Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information For

Ring-expansion from Tellurophenes to Telluropyrans: Inhibition of C-Te Bond Cleavages in Transition Metal-Catalyzed Reactions

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Experimental Section

1. Materials and reagents.

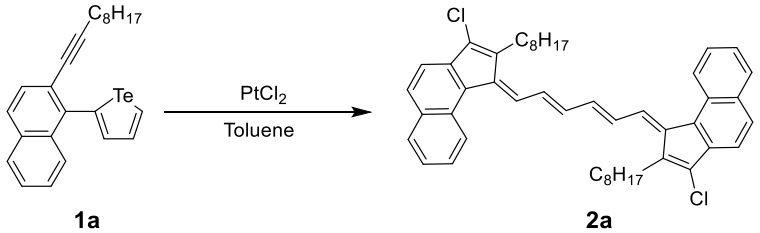
All chemicals and reagents were purchased from commercial sources and were used without further purification unless otherwise specified. Anhydrous tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. *N*,*N*-dimethylformamide (DMF) was distilled from CaH_2. Synthesis of bis[tris(pentafluorophenyl)phosphine]platinum(II) dichloride/bromide[S1] and 2-alkynyl-1-tellurophenyl substituted aromatics[S2] were followed the previously reported methods. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.

2. Characterizations.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). HRMS (High-resolution mass spectra were recorded on an Agilent QTOF-6550 spectrometer using ESI for ionization. The single crystals suitable for X-ray analysis were obtained by the slow solvent volatilization method. The X-ray measurement of single crystals was recorded on a Bruker Sc XRD D8 venture.

3. Synthetic procedures.

Synthesis of 1,6-bis(3-chloro-2-octylcyclopenta[*a*]-1-naphthalenylidene)hexa-2,4-diene (2a).

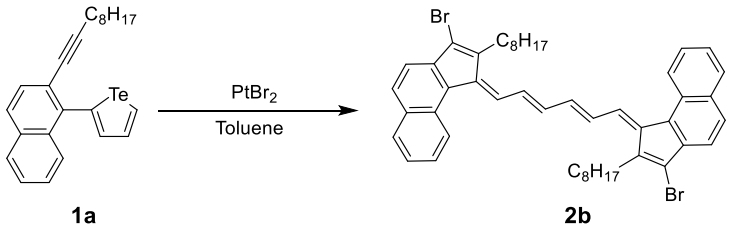


1a **2a**

Under nitrogen atmosphere, a mixture of **1** (168 mg, 0.38 mmol) and $PtCl_2$ (10 mg,

0.038 mmol, 10 mol%) in dry toluene (5 mL) was stirred at 110 °C overnight. After cooling to room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified using column chromatography on silica gel (eluent: DCM : PE = 1:10) to yield product **2a** (18 mg) as a red solid. The yield is 14% if calculated from compound **1a** while 68% if calculated from $PtCl_2$. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (d, J = 8.8 Hz, 2H), 7.91-7.85 (m, 4H), 7.76 (d, J = 8.0 Hz, 2H), 7.55-7.49 (m, 4H), 7.40-7.33 (m, 4H), 6.99-6.95 (m, 2H), 2.90 (t, J = 7.6 Hz, 4H), 1.74-1.67 (m, 4H), 1.56-1.48 (m, 4H), 1.44-1.39 (m, 16H), 0.89-0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 141.2, 140.8, 138.0, 135.3, 134.4, 133.8, 132.9, 130.4, 129.6, 129.4, 129.2, 129.1, 127.7, 124.4, 123.3, 117.9, 32.1, 29.8, 29.7, 29.7, 29.7, 29.5, 22.9, 14.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{48}H_{53}Cl_2$ 699.3519 found 699.3529.

Synthesis of 1,6-bis(3-bromo-2-octylcyclopenta[*a*]-1-naphthalenylidene)hexa-2,4-diene (2b).

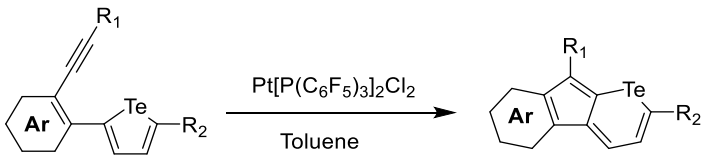


1a **2b**

Under nitrogen atmosphere, a mixture of **1** (200 mg, 0.45 mmol) and $PtBr_2$ (16 mg, 0.045 mmol, 10 mol%) in dry toluene (5 mL) was stirred at 110 °C overnight. After cooling to room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified using column chromatography on silica gel (eluent: DCM : PE = 1:10) to yield product **2b** (27 mg) as a red solid. The yield is 15% if calculated from compound **1a** while 76% if calculated from $PtBr_2$. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (d, J = 8.8 Hz, 2H), 7.89-7.84 (m, 4H), 7.76 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 7.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.40-7.31 (m, 4H), 7.02-6.96 (m, 2H), 2.91 (t, J = 7.6 Hz, 4H), 1.75-1.69 (m, 4H), 1.56-1.51 (m, 4H), 1.45-

1.25 (m, 16H), 0.89-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.4, 141.2, 139.1, 138.5, 134.2, 133.9, 133.1, 130.4, 129.6, 129.4, 129.0, 127.7, 125.4, 124.4, 123.3, 119.3, 32.1, 29.9, 29.9, 29.7, 29.7, 29.5, 22.9, 14.3. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{48}H_{53}Br_2$ 789.2488 found 789.2482.

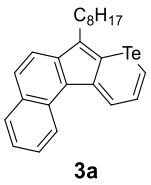
General procedure for the synthesis of 3a-3n.



Scheme S1. Synthetic route for compounds **3a-3n**.

To a degassed solution of alkyne precursor 2-alkynyl-1-tellurophenyl substituted aromatics (0.15 mmol) in dry toluene (5 mL) was added $Pt[P(C_6F_5)_3]_2Cl_2$ (10 mol% 20 mg, 0.015mmol). The mixture was heated at 110 °C overnight under nitrogen atmosphere and then cooled to room temperature. After removing toluene in vacuo, the product was purified by column chromatography to produce the target product.

Synthesis of 7-octylbenzo[6,7]indeno[2,1-*b*]telluropyran (3a).

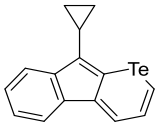


3a

Eluent (PE). Blue solid.48 mg, 73% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.68 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 4.0 Hz, 1H), 8.38 (d, J = 6.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.79-7.74 (m, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 2.77 (t, J = 7.6 Hz, 2H), 1.75 (t, J = 7.6 Hz, 2H), 1.45-1.41 (m, 2H), 1.38-1.26 (m, 8H), 0.89-0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.2, 138.9, 131.1, 130.9, 130.1, 129.4, 128.6, 127.5, 127.4, 127.2,

125.2, 123.4, 123.0, 117.4, 114.4, 107.4, 32.1, 30.3, 30.2, 29.8, 29.5, 27.6, 22.9, 14.3. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{27}Te$ 445.1170; found 445.1168.

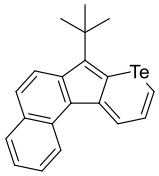
Synthesis of 9-cyclopropylindeno[2,1-*b*]telluropyran (3b).



3b

Eluent (PE). Violet solid. 29 mg, 61% yield. ^1H NMR (400 MHz, $CDCl_3$) : 8.15-8.12 (m, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 1.83-1.78 (m, 1H), 1.05-1.00 (m, 2H), 0.79-0.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.2, 138.2, 135.2, 130.5, 129.3 127.6, 126.9, 122.6, 121.7, 119.9, 116.9, 114.1, 10.2, 5.0. HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{15}H_{12}Te$ 322.0001 found 321.9987.

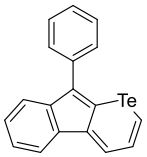
Synthesis of 7-(*tert*-butyl)benzo[6,7]indeno[2,1-*b*]telluropyran (3c).



3c

Eluent (PE). Violet solid. 5 mg, 8% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.69 (d, *J* = 8.8 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 10.0 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 1.69 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 131.9, 130.5, 129.9, 129.7, 128.8, 128.2, 128.1, 127.3, 127.1, 126.8, 123.6, 123.3, 123.0, 120.5, 119.8, 118.1, 31.1, 29.6. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{19}Te$ 389.0543; found 389.0536.

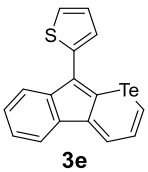
Synthesis of 9-phenylindeno[2,1-*b*]telluropyran (3d).



3d

Eluent (PE). Violet solid. 44 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.14(d, J = 10.4 Hz, 1H),8.10 (d, J = 7.6 Hz, 1H), 7.70 (t, J = 6.8 Hz, 3H), 7.63 (d, J = 7.6 Hz, 1H), 7.59-7.46 (m, 4H), 7.38 (t, J = 7.2 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.0, 137.8, 135.7, 131.5, 129.7, 129.4, 128.0, 127.7, 127.4, 126.9, 124.6, 122.3, 120.5, 117.9, 117.4, 113.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}Te$ 359.0074; found 359.0069.

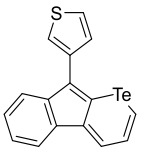
Synthesis of 2-(9-indeno[2,1-*b*]telluropyranyl)thiophene (3e).



3e

Eluent (PE). Violet solid. 41 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.24 (d, J = 10.4 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.65-7.60 (m, 1H), 7.56-7.52 (m, 2H), 7.43 (d, J = 4.8 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.26-7.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.4, 140.2, 135.9, 131.7, 131.7, 128.7, 128.1, 128.1, 127.5, 124.8, 124.4, 123.5, 122.6, 120.3, 117.9, 116.0. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{16}H_{10}STe$ 363.9565; found 363.9551.

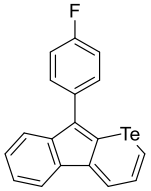
Synthesis of 3-(9-indeno[2,1-*b*]telluropyranyl)thiophene (3f).



3f

Eluent (PE). Violet solid. 38 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, J = 10.0 Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.63-7.57 (m, 2H), 7.55-7.47 (m, 2H), 7.31-7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.1, 138.5, 135.6, 134.0, 131.5, 128.1, 127.4, 126.6, 126.4, 124.3, 122.3, 121.7, 120.4, 117.5, 114.2, 109.9. HRMS (ESI) m/z: $[M]^+$ calcd for $C_{16}H_{10}STe$ 363.9565; found 363.9548.

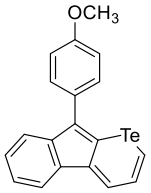
Synthesis of 9-(4-fluorophenyl)indeno[2,1-*b*]telluropyran (3g).



3g

Eluent (PE). Violet solid. 48 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (d, J = 10.0 Hz, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.70-7.67 (m, 3H), 7.58-7.54 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.22 (t, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.7, 141.0, 137.5, 133.7 (d, J = 3.7 Hz, 1C), 131.4, 128.7, 128.6, 128.1, 127.4, 124.7, 122.3, 120.6, 117.2, 116.5, 116.3, 113.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{12}FTe$ 376.9980; found 376.9953.

Synthesis of 9-(4-methoxyphenyl)indeno[2,1-*b*]telluropyran (3h).

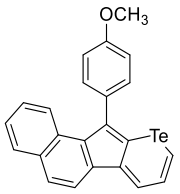


3h

Eluent (DCM : PE = 1:15). Violet solid. 47 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08-8.04 (m, 2H), 7.67-7.59 (m, 4H), 7.56-7.51 (m, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.0, 144.2, 131.6, 130.1, 128.2, 127.9, 127.4, 125.0, 125.0,

124.1, 122.2, 120.4, 119.0, 117.4, 114.8, 113.3, 55.6. HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{19}H_{14}OTe$ 388.0107; found 388.0105.

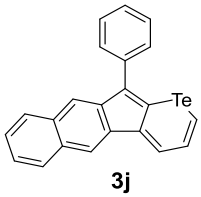
Synthesis of 11-(4-methoxyphenyl)benzo[4,5]indeno[2,1-*b*]telluropyran (3i).



3i

Eluent (DCM : PE = 1:10). Blue solid. 42 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.45 (d, J = 10.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.97-7.91 (m, 3H), 7.75-7.70 (m, 2H), 7.52-7.48 (m, 2H), 7.43 (t, J = 6.8 Hz, 1H), 7.29-7.25(m, 1H), 7.13-7.09 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 159.3, 139.4, 137.0, 134.6, 132.9, 132.0, 131.5, 130.0, 129.7, 128.8, 127.2, 126.7, 126.4, 125.4, 125.3, 122.4, 119.0, 117.9, 115.1, 113.4, 55.6. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{17}OTe$ 439.0336; found 439.0321.

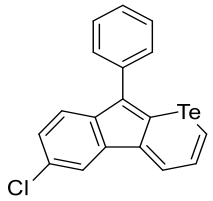
Synthesis of 11-octylbenzo[5,6]indeno[2,1-*b*]telluropyran (3j).



3j

Eluent (PE). Violet solid. 38 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.43 (s, 1H), 8.00-7.98 (m, 1H), 7.92-7.89 (m, 2H), 7.81-7.75 (m, 3H), 7.59-7.54 (m, 3H), 7.50-7.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.6, 139.5, 137.6, 135.3, 133.8, 132.5, 130.0, 129.5, 128.8, 128.7, 128.0, 127.8, 126.9, 126.1, 124.9, 122.0, 119.5, 114.7, 114.6, 110.2. HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{22}H_{14}Te$ 408.0158; found 408.0156.

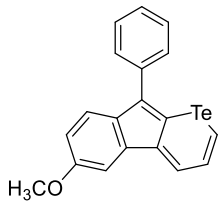
Synthesis of 6-chloro-9-phenylindeno[2,1-*b*]telluropyran (3k).



3k

Eluent (PE). Violet solid. 42 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.24-8.21 (m, 1H), 8.03 (m, 1H), 7.70-7.67 (m, 3H), 7.62-7.58 (m, 1H), 7.57-7.52 (m, 3H), 7.46-7.43 (m, 1H), 7.25-7.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.0, 137.5, 137.2, 136.9, 130.4, 129.3, 128.1, 127.7, 127.6, 127.2, 126.6, 125.4, 120.5, 118.1, 115.4, 110.8. HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{18}H_{11}ClTe$ 391.9612; found 391.9596.

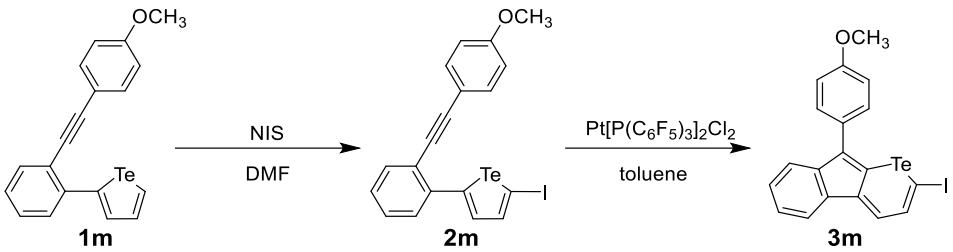
Synthesis of 6-methoxy-9-phenylindeno[2,1-*b*]telluropyran (3l).



3l

Eluent (DCM : PE = 1:10). Violet solid. 39 mg, 70% yield. (40 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, J = 10.0 Hz, 1H), 7.70-7.67 (m, 2H), 7.62 (d, J = 2.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.53-7.47 (m, 4H), 7.36 (t, J = 7.2 Hz 1H), 7.04 (dd, J = 8.4, 2.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.7, 156.3, 138.4, 137.9, 137.3, 135.0, 131.6, 129.4, 127.6, 127.2, 126.8, 124.3, 118.1, 114.4, 113.6, 106.3, 56.1. HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{19}H_{14}OTe$ 388.0107; found 388.0102.

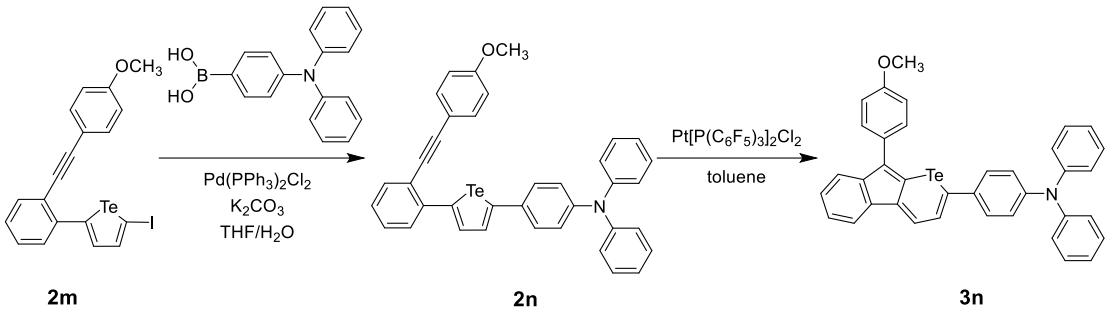
Synthesis of 2-iodo-9-(4-methoxyphenyl)indeno[2,1-*b*]telluropyran (3m).



To a solution of **1m** (100 mg, 0.26 mmol) in DMF (5 mL) was added *N*-iodosuccinimide (NIS) (68 mg, 0.3 mmol) in small portions and the mixture was stirred for 12 h at room temperature. Then water was added and the aqueous phase was extracted twice with dichloromethane. The combined organic layer was dried with Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography (eluent: DCM/PE = 1/10) to get a yellow solid **2m** in 65% yield (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.17 (d, J = 4.4 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 4.8 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.58-7.55 (m, 2H), 7.36-7.32 (m, 1H), 7.28-7.24 (m, 1H), 6.95-6.94 (m, 2H), 3.86 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.5, 149.6, 147.2, 140.7, 135.5, 134.2, 133.8, 128.8, 127.2, 125.5, 120.8, 114.8, 114.6, 98.2, 88.6, 74.1, 55.6.

Following the general procedure of the ring-expansion reaction, the crude product was purified using column chromatography on silica gel (eluent: DCM/PE = 1/10) to yield product **3m** (61 mg, 79%) as a violet solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.10 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.56-7.52 (m, 3H), 7.47 (t, J = 7.2 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.05-7.01 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.2, 141.6, 139.3, 138.2, 136.6, 131.5, 129.6, 128.4, 127.9, 123.6, 122.8, 120.4, 117.7, 115.8, 114.9, 62.8, 55.6. HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{19}H_{13}IOTe$ 513.9073; found 513.9058.

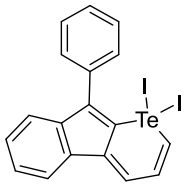
Synthesis of 4-(9-(4-methoxyphenyl)indeno[2,1-*b*]-2-telluropyranyl)-*N*,*N*-diphenylaniline (3n).



Compound **2m** (100 mg, 0.2 mmol), 4-(diphenylamino)phenylboronic acid (86 mg, 0.3 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) were dissolved in deoxygenated THF (5 mL). The sealed tube was evacuated and backfilled with nitrogen. Deoxygenated 2 M K_2CO_3 (aq) (3 mL) was added via syringe. The reaction mixture was stirred and refluxed overnight. After removing the solvents in vacuum, the mixture was separated and purified by column chromatography on silica gel (eluent: DCM/PE = 1/5) to yield product **2n** (104 mg, yield: 83%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.12 (d, *J* = 4.4 Hz, 1H), 7.80 (d, *J* = 4.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.57-7.55 (m, 2H), 7.38-7.33 (m, 3H), 7.29-7.27 (m, 2H), 7.26-7.23 (m, 3H), 7.14-7.11 (m, 4H), 7.06-7.01 (m, 4H), 6.94-6.91 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.2, 151.3, 147.7, 141.6, 141.2, 136.8, 134.6, 134.1, 133.6, 131.6, 129.7, 129.5, 128.6, 127.7, 126.7, 126.1, 124.8, 123.8, 123.3, 120.7, 115.4, 114.4, 97.5, 88.8, 55.6.

Following the general procedure of the ring-expansion reaction, the crude product was purified using column chromatography on silica gel (eluent: DCM/PE = 1/10) to yield product **3n** (68 mg, 76%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, *J* = 7.6 Hz, 1H), 7.68-7.65 (m, 3H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.48-7.41 (m, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.32-7.24 (m, 5H), 7.16-7.15 (m, 4H), 7.11-7.05 (m, 6H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 158.9, 149.0, 147.4, 141.8, 136.1, 135.9, 133.5, 130.7, 130.2, 129.7, 128.3, 128.0, 127.6, 125.3, 124.9, 123.9, 123.7, 122.9, 122.2, 120.3, 117.6, 114.7, 111.7, 55.6. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{37}H_{28}NOTe$ 632.1228; found 632.1234.

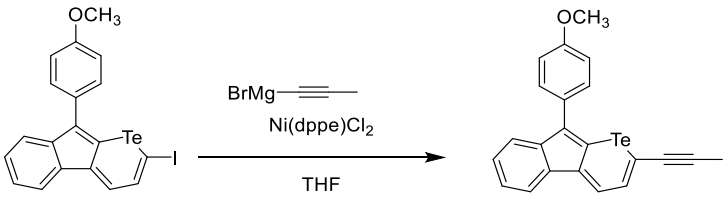
Synthesis of 1,1-diiodo-9-phenyl-indeno[2,1-*b*]telluropyran (3d•I_2)



3d•I_2

The 3 mL chloroform solution of I_2 (51 mg, 0.20 mmol) was slowly added to **3d** (70 mg, 0.20 mmol) in 3 mL chloroform solution. After stirring for 2 min, PE could be added, then the crude was filtered. **3d•I_2** (118 mg, yield: 98%) could be purified as an red solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.87 (d, J = 7.2 Hz, 2H), 7.83-7.81 (m, 1H), 7.68-7.65 (m, 2H) 7.62-7.58 (m, 1H) 7.48-7.42 (m, 4H), 7.20 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H). ^{13}C NMR of **3d•I_2** can't be obtained because of the poor solubility of **3d•I_2** in $CDCl_3$ and the HRMS (ESI) of it shows deiodized.

Synthesis of 2-(1-propynyl)-9-(4-methoxyphenyl)indeno[2,1-*b*]telluropyran (4a).

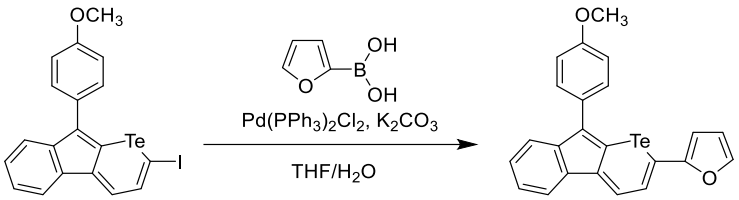


4a

$Ni(dppe)Cl_2$ (5 mg, 0.01 mmol) and compound **3m** (50 mg, 0.1 mmol) were dissolved in deoxygenated THF (3 mL). The sealed tube was evacuated and backfilled with nitrogen. Deoxygenated 1-propynylmagnesium bromide (0.5 mol/L in deoxygenated THF) (3 mL) was added via syringe at 0 ºC for 1 h. Then the reaction mixture was stirred and refluxed overnight. After removing the solvents in vacuum, the mixture was separated and purified by column chromatography on silica gel (eluent: DCM : PE = 1:10) to yield product **4a** (31 mg, yield: 72%) as a green solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.14 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 3H), 7.51(d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.12

(d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 159.36, 141.58, 138.27, 136.07, 132.50, 130.91, 129.29, 128.62, 128.16, 125.26, 123.18, 121.63, 117.76, 115.54, 110.62, 108.48, 100.89, 82.11, 79.6, 55.93, 5.54. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}OTe$ 427.0336; found 427.0334.

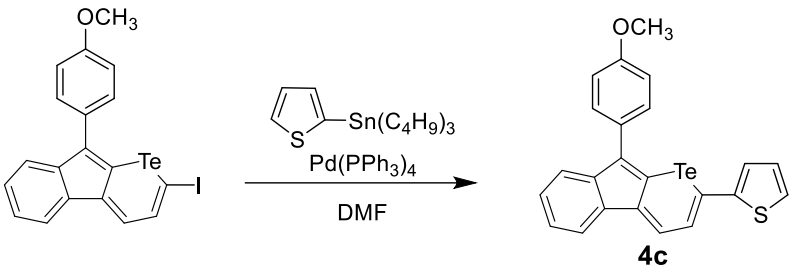
Synthesis of 2-(9-(4-methoxyphenyl)indeno[2,1-*b*]-2-telluropyranyl)furan (4b).



4b

Compound **3m** (50 mg, 0.1 mmol), 2-furanboronic acid (17 mg, 0.15 mmol), and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) were dissolved in deoxygenated THF (5 mL). The sealed tube was evacuated and backfilled with nitrogen. Deoxygenated 2 M K_2CO_3 (aq) (1.5 mL) was added via syringe. The reaction mixture was stirred and refluxed overnight. After removing the solvents in vacuum, the mixture was separated and purified by column chromatography on silica gel (eluent: DCM : PE = 1:10) to yield product **4b** (41 mg, yield: 91%) as green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00 (d, J = 7.6 Hz, 1H), 7.60-7.66 (m, 4H), 7.57 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.23-7.27 (m, 1H), 7.06-7.08 (m, 2H), 6.67 (d, J = 3.6 Hz, 1H), 6.50-6.52(m, 1H), 3.90(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.0, 155.4, 143.6, 141.7, 137.9, 136.0, 131.3, 130.1, 128.2, 127.7, 124.6, 122.4, 121.1, 120.4, 117.9, 117.6, 114.8, 113.0, 109.7, 107.2, 55.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{17}O_2Te$ 455.0285; found 455.0285.

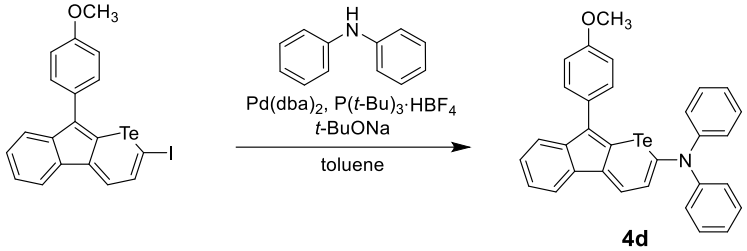
Synthesis of 2-(9-(4-methoxyphenyl)indeno[2,1-*b*]-2-telluropyranyl)thiophene (4c).



4c

Compound **3m** (50 mg, 0.1 mmol), 2-(tributylstannyl)thiophene (38 mg, 0.15 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) were dissolved in deoxygenated DMF (5 mL). The sealed tube was evacuated and backfilled with nitrogen. The reaction mixture was stirred and heated at 120 °C overnight. After removing the solvents in vacuum, the mixture was separated and purified by column chromatography on silica gel (eluent: DCM : PE = 1:10) to yield product **4c** (39 mg, yield: 83%) as green solid.^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.12 (d, J = 7.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 4.8 Hz, 1H), 7.64-7.59 (m, 3H), 7.51 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 4.0 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.17-7.13 (m, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 159.5, 145.8, 141.7, 137.9, 136.2, 131.4, 129.6, 129.4, 129.0, 128.5, 128.5, 127.6, 126.0, 124.2, 123.2, 122.8, 121.5, 117.9, 115.6, 110.4, 56.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{17}OSTe$ 471.0057; found 471.0051.

Synthesis of 9-(4-methoxyphenyl)-*N*,*N*-diphenylindeno[2,1-*b*]telluropyran-2-amine (4d).

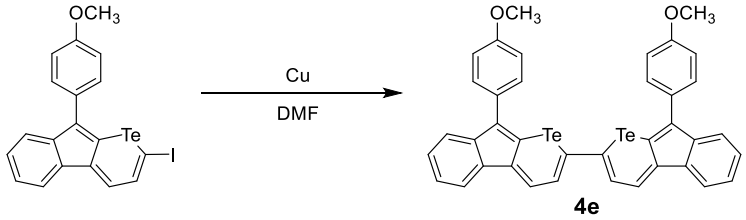


4d

Compound **3m** (50 mg, 0.1 mmol), diphenylamine (25 mg, 0.15 mmol), $Pd(dba)_2$ (6 mg, 0.01 mmol), P(t-Bu)·HBF_4 (11 mg, 0.04 mmol), and t-BuONa (10 mg, 0.1 mmol) were dissolved in deoxygenated toluene (5 mL). The sealed tube was evacuated and

backfilled with nitrogen. The reaction mixture was stirred and heated at 110 °C overnight. After removing the solvents in vacuum, the mixture was separated and purified by column chromatography on silica gel (eluent: DCM : PE = 1:10) to yield product **4d** (41 mg, yield: 75%) as brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.92 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 9.2 Hz, 1H), 7.48-7.39 (m, 11H), 7.35-7.31 (m, 2H) 7.25 (d, J = 7.2 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.05-7.02 (m, 2H), 6.31 (d, J = 9.2 Hz, 1H), 3.77(s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 158.9, 146.5, 143.8, 140.6, 136.4, 134.0, 131.0, 130.6, 130.1, 128.9, 128.3, 128.1, 128.0, 126.0, 125.6, 123.3, 122.2, 120.0, 117.6, 115.5, 111.7, 108.3, 55.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}NOTe$ 556.0915; found 556.0914.

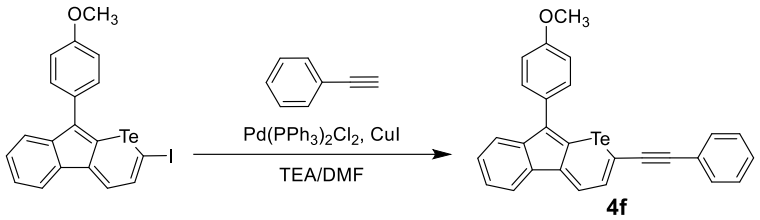
Synthesis of 9,9'-bis(4-methoxyphenyl)-2,2'-biindeno[2,1-*b*]telluropyran (4e).



4e

To a stirred mixture of 100 mg (0.2 mmol) of **3m** of DMF was added 50 mg (0.8 mol) of copper powder. The mixture was heated to 150 °C and maintained at this temperature for 48 hours. After removing the solvents in vacuum, the mixture was separated and purified by column chromatography on silica gel (eluent: DCM : PE = 1:5) to yield product **4e** (52 mg, yield: 68%) as green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.4 Hz, 4H), 7.48-7.52 (m, 4H), 7.38-7.44 (m, 4H), 7.22 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 8.4 Hz, 4H), 3.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.2, 142.2, 139.1, 135.9, 134.2, 133.6, 133.0, 130.4, 129.7, 128.4, 128.4, 127.7, 123.6, 123.0, 120.9, 118.1, 114.9, 111.6, 55.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{27}O_2Te_2$ 771.0100; found 771.0115.

Synthesis of 9-(4-methoxyphenyl)-2-(phenylethynyl)indeno[2,1-*b*]telluropyran (4f).



$Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), CuI (5 mg, 0.03 mmol) and ethynylbenzene (15 mg, 0.15 mmol) were added to a degassed solution of **3m** (50 mg, 0.1 mmol) and TEA (3 mL) in dry DMF (5 mL). The mixture was stirred overnight at room temperature. The resulting mixture was extracted with dichloromethane, and the combined organic layer was dried with Na_2SO_4 and concentrated in vacuum. The product was separated and purified by column chromatography on silica gel (eluent: DCM : PE = 1:10) to yield product **4f** (43 mg, yield: 89%) as green solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.16 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.59-7.50 (m, 5H), 7.47-7.41 (m, 4H), 7.27 (t, J = 7.2 Hz, 1H), 7.13-7.10 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 159.4, 141.6, 138.5, 136.0, 133.6, 132.1, 131.6, 130.3, 129.6, 129.3, 128.9, 128.2, 125.2, 123.3, 122.3, 121.8, 117.9, 115.5, 110.6, 106.3, 101.5, 91.3, 55.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{19}OTe$ 489.0493; found 489.0492.

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4. X-ray crystallographic data.

Figure S1. ORTEP diagram (ellipsoid contour probability level 50%) and crystal packings of compound **2a**.

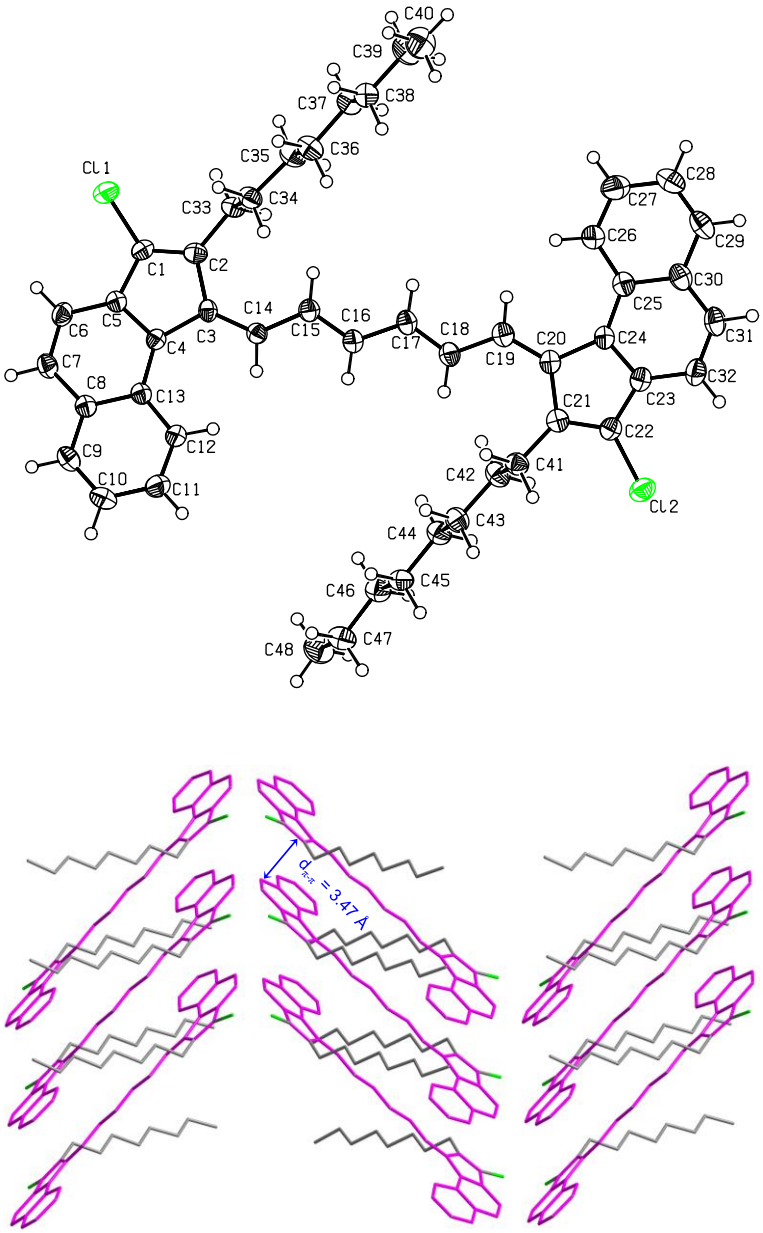


Figure S2. ORTEP diagram (ellipsoid contour probability level 50%) and crystal packings of compound **2b**.

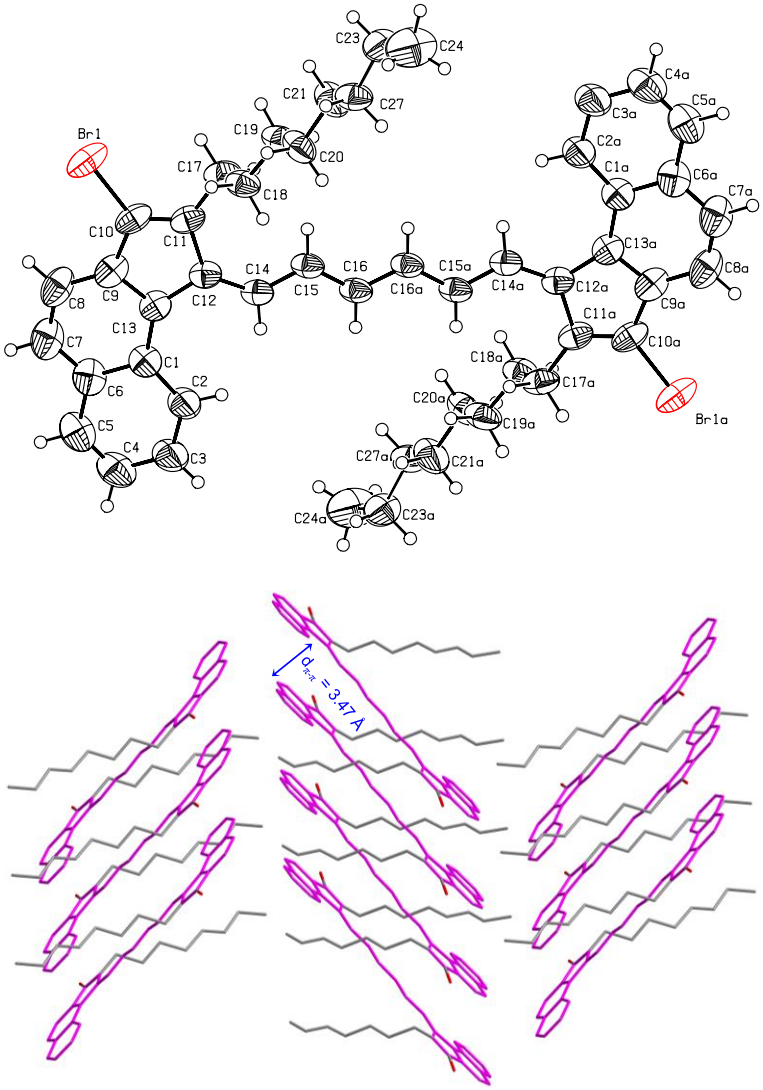


Figure S3. ORTEP diagram (ellipsoid contour probability level 50%) and crystal packings of compound **3g**.

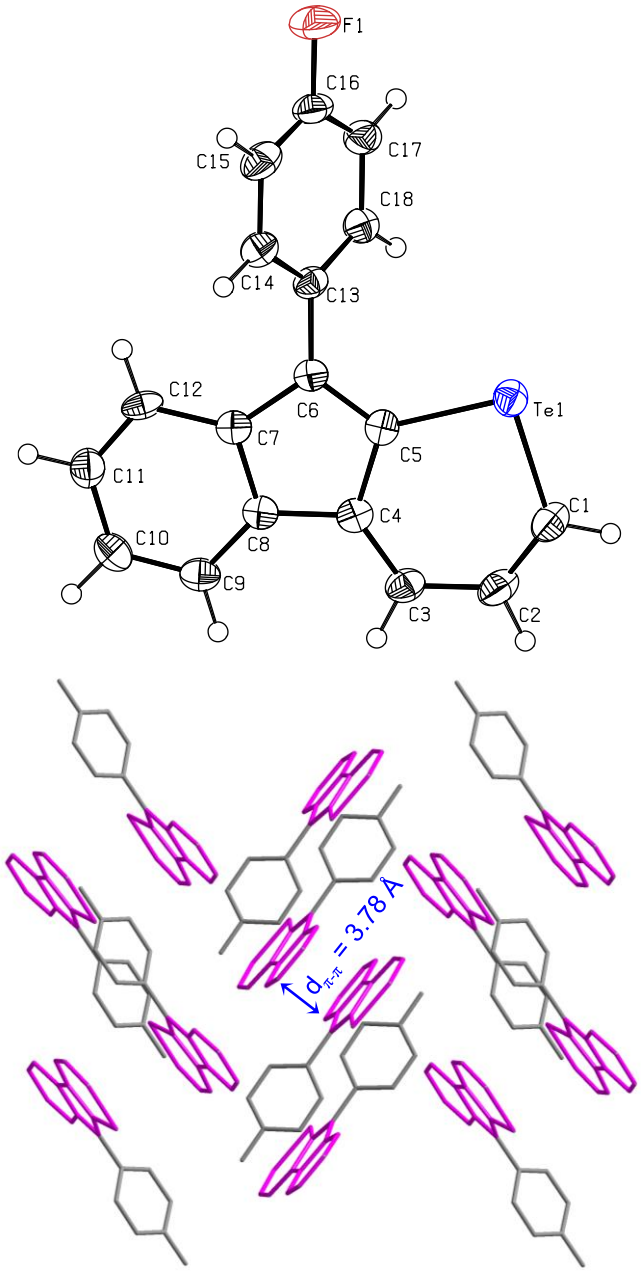


Figure S4. ORTEP diagram for the crystal structure of **Pt[P(C$_6$F$_5$)$_3$]$_2$Cl$_2$** with an ellipsoid contour probability level of 50%.

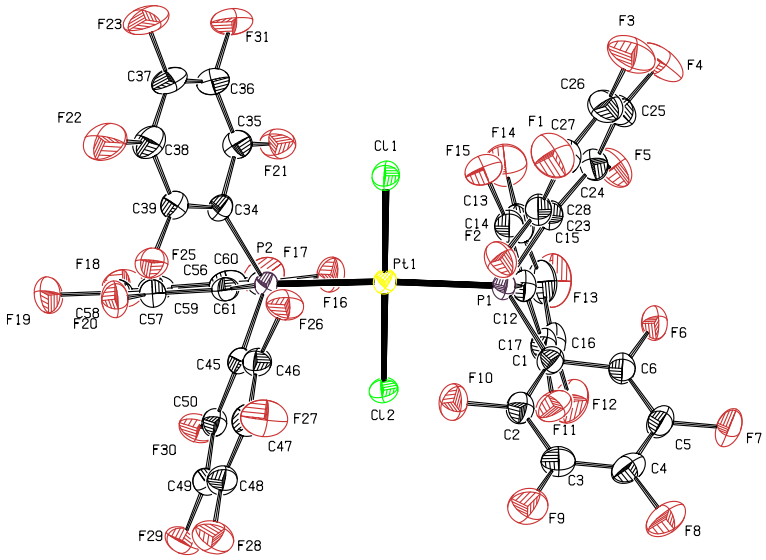


Table S1. Single crystal data and structure refinements for **2a, 2b**, **3g,** and **Pt[P(C$_6$F$_5$)$_3$]$_2$Cl$_2$**.

	2a	**2b**	**3g**	**Pt[P(C$_6$F$_5$)$_3$]$_2$Cl$_2$**
CCDC No.	2132835	2132837	2132833	2132838
formula	$C_{48}H_{52}Cl_2$	$C_{48}H_{52}Br_2$	$C_{18}H_{11}FTe$	$C_{36}Cl_2F_{30}P_2Pt$
formula wt.	699.79	788.75	373.87	1330.29
T (K)	173(2)	173(2)	173(2)	173(2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178
crystal size(mm)	0.160 × 0.140 × 0.120	0.200 × 0.180 × 0.150	0.220 × 0.200 × 0.160	0.180 × 0.160× 0.140
crystal syst.	Monoclinic	Monoclinic	Orthorhombic	Triclinic
space group	$P2_1$	$P2_1$/n	*Pccn*	$P\bar{1}$
a (Å)	4.98570(10)	15.8510(17)	14.5848(4)	12.7283(13)
b (Å)	24.9845(6)	5.0925(10)	23.5345(7)	14.371(3)
c (Å)	15.7241(4)	24.933(4)	8.1922(3)	14.6091(19)
α (deg.)	90.0000	90.0000	90.0000	101.005(15)
β (deg.)	92.193(2)	100.051(7)	90.0000	115.013(10)
γ (deg.)	90.0000	90.0000	90.0000	108.814(7)
V (Å^3)	1957.24(8)	1981.8(5)	2811.94(15)	2118.9(6)
Z / $D_{calcd.}$ (mg/m^3)	2 / 1.187	2 / 1.322	8 / 1.766	2 / 2.085
μ (mm^{-1})	1.720	2.821	16.678	9.610
F(000)	748	820	1440	1256
	$R1$ = 0.0403	$R1$ = 0.0515	$R1$ = 0.0263	$R1$ = 0.0202
[$I > 2\theta(I)$]	$wR2$ = 0.0937	$wR2$ = 0.1297	$wR2$ = 0.0732	$wR2$ = 0.0510
R indices (all data)	R = 0.0530	R = 0.0558	R = 0.0307	R = 0.0222
	$wR2$ = 0.1005	$wR2$ = 0.1332	$wR2$ = 0.0762	$wR2$ = 0.0519

Table S2. Selected bond lengths for **2a**

Bond	Length/Å	Bond	Length/Å
Cl1-C1	1.734(4)	C21-C22	1.349(6)
Cl2-C22	1.727(4)	C21-C41	1.498(6)
C1-C2	1.341(6)	C22-C23	1.455(6)
C2-C3	1.487(6)	C23-C24	1.392(6)
C4-C3	1.486(5)	C23-C32	1.400(6)
C1-C5	1.456(6)	C24-C25	1.429(6)
C4-C5	1.399(5)	C25-C26	1.419(7)
C5-C6	1.394(5)	C25-C30	1.443(6)
C3-C14	1.359(5)	C26-C27	1.363(7)
C4-C13	1.435(5)	C27-C28	1.403(7)
C7-C8	1.425(6)	C28-C29	1.362(7)
C6-C7	1.361(6)	C29-C30	1.411(6)
C2-C33	1.500(5)	C30-C31	1.414(6)
C9-C10	1.360(6)	C33-C34	1.525(6)
C9-C8	1.410(6)	C34-C35	1.521(6)
C8-C13	1.427(5)	C35-C36	1.525(6)
C10-C11	1.404(6)	C36-C37	1.524(6)
C11-C12	1.356(6)	C37-C38	1.525(6)
C13-C12	1.426(5)	C38-C39	1.513(7)
C14-C15	1.429(5)	C39-C40	1.522(7)
C15-C16	1.356(6)	C41-C42	1.528(6)
C16-C17	1.428(6)	C42-C43	1.533(6)
C17-C18	1.341(6)	C43-C44	1.519(6)
C18-C19	1.436(6)	C44-C45	1.531(6)
C19-C20	1.364(6)	C45-C46	1.521(6)
C20-C21	1.483(7)	C46-C47	1.519(7)
C20-C24	1.495(6)	C47-C48	1.523(7)

Table S3. Selected bond lengths for **2b**

Bond	Length/Å
Br1-C10	1.890(4)
C1-C2	1.418(6)
C1-C13	1.434(4)
C1-C6	1.437(6)
C2-C3	1.367(5)
C3-C4	1.389(6)
C4-C5	1.348(6)
C5-C6	1.420(5)
C7-C8	1.360(6)
C7-C6	1.411(6)
C8-C9	1.399(5)
C9-C13	1.391(5)
C9-C10	1.465(5)
C10-C11	1.338(5)
C11-C12	1.489(4)
C11-C17	1.505(4)
C12-C14	1.360(4)
C12-C13	1.485(4)
C14-C15	1.425(4)
C15-C16	1.348(5)

Table S4. Selected bond lengths for **3g**.

Bond	Length/Å
Te1-C5	2.066(3)
Te1-C1	2.067(3)
C1-C2	1.336(5)
F1-C16	1.366(4)
C3-C4	1.351(4)
C3-C2	1.444(5)
C4-C8	1.466(4)
C4-C5	1.466(4)
C5-C6	1.371(4)
C6-C13	1.469(4)
C6-C7	1.470(4)
C8-C9	1.391(4)
C8-C7	1.416(4)
C7-C12	1.458(5)
C9-C10	1.390(5)
C10-C11	1.392(5)
C11-C12	1.349(5)
C13-C18	1.394(5)
C13-C14	1.400(5)
C14-C15	1.398(5)
C15-C16	1.364(6)
C16-C17	1.378(5)
C17-C18	1.391(5)

5. Density functional theory calculations.

Density-functional theory (DFT) calculations were performed with Gaussian 16 program[S3]. Geometry optimizations were performed with the ωB97X-D[S4] functional. The LANL2DZ basis set with effective core potential (ECP) was used for Pt and Te, and the 6-31G(d) basis set was used for other atoms. Frequency calculations were performed at the same level of theory as for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency) on the potential energy surface, as well as to obtain thermal Gibbs free energy corrections. Intrinsic reaction coordinate calculations were performed to ensure that the first-order saddle points found were true transition states (TS) connecting the reactants and the products. Single-point energies were calculated with ORCA package[S5] with the ωB97M-V functional[S6] and the def2-TZVPP basis set.[S7] Solvation effects were incorporated with single-point energy calculations using the SMD[S8] solvation model. Molecular structure visualizations were obtained using CYLview.[S9]

Figure S5. Calculated pathway from compound **a** to intermediate **i** and the relative free energies (in kcal/mol) of each stationary point.

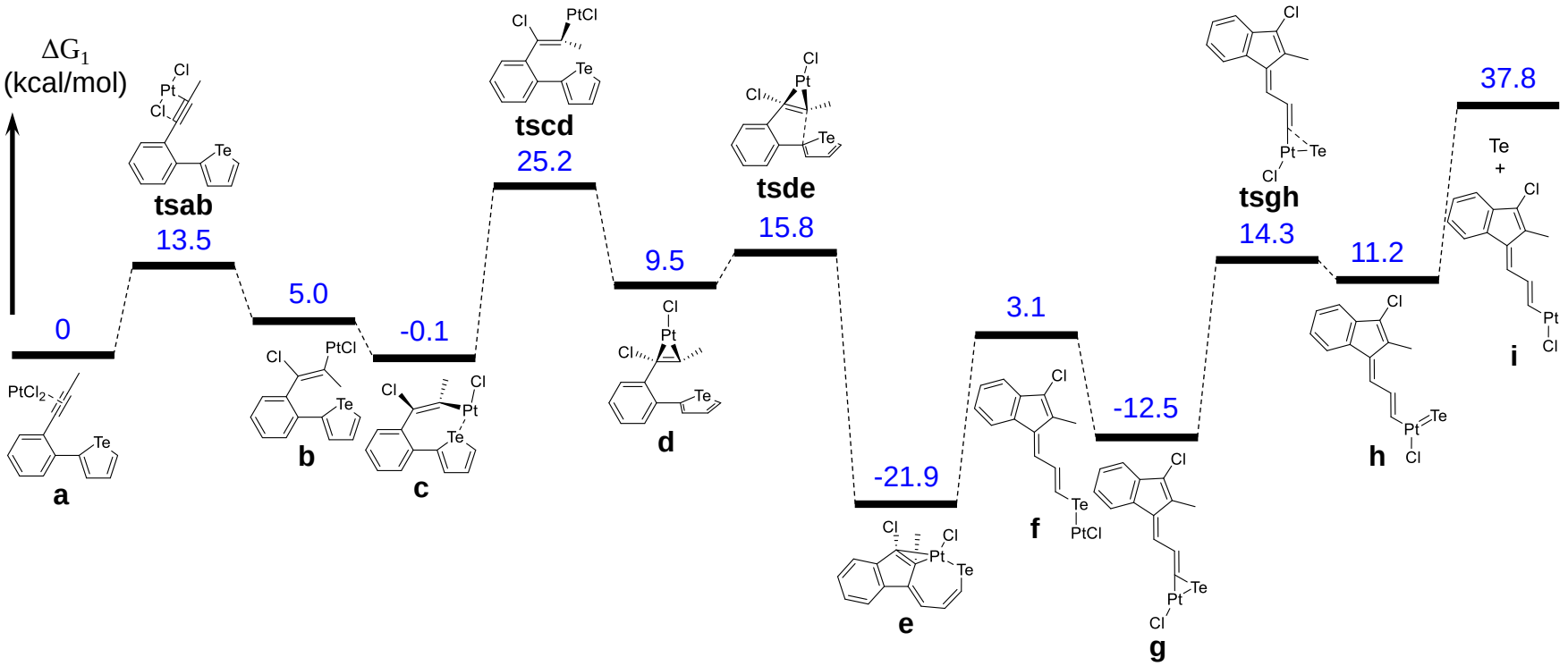


Figure S6. Calculated pathway from intermediate **i** to intermediate **q** and the relative free energies (in kcal/mol) of each stationary point.

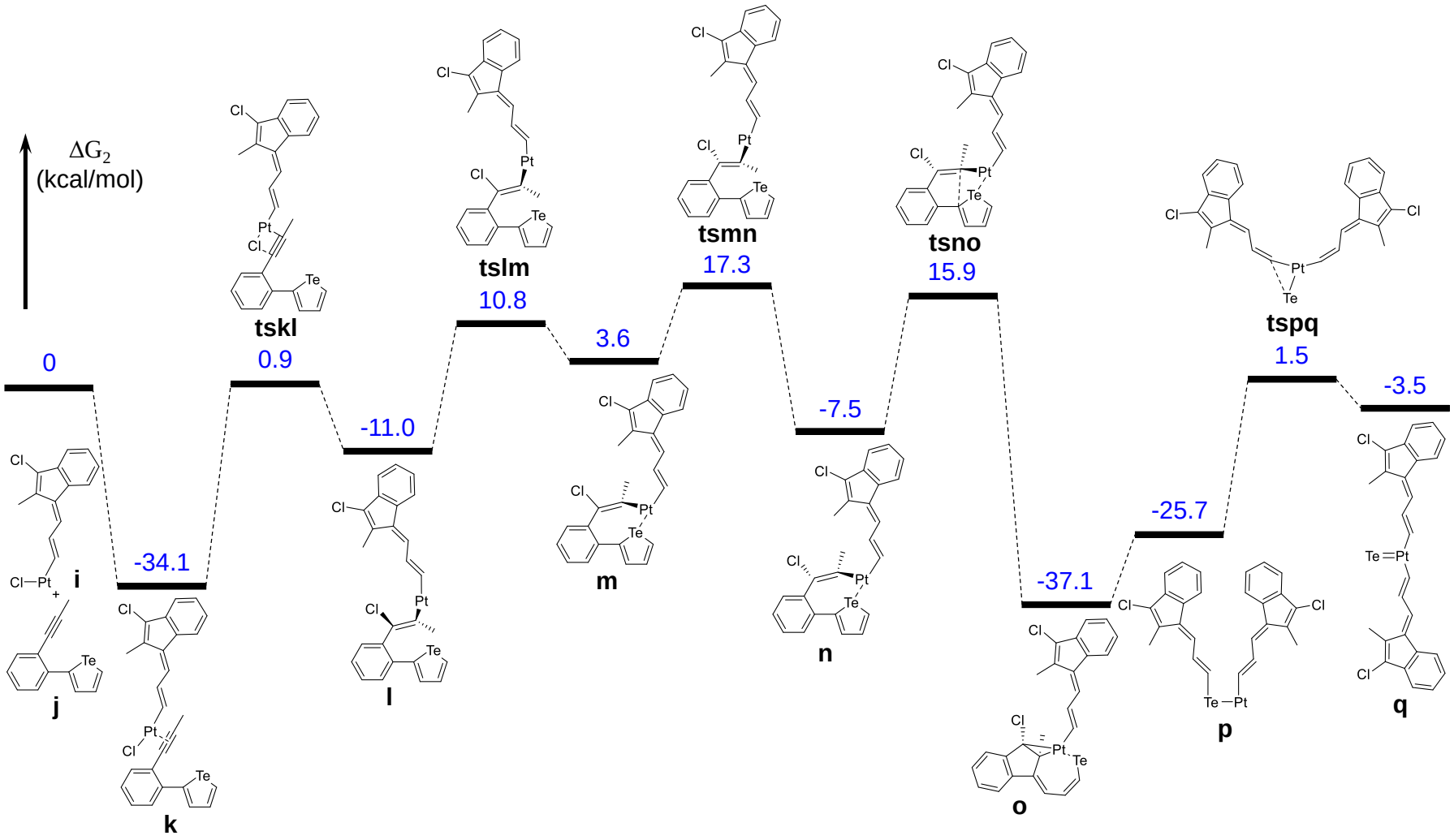


Figure S7. Calculated pathway from intermediate **r** to compound **t** and the relative free energies (in kcal/mol) of each stationary point.

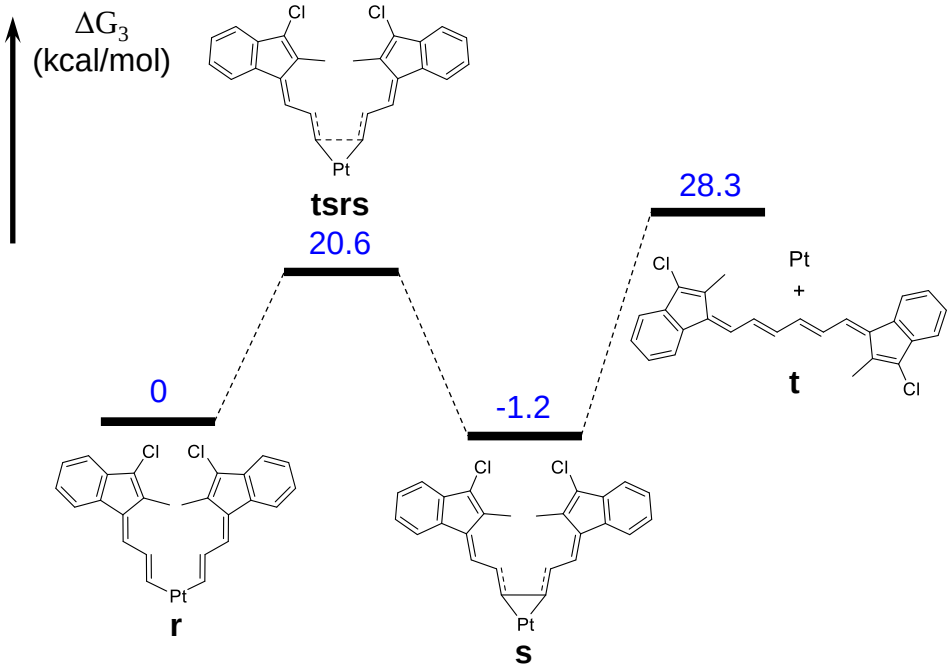


Figure S8. Calculated pathway from compound **j** to compound **y** and the relative free energies (in kcal/mol) of each stationary point.

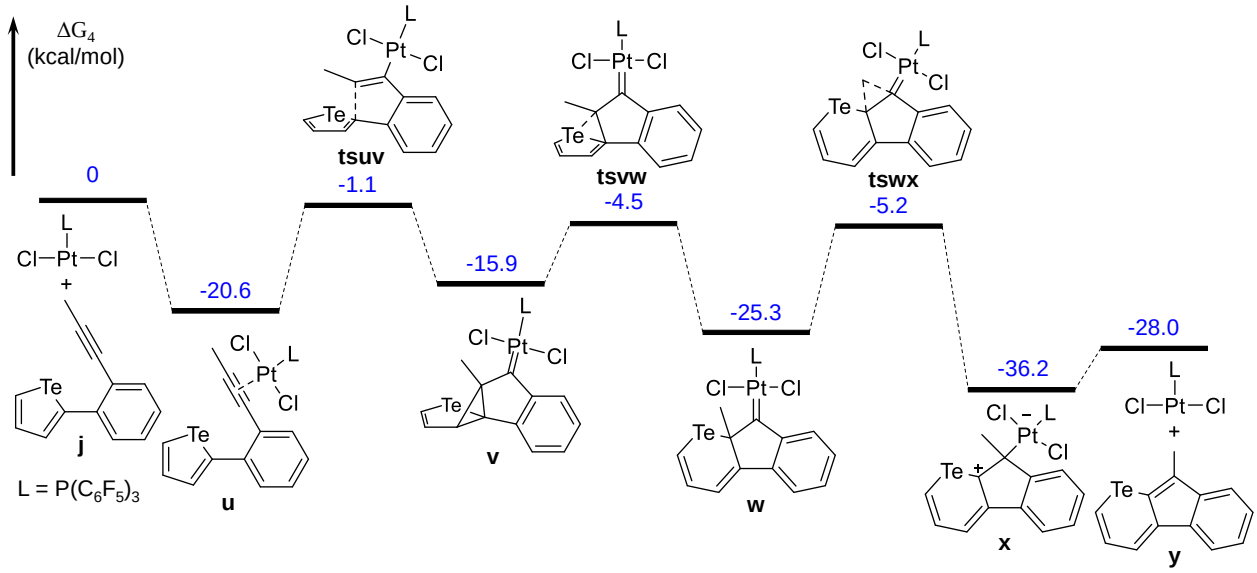
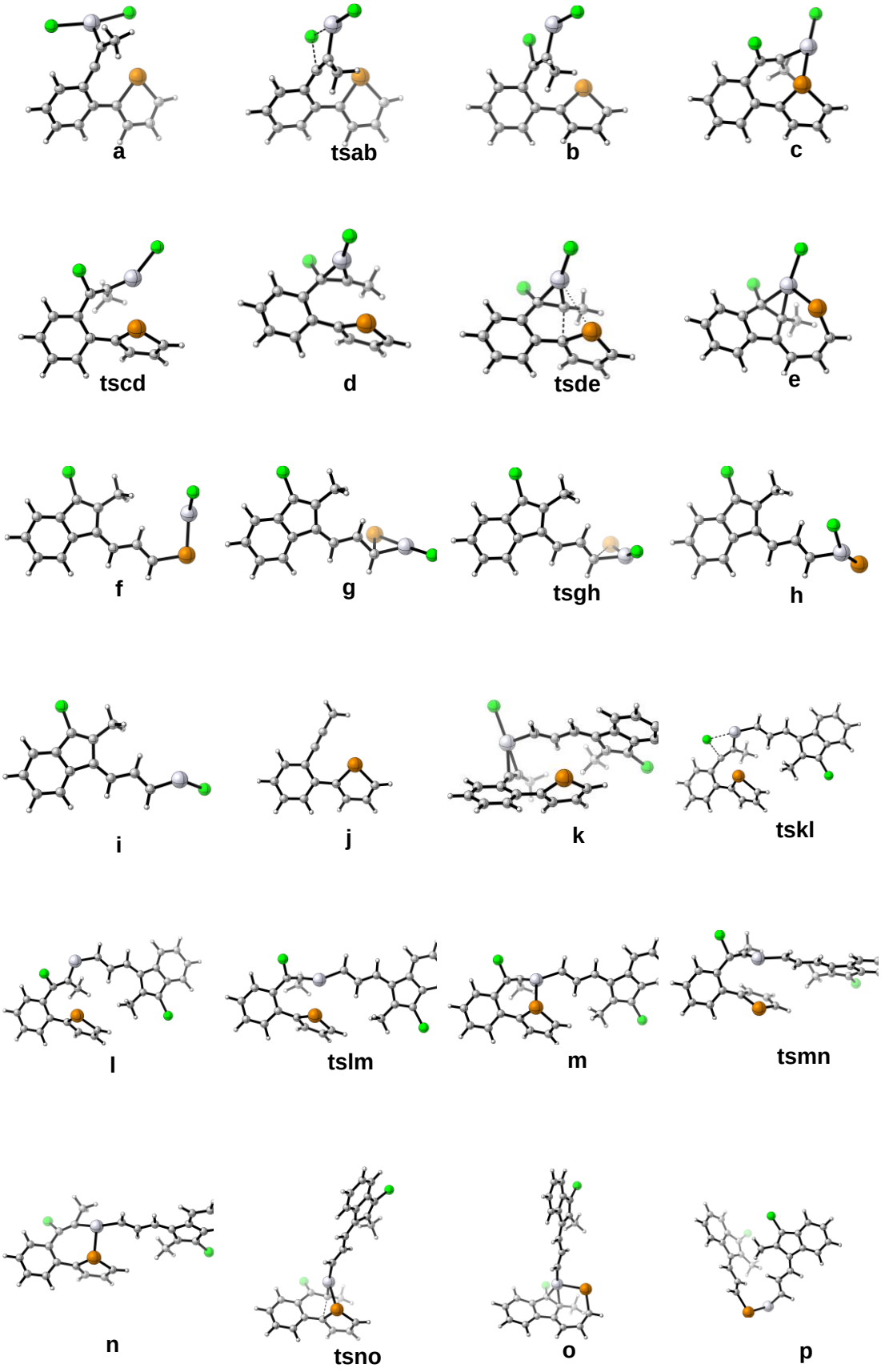
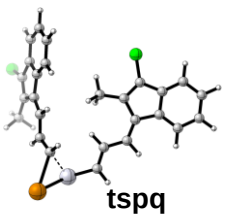
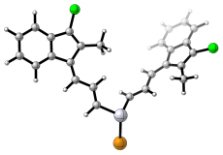


Table S5. Calculated geometries of all the stationary points in the ring-opening pathway.

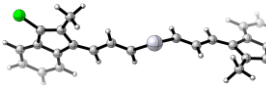




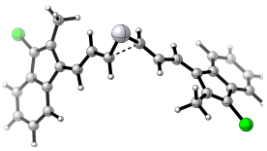
tspq



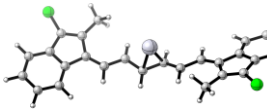
q



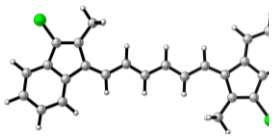
r



tsrs

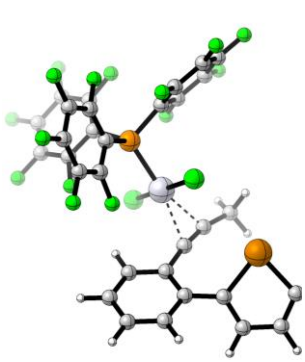


s

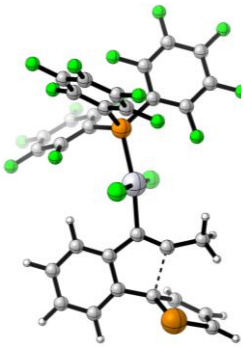


t

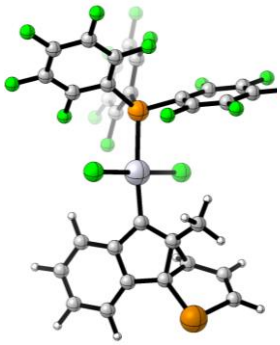
Table S6. Calculated geometries of all the stationary points in the ring-expansion pathway.



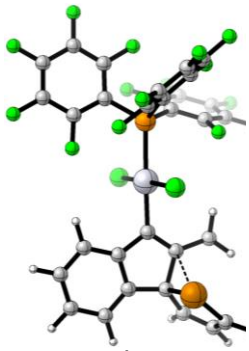
u



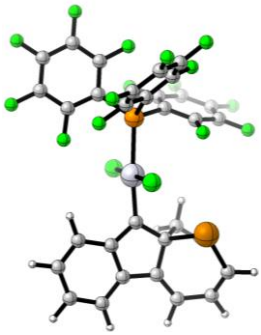
tsuv



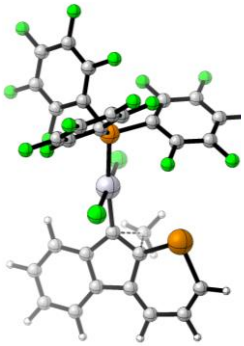
v



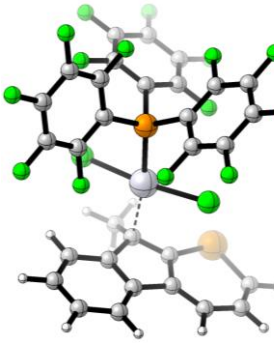
tsvw



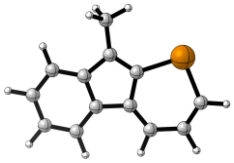
w



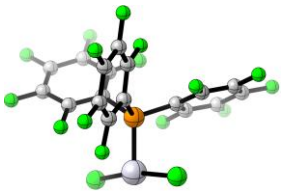
tswx



x



y



$Pt[P(C_6F_5)_3]Cl_2$

Table S7. Calculated orientation for intermediate **a** (*E* = -1808.921261 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	0.090491	3.978266	-0.5432
C	-1.28854	4.120616	-0.41026
C	-2.0714	3.033826	-0.03236
C	-1.49431	1.789269	0.222114
C	-0.09674	1.656982	0.08578
C	0.686869	2.749261	-0.2957
C	-2.32283	0.638948	0.637913
C	0.487614	0.367203	0.352785
C	0.481415	-0.82934	0.764034
C	-2.67952	0.343875	1.916376
C	-3.48334	-0.82926	2.143715
C	-3.8308	-1.56777	1.060148
Te	-3.0891	-0.77268	-0.6902
C	0.068711	-2.09471	1.365352
Pt	2.332255	-0.40358	-0.13858
Cl	3.340468	0.245218	1.862379
Cl	1.636171	-1.08817	-2.25464
H	0.703055	4.823953	-0.83852
H	-1.75807	5.080641	-0.6015
H	-3.14702	3.140493	0.06992
H	1.76128	2.628971	-0.39048
H	-2.35805	0.975204	2.740751
H	-3.79702	-1.10596	3.146496
H	-4.43369	-2.46786	1.082417
H	0.740242	-2.37002	2.184021
H	-0.94699	-1.96793	1.758216
H	0.064989	-2.89185	0.615895

Table S8. Calculated orientation for transition state **tsab** (*E* = -1808.899774 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-2.45642	4.00398	0.078179
C	-3.66861	3.307483	-0.03261
C	-3.72702	1.923073	0.050053
C	-2.57614	1.153185	0.264356
C	-1.33866	1.868644	0.400085
C	-1.30192	3.288632	0.284705
C	-2.70101	-0.29849	0.347468
C	-0.15724	1.235404	0.708928
C	0.954443	0.738885	1.134817
C	-3.76715	-0.91518	0.950757
C	-3.84266	-2.34092	0.908246
C	-2.8525	-2.99132	0.24041
Te	-1.43928	-1.71633	-0.52017
C	1.227852	0.611179	2.617295
Pt	2.214186	0.120616	-0.23932
Cl	0.94613	1.082322	-1.97635
Cl	3.72842	-0.97975	1.154128
H	-2.43206	5.084337	-0.00876
H	-4.5868	3.860199	-0.20938
H	-4.67769	1.420798	-0.08968
H	-0.33866	3.780765	0.366342
H	-4.52454	-0.33396	1.47082
H	-4.65831	-2.87426	1.387413
H	-2.78597	-4.06661	0.12142
H	2.171309	1.106139	2.858052
H	0.42029	1.058329	3.204969
H	1.323024	-0.44575	2.876371

Table S9. Calculated orientation for intermediate **b** (*E* = -1808.913329 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-2.90519	3.813865	0.229086
C	-3.99087	2.974003	0.467448
C	-3.8055	1.599659	0.546671
C	-2.53631	1.022946	0.397788
C	-1.43839	1.883874	0.179868
C	-1.63778	3.266831	0.090039
C	-2.41915	-0.44571	0.48985
C	-0.07793	1.352329	0.081612
C	0.71358	0.608731	0.846688
C	-2.90632	-1.18759	1.522976
C	-2.78684	-2.61927	1.456816
C	-2.20801	-3.14637	0.35051
Te	-1.62107	-1.6898	-0.98175
C	0.424543	0.088899	2.211882
Pt	2.351285	0.233716	-0.14897
Cl	0.844986	1.674125	-1.48389
Cl	3.584432	-1.11326	1.224022
H	-3.04423	4.888074	0.16059
H	-4.98786	3.388913	0.581331
H	-4.65698	0.944995	0.703912
H	-0.78049	3.91363	-0.07398
H	-3.35911	-0.70313	2.384925
H	-3.14522	-3.24837	2.266812
H	-2.04733	-4.20189	0.16649
H	1.253341	0.313311	2.888969
H	-0.49377	0.535367	2.605222
H	0.302129	-0.99897	2.176606

Table S10. Calculated orientation for intermediate **c** (*E* = -1808.921346 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-4.55617	-2.1216	0.213755
C	-4.98657	-0.80521	0.359796
C	-4.06489	0.235458	0.372038
C	-2.69212	-0.01754	0.250538
C	-2.26434	-1.35858	0.096396
C	-3.1997	-2.39163	0.073232
C	-1.74823	1.121689	0.351858
C	-0.81592	-1.56469	-0.12386
C	0.112384	-1.08932	0.717161
C	-1.85692	2.109385	1.268373
C	-0.86982	3.176356	1.307754
C	0.135376	3.14467	0.41679
Te	-0.05474	1.535472	-0.88588
C	-0.11451	-0.93009	2.191499
Pt	1.744158	-0.21757	0.06298
Cl	-0.41921	-1.91941	-1.81805
H	-5.27565	-2.93447	0.20035
H	-6.04558	-0.58464	0.454103
H	-4.41035	1.260863	0.462635
H	-2.85138	-3.41216	-0.05391
H	-2.65511	2.083335	2.006155
H	-0.94337	3.961544	2.055031
H	0.940919	3.864115	0.33409
H	-0.01399	0.114905	2.50468
H	-1.10359	-1.29843	2.48314
H	0.641273	-1.51082	2.731949
Cl	3.363186	-1.69658	0.818232

Table S11. Calculated orientation for transition state **tscd** (*E* = -1808.881121 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	4.061835	-2.59638	0.058474
C	4.615152	-1.4117	0.538812
C	3.808776	-0.29691	0.731573
C	2.435252	-0.33918	0.463621
C	1.879035	-1.54606	-0.00963
C	2.702853	-2.6584	-0.21683
C	1.628552	0.883663	0.667528
C	0.419619	-1.6759	-0.24816
C	-0.48228	-1.51239	0.769196
C	1.229588	1.382372	1.866107
C	0.430536	2.581225	1.875114
C	0.13764	3.146956	0.679551
Te	0.961874	2.098081	-0.89329
C	-0.32609	-1.81049	2.217248
Pt	-1.71746	-0.31673	0.039186
Cl	-0.02512	-2.23945	-1.85827
Cl	-3.99758	-0.33064	0.211332
H	4.685633	-3.47051	-0.09975
H	5.67728	-1.35323	0.756457
H	4.239125	0.634116	1.087322
H	2.265798	-3.58165	-0.58544
H	1.486982	0.872298	2.791156
H	0.074829	3.008807	2.808215
H	-0.449	4.046417	0.536321
H	0.714374	-2.06199	2.447923
H	-0.66473	-0.9884	2.850922
H	-0.94311	-2.69026	2.443654

Table S12. Calculated orientation for intermediate **d** (*E* = -1808.906135 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-0.50216	3.818566	-1.514
C	0.830227	3.69597	-1.90049
C	1.61916	2.697956	-1.3437
C	1.103489	1.811436	-0.39201
C	-0.2423	1.940752	-0.00582
C	-1.03222	2.945716	-0.57535
C	-0.87934	0.996842	0.959882
C	1.994389	0.783086	0.184283
C	2.770501	0.947637	1.290377
C	3.619343	-0.14076	1.691916
C	3.604144	-1.26097	0.922988
Te	2.325269	-1.08898	-0.67554
Cl	-1.91304	1.792118	2.193744
C	-0.45999	-0.29059	1.345049
Pt	-1.6562	-0.6851	-0.01431
C	0.17681	-0.99783	2.456594
Cl	-2.80476	-1.93383	-1.59319
H	-1.13191	4.588929	-1.94755
H	1.253759	4.375199	-2.63378
H	2.65971	2.595019	-1.6366
H	-2.07457	3.032178	-0.28607
H	2.737817	1.875696	1.855179
H	4.247619	-0.0653	2.575045
H	4.189484	-2.15375	1.108811
H	1.228369	-0.70633	2.554539
H	-0.33616	-0.67489	3.374292
H	0.085832	-2.07988	2.353094

Table S13. Calculated orientation for transition state **tsde** (*E* = -1808.896089 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-0.77834	3.883875	-1.62201
C	0.573846	3.750754	-1.93368
C	1.336928	2.758129	-1.32491
C	0.745148	1.898593	-0.40202
C	-0.61623	2.030681	-0.10207
C	-1.37867	3.025943	-0.70622
C	-1.13132	1.011873	0.841445
C	1.501023	0.844029	0.31991
C	2.284798	1.140889	1.4368
C	3.268796	0.218443	1.843268
C	3.464174	-0.87125	1.02752
Te	2.240516	-0.90393	-0.59407
Cl	-2.41053	1.55704	1.958282
C	-0.25321	-0.00808	1.288892
Pt	-1.33921	-0.83649	-0.06378
C	0.154991	-0.54878	2.60684
Cl	-2.15085	-2.50144	-1.47578
H	-1.37113	4.65755	-2.10012
H	1.035972	4.423089	-2.64977
H	2.392683	2.653079	-1.55822
H	-2.43375	3.120522	-0.47041
H	2.107948	2.063944	1.983009
H	3.842689	0.360876	2.75338
H	4.166755	-1.66931	1.242021
H	0.943229	-1.29969	2.492782
H	0.493048	0.239069	3.286347
H	-0.71411	-1.05492	3.041804

Table S14. Calculated orientation for intermediate **e** (*E* =-1808.956104 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-4.23991	0.034051	-1.71029
C	-4.13774	1.425902	-1.60867
C	-3.18535	2.019163	-0.78535
C	-2.3477	1.197079	-0.03695
C	-2.45427	-0.19698	-0.15218
C	-3.38972	-0.79552	-0.98644
C	-1.2098	1.51837	0.83864
C	-1.43565	-0.78431	0.726411
C	-0.68353	0.21594	1.395782
C	-0.70326	2.744306	1.046032
C	0.644251	2.992878	1.555367
C	1.730981	2.43132	1.00632
Te	1.78311	1.223388	-0.73392
C	-0.18185	0.122848	2.813042
Pt	0.548711	-0.96058	0.024529
Cl	-1.6342	-2.42098	1.33849
H	-4.98653	-0.40248	-2.36613
H	-4.81076	2.053392	-2.18497
H	-3.10849	3.10072	-0.72619
H	-3.45432	-1.87579	-1.07112
H	-1.2698	3.613319	0.712133
H	0.772966	3.714228	2.36273
H	2.7148	2.660267	1.40982
H	0.749789	0.6766	2.941085
H	-0.93144	0.552561	3.488754
H	-0.0083	-0.91515	3.105956
Cl	2.126684	-2.25072	-1.10508

Table S15. Calculated orientation for intermediate **f** (*E* = -1808.916374 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-6.94666	-1.10971	0.545692
C	-6.16728	-2.24994	0.731744
C	-4.77988	-2.2044	0.563969
C	-4.19343	-0.99913	0.21065
C	-4.98613	0.14505	0.024573
C	-6.36089	0.107828	0.187332
C	-2.78283	-0.62669	-0.04636
C	-4.06856	1.228723	-0.33537
C	-2.77953	0.817187	-0.38401
C	-1.75821	-1.50659	0.045549
C	-0.36495	-1.24119	-0.22203
C	0.6165	-2.1314	0.025815
Te	2.634064	-1.70103	-0.2504
C	-1.59086	1.673023	-0.68572
Pt	2.618191	0.770778	-0.12306
Cl	-4.63602	2.834414	-0.63972
H	-8.02255	-1.16642	0.680813
H	-6.64194	-3.18583	1.010464
H	-4.18513	-3.1015	0.71185
H	-6.96767	0.99642	0.041897
H	-1.99474	-2.52321	0.356018
H	-0.09014	-0.27389	-0.62712
H	0.400448	-3.11363	0.441153
H	-0.85836	1.643798	0.12969
H	-1.08569	1.356207	-1.60581
H	-1.89345	2.71445	-0.81997
Cl	2.702203	2.081473	1.717923

Table S16. Calculated orientation for intermediate **g** (*E* = -1808.941225 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	6.367248	-1.81418	-0.79325
C	5.302882	-2.69375	-0.98045
C	3.981001	-2.25663	-0.85027
C	3.751704	-0.92824	-0.52909
C	4.829449	-0.04818	-0.34249
C	6.140941	-0.47295	-0.47041
C	2.49812	-0.1653	-0.31884
C	4.247403	1.257354	-0.01634
C	2.894983	1.225869	0.004284
C	1.273949	-0.72592	-0.4071
C	-0.01416	-0.06994	-0.24054
C	-1.23754	-0.77935	-0.51416
Te	-1.24715	-0.57203	1.70067
C	1.980649	2.366642	0.312487
Pt	-2.95541	0.079844	-0.3106
Cl	5.236389	2.63872	0.302799
H	7.386103	-2.17408	-0.89932
H	5.500507	-3.73145	-1.23091
H	3.161926	-2.95429	-1.00112
H	6.970136	0.212491	-0.32463
H	1.221277	-1.79339	-0.61682
H	-0.05948	1.012191	-0.26158
H	-1.18778	-1.78105	-0.94412
H	1.373467	2.641117	-0.55848
H	1.301976	2.125312	1.13864
H	2.553174	3.250998	0.602584
Cl	-4.35097	0.734069	-2.02251

Table S17. Calculated orientation for transition state **tsgh** (*E* = -1808.898441 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	6.525697	-1.63011	-1.17342
C	5.454803	-2.26104	-1.805
C	4.141326	-1.83988	-1.57957
C	3.922376	-0.77881	-0.71344
C	5.007527	-0.14774	-0.0819
C	6.312139	-0.5605	-0.30014
C	2.68036	-0.10623	-0.27051
C	4.440052	0.916009	0.747694
C	3.089547	0.969379	0.659503
C	1.449602	-0.48292	-0.69209
C	0.169585	0.081876	-0.33665
C	-0.97324	-0.42105	-0.86211
Te	-2.54807	-1.34589	1.366369
C	2.19124	1.933557	1.364138
Pt	-2.74991	0.322202	-0.50451
Cl	5.439359	1.95478	1.706585
H	7.538628	-1.97268	-1.36245
H	5.642088	-3.08937	-2.48162
H	3.317834	-2.34068	-2.08117
H	7.145784	-0.06801	0.191314
H	1.403282	-1.32043	-1.38667
H	0.122313	0.926226	0.340193
H	-0.95855	-1.26078	-1.55612
H	1.606499	2.528037	0.653002
H	1.490336	1.415113	2.028757
H	2.774056	2.626998	1.975471
Cl	-2.47206	2.361379	-1.57475

Table S18. Calculated orientation for intermediate **h** (*E* = -1808.903489 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	6.663164	-1.98614	-0.72625
C	5.579953	-2.70154	-1.23641
C	4.27593	-2.21811	-1.1035
C	4.076224	-1.0084	-0.45366
C	5.173465	-0.29411	0.057404
C	6.470007	-0.76861	-0.07045
C	2.847819	-0.23841	-0.15342
C	4.628776	0.916678	0.670234
C	3.280348	0.982122	0.565387
C	1.611396	-0.65218	-0.51277
C	0.342341	0.003686	-0.27282
C	-0.79779	-0.51719	-0.75202
Te	-3.37155	-1.16537	1.222003
C	2.404536	2.082719	1.070442
Pt	-2.54676	0.335596	-0.56715
Cl	5.650773	2.095879	1.424495
H	7.668853	-2.37965	-0.84032
H	5.750997	-3.64628	-1.74385
H	3.443293	-2.78792	-1.50702
H	7.312289	-0.21011	0.326859
H	1.546027	-1.59457	-1.05514
H	0.317525	0.930374	0.286079
H	-0.83125	-1.45758	-1.30247
H	1.827783	2.540302	0.258561
H	1.696694	1.71727	1.823511
H	3.004395	2.869115	1.535438
Cl	-1.95109	2.424057	-1.39985

Table S19. Calculated orientation for intermediate **i** (*E* = -1540.882591 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	5.960354	-1.96207	-0.04017
C	4.901205	-2.86707	0.019125
C	3.579216	-2.41882	0.084226
C	3.339696	-1.05273	0.088895
C	4.412536	-0.14766	0.02996
C	5.726038	-0.58497	-0.03508
C	2.082383	-0.27156	0.142691
C	3.823842	1.192137	0.051574
C	2.472042	1.157344	0.117533
C	0.860549	-0.84977	0.192378
C	-0.43442	-0.20278	0.234392
C	-1.58107	-0.91823	0.185114
C	1.556282	2.337613	0.158879
Pt	-3.14789	-0.01	-0.38041
Cl	4.803571	2.61885	-0.00349
H	6.980241	-2.33129	-0.09098
H	5.104729	-3.93362	0.014598
H	2.764195	-3.13599	0.130491
H	6.55044	0.120234	-0.08142
H	0.828682	-1.93831	0.188161
H	-0.48582	0.880002	0.286924
H	-1.6316	-2.00201	0.305134
H	0.869879	2.342663	-0.69599
H	0.956162	2.346008	1.075905
H	2.1269	3.269158	0.129715
Cl	-4.72828	0.010223	1.240701

Table S20. Calculated orientation for intermediate **j** (*E* = -769.1789245 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-0.07112	-0.96986	0.313432
C	1.216747	1.740499	0.319056
C	0.61465	2.776723	0.482997
C	-0.16518	3.992552	0.681225
Te	-1.63099	0.157164	-0.50113
C	-2.7667	-1.32908	0.35852
C	-2.0012	-2.23473	1.015463
C	-0.57796	-2.04672	0.981082
H	-1.2325	3.787176	0.538118
H	-0.03001	4.384229	1.695374
H	0.131707	4.773299	-0.02731
H	-3.84932	-1.33963	0.311804
H	-2.43996	-3.07186	1.551686
H	0.084042	-2.74554	1.486376
C	4.154944	-0.45921	-0.27165
C	3.359733	0.659346	-0.07052
C	1.974027	0.541014	0.115948
C	1.369145	-0.73762	0.10189
C	2.194859	-1.84973	-0.12389
C	3.566168	-1.72079	-0.29973
H	5.225097	-0.34583	-0.41515
H	3.802314	1.650299	-0.05109
H	1.739588	-2.83335	-0.18162
H	4.171516	-2.60571	-0.47233

Table S21. Calculated orientation for intermediate **k** (*E* = -2310.115869 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	4.70878	3.079869	-0.01756
C	3.723814	4.058732	-0.12812
C	2.40104	3.754577	0.16758
C	2.018766	2.474276	0.587334
C	3.025269	1.488169	0.692325
C	4.356113	1.800393	0.384949
C	0.605496	2.179917	0.875702
C	2.70204	0.127143	1.058975
C	2.301999	-0.87623	1.703116
C	0.104395	1.609331	2.004714
C	-1.31607	1.399427	2.08939
C	-2.07132	1.778808	1.0292
Te	-0.92929	2.595756	-0.47324
C	1.776112	-1.61863	2.859678
Pt	2.745879	-1.54366	-0.22282
Cl	3.423757	-2.93608	-1.99269
H	5.743538	3.309448	-0.25035
H	3.985615	5.063706	-0.44471
H	1.639535	4.525481	0.087759
H	5.108899	1.021501	0.460769
H	0.758169	1.345563	2.832009
H	-1.76663	0.959321	2.975011
H	-3.14628	1.670396	0.95116
H	2.391148	-2.49578	3.078488
H	1.757594	-0.9676	3.739533
H	0.756564	-1.96351	2.658018
C	0.980786	-1.25488	-1.00289
C	-0.18176	-1.47889	-0.37667
H	1.028824	-0.86719	-2.02073

C	-1.43819	-1.15989	-1.02318
H	-0.19448	-1.86153	0.635039
C	-2.683	-1.1869	-0.4976
H	-1.34488	-0.79631	-2.04571
C	-3.86988	-0.67119	-1.20968
C	-3.1426	-1.5847	0.849929
C	-4.03103	-0.14991	-2.48744
C	-4.96664	-0.72776	-0.33002
C	-4.46549	-1.30005	0.915792
C	-2.31147	-2.18401	1.936737
C	-5.29331	0.302982	-2.87449
H	-3.19735	-0.09417	-3.18229
C	-6.22343	-0.27509	-0.70937
Cl	-5.49703	-1.55528	2.289225
H	-2.93374	-2.46711	2.789828
H	-1.78906	-3.08241	1.589503
H	-1.5602	-1.46899	2.293139
C	-6.37698	0.241161	-1.99607
H	-5.43345	0.708319	-3.87227
H	-7.06422	-0.32021	-0.02332
H	-7.35026	0.600154	-2.31748

Table S22. Calculated orientation for transition state **tskl** (*E* = -2310.060142 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	6.157425	0.575192	2.106572
C	5.990924	1.943393	1.872288
C	4.817541	2.443384	1.318181
C	3.757902	1.596331	0.978061
C	3.921332	0.205099	1.246174
C	5.126683	-0.28782	1.795207
C	2.538075	2.181654	0.402862
C	2.850193	-0.67449	1.061294
C	1.663382	-1.18726	1.134567
C	1.885217	3.244102	0.958473
C	0.766304	3.801818	0.254905
C	0.452016	3.24934	-0.94433
Te	1.678657	1.672992	-1.42835
C	0.794491	-0.91938	2.341615
Pt	1.172142	-2.24798	-0.43968
Cl	3.562317	-2.04488	-1.03538
H	7.083183	0.198074	2.527203
H	6.7959	2.631325	2.113643
H	4.723592	3.505554	1.118295
H	5.216971	-1.35566	1.963897
H	2.20244	3.648937	1.916508
H	0.202704	4.633902	0.666837
H	0.357876	3.572872	-1.58762

H	0.433141	-1.86506	2.753323
H	1.340452	-0.37174	3.115771
H	0.074324	-0.33321	2.032375
C	0.753661	-2.33635	-0.04083
C	1.614827	-1.29657	-0.11901
H	1.174129	-3.3158	0.22324
C	3.034316	-1.4448	0.114841
H	1.227471	-0.30825	-0.34581
C	4.002649	-0.49709	0.138821
H	3.355253	-2.46961	0.307016
C	5.425155	-0.79548	0.402828
C	3.912568	0.966154	-0.05739
C	6.09219	-1.988	0.656333
C	6.141741	0.415273	0.368503
C	5.166579	1.461326	0.083088
C	2.678442	1.757064	-0.35046
C	7.470105	-1.95624	0.874337
H	5.559371	-2.93482	0.686123
C	7.513214	0.451934	0.584844
Cl	5.624773	3.132722	-0.04722
H	2.913928	2.821038	-0.43929
H	1.929463	1.647506	0.441675
H	2.213869	1.435153	-1.28948
C	8.17314	-0.74991	0.83942
H	8.00205	-2.88206	1.073547
H	8.05802	1.391143	0.556647
H	9.245478	-0.74749	1.011873

Table S23. Calculated orientation for intermediate **I** (*E* = -2310.078973 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	5.985003	0.630583	2.395213
C	5.709412	1.994853	2.340471
C	4.567488	2.44692	1.692622
C	3.66457	1.557737	1.090315
C	3.941203	0.175145	1.16736
C	5.102948	-0.26716	1.811069
C	2.481096	2.128777	0.415218
C	3.013131	-0.81665	0.601679
C	1.718302	-1.0569	0.818037
C	1.655997	3.055378	0.978327
C	0.593642	3.608028	0.18167
C	0.489858	3.182108	-1.10135
Te	1.92714	1.782297	-1.56664
C	0.892021	-0.35484	1.846857
Pt	1.06528	-2.42114	-0.42884
Cl	3.705946	-1.91337	-0.67166
H	6.878582	0.268239	2.893838
H	6.391116	2.709941	2.79111
H	4.370829	3.512262	1.622375
H	5.300975	-1.33405	1.862076
H	1.793463	3.359077	2.013416
H	0.096678	4.336929	0.597261
H	0.256737	3.511803	-1.81397
H	1.524065	0.214706	2.535187

H	0.195707	0.341397	1.367349
H	0.300551	-1.07547	2.418127
C	0.839679	-2.41846	-0.03054
C	1.66447	-1.35416	-0.11469
H	1.266408	-3.39227	0.240024
C	3.08507	-1.46512	0.138859
H	1.252218	-0.38199	-0.36011
C	4.023909	-0.48996	0.162331
H	3.431445	-2.47863	0.343904
C	5.453706	-0.74668	0.436423
C	3.893182	0.969241	-0.04662
C	6.151073	-1.91748	0.705546
C	6.135983	0.482769	0.392225
C	5.132258	1.499318	0.093304
C	2.636491	1.72278	-0.34083
C	7.526949	-1.84515	0.929381
H	5.644334	-2.87816	0.744362
C	7.504313	0.56027	0.613674
Cl	5.5445	3.18061	-0.04777
H	1.891461	1.586987	0.450884
H	2.181026	1.393231	-1.28157
H	2.838463	2.793907	-0.42442
C	8.196083	-0.6206	0.884098
H	8.083176	-2.75352	1.141841
H	8.023	1.513826	0.578002
H	9.267049	-0.58652	1.061418

Table S24. Calculated orientation for transition state **tslm** (*E* = -2310.044324 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-6.88673	-0.03713	0.580893
C	-6.60243	-1.39376	0.712288
C	-5.28518	-1.82861	0.660025
C	-4.22281	-0.93023	0.486976
C	-4.51494	0.448534	0.3657
C	-5.85012	0.867923	0.405876
C	-2.8587	-1.51	0.451353
C	-3.42724	1.449394	0.210696
C	-2.41135	1.561089	1.144692
C	-2.24827	-2.11351	1.501518
C	-0.94552	-2.70566	1.310592
C	-0.40272	-2.64906	0.074307
Te	-1.64072	-1.67255	-1.26143
C	-2.44903	1.28108	2.603879
Pt	-1.06148	1.138304	-0.08771
Cl	-3.70733	2.661517	-1.04802
H	-7.91266	0.31583	0.617113
H	-7.40408	-2.11317	0.847881
H	-5.05781	-2.88692	0.742388
H	-6.06749	1.926601	0.30494
H	-2.73257	-2.1335	2.474683
H	-0.42359	-3.1799	2.136647
H	0.561494	-3.05097	-0.21073

H	-3.43815	0.920488	2.908015
H	-1.67589	0.564979	2.895132
H	-2.25007	2.219797	3.136166
C	0.8159	1.75326	-0.08003
C	1.835141	0.870567	0.01242
H	1.051579	2.816767	-0.16155
C	3.225418	1.27477	-0.0151
H	1.610609	-0.18625	0.119461
C	4.337262	0.506226	0.056204
H	3.38085	2.350656	-0.10056
C	5.709189	1.054849	0.03797
C	4.478247	-0.96162	0.166822
C	6.187158	2.355487	-0.05138
C	6.612172	-0.01837	0.137213
C	5.804904	-1.23163	0.212284
C	3.374193	-1.96937	0.204241
C	7.566389	2.567745	-0.04194
H	5.508693	3.200908	-0.1285
C	7.984501	0.186428	0.14797
Cl	6.523412	-2.80485	0.338146
H	2.714585	-1.81267	1.065549
H	2.758859	-1.9089	-0.7014
H	3.782214	-2.98132	0.26972
C	8.455333	1.495924	0.056753
H	7.952392	3.58036	-0.11244
H	8.671062	-0.65134	0.225043
H	9.524852	1.683876	0.062498

Table S25. Calculated orientation for intermediate **m** (*E* = -2310.055764 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	6.677554	0.596751	0.953087
C	6.339379	1.89469	0.581527
C	5.030331	2.185454	0.224932
C	4.027973	1.202745	0.236414
C	4.373521	-0.11635	0.617467
C	5.702291	-0.3901	0.965129
C	2.671746	1.650682	-0.15093
C	3.35701	-1.21231	0.701086
C	2.313415	-1.20194	1.639072
C	1.969321	2.636967	0.451637
C	0.658914	2.985354	-0.06568
C	0.185092	2.296258	-1.12208
Te	1.55223	0.883202	-1.78486
C	2.2442	-0.56031	2.970434
Pt	1.224461	-1.05021	0.103414
Cl	3.91619	-2.76358	-0.00195
H	7.696774	0.352348	1.236075
H	7.091601	2.677368	0.563028
H	4.764499	3.191694	-0.08416
H	5.96774	-1.39998	1.261264
H	2.363914	3.134284	1.334015
H	0.074317	3.772342	0.403142
H	0.770738	2.44714	-1.60851
H	3.036572	0.189481	3.092131

H	1.265	-0.11184	3.155574
H	2.40743	-1.3373	3.730295
C	0.706292	-1.5326	-0.2121
C	1.749411	-0.72072	0.075268
H	0.945688	-2.52863	-0.60047
C	3.124202	-1.1235	-0.11266
H	1.554533	0.276143	0.457717
C	4.264165	-0.42488	0.117381
H	3.247312	-2.13403	-0.50542
C	5.61411	-0.9585	-0.15033
C	4.453914	0.943311	0.643044
C	6.049033	-2.18221	-0.64713
C	6.554602	0.032628	0.190194
C	5.789838	1.175836	0.670752
C	3.384724	1.894907	1.074723
C	7.418528	-2.40107	-0.79709
H	5.342571	-2.96285	-0.91682
C	7.919521	-0.18115	0.04182
Cl	6.561994	2.638936	1.206687
H	2.777655	1.471318	1.882786
H	2.708025	2.139833	0.247854
H	3.822254	2.828892	1.437542
C	8.344425	-1.4117	-0.45647
H	7.769047	-3.35389	-1.18327
H	8.636837	0.590068	0.3074
H	9.406305	-1.60318	-0.58114

Table S26. Calculated orientation for transition state **tsmn** (*E* = -2310.033874 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-6.62677	0.498986	-0.23168
C	-6.23835	1.827291	-0.35253
C	-4.90207	2.154598	-0.1676
C	-3.94144	1.186725	0.14667
C	-4.33796	-0.16614	0.284042
C	-5.68974	-0.47702	0.082763
C	-2.54112	1.646154	0.271885
C	-3.36317	-1.24626	0.625379
C	-2.20683	-1.10212	1.417515
C	-1.87108	1.97264	1.410463
C	-0.51232	2.432279	1.292907
C	0.007459	2.538984	0.043785
Te	-1.34829	2.003084	-1.40508
C	-1.81913	-0.94929	2.821239
Pt	-1.32639	-1.41268	-0.16368
Cl	-4.07004	-2.88525	0.878258
H	-7.6633	0.211751	-0.38034
H	-6.96194	2.599778	-0.59318
H	-4.57529	3.185618	-0.26832
H	-6.02207	-1.50349	0.171499
H	-2.35453	1.895078	2.380542
H	0.067871	2.692964	2.174147
H	1.008444	2.879409	-0.19306

H	-2.53663	-0.32546	3.362928
H	-1.8564	-1.95913	3.257325
H	-0.79845	-0.57471	2.92333
C	0.635661	-1.65222	-0.66064
C	1.665862	-0.95255	-0.13023
H	0.917125	-2.39054	-1.42355
C	3.039678	-1.14487	-0.54585
H	1.462719	-0.20304	0.627505
C	4.165604	-0.53529	-0.10236
H	3.16984	-1.88516	-1.33657
C	5.509154	-0.81188	-0.65189
C	4.348717	0.484823	0.953075
C	5.943768	-1.67255	-1.65249
C	6.437019	-0.00048	0.026843
C	5.672504	0.771944	0.999975
C	3.284576	1.077116	1.819325
C	7.304031	-1.71309	-1.96194
H	5.246012	-2.30841	-2.19086
C	7.791229	-0.03604	-0.27834
Cl	6.434133	1.90819	2.071325
H	2.53631	1.612002	1.224025
H	2.759304	0.301265	2.388025
H	3.715374	1.784322	2.533163
C	8.217762	-0.90406	-1.28318
H	7.655696	-2.38298	-2.74125
H	8.499731	0.594582	0.250837
H	9.271945	-0.95092	-1.54034

Table S27. Calculated orientation for intermediate **n** (*E* = -2310.073502 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	-6.96625	0.582147	-0.87325
C	-6.45345	1.819051	-1.25178
C	-5.14698	2.137996	-0.91257
C	-4.33875	1.249077	-0.18991
C	-4.85526	-0.0035	0.206475
C	-6.17817	-0.30421	-0.15362
C	-4.08094	-1.01063	0.978776
C	-2.95775	1.68811	0.081001
C	-2.49936	2.502641	1.046427
C	-1.07414	2.823353	1.071612
C	-0.27292	2.272935	0.14531
Te	-1.37375	1.114619	-1.19906
Cl	-5.07155	-1.82339	2.248768
C	-2.82281	-1.41651	0.832032
Pt	-1.0555	-1.13514	-0.12394
C	-2.18673	-2.54602	1.590983
H	-7.98273	0.304529	-1.13534
H	-7.06223	2.52742	-1.80504
H	-4.72929	3.09804	-1.20265
H	-6.59605	-1.2607	0.140644
H	-3.16653	2.892332	1.810397
H	-0.67765	3.484745	1.837375
H	0.7935	2.42474	0.038322
H	-2.05304	-2.33265	2.656288

H	-2.7079	-3.49876	1.451376
H	-1.12774	-2.76639	1.219404
C	0.9041	-1.25594	-0.73166
C	1.963991	-0.64921	-0.14527
H	1.15746	-1.90426	-1.58262
C	3.327136	-0.8551	-0.58718
H	1.793524	0.019108	0.694495
C	4.485279	-0.33653	-0.10944
H	3.419824	-1.53075	-1.43925
C	5.809713	-0.63545	-0.69031
C	4.724498	0.59124	1.016079
C	6.197987	-1.43973	-1.75591
C	6.781	0.075238	0.040225
C	6.061621	0.80935	1.073332
C	3.695888	1.174865	1.930136
C	7.552577	-1.5243	-2.07855
H	5.467246	-1.99909	-2.33416
C	8.131085	-0.00568	-0.27805
Cl	6.883266	1.8271	2.2186
H	2.975455	1.792075	1.380652
H	3.132379	0.390699	2.44782
H	4.165776	1.807086	2.688284
C	8.509297	-0.81503	-1.34821
H	7.866821	-2.15068	-2.9085
H	8.872639	0.54661	0.291952
H	9.558749	-0.89538	-1.6164

Table S28. Calculated orientation for transition state **tsno** (*E* = -2310.036109 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-4.99548	0.622975	3.369085
C	-5.56307	-0.52655	2.819486
C	-5.22647	-0.92096	1.528551
C	-4.33843	-0.15253	0.777483
C	-3.76524	1.004477	1.335707
C	-4.09953	1.390088	2.633594
C	-2.88244	1.755791	0.424597
C	-3.88089	-0.55274	-0.56385
C	-4.55238	-0.52139	-1.76694
C	-3.93428	-1.15647	-2.87503
C	-2.7806	-1.86783	-2.67422
Te	-2.19182	-1.92816	-0.72062
Cl	-2.7829	3.50846	0.700279
C	-2.57664	1.242069	-0.81602
Pt	-1.01078	0.300688	0.005221
C	-2.60119	1.846751	-2.17229
H	-5.25241	0.923605	4.38007
H	-6.26804	-1.1155	3.397813
H	-5.65531	-1.82016	1.095661
H	-3.6615	2.28433	3.064029
H	-5.48159	0.031302	-1.86675
H	-4.37445	-1.09225	-3.86675
H	-2.22916	-2.38005	-3.45345

H	-2.42729	1.083696	-2.93722
H	-3.55136	2.354031	-2.36937
H	-1.7948	2.584077	-2.25401
C	0.828851	-0.26928	0.672583
C	2.025551	0.119434	0.163414
H	0.905676	-0.97572	1.511595
C	3.279529	-0.35613	0.698512
H	2.054666	0.814101	-0.67127
C	4.556787	-0.08346	0.325323
H	3.168239	-1.04453	1.538614
C	5.737181	-0.66532	0.990948
C	5.072059	0.785915	-0.74993
C	5.863997	-1.54623	2.06015
C	6.891562	-0.17372	0.349723
C	6.426464	0.710465	-0.70878
C	4.260366	1.599483	-1.70533
C	7.13994	-1.9256	2.47578
H	4.988307	-1.93757	2.571676
C	8.165047	-0.54991	0.761479
Cl	7.530679	1.54549	-1.76341
H	3.596146	0.965129	-2.30348
H	3.63566	2.327587	-1.17547
H	4.907507	2.150284	-2.39331
C	8.279401	-1.43286	1.833502
H	7.249071	-2.61245	3.310386
H	9.048703	-0.1646	0.260679
H	9.264027	-1.74085	2.173623

Table S29. Calculated orientation for intermediate **o** (*E* = -2310.120708 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	3.695173	4.230728	-0.5283
C	4.494957	3.649614	-1.51655
C	4.73675	2.276815	-1.53403
C	4.191912	1.490152	-0.52606
C	3.382778	2.084732	0.464808
C	3.119808	3.449591	0.470925
C	2.922928	1.003496	1.353971
C	4.197241	0.029049	-0.30774
C	4.674121	-0.88517	-1.18484
C	4.362778	-2.29555	-1.26429
C	3.18426	-2.9187	-1.04411
Te	1.212255	-2.37664	-0.60792
Cl	2.3669	1.344592	2.97439
C	3.452453	-0.22248	0.945704
Pt	1.287671	0.117891	0.086057
C	3.672916	-1.37919	1.877178
H	3.517528	5.301556	-0.54186
H	4.933936	4.278046	-2.28563
H	5.348242	1.838424	-2.31725
H	2.489039	3.892228	1.235846
H	5.327097	-0.51637	-1.97604
H	5.160018	-2.92217	-1.6654
H	3.172318	-3.99336	-1.23414
H	3.941348	-2.29027	1.345119

H	4.496668	-1.12338	2.556115
H	2.785915	-1.57785	2.483101
C	0.464805	0.190289	-0.82127
C	1.643626	0.006114	-0.18319
H	0.479393	0.504191	-1.87009
C	2.909439	0.321459	-0.81123
H	1.643533	-0.37569	0.832507
C	4.160369	0.242144	-0.29947
H	2.825854	0.67362	-1.83962
C	5.373216	0.597669	-1.06787
C	4.622749	-0.18035	1.041402
C	5.547267	1.053107	-2.36811
C	6.490763	0.400886	-0.23704
C	5.973419	-0.07562	1.042786
C	3.769193	-0.6354	2.180516
C	6.842253	1.308085	-2.82378
H	4.699415	1.211603	-3.02907
C	7.779994	0.652617	-0.68445
Cl	7.024613	-0.44733	2.372752
H	4.384028	-0.87123	3.053007
H	3.201785	-1.53606	1.919234
H	3.052074	0.138712	2.476332
C	7.94558	1.110502	-1.9922
H	6.991574	1.664538	-3.83877
H	8.636957	0.49744	-0.0356
H	8.944398	1.314616	-2.36664

Table S30. Calculated orientation for intermediate **p** (*E* = -2310.102399 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	4.954734	-4.67395	-0.91332
C	4.151511	-4.5322	-2.04593
C	2.880368	-3.96194	-1.95549
C	2.425832	-3.53701	-0.71411
C	3.241269	-3.68412	0.421608
C	4.505804	-4.2491	0.337598
C	1.161892	-2.89573	-0.29237
C	2.483158	-3.14363	1.546983
C	1.267082	-2.68121	1.169852
C	0.177308	-2.55223	-1.15378
C	-1.0699	-1.88339	-0.85039
C	-1.91754	-1.46352	-1.80484
Te	-3.70542	-0.41015	-1.50506
C	0.245991	-2.05512	2.065463
Pt	-3.37078	0.239946	0.938083
Cl	3.128299	-3.12204	3.156659
H	5.940984	-5.11888	-1.00642
H	4.519453	-4.86886	-3.01059
H	2.2674	-3.85842	-2.84686
H	5.129988	-4.35632	1.219742
H	0.339499	-2.77719	-2.20761
H	-1.32126	-1.69524	0.187306
H	-1.69261	-1.63754	-2.85731
H	0.022988	-1.02372	1.765942

H	-0.69584	-2.6158	2.055529
H	0.605483	-2.02738	3.097259
C	-2.1689	1.724726	0.729451
C	-0.8855	1.653546	0.323739
H	-2.61453	2.684566	1.015061
C	-0.02301	2.817436	0.364658
H	-0.49321	0.712833	-0.04819
C	1.283927	2.918343	0.030689
H	-0.50903	3.729732	0.710262
C	2.04085	4.187969	0.104176
C	2.231932	1.891651	-0.45678
C	1.668325	5.467874	0.490515
C	3.357871	3.93526	-0.31813
C	3.419595	2.512802	-0.64888
C	1.9386	0.444396	-0.67543
C	2.623362	6.486367	0.451158
H	0.655506	5.685514	0.818906
C	4.310602	4.942492	-0.35994
Cl	4.879579	1.766534	-1.21234
H	1.600861	-0.03257	0.25092
H	1.155476	0.30104	-1.42842
H	2.829903	-0.09012	-1.01311
C	3.928309	6.226942	0.031046
H	2.345615	7.492498	0.751129
H	5.325875	4.738493	-0.68701
H	4.655613	7.033135	0.007613

Table S31. Calculated orientation for transition state **tspq** (*E* = -2310.059144 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	-2.75867	5.565728	-1.52815
C	-2.59959	4.379477	-2.24597
C	-1.55807	3.497846	-1.94906
C	-0.68035	3.822444	-0.92302
C	-0.84908	5.018815	-0.2034
C	-1.88117	5.898866	-0.49508
C	0.482233	3.107632	-0.35632
C	0.213552	5.049992	0.798883
C	1.004635	3.951359	0.738042
C	0.887076	1.89198	-0.79767
C	1.926955	1.035023	-0.28324
C	2.043578	-0.23702	-0.74525
Te	4.165557	-1.59168	-1.15914
C	2.182999	3.652786	1.606894
Pt	2.46252	-1.62833	0.726213
Cl	0.385507	6.369545	1.910534
H	-3.57586	6.237014	-1.77469
H	-3.2937	4.137496	-3.04521
H	-1.44848	2.577628	-2.51674
H	-2.0059	6.820239	0.066055
H	0.324506	1.466384	-1.62862
H	2.599096	1.399418	0.485063
H	1.376882	-0.58521	-1.52991
H	2.027976	2.736687	2.188925

H	3.093787	3.522589	1.011335
H	2.360421	4.468147	2.3128
C	0.848239	-2.66641	0.434685
C	-0.34573	-2.05409	0.328073
H	0.971872	-3.75079	0.424289
C	-1.60289	-2.77376	0.331377
H	-0.37336	-0.97324	0.250952
C	-2.84539	-2.25178	0.216975
H	-1.52297	-3.8546	0.439089
C	-4.0735	-3.07896	0.240409
C	-3.2877	-0.84623	0.042546
C	-4.26448	-4.4464	0.374808
C	-5.17863	-2.22367	0.095747
C	-4.63979	-0.86899	-0.02344
C	-2.42249	0.369064	-0.06346
C	-5.56935	-4.94576	0.362365
H	-3.4244	-5.12635	0.486702
C	-6.47598	-2.71204	0.083518
Cl	-5.67113	0.506838	-0.2319
H	-1.83526	0.531841	0.847423
H	-1.72308	0.285845	-0.90304
H	-3.02821	1.263692	-0.22724
C	-6.66094	-4.08959	0.219106
H	-5.73438	-6.01404	0.465625
H	-7.32482	-2.04407	-0.02801
H	-7.66705	-4.49803	0.212516

Table S32. Calculated orientation for transition state **q** (*E* = -2310.067075 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	5.375555	-4.76637	1.913422
C	4.30895	-4.22501	2.630628
C	3.63221	-3.09508	2.16436
C	4.041573	-2.51915	0.970451
C	5.11703	-3.07118	0.254395
C	5.793114	-4.19189	0.711087
C	3.545344	-1.34312	0.21906
C	5.288777	-2.24184	-0.93814
C	4.3927	-1.22846	-0.99101
C	2.505339	-0.5876	0.637847
C	1.92098	0.575021	-0.00278
C	0.81712	1.157881	0.497546
Te	0.23924	4.664101	0.910622
C	4.283473	-0.19928	-2.06916
Pt	-0.06572	2.594707	-0.48964
Cl	6.51867	-2.57619	-2.11141
H	5.887918	-5.64493	2.293882
H	3.999534	-4.68633	3.563638
H	2.80391	-2.68509	2.735536
H	6.623334	-4.61202	0.151271
H	2.025256	-0.881	1.570749
H	2.376081	0.962118	-0.90835
H	0.351683	0.833068	1.425882

H	3.29868	-0.22657	-2.5501
H	4.441186	0.81145	-1.67529
H	5.034301	-0.37219	-2.84416
C	-1.87281	1.858635	-0.3077
C	-2.14427	0.546084	-0.20878
H	-2.66204	2.609858	-0.3613
C	-3.50396	0.043663	-0.23846
H	-1.33441	-0.16683	-0.12115
C	-3.90906	-1.24432	-0.16948
H	-4.27733	0.805453	-0.32761
C	-5.33283	-1.64942	-0.20812
C	-3.11966	-2.49323	-0.04255
C	-6.50307	-0.91168	-0.31823
C	-5.39032	-3.05004	-0.11022
C	-4.00758	-3.51478	-0.01073
C	-1.63153	-2.6165	0.039251
C	-7.72477	-1.58907	-0.32819
H	-6.48402	0.171943	-0.39552
C	-6.59957	-3.7286	-0.11965
Cl	-3.62048	-5.19817	0.130544
H	-1.14356	-2.20942	-0.85384
H	-1.23202	-2.08796	0.912858
H	-1.33677	-3.6653	0.126025
C	-7.77257	-2.97973	-0.23008
H	-8.64844	-1.02452	-0.41323
H	-6.63463	-4.81125	-0.04357
H	-8.73289	-3.48653	-0.23976

Table S33. Calculated orientation for intermediate **r** (*E* = -2310.042144 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	-1.8104	7.016347	-3.26147
C	-1.49097	5.884786	-2.50847
C	-0.6452	6.025213	-1.41613
C	-0.12656	7.290298	-1.08767
C	-0.44018	8.418409	-1.83257
C	-1.29168	8.268369	-2.92767
C	-0.1246	5.046119	-0.43644
C	0.737483	5.806042	0.496848
C	0.71342	7.098182	0.091408
C	-0.43666	3.730195	-0.4694
C	0	2.664602	0.411532
C	-0.43318	1.398524	0.24138
Cl	1.556219	8.417958	0.838911
C	1.490509	5.260058	1.666668
C	-1.49051	-5.26006	1.666668
Cl	-1.55622	-8.41796	0.838911
C	0.433181	-1.39852	0.24138
C	0	-2.6646	0.411532
C	0.436663	-3.7302	-0.4694
C	-0.71342	-7.09818	0.091408
C	-0.73748	-5.80604	0.496848
C	0.124601	-5.04612	-0.43644
C	1.291675	-8.26837	-2.92767

C	0.44018	-8.41841	-1.83257
C	0.126562	-7.2903	-1.08767
C	0.645197	-6.02521	-1.41613
C	1.49097	-5.88479	-2.50847
C	1.810404	-7.01635	-3.26147
H	-2.47129	6.919907	-4.11784
H	-1.90297	4.917564	-2.78323
H	-0.03472	9.391361	-1.57102
H	-1.5531	9.135644	-3.52676
H	-1.10925	3.408754	-1.26467
H	0.685676	2.900559	1.218409
H	-1.08789	1.143269	-0.59357
H	2.219129	4.502898	1.354958
H	2.037295	6.055797	2.17905
H	0.81425	4.798441	2.395506
H	-2.21913	-4.5029	1.354958
H	-2.0373	-6.0558	2.17905
H	-0.81425	-4.79844	2.395506
H	1.087886	-1.14327	-0.59357
H	-0.68568	-2.90056	1.218409
H	1.109246	-3.40875	-1.26467
H	1.553096	-9.13564	-3.52676
H	0.034721	-9.39136	-1.57102
H	1.902973	-4.91756	-2.78323
H	2.471293	-6.91991	-4.11784
Pt	0	0	1.503578

Table S34. Calculated orientation for transition state **tsrs** (*E* = -2310.00932 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	-1.54794	5.672798	-3.10607
C	-1.24579	4.698595	-2.1527
C	0.041669	4.64644	-1.63387
C	1.013562	5.56464	-2.0725
C	0.718735	6.534205	-3.02036
C	-0.57768	6.579903	-3.53494
C	0.669232	3.75479	-0.63748
C	2.072246	4.196141	-0.50259
C	2.238933	5.244128	-1.34651
C	0	2.750547	-0.01444
C	0.478078	1.808222	0.957576
C	-0.34985	0.858767	1.489648
Cl	3.705078	6.141328	-1.58161
C	3.111222	3.609088	0.396911
C	-3.11122	-3.60909	0.396911
Cl	-3.70508	-6.14133	-1.58161
C	0.349845	-0.85877	1.489648
C	-0.47808	-1.80822	0.957576
C	0	-2.75055	-0.01444
C	-2.23893	-5.24413	-1.34651
C	-2.07225	-4.19614	-0.50259
C	-0.66923	-3.75479	-0.63748
C	0.577677	-6.5799	-3.53494

C	-0.71874	-6.53421	-3.02036
C	-1.01356	-5.56464	-2.0725
C	-0.04167	-4.64644	-1.63387
C	1.245789	-4.6986	-2.1527
C	1.547939	-5.6728	-3.10607
H	-2.55115	5.72437	-3.51877
H	-2.01328	3.999543	-1.83119
H	1.475135	7.238601	-3.35376
H	-0.83363	7.329555	-4.27781
H	-1.0507	2.632943	-0.2799
H	1.522571	1.818716	1.245684
H	-1.38873	0.840488	1.156689
H	3.311246	2.560795	0.146254
H	4.053188	4.156451	0.308443
H	2.798271	3.649964	1.446484
H	-3.31125	-2.5608	0.146254
H	-4.05319	-4.15645	0.308443
H	-2.79827	-3.64996	1.446484
H	1.388732	-0.84049	1.156689
H	-1.52257	-1.81872	1.245684
H	1.050698	-2.63294	-0.2799
H	0.833632	-7.32956	-4.27781
H	-1.47514	-7.2386	-3.35376
H	2.013279	-3.99954	-1.83119
H	2.551154	-5.72437	-3.51877
Pt	0	0	3.254082

Table S35. Calculated orientation for intermediate **s** (*E* = -2310.044013 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	-2.1817	7.194768	-0.8237
C	-1.74762	5.870719	-0.89941
C	-0.43752	5.57366	-0.54376
C	0.427031	6.601816	-0.12233
C	0	7.921027	-0.04845
C	-1.31785	8.208506	-0.4034
C	0.314959	4.305248	-0.52017
C	1.675375	4.630597	-0.04977
C	1.707508	5.968232	0.172032
C	-0.22632	3.107489	-0.85589
C	0.407464	1.815232	-0.91174
C	-0.32205	0.658934	-1.23702
Cl	3.071161	6.873409	0.750498
C	2.788685	3.661748	0.184293
C	-2.78869	-3.66175	0.184293
Cl	-3.07116	-6.87341	0.750498
C	0.322052	-0.65893	-1.23702
C	-0.40746	-1.81523	-0.91174
C	0.226317	-3.10749	-0.85589
C	-1.70751	-5.96823	0.172032
C	-1.67538	-4.6306	-0.04977
C	-0.31496	-4.30525	-0.52017
C	1.317847	-8.20851	-0.4034

C	0	-7.92103	-0.04845
C	-0.42703	-6.60182	-0.12233
C	0.437521	-5.57366	-0.54376
C	1.747622	-5.87072	-0.89941
C	2.181699	-7.19477	-0.8237
H	-3.20413	7.439506	-1.09627
H	-2.43071	5.093673	-1.23272
H	0.673382	8.708479	0.277264
H	-1.6757	9.232663	-0.35307
H	-1.28629	3.106962	-1.11132
H	1.489831	1.752363	-0.8926
H	-1.37857	0.740791	-1.49419
H	3.14012	3.216901	-0.75462
H	3.642423	4.157578	0.653574
H	2.468609	2.844956	0.842221
H	-3.14012	-3.2169	-0.75462
H	-3.64242	-4.15758	0.653574
H	-2.46861	-2.84496	0.842221
H	1.37857	-0.74079	-1.49419
H	-1.48983	-1.75236	-0.8926
H	1.286291	-3.10696	-1.11132
H	1.675696	-9.23266	-0.35307
H	-0.67338	-8.70848	0.277264
H	2.430709	-5.09367	-1.23272
H	3.204129	-7.43951	-1.09627
Pt	0	0	0.737413

Table S36. Calculated orientation for intermediate **t** (*E* = -1922.829753 Hartree).

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	4.342079	0.119685	-5.2E-05
C	3.057888	0.549326	-0.00018
C	1.838482	-0.22094	-0.00017
C	0.620781	0.366865	-0.00021
C	-0.62078	-0.36686	-0.0002
C	-1.83848	0.22094	-0.00019
C	-3.05789	-0.54932	-0.00018
C	-4.34208	-0.11968	-0.00007
C	-4.89434	1.252861	0.00008
C	-6.24316	1.134049	0.000111
C	-6.67374	-0.26194	-4E-06
C	-5.50174	-1.03826	-0.00011
C	-7.93086	-0.84739	-1.2E-05
C	-8.00782	-2.24076	-0.00013
C	-6.8501	-3.01901	-0.00024
C	-5.58716	-2.42358	-0.00023
Cl	-7.38288	2.442058	0.000274
C	4.894335	-1.25286	0.000139
C	6.243161	-1.13405	0.000184
C	6.673737	0.261934	0.000038
C	5.50174	1.038264	-0.00011
C	7.930856	0.847385	0.00003
C	8.007818	2.240754	-0.00013

C	6.850103	3.019005	-0.00027
C	5.587163	2.423583	-0.00026
Cl	7.382883	-2.44206	0.000395
C	-4.11688	2.528706	0.000203
C	4.116876	-2.52871	0.000282
H	2.908662	1.629095	-0.00031
H	1.891426	-1.30473	-0.00014
H	0.555093	1.455141	-0.00025
H	-0.55509	-1.45514	-0.00021
H	-1.89143	1.304727	-0.00019
H	-2.90866	-1.62909	-0.00027
H	-8.83088	-0.23975	0.00007
H	-8.98029	-2.72396	-0.00014
H	-6.93084	-4.10192	-0.00034
H	-4.69532	-3.04449	-0.00032
H	8.830879	0.239743	0.00014
H	8.98029	2.723956	-0.00014
H	6.930846	4.101917	-0.00039
H	4.69532	3.044489	-0.00038
H	-4.78836	3.390883	0.000377
H	-3.47660	2.604645	0.886328
H	-3.47673	2.604905	-0.886
H	4.788356	-3.39088	0.000466
H	3.4766	-2.60463	0.886409
H	3.47673	-2.60492	-0.88592

Table S37. Calculated orientation for intermediate **u** (*E* = -4334.072777 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	5.384791	-0.7178	-0.27325
C	2.639536	-0.56839	-1.36587
C	2.465566	0.550185	-1.8588
C	2.550152	1.842539	-2.5373
Te	5.025695	1.127841	0.640677
C	6.993344	1.431307	0.11324
C	7.521776	0.364752	-0.53513
C	6.669073	-0.77562	-0.72709
H	3.544999	1.944369	-2.98266
H	1.794239	1.911421	-3.32504
H	2.396909	2.65771	-1.82298
H	7.517168	2.356987	0.322171
H	8.545838	0.363875	-0.89846
H	7.033954	-1.66764	-1.23075
C	2.833521	-4.1717	-0.42569
C	2.3554	-2.96029	-0.90228
C	3.154743	-1.81076	-0.85201
C	4.461852	-1.86739	-0.3198
C	4.91485	-3.10379	0.158296
C	4.118056	-4.24118	0.106572
H	2.204419	-5.05504	-0.4671
H	1.358175	-2.88934	-1.32459
H	5.908863	-3.15797	0.590834
H	4.500836	-5.18205	0.490367
Pt	0.516383	0.001476	-0.85196
Cl	-0.21413	-0.77437	-2.9589
Cl	1.28299	0.894723	1.215975
P	-1.59937	0.112916	0.051368
C	-1.88812	1.881608	0.394484

C	-1.88363	-0.83145	1.582852
C	-2.97685	-0.52131	-0.9681
C	-1.88875	2.739373	-0.70643
C	-1.8915	2.471537	1.656065
C	-3.08362	-0.67232	2.278604
C	-1.00898	-1.81898	2.035211
C	-2.87569	-1.86166	-1.3469
C	-4.09938	0.177246	-1.40475
C	-1.93146	4.11537	-0.57668
F	-1.84369	2.224549	-1.93494
C	-1.9361	3.851103	1.811146
F	-1.83299	1.746742	2.768585
C	-3.39126	-1.41509	3.403255
F	-3.97136	0.232059	1.86175
C	-1.29894	-2.57818	3.162978
F	0.114583	-2.10548	1.395361
C	-3.81623	-2.4778	-2.15373
F	-1.85594	-2.59591	-0.90213
C	-5.05439	-0.41901	-2.2178
F	-4.31844	1.440373	-1.04801
C	-1.95632	4.673686	0.695362
F	-1.94207	4.896338	-1.65065
F	-1.94845	4.382721	3.028203
C	-2.48658	-2.37296	3.847969
F	-4.53517	-1.22552	4.05075
F	-0.44969	-3.51212	3.573284
C	-4.90954	-1.74536	-2.59749
F	-3.6828	-3.75352	-2.49528
F	-6.11379	0.274488	-2.61986
F	-1.99821	5.988922	0.84088
F	-2.76756	-3.09697	4.919107
F	-5.82238	-2.31788	-3.36661

Table S38. Calculated orientation for transition state **tsuv** (E = -4334.044223 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-4.6512	1.439004	-0.0204
C	-5.43694	2.548777	0.276539
C	-4.8235	3.729038	0.691531
C	-3.43629	3.798581	0.81031
C	-2.64609	2.692201	0.514646
C	-3.25258	1.510172	0.095537
C	-2.56715	0.265396	-0.23506
C	-3.21404	-0.77888	-0.6504
C	-5.18694	0.145083	-0.4845
Te	-6.36361	-1.12623	0.682024
C	-6.66733	-2.00738	-1.14693
C	-6.03029	-1.36864	-2.16812
C	-5.26848	-0.2131	-1.82506
C	-3.16052	-2.17234	-1.09484
Cl	-0.35521	0.400818	-2.42879
Cl	-0.84962	-0.39003	2.234624
H	-6.51766	2.49252	0.184828
H	-5.43276	4.596006	0.928168
H	-2.96715	4.719225	1.143441
H	-1.56728	2.733809	0.62272
H	-7.25989	-2.9079	-1.26435
H	-6.08949	-1.72039	-3.1929
H	-4.78245	0.398749	-2.58049
H	-2.29718	-2.62864	-0.59773
H	-3.03098	-2.25271	-2.17866
H	-4.04825	-2.73635	-0.7921
P	1.780032	-0.04614	-0.00788
Pt	-0.54267	-0.02351	-0.08372

C	2.698165	-1.26027	-1.01898
C	4.086799	-1.18274	-1.13357
C	2.07172	-2.35809	-1.60644
C	4.827179	-2.11958	-1.83113
C	2.79575	-3.31277	-2.31193
C	4.171526	-3.19134	-2.42634
C	2.27635	1.622914	-0.57478
C	2.833253	1.927515	-1.81334
C	1.833397	2.699241	0.194947
C	2.975478	3.239953	-2.24699
C	1.959415	4.013481	-0.21568
C	2.537612	4.284631	-1.44897
C	2.584149	-0.34982	1.610872
C	3.436374	0.496239	2.314776
C	2.276482	-1.57419	2.206611
C	3.922449	0.159981	3.571454
C	2.752958	-1.93441	3.455701
C	3.575662	-1.05419	4.145126
F	3.84139	1.659812	1.809152
F	4.733285	0.9923	4.218314
F	4.045608	-1.38183	5.340459
F	2.437163	-3.10999	3.988154
F	1.525185	-2.45629	1.548423
F	4.740673	-0.16637	-0.56814
F	6.147466	-2.00518	-1.93362
F	4.865055	-4.10091	-3.09432
F	2.17358	-4.34993	-2.86308
F	0.766428	-2.56183	-1.49499
F	3.238125	0.977676	-2.65301
F	3.520751	3.493338	-3.43276
F	2.669214	5.537936	-1.86025
F	1.527346	5.007308	0.554527
F	1.254351	2.469005	1.374893

Table S39. Calculated orientation for intermediate **v** (*E* = -4334.067896 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	3.424113	-4.34649	-0.5657
C	4.812612	-4.15257	-0.58576
C	5.384293	-2.88769	-0.44461
C	4.536376	-1.81031	-0.24657
C	3.134083	-1.99377	-0.2282
C	2.571345	-3.26843	-0.3956
C	2.470835	-0.73442	-0.06923
C	4.823258	-0.3598	-0.13411
C	4.304272	0.422417	-1.32402
C	5.045643	1.664737	-1.60794
C	6.146913	1.930987	-0.89447
Te	6.622983	0.513435	0.580159
C	3.475934	0.321892	0.026523
C	3.175253	1.571134	0.815766
H	3.021285	-5.34715	-0.68128
H	5.462943	-5.01326	-0.71287
H	6.461673	-2.75727	-0.4738
H	1.493144	-3.39237	-0.37941
H	3.885906	-0.11922	-2.16793
H	4.710319	2.315573	-2.41054
H	6.761224	2.81452	-1.0331
H	2.308058	2.081482	0.386036
H	2.942567	1.310254	1.852341
H	4.019652	2.263311	0.811882
Pt	0.54458	-0.44235	-0.00299
Cl	0.566385	-1.19462	2.248537
Cl	0.585516	0.383635	-2.24793
P	1.79865	0.098406	0.001607
C	2.895098	-0.68632	-1.22922

C	2.49155	-1.79986	-1.96366
C	4.21485	-0.26164	-1.38666
C	3.356116	-2.4376	-2.84613
C	5.092036	-0.8789	-2.25967
C	4.653723	-1.97388	-2.99615
C	1.852209	1.904202	-0.28889
C	2.227247	2.527297	-1.47528
C	1.237634	2.704602	0.6747
C	2.033445	3.888293	-1.67692
C	1.032157	4.060795	0.497875
C	1.435492	4.656359	-0.69036
C	2.757981	-0.25397	1.522119
C	3.456324	0.644463	2.323711
C	2.760043	-1.59134	1.921287
C	4.088331	0.238295	3.491773
C	3.387439	-2.02195	3.077995
C	4.049146	-1.09517	3.872144
F	2.16893	-2.50637	1.152935
F	3.366582	-3.30461	3.422981
F	4.658765	-1.48645	4.982012
F	4.744187	1.122082	4.237935
F	3.564931	1.931486	1.999671
F	2.771788	1.847667	-2.48177
F	2.411912	4.452271	-2.81977
F	1.248082	5.955049	-0.87935
F	0.450615	4.787679	1.446605
F	0.823318	2.151935	1.81541
F	1.278737	-2.31988	-1.83058
F	2.946913	-3.49842	-3.53375
F	5.48227	-2.57961	-3.83323
F	6.338782	-0.43943	-2.39699
F	4.660452	0.783381	-0.68756

Table S40. Calculated orientation for transition state **tsvw** (*E* = -4334.049644 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	3.686453	-4.21765	-0.76522
C	5.045423	-3.99187	-1.01369
C	5.55833	-2.69679	-1.04193
C	4.674233	-1.6417	-0.85951
C	3.306143	-1.85705	-0.61317
C	2.808247	-3.15908	-0.5565
C	2.610836	-0.57768	-0.49103
C	4.938493	-0.18662	-0.77867
C	5.986825	0.486807	-1.52648
C	6.651199	1.539426	-0.95451
C	6.428955	1.794331	0.417074
Te	5.17947	0.539331	1.321306
C	3.51046	0.442474	-0.64778
C	3.201523	1.8748	-0.95585
H	3.312524	-5.23683	-0.73954
H	5.706648	-4.83559	-1.18688
H	6.616793	-2.52079	-1.21437
H	1.753549	-3.33114	-0.36516
H	6.23408	0.121418	-2.5193
H	7.356377	2.145164	-1.51509
H	6.852779	2.655584	0.92387
H	2.296769	2.184563	-0.42564
H	4.011228	2.563827	-0.69202
H	3.017786	1.980224	-2.03235
Pt	0.647625	-0.36211	-0.22529
Cl	1.119538	-0.15713	2.102964
Cl	0.314315	-0.50897	-2.58588
P	1.680225	0.052408	-0.01503

C	2.894238	-1.18294	-0.60277
C	2.513704	-2.48768	-0.9109
C	4.256896	-0.88791	-0.655
C	3.448386	-3.44513	-1.29023
C	5.20427	-1.82284	-1.03049
C	4.791707	-3.11072	-1.35309
C	1.963632	1.581148	-0.98636
C	2.582135	1.651335	-2.23074
C	1.282694	2.722591	-0.56186
C	2.557042	2.810899	-2.99634
C	1.240292	3.887717	-1.30538
C	1.885488	3.93109	-2.5343
C	2.359182	0.337727	1.666251
C	2.993581	1.474814	2.157346
C	2.176535	-0.71785	2.560962
C	3.384902	1.575636	3.48613
C	2.563085	-0.64421	3.88875
C	3.16451	0.516793	4.354248
F	1.642653	-1.86028	2.130401
F	2.371063	-1.67221	4.709071
F	3.544706	0.606807	5.621805
F	3.985911	2.679031	3.9242
F	3.270962	2.515238	1.37257
F	3.213781	0.605526	-2.75986
F	3.168511	2.842723	-4.17702
F	1.857732	5.040257	-3.26155
F	0.585127	4.954808	-0.85558
F	0.636854	2.706608	0.605777
F	1.251639	-2.8844	-0.82725
F	3.059054	-4.68298	-1.57852
F	5.686906	-4.02008	-1.71083
F	6.494049	-1.50308	-1.08312
F	4.680711	0.339956	-0.34874

Table S41. Calculated orientation for intermediate **w** (*E* = -4334.08287 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	-3.41162	4.667258	0.188264
C	-4.80551	4.586855	-0.01879
C	-5.45063	3.381452	-0.24523
C	-4.67948	2.216863	-0.27771
C	-3.27655	2.290015	-0.07031
C	-2.63911	3.52761	0.165016
C	-2.68976	1.004139	-0.16686
C	-5.05479	0.828575	-0.46128
C	-6.30265	0.321155	-0.57331
C	-6.61216	-1.0889	-0.46651
C	-5.8351	-1.97836	0.187243
Te	-3.99268	-1.51793	1.063315
C	-3.7681	0.024471	-0.47585
C	-3.50644	-0.66204	-1.83052
H	-2.9548	5.635276	0.364644
H	-5.3898	5.502432	0.000498
H	-6.52483	3.350461	-0.39738
H	-1.56544	3.561838	0.319527
H	-7.14234	1.006443	-0.66965
H	-7.57607	-1.42031	-0.8469
H	-6.17006	-3.00616	0.303258
H	-2.56211	-1.21083	-1.80955
H	-4.3197	-1.35444	-2.06385
H	-3.44978	0.094439	-2.62034
Pt	-0.77503	0.602813	-0.03397
Cl	-1.09812	0.048237	2.253482
Cl	-0.46903	1.191845	-2.3273
P	1.534083	-0.04678	-0.05305
C	2.812929	1.16524	-0.52815

C	2.546497	2.532924	-0.55385
C	4.128462	0.766065	-0.76605
C	3.540792	3.459355	-0.84642
C	5.13369	1.669235	-1.06069
C	4.83213	3.025979	-1.10372
C	1.577442	-1.41035	-1.27252
C	2.089365	-1.32776	-2.56393
C	0.814067	-2.53867	-0.96902
C	1.88063	-2.3363	-3.49659
C	0.591304	-3.55546	-1.87976
C	1.130861	-3.45077	-3.15547
C	2.271813	-0.66333	1.505972
C	2.833173	-1.91259	1.75376
C	2.2448	0.240541	2.569016
C	3.30304	-2.2619	3.01315
C	2.712576	-0.08155	3.831712
C	3.238104	-1.34721	4.054118
F	1.783673	1.474858	2.368019
F	2.669915	0.807436	4.817665
F	3.694686	-1.6749	5.254373
F	3.830331	-3.46495	3.219088
F	2.960471	-2.8243	0.791706
F	2.785778	-0.27067	-2.97452
F	2.391203	-2.22836	-4.71919
F	0.928892	-4.41449	-4.04289
F	-0.13467	-4.6174	-1.54575
F	0.267663	-2.65294	0.242128
F	1.343961	3.013549	-0.26706
F	3.260428	4.758074	-0.86422
F	5.784053	3.904317	-1.37993
F	6.373814	1.254371	-1.29767
F	4.443992	-0.52919	-0.72246

Table S42. Calculated orientation for transition state **tswx** (*E* = -4334.050852 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
Cl	1.246508	-0.51027	2.05761
Cl	0.312074	-0.68777	-2.60879
C	4.673607	-2.32243	-0.07112
C	5.410869	-3.4993	0.042695
C	4.758957	-4.71029	-0.1679
C	3.399018	-4.75271	-0.49623
C	2.662196	-3.57936	-0.62409
C	3.310731	-2.36861	-0.4073
C	2.75587	-0.99299	-0.47817
C	3.84723	-0.13312	-0.20368
C	5.070599	-0.91841	0.079118
Te	3.715274	1.832806	0.486301
C	5.777664	2.012212	0.503632
C	6.647013	0.982292	0.437733
C	6.301288	-0.414	0.334479
C	3.466395	-0.22098	-2.01888
H	6.46605	-3.47986	0.300405
H	5.313384	-5.63909	-0.07126
H	2.915034	-5.7121	-0.65092
H	1.606695	-3.60082	-0.87775
H	6.145039	3.026906	0.631455
H	7.707965	1.210992	0.508764
H	7.112927	-1.12287	0.482145
H	4.526611	-0.17706	-2.27384
H	2.942805	0.706308	-2.23151
H	3.018716	-1.043	-2.581
Pt	0.782533	-0.58494	-0.26608
P	1.478595	0.038413	-0.01516

C	1.590811	1.632549	-0.90994
C	2.792994	-1.05278	-0.65907
C	2.120982	0.30454	1.679987
C	0.803908	2.677109	-0.42287
C	2.185076	1.824401	-2.15363
C	4.116052	-0.6158	-0.72876
C	2.542715	-2.38352	-0.98965
C	2.044494	-0.80565	2.522394
C	2.651644	1.471742	2.221586
C	0.633254	3.865874	-1.10817
F	0.17897	2.538341	0.748335
C	2.032206	3.011122	-2.86042
F	2.911754	0.874772	-2.73678
C	5.145658	-1.43636	-1.15206
F	4.416167	0.639282	-0.38983
C	3.56205	-3.22756	-1.41544
F	1.332211	-2.91336	-0.87991
C	2.431788	-0.75963	3.850995
F	1.614053	-1.96902	2.036759
C	3.041229	1.544809	3.552573
F	2.824988	2.568328	1.485631
C	1.255495	4.033288	-2.33864
F	0.122768	4.835922	-0.60211
F	2.621777	3.162087	-4.04219
C	4.861215	-2.75174	-1.501
F	6.392841	-0.98233	-1.22284
F	3.297102	-4.49201	-1.72595
C	2.925941	0.429625	4.369447
F	2.342211	-1.83821	4.62088
F	3.54046	2.676512	4.04107
F	1.104891	5.166011	-3.01071
F	5.836131	-3.55248	-1.90425
F	3.305612	0.494438	5.637639

Table S43. Calculated orientation for intermediate **x** (*E* = -4334.100238 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
Cl	1.544982	-0.03288	1.73191
Cl	-0.03322	-0.22376	-2.77592
C	3.64472	-2.48339	-0.2149
C	3.733841	-3.83765	0.10004
C	3.108313	-4.75564	-0.7355
C	2.406256	-4.32332	-1.86689
C	2.300762	-2.97112	-2.17407
C	2.915891	-2.04514	-1.33311
C	2.910499	-0.5505	-1.38969
C	3.797496	-0.17257	-0.31813
C	4.226753	-1.30685	0.438284
Te	4.494588	1.70011	0.044189
C	5.571052	1.122701	1.67049
C	5.656073	-0.15591	2.131132
C	5.046939	-1.29268	1.54346
C	3.111357	0.149815	-2.72819
H	4.283468	-4.17635	0.974122
H	3.166557	-5.81645	-0.51094
H	1.926816	-5.05572	-2.51003
H	1.724254	-2.63864	-3.03136
H	6.100599	1.923692	2.17804
H	6.263789	-0.32901	3.015663
H	5.268176	-2.25	2.008822
H	4.155705	0.03776	-3.05053
H	2.875328	1.218374	-2.67203
H	2.467108	-0.27458	-3.49704
Pt	0.865423	-0.19775	-0.54654
P	-1.33827	0.133812	0.032986
C	-1.83875	1.716651	-0.73986

C	-2.55096	-1.13923	-0.47177
C	-1.77413	0.22349	1.813458
C	-1.15261	2.857302	-0.32138
C	-2.67274	1.858288	-1.84574
C	-3.91754	-0.90921	-0.30646
C	-2.16873	-2.40864	-0.90495
C	-1.46961	-0.91551	2.561877
C	-2.36283	1.284054	2.496129
C	-1.30481	4.0872	-0.93549
F	-0.31498	2.777988	0.712639
C	-2.84269	3.082985	-2.47909
F	-3.33423	0.827353	-2.36347
C	-4.87358	-1.86315	-0.60354
F	-4.34004	0.274434	0.143796
C	-3.11318	-3.38319	-1.20895
F	-0.89722	-2.76091	-1.01202
C	-1.69481	-0.99213	3.925532
F	-0.96569	-1.98837	1.954824
C	-2.59326	1.232941	3.864971
F	-2.7538	2.392422	1.869481
C	-2.15862	4.199221	-2.02479
F	-0.63974	5.150981	-0.49424
F	-3.65341	3.1825	-3.52823
C	-4.46369	-3.10933	-1.06236
F	-6.16771	-1.6003	-0.44936
F	-2.72186	-4.58414	-1.62227
C	-2.25329	0.096094	4.58194
F	-1.38606	-2.09351	4.601826
F	-3.15551	2.266373	4.485466
F	-2.31763	5.369422	-2.62712
F	-5.36516	-4.0376	-1.34678
F	-2.47853	0.041369	5.887227

Table S44. Calculated orientation for intermediate **y** (*E* = -769.2235746 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
C	1.951373	0.729473	-0.00003
C	3.060581	1.566782	-5.7E-05
C	4.331732	0.993814	-1.9E-05
C	4.485718	-0.39583	0.000033
C	3.37655	-1.24018	0.00005
C	2.104418	-0.67199	0.000016
C	0.778432	-1.29825	-6E-06
C	-0.1464	-0.30382	-0.00001
C	0.510205	1.014565	-1.2E-05
Te	-2.22693	-0.46066	-4E-06
C	-2.48455	1.59777	0.00002
C	-1.49377	2.509106	0.000035
C	-0.07352	2.235429	0.000019
C	0.568371	-2.7768	-1.4E-05
H	2.947239	2.6479	-9.5E-05
H	5.210289	1.632331	-3.1E-05
H	5.484723	-0.82297	0.000064
H	3.506082	-2.31927	0.00009
H	-3.52296	1.916879	0.000031
H	-1.77915	3.559121	0.000065
H	0.580399	3.104698	0.000023
H	1.026851	-3.24076	-0.88259
H	-0.49376	-3.04366	-0.00055
H	1.025969	-3.24067	0.883068

Table S45. Calculated orientation for catalyst **Pt[P(C$_6$F$_5$)$_3$]Cl$_2$** (*E* = -3564.863562 Hartree).

Atomic	Coordinates (Angstroms)		
Name	X	Y	Z
Cl	1.426024	1.90765	2.343108
Cl	-0.43324	-2.33424	2.684219
P	0.040294	0.008675	0.154791
C	1.682913	0.113171	-0.61659
C	-0.963	1.438476	-0.35045
C	-0.90773	-1.35015	-0.60367
C	2.511115	-1.00792	-0.51773
C	2.250857	1.284031	-1.11798
C	-1.07909	1.711278	-1.71601
C	-1.72766	2.209971	0.525579
C	-2.18191	-1.58225	-0.07619
C	-0.51059	-2.14303	-1.68003
C	3.827766	-0.99199	-0.94015
F	2.030276	-2.13626	-0.00225
C	3.570303	1.321065	-1.54719
F	1.560371	2.416027	-1.19337
C	-1.86908	2.735441	-2.20145
F	-0.39845	0.970579	-2.5927
C	-2.52991	3.24412	0.056316
F	-1.75241	1.9797	1.827917
C	-3.00589	-2.58781	-0.54995
F	-2.6434	-0.80441	0.899294
C	-1.32168	-3.15786	-2.16897
F	0.647674	-1.94981	-2.30235
C	4.358821	0.183143	-1.4582
F	4.579657	-2.0806	-0.84792
F	4.079607	2.445582	-2.03356
C	-2.59641	3.50908	-1.30296

F	-1.9406	2.978007	-3.50384
F	-3.24473	3.9673	0.907372
C	-2.56656	-3.38453	-1.59976
F	-4.20573	-2.78256	-0.02082
F	-0.91489	-3.89849	-3.1923
F	5.615328	0.21581	-1.86697
F	-3.36141	4.48988	-1.74937
F	-3.34292	-4.34529	-2.07025
Pt	0.390887	-0.19657	2.295843

6. ^{1}H and ^{13}C NMR spectra.

Figure S9. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

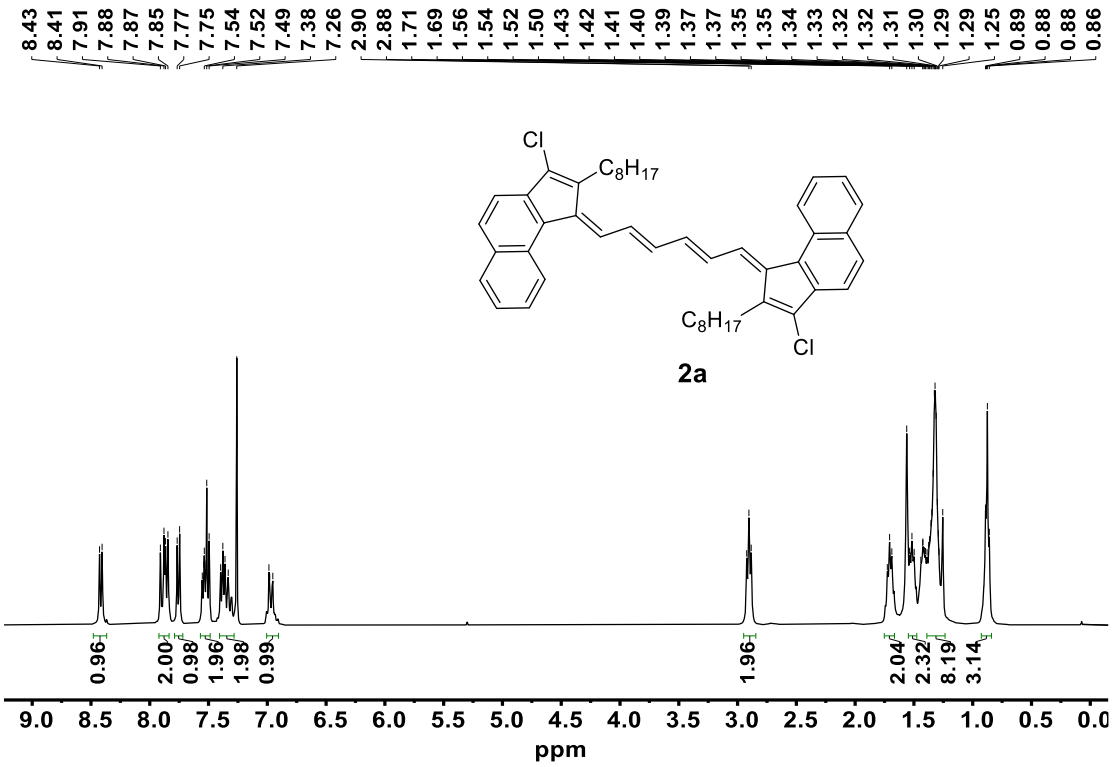


Figure S10. ^{13}C NMR spectrum of **2a** in $CDCl_3$.

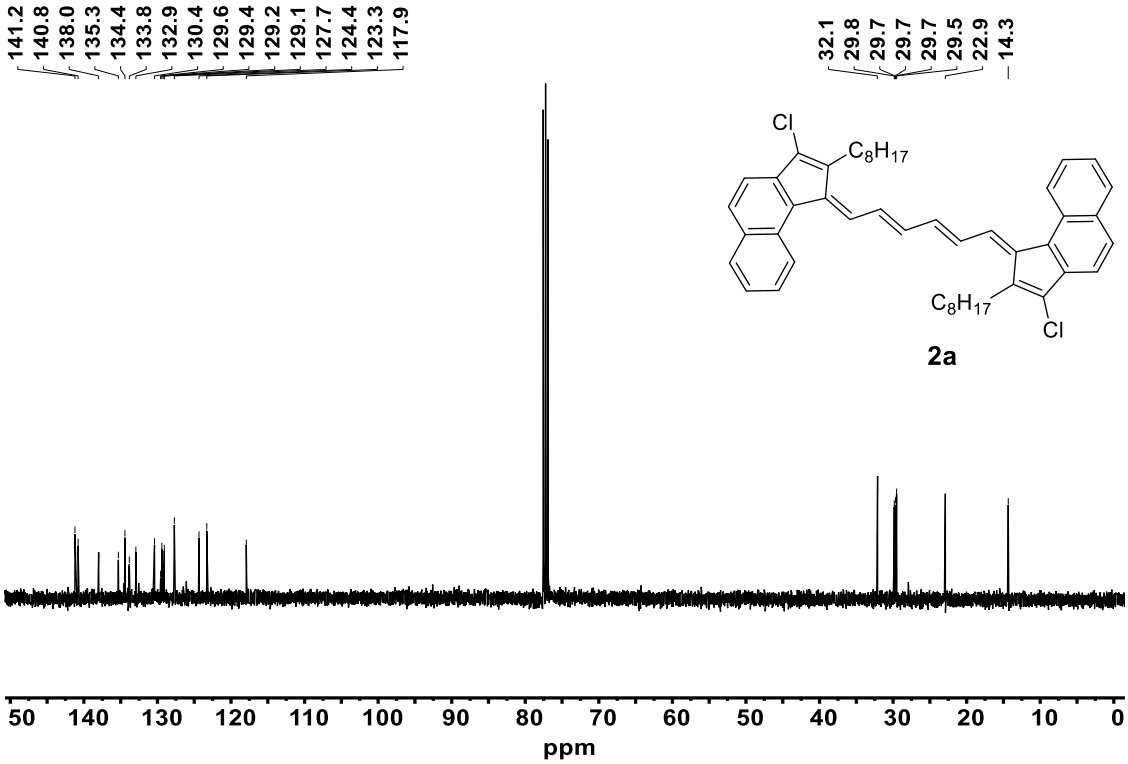


Figure S11. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

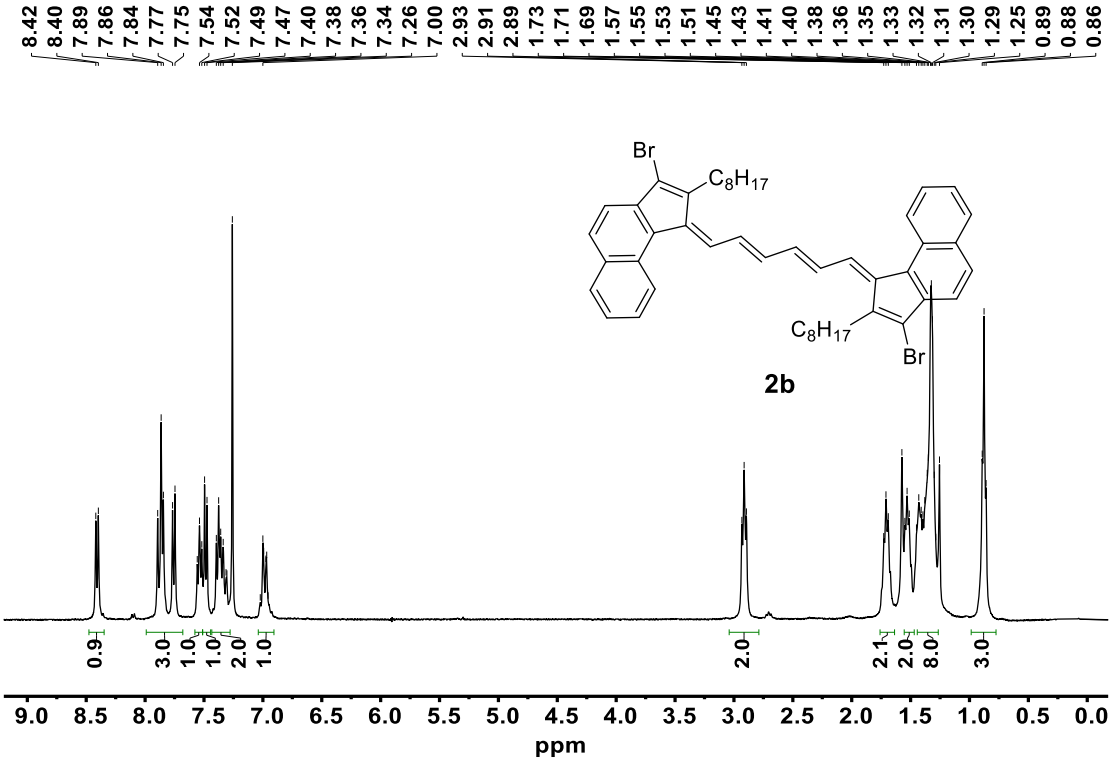


Figure S12. ^{13}C NMR spectrum of **2b** in $CDCl_3$.

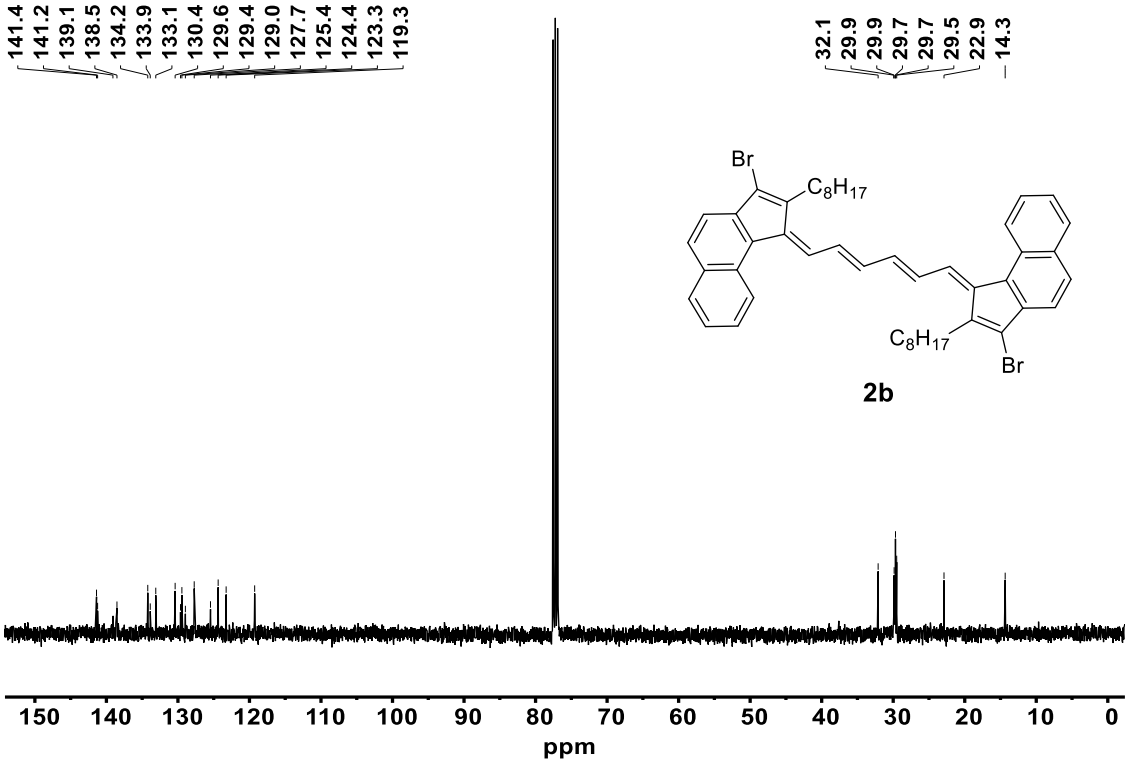


Figure S13. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

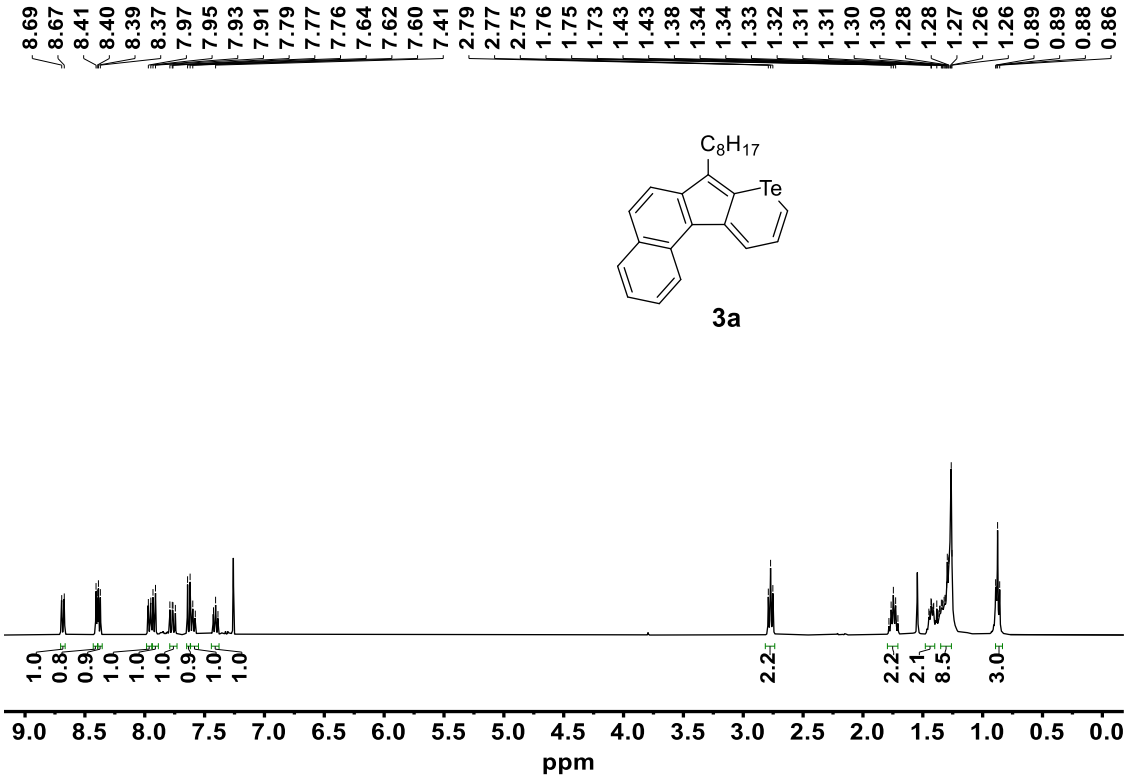


Figure S14. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

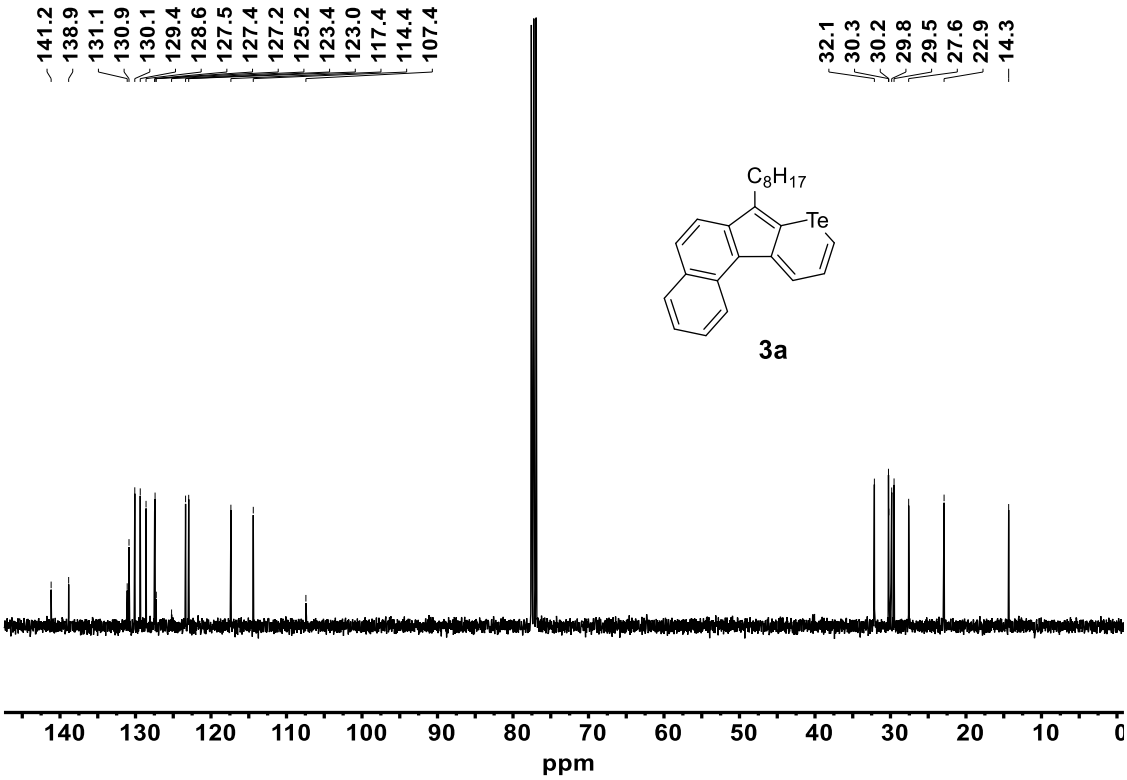


Figure S15. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

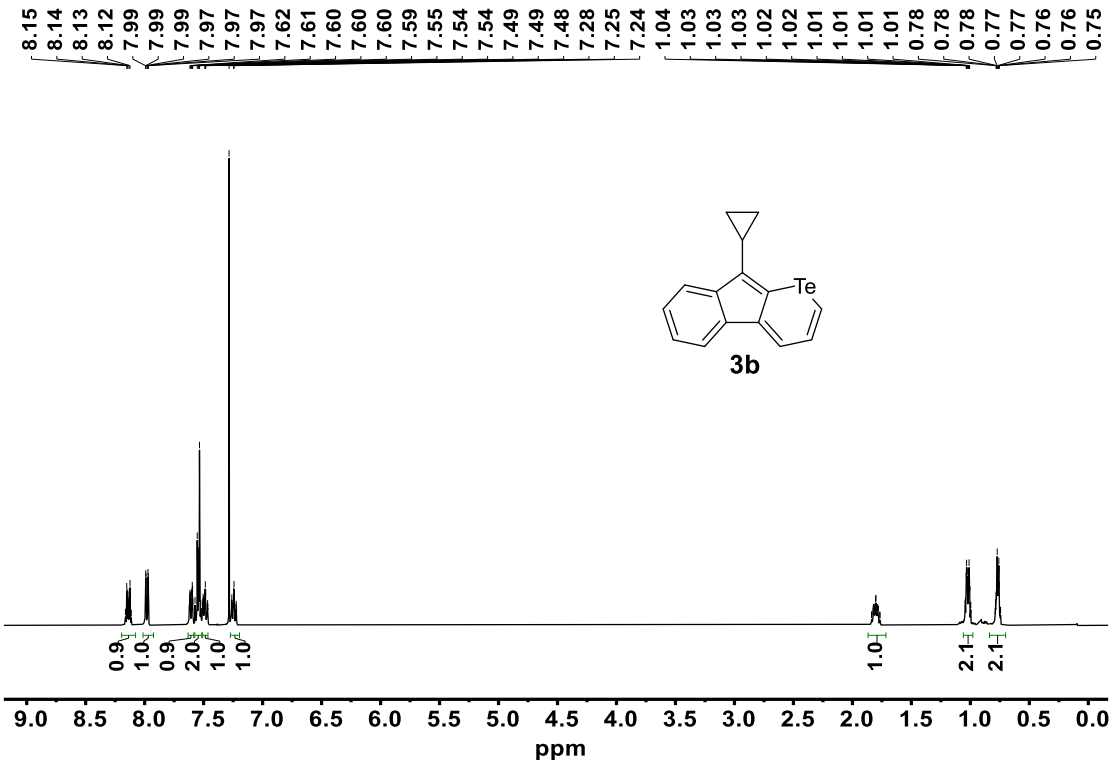


Figure S16. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

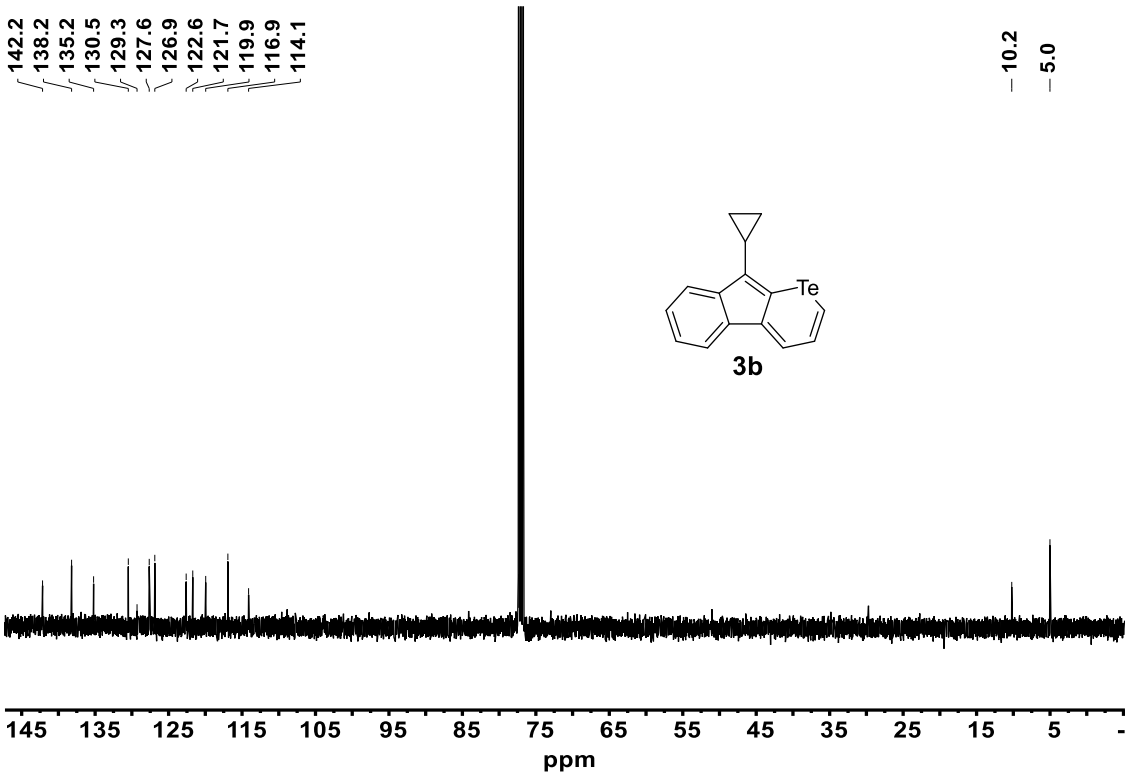


Figure S17. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

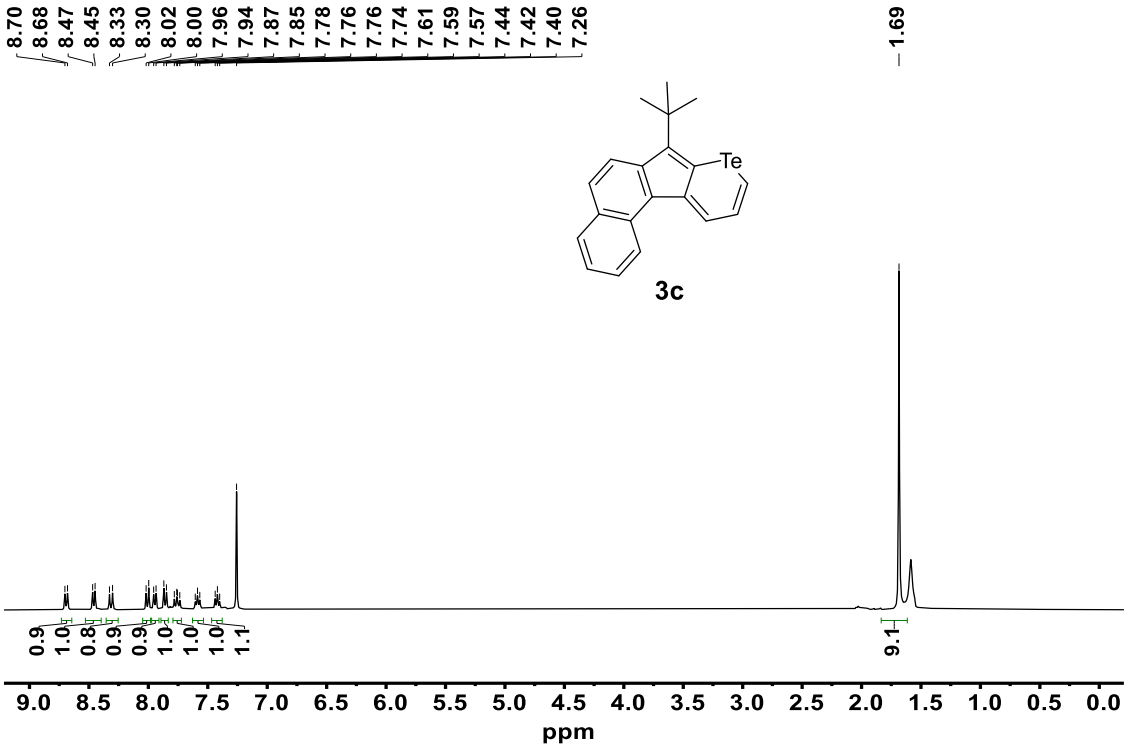


Figure S18. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

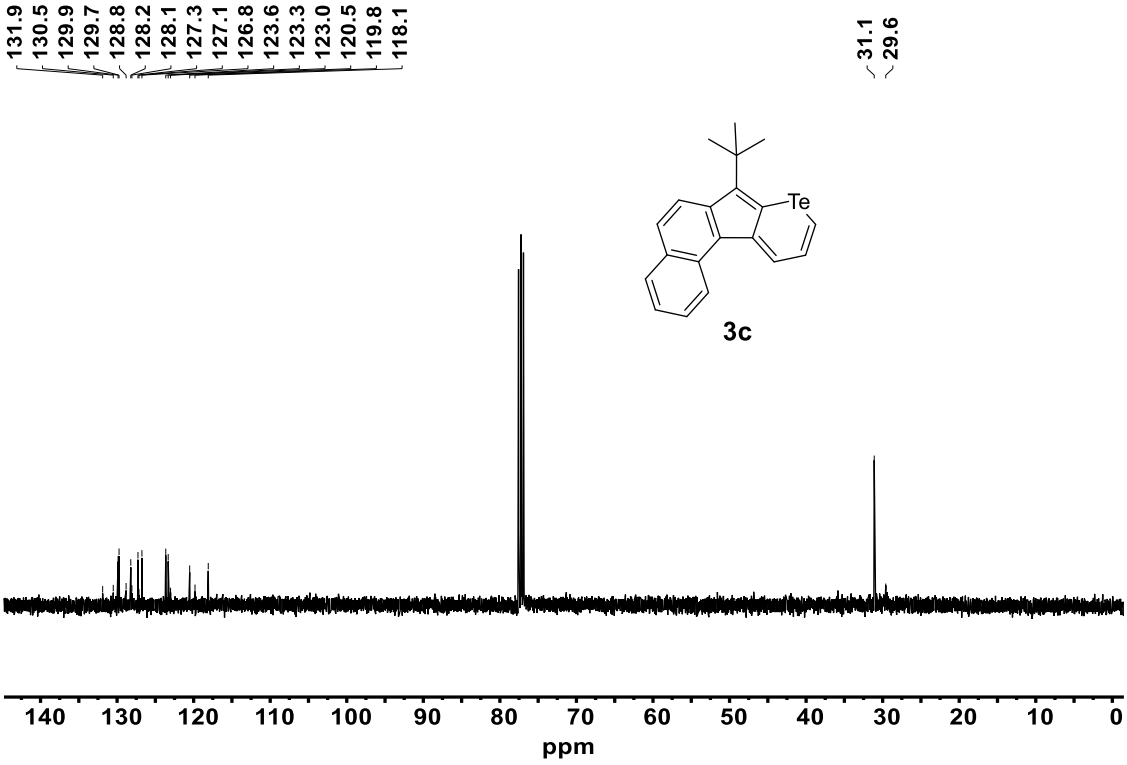


Figure S19. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

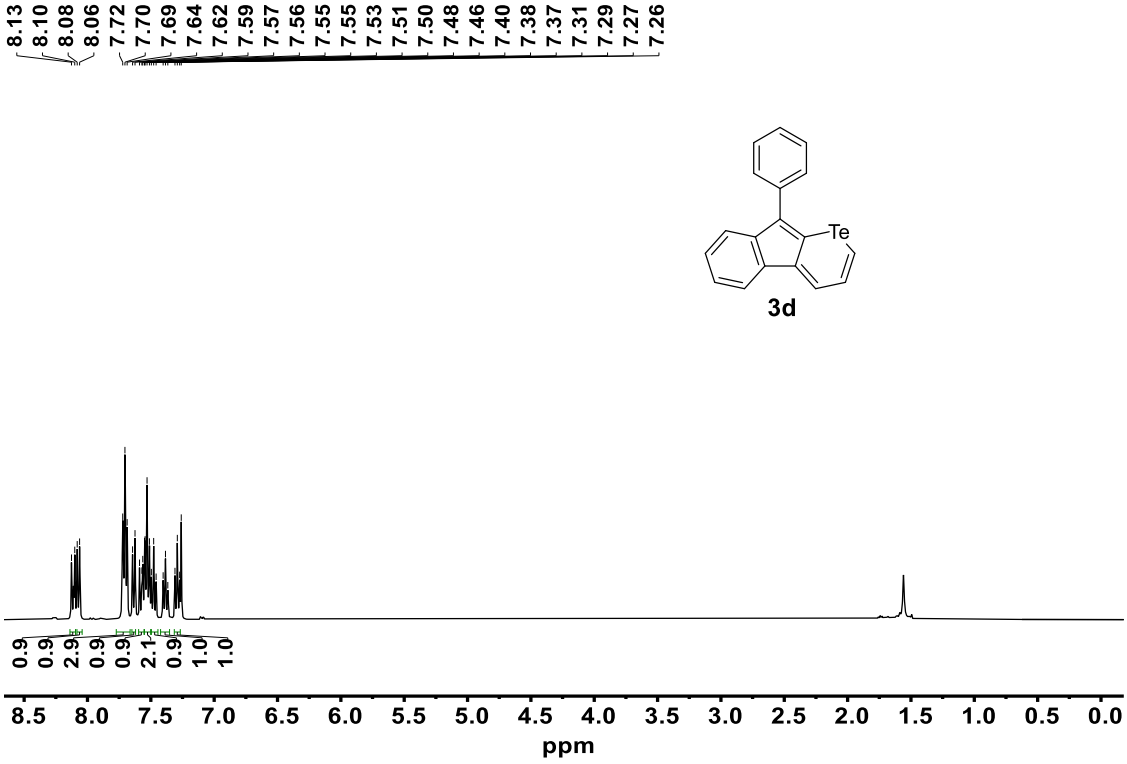


Figure S20. ^{13}C NMR spectrum of **3d** in $CDCl_3$.

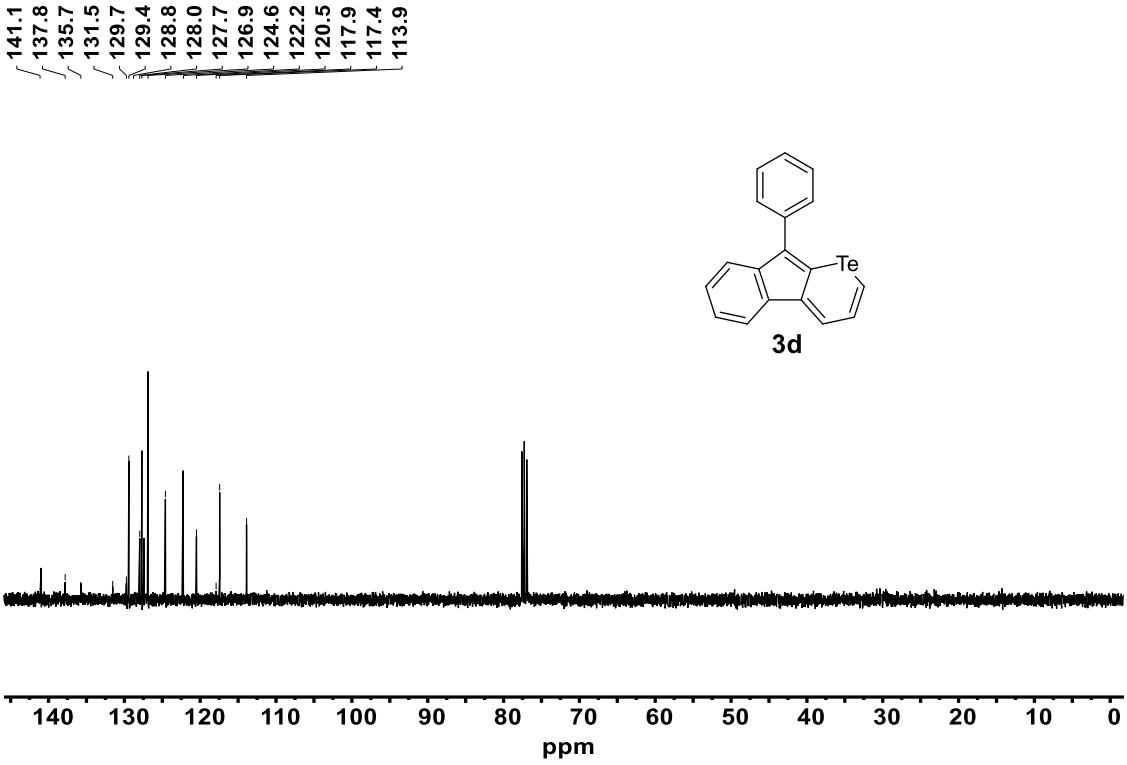


Figure S21. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

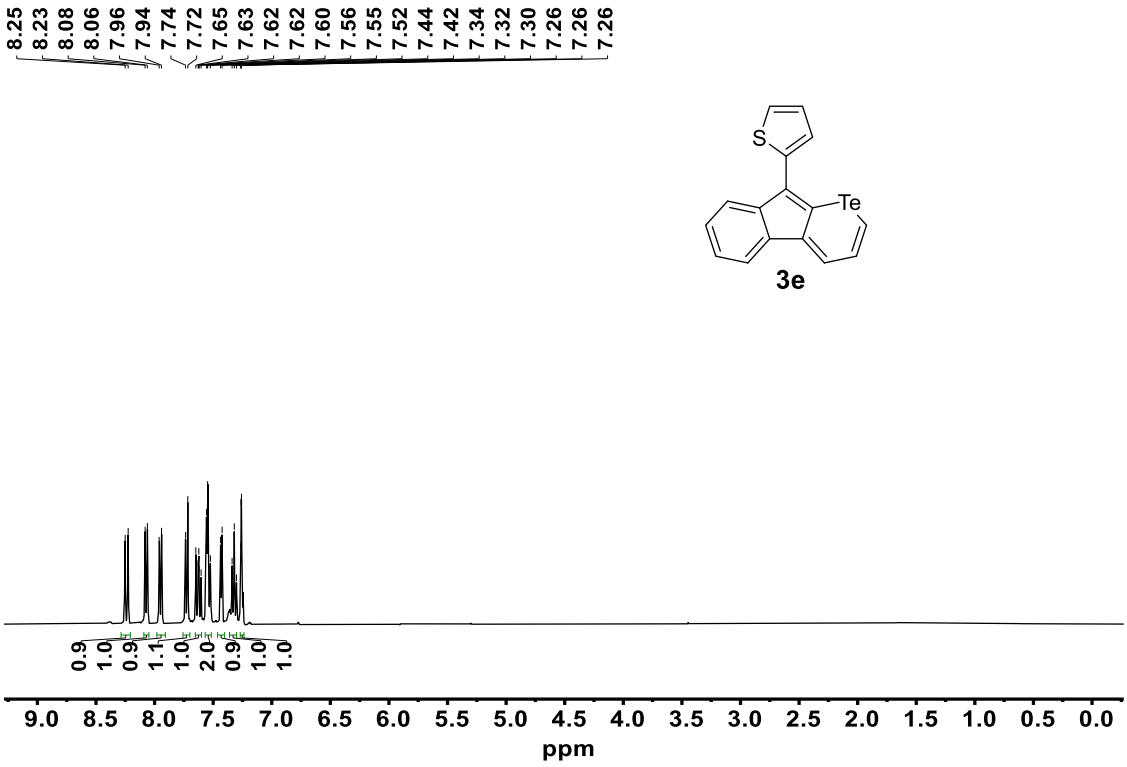


Figure S22. ^{13}C NMR spectrum of **3e** in $CDCl_3$.

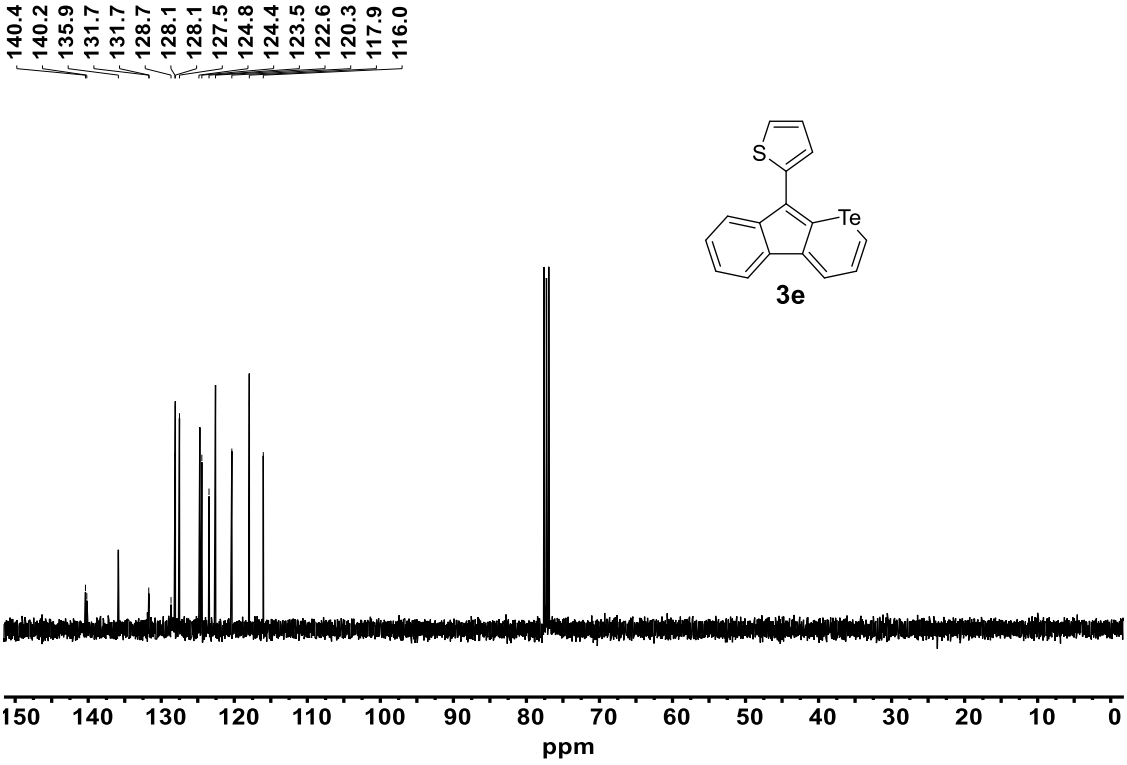


Figure S23. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

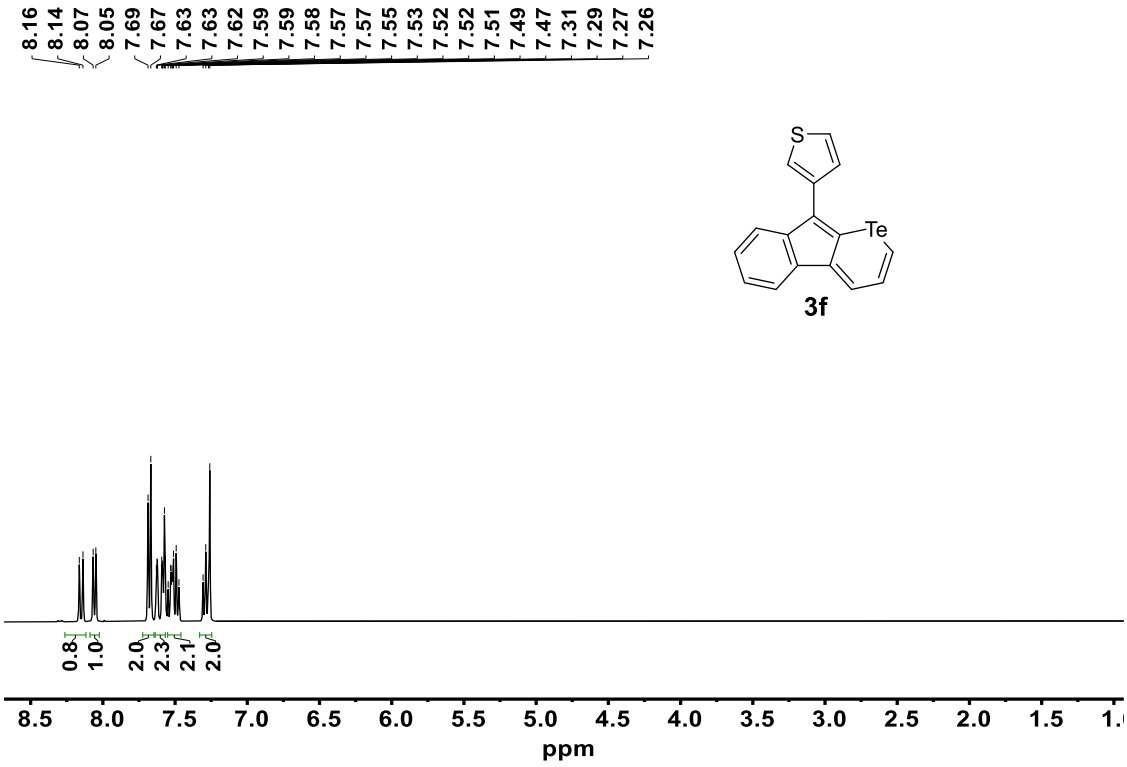


Figure S24. ^{13}C NMR spectrum of **3f** in $CDCl_3$.

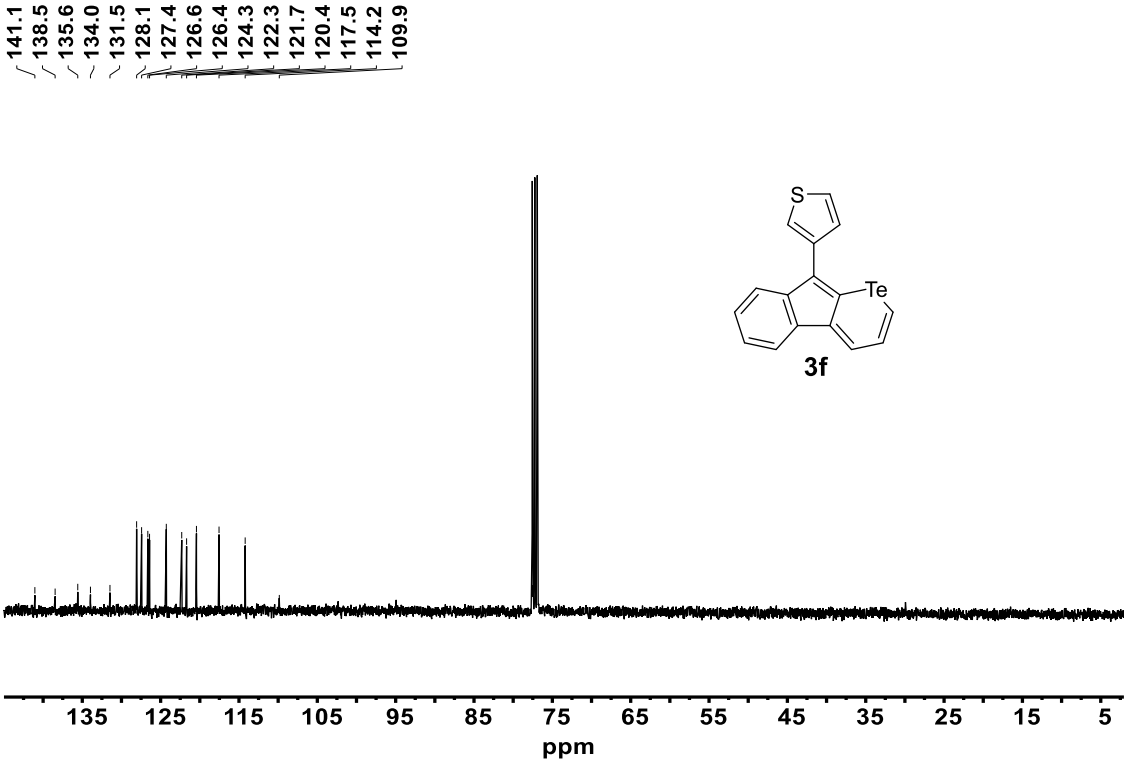


Figure S25 ^{1}H NMR spectrum of **3g** in $CDCl_3$.

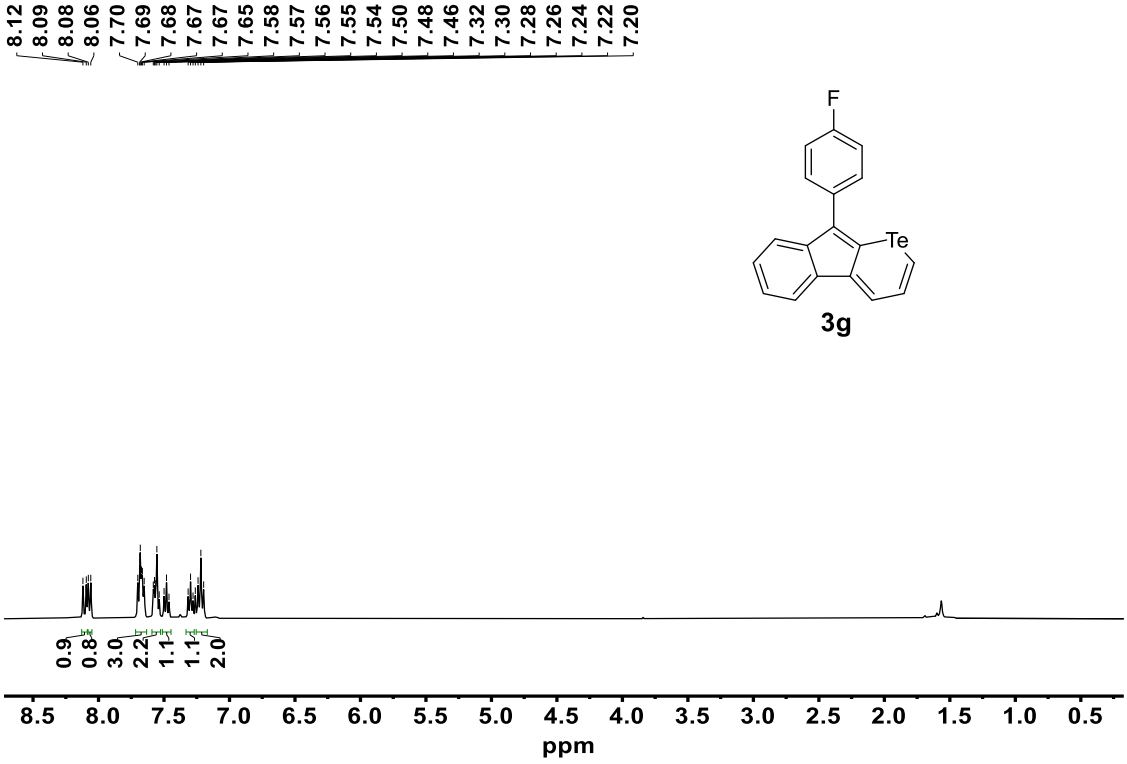


Figure S26. ^{13}C NMR spectrum of **3g** in $CDCl_3$.

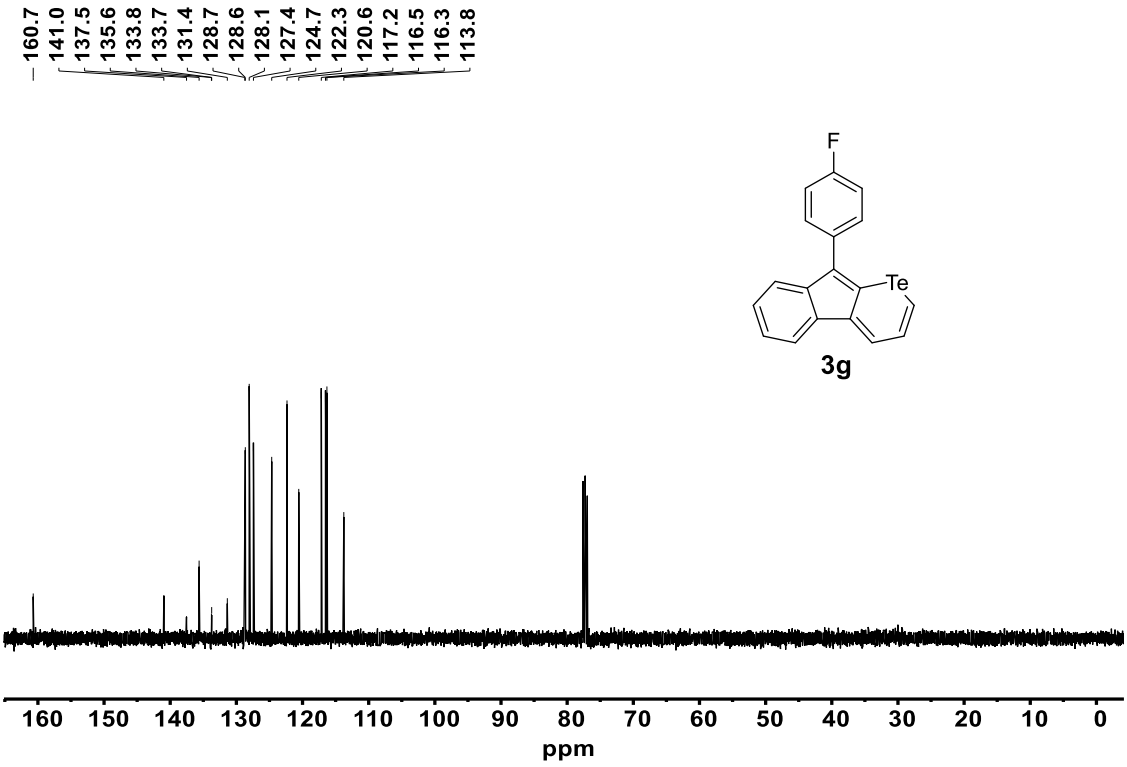


Figure S27. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

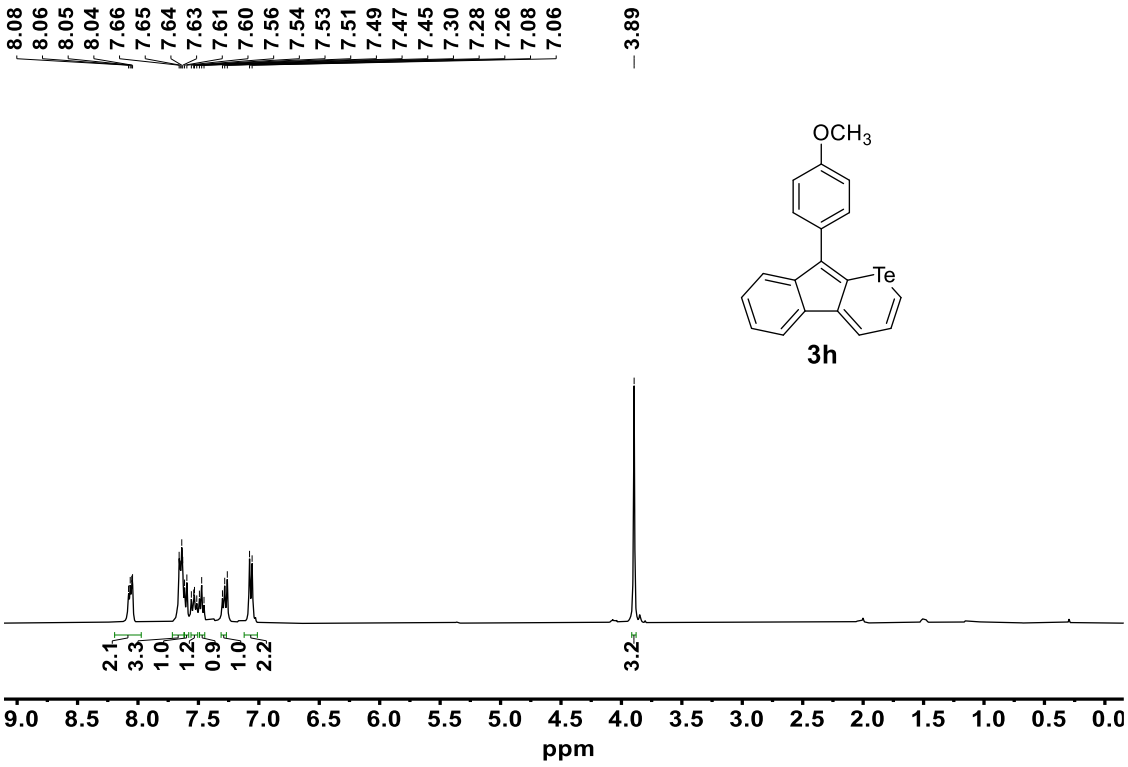


Figure S28. ^{13}C NMR spectrum of **3h** in $CDCl_3$.

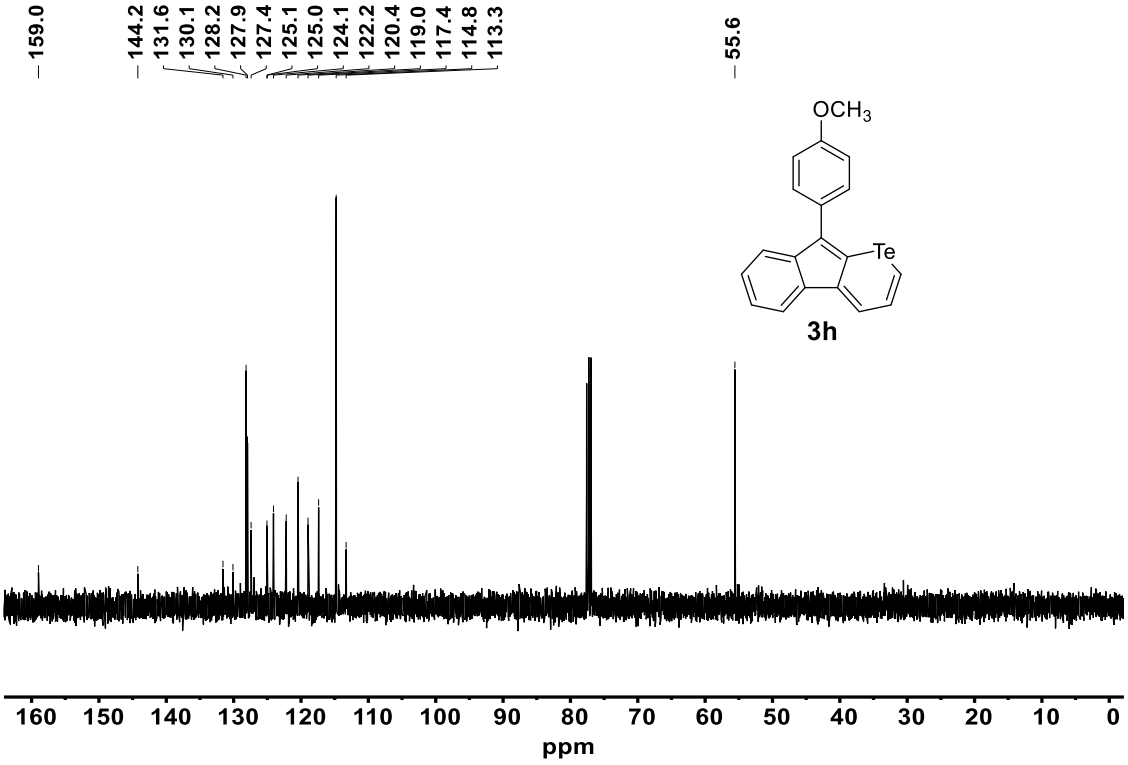


Figure S29. ^{1}H NMR spectrum of **3i** in $CDCl_3$

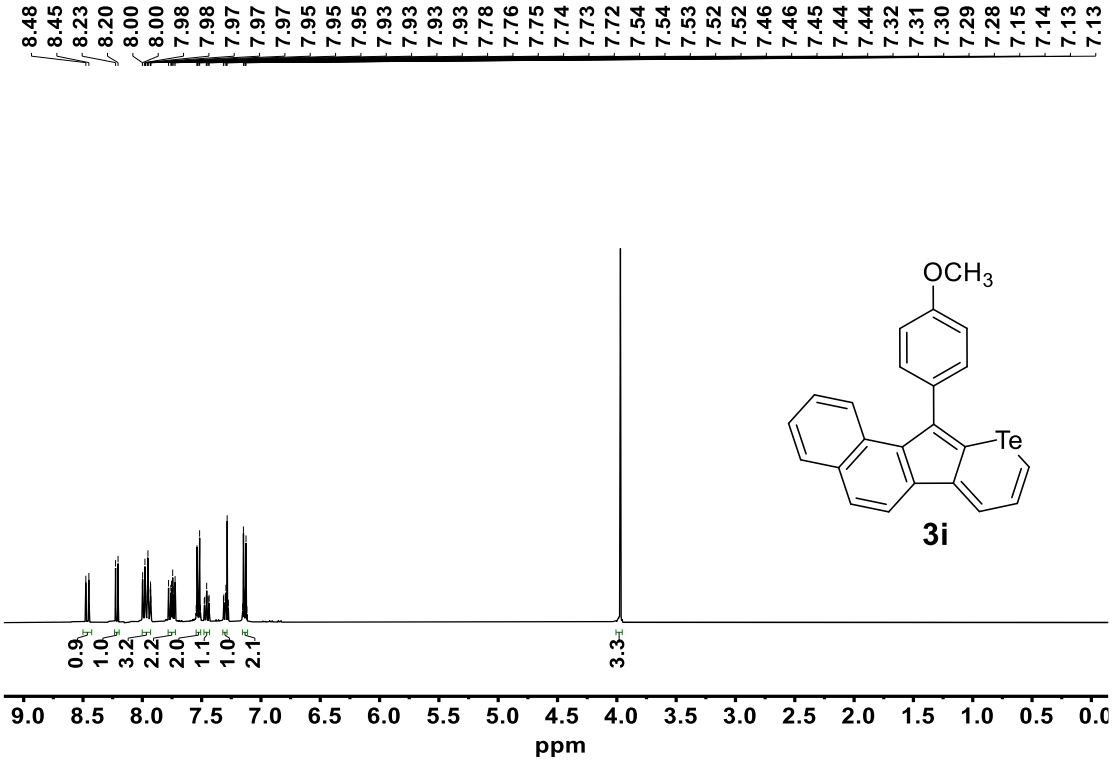


Figure S30. ^{13}C NMR spectrum of **3i** in $CDCl_3$.

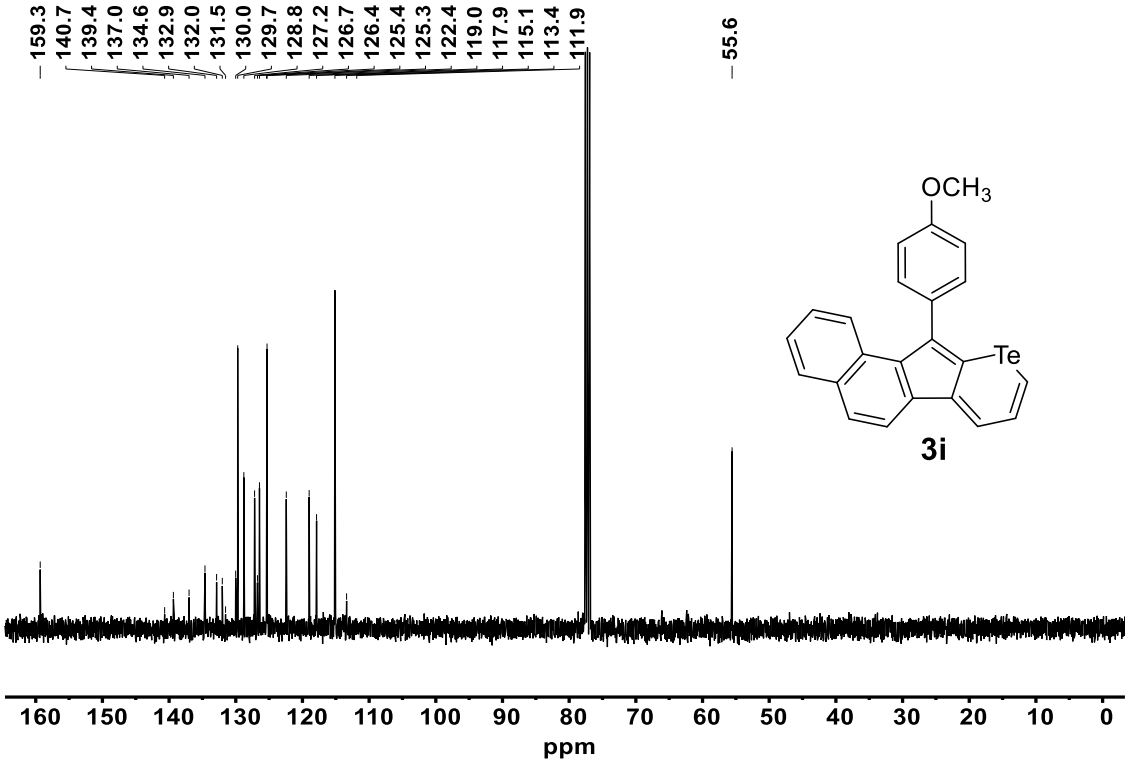


Figure S31. ^{1}H NMR spectrum of **3j** in $CDCl_3$.

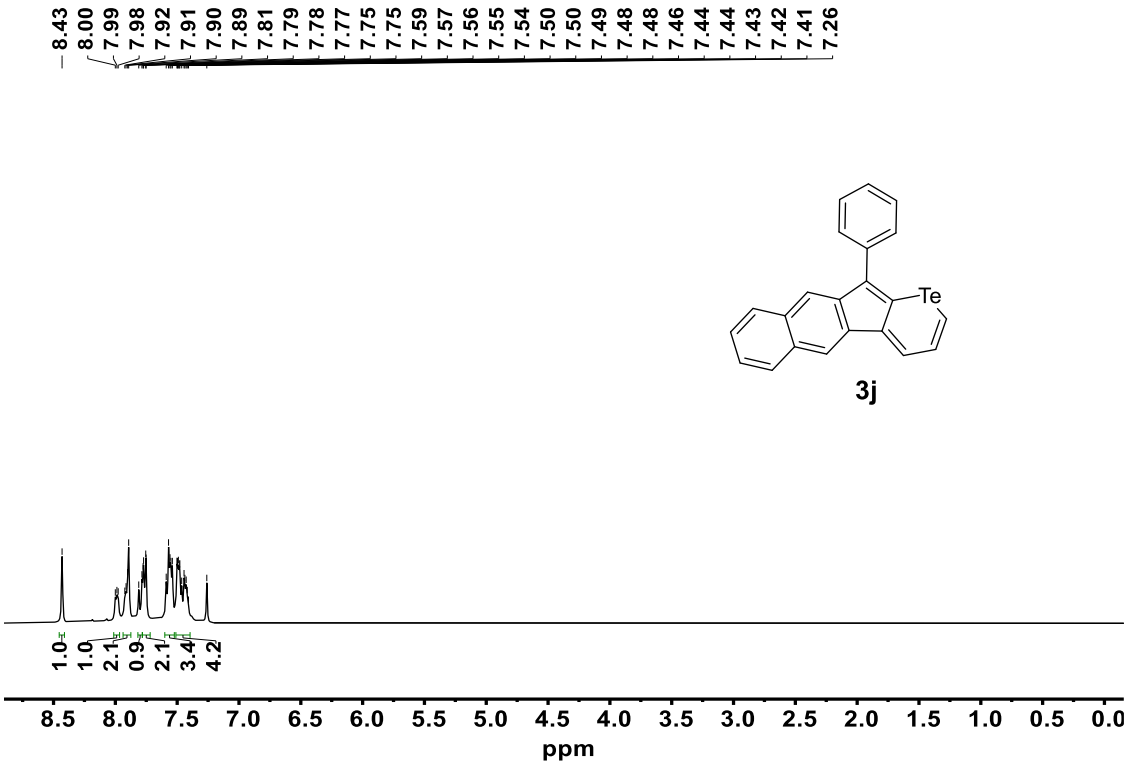


Figure S32. ^{13}C NMR spectrum of **3j** in $CDCl_3$.

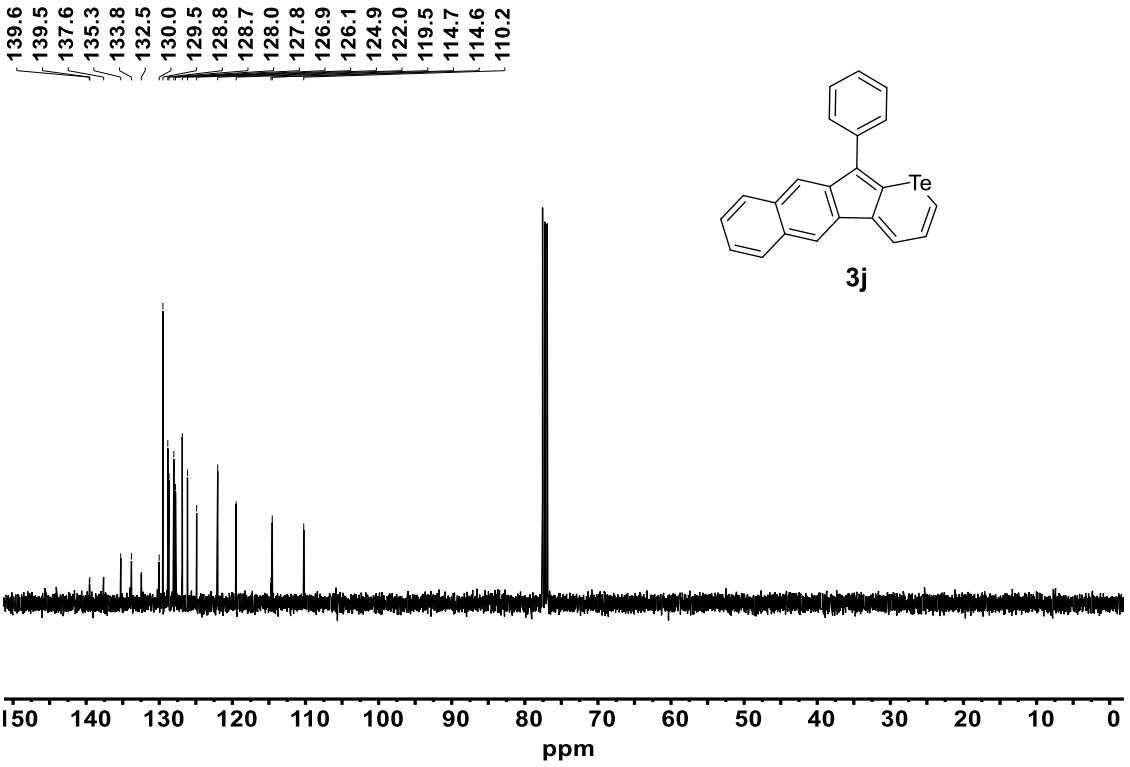


Figure S33. ^{1}H NMR spectrum of **3k** in $CDCl_3$.

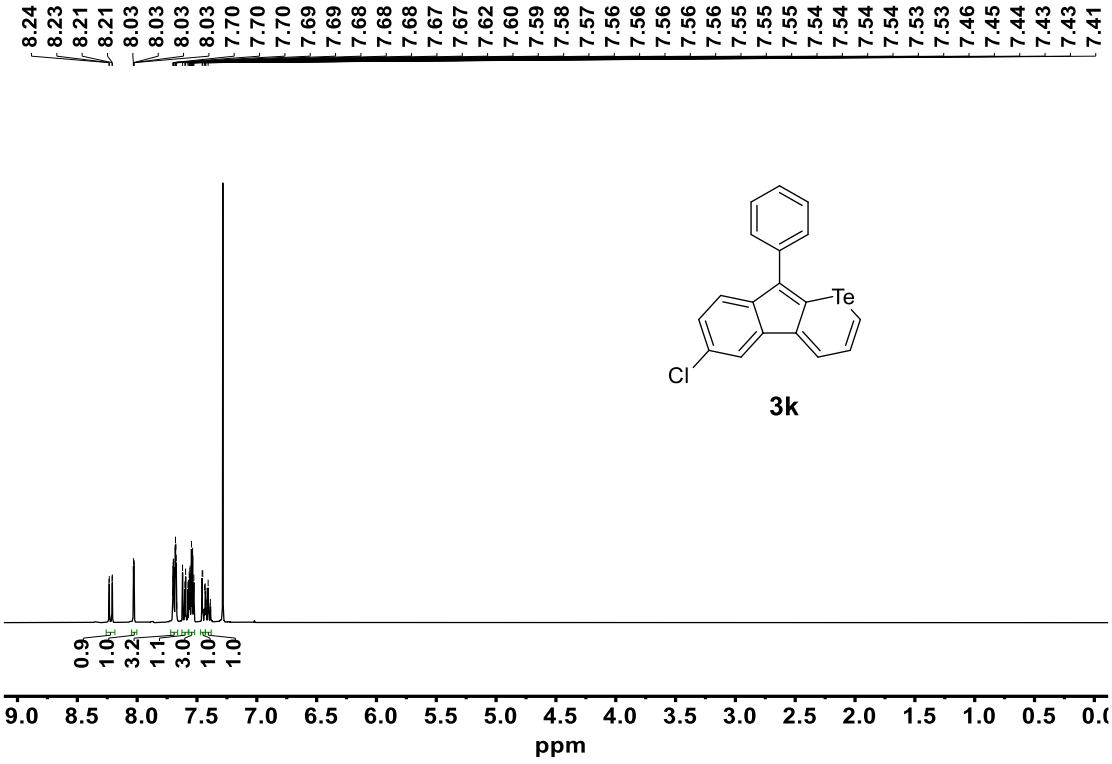


Figure S34. ^{13}C NMR spectrum of **3k** in $CDCl_3$.

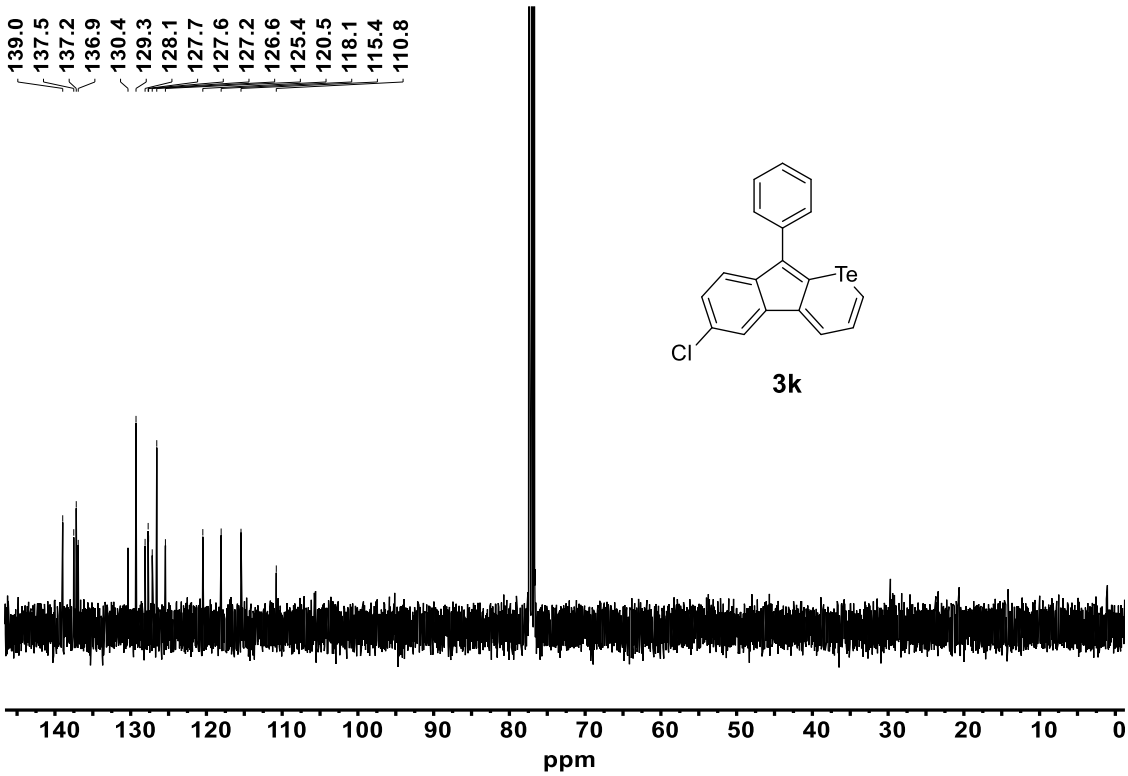


Figure S35. ^{1}H NMR spectrum of **3l** in $CDCl_3$.

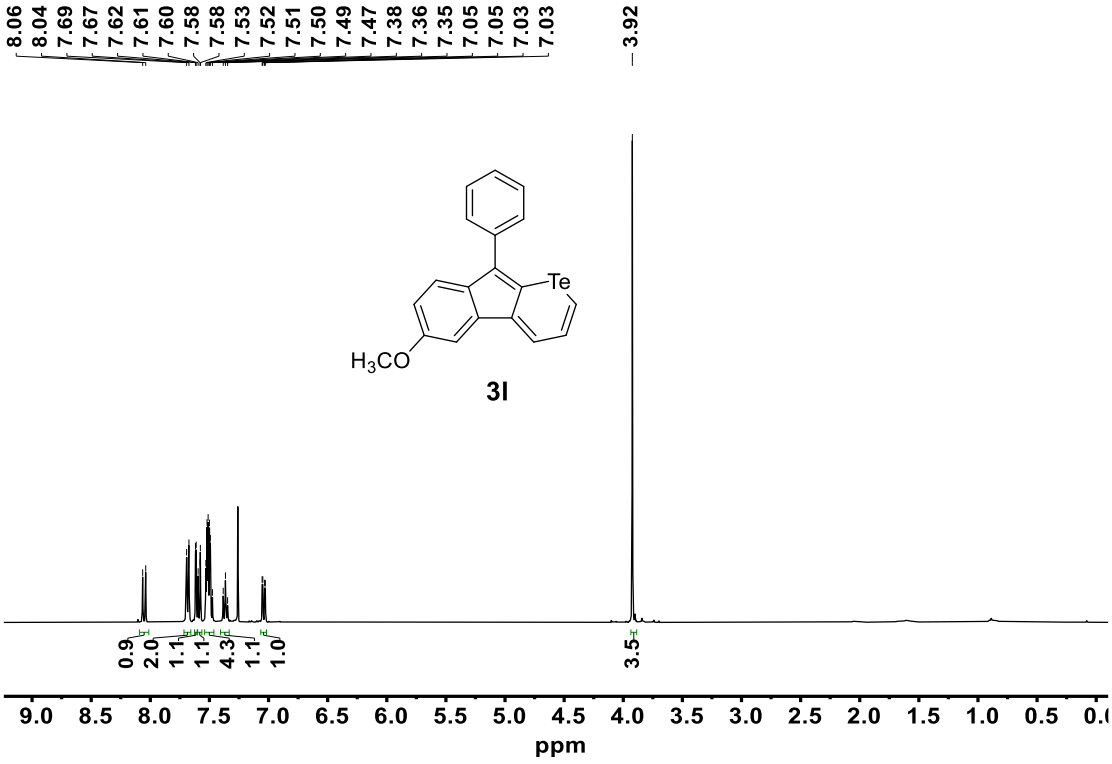


Figure S36. ^{13}C NMR spectrum of **3l** in $CDCl_3$.

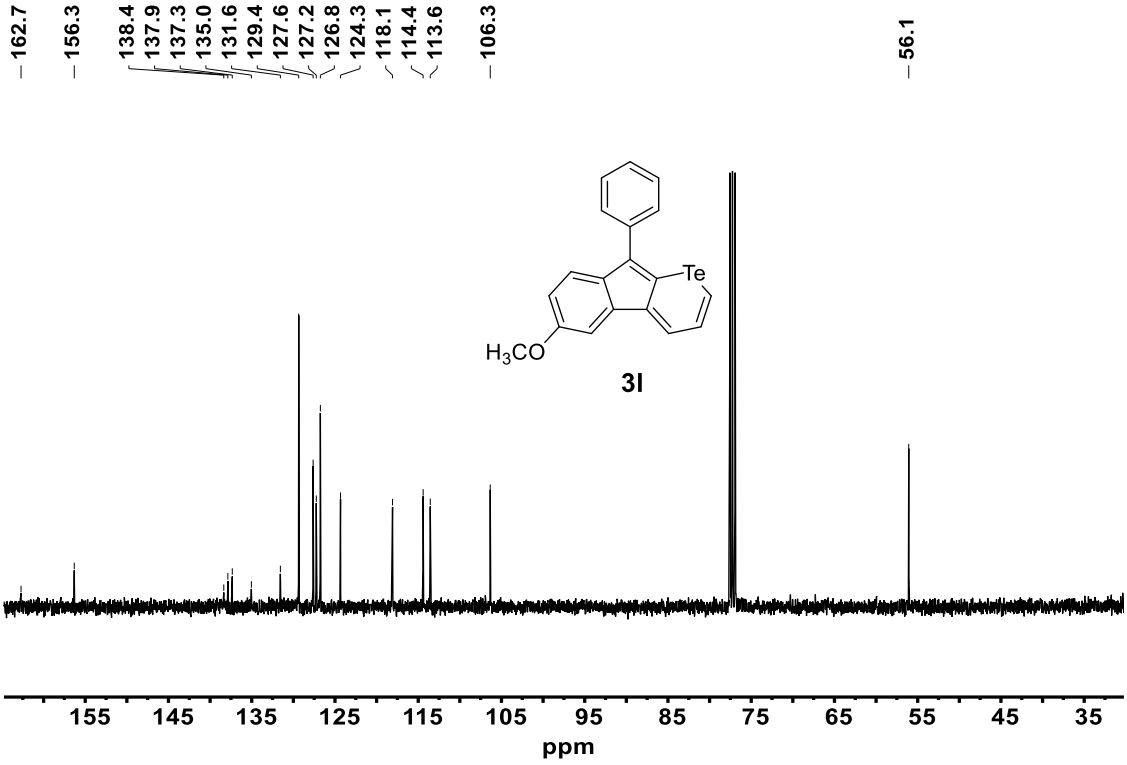


Figure S37. ^{1}H NMR spectrum of **2m** in $CDCl_3$.

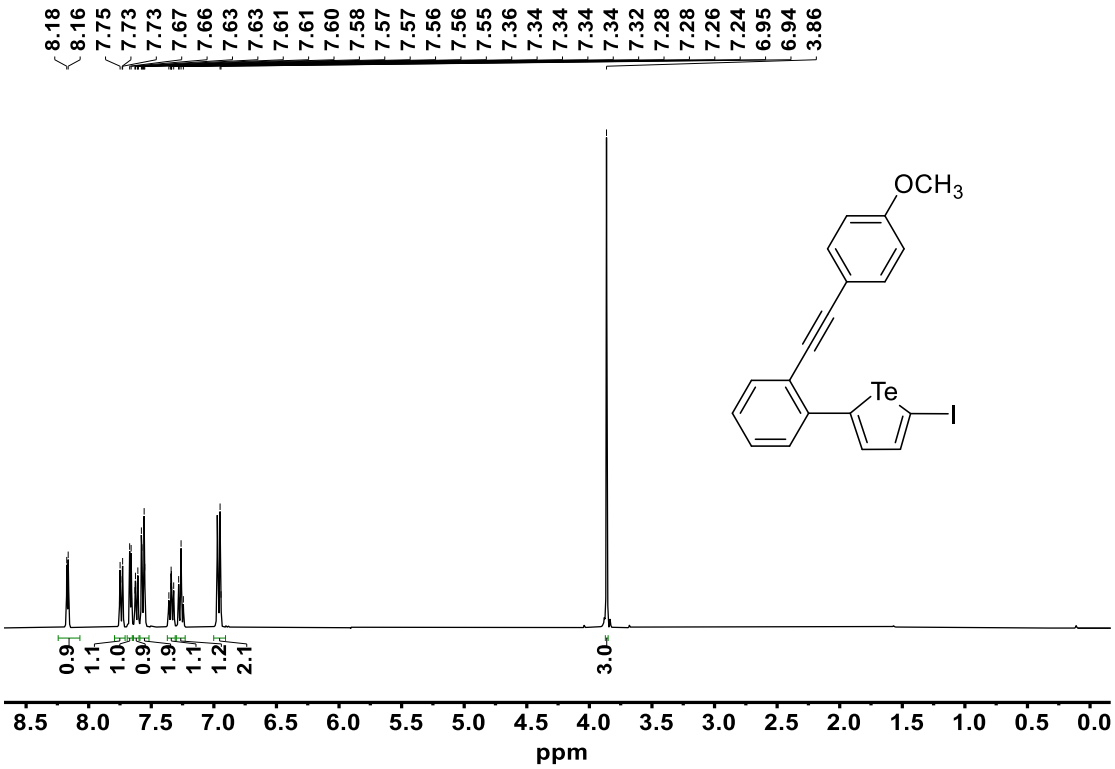


Figure S38. ^{1}H NMR spectrum of **2m** in $CDCl_3$.

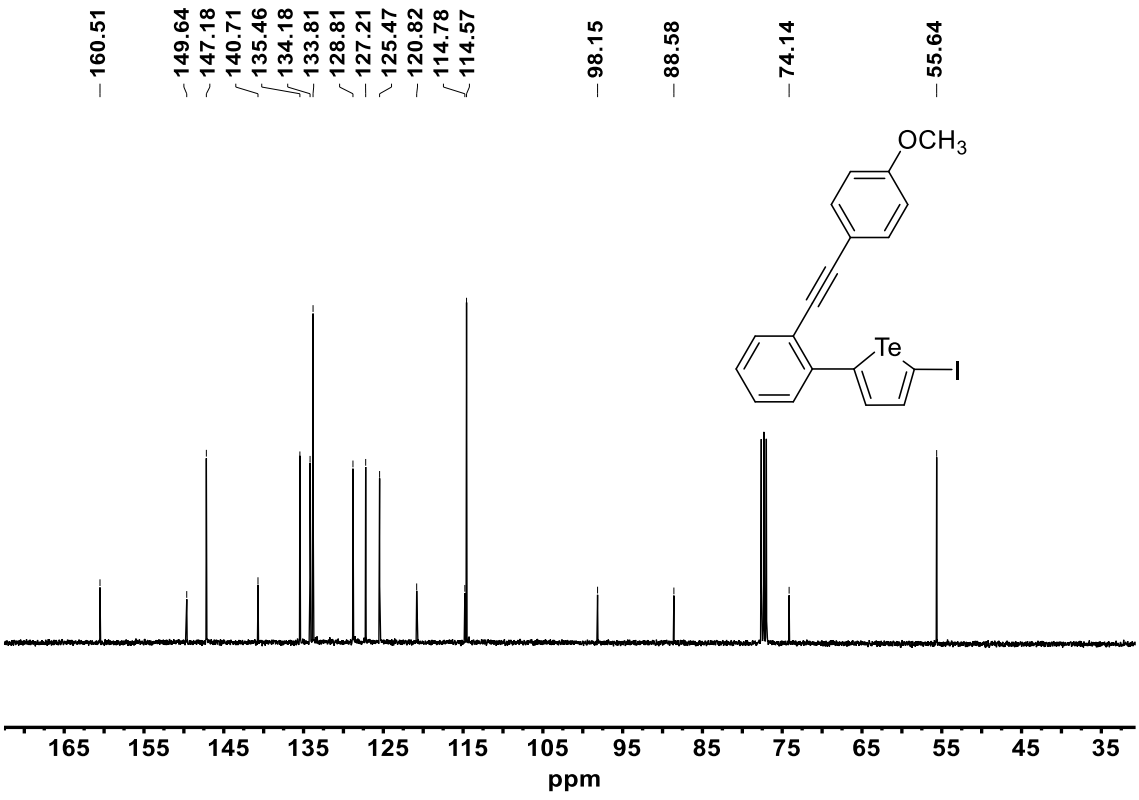


Figure S39. ^{1}H NMR spectrum of **3m** in $CDCl_3$.

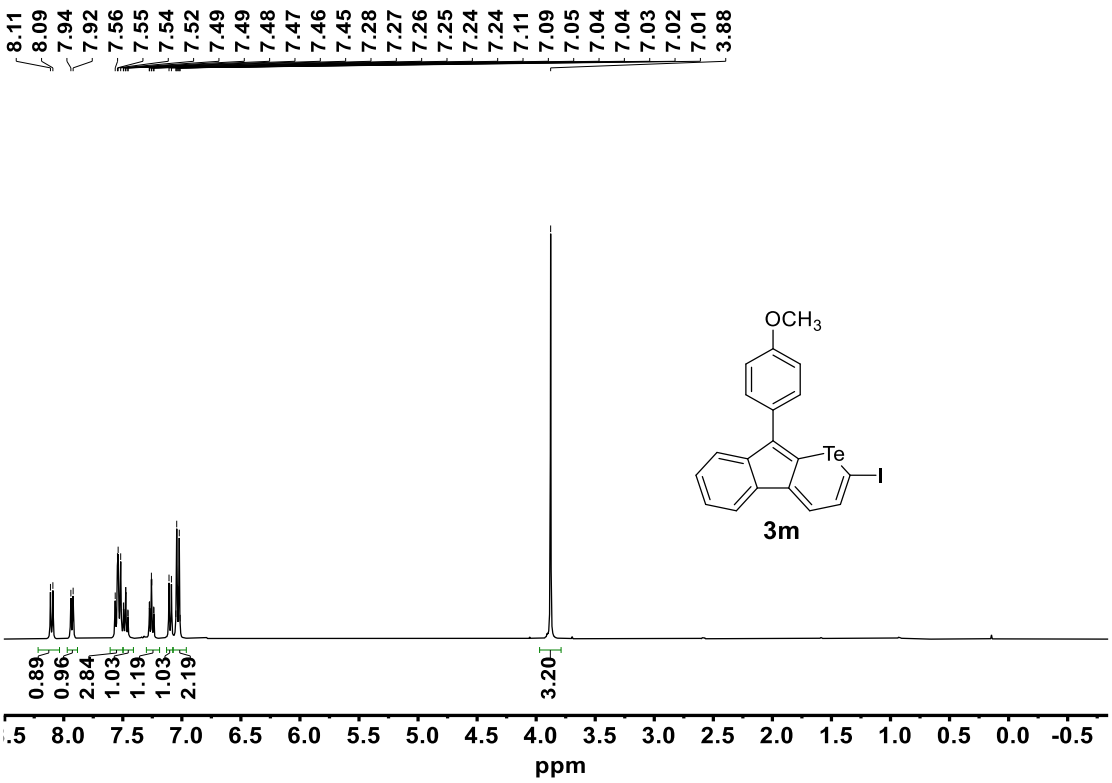


Figure S40. ^{1}H NMR spectrum of **3m** in $CDCl_3$.

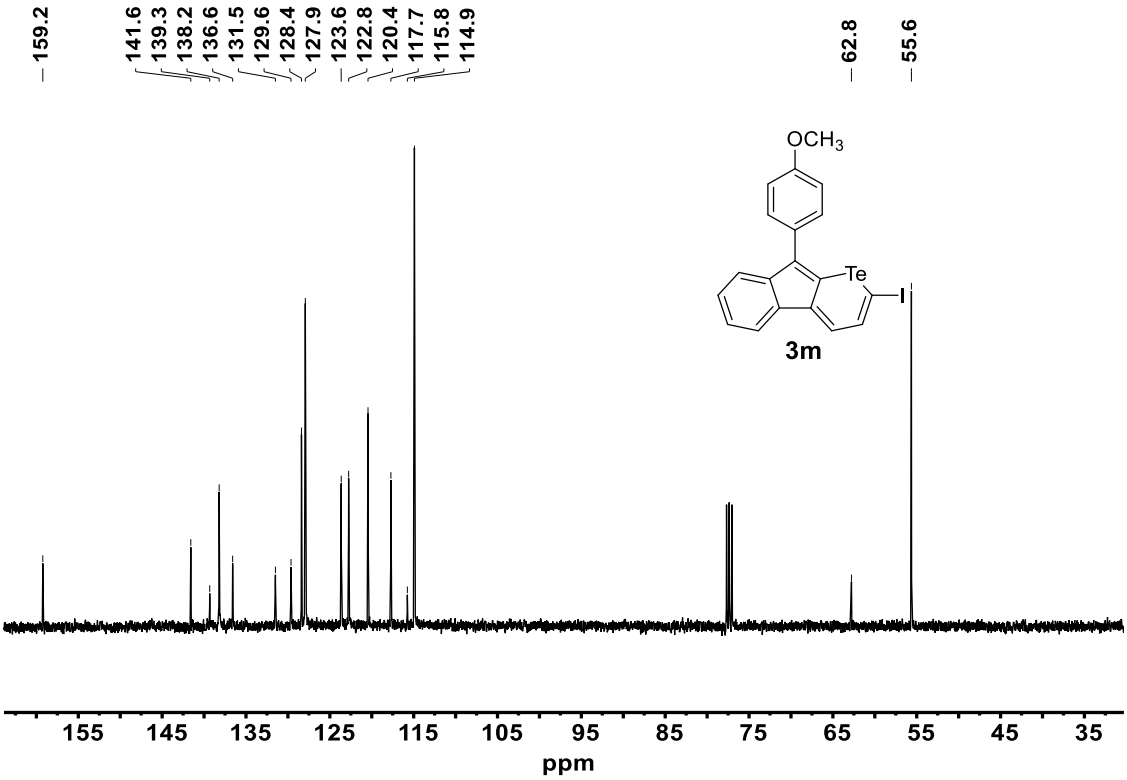


Figure S41. ^{1}H NMR spectrum of **2n** in $CDCl_3$

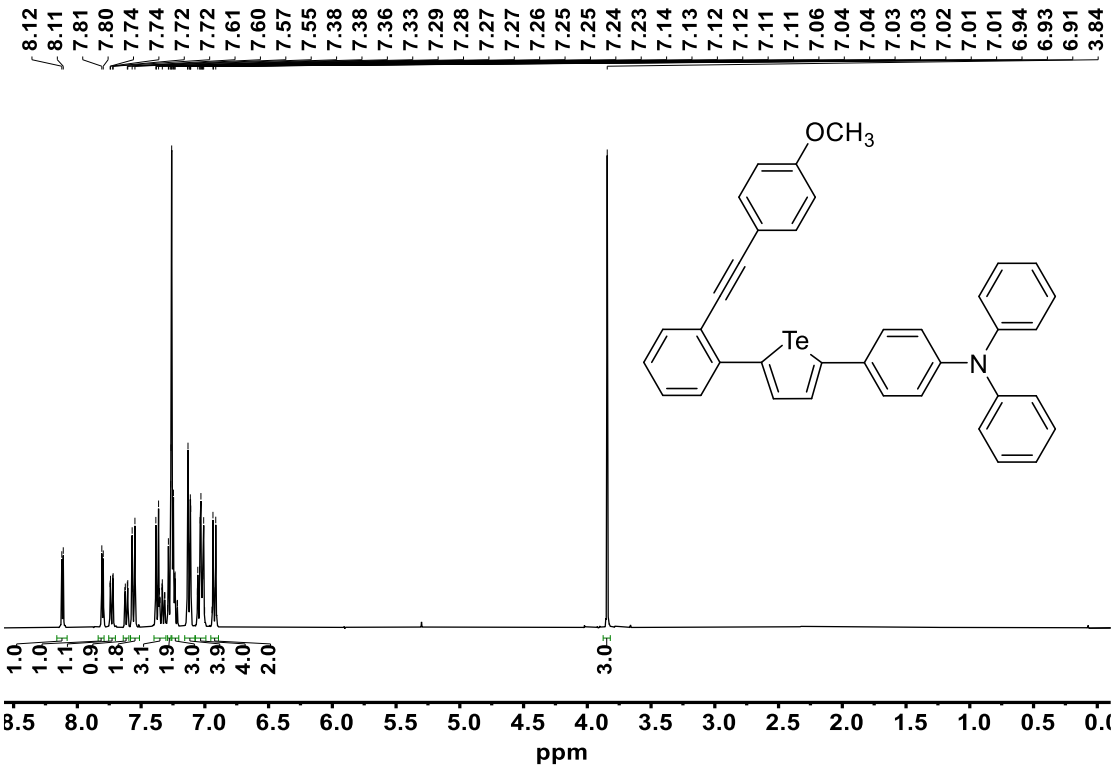


Figure S42. ^{13}C NMR spectrum of **2n** in $CDCl_3$.

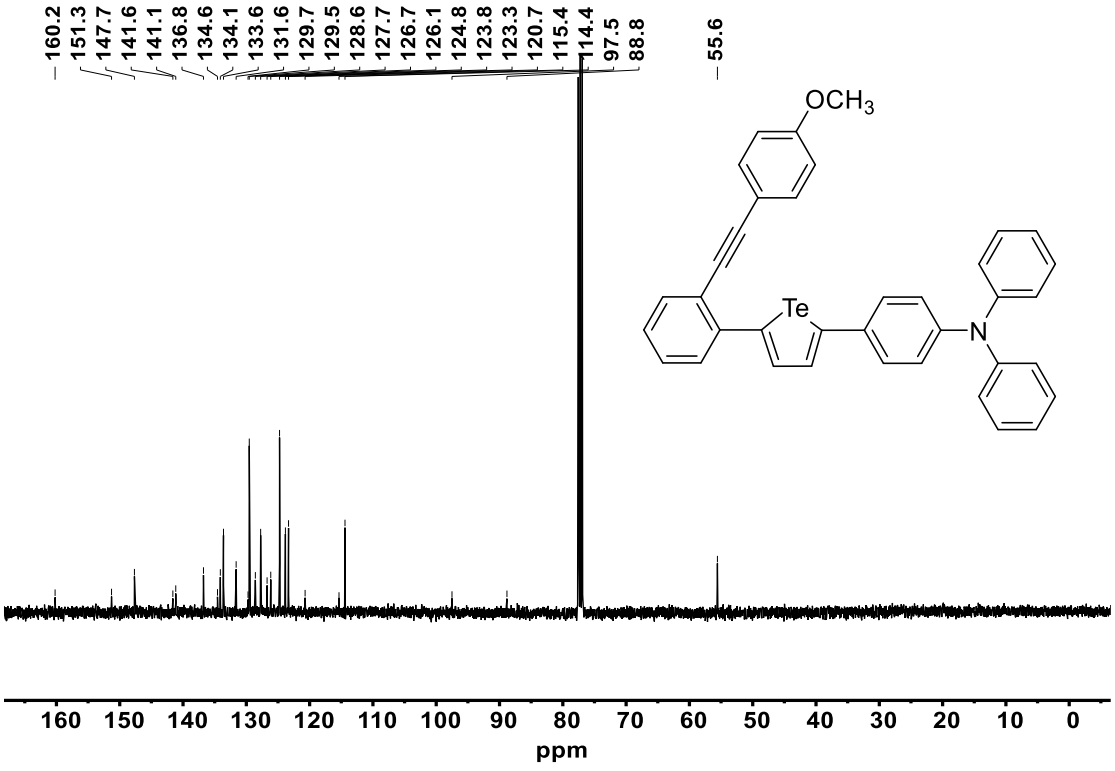


Figure S43. ^{1}H NMR spectrum of **3n** in $CDCl_3$.

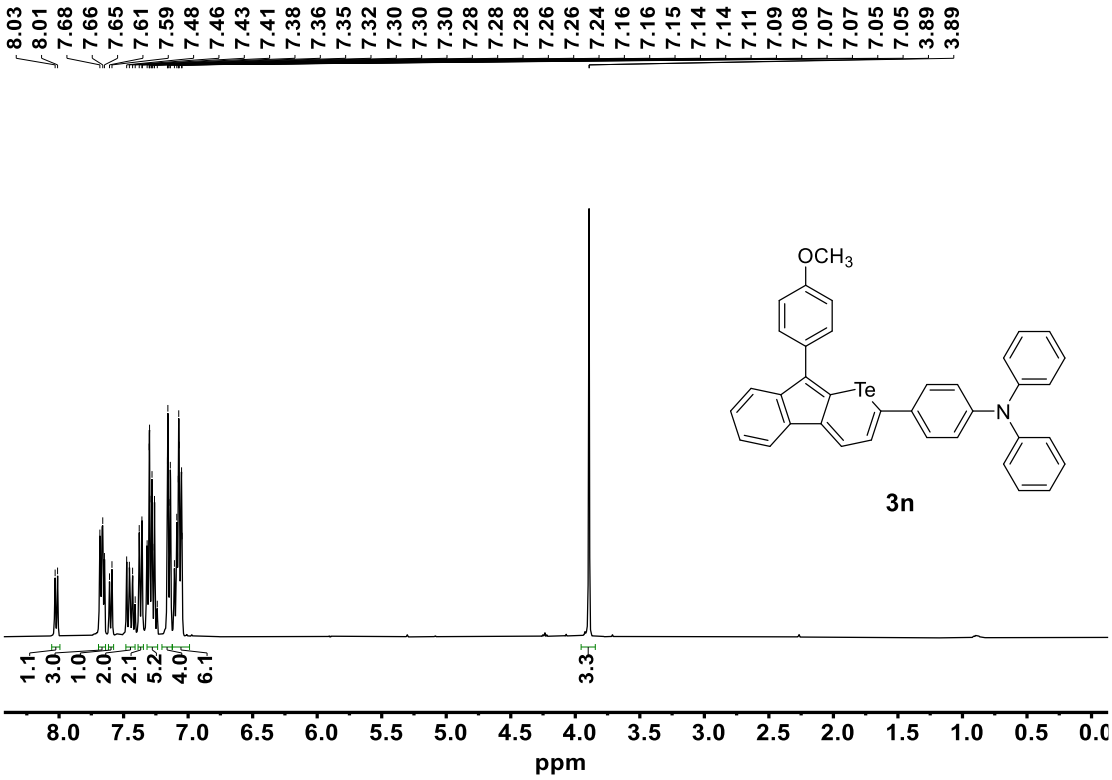


Figure S44. ^{13}C NMR spectrum of **3n** in $CDCl_3$.

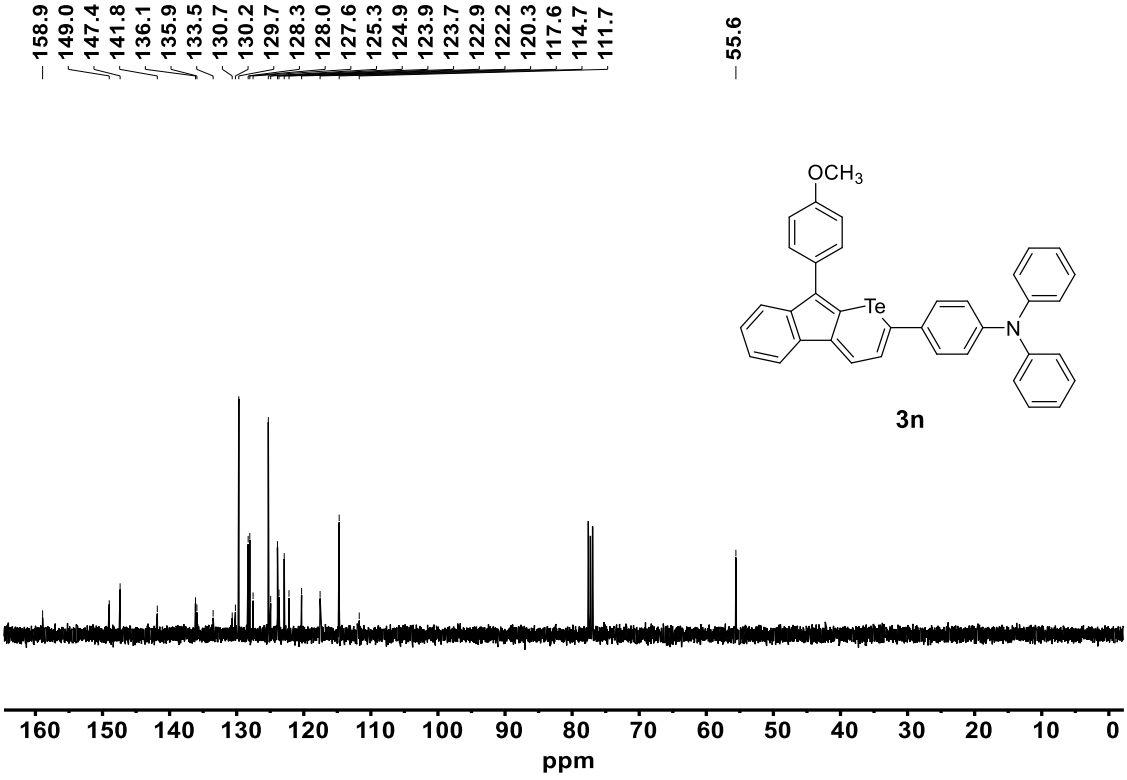


Figure S45. ^{1}H NMR spectrum of **3d•I$_2$** in $CDCl_3$.

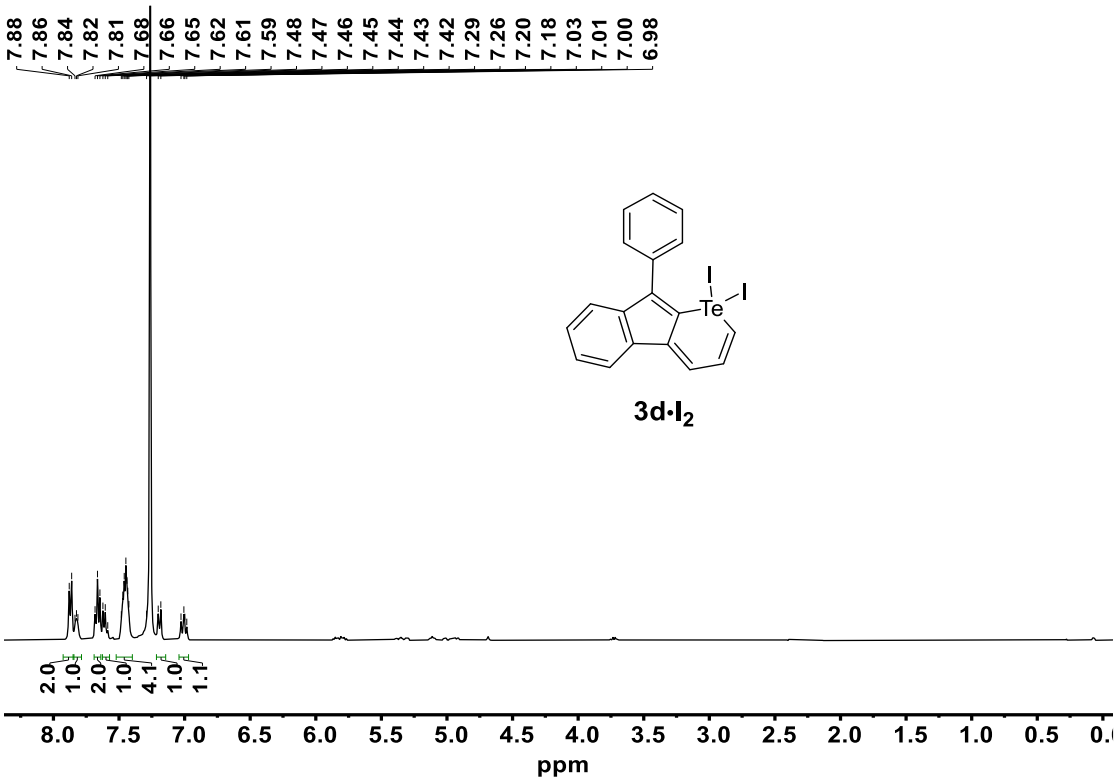


Figure S46. ^{1}H NMR spectrum of **4a** in DMSO-d_6.

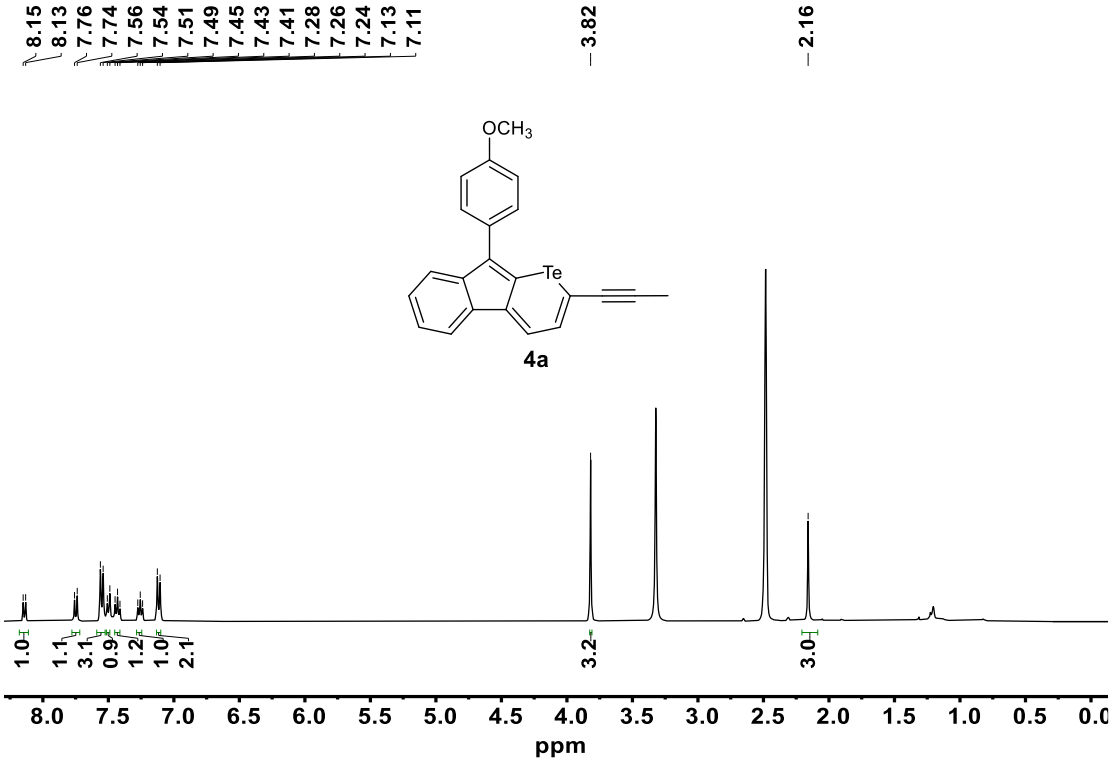


Figure S47. ^{13}C NMR spectrum of **4a** in DMSO-d_6.

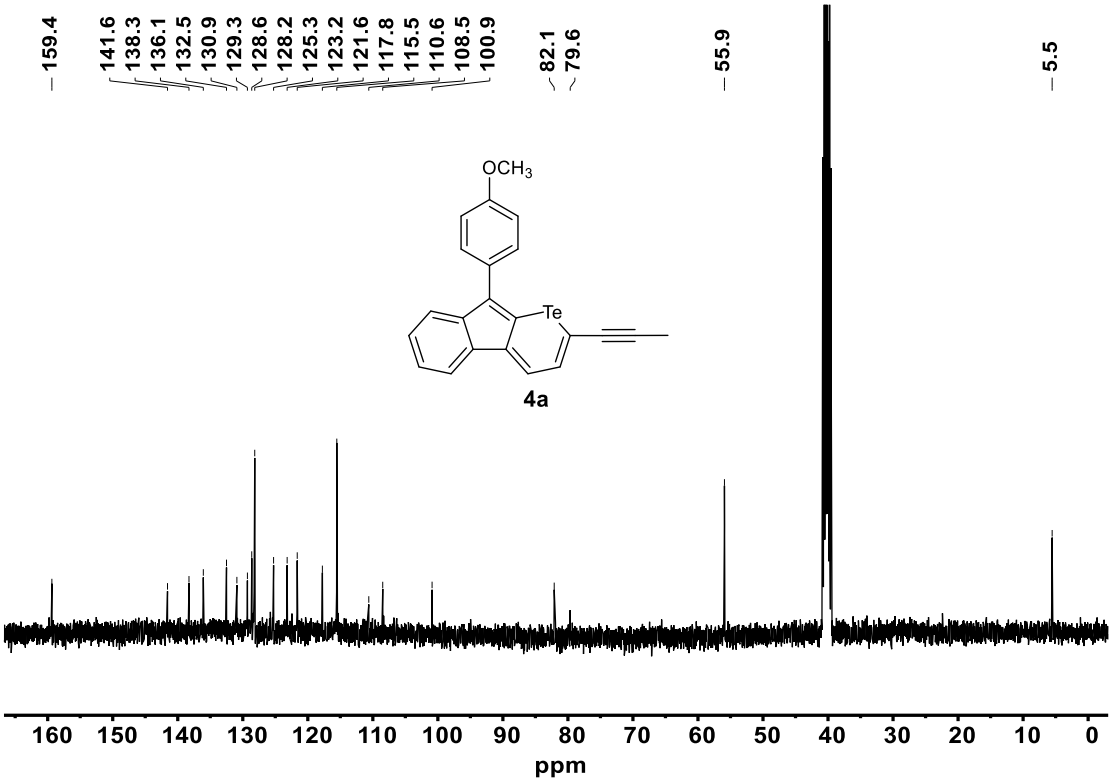


Figure S48. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

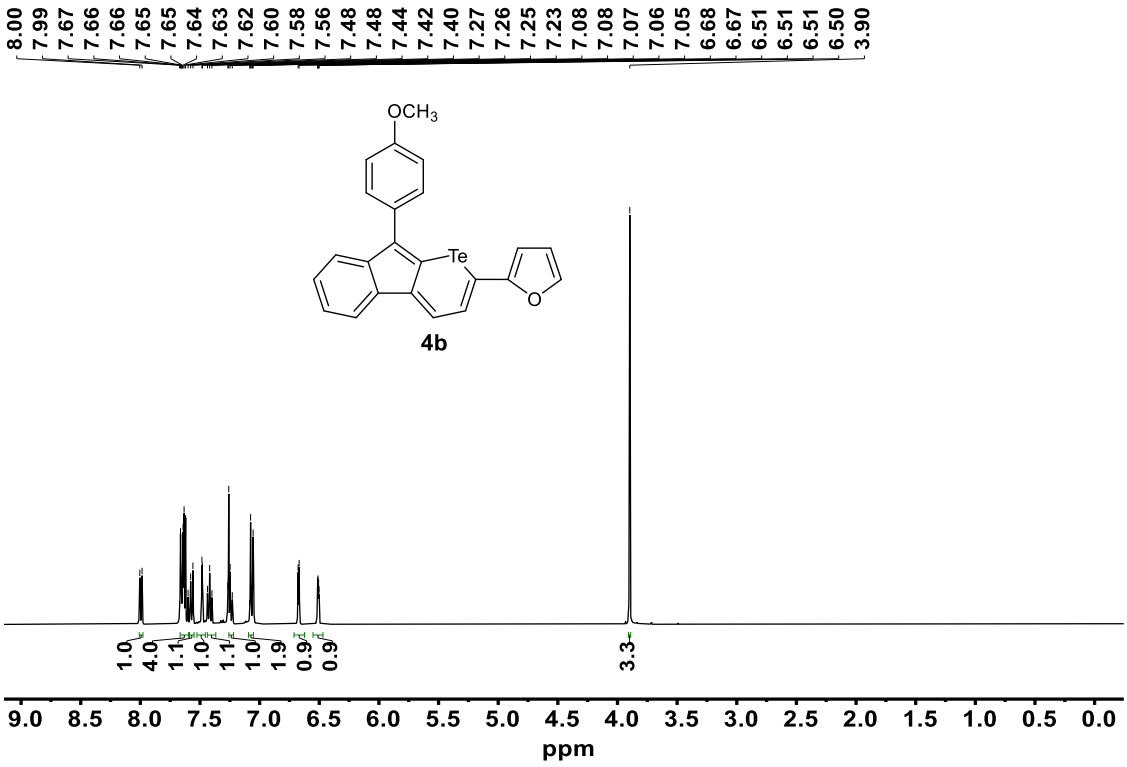


Figure S49. ^{13}C NMR spectrum of **4b** in $CDCl_3$.

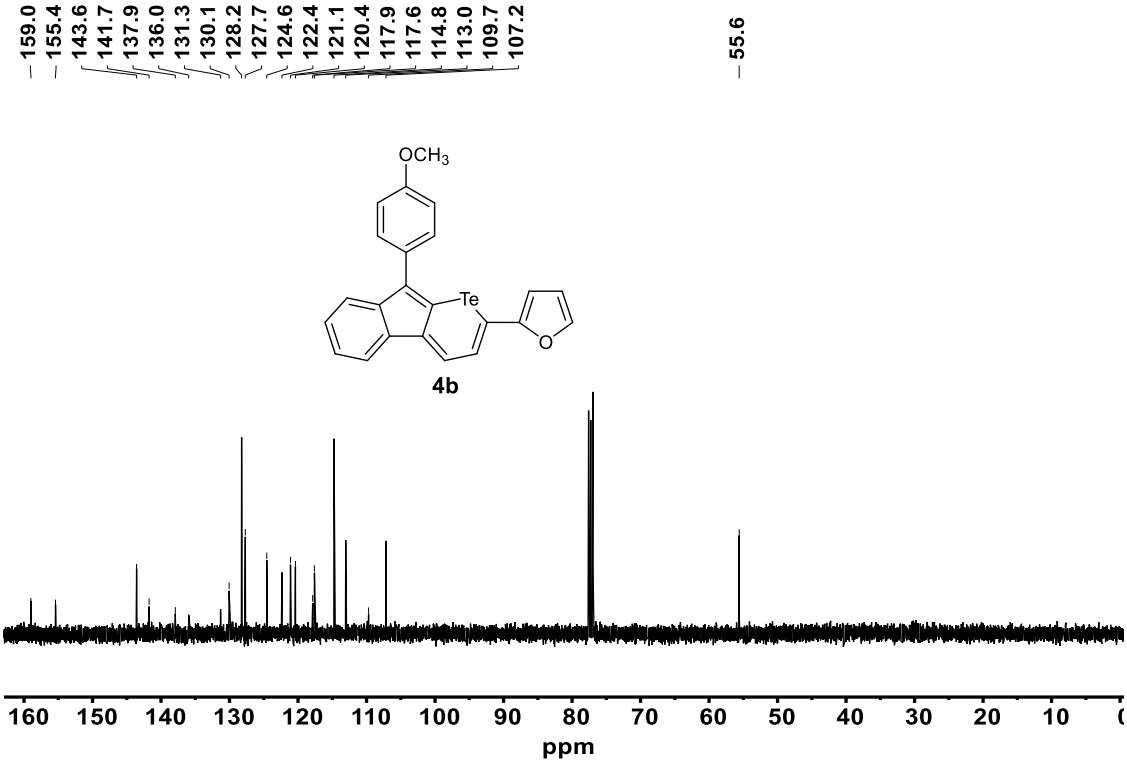


Figure S50. ^{1}H NMR spectrum of **4c** in DMSO-d_6.

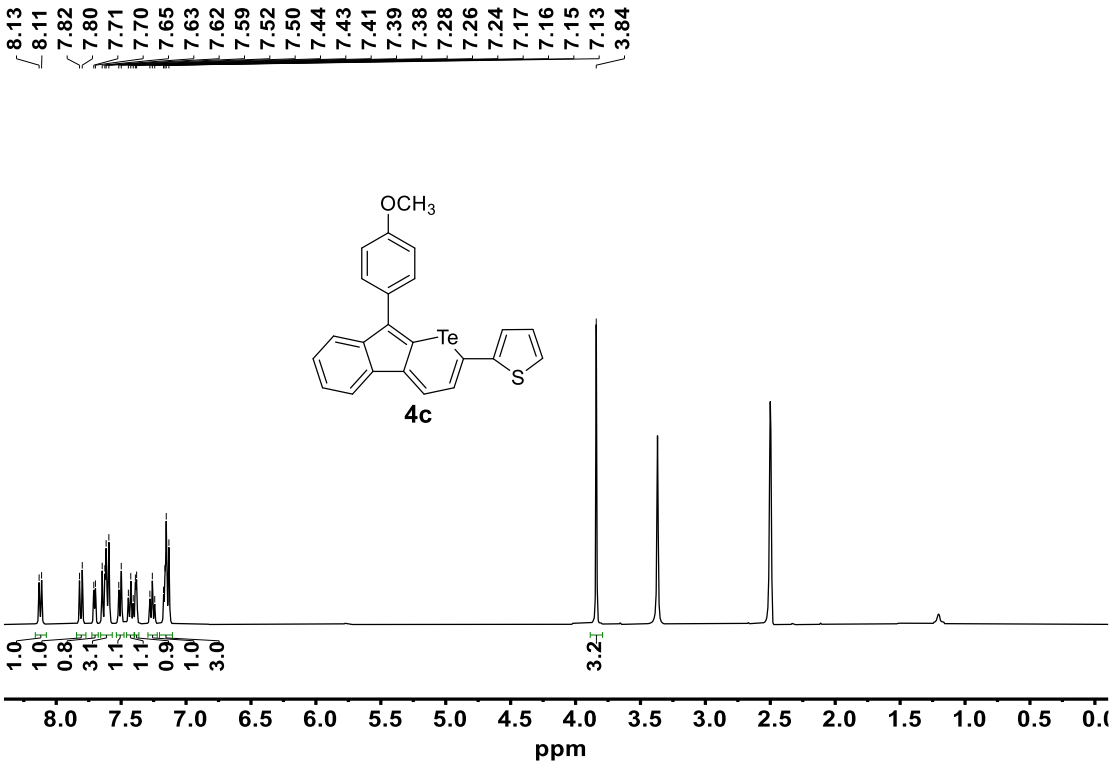


Figure S51. ^{13}C NMR spectrum of **4c** in DMSO-d_6.

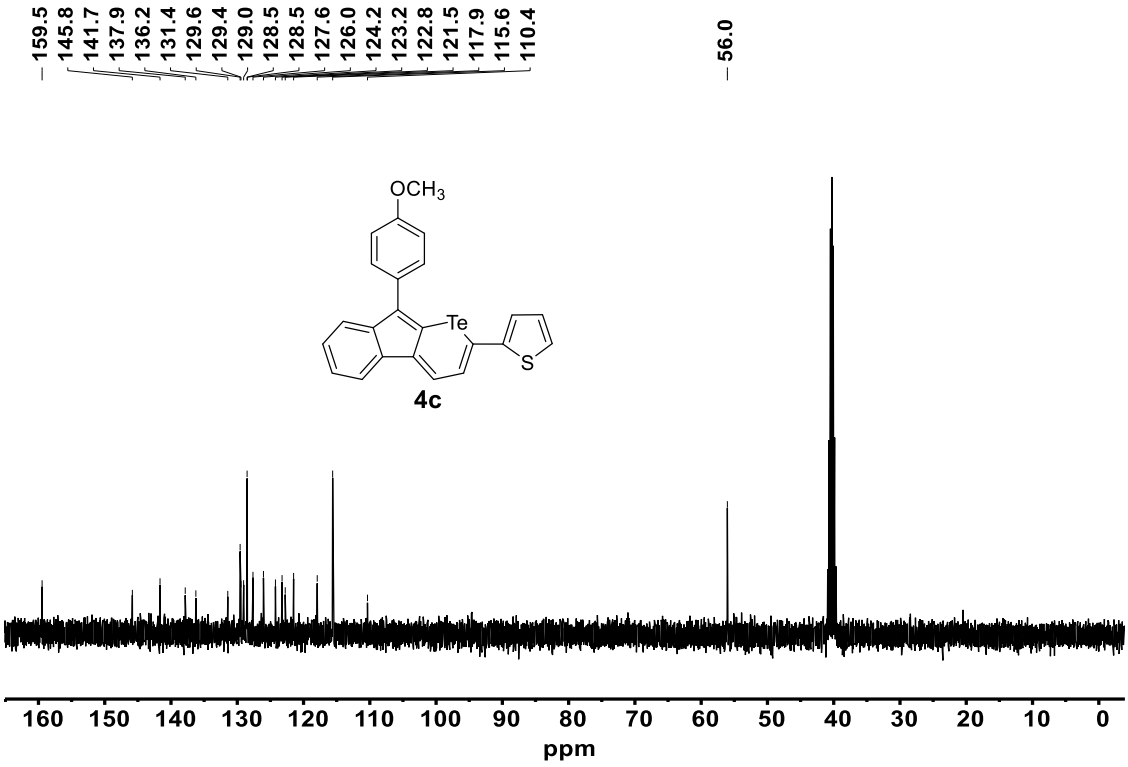


Figure S52. ^{1}H NMR spectrum of **4d** in DMSO-d_6.

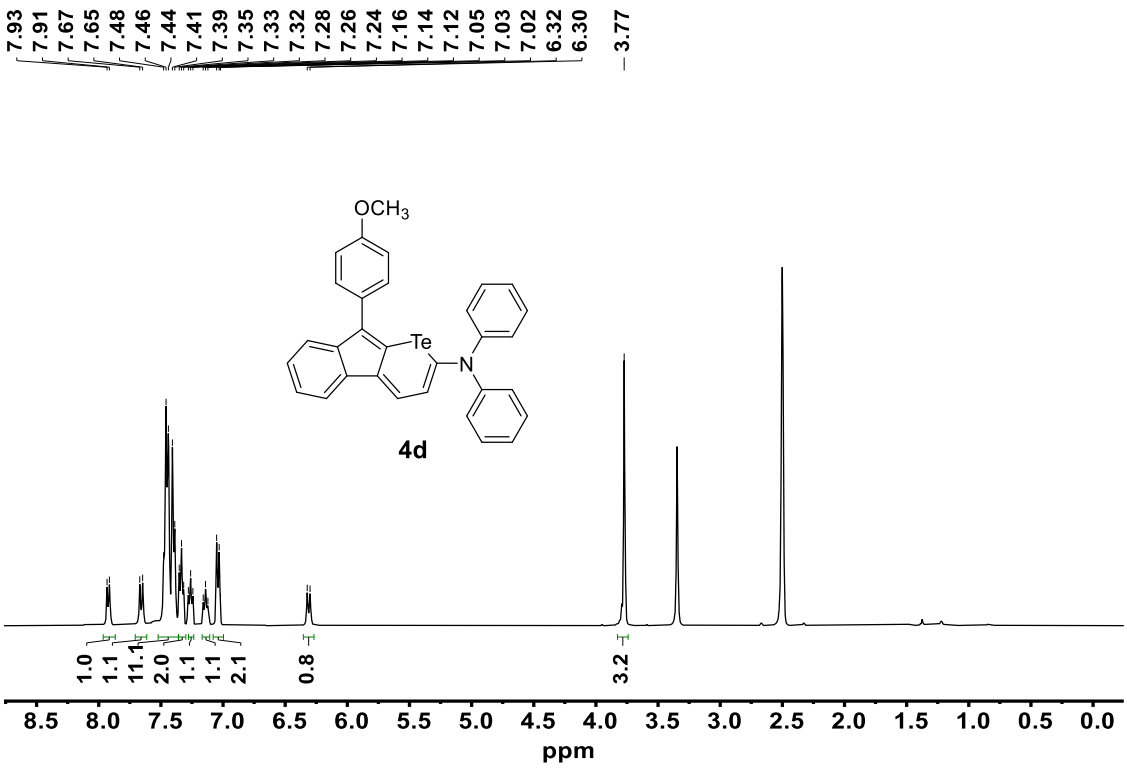


Figure S53. ^{13}C NMR spectrum of **4d** in DMSO-d_6.

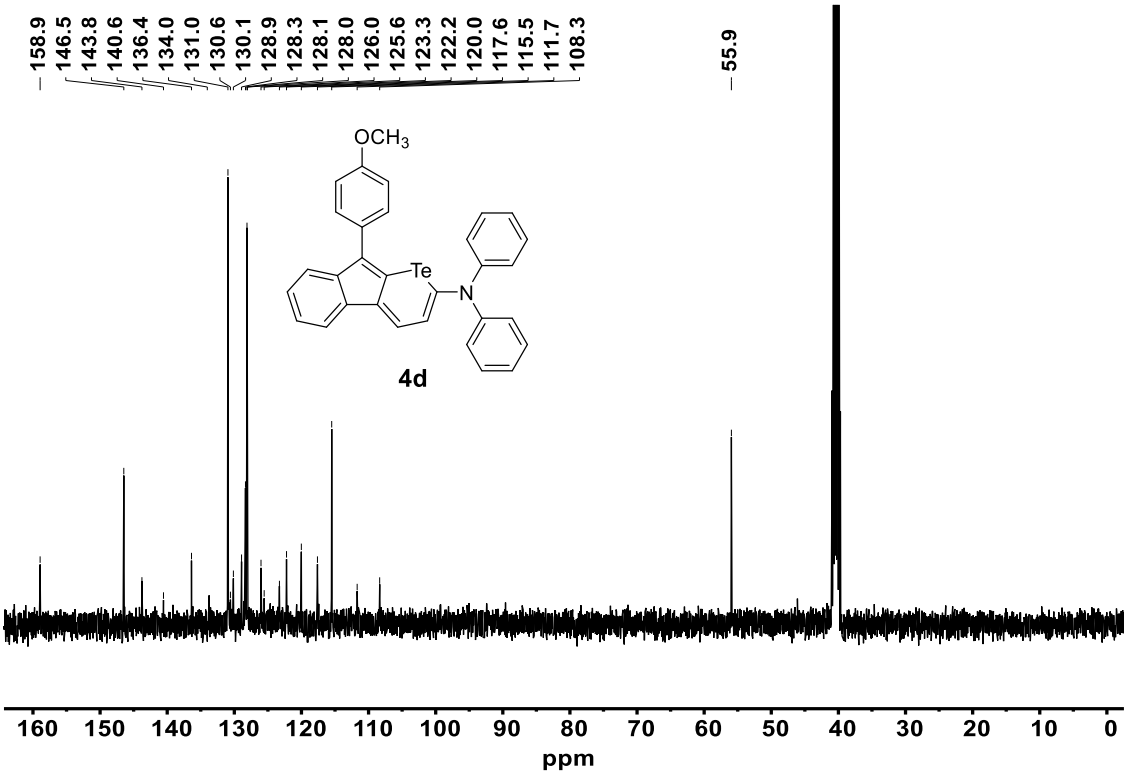


Figure S54. ^{1}H NMR spectrum of **4e** in $CDCl_3$.

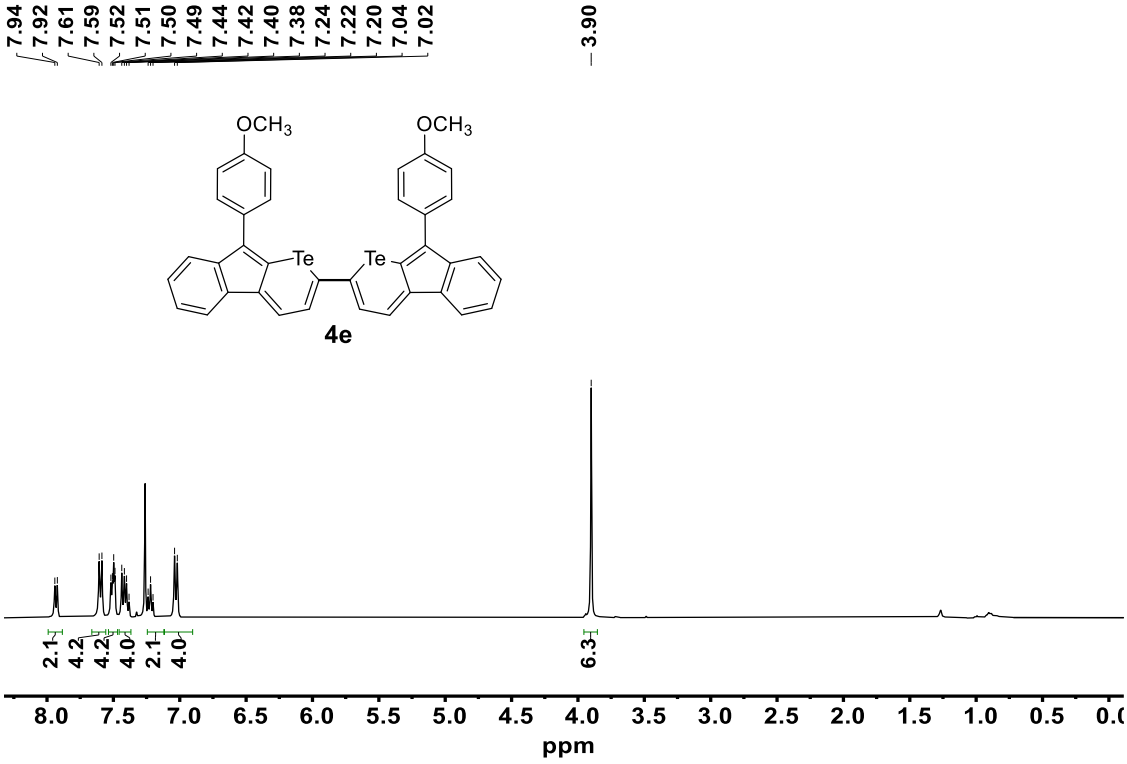


Figure S55. ^{13}C NMR spectrum of **4e** in $CDCl_3$.

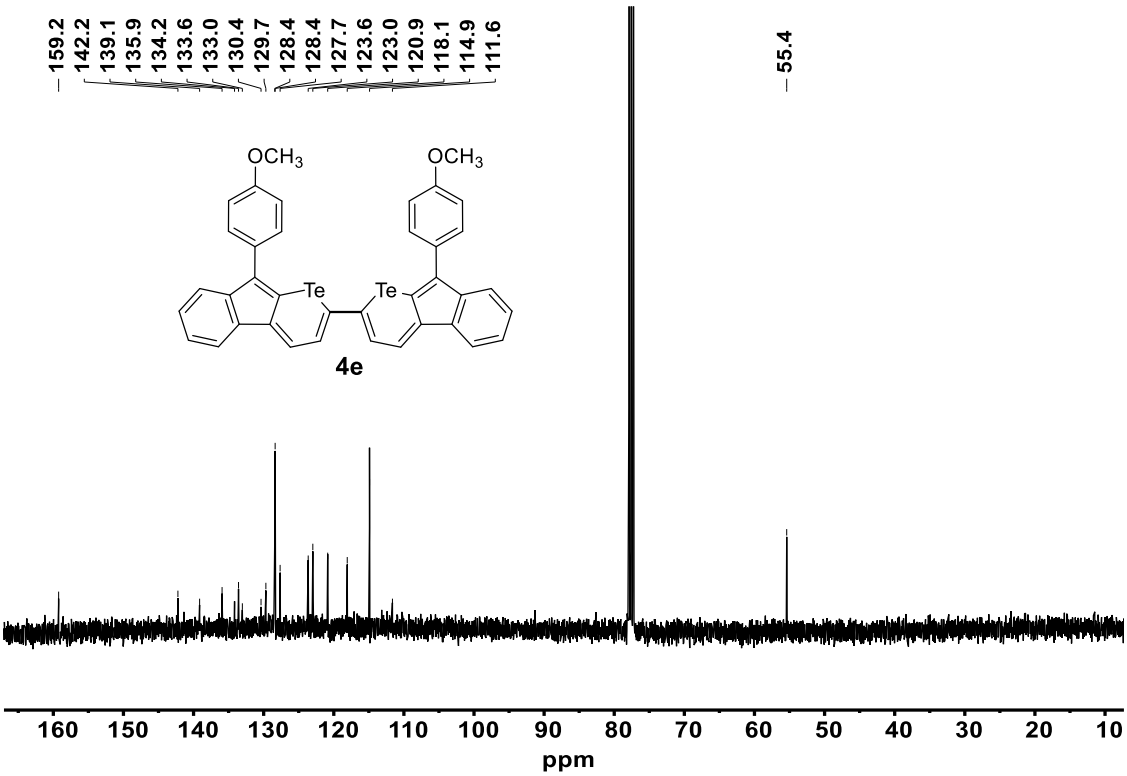


Figure S56. ^{1}H NMR spectrum of **4f** in DMSO-d_6.

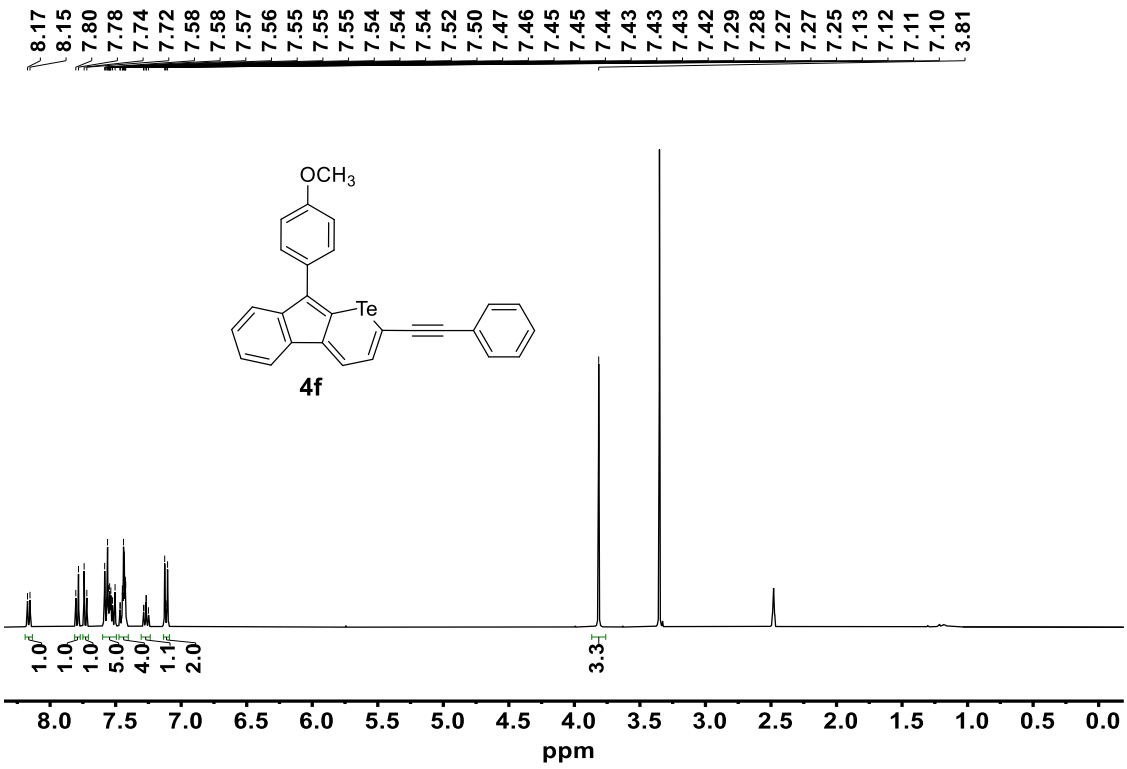
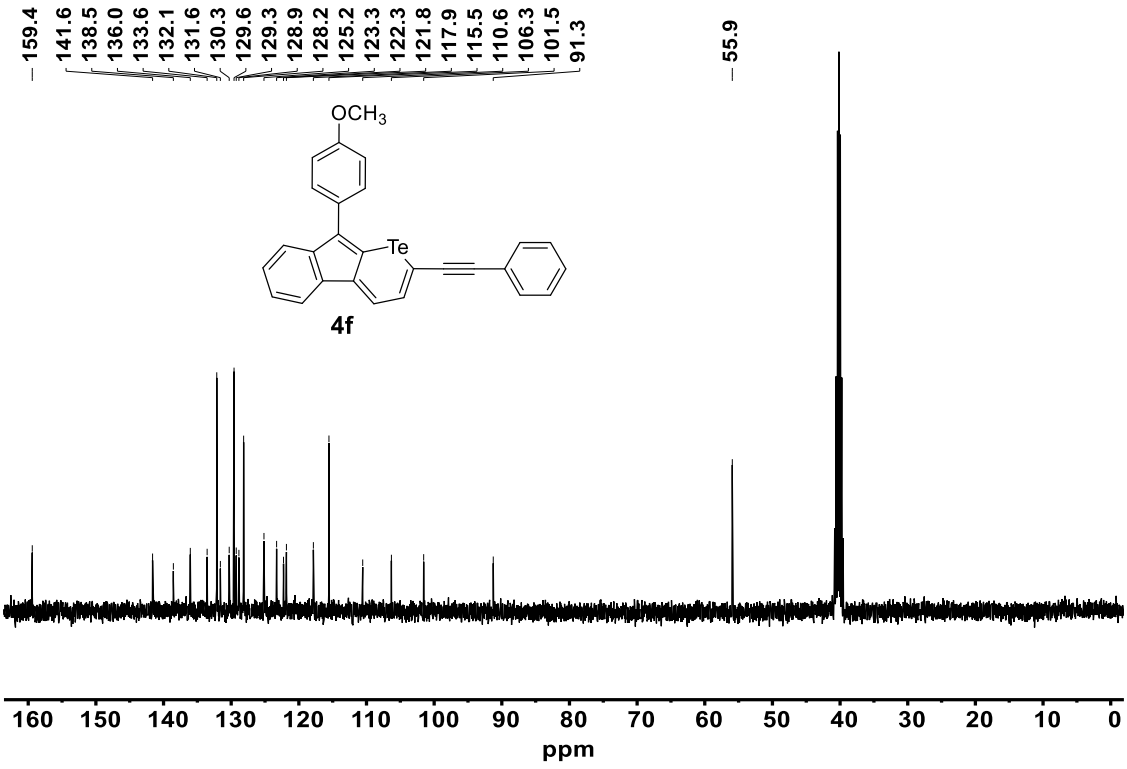


Figure S57. ^{13}C NMR spectrum of **4f** in DMSO-d_6.



References.

S1 a) Schaefer, W. P.; Lyon, D. K.; Labinger, J. A.; Bercaw, J. E., A Platinum Chloro (Fluoroaryl)Phosphine Complex. *Acta Crystallogr C* **1992,** *48*, 1582-1584; b) Kemmitt, R. D. W.; Nichols, D. I.; Peacock, R. D., Trispentafluorophenylphosphine Complexes of Rhodium Palladium and Platinum. *Chem Commun* **1967,** 599.

S2 a) Lu, Y.; Qiao, Y.; Xue, H.; Zhou, G., From Colorless to Near-Infrared S-Heteroarene Isomers: Unexpected Cycloaromatization of Cyclopenta[*b*]thiopyran Catalyzed by $PtCl_2$. *Org. Lett.* **2018,** *20*, 6632-6635; b) Jahnke, A. A.; Howe, G. W.; Seferos, D. S., Polytellurophenes with Properties Controlled by Tellurium-Coordination. *Angew. Chem. Int. Ed.* **2010,** *49* (52), 10140-10144.

S3 *Gaussian 16, Revision C.01,* M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers,0 K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2019**.

S4 Chai, J. D.; Head-Gordon, M., Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008,** *10*, 6615-6620.

S5 Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C., The ORCA quantum chemistry program package. *J Chem Phys* **2020,** *152*, 224108.

S6 Mardirossian, N.; Head-Gordon, M., omegaB97M-V: A combinatorially optimized, range-separated hybrid, meta-GGA density functional with VV10 nonlocal correlation. *J. Chem. Phys.* **2016,** *144*, 214110.

S7 Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005,** *7*, 3297-3305

S8 Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B.* **2009,** *113*, 6378-6396.

S9 CYLview20; C. Y. Legault, Université de Sherbrooke, **2020** (http://www.cylview.org).