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Supporting Information

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Experimental Procedures

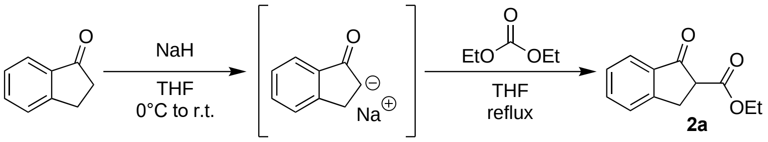
General methods and materials

^{1}H-NMR spectra were recorded on Varian Mercury 400, Varian Inova 600 or Bruker 600 spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CDCl_3$: $\delta = 7.26$ ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m= multiplet, dt = double triplet, td = triple doublet, ddd = doublet of doublets of doublets), coupling constants (Hz), number of protons. ^{13}C-NMR spectra were recorded on Varian Mercury 400, Varian Inova 600 or Bruker 600 spectrometers. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard ($CDCl_3$: $\delta = 77.0$ ppm). Chromatographic purifications were done with 240-400 mesh silica gel. All reactions were setup under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. All the reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Fluorochem, Strem Chemicals, TCI) and used without further purification unless specified. Anhydrous solvents were supplied by Aldrich in Sureseal® bottles and, unless specified, were used without further treatment.

1[24] was prepared following the reported procedure.

Preparation and characterization. of the starting materials

*Preparation of compound **2a***



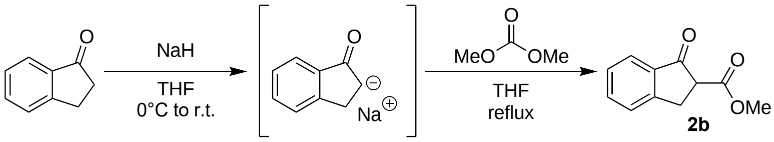
Product **2a** was synthetized slightly modifying the procedure reported by Marques and co-workers.[37] In a three-necked 50 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, NaH (60% w/w in mineral oil, 7.6 mmol, 304 mg, 2.0 equiv.) suspended in 3 mL of reagent-grade dry THF. The suspension was cooled at 0°C and a solution of 1-indanone (3.8 mmol, 502 mg, 1.0 equiv) in THF (5 mL) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was stirred at 0° C for 20 minutes and diethyl carbonate (19 mmol, 2.3 mL, 5.0 equiv.) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was warmed at room temperature and allowed to stir for 1 h. When TLC analysis (eluent 20% EtOAc in Cyclohexane) showed complete conversion of the starting material the reaction was quenched with HCl (2N, 10 mL) and extracted with Et_2O (3 x 10mL). The organic phase was washed with brine (1 x 10mL) and dried over Na_2SO_4 and the solvent was removed under vacuum. Product **2a** was isolated as a yellow oil after flash chromatography (SiO_2, 20% EtOAc in Cyclohexane) in 75% yield (2.85 mmol, 582 mg) Spectroscopic data agree with those reported in literature.

Mixture of ketonic and enol forms; keto:enol 5:1

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.81 – 7.74 (m, 1H), 7.68 – 7.55 (m, 1H), 7.54 – 7.47 (m, 1H), 7.43 – 7.33 (m, 1H) 4.25 (q, *J* = 7.1 Hz, 2H), 3.71 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.53 (m, 1H), 3.37 (dd, *J* = 17.3, 8.3 Hz, 1H) 1.31 (t, *J* = 7.1 Hz, 3H). Minor peaks corresponding to the enol form observed at 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ/ppm = 199.7, 169.3, 153.8, 135.5, 135.4, 129.5, 127.9, 126.9, 126.7, 124.8 120.8, 61.9, 60.2, 53.5, 32.7, 30.4, 14.6, 14.3.

*Preparation of compound **2b***

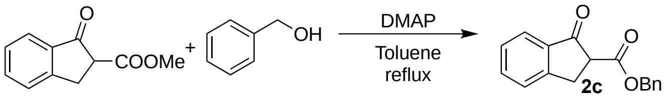


Product **2b** was synthetized slightly modifying the procedure reported by Marques and co-workers.[37] In a two-necked 50 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, NaH (60% w/w in mineral oil, 7.6 mmol, 304 mg, 2.0 equiv.) suspended in 8 mL of reagent-grade dry THF. The suspension was cooled at 0°C and a solution of 1-indanone (3.8 mmol, 502 mg, 1.0 equiv) in THF (2 mL) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was stirred at room temperature for 60 minutes and dimethyl carbonate (19 mmol, 1.6 mL, 5 equiv.) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was warmed to reflux and allowed to stir for 3 h. When TLC analysis (eluent 20% EtOAc in Cyclohexane) showed complete conversion of the starting material the reaction was quenched with HCl (2N, 10 mL) and extracted with EtOAc (3 x 10mL). The organic phase was washed with brine (1 x 10mL) and dried over Na_2SO_4 and the solvent was removed under vacuum. Product **2a** was isolated as a yellow oil after flash chromatography (SiO_2, 20% EtOAc in Cyclohexane) in 70% yield (2.66 mmol, 506 mg). Spectroscopic data agree with those reported in literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.81 – 7.77 (m, 1H), 7.68 – 7.61 (m, 1H), 7.53 – 7.48 (m, 1H), 7.47 – 7.39 (m, 1H), 3.79 (s, 3H), 3.74 (t, *J* = 3.9 Hz, 1H), 3.56 (d, *J* = 16.9 Hz, 1H), 3.37 (dd, *J* = 17.0, 7.9 Hz, 1H).

^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ/ppm = 199.6, 169.7, 153.7, 135.6, 135.4, 128.0, 126.7, 124.9, 53.3, 52.9, 30.4

*Preparation of compound **2c***



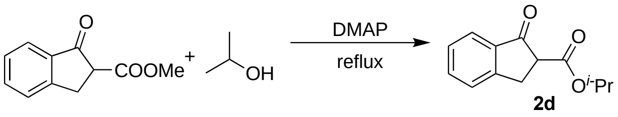
Product **2c** was synthetized slightly modifying the reported procedure.[37] In a two-necked 50 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **2b** (100 mg, 0.53 mmol, 1.0 equiv.) and DMAP (0.05 mmol, 6 mg, 0.1 equiv.) were dissolved in 5 mL of reagent-grade dry toluene. Benzyl alcohol (5.3 mmol, 548 µL, 573 mg, 10.0 equiv.) was added dropwise and the reaction was warmed to reflux and allowed to stir for 18 h. When TLC analysis (eluent 10% EtOAc in Cyclohexane) showed complete conversion of the starting material the reaction was quenched with HCl (2N, 10 mL) and extracted with EtOAc (3 x 10mL). The organic phase was washed with brine (1 x 10mL), then with $NaHCO_3$ aq. (5% w/w; 2*10mL), dried over Na_2SO_4 and the solvent was removed under vacuum. Product **2c** was isolated as a yellow oil after flash chromatography (SiO_2, 10% EtOAc in Cyclohexane) in 52% (0.28 mmol, 73 mg). Spectroscopic data agree with those reported in literature.

Mixture of ketonic and enol forms; keto:enol 4.5:1

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = δ 7.80 – 7.73 (m, 4.5H, keto), 7.68 – 7.56 (m, 1+4.5H), 7.54 – 7.49 (m, 4.5H, keto), 7.48 – 7.35 (m, 30.5H, keto+enol), 7.35 – 7.29 (m, 4.5H, keto), 5.32 (s, 2H, enol), 5.25 (d, *J* = 12.4 Hz, 4.5H, keto), 5.22 (d, *J* = 12.4 Hz, 4.5H, keto), 3.79 (dd, *J* = 8.3, 4.1 Hz, 4.5H, keto), 3.57 (dd, *J* = 17.2, 4.1 Hz, 4.5H, keto), 3.56 (s, 2H, enol), 3.39 (dd, *J* = 17.2, 8.3 Hz, 4.5H, keto).

^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ/ppm = δ 199.1, 168.9, 153.4, 135.3, 128.5 (2C), 128.2, 128.0 (2C), 127.7, 126.5, 124.6, 67.2, 53.2, 30.2.

*Preparation of compound **2d***



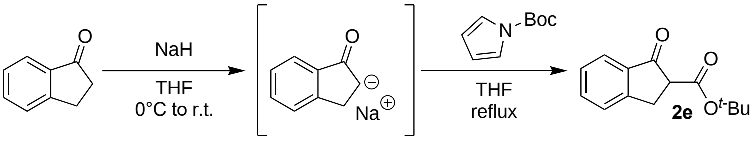
Product **2d** was synthetized slightly modifying the reported procedure.[37] In a two-necked 25 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **2b** (0.7 mmol, 133 mg, 1.0 equiv.) and DMAP (0.07 mmol, 8.6 mg, 0.1 equiv.) were dissolved in isopropyl alcohol (65.3 mmol, 5 mL, 93.3 equiv.). The reaction was warmed to reflux and allowed to stir for 26 h. When TLC analysis (eluent 10% EtOAc in Cyclohexane) showed complete conversion of the starting material the solvent was removed under vacuum. Product **2d** was isolated as a yellow oil after flash chromatography (SiO_2, 10% EtOAc in Cyclohexane) in 76% (0.53 mmol, 116 mg). Spectroscopic data agree with those reported in literature.[38]

Mixture of ketonic and enol forms; keto:enol 6:1

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.86 – 7.75 (m, 1H, enol), 7.72 (m, 6H, keto), 7.58 (m, 6H, keto), 7.55 – 7.50 (m, 1H, enol), 7.46 (m, 6H, keto), 7.44 – 7.31 (m, 6+2H keto+enol), 5.18 (hept, J = 6.3 Hz, 1H, enol), 5.06 (hept, J = 6.3 Hz, 6H, keto), 3.99 (bs, 1H, keto), 3.64 (dd, J = 8.3, 4.1 Hz, 6H, enol), 3.50 (dd, J = 17.2, 4.1 Hz, 6H, enol), 3.46 (s, 2H, keto), 3.33 (dd, J = 17.2, 8.3 Hz, 6H, enol), 1.32 (d, J = 6.2 Hz, 6H, keto), 1.27 (d, J = 6.2 Hz, 18H, keto), 1.26 (d, J = 6.2 Hz, 18H, keto).

^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ/ppm = δ =199.5, 168.6, 153.5, 135.2, 127.6, 126.4, 124.4, 69.1, 53.4, 30.1, 21.6, 21.6.

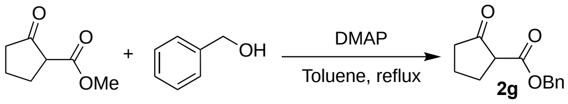
*Preparation of compound **2e***



Product **2e** was synthetized slightly modifying the procedure reported by Dixon and co-workers.[39] In a three-necked 50 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, NaH (60% w/w in mineral oil, 7.6 mmol, 304 mg, 2.0 equiv.) suspended in 3 mL of reagent-grade dry THF. The suspension was cooled at 0°C and a solution of 1-indanone (3.8 mmol, 500 mg, 1.0 equiv.) in dry THF (5mL) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was stirred at 0° C for 20 minutes and *tert*-butyl-1H-pyrrole-1-carboxylate (7.6 mmol, 1.27 g, 2.0 equiv.) in THF (5mL) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was warmed up and allowed to stir under reflux for 18 h. When TLC analysis (eluent 20% EtOAc in Cyclohexane) showed complete conversion of the starting material the reaction was quenched with HCl (2N, 10 mL) and extracted with Et_2O (3 x 10mL). The organic phase was washed with brine (1 x 10 mL), dried over Na_2SO_4 and the solvent was removed under vacuum. Product **2e** was isolated as a yellow oil after flash chromatography (SiO_2, 20% EtOAc in Cyclohexane) in 68% yield (2.58 mmol, 600 mg) Spectroscopic data agree with those reported in literature.

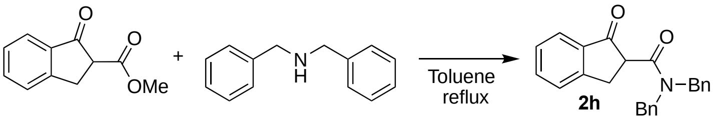
^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm = 7.78 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.52 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.39 (m, 1H), 3.65 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 3.52 (dd, *J* = 17.2, 4.0, 1H), 3.36 (dd, *J* = 17.2, 8.4, 1H) 1.51 (s, 9H). Minor peaks due to enol observed at 3.49 (s, 2H), 1.60 (s, 9H).
^{13}C{1H}-NMR (100 MHz, CDCl$_3$): δ/ppm = 200.1, 168.4, 153.7, 135.5, 135.2, 127.7, 126.5, 124.6, 82.1, 54.3, 30.3, 28.0. Minor peaks due to enol observed at 129.0, 126.7, 120.5, 32.9, 28.5.

*Preparation of compound **2g***



Product **2g** was synthetized slightly modifying the reported procedure.[40] In a two-necked 50 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, methyl 2-oxocyclopentane-1-carboxylate (1.92 mmol, 0.24 mL, 1.0 equiv.) and DMAP (0.19 mmol, 23 mg, 0.1 equiv.) were dissolved in 10 mL of reagent-grade dry toluene. Benzyl alcohol (2.32 mmol, 0.24 mL, 1.21 equiv.) was added dropwise and the reaction was warmed to reflux and allowed to stir for 48 h. When TLC analysis (eluent 10% EtOAc in Cyclohexane) showed complete conversion of the starting material the reaction was quenched with HCl (2N, 10 mL) and extracted with EtOAc (3*10mL). The organic phase was washed with brine (1 x 10mL), then with NaHCO$_3$ (5 % w/w; 1 x 10mL) and dried over Na$_2$SO$_4$ and the solvent was removed under vacuum. Product **2f** was isolated as a yellow oil after flash chromatography (SiO$_2$, 10% EtOAc in Cyclohexane) in 71% (1.36 mmol, 298 mg). Spectroscopic data agree with those reported in literature.
Mixture of ketonic and enol forms, keto:enol 20:1
^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm = 7.38 – 7.34 (m, 100H, keto), 7.34 – 7.30 (m, 5H, enol), 5.21 (s, 2H, enol), 5.18 (s, 40H, keto), 3.21 (t, *J* = 9.0 Hz, 20H, keto), 2.52 (t, *J* = 7.7 Hz, 2H, enol), 2.38 – 2.24 (m, 80H + 2H, keto + enol), 2.17 – 2.08 (m, 20H), 1.91 – 1.80 (m, 20H + 2H, keto + enol).
^{13}C{1H}-NMR (100 MHz, CDCl$_3$): δ/ppm = 212.0, 169.2, 135.5, 128.5 (2C), 128.2, 128.0 (2C), 66.9, 54.7, 38.0, 27.3, 20.9.

*Preparation of compound **2h***



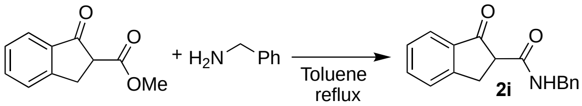
Product **2h** was synthetized slightly modifying the reported procedure.[41] In a two-necked 25 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **2b** (0.53 mmol, 100 mg, 1.0 equiv.) and *N,N*-dibenzylamine (0.80 mmol, 154 mg, 1.5 equiv.) were dissolved in 3.5 mL of reagent-grade dry toluene. The reaction was warmed to reflux and allowed to stir for 18 h. When TLC analysis (eluent 10% EtOAc in Cyclohexane) showed complete conversion of the starting material the solvent was removed under vacuum.

Product **2g** was isolated as a yellow oil after flash chromatography (SiO_2, 25% EtOAc in Cyclohexane) in 52% (0.28 mmol, 98 mg).

^{1}H-NMR (600 MHz, $CDCl_3$): δ/ppm = 7.76 (d, *J* = 7.5 Hz, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.50 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.44 – 7.26 (m, 12H), 5.35 – 5.29 (m, 1H), 4.50 (s, 1H), 4.16 – 4.08 (m, 2H), 3.85 (dd, *J* = 16.9, 3.9 Hz, 1H), 3.22 (dd, *J* = 17.0, 7.9 Hz, 1H).

^{13}C{1H}-NMR (151 MHz, $CDCl_3$): δ/ppm = 202.2, 169.7, 155.1, 137.2, 137.1, 136.0, 135.7, 129.4, 129.1, 128.9, 128.1, 127.9, 127.9, 127.6, 126.9, 126.69, 125.4, 124.8, 51.2, 50.8, 49.5, 31.2.

*Preparation of compound **2i***

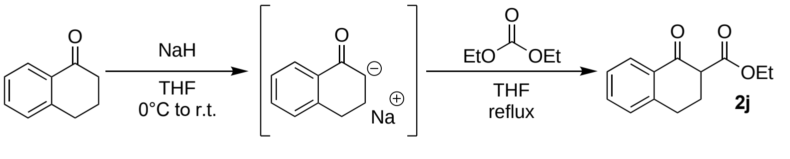


Product **2i** was synthetized slightly modifying the reported procedure.[41] In a two-necked 25 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **2b** (0.53 mmol, 100 mg, 1,0 equiv.) and benzylamine (0.80 mmol, 87 mg, 1.5 equiv.) were dissolved in 3.5 mL of reagent-grade dry toluene. The reaction was warmed to reflux and allowed to stir for 18 h. When TLC analysis (eluent 10% EtOAc in Cyclohexane) showed complete conversion of the starting material the solvent was removed under vacuum. Product **2h** was isolated as a yellow oil after flash chromatography (SiO_2, 25% EtOAc in Cyclohexane) in 69% (0.37 mmol, 97 mg). Spectroscopic data agree with those reported in literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.43 (bs, 1H), 7.36 – 7.18 (m, 5H), 4.50 (dd, *J* = 14.9, 5.9 Hz, 1H), 4.40 (dd, *J* = 14.9, 5.7 Hz, 1H), 3.77 (dd, *J* = 17.7, 4.1 Hz, 1H), 3.54 (dd, *J* = 8.4, 4.1 Hz, 1H), 3.31 (dd, *J* = 17.7, 8.4 Hz, 1H).

^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ 203.2, 166.4, 154.3, 138.0, 135.7, 135.3, 128.7 (2C), 127.6 (2C), 127.6, 127.4, 126.7, 124.3, 52.9, 43.8, 28.7.

*Preparation of compound **2j***



Product **2j** was synthetized slightly modifying the procedure reported by Christoffers and co-workers.[42] In a three-necked 50 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, NaH (60 % w/w in mineral oil, 6.84 mmol, 274 mg, 2.0 equiv.) suspended in 3 mL of reagent-grade dry THF. The suspension was cooled at 0°C and a solution of 3,4-dihydronaphthalen-1(2*H*)-one (3.42 mmol, 0.455 mL, 1.0 equiv.) in THF (5 mL) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was stirred at 0° C for 20 minutes and diethyl carbonate (17.1 mmol, 2 mL, 5 equiv.) was added dropwise through a dropping funnel over 5 minutes. The reaction mixture was warmed at reflux and allowed to stir for

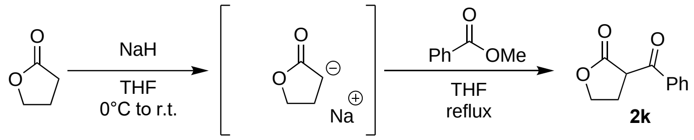
18 h. When TLC analysis (eluent 20% EtOAc in Cyclohexane) showed complete conversion of the starting material the reaction was quenched with HCl (2N, 10 mL) and extracted with Et$_2$O (3 x 10 mL). The organic phase was washed with brine (1 x 10 mL) and dried over Na$_2$SO$_4$, and the solvent was removed under vacuum. Product **2i** was isolated as a yellow oil after flash chromatography (SiO$_2$, 20% EtOAc in Cyclohexane) in 65% yield (2.22 mmol, 485 mg). Spectroscopic data agree with those reported in literature.

Mixture of ketonic and enol forms, keto:enol 1:4

^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm = keto+enol δ = 12.49 (bs, 4H, enol), 8.05 (dd, J = 7.9, 1.4 Hz, 1H, keto), 7.80 (dd, J = 7.6, 1.5 Hz, 4H, enol), 7.49 (td, J = 7.5, 1.5 Hz, 1H, keto), 7.35 – 7.23 (m, 2+8H, keto+enol), 7.17 (dt, J = 7.3, 0.9 Hz, 4H, enol), 4.29 (q, J = 7.1 Hz, 8H, enol), 4.27 – 4.21 (m, 2H, keto), 3.60 (dd, J = 10.5, 4.7 Hz, 1H, keto), 3.07 (dt, J = 16.8, 5.2 Hz, 1H, keto), 3.00 (ddd, J = 16.9, 9.7, 4.7 Hz, 1H, keto), 2.84 – 2.79 (m, 8H, enol), 2.61 – 2.55 (m, 8H, enol),2.55 – 2.46 (m, 1H, keto), 2.40 – 2.33 (m, 1H, keto), 1.35 (t, J = 7.1 Hz, 8H), 1.30 (t, J = 7.1 Hz, 3H).

^{13}C{1H}-NMR (100 MHz, CDCl$_3$): δ/ppm = keto + enol δ = 193.2 (keto), 172.7, 170.2, 165.0, 143.6, 139.3, 133.8, 131.7, 130.4, 130.0, 128.7, 127.7, 127.3, 126.8, 126.5, 124.2, 97.0 (enol), 61.2 (keto), 60.5 (enol), 54.5, 27.7, 27.6, 26.3, 20.5, 14.3, 14.1.

*Preparation of compound **2k***



Product **2k** was synthetized slightly modifying the procedure reported by Tardella and co-workers.[43] In a two-necked 50 mL round bottom flask equipped with a magnetic stirring bar, under nitrogen atmosphere, NaH (60 % w/w in mineral oil, 6.0 mmol, 240 mg, 2.0 equiv.) suspended in 2 mL of reagent-grade dry THF. The suspension was cooled at 0°C and a solution γ-butyrolactone (3.0 mmol, 231 µL, 1.0 equiv.) in THF (10 mL) was added. Then a solution of methyl benzoate (3.6 mmol, 450 µL, 1.2 equiv.) in anhydrous THF (5 mL) was added dropwise and the reaction was refluxed 5h. When TLC analysis (eluent 50% EtOAc in Cyclohexane) showed complete conversion of the starting material the reaction was quenched with HCl (2N, 10 mL) and extracted with EtOAc (3 x 10 mL). The organic phase was washed with brine (1 x 10 mL) and dried over Na$_2$SO$_4$, and the solvent was removed under vacuum. Product **2j** was isolated as a yellow oil after flash chromatography (SiO$_2$, 40% EtOAc in Cyclohexane) in 51% yield (1.53 mmol, 291 mg). Spectroscopic data agree with those reported in literature.

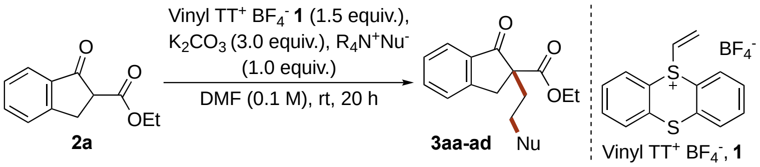
Mixture of ketonic and enol forms, keto:enol 10:1.

^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm = 11.88 (s, 1H, enol), 8.13 – 8.09 (m, 2H, enol), 8.09 – 8.06 (m, 20H, keto), 7.76 – 7.69 (m, 2H, enol), 7.65 – 7.57 (m, 1H, keto), 7.53 – 7.49 (m, 20H, keto), 7.48 – 7.44 (m, 1H, enol), 4.57 (dd, J = 9.2, 5.7 Hz, 10H, keto), 4.51 (ddd, J = 8.8, 7.8, 6.9 Hz, 10H, keto), 4.47 – 4.38 (m, 10+2H, keto + enol), 3.22 – 3.16 (m, 2H, enol), 2.89 – 2.81 (m, 10H, keto), 2.55 – 2.46 (m, 10H, keto).

^{13}C{1H}-NMR (100 MHz, CDCl$_3$): δ/ppm = 193.0, 172.8, 135.2, 134.0, 134.0, 129.4 (2C), 128.7 (2C), 67.7, 47.9, 26.0.

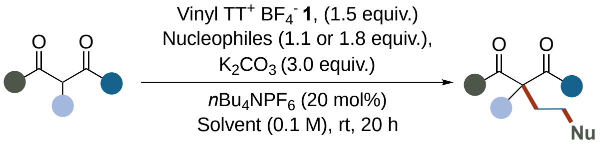
General procedure for the one-pot difunctionalization of vinylthiathrene

Procedure A (Table 1)



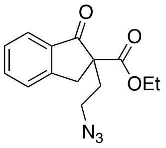
In a screw vial, 1,3-dicarbonyl compound (0.1 mmol), **1** (0.15 mmol, 50 mg, 1.5 equiv.), potassium carbonate (0.3 mmol, 41 mg, 3 equiv.) and tetrabutylammonium salt (0.1 mmol, 1,0 equiv.) were added to the DMF (1 mL). After 20 h under vigorous stirring, water (10 mL) and EtOAc (10 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The organic phase was washed with brine (1 x 10 mL), dried over Na_2SO_4 and the solvent was removed under vacuum. Products were isolated after flash chromatography (SiO_2).

Procedure B



In a screw vial, 1,3-dicarbonyl compound (0.1 mmol), **1** (0.15 mmol, 50 mg, 1.5 equiv.), nucleophile (1.1 or 1.8 equiv.), potassium carbonate (0.3 mmol, 41 mg, 3 equiv.) and tetrabutylammonium tetrafluoroborate (0.02 mmol, 6.6 mg, 0.2 equiv.) were added to the stated solvent (DMF, CH_3CN or DMSO, 1 mL). After 20 h under vigorous stirring, water (10 mL) and EtOAc (10 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The organic phase was washed with brine (1*10 mL), dried over Na_2SO_4 and the solvent was removed under vacuum. Product were isolated after flash chromatography (SiO_2).

Characterization of the products



3aa Ethyl 2-(2-azidoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

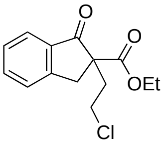
Yield (Cond. A, Scheme 2) 85% (0.085 mmol, 23.2 mg)

3aa was obtained following the general procedure as stated above employing 0.1 mmol (16.3 mg, 1 equiv.) of **2a**.

The title compound was isolated by flash column chromatography (SiO_2, 10% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.72 – 3.15 (dd, *J* = 17.3, 17.3 Hz, 2H), 3.49 – 3.33 (m, 2H), 2.66 – 2.44 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): 201.7, 170.6, 152.8, 135.7, 134.9, 128.1, 126.5, 125.1, 62.1, 59.1, 47.9, 37.2, 33.72, 14.1.



3ab Ethyl 2-(2-chloroethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

Yield in CH_3CN 80% (0.04 mmol, 10.7 mg)

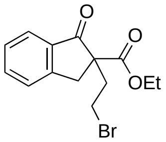
Yield in DMF 34% (0.017 mmol, 4.5 mg)

3ab was obtained following the general procedure as stated above employing 0.05 mmol (8.16 mg, 1 equiv.) of **2a** and 0.055 mmol (3.2 mg, 1.1 equiv.) of NaCl.

The title compound was isolated by flash column chromatography (SiO_2, 10% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.77 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.71 (d, *J* = 17.3, 1H), 3.69 – 3.51 (m, 2H), 3.14 (d, *J* = 17.3, 1H), 2.65 – 2.53 (m, 1H), 2.40 – 2.28 (m, 1H) 1.19 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 201.5, 170.4, 152.8, 135.8, 134.8, 128.1, 126.6, 126.5, 125.1, 62.1, 59.8, 40.5, 37.6, 37.3, 14.1.



3ac Ethyl 2-(2-bromoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

Yield in CH_3CN 71% (0.036 mmol, 11.0 mg)

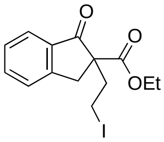
Yield in DMF 55% (0.028 mmol, 8.6 mg)

3ac was obtained following the general procedure as stated above employing 0.05 mmol (8.16 mg, 1 equiv.) of **2a** and 0.055 mmol (6.5 mg, 1.1 equiv.) of KBr.

The title compound was isolated by flash column chromatography (SiO_2, 10% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H,), 7.45 (t, *J* = 7.3 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.72 (d, *J* = 17.3, Hz, 1H), 3.54 – 3.32 (m, 1H), 3.15 (d, *J* = 17.3 Hz, 1H), 2.72 – 2.60 (m, 1H), 2.50 – 2.38 (m, 1H), 1.21 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 201.7, 170.3, 152.7, 135.8, 134.8, 128.2, 126.6, 125.1, 62.1, 60.7, 38.2, 37.3, 27.6, 14.2.



3ad Ethyl 2-(2-iodoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

Yield in CH_3CN 85% (0.043 mmol, 15.2 mg)

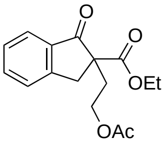
Yield in DMF 67% (0.034 mmol, 12.0 mg)

3ad was obtained following the general procedure as stated above employing 0.05 mmol (8.16 mg, 1 equiv.) of **2a** and 0.055 mmol (9.1 mg, 1.1 equiv.) of KI.

The title compound was isolated by flash column chromatography (SiO_2, 10% EtOAc in Cyclohexane).

^{1}H-NMR (600 MHz, $CDCl_3$): δ/ppm = 7.78 – 7.76 (m, 1H), 7.64 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.43 – 7.40 (m, 1H), 4.21 – 4.14 (m, 2H), 3.70 (d, *J* = 17.0 Hz, 1H), 3.23 (ddd, *J* = 12.4, 9.5, 4.7 Hz, 1H), 3.15 – 3.09 (m, 2H), 2.68 (ddd, *J* = 13.9, 12.4, 4.7 Hz, 1H), 2.50 (ddd, *J* = 13.9, 12.4, 4.9 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 200.9, 170.0, 152.5, 135.6, 134.8, 128.0, 126.4, 125.0, 61.93, 61.91, 39.6, 36.8, 14.0, -2.1.



3ae Ethyl 2-(2-acetoxyethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

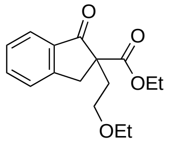
Yield in CH_3CN 68% (0.034 mmol, 9.9 mg)

3ae was obtained following the general procedure as stated above employing 0.05 mmol (8.16 mg, 1.0 equiv.) of **2a** and 0.055 mmol (4.5 mg, 1.1 equiv.) of AcONa.

The title compound was isolated by flash column chromatography (SiO_2, 10% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.77 (m, *J* = 0.9 Hz, 1H), 7.63 (m, *J* = 1.2 Hz, 1H), 7.49 (m, *J* = 0.9 Hz, 1H), 7.45 – 7.36 (m, 1H), 4.24 – 4.10 (m, 4H), 3.72 (d, *J* = 17.3 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 1H), 2.50 (ddd, *J* = 14.3, 6.9, 5.7 Hz, 1H), 2.35 – 2.18 (m, 1H), 1.90 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 201.8, 170.8, 170.7, 153.0, 135.6, 135.1, 128.0, 126.5, 125.0, 62.0, 61.0, 59.0, 36.6, 33.2, 20.8, 14.1.



3af Ethyl 2-(2-ethoxyethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

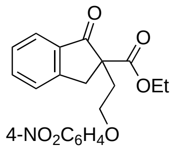
Yield in CH_3CN 81% (0.004 mmol, 11.2 mg)

3af was obtained following the general procedure as stated above employing 0.05 mmol (8.16 mg, 1.0 equiv.) of **2a** and 3 mmol (0.169 mL, 60 equiv.) of EtOH.

The title compound was isolated by flash column chromatography (SiO_2, 10-20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.76 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.69 (d, *J* = 17.3 Hz, 1H), 3.47 (t, *J* = 6.4 Hz, 2H), 3.32-3.22 (m, 3H), 2.41 (dt, *J* = 14.2, 6.1 Hz, 1H), 2.23 (dt, *J* = 14.3, 6.6 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H)

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 202.5, 171.2, 153.4, 135.4, 135.3, 127.7, 126.4, 124.8, 67.0, 66.3, 61.7, 59.4, 36.9, 34.4, 15.1, 14.2.



3ag Ethyl 2-(2-(4-nitrophenoxy)ethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

Yield in CH_3CN 51% (0.026 mmol, 9.4 mg)

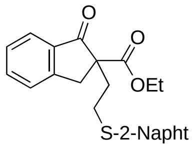
Yield in DMF 71% (0.036 mmol, 13.1 mg)

3ag was obtained following the general procedure as stated above employing 0.05 mmol (8.16 mg, 1.0 equiv.) of **2a** and 0.055 mmol (7.7 mg, 1.1 equiv.) of 4-nitrophenol.

The title compound was isolated by flash column chromatography (SiO_2, 10-20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 8.11 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 4.0 Hz, 1H), 7.63 (q, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 4.17 (m, 2H), 3.70 (d, *J* = 20.0 Hz, 1H), 3.28 – 3.00 (m, 1H), 2.43 – 2.13 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 1H), 0.86 (t, *J* = 8.0 Hz, 1H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 201.7, 170.8, 152.5, 146.9, 136.6, 135.8, 135.0, 128.3, 126.6, 126.4, 125.2, 124.2, 123.7, 62.1, 59.9, 37.8, 34.4, 27.3, 14.2.



3ah Ethyl 2-(2-(naphthalen-1-ylthio)ethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

Yield in CH_3CN 62% (0.031 mmol, 12.1 mg)

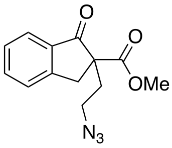
Yield in DMF 68% (0.034 mmol, 13.3 mg)

3ah was obtained following the general procedure as stated above employing 0.05 mmol (8.16 mg, 1 equiv.) of **2a** and 0.055 mmol (8.8 mg, 1.1 equiv.) of 2-naphthalenethiol.

The title compound was isolated by flash column chromatography (SiO_2, 10-20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.81 – 7.67 (m, 4H), 7.63 (m, *J* = 1.2 Hz, 1H), 7.51 – 7.36 (m, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 17.3 Hz, 1H), 3.20 – 3.05 (m, 2H), 3.01 (ddd, *J* = 13.2, 11.6, 4.9 Hz, 1H), 2.45 (ddd, *J* = 14.0, 11.5, 4.9 Hz, 1H), 2.26 (ddd, *J* = 14.0, 11.6, 4.9 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 1H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 201.8, 170.7, 152.8, 135.6, 135.2, 133.9, 133.4, 131.9, 128.6, 128.1, 127.8, 127.4, 127.3, 127.2, 126.7, 126.5, 125.8, 125.1, 62.0, 60.4, 37.4, 35.0, 29.0, 14.2.



3ba Methyl 2-(2-azidoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

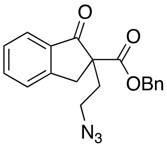
Yield (Cond. A, Scheme 2) 75% (0.075 mmol, 19.4 mg)

3ba was obtained following the general procedure as stated above employing 0.1 mmol (19.0 mg, 1 equiv.) of **2b**.

The title compound was isolated by flash column chromatography (SiO_2, 10-20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.79 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 3.75 (dd, *J* = 17.6, 17.1 Hz, 2H), 3.71 (s, 3H), 3.41 (m, 2H), 2.42 (m, 1H), 2.17 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 201.6, 171.1, 152.8, 135.8, 134.9, 128.2, 126.6, 125.1, 59.0, 53.1, 47.9, 37.1, 33.7.



3ca Benzyl 2-(2-azidoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

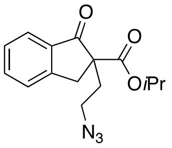
Yield (Cond. A, Scheme 2) 76% (0.076 mmol, 25.5 mg)

3ca was obtained following the general procedure as stated above employing 0.1 mmol (26.6 mg, 1 equiv.) of **2c**.

The title compound was isolated by flash column chromatography (SiO_2, 10-20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.77 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.4, 1.3 Hz, 1H), 7.46 – 7.36 (m, 1H), 7.34 – 7.26 (m, 3H), 7.25 – 7.19 (m, 2H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 3.71 (d, *J* = 17.3 Hz, 1H), 3.44 – 3.27 (m, 2H), 3.14 (d, *J* = 17.3 Hz, 1H), 2.40 (ddd, *J* = 14.0, 8.2, 6.0 Hz, 1H), 2.15 (ddd, *J* = 14.0, 8.4, 6.7 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ/ppm = 201.4, 170.3, 152.7, 135.8, 135.5, 134.9, 128.7, 128.4, 128.2, 127.9, 126.5, 125.1, 67.5, 59.2, 47.8, 37.1, 33.7.



3da Isopropyl 2-(2-azidoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

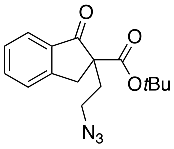
Yield (Cond. A, Scheme 2) 78% (0.078 mmol, 22.4 mg)

3da was obtained following the general procedure as stated above employing 0.1 mmol (21.8 mg, 1 equiv.) of **2d**.

The title compound was isolated by flash column chromatography (SiO_2, 10-20% EtOAc in Cyclohexane).

^{1}H-NMR (600 MHz, CDCl$_3$): δ/ppm = 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (td, *J* = 7.4, 1.2 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 5.01 (hept, *J* = 6.3 Hz, 1H), 3.70 (d, *J* = 17.2 Hz, 1H), 3.43 (ddd, *J* = 12.5, 8.6, 5.8 Hz, 1H), 3.37 (ddd, *J* = 12.5, 8.5, 6.5 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 2.38 (ddd, *J* = 14.2, 8.5, 5.8 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.18 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H).

^{13}C-NMR (151 MHz, CDCl$_3$): δ/ppm = 201.6, 169.9, 152.7, 135.5, 134.8, 127.9, 126.4, 124.9, 69.5, 59.1, 47.8, 37.0, 33.5, 21.5, 21.4.



3ea *tert*-Butyl 2-(2-azidoethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

Yield (Cond. A, Scheme 2) 21% (0.021 mmol, 6.3 mg)

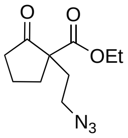
Yield (Cond. B, Scheme 2) 35% (0.035 mmol, 10.5 mg)

3ea was obtained following the general procedure as stated above employing 0.1 mmol (23.2 mg, 1 equiv.) of **2e**.

The title compound was isolated by flash column chromatography (SiO_2, 20% EtOAc in Cyclohexane).

^{1}H-NMR (600 MHz, CDCl$_3$): δ/ppm = 7.78 (d, *J* = 7.7 Hz, 1H), 7.63 (td, *J* = 7.5, 1.3 Hz, 1H), 7.49 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.45 – 7.36 (m, 1H), 3.66 (d, *J* = 17.2 Hz, 1H), 3.50 – 3.31 (m, 2H), 3.12 (d, *J* = 17.2 Hz, 1H), 2.35 (ddd, *J* = 14.3, 8.5, 5.9 Hz, 1H), 2.12 (ddd, *J* = 14.0, 8.7, 6.5 Hz, 1H), 1.39 (s, 9H).

^{13}C-NMR (151 MHz, CDCl$_3$): δ/ppm = 202.0, 169.4, 152.7, 135.4, 135.0, 127.8, 126.3, 124.8, 82.4, 59.7, 47.8, 37.1, 33.4, 27.7 (3C).



3fa Ethyl 1-(2-azidoethyl)-2-oxocyclopentane-1-carboxylate

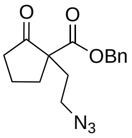
Yield (Cond. B, Scheme 2) 80% (0.08 mmol, 18.0 mg)

3fa was obtained following the general procedure as stated above employing 0.1 mmol (15.6 mg, 1.0 equiv.) of ethyl 2-oxocyclopentane-1-carboxylate.

The title compound was isolated by flash column chromatography (SiO_2, 10-20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm = 4.17 (q, *J* = 7.1 Hz, 2H), 3.50 – 3.39 (m, 1H), 3.8 – 3.26 (m, 1H), 2.59 – 2.38 (m, 2H), 2.37 – 2.14 (m, 2H), 2.12 – 1.82 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H)

^{13}C-NMR (101 MHz, CDCl$_3$): δ/ppm = 213.9, 170.5, 61.6, 58.5, 47.5, 37.5, 33.2, 32.5, 19.6, 13.9.



3ga Benzyl 1-(2-azidoethyl)-2-oxocyclopentane-1-carboxylate

Yield (Cond. A, Scheme 2) 57% (0.057 mmol, 16,4 mg)

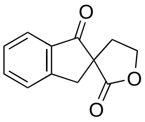
Yield (Cond. B, Scheme 2) 84% (0.084 mmol, 24.1 mg)

3ga was obtained following the general procedure as stated above employing 0.1 mmol (21.8 mg, 1 equiv.) of **2f**.

The title compound was isolated by flash column chromatography (SiO$_2$, 20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm = 7.40 – 7.29 (m, 5H), 5.17 (d, *J* = 12.5 Hz, 1H), 5.12 (d, *J* = 12.5 Hz, 1H), 3.40 (ddd, *J* = 12.4, 8.5, 5.8 Hz, 1H), 3.28 (ddd, *J* = 12.4, 8.4, 6.7 Hz, 1H), 2.65 – 2.50 (m, 1H), 2.49 – 2.36 (m, 1H), 2.36 – 2.15 (m, 2H), 2.09 – 1.80 (m, 4H).

^{13}C-NMR (101 MHz, CDCl$_3$): δ/ppm = 213.7, 170.4, 135.3, 128.6 (2C), 128.4, 128.0 (2C), 67.3, 58.6, 47.5, 37.6, 33.2, 32.6, 19.6.



4a 4,5-dihydro-2*H*-spiro[furan-3,2'-indene]-1',2(3'*H*)-dione

Yield (Cond. A, Scheme 2) 84% (0.084 mmol, 17.0 mg)

Yield (Cond. B, Scheme 2) 86% (0.086 mmol, 17.4 mg)

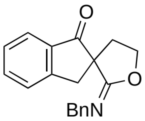
Yield (Scheme 1) 70% (0.070 mmol, 14.2 mg)

4a was obtained following the general procedure employing different substrates or nucleophiles.

The title compound was isolated by flash column chromatography (SiO$_2$, 20% EtOAc in Cyclohexane).

^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm = 7.80 (m, 1H), 7.68 (m, 1H), 7.53 (m, 1H), 7.45 (m, 1H), 4.78 (m, 1H), 4.49 (dt, *J* = 9.0, 3.0 Hz, 1H), 3.78 (d, *J* = 17.1 Hz, 1H), 3.14 (d, *J* = 17.1 Hz. 1H), 2.77 (ddd, *J* = 12.8, 7.2, 3.0 Hz, 1H), 2.48 (td, *J* = 12.8, 9.0 Hz, 1H).

^{13}C-NMR (101 MHz, CDCl$_3$): δ/ppm = 201.7, 175.6, 152.9, 135.8, 134.1, 128.2, 126.4, 125.0, 66.4, 56.6, 37.7, 33.5.



4i 2-(benzylimino)-4,5-dihydro-2*H*-spiro[furan-3,2'-inden]-1'(3'*H*)-one

Yield (Cond. B, Scheme 2) 62% (0.062 mmol, 18.1 mg)

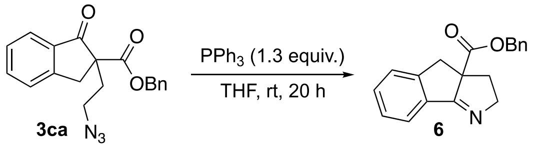
4i was obtained following the general procedure as stated above employing 0.1 mmol (26.5 mg, 1 equiv.) of **2i**.

The title compound was isolated by flash column chromatography (SiO_2, 20% EtOAc in Cyclohexane).

^{1}H-NMR (600 MHz, $CDCl_3$): δ/ppm = 7.75 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.48 – 7.42 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.19 – 7.11 (m, 1H), 4.71 – 4.61 (m, 1H), 4.51 (d, *J* = 15.3 Hz, 1H), 4.44 (d, *J* = 15.3 Hz, 1H), 4.39 (td, *J* = 8.4, 3.3 Hz, 1H), 3.84 (d, *J* = 17.1 Hz, 1H), 3.13 (d, *J* = 17.1 Hz, 1H), 2.57 (ddd, *J* = 12.5, 6.8, 3.3 Hz, 1H), 2.35 – 2.23 (m, 1H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ/ppm = 204.5, 163.4, 153.3, 140.7, 135.4, 134.4, 128.1 (2C), 127.8, 127.3 (2C), 126.4, 126.2,124.9, 67.8, 56.5, 51.1, 39.4, 35.3.

Procedure for Staudinger-Aza-Wittig



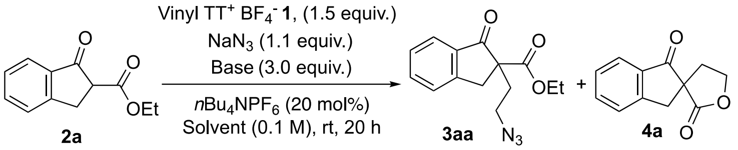
In round bottom flask under inert atmosphere, substrate **3ca** (0.055 mmol, 18.4 mg, 1 equiv.) and triphenylphosphine (0.072 mmol, 18.8 mg, 1.3 equiv.) were added in 1 mL of dry THF. The reaction was left overnight at room temperature and the solvent was evaporated under reduced pressure. The resulting crude was subjected to column chromatography (SiO_2, 30% EtOAc in Cyclohexane). The product was obtained with a yield of 98% (0.054 mmol, 15.7 mg). Spectroscopic data are in agreement with those reported in literature.[44]

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.75 (d, *J* = 7.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 (ddt, *J* = 14.6, 7.3, 1.1 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.15 – 7.09 (m, 2H), 5.09 (d, *J* = 12.7 Hz, 1H), 5.01 (d, *J* = 12.7 Hz, 1H), 4.46 – 4.41 (m, 2H), 3.62 (d, *J* = 15.6 Hz, 1H), 2.78 (d, *J* = 15.6 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.09 – 2.00 (m, 1H).

^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ/ppm = 181.8, 171.8, 151.5, 135.6, 132.5, 131.6, 128.5 (2C), 128.0, 127.6, 127.4 (2C), 126.0, 123.4, 67.4, 67.2, 66.8, 38.7, 37.0.

Optimization Studies and other tests

***Table S1**. Condition screening for functionalization of **1** with **2a** and NaN_3 as nucleophile .*

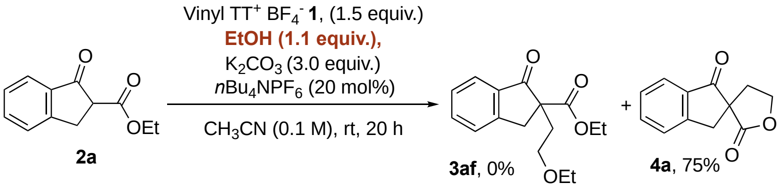


2a **3aa** **4a**

Entry[a]	Solvent	Base	Yield% **3aa**[b]	Yield% **4a**[b]
1	DMF	K_2CO_3	83 (72)[c]	3
2	CH_3CN	K_2CO_3	92 (85)[c]	0
3	DMSO	K_2CO_3	90 (78)[c]	0
4	DCM	K_2CO_3	34	57
5	THF	K_2CO_3	45	0
6	Toluene	K_2CO_3	29	61
7[d]	CH_3CN	KOH	41	10
8	CH_3CN	Cs_2CO_3	80 (61)[c]	0
9	DMF	Cs_2CO_3	87 (66)[c]	0
10[e]	CH_3CN	K_2CO_3	66 (58)[c]	0
11[e]	DMSO	K_2CO_3	84 (72)[c]	0
12[e]	DMF	K_2CO_3	40	0
13[f]	CH_3CN	K_2CO_3	-	82 (73)[c]
14[f]	DCM	K_2CO_3	-	93 (75)[c]

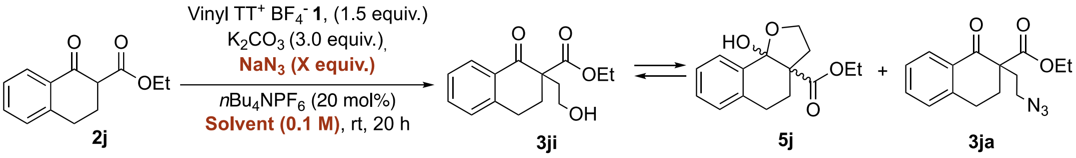
[a] Reaction was performed on 0.05 mmol scale. [b] ^{1}H-NMR yield determined with trichlorethylene as internal standard. [c] Isolated yield after purification by flash column chromatography. [d] Decomposition of **2a** was observed. [e] Reaction performed in absence of $^nBu_4NPF_6$. [f] Reaction performed in absence of NaN_3.

*Reaction of vinylthianthrenium **1** with **2a** in the presence of 1.1. equiv. of ethanol.*



2a **3af**, 0% **4a**, 75%

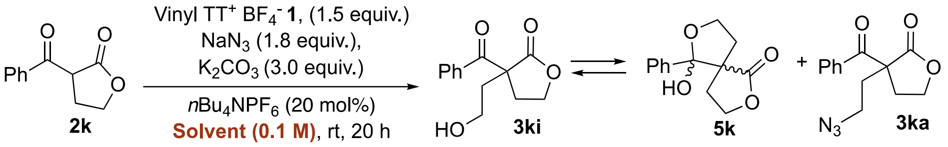
***Table S2**. Condition screening for functionalization of **1** with **2j**.*



Entry[a]	Solvent	NaN_3 equiv.	**3ji:5j:3ja**[b]	Yield% **5j**[c]	Yield% **5j+3ja**[d]	**5j+3ja**[e]
1	CH_3CN	1.8	0:100:0	74	-	-
2	CH_3CN	0	50:50:0	62	-	-
3	DMF	1.8	25:25:50	-	64	26:74
4	DMSO	1.8	22:18:60	-	78	32:68

[a] Reaction was performed on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis on the reaction crude. [c] Isolated yield after purification by flash column chromatography. [d] Isolated yield after purification by flash column chromatography as inseparable mixture of products; ratio determined by ^{1}H-NMR analysis. [e] Determined by ^{1}H-NMR analysis

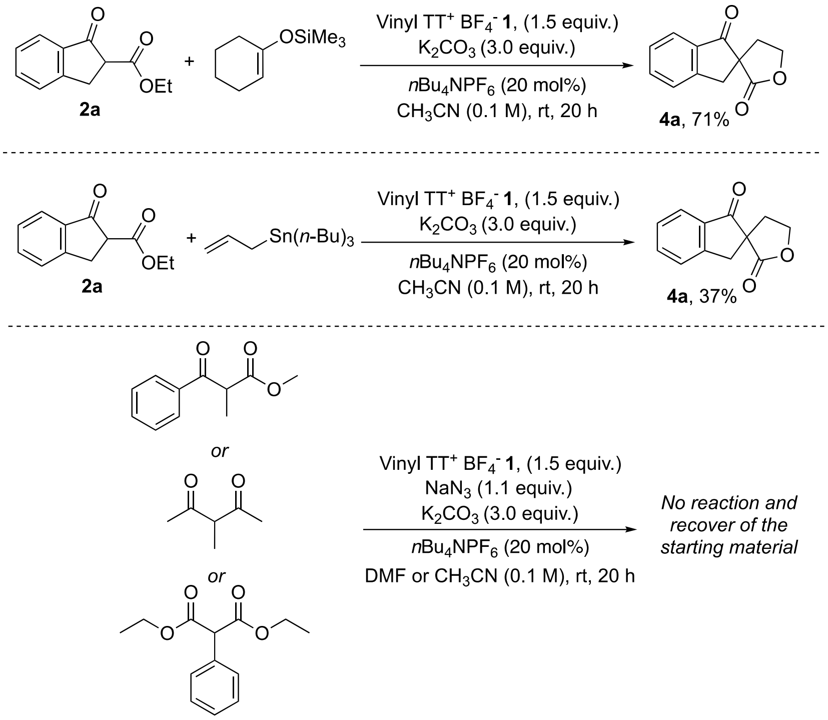
***Table S3**. Condition screening for functionalization of **1** with **2k**.*



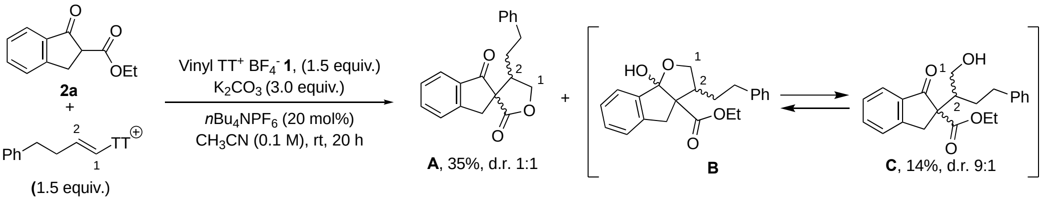
Entry[a]	Solvent	NaN_3 equiv.	**3ki:5k:3ka**[b]	Yield% **5k**[c]	Yield% **3ki+3ka**[d]	**3ki+3ka**[e]
1	CH_3CN	1.8	15:55:30	20	51	46:54
2	CH_3CN	0	100:0:0	84	-	-
3	DMSO	1.8	14:47:39	18	62	42:58

[a] Reaction was performed on 0.1 mmol scale. [b] Determined by ^{1}H-NMR analysis on the reaction crude. [c] Isolated yield after purification by flash column chromatography. [d] Isolated yield after purification by flash column chromatography as inseparable mixture of products; ratio determined by ^{1}H-NMR analysis. [e] Determined by ^{1}H-NMR analysis

Unsuccessful substrates tested

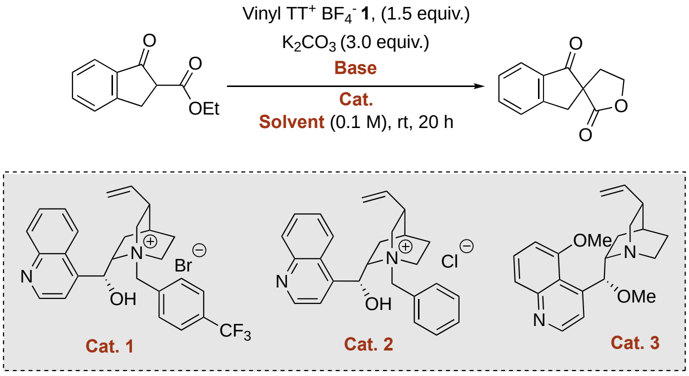


Reaction with substituted alkenyl thianthrenium salts



The substrate **2a** was subjected to a reaction in the presence of (*E*)-5-(4-phenylbut-1-en-1-yl)-5H-thianthren-5-ium under standard conditions in CH_3CN. A mixture of products was obtained as a result of intramolecular attack by the carbonyl groups present in **2a.** The enolate of **2a** reacts with the in position 2 of the thianthrenium salt, resulting in the formation of a stabilized sulfur ylide that underwent protonation, yielding the monosulfonium salt intermediate. Intramolecular nucleophilic attack by the C=O ester function lead to the formation of the spiro-lactone **A**. In cases where the C=O keto group attacked the monosulfonium salt, emiacetal **B** was formed, which existed in equilibrium with keto form **C**.

***Table S4**. Tests for enantioselective formation of the spirolactone **4a**.*



Entry[a]	Solvent	**Cat**. equiv.	**Base** equiv.	Yield% **4a**[b]	ee% **4a**[c]
1	CH_3CN	**Cat. 1** (0.2)	K_2CO_3	95	0
2	C_6H_5Cl	**Cat. 2** (0.2)	K_2CO_3	98	0
3	C_6H_5Cl	**Cat. 1** (0.2)	Cs_2CO_3	93	0
4	C_6H_5Cl	**Cat. 1** (0.2)	DMAP	91	0
5	C_6H_5Cl	**Cat. 3** (1.5)	-	94	0

[a] Reaction was performed on 0.05 mmol scale. [b] ^{1}H-NMR yield determined with trichlorethylene as internal standard. [c] Determined by HPLC analysis on chiral column: Lux-Cellulose-3, Hex:*i*PrOH 90:10, 1 mL/min, 40°C, t_R = 19.2 – 23.7 min..

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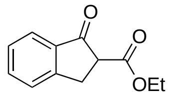
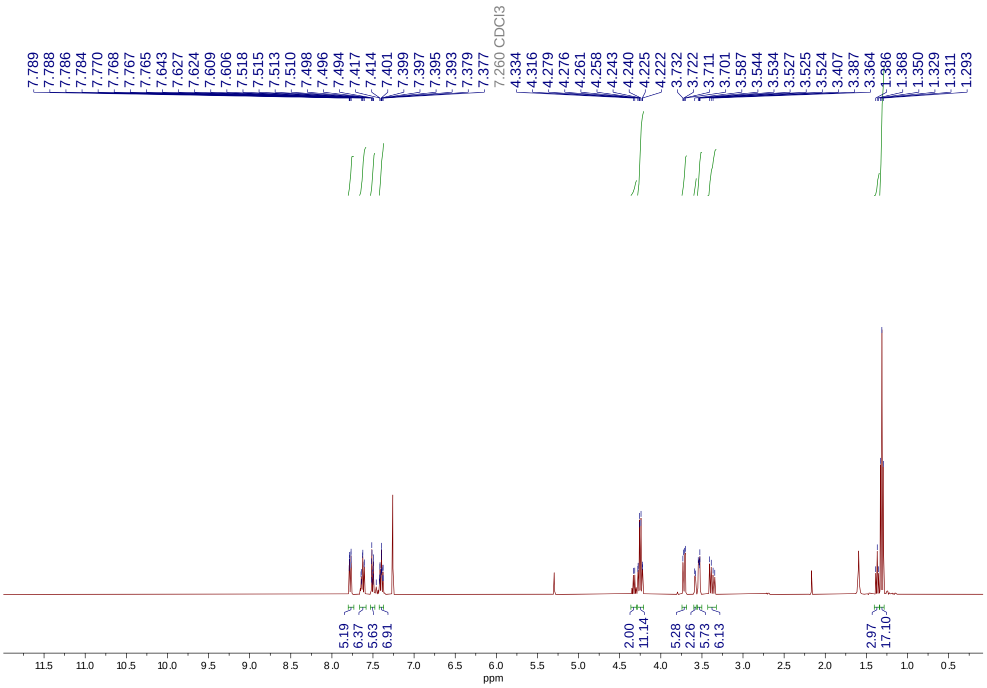
Copies of NMR spectra

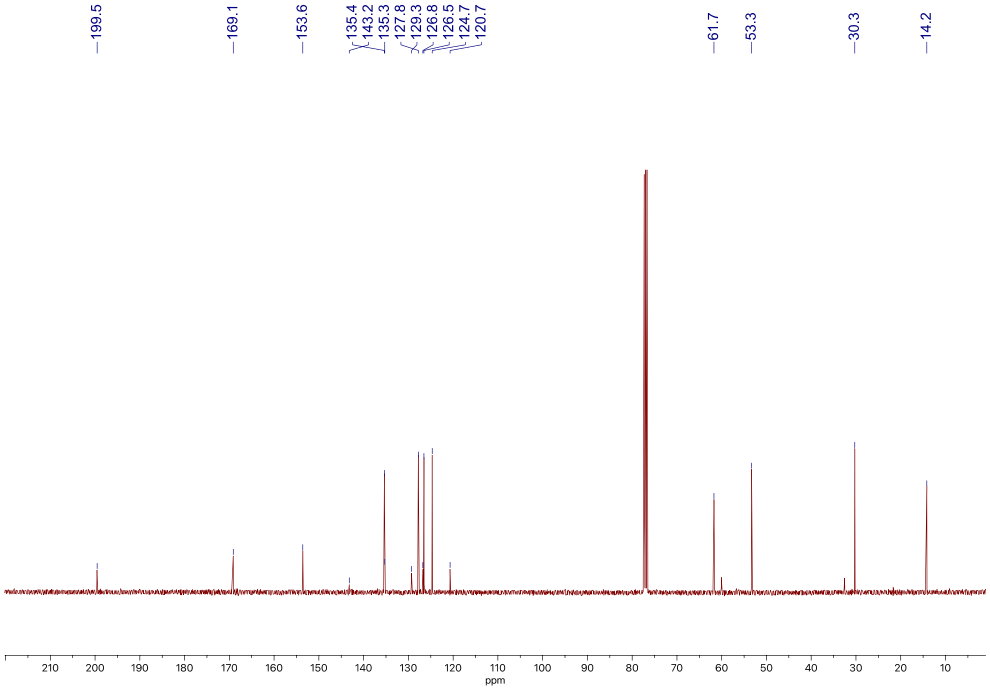


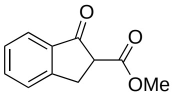
2a

^{1}**H NMR** (400 MHz, CDCl$_3$)



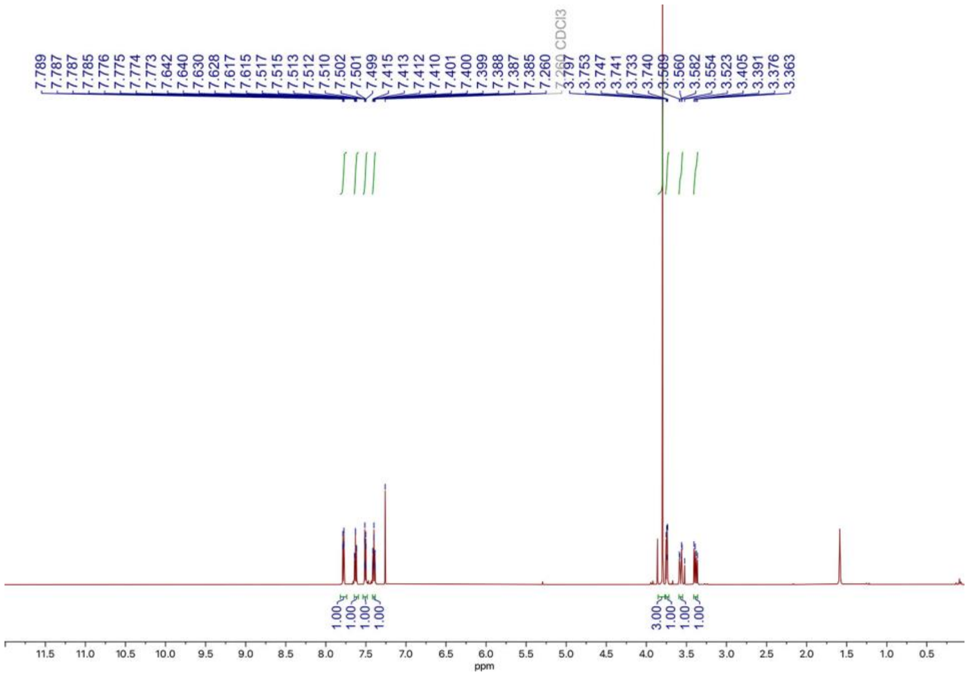
^{13}**C{^{1}H} NMR** (101 MHz, CDCl$_3$)



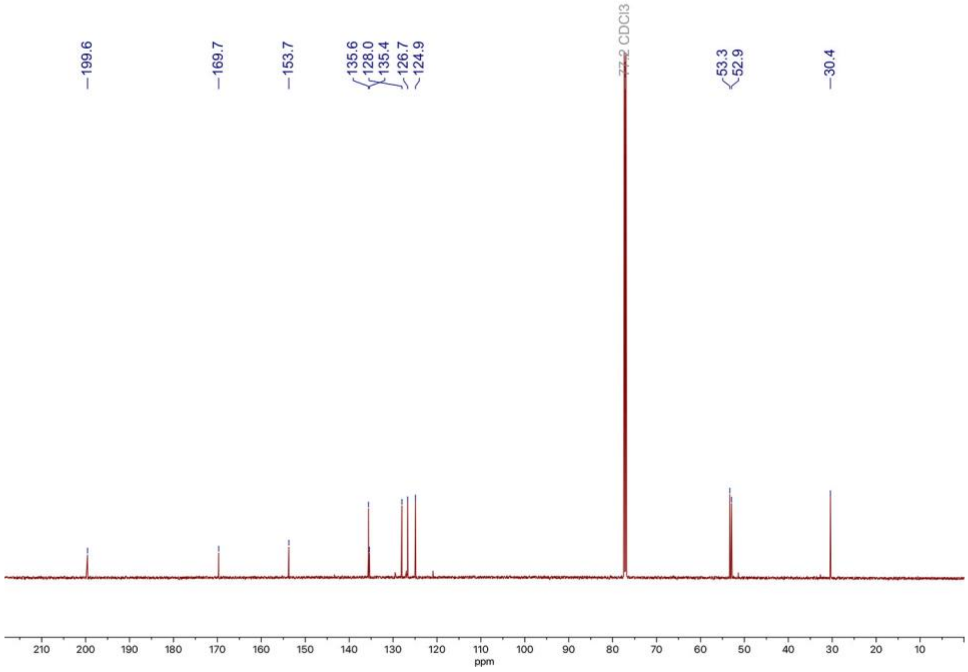


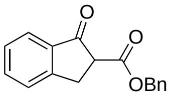
2b

^{1}H NMR (400 MHz, CDCl$_3$)



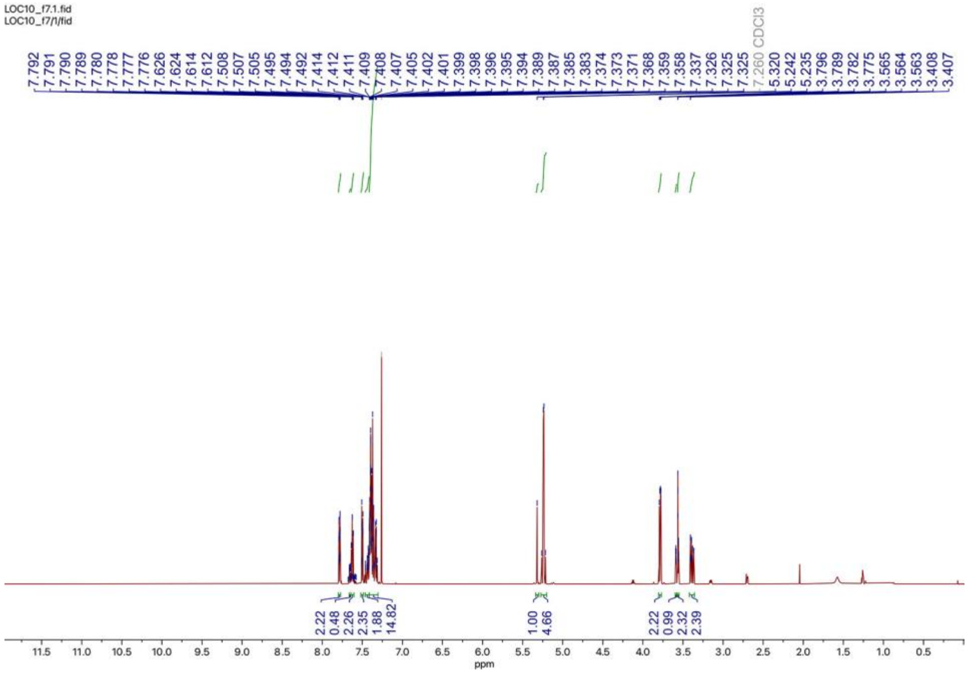
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



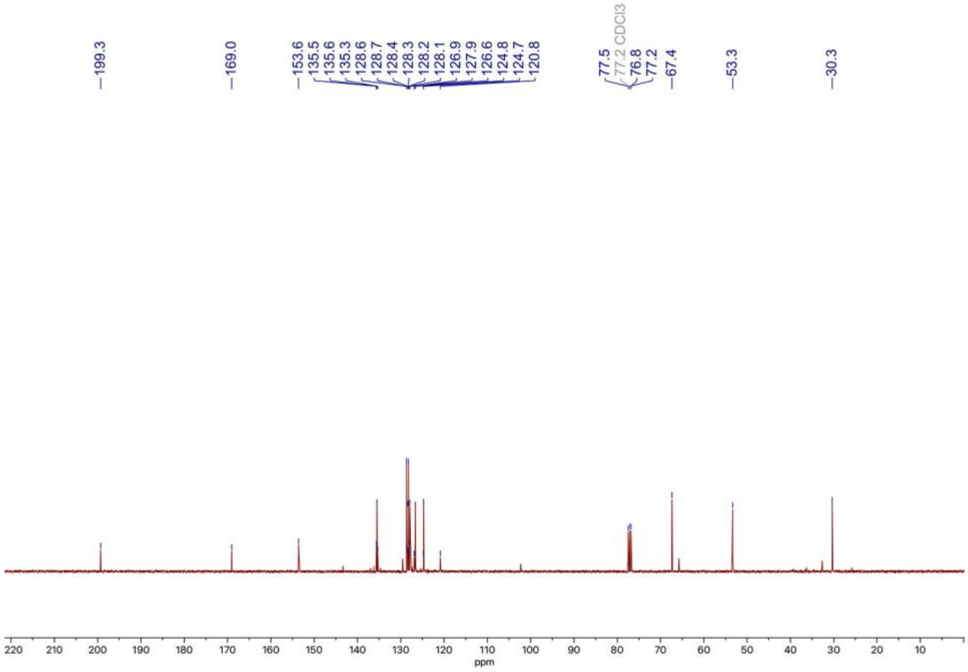


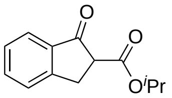
2c

^{1}H NMR (400 MHz, CDCl$_3$)



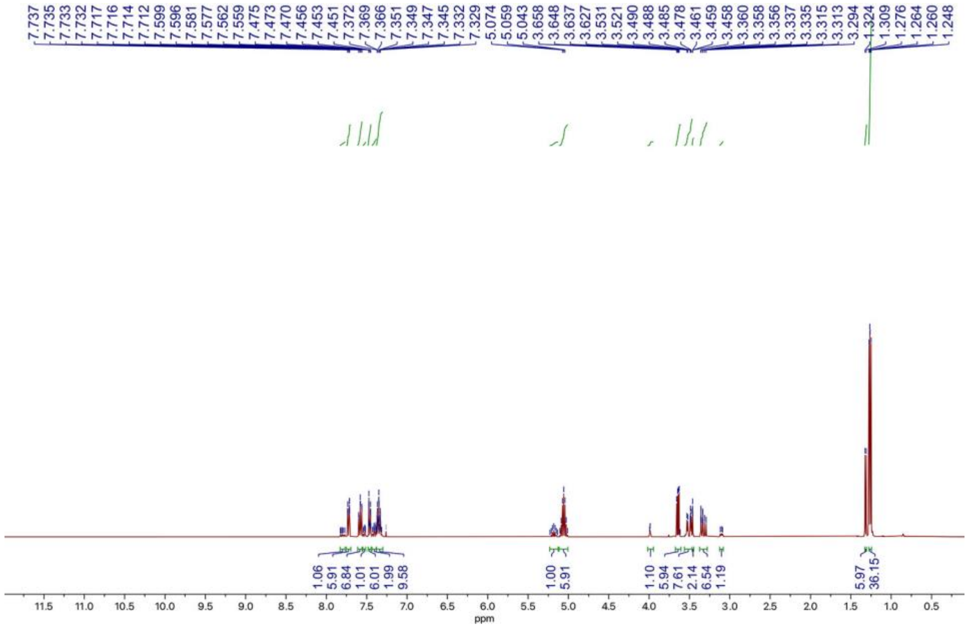
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)





2d

^{1}H NMR (400 MHz, CDCl$_3$)



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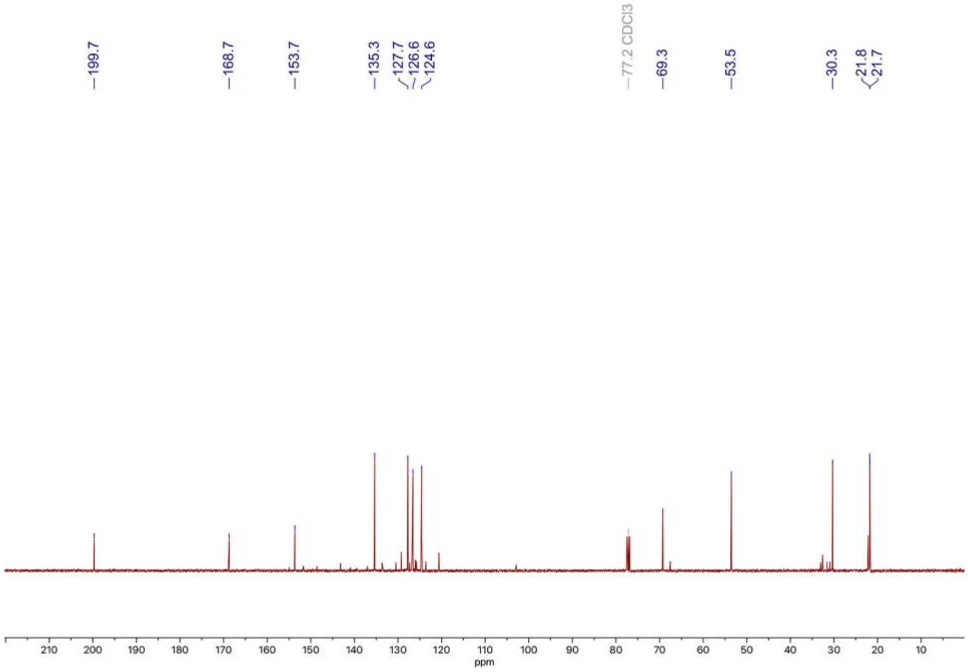
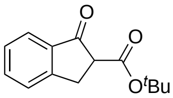
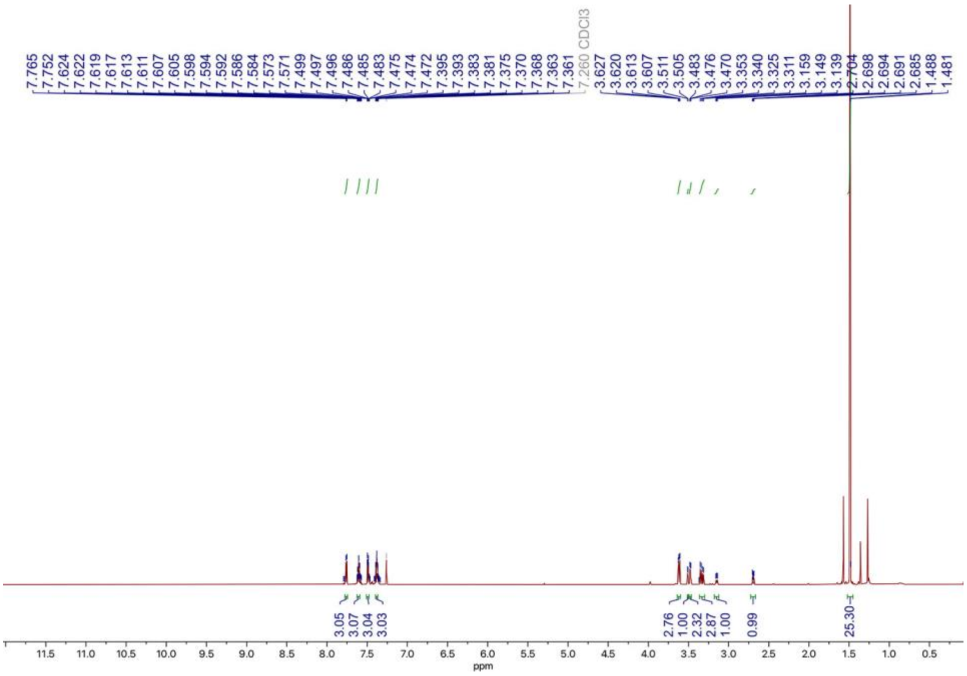




2e

^{1}H NMR (400 MHz, CDCl$_3$)



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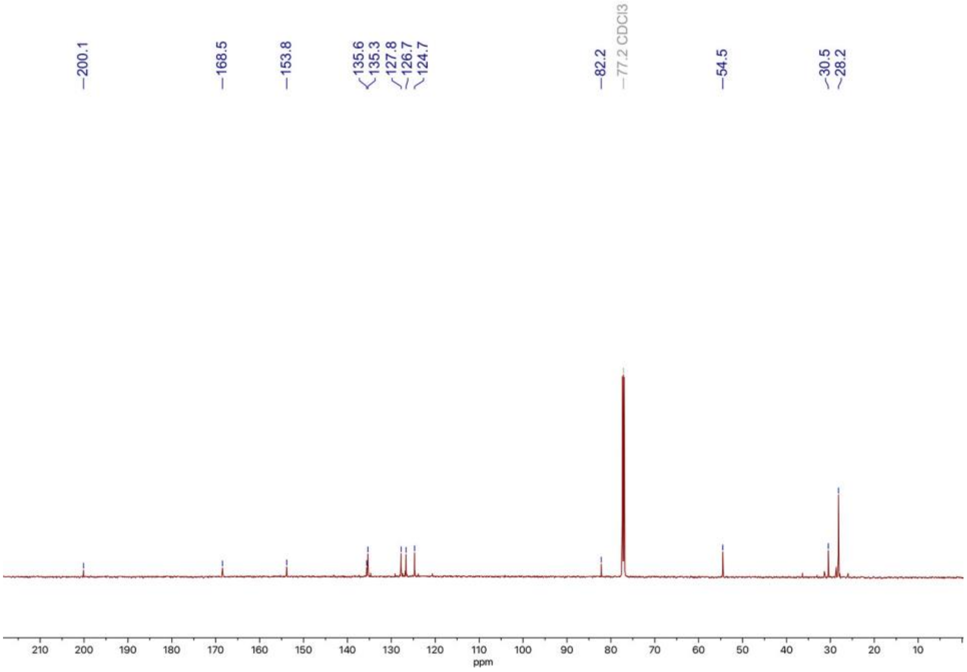
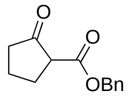
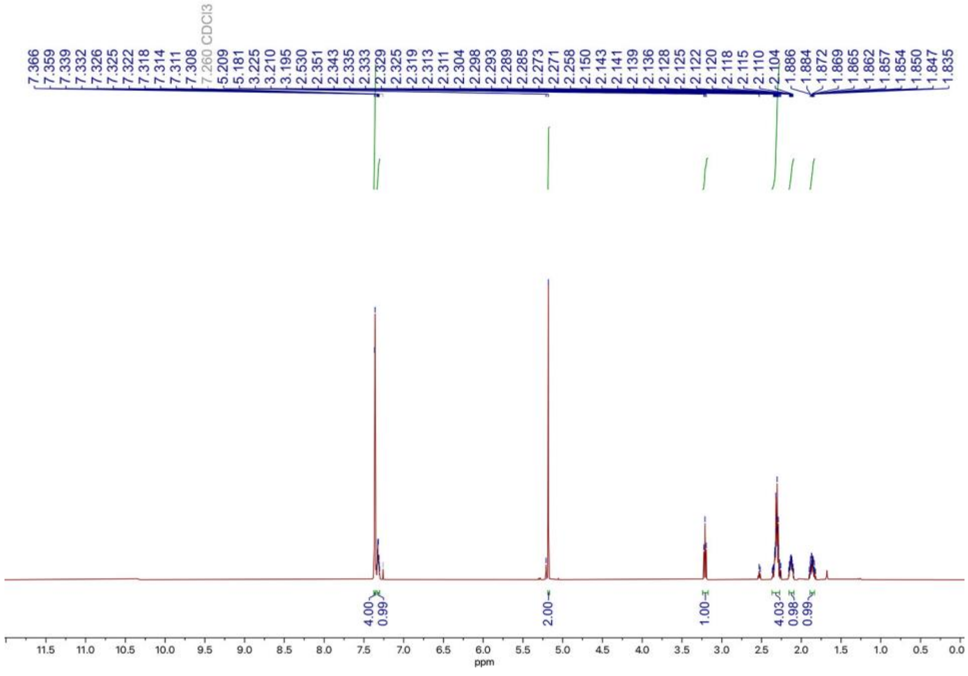




2f

^{1}H NMR (400 MHz, CDCl$_3$)



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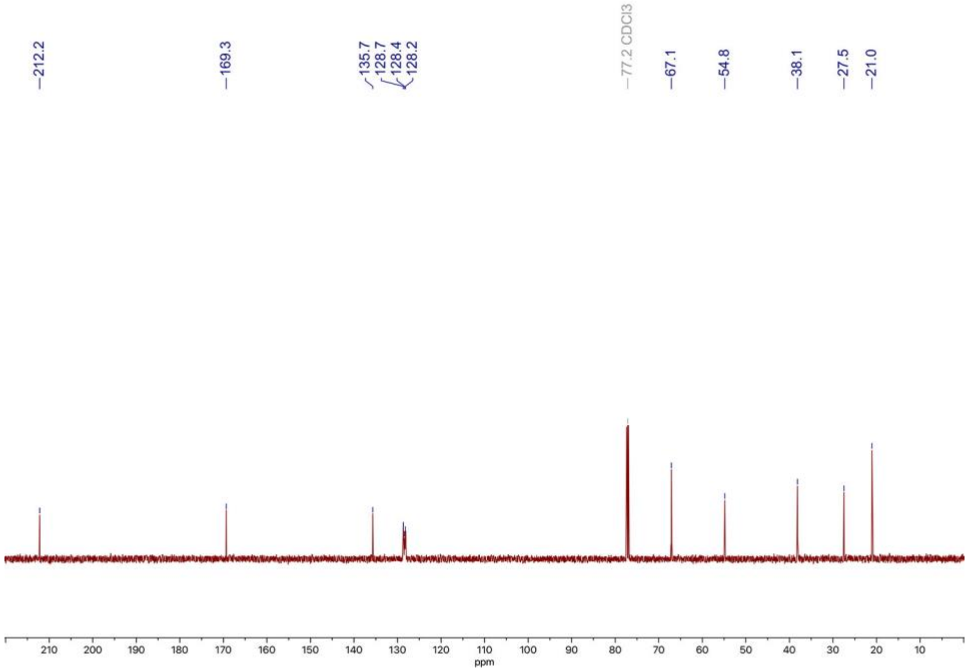
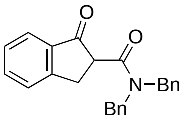
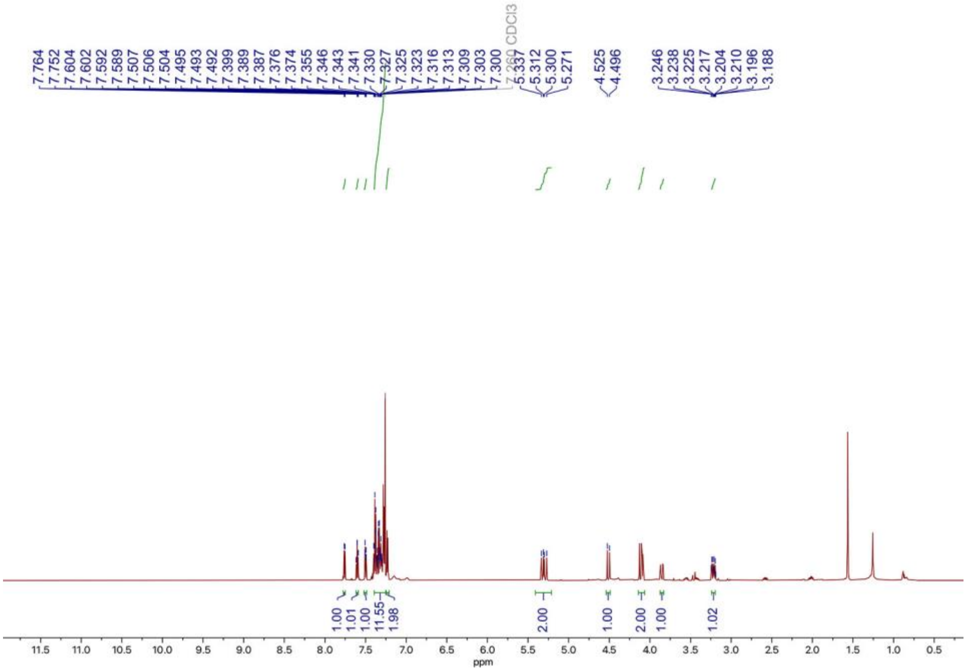


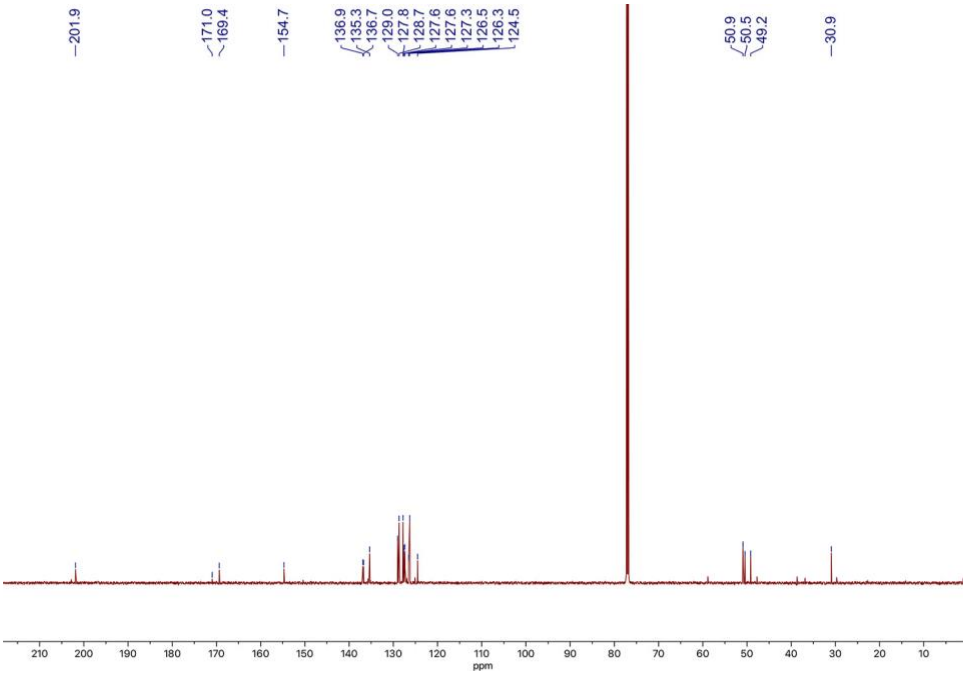


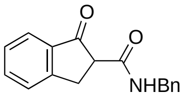
2g

^{1}H NMR (400 MHz, $CDCl_3$)



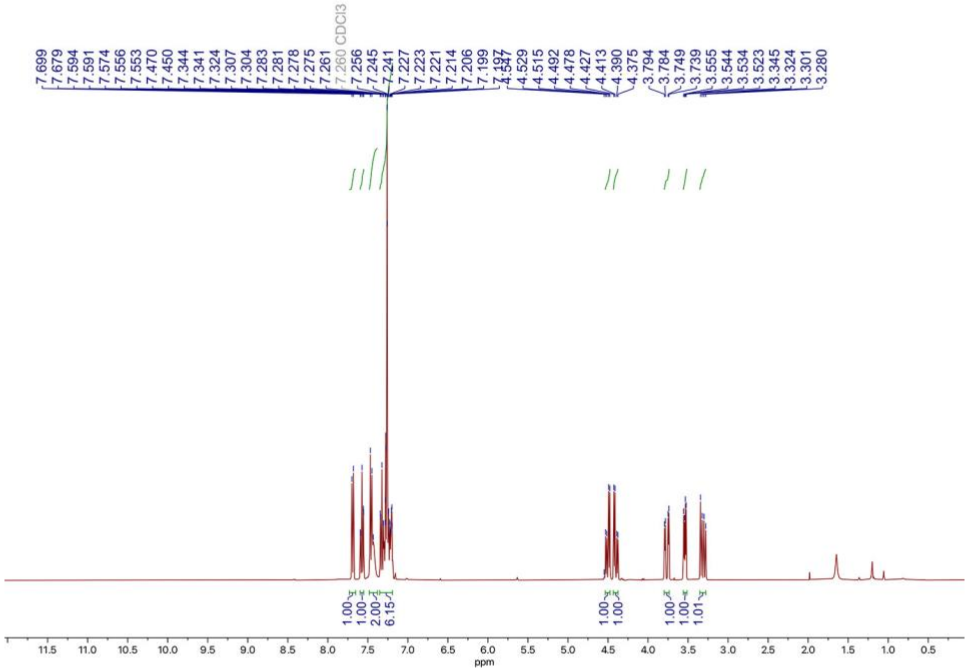
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



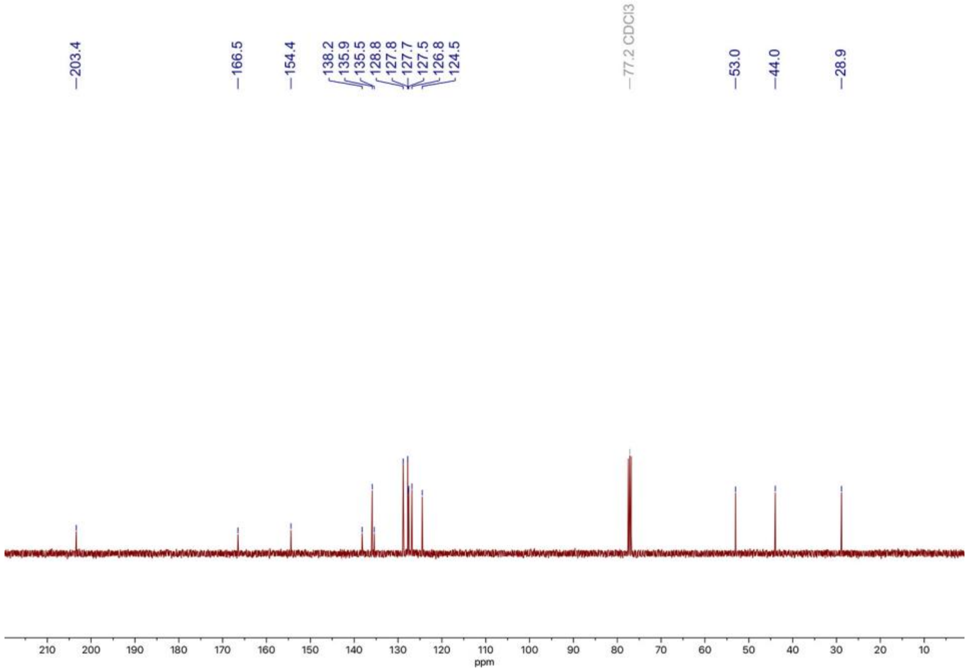


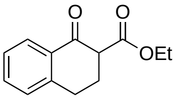
2h

^{1}H NMR (400 MHz, CDCl$_3$)



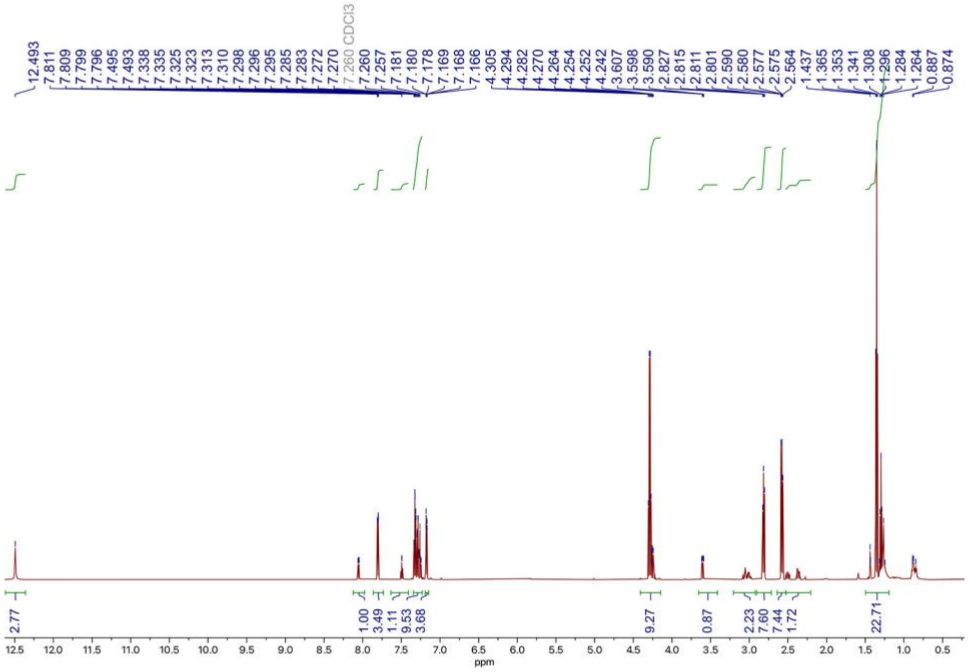
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



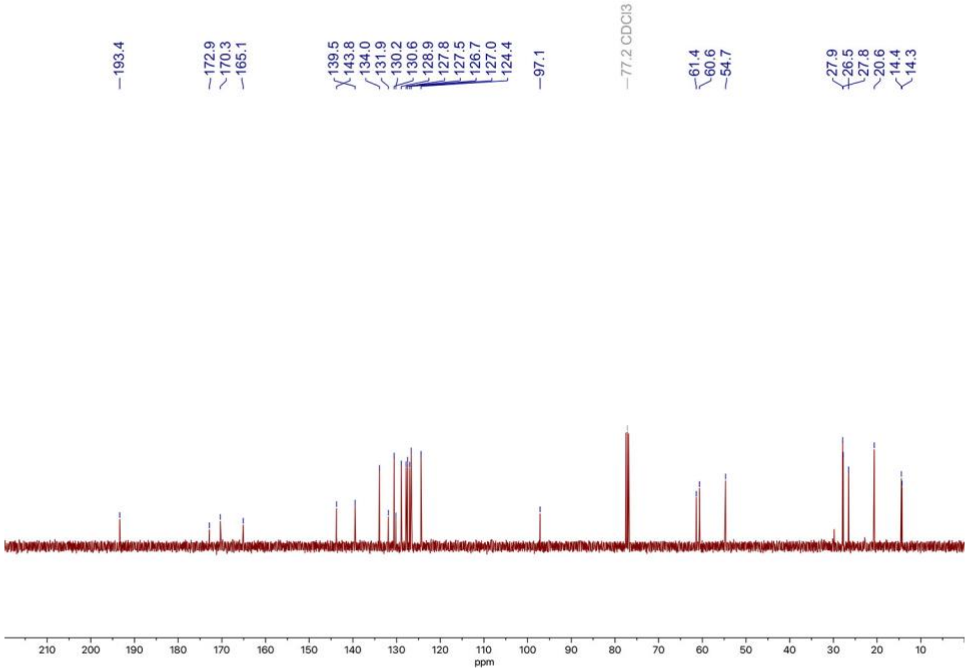


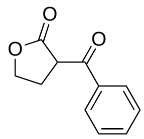
2i

^{1}H NMR (400 MHz, $CDCl_3$)



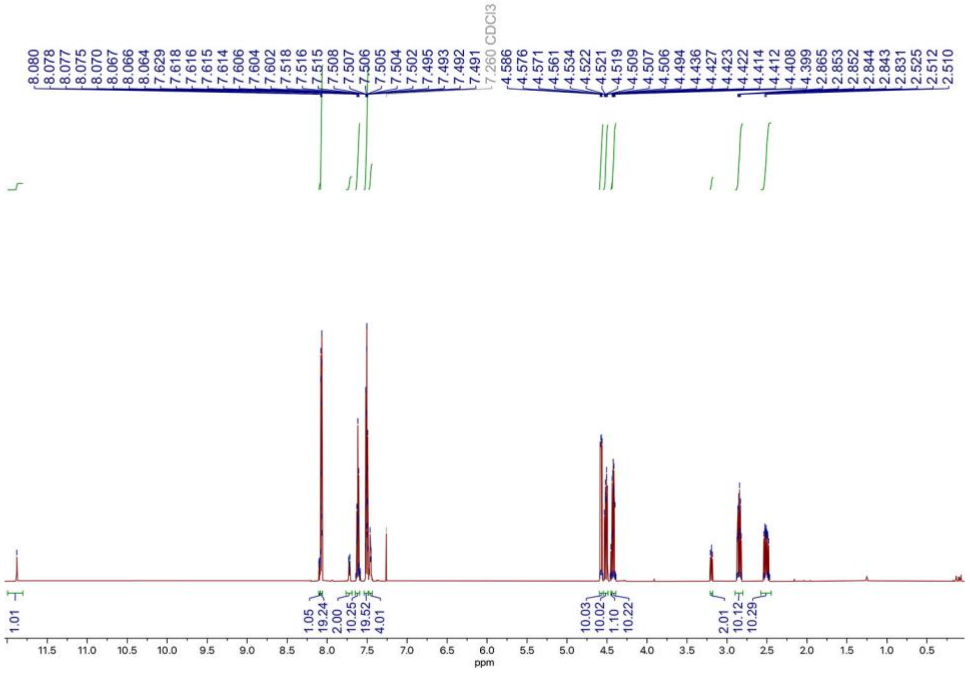
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



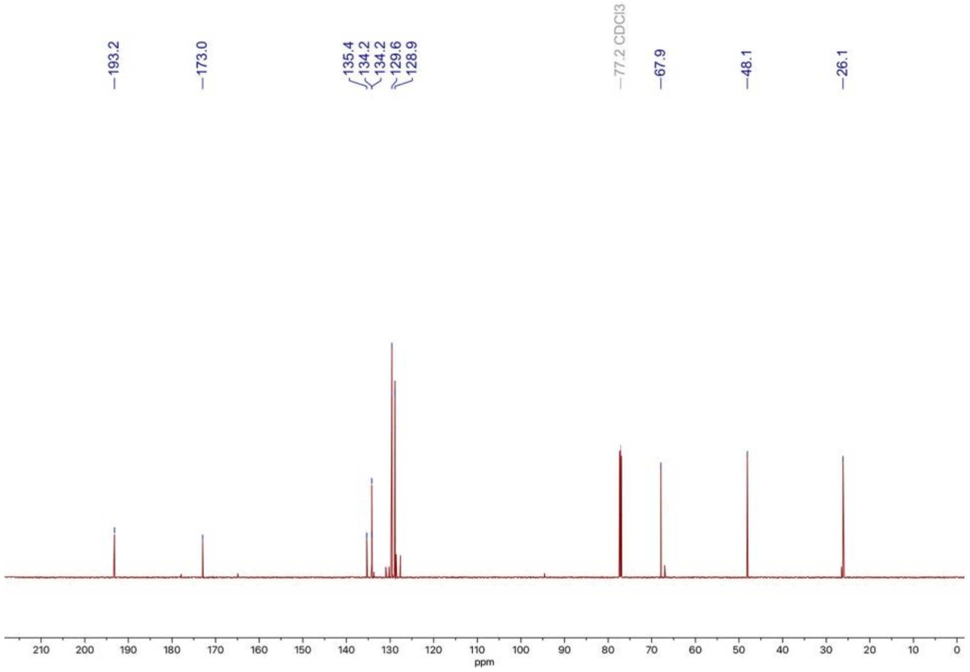


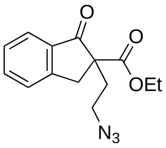
2j

^{1}H NMR (400 MHz, $CDCl_3$)



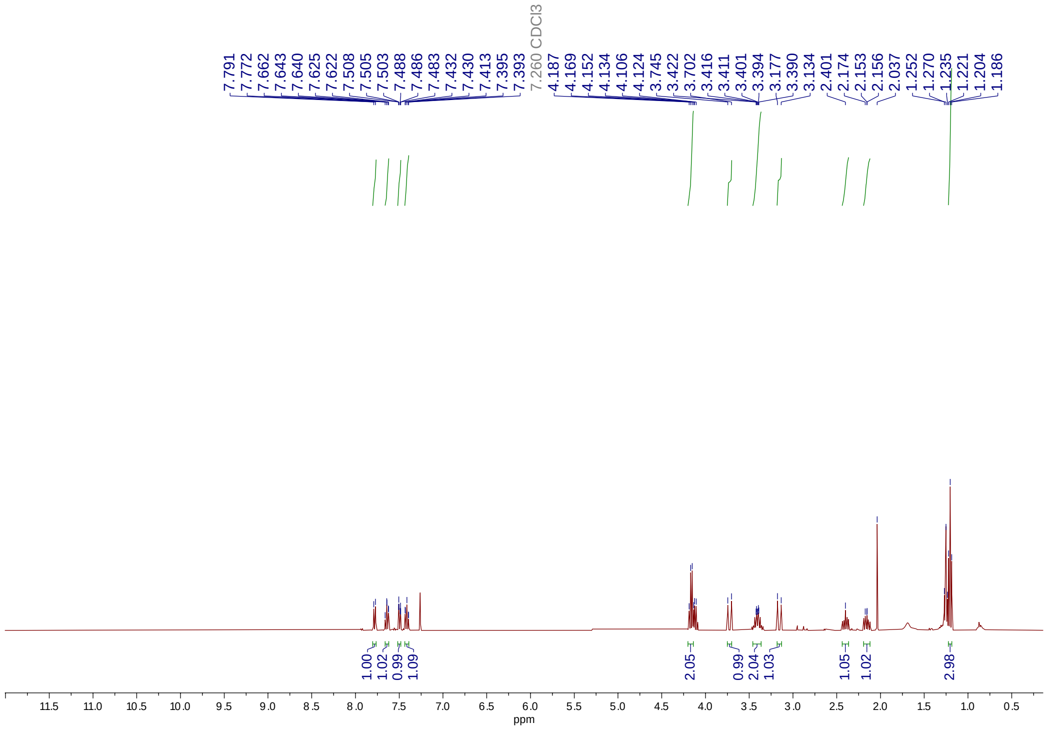
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



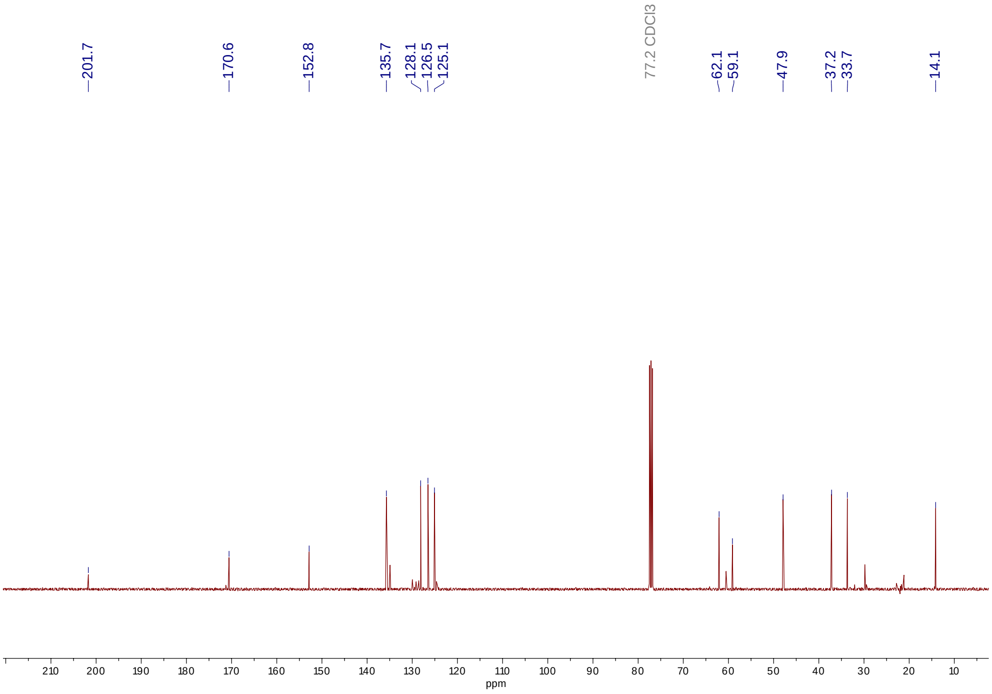


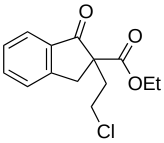
3aa

^{1}H NMR (400 MHz, CDCl$_3$)



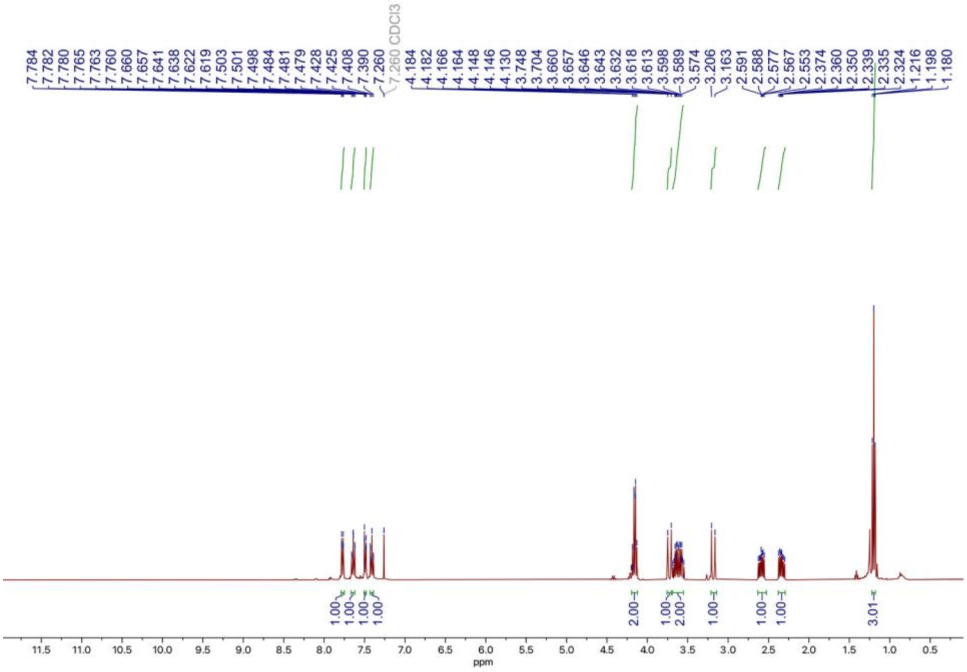
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



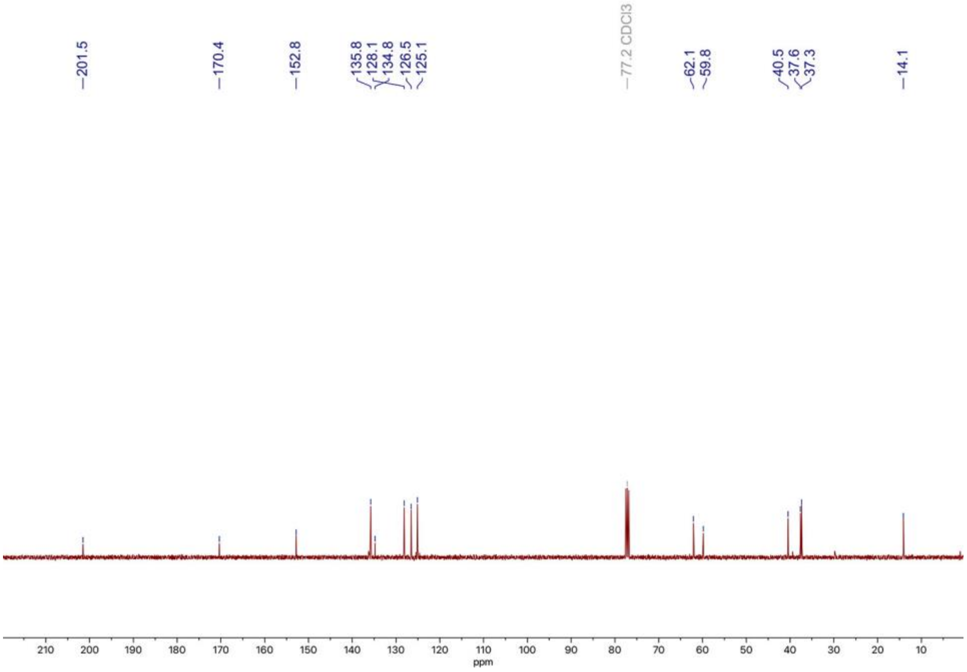


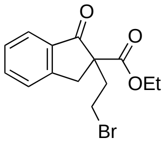
3ab

^{1}H NMR (400 MHz, CDCl$_3$)



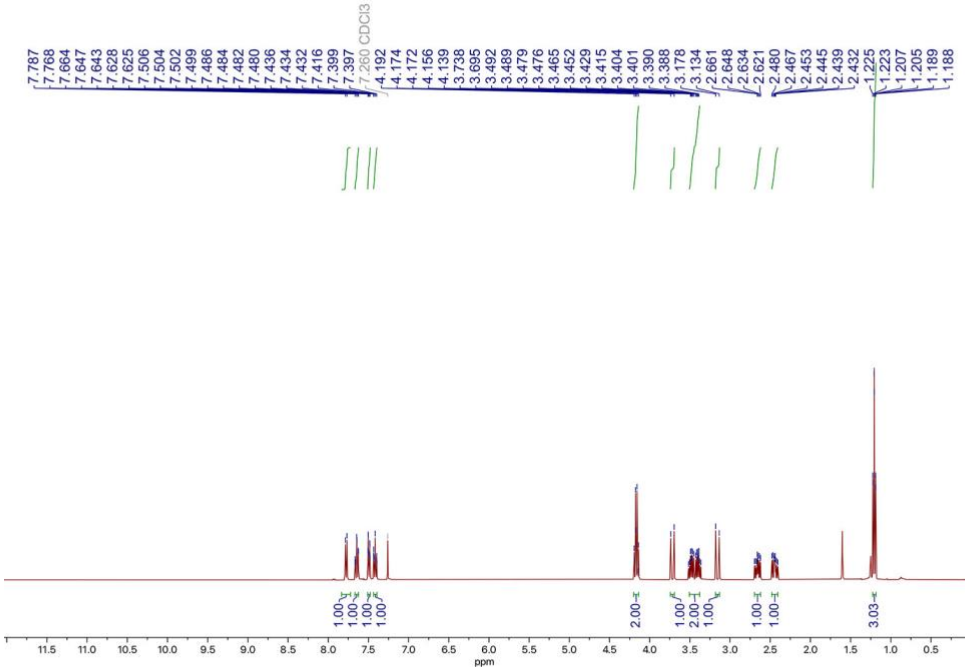
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



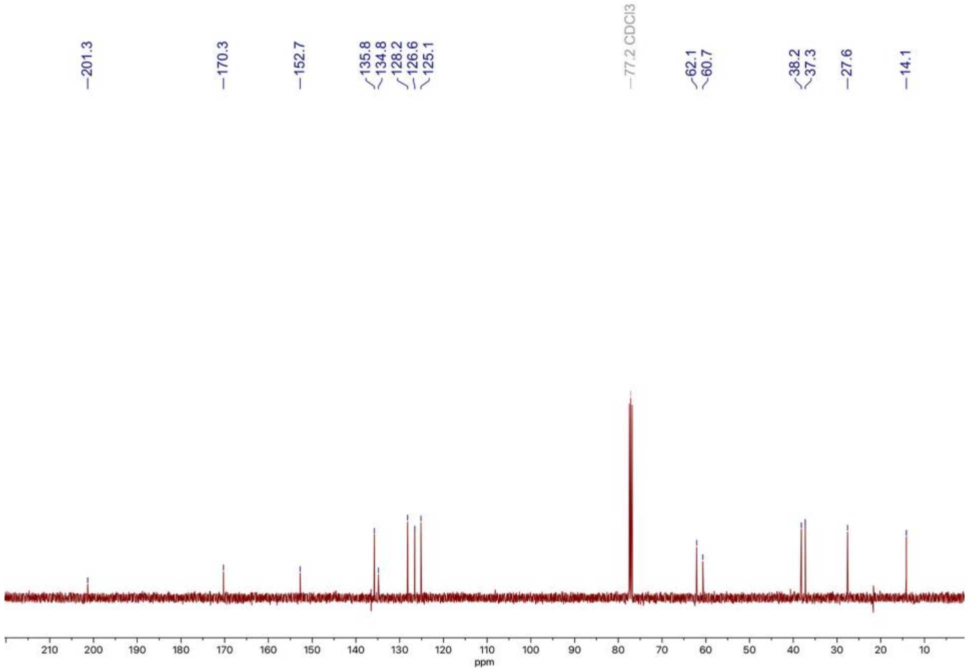


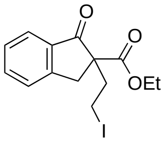
3ac

^{1}H NMR (400 MHz, CDCl$_3$)



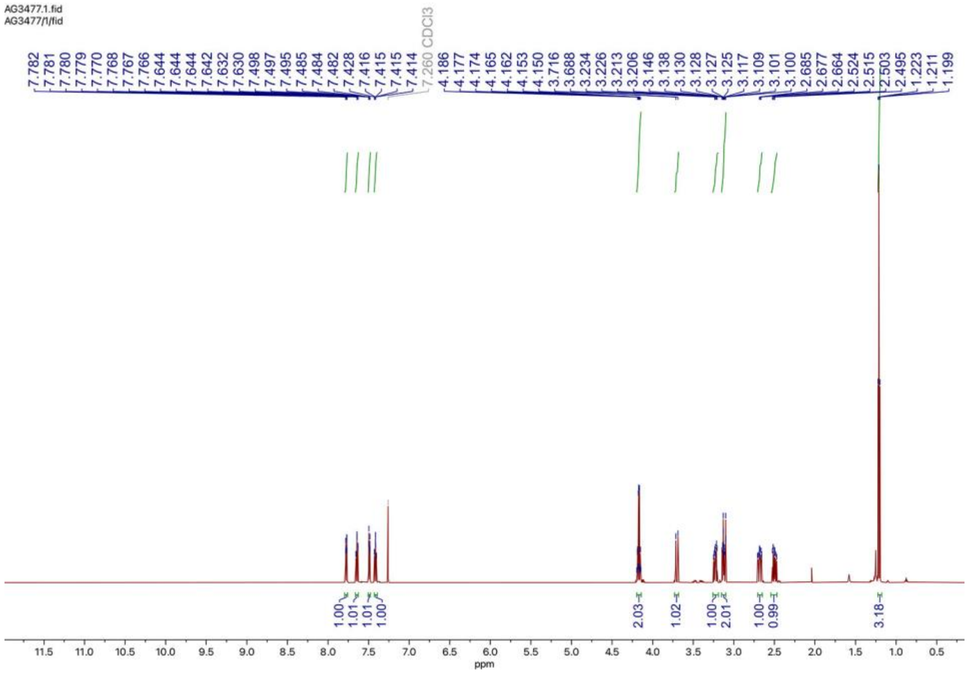
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



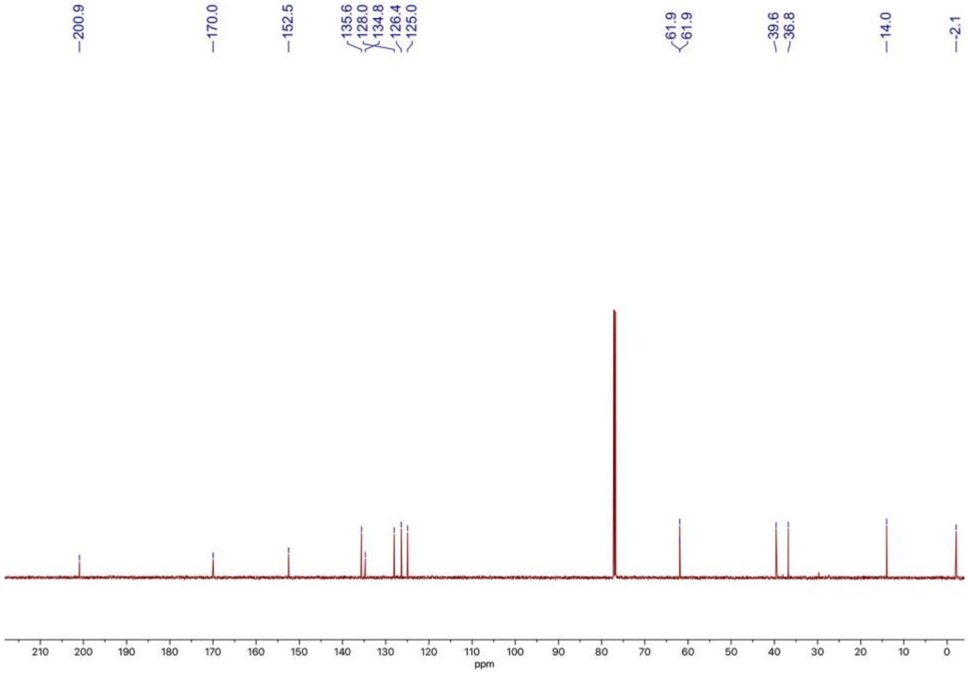


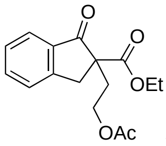
3ad

^{1}H NMR (400 MHz, $CDCl_3$)



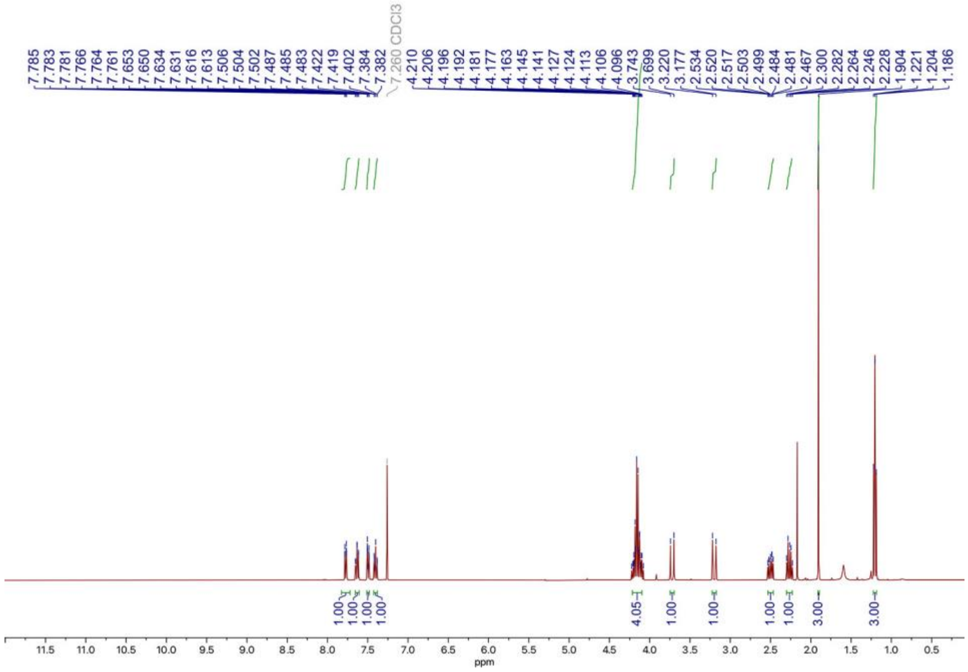
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



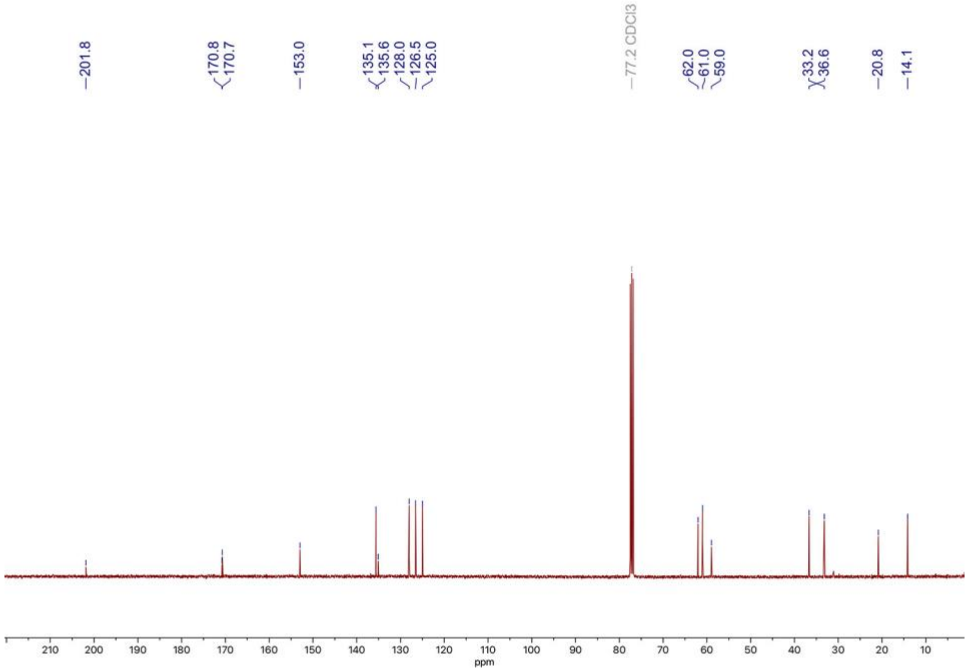


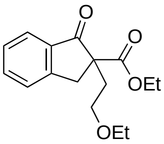
3ae

^{1}H NMR (400 MHz, $CDCl_3$)



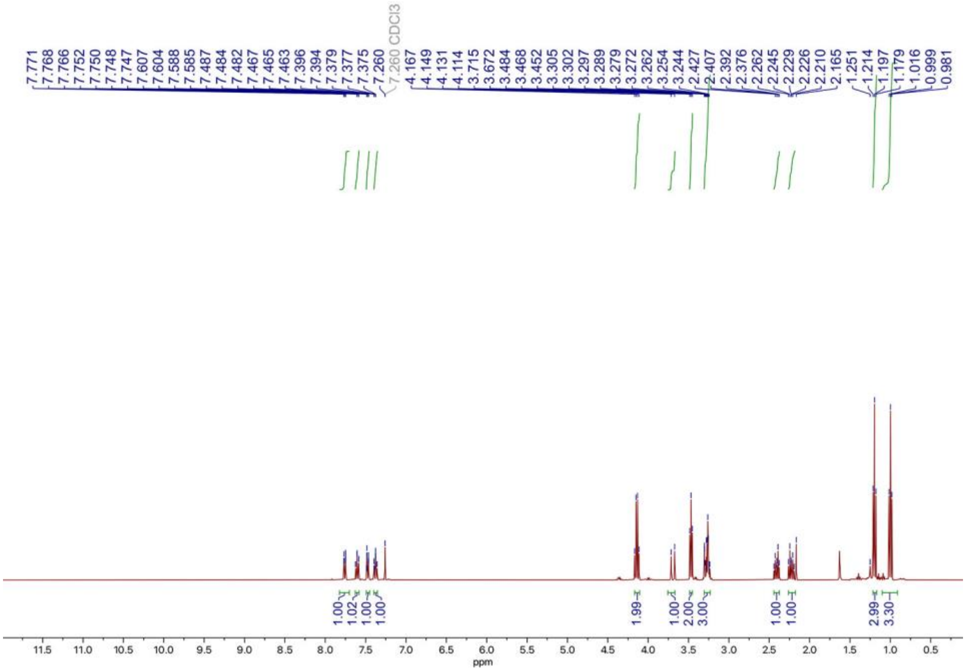
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



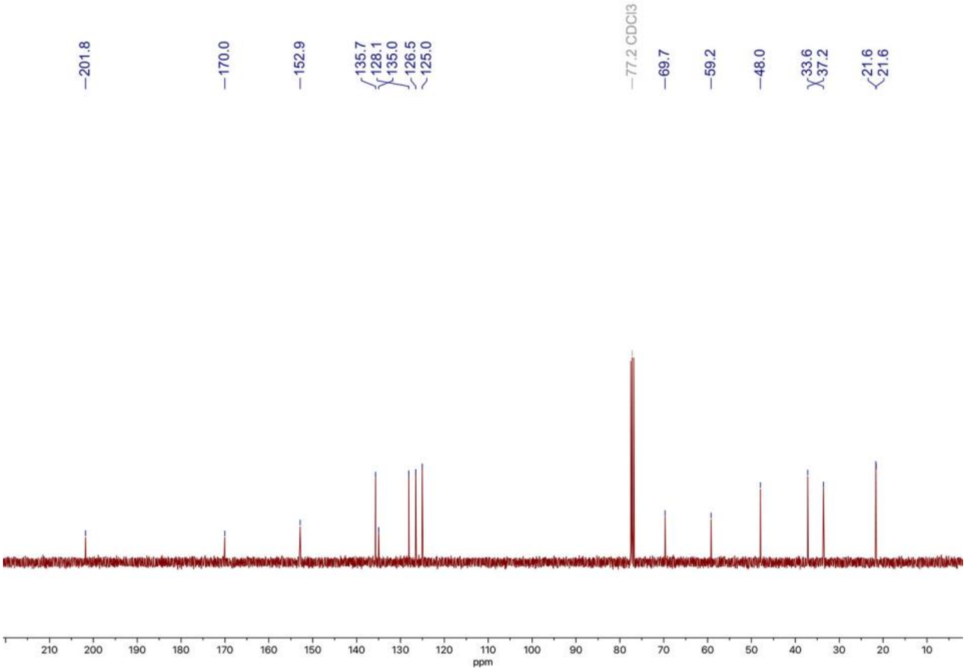


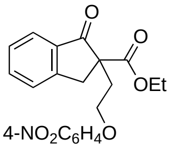
3af

^{1}H NMR (400 MHz, $CDCl_3$)



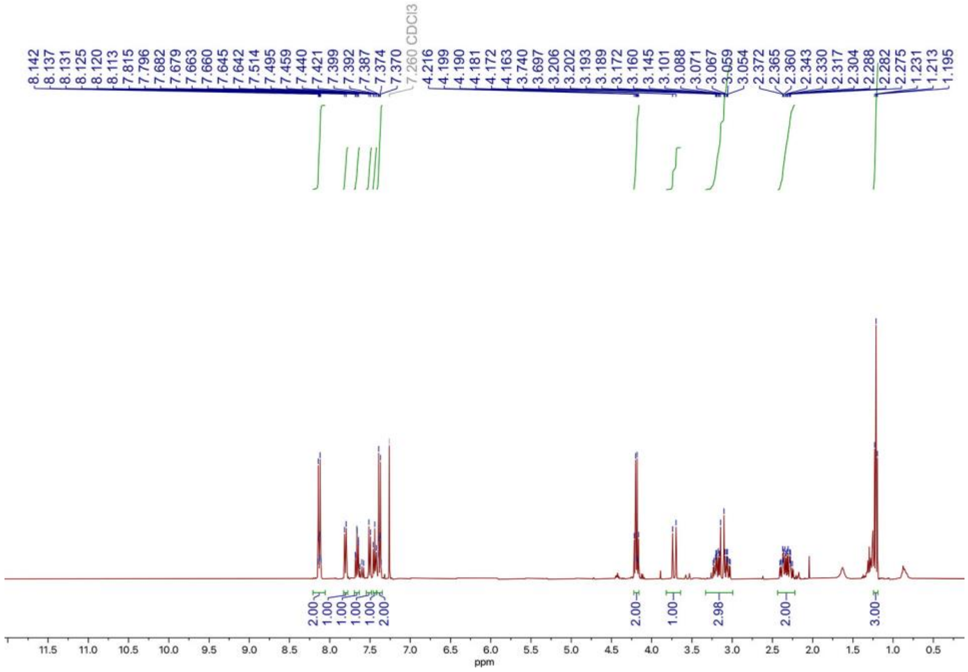
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



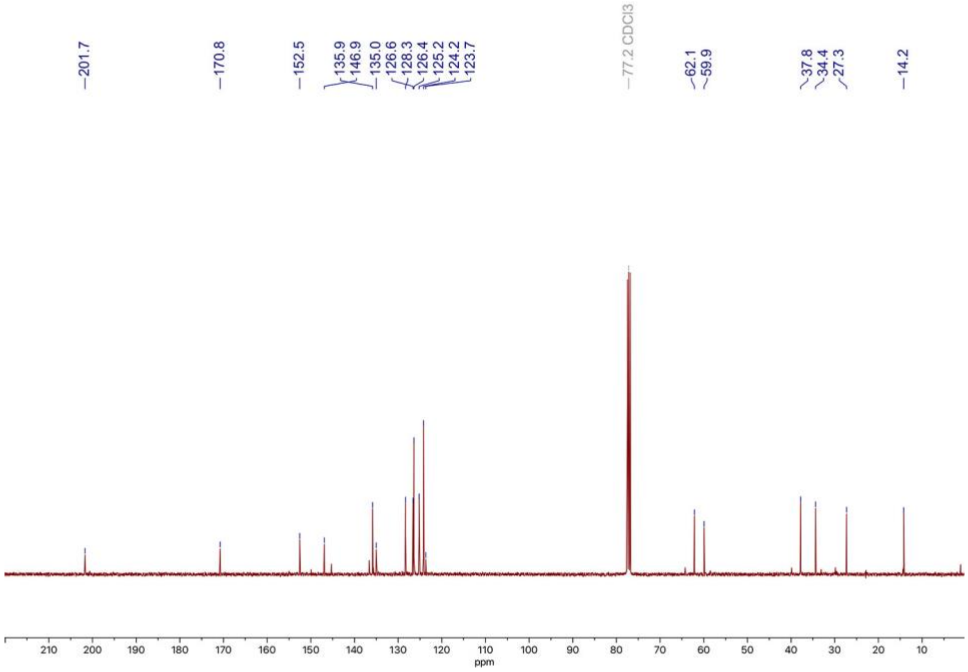


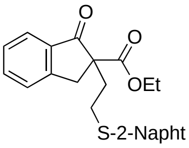
3ag

^{1}H NMR (400 MHz, $CDCl_3$)



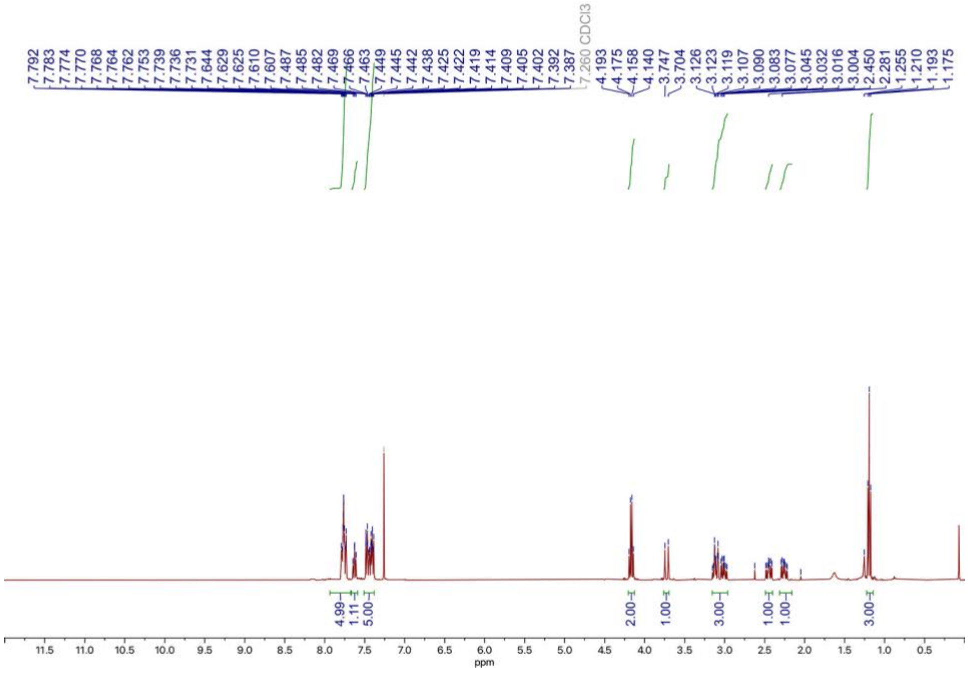
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



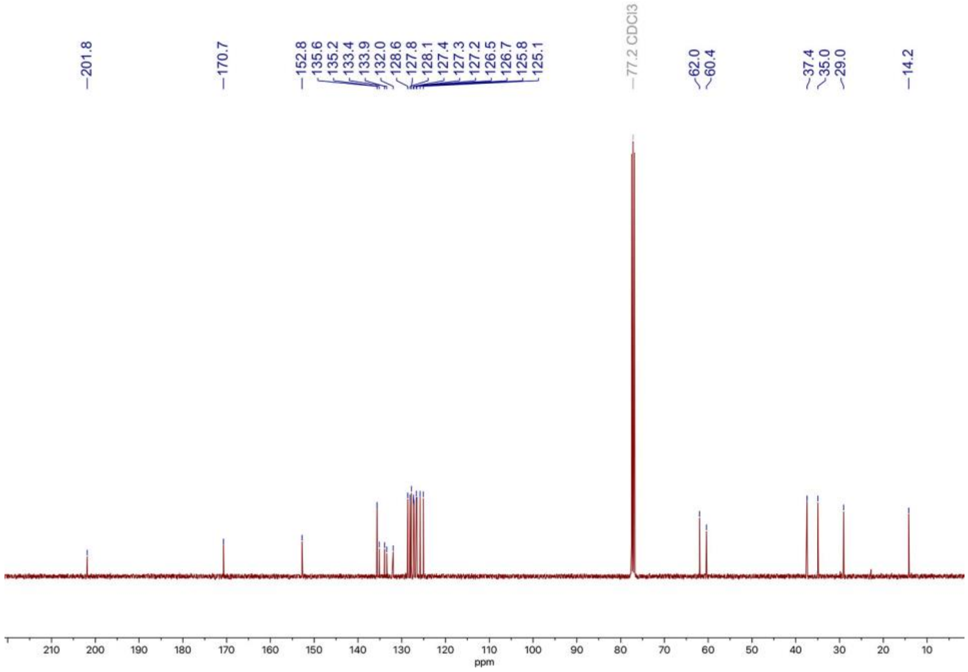


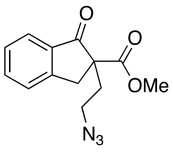
3ah

^{1}H NMR (400 MHz, CDCl$_3$)



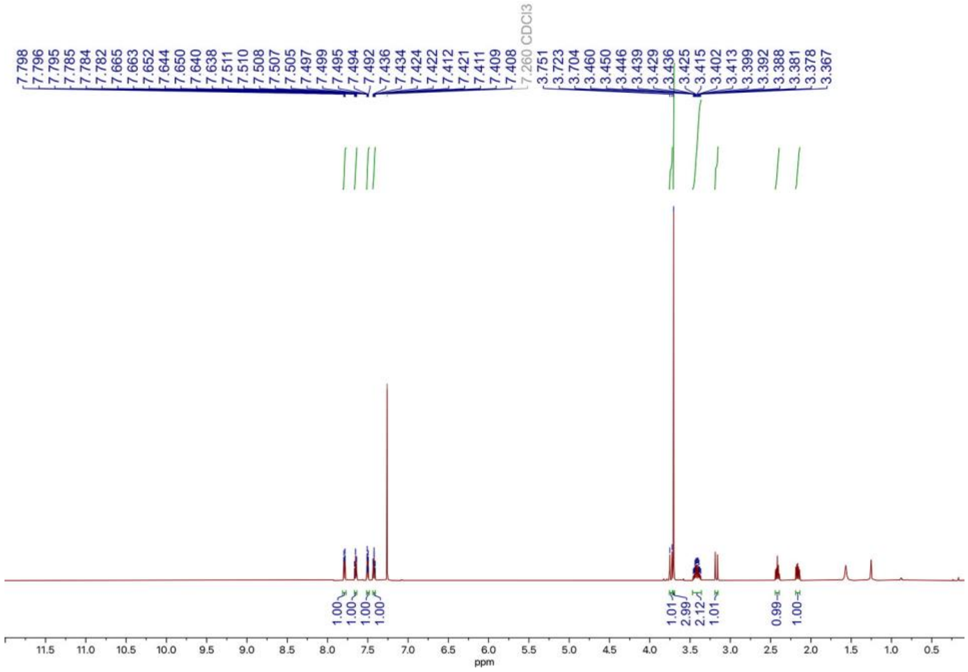
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



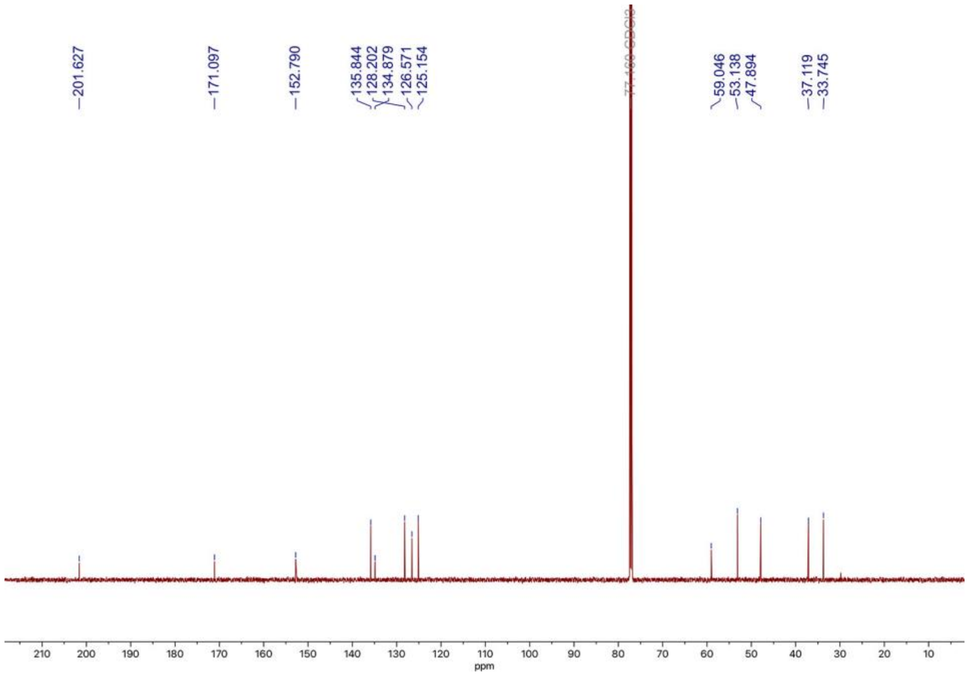


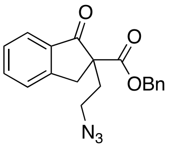
3ba

^{1}H NMR (400 MHz, $CDCl_3$)



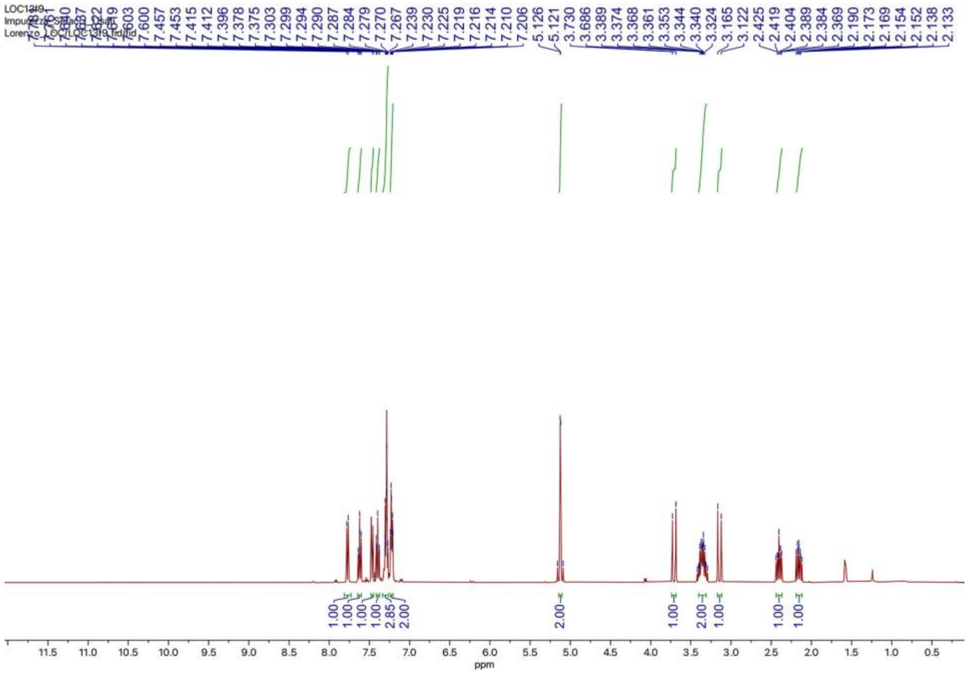
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



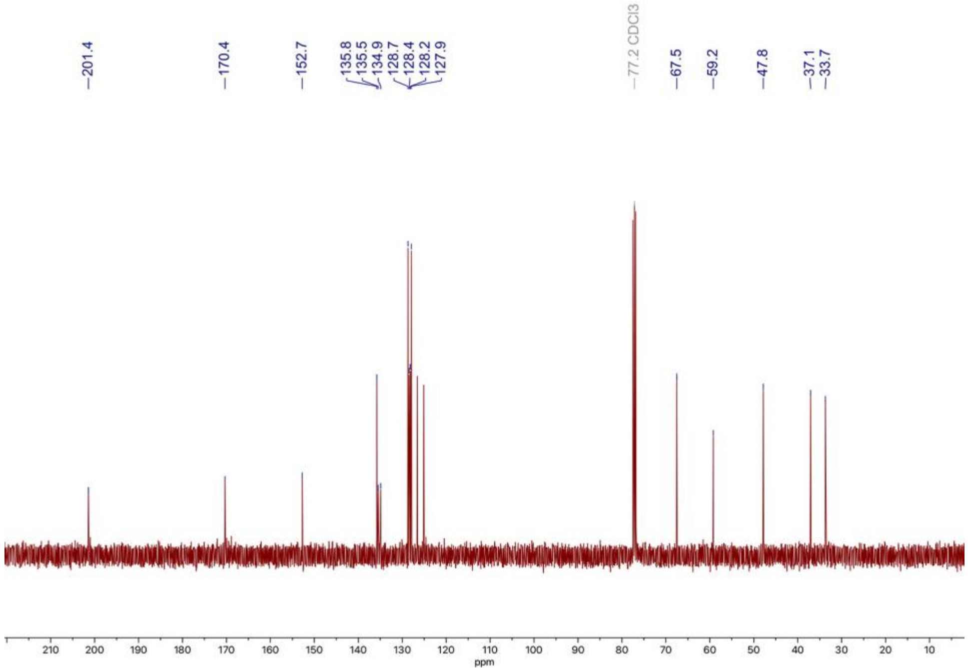


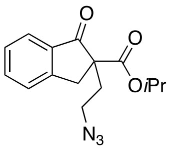
3ca

^{1}H NMR (400 MHz, $CDCl_3$)



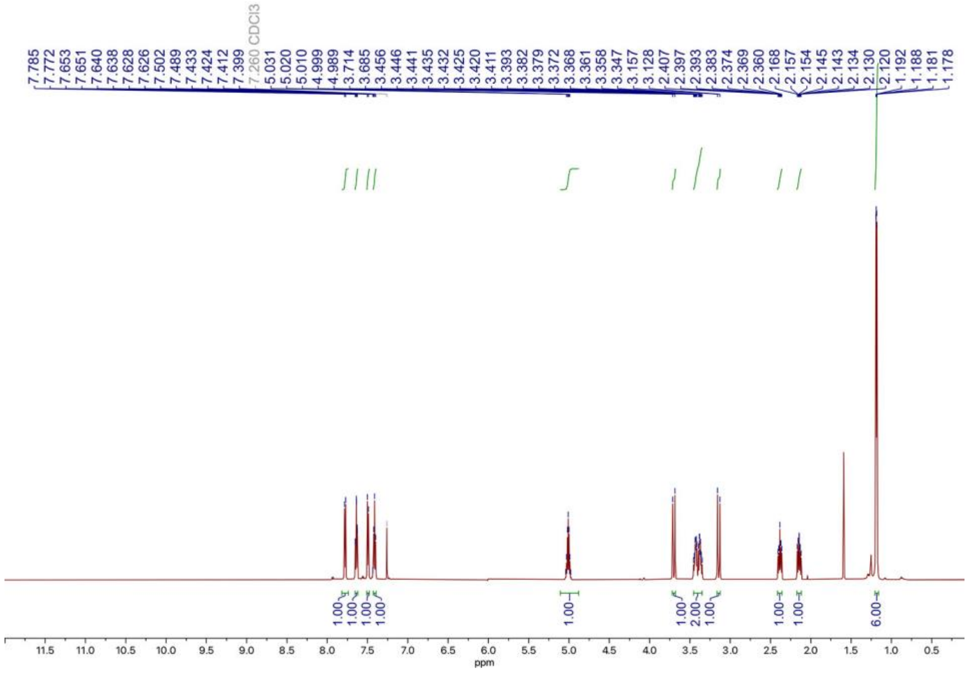
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



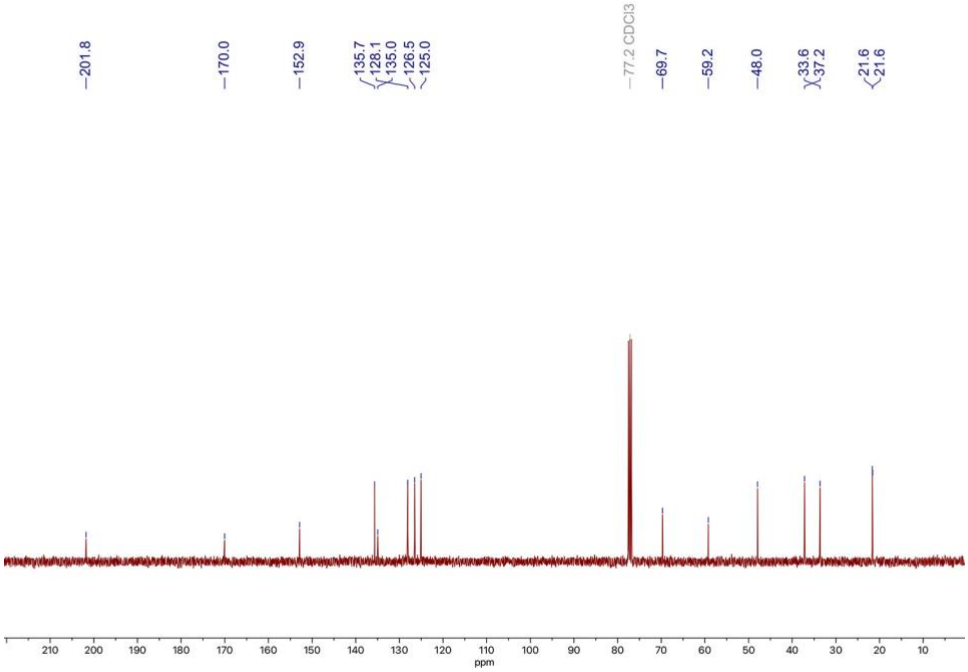


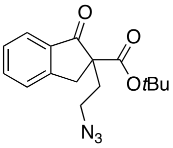
3da

^{1}H NMR (400 MHz, $CDCl_3$)



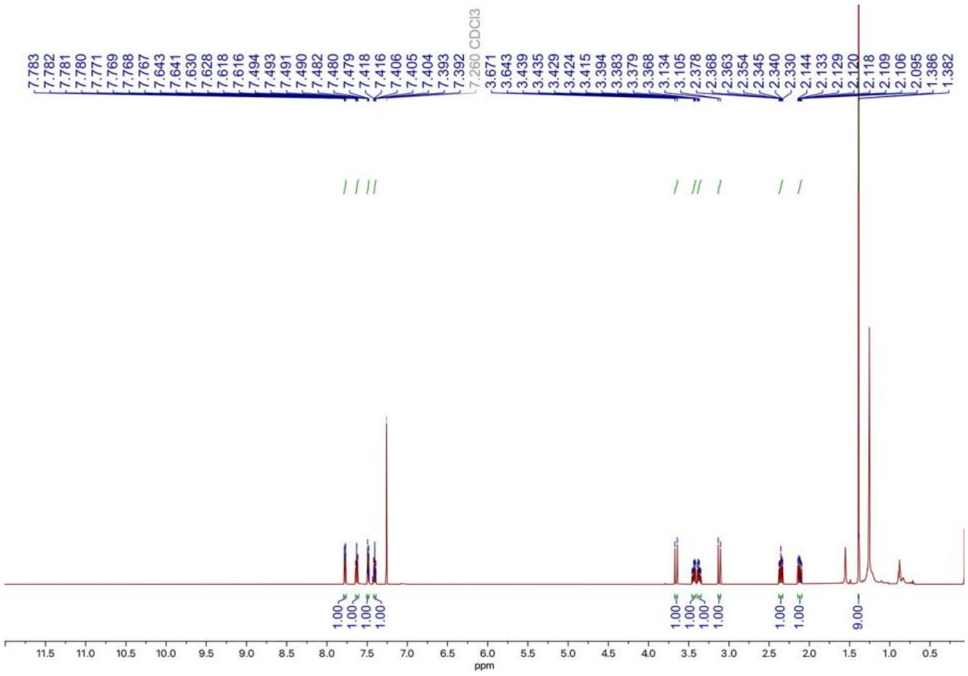
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



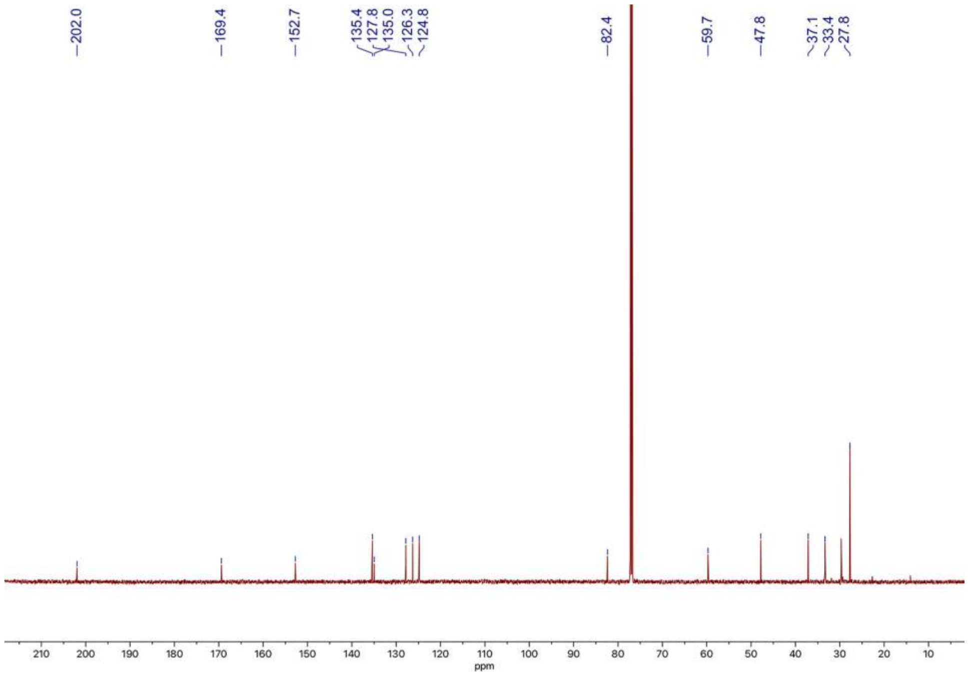


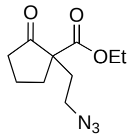
3ea

^{1}H NMR (400 MHz, $CDCl_3$)



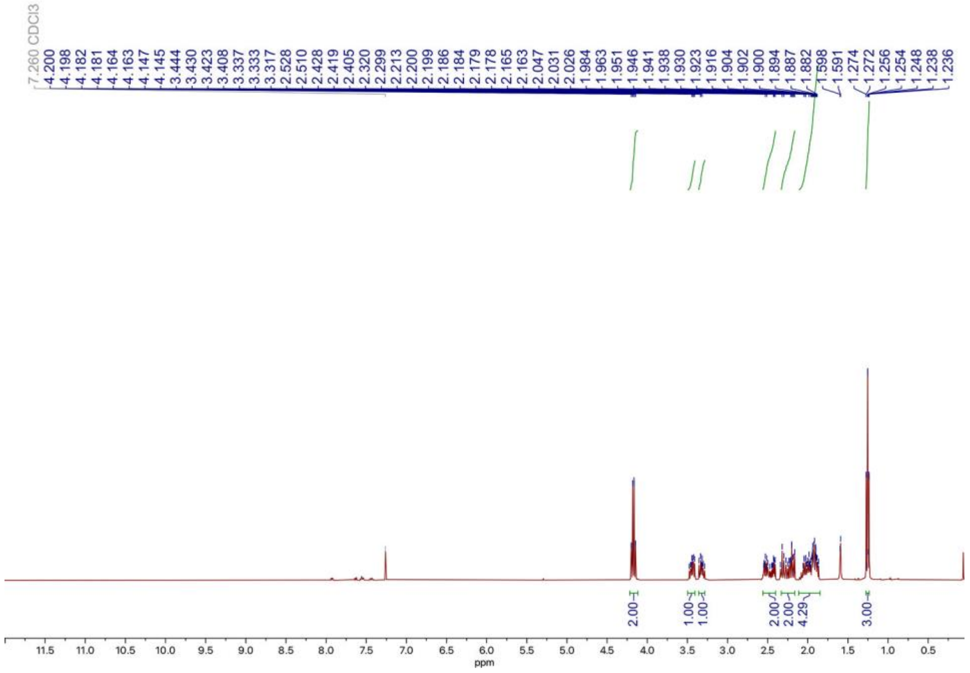
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



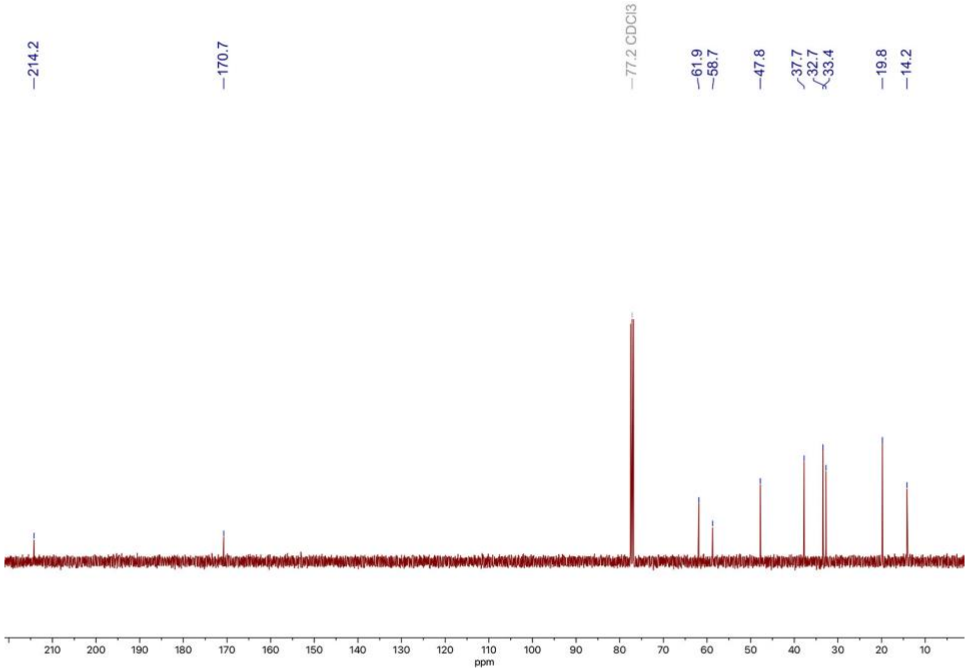


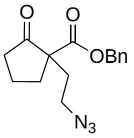
3fa

^{1}H NMR (400 MHz, $CDCl_3$)



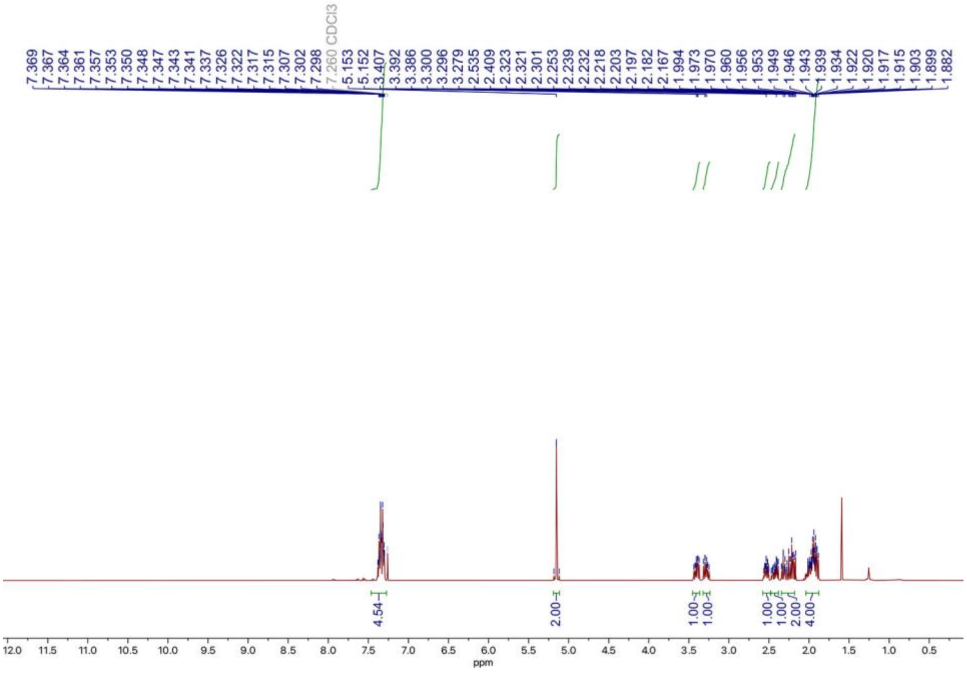
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



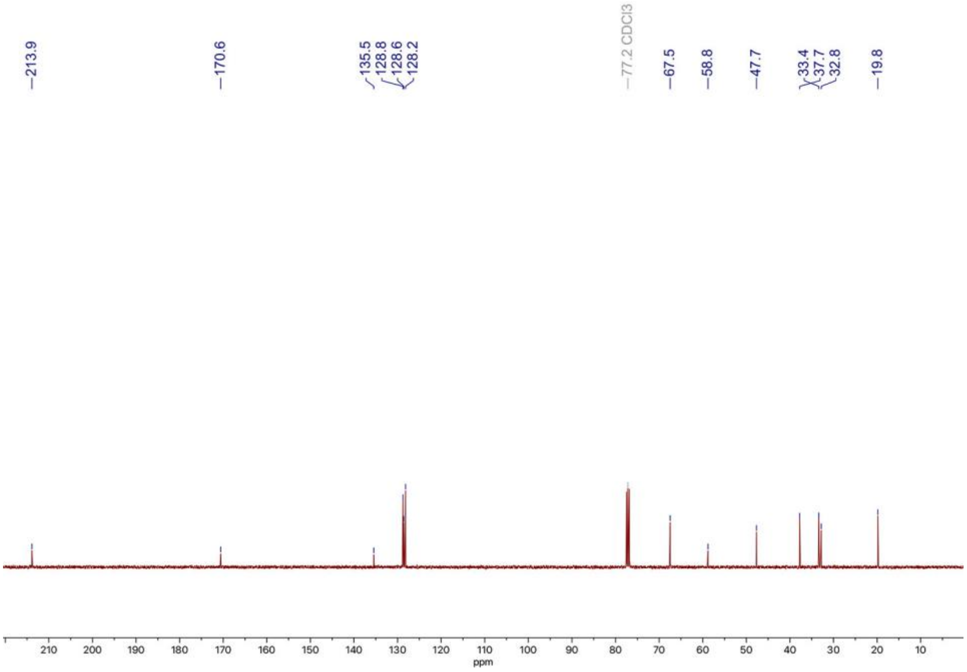


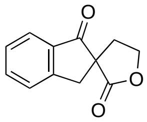
3ga

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

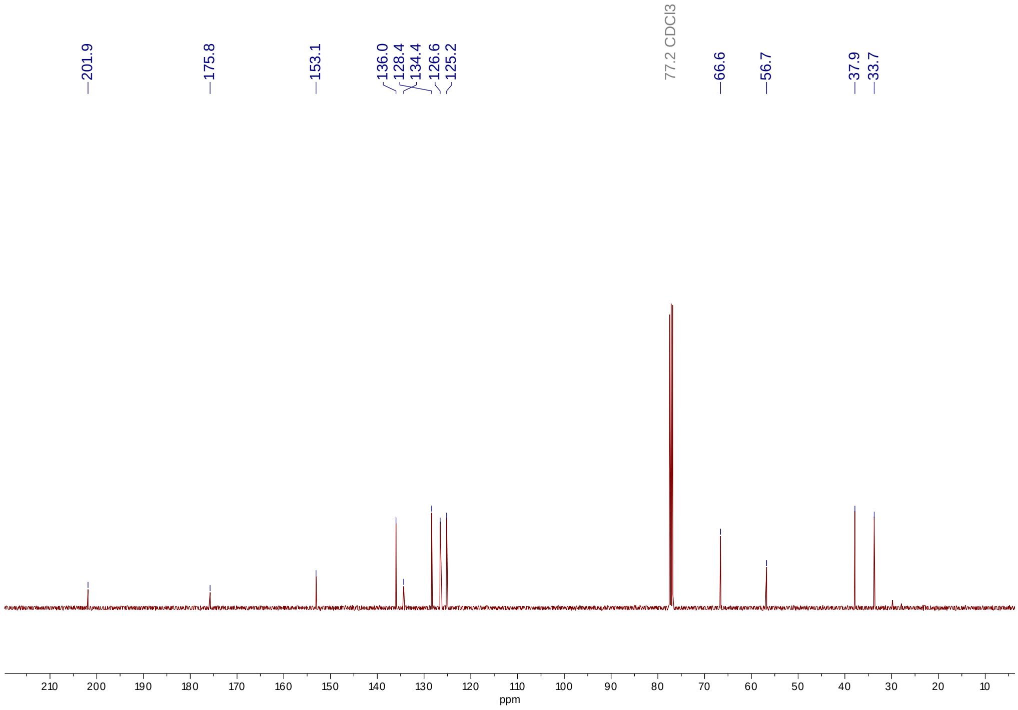


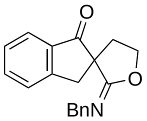


4a

^{1}H NMR (400 MHz, CDCl$_3$)

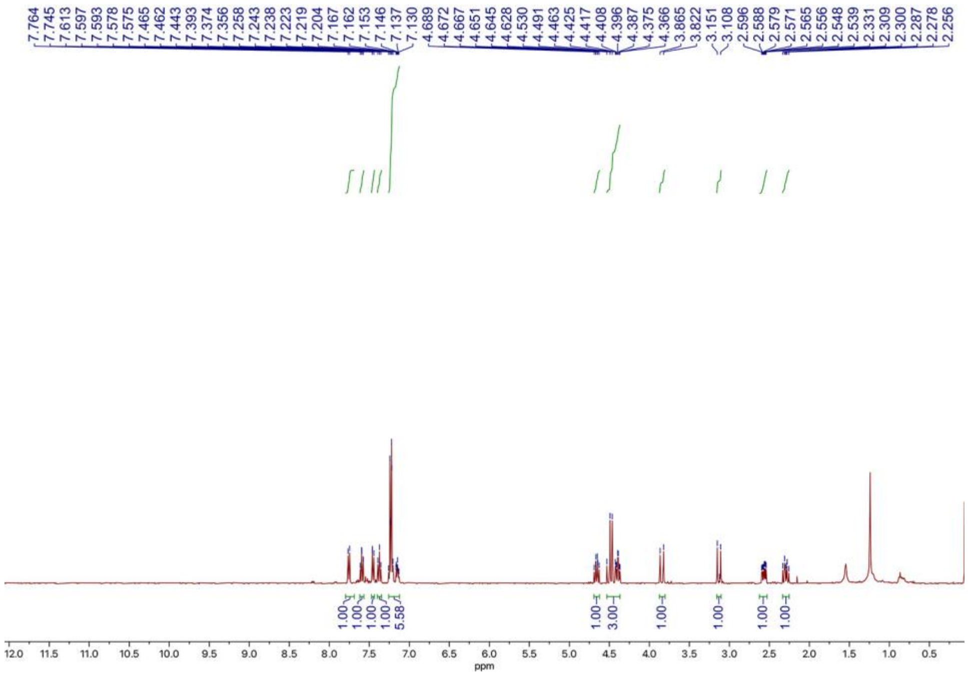
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)



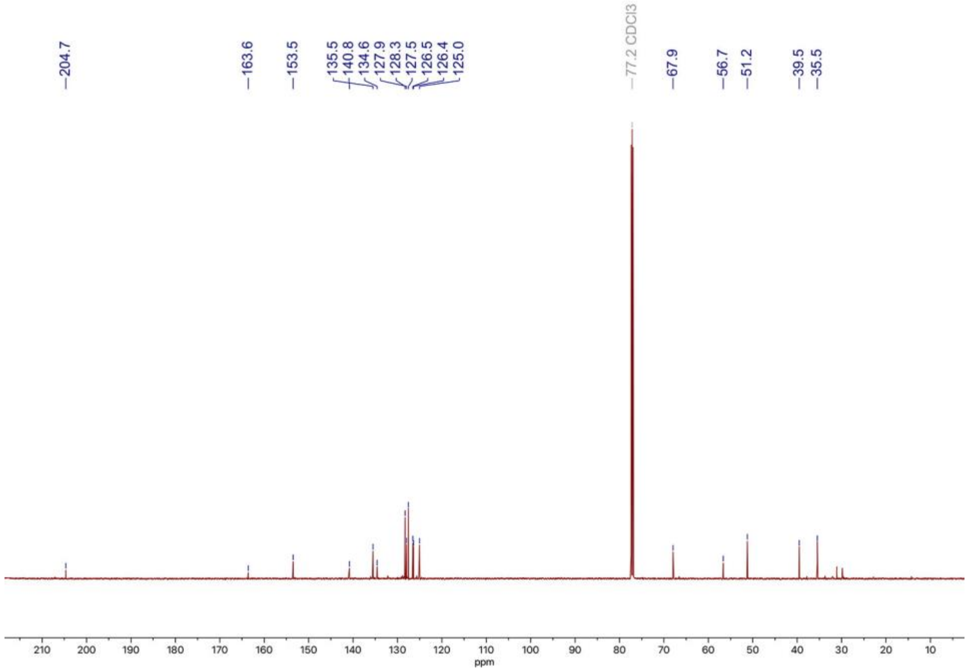


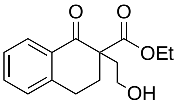
4i

^{1}H NMR (400 MHz, $CDCl_3$)



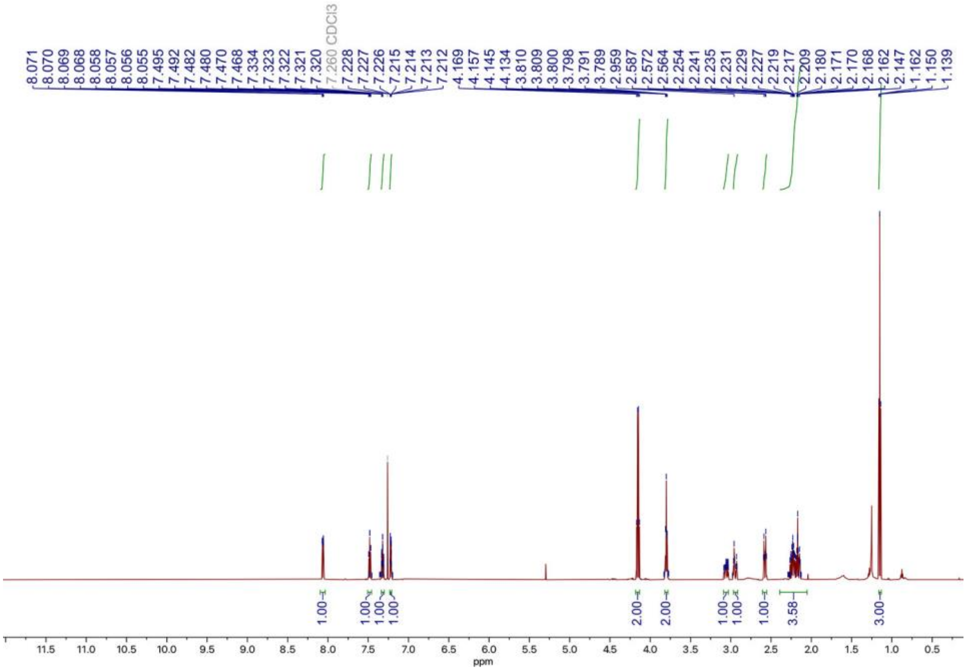
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



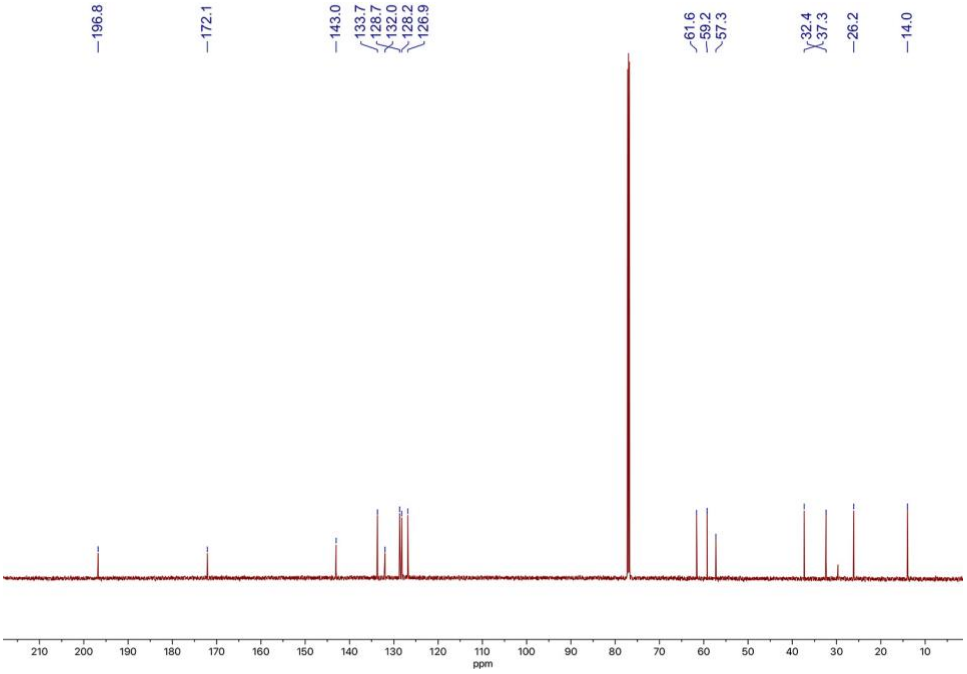


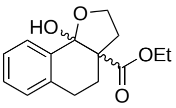
3ji

^{1}H NMR (400 MHz, $CDCl_3$)



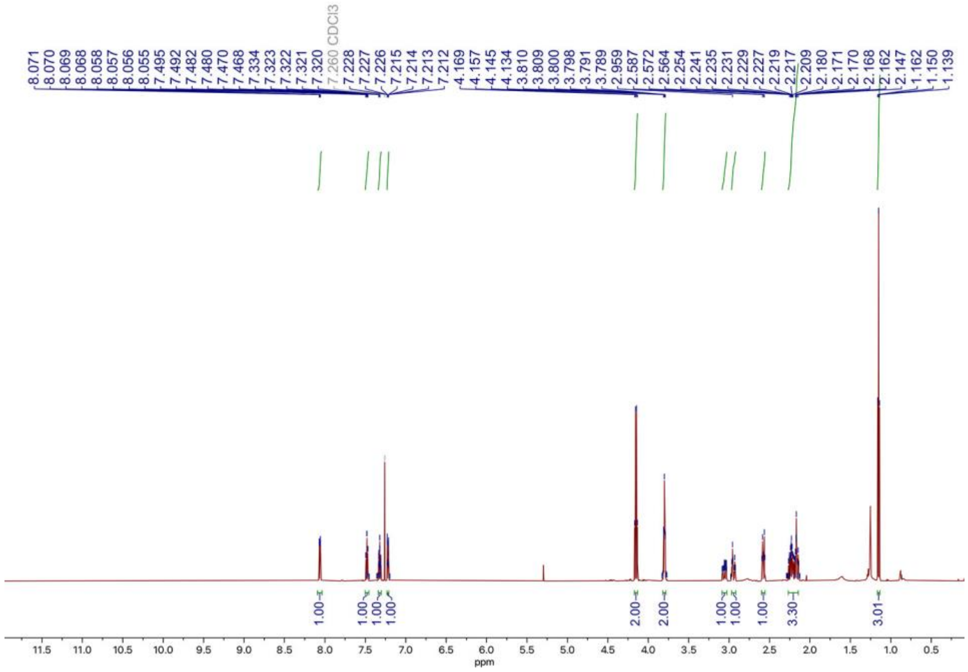
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



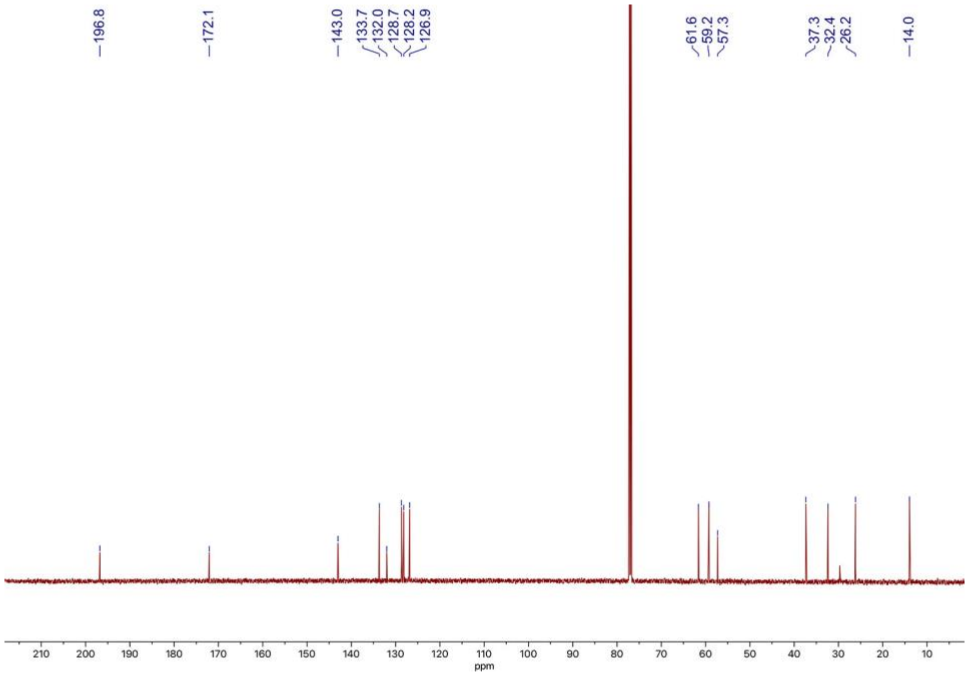


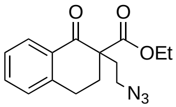
5j

^{1}H NMR (400 MHz, $CDCl_3$)



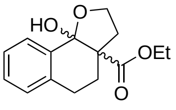
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)





3ja

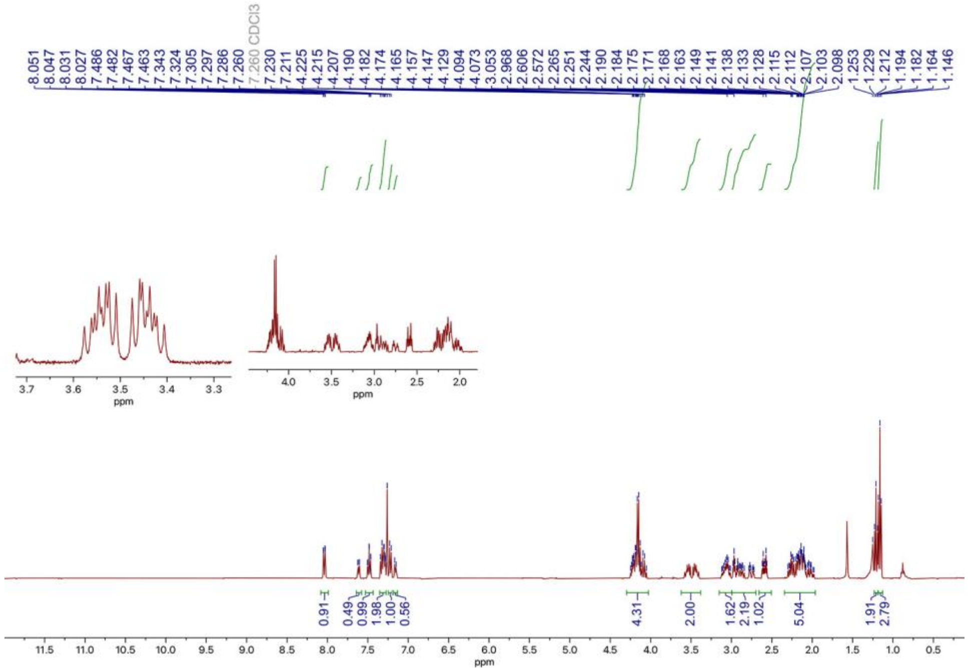
+

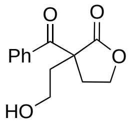


5j

3ja+5j

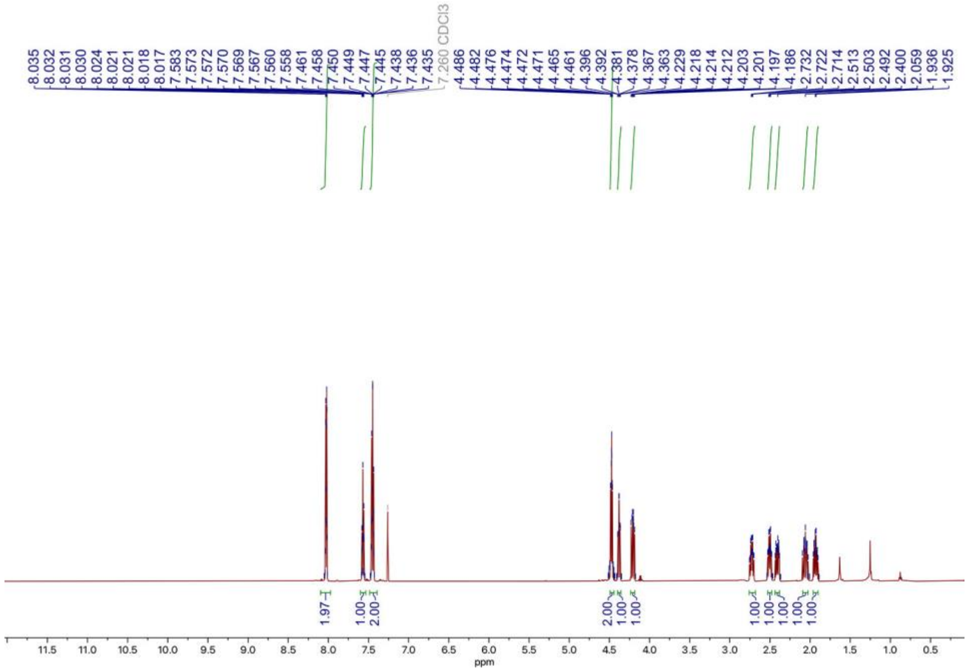
^{1}H NMR (400 MHz, $CDCl_3$)



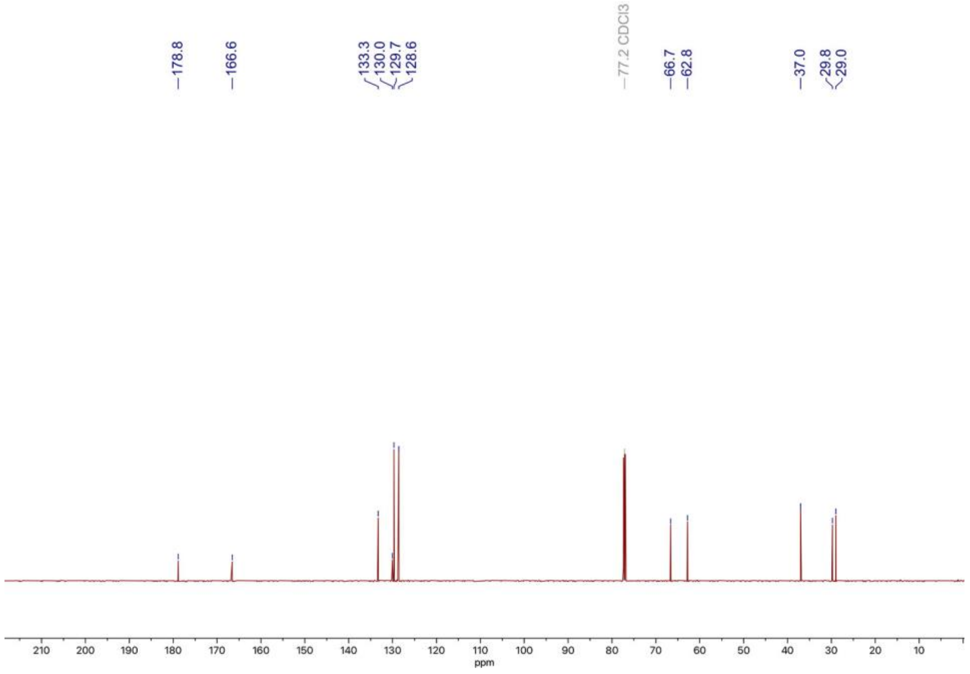


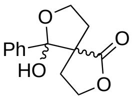
3ki

^{1}H NMR (400 MHz, $CDCl_3$)



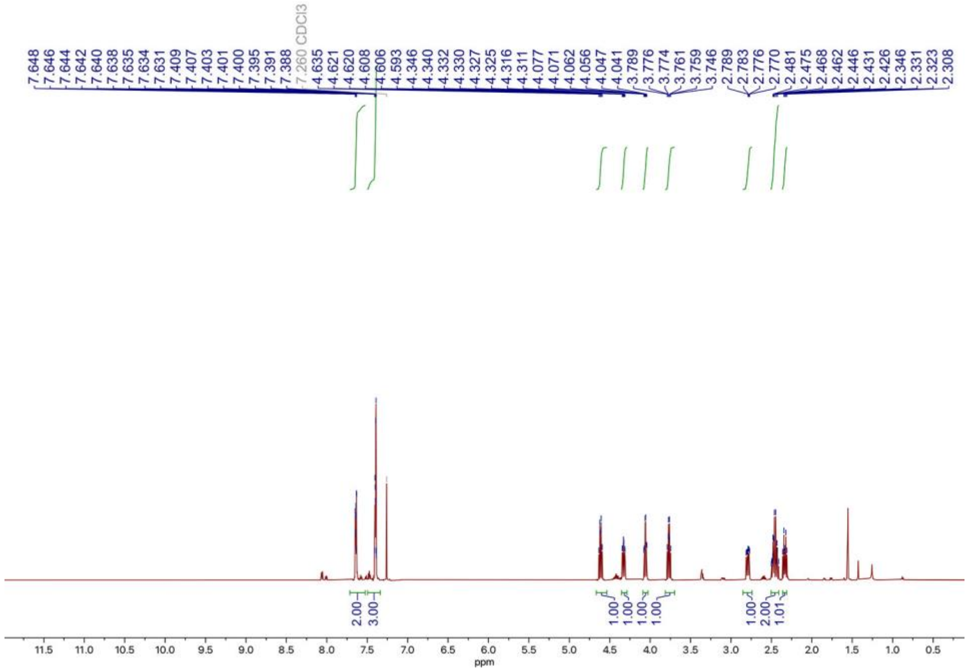
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



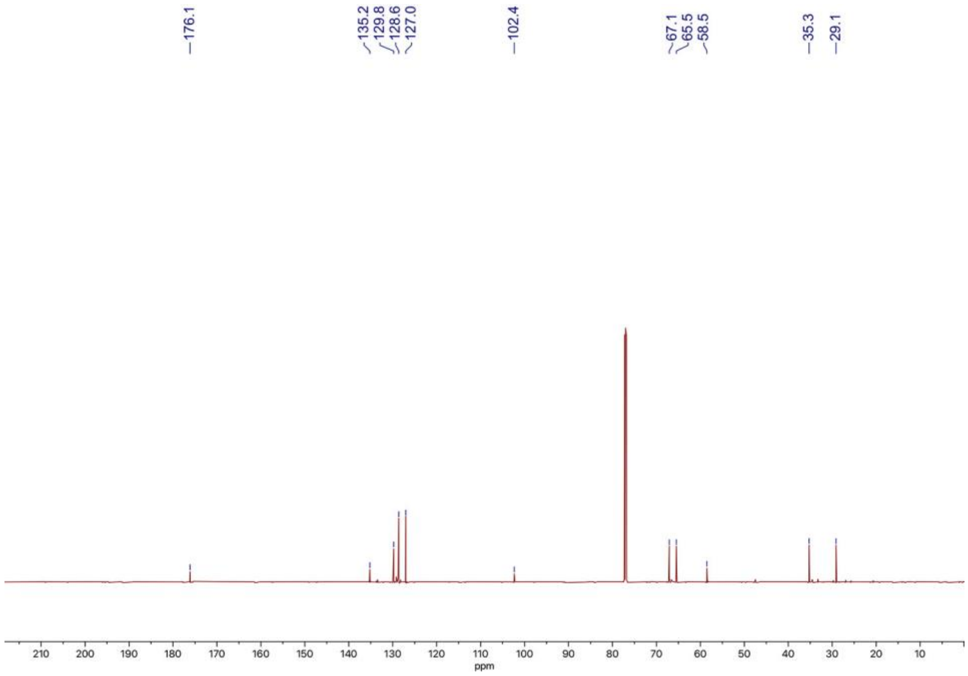


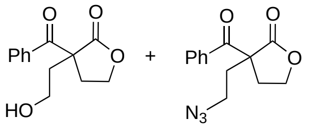
5k

^{1}H NMR (400 MHz, CDCl$_3$)



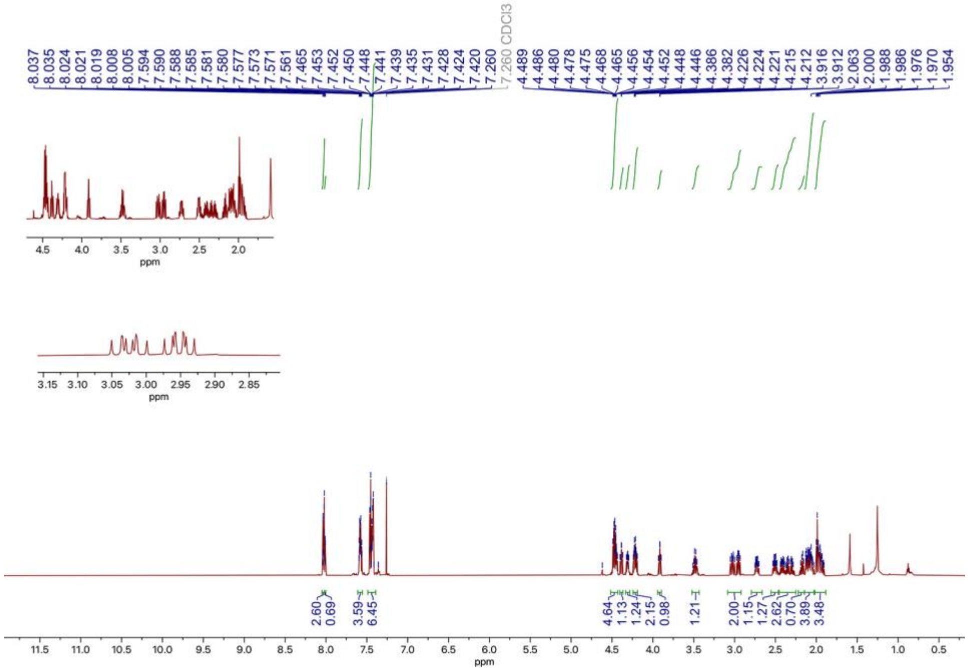
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

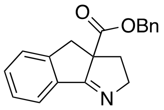




3ki+3ka

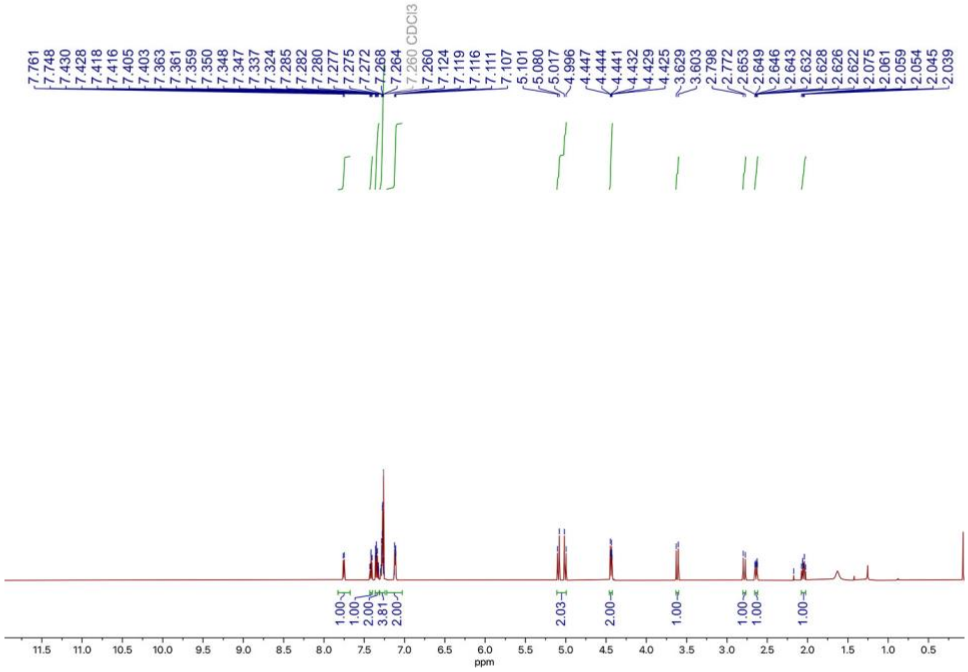
^{1}H NMR (400 MHz, $CDCl_3$)





6

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)