Silver-Catalyzed Synthesis of Symmetrical Diaryl Tellurides from Arylboronic Acids and Tellurium

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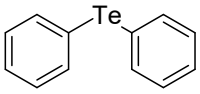
General Information: The reactions were monitored by TLC carried out on Merck silica gel (60 F254) by using UV light as visualizing agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. Baker silica gel (particle size 0.040–0.063mm) was used for flash chromatography. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400 MHz on Bruker Avance III HD spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the external reference. Coupling constants (*J*) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (double doublet), q (quartet) and m (multiplet). Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz on Bruker Avance HD III spectrometer. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Low-resolution mass spectra were obtained with a Shimadzu GCMS-QP 2010 Plus mass spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Micro TOF-QII spectrometer 10416.

General procedure for the synthesis of diorganyl tellurides 3a-n

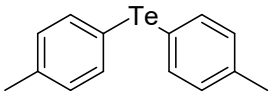
The corresponding arylboronic acid **1a-n** (0.3 mmol), Te^0 (0.9 mmol; 0.114 g), DMSO (1.5 mL) and $AgNO_3$ (0.03 mmol; 0.005 g) were added to a 5.0 mL glass tube. Then, the reaction mixture was allowed to react at 120 °C for 6 hours. After this time, the mixture was diluted with ethyl acetate (30 mL), washed with water (3 x 20 mL), dried over $MgSO_4$ and concentrated under vacuum. The obtained products **3a-n** were purified by chromatography on silica gel using hexane as eluent.

Characterization data of diorganyl tellurides 3a-n

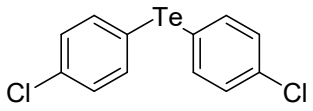


Diphenyltelluride[1] (3a): Yield: 0.0362 g (85%); Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.69 (d, *J* = 6.9 Hz, 4H), 7.29-7.25 (m, 2H), 7.21-7.18 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 137.9 (4C), 129.5 (4C), 127.8 (2C),

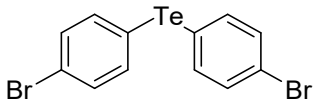
114.6 (2C). GC-MS (relative intensity *m/z*): 284 (M+, 19), 282 (18), 154 (85), 153 (26), 77 (62), 51 (32), 44 (100), 40 (90).



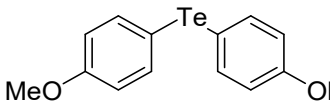
Bis(4-methylphenyl)telluride[1] (3b): Yield: 0.0314 g (67%); Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.57 (d, *J* = 7.8 Hz, 4H), 7.01 (d, *J* = 7.8 Hz, 4H), 2.31 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ: 138.0 (4C), 137.7 (2C), 130.3 (4C), 110.7 (2C), 21.2 (2C). GC-MS (relative intensity *m/z*): 312 (M+, 32), 310 (29), 182 (100), 181 (31), 167 (62), 91 (66), 89 (20), 65 (52).



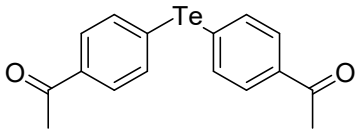
Bis(4-chlorophenyl)telluride[1] (3c): Yield: 0.0394 g (75%); Yellow solid; m.p. 95-97 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.58 (d, *J* = 7.6 Hz, 4H), 7.18 (d, *J* = 7.6 Hz, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ: 139.3 (4C), 134.6 (2C), 129.8 (4C), 112.0 (2C). GC-MS (relative intensity *m/z*): 351 (M+, 28), 349 (22), 223 (62), 221 (100), 152 (23), 111 (30), 75 (53), 50 (22).



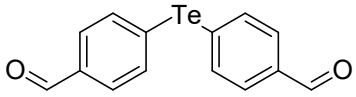
Bis(4-bromophenyl)telluride[1] (3d): Yield: 0.0464 g (70%); beige solid; m.p. 118-120 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.51 (d, *J* = 8.3 Hz, 4H), 7.33 (d, *J* = 8.3 Hz, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ: 139.6 (4C), 132.8 (4C), 122.9 (2C), 112.7 (2C). GC-MS (relative intensity *m/z*): 443 (M+, 29), 441 (83), 439 (100), 437 (67), 281 (61), 279 (57), 205 (56), 152 (76), 76 (97), 50 (87).



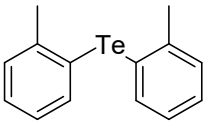
Bis(4-methoxyphenyl)telluride[1] (3e): Yield: 0.0268 g (52%); Yellow solid; m.p. 57-59 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.62 (d, *J* = 8.6 Hz, 4H), 6.75 (d, *J* = 8.6 Hz, 4H), 3.76 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ: 159.6 (2C), 139.7 (4C), 115.3 (4C), 104.3 (2C), 55.1 (2C). GC-MS (relative intensity *m/z*): 343 (M+, 28), 341 (25), 214 (98), 199 (100), 171 (29), 64 (21), 63 (24).



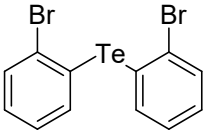
Bis(4-acetylphenyl) telluride (3f): Yield: 0.0397 g (72%); Yellow solid; m.p. 113-115 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.80-7.74 (m, 8H), 2.58 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 197.5 (2C), 137.6 (4C), 136.6 (2C), 129.1 (4C), 121.9 (2C), 26.5 (2C). GC-MS (relative intensity *m/z*): 367 (M+, 21), 365 (19), 223 (46), 76 (21), 44 (14), 43 (100). HRMS calculated for $C_{16}H_{15}O_2Te$ 369.0129, found: 369.0133.



Bis(4-formyilphenyl)telluride[1] (3g): Yield: 0.0326 g (64%); Yellow solid; m.p. 113-115 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.97 (s, 2H), 7.83 (d, *J* = 8.1 Hz, 4H), 7.72 (d, *J* = 8.1 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 191.5 (2C), 137.9 (4C), 135.8 (2C), 130.3 (4C), 123.8 (2C). GC-MS (relative intensity *m/z*): 339 (M+, 46), 337 (43), 335 (27), 209 (100), 181 (33), 153 (23), 77 (67), 51 (60).

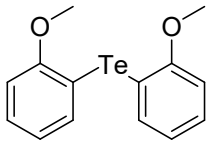


Bis(2-methylphenyl)telluride[2] (3h): Yield: 0.0243 g (52%); Beige solid; m.p. 48-50 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.49 (d, *J* = 7.6 Hz, 2H), 7.27-7.19 (m, 4H), 6.98-6.94 (m, 2H), 2.43 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$,100 MHz) δ: 142.6 (2C), 138.2 (2C), 129.4 (2C), 128.4 (2C), 126.8 (2C), 118.5 (2C), 26.2 (2C). GC-MS (relative intensity *m/z*): 311 (M+, 31), 309 (27), 167 (26), 91 (100), 90 (21), 89 (22), 65 (51).

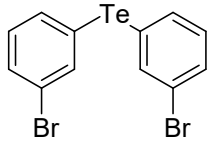


Bis(2-bromophenyl) telluride[3] (3i): Yield: 0.0198 g (30%); Brown solid; m.p. 115-117 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.63 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.47 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.16 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ: 138.8 (2C), 132.4 (2C), 130.4 (2C), 129.8 (2C), 128.3 (2C), 122.9

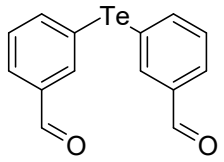
(2C). GC-MS *m/z* (relative intensity %): 443 (M+, 25), 439 (87), 282 (63), 205 (42), 152 (56), 76 (57), 44 (100).



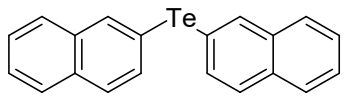
Bis(2-methoxyphenyl)telluride[4] (3j): Yield 0.0144 g (28%); Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.28 (m, 2H), 6.88 – 6.86 (m, 2H), 6.80 (m, 2H), 3.85 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ: 159.7 (2C), 138.1 (2C), 129.4 (2C), 122.2 (2C), 109.9 (2C), 105.2 (2C), 55,9 (2C). GC-MS (relative intensity *m/z*): 343 (M+, 64), 214 (75), 199 (32), 184 (34), 168 (21), 107 (75), 77 (100), 63 (40), 51 (26).



Bis(3-bromophenyl)telluride (3k): Yield: 0.0410 g (62%); Yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: δ 7.85 (s, 2H), 7.59 (m, 2H), 7.43 (m, 2H), 7.09 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$,100 MHz) δ: 140.2 (2C), 136.4 (2C), 131.3 (2C) 131.0 (2C), 123.4 (2C), 115.8 (2C). GC-MS (relative intensity *m/z*): 442 (M+, 49), 312 (95), 152 (90), 76 (100), 50 (77). HRMS calculated for $C_{12}H_9Br_2Te$ 440.8128, found: 440.8123.

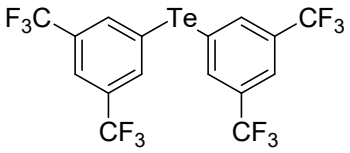


Bis(3-formyilphenyl)telluride (3l): Yield 0.0332 g (65%); Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.95 (s, 2H), 8.21 (m, 2H), 7.94 (m, 2H), 7.82 (m, 2H), 7.41 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$,100 MHz) δ: 191.4 (2C), 143.7 (2C), 139.0 (2C), 137.3 (2C), 130.2 (2C), 129.5 (2C), 115.1 (2C). GC-MS (relative intensity *m/z*): 339 (M+, 64), 209 (89), 181 (54), 153 (43), 105 (22), 77 (100), 51 (81). HRMS calculated for $C_{14}H_{11}O_2Te$ 340.9816, found: 340.9817.



Bis(2-naphthyl)telluride[3] (3m): Yield: 0.0288 g (50%); Beige solid; m.p. 153-155 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.26 (s, 2H), 7.79 –

7.64 (m, 8H), 7.45 (dd, *J* = 5.6, 3.8 Hz, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$,100 MHz) δ: 137.6 (2C), 134.6 (2C), 134.3 (2C), 132.6 (2C), 128.7 (2C), 127.8 (2C), 127.4 (2C), 126.4 (2C), 126.3 (2C), 112.1 (2C). GC-MS (relative intensity *m/z*): 383 (M+, 17), 254 (100), 253 (24), 127 (48).



Bis(3,5-bis(trifluormethyl)phenyl)telluride[5] (3n): Yield 0.0242 g (29%); Yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.13 (s, 4H), 7.85 (s, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$,100 MHz) δ: 137.9 (q, *J* = 3 Hz), 132.9 (q, *J* = 32 Hz), 122.7 (q, *J* = 272 Hz), 122.9 (q, *J* = 3 Hz), 115.5. GC-MS (relative intensity *m/z*): 556 (M+, 84), 343 (32), 275 (100), 206 (44), 180 (61), 153 (23).

References:

1- N. Taniguchi, *Tetrahedron*, 2016, **72**, 5818.

2- Y. Takaguchi, H. Fujihara and N. Furukawa, *Organometallics*, 1996, **15**, 1913.

3- L. Engman, *J. Org. Chem.*, 1983, **48**, 2920.

4- L. Engman, D. Stern and M. Pelcman, *J. Org. Chem.*, 1994, **59**, 1973.

5- B. Zhou and F. P. Gabbaï, *Organometallics*, 2021, **40**, 237.

^{1}H and ^{13}C NMR spectrum of products

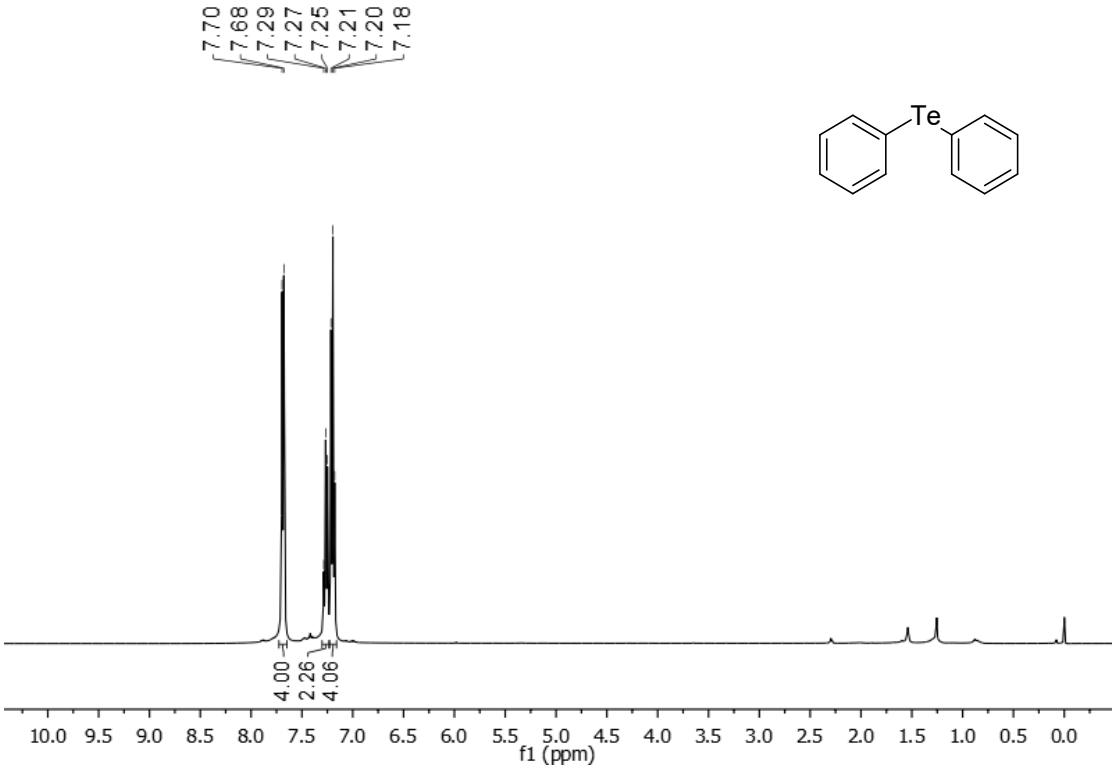


Figure S1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3a**.

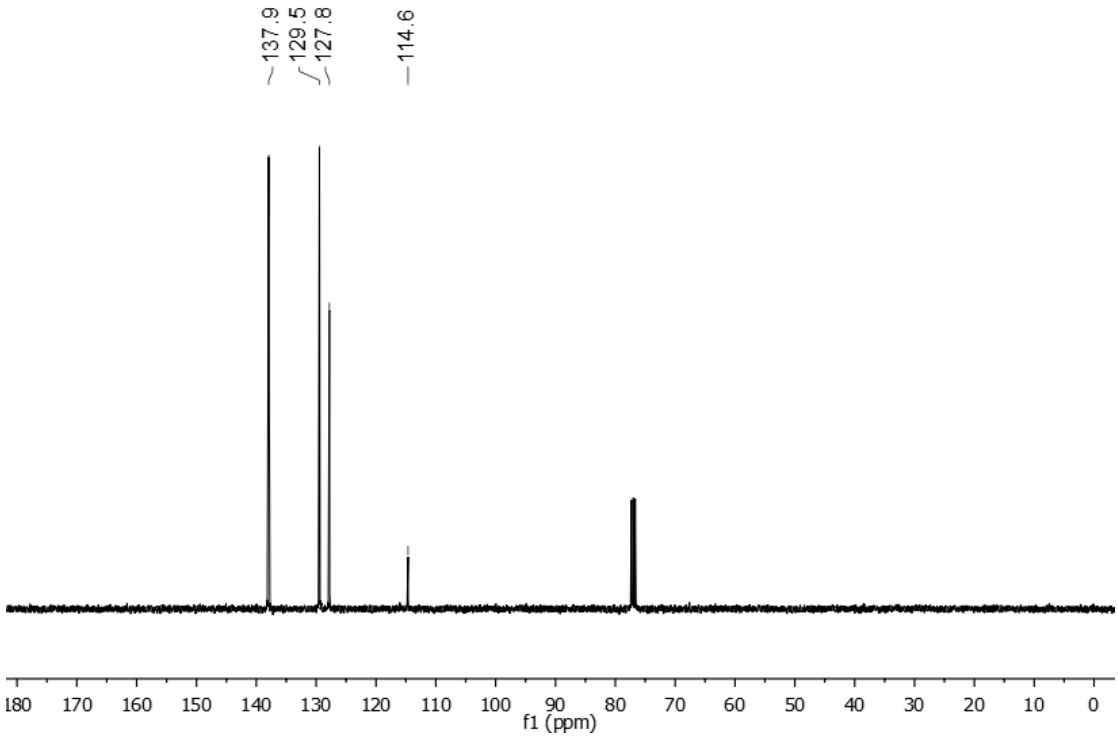


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3a**.

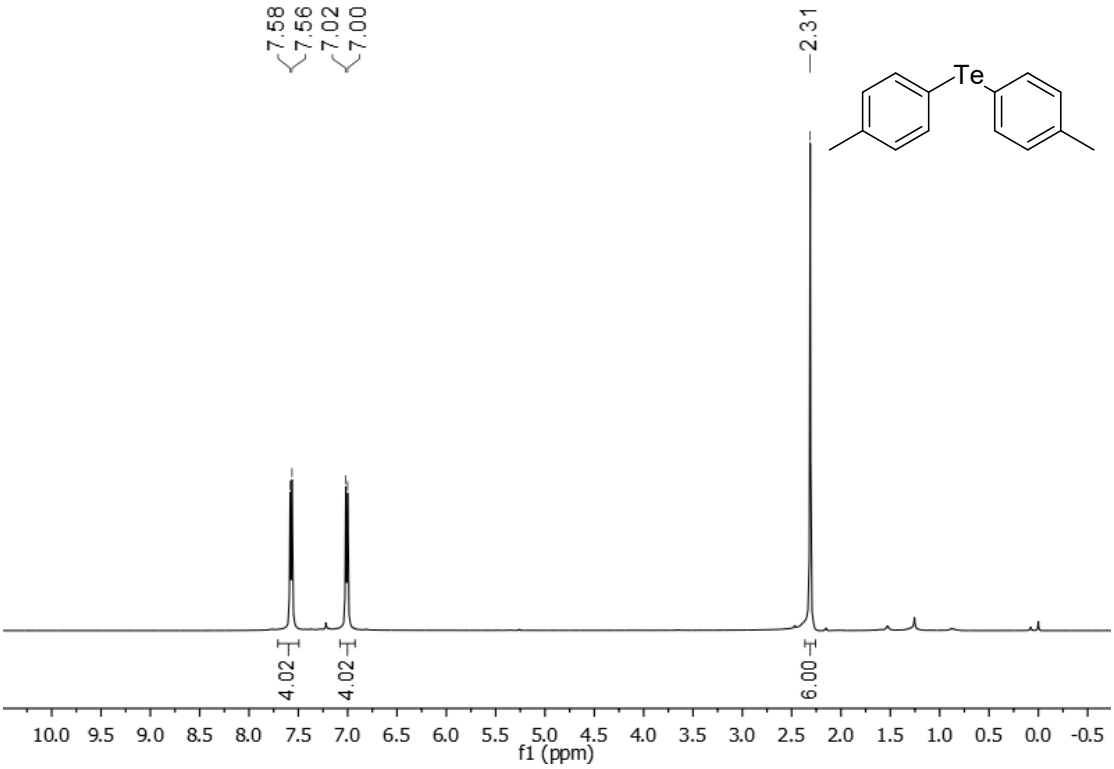


Figure S3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3b**

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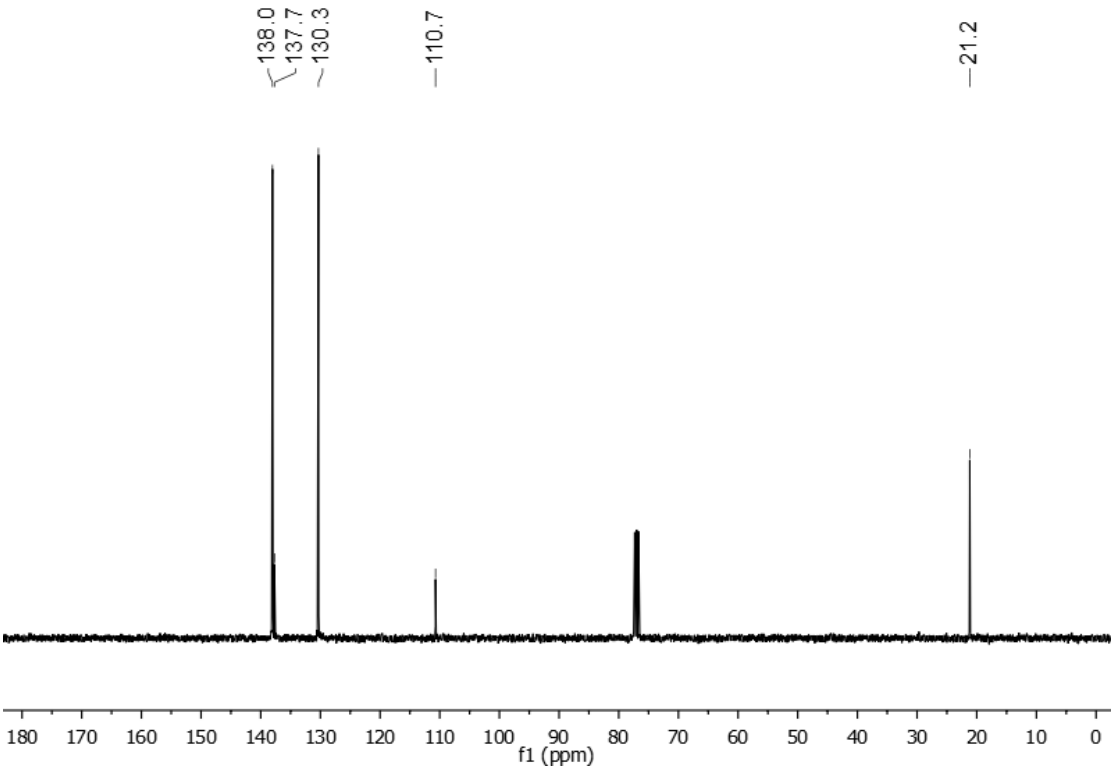

Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3b**

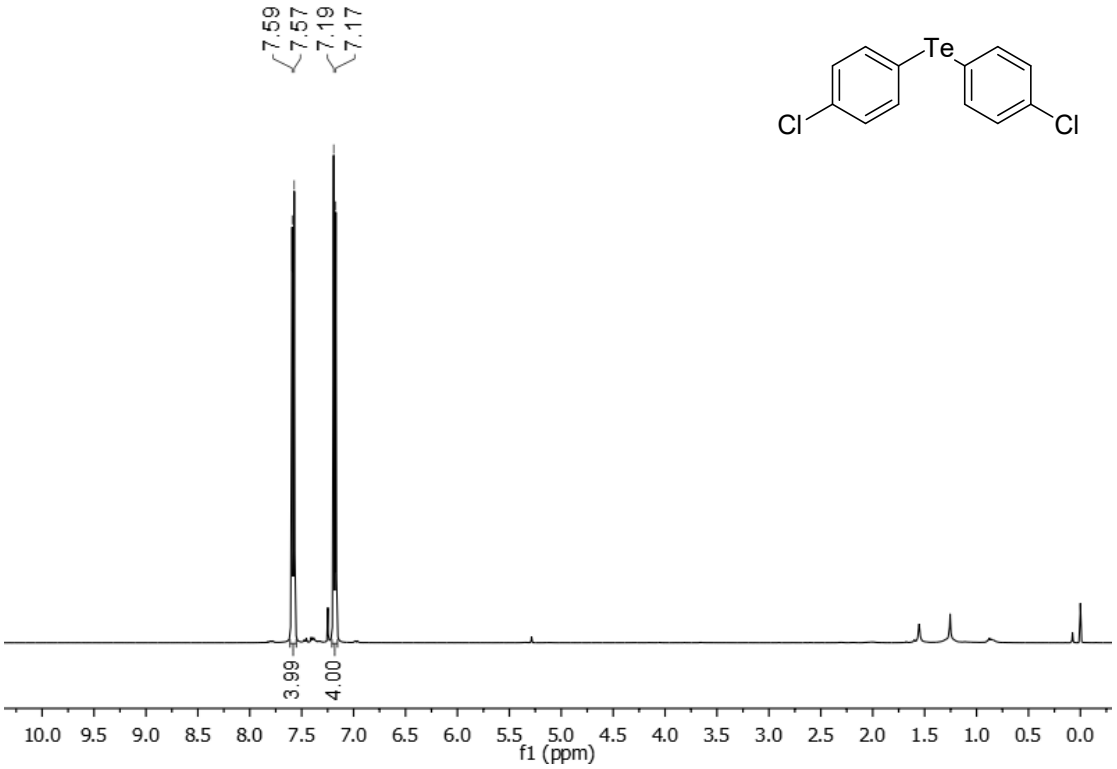

Figure S5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3c**

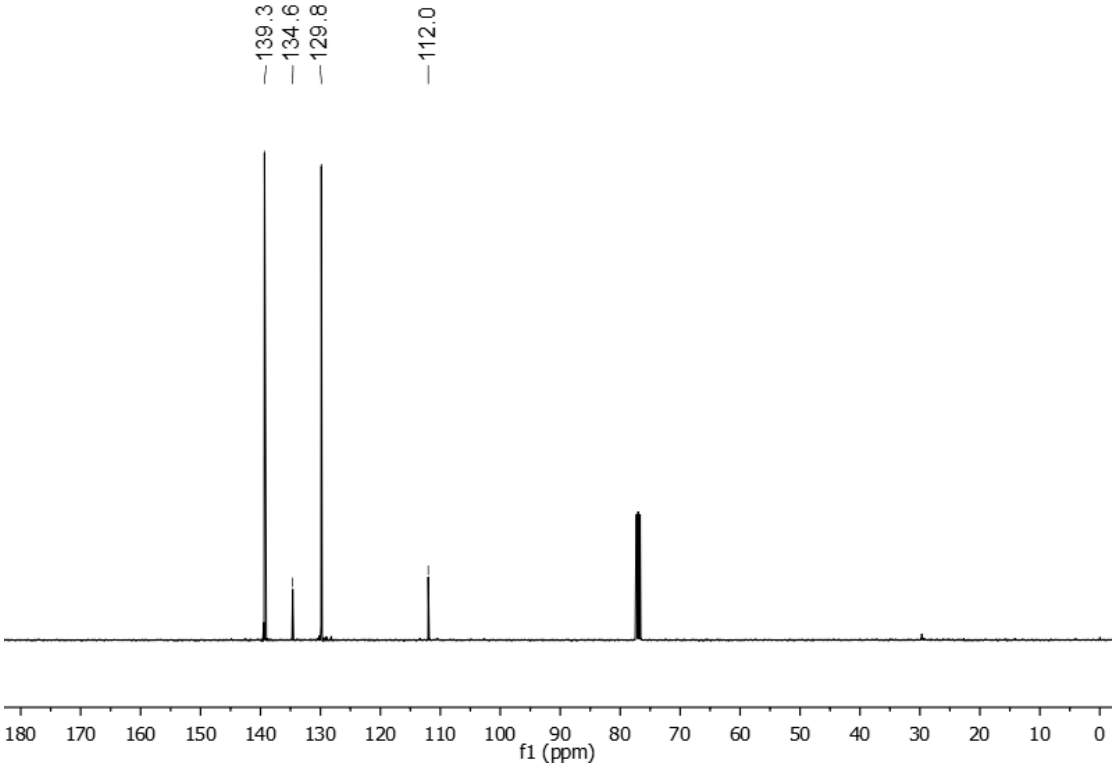

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3c**

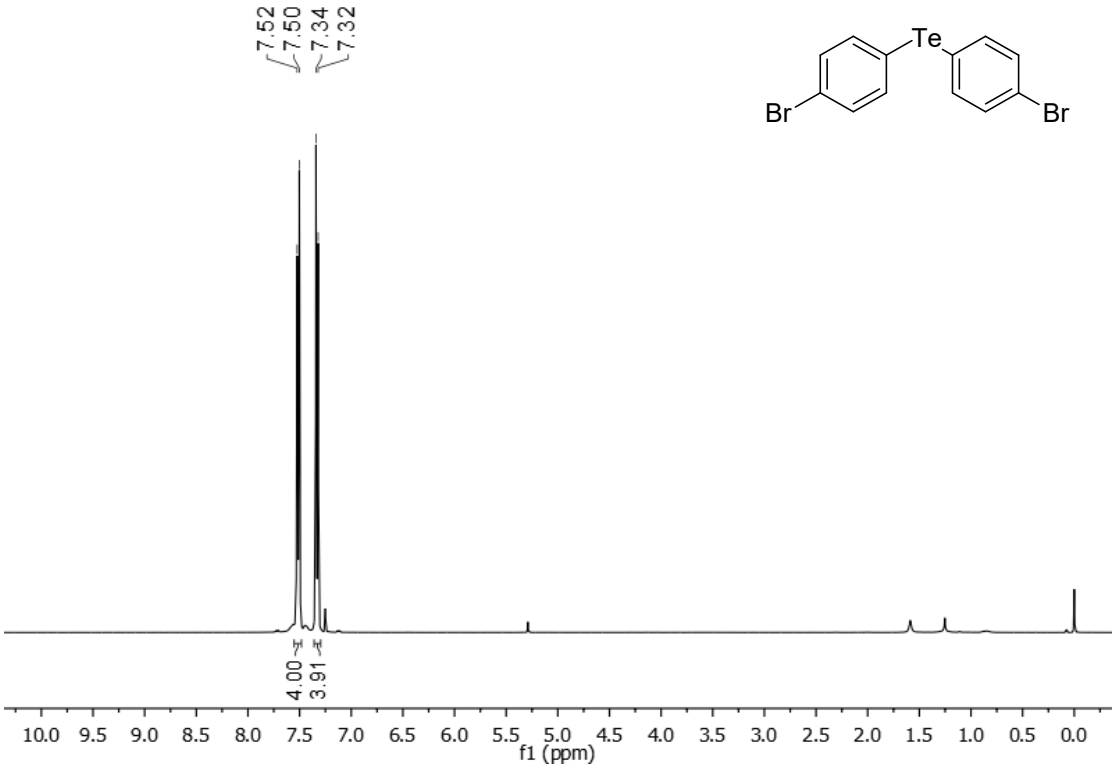

Figure S7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3d**

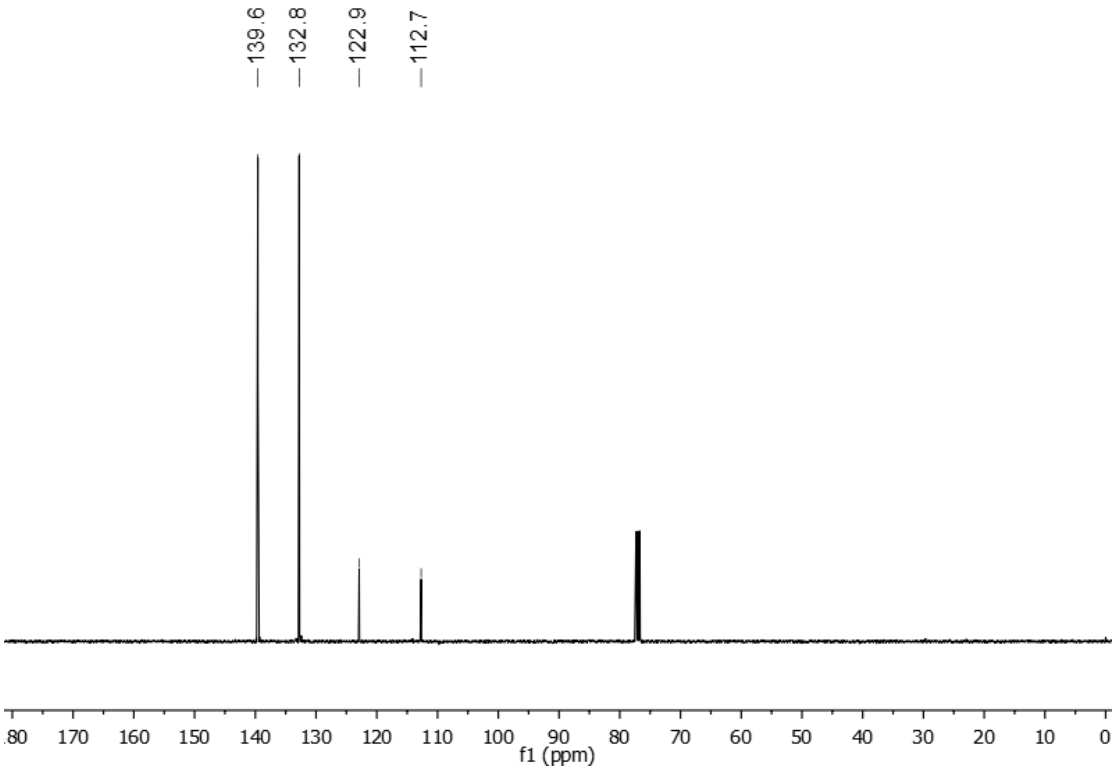

Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3d**

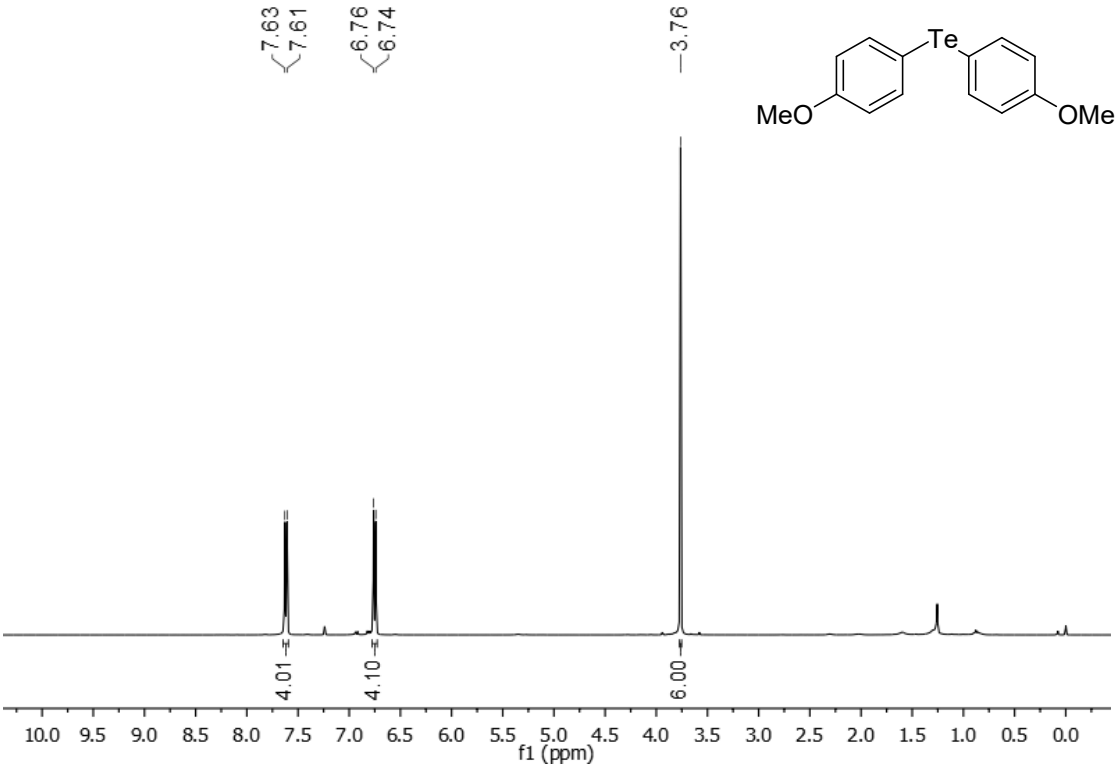

Figure S9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3e**

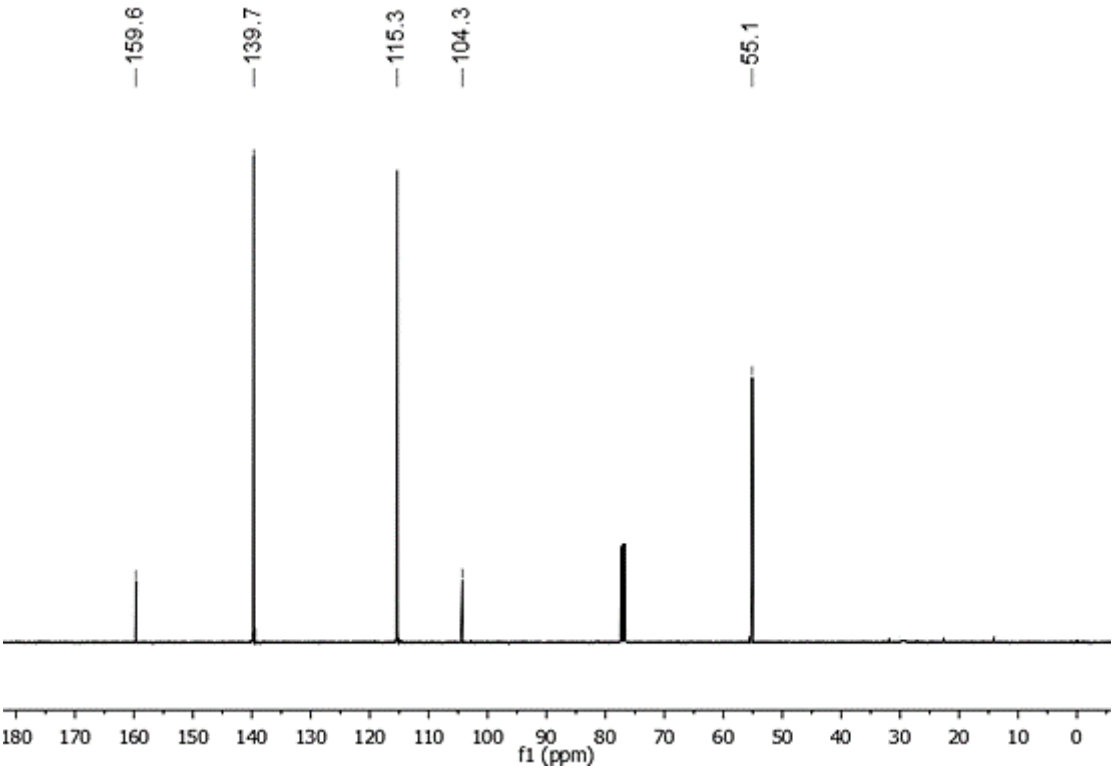

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3e**

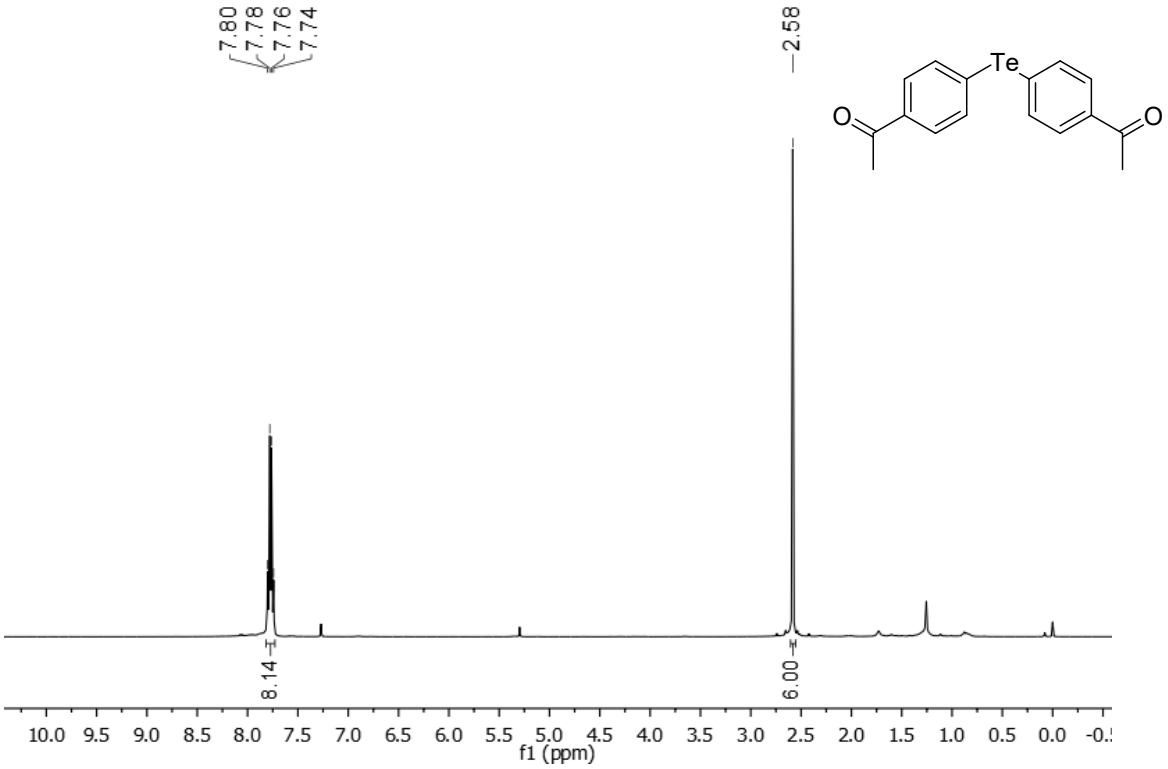

Figure S11: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3f**

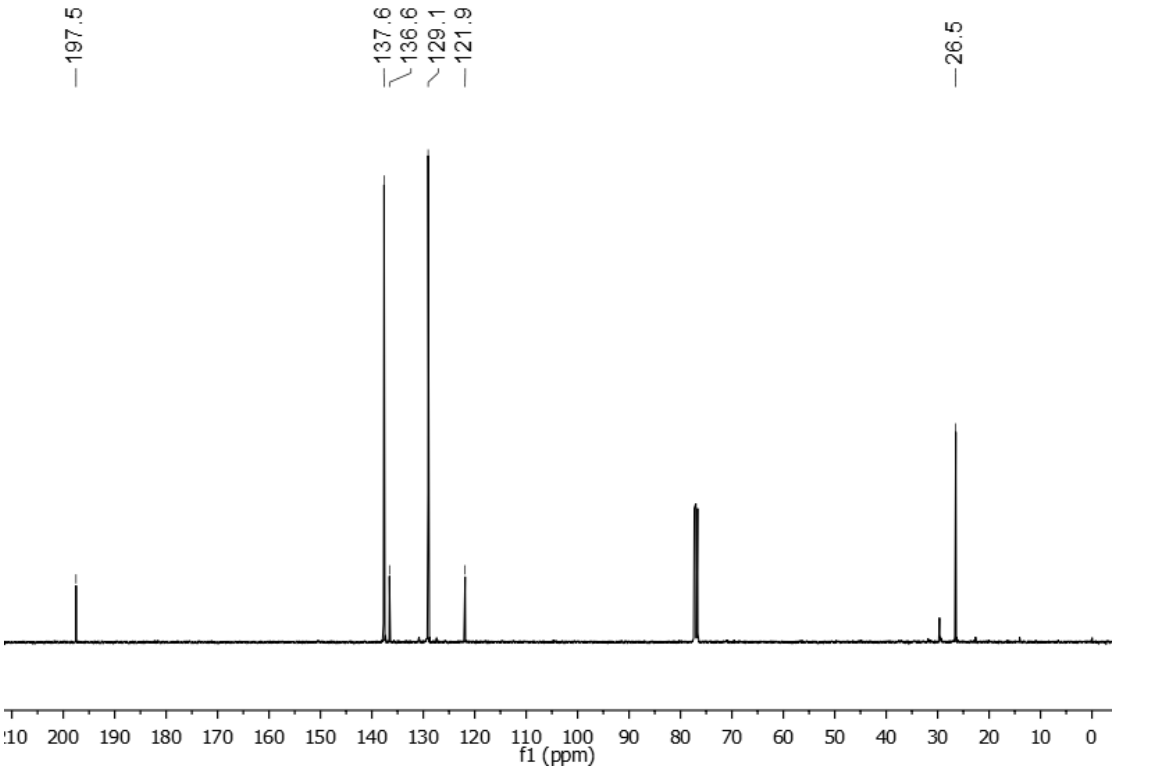

Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3f**

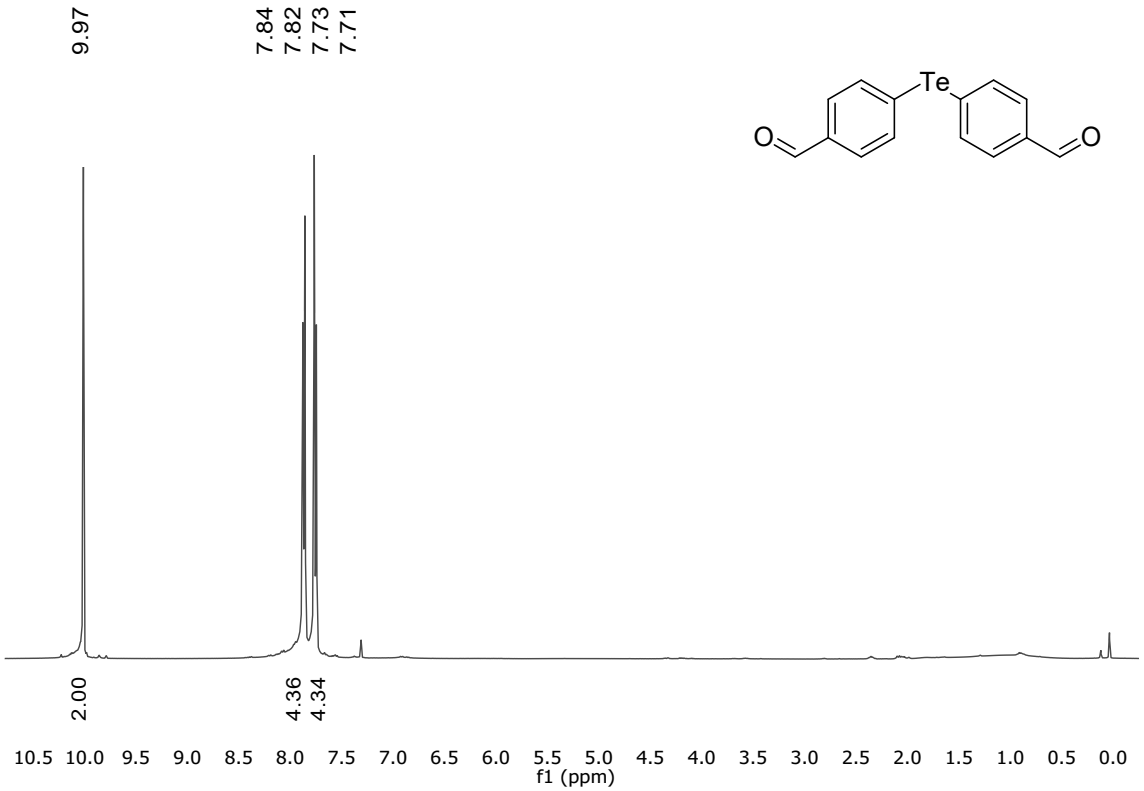

Figure S13: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3g**

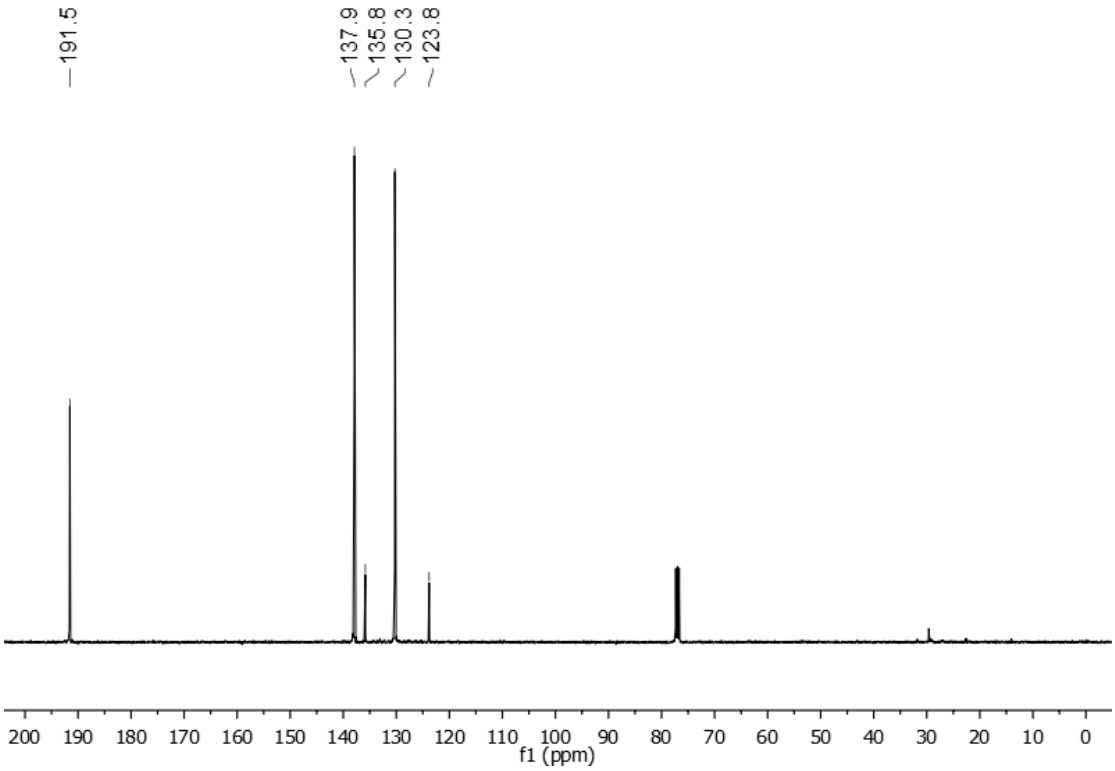

Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3g**

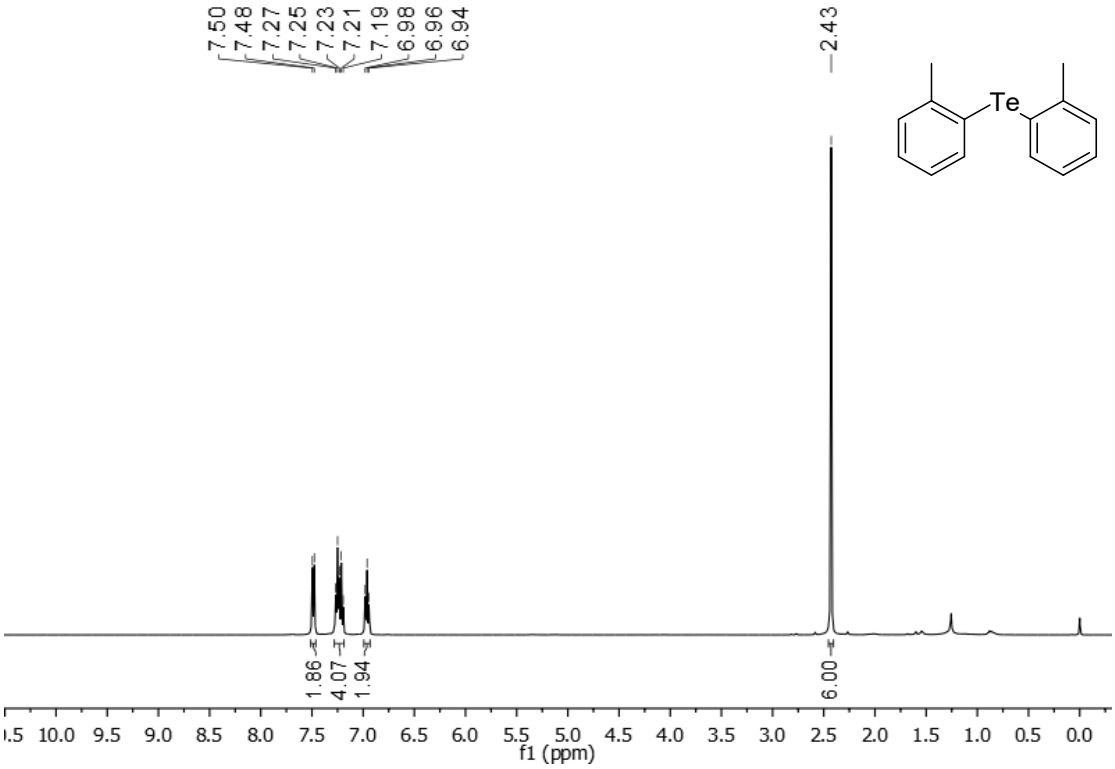

Figure S15: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3h**

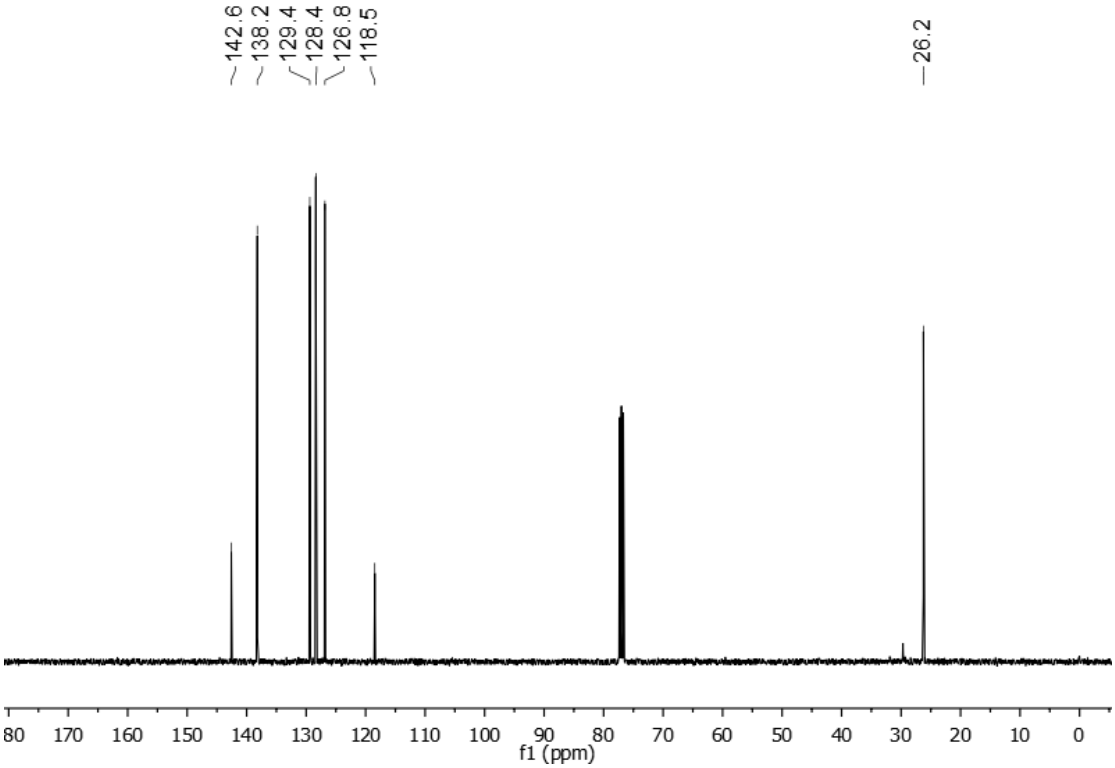

Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3h**

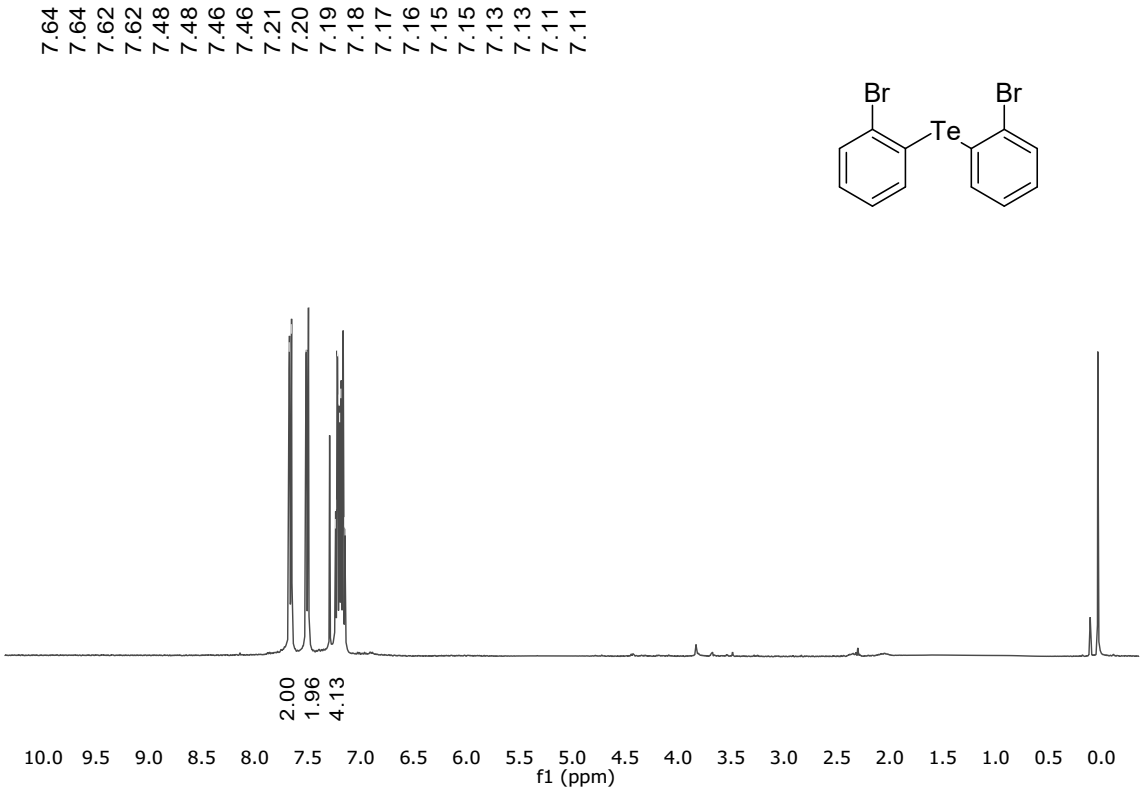

Figure S17: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3i**

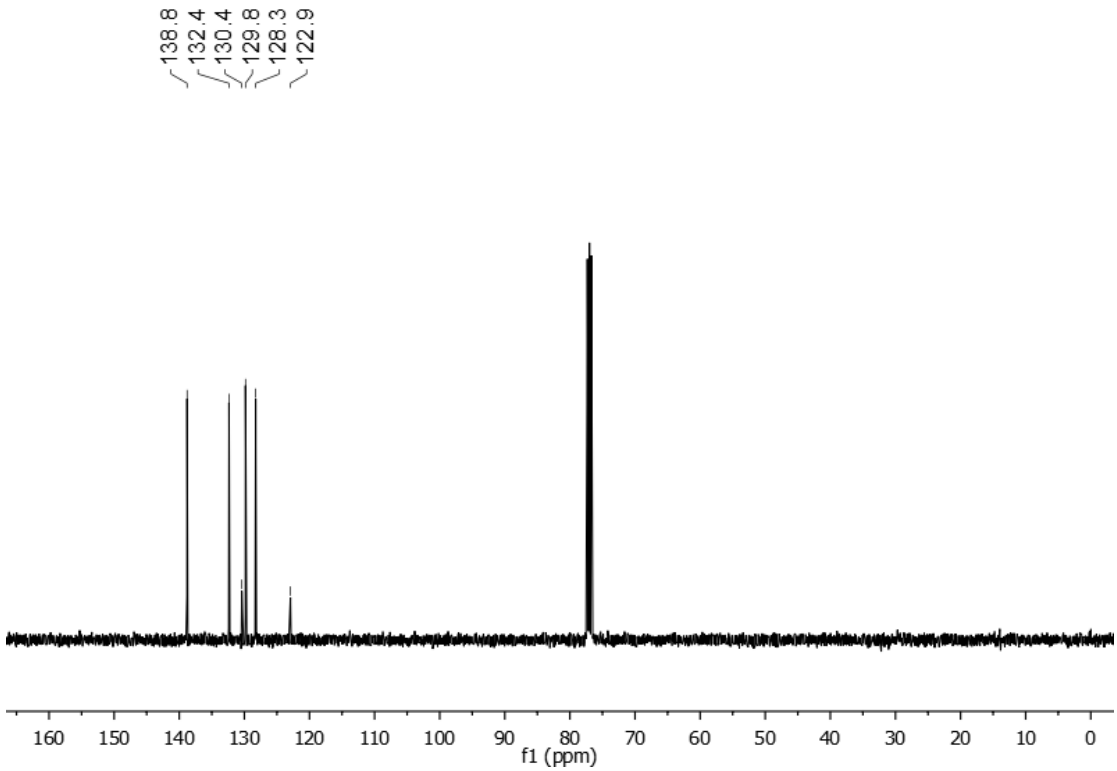

Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3i**

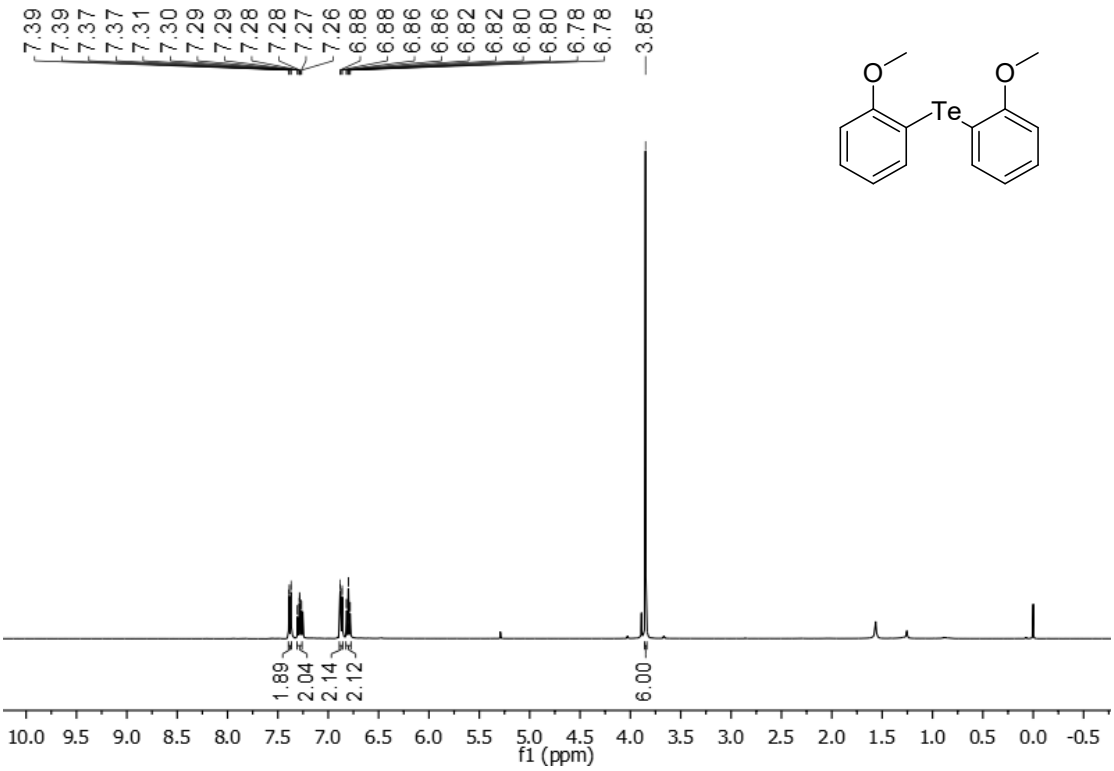

Figure S19: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3j**

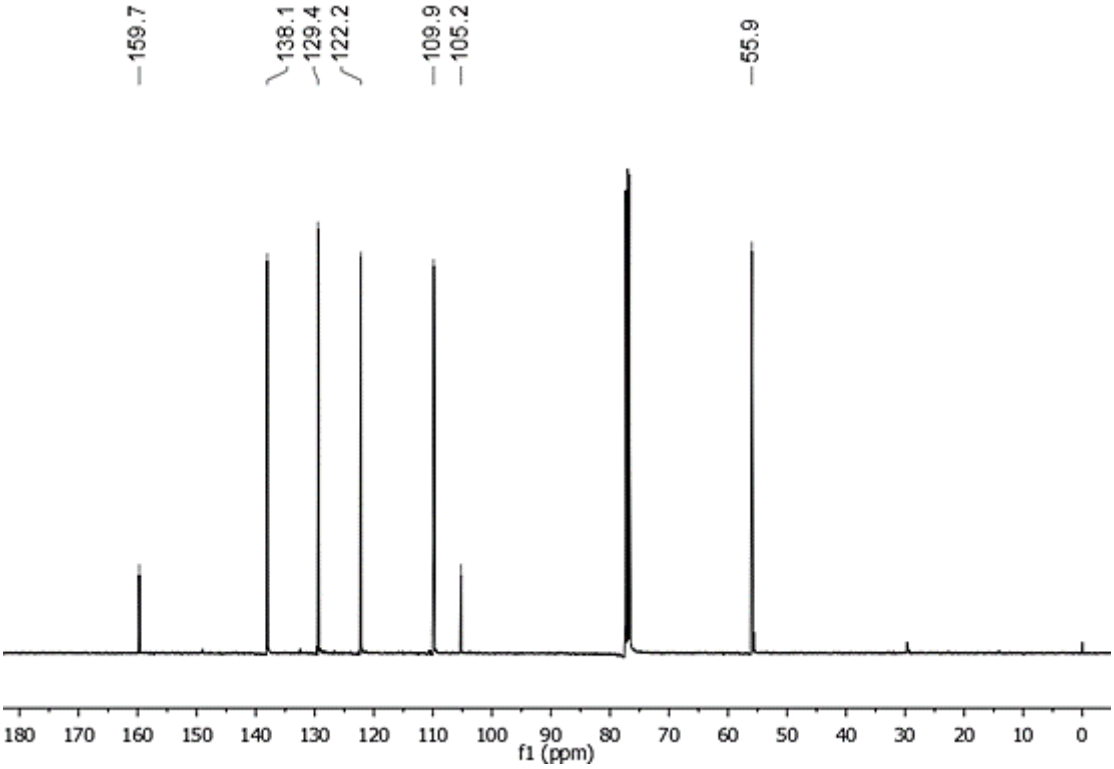

Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3j**

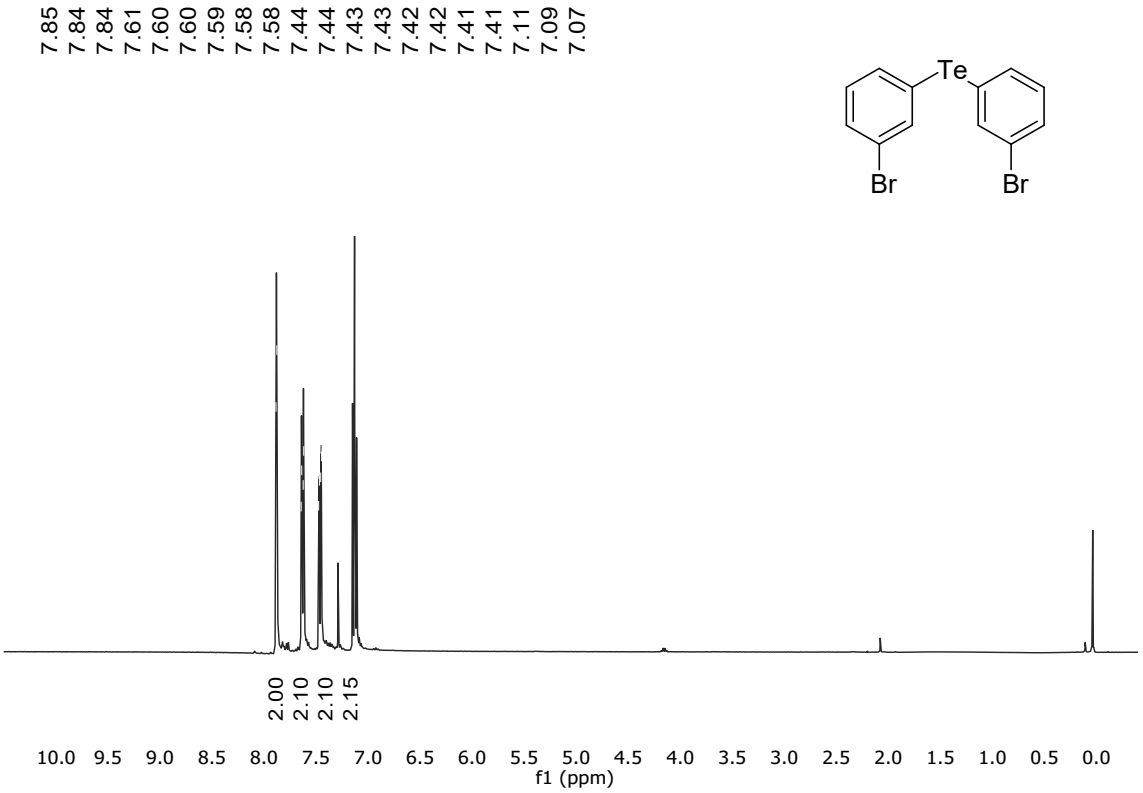

Figure S21: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3k**

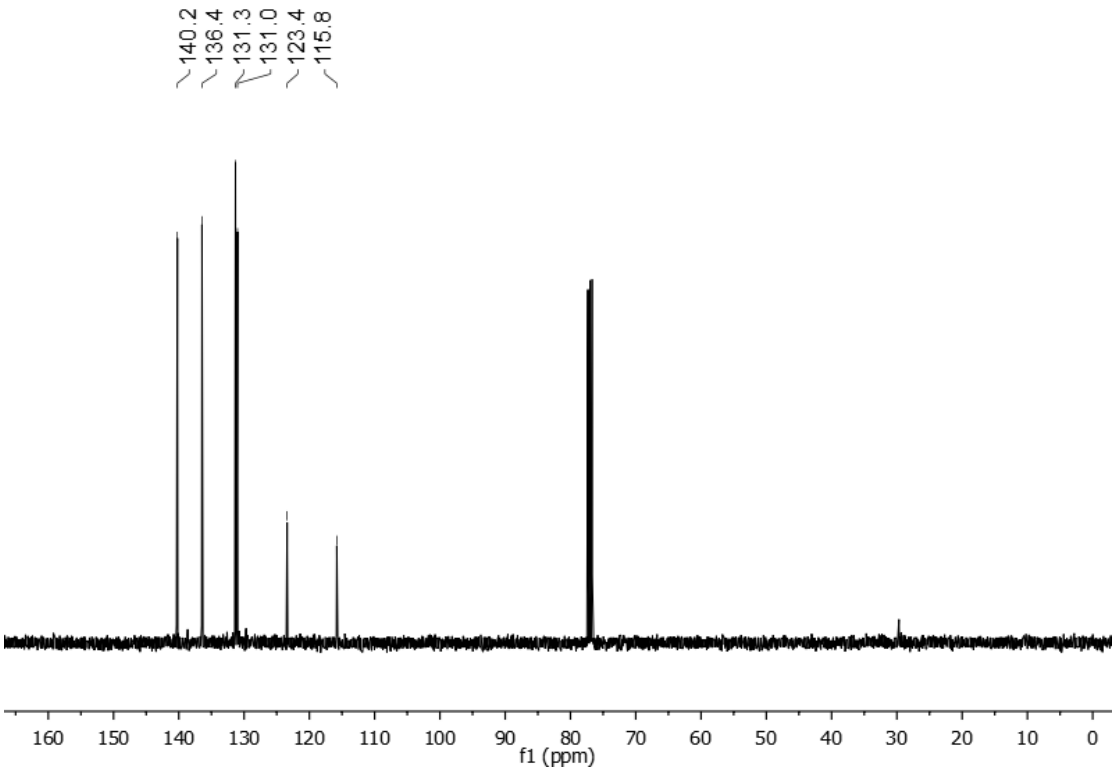

Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3k**

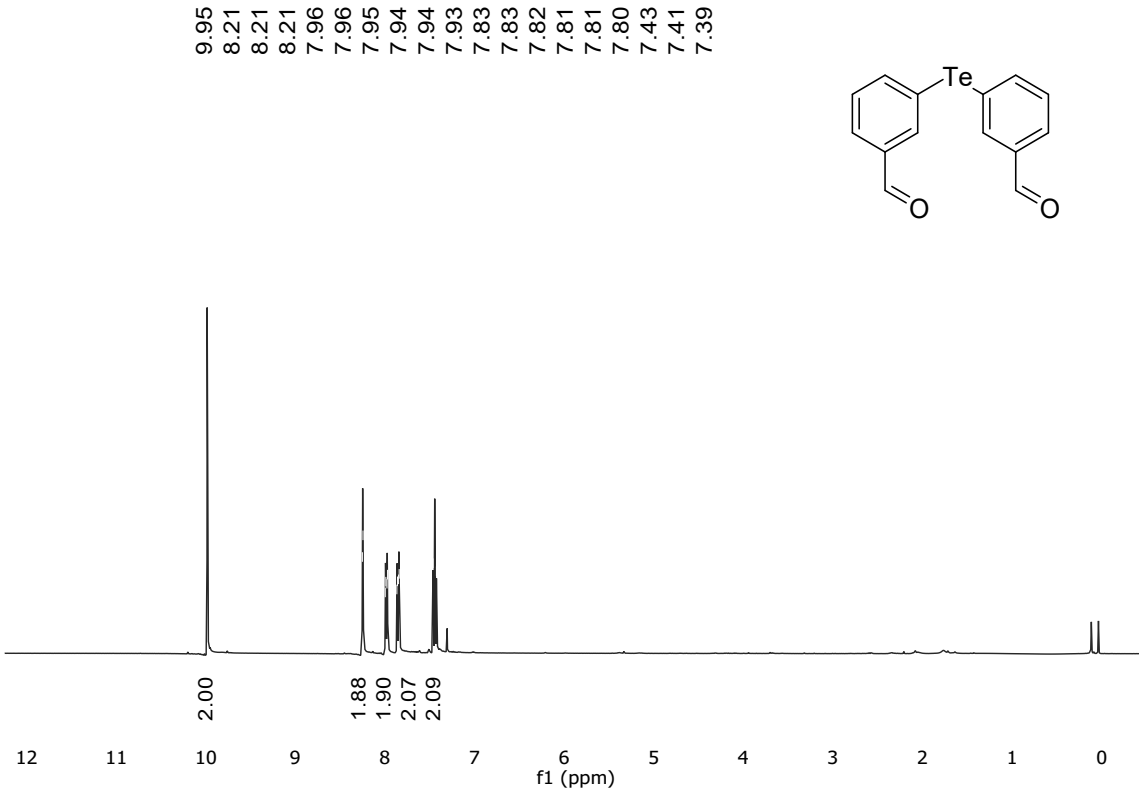

Figure S23: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3l**

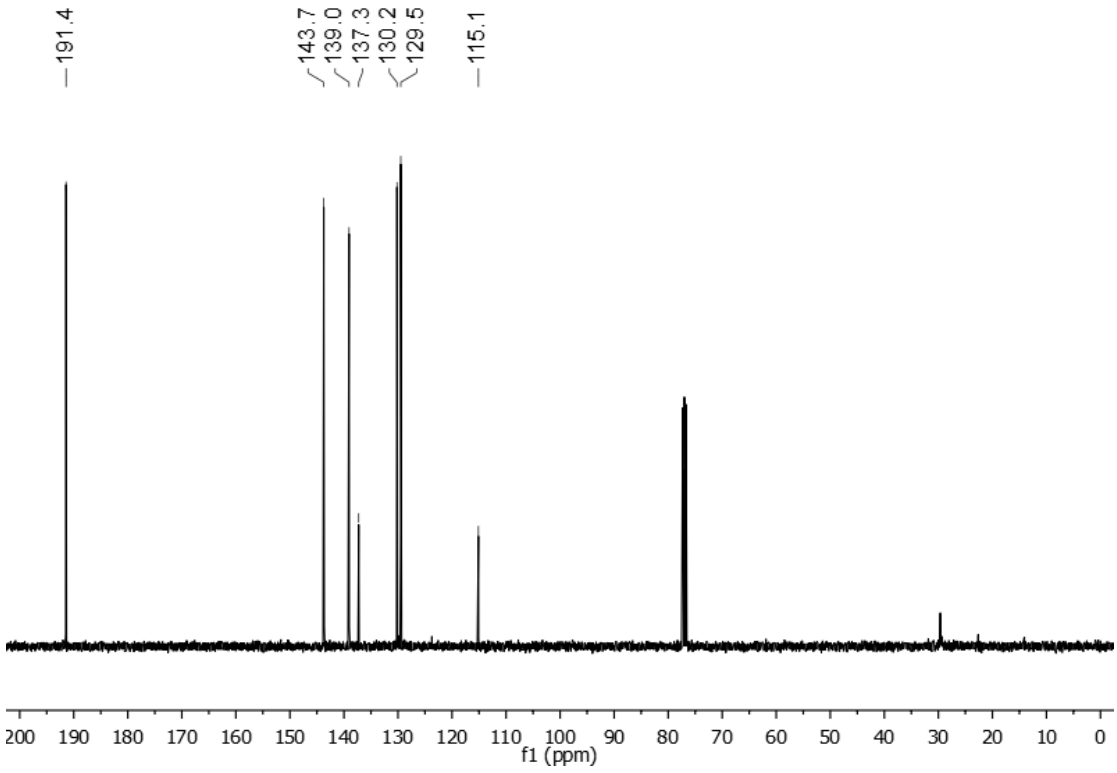

Figure S24: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3l**

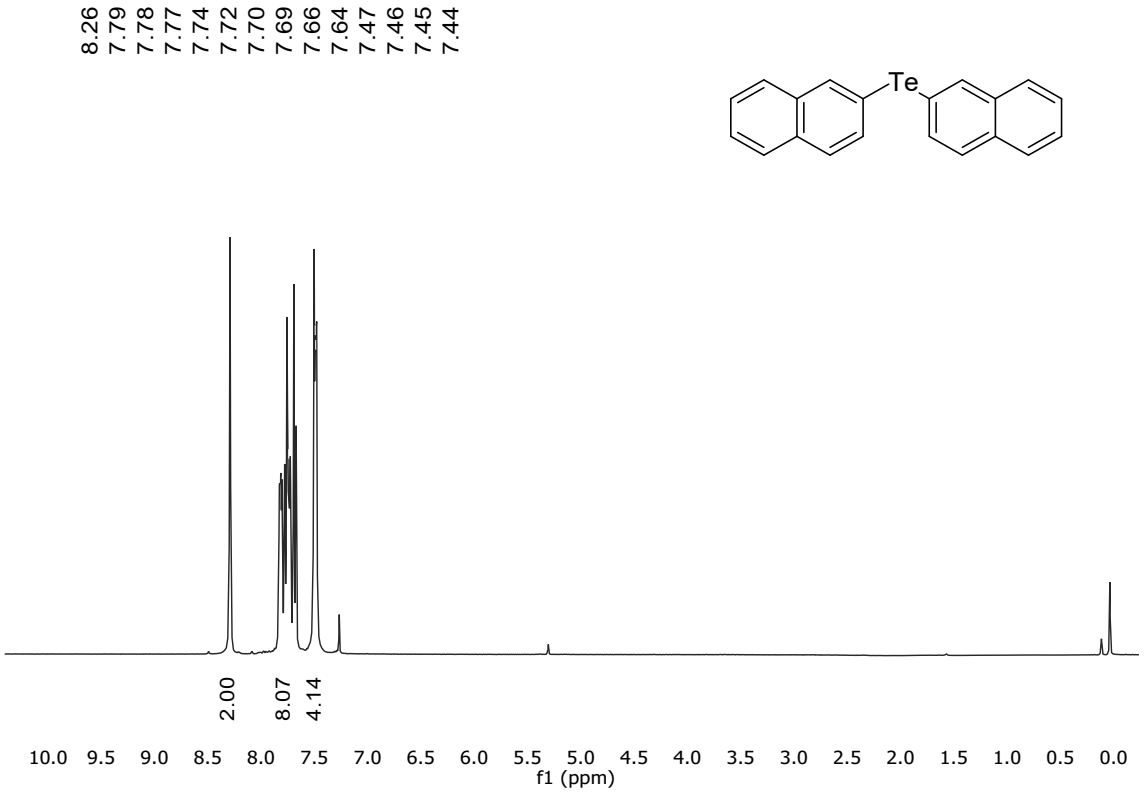

Figure S25: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3m**

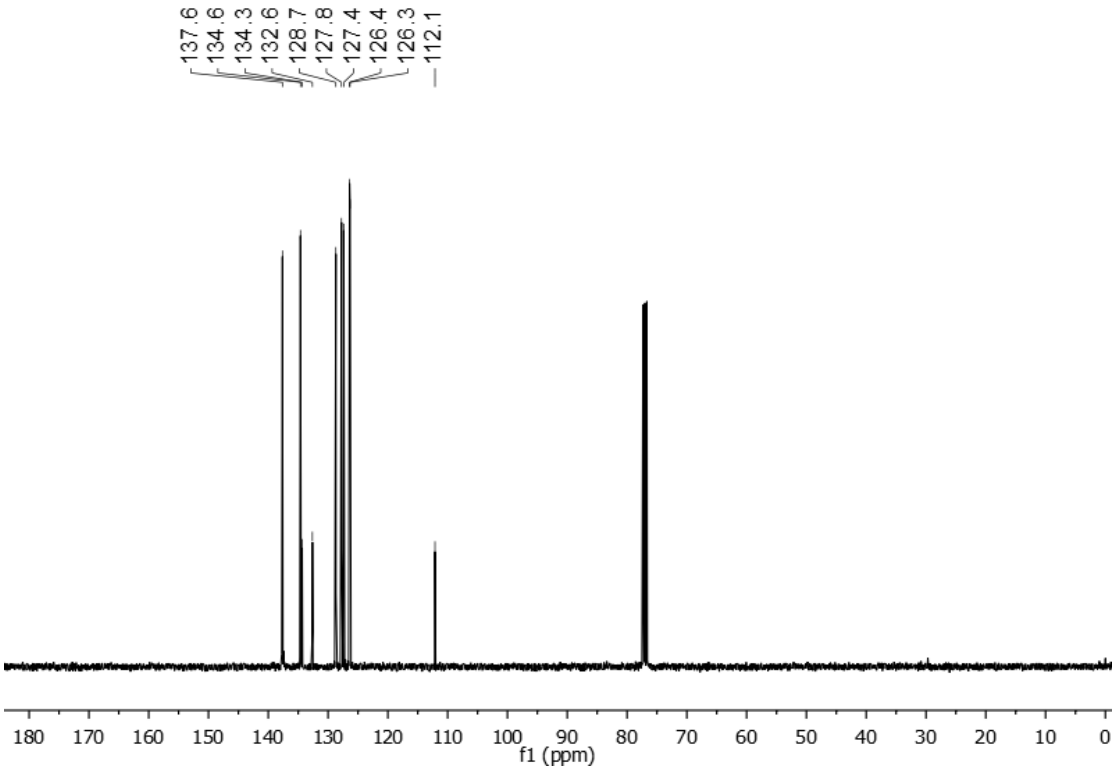

Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3m**

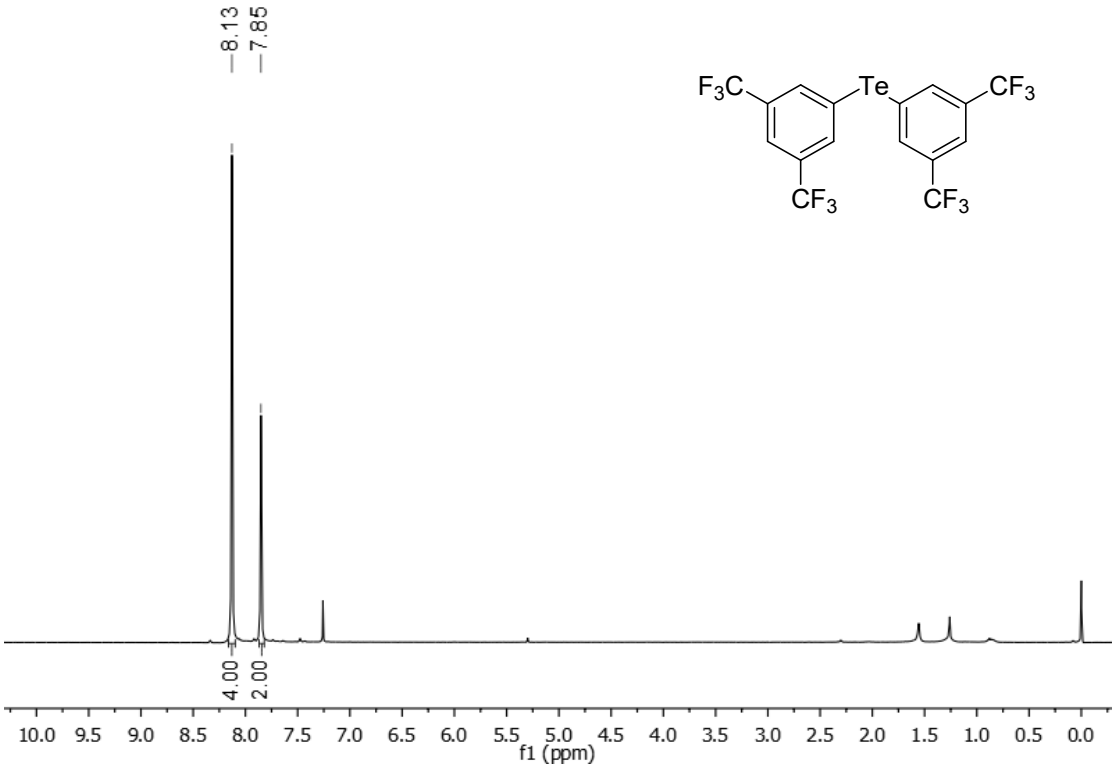

Figure S27: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3n**

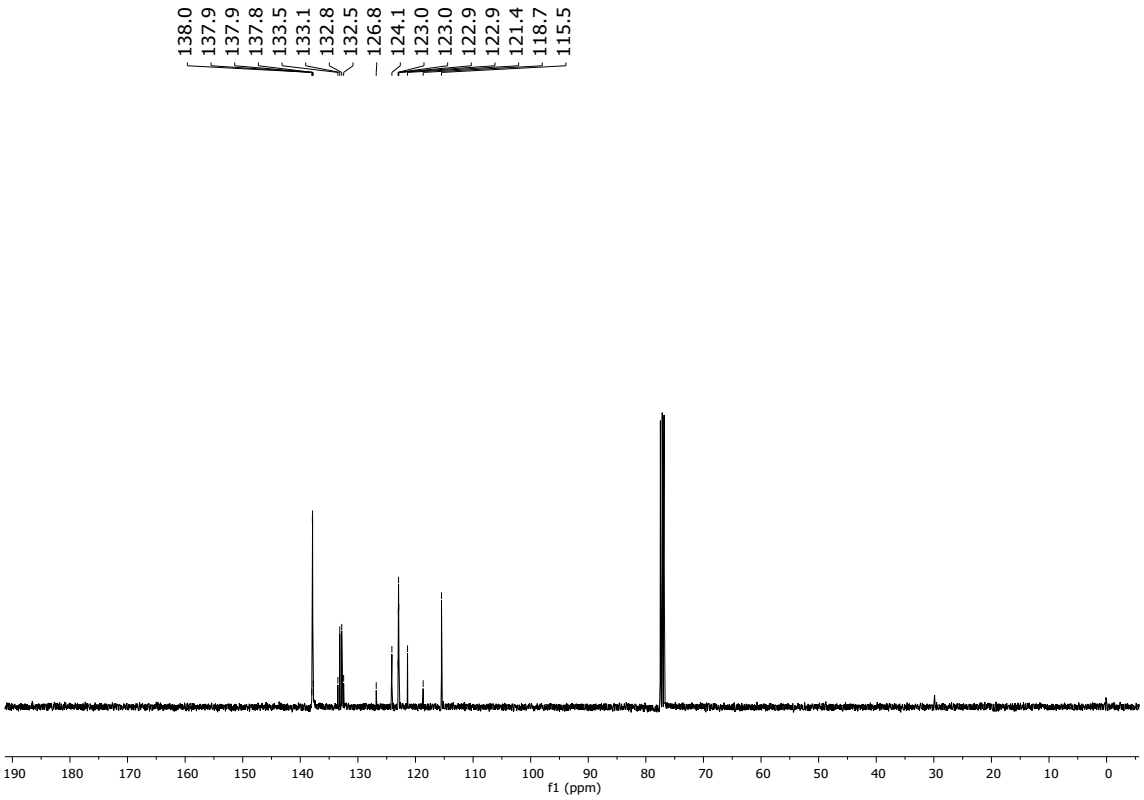

Figure S28: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3n**