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Supporting Information

for

Synthesis of novel alkynyl imidazopyridinyl selenides: copper-catalyzed tandem selenation of selenium with 2-arylimidazo[1,2-*a*]pyridines and terminal alkynes

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Characterization data of all new compounds, synthetic procedures for compounds 6–8, X-ray crystallography details, and copies of spectra

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1. General information

Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and are not corrected. ^{1}H NMR (400 MHz, TMS: δ = 0.00 ppm as an internal standard), ^{13}C NMR (100 MHz, $CDCl_3$: δ = 77.00 or benzene-d_6: δ = 128.06 ppm as an internal standard), ^{19}F NMR (376 MHz, benzotrifluoride; δ = −64.0 ppm as an external standard) and ^{77}Se NMR (76 MHz, diphenyldiselenide; δ = 463.15 ppm as an external standard) spectra were recorded on JEOL ECZ-400S spectrometer (JEOL Ltd., Tokyo, Japan) in $CDCl_3$ or benzene-d_6. GC–MS (EI) spectra were recorded on an Agilent 5977E Diff-SST MSD-230V spectrometer (Agilent Technologies Japan, Ltd., Tokyo, Japan). ESI mass spectra were measured on an Agilent Technologies 6230 LC/TOF mass spectrometer (Agilent Technologies Japan, Ltd., Tokyo, Japan). IR spectra were recorded on a SHIMADZU FTIR-8400S spectrometer (SHIMADZU CORPORATION, Kyoto, Japan) and are reported in frequency of absorption (cm^{-1}). Only selected IR peaks are reported. The X-ray diffraction measurements were carried out using an XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer (Rigaku, Tokyo, Japan). All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc., Tokyo, Japan). Thin-layer chromatography (TLC) was performed with Macherey–Nagel precoated TLC plates Sil G25 UV_{254}. Most of the reagents were used without further purification unless otherwise specified.

Various imidazo[1,2-*a*]pyridine derivatives (**1a**–**m**) were prepared according to the reported procedures [1]. The spectroscopic data of known selanylimidazo[1,2-*a*]pyridines **5a** [1], **5b** [2], and **6** [3] are in accordance with the literature.

2. Experimental details and characterization data

Preparation and characterization of alkynyl imidazopyridinyl selenides

Compounds 4aa–**ma** were prepared following the general procedure provided in the Experimental.

2-Phenyl-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4aa**)

Colorless prisms (275 mg, 74%), m.p. 84–86°C (CH_2Cl_2/hexane/Et_2O). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.58 (d, *J* = 6.7 Hz, 1H), 8.13 (dt, *J* = 8.2, 1.4 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.52 (t, *J* = 8.2 Hz, 2H), 7.43 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.39–7.34 (m, 3H), 7.29–7.23 (m, 3H), 7.02 (td, *J* = 6.9, 1.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.2 (C), 147.3 (C), 133.2 (C), 131.7 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH),

126.7 (CH), 125.9 (CH), 122.5 (C), 117.5 (CH), 113.3 (CH), 100.1 (C), 97.4 (C), 67.5 (C). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 119.5 (s). FTIR (KBr): 2149 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{21}H_{15}N_2Se$: 375.0400. found: 375.0411.

3-{[2-(4-Methoxyphenyl)ethynyl]selanyl}-2-phenylimidazo[1,2-*a*]pyridine (**4ab**)

Colorless needle (231 mg, 57%), m.p. 120–122°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.58 (dd, *J* = 6.9, 0.9 Hz, 1H), 8.13 (d, *J* = 7.3 Hz, 2H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.52 (td, *J* = 7.3, 1.8 Hz, 2H), 7.43 (tt, *J* = 6.8, 1.3 Hz, 1H), 7.38–7.26 (m, 3H), 7.01 (t, *J* = 6.9 Hz, 1H), 6.78 (dt, *J* = 8.7, 1.8 Hz, 2H), 3.77 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 159.9 (C), 150.1 (C), 147.3 (C), 133.5 (CH), 133.3 (C), 129.1 (CH), 128.5 (CH), 128.4 (CH), 126.6 (CH), 126.0 (CH), 117.5 (CH), 114.6 (C), 113.9 (CH), 113.2 (CH), 100.4 (C), 97.4 (C), 65.7 (C), 55.2 (CH_3). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 117.4 (s). FTIR (KBr): 2160 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{22}H_{17}N_2OSe$: 405.0502. found: 405.0494.

3-{[2-(4-Methylphenyl)ethynyl]selanyl}-2-phenylimidazo[1,2-*a*]pyridine (**4ac**)

Colorless powder (194 mg, 51%), m.p. 100–101°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.59 (dd, *J* = 6.0, 0.9 Hz, 1H), 8.15 (d, *J* = 4.9 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.54 (t, *J* = 6.4 Hz, 2H), 7.44 (td, *J* = 6.4, 1.0 Hz, 1H), 7.37 (td, *J* = 6.8, 1.4 Hz, 1H), 7.27 (dd, *J* = 5.9, 2.3 Hz, 2H), 7.09–7.01 (m, 3H), 2.32 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.1 (C), 147.3 (C), 139.0 (C), 133.2 (C), 131.7 (CH), 129.1 (CH), 129.0 (CH), 128.6 (CH), 128.4 (CH), 126.6 (CH), 126.0 (CH), 119.4 (C), 117.5 (CH), 113.2 (CH), 100.3 (C), 97.6 (C), 66.5 (C), 21.5 (CH_3). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 118.3 (s). FTIR (KBr): 2155 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{22}H_{17}N_2Se$: 389.0553. found: 389.0547.

3-{[2-(4-Bromophenyl)ethynyl]selanyl}-2-phenylimidazo[1,2-*a*]pyridine (**4ad**)

Colorless plate (185 mg, 41%), m.p. 150–151°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.54 (d, *J* = 5.9 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.78–7.73 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45–7.37 (m, 4H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.06–7.02 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.5 (C), 147.4 (C), 133.3 (CH), 133.1 (C), 131.5 (CH), 129.1 (CH), 128.6 (CH), 128.4 (CH), 126.6 (CH), 125.8 (CH), 123.0 (C), 121.4 (C), 117.6 (CH), 113.5 (C), 113.3 (CH), 99.7 (C), 69.2 (C). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 120.0 (s). FTIR (KBr): 2152 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{21}H_{14}BrN_2Se$: 452.9498. found: 452.9493.

3-{[2-(4-Trifluoromethylphenyl)ethynyl]selanyl}-2-phenylimidazo[1,2-*a*]pyridine (**4ae**)

Colorless needle (213 mg, 48%), m.p. 126–127°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.55 (d, *J* = 6.9 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.54–7.50 (m, 4H), 7.45–7.42 (m, 3H), 7.37 (td, *J* = 6.9, 1.4 Hz, 1H), 7.03 (t, *J* = 6.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.8 (C), 147.6 (C), 133.3 (C), 131.8 (CH), 130.1 (q, *J* = 33 Hz, C), 129.1 (CH), 128.4 (CH), 126.6 (CH), 126.3 (C), 125.8 (CH), 125.2 (q, *J* = 3.9 Hz, CH), 123.9 (q, *J* = 273 Hz, C), 117.7 (CH), 113.3 (CH), 99.3 (C), 96.0 (C), 71.3 (C). ^{19}F-NMR (376 MHz, $CDCl_3$) δ (ppm): −64.1 (s). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 121.4 (s). FTIR (KBr): 2554 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{22}H_{14}F_3N_2Se$: 443.0270. found: 443.0265.

2-Phenyl-3-{[2-(2-thienyl)ethynyl]selanyl}imidazo[1,2-*a*]pyridine (**4af**)

Yellow plate (232 mg, 61%), m.p. 78–80°C (AcOEt/Et_2O/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.55 (dt, *J* = 6.9 Hz, 1H), 8.13 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.51 (t, *J* = 6.0 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.40 (dd, *J* = 3.1, 1.0 Hz, 1H), 7.33 (ddd, *J* = 9.1, 6.9, 1.4 Hz, 1H), 7.19 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.03 (dd, *J* = 5.0, 1.1 Hz, 1H), .6.99 (td, *J* = 6.7, 1.1 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.5 (C), 147.4 (C), 133.4 (C), 130.0 (CH), 129.8 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 126.4 (CH), 125.9 (CH), 125.3 (CH), 121.6 (C), 117.6 (CH), 113.1 (CH), 99.9 (C), 92.2 (C), 67.3 (C). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 117.9 (s). FTIR (KBr): 2153 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{19}H_{13}N_2SSe$: 380.9959. found:.380.9965.

3-{[2-(1-Cyclohexenyl)ethynyl]selanyl}-2-phenylimidazo[1,2-*a*]pyridine (**4ag**)

Colorless needle (269 mg, 71%), m.p. 93–94°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.51 (dd, *J* = 5.9, 1.0 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.69 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.41 (td, *J* = 7.4, 0.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 6.8 Hz, 1H), 6.10–6.03 (m, 1H), 2.05–2.03 (m, 4H), 1.60–1.49 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.2 (C), 147.4 (C), 136.7 (CH), 133.5 (C), 129.1 (CH), 128.4 (CH), 128.3 (CH), 126.3 (CH), 126.0 (CH), 120.4 (C), 117.5 (CH), 112.9 (CH), 100.5 (C), 99.3 (C), 64.1 (C), 28.9 (CH_2), 25.6 (CH_2), 22.1 (CH_2), 21.2 (CH_2). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 115.9 (s). FTIR (KBr): 2147 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{21}H_{19}N_2Se$: 379.0700. found: 375.0411.

3-(1-Hexyn-1-ylselanyl)-2-phenylimidazo[1,2-*a*]pyridine (**4ah**)

Pale yellow oil (111 mg, 31%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.50 (d, *J* = 6.9 Hz, 1H), 8.10 (dd, *J* = 7.4, 1.0 Hz, 2H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 6.9 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 6.9 Hz, 1H), 2.25 (t, *J* = 6.9 Hz, 2H), 1.43 (qui, *J* = 6.9 Hz, 2H), 1.32 (six, *J* = 6.9 Hz, 2H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.1 (C), 147.3 (C), 133.6 (C), 129.0 (CH), 128.4 (CH), 128.3 (CH), 126.2 (CH), 126.0 (CH), 117.5 (CH), 112.8 (CH), 100.8 (C), 98.9 (C), 56.2 (C), 30.4 (CH_2), 21.8 (CH_2), 19.8 (CH_2), 13.5 (CH_3). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 111.2 (s). FTIR (neat): 2180 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{19}H_{19}N_2Se$: 355.0709. found: 355.0713.

6-Methoxy-2-phenyl-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ba**)

Colorless powder (279 mg, 69%), m.p. 118–120°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12–8.08 (m, 3H), 7.65 (d, *J* = 9.6 Hz, 1H), 7.51 (t, *J* = 6.0 Hz, 2H), 7.48–7.32 (m, 3H), 7.31–7.25 (m, 3H), 7.16 (dd, *J* = 9.6, 2.3 Hz, 1H), 3.93 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 149.9 (C), 144.0 (C), 133.2 (C), 131.9 (C), 131.7 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 122.5 (C), 121.7 (CH), 117.6 (CH), 107.8 (CH), 100.8 (C), 97.6 (C), 67.3 (C), 56.3 (CH_3). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 122.8 (s). FTIR (KBr): 2155 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{22}H_{17}N_2OSe$: 405.0502. found: 405.0490.

6-Methyl-2-phenyl-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ca**)

Colorless needle (225 mg, 58%), m.p. 137–138°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.48–7.20 (m, 7H), 2.44 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.0 (C), 146.3 (C), 133.3 (C), 131.7 (CH), 129.8 (CH), 129.0 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 123.7 (CH), 123.1 (C), 122.5 (C), 116.8 (CH), 99.6 (C), 97.2 (C), 68.0 (C), 18.5 (CH_3). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 118.7 (s). FTIR (KBr): 2153 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{22}H_{17}N_2Se$: 389.0553. found: 389.0542.

6-Fluoro-2-phenyl-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4da**)

Colorless needle (302 mg, 77%), m.p. 105–107°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.54–8.52 (m, 1H), 8.14–8.11 (m, 2H), 7.73 (dd, *J* = 9.6, 5.0 Hz, 1H), 7.53 (td, *J* = 7.8, 2.3 Hz, 2H), 7.45 (t, *J* = 5.0 Hz, 1H), 7.43–7.33 (m, 2H), 7.31–7.26 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7 (d, *J* = 239 Hz, C), 151.3 (C), 144.9 (C), 133.0 (C), 131.8 (C), 128.9 (CH), 128.84 (CH), 128.77 (CH), 128.5 (CH), 128.3 (CH), 122.3 (CH),

118.5 (d, *J* = 25 Hz, CH), 118.0 (d, *J* = 8.7 Hz, CH), 112.9 (d, *J* = 41 Hz, CH), 101.6 (C), 97.9 (C), 66.8 (C). ^{19}F-NMR (376 MHz, $CDCl_3$) δ (ppm): −139.0 (s). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 124.1 (s). FTIR (KBr): 2154 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{21}H_{14}FN_2Se$: 393.0302. found: 393.0292.

6-Bromo-2-phenyl-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ea**)

Colorless needle (187 mg, 41%), m.p. 147–149°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.72 (s, 1H), 8.11 (d, *J* = 6.9 Hz, 2H), 7.65 (d, *J* = 9.1 Hz, 1H), 7.53 (td, *J* = 8.2, 1.8 Hz, 2H), 7.47–7.38 (m, 4H), 7.33–7.26 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.5 (C), 145.6 (C), 132.6 (C), 131.9 (CH), 130.3 (CH), 129.0 (CH), 128.94 (CH), 128.91 (CH), 128.5 (CH), 128.3 (CH), 126.2 (CH), 122.2 (C), 118.1 (CH), 108.2 (C), 100.7 (C), 98.1 (C), 66.7 (C). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 124.4 (s). FTIR (KBr): 2156 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{21}H_{14}BrN_2Se$: 452.9498. found: 452.9488.

2-(4-Methoxyphenyl)-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ga**)

Colorless needle (274 mg, 68%), m.p. 147–149°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, benzene-d_6) δ (ppm): 8.57 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 6.9 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.20 (dd, *J* = 7.3, 0.9 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.87–6.79 (m, 3H), 6.59 (t, *J* = 7.8 Hz, 1H), 6.19 (t, *J* = 6.8 Hz, 1H), 3.30 (s, 3H). ^{13}C-NMR (100 MHz, benzene-d_6) δ (ppm): 160.6 (C), 151.2 (C), 147.8 (C), 132.0 (CH), 130.9 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.2 (C), 125.7 (CH), 123.2 (C), 117.8 (CH), 114.3 (CH), 112.5 (CH), 99.0 (C), 97.4 (C), 69.5 (C), 54.8 (CH_3). ^{77}Se-NMR (76 MHz, benzene-d_6) δ (ppm): 114.5 (s). FTIR (KBr): 2155 (C≡N) cm^{-1}. HRMS: *m*/*z* $[M+H]^+$ calculated for $C_{22}H_{17}N_2OSe$: 405.0502. found: 405.0495.

2-(4-Methylphenyl)-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ha**)

Colorless needle (236 mg, 61%), m.p. 111–113°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.57 (dd, *J* = 6.4, 0.9 Hz, 1H), 8.04 (dd, *J* = 6.4, 1.8 Hz, 2H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.39–7.30 (m, 5H), 7.29–7.23 (m, 3H), 7.03 (t, *J* = 6.9 Hz, 1H), 2.43 (s, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 150.3 (C), 147.3 (C), 138.8 (C), 131.9 (CH), 130.3 (C), 129.3 (CH), 129.1 (CH), 128.8 (CH), 128.4 (CH), 126.9 (CH), 126.1 (CH), 122.6 (C), 117.5 (CH), 113.4 (CH), 100.0 (C), 97.5 (C), 67.7 (C), 21.5 (CH_3). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 119.0 (s). FTIR (KBr): 2153 (C≡N) cm^{-1}. HRMS: *m/z* $[M+H]^+$ calculated for $C_{22}H_{17}N_2Se$: 389.0553. found: 389.0553.

2-(4-Fluorophenyl)-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ia**)

Colorless needle (270 mg, 69%), m.p. 126–128°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.57 (d, *J* = 6.9 Hz, 1H), 8.15–8.11 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.40–7.18 (m, 8H), 7.04 (t, *J* = 6.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 163.1 (d, *J* = 248 Hz, C), 149.4 (C), 147.3 (C), 131.7 (CH), 130.8 (d, *J* = 7.7 Hz, CH), 129.4 (C), 128.7 (CH), 128.3 (CH), 126.8 (CH), 125.9 (CH), 122.4 (C), 117.5 (CH), 115.4 (d, *J* = 21 Hz, CH), 113.4 (CH), 99.9 (C), 97.4 (C), 67.4 (C). ^{19}F-NMR (376 MHz, $CDCl_3$) δ (ppm): −114.2 (s). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 117.6 (s). FTIR (KBr): 2156 (C≡N) cm^{-1}. HRMS: *m/z* $[M+H]^+$ calculated for $C_{21}H_{14}FN_2Se$: 393.0302. found: 393.0296.

2-(4-Chlorophenyl)-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ja**)

Colorless needle (270 mg, 66%), m.p. 134–137°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.57 (d, *J* = 6.9 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.49–7.34 (m, 3H), 7.31–7.24 (m, 3H), 7.04 (t, *J* = 6.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 149.1 (C), 147.3 (C), 134.6 (C), 131.7 (CH), 130.3 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 126.9 (CH), 125.9 (CH), 122.3 (C), 117.5 (CH), 113.4 (CH), 100.2 (C), 97.5 (C), 67.3 (C). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 118.2 (s). FTIR (KBr): 2156 (C≡N) cm^{-1}. HRMS: *m/z* $[M+H]^+$ calculated for $C_{21}H_{14}ClN_2Se$: 409.0004. found: 408.9995.

2-(4-Bromophenyl)-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ka**)

Colorless needle (325 mg, 72%), m.p. 144–145°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.58 (d, *J* = 6.4 Hz, 1H), 8.04 (dt, *J* = 6.9, 2.3 Hz, 2H), 7.76 (t, *J* = 9.1 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.42–7.24 (m, 6H), 7.06 (t, *J* = 6.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 147.2 (C), 131.9 (C), 131.8 (CH), 131.6 (CH), 131.0 (CH), 130.6 (C), 128.8 (CH), 128.3 (CH), 127.1 (CH), 126.0 (CH), 123.1 (C), 122.3 (C), 117.4 (CH), 113.6 (CH), 100.4 (C), 97.6 (C), 67.1 (C). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 118.6 (s). FTIR (KBr): 2155 (C≡N) cm^{-1}. HRMS: *m/z* $[M+H]^+$ calculated for $C_{21}H_{14}BrN_2Se$: 452.9498. found: 452.9487.

2-(4-Trifluoromethylphenyl)-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4la**)

Colorless needle (225 mg, 51%), m.p. 123–124°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.61 (d, *J* = 6.9 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 2H), 7.79–7.76 (m, 3H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 7.4, 1.4 Hz, 2H), 7.31–7.25 (m, 3H), 7.08 (t, *J* = 6.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 148.5 (C), 147.4 (C), 136.7 (C), 131.8 (CH), 130.4 (q, *J* = 34 Hz, C), 129.3 (CH), 128.9 (CH), 128.3 (CH), 127.2 (CH), 126.0 (CH), 125.3 (q, *J*

= 3.9 Hz, CH), 124.2 (q, *J* = 273 Hz, C), 122.3 (C), 117.7 (CH), 113.7 (CH), 101.1 (C), 97.7 (C), 67.0 (C). ^{19}F-NMR (376 MHz, $CDCl_3$) δ (ppm): −63.9 (s). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 118.6 (s). FTIR (KBr): 2158 (C≡N) cm^{-1}. HRMS: *m/z* $[M+H]^+$ calculated for $C_{22}H_{14}F_3N_2Se$: 443.0270. found: 443.0257.

2-(2-Methylphenyl)-3-[(2-phenylethynyl)selanyl]imidazo[1,2-*a*]pyridine (**4ma**)

Colorless needle (229 mg, 59%), m.p. 105–107°C (CH_2Cl_2/hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.55 (d, *J* = 6.9 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.40–7.26 (m, 9H), 7.04 (t, *J* = 6.8 Hz, 1H), 2.41 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 152.0 (C), 147.2 (C), 137.6 (C), 133.0 (C), 131.7 (CH), 131.1 (CH), 130.3 (CH), 128.6 (CH), 128.3 (CH), 126.3 (CH), 125.9 (CH), 125.3 (CH), 122.6 (C), 117.6 (CH), 113.2 (CH), 101.9 (C), 97.3 (C), 67.7 (C), 20.4 (CH_3). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 111.5 (s). FTIR (KBr): 2152 (C≡N) cm^{-1}. HRMS: *m/z* $[M+H]^+$ calculated for $C_{22}H_{17}N_2Se$: 389.0553. found: 389.0545.

Reaction of 3-(ethynylselanyl)imidazo[1,2-*a*]pyridine:

Reaction with phenyllithium

A solution of PhLi (1.12 M solution in cyclohexane/diethyl ether, 0.9 mL, 1.0 mmol, 2 equiv) was added dropwise to a solution of **4aa** (187 mg, 0.5 mmol) in dry THF (2 mL) at −78 °C under an Ar atmosphere. After 1 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and water (20 mL) at 0 °C. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with water (10 mL × 3), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane/AcOEt as eluent to give 2-phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (**6a**) [1] as a yellow oil (85 mg, 49%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.36 (dt, *J* = 6.9, 1.4 Hz, 1H), 8.16 (d, *J* = 7.3 Hz, 2H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.45 (tt, *J* = 6.9, 2.3 Hz, 2H), 7.41–7.33 (m, 2H), 7.20–7.16 (m, 3H), 7.13–7.10 (m, 2H), 6.89 (td, *J* = 6.9, 0.9 Hz, 1H). LRMS (EI) *m/z*: 350.0 ($[M]^+$, 40%), 270.1 (100%). HRMS: *m/z* $[M]^+$ calculated for $C_{19}H_{14}N_2Se$: 350.0322. Found: 350.0319.

Reaction with *n*-butyllithium

A solution of *n*-BuLi (1.55 M solution in hexane, 2.0 mL, 3.0 mmol, 6 equiv) was added dropwise to a solution of **4aa** (187 mg, 0.5 mmol) in dry THF (2 mL) at −78 °C under an Ar atmosphere. After 1 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and water (20 mL) at 0 °C. The phases were separated, and the aqueous layer was

extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with water (10 mL × 3), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane/AcOEt as eluent to give 3-(butylselanyl)-2-phenylimidazo[1,2-*a*]pyridine (**6b**) [2] as a yellow oil (104 mg, 63%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.56 (d, *J* = 6.9 Hz, 1H), 8.24 (dt, *J* = 8.2, 1.8 Hz, 2H)), 7.69 (d, *J* = 9.1 Hz, 1H), 7.47 (td, *J* = 7.3, 1.4 Hz, 2H), 7.38 (tt, *J* = 7.8, 1.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 6.92 (t, *J* = 6.9 Hz, 1H), 2.68 (t, *J* = 7.8 Hz, 2H), 1.47 (qui, *J* = 7.3 Hz, 2H), 1.29 (six, *J* = 7.8 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). LRMS (EI) *m/z*: 330.1 ([M]$^+$, 30%), 273.0 (100%) 194.1 (99%). HRMS: *m/z* [M]$^+$ calculated for $C_{17}H_{18}N_2Se$: 330.0635. Found: 330.0639.

Reaction with $TMSCF_3$

To a solution of **4aa** (187 mg, 0.5 mmol) and cesium carbonate (652 mg, 2.0 mmol, 4 equiv) in dry acetonitrile (4 mL) was added (trifluoromethyl)trimethylsilane (111 µL, 0.75 mmol, 1.5 equiv) at 0 °C. The solution was stirred for 1 h at 0 °C and then warmed to room temperature. After 48 h, the reaction mixture was filtered through a short pad of silica, rinsed with dichloromethane (30 mL) and the collected solution was concentrated under reduced pressure. The residue was purified by column chromatography using hexane/AcOEt as eluent to give 3-(trifluoromethylselanyl)-2-phenylimidazo[1,2-*a*]pyridine (**7**) [3] as a yellow oil (75 mg, 44%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.54 (d, *J* = 6.9 Hz, 1H), 8.07 (d, *J* = 6.9 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.53–7.39 (m, 4H), 7.02 (td, *J* = 6.8, 1.0 Hz, 1H). LRMS (EI) *m/z*: 342.0 ([M]$^+$, 30%), 273.0 (100%), 78.0 (30%). HRMS: *m/z* [M]$^+$ calculated for $C_{14}H_9F_3N_2Se$: 341.9883. Found: 341.9882.

Reaction with benzylazide

A solution of **4aa** (187 mg, 0.5 mmol), benzylazide (147 mg, 1.1 mmol, 2.2 equiv) CuI (95 mg, 0.5 mmol, 1 equiv) and *N*,*N*,*N*',*N*",*N*"-pentamethyldiethylenetriamine (87 mg, 0.5 mmol, 1 equiv) in dry THF (2 mL) was heated at 60 °C under an Ar atmosphere. After 5.5 h, the mixture was allowed to cool to room temperature, and diluted with AcOEt (20 mL) and saturated aqueous NH_4Cl (20 mL) at 0°C. The phases were separated and the aqueous layer was extracted with AcOEt (10 mL × 2). The combined organic layer was washed with saturated aqueous NH_4Cl (20 mL × 6), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane/AcOEt as eluent to give 3-[(1-benzyl-4-phenyl)-1*H*-1,2,3-triazolyl]-2-phenylimidazo[1,2-*a*]pyridine (**8**) as colorless prisms (182 mg, 72%). m.p. 118–121°C (EtOH). ^{1}H-NMR

(400 MHz, $CDCl_3$) δ (ppm): 7.92 (dd, J = 7.8, 1.8 Hz, 2H), 7.87–7.85 (m, 2H), 7.58–7.48 (m, 8H), 7.24–7.14 (m, 4H), 6.64 (d, J = 6.9 Hz, 2H), 6.44 (td, J = 6.9, 0.9 Hz, 1H), 5.11 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 151.7 (C), 151.2 (C), 147.0 (C), 134.6 (C), 132.9 (C), 130.5 (C), 129.7 (CH), 129.1 (CH), 128.9 (CH), 128.7 (CH), 128.62 (CH), 128.57 (CH), 128.5 (CH), 128.0 (CH), 126.9 (CH), 126.6 (CH), 125.5 (CH), 117.6 (C), 117.3 (CH), 113.1 (CH), 102.1 (C), 52.6 (CH_2). ^{77}Se-NMR (76 MHz, $CDCl_3$) δ (ppm): 46.8 (s). IR (KBr): v = 3422, 3065, 3028, 1460, 1343 cm^{-1}. HRMS: m/z $[M]^+$ calculated for $C_{28}H_{21}N_5Se$: 507.0962. found: 507.0966.

3. Single crystal X-ray diffraction experiment

A suitable crystal was selected and measured on an XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer (Rigaku, Tokyo, Japan). The crystal was kept at 103 K in the N_2 cold stream during data collection. Using Olex2 [4], the structure was solved with the SHELXT [5] structure solution program using Intrinsic Phasing and refined with the SHELXL [6] refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

Data of compound **4aa**

The colorless prism crystal (0.105 × 0.096 × 0.056 mm^3), obtained from CH_2Cl_2/hexane, was immersed in Paraton-N oil. $C_{21}H_{14}N_2Se$, *M*r = 373.30; monoclinic, space group $P2_1/c$, $Z = 4$, $D_{calc} = 1.506$ g·cm^{-3}, μ(Cu Kα) = 3.097 mm^{-1}, $a = 8.60000(10)$, $b = 11.4839(2)$, $c = 16.6687(2)$ Å, $\beta = 90.8590(10)°$, $V = 1646.04(4)$ $Å^3$, 7991 measured and 2989 independent [$I > 2\sigma(I)$] reflections, 217 parameters, final $R_1 = 0.0274$, $wR_2 = 0.0667$, $S = 1.056$ [$I > 2\sigma(I)$]. CCDC 2156343.

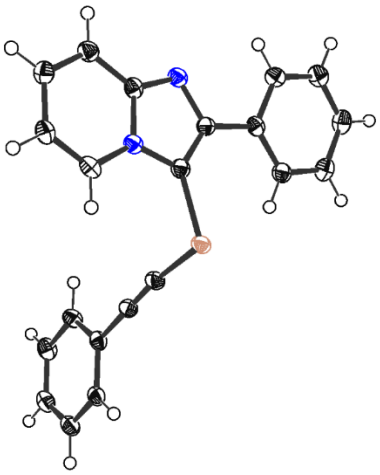

Figure S1. Ortep drawing of **2a** (50% probability)

Data of compound **8**

The colorless prism crystal (0.296 × 0.195 × 0.064 mm^3), obtained from EtOH, was immersed in Paraton-N oil. $C_{28}H_{21}N_5Se$, *M*r = 506.46; triclinic, space group $P\bar{1}$, $Z = 2$, $D_{calc} = 1.473$ g·cm^{-3}, μ(Cu Kα) = 2.434 mm^{-1}, $a = 9.1538(2)$, $b = 10.0410(3)$, $c = 13.2207(6)$ Å, $\alpha = 105.832(3)$, $\beta = 90.8590(10)$, $\gamma = 100.780(2)°$, $V = 1141.77(7)$ $Å^3$, 9609 measured and 9609 independent [$I > 2\sigma(I)$] reflections, 308 parameters, final $R_1 = 0.0459$, $wR_2 = 0.1285$, $S = 1.084$ [$I > 2\sigma(I)$]. CCDC 2156344.

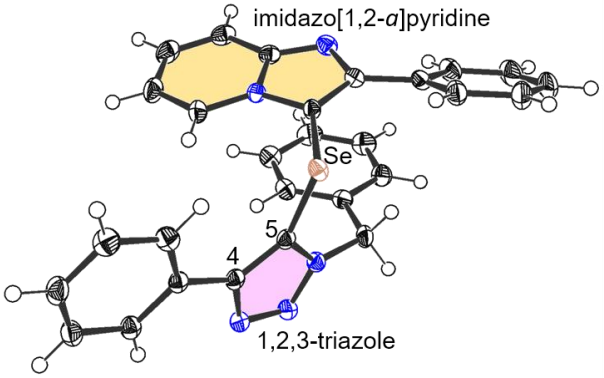

Figure S2. Ortep drawing of 8 (50% probability)

4. References

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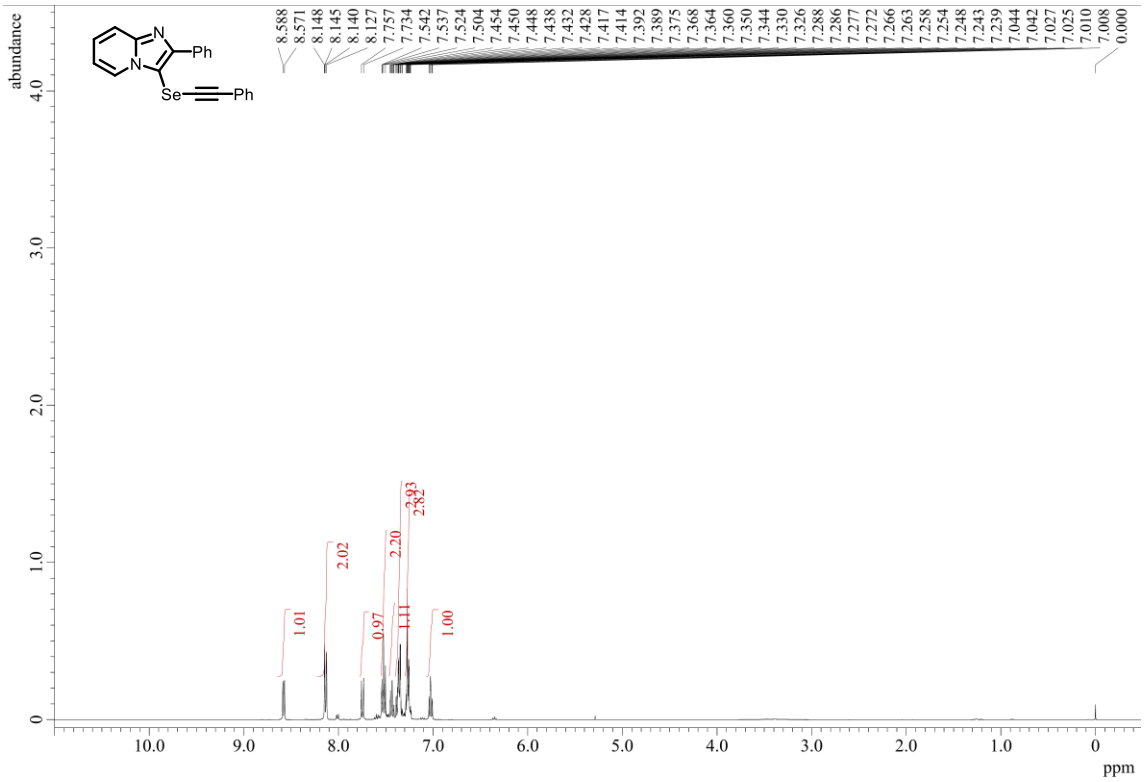
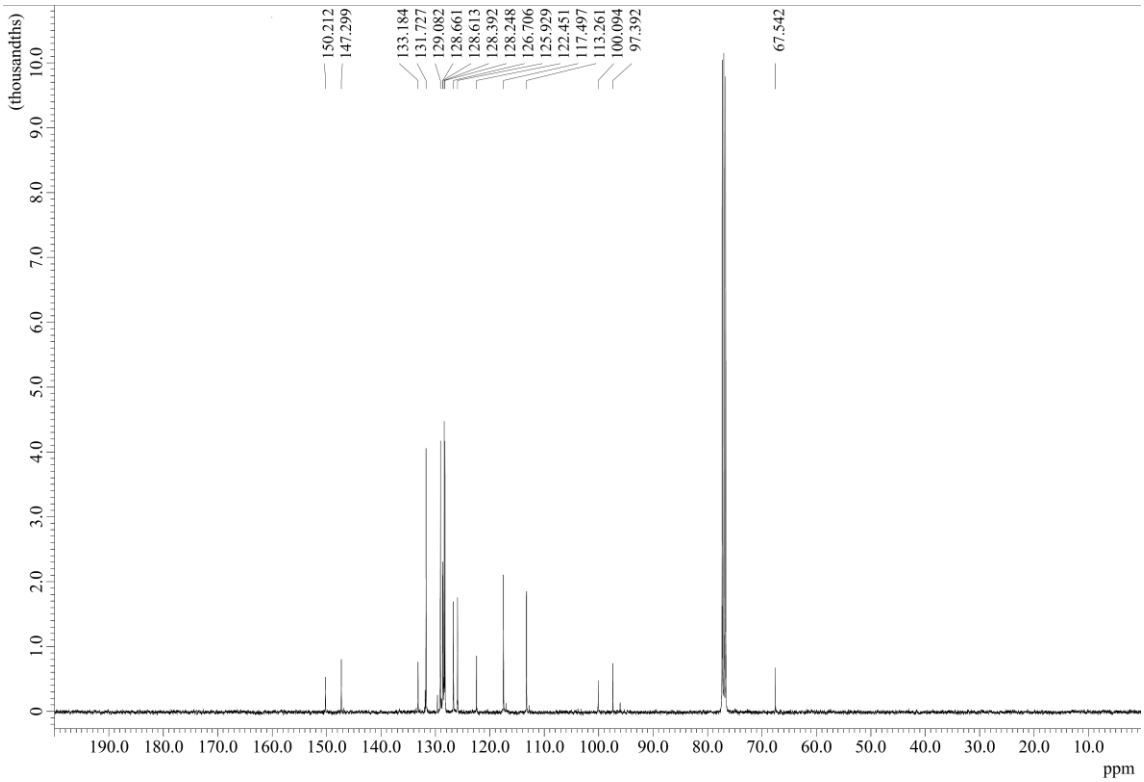
NMR data of novel compounds

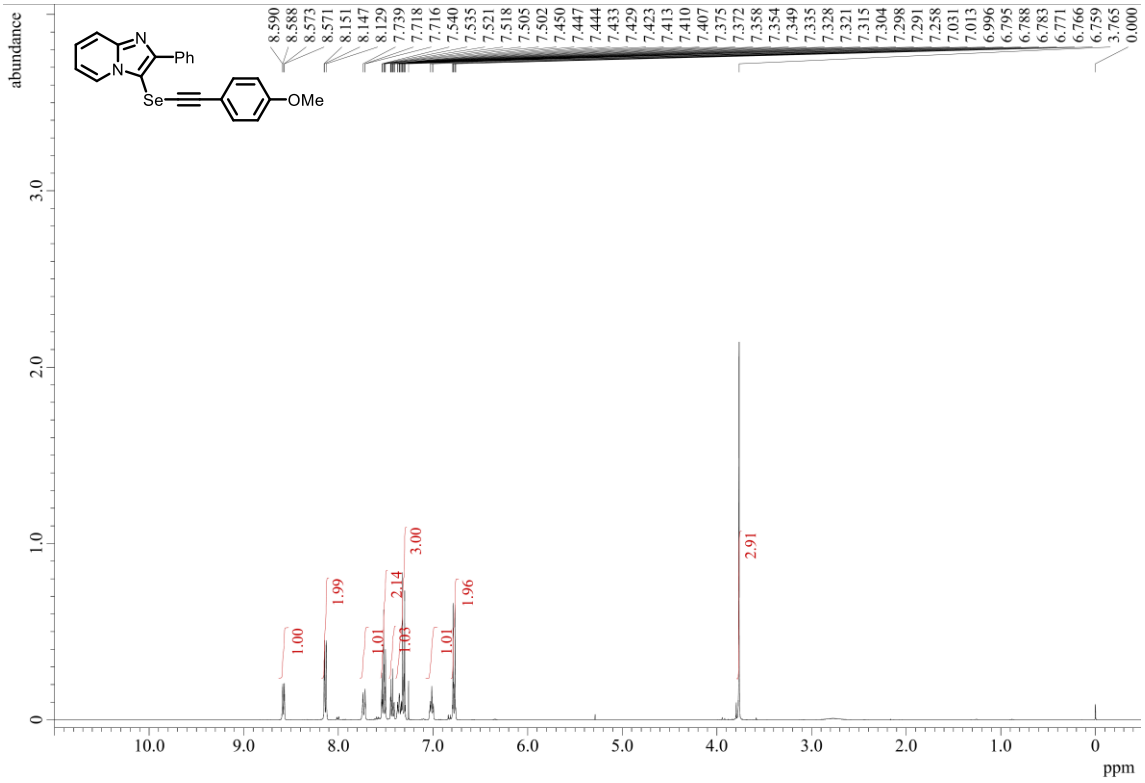
^{1}H NMR of **4aa**



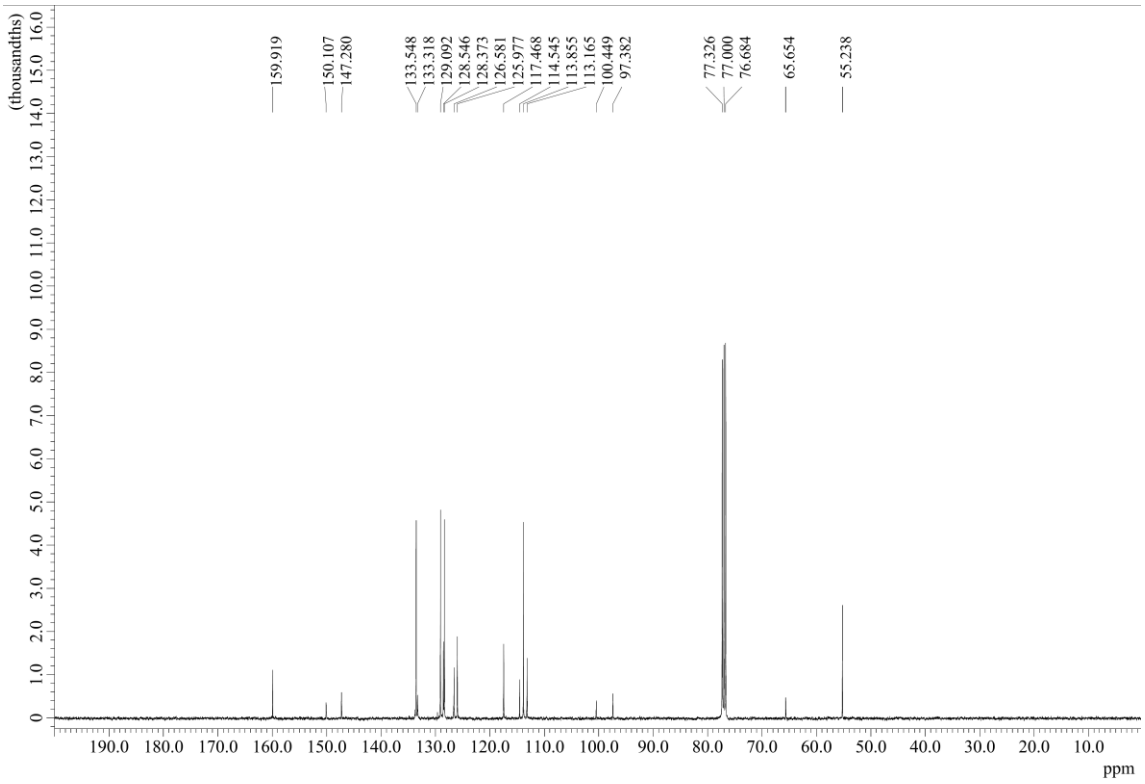
^{13}C NMR of **4aa**



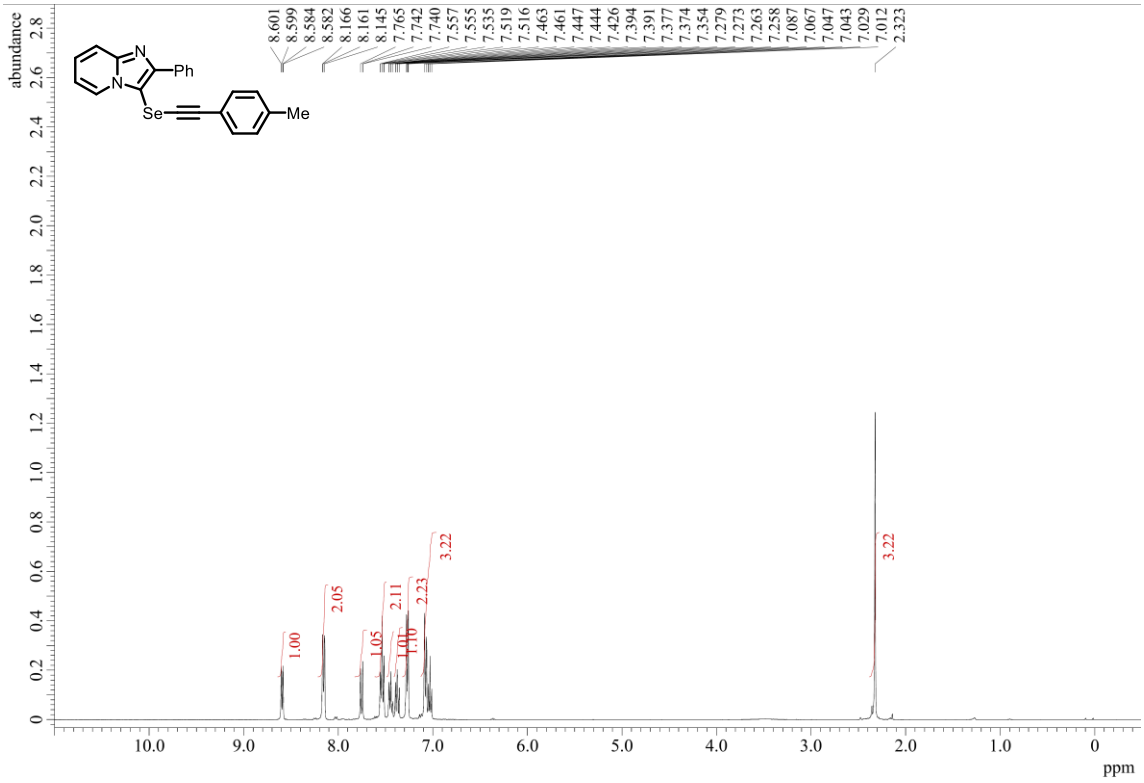
^{1}H NMR of **4ab**



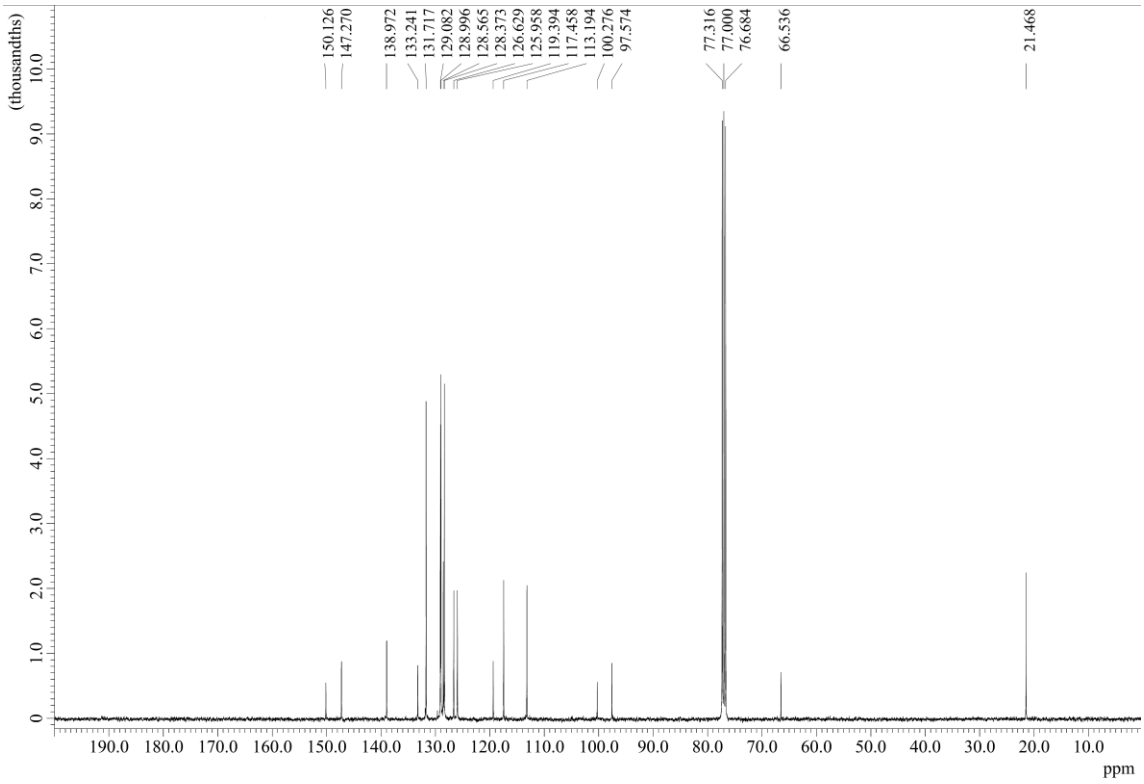
^{13}C NMR of **4ab**



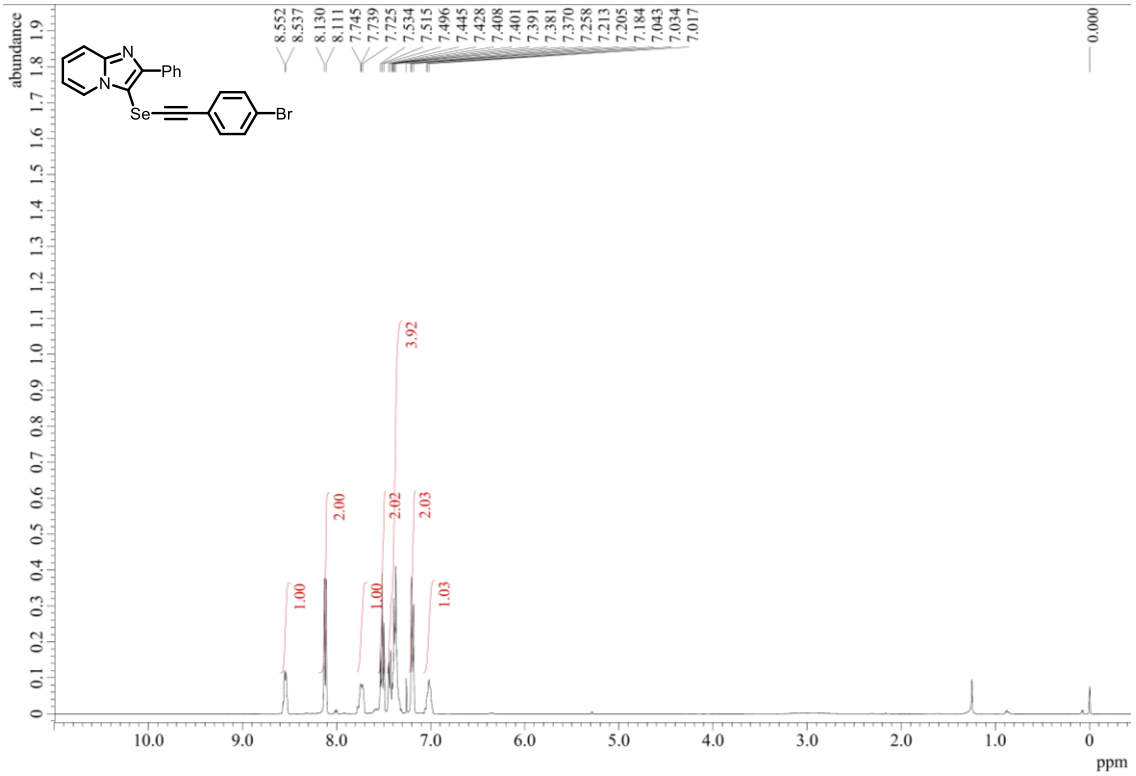
^{1}H NMR of **4ac**



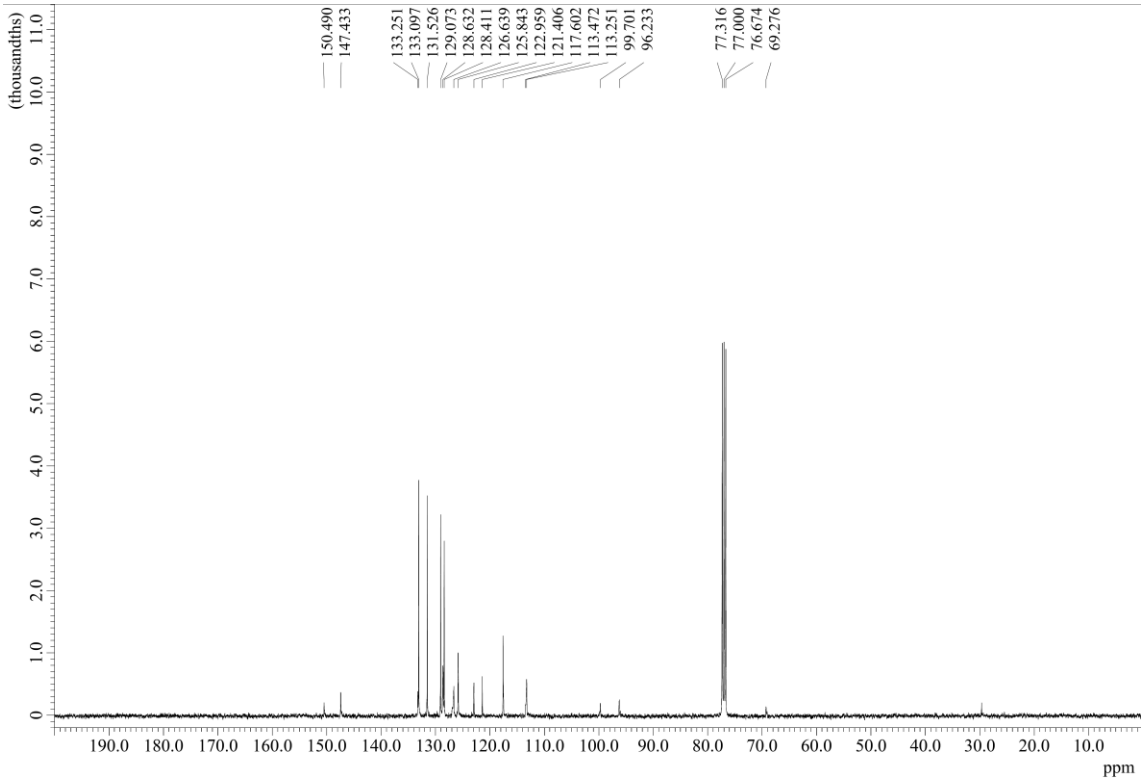
^{13}C NMR of **4ac**



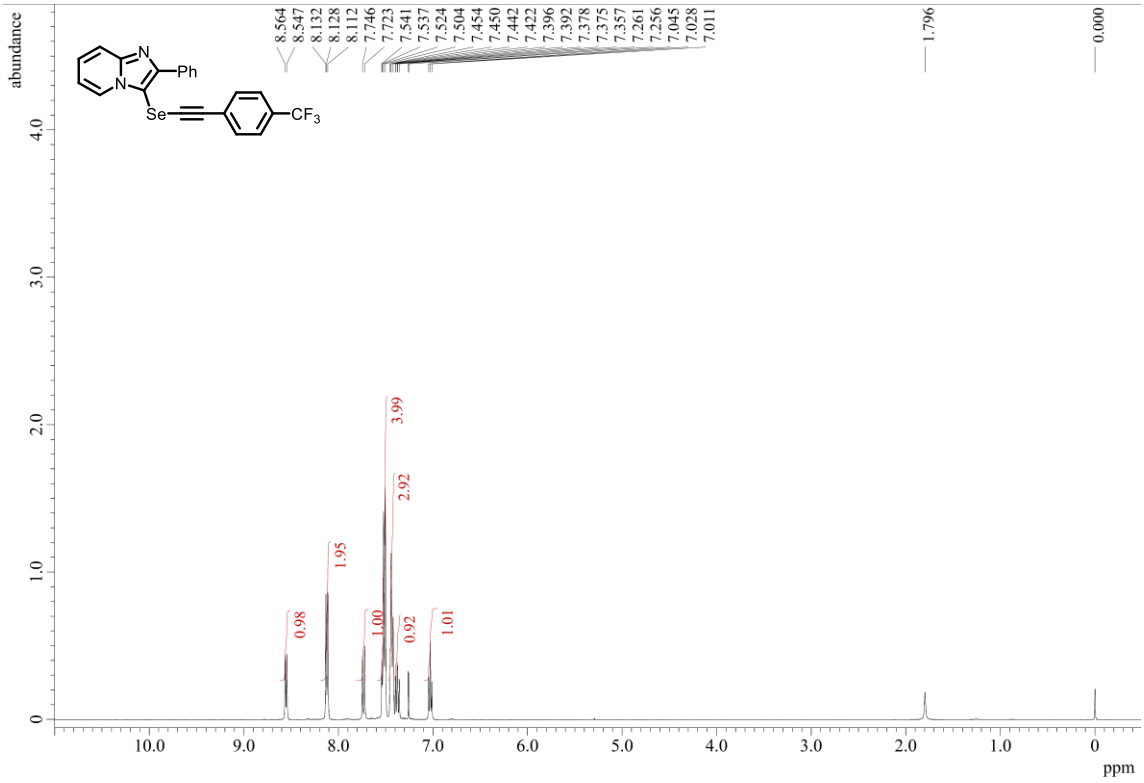
^{1}H NMR of **4ad**



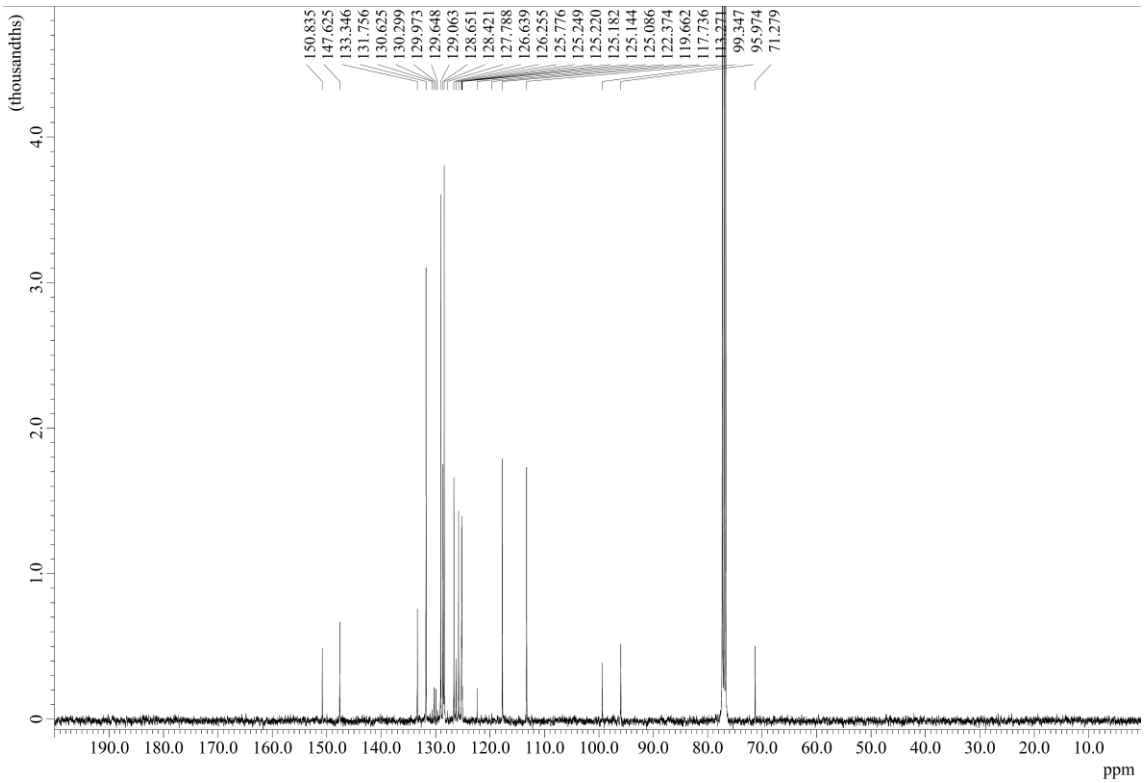
^{13}C NMR of **4ad**



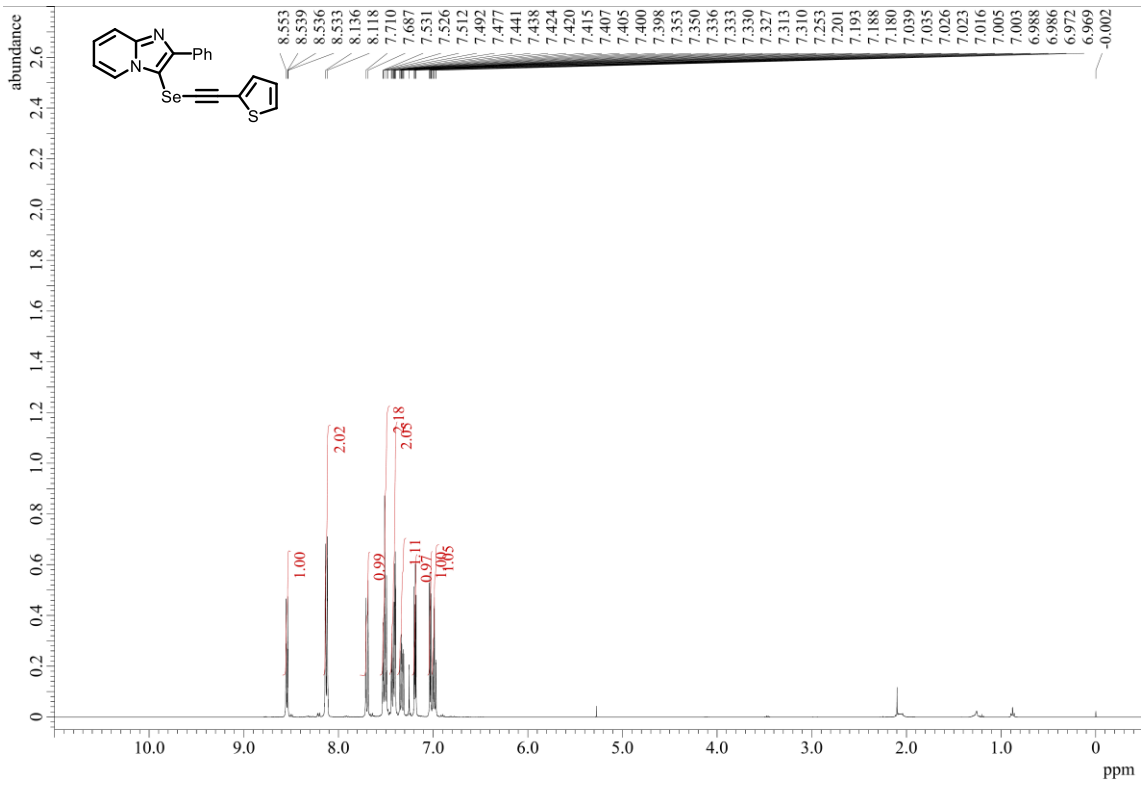
^{1}H NMR of **4ae**



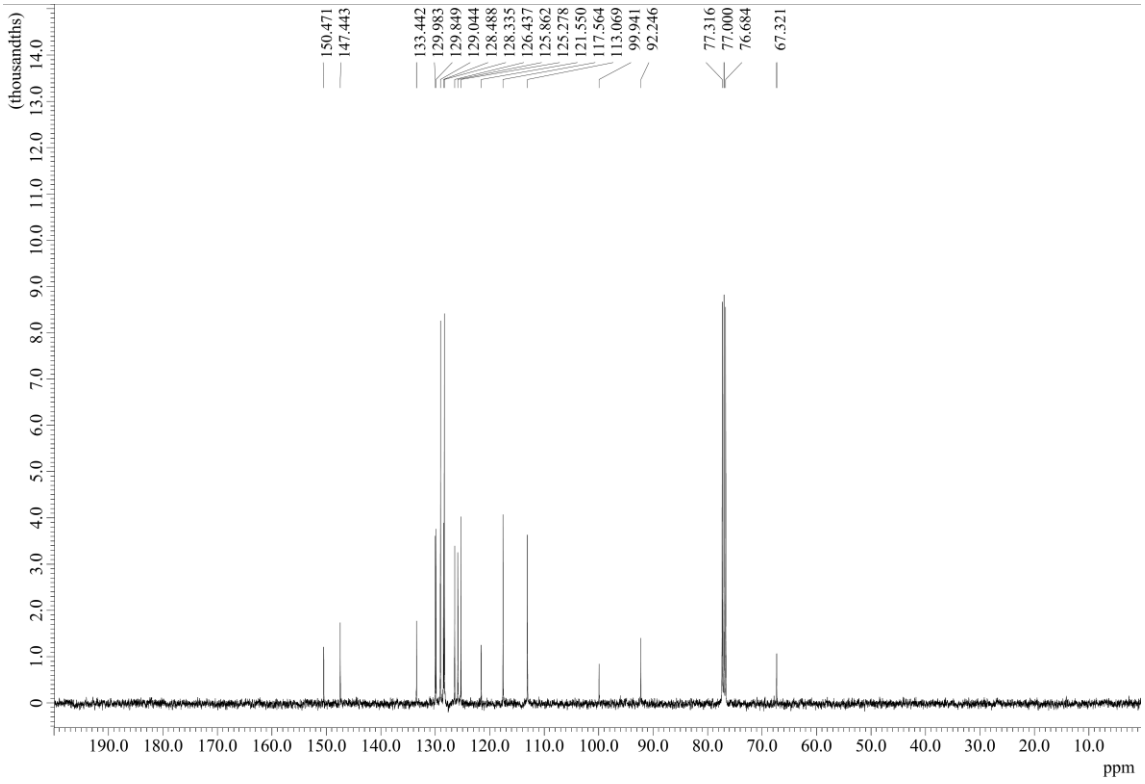
^{13}C NMR of **4ea**



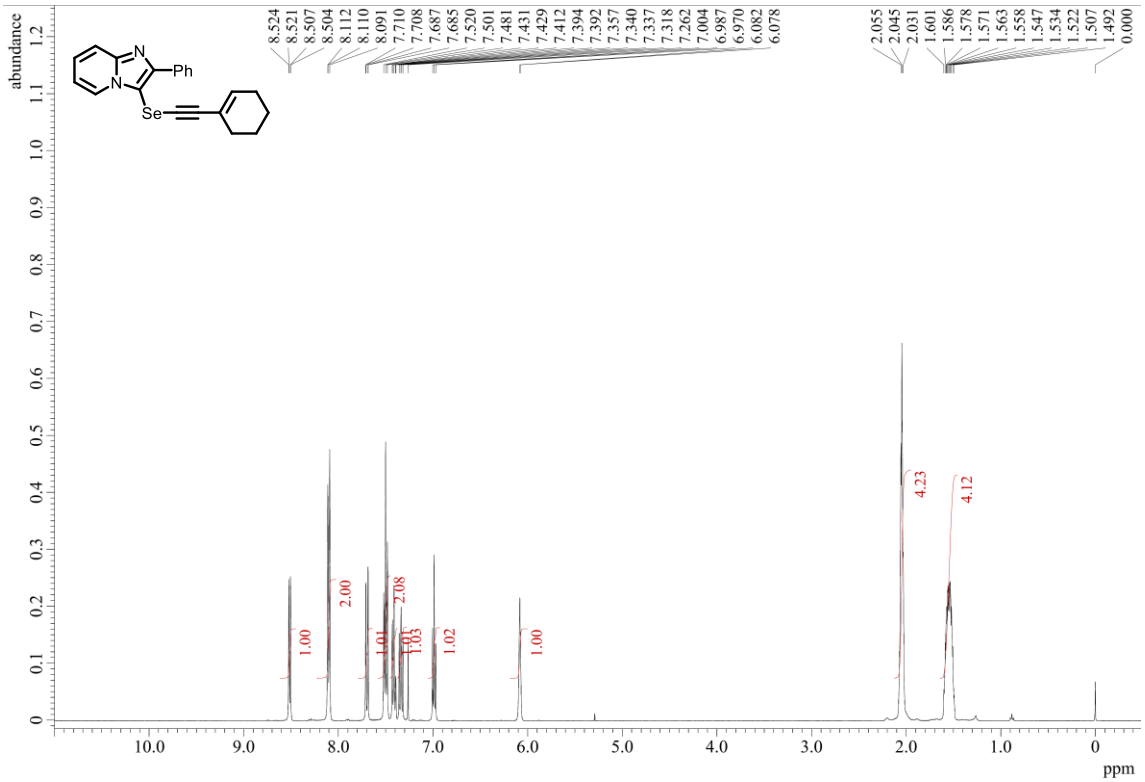
^{1}H NMR of **4af**



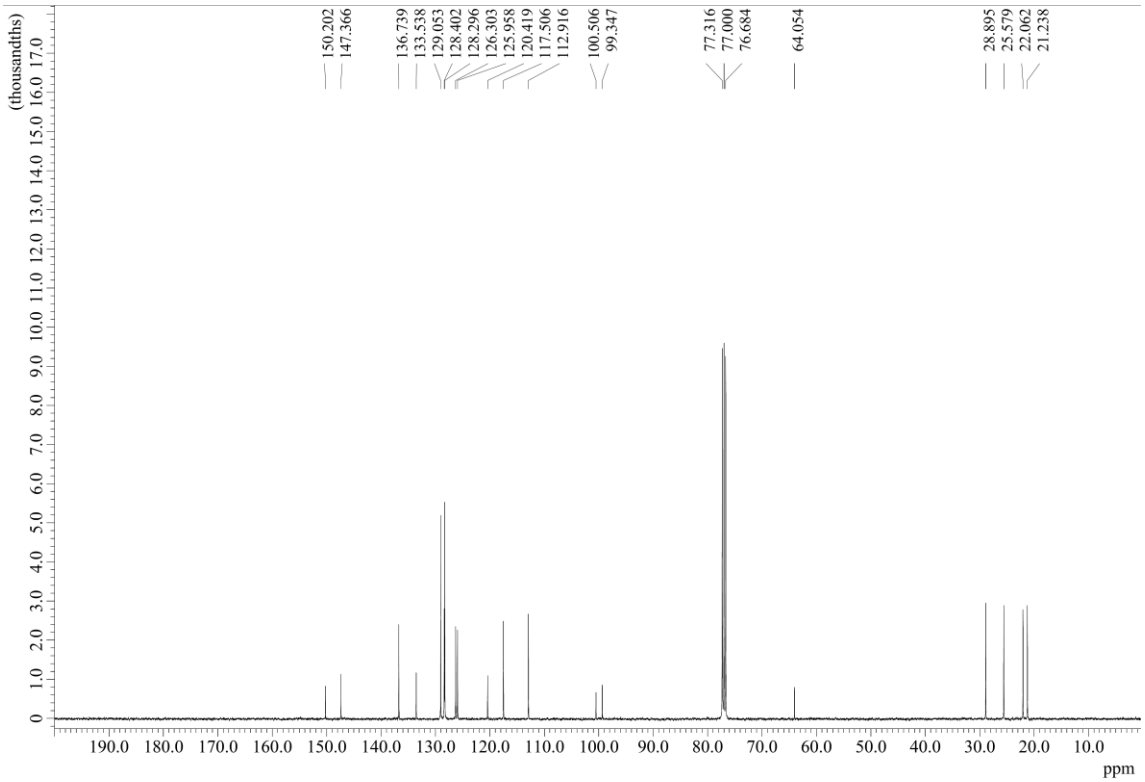
^{13}C NMR of **4af**



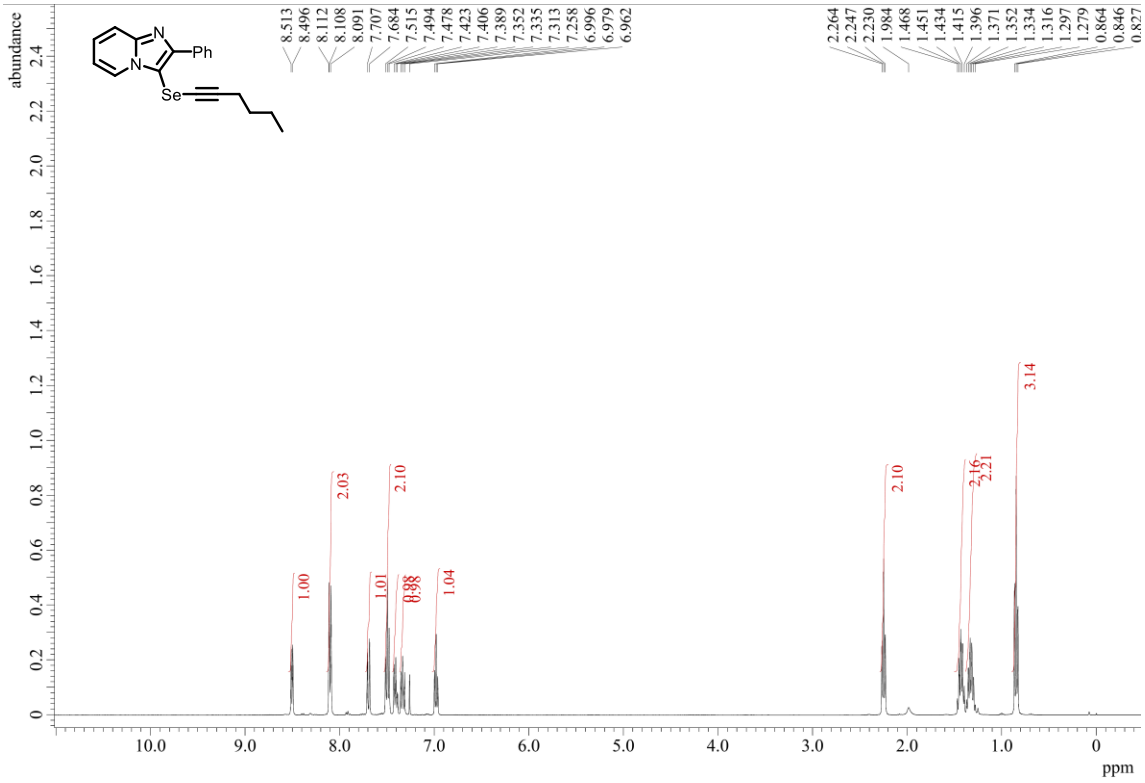
^{1}H NMR of **4ag**



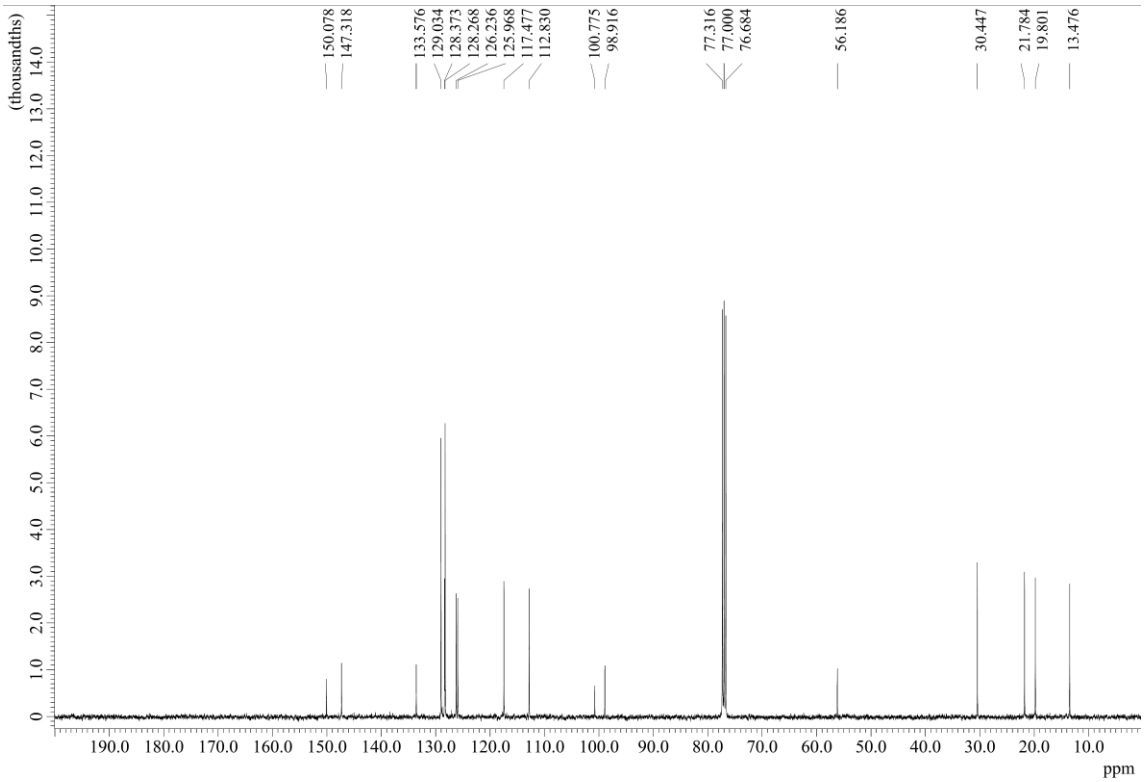
^{13}C NMR of **4ag**



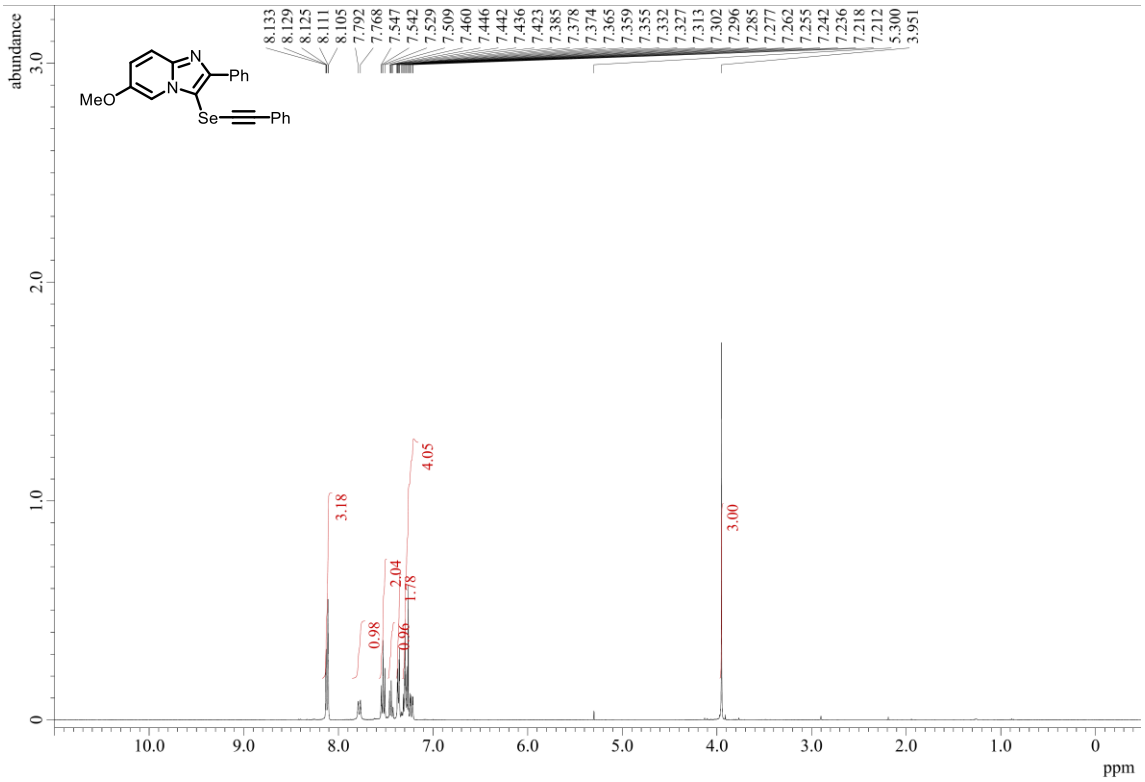
^{1}H NMR of **4ah**



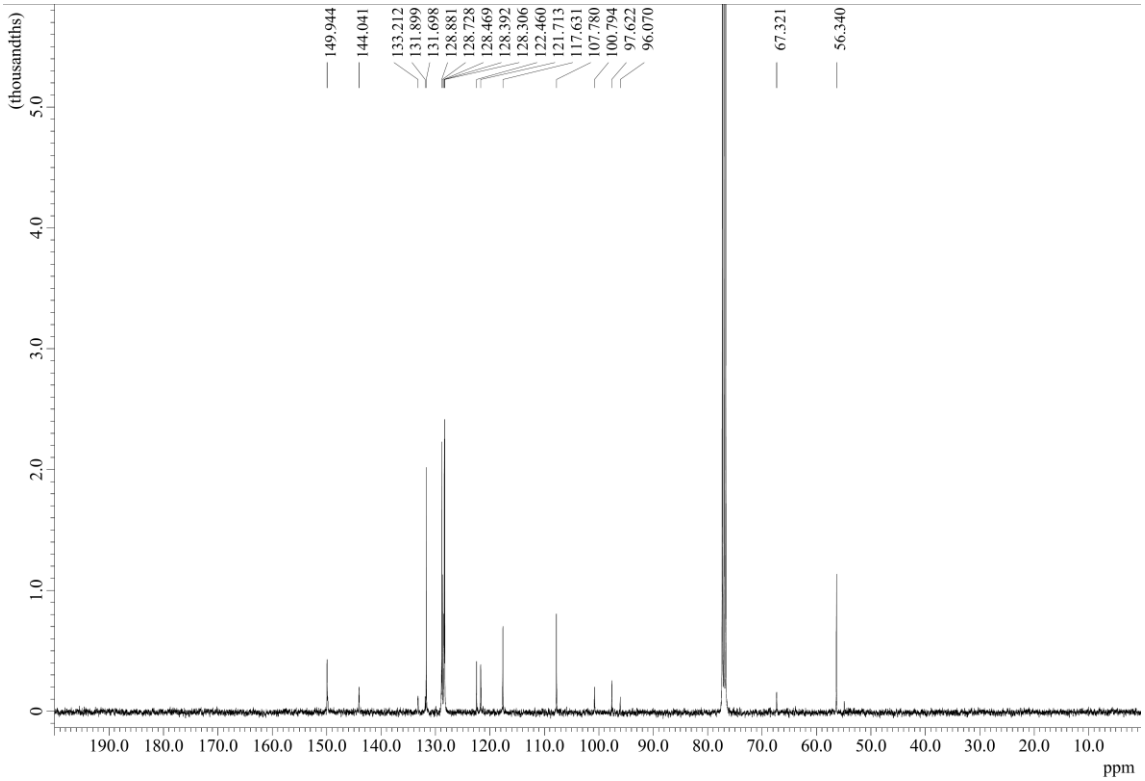
^{13}C NMR of **4ah**



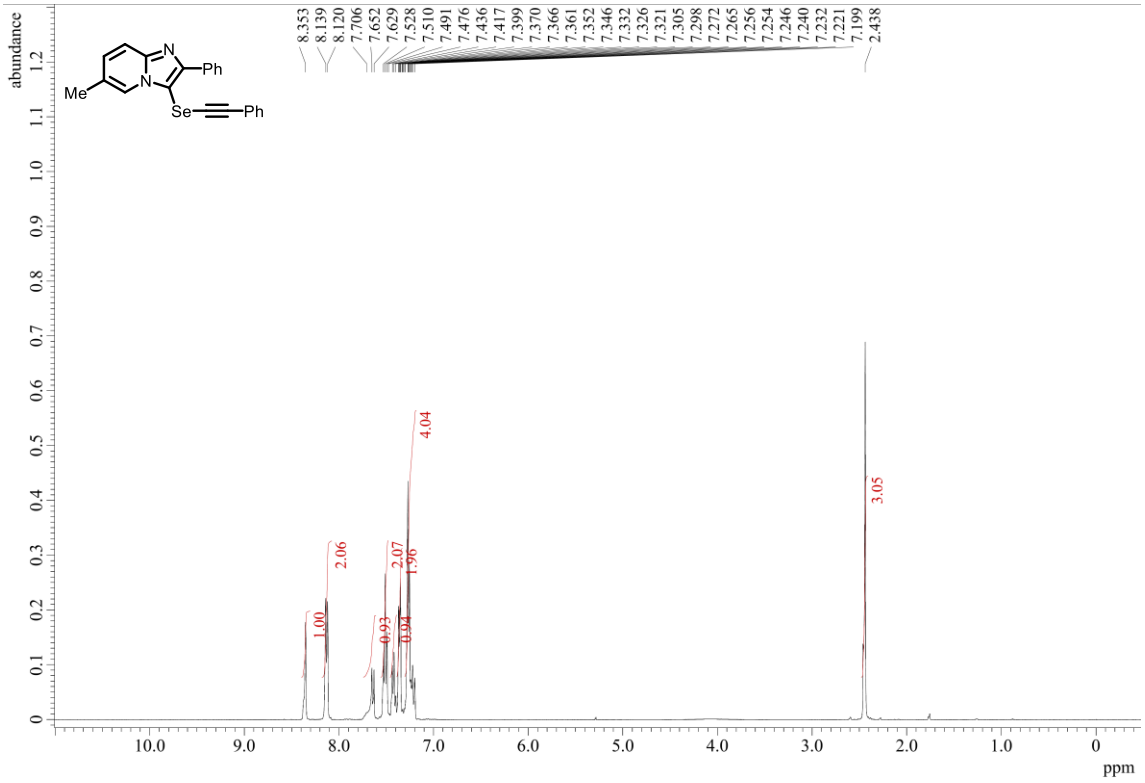
^{1}H NMR of **4ba**



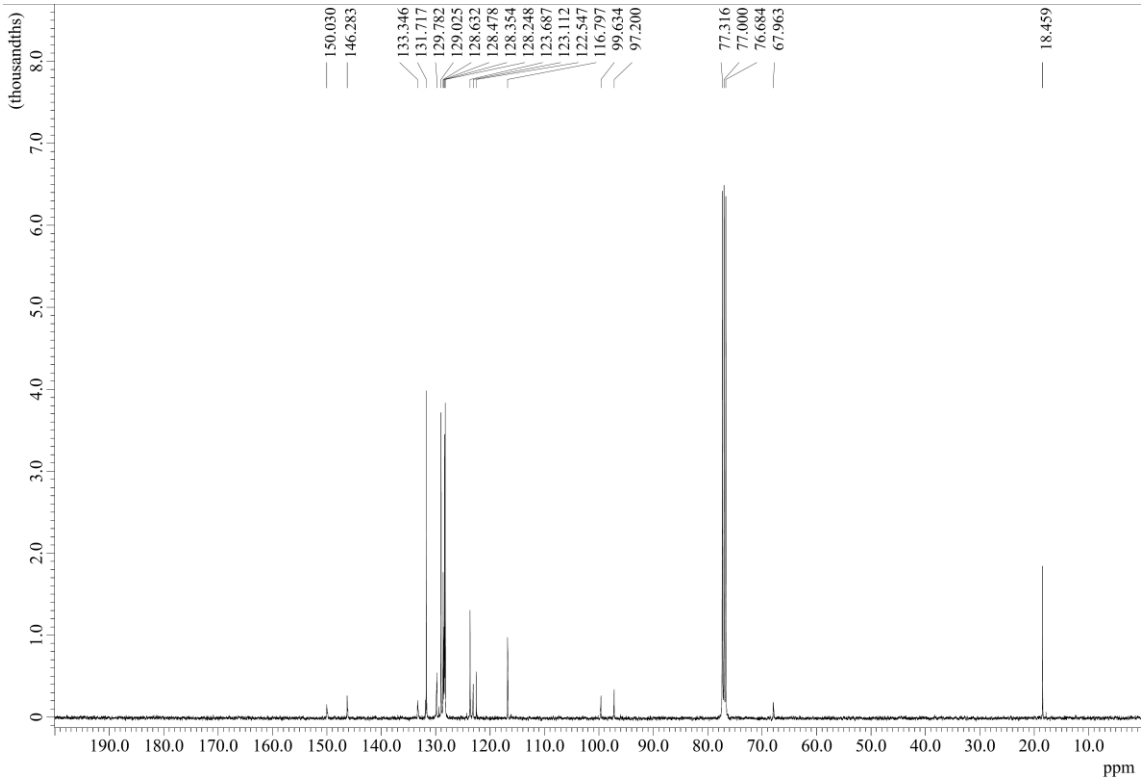
^{13}C NMR of **4ba**



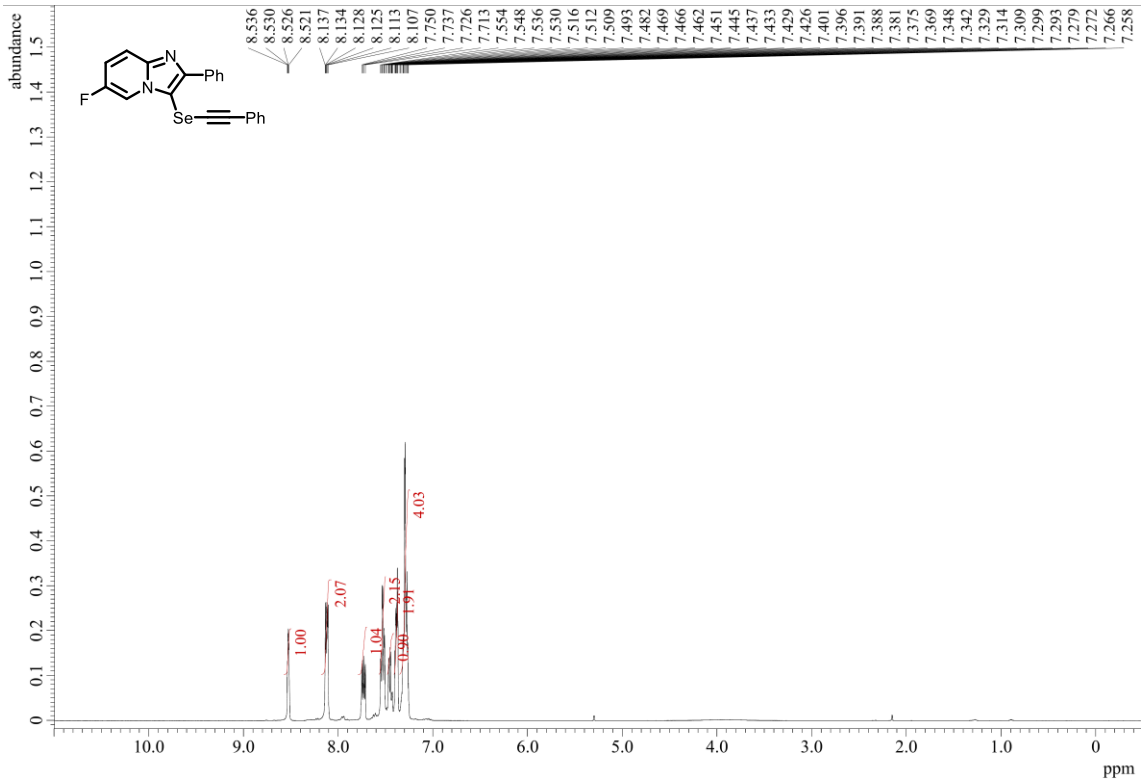
^{1}H NMR of **4ca**



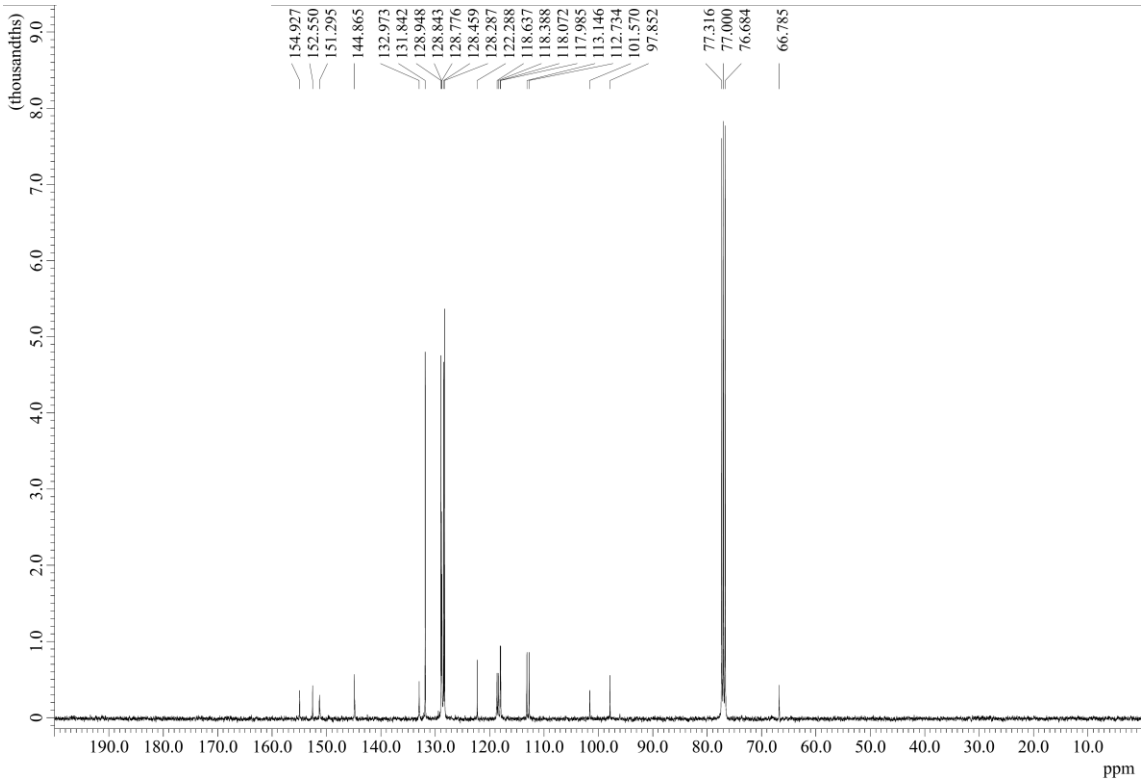
^{13}C NMR of **4ca**



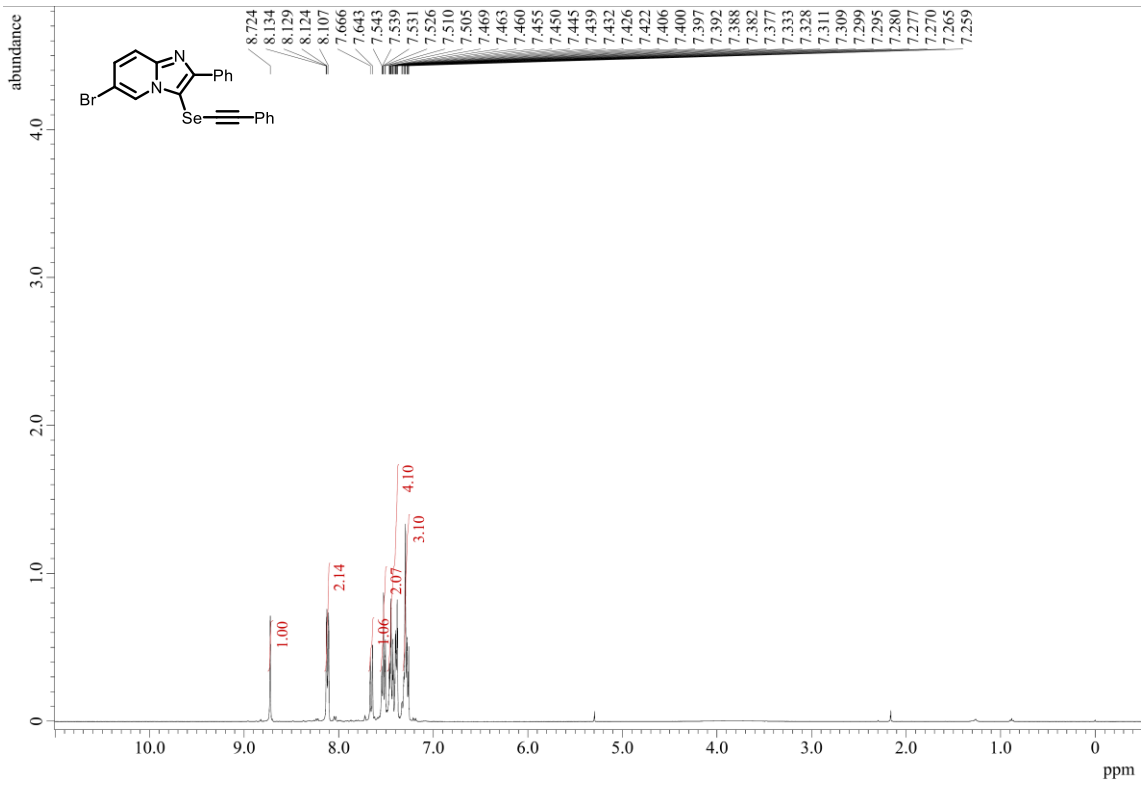
^{1}H NMR of **4da**



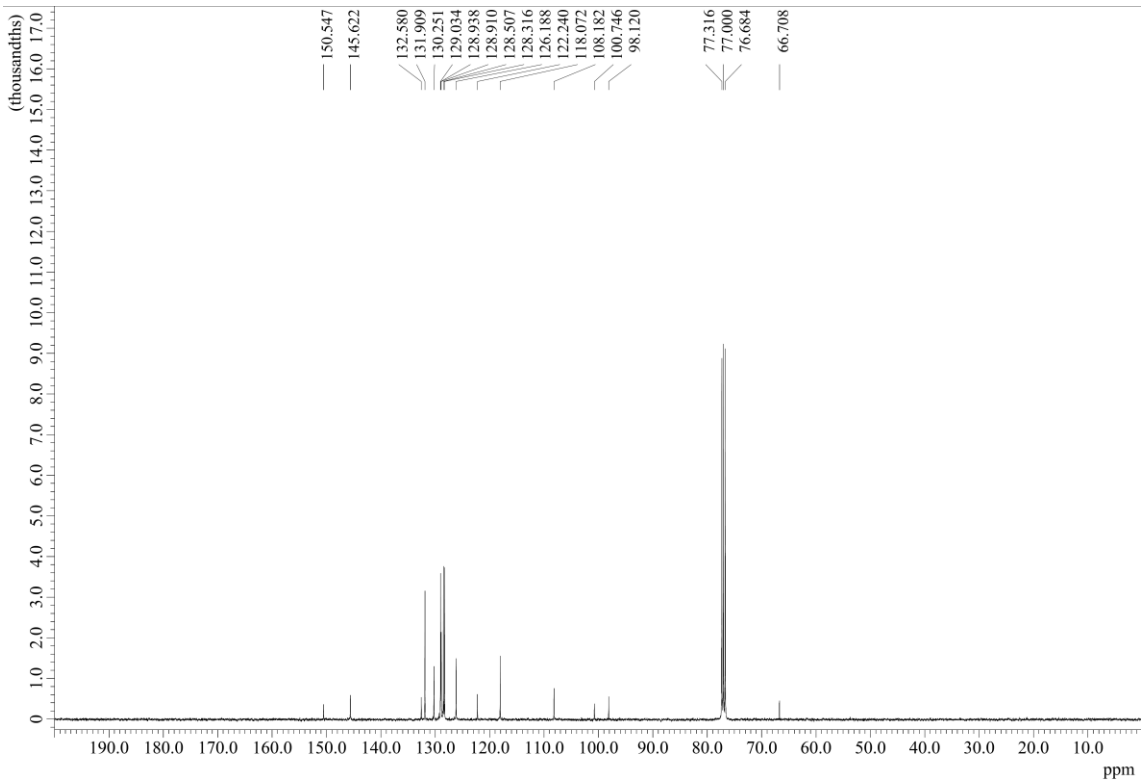
^{13}C NMR of **4da**



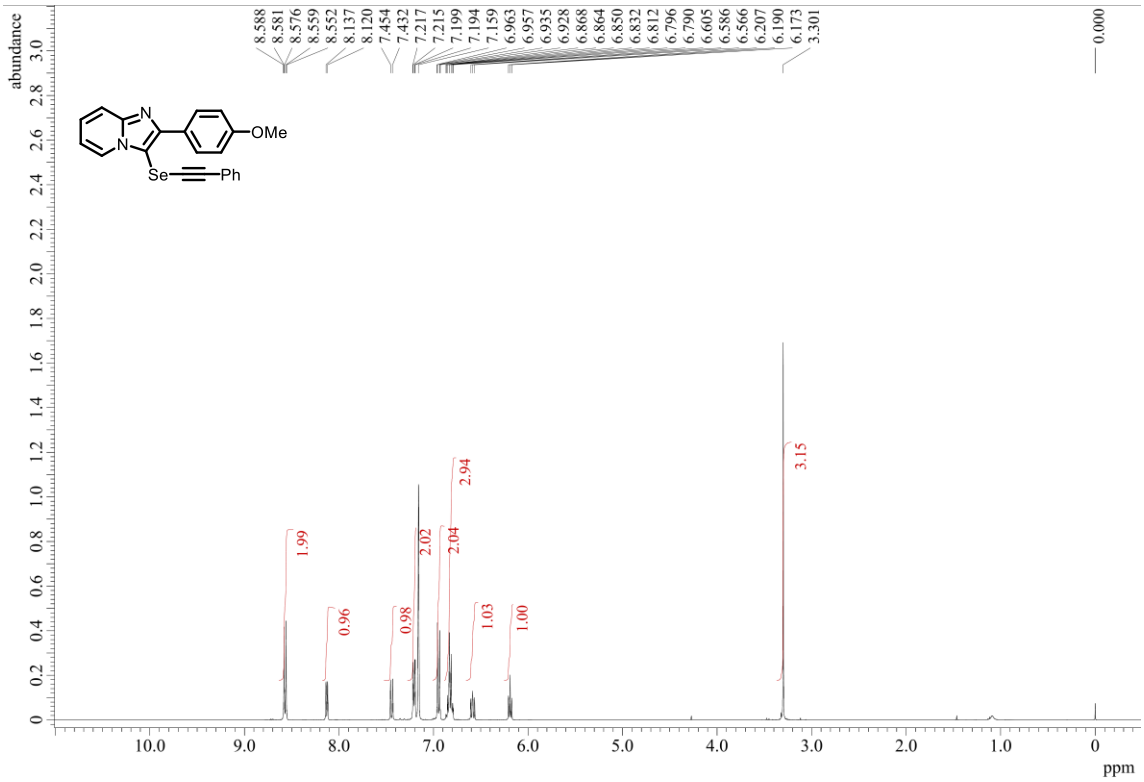
^{1}H NMR of **4ea**



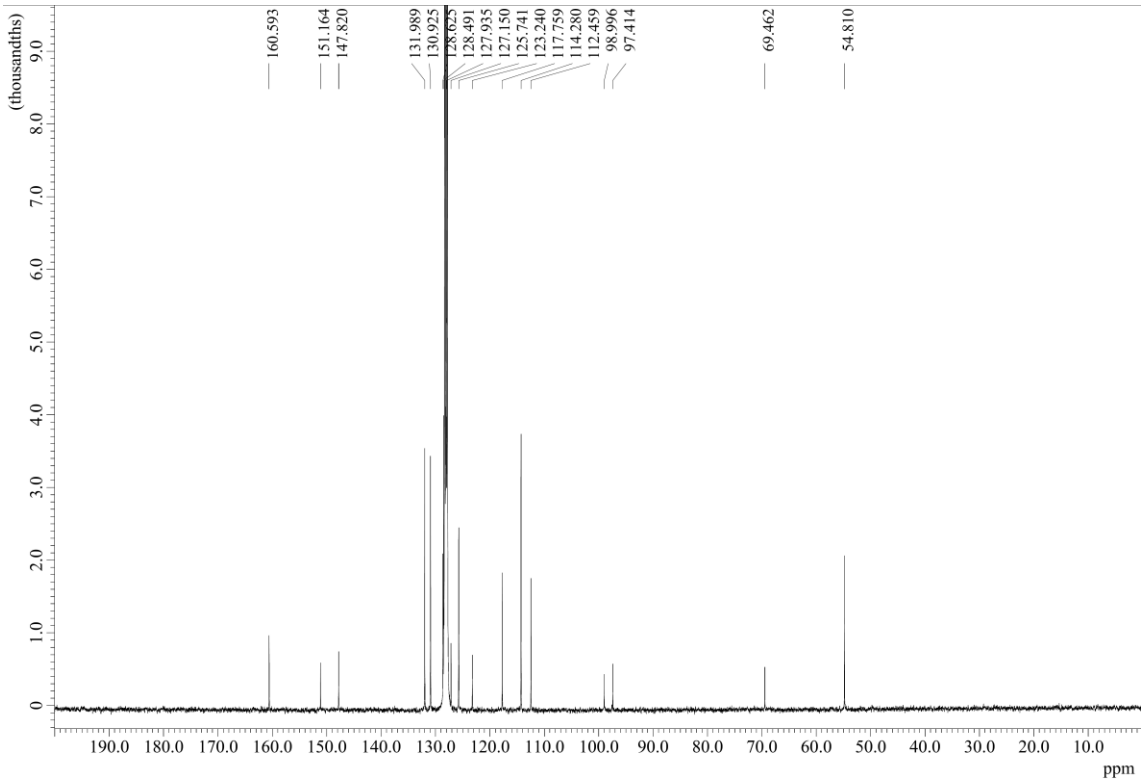
^{13}C NMR of **4ea**



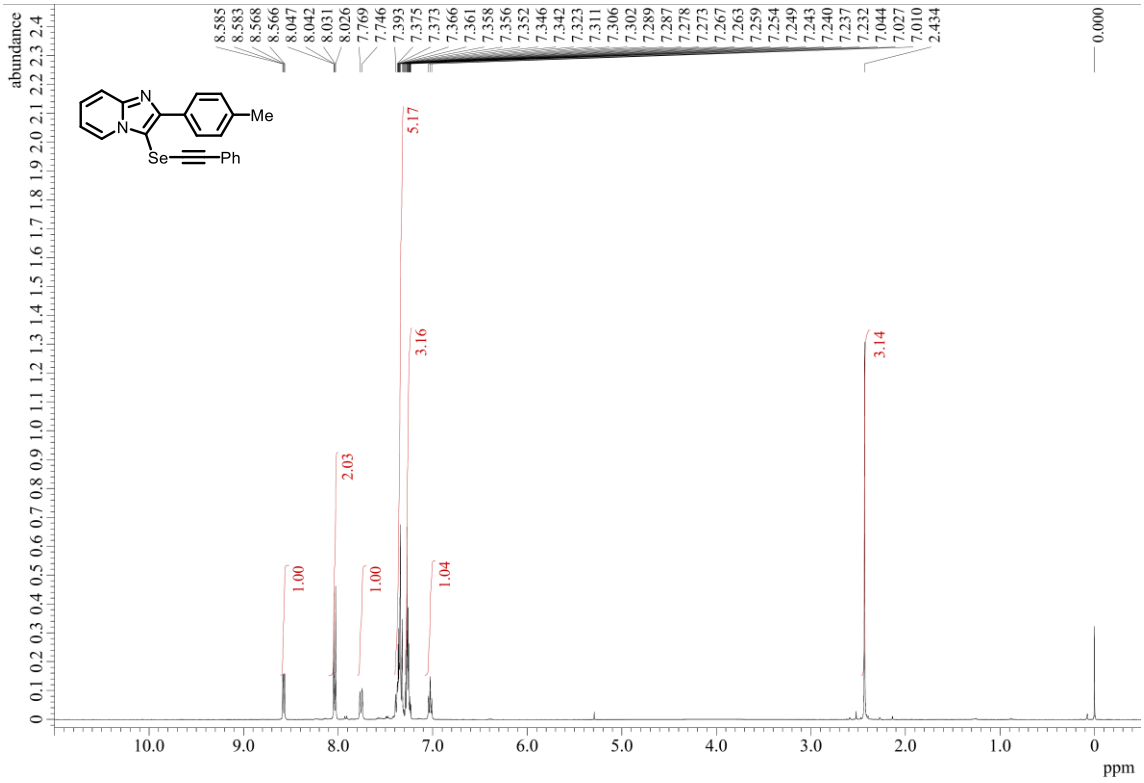
^{1}H NMR of **4ga**



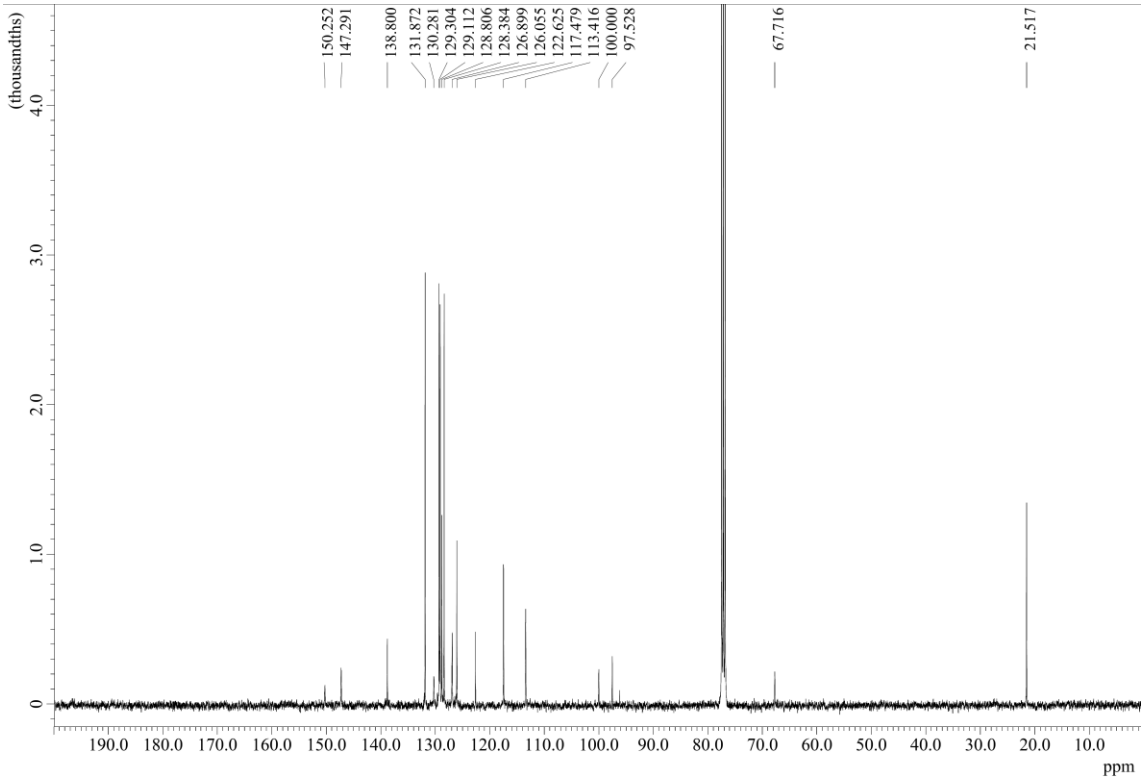
^{13}C NMR of **4ga**



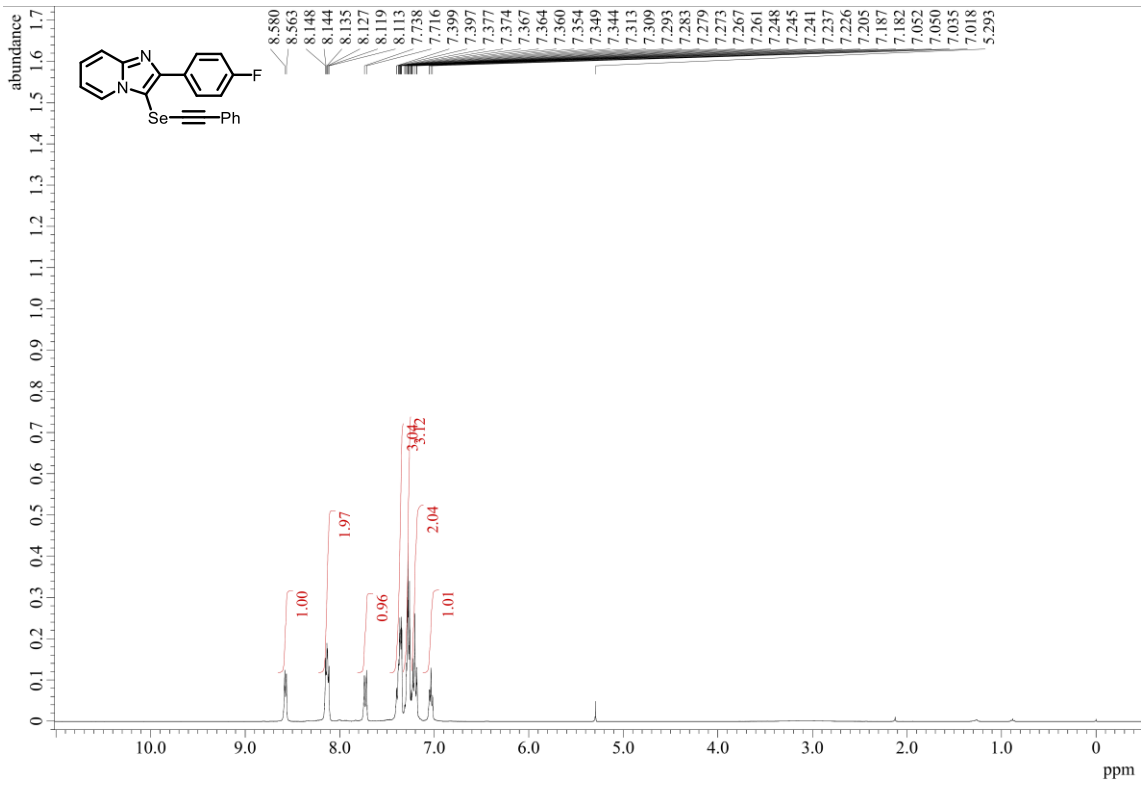
^{1}H NMR of **4ha**



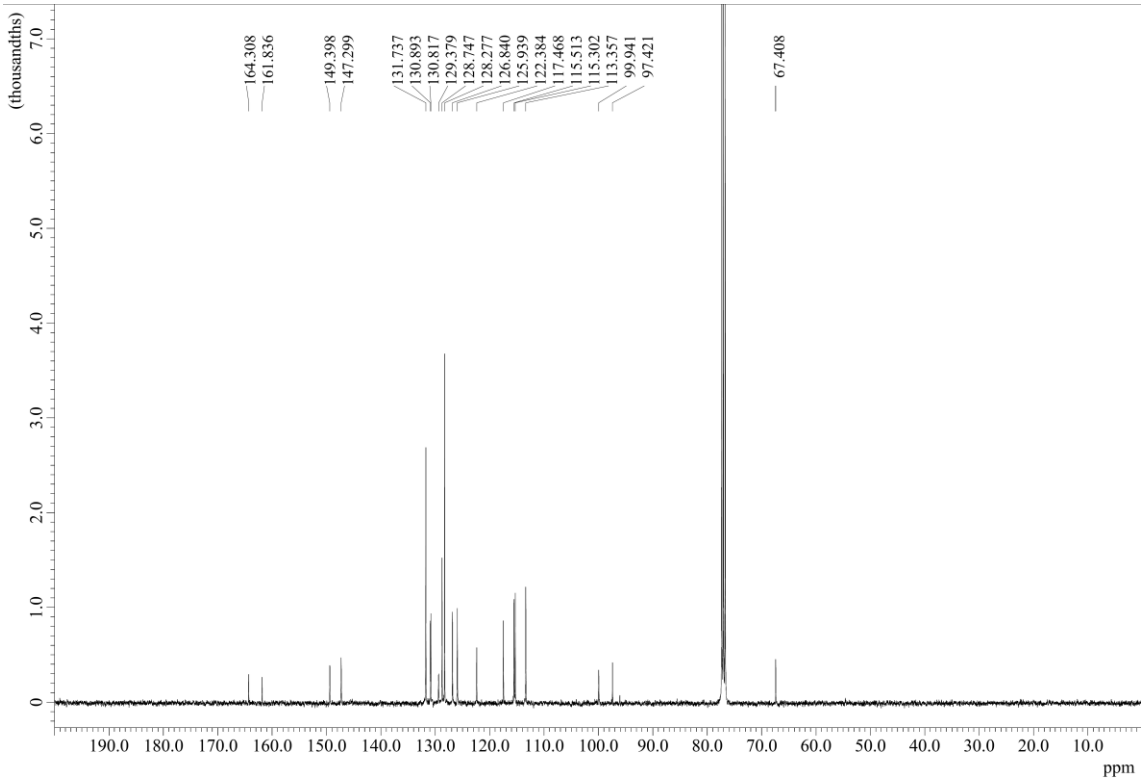
^{13}C NMR of **4ha**



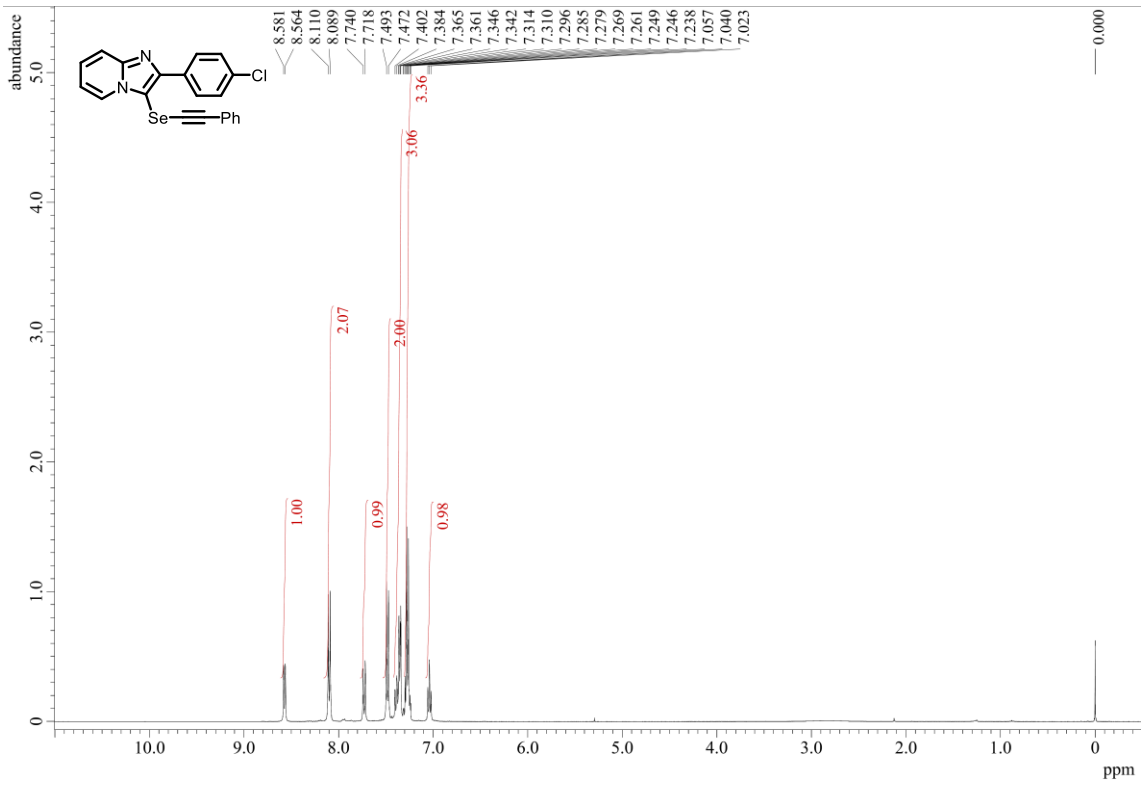
^{1}H NMR of **4ia**



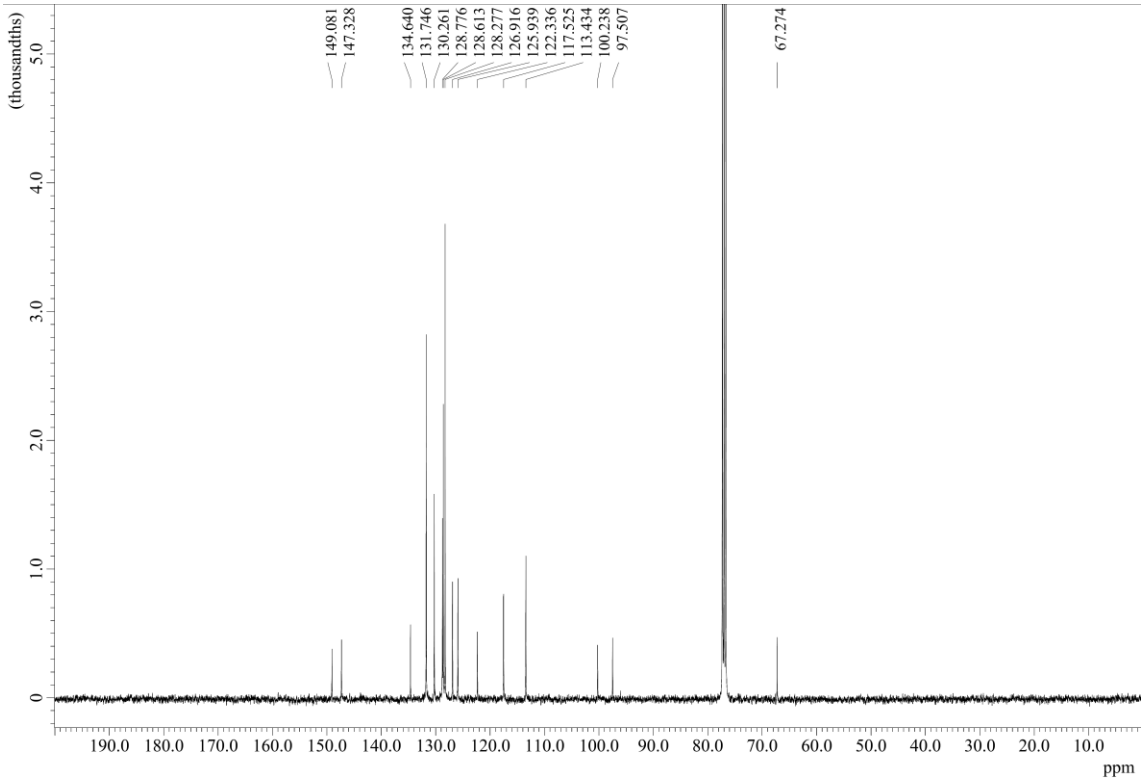
^{13}C NMR of **4ia**



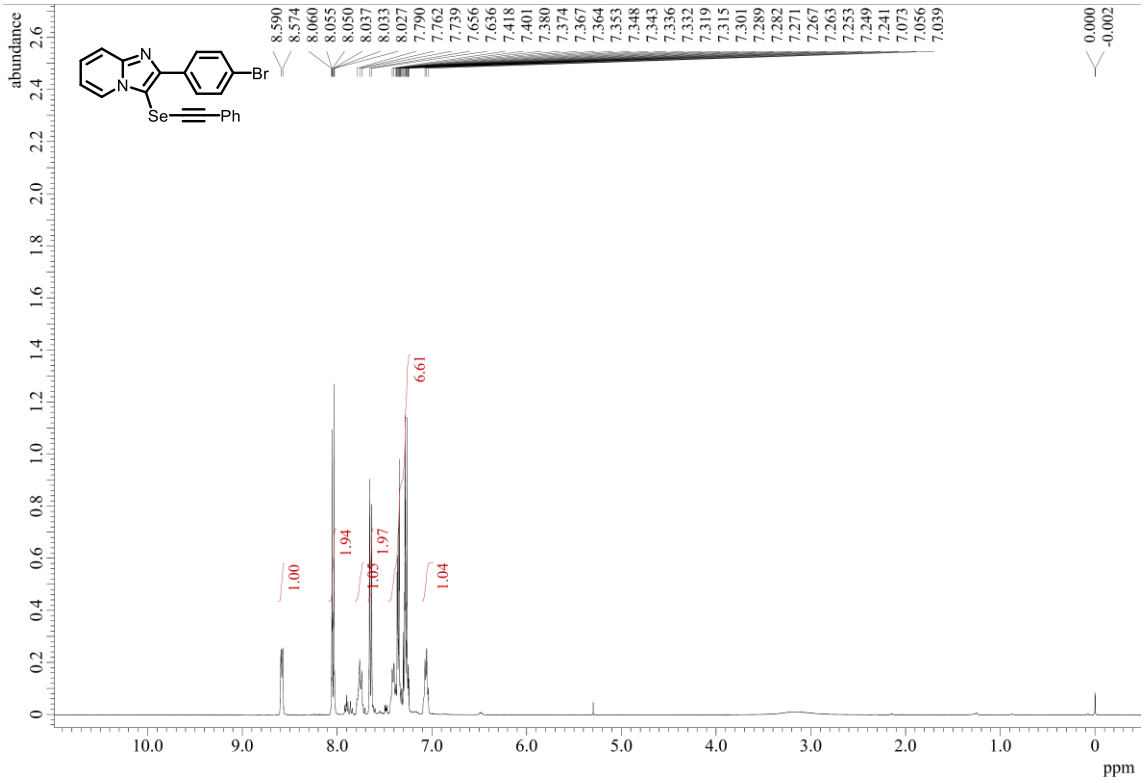
^{1}H NMR of **4ja**



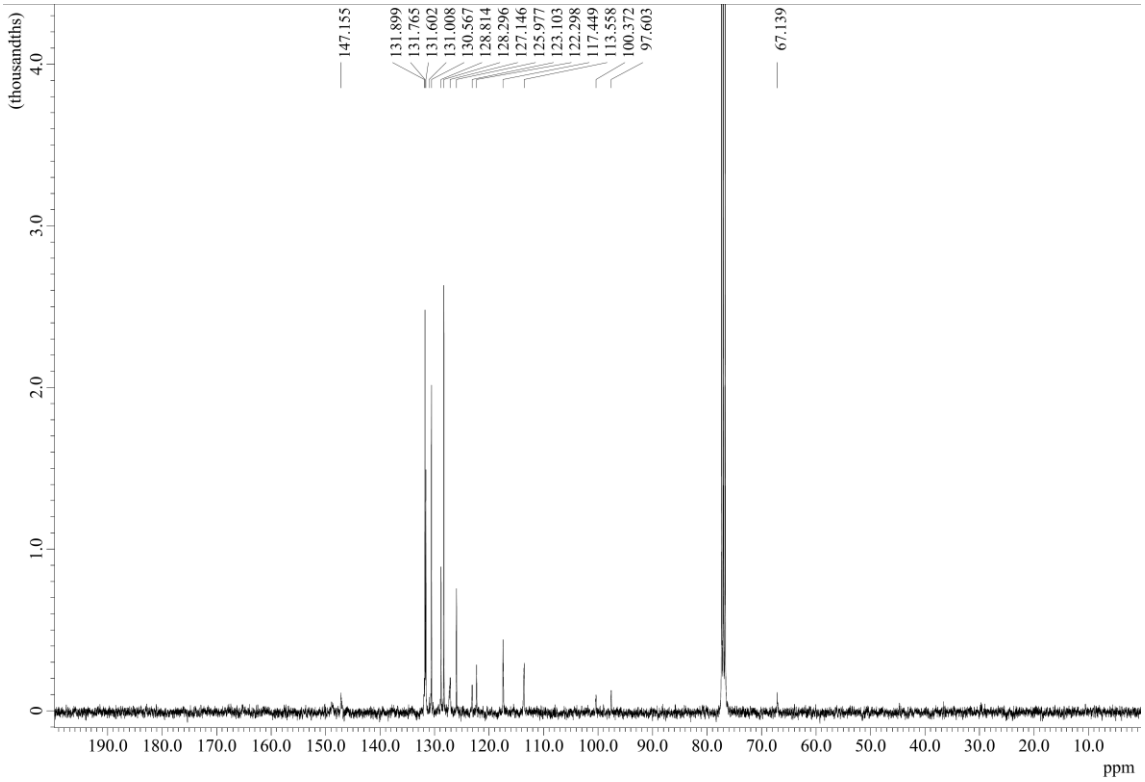
^{13}C NMR of **4ja**



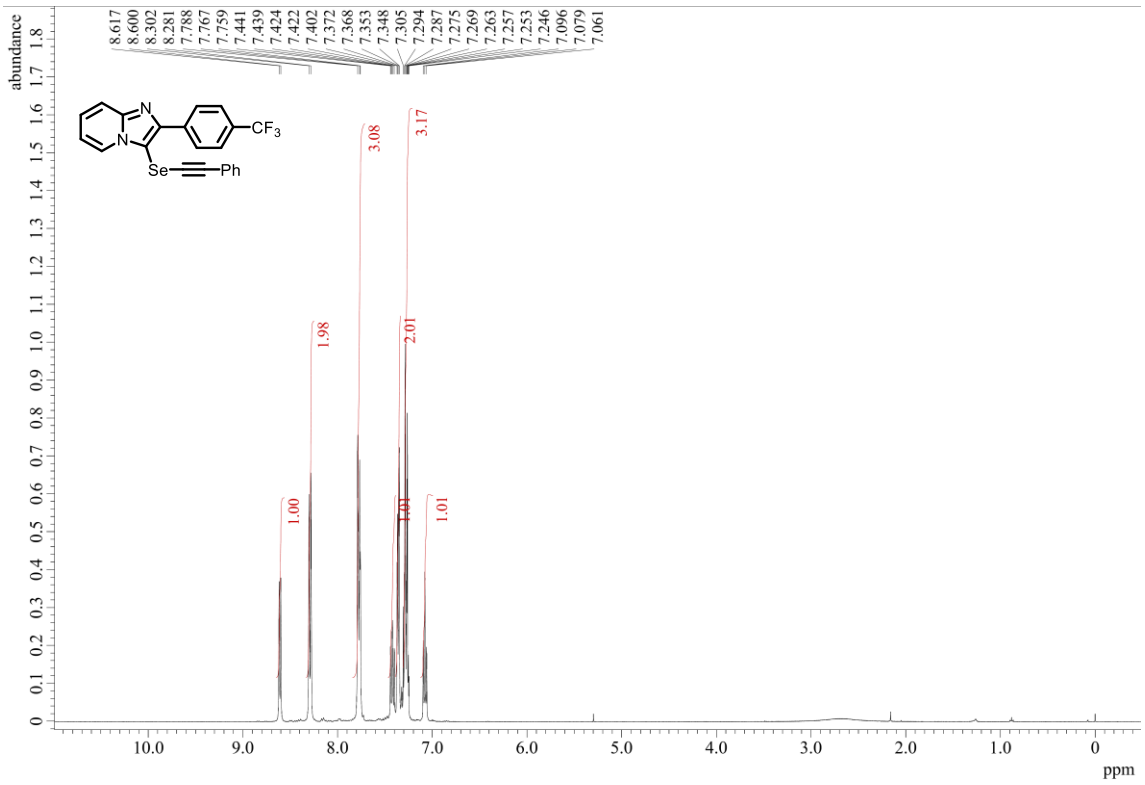
^{1}H NMR of **4ka**



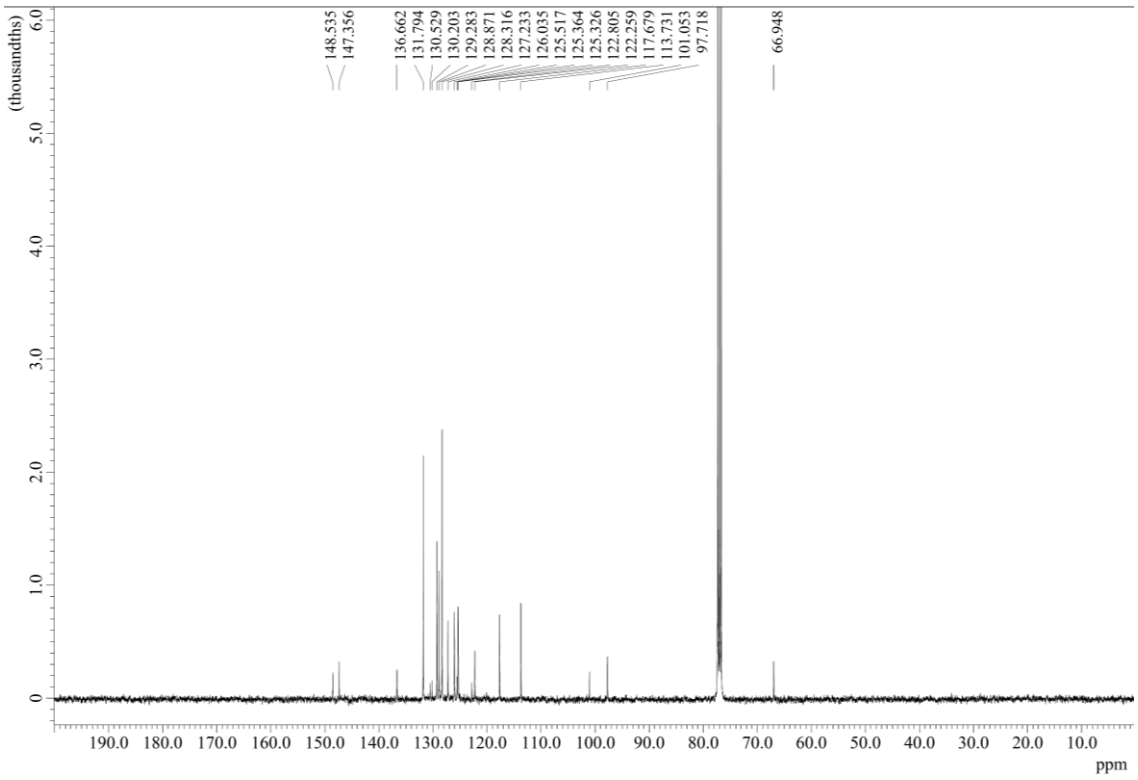
^{13}C NMR of **4ka**



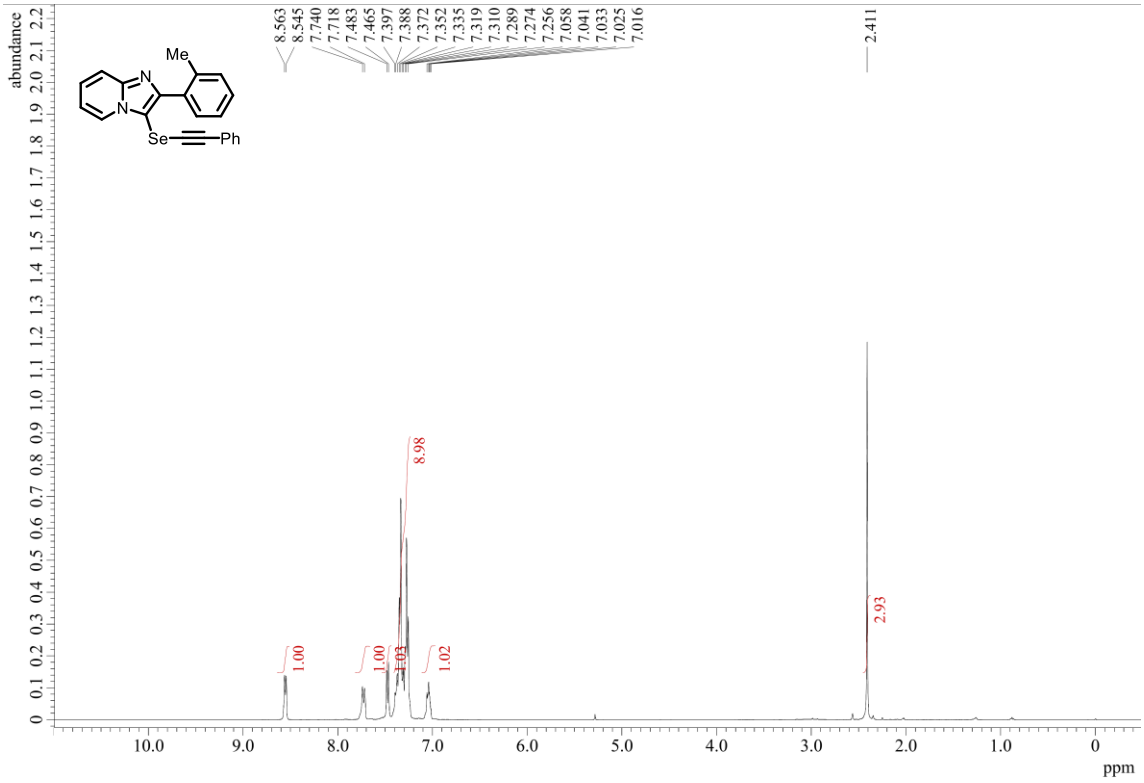
^{1}H NMR of **4la**



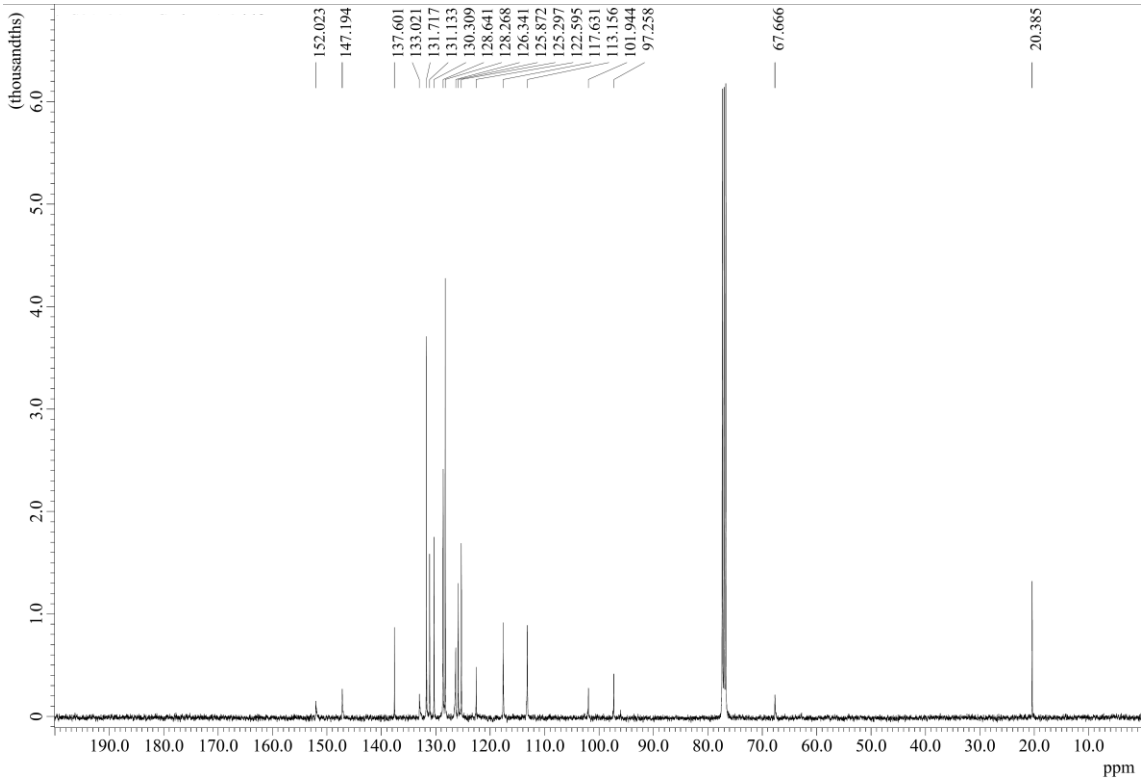
^{13}C NMR of **4la**



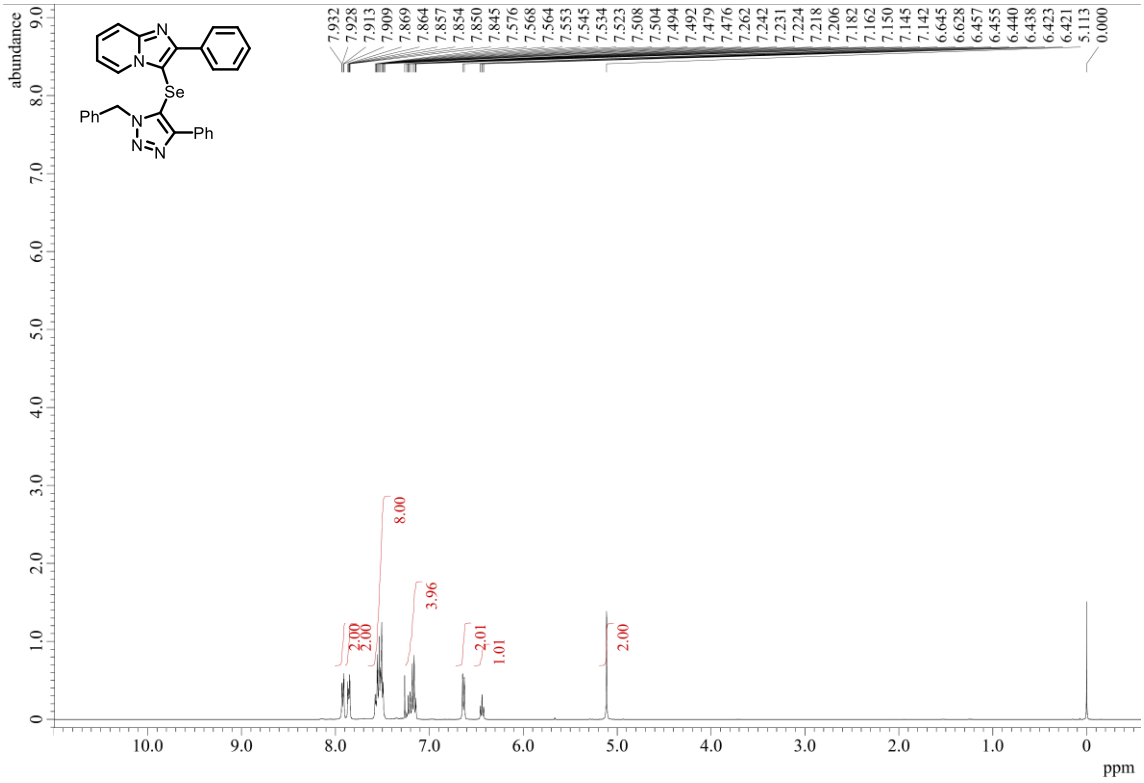
^{1}H NMR of **4ma**



^{13}C NMR of **4ma**



^{1}H NMR of **8**



^{13}C NMR of **8**