Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting material

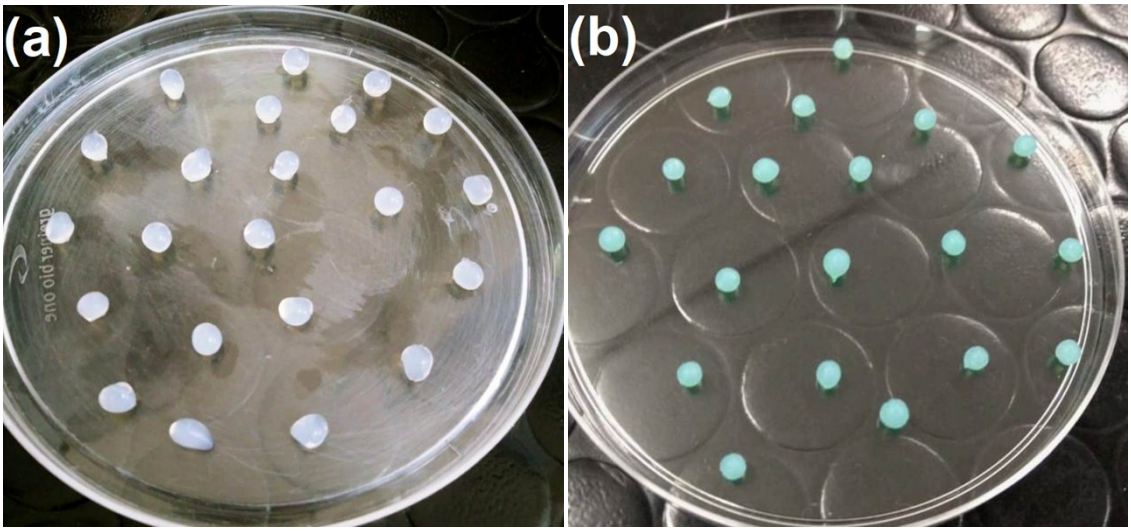


Figure S1. Photographic images taken from the as-prepared microspheres (a) Alg-Ca^{2+} and (b) Alg-Cu^{2+}.

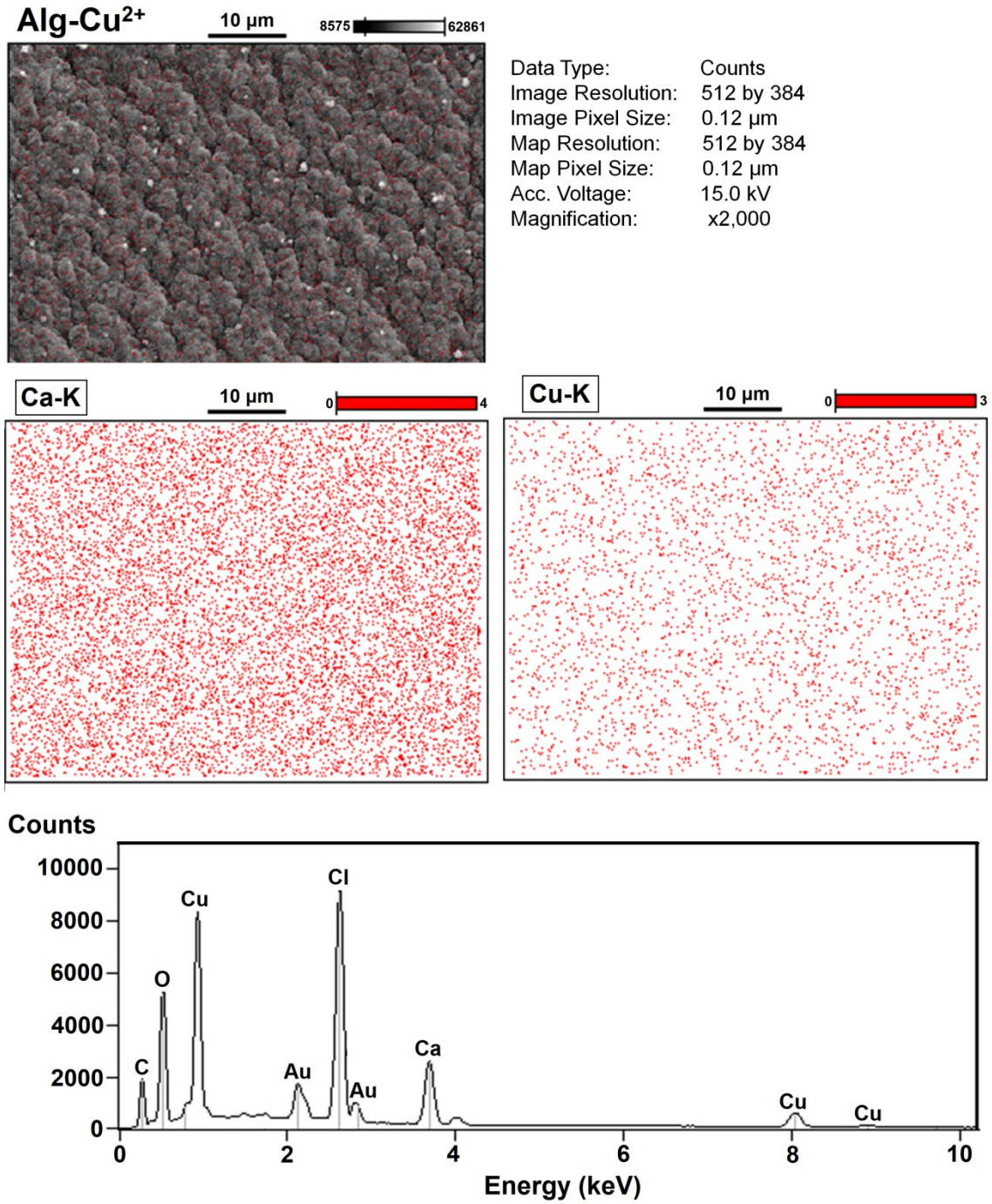
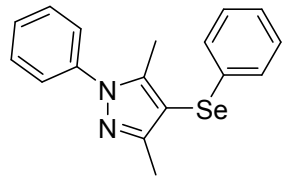
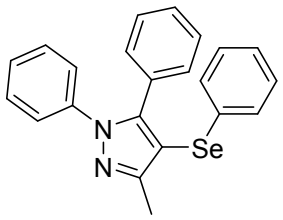


Figure S2. EDX analysis and elemental mapping of Alg-Cu^{2+} microspheres.

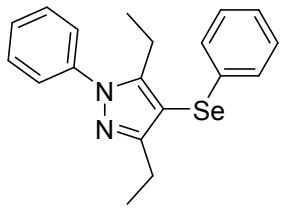
Spectral information of the synthesized products



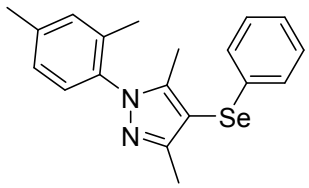
3,5-Dimethyl-1-phenyl-4-(phenylselanyl)-1H-pyrazole **(4a)**
Yield: 0.262 g (80%); orange solid; mp 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.33 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.13-7.19 (m, 5H, Ar-H), 7.37-7.48 (m, 5H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) = 12.5, 12.9, 102.6, 124.8, 125.8, 127.8, 128.4, 129.1, 129.2, 133.0, 139.9, 144.1, 153.3; MS (relative intensity, %) *m/z*: 77 (96.2), 118 (55.0), 157 (3.8), 171 (5.2), 248 (100.0), 328 (75.4).



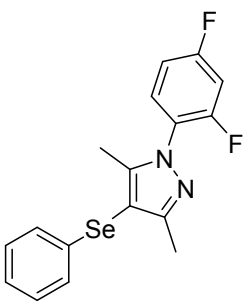
3-Methyl-1,5-diphenyl-4-(phenylselanyl)-1H-pyrazole **(4b)**
Yield: 0.347 g (89%); beige solid; mp 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.39 (s, 3H, CH_3), 7.13-7.19 (m, 7H, Ar-H), 7.24-7.30 (m, 8H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) =13.0, 103.5, 124.8, 125.8, 127.2, 128.2, 128.5, 128.7, 128.8, 129.1, 129.9, 130.1, 133.3, 139.9, 147.0, 154.0; MS (relative intensity, %) *m/z*: 77 (71.6), 157 (0.9), 180 (18.8), 233 (5.3), 310 (100.0), 390 (69.5).



3,5-Diethyl-1-phenyl-4-(phenylselanyl)-1H-pyrazole **(4c)**
Yield: 0.213 g (78%); orange oil; ; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.00 (t, 3H, *J* 7.6 Hz, CH_3), 1.23 (t, 3H, *J* 7.6 Hz, CH_3), 2.71 (q, 2H, *J* 7.6 Hz, CH_2), 2.79 (q, 2H, *J* 7.6 Hz, CH_2), 7.19-7.26 (m, 5H, Ar-H), 7.41-7.47 (m, 5H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) = 14.2, 14.4, 19.6, 21.3, 100.7, 125.8, 126.0, 128.5, 128.6, 129.5, 129.6 134.1, 140.5, 150.2, 158.8; MS (relative intensity, %) *m/z*: 77 (48.4); 132 (17.0), 157 (2.1), 199 (3.2), 275 (100.0), 356 (36.8).

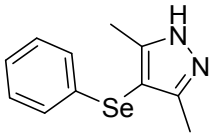


1-(2,4-Dimethylphenyl)-3,5-dimethyl-4-phenylselanyl-1H-pyrazole **(4d)**
Yield: 0.249 g (70%); yellowish solid; mp 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.03 (s, 3H, Ar-CH_3), 2.11 (s, 3H, Ar-CH_3), 2.31 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.07-7.22 (m, 8H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) = 11.3, 12.9, 17.1, 21.2, 100.4, 125.6, 127.2, 127.4, 128.0, 129.1, 131.5, 133.3, 135.6, 136.2, 139.2, 145.2, 152.8; MS (relative intensity, %) *m/z*: 77 (45.0), 105 (28.4), 118 (4.5), 157 (12.9), 199 (11.0), 275 (66.4), 356 (100.0).



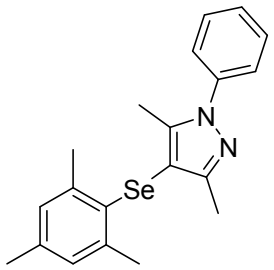
1-(2,4-Difluorophenyl)-3,5-dimethyl-4-(phenylselanyl)-1H-pyrazole **(4e)**
Yield: 0.254 g (71%); yellow oil; ; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.24 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 6.98–7.04 (m, 2 H, Ar-H), 7.15–7.26 (m, 5 H, Ar-H), 7.45 -7.51 (m, 1 H, Ar-H);); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) = 11.2 (d, *J* 3.4 Hz), 12.9, 102.0, 105.0 (dd, *J* 25.9 and 23.4 Hz), 112.0 (dd, *J* 23.5 and 4.1 Hz), 124.1 (dd, *J* 12.6 and 4.3 Hz), 125.8, 128.3, 129.2, 129.7 (dd, *J* 10.1 and 1.4 Hz), 132.7, 146.2,

154.09, 161.3 (dd, *J* 254.7 and 12.8 Hz), 163.9 (dd, *J* 254.2 and 12.6 Hz); MS(relative intensity, %) *m/z*: 41 (6), 63 (3), 65 (11), 77 (32), 91 (6), 103 (9), 113 (42), 127 (28), 128 (16), 140 (7), 143 (5), 154 (100), 155 (13), 166 (6), 194 (2), 207 (8), 222 (5), 236 (4), 242 (16), 243 (11), 256 (8), 263 (9), 268 (18), 269 (7), 283 (63), 284 (99), 362 364. (M^+ 59), (30), 365 (6), 366 (12).

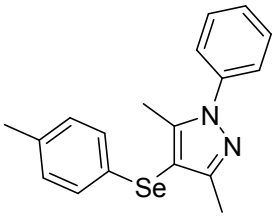


3,5-dimethyl-4-(phenylselanyl)-1H-pyrazole **(4f)**

Yield: 0.131 g (52%); white solid, m.p: 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.34 (s, 6H, CH_3), 7.10-7.18 (m, 5H, Ar-H), 11.65 (s, 1H, N-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 12.0, 100.1, 125.7, 128.3, 129.2, 133.2, 149.1; MS (relative intensity, %) *m/z*: 77 (16.3), 95 (13.2), 118 (1.6), 157 (10.6), 172 (100.0), 252 (58.9).

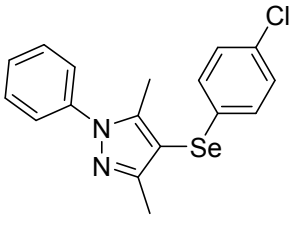


4-(Mesitylselanyl)-3,5-dimethyl-1-phenyl-1H-pyrazole ***(4g):*** Yield: 0.281 g (76%); yellow oil; ; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.15 (s, 3 H, Ar-CH_3) 2.25 (s, 6 H, Ar-CH_3), 2.44 (s, 6 H, CH_3), 6.80-6.88 (s, 2 H, Ar-H), 7.38-7.45 (m, 5 H, Ar-H);); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) = 12.2, 12.9, 20.8, 24.0, 104.2, 124.7, 127.5, 127.8, 128.8, 129.0 137.5, 139.8, 141.5, 141.7, 151.8; (relative intensity, %) *m/z*: 41 (5). 51 (11), 65 (7), 77 (61), 91 (19), 115 (14), 117 (19), 118 (42), 130 (7), 158 (16), 171 (12), 183 (10), 195 (22), 196 (26), 196 (51), 198 (100), 200 (28), 251 (2), 278 (3), 289 (9), 366 (14), 367 (15), 368 (40), 369 (18), 370 (M^+ 74), 371 (17), 372 (14).



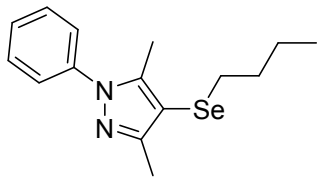
3,5-dimethyl-1-phenyl-4-(p-tolylselanyl)-1H-pyrazole **(4h)**

Yield: 0.0.273 g (80%); slightly orange solid, m.p: 95-97 °C; ; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.27 (s, 3H, Ar- CH_3), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.01-7.03 (m, 2H, Ar-H), 7.10-7.12 (m, 2H, Ar-H), 7.34-7.39 (m, 1H, Ar-H), 7.45-7.46 (m, 4H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) =12.6, 13.0, 21.0, 103.2, 124.8, 127.8, 128.9, 129.1, 129.20, 130.0, 135.8, 140.0, 144.0, 153.3; MS (relative intensity, %) *m/z*: 77 (55.1), 118 (32.1), 170 (3.9), 171 (5.7), 262 (100.0), 342 (46.7).



4-[(4-Chlorophenyl)selanyl]-3,5-dimethyl-1-phenyl-1H-pyrazole **(4i)**

Yield: 0.147 g (45%); yellowish solid, m.p: 124-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.32 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.11-7.17 (m, 3H, Ar-H), 7.26 (s, 1H, Ar-H), 7.39 (s, 1H, Ar-H), 7.47-7.51 (m, 4H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) =12.4, 12.9, 102.3, 124.8, 127.9, 129.1, 129.2, 129.6, 131.2, 131.8, 139.7, 144.1, 153.1; MS (relative intensity, %) *m/z*: = 77 (100.0), 118 (59.5), 171 (3.9), 191 (2.3), 282 (83.9), 362 (66.3).



4-(Butylselanyl)-3,5-dimethyl-1-phenyl-1H-pyrazole **(4j)**

Yield: 0.194 g (63%); yellowish oil. ; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.90 (t, J 7.5 Hz, 3H, CH_3), 1.42 (sext, J 7.5 Hz, 2H, CH_2), 1.58 (quint, J 7.5 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.58 (t, J 7.5 Hz, 2H, CH_2), 7.34-7.36 (m, 1H, Ar-H), 7.44-7.48 (m, 4H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$,) δ (ppm) = 12.6, 13.1, 13.6, 22.8, 28.4, 32.4, 103.2, 124.7, 127.5, 129.0, 140.0, 143.3, 152.9; MS (relative intensity, %) *m/z*: 57 (6.1), 77 (72.3), 118 (75.4), 171 (100.0), 251 (24.3), 308 (43.9).

Selected NMR spectra

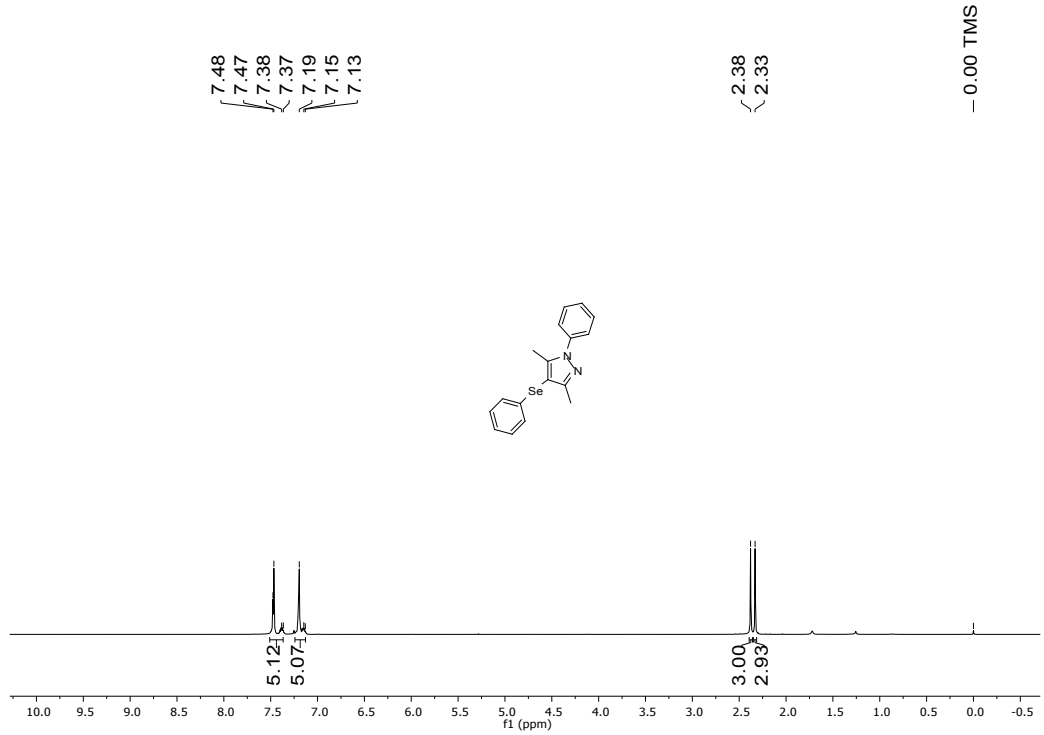


Figure S3. ^{1}H NMR (400 MHz) spectrum for product **4a** in $CDCl_3$.

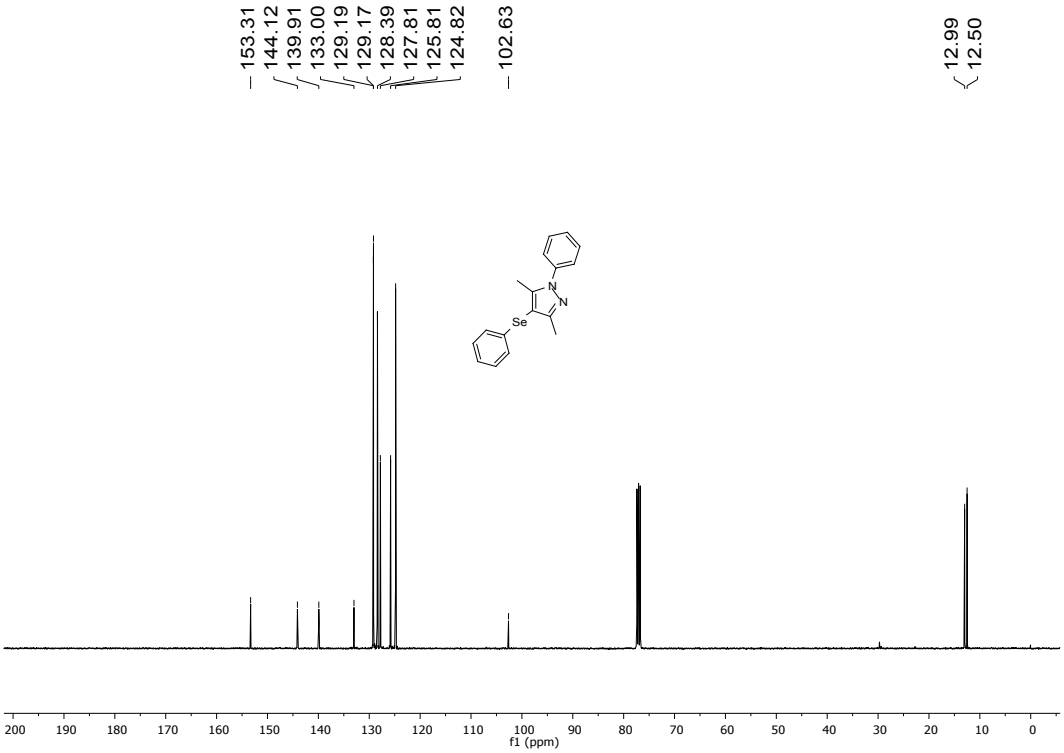


Figure S4. ^{13}C NMR (100 MHz) spectrum for product **4a** in $CDCl_3$.

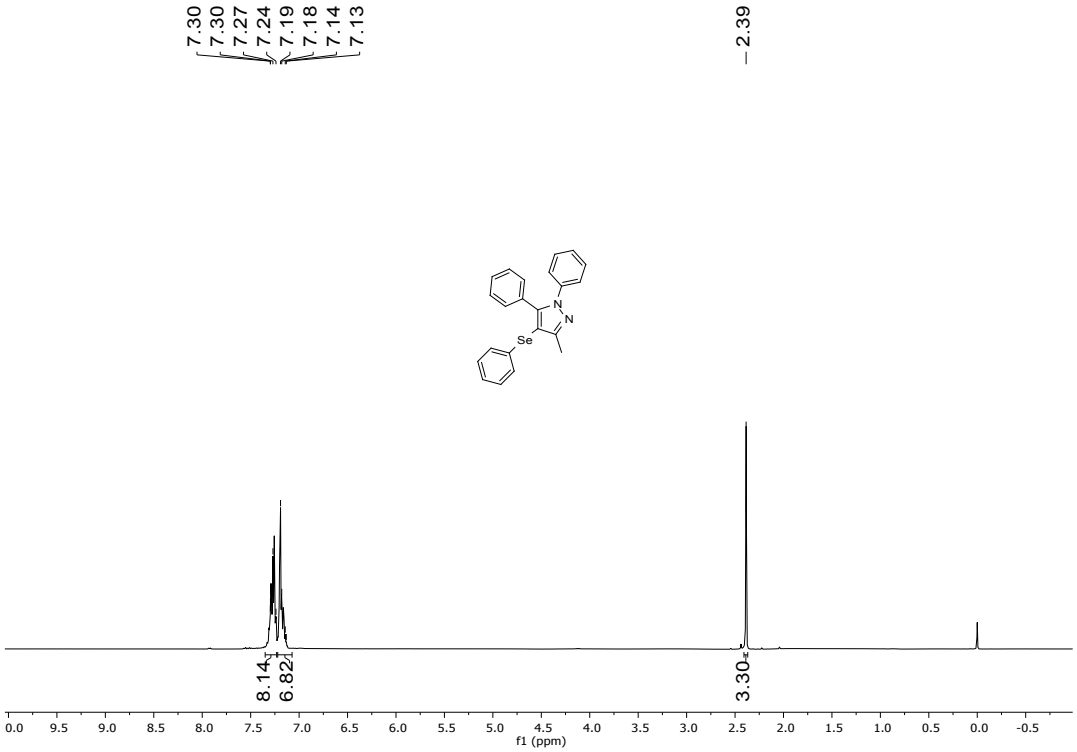


Figure S5. ^{1}H NMR (400 MHz) spectrum for product **4b** in $CDCl_3$.

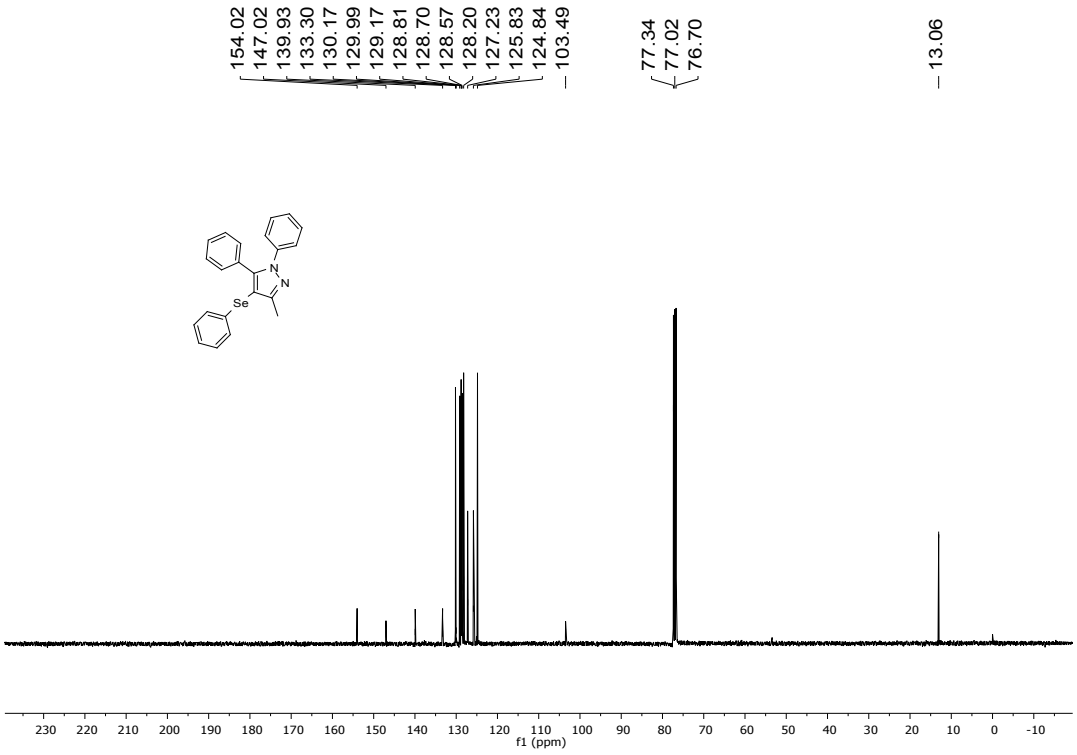


Figure S6. ^{13}C NMR (100 MHz) spectrum for product **4b** in $CDCl_3$.

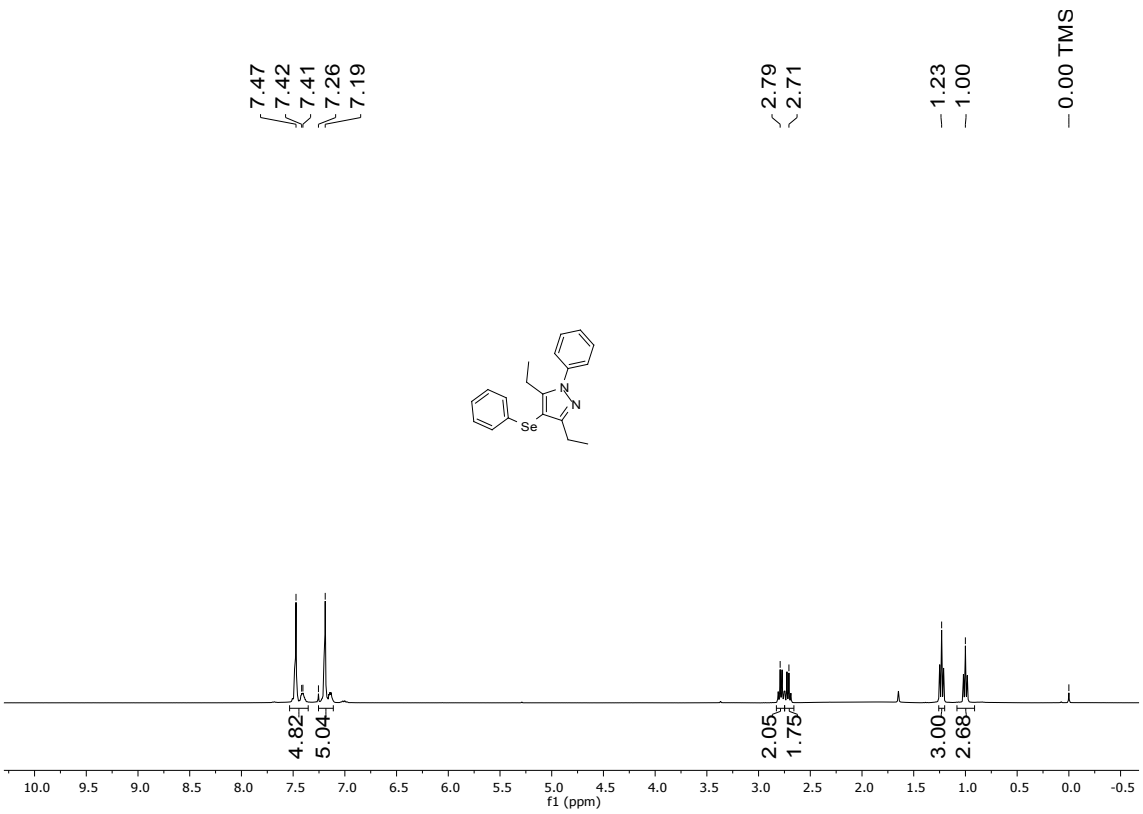


Figure S7. ^{1}H NMR (400 MHz) spectrum for product **4c** in $CDCl_3$.

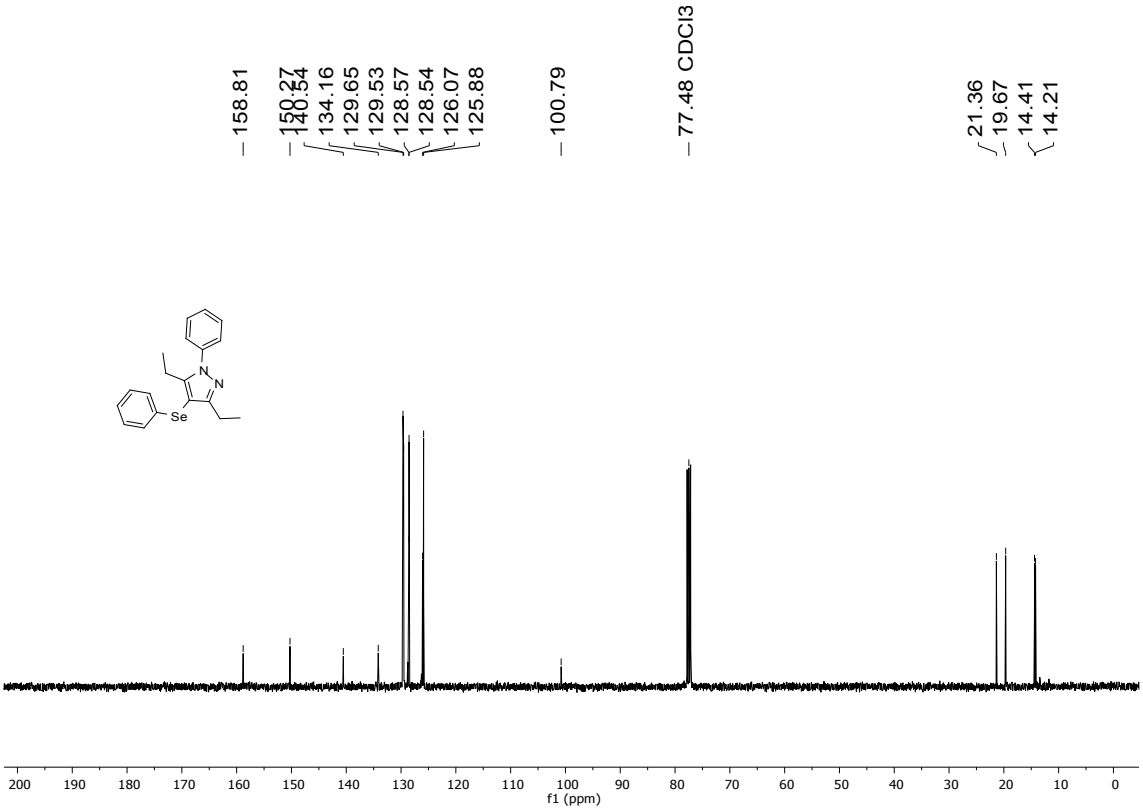


Figure S8. ^{13}C NMR (100 MHz) spectrum for product **4c** in $CDCl_3$.

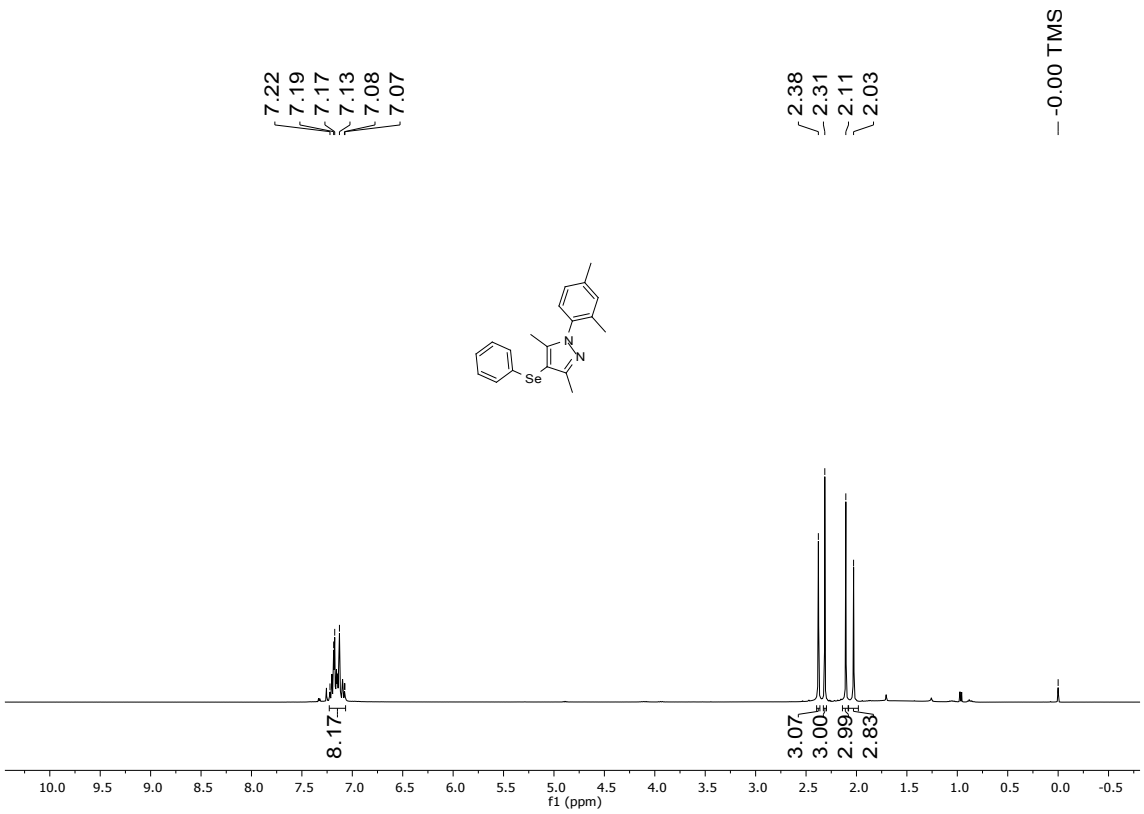


Figure S9. ^{1}H NMR (400 MHz) spectrum for product **4d** in $CDCl_3$.

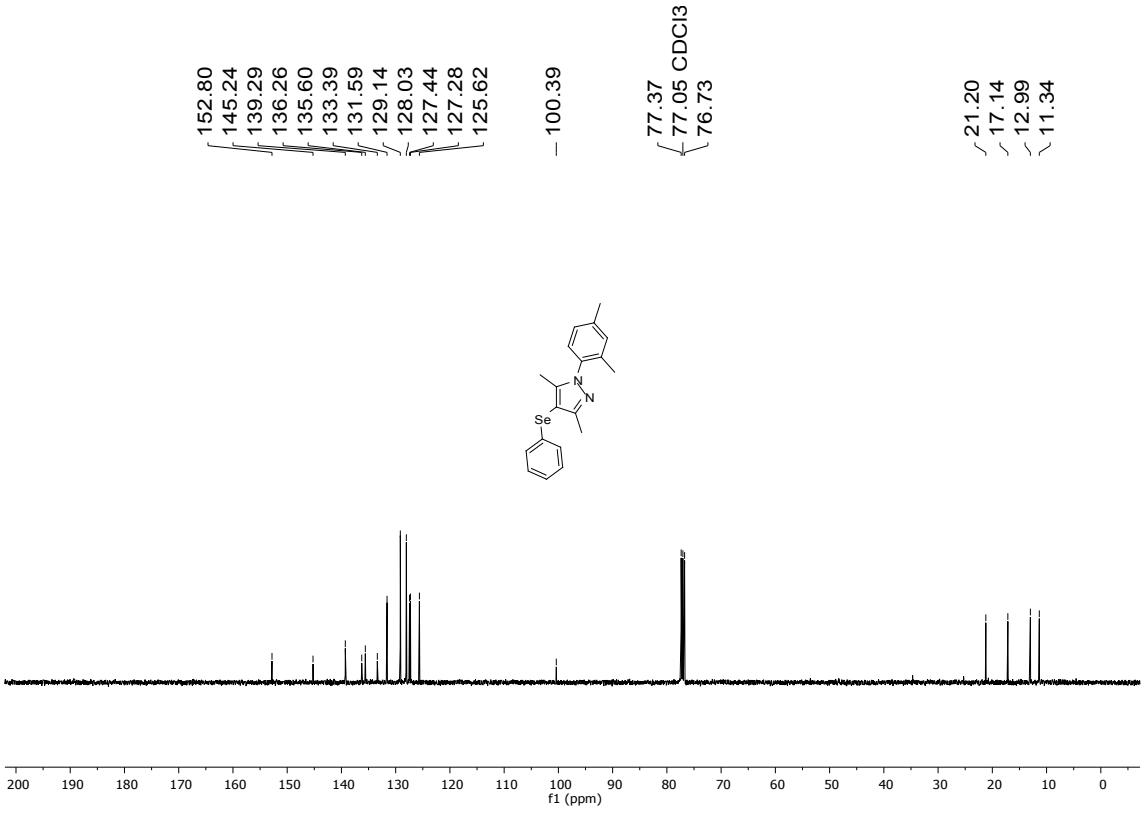


Figure S10. ^{13}C NMR (100 MHz) spectrum for product **4d** in $CDCl_3$.

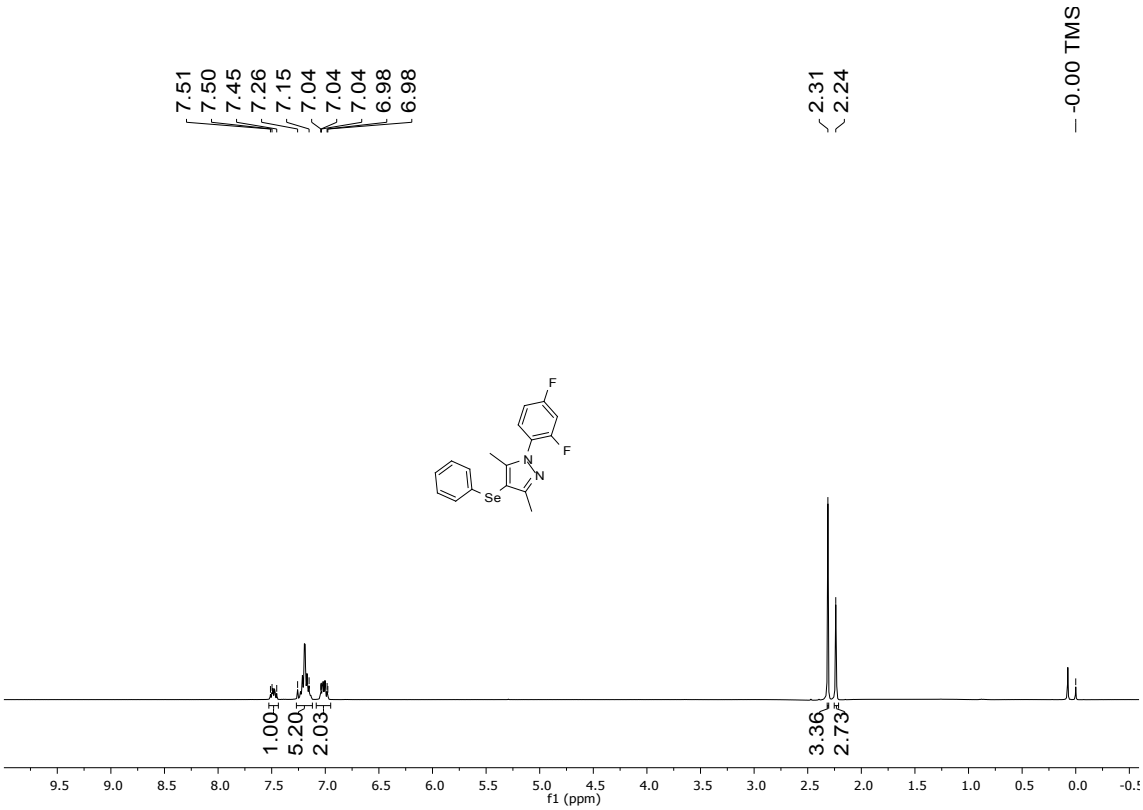


Figure S11. ^{1}H NMR (400 MHz) spectrum for product **4e** in $CDCl_3$.

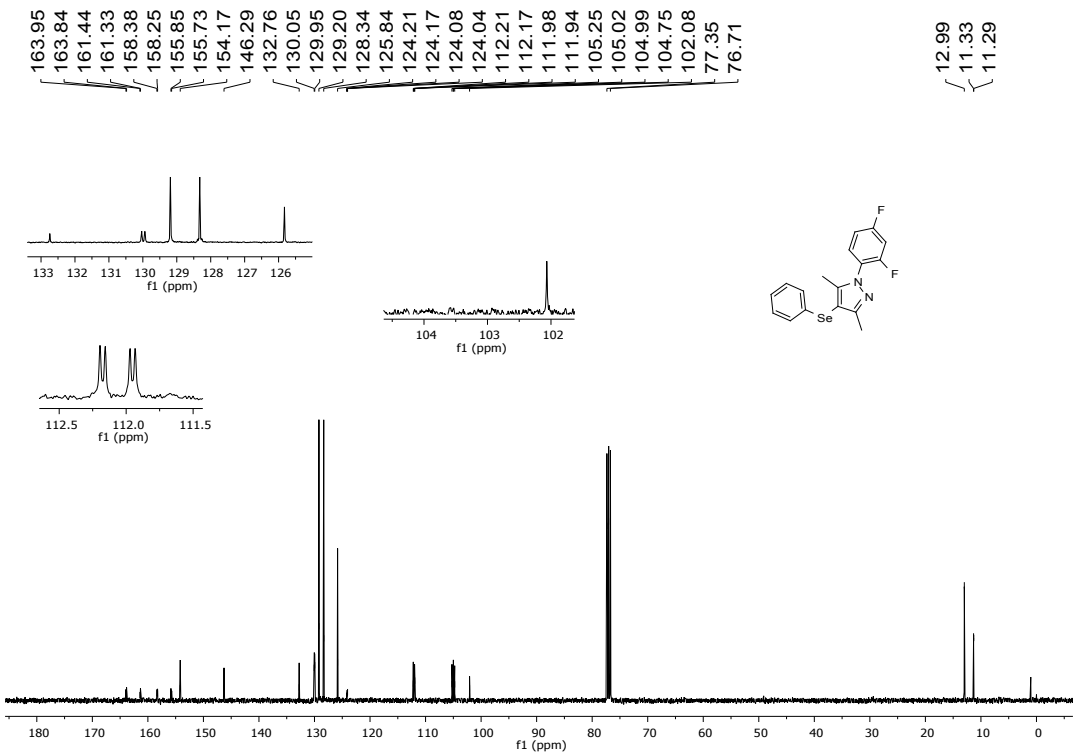


Figure S12. ^{13}C NMR (100 MHz) spectrum for product **4e** in $CDCl_3$.

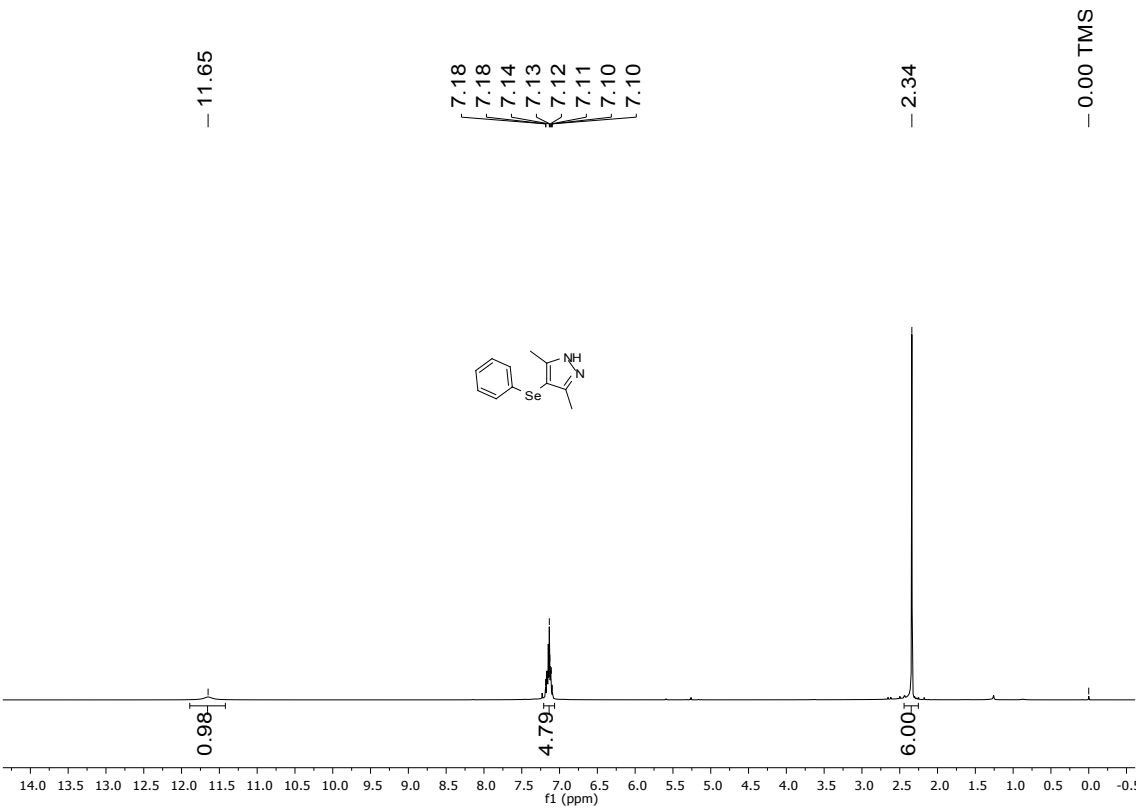


Figure S13. ^{1}H NMR (400 MHz) spectrum for product **4f** in $CDCl_3$.

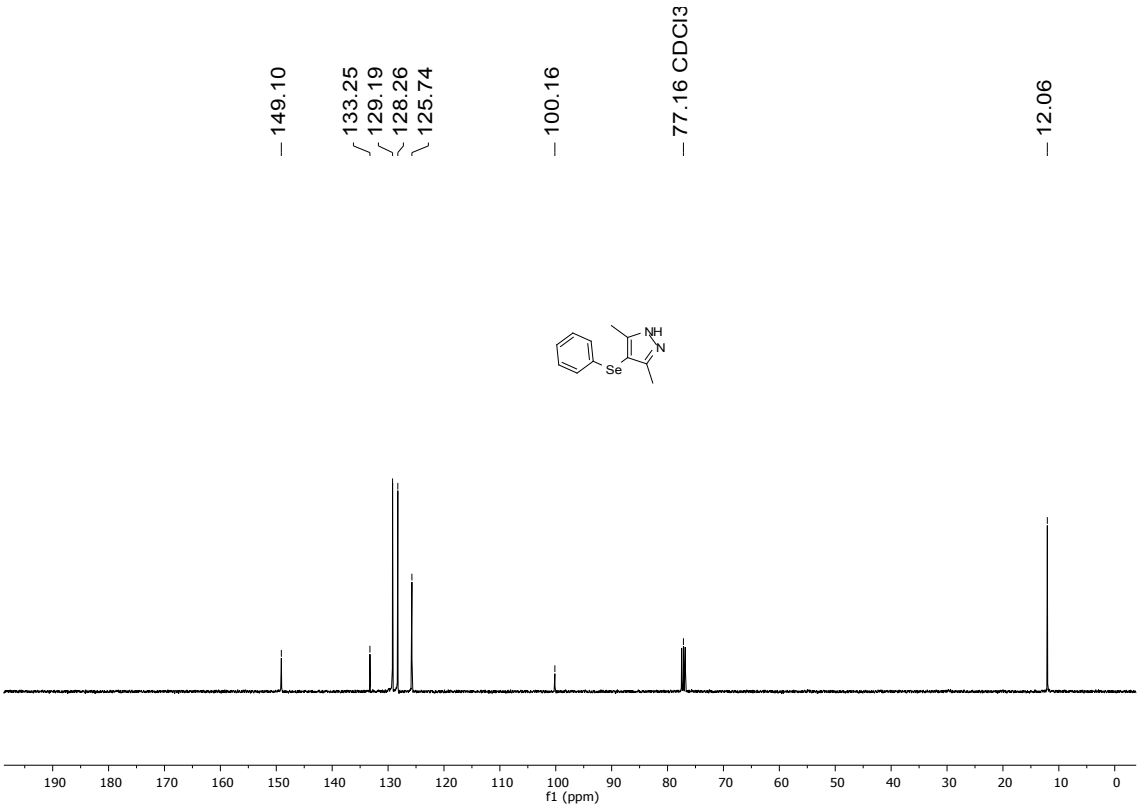


Figure S14. ^{13}C NMR (100 MHz) spectrum for product **4f** in $CDCl_3$.

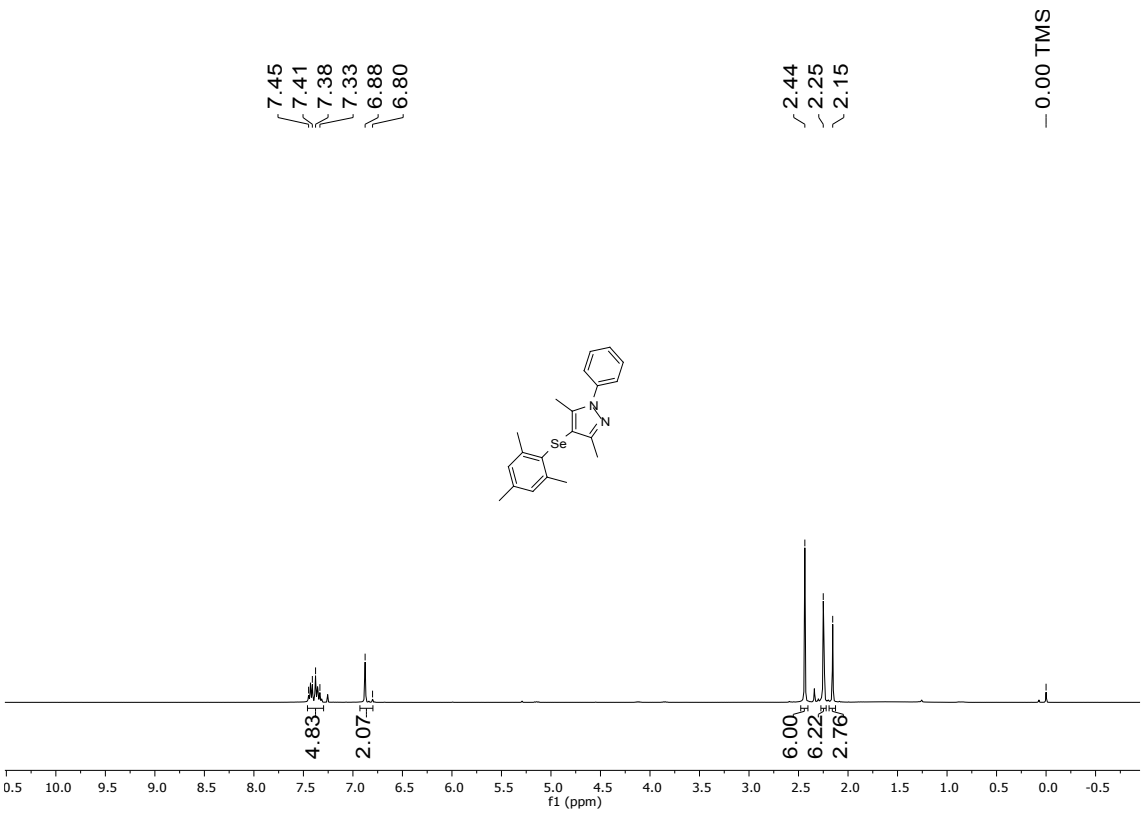


Figure S15. ^{1}H NMR (400 MHz) spectrum for product **4g** in $CDCl_3$.

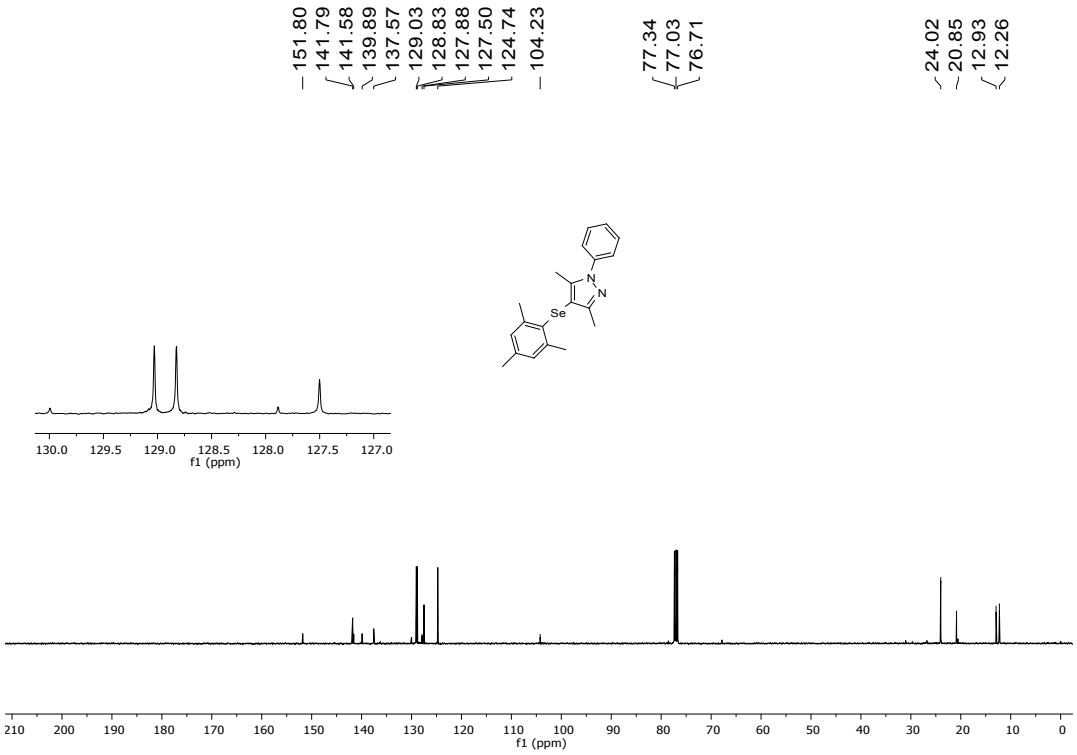


Figure S16. ^{13}C NMR (100 MHz) spectrum for product **4g** in $CDCl_3$.

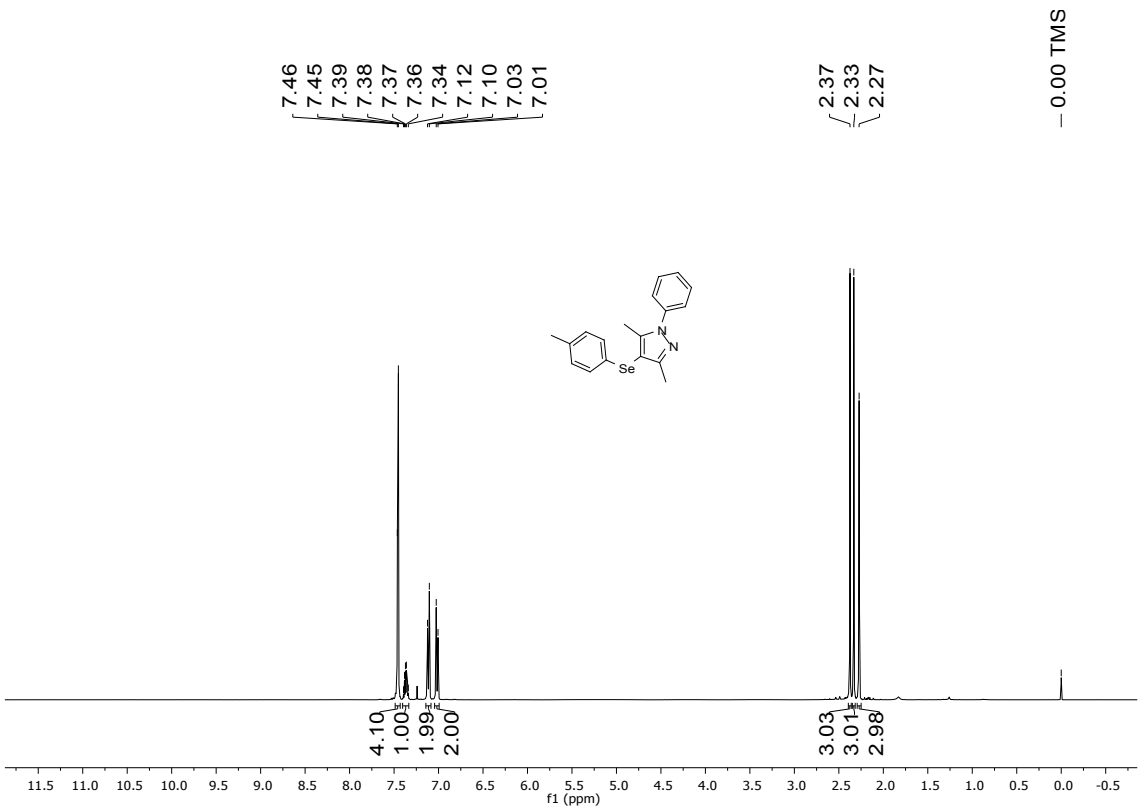


Figure S17. ^{1}H NMR (400 MHz) spectrum for product **4h** in $CDCl_3$.

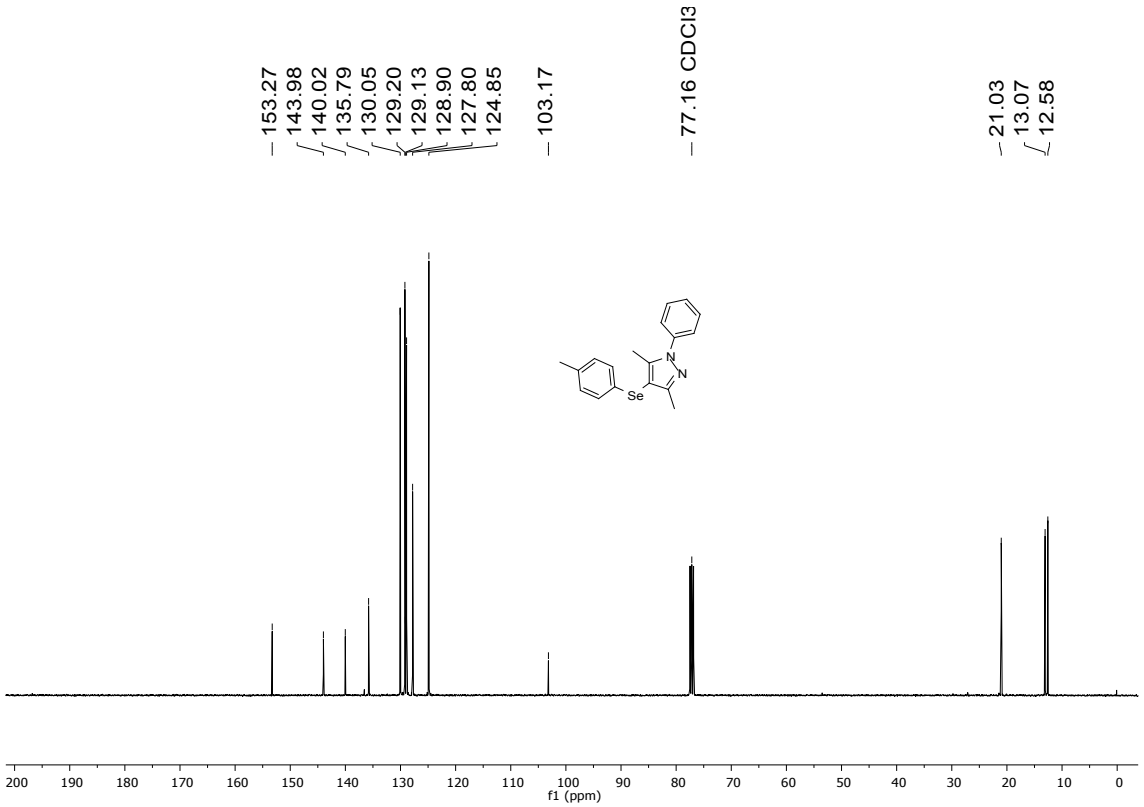


Figure S18. ^{13}C NMR (100 MHz) spectrum for product **4h** in $CDCl_3$.

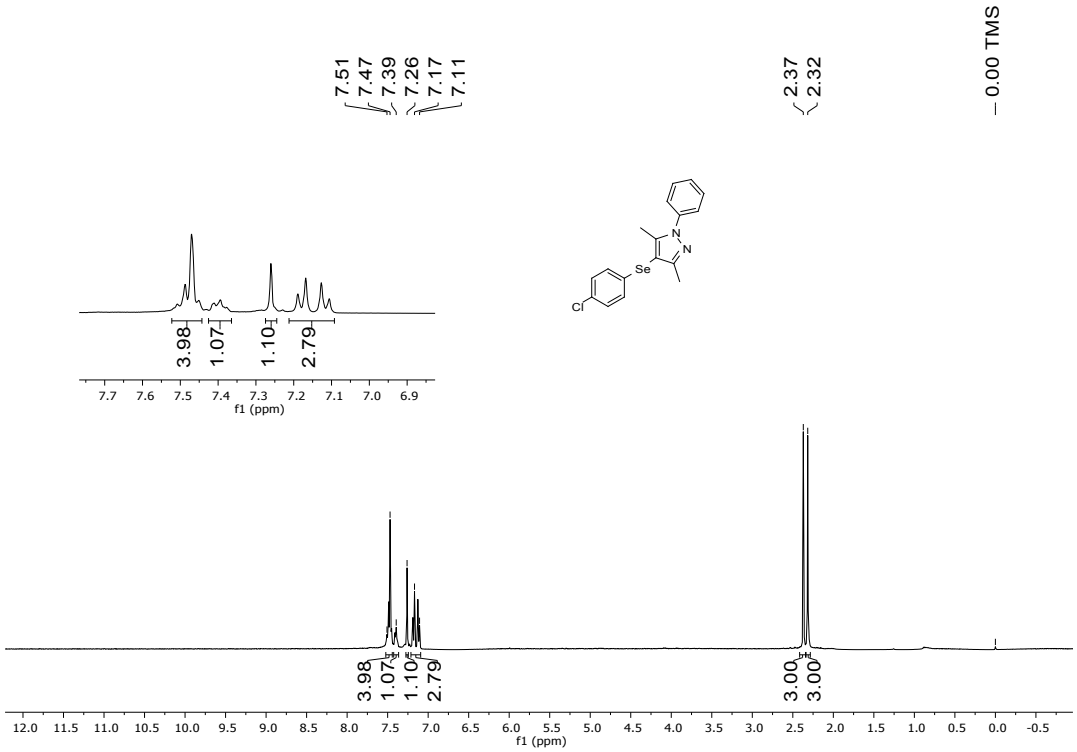


Figure S19. ^{1}H NMR (400 MHz) spectrum for product **4i** in $CDCl_3$.

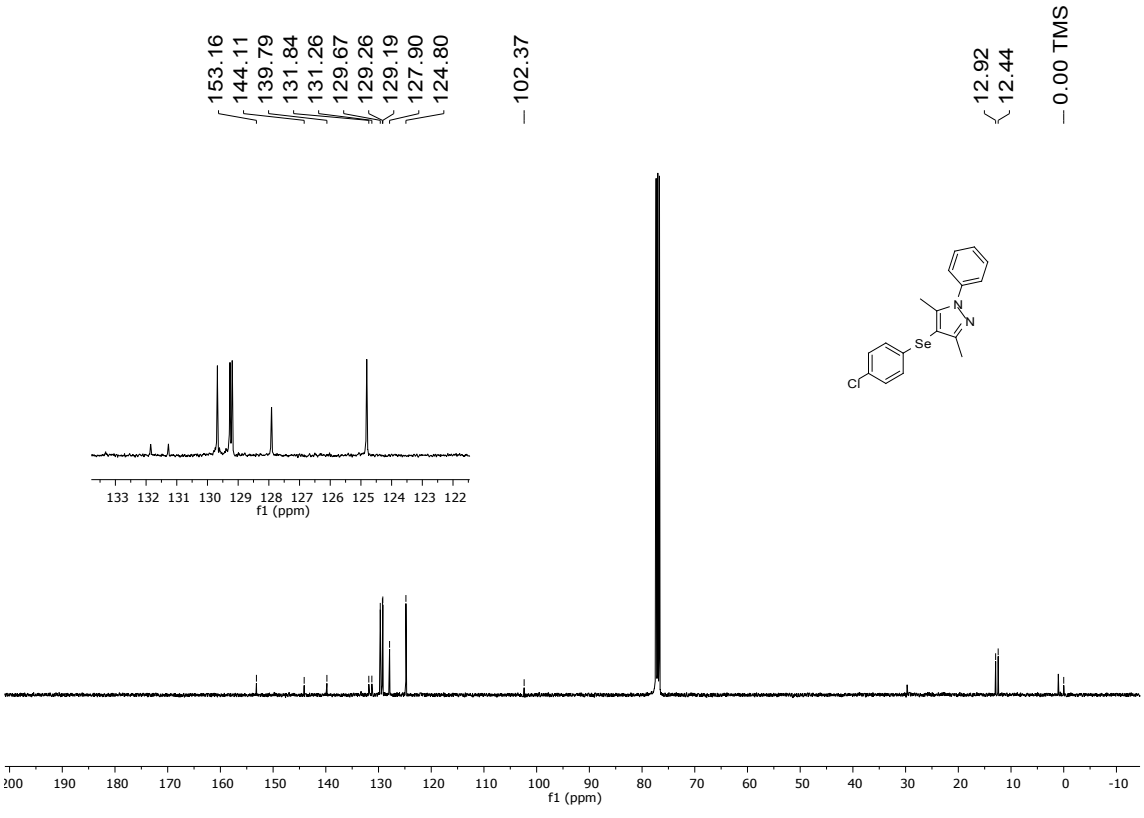


Figure S20. ^{13}C NMR (100 MHz) spectrum for product **4i** in $CDCl_3$.

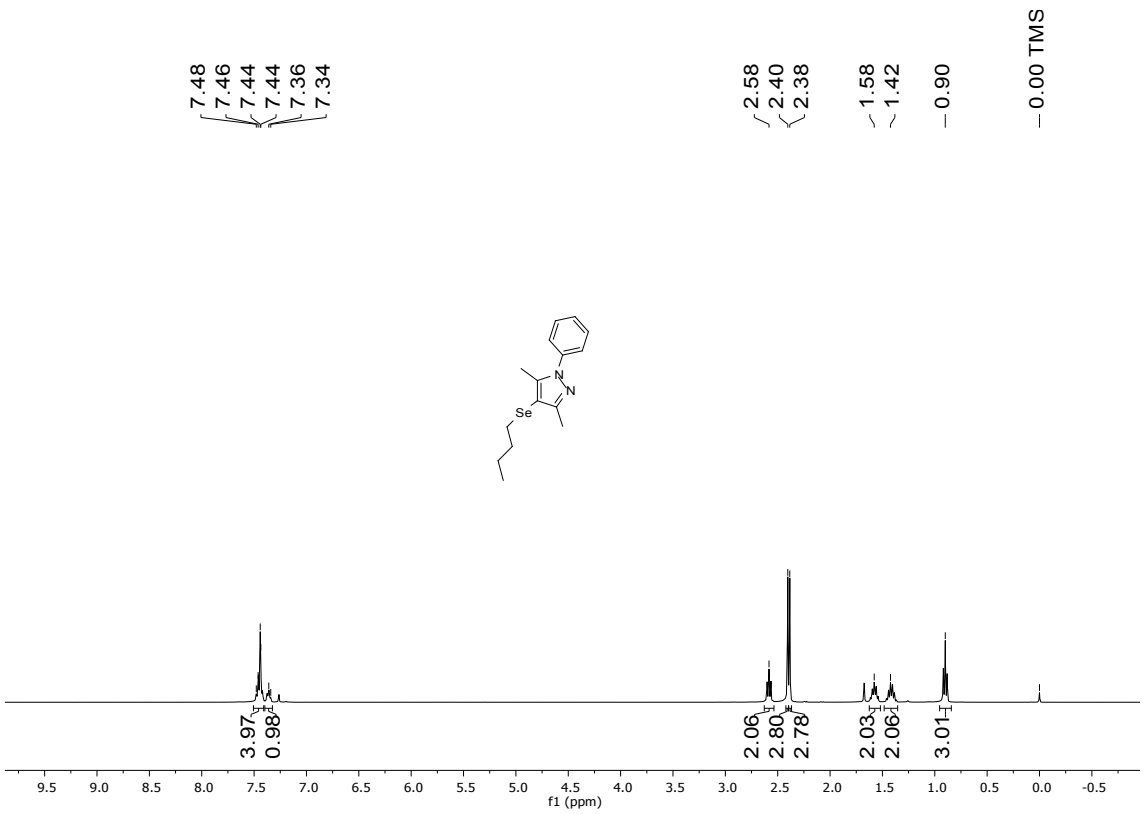


Figure S21. ^{1}H NMR (400 MHz) spectrum for product **4j** in $CDCl_3$.

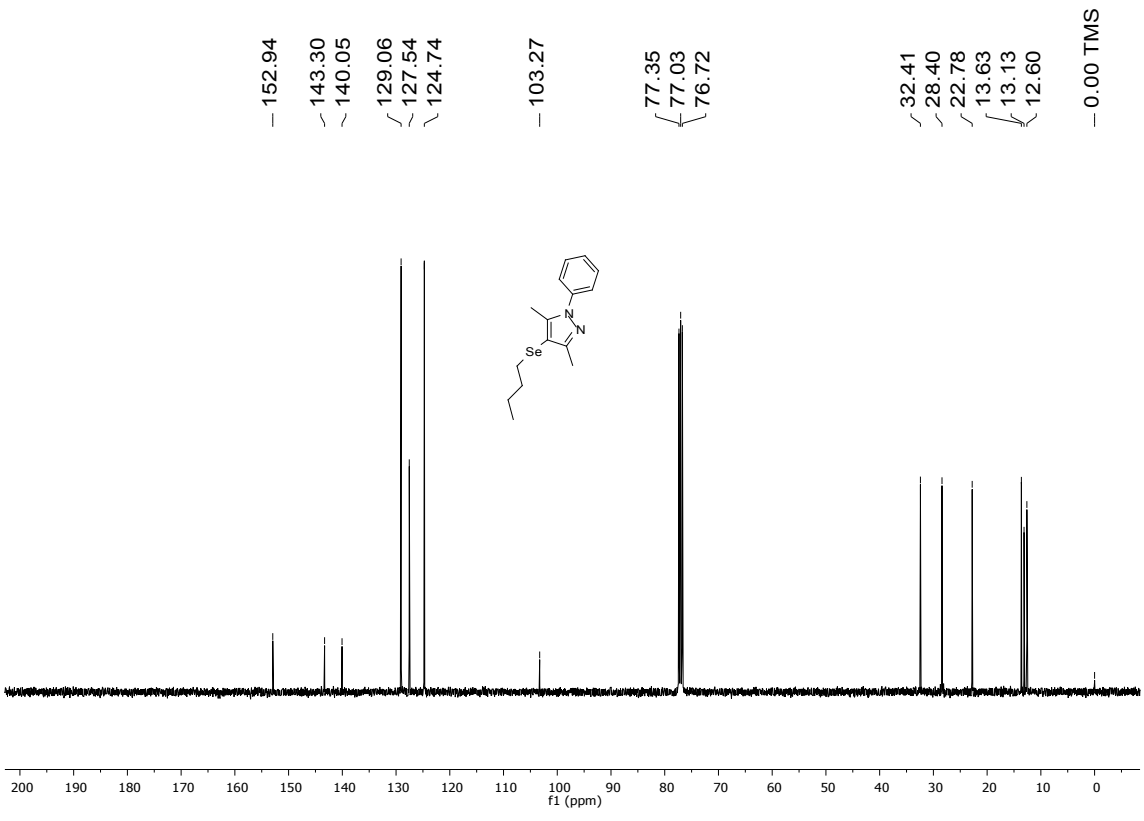


Figure S22. ^{13}C NMR (100 MHz) spectrum for product **4j** in $CDCl_3$.