Supplementary Information

Efficient asymmetric synthesis of spiro-2(3*H*)-furanones via phase-transfer-catalyzed alkynylation

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General Information

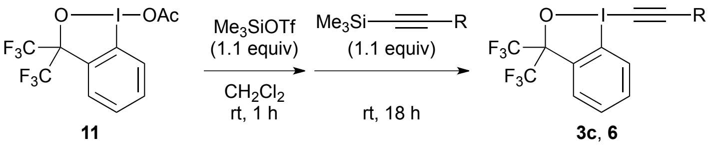
^{1}H NMR spectra were measured on JEOL JNM-FX 400 NMR instrument (400 MHz for ^{1}H NMR). ^{13}C NMR spectra were measured on JEOL JNM-FX 400 NMR instrument (100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using Daicel Chiralpak AD-3, IA-3, or IC-3 (4.6 mm × 250 mm) columns. High-resolution mass spectra (HRMS) were performed on BRUKER microTOF focus–KR. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. All reactions were monitored by thin-layer chromatography carried out on Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), visualization by using UV (254 nm), or dyes such as $KMnO_4$. The products were purified by flash column chromatography on silica gel 60N [Kanto Chemical Co., Inc. (spherical, neutral)] or Merck preparative thin layer chromatography on silica gel (PLC 60 F254, 0.5 mm). All simple chemicals were purchased and used as received.

Experimental Section

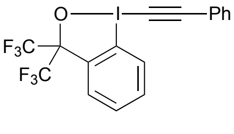
Synthesis of Iodine Reagents 3a and 3b.

Iodine reagents **3a** and **3b** were prepared according to the literature.[1]

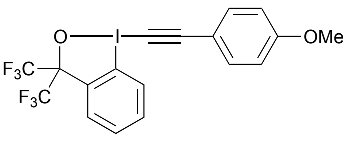
General Procedure for the Synthesis of Iodine Reagents 3c and 6.



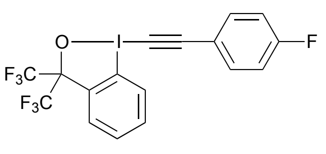
To a solution of iodine reagent **11**[2] (0.20 mmol) in dichloromethane (1.0 mL) was added trimethylsilyl triflate (0.22 mmol) at room temperature, and the reaction mixture was stirred for 1 h. To the resulting solution was added trimethylsilylacetylene compound (0.22 mmol), and the mixture was stirred for 18 h at room temperature. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with dichloromethane (3 × 5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane as eluent) to give compound **3c** or **6** (70–95% yield).



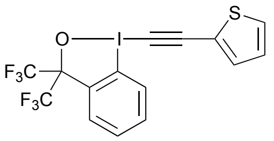
3c:[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.30 (m, 1H), 7.83–7.88 (m, 1H), 7.67–7.73 (m, 2H), 7.54–7.57 (m, 2H), 7.37–7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 132.6, 131.2, 130.13, 130.08, 129.9, 128.6, 128.3, 123.6 (q, J = 292 Hz), 121.3, 111.4, 105.3, 81.7 (septet, J = 29.6 Hz), 54.4; IR (neat) 2131, 1265, 1255, 1179, 1157, 963, 946, 761, 729 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_9F_6INaO^+$: 492.9494 ([M+Na]$^+$), found 492.9502.



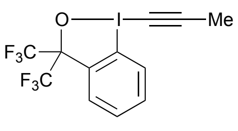
6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.29 (m, 1H), 7.83–7.85 (br m, 1H), 7.66–7.71 (m, 2H), 7.50 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 134.4, 132.8, 131.1, 130.1, 129.8, 128.3, 123.7 (q, J = 292 Hz), 114.3, 113.2, 111.6, 105.9, 81.7 (septet, J = 29.6 Hz), 55.4, 52.7; IR (neat) 2118, 1508, 1254, 1183, 1151, 1023, 755, 730, 692, 663 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{12}F_6IO_2^+$: 500.9781 ([M+H]$^+$), found 500.9764.



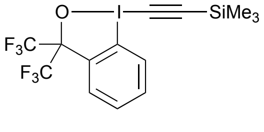
6b: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.24–8.27 (m, 1H), 7.84–7.87 (br m, 1H), 7.67–7.74 (m, 2H), 7.53–7.57 (m, 2H), 7.08–7.12 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.5 (d, J = 254 Hz), 134.7 (d, J = 9.1 Hz), 132.9, 131.2, 130.1, 129.9, 128.3, 123.6 (q, J = 292 Hz), 117.5 (d, J = 3.3 Hz), 116.0 (d, J = 23.0 Hz), 111.3, 104.1, 81.7 (septet, J = 29.6 Hz), 54.4; IR (neat) 2120, 1505, 1264, 1209, 1181, 1165, 1150, 966, 950, 840, 739, 730 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_9F_7IO^+$: 488.9581 ([M+H]$^+$), found 488.9582.



6c: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22–8.25 (m, 1H), 7.84–7.87 (m, 1H), 7.67–7.74 (m, 2H), 7.40–7.42 (m, 2H), 7.05–7.08 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 135.0, 133.0, 131.2, 130.1, 129.9, 129.7, 128.3, 127.3, 123.6 (q, J = 292 Hz), 121.2, 111.7, 98.3, 81.7 (septet, J = 29.6 Hz), 59.6; IR (neat) 2095, 1266, 1183, 1165, 1149, 966, 952, 730, 704 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_8F_6IOS^+$: 476.9239 ([M+H]$^+$), found 476.9238.



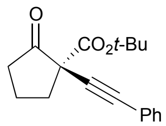
6d: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.21–8.24 (m, 1H), 7.81–7.84 (br m, 1H), 7.66–7.71 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 132.7, 131.0, 130.1, 129.8, 128.2, 123.7 (q, J = 291 Hz), 110.9, 103.1, 81.6 (septet, J = 29.7 Hz), 43.0, 5.3; IR (neat) 2140, 1266, 1226, 1198, 1182, 1157, 962, 762, 729 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_8F_6IO^+$: 408.9519 ([M+H]$^+$), found 408.9511.



6e:[3] ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22–8.26 (m, 1H), 7.82–7.85 (br m, 1H), 7.67–7.72 (m, 2H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 132.9, 131.1, 129.98, 129.90, 128.2, 123.6 (q, J = 292 Hz), 115.2, 110.8, 81.6 (septet, J = 29.6 Hz), 69.2, –0.3; IR (neat) 2229, 1187, 1153, 906, 846, 728, 687 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{14}F_6IOSi^+$: 466.9757 ([M+H]$^+$), found 466.9746.

General Procedure for Asymmetric Alkynylation of 2-Oxocyclopentanecarboxylate (Table 1).

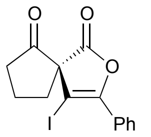
To a solution of 2-oxocyclopentanecarboxylate (0.025 mmol), iodine reagent **3** (0.030 mmol), and chiral phase-transfer catalyst (*S*,*S*)-**1** or (*S*)-**2** (3 mol %) in dichloromethane or toluene (2 mL) was added K_2CO_3 (0.038 mmol) at 0 °C. The reaction mixture was vigorously stirred for 72 h at 0 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (3 × 5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography or preparative thin layer chromatography on silica gel (ethyl acetate/hexane/dichloromethane as eluent) to give alkynylation product **4**.



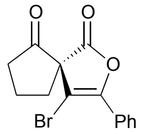
4a: $[\alpha]^{23}_{D} = +46.3$ (c = 0.25, $CHCl_3$, 94% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 254 nm; retention time: 7.3 min (minor) and 8.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.45 (m, 2H), 7.27–7.30 (m, 3H), 2.61–2.68 (m, 1H), 2.38–2.55 (m, 3H), 2.08–2.17 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 167.4, 131.8, 128.2, 128.0, 122.6, 85.1, 84.7, 82.9, 57.3, 36.9, 36.7, 27.7, 19.9; IR (neat) 1757, 1735, 1719, 1369, 1250, 1147, 845, 757, 730, 692 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{20}NaO_3^+$: 307.1305 ([M+Na]$^+$), found 307.1318.

General Procedure for Cyclization of Alkynylation Product 4a (Scheme 2).

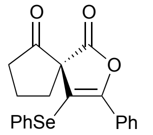
A solution of *N*-iodosuccinimide, bromine, or phenylselenyl chloride (0.030 mmol) in dichloromethane (1 mL) was added dropwise to a solution of the alkynylated compound **4a** (0.015 mmol) in dichloromethane (1 mL) at room temperature. The reaction mixture was stirred for 6–12 h at room temperature. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (NIS and Br_2) or $NaHCO_3$ (PhSeCl) and extracted with dichloromethane (3 × 5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography or preparative thin layer chromatography on silica gel (ethyl acetate/hexane/dichloromethane as eluent) to give cyclization product **5**.



5a:[4] $[\alpha]^{22}_D = -63.7$ (*c* = 0.35, $CHCl_3$, 94% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 254 nm; retention time: 13.7 min (major) and 16.4 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.98 (m, 2H), 7.41–7.46 (m, 3H), 2.20–2.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 172.7, 152.8, 130.6, 128.4, 127.7, 127.6, 67.6, 65.6, 38.1, 33.5, 19.4; IR (neat) 1795, 1747, 1199, 1091, 1018, 942, 767, 691 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{11}INaO_3^+$: 376.9645 ($[M+Na]^+$), found 376.9645.



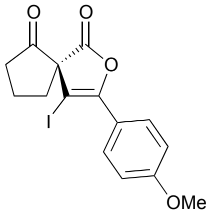
5b: $[\alpha]^{28}_D = -61.4$ (*c* = 0.10, $CHCl_3$, 94% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 254 nm; retention time: 12.2 min (major) and 13.9 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–8.01 (m, 2H), 7.40–7.50 (m, 3H), 2.15–2.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 171.9, 149.8, 130.5, 128.5, 127.2, 127.0, 95.9, 66.3, 38.1, 32.5, 19.5; IR (neat) 1800, 1750, 1022, 904, 726, 650 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{11}BrNaO_3^+$: 328.9784 ($[M+Na]^+$), found 328.9769 (and 330.98).



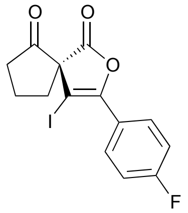
5c: $[\alpha]^{27}_D = -206.8$ (*c* = 0.25, $CHCl_3$, 94% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 254 nm; retention time: 17.9 min (minor) and 24.2 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03–8.06 (m, 2H), 7.36–7.45 (m, 5H), 7.23–7.26 (m, 3H), 2.24–2.53 (m, 4H), 2.06–2.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 173.9, 157.6, 130.7, 130.2, 129.5, 129.4, 128.4, 128.0, 127.7, 127.3, 102.8, 67.5, 38.1, 32.7, 19.8; IR (neat) 1796, 1745, 1035, 1018, 941, 737, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{16}NaO_3Se^+$: 407.0158 ($[M+Na]^+$), found 407.0139 (and 405.02).

General Procedure for Efficient Asymmetric Synthesis of Spiro Compounds 7 and 8 (Table 2, Scheme 3).

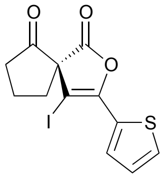
To a solution of β-keto ester (0.025 mmol), iodine reagent **3c** or **6** (0.030 mmol), and chiral phase-transfer catalyst (*S*)-**2** (3 mol %) in toluene (2 mL) was added K_2CO_3 (0.038 mmol) at 0 °C. The reaction mixture was vigorously stirred for 72 h at 0 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (3 × 5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was dissolved in dichloromethane (1 mL), and to this solution was added a solution of *N*-iodosuccinimide or phenylselenyl chloride (0.075 mmol) in dichloromethane (1 mL) at room temperature. The reaction mixture was stirred for 6–12 h at room temperature. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (NIS) or $NaHCO_3$ (PhSeCl) and extracted with dichloromethane (3 × 5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography or preparative thin layer chromatography on silica gel (ethyl acetate/hexane/dichloromethane as eluent) to give cyclization product **7** or **8**.



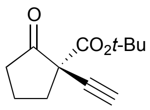
7a: $[\alpha]^{23}_{D} = -70.3$ (*c* = 0.40, $CHCl_3$, 95% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 260 nm; retention time: 24.8 min (major) and 32.0 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H), 2.22–2.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 172.9, 161.3, 152.6, 129.3, 120.1, 113.8, 67.5, 63.1, 55.4, 38.1, 33.6, 19.4; IR (neat) 1792, 1747, 1605, 1509, 1255, 1178, 1089, 1021, 1005, 909, 835, 730 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{14}IO_4^+$: 384.9931 ($[M+H]^+$), found 384.9914.



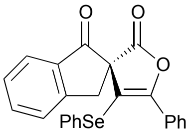
7b: $[\alpha]^{22}_{D} = -55.0$ (*c* = 0.23, $CHCl_3$, 90% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 250 nm; retention time: 12.1 min (major) and 15.2 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96–8.00 (m, 2H), 7.12–7.16 (m, 2H), 2.24–2.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 172.5, 163.8 (d, *J* = 254 Hz), 151.9, 129.9 (d, *J* = 9.1 Hz), 123.9 (d, *J* = 3.3 Hz), 115.6 (d, *J* = 22.3 Hz), 67.6, 65.3 (d, *J* = 1.7 Hz), 38.1, 33.5, 19.4; IR (neat) 1797, 1749, 1508, 1265, 1238, 1162, 1089, 1023, 1012, 841, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{10}FINaO_3^+$: 394.9551 ($[M+Na]^+$), found 394.9558.



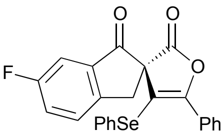
7c: $[\alpha]^{23}_{D} = -66.3$ (*c* = 0.40, $CHCl_3$, 93% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 254 nm; retention time: 19.9 min (major) and 21.2 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 4.0 Hz, 1H), 7.51 (d, *J* = 5.2 Hz, 1H), 7.15 (dd, *J* = 4.0, 5.2 Hz, 1H), 2.21–2.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 172.1, 149.5, 129.5, 129.4, 128.7, 127.4, 67.2, 63.8, 38.0, 33.7, 19.4; IR (neat) 1266, 1183, 1065, 1149, 966, 952, 730 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_9INaO_3S^+$: 382.9209 ([M+Na]$^+$), found 382.9197.



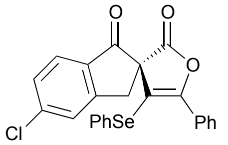
4e:[5] [α]$^{28}_{D}$ = +5.1 (*c* = 0.30, $CHCl_3$, 93% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 220 nm; retention time: 13.9 min (minor) and 14.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56–2.63 (m, 1H), 2.31–2.49 (m, 4H), 2.04–2.11 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 167.1, 83.3, 79.5, 73.3, 56.7, 36.7, 27.8, 19.8; IR (neat) 3258, 1757, 1735, 1370, 1283, 1255, 1150 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{16}NaO_3^+$: 231.0992 ([M+Na]$^+$), found 231.1003.



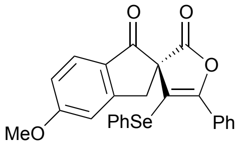
8a: [α]$^{22}_{D}$ = –19.4 (*c* = 0.30, $CHCl_3$, 90% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 248 nm; retention time: 38.3 min (minor) and 58.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.14 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.42–7.46 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 3.57 (d, *J* = 17.6 Hz, 1H), 3.47 (d, *J* = 17.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 174.1, 156.8, 153.1, 135.8, 134.6, 131.7, 130.6, 129.2, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 126.3, 125.4, 103.9, 67.7, 36.1; IR (neat) 1795, 1720, 1272, 1202, 1034, 1020, 901, 736, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{16}NaO_3Se^+$: 455.0158 ([M+Na]$^+$), found 455.0163 (and 453.02).



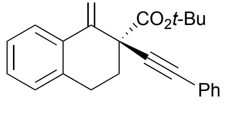
8b: [α]$^{25}_{D}$ = –26.7 (*c* = 0.50, $CHCl_3$, 80% *ee*); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 240 nm; retention time: 18.5 min (minor) and 28.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.13 (m, 2H), 7.08–7.47 (m, 11H), 3.53 (d, *J* = 17.2 Hz, 1H), 3.44 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 166.7, 155.4 (d, *J* = 251 Hz), 149.7, 141.5, 129.3 (d, *J* = 7.4 Hz), 125.0, 123.7, 122.2, 121.5, 121.1, 120.84, 120.79, 120.6 (d, *J* = 8.3 Hz), 116.6 (d, *J* = 23.8 Hz), 103.9 (d, *J* = 22.2 Hz), 96.9, 61.4, 28.5; IR (neat) 1798, 1720, 1488, 1438, 1290, 1264, 1201, 1035, 1018, 768, 738, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{15}FNaO_3Se^+$: 473.0064 ([M+Na]$^+$), found 473.0054 (and 471.01).



8c: $[\alpha]^{24}_{\mathrm{D}}$ = –22.7 (*c* = 0.20, $\mathrm{CHCl_3}$, 85% *ee*); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 5:1, flow rate = 0.5 mL/min, 310 nm; retention time: 18.2 min (minor) and 20.2 min (major). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 8.09–8.12 (m, 2H), 7.42–7.46 (m, 5H), 7.07–7.32 (m, 6H), 3.53 (d, *J* = 17.2 Hz, 1H), 3.44 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 195.9, 173.7, 156.8, 154.4, 142.6, 133.0, 131.8, 130.8, 129.3, 128.9, 128.5, 128.1, 127.90, 127.85, 127.78, 126.5, 126.3, 103.7, 67.8, 35.7; IR (neat) 1797, 1716, 1597, 1578, 1264, 1200, 1066, 1035, 1018, 904, 737, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $\mathrm{C_{24}H_{15}ClNaO_3Se^+}$: 488.9766 ($[\mathrm{M+Na}]^+$), found 488.9785 (and 486.98).



8d: $[\alpha]^{25}_{\mathrm{D}}$ = –46.8 (*c* = 0.30, $\mathrm{CHCl_3}$, 92% *ee*); HPLC analysis: Daicel Chiralpak AD-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 280 nm; retention time: 35.9 min (minor) and 46.4 min (major). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 8.10–8.13 (m, 2H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.42–7.44 (m, 3H), 7.25–7.27 (m, 2H), 7.10–7.19 (m, 3H), 6.86–6.88 (m, 2H), 3.89 (s, 3H), 3.50 (d, *J* = 17.6 Hz, 1H), 3.38 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 195.0, 174.4, 166.3, 156.9, 156.2, 131.3, 130.6, 129.2, 128.5, 128.4, 128.1, 127.9, 127.8, 127.5, 127.1, 116.3, 109.4, 103.8, 68.0, 55.8, 35.9; IR (neat) 1799, 1707, 1596, 1491, 1303, 1265, 1207, 1094, 1034, 1019, 738, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $\mathrm{C_{25}H_{18}NaO_4Se^+}$: 485.0264 ($[\mathrm{M+Na}]^+$), found 485.0248 (and 483.03).



9: $[\alpha]^{27}_{\mathrm{D}}$ = +12.3 (*c* = 0.10, $\mathrm{CHCl_3}$, 57% *ee*); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 10:1, flow rate = 0.8 mL/min, 254 nm; retention time: 9.2 min (major) and 10.2 min (minor). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ 8.09 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.24–7.42 (m, 7H), 3.34–3.42 (m, 1H), 2.98–3.05 (m, 1H), 2.77–2.84 (m, 1H), 2.45–2.51 (m, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 190.0, 167.9, 143.2, 133.8, 132.0, 130.8, 128.7, 128.4, 128.1, 126.9, 122.7, 86.4, 83.8, 83.0, 56.7, 33.2, 27.9, 26.1; IR (neat) 2124, 1734, 1691, 1491, 1281, 1252, 1233, 1154, 756, 742 cm^{-1}; HRMS (ESI-TOF) calcd for $\mathrm{C_{23}H_{22}NaO_3^+}$: 369.1461 ($[\mathrm{M+Na}]^+$), found 369.1455.

Determination of Absolute Configuration of Products.

X-Ray Diffraction Analysis of Product 8a.

Product **8a** was recrystallized from benzene/hexane. Data of X-ray diffraction were collected by a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated CuKα (λ = 1.54187 Å) radiation. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[6] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The absolute configuration was determined by reference to the Flack parameter[7] –0.01(5).

The crystallographic data of **8a** were summarized in the following table.

empirical formula	$C_{24}H_{16}O_3Se$
formula weight	431.35
crystal system	orthorhombic
space group	$P2_12_12_1$ (#19)
a, Å	9.9638(2)
b, Å	10.0483(2)
c, Å	19.6441(4)
V, Å^3	1966.75(7)
Z	4
*D*calc, g/cm^3	1.457
T, °C	–150
μ (CuKα), cm^{-1}	27.607
no. of reflns obsd	3526
no. of reflns variable	253
R_1 (I >2σ(I))	0.0541
Rw (All reflections)	0.2220
Goodness of Fit	1.604
Flack Parameter (Friedel pairs = 1494)	–0.01(5)

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 986764). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

References

[1] M. J. Bouma and B. Olofsson, *Chem.–Eur. J.* 2012, **18**, 14242.

[2] P. Eisenberger, S. Gischig and A. Togni, *Chem.–Eur. J.* 2006, **12**, 2579.

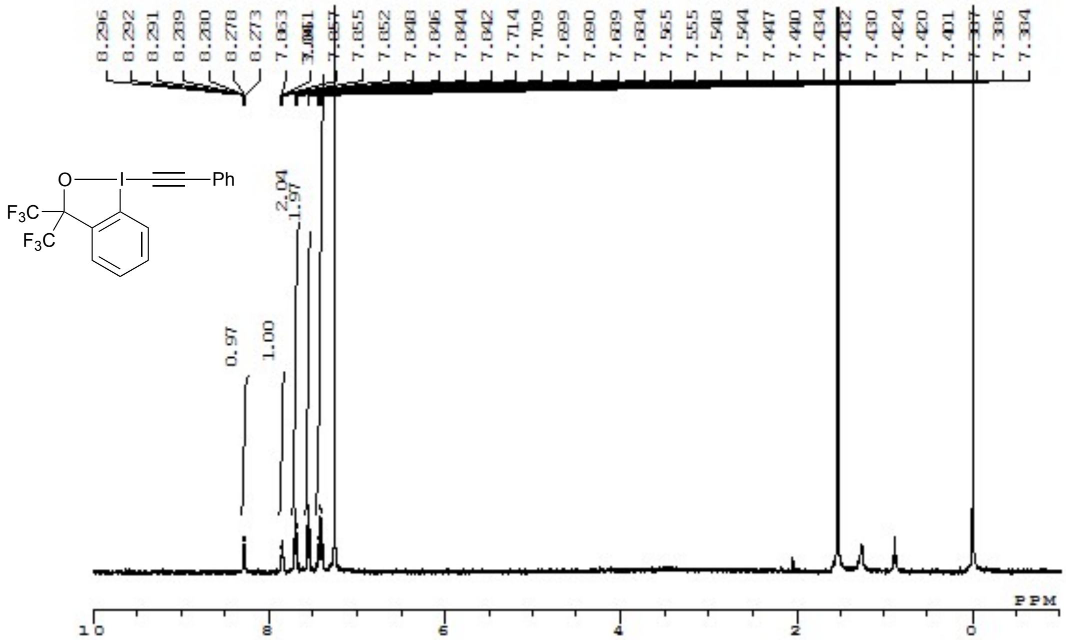
[3] V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz and A. J. Simonsen, *J. Org. Chem.* 1996, **61**, 6547.

[4] Z. W. Just, R. C. Larock, *J. Org. Chem.* 2008, **73**, 2662.

[5] T. B. Poulsen, L. Bernardi, J. Alemán, J. Overgaard and K. A. Jørgensen, *J. Am. Chem. Soc.* 2007, **129**, 441.

[6] G. M. Sheldrick, SHELX-97: Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.

[7] H. D. Flack, *Acta Cryst.* 1983, **A39**, 876.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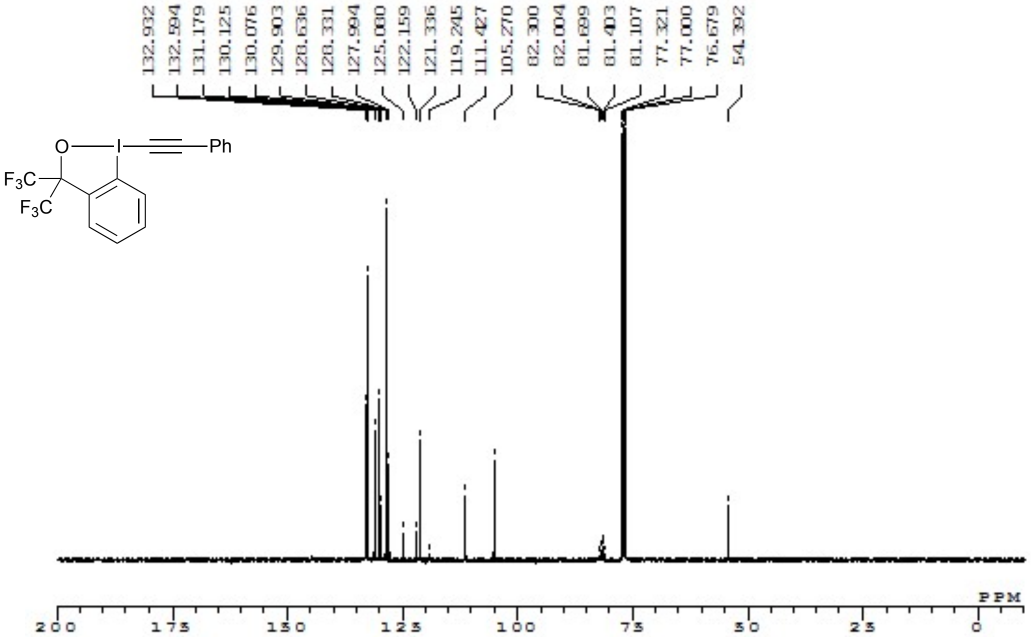
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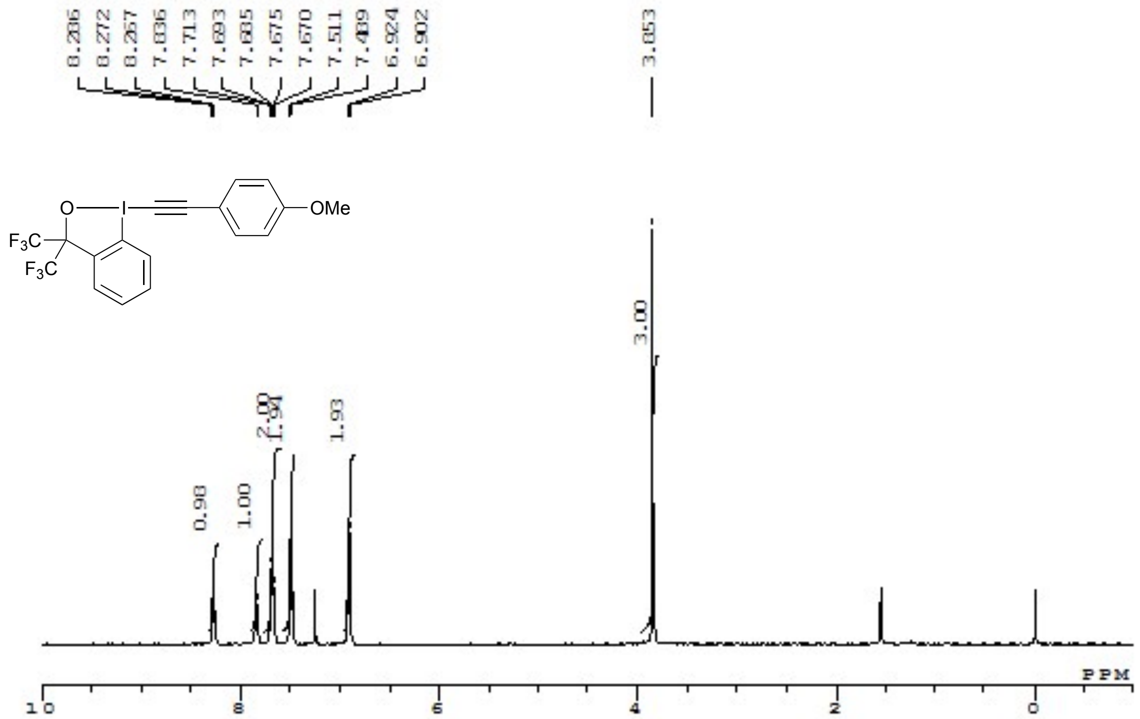
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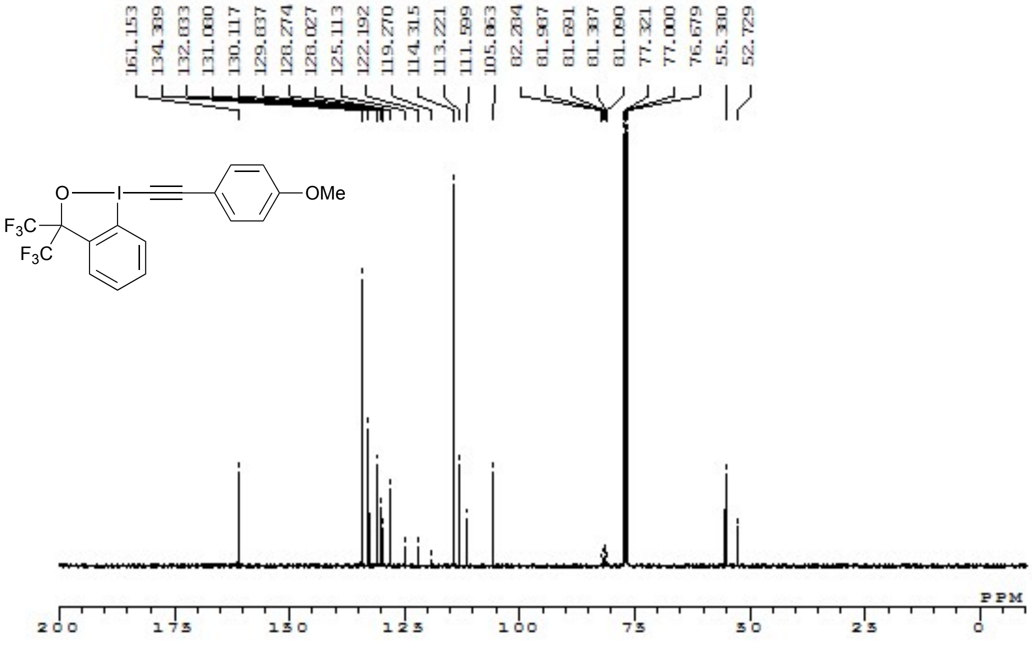
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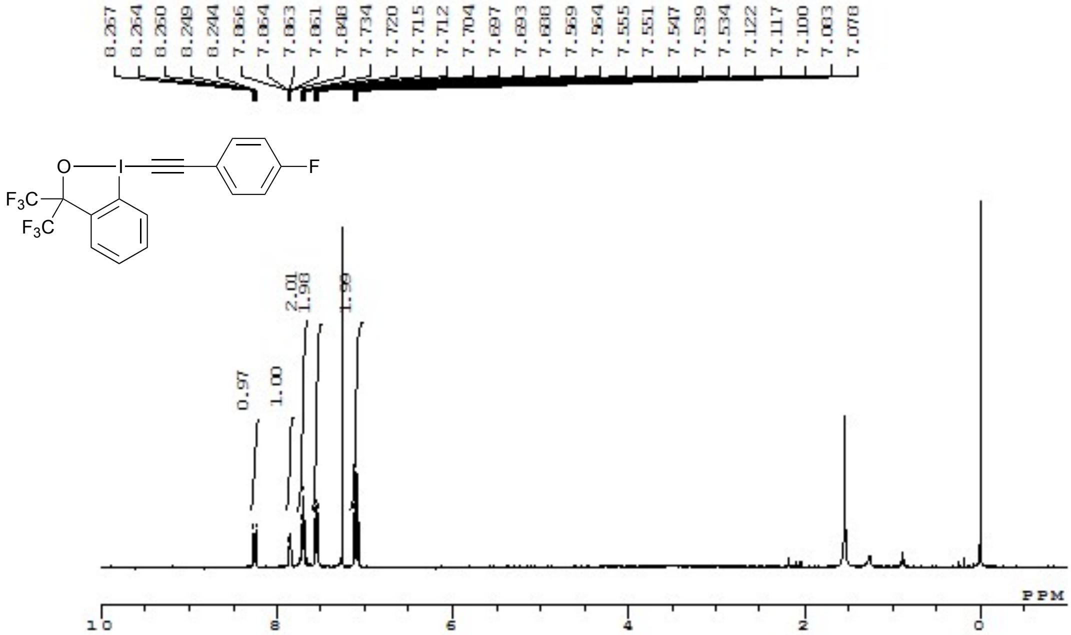
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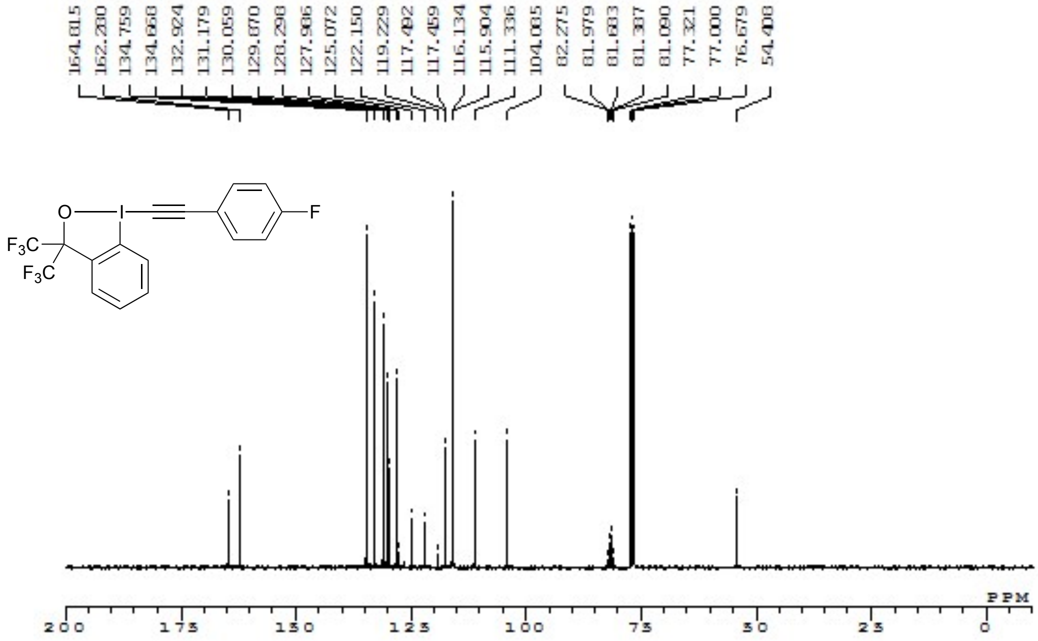
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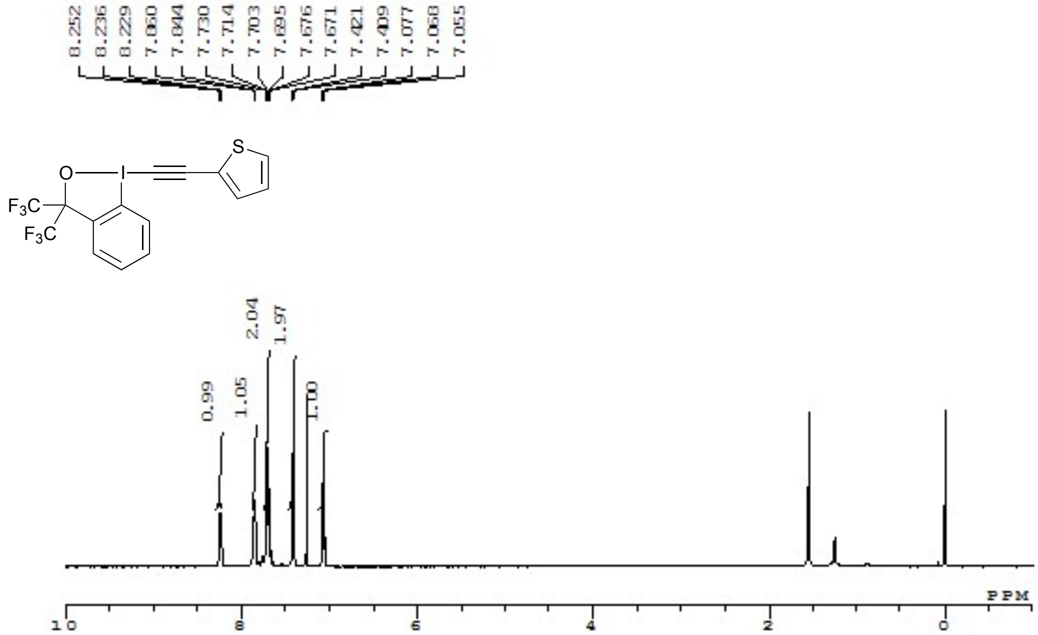
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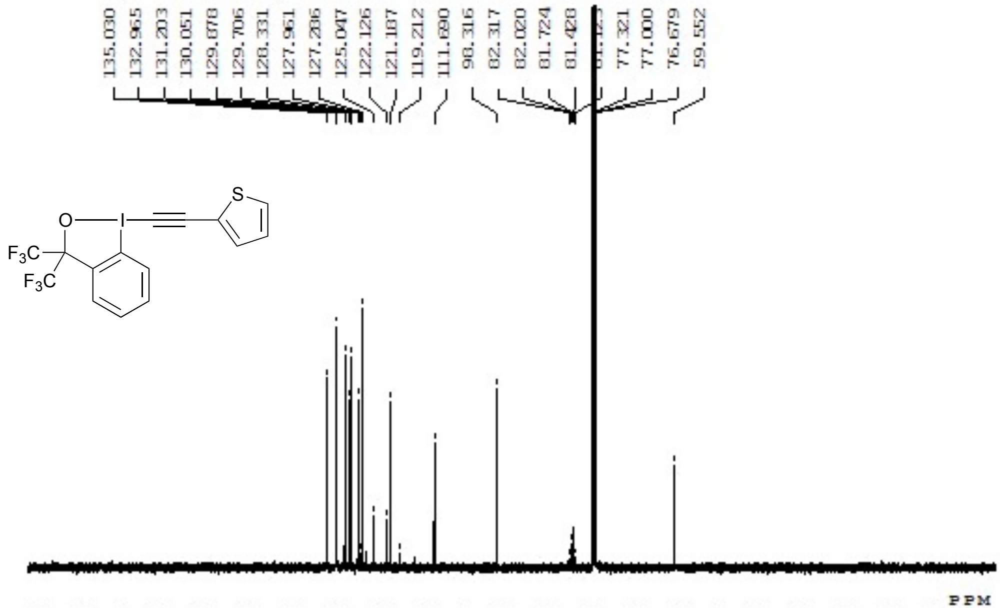
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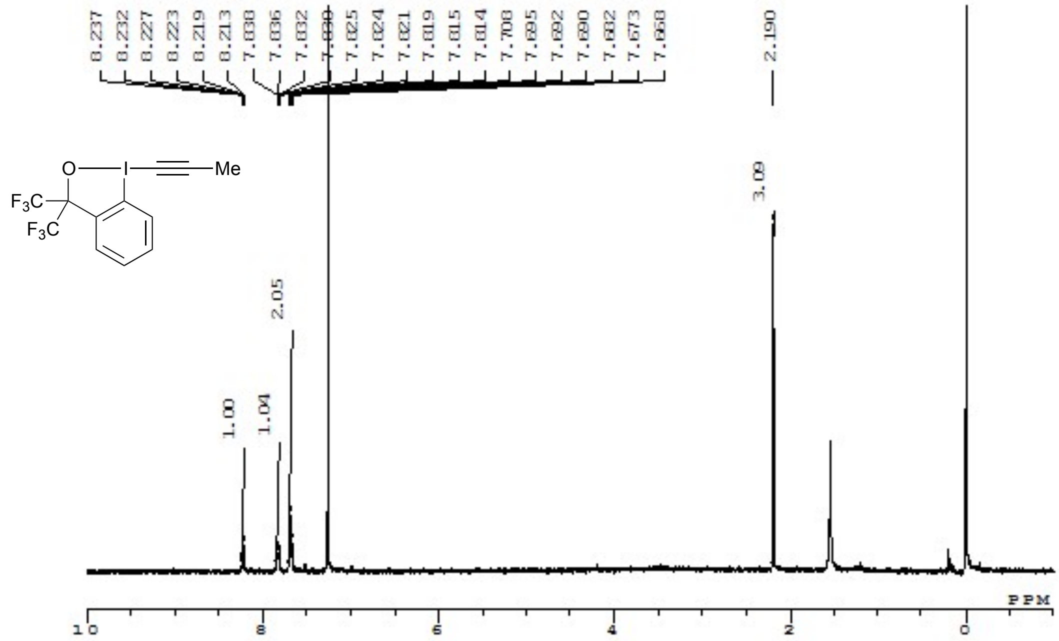
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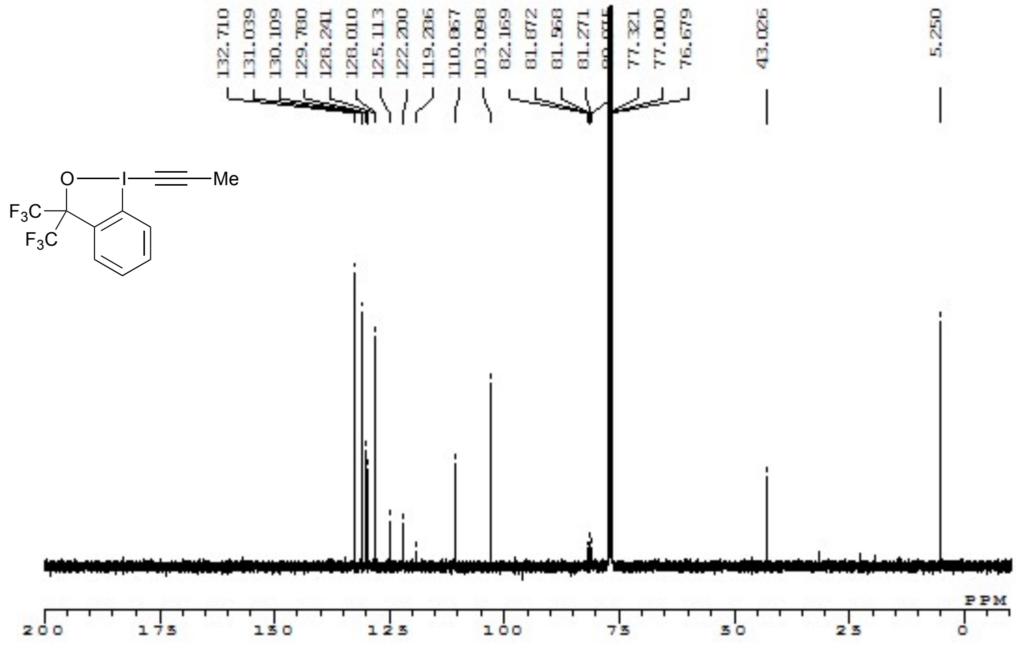
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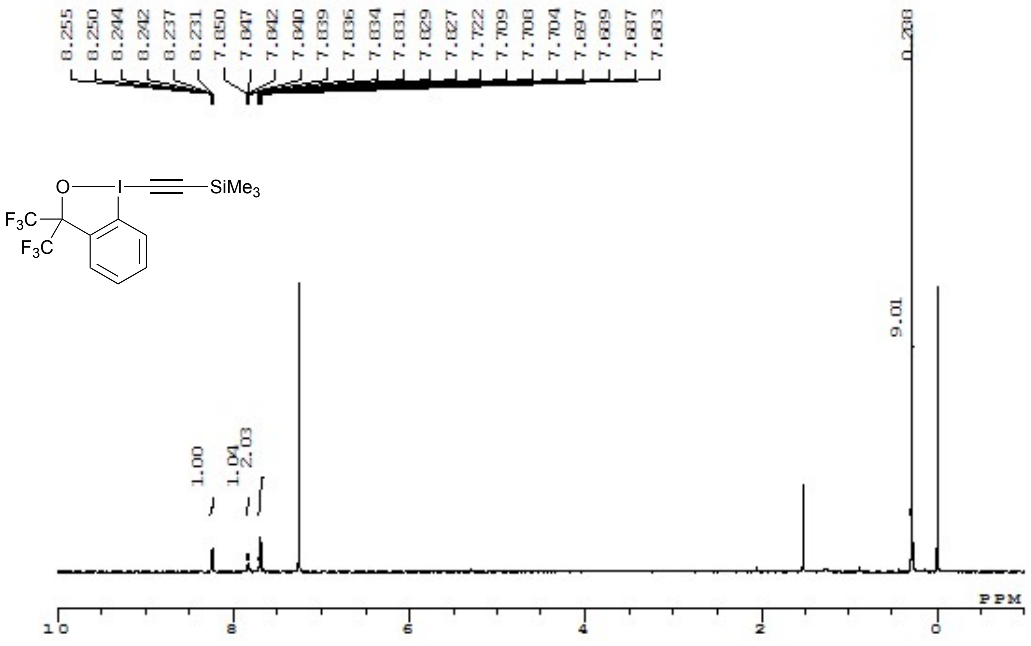
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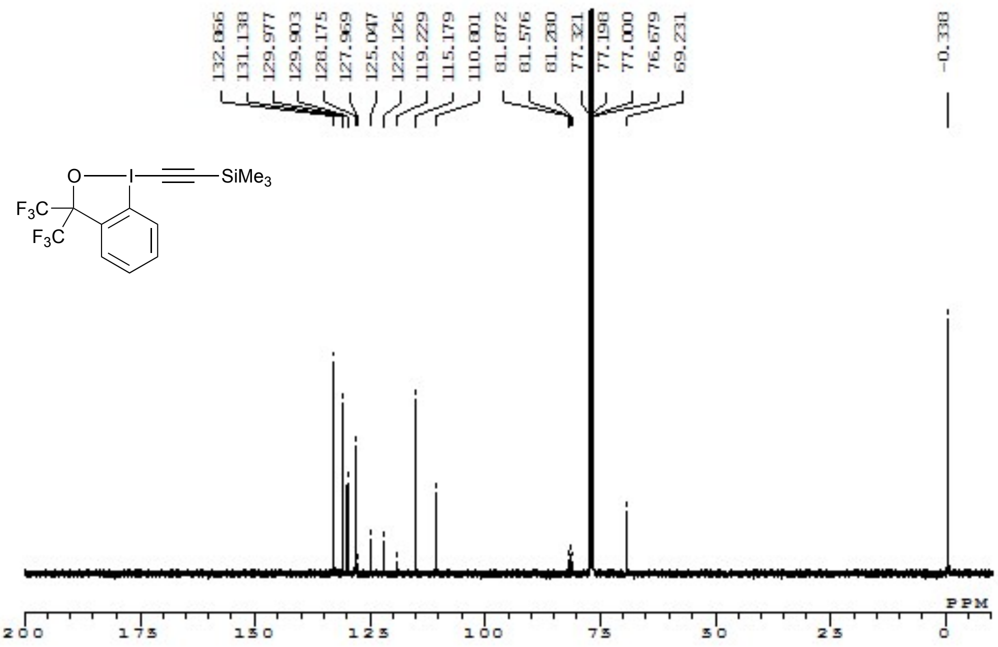
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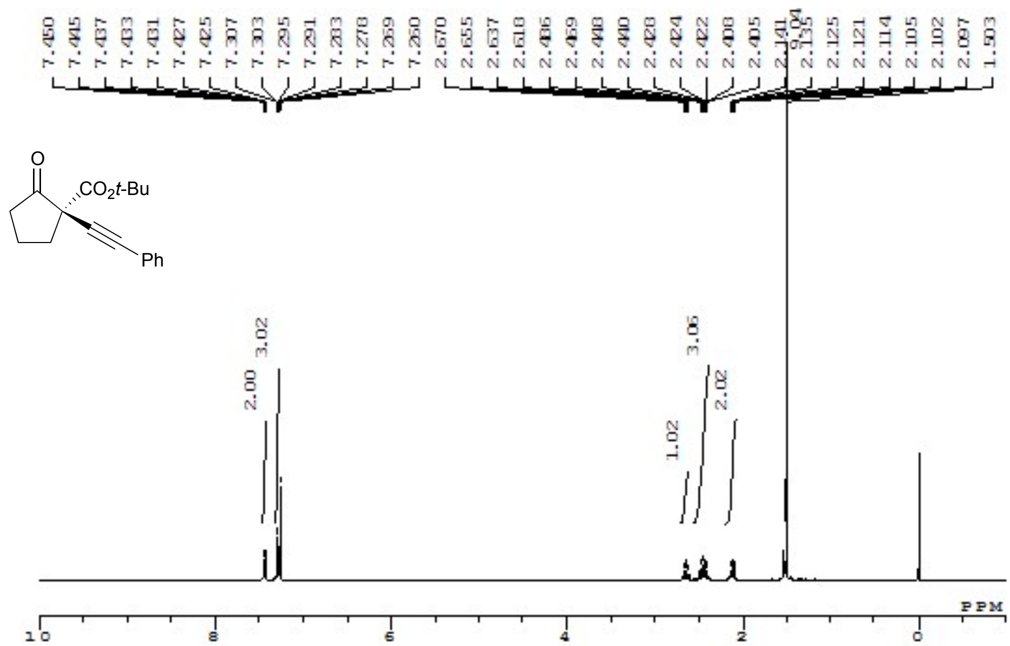
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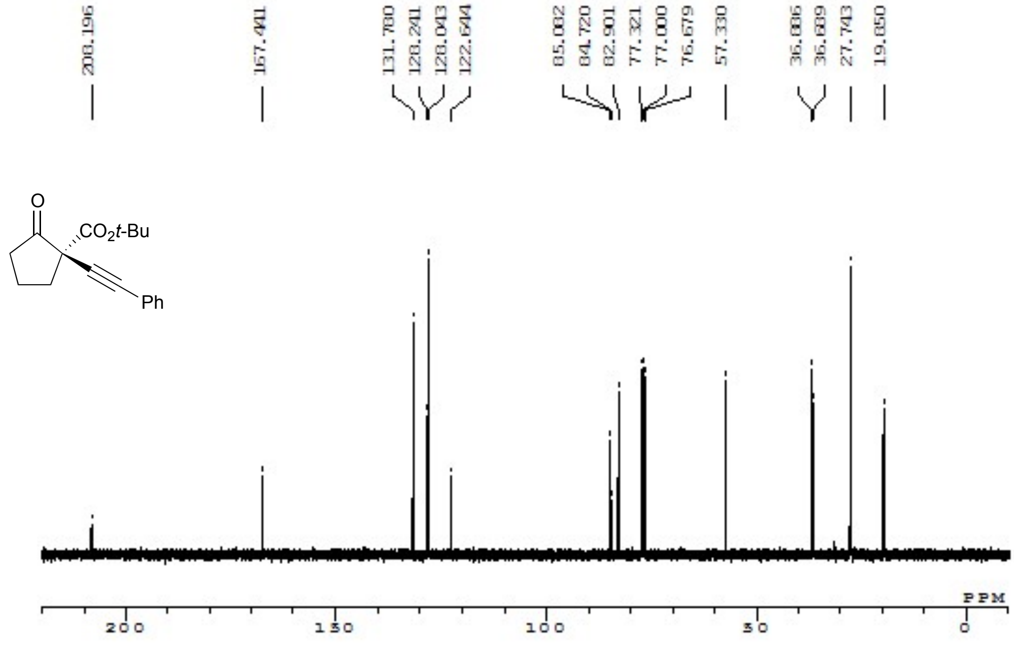
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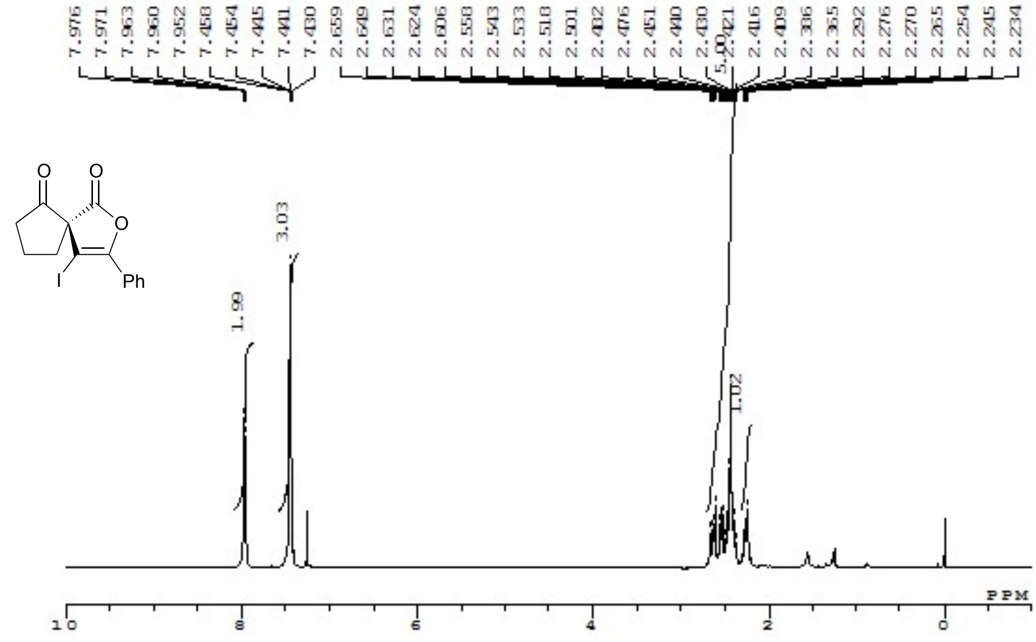
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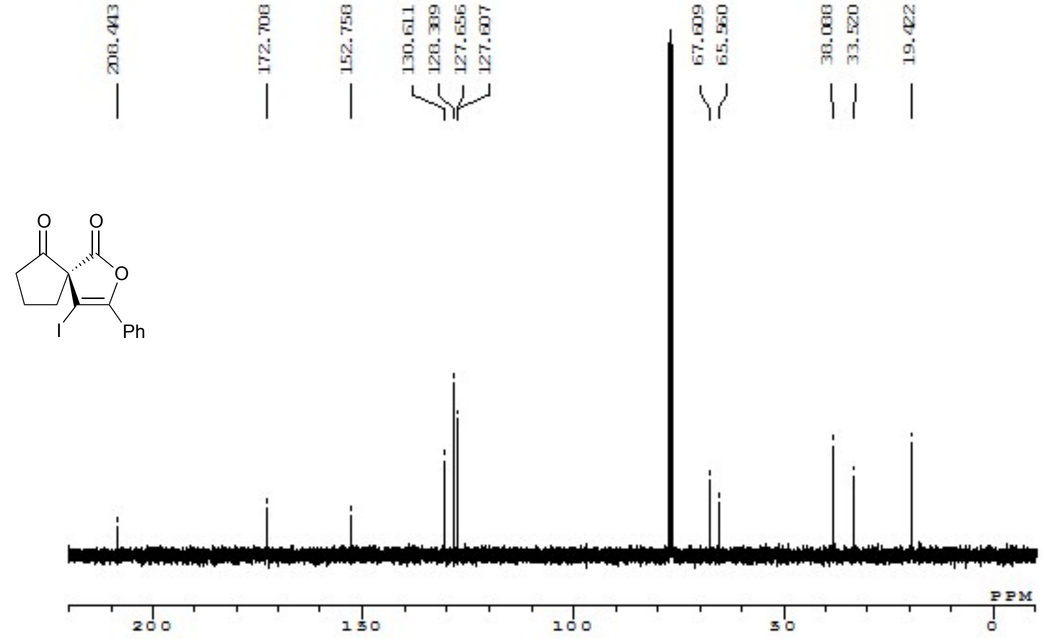
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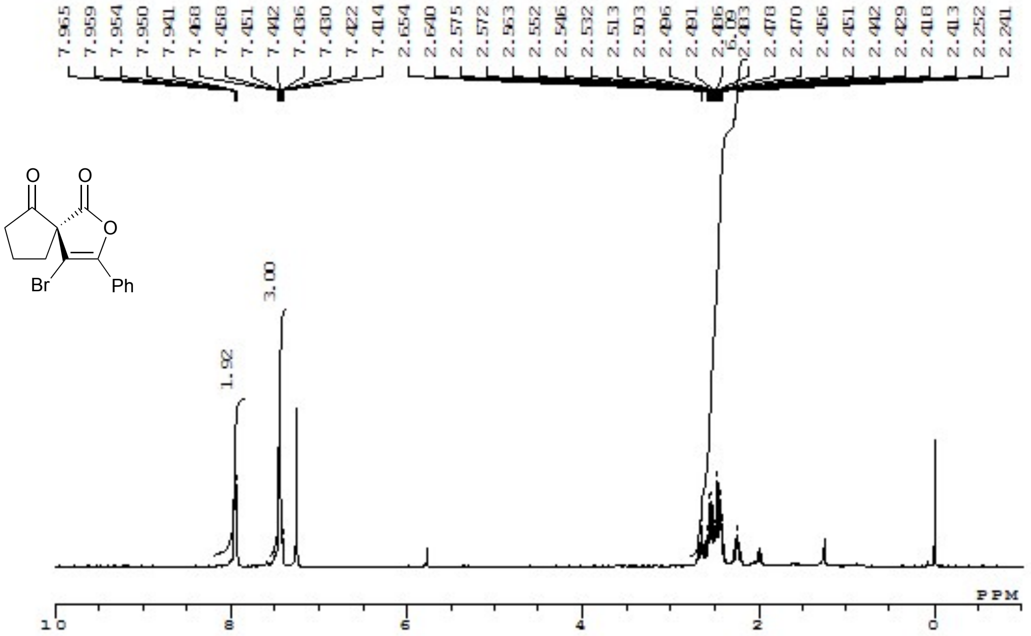
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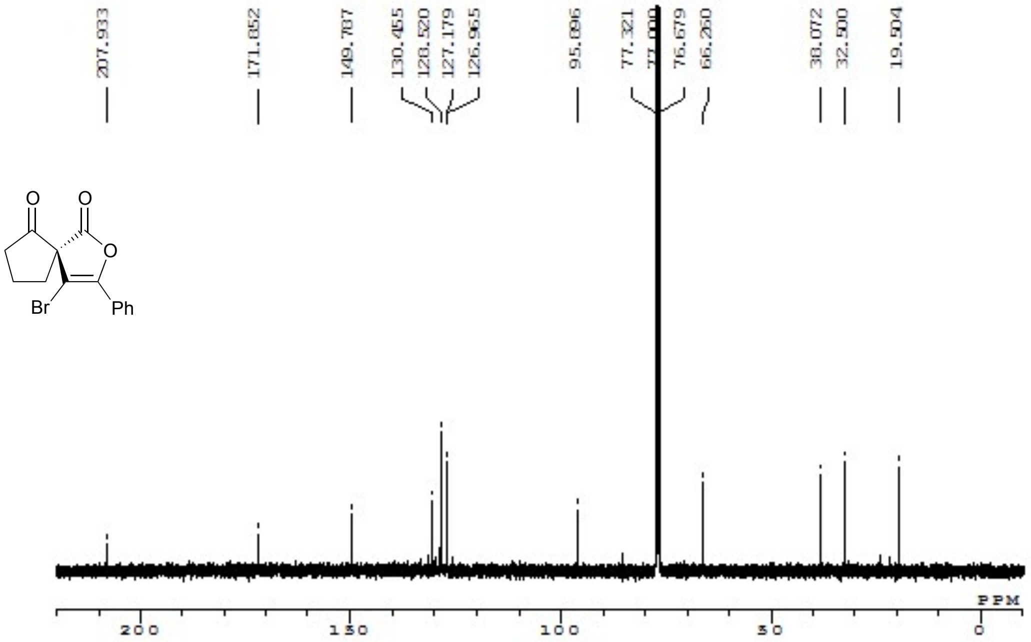
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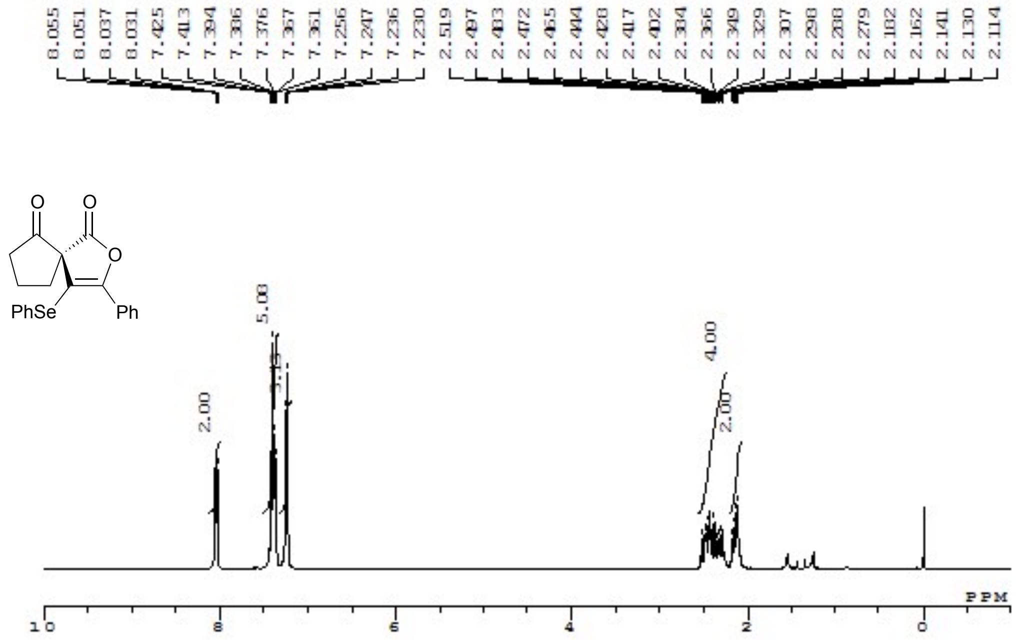
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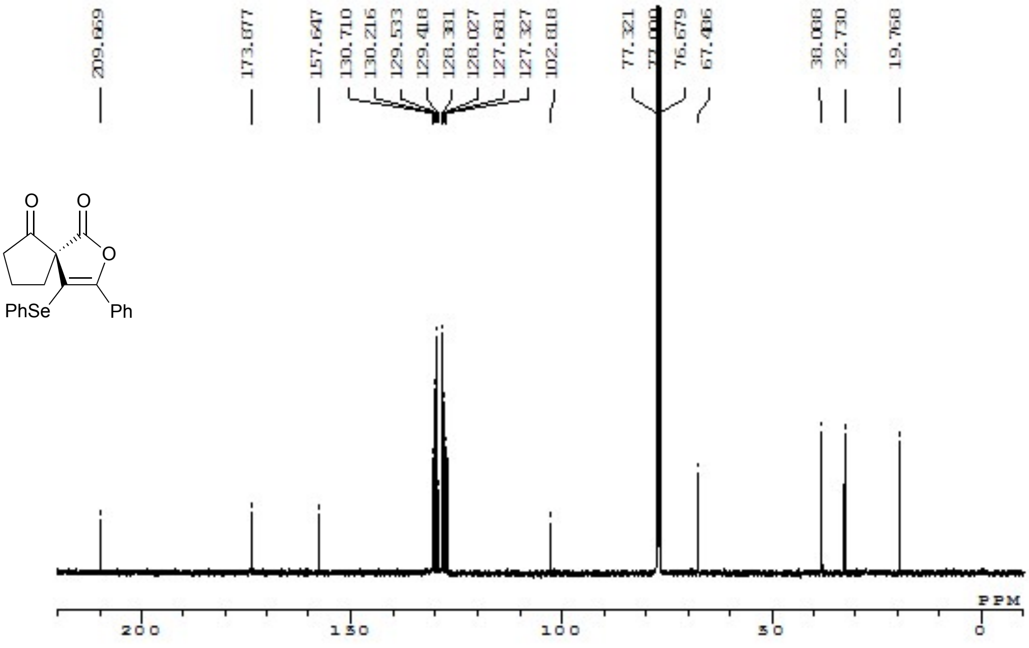
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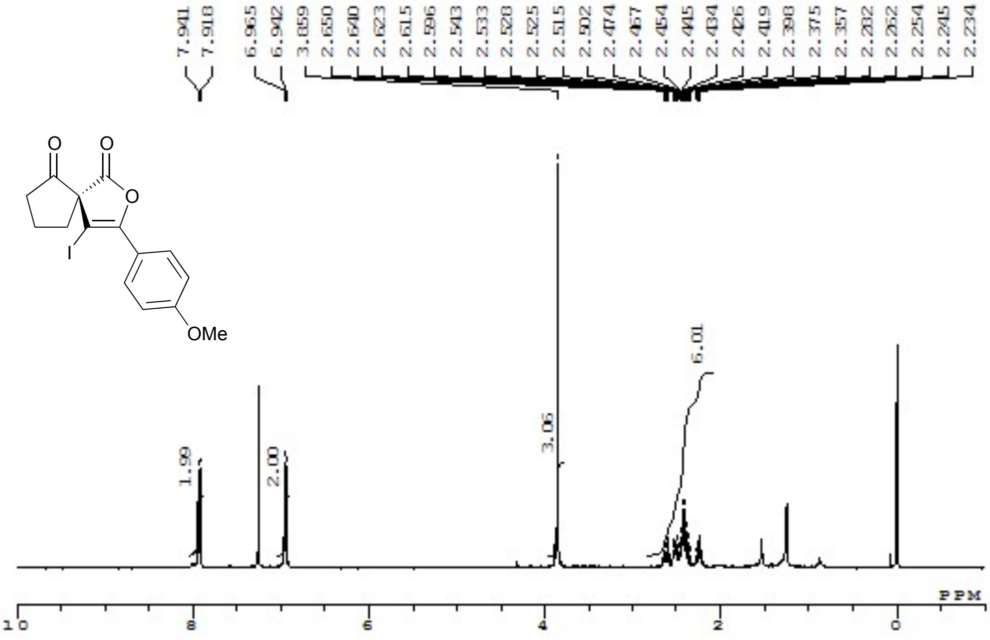
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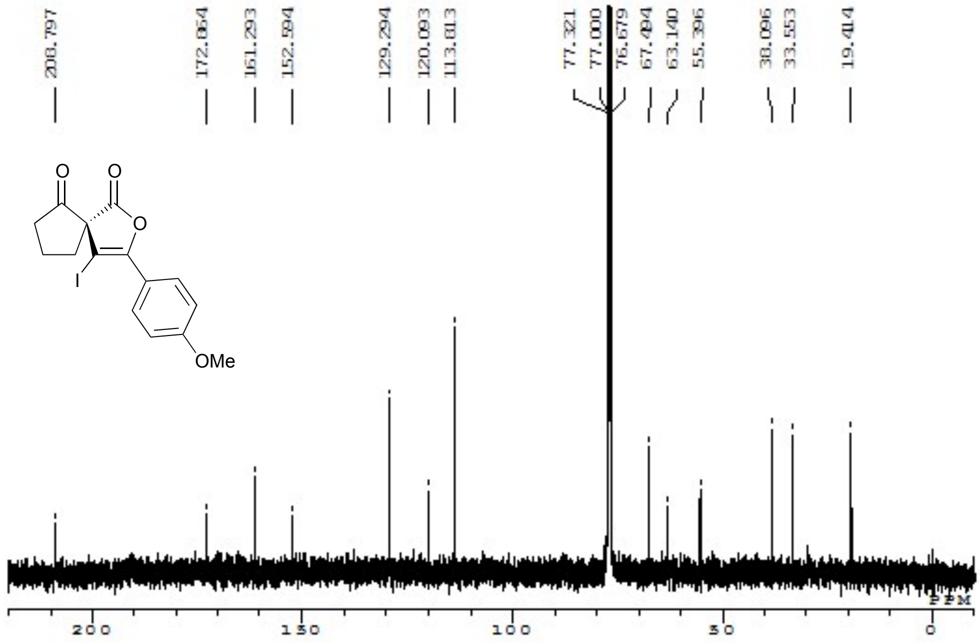
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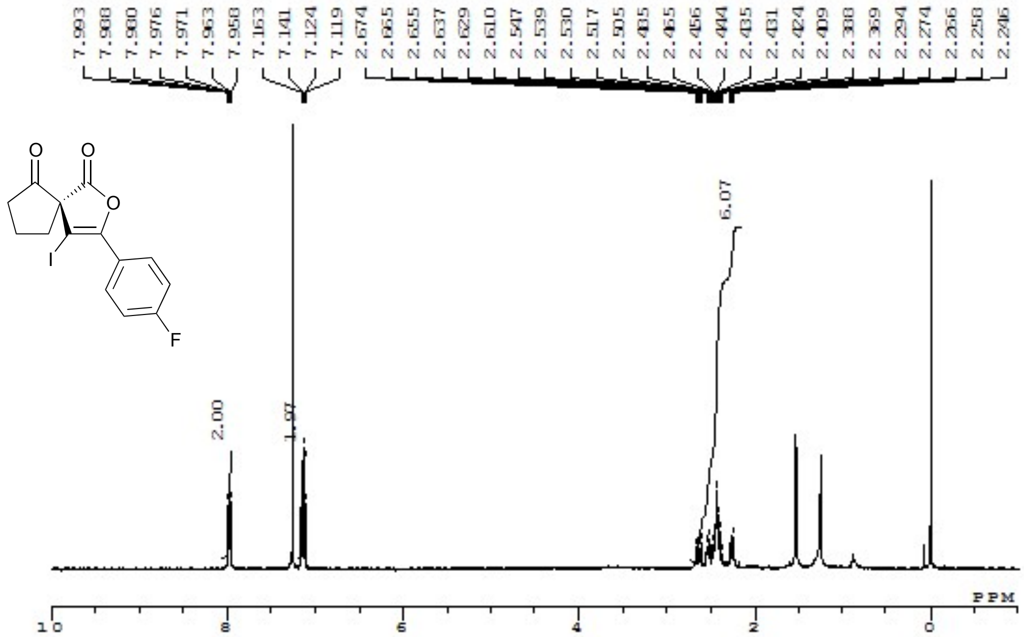
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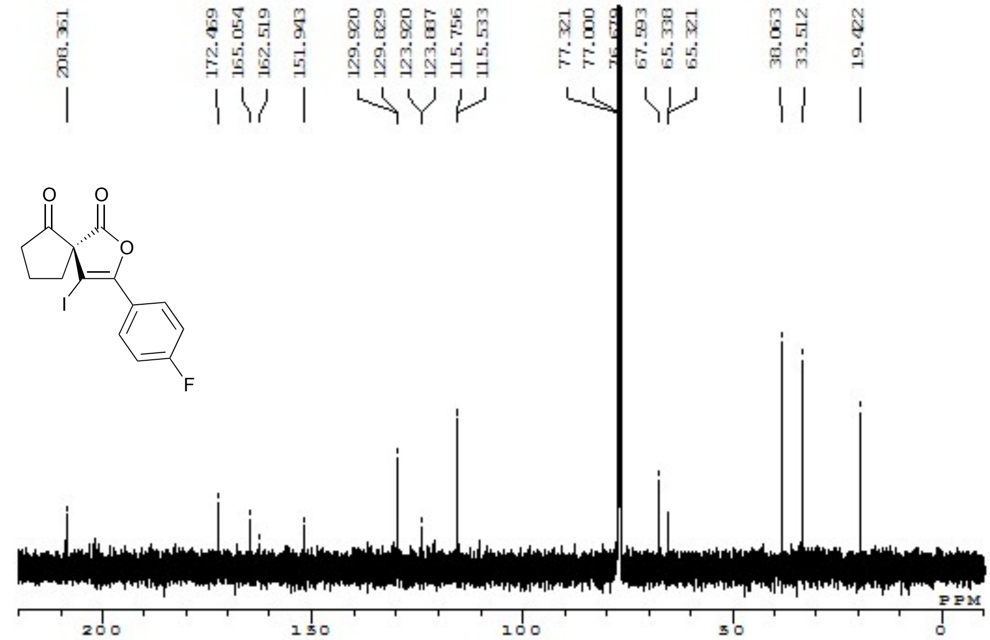
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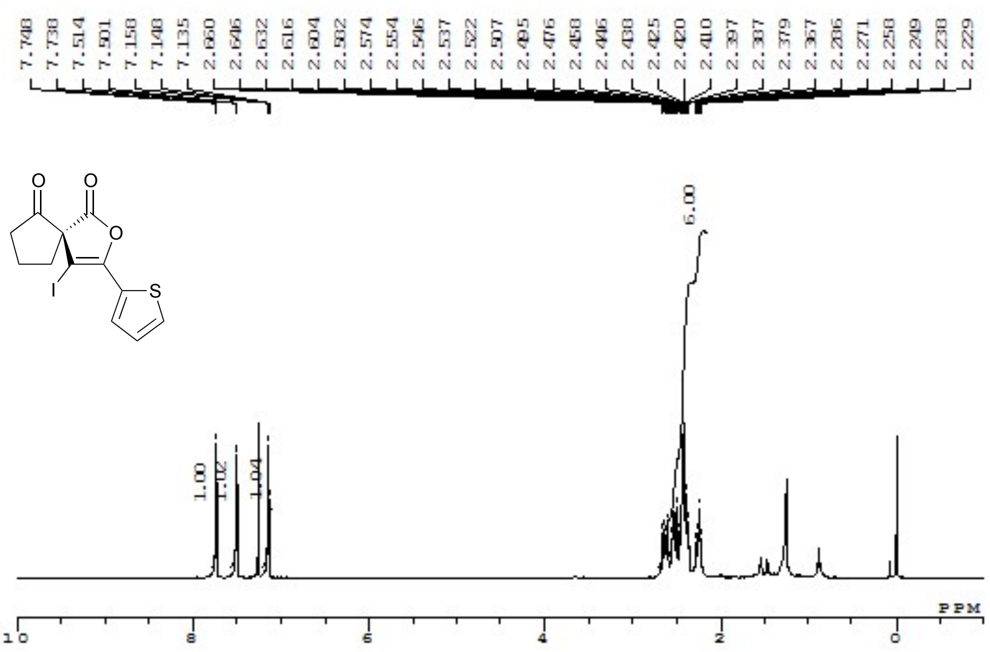
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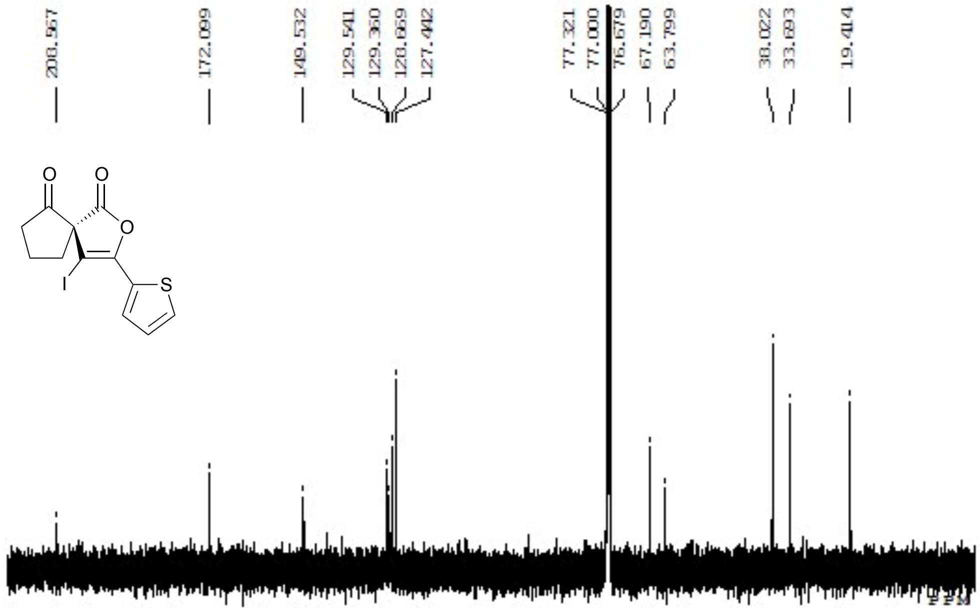
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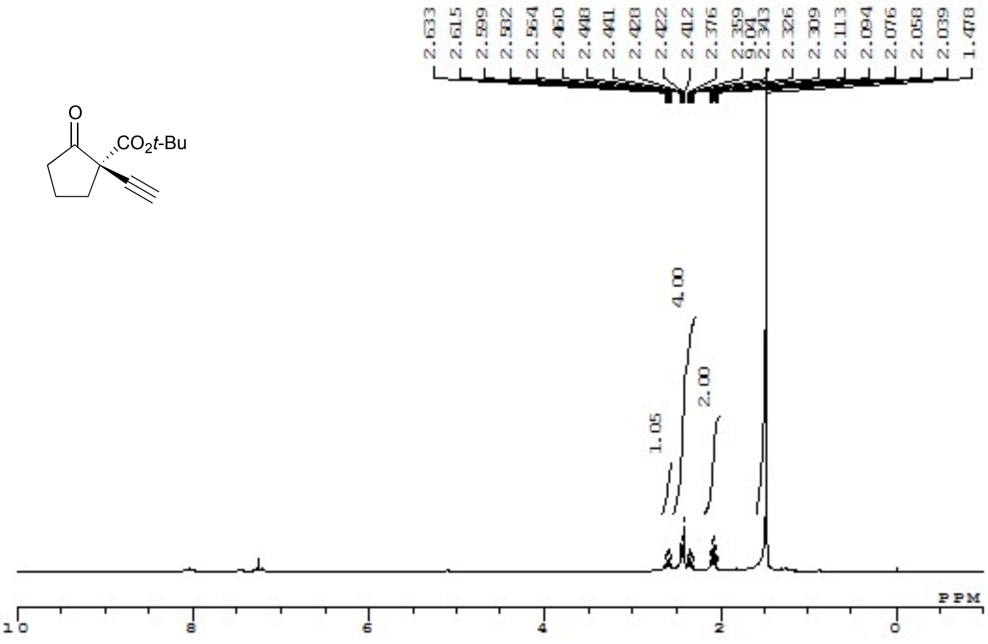
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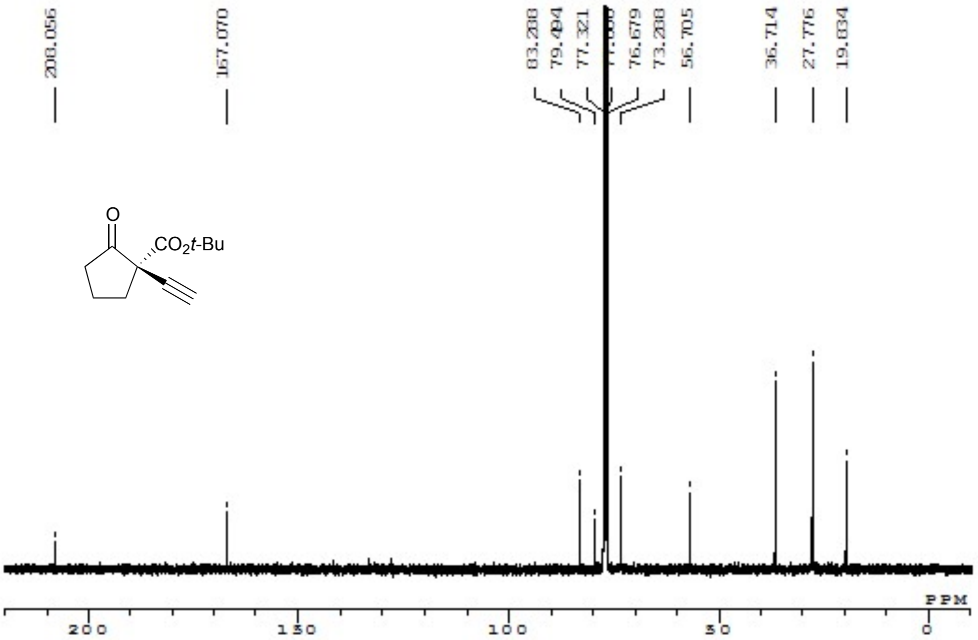
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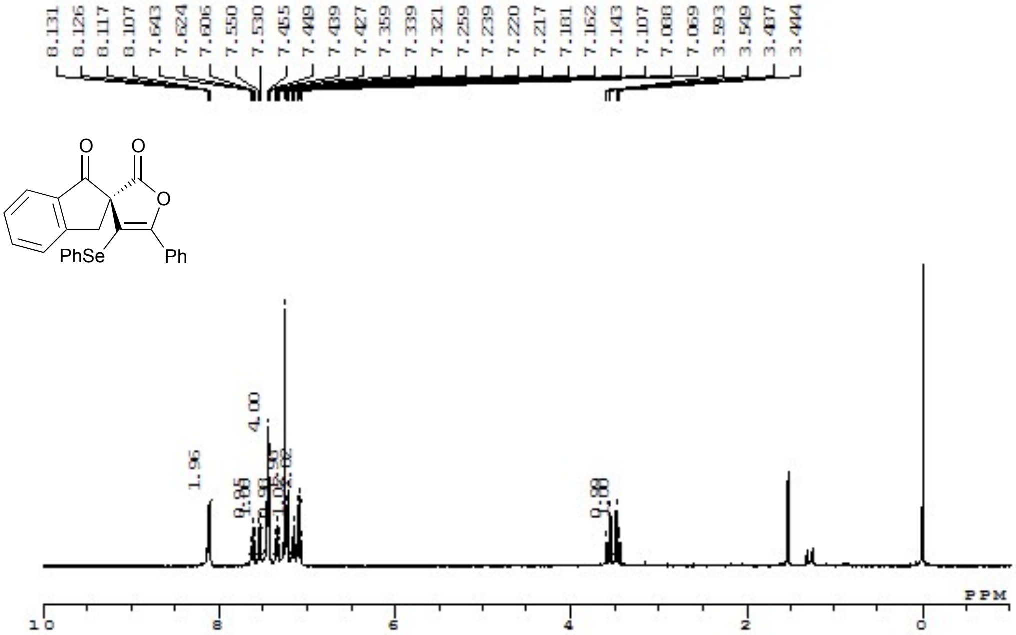
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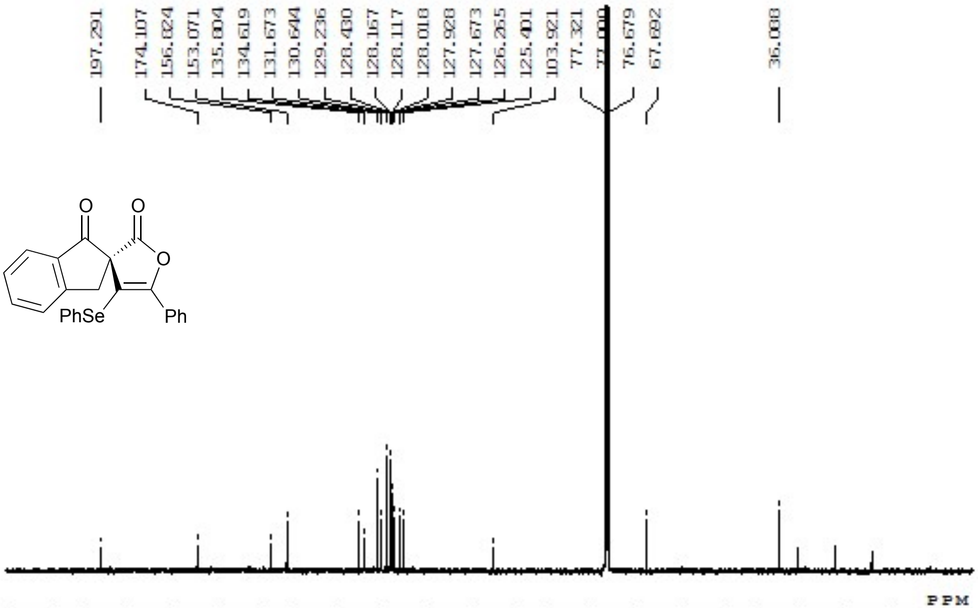
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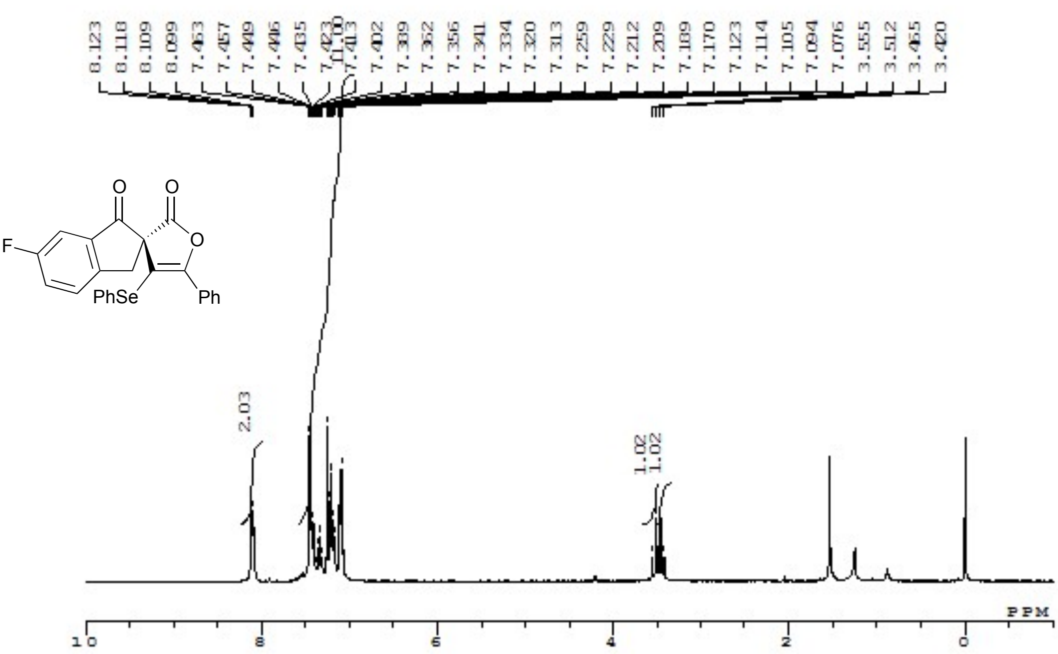
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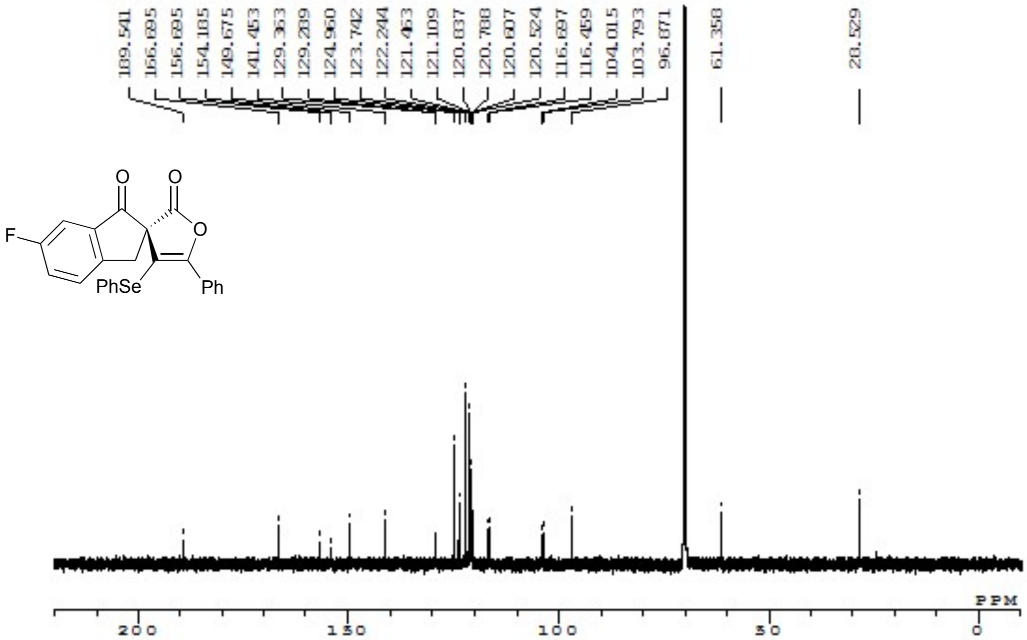
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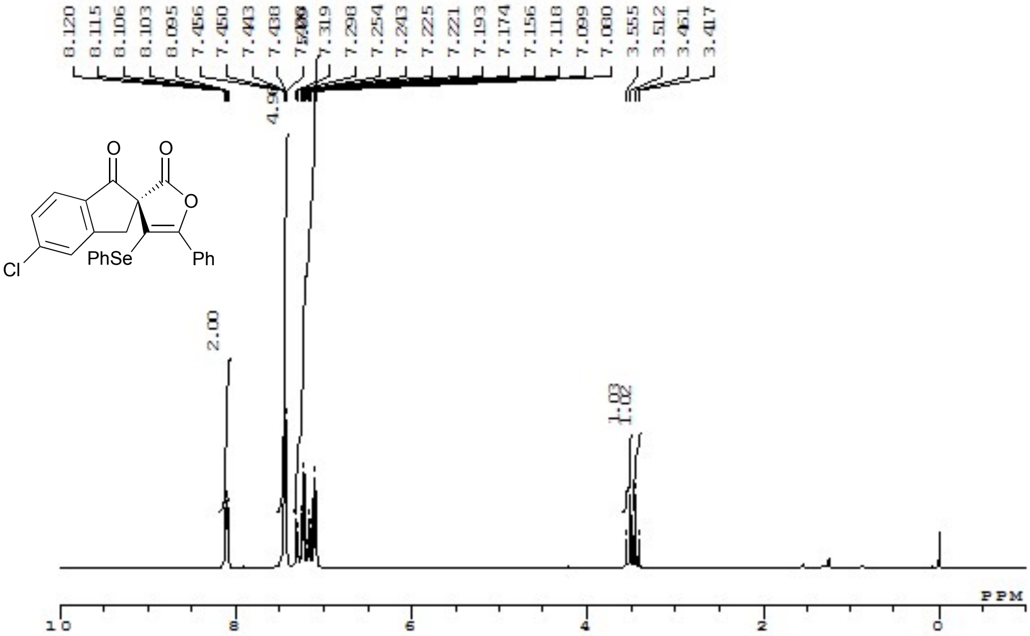
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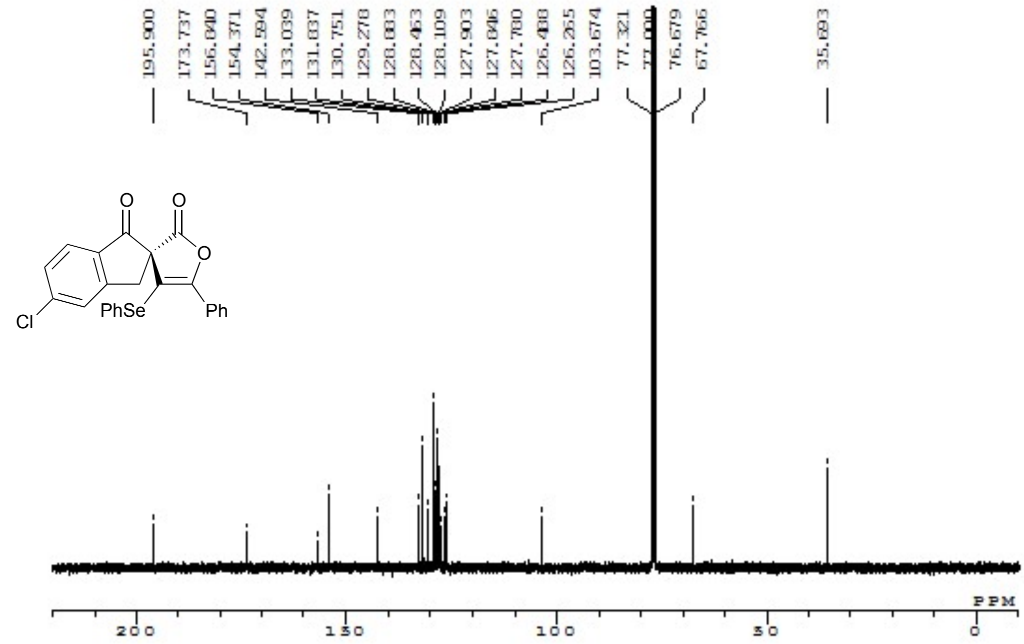
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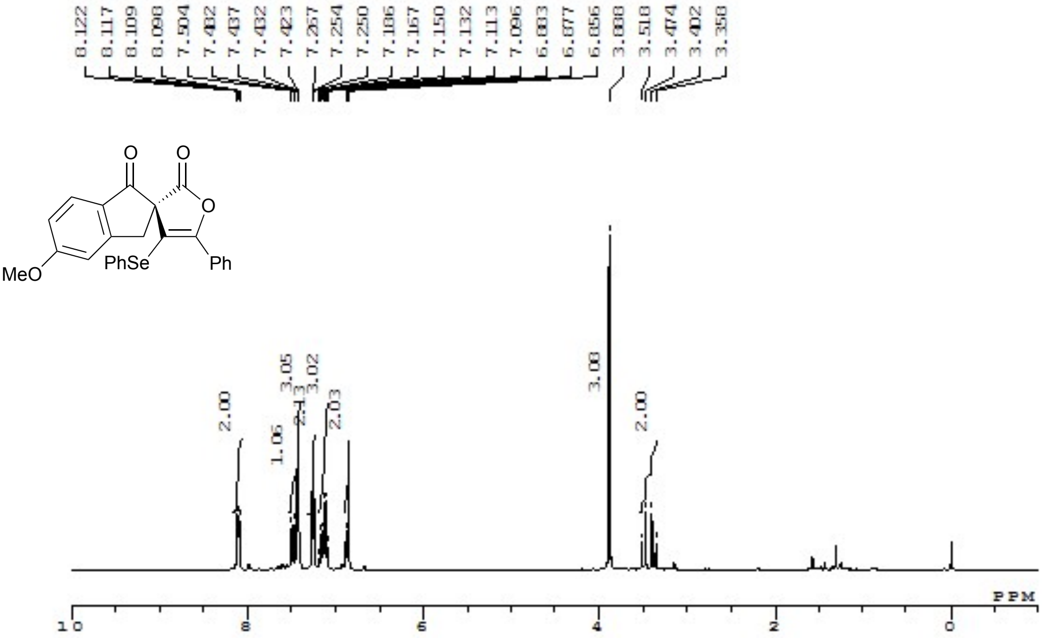
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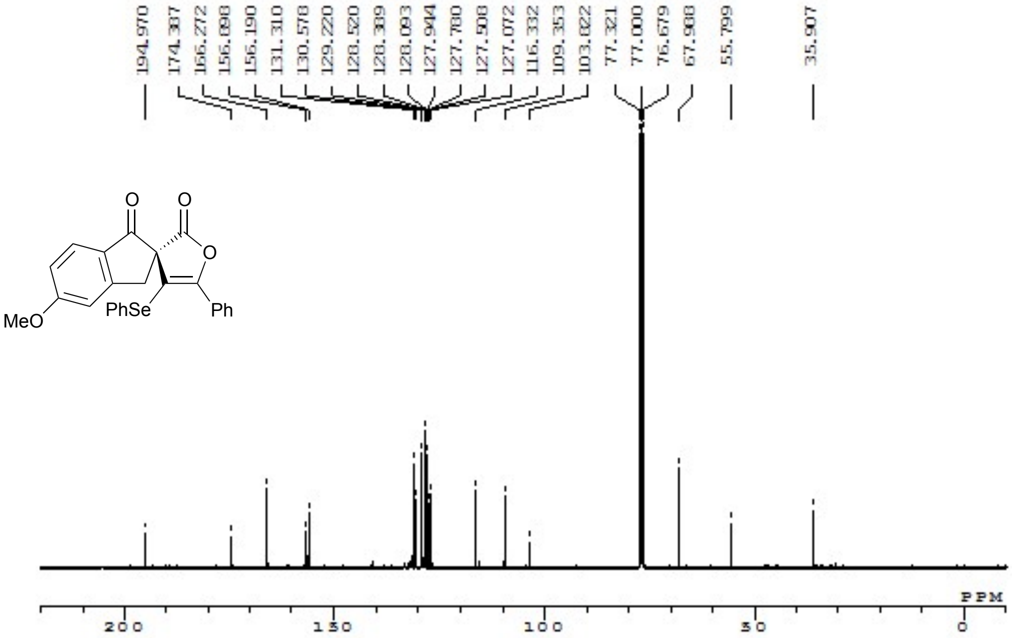
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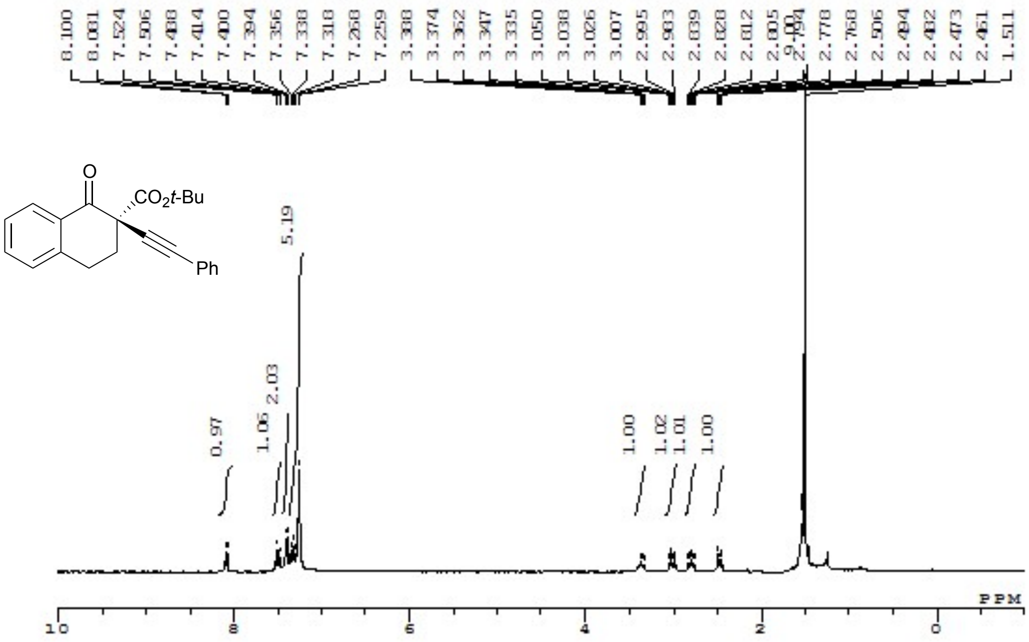
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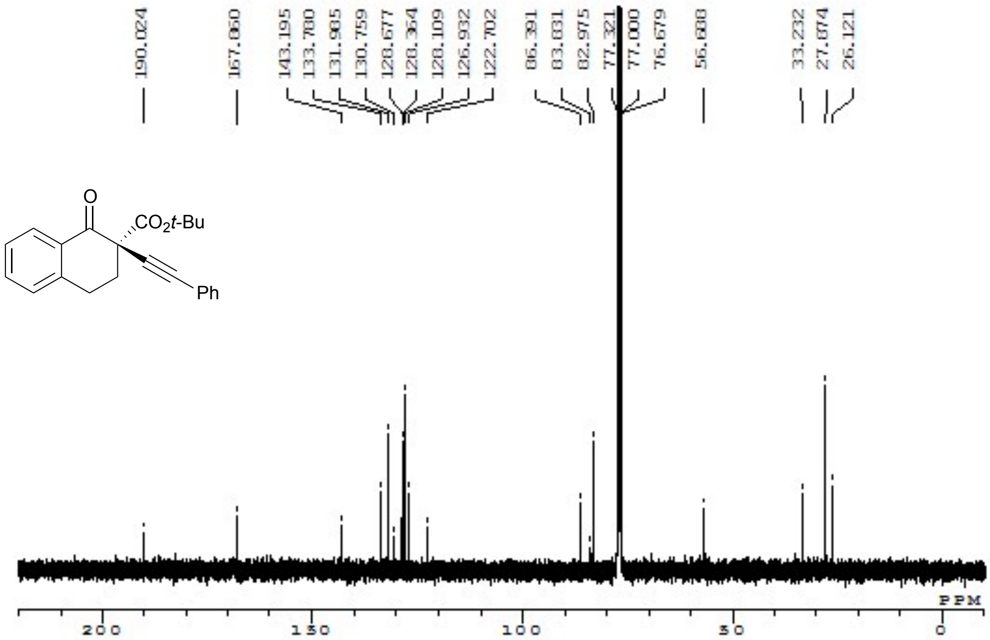
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