

Electronic Supporting Information

Iodine-Catalyzed Intermolecular 1,2-Thio (Seleno)amination of Alkenes with 1,2,3-Triazoles and Disulfides (Diselenides) in Air

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1. General information

All reactions and manipulations were carried out in air, in a 4 mL sealed vial equipped with a stir bar. ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using a Bruker 400 MHz spectrometer in CDCl_3 . Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^1H NMR, and CDCl_3 was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s=singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). High-resolution mass spectrometry (HRMS) was performed on IonSpec FT-ICR or Waters Micromass Q-TOF micro Synapt High-Definition Mass Spectrometer. Mass spectra were recorded on the HP-5989 instrument by ESI methods. The X-ray diffraction analysis was performed using a Bruker Smart-1000 X-ray diffractometer.

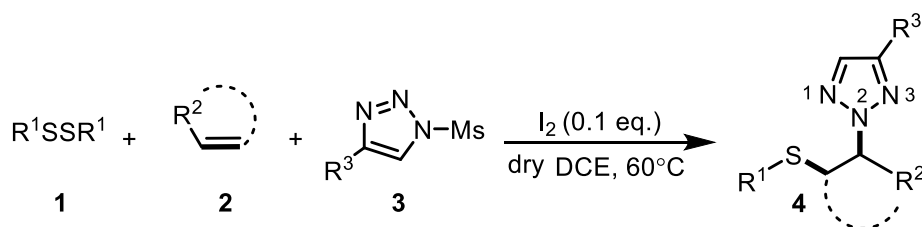
2. Starting materials

N-sulfonyl-1,2,3-triazoles **3**

1-sulfonyl-1,2,3-triazoles **3** were prepared from the corresponding alkynes and sulfonyl azides according to previously reported synthetic procedures.¹ Attention! Sulfonyl azides are potentially explosive materials and must be handled with caution! Due to the potential danger of methane sulfonyl azide, we strongly recommend to avoid isolating this compound in large quantities.

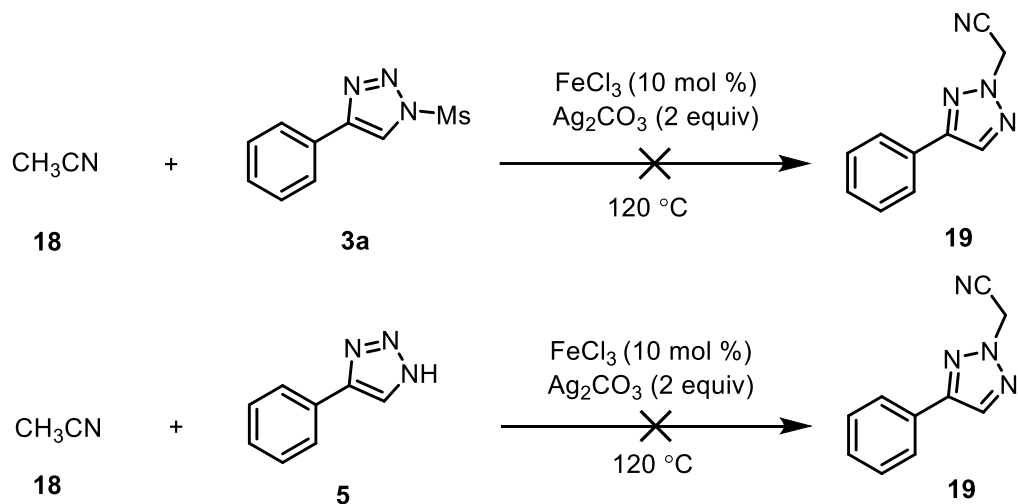
3. Experimental procedures

General procedures for products **4**:

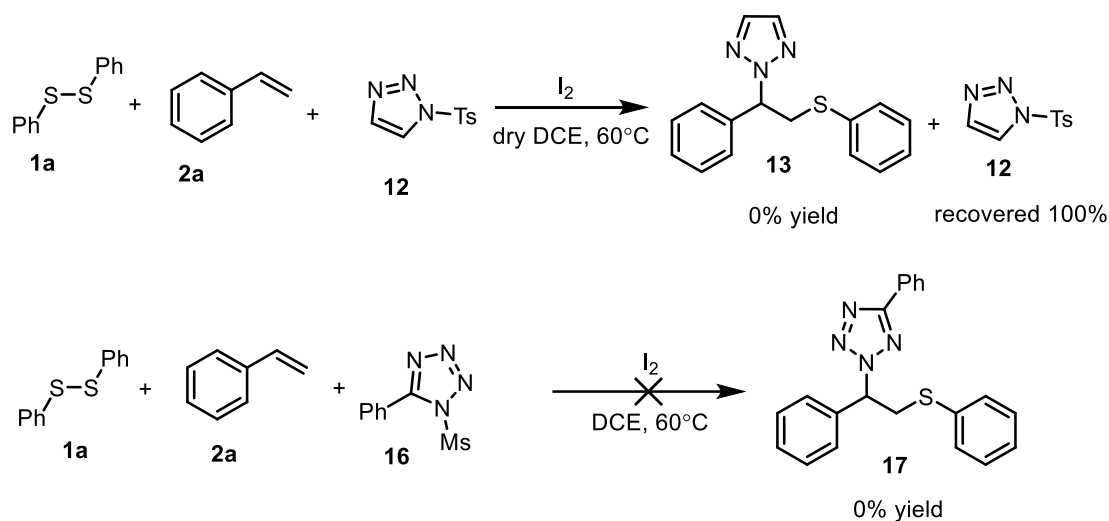


To a flame-dried Schlenk tube was added *N*-sulfonyl-1,2,3-triazoles **3** (0.2 mmol, 1.0 equiv), then disulfides (diselenides) **1** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) were added respectively, I_2 (0.02 mmol, 0.1 equiv), and dry DCE (2 mL) was

added to the tube and the mixture was stirred at 60 °C for 12 h. After completion as detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was purified by silica gel chromatography with eluent (petroleum ether/ethyl acetate = 20/1 - 15/1) to give the desired product **4**.

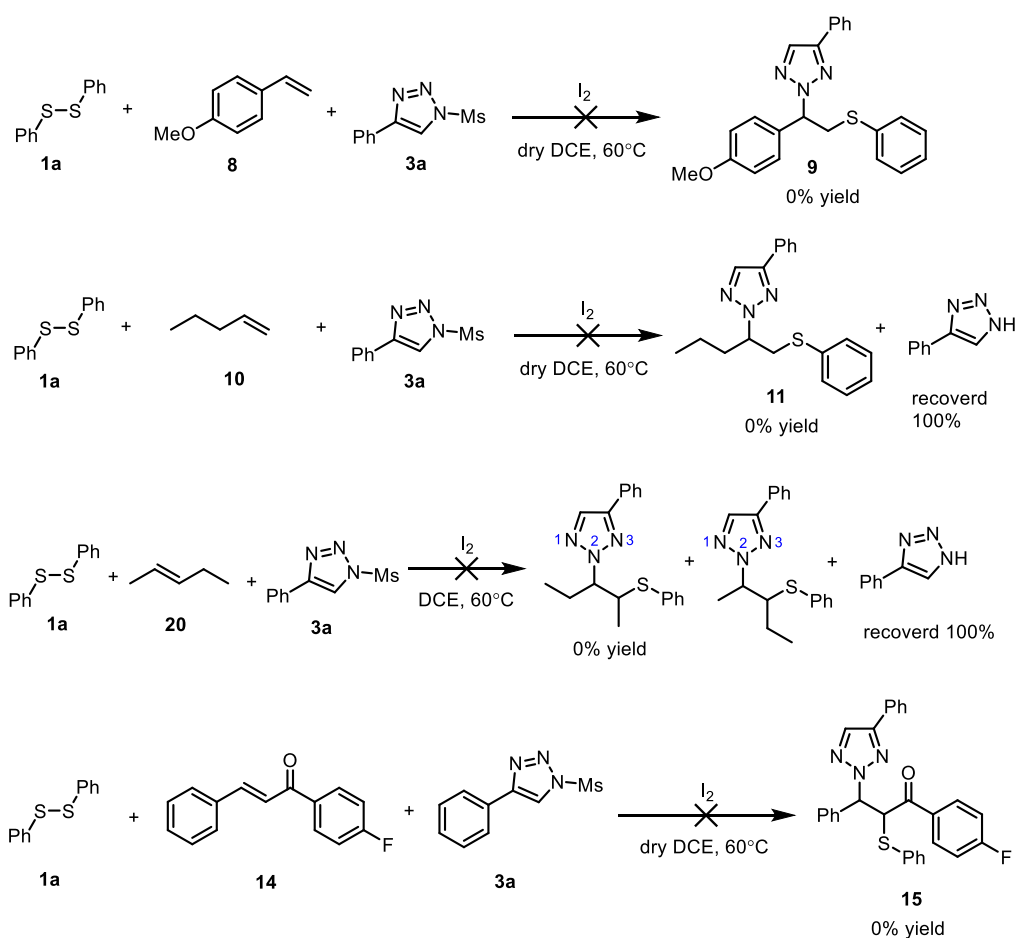


Scheme S1 Acetonitrile to generat a carbon radical intermediate to react with Ms-triazole and the unprotected triazole

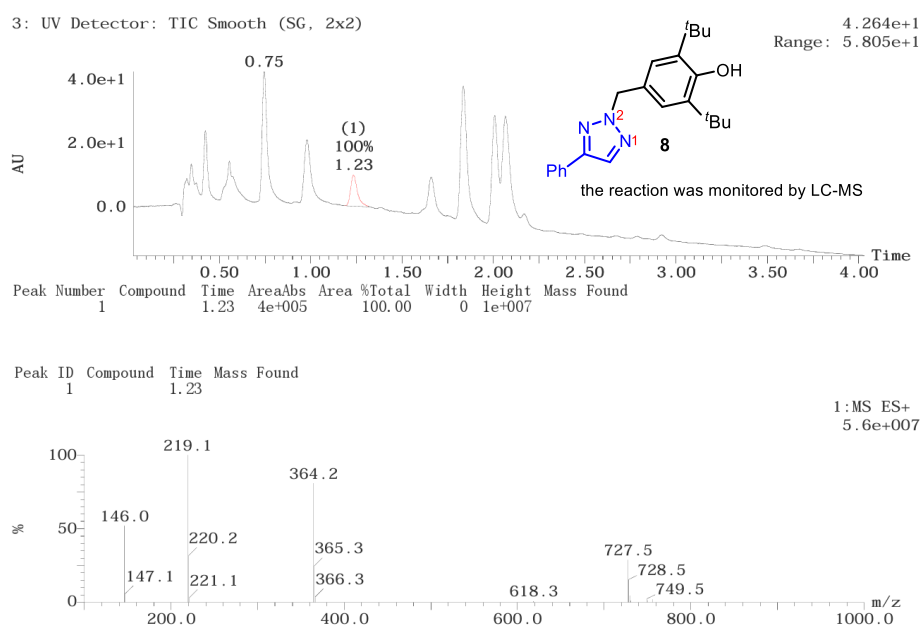


Scheme S2 Using the sulfonyl-1,2,3-triazole without substituent and Ms-tetrazole to test this reaction.

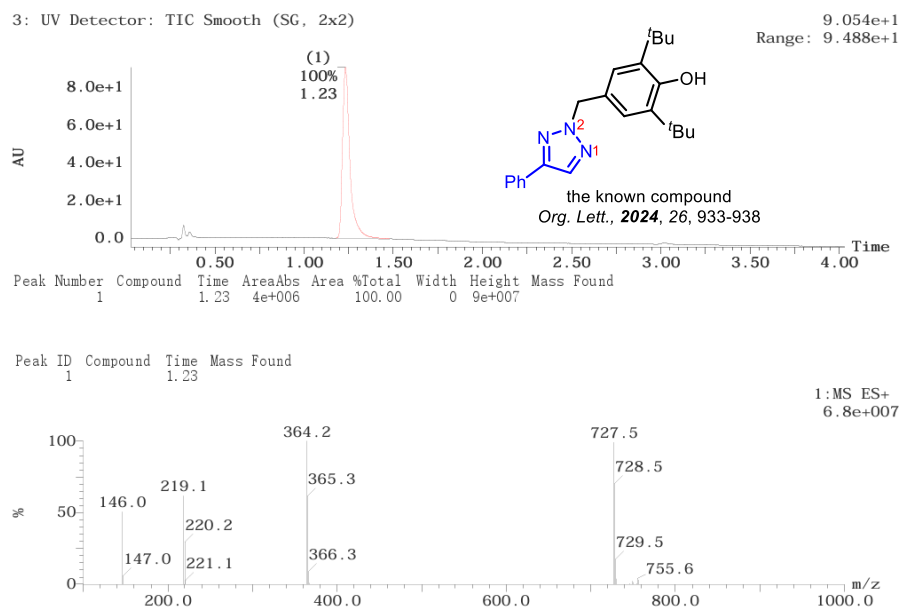
Electronic Supporting Information



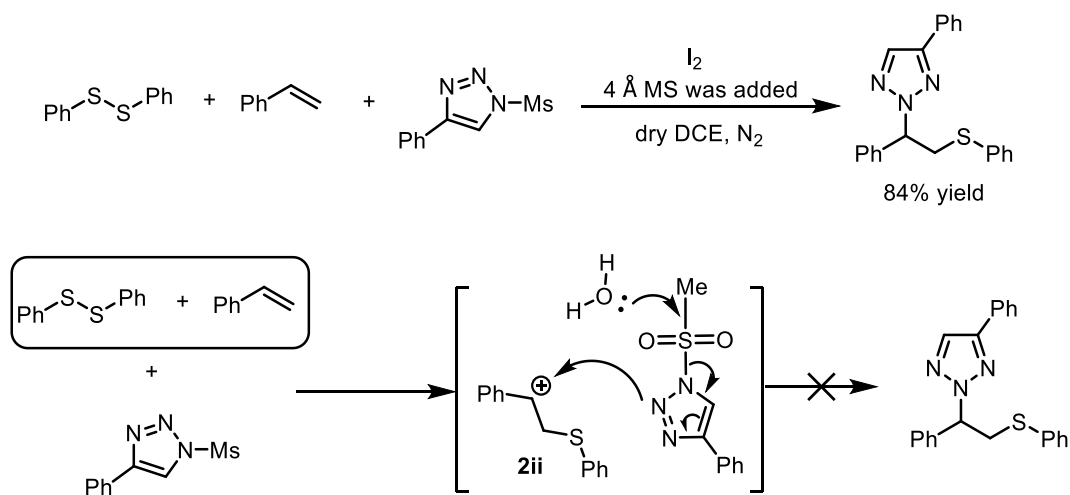
Scheme S3 Using 4-methoxy styrene **8**, 1-pentene **10**, 2-pentene **10**, and chalcone **14** as the raw material to test this reaction.



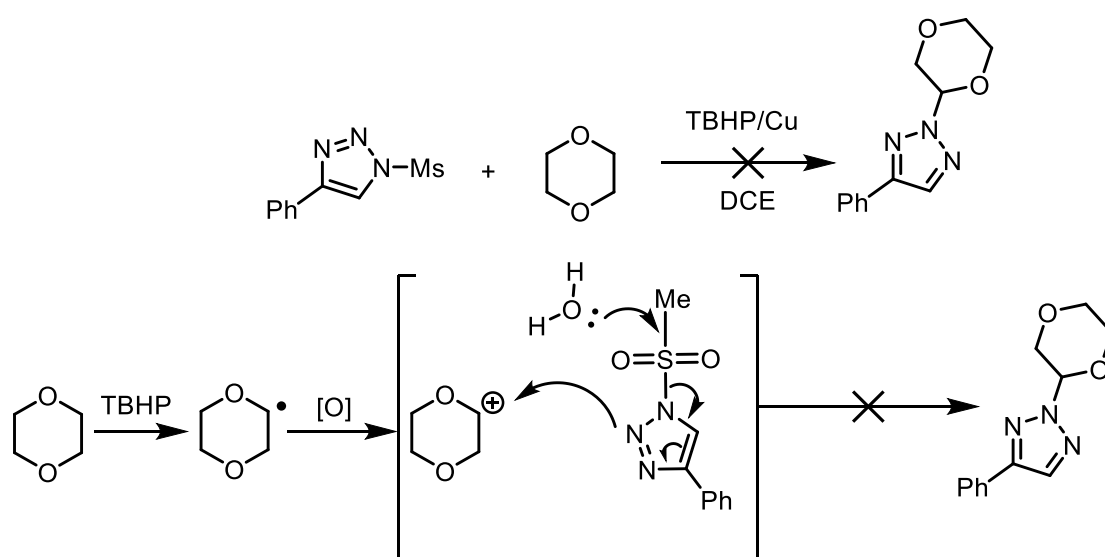
Electronic Supporting Information



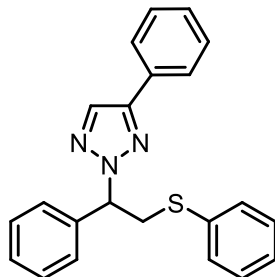
Scheme S4 The LC-MS of product **8**



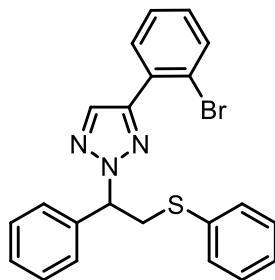
Scheme S5 Exclude the possibility of the reaction of intermediate **2ii** with Ms-triazole



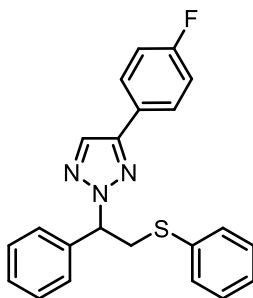
Scheme S6 Using Ms-triazole to react with carbocations

4. ^1H NMR, ^{19}F NMR and ^{13}C NMR data of compounds 4**4-phenyl-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4a)**

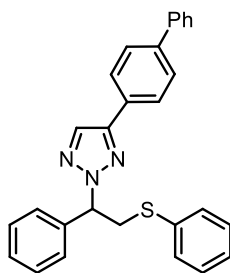
Following the procedure, product **4a** was obtained as a colorless oil. (82% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 7.7 Hz, 6H), 7.28 (dt, J = 15.1, 8.2 Hz, 6H), 7.19 (t, J = 7.2 Hz, 1H), 5.81 – 5.76 (m, 1H), 4.16 – 4.03 (m, 1H), 3.66 (dd, J = 14.1, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.9, 138.3, 134.8, 131.3, 131.2, 130.5, 129.2, 128.9, 128.7, 128.5, 127.1, 127.0, 126.1, 68.5, 40.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 380.1192, Found: 380.1200.

4-(2-bromophenyl)-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4b)

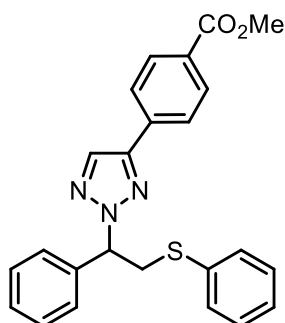
Following the procedure, product **4b** was obtained as a colorless oil. (80% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.73 (dd, J = 7.8, 1.6 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.40 – 7.37 (m, 4H), 7.35 – 7.25 (m, 6H), 7.23 – 7.17 (m, 2H), 5.80 (dd, J = 9.6, 5.5 Hz, 1H), 4.10 (dd, J = 14.1, 9.6 Hz, 1H), 3.67 (dd, J = 14.1, 5.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.9, 141.6, 140.5, 137.2, 134.7, 131.3, 131.2, 130.5, 129.2, 128.8, 128.9, 128.5, 127.6, 127.5, 127.2, 126.1, 68.3, 40.0. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{18}\text{BrN}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 458.0297, Found: 458.0290.

4-(4-fluorophenyl)-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4c)

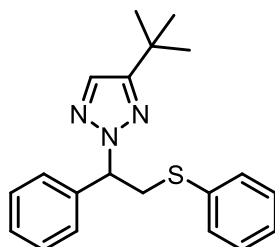
Following the procedure, product **4c** was obtained as a colorless oil. (78% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.72 (dd, J = 8.6, 5.4 Hz, 2H), 7.38 (d, J = 7.5 Hz, 4H), 7.34 – 7.25 (m, 5H), 7.21 (d, J = 7.0 Hz, 1H), 7.08 (t, J = 8.6 Hz, 2H), 5.77 (dd, J = 9.7, 5.3 Hz, 1H), 4.09 (dd, J = 14.1, 9.8 Hz, 1H), 3.65 (dd, J = 14.1, 5.3 Hz, 1H). **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -113.02. **¹³C NMR** (100 MHz, Chloroform-*d*) δ 162.9 (d, J = 247.6 Hz), 147.0, 138.2, 134.7, 131.2, 130.9, 129.2, 128.9, 128.7, 127.8 (d, J = 8.2 Hz), 127.2, 127.0, 126.7 (d, J = 3.3 Hz), 115.8 (d, J = 21.8 Hz), 68.6, 40.0. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for C₂₂H₁₉FN₃S (M+H)⁺ 376.4654, Found: 376.4661.

4-([1,1'-biphenyl]-4-yl)-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4d)

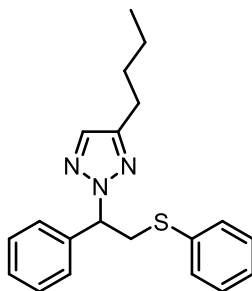
Following the procedure, product **4d** was obtained as a colorless oil. (76% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 8.0 Hz, 4H), 7.41 (dt, J = 23.1, 7.7 Hz, 6H), 7.35 – 7.25 (m, 6H), 7.21 (t, J = 7.1 Hz, 1H), 5.80 (dd, J = 8.9, 5.5 Hz, 1H), 4.11 (dd, J = 13.8, 9.9 Hz, 1H), 3.68 (dd, J = 14.0, 5.1 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.5, 141.2, 140.6, 138.3, 134.8, 131.3, 131.2, 129.4, 129.2, 128.9, 128.8, 128.6, 127.5, 127.2, 127.1, 127.0, 126.5, 68.6, 40.1. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₈H₂₃N₃SNa (M+Na)⁺ 456.1505, Found: 456.1508.

methyl 4-(2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazol-4-yl) benzoate (4e)

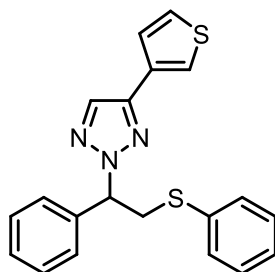
Following the procedure, product **4e** was obtained as a colorless oil. (77% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, J = 8.1 Hz, 2H), 7.90 (s, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 6.1 Hz, 4H), 7.33 – 7.23 (m, 5H), 7.20 (d, J = 7.2 Hz, 1H), 5.80 (dd, J = 9.6, 5.2 Hz, 1H), 4.10 (dd, J = 14.0, 9.9 Hz, 1H), 3.90 (s, 3H), 3.66 (dd, J = 14.1, 5.1 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 166.8, 146.8, 138.1, 134.8, 134.6, 131.8, 131.2, 130.2, 129.8, 129.2, 128.9, 128.7, 127.2, 127.0, 125.9, 68.8, 52.2, 40.02. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₄H₂₁N₃O₂SNa ($M+Na$)⁺ 438.1247, Found: 438.1256.

4-(tert-butyl)-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4f)

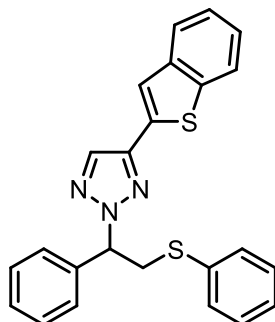
Following the procedure, product **4f** was obtained as a colorless oil. (75% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 4H), 7.29 – 7.25 (m, 3H), 7.22 (d, J = 7.4 Hz, 1H), 5.69 (dd, J = 9.4, 5.6 Hz, 1H), 4.01 (dd, J = 14.0, 9.5 Hz, 1H), 3.61 (dd, J = 14.0, 5.6 Hz, 1H), 1.31 (s, 9H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 157.6, 138.7, 134.9, 131.0, 130.6, 129.1, 128.7, 128.4, 127.0, 126.9, 68.0, 40.2, 30.8, 30.4. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₀H₂₃N₃SNa ($M+Na$)⁺ 360.1505, Found: 360.1515.

4-butyl-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4g)

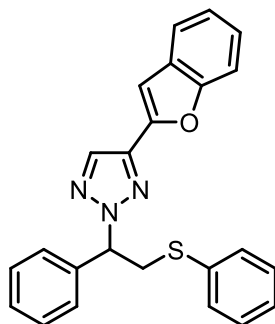
Following the procedure, product **4g** was obtained as a colorless oil. (74% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.37 (d, $J = 7.4$ Hz, 3H), 7.33 – 7.26 (m, 7H), 7.25 – 7.22 (m, 1H), 5.69 (dd, $J = 9.5, 5.6$ Hz, 1H), 4.02 (dd, $J = 14.0, 9.6$ Hz, 1H), 3.61 (dd, $J = 14.0, 5.6$ Hz, 1H), 2.65 (t, $J = 8.0$ Hz, 2H), 1.67 – 1.58 (m, 2H), 1.42 – 1.32 (m, 2H), 0.92 (t, $J = 8.0$ Hz, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 148.8, 138.5, 134.8, 132.7, 131.0, 129.1, 128.7, 128.4, 127.0, 126.9, 67.9, 39.9, 31.3, 25.3, 22.4, 13.8. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{23}N_3SNa$ ($M+Na$) $^+$ 360.1505, Found: 360.1515.

2-(1-phenyl-2-(phenylthio) ethyl)-4-(thiophen-3-yl)-2H-1,2,3-triazole (4h)

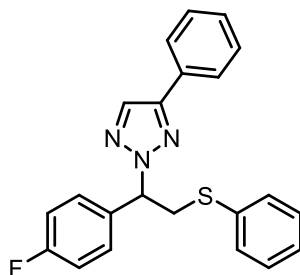
Following the procedure, product **4h** was obtained as a colorless oil. (70% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.40 – 7.34 (m, 6H), 7.33 (s, 1H), 7.30 (d, $J = 6.9$ Hz, 4H), 7.25 (d, $J = 3.9$ Hz, 1H), 7.07 (t, $J = 4.0$, 1H), 5.75 (dd, $J = 9.6, 5.4$ Hz, 1H), 4.07 (dd, $J = 14.1, 9.7$ Hz, 1H), 3.65 (dd, $J = 14.1, 5.4$ Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 143.0, 138.1, 134.6, 132.7, 131.2, 130.9, 129.2, 128.8, 128.6, 127.6, 127.1, 127.0, 125.5, 124.8, 68.5, 39.9. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{17}N_3S_2Na$ ($M+Na$) $^+$ 386.0756, Found: 386.0765.

4-(benzo[b]thiophen-2-yl)-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4i)

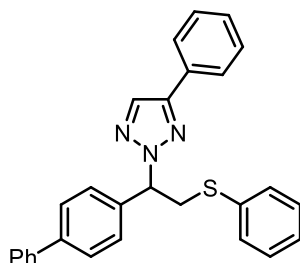
Following the procedure, product **4i** was obtained as a colorless oil. (72% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.77 (d, J = 7.4 Hz, 1H), 7.59 (s, 1H), 7.40 (d, J = 7.1 Hz, 4H), 7.37 – 7.31 (m, 6H), 7.29 (d, J = 7.6 Hz, 2H), 7.25 (s, 1H), 5.78 (dd, J = 9.6, 5.4 Hz, 1H), 4.10 (dd, J = 14.1, 9.7 Hz, 1H), 3.67 (dd, J = 14.1, 5.4 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 142.9, 139.9, 139.5, 137.9, 134.5, 132.8, 131.5, 131.3, 129.2, 128.8, 128.7, 127.2, 127.1, 124.7, 124.6, 123.7, 122.4, 121.1, 68.7, 40.0. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₄H₁₉N₃S₂ ($M+Na$)⁺ 436.0913, Found: 436.0903.

4-(benzofuran-2-yl)-2-(1-phenyl-2-(phenylthio) ethyl)-2H-1,2,3-triazole (4j)

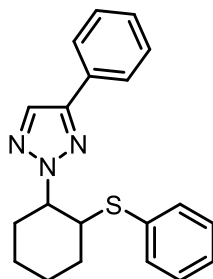
Following the procedure, product **4j** was obtained as a colorless oil. (75% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 7.4 Hz, 4H), 7.35 – 7.26 (m, 6H), 7.24 (d, J = 7.8 Hz, 2H), 7.08 (s, 1H), 5.83 (dd, J = 9.6, 5.4 Hz, 1H), 4.11 (dd, J = 14.1, 9.7 Hz, 1H), 3.69 (dd, J = 14.1, 5.4 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 154.8, 147.7, 140.0, 137.9, 134.4, 132.1, 131.3, 129.2, 128.9, 128.7, 128.5, 127.2, 127.0, 124.8, 123.2, 121.2, 111.4, 103.6, 68.8, 39.9. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₄H₁₉N₃OSNa ($M+Na$)⁺ 420.1141, Found: 420.1142.

2-(1-(4-fluorophenyl)-2-(phenylthio) ethyl)-4-phenyl-2H-1,2,3-triazole (4k)

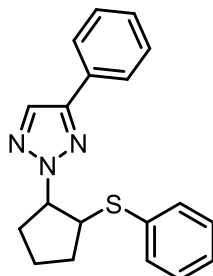
Following the procedure, product **4k** was obtained as a colorless oil. (82% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.76 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.33 (m, 7H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.19 (m, 1H), 6.99 (t, *J* = 8.6 Hz, 2H), 5.76 (dd, *J* = 9.2, 5.9 Hz, 1H), 4.05 (dd, *J* = 14.0, 9.2 Hz, 1H), 3.64 (dd, *J* = 14.0, 5.9 Hz, 1H). **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -112.98. **¹³C NMR** (100 MHz, Chloroform-*d*) δ 162.7 (d, *J* = 247.6 Hz), 147.9, 134.5, 134.0 (d, *J* = 3.2 Hz), 131.3, 131.2, 130.3, 129.2, 129.0 (d, *J* = 8.4 Hz), 128.8, 128.5, 127.2, 126.1, 115.7 (d, *J* = 21.6 Hz), 67.7, 40.1. **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₂H₁₈FN₃SNa (M+Na)⁺ 398.1098, Found: 398.1094.

2-(1-([1,1'-biphenyl]-4-yl)-2-(phenylthio) ethyl)-4-phenyl-2H-1,2,3-triazole (4l)

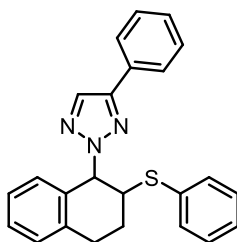
Following the procedure, product **4l** was obtained as a colorless oil. (77% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.50 (m, 4H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.37 (m, 6H), 7.33 (dd, *J* = 7.2, 3.8 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 1H), 5.83 (dd, *J* = 9.5, 5.6 Hz, 1H), 4.12 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.71 (dd, *J* = 14.1, 5.6 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.9, 141.6, 140.5, 137.2, 134.7, 131.3, 131.2, 130.5, 129.2, 128.9, 128.8, 128.5, 127.6, 127.5, 127.2, 126.1, 68.3, 40.0. **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₈H₂₃N₃SNa (M+Na)⁺ 456.1515, Found: 456.1522.

4-phenyl-2-(2-(phenylthio) cyclohexyl)-2H-1,2,3-triazole (4m)

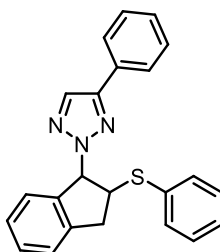
Following the procedure, product **4m** was obtained as a colorless oil. (71% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (s, 1H), 7.73 (d, J = 2.8 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.20 – 7.13 (m, 3H), 4.47 (td, J = 11.3, 4.2 Hz, 1H), 3.64 (td, J = 11.3, 3.9 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.24 – 2.16 (m, 1H), 2.05 (qd, J = 12.6, 3.6 Hz, 1H), 1.91 – 1.78 (m, 2H), 1.57 – 1.31 (m, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.2, 134.0, 132.7, 130.7, 130.5, 128.8, 128.6, 128.2, 127.5, 125.9, 68.3, 51.9, 33.8, 33.4, 25.8, 24.8. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for C₂₀H₂₂N₃S (M+H)⁺ 336.1534, Found: 336.1530. (known product)²

4-phenyl-2-(2-(phenylthio)cyclopentyl)-2H-1,2,3-triazole (4n)

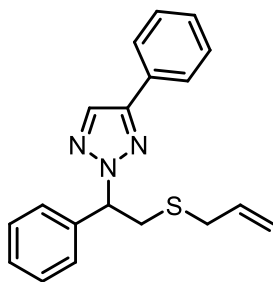
Following the procedure, product **4n** was obtained as a colorless oil. (82% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 7.7 Hz, 3H), 7.41 (t, J = 7.5 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.20 (t, J = 7.4 Hz, 2H), 7.13 (t, J = 7.2 Hz, 1H), 4.95 (q, J = 6.4 Hz, 1H), 4.13 (q, J = 7.2 Hz, 1H), 2.45 – 2.34 (m, 2H), 2.33 – 2.24 (m, 1H), 2.07 – 1.96 (m, 1H), 1.96 – 1.86 (m, 1H), 1.84 – 1.74 (m, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.5, 134.3, 131.6, 130.8, 130.6, 128.8, 128.8, 128.3, 126.9, 125.9, 71.6, 51.9, 31.9, 31.8, 22.8. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₁₉H₁₉N₃SNa (M+Na)⁺ 344.1192, Found: 344.1201.

4-phenyl-2-(2-(phenylthio)-1,2,3,4-tetrahydronaphthalen-1-yl)-2H-1,2,3-triazole (4o)

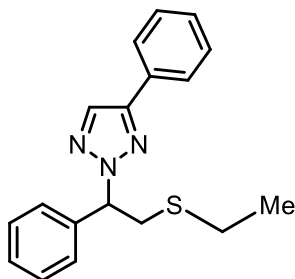
Following the procedure, product **4o** was obtained as a colorless oil. (71% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.69 (d, J = 7.3 Hz, 2H), 7.38 (d, J = 6.8 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.19 – 7.11 (m, 3H), 7.09 – 7.02 (m, 2H), 6.96 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 5.78 (d, J = 8.9 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.05 – 2.94 (m, 1H), 2.88 (dt, J = 17.1, 4.9 Hz, 1H), 2.41 (dq, J = 13.2, 4.8 Hz, 1H), 2.01 – 1.84 (m, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 136.1, 133.9, 133.6, 132.3, 131.3, 130.5, 128.90, 128.9, 128.8, 128.4, 128.1, 127.9, 127.8, 126.6, 126.1, 68.2, 49.2, 28.6, 28.5. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for C₂₄H₂₂N₃S (M+H)⁺ 384.1456, Found: 384.1451.

4-phenyl-2-(2-(phenylthio)-2,3-dihydro-1H-inden-1-yl)-2H-1,2,3-triazole (4p)

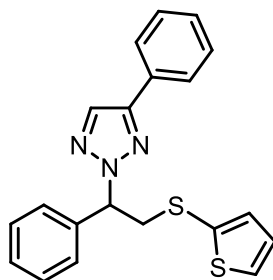
Following the procedure, product **4p** was obtained as a colorless oil. (75% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.42 – 7.38 (m, 4H), 7.34 (d, J = 7.3 Hz, 1H), 7.28 (d, J = 5.2 Hz, 2H), 7.25 – 7.14 (m, 4H), 7.03 (d, J = 7.6 Hz, 1H), 6.13 (d, J = 6.7 Hz, 1H), 4.64 (q, J = 7.4 Hz, 1H), 3.68 (dd, J = 16.2, 8.0 Hz, 1H), 3.10 (dd, J = 16.2, 7.5 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 148.0, 140.9, 139.5, 133.4, 132.4, 131.5, 130.4, 129.2, 129.0, 128.8, 128.5, 127.5, 127.4, 126.0, 124.9, 124.5, 75.1, 51.9, 37.9. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₃H₁₉N₃SSNa (M+Na)⁺ 392.1192, Found: 392.1184.

2-(2-(allylthio)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4q)

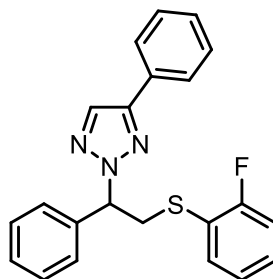
Following the procedure, product **4q** was obtained as a colorless oil. (71% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.37 – 7.29 (m, 4H), 5.84 – 5.75 (m, 2H), 5.16 (d, *J* = 5.3 Hz, 1H), 5.12 (s, 1H), 3.65 (dd, *J* = 14.1, 9.7 Hz, 1H), 3.25 (dd, *J* = 14.1, 5.6 Hz, 1H), 3.08 (dd, *J* = 7.0, 4.4 Hz, 2H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 138.5, 134.2, 131.1, 130.5, 128.8, 128.8, 128.5, 128.4, 127.0, 126.0, 117.7, 69.2, 35.7, 35.1. **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₉H₂₀N₃S (M+H)⁺ 322.1300, Found: 322.1306.

2-(2-(methylthio)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4r)

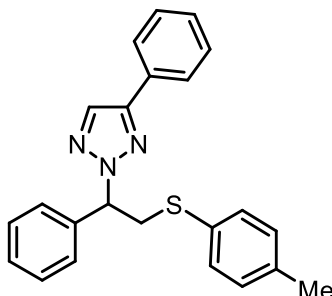
Following the procedure, product **4r** was obtained as a colorless oil. (78% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.27 (m, 4H), 5.82 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.73 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.32 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.47 (q, *J* = 7.4 Hz, 2H), 1.21 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 138.6, 131.2, 130.5, 128.9, 128.8, 128.6, 128.5, 127.1, 126.1, 69.6, 36.9, 26.5, 14.8. **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₁₉N₃SSNa (M+Na)⁺ 332.1192, Found: 332.1194.

4-phenyl-2-(1-phenyl-2-(thiophen-2-ylthio) ethyl)-2H-1,2,3-triazole (4s)

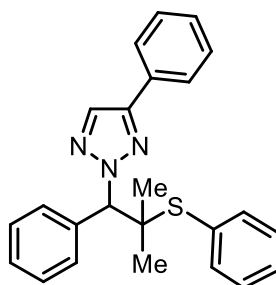
Following the procedure, product **4s** was obtained as a colorless oil. (72% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.38 – 7.27 (m, 7H), 7.13 (d, J = 3.4 Hz, 1H), 6.97 (dd, J = 5.2, 3.7 Hz, 1H), 5.81 (dd, J = 10.0, 5.1 Hz, 1H), 3.97 (dd, J = 14.0, 10.1 Hz, 1H), 3.50 (dd, J = 14.1, 5.1 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 138.1, 135.3, 132.7, 131.3, 130.5, 130.3, 128.8, 128.8, 128.6, 128.5, 127.8, 127.0, 126.1, 68.1, 43.8. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₀H₁₇N₃S ($M+Na$)⁺ 386.0756, Found: 386.0765.

2-(2-((2-fluorophenyl) thio)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4t)

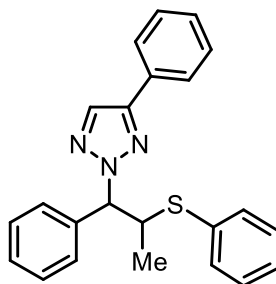
Following the procedure, product **4t** was obtained as a colorless oil. (79% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.34 – 7.25 (m, 5H), 7.22 – 7.15 (m, 1H), 7.01 (q, J = 7.7, 6.8 Hz, 2H), 5.78 (dd, J = 9.8, 5.2 Hz, 1H), 4.10 (dd, J = 14.1, 9.9 Hz, 1H), 3.64 (dd, J = 14.1, 5.2 Hz, 1H). **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -107.85. **¹³C NMR** (100 MHz, Chloroform-*d*) δ 162.2 (d, J = 246.2 Hz), 147.8, 138.2, 134.3 (d, J = 1.3 Hz), 131.2, 130.5, 129.7 (d, J = 8.0 Hz), 128.8, 128.8, 128.6, 128.4, 127.0, 126.0, 124.5 (d, J = 3.8 Hz), 121.3 (d, J = 17.7 Hz), 116.0 (d, J = 22.7 Hz), 69.2, 39.2. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₂H₁₈FN₃SNa ($M+Na$)⁺ 398.1098, Found: 398.1094.

4-phenyl-2-(1-phenyl-2-(p-tolylthio) ethyl)-2H-1,2,3-triazole (4u)

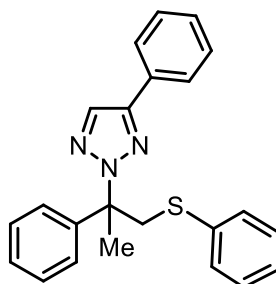
Following the procedure, product **4u** was obtained as a colorless oil. (82% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.75 (d, J = 7.4 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.33 – 7.25 (m, 6H), 7.07 (d, J = 7.9 Hz, 2H), 5.76 (dd, J = 9.7, 5.3 Hz, 1H), 4.05 (dd, J = 14.1, 9.8 Hz, 1H), 3.60 (dd, J = 14.1, 5.3 Hz, 1H), 2.27 (s, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 138.4, 137.4, 132.0, 131.2, 130.9, 130.5, 129.9, 128.8, 128.8, 128.6, 128.4, 127.1, 126.1, 68.6, 40.8, 21.2. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₃H₂₁N₃SSa ($M+Na$)⁺ 394.1348, Found: 394.1357.

2-(2-methyl-1-phenyl-2-(phenylthio) propyl)-4-phenyl-2H-1,2,3-triazole (4v)

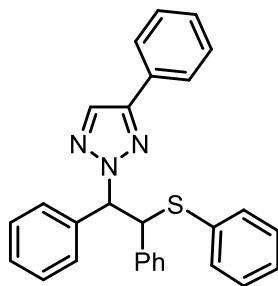
Following the procedure, product **4v** was obtained as a colorless oil. (50% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (d, J = 7.6 Hz, 2H), 7.48 (s, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.13 (s, 5H), 7.08 – 7.00 (m, 5H), 4.78 (s, 1H), 1.92 (s, 3H), 1.64 (s, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 146.5, 138.2, 134.6, 131.5, 130.8, 129.5, 128.8, 128.7, 128.1, 127.9, 127.7, 127.2, 125.7, 118.7, 65.3, 65.0, 26.0, 25.5. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for C₂₄H₂₃N₃SSa ($M+Na$)⁺ 408.1505, Found: 408.1515.

4-phenyl-2-(1-phenyl-2-(phenylthio) propyl)-2H-1,2,3-triazole (4w)

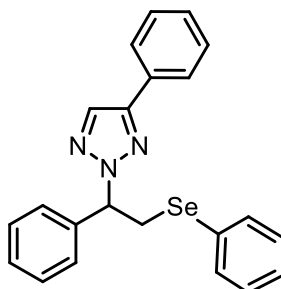
Following the procedure, product **4w** was obtained as a colorless oil. (53% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 7.5 Hz, 2H), 7.62 (s, 1H), 7.39 (t, J = 7.5 Hz, 3H), 7.32 (t, J = 5.4 Hz, 4H), 7.23 – 7.12 (m, 6H), 4.24 (d, J = 13.6 Hz, 1H), 3.92 (d, J = 13.6 Hz, 1H), 2.19 (s, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.5, 142.5, 136.1, 130.7, 130.6, 128.9, 128.8, 128.7, 128.4, 128.1, 126.8, 125.7, 125.6, 119.4, 67.8, 46.7, 26.9. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for C₂₃H₂₂N₃S (M+H)⁺ 372.1456, Found: 372.1448.

4-phenyl-2-(2-phenyl-1-(phenylthio) propan-2-yl)-2H-1,2,3-triazole (4x)

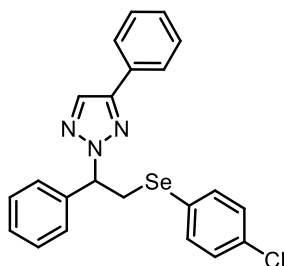
Following the procedure, product **4x** was obtained as a colorless oil. (48% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 7.5 Hz, 2H), 7.62 (s, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 5.5 Hz, 4H), 7.26 (d, J = 4.8 Hz, 2H), 7.23 – 7.13 (m, 5H), 4.24 (d, J = 13.6 Hz, 1H), 3.92 (d, J = 13.6 Hz, 1H), 2.19 (s, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 142.5, 136.0, 130.6, 130.6, 128.9, 128.8, 128.7, 128.4, 128.1, 126.8, 125.7, 125.7, 119.4, 67.8, 46.7, 26.9. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for C₂₃H₂₂N₃S (M+H)⁺ 372.1534, Found: 372.1530. (known product)²

2-(1,2-diphenyl-2-(phenylthio) ethyl)-4-phenyl-2H-1,2,3-triazole (4y)

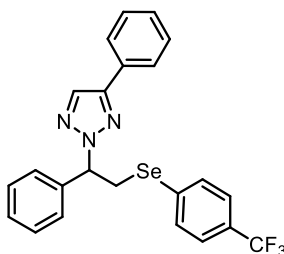
Following the procedure, product **4y** was obtained as a colorless oil. (78% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.74 (m, 2H), 7.62 – 7.59 (m, 2H), 7.54 (s, 1H), 7.34 (t, J = 7.6 Hz, 5H), 7.29 – 7.23 (m, 3H), 7.14 – 7.02 (m, 8H), 6.08 (d, J = 11.6 Hz, 1H), 5.31 (d, J = 11.6 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.4, 138.9, 136.7, 133.7, 133.4, 130.7, 130.4, 128.8, 128.7, 128.6, 128.6, 128.5, 128.3, 128.1, 128.0, 127.7, 127.3, 125.9, 73.2, 58.2. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd for C₂₈H₂₃N₃SSNa (M+Na)⁺ 456.1505, Found: 456.1515.

4-phenyl-2-(1-phenyl-2-(phenylselanyl) ethyl)-2H-1,2,3-triazole (4z)

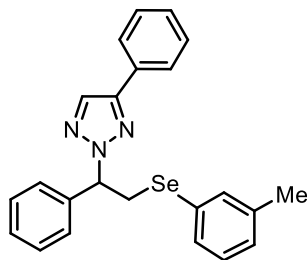
Following the procedure, product **4z** was obtained as a colorless oil. (83% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, J = 1.5 Hz, 1H), 7.79 – 7.75 (m, 2H), 7.53 – 7.49 (m, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.37 – 7.26 (m, 6H), 7.25 – 7.22 (m, 3H), 5.86 – 5.80 (m, 1H), 4.09 – 4.01 (m, 1H), 3.66 – 3.57 (m, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 138.9, 133.9, 131.2, 130.5, 129.2, 129.2, 128.9, 128.8, 128.6, 128.5, 127.7, 126.9, 126.1, 69.4, 32.9. **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₂₂H₂₀N₃Se (M+H)⁺ 406.0766, Found: 406.0760.

2-(2-((4-chlorophenyl) selanyl)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4aa)

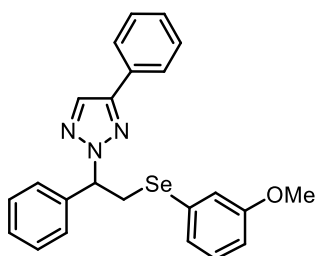
Following the procedure, product **4aa** was obtained as a colorless oil. (81% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.75 (d, J = 7.5 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.36 – 7.26 (m, 6H), 7.18 (d, J = 8.2 Hz, 2H), 5.81 (dd, J = 9.9, 5.3 Hz, 1H), 4.03 (dd, J = 12.7, 10.3 Hz, 1H), 3.58 (dd, J = 13.1, 5.3 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 138.7, 135.4, 134.0, 131.2, 130.3, 129.3, 128.8, 128.6, 128.5, 127.1, 126.9, 126.0, 69.4, 33.2. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $C_{22}H_{18}ClN_3SeNa$ ($M+Na$)⁺ 462.0247, Found: 462.0249.

4-phenyl-2-(1-phenyl-2-((4-(trifluoromethyl) phenyl) selanyl) ethyl)-2H-1,2,3-triazole (4ab)

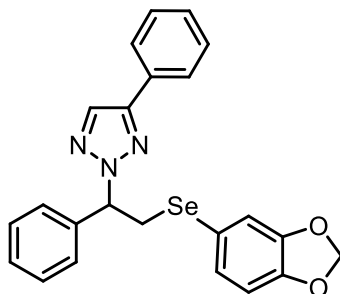
Following the procedure, product **4ab** was obtained as a colorless oil. (55% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.75 (d, J = 7.4 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.47 – 7.29 (m, 10H), 5.86 (dd, J = 9.8, 5.3 Hz, 1H), 4.12 (dd, J = 12.9, 10.1 Hz, 1H), 3.68 (dd, J = 13.1, 5.3 Hz, 1H). **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -62.69. **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 138.5, 134.4, 132.9, 131.2, 130.2, 129.6, 129.2, 128.9, 128.8, 128.7, 128.5, 126.8, 125.9, 125.8 (q, J = 3.6 Hz), 69.5, 32.6. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for $C_{23}H_{19}F_3N_3Se$ ($M+H$)⁺ 474.0618, Found: 474.0610.

4-phenyl-2-(1-phenyl-2-(m-tolylselanyl) ethyl)-2H-1,2,3-triazole (4ac)

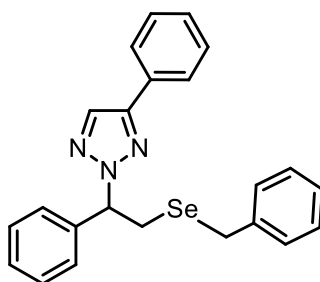
Following the procedure, product **4ac** was obtained as a colorless oil. (85% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.76 (d, $J = 7.7$ Hz, 2H), 7.42 – 7.26 (m, 10H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 1H), 5.84 (dd, $J = 9.7, 5.6$ Hz, 1H), 4.04 (dd, $J = 12.6, 10.1$ Hz, 1H), 3.61 (dd, $J = 13.0, 5.5$ Hz, 1H), 2.27 (s, 3H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 147.7, 139.0, 138.9, 134.5, 131.1, 130.8, 130.5, 129.0, 128.9, 128.8, 128.8, 128.5, 128.4, 128.4, 126.9, 126.0, 69.5, 32.8, 21.3. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{23}H_{21}N_3SeNa$ ($M+Na$) $^+$ 442.0793, Found: 442.0789.

2-(2-((3-methoxyphenyl) selanyl)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4ad)

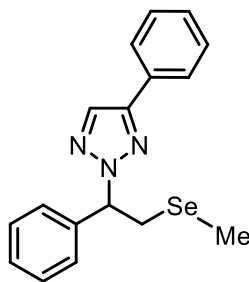
Following the procedure, product **4ad** was obtained as a colorless oil. (78% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.77 (d, $J = 7.6$ Hz, 2H), 7.44 – 7.27 (m, 9H), 7.16 (t, $J = 7.8$ Hz, 1H), 7.09 (d, $J = 7.5$ Hz, 1H), 6.78 (d, $J = 8.1$ Hz, 1H), 5.85 (dd, $J = 9.8, 5.4$ Hz, 1H), 4.05 (dd, $J = 12.7, 10.2$ Hz, 1H), 3.74 (s, 3H), 3.62 (dd, $J = 13.2, 5.2$ Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 159.7, 147.7, 138.9, 131.2, 130.4, 130.1, 130.0, 128.8, 128.8, 128.6, 128.4, 126.9, 126.0, 125.8, 119.0, 113.5, 69.4, 55.3, 32.8. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $C_{23}H_{21}N_3OSeNa$ ($M+Na$) $^+$ 458.0742, Found: 458.0739.

2-(2-(benzo[d][1,3] dioxol-5-ylselanyl)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4ae)

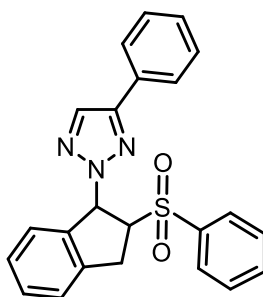
Following the procedure, product **4ae** was obtained as a colorless oil. (68% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.42 – 7.25 (m, 8H), 7.03 – 6.97 (m, 2H), 6.67 (d, J = 7.9 Hz, 1H), 5.84 (s, 2H), 5.83 – 5.79 (m, 1H), 4.02 – 3.94 (m, 1H), 3.51 (dd, J = 13.0, 5.3 Hz, 1H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 148.0, 147.9, 147.7, 138.9, 131.1, 130.5, 129.1, 128.9, 128.8, 128.5, 128.4, 126.9, 126.0, 119.9, 115.3, 109.1, 101.3, 69.5, 33.9. **HRMS** (ESI) m/z : [M+Na]⁺ Calcd for C₂₃H₁₉N₃O₂SeNa (M+Na)⁺ 472.0535, Found: 472.0529.

2-(2-(benzylselanyl)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4af)

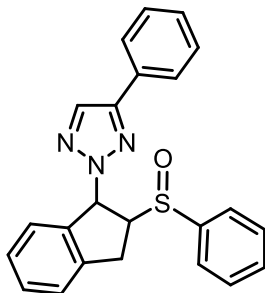
Following the procedure, product **4af** was obtained as a colorless oil. (85% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.6 Hz, 2H), 7.57 (s, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.35 – 7.24 (m, 11H), 5.40 (t, J = 7.5 Hz, 1H), 3.69 (s, 2H), 3.64 (dd, J = 13.3, 8.7 Hz, 1H), 3.27 (dd, J = 13.2, 6.5 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 147.5, 138.9, 138.3, 130.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.2, 127.1, 127.0, 125.7, 119.6, 66.1, 28.3, 28.1. **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₂₃H₂₂N₃Se (M+H)⁺ 420.0901, Found: 420.0909.

2-(2-(methylselanyl)-1-phenylethyl)-4-phenyl-2H-1,2,3-triazole (4ag)

Following the procedure, product **4ag** was obtained as a colorless oil. (86% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.79 (d, J = 7.9 Hz, 2H), 7.46 – 7.38 (m, 4H), 7.36 – 7.28 (m, 4H), 5.86 (dd, J = 9.1, 6.3 Hz, 1H), 3.71 (dd, J = 12.9, 9.6 Hz, 1H), 3.31 (dd, J = 13.0, 6.0 Hz, 1H), 1.91 (s, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 147.7, 138.9, 131.1, 130.5, 128.8, 128.8, 128.5, 128.4, 127.0, 126.0, 70.0, 29.8, 5.1. **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $C_{17}H_{17}N_3SeNa$ ($M+Na$) $^+$ 366.0480, Found: 366.0482.

4-phenyl-2-(2-(phenylsulfonyl)-2,3-dihydro-1H-inden-1-yl)-2H-1,2,3-triazole (6)

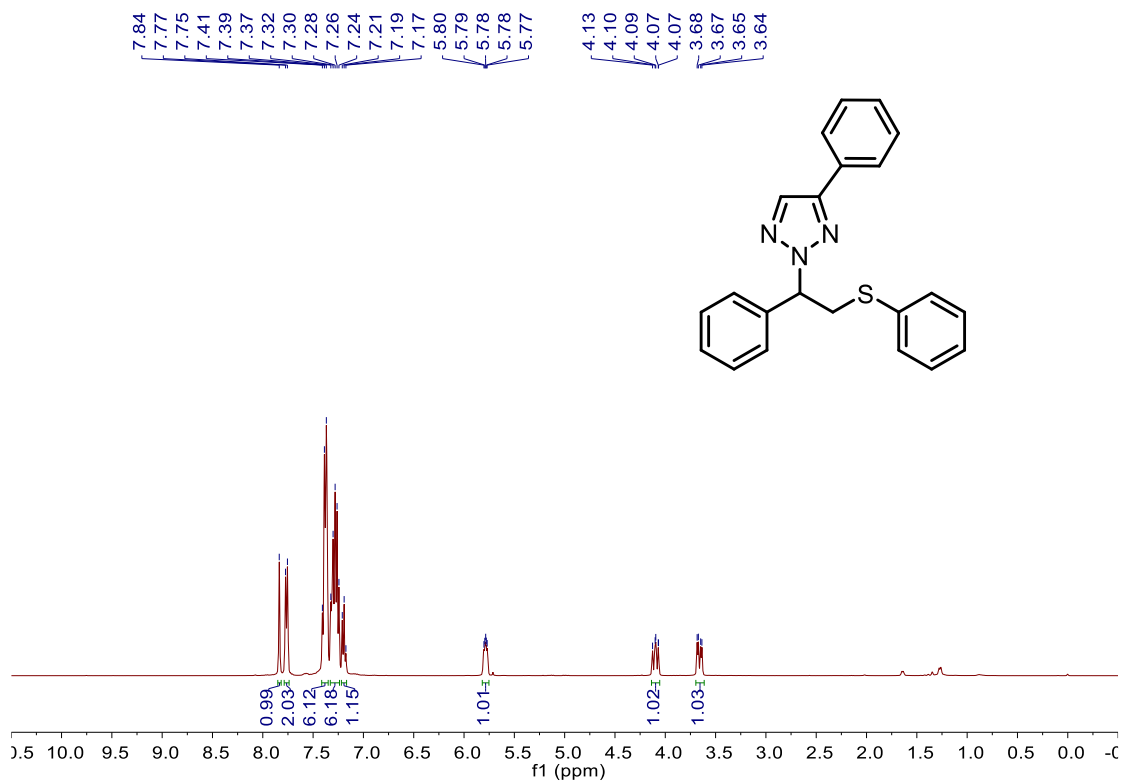
Product **6** was obtained as a white solid. (90% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 7.3 Hz, 2H), 7.62 (d, J = 8.7 Hz, 3H), 7.45 – 7.29 (m, 9H), 6.94 (d, J = 7.6 Hz, 1H), 6.57 (d, J = 7.6 Hz, 1H), 5.01 (q, J = 8.3 Hz, 1H), 3.74 (dd, J = 16.3, 8.4 Hz, 1H), 3.63 (dd, J = 16.4, 9.1 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 148.0, 138.5, 137.8, 133.8, 131.6, 129.9, 129.7, 129.1, 128.8, 128.6, 128.4, 127.9, 125.9, 125.0, 123.9, 69.9, 68.2, 31.1. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_2S$ ($M+H$) $^+$ 402.1198, Found: 402.1190.

4-phenyl-2-(2-(phenylsulfinyl)-2,3-dihydro-1H-inden-1-yl)-2H-1,2,3-triazole (7)

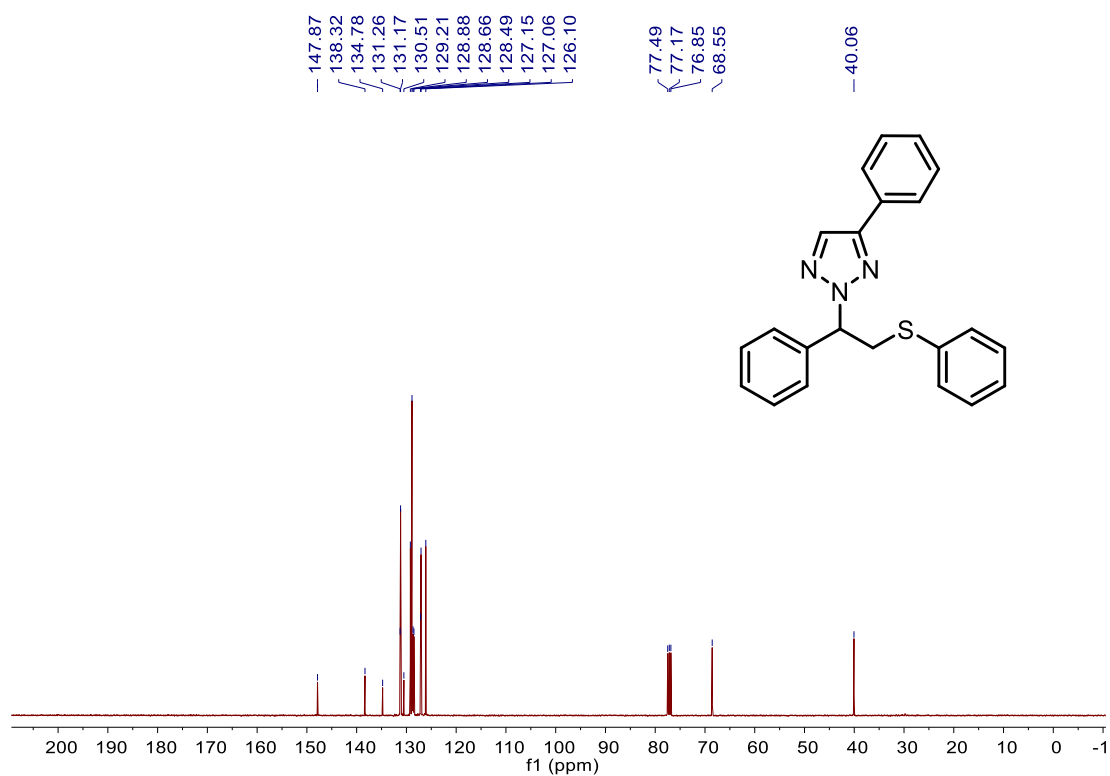
Product **7** was obtained as a white solid. (85% yield). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.1 Hz, 2H), 7.51 – 7.41 (m, 5H), 7.40 – 7.33 (m, 1H), 7.28 – 7.14 (m, 3H), 7.06 (d, J = 7.6 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 4.46 (q, J = 8.2 Hz, 1H), 3.59 (dd, J = 16.4, 8.1 Hz, 1H), 2.96 (dd, J = 16.4, 8.8 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 148.3, 141.8, 139.7, 138.7, 131.8, 131.2, 130.1, 129.4, 129.2, 128.9, 128.6, 127.6, 126.0, 125.0, 124.3, 124.2, 69.1, 68.6, 27.8. **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for C₂₃H₂₀N₃OS ($M+H$)⁺ 386.1249, Found: 386.1241.

5. ^1H , ^{19}F and ^{13}C NMR Spectra of products 4

^1H NMR (400 MHz, CDCl_3) spectrum for 4a

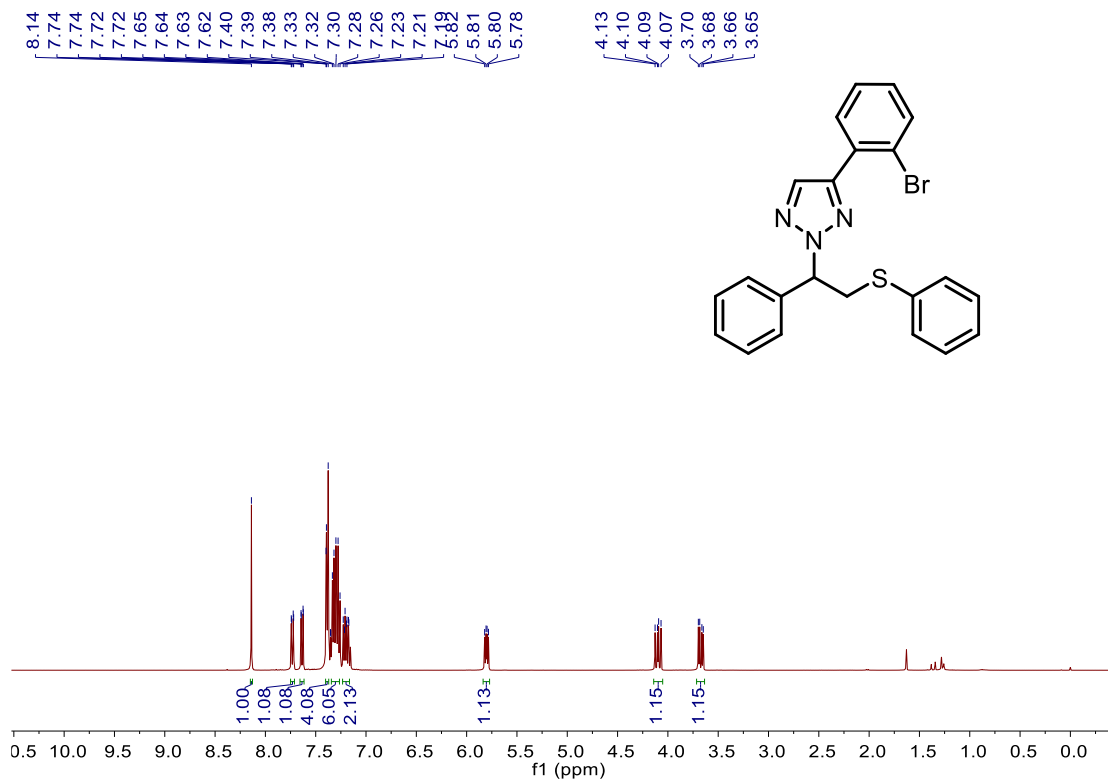


^{13}C NMR (100 MHz, CDCl_3) spectrum for 4a

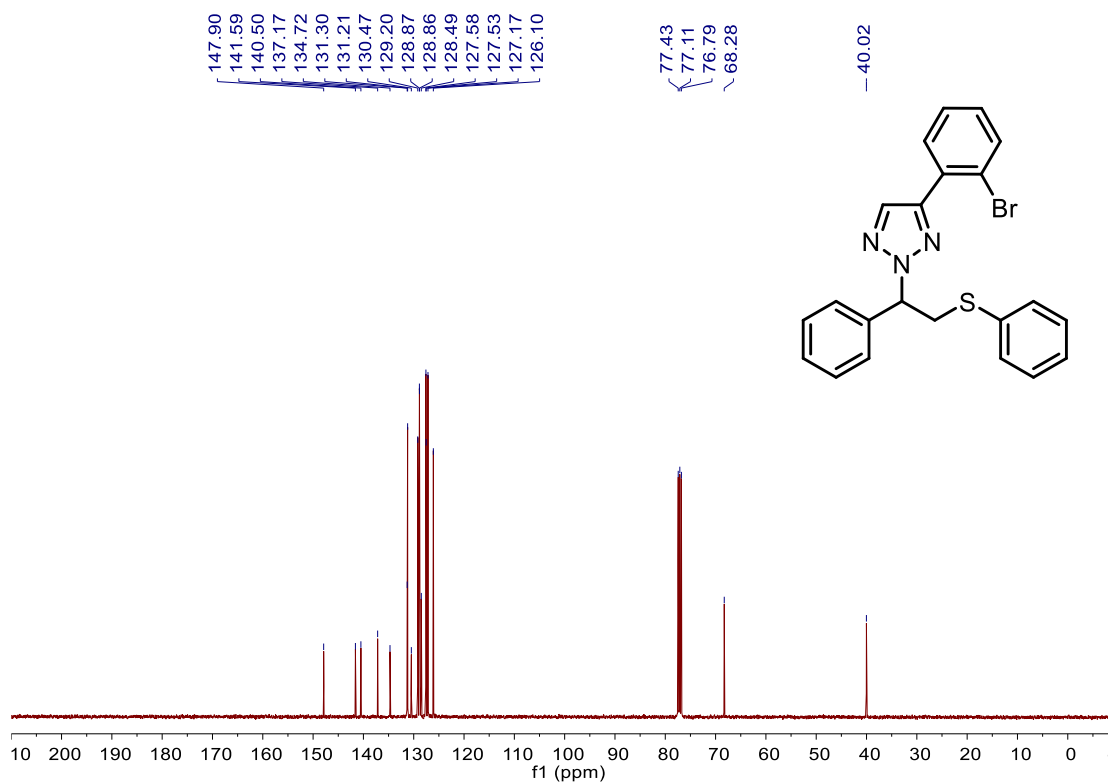


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4b**

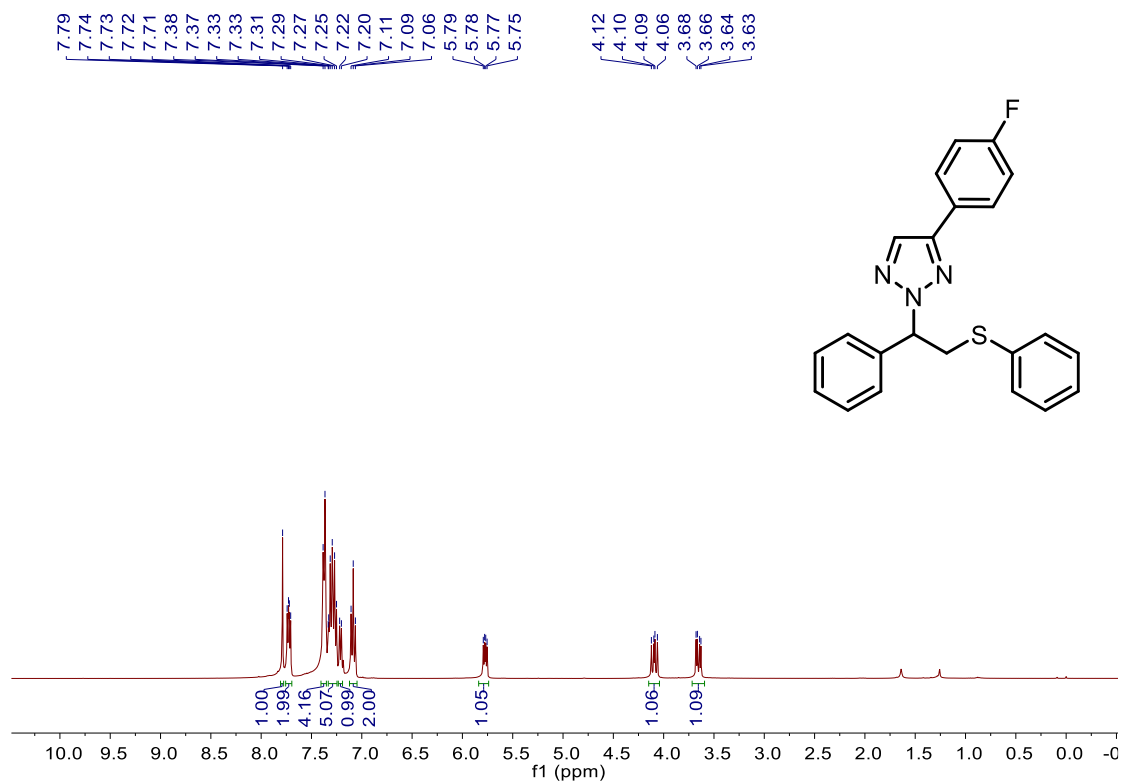


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4b**

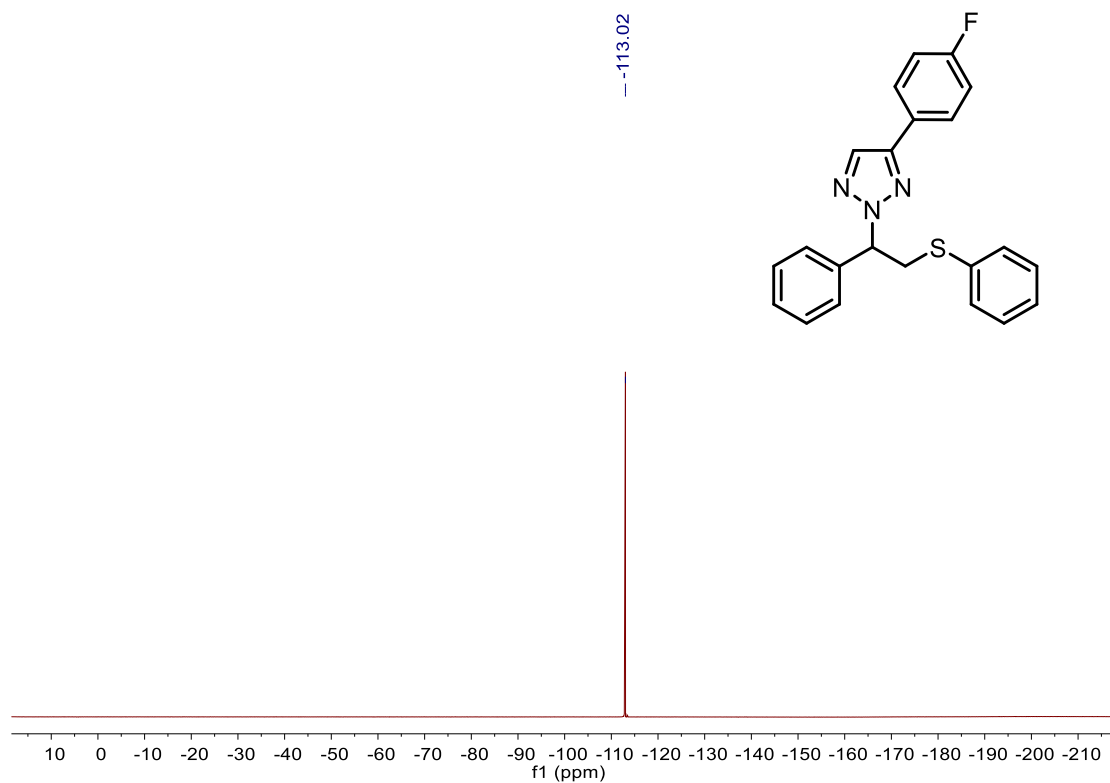


Electronic Supporting Information

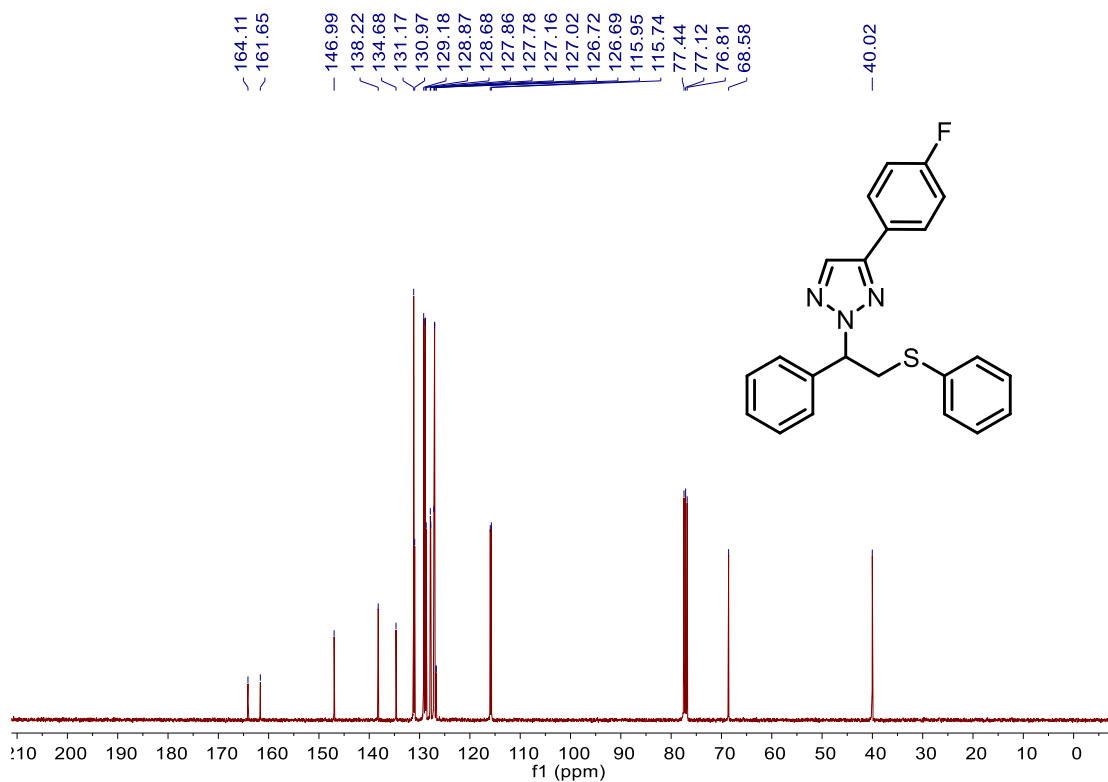
^1H NMR (400 MHz, CDCl_3) spectrum for **4c**



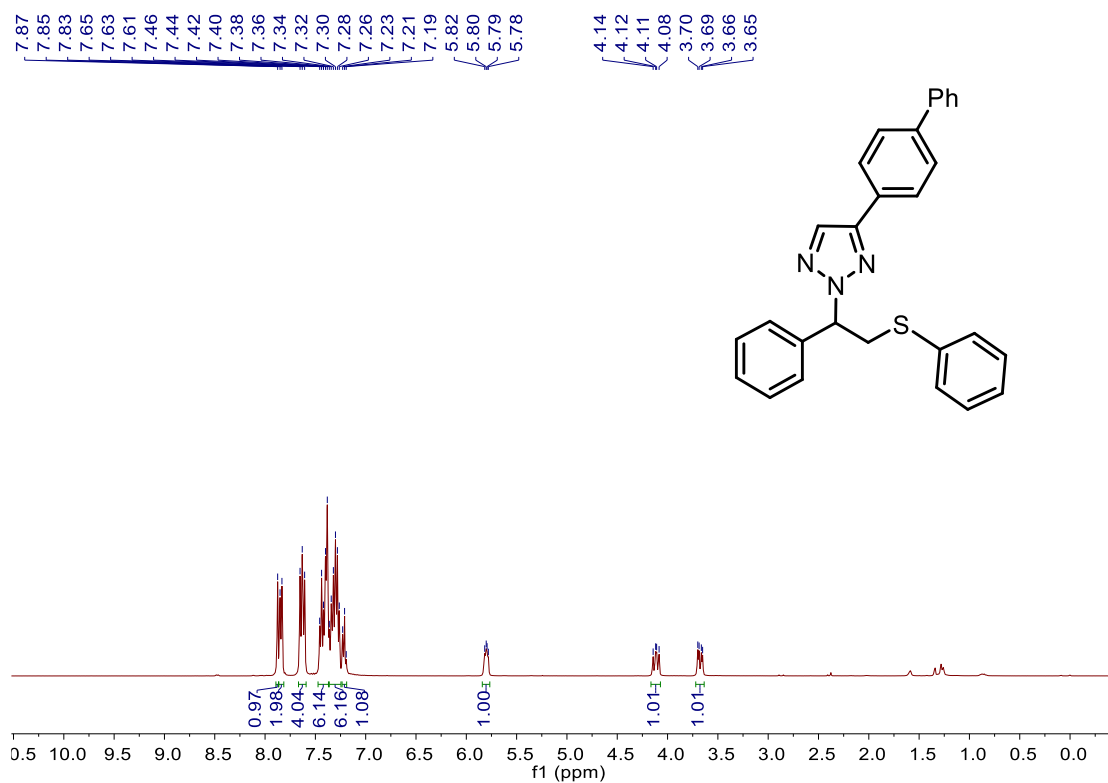
^{19}F NMR (376 MHz, CDCl_3) spectrum for **4c**



^{13}C NMR (100 MHz, CDCl_3) spectrum for **4c**

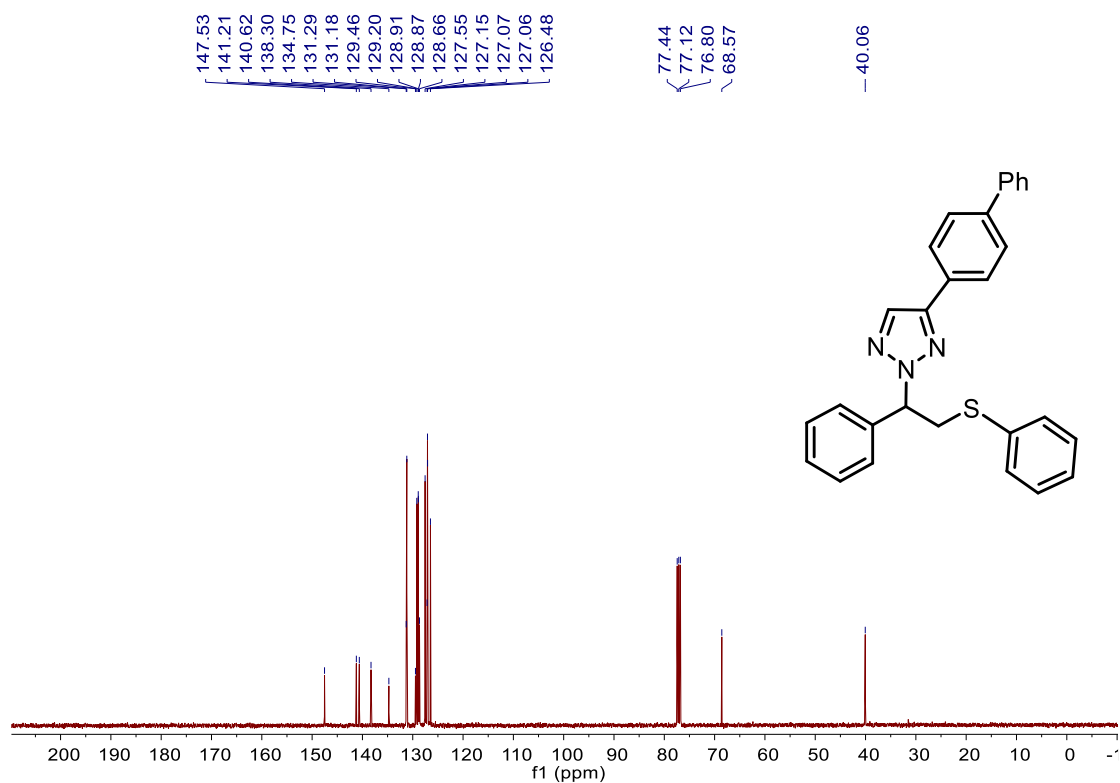


^1H NMR (400 MHz, CDCl_3) spectrum for **4d**

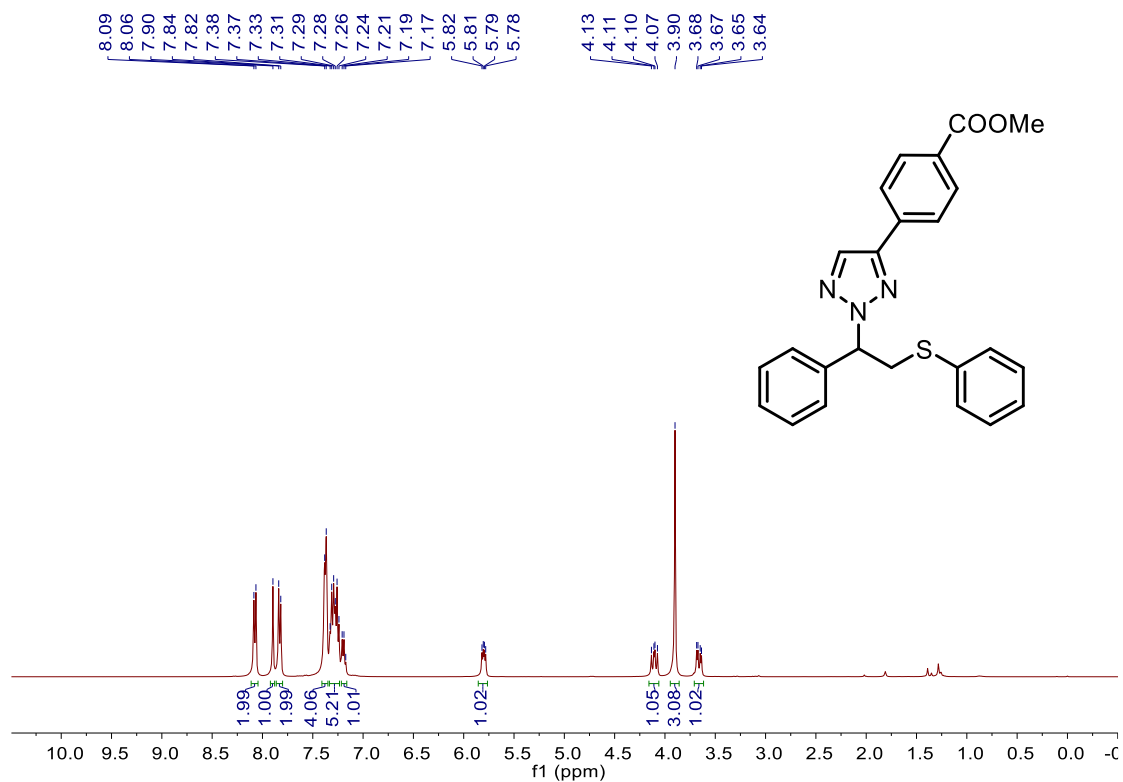


Electronic Supporting Information

^{13}C NMR (100 MHz, CDCl_3) spectrum for **4d**

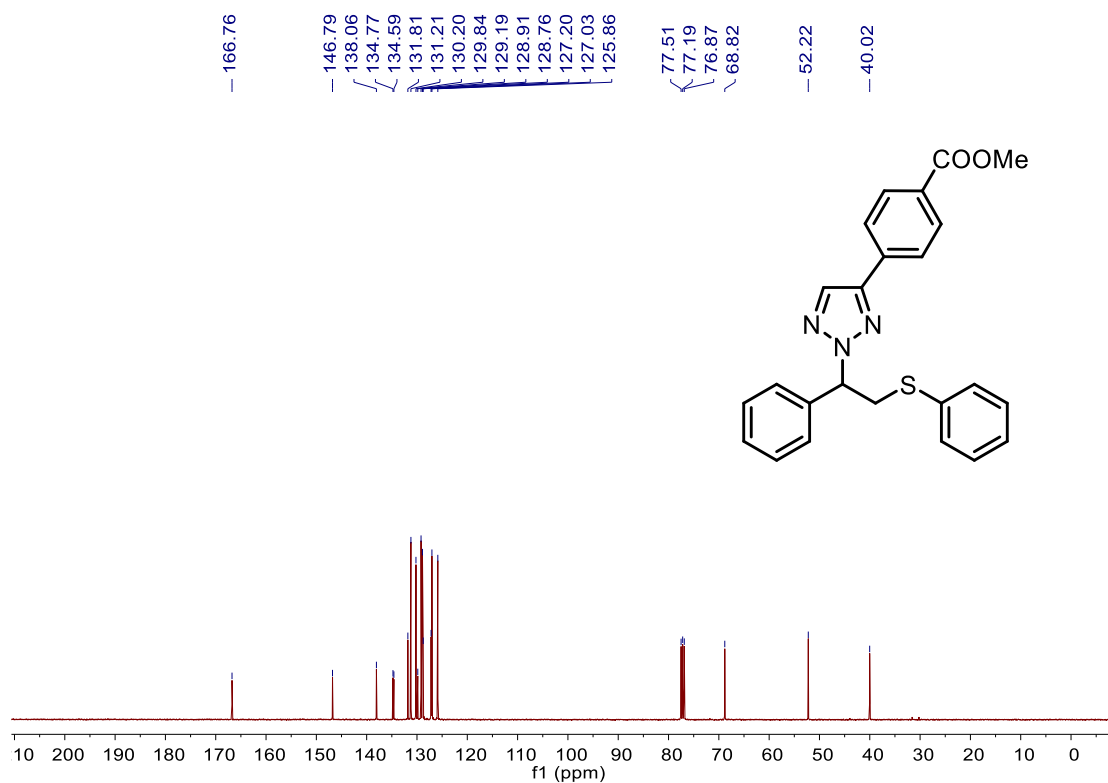


^1H NMR (400 MHz, CDCl_3) spectrum for **4e**

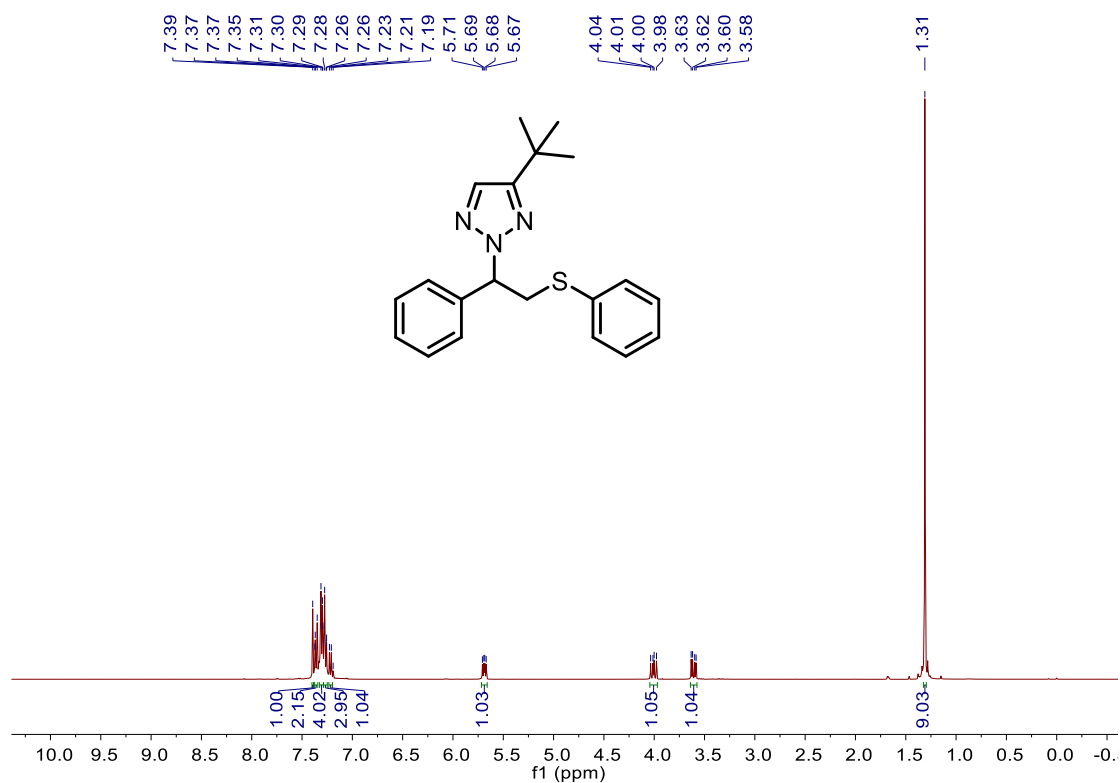


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for 4e

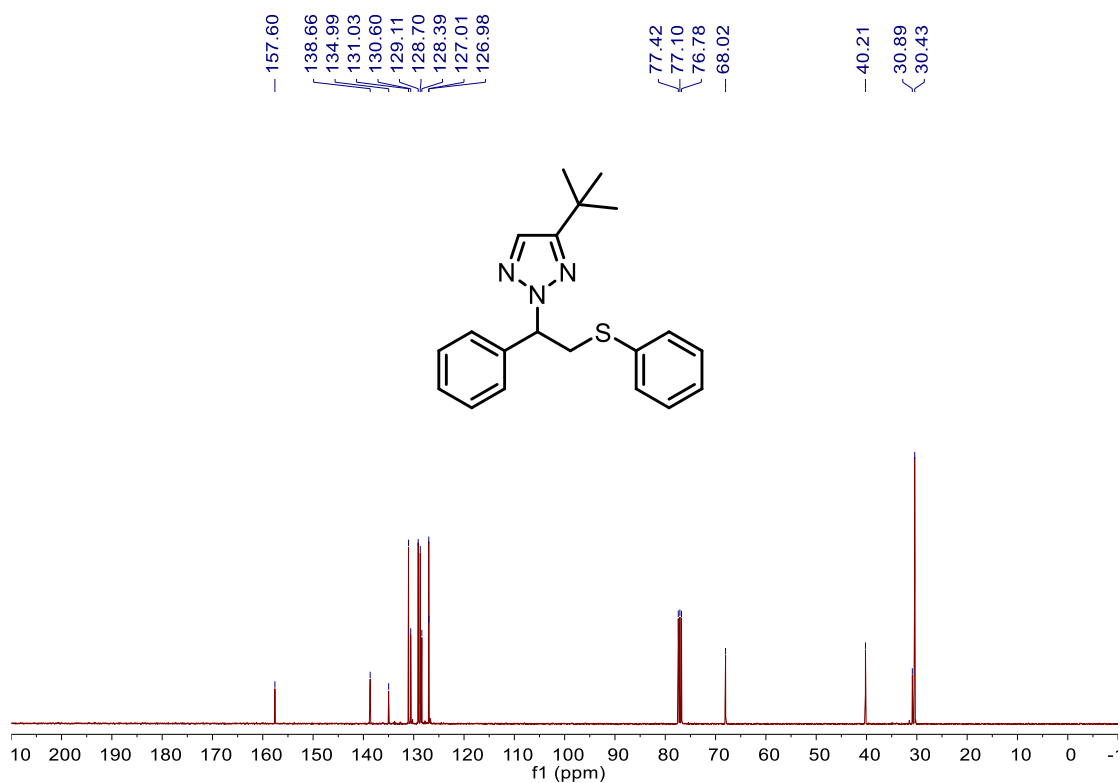


¹H NMR (400 MHz, CDCl₃) spectrum for 4f

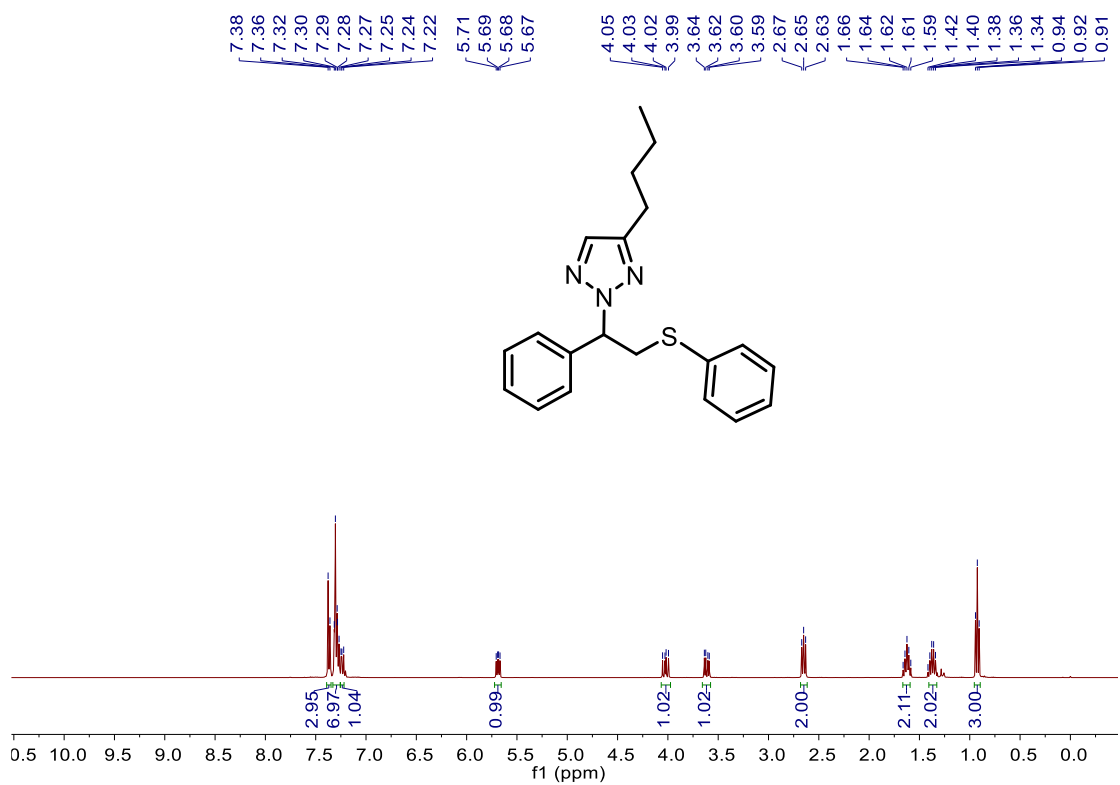


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for **4f**

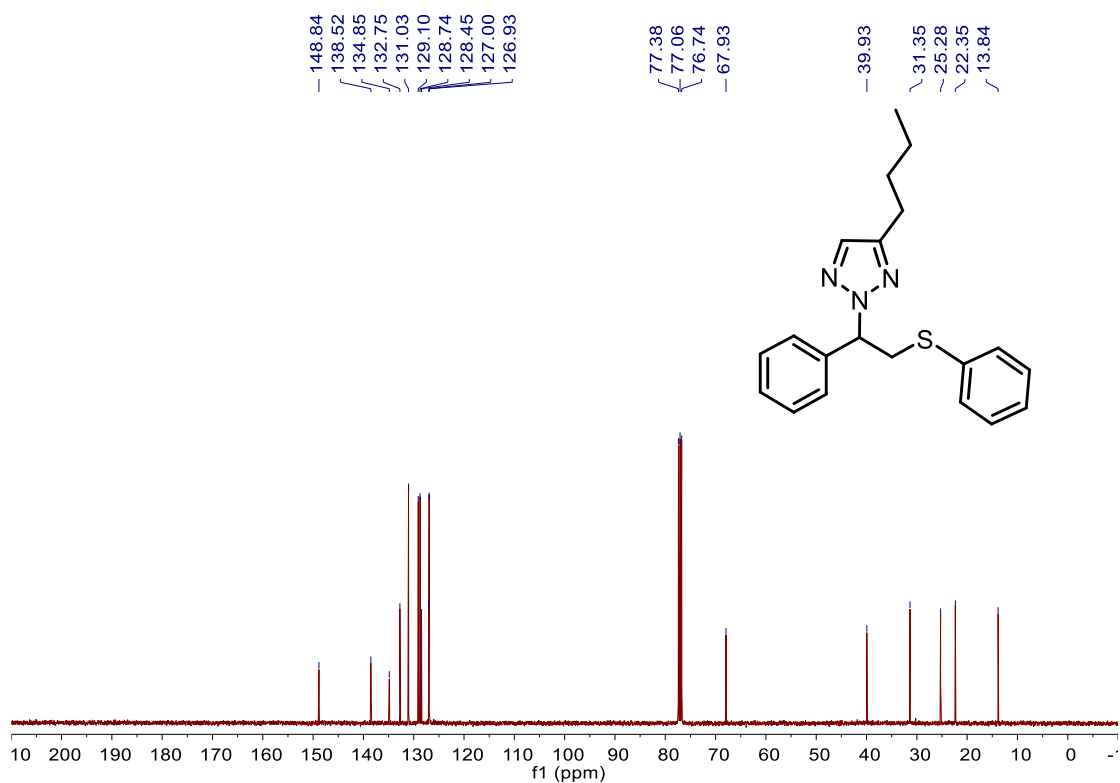


¹H NMR (400 MHz, CDCl₃) spectrum for **4g**

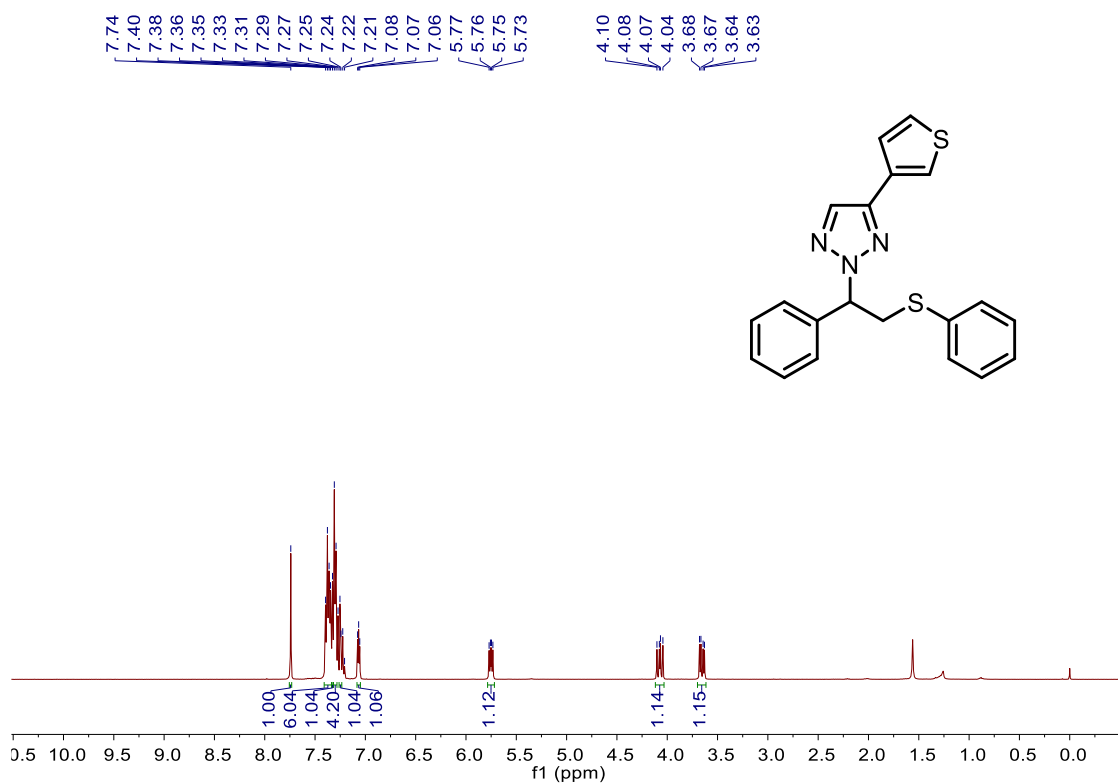


Electronic Supporting Information

^{13}C NMR (100 MHz, CDCl_3) spectrum for **4g**

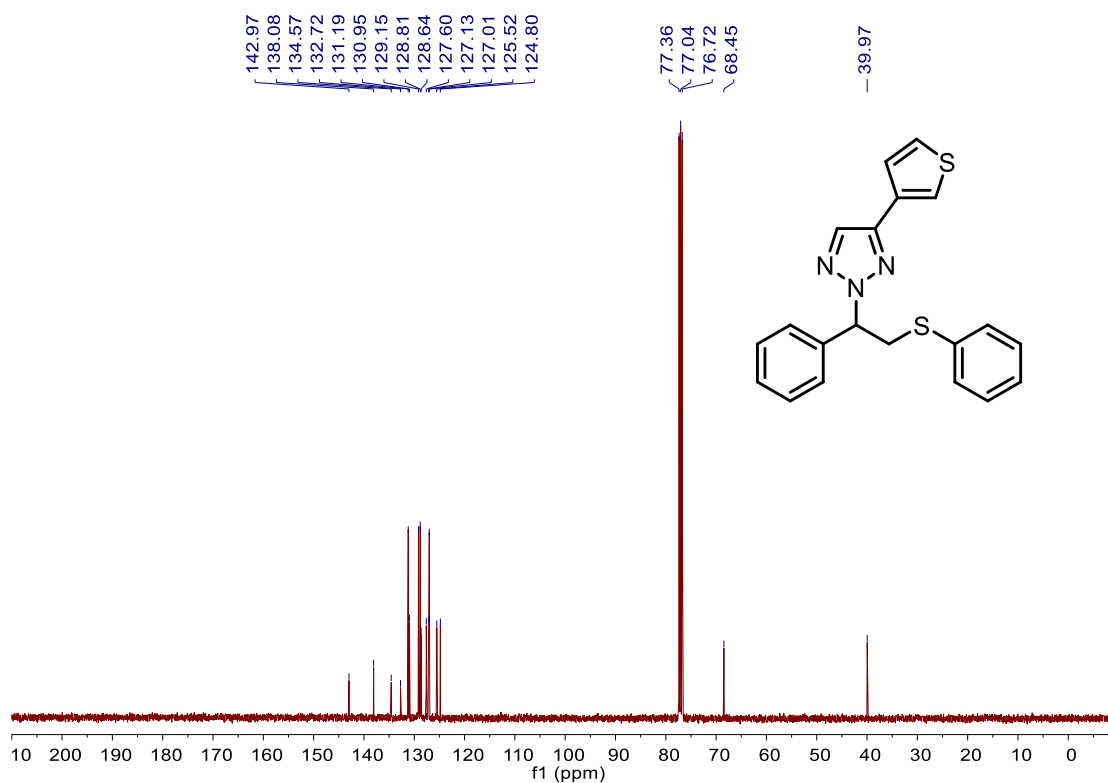


^1H NMR (400 MHz, CDCl_3) spectrum for **4h**

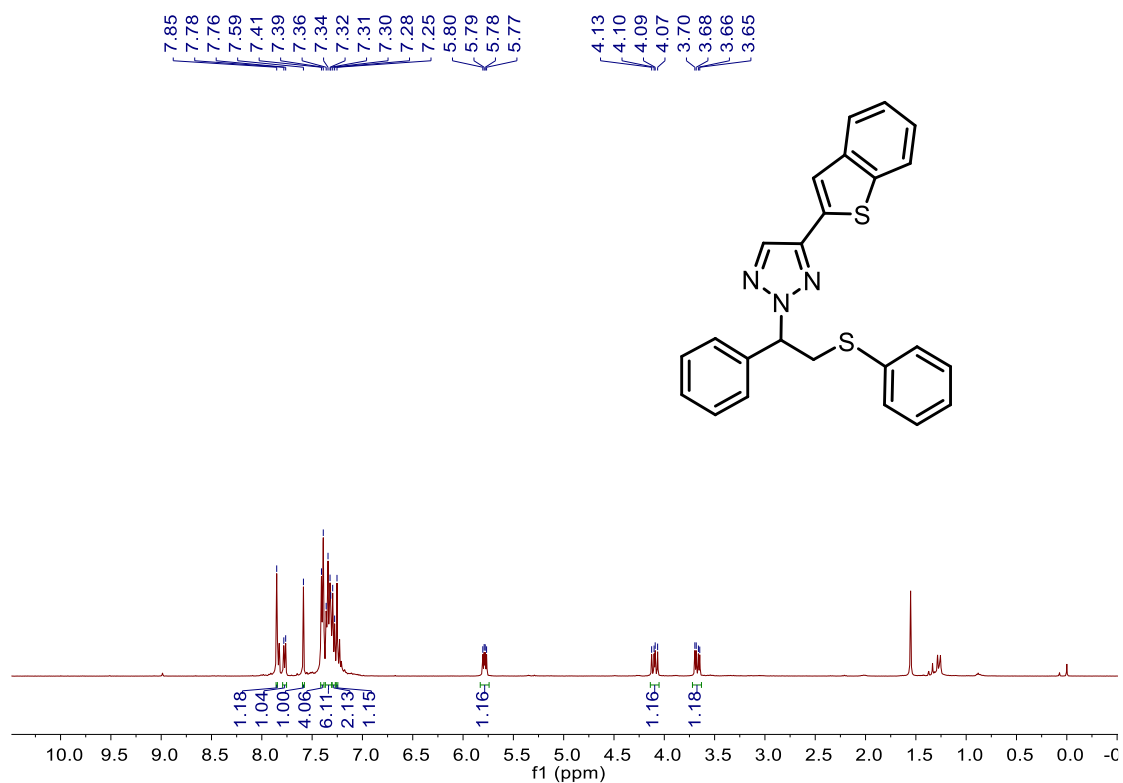


Electronic Supporting Information

^{13}C NMR (100 MHz, CDCl_3) spectrum for **4h**

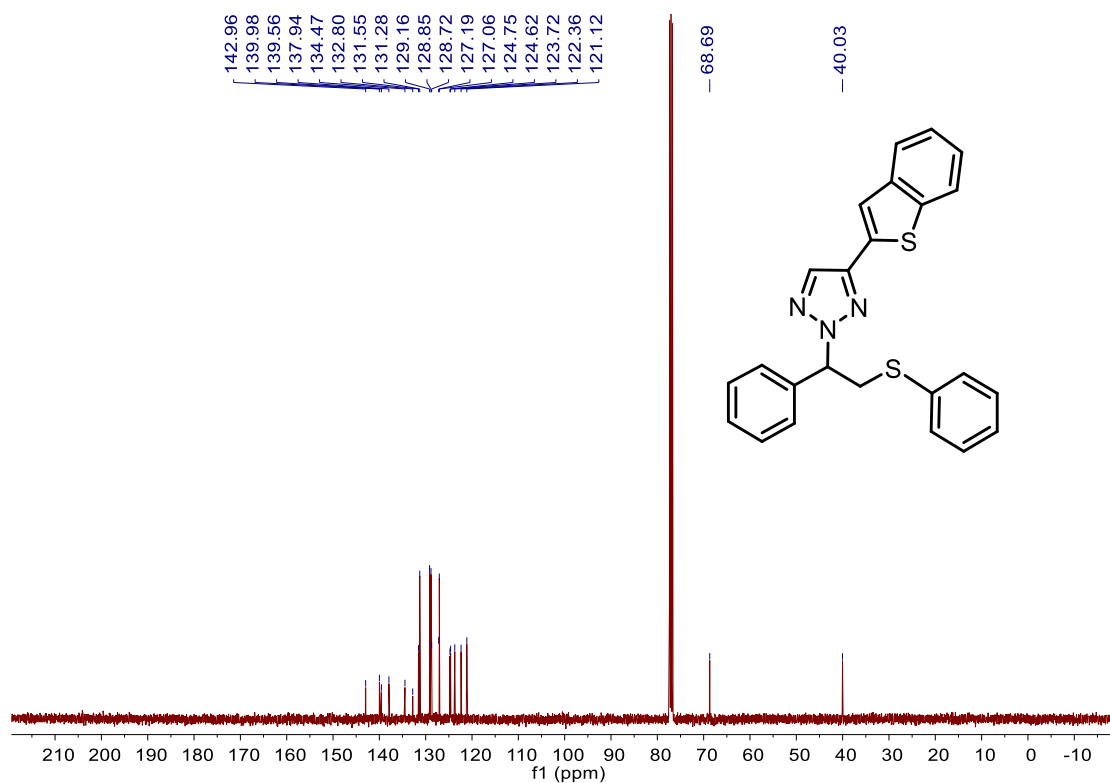


^1H NMR (400 MHz, CDCl_3) spectrum for **4i**

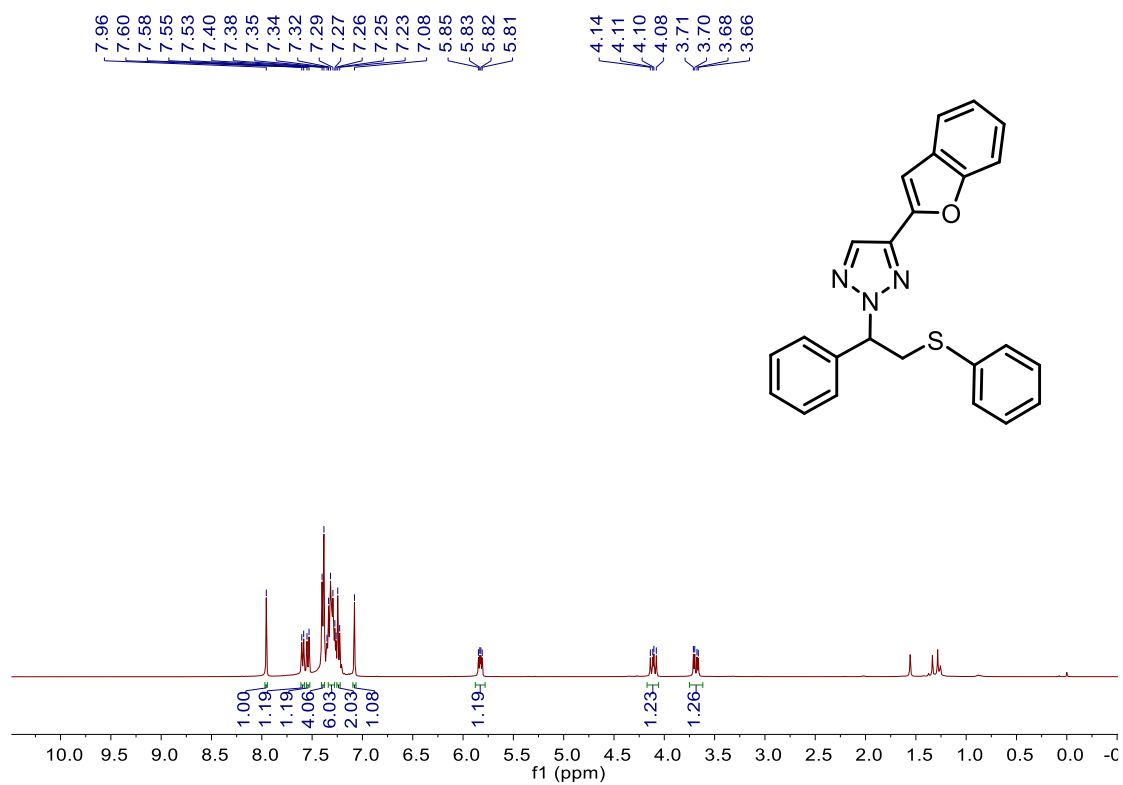


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for **4i**

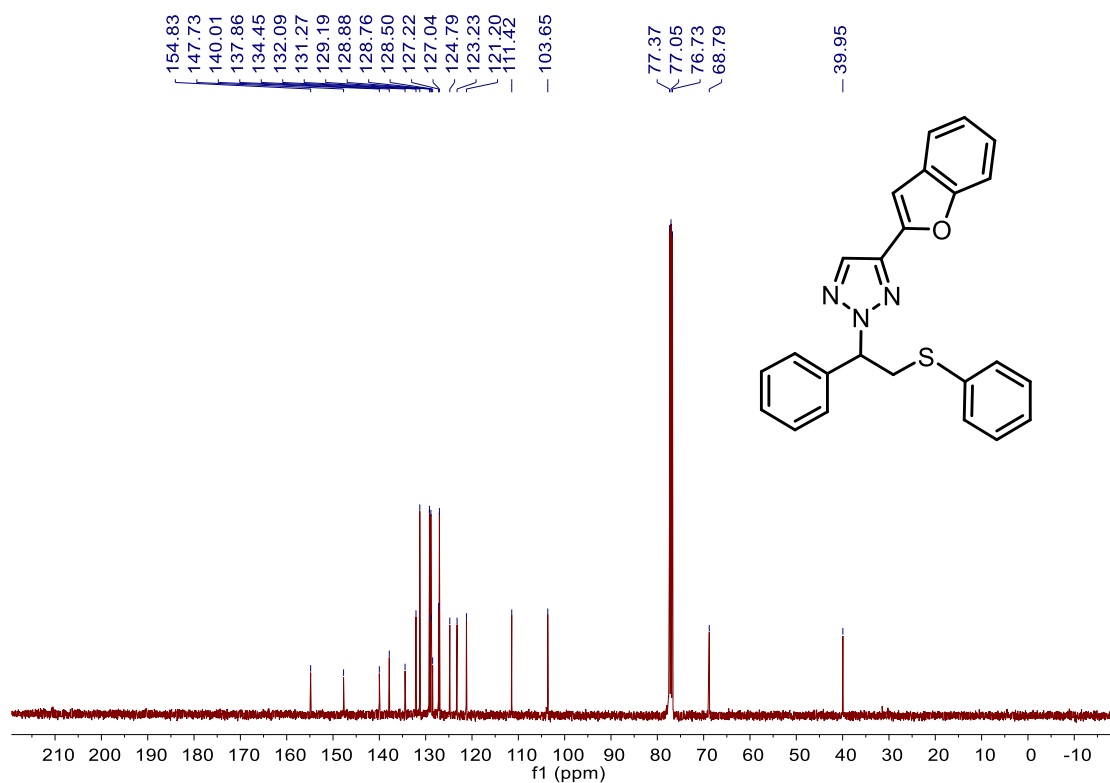


¹H NMR (400 MHz, CDCl₃) spectrum for **4j**

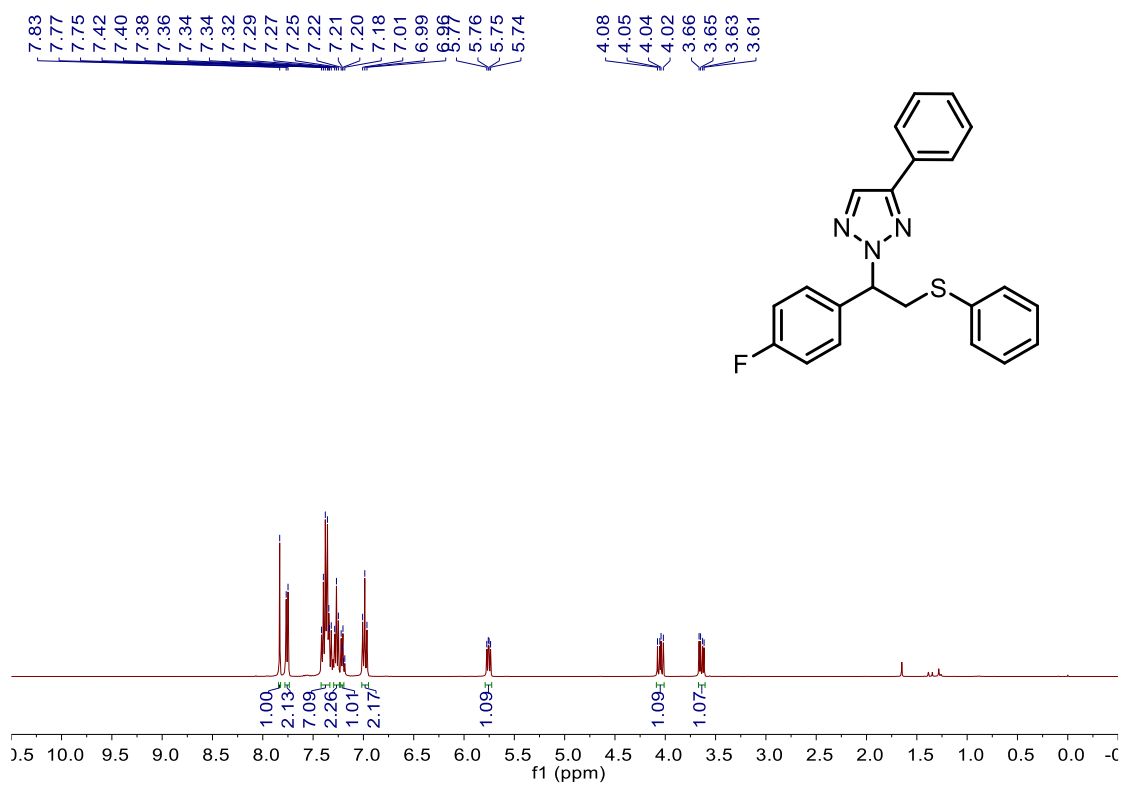


Electronic Supporting Information

^{13}C NMR (100 MHz, CDCl_3) spectrum for **4j**

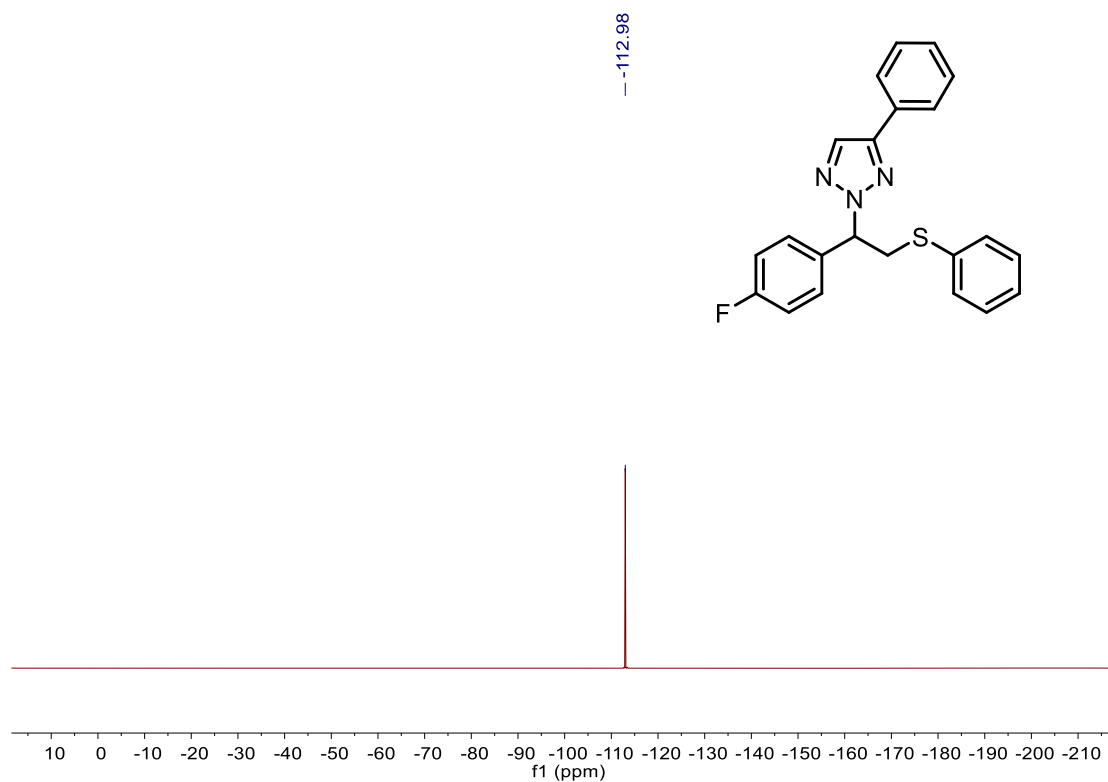


^1H NMR (400 MHz, CDCl_3) spectrum for **4k**

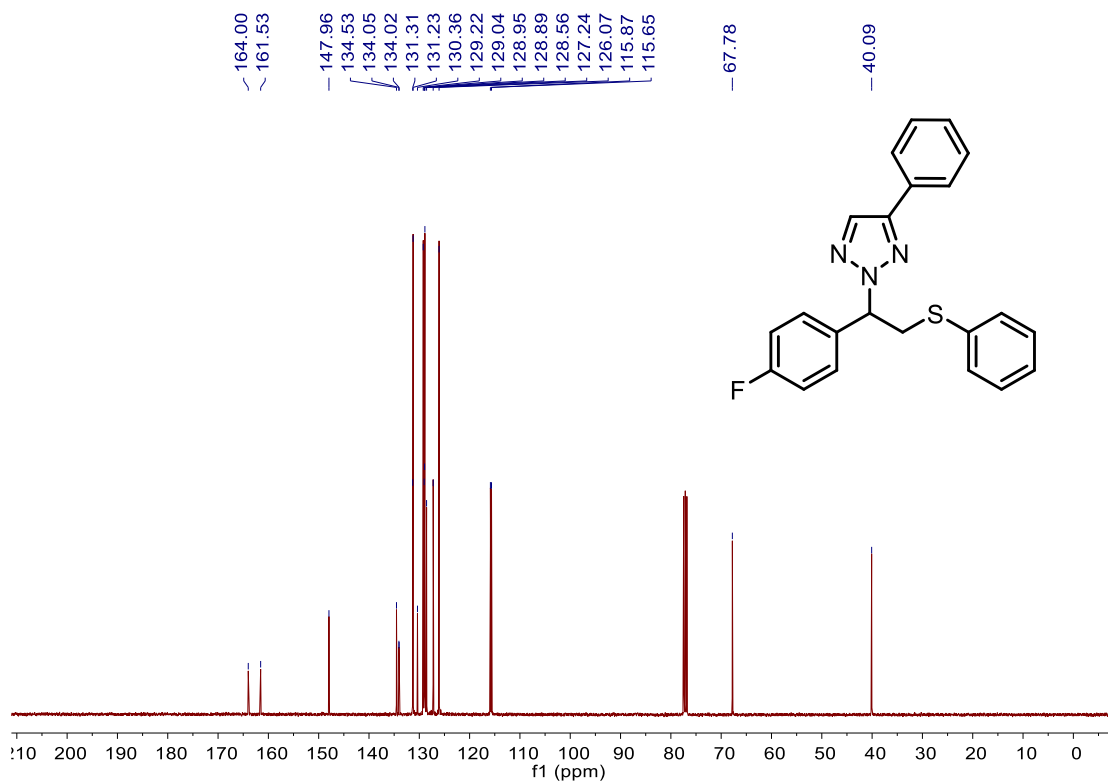


Electronic Supporting Information

^{19}F NMR (376 MHz, CDCl_3) spectrum for 4k

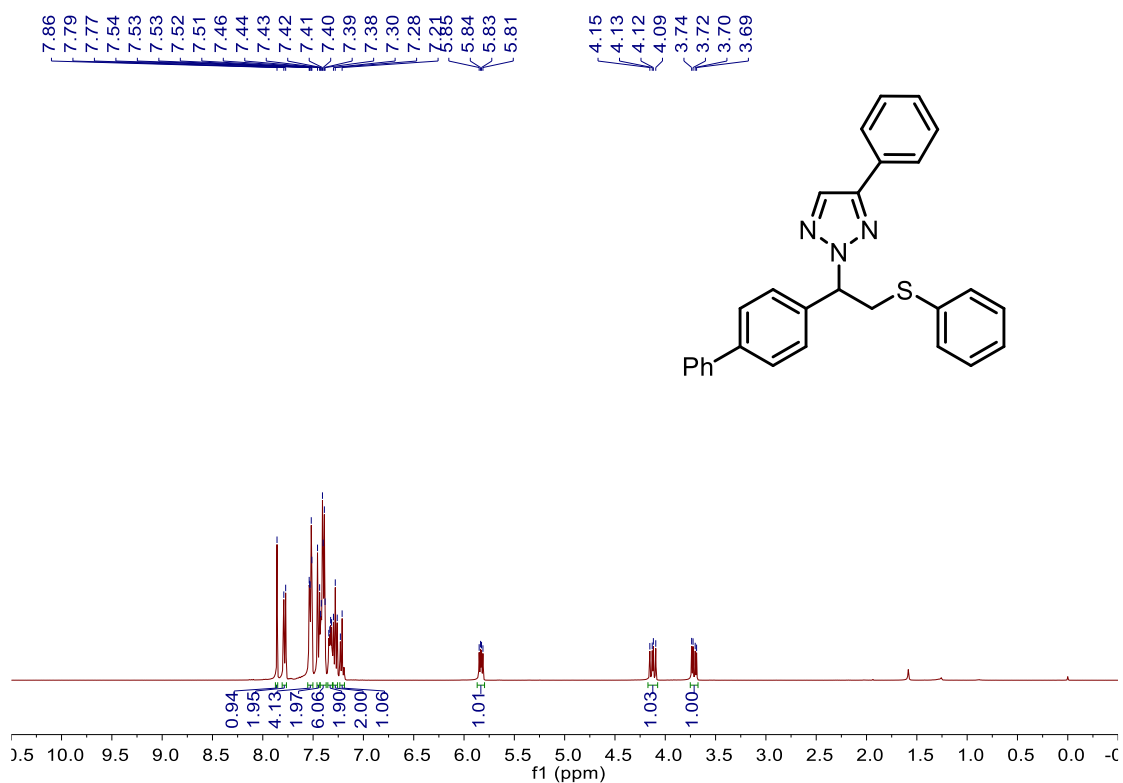


^{13}C NMR (100 MHz, CDCl_3) spectrum for 4k

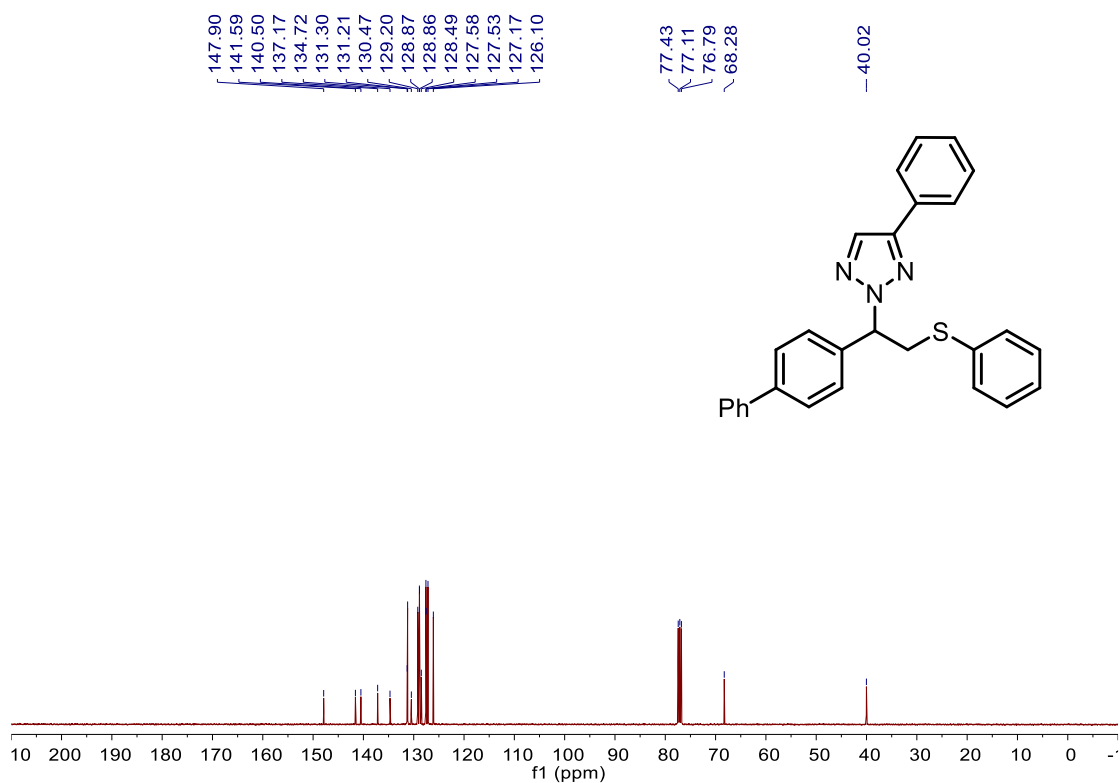


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4l**

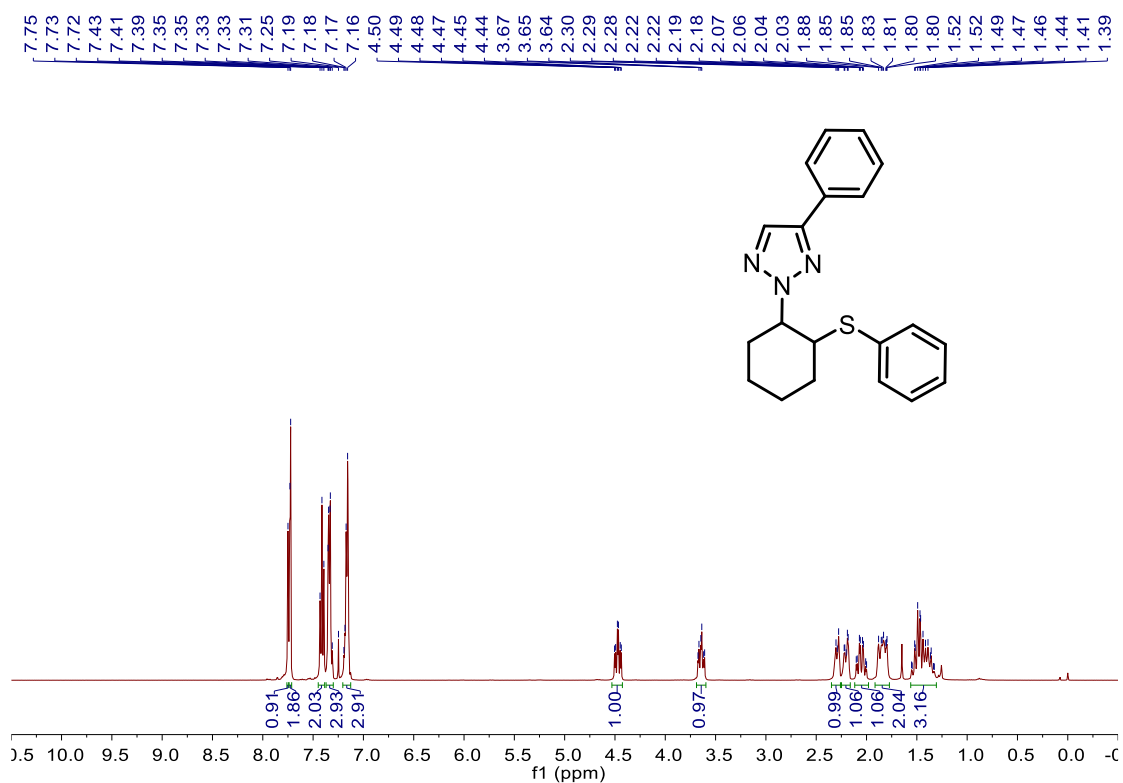


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4l**

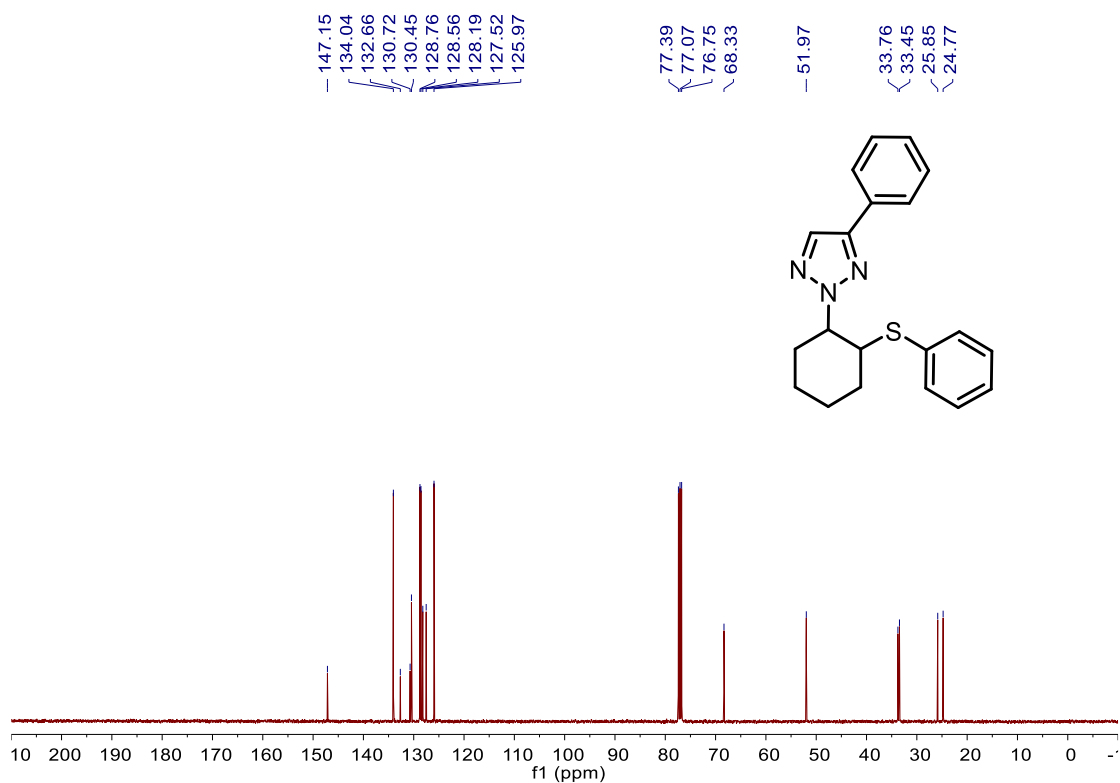


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4m**

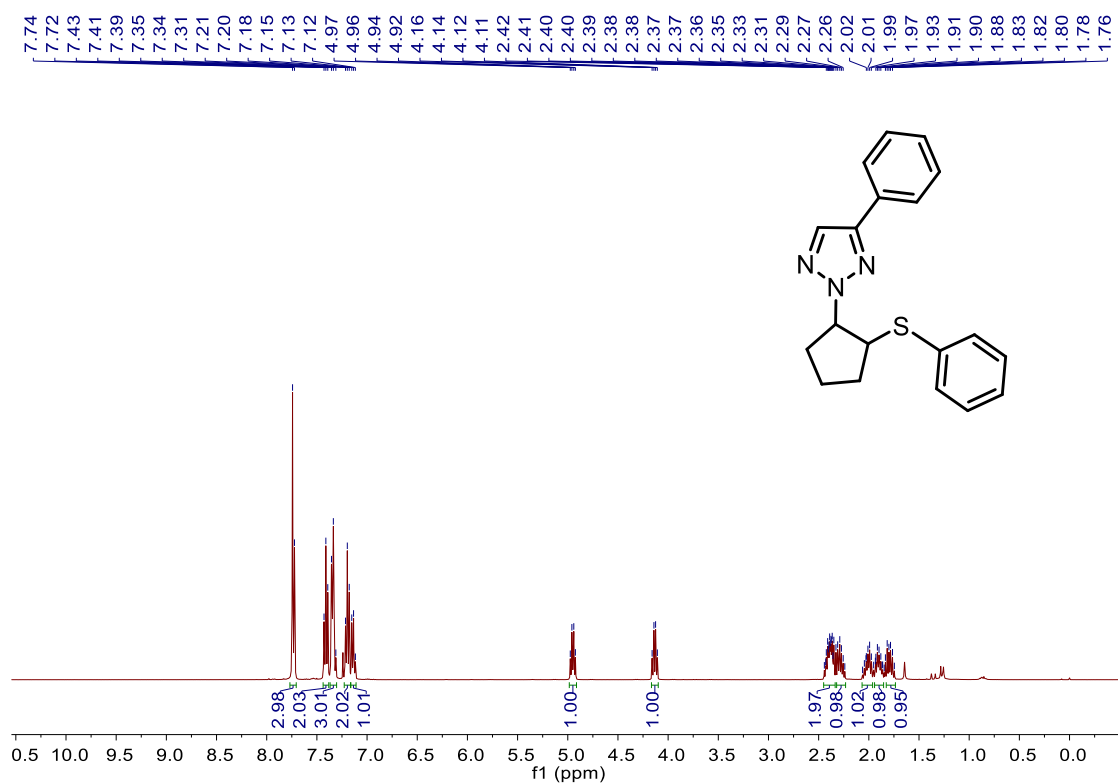


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4m**

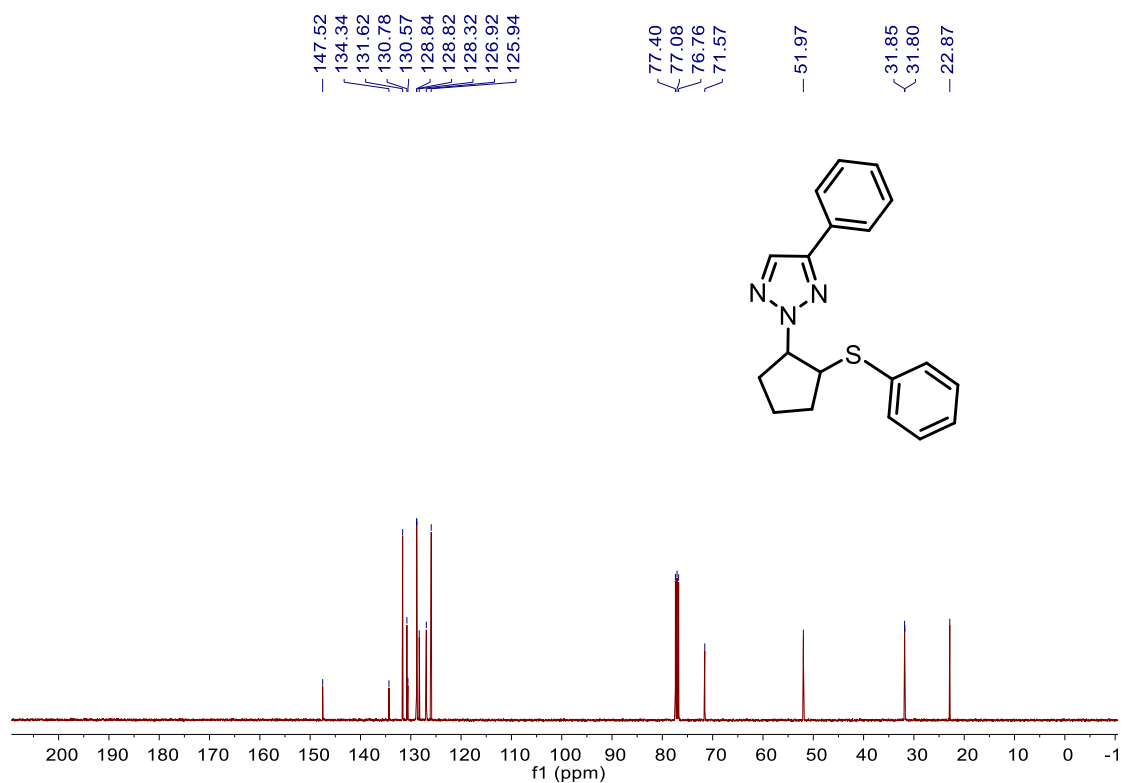


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4n**

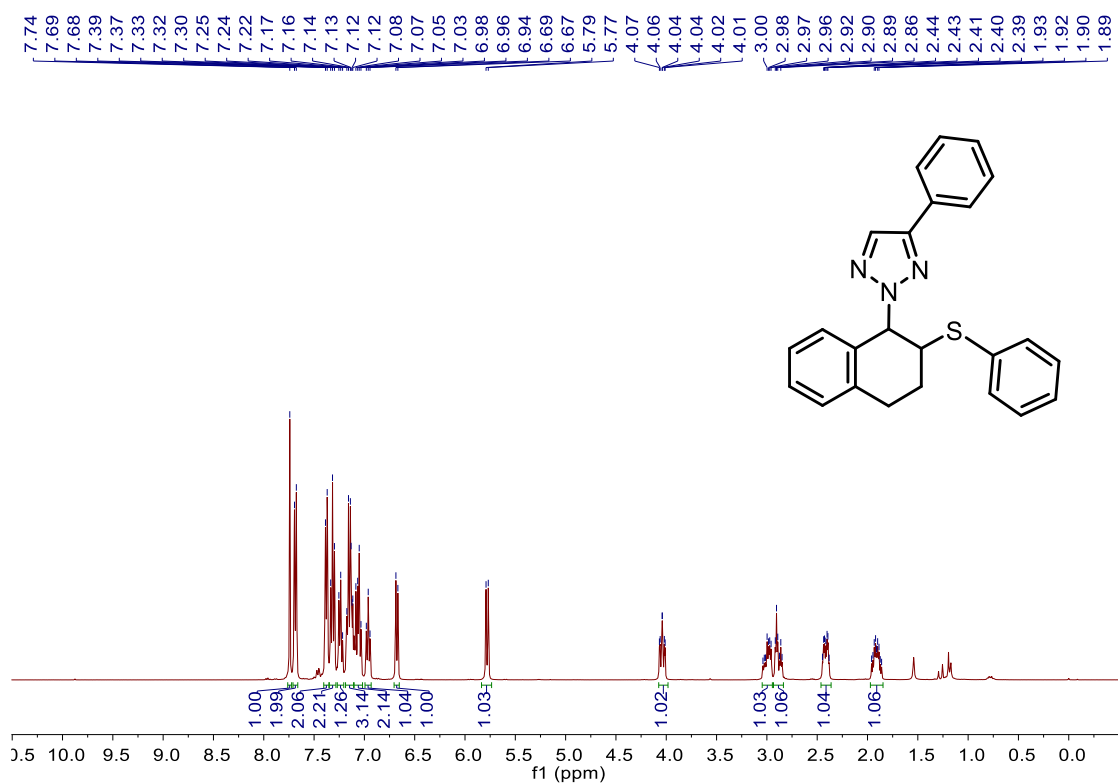


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4n**

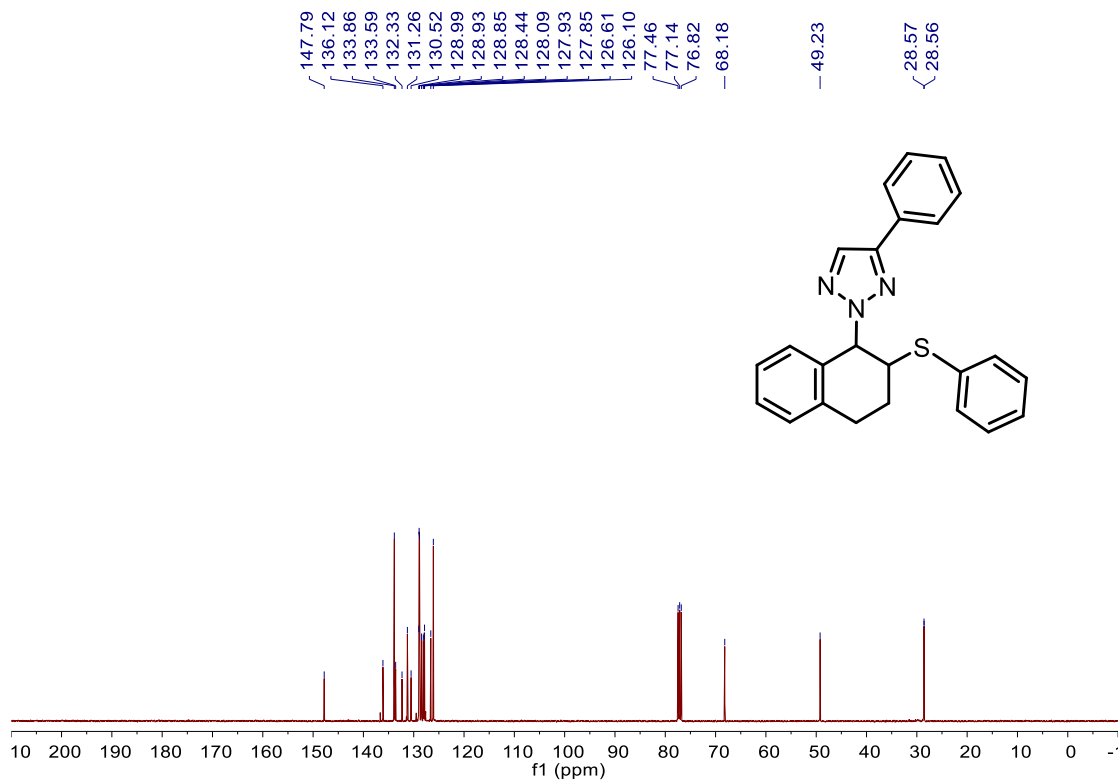


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4o**

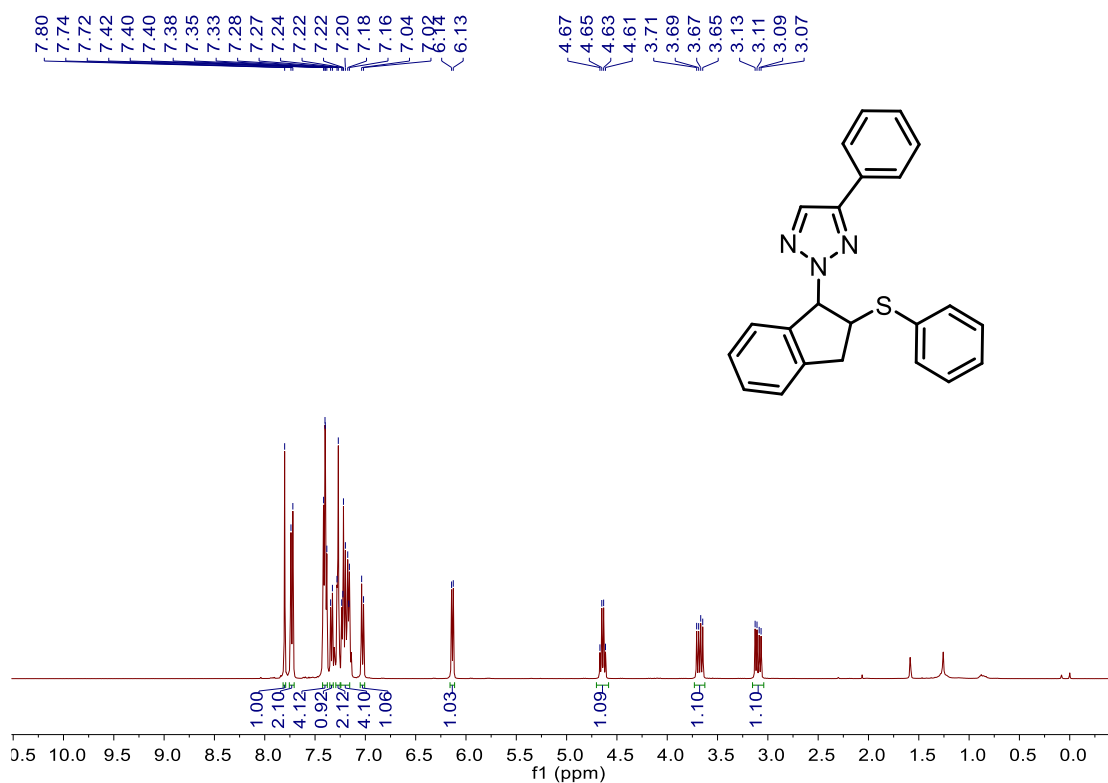


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4o**

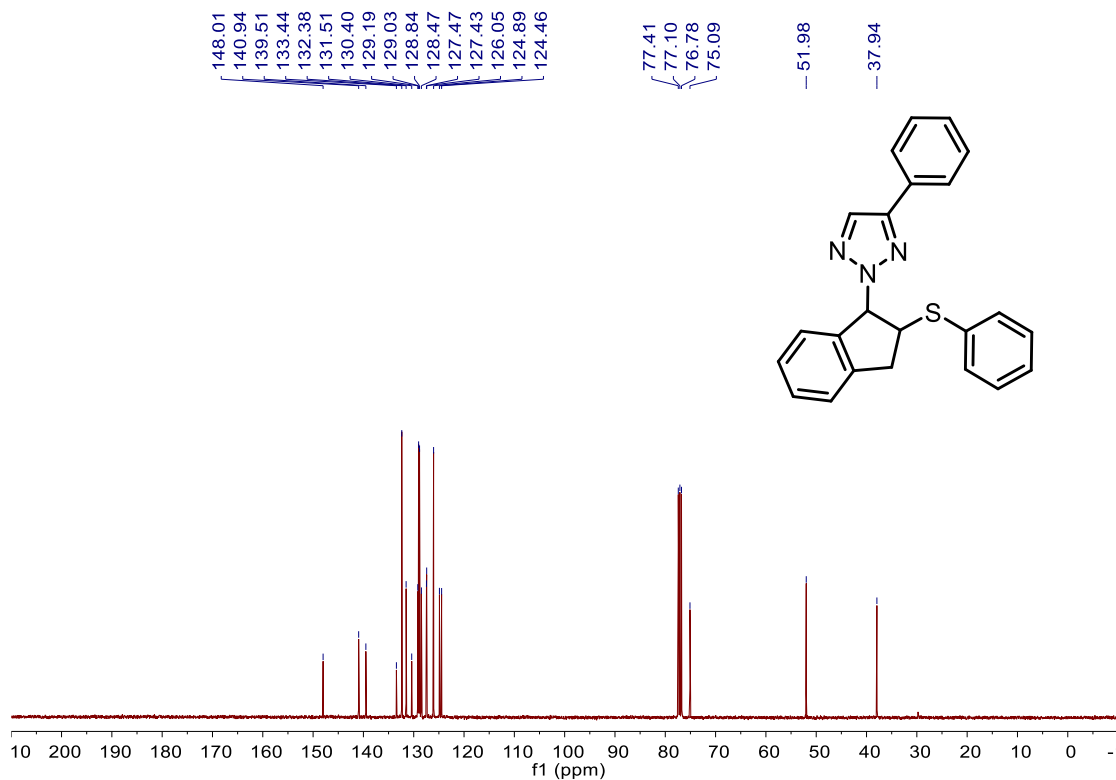


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4p**

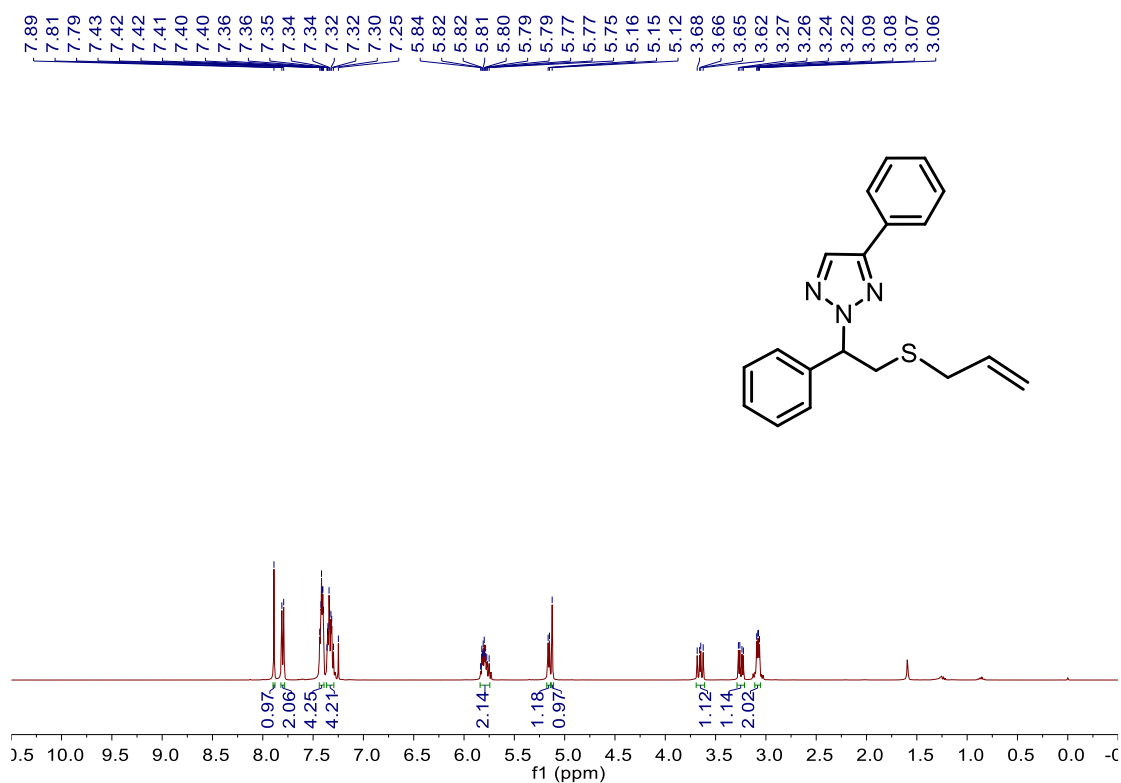


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4p**

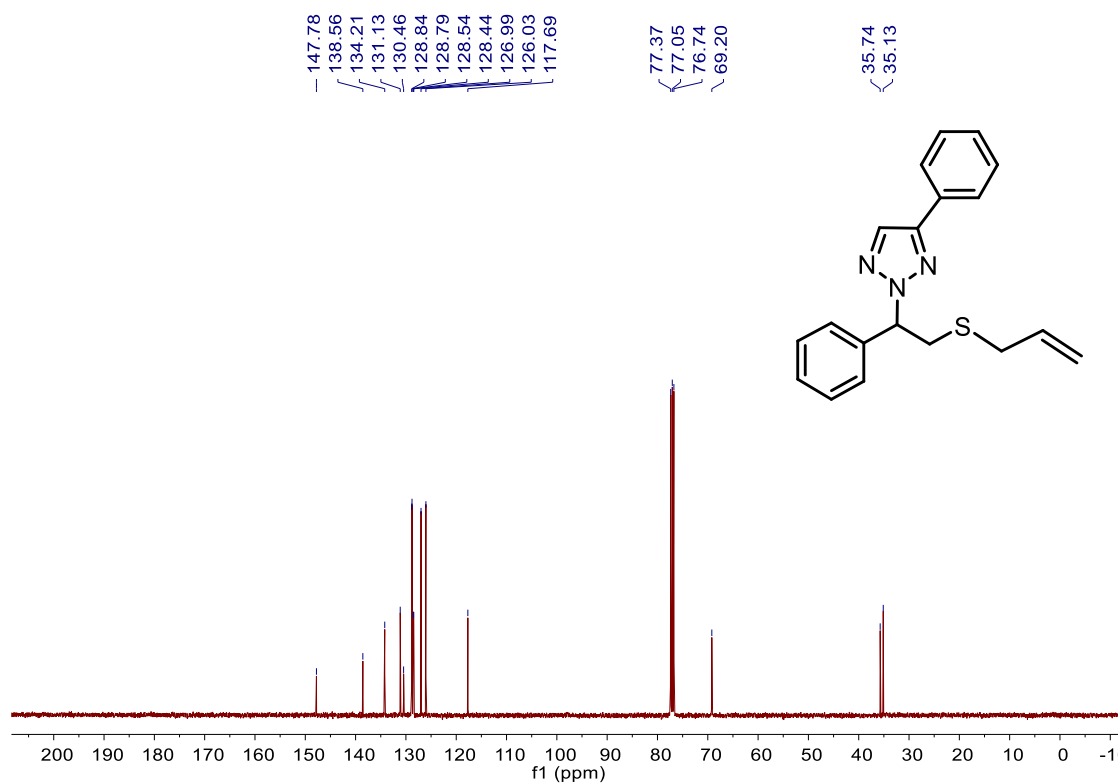


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4q**

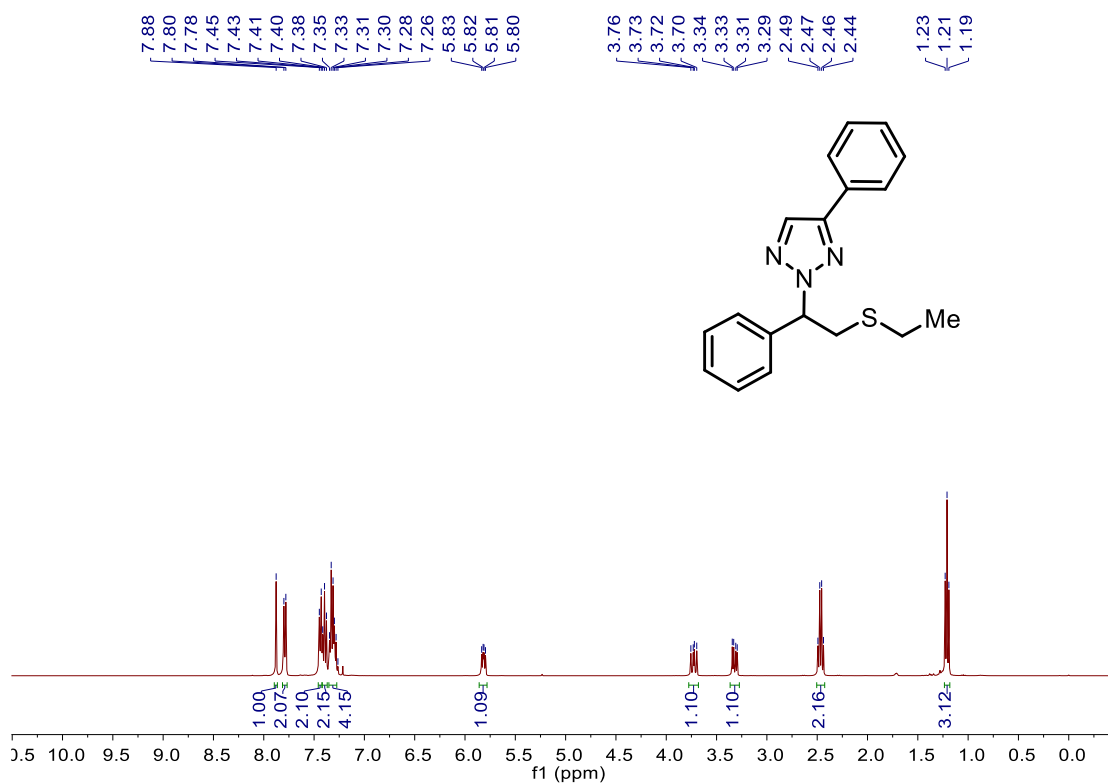


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4q**

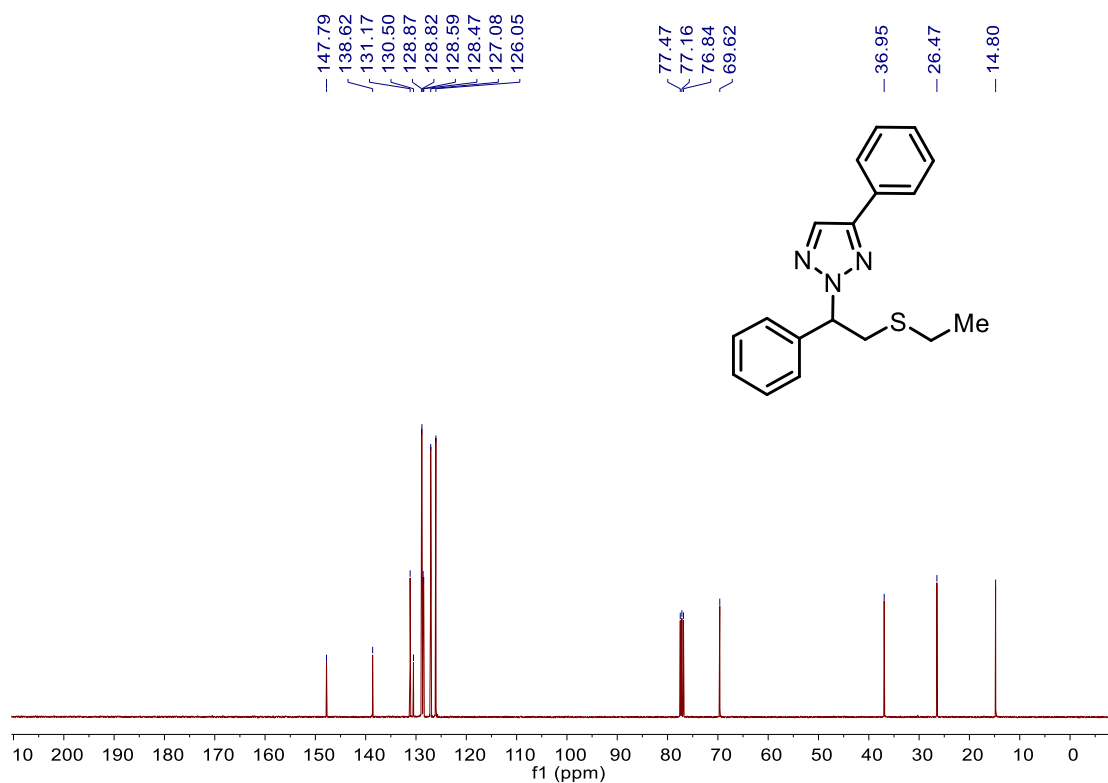


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4r**

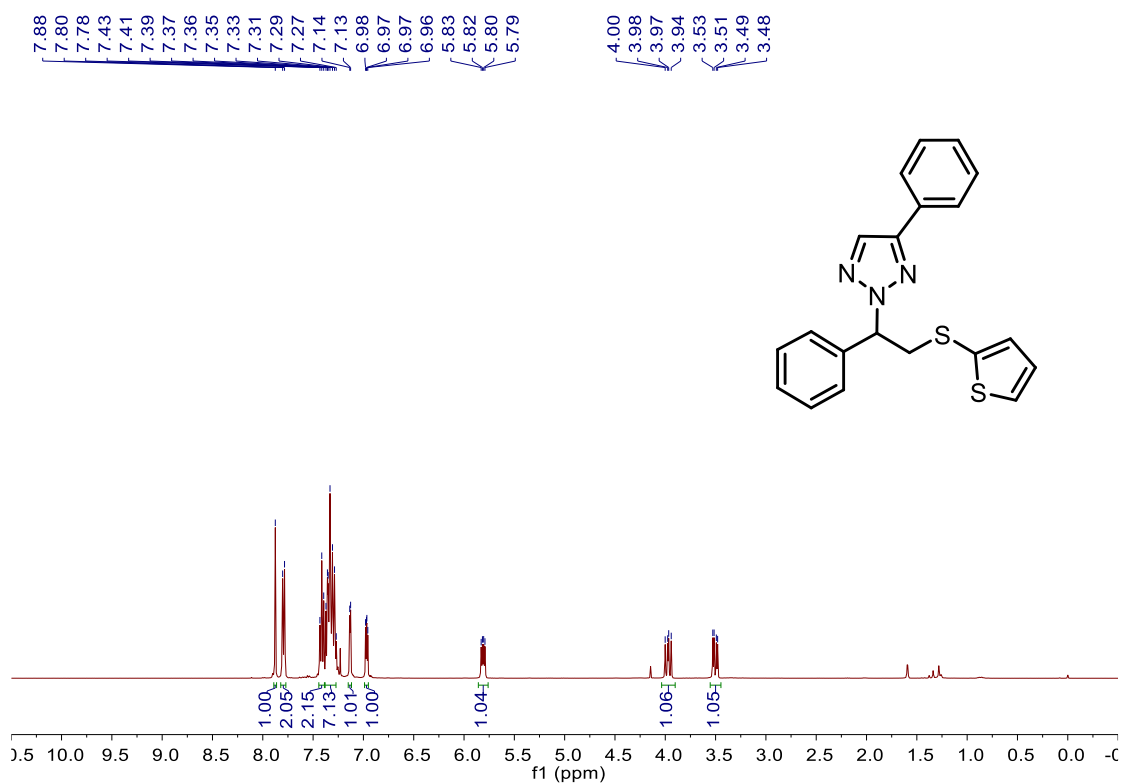


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4r**

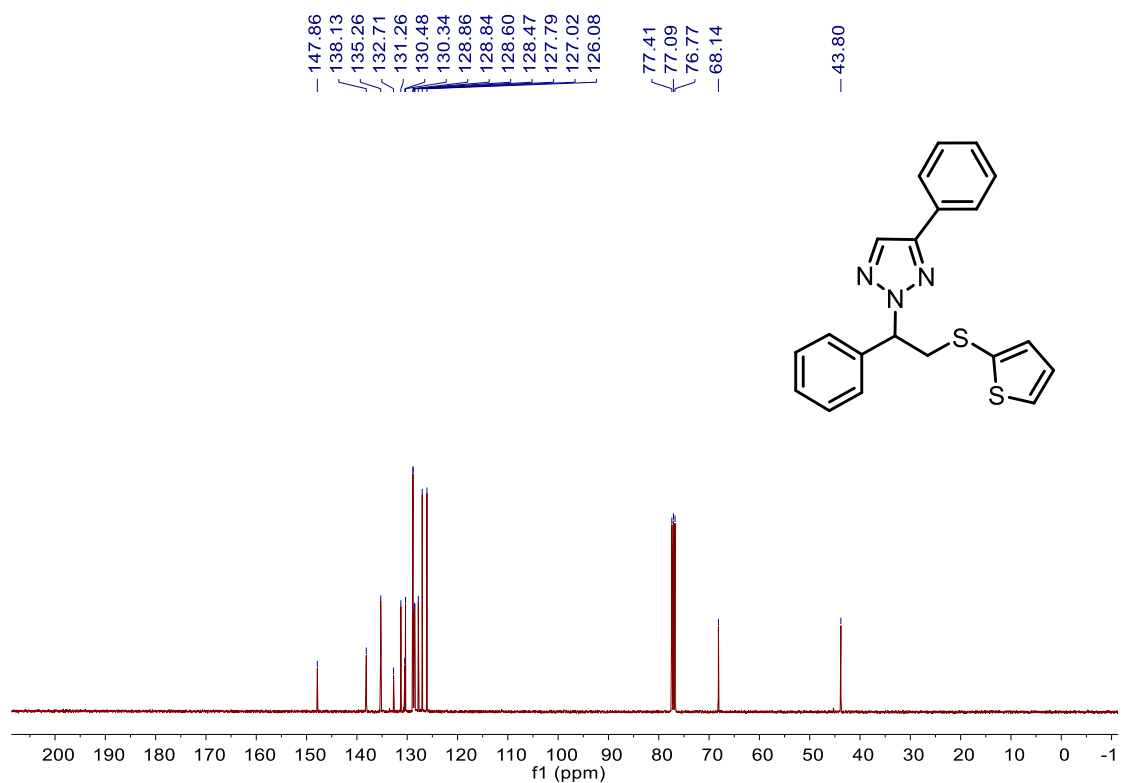


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4s**

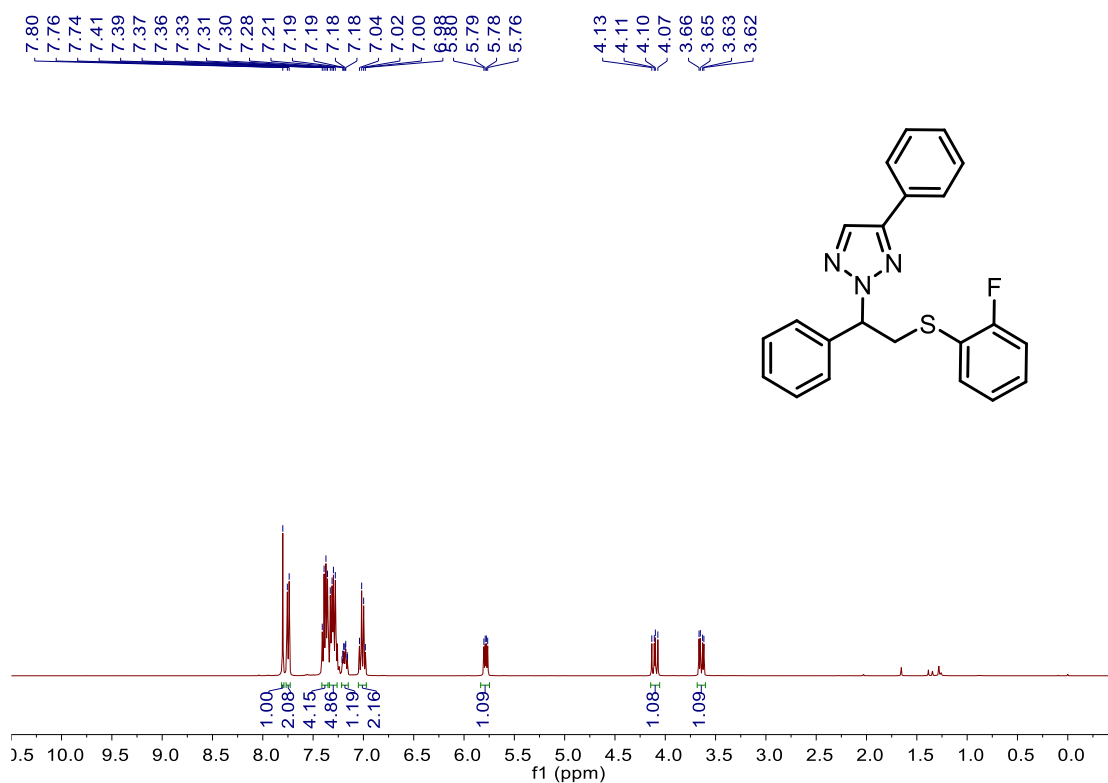


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4s**

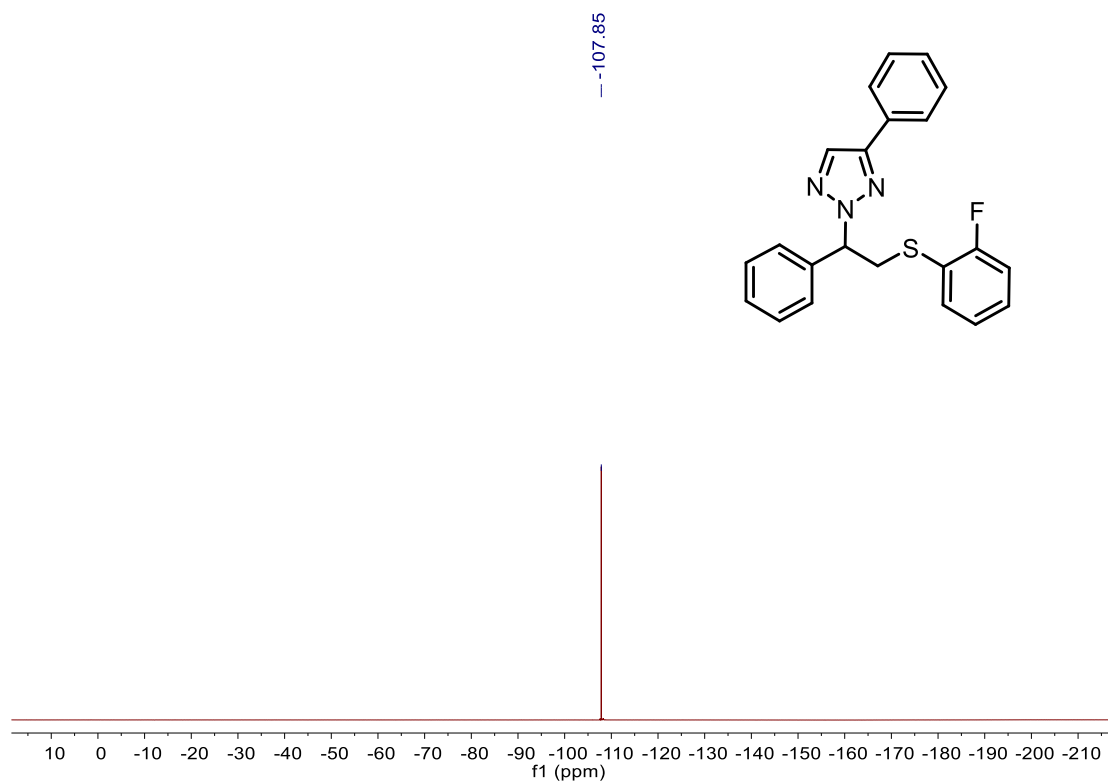


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4t**

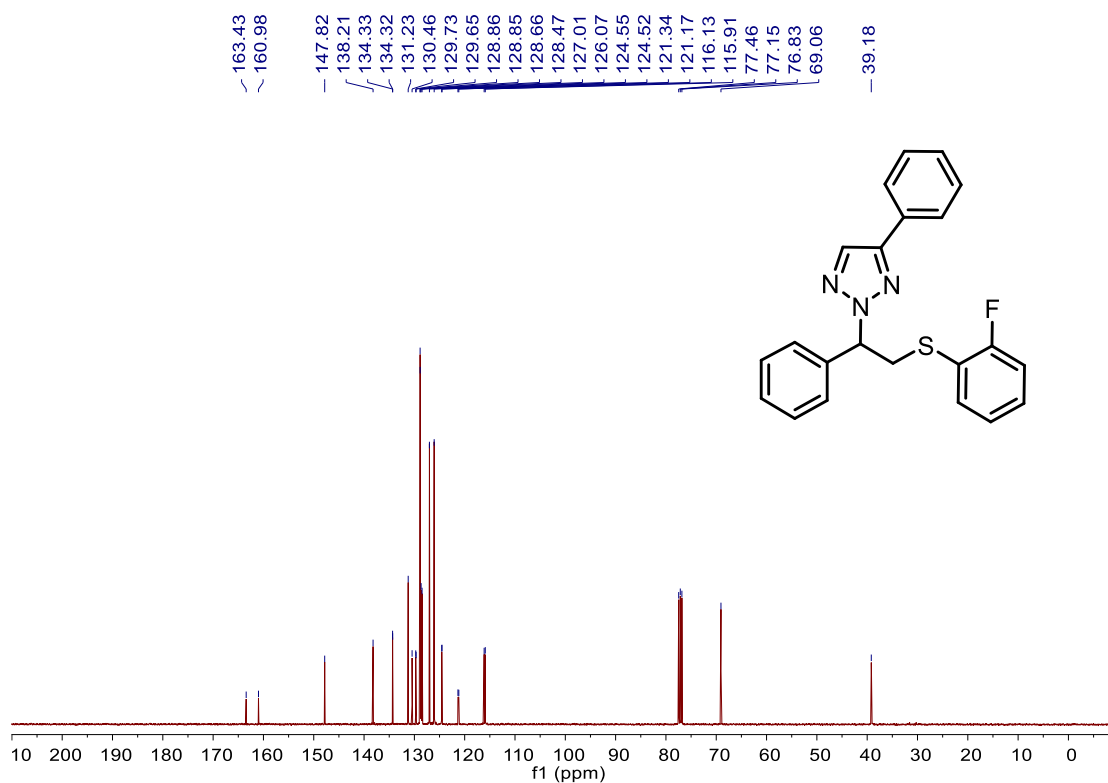


^{19}F NMR (376 MHz, CDCl_3) spectrum for **4t**

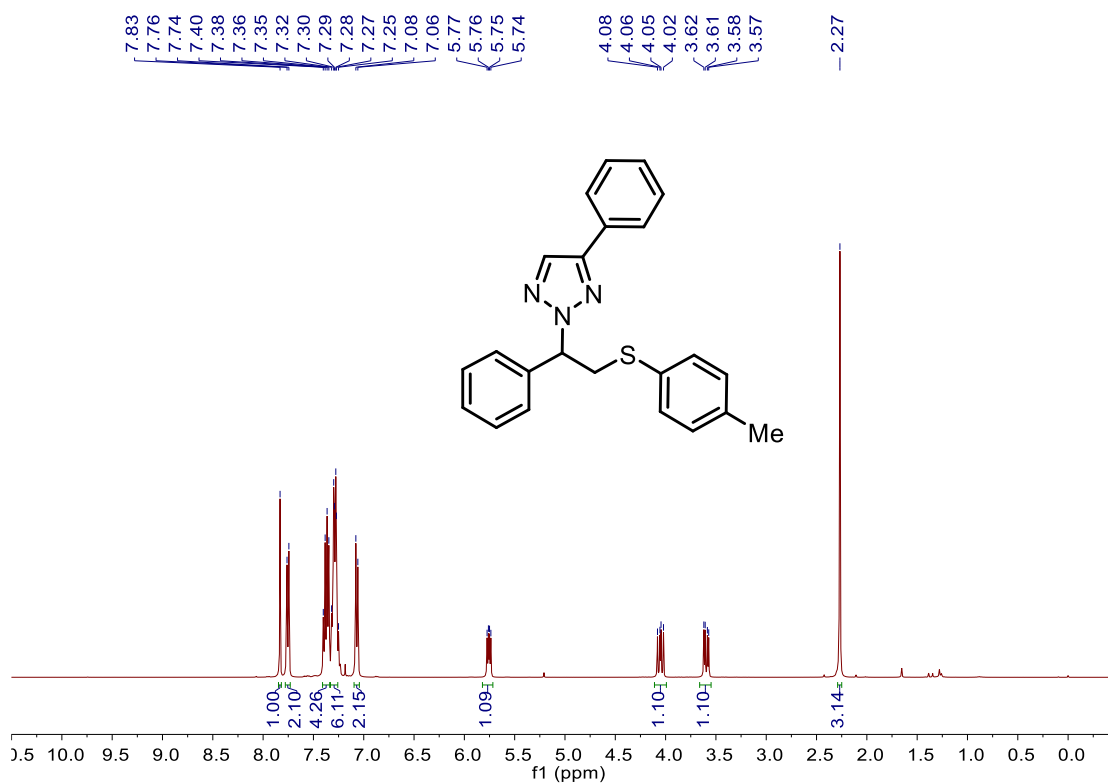


Electronic Supporting Information

^{13}C NMR (100 MHz, CDCl_3) spectrum for **4t**

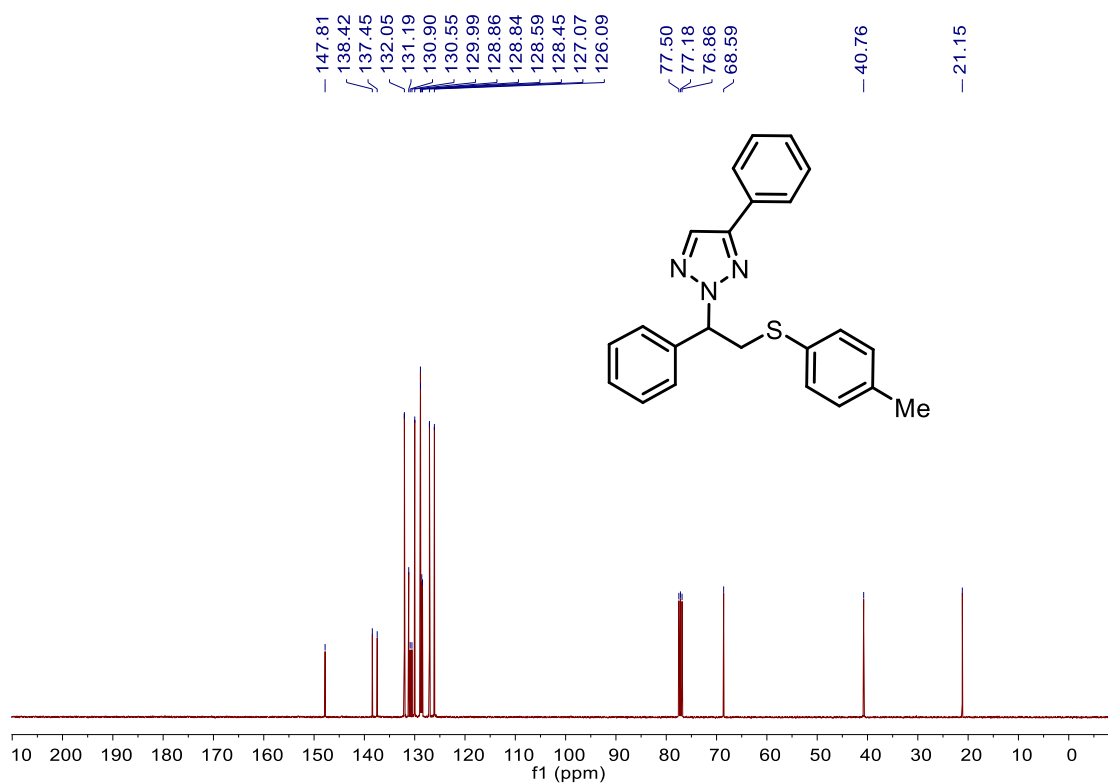


^1H NMR (400 MHz, CDCl_3) spectrum for **4u**

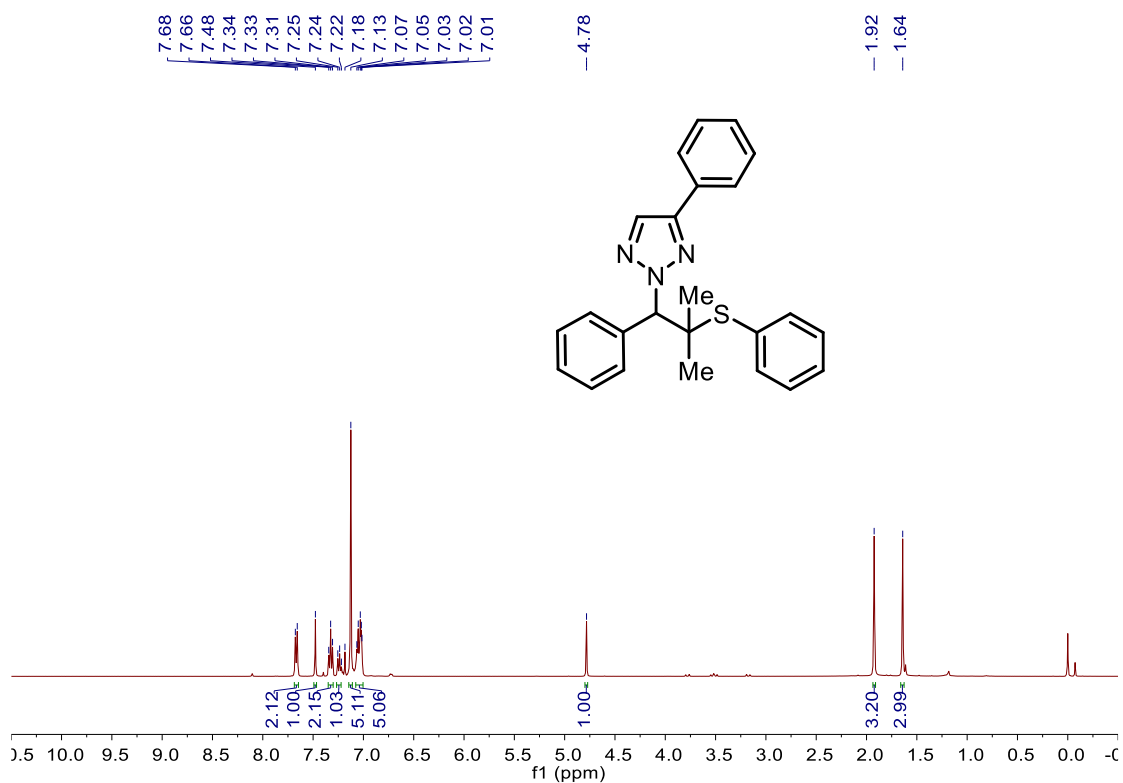


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for 4u

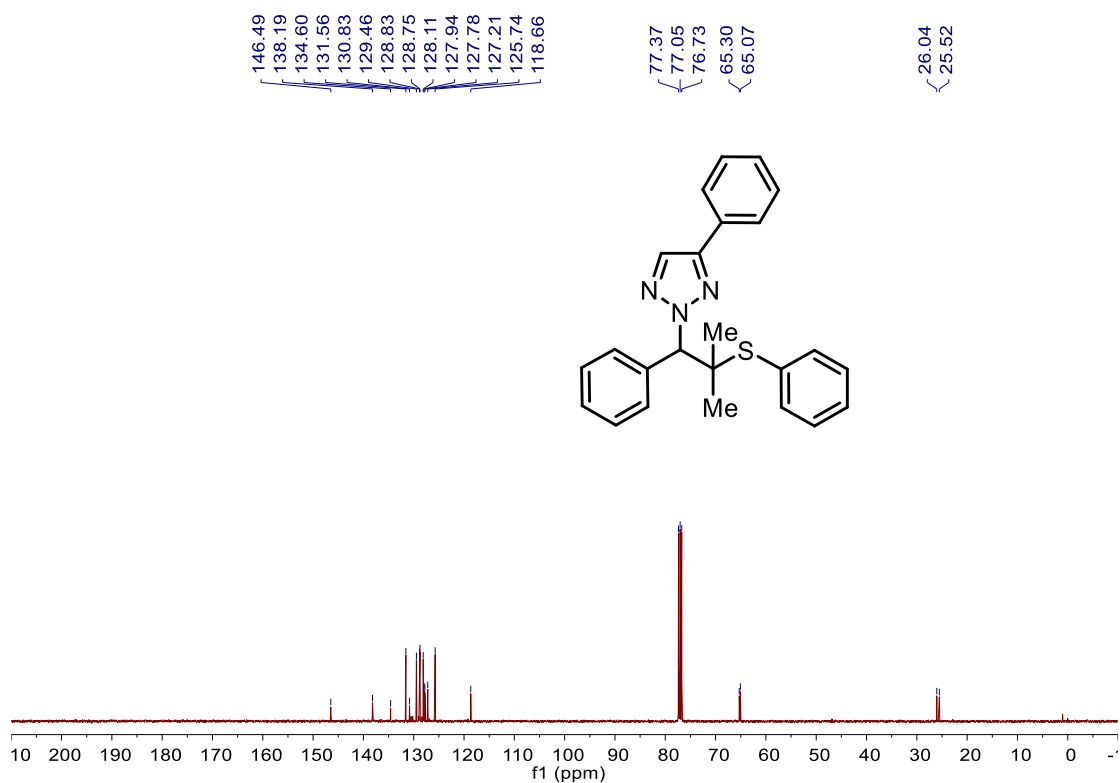


¹H NMR (400 MHz, CDCl₃) spectrum for 4v

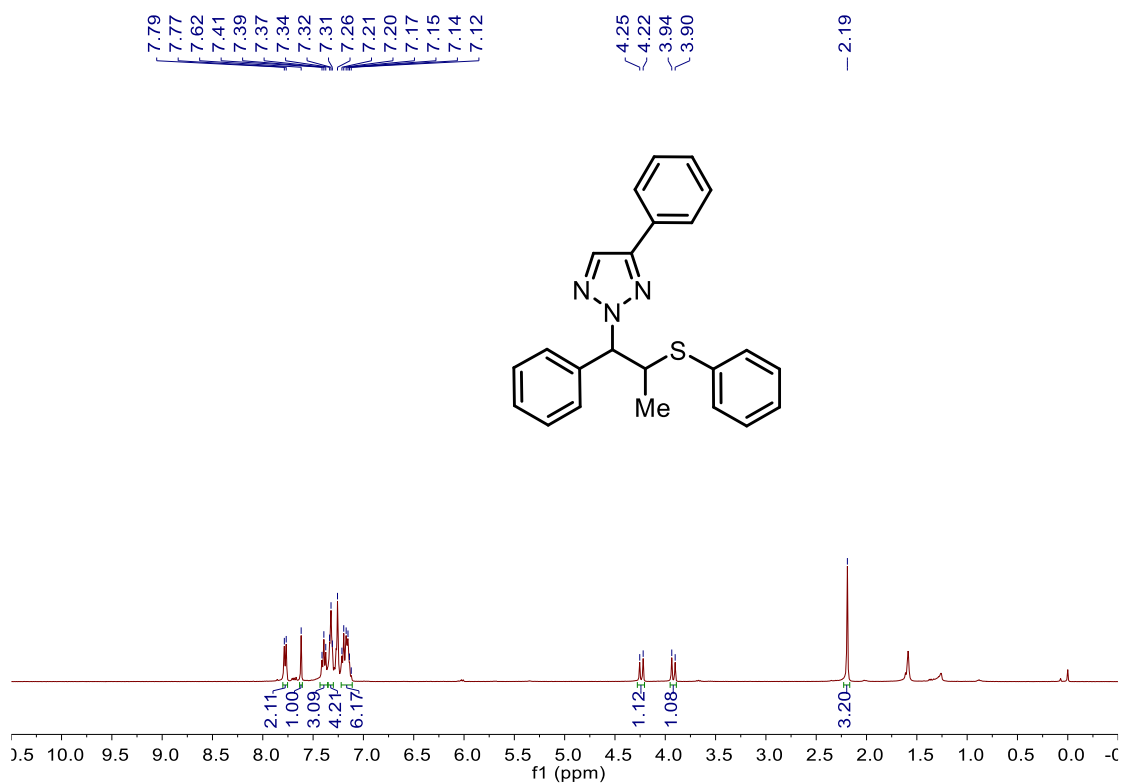


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for **4v**

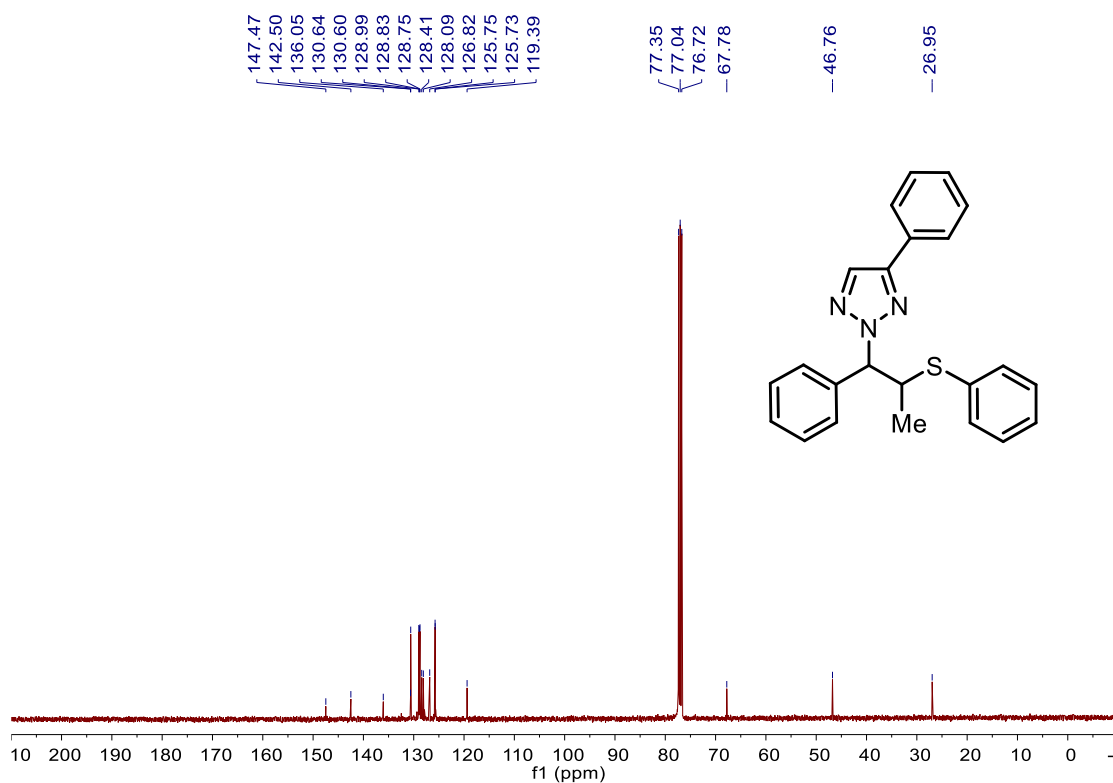


¹H NMR (400 MHz, CDCl₃) spectrum for **4w**

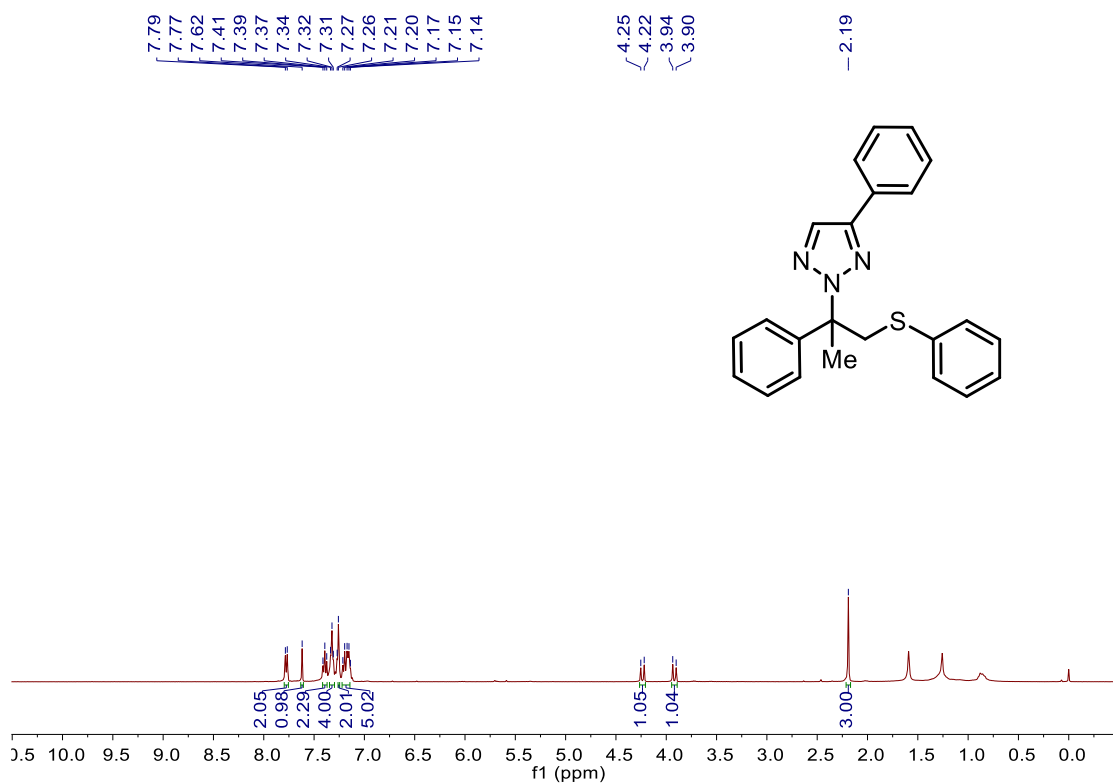


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for **4w**

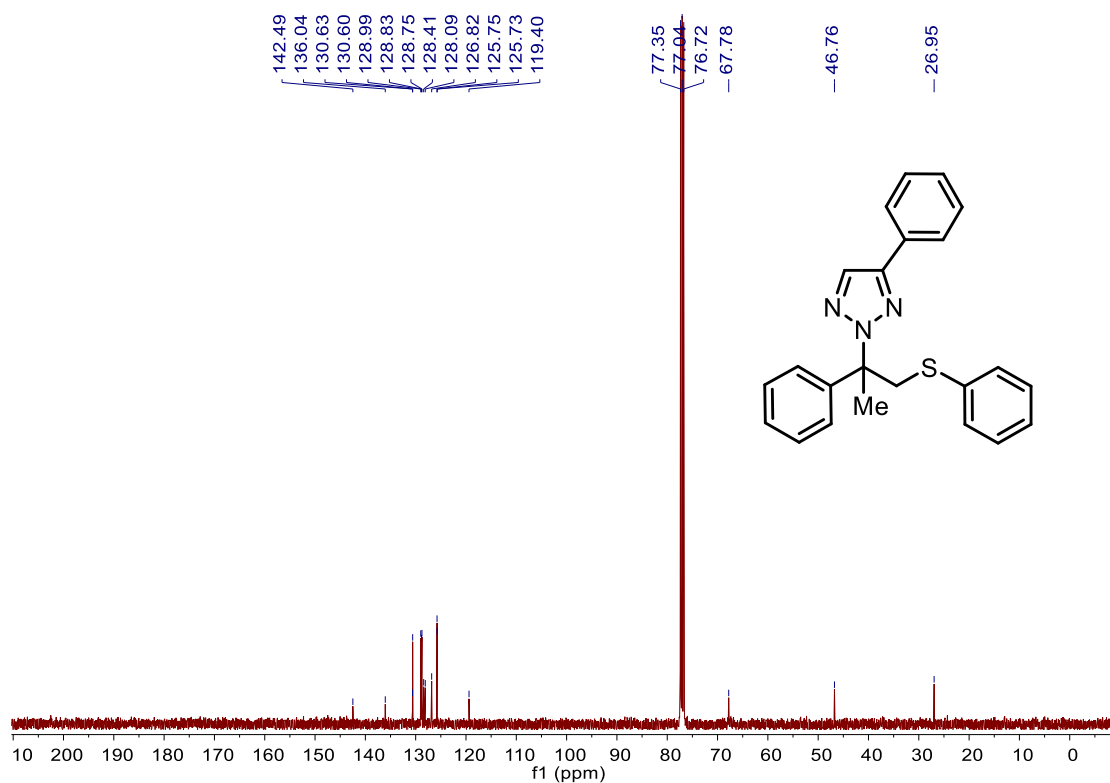


¹H NMR (400 MHz, CDCl₃) spectrum for **4x**

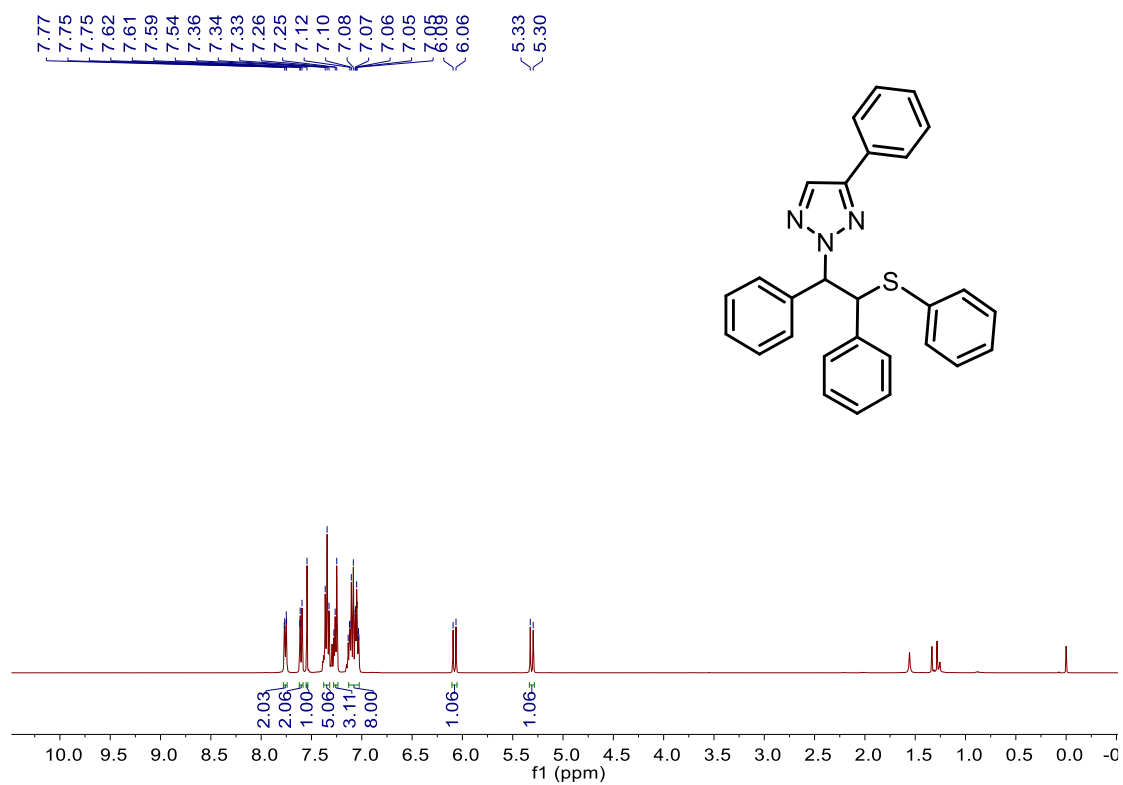


Electronic Supporting Information

^{13}C NMR (100 MHz, CDCl_3) spectrum for **4x**

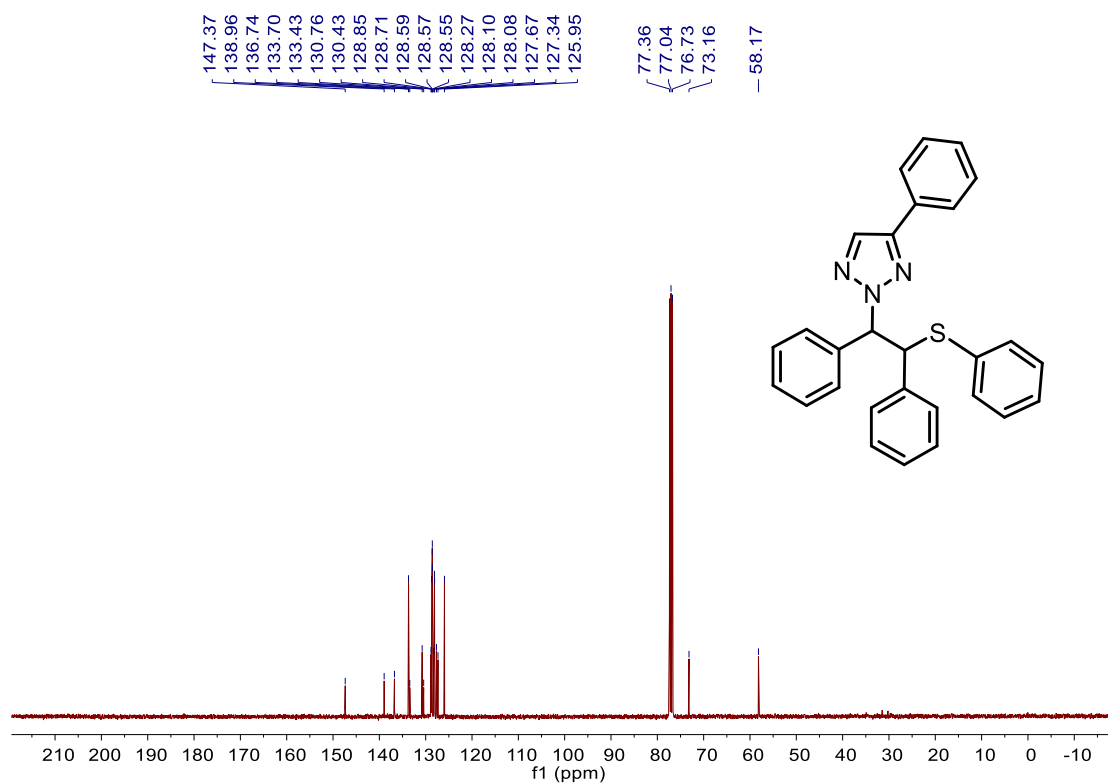


^1H NMR (400 MHz, CDCl_3) spectrum for **4y**

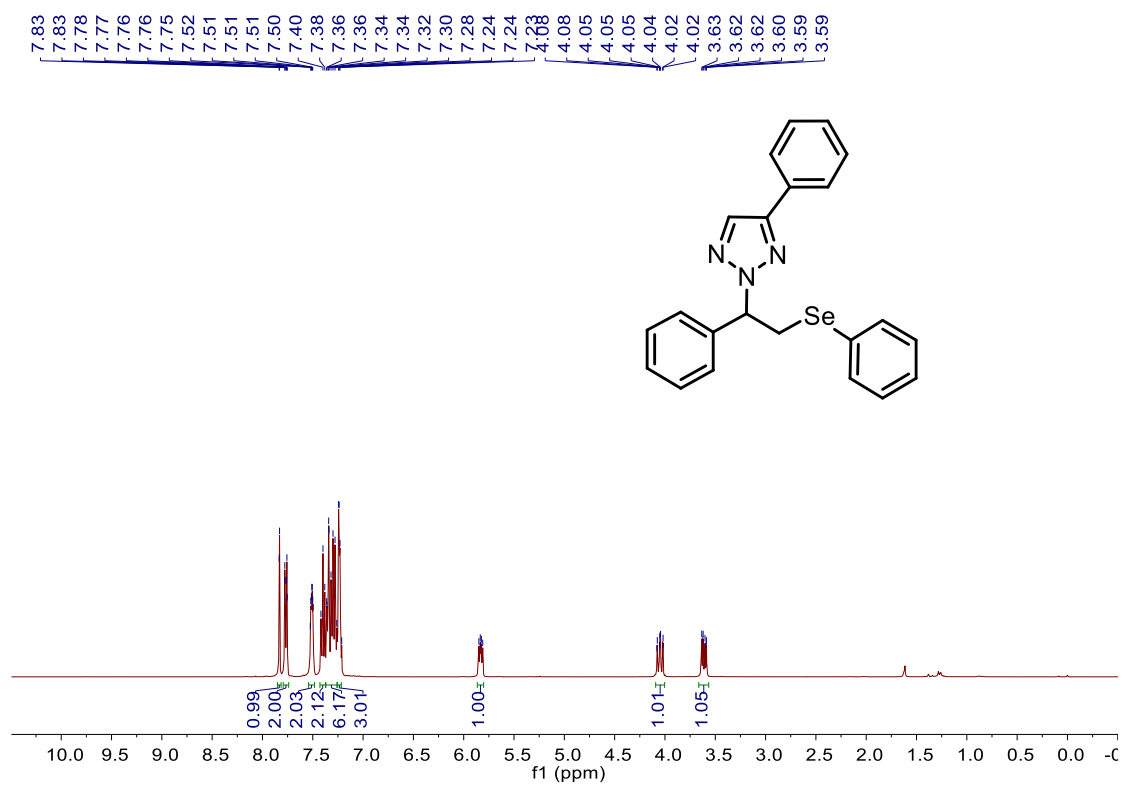


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for **4y**

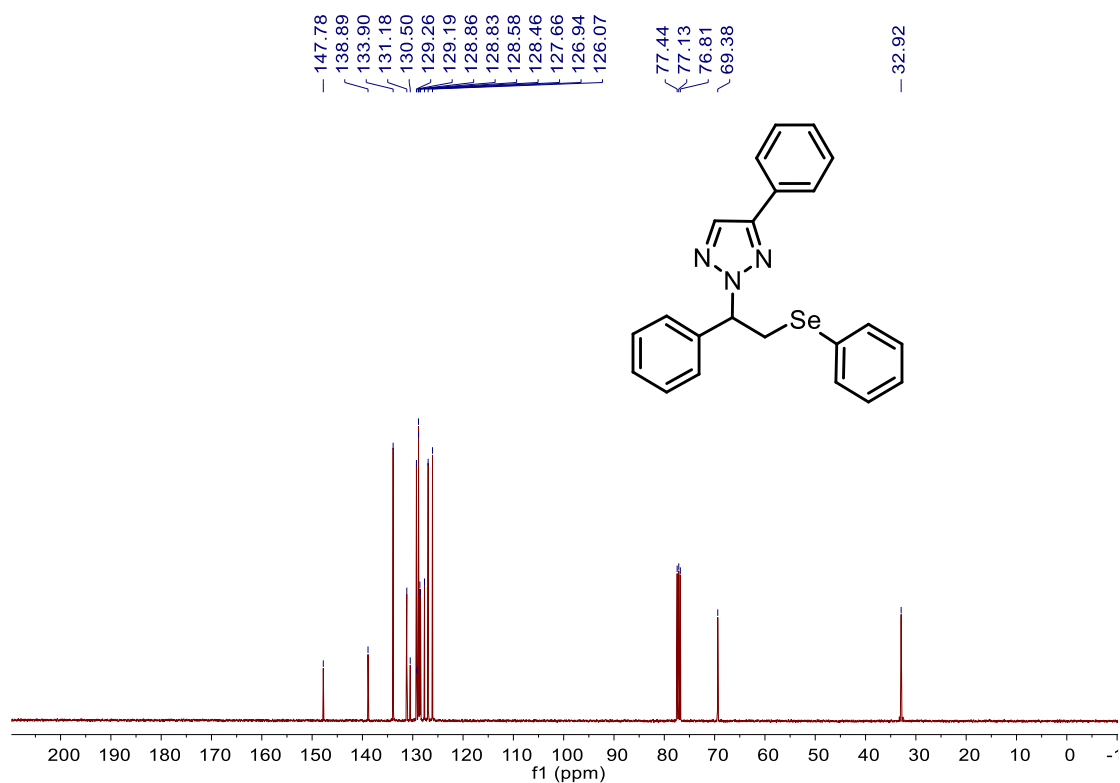


¹H NMR (400 MHz, CDCl₃) spectrum for **4z**

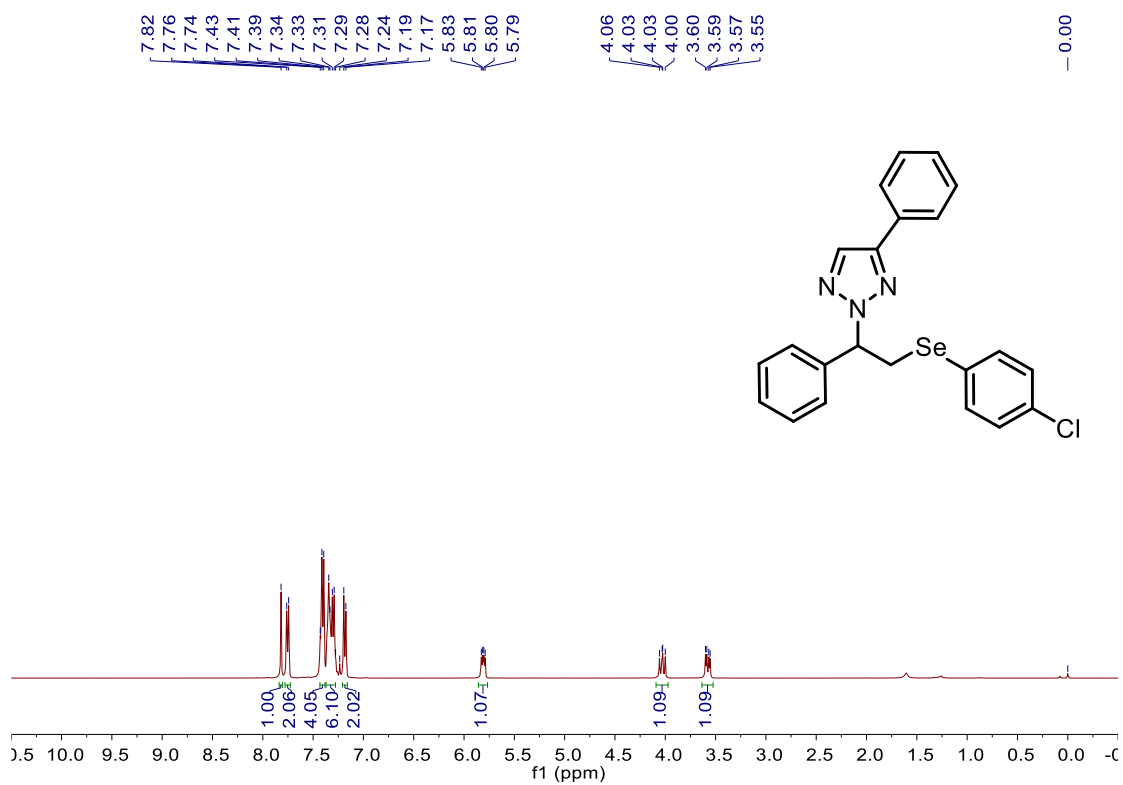


Electronic Supporting Information

¹³C NMR (100 MHz, CDCl₃) spectrum for **4z**

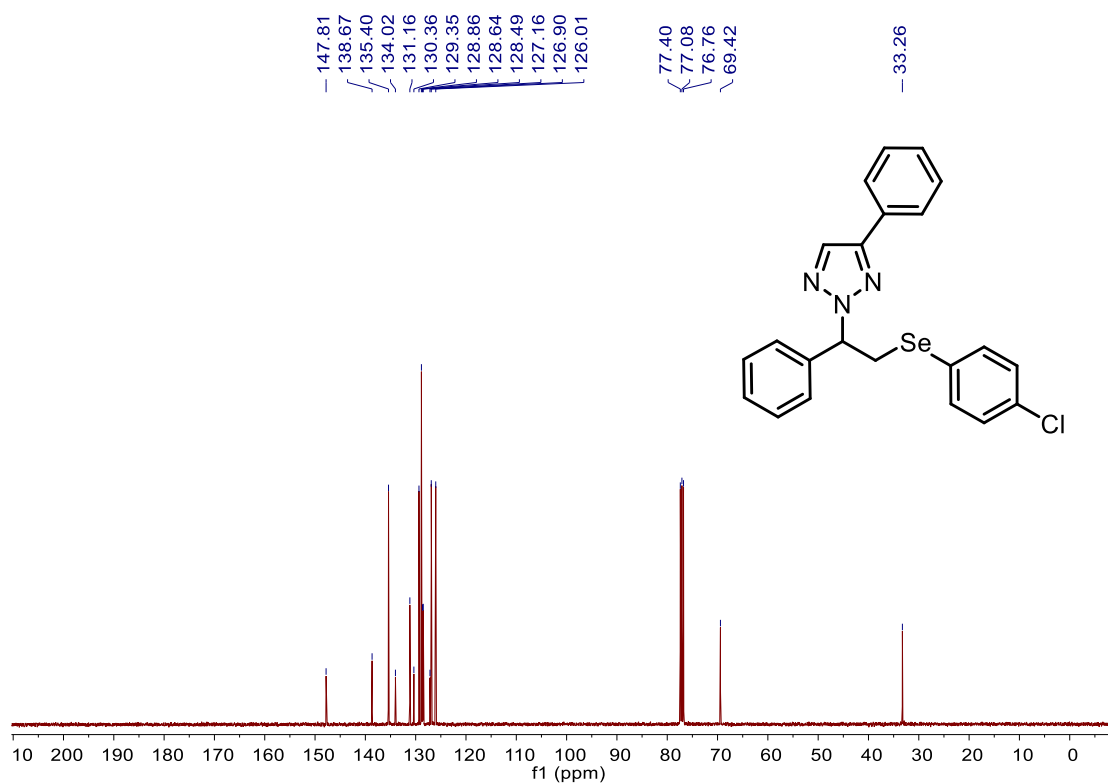


¹H NMR (400 MHz, CDCl₃) spectrum for **4aa**

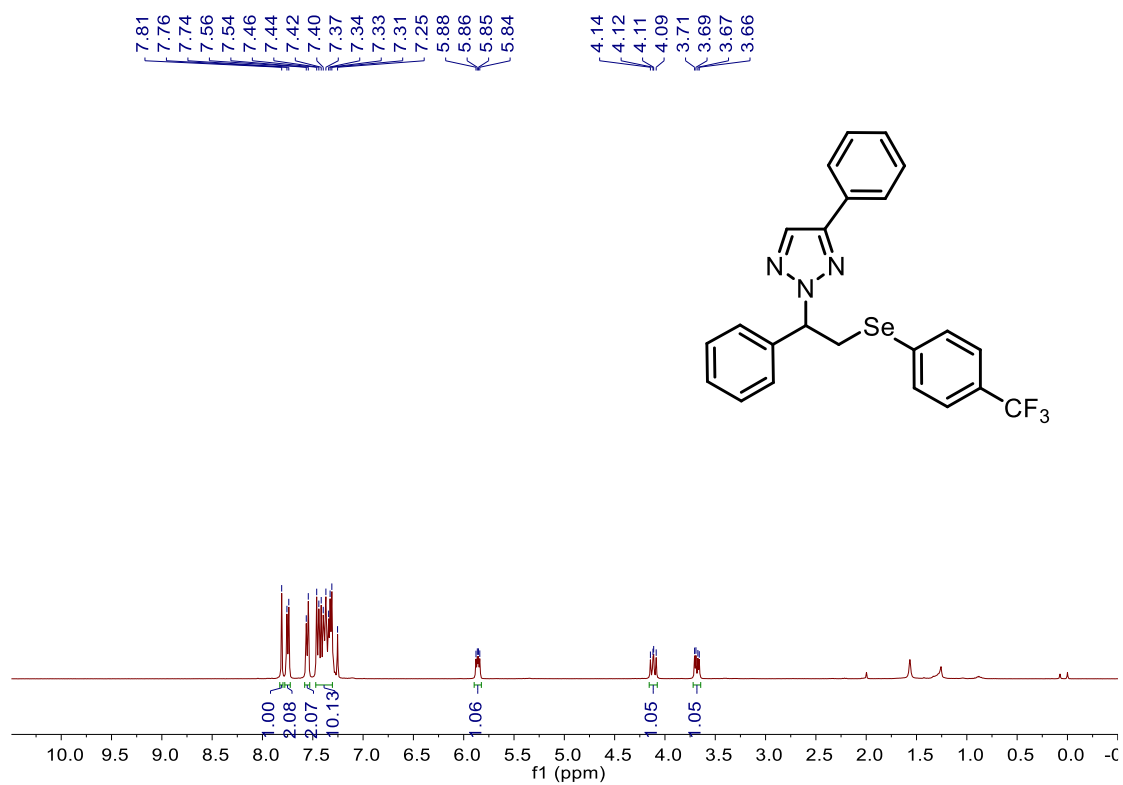


Electronic Supporting Information

^{13}C NMR (100 MHz, CDCl_3) spectrum for **4aa**

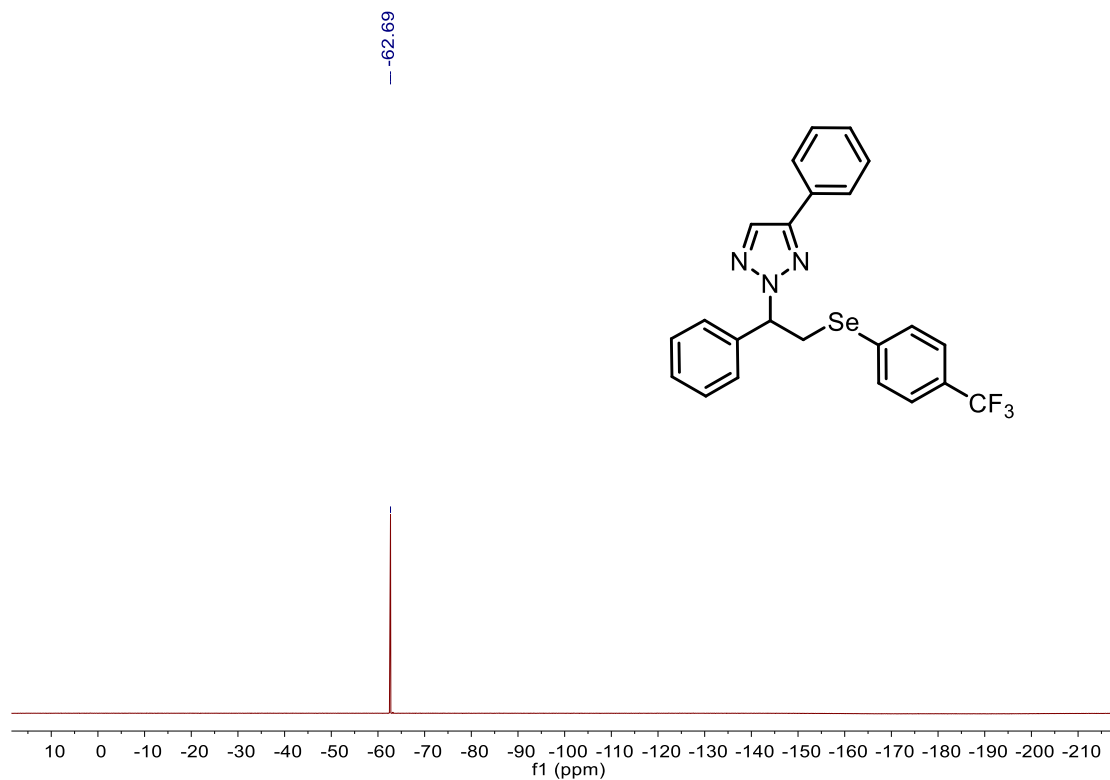


^1H NMR (400 MHz, CDCl_3) spectrum for **4ab**

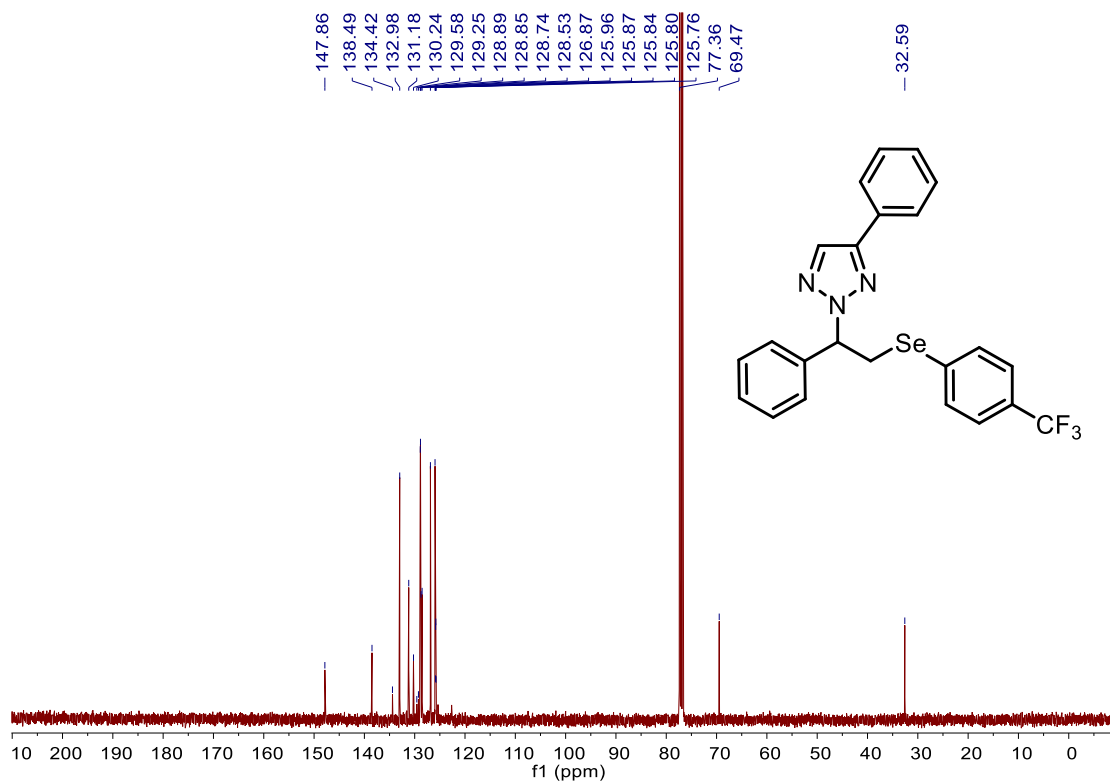


Electronic Supporting Information

^{19}F NMR (376 MHz, CDCl_3) spectrum for 4ab

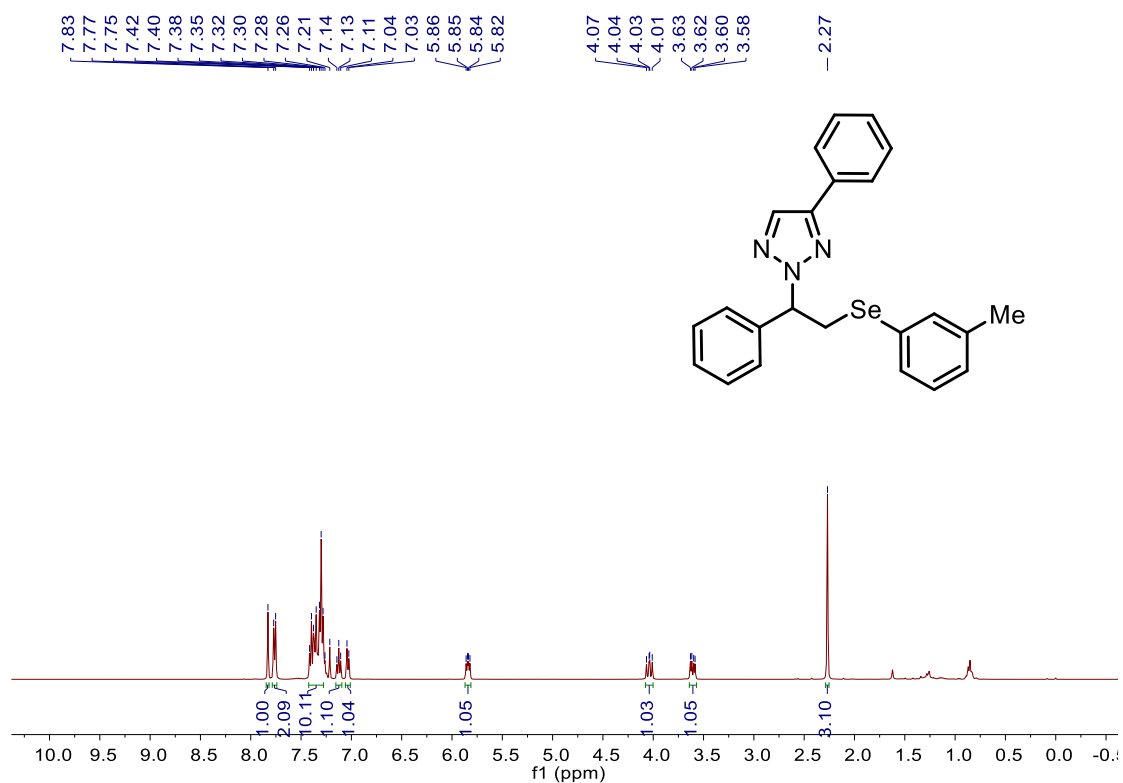


^{13}C NMR (100 MHz, CDCl_3) spectrum for 4ab

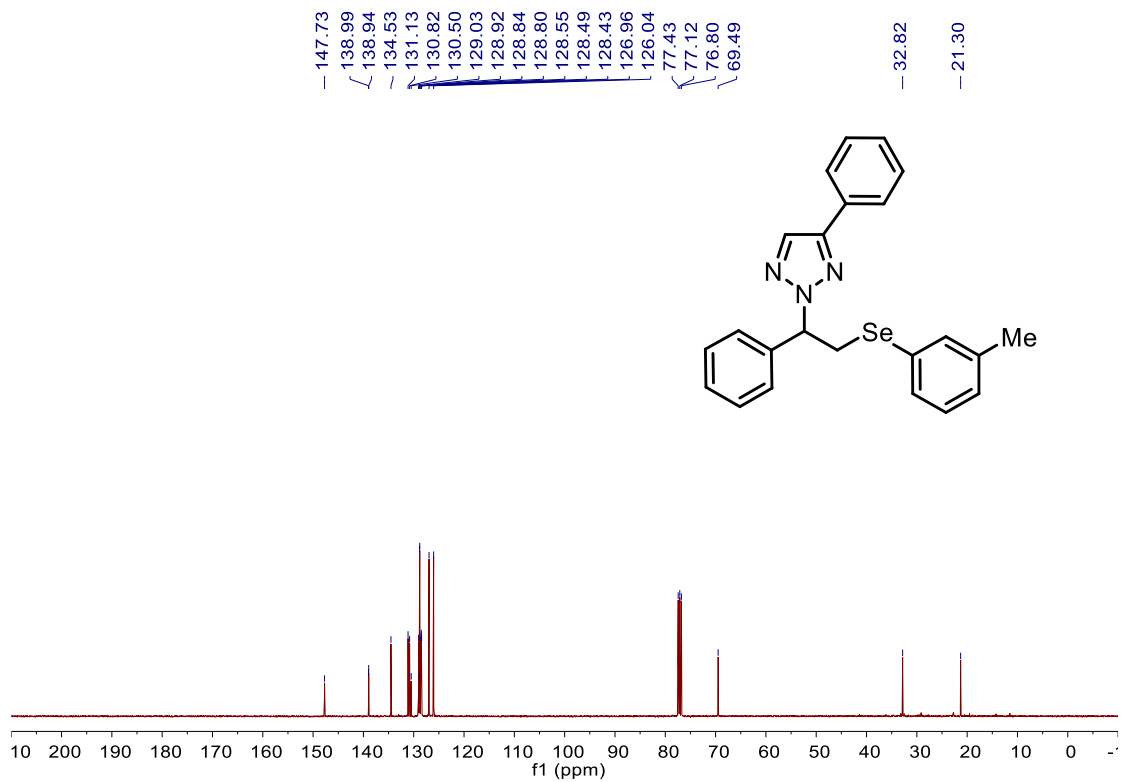


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4ac**

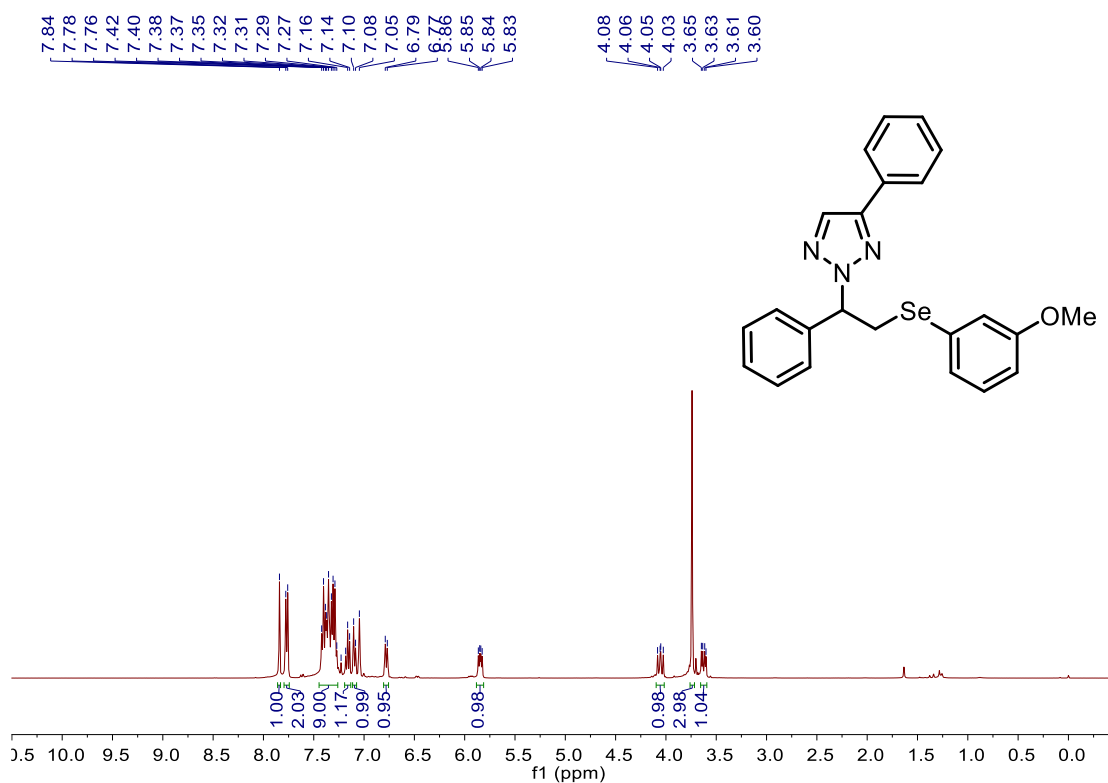


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4ac**

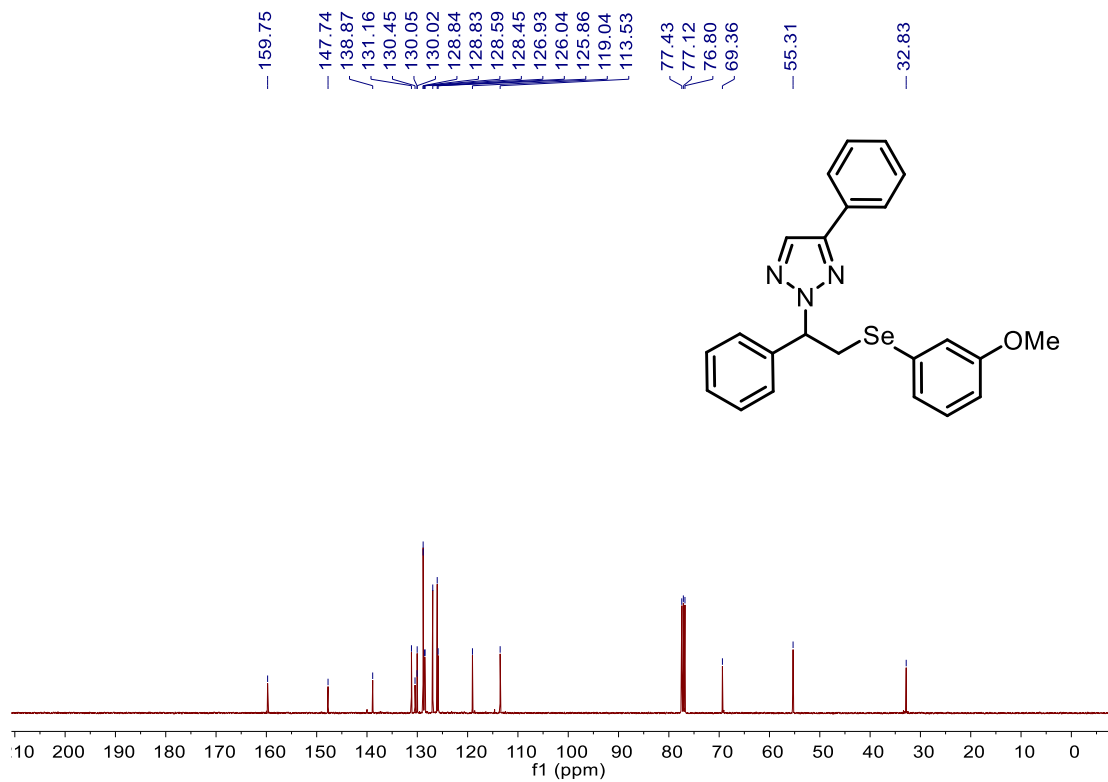


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4ad**

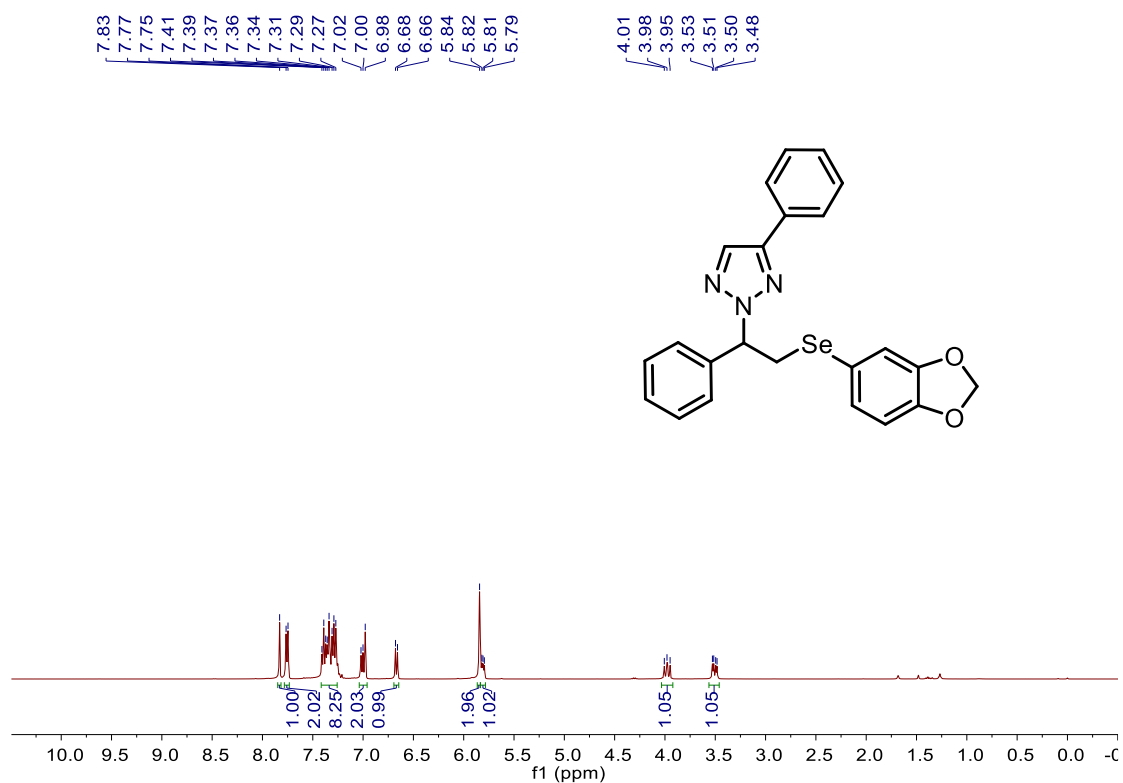


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4ad**

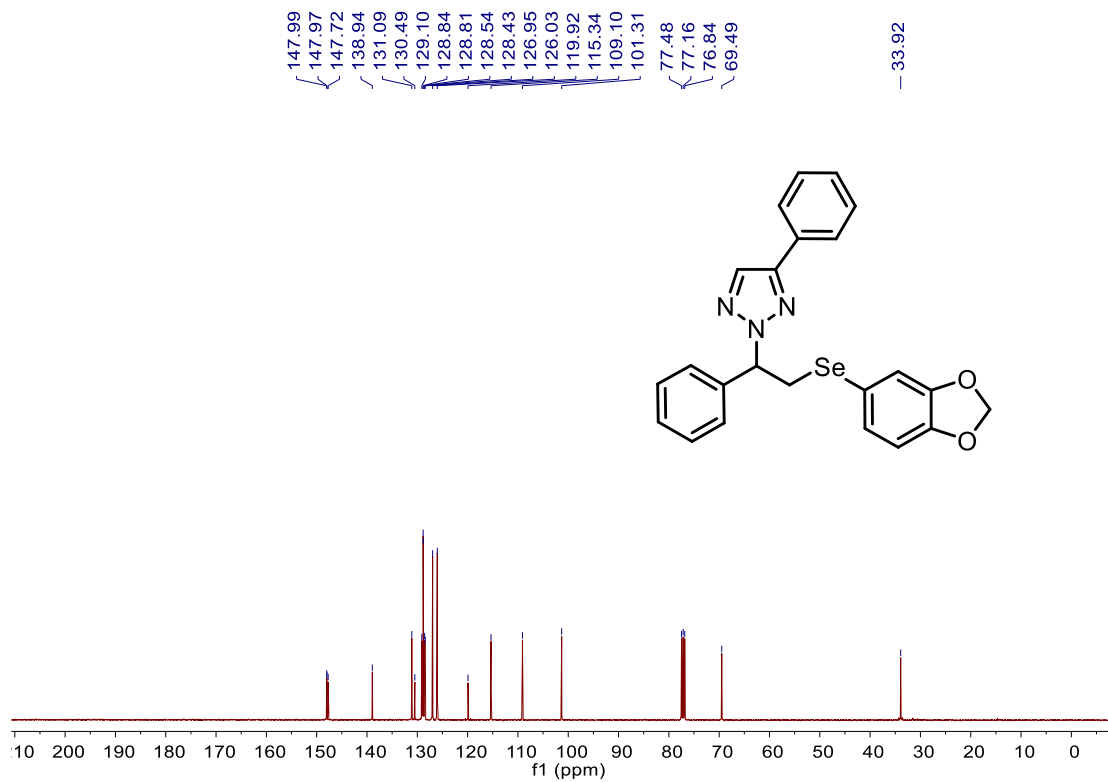


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4ae**

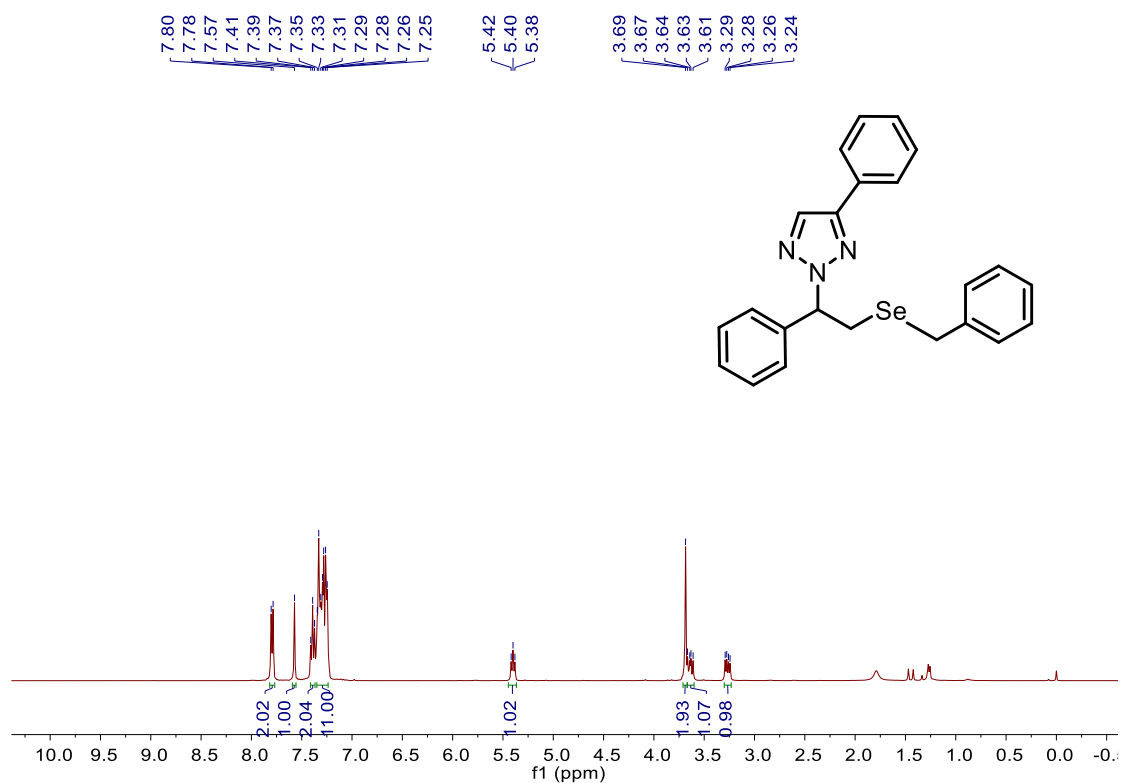


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4ae**

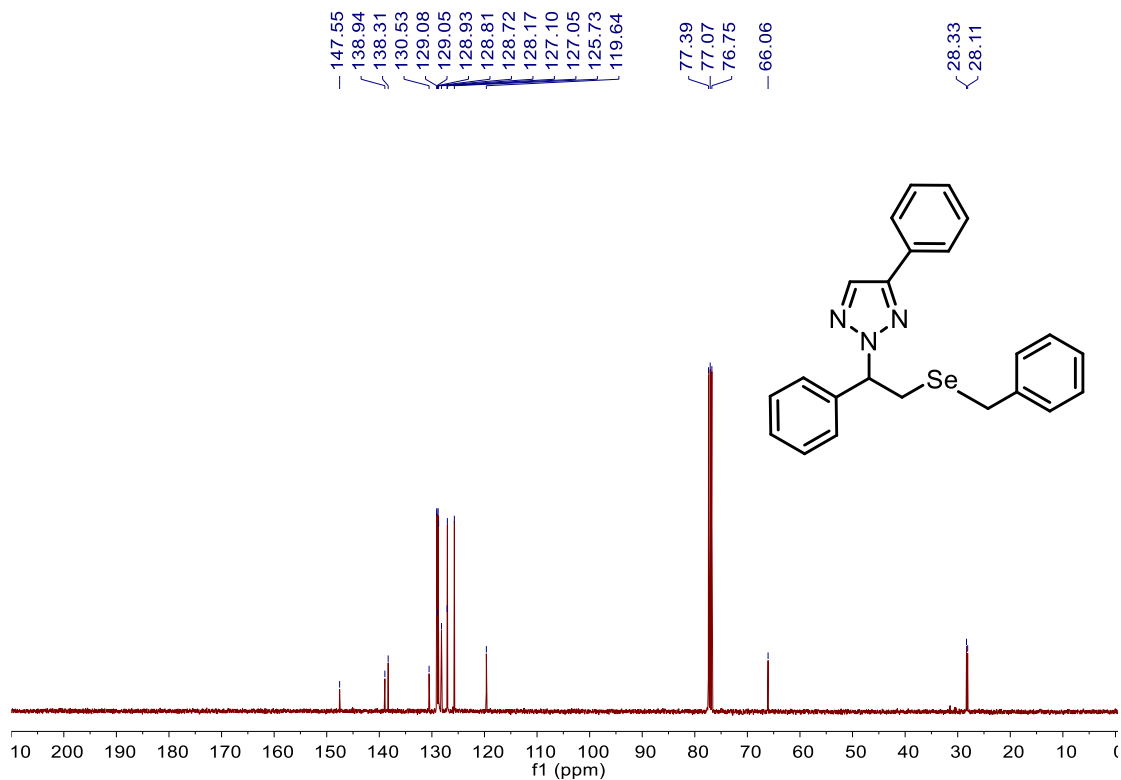


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4af**

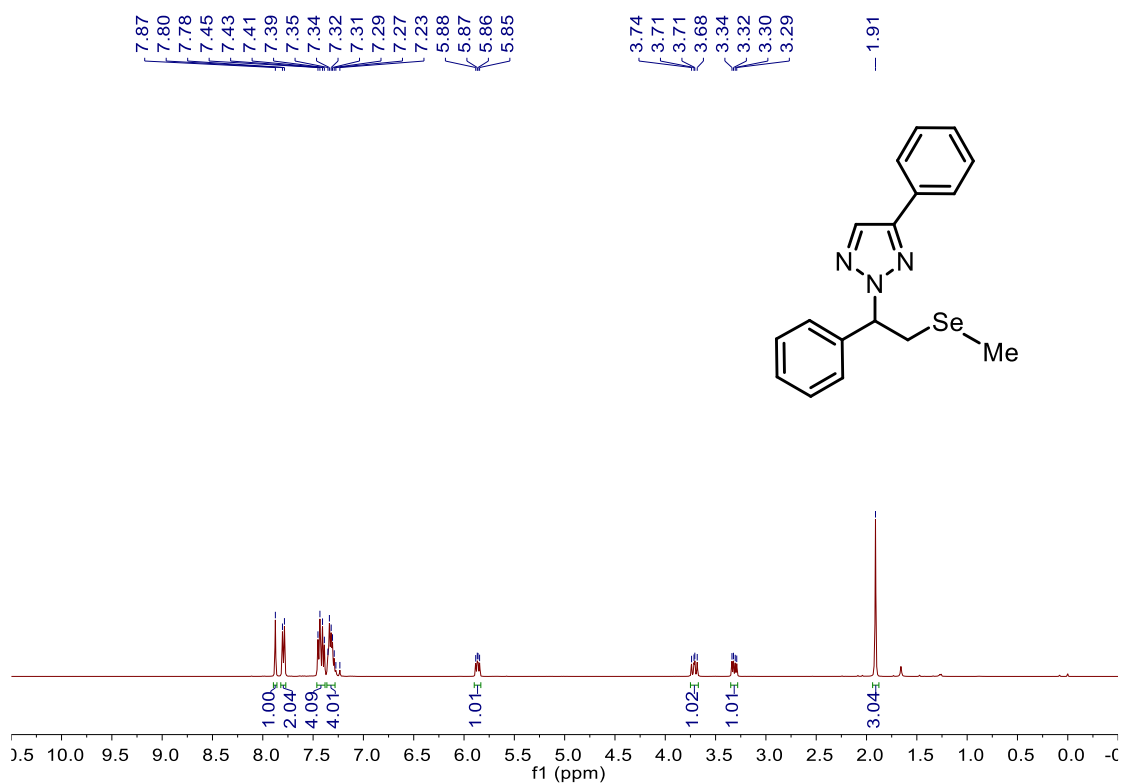


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4af**

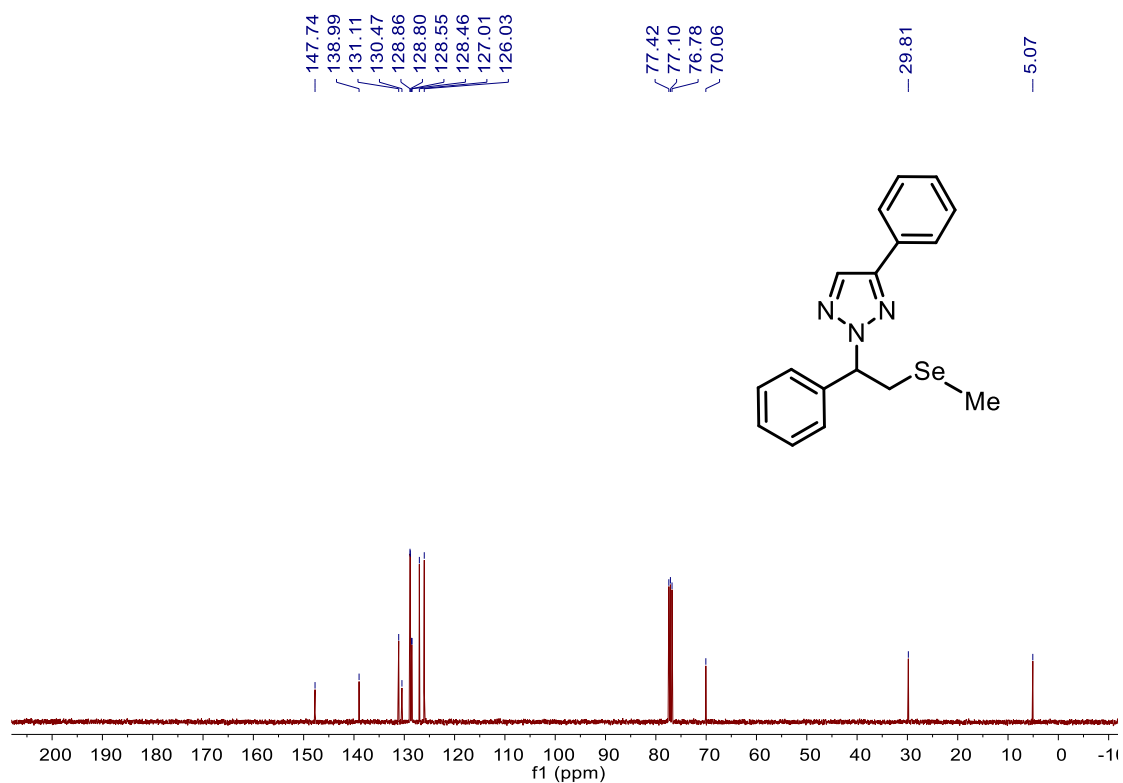


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **4ag**

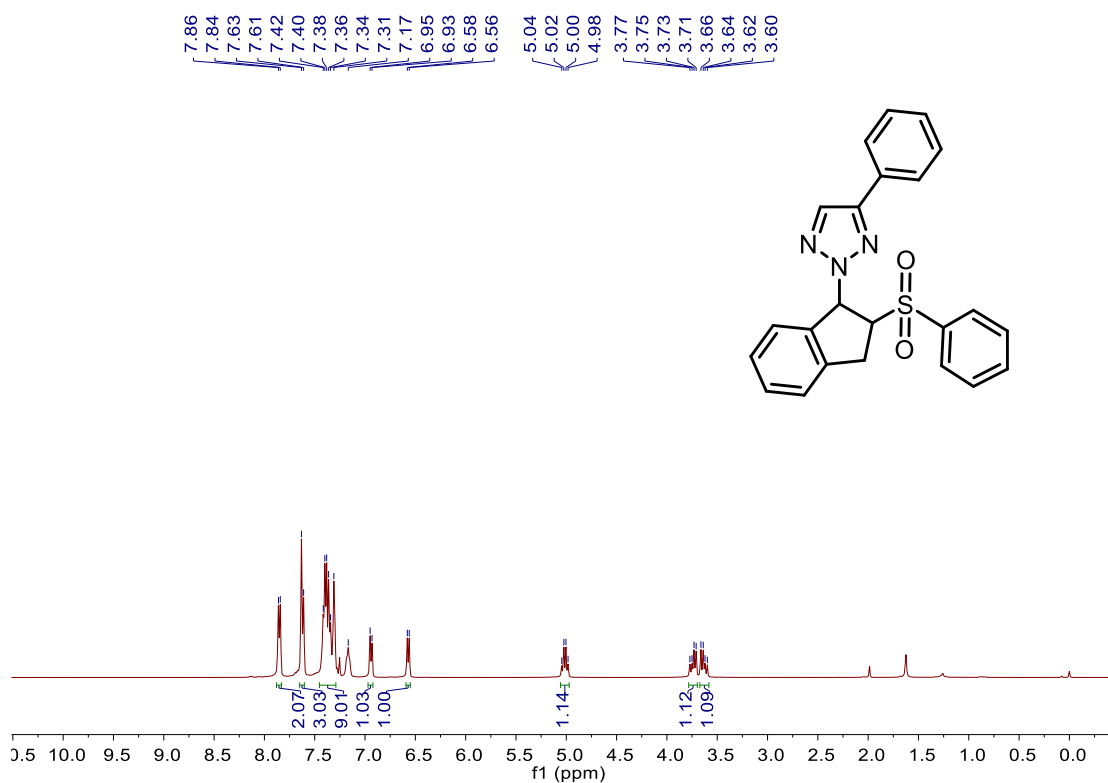


^{13}C NMR (100 MHz, CDCl_3) spectrum for **4ag**

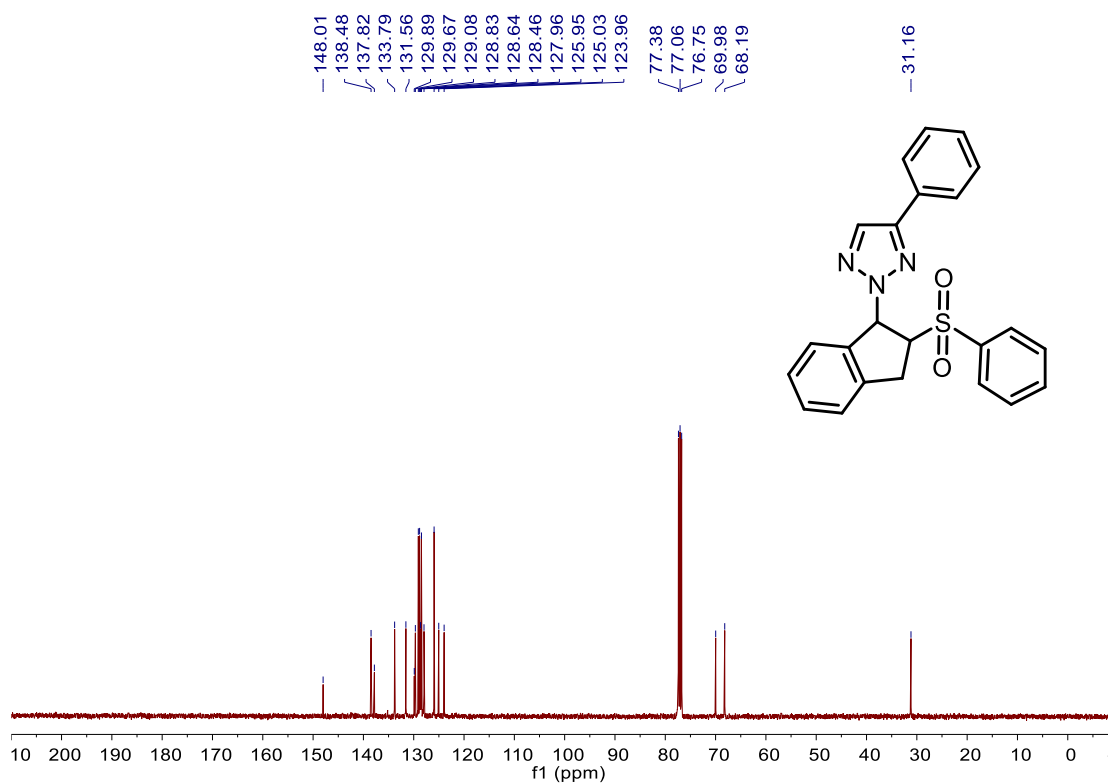


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **6**

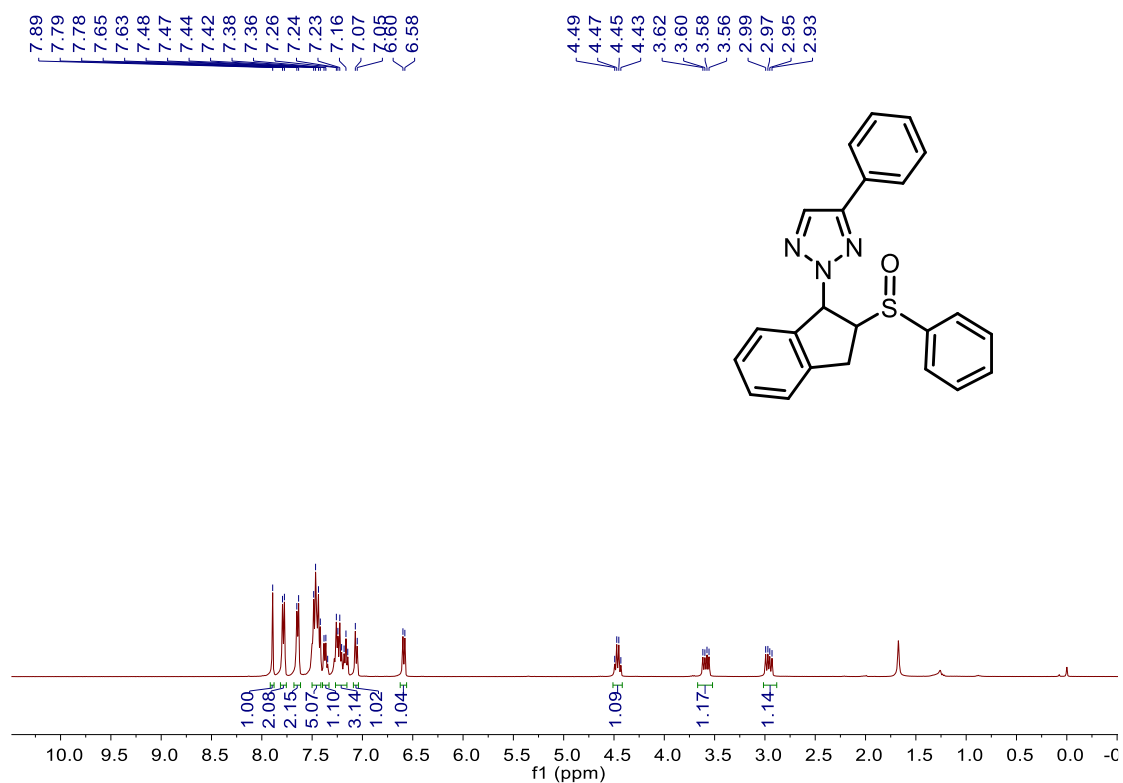


^{13}C NMR (100 MHz, CDCl_3) spectrum for **6**

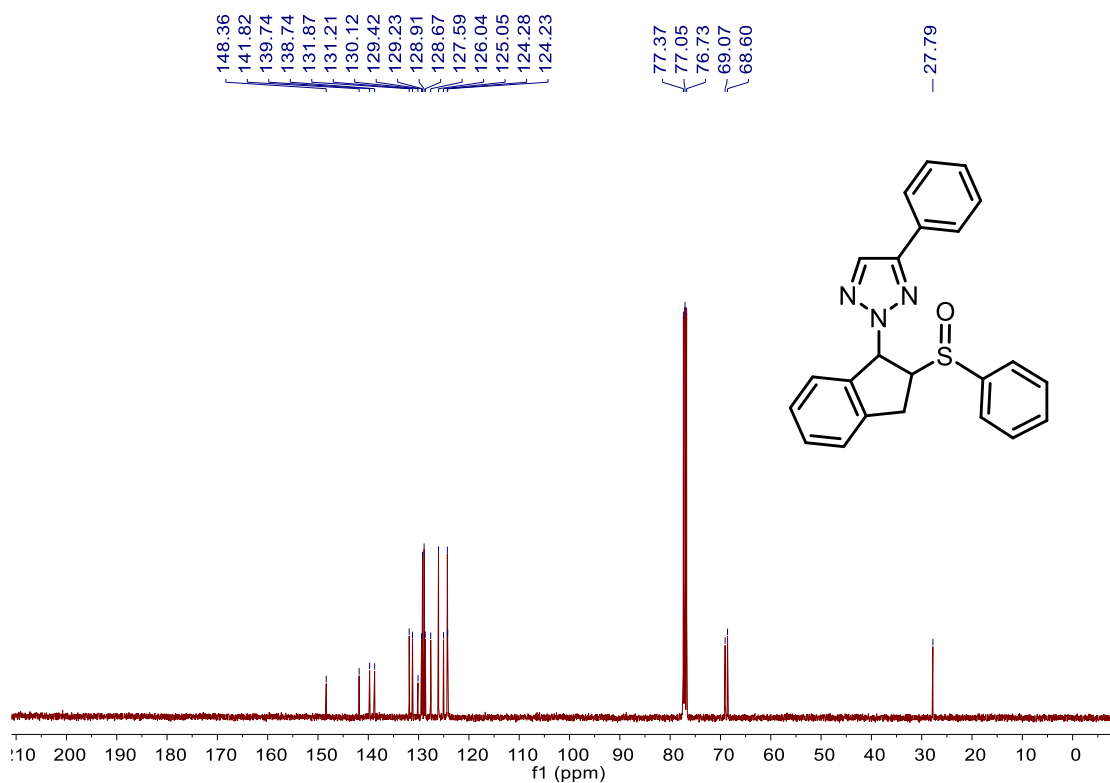


Electronic Supporting Information

^1H NMR (400 MHz, CDCl_3) spectrum for **7**



^{13}C NMR (100 MHz, CDCl_3) spectrum for **7**



Supplementary References

- (1) Kwok, S. W.; Zhang, L.; Grimster, N. P.; Fokin, V. V., Catalytic Asymmetric Transannulation of NH-1,2,3-Triazoles with Olefins. *Angew. Chem., Int. Ed.*, **2014**, *53*, 3452–3456.
- (2) Zhu, L.-L.; Tian, L. F.; Sun, K. H.; Li, Y. W.; Liu, G. L.; Cai, B.; Zhang, H.; Wang, Y. H. *N*²-selective β -thioalkylation of benzotriazoles with alkenes. *J. Org. Chem.* **2022**, *87*, 12963–12974.