Supporting Information for

Catalytic asymmetric Staudinger–aza-Wittig reaction for the synthesis of heterocyclic amines

Lingchao Cai,[1] Kui Zhang,[1] Shuming Chen,[1] Romain J. Lepage,[2] K. N. Houk,[1] Elizabeth H. Krenske,[2] and Ohyun Kwon[1*]

[1]Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, USA.
[2]School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Queensland 4072, AUS.

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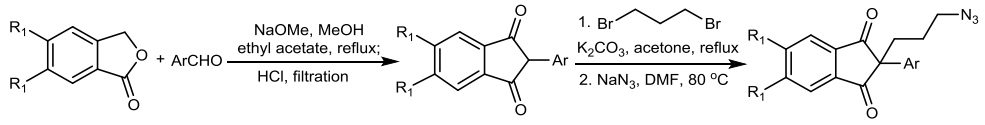
1. Materials and Methods

Unless otherwise stated, reactions were performed in dry solvents under an Ar atmosphere and anhydrous conditions. Dichloromethane (DCM), MeCN, and Et_3N were freshly distilled over CaH_2; toluene, tetrahydrofuran (THF), and benzene were freshly distilled over Na; and MeOH was freshly distilled over Mg prior to use. All other reagents were used as received from commercial sources. Reactions were monitored through thin layer chromatography (TLC) on 0.25-mm SiliCycle silica gel plates and visualized under UV light. Flash column chromatography (FCC) was performed using SiliCycle Silica-P Flash silica gel (60-Å pore size, 40–63 μm). Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance-500 instruments, calibrated to $CD(H)Cl_3$ as the internal reference (7.26 and 77.0 ppm for ^1H and ^{13}C NMR spectra, respectively), unless otherwise noted. ^1H NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data are reported in terms of chemical shift (δ, ppm). The following abbreviations indicate the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; quint = quintet; m = multiplet. High-resolution mass spectra were recorded using a Waters LCT Premier XE time-of-flight instrument controlled by MassLynx 4.1 software. Samples were infused through direct loop injection from a Waters Acquity UPLC into the multi-mode ionization source. The lock mass standard for accurate mass determination was leucine enkephalin (Sigma L9133). X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 100 K. Optical rotations were recorded using a Rudolph Autopol IV automatic polarimeter. Enantiomeric excesses were measured using high-performance liquid chromatography (HPLC), with a Shimadzu CBM Lite system and a REGIS (*S*,*S*)-Whelk-O1 analytical (250 mm × 4.5 mm × 5 μm) chiral column and CHIRALCEL AD-H, OD-H, and OJ-H analytical (250 mm × 4.6 mm × 5 μm) chiral columns.

2. Preparation of Azidodiones 1

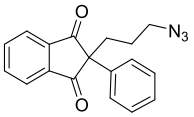
General Procedure for Preparation of Compounds 1a, 1b, 1c, 1e, 1n, and 1o



EtOAc (18.0 mL) was added to a suspension of the aldehyde (75.0 mmol, 1.0 equiv.) and the phthalide (75.0 mmol, 1.0 equiv.) in anhydrous MeOH (100 mL), followed by the addition of NaOMe (25% wt in MeOH, 40.0 mL) at room temperature. The mixture was heated under reflux for 3 h and then cooled to room temperature. After concentration *in vacuo*, water (50.0 mL) was added to the residue and the solution was acidified with conc. HCl to pH 1.0. The 2-substituted indanedione was collected by filtration and dried *in vacuo* to give a yellow powder, which was used for the next step without further purification[1].

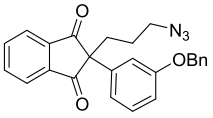
Dibromopropane (2.03 mL, 20.0 mmol, 2.0 equiv.) and K_2CO_3 (2.76 g, 20.0 mmol, 2.0 equiv.) were added to a solution of the 2-substituted indanedione (10.0 mmol, 1.0 equiv.) in acetone (100 mL). The mixture was heated under reflux overnight and then cooled to room temperature. After concentration *in vacuo*, the residue was purified through FCC (5% to 20% EtOAc in hexanes) to provide the alkyl bromide as a yellow oil[2].

Sodium azide (0.640 g, 10.0 mmol, 2.0 equiv.) was added to a solution of the alkyl bromide (5.00 mmol, 1.0 equiv.) in DMF (30.0 mL). The mixture was heated at 80 °C for 8 h and then cooled to room temperature. The reaction was quenched through the addition of water (50.0 mL) and EtOAc (50.0 mL). The aqueous phase was extracted with EtOAc (2 × 50.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired azidoindanedione.



1a

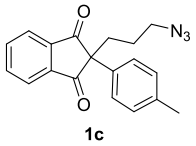
1a. 81% yield. IR (ATR): 2944, 2096, 1706, 1256, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 3.2, 6.0 Hz, 2H), 7.87 (dd, *J* = 3.2, 6.0 Hz, 2H), 7.40 (dd, *J* = 1.2, 8.2 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.26–7.24 (m, 1H), 3.21 (t, *J* = 7.2 Hz, 2H), 2.29 (quint, *J* = 4.6 Hz, 2H), 1.54–1.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.2, 141.7, 136.3, 136.1, 128.9, 127.8, 126.8, 123.7, 61.5, 51.3, 32.9, 24.6; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{16}N_3O_2$ 306.1243, found 306.1248.



1b

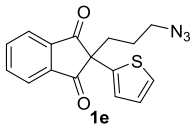
1b. 20% yield. IR (ATR): 3065, 2928, 2098, 1705, 1264, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 3.1, 6.0 Hz, 2H), 7.86 (dd, *J* = 3.2, 6.1 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.05 (quint, *J* = 2.0 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.85 (dd, *J* = 2.0, 7.8 Hz, 1H), 5.02 (s, 2H), 3.20 (t, *J* = 7.1 Hz,

2H), 2.25 (quint, J = 4.6 Hz, 2H), 1.58–1.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.0, 159.0, 141.7, 137.7, 136.6, 136.1, 129.8, 128.5, 128.0, 127.6, 123.7, 119.3, 113.96, 113.94, 70.0, 61.4, 51.3, 32.8, 24.5; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{25}H_{22}N_3O_3$ 412.1661, found 412.1660.



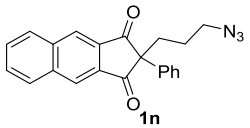
1c

1c. 71% yield. IR (ATR): 3061, 2920, 2095, 1741, 1703, 1252, 765 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 3.2, 6.0 Hz, 2H), 7.85 (dd, J = 3.2, 6.0 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.10 (t, J = 8.0 Hz, 2H), 3.21 (t, J = 7.2 Hz, 2H), 2.27 (s, 3H), 2.25 (quint, J = 4.6 Hz, 2H), 1.58–1.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.3, 141.7, 137.6, 136.0, 133.4, 129.6, 126.6, 123.6, 61.2, 51.3, 32.7, 24.6, 20.9; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{19}H_{18}N_3O_2$ 320.1399, found 320.1396.



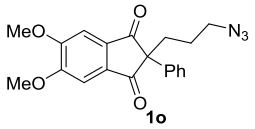
1e

1e. 45% yield. IR (ATR): 3077, 2932, 2094, 1744, 1706, 1254, 760 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 3.0, 6.0 Hz, 2H), 7.88 (dd, J = 3.0, 6.0 Hz, 2H), 7.24 (dd, J = 1.2, 5.2 Hz, 1H), 6.99 (dd, J = 1.2, 3.8 Hz, 1H), 6.92 (dd, J = 3.8, 5.2 Hz, 1H), 3.20 (t, J = 7.2 Hz, 2H), 2.26 (quint, J = 4.6 Hz, 2H), 1.54–1.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.6, 140.9, 138.3, 136.3, 126.8, 125.8, 125.7, 124.0, 58.6, 51.1, 34.5, 24.4; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{16}H_{14}N_3O_2S$ 312.0807, found 312.0811.



1n

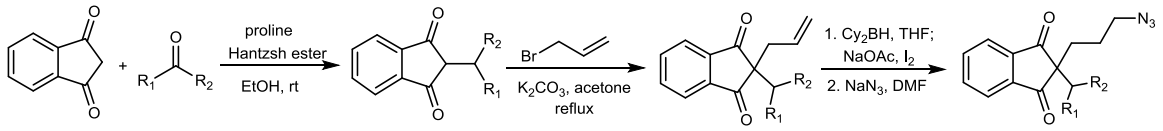
1n. 70% yield. IR (ATR): 3029, 2928, 2095, 1740, 1705, 1222 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 2H), 8.09 (dd, J = 3.0, 6.0 Hz, 2H), 7.70 (dd, J = 3.0, 6.0 Hz, 2H), 7.44 (td, J = 1.5, 7.8 Hz, 2H), 7.29 (tt, J = 1.5, 7.8 Hz, 2H), 7.23 (tt, J = 1.5, 7.8 Hz, 1H), 3.22 (t, J = 7.0 Hz, 2H), 2.36 (quint, J = 6.8 Hz, 2H), 1.57–1.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.5, 136.173, 136.70, 136.5, 130.6, 129.8, 128.9, 127.8, 126.9, 124.9, 63.1, 51.4, 33.1, 24.7; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{22}H_{18}N_3O_2$ 356.1399, found 356.1391.



1o

1o. 68% yield. IR (ATR): 3089, 2940, 2094, 1731, 1691, 1577, 1299, 1005, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.35 (s, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.8 Hz, 1H), 4.00 (s, 6H), 3.19 (t, J = 7.0 Hz, 2H), 2.25 (quint, J = 6.8 Hz, 2H), 1.50–1.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.1, 156.3, 137.1, 136.8, 128.7, 127.6, 126.7, 103.6, 61.0, 56.7, 51.3, 32.5, 24.6; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{20}H_{20}N_3O_4$ 366.1454, found 366.1459.

General Procedure for Preparation of Compounds 1d, 1f, 1g, 1h, 1i, 1j, 1k, 1l, and 1m

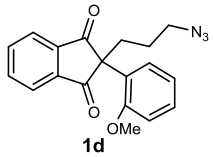


Proline (57.0 mg, 0.500 mmol, 0.05 equiv.) was added to a mixture of the aldehyde or ketone (10.0 mmol, 1.0 equiv.), 1,3-indanedione (1.46g, 10.0 mmol, 1.0 equiv.), and Hantzsch ester (2.53 g, 10.0 mmol, 1.0 equiv.) in EtOH (50.0 mL). The reaction mixture was stirred at room temperature overnight and then diluted with water (50.0 mL) and EtOAc (50.0 mL). The aqueous phase was extracted with EtOAc (2 × 50.0 mL). The combined organic phases were washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 40% EtOAc in hexanes) to give the 2-substituted indanedione[3].

Allyl bromide (1.72 mL, 20.0 mmol, 2.0 equiv.) and K_2CO_3 (2.76 g, 20.0 mmol, 2.0 equiv.) were added to a solution of the 2-substituted indanedione (10.0 mmol, 1.0 equiv.) in acetone (100 mL). The mixture was heated under reflux for 1 h and then cooled to room temperature. After concentration *in vacuo*, the residue was purified through FCC (5% to 20% EtOAc in hexanes) to give the 2-allylindanedione as a yellow oil.

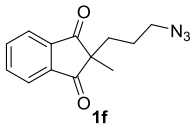
A solution of $BH_3{\cdot}SMe_2$ (0.710 mL, 7.50 mmol, 1.5 equiv.) was added carefully *via* syringe to a solution of freshly distilled cyclohexene (1.56 mL, 15.0 mmol, 3.0 equiv.) in dry THF (10.0 mL) at 0 °C. A thick white precipitate appeared after a few minutes. The mixture was stirred at 0 °C for 1 h, then a solution of the 2-allylindanedione (5.00 mmol, 1.0 equiv.) in dry THF (10.0 mL) was added dropwise at 0 °C. The mixture was stirred overnight at room temperature and then cooled again to 0 °C. A solution of sodium acetate (1.23 g, 15.0 mmol, 3.0 equiv.) in MeOH (10.0 mL) was added slowly, immediately followed by the dropwise addition of a solution of iodine (1.90 g, 7.50 mmol, 1.5 equiv.) in MeOH (10.0 mL) and THF (10.0 mL). The resulting solution was stirred at room temperature overnight and then quenched through a slow addition of saturated aqueous sodium thiosulfate until the mixture turned pale-yellow. The solution was stirred for 15 min, then diluted with water (20.0 mL) and extracted with Et_2O (3 × 20.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired alkyl iodide[4].

Sodium azide (0.325 g, 5.00 mmol, 2.0 equiv.) was added to a solution of the alkyl iodide (2.50 mmol, 1.0 equiv.) in DMF (15.0 mL). The mixture was heated at 80 °C for 8 h and then cooled to room temperature. The reaction was quenched through the addition of water (25.0 mL) and EtOAc (25.0 mL). The aqueous phase was extracted with EtOAc (2 × 25.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired azidoindanedione product.



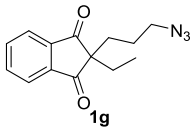
1d

Starting from 2-*o*-anisylindanedione, allylation, hydroboration/iodine oxidation, and NaN_3 displacement (the last three steps of the procedure above) gave the desired product **1d** in 58% yield. IR (ATR): 3073, 2944, 2098, 1747, 1708, 1491, 1252, 1025, 761 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.86 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.71 (dd, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 3.25 (t, *J* = 7.1 Hz, 2H), 2.27 (quint, *J* = 4.6 Hz, 2H), 1.50–1.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.0, 156.0, 141.2, 135.3, 129.3, 128.7, 126.3, 122.8, 121.5, 111.1, 59.2, 54.9, 51.5, 30.1, 24.4; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{18}N_3O_3$ 336.1348, found 336.1350.



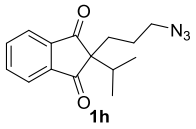
1f

Starting from 2-methylindanedinone, allylation, hydroboration/iodine oxidation, and NaN_3 displacement (the last three steps of the procedure above) gave the desired product **1f** in 62% yield. IR (ATR): 2972, 2867, 2096, 1743, 1707, 1594, 1287 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.84 (dd, *J* = 3.0, 6.0 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 1.84 (quint, *J* = 4.6 Hz, 2H), 1.40–1.36 (m, 2H), 1.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.0, 141.0, 136.0, 123.4, 53.3, 51.3, 32.2, 24.4, 19.7; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{13}H_{14}N_3O_2$ 244.1086, found 244.1082.



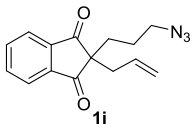
1g

1g. 33% yield. IR (ATR): 2965, 2876, 2097, 1740, 1705, 1596, 1270, 790 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.84 (dd, *J* = 3.0, 6.0 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 1.84 (m, 4H), 1.35–1.29 (m, 2H), 0.67 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4, 142.3, 135.8, 123.0, 58.2, 51.3, 31.4, 28.3, 24.3, 9.1; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{13}H_{14}N_3O_2$ 258.1243, found 258.1241.



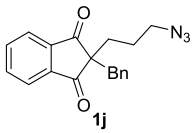
1h

1h. 34% yield. IR (ATR): 2960, 2928, 2096, 1740, 1702, 1594, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.80 (dd, *J* = 3.0, 6.0 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.13 (quint, *J* = 6.8 Hz, 1H), 1.88 (quint, *J* = 4.6 Hz, 2H), 1.27–1.19 (m, 2H), 0.86 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.6, 142.7, 135.7, 122.7, 60.3, 51.4, 33.9, 29.4, 24.4, 18.0; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{13}H_{14}N_3O_2$ 272.1399, found 272.1401.



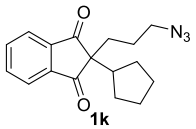
1i

Starting from 2,2-diallylindanedinone[5], hydroboration/iodine oxidation and NaN_3 displacement (the last two steps of the procedure above) gave the desired product **1i** in 54% yield. IR (ATR): 2932, 2856, 2097, 1742, 1705, 1594, 1245, 926 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.85 (dd, *J* = 3.0, 6.0 Hz, 2H), 5.48–5.41 (m, 1H), 5.02 (qd, *J* = 1.5, 17.0 Hz, 1H), 4.89 (qd, *J* = 0.8, 10.0 Hz, 1H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.52 (d, *J* = 7.6 Hz, 2H), 1.87 (quint, *J* = 6.8 Hz, 2H), 1.38–1.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.5, 142.1, 135.9, 131.2, 123.1, 119.6, 57.7, 51.3, 39.2, 31.4, 24.2; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{15}H_{16}N_3O_2$ 270.1243, found 270.1240.



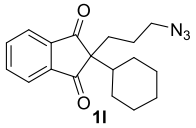
1j

1j. 33% yield. IR (ATR): 3037, 2916, 2852, 2095, 1740, 1702, 1594, 1247, 934 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.67 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.00–6.92 (m, 5H), 3.17 (t, *J* = 7.0 Hz, 2H), 3.12 (s, 2H), 1.98 (quint, *J* = 6.8 Hz, 2H), 1.39–1.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.7, 142.4, 135.6, 135.1, 129.7, 128.0, 126.7, 122.7, 59.7, 51.3, 41.3, 32.2, 24.4; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{18}N_3O_2$ 320.1399, found 320.1397.



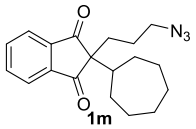
1k

1k. 28% yield. IR (ATR): 2960, 2867, 2095, 1740, 1702, 1587, 1249 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.84 (dd, *J* = 3.0, 6.0 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.24 (tt, *J* = 7.0, 10.2 Hz, 1H), 1.96 (quint, *J* = 6.8 Hz, 2H), 1.59–1.54 (m, 2H), 1.53–1.48 (m, 2H), 1.47–1.41 (m, 2H), 1.35–1.26 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4, 142.3, 135.8, 122.8, 59.1, 51.4, 46.2, 30.3, 27.5, 24.6, 24.4; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{17}H_{20}N_3O_2$ 298.1556, found 298.1550.



1l

1l. 33% yield. IR (ATR): 2929, 2852, 2095, 1739, 1701, 1594, 1257 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.82 (dd, *J* = 3.0, 6.0 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 1.90 (quint, *J* = 6.8 Hz, 2H), 1.87 (tt, *J* = 7.0, 10.2 Hz, 1H), 1.65–1.63 (m, 2H), 1.58–1.55 (m, 3H), 1.29–1.23 (m, 2H), 1.14–1.02 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.9, 142.6, 135.7, 122.6, 60.8, 51.5, 43.8, 28.9, 28.1, 26.5, 25.9, 24.3; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{22}N_3O_2$ 312.1712, found 312.1713.

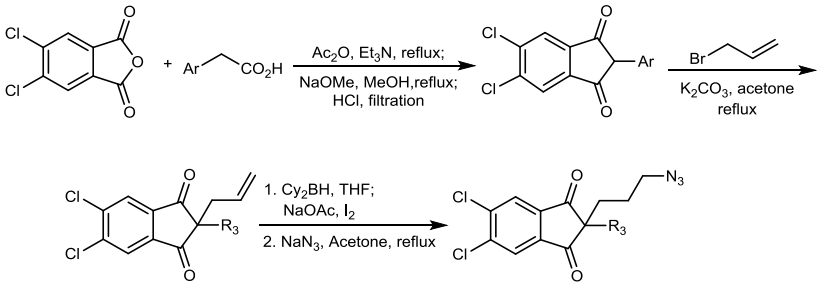


1m

1m. 31% yield. IR (ATR): 2922, 2848, 2094, 1738, 1701, 1598, 1240 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 3.0, 6.0 Hz, 2H), 7.83 (dd, *J* = 3.0, 6.0 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.03–1.99 (m, 1H), 1.91 (quint, *J* = 6.8 Hz, 2H), 1.67–1.59 (m, 4H), 1.52–1.49 (m,

2H), 1.40–1.32 (m, 2H), 1.31–1.27 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.9, 142.5, 135.7, 122.8, 60.8, 51.5, 45.1, 29.8, 29.4, 27.4, 27.0, 24.3; HRMS–ESI (*m*/z) $[M + H]^+$ calcd $C_{19}H_{24}N_3O_2$ 326.1869, found 326.1867.

General Procedure for Preparation of Compounds 1p, 1q, 1r, 1s, 1t, 1u, and 1v



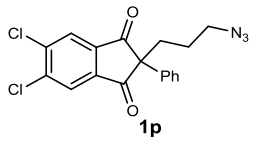
A mixture of 4,5-dichlorophthalic anhydride (2.14 g, 10.0 mmol, 1.0 equiv.), Et_3N (4.30 mL, 30.0 mmol, 3.0 equiv.), the arylacetic acid (15.0 mmol, 1.5 equiv.), and acetic anhydride (3.80 mL, 40.0 mmol, 4.0 equiv.) was heated under reflux for 2 h. The mixture was cooled to room temperature and diluted with MeOH (50.0 mL), followed by the addition of NaOMe (25% wt in MeOH, 18.0 mL). The mixture was heated under reflux for another 1 h and then cooled to room temperature. After concentration *in vacuo*, water (50.0 mL) was added to the residue and the solution was acidified with conc. HCl to pH 1.0. The 2-substituted indanedione was collected by filtration and dried *in vacuo* as a yellow powder, which was used in the next step without further purification[2].

Allyl bromide (1.72 mL, 20.0 mmol, 2.0 equiv.) and K_2CO_3 (2.76 g, 20.0 mmol, 2.0 equiv.) were added to a solution of the 2-substituted indanedione (10.0 mmol, 1.0 equiv.) in acetone (100 mL). The mixture was heated under reflux for 1 h and then cooled to room temperature. After concentration *in vacuo*, the residue was purified through FCC (5% to 20% EtOAc in hexanes) to give the 2-allylindanedione as a yellow oil.

A solution of $BH_3{\cdot}SMe_2$ (0.710 mL, 7.50 mmol, 1.5 equiv.) was added carefully *via* syringe to a solution of freshly distilled cyclohexene (1.56 ml, 15.0 mmol, 3.0 equiv.) in dry THF (10.0 mL) at 0 °C. A thick white precipitate appeared after a few minutes. The mixture was stirred at 0 °C for 1 h and then a solution of the 2-allylindanedione (5.00 mmol, 1.0 equiv.) in dry THF (10.0 mL) was added dropwise at 0 °C. The mixture was stirred overnight at room temperature and then cooled again to 0 °C. A solution of sodium acetate (1.23 g, 15.0 mmol, 3.0 equiv.) in MeOH (10.0 mL) was added slowly, immediately followed by the dropwise addition of a solution of iodine (1.90 g, 7.50 mmol, 1.5 equiv.) in MeOH (10.0 mL) and THF (10.0 mL). The resulting solution was stirred at room temperature overnight and then quenched through slow addition of saturated aqueous sodium thiosulfate until the mixture turned pale-yellow. The solution was stirred for 15 min, then diluted with water (20.0 mL) and extracted with Et_2O (3 × 20.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired alkyl iodide product.

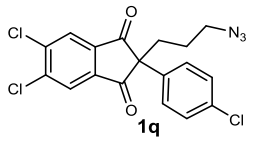
Sodium azide (0.325 g, 5.00 mmol, 2.0 equiv.) was added to a solution of the alkyl iodide (2.50 mmol, 1.0 equiv.) in DMF (15.0 mL). The mixture was heated at 80 °C for 8 h and then cooled to room temperature. The reaction was quenched through addition of water (25.0

mL) and EtOAc (25.0 mL). The aqueous phase was extracted with EtOAc (2 × 25.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired azidoindanedione product.



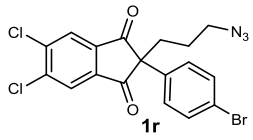
1p

1p. 71% yield. IR (ATR): 3065, 2924, 2094, 1744, 1709, 1579, 1296, 1249, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.0 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H), 3.21 (t, J = 7.0 Hz, 2H), 2.27 (quint, J = 6.8 Hz, 2H), 1.51–1.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.9, 141.6, 140.2, 135.5, 129.1, 128.1, 126.7, 125.4, 61.9, 51.2, 33.0, 24.5; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{18}H_{14}Cl_2N_3O_2$ 374.0463, found 374.0458.



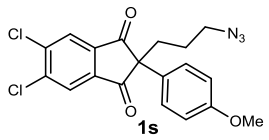
1q

1q. 41% yield. IR (ATR): 3089, 2936, 2098, 1744, 1711, 1493, 1264, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.32 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 3.21 (t, J = 7.0 Hz, 2H), 2.22 (quint, J = 6.8 Hz, 2H), 1.48–1.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 141.8, 140.0, 134.3, 133.9, 129.2, 128.1, 125.5, 61.1, 51.1, 33.4, 24.5; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{18}H_{13}Cl_3N_3O_2$ 408.0073, found 408.0081.



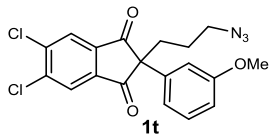
1r

1r. 38% yield. IR (ATR): 3089, 2932, 2096, 1744, 1709, 1580, 1298, 1251, 1010 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.44 (d, J = 9.0 Hz, 2H), 7.26 (d, J = 9.0 Hz, 2H), 3.21 (t, J = 7.0 Hz, 2H), 2.22 (quint, J = 6.8 Hz, 2H), 1.48–1.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 141.9, 140.0, 134.4, 132.1, 128.4, 125.5, 122.5, 61.1, 51.1, 33.3, 24.5; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{18}H_{13}BrCl_2N_3O_2$ 451.9568, found 451.9572.



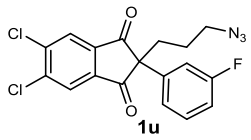
1s

1s. 52% yield. IR (ATR): 3093, 2944, 2095, 1743, 1708, 1580, 1509, 1295, 1249, 1032, 831 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.26 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 3.74 (s, 3H), 3.20 (t, J = 7.0 Hz, 2H), 2.22 (quint, J = 6.8 Hz, 2H), 1.49–1.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.1, 159.3, 141.5, 140.1, 127.9, 127.4, 125.4, 114.4, 61.2, 55.2, 51.2, 32.9, 24.5; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{19}H_{16}Cl_2N_3O_3$ 404.0569, found 404.0571.



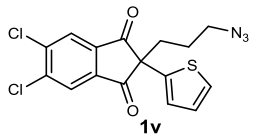
1t

1t. 48% yield. IR (ATR): 3069, 2944, 2095, 1743, 1709, 1579, 1294, 1246, 1049, 897 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.92–6.89 (m, 2H), 6.80 (dd, *J* = 2.0, 8.0 Hz, 1H), 3.76 (s, 3H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.25 (quint, *J* = 6.8 Hz, 2H), 1.50–1.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.7, 160.0, 141.6, 140.2, 136.9, 130.0, 125.4, 118.9, 113.3, 112.8, 61.8, 55.2, 51.21, 32.8, 24.5; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{16}Cl_2N_3O_3$ 404.0569, found 404.0565.



1u

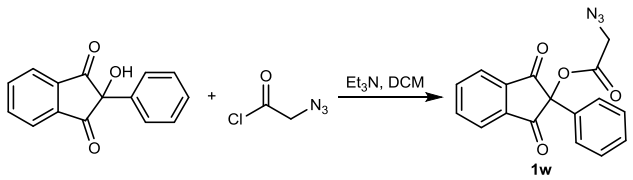
1u. 28% yield. IR (ATR): 3085, 2924, 2097, 1746, 1712, 1582, 1298, 1243, 764 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.28–7.26 (m, 1H), 7.13 (t, *J* = 9.0 Hz, 2H), 6.98 (t, *J* = 8.8 Hz, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.23 (quint, *J* = 6.8 Hz, 2H), 1.55–1.450 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4, 162.9 (d, *J* = 248.8 Hz, 1C), 141.9, 140.0, 137.7 (d, *J* = 7.2 Hz, 1C), 130.5 (d, *J* = 8.0 Hz, 1C), 125.5, 122.4 (d, *J* = 3.0 Hz, 1C), 115.2 (d, *J* = 21.6 Hz, 1C), 114.2 (d, *J* = 21.0 Hz, 1C), 61.3, 51.5, 33.3, 24.5; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{13}Cl_2FN_3O_2$ 392.0369, found 392.0372.



1v

1v. 37% yield. IR (ATR): 3089, 2928, 2097, 1747, 1713, 1580, 1298, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.25 (dd, *J* = 1.2, 5.2 Hz, 1H), 6.95 (dd, *J* = 1.2, 4.0 Hz, 1H), 6.92 (dd, *J* = 4.2, 5.2 Hz, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.25 (quint, *J* = 6.8 Hz, 2H), 1.52–1.49 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 141.9, 139.5, 137.3, 126.9, 126.2, 125.9, 125.7, 59.0, 51.0, 34.5, 24.4; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{16}H_{12}Cl_2SN_3O_2$ 380.0027, found 380.0032.

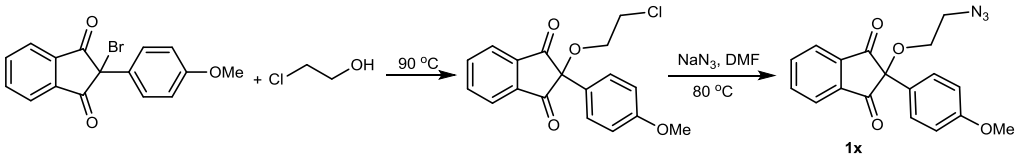
Procedure for Preparation of Compound 1w



1w

Azidoacetyl chloride (0.710 g, 6.00 mmol, 1.2 equiv.) was added slowly to a mixture of the hydroxyl indane (1.19 g, 5.00 mmol, 1.0 equiv.; prepared according to a known procedure[6]) and Et_3N (6.10 g, 6.00 mmol, 1.2 equiv.) in DCM (100 mL) at 0 °C. The resulting mixture was stirred for 30 min. After concentration *in vacuo*, the crude material was purified through FCC (5% to 50% EtOAc in hexanes) to yield a yellow oil (83.0% yield). IR (ATR): 3057, 2920, 2110, 1747, 1721, 1256, 1176, 763 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 3.2, 6.2 Hz, 2H), 7.91 (dd, *J* = 3.2, 6.0 Hz, 1H), 7.43–7.41 (m, 2H), 7.36–7.34 (m, 3H), 4.08 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.7, 167.6, 139.7, 136.5, 130.9, 129.9, 129.1, 127.2, 124.2, 83.7, 49.4; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{17}H_{12}N_3O_4$ 322.0828, found 322.0830.

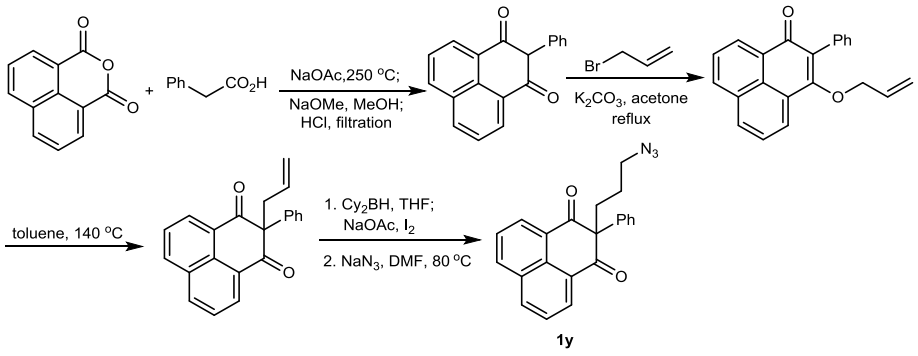
Procedure for Preparation of Compound 1x



A solution of the 2-bromoindanedione (0.660 g, 2.00 mmol, 1.0 equiv.; prepared according to the known procedure[7]) in 2-chloroethanol (20.0 mL) was heated at 90 °C for 3 h and then cooled to room temperature. The reaction mixture was diluted with water (50.0 mL) and extracted with Et_2O (3 × 50.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 50% EtOAc in hexanes) to give the desired chloroethyl ether product, which was used for the next step without purification.

Sodium azide (0.640 g, 10.0 mmol, 2.0 equiv.) was added to a solution of the chloroethyl ether (1.65 g, 5.00 mmol, 1.0 equiv.) in DMF (30.0 mL). The mixture was heated at 80 °C for 8 h and then cooled to room temperature. The mixture was diluted with water (50.0 mL) and EtOAc (50.0 mL). The aqueous phase was extracted with EtOAc (2 × 50.0 mL). The combined organic phases were washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired azide product **1x** (68% yield). IR (ATR): 3073, 2932, 2105, 1747, 1711, 1580, 1509, 1252, 1178, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 3.2, 6.2 Hz, 2H), 7.87 (dd, J = 3.2, 6.0 Hz, 2H), 7.40 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 3.76 (t, J = 5.2 Hz, 2H), 3.73 (s, 3H), 3.37 (d, J = 5.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.6, 160.4, 140.7, 136.7, 129.1, 125.2, 1243.9, 114.3, 83.2, 65.3, 55.2, 50.7; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{17}H_{14}N_3O_3$ 308.1035, found 308.1042.

Procedure for Preparation of Compound 1y



A mixture of 1,8-naphthoic anhydride (19.8 g, 100 mmol, 1.0 equiv.), phenylacetic acid (14.9 g. 110 mmol, 1.1 equiv.), and sodium acetate (1.00 g) was heated at 250 °C. Within 30 min, the mixture melted, and carbon dioxide and water began to evolve. After 2 h at 250 °C, the mixture was cooled to room temperature and diluted with MeOH (300 mL). A solution of NaOMe (25% wt in MeOH, 50.0 mL) was added and then the mixture was heated under reflux for another 2 h. The mixture was cooled to room temperature. After concentration *in vacuo*, water (200 mL)

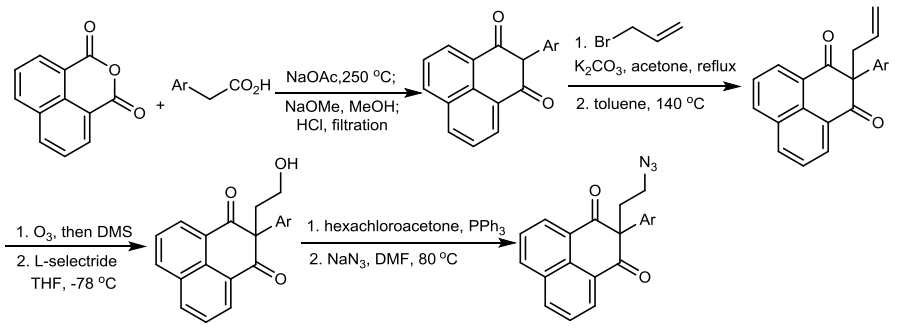
was added to the residue and then the solution was acidified with conc. HCl to pH 1.0. The product was collected by filtration and dried *in vacuo* to give a yellowish powder, which was used in the next step without purification[8].

Allyl bromide (3.40 mL, 40.0 mmol, 2.0 equiv.) and K_2CO_3 (5.50 g, 40.0 mmol, 2.0 equiv.) were added to a solution of the product (5.44 g, 20.0 mmol, 1.0 equiv.) from the previous step in acetone (100 mL). The mixture was heated under reflux for 1 h and then cooled to room temperature. After filtration and concentration *in vacuo*, the residue was dissolved in toluene (100 mL) in a sealed flask. The solution was heated at 140 °C overnight. The mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified through FCC (5% to 20% EtOAc in hexanes) to furnish 2-allylphenalendione.

A solution of $BH_3{\cdot}SMe_2$ (0.710 mL, 7.50 mmol, 1.5 equiv.) was added carefully *via* syringe to a solution of freshly distilled cyclohexene (1.56 ml, 15.0 mmol, 3.0 equiv.) in dry THF (10.0 mL) at 0 °C. A thick white precipitate appeared after a few minutes. The mixture was stirred at 0 °C for 1 h and then a solution of the 2-allylindanedione (5.00 mmol, 1.0 equiv.) in dry THF (10.0 mL) was added dropwise at 0 °C. The mixture was stirred overnight at room temperature and then cooled again to 0 °C. A solution of sodium acetate (1.23 g, 15.0 mmol, 3.0 equiv.) in MeOH (10.0 mL) was added slowly, immediately followed by the dropwise addition of a solution of iodine (1.90 g, 7.50 mmol, 1.5 equiv.) in MeOH (10.0 mL) and THF (10.0 mL). The resulting solution was stirred at room temperature overnight and then quenched through slow addition of saturated aqueous sodium thiosulfate until the mixture turned pale-yellow. The solution was stirred for 15 min, then diluted with water (20.0 mL) and extracted with Et_2O (3 × 20.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired alkyl iodide product.

Sodium azide (0.325 g, 5.00 mmol, 2.0 equiv.) was added to a solution of the alkyl iodide (1.10 g, 2.50 mmol, 1.0 equiv.) in DMF (15.0 mL). The mixture was heated at 80 °C for 8 h and then cooled to room temperature. The reaction was quenched through addition of water (25.0 mL) and EtOAc (25.0 mL). The aqueous phase was extracted with EtOAc (2 × 25.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired azide **1y** in 34% yield. IR (ATR): 3061, 2924, 2095, 1697, 1671, 1580, 1304, 844 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 8.2 Hz, 2H), 8.10 (d, J = 8.2 Hz, 2H), 7.67 (t, J = 8.2 Hz, 2H), 7.16–7.09 (m, 5H), 3.32 (t, J = 6.2 Hz, 2H), 2.48 (quint, J = 6.8 Hz, 2H), 1.72–1.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.1, 138.1, 134.3, 132.7, 130.7, 129.08, 129.00, 128.5, 127.8, 126.7, 126.2, 71.9, 51.7, 32.9, 25.6; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{22}H_{18}N_3O_2$ 356.1399, found 356.1395.

General Procedure for Preparation of Compounds 1z, 1aa, and 1ab



A mixture of 1,8-naphthoic anhydride (19.8 g, 100 mmol, 1.0 equiv.), phenylacetic acid (14.9 g. 110 mmol, 1.1 equiv.), and sodium acetate (1.00 g, 12.2 mmol) was heated at 250 °C. Within 30 min, the mixture melted, and carbon dioxide and water began to evolve. After 2 h at 250 °C, the mixture was cooled to room temperature and diluted with MeOH (300 mL). A solution of NaOMe (25% wt in MeOH, 50.0 mL) was added and then the mixture was heated under reflux for another 2 h. The mixture was cooled to room temperature. After concentration *in vacuo*, water (200 mL) was added to the residue and the solution was acidified with conc. HCl to pH 1.0. The product was collected by filtration and dried *in vacuo* to give a yellowish powder, which was used in the next step without purification.

Allyl bromide (3.40 mL, 40.0 mmol, 2.0 equiv.) and K_2CO_3 (5.50 g, 40.0 mmol, 2.0 equiv.) were added to a solution of the product (20.0 mmol, 1.0 equiv.) from the previous step in acetone (100 mL). The mixture was heated under reflux for 1 h and then cooled to room temperature. After filtration and concentration *in vacuo*, the residue was dissolved in toluene (100 mL) in a sealed flask. The solution was heated at 140 °C overnight. The mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified through FCC (5% to 20% EtOAc in hexanes) to furnish 2-allylphenalendione.

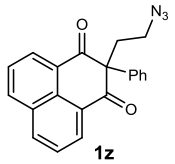
A solution of the 2-allylphenalendione (20.0 mmol, 1.0 equiv.) in MeOH (50.0 mL) and DCM (200 mL) was cooled in a dry ice/acetone bath. A flow of O_3/O_2 was bubbled into the solution. The reaction was monitored using TLC. After it had reached completion, a flow of argon was bubbled into the solution for 30 min. DMS (6.20 g, 100 mmol, 5.0 equiv.) was added to the solution at –78 °C. The mixture was warmed slowly to room temperature and stirred overnight. The mixture was diluted with water (50.0 mL) and extracted with DCM (3 × 50.0 mL). The combined organic phases were washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 50% EtOAc in hexanes) to give the corresponding aldehyde for the next step.

L-selectride in THF (1.00 M, 12.0 mL, 12.0 mmol, 1.2 equiv.) was added slowly to a solution of the aldehyde (10.0 mmol, 1.0 equiv.) in THF (100 mL) at –78 °C. The reaction was monitored using TLC. After it had reached completion, the mixture was diluted with water (50.0 mL) and extracted with Et_2O (3 × 50.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (20% to 50% EtOAc in hexanes) to give the desired alcohol for the next step.

PPh_3 (3.14 g, 12.0 mmol, 1.2 equiv.) was added to a solution of the alcohol (10.0 mmol, 1.0 equiv.) in DCM (100 mL) and hexachloroacetone (10.0 mL) at room temperature. The

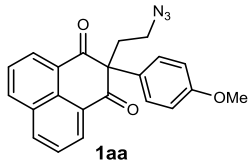
mixture was stirred for 2 days. After concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired alkyl chloride for the next step.

Sodium azide (0.640 g, 10.0 mmol, 2.0 equiv.) was added to a solution of the alkyl chloride (5.00 mmol, 1.0 equiv.) in DMF (30.0 mL). The mixture was heated at 80 °C for 8 h and then cooled to room temperature. The reaction was quenched through the addition of water (50.0 mL) and EtOAc (50.0 mL). The aqueous phase was extracted with EtOAc (2 × 50.0 mL). The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting yellow oil was purified through FCC (5% to 20% EtOAc in hexanes) to give the desired azidophenalendione.



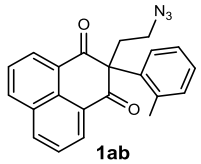
1z

1z. 28% yield. IR (ATR): 3053, 2936, 2080, 1693, 1666, 1577, 1305, 1252, 1006, 829 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.2 Hz, 2H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.70 (t, *J* = 8.2 Hz, 2H), 7.25–7.13 (m, 5H), 3.39 (t, *J* = 6.2 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 137.3, 134.4, 130.7, 129.19, 129.18, 128.2, 128.0, 126.77, 126.71, 70.0, 48.1, 34.2; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{21}H_{16}N_3O_2$ 342.1243, found 342.1247.



1aa

1aa. 25% yield. IR (ATR): 3013, 2932, 2095, 1697, 1669, 1579, 1509, 1296, 1275, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.70 (t, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.68 (td, *J* = 8.4 Hz, 2H), 3.64 (s, 3H), 3.38 (t, *J* = 6.2 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 159.2, 134.3, 132.6, 130.5, 129.1, 128.2, 128.0, 126.7, 114.5, 69.4, 55.1, 48.1, 34.0; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{22}H_{18}N_3O_3$ 372.1348, found 372.1344.



1ab

1ab. 21% yield. IR (ATR): 3057, 2960, 2095, 1696, 1666, 1577, 1285, 1263, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 1.2, 7.2 Hz, 2H), 8.28 (dd, *J* = 1.4, 7.2 Hz, 2H), 7.96 (dt, *J* = 1.2, 7.2 Hz, 2H), 7.36 (dd, *J* = 0.8, 7.8 Hz, 1H), 7.29 (dt, *J* = 1.0, 8.0 Hz, 1H), 7.22 (dt, *J* = 1.0, 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.39 (t, *J* = 6.2 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 1.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.8, 137.1, 135.9, 134.8, 133.0, 129.4, 128.0, 127.6, 126.9, 126.1, 69.2, 47.6, 35.0, 21.7; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{22}H_{18}N_3O_2$ 356.1399, found 356.1392.

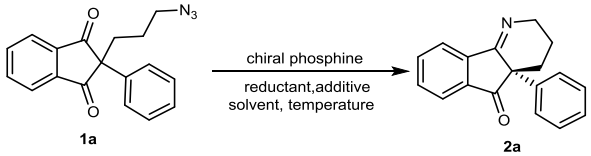
3. Optimization of Enantioselective Staudinger–aza-Wittig Reaction

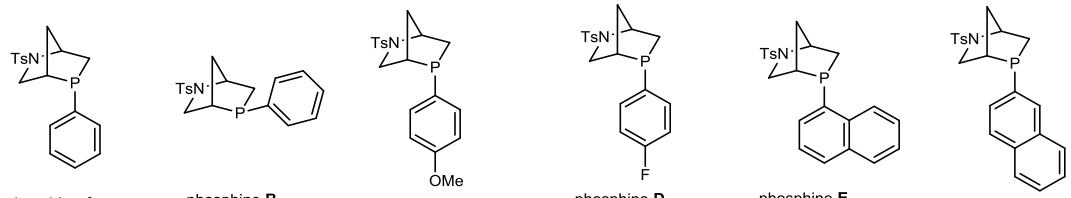
A flame-dried round-bottom flask was charged with the azide **1a** (15.2 mg, 0.0500 mmol, 1.0 equiv.), the phosphine **A** (0.0100 mmol, 0.2 equiv.), and the additive under argon. The solid mixture was dissolved in freshly dried toluene (1 mL), followed by the addition of the reducing reagent (0.1 mmol, 2.0 equiv.). The mixture was stirred until the starting material was consumed (as determined using TLC). The crude reaction mixture was loaded directly onto a SiO_2 column and purified through FCC (20% EA in hexanes) to deliver compound **2a**.

Table S1 summarizes the conditions screened for the enantioselective Staudinger–aza-Wittig reaction. The main parameters varied were the Brønsted acid additive, the solvent, the catalyst, and the silane. Treating **1a** with stoichiometric amounts of the phosphine **A** or **B** at room temperature resulted in both reactions being complete within 12 h in quantitative yields, with ee's of 79 and 11%, respectively (entries 1 and 2). When a catalytic amount of the phosphine **A** was used in the presence of phenylsilane at room temperature, **1a** (>50%) was recovered after two weeks (entry 3). At higher temperatures (100 or 80 °C), lower enantioselectivities were observed (entries 4 and 5).

To test whether the catalytic variant of this reaction could proceed at appreciable rates, various additives known to accelerate the reduction of phosphine oxides were introduced (entries 6–20). Among the acid additives, we found that 2-nitrobenzoic acid gave the best results, facilitating the reaction at room temperature in 99% yield with 86% ee after 28 h (entry 20). Increasing the loading of 2-nitrobenzoic acid to 50 and 100 mol% decreased the enantioselectivity (entries 21 and 22)[9]. From a screen of various solvents for this reaction, toluene gave the optimal results (entries 23–28). Next, several chiral phosphines (**C**–**F**) were screened for this reaction, but the phosphine **A** still provided the best results (entries 29–32). O'Brien's conditions (a combination of 2-nitrobenzoic acid and Hünig's base) led to lower enantioselectivity (entries 33 and 34)[10, 11] Additionally, the chiral phosphine **A** underwent partial inversion at the P center[12–15]. The reaction did not reach completion within one week when employing other silanes (entries 35–38). When molecular sieves (MS) were added as a water scavenger, the enantioselectivity improved further to 90%, while the yield remained near-quantitative at 99% (entry 39). Lowering the catalyst loading to 15 mol% provided a reaction that retained its yield and ee, but at the expense of a lower reaction rate (entry 40).

Table S1. Conditions Tried for the Catalytic Staudinger–aza-Wittig Reaction





phosphine **A** Aldrich # L512398 | phosphine **B** Aldrich # L512389 | phosphine **C** Aldrich # L512478 | phosphine **D** Aldrich # L512451 | phosphine **E** Aldrich # L512486 | phosphine **F** Aldrich # L512494

entry	catalyst	solvent	temp	reductant	additive	time (h)	yield (%)[a]	ee (%)[b]
1	**A** (110 mol%)	toluene	rt	none	none	12	99	79
2	**B** (110 mol%)	toluene	rt	none	none	12	99	11
3[c]	**A** (20 mol%)	toluene	rt	$PhSiH_3$	none	NA	NA	NA
4	**A** (20 mol%)	toluene	100 ℃	$PhSiH_3$	none	12	96	65
5	**A** (20 mol%)	toluene	80 ℃	$PhSiH_3$	none	24	95	71
6	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	benzoic acid	24	99	54
7	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	2-nitro-4-trifluoromethylbenzoic acid	24	99	70
8	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	4-trifluomethylbenzoic acid	24	99	60
9	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	2,4-dinitrobenzoic acid	24	99	60
10	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	4-nitrobenzoic acid	24	99	75
11[c]	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	*r*-Binol	NA	NA	NA
12[c]	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	*s*-Binol	NA	NA	NA
13	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	2-thiophenecarboxylic acid	24	97	59
14[c]	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	*s*-1,1′-binaphthyl-2,2’-dicarboxylic acid	NA	NA	NA
15[c]	**A** (20 mol%)	toluene	30 ℃	$PhSiH_3$	*r*-1,1′-binaphthyl-2,2’-dicarboxylic acid	NA	NA	NA
16	**A** (20 mol%)	toluene/THF (1:9)	30 ℃	$PhSiH_3$	*s*-1,1′-binaphthyl-2,2’-dicarboxylic acid	24	88	66
17	**A** (20 mol%)	toluene/THF (1:9)	30 ℃	$PhSiH_3$	*r*-1,1′-binaphthyl-2,2’-dicarboxylic acid	24	76	74
18[c]	**A** (20 mol%)	toluene	rt	$PhSiH_3$	bis(4-nitrophenyl)phosphinic acid	NA	NA	NA
19[c]	**A** (20 mol%)	EtOAc	rt	$PhSiH_3$	bis(4-nitrophenyl)phosphinic acid	NA	NA	NA
20	**A** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid	28	99	86
21	**A** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid (50%)	24	99	75
22	**A** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid (100%)	24	99	68
23	**A** (20 mol%)	CH_3CN	rt	$PhSiH_3$	2-nitrobenzoic acid	32	90	60
24	**A** (20 mol%)	benzene	rt	$PhSiH_3$	2-nitrobenzoic acid	30	90	84
25	**A** (20 mol%)	THF	rt	$PhSiH_3$	2-nitrobenzoic acid	54	99	79
26[c]	**A** (20 mol%)	dioxane	rt	$PhSiH_3$	2-nitrobenzoic acid	NA	NA	NA
27[c]	**A** (20 mol%)	$CHCl_3$	rt	$PhSiH_3$	2-nitrobenzoic acid	NA	NA	NA
28[c]	**A** (20 mol%)	xylene	rt	$PhSiH_3$	2-nitrobenzoic acid	NA	NA	NA
29	**C** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid	28	99	84

30	**D** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid	28	99	84
31	**E** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid	36	99	66
32	**F** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid	36	99	84
33[d]	**A** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid (0.2 equiv)/Hünig's base (0.2 equiv)	30	97	80
34[e]	**A** (20 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid (0.2 equiv)/Hünig's base (1 equiv)	32	98	75
35[f]	**A** (20 mol%)	toluene	rt	Ph_2SiH_2	2-nitrobenzoic acid	NA	NA	NA
36[f]	**A** (20 mol%)	toluene	rt	Ph_3SiH	2-nitrobenzoic acid	NA	NA	NA
37[f]	**A** (20 mol%)	toluene	rt	$(EtO)_3SiH$	2-nitrobenzoic acid	NA	NA	NA
38[f]	**A** (20 mol%)	toluene	rt	Et_3SiH	2-nitrobenzoic acid	NA	NA	NA
39[g]	**A (20 mol%)**	**toluene**	**rt**	**$PhSiH_3$**	**2-nitrobenzoic acid**	**32**	**99**	**90**
40[g]	**A** (15 mol%)	toluene	rt	$PhSiH_3$	2-nitrobenzoic acid	70	99	90

[a] Isolated yield after silica gel FCC. [b] determined using HPLC. No racemization was observed over months after exposure to air at room temperature. [c] Incomplete reaction after two weeks; NA, not available. [d] Upon completion, the crude ^{31}P NMR spectrum revealed **A**:**B** = 5.5:1. [e] Upon completion, the crude ^{31}P NMR spectrum revealed **A**:**B** = 3:1. [f] Incomplete reaction after 1 week. [g] 4-Å MS (5 mg).

4. Computational Studies

4a. Acid-Free Aza-Wittig Reaction of 3

To explore the enantioselectivity of the aza-Wittig reaction in the absence of an acid catalyst, we computed the reaction of the iminophosphorane **3** derived from HypPhos **A** (Fig. S1). This reaction was calculated to follow a conventional [2+2]/retro-[2+2] cycloaddition pathway through the oxazaphosphetidine intermediate **4**. The [2+2] cycloaddition step has a barrier ($\Delta G^{\ddagger}$) of 11.3 kcal/mol for the major enantiomer (**TS3a**) and 16.9 kcal/mol for the minor enantiomer (**TS3b**). These relatively low barriers mean that the [2+2] cycloaddition would be reversible at room temperature. The enantioselectivity is determined in the retro-[2+2] cycloaddition step. The retro-[2+2] transition state leading to the major (*R*)-enantiomer of the iminoketone product (**TS4a**) is 1.3 kcal/mol lower in energy than that leading to the minor (*S*)-enantiomer (**TS4b**). This energy difference would correspond to an ee of 80% at 25 °C, in agreement with the experimental ee (79%).

Close steric contacts of similar magnitude (2.0 Å) between the iminoketone and phosphine oxide are present in both **TS4a** and **TS4b**. To relieve steric clashing with the iminoketone, the phosphine oxide in **TS4b** takes on a more distorted conformation than the phosphine oxide in **TS4a**. In isolation, the phosphine oxide fragment of **TS4b** was calculated to be 1.3 kcal/mol higher in energy than the corresponding fragment of **TS4a** ($\Delta\Delta E$). The phosphine oxide distortion in **TS4b** translates to a weakened ability to stabilize the breaking P–N bond, as the phenyl group in the distorted phosphine has twisted away from perpendicular alignment with the P–N bond, diminishing resonance stabilization [see insets to Fig. S1(b)]. The C_{Ph}–C_{Ph}–P–N dihedral angle in **TS4b** is –55°, compared with –75° in **TS4a**. The role of the phenyl group in stabilizing the TS is demonstrated by artificially realigning the dihedral angle to –75°, which causes the energy difference between the two phosphine oxide fragments to disappear almost entirely ($\Delta\Delta E$ = 0.1 kcal/mol).

The overall enantioselectivity of the uncatalyzed aza-Wittig reaction of **3** was calculated based on the free energies of **TS4a** and **TS4b** relative to that of the resting state **4b**. The overall barrier for the reaction leading to the major (*R*)-enantiomer of the iminoketone product is 19.7 kcal/mol, as compared with 21.0 kcal/mol for the minor (*S*)-enantiomer, a difference of 1.3 kcal/mol. In comparison, in the presence of benzoic acid (Fig. 2 of the paper), the overall barrier for the reaction leading to the major enantiomer of the iminoketone product was 12.2 kcal/mol, as compared with 15.2 kcal/mol for the minor enantiomer, a difference of 3.0 kcal/mol. Thus, the acid increases the enantioselectivity, relative to that of the acid-free reaction, as observed experimentally.

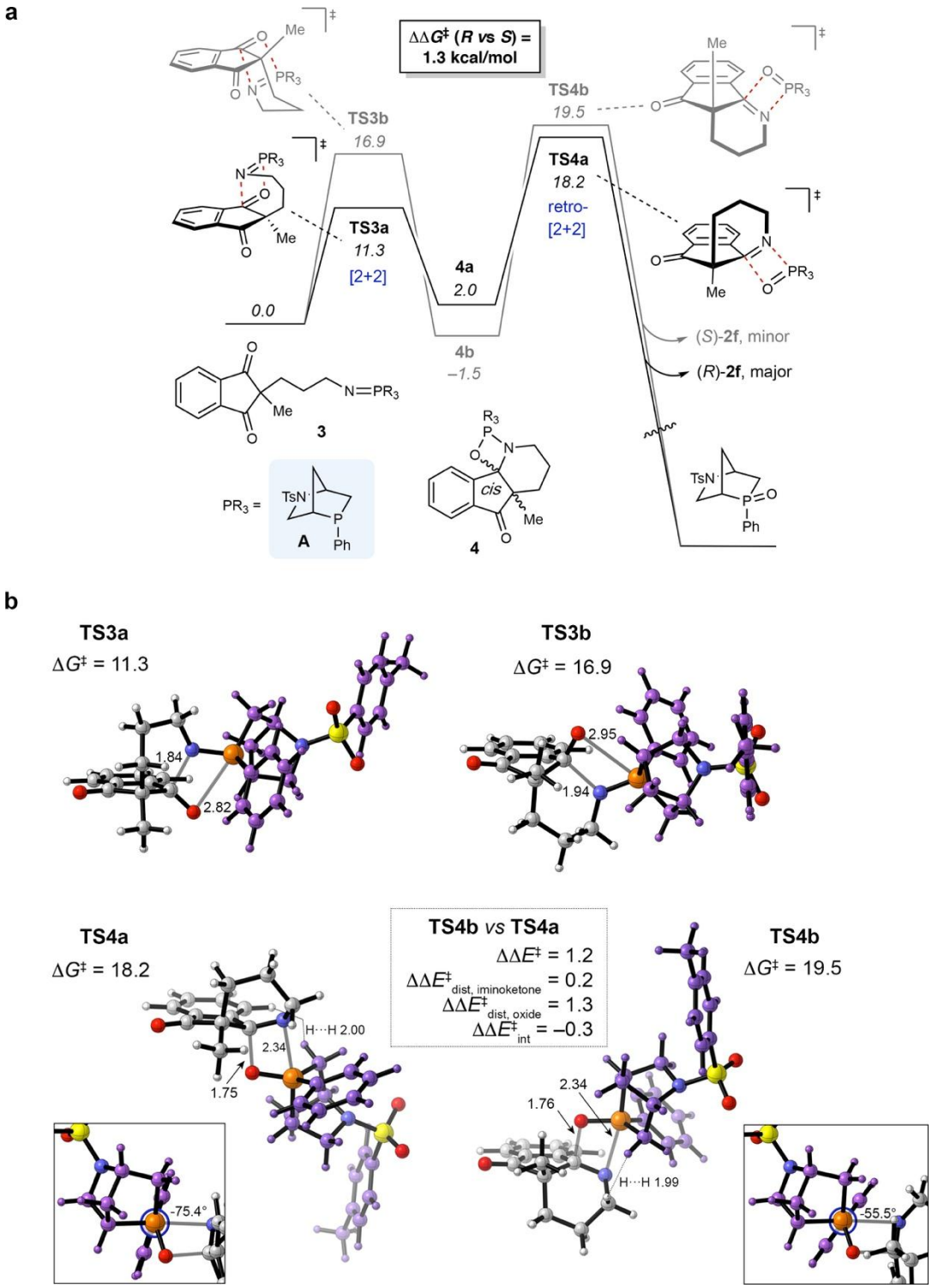


Fig. S1. a Free energy profile and **b** structures of transition states in the non-acid-catalyzed aza-Wittig reaction of the phosphine imine **3**. The HypPhos moiety is highlighted in purple. Newman projections in the insets to **b** provide the dihedral angle between the phenyl ring on the HypPhos unit and the breaking P–N bond. The relative distortion energies and interaction energies of the iminoketone and phosphine oxide fragments of **TS4a** and **TS4b** are also presented in **b**. Distances in Å, $\Delta G^{\ddagger}$ and $\Delta E^{\ddagger}$ in kcal/mol. $\Delta G^{\ddagger}$, Gibbs free energy barriers; $\Delta E^{\ddagger}$, electronic potential energy barriers.

4b. Transition State Geometries for Benzoic Acid–Catalyzed Aza-Wittig Reaction of 3

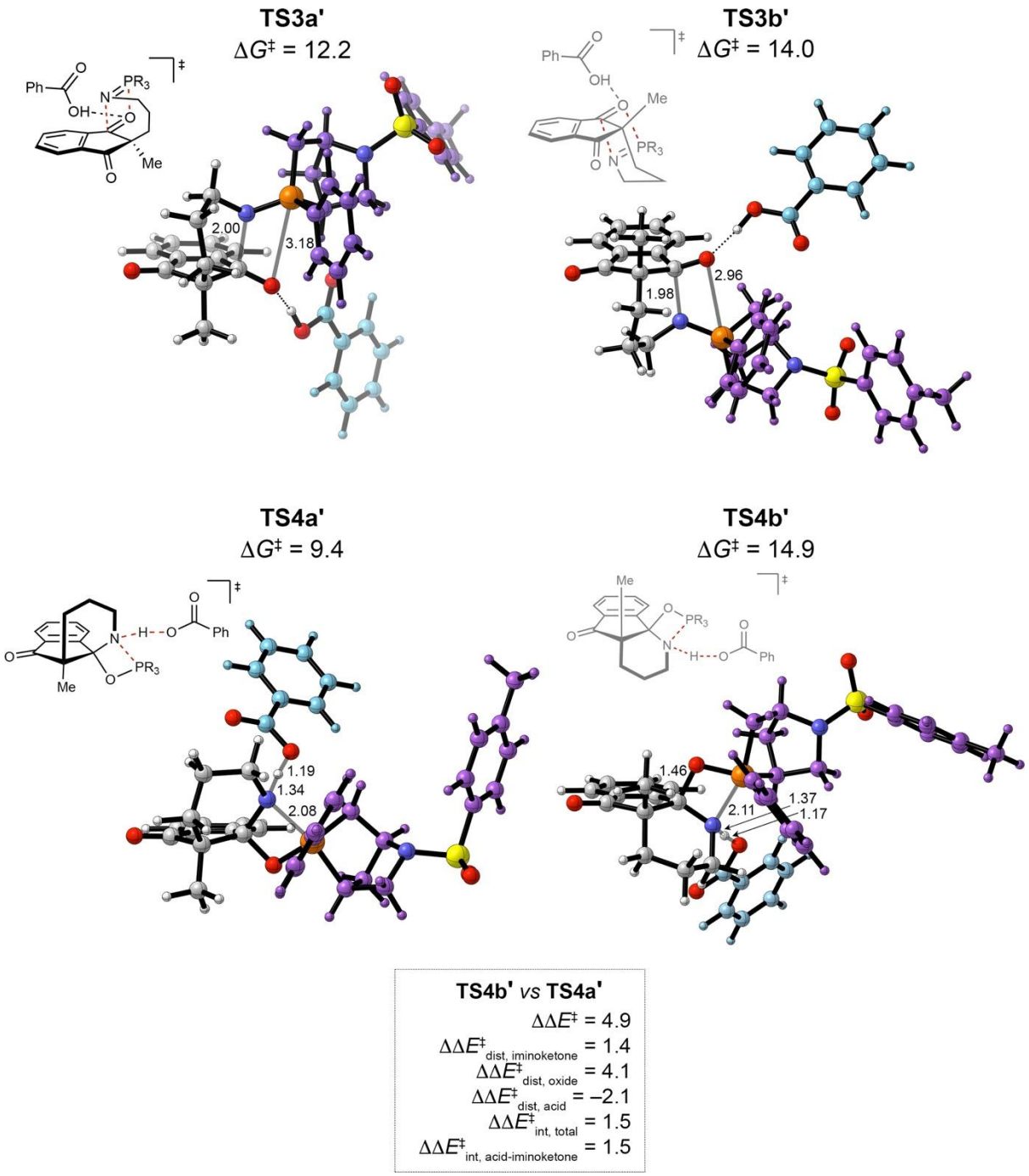
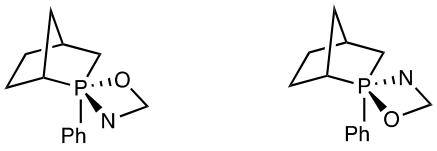


Fig. S2. Structures of transition states in the benzoic acid–catalyzed aza-Wittig reaction of the phosphine imine **3**. The HypPhos moiety is highlighted in purple; the benzoic acid unit, light blue. The relative distortion energies and interaction energies of the iminoketone, phosphine oxide, and benzoic acid fragments of **TS4a´** and **TS4b´** are also presented in **b**. Distances in Å, $\Delta G^{\ddagger}$ in kcal/mol.

4c. Further Discussion of the Mechanistic Pathways and Origins of Enantioselectivity in the Aza-Wittig Reaction

In the aza-Wittig reactions mediated by HypPhos **A** and related bicyclic phosphines (*e.g.*, **B**), two different classes of mechanism can be discerned that differ with respect to (i) the stereochemistry at the phosphorus atom in the transition states and (ii) the intermediates formed during the reaction. With respect to the rigid bicyclic phosphine, the oxygen and nitrogen atoms adopt one of two different arrangements, which we denote "Type I" and "Type II," as displayed below.



"Type I" "Type II"

In the acid-free aza-Wittig reaction of **3** described in Section **4a** above, the lowest-energy pathways leading to the (*R*)- and (*S*)-enantiomers of the iminoketone product both involve Type II structures. In contrast, in the benzoic acid–catalyzed aza-Wittig reaction of **3** described in Section **4b** and in the paper, the lowest-energy pathway leading to the major (*R*)-enantiomer of the iminoketone features Type II structures, but the lowest-energy pathway leading to the minor (*S*)-enantiomer features Type I structures. This switch in structural preference from Type II to Type I for the (*S*)-enantiomer contributes indirectly to the overall enantioselectivity, as described further below.

We studied the relative importance of the Type I and Type II mechanistic pathways for the (*S*)-enantiomer by performing computations on the aza-Wittig reaction mediated by the bicyclic phosphine **B**. Figure S3 presents free energy profiles for two pathways (Type I and Type II) leading only to the formation of the (*S*)-iminoketone product [the profiles for the (*R*)-enantiomer are not shown] in the absence and presence of a benzoic acid catalyst. The structures of the transition states and intermediates are displayed in Figures S4 and S5.

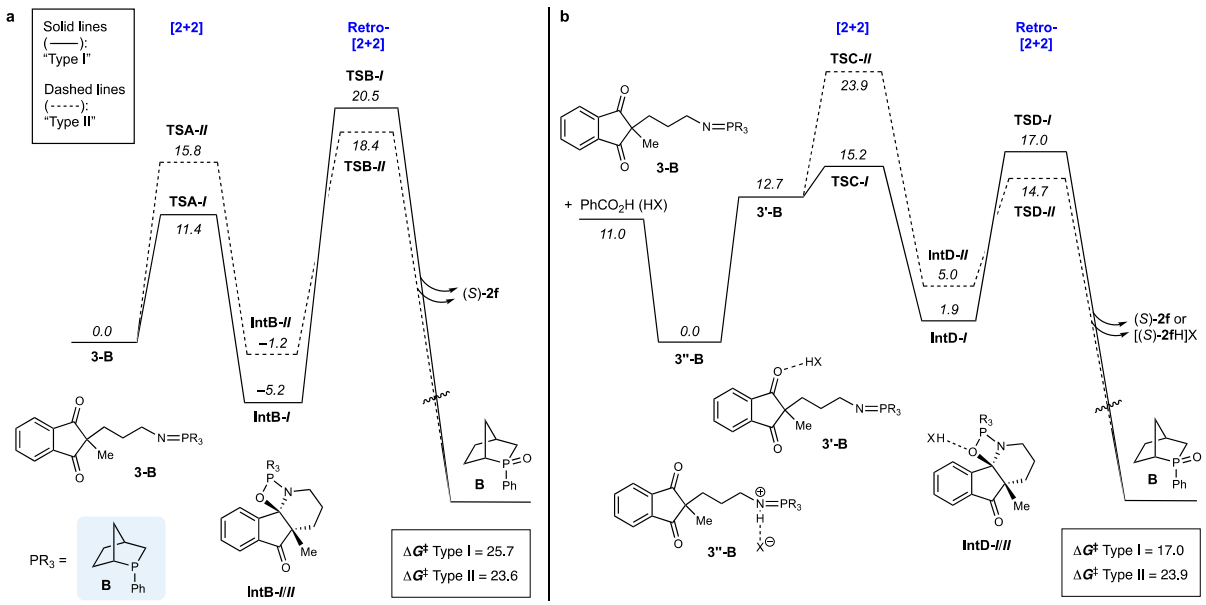


Fig. S3. Type I and Type II pathways leading to the minor (*S*)-enantiomer of the iminoketone product in the **a** acid-free and **b** benzoic acid–catalyzed aza-Wittig reactions of the phosphine imine **3-B** (formed from the azide **1f** and the phosphine **B**). Gibbs free energies (kcal/mol) are given in italics.

In the absence of acid (Fig. S3a), the Type I transition state for the initial [2+2] cycloaddition is lower in energy ($\Delta G^{\ddagger}$ = 11.4 kcal/mol) than the Type II transition state (15.8 kcal/mol). Bond formation is more advanced in the Type I [2+2] transition state (**TSA-*I***) than in the Type II [2+2] transition state (**TSA-*II***). The forming C–N bond is 0.08 Å shorter (1.87 vs 1.95 Å) and the forming P–O bond is 0.12 Å shorter (2.77 vs 2.89 Å) in **TSA-*I*** than they are in **TSA-*II*** (see Fig. S4). In **TSA-*I***, the apical positions of the phosphorus trigonal bipyramid are occupied by the forming P–O bond and the P–C bond to the bridgehead carbon, whereas in **TSA-*II***, the apical positions are occupied by the forming P–O bond and the P–C bond to the methylene bridge—a less preferred arrangement.

In the oxazaphosphetidine intermediate **IntB**, the Type I stereochemistry is also preferred. In the favored **IntB-*I***, the apical positions of the phosphorus trigonal bipyramid are occupied by the P–O bond and the P–C bond to the bridgehead carbon of the bicyclic phosphine. In the disfavored **IntB-*II***, the apical positions are occupied by the P–O bond and the P–C bond to the bridging methylene group—a less stable arrangement. Both **IntB-*I*** and **IntB-*II*** contain close steric contacts between the bicyclic phosphine and the iminoketone, but the steric clash in **IntB-*II*** is stronger (H···H, 1.96 Å vs 2.04 Å).

In the retro-[2+2] cycloaddition, the energy ordering of the Type I and Type II structures reverses. The Type II transition state is now lower in energy than the Type I transition state. Type II retro-[2+2] transition state **TSB-*II*** benefits from stronger partial bonds within the breaking four-membered ring: between carbon and oxygen and, especially, between phosphorus and nitrogen. The P–N distance is 0.11 Å shorter in **TSB-*II*** than it is in **TSB-*I***. Furthermore, in **TSB-*II***, the apical positions of the phosphorus trigonal bipyramid are occupied by the breaking P–N bond and the P–C bond to the bridgehead carbon atom—a more stable arrangement than in **TSB-*I***, where the apical positions are occupied by the breaking P–N bond

and the P–C bond to the methylene bridge.

The rate-determining steps of both the Type I and the Type II pathways leading to the (*S*)-iminoketone from the phosphine imine **3-B** are the retro-[2+2] cycloadditions. The overall aza-Wittig reaction of **3-B** represents a Curtin–Hammett scenario. The [2+2] cycloaddition of **3-B** to give **IntB** is reversible, and the intermediate **IntB-*I*** represents the resting state of the system. Overall, in this non-acid-catalyzed reaction, the preferred mechanistic pathway to form the (*S*)-iminoketone is the one involving Type II structures. Its total activation barrier ($\Delta G^{\ddagger}$ = 23.6 kcal/mol) is 2.1 kcal/mol lower than the Type I pathway barrier ($\Delta G^{\ddagger}$ = 25.7 kcal/mol).

The corresponding benzoic acid–catalyzed aza-Wittig reaction of the phosphine imine **3-B** is displayed in Fig. S3b. In this reaction, the energy ordering of the Type I versus Type II structures at each stationary point (**TSC**, **IntD**, **TSD**) resembles those in the non-acid-catalyzed reaction. That is, the [2+2] cycloaddition transition state and oxazaphosphetidine intermediate prefer the Type I stereochemistry, but the retro-[2+2] cycloaddition transition state prefers Type II. The acid-catalyzed reaction differs from the acid-free reaction in that, unlike the acid-free reaction, the acid-catalyzed reaction is not a Curtin–Hammett scenario. The Type I and Type II pathways feature different rate-limiting steps. The retro-[2+2] cycloaddition is rate-limiting for Type I, while the [2+2] cycloaddition is rate-limiting for Type II. The overall barrier for the Type I pathway is 17.0 kcal/mol, compared with 23.9 kcal/mol for Type II. This situation is due mainly to the high energy of the Type II [2+2] cycloaddition transition state **TSC-*II*** (23.9 kcal/mol), which, compared to the other transition states, has been stabilized only weakly by the acid catalyst. Bond formation in **TSC-*II*** is less advanced than in **TSC-*I***: the forming C–N bond is 0.07 Å longer (2.07 vs 2.00 Å) and the forming P–O bond is 0.29 Å longer (3.34 vs 3.05 Å) in **TSC-*II*** than they are in **TSC-*I***. The difference between the forming P–O bond lengths in these Type I and Type II transition states is even greater than was the case in the acid-free reaction, such that **TSC-*II*** derives little stabilization from the P–O interaction.

Overall, the benzoic acid–catalyzed aza-Wittig reaction leading to the (*S*)-iminoketone from **3-B** favors a Type I pathway, in contrast to the acid-free reaction, which favored a Type II pathway. The rate-limiting step in the acid-catalyzed reaction is the retro-[2+2] cycloaddition that takes place through transition state **TSD-*I***. Even though there is a lower-energy retro-[2+2] transition state present on the energy surface (**TSD-*II***), it is inaccessible because of the high energy of its upstream steps; hence, transition state **TSD-*I*** determines the rate of (*S*)-product formation. The switch from a Type II to a Type I mechanism for the (*S*)-enantiomer upon going from acid-free to acid-catalyzed conditions plays an important and indirect role in determining the overall enantioselectivity of the aza-Wittig reaction.

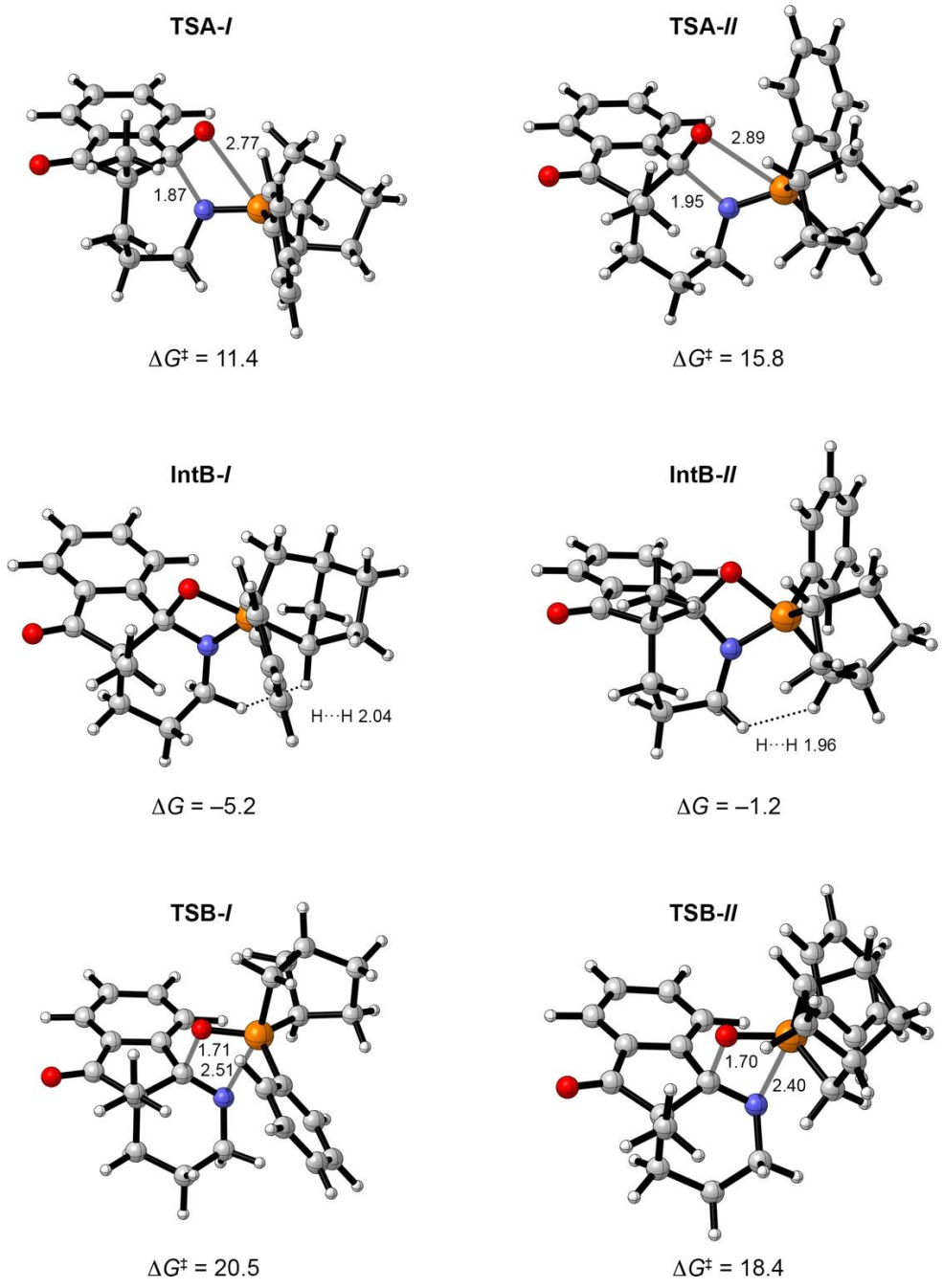


Fig. S4. Structures of Type I and Type II transition states in the non-acid-catalyzed aza-Wittig reaction of the phosphine imine **3-B** leading to the minor enantiomer of the iminoketone product. Distances in Å, $\Delta G^{\ddagger}$ in kcal/mol.

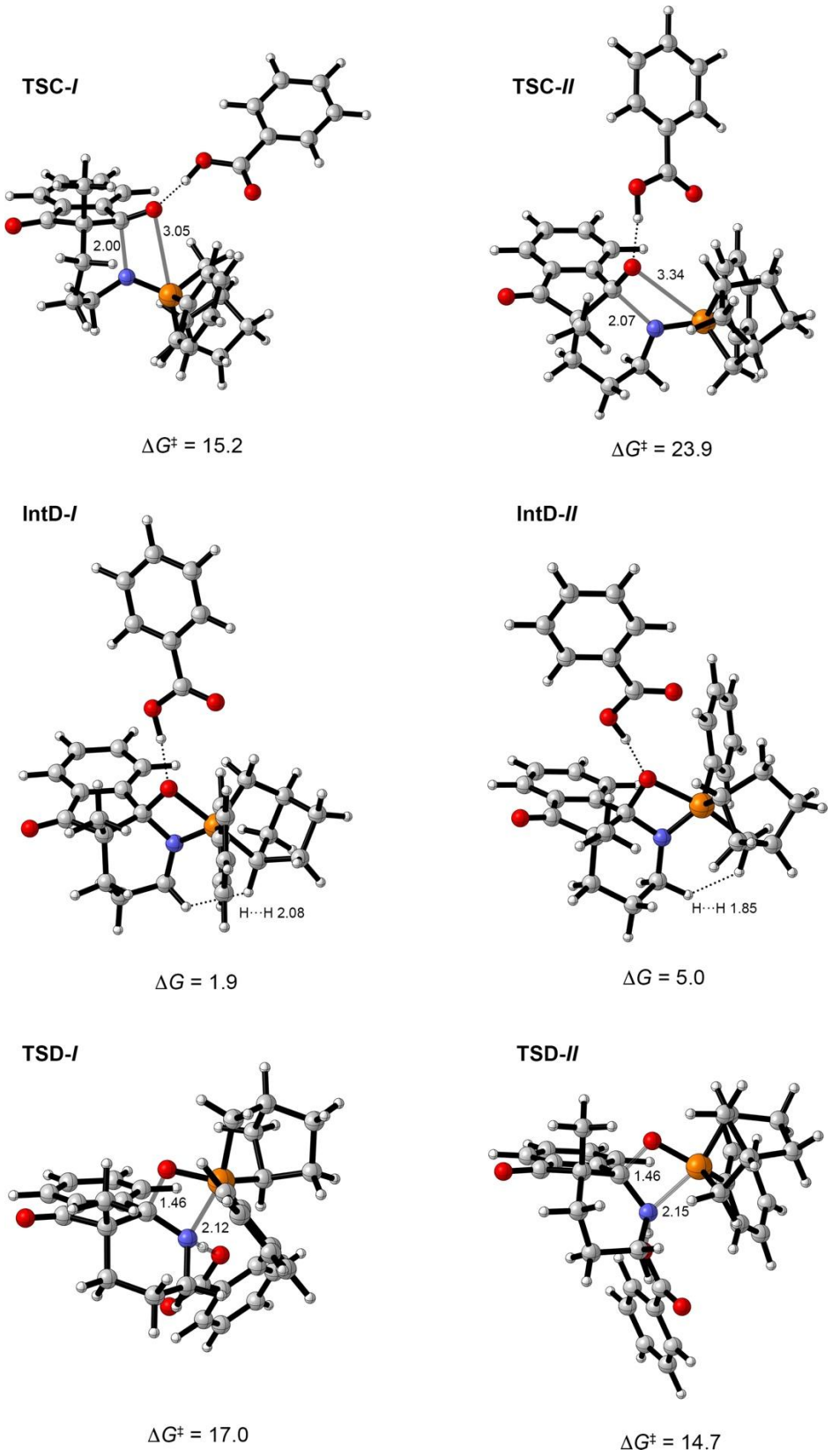


Fig. S5. Structures of Type I and Type II transition states in the benzoic acid–catalyzed aza-Wittig reaction of the phosphine imine **3-B** leading to the minor (*S*)-enantiomer of the iminoketone product. Distances in Å, $\Delta G^{\ddagger}$ in kcal/mol.

4d. Computational Methods and Data

Density functional theory calculations were performed in Gaussian 09[16]. Geometry optimizations were performed at the B3LYP/6-31G(d) level of theory[17–20], modeling the solvent (toluene) with the SMD implicit solvent model[21]. Vibrational frequency calculations at this level confirmed the nature of each stationary point (local minimum or transition state) and provided thermochemical data. Intrinsic reaction coordinate[22,23] calculations identified the species immediately preceding and following each transition state. Single-point energies were calculated with the M06-2X/6-311++G(d,p) level[24] in SMD toluene. The total free energy of each species was calculated by adding the B3LYP thermochemical corrections to the M06-2X potential energies; they are reported at a standard state of 1 mol/L and 298.15 K.

4e. Computational Geometries and Energies

Cartesian coordinates are listed below, along with the following energies (in Hartree):

E: Sum of B3LYP/6-31G(d) electronic potential energy and free energy of solvation

H: B3LYP/6-31G(d) enthalpy in solution at 298.15 K

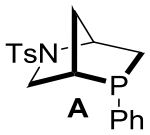
G: B3LYP/6-31G(d) Gibbs free energy in solution at 1 mol/L and 298.15 K

E_{LBS}: Sum of M06-2X/6-311++G(d,p) electronic potential energy and free energy of solvation

G_{tot}: Total Gibbs free energy in toluene at the M06-2X/6-311++G(d,p)-SMD//B3LYP/6-31G(d)-SMD level of theory at 1 mol/L and 298.15 K

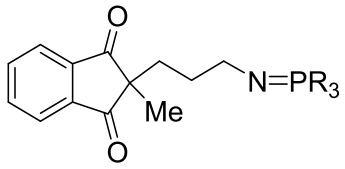
Part A – Reactions Mediated by Chiral Phosphine A

In this Part, PR_3 refers to the phosphine **A**.



Non-Acid-Catalyzed Reaction

Phosphine imine 3



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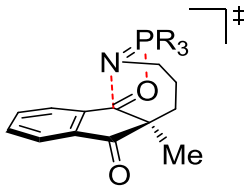

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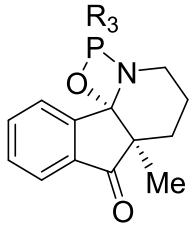

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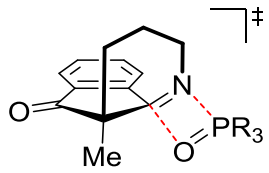

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C	-4.202425	-2.481803	0.405601
C	-3.258928	-1.896236	-0.446684
C	-2.636460	-2.675118	-1.422281
C	-2.915532	-4.042678	-1.470116
C	-3.822530	-4.632898	-0.575258
C	-4.488301	-3.848533	0.363663
C	-4.244343	0.935507	1.806520
O	-5.653146	-1.599426	2.125357
C	0.777320	0.016192	1.224922
C	1.276576	-1.279100	0.546724
C	1.549101	-0.644871	-0.828201
C	1.964949	0.955030	0.941095
C	0.169324	-0.217765	-1.361694
H	-1.976306	-2.222802	-2.154202
H	-5.228834	-4.271847	1.036625
H	-4.023249	-5.699005	-0.637526
H	-2.432725	-4.660358	-2.223361
H	-3.097323	2.151266	-2.235023
H	-3.342511	2.373295	-0.512842
H	-6.271543	0.948996	0.221145
H	-6.003984	-0.451086	-0.794846
H	-5.073066	0.788188	-2.456751
H	-5.530093	2.243018	-1.572956
H	-3.446354	0.625261	2.485157
H	-5.180189	0.968026	2.374928
H	-4.025473	1.945327	1.450895
H	0.224073	0.524165	-2.159811
H	-0.392821	-1.074040	-1.735455
H	1.736622	2.018636	1.017811
H	2.793209	0.722645	1.625101
H	2.107273	-1.246513	-1.545941
H	0.528869	-0.058314	2.284200
H	2.188742	-1.665364	1.014636
H	0.528783	-2.076547	0.511054
H	-0.165359	2.676474	-1.791497
H	-0.191613	5.119878	-1.509848
H	-0.846664	6.127468	0.667792
H	-1.464068	4.653497	2.574597
H	-1.422476	2.199325	2.308969
N	2.296641	0.596033	-0.464405
S	3.812280	0.917041	-1.083871
O	4.138201	2.279014	-0.648091
O	3.755103	0.554749	-2.505027

C	4.986260	-0.190373	-0.294094
C	5.232853	-1.451160	-0.849372
C	5.627570	0.205657	0.881912
C	6.116448	-2.316280	-0.210653
H	4.760671	-1.736192	-1.783693
C	6.509885	-0.675281	1.507851
H	5.460772	1.199221	1.283809
C	6.764933	-1.947207	0.979194
H	6.315838	-3.291409	-0.648719
H	7.016004	-0.362877	2.417679
C	7.711954	-2.901874	1.663368
H	7.170813	-3.756616	2.089900
H	8.447113	-3.307787	0.958458
H	8.256872	-2.413729	2.477235

1 imaginary frequency

E = -2351.036873

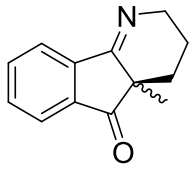
H = -2350.415110

G = -2350.515326

E_{LBS} = -2350.808091

G_{tot} = -2350.286544

Product 2f



N	-1.189408	-1.832312	-0.127734
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C	-1.061171	0.661548	0.220978
C	-2.328034	0.789881	-0.636105
C	-3.294512	-0.345225	-0.254502
C	-2.633439	-1.737274	-0.360096
C	0.951227	-0.701783	0.099942
C	1.352488	0.625039	-0.129286
C	0.155041	1.503635	-0.219438
C	2.700901	0.963480	-0.259319
C	3.647695	-0.052745	-0.142738
C	3.247526	-1.380798	0.086206
C	1.899170	-1.720964	0.201367
O	0.131294	2.679477	-0.536739
C	-1.319410	1.045564	1.702479
H	-2.783778	-2.147542	-1.369051
H	-3.126076	-2.447162	0.316999

H	-4.178918	-0.322223	-0.902251
H	-3.658940	-0.182212	0.766170
H	2.993270	1.992862	-0.446087
H	4.705560	0.178369	-0.232707
H	4.004631	-2.156110	0.170015
H	1.588210	-2.748466	0.364163
H	-2.104486	0.426491	2.145892
H	-1.626244	2.095735	1.760869
H	-0.416886	0.920387	2.310786
H	-2.797587	1.769322	-0.493169
H	-2.059845	0.713452	-1.698073

0 imaginary frequencies

E = -633.203436

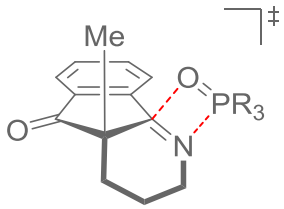
H = -632.957768

G = -633.005354

E_{LBS} = -633.102819

G_{tot} = -632.904737

Transition state TS3b

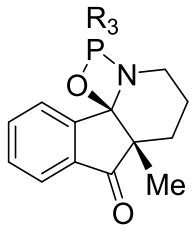


C	1.328589	2.383534	-1.261671
C	0.801897	2.250742	0.036471
C	0.506632	3.403390	0.780341
C	0.725303	4.668615	0.233236
C	1.234414	4.795077	-1.059714
C	1.536743	3.651941	-1.803295
P	0.563107	0.570572	0.727348
O	2.143888	-0.671952	-1.431186
C	2.894234	-0.897283	-0.443755
N	1.936920	-0.205764	1.094213
C	2.336618	-0.649228	2.425429
C	2.464940	-2.173925	2.453128
C	3.519789	-2.659720	1.457328
C	3.240415	-2.387674	-0.058409
C	4.652804	-2.497889	-0.686752
C	5.244762	-1.135051	-0.680510
C	4.248698	-0.187025	-0.404742
C	4.585095	1.160923	-0.304542
C	5.920641	1.533307	-0.484669

C	6.910531	0.582104	-0.777151
C	6.577269	-0.766971	-0.880724
C	2.260105	-3.397067	-0.643019
O	5.193911	-3.527218	-1.051886
C	-0.610191	-0.379573	-0.384372
C	-1.338311	-1.250285	0.663873
C	-1.909077	-0.087389	1.490047
C	-1.759005	0.534831	-0.848408
C	-0.689016	0.627742	2.117079
H	3.828664	1.908154	-0.088946
H	7.327034	-1.522446	-1.099305
H	7.939486	0.902350	-0.917774
H	6.198739	2.581193	-0.400781
H	3.310997	-0.202880	2.677209
H	1.642374	-0.315025	3.208038
H	3.670081	-3.741473	1.562967
H	4.472693	-2.194608	1.743878
H	2.761898	-2.495500	3.461318
H	1.486986	-2.628766	2.246228
H	1.991466	-3.120090	-1.665573
H	2.712269	-4.394581	-0.655277
H	1.336960	-3.446590	-0.053885
H	-0.939951	1.641474	2.430224
H	-0.319339	0.076700	2.986587
H	-1.438693	1.465765	-1.317895
H	-2.399895	-0.013306	-1.552586
H	-2.665893	-0.336833	2.233383
H	-0.074075	-0.890821	-1.180706
H	-2.122175	-1.861020	0.203981
H	-0.674150	-1.900865	1.240652
H	0.106746	3.330123	1.786316
H	0.490511	5.553715	0.818018
H	1.397022	5.781497	-1.485814
H	1.940612	3.745189	-2.807814
H	1.600576	1.490392	-1.818412
N	-2.459206	0.809975	0.435245
S	-4.044999	1.329890	0.448083
O	-4.374897	1.581117	1.856165
O	-4.122258	2.387838	-0.563987
C	-5.080210	-0.023313	-0.119966
C	-5.588585	-0.943459	0.802873
C	-5.349014	-0.161243	-1.484378
C	-6.359157	-2.009820	0.347278
H	-5.402411	-0.810678	1.863440

C -6.121273 -1.236723 -1.921747
H -4.979045 0.575811 -2.188970
C -6.636960 -2.176437 -1.018775
H -6.760301 -2.721019 1.065347
H -6.333153 -1.341526 -2.982824
C -7.499061 -3.319611 -1.494154
H -7.352813 -3.517093 -2.560756
H -7.282984 -4.241419 -0.942758
H -8.563704 -3.095527 -1.344084
1 imaginary frequency
E = -2351.038235
H = -2350.416761
G = -2350.517222
E_{LBS} = -2350.809610
G_{tot} = -2350.288598

Intermediate 4b



C -6.690838 -2.080827 -0.750054
C -6.275143 -1.935168 0.583615
C -5.474251 -0.867227 0.977866
C -5.075348 0.079071 0.026951
C -5.487353 -0.035548 -1.302861
C -6.289310 -1.113334 -1.679896
S -3.999175 1.435715 0.513321
O -4.221710 1.677740 1.943782
N -2.415042 0.934317 0.367278
C -1.808761 -0.037316 1.326265
C -1.460015 -1.220497 0.409980
C -0.757713 -0.383382 -0.676515
C -1.842980 0.672760 -0.978138
P 0.712896 0.358338 0.268343
C -0.464926 0.550075 1.792905
C 1.002319 2.135811 -0.143890
C 1.129155 2.533095 -1.485849
C 1.363438 3.868203 -1.813149
C 1.513211 4.822710 -0.804493
C 1.422893 4.434913 0.532511
C 1.157706 3.103252 0.859850

O	1.881084	-0.213432	-1.055086
C	2.757440	-0.822779	-0.148242
N	1.967956	-0.505968	1.050788
C	2.227511	-1.084072	2.368202
C	3.069033	-2.368071	2.215555
C	2.663319	-3.144192	0.957048
C	3.001953	-2.370912	-0.346078
C	4.518458	-2.498335	-0.611725
C	5.135986	-1.162854	-0.499061
C	4.161602	-0.210149	-0.193879
C	4.531469	1.123954	-0.011824
C	5.877721	1.468360	-0.141017
C	6.852763	0.504771	-0.452495
C	6.487638	-0.824571	-0.634503
C	2.239082	-2.961298	-1.538147
O	5.096003	-3.545917	-0.856471
O	-4.172284	2.497531	-0.484266
H	3.791760	1.882442	0.222132
H	7.219936	-1.590863	-0.872620
H	7.892843	0.804571	-0.548445
H	6.179541	2.503440	-0.001314
H	2.735032	-0.369787	3.031808
H	1.276644	-1.346596	2.840757
H	1.583213	-3.343496	0.984752
H	3.165173	-4.118002	0.923775
H	2.931601	-2.984422	3.111251
H	4.135813	-2.117922	2.174277
H	2.461796	-2.424217	-2.464915
H	2.523065	-4.011201	-1.670003
H	1.157727	-2.912036	-1.374949
H	-0.604072	1.590003	2.090892
H	-0.110925	0.002916	2.670582
H	-1.470330	1.597932	-1.420430
H	-2.588831	0.237973	-1.657891
H	-2.494486	-0.242726	2.148804
H	-0.422999	-0.913840	-1.566010
H	-2.350027	-1.730113	0.024670
H	-0.811231	-1.959332	0.891950
H	1.091126	2.824603	1.906911
H	1.549883	5.168096	1.324565
H	1.705415	5.861467	-1.059762
H	1.442747	4.160245	-2.856964
H	1.063119	1.791102	-2.273993
H	-5.184145	-0.750660	2.016780

H	-5.207906	0.724158	-2.024764
H	-6.594020	-2.663196	1.325863
H	-6.616154	-1.196075	-2.713373
C	-7.548818	-3.251755	-1.161550
H	-7.928835	-3.133044	-2.180876
H	-6.979963	-4.190159	-1.125368
H	-8.407741	-3.371708	-0.490815

0 imaginary frequencies

E = -2351.067058

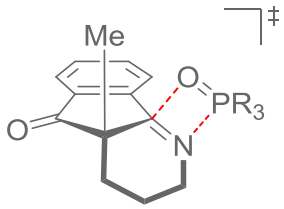
H = -2350.443196

G = -2350.543622

E_{LBS} = -2350.841397

G_{tot} = -2350.317962

Transition state TS4b



C	-6.942261	-1.589198	-1.318900
C	-6.404535	-2.061742	-0.110739
C	-5.503680	-1.298547	0.626477
C	-5.127430	-0.036491	0.153619
C	-5.659187	0.463121	-1.037785
C	-6.560203	-0.316542	-1.763217
S	-3.925949	0.936349	1.069621
O	-3.981631	0.499315	2.469504
N	-2.401950	0.534480	0.520937
C	-1.766221	-0.771373	0.860946
C	-1.475777	-1.366063	-0.527151
C	-0.840275	-0.088024	-1.118095
C	-1.965116	0.930522	-0.844532
P	0.637085	0.154754	0.051448
C	-0.386103	-0.476865	1.477574
C	0.904364	1.959027	0.045665
C	0.997437	2.616607	-1.190374
C	1.183415	3.999402	-1.239433
C	1.263301	4.735424	-0.056339
C	1.169770	4.084858	1.176794
C	1.001375	2.701990	1.229266
O	1.667779	-0.763480	-0.743462
C	3.062917	-0.731005	0.327469

N	2.532388	-0.075851	1.395867
C	2.564495	-0.827816	2.647553
C	3.973708	-1.387535	2.890373
C	4.448706	-2.303420	1.733105
C	3.574765	-2.194725	0.427121
C	4.523727	-2.332431	-0.780487
C	4.856580	-0.967776	-1.245239
C	4.051330	-0.034714	-0.581637
C	4.279460	1.330301	-0.757723
C	5.276881	1.729071	-1.649657
C	6.054719	0.788248	-2.345299
C	5.856620	-0.574526	-2.138574
C	2.511861	-3.298265	0.392939
O	4.945366	-3.384187	-1.232624
O	-4.124907	2.339052	0.690104
H	3.703260	2.062252	-0.203561
H	6.468404	-1.321243	-2.637214
H	6.826789	1.129778	-3.029568
H	5.462661	2.789367	-1.802519
H	2.296158	-0.145739	3.464274
H	1.842540	-1.664251	2.703657
H	4.435138	-3.354807	2.039739
H	5.493315	-2.070581	1.498424
H	4.006719	-1.935527	3.840535
H	4.655355	-0.534381	2.985957
H	1.870613	-3.203813	-0.486427
H	3.017044	-4.268856	0.344614
H	1.881006	-3.289647	1.286849
H	-0.432557	0.254608	2.287035
H	0.063760	-1.394879	1.862279
H	-1.652317	1.974842	-0.854429
H	-2.769672	0.796948	-1.581519
H	-2.399836	-1.358089	1.526416
H	-0.551847	-0.139487	-2.168484
H	-2.391545	-1.652569	-1.055577
H	-0.799334	-2.224567	-0.495809
H	0.962474	2.199807	2.189751
H	1.235358	4.653782	2.100033
H	1.401068	5.812680	-0.093695
H	1.263330	4.498404	-2.201323
H	0.937295	2.051723	-2.116624
H	-5.118086	-1.662356	1.573060
H	-5.393915	1.459202	-1.375573
H	-6.705241	-3.037534	0.263342

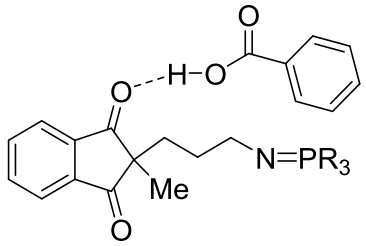
H -6.980349 0.077116 -2.685345
C -7.903764 -2.437829 -2.113866
H -8.402727 -1.855975 -2.894927
H -7.381801 -3.270797 -2.603296
H -8.675371 -2.876432 -1.470654
1 imaginary frequencies
E = -2351.035831
H = -2350.414260
G = -2350.514198
E_{LBS} = -2350.806111
G_{tot} = -2350.284478

Benzoic Acid–Catalyzed Reaction

In the structures below, X^- refers to $PhCO_2^-$.

Benzoic acid
C 0.087684 1.706302 0.000000
C -0.000000 0.222938 0.000000
O 1.362578 2.165697 -0.000000
O -0.866912 2.460775 0.000000
H 1.297961 3.140080 -0.000000
C -1.275055 -0.360382 0.000000
C -1.409292 -1.746151 0.000000
C -0.271120 -2.557363 0.000000
C 1.001361 -1.980260 -0.000000
C 1.140656 -0.593586 -0.000000
H -2.146416 0.286313 0.000000
H -2.398991 -2.194234 0.000000
H -0.375957 -3.639102 0.000000
H 1.885844 -2.611268 -0.000000
H 2.126832 -0.142559 -0.000000
0 imaginary frequencies
E = -420.832522
H = -420.708628
G = -420.745802
E_{LBS} = -420.784094
G_{tot} = -420.697375

Complex of phosphine imine 3 with benzoic acid, bound through oxygen (3´)

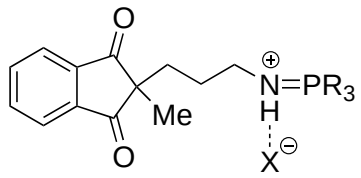


C	1.634865	1.980939	2.504615
C	1.481018	1.766012	1.125109
C	0.866973	2.759964	0.346819
C	0.437148	3.950805	0.931445
C	0.604230	4.158865	2.302406
C	1.199943	3.171598	3.089014
P	1.902500	0.142419	0.382403
N	0.748037	-0.937982	0.340825
C	-0.089094	-1.280669	1.482276
C	-1.368136	-1.973044	0.992298
C	-2.272084	-2.423210	2.146753
C	-3.595247	-3.111284	1.731995
C	-4.453654	-2.214459	0.827990
C	-4.720725	-2.923624	-0.443889
C	-4.079571	-4.172451	-0.427360
C	-3.354003	-4.357331	0.857606
C	-5.476545	-2.511243	-1.544802
C	-5.569116	-3.386209	-2.627798
C	-4.926971	-4.636597	-2.612396
C	-4.174584	-5.044838	-1.510631
O	-4.851370	-1.100917	1.150804
C	-4.404789	-3.508889	2.985734
O	-2.697069	-5.330687	1.179764
C	3.594379	-0.365815	1.064570
C	4.096023	-1.205735	-0.134322
C	4.072501	-0.060746	-1.162612
C	4.597126	0.805035	1.040706
C	2.589139	0.339515	-1.328519
H	-5.972918	-1.544054	-1.553892
H	-3.674523	-6.008401	-1.488972
H	-5.019881	-5.292404	-3.473823
H	-6.147690	-3.097099	-3.500780
H	0.430275	-1.965630	2.177583
H	-0.377776	-0.399701	2.083395
H	-2.535286	-1.558566	2.769679

H	-1.728687	-3.128835	2.788184
H	-1.075916	-2.831917	0.374090
H	-1.901612	-1.275594	0.333331
H	-5.351171	-3.995297	2.722223
H	-3.821446	-4.206672	3.594729
H	-4.632237	-2.619716	3.582141
H	2.489440	1.352763	-1.723139
H	2.048398	-0.359023	-1.975368
H	4.249598	1.712795	1.536274
H	5.544317	0.494530	1.503293
H	4.563875	-0.251644	-2.116373
H	3.546986	-0.883557	2.024648
H	5.105879	-1.596840	0.030027
H	3.428381	-2.030825	-0.399438
H	0.721073	2.604792	-0.718788
H	-0.028209	4.716258	0.316475
H	0.268927	5.087370	2.756599
H	1.327587	3.327427	4.156920
H	2.097604	1.220310	3.128943
H	-5.818381	0.303298	0.571488
O	-6.264373	1.187038	0.553060
C	-6.938659	1.330650	-0.592269
O	-6.976020	0.473333	-1.464117
C	-7.642355	2.640652	-0.702862
C	-7.588467	3.600261	0.318230
C	-8.262889	4.811527	0.171598
C	-8.991977	5.071764	-0.991379
C	-9.047414	4.117654	-2.011246
C	-8.375435	2.906316	-1.867677
H	-7.020485	3.393314	1.218477
H	-8.219533	5.552934	0.964839
H	-9.516396	6.017249	-1.103137
H	-9.613887	4.319288	-2.916330
H	-8.406687	2.153203	-2.648238
N	4.752027	1.042522	-0.419434
S	6.130692	1.774061	-1.008383
O	5.903776	1.974124	-2.444214
O	6.399428	2.897949	-0.104741
C	7.497923	0.619466	-0.838100
C	7.770787	-0.288146	-1.864449
C	8.264502	0.621498	0.332406
C	8.809021	-1.205431	-1.705989
H	7.197122	-0.259001	-2.784820
C	9.297336	-0.301986	0.472621

H 8.069538 1.356188 1.106217
C 9.583963 -1.232578 -0.538368
H 9.027419 -1.904764 -2.509039
H 9.898370 -0.293538 1.378907
C 10.703084 -2.229999 -0.366223
H 10.478252 -2.941171 0.439121
H 10.873401 -2.805244 -1.281396
H 11.642815 -1.731405 -0.099974
0 imaginary frequencies
E = -2771.918001
H = -2771.168963
G = -2771.301135
E_{LBS} = -2771.625686
G_{tot} = -2771.008820

Complex of phosphine imine 3 with benzoic acid, bound through nitrogen (3 ´)



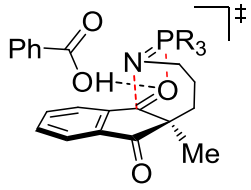
C 2.002535 -1.083553 2.809237
C 1.588130 -0.042040 1.960100
C 1.639741 1.289102 2.408418
C 2.130977 1.564933 3.684604
C 2.555194 0.529998 4.520538
C 2.484851 -0.794885 4.085238
P 0.882689 -0.423724 0.326809
N -0.762084 -0.480117 0.255585
C -1.572310 -1.138741 1.293975
C -3.012101 -1.303090 0.798396
C -3.890218 -2.013916 1.837177
C -5.364260 -2.229713 1.423588
C -6.088887 -0.899459 1.134966
C -6.627529 -0.950862 -0.250822
C -6.282141 -2.167923 -0.853987
C -5.487975 -2.996468 0.092199
C -7.369907 0.009602 -0.939035
C -7.757411 -0.279153 -2.247215
C -7.412168 -1.500807 -2.852267
C -6.670999 -2.459660 -2.162341
O -6.211443 0.021692 1.921712
C -6.117196 -2.993424 2.533486
O -5.019557 -4.098475 -0.134462

C	1.612562	-1.998337	-0.348483
C	1.357244	-1.768636	-1.858780
C	2.190015	-0.481284	-1.978648
C	3.156836	-1.927545	-0.303863
C	1.481402	0.578076	-1.103672
H	-7.628994	0.951334	-0.464680
H	-6.398377	-3.405001	-2.622017
H	-7.727816	-1.695110	-3.873611
H	-8.332739	0.449150	-2.812063
H	-1.146031	-2.125665	1.517931
H	-1.563504	-0.560634	2.229420
H	-3.892784	-1.441535	2.773418
H	-3.466271	-3.001387	2.061545
H	-2.993004	-1.869098	-0.141108
H	-3.412517	-0.308576	0.566248
H	-7.167695	-3.161076	2.269255
H	-5.648815	-3.968830	2.700620
H	-6.088917	-2.419569	3.465437
H	2.139608	1.388143	-0.790572
H	0.606663	1.007112	-1.598467
H	3.571929	-1.675625	0.674122
H	3.569413	-2.889938	-0.626994
H	2.384760	-0.116442	-2.985662
H	1.201229	-2.914429	0.078267
H	1.768216	-2.586561	-2.458718
H	0.302264	-1.628624	-2.109055
H	1.264319	2.084904	1.771457
H	2.172992	2.594573	4.028629
H	2.933526	0.754063	5.514303
H	2.804109	-1.603703	4.736441
H	1.950870	-2.118920	2.484409
H	-1.189290	0.425970	-0.122638
O	-1.858955	1.786950	-0.698568
C	-1.204592	2.781648	-0.245244
O	-0.081627	2.725679	0.318940
C	-1.843336	4.149439	-0.420191
C	-3.098970	4.280610	-1.026746
C	-3.681319	5.538364	-1.186173
C	-3.012323	6.681215	-0.739566
C	-1.759128	6.559006	-0.132899
C	-1.180185	5.299776	0.025086
H	-3.603309	3.381885	-1.366497
H	-4.657062	5.629321	-1.657999
H	-3.465293	7.662139	-0.863264

H	-1.235197	7.445998	0.216055
H	-0.207944	5.183073	0.493237
N	3.470746	-0.849170	-1.289312
S	4.838456	-1.095219	-2.266420
O	4.989128	-2.514829	-2.632982
O	4.760615	-0.081083	-3.326279
C	6.160334	-0.684020	-1.132372
C	7.133158	-1.638517	-0.841854
C	6.231969	0.606305	-0.595906
C	8.187943	-1.294688	0.005408
H	7.064254	-2.631624	-1.272237
C	7.288929	0.929164	0.246762
H	5.470020	1.341938	-0.832423
C	8.284143	-0.013238	0.560461
H	8.948315	-2.036561	0.235237
H	7.347406	1.929714	0.668178
C	9.429236	0.361436	1.468090
H	10.057057	1.136313	1.009945
H	9.066032	0.765839	2.420682
H	10.067543	-0.499952	1.686973

0 imaginary frequencies
E = -2771.929085
H = -2771.180368
G = -2771.311304
ELBS = -2771.642179
Gtot = -2771.024399

Transition state TS3a´



C	4.415012	0.857608	-3.524798
C	4.164678	0.298607	-2.267553
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C	2.083651	1.524734	-2.056091
C	2.331818	2.085296	-3.310057
C	3.483863	1.752760	-4.044003
C	2.997283	-0.104920	-0.212405
C	4.410542	-0.775940	-0.082118
C	5.024522	-0.622820	-1.484340

O	2.409633	0.373705	0.801832
C	4.416885	-2.225167	0.437095
C	3.839299	-3.286366	-0.519988
C	2.736305	-2.725804	-1.436526
N	1.926471	-1.688442	-0.800798
P	0.530793	-2.040630	-0.059154
C	0.620007	-2.819433	1.598676
C	1.318877	-2.123037	2.602817
C	1.429492	-2.666890	3.881789
C	0.856336	-3.908057	4.170451
C	0.168570	-4.605632	3.177165
C	0.046359	-4.064856	1.895884
C	5.241908	0.110261	0.876880
O	6.062953	-1.141149	-1.863935
C	-0.566659	-0.543294	-0.000583
C	-1.811224	-0.852871	0.853955
C	-1.821490	-1.978014	-1.295278
C	-1.177355	-0.588762	-1.422441
C	-0.651585	-2.982183	-1.161473
H	1.198231	1.799627	-1.490226
H	5.321711	0.601614	-4.065774
H	3.649978	2.208404	-5.016528
H	1.624248	2.797981	-3.726406
H	3.198533	-2.269444	-2.322748
H	2.120793	-3.550283	-1.826770
H	3.852905	-2.226630	1.376209
H	5.447127	-2.496038	0.694621
H	4.633914	-3.701808	-1.151792
H	3.445561	-4.118592	0.076812
H	5.248036	1.160095	0.563661
H	6.277293	-0.244822	0.907101
H	4.815810	0.065356	1.883616
H	-0.987219	-3.938621	-0.759702
H	-0.165053	-3.153109	-2.127476
H	-1.595925	-1.230803	1.854463
H	-2.417527	0.057876	0.942255
H	-2.526043	-2.266183	-2.075284
H	-0.054329	0.374058	0.284546
H	-1.919450	0.205144	-1.555397
H	-0.436866	-0.527920	-2.224048
H	-0.501524	-4.620087	1.142523
H	-0.280174	-5.570334	3.397051
H	0.945851	-4.329989	5.167896
H	1.965316	-2.120625	4.653323

H	1.777259	-1.164608	2.369559
H	2.021588	1.938773	1.045283
O	1.927383	2.905789	1.327829
C	0.732432	3.380075	0.996391
O	-0.129847	2.723085	0.418905
C	0.526548	4.807526	1.387437
C	1.518320	5.543762	2.050948
C	1.286260	6.874954	2.394371
C	0.066415	7.478374	2.078562
C	-0.924896	6.747691	1.417563
C	-0.695538	5.417634	1.073681
H	2.463304	5.069840	2.292536
H	2.057635	7.442235	2.908233
H	-0.111506	8.516569	2.346941
H	-1.874149	7.215855	1.171096
H	-1.452040	4.833734	0.559644
N	-2.487913	-1.897527	0.036753
S	-4.118439	-2.203240	0.223752
O	-4.410266	-3.363821	-0.626219
O	-4.351327	-2.229066	1.671174
C	-5.026908	-0.803853	-0.440165
C	-5.404617	-0.797881	-1.787470
C	-5.321379	0.283453	0.386299
C	-6.067712	0.311826	-2.303538
H	-5.202606	-1.660581	-2.413556
C	-5.985337	1.386795	-0.149493
H	-5.055403	0.256554	1.437511
C	-6.365704	1.422322	-1.497456
H	-6.367236	0.313702	-3.348873
H	-6.216670	2.231304	0.494598
C	-7.102742	2.608124	-2.069243
H	-6.681129	2.913210	-3.033963
H	-8.160134	2.367934	-2.242071
H	-7.065446	3.468613	-1.394139

1 imaginary frequency

E = -2771.904467

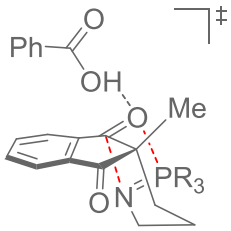
H = -2771.156699

G = -2771.279933

E_{LBS} = -2771.629556

G_{tot} = -2771.005023

Transition state TS3b´



C	1.838333	-2.505301	-1.445922
C	0.311157	-2.571595	-1.660917
C	0.151156	-1.621767	-2.871855
C	0.893467	-0.428186	-2.249488
P	-0.570556	-1.567201	-0.345332
C	0.035605	0.033440	-1.049559
C	0.196648	-1.923680	1.278743
C	0.443165	-3.258821	1.643346
C	0.963905	-3.562200	2.900757
C	1.242798	-2.534561	3.804722
C	0.997602	-1.207290	3.448738
C	0.473510	-0.894653	2.192879
N	-2.186656	-1.673303	-0.485558
C	-2.903874	-2.945955	-0.515833
C	-3.264826	-3.496694	0.879496
C	-3.480658	-2.382946	1.920729
C	-4.088826	-1.077355	1.380414
C	-3.135039	-0.226108	0.469532
C	-3.998968	0.251282	-0.679746
C	-5.245984	-0.385330	-0.659949
C	-5.340292	-1.289440	0.513509
C	-3.726719	1.221941	-1.645033
C	-4.702630	1.504194	-2.602000
C	-5.941046	0.839960	-2.596813
C	-6.226382	-0.107369	-1.617102
O	-2.229506	0.494274	0.985773
C	-4.498589	-0.174920	2.568808
O	-6.266984	-2.041625	0.772630
H	-2.786522	1.765010	-1.641715
H	-7.186758	-0.613756	-1.577697
H	-6.682083	1.081510	-3.353976
H	-4.505818	2.256305	-3.361810
H	-3.827193	-2.762289	-1.081384
H	-2.360832	-3.707502	-1.095264
H	-2.524491	-2.114623	2.384404
H	-4.121232	-2.763052	2.724562
H	-2.472713	-4.163371	1.242879
H	-4.169354	-4.109594	0.786240

H	-4.919727	0.779372	2.233505
H	-5.249084	-0.684245	3.182534
H	-3.618521	0.044918	3.180266
H	0.591527	0.636082	-0.331201
H	-0.831869	0.600705	-1.389958
H	2.166888	-2.791264	-0.444484
H	2.339757	-3.146058	-2.180661
H	1.147426	0.391994	-2.918602
H	-0.066243	-3.587349	-1.786375
H	0.662892	-2.014502	-3.756736
H	-0.889342	-1.398984	-3.123173
H	0.274007	0.141166	1.937645
H	1.211266	-0.405998	4.150778
H	1.648988	-2.769593	4.784949
H	1.153137	-4.597288	3.171788
H	0.232684	-4.067255	0.947308
H	-1.752660	1.999949	0.704771
O	-1.536450	2.980376	0.547833
C	-0.279206	3.263422	0.875110
O	0.531281	2.434367	1.278129
C	0.069835	4.706424	0.699991
C	-0.877224	5.652163	0.281845
C	-0.509823	6.988649	0.131242
C	0.802322	7.389098	0.395371
C	1.749256	6.449845	0.812978
C	1.384145	5.114427	0.965620
H	-1.894419	5.335357	0.079687
H	-1.247305	7.718318	-0.192237
H	1.086645	8.431482	0.276468
H	2.770486	6.759458	1.018299
H	2.105505	4.371436	1.289479
N	2.132586	-1.066223	-1.700477
S	3.628950	-0.681927	-2.383685
O	4.091264	-1.756107	-3.279899
O	3.501234	0.687342	-2.901805
C	4.702625	-0.678694	-0.949784
C	5.834765	-1.491008	-0.945435
C	4.427416	0.180776	0.119691
C	6.698698	-1.445283	0.150290
H	6.033694	-2.146686	-1.786087
C	5.299012	0.211244	1.201847
H	3.543798	0.810807	0.110120
C	6.447671	-0.598656	1.236129
H	7.582176	-2.078473	0.157385

H 5.085853 0.874584 2.036551
C 7.381166 -0.546799 2.420204
H 6.858025 -0.804565 3.349546
H 8.219510 -1.239960 2.302246
H 7.793810 0.460948 2.554502
1 imaginary frequency
E = -2771.900649
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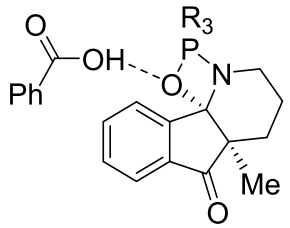
G = -2771.275973
E_{LBS} = -2771.626792
G_{tot} = -2771.002117

Intermediate 4a´



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C 2.982108 1.305999 -3.660408
C 4.230206 0.834487 -4.101352
C 2.498250 -1.076482 -0.654412
C 3.791447 -1.830815 -0.155198
C 4.744515 -1.775333 -1.366053
O 1.780486 -0.346886 0.287089
C 3.492188 -3.271956 0.288440
C 2.767905 -4.124900 -0.773433
C 1.780028 -3.294486 -1.631629
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P 0.208809 -1.568008 0.102795
C 0.323747 -1.998290 1.893279
C 0.654652 -1.013147 2.839736
C 0.733768 -1.330638 4.194918
C 0.515889 -2.641733 4.624205
C 0.210763 -3.632420 3.691567
C 0.102874 -3.310970 2.337014
C 4.464836 -1.046913 0.988996
O 5.748694 -2.454639 -1.507534
C -0.896023 -0.083856 -0.248164
C -2.047156 -0.007885 0.777788

C	-2.341736	-1.752592	-0.865135
C	-1.664253	-0.534096	-1.507488
C	-1.198443	-2.720617	-0.505324
H	1.399684	1.145881	-2.198166
H	5.849534	-0.559032	-3.727069
H	4.695167	1.283830	-4.974724
H	2.501819	2.120445	-4.196807
H	2.238650	-3.047835	-2.597936
H	0.880004	-3.866697	-1.860533
H	2.881440	-3.218324	1.196704
H	4.432775	-3.757629	0.570716
H	3.497762	-4.595979	-1.441721
H	2.236695	-4.940459	-0.268529
H	4.671256	-0.008662	0.707329
H	5.414670	-1.522313	1.257578
H	3.814521	-1.031879	1.868239
H	-1.535577	-3.437293	0.243710
H	-0.906801	-3.275500	-1.401166
H	-1.738151	-0.067305	1.822293
H	-2.589968	0.935354	0.627550
H	-3.136523	-2.231310	-1.437562
H	-0.330191	0.843645	-0.317871
H	-2.382191	0.227100	-1.830847
H	-1.019349	-0.797715	-2.351255
H	-0.143339	-4.098940	1.632792
H	0.046951	-4.656828	4.014490
H	0.587383	-2.889352	5.679840
H	0.976787	-0.553415	4.914254
H	0.866927	-0.000520	2.516882
H	2.096433	1.209594	0.670588
O	2.364709	2.112368	1.041540
C	1.603123	3.082412	0.539654
O	0.673863	2.890732	-0.237799
C	1.982023	4.445548	1.019395
C	3.062717	4.651465	1.888702
C	3.381693	5.941014	2.312070
C	2.625447	7.030445	1.872694
C	1.547361	6.829402	1.006198
C	1.227235	5.542311	0.581038
H	3.645962	3.801900	2.226321
H	4.220561	6.096293	2.985159
H	2.875790	8.034779	2.204575
H	0.958290	7.675826	0.663373
H	0.394343	5.366601	-0.091920

N	-2.870914	-1.187764	0.410476
S	-4.491011	-1.243202	0.796343
O	-4.959139	-2.575762	0.396443
O	-4.584098	-0.777730	2.184300
C	-5.358914	-0.043191	-0.222075
C	-5.849845	-0.422877	-1.476300
C	-5.514083	1.267946	0.234199
C	-6.486226	0.523564	-2.274152
H	-5.755523	-1.451341	-1.808527
C	-6.154146	2.202817	-0.579701
H	-5.161254	1.544826	1.221773
C	-6.646812	1.850388	-1.842823
H	-6.874573	0.226016	-3.245375
H	-6.278974	3.221550	-0.221611
C	-7.357933	2.857596	-2.712530
H	-6.977426	2.837266	-3.740520
H	-8.433486	2.643253	-2.764054
H	-7.240924	3.875144	-2.327143

0 imaginary frequencies

E = -2771.920954

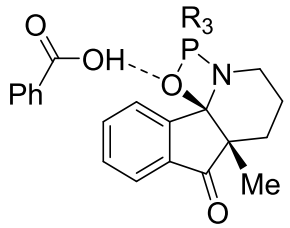
H = -2771.171020

G = -2771.294158

E_{LBS} = -2771.649998

G_{tot} = -2771.023203

Intermediate 4b´



C	6.889074	1.265493	1.119464
C	7.276556	0.122325	0.410240
C	6.457366	-0.427719	-0.576880
C	5.231448	0.174554	-0.853654
C	4.818725	1.319088	-0.163019
C	5.647395	1.851313	0.818217
S	4.210949	-0.483600	-2.170157
O	3.937393	0.569560	-3.159520
C	7.782250	1.869759	2.174528
N	2.751903	-0.749569	-1.354274
C	2.692400	-1.953437	-0.467367
C	1.277156	-2.517146	-0.728539

C	1.155116	-2.262444	-2.246907
C	1.506422	-0.765426	-2.188348
P	-0.082268	-1.347035	-0.041772
O	-1.691977	-0.332948	0.290746
C	-2.508628	-1.467456	0.148888
N	-1.416105	-2.393526	-0.206409
C	-1.534809	-3.854357	-0.159236
C	-2.758991	-4.267610	0.679689
C	-2.948426	-3.330340	1.877174
C	-3.325776	-1.895362	1.432423
C	-3.572057	-1.301004	-0.940945
C	-4.861943	-1.505699	-0.447780
C	-4.801942	-1.889688	0.977025
C	-5.994251	-1.377679	-1.259951
C	-5.809799	-1.037624	-2.596010
C	-4.514117	-0.836563	-3.101337
C	-3.390617	-0.965514	-2.283410
C	0.389636	-0.111745	-1.365463
C	-3.175351	-0.908873	2.600475
O	-5.751292	-2.172568	1.689741
C	0.558852	-0.976275	1.639286
C	0.980881	-2.029800	2.465115
C	1.433790	-1.776562	3.761344
C	1.487500	-0.465276	4.236478
C	1.077335	0.588159	3.416050
C	0.603799	0.337862	2.127386
O	4.830836	-1.743136	-2.624668
O	-2.664758	2.139634	0.095984
C	-1.751983	3.108544	0.110052
C	-2.336552	4.477659	-0.011727
C	-3.718631	4.685958	-0.124208
C	-4.221525	5.981537	-0.235887
C	-3.350792	7.074135	-0.236610
C	-1.972566	6.870389	-0.125050
C	-1.467428	5.577250	-0.012892
O	-0.545863	2.909555	0.210904
H	-2.397966	-0.811099	-2.694722
H	-6.983959	-1.544952	-0.844615
H	-6.666037	-0.929109	-3.256034
H	-4.386121	-0.574553	-4.148504
H	-1.602805	-4.278985	-1.170362
H	-0.635748	-4.268778	0.305935
H	-2.023464	-3.292354	2.467767
H	-3.737315	-3.704143	2.539597

H	-2.619899	-5.302434	1.012542
H	-3.661220	-4.263262	0.055991
H	-3.453129	0.109154	2.309882
H	-3.829000	-1.220183	3.422730
H	-2.143000	-0.882880	2.959294
H	0.671981	0.841947	-0.912507
H	-0.496417	0.069847	-1.979425
H	2.883269	-1.663906	0.567240
H	3.442388	-2.693463	-0.770504
H	1.678171	-0.264172	-3.140046
H	1.203626	-3.562075	-0.424623
H	1.888107	-2.833593	-2.827047
H	0.155714	-2.453464	-2.650661
H	0.258935	1.163358	1.511411
H	1.114800	1.610672	3.782322
H	1.845610	-0.265396	5.242946
H	1.748670	-2.602185	4.393978
H	0.961182	-3.053842	2.101430
H	-2.225787	1.236248	0.168314
H	-4.389463	3.833903	-0.123173
H	-5.293257	6.139130	-0.322322
H	-3.745525	8.083145	-0.324047
H	-1.293987	7.719197	-0.126054
H	-0.400662	5.398526	0.073823
H	6.760573	-1.313857	-1.123849
H	3.859709	1.776503	-0.383468
H	8.231965	-0.347153	0.630319
H	5.327597	2.737137	1.361548
H	7.227280	2.076763	3.097147
H	8.617696	1.207561	2.421549
H	8.203913	2.824190	1.832900

0 imaginary frequencies

E = -2771.923847

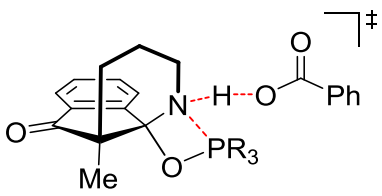
H = -2771.174019

G = -2771.296677

E_{LBS} = -2771.652113

G_{tot} = -2771.024943

Transition state TS4a´



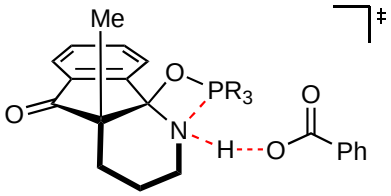
C	2.535419	-2.458971	-1.337373
C	1.070602	-2.244968	-1.760762
C	1.222749	-1.003444	-2.662678
C	1.940137	-0.137719	-1.613738
P	0.016792	-1.547949	-0.321356
C	0.917516	0.082077	-0.490078
C	0.576434	-2.604772	1.062273
C	0.285000	-3.976753	1.012419
C	0.727487	-4.828884	2.024802
C	1.474529	-4.322097	3.089945
C	1.774520	-2.960122	3.141506
C	1.324840	-2.102026	2.136031
O	-1.384203	-1.963832	-1.116235
C	-2.444149	-1.350998	-0.320919
N	-1.583156	-0.674144	0.672333
C	-1.843051	-0.821260	2.131736
C	-3.230094	-1.363526	2.460942
C	-3.473640	-2.659554	1.692910
C	-3.510782	-2.396096	0.179108
C	-4.869873	-1.749337	-0.196882
C	-4.615890	-0.620562	-1.107158
C	-3.241804	-0.403805	-1.217777
C	-2.766659	0.587345	-2.077229
C	-3.688968	1.351336	-2.793807
C	-5.070916	1.139260	-2.662349
C	-5.547535	0.145339	-1.814603
C	-3.441532	-3.720573	-0.609022
O	-5.954065	-2.159031	0.179301
H	-1.704951	0.777665	-2.188326
H	-6.610100	-0.047869	-1.700242
H	-5.764774	1.753829	-3.228959
H	-3.330722	2.128997	-3.462983
H	-1.713008	0.165588	2.586481
H	-1.096550	-1.492416	2.567958
H	-2.685024	-3.386365	1.929347
H	-4.430079	-3.115046	1.972379
H	-3.989635	-0.612270	2.214800
H	-3.287514	-1.535678	3.542412
H	-3.491614	-3.562003	-1.691151
H	-4.288140	-4.350458	-0.315802
H	-2.517147	-4.261622	-0.389362
H	1.370270	0.372987	0.461886
H	0.198472	0.861712	-0.751271
H	2.671188	-3.054947	-0.434402

H	3.090253	-2.939835	-2.150827
H	2.367819	0.797272	-1.977711
H	0.631946	-3.126458	-2.230875
H	1.857689	-1.193389	-3.534417
H	0.273355	-0.577340	-3.001371
H	1.560371	-1.044319	2.197472
H	2.356023	-2.559970	3.967369
H	1.823627	-4.986687	3.875210
H	0.494104	-5.888789	1.975897
H	-0.278472	-4.384824	0.178289
H	-1.575468	0.657482	0.536301
O	-1.441014	1.832265	0.452639
C	-2.392345	2.530264	1.028234
O	-3.287502	2.054492	1.727961
C	-2.316130	4.015079	0.779044
C	-1.303009	4.585491	-0.003029
C	-1.265067	5.964467	-0.211008
C	-2.239766	6.786183	0.360490
C	-3.252690	6.223647	1.142123
C	-3.289153	4.845983	1.349983
H	-0.549263	3.941151	-0.442611
H	-0.475393	6.399104	-0.819018
H	-2.210238	7.860688	0.197401
H	-4.012904	6.859723	1.588516
H	-4.067126	4.389525	1.953349
N	3.006790	-1.054214	-1.095417
S	4.600155	-0.722874	-1.557107
O	4.677067	-0.215578	-2.939287
O	5.368018	-1.920133	-1.188496
C	5.021855	0.628746	-0.459840
C	5.001764	0.424695	0.924570
C	5.418194	1.851053	-0.998507
C	5.370222	1.467020	1.766973
H	4.699988	-0.535176	1.331644
C	5.785288	2.886158	-0.136427
H	5.438207	1.986900	-2.074393
C	5.766004	2.714556	1.252509
H	5.355027	1.313455	2.843393
H	6.093159	3.841165	-0.554152
C	6.154835	3.834567	2.185274
H	5.308454	4.135505	2.815734
H	6.963141	3.526504	2.859721
H	6.492772	4.717659	1.634779

1 imaginary frequency

E = -2771.902272
H = -2771.157439
G = -2771.277799
E_{LBS} = -2771.633967
G_{tot} = -2771.009495

Transition state TS4b´



C	-1.176196	-1.358445	2.258453
C	-0.868341	-2.042356	1.071630
C	-1.219849	-3.396845	0.954439
C	-1.846022	-4.058053	2.011424
C	-2.151537	-3.369006	3.186844
C	-1.823651	-2.017499	3.304858
P	-0.049287	-1.196223	-0.333499
O	1.259499	-1.811048	-1.158668
C	2.414659	-1.549613	-0.302268
N	1.723000	-0.753074	0.718932
C	2.059579	-0.979053	2.147858
C	2.432714	-2.411169	2.510509
C	3.566241	-2.873508	1.598624
C	3.113944	-2.906667	0.113848
C	4.396748	-2.953867	-0.740511
C	4.564299	-1.654158	-1.413893
C	3.463727	-0.833861	-1.157414
C	3.405249	0.438152	-1.730424
C	4.464168	0.859532	-2.536786
C	5.569985	0.030597	-2.784110
C	5.627327	-1.240175	-2.222462
C	2.287081	-4.171487	-0.160270
O	5.143832	-3.915226	-0.814402
C	-0.558118	0.592188	-0.596441
C	-0.594608	0.661689	-2.141617
C	-1.726977	-0.358613	-2.336146
C	-2.056234	0.806203	-0.266372
C	-1.201710	-1.694909	-1.780112
H	2.573263	1.105722	-1.539469
H	6.467364	-1.906047	-2.397564
H	6.379492	0.387322	-3.414859
H	4.431803	1.851342	-2.979916

H	2.902867	-0.320353	2.394555
H	1.209508	-0.632859	2.740816
H	3.929580	-3.871478	1.866935
H	4.414093	-2.185287	1.717880
H	2.761335	-2.431443	3.557188
H	1.568094	-3.080392	2.433160
H	1.915289	-4.198128	-1.188037
H	2.932405	-5.042630	-0.009082
H	1.432058	-4.258370	0.515768
H	-2.031689	-2.328199	-1.461113
H	-0.628568	-2.226296	-2.544766
H	-2.380186	0.392536	0.689694
H	-2.253068	1.884064	-0.264725
H	-2.135728	-0.445008	-3.341994
H	0.089533	1.307144	-0.095475
H	-0.873605	1.663542	-2.483722
H	0.340978	0.366766	-2.625350
H	-1.003331	-3.940963	0.039964
H	-2.103012	-5.108860	1.910928
H	-2.647549	-3.882362	4.005884
H	-2.066385	-1.472944	4.213051
H	-0.924199	-0.308569	2.367891
H	1.958445	0.599321	0.684772
O	1.992294	1.764705	0.754259
C	3.085524	2.278976	1.280922
O	4.004498	1.620887	1.765972
C	3.139465	3.783243	1.254653
C	2.109948	4.555716	0.700206
C	2.198146	5.947857	0.696489
C	3.315318	6.580413	1.247270
C	4.345389	5.815838	1.802060
C	4.256960	4.425193	1.805299
H	1.244969	4.059452	0.273881
H	1.395495	6.539681	0.263767
H	3.383322	7.665413	1.243927
H	5.216249	6.304681	2.231244
H	5.046389	3.814215	2.230734
N	-2.779822	0.130183	-1.385956
S	-4.061671	1.005844	-2.075258
O	-4.458706	0.258161	-3.277050
O	-3.749818	2.442674	-2.197688
C	-5.317046	0.831185	-0.810411
C	-5.899470	1.974544	-0.266876
C	-5.746841	-0.445779	-0.432735

C	-6.920423	1.833886	0.674755
H	-5.558252	2.956066	-0.577596
C	-6.763500	-0.565730	0.507446
H	-5.286801	-1.328256	-0.865282
C	-7.367570	0.569563	1.075826
H	-7.376132	2.723656	1.101258
H	-7.099283	-1.556029	0.805752
C	-8.470350	0.416667	2.093721
H	-8.114607	-0.111537	2.987465
H	-8.861963	1.387748	2.411171
H	-9.305331	-0.167700	1.687930

1 imaginary frequency

E = -2771.897928

H = -2771.152345

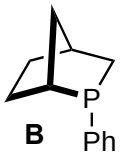
G = -2771.272487

E_{LBS} = -2771.626145

G_{tot} = -2771.000704

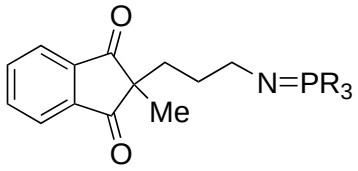
Part B – Reactions Mediated by Chiral Phosphine B

In this Part, PR_3 refers to the phosphine **B**.



Non-Acid-Catalyzed Reaction

Phosphine imine 3-B

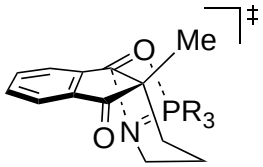


C	-3.567567	-2.949827	-0.763551
C	-3.793734	-1.480675	-1.199955
C	-5.295177	-1.284069	-0.869008
C	-5.532881	-2.184449	0.384459
C	-4.150652	-2.824059	0.663518
P	-2.701292	-0.634196	0.072197
C	-3.225152	-1.817127	1.395927
N	-1.124829	-0.708821	-0.077464
C	3.831013	1.391153	0.110133
C	3.513842	0.876668	-1.307650
C	1.994095	0.887256	-1.600784

C	1.125478	0.060749	-0.644022
C	-0.367422	0.135160	-0.991472
C	4.093256	-0.551182	-1.303351
C	4.726782	-0.797683	0.021163
C	4.574332	0.328052	0.840770
C	5.395795	-1.934876	0.476120
C	5.906986	-1.916854	1.773564
C	5.753372	-0.786884	2.596585
C	5.085931	0.348941	2.139100
O	4.054549	-1.334931	-2.235174
O	3.538269	2.489713	0.547677
C	4.262003	1.735285	-2.349343
C	-3.387064	1.048398	0.363605
H	4.961937	1.226211	2.767070
H	5.508450	-2.803058	-0.166421
H	6.431613	-2.786959	2.158785
H	6.161710	-0.803854	3.603385
H	-0.491841	-0.179527	-2.044584
H	-0.679530	1.195235	-0.954959
H	1.668041	1.935350	-1.583337
H	1.858072	0.524898	-2.628138
H	1.428255	-0.994366	-0.663590
H	1.253069	0.407519	0.389869
H	5.342375	1.750951	-2.163264
H	4.095612	1.331610	-3.353317
H	3.895858	2.766463	-2.314842
H	-3.719173	-1.325702	2.239645
H	-2.309605	-2.294189	1.760534
H	-5.904292	-1.616099	1.244317
H	-6.273343	-2.962280	0.167804
H	-5.565577	-0.239766	-0.692820
H	-5.898562	-1.632053	-1.715849
H	-4.217853	-3.768454	1.212131
H	-3.518169	-1.247652	-2.231661
H	-4.144048	-3.645641	-1.385744
H	-2.516033	-3.255678	-0.780115
C	-3.427272	1.587268	1.659361
C	-3.827886	2.907226	1.867322
C	-4.180514	3.712203	0.781742
C	-4.128763	3.193605	-0.513292
C	-3.733791	1.870900	-0.721176
H	-3.138287	0.977366	2.511313
H	-3.861790	3.308329	2.876888
H	-4.490240	4.741101	0.944558

H -4.395612 3.817376 -1.362402
H -3.700446 1.478226 -1.734582
0 imaginary frequencies
E = -1516.090830
H = -1515.584836
G = -1515.668622
E_{LBS} = -1515.898693
G_{tot} = -1515.476486

Transition state TSA-*I*



C 3.215024 1.382620 0.821651
C 2.386927 0.855522 -0.184041
C 2.292336 1.525216 -1.415445
C 3.036253 2.683458 -1.641120
C 3.866030 3.195257 -0.640522
C 3.948895 2.548057 0.593243
P 1.354710 -0.622958 0.144866
O -0.576818 0.222742 -1.647485
C -1.269349 0.298797 -0.587031
N -0.135406 -0.327457 0.763233
C -0.223025 0.067982 2.180219
C -1.315781 1.124192 2.382069
C -1.261857 2.191758 1.285364
C -1.803404 1.705657 -0.080178
C -3.323822 1.484372 0.084439
C -3.634338 0.057025 -0.134949
C -2.469304 -0.644969 -0.452928
C -2.545444 -2.013755 -0.718739
C -3.783682 -2.650081 -0.636896
C -4.950757 -1.936506 -0.309190
C -4.884110 -0.570638 -0.058992
C -1.562083 2.782003 -1.148356
O -4.129835 2.358260 0.367986
C 2.287446 -1.803155 1.245947
C 1.634871 -3.134061 0.790778
C 2.075998 -3.073294 -0.688882
C 3.600329 -2.843094 -0.554912
C 3.745067 -1.992738 0.746681
C 1.385607 -1.814269 -1.272940

H	-1.656745	-2.580270	-0.979407
H	-5.769756	0.008441	0.187919
H	-5.902875	-2.457873	-0.256785
H	-3.852176	-3.717559	-0.833311
H	-0.421972	-0.804465	2.822123
H	0.722791	0.509192	2.533164
H	-0.227992	2.541419	1.161397
H	-1.859897	3.063032	1.579719
H	-1.176657	1.581846	3.369587
H	-2.303992	0.648902	2.400928
H	-1.969220	2.482585	-2.118775
H	-2.038852	3.721010	-0.846067
H	-0.489681	2.953815	-1.279673
H	1.918156	-1.387834	-2.127374
H	0.357516	-1.988250	-1.586546
H	4.016666	-2.337034	-1.432366
H	4.123837	-3.799767	-0.453761
H	4.275569	-1.053204	0.578516
H	4.303550	-2.543370	1.512195
H	1.825670	-3.961702	-1.276426
H	2.200570	-1.572880	2.309461
H	2.078819	-3.984799	1.321415
H	0.549537	-3.164497	0.928580
H	1.603848	1.158199	-2.168834
H	2.960009	3.191723	-2.598567
H	4.441443	4.099540	-0.819962
H	4.586808	2.945578	1.378007
H	3.298465	0.884638	1.783581

1 imaginary frequency

E = -1516.062451

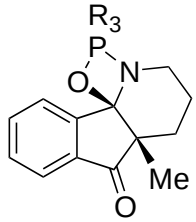
H = -1515.557698

G = -1515.634424

E_{LBS} = -1515.886296

G_{tot} = -1515.458269

Intermediate IntB-*I*



C	-1.739984	2.995211	0.988715
C	-2.254219	1.550393	1.184748

C	-3.701118	1.682681	0.633423
C	-3.593191	2.734824	-0.512759
C	-2.099290	3.125430	-0.509936
P	-1.113079	0.588957	-0.027229
C	-1.259723	2.040005	-1.206655
N	0.250098	0.435432	1.007296
C	1.165478	-0.156060	0.029073
C	1.726139	-1.580800	0.407320
C	1.988674	-1.647503	1.947806
C	0.805967	-1.157644	2.793321
C	0.459217	0.294337	2.442284
C	3.118132	-1.607636	-0.252594
C	3.518127	-0.205230	-0.518141
C	2.436027	0.645310	-0.276937
C	4.766468	0.283317	-0.913894
C	4.921598	1.660717	-1.049750
C	3.843402	2.522348	-0.790320
C	2.595958	2.024339	-0.405691
O	3.784737	-2.606394	-0.468181
O	0.275145	-0.117535	-1.055141
C	0.867148	-2.752428	-0.063895
C	-2.187756	-0.857136	-0.437667
H	1.770844	2.702124	-0.206892
H	5.588695	-0.402683	-1.097946
H	5.879940	2.075185	-1.350896
H	3.983701	3.595665	-0.892540
H	1.282851	0.955169	2.753660
H	-0.432183	0.629455	2.975981
H	2.251802	-2.679814	2.206347
H	2.864387	-1.033096	2.200335
H	1.064398	-1.225682	3.858048
H	-0.073020	-1.794305	2.632153
H	0.631240	-2.660123	-1.126636
H	1.415120	-3.688140	0.091096
H	-0.079128	-2.810002	0.482182
H	-1.676892	1.701673	-2.161751
H	-0.239124	2.376599	-1.409149
H	-3.909125	2.334555	-1.482777
H	-4.221399	3.608277	-0.304310
H	-4.130110	0.737900	0.294466
H	-4.351109	2.056189	1.434385
H	-1.910757	4.115144	-0.939508
H	-2.239307	1.193646	2.217057
H	-2.293190	3.715479	1.605544

H	-0.670655	3.121068	1.193426
C	-2.305231	-1.309693	-1.760202
C	-3.098856	-2.415976	-2.063506
C	-3.764250	-3.104129	-1.045877
C	-3.639895	-2.674119	0.275826
C	-2.865217	-1.550939	0.575227
H	-1.758345	-0.808448	-2.552513
H	-3.186409	-2.749552	-3.094258
H	-4.372876	-3.973012	-1.282188
H	-4.149820	-3.206458	1.074578
H	-2.794714	-1.215458	1.606532

0 imaginary frequencies

E = -1516.090460

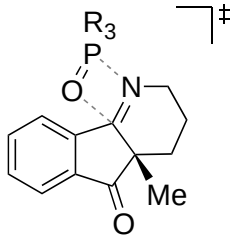
H = -1515.583751

G = -1515.658542

E_{LBS} = -1515.916658

G_{tot} = -1515.484740

Transition state TSB-*I*



C	-2.934350	-0.941060	1.106658
C	-2.348287	-0.642814	-0.133542
C	-2.710519	-1.399700	-1.261408
C	-3.633695	-2.438938	-1.146451
C	-4.220331	-2.721987	0.088909
C	-3.872082	-1.968931	1.212017
P	-1.162567	0.719816	-0.360235
O	0.271663	0.375093	-0.953219
C	1.182612	-0.408387	0.260101
N	0.315235	-0.444777	1.307157
C	0.161132	-1.667236	2.078930
C	0.556144	-2.977027	1.382476
C	1.893602	-2.797504	0.663001
C	1.773146	-1.697364	-0.426152
C	3.190251	-1.290539	-0.865160
C	3.492854	0.038746	-0.298670
C	2.362028	0.552242	0.343002
C	2.451091	1.764728	1.031187
C	3.659671	2.459890	1.014804

C	4.786757	1.949646	0.344818
C	4.712805	0.725603	-0.310566
C	1.004944	-2.231552	-1.644005
O	3.936354	-1.976199	-1.548513
C	-1.313065	2.141588	0.821108
C	-0.863232	3.298036	-0.110141
C	-1.996485	3.174650	-1.153019
C	-3.253921	3.222198	-0.255920
C	-2.806203	2.508125	1.057025
C	-1.832092	1.761582	-1.769751
H	1.597452	2.151518	1.578303
H	5.574641	0.294816	-0.813003
H	5.718145	2.509532	0.356048
H	3.738110	3.410431	1.537283
H	0.764743	-1.591380	3.005434
H	-0.879936	-1.745553	2.423131
H	2.238382	-3.725710	0.191806
H	2.659599	-2.511871	1.398549
H	0.632124	-3.779387	2.128562
H	-0.219231	-3.280035	0.668596
H	0.944746	-1.481747	-2.436639
H	1.533103	-3.106062	-2.039608
H	-0.014582	-2.529042	-1.384700
H	-2.773944	1.369436	-2.164390
H	-1.093650	1.760914	-2.576102
H	-4.114629	2.734414	-0.725853
H	-3.539687	4.260269	-0.054392
H	-3.437132	1.652691	1.305800
H	-2.851778	3.193464	1.910826
H	-1.988393	3.949487	-1.925316
H	-0.732313	1.976433	1.725653
H	-0.894382	4.254916	0.424826
H	0.138718	3.168067	-0.530320
H	-2.266845	-1.183552	-2.229537
H	-3.899230	-3.021930	-2.024135
H	-4.944994	-3.526943	0.176064
H	-4.323561	-2.186236	2.176195
H	-2.654405	-0.375862	1.988693

1 imaginary frequency

E = -1516.055581

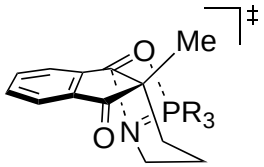
H = -1515.550934

G = -1515.625973

E_{LBS} = -1515.873353

G_{tot} = -1515.443746

Transition state TSA-*II*



C	-1.560116	2.005001	-1.116993
C	-1.956255	1.363981	0.069905
C	-2.623238	2.106811	1.057529
C	-2.905676	3.458877	0.856299
C	-2.529109	4.082708	-0.334091
C	-1.853813	3.354382	-1.315919
P	-1.543642	-0.401959	0.355700
O	0.617132	-0.182247	-1.556192
C	1.293907	-0.341222	-0.506090
N	-0.027985	-0.610487	0.902263
C	0.360635	-1.298237	2.127198
C	1.200828	-2.536960	1.806157
C	2.470867	-2.163578	1.041070
C	2.272961	-1.573802	-0.393144
C	3.625459	-0.868686	-0.662237
C	3.482932	0.544930	-0.229680
C	2.130105	0.838747	-0.007805
C	1.762490	2.105793	0.439904
C	2.763725	3.056580	0.657191
C	4.115490	2.761423	0.418653
C	4.486756	1.496546	-0.031950
C	1.975774	-2.666034	-1.414137
O	4.635454	-1.401515	-1.089732
C	-2.063487	-1.431584	-1.109259
C	-2.437660	-2.746805	-0.384359
C	-3.567623	-2.178370	0.500260
C	-4.453620	-1.446889	-0.537746
C	-3.446079	-0.966287	-1.629611
C	-2.869715	-1.157019	1.436198
H	0.721494	2.350792	0.620770
H	5.526636	1.242123	-0.218415
H	4.871241	3.523263	0.590815
H	2.491121	4.046999	1.014112
H	0.961787	-0.615440	2.748528
H	-0.501172	-1.584848	2.744467
H	3.122373	-3.040252	0.936437
H	3.027388	-1.447399	1.661146
H	1.488878	-3.029875	2.745547

H	0.596909	-3.256647	1.237933
H	1.725724	-2.226386	-2.382986
H	2.852655	-3.311116	-1.535088
H	1.131033	-3.290294	-1.101204
H	-3.561420	-0.407141	1.827008
H	-2.410449	-1.661686	2.290729
H	-5.012495	-0.618382	-0.088748
H	-5.188883	-2.138660	-0.962435
H	-3.500508	0.108884	-1.815425
H	-3.641342	-1.465415	-2.585541
H	-4.113728	-2.926100	1.083345
H	-1.269609	-1.483530	-1.851154
H	-2.801295	-3.496022	-1.097564
H	-1.616568	-3.191366	0.189010
H	-2.919020	1.642239	1.993621
H	-3.421365	4.021576	1.629898
H	-2.754119	5.134113	-0.492596
H	-1.544507	3.838916	-2.238142
H	-0.984163	1.452681	-1.852076

1 imaginary frequency

E = -1516.058913

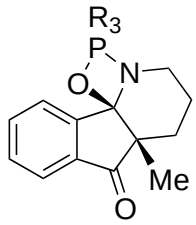
H = -1515.554119

G = -1515.630280

E_{LBS} = -1515.879998

G_{tot} = -1515.451365

Intermediate IntB-*II*

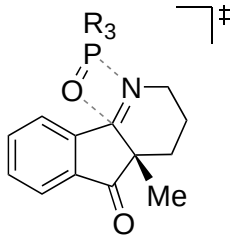


C	-1.946735	1.952026	-1.293095
C	-1.886362	1.323329	-0.037966
C	-2.241506	2.063992	1.099066
C	-2.655639	3.393951	0.986606
C	-2.743010	3.995425	-0.268996
C	-2.389473	3.269343	-1.409099
P	-1.274953	-0.419466	0.103081
O	0.093636	-0.069199	-1.125228
C	1.108429	-0.347186	-0.206370
N	0.213481	-0.688567	0.910792
C	0.660108	-1.333917	2.144169

C	2.033576	-1.998049	1.918802
C	2.127168	-2.601301	0.512656
C	2.105965	-1.512024	-0.592292
C	3.496390	-0.840807	-0.641794
C	3.356581	0.576285	-0.253781
C	2.020736	0.861149	0.035624
C	1.661625	2.145237	0.450085
C	2.658707	3.114429	0.567038
C	4.001818	2.821090	0.272303
C	4.362467	1.543814	-0.142491
C	1.809550	-2.137119	-1.961159
O	4.534451	-1.411027	-0.939830
C	-2.114989	-1.617771	-1.083720
C	-2.323022	-2.858620	-0.190937
C	-3.277681	-2.205710	0.830631
C	-4.367184	-1.614964	-0.094177
C	-3.581376	-1.201923	-1.375965
C	-2.457090	-1.069982	1.485780
H	0.628402	2.389592	0.673758
H	5.392546	1.288675	-0.375318
H	4.755618	3.597674	0.370912
H	2.392670	4.118256	0.889227
H	0.713872	-0.620528	2.979289
H	-0.057667	-2.109754	2.426003
H	1.286381	-3.290169	0.354022
H	3.045736	-3.189311	0.403240
H	2.177564	-2.770799	2.682717
H	2.836826	-1.265966	2.065653
H	1.781540	-1.381183	-2.751573
H	2.589341	-2.866707	-2.206540
H	0.842680	-2.650048	-1.955550
H	-3.117445	-0.284194	1.861741
H	-1.907016	-1.451734	2.349739
H	-4.886265	-0.769809	0.370839
H	-5.124890	-2.371399	-0.328799
H	-3.693122	-0.142029	-1.617488
H	-3.933162	-1.765307	-2.248535
H	-3.682878	-2.897810	1.576859
H	-1.506581	-1.758438	-1.976052
H	-2.801610	-3.674413	-0.747551
H	-1.400924	-3.247254	0.257553
H	-2.177377	1.614946	2.085632
H	-2.914096	3.954861	1.881114
H	-3.076695	5.025901	-0.359166

H -2.443571 3.734216 -2.390087
H -1.628960 1.412314 -2.178438
0 imaginary frequencies
E = -1516.086355
H = -1515.579157
G = -1515.654792
E_{LBS} = -1515.910000
G_{tot} = -1515.478437

Transition state TSB-*II*



C -1.958727 2.135294 -0.735568
C -1.838262 1.148552 0.254799
C -2.156553 1.466105 1.582074
C -2.609206 2.743743 1.909165
C -2.726869 3.722810 0.918842
C -2.394974 3.418958 -0.402338
P -1.286134 -0.520044 -0.240072
O 0.150356 -0.644443 -0.933491
C 1.244580 -0.378189 0.335273
N 0.426294 -0.362434 1.431275
C 0.688168 -1.425120 2.393506
C 2.176308 -1.469163 2.782309
C 3.115179 -1.538308 1.546649
C 2.367930 -1.445051 0.169400
C 3.344996 -0.792937 -0.829999
C 3.063348 0.659984 -0.844504
C 1.886708 0.916663 -0.131529
C 1.494647 2.233500 0.109138
C 2.265026 3.267377 -0.427480
C 3.422757 3.003120 -1.178162
C 3.838751 1.690074 -1.383657
C 1.947796 -2.832293 -0.326015
O 4.215867 -1.376947 -1.454249
C -2.346145 -0.966760 -1.728205
C -2.370499 -2.509202 -1.609250
C -3.051642 -2.582249 -0.224572
C -4.300222 -1.691257 -0.429310
C -3.838645 -0.631721 -1.478656

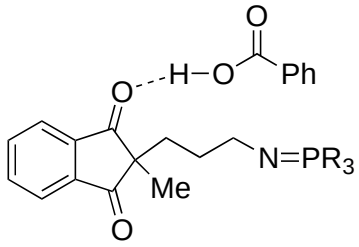
C	-2.043804	-1.910195	0.736064
H	0.618424	2.447455	0.710432
H	4.749261	1.460001	-1.930265
H	4.003699	3.829131	-1.579866
H	1.968168	4.298982	-0.254120
H	0.088676	-1.231519	3.293079
H	0.393024	-2.437083	2.054031
H	3.693160	-2.468860	1.540691
H	3.848912	-0.727309	1.613238
H	2.361312	-2.321166	3.449073
H	2.400778	-0.560881	3.353352
H	1.373522	-2.763745	-1.252931
H	2.850205	-3.419625	-0.527714
H	1.350429	-3.373773	0.413450
H	-2.488868	-1.540733	1.664535
H	-1.248665	-2.608045	1.006820
H	-4.635632	-1.234947	0.508808
H	-5.135916	-2.285499	-0.814171
H	-4.008645	0.394996	-1.147395
H	-4.386595	-0.758325	-2.419787
H	-3.294170	-3.594322	0.114725
H	-1.944731	-0.572227	-2.663394
H	-2.986670	-2.959596	-2.397050
H	-1.380116	-2.975415	-1.636973
H	-2.024939	0.724068	2.361828
H	-2.857649	2.978774	2.940610
H	-3.071065	4.720459	1.178249
H	-2.476123	4.177870	-1.175755
H	-1.705492	1.907728	-1.767255

1 imaginary frequency
E = -1516.055418
H = -1515.550800
G = -1515.626603
E_{LBS} = -1515.875967
G_{tot} = -1515.447152

Benzoic Acid–Catalyzed Reaction

In the structures below, X^- refers to $PhCO_2^-$.

Complex of phosphine imine 3 with benzoic acid, bound through oxygen (3´-B)



C	-4.318373	-2.281995	1.665207
C	-3.945415	-2.095827	0.323867
C	-3.254102	-3.125246	-0.334519
C	-2.964885	-4.320432	0.324274
C	-3.350770	-4.498492	1.654768
C	-4.024044	-3.476046	2.325766
P	-4.177746	-0.461489	-0.488571
N	-2.958302	0.543848	-0.357957
C	-2.335443	0.873833	0.916472
C	-1.024969	1.633176	0.669745
C	-0.326979	2.030807	1.976402
C	0.994775	2.822928	1.822193
C	2.035853	2.057589	0.992538
C	2.428772	2.883193	-0.172182
C	1.706560	4.086805	-0.157696
C	0.798718	4.123891	1.019740
C	3.356984	2.607081	-1.180031
C	3.536621	3.570647	-2.173065
C	2.812729	4.775566	-2.160019
C	1.889218	5.048346	-1.150453
O	2.464493	0.948333	1.290017
C	1.581485	3.154180	3.211441
O	0.042446	5.030834	1.316683
C	-5.911479	0.135748	-0.080942
C	-6.162294	1.004934	-1.338114
C	-6.056919	-0.127199	-2.385897
C	-7.047837	-1.173836	-1.820249
C	-6.952647	-0.996678	-0.271095
C	-4.599790	-0.648682	-2.280452
H	3.917397	1.675580	-1.186863
H	1.324693	5.975670	-1.131101
H	2.977321	5.502962	-2.950342
H	4.248906	3.387876	-2.972847
H	-2.985452	1.509767	1.546496
H	-2.108331	-0.020396	1.526140
H	-0.102680	1.131528	2.564308
H	-1.001993	2.650261	2.580986
H	-1.252171	2.522890	0.068080

H	-0.370911	0.996796	0.059230
H	2.522578	3.710927	3.133719
H	0.869912	3.765265	3.775637
H	1.775605	2.230516	3.765884
H	-4.492671	-1.675682	-2.642589
H	-3.897680	-0.012636	-2.829189
H	-6.799822	-2.191415	-2.141804
H	-8.063626	-0.962959	-2.172364
H	-6.680947	-1.923094	0.241422
H	-7.915668	-0.673594	0.141863
H	-6.293020	0.177332	-3.410047
H	-5.975718	0.660387	0.875653
H	-7.161072	1.458349	-1.318675
H	-5.420854	1.799064	-1.476947
H	-2.932226	-2.992744	-1.364311
H	-2.435568	-5.111613	-0.200193
H	-3.123309	-5.429083	2.167963
H	-4.320678	-3.606815	3.363165
H	-4.845787	-1.494027	2.197485
H	3.619566	-0.328833	0.770271
O	4.143539	-1.169145	0.767648
C	4.992518	-1.172091	-0.264653
O	5.078127	-0.255032	-1.069744
C	5.827586	-2.405487	-0.338616
C	5.707743	-3.439636	0.600789
C	6.510056	-4.574609	0.493043
C	7.433916	-4.683759	-0.549222
C	7.555951	-3.654792	-1.487266
C	6.755904	-2.519677	-1.382581
H	4.989442	-3.349489	1.408140
H	6.414926	-5.374129	1.222780
H	8.058471	-5.569654	-0.630349
H	8.274140	-3.738580	-2.298412
H	6.836015	-1.710388	-2.100934

0 imaginary frequencies

E = -1936.938114

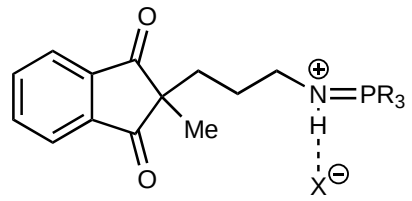
H = -1936.305897

G = -1936.413916

E_{LBS} = -1936.695279

G_{tot} = -1936.171081

Complex of phosphine imine 3 with benzoic acid, bound through nitrogen (3´´-B)



C	4.024733	-2.212900	1.534184
C	3.614448	-1.002261	0.949309
C	3.874382	0.214723	1.603255
C	4.565160	0.209058	2.815516
C	4.985150	-0.994072	3.386709
C	4.708978	-2.205468	2.749383
P	2.634347	-1.003032	-0.585210
N	1.010592	-0.815168	-0.357297
C	0.274749	-1.562906	0.674630
C	-1.232540	-1.430872	0.436893
C	-2.039358	-2.240812	1.460808
C	-3.576638	-2.145165	1.322302
C	-4.082497	-0.698535	1.494357
C	-4.846605	-0.321352	0.274855
C	-4.836973	-1.380677	-0.642502
C	-4.063540	-2.524787	-0.090031
C	-5.506956	0.874285	-0.010903
C	-6.157757	0.982932	-1.239530
C	-6.149129	-0.080160	-2.160113
C	-5.488796	-1.274243	-1.872105
O	-3.899545	0.000386	2.474417
C	-4.258172	-3.055907	2.365666
O	-3.857877	-3.589319	-0.646596
C	3.000052	-2.490715	-1.625494
C	2.534474	-1.942083	-3.000356
C	3.517805	-0.752674	-3.086799
C	4.877504	-1.443846	-2.825446
C	4.534129	-2.610242	-1.844854
C	3.146528	0.179902	-1.902908
H	-5.504873	1.690529	0.705172
H	-5.475607	-2.099737	-2.577606
H	-6.664087	0.036002	-3.109800
H	-6.678734	1.901711	-1.494422
H	0.562965	-2.621757	0.630633
H	0.523897	-1.200955	1.683036
H	-1.784216	-1.912867	2.476528
H	-1.767319	-3.301630	1.385015
H	-1.455212	-1.770095	-0.582298
H	-1.496937	-0.367386	0.485958

H	-5.350912	-2.998797	2.301253
H	-3.961904	-4.097255	2.202575
H	-3.961169	-2.754645	3.375457
H	3.960793	0.827289	-1.572818
H	2.281553	0.811624	-2.117313
H	5.615707	-0.751301	-2.407792
H	5.291539	-1.834819	-3.760595
H	5.113622	-2.566878	-0.920057
H	4.740280	-3.582176	-2.305952
H	3.485537	-0.204175	-4.032038
H	2.509568	-3.405261	-1.285983
H	2.708695	-2.683760	-3.788396
H	1.481085	-1.647182	-3.022855
H	3.504494	1.144033	1.176117
H	4.767803	1.150526	3.318587
H	5.520950	-0.989325	4.332188
H	5.024527	-3.144088	3.196373
H	3.812633	-3.161663	1.049464
H	0.686185	0.195855	-0.475731
O	0.121636	1.720567	-0.659919
C	0.973071	2.560576	-0.222365
O	2.167649	2.313089	0.081784
C	0.489805	3.995461	-0.071754
C	-0.831714	4.343947	-0.378002
C	-1.268820	5.661491	-0.236810
C	-0.386392	6.647701	0.212652
C	0.934229	6.308534	0.520008
C	1.367073	4.990066	0.378224
H	-1.502017	3.564298	-0.725180
H	-2.297604	5.921156	-0.476364
H	-0.726103	7.674903	0.323324
H	1.624378	7.072726	0.870565
H	2.387928	4.704985	0.612026

0 imaginary frequencies

E = -1936.952402

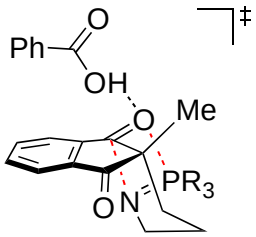
H = -1936.320218

G = -1936.427056

E_{LBS} = -1936.716666

G_{tot} = -1936.191321

Transition state TSC-*I*



C	1.241038	3.568641	-2.551779
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C	0.994864	1.366388	-3.471775
C	-0.389127	1.767845	-2.915387
C	-0.272546	3.310471	-2.839673
P	1.281890	1.320098	-0.875038
C	-0.453481	1.154950	-1.492128
C	1.377825	2.509838	0.516155
C	2.528094	3.302018	0.675744
C	2.648770	4.159497	1.768825
C	1.621908	4.233883	2.712983
C	0.478101	3.448344	2.561284
C	0.350818	2.584786	1.471309
N	1.952737	-0.147285	-0.669491
C	3.396798	-0.362584	-0.693542
C	4.082383	-0.177984	0.676144
C	3.163087	-0.545280	1.855793
C	2.169578	-1.690026	1.591775
C	0.989259	-1.336581	0.620766
C	0.848753	-2.532513	-0.297455
C	1.909593	-3.427269	-0.110568
C	2.813776	-2.933798	0.958447
C	-0.174367	-2.842029	-1.195230
C	-0.090262	-4.032096	-1.919055
C	0.991070	-4.913493	-1.748934
C	1.999119	-4.620200	-0.834587
O	-0.003017	-0.672495	1.035922
C	1.532988	-2.132995	2.930960
O	3.866207	-3.446586	1.306792
H	-1.029386	-2.183987	-1.315991
H	2.831560	-5.298272	-0.668294
H	1.028605	-5.833781	-2.325633
H	-0.878203	-4.287126	-2.623296
H	3.548863	-1.396003	-1.034192
H	3.893626	0.262315	-1.450762
H	2.566290	0.325434	2.149799
H	3.779810	-0.807573	2.723123

H	4.408770	0.862029	0.801476
H	4.989605	-0.794161	0.695556
H	0.800480	-2.935851	2.791536
H	2.310853	-2.493046	3.612594
H	1.015343	-1.284275	3.387615
H	-1.186046	1.636227	-0.841363
H	-0.683258	0.089432	-1.531937
H	-0.921620	3.730288	-2.064149
H	-0.568718	3.763573	-3.791605
H	1.404979	4.181651	-1.662756
H	1.715176	4.087656	-3.392584
H	-1.237773	1.431576	-3.518201
H	2.935259	2.106840	-2.598045
H	1.161656	1.747904	-4.486256
H	1.174193	0.286741	-3.468422
H	-0.537084	1.966771	1.379434
H	-0.322053	3.502034	3.294499
H	1.714595	4.902653	3.564631
H	3.540882	4.769817	1.880754
H	3.331513	3.257820	-0.055773
H	-1.564882	-0.835411	0.753712
O	-2.553653	-1.024643	0.601874
C	-3.287337	0.075134	0.746785
O	-2.826154	1.184358	0.993451
C	-4.753936	-0.162223	0.571296
C	-5.273169	-1.439025	0.314294
C	-6.647348	-1.615352	0.156792
C	-7.510467	-0.521168	0.254955
C	-6.997203	0.753105	0.512345
C	-5.624764	0.931469	0.670366
H	-4.598280	-2.284757	0.242081
H	-7.045565	-2.607034	-0.040874
H	-8.581411	-0.661385	0.132271
H	-7.667306	1.605111	0.590409
H	-5.207322	1.912492	0.872523

1 imaginary frequency

E = -1936.922769

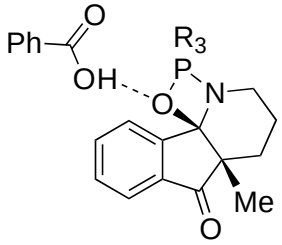
H = -1936.291986

G = -1936.390884

E_{LBS} = -1936.699052

G_{tot} = -1936.167167

Intermediate IntD-*I*



C	3.107787	-3.114725	1.711788
C	3.107124	-1.562440	1.674190
C	2.606390	-1.238730	3.101591
C	1.333555	-2.115734	3.062636
C	1.900350	-3.486102	2.627256
P	1.660068	-0.898880	0.624682
C	0.478318	-1.500564	1.940084
C	1.749275	-1.940230	-0.887669
C	2.982689	-2.114317	-1.534253
C	3.069520	-2.870320	-2.704867
C	1.926924	-3.476905	-3.229064
C	0.698044	-3.315358	-2.585078
C	0.602892	-2.542354	-1.426838
N	2.129221	0.736266	0.509153
C	3.447753	1.376842	0.523403
C	3.540647	2.450771	-0.578643
C	2.760950	2.030816	-1.829013
C	1.237856	1.963342	-1.559197
C	0.940383	1.316434	-0.145850
C	0.282151	2.447071	0.653950
C	0.118187	3.603960	-0.109799
C	0.689159	3.403283	-1.457020
C	-0.155388	2.427113	1.979252
C	-0.754577	3.571824	2.506717
C	-0.921504	4.730632	1.729369
C	-0.482208	4.756252	0.409945
O	0.181951	0.140081	-0.158712
C	0.513835	1.251951	-2.712291
O	0.738723	4.233313	-2.350712
H	-0.029730	1.543500	2.597096
H	-0.593049	5.640281	-0.211634
H	-1.392617	5.606963	2.166177
H	-1.099994	3.568526	3.537450
H	3.662362	1.818574	1.506681
H	4.211343	0.616276	0.338282
H	3.108945	1.047773	-2.172774
H	2.935154	2.738425	-2.647622

H	4.597680	2.617287	-0.815916
H	3.155633	3.407549	-0.205218
H	-0.564672	1.190840	-2.536643
H	0.679092	1.808760	-3.641363
H	0.888408	0.233096	-2.840008
H	-0.256469	-2.178491	1.495070
H	-0.076399	-0.626160	2.290082
H	1.149106	-4.090867	2.107768
H	2.232003	-4.060442	3.499369
H	3.044663	-3.576700	0.724484
H	4.048625	-3.453512	2.162223
H	0.778772	-2.157835	4.005571
H	4.085787	-1.146899	1.427184
H	3.317786	-1.576509	3.865873
H	2.397708	-0.176428	3.274378
H	-0.364949	-2.397406	-0.955506
H	-0.195318	-3.783379	-2.990130
H	1.993537	-4.071749	-4.136272
H	4.029430	-2.989714	-3.200404
H	3.884018	-1.665621	-1.125143
H	-1.455593	0.099749	-0.160793
O	-2.462547	0.193317	-0.183781
C	-3.055819	-0.992676	-0.088426
O	-2.453275	-2.056653	0.011480
C	-4.548486	-0.913667	-0.110776
C	-5.223908	0.311631	-0.202659
C	-6.617819	0.340269	-0.218957
C	-7.344688	-0.850540	-0.144695
C	-6.675030	-2.073924	-0.053510
C	-5.282587	-2.105210	-0.036071
H	-4.653809	1.232291	-0.261008
H	-7.137519	1.291993	-0.290603
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0 imaginary frequencies

E = -1936.943230

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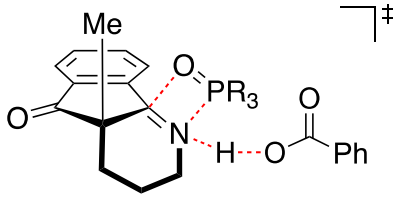
E_{LBS} = -1936.722628

G_{tot} = -1936.188296

Transition state TSD-*I*



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C	4.911465	-1.917184	2.423195
C	3.624077	-2.445315	2.532413
P	1.699030	-0.803537	-0.741491
O	1.465939	0.776101	-1.222943
C	0.651851	1.391773	-0.176959
N	0.394178	0.184567	0.612727
C	0.453663	0.269463	2.091721
C	1.462243	1.267594	2.647978
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C	-0.547518	2.046212	-0.871227
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1 imaginary frequency

E = -1936.918889

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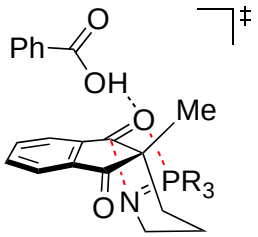
G = -1936.384866

E_{LBS} = -1936.698227

G_{tot} = -1936.164204

Transition state TSC-*II*



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C	1.053097	-3.161845	-1.845223

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1 imaginary frequency

E = -1936.912281

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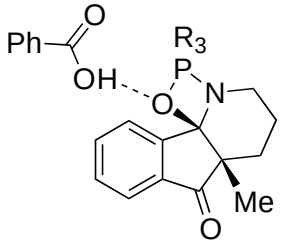
G = -1936.381670

E_{LBS} = -1936.683919

G_{tot} = -1936.153308

Intermediate IntD-*II*



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C	-7.265868	-0.649939	-0.243793
C	-6.517640	0.529517	-0.213120
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C	0.362335	4.184644	2.782541
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C	1.667889	-1.583887	1.412534
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0 imaginary frequencies

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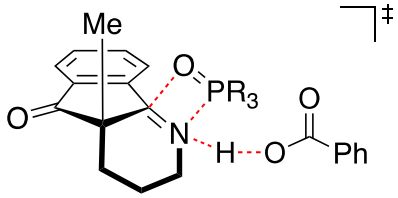
G = -1936.405443

E_{LBS} = -1936.717711

G_{tot} = -1936.183293

Transition state TSD-*II*



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C	-1.439146	-3.655694	-1.776814
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C	3.462094	-1.737120	-0.974238
C	4.596109	-1.456971	0.037035
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1 imaginary frequency

E = -1936.919022

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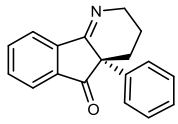
G = -1936.386481

E_{LBS} = -1936.700382

G_{tot} = -1936.167841

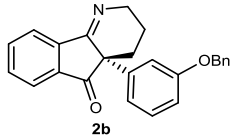
5. Catalytic Asymmetric Staudinger–aza-Wittig Reaction

A flame-dried round-bottom flask was charged with the azide **1** (0.0500 mmol), 2-nitrobenzoic acid (1.68 mg, 0.0100 mmol), 4-Å MS (5.00 mg), and the phosphine **A** (3.45 mg, 0.0100 mmol) under argon. The solid mixture was dissolved in freshly dried toluene (1 mL), followed by the addition of the phenylsilane (12.3 μL, 0.100 mmol). The mixture was stirred at room temperature until the starting material had been consumed (as determined using TLC). The crude reaction product was loaded directly onto a column of SiO_2 and purified through FCC (20% EA in hexanes) to deliver compound **2**.



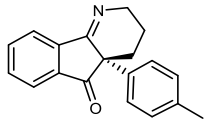
2a
99% yield
90% ee

2a. Pale-yellow oil (13.10 mg, 99% yield; 90% ee, determined through HPLC using an AD column: 2% iPrOH in hexane, 1 mL/min). IR (ATR): 3026, 1722, 1598, 1271, 947, 733, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.28–7.25 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.96 (td, *J* = 8.3, 19.1 Hz, 1H), 3.88 (ddd, *J* = 3.0, 7.6, 19.1 Hz, 1H), 2.57 (td, *J* = 4.0, 13.6 Hz, 1H), 1.84 (dt, *J* = 4.8, 12.7 Hz, 1H), 1.69–1.66 (m, 1H), 1.56–1.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.1, 169.2, 146.4, 137.7, 137.0, 135.5, 132.0, 128.8, 127.5, 127.3, 124.0, 121.8, 55.4, 49.4, 27.4, 17.9; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{16}NO$, 262.1232, found 262.1234; $[\alpha]_{589}^{24.2}$ –167.2° (C = 1.0, CH_2Cl_2).



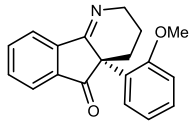
2b
99% yield
90% ee

2b. (18.35 mg, 99% yield; 90% ee, determined through HPLC using an OD column: 5% iPrOH in hexane, 1 mL/min). IR (ATR): 3068, 2943, 1727, 1599, 1256, 895, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.39–7.30 (m, 5H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.68 (dd, *J* = 1.9, 8.0 Hz, 1H), 4.99 (s, 2H), 3.93 (td, *J* = 8.2, 18.8 Hz, 1H), 3.84 (ddd, *J* = 3.0, 8.1, 18.4 Hz, 1H), 2.54 (td, *J* = 3.8, 14.1 Hz, 1H), 1.81 (dt, *J* = 4.4, 13.1 Hz, 1H), 1.70–1.63 (m, 1H), 1.57–1.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.9, 169.0, 159.0, 146.4, 139.2, 137.0, 136.6, 135.5, 132.0, 129.7, 128.5, 128.0, 127.6, 124.0, 121.9, 120.0, 114.3, 113.7, 70.0, 55.3, 49.4, 27.4, 18.0. HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{25}H_{22}NO_2$, 368.1651; found 368.1650; $[\alpha]_{589}^{24.0}$ –135.0° (C = 1.0, CH_2Cl_2).



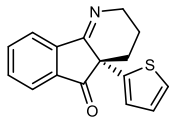
2c
99% yield
91% ee

2c. (13.75 mg, 99% yield; 90% ee, determined through HPLC using an AD column: 2% iPrOH in hexane, 1 mL/min). IR (ATR): 2947, 1723, 1592, 1275, 958 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.71 (dt, *J* = 1.0, 7.6 Hz, 1H), 7.55 (dt, *J* = 1.0, 7.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.93 (ddd, *J* = 7.0, 8.8, 18.6 Hz, 1H), 3.84 (ddd, *J* = 3.3, 8.6, 19.0 Hz, 1H), 2.55 (ddd, *J* = 3.1, 4.6, 12.6 Hz, 1H), 2.26 (s, 1H), 1.82 (dt, *J* = 4.4, 12.1 Hz, 1H), 1.70–1.64 (m, 1H), 1.61–1.51 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.2, 169.3, 146.4, 137.3, 137.0, 135.4, 134.7, 132.0, 129.5, 127.2, 124.0, 121.8, 55.0, 49.4, 27.4, 20.9, 17.9; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{18}NO$ 276.1388, found 276.1390; $[\alpha]_{589}^{23.5}$ –168.2° (C = 1.0, CH_2Cl_2).



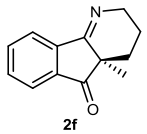
2d
95% yield
84% ee

2d. (13.82 mg, 95% yield; 84% ee, determined through HPLC using an AD column: 5% iPrOH in hexane, 1 mL/min). IR (ATR): 2943, 1722, 1491, 1249, 650 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 1H), 3.91 (td, *J* = 7.9, 18.8 Hz, 1H), 3.42 (s, 3H), 3.37 (q, *J* = 7.8 Hz, 1H), 2.86 (td, *J* = 3.8, 14.0 Hz, 1H), 1.84–1.79 (m, 2H), 1.61–1.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.9, 173.5, 157.6, 146.2, 137.0, 135.3, 131.5, 129.4, 129.0, 123.6, 121.4, 111.9, 55.2, 53.1, 47.5, 25.6, 19.0; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{18}NO_2$ 292.1338, found 292.1338; $[\alpha]_{589}^{23.4}$ –42.0° (C = 1.0, CH_2Cl_2).



2e
91% yield
85% ee

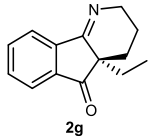
2e. (12.15 mg, 91% yield; 85% ee, determined through HPLC using an AD column: 2% iPrOH in hexane, 1 mL/min). IR (ATR): 2952, 1724, 1679, 1285, 935, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.83 (dd, *J* = 3.7, 5.0 Hz, 1H), 6.76 (dd, *J* = 1.0, 5.0 Hz, 1H), 3.91 (dd, *J* = 7.4, 13.4 Hz, 2H), 2.55 (td, *J* = 4.2, 12.6 Hz, 1H), 1.82 (dt, *J* = 4.6, 12.7 Hz, 1H), 1.70–1.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.6, 168.0, 146.1, 141.1, 136.5, 135.7, 132.2, 126.8, 126.3, 125.7, 124.4, 122.1, 52.3, 49.2, 27.7, 18.0; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{16}H_{14}NOS$ 268.0796, found 268.0791; $[\alpha]_{589}^{24.0}$ –135.5° (C = 1.0, CH_2Cl_2).



2f
96% yield
90% ee

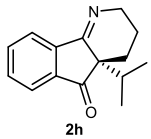
2f. (9.55 mg, 96% yield; 91% ee, determined through HPLC using an OJ column: 2% iPrOH in hexane, 1 mL/min). IR (ATR): 2952, 1693, 1664, 1600, 1286, 776, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (td, *J* = 1.0, 8.2 Hz, 1H), 7.73 (dt, *J* = 1.1, 7.5

Hz, 1H), 7.60 (dt, *J* = 1.0, 7.6 Hz, 1H), 3.91 (d, *J* = 7.1 Hz, 1H), 3.90 (d, *J* = 7.6 Hz, 1H), 2.04 (ddd, *J* = 4.0, 6.1, 12.8 Hz, 1H), 2.00–1.94 (m, 1H), 1.78–1.72 (m, 1H), 1.66 (ddd, *J* = 6.4, 11.0, 16.8 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.0, 171.4, 145.5, 136.6, 135.4, 131.8, 123.7, 122.2, 48.7, 45.9, 24.9, 22.0, 18.4; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{13}H_{14}NO$ 200.1075, found 200.1076; $[\alpha]_{589}^{22.7}$ +42.0° (C = 1.0, CH_2Cl_2).



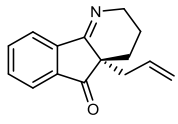
2g
97% yield
91% ee

2g. (10.33 mg, 97% yield; 95% ee, determined through HPLC using an OJ column: 1% iPrOH in hexane, 1 mL/min). IR (ATR): 2937, 1721, 1662, 1599, 1262, 943, 777 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.75 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.63 (dt, *J* = 1.1, 7.6 Hz, 1H), 4.00 (td, *J* = 6.5, 17.4 Hz, 1H), 3.87 (ddd, *J* = 4.9, 6.9, 17.6 Hz, 1H), 2.17 (ddd, *J* = 3.8, 6.2, 12.7 Hz, 1H), 2.04–1.59 (m, 5H), 0.81 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.8, 171.7, 146.1, 137.7, 135.3, 131.8, 123.1, 121.7, 49.9, 48.4, 28.1, 23.0, 18.4, 9.1; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{14}H_{16}NO$ 214.1232, found 214.1233; $[\alpha]_{589}^{23.1}$ +38.5° (C = 1.0, CH_2Cl_2).



2h
95% yield
90% ee

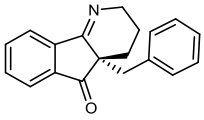
2h. (11.01 mg, 95% yield; 90% ee, determined through HPLC using an OJ column: 1% iPrOH in hexane, 1 mL/min). IR (ATR): 2962, 1660, 1599, 1467, 1273, 637, 773 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 4.00 (td, *J* = 6.8, 17.3 Hz, 1H), 3.78 (td, *J* = 6.8, 17.4 Hz, 1H), 2.19 (ddd, *J* = 3.5, 6.3, 12.4 Hz, 1H), 2.17 (p, *J* = 6.3 Hz, 1H), 1.94–1.90 (m, 1H), 1.70–1.60 (m, 1H), 1.58–1.55 (m, 1H), 1.08 (d, *J* = 7.2 Hz, 3H), 0.65 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4, 172.4, 146.4, 138.2, 135.3, 131.7, 122.6, 121.3, 53.2, 48.1, 31.0, 22.4, 19.4, 18.8, 17.2; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{15}H_{18}NO$ 228.1388, found 228.1389; $[\alpha]_{589}^{23.1}$ +47.8° (C = 1.0, CH_2Cl_2).



2i
89% yield
85% ee

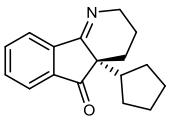
2i. (10.01 mg, 89% yield; 84% ee, determined through HPLC using an OJ column: 1% iPrOH in hexane, 1 mL/min). IR (ATR): 2946, 1723, 1662, 1352, 922, 776 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.82 (td, *J* = 1.0, 8.0 Hz, 1H), 7.72 (dt, *J* = 1.0, 8.0 Hz, 1H), 7.56 (dt, *J* = 1.0, 8.0 Hz, 1H), 5.56 (dddd, *J* = 6.5, 8.4, 10.2, 16.7 Hz, 1H), 5.00 (qd, *J* = 1.5, 16.9 Hz, 1H), 4.96 (qd, *J* = 1.5, 10.2 Hz, 1H), 3.95 (td, *J* = 7.4, 18.00 Hz, 1H), 3.86 (dd, *J* = 5.0, 7.2, 12.4 Hz, 1H), 2.48 (dd, *J* = 8.6, 14.4 Hz, 1H), 2.40 (dd, *J* = 8.4, 14.2 Hz, 1H), 2.14 (ddd, *J* = 4.2, 6.4, 10.2 Hz, 1H), 1.97–1.90 (m, 1H), 1.73–1.65 (m, 1H), 1.63–1.59 (m, 1H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 204.0, 170.8, 145.9, 137.4, 135.4, 132.0, 131.9, 123.3, 121.9, 118.9, 49.7, 48.4, 39.3, 23.1, 18.1; HRMS–ESI (*m*/*z*) [M + H]$^+$ calcd $C_{15}H_{16}NO$ 226.1232, found 226.1230; $[\alpha]_{589}^{23.1}$ +22.5° (C = 1.0, CH_2Cl_2).



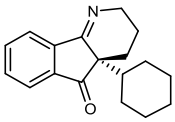
2j
94% yield
99% ee

2j. (12.93 mg, 94% yield; 99% ee, determined through HPLC using an OJ column: 5% iPrOH in hexane, 1 mL/min). IR (ATR): 2952, 1718, 1661, 1269, 776 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.02–6.98 (m, 3H), 6.90–6.88 (m, 2H), 4.01 (td, *J* = 6.8, 17.8 Hz, 1H), 3.82 (td, *J* = 6.0, 16.6 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.17 (ddd, *J* = 4.4, 6.8, 12.6 Hz, 1H), 2.09–2.00 (m, 1H), 1.78–1.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.6, 171.1, 146.4, 137.8, 135.6, 135.1, 131.4, 129.5, 127.9, 126.9, 126.7, 122.8, 121.4, 51.5, 48.2, 41.8, 24.4, 18.7; HRMS–ESI (*m*/*z*) [M + H]$^+$ calcd $C_{19}H_{18}NO$ 276.1388, found 276.1390; $[\alpha]_{589}^{22.8}$ +11.7° (C = 1.0, CH_2Cl_2).



2k
94% yield
90% ee

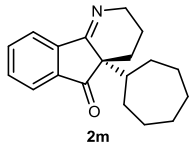
2k. (11.89 mg, 94% yield; 90% ee, determined through HPLC using an OD column: 0.5% iPrOH in hexane, 1 mL/min). IR (ATR): 2929, 2851, 1719, 1599, 1273, 774, 727 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.79 (td, *J* = 0.8, 7.8 Hz, 1H), 7.71 (dt, *J* = 1.0, 7.8 Hz, 1H), 7.58 (dt, *J* = 1.0, 8.0 Hz, 1H), 3.98 (td, *J* = 6.8, 17.5 Hz, 1H), 3.86 (ddd, *J* = 5.0, 6.8, 17.4 Hz, 1H), 2.26–2.19 (m, 2H), 2.00–1.94 (m, 1H), 1.78–1.58 (m, 5H), 1.53–1.45 (m, 2H), 1.37–1.32 (m, 1H), 1.27–1.21 (m, 2H), 0.82–0.76 (m, 1H),; ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.6, 172.0, 146.3, 138.3, 135.3, 131.7, 122.5, 121.5, 51.2, 48.3, 44.7, 29.3, 26.4, 25.0, 23.6, 23.5, 18.6; HRMS–ESI (*m*/*z*) [M + H]$^+$ calcd $C_{17}H_{20}NO$ 254.1545, found 254.1540; $[\alpha]_{589}^{23.1}$ +41.5° (C = 1.0, CH_2Cl_2).



2l
99% yield
94% ee

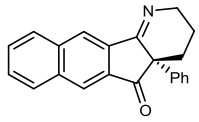
2l. (13.35 mg, 99% yield; 94% ee, determined through HPLC using an OD column: 0.4% iPrOH in hexane, 1 mL/min). IR (ATR): 2925, 2855, 1718, 1599, 773 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.80 (td, *J* = 1.0, 8.2 Hz, 1H), 7.70 (dt, *J* = 1.1, 7.6 Hz, 1H), 7.57 (dt, *J* = 1.1, 7.5 Hz, 1H), 4.00 (ddd, *J* = 6.0, 7.1, 18.2 Hz, 1H), 3.82 (ddd, *J* = 5.9, 7.2, 18.1 Hz, 1H), 2.29 (ddd, *J* = 4.6, 6.4, 13.6 Hz, 1H), 1.94–1.86 (m, 2H), 1.78 (tt, *J* = 2.9, 12.8 Hz, 2H), 1.70–1.64 (m, 1H), 1.59–1.49 (m, 3H), 1.37–1.24 (m, 2H), 1.78 (tq, *J* = 3.1, 12.9 Hz, 1H), 1.06–0.97 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.5, 172.4, 146.7, 138.3, 135.3,

131.7, 122.7, 121.1, 53.4, 48.0, 41.7, 30.2, 26.9, 26.7, 26.6, 25.9, 22.1, 18.5; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{22}NO$ 268.1701, found 268.1700; $[\alpha]_{589}^{22.9}$ +35.3° (C = 1.0, CH_2Cl_2).



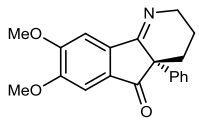
2m
92% yield
96% ee

2m. (12.93 mg, 92% yield; 96% ee, determined through HPLC using an OD column: 0.5% iPrOH in hexane, 1 mL/min). IR (ATR): 2966, 2851, 1721, 1601, 765 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.79 (td, *J* = 1.0, 8.0 Hz, 1H), 7.70 (dt, *J* = 1.0, 7.8 Hz, 1H), 7.57 (dt, *J* = 1.0, 7.6 Hz, 1H), 4.02 (ddd, *J* = 6.0, 7.4, 18.0 Hz, 1H), 3.76 (ddd, *J* = 6.4, 7.0, 18.0 Hz, 1H), 2.25 (ddd, *J* = 4.8, 7.0, 11.6 Hz, 1H), 2.00–1.89 (m, 3H), 1.73–1.58 (m, 4H), 1.58–1.48 (m, 3H), 1.47–1.41 (m, 3H), 1.36–1.29 (m, 2H), 1.17 (tq, *J* = 3.7, 10.9 Hz, 1H), 0.90–0.83 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.6, 172.7, 146.6, 138.2, 135.3, 131.7, 122.8, 121.3, 53.9, 48.0, 43.6, 31.0, 28.4, 27.7, 27.27, 27.24, 26.8, 23.0, 19.1; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{24}NO$ 282.1858, found 282.1850; $[\alpha]_{589}^{22.6}$ +36.1° (C = 1.0, CH_2Cl_2).



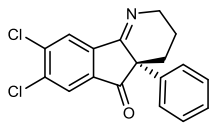
2n
92% yield
89% ee

2n. (14.31 mg, 92% yield; 89% ee, determined through HPLC using an OD column: 1.5% iPrOH in hexane, 1 mL/min). IR (ATR): 2944, 1721, 1622, 1287, 906, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.31 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.20–7.19 (m, 1H), 3.98 (ddd, *J* = 5.8, 6.4, 17.8 Hz, 1H), 3.92 (ddd, *J* = 5.8, 6.2, 16.8 Hz, 1H), 2.63 (ddd, *J* = 3.0, 4.6, 12.6 Hz, 1H), 1.94 (dt, *J* = 4.8, 12.8 Hz, 1H), 1.78–1.65 (m, 1H), 1.59–1.54 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.4, 169.0, 140.7, 137.8, 137.0, 134.9, 133.7, 130.3, 129.4, 129.1, 128.8, 127.7, 127.5, 125.1, 121.2, 56.6, 49.6, 27.5, 18.0; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{22}H_{18}NO$ 312.1388, found 312.1380; $[\alpha]_{589}^{22.8}$ –111.6° (C = 1.0, CH_2Cl_2).



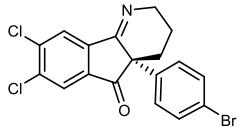
2o
93% yield
86% ee

2o. (14.92 mg, 93% yield; 86% ee, determined through HPLC using an OJ column: 10% iPrOH in hexane, 1 mL/min). IR (ATR): 2940, 1710, 1661, 1498, 1315, 937, 867 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.27–7.24 (m, 3H), 7.21–7.19 (m, 1H), 7.14 (s, 1H), 4.03 (s, 3H), 3.89 (s, 3H), 3.88 (td, *J* = 6.4, 17.8 Hz, 1H), 3.75 (dd, *J* = 6.2, 7.8, 16.8 Hz, 1H), 2.57 (ddd, *J* = 3.0, 4.8, 12.8 Hz, 1H), 1.80 (dt, *J* = 4.8, 13.0 Hz, 1H), 1.71–1.65 (m, 1H), 1.56–1.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7, 169.3, 156.0, 153.2, 141.3, 138.1, 130.8, 128.8, 127.3, 127.1, 104.2, 102.5, 56.6, 56.3, 55.0, 48.9, 27.2, 18.1; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{20}H_{20}NO_3$ 322.1443, found 322.1449; $[\alpha]_{589}^{23.7}$ –135.7° (C = 1.0, CH_2Cl_2).



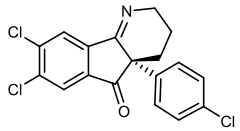
2p
92% yield
92% ee

2p. (15.13 mg, 92% yield; 92% ee, determined through HPLC using an AD column: 1% iPrOH in hexane, 1 mL/min). IR (ATR): 2942, 1727, 1596, 1296, 711, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.82 (s, 1H), 7.30–7.20 (m, 5H), 3.93–3.90 (m, 2H), 2.55 (td, J = 4.0, 12.6 Hz, 1H), 1.83 (dt, J = 4.2, 12.8 Hz, 1H), 1.69–1.66 (m, 1H), 1.52–1.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.8, 166.9, 145.2, 140.5, 137.0, 136.9, 129.0, 127.8, 127.2, 125.6, 123.8, 55.7, 49.7, 27.4, 17.7; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{18}H_{14}NOCl_2$ 330.0452, found 330.0456; $[\alpha]_{589}^{24.2}$ –260.4° (C = 1.0, CH_2Cl_2).



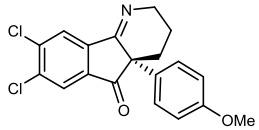
2q
96% yield
93% ee

2q. (19.49 mg, 96% yield; 93% ee, determined through HPLC using a (*S*,*S*)-WHELK-O1 column: 1% iPrOH in hexane, 1 mL/min). IR (ATR): 2944, 1727, 1592, 1486, 1296, 908, 737 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.83 (s, 1H), 7.41 (d, J = 9.0 Hz, 2H), 7.17 (d, J = 9.0 Hz, 2H), 3.94 (ddd, J = 5.6, 6.8, 17.4 Hz, 1H), 3.87 (ddd, J = 5.2, 6.4, 17.0 Hz, 1H), 2.50 (ddd, J = 3.2, 4.8, 13.6 Hz, 1H), 1.82 (dt, J = 4.4, 12.8 Hz, 1H), 1.69–1.64 (m, 1H), 1.50–1.44 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4, 166.4, 145.0, 140.7, 137.1, 136.1, 135.8, 132.2, 128.3, 125.6, 123.9, 122.2, 55.1, 49.7, 27.3, 17.6; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{18}H_{13}NOCl_2Br$ 407.9558, found 407.9550; $[\alpha]_{589}^{23.2}$ –109.3° (C = 1.0, CH_2Cl_2).



2r
95% yield
95% ee

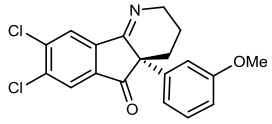
2r. (17.24 mg, 95% yield; 95% ee, determined through HPLC using a (*S*,*S*)-WHELK-O1 column: 0.5% iPrOH in hexane, 1 mL/min). IR (ATR): 2946, 1728, 1596, 1297, 908, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.83 (s, 1H), 7.25–7.20 (m, 4H), 3.94 (ddd, J = 5.6, 6.8, 17.4 Hz, 1H), 3.89 (ddd, J = 5.2, 6.4, 17.0 Hz, 1H), 2.50 (ddd, J = 3.2, 4.8, 13.6 Hz, 1H), 1.82 (dt, J = 4.4, 12.8 Hz, 1H), 1.71–1.67 (m, 1H), 1.50–1.44 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4, 166.4, 145.1, 140.7, 137.1, 135.8, 135.6, 134.0, 129.2, 128.6, 125.6, 123.9, 55.0, 49.7, 27.4, 17.6; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{18}H_{13}NOCl_3$ 364.0063, found 364.0058; $[\alpha]_{589}^{24.0}$ –145.6° (C = 1.0, CH_2Cl_2).



2s
87% yield
92% ee

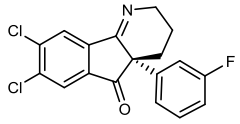
2s. (15.62 mg, 87% yield; 92% ee, determined through HPLC using an AD column: 2% iPrOH

in hexane, 1 mL/min). IR (ATR): 2950, 1725, 1600, 1508, 1250, 909, 728 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.81 (s, 1H), 7.19 (d, *J* = 9.2 Hz, 1H), 6.80 (d, *J* = 9.2 Hz, 1H), 3.92–3.89 (m, 2H), 3.73 (s, 3H), 2.50 (ddd, *J* = 3.4, 4.4, 13.8 Hz, 1H), 1.80 (dt, *J* = 4.2, 12.6 Hz, 1H), 1.69–1.65 (m, 1H), 1.53–1.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.9, 167.0, 159.1, 145.1, 140.7, 140.3, 136.8, 136.0, 128.9, 128.4, 125.6, 123.8, 114.4, 55.2, 54.9, 49.8, 27.2, 17.6; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{16}NO_2Cl_2$ 360.0558, found 360.0560; $[\alpha]_{589}^{23.7}$ –220.7° (C = 1.0, CH_2Cl_2).



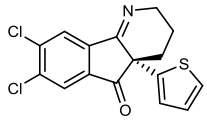
2t
85% yield
91% ee

2t. (15.26 mg, 85% yield; 91% ee, determined through HPLC using an OJ column: 2% iPrOH in hexane, 1 mL/min). IR (ATR): 2946, 1727, 1595, 1297, 907, 714 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.81 (s, 1H), 7.17 (t, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.92–3.90 (m, 2H), 3.75 (s, 3H), 2.53 (ddd, *J* = 3.4, 4.4, 13.8 Hz, 1H), 1.80 (dt, *J* = 4.2, 12.6 Hz, 1H), 1.69–1.65 (m, 1H), 1.54–1.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 166.8, 159.9, 145.2, 140.5, 138.5, 136.9, 136.0, 129.9, 125.6, 123.9, 119.6, 113.4, 112.8, 55.6, 55.2, 49.7, 27.3, 17.7; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{16}NO_2Cl_2$ 360.0558, found 360.0554; $[\alpha]_{589}^{23.0}$ –160.3° (C = 1.0, CH_2Cl_2).



2u
91% yield
92% ee

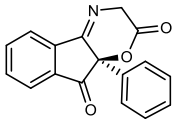
2u. (15.79 mg, 91% yield; 92% ee, determined through HPLC using an AD column: 2% iPrOH in hexane, 1 mL/min). IR (ATR): 2950, 1729, 1586, 1297, 900, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.84 (s, 1H), 7.25–7.22 (m, 1H), 7.05 (t, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 8.0 Hz, 1H), 3.94–3.90 (m, 2H), 2.52 (ddd, *J* = 3.2, 4.6, 13.6 Hz, 1H), 1.82 (dt, *J* = 4.4, 12.8 Hz, 1H), 1.71–1.67 (m, 1H), 1.51–1.46 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.3, 166.3, 163.0 (d, *J* = 248.8 Hz, 1C), 145.1, 140.8, 139.6 (d, *J* = 7.2 Hz, 1C), 137.1, 135.8, 130.5, 130.4, 125.6, 123.9, 123.0, 122.9, 114.9 (d, *J* = 21.5 Hz, 1C), 114.5 (d, *J* = 21.5 Hz, 1C), 55.34, 55.33, 49.7, 27.4, 17.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ 111.09; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{13}NOFCl_2$ 348.0358, found 348.0350; $[\alpha]_{589}^{23.4}$ –134.3° (C = 1.0, CH_2Cl_2).



2v
87% yield
90% ee

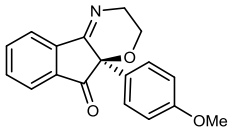
2v. (14.57 mg, 87% yield; 90% ee, determined through HPLC using a (*S*,*S*)-WHELK-O1 column: 5% iPrOH in hexane, 1 mL/min). IR (ATR): 2944, 1731, 1595, 1295, 906, 720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.87 (s, 1H), 7.21 (dd, *J* = 1.2, 6.4 Hz, 1H), 6.87 (dd, *J* = 3.8, 6.4 Hz, 1H), 6.76 (dd, *J* = 1.2, 3.8 Hz, 1H), 3.95–3.92 (m, 2H), 2.54 (ddd, *J* = 3.2, 4.6, 13.6 Hz, 1H), 1.82 (dt, *J* = 5.4, 12.8 Hz, 1H), 1.76–1.72 (m, 2H); ^{13}C NMR (125 MHz,

$CDCl_3$): δ 197.3, 165.8, 144.9, 140.7, 140.2, 137.1, 135.5, 127.0, 126.6, 126.1, 125.9, 124.0, 52.6, 49.5, 27.6, 17.8; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{16}H_{12}NOSCl_2$ 336.0017, found 336.0020; $[\alpha]_{589}^{23.9}$ –116.6° (C = 1.0, CH_2Cl_2).



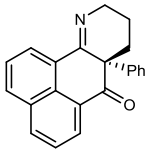
2w
90% yield
80% ee

2w. (12.47 mg, 90% yield; 80% ee, determined through HPLC using a (*S*,*S*)-WHELK-O1 column: 20% iPrOH in hexane, 2 mL/min). IR (ATR): 3065, 1763, 1744, 1598, 1233, 1024, 633 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.41–7.32 (m, 5H), 4.77 (d, *J* = 19.4 Hz, 1H), 3.94 (d, *J* = 19.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.2, 168.4, 167.7, 142.3, 138.1, 137.0, 134.2, 132.5, 129.9, 129.5, 125.9, 125.6, 122.6, 83.5, 52.5; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{17}H_{12}NO_3$ 278.0817, found 278.0821; $[\alpha]_{589}^{24.1}$ –282.8° (C = 1.0, CH_2Cl_2).



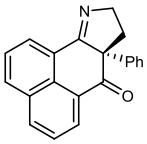
2x
92% yield
87% ee

2x. (13.48 mg, 92% yield; 87% ee, determined through HPLC using an AD column: 15% iPrOH in hexane, 1 mL/min). IR (ATR): 2934, 1734, 1603, 1416, 1250, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.83–7.80 (m, 2H), 7.63 (t, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.99 (td, *J* = 5.8, 16.8 Hz, 1H), 3.94 (dd, *J* = 6.0, 16.8 Hz, 1H), 3.83 (dd, *J* = 6.2, 17.0 Hz, 1H), 3.74 (s, 3H), 3.61 (td, *J* = 6.2, 16.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.3, 170.0, 159.9, 144.6, 136.9, 136.1, 132.8, 128.4, 127.7, 124.9, 121.7, 114.3, 78.6, 61.0, 55.2, 48.1; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{16}NO_3$ 294.1130, found 294.1138; $[\alpha]_{589}^{23.0}$ –162.3° (C = 1.0, CH_2Cl_2).



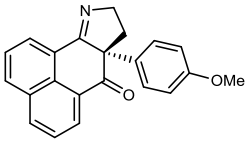
2y
63% yield
71% ee

2y. (9.80 mg, 63% yield; 71% ee, determined through HPLC using an OJ column: 10% iPrOH in hexane, 1 mL/min). IR (ATR): 2935, 1685, 1731, 1580, 1306, 829 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.6 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 4.16 (td, *J* = 5.2, 19.2 Hz, 1H), 3.92 (ddd, *J* = 5.6, 11.2, 18.8 Hz, 1H), 2.52 (dt, *J* = 3.8, 13.8 Hz, 1H), 3.35 (td, *J* = 4.6, 14.4 Hz, 1H), 1.71–1.68 (m, 1H), 1.59–1.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1, 162.9, 139.9, 133.8, 132.6, 131.8, 129.9,129.8, 128.5, 128.4, 127.4, 127.3, 127.2, 126.8, 125.8, 125.5, 60.0, 50.8, 30.7, 18.4; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{22}H_{18}NO$ 312.1388, found 312.1340; $[\alpha]_{589}^{23.4}$ –39.0° (C = 1.0, CH_2Cl_2).



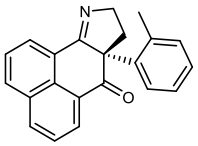
2z
95% yield
87% ee

2z. (14.11 mg, 95% yield; 87% ee, determined through HPLC using an AD column: 10% iPrOH in hexane, 1 mL/min). IR (ATR): 2853, 1686, 1590, 1578, 1321, 1244, 996, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.17–7.09 (m, 5H), 4.32 (td, *J* = 8.2, 16.2 Hz, 1H), 3.86 (ddd, *J* = 6.2, 10.0, 16.2 Hz, 1H), 2.91 (ddd, *J* = 8.8, 10.0, 19.2 Hz, 1H), 2.38 (ddd, *J* = 1.0, 4.8 16.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4, 171.3, 137.9, 134.0, 133.0, 131.1, 129.5,129.0, 127.9, 127.6, 127.1, 126.7, 126.2, 125.6, 71.6, 58.1, 35.6; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{21}H_{16}NO$ 298.1232, found 298.1232; $[\alpha]_{589}^{23.2}$ –168.1° (C = 1.0, CH_2Cl_2).



2aa
85% yield
84% ee

2aa. (13.89 mg, 85% yield; 84% ee, determined through HPLC using an AD column: 10% iPrOH in hexane, 1 mL/min). IR (ATR): 2997, 1687, 1590, 1248, 1031, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.6 Hz, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.30 (td, *J* = 8.0, 16.0 Hz, 1H), 3.83 (ddd, *J* = 6.0, 9.8, 16.4 Hz, 1H), 3.64 (s, 3H), 2.86 (ddd, *J* = 8.9, 10.2, 19.0 Hz, 1H), 2.36 (ddd, *J* = 1.1, 4.7 16.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4, 171.5, 159.0, 134.0, 133.0, 131.17, 131.15, 129.8, 129.5, 127.9, 127.4, 127.1, 126.7, 126.2, 125.6, 114.3, 70.8, 58.0, 55.1, 35.6; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{22}H_{18}NO_2$ 328.1338, found 328.1341; $[\alpha]_{589}^{23.8}$ –156.0° (C = 1.0, CH_2Cl_2).



2ab
92% yield
85% ee

2ab. (14.31 mg, 92% yield; 85% ee, determined through HPLC using an AD column: 10% iPrOH in hexane, 1 mL/min). IR (ATR): 2954, 1693, 1626, 1318, 997, 907 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.4 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.96 (dd, *J* = 4.4, 7.8 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.80 (t, *J* = 7.8 Hz, 1H), 4.35 (dd, *J* = 7.8, 16.0 Hz, 1H), 3.88 (ddd, *J* = 7.4, 9.8, 16.4 Hz, 1H), 3.17 (td, *J* = 8.8, 18.8 Hz, 1H), 2.40 (s, 3H), 2.30 (dd, *J* = 7.4, 13.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 171.6, 137.1, 136.5, 132.0, 131.7, 130.7, 130.5, 127.9, 127.6, 127.2, 126.8, 126.7, 126.2, 126.1, 125.3, 73.4, 59.1, 32.0, 20.7; HRMS–

ESI (*m*/*z*) $[M + H]^+$ calcd $C_{22}H_{18}NO$ 312.1388, found 312.1386; $[\alpha]_{589}^{23.9}$ –142.4° (C = 1.0, CH_2Cl_2).

6. Transformation of the Staudinger–aza-Wittig Product 2a

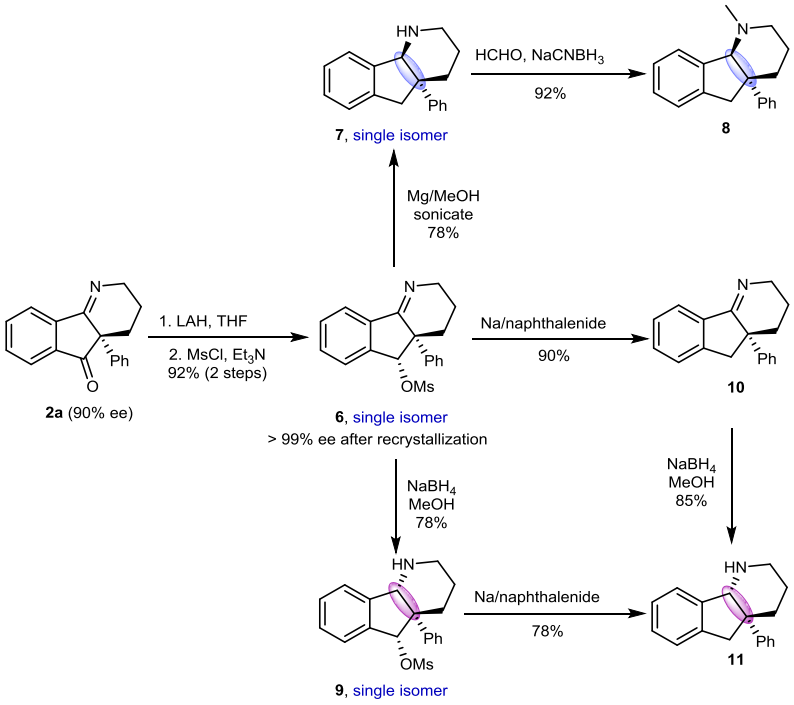


Fig. S4. Transformations of a Staudinger–aza-Wittig product: Syntheses of NMDAR antagonists.

Mesylate 6. LAH (0.380 g, 10.0 mmol, 1.0 equiv) was added to a solution of the iminoketone **2a** (2.61 g, 10.0 mmol, 1.0 equiv.) in THF (50.0 mL) at room temperature. After the starting material had been consumed, the reaction was quenched through the slow addition of water (0.380 mL). After stirring for 30 min, 20% aqueous NaOH (0.380 mL) was added, followed by the addition of water (1.00 mL). After stirring for 1 h, the mixture was treated with anhydrous Na_2SO_4. The organic solution was filtered through a plug of Celite and the solids were washed with DCM. The combined organic phases were concentrated *in vacuo*. The residue was used directly in the next step.

MsCl (1.37 g, 12.0 mmol, 1.2 equiv) was added to a solution of the alcohol product from the previous step in DCM (50.0 mL) containing Et_3N (1.52g, 15.0 mmol, 1.5 equiv) at 0 °C. After the starting material had been consumed, the mixture was concentrated *in vacuo* and the residue was purified through FCC to produce **6** as a yellow solid (3.14 g, 92% yield). After a single recrystallization [EtOAc/hexanes, 1:3 (v/v)], the ee of mother liquor had enriched to 99% (determined through HPLC using an AD column: 20% iPrOH in hexane, 1 mL/min). IR (ATR): 2939, 1669, 1350, 1175, 941 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, J = 2.3, 7.4 Hz, 1H), 7.51–7.27 (m, 3H), 7.26–7.17 (m, 5H), 6.00 (s, 1H), 3.83 (td, J = 8.0, 18.0 Hz, 1H), 3.57 (ddd, J = 3.2, 8.2, 18.2 Hz, 1H), 3.00 (ddd, J = 3.2, 5.3, 13.4 Hz, 1H), 2.93 (s, 3H), 1.86 (dt, J = 5.2, 13.2 Hz, 1H), 1.71–1.67 (m, 1H), 1.50–1.46 (m, 1H); ^{13}C MR (125 MHz, $CDCl_3$): δ 171.6, 141.5, 139.1, 137.5, 132.0, 128.8, 128.2, 127.2, 125.5, 121.2, 84.3, 54.9, 48.2, 38.1, 29.7, 18.0; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{20}NO_3S$ 342.1164, found 342.1162; $[\alpha]_{589}^{23.3}$ –141.4° (C = 1.0, CH_2Cl_2).

***cis*-Indanopiperidine 7.** The mesylate **6** (1.70 g, 5.00 mmol, 1.0 equiv.) was dissolved in freshly distilled THF (7.00 mL) and freshly distilled MeOH (63.0 mL). Powdered Mg (1.21 g, 50.0 mmol, 10 equiv) was added and then the flask was equipped with a reflux condenser and placed under a pressure of Ar. The heterogeneous mixture was sonicated for 30 min and then a second aliquot of Mg powder (1.21 g, 50.0 mmol, 10 equiv) was added and sonication continued for another 30 min. Once the starting material had been consumed, the mixture was cooled to 0 °C and the reaction quenched through the dropwise addition of 2 M HCl (aq) until all of the solid Mg had dissolved to form a homogeneous solution, which was transferred to a separatory funnel. The aqueous phase was extracted five times with Et_2O. The combined organic phases were washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting oil was purified through FCC to give the secondary amine **7** as a colorless oil (0.970 g, 78%). IR (ATR): 3060, 2928, 2856, 1444, 1059 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 4.9 Hz, 1H), 7.48 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 4.4, 7.6 Hz, 2H), 7.25–7.20 (m, 4H), 4.95 (s, 1H), 3.34 (d, J = 16.0 Hz, 1H), 3.13 (d, J = 16.0 Hz, 1H), 2.93–2.90 (m, 2H), 2.05–2.01 (m, 1H), 1.91–1.88 (m, 1H), 1.67 (d, J = 5.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8, 141.5, 138.8, 128.7, 128.5, 127.0, 126.69, 126.60, 125.5, 125.0, 63.8, 49.4, 45.0, 40.6, 33.0, 20.0; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{20}N$ 250.1596, found 250.1590; $[\alpha]_{589}^{27.5}$ –27.4° (C = 1.0, CH_2Cl_2).

Tertiary amine 8. Formaldehyde in H_2O (37 wt.%, 1.00 mL) was added to a solution of the secondary amine **7** (498 mg, 2.00 mmol, 1.0 equiv.) in MeOH (50.0 mL). $NaCNBH_3$ (251 mg, 4.00 mmol, 2.0 equiv) was added slowly. After stirring for 30 min, if the reaction was not complete, another portion of $NaCNBH_3$ (251 mg, 4.00 mmol, 2.0 equiv) was added to the reaction mixture. After repeating this procedure until the starting material was consumed, the reaction mixture was diluted with water and extracted three times with Et_2O. The combined organic phases were washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting oil was purified through FCC to give the amine **8** as colorless oil (484 mg, 92%). IR (ATR): 2929, 2850, 1444, 1294, 1059, 763, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, J = 1.3, 8.6 Hz, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 7.19–7.14 (m, 3H), 4.16 (s, 1H), 3.32 (d, J = 16.0 Hz, 1H), 3.03 (d, J = 16.0 Hz, 1H), 2.85 (ddd, J = 3.4, 8.4, 11.6 Hz, 1H), 2.69 (s, 3H), 2.51 (ddd, J = 3.4, 8.4, 11.6 Hz, 1H), 1.86 (dd, J = 2.0, 5.4 Hz, 1H), 1.85 (d, J = 5.4 Hz, 1H), 1.69–1.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.0, 144.1, 142.2, 127.9, 127.12, 127.11, 125.7, 125.69, 125.64, 125.5, 73.0, 50.7, 50.4, 43.9, 43.6, 33.9, 22.2; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{22}N$ 264.1752, found 264.1758; $[\alpha]_{589}^{23.5}$ –5.5° (C = 1.0, CH_2Cl_2).

***trans*-Indanopiperidine 9.** The mesylate **3** (1.70 g. 5.00 mmol, 1.0 equiv.) was dissolved in freshly distilled MeOH (50.0 mL). $NaBH_4$ (189 mg, 5.00 mmol, 1.0 equiv) was added to the solution in one portion at room temperature. After stirring for 15 min, another portion of $NaBH_4$ (189 mg, 5.00 mmol, 1.0 equiv) was added. After repeating this procedure until the starting material was consumed, the reaction mixture was diluted with water and extracted three times with Et_2O. The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting oil was purified through FCC to give the amine **9** as a colorless foam (1.33 g, 78%). IR (ATR): 2997, 1355, 1173, 957, 708 cm^{-1}; ^1H NMR (500 MHz,

$CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 5.86 (s, 1H), 4.23 (s, 1H), 3.18 (dd, *J* = 4.8, 13.5 Hz, 1H), 3.06 (s, 3H), 3.05 (td, *J* = 4.0, 11.0 Hz, 1H), 2.95 (dt, *J* = 4.0, 13.6 Hz, 1H), 2.18 (dt, *J* = 4.0, 13.6 Hz, 1H), 1.92 (s, 1H, NH), 1.49 (dd, *J* = 2.6, 14.4 Hz, 1H), 1.29 (tq *J* = 4.4, 13.4 Hz, 1H), 1.85 (d, *J* = 5.4 Hz, 1H), 1.69–1.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.9, 136.37, 136.30, 130.3, 129.0, 128.1, 127.3, 126.5, 124.4, 120.1, 85.9, 67.9, 59.3, 48.2, 38.2, 35.8, 22.7; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{19}H_{22}NO_3S$ 344.1320, found 344.1328; $[\alpha]_{589}^{27.5}$ –74.0° (C = 1.0, CH_2Cl_2).

Imine 10. The mesylate **3** (1.70 g. 5.00 mmol, 1.0 equiv.) was dissolved in freshly distilled THF (50.0 mL) and then freshly prepared Na/naphthalenide solution in THF (11.0 mL, 1.0 M) was added slowly at room temperature. After the starting material had been consumed, the reaction was quenched through the slow addition of water. The mixture was extracted three times with Et_2O. The organic phase was washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting oil was purified through FCC to give the imine **10** as a red foam (1.11 g, 90%). IR (ATR): 2940, 2859, 1691, 1663, 1093 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 3H), 7.17 (d, *J* = 7.8 Hz, 1H), 3.87 (td, *J* = 8.2, 17.8 Hz, 1H), 3.76 (dd, *J* = 8.2, 18.2 Hz, 1H), 3.42 (d, *J* = 16.4 Hz, 1H), 3.27 (d, *J* = 16.4 Hz, 1H), 2.53 (td, *J* = 4.0, 12.6 Hz, 1H), 1.88 (dt, *J* = 4.2, 13.6 Hz, 1H), 1.65–1.62 (m, 1H), 1.42–1.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.0, 145.8, 144.7, 138.0, 132.4, 128.5, 127.7, 126.9, 126.6, 125.6, 123.1, 51.0, 47.4, 46.7, 32.2, 17.8; HRMS–ESI (*m*/*z*) $[M + H]^+$ calcd $C_{18}H_{18}N$ 248.1439, found 248.1442; $[\alpha]_{589}^{27.5}$ –83.8° (C = 1.0, CH_2Cl_2).

***trans*-Indanopiperidine 11.**

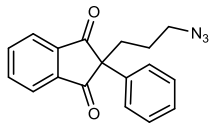
From the mesylate **9**: The mesylate **9** (343 mg, 1.00 mmol, 1.0 equiv.) was dissolved in freshly distilled THF (20.0 mL) and then freshly prepared Na/naphthalenide solution in THF (2.20 mL, 1.0 M) was added slowly at room temperature. After the starting material had been consumed, the reaction was quenched through the slow addition of water. The reaction mixture was extracted three times with Et_2O. The combined organic phases were washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting oil was purified through FCC to give the desired product as **11** colorless oil (194 mg, 78%).

From the imine **10**: The imine **10** (247 mg, 1.00 mmol, 1.0 equiv.) was dissolved in freshly distilled MeOH (30.0 mL). $NaBH_4$ (38.0 mg, 1.00 mmol, 1.0 equiv) was added to the solution in one portion at room temperature. After stirring for 30 min, another portion of (38.0 mg, 1.00 mmol, 1.0 equiv) was added to the reaction mixture. After repeating this procedure until the starting material had been consumed, the reaction mixture was diluted with water and extracted three times with Et_2O. The combined organic phases were washed with brine and dried (Na_2SO_4). After filtration and concentration *in vacuo*, the resulting oil was purified through FCC to provide the desired product as colorless oil (212 mg, 85%).

IR (ATR): 2941, 1458, 1163, 913, 736 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 2H), 7.07 (q, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 4.20 (s, 1H), 3.24 (dd, *J* = 4.2, 13.8 Hz, 1H), 2.96 (dt, *J* = 4.2, 13.2 Hz, 1H), 2.91 (d, *J* = 5.55 Hz, 2H), 2.72 (td, *J* = 3.6, 13.4 Hz, 1H), 2.06 (dt, *J* = 3.8,

13.4 Hz, 1H), 1.45 (d, J = 13.6 Hz, 1H), 1.27 (tq, J = 4.0, 13.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1, 144.3, 139.1, 128.5, 128.0, 126.5, 126.4, 125.5, 125.3, 119.8, 71.7, 53.7, 48.4, 46.3, 37.7, 23.3; HRMS–ESI (m/z) $[M + H]^+$ calcd $C_{18}H_{20}N$ 250.1596, found 250.1592; $[\alpha]_{589}^{23.5}$ –133.4° (C = 1.0, CH_2Cl_2).

7. ^{1}H and ^{13}C NMR Spectra



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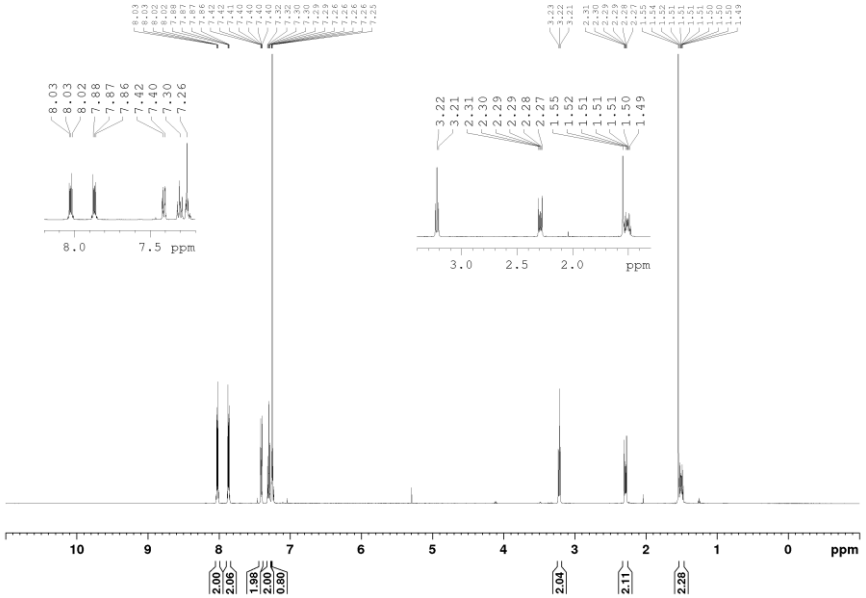

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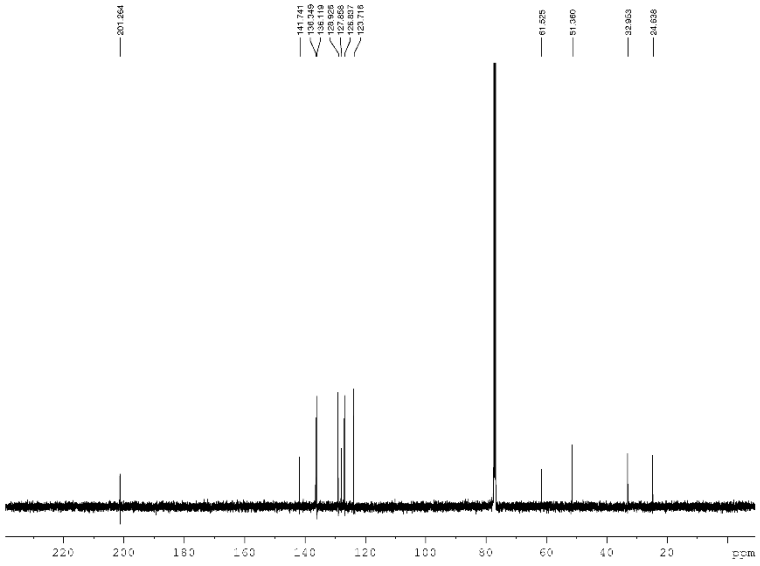

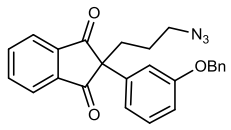

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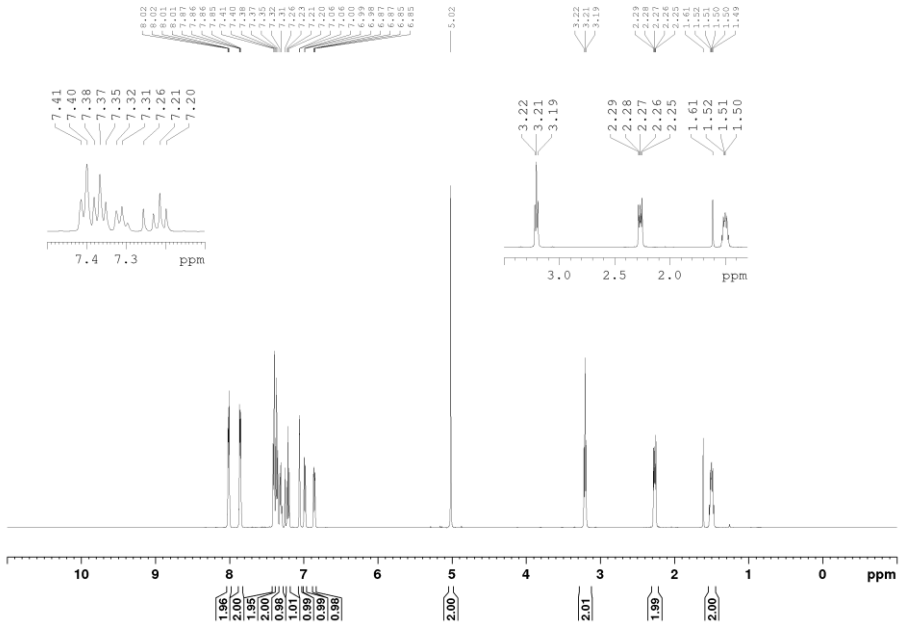

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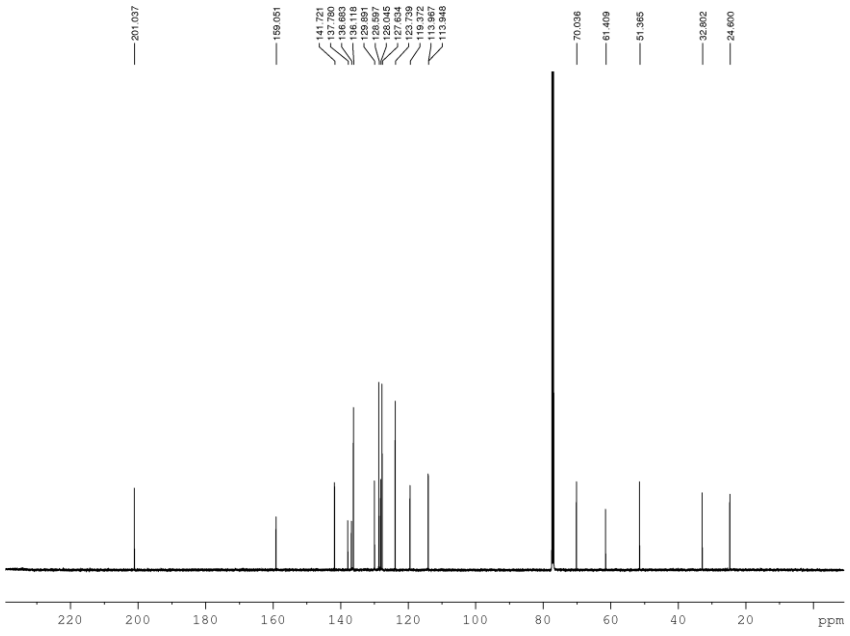

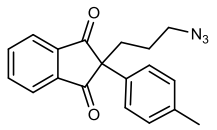

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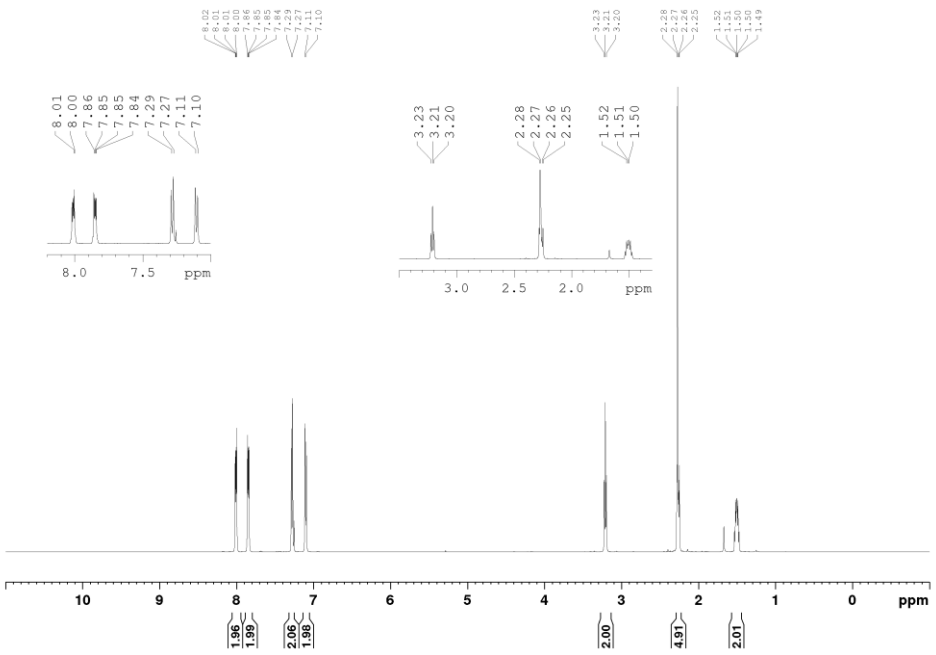

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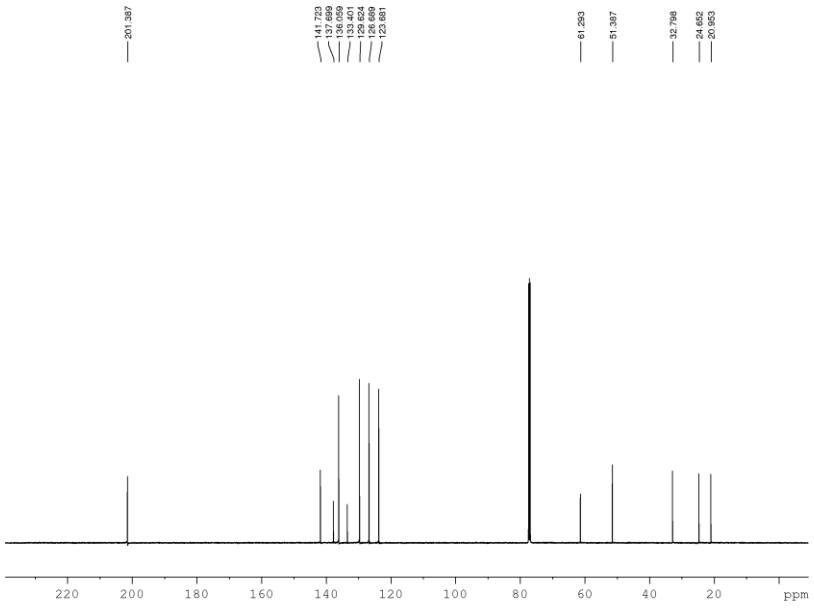

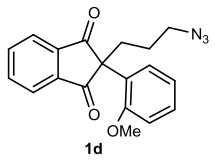

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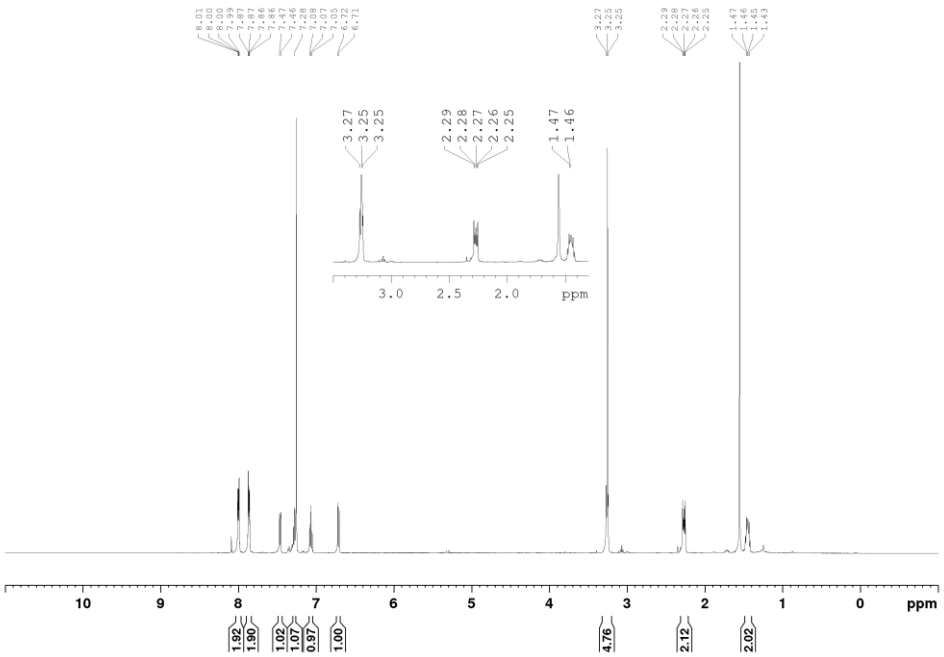

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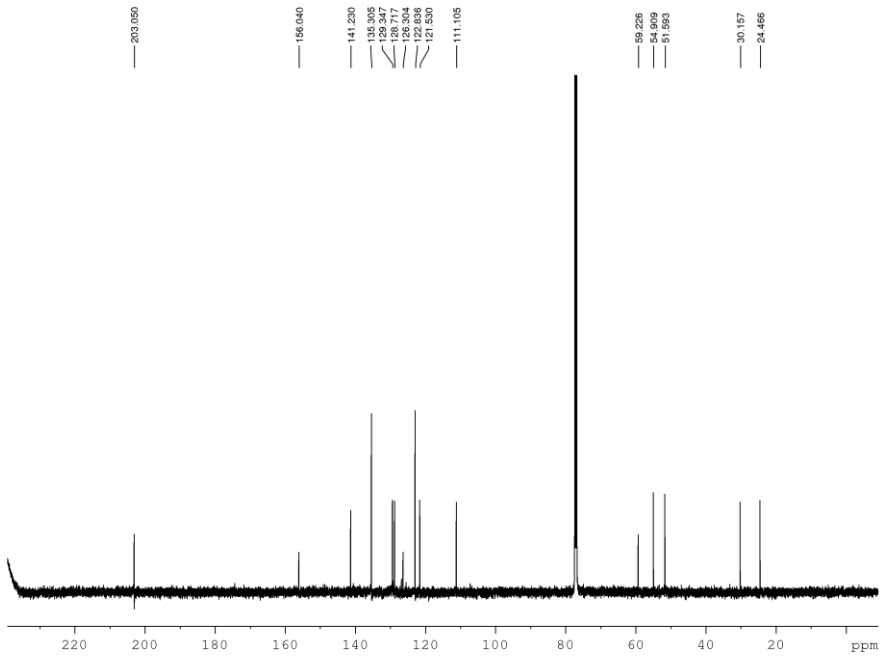

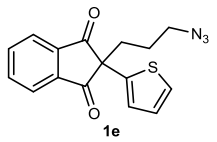

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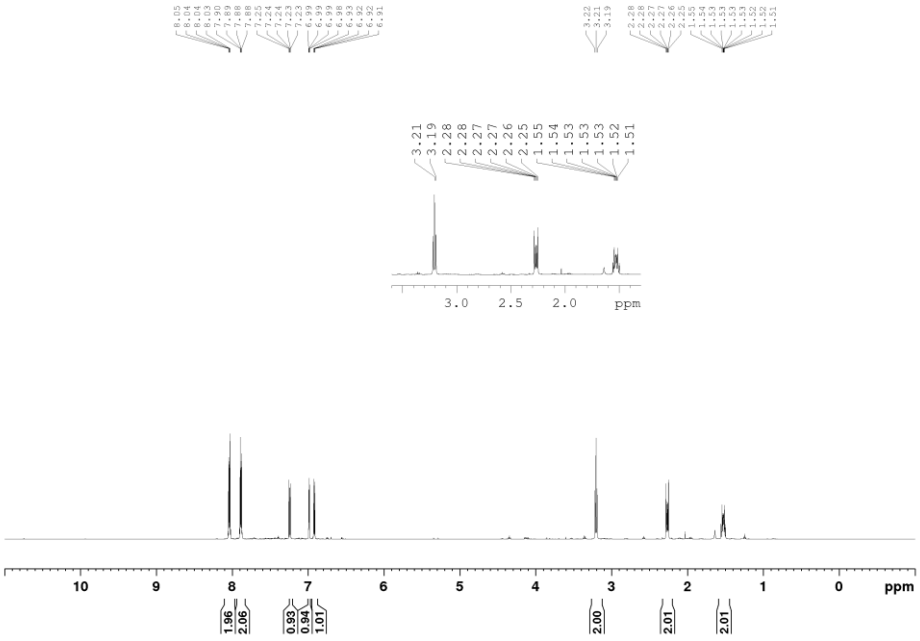

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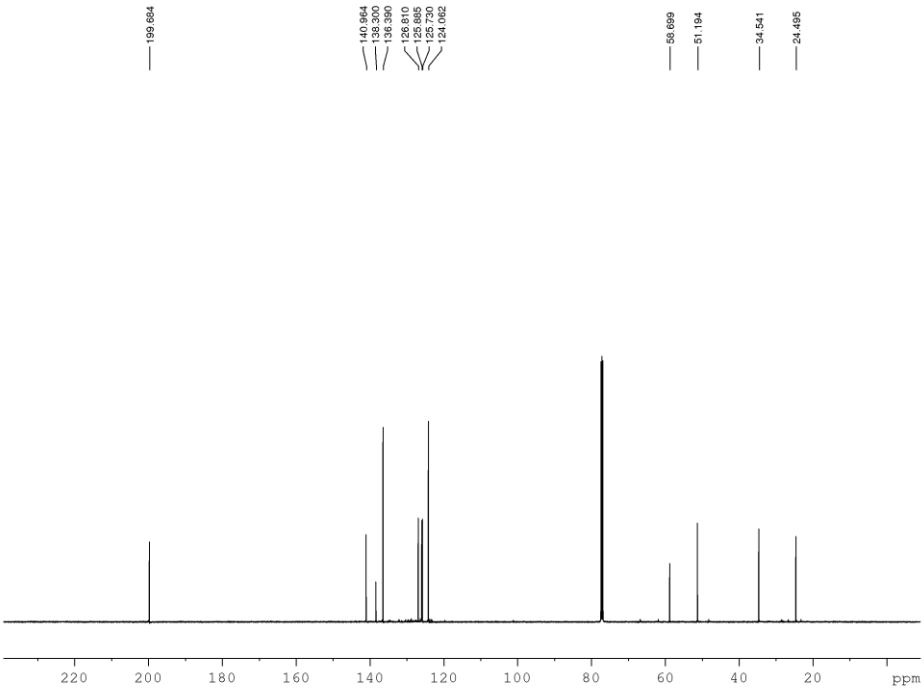

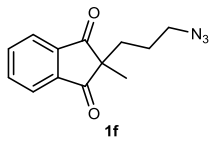

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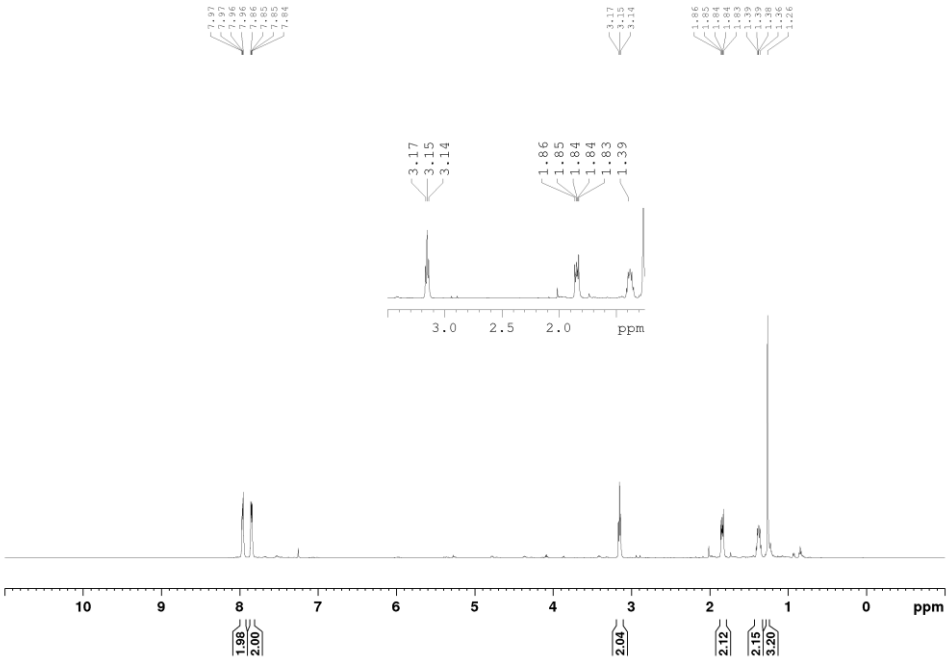

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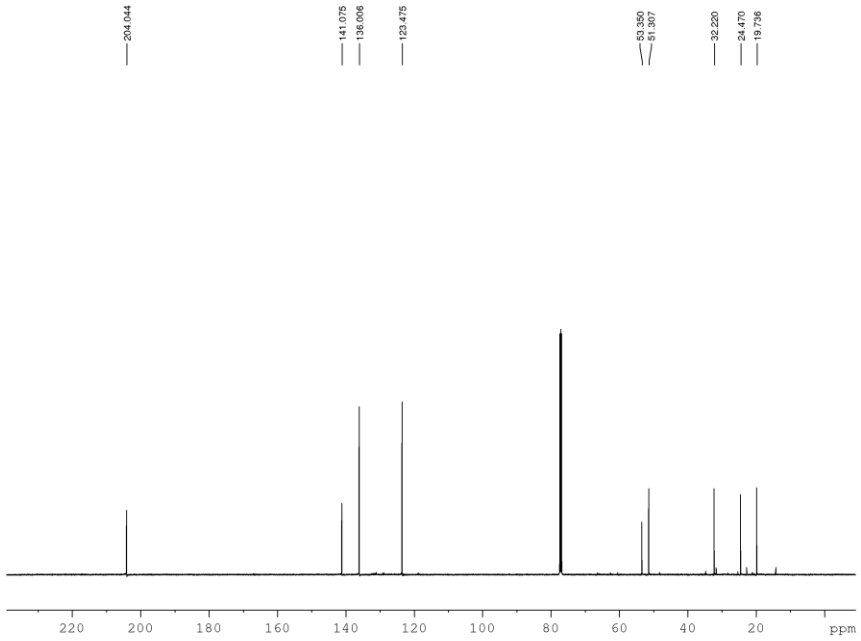

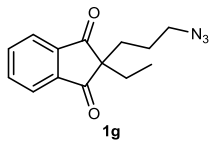

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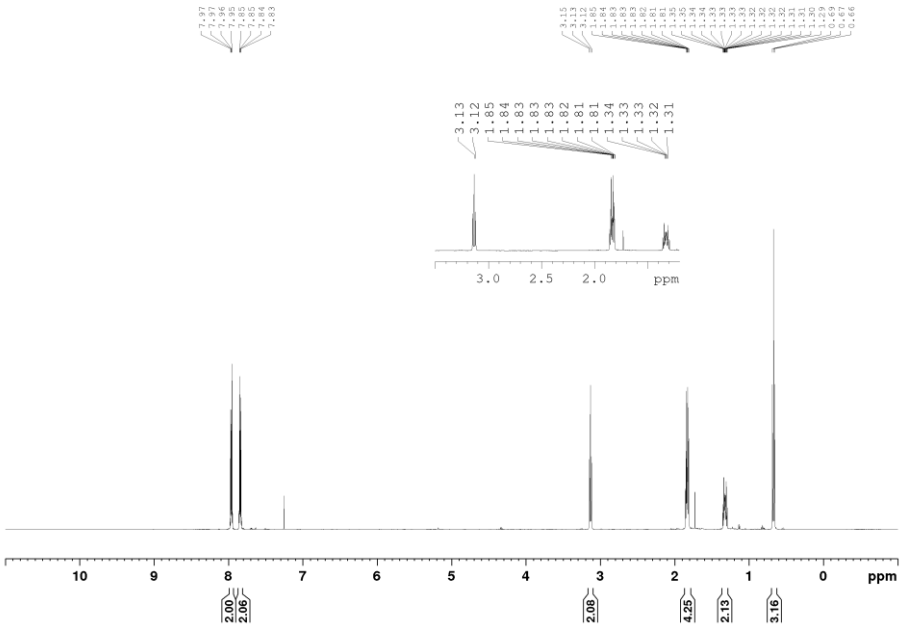

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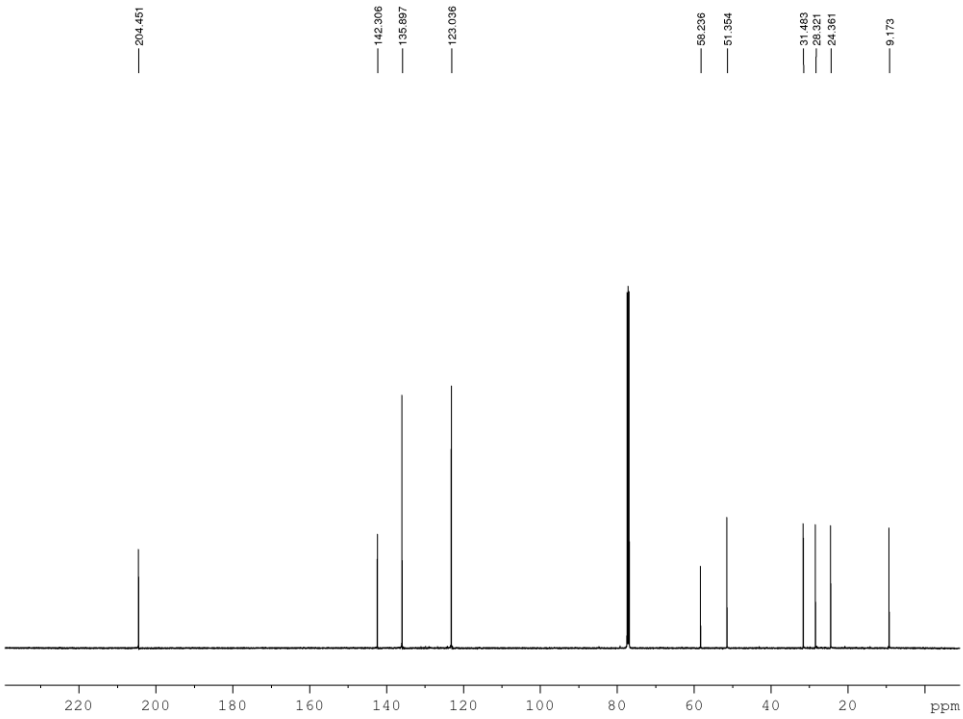

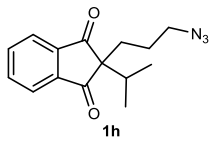

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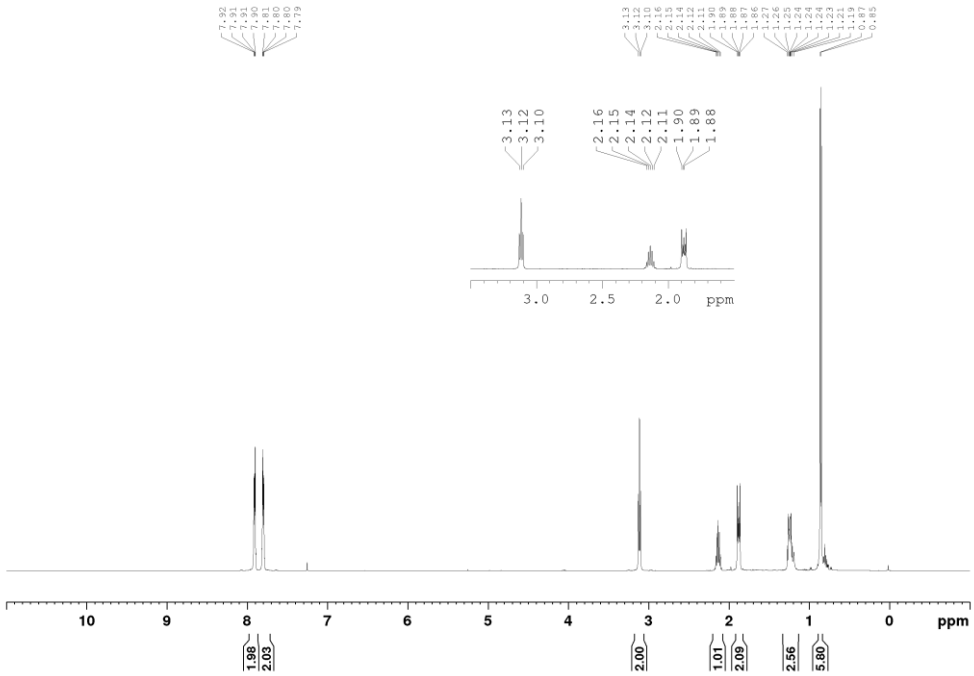

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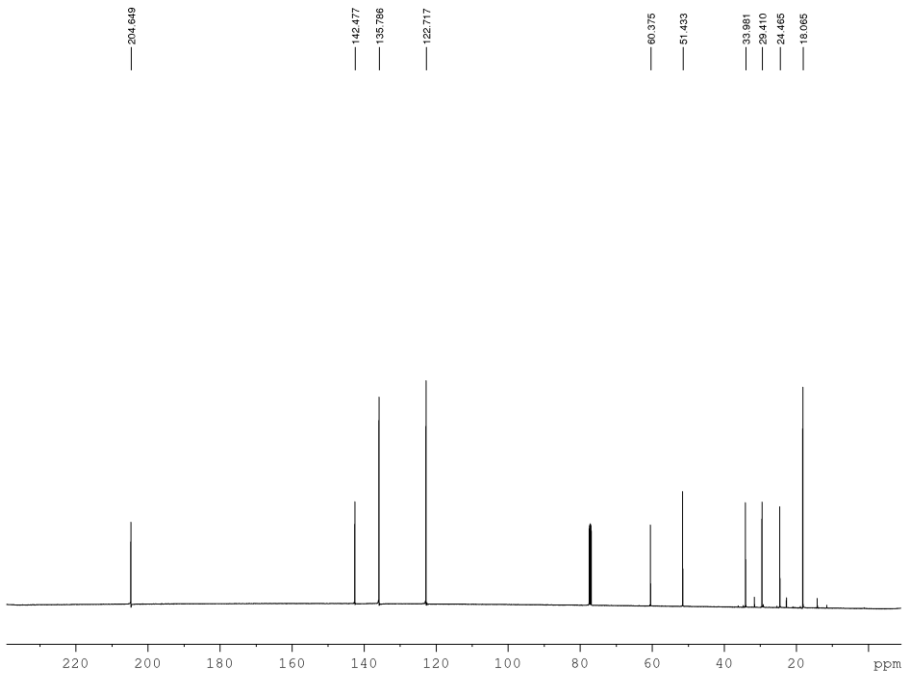

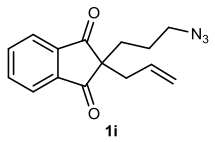

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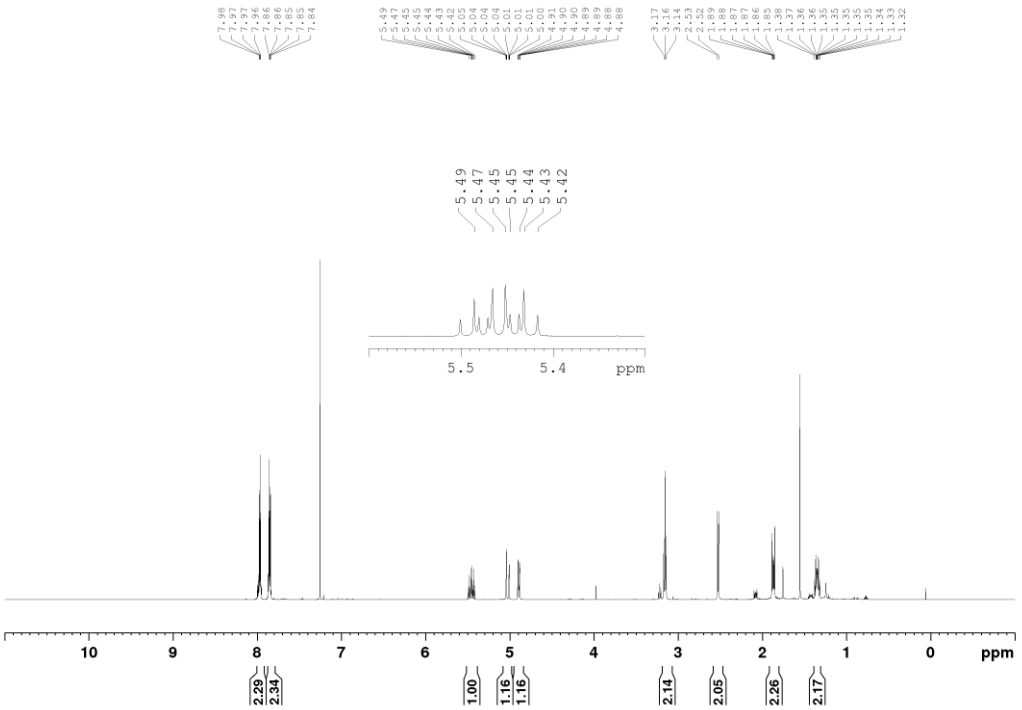
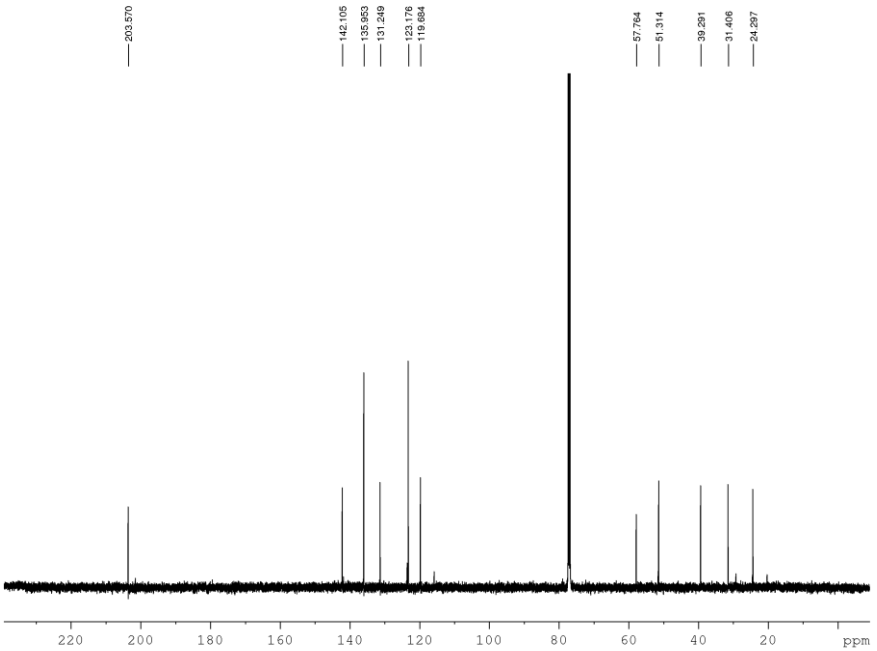
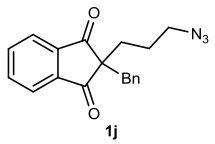
(^{1}H NMR, $CDCl_3$, 500 MHz)



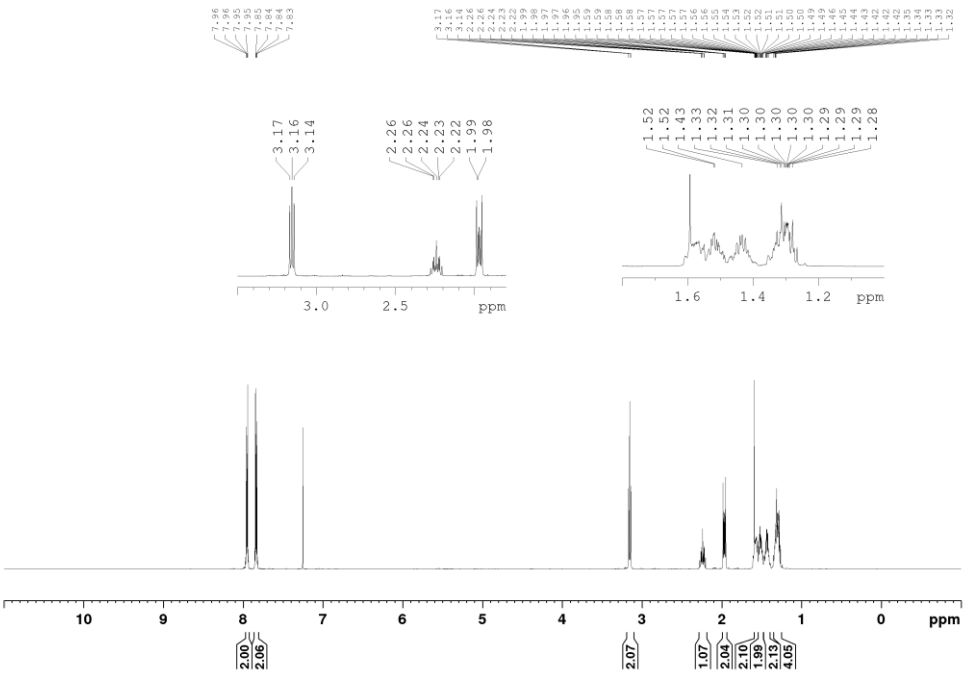
(^{13}C NMR, $CDCl_3$, 125 MHz)



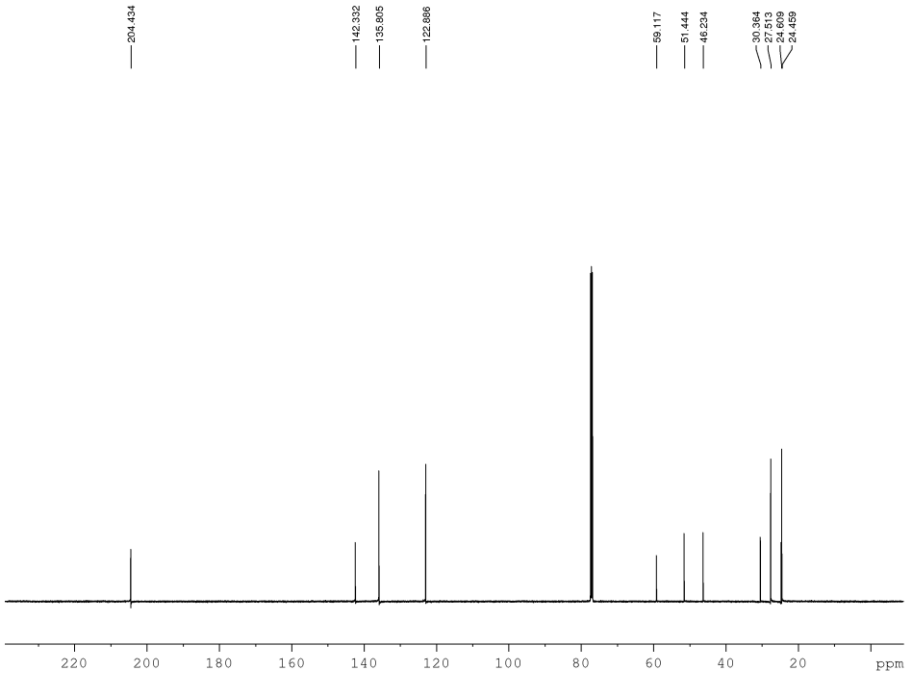


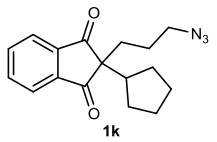
1j

(^{1}H NMR, $CDCl_3$, 500 MHz)

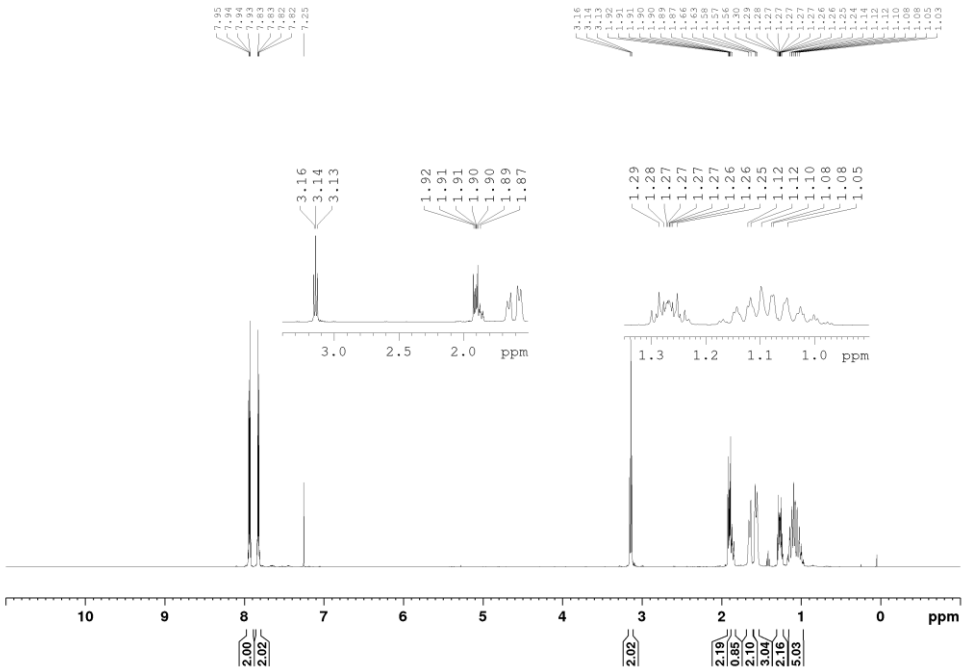


(^{13}C NMR, $CDCl_3$, 125 MHz)

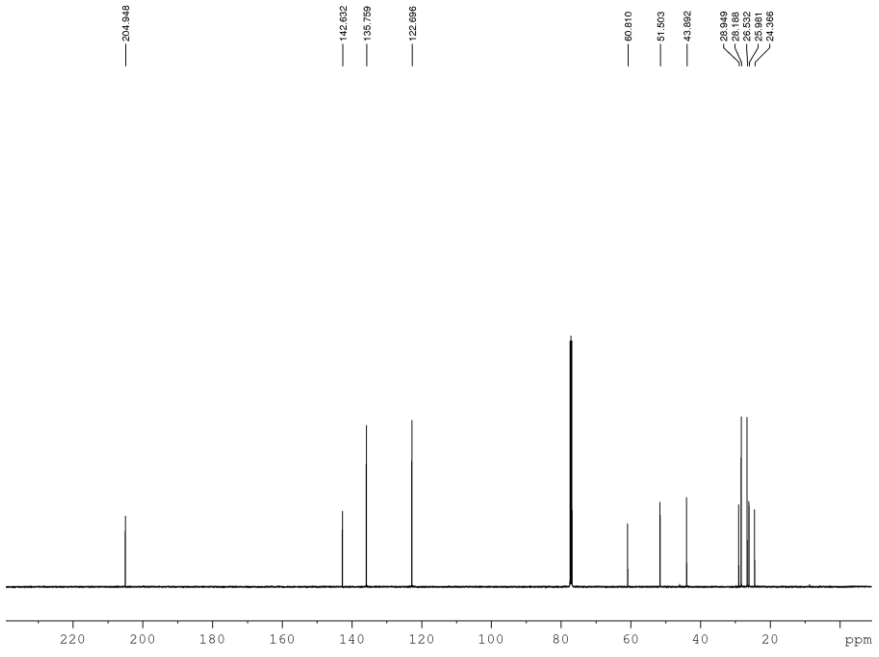


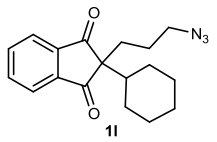


(^{1}H NMR, $CDCl_3$, 500 MHz)



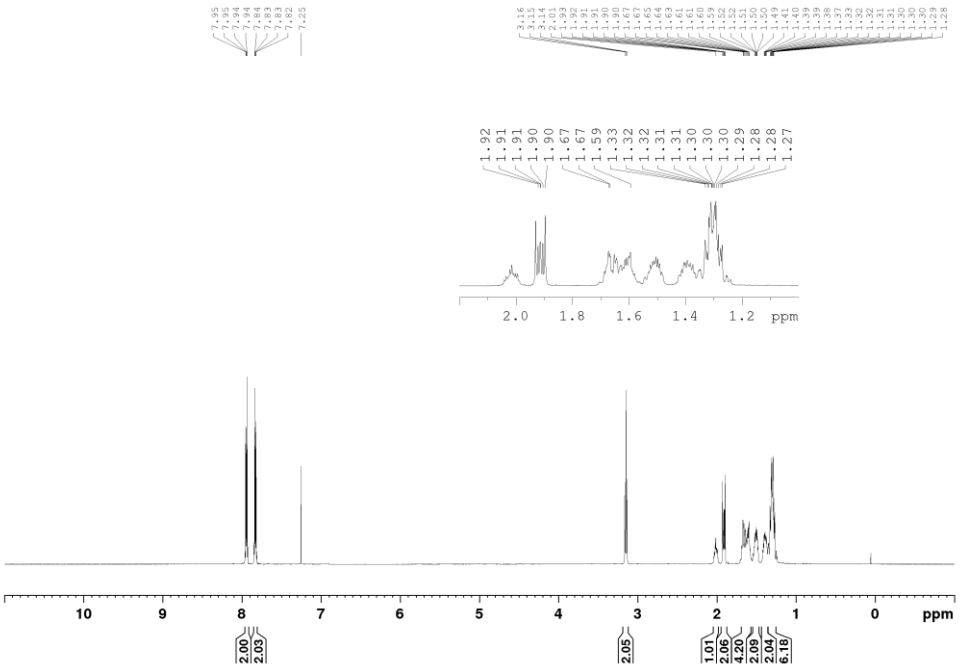
(^{13}C NMR, $CDCl_3$, 125 MHz)



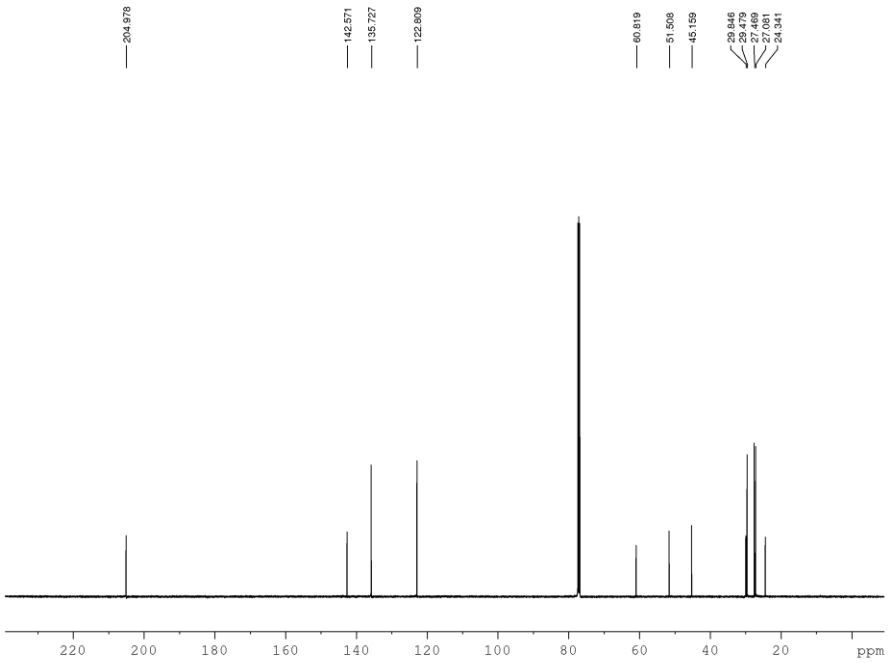


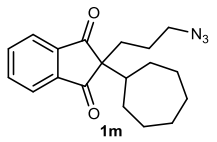
1l

(^{1}H NMR, $CDCl_3$, 500 MHz)

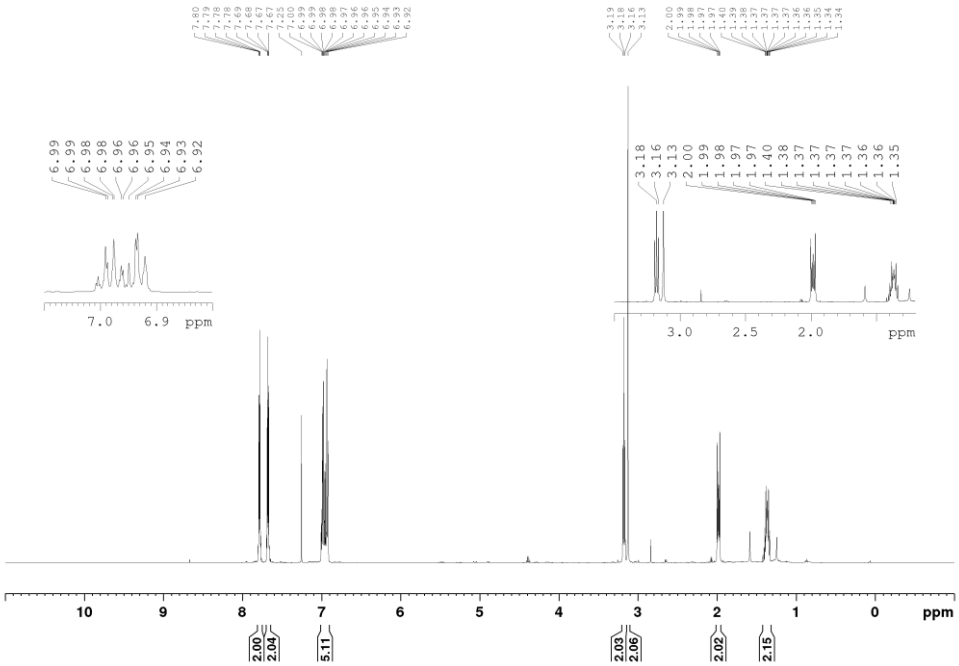


(^{13}C NMR, $CDCl_3$, 125 MHz)

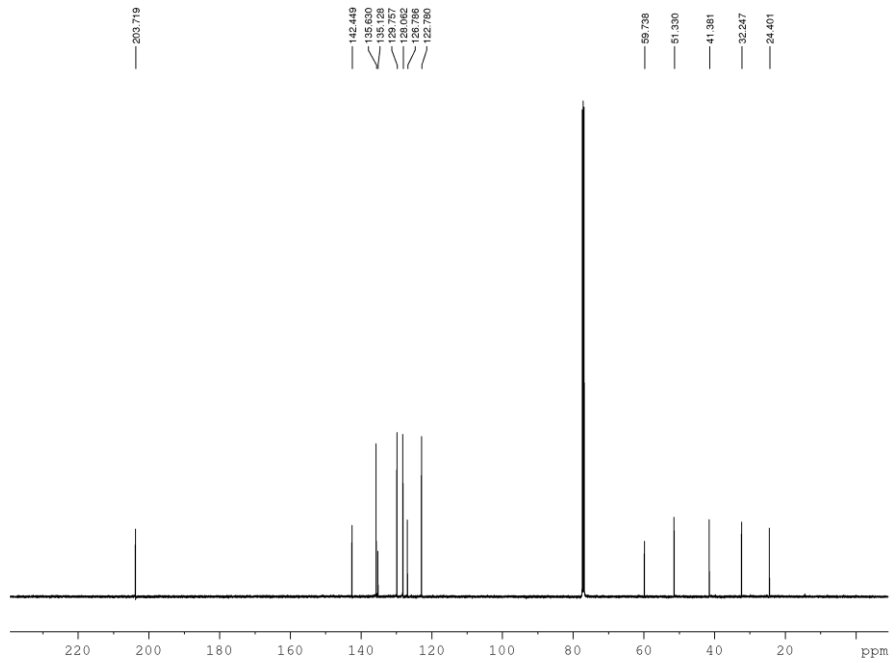


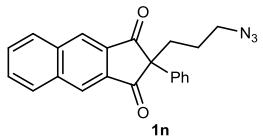


(^{1}H NMR, $CDCl_3$, 500 MHz)



(^{13}C NMR, $CDCl_3$, 125 MHz)





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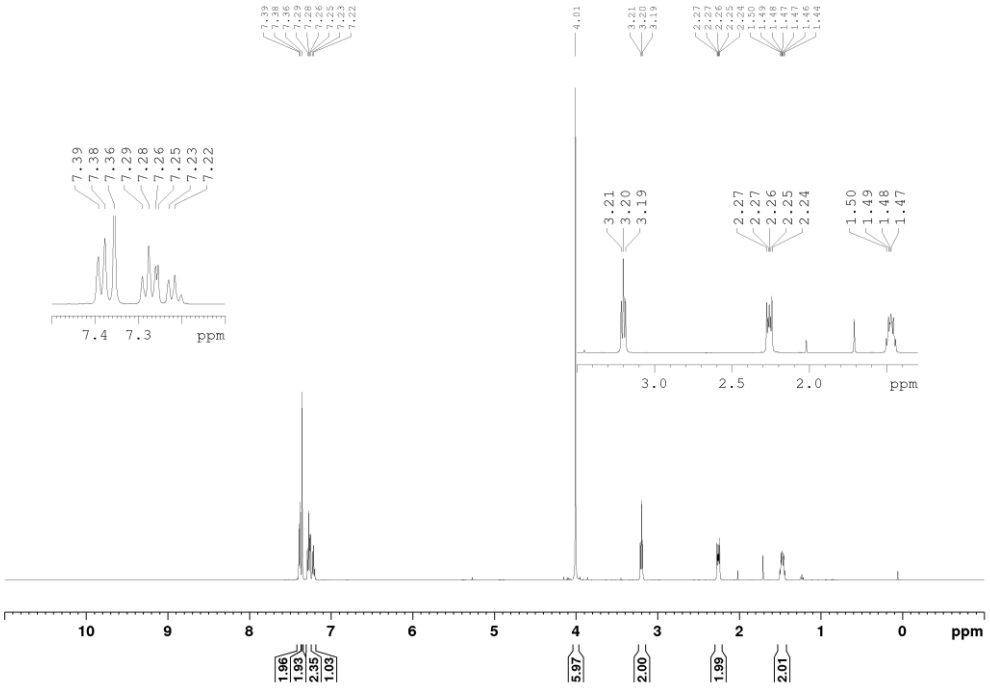
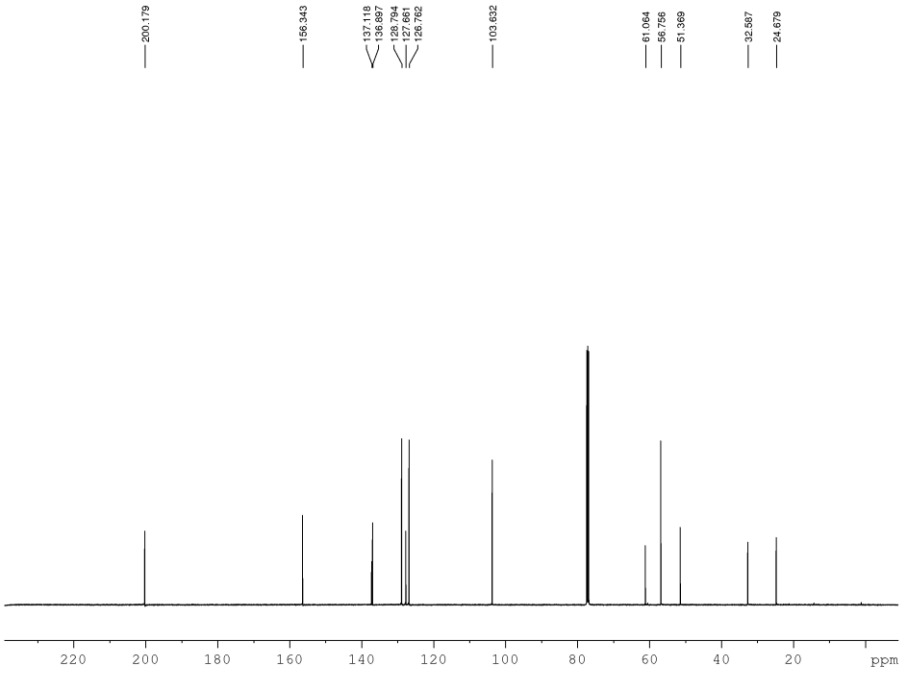
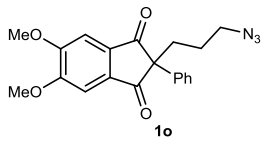
(^{1}H NMR, $CDCl_3$, 500 MHz)



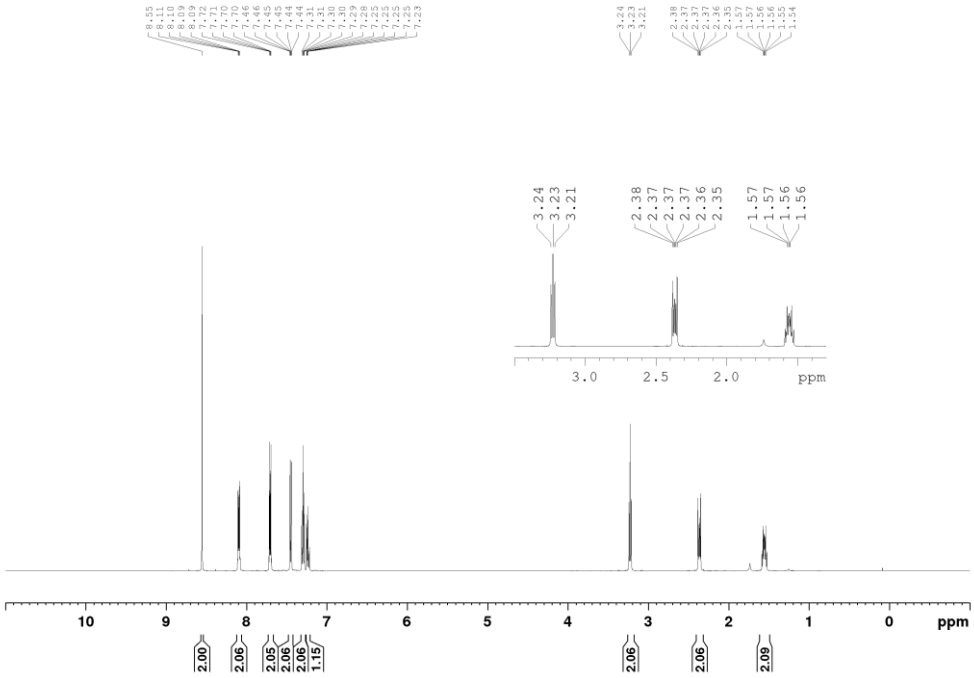
(^{13}C NMR, $CDCl_3$, 125 MHz)



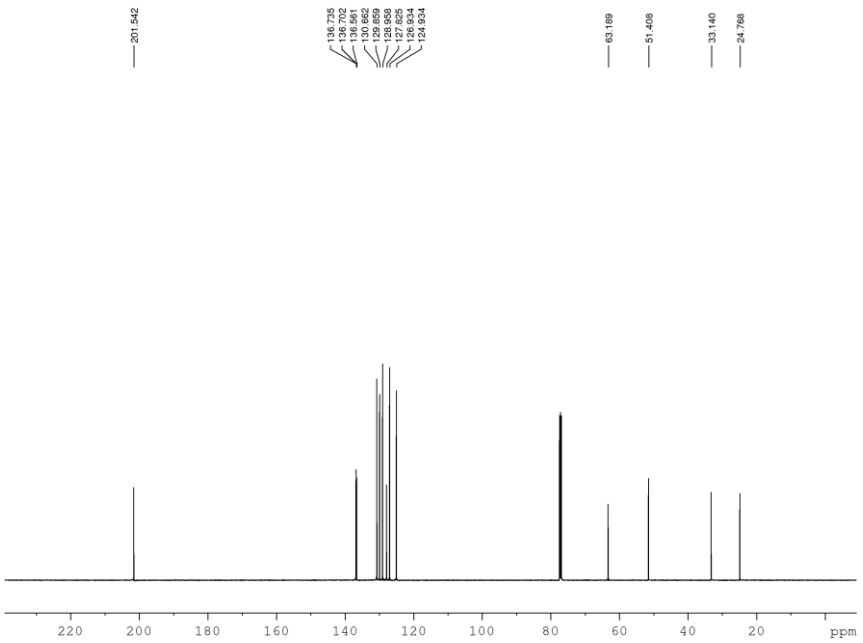


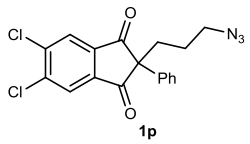
1o

(^{1}H NMR, $CDCl_3$, 500 MHz)



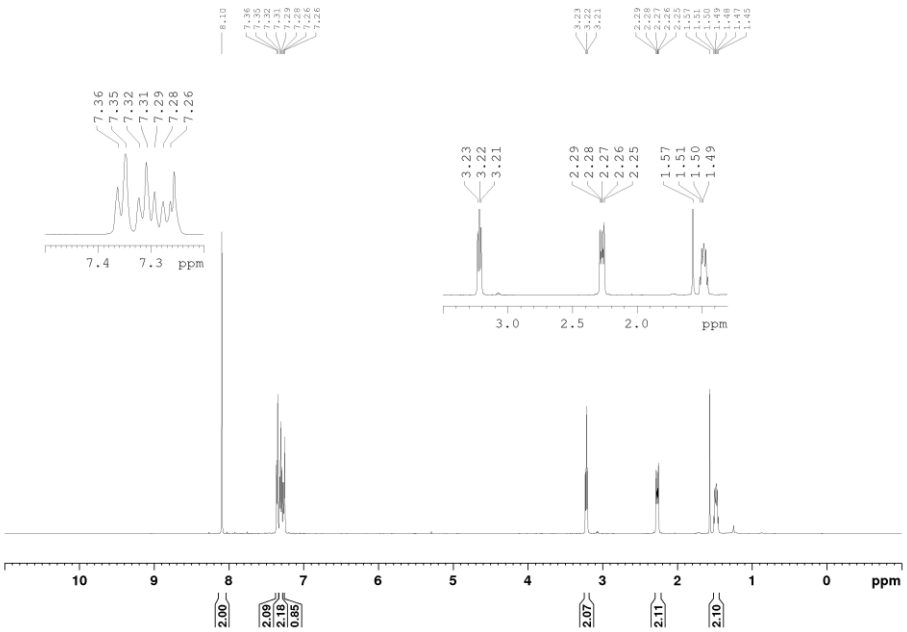
(^{13}C NMR, $CDCl_3$, 125 MHz)



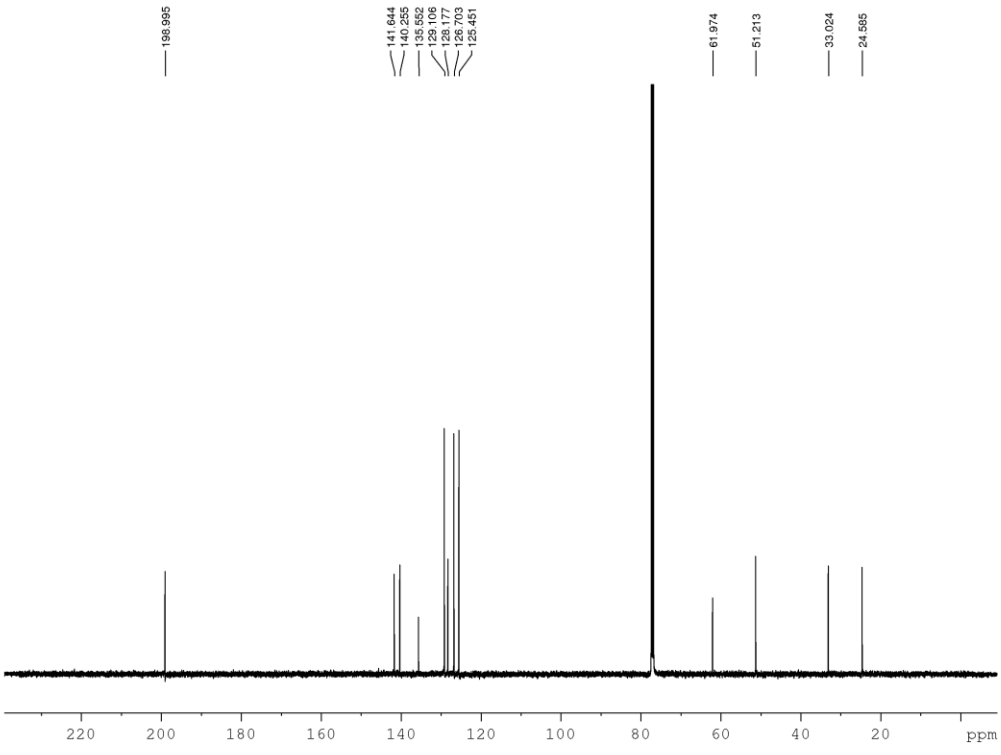


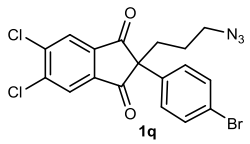
1p

(^{1}H NMR, $CDCl_3$, 500 MHz)



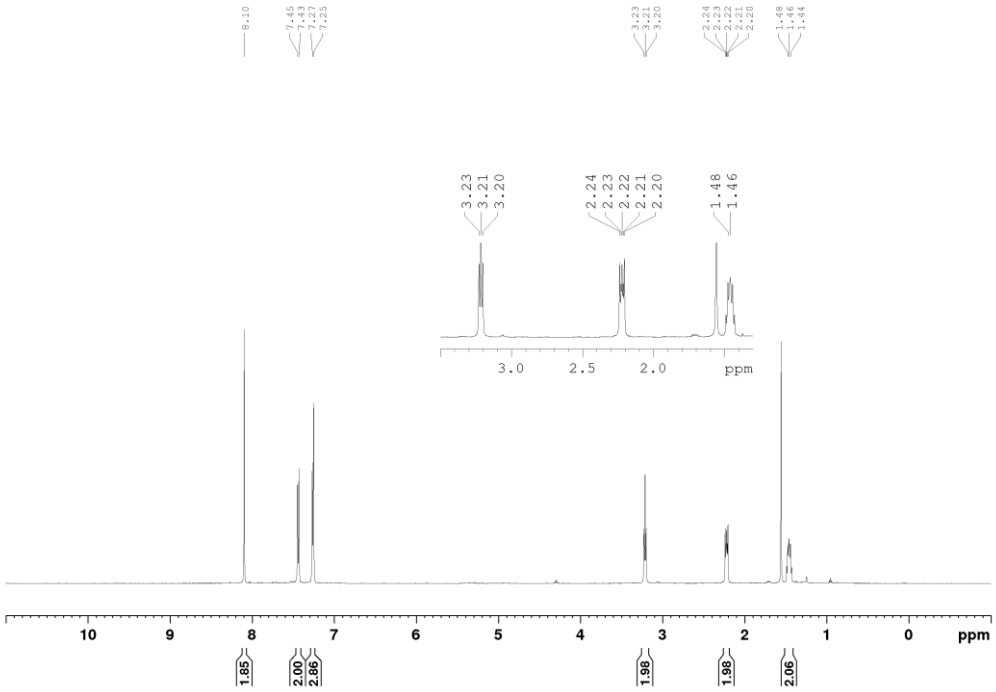
(^{13}C NMR, $CDCl_3$, 125 MHz)



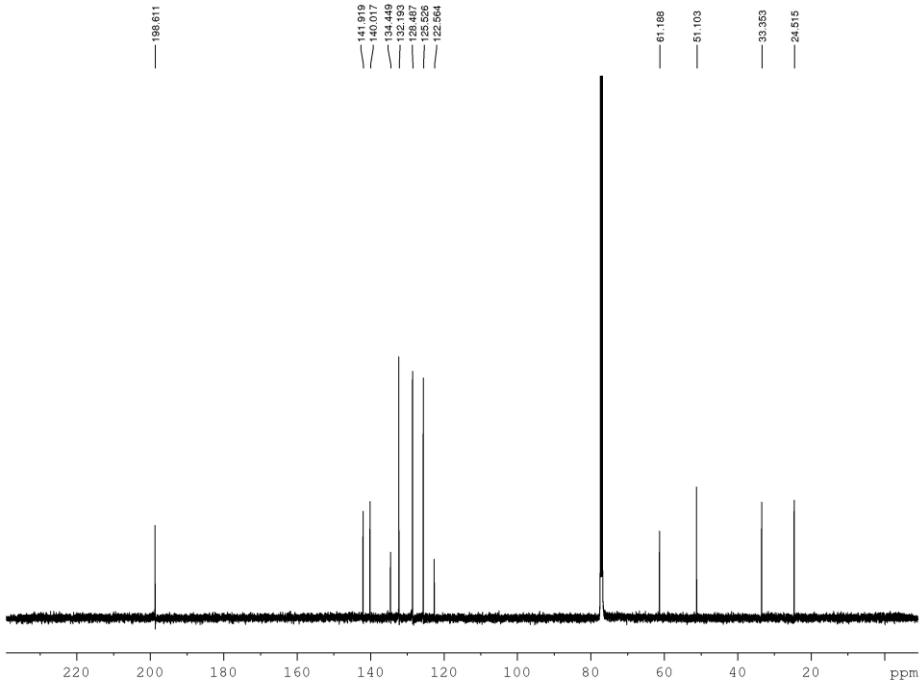


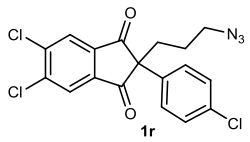
1q

(^{1}H NMR, $CDCl_3$, 500 MHz)

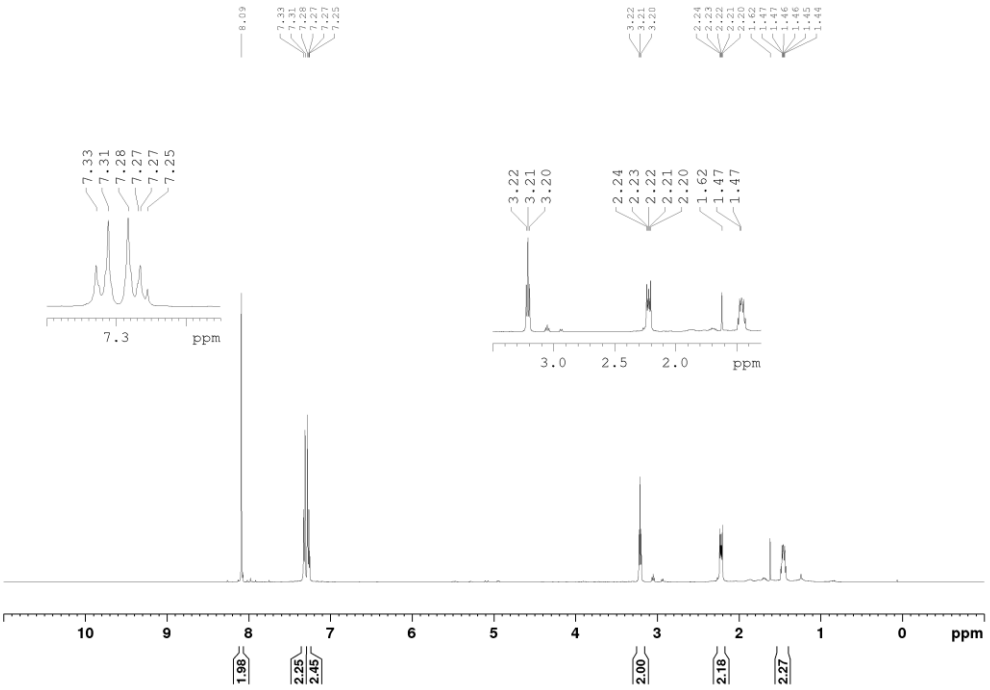


(^{13}C NMR, $CDCl_3$, 125 MHz)

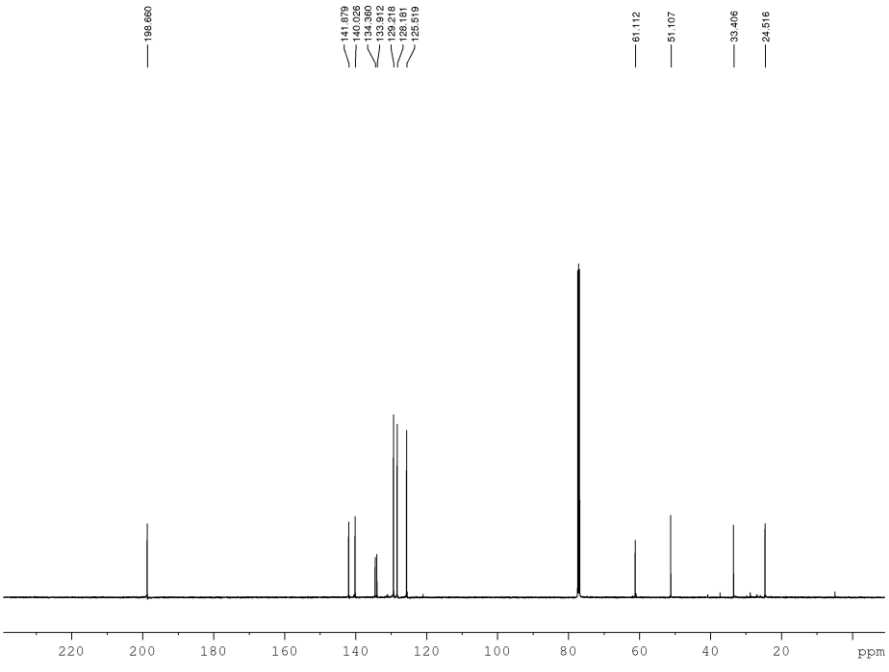


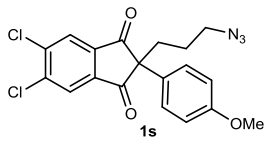


(^{1}H NMR, $CDCl_3$, 500 MHz)

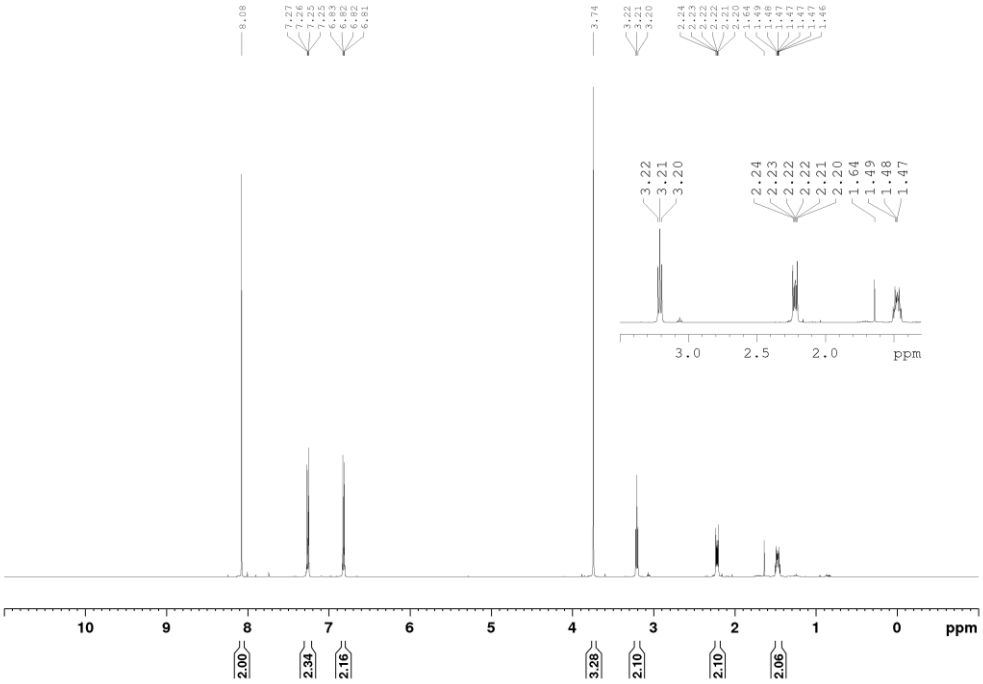


(^{13}C NMR, $CDCl_3$, 125 MHz)

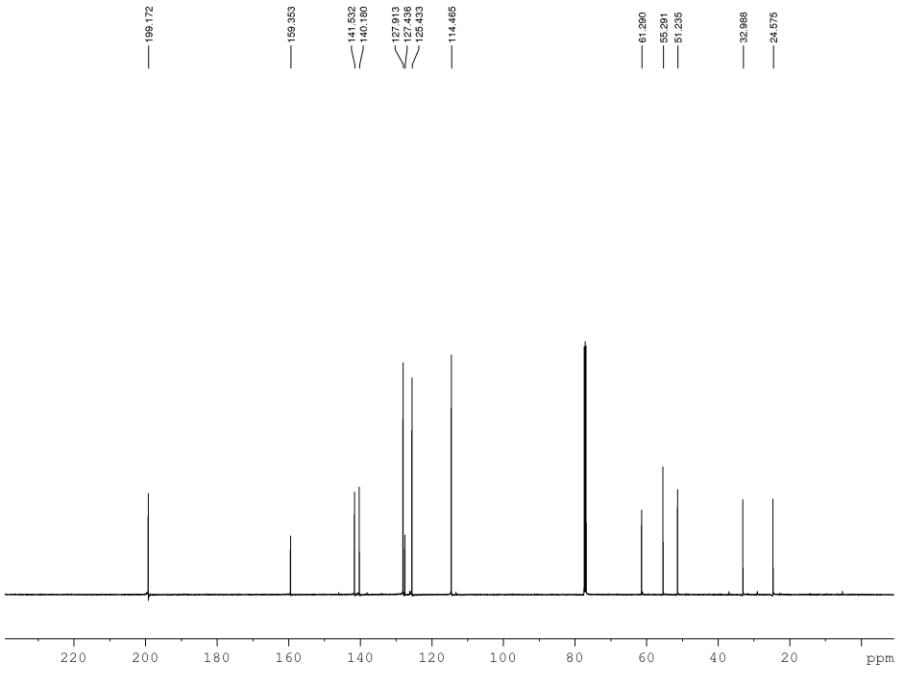


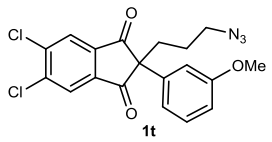


(^{1}H NMR, $CDCl_3$, 500 MHz)



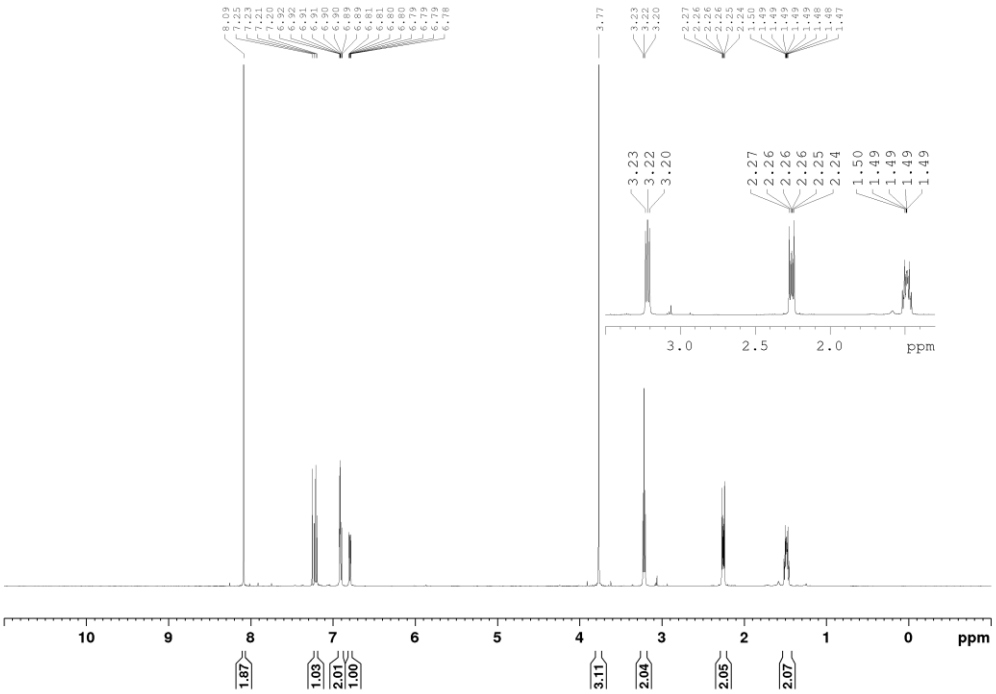
(^{13}C NMR, $CDCl_3$, 125 MHz)



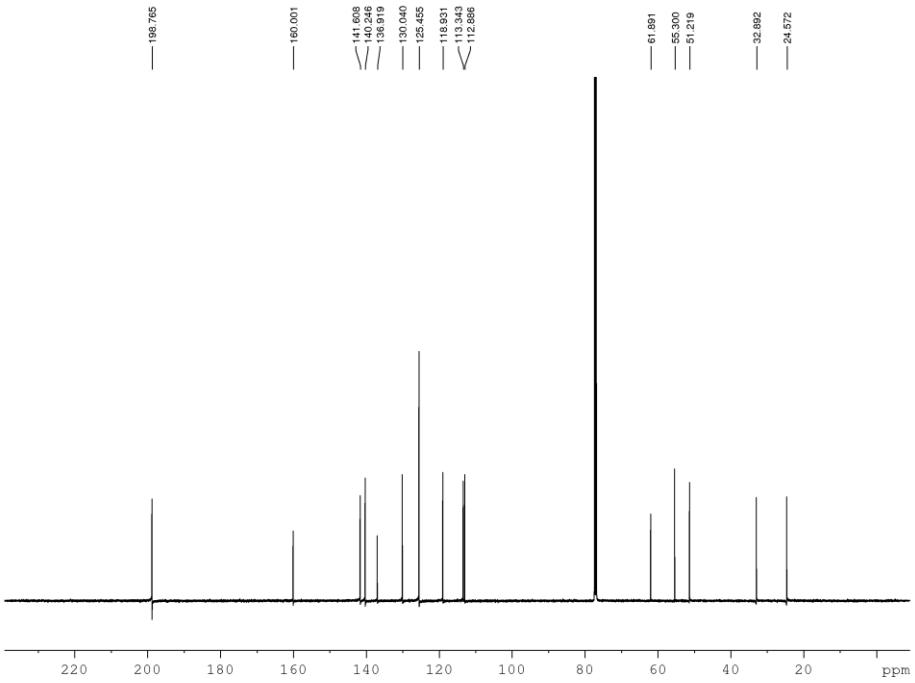


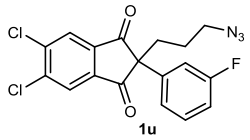
1t

(^{1}H NMR, $CDCl_3$, 500 MHz)

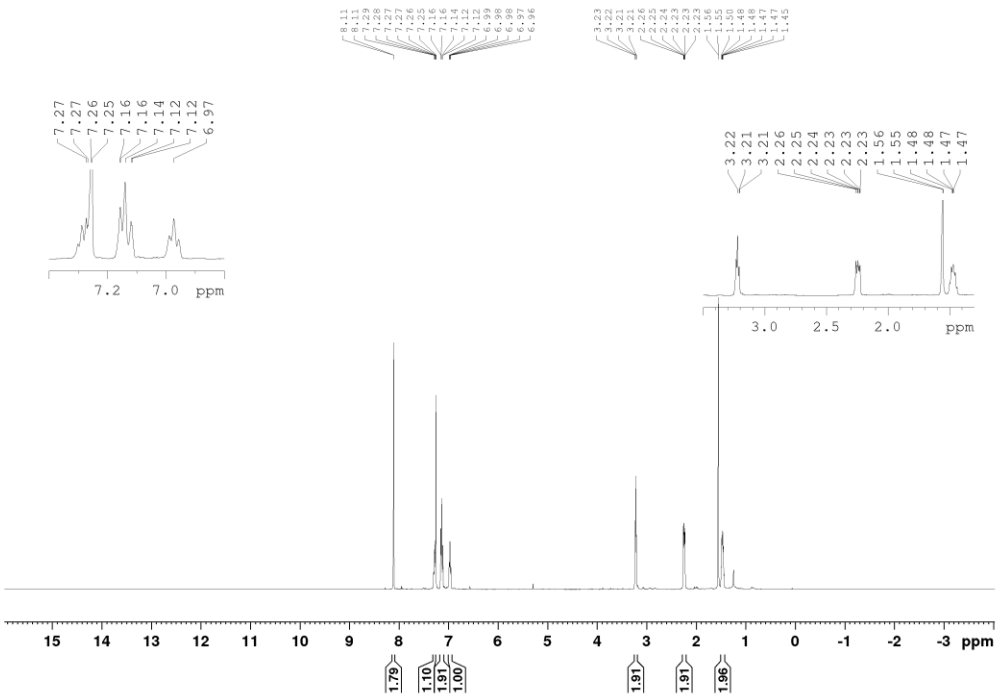


(^{13}C NMR, $CDCl_3$, 125 MHz)

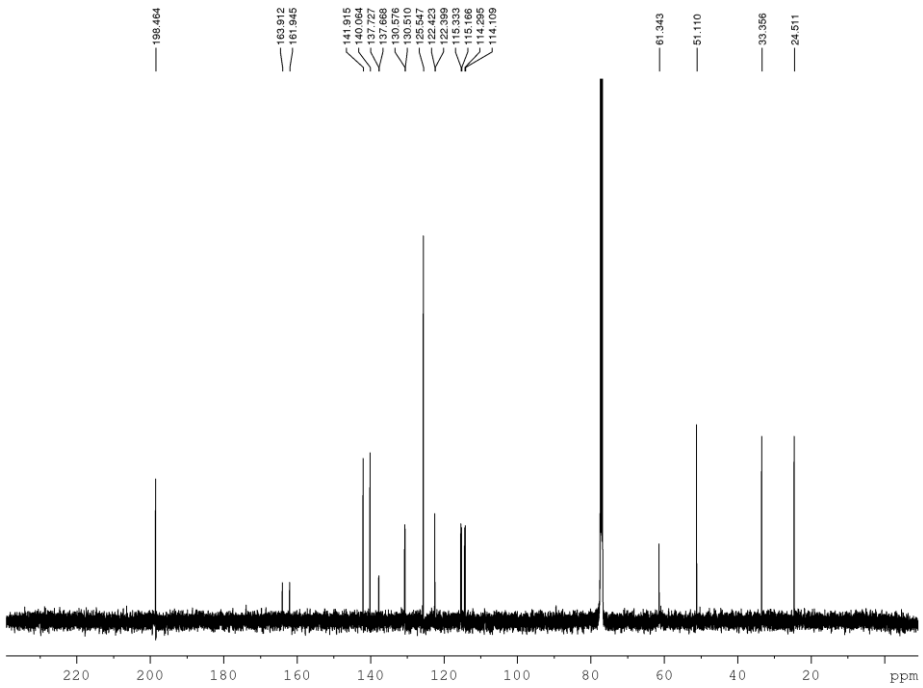


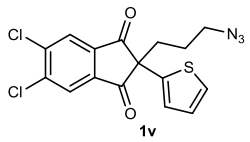


(^{1}H NMR, $CDCl_3$, 500 MHz)



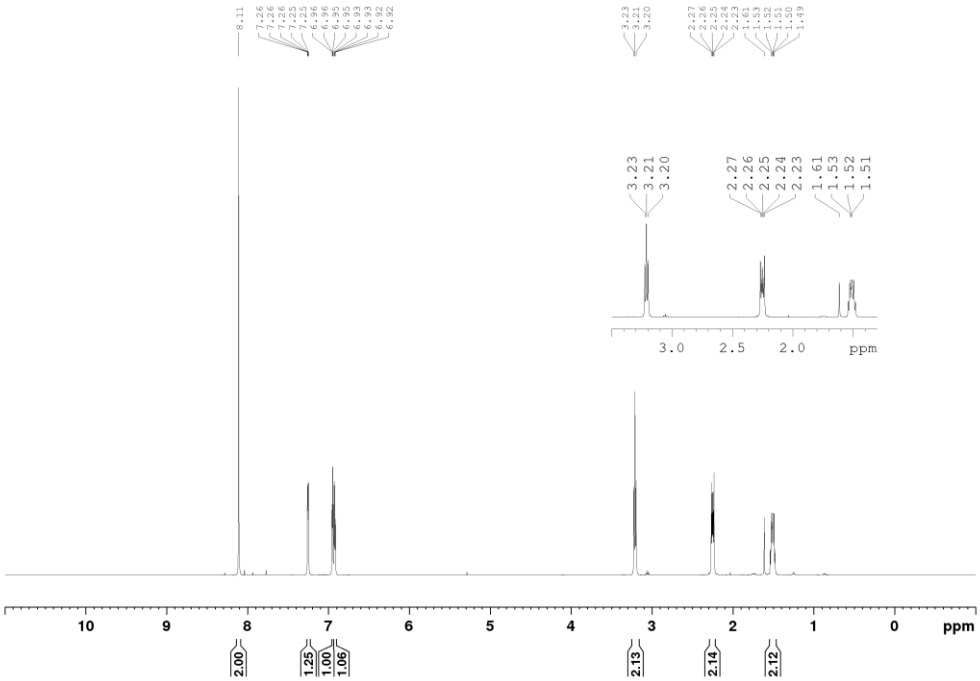
(^{13}C NMR, $CDCl_3$, 125 MHz)



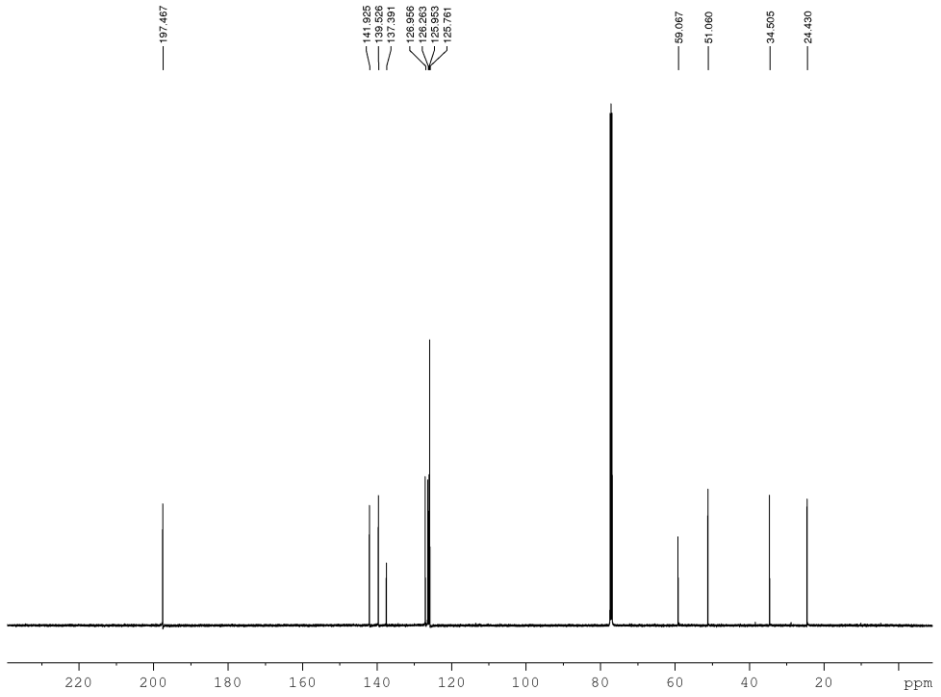


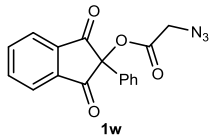
1v

(^{1}H NMR, $CDCl_3$, 500 MHz)



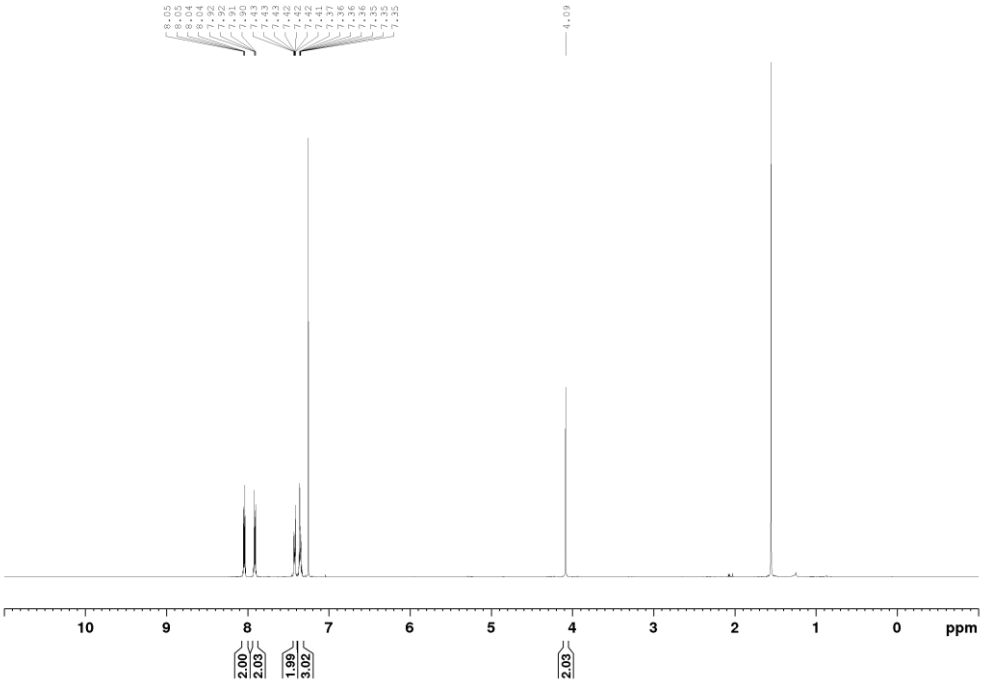
(^{13}C NMR, $CDCl_3$, 125 MHz)



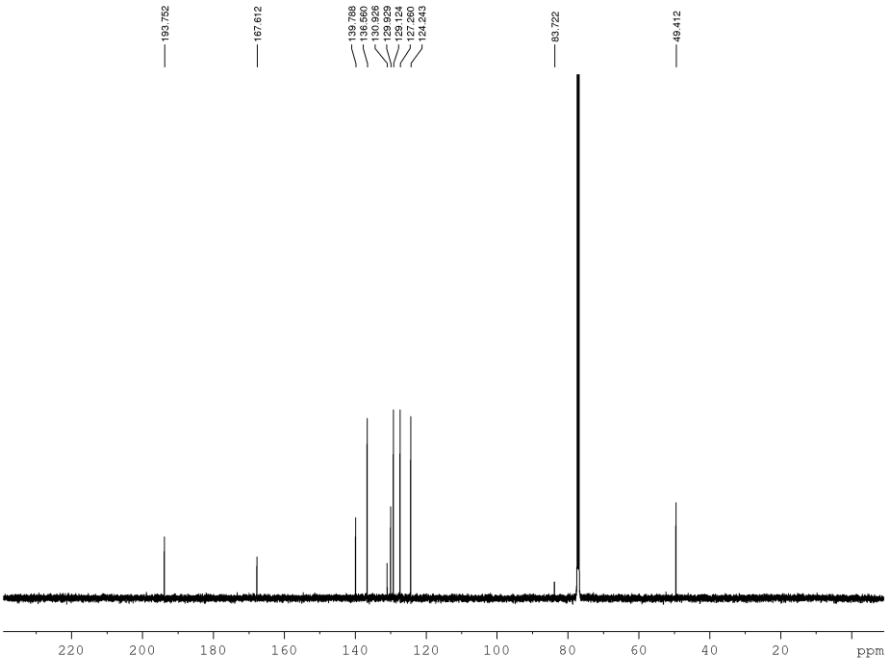


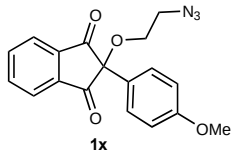
1w

(^{1}H NMR, $CDCl_3$, 500 MHz)



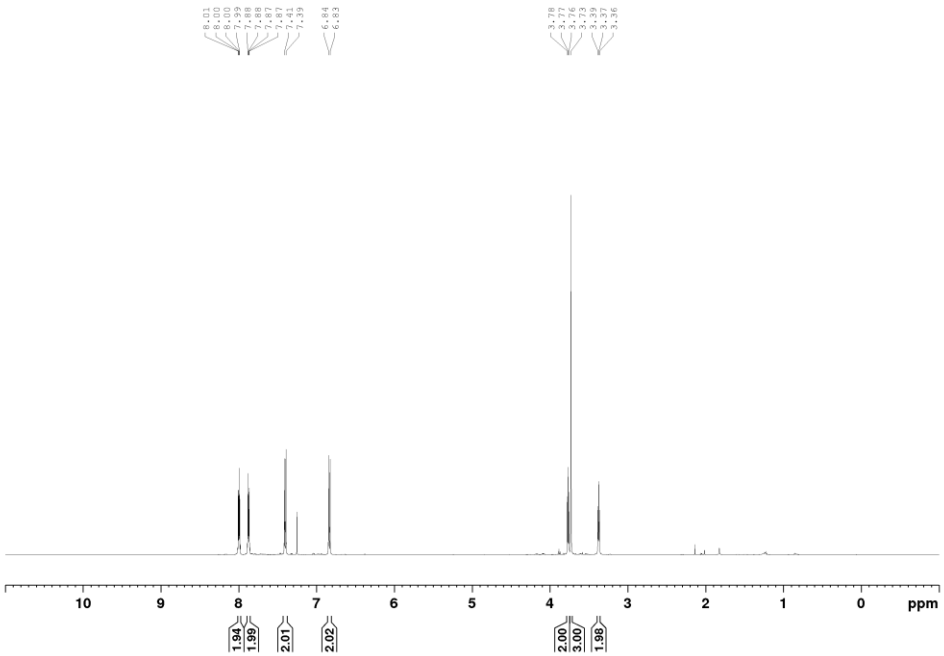
(^{13}C NMR, $CDCl_3$, 125 MHz)



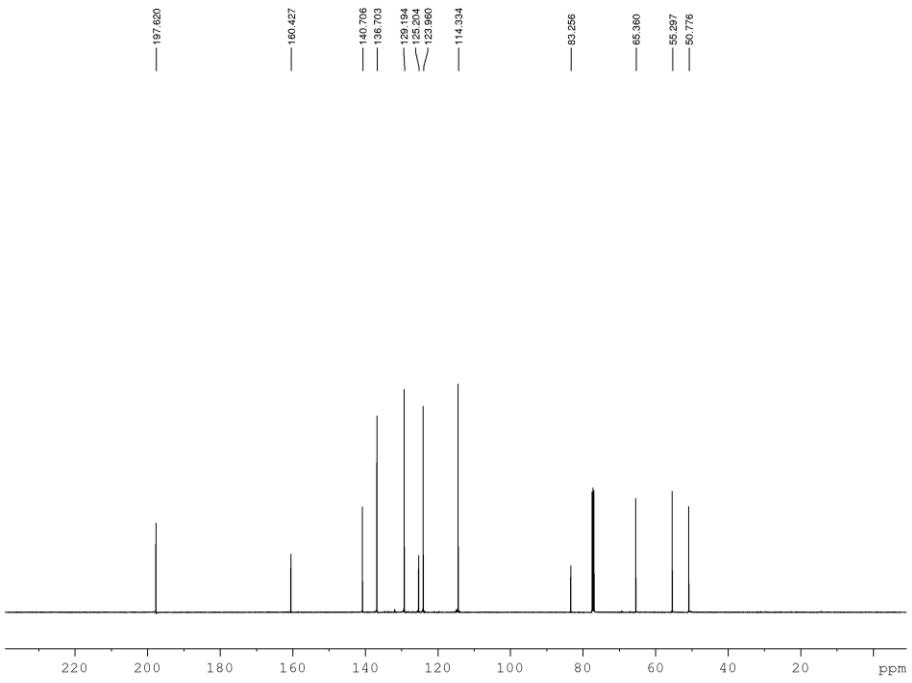


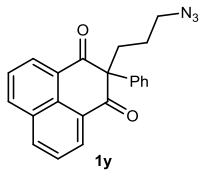
1x

(^{1}H NMR, $CDCl_3$, 500 MHz)



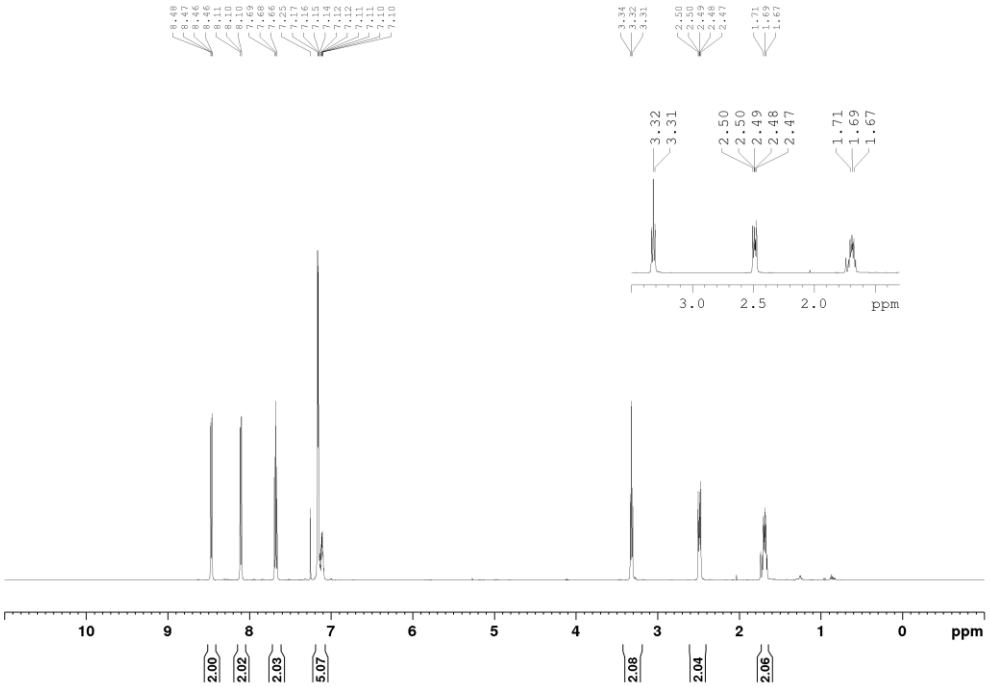
(^{13}C NMR, $CDCl_3$, 125 MHz)



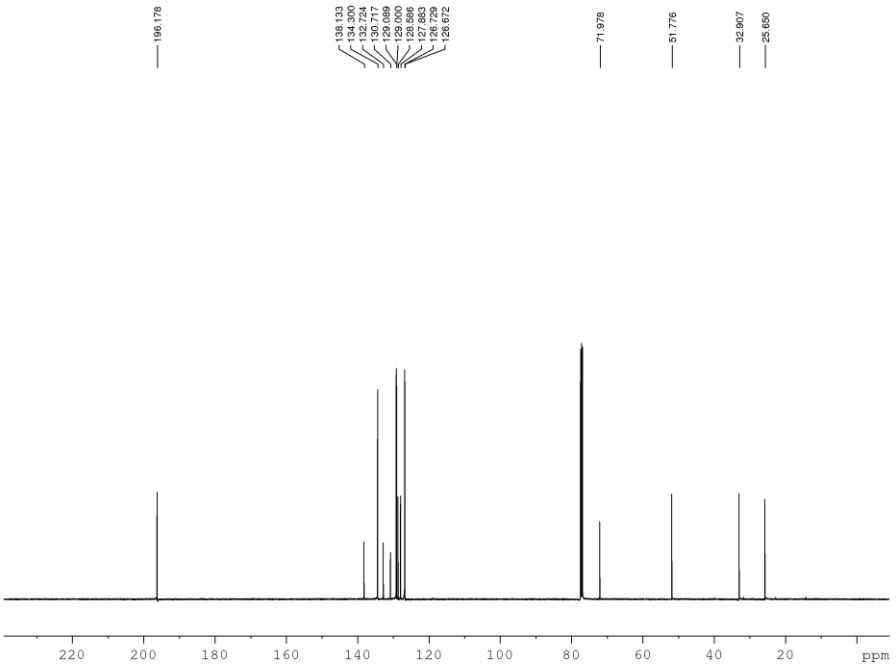


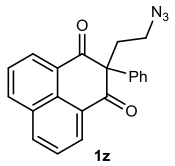
1y

(^{1}H NMR, $CDCl_3$, 500 MHz)



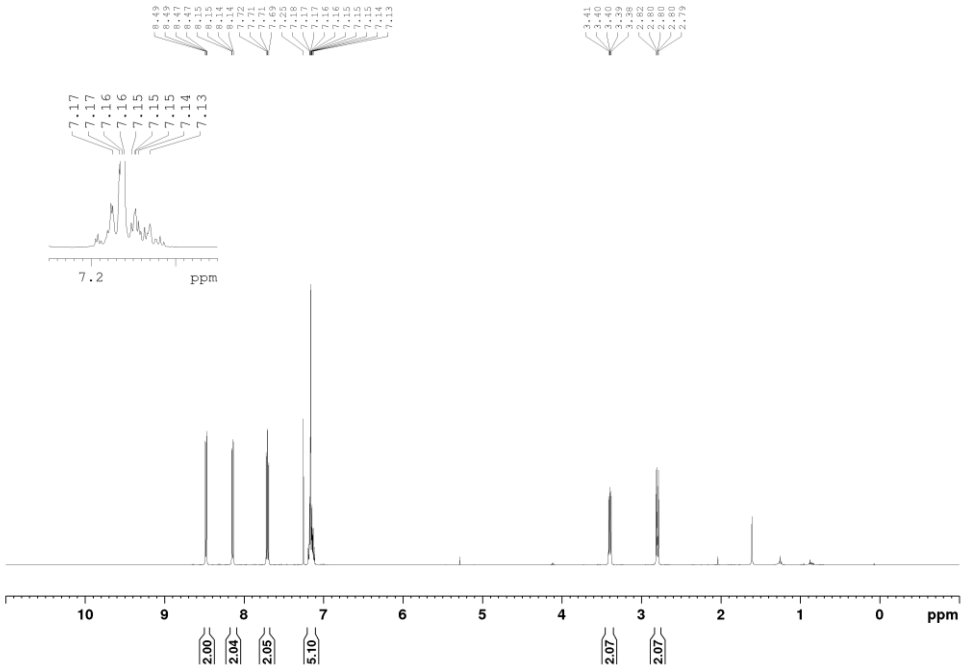
(^{13}C NMR, $CDCl_3$, 125 MHz)



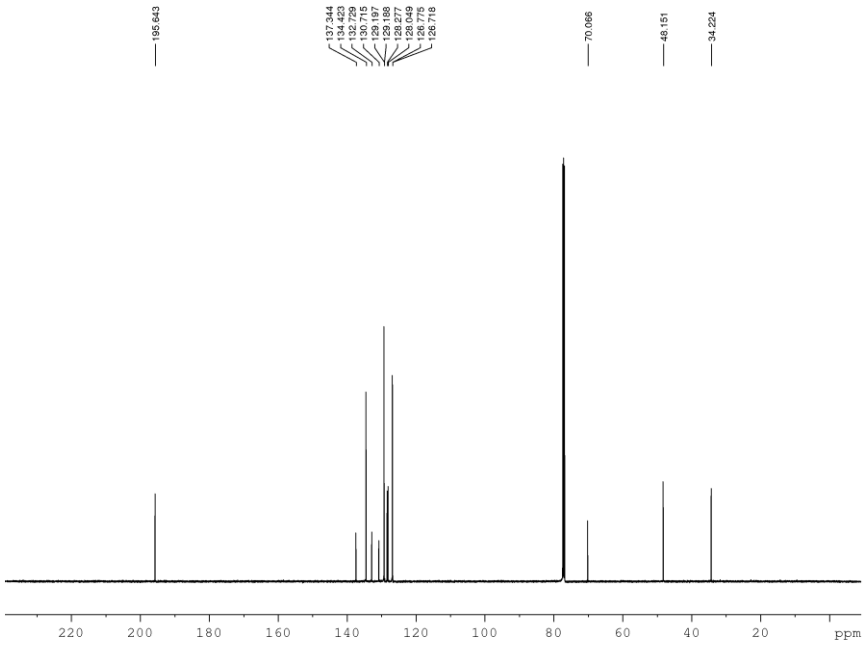


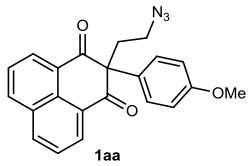
1z

(^{1}H NMR, $CDCl_3$, 500 MHz)



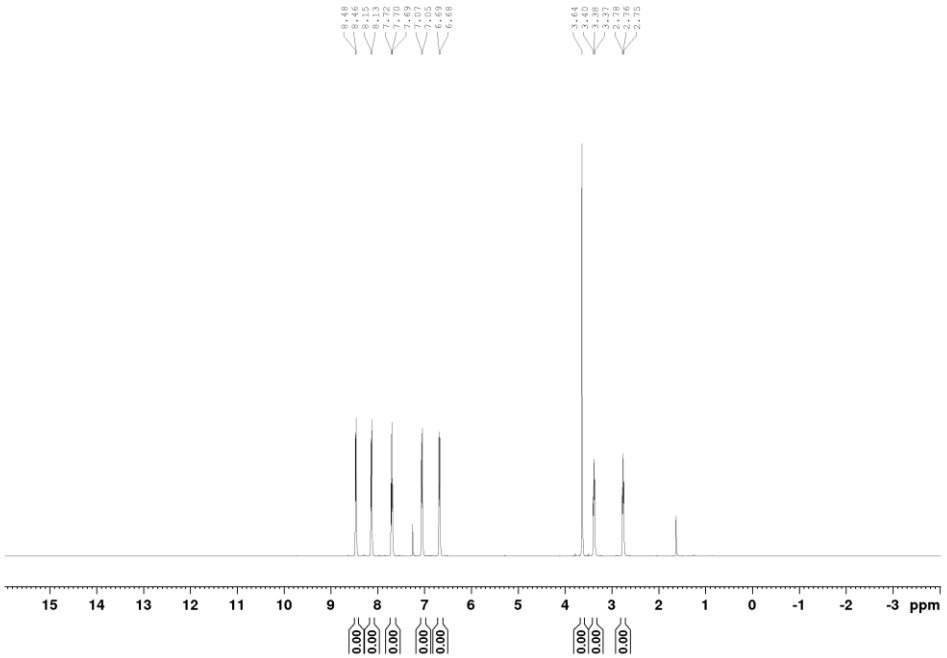
(^{13}C NMR, $CDCl_3$, 125 MHz)



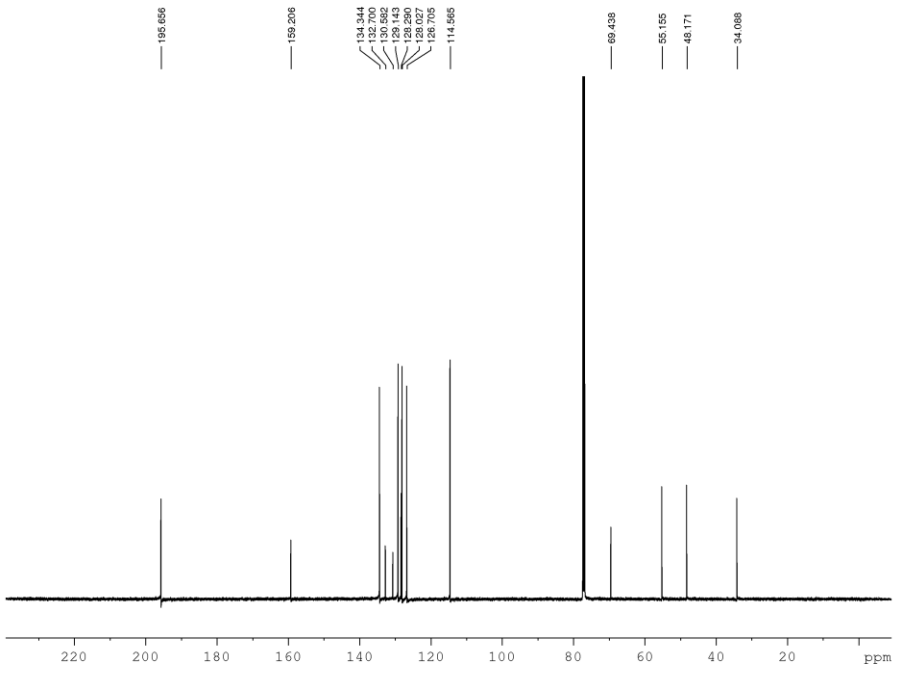


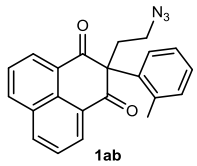
1aa

(^{1}H NMR, $CDCl_3$, 500 MHz)



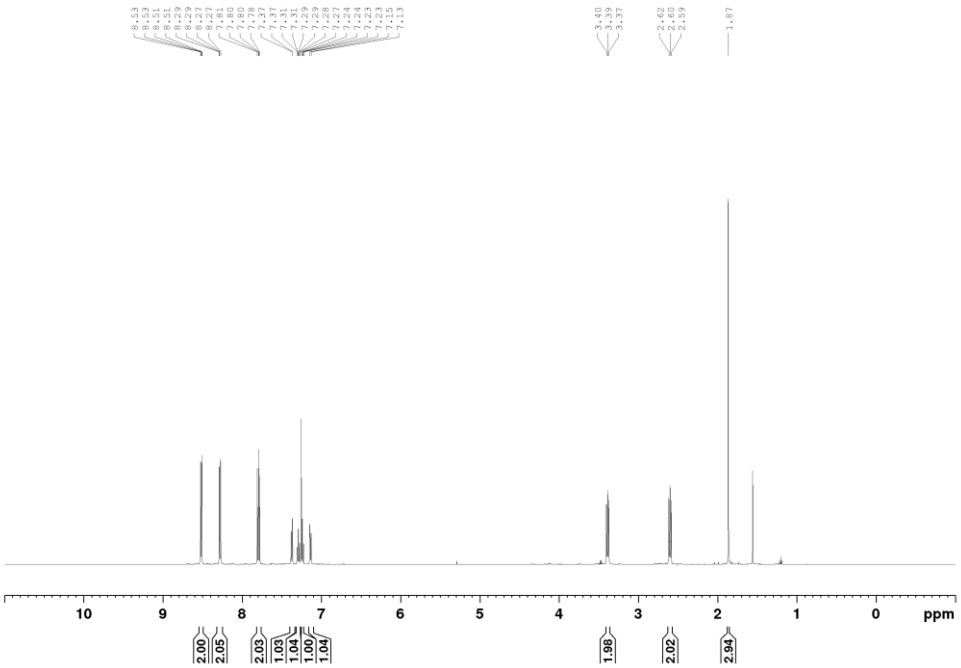
(^{13}C NMR, $CDCl_3$, 125 MHz)



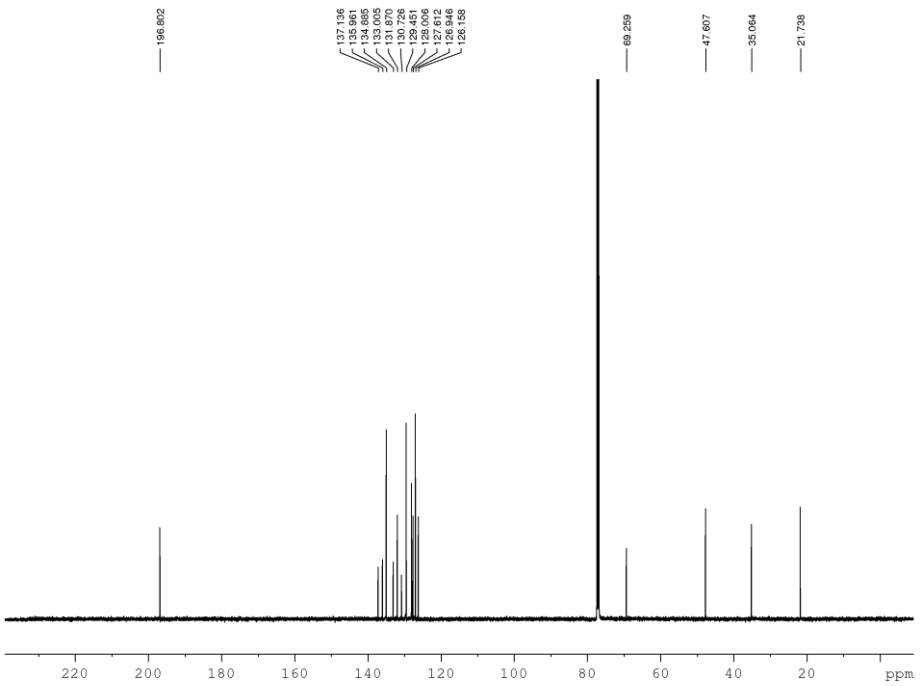


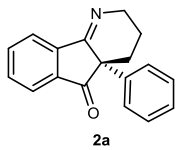
1ab

(^{1}H NMR, $CDCl_3$, 500 MHz)



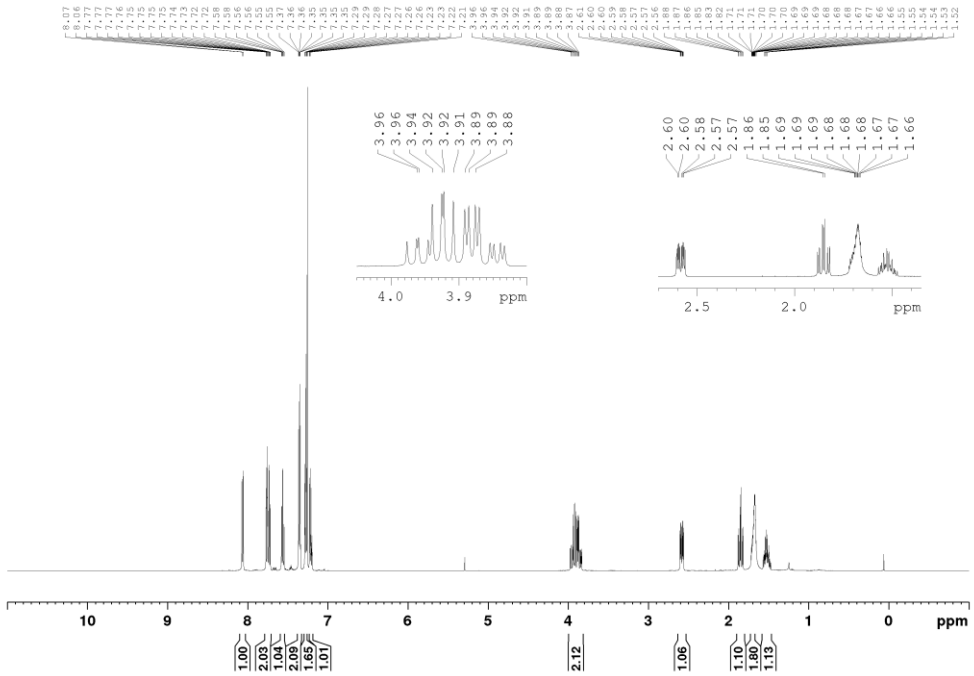
(^{13}C NMR, $CDCl_3$, 125 MHz)



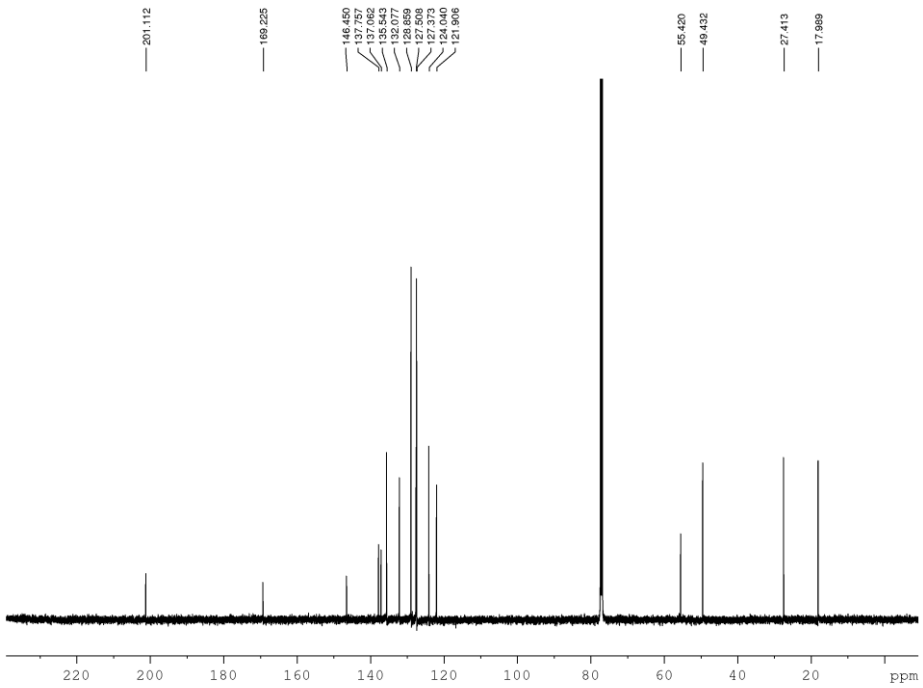


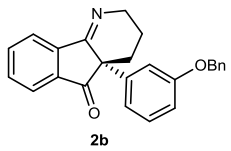
2a

(^{1}H NMR, $CDCl_3$, 500 MHz)



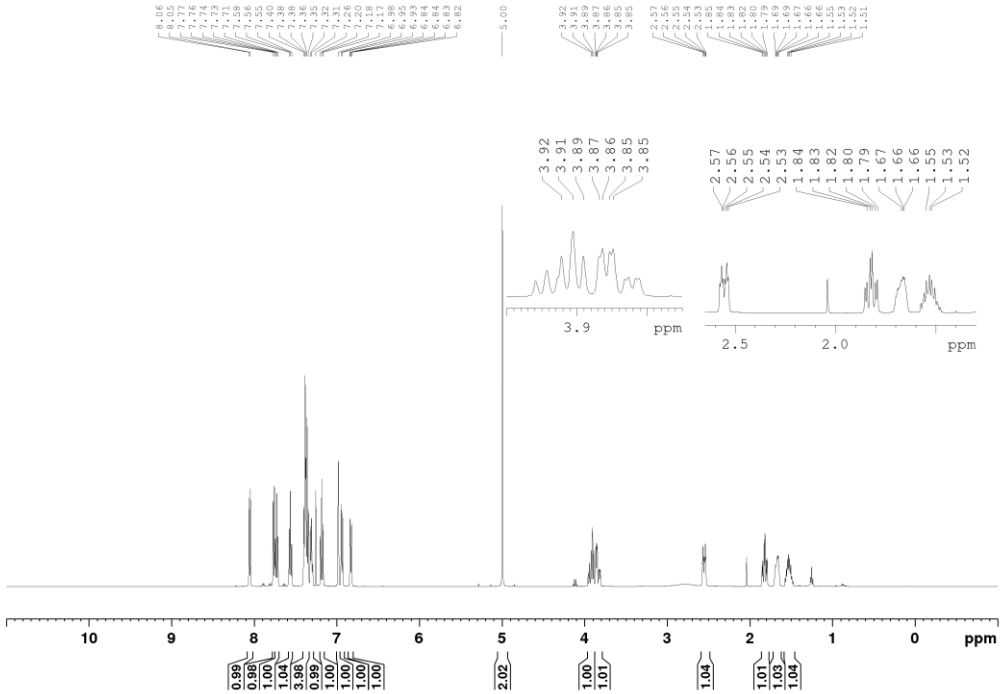
(^{13}C NMR, $CDCl_3$, 125 MHz)



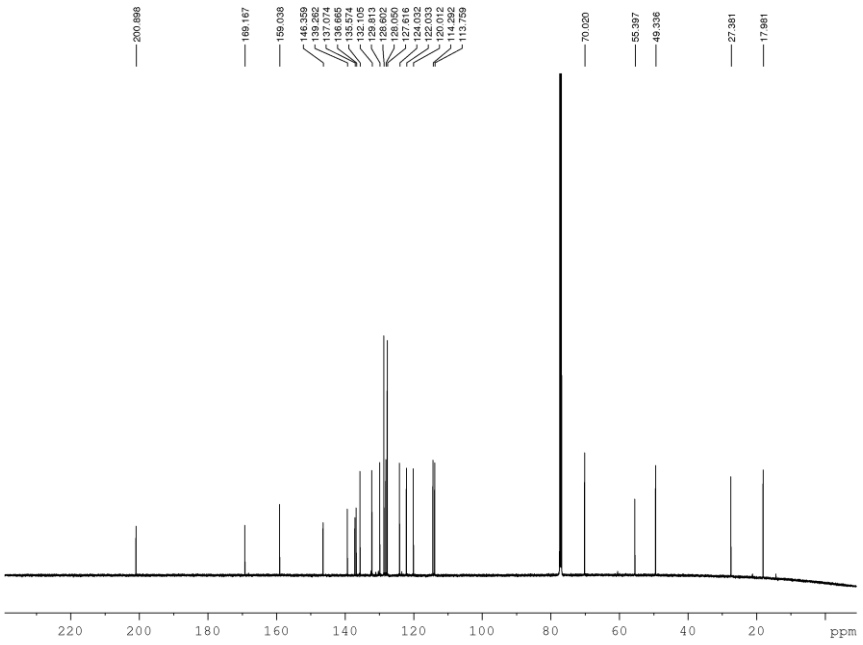


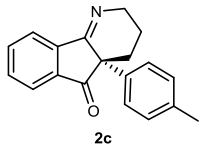
2b

(^{1}H NMR, $CDCl_3$, 500 MHz)



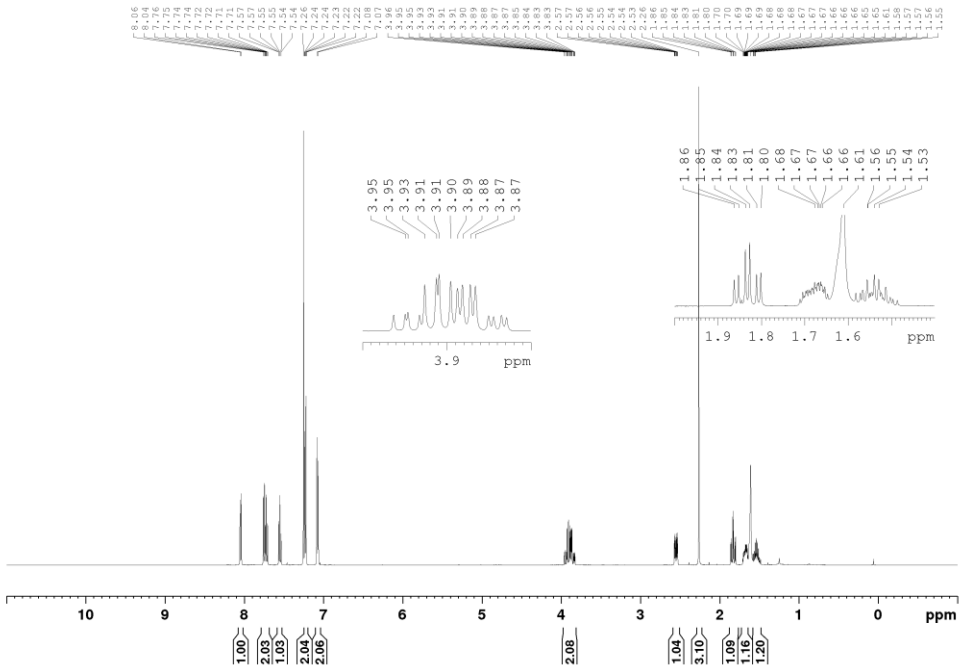
(^{13}C NMR, $CDCl_3$, 125 MHz)



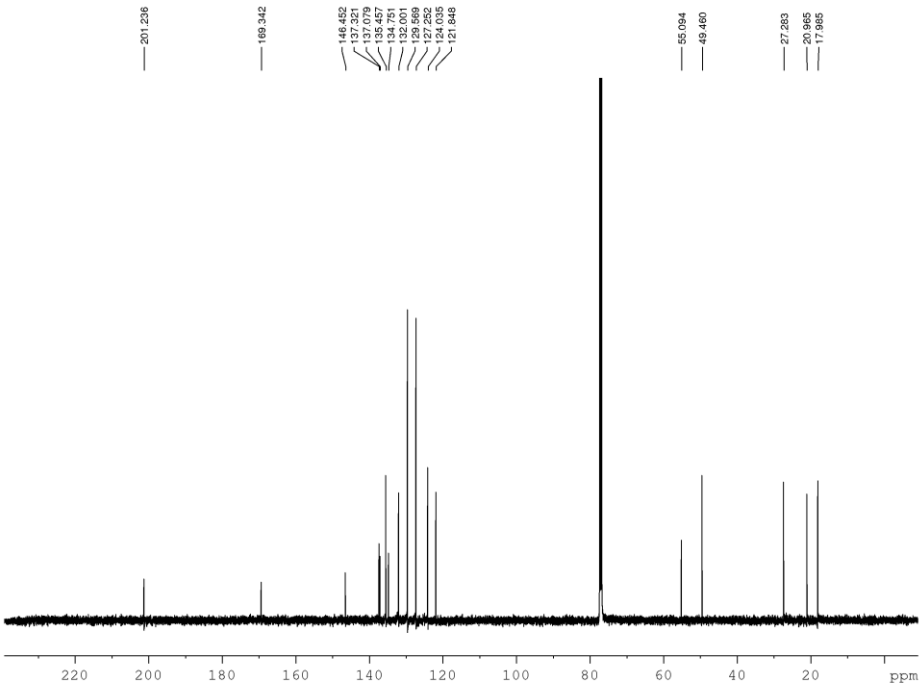


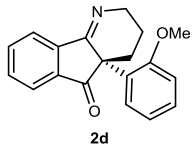
2c

(^{1}H NMR, $CDCl_3$, 500 MHz)



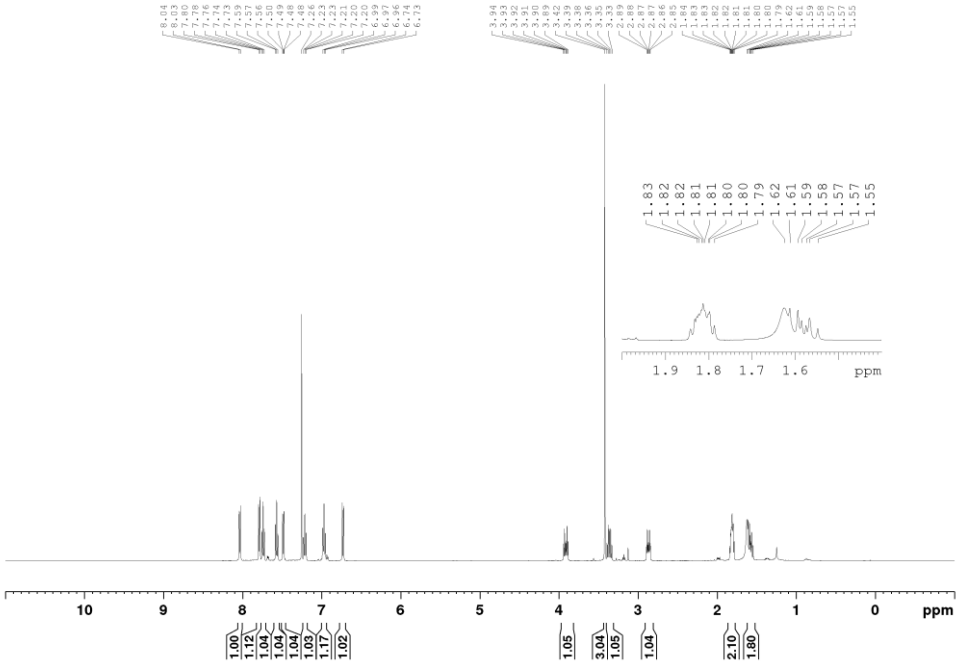
(^{13}C NMR, $CDCl_3$, 125 MHz)



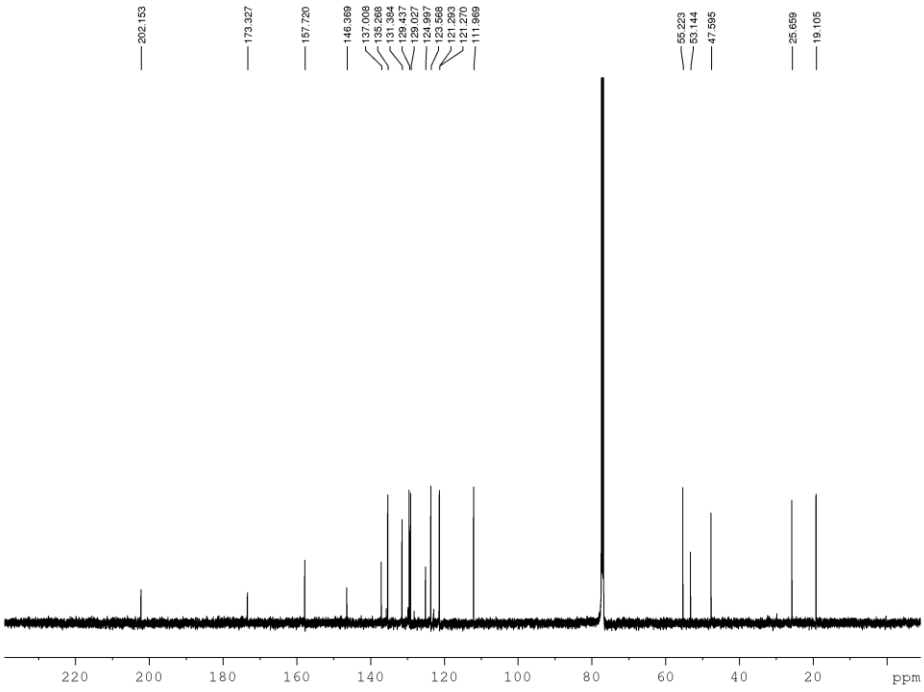


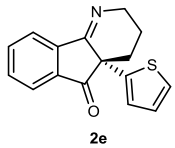
2d

(^{1}H NMR, $CDCl_3$, 500 MHz)



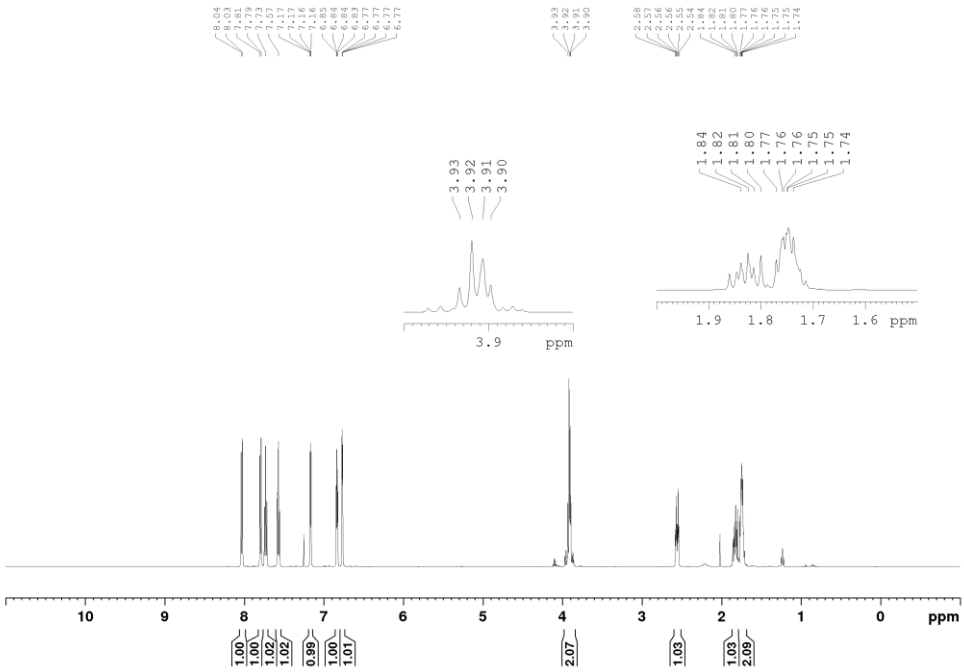
(^{13}C NMR, $CDCl_3$, 125 MHz)



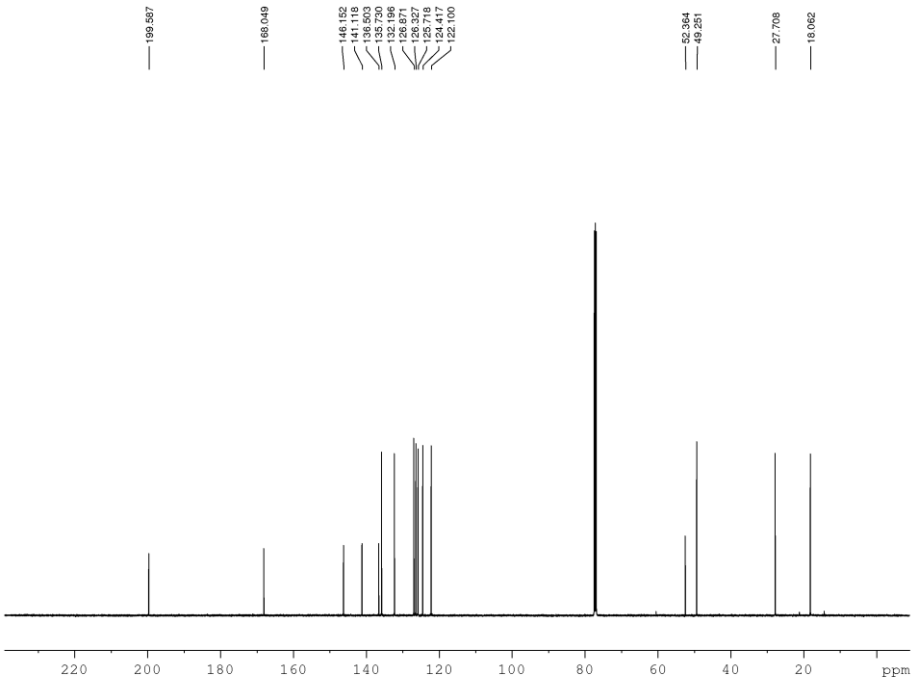


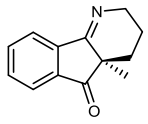
2e

(^{1}H NMR, $CDCl_3$, 500 MHz)



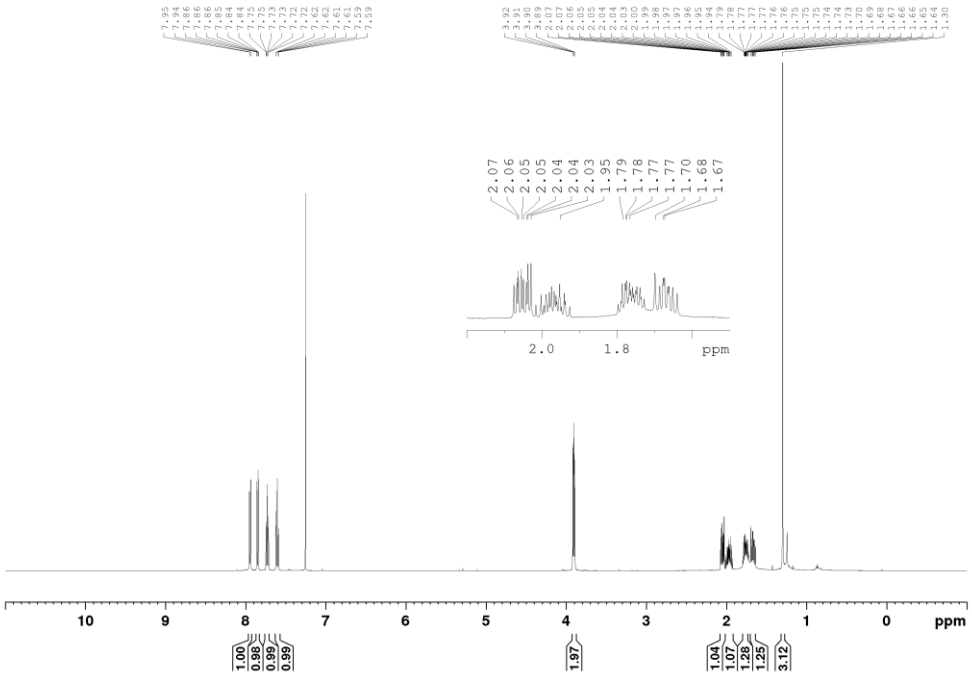
(^{13}C NMR, $CDCl_3$, 125 MHz)



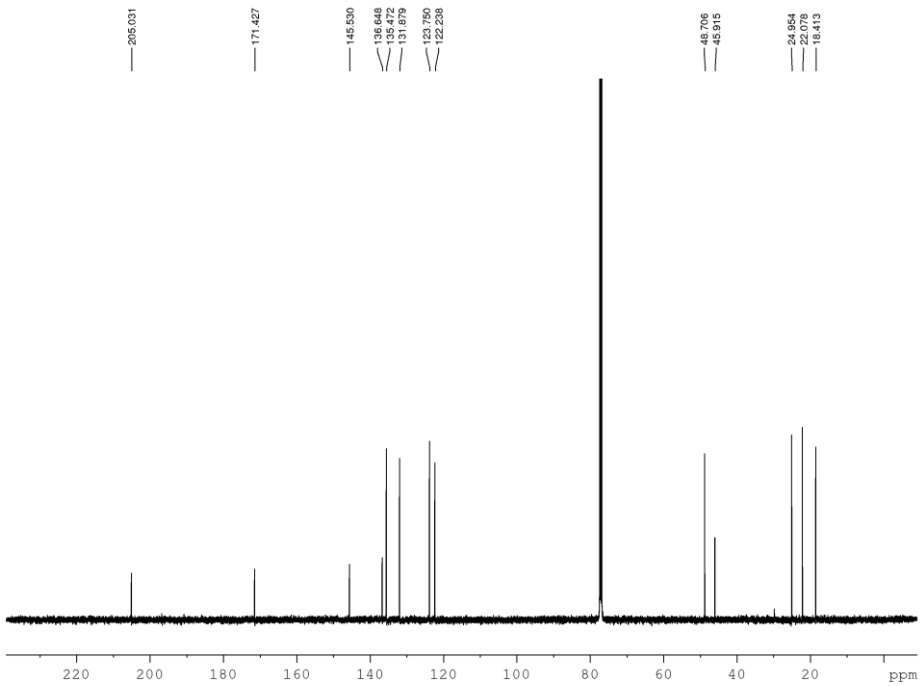


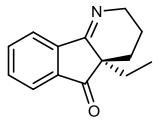
2f

(^{1}H NMR, $CDCl_3$, 500 MHz)



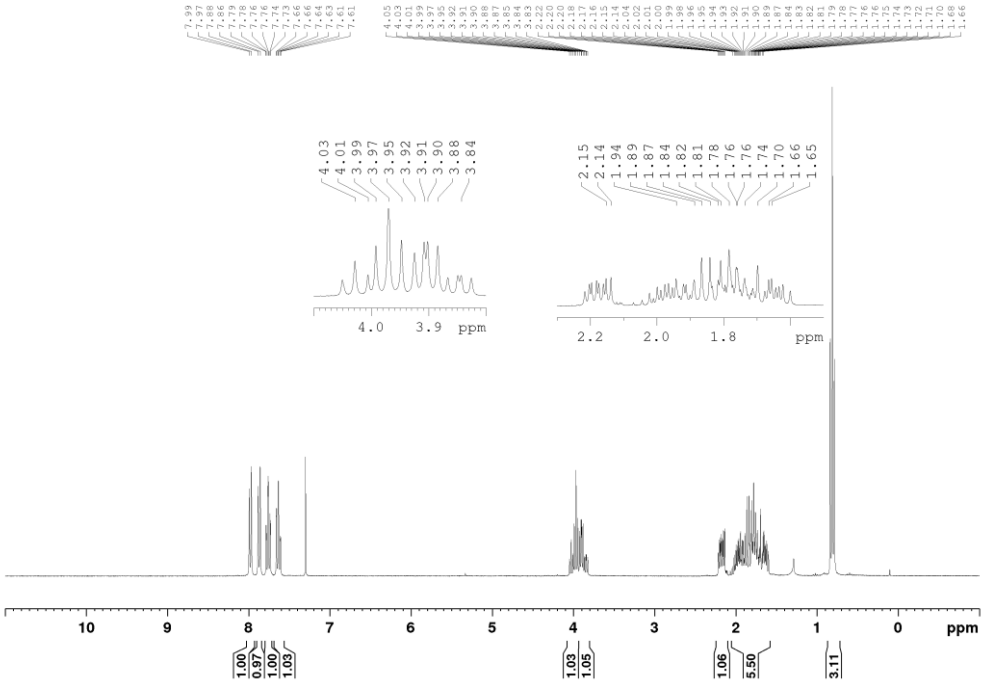
(^{13}C NMR, $CDCl_3$, 125 MHz)



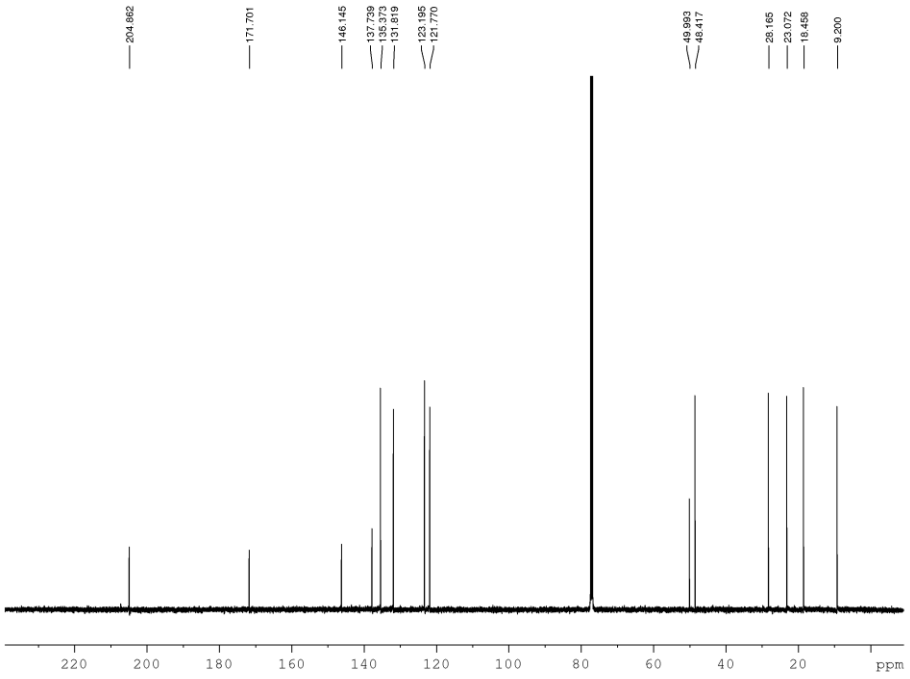


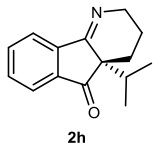
2g

(^{1}H NMR, $CDCl_3$, 500 MHz)



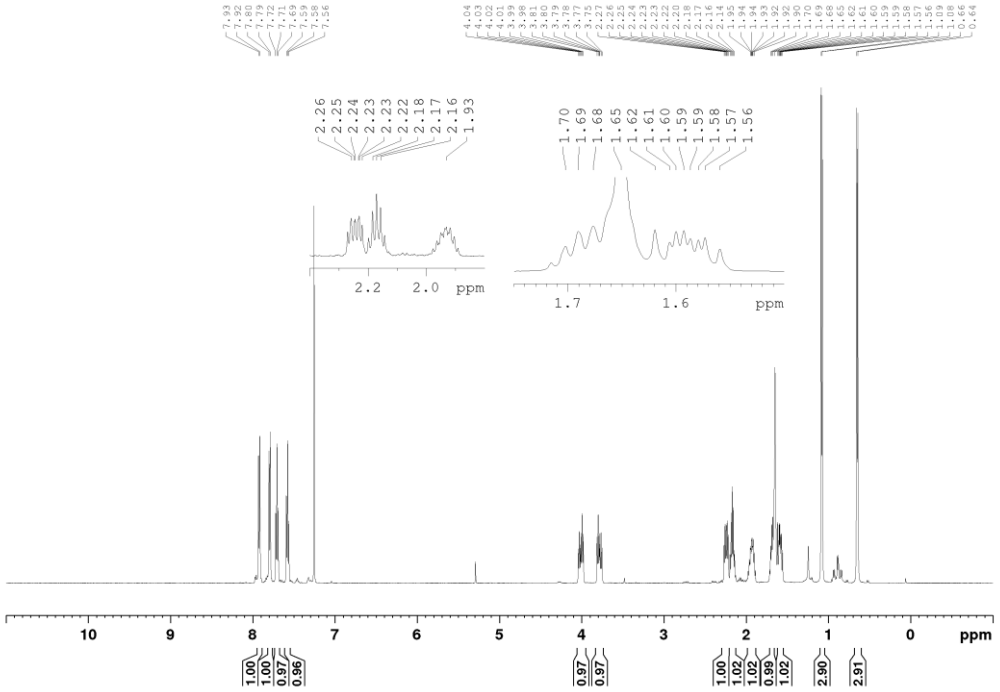
(^{13}C NMR, $CDCl_3$, 125 MHz)



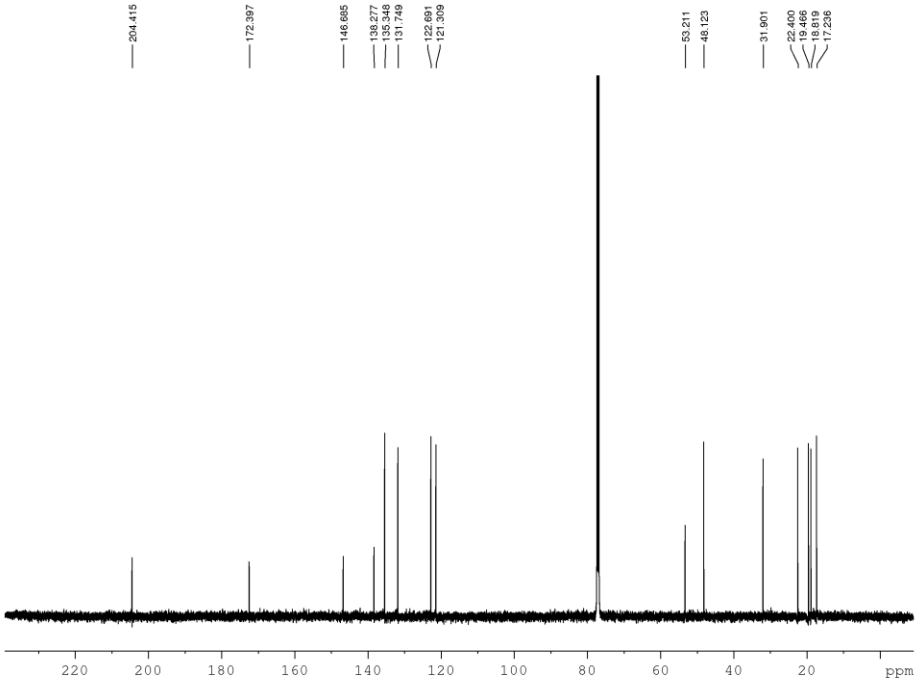


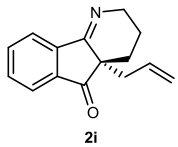
2h

(^{1}H NMR, $CDCl_3$, 500 MHz)



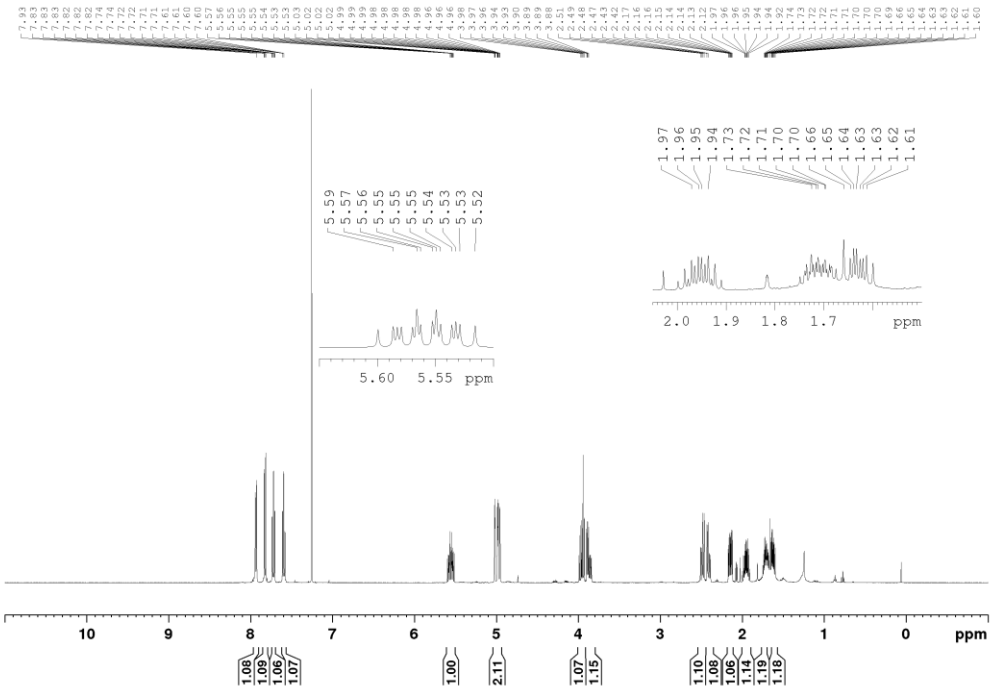
(^{13}C NMR, $CDCl_3$, 125 MHz)



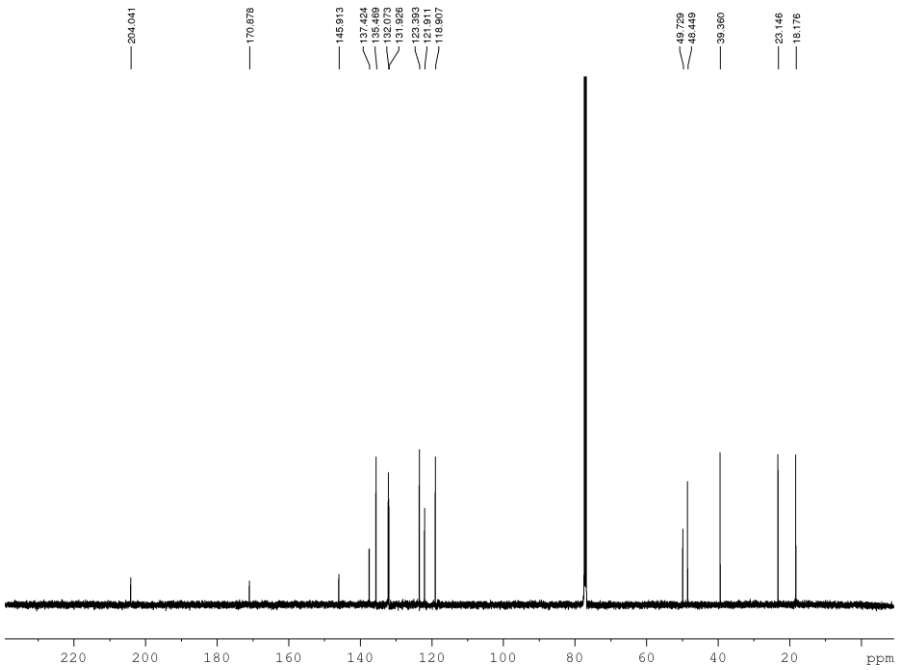


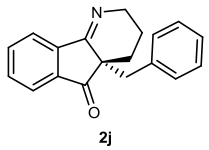
2i

(^{1}H NMR, $CDCl_3$, 500 MHz)



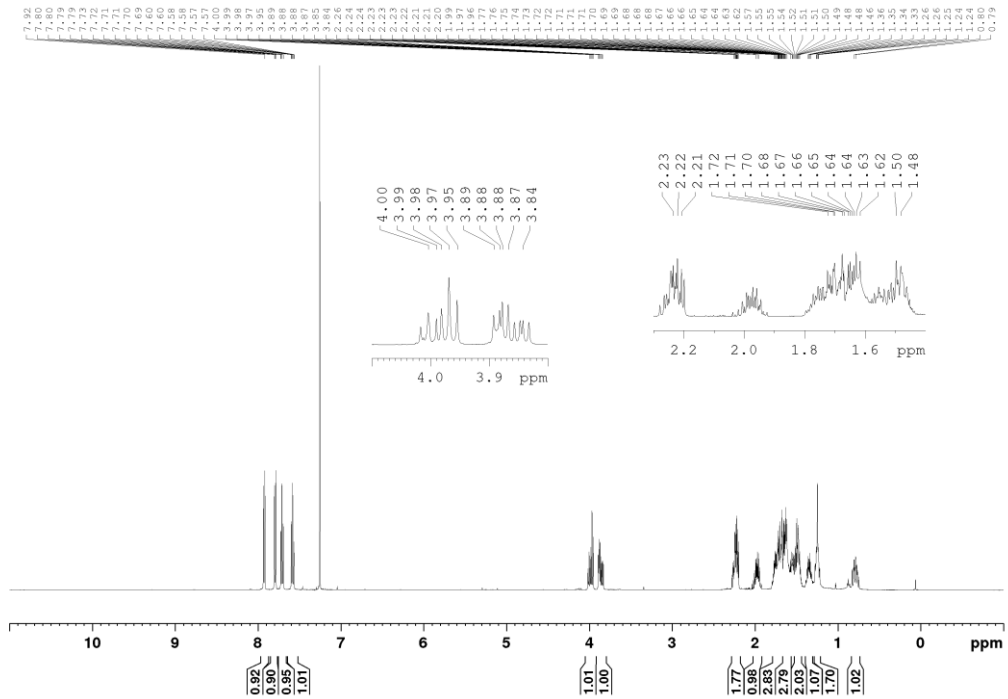
(^{13}C NMR, $CDCl_3$, 125 MHz)



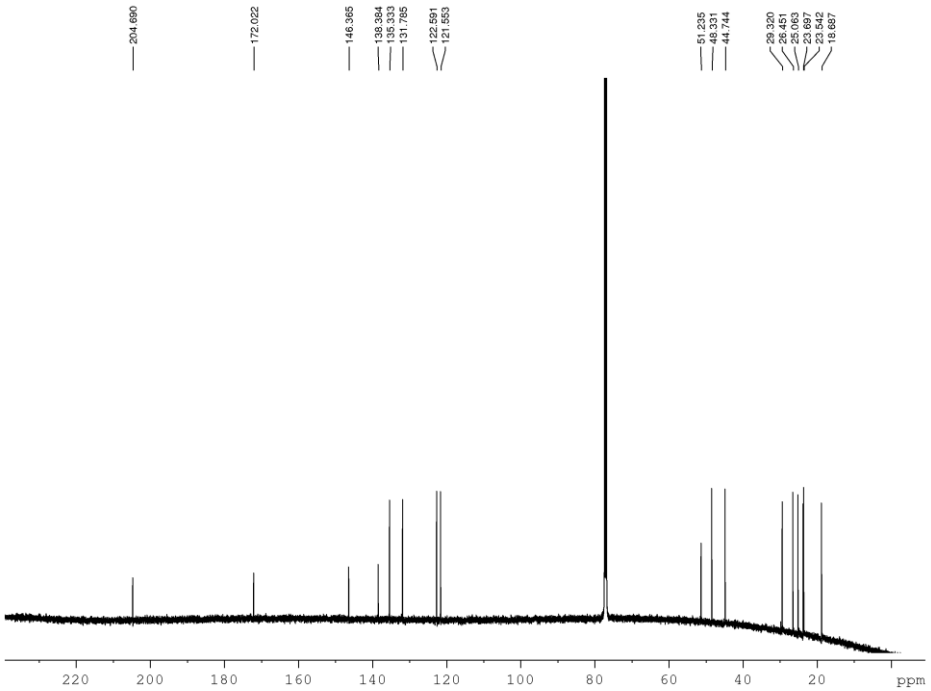


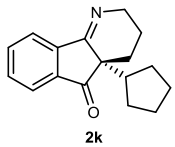
2j

(^{1}H NMR, $CDCl_3$, 500 MHz)



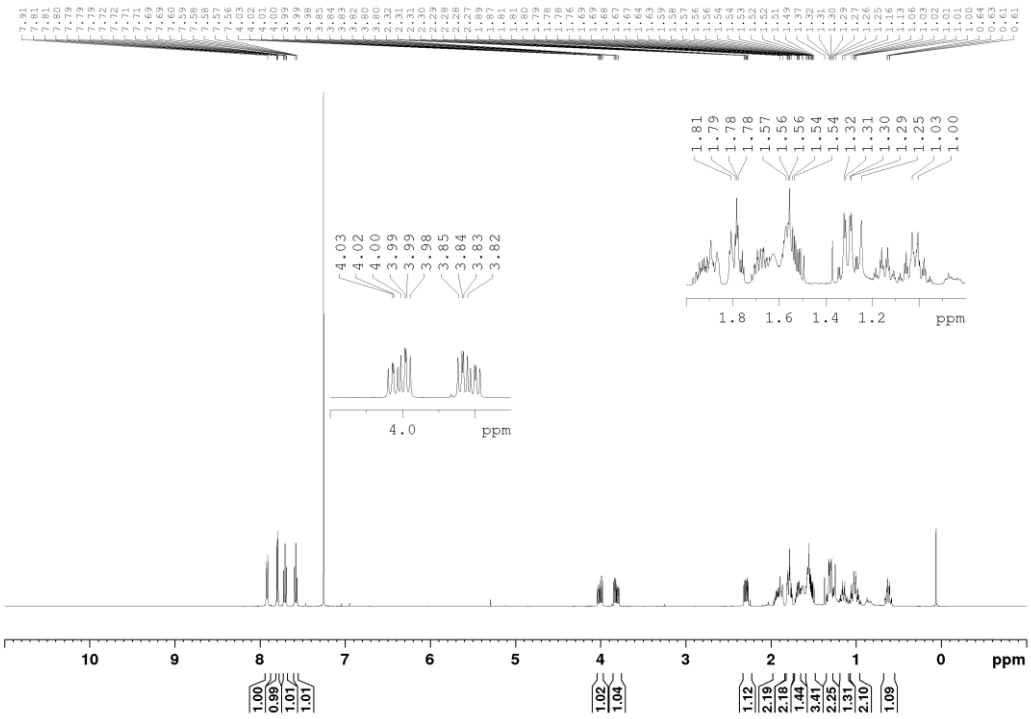
(^{13}C NMR, $CDCl_3$, 125 MHz)



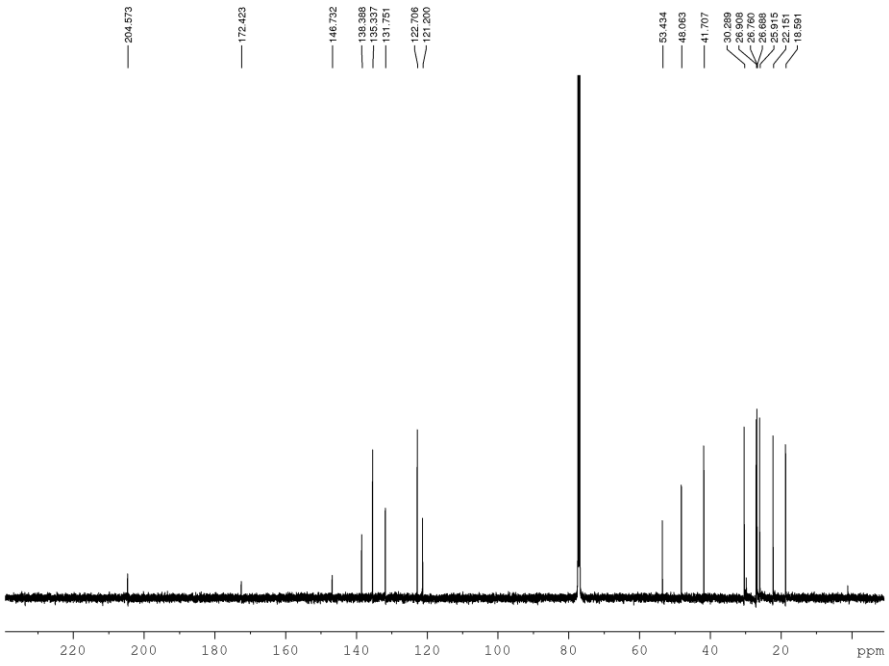


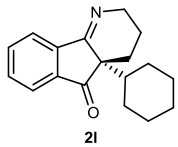
2k

(^{1}H NMR, $CDCl_3$, 500 MHz)



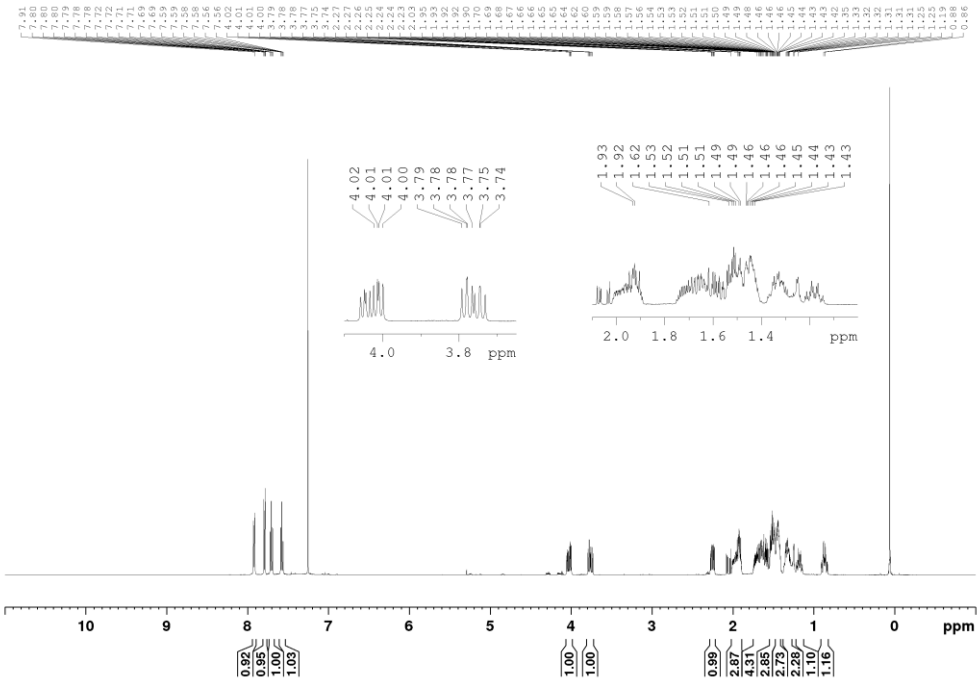
(^{13}C NMR, $CDCl_3$, 125 MHz)



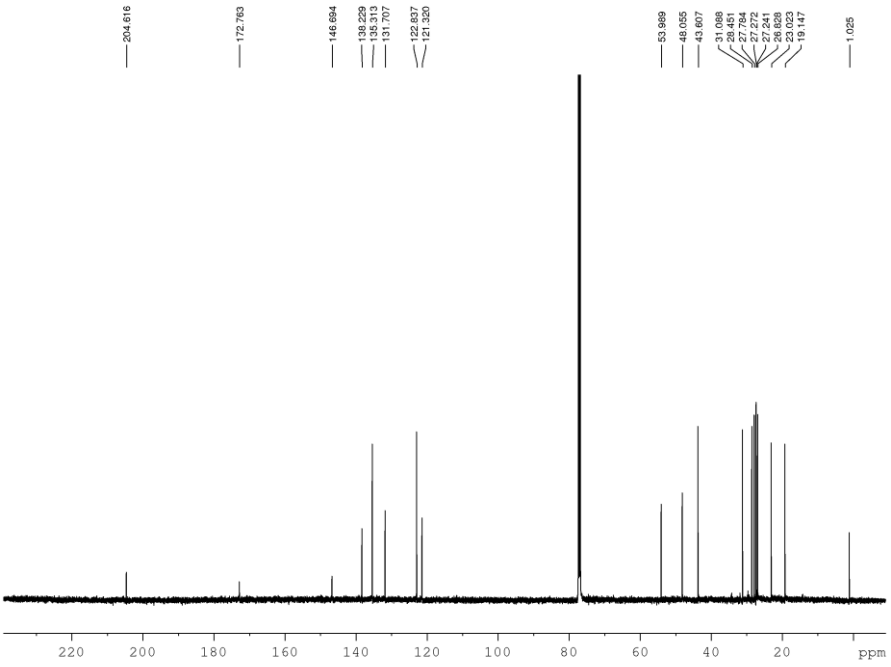


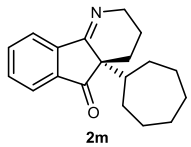
2l

(^{1}H NMR, $CDCl_3$, 500 MHz)



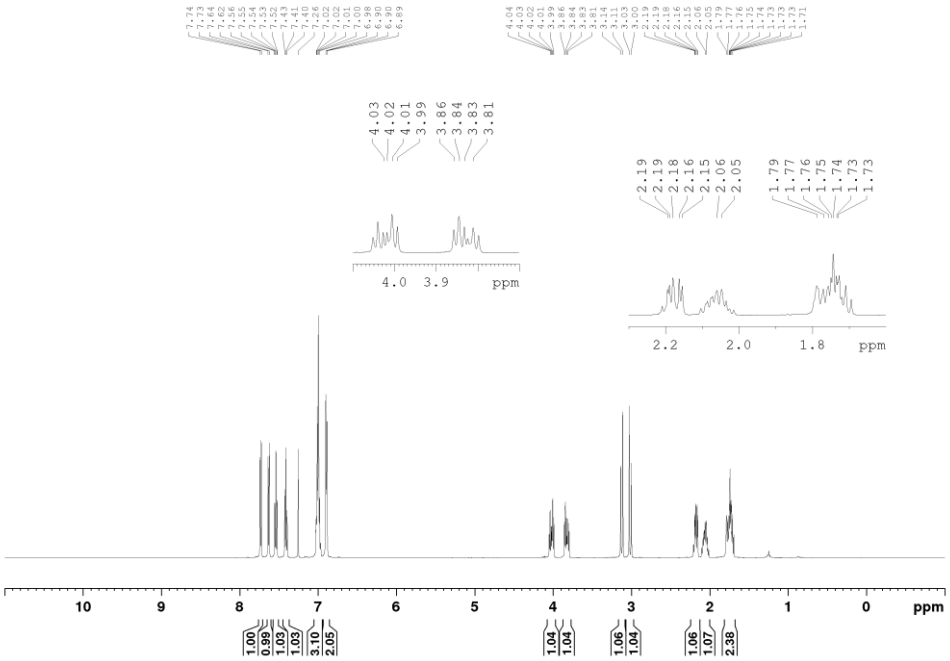
(^{13}C NMR, $CDCl_3$, 125 MHz)



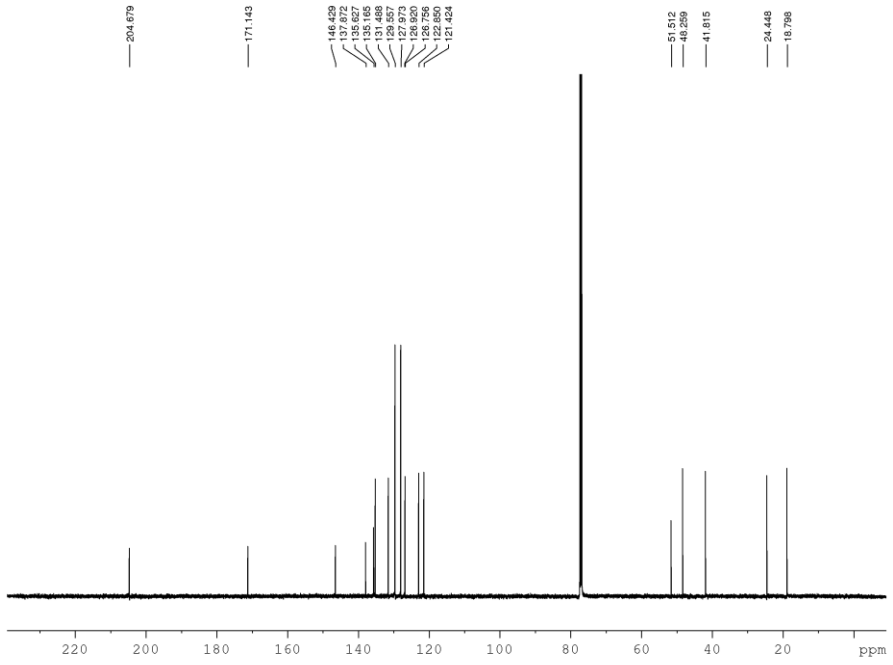


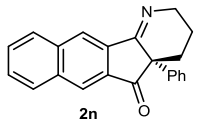
2m

(^{1}H NMR, $CDCl_3$, 500 MHz)



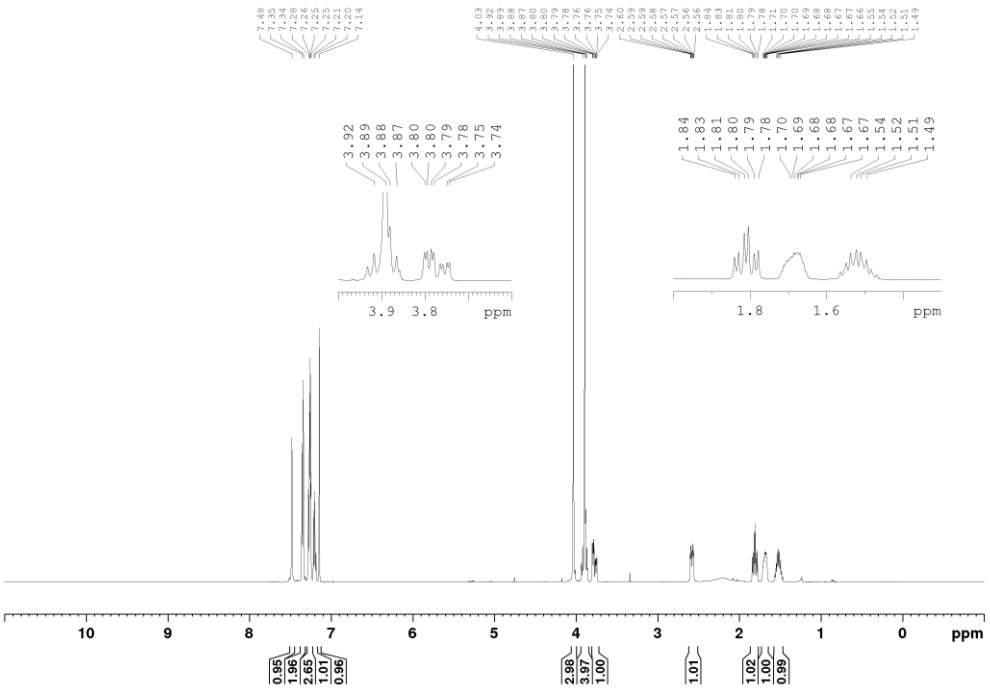
(^{13}C NMR, $CDCl_3$, 125 MHz)



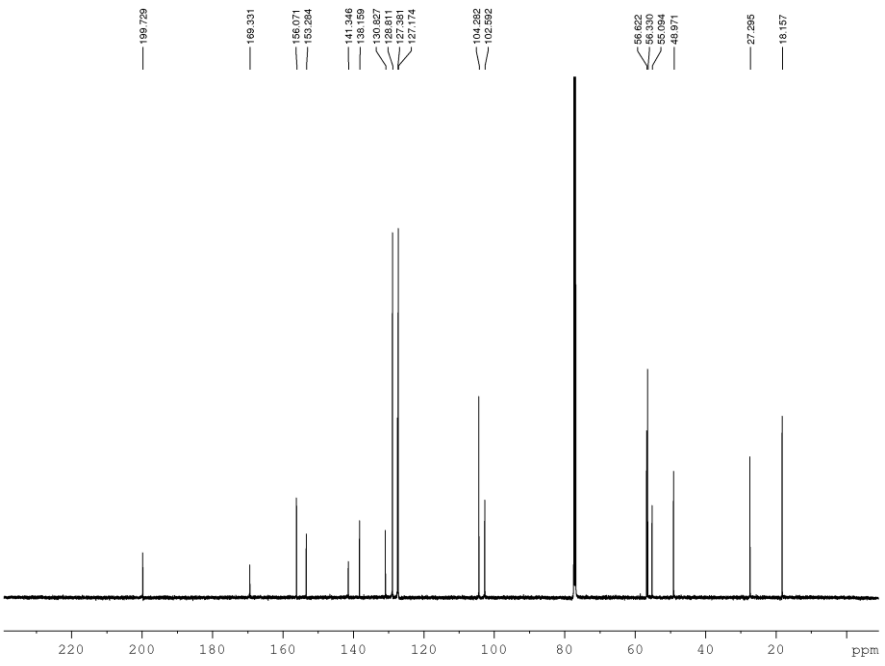


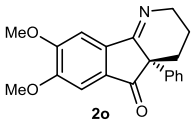
2n

(^{1}H NMR, $CDCl_3$, 500 MHz)



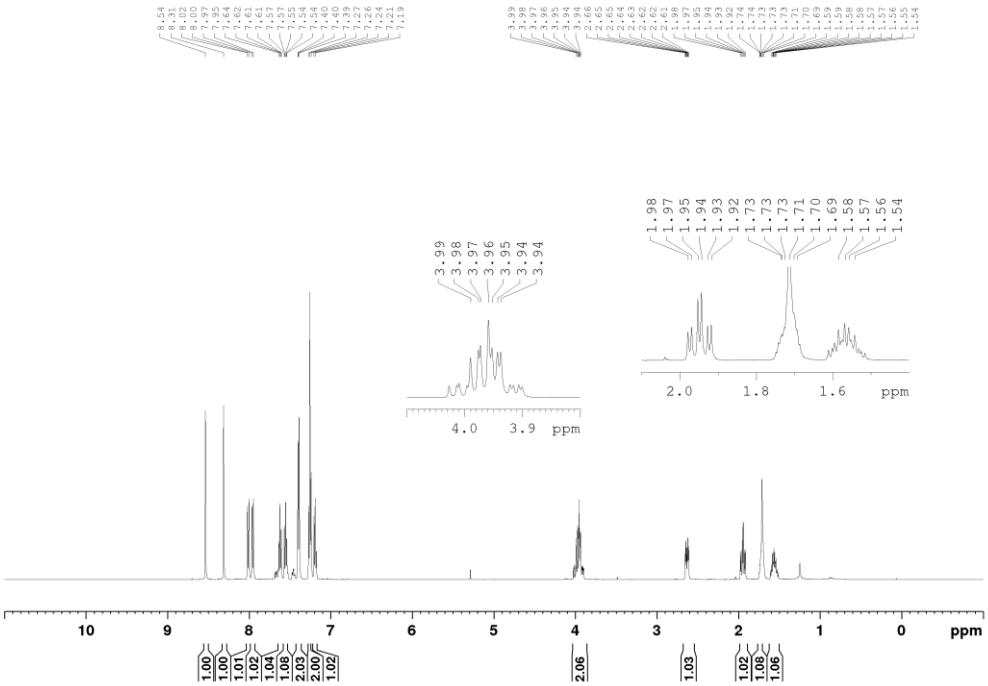
(^{13}C NMR, $CDCl_3$, 125 MHz)



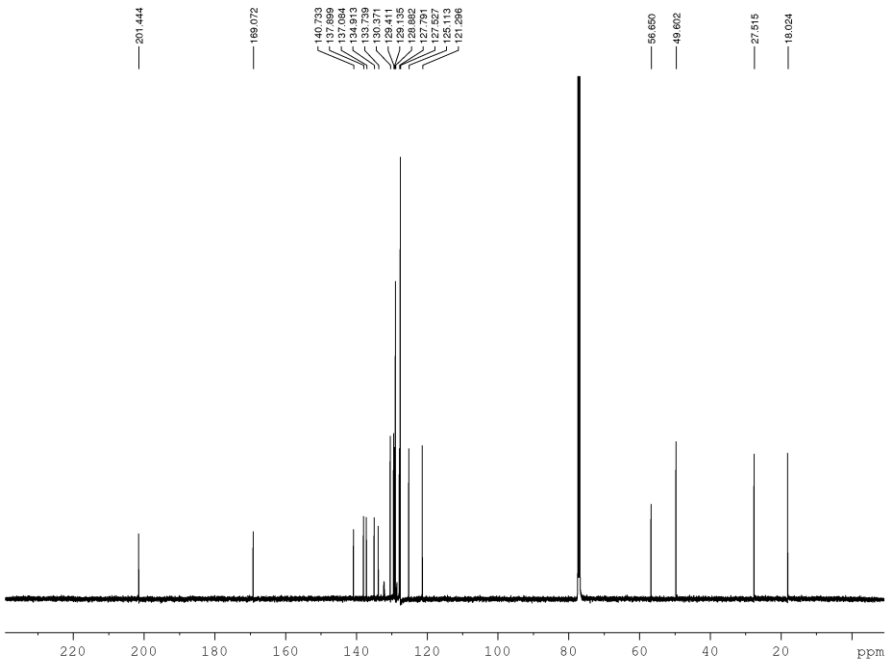


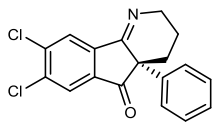
2o

(^{1}H NMR, $CDCl_3$, 500 MHz)



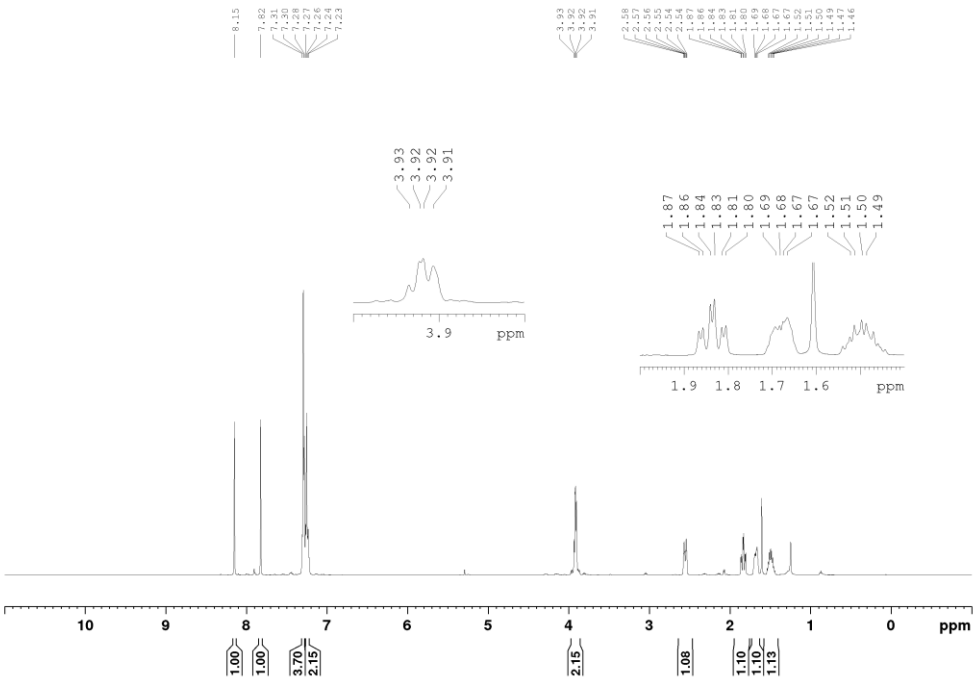
(^{13}C NMR, $CDCl_3$, 125 MHz)



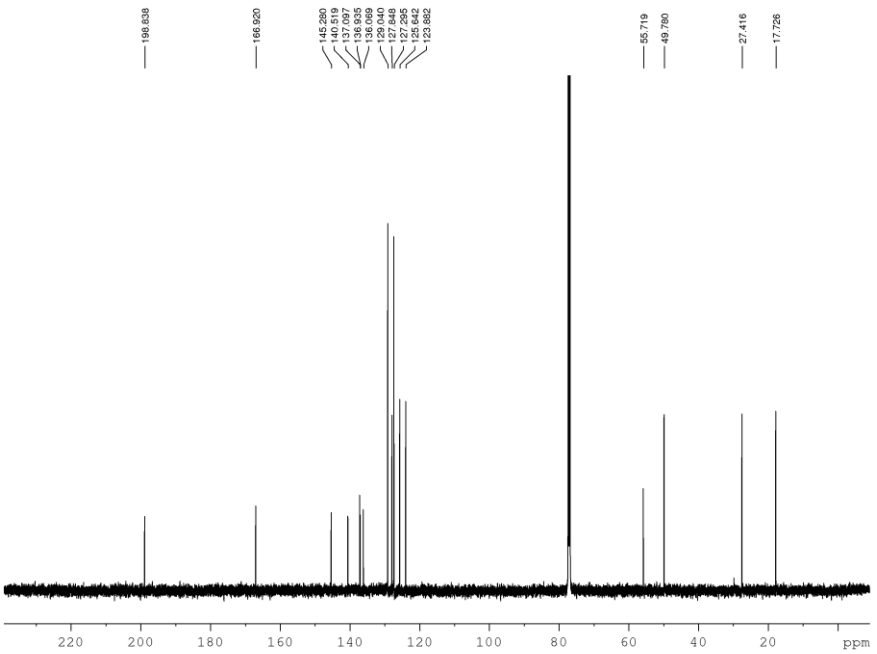


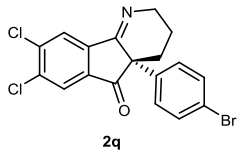
2p

(^{1}H NMR, $CDCl_3$, 500 MHz)



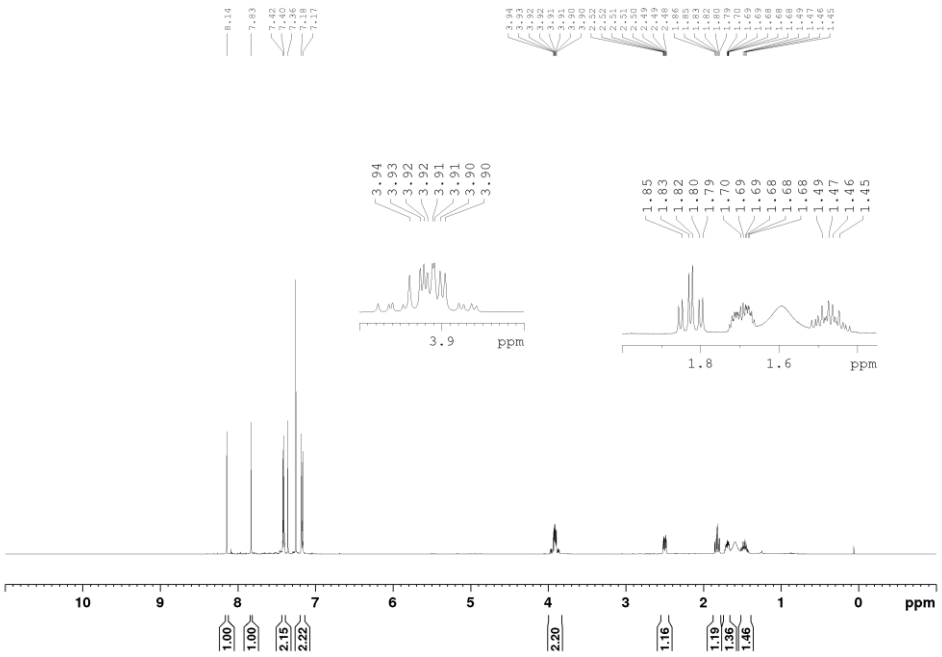
(^{13}C NMR, $CDCl_3$, 125 MHz)



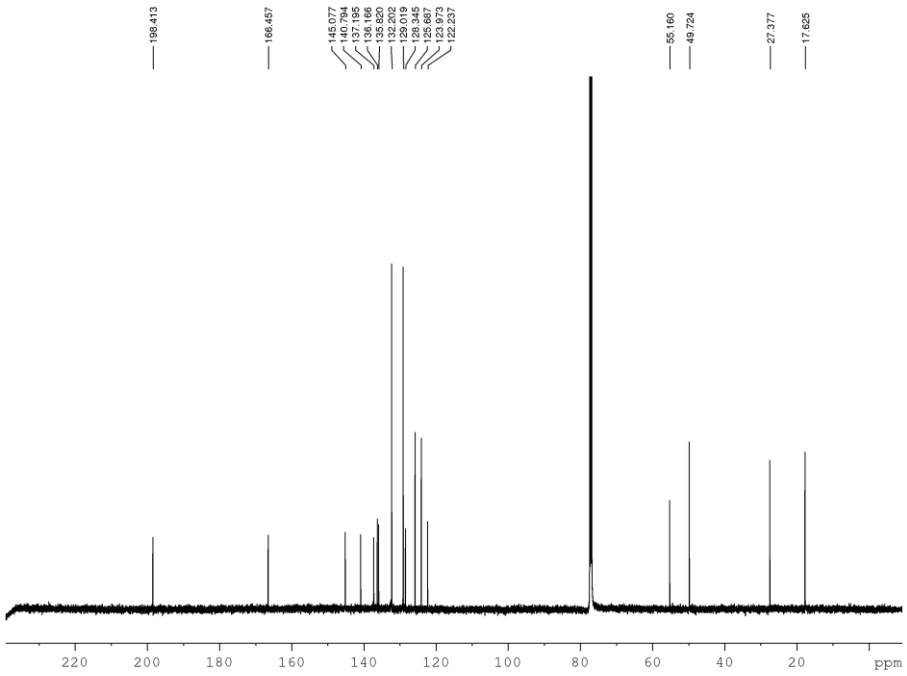


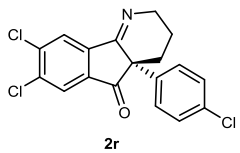
2q

(^{1}H NMR, $CDCl_3$, 500 MHz)



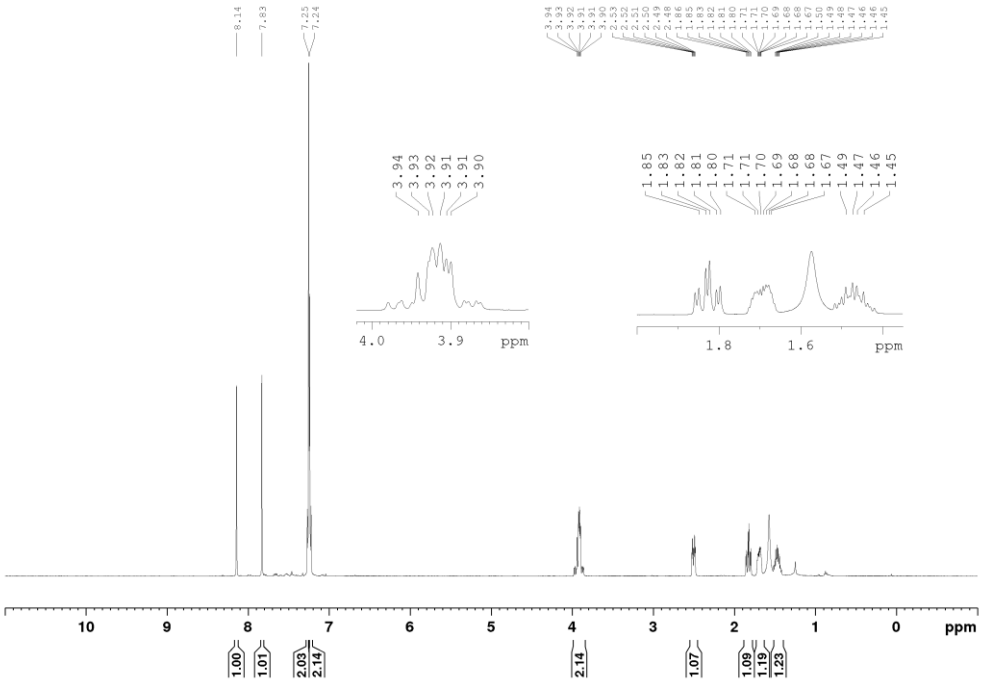
(^{13}C NMR, $CDCl_3$, 125 MHz)



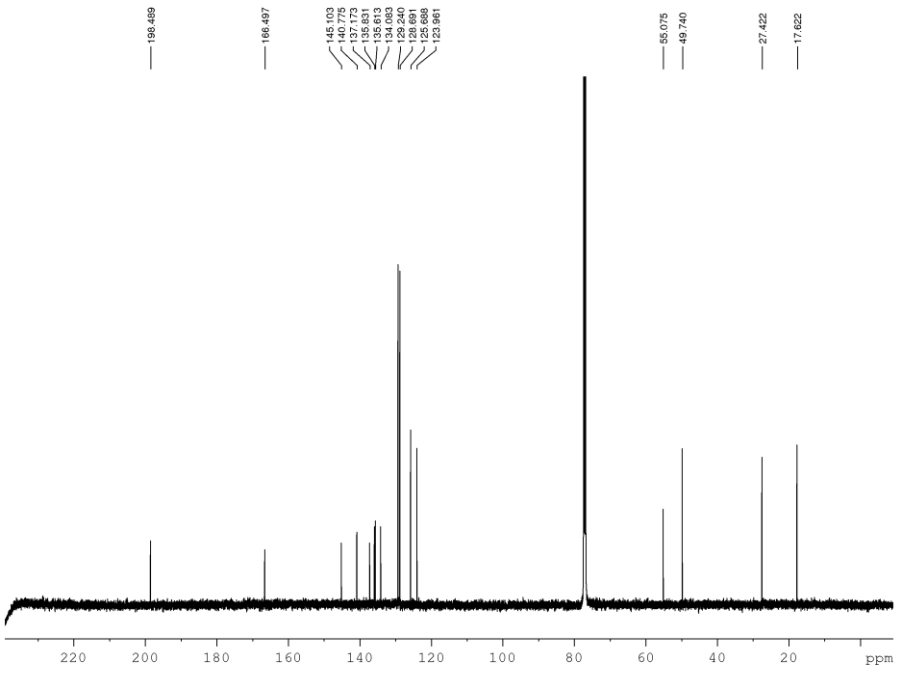


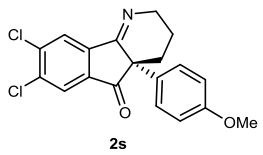
2r

(^{1}H NMR, $CDCl_3$, 500 MHz)



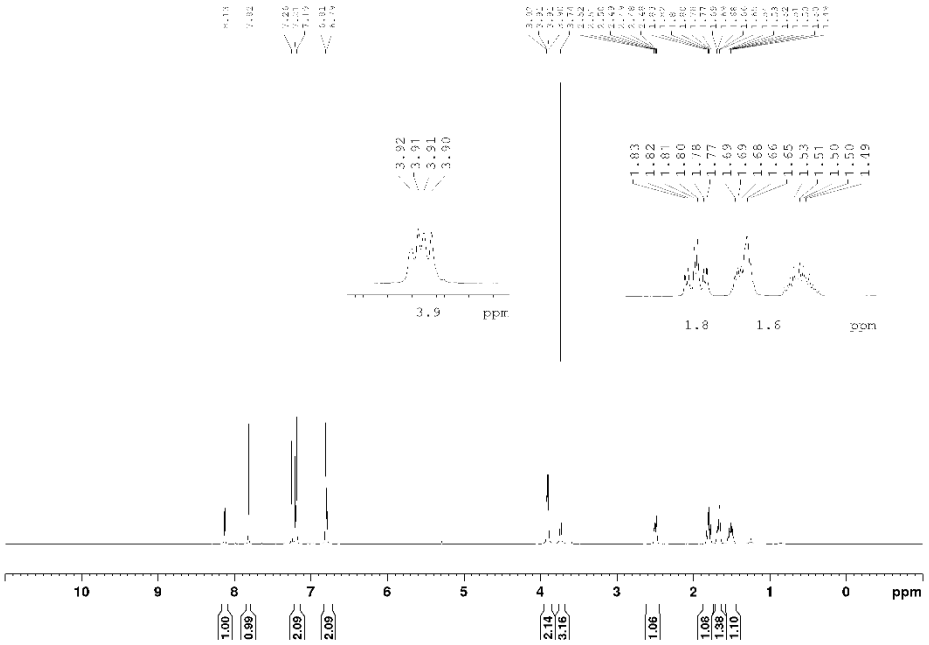
(^{13}C NMR, $CDCl_3$, 125 MHz)



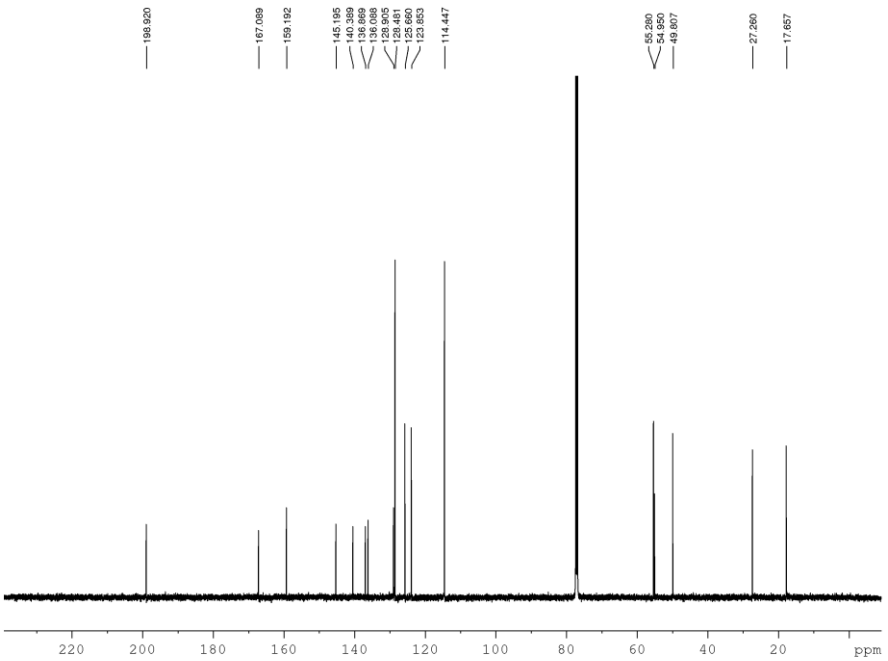


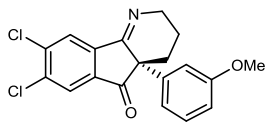
2s

(^{1}H NMR, $CDCl_3$, 500 MHz)



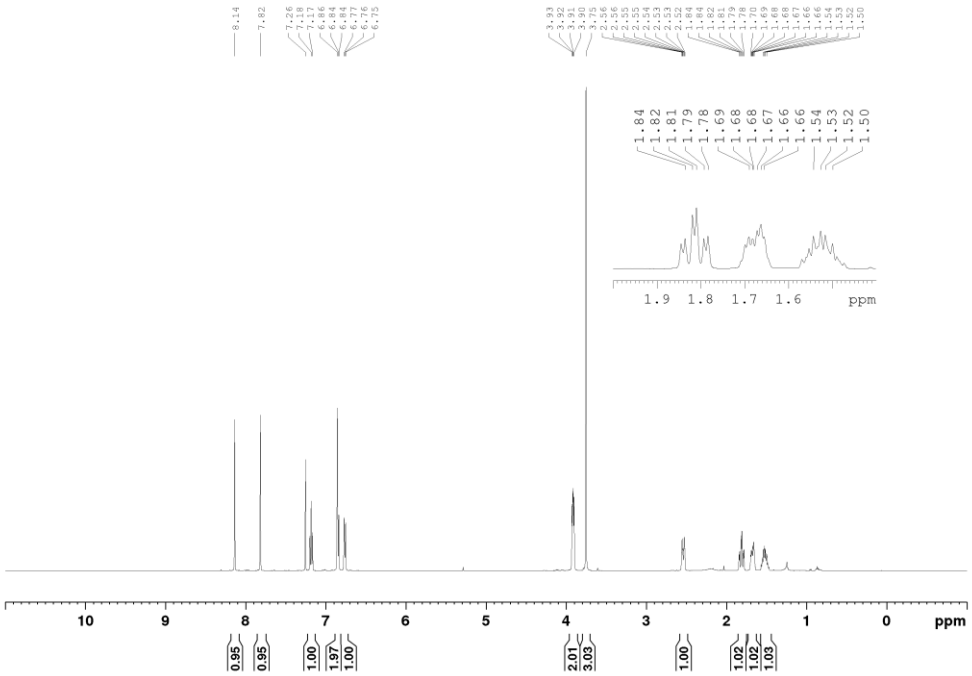
(^{13}C NMR, $CDCl_3$, 125 MHz)



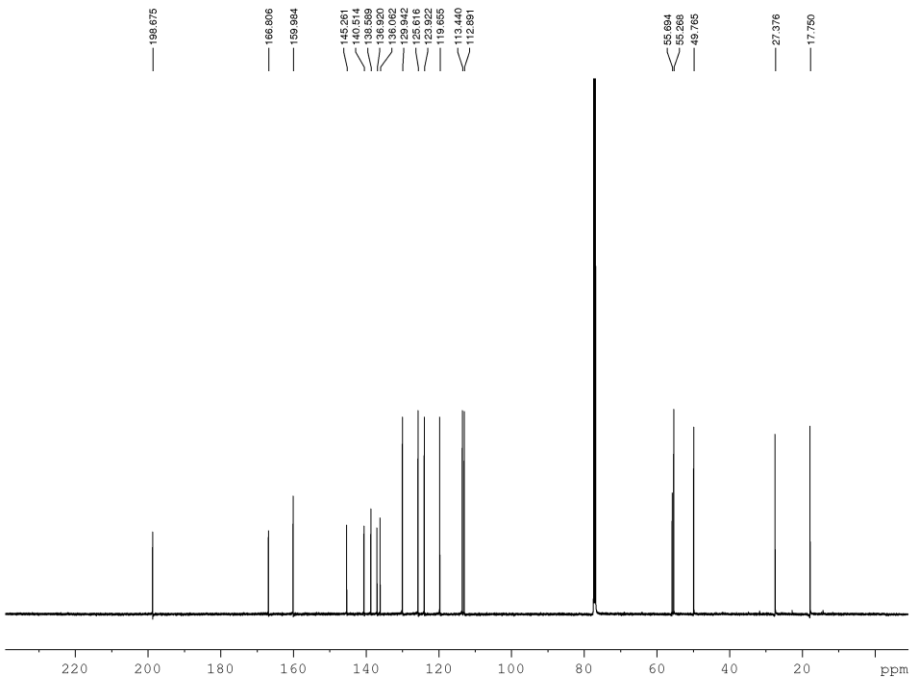


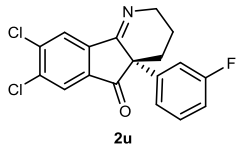
2t

(^{1}H NMR, $CDCl_3$, 500 MHz)



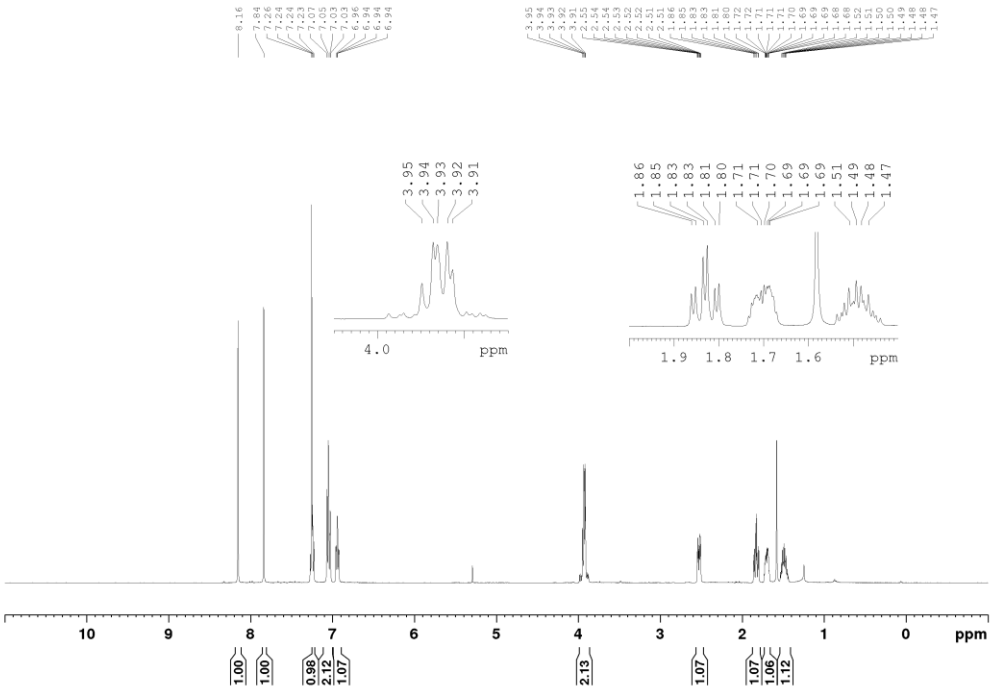
(^{13}C NMR, $CDCl_3$, 125 MHz)



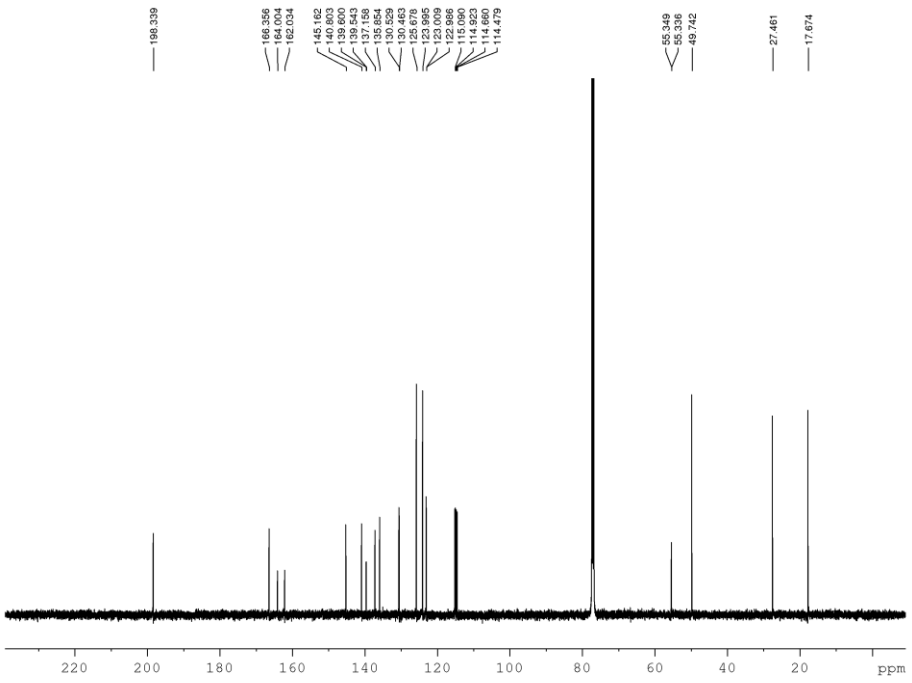


2u

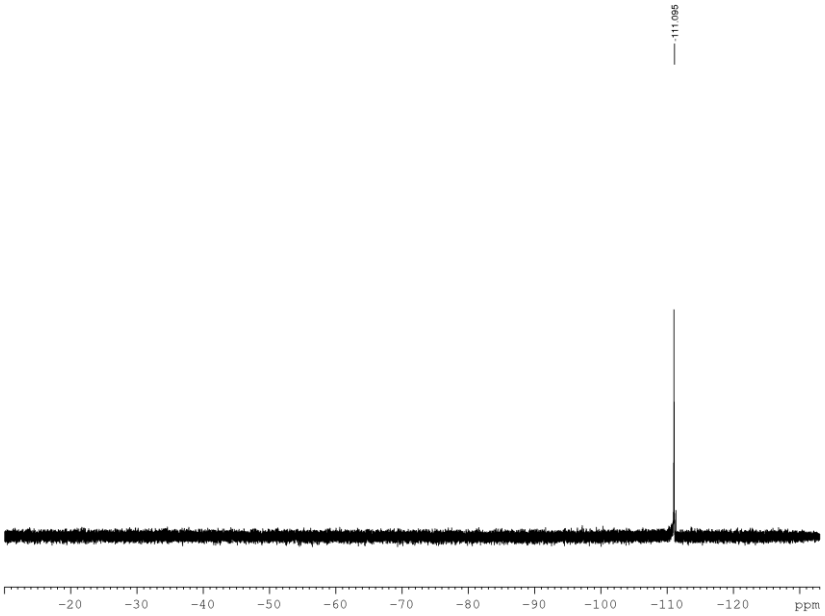
(^{1}H NMR, $CDCl_3$, 500 MHz)

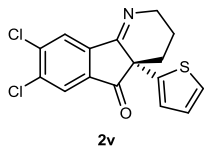


(^{13}C NMR, $CDCl_3$, 125 MHz)



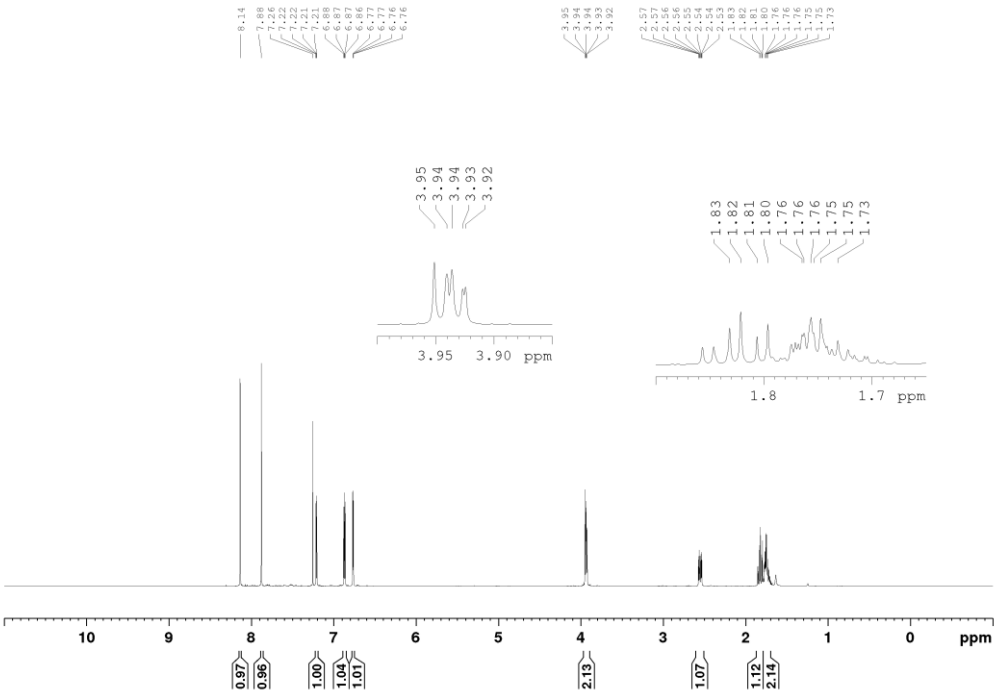
(^{19}F NMR, $CDCl_3$, 282 MHz)



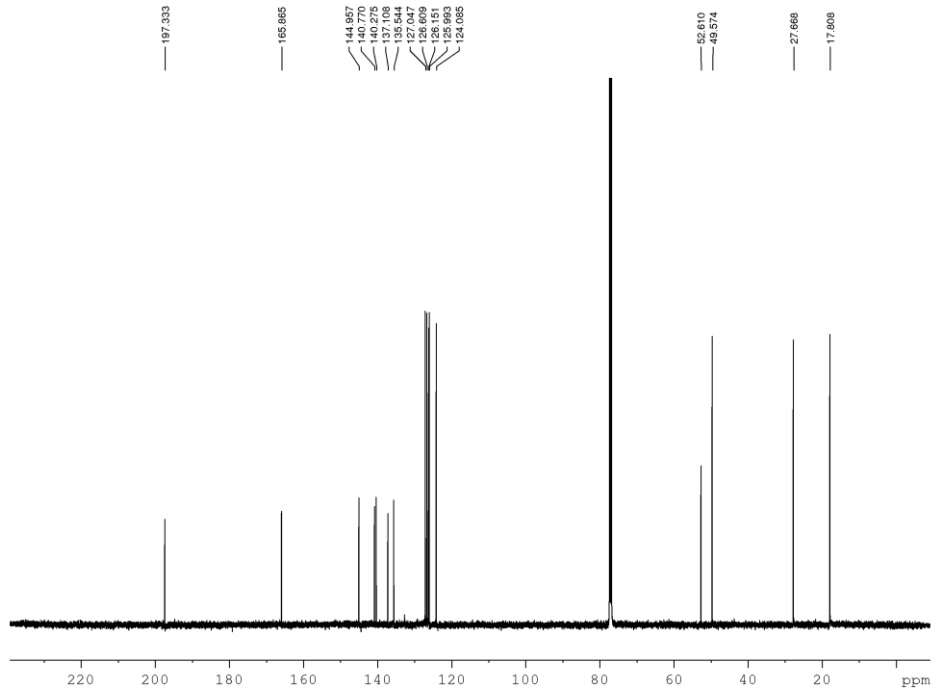


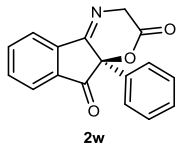
2v

(^{1}H NMR, $CDCl_3$, 500 MHz)



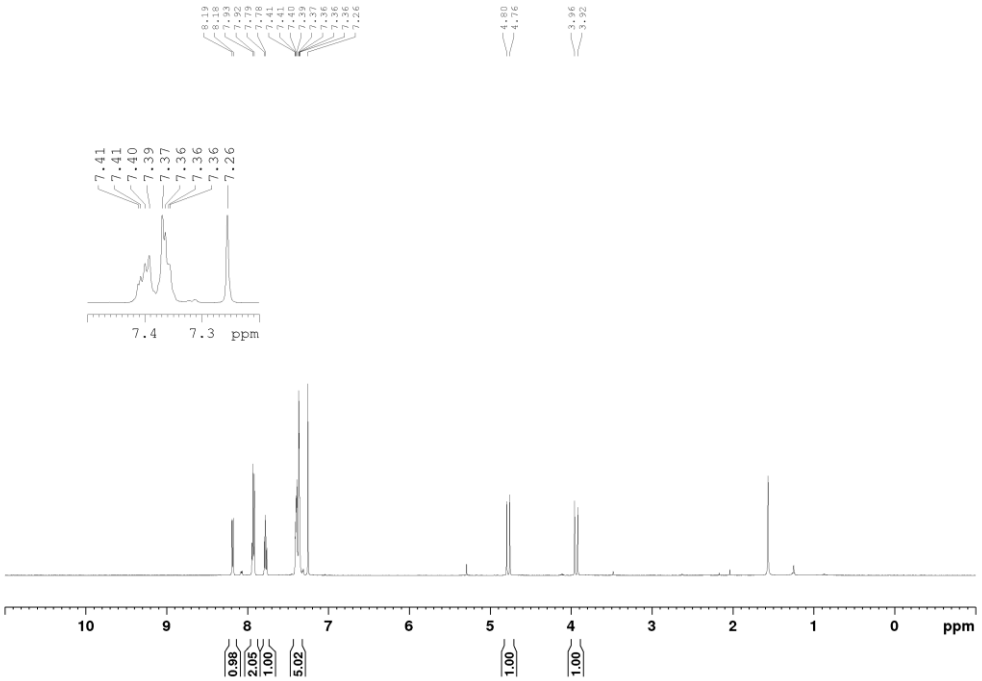
(^{13}C NMR, $CDCl_3$, 125 MHz)



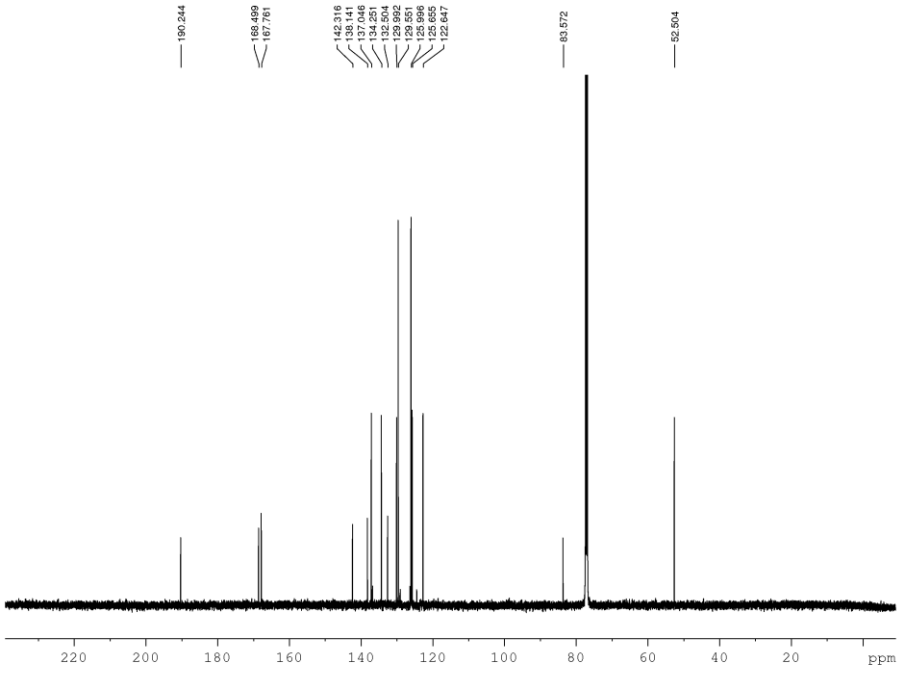


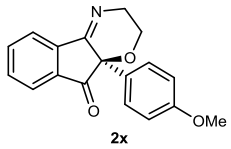
2w

(^{1}H NMR, $CDCl_3$, 500 MHz)



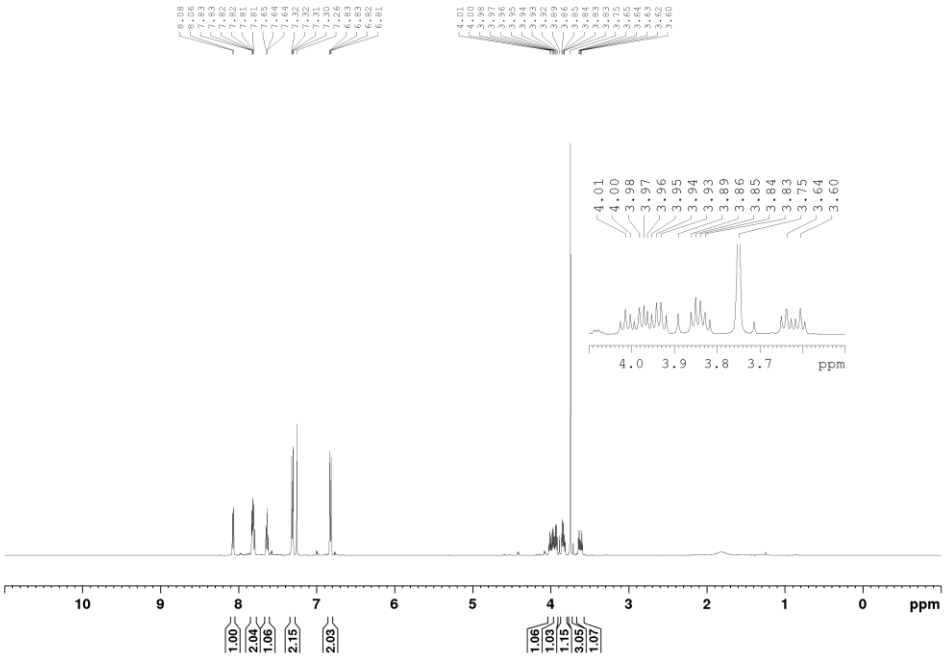
(^{13}C NMR, $CDCl_3$, 125 MHz)



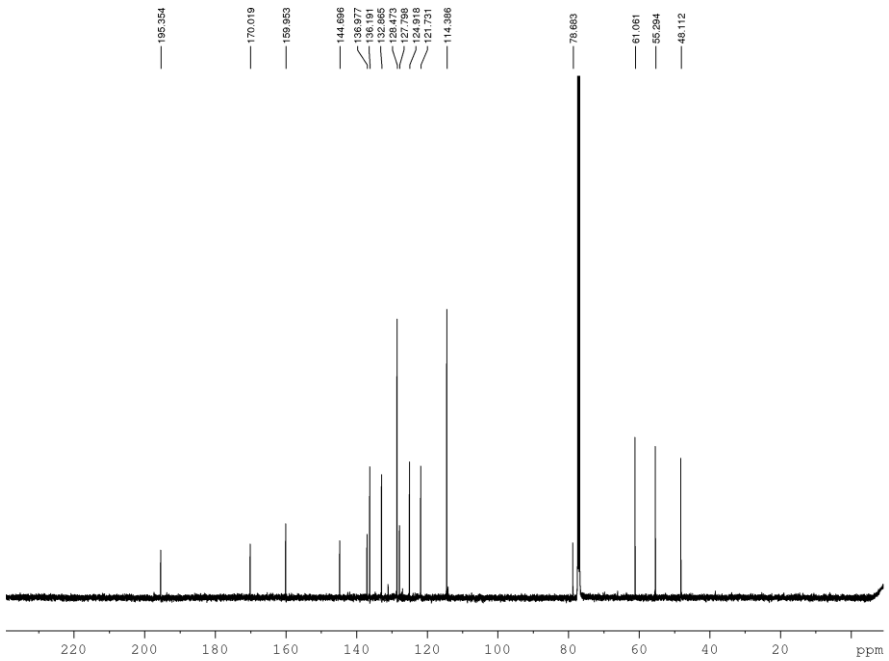


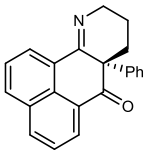
2x

(^{1}H NMR, $CDCl_3$, 500 MHz)



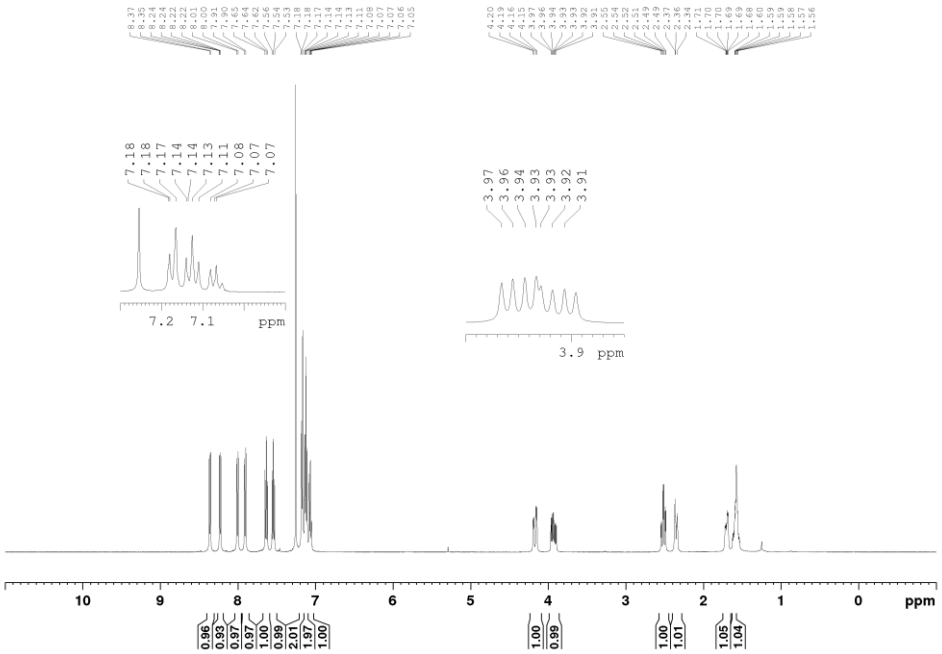
(^{13}C NMR, $CDCl_3$, 125 MHz)



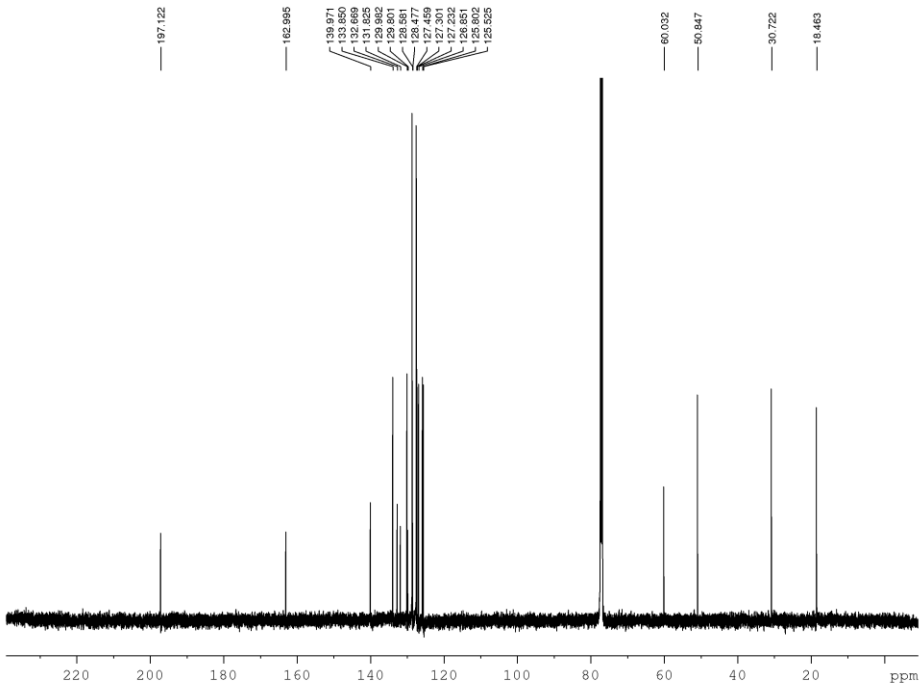


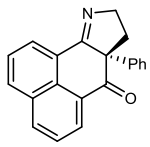
2y

(^{1}H NMR, $CDCl_3$, 500 MHz)



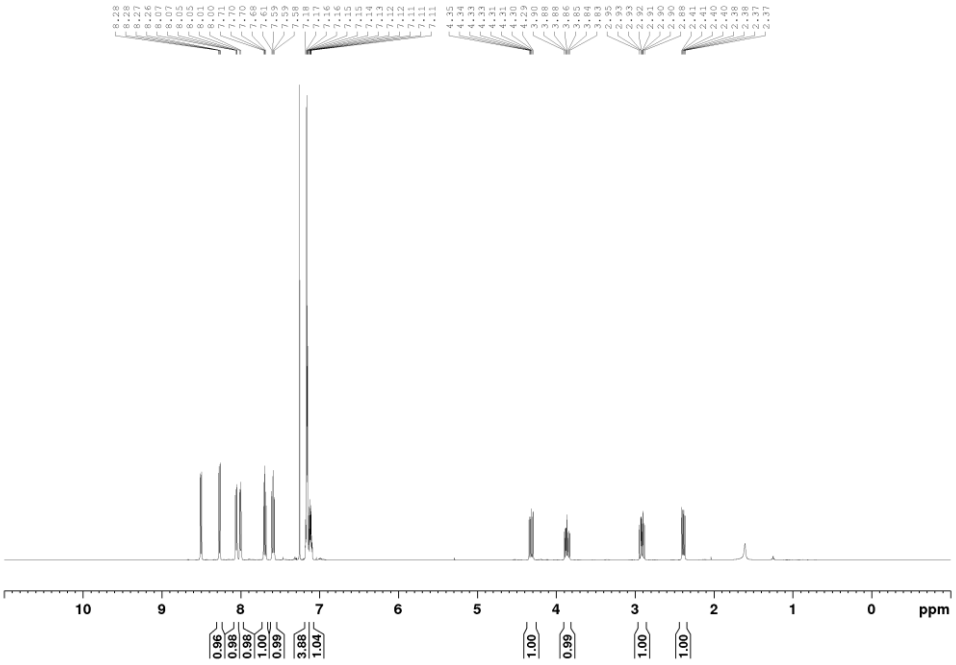
(^{13}C NMR, $CDCl_3$, 125 MHz)



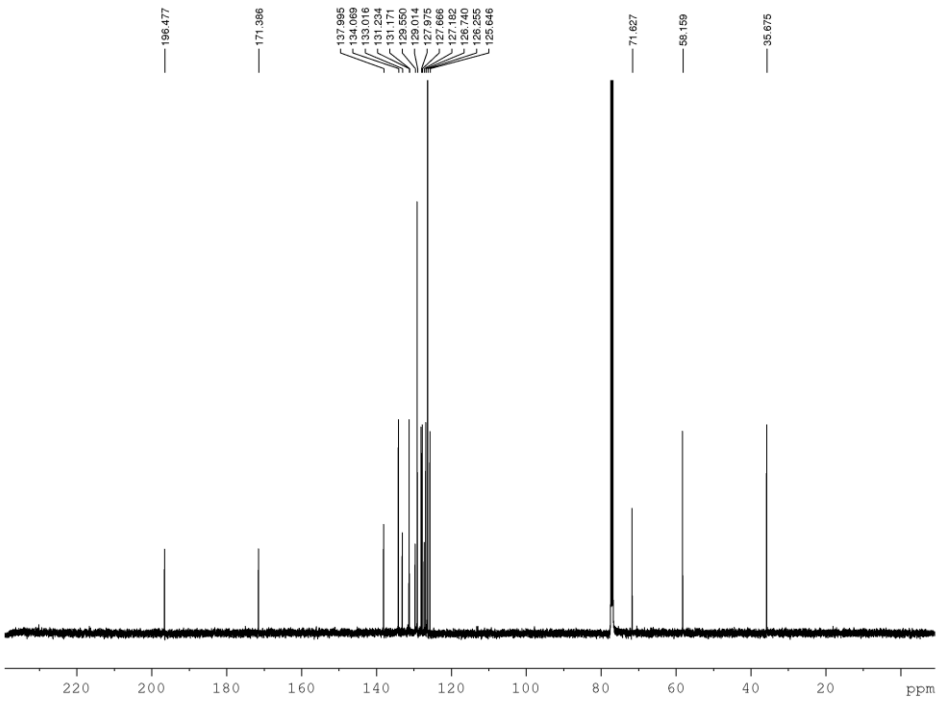


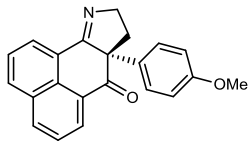
2z

(^{1}H NMR, $CDCl_3$, 500 MHz)



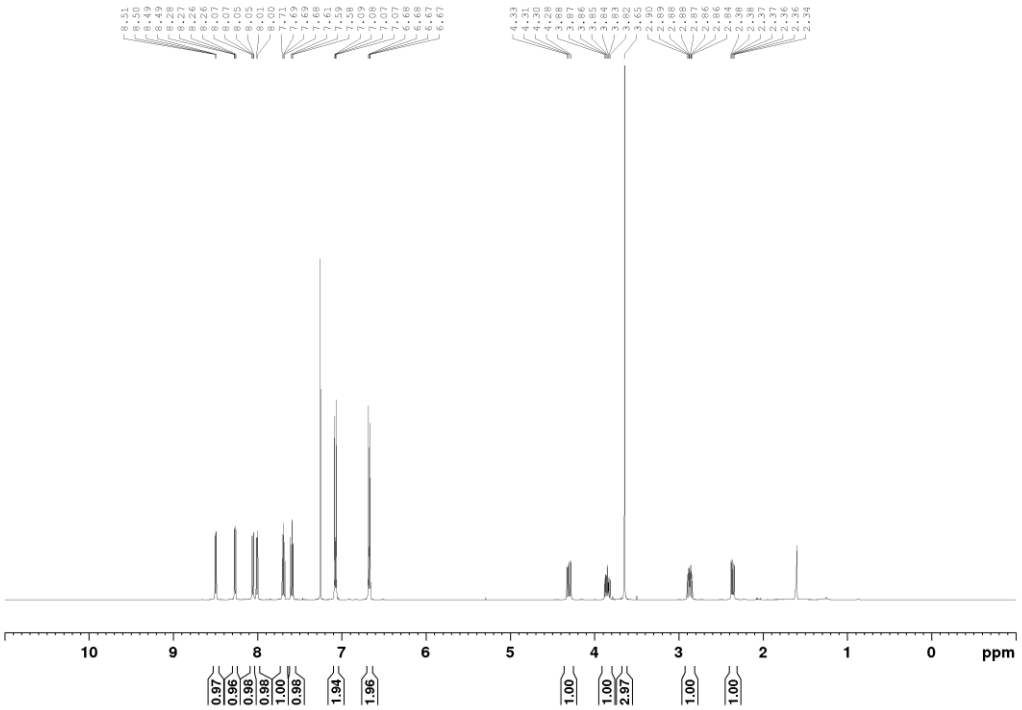
(^{13}C NMR, $CDCl_3$, 125 MHz)



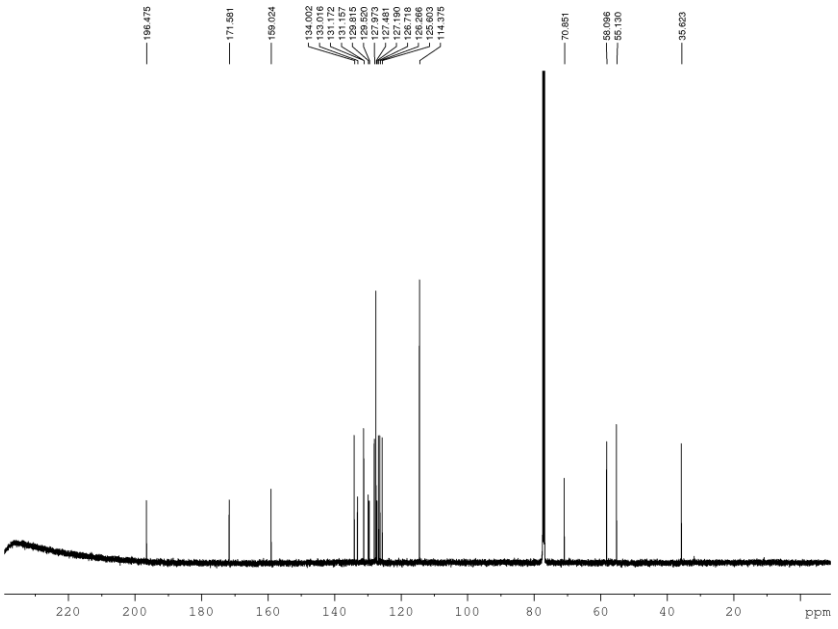


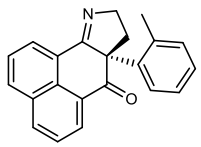
2aa

(^{1}H NMR, $CDCl_3$, 500 MHz)



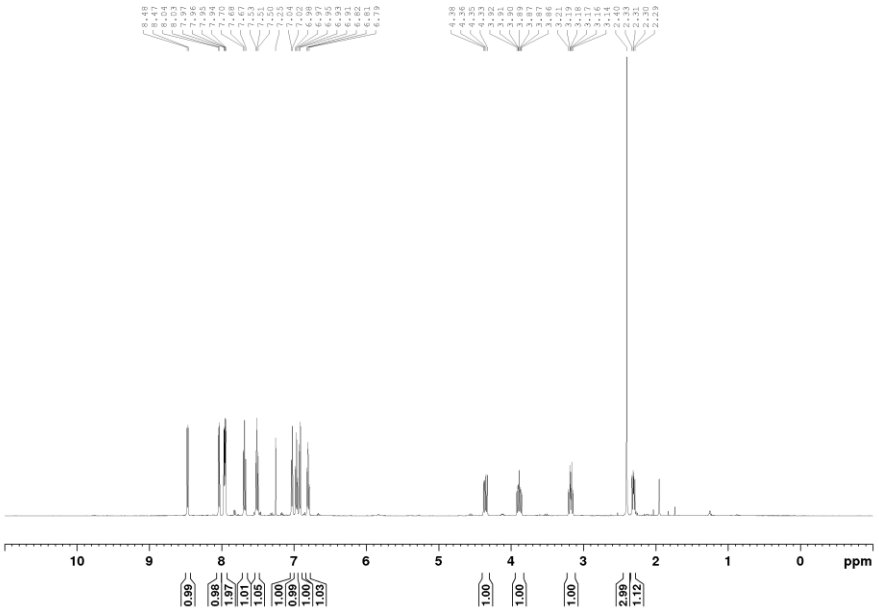
(^{13}C NMR, $CDCl_3$, 125 MHz)



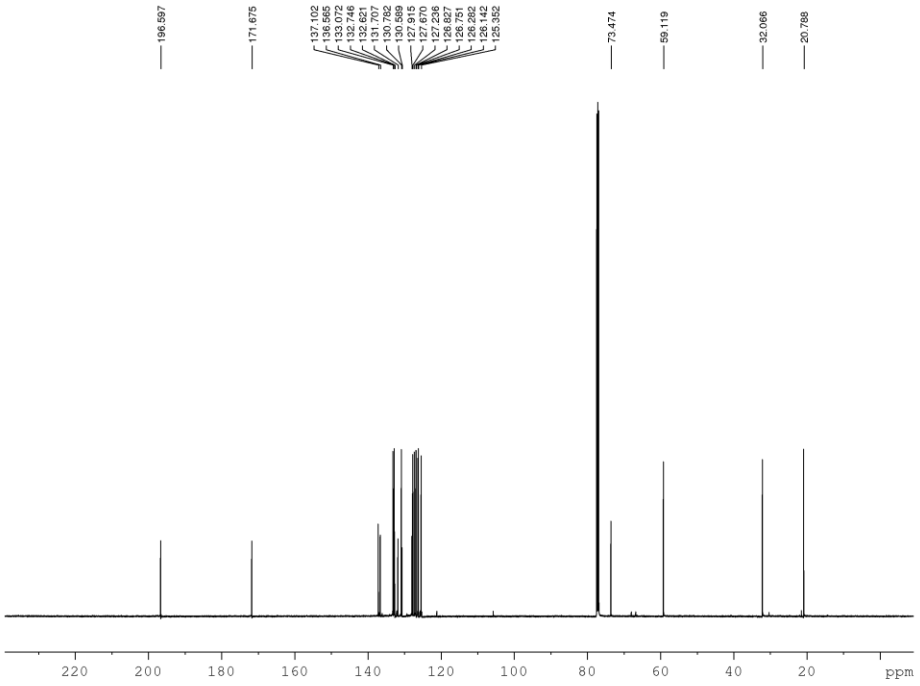


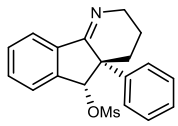
2ab

(^{1}H NMR, $CDCl_3$, 500 MHz)



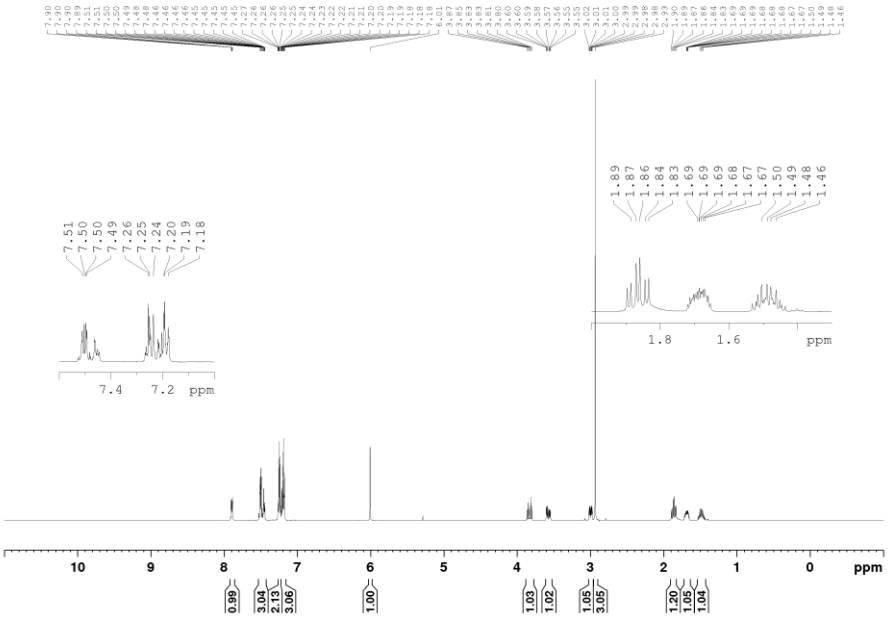
(^{13}C NMR, $CDCl_3$, 125 MHz)



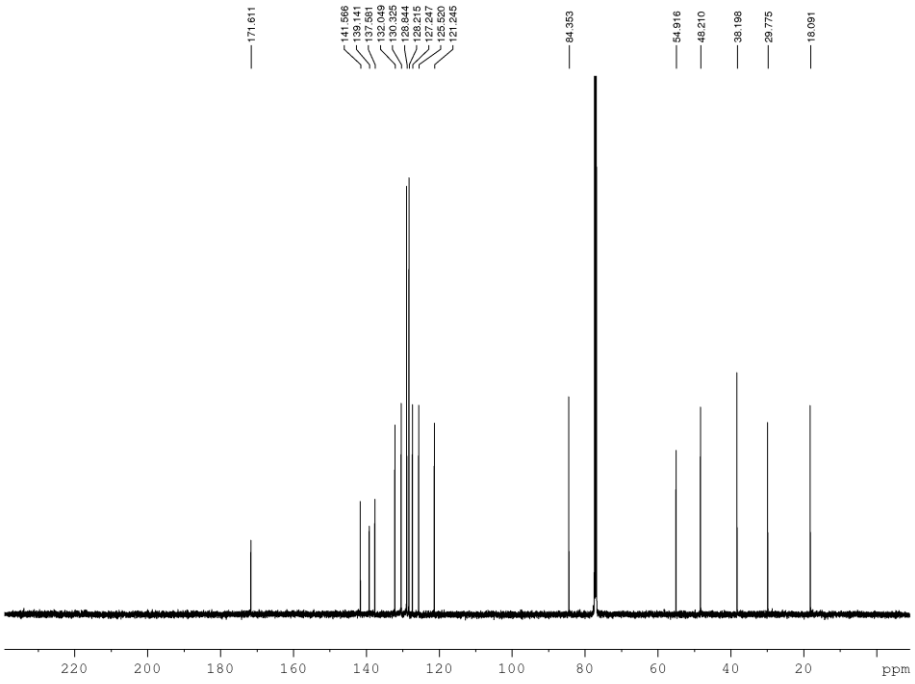


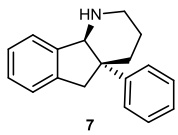
6

(^{1}H NMR, $CDCl_3$, 500 MHz)



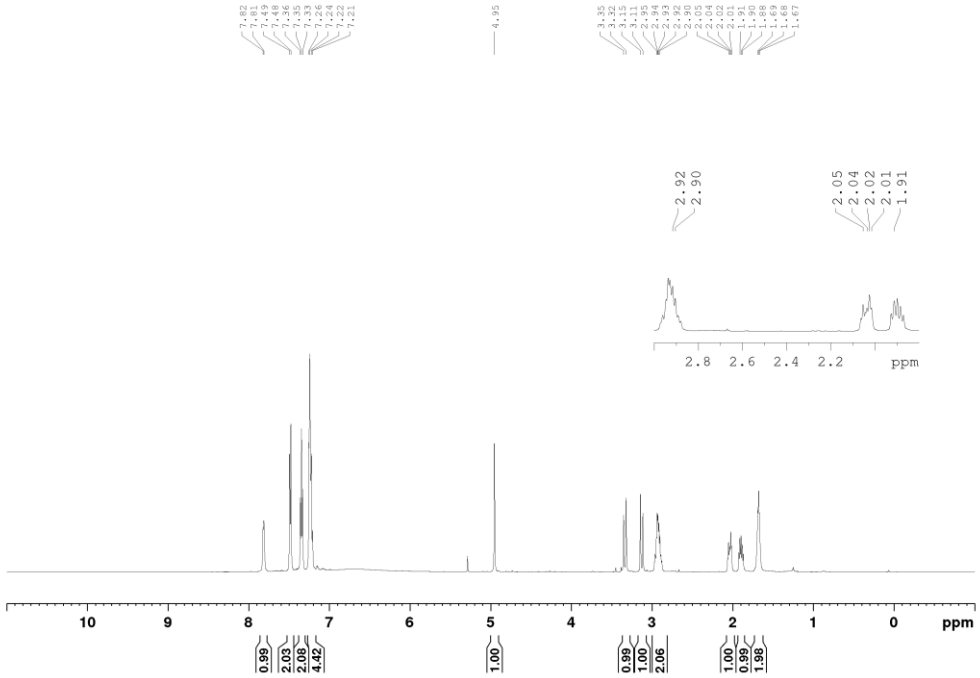
(^{13}C NMR, $CDCl_3$, 125 MHz)



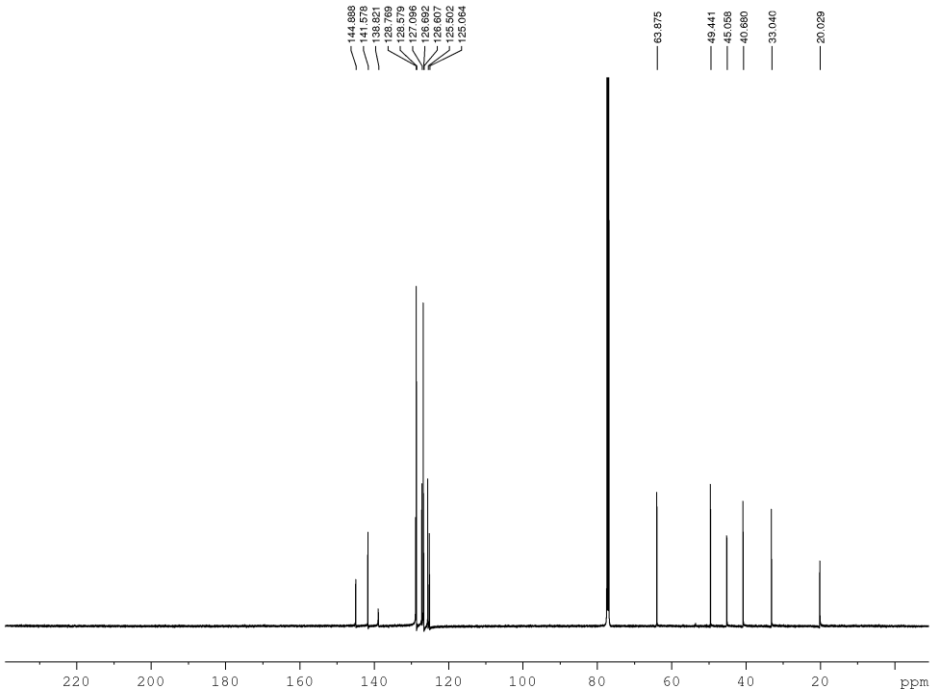


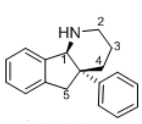
7

(^{1}H NMR, $CDCl_3$, 500 MHz)

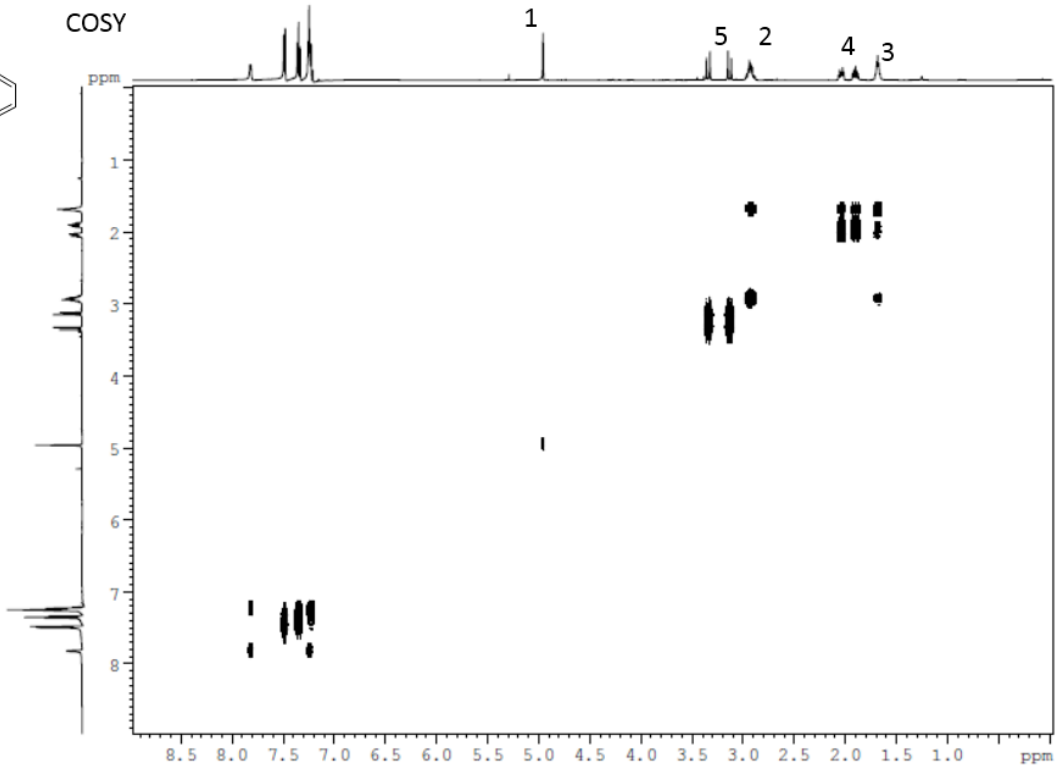


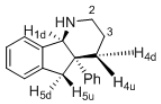
(^{13}C NMR, $CDCl_3$, 125 MHz)



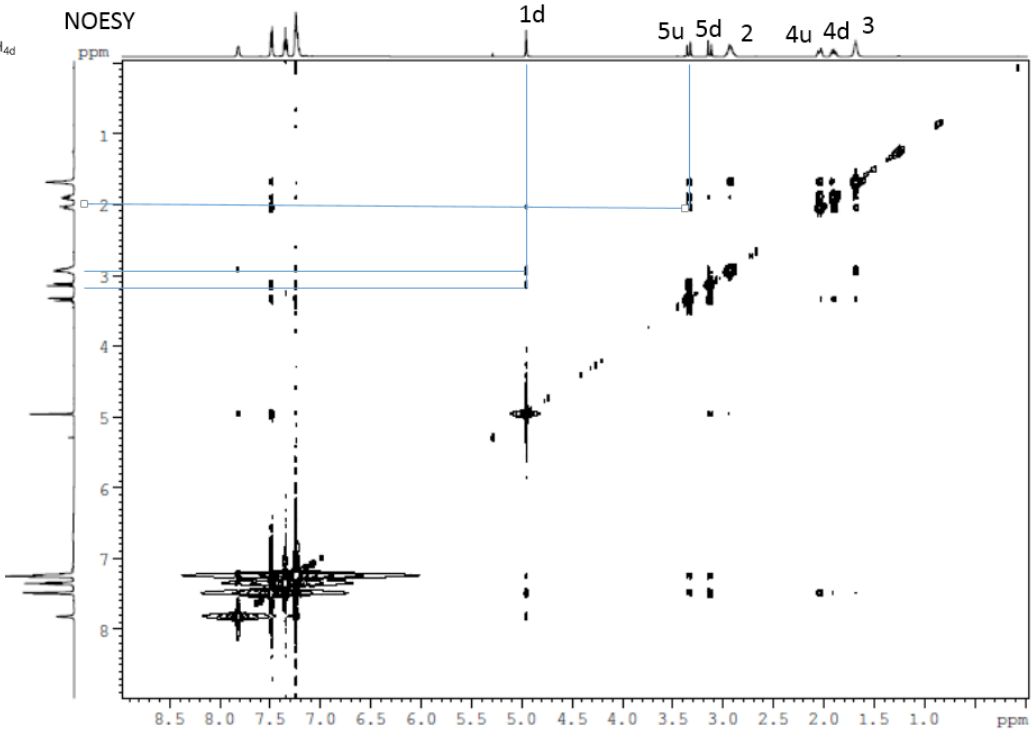

HN
2
3
1
4
5

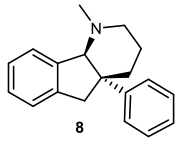
COSY


1
5
2
4
3
ppm
1
2
3
4
5
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


HN
2
3
H1d
H4d
Ph
H5d
H5u
H4u

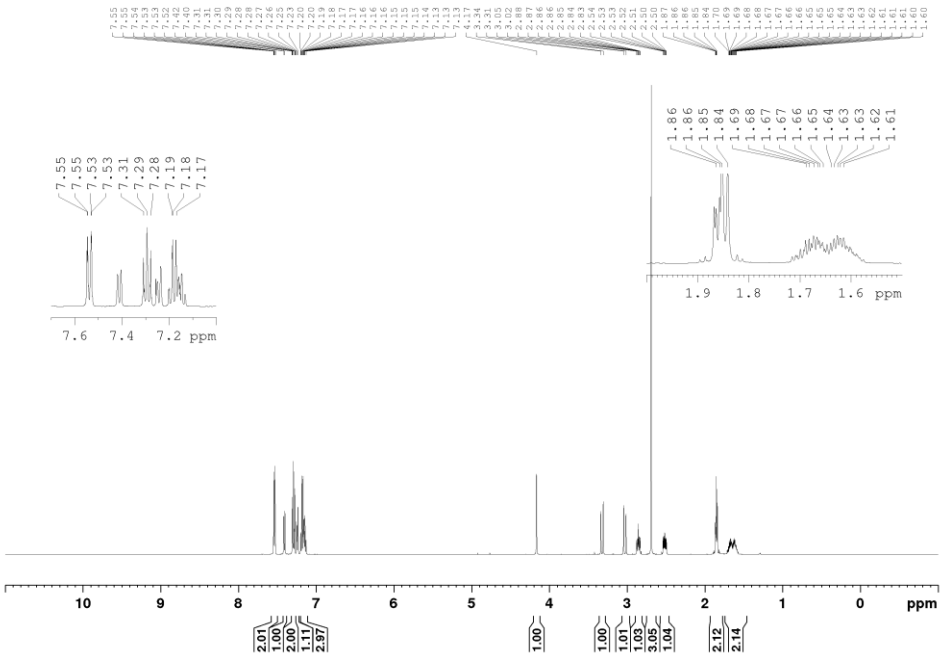
NOESY


1d
5u
5d
2
4u
4d
3
ppm
1
2
3
4
5
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

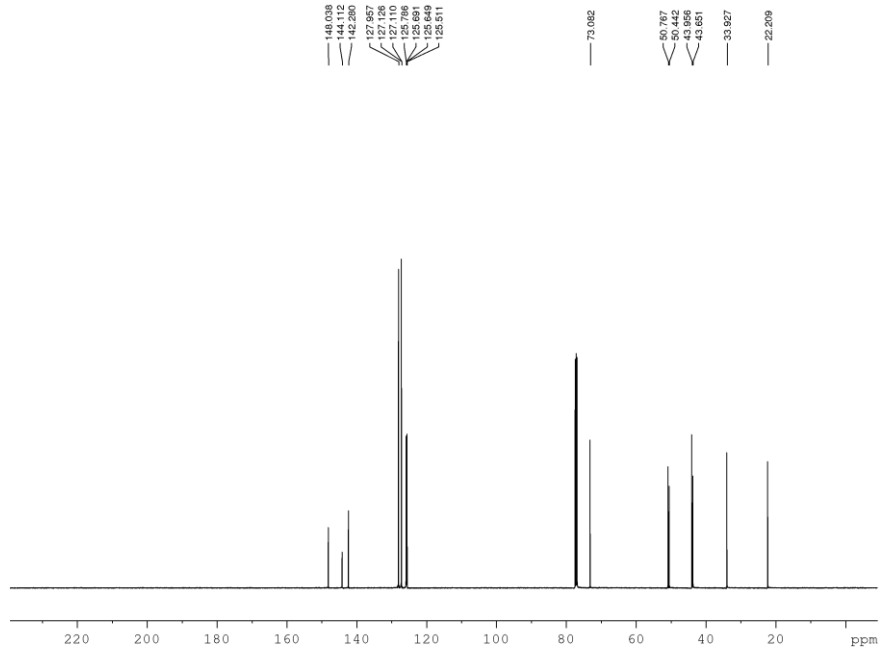


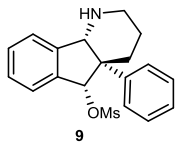
8

(^{1}H NMR, $CDCl_3$, 500 MHz)



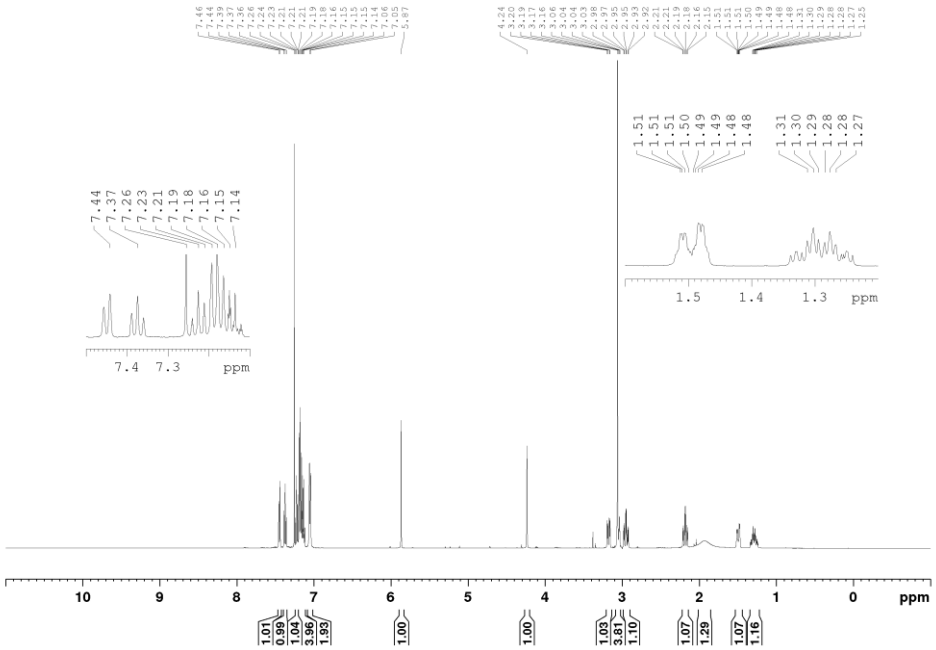
(^{13}C NMR, $CDCl_3$, 125 MHz)



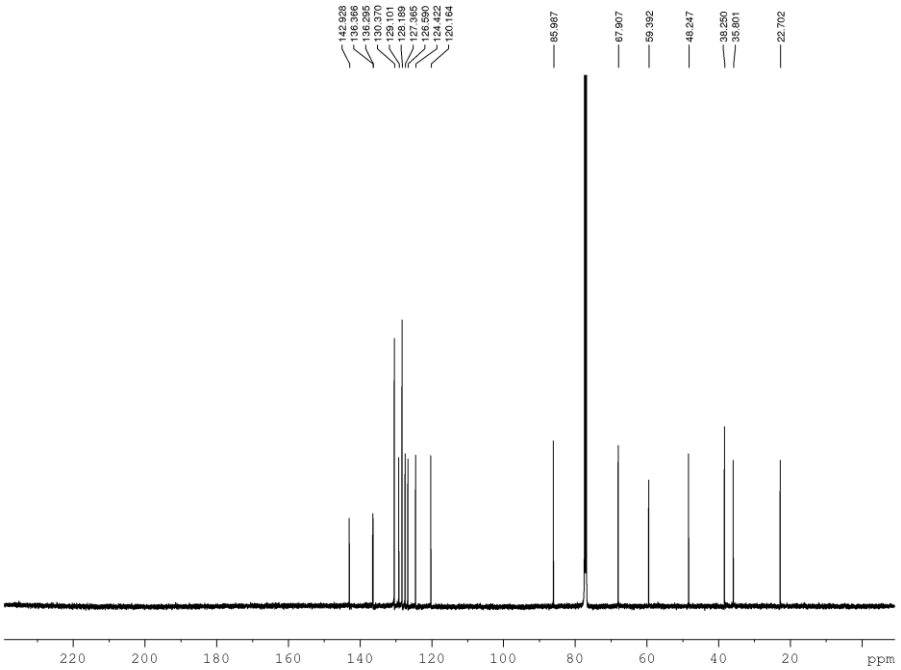


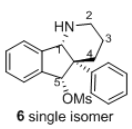
9

(^{1}H NMR, $CDCl_3$, 500 MHz)



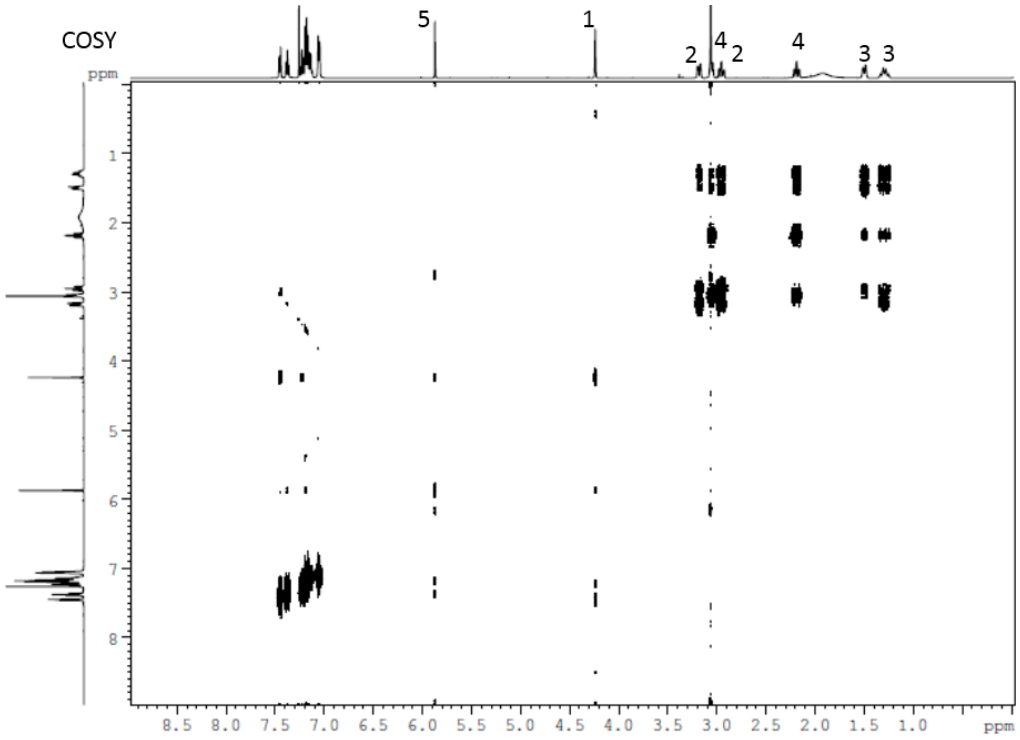
(^{13}C NMR, $CDCl_3$, 125 MHz)

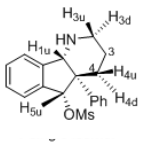




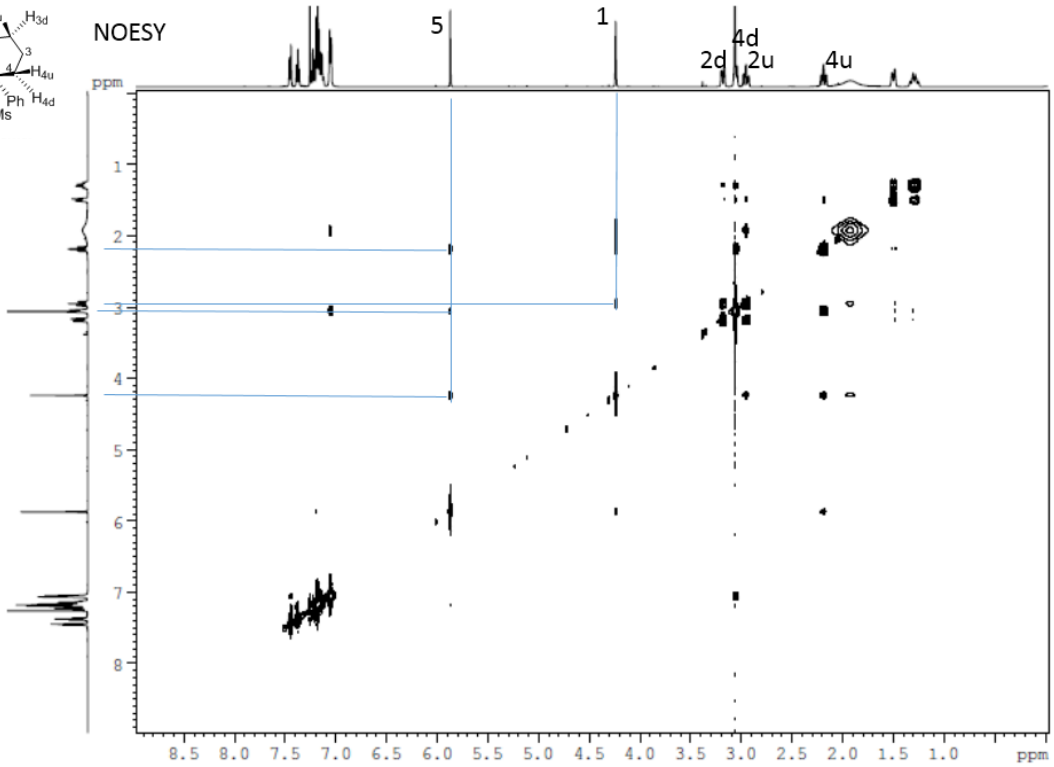
6 single isomer

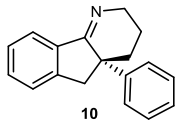
COSY



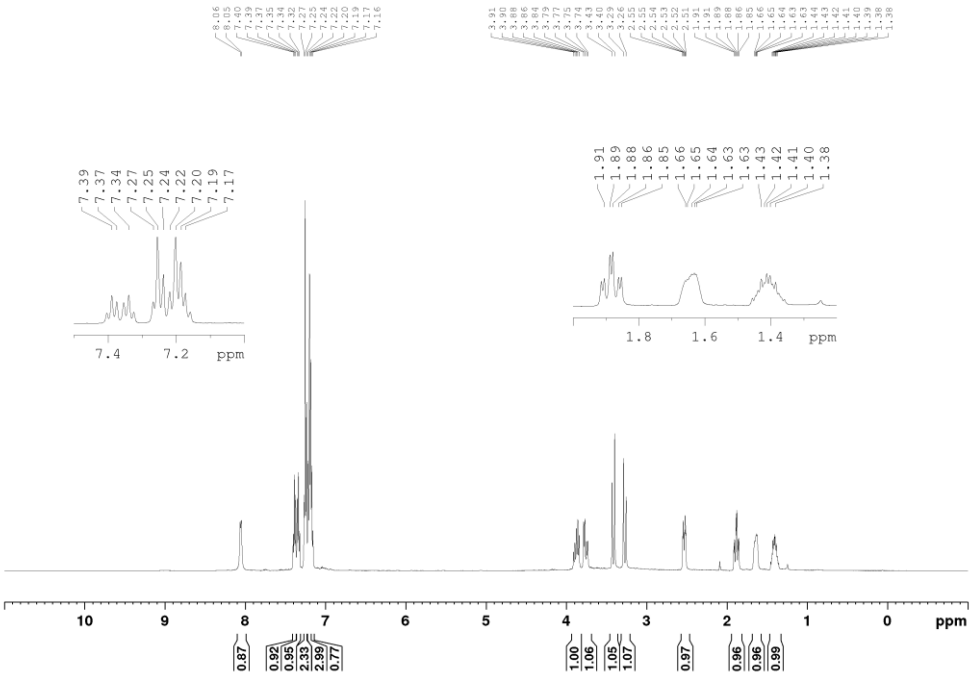


NOESY

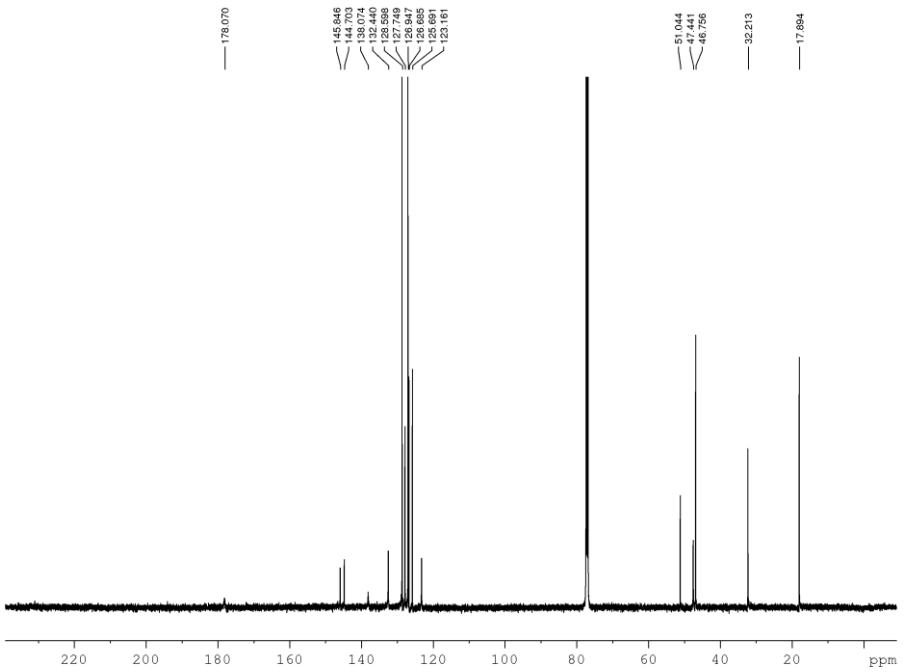


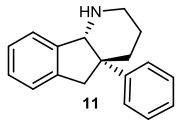


(^{1}H NMR, $CDCl_3$, 500 MHz)



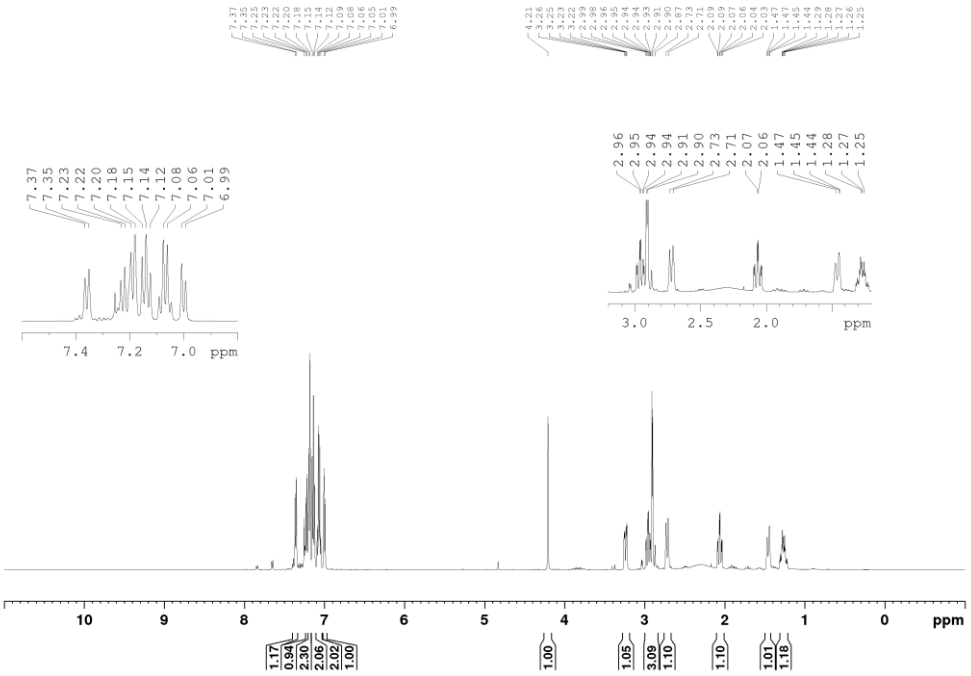
(^{13}C NMR, $CDCl_3$, 125 MHz)



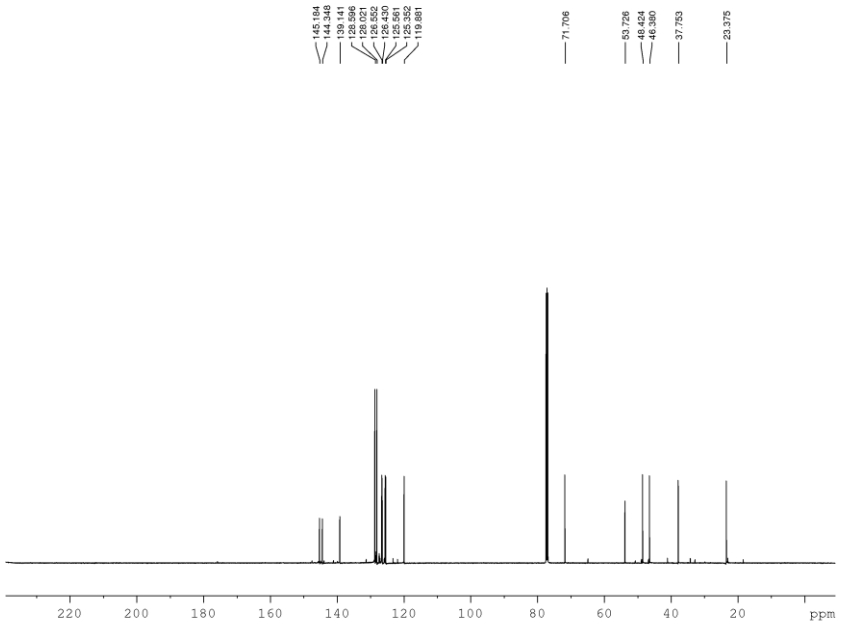


11

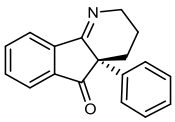
(^{1}H NMR, $CDCl_3$, 500 MHz)



(^{13}C NMR, $CDCl_3$, 125 MHz)



8. HPLC Traces for Compounds 2 and 6



2a

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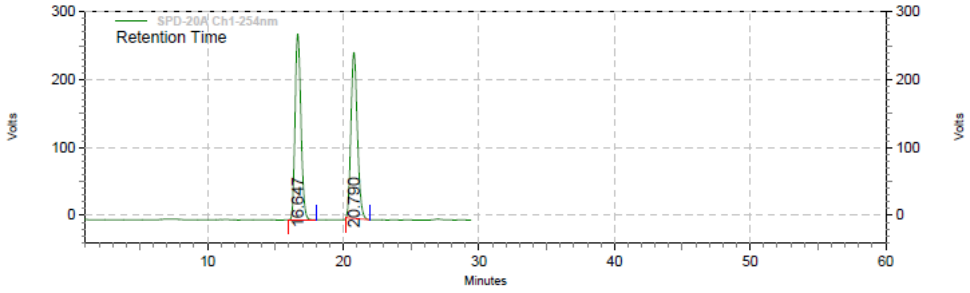
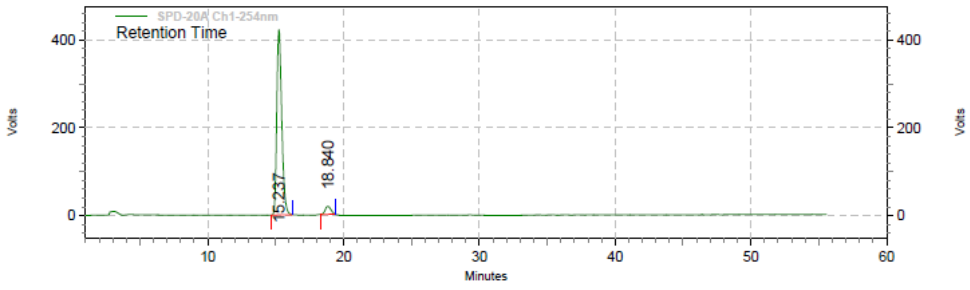
Printed: 7/17/2017 12:36:31 PM



SPD-20A
Ch1-254nm
Results

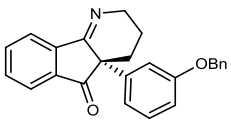
Retention Time	Area	Area %	Height	Height %
16.647	8220417	50.56	273579	52.82
20.790	8037243	49.44	244333	47.18
Totals				
	16257660	100.00	517912	100.00

User: System
Acquired: 7/1/2017 2:06:01 PM
Printed: 7/17/2017 12:34:57 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
15.237	10739872	95.28	421927	95.86
18.840	531575	4.72	18223	4.14
Totals				
	11271447	100.00	440150	100.00



2b

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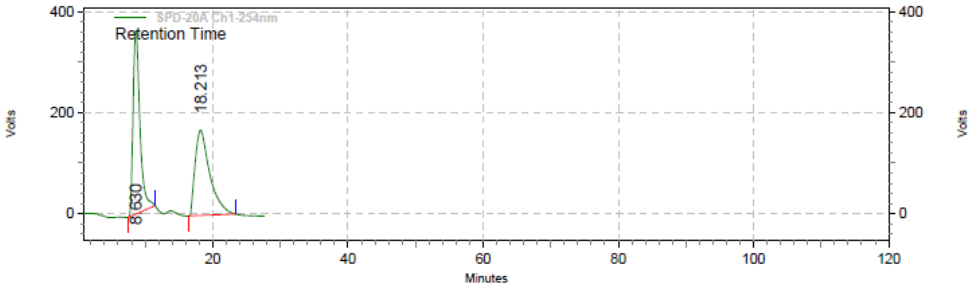
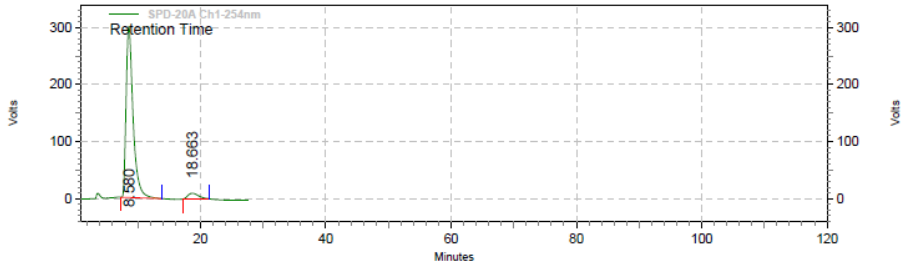


SPD-20A
Ch1-254nm
Results

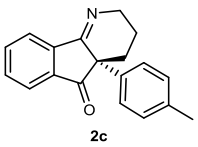
Retention Time	Area	Area %	Height	Height %
8.630	25579137	50.15	362527	68.20
18.213	25422210	49.85	169011	31.80
Totals				
	51001347	100.00	531538	100.00

User: System
Acquired: 1/30/2017 12:58:54 PM
Printed: 10/12/2017 11:23:02 AM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
8.580	23193232	95.11	299839	96.79
18.663	1191619	4.89	9950	3.21
Totals				
	24384851	100.00	309789	100.00



2c

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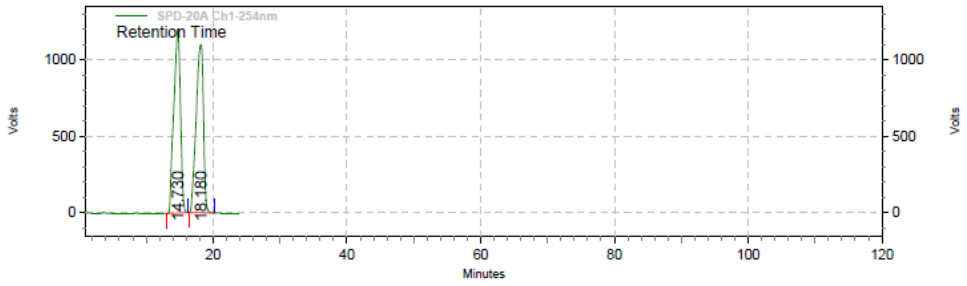
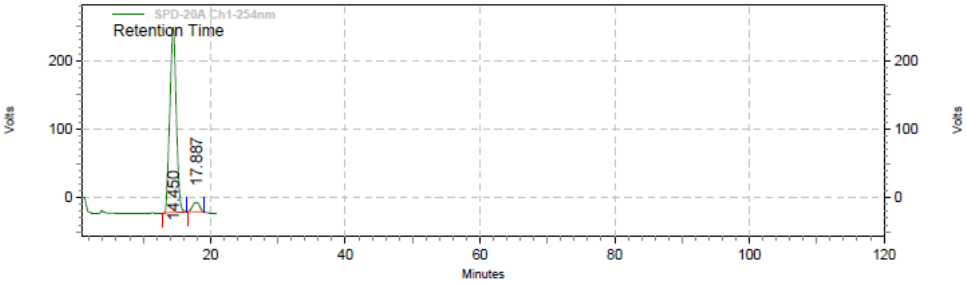
Printed: 10/12/2017 11:43:49 AM



SPD-20A
Ch1-254nm
Results

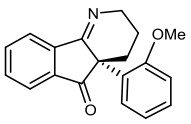
Retention Time	Area	Area %	Height	Height %
14.730	84088234	50.00	1206405	52.25
18.180	84090310	50.00	1102579	47.75
Totals	168178544	100.00	2308984	100.00

User: System
Acquired: 1/27/2017 6:46:20 PM
Printed: 10/12/2017 11:40:56 AM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
14.450	17956472	94.79	270062	95.27
17.887	986280	5.21	13411	4.73
Totals	18942752	100.00	283473	100.00



2d

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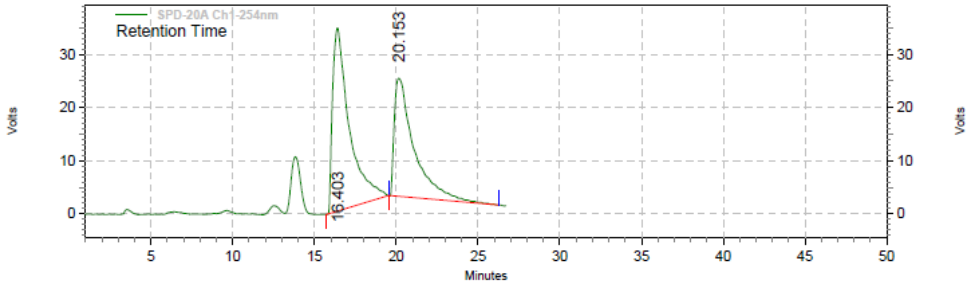
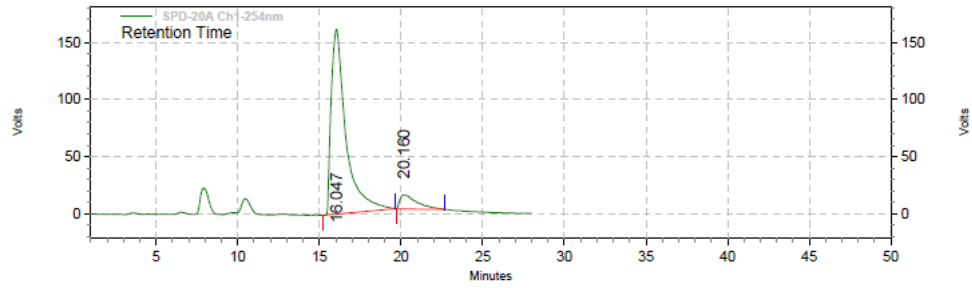
Printed: 10/12/2017 11:47:00 AM



SPD-20A
Ch1-254nm
Results

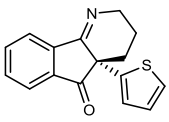
Retention Time	Area	Area %	Height	Height %
16.403	2449974	56.83	34465	60.82
20.153	1861391	43.17	22206	39.18
Totals	4311365	100.00	56671	100.00

User: System
Acquired: 4/17/2017 12:15:26 PM
Printed: 10/12/2017 11:48:40 AM



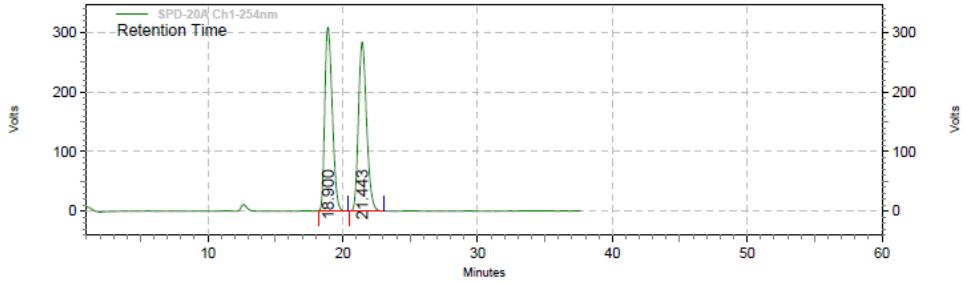
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
16.047	10093396	91.82	161383	92.94
20.160	898949	8.18	12260	7.06
Totals	10992345	100.00	173643	100.00



2e

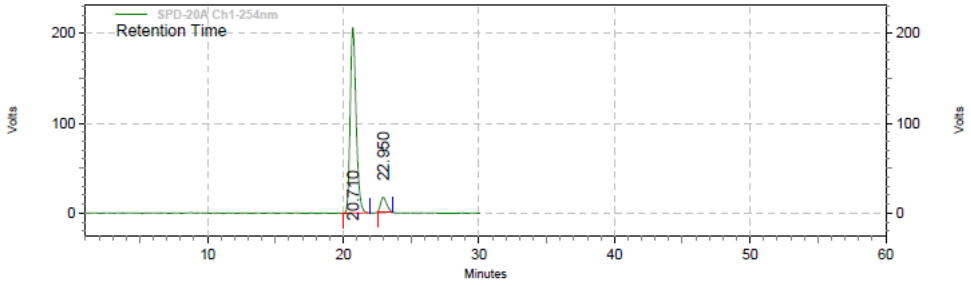
User: System
Acquired: 7/19/2017 12:48:09 PM
Printed: 7/28/2017 12:50:11 PM



SPD-20A
Ch1-254nm
Results

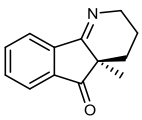
Retention Time	Area	Area %	Height	Height %
18.900	11912800	49.91	308924	52.07
21.443	11956019	50.09	284408	47.93
Totals	23868819	100.00	593332	100.00

User: System
Acquired: 7/28/2017 11:47:09 AM
Printed: 7/28/2017 12:50:46 PM



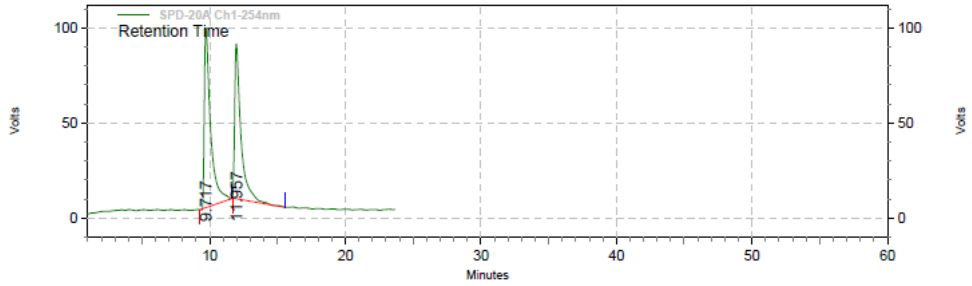
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
20.710	6245955	92.52	206447	92.70
22.950	505237	7.48	16269	7.30
Totals	6751192	100.00	222716	100.00



2f

User: System
Acquired: 4/13/2017 2:29:27 PM
Printed: 5/24/2017 7:48:37 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.717	3036157	53.87	94368	53.70
11.957	2600374	46.13	81359	46.30
Totals	5636531	100.00	175727	100.00

User: System
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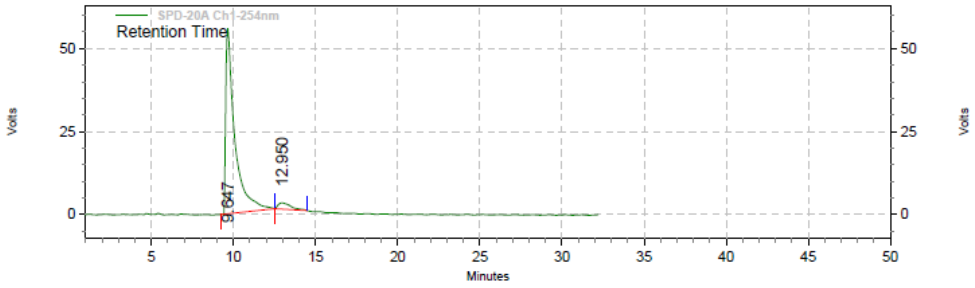
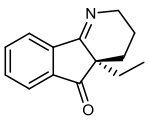
Printed: 5/24/2017 7:49:13 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.647	2136214	95.46	55748	96.74
12.950	101512	4.54	1877	3.26
Totals	2237726	100.00	57625	100.00



2g

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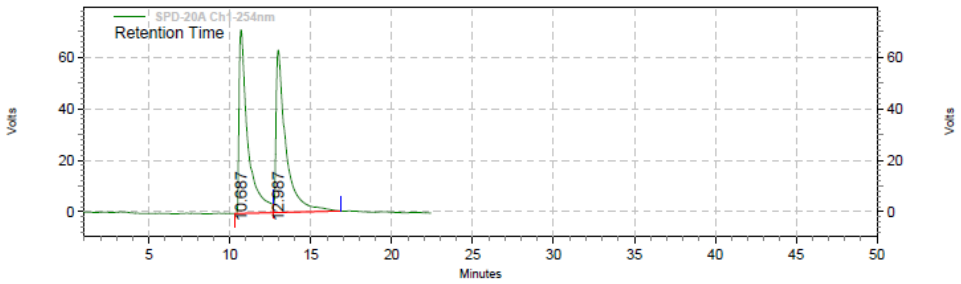
Printed: 5/24/2017 7:44:38 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
10.687	2692140	50.27	71279	53.06
12.987	2663010	49.73	63052	46.94
Totals	5355150	100.00	134331	100.00

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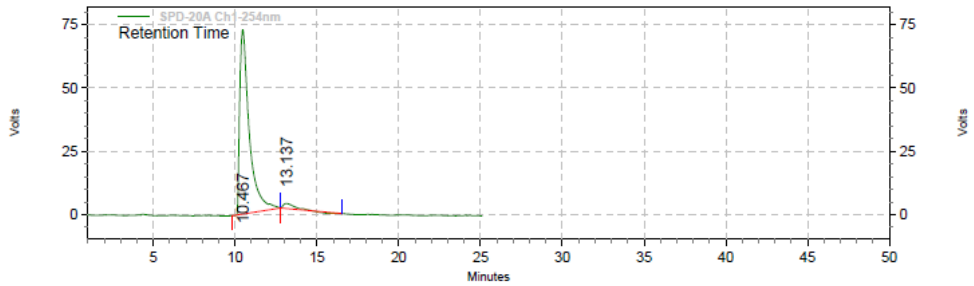
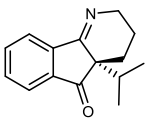
Printed: 5/24/2017 7:45:24 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
10.467	2955322	97.53	72782	97.31
13.137	74930	2.47	2014	2.69
Totals	3030252	100.00	74796	100.00



2h

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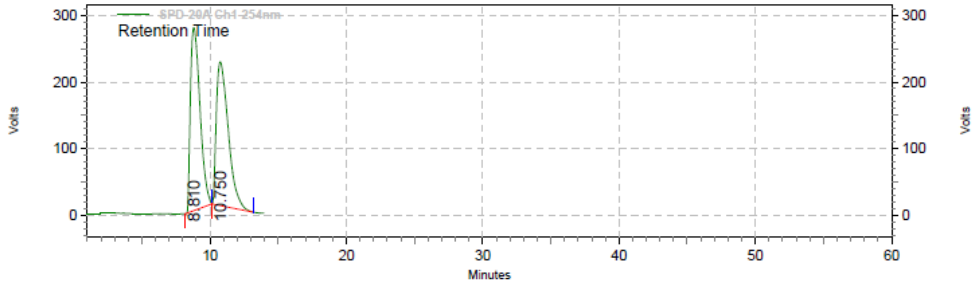
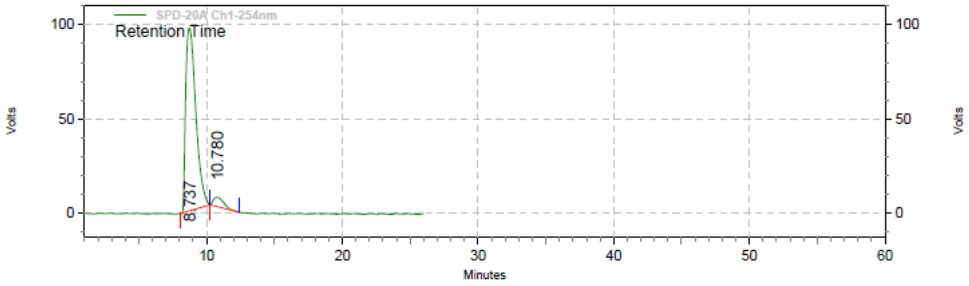
Printed: 6/1/2017 10:56:50 AM



SPD-20A
Ch1-254nm
Results

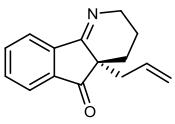
Retention Time	Area	Area %	Height	Height %
8.810	13377497	50.51	274256	56.00
10.750	13104770	49.49	215511	44.00
Totals	26482267	100.00	489767	100.00

User: System
Acquired: 6/1/2017 10:01:09 AM
Printed: 6/1/2017 10:57:21 AM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
8.737	5026424	95.07	96987	95.08
10.780	260631	4.93	5023	4.92
Totals	5287055	100.00	102010	100.00



2i

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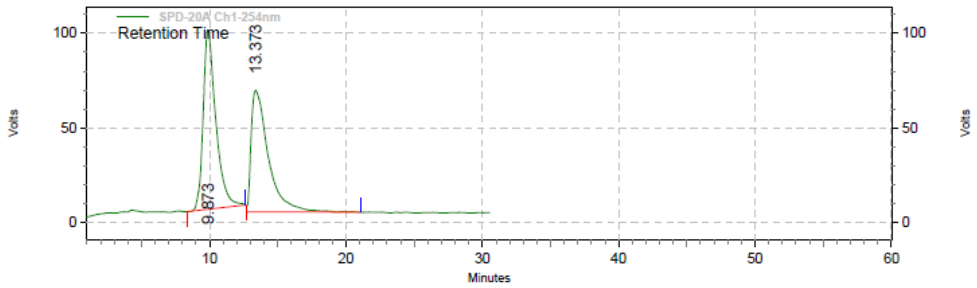
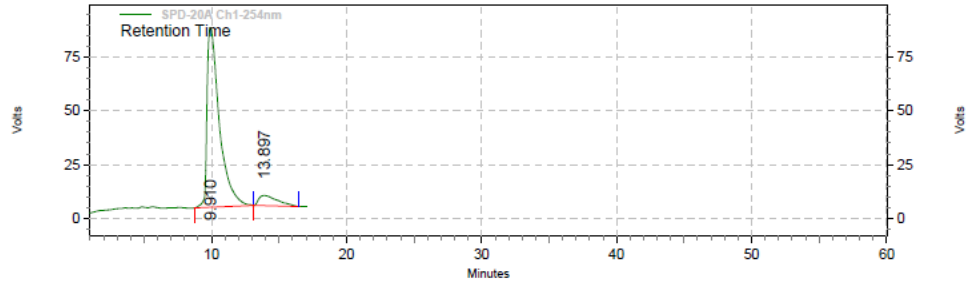
Printed: 5/29/2017 4:43:42 PM



SPD-20A
Ch1-254nm
Results

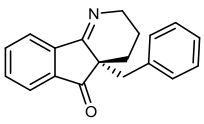
Retention Time	Area	Area %	Height	Height %
9.873	6111250	51.98	94639	59.59
13.373	5645650	48.02	64168	40.41
Totals				
	11756900	100.00	158807	100.00

User: System
Acquired: 5/8/2017 1:08:36 PM
Printed: 5/29/2017 3:39:08 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.910	5295634	92.02	83394	94.66
13.897	459183	7.98	4705	5.34
Totals				
	5754817	100.00	88099	100.00



2j

User: System
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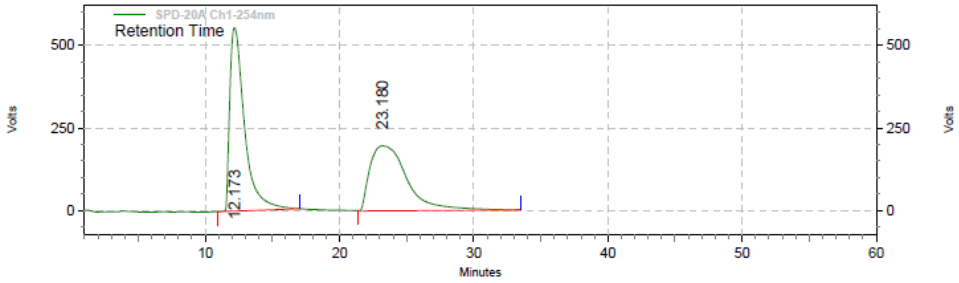
Printed: 5/24/2017 7:38:23 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
12.173	42547583	52.84	555779	73.77
23.180	37970556	47.16	197662	26.23
Totals	80518139	100.00	753441	100.00

User: System
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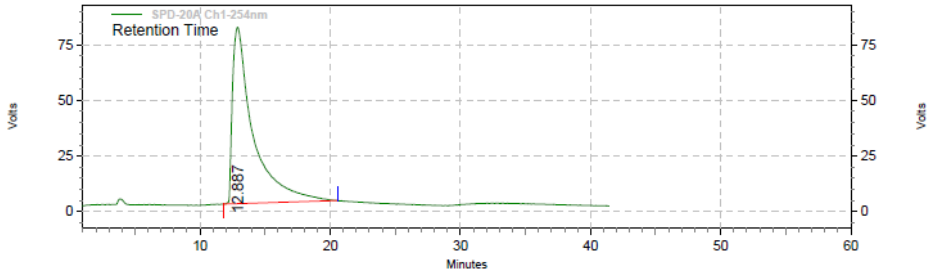
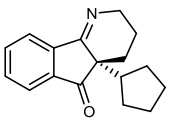


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
12.887	8714347	100.00	79261	100.00
Totals	8714347	100.00	79261	100.00



2k

Area % Report

Method Name: C:\EZStart\Projects\Default\Method\kui zhang\10% iproh.met
Data: C:\EZStart\Projects\Default\Data\kui zhang\aza-wittig\zuihou\3-320-rac-OD-0.5% iproh-3.dat
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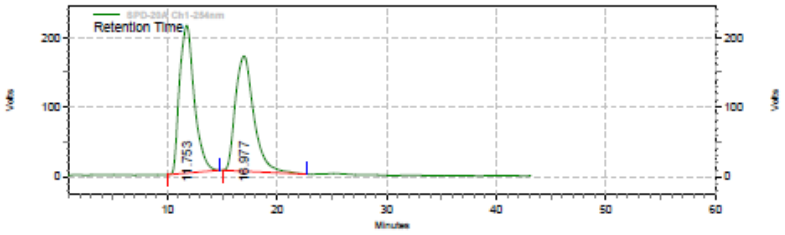
Acquired: 5/3/2017 2:24:43 PM
Printed: 5/24/2017 7:41:33 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.753	19763869	50.53	212022	56.20
16.977	19351562	49.47	165209	43.80
Totals	39115431	100.00	377231	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Method\kui zhang\10% iproh.met
Data: C:\EZStart\Projects\Default\Data\kui zhang\aza-wittig\zuihou\3-320-asy-second-2.dat
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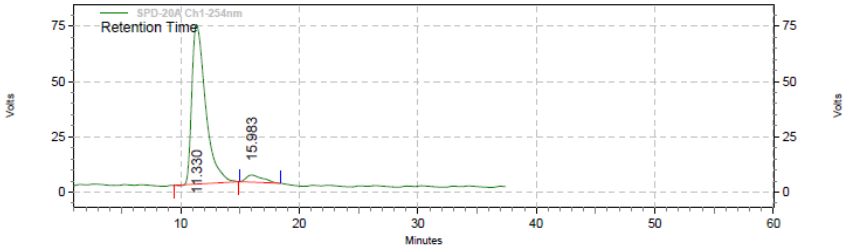
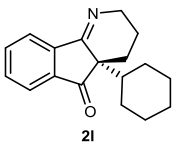
Printed: 5/24/2017 7:42:13 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.330	5822403	94.95	72036	95.71
15.983	309441	5.05	3228	4.29
Totals	6131844	100.00	75264	100.00



2l

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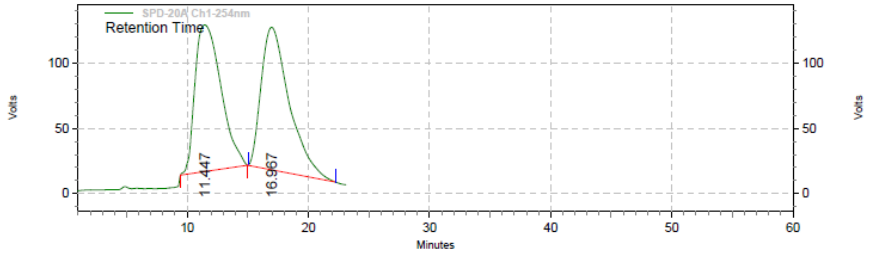
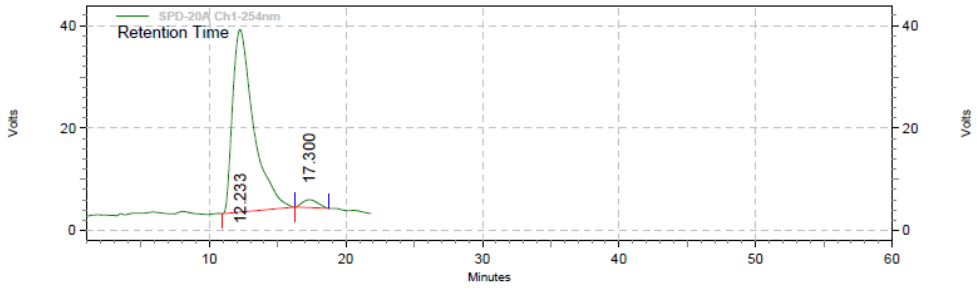
Printed: 5/24/2017 7:46:18 PM



SPD-20A
Ch1-254nm
Results

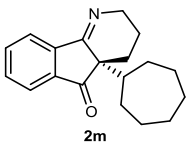
Retention Time	Area	Area %	Height	Height %
11.447	16779225	48.79	112399	50.72
16.967	17608762	51.21	109194	49.28
Totals	34387987	100.00	221593	100.00

User: System
Acquired: 4/12/2017 7:58:50 PM
Printed: 5/24/2017 7:46:49 PM



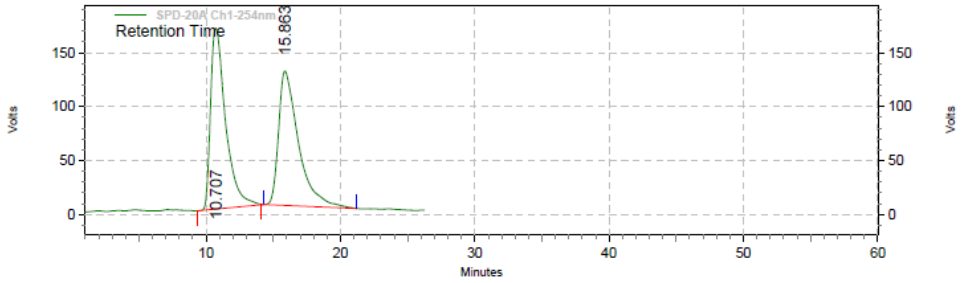
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
12.233	3795316	96.92	35657	95.90
17.300	120453	3.08	1523	4.10
Totals	3915769	100.00	37180	100.00



2m

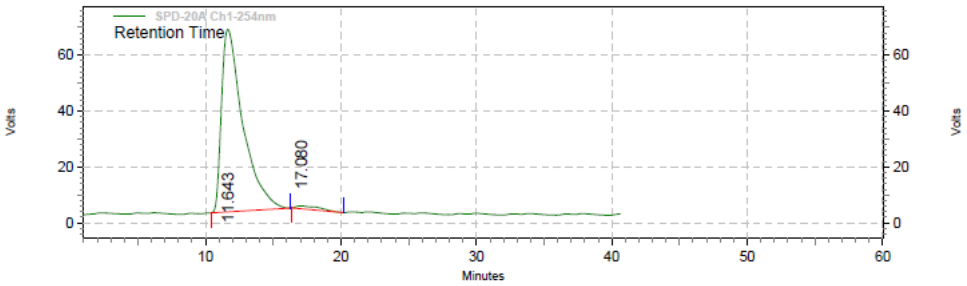
User: System
Acquired: 5/8/2017 7:17:35 PM
Printed: 5/24/2017 6:07:16 PM



SPD-20A
Ch1-254nm
Results

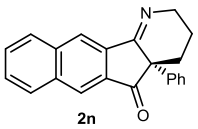
Retention Time	Area	Area %	Height	Height %
10.707	13051904	50.51	167881	57.39
15.863	12787204	49.49	124663	42.61
Totals				
	25839108	100.00	292544	100.00

User: System
Acquired: 5/10/2017 4:18:48 PM
Printed: 5/24/2017 6:04:42 PM



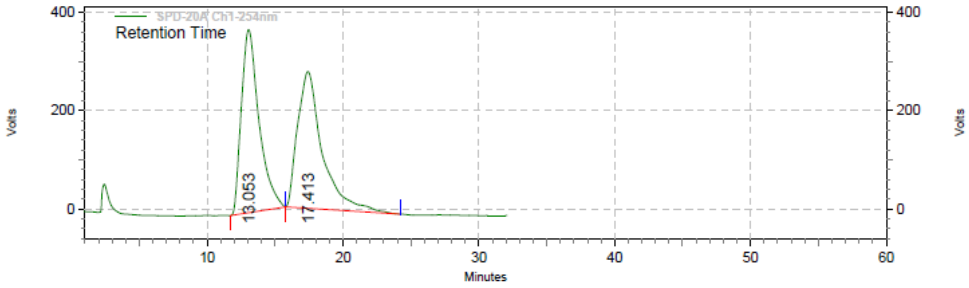
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.643	7174221	98.11	65286	98.44
17.080	138075	1.89	1035	1.56
Totals				
	7312296	100.00	66321	100.00



2n

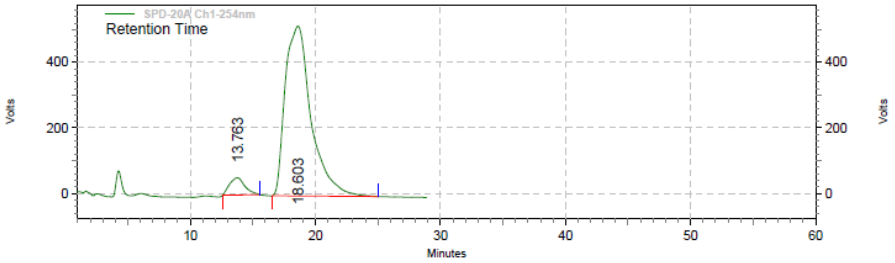
User: System
Acquired: 7/20/2017 5:12:39 PM
Printed: 10/12/2017 12:17:25 PM



SPD-20A
Ch1-254nm
Results

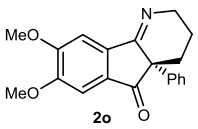
Retention Time	Area	Area %	Height	Height %
13.053	33697937	49.02	372720	57.25
17.413	35049162	50.98	278304	42.75
Totals	68747099	100.00	651024	100.00

User: System
Acquired: 8/2/2017 5:57:03 PM
Printed: 10/12/2017 12:15:05 PM



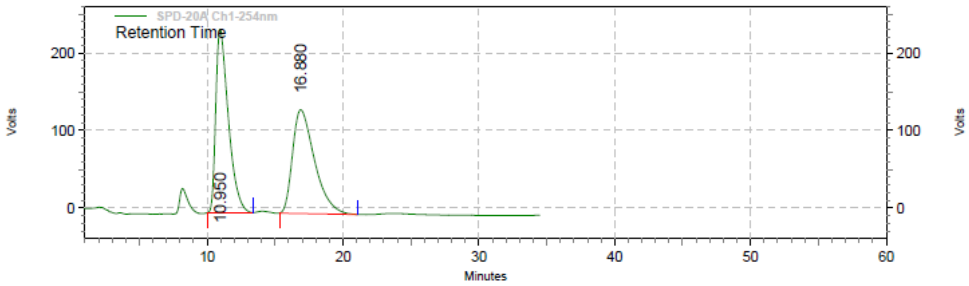
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
13.763	4506005	5.68	52708	9.23
18.603	74804663	94.32	518645	90.77
Totals	79310668	100.00	571353	100.00



2o

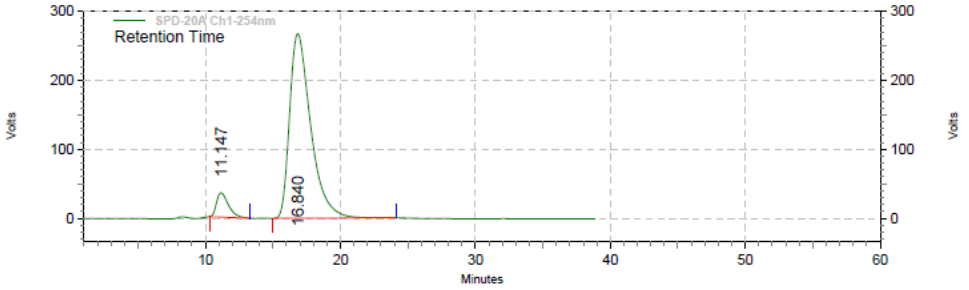
User: System
Acquired: 7/19/2017 3:30:50 PM
Printed: 8/2/2017 1:37:48 PM



SPD-20A
Ch1-254nm
Results

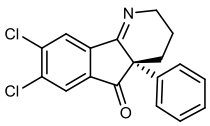
Retention Time	Area	Area %	Height	Height %
10.950	15214048	50.28	236128	63.86
16.880	15045213	49.72	133641	36.14
Totals				
	30259261	100.00	369769	100.00

User: System
Acquired: 8/2/2017 12:34:30 PM
Printed: 8/2/2017 1:38:38 PM



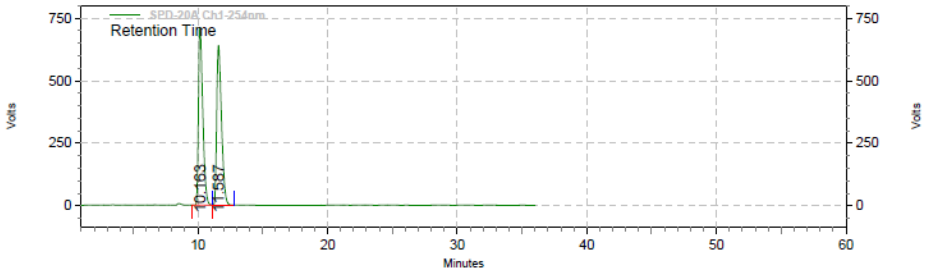
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.147	2153603	6.91	35240	11.64
16.840	29035294	93.09	267430	88.36
Totals				
	31188897	100.00	302670	100.00



2p

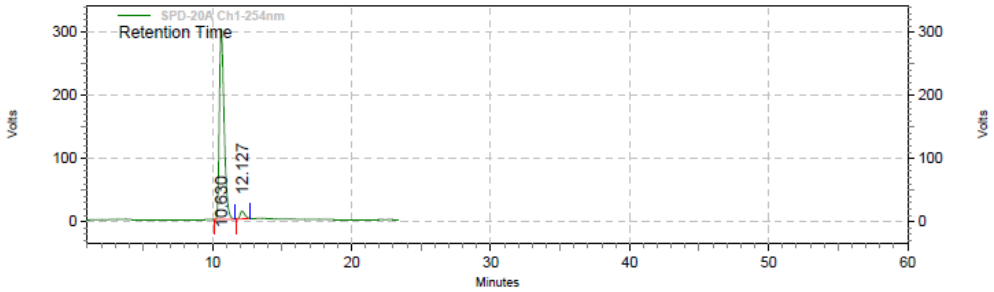
User: System
Acquired: 5/24/2017 10:32:22 AM
Printed: 5/29/2017 9:55:30 PM



SPD-20A
Ch1-254nm
Results

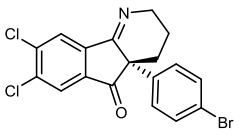
Retention Time	Area	Area %	Height	Height %
10.163	16434511	49.99	709556	52.67
11.587	16441459	50.01	637715	47.33
Totals	32875970	100.00	1347271	100.00

User: System
Acquired: 5/29/2017 9:44:19 PM
Printed: 5/29/2017 10:43:28 PM



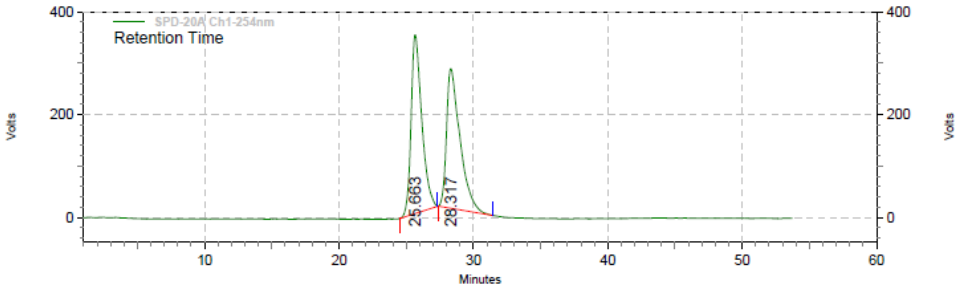
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
10.630	7154641	96.22	301772	96.08
12.127	280916	3.78	12306	3.92
Totals	7435557	100.00	314078	100.00



2q

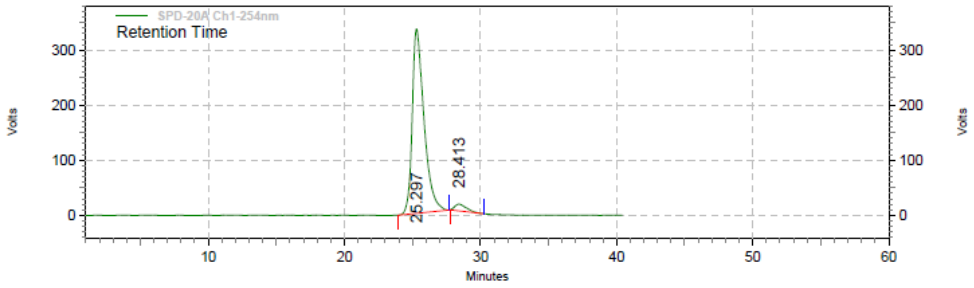
User: System
Acquired: 7/17/2017 6:22:39 PM
Printed: 7/21/2017 1:10:08 PM



SPD-20A
Ch1-254nm
Results

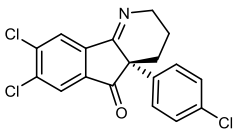
Retention Time	Area	Area %	Height	Height %
25.663	19220589	50.32	347933	56.15
28.317	18976341	49.68	271676	43.85
Totals				
	38196930	100.00	619609	100.00

User: System
Acquired: 7/21/2017 11:54:51 AM
Printed: 7/21/2017 1:12:13 PM



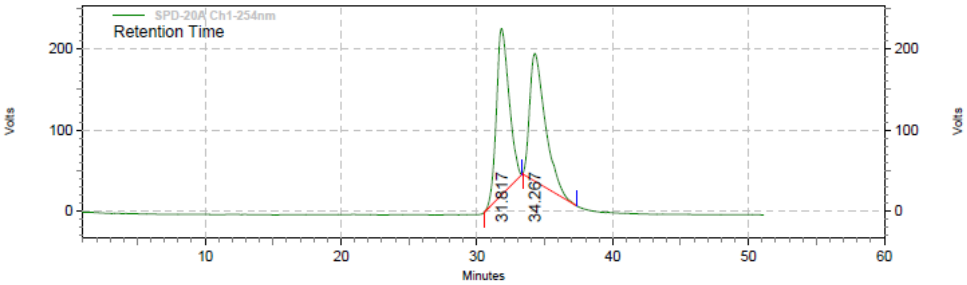
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
25.297	20113536	96.48	334747	96.49
28.413	734838	3.52	12182	3.51
Totals				
	20848374	100.00	346929	100.00



2r

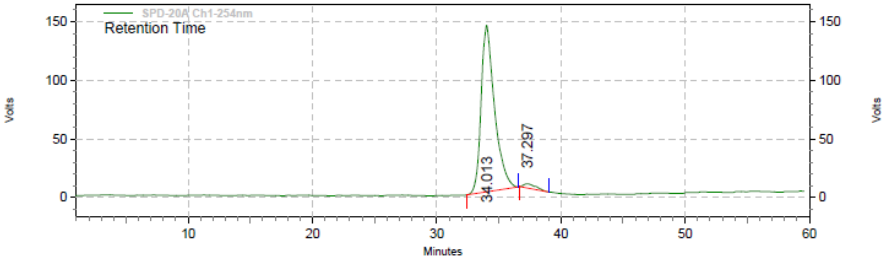
User: System
Acquired: 7/21/2017 9:18:18 PM
Printed: 10/12/2017 12:23:51 PM



SPD-20A
Ch1-254nm
Results

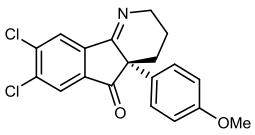
Retention Time	Area	Area %	Height	Height %
31.817	13135080	51.10	204434	56.56
34.267	12567855	48.90	157008	43.44
Totals				
	25702935	100.00	361442	100.00

User: System
Acquired: 7/26/2017 11:02:54 AM
Printed: 10/12/2017 12:22:32 PM



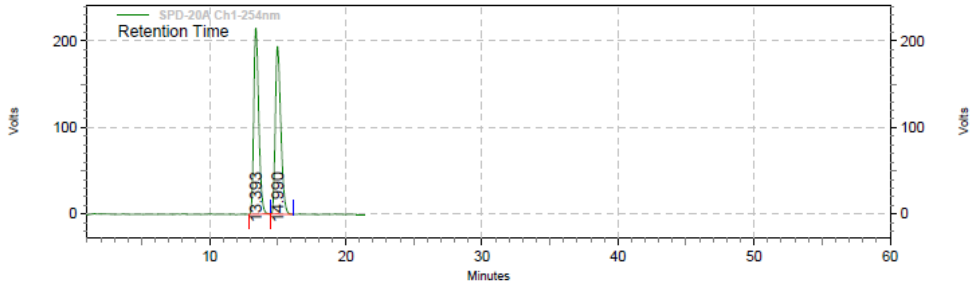
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
34.013	10710845	97.61	142212	97.56
37.297	261997	2.39	3556	2.44
Totals				
	10972842	100.00	145768	100.00



2s

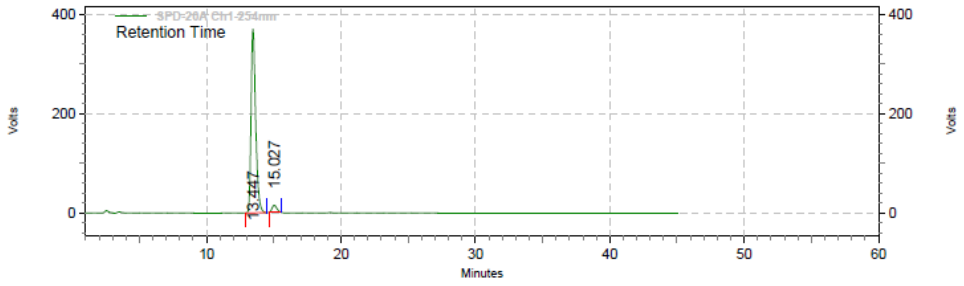
User: System
Acquired: 8/3/2017 6:29:50 PM
Printed: 8/8/2017 8:22:06 PM



SPD-20A
Ch1-254nm
Results

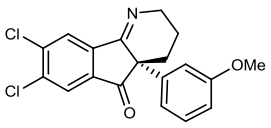
Retention Time	Area	Area %	Height	Height %
13.393	5464911	50.03	214869	52.62
14.990	5458529	49.97	193505	47.38
Totals	10923440	100.00	408374	100.00

User: System
Acquired: 8/8/2017 7:36:04 PM
Printed: 8/8/2017 8:23:22 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
13.447	8798853	95.95	369847	96.19
15.027	371145	4.05	14638	3.81
Totals	9169998	100.00	384485	100.00



2t

User: System
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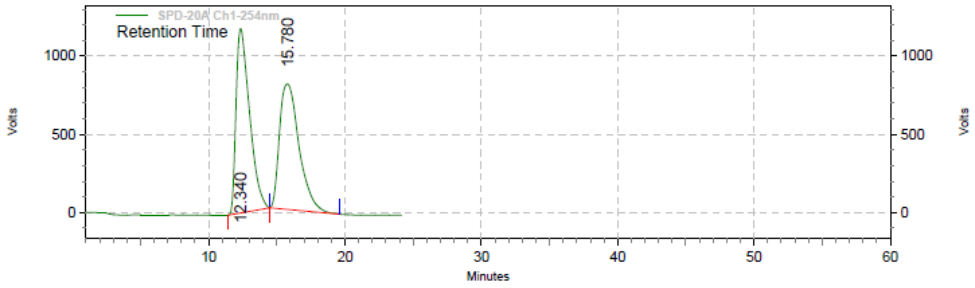
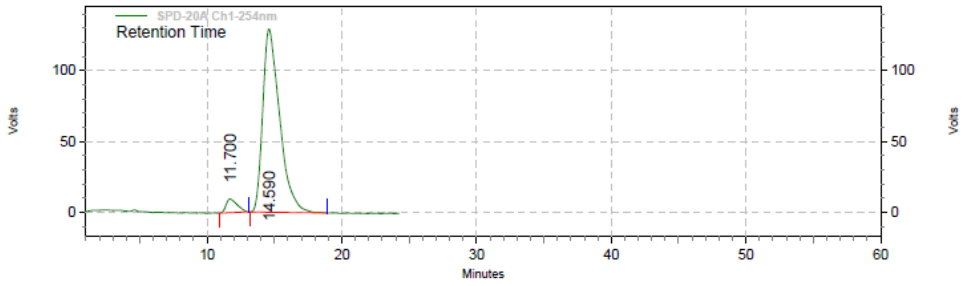
Printed: 8/8/2017 6:32:31 PM



SPD-20A
Ch1-254nm
Results

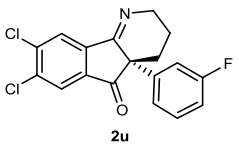
Retention Time	Area	Area %	Height	Height %
12.340	81252521	50.38	1178979	59.50
15.780	80027600	49.62	802541	40.50
Totals				
	161280121	100.00	1981520	100.00

User: System
Acquired: 8/8/2017 12:51:40 PM
Printed: 8/8/2017 6:36:57 PM



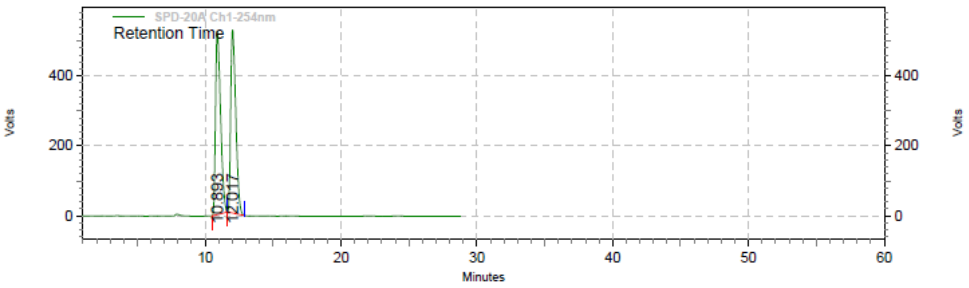
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.700	549465	4.64	9610	6.92
14.590	11294241	95.36	129225	93.08
Totals				
	11843706	100.00	138835	100.00



2u

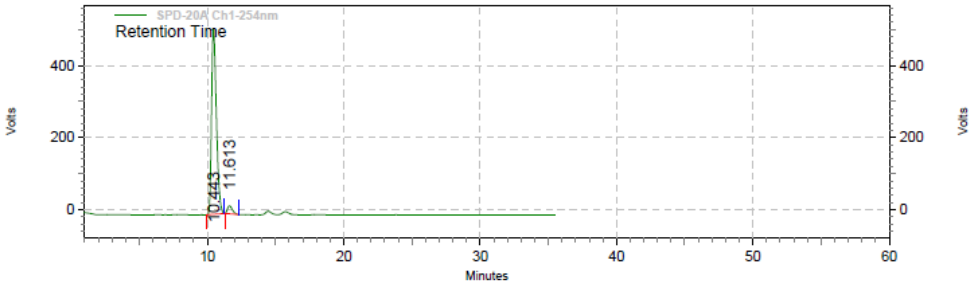
User: System
Acquired: 8/11/2017 3:29:37 PM
Printed: 8/14/2017 1:40:51 PM



SPD-20A
Ch1-254nm
Results

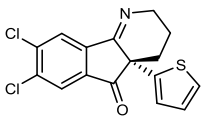
Retention Time	Area	Area %	Height	Height %
10.893	13506788	49.91	522566	49.98
12.017	13553383	50.09	523036	50.02
Totals				
	27060171	100.00	1045602	100.00

User: System
Acquired: 8/14/2017 12:46:02 PM
Printed: 8/14/2017 1:40:10 PM



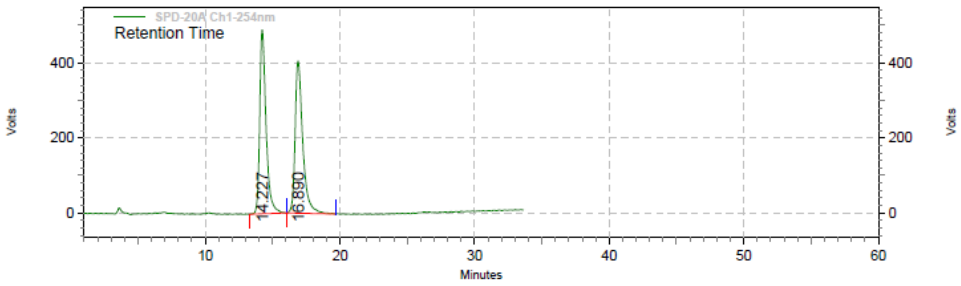
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
10.443	12703491	95.78	515602	95.90
11.613	559876	4.22	22024	4.10
Totals				
	13263367	100.00	537626	100.00



2v

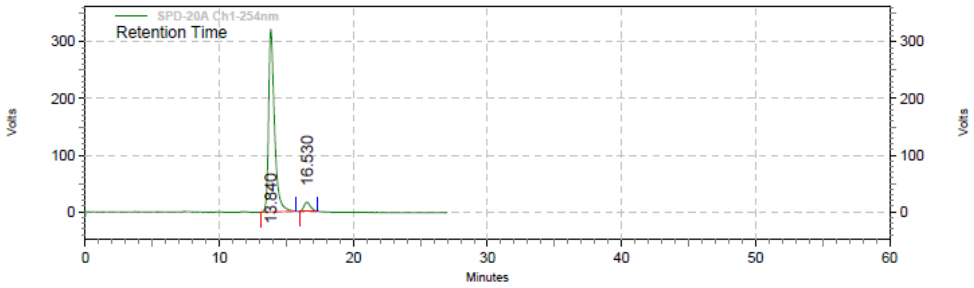
User: System
Acquired: 8/14/2017 9:01:49 PM
Printed: 10/12/2017 12:28:43 PM



SPD-20A
Ch1-254nm
Results

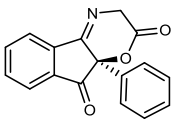
Retention Time	Area	Area %	Height	Height %
14.227	16001579	50.06	489292	54.72
16.890	15961361	49.94	404875	45.28
Totals	31962940	100.00	894167	100.00

User: System
Acquired: 8/17/2017 12:24:15 PM
Printed: 10/12/2017 12:33:04 PM



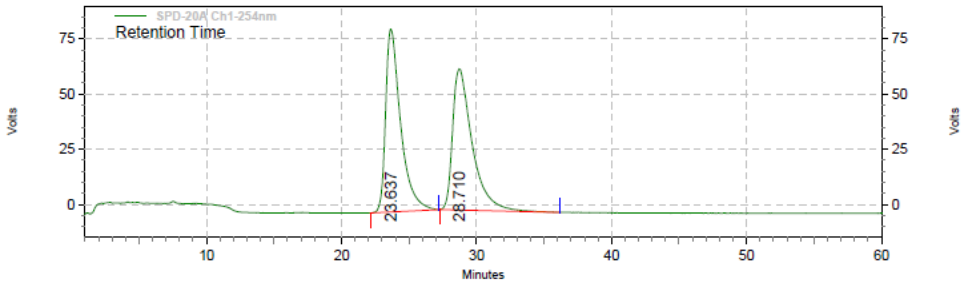
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
13.840	9840685	94.92	322272	95.32
16.530	526236	5.08	15831	4.68
Totals	10366921	100.00	338103	100.00



2w

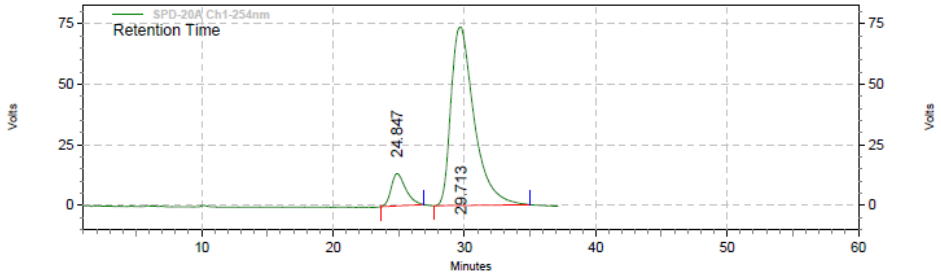
User: System
Acquired: 5/24/2017 5:34:00 PM
Printed: 10/12/2017 12:34:43 PM



SPD-20A
Ch1-254nm
Results

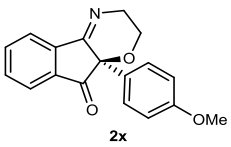
Retention Time	Area	Area %	Height	Height %
23.637	6411620	49.84	82862	56.44
28.710	6452184	50.16	63946	43.56
Totals	12863804	100.00	146808	100.00

User: System
Acquired: 6/1/2017 11:41:35 AM
Printed: 10/12/2017 12:37:07 PM



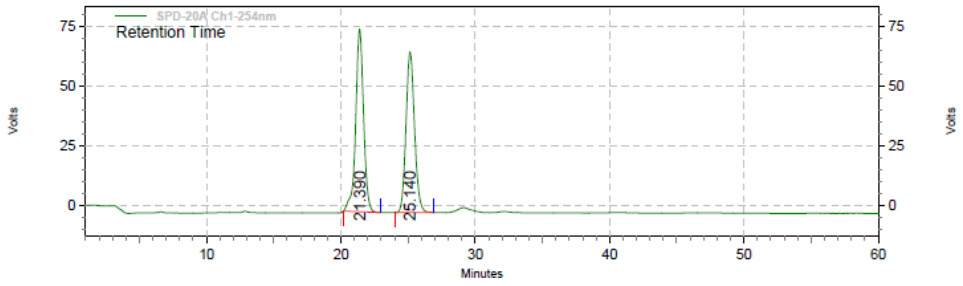
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
24.847	1020806	10.15	13319	15.31
29.713	9034767	89.85	73673	84.69
Totals	10055573	100.00	86992	100.00



2x

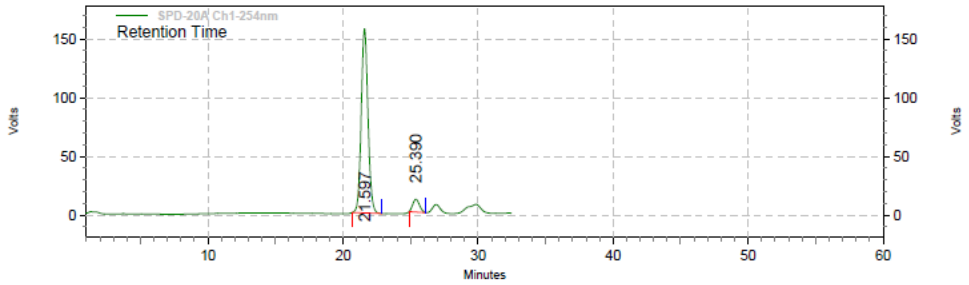
User: System
Acquired: 6/23/2017 11:40:20 AM
Printed: 10/12/2017 12:38:57 PM



SPD-20A
Ch1-254nm
Results

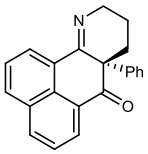
Retention Time	Area	Area %	Height	Height %
21.390	3147266	51.33	76897	53.23
25.140	2984364	48.67	67566	46.77
Totals	6131630	100.00	144463	100.00

User: System
Acquired: 6/23/2017 4:24:59 PM
Printed: 10/12/2017 12:42:41 PM



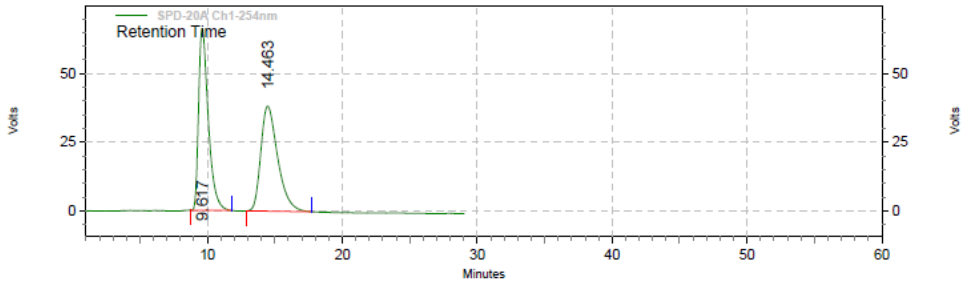
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
21.597	5451511	93.47	156931	93.50
25.390	381014	6.53	10912	6.50
Totals	5832525	100.00	167843	100.00



2y

User: System
Acquired: 8/9/2017 11:49:44 AM
Printed: 10/12/2017 12:49:08 PM



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.617	3310042	49.82	66225	63.34
14.463	3333676	50.18	38324	36.66
Totals	6643718	100.00	104549	100.00

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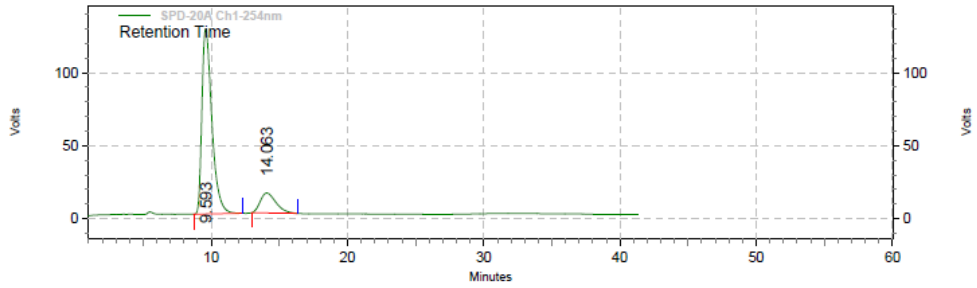
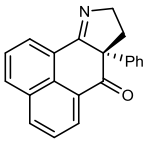


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.593	6428152	85.40	126725	90.24
14.063	1099223	14.60	13705	9.76
Totals	7527375	100.00	140430	100.00



2z

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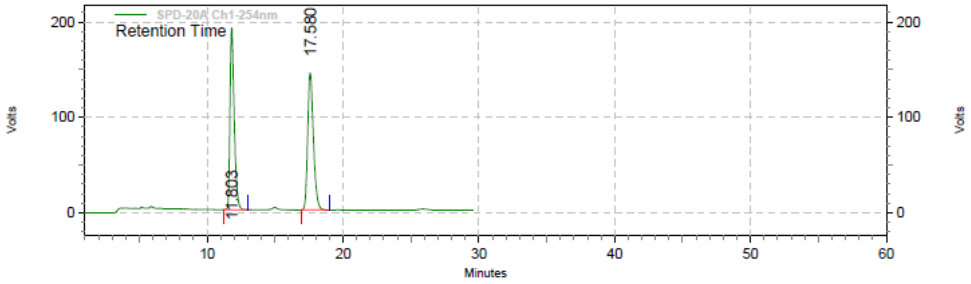

SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.803	4098187	49.25	190647	57.03
17.580	4223016	50.75	143645	42.97
Totals				
	8321203	100.00	334292	100.00

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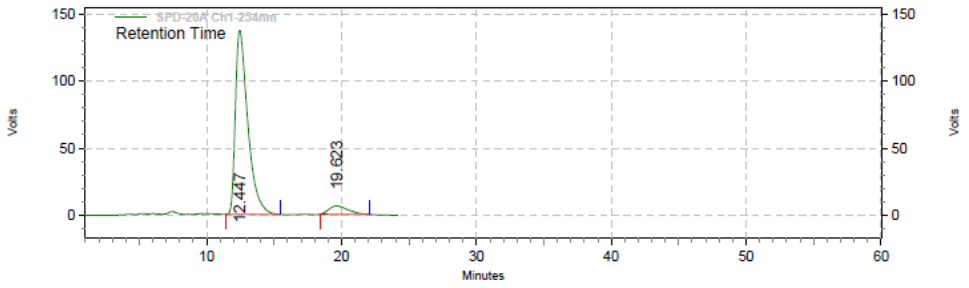
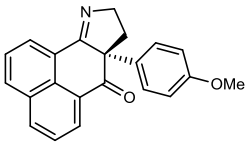


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
12.447	8854556	93.56	137954	95.72
19.623	609693	6.44	6161	4.28
Totals				
	9464249	100.00	144115	100.00



2aa

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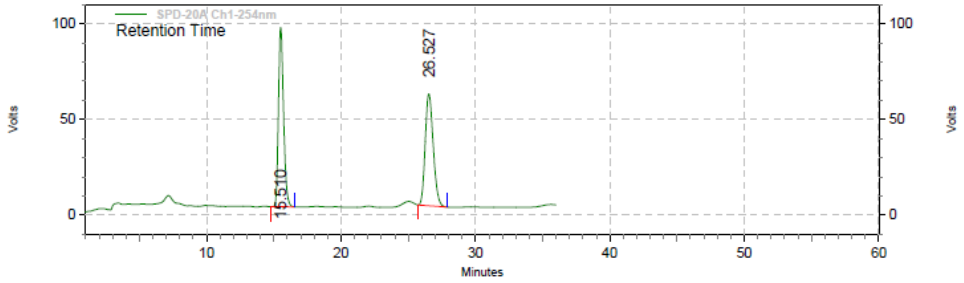

SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
15.510	2472374	50.49	93637	61.59
26.527	2424121	49.51	58387	38.41
Totals	4896495	100.00	152024	100.00

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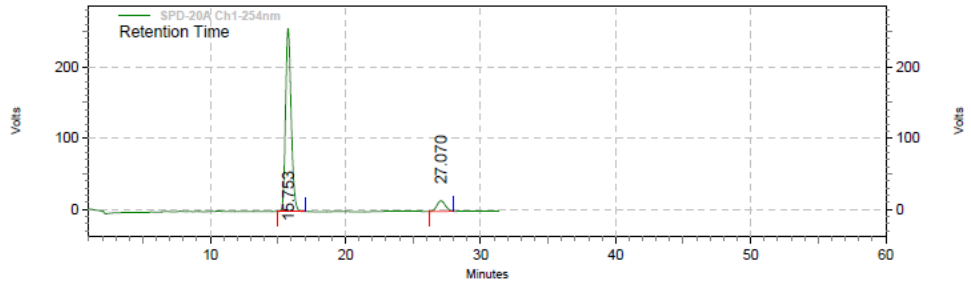
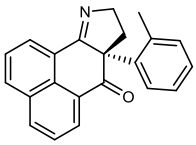


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
15.753	7434131	91.87	256918	94.48
27.070	657895	8.13	15005	5.52
Totals	8092026	100.00	271923	100.00



2ab

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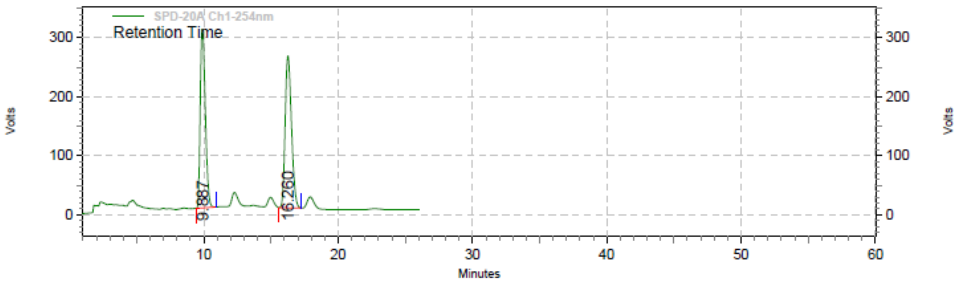

SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.887	7962260	48.59	302791	54.05
16.260	8424007	51.41	257455	45.95
Totals	16386267	100.00	560246	100.00

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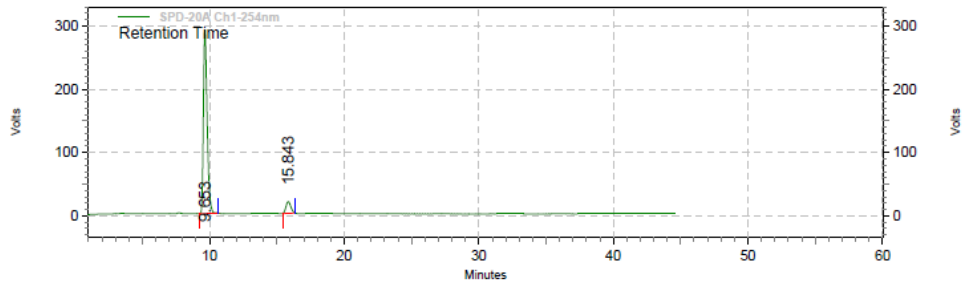
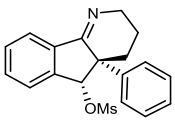


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.653	5605426	92.39	290044	94.01
15.843	461682	7.61	18476	5.99
Totals	6067108	100.00	308520	100.00



6

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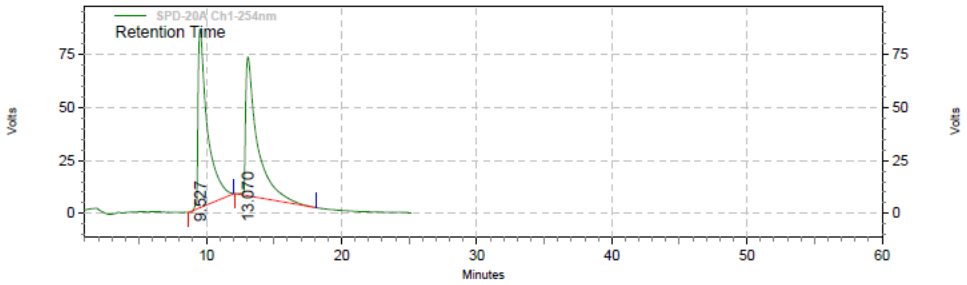

SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.527	4026764	50.90	84204	56.29
13.070	3884128	49.10	65378	43.71
Totals	7910892	100.00	149582	100.00

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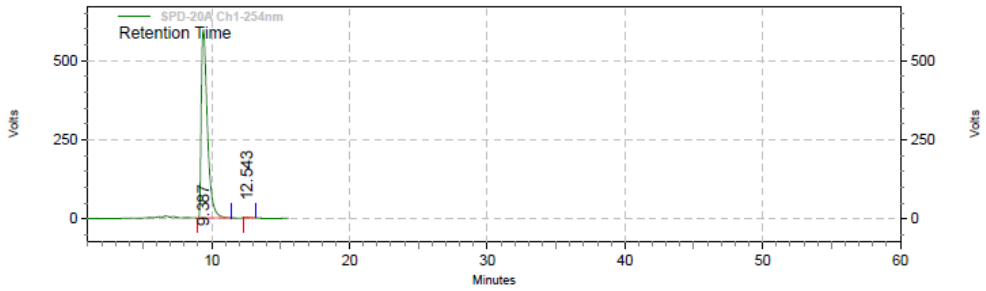

SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.387	18292327	99.83	593995	99.78
12.543	31956	0.17	1317	0.22
Totals	18324283	100.00	595312	100.00

9. References

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