Supplementary Information

Copper free Heck-Cassar-Sonogashira and Suzuki-Miyaura Reactions of Aryl Chlorides: a Sustainable Approach

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1. General Information

Commercial reagents (reagent grade, >99%) were used as received without additional purification.

Solvents (cyclohexane (Cy), dichloromethane (DCM), methyl-*tert*-butyl ether (MTBE), N-hydroxyethylpyrrolidone (HEP), toluene, 2-methyltetrahydrofuran (2-MeTHF), isobutylacetate (IBA), isopropyl alcohol (IPA) and deuterated N,N-Dimethylformamide (DMF-d_7)) are commercially available and were used after degassing.

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded with an Agilent-Technologies-Varian INOVA 400 MHz and 100 MHz instrument ^{1}H/^{19}F/X 5 mm PFG ATB Broadband Probe, VT, single, double and triple resonance, z-axis pulsed field gradients, serves broadband probe and customized variable temperature – 5 mm Broadband probe. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, spt = septet, m = multiplet, bs = broad signal. Coupling constants *J* are given in Hz. All ^{1}H and ^{13}C chemical shifts are calibrated to residual proto-solvents.

HPLC-UV analysis were recorded with an Agilent 1260 InfinityLab instrument. Column: Zorbax® SB-C18; particle size 5 µm; pore size 100 Å; length 250 mm, internal diameter: 4.6 mm. Mobile phase A: H_2O, mobile phase B: ACN. Gradient (Time(min), %B): 0, 30; 8, 80; 22, 80; 24, 10; 30, 10; flow 0.5 mL min^{-1}column temperature 30°C; injection volume: 20 µL.

NE-1010 Higher Pressure Syringe Pump used to perform slow-addition of acetylenes in the Heck-Cassar-Sonogashira cross-coupling reactions.

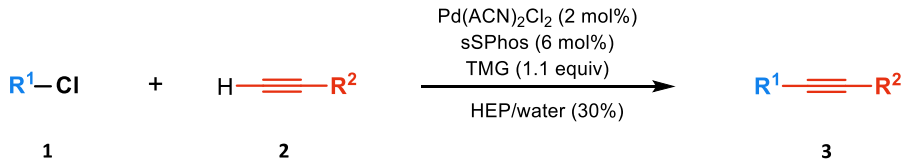
Mass Spectrometry analysis were recorded on a QTRAP 3200 mass spectrometer in ESI^{+} mode.

Spectrometer ICP-OES AGILENT 5110 was used to determine the concentration of Pd in the solution. Power: 1200 W; Auxiliary gas: Argon (1.0 L min^{-1}); nebulizer gas: nitrogen (0.7 L min^{-1}); peristaltic pump speed: 12 rpm. Samples for ICP-OES were digested with 8 mL HNO_3/HCl (1:3) using a microwave digestion system held at 175 °C for 10 minutes. The volume of the digests was then made up to 50 mL with de-ionized water before analysis by ICP-OES. Calibration standards for the quantification of the digested samples were prepared in 5% HNO_3. Palladium standards from Faggi Enrico and 2'-Dicyclohexylphosphino-2,6-dimethoxy-3-sulfonato-1,1'-biphenyl hydrate sodium (sSPhos) from Chemieliva Pharmaceutical Co., Ltd**.**

2. General Procedures

2.1. General procedure for Heck-Cassar cross-coupling with aryl chlorides[1]:

2.1.1. Heck-Cassar reactions with 2 mol% of catalyst

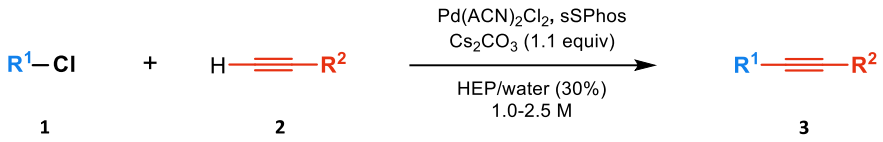


Procedure:

Figure S1: NE-1010 Higher Pressure Syringe Pump used to perform slow-addition of acetylenes

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, the palladium pre-catalyst $Pd(ACN)_2Cl_2$ (0.02 mmol, 2 mol%, 5.2 mg), sSPhos, (0.06 mmol ,6 mol%, 30.8 mg) were dissolved in HEP and water as co-solvent in a 7/3 ratio. The other reagents were then added in the following order: TMG (126.9 mg, 138.0 µL, 1.1 mmol, 1.1 equiv) and aryl chloride (1.0 mmol, 1.0 equiv). The reaction mixture was heated to 80-90°C with an oil bath and alkyne (from 1.05 to 1.5 equiv) was added slowly with a syringe pump over the course of the reaction; the conversion was evaluated through HPLC-UV analysis at 210 nm considering the appropriate RRF (see *Chapter 9* for RRF calculation). At reaction completion, the mixture was extracted with an appropriate organic solvent (3x1 mL). The collected organic phases were concentrated under reduced pressure. The reaction crude was purified, when necessary, by flash chromatography (eluents and isolated yields specified below in *Compound Characterization section).*

2.1.2. Heck-Cassar reactions with 0.2-0.4 mol% of catalyst



Preparation of stock solution of the HCS catalyst:

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, palladium pre-catalyst $Pd(ACN)_2Cl_2$ (0.02 mmol, 5.2 mg) and ligand sSPhos, (0.06 mmol, 30.8 mg) were dissolved in 2 mL of HEP/water(30%) solution. The mixture was stirred for 5 min at room temperature. A yellow-orange solution was obtained for subsequent HCS reactions (stock solution is stable and can be used even after one week).

Procedure:

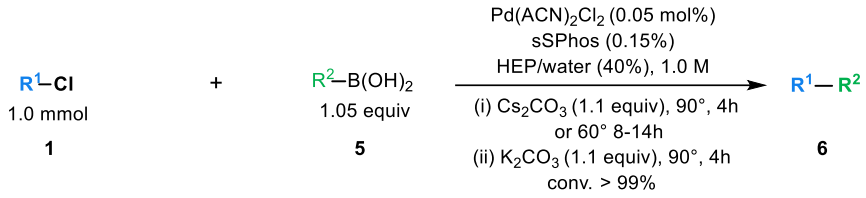
To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, 200 µL of the stock solution (0.2 mol% of palladium catalyst) was added along with the amount of HEP/water (30%) solution needed to achieve the desired concentration. The other reagents were then added in the following order: Cs_2CO_3 (358 mg, 1.1 mmol, 1.1 equiv) and aryl chloride (1.0 mmol, 1.0 equiv). The reaction mixture was heated to 80-90°C with an oil bath and alkyne (1.05 mmol, 1.05 equiv) was added slowly with a syringe pump over the course of the reaction; the conversion was evaluated through HPLC-UV analysis at 210 nm considering the appropriate RRF (see *Chapter 9* for RRF calculation). At reaction completion, the mixture was extracted with an appropriate organic solvent (3x1 mL). The collected organic phases were concentrated under reduced pressure. The reaction crude was purified, when necessary, by flash chromatography (eluents and isolated yields specified below in *Compound Characterization section*).

2.2. General procedure for Suzuki-Miyaura cross-coupling[1]

Preparation of stock solution of the SM catalyst:

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, palladium pre-catalyst $Pd(ACN)_2Cl_2$ (0.04 mmol, 10.4 mg) and ligand sSPhos, (0.12 mmol, 61.6 mg) were dissolved in 4 mL of HEP/water(40%) solution. The mixture was stirred for 5 min at room temperature. A yellow-orange solution was obtained for subsequent SM reactions (stock solution is stable and can be used even after one week)

Procedure



To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, 50 µL of the stock solution (0.05 mol% of palladium catalyst) was added along with the amount of HEP/water (40%) solution needed to achieve the desired concentration. The other reagents were then added in the following order:base (1.1 mmol, 1.1 equiv), aryl chloride (1.0 mmol, 1.0 equiv) and boronic acid (1.05 mmol, 1.05 equiv). The reaction mixture was heated to the desired temperature with an oil bath and maintained at this temperature under stirring; the conversion was evaluated through HPLC-UV analysis at 210 nm considering the appropriate RRF (see *Chapter 9* for RRF calculation). At reaction completion, the mixture was extracted with an appropriate organic solvent (3x1 mL). The collected organic phases were concentrated under reduced pressure. The product was isolated without need of purification (yields specified below in *Compound Characterization section*).

2.3. Recycling protocol for HCS coupling[1]

After complete conversion of the desired reaction (monitored with HPLC-UV at 210 nm), the mixture was extracted three times under N_2 with an appropriate organic solvent, not miscible with the HEP/water solution (Cy, MTBE, toluene, 2-MeTHF, IBA and IPA). The organic layer was removed with a syringe, another portion of base, aryl chloride and acetylene (slowly over the curse of the reaction) were added to the HEP/water phase and another catalytic cycle was performed at 80-90°C. The conversion of the new cycle of reaction was monitored by the previously mentioned analysis. The organic phases obtained from the different cycles were combined, distilled to recover the organic solvent, and the residue purified, when necessary, by flash chromatography (yields and recycles are reported in Table 2).

2.4. Thermomorphic protocol for HCS coupling

To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, palladium pre-catalyst $Pd(ACN)_2Cl_2$ (0.02 mmol, 2 mol%, 5.2 mg), sSPhos, (0.06 mmol ,6 mol%, 30.8 mg) were dissolved in HEP and water as co-solvent. The other reagents were then added in the following order: TMG (126.9 mg, 138.0 µL, 1.1 mmol, 1.1 equiv) and aryl chloride (1.0 mmol, 1.0 equiv). The reaction mixture was heated to 90°C with an oil bath and phenylacetylene **2a** (1.7.2 mg, 115.3 µL, 1.05 mmol, 1.05 equiv) was added slowly with a syringe pump over the course of the reaction in 0.5 mL of toluene or IBA in a HEP/water/toluene or HEP/water/IBA 7/3/5 ratio;

the conversion was evaluated through HPLC-UV analysis at 210 nm considering the appropriate RRF (see *Chapter 9* for RRF calculation). At reaction completion, by simply cooling the reaction mixture at room temperature, the separation of toluene (or IBA) containing the product **3a** occurred, that was simply extracted with a syringe. It was possible to recycle the catalyst and the HEP/water solution three times. The organic phases obtained from the different cycles were combined, distilled to recover the organic solvent, and the residue purified by flash chromatography (yields and recycles are reported in Table 2).

3. Calculation of TON, PMI and PMIr

Turnover number (TON):

TON can be calculated by the ratio between the yield of the product at the end of the cycle, and the percentage of the mmol of catalyst divided from the number of the cycle.[2]

$$TON = \frac{average\ yield_{product}}{\%\ mmol_{catalyst}/n\ cycle}$$

Complete Environmental Factor (cEF)[3]

The general environmental factor for an entire API process is computed by the ratio between the total mass of waste generated in the synthetic scheme and the mass of the isolated product. The simple environmental factor (sEF) neglects the solvents and water, and it is usually applied at the stage of initial research. This is the reason why, for an industrial point of view, it is better to use the complete environmental factor (cEF), that includes all the components utilized for the entire synthesis including solvents and water:

$$cEF = \frac{\sum mass\ of\ waste}{mass\ of\ isolated\ product} = \frac{\sum mass\ of\ materials - mass\ of\ isolated\ product}{mass\ of\ isolated\ product}$$

Process Mass Intensity (PMI)[4]

The process mass intensity (PMI) is defined as the ratio between the total mass of materials and the mass of the isolated product.

$$PMI = \frac{\sum mass\ of\ materials}{mass\ of\ isolated\ product} = cEF + 1$$

Recovery of HEP, and Pd

3.1. Recovery of HEP and Pd in the HCS cross-coupling with 2 mol%

At the given time, the reaction was cooled at rt, extracted with cyclohexane and the HEP/water phase containing the catalyst was recycled.

After the final cycle, product **3** was again extracted with cyclohexane and the combined organic extracts were distilled and the product could be recovered without further purification. The reaction mixture, containing HEP/water, conjugated TMG acid and the catalyst complex, was treated with sodium formate (0.15 mmol, 10.0 mg) for 1h at 60°C to generate palladium black. At reaction completion, the mixture was filtered out with the aid of charcoal (30 mg) and the palladium metal was recovered. The filtrate was distilled under reduced pressure to recover HEP in 95% yield.

Table S1: Example of PMI calculation on the optimized HCS reaction on 5 mmol scale

Reagents	**Single run (mg)**	**5 cycles (g)[a]**	**5 cycles and final recovery (g)[b]**	**% of recovery**
1a	563	2.8	2.8	-
2a	536	2.68	2.68	-
TMG	633	3.17	3.17	-
$Pd(ACN)_2Cl_2$	25.5	0.025	0.0025	90
sSPhos	154	0.154	0.154	-
HEP	4000	4.0	0.2	95
Water	1500	1.5	300	-
Sodium formate	-	-	0.01	-
Charcoal	-	-	0.03	-
Cyclohexane[c]	11685	58.4	58.4	95
3a[d]	870	4.2	4.2	-
PMI	21	-	-	-
PMI after Pd/sSPhos and HEP/water recycle	-	18.1	-	-
PMI after final recovery of Pd, HEP, Cy	-	-	3.3	-

[a]PMI calculated after 5 cycles and recycle of Pd complex and HEP/water. [b]PMI calculated after 5 cycles and recycle of Pd complex, HEP/water and final recovery of Pd metal, HEP and cyclohexane. [c]The organic phases obtained from the different cycles were combined and distilled to recover 95% of cyclohexane. It is possible to distill the cyclohexane also after each cycle. [d]Product **3a** obtained without need of purification.

3.2. Recovery of HEP and Pd in the HCS cross-coupling with 0.2 mol%

At the given time, the reaction was cooled at rt, extracted with cyclohexane achieving product **3a** with 93% yield with no need of purification. The reaction mixture, containing HEP/water, conjugated Cs_2CO_3 acid and the catalyst complex, was treated with sodium formate (0.1 mmol, 10.0 mg) for 1h at 60°C in order to generate palladium black. At reaction completion, the mixture was filtered out with the aid of charcoal (60 mg) and the palladium metal was recovered. The filtrate was distilled under reduced pressure to recover HEP in 95% yield.

Table S2: Example of PMI calculation on the direct HCS reaction on 10 mmol scale

Reagents	**Single run (g)**	**Single run and final recovery (g)[b]**	**% of recovery**
1a	1.12	1.12	-
2a	1.07	1.07	-
Cs_2CO_3	3.58	3.58	-
$Pd(ACN)_2Cl_2$	0.005	0.0005	90
sSPhos	0.03	0.03	-
HEP	3.2	0.16	95
Water	1.2	0.12	-
Sodium formate	-	0.01	-
Charcoal	-	0.06	-
Cyclohexane[c]	9.3	0.46	95
3a[d]	1.7	1.7	-
PMI[a]	11.1	-	-
PMI after Pd/sSPhos and HEP/water recycle	-	-	-
PMI after final recovery of Pd, HEP, Cy	-	4.4	-

[a]PMI calculated considering all the reagents used without recovery. [b]PMI calculated after final recovery of Pd metal, HEP and cyclohexane. [c]The organic phases obtained from the different cycles were combined and distilled to recover 95% of cyclohexane. [d]Product **3a** obtained without need of purification.

3.3. Recovery of HEP and Pd in the SM cross-coupling with 0.05 mol%

At the given time, the reaction was cooled at rt, extracted with cyclohexane achieving product **6a** and **6k** both with 95% yield with no need of purification. The reaction mixture, containing HEP/water, conjugated base (K_2CO_3 or Cs_2CO_3 acid and the catalyst complex, was treated with sodium formate (0.1 mmol, 10.0 mg) for 1h at 60°C in order to generate palladium black. At reaction completion, the mixture was filtered out with the aid of charcoal (60 mg) and the palladium metal was recovered. The filtrate was distilled under reduced pressure to recover HEP in 95% yield.

Table S3. Example of PMI calculation on the SM reaction of Scheme 4 with 10 mmol scale

Reagents	**Single run (g)**	**Single run and final recovery (g)[b]**	**% of recovery**
1a	1.1	1.1	-
5a	1.2	1.2	-
Cs_2CO_3	3.57	3.57	-
$Pd(ACN)_2Cl_2$	0.001	0.0001	90
sSPhos	0.007	0.007	-
HEP	6.8	0.34	95
Water	4	4	-
Sodium formate	-	0.01	-
Charcoal	-	0.06	-
Cyclohexane[c]	23.4	1.16	95
6a[d]	1.47	1.47	-
PMI[a]	27.2	-	-
PMI after final recovery of Pd, HEP, Cy	-	7.7	-

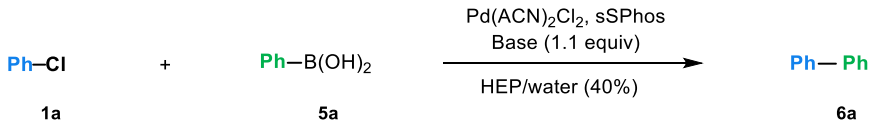
[a]PMI calculated considering all the reagents used without recovery. [b]PMI calculated after final recovery of Pd metal, HEP and cyclohexane. [c]The organic phases obtained from the different cycles were combined and distilled to recover 95% of cyclohexane. [d]Product **6a** obtained without need of purification.

Table S4. Example of PMI calculation on the SM reaction of Scheme 5 with 10 mmol scale

Reagents	Single run (g)	Single run and final recovery (mg)[b]	% of recovery
1g	1.1	1.1	-
5e	1.56	1.56	-
Cs_2CO_3	3.57	3.57	-
$Pd(ACN)_2Cl_2$	0.001	0.0001	90
sSPhos	0.007	0.007	-
HEP	6.8	0.34	95
Water	4	4	-
Sodium formate	-	0.01	-
Charcoal	-	0.06	-
Cyclohexane[c]	23.4	1.16	95
6k[d]	2.24	2.24	-
PMI[a]	18.0	-	-
PMI after final recovery of Pd, HEP, Cy	-	5.3	-

[a]PMI calculated considering all the reagents used without recovery. [b]PMI calculated after final recovery of Pd metal, HEP and cyclohexane. [c]The organic phases obtained from the different cycles were combined and distilled to recover 95% of cyclohexane. [d]Product **6k** obtained without need of purification.

4. Base Screening in the SM coupling

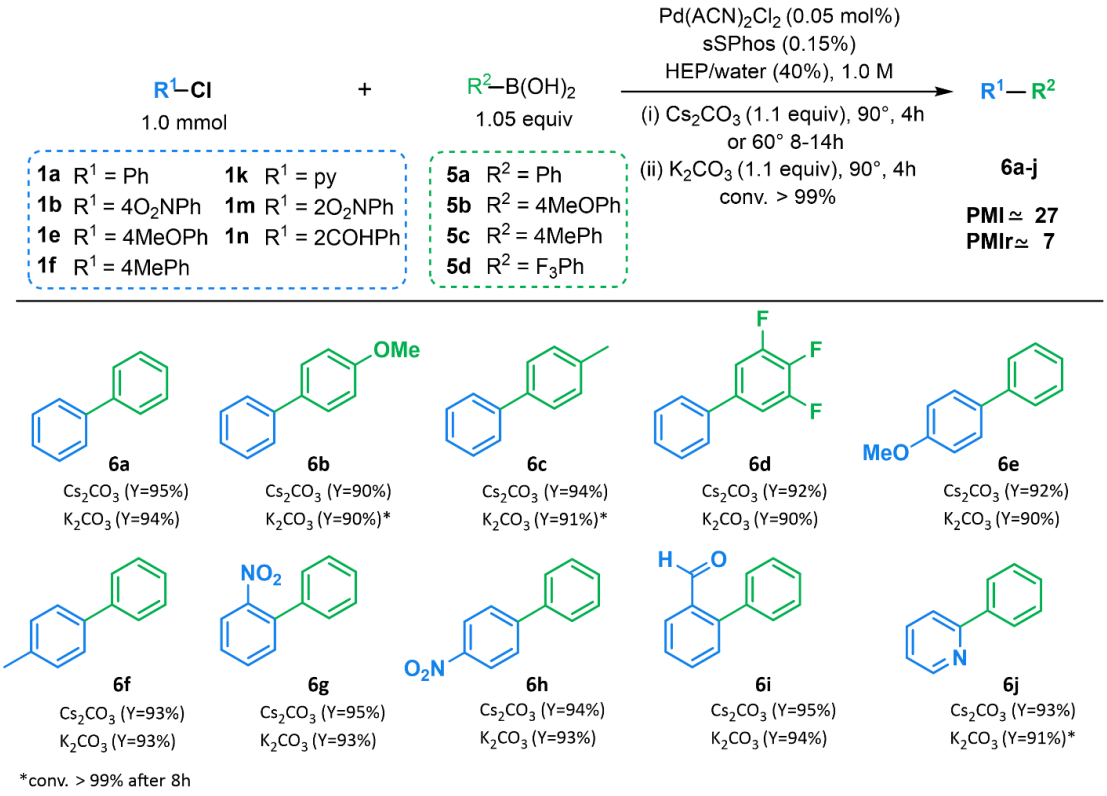


To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, an aliquot of the stock solution was added along with the amount of HEP/water (40%) solution needed to achieve the desired concentration. The other reagents were then added in the following order: base (1.1 mmol, 1.1 equiv), chlorobenzene (50.6 µL, 1.0 mmol, 1.0 equiv) and phenyl boronic acid (1.05 or 1.2 equiv, see the following table). The reaction mixture was heated at the desired temperature with an oil bath and maintained at this temperature under stirring; the conversion was evaluated through HPLC-UV analysis at 210 nm considering the appropriate RRF (see *Chapter 9* for RRF calculation).

Table S5. Base screening in SM coupling

Entry	Conc. (M)	Pd (mmol%)	R-B(OH)$_2$ (equiv)	Base	T (°C)	Time (h)	Conv. (%)
1	1.0	0.1	1.2	Cs_2CO_3	45	16	100
2	1.0	0.2	1.05	Cs_2CO_3	45	16	100
3	1.0	0.1	1.2	K_2CO_3	45	16	63
4	1.0	0.2	1.05	K_2CO_3	45	16	100
5	0.5	0.1	1.2	K_2CO_3	45	16	100
6	1.0	0.1	1.2	Na_2CO_3	45	16	51
7	1.0	0.2	1.05	Na_2CO_3	45	16	100
8	0.5	0.1	1.2	Na_2CO_3	45	16	76
9	1.0	0.1	1.2	K_3PO_4	45	16	38
10	1.0	0.2	1.05	K_3PO_4	45	16	100
11	0.5	0.1	1.2	K_3PO_4	45	16	67
12	1.0	0.05	1.05	Cs_2CO_3	60	8	100
13	1.0	0.05	1.05	K_2CO_3	60	16	85
14	0.5	0.05	1.05	K_2CO_3	60	16	87
15	1.0	0.05	1.05	Na_2CO_3	60	16	83
16	0.5	0.05	1.05	Na_2CO_3	60	16	85
17	1.0	0.05	1.05	K_3PO_4	60	16	76
18	0.5	0.05	1.05	K_3PO_4	60	16	79
19	1.0	0.05	1.05	Cs_2CO_3	90	4	100
20	1.0	0.05	1.05	K_2CO_3	90	4	100
21	1.0	0.05	1.05	Na_2CO_3	90	4	88
22	1.0	0.05	1.05	K_3PO_4	90	4	84

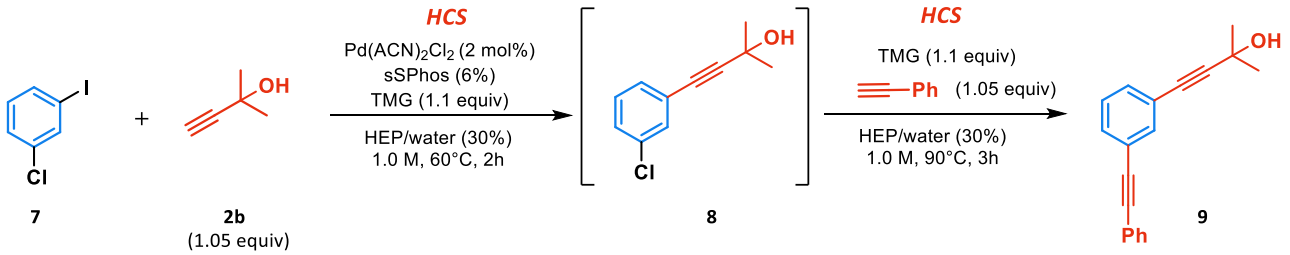
5. SM Scope with Cs_2CO_3 and K_2CO_3



To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, an aliquot of the stock solution was added along with the amount of HEP/water (40%) solution needed to achieve the desired concentration. The other reagents were then added in the following order: Cs_2CO_3 (1.1 mmol, 357 mg, 1.1 equiv) or K_2CO_3 (1.1 mmol, 152.1 mg, 1.1 equiv), aryl chloride **1a-1n** (1.0 mmol, 1.0 equiv) and aryl boronic acid **5a-5d** (1.05 mmol, 1.05 equiv). The reaction mixture was heated at the desired temperature with an oil bath and maintained at this temperature under stirring; the conversion was evaluated through HPLC-UV analysis at 210 nm considering the appropriate RRF (see *Chapter 9* for RRF calculation). At reaction completion, the mixture was extracted with an appropriate organic solvent (3x1 mL). The collected organic phases were concentrated under reduced pressure. The product was isolated without need of purification (yields specified below in *Compound Characterization section*).

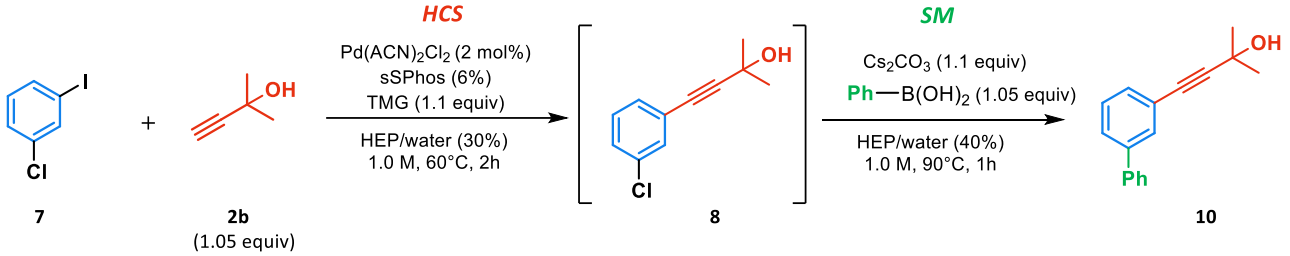
6. Selectivity Studies

6.1. One-pot HCS-HCS cross-coupling reactions



To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, palladium pre-catalyst $Pd(ACN)_2Cl_2$ (0.02 mmol, 2 mol%, 5.2 mg), sSPhos, (0.06 mmol ,6 mol%, 30.4 mg) were dissolved in HEP and water as co-solvent. The other reagents were then added in the following order: TMG (126.7 mg, 138.0 µL, 1.1 mmol, 1.1 equiv), 1-chloro-3-iodobenzene **7** (238.4 mg, 123.8 µL, 1.0 mmol, 1.0 equiv) and alkyne **2b** (92.5 mg, 106.6 µL, 1.1 mmol, 1,1 equiv). The reaction mixture was heated to 60°C with an oil bath and the conversion was evaluated through HPLC-UV analysis at 210 nm. After 2h, intermediate **8** was achieved with a complete conversion and a selectivity >99%. The mixture was then heated to 90°C, TMG (1.1 equiv) was directly added and phenylacetylene **2a** was added slowly in 4h with a syringe pump in order to achieve product **9** with 95% of conversion. The mixture was extracted with IBA (3x5 mL). The collected organic phases were concentrated under reduced pressure. The reaction crude was purified by flash chromatography (eluents and isolated yields specified below in *Compound Characterization section*).

6.2. One-pot HCS-SM cross-coupling reactions



To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, palladium pre-catalyst $Pd(ACN)_2Cl_2$ (0.02 mmol, 2 mol%, 5.2 mg), sSPhos, (0.06 mmol, 6 mol%, 30.4 mg) were dissolved in HEP and water as co-solvent. The other reagents were then added in the following order: TMG (126.7 mg, 138.0 µL, 1.1 mmol, 1.1 equiv), 1-chloro-3-iodobenzene **7** (238.4 mg, 123.8 µL, 1.0 mmol, 1.0 equiv) and alkyne **2b** (92.5 mg, 106.6 µL, 1.1 mmol, 1,1 equiv). The reaction mixture was heated to 60°C with an oil bath and the conversion was evaluated through HPLC-UV analysis at 210 nm. After 2h, intermediate **8** was achieved with a complete conversion and a selectivity >99%. The mixture was then heated to 90°C, Cs_2CO_3 (358.4 mg, 1.1 mmol, 1.1 equiv) and phenyl boronic acid **5a** (128.0 mg, 1.05 mmol, 1.05 equiv) were directly added to the solution. The reaction was complete in 1h giving product **10** with a complete conversion. The mixture was extracted with

IBA (3x5 mL). The collected organic phases were concentrated under reduced pressure in order to achieve compound 10 without need of purification.

7. $PdCl_2(sSPhos)_2$ Reduction

To an oven-dried 20 mL Schlenk purged under nitrogen atmosphere, the pre-catalyst $PdCl_2(ACN)_2$ (3.37 mg, 0.013 mmol, 1.0 equiv), the ligand sSPhos (13.32 mg, 0.026 mmol, 2.0 equiv) and Cs_2CO_3 (21.18 mg, 0.065 mmol, 5.0 equiv) were dissolved in DMF-d_7 (0.4 mL) and HEP/H_2O (ratio 7:3, 0.2 mL). The reaction was stirred at 60°C and after 10 minutes the ^{31}P NMR spectrum was collected (A). Chlorobenzene (6.6 µL, 0.026 mmol, 5 equiv) was added and the reaction stirred at 60°C for 30 minutes (B). The chemical shift of ArPd(sSPhos)Cl at 44.81 ppm and the shape of the signal is in line with the chemical shift of ArPd(SPhos)Cl in toluene reported by Barder et al.[5] The disappearance of the signals at 64.24 ppm and at 63.02 ppm confirmed that the reduction process occurred.

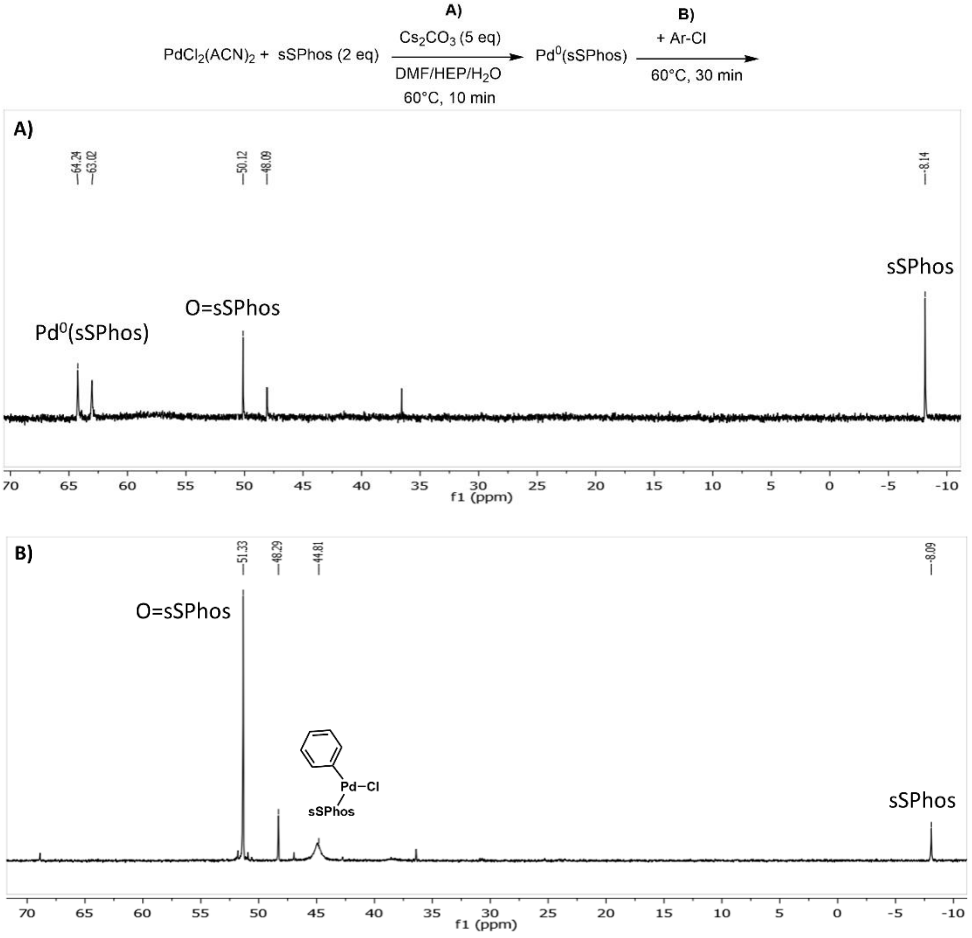


Figure S2: ^{31}P NMR spectra of the reduction of $PdCl_2(sSPhos)_2$ in DMF-d_7/HEP/H_2O with Cs_2CO_3 5 equiv at 60°C (A) and after the addition of Ar-Cl (5 equiv) (B).

To further demonstrate that HEP plays a fundamental role in the Pd(II) reduction process, the previous reaction was repeated in only DMF-d_7 as solvent. To an oven-dried 20 mL Schlenk purged under nitrogen atmosphere, the pre-catalyst $PdCl_2(ACN)_2$ (3.37 mg, 0.013 mmol, 1.0 equiv), the ligand sSPhos (13.32 mg, 0.026 mmol, 2.0 equiv) and Cs_2CO_3 (21.18 mg, 0.065 mmol, 5.0 equiv) were dissolved in DMF-d_7 (0.6 mL) and the reaction was stirred at 60°C. After 10 minutes the ^{31}P NMR spectra was collected.

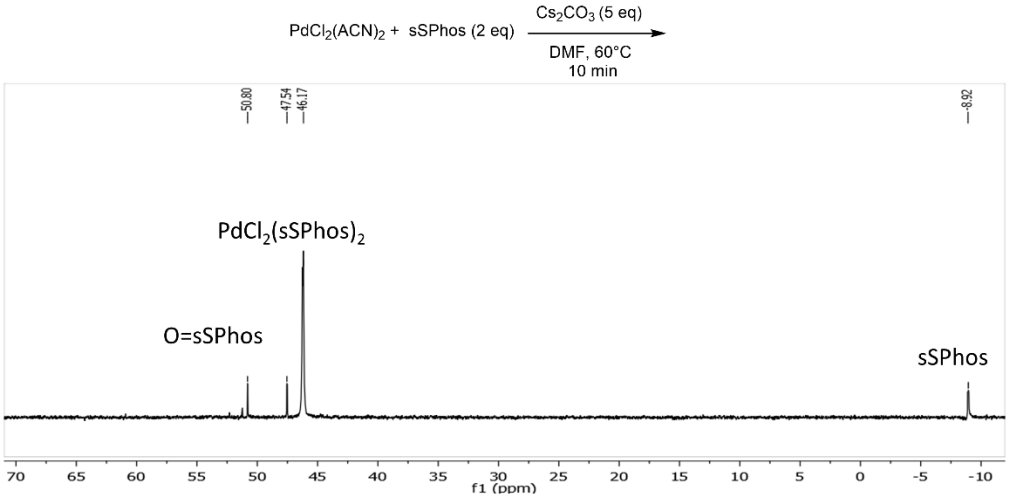


Figure S3: ^{31}P NMR spectrum of the reduction of $PdCl_2(sSPhos)_2$ in DMF-d_7 with Cs_2CO_3 5 equiv at 60°C.

As reference, the following spectra show the chemical shifts of the pre-catalyst $PdCl_2(sSPhos)_2$, the ligand sSPhos and OsSPhos:

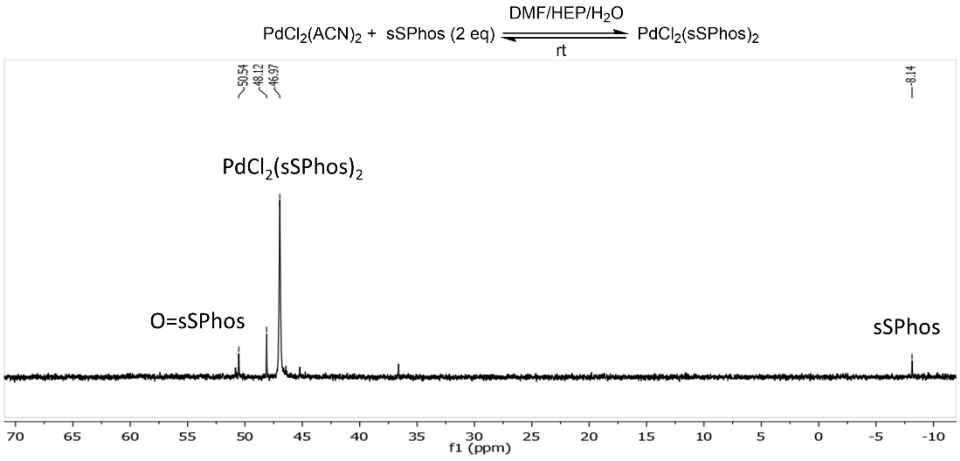


Figure S4: ^{31}P NMR spectrum of $PdCl_2(sSPhos)_2$ in DMF-d_7/HEP/H_2O. $PdCl_2(ACN)_2$ (3.37 mg, 0.013 mmol, 1 equiv) and sSPhos (13.32 mg, 0.026 mmol, 2 equiv) were dissolved in DMF-d_7 (0.4 mL) and HEP/H_2O (ratio 7:3, 0.2 mL).

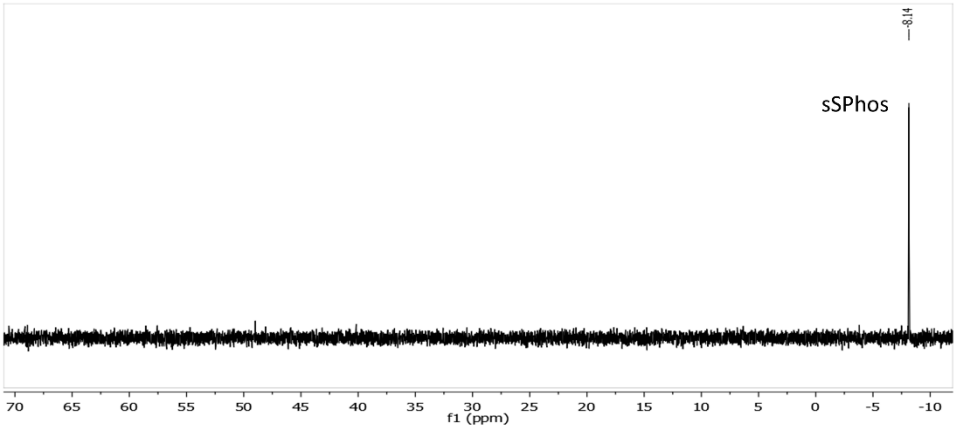


Figure S5: ^{31}P NMR spectrum of sSPhos in DMF-d_7/HEP/H_2O.

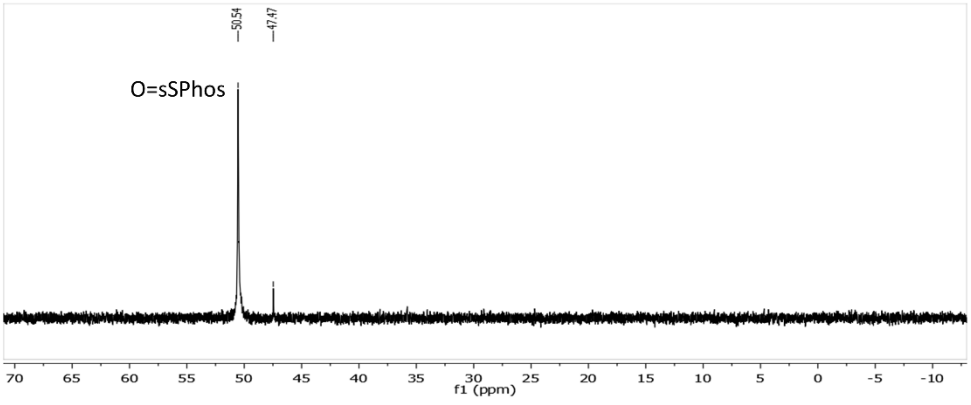


Figure S6: ^{31}P NMR spectrum of OsSPhos in DMF-d_7/HEP/H_2O. The spectrum shows an unknown peak present also in the previous spectra.

8. Compound Characterization

Yields of the HCS reactions reported considering the single run of the entries in Table 3

*1,2-diphenylacetylene, **3a***

The product **3a** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

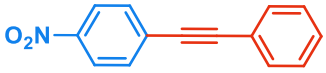
White solid (93% yield), extraction solvent: Cy

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 – 7.56 (m, 4H), 7.39 – 7.36 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 131.27, 128.00, 127.91, 122.94, 89.04.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.33; H, 5.67; found: C, 94.62; H, 5.69.

*1-nitro-4-(phenylethynyl)benzene, **3b***



The product **3b** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

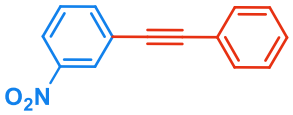
Yellow solid (94% yield), extraction solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 – 8.17 (m, 2H), 7.64 – 7.62 (m, 2H), 7.56 – 7.53 (m, 2H), 7.38 – 7.36 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.95, 132.27, 131.84, 130.22, 129.28, 128.57, 123.58, 122.10, 94.75, 87.59.

Anal. Calcd. for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27; found: C, 75.26; H, 4.06; N, 6.27.

*1-nitro-3-(phenylethynyl)benzene, **3c***



The product **3c** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

Yellow solid (95% yield), extraction solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.36 – 8.35 (m, 1H), 8.17 – 8,15 (d, 1H, J = 8.2 Hz), 7.82 – 7.80 (d, 1H, J = 7.7 Hz), 7.53 – 7.49 (m, 3H), 7.40 – 7.38 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.11, 137.19, 131.77, 129.35, 129.06, 128.53, 126.28, 125.10, 122.84, 122.19, 91.92, 86.91.

Anal. Calcd. for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27; found: C, 75.14; H, 4.06; N, 6.26.

4-(phenylethynyl)benzonitrile, ***3d***

The product **3d** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

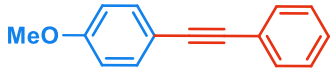
Yellow solid (93% yield); extraction solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66– 7.61 (m, 4H), 7.57 – 7.55 (m, 2H), 7.40 – 7.38 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 132.05, 132.02, 131.77, 129.10, 128.49, 128.23, 122.21, 118.50, 111.45, 93.76, 87.70.

Anal. Calcd. for $C_{14}H_9N$: C, 88.64; H, 4.46; N, 6.89; found C, 88.69; H, 4.38; N, 6.92.

1-methoxy-4-(phenylethynyl)benzene, ***3e***



The product **3e** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

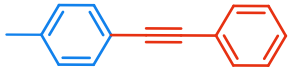
White solid (90% yield), extraction solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55 – 7.49 (m, 4H), 7.37 – 7.33 (m, 3H), 6.91 – 6.89 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.60, 133.02, 131.42, 128.28, 127.90, 123.58, 115.36, 113.98, 89.35, 88.05, 55.26.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81; found: C, 86.72; H, 5.81.

1-methyl-4-(phenylethynyl)benzene, ***3f***



The product **3f** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

White solid (91% yield), extraction solvent: Cy

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 – 7.54 (m, 2H), 7.47 – 7.45 (d, J = 8.1 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.19 – 7.17 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.36, 131.53, 131.48, 129.09, 128.29, 128.04, 89.55, 88.71, 21.49.

Anal. Calcd. for $C_{15}H_{12}$: C, 93.79; H, 6.21; found: C, 93.57, H: 6.23.

2-methyl-4-phenylbut-3-yn-2-ol, ***3g***

The product **3g** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

Yellow oil (90% yield); extraction solvent: ^{t}BuOAc and purification by flash chromatography (Cy/EtOAc = 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 – 7.42 (m, 2H), 7.31 – 7.29 (m, 3H), 2.53 (s, OH), 1.64 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 131.23, 127.83, 127.81, 122.37, 93.50, 81.69, 65.17, 31.08.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55; found: C, 82.78; H, 7.54.

N,N-dimethyl-3-phenylprop-2-yn-1-amine, ***3h***

The product **3h** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

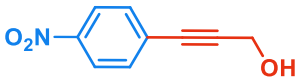
Colourless liquid (91% yield); extraction solvent: ^{t}BuOAc and purification by flash chromatography (Cy/EtOAc = 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 – 7.43 (m, 2H), 7.30 – 7.28 (m, 3H), 3.47 (s, 2H), 2.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 131.27, 127.82, 127.59, 122.80, 84.86, 84.13, 48.15, 43.81.

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80; found: C, 82.99; H, 8.22; N, 8.77.

3-(4-nitrophenyl)prop-2-yn-1-ol, ***3i***



The product **3i** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

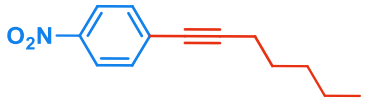
Yellow oil (90% yield); extraction solvent: ^{t}BuOAc and purification by flash chromatography (Cy/EtOAc = 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 – 8.18 (dd, J = 8.0, 4.0 Hz, 2H), 7.60 – 7.57 (dd, J = 8.0, 4.0 Hz, 2H), 4.55 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.25, 132.39, 129.41, 123.57, 92.46, 83.81, 51.49.

Anal. Calcd. for $C_9H_7NO_3$: C, 61.02; H, 3.98; N, 7.91; O, 27.09; found: C, 61.11; H, 3.95; N, 7.87; O, 28.1.

1-(hept-1-yn-1-yl)-4-nitrobenzene, ***3j***



The product **3j** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

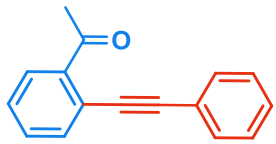
Yellow oil (90% yield); extraction solvent: Cy and Purification by flash chromatography (Cy 100%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 – 8.14 (dd, J = 8.0, 4.0 Hz, 2H), 7.52 – 7.50 (dd, J = 8.0, 4.0 Hz, 2H), 2.46 – 2.43 (t, *J* = 12.0 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.48 – 1.34 (m, 4H), 0.95 – 0.91 (t, *J* = 12.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.53, 132.19, 131.20, 123.43, 96.79, 79.25, 31.08, 28.08, 22.16, 19.50, 13.93.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45; O, 14.73; found: C, 71.93; H, 6.92; N, 6.50; O, 14.69.

1-(2-(phenylethynyl)phenyl)ethan-1-one, ***3k***



The product **3k** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

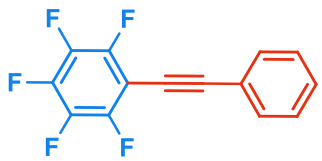
Yellow oil (94% yield); extraction solvent: ^{t}BuOAc and purification by flash chromatography (Cy/EtOAc = 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 – 7.75 (d, J = 8.0 Hz, 1H), 7.64 – 7.62 (d, J = 8.0 Hz, 1H), 7.56 – 7.55 (m, 2H), 7.49 – 7.47 (t, J = 4.0 Hz, 1H), 7.42 – 7.37 (m, 4H), 2.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.35, 140.76, 133.91, 131.54, 131.34, 128.80, 128.73, 128.49, 128.31, 122.91, 121.71, 95.06, 88.53, 30.01.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.25; H, 5.49; O, 7.26; found C, 87.28; H, 5.52; O, 7.24

1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene, ***3l***



The product **3l** is prepared by general procedure for Heck-Cassar cross-coupling (*Chapter 2.1.*).

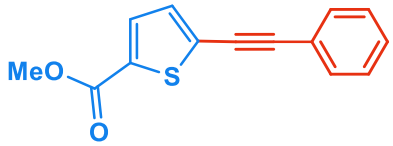
White solid (92% yield); extraction solvent: Cy and purification by flash chromatography (Cy 100%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59 – 7.57 (m, 2H), 7.42 – 7.38 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.1 (dm, J_{F-C} = 250 Hz), 141.4 (dm, J_{F-C} = 250 Hz), 137.6 (dm, J_{F-C} = 250 Hz), 131.90, 129.64, 128.52, 121.55, 101.55 (m), 100.31, 73.04 (m).

Anal. Calcd. for $C_{14}H_5F_5$: C, 62.70; H, 1.88; F, 35.42; found C, 62.71; H, 1.31; F, 35.40

methyl 5-(phenylethynyl)thiophene-2-carboxylate, ***3m***



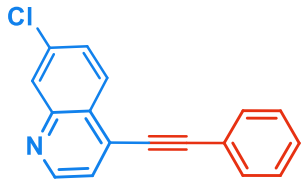
The product **3m** is prepared by general procedure for Heck-Cassar-Sonogashira cross-coupling (Chapter 2.1.). Yellow solid (93% yield); Extraction solvent: ^{t}BuOAc; Purification by flash chromatography (Cy/EtOAc = 90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.70 (d, 1H, J = 3.9 Hz), 7.55 – 7.53 (m, 2H), 7.38 (m, 3H), 7.23 (d, 1H, J = 3.9 Hz), 3.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.03, 133.79, 133.32, 132.14, 131.62, 130.05, 129.06, 128.49, 122.20, 95.62, 91.99, 52.34.

Anal. Calcd. for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16; O, 13.21; S, 13.23; found: C, 68.87; H, 4.01; O, 13.29; S, 13.40.

7-chloro-4-(phenylethynyl)quinoline, ***3n***



The product **3n** is prepared by general procedure for Heck-Cassar-Sonogashira cross-coupling (*Chapter 2.1.*). White solid (90% yield); Extraction solvent: ^{t}BuOAc; Purification by flash chromatography (Cy/EtOAc = 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 8.90 (d, J = 4.5 Hz, 1H), 8.30 (d, J = 8.9 Hz, 1H), 8.13 (d, J = 2.1 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.61 – 7.54 (m, 2H), 7.44 (dd, J = 5.1, 1.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.85, 148.50, 135.87, 132.00, 129.88, 129.58, 128.81, 128.65, 128.19, 127.43, 126.18, 123.64, 121.98, 99.20, 84.60.

Anal. Calcd. for $C_{17}H_{10}ClN$: C, 77.42; H, 3.82; Cl, 13.44; N, 5.31; found: C, 77.54; H, 3.76; Cl, 13.63; N, 5.22

2-(phenylethynyl)pyridine, ***3o***

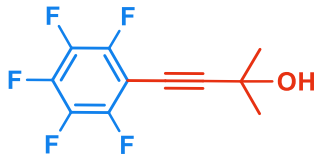
The product **3o** is prepared by general procedure for Heck-Cassar-Sonogashira cross-coupling (*Chapter 2.1.*). Yellow oil (91% yield); Extraction solvent: ^{t}BuOAc; Purification by flash chromatography (Cy/EtOAc = 95/5).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.70 – 7.67 (m, 1H), 7.61 (m, 2H), 7.54 (d, J = 8.1 Hz, 1H), 7.38, (m, 3H), 7.26 – 7.23 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.09, 143.50, 136.17, 132.07, 128.99, 128.41, 127.18, 122.76, 122.29, 89.25, 88.62.

Anal. Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82; found: C, 87.09; H, 5.09; N, 7.87.

2-methyl-4-(perfluorophenyl)but-3-yn-2-ol, ***3p***



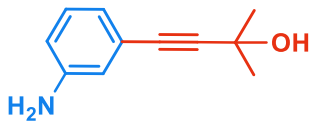
The product **3p** is prepared by general procedure for Heck-Cassar-Sonogashira cross-coupling (*Chapter 2.1.*). Yellow solid (91% yield); Extraction solvent: ^{t}BuOAc; Purification by flash chromatography (Cy/EtOAc = 80/20).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 1.65 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.11 – 145.33 (dm, $J_{F\text{-}C}$ = 168,0 Hz), 141.22 – 139.60 (dm, $J_{F\text{-}C}$ = 173,0 Hz), 137.40 – 135.76 (dm, $J_{F\text{-}C}$ = 164,0 Hz), 105.35, 98.61, 65.41, 64.78, 30.01.

Anal. Calcd. for $C_{11}H_7F_5O$: C, 52.81; H, 2.82; F, 37.97; O, 6.40; found: C, 52.72; H, 2.98; F, 37.90; O, 6.54

4-(3-aminophenyl)-2-methylbut-3-yn-2-ol, ***3q***



The product **3q** is prepared by general procedure for Heck-Cassar-Sonogashira cross-coupling (*Chapter 2.1.*). Pale yellow solid (52%); Extraction solvent: ^{t}BuOAc; Purification by flash chromatography (Cy/EtOAc = 90/10)

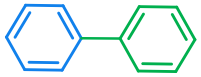
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.08 (t, J = 7.8 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.75 (s, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.67 (s, NH_2), 2.21 (s, OH), 1.61 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.13, 129.15, 123.38, 122.03, 117.91, 115.28, 93.17, 82.26, 65.53, 31.47.

Anal. Calcd for $C_{11}H_{12}NO$: C, 75.40; H, 7.48; N, 7.99; found: C, 75.50; H, 7.43; N, 7.95;

Yields of the SM reactions reported considering Scheme 4

1,1'-biphenyl, ***6a***



The product **6a** is prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

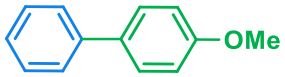
White solid (95% yield); extraction solvent: Cy

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69 – 7.66 (m, 4H), 7.54 – 7.49 (m, 4H), 7.44 – 7.40 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.28, 128.80, 127.29, 127.21.

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54; found: C, 93.37; H, 6.62.

4-methoxy-1,1'-biphenyl, ***6b-6e***



The products **6b-6e** are prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

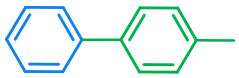
White solid (90 and 92% yield); extraction solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 – 7.52 (m, 4H), 7.45 – 7.41 (m, 2H), 7.33 – 7.29 (m, 1H), 7.00 – 6.98 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)159.11, 140.81, 133.76, 128.68, 128.12, 126.71, 126.62, 114.17, 55.32.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57; O, 8.68; found: C, 84.77; H, 6.51; O, 8.70.

4-methyl-1,1'-biphenyl, ***6c-6f***



The products **6c-6f** are prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

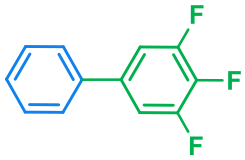
White solid (94 and 93% yield), extraction solvent: Cy

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68 – 7.66 (m, 2H), 7.60 – 7.58 (m, 2H), 7.53 – 7.49 (m, 2H), 7.43 – 7.39 (m, 1H), 7.35 – 7.33 (d, J = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.22, 138.44, 137.06, 129.57, 128.79, 127.04, 127.02, 21.14.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19; found: C, 92.75; H, 7.23.

3,4,5-trifluoro-1,1'-biphenyl, ***6d***



The product **6d** is prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

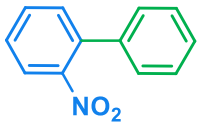
White solid (92% yield); extraction solvent: Cy

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.42 (m, 5H), 7.22 – 7.18 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.72 – 152.58 (dd, J_{C-F} = 9.9, 4.2 Hz), 150.25 – 150.11 (dd, J_{C-F} = 10.1, 4.4 Hz), 140.63 – 140.32 (t, J_{C-F} = 15.1 Hz), 138.17 – 137.43 (m), 137.45 – 137.25 (m), 129.06, 128.37, 126.81, 111.10 – 110.88 (dd, J_{C-F} = 16.1, 6.0 Hz).

Anal. Calcd. for $C_{12}H_7F_3$: C, 69.23; H, 3.39; F, 27.38; found: C, 69.20; H, 3.45; F, 27.44.

2-nitro-1,1'-biphenyl, ***6g***



The product **6g** is prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

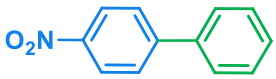
Yellow oil (95% yield); extraction solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89– 7.87 (dd, J = 8.0, 1.3 Hz, 1H), 7.65 – 7.61 (td, J = 7.6, 1.3 Hz, 1H), 7.52 – 7.44 (m, 5H), 7.38 – 7.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.32, 137.42, 136.32, 132.31, 131.97, 128.70, 128.24, 128.20, 127.91, 124.06.

Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03; O, 16.06; found: C, 72.39; H, 4.52; N, 7.01; O, 16.09.

4-nitro-1,1'-biphenyl, ***6h***



The product **6h** is prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

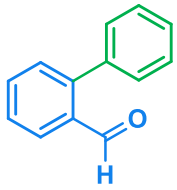
Yellow solid (94% yield); extraction solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 – 8.30 (m, 2H), 7.76 – 7.74 (m, 2H), 7.65 (m, 2H), 7.54 – 7.46 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.61, 147.07, 138.75, 129.16, 128.89, 127.80, 127.36, 124.08.

Anal. Calcd. for $C_{12}H_{14}$: C, 72.35; H, 4.55; N, 7.03; O, 16.06; found: C, 72.25; H, 4.61; N, 7.07; O, 15.9.

[1,1'-biphenyl]-2-carbaldehyde, ***6i***



The product **6i** is prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

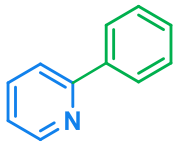
Colorless oil (95% yield), extractions solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.88 (s, 1H), 7.94 – 7.92 (J= 8.0 Hz, d, 1H), 7.54-7.52 (m, 1H), 7.40 – 7.33 (m, 5H), 7.28-7.27 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.42, 145.97, 137.77, 133.74, 133.57, 130.79, 130.12, 128.45, 128.14, 127.79, 127.58

Anal. Calcd. for $C_{13}H_{10}O$, C, 85.69; H, 5.53; O, 8.78; found 85.70; H, 5.51; O, 8.76

2-phenylpyridine, ***6j***



The product **6j** is prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.1.*).

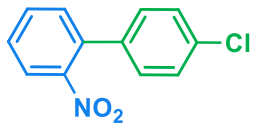
Colourless oil (93% yield). Extraction solvent: ^{t}BuOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 8.71 (d, J = 3.5 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.75 (m, 2H), 7.50 – 7.42 (m, 3H), 7.23 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.44, 148.63, 138.37, 135.70, 127.91, 127.71, 125.88, 121.05, 119.53.

Anal. Calcd. for $C_{11}H_9N$: C, 85.13; H, 5.85; N, 9.03; found: C, 85.16; H, 5.89; N, 9.01

4'-chloro-2-nitro-1,1'-biphenyl, ***6k***



The product **6k** is prepared by general procedure for Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

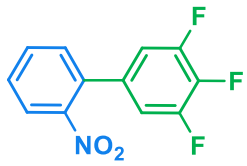
Yellow solid (95% yield); extractions solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 – 7.87 (dd, J = 8.1, 1.3 Hz, 1H), 7.65 – 7.61 (td, J = 7.6, 1.3 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.43 – 7.39 (m, 3H), 7.27 – 7.25 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.03, 135.95, 135.15, 134.41, 132.55, 131.85, 129.30, 128.89, 128.61, 124.25.

Anal. Calcd. for $C_{12}H_8ClNO_2$: C, 61.69; H, 3.45; Cl, 15.17; N, 5.99; O, 13.69; found: C, 61.74; H, 3.38; Cl, 15.13; N, 6.04; O, 13.74.

3',4',5'-trifluoro-2-nitro-1,1'-biphenyl, ***6l***



The product **6l** is prepared by general procedure Suzuki-Miyaura cross-coupling (*Chapter 2.2.*).

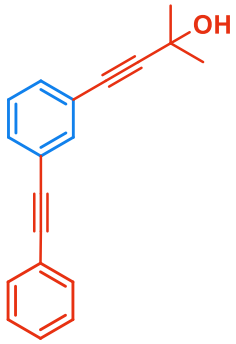
Yellow solid (97% yield); extractions solvent: Cy

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 – 7.93 (dd, J = 8.1, 1.3 Hz, 1H), 7.69 – 7.65 (td, J = 7.5, 1.3 Hz, 1H), 7.60 – 7.55 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.41 – 7.39 (dd, J = 7.6, 1.5 Hz, 1H), 6.97 – 6.94 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.41 – 152.27 (dd, J^F = 10.3, 4.2 Hz), 149.92 – 149.77 (dd, J^F = 10.1, 4.4 Hz), 148.68, 141.19 – 140.89 (t, J^F = 15.1 Hz), 138.68 – 138.38 (t, J^F = 15.1 Hz), 133.51 – 133.46 (m), 132.79, 131.63, 129.37, 124.49, 112.68 – 112.46 (dd, J^F = 16.1, 6.0 Hz).

Anal. Calcd. for $C_{12}H_6F_3NO_2$: C, 56.93; H, 2.39; F, 22.51; N, 5.53; O, 12.64; found: C, 56.98; H, 2.35; F, 22.46; N, 5.61; O, 12.60.

2-methyl-4-(3-(phenylethynyl)phenyl)but-3-yn-2-ol, ***9***



The product **9** is prepared by one-pot Heck-Cassar cross-coupling (*Chapter 4.1.*).

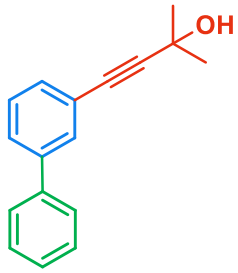
Yellow oil (92% yield); extractions solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63 (s, 1H), 7.56 – 7.53 (m, 2H), 7.49 – 7.47 (m, 1H), 7.40 – 7.30 (m, 5H), 1.65 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 134.68, 131.62, 131.29, 128.47, 128,37, 123.53, 123.08, 122.98, 94.39, 89.94, 88.47, 81.35, 65.58, 31.43.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.20; O, 6.15; found: C, 87.61; H, 6.29; O, 6.14.

4-([1,1'-biphenyl]-3-yl)-2-methylbut-3-yn-2-ol, ***10***



The product **10** is prepared by a one-pot Heck-Cassar and Suzuki-Miyaura cross-coupling (*Chapter 4.2.*).

Yellow oil (96% yield); extractions solvent: ^{t}BuOAc

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 – 7.55 (m, 4H), 7.49 – 7.38 (m, 5H), 1.70 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.34, 140.32, 130.45, 128.89, 128.79, 127.66, 127.11, 123.30, 94.13, 82.21, 65.70, 31.57.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.82; O, 6.77; found: C, 86.44; H, 6.74; O, 6.81.

9. Calculation of Relative Response Factor (RRF)

In HPLC with UV-DAD, the response of the detector is the absorbance of the compound at a fixed wavelength. Exploiting the Lambert-Beer law, it is possible to evaluate the RRF.

$$A = l \cdot c \cdot \varepsilon$$

Where:

ε is the molar attenuation coefficient or absorptivity (corresponding to the absorbance of a 1M solution).

c is expressed in molarity (mol/L).

The response factor, in analytical chemistry, is defined as the ratio between the molar concentration of a compound being analyzed and the response of the detector to that compound. In this way, the calculation of RRF is described below:

$$Response\ Factor\ (RF) = \frac{Peak\ Area}{Concentration\ [M]}$$

Thus, considering two substances in which one is the product (B) and the second is the reagent (A), the RRF is:

$$RF = \frac{RF_A}{RF_B} = \frac{PeakArea_A / Concentration_A}{PeakArea_B / Concentration_B} = \frac{PeakArea_A}{PeakArea_B} \cdot \frac{Concentration_B}{Concentration_A}$$

Table S6: Calculation of RRF between chlorobenzene **1a** and diphenylacetylene **3a** at several concentrations

Concentration (M)	Chlorobenzene area (mAu)	Diphenylacetylene area (mAu)	RRF	Δ_{RRF}
0,0025	2142.2	5633.3	2.63	
0,0005	438.7	1126.4	2.57	**2.59**
0,00025	256.0	658.6	2.57	

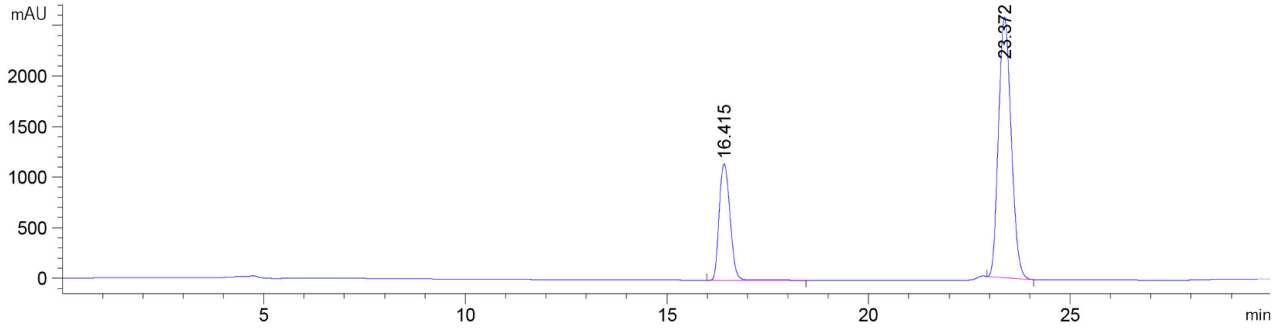


Figure S7: HPLC-UV spectrum of equimolar mixture of chlorobenzene **1a** and diphenylacetylene **3a** at 0.0025 M concentration

Table S7: Calculation of RRF between chlorobenzene **1a** and biphenyl **6a** at several concentrations

Concentration (M)	Chlorobenzene area (mAu)	Biphenyl area (mAu)	RRF	Δ_{RRF}
0,0025	1923.8	4230.5	2.19	
0,0005	496.3	1124.2	2.26	**2.23**
0,00025	351.0	790.1	2.25	

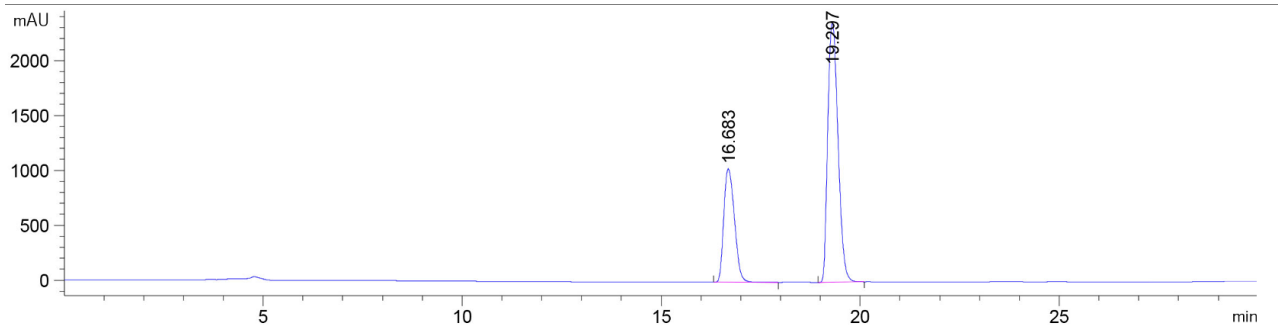


Figure S8: HPLC-UV spectrum of equivuimolar mixture of chlorobenzene **1a** and biphenyl **6a** at 0.0025 M concentration

Table S8: Calculation of RRF between diphenylacetylene **3a** and 1,4-diphenyl-1-buten-3-yne **4a** at several concentrations.

Concentration (M)	Diphenylacetylene area (mAu)	1,4-diphenyl-1-buten-3-yne area (mAu)	RRF	Δ_{RRF}
0,0025	75423.4	59859.8	1.26	**1,24**
0,0005	17645.2	13573.2	1.30	
0,00025	7982.4	6597.0	1.21	
0,000025	3426.5	2879.4	1.19	

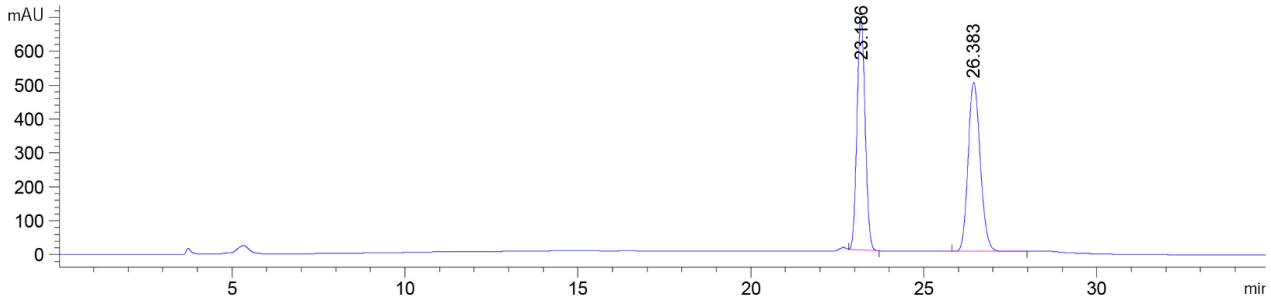


Figure S9: HPLC-UV spectrum of equivuimolar mixture of diphenylacetylene **3a** and 1,4-diphenyl-1-buten-3-yne **4** at 0.0005 M concentration.

10. Computational Methods

DFT calculations were conducted at CINECA, through the Italian SuperComputing Resource Allocation – ISCRA, using the Gaussian 16 software package[6]. Geometry optimizations for all reported structures were performed with the dispersion corrected B3LYP-D3 functional with a mixed basis set of LANL2DZ (for Pd, I, Br, Cl) and 6-31G(d) (for other atoms).[7] Frequency calculations were performed on all optimized structures to ensure that each local minimum lacked imaginary frequency and that each transition state contained exactly one imaginary frequency. Solvation in DMF were introduced through single point calculations at optimized gas-phase geometries for all the minima and transition state using def2-TZVP for all atoms and the SMD implicit solvation model.[8] The reported Gibbs free energies were corrected considering the thermal correction computed at 298.15 K.

Computed free energy profile of 4-NO_2-phenyl halides

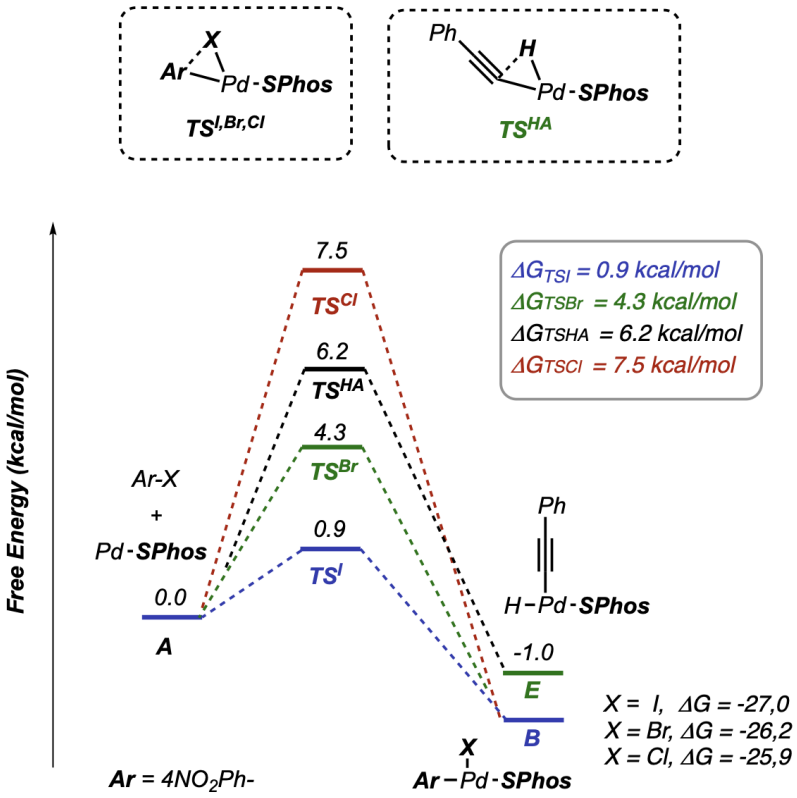


Figure S10. DFT calculations in DMF of the OA of 4-NO2-Phenyl halides and the first step of the phenylacetylene insertion to give the enyne byproduct **4**.

Cartesian Coordinates (Å) of Optimized Structures

PhI

E (DMF) = - 529.48941

C	-2.66243000	-1.20718400	0.00000100
C	-1.26514500	-1.21595700	-0.00000100
C	-0.58205300	-0.00002000	-0.00000400
C	-1.26513600	1.21594900	-0.00000300
C	-2.66239500	1.20720400	0.00000200
C	-3.36283100	0.00000600	0.00000000
H	-3.19930500	-2.15148900	0.00000600
H	-0.72316200	-2.15489400	-0.00000400
H	-0.72310800	2.15486100	-0.00000500
H	-3.19928900	2.15149800	0.00000800
H	-4.44859100	0.00003500	-0.00000200
I	1.56780000	0.00000000	0.00000000

PhBr

E (DMF) = - 2805.873389

C	-2.20544000	-1.20824800	0.00000100
C	-0.80819800	-1.21817700	-0.00000600
C	-0.13437400	-0.00001600	-0.00000600
C	-0.80819200	1.21816900	-0.00000500
C	-2.20541200	1.20826600	0.00000000
C	-2.90496400	0.00000400	0.00000400
H	-2.74317300	-2.15189000	0.00001100
H	-0.25710600	-2.15151500	-0.00001100
H	-0.25706100	2.15148500	-0.00000700
H	-2.74316400	2.15189700	0.00000900
H	-3.99062100	0.00002900	0.00000500
Br	1.83973200	0.00000000	0.00000200

PhCl

E (DMF) = - 691.916436

C	-1.58336400	-1.20850600	0.00000000
C	-0.18671300	-1.21806400	0.00001800
C	0.48580500	-0.00000500	-0.00001400
C	-0.18670800	1.21805500	-0.00000300
C	-1.58335000	1.20851600	0.00002000
C	-2.28297600	0.00000200	-0.00001700
H	-2.12124800	-2.15177700	-0.00000300
H	0.37067900	-2.14757000	0.00001100
H	0.37070100	2.14755300	-0.00001200
H	-2.12124400	2.15177900	0.00002300
H	-3.36845200	0.00001600	-0.00003100
Cl	2.28784700	0.00000000	-0.00000100

PhI^{NO2}

E (DMF) = -734.086546

C	1.66221200	1.21885400	0.00009200
C	0.26923300	1.21814200	0.00004700
C	-0.41590200	0.00000000	0.00002600
C	0.26923300	-1.21814200	0.00004700
C	1.66221100	-1.21885400	0.00009200
C	2.33675700	0.00000000	0.00011500
H	2.22656500	2.14302400	0.00011000
H	-0.27146200	2.15727700	0.00003000
H	-0.27146300	-2.15727600	0.00003000
H	2.22656500	-2.14302300	0.00011000
I	-2.55345000	0.00000000	-0.00004300
N	3.80933200	0.00000000	0.00016500
O	4.37842800	-1.09067500	-0.00010500
O	4.37842800	1.09067500	-0.00010400

PhBr^{NO2}

E (DMF) = -3010.469407

C	-2.20544000	-1.20824800	0.00000100
C	-0.80819800	-1.21817700	-0.00000600
C	-0.13437400	-0.00001600	-0.00000600
C	-0.80819200	1.21816900	-0.00000500
C	-2.20541200	1.20826600	0.00000000
C	-2.90496400	0.00000400	0.00000400
H	-2.74317300	-2.15189000	0.00001100
H	-0.25710600	-2.15151500	-0.00001100
H	-0.25706100	2.15148500	-0.00000700
H	-2.74316400	2.15189700	0.00000900
Br	1.83973200	0.00000000	0.00000200
N	-4.37496400	0.00003785	0.00000535
O	-4.94525411	1.05511511	0.00000865
O	-4.94528735	-1.05501667	0.00000202

PhCl^{NO2}

E (DMF) = -896.512823

C	0.43603300	1.22015700	-0.00000400
C	-0.95617800	1.22064100	0.00000700
C	-1.62959300	0.00000000	0.00001200
C	-0.95617800	-1.22064100	0.00000600
C	0.43603300	-1.22015700	-0.00000500
C	1.10998600	0.00000000	-0.00001000
H	1.00157000	2.14336500	-0.00000900
H	-1.51227800	2.15049100	0.00001200
H	-1.51227800	-2.15049100	0.00001100
H	1.00157000	-2.14336400	-0.00001000
Cl	-3.41933800	0.00000000	0.00002700
N	2.58279300	0.00000000	-0.00002400
O	3.15187500	-1.09068300	-0.00002200
O	3.15187500	1.09068300	-0.00001900

DMF

E (DMF) = - 248.558162

C	-0.82327700	-0.69498100	-0.00018200
O	-1.92170700	-0.16087000	0.00016600
N	0.35768800	-0.01634700	-0.00029000
H	-0.68364300	-1.79529300	-0.00003500
C	0.30255500	1.44168600	0.00002400
H	-0.23238300	1.80716400	0.88222100
H	1.31898200	1.83951900	0.00348000
H	-0.22659300	1.80805900	-0.88533300
C	1.64408800	-0.68663000	0.00012500
H	2.23170900	-0.42382400	-0.88842000
H	2.23043000	-0.42552900	0.89004400
H	1.49114200	-1.76916100	-0.00106600

PdSPhos

E (DMF) = - 1880.265963

H	-3.61593000	-3.38653600	0.25914500
H	-2.92366200	0.92924900	-1.34270300
H	-3.72866000	-1.39898300	-1.20715900
H	-0.57117300	5.20658600	-0.12292300
H	-3.53641900	0.16820600	-2.85031100
C	-2.70275500	-2.97892400	-0.16516100
C	-2.77418200	-1.86277000	-0.99579800
C	-2.66222500	0.62319100	-2.36307200
H	0.61730100	6.31947700	-0.79798700
H	1.33723700	5.45308500	1.45031700
H	-2.35360900	1.49967600	-2.93564800
C	0.44929100	5.26969300	-0.52783100
H	0.27206800	3.19961400	1.38902500
H	-1.45833700	-4.45345700	0.78140400

H	-0.65841600	2.73646200	-1.01591700
Pd	-0.96696700	0.36048100	1.10700700
H	-0.18798400	4.67082500	-2.52141300
C	1.44447000	4.82856700	0.55492800
C	-1.48541400	-3.58828900	0.13136000
C	-1.59098800	-1.33972100	-1.53240000
O	-1.54565900	-0.24914300	-2.35283200
C	1.25663600	3.34826000	0.92496400
C	0.55188200	4.37081700	-1.76853000
H	2.00245300	3.05754600	1.67409700
C	0.35871500	2.89214000	-1.40170200
H	2.46876400	4.98364100	0.18563800
H	0.72154400	-4.18605000	1.77420100
C	-0.31132900	-3.06680300	-0.42983000
C	-0.34936900	-1.93839500	-1.26198400
H	1.54032100	4.50519300	-2.23132800
C	1.35657900	2.44092100	-0.31610900
H	0.45616700	2.25850600	-2.29041200
P	1.02406700	0.64868000	0.13359700
H	2.14920900	0.77530800	2.22330700
H	0.57396300	-5.49908200	0.56642400
H	1.31027400	-1.53534100	1.99577000
C	1.08841600	-4.55971900	0.80961700
O	0.93315400	-3.59120800	-0.21453800
H	3.06025600	-1.15742000	3.71178300
H	2.37194800	2.54042700	-0.72016800
C	2.41957500	0.20427300	1.32397900
H	2.16078300	-4.74942300	0.88215100
C	0.89045900	-1.39262500	-1.88807000
C	2.33196300	-1.29345900	1.68039500
C	1.55137600	-0.23239800	-1.42736200
C	3.33641000	-1.67057800	2.77939500
H	3.27892200	-2.74700600	2.98610000
H	4.62853500	0.81198500	2.93640800
H	0.85512200	-2.95940300	-3.35028500
H	2.52774600	-1.88988700	0.78080200
H	3.93179700	1.65130100	0.69936700

C	1.37551100	-2.06543400	-3.01958800
C	3.85689400	0.58099900	0.92604300
C	4.85275200	0.21516500	2.04063400
C	2.66137000	0.22464900	-2.16227600
C	4.76931000	-1.27687800	2.39315000
H	5.46732000	-1.51835000	3.20417800
H	3.18259800	1.12184800	-1.84974700
H	4.13524800	0.03946000	0.01403100
C	2.48629400	-1.60526700	-3.72020100
H	5.87225900	0.47983500	1.73367900
H	5.08149000	-1.86812000	1.52020200
C	3.12733200	-0.44344500	-3.29290500
H	2.84080000	-2.14241300	-4.59547800
H	3.98825900	-0.05767900	-3.83206200
C	-3.70856300	0.98884400	1.40838300
O	-2.93508600	0.36583500	2.15264500
N	-4.85852400	0.47868500	0.90784200
H	-3.52153000	2.03266400	1.11197900
C	-5.76136100	1.28068700	0.10284100
H	-5.91791100	0.81643100	-0.87838300
H	-6.73655600	1.38702200	0.59403000
H	-5.33887400	2.27691300	-0.04913600
C	-5.26495100	-0.88059300	1.23285300
H	-4.41357900	-1.40056400	1.66941800
H	-6.09896600	-0.87497400	1.94561100
H	-5.58547500	-1.40100800	0.32430400

PhCCH

E (DMF) = - 308.448227

C	-1.51232600	-1.20901900	-0.00000500
C	-0.11946500	-1.21382800	0.00000300
C	0.59407500	-0.00002000	0.00001300
C	-0.11944700	1.21381800	0.00000400
C	-1.51229400	1.20903900	-0.00000700
C	-2.21276500	0.00001200	-0.00000800

H	-2.05286700	-2.15109200	-0.00000800
H	0.42908700	-2.15022800	0.00000700
H	0.42914500	2.15019500	0.00000900
H	-2.05283200	2.15111500	-0.00001000
H	-3.29885300	0.00003300	-0.00001500
C	2.02332600	-0.00001400	0.00002900
C	3.23348800	0.00000300	0.00000300
H	4.29876700	0.00002500	-0.00017700

TS^{I}

E (DMF) = - 2161.195471

C	-2.09112000	-1.71719900	-1.10503100
C	-0.92267100	-2.39476200	-1.49553500
C	-0.53462200	-3.58128900	-0.86117700
C	-1.31821300	-4.08302200	0.17388400
C	-2.48538600	-3.44027900	0.58282700
C	-2.87069400	-2.26353800	-0.07105700
C	-2.54049000	-0.48878700	-1.82903500
C	-2.08425500	0.80827700	-1.50211300
C	-2.59523500	1.89756200	-2.22756300
C	-3.51967500	1.72066700	-3.25681000
C	-3.96105900	0.43871700	-3.57830800
C	-3.47340100	-0.65143300	-2.86102600
H	0.37615800	-4.09187000	-1.14198100
H	-3.07780900	-3.85583500	1.38771900
H	-2.27664100	2.90660600	-1.99362800
H	-3.89310100	2.58441900	-3.79978300
H	-4.68074600	0.28734300	-4.37774800
H	-3.81462700	-1.65546700	-3.09512500
P	-0.88051400	1.02761600	-0.10857900
Pd	1.15538200	-0.17888500	0.07694900
C	-4.82031200	-2.01855700	1.30263000
H	-4.27194200	-2.04563300	2.25342800
H	-5.63990600	-1.30242400	1.38322400

H	-5.22949600	-3.01592100	1.09567600
C	0.97091100	-2.43571800	-2.95438900
H	1.70139000	-2.53038300	-2.14261800
H	0.76867000	-3.42852400	-3.37789500
H	1.37407600	-1.78714800	-3.73382100
H	-1.01045400	-4.99519900	0.67654200
O	-4.00374100	-1.55573100	0.23901100
O	-0.22287600	-1.80771400	-2.50818000
C	-0.31321900	2.81227900	-0.28267500
C	0.46436100	3.28060500	0.96664400
C	0.57382100	2.96084100	-1.54059200
H	-1.19412700	3.45936900	-0.38562200
C	0.99346600	4.71424300	0.79727100
H	1.30964500	2.60172800	1.13822400
H	-0.16965600	3.22930900	1.85683800
C	1.09084800	4.39747500	-1.70544800
H	1.43307100	2.28291900	-1.44448900
H	0.03032500	2.64694500	-2.43757500
C	1.86310900	4.85091000	-0.45953400
H	1.56116400	5.00359600	1.69014200
H	0.14366100	5.40874300	0.72736800
H	1.72784400	4.46059800	-2.59592800
H	0.24237000	5.07607700	-1.87654600
H	2.20943100	5.88509600	-0.57500900
H	2.75725800	4.22209900	-0.34770900
C	-2.06478900	0.98156000	1.34779300
C	-1.36567200	0.66597700	2.68364700
C	-3.00531400	2.19386100	1.46664000
H	-2.69108900	0.11769600	1.10022700
C	-2.40228200	0.45470700	3.79886600
H	-0.69690700	1.48816200	2.96739700
H	-0.73566700	-0.22324700	2.56841400
C	-4.03677800	1.96797400	2.58502300
H	-2.42719600	3.09925100	1.69409100
H	-3.51505700	2.36985000	0.51253700
C	-3.35121100	1.65639600	3.92384200
H	-1.89568400	0.26535800	4.75279400

H	-2.99052400	-0.44644700	3.57234900
H	-4.68653000	2.84628300	2.68225100
H	-4.68514100	1.12553000	2.30473600
H	-4.10088800	1.47243700	4.70293700
H	-2.77486200	2.53633600	4.24433800
C	3.20007600	-0.24049500	0.17481400
C	3.57708000	0.69283500	1.16251600
C	3.65232600	-0.10554800	-1.15284400
C	4.32713900	1.80891300	0.78742400
H	3.27964900	0.54202200	2.19376700
C	4.39849400	1.02328500	-1.50210700
H	3.41558700	-0.86228200	-1.89127300
C	4.73348100	1.97993300	-0.54003100
H	4.59629800	2.54608400	1.53888800
H	4.72257500	1.14849400	-2.53163800
H	5.32139600	2.84882200	-0.81979200
I	2.69487400	-2.44937900	0.95840400

B^I

E (DMF) = - 2161.24222

C	-1.58559700	-1.96799700	0.62620300
C	-2.55760700	-1.27228800	1.39017000
C	-3.84677400	-1.06115800	0.88959400
C	-4.15724100	-1.50315100	-0.39055900
C	-3.22342200	-2.16571500	-1.18647200
C	-1.95198300	-2.41891500	-0.66733200
C	-0.39688300	-2.56187700	1.32617800
C	0.91272200	-2.05080100	1.26429200
C	1.93366700	-2.70437000	1.97571800
C	1.67194900	-3.84285000	2.73453300
C	0.37441400	-4.35102900	2.79145400
C	-0.64476700	-3.71199600	2.09109000
H	-4.57932300	-0.50777800	1.46001200
H	-3.49550200	-2.48420300	-2.18401000
H	2.94739900	-2.32091300	1.95131900

H	2.47769800	-4.32637000	3.27910700
H	0.15566900	-5.23658300	3.38093800
H	-1.65920800	-4.09673000	2.13559700
P	1.23568200	-0.57542600	0.20568500
Pd	-0.76086600	0.63216300	-0.07978600
C	-1.22715300	-3.50960100	-2.67260200
H	-1.41180400	-2.63016600	-3.30190700
H	-0.31523000	-4.00790300	-3.00534400
H	-2.07168900	-4.20399000	-2.76015300
C	-2.92145700	0.12403200	3.29022200
H	-3.09320200	0.98772300	2.63737400
H	-3.88175900	-0.28127700	3.63316200
H	-2.33184500	0.42469600	4.15734400
H	-5.14540900	-1.30333100	-0.79160800
O	-0.99371000	-3.13922200	-1.31945200
O	-2.14349400	-0.86883200	2.62073000
C	2.75526300	0.18853000	0.98055700
C	3.42318700	1.28434200	0.12377700
C	2.43410200	0.70514400	2.39876100
H	3.48419800	-0.62796800	1.07139600
C	4.68108300	1.82484400	0.82222500
H	2.72883900	2.10804500	-0.03859900
H	3.68699500	0.89312300	-0.86379000
C	3.68924500	1.27239800	3.07995300
H	1.67668200	1.49104300	2.32243100
H	2.00313600	-0.09598500	3.00838800
C	4.34989900	2.36047500	2.22175900
H	5.12714300	2.61415100	0.20605800
H	5.43167300	1.02491000	0.90569400
H	3.42465700	1.66809400	4.06767500
H	4.40894600	0.45825300	3.25050200
H	5.25495200	2.73739800	2.71265300
H	3.66042300	3.20961800	2.12119700
C	1.78690600	-1.39183800	-1.39347500
C	1.63248700	-0.48087300	-2.62638700
C	3.17777600	-2.05108200	-1.33693600
H	1.04315200	-2.19117800	-1.48702700

C	1.94719800	-1.25227400	-3.91792600
H	2.29852500	0.38682300	-2.54719800
H	0.61056500	-0.08850600	-2.66211400
C	3.46734100	-2.81844900	-2.63818400
H	3.95271500	-1.28665400	-1.19922100
H	3.24072900	-2.73236500	-0.48147000
C	3.33518100	-1.90583500	-3.86550700
H	1.86971800	-0.58038700	-4.78070200
H	1.18744800	-2.03443000	-4.06025800
H	4.46915100	-3.26200400	-2.59386400
H	2.75726500	-3.65303200	-2.72766900
H	3.52689100	-2.47164600	-4.78480600
H	4.10212700	-1.11985400	-3.81361200
C	0.19730900	2.37799100	-0.29845300
C	0.69127800	2.78864600	-1.53922700
C	0.38452400	3.18673000	0.82654700
C	1.42728000	3.97437200	-1.63796700
H	0.50921900	2.19661900	-2.42799000
C	1.12407600	4.36972900	0.72119600
H	-0.04464900	2.90642100	1.78276300
C	1.66020200	4.76045000	-0.50770100
H	1.81751100	4.28047900	-2.60530500
H	1.27258500	4.98691400	1.60370600
H	2.23735800	5.67715400	-0.58681000
I	-3.00069400	2.03650300	-0.66155100

TS^{Br}

E (DMF) = - 4437.56995

C	-2.19254800	-1.61796700	-0.92659100
C	-1.14032400	-2.51583400	-1.18060900
C	-0.94980400	-3.64501900	-0.37451000
C	-1.81747000	-3.86973200	0.69046100
C	-2.87811700	-3.00726400	0.96284200
C	-3.06396200	-1.88811200	0.14204700
C	-2.41365900	-0.43292900	-1.81025000

C	-1.76444800	0.80544300	-1.60374200
C	-2.06119300	1.86917300	-2.47205900
C	-2.96232500	1.72012100	-3.52609300
C	-3.59435300	0.49472300	-3.72870300
C	-3.31962500	-0.56718100	-2.86960600
H	-0.12167900	-4.31891400	-0.54491500
H	-3.54087700	-3.21115300	1.79392000
H	-1.58896100	2.83488900	-2.33307400
H	-3.16862100	2.56145100	-4.18176500
H	-4.29763700	0.36595700	-4.54649000
H	-3.81038700	-1.52541900	-3.01164000
P	-0.59580200	0.99318400	-0.17750000
Pd	1.14710700	-0.57697400	0.29183600
C	-4.97544700	-1.16155200	1.39338600
H	-4.45698000	-1.14473600	2.36102600
H	-5.67330700	-0.32371000	1.34714500
H	-5.53253800	-2.10288200	1.30124100
C	0.75080700	-3.04373100	-2.54726000
H	1.44754300	-3.12473000	-1.70511700
H	0.40792900	-4.04702000	-2.83295800
H	1.25541100	-2.58162100	-3.39745500
H	-1.66183000	-4.73687900	1.32541100
O	-4.07545100	-0.97741100	0.31238400
O	-0.34296700	-2.18953200	-2.23769400
C	0.31559500	2.59410500	-0.54807800
C	1.14455800	3.06389200	0.66688800
C	1.23811000	2.40844700	-1.77430300
H	-0.42063000	3.37764900	-0.77007600
C	1.93519300	4.34292400	0.34617700
H	1.84478200	2.26860200	0.95333500
H	0.49661900	3.24267400	1.53032200
C	2.02008200	3.69152900	-2.09268200
H	1.95052600	1.60133900	-1.55748100
H	0.66130400	2.08856700	-2.64804300
C	2.83818400	4.15580200	-0.88025000
H	2.53075300	4.63480000	1.21978100
H	1.23127900	5.16641200	0.15689400

H	2.67599100	3.51960100	-2.95464400
H	1.31775200	4.48574500	-2.38537500
H	3.37116400	5.08674000	-1.10859400
H	3.59864500	3.39653900	-0.65224100
C	-1.81752800	1.37617900	1.19694500
C	-1.24293100	1.11266500	2.60179700
C	-2.49515200	2.75506500	1.10609900
H	-2.59594300	0.62568500	1.01931300
C	-2.33556000	1.26653300	3.67206700
H	-0.42828900	1.81522100	2.81788000
H	-0.80642800	0.10802900	2.63786300
C	-3.58660900	2.89208400	2.18118200
H	-1.75247800	3.55061700	1.25155900
H	-2.92742700	2.89757200	0.10910100
C	-3.02163200	2.63824700	3.58669600
H	-1.90863400	1.11239800	4.67026800
H	-3.08894300	0.47848100	3.52840900
H	-4.04680100	3.88617600	2.12653200
H	-4.38370500	2.16386800	1.97353100
H	-3.81711800	2.71537300	4.33769400
H	-2.28788600	3.42184800	3.82487300
C	3.15832100	-0.83992900	0.43754800
C	3.66260500	-0.01209700	1.45491400
C	3.69864700	-0.82709200	-0.85923700
C	4.63503800	0.93242000	1.12125600
H	3.28643900	-0.10298900	2.46719300
C	4.66969200	0.12983300	-1.16468300
H	3.35104800	-1.53190200	-1.60522400
C	5.13453100	1.01062800	-0.18336900
H	5.00783300	1.60510400	1.88872800
H	5.06841000	0.17834800	-2.17423100
H	5.89816600	1.74226200	-0.42870800
Br	2.37202500	-2.86256100	1.16362400

B^{Br}

E (DMF) = - 4437.617727

C	2.47350900	0.69467300	0.56110500
C	2.97219300	-0.50554900	1.12626900
C	3.92444900	-1.27565900	0.44575400
C	4.35180200	-0.87010400	-0.81074200
C	3.87621900	0.29816100	-1.40836700
C	2.96224100	1.08878000	-0.71018500
C	1.76102200	1.68406600	1.43609200
C	0.36698000	1.88317300	1.44621600
C	-0.17641600	2.84788600	2.31173900
C	0.63608500	3.60317900	3.15460800
C	2.01641800	3.40530500	3.14279300
C	2.56658100	2.45412000	2.28797000
H	4.27760200	-2.20940800	0.85890500
H	4.22902000	0.58277400	-2.39086900
H	-1.24742300	3.01265100	2.34256500
H	0.19037600	4.33901100	3.81752900
H	2.66094700	3.98510200	3.79697300
H	3.63982900	2.28998000	2.27503800
P	-0.67883000	0.90397500	0.28196100
Pd	0.40932400	-1.10339400	-0.21984000
C	2.85747900	2.71345000	-2.46778200
H	2.52883900	1.98912700	-3.22361400
H	2.34097700	3.66133700	-2.62722500
H	3.93921900	2.86970600	-2.56050400
C	2.66732100	-2.15144800	2.82994300
H	2.32598900	-2.87789400	2.08386200
H	3.71706300	-2.34100000	3.08715200
H	2.05989700	-2.22854500	3.73274700
H	5.05886500	-1.49016400	-1.35212600
O	2.50134400	2.29461900	-1.15662700
O	2.48087900	-0.81562300	2.35545200
C	-2.36512200	0.92052400	1.08735500
C	-3.50670200	0.41913000	0.17772000
C	-2.33560800	0.14890500	2.42347100
H	-2.57749800	1.97576700	1.30560900
C	-4.85690600	0.50828400	0.90647400

H	-3.32873300	-0.61678900	-0.10978800
H	-3.54586800	1.00255300	-0.74747700
C	-3.69712200	0.21642200	3.13264200
H	-2.08563000	-0.89633200	2.21898000
H	-1.54981900	0.54345400	3.07605500
C	-4.82857500	-0.28128500	2.22223000
H	-5.64907100	0.12999700	0.24998400
H	-5.09547100	1.56123200	1.11768100
H	-3.65946900	-0.37146900	4.05734300
H	-3.90094200	1.25577000	3.42947600
H	-5.79411000	-0.20560700	2.73618500
H	-4.66757600	-1.34360900	1.99386400
C	-0.76376900	2.06339300	-1.19111300
C	-1.11359200	1.35075200	-2.51128000
C	-1.62352500	3.32231700	-0.97062600
H	0.28102000	2.38479700	-1.26478300
C	-1.01187700	2.32177800	-3.69832800
H	-2.12684300	0.93365200	-2.46584400
H	-0.43294000	0.50532600	-2.65784900
C	-1.50103200	4.27801100	-2.16941500
H	-2.67770200	3.04362200	-0.84921200
H	-1.31705600	3.83460900	-0.05197900
C	-1.87169800	3.57520200	-3.48300700
H	-1.30162100	1.80990400	-4.62344500
H	0.03790100	2.62439200	-3.82275100
H	-2.13580700	5.15789600	-2.01079000
H	-0.46607000	4.64373700	-2.23206600
H	-1.76245700	4.26401800	-4.32892800
H	-2.93134700	3.28427100	-3.44861300
C	-1.29625600	-2.08954700	-0.54406300
C	-1.92410100	-2.05549100	-1.79105200
C	-1.85522700	-2.83363600	0.49868500
C	-3.14596000	-2.71328300	-1.97194100
H	-1.47683300	-1.52126400	-2.62059600
C	-3.07902200	-3.48494600	0.31178400
H	-1.34314500	-2.91599100	1.45144000
C	-3.73564800	-3.41492300	-0.91890900

H	-3.63492400	-2.67228500	-2.94196300
H	-3.51184600	-4.05361600	1.13093800
H	-4.68790600	-3.91776600	-1.06071100
Br	1.56147100	-3.29680700	-0.86327900

TS^{Cl}

E (DMF) = - 2323.60394

C	2.46838100	-1.32677600	0.61566600
C	1.71899400	-2.49255800	0.86101300
C	1.71146000	-3.54823100	-0.06055300
C	2.45598100	-3.42840000	-1.23100200
C	3.21936500	-2.29316000	-1.49817500
C	3.22633500	-1.24955100	-0.56403700
C	2.48037900	-0.21274700	1.61172500
C	1.52801500	0.83209700	1.60116000
C	1.63401300	1.84143600	2.57306800
C	2.64111500	1.82346900	3.53766200
C	3.57434100	0.78848600	3.54481000
C	3.48891900	-0.21614900	2.58335100
H	1.11244600	-4.43251500	0.10921200
H	3.79431900	-2.23229000	-2.41316600
H	0.92427400	2.66077000	2.58717000
H	2.69376300	2.61799300	4.27680200
H	4.36320900	0.76272100	4.29112900
H	4.21140800	-1.02683000	2.57552000
P	0.21683600	0.86848900	0.28801100
Pd	-0.85708200	-1.11732900	-0.41331600
C	4.69257600	0.08332700	-1.91274900
H	4.05273600	0.05121300	-2.80431600
H	5.15016600	1.07119100	-1.83608000
H	5.48085600	-0.67450300	-2.00913700
C	0.12493500	-3.57219600	2.28038000
H	-0.62605600	-3.66115300	1.48648400
H	0.66149800	-4.52454500	2.38507400
H	-0.36720200	-3.33454200	3.22481300

H	2.44136100	-4.23984400	-1.95265300
O	3.94173200	-0.09046900	-0.72164000
O	1.01828500	-2.49421400	2.02961100
C	-1.05644800	2.06601900	0.96180700
C	-2.11569500	2.41203600	-0.10479400
C	-1.74285800	1.47469100	2.21153500
H	-0.54895800	2.99806600	1.24311000
C	-3.17736100	3.37251700	0.45595900
H	-2.59930100	1.48907100	-0.44432300
H	-1.64544500	2.86420000	-0.98361400
C	-2.79438900	2.44126300	2.77815600
H	-2.22886700	0.53315600	1.92553200
H	-1.00330200	1.22735500	2.97988500
C	-3.84265500	2.80869900	1.71878300
H	-3.93204500	3.57447400	-0.31385400
H	-2.70439100	4.33650200	0.69377600
H	-3.27751300	1.99209900	3.65449800
H	-2.29509600	3.35582100	3.13031200
H	-4.56348100	3.52872700	2.12497900
H	-4.40652700	1.90735500	1.44734600
C	1.15005000	1.78866300	-1.06297600
C	0.55139400	1.57105700	-2.46615200
C	1.40495100	3.28025100	-0.78109000
H	2.12322100	1.28379300	-1.04332500
C	1.44831100	2.19901500	-3.54520800
H	-0.44898800	2.01773200	-2.52612200
H	0.42349400	0.49762900	-2.64741800
C	2.30628600	3.89241300	-1.86669800
H	0.45278700	3.82697200	-0.76294000
H	1.86610000	3.40494100	0.20511500
C	1.71130500	3.68653400	-3.26736200
H	0.99398700	2.06791800	-4.53471100
H	2.40870200	1.66389800	-3.56777900
H	2.46188500	4.95999000	-1.66896700
H	3.29589700	3.41567000	-1.81906100
H	2.37667700	4.10684100	-4.03115500
H	0.76280800	4.23826300	-3.33861300

C	-2.86276700	-1.64371600	-0.80181400
C	-3.30539300	-0.97013100	-1.95170000
C	-3.58358300	-1.60428100	0.40265200
C	-4.41011100	-0.12621500	-1.83822400
H	-2.77890500	-1.09596200	-2.89014300
C	-4.68546200	-0.75273600	0.48454000
H	-3.26880500	-2.20866500	1.24489500
C	-5.09911600	-0.00916100	-0.62598100
H	-4.73842600	0.43563400	-2.70819300
H	-5.22824400	-0.67846400	1.42274600
Cl	-1.88823500	-3.40417000	-1.16438900
H	-5.96452900	0.64165900	-0.55212900ù

B^{Cl}

E (DMF) = - 2323.657987

C	2.62438500	-0.15668600	0.43109900
C	2.83141900	-1.51768200	0.76571500
C	3.53786400	-2.36689500	-0.09811000
C	4.01106200	-1.86756800	-1.30235000
C	3.82353700	-0.53370700	-1.67148900
C	3.15637700	0.32086300	-0.79341200
C	2.17556600	0.80950200	1.48724700
C	0.86391300	1.31097500	1.60000900
C	0.56942200	2.22042600	2.63000800
C	1.54634300	2.62826000	3.53588600
C	2.84394100	2.13020000	3.42325200
C	3.14867500	1.23095100	2.40498500
H	3.65894600	-3.41453400	0.13558500
H	4.20704300	-0.17780600	-2.61867100
H	-0.43464800	2.61372200	2.74110500
H	1.29140500	3.32847800	4.32598900
H	3.61377300	2.43717800	4.12514900
H	4.15525700	0.83478100	2.31156000
P	-0.39933100	0.79063400	0.35692000
Pd	0.17578300	-1.31400800	-0.45113000

C	3.40962600	2.20032800	-2.25711100
H	2.89416000	1.71717700	-3.09674300
H	3.14008700	3.25733000	-2.22812400
H	4.49385700	2.10597400	-2.39418200
C	2.19278000	-3.30837200	2.21382100
H	1.65658100	-3.79481500	1.39161900
H	3.17256500	-3.78047200	2.35951800
H	1.61841400	-3.38807400	3.13784000
H	4.52420100	-2.53716900	-1.98507400
O	2.99249700	1.66007300	-1.01023600
O	2.32537900	-1.90481400	1.96652600
C	-2.02354900	1.05667100	1.24145400
C	-3.26441600	0.97392000	0.32688400
C	-2.14834000	0.09532300	2.44229100
H	-1.98530000	2.08418300	1.62737500
C	-4.54681200	1.24242700	1.13032900
H	-3.33197500	-0.01563200	-0.12476200
H	-3.18494100	1.69232200	-0.49510100
C	-3.44764600	0.34831600	3.22252700
H	-2.14355100	-0.93326000	2.06987400
H	-1.28317700	0.19772800	3.10555400
C	-4.67692100	0.26537900	2.30679800
H	-5.41489900	1.15979500	0.46611300
H	-4.53628800	2.27412100	1.51206500
H	-3.52934800	-0.37325500	4.04394400
H	-3.40589600	1.34593800	3.68393300
H	-5.59181300	0.46920600	2.87560500
H	-4.76440100	-0.75550900	1.91086500
C	-0.23789800	2.15694600	-0.91881900
C	-0.75705600	1.75705500	-2.31275900
C	-0.78799900	3.52326700	-0.46788100
H	0.85131200	2.24748200	-0.99304200
C	-0.45817200	2.85796000	-3.34291700
H	-1.83719900	1.57024600	-2.28078700
H	-0.28463900	0.81752300	-2.61906600
C	-0.47208000	4.60603300	-1.51345800
H	-1.87578800	3.46839900	-0.33620200

H	-0.35943300	3.80294800	0.50085000
C	-1.01178900	4.21865800	-2.89753000
H	-0.86937100	2.57535800	-4.31906100
H	0.63063700	2.93939300	-3.47269500
H	-0.89012500	5.56739800	-1.19211000
H	0.61750700	4.74054100	-1.57264400
H	-0.76441600	4.99198900	-3.63423000
H	-2.10898800	4.16490500	-2.85363200
C	-1.70880200	-1.81795200	-0.85742500
C	-2.30787400	-1.44997100	-2.06377000
C	-2.42037400	-2.58209700	0.07148300
C	-3.64269800	-1.79209300	-2.30936800
H	-1.75240600	-0.89621600	-2.81089200
C	-3.75555400	-2.91548100	-0.17842800
H	-1.94240000	-2.92550400	0.98260800
C	-4.37560200	-2.50903100	-1.36222800
H	-4.10664200	-1.49146200	-3.24537600
H	-4.30564300	-3.50156700	0.55344300
Cl	0.75320500	-3.52509300	-1.27109900
H	-5.41397300	-2.76503800	-1.55208100

TS^{HA}

E (DMF) = - 1940.146347

C	0.73964800	-2.23801700	0.93773900
C	-0.60070500	-2.14946200	1.37607800
C	-1.62829500	-2.79715400	0.66623300
C	-1.30609800	-3.54447900	-0.46174800
C	0.01067300	-3.67138400	-0.90353000
C	1.02736400	-3.01858200	-0.19842100
C	1.83981000	-1.58082400	1.70941400
C	2.28173300	-0.26957600	1.42635500
C	3.33412900	0.26711700	2.18470800
C	3.93722700	-0.46600100	3.20629200
C	3.49541200	-1.75904200	3.48410100
C	2.45585700	-2.30756300	2.73541100

H	-2.66035000	-2.69419400	0.97074200
H	0.22889200	-4.26224300	-1.78362700
H	3.68969400	1.27243700	1.98549500
H	4.74754800	-0.02646500	3.78093800
H	3.95658100	-2.33809300	4.27897700
H	2.10581900	-3.31430600	2.94283300
P	1.47579400	0.66072600	0.04640900
Pd	-0.83884100	0.22189700	-0.20893600
C	2.71704000	-3.79143600	-1.71172100
H	2.23006700	-3.38279300	-2.60663700
H	3.79796500	-3.67607800	-1.80691800
H	2.47284700	-4.85777500	-1.62357300
C	-2.13584300	-1.17985400	2.93801800
H	-2.70180200	-0.65994400	2.15650400
H	-2.64751100	-2.10989600	3.21686400
H	-2.04893200	-0.54035000	3.81730200
H	-2.10154400	-4.03414200	-1.01495700
O	2.35170000	-3.07268400	-0.54306000
O	-0.79511300	-1.43382100	2.51770800
C	1.81151100	2.45560500	0.43839600
C	1.37157500	3.36878000	-0.72490900
C	1.08232300	2.85471000	1.73958400
H	2.89207300	2.58913200	0.58071800
C	1.58783700	4.85198400	-0.38344700
H	0.30919200	3.18863400	-0.93497700
H	1.91990000	3.12020800	-1.63925800
C	1.30366900	4.33731800	2.07509400
H	0.00858400	2.66468000	1.60820700
H	1.41160800	2.22481300	2.57235700
C	0.86887100	5.24297500	0.91474700
H	1.24272800	5.47592200	-1.21642000
H	2.66497800	5.04386200	-0.27229400
H	0.75632700	4.59534700	2.98943700
H	2.36921300	4.50691500	2.28831600
H	1.06071400	6.29530000	1.15581200
H	-0.21584700	5.14359600	0.76884300
C	2.58523500	0.18478200	-1.39004800

C	1.89437000	0.35275900	-2.75790100
C	3.98450700	0.82508800	-1.37656500
H	2.71412400	-0.89134200	-1.22053500
C	2.77650200	-0.20914300	-3.88420000
H	1.69418700	1.41350500	-2.95415500
H	0.91970300	-0.14749200	-2.74310600
C	4.85443700	0.25413300	-2.50927400
H	3.90012300	1.91186100	-1.50877300
H	4.46915800	0.65572800	-0.40829600
C	4.17526900	0.42511000	-3.87613100
H	2.29001800	-0.05407500	-4.85445900
H	2.87595500	-1.29654500	-3.75287300
H	5.83912500	0.73694700	-2.50665000
H	5.02756500	-0.81530300	-2.32159600
H	4.79715300	-0.00900400	-4.66812600
H	4.08439700	1.49769600	-4.10016700
C	-2.80741100	0.34093700	-0.42698400
C	-4.03413300	0.37897900	-0.49680200
C	-5.45701300	0.36462600	-0.56172800
C	-6.12414900	-0.10844700	-1.71168200
C	-6.23382200	0.82230200	0.52388700
C	-7.51543400	-0.12153900	-1.76943500
H	-5.53377700	-0.46111600	-2.55155500
C	-7.62471800	0.80567200	0.45846300
H	-5.72848400	1.19077000	1.41136200
C	-8.27275900	0.33424600	-0.68666200
H	-8.01214700	-0.48872100	-2.66344700
H	-8.20652700	1.16286700	1.30389000
H	-9.35785300	0.32285000	-0.73507600
H	-1.63210700	1.45299200	-0.72338700

E

E (DMF) = - 1940.157818

C	2.87307800	-0.83217500	0.04530700
C	2.55069800	-2.19203400	0.23761300

C	2.62271900	-3.10335900	-0.83051300
C	3.03015600	-2.64909900	-2.08176700
C	3.36408200	-1.31315400	-2.29934500
C	3.28369000	-0.41100400	-1.23180700
C	2.83366500	0.11939100	1.19794100
C	1.66752500	0.83419100	1.55157400
C	1.72066000	1.69171200	2.66220300
C	2.88947200	1.84756000	3.40721000
C	4.03878400	1.14552200	3.04729100
C	4.00363300	0.28950500	1.94833100
H	2.36424300	-4.14420100	-0.68765500
H	3.67494200	-0.98933600	-3.28424100
H	0.83883800	2.24828500	2.96026400
H	2.89903300	2.51648600	4.26329400
H	4.95535200	1.25963500	3.61904100
H	4.89117800	-0.26674800	1.66146200
P	0.14583200	0.63827300	0.50871500
Pd	-0.18519300	-1.47131000	-0.46390300
C	3.88212800	1.44932700	-2.61719700
H	3.05871000	1.28609800	-3.32476300
H	4.02450700	2.52166400	-2.47294600
H	4.80266300	1.01520600	-3.02861100
C	1.63557700	-3.81256100	1.73979000
H	0.73939400	-3.94567600	1.12097000
H	2.34770600	-4.62568300	1.54628900
H	1.35572800	-3.82765000	2.79407000
H	3.08530400	-3.35113900	-2.90849400
O	3.58004700	0.92192200	-1.33482400
O	2.22072700	-2.53620800	1.51397200
C	-1.23892200	1.18192600	1.64693200
C	-2.55923500	1.35868100	0.87120200
C	-1.41158700	0.13815800	2.77087300
H	-0.98059900	2.14992600	2.09629000
C	-3.72823600	1.70586100	1.80578900
H	-2.78908200	0.43121200	0.34065700
H	-2.45821400	2.13851100	0.11027900
C	-2.58063600	0.49278500	3.70190000

H	-1.59700000	-0.83951000	2.30528800
H	-0.48401000	0.04006000	3.34556400
C	-3.88811000	0.65842100	2.91518900
H	-4.64981500	1.78141700	1.21700600
H	-3.55546600	2.69257500	2.26019900
H	-2.68983000	-0.28147500	4.47119400
H	-2.35421100	1.43031400	4.23059800
H	-4.70978300	0.93348100	3.58783600
H	-4.15817300	-0.30252400	2.45630700
C	0.41631500	2.04250100	-0.71547300
C	-0.40827200	1.86742300	-2.00659000
C	0.27553500	3.46262400	-0.14002700
H	1.47095900	1.89921900	-0.98323000
C	-0.03186800	2.93548700	-3.04549200
H	-1.48044500	1.94110900	-1.78610600
H	-0.24596400	0.86058000	-2.40744900
C	0.65395900	4.51950400	-1.19153600
H	-0.76045800	3.63672600	0.17917300
H	0.90715600	3.57468800	0.74824500
C	-0.17427700	4.35403500	-2.47410000
H	-0.64912600	2.82034300	-3.94495000
H	1.01096400	2.77917500	-3.35866400
H	0.52312800	5.52685600	-0.77760200
H	1.72133600	4.41525700	-1.43436500
H	0.12356700	5.10023900	-3.22071200
H	-1.23285900	4.54363700	-2.24457100
C	-3.51595700	-0.57392800	-2.08679100
C	-4.22777600	-1.94379100	-0.21623500
C	-4.71043800	0.13733900	-2.01570100
H	-2.75620200	-0.31023100	-2.81500200
C	-5.41869500	-1.22273600	-0.14801200
H	-4.02580900	-2.74354600	0.48909100
C	-5.66488400	-0.17851100	-1.04342400
H	-4.89402000	0.94911900	-2.71396200
H	-6.15426700	-1.47278600	0.61126900
H	-6.59107600	0.38534200	-0.98318800
C	-1.99248400	-2.31110500	-1.20791000

C	-1.08178500	-3.16869400	-1.35354300
C	-3.25740300	-1.62445500	-1.18476100
H	-0.75974000	-4.12831400	-1.71575100

B^{L_NO2}

E (DMF) = -2365.845457

C	-2.86100500	-0.19730300	-0.50728300
C	-2.93935200	-1.34338200	-1.34776800
C	-3.46901200	-2.54643800	-0.87647800
C	-3.88965500	-2.62823000	0.44740500
C	-3.80515800	-1.54268700	1.31612600
C	-3.31480900	-0.32669700	0.83348500
C	-2.78961900	1.15916500	-1.15453900
C	-1.66663000	2.00479000	-1.13209300
C	-1.72676200	3.24529800	-1.78967100
C	-2.88011300	3.65112900	-2.45657200
C	-3.99780100	2.81617100	-2.47184500
C	-3.94668800	1.58418500	-1.82599900
H	-3.50577900	-3.42411800	-1.50652600
H	-4.12198100	-1.65035400	2.34467900
H	-0.86345500	3.90140500	-1.79677000
H	-2.90291300	4.61142100	-2.96317800
H	-4.90310200	3.11984900	-2.98916800
H	-4.80996400	0.92575300	-1.84303700
P	-0.18323700	1.45742600	-0.19285600
Pd	-0.32686800	-0.87259000	0.08266800
C	-3.56225000	0.74640000	2.95943400
H	-2.88825000	0.04519600	3.46603800
H	-3.39969200	1.75251600	3.34868700
H	-4.60253400	0.45198100	3.14243800
C	-2.27679200	-2.30311700	-3.42983700
H	-1.61940200	-3.02169400	-2.92673900
H	-3.22396700	-2.78969700	-3.69411300
H	-1.79764900	-1.93653000	-4.33841000
H	-4.26884100	-3.57347500	0.82133500

O	-3.27781900	0.82061200	1.56639400
O	-2.48927200	-1.15213600	-2.61434300
C	1.23652700	2.26436500	-1.09989100
C	2.58694100	2.18454200	-0.35776800
C	1.34777500	1.70120400	-2.53240900
H	0.97497300	3.32872100	-1.17181400
C	3.69111800	2.89339700	-1.15814600
H	2.87065100	1.14244100	-0.21466500
H	2.50653200	2.62929000	0.63902100
C	2.47348400	2.39466200	-3.31581800
H	1.55436800	0.62787800	-2.47447300
H	0.39461200	1.81410000	-3.05976800
C	3.81356500	2.30883900	-2.57183500
H	4.64287800	2.80292300	-0.62240800
H	3.46569000	3.96781100	-1.22539400
H	2.55651900	1.94666900	-4.31289500
H	2.21027300	3.45163400	-3.46748500
H	4.59664200	2.82979500	-3.13443200
H	4.12210600	1.25724400	-2.49726900
C	-0.39807300	2.37600300	1.43181000
C	0.36017600	1.71807600	2.60084600
C	-0.13592900	3.89231400	1.35685500
H	-1.46827800	2.22955100	1.61545400
C	0.03936500	2.42012700	3.92982500
H	1.44169700	1.75359600	2.42208600
H	0.08599900	0.65920800	2.65967200
C	-0.46991100	4.56855000	2.69751500
H	0.91810000	4.08263600	1.12002700
H	-0.73299500	4.34210400	0.55653700
C	0.30939600	3.92907500	3.85487800
H	0.61997100	1.96365600	4.73979400
H	-1.02042300	2.25695000	4.17337400
H	-0.25544700	5.64185200	2.63469500
H	-1.54830000	4.47337300	2.88865700
H	0.04853500	4.41167600	4.80386000
H	1.38497700	4.09647000	3.70152600
C	1.65709300	-1.10330700	0.17114800

C	2.37783200	-0.93097200	1.36131900
C	2.34616800	-1.40674200	-1.01339800
C	3.76989900	-0.97777500	1.35682100
H	1.85910300	-0.75377700	2.29489500
C	3.73758200	-1.45155300	-1.03158700
H	1.79947400	-1.60602700	-1.92829500
C	4.43574100	-1.21338300	0.15323600
H	4.34504100	-0.82656500	2.26212100
H	4.28692500	-1.66246000	-1.94092500
I	-0.37862900	-3.50853900	0.69258100
N	5.89983900	-1.20958200	0.13108300
O	6.45992300	-1.39134800	-0.95267000
O	6.49244700	-1.01411000	1.19461800

B^{Br_NO2}

E (DMF) = -4642.222603

C	2.86225100	-0.57421000	0.37356600
C	2.85808500	-1.81859600	1.06278500
C	3.27946200	-2.99138100	0.43099500
C	3.66833600	-2.94016800	-0.90271200
C	3.66659200	-1.74879800	-1.62607300
C	3.29113000	-0.56781400	-0.98180900
C	2.87290100	0.69674500	1.17744400
C	1.79905200	1.60157700	1.25992400
C	1.93004400	2.75414700	2.05275900
C	3.10526700	3.01519800	2.75338100
C	4.17280300	2.12111800	2.66734000
C	4.05172000	0.97543800	1.88577800
H	3.24772200	-3.94162300	0.94508000
H	3.96161300	-1.74997200	-2.66678600
H	1.10568800	3.45324500	2.14033000
H	3.18338100	3.90904600	3.36513100
H	5.09367400	2.31181700	3.21050200
H	4.87582100	0.27134300	1.82202400
P	0.28309700	1.24801800	0.27946700

Pd	0.28442700	-1.03603400	-0.20675000
C	3.61819500	0.74611300	-2.95660800
H	2.88291100	0.17890300	-3.54019600
H	3.54502000	1.80457700	-3.21068600
H	4.62733600	0.38703700	-3.19118700
C	2.07356600	-2.98278700	2.99087200
H	1.35568200	-3.54070100	2.37877100
H	2.95313500	-3.60608700	3.19448000
H	1.61306000	-2.69622700	3.93717900
H	3.95757000	-3.85899900	-1.40199500
O	3.34568800	0.66367700	-1.56192700
O	2.43663900	-1.75801900	2.35219100
C	-1.08763800	2.02829600	1.27921600
C	-2.44228300	2.10179000	0.54313100
C	-1.22658500	1.32222700	2.64436900
H	-0.76778200	3.06309400	1.46195300
C	-3.50332000	2.78071200	1.42380200
H	-2.78376500	1.09780600	0.29158300
H	-2.33960700	2.64578300	-0.40100600
C	-2.31043400	1.98865900	3.50626200
H	-1.49253900	0.27430300	2.47422900
H	-0.26738400	1.32528300	3.17272400
C	-3.65468900	2.05565500	2.76779800
H	-4.45988300	2.80098600	0.88940600
H	-3.21808300	3.82757600	1.60375400
H	-2.41589900	1.44179500	4.45046100
H	-1.98914400	3.00743400	3.76770200
H	-4.40719300	2.55469900	3.38893000
H	-4.01955800	1.03602100	2.58367800
C	0.54567200	2.31987600	-1.23937900
C	-0.24713200	1.83045500	-2.46656600
C	0.36443100	3.83117400	-1.00141700
H	1.60652300	2.13828900	-1.44414200
C	0.11020700	2.65168400	-3.71548600
H	-1.32514900	1.90399000	-2.27851200
H	-0.02979600	0.77054100	-2.63807100
C	0.73306000	4.62744700	-2.26481200

H	-0.67773600	4.05052700	-0.73883400
H	0.98521400	4.16040200	-0.16133300
C	-0.07946200	4.15623900	-3.47879800
H	-0.49419500	2.31543100	-4.56585900
H	1.15974000	2.45964600	-3.98119200
H	0.57554600	5.69775900	-2.08736900
H	1.80483500	4.49675300	-2.47149700
H	0.20615900	4.72267500	-4.37269300
H	-1.14461900	4.36266200	-3.30209000
C	-1.70307200	-1.14630100	-0.32035400
C	-2.39655000	-0.83048700	-1.49635400
C	-2.41986100	-1.54671300	0.81742000
C	-3.78965400	-0.83313900	-1.51580400
H	-1.85796700	-0.57289700	-2.39954300
C	-3.81206900	-1.54892000	0.81179300
H	-1.89450800	-1.85734100	1.71347400
C	-4.48215100	-1.16901900	-0.35214600
H	-4.34464700	-0.57185000	-2.40850900
H	-4.38307500	-1.83515200	1.68653800
Br	0.19642300	-3.49978300	-0.88436100
N	-5.94624600	-1.12398300	-0.35138400
O	-6.53058100	-1.40593900	0.69735500
O	-6.51380900	-0.79701100	-1.39605800

B^{Cl_NO2}

E (DMF) = -2528.261305

C	2.86943900	-0.87444400	0.18877300
C	2.77718300	-2.21624600	0.64534500
C	3.12379100	-3.28374200	-0.19162200
C	3.52623500	-3.02170100	-1.49342800
C	3.61761300	-1.72012300	-1.98958900
C	3.32036600	-0.65280200	-1.14140500
C	2.90526600	0.24362700	1.19211700
C	1.85411000	1.15470600	1.40692200
C	2.00807200	2.16607100	2.36984000

C	3.18100300	2.27915300	3.11295000
C	4.22301600	1.37660900	2.89979500
C	4.08077900	0.37174200	1.94656800
H	3.01929300	-4.30528900	0.14466600
H	3.93110600	-1.55403200	-3.01166100
H	1.20402800	2.86903300	2.55748000
H	3.27640300	3.06496200	3.85639000
H	5.14077000	1.45176400	3.47550900
H	4.88564100	-0.33756400	1.77949500
P	0.33497800	1.00009600	0.37790200
Pd	0.22584400	-1.20326700	-0.35611500
C	3.80445300	0.97093500	-2.83414600
H	3.05421000	0.57988800	-3.53250000
H	3.81845700	2.06043100	-2.89039900
H	4.79307300	0.58130100	-3.10482400
C	1.84284500	-3.64686900	2.31020900
H	1.10051900	-3.99593000	1.58378500
H	2.64921200	-4.38380600	2.41050200
H	1.37583900	-3.49615200	3.28443700
H	3.75618600	-3.85363000	-2.15116400
O	3.47154700	0.65750600	-1.48671300
O	2.35320200	-2.36532100	1.92674200
C	-1.01323200	1.71070000	1.45684300
C	-2.35237700	1.94184500	0.72455800
C	-1.20578200	0.84568800	2.72035700
H	-0.64877000	2.69800500	1.77106400
C	-3.39147600	2.55764400	1.67511600
H	-2.73868000	0.99483600	0.34755800
H	-2.21034800	2.59289600	-0.14369900
C	-2.26852000	1.45141400	3.65055800
H	-1.51922900	-0.15776000	2.41614400
H	-0.25590900	0.73345600	3.25338100
C	-3.59704300	1.67764400	2.91547700
H	-4.33814100	2.69301600	1.13986100
H	-3.05805000	3.55793600	1.98800900
H	-2.41392300	0.79599800	4.51710600
H	-1.90224000	2.41196000	4.04129700

H	-4.33357800	2.13120300	3.58846700
H	-4.00766200	0.70854400	2.60080300
C	0.66614600	2.23941300	-0.99045300
C	-0.12961000	1.95057800	-2.27752400
C	0.55468200	3.71468500	-0.56084000
H	1.71994700	2.03457600	-1.20798500
C	0.29004800	2.90539900	-3.40651600
H	-1.20589700	2.05399900	-2.09334700
H	0.03965800	0.91186600	-2.58185100
C	0.98426600	4.64610600	-1.70702400
H	-0.48008800	3.95137400	-0.28430400
H	1.17564500	3.90036200	0.32230500
C	0.17126600	4.37526400	-2.98063200
H	-0.31496600	2.71244200	-4.29993900
H	1.33339600	2.69484700	-3.68232000
H	0.87608200	5.69170200	-1.39580800
H	2.05195400	4.48873000	-1.91648200
H	0.50044600	5.03549900	-3.79132100
H	-0.88530700	4.61210300	-2.79104800
C	-1.75697600	-1.20203100	-0.50466700
C	-2.40383300	-0.72012800	-1.64985700
C	-2.51701400	-1.72012400	0.55409900
C	-3.79564100	-0.68013500	-1.70810700
H	-1.83141200	-0.36312700	-2.49663000
C	-3.90797500	-1.68016700	0.50970100
H	-2.02747100	-2.15710400	1.41692400
C	-4.53148300	-1.13871200	-0.61558000
H	-4.31589000	-0.29223300	-2.57531200
H	-4.51320700	-2.05696100	1.32508700
Cl	0.04508300	-3.50355100	-1.11122400
N	-5.99392300	-1.05329300	-0.65071800
O	-6.61779100	-1.45190100	0.33526100
O	-6.51961400	-0.57888900	-1.66005300

TS^{L_NO2}

E (DMF) = -2365.793085

C	2.75385200	-0.98903400	1.30947500
C	1.86905300	-2.04772400	1.58085900
C	2.01521000	-3.28834600	0.94767200
C	3.05266100	-3.46440200	0.03616900
C	3.95569100	-2.44132800	-0.24696600
C	3.80703000	-1.21083500	0.40500400
C	2.63369300	0.31272800	2.03577300
C	1.81247300	1.37320100	1.58906000
C	1.79379800	2.56389500	2.33437000
C	2.55180400	2.70922800	3.49596000
C	3.35552500	1.65882200	3.93431000
C	3.39360200	0.47491100	3.20094000
H	1.32260200	-4.09687100	1.13757300
H	4.75849500	-2.60927800	-0.95315000
H	1.18254300	3.39932800	2.01393100
H	2.51279600	3.64211900	4.05112200
H	3.95012300	1.75939200	4.83769300
H	4.02106300	-0.34906100	3.52744200
P	0.82981600	1.17441100	0.03113600
Pd	-0.58405000	-0.73361300	-0.28223100
C	5.72561800	-0.28204100	-0.69367600
H	5.37266800	-0.49414700	-1.71131000
H	6.24481400	0.67772600	-0.68844900
H	6.42028100	-1.07238700	-0.38171800
C	0.00570000	-2.81090600	2.87115400
H	-0.55866300	-3.20512600	2.01771300
H	0.55228600	-3.63276800	3.35174400
H	-0.68420900	-2.36746000	3.59098200
H	3.16083300	-4.42182100	-0.46489100
O	4.64660500	-0.14403500	0.21804800
O	0.88181800	-1.76348200	2.47945800
C	-0.34372100	2.64065300	0.03907300
C	-1.03291500	2.83508400	-1.32820000
C	-1.41492000	2.46940900	1.14027400
H	0.23947400	3.54800600	0.24355200

C	-1.99295400	4.03638300	-1.29493700
H	-1.59232000	1.92492900	-1.58087600
H	-0.29263200	2.98292200	-2.11964400
C	-2.38296800	3.66231400	1.17840100
H	-1.98391700	1.55343100	0.93416700
H	-0.94779700	2.32857500	2.12044600
C	-3.04488800	3.89584100	-0.18695400
H	-2.47961600	4.14584500	-2.27157400
H	-1.41004900	4.95434900	-1.13087200
H	-3.14694700	3.49185700	1.94613600
H	-1.83224100	4.56638500	1.47630200
H	-3.68392600	4.78556600	-0.15258600
H	-3.70660700	3.05317000	-0.42036100
C	2.14735100	1.54437600	-1.25148500
C	1.79735800	1.00450400	-2.65103000
C	2.61589500	3.00973700	-1.30039500
H	2.99234200	0.95508700	-0.88062900
C	2.98982100	1.17230700	-3.60656700
H	0.93164800	1.53893200	-3.06143100
H	1.50732300	-0.04985800	-2.57682400
C	3.80910100	3.15992900	-2.25927500
H	1.79939900	3.65721600	-1.64546500
H	2.89260100	3.34937600	-0.29577300
C	3.47004400	2.63060300	-3.66081100
H	2.72063600	0.81961800	-4.60924900
H	3.81572100	0.53368000	-3.26104400
H	4.12066900	4.21011300	-2.31104900
H	4.66272900	2.59726200	-1.85517400
H	4.33879000	2.72211800	-4.32370300
H	2.67577100	3.25363800	-4.09657700
C	-2.51106800	-1.38926500	-0.39753100
C	-3.14820000	-0.62300600	-1.40237400
C	-3.01148800	-1.39537900	0.92518500
C	-4.17728300	0.23960500	-1.04949800
H	-2.81298500	-0.68889400	-2.43028900
C	-4.04111100	-0.52730500	1.26756000
H	-2.57320300	-2.04373200	1.67292700

C	-4.59832000	0.29406500	0.28358200
H	-4.65145300	0.87989400	-1.78277100
H	-4.40981200	-0.46314200	2.28376400
I	-1.36274000	-3.33135700	-1.13833600
N	-5.63732400	1.24692500	0.66101100
O	-6.07144800	2.00264000	-0.21444500
O	-6.01401800	1.25729100	1.83562400

TS^{Br_NO2}

E (DMF) = -4642.170473

C	-2.70266500	1.18252600	1.11542000
C	-1.88931700	2.32775400	1.19211000
C	-2.12113700	3.43298100	0.36282800
C	-3.17945400	3.38967000	-0.54104400
C	-4.02159900	2.28251000	-0.62458300
C	-3.78453300	1.18891100	0.21779600
C	-2.47188100	0.01955000	2.02727600
C	-1.60092300	-1.04893300	1.70950200
C	-1.47756500	-2.10545300	2.62723000
C	-2.17951500	-2.11097100	3.83238200
C	-3.03131900	-1.05292800	4.14258100
C	-3.17375800	-0.00222800	3.23877500
H	-1.48005900	4.30326700	0.40027700
H	-4.84548300	2.28221100	-1.32643400
H	-0.82646700	-2.94406400	2.41009300
H	-2.05930000	-2.94197900	4.52156800
H	-3.58276400	-1.04508500	5.07831200
H	-3.83962200	0.82523400	3.46498500
P	-0.68755600	-1.04222400	0.09644400
Pd	0.49116500	0.94039200	-0.54478500
C	-5.67403200	-0.01160900	-0.64259700
H	-5.36743000	0.04867700	-1.69485100
H	-6.13506500	-0.98367300	-0.46030300
H	-6.40336000	0.78152000	-0.43420000

C	-0.08536500	3.42343700	2.31552000
H	0.45613300	3.70768000	1.40543600
H	-0.69291100	4.27293700	2.65358300
H	0.62803900	3.15846600	3.09770600
H	-3.35523500	4.24086000	-1.19218000
O	-4.56005200	0.05949400	0.23429600
O	-0.88189700	2.26456500	2.11066300
C	0.57481300	-2.41736500	0.27198000
C	1.22257000	-2.77298600	-1.08251800
C	1.67349400	-2.02434300	1.28367800
H	0.05571800	-3.31468500	0.63328700
C	2.24415400	-3.91027100	-0.91727400
H	1.72254600	-1.88206600	-1.48474300
H	0.46380400	-3.06875000	-1.81233500
C	2.71787700	-3.13974900	1.45027600
H	2.16957000	-1.11807600	0.91846500
H	1.23736500	-1.76723800	2.25456800
C	3.33123000	-3.55218600	0.10408300
H	2.69596200	-4.14483400	-1.88859000
H	1.71699100	-4.81804700	-0.58945700
H	3.50490400	-2.80519100	2.13647100
H	2.24175000	-4.01457400	1.91640500
H	4.01831700	-4.39462300	0.24300600
H	3.93583700	-2.72754900	-0.29026400
C	-2.02520900	-1.69175600	-1.05074500
C	-1.77321400	-1.35424600	-2.53246000
C	-2.38667900	-3.17492400	-0.85130800
H	-2.89567500	-1.11002200	-0.73137300
C	-2.98491300	-1.75193300	-3.39097700
H	-0.88539300	-1.88292800	-2.90043800
H	-1.56367500	-0.28318700	-2.63473500
C	-3.60202800	-3.55270200	-1.71502900
H	-1.53959400	-3.81340200	-1.13326300
H	-2.59875000	-3.37076900	0.20598000
C	-3.35628700	-3.22976100	-3.19634200
H	-2.78063600	-1.54369100	-4.44792800
H	-3.84313600	-1.12521300	-3.10855600

H	-3.83748000	-4.61623800	-1.58819000
H	-4.47848100	-2.99127000	-1.36118600
H	-4.23994600	-3.48330400	-3.79413200
H	-2.53453100	-3.85827600	-3.56861400
C	2.42659800	1.62556500	-0.67022400
C	3.10899500	0.82471000	-1.61429200
C	2.91353500	1.77029700	0.64851500
C	4.17245000	0.04289200	-1.18684600
H	2.78122100	0.80526200	-2.64633800
C	3.97550000	0.97968000	1.06345000
H	2.43843200	2.46016500	1.33306800
C	4.58257000	0.11129800	0.15008900
H	4.68768000	-0.62468700	-1.86602700
H	4.33689400	1.01331300	2.08361100
N	5.66092700	-0.75476300	0.60702900
O	6.18527800	-1.50946000	-0.21910300
O	5.98118100	-0.70175900	1.79823500
Br	1.38447600	3.35271900	-1.49299100

TS^{Cl_NO2}

E (DMF) = -2528.20883

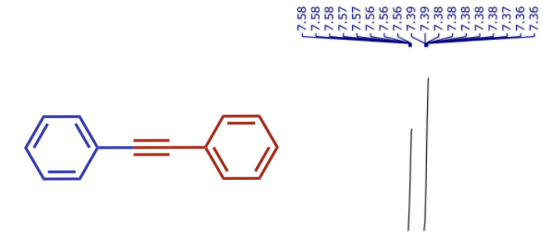
C	3.05457900	-0.92899400	0.48280800
C	2.55203800	-2.19962700	0.82341800
C	2.63261300	-3.26984500	-0.07895100
C	3.21421200	-3.05865600	-1.32687100
C	3.73150900	-1.81669600	-1.69025200
C	3.65641800	-0.75860700	-0.77515900
C	2.97840200	0.19961200	1.45943800
C	1.87340800	1.07872600	1.52851200
C	1.90120600	2.11415400	2.47799000
C	2.98167400	2.28091100	3.34363400
C	4.06704600	1.40964200	3.27186100
C	4.05838400	0.38099200	2.33231400
H	2.22998000	-4.24215700	0.17109000

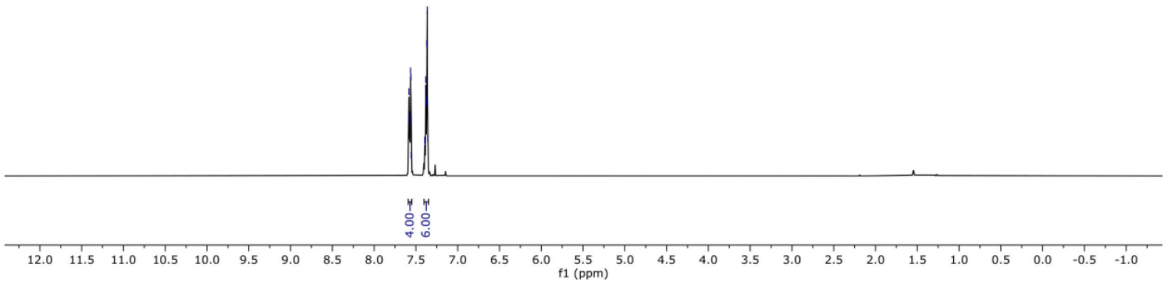
H	4.18529600	-1.68553900	-2.66401500
H	1.07071200	2.80686300	2.55251100
H	2.97175900	3.09026700	4.06813700
H	4.91424900	1.52863500	3.94106900
H	4.89848200	-0.30379000	2.26549700
P	0.45785100	0.88057800	0.34711500
Pd	-0.19726800	-1.30944800	-0.28577600
C	4.71332100	0.76566300	-2.29389600
H	3.99611900	0.59836900	-3.10794900
H	4.99706600	1.81921200	-2.27739000
H	5.60652500	0.15242400	-2.46881400
C	1.29696700	-3.47897300	2.40634800
H	0.49353300	-3.68994800	1.68915600
H	1.97211300	-4.34290200	2.46126700
H	0.86707900	-3.29832200	3.39257800
H	3.26803800	-3.88286100	-2.03189600
O	4.13636100	0.49947700	-1.02432700
O	1.99357000	-2.28831600	2.06370700
C	-0.93780200	1.83478600	1.14648200
C	-2.13202400	1.97463600	0.18225700
C	-1.38685800	1.13776200	2.44803300
H	-0.58013500	2.84376000	1.38922400
C	-3.31436000	2.70592300	0.84014700
H	-2.44593000	0.97487300	-0.13110400
H	-1.83681800	2.50851000	-0.72631400
C	-2.54140700	1.90159800	3.11458300
H	-1.71617500	0.11977700	2.19974000
H	-0.54626300	1.03606300	3.14222300
C	-3.73572900	2.04983200	2.16277300
H	-4.15995000	2.73129400	0.14298200
H	-3.02763900	3.75038700	1.03001400
H	-2.84582800	1.38576100	4.03322700
H	-2.18706700	2.89774900	3.41759600
H	-4.53449300	2.63332900	2.63450500
H	-4.16146300	1.06092700	1.95718200
C	1.07711000	1.92683800	-1.08824000
C	0.39265200	1.58434600	-2.42611700

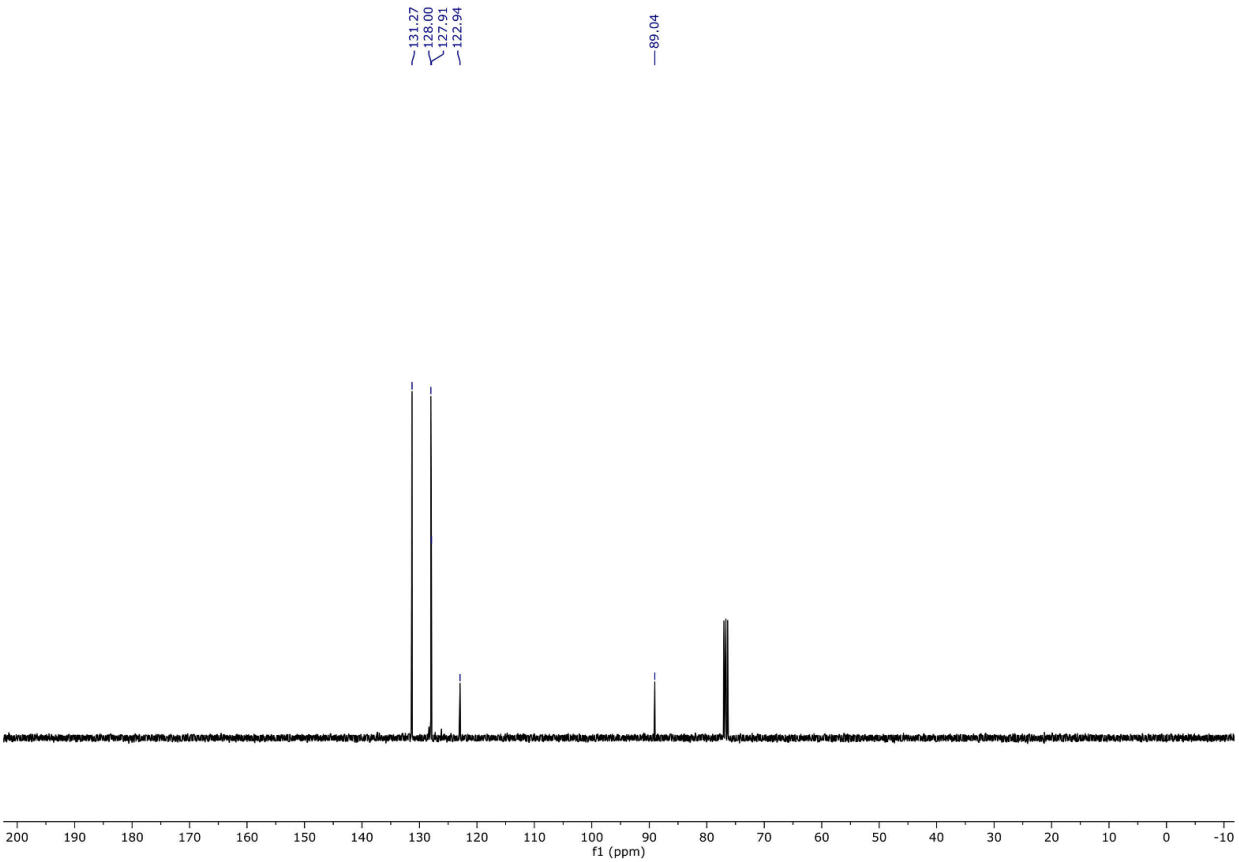
C	1.08721400	3.44397700	-0.82712900
H	2.12158300	1.60185400	-1.16486800
C	1.04889900	2.34964400	-3.58658400
H	-0.67363900	1.83845700	-2.38436600
H	0.44758600	0.50305200	-2.59869700
C	1.74996600	4.19234300	-1.99599200
H	0.05949700	3.81162100	-0.70992700
H	1.61562100	3.66254900	0.10759300
C	1.06341100	3.86371700	-3.32959100
H	0.52950700	2.12453000	-4.52575600
H	2.08357400	1.99733500	-3.70774400
H	1.72939500	5.27281500	-1.80964600
H	2.80907300	3.90219800	-2.05144200
H	1.56098000	4.38673100	-4.15496900
H	0.02841800	4.23340800	-3.30136300
C	-2.08405400	-2.15635300	-0.76725400
C	-2.59822000	-1.47506300	-1.89539600
C	-2.81992800	-2.23439900	0.43795900
C	-3.74613600	-0.71573500	-1.74864700
H	-2.07072800	-1.52380700	-2.83980200
C	-3.97152300	-1.47530300	0.56675700
H	-2.46419400	-2.85806100	1.24858900
C	-4.41492500	-0.70525800	-0.51610200
H	-4.13588000	-0.12180400	-2.56569800
H	-4.53621100	-1.46461000	1.49037900
Cl	-0.96203700	-3.70128500	-1.15547600
N	-5.58012400	0.14387200	-0.34983300
O	-6.17956300	0.10244500	0.73126600
O	-5.90037800	0.88041600	-1.29023200

11. NMR Spectra

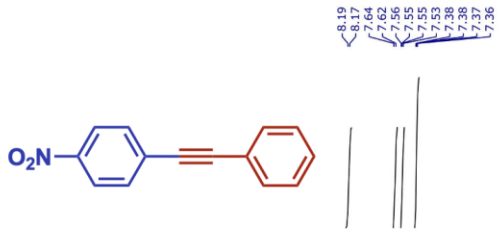
1,2-diphenylacetylene, ***3a***

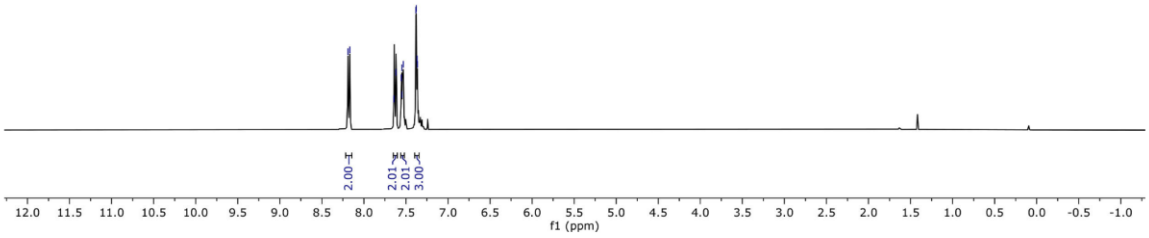


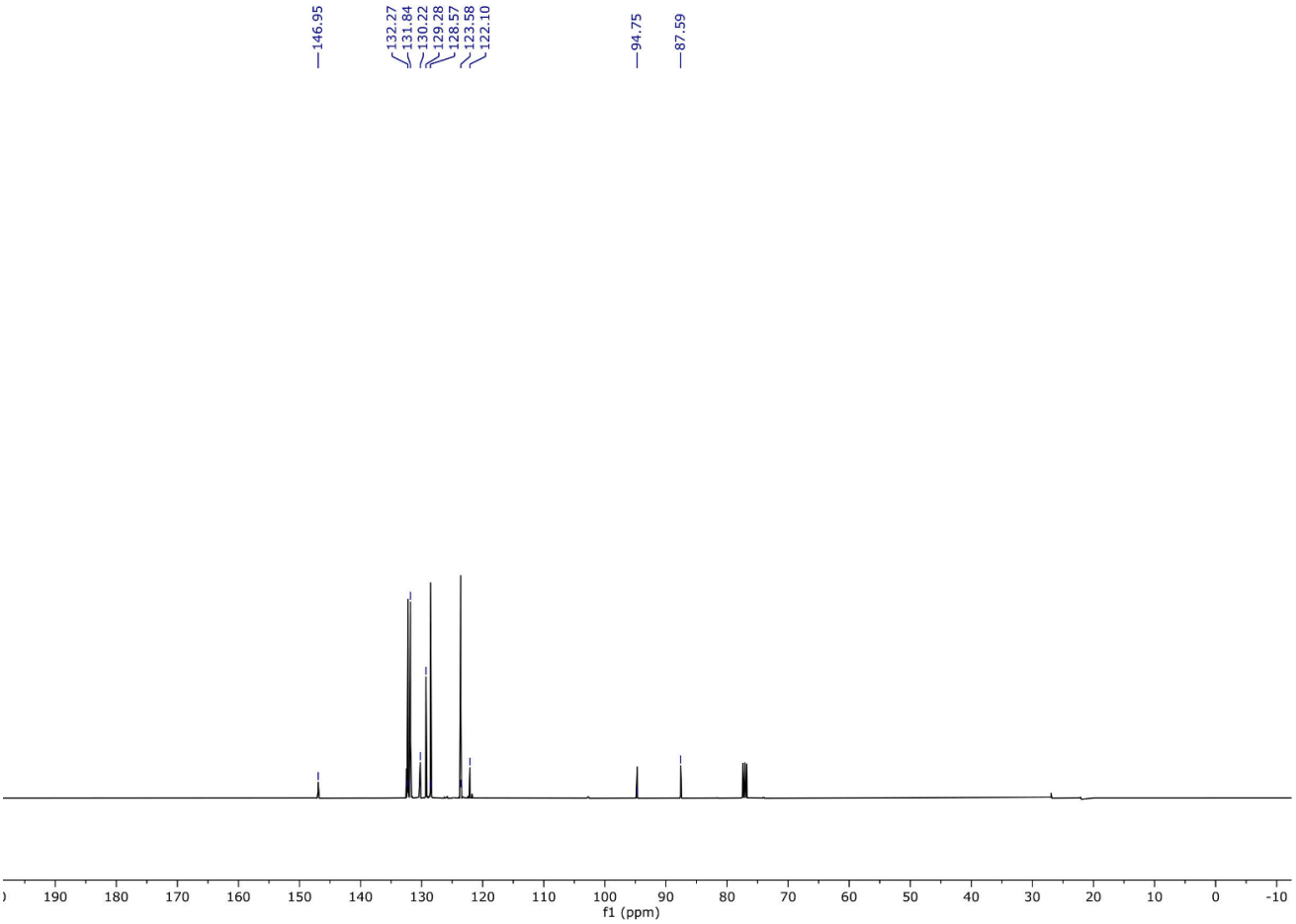




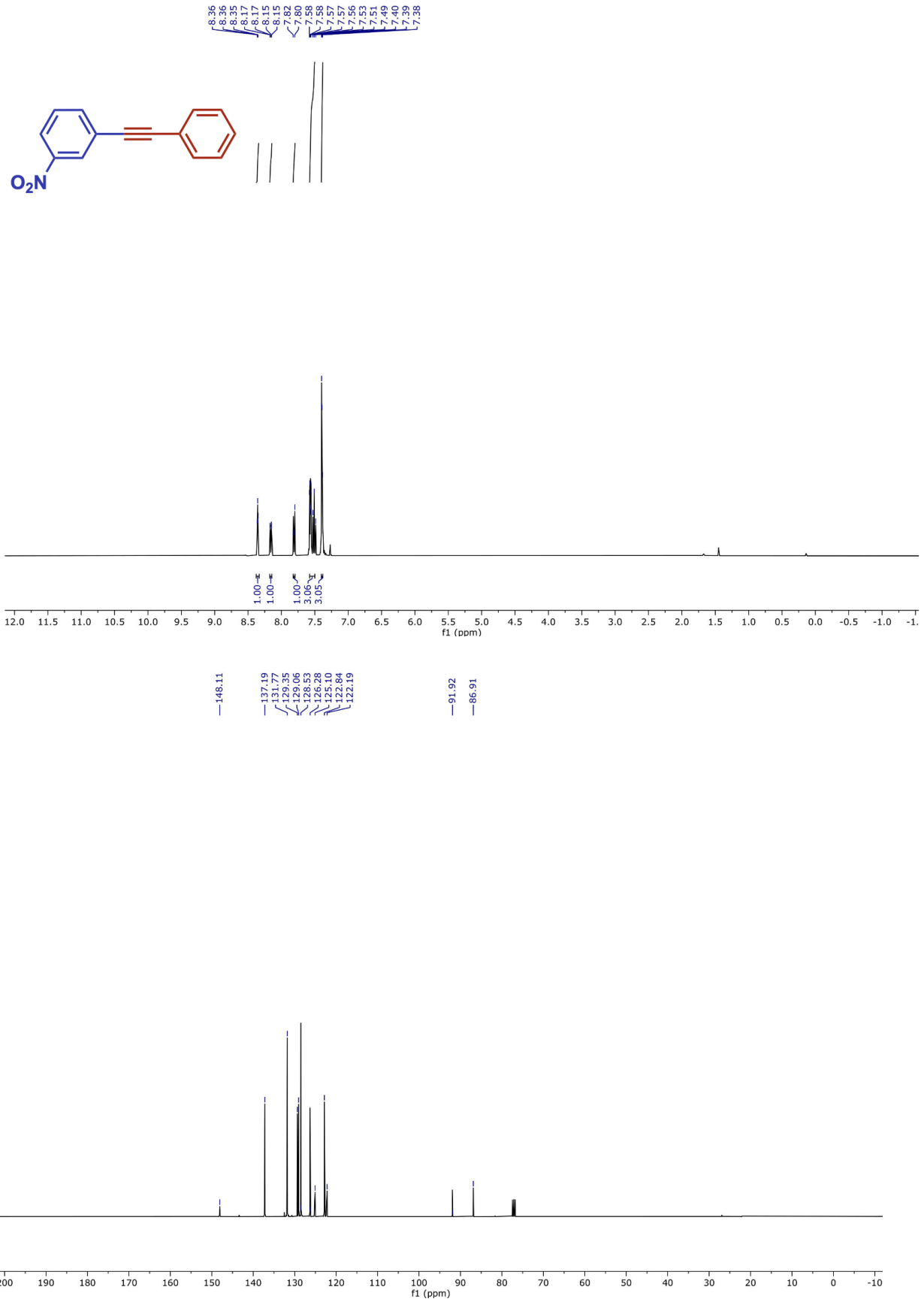
1-nitro-4-(phenylethynyl)benzene, ***3b***



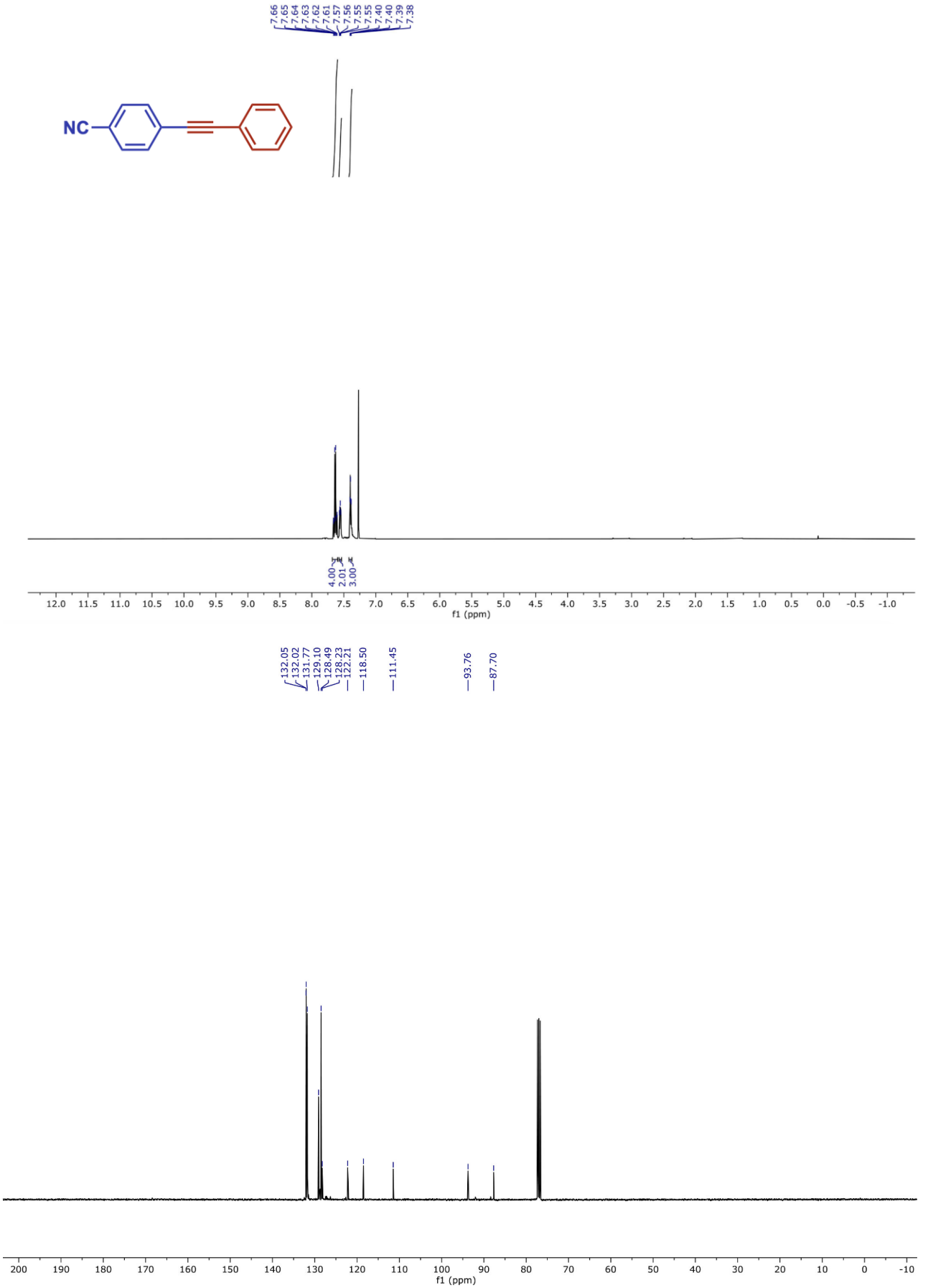




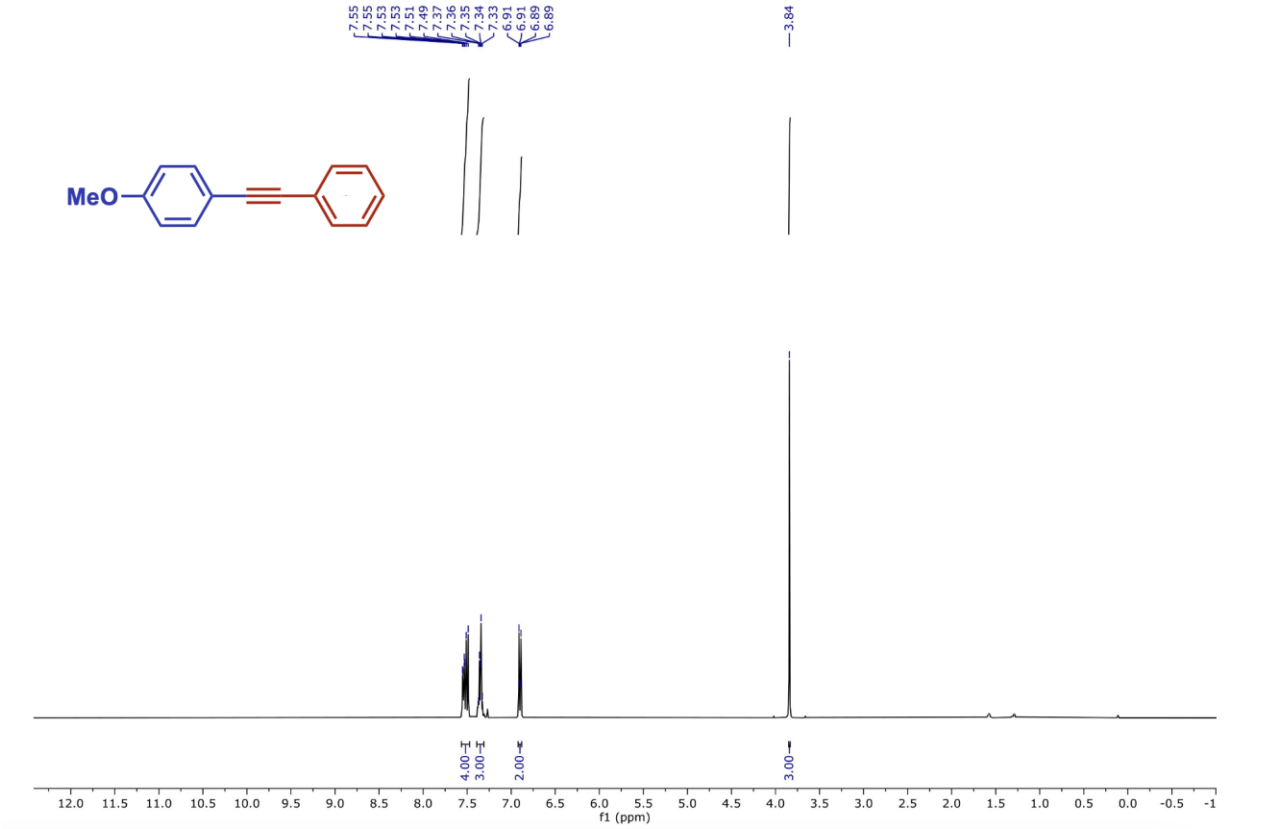
1-nitro-3-(phenylethynyl)benzene, ***3c***

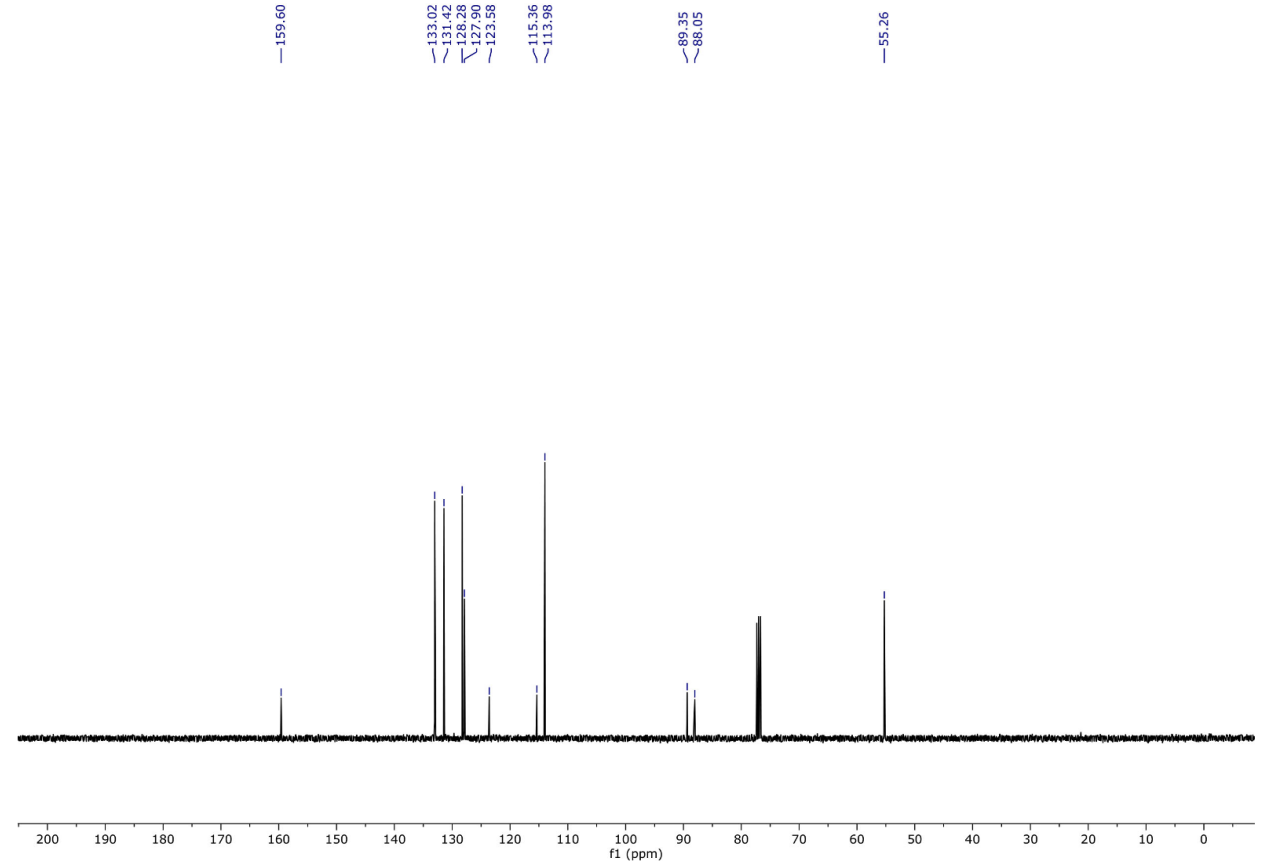


4-(phenylethynyl)benzonitrile, ***3d***

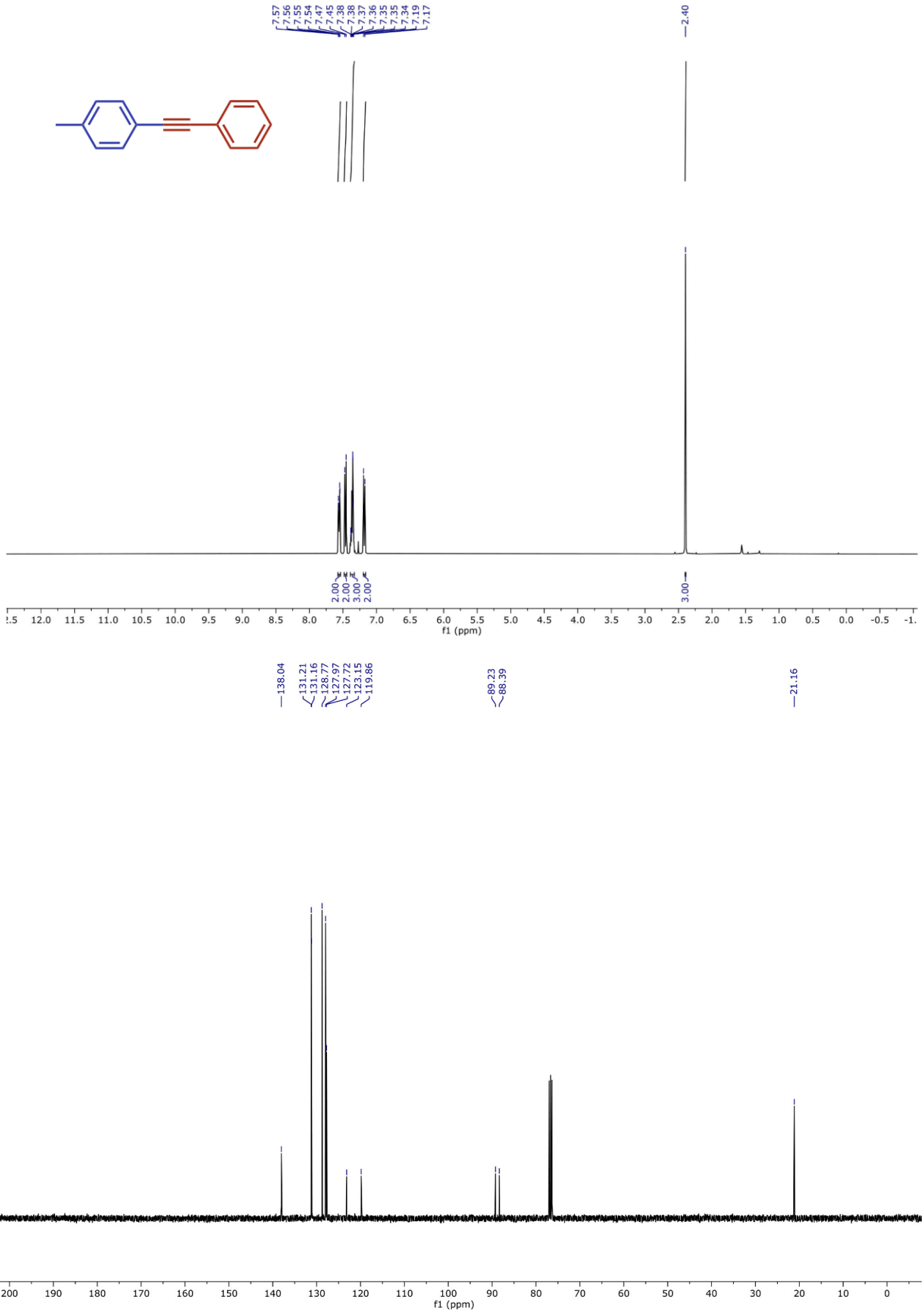


1-methoxy-4-(phenylethynyl)benzene, ***3e***

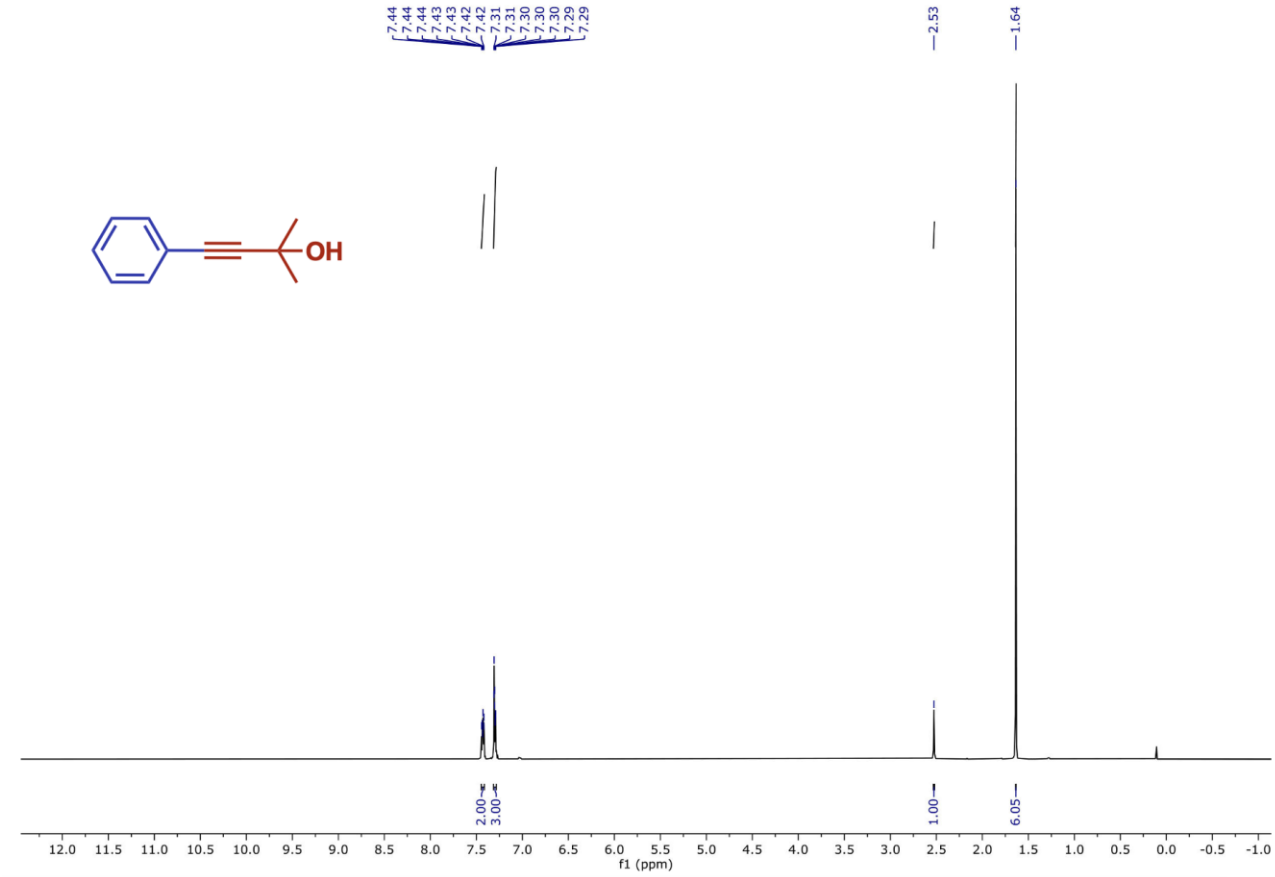


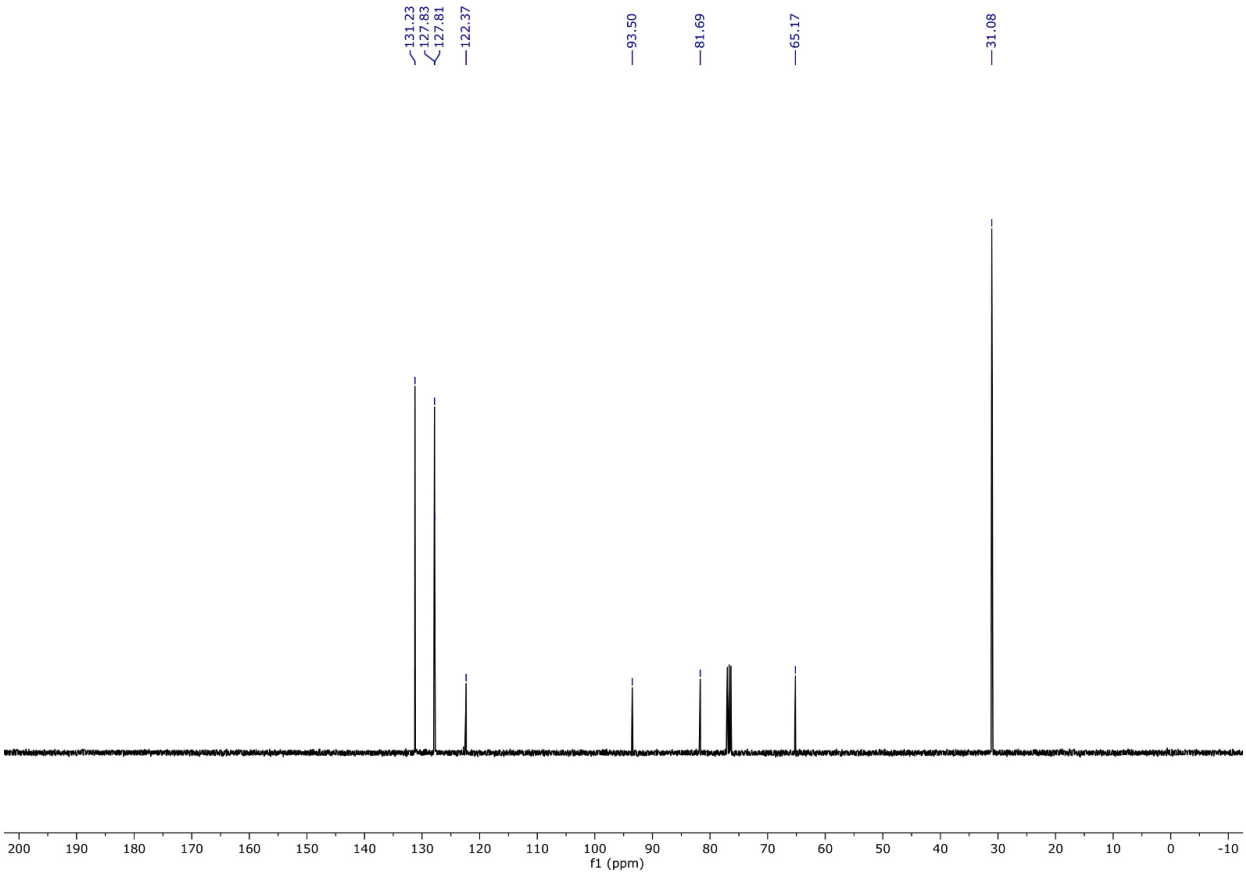


1-methyl-4-(phenylethynyl)benzene, ***3f***

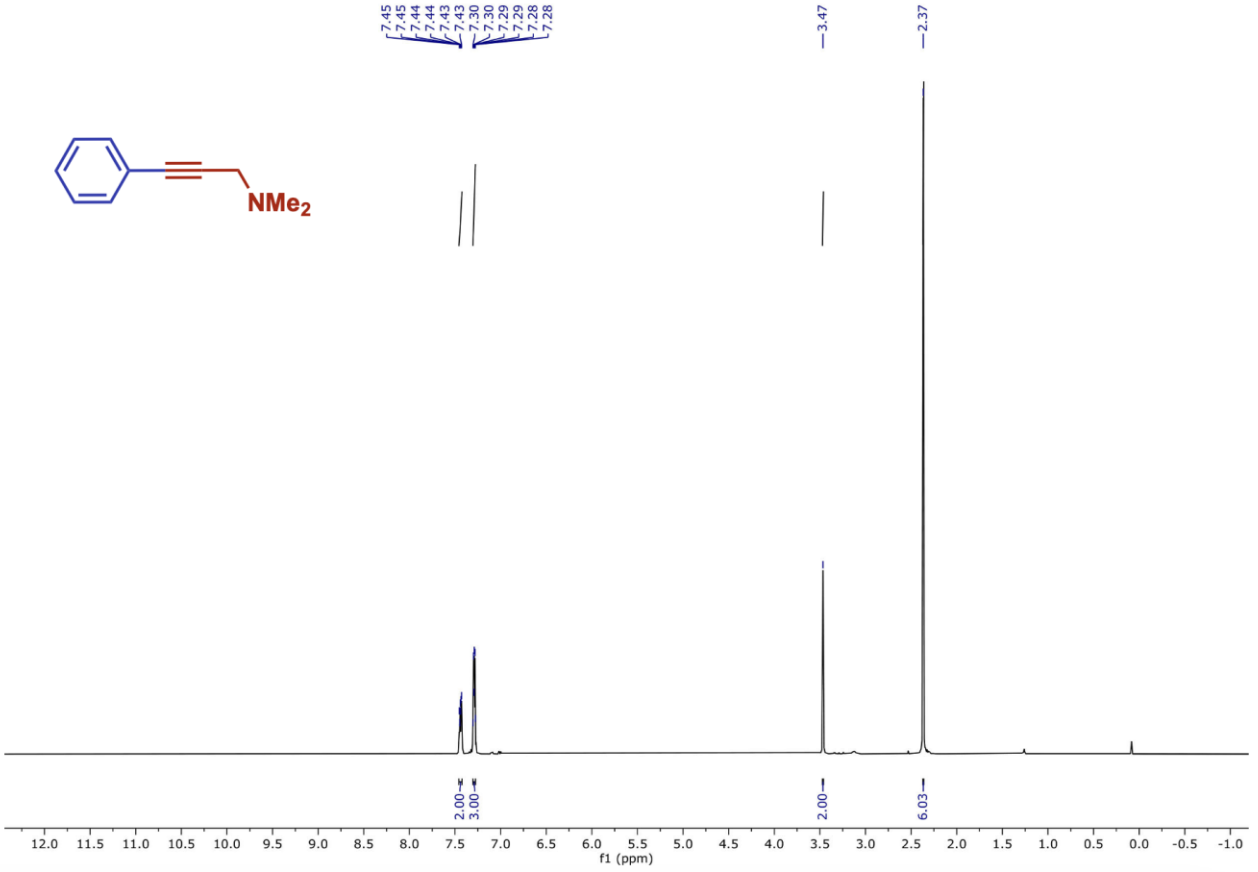


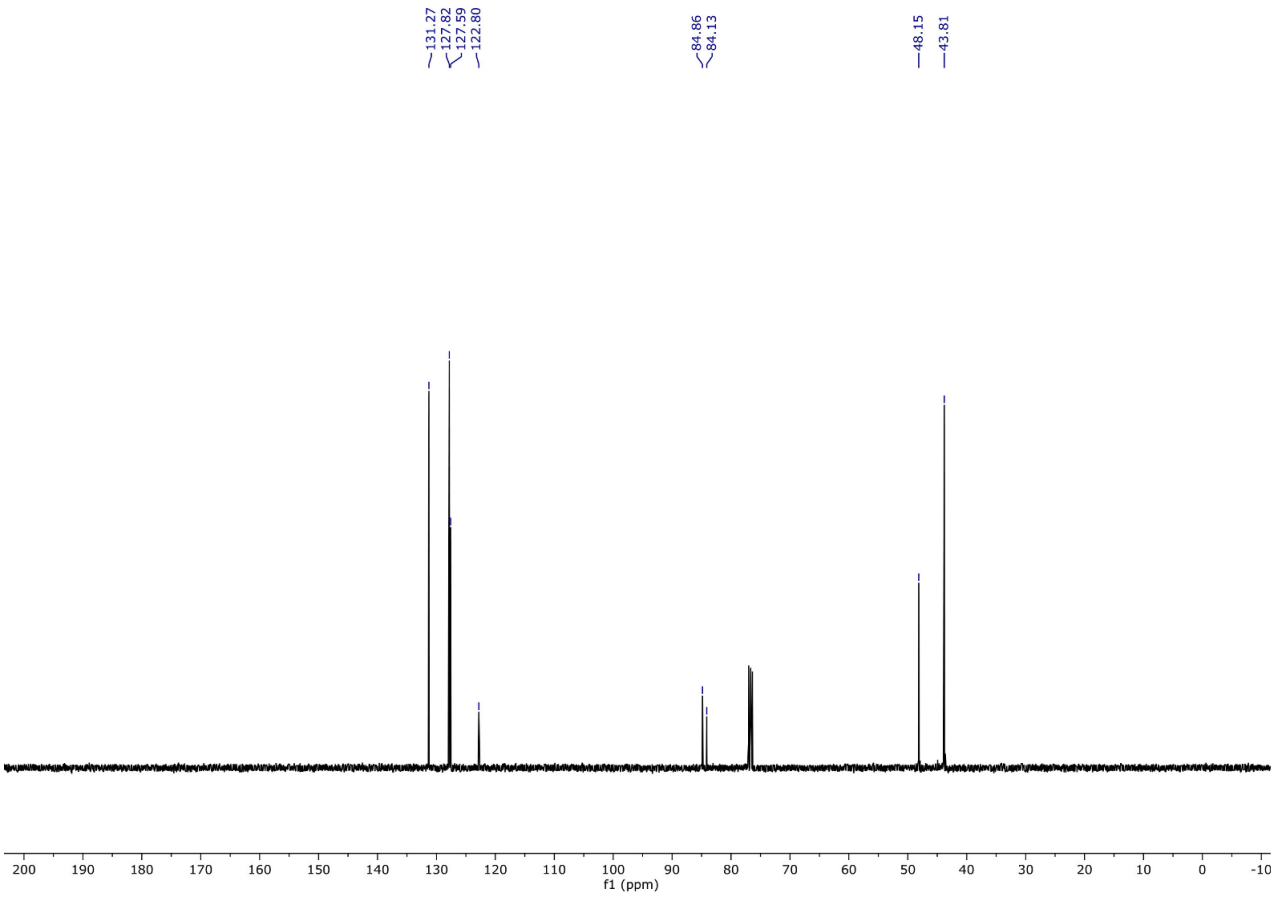
2-methyl-4-phenylbut-3-yn-2-ol, ***3g***



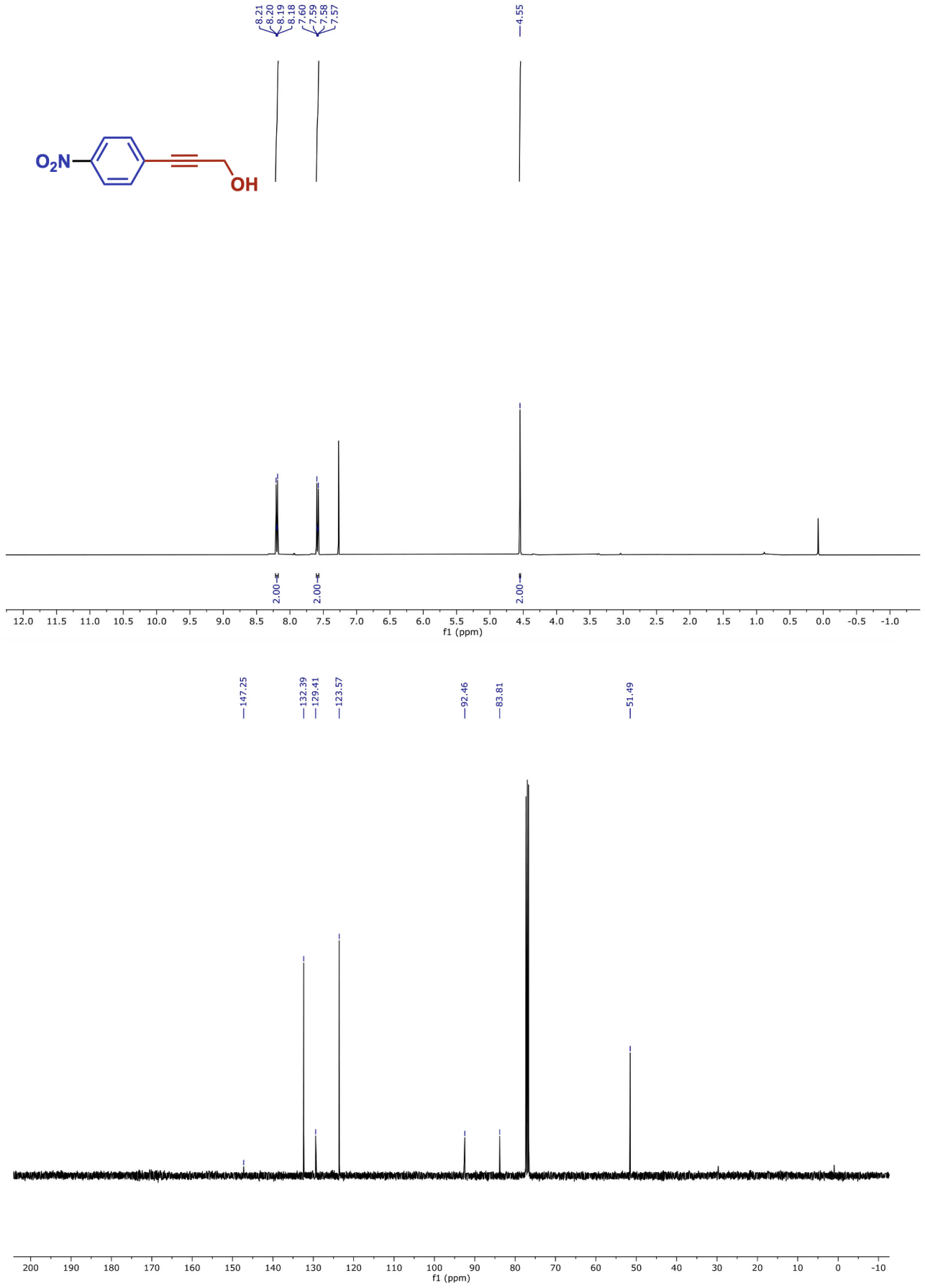


N,N-dimethyl-3-phenylprop-2-yn-1-amine, ***3h***

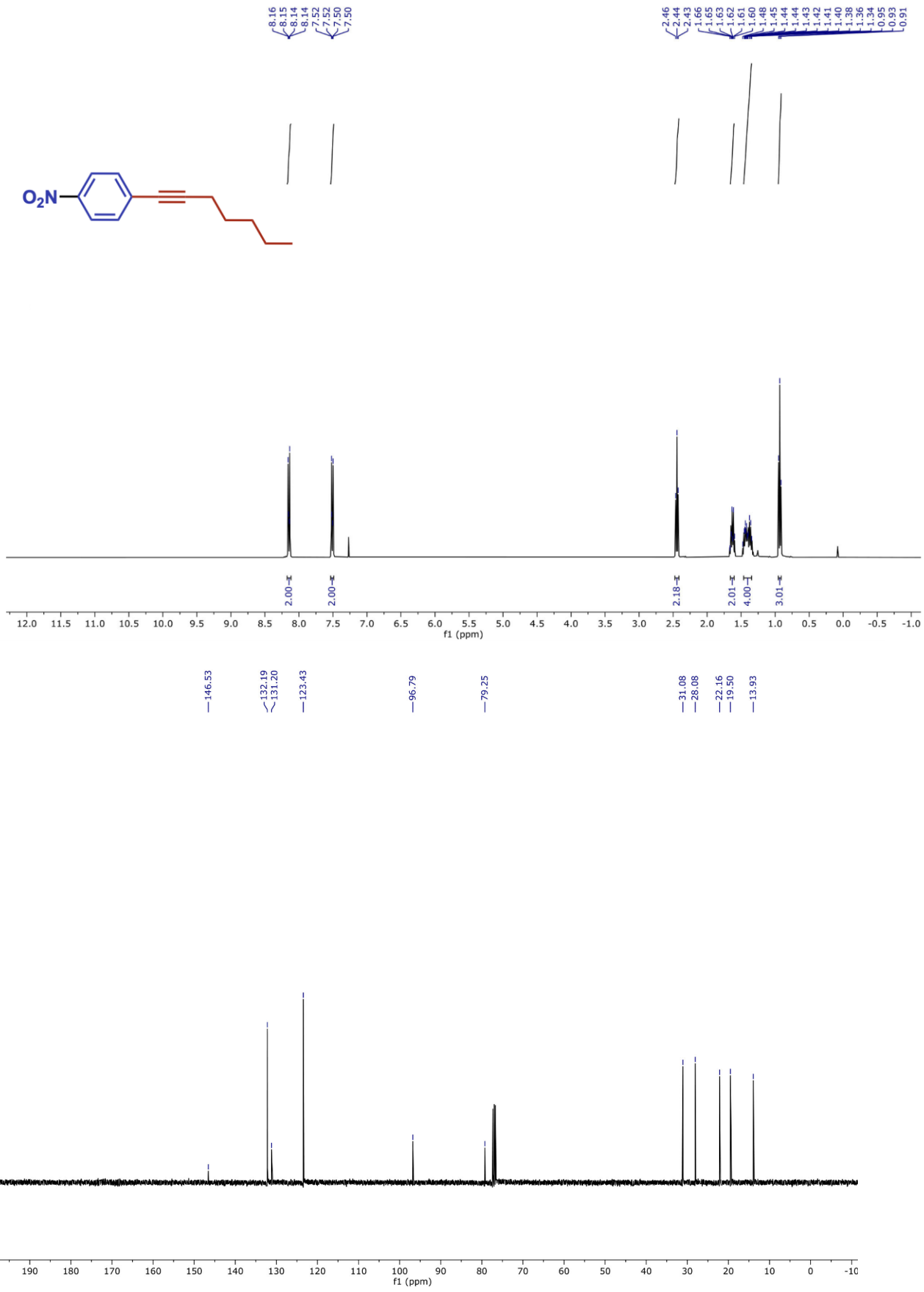




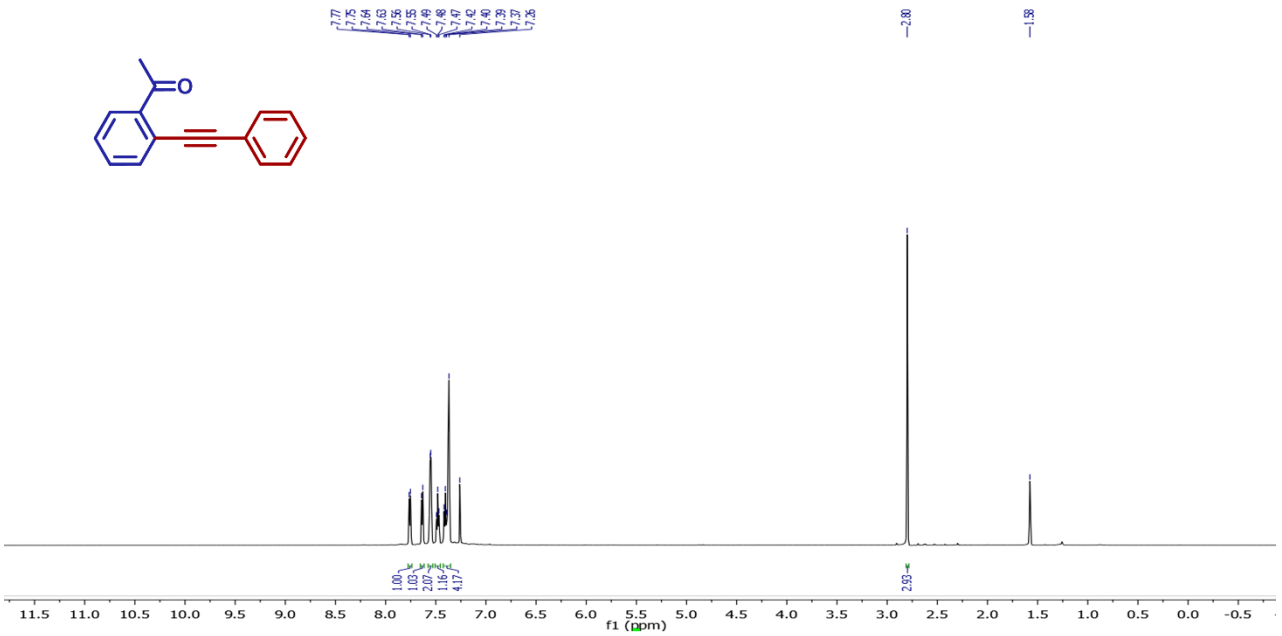
3-(4-nitrophenyl)prop-2-yn-1-ol, ***3i***

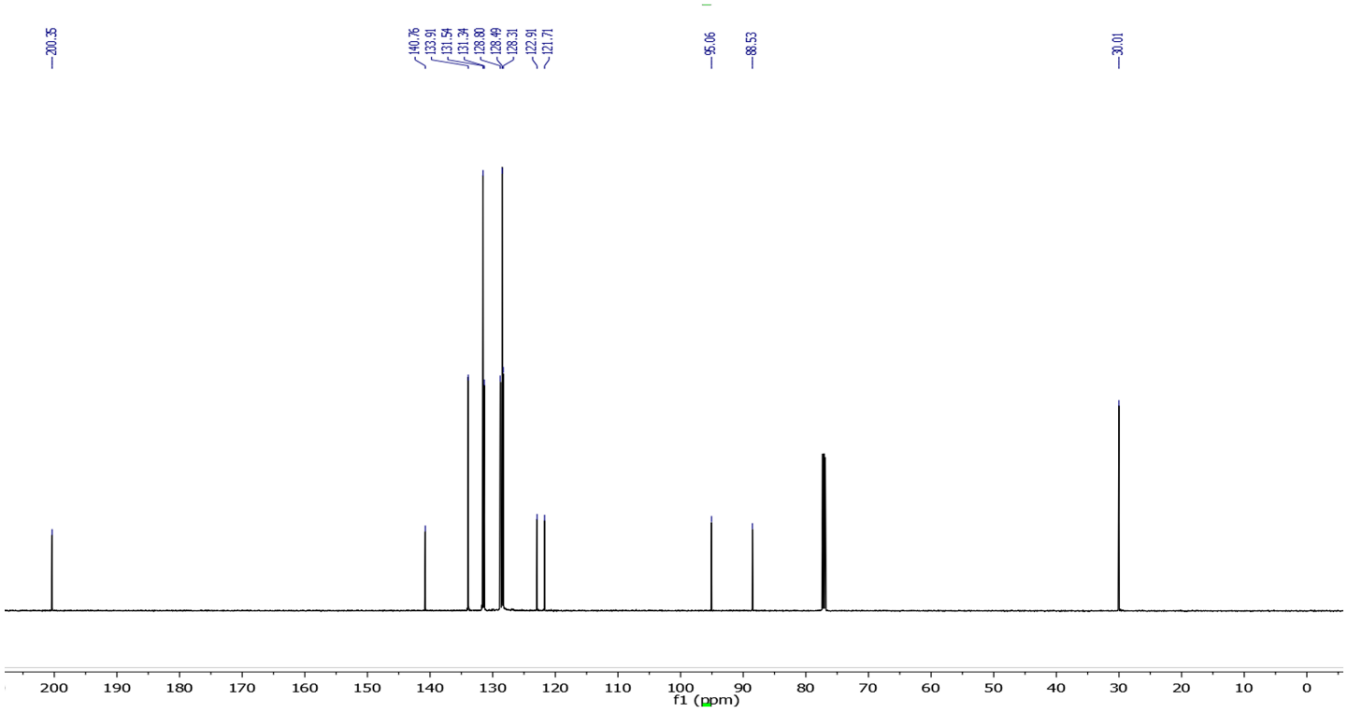


1-(hept-1-yn-1-yl)-4-nitrobenzene, ***3j***

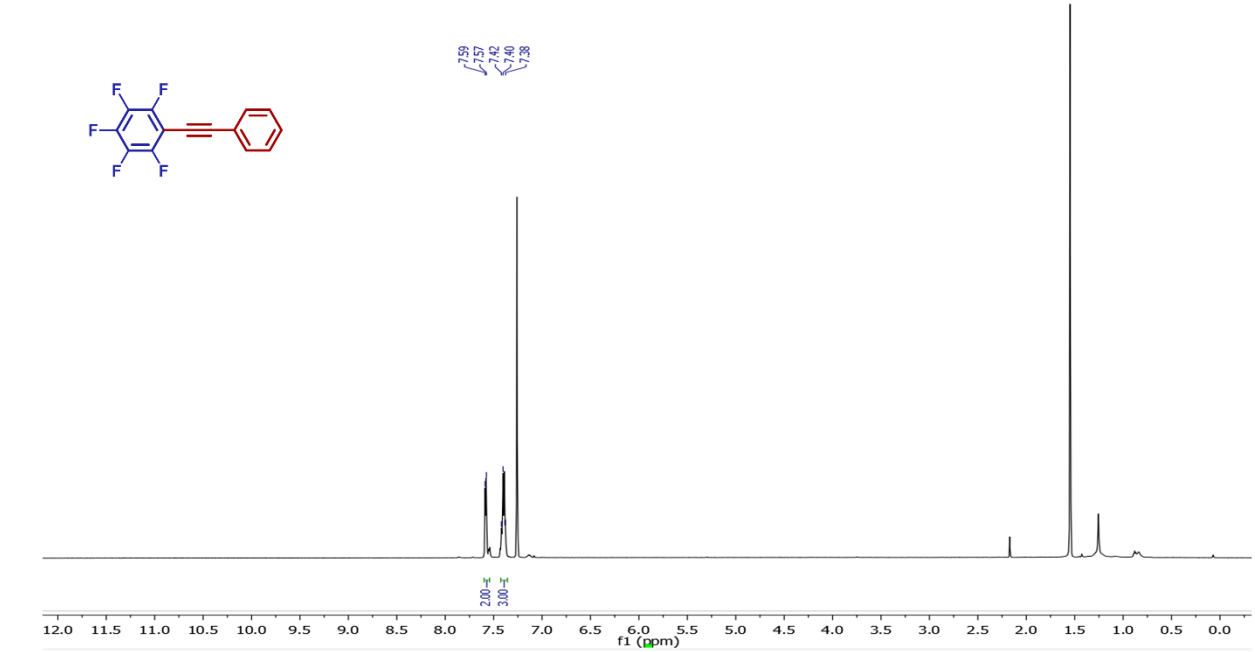


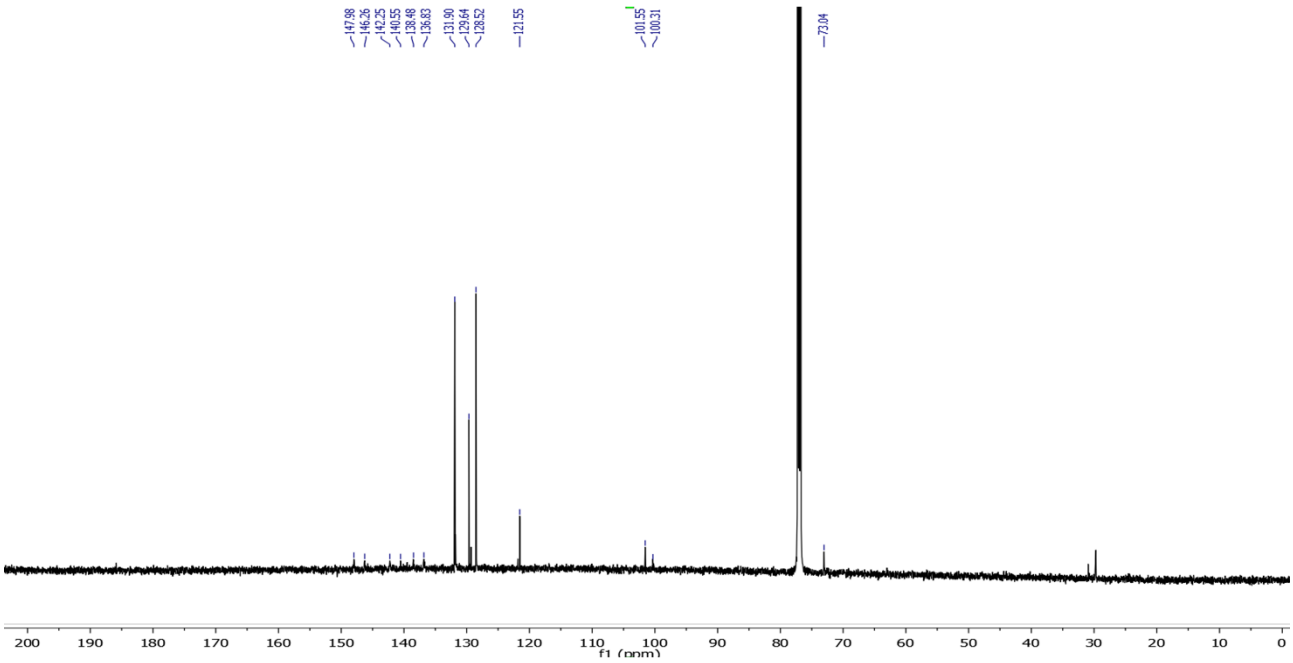
1-(2-(phenylethynyl)phenyl)ethan-1-one, ***3k***



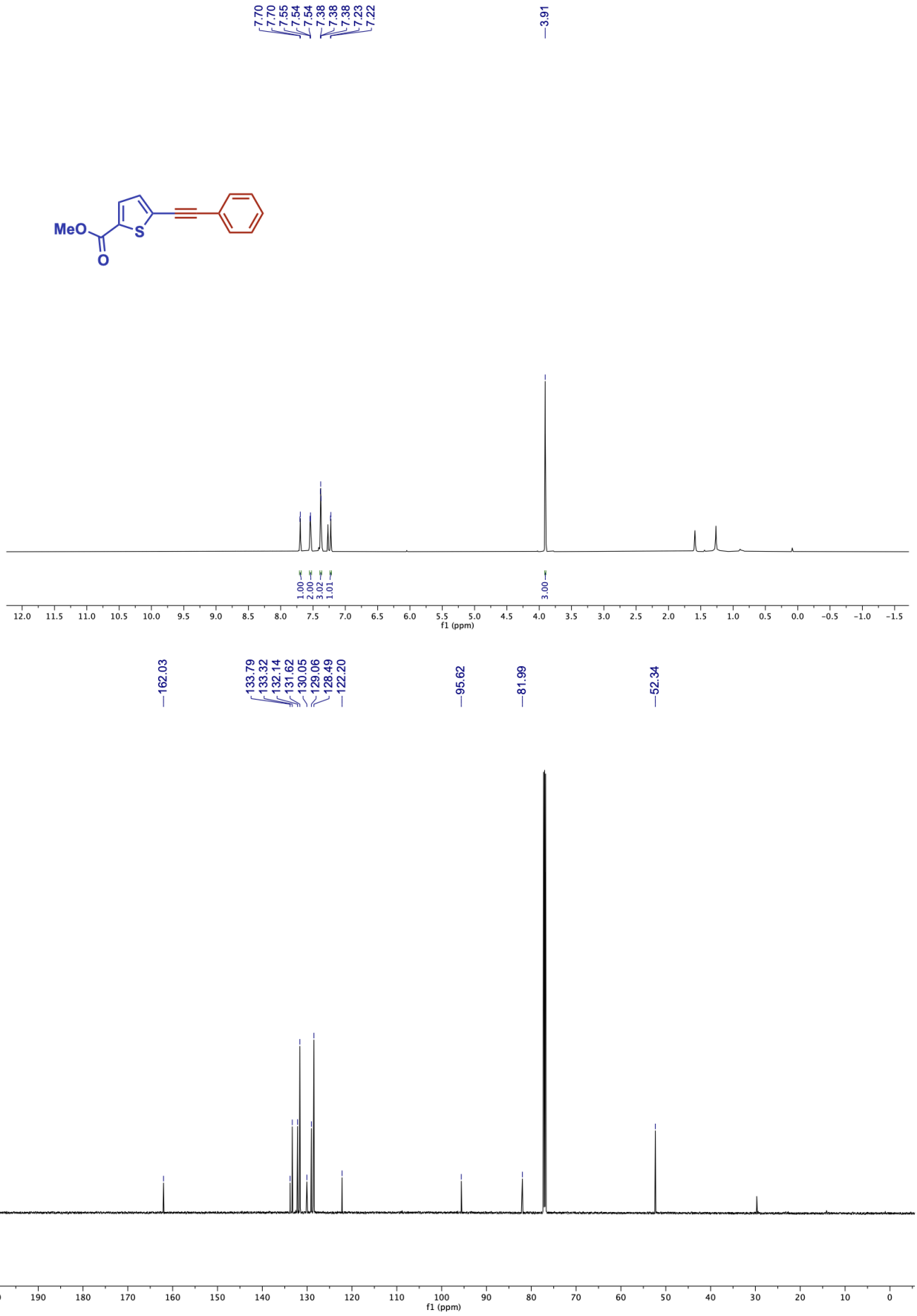


1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene, ***3l***

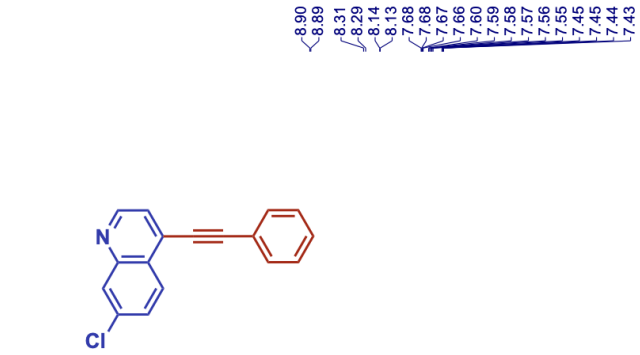


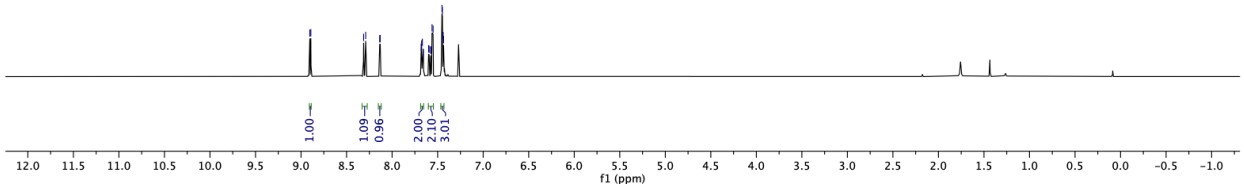


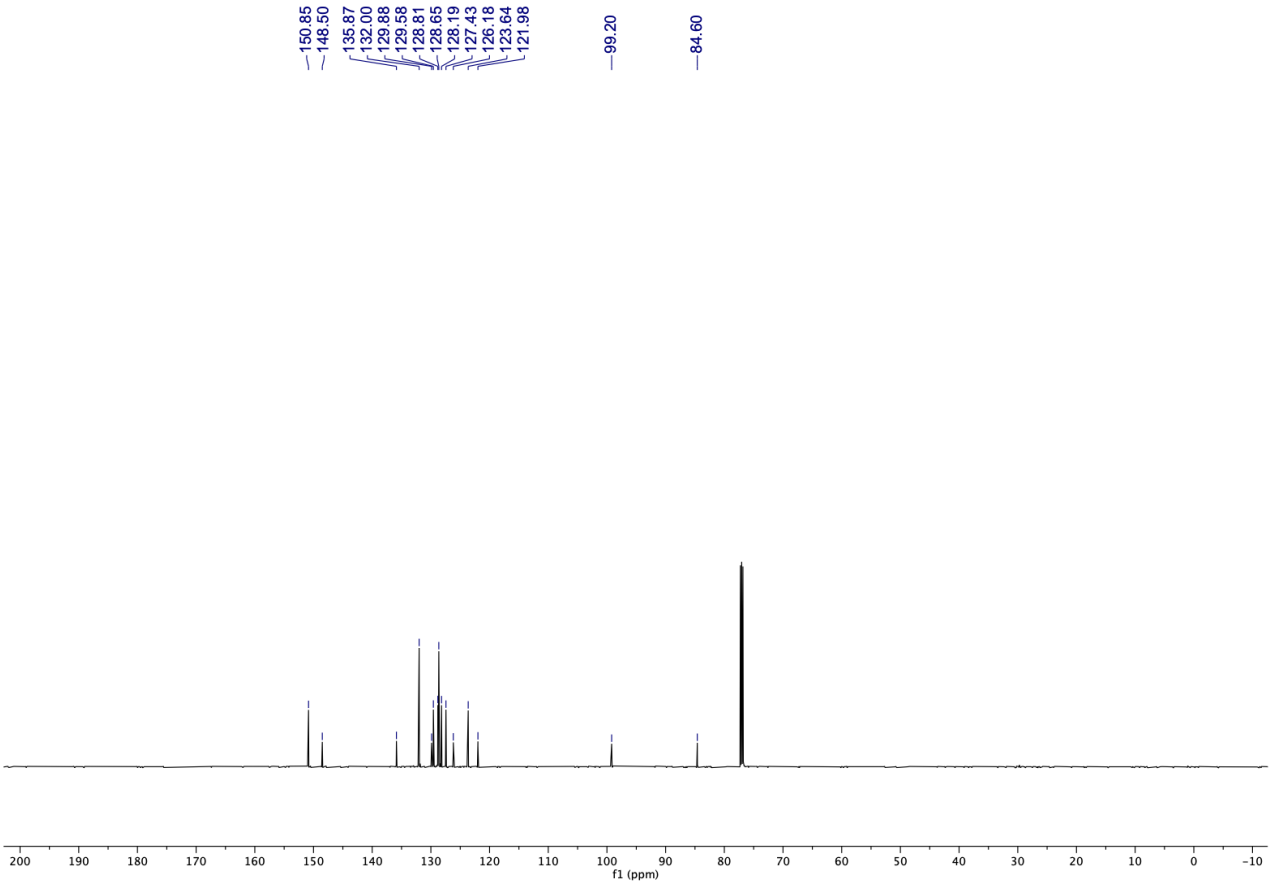
methyl 5-(phenylethynyl)thiophene-2-carboxylate, ***3m***



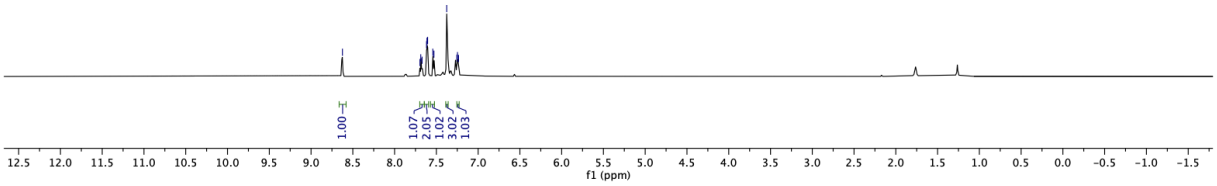
7-chloro-4-(phenylethynyl)quinoline, ***3n***

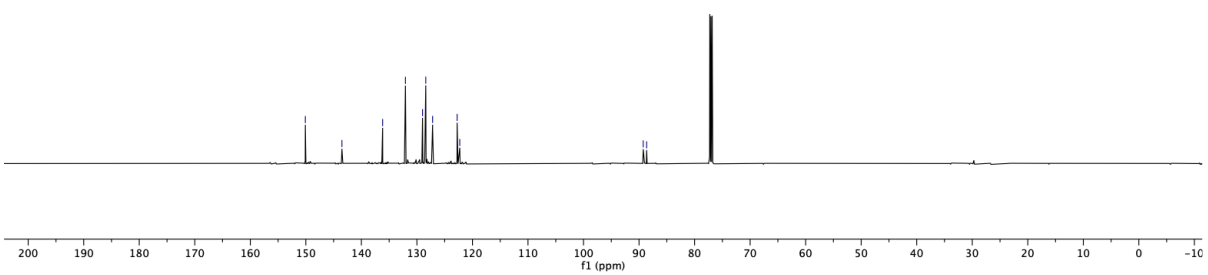




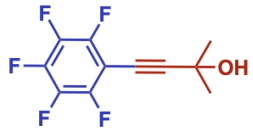


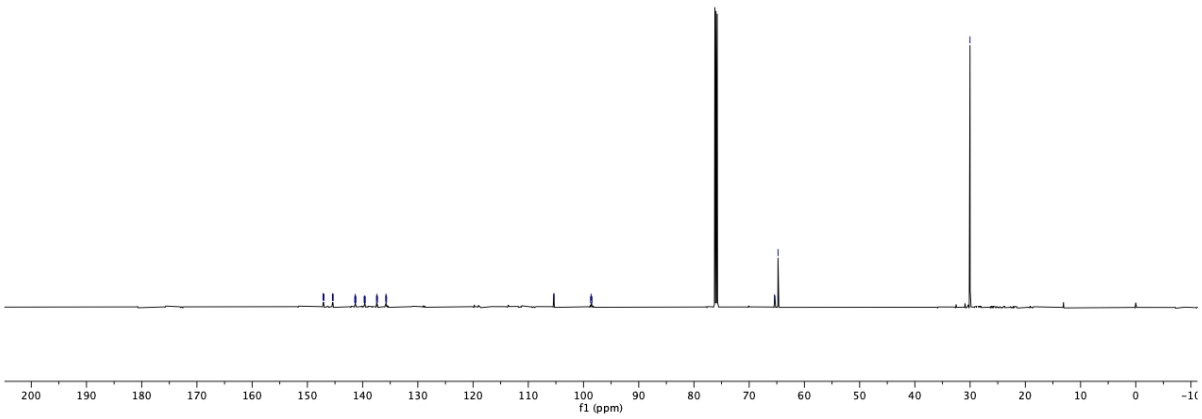
2-(phenylethynyl)pyridine, ***3o***



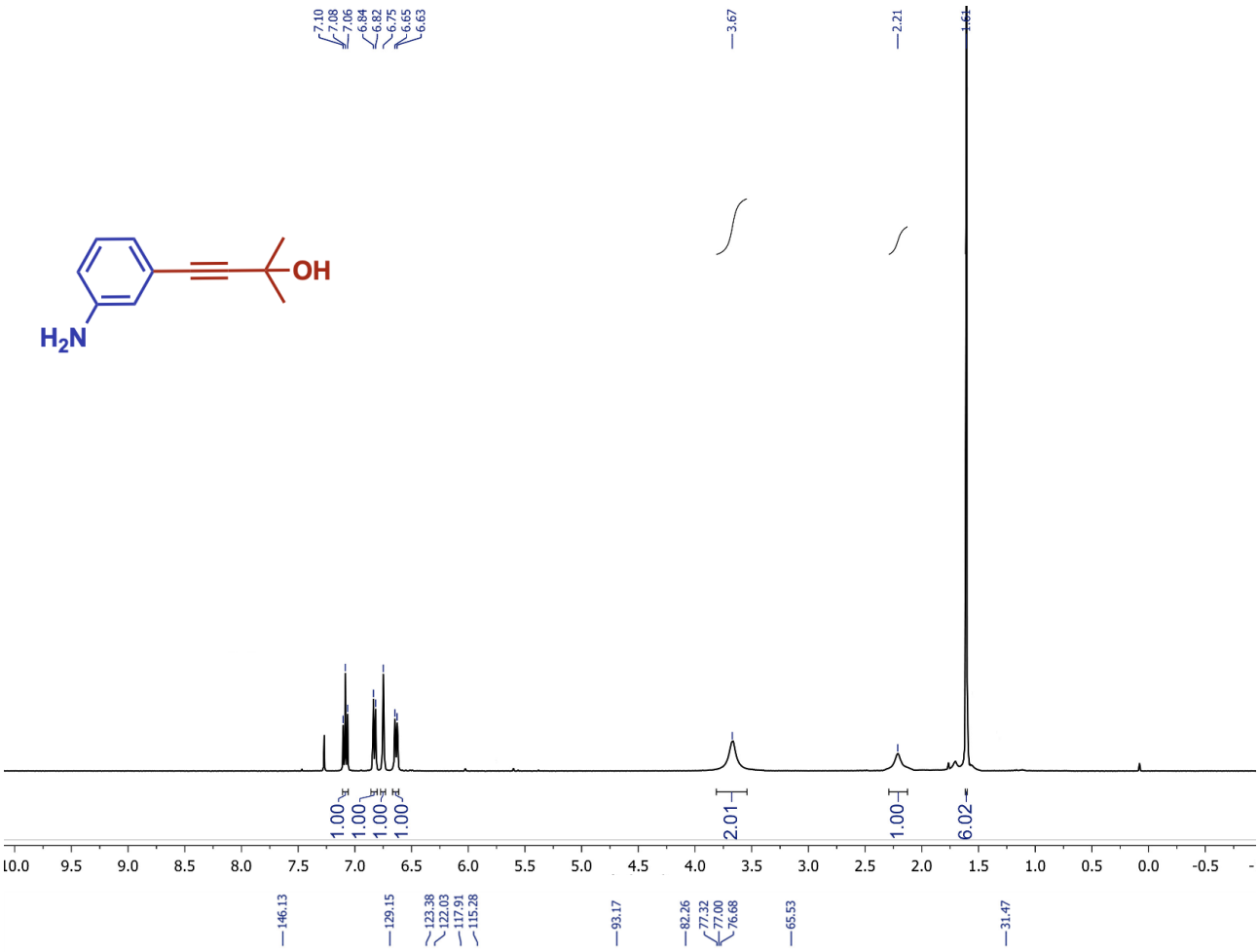


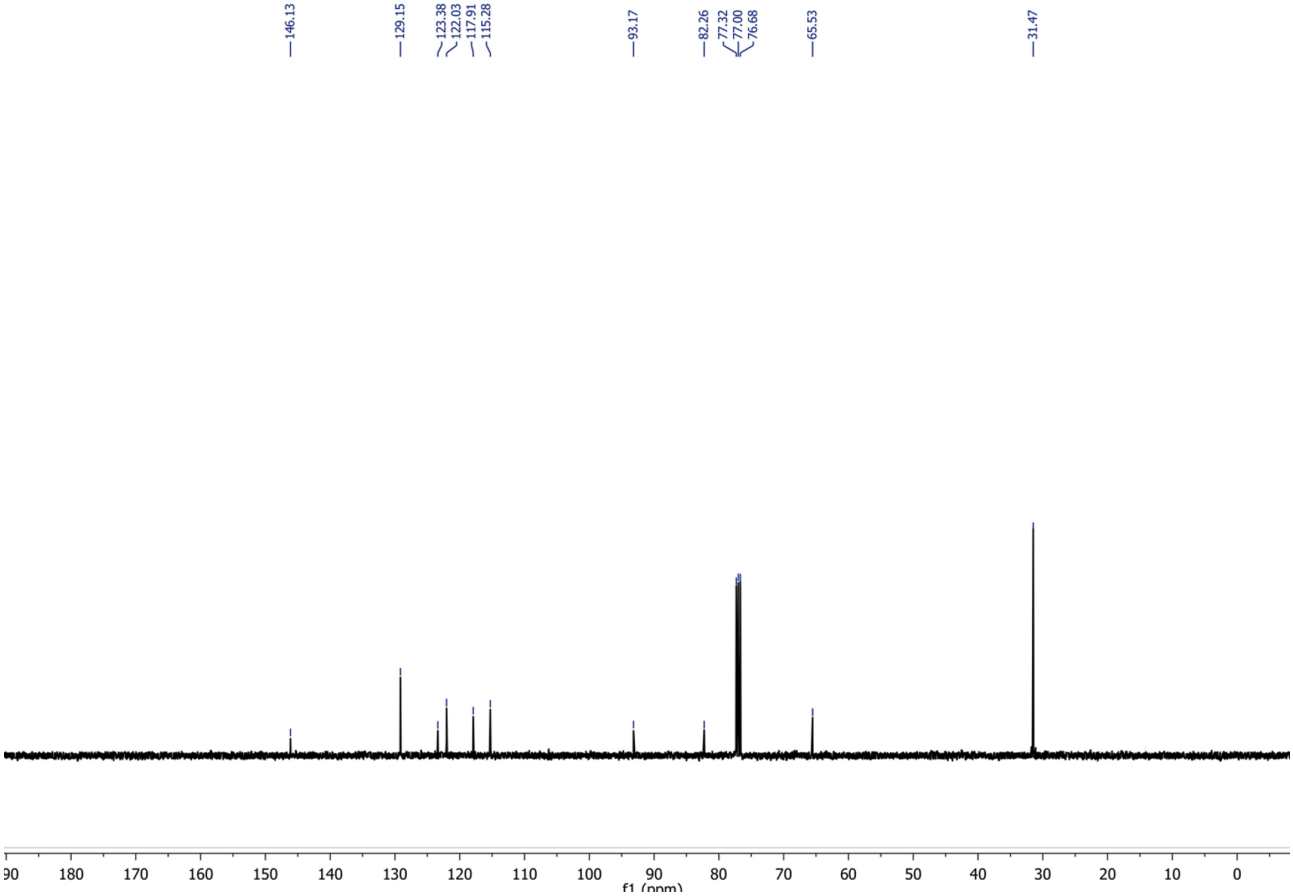
2-methyl-4-(perfluorophenyl)but-3-yn-2-ol, ***3p***



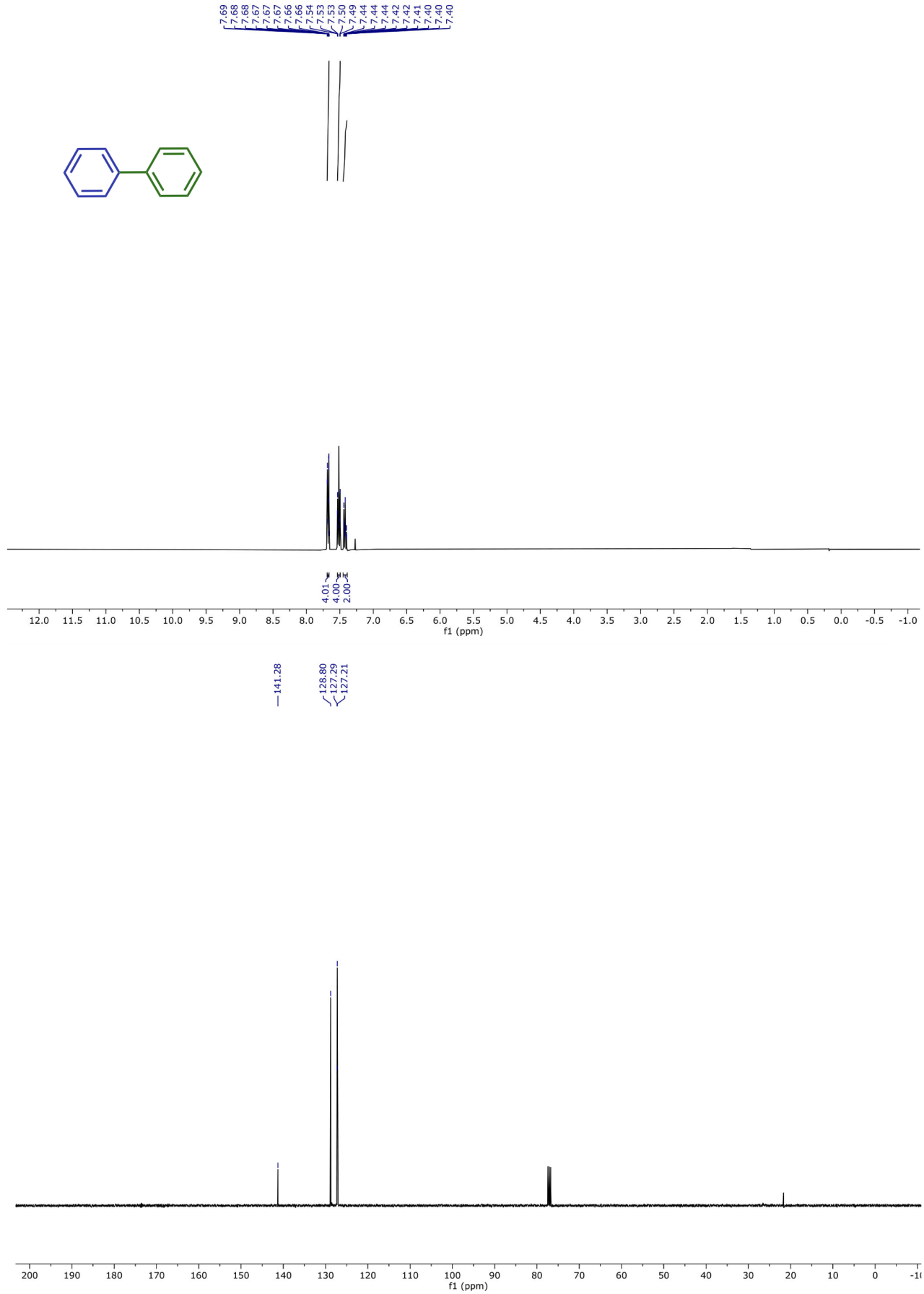


4-(3-aminophenyl)-2-methylbut-3-yn-2-ol, ***3q***

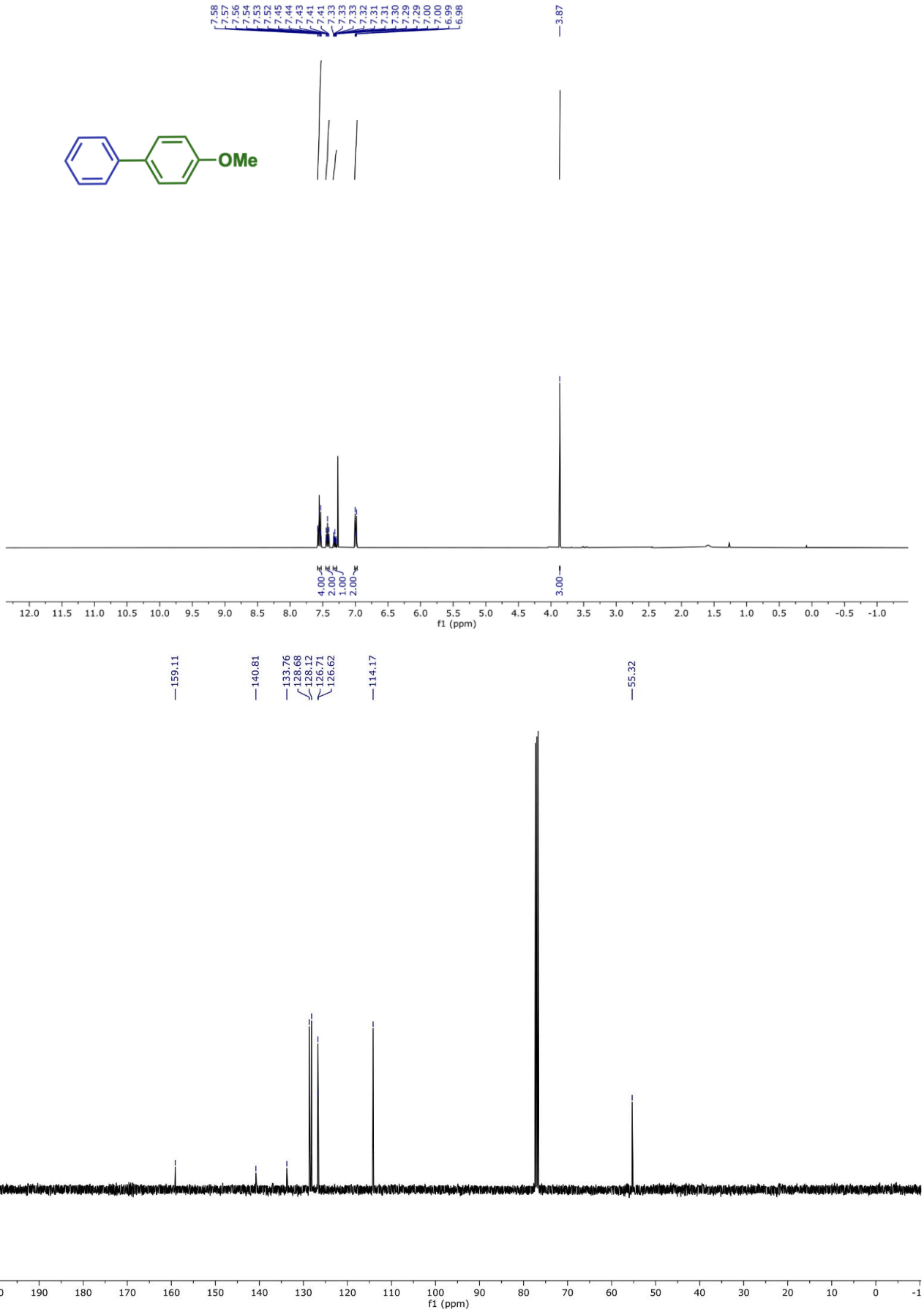




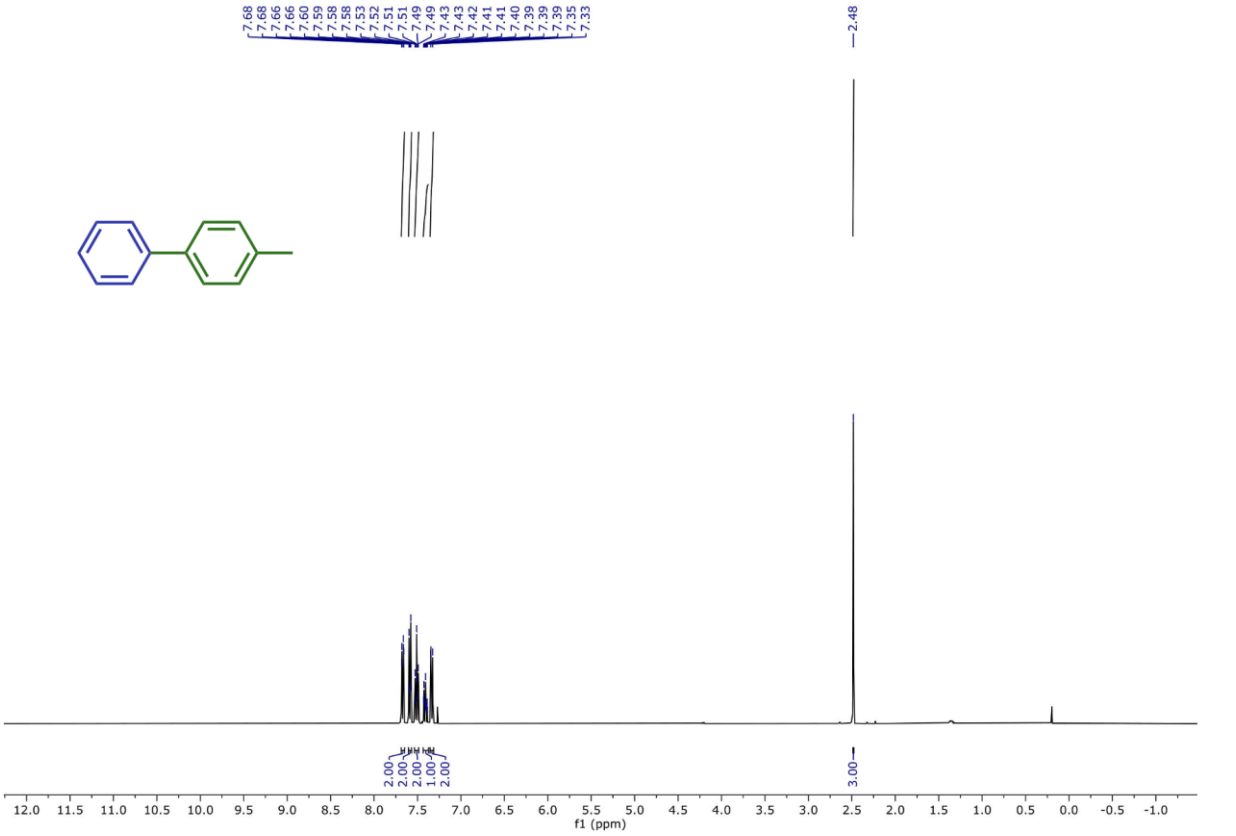
1,1'-biphenyl, ***6a***

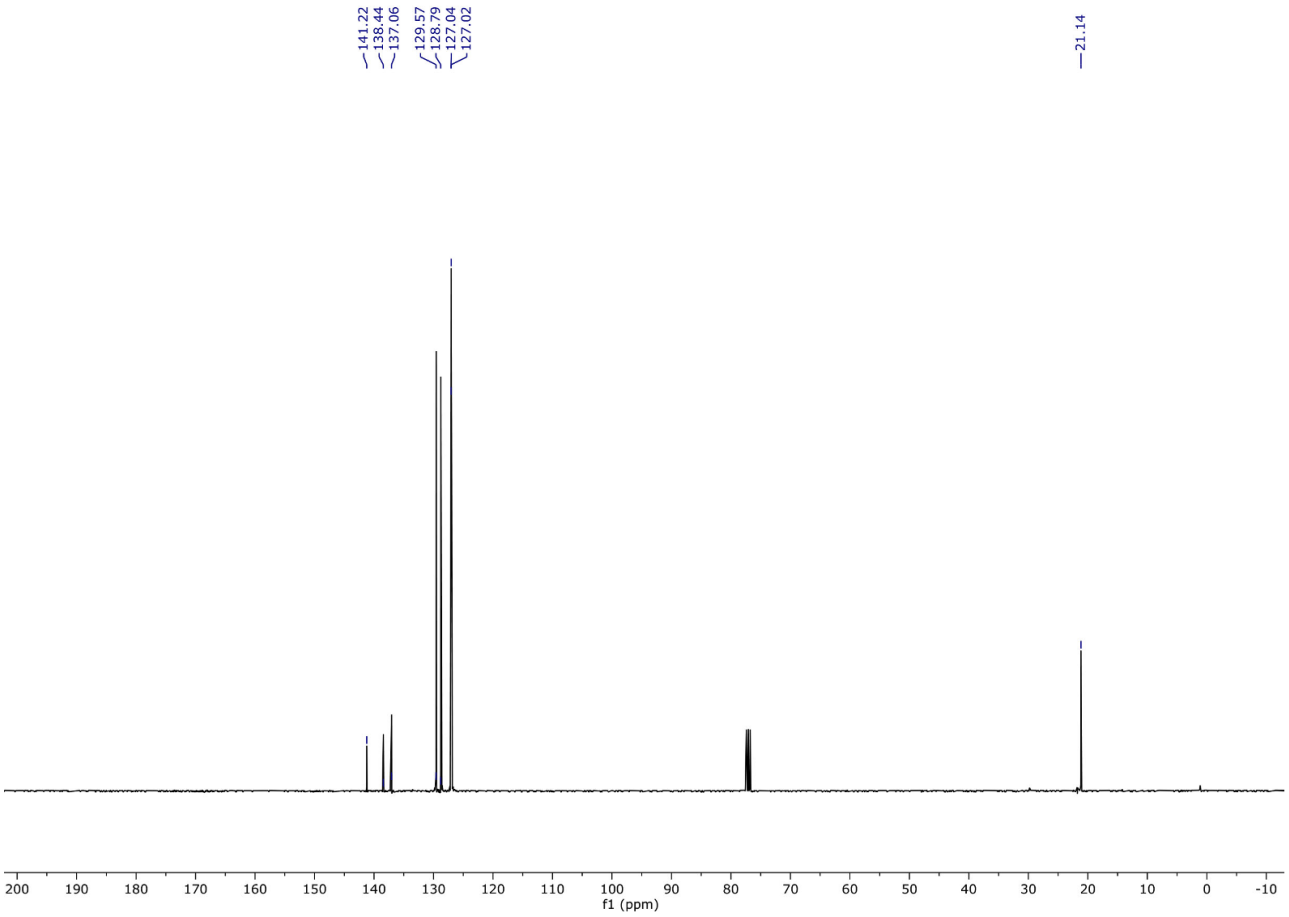


4-methoxy-1,1'-biphenyl, ***6b-6e***

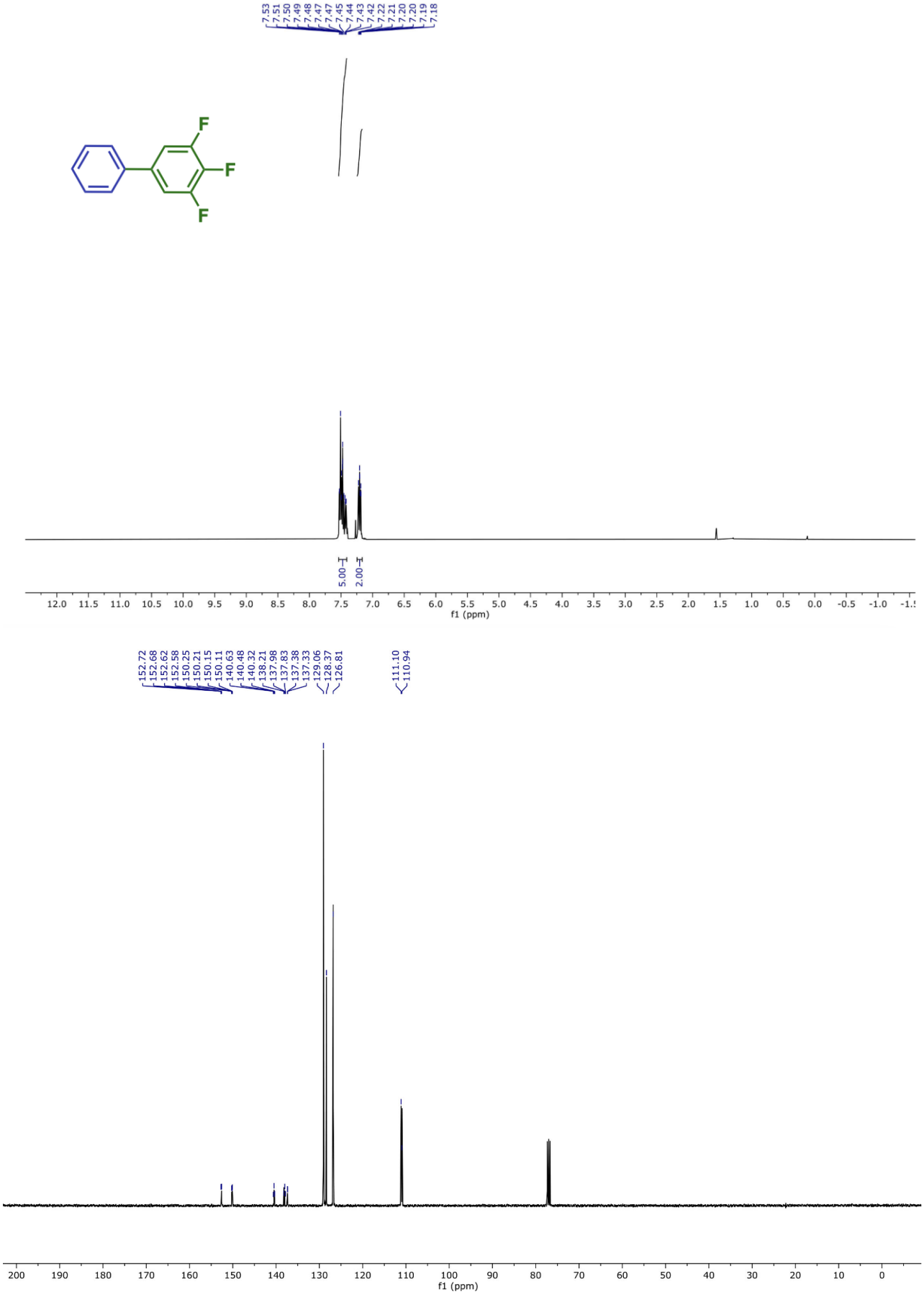


4-methyl-1,1'-biphenyl, ***6c-6f***

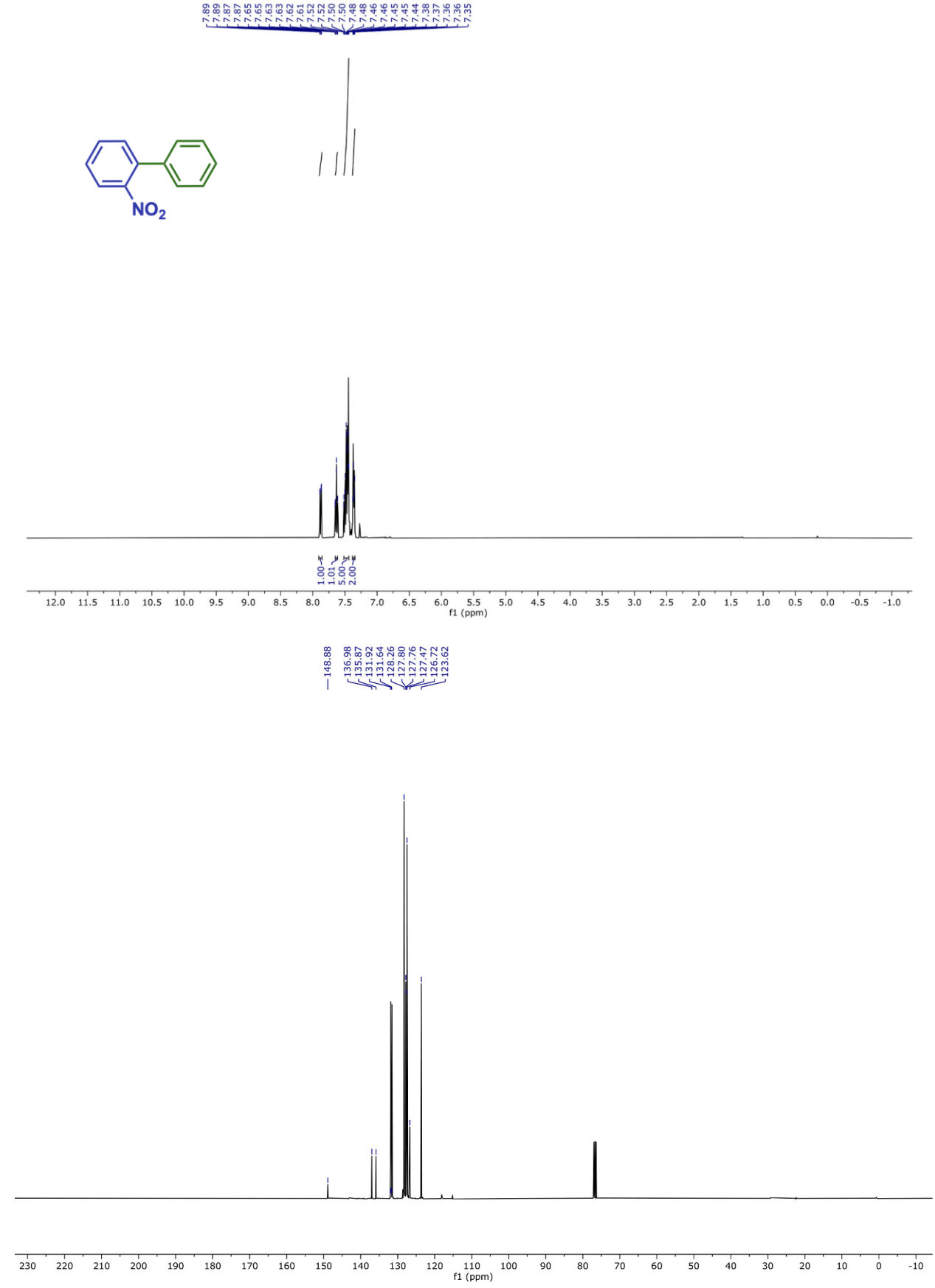




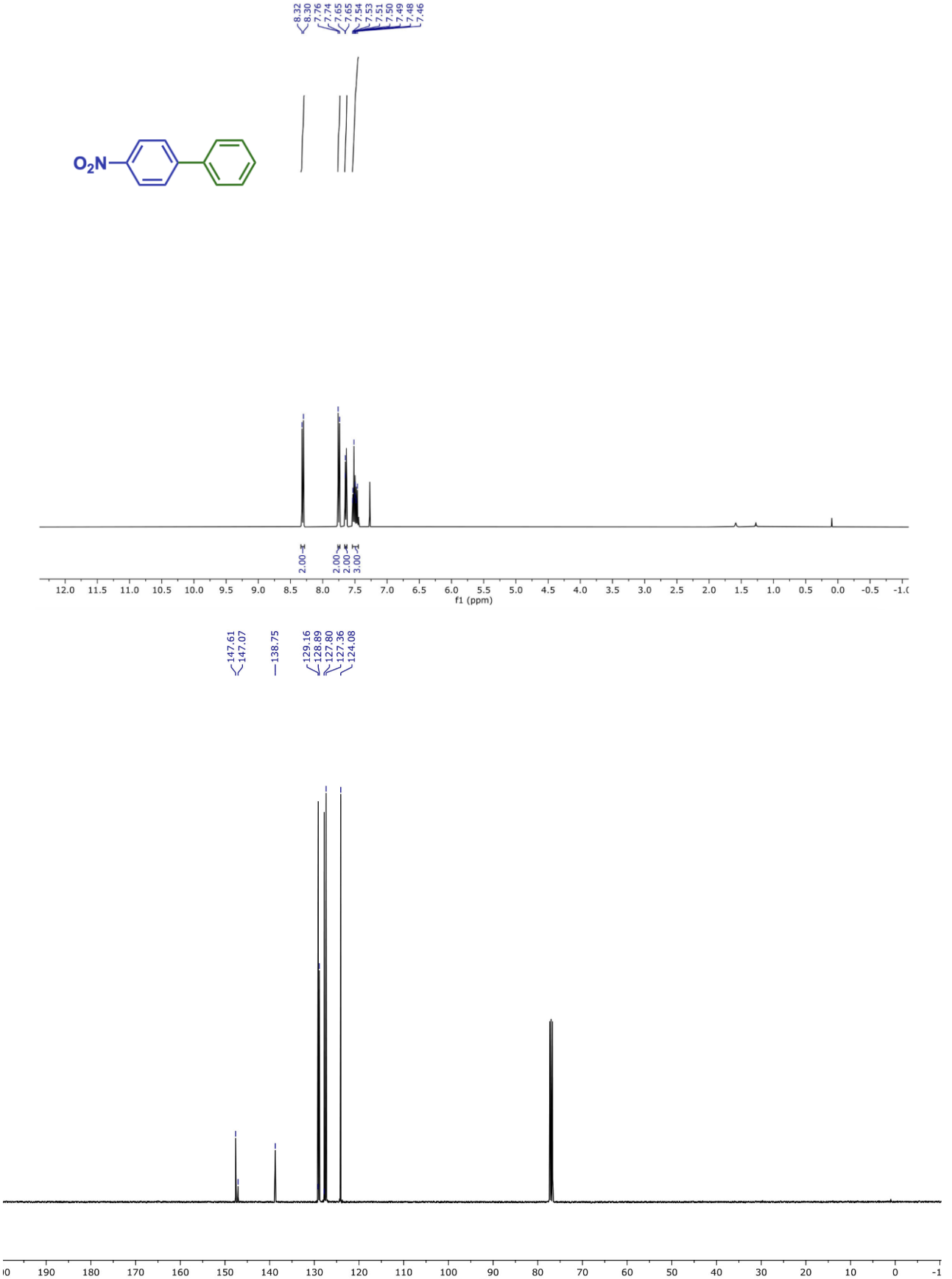
3,4,5-trifluoro-1,1'-biphenyl, ***6d***



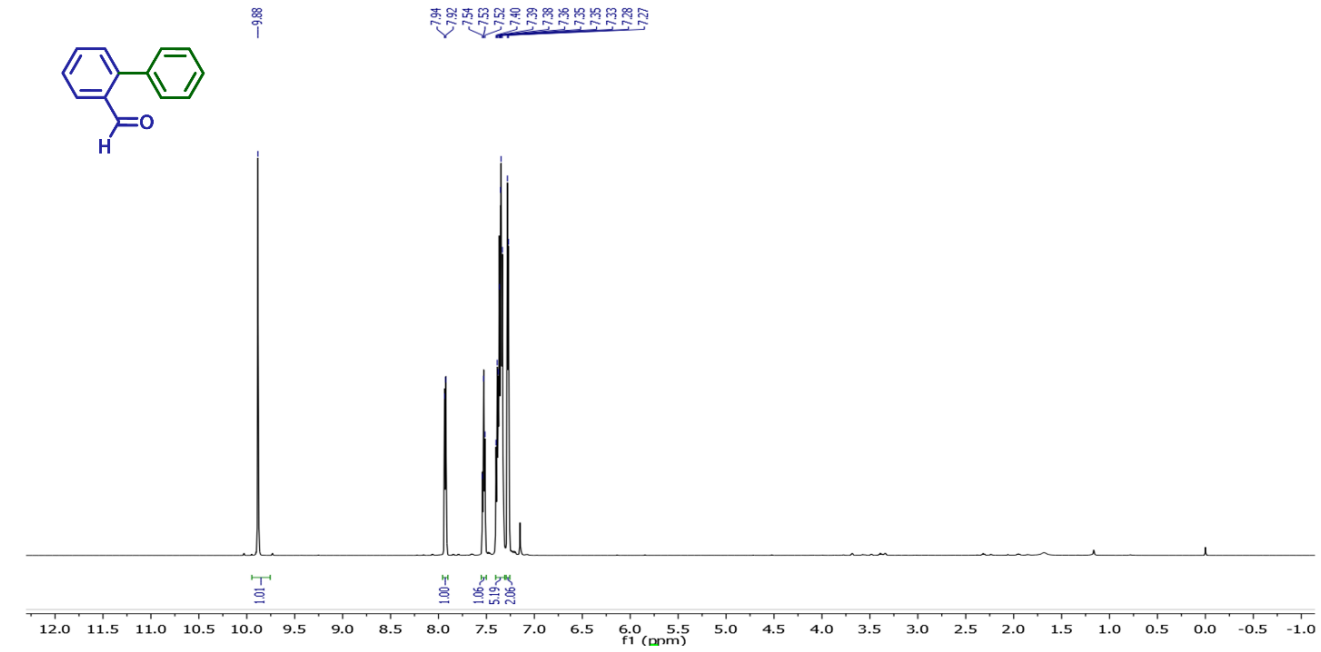
2-nitro-1,1'-biphenyl, ***6g***

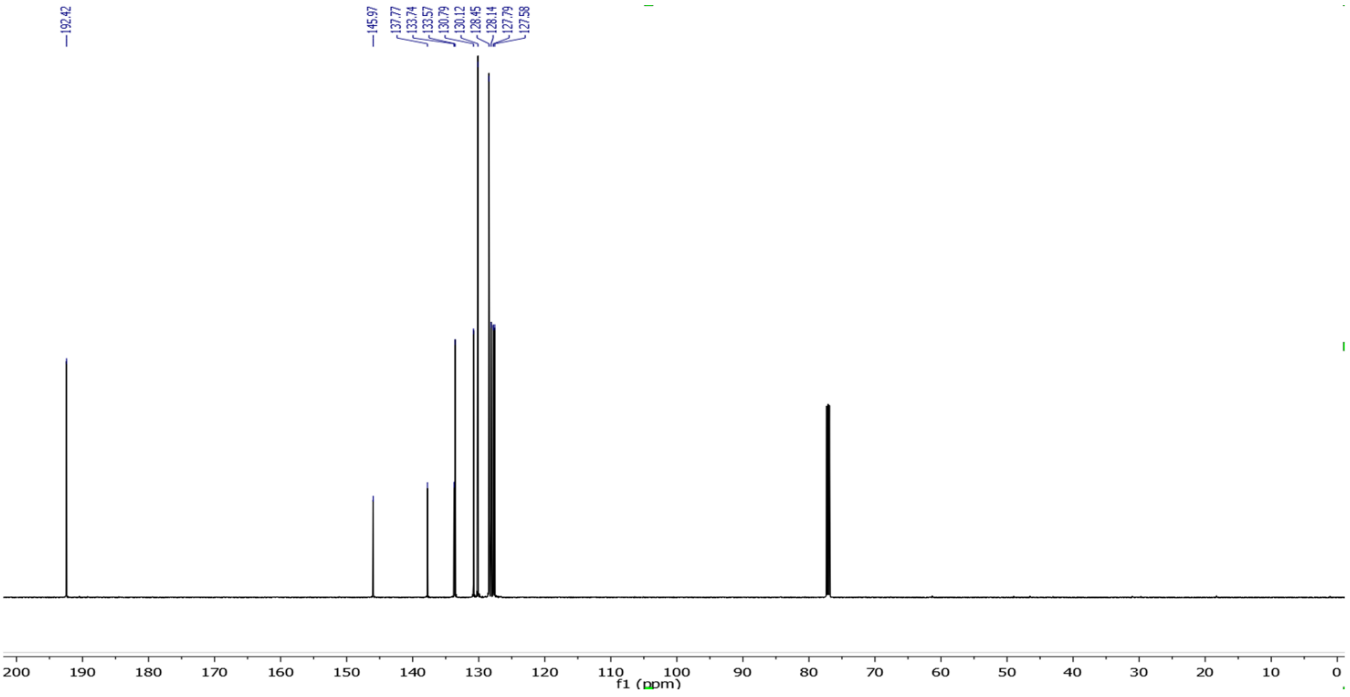


4-nitro-1,1'-biphenyl, ***6h***

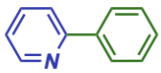


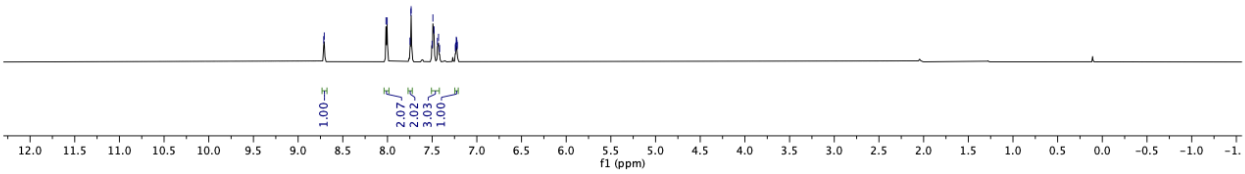
[1,1'-biphenyl]-2-carbaldehyde, ***6i***

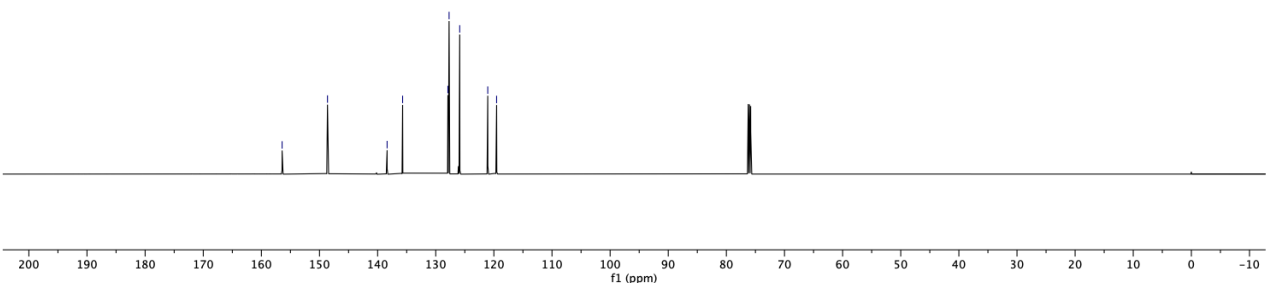




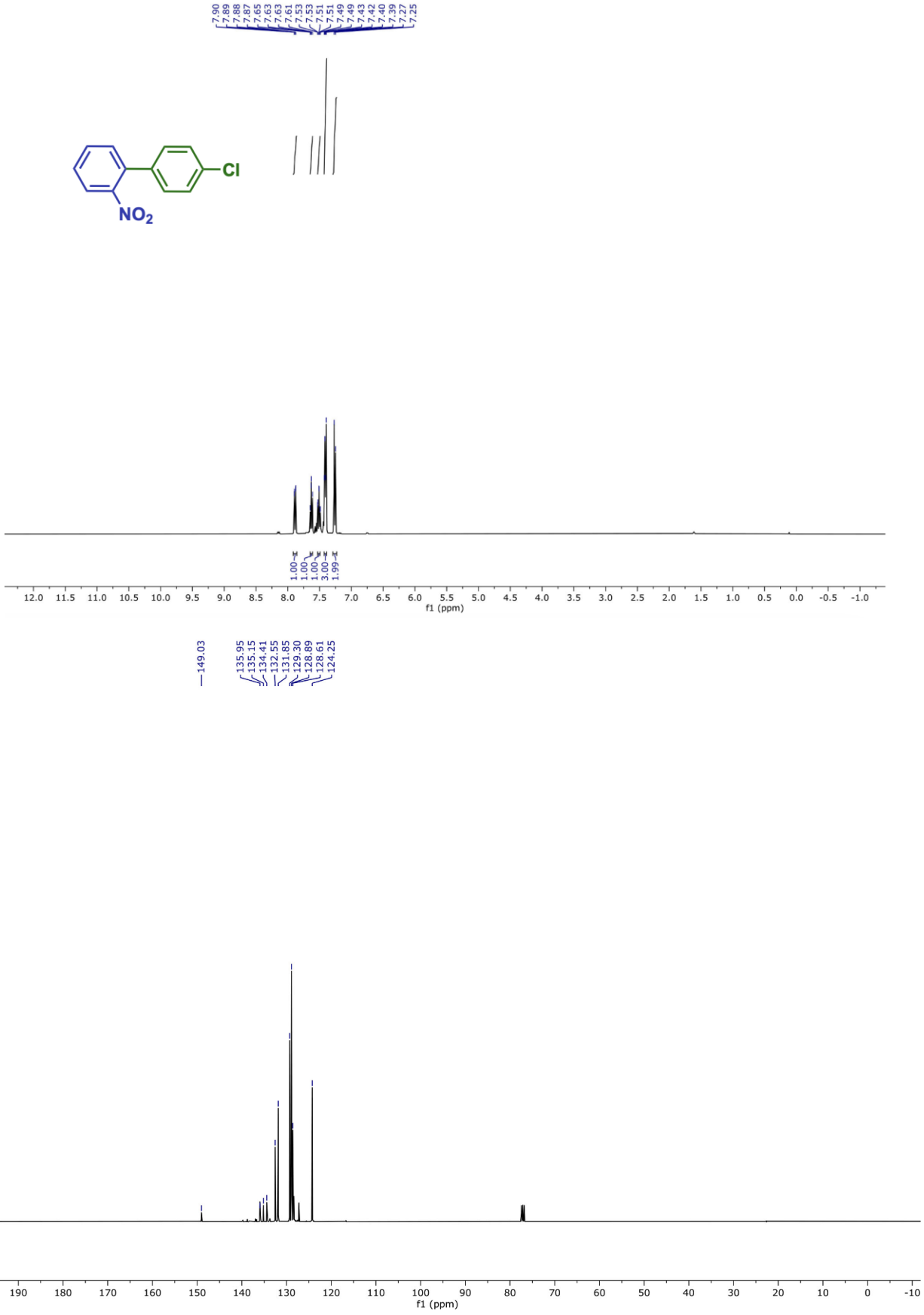
2-phenylpyridine, ***6j***



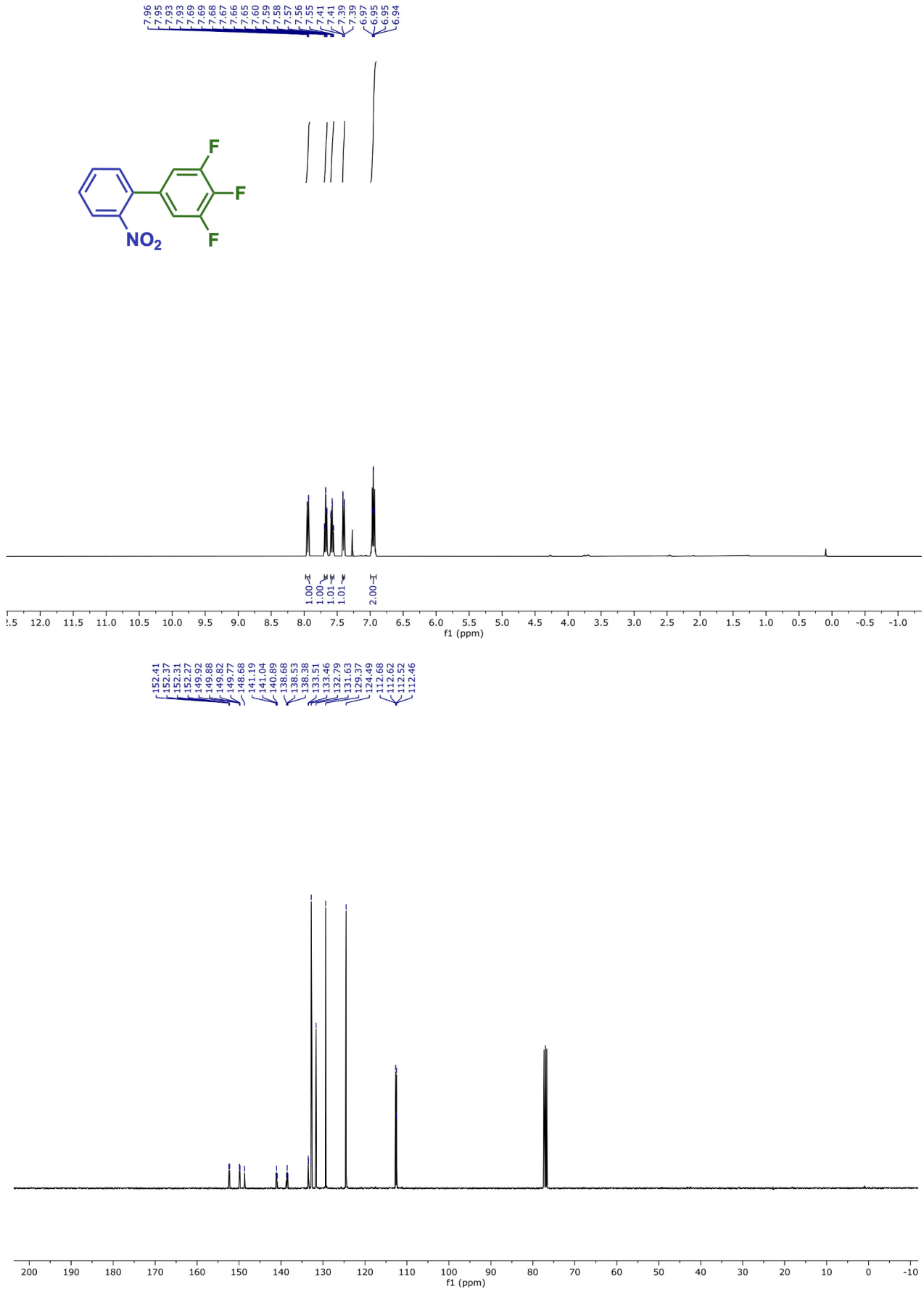




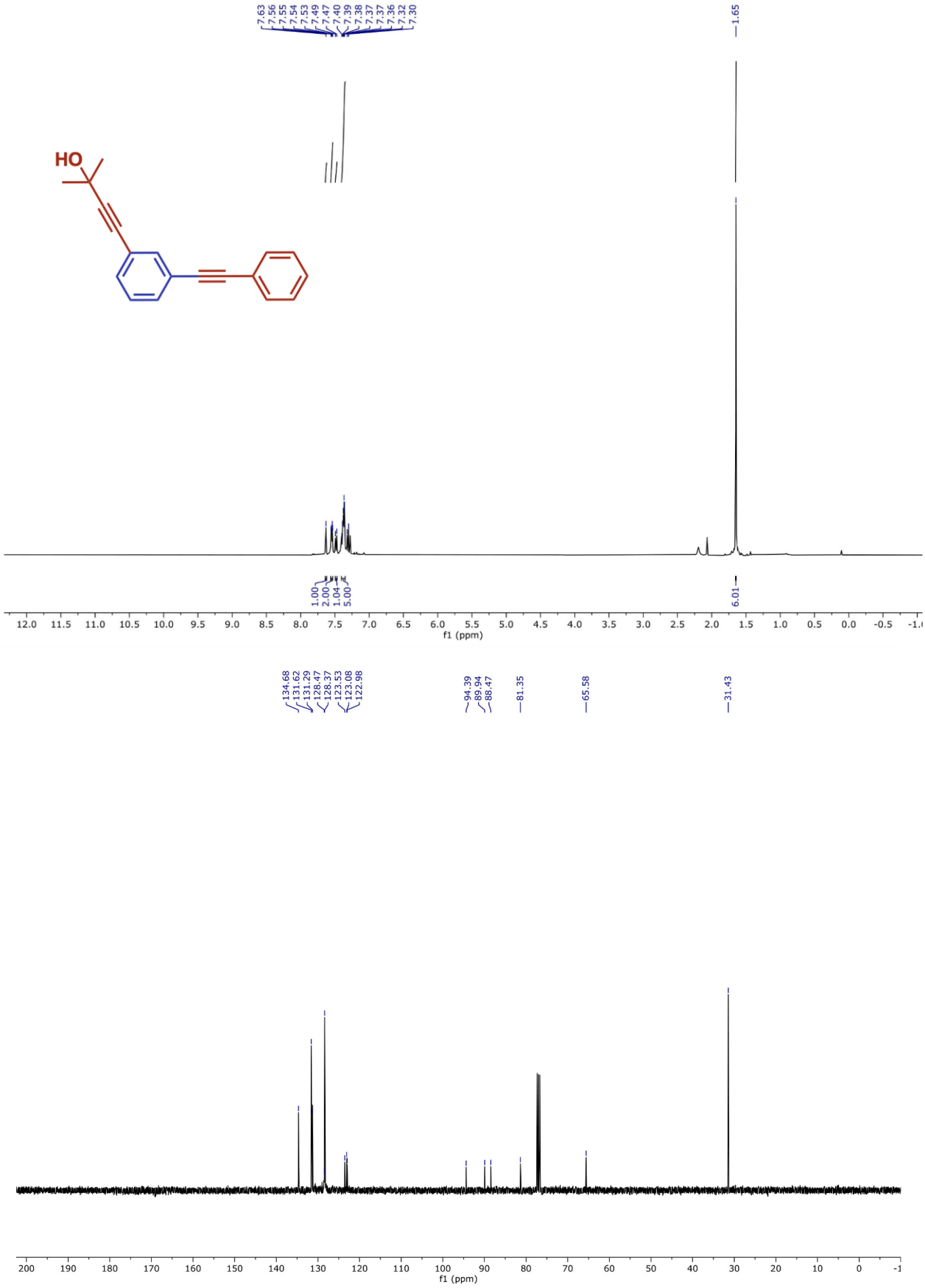
4'-chloro-2-nitro-1,1'-biphenyl, ***6k***



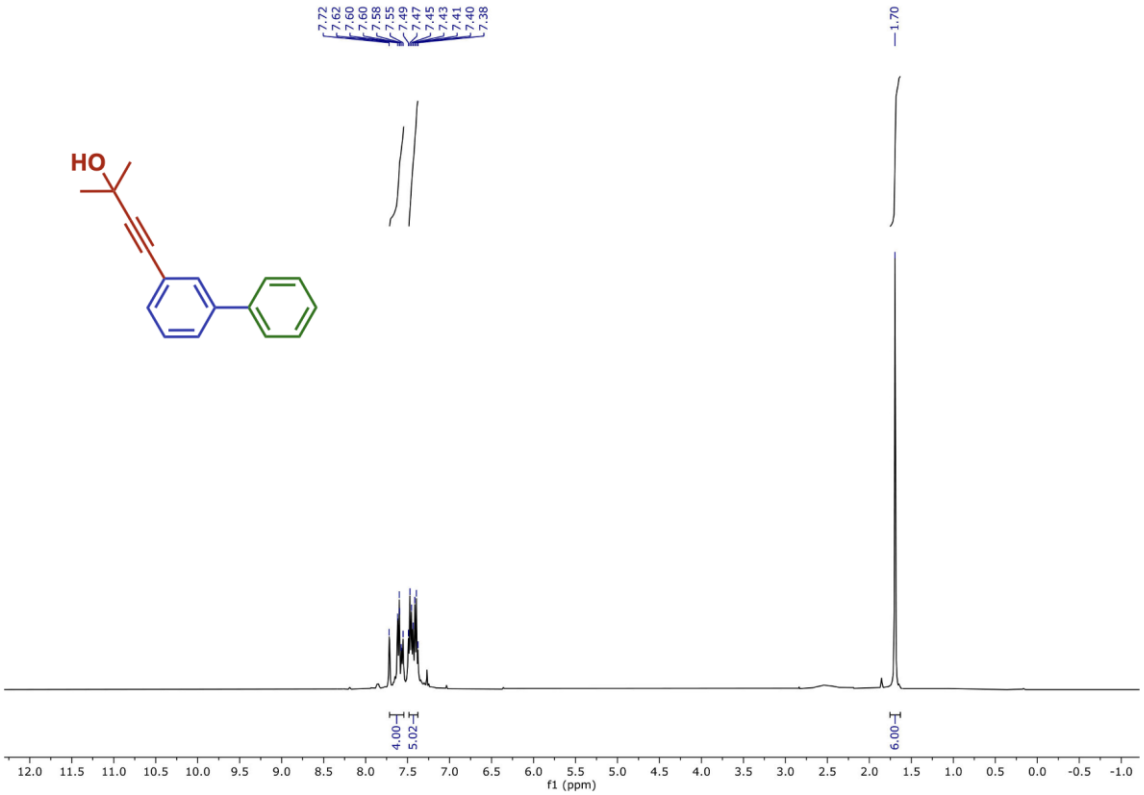
3',4',5'-trifluoro-2-nitro-1,1'-biphenyl, ***6l***

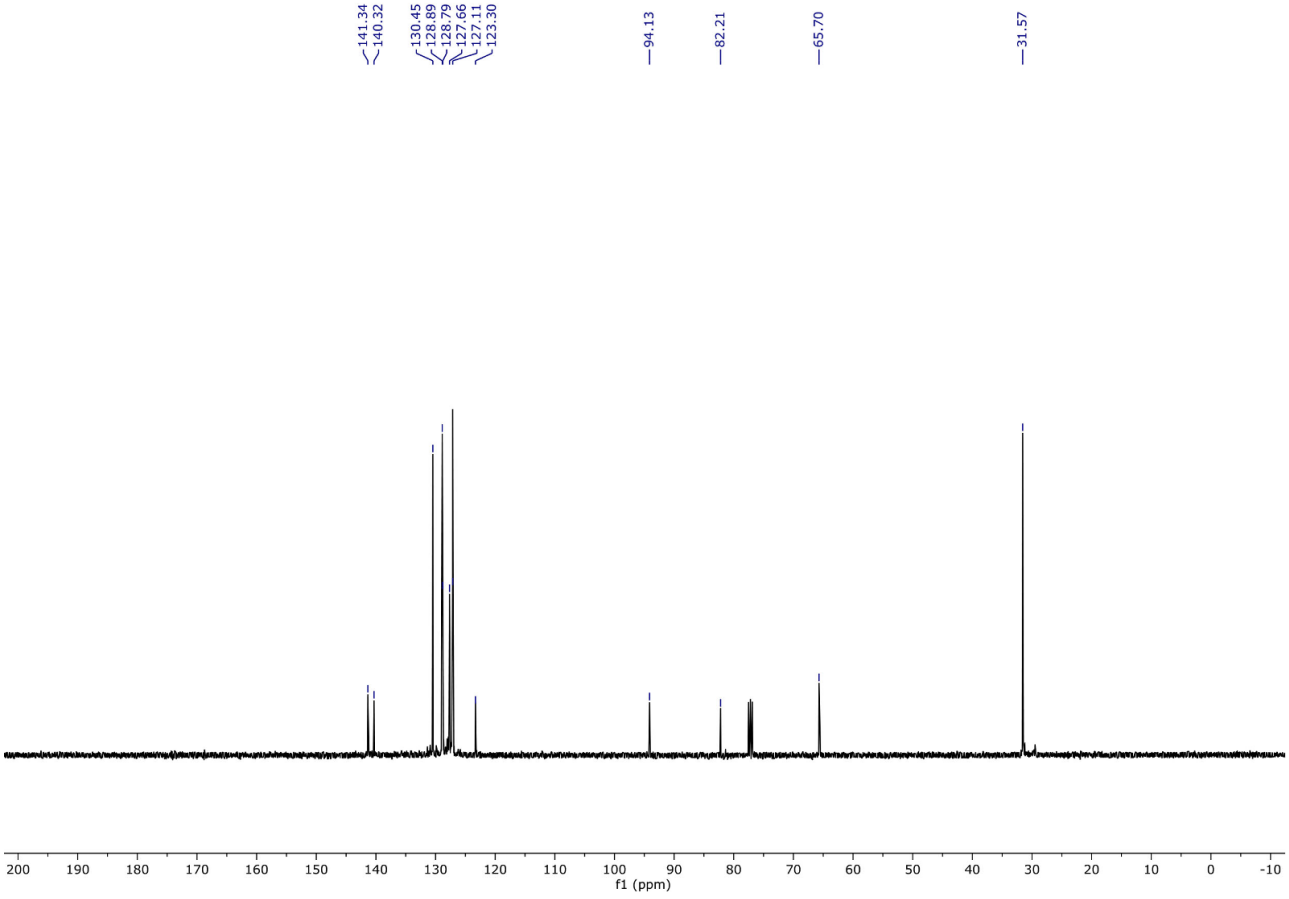


2-methyl-4-(3-(phenylethynyl)phenyl)but-3-yn-2-ol, ***9***



4-([1,1'-biphenyl]-3-yl)-2-methylbut-3-yn-2-ol, ***10***





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