



Supporting Information

Catalytic Photoredox Allylation of Aldehydes Promoted by a Cobalt Complex

Andrea Gualandi,* Giacomo Rodeghiero, Rossana Perciaccante, Thomas Paul Jansen, Cristina Moreno-Cabrerizo, Charles Foucher, Marianna Marchini,* Paola Ceroni, and Pier Giorgio Cozzi*

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General Methods and Synthesis

All commercial chemicals and dry solvents were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 NMR instrument with a 5 mm probe. All chemical shifts are referenced using deuterated solvent signals; chemical shifts (δ) are reported in ppm from TMS and coupling constants (J) are reported in Hertz. Multiplicity is reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad signal). GC-MS spectra were obtained by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection; they are reported as: m/z (rel. intensity). HPLC-MS analyses were performed on an Agilent Technologies HP1100 instrument coupled with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer using a Phenomenex Gemini C18 3 μm (100 x 3 mm) column; mass spectrometric detection was performed in full-scan mode from m/z 50 to 2500, scan time 0.1 s in positive ion mode, ESI spray voltage 4500 V, nitrogen gas 35 psi, drying gas flow rate 11.5 mL min^{-1} , fragmentor voltage 30 V. HPLC analyses were performed on an Agilent Technologies Series 1200 instrument. The enantiomeric compositions were checked against the corresponding racemic products. Flash chromatography purifications were carried out using VWR or Merck silica gel (40-63 μm particle size). Thin-layer chromatography was performed on Merck 60 F254 plates.

3-Phenylprop-2-enyl acetate (**2b**, cinnamyl acetate) and (E)-hex-2-en-1-yl acetate (**2c**) were prepared according to the literature procedure.^[1]

$[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ was prepared according to the reported procedure^[2] or purchased from Sigma-Aldrich.

Photochemical reactions

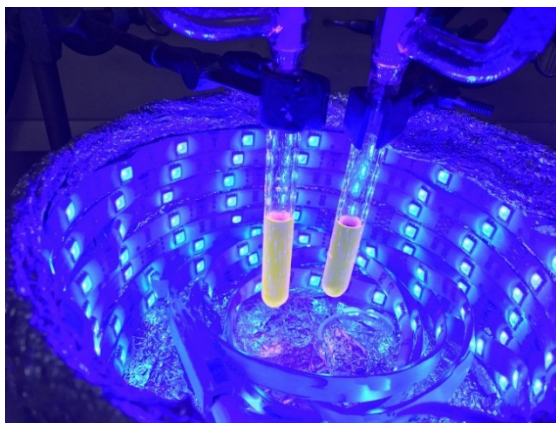


Figure S1. Reaction set-up for the photochemical reaction.

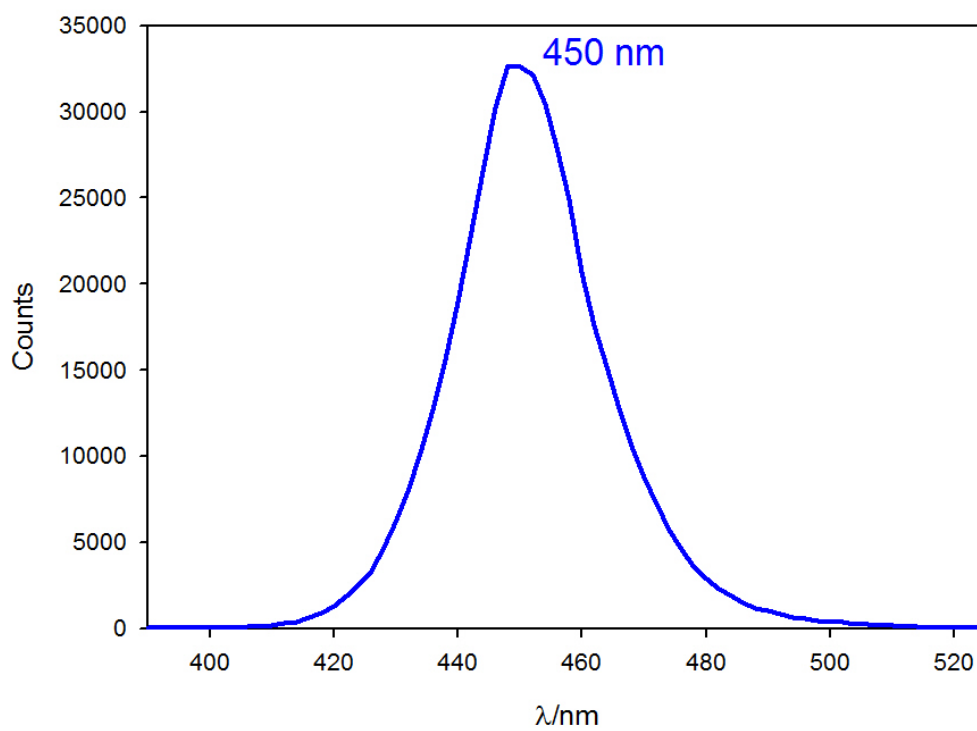
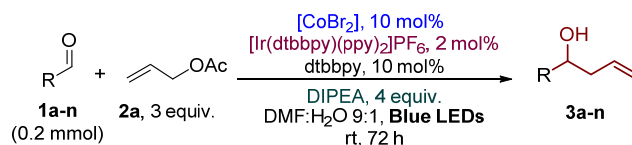


Figure S2. Emission spectrum of 23W blue LEDs used for the irradiation of the reaction mixture.

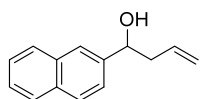
General procedure for photoredox titanium-catalyzed allylation of aldehydes.



A dry 10 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar and an argon supply tube, was first charged with cobalt di bromide (0.02 mmol, 4 mg) and the salt was dried under vacuum and gently heating until color changed from purple to green. The tube was filled with argon and dtbbpy (0.02 mmol, 5 mg), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (0.004 mmol, 3.7 mg), DMF (0.9 mL) and water (0.1 mL) were added. The reaction mixture was further subjected to a freeze-pump-thaw procedure (three cycles) and the vessel refilled with argon. Then, DIPEA (0.8 mmol, 0.103 g, 0.139 mL), allyl acetate (0.6 mmol, 0.060 g, 0.065 mL) and aldehyde (0.2 mmol) were added. The reaction was irradiated under vigorous stirring for the 72 h. After that the reaction was quenched with water (approx. 4 mL) and extracted with AcOEt (4 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was subject of flash column chromatography (SiO_2) to afford the products **3** in the stated yields.

Preparative scale reaction: The reaction was performed on 0.8 mmol of aldehyde **1a** following the general procedure irradiating with Kessil® PR160L@456 nm³ for 72 hours. Product **3a** was obtained in 74% yield (0.59 mmol, 117 mg) after chromatographic purification.

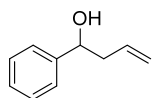
The discrepancies observed in the yields determined by ¹H NMR and the ones after chromatographic purification are ascribable to the difficulties encountered in the latter. In fact, the products partially elute together with dtbbpy although acetic acid was used as additive in the eluent.



1-(Naphthalen-2-yl)but-3-en-1-ol (3a): yellowish oil, 76% (0.15 mmol, 30 mg). The general procedure was applied using **1a** (0.2 mmol, 32 mg) as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

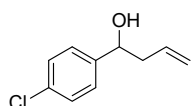
¹H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.86 – 7.78 (m, 4H), 7.50 – 7.43 (m, 3H), 5.91 – 5.74 (m, 1H), 5.25 – 5.05 (m, 2H), 4.90 (dd, J = 7.6, 5.2 Hz, 1H), 2.73 – 2.47 (m, 2H), 2.17

(bs, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): $\delta = 141.1, 134.3, 133.2, 132.9, 128.1, 127.9, 127.6, 126.0, 125.7, 124.4, 123.9, 118.5, 73.3, 43.7$; MS (ESI): $m/z = 181.1$ $[\text{M-OH}]^+$.



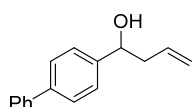
1-Phenylbut-3-en-1-ol (3b): brown oil, 61% (0.15 mmol, 12 mg). The general procedure was applied using **1b** (0.2 mmol, 20.4 μL) previously distilled as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): $\delta = 7.43 - 7.19$ (m, 5H), 5.80 (dddd, $J = 16.9, 10.2, 7.6, 6.6$ Hz, 1H), 5.21 – 5.07 (m, 2H), 4.72 (dd, $J = 7.6, 5.3$ Hz, 1H), 2.67 – 2.39 (m, 2H), 2.03 (bs, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): $\delta = 143.7, 134.4, 128.4$ (2C), 127.5, 125.8 (2C), 118.4, 73.2, 43.8; MS (ESI): $m/z = 131.2$ $[\text{M-OH}]^+$.



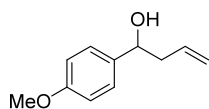
1-(4-Chlorophenyl)but-3-en-1-ol (3c): brown oil, 85% (0.17 mmol, 31 mg). The general procedure was applied using **1c** (0.2 mmol, 28 mg) as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): $\delta = 7.30$ (d, $J = 8.9$ Hz, 2H), 7.26 (d, $J = 7.5$ Hz, 2H), 5.88 – 5.66 (m, 1H), 5.24 – 5.02 (m, 2H), 4.70 (t, $J = 7.2$ Hz, 1H), 2.63 – 2.31 (m, 2H), 2.11 (bs, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): $\delta = 142.3, 133.9, 133.2, 128.5$ (2C), 127.2 (2C), 118.9, 72.5, 43.9; MS (ESI): $m/z = 165.2$ $[\text{M-OH}^-, 100]^+$; 167.2 $[\text{M-OH}^-, 30]^+$.



1-([1,1'-Biphenyl]-4-yl)but-3-en-1-ol (3d): brown oil, 70% (0.14 mmol, 31 mg). The general procedure was applied using **1d** (0.2 mmol, 36 mg) as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

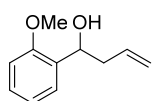
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): $\delta = 7.61 - 7.53$ (m, 4H), 7.43 (tdd, $J = 6.5, 1.6, 0.8$ Hz, 4H), 7.37 – 7.31 (m, 1H), 5.84 (dddd, $J = 16.9, 10.2, 7.6, 6.7$ Hz, 1H), 5.23 – 5.11 (m, 2H), 4.78 (dd, $J = 7.7, 5.3$ Hz, 1H), 2.74 – 2.43 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): $\delta = 142.9, 140.8, 140.4, 134.4, 128.7$ (2C), 127.2, 127. (2C), 127.0 (2C), 126.3 (2C), 118.5, 73.0, 43.8; MS (ESI): $m/z = 207.1$ $[\text{M-OH}]^+$.



1-(4-methoxyphenyl)but-3-en-1-ol (3e): yellowish oil, 67% (0.13 mmol, 24 mg). The general procedure was applied using **1e** (0.2 mmol, 26 μ L) as

aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

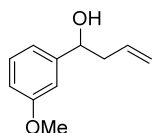
¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 7.27 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.87 – 5.66 (m, 1H), 5.16 – 4.97 (m, 2H), 4.67 (t, *J* = 6.5 Hz, 1H), 3.79 (s, 3H), 2.48 (t, *J* = 6.8 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 159.0, 136.0, 134.6, 127.0 (2C), 118.2, 113.8 (2C), 73.0, 55.3, 43.7; MS (ESI): *m/z* = 161.1 [M-OH]⁺.



1-(2-Methoxyphenyl)but-3-en-1-ol (3f): yellowish oil, 58% (0.12 mmol, 21 mg). The general procedure was applied using **1f** (0.2 mmol, 24 μ L) as

aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[5]

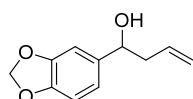
¹H NMR (400 MHz, CDCl₃, 25°C): δ = 7.32 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.27 – 7.18 (m, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.0 Hz, 1H), 5.84 (dddd, *J* = 16.9, 10.2, 7.5, 6.6 Hz, 1H), 5.19 – 5.04 (m, 2H), 4.95 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.84 (s, 3H), 2.63 – 2.43 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, 25°C): δ = 156.4, 135.2, 131.7, 128.3, 126.8, 120.7, 117.5, 110.4, 69.7, 55.2, 41.8; MS (ESI): *m/z* = 161.1 [M-OH]⁺.



1-(3-Methoxyphenyl)but-3-en-1-ol (3g): yellowish oil, 73% (0.15 mmol, 26 mg). The general procedure was applied using **1g** (0.2 mmol, 24 μ L) as

aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[5]

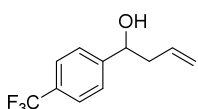
¹H NMR (400 MHz, CDCl₃, 25°C): δ = 7.24 (t, *J* = 8.1 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.79 (ddd, *J* = 8.2, 2.6, 1.1 Hz, 1H), 5.92 – 5.58 (m, 1H), 5.25 – 5.06 (m, 2H), 4.69 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.79 (s, 3H), 2.61 – 2.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, 25°C): δ = 159.7, 145.6, 134.4, 129.4, 118.4, 118.1, 113.0, 111.3, 73.2, 55.2, 43.8; MS (ESI): *m/z* = 161.2 [M-OH]⁺.



1-(Benzo[d][1,3]dioxol-5-yl)but-3-en-1-ol (3h): brown oil, 74% (0.15 mmol, 28 mg). The general procedure was applied using **1h** (0.2 mmol, 38

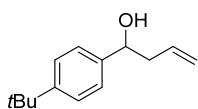
mg) and as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 90/10/1). Spectroscopic data were according to the literature.^[4]

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 6.85 (s, 1H), 6.81 – 6.68 (m, 2H), 5.93 (s, 2H), 5.77 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.23 – 5.01 (m, 2H), 4.62 (t, J = 6.5 Hz, 1H), 2.45 (t, J = 6.8 Hz, 2H), 2.04 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 147.7, 146.9, 138.0, 134.4, 119.2, 118.3, 108.0, 106.4, 100.9, 73.2, 43.8; MS (ESI): *m/z* = 175.2 [M-OH]⁺.



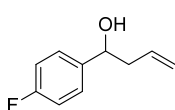
1-(4-(Trifluoromethyl)phenyl)but-3-en-1-ol (3i): brown oil, 30% (0.06 mmol, 13 mg). The general procedure was applied using **1i** (0.2 mmol, 28 μL) previously distilled as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 97/3/1). Spectroscopic data were according to the literature.^[4]

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 7.59 (d, J = 7.7 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 5.89 – 5.63 (m, 1H), 5.21 – 5.11 (m, 2H), 4.80 (dd, J = 8.0, 4.8 Hz, 2H), 2.58 – 2.40 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 147.7 (q, J = 1.2 Hz), 133.7, 129.6 (q, J = 32.8 Hz), 126.1 (2C), 125.3 (q, J = 3.8 Hz), 124.2 (q, J = 274.1 Hz), 119.2 (2C), 72.5, 43.9; ¹⁹F-NMR (377 MHz, CDCl₃, 25°C): δ = 61.28; MS (ESI): *m/z* = 199.3 [M-OH]⁺.



1-(4-(tert-butyl)phenyl)but-3-en-1-ol (3j): brown oil, 70% (0.14 mmol, 29 mg). The general procedure was applied using **1j** (0.2 mmol, 32 μL) previously distilled as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 7.39 – 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 6.05 – 5.65 (m, 1H), 5.27 – 5.01 (m, 2H), 4.70 (dd, J = 7.5, 5.4 Hz, 1H), 2.59 – 2.40 (m, 2H), 1.31 (s, 9H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 150.5, 140.9, 134.7, 125.5 (2C), 125.3 (2C), 118.2, 73.1, 43.6, 34.5, 31.4 (3C); MS (ESI): *m/z* = 187.1 [M-OH]⁺.

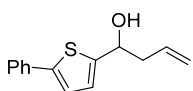


1-(4-Fluorophenyl)but-3-en-1-ol (3k): brown oil, 52% (0.10 mmol, 17 mg).

The general procedure was applied using **1k** (0.2 mmol, 21 μL) as aldehyde.

The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 90/10/1). Spectroscopic data were according to the literature.^[6]

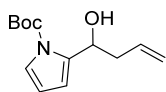
^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.30 (m, 2H), 7.06 – 6.96 (m, 2H), 5.83 – 5.69 (m, 1H), 5.19 – 5.09 (m, 2H), 4.70 (t, J = 5.7 Hz, 1H), 2.59 – 2.35 (m, 2H); 2.12 (bs, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 162.1 (d, J = 245.3 Hz), 139.5, 134.1, 127.4 (d, J = 8.0 Hz, 2C), 118.6, 115.2 (d, J = 21.4 Hz, 2C), 72.6, 43.9; ^{19}F NMR (377 MHz, CDCl_3 , 25°C): δ = -114.01 (dq, J = 9.2, 5.4, 4.5 Hz); MS (ESI): m/z = 149.0 $[\text{M-OH}]^+$.



1-(5-Phenylthiophen-2-yl)but-3-en-1-ol (3l): brown oil, 42% (0.08 mmol, 19 mg). The general procedure was applied using **1l** (0.2 mmol, 23 mg) as

aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate 95/5). Spectroscopic data were according to the literature.^[4]

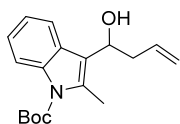
^1H -NMR (400 MHz, CDCl_3 , 25°C): δ = 7.61 – 7.52 (m, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.21 (m, 2H), 7.15 (dd, J = 3.7, 0.9 Hz, 1H), 6.93 (d, J = 3.6 Hz, 1H), 5.85 (ddt, J = 17.2, 10.2, 7.1 Hz, 1H), 5.25 – 5.12 (m, 2H), 4.96 (t, J = 6.4 Hz, 1H), 2.69 – 2.60 (m, 2H), 2.21 (bs, 1H); ^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ = 147.1, 143.5, 134.4, 133.7, 128.8 (2C), 127.4, 125.7 (2C), 124.7, 122.5, 118.9, 69.5, 43.6; MS (ESI): m/z = 213.2 $[\text{M-OH}]^+$.



tert-Butyl 2-(1-hydroxybut-3-en-1-yl)-1H-pyrrole-1-carboxylate (3m): brown oil, 67% (0.11 mmol, 24 mg). The general procedure was applied

using **1m** (0.2 mmol, 39 mg) as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate 95/5). Spectroscopic data were according to the literature.^[4]

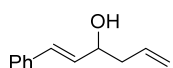
^1H -NMR (400 MHz, CDCl_3 , 25°C): δ = 7.17 (dd, J = 3.3, 1.7 Hz, 1H), 6.23 – 6.19 (m, 1H), 6.11 (t, J = 3.3 Hz, 1H), 5.93 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.21 – 5.05 (m, 2H), 4.96 (t, J = 6.1 Hz, 1H), 3.97 (bs, 1H), 2.68 (t, J = 7.3 Hz, 2H), 1.62 (s, 9H); ^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ = 150.3, 137.6, 135.4, 122.0, 117.0, 111.8, 110.3, 84.6, 66.3, 39.2, 28.0 (3C); MS (ESI): m/z = 220.4 $[\text{M-OH}]^+$.



tert-Butyl 3-(1-hydroxybut-3-en-1-yl)-2-methyl-1H-indole-1-carboxylate (3n): brown oil, 57% (0.11 mmol, 34 mg). The general procedure was applied using **1n** (0.2 mmol, 52 mg) as aldehyde. The title compound was

isolated by flash column chromatography (cyclohexane/ethyl acetate 95/5). Spectroscopic data were according to the literature.^[4]

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ = 8.09 (d, J = 8.0 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.25 – 7.14 (m, 2H), 5.78 (ddt, J = 17.1, 10.1, 7.5 Hz, 1H), 5.30 – 5.07 (m, 2H), 5.04 (dd, J = 8.0, 6.3 Hz, 1H), 2.79 (dt, J = 15.2, 7.8 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.55 (s, 3H), 1.67 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ = 150.7, 136.0, 134.6, 133.6, 127.7, 123.4, 122.4, 119.7, 119.5, 118.0, 115.4, 83.8, 67.8, 41.6, 28.3 (3C), 14.2 (9C); MS (ESI): m/z = 284.3 $[\text{M-OH}]^+$.

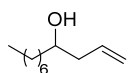


(E)-1-Phenylhexa-1,5-dien-3-ol (3o): yellow oil, 43%. (0.11 mmol, 20 mg).

The general procedure was applied using **1o** (0.2 mmol, 26 μL) as aldehyde.

The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate 95/5). Spectroscopic data were according to the literature.^[4]

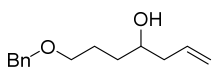
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ = 7.40 – 7.35 (m, 2H), 7.30 (dd, J = 8.4, 6.7 Hz, 2H), 7.23 – 7.19 (m, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.23 (dd, J = 15.9, 6.3 Hz, 1H), 5.85 (ddt, J = 17.2, 10.2, 7.1 Hz, 1H), 5.26 – 5.01 (m, 2H), 4.35 (q, J = 6.7, 6.3 Hz, 1H), 2.56 – 2.31 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ = 136.6, 134.0, 131.5, 130.4, 128.6 (2C), 127.7, 126.5 (2C), 118.5, 71.7, 42.0; MS (ESI): m/z = 160.2 $[\text{M-OH}]^+$.



Undec-1-en-4-ol (3p): brown oil, 30% (0.06 mmol, 10 mg). The general procedure was applied using **1p** (0.2 mmol, 32 μL) freshly distilled at $59^\circ\text{C}/21$ mbar as aldehyde.

The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

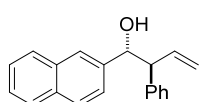
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ = 5.91 – 5.72 (m, 1H), 5.17 – 5.04 (m, 2H), 3.68 – 3.60 (m, 1H), 2.28 (dddt, J = 13.7, 6.8, 4.2, 1.4 Hz, 1H), 2.18 – 2.05 (m, 1H), 1.44 (q, J = 4.3, 2.9 Hz, 3H), 1.33 – 1.15 (m, 10H), 0.86 (t, J = 6.8 Hz, 3H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ = 134.9, 118.0, 70.7, 41.9, 36.8, 31.8, 29.6, 29.3, 25.7, 22.6, 14.1; GC-MS: rt 10.8; m/z = 170 (M^+ , 1), 152 ($[\text{M-H}_2\text{O}]^+$, 1.8), 129 ($[\text{M-CH}_2=\text{CHCH}_2]^+$, 16), 111 ($[\text{M-H}_2\text{O-CH}_2=\text{CHCH}_2]^+$, 20), 69 ($[\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2]^+$, 100), 55 ($[\text{CH}_2=\text{CHCH}_2\text{CH}_2]^+$, 49).



7-(Benzyloxy)hept-1-en-4-ol (3q): brown oil, 34% (0.07 mmol 15 mg).

The general procedure was applied using **1q** (0.2 mmol, 30 mg) previously synthesized as aldehyde. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 95/5/1). Spectroscopic data were according to the literature.^[4]

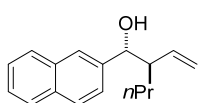
¹H-NMR (400 MHz, CDCl₃, 25°C): δ = 7.31 – 7.08 (m, 5H), 5.84 – 5.63 (m, 1H), 5.12 – 4.95 (m, 2H), 4.44 (s, 2H), 3.58 (tt, J = 8.2, 4.4 Hz, 1H), 3.43 (t, J = 6.0 Hz, 2H) 2.28 (bs, 1H), 2.24 – 2.15 (m, 1H), 2.15 – 2.05 (m, 1H), 1.77 – 1.62 (m, 2H), 1.62 – 1.51 (m, 1H), 1.49 – 1.35 (m, 1H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 138.2, 135.0, 128.4 (2C), 127.7 (2C), 127.6, 117.8, 73.0, 70.6, 70.5, 42.0, 34.0, 26.2; MS (ESI): *m/z* = MS (ESI): *m/z* = 221.1 [M+H]⁺, 203.1 [M-OH]⁺.



1-(Naphthalen-2-yl)-2-phenylbut-3-en-1-ol (4b) and **(E)-1-(naphthalen-2-yl)-4-phenylbut-3-en-1-ol (4b')**: isolated as mixture of isomers; **4b:4b'**

3:1, *anti:syn* 3:1; brown oil, 52% (0.10 mmol, 28 mg). The general procedure was applied using **1a** (0.2 mmol, 36 mg) as aldehyde and acetate **2b** (0.3 mmol, 53 mg). Isomers ratio was determined by comparison of ¹H-NMR signals with data reported in literature.^[7] The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 97/3/1) as mixture of isomers (42%) and single isomer **4b** (10%). Spectroscopic data were according to the literature.^[4,7]

¹H-NMR (400 MHz, CDCl₃, 25°C) major isomer: δ = 7.76 – 7.68 (m, 2H), 7.66 (d, J = 8.6 Hz, 1H), 7.58 (s, 1H), 7.39 (dt, J = 6.4, 3.6 Hz, 2H), 7.25 (dd, J = 8.5, 1.7 Hz, 1H), 7.19 – 7.10 (m, 3H), 7.10 – 7.00 (m, 3H), 6.26 (ddd, J = 17.0, 10.2, 8.9 Hz, 1H), 5.34 – 5.12 (m, 2H), 5.00 (d, J = 7.6 Hz, 1H), 3.64 (t, J = 8.3 Hz, 1H), 2.41 (bs, 1H); ¹³C-NMR (100 MHz, CDCl₃, 25°C): δ = 140.6, 139.4, 137.8, 133.1, 132.9, 128.4, 128.4, 128.0, 127.6 (2C), 126.7, 125.9, 125.7 (2C), 124.7, 118.5, 59.0; MS (ESI): *m/z* = 257.2 [M-OH]⁺.



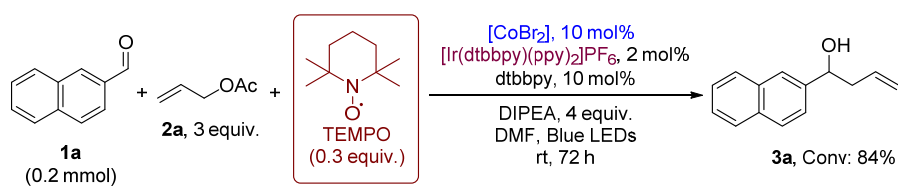
1-(Naphthalen-2-yl)-2-vinylpentan-1-ol (4c) and **(E)-1-(naphthalen-2-yl)hept-3-en-1-ol (4c')**: isolated as mixture of isomers; **4c:4c'**

2.8:1, *anti:syn* 1:1; brown oil, 43% (0.086 mmol, 20 mg). The general procedure was applied using **1a** (0.2 mmol, 36 mg) as aldehyde and acetate **2c** (0.3 mmol, 43 mg). Isomers ratio was determined by comparison of ¹H-NMR signals with data reported in literature.^[4] The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate/acetic acid, 97/3/1) as mixture of isomers. Spectroscopic data were according to the literature.^[4]

¹H-NMR (400 MHz, CDCl₃, 25°C) mixture of isomers: δ = 7.87 – 7.79 (m, 6H), 7.79 – 7.68 (m, 3H), 7.50 – 7.43 (m, 5H), 7.40 (dd, J = 8.5, 1.7 Hz, 1H), 5.69 (ddd, J = 17.0, 10.2, 9.1 Hz, 1H), 5.55 (ddd, J = 17.0, 10.3, 9.1 Hz, 1H), 5.28 – 5.16 (m, 2H), 5.10 – 4.97 (m, 2H), 4.78 (d, J = 5.8 Hz, 1H), 4.55 (d, J = 7.9 Hz, 1H), 2.52 (dt, J = 9.8, 5.2 Hz, 1H), 2.41 (qd, J

= 8.9, 3.9 Hz, 1H), 1.57 (dtd, J = 12.2, 5.9, 2.8 Hz, 1H), 1.44 – 1.04 (m, 5H), 0.85 (t, J = 7.1 Hz, 3H), 0.76 (t, J = 7.2 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, 25°C) mixture of isomers: δ = 140.1, 139.9, 139.3, 138.6, 133.2, 133.1, 133.0, 132.9, 128.0, 127.9, 127.6, 127.6, 126.1, 126.0, 125.8, 125.7, 125.5, 124.9, 124.7, 118.8, 117.3, 77.1, 76.8, 52.4, 51.2, 32.6, 31.7, 20.4, 20.3, 14.0, 13.9; MS (ESI): *m/z* = 223.1 [M-OH]⁺.

Effect of radical inhibitor on reaction outcome

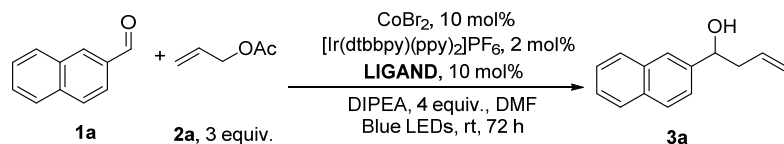


The reaction was performed following the general procedure but adding TEMPO (0.06 mmol, 9 mg) before freeze-pump-thaw procedure.

Results and discussion

Screening of reaction conditions

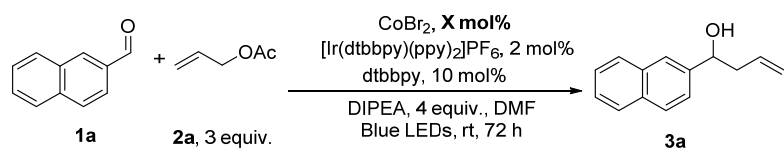
Table S1. Screening of cobalt ligand.



Entry ^[a]	Ligand	Yield (%) ^[b]
1	dtbbpy; di- <i>tert</i> -butylbipyridine	91 (60)
2	No ligand	0
3	dppe; 1,2-bis(diphenylphosphino)ethane	0
4	dppf; 1,1'-ferrocenediyl-bis(diphenylphosphine).	0
5	PPh_3 ^[c]	32 (23)
6	pyridine	0
7	bpy; 2,2'-bipyridine	44 (38)
8	<i>o</i> -phen; <i>ortho</i> -phenanthroline	39 (30)
9	3,3'-dimethyl-2,2'-bipyridine	30 (22)
10	4,4'-dimethyl-2,2'-bipyridine	51 (39)

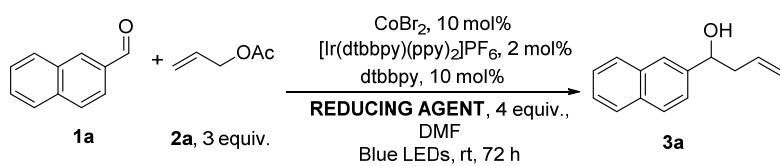
[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ^1H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification. [c] 20 mol% was used in the reaction.

Table S2. Screening of cobalt salt amount.



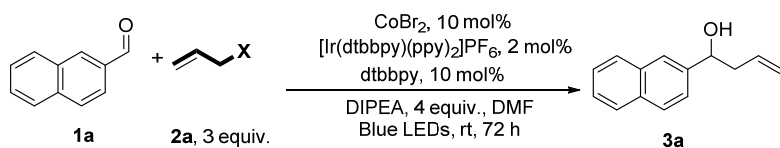
Entry ^[a]	Cobalt bromide (mol%)	Yield (%) ^[b]
1	10	91 (60)
2	5	28
3	20	70 (64)
4	0	0

[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ^1H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

Table S3. Screening of the reducing agent.

Entry ^[a]	Reducing agent	Yield (%) ^[b]
1	DIPEA	91 (60)
2	TEA	85 (53)
3	Ph ₃ N	0
4	4-Methoxy-N,N-diphenylaniline	0
5	1,3-Dimethyl-2-phenyl-2,3-dihydro-1H-benzimidazole (BIH)	63 (49)

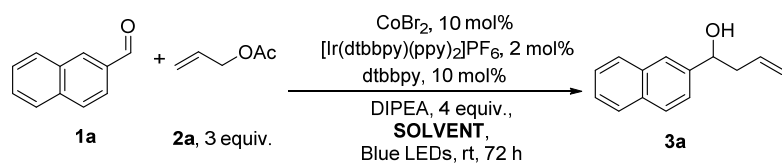
[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ¹H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

Table S4. Allylating reagent.

Entry ^[a]	X	Yield (%) ^[b]
1	OAc	91 (60)
2	OPiv	10
3	OC(O)OEt	40
4	Br	0

[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ¹H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

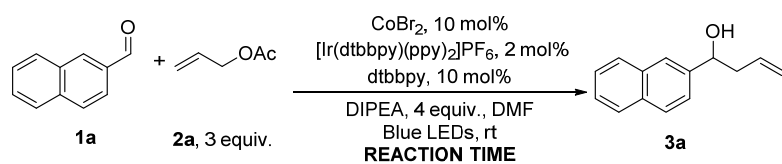
Table S5. Screening of the reaction solvent.



Entry ^[a]	Reaction time (h)	Yield (%) ^[b]
1	DMF	91 (60)
2	CH ₃ CN	55 (33)
3	DCE	64 (50)
4	DMSO	33 (25)
5	DMF:H ₂ O 9:1	97 (76)
6	THF	0

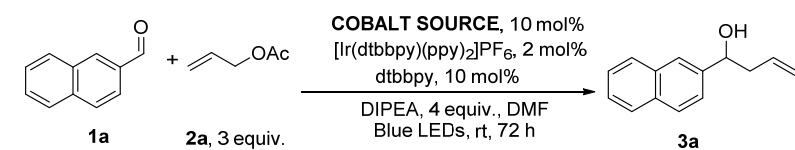
[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ¹H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

Table S6. Influence of reaction time on the reaction outcome.



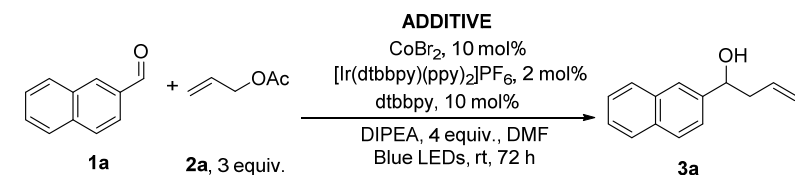
Entry ^[a]	Reaction time (h)	Yield (%) ^[b]
1	24	50 (33)
2	48	75 (53)
3	72	91 (60)
4	120	92 (62)

[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ¹H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

Table S7. Screening of cobalt source.

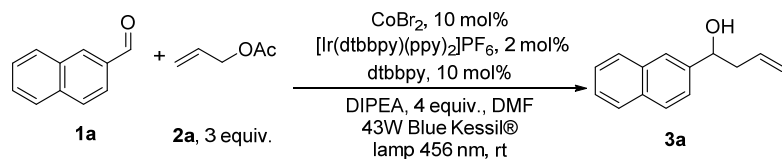
Entry ^[a]	Cobalt source	Yield (%) ^[b]
1	CoBr ₂	91 (60)
2	Co(OAc) ₂	89 (56)
3	CoCl ₂	91 (58)

[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ¹H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

Table S8. Screening of additives.

Entry ^[a]	Additives (equiv.)	Yield (%) ^[b]
1	None	91 (60)
2	TMSCl (1)	0
3	ZnBr ₂ (1)	0
4	TFE (2)	0
5	PhCOF (1)	0
6	Ac ₂ O (2)	0
7	CbzCl (2)	0
8	AcCl (2)	0
9	KHF ₂ (2)	0
10	PhB(OH) ₂	0
11	Oxalic acid	0
12	Al(OTf) ₃ (0.1)	66 (52)
13	Sc(OTf) ₃ (0.1)	49 (35)

[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ¹H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

Table S9. Influence of reaction time on the reaction outcome.

Entry ^[a]	Note	Yield (%) ^[b]
1	Reaction time 14 hours	72
2	Reaction time 14 hours under irradiation and 10 hours in the dark	73
3	Reaction time 24 hours	97 (75)
4	The reaction was settled with 0.2 mmol of aldehyde, 0.6 mmol of allyl acetate and 0.8 mmol of DIPEA, and irradiated for 24 hours. An aliquot of 50% of the reaction mixture was sampled and quenched. ¹ H NMR analysis of the reaction mixture shown full conversion (97%). To the remaining 50% of the sample 0.1 mmol of fresh aldehyde, 0.3 mmol of allyl acetate and 0.4 mmol of DIPEA were added, and the reaction was performed for other 24 hours, then quenched.	76 referred to the total amount of aldehyde used

[a] Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL). [b] Determined by ¹H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification.

These experiments were performed using a KESSIL® Lamp (40 W, 456nm), recently purchased in our laboratory. The first experiment was performed with three reactions that were settled under same conditions (entry 1, 2, and 3). The first reaction was performed under irradiation for 14 hours, then the reaction was quenched (entry 1). The second reaction was irradiated 14 hours, then kept under dark for 10 hours, before quenching (entry 2). The yields for the two reactions are indicating that under dark the reaction is not progressing, and irradiation with light is essential for yields. The third reaction was kept under irradiation of 24 hours, before quenching, showing good yields, and that was necessary 24 hours with KESSIL® lamp to reach full conversion.

In the second experiment, (entry 4) after 24 hours the Schlenk tube was opened, a sample of 50% (by volume) of the reaction transferred in another flask and quenched. The conversion was measured on this sample and determined to be 97%. To the original flask more aldehyde (0.1 mmol), allyl acetate (0.3mmol), and DIPEA (0.4 mmol) were added. The reaction was kept under irradiation for 24 hours and then quenched. The final yields for the reaction, referred to aldehydes (0.1 mmol + 0.1 mmol), were 76%. The photocatalyst (Ir complex) and cobalt catalyst are still able to perform the transformation, but with a reduced efficiency (probably due to the opening of the reaction flask).

Photochemical Investigations

Photochemical experiments were carried out at room temperature in air-equilibrated solutions (Milli-q water and DMF Uvasol®), in a quartz cuvette (optical pathlength 1 cm). All absorption spectra were recorded with a spectrophotometer Varian Cary 300 UV-Vis. Phosphorescence spectra were recorded with Perkin Elmer LS 50 spectrofluorometers equipped with Hamamatsu R928 photomultiplier. Lifetime decays measurements were performed using an Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a LDH-P-C-405 pulsed diode laser.

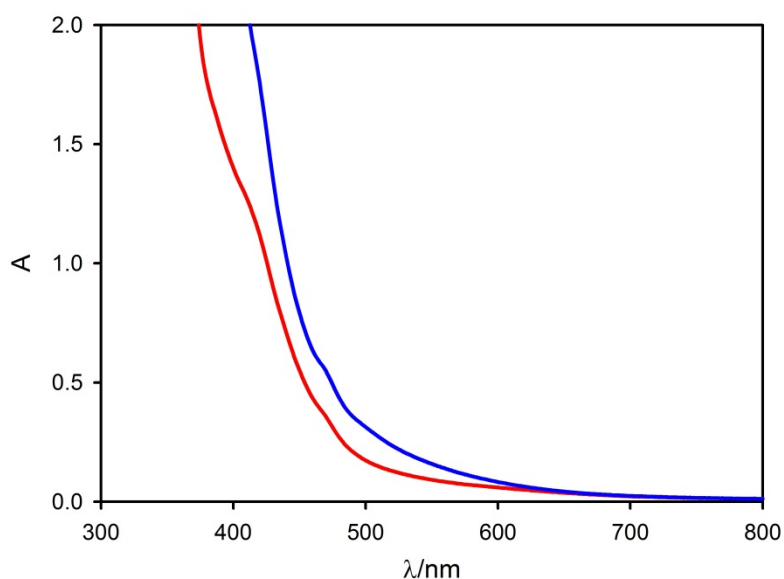


Figure S3. Absorption spectrum of the reaction mixture under standard conditions diluted 1:20 before (red solid line) and upon 72 hours irradiation with blue LEDs (blue solid line).

Upon 72 hours of irradiation with blue LEDs, the absorption spectrum of the reaction mixture shows the typical feature of the iridium photocatalyst; that suggests the $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ does not decompose during the irradiation.

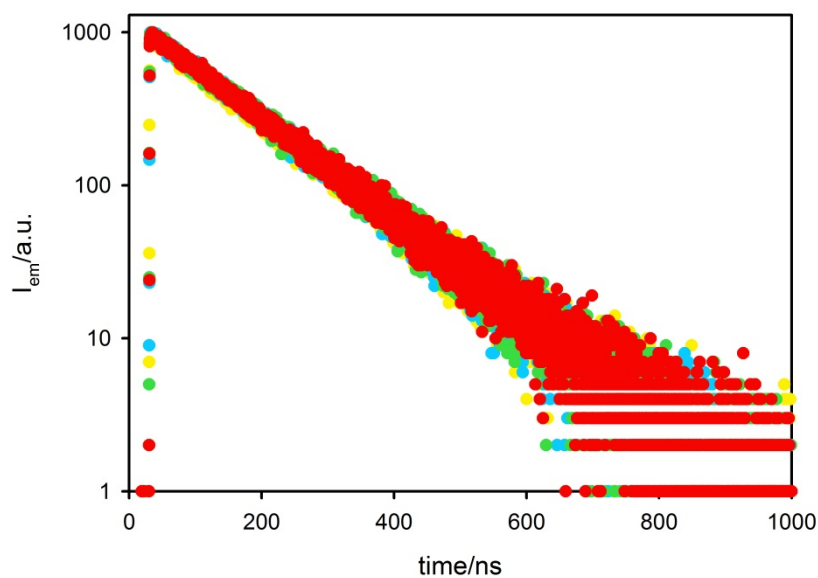


Figure S4. Emission intensity decays of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (2×10^{-4} M) in DMF:H₂O 9:1 solution in absence (yellow dots) and in presence of allyl acetate 0.6 M (light blue dots), di-tert-butylbipyridine 0.02 M (red dots) and CoBr₂ 0.02 M (green dots), upon excitation at 405 nm.

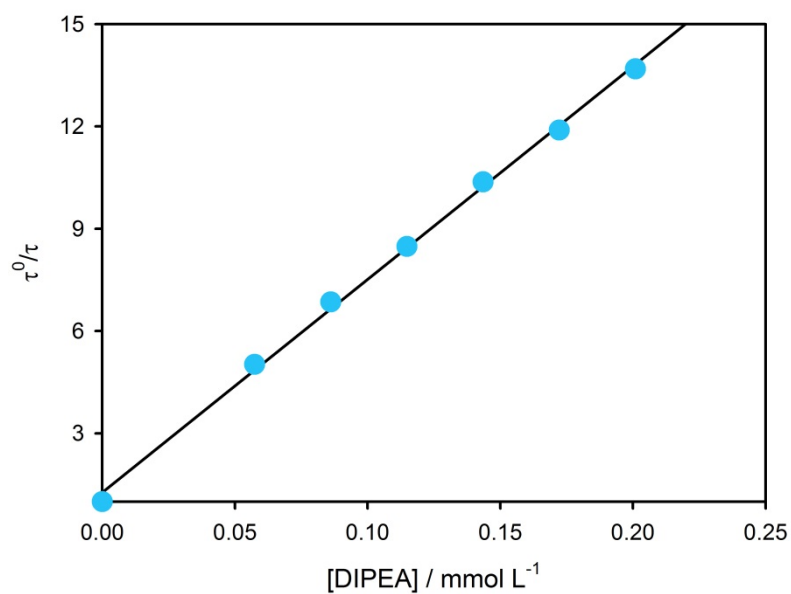


Figure S5. Emission intensity decays of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ in DMF:H₂O 9:1 solution in absence (τ^0) and in the presence (τ) of increasing amount of DIPEA (blue dots). The slopes represent the Stern-Volmer constant (K_{SV}), i.e. the product of the quenching constant (k_q) and τ^0 .

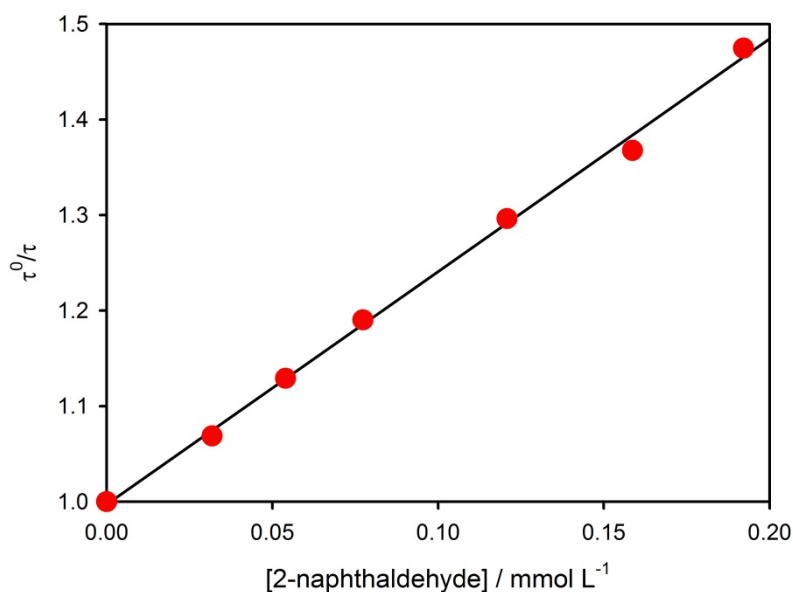


Figure S6. Emission intensity decays of [Ir(dtbbpy)(ppy)₂]PF₆ in DMF:H₂O 9:1 solution in absence (τ^0) and in the presence (τ) of increasing amount of 2-naphthaldehyde (red dots). The slopes represent the Stern-Volmer constant (K_{SV}), i.e. the product of the quenching constant (k_q) and τ^0 .

The Stern-Volmer plots show a linear correlation between the ratio τ^0/τ and the quencher concentration, as expected for a dynamic quenching process according to the Stern-Volmer equation:

$$(1) \quad \tau^0/\tau = 1 + K_{SV}[Q] = 1 + k_q \tau^0 [Q]$$

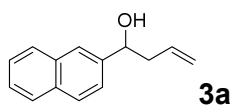
where τ^0 and τ are the lifetimes in the absence and in the presence of the quencher Q, respectively, K_{SV} is the Stern-Volmer constant and k_q is the quenching constant.

The analysis of the plots reported above yields the following quenching constants:

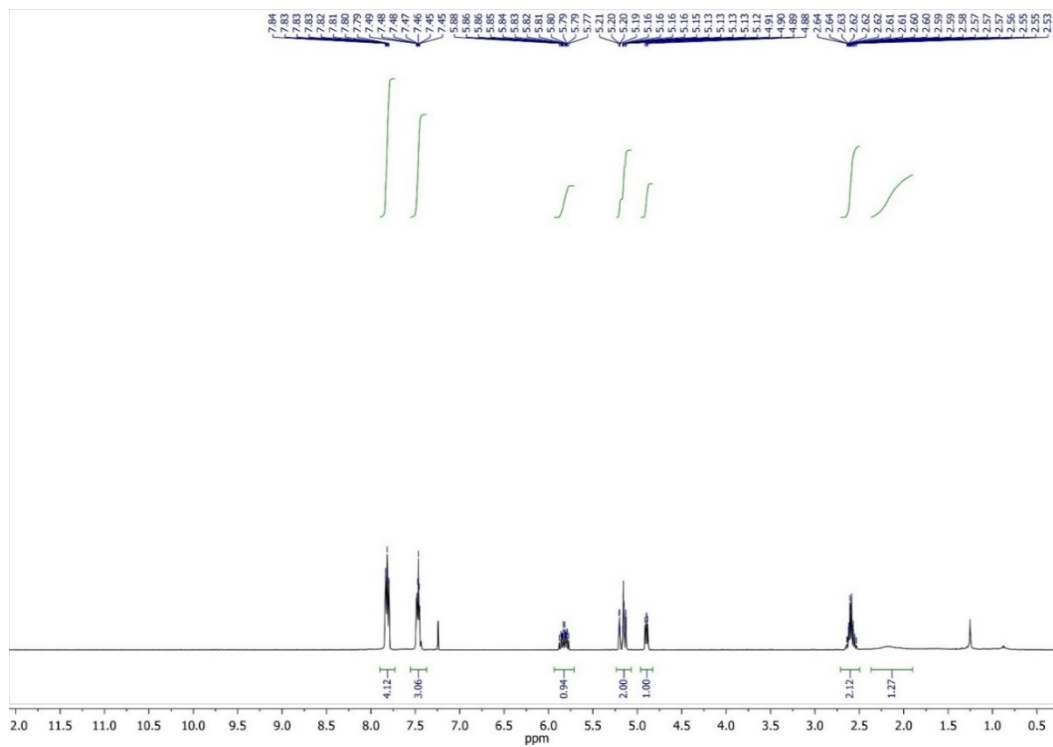
$$(2) \quad k_q = 4.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \text{ for DIPEA}$$

$$(3) \quad k_q = 1.9 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \text{ for 2-naphthaldehyde}$$

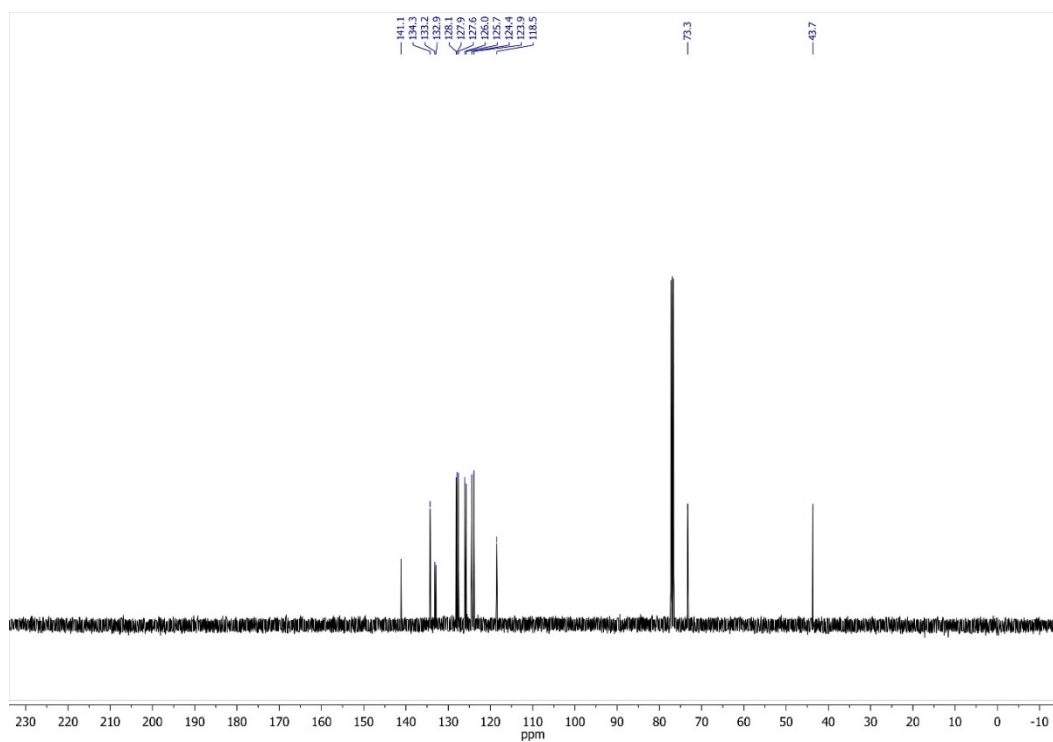
Copies of NMR spectra

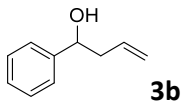


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

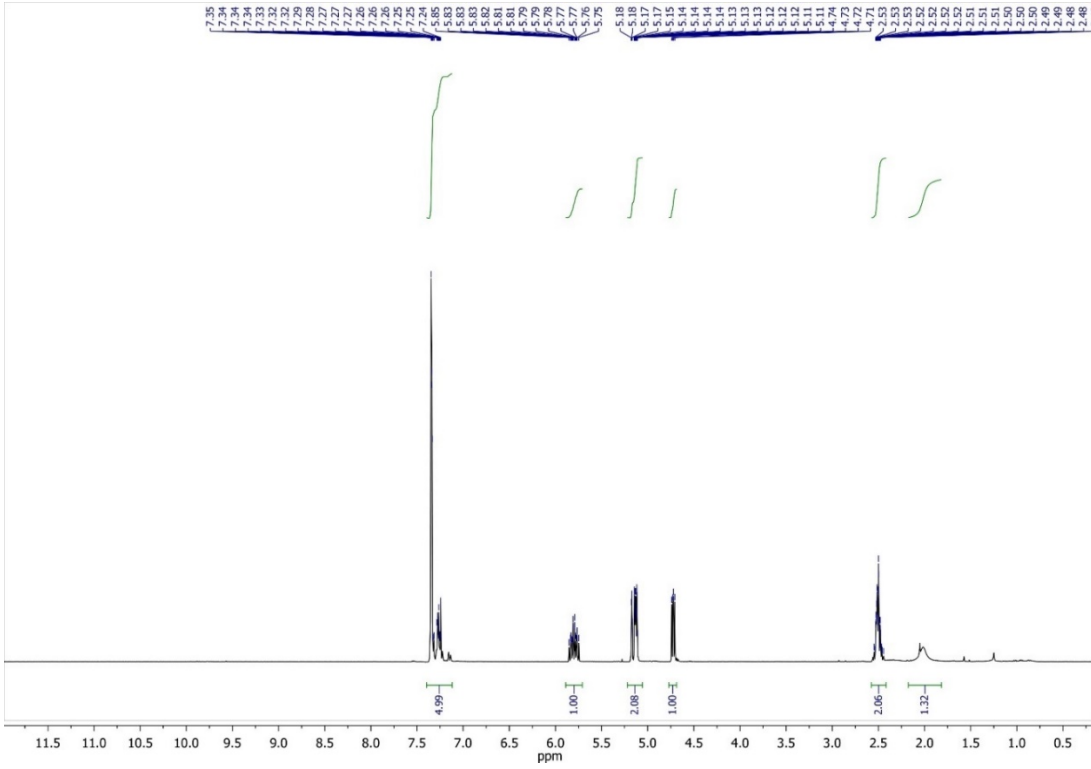


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

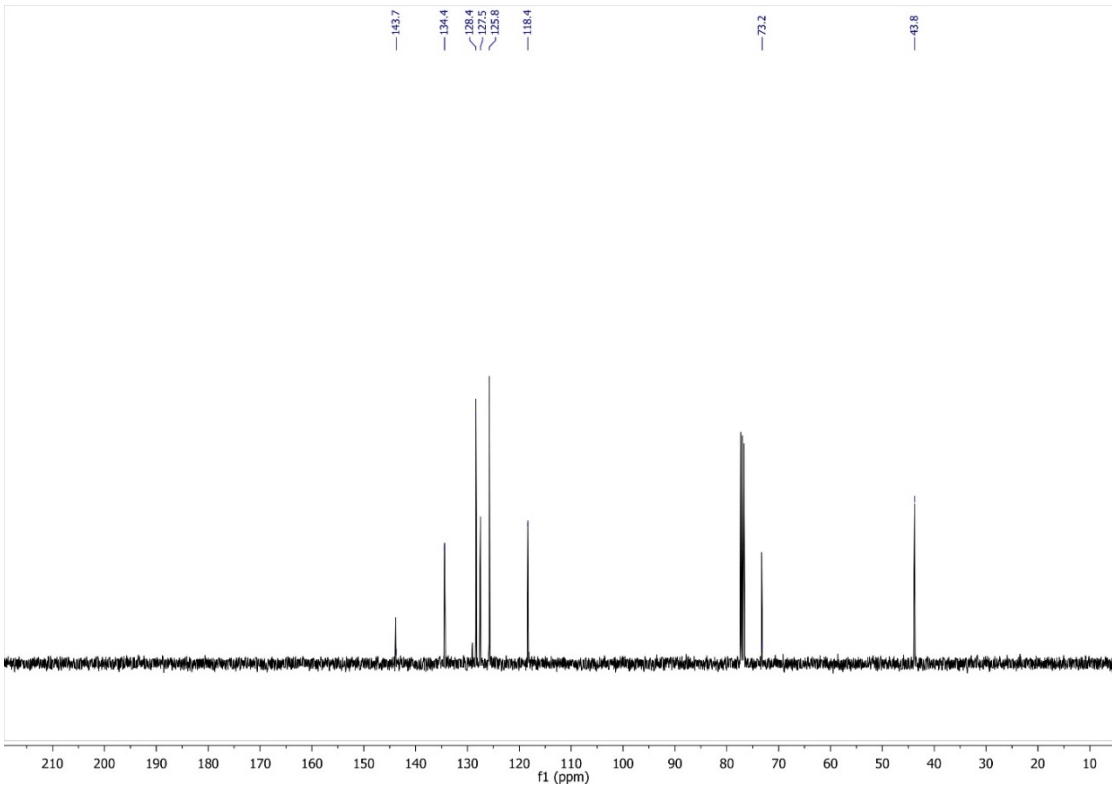


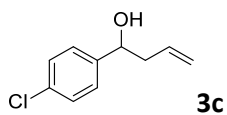


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

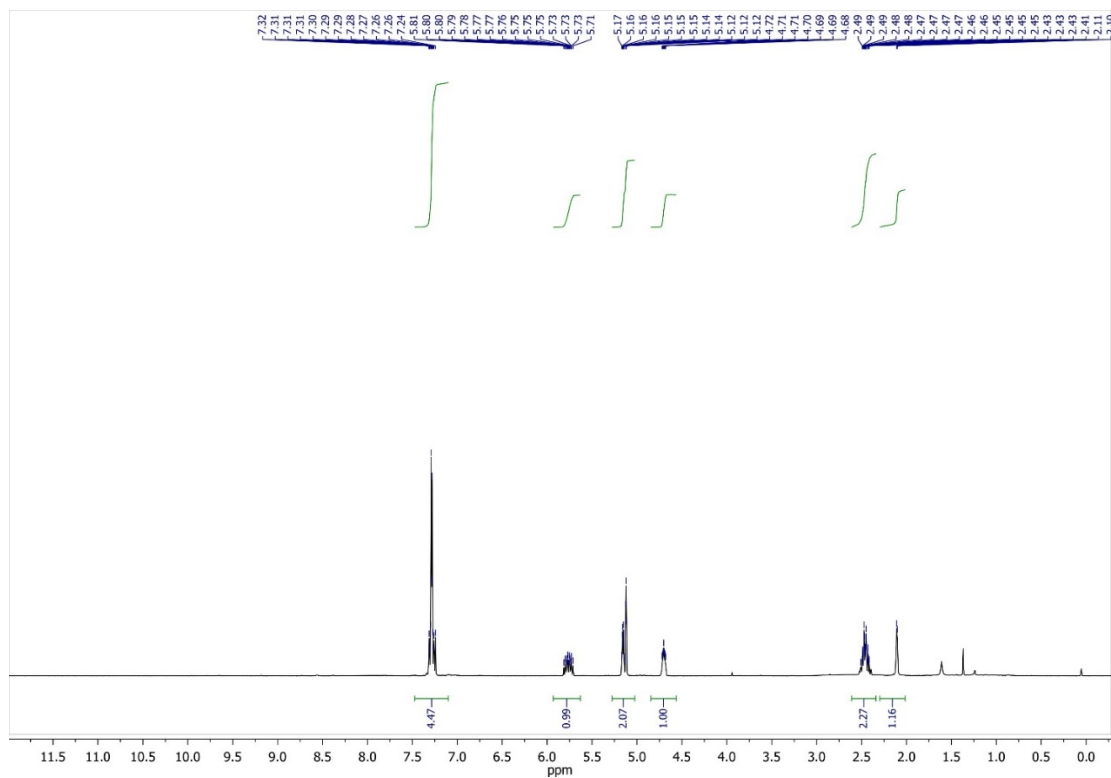


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

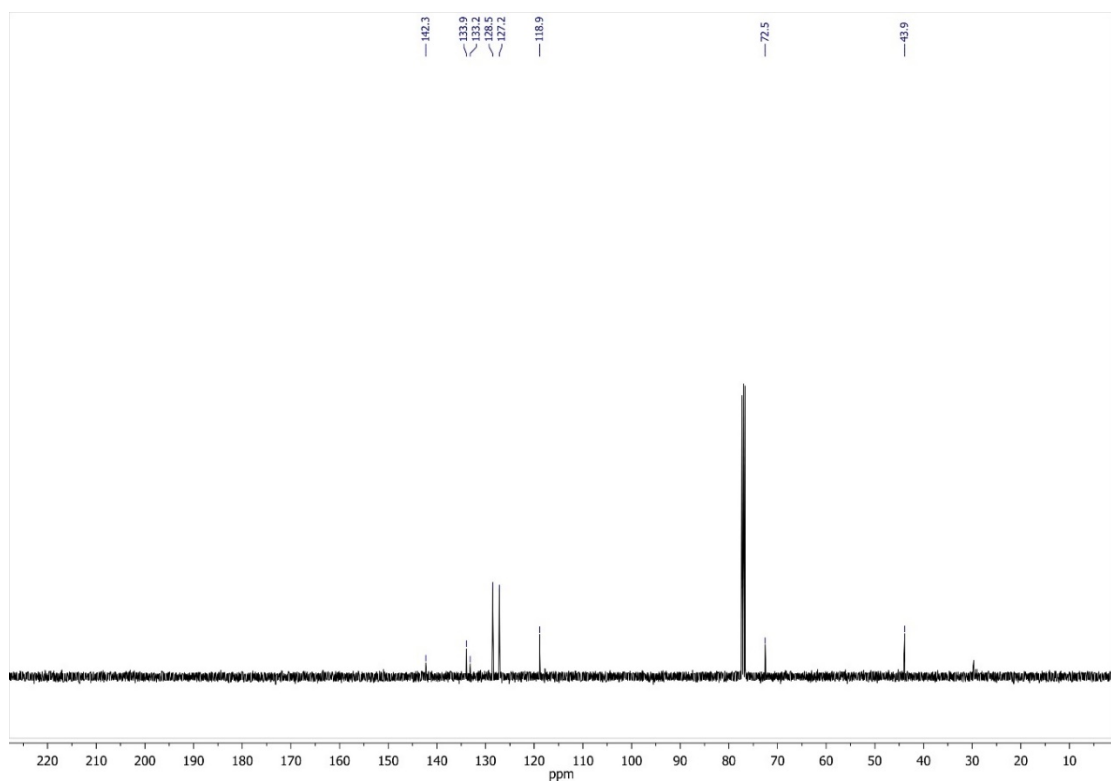


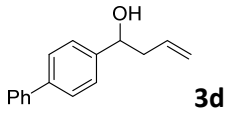


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

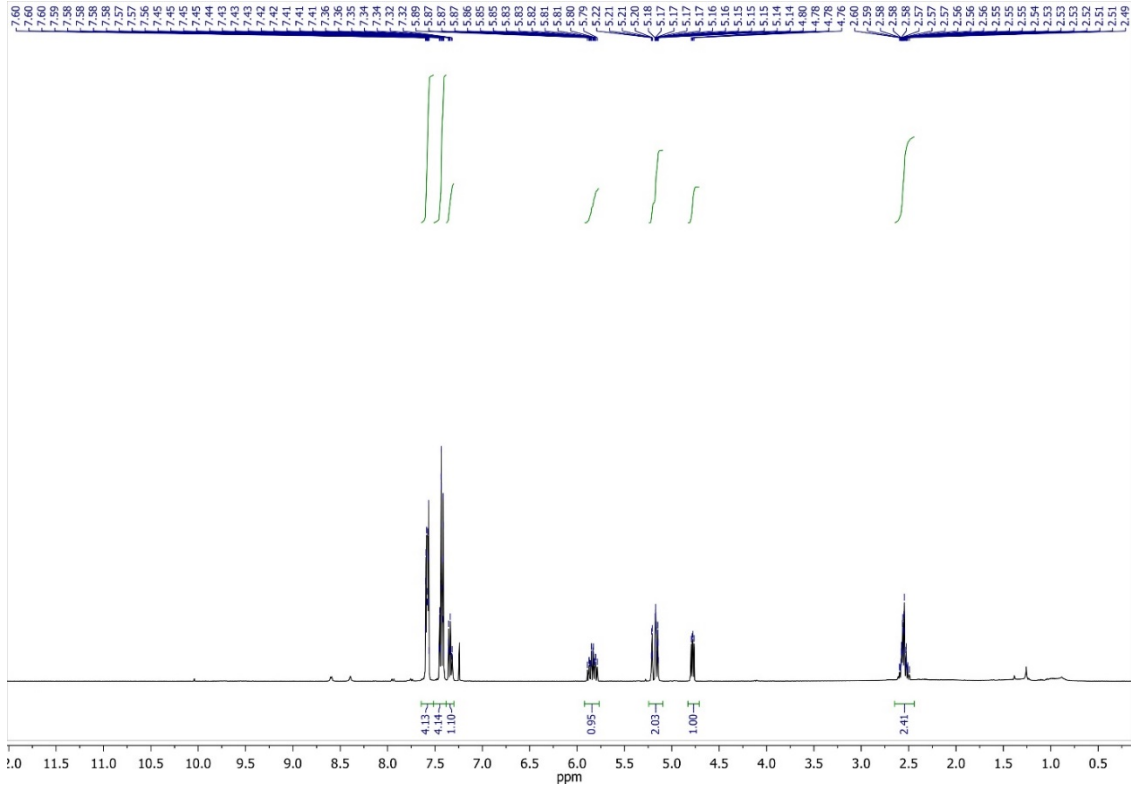


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

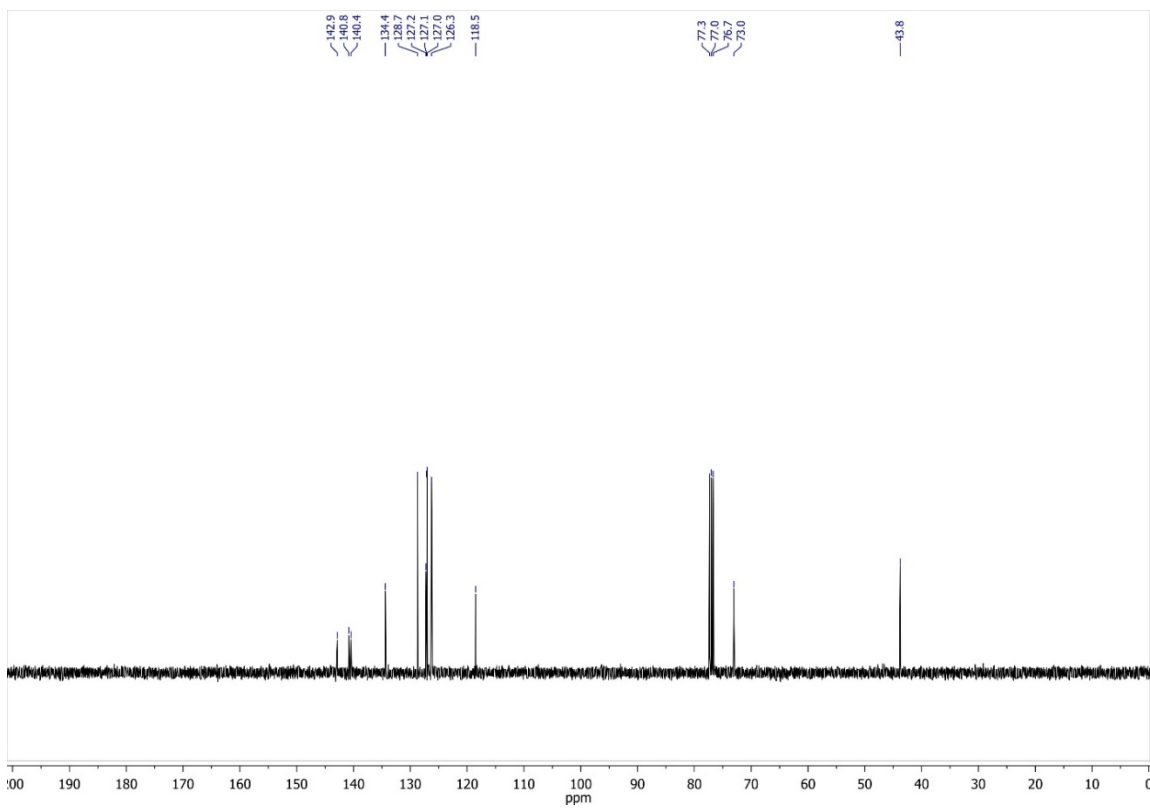


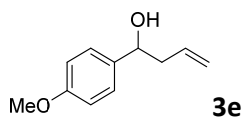


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

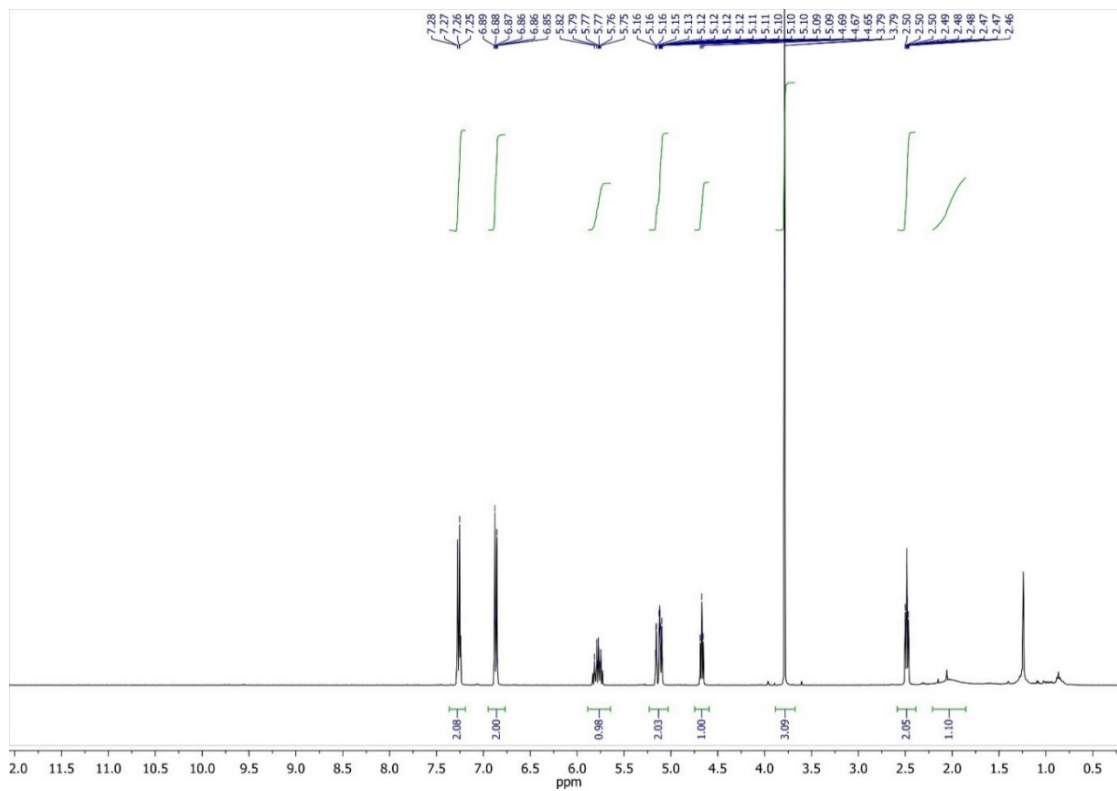


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

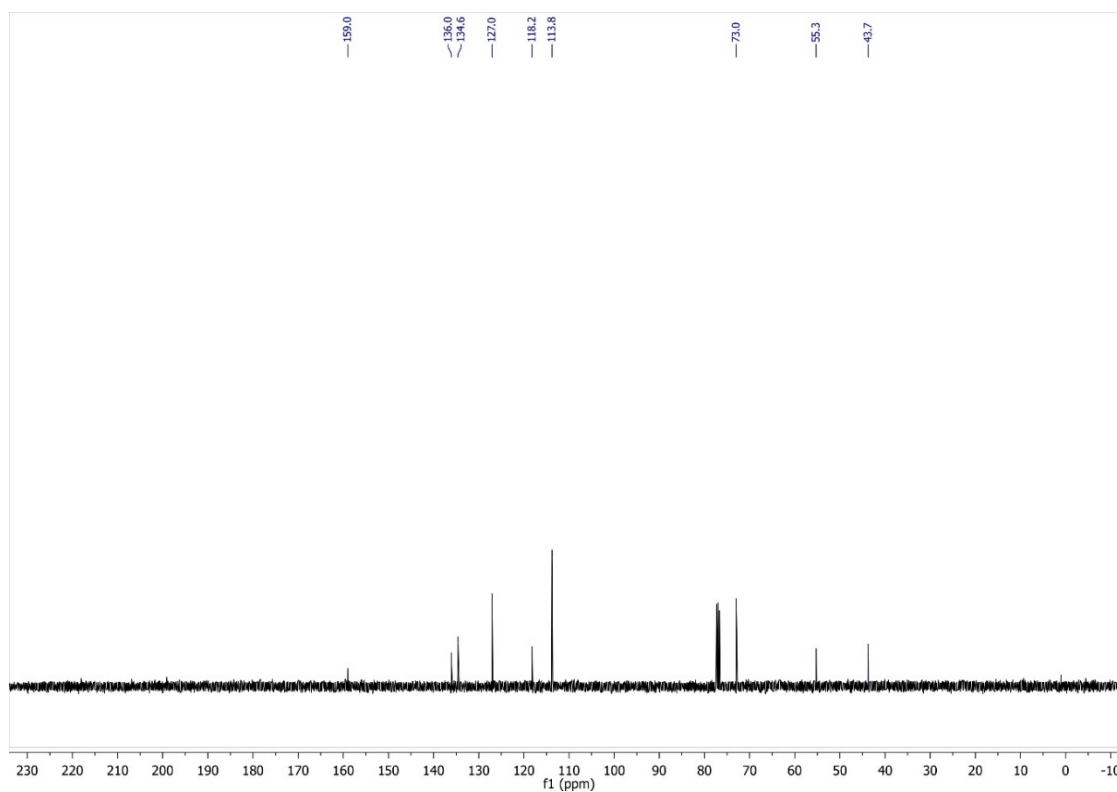


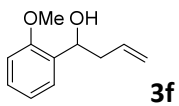


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

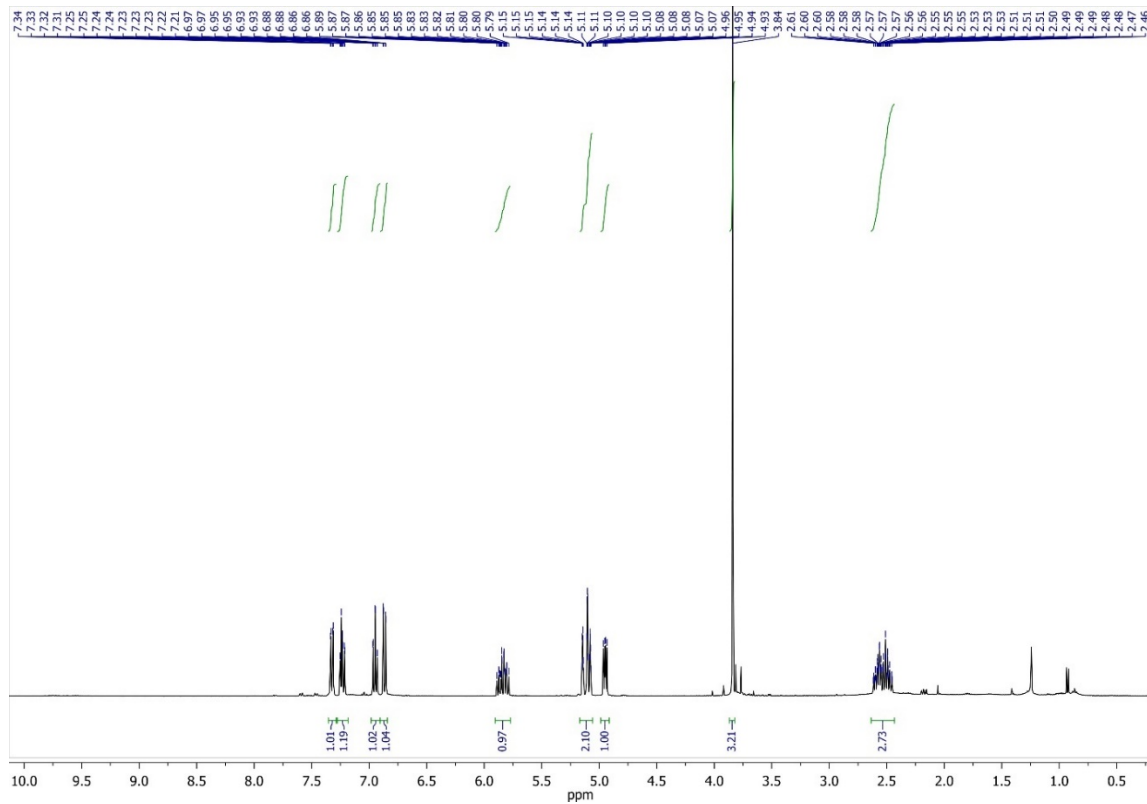


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

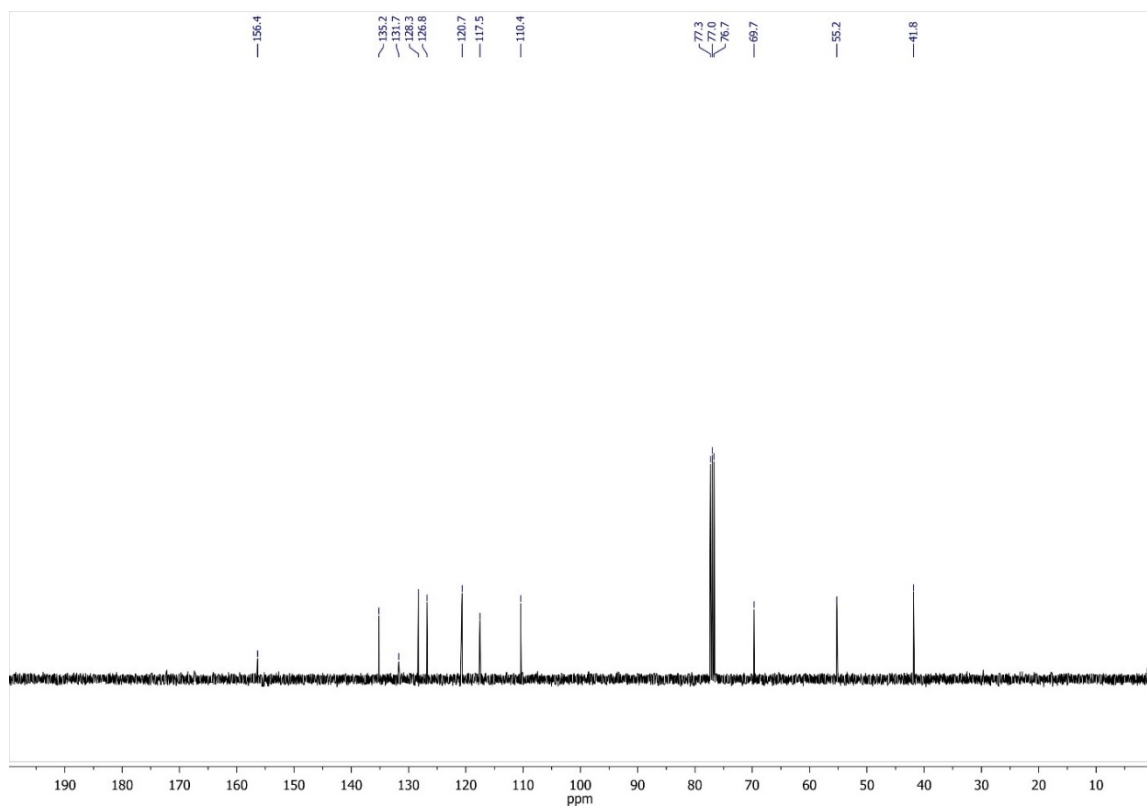


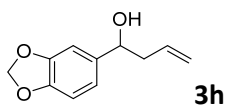


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

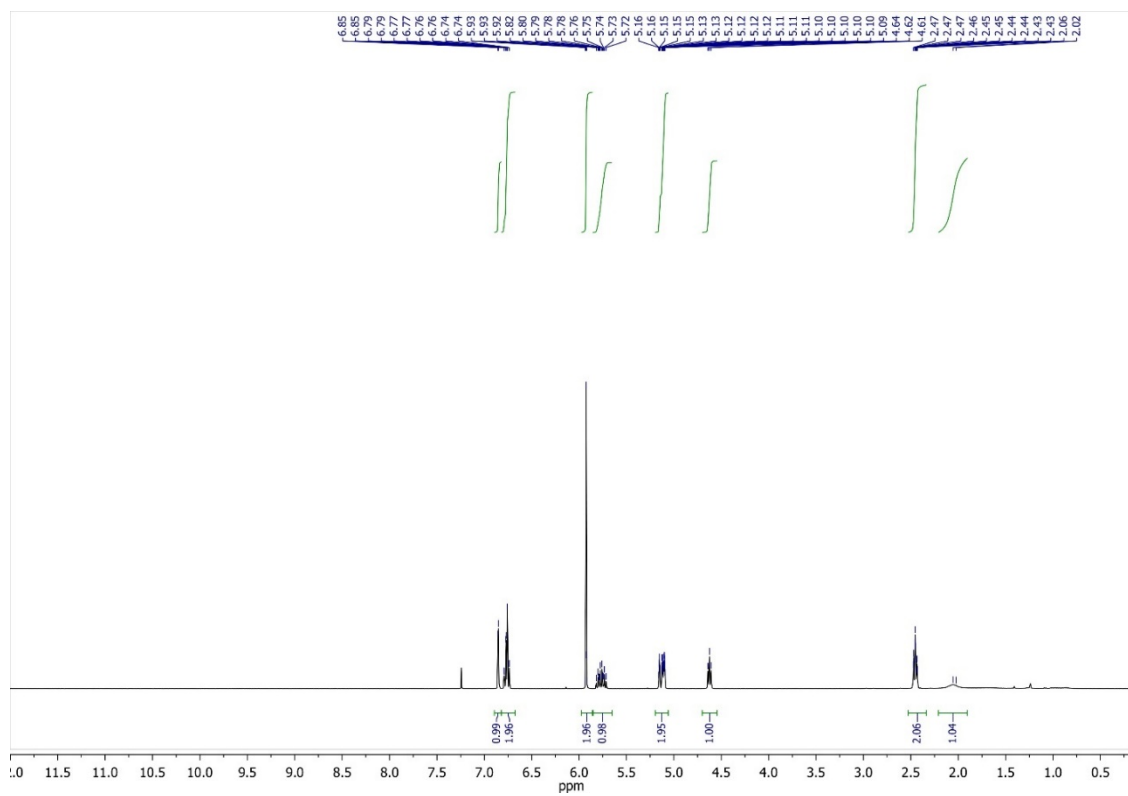


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

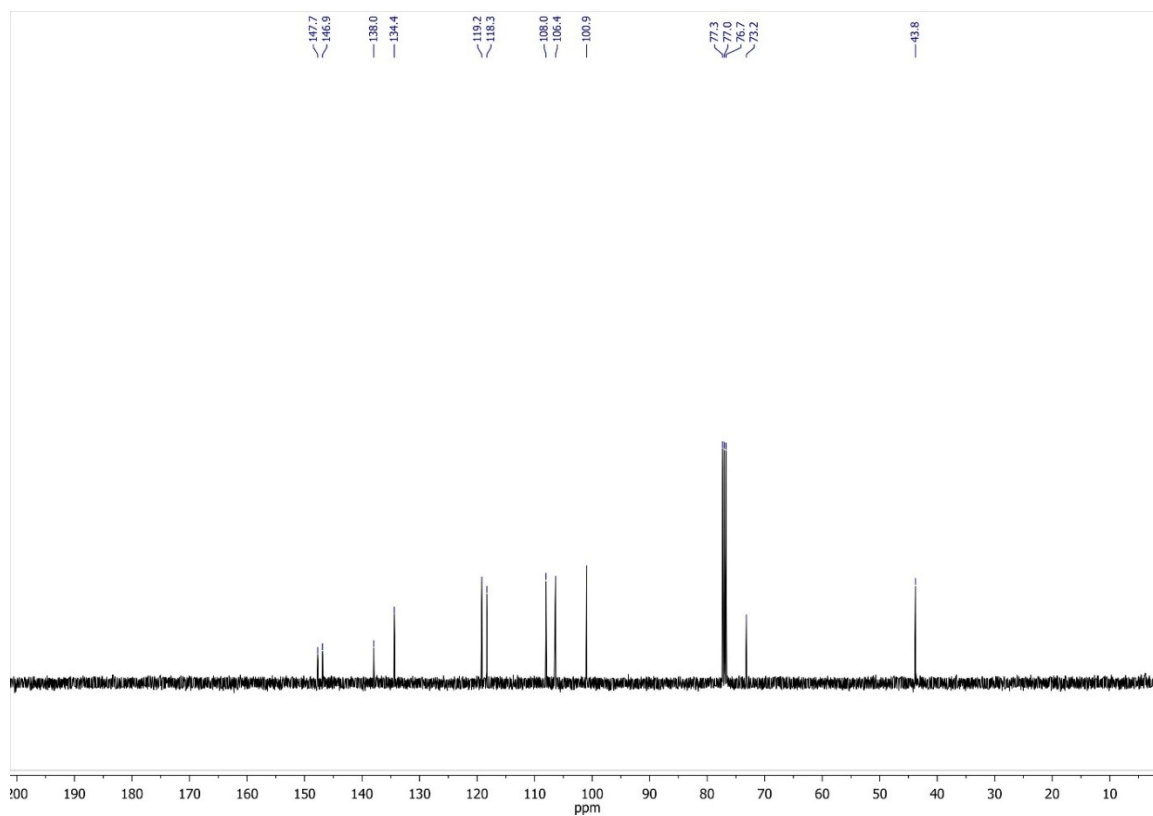


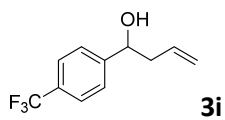


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

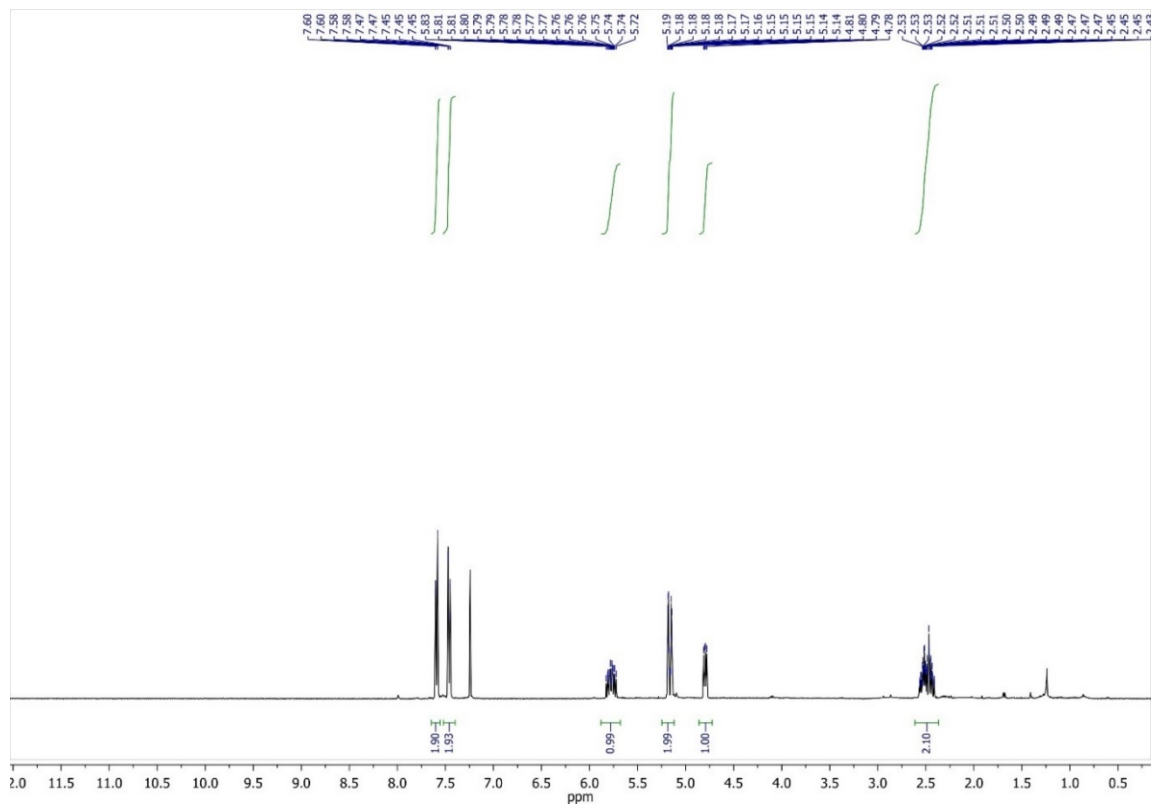


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

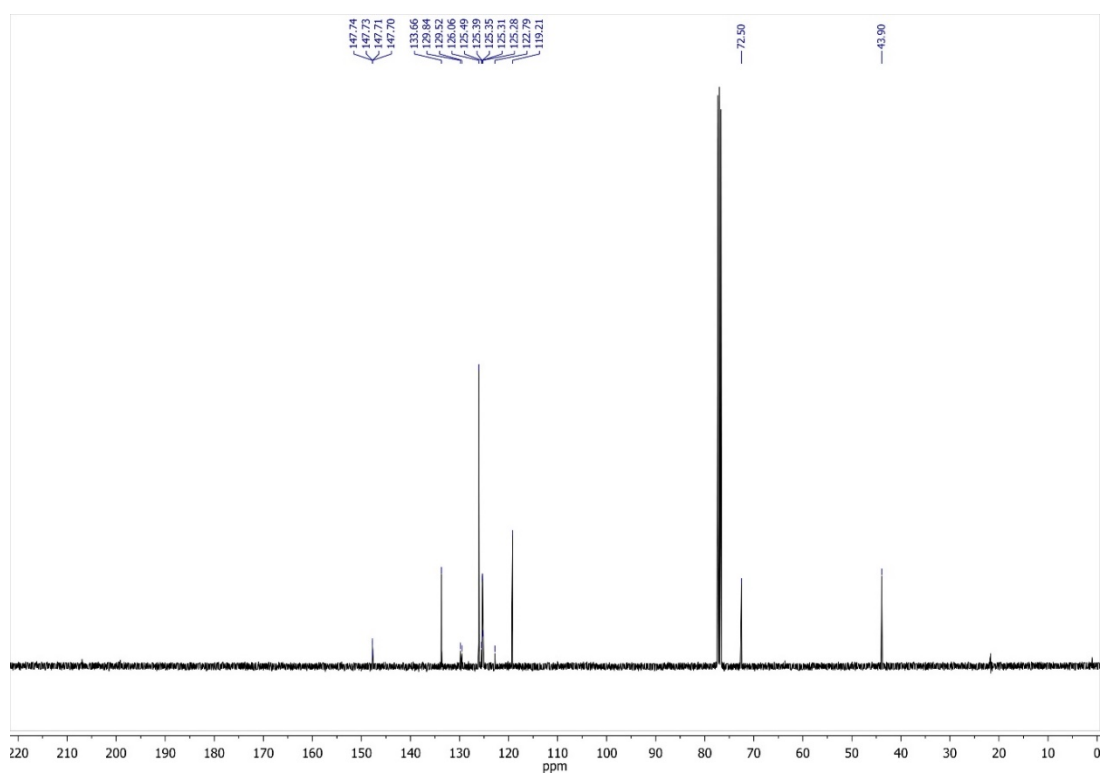




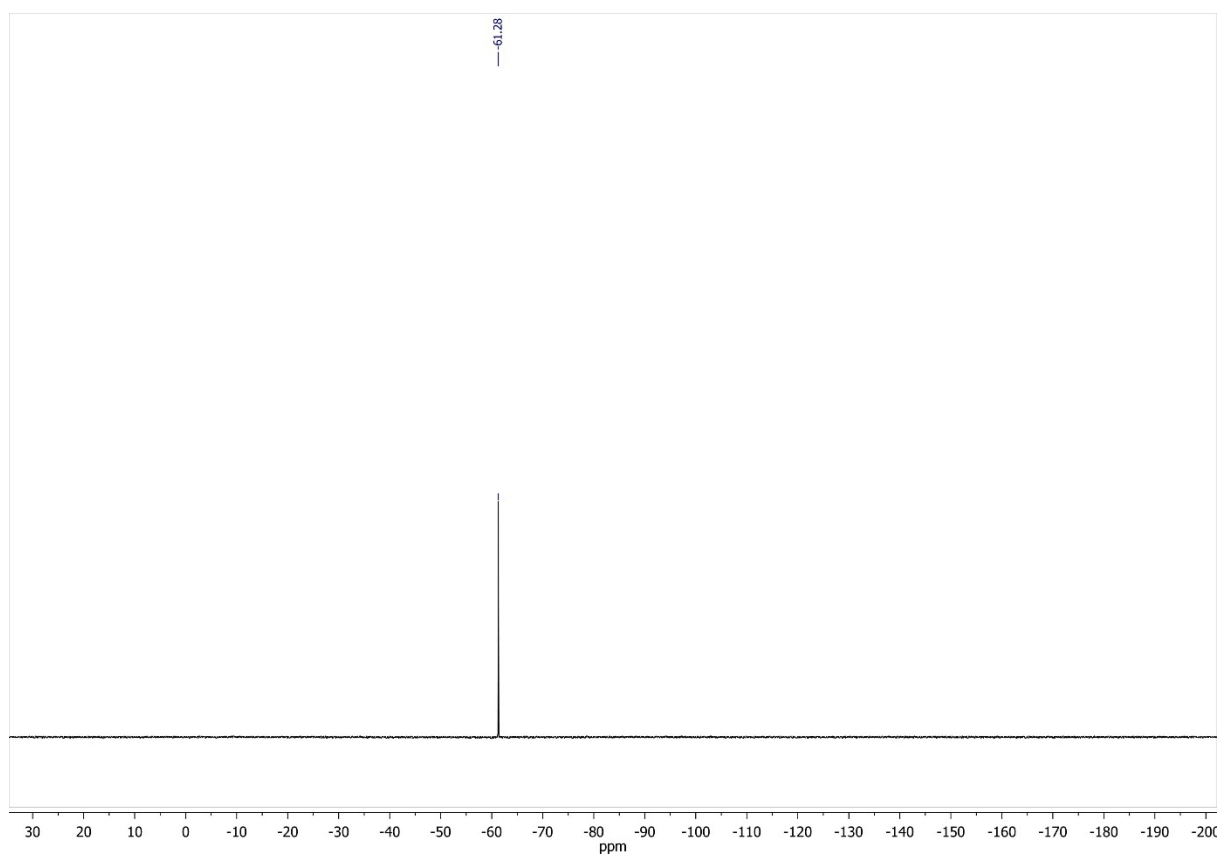
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

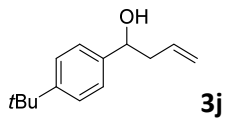


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

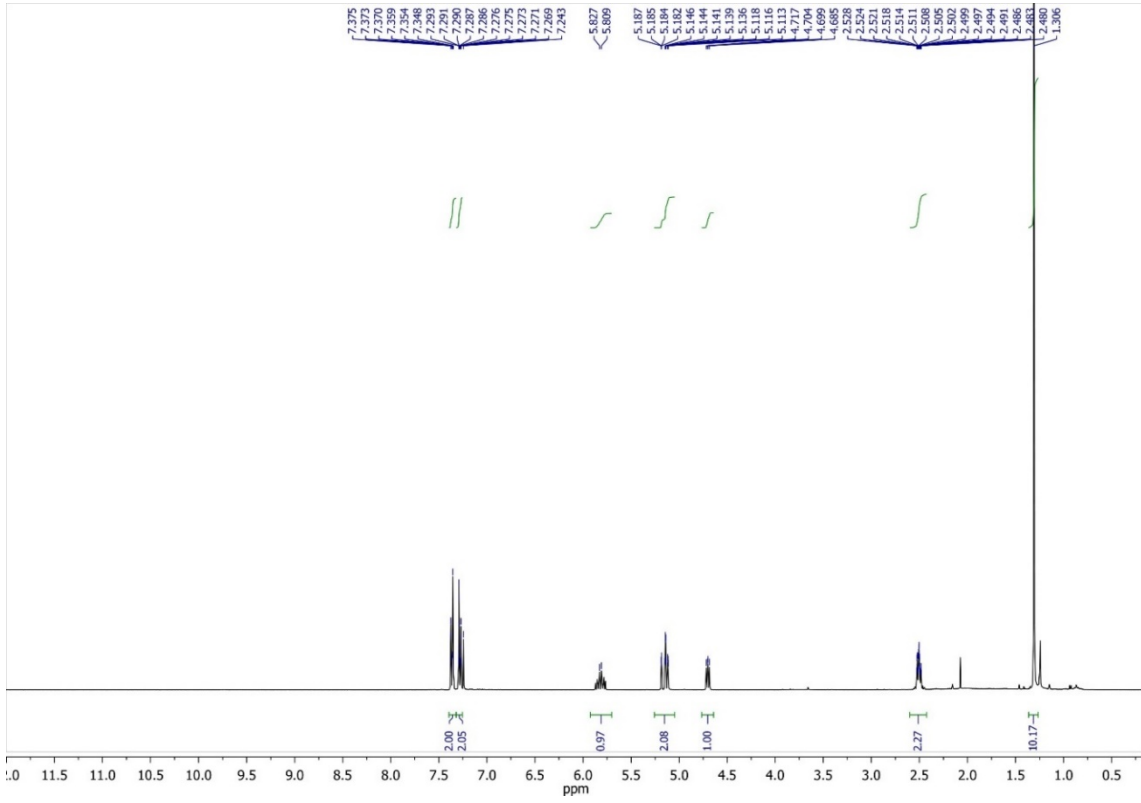


^{19}F -NMR (376.5 MHz, CDCl_3 , 25°C)

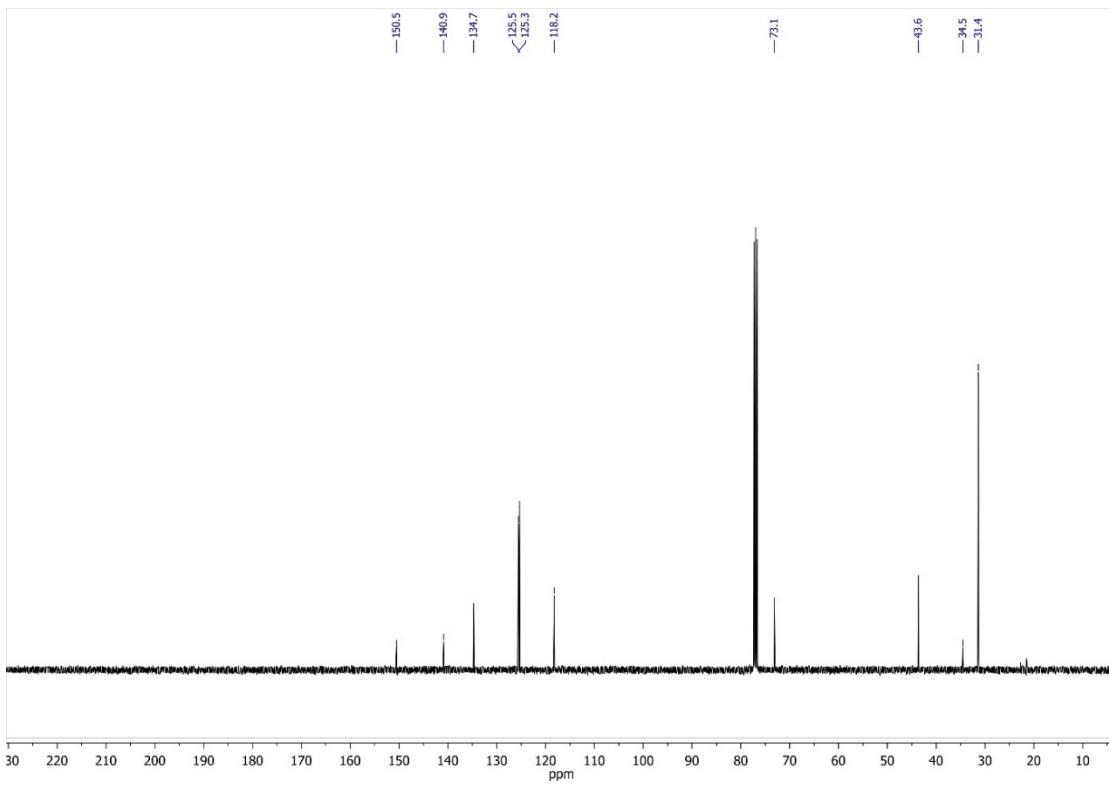


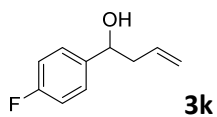


¹H-NMR (400 MHz, CDCl₃, 25°C)

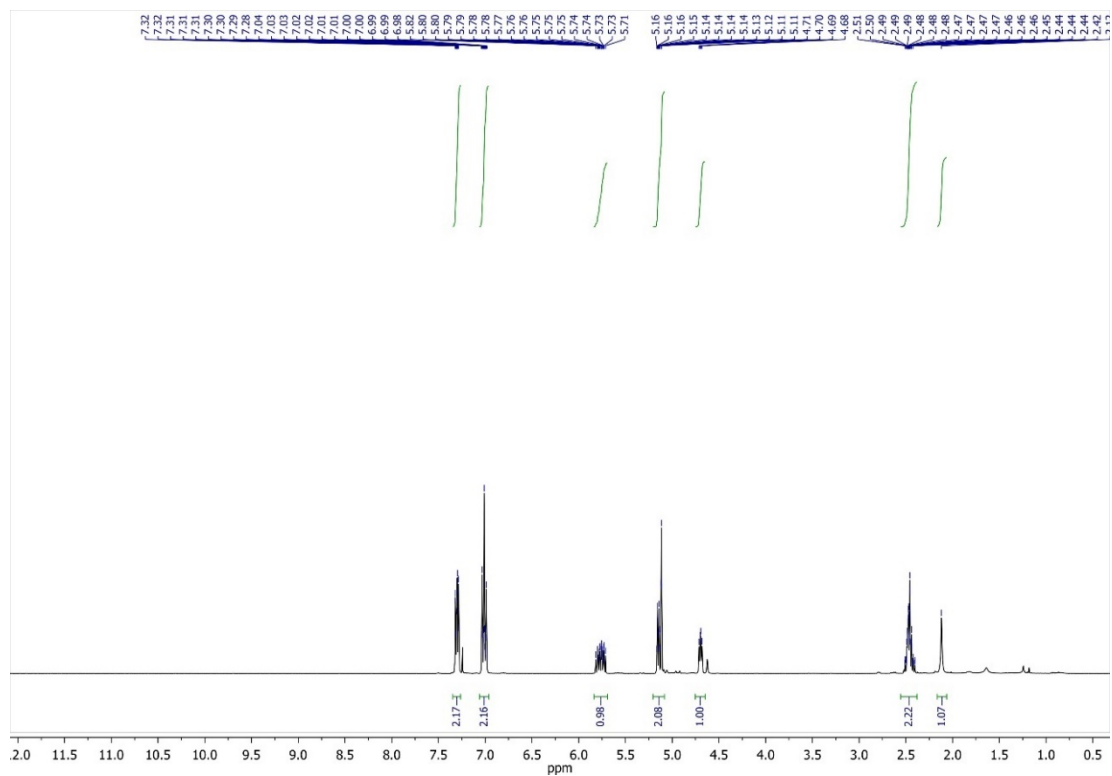


¹³C-NMR (100 MHz, CDCl₃, 25°C)

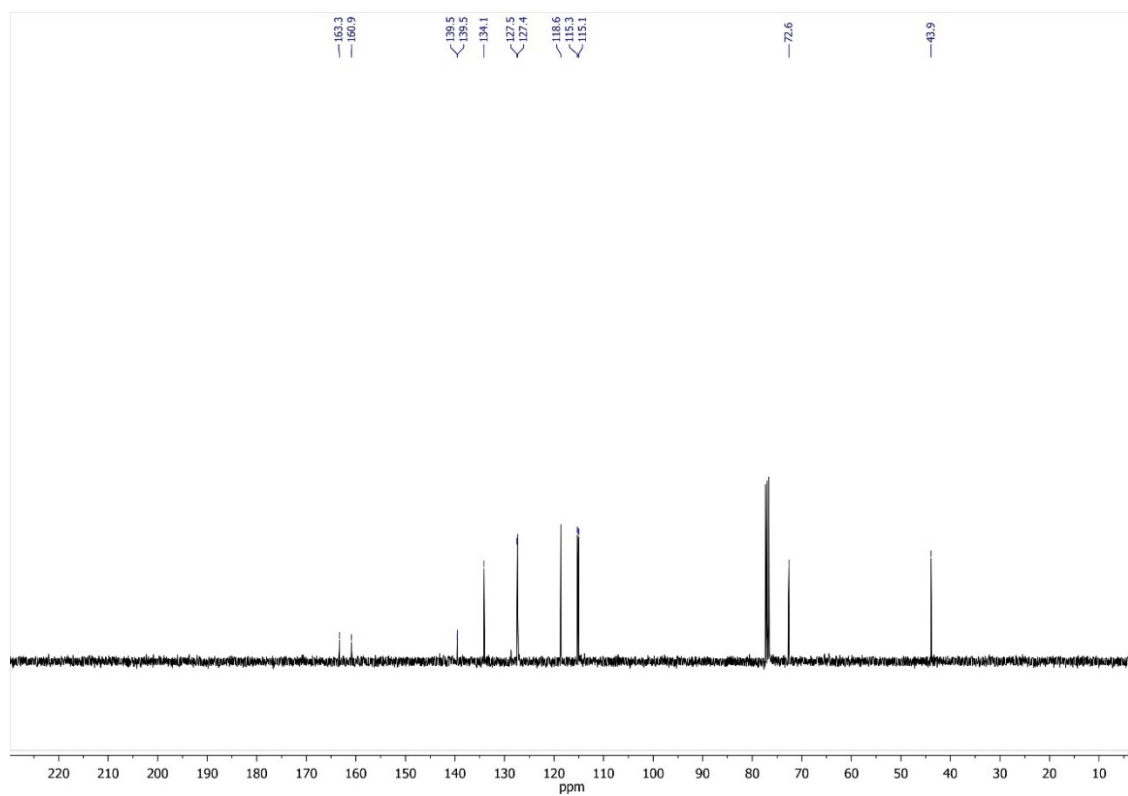




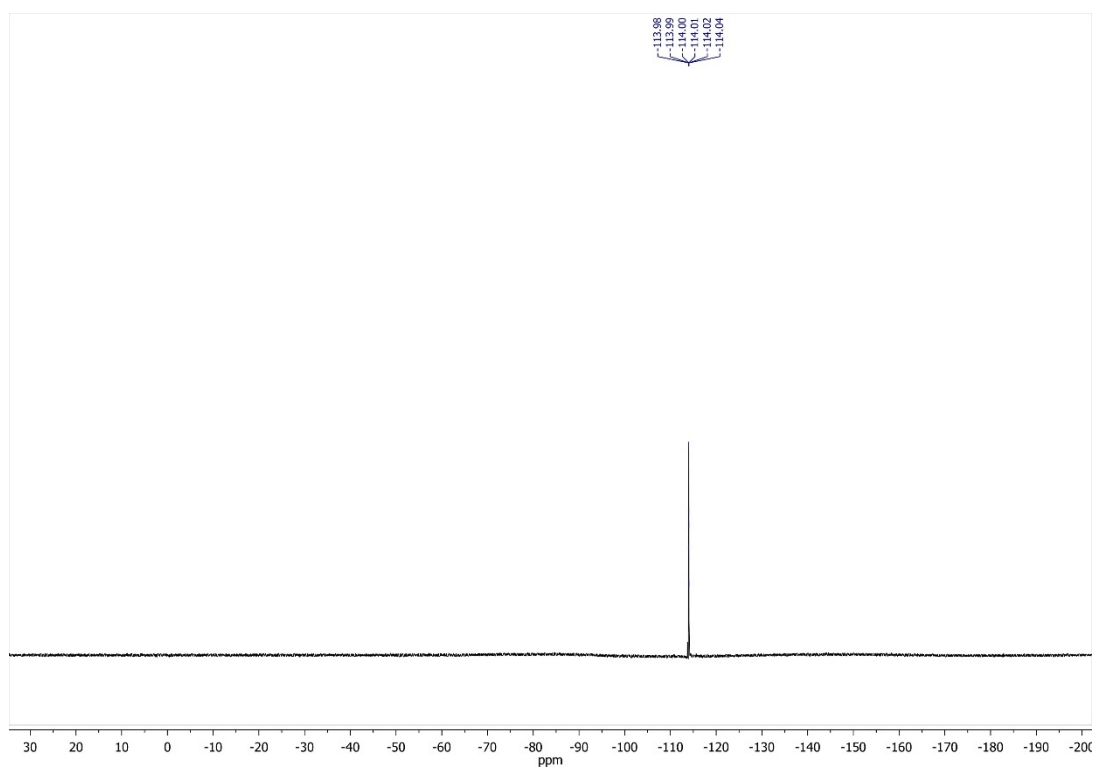
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

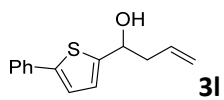


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

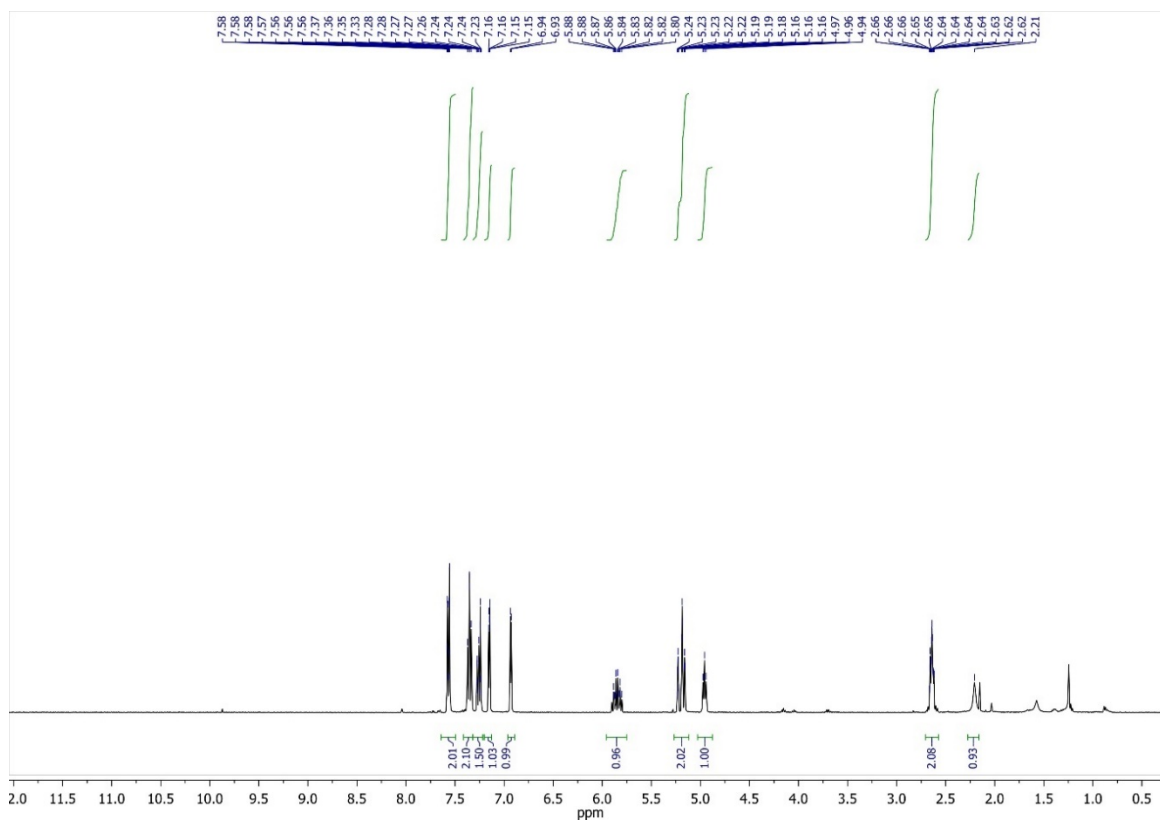


^{19}F -NMR (376.5 MHz, CDCl_3 , 25°C)

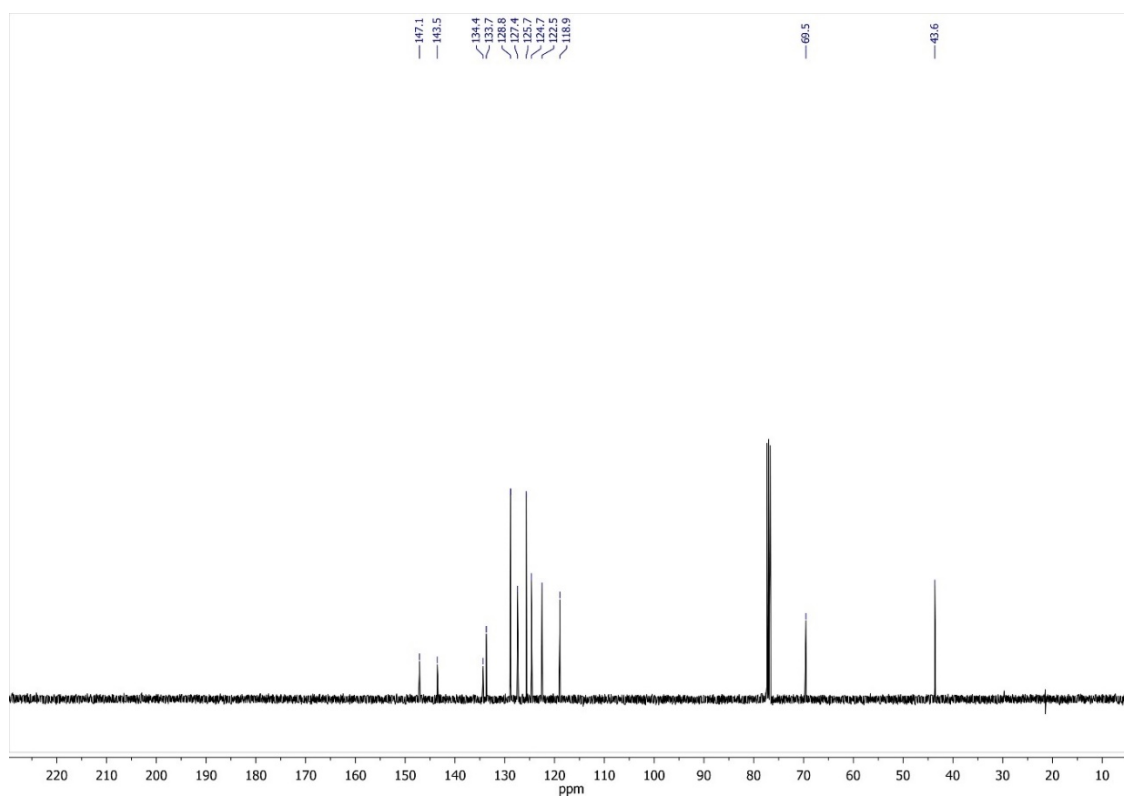


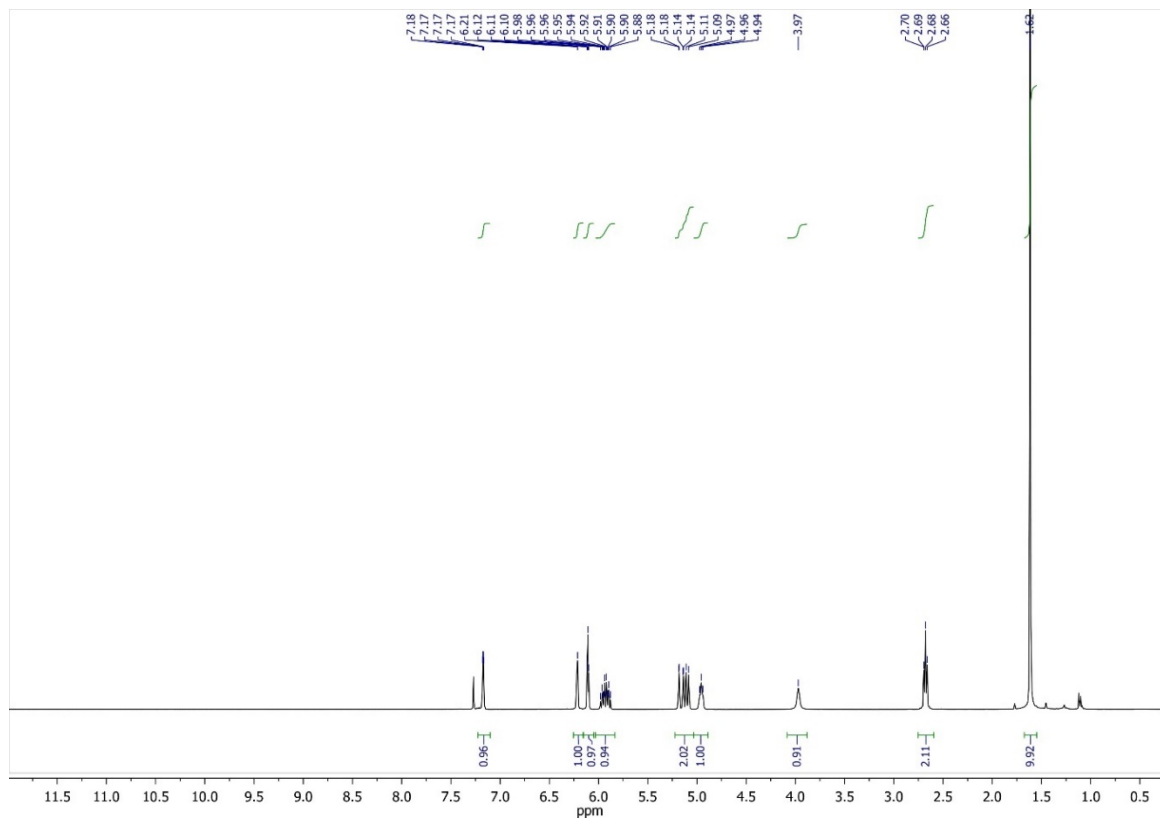
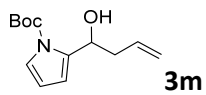


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

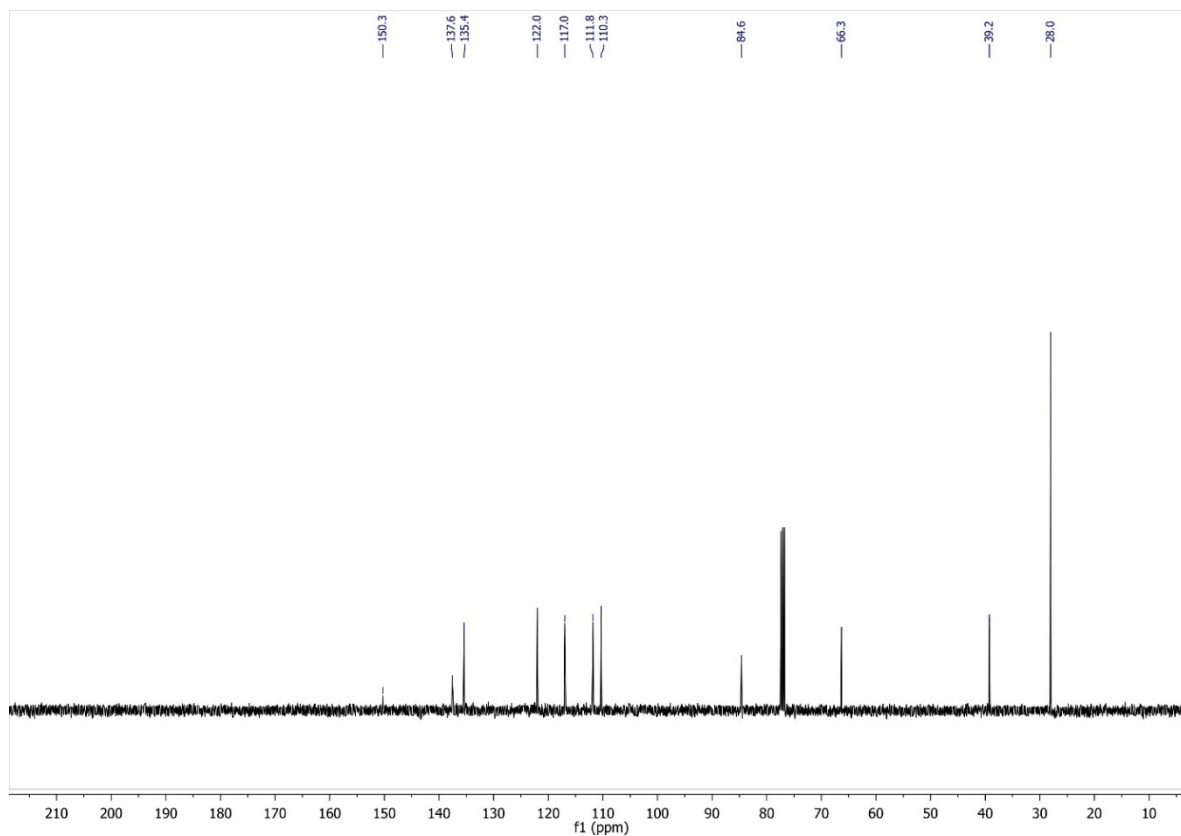


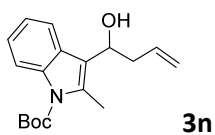
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)



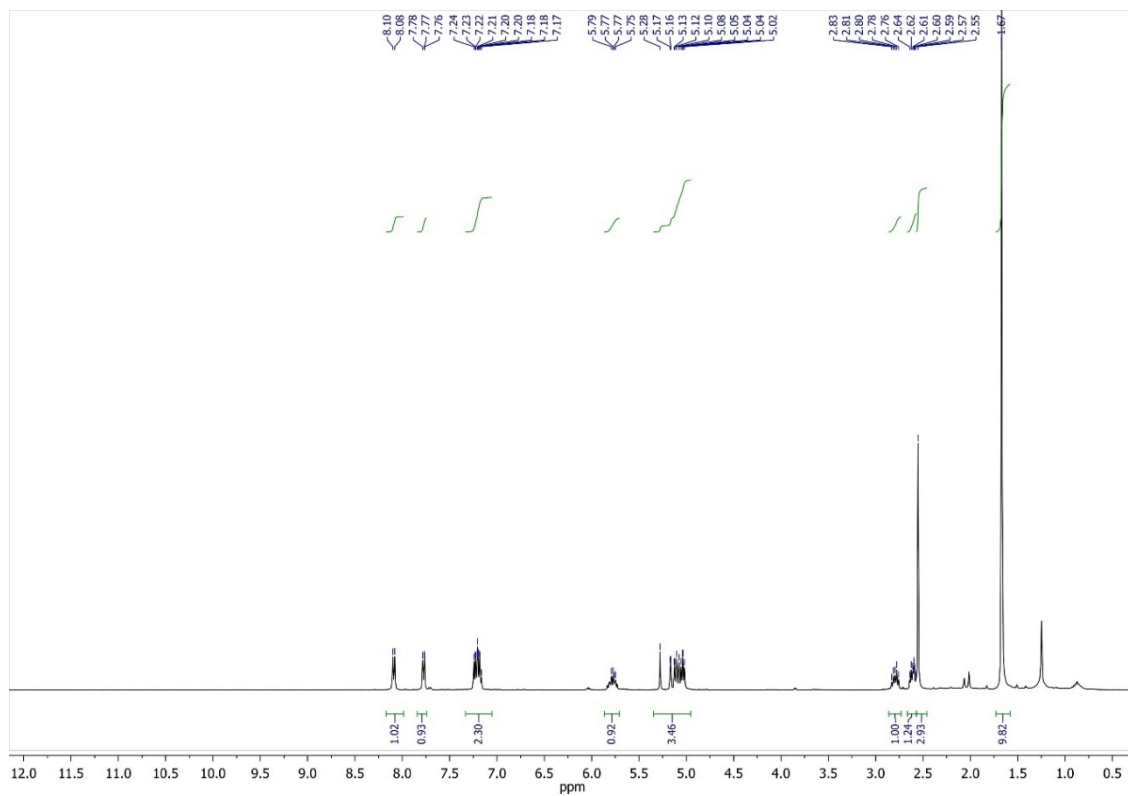


¹³C-NMR (100 MHz, CDCl₃, 25°C)

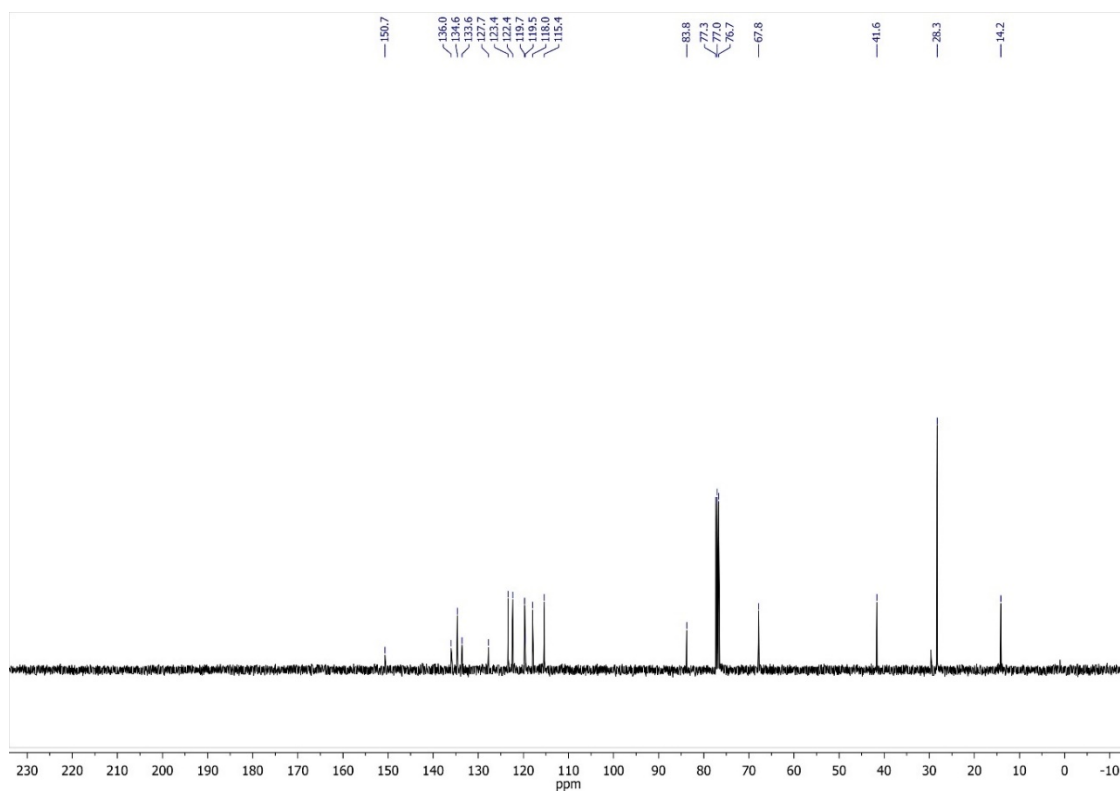


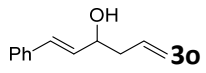


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

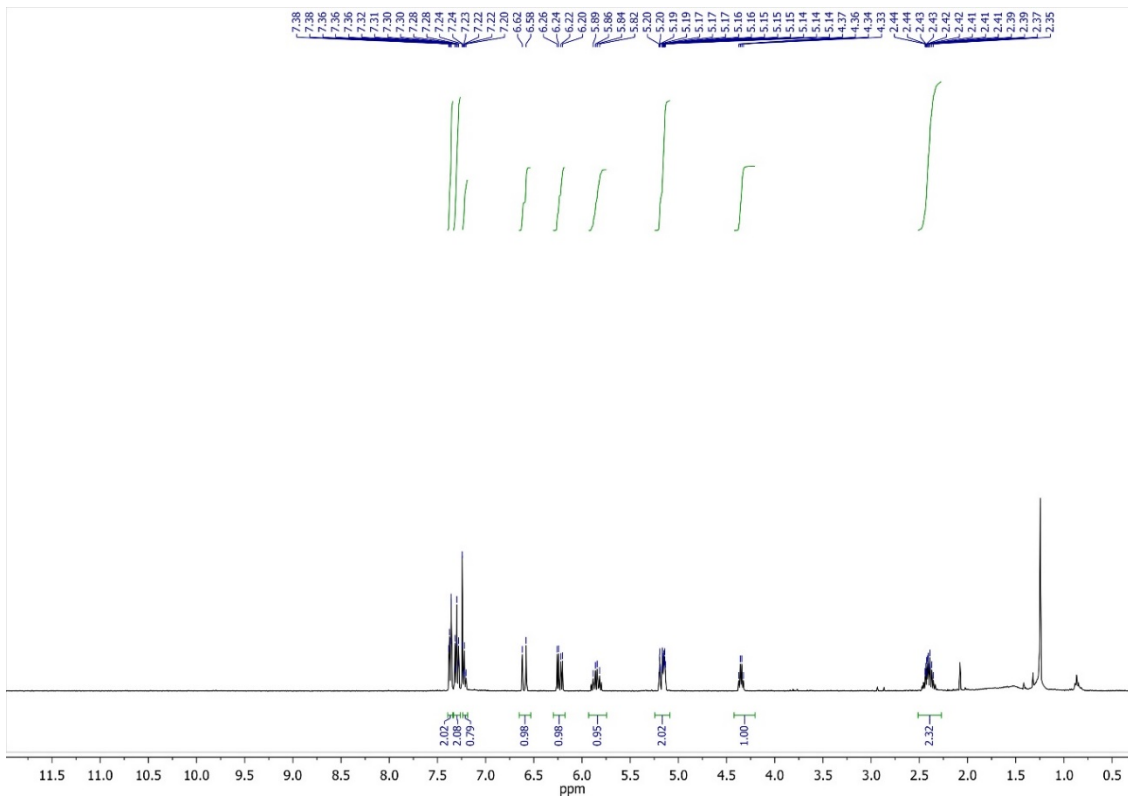


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

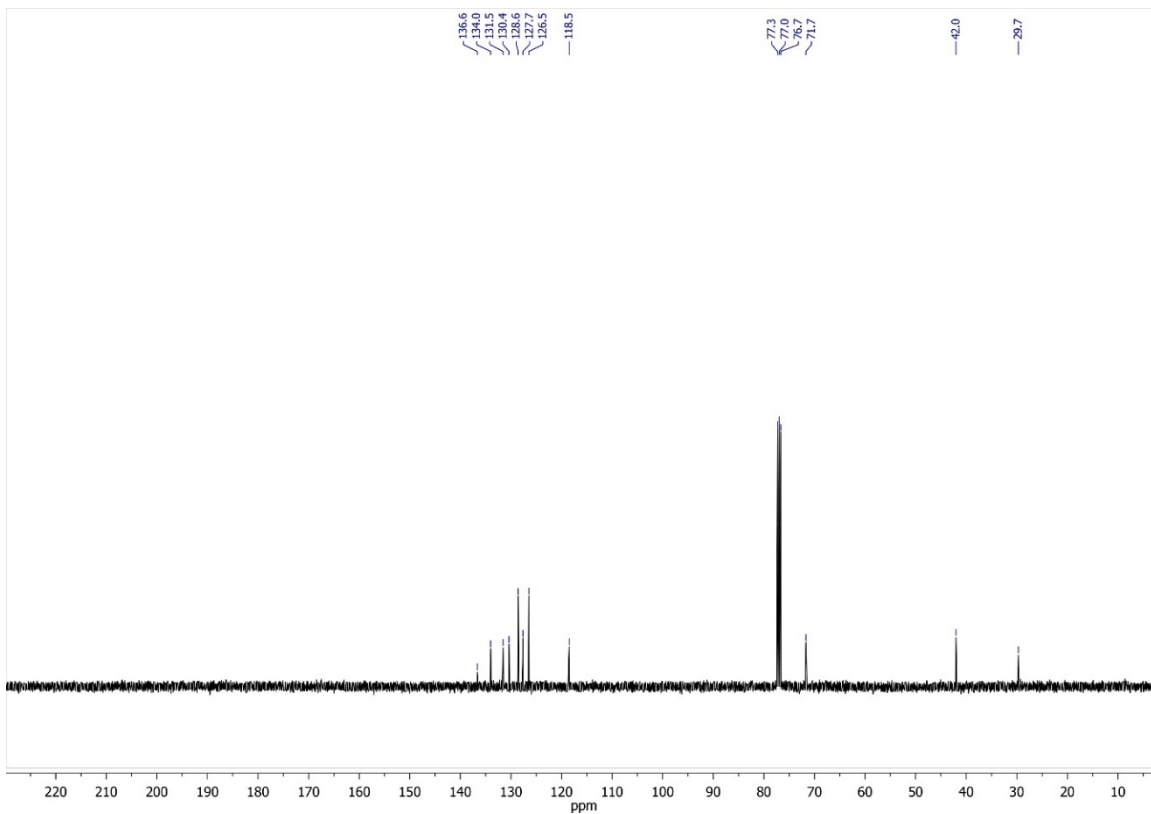


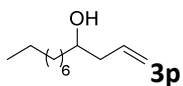


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

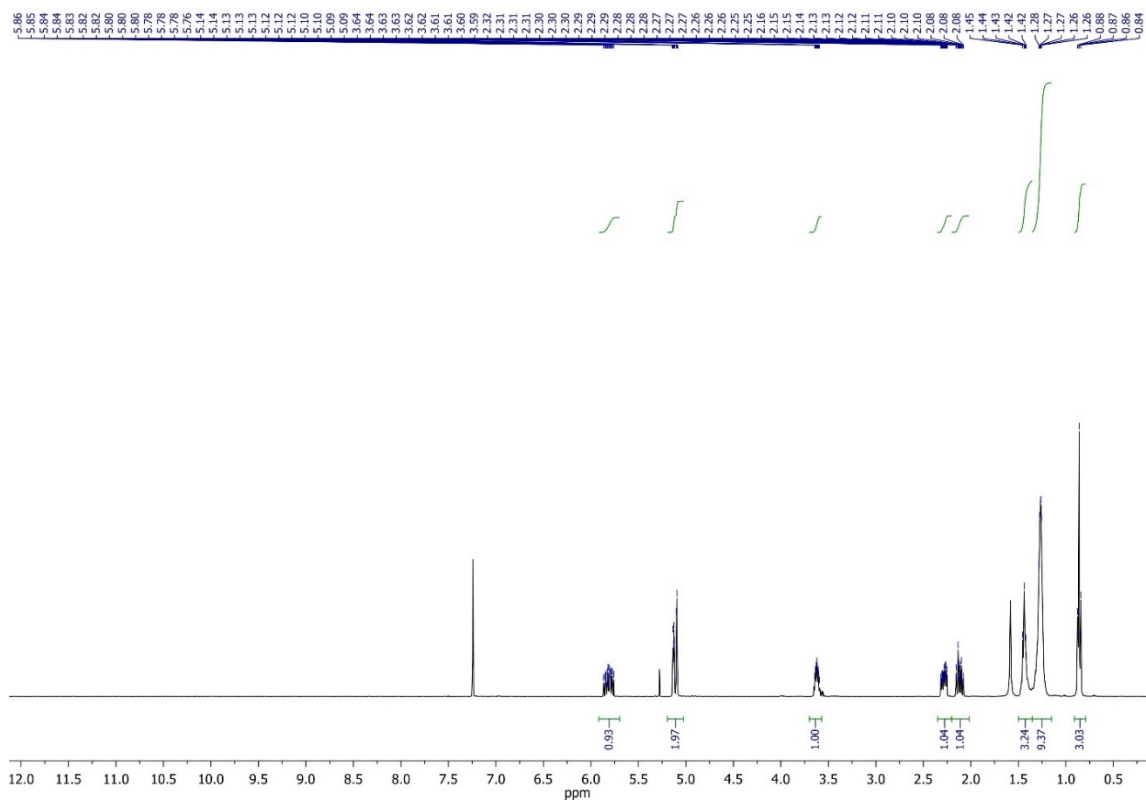


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

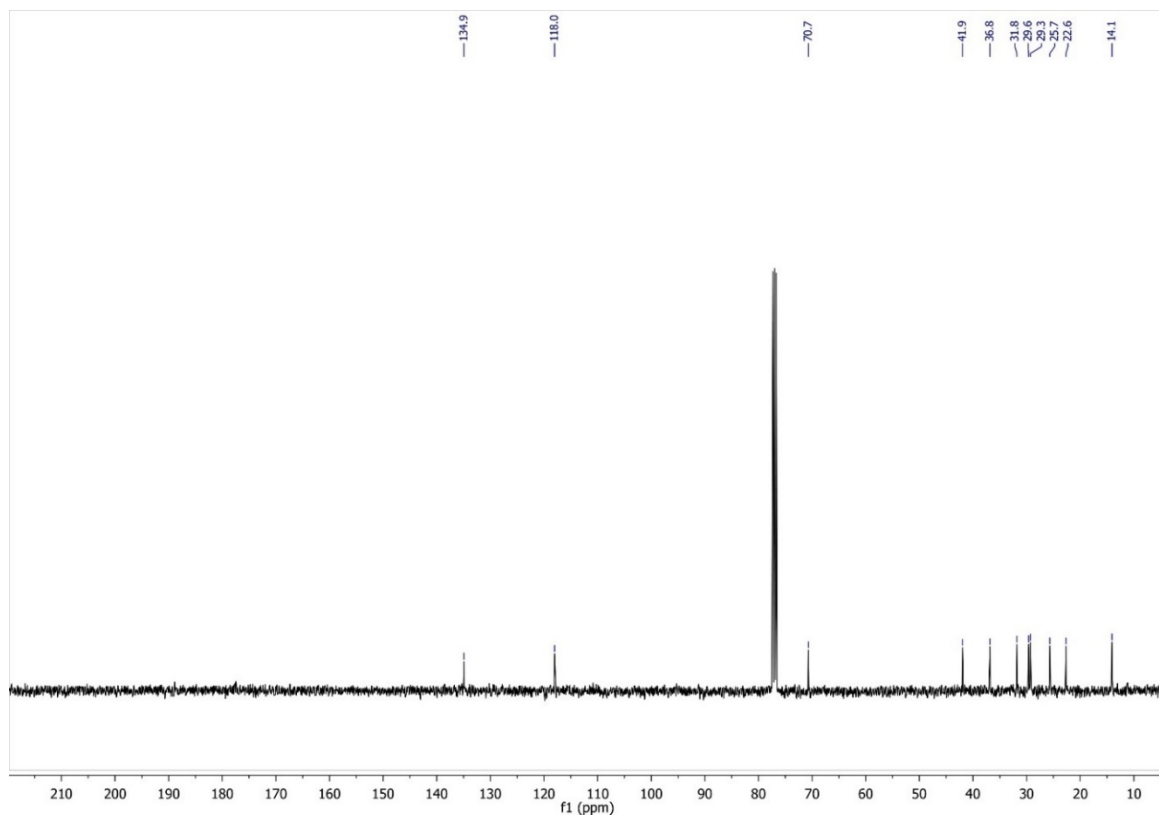


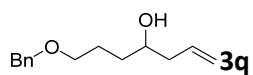


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

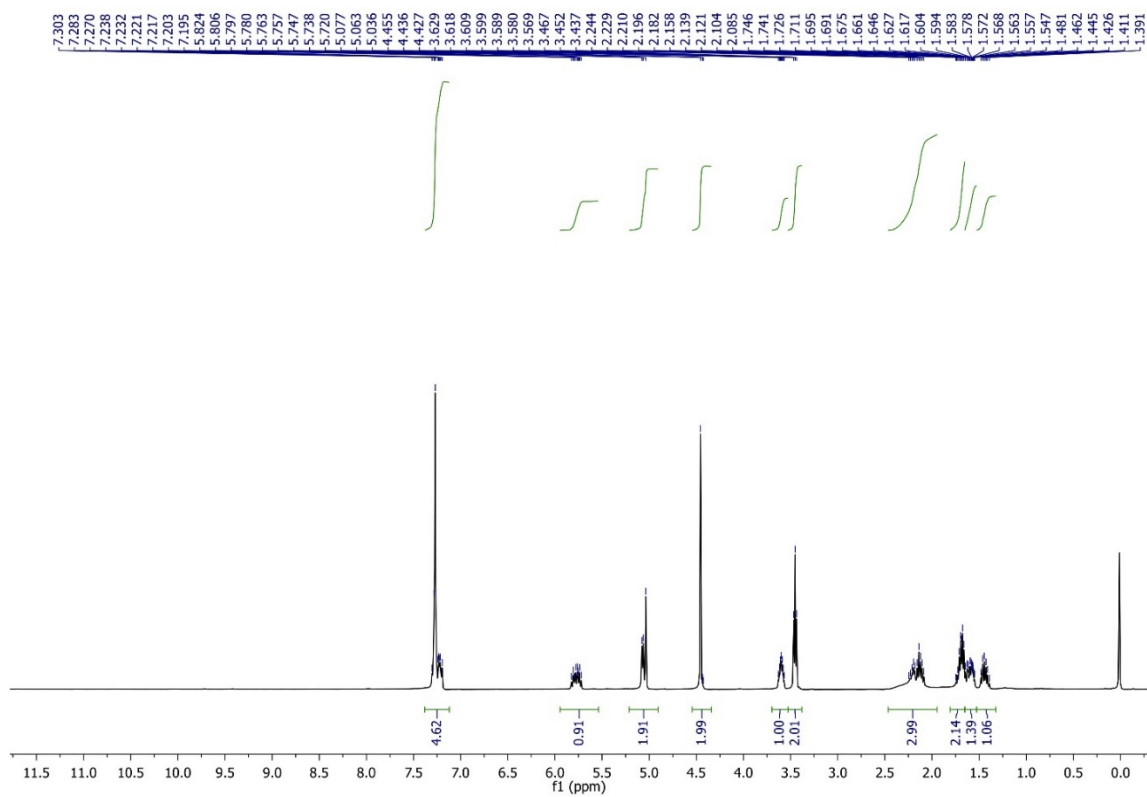


$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)

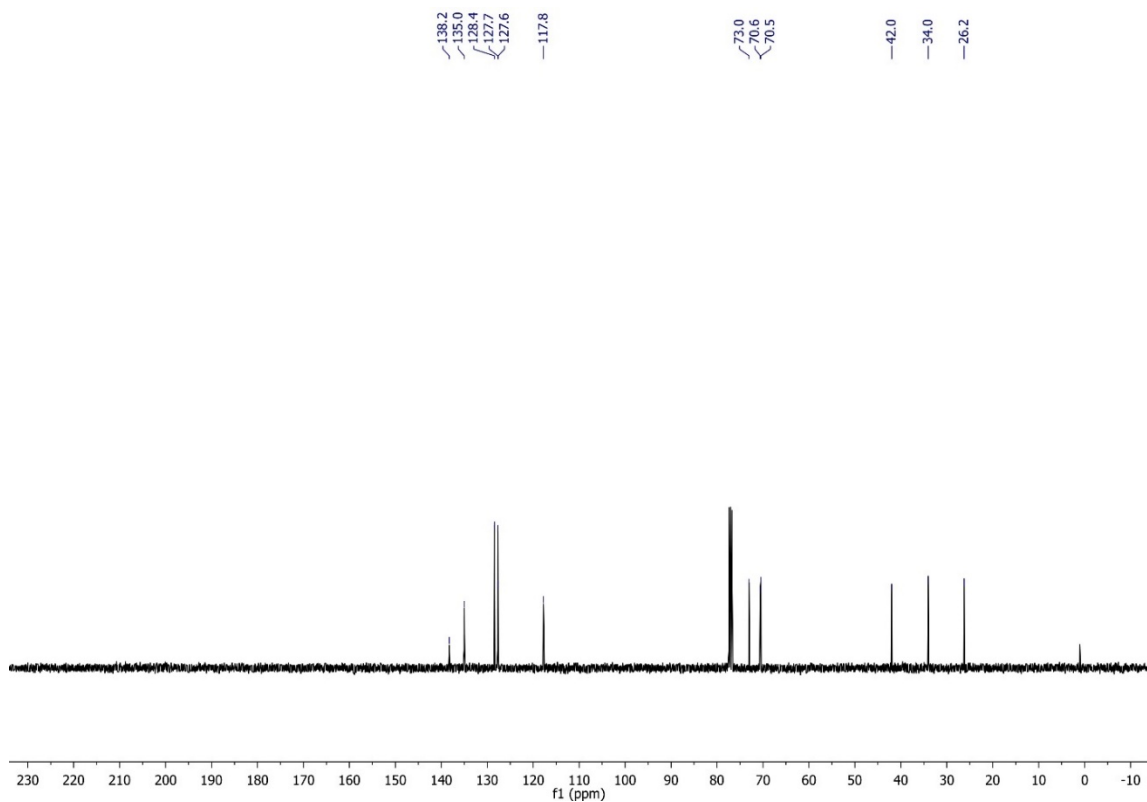


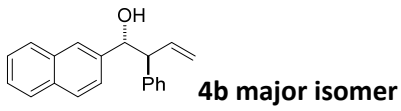


¹H-NMR (400 MHz, CDCl₃, 25°C)

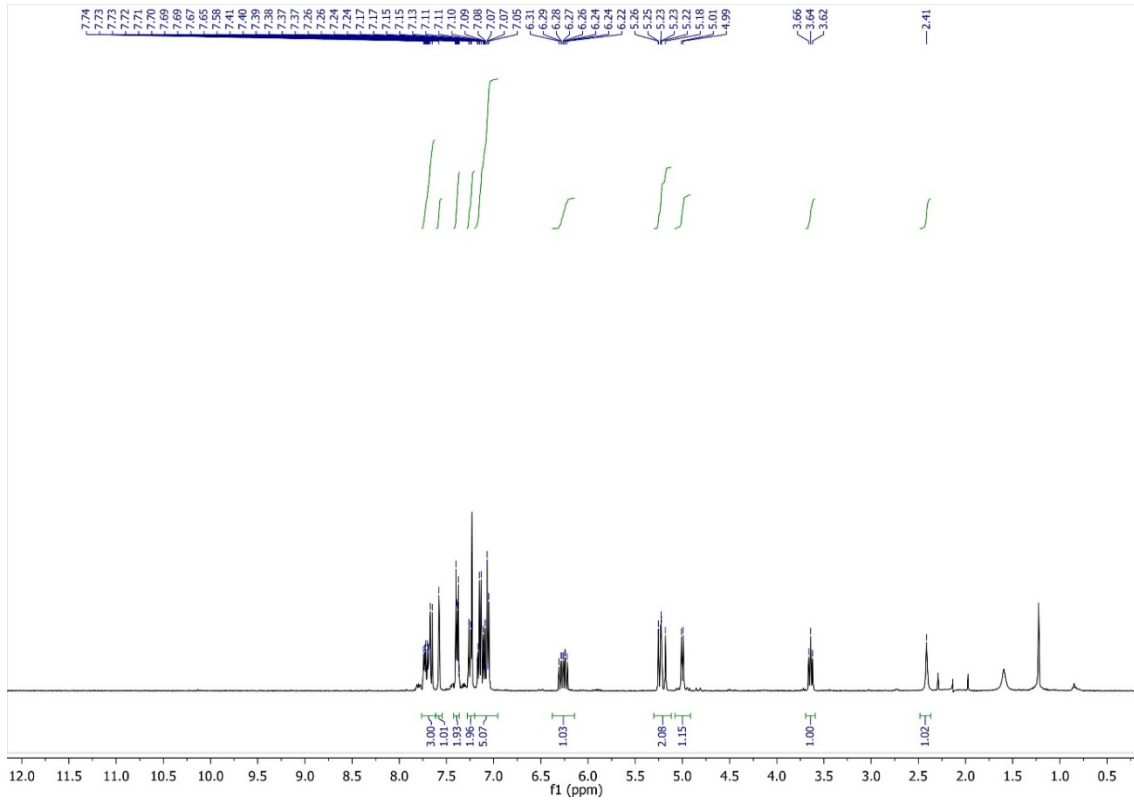


¹³C-NMR (100 MHz, CDCl₃, 25°C)

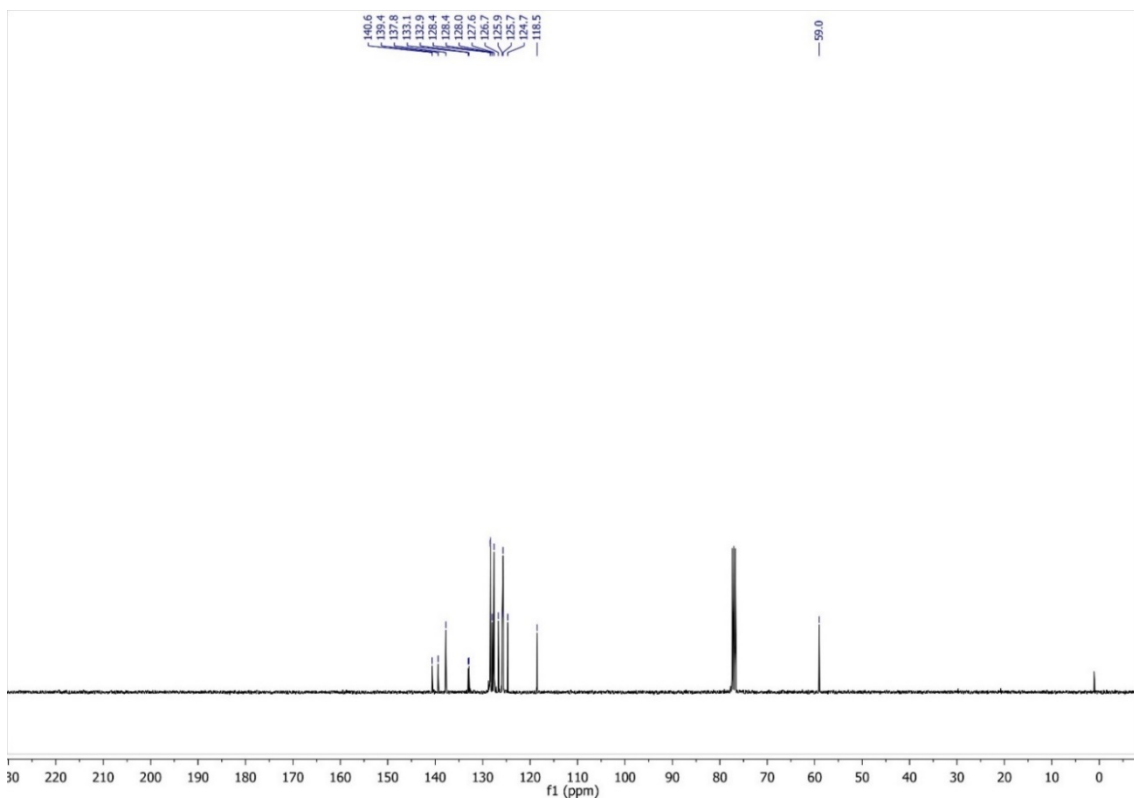


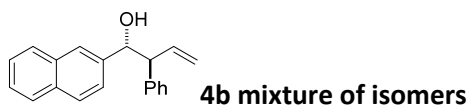


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

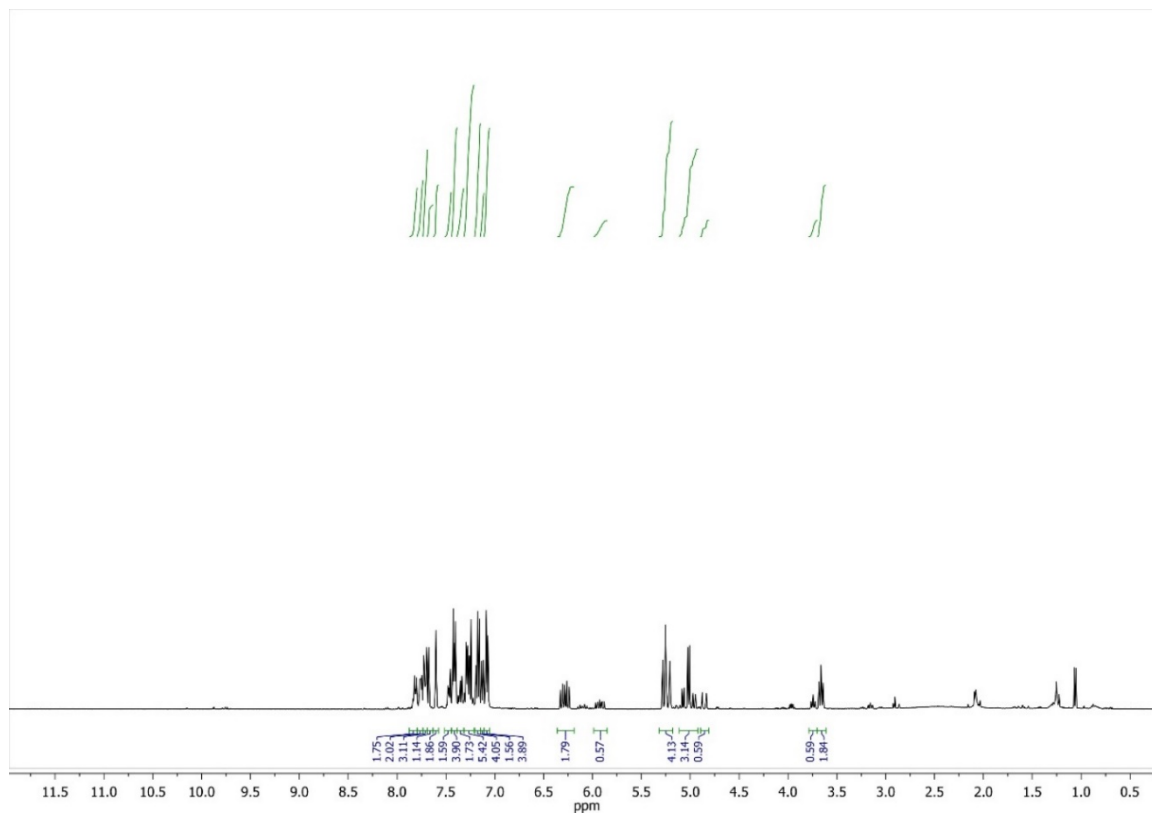


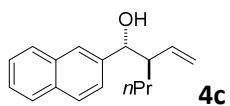
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)



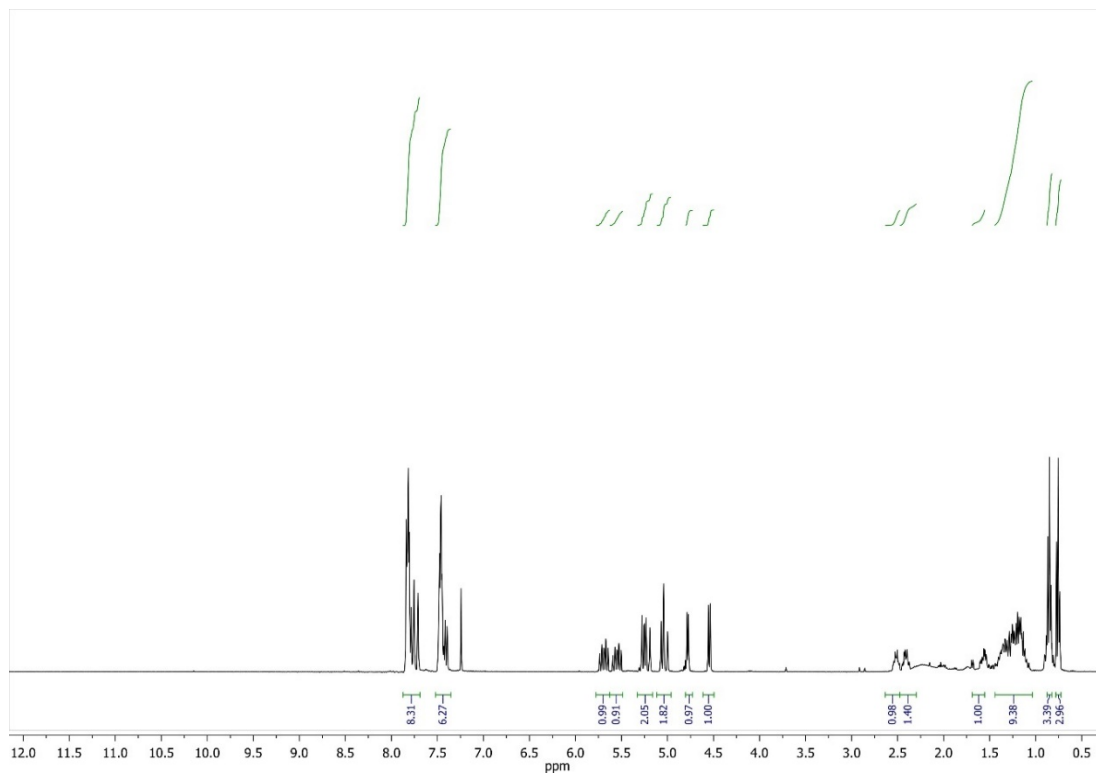


$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)

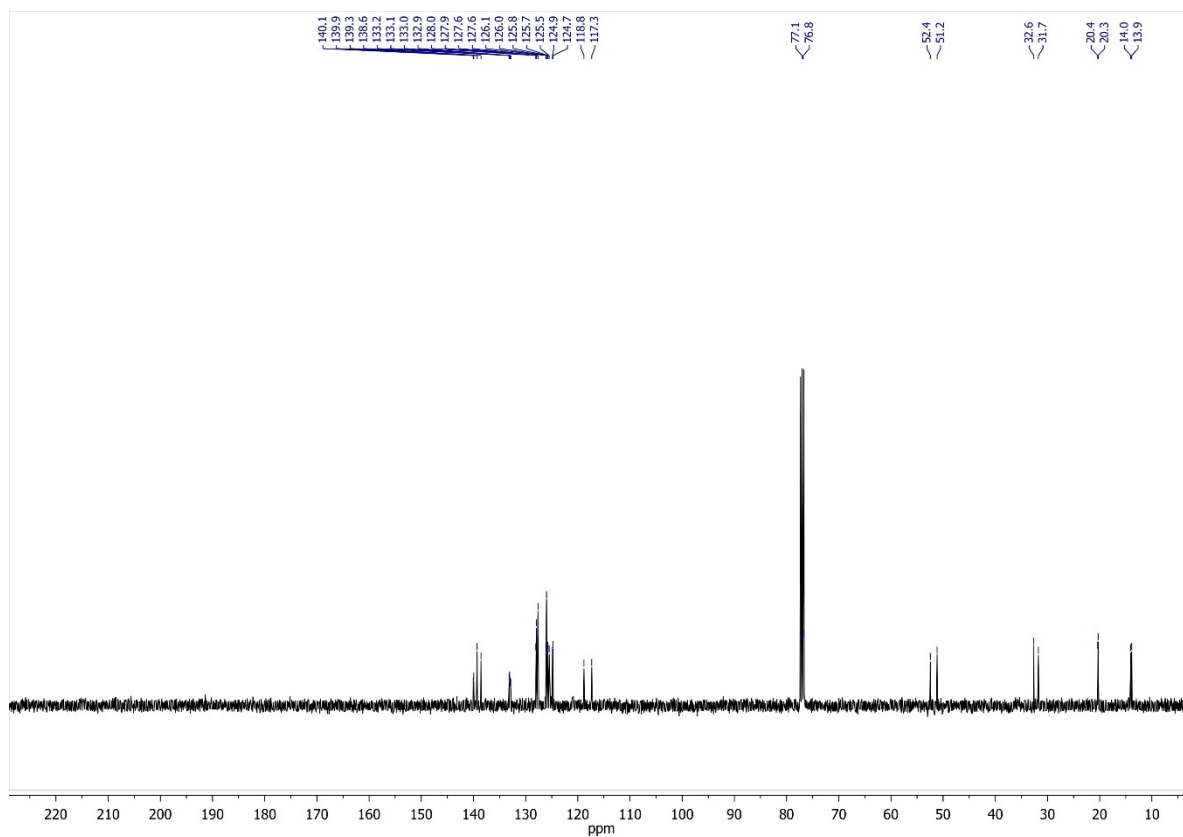




$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C)



$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C)



References

- [1] F. Krätzschar, M. Kaßel, D. Delony, A. Breder, *Chem. --Eur. J.* **2015**, *21*, 7030-7034.
- [2] J. Zhang, Y. Li, F. Zhang, C. Hu, Y. Chen, *Angew. Chem.* **2016**, *128*, 1904-1907; *Angew. Chem. Int. Ed.* **2016**, *55*, 1872-1875.
- [3] <https://www.kessil.com/photoreaction/PR160L.php>.
- [4] A. Gualandi, G. Rodeghiero, A. Faraone, F. Patuzzo, M. Marchini, F. Calogero, R. Perciaccante, T. P. Jansen, P. Ceroni, P. G. Cozzi, *Chem. Commun.* **2019**, *55*, 6838-6841.
- [5] T. Wang, X.-Q. Hao, J.-J. Huang, J.-L. Niu, J.-F. Gong, M.-P. Song, *J. Org. Chem.* **2013**, *78*, 8712-8721.
- [6] M. Bandini, P. G. Cozzi and A. Umami-Ronchi, *Tetrahedron*, **2001**, *57*, 835-843.
- [7] S. E. Denmark, Z. D. Matesich, S. T. Nguyen, S. Milicevic Sephton, *J. Org. Chem.* **2018**, *83*, 23-48.