Electronic supplementary information

Constructing Fused *N*-Heterocycles from Unprotected Mesoionic *N*-Heterocyclic Olefins and Organic Azides via Diazo Transfer

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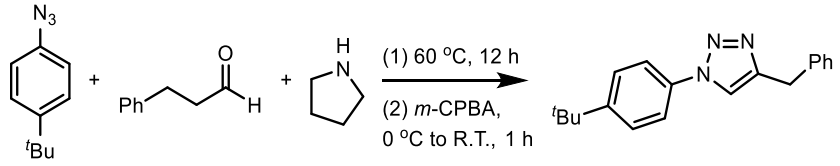
1. Experimental section

All reactions were carried out in a dinitrogen-filled glovebox or using the standard Schlenk techniques under dinitrogen. Glassware was dried in a 180 °C oven overnight. Diethyl ether, hexanes, and pentane solvents were dried by refluxing and distilling over sodium under dinitrogen. THF and toluene solvents were dried by refluxing and distilling over sodium benzophenone ketyl under dinitrogen. C_6D_6, $CDCl_3$, and THF-d_8 solvents were degassed through three consecutive freeze−pump−thaw cycles. All solvents were stored over 3 Å molecular sieves prior to use. Unless otherwise noted, all NMR spectra were recorded at 25 °C on an Agilent DD2 600 MHz or 500 MHz spectrometer with ^{13}C-sensitive cryogenically cooled probe. Chemical shifts are referenced to the solvent signals. The NMR signal assignments were made based on ^{1}H-COSY, ^{1}H-^{13}C-HSQC, and ^{1}H-^{13}C-HMBC NMR experiments. Elemental analyses were carried out at the ANALEST at the University of Toronto. High-resolution mass spectrograms were recorded at the AIMS Mass Spectrometry Laboratory at the University of Toronto. Unless otherwise noted, all chemicals were purchased from commercial sources and used as received.

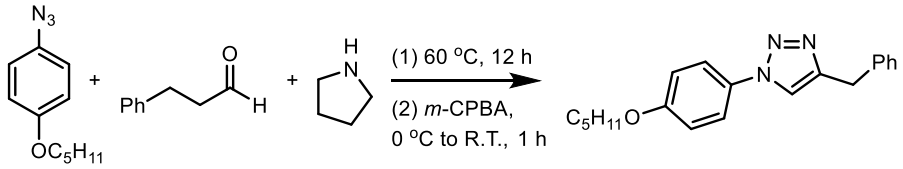
Notes: *Although we have not experienced any problems, cautions should be exercised when handling azide reagents due to their potentially explosive nature, especially for large scale reactions.*

Syntheses of triazoles:

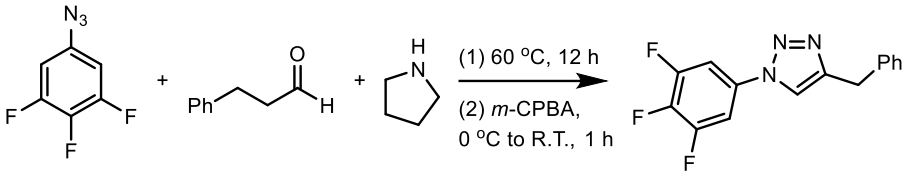
Triazoles 4-benzyl-1-mesityl-1,2,3-triazole,[1] 4-benzyl-1-phenyl-1,2,3-triazole,[2] 4-benzyl-1-(4-fluorophenyl)-1,2,3-triazole[2] and 4-benzyl-1-(4-(trifluoromethyl)phenyl)-1,2,3-triazole[3] were synthesized according to literatures.



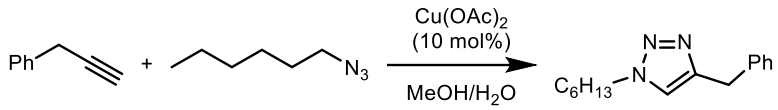
Pyrrolidine (1.6 mL, 20 mmol), 3-phenylpropionaldehyde (3.0 g, 22 mmol), and 1-azido-4-(*tert*-butyl)benzene[4] (3.5 g, 20 mmol) were dissolved in 50 mL of THF. The reaction mixture was stirred at 60 °C for 12 h. Solid *m*-CPBA (10.4 g, 50% active oxidant, 30 mmol) was added to the reaction mixture at 0 °C and the mixture was warmed up to room temperature and stirred for 1 h. The reaction mixture was then concentrated to dryness under reduced pressure. The crude product was dissolved in EtOAc, washed with sat. $Na_2S_2O_3$ solution, 2M NaOH solution and brine, sequentially. The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel eluted with ethyl acetate (0–20% gradient by volume) in hexanes to afford 4-benzyl-1-(*tert*-butylphenyl)-1,2,3-triazole as a white solid. Yield: 4.8 g, 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 – 7.58 (m, 2H, ^{t}Bu-C$_6$*H*$_4$), 7.56 (m, 1H, Ph-*H*), 7.52 – 7.45 (m, 2H, ^{t}Bu-C$_6$*H*$_4$), 7.35 – 7.31 (m, 4H, overlapping, triazole-*H* and Ph-*H*), 7.28 – 7.23 (m, 1H, Ph-*H*), 4.17 (s, 2H, C*H*$_2$), 1.34 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.00 ^{t}Bu-*C*$_6$H$_4$), 148.42 (triazole-*C*), 139.06 (Ph-*C*), 134.90 (^{t}Bu-*C*$_6$H$_4$), 128.93 (^{t}Bu-*C*$_6$H$_4$), 128.83 (Ph-*C*), 126.74 (Ph-*C*), 126.65 (Ph-*C*), 120.28 (^{t}Bu-*C*$_6$H$_4$), 119.81 (triazole-*C*), 34.88 (*C*(CH$_3$)$_3$), 32.45 (*C*H$_2$), 31.40 (C(*C*H$_3$)$_3$). $C_{19}H_{22}N_3$ $[M+H]^+$ 292.18082, found 292.18091.



Pyrrolidine (1.6 mL, 20 mmol), 3-phenylpropionaldehyde (3.0 g, 22 mmol), and 1-azido-4-(pentyloxy)benzene (4.1 g, 20 mmol) were dissolved in 50 mL of THF. The reaction mixture was stirred at 60 °C for 12 h. Solid *m*-CPBA (10.4 g, 50% active oxidant, 30 mmol) was added to the reaction mixture at 0 °C and the mixture was warmed up to room temperature and stirred for 1 h. The reaction mixture was then concentrated to dryness under reduced pressure. The crude product was dissolved in EtOAc, washed with sat. $Na_2S_2O_3$ solution, 2M NaOH solution and brine, sequentially. The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel eluted with ethyl acetate (0–20% gradient by volume) in hexanes to afford 4-benzyl-1-(4-pentoxyphenyl)-1,2,3-triazole as a white solid. Yield: 4.9 g, 76%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 – 7.52 (m, 2H, pentoxy- C_6H_4), 7.51 (s, 1H, triazole-*H*), 7.34 – 7.31 (m, 4H, Ph-*H*), 7.28 – 7.21 (m, 1H, Ph-*H*), 6.99 – 6.93 (m, 2H, pentoxy-C_6H_4), 4.16 (s, 2H. CH_2), 3.98 (t, *J* = 6.6 Hz, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.80 (dt, *J* = 14.6, 6.6 Hz, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.49 – 1.41 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.43 – 1.35 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 0.94 (t, *J* = 7.2 Hz, 3H, $CH_2CH_2CH_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.32 (pentoxy-C_6H_4), 148.27 (triazole-*C*), 139.05 (pentoxy-C_6H_4), 130.54 (Ph-*C*), 128.87 (Ph-*C*), 128.77 (Ph-*C*), 126.67 (Ph-*C*), 122.07 (pentoxy-C_6H_4), 119.92 (triazole-*C*), 115.26 (pentoxy-C_6H_4), 68.50 ($CH_2CH_2CH_2CH_2CH_3$), 32.41 (CH_2), 28.94 ($CH_2CH_2CH_2CH_2CH_3$), 28.23 ($CH_2CH_2CH_2CH_2CH_3$), 22.53 ($CH_2CH_2CH_2CH_2CH_3$), 14.10 ($CH_2CH_2CH_2CH_2CH_3$). HRMS (ESI): *m/z* calcd for $C_{20}H_{24}N_3O$ $[M+H]^+$ 322.1914, found 322.1912.

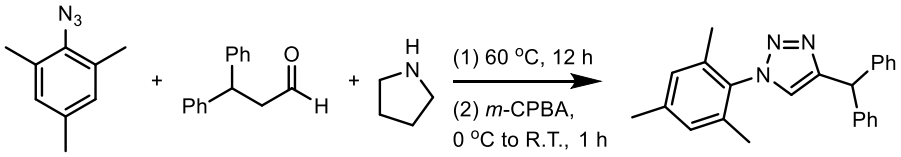


Pyrrolidine (1.6 mL, 20 mmol), 3-phenylpropionaldehyde (3.0 g, 22 mmol), and 5-azido-1,2,3-trifluorobenzene[5] (3.5 g, 20 mmol) were dissolved in 50 mL of THF. The reaction mixture was stirred at 60 °C for 12 h. Solid *m*-CPBA (10.4 g, 50% active oxidant, 30 mmol) was added to the reaction mixture at 0 °C and the mixture was warmed up to room temperature and stirred for 1 h. The reaction mixture was then concentrated to dryness under reduced pressure. The crude product was dissolved in EtOAc, washed with sat. $Na_2S_2O_3$ solution, 2M NaOH solution and brine, sequentially. The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel eluted with ethyl acetate (0–20% gradient by volume) in hexanes to afford 4-benzyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazole as a white solid. Yield: 4.7 g, 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.45 – 7.36 (m, 2H, $C_6H_2F_3$), 7.36 – 7.28 (m, 4H, Ph-*H*), 7.29 – 7.22 (m, 1H, Ph-*H*), 4.16 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.57 (ddd, J = 252.3, 10.7, 4.8 Hz, $C_6H_2F_3$), 149.36 (triazole-*C*), 139.60 (dt, J = 254.4, 15.1 Hz, $C_6H_2F_3$), 138.28 (Ph-*C*), 132.32 (td, J = 10.7, 4.4 Hz, $C_6H_2F_3$), 128.82 (Ph-*C*), 128.74 (Ph-*C*), 126.83 (Ph-*C*), 119.46 (triazole-*C*), 106.25 – 104.26 (m, $C_6H_2F_3$), 32.19 (CH_2). ^{19}F NMR (564 MHz, $CDCl_3$): δ −130.52 (dd, J = 20.6, 7.9 Hz), −159.37 (tt, J = 20.5, 6.4 Hz). HRMS (ESI): *m/z* calcd for $C_{15}H_{11}N_3F_3$ $[M+H]^+$ 290.08996, found 290.09068.



An aqueous solution of $Cu(OAc)_2$ (2.5 mL, 0.4 M, 1 mmol) was added into a mixture of 3-phenyl-1-propyne (1.25 mL, 10 mmol) and hexyl azide[6] (12 mmol) in MeOH (50 mL). The reaction mixture was

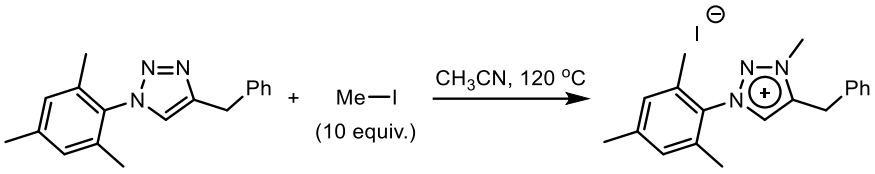
stirred at room temperature for 24 h. All volatiles were removed under vacuum. The residue was purified by column chromatography on silica eluted with ethyl acetate (0–20% gradient by volume) in hexanes. The product was isolated as a colorless oil. Yield: 2.2 g, 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 2H, Ph-*H*), 7.26 (ddd, *J* = 7.9, 1.7, 0.7 Hz, 2H, Ph-*H*), 7.24 – 7.19 (m, 1H, Ph-*H*), 7.13 (s, 1H, triazole-*H*), 4.31 – 4.23 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.09 (s, 2H, C*H*$_2$), 1.90 – 1.79 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.36 – 1.23 (m, 6H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.95 – 0.78 (m, 3H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.72 (triazole-*C*), 139.33 (Ph-*C*), 128.84 (Ph-*C*), 128.72 (Ph-*C*), 126.57 (Ph-*C*), 121.32 (triazole-*C*), 50.40 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 32.43 (*C*H$_2$), 31.24 (CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 30.37 (CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 26.26 (CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.51 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 14.03 (CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{15}H_{22}N_3$ $[M+H]^+$ 244.18082, found 244.18109.



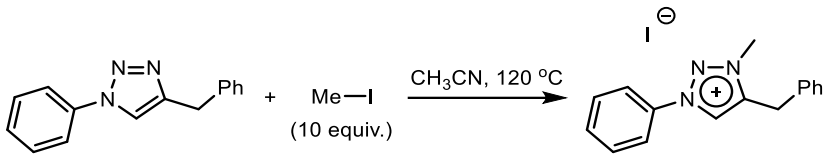
Pyrrolidine (1.6 mL, 20 mmol), 3,3-diphenylpropanal[7] (4.9 g, 22 mmol), and 2-azido-1,3,5-trimethylbenzene[8] (3.5 g, 20 mmol) were dissolved in 50 mL of THF. The reaction mixture was stirred at 60 °C for 12 h. Solid *m*-CPBA (10.4 g, 50% active oxidant, 30 mmol) was added to the reaction mixture at 0 °C and the mixture was warmed up to room temperature and stirred for 1 h. The reaction mixture was then concentrated to dryness under reduced pressure. The crude product was dissolved in EtOAc, washed with sat. $Na_2S_2O_3$ solution, 2M NaOH solution and brine, sequentially. The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel eluted with ethyl acetate (0–20% gradient by volume) in hexanes to afford 4-benzhydryl-1-mesityl-1H-1,2,3-triazole as a white solid. Yield: 5.1 g, 72%. ^{1}H NMR (600 MHz, $CDCl_3$):

δ 7.31 (td, *J* = 7.2, 1.4 Hz, 4H, Ph-*H*), 7.26 – 7.21 (m, 6H, Ph-*H*), 7.17 (d, *J* = 0.7 Hz, 1H, triazole-*H*), 7.00 – 6.89 (m, 2H, Mes-*H*), 5.76 (s, 1H, C*H*Ph$_2$), 2.33 (s, 3H, Mes-C*H*$_3$), 1.97 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.77 (triazole-*C*), 142.85 (Ph-*C*), 140.02 (Mes-*C*), 135.17 (Mes-*C*), 133.73 (Mes-*C*), 129.13 (Mes-*C*), 128.86 (Ph-*C*), 128.71 (Ph-*C*), 126.85 (Ph-*C*), 124.73 (triazole-*C*), 48.85 (*C*HPh$_2$), 21.24 (Mes-*C*H$_3$), 17.44 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{24}H_{23}N_3$ $[M+H]^+$ 354.1961, found 354.1961.

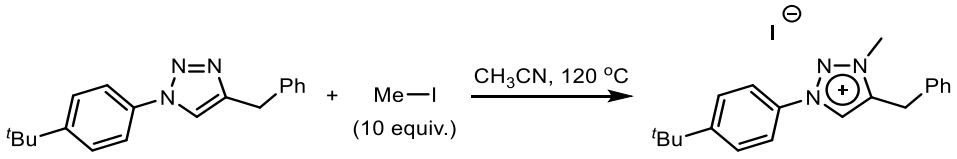
Syntheses of triazolium salts:



4-Benzyl-1-mesityl-1,2,3-triazole [1] (2.8 g, 10 mmol) and iodomethane (6.2 mL, 100 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording a white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. White solid. Yield: 3.5 g, 83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 1H, triazolium-*H*), 7.47 (dt, *J* = 6.2, 1.3 Hz, 2H, Ph-*H*), 7.35 – 7.30 (m, 2H, Ph-*H*), 7.30 – 7.24 (m, 1H, Ph-*H*), 6.98 (s, 2H, Mes-*H*) 4.76 (s, 2H, C*H*$_2$), 4.47 (s, 3H, N-C*H*$_3$), 2.32 (s, 3H, Mes-C*H*$_3$), 2.07 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.91 (triazolium-*C*), 142.54 (Mes-*C*), 134.42 (Mes-*C*), 133.28 (Ph-*C*), 131.20 (Mes-*C*), 131.00 (triazolium-*C*), 129.88 (Mes-*C*), 129.49 (Ph-*C*), 129.36 (Ph-*C*), 128.11 (Ph-*C*), 40.42 (N-*C*H$_3$), 30.63 (*C*H$_2$), 21.26 (Mes-*C*H$_3$), 18.12 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{19}H_{22}N_3$ $[M-I]^+$ 292.1808, found 292.1810.



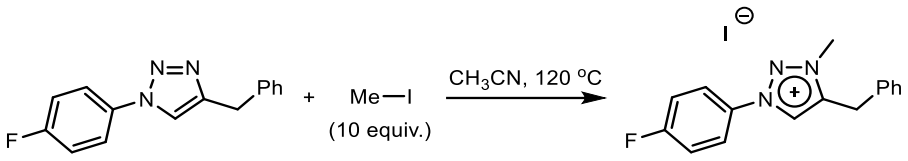
4-Benzyl-1-phenyl-1,2,3-triazole[2] (2.4 g, 10 mmol) and iodomethane (6.2 mL, 100 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording a white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. White solid. Yield: 2.6 g, 69%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.27 (s, 1H, triazolium-*H*), 7.91 – 7.79 (m, 2H, Ph-*H*), 7.52 – 7.46 (m, 3H, Ph-*H*), 7.46 – 7.41 (m, 2H, Ph-*H*), 7.27 – 7.21 (m, 2H, Ph-*H*), 7.22 – 7.17 (m, 1H, Ph-*H*), 4.59 (s, 2H, CH_2), 4.34 (s, 3H, N-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.18 (triazolium-*C*), 134.45 (Ph-*C*), 132.85 (Ph-*C*), 131.84 (Ph-*C*), 130.31 (Ph-*C*), 129.28 (Ph-*C*), 129.26 (Ph-*C*), 127.95 (Ph-*C*), 127.62 (triazolium-*C*), 121.34 (Ph-*C*), 40.03 (N-*C*H_3), 29.88 (*C*H_2). HRMS (ESI): *m/z* calcd for $C_{16}H_{16}N_3$ $[M-I]^+$ 250.1339, found 250.1339.



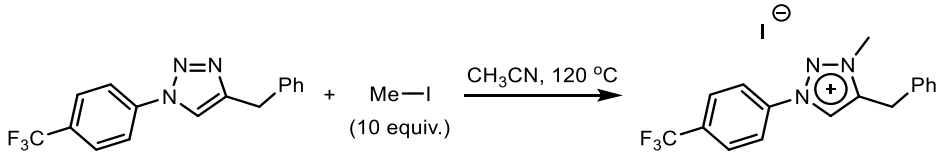
4-benzyl-1-(4-(*tert*-butyl)phenyl)-1,2,3-triazole (2.9 g, 10 mmol) and iodomethane (6.2 mL, 100 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording a white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. White solid. Yield: 3.3 g, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (s, 1H, triazolium-*H*), 7.86 – 7.77 (m, 2H, ^{t}Bu-C_6H_4-), 7.55 – 7.51 (m, 2H, ^{t}Bu-C_6H_4-), 7.47 – 7.43 (m, 2H, Ph-*H*), 7.30 – 7.26 (m, 2H, Ph-*H*), 7.25 – 7.21 (m, 1H, Ph-*H*), 4.65 (s, 2H, CH_2), 4.37 (s, 3H, N-

CH_3), 1.29 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.76 (^{t}Bu-C_6H_4-), 145.18 (triazolium-*C*), 133.07 (Ph-*C*), 132.18 (^{t}Bu-C_6H_4-), 129.40 (Ph-*C*), 129.38 (Ph-*C*), 128.06 (Ph-*C*), 127.68 (triazolium-*C*), 127.39 (^{t}Bu-C_6H_4-), 121.08 (^{t}Bu-C_6H_4-), 39.98 (N-*C*H_3), 35.15 (*C*(CH$_3$)$_3$), 31.10 (C(*C*H$_3$)$_3$), 30.04 (*C*H$_2$). HRMS (ESI): *m/z* calcd for $C_{20}H_{24}N_3$ $[M-I]^+$ 306.1965, found 306.1965.

Trimethyloxonium tetrafluoroborate (887.5 mg, 6 mmol, 1.2 equiv.) was added as solid to a stirring solution of 4-benzyl-1-(4-(pentyloxy)phenyl)-1,2,3-triazole (1.6 g, 5 mmol) in DCM (20 mL). The mixture was stirred at room temperature overnight. It was then filtered, concentrated under vacuum to ~10 mL and dropwise added into rapid stirring diethyl ether (50 mL). The white precipitate that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. White solid. Yield: 1.6 g, 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (s, 1H, triazolium-*H*), 7.74 – 7.61 (m, 2H, pentoxy-C_6H_4-), 7.34 – 7.27 (m, 4H, Ph-*H*), 7.28 – 7.21 (m, 1H, Ph-*H*), 7.00 – 6.90 (m, 2H, pentoxy-C_6H_4-), 4.28 (s, 2H, CH_2), 4.17 (s, 3H, N-CH_3), 3.95 (t, *J* = 6.5 Hz, 2H, CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.78 (dq, *J* = 8.2, 6.5 Hz, 2H, CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.49 – 1.30 (m, 4H, CH$_2$CH$_2$CH_2CH_2CH$_3$), 0.93 (t, *J* = 7.1 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.70 (pentoxy-C_6H_4-), 145.02 (triazolium-*C*), 133.41 (Ph-*C*), 129.48 (Ph-*C*), 129.26 (Ph-*C*), 128.03 (Ph-*C*), 127.69 (pentoxy-C_6H_4-), 126.44 (triazolium-*C*), 123.05 (pentoxy-C_6H_4-), 115.83 (pentoxy-C_6H_4-), 68.78 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 38.17 (N-*C*H$_3$), 29.16 (*C*H$_2$), 28.82 (CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.19 (CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.53 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$), 14.11 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{21}H_{26}N_3O$ $[M-BF_4]^+$ 336.2070, found 330.2071.

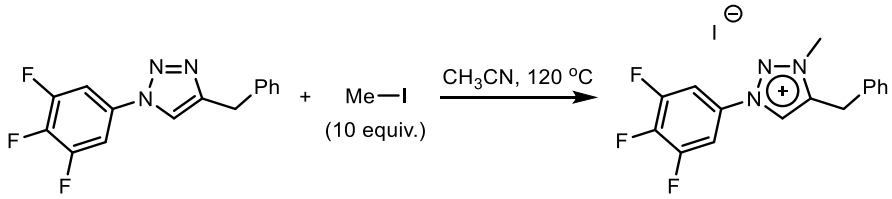


4-Benzyl-1-(4-fluorophenyl)-1,2,3-triazole[2] (2.5 g, 10 mmol) and iodomethane (6.2 mL, 100 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording a white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. Off-white solid. Yield: 2.9 g, 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.40 (s, 1H, triazolium-*H*), 7.99 (ddd, *J* = 9.1, 5.0, 2.5 Hz, 2H, F-C$_6$*H*$_4$-), 7.50 – 7.40 (m, 2H, Ph-*H*), 7.34 – 7.29 (m, 2H, Ph-*H*), 7.27 (dd, *J* = 6.9, 1.8 Hz, 1H, Ph-*H*), 7.26 – 7.20 (m, 2H, F-C$_6$*H*$_4$-), 4.59 (s, 2H, C*H*$_2$), 4.35 (s, 3H, N-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.21 (d, *J* = 254.6 Hz, F-*C*$_6$H$_4$-), 145.38 (triazolium-*C*), 132.83 (Ph-*C*), 130.82 (d, *J* = 3.3 Hz, F-*C*$_6$H$_4$-), 129.54 (Ph-*C*), 129.39 (Ph-*C*), 128.29 (triazolium-*C*), 128.25 (Ph-*C*), 124.18 (d, *J* = 9.1 Hz, F-*C*$_6$H$_4$-), 117.67 (d, *J* = 23.7 Hz, F-*C*$_6$H$_4$-), 40.03 (N-*C*H$_3$), 30.17 (*C*H$_2$). ^{19}F NMR (470 MHz, $CDCl_3$): δ −106.14 (tt, *J* = 8.0, 4.3 Hz). HRMS (ESI): *m/z* calcd for $C_{16}H_{15}N_3F$ $[M-I]^+$ 268.1245, found 268.1247.

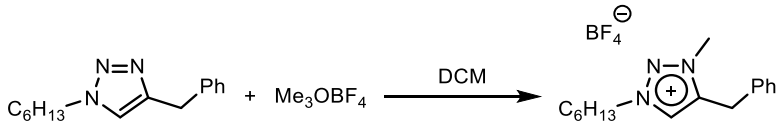


4-benzyl-1-(4-(trifluoromethyl)phenyl)-1,2,3-triazole[3] (3.0 g, 10 mmol) and iodomethane (6.2 mL, 100 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording an off-white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. Off-white solid. Yield: 3.8 g, 85%. ^{1}H NMR

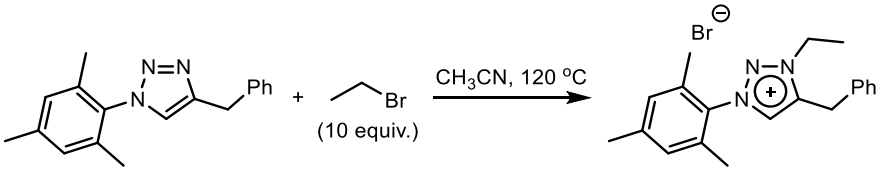
(500 MHz, $CDCl_3$): δ 9.70 (s, 1H, triazolium-*H*), 8.30 – 8.09 (m, 2H, CF_3-C_6H_4), 7.89 – 7.74 (m, 2H, CF_3-C_6H_4), 7.46 – 7.41 (m, 2H, Ph-*H*), 7.31 (ddt, *J* = 8.0, 6.4, 1.2 Hz, 2H, Ph-*H*), 7.28 – 7.24 (m, 1H, Ph-*H*), 4.61 (s, 2H, CH_2), 4.38 (s, 3H, N-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.68 (triazolium-*C*), 136.99 (m, CF_3-C_6H_4), 133.84 (q, *J* = 33.6 Hz, CF_3-C_6H_4), 132.66 (Ph-*C*), 129.58 (Ph-*C*), 129.35 (Ph-*C*), 128.61 (triazolium-*C*), 128.32 (Ph-*C*), 127.75 (q, *J* = 3.7 Hz, CF_3-C_6H_4), 123.00 (q, *J* = 273.0 Hz, CF_3), 122.34 (CF_3-C_6H_4), 40.28 (CH_2), 30.21 (N-CH_3). ^{19}F NMR (564 MHz, $CDCl_3$): δ −63.06. HRMS (ESI): *m/z* calcd for $C_{17}H_{15}N_3F_3$ $[M-I]^+$ 318.1213, found 318.1211.



4-Benzyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazole (2.9 g, 10 mmol) and iodomethane (6.2 mL, 100 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording an off-white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. White solid. Yield: 4.0 g, 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (s, 1H, triazolium-*H*), 7.93 – 7.83 (m, 2H, $C_6H_2F_3$), 7.47 – 7.41 (m, 2H, Ph-*H*), 7.36 – 7.25 (m, 3H, Ph-*H*), 4.57 (s, 2H, CH_2), 4.35 (s, 3H, N-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.69 (ddd, *J* = 256.0, 10.9, 4.5 Hz, $C_6H_2F_3$), 145.79 (triazolium-*C*), 142.05 (dt, *J* = 260.4, 14.8 Hz, $C_6H_2F_3$), 132.53 (Ph-*C*), 129.72 (dd, *J* = 10.7, 4.8 Hz, $C_6H_2F_3$), 129.59 (Ph-*C*), 129.37 (Ph-*C*), 129.06 (triazolium-*C*), 128.35 (Ph-*C*), 108.17 – 107.77 (m, $C_6H_2F_3$), 40.26 (N-CH_3), 30.23 (CH_2). ^{19}F NMR (470 MHz, $CDCl_3$): δ −127.69 (dt, *J* = 20.2, 6.5 Hz), −152.63 (tt, *J* = 20.5, 5.8 Hz). HRMS (ESI): *m/z* calcd for $C_{16}H_{13}N_3F_3$ $[M-I]^+$ 304.1056, found 304.1056.

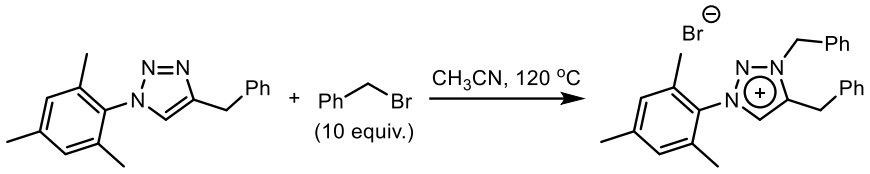


Trimethyloxonium tetrafluoroborate (700 mg, 4.7 mmol, 1.05 equiv.) was added as solid to a stirring solution of 4-benzyl-1-hexyl-1,2,3-triazole (1.1 g, 4.5 mmol) in DCM (20 mL). The mixture was stirred at room temperature overnight. It was then filtered, concentrated under vacuum to dryness leaving a pale yellow oil. Yield: 1.4 g, 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H, triazolium-*H*), 7.36 – 7.31 (m, 2H, Ph-*H*), 7.29 – 7.25 (td, *J* = 6.0, 1.4 Hz, 3H, Ph-*H*), 4.52 – 4.37 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.22 (s, 2H, C*H*$_2$), 4.10 (s, 3H, N-C*H*$_3$), 2.00 – 1.90 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.38 – 1.20 (m, 6H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.90 – 0.79 (m, 3H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.11 (triazolium-*C*), 133.35 (Ph-*H*), 129.54 (Ph-*H*), 129.09 (Ph-*H*), 128.92 (triazolium-*C*), 128.11 (Ph-*H*), 54.12 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 37.89 (N-*C*H$_3$), 31.01 (CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 29.20, 29.18, 25.86 (CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 22.40 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.99 (CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{16}H_{24}N_3$ $[M-BF_4]^+$ 258.1965, found 258.1961.

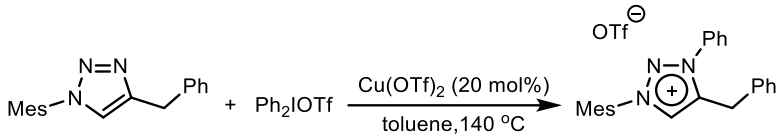


4-Benzyl-1-mesityl-1,2,3-triazole[1] (2.5 g, 8.9 mmol) and bromoethane (6.6mL, 89 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording an off-white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. Off-white solid. Yield: 2.6 g, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.99 (s, 1H, triazolium-*H*), 7.50 – 7.37 (m, 2H, Ph-*H*), 7.33 – 7.27 (m, 2H, Ph-*H*), 7.26 – 7.21 (m, 1H, Ph-*H*),

6.98 (s, 2H, Mes-*H*), 4.82 (s, 2H, CH_2), 4.77 (q, J = 7.3 Hz, 2H, CH_2CH$_3$), 2.32 (s, 3H, Mes-CH_3), 2.03 (s, 6H, Mes-CH_3), 1.47 (t, J = 7.2 Hz, 3H, CH$_2$CH_3). ^{13}C NMR (126 MHz, CDCl$_3$): δ 145.02 (triazolium-*C*), 142.45 (Mes-*C*), 134.28 (Ph-*C*), 133.97 (Mes-*C*), 131.70 (triazolium-*C*), 131.40 (Mes-*C*), 129.87 (Mes-*C*), 129.41 (Ph-*C*), 129.17 (Ph-*C*), 127.89 (Ph-*C*), 48.41 (*C*H$_2$CH$_3$), 29.83 (*C*H$_2$), 21.24 (Mes-*C*H$_3$), 17.67 (Mes-*C*H$_3$), 13.58 (CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd for C$_{20}$H$_{24}$N$_3$ [M−Br]$^+$ 306.1965, found 306.1964.



4-Benzyl-1-mesityl-1,2,3-triazole[1] (1.8 g, 6.5 mmol) and benzyl bromide (7.7 mL, 65 mmol, 10 equiv.) were mixed in 20 mL of acetonitrile. The mixture was stirred at 120 °C overnight. All volatiles were removed under vacuum. The oily residue was stirred with 50 mL of diethyl ether affording an off-white suspension. The solid that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. Off-white solid. Yield: 2.1 g, 72%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.68 (s, 1H, triazolium-*H*), 7.34 – 7.27 (m, 5H, Ph-*H*), 7.25 – 7.18 (m, 5H, Ph-*H*), 6.96 (s, 2H, Mes-*H*), 6.03 (s, 2H, CH_2), 4.67 (s, 2H, CH_2), 2.30 (s, 3H, Mes-CH_3), 2.02 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, CDCl$_3$): δ 145.64 (triazolium-*C*), 142.54 (Mes-*C*), 134.19 (Mes-*C*), 133.64 (Ph-*C*), 131.79 (Ph-*C*), 131.24 (triazolium-*C*), 131.03 (Mes-*C*), 129.85 (Ph-*C*), 129.60 (Mes-*C*), 129.43 (Ph-*C*), 129.35 (Ph-*C*), 129.16 (Ph-*C*), 128.43 (Ph-*C*), 127.91 (Ph-*C*), 56.39 (*C*H$_2$), 30.18 (*C*H$_2$), 21.21 (Mes-*C*H$_3$), 17.67 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd for C$_{16}$H$_{15}$N$_3$ [M−Br−C$_9$H$_{11}$+H]$^+$ 250.1339, found 250.1340.



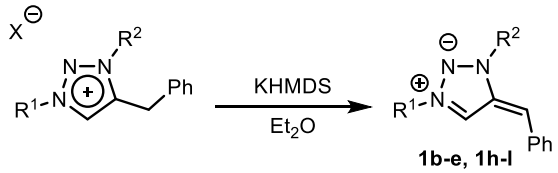
4-Benzyl-1-mesityl-1,2,3-triazole[1] (1.2 g, 4.3 mmol), diphenyliodonium triflate[9] (2.8 g, 6.5 mmol, 1.5 equiv.), $Cu(OTf)_2$ (311 mg, 0.86 mmol) and toluene (20 mL) were mixed in a Schlenk tube. The tube was sealed and the mixture was stirred at 140 °C overnight. All volatiles were removed under vacuum. The residue was purified by chromatography eluted with acetone (0–20% gradient by volume) in DCM to afford a pale brown sticky foam. Yield: 1.1 g, 51%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (s, 1H, triazolium-*H*), 7.72 – 7.66 (m, 3H, Ph-*H*), 7.62 (ddt, *J* = 8.5, 7.6, 1.4 Hz, 2H, Ph-*H*), 7.29 – 7.18 (m, 3H, Ph-*H*), 7.18 – 7.09 (m, 2H, Ph-*H*), 7.03 (s, 2H, Mes-*H*), 4.42 (s, 2H, C*H*$_2$), 2.35 (s, 3H, Mes-C*H*$_3$), 2.14 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.50 (triazolium-*C*), 142.77 (Mes-*C*), 134.46 (Mes-*C*), 134.01, 133.36, 132.62 (Ph-*C*), 131.66 (triazolium-*C*), 131.36 (Mes-*C*), 130.43 (Ph-*C*), 130.04 (Mes-*C*), 129.38 (Ph-*C*), 129.01 (Ph-*C*), 127.96 (Ph-*C*), 126.04 (Ph-*C*), 120.87 (q, *J* = 320.5 Hz, *C*F_3SO_3), 30.35 (*C*H_2), 21.31 (Mes-*C*H_3), 17.44 (Mes-*C*H_3). HRMS (ESI): *m/z* calcd for $C_{24}H_{24}N_3$ $[M-OTf]^+$ 354.1965, found 354.1957.

Methyl triflate (1.3 mL, 12 mmol, 1.2 equiv.) was added to a stirring solution of 4-benzhydryl-1-mesityl-1,2,3-triazole (3.5 g, 10 mmol) in DCM (20 mL). The mixture was stirred at room temperature overnight. It was then filtered, concentrated under vacuum to ~10 mL and dropwise added into rapid stirring diethyl ether (50 mL). The white precipitate that formed was collected by filtration, washed with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum. White solid. Yield: 4.4 g, 85%. ^{1}H NMR (500

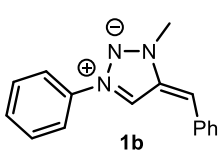
MHz, $CDCl_3$): δ 7.43 – 7.37 (m, 5H, Ph-*H*, triazolium-*H*, overlap), 7.35 – 7.31 (m, 2H, Ph-*H*), 7.31 – 7.28 (m, 4H, Ph-*H*), 7.02 (q, *J* = 0.7 Hz, 2H, Mes-*H*), 6.24 (s, 1H, C*H*Ph_2), 4.16 (s, 3H, N-CH_3), 2.34 (s, 3H, Mes-CH_3), 2.09 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.23 (triazolium-*C*), 142.83 (Mes-*C*), 137.33 (Ph-*C*), 134.57 (Mes-*C*), 131.25 (triazolium-*C*), 130.93 (Mes-*C*), 129.98 (Mes-*C*), 129.79 (Ph-*C*), 128.74 (Ph-*C*), 128.56 (Ph-*C*), 124.77 – 117.12 (q, *J* = 320.4 Hz, *C*F_3SO_3), 46.08 (*C*HPh_2), 39.61 (N-*C*H_3), 21.31 (Mes-*C*H_3), 17.35 (Mes-*C*H_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{26}N_3$ $[M-OTf]^+$ 368.2121, found 368.2120.

Syntheses of mNHOs:

mNHO **1a**[1] was synthesized according to literature. mNHO **1f** and **1g** were prepared in *situ* at low temperatures due to their thermal instabilities.

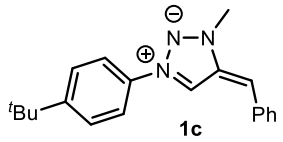


To a mixture of triazolium salt (2 mmol) and KHMDS (399.0 mg, 2 mmol) was added diethyl ether (10 mL). The reaction mixture instantaneously turned dark color. The reaction mixture was stirred for 1 h at room temperature and then filtered through Celite. All volatiles were removed under reduced pressure to afford a crystalline solid of **1b–e** and **1h–l**. The solid was washed with *n*-pentane (3 × 5 mL) and dried under vacuum.



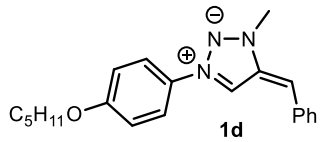
Blue purple crystalline solid. Yield: 395.2 mg, 79%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.50 – 7.41 (m, 2H, Ph-*H*), 7.27 – 7.22 (m, 2H,

Ph-*H*), 7.17 (s, 1H, triazole-*H*), 7.07 (dt, *J* = 6.7, 1.7 Hz, 2H, Ph-*H*), 6.97 – 6.84 (m, 4H, Ph-*H*), 4.29 (s, 1H, C*H*), 2.89 (s, 3H, N-CH_3). ^{13}C NMR (126 MHz, C_6D_6): δ 143.68, 143.57, 136.64 (Ph-*C*), 129.52 (Ph-*C*), 129.51 (Ph-*C*), 129.05 (Ph-*C*), 121.42 (Ph-*C*), 120.44 (Ph-*C*), 117.06 (Ph-*C*), 105.76 (triazole-*C*), 65.62 (*C*H), 33.61 (N-*C*H_3). Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 76.83; H, 6.27; N, 16.75.



1c

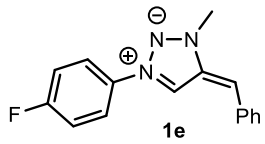
Blue purple crystalline solid. Yield: 517.2 mg, 85%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.47 (t, *J* = 7.6 Hz, 2H, Ph-*H*), 7.33 – 7.25 (m, 3H, overlapping, , Ph-*H* and triazole-*H*), 7.15 (d, *J* = 8.4 Hz, 2H, ^{t}Bu-C$_6H_4$), 7.08 (d, *J* = 8.7 Hz, 2H, ^{t}Bu-C$_6H_4$), 6.93 (t, *J* = 7.2 Hz, 1H, Ph-*H*), 4.34 (s, 1H, C*H*), 2.93 (s, 3H, N-CH_3), 1.11 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (126 MHz, C_6D_6): δ 153.00 (^{t}Bu-*C*$_6$H$_4$), 143.75 (triazole-*C*), 143.65 (Ph-*C*), 134.48 (^{t}Bu-*C*$_6$H$_4$), 129.07, 126.55 (^{t}Bu-*C*$_6$H$_4$), 121.46 (Ph-*C*), 120.48 (^{t}Bu-*C*$_6$H$_4$), 117.08 (Ph-*C*), 106.05 (triazole-*C*), 65.65 (*C*H), 34.66 (*C*(CH$_3$)$_3$), 33.61 (N-*C*H$_3$), 31.13 (C(*C*H$_3$)$_3$). Anal. Calcd for $C_{20}H_{23}N_3$: C, 78.65; H, 7.59; N, 13.76. Found: C, 78.20; H, 7.69; N, 13.88.



1d

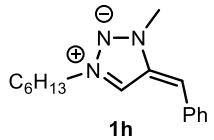
Blue purple crystalline solid. Yield: 472.3 mg, 70%. Crystals suitable for X-ray crystallography were obtained by slow evaporation of a concentrated diethyl ether solution at room temperature. ^{1}H NMR (500 MHz, C_6D_6): δ 7.46 (t, *J* = 7.5 Hz, 2H, Ph-*H*), 7.32 – 7.25 (m, 2H, Ph-*H*), 7.22 (s, 1H, triazole-*H*), 7.10 (d, *J* = 9.1 Hz, 2H, pentoxy-C$_6H_4$-), 6.93 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.64 – 6.57 (m, 2H, pentoxy-C$_6H_4$-), 4.34 (s, 1H, C*H*), 3.51 (t, *J* = 6.5 Hz, 2H, CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 2.95 (s, 3H, N-CH_3), 1.64 – 1.46 (m, 2H, CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.34 – 1.14 (m, 4H, CH$_2$CH$_2$CH_2CH_2CH$_3$), 0.87 (t, *J* = 7.1 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (126

MHz, C_6D_6): δ 160.35 (pentoxy-*C*$_6$H$_4$-), 143.74, 143.69, 129.92 (pentoxy-*C*$_6$H$_4$-), 129.06 (Ph-*C*), 122.03 (Ph-*C*), 121.41 (pentoxy-*C*$_6$H$_4$-), 116.98 (Ph-*C*), 115.14 (pentoxy-*C*$_6$H$_4$-), 105.96 (triazole-*C*), 68.35 (*C*H), 65.56 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 33.57 (N-*C*H$_3$), 29.12 (CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.42 (CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.76 (CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 14.20 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd. for $C_{21}H_{25}N_3O$•0.1$C_4H_{10}O$: C, 74.94; H, 7.64; N, 12.26. Found: C, 74.40; H, 8.19; N, 12.77.



1e

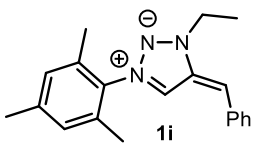
Blue purple crystalline solid. Yield: 469.5 mg, 88%. Crystals suitable for X-ray crystallography were obtained by top-layering a concentrated THF solution with pentane and cooled to −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.52 – 7.42 (m, 2H, Ph-*H*), 7.30 – 7.22 (m, 2H, Ph-*H*), 7.05 (s, 1H, triazole-*H*), 6.94 (tt, *J* = 7.2, 1.2 Hz, 1H, Ph-*H*), 6.82 (dd, *J* = 9.0, 4.5 Hz, 2H, F-C$_6$*H*$_4$-), 6.58 – 6.46 (m, 2H, 2H, F-C$_6$*H*$_4$-), 4.31 (s, 1H, C*H*), 2.88 (s, 3H, N-C*H*$_3$). ^{13}C NMR (126 MHz, C_6D_6): δ 162.92 (d, *J* = 249.7 Hz, F-*C*$_6$H$_4$-), 143.62 (triazole-*C*), 143.40 (Ph-*C*), 132.77 (d, *J* = 3.0 Hz, F-*C*$_6$H$_4$-), 129.07 (Ph-*C*), 122.40 (d, *J* = 8.7 Hz, F-*C*$_6$H$_4$-), 121.54 (Ph-*C*), 117.44 (Ph-*C*), 116.35 (d, *J* = 23.2 Hz, F-*C*$_6$H$_4$-), 105.92 (triazole-*C*), 65.87 (*C*H), 33.55 (N-*C*H$_3$). ^{19}F NMR (470 MHz, C_6D_6): δ −110.86 (tt, *J* = 8.2, 4.4 Hz). Anal. Calcd for $C_{16}H_{14}N_3F$: C, 71.89; H, 5.28; N, 15.72. Found: C, 70.49; H, 5.64; N, 15.59.



1h

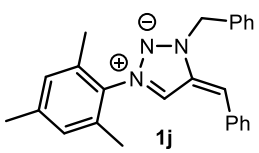
Red crystalline solid. Yield: 377.6 mg, 73%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.47 – 7.40 (m, 2H, Ph-*H*), 7.20 (dd, *J* = 8.5, 1.2 Hz, 2H, Ph-*H*), 6.88 (tt, *J* = 7.2, 1.2 Hz, 1H, Ph-*H*), 6.74 (s, 1H, triazole-*H*), 4.29 (s, 1H, C*H*), 3.15 (t, *J* = 7.3 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 2.90 (s, 3H, N-CH$_3$), 1.24 (p, J = 7.3 Hz, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.13 – 1.06 (m, 2H, CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.97 (ddd, *J* = 13.7, 9.1, 6.8 Hz, 2H, CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_3$),

0.94 – 0.83 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 0.80 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$). ^{13}C NMR (126 MHz, C_6D_6): δ 143.95, 143.63, 129.02 (Ph-*C*), 121.14 (Ph-*C*), 116.52 (Ph-*C*), 108.06 (triazole-*C*), 65.04 (*C*H), 51.72 ($CH_2CH_2CH_2CH_2CH_2CH_3$), 33.34 (N-CH_3), 31.30 ($CH_2CH_2CH_2CH_2CH_2CH_3$), 29.29 ($CH_2CH_2CH_2CH_2CH_2CH_3$), 26.13 ($CH_2CH_2CH_2CH_2CH_2CH_3$), 22.66 ($CH_2CH_2CH_2CH_2CH_2CH_3$), 14.13 ($CH_2CH_2CH_2CH_2CH_2CH_3$). Anal. Calcd. for $C_{16}H_{23}N_3$: C, 74.67; H, 9.01; N, 16.33. Found: C, 74.30; H, 8.51; N, 15.90.



1i

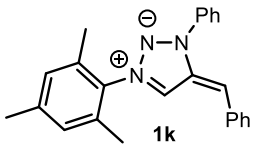
Purple crystalline solid. Yield: 550.7 mg, 90%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.44 – 7.36 (m, 2H, Ph-*H*), 7.18 – 7.12 (m, 2H, Ph-*H*), 6.90 (tt, J = 7.2, 1.2 Hz, 1H, Ph-*H*), 6.83 (s, 1H, triazole-*H*), 6.54 (s, 2H, Mes-*H*), 4.47 (s, 1H, C*H*), 3.52 (q, J = 7.2 Hz, 2H, CH_2CH_3), 1.99 (s, 3H, Mes-CH_3), 1.85 (s, 6H, Mes-CH_3), 1.10 (t, J = 7.2 Hz, 3H, CH_2CH_3). ^{13}C NMR (126 MHz, C_6D_6): δ 143.70 (Ph-*C*), 142.57 (triazole-*C*), 140.25 (Mes-*C*), 134.93 (Mes-*C*), 133.91 (Mes-*C*), 129.27 (Mes-*C*), 128.99 (Ph-*C*), 121.40 (Ph-*C*), 116.77 (Ph-*C*), 110.73 (triazole-*C*), 65.52 (*C*H), 42.08 (CH_2CH_3), 20.93 (Mes-CH_3), 16.65 (Mes-CH_3), 12.20 (CH_2CH_3). Anal. Calcd for $C_{20}H_{23}N_3$: C, 78.65; H, 7.59; N, 13.76. Found: C, 78.11; H, 7.83; N, 13.95.



1j

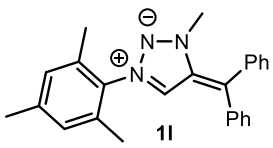
Purple crystalline solid. Yield: 620.5 mg, 84%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.37 – 7.32 (m, 2H, Ph-*H*), 7.21 – 7.17 (m, 2H, Ph-*H*), 7.11 (t, J = 7.6 Hz, 2H, Ph-*H*), 7.09 – 7.06 (m, 2H, Ph-*H*), 7.05 – 7.00 (m, 1H, Ph-*H*), 6.91 – 6.85 (m, 1H, Ph-*H*), 6.84 (s, 1H, triazole-*H*), 6.52 (s, 2H, Mes-*H*), 4.81 (s, 2H, CH_2), 4.58 (s, 1H, C*H*), 1.98 (s, 3H, Mes-CH_3), 1.87 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, C_6D_6): δ 143.29, 143.05, 140.29

(Mes-*C*), 135.78 (Ph-*C*), 134.90 (Mes-*C*), 133.84 (Mes-*C*), 129.28 (Mes-*C*), 128.96 (Ph-*C*), 128.91 (Ph-*C*), 127.91 (Ph-*C*), 127.78 (Ph-*C*), 121.70 (Ph-*C*), 117.26 (Ph-*C*), 111.12 (triazole-*C*), 66.71 (*C*H), 50.37 (*C*H_2), 20.92 (Mes-*C*H_3), 16.69 (Mes-*C*H_3). Anal. Calcd. for $C_{25}H_{25}N_3$: C, 81.71; H, 6.86; N, 11.43. Found: C, 81.33; H, 7.59; N, 12.07.



1k

From 1.1 g (2.2 mmol) of 4-benzyl-1-mesityl-3-phenyl-1,2,3-triazolium triflate and 438.9 mg, 2.2 mmol of KHMDS. Blue green crystalline solid. Yield: 551.0 mg, 71%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.79 – 7.74 (m, 2H, Ph-*H*), 7.38 – 7.31 (m, 2H, Ph-*H*), 7.15 – 7.12 (m, 2H, Ph-*H*), 7.11 – 7.06 (m, 2H, Ph-*H*), 6.97 (d, *J* = 0.7 Hz, 1H, triazole-*H*), 6.92 (tq, *J* = 7.2, 1.3 Hz, 2H, Ph-*H*), 6.54 (q, *J* = 0.8 Hz, 1H, Mes-*H*), 5.45 (s, 1H, C*H*), 1.98 (s, 3H, Mes-CH_3), 1.93 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, C_6D_6): δ 142.71, 142.69, 140.33 (Mes-*C*), 138.63 (Ph-*C*), 134.89 (Mes-*C*), 133.82 (Mes-*C*), 129.63 (Ph-*C*), 129.32 (Mes-*C*), 128.98 (Ph-*C*), 127.11 (Ph-*C*), 123.83 (Ph-*C*), 122.54 (Ph-*C*), 118.53 (Ph-*C*), 111.25 (triazole-*C*), 70.21 (*C*H), 20.92 (Mes-*C*H_3), 16.71 (Mes-*C*H_3). Anal. Calcd. for $C_{24}H_{23}N_3$•0.2$C_4H_{10}O$: C, 80.88; H, 6.84; N, 11.41. Found: C, 80.82; H, 6.64; N, 11.64.

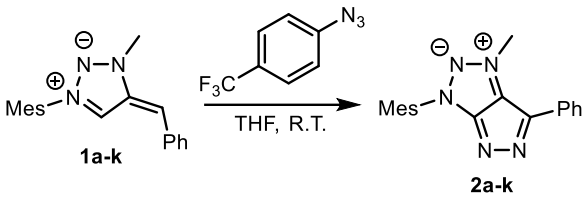


1l

Dark green crystalline solid. Yield: 541.2 mg, 74%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.55 (dq, *J* = 8.6, 1.8 Hz, 4H, Ph-*H*), 7.29 – 7.20 (m, 4H, Ph-*H*), 6.97 (s, 1H, triazole-*H*), 6.92 (tt, *J* = 7.2, 1.2 Hz, 2H, Ph-*H*), 6.51 – 6.44 (m, 2H, Mes-*H*), 2.94 (s, 3H, N-CH_3), 1.96 (s, 3H, Mes-CH_3), 1.86 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, C_6D_6): δ 146.66 (triazole-*C*), 146.07 (Ph-*C*), 140.21 (Mes-*C*), 134.56 (Mes-*C*), 133.44 (Mes-*C*), 129.29 (Mes-*C*),

128.87 (Ph-*C*), 127.44 (Ph-*C*), 121.07 (Ph-*C*), 118.91 (triazole-*C*), 79.04 (*C*Ph$_2$), 38.40 (N-*C*H$_3$), 20.89 (Mes-*C*H$_3$), 16.70 (Mes-*C*H$_3$). Anal. Calcd. for $C_{25}H_{25}N_3$•0.1C_5H_{12}: C, 81.74; H, 7.05; N, 11.21. Found: C, 82.39; H, 6.76; N, 10.83.

Syntheses of pyrazolo[3,4-d][1,2,3]triazoles:

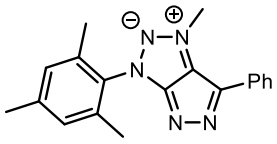


From isolated mNHO 1a-e and 1h-k:

To a stirring solution of mNHO (0.5 mmol) in THF (5 mL) was added 1-azido-4-(trifluoromethyl)benzene (93.6 mg, 0.5 mmol) in THF (2 mL). The reaction mixture instantaneously turned from dark color to orange brown color. The reaction mixture was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel eluted with DCM with 1% Et$_3$N to afford desired pyrazolo[3,4-d][1,2,3]triazoles.

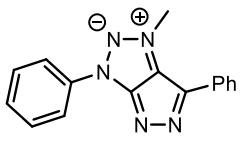
From *in situ* generated mNHO 1f/1g:

To a cold (−80°C) mixture of triazolium salt (0.5 mmol) and KHMDS (99.7 mg, 0.5 mmol) was added pre-cooled (−80°C) THF (5 mL). The reaction mixture was stirred at −80°C for 30 min. A pre-cooled (−80°C) solution of 1-azido-4-(trifluoromethyl)benzene (93.6 mg, 0.5 mmol) in THF (5 mL) was then added to the mixture. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. All volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel eluted with DCM with 1% Et$_3$N to afford desired pyrazolo[3,4-d][1,2,3]triazoles.



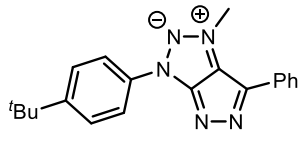
2a

Yellow solid. 136.7 mg, 86%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 – 7.85 (m, 2H, Ph-*H*), 7.54 – 7.40 (m, 2H, Ph-*H*), 7.36 – 7.29 (m, 1H, Ph-*H*), 7.04 (s, 2H, Mes-*H*), 4.49 (s, 3H, N-CH_3), 2.37 (s, 3H, Mes-CH_3), 2.11 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.82 (N-*C*-N), 141.38 (Mes-*C*), 135.53 (Mes-*C*), 133.93 (triazole-*C*(N)-Ph), 133.07 (Ph-*C*), 130.32 (N-*C*-C), 129.80 (Mes-*C*), 129.69 (Mes-*C*), 129.04 (Ph-*C*), 127.22 (Ph-*C*), 126.65 (Ph-*C*), 40.07 (N-*C*H_3), 21.33 (Mes-*C*H_3), 17.86 (Mes-*C*H_3). HRMS (ESI): *m/z* calcd for $C_{19}H_{20}N_5$ $[M+H]^+$ 318.1713, found 318.1727. The reaction at 5 mmol scale (1.46 g of **1a**, 0.94 g of 1-azido-4-(trifluoromethyl)benzene) afforded 1.29 g of **2a** (81% yield).



2b

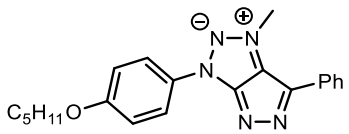
Yellow solid. 125.6 mg, 91%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (dd, *J* = 7.5, 1.3 Hz, 2H, Ph-*H*), 7.85 – 7.73 (m, 2H, Ph-*H*), 7.63 – 7.52 (m, 2H, Ph-*H*), 7.50 – 7.43 (m, 1H, Ph-*H*), 7.38 (dd, *J* = 8.4, 7.1 Hz, 2H, Ph-*H*), 7.31 – 7.18 (m, 1H, Ph-*H*), 4.45 (s, 3H, N-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.77 (N-*C*-N), 135.63 (Ph-*C*), 133.84 (Ph-*C*), 132.44 (triazole-*C*(N)-Ph), 130.60 (N-*C*-C), 129.98 (Ph-*C*), 129.31 (Ph-*C*), 129.00 (Ph-*C*), 127.37 (Ph-*C*), 126.59 (Ph-*C*), 119.75 (Ph-*C*), 40.23 (N-CH_3). HRMS (ESI): *m/z* calcd for $C_{16}H_{14}N_5$ $[M+H]^+$ 276.12437, found 276.12444.



2c

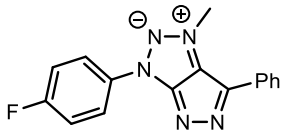
Yellow solid. 146.5 mg, 88%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 – 8.19 (m, 2H, ^{t}Bu-C_6H_4-), 7.80 – 7.77 (m, 2H, Ph-*H*), 7.62 – 7.55 (m, 2H, ^{t}Bu-C_6H_4-), 7.42 – 7.34 (m, 2H, Ph-*H*), 7.25 – 7.21 (m,

1H, Ph-*H*), 4.44 (s, 3H, N-CH_3), 1.38 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.77 (N-*C*-N), 152.81 (^{t}Bu-*C*$_6$H$_4$-), 133.71 (Ph-*C*), 133.15 (^{t}Bu-*C*$_6$H$_4$-), 132.55 (triazole-*C*(N)-Ph), 130.48 (N-*C*-C), 128.96 (Ph-*C*), 127.27 (Ph-*C*), 126.88 (Ph-*C*), 126.55 (^{t}Bu-*C*$_6$H$_4$-), 119.48 (^{t}Bu-*C*$_6$H$_4$-), 40.13 (N-*C*H$_3$), 35.05 (*C*(CH$_3$)$_3$), 31.37 (C(*C*H$_3$)$_3$). HRMS (ESI): *m/z* calcd for $C_{20}H_{22}N_5$ $[M+H]^+$ 332.18697, found 332.18755.



2d

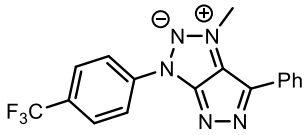
Yellow solid. 174.9 mg, 97%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 – 8.05 (m, 2H, pentoxy-C$_6$*H*$_4$-), 7.73 – 7.61 (m, 2H, Ph-*H*), 7.27 (t, *J* = 7.6 Hz, 2H, Ph-*H*), 7.19 – 7.09 (m, 1H, Ph-*H*), 7.03 – 6.88 (m, 2H, pentoxy-C$_6$*H*$_4$-), 4.28 (s, 3H, N-C*H*$_3$), 3.95 (t, *J* = 6.6 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.92 – 1.71 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.57 – 1.28 (m, 4H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.94 (t, *J* = 7.1 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.55 (pentoxy-*C*$_6$H$_4$-), 156.55 (N-*C*-N), 133.45 (triazole-*C*(N)-Ph), 132.60 (Ph-*C*), 130.23 (N-*C*-C), 128.76 (Ph-*C*), 128.62 (pentoxy-*C*$_6$H$_4$-), 126.87 (Ph-*C*), 126.06 (Ph-*C*), 120.95 (pentoxy-*C*$_6$H$_4$-), 115.26 (pentoxy-*C*$_6$H$_4$-), 68.50 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 39.97 (N-*C*H$_3$), 28.92 (CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.21 (CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.53 (CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 14.09 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{21}H_{24}N_5O$ $[M+H]^+$ 362.1975, found 362.1978.



2e

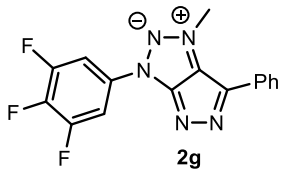
Yellow solid. 108.7 mg, 74%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 – 8.29 (m, 2H, F-C$_6$*H*$_4$-), 7.85 – 7.76 (m, 2H, Ph-*H*), 7.48 – 7.36 (m, 2H, Ph-*H*), 7.32 – 7.24 (m, 3H, overlapping, F-C$_6$*H*$_4$- and Ph-*H*), 4.46 (s, 3H, N-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.65 (d, *J* = 250.6 Hz, F-*C*$_6$H$_4$-), 156.66 (N-*C*-N),

134.06 (triazole-*C*(N)-Ph), 132.44 (Ph-*C*), 131.84 (d, *J* = 3.1 Hz, F-*C*$_6$H$_4$-), 130.69 (N-*C*-C), 129.05 (Ph-*C*), 127.47 (Ph-*C*), 126.65 (Ph-*C*), 121.76 (d, *J* = 8.7 Hz, F-*C*$_6$H$_4$-), 117.08 (d, *J* = 23.4 Hz, F-*C*$_6$H$_4$-), 40.22 (N-*C*H$_3$). ^{19}F NMR (470 MHz, CDCl$_3$): δ −110.72 (tt, *J* = 8.2, 5.3 Hz). HRMS (ESI): *m/z* calcd for C$_{16}$H$_{13}$N$_5$F [M+H]$^+$ 294.1150, found 294.1162.



2f

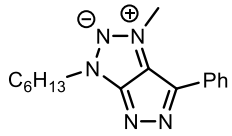
Yellow solid. 119.8 mg, 70%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.48 (dd, *J* = 8.7, 2.3 Hz, 2H, CF$_3$-C$_6$*H*$_4$-), 7.85 (ddt, *J* = 8.4, 1.5, 0.8 Hz, 2H, CF$_3$-C$_6$*H*$_4$-), 7.81 – 7.75 (m, 2H, Ph-*H*), 7.39 (td, *J* = 8.0, 2.4 Hz, 2H, Ph-*H*), 7.30 – 7.23 (m, 1H, Ph-*H*), 4.49 (d, *J* = 1.0 Hz, 3H, N-C*H*$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 156.81 (N-*C*-N), 138.05 (m, CF$_3$-*C*$_6$H$_4$-), 134.33 (triazole-*C*(N)-Ph), 132.23 (Ph-*C*), 131.06 (q, *J* = 33.3 Hz, CF$_3$-*C*$_6$H$_4$-), 130.83 (N-*C*-C), 129.04 (Ph-*C*), 127.55 (Ph-*C*), 127.25 (q, *J* = 3.8 Hz, CF$_3$-*C*$_6$H$_4$-), 126.54 (Ph-*C*), 123.61 (q, *J* = 272.3 Hz, *C*F$_3$), 119.91 (CF$_3$-*C*$_6$H$_4$-), 40.49 (N-CH$_3$). ^{19}F NMR (470 MHz, CDCl$_3$): δ −62.68. HRMS (ESI): *m/z* calcd for C$_{17}$H$_{13}$N$_5$F$_3$ [M+H]$^+$ 344.11176, found 344.11185.



2g

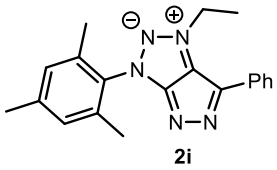
Yellow solid. 79.6 mg, 48%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.19 – 8.03 (m, 2H, C$_6$*H*$_2$F$_3$), 7.86 – 7.75 (m, 2H, Ph-*H*), 7.50 – 7.40 (m, 2H, Ph-*H*), 7.36 – 7.28 (m, 1H, Ph-*H*), 4.50 (s, 3H, N-C*H*$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 156.55 (N-*C*-N), 153.43 – 150.30 (m, *C*$_6$H$_2$F$_3$), 140.22 (d, *J* = 255.9 Hz, *C*$_6$H$_2$F$_3$), 134.69 (triazole-*C*(N)-Ph), 132.20 (Ph-*C*), 131.03 (N-*C*-C), 130.69 (m, *C*$_6$H$_2$F$_3$), 129.14 (Ph-*C*), 127.76 (Ph-*C*), 126.73 (Ph-*C*), 105.36 – 104.80 (m, *C*$_6$H$_2$F$_3$), 40.46 (N-*C*H$_3$). ^{19}F NMR (564 MHz, CDCl$_3$): δ

−129.43 (dd, J = 20.5, 7.7 Hz), −157.58 (t, J = 20.7 Hz). HRMS (ESI): *m/z* calcd for $C_{16}H_{11}N_5F_3$ $[M+H]^+$ 330.09611, found 330.09652.



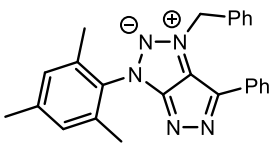
2h

Pale yellow to colorless solid. 105.9 mg, 75%. Crystals suitable for X-ray crystallography were obtained by slow evaporation of an acetone solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 – 7.76 (m, 2H, Ph-*H*), 7.45 – 7.38 (m, 2H, Ph-*H*), 7.31 – 7.26 (m, 1H, Ph-*H*), 4.49 (t, J = 7.4 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.34 (s, 3H, N-C*H*$_3$), 2.19 – 2.05 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.47 – 1.26 (m, 6H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.95 – 0.80 (m, 3H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.43 (N-*C*-N), 133.54 (triazole-*C*(N)-Ph), 133.08 (Ph-*C*), 129.86 (N-*C*-C), 128.97 (Ph-*C*), 127.05 (Ph-*C*), 126.49 (Ph-*C*), 50.29 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 39.71 (N-*C*H$_3$), 31.17 (CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 28.63 (CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 26.30 (CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 22.50 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 14.06 (CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). $C_{16}H_{22}N_5$ $[M+H]^+$ 284.18697, found 284.18649.



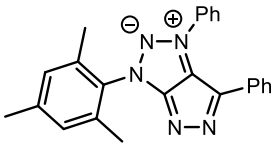
2i

Pale yellow solid. 131.7 mg, 79%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 – 7.81 (m, 2H, Ph-*H*), 7.48 – 7.41 (m, 2H, Ph-*H*), 7.35 – 7.28 (m, 1H, Ph-*H*), 7.02 (s, 2H, Mes-*H*), 4.78 (q, J = 7.3 Hz, 2H, C*H*$_2$CH$_3$), 2.36 (s, 3H, Mes-C*H*$_3$), 2.10 (s, 6H, Mes-C*H*$_3$), 1.65 (t, J = 7.3 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.75 (N-*C*-N), 141.25 (Mes-*C*), 135.46 (Mes-*C*), 133.74 (Ph-*C*), 133.23 (triazole-*C*(N)-Ph), 130.42 (Mes-*C*), 129.60 (Mes-*C*), 128.91 (Ph-*C*), 128.70 (N-*C*-C), 127.14 (Ph-*C*), 126.72 (Ph-*C*), 48.72 (*C*H$_2$CH$_3$), 21.26 (Mes-*C*H$_3$), 17.80 (Mes-*C*H$_3$), 15.32 (CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{20}H_{22}N_5$ $[M+H]^+$ 332.18697, found 332.18716.



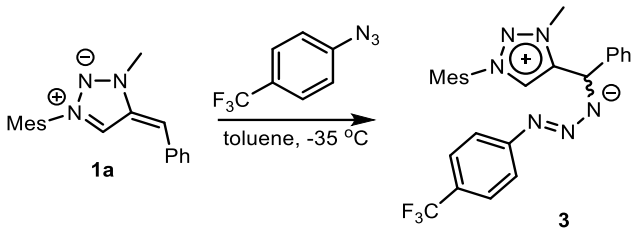
2j

Pale yellow solid. 163.1 mg, 83%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 – 7.69 (m, 2H, Ph-*H*), 7.41 (t, *J* = 7.7 Hz, 2H, Ph-*H*), 7.35 – 7.27 (m, 4H, Ph-*H*), 7.24 – 7.18 (m, 2H, Ph-*H*), 7.04 (s, 2H, Mes-*H*), 5.85 (s, 2H, C*H*$_2$), 2.37 (s, 3H, Mes-C*H*$_3$), 2.10 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.83 (N-*C*-N), 141.41 (Mes-*C*), 135.48 (Mes-*C*), 134.06, 133.04, 133.02, 130.40 (Mes-*C*), 129.68 (Mes-*C*), 129.40 (Ph-*C*), 129.39 (Ph-*C*), 129.25, 128.81 (Ph-*C*), 127.57 (Ph-*C*), 127.28 (Ph-*C*), 127.26 (Ph-*C*), 56.59 (*C*H$_2$), 21.32 (Mes-*C*H$_3$), 17.87 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{25}H_{24}N_5$ $[M+H]^+$ 394.20262, found 394.20204.

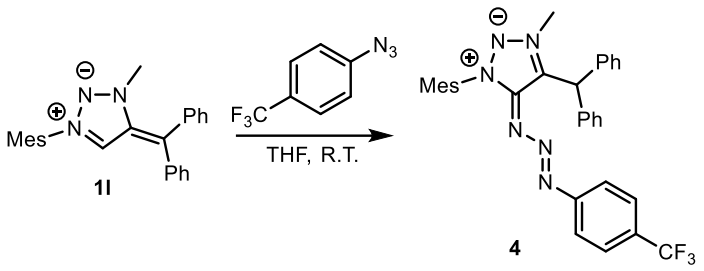


2k

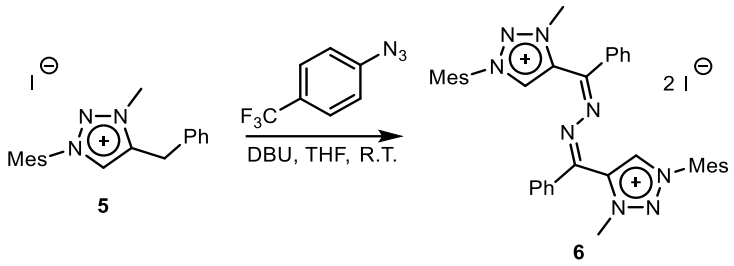
Yellow solid. 165.4 mg, 87%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.64 (m, 2H, Ph-*H*), 7.63 – 7.59 (m, 1H, Ph-*H*), 7.58 – 7.51 (m, 4H, Ph-*H*), 7.37 – 7.26 (m, 3H, Ph-*H*), 7.09 (s, 2H, Mes-*H*), 2.40 (s, 3H, Mes-C*H*$_3$), 2.21 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.58 (N-*C*-N), 141.60 (Mes-*C*), 135.99 (Ph-*C*), 135.51 (Mes-*C*), 134.10 (triazole-*C*(N)-Ph), 132.54 (N-*C*-C), 130.90 (Ph-*C*), 130.42 (Mes-*C*), 129.80 (Ph-*C*), 129.74 (Mes-*C*), 128.56 (Ph-*C*), 128.22 (Ph-*C*), 127.58 (Ph-*C*), 127.28 (Ph-*C*), 123.92 (Ph-*C*), 21.36 (Mes-*C*H$_3$), 18.02 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd for $C_{24}H_{22}N_5$ $[M+H]^+$ 380.18697, found 380.18694.



To a cold (−35 °C) solution of **1a** (183.7 mg, 0.5 mmol) in toluene (2 mL) was added a cold (−35 °C) solution of 1-azido-4-(trifluoromethyl)benzene (93.6 mg, 0.5 mmol) in *n*-pentane (2 mL). The reaction mixture was stirred for 3 h at −35 °C, affording an off-white suspension. The solid that formed was collected by filtration, washed with cold pentane (3 × 5 mL), and dried under vacuum. Off-white solid. Yield: 294.3 g, 62%. Crystals suitable for X-ray crystallography were obtained by top-layering a cold (−35 °C) solution of 1-azido-4-(trifluoromethyl)benzene in *n*-pentane onto a cold (−35 °C) solution of **1a** in toluene solution and storing at −35 °C. Compound **3** is highly thermally unstable in solution. It can be detected by NMR at low temperatures (See section 4). Anal. Calcd. for $C_{26}H_{25}N_6F_3$•0.2C_7H_8: C, 66.22; H, 5.40; N, 16.91. Found: C, 66.19; H, 5.49; N, 16.74.



To a stirring solution of **1l** (183.7 mg, 0.5 mmol) in THF (5 mL) was added 1-azido-4-(trifluoromethyl)benzene (93.6 mg, 0.5 mmol) in THF (2 mL). The reaction mixture instantaneously turned for dark green to yellow. The reaction mixture was stirred for 3 h at room temperature, then filtered. The filtrate was concentrated to ~2 mL. Top-layering with 5 mL of *n*-pentane and cooling to −35 °C afforded crystals of **4** that are suitable for X-ray crystallography. The supernatant was decanted off, and the solid was washed with *n*-pentane (3 × 5 mL) and dried under vacuum (230.4 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 4H, Ph-*H*), 7.35 – 7.30 (m, 2H, Ph-*H*), 7.30 – 7.25 (m, 2H, CF_3-C_6H_4-), 7.19 (ddd, *J* = 8.2, 1.5, 0.8 Hz, 4H, Ph-*H*), 7.02 (s, 2H, Mes-*H*), 6.87 (d, *J* = 8.0 Hz, 2H, CF_3-C_6H_4-), 6.83 (s, 1H, C*H*), 3.59 (s, 3H, N-CH_3), 2.38 (s, 3H, Mes-CH_3), 2.09 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.16 (m, CF_3-C_6H_4-), 152.73 (triazole-*C*), 140.37 (Mes-*C*), 138.53 (Ph-*C*), 134.63 (Mes-*C*), 133.01 (Mes-*C*), 129.41 (Mes-*C*), 129.16 (Ph-*C*), 128.84 (Ph-*C*), 127.73 (Ph-*C*), 126.71 (triazole-*C*), 125.52 (q, *J* = 32.0 Hz, CF_3-C_6H_4-) 125.31 (q, *J* = 3.8 Hz, CF_3-C_6H_4-), 124.80 (q, *J* = 271.3 Hz, *C*F_3), 120.63 (CF_3-C_6H_4-), 44.96 (*C*H), 40.07 (N-*C*H_3), 21.21 (Mes-*C*H_3), 17.77 (Mes-*C*H_3). ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.67. HRMS (ESI): *m/z* calcd for $C_{32}H_{30}N_6F_3$ $[M+H]^+$ 555.2479, found 555.2475.



To a stirring suspension of 4-benzyl-3-methyl-1-phenyl-1,2,3-triazolium iodide (430.7 mg, 1.03 mmol) in THF (3 mL) was added DBU (155 µL, 1.03 mmol) then 1-azido-4-(trifluoromethyl)benzene (210.6 mg, 1.13 mmol) in THF (2 mL). The reaction mixture was stirred overnight resulting a yellow suspension. The solid was collected by filtration and washed with diethyl ether (3 × 1 mL) and *n*-pentane (3 × 1 mL), then filtered. The solid was recrystallized by vapor diffusion of *n*-pentane into its DCM solution. The crystals were washed with cold DCM (−35 °C, 1 mL) and *n*-pentane (3 × 1 mL) and dried under vacuum. (262.2 mg, 61%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.67 (s, 1H, triazolium-*H*), 7.87 – 7.82 (m, 2H, Ph-*H*), 7.75 (ddt, *J* = 8.7, 7.1, 1.2 Hz, 1H, Ph-*H*), 7.67 – 7.55 (m, 2H, Ph-*H*), 7.31 – 7.22 (m, 2H, Mes-*H*), 4.35 (s, 3H, N-CH_3), 2.39 (s, 3H, Mes-CH_3), 2.18 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, DMSO-d_6): δ 154.18 (Ph-*C*(N)-triazolium), 142.30 (Mes-*C*), 135.62 (triazolium-*C*), 134.37 (Mes-*C*), 134.26 (Ph-*C*), 133.95 (triazolium-*C*), 132.29 (Ph-*C*), 131.03 (Mes-*C*), 129.64 (Mes-*C*), 129.41 (Ph-*C*), 128.93 (Ph-*C*), 40.45 (N-*C*H$_3$), 20.74 (Mes-*C*H$_3$), 16.71 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd for ½($C_{38}H_{40}N_8$) ½$[M-2I]^{2+}$ 304.1682, found 304.1687.

2. NMR spectra

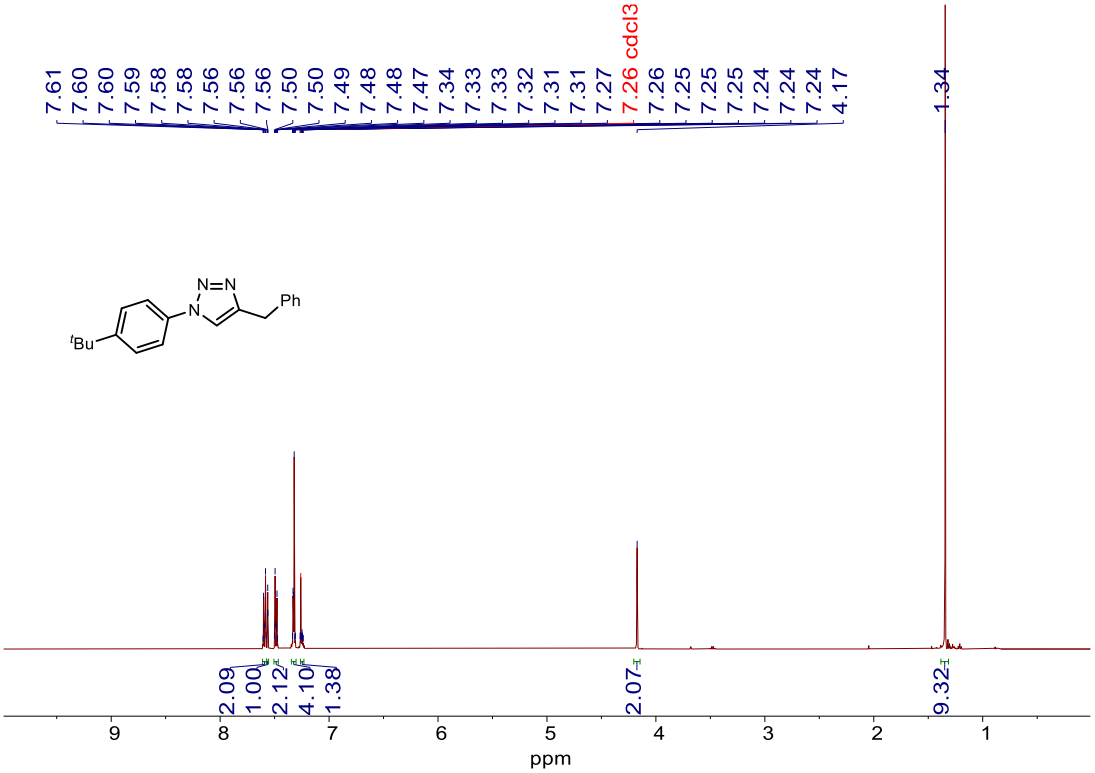


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(*tert*-butylphenyl)-1,2,3-triazole.

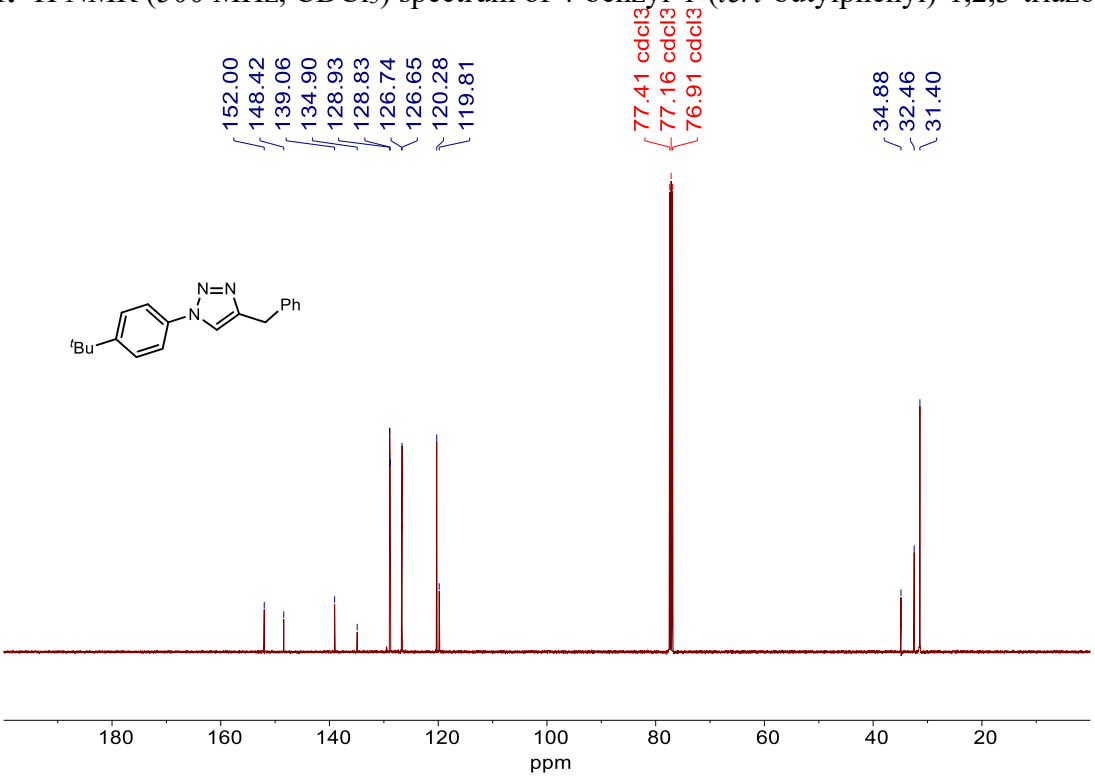


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(*tert*-butylphenyl)-1,2,3-triazole.

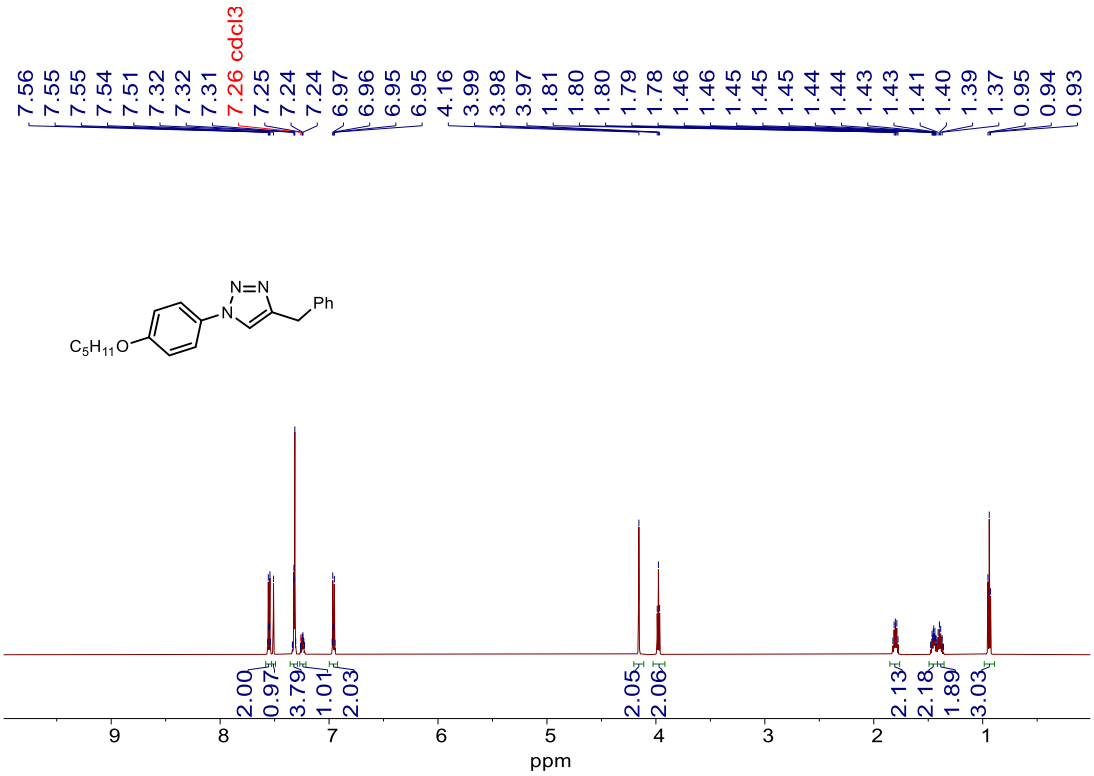


Figure S3. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(4-pentoxyphenyl)-1,2,3-triazole.

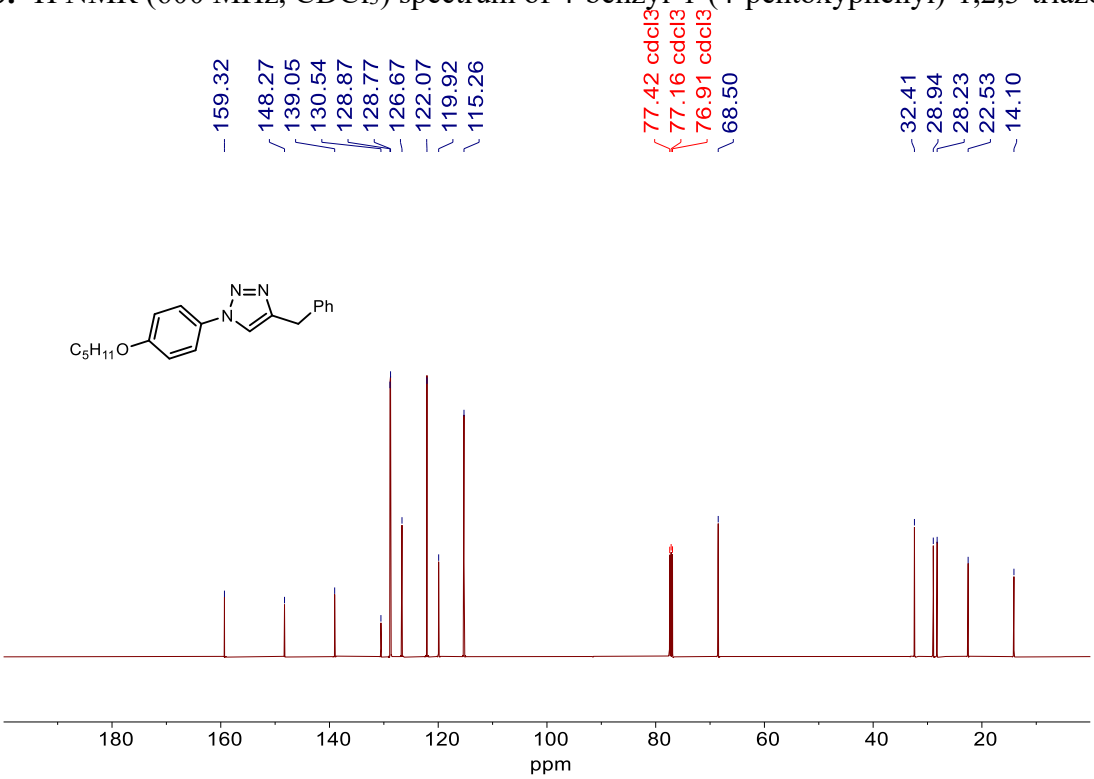


Figure S4. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(4-pentoxyphenyl)-1,2,3-triazole.

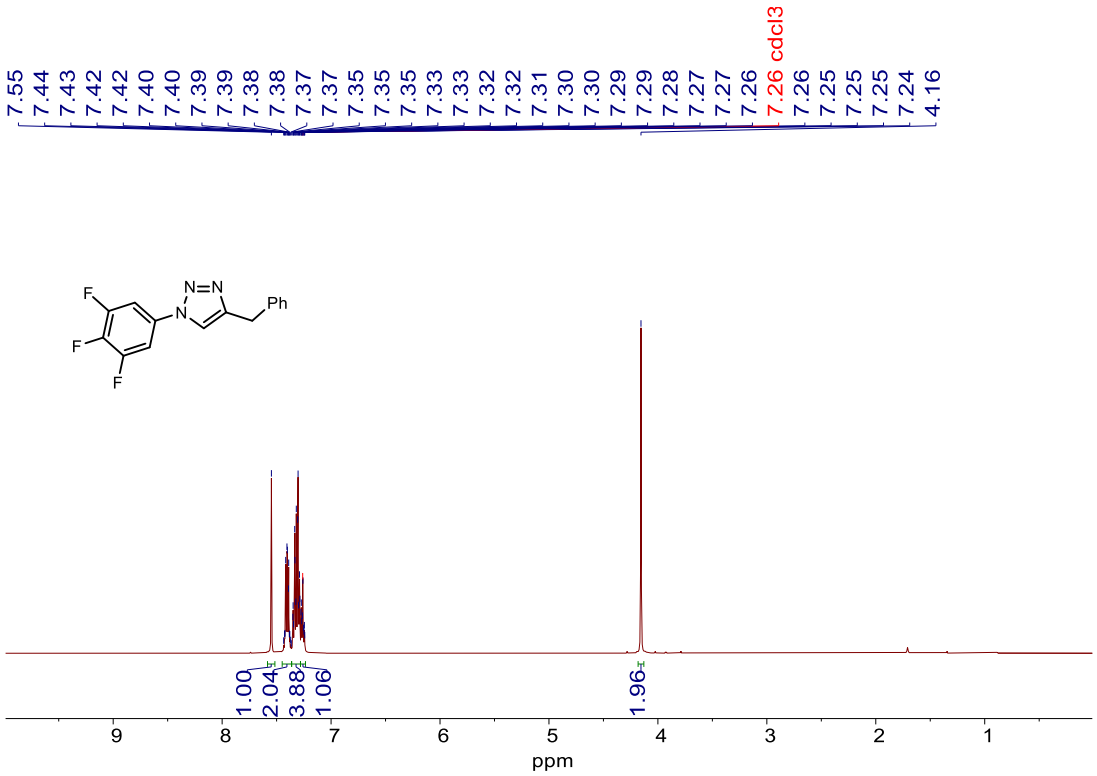


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazole.

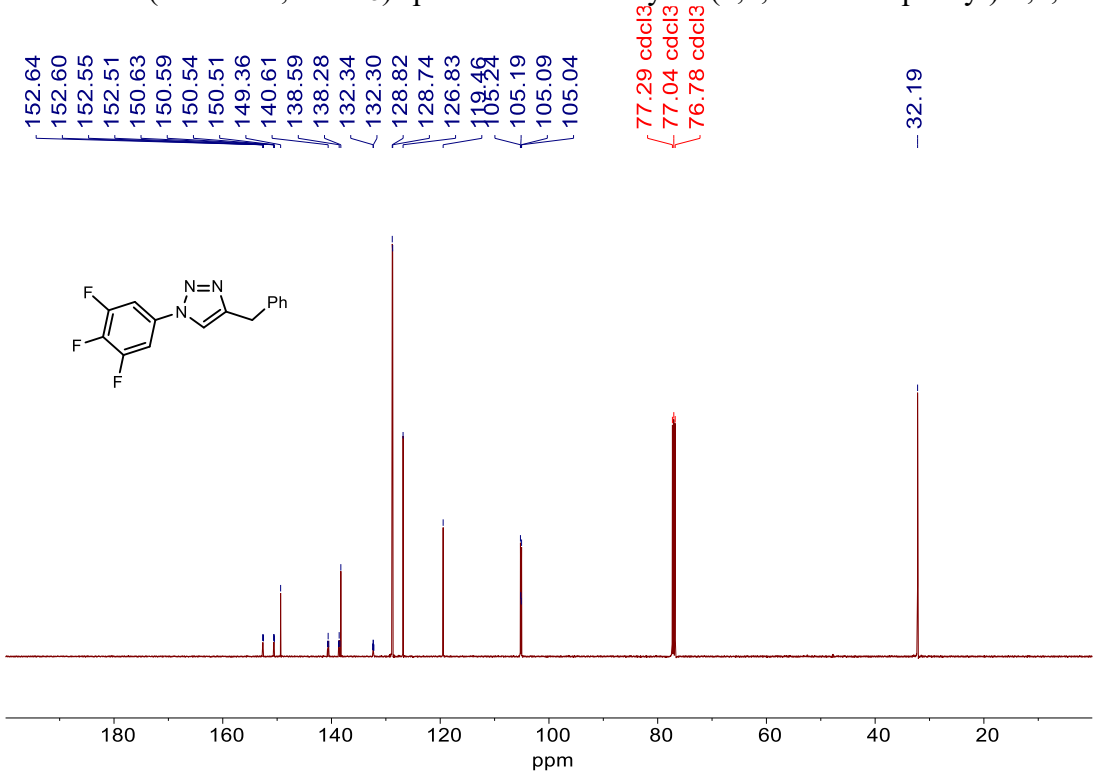


Figure S6. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazole.

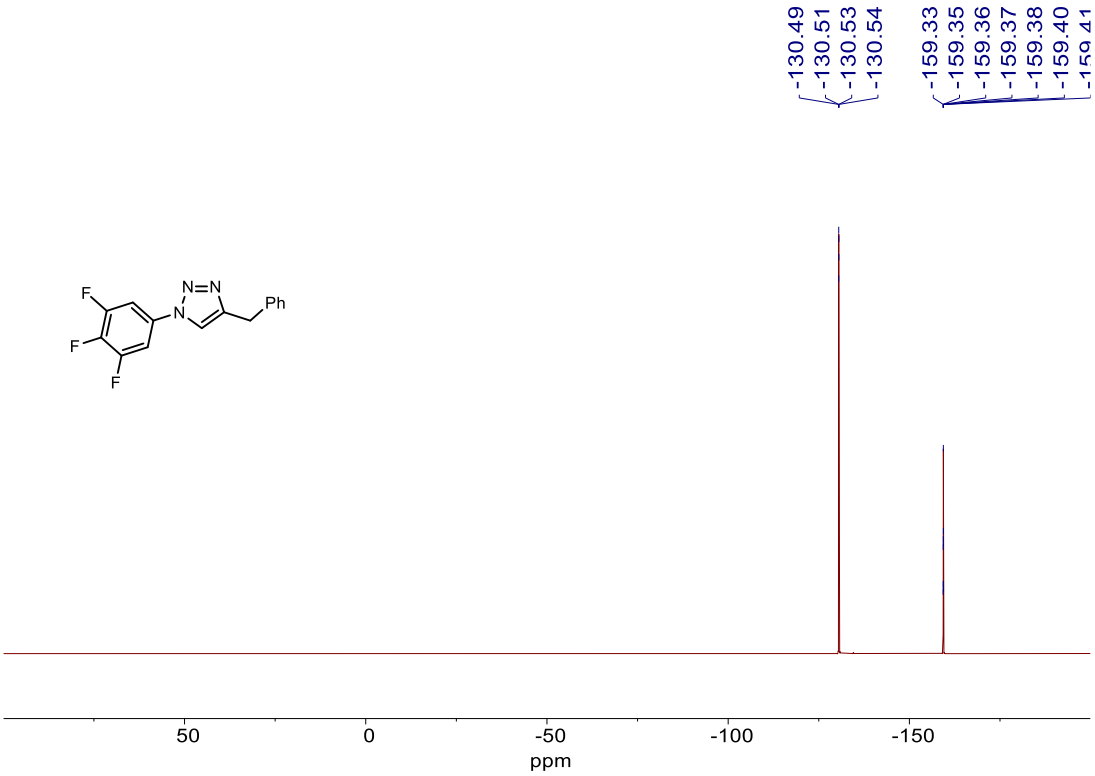


Figure S7. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazole.

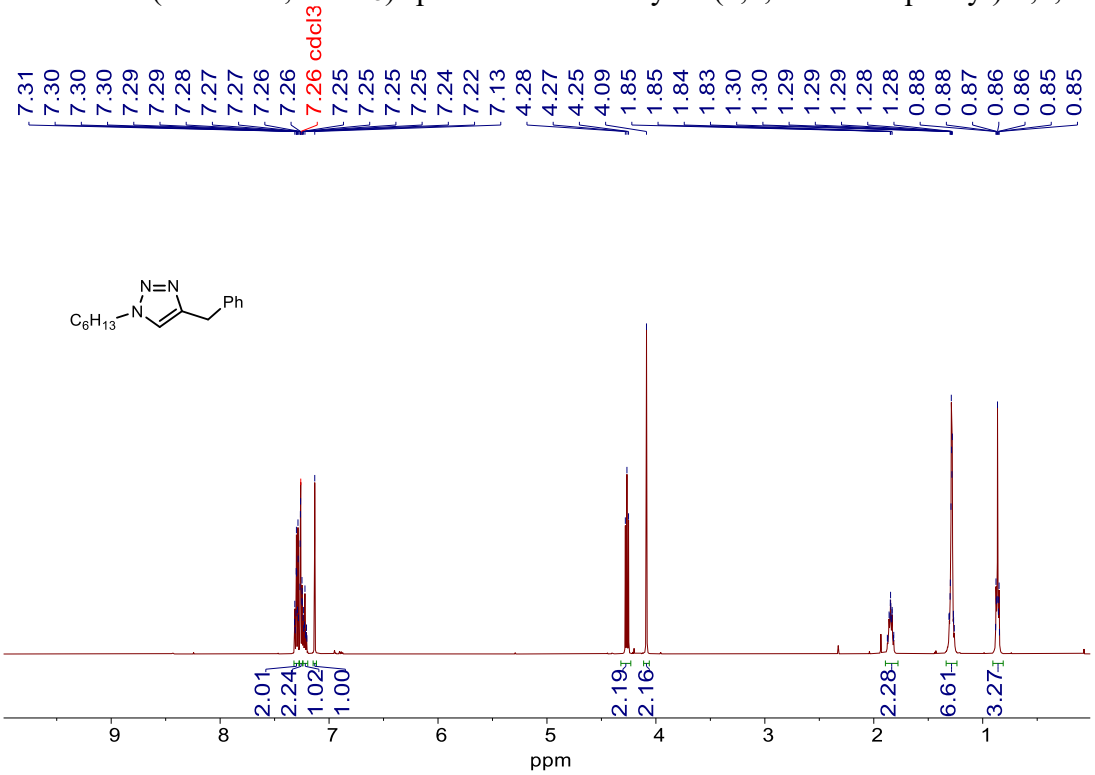


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-1-hexyl-1,2,3-triazole.

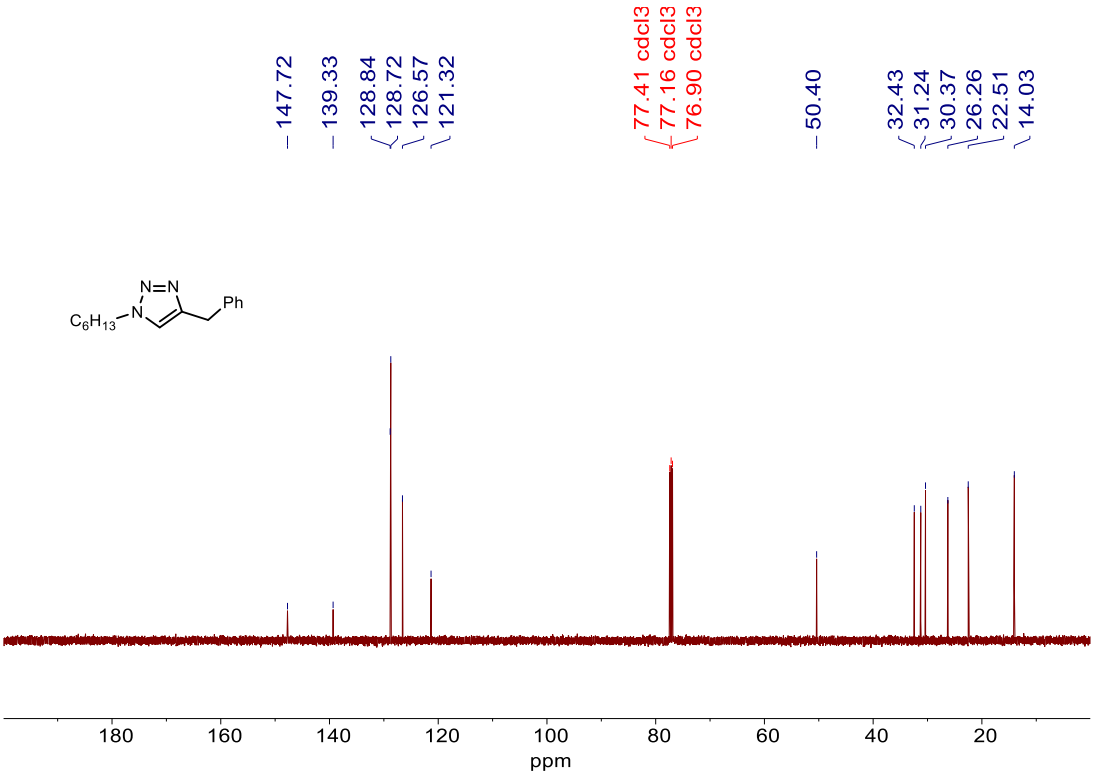


Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-hexyl-1,2,3-triazole.

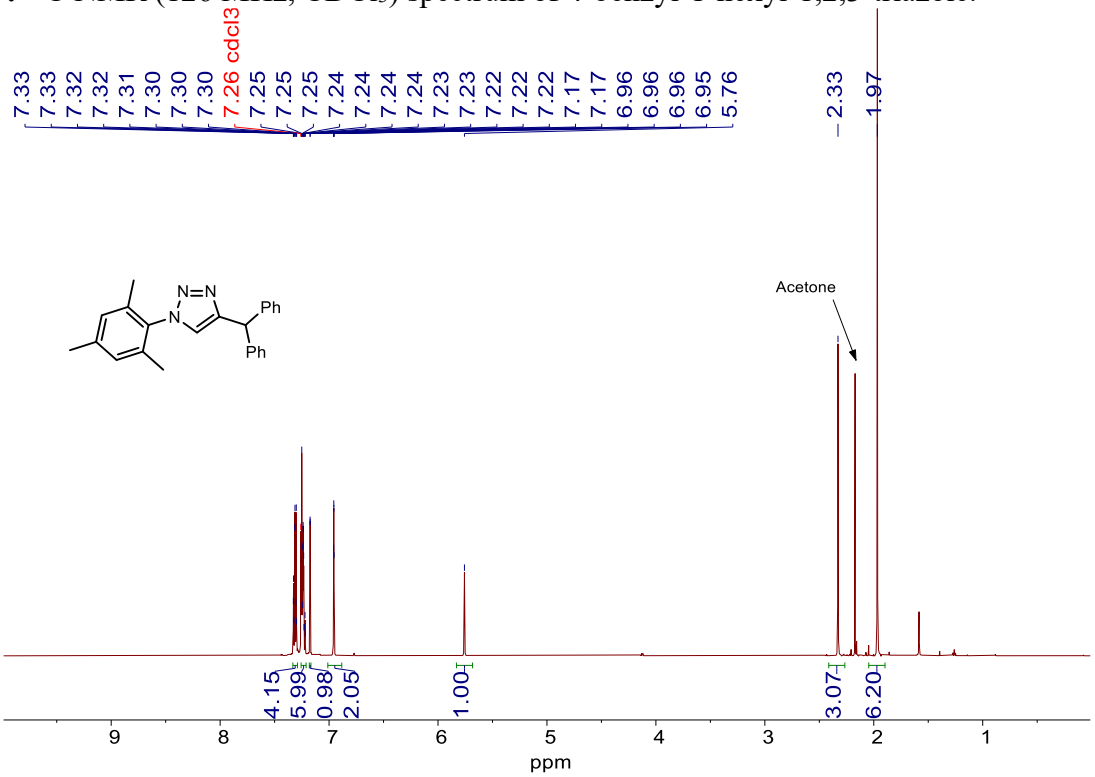


Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-benzhydryl-1-mesityl-1,2,3-triazole.

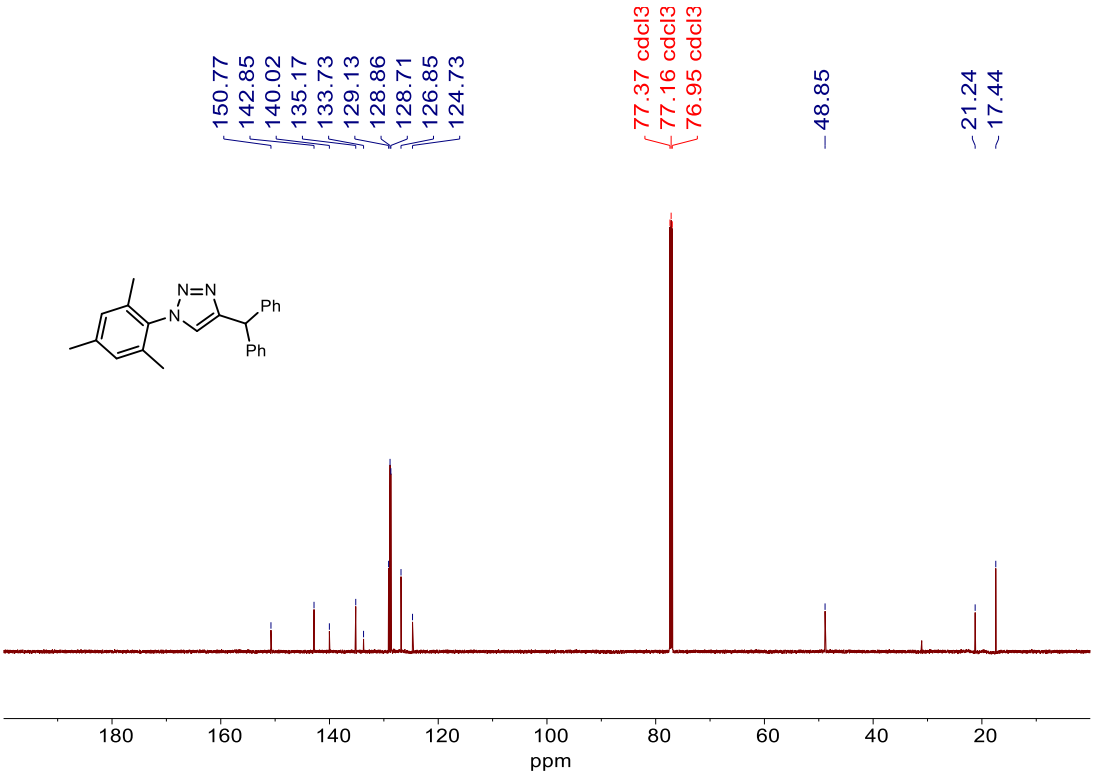


Figure S11. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4-benzhydryl-1-mesityl-1,2,3-triazole.

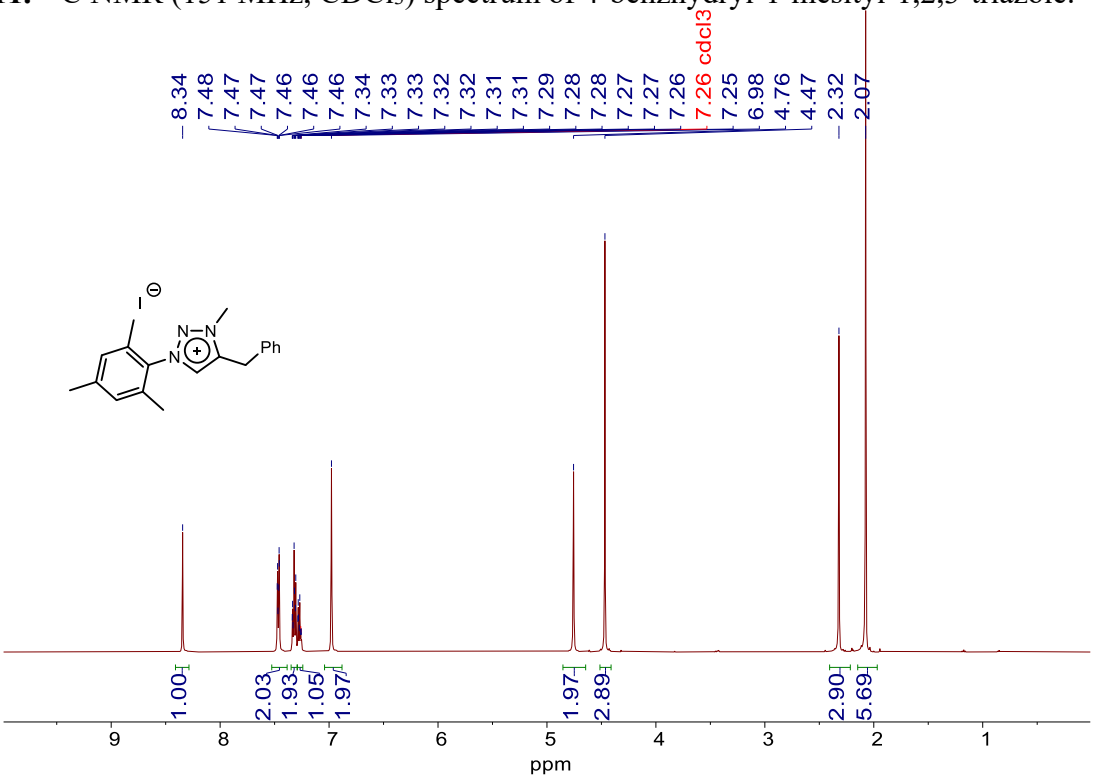


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-phenyl-1,2,3-triazolium iodide.

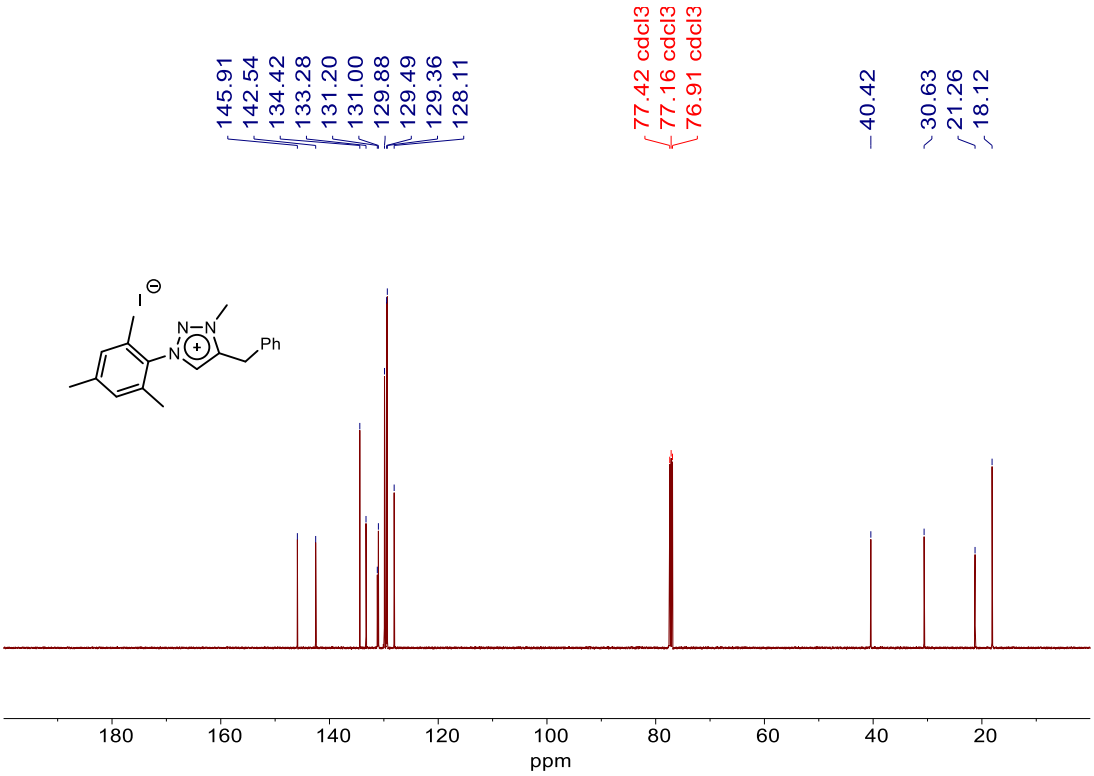


Figure S13. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-phenyl-1,2,3-triazolium iodide.

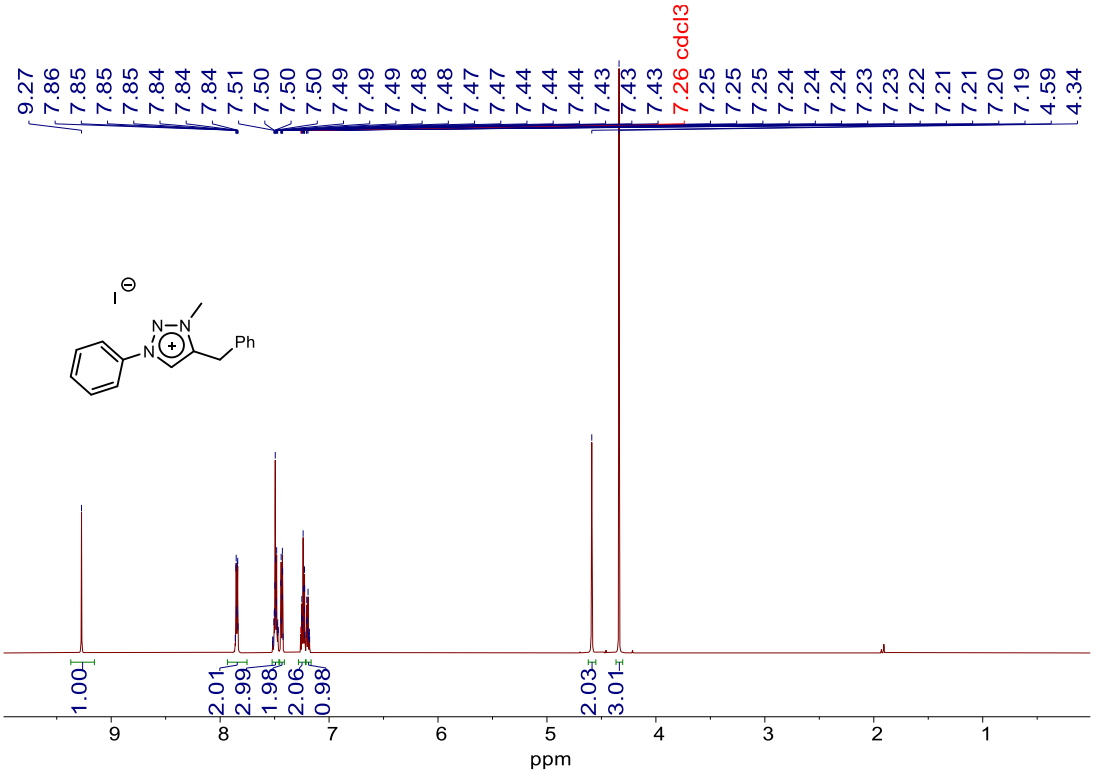


Figure S14. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-phenyl-1,2,3-triazolium iodide.

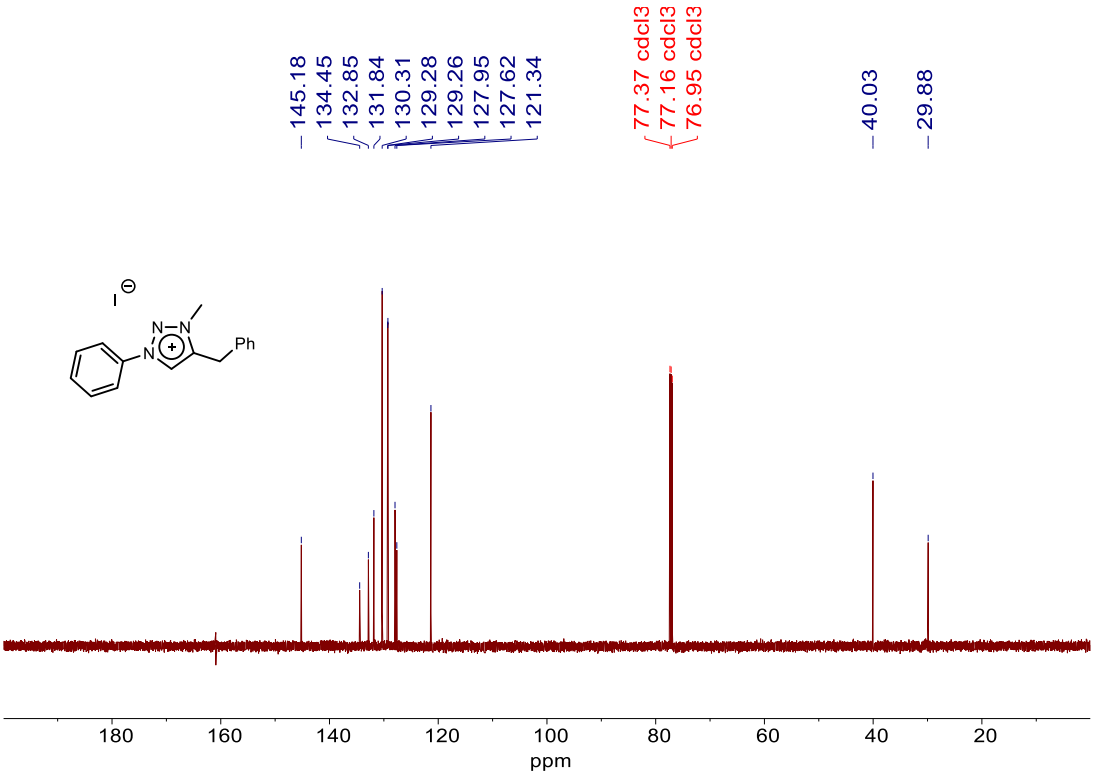


Figure S15. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-phenyl-1,2,3-triazolium iodide.

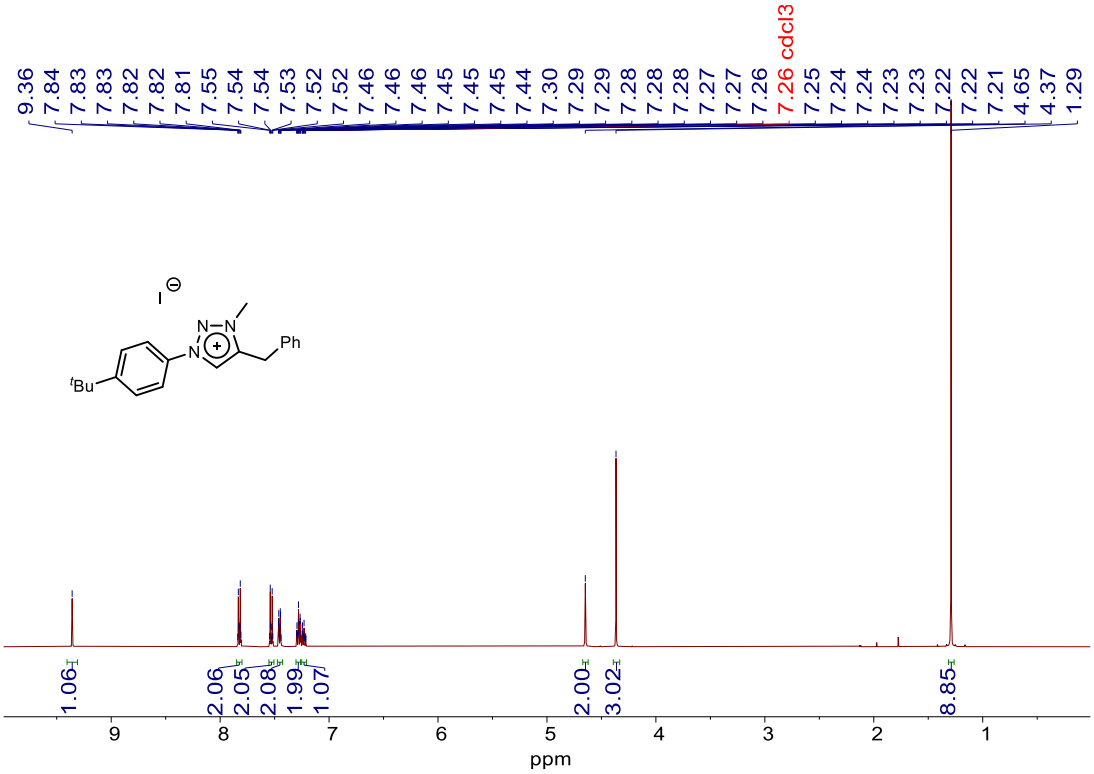


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(4-(*tert*-butyl)phenyl)-3-methyl-1,2,3-triazolium iodide.

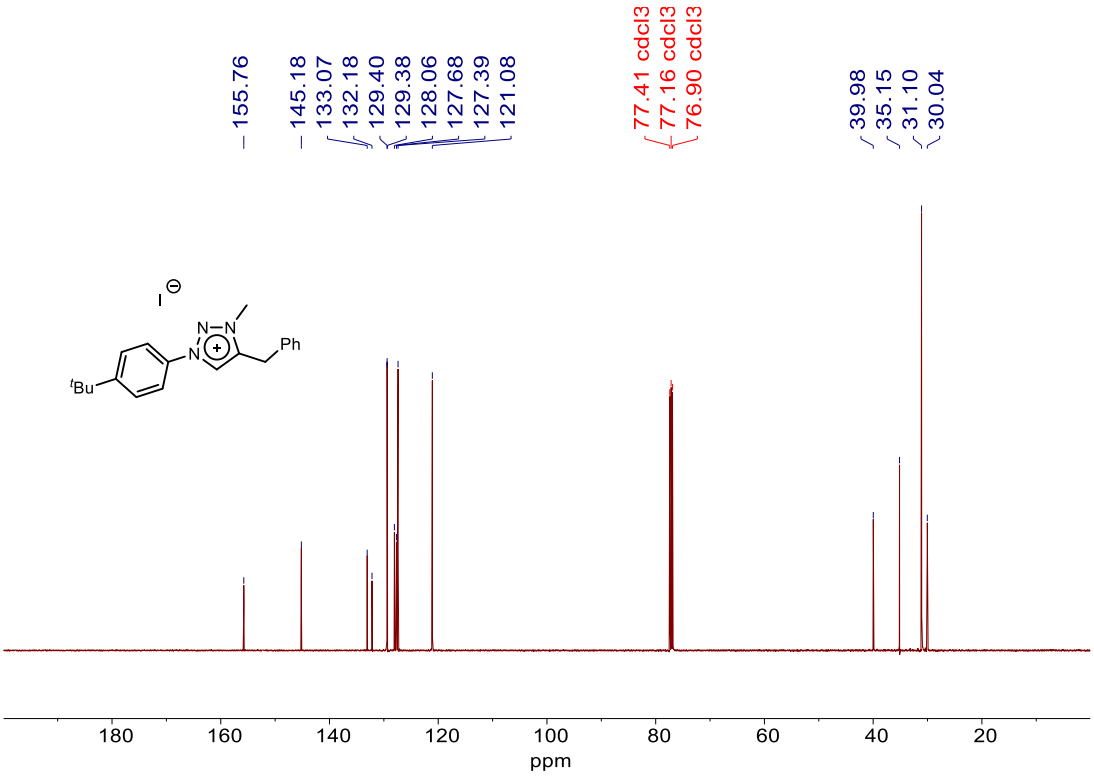


Figure S17. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(4-(*tert*-butyl)phenyl)-3-methyl-1,2,3-triazolium iodide.

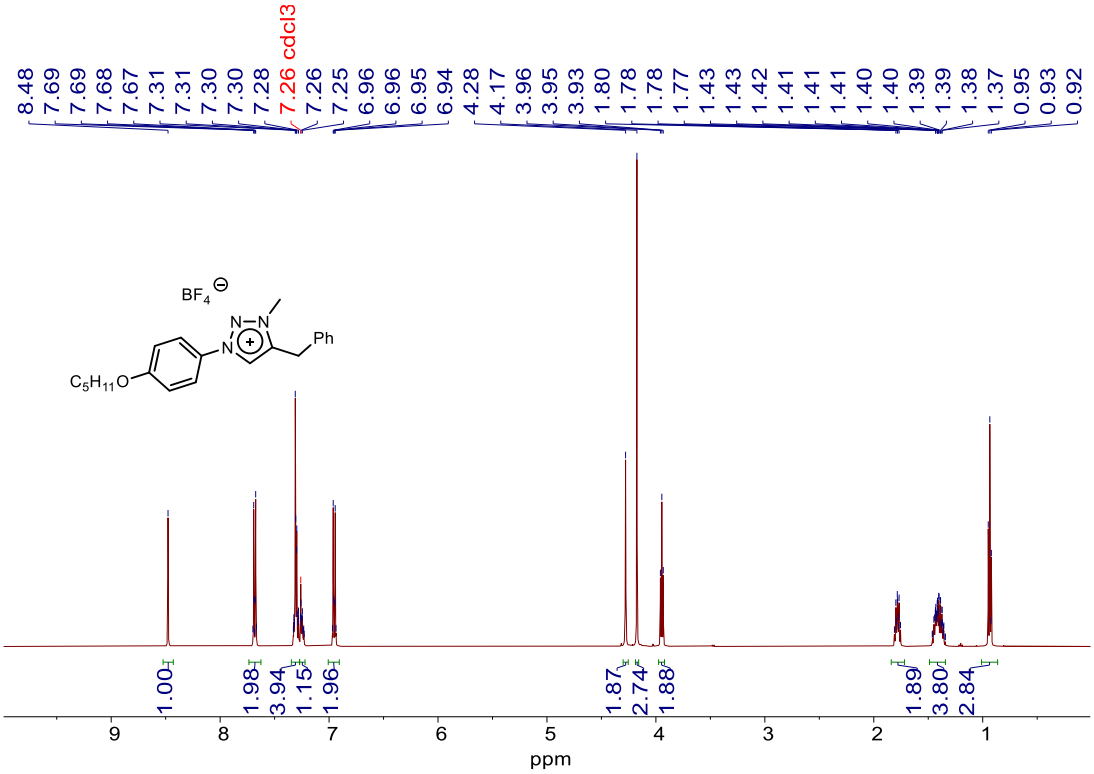


Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(4-(pentyloxy)phenyl)-1,2,3-triazolium tetrafluoroborate.

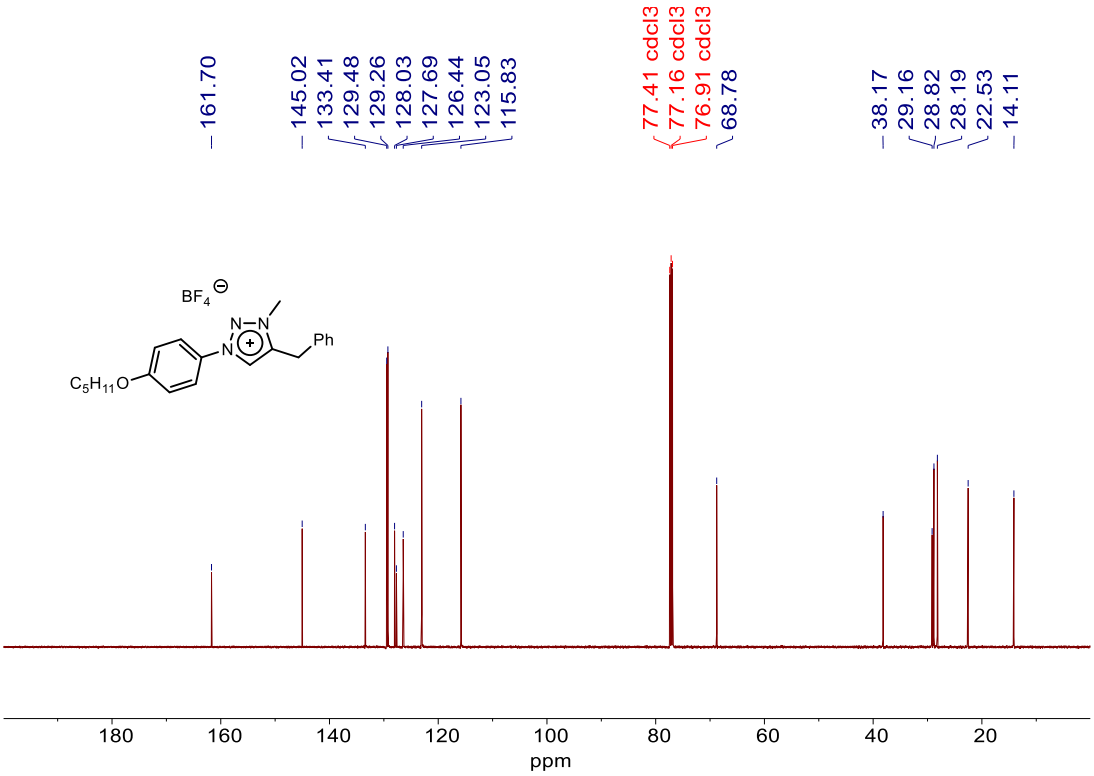


Figure S19. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(4-(pentyloxy)phenyl)-1,2,3-triazolium tetrafluoroborate.

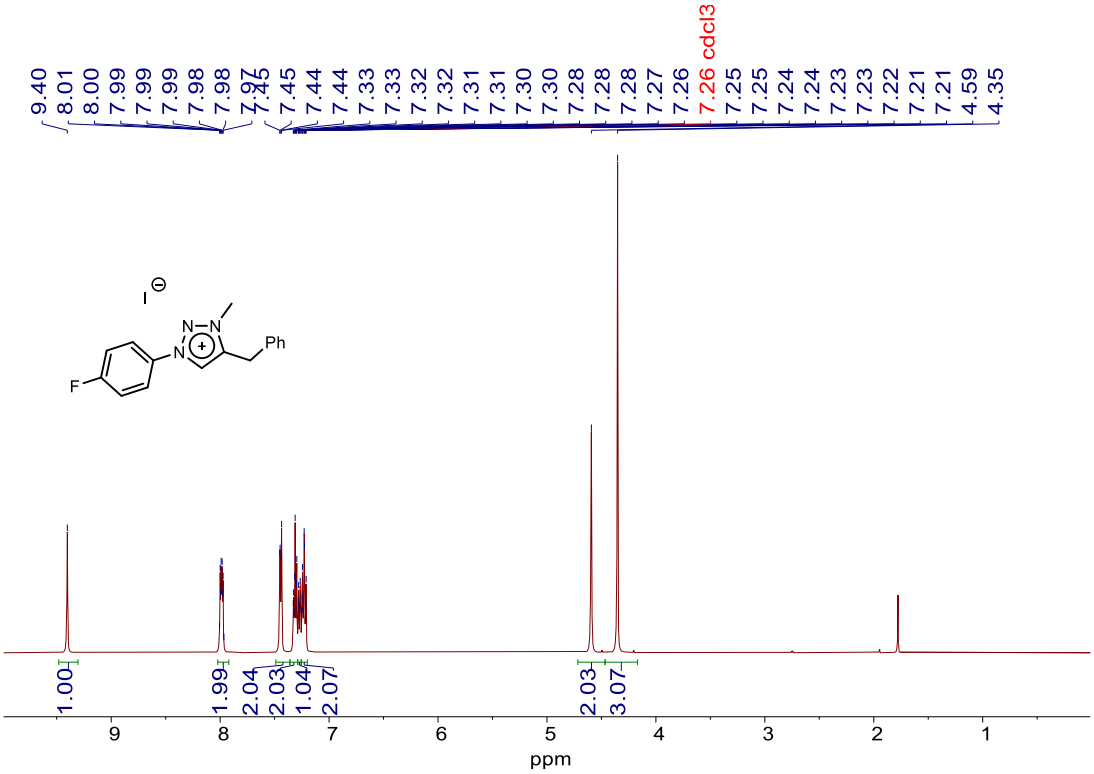


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(4-fluorophenyl)-3-methyl-1,2,3-triazolium iodide.

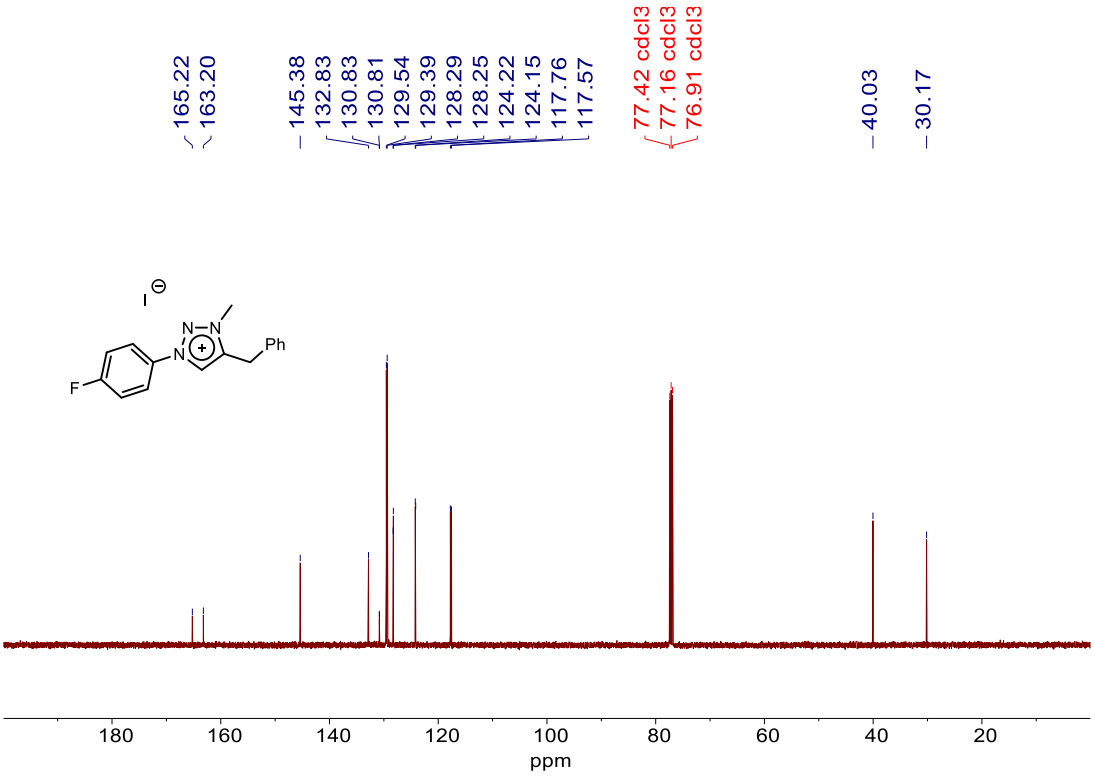


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(4-fluorophenyl)-3-methyl-1,2,3-triazolium iodide.

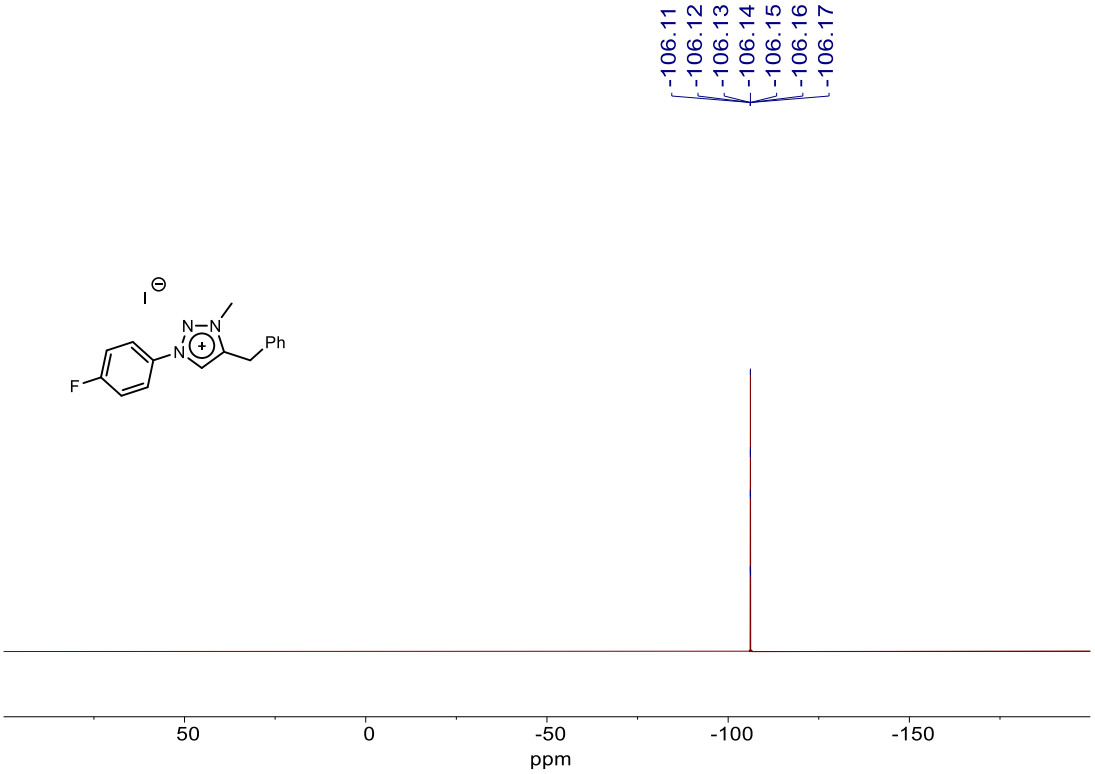


Figure S22. ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of 4-benzyl-1-(4-fluorophenyl)-3-methyl-1,2,3-triazolium iodide.

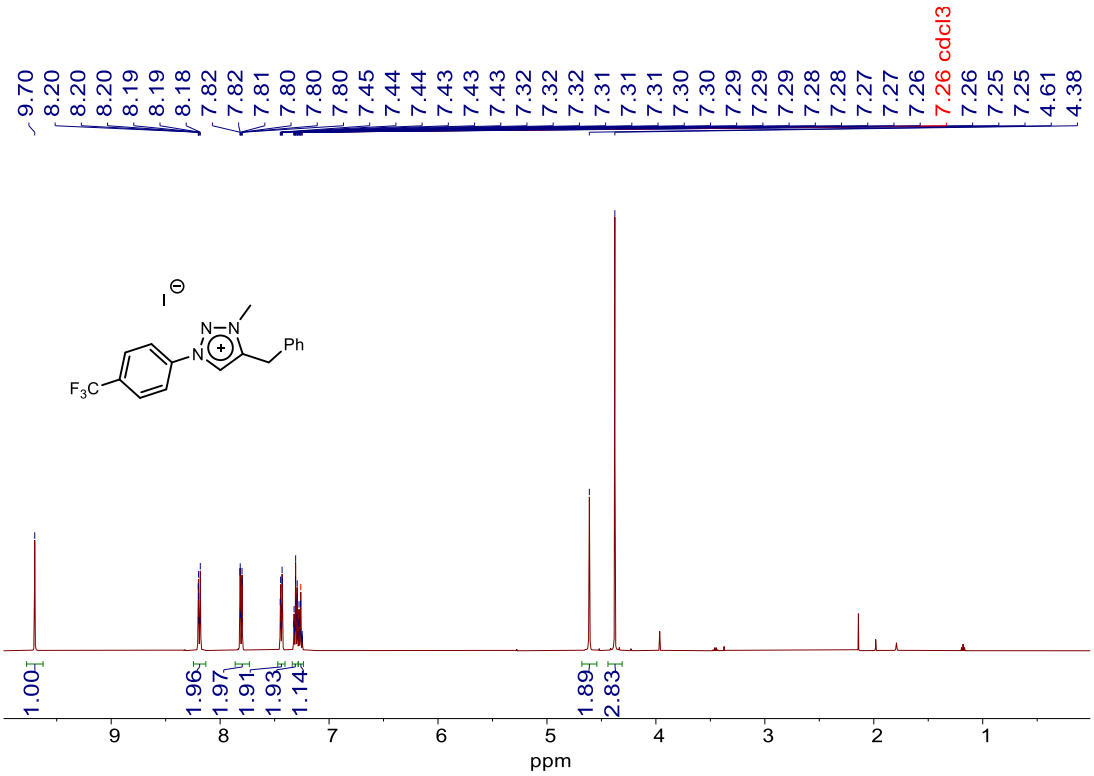


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(4-(trifluoromethyl)phenyl)-1,2,3-triazolium iodide.

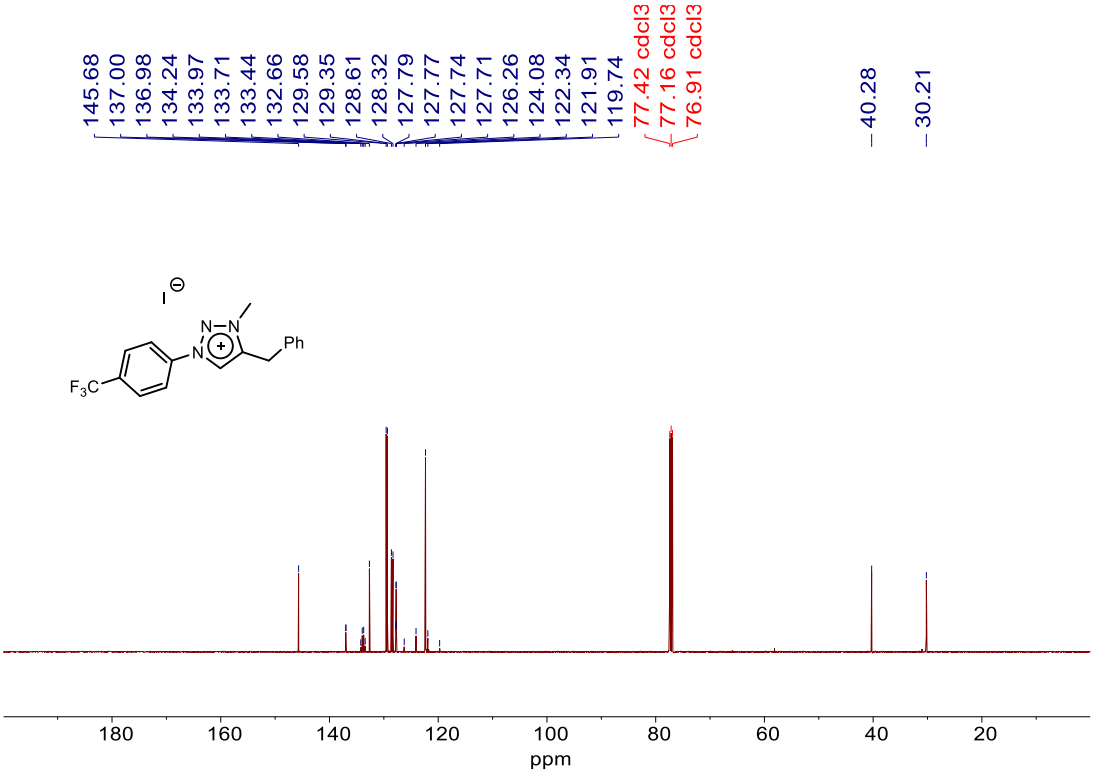


Figure S24. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(4-(trifluoromethyl)phenyl)-1,2,3-triazolium iodide.

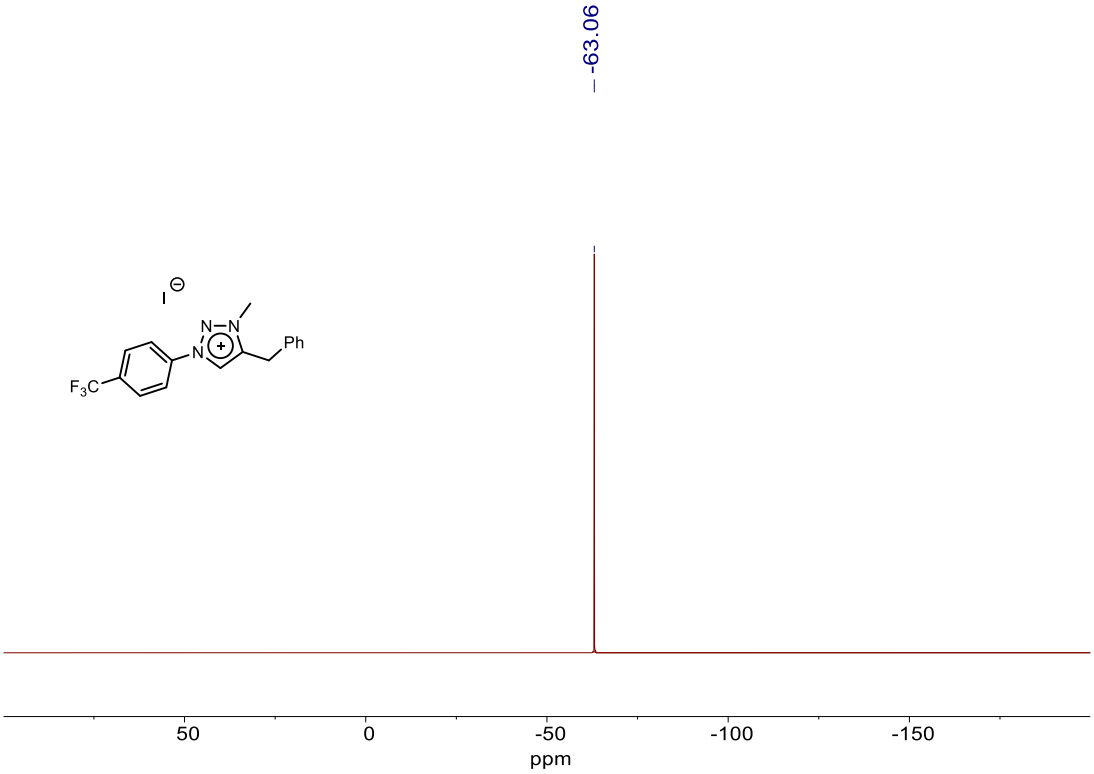


Figure S25. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(4-(trifluoromethyl)phenyl)-1,2,3-triazolium iodide.

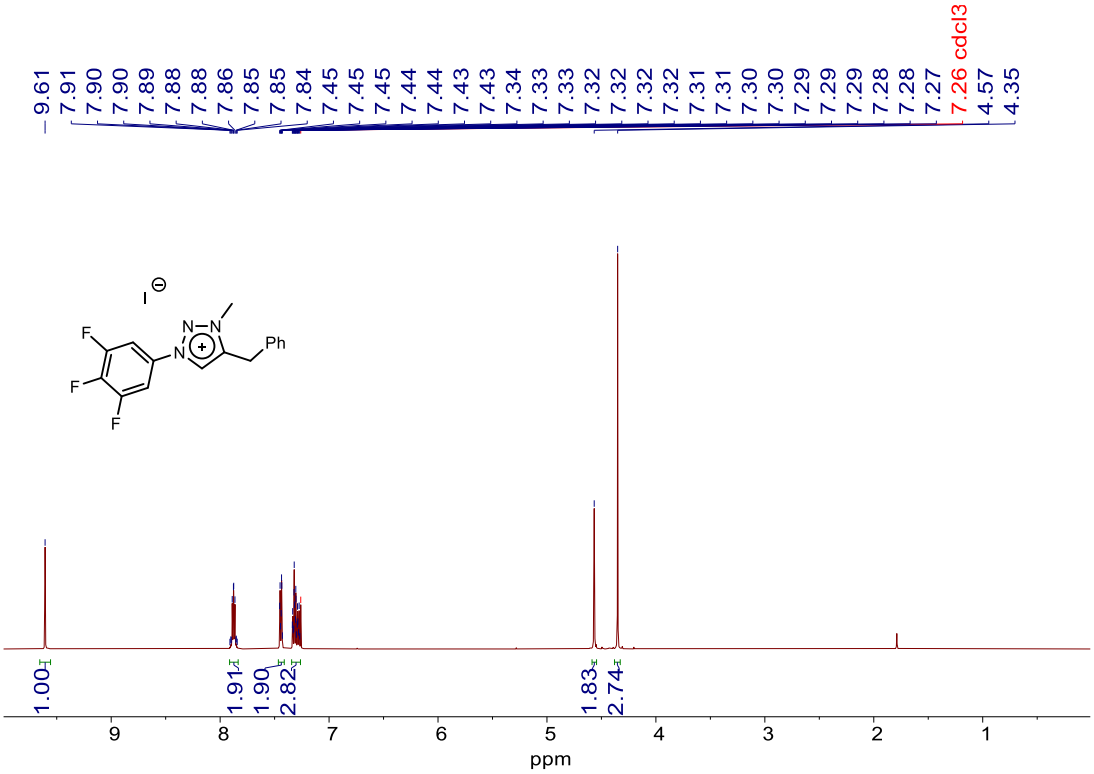


Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazolium iodide.

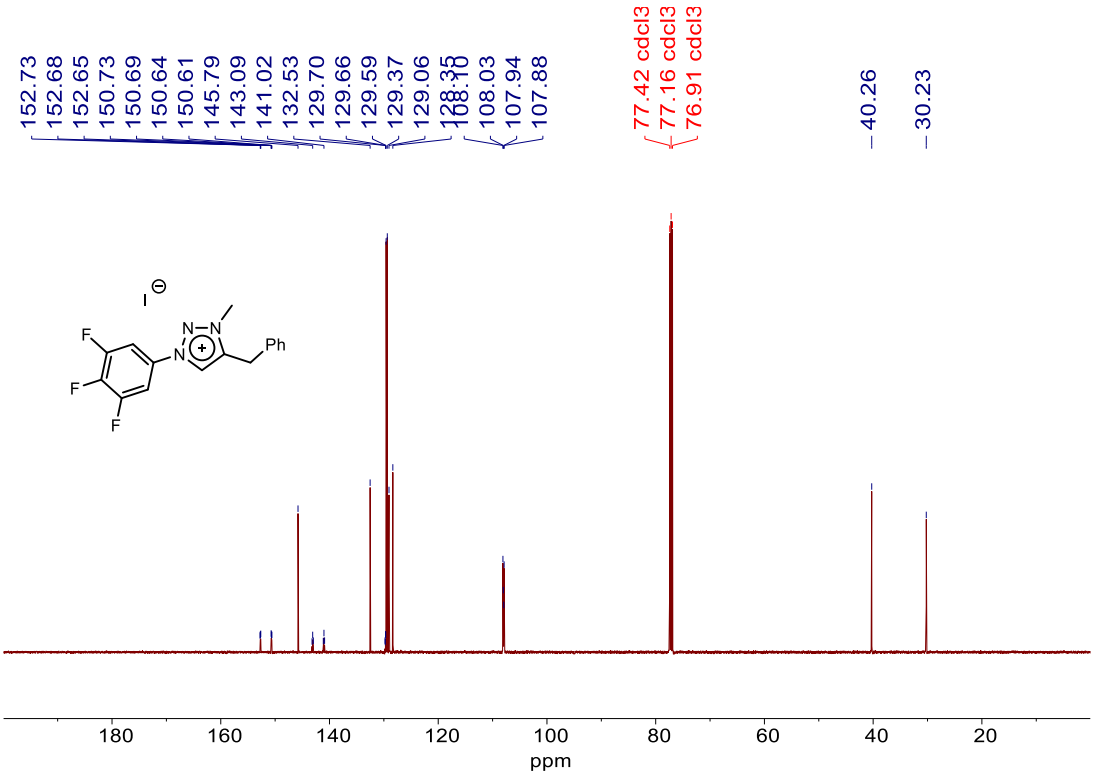


Figure S27. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazolium iodide.

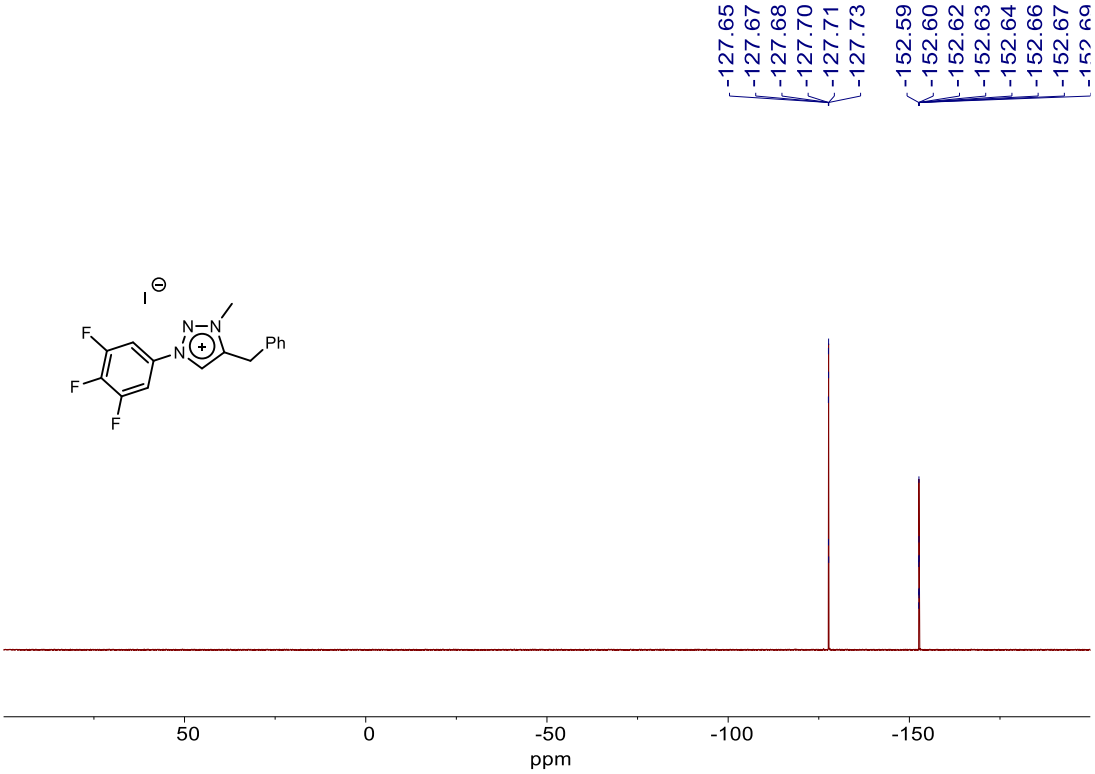


Figure S28. ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of 4-benzyl-3-methyl-1-(3,4,5-trifluorophenyl)-1,2,3-triazolium iodide.

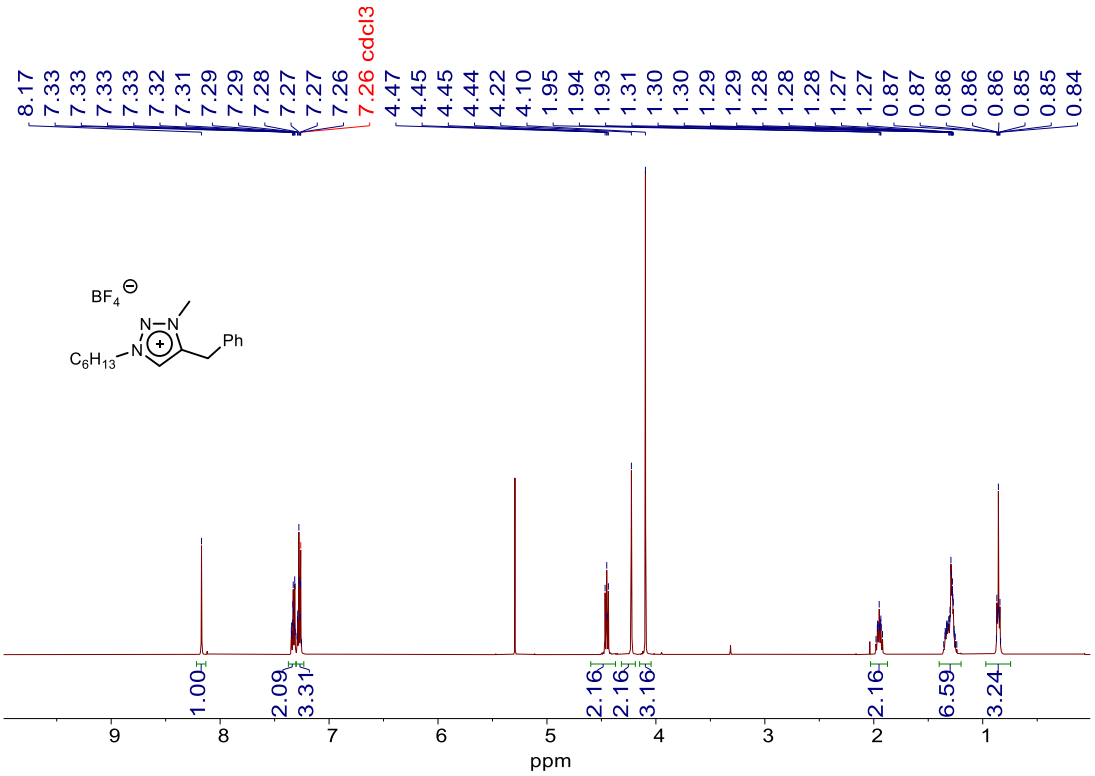


Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-1-hexyl-3-methyl-1,2,3-triazolium tetrafluoroborate.

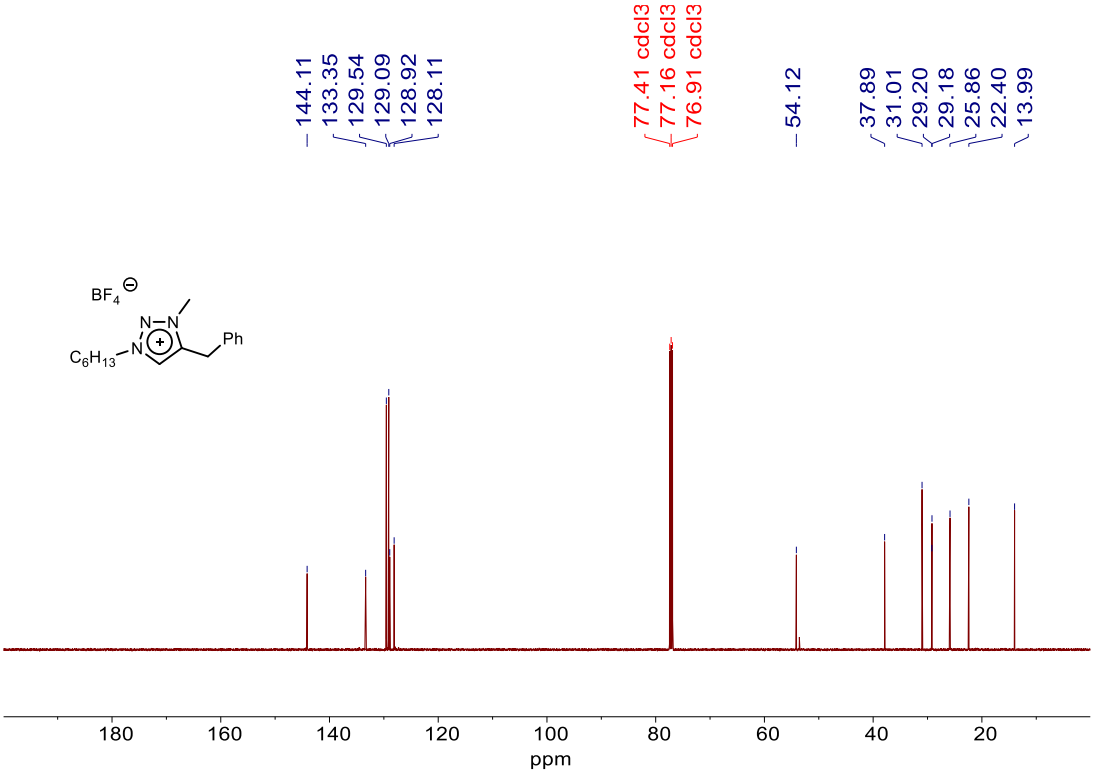


Figure S30 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-hexyl-3-methyl-1,2,3-triazolium tetrafluoroborate.

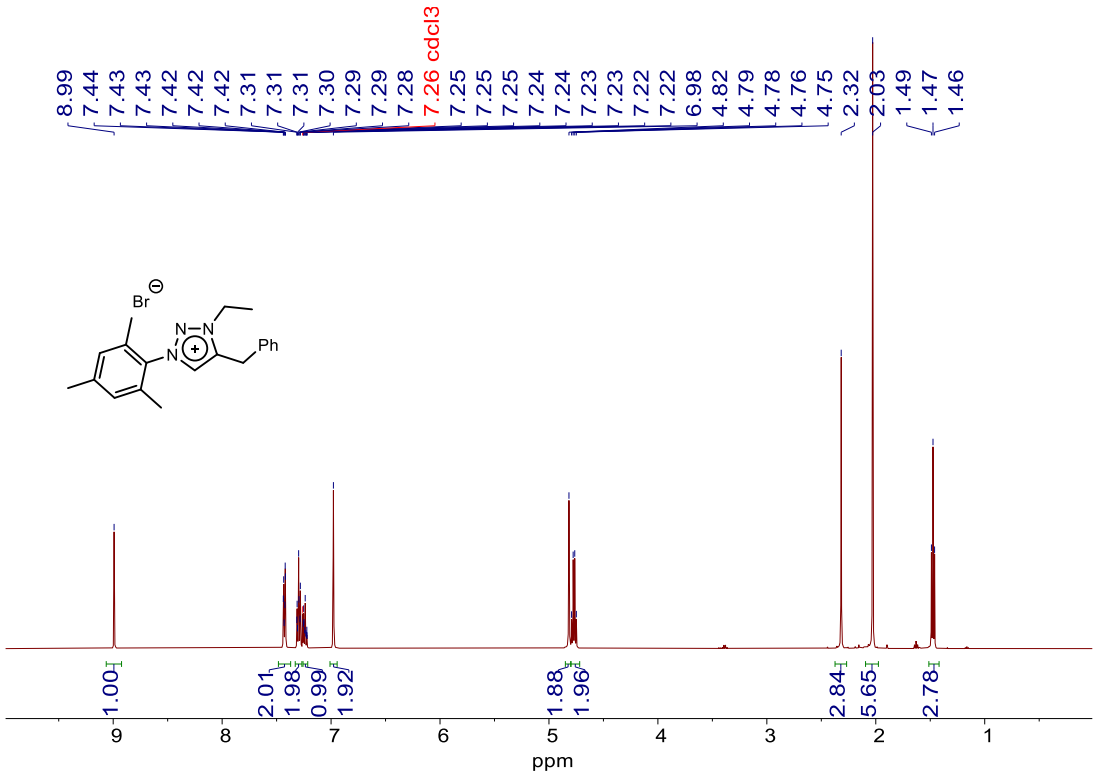


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-3-ethyl-1-mesityl-1,2,3-triazolium bromide.

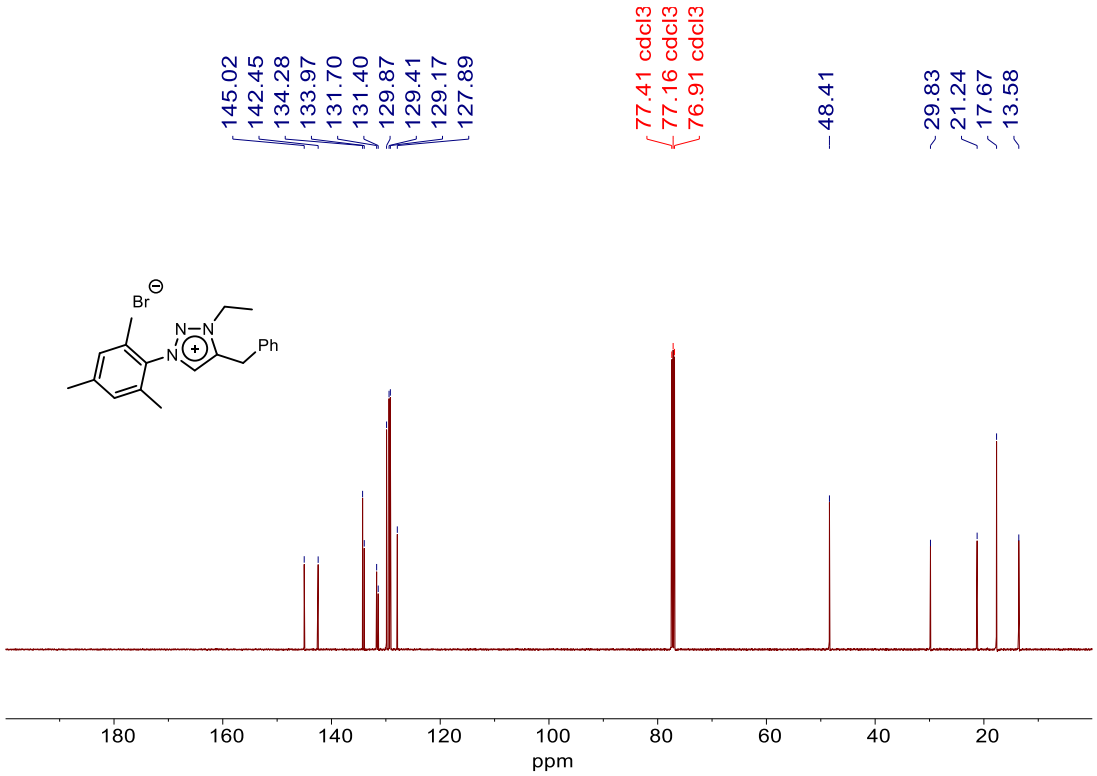


Figure S32. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-3-ethyl-1-mesityl-1,2,3-triazolium bromide.

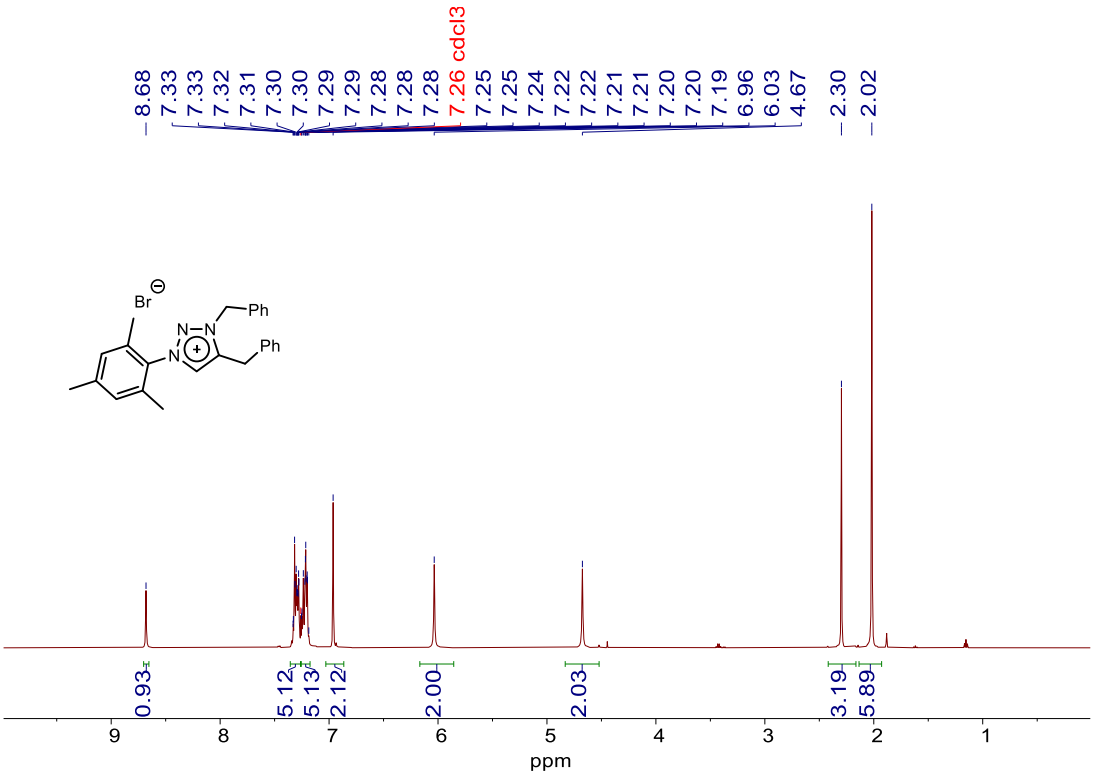


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3,4-dibenzyl-1-mesityl-1,2,3-triazolium bromide.

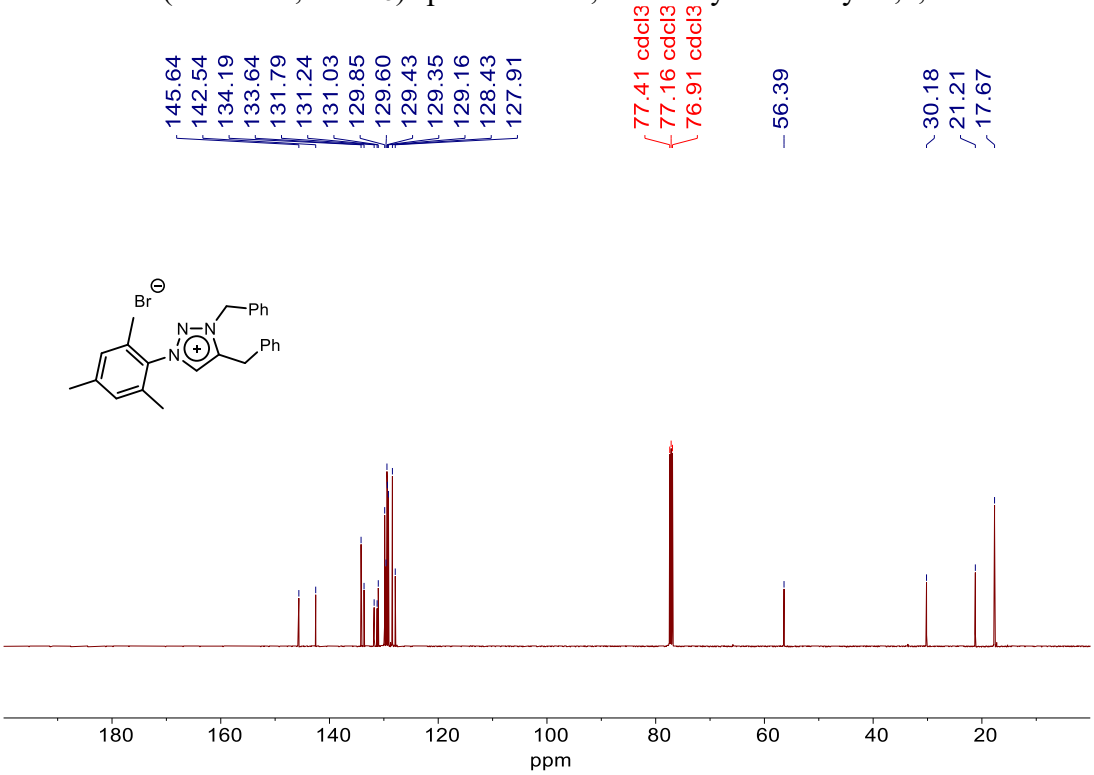


Figure S34. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3,4-dibenzyl-1-mesityl-1,2,3-triazolium bromide.

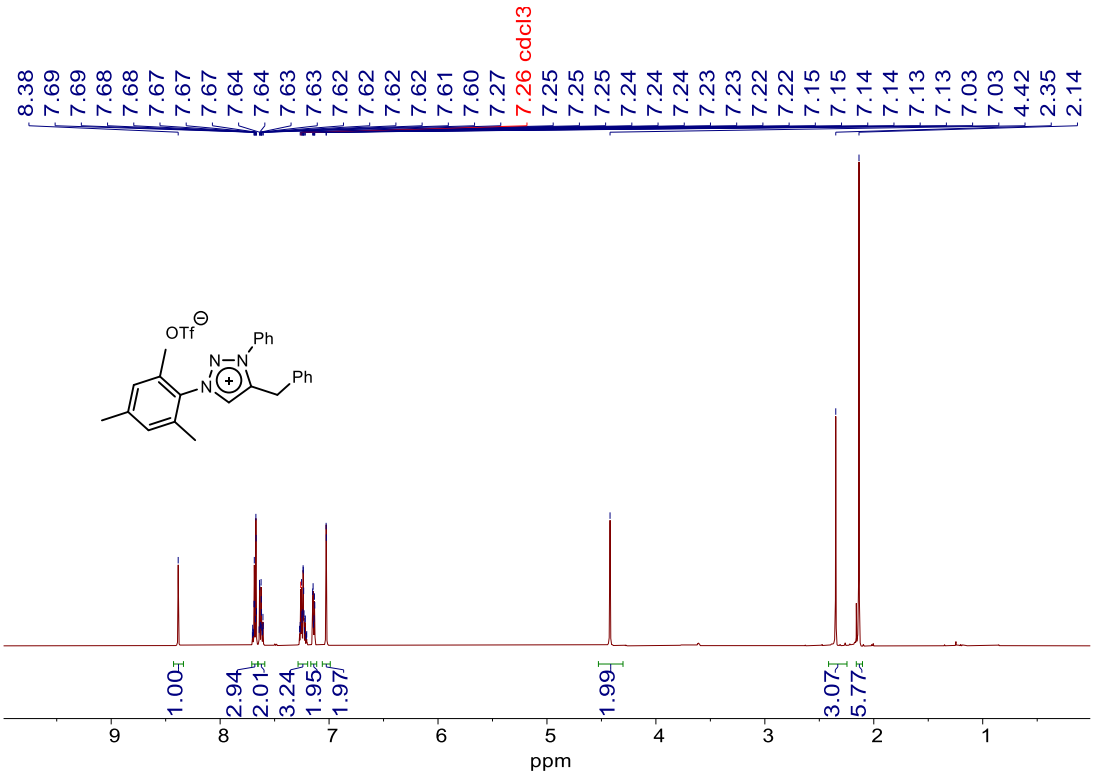


Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-3-phenyl-1,2,3-triazolium triflate.

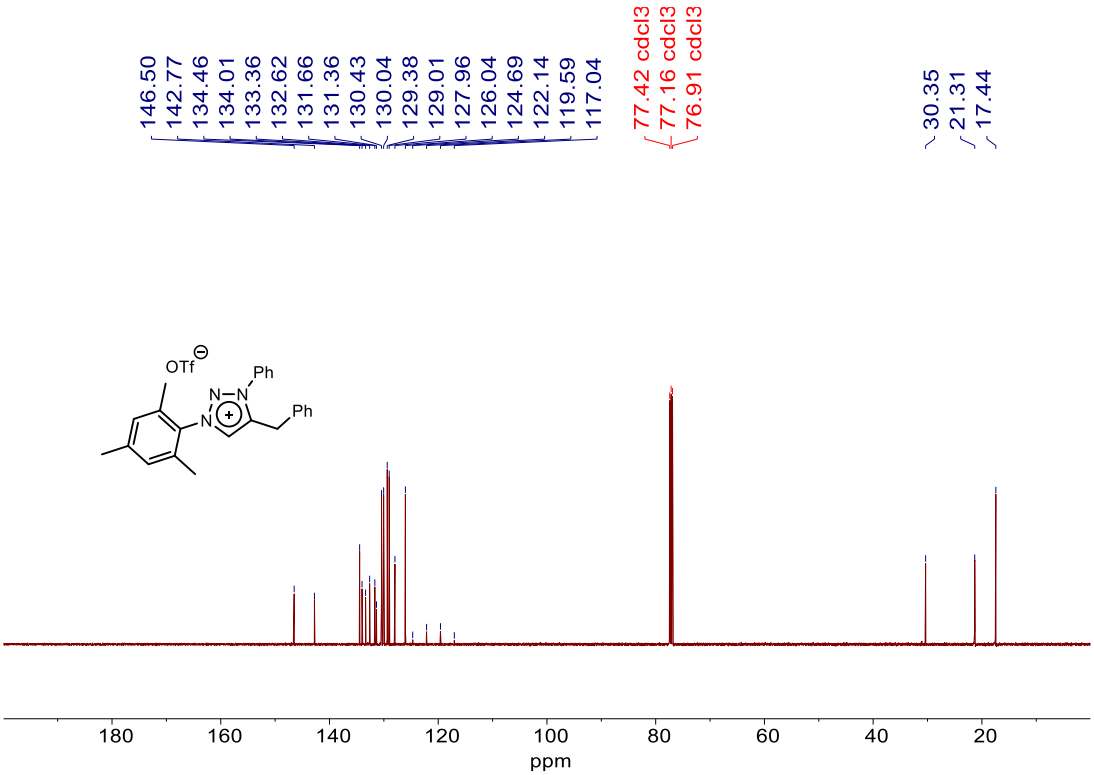


Figure S36. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-3-phenyl-1,2,3-triazolium triflate.

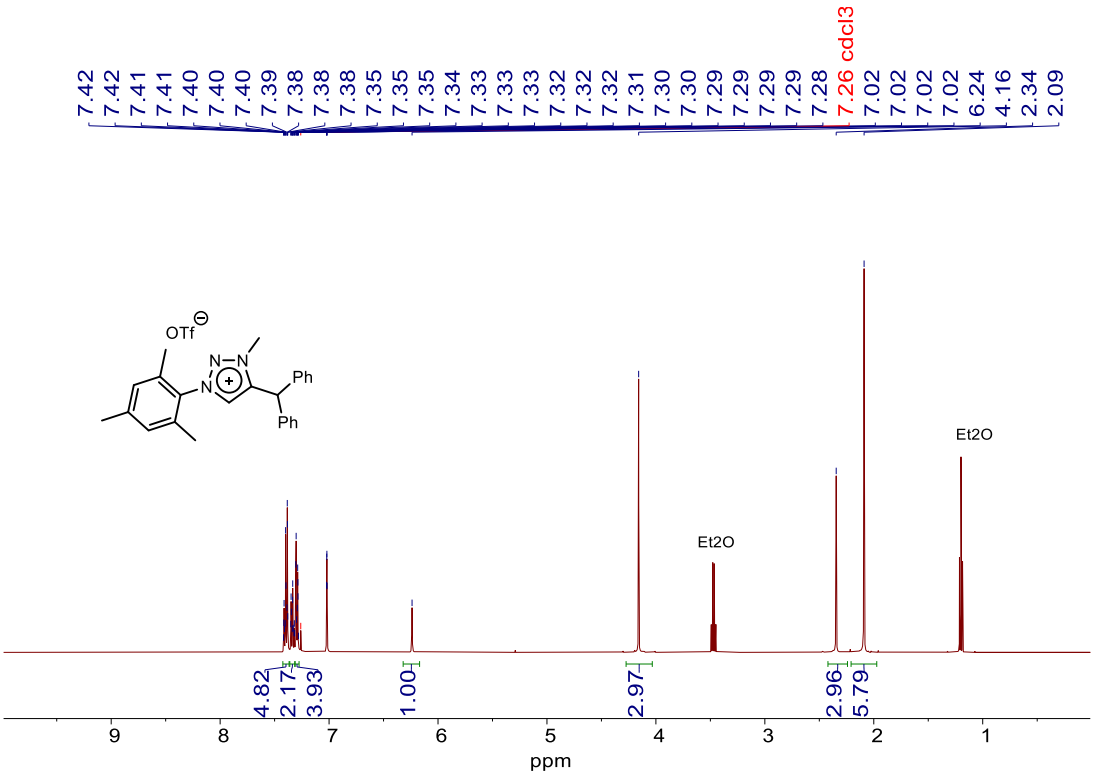


Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4-benzhydryl-1-mesityl-3-methyl-1,2,3-triazolium triflate.

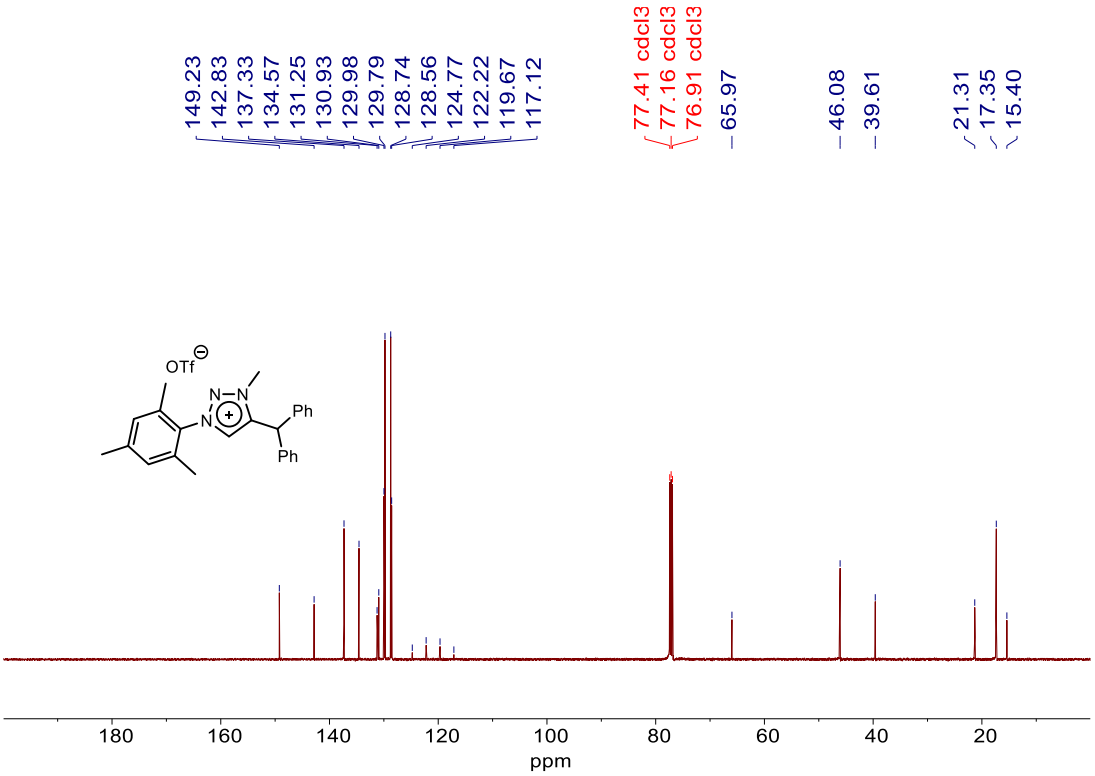


Figure S38. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4-benzhydryl-1-mesityl-3-methyl-1,2,3-triazolium triflate.

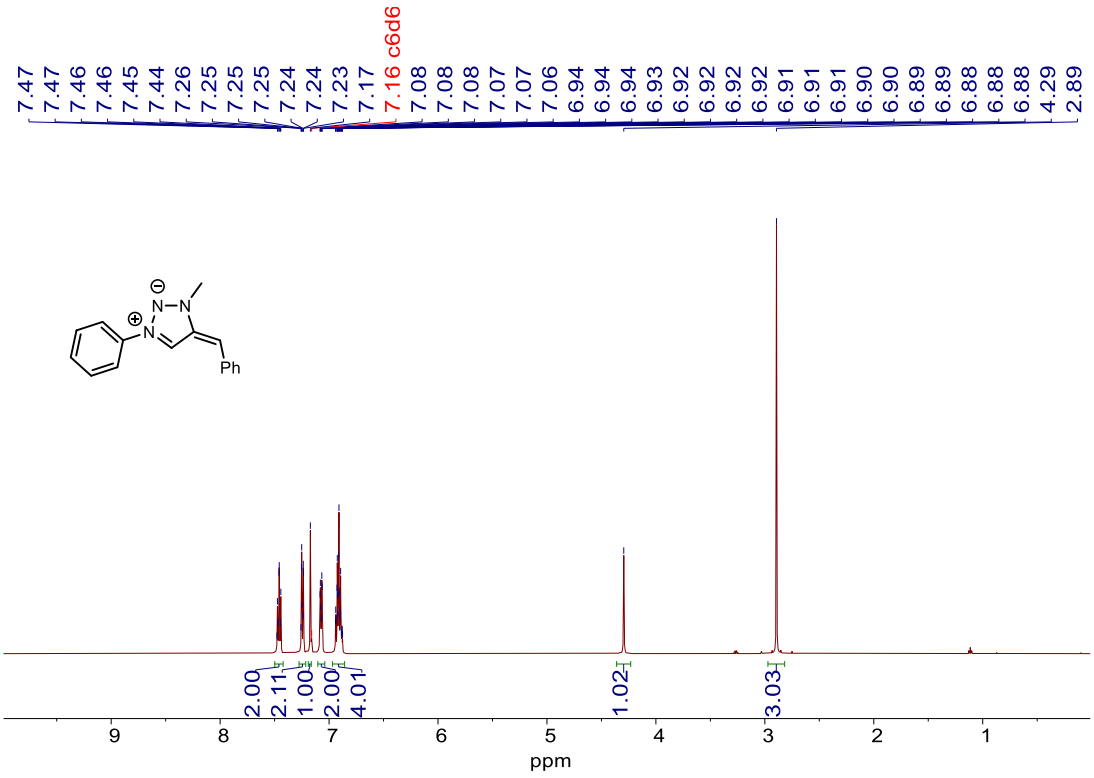


Figure S39. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1b**.

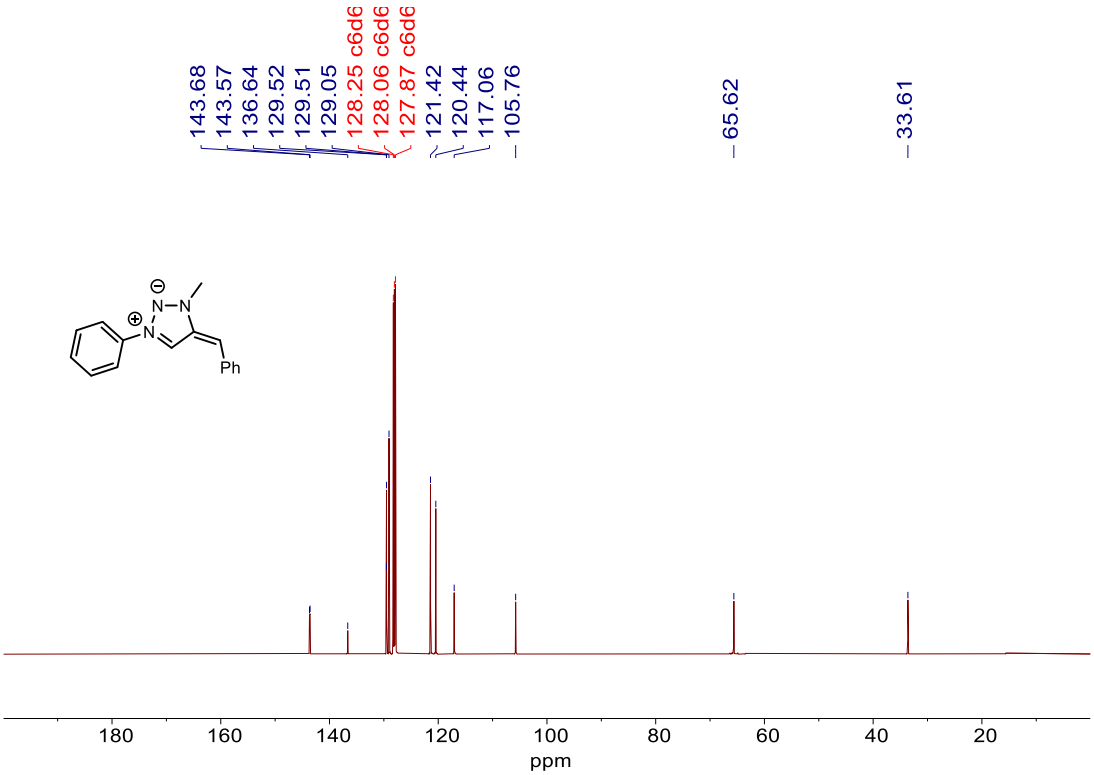


Figure S40. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1b**.

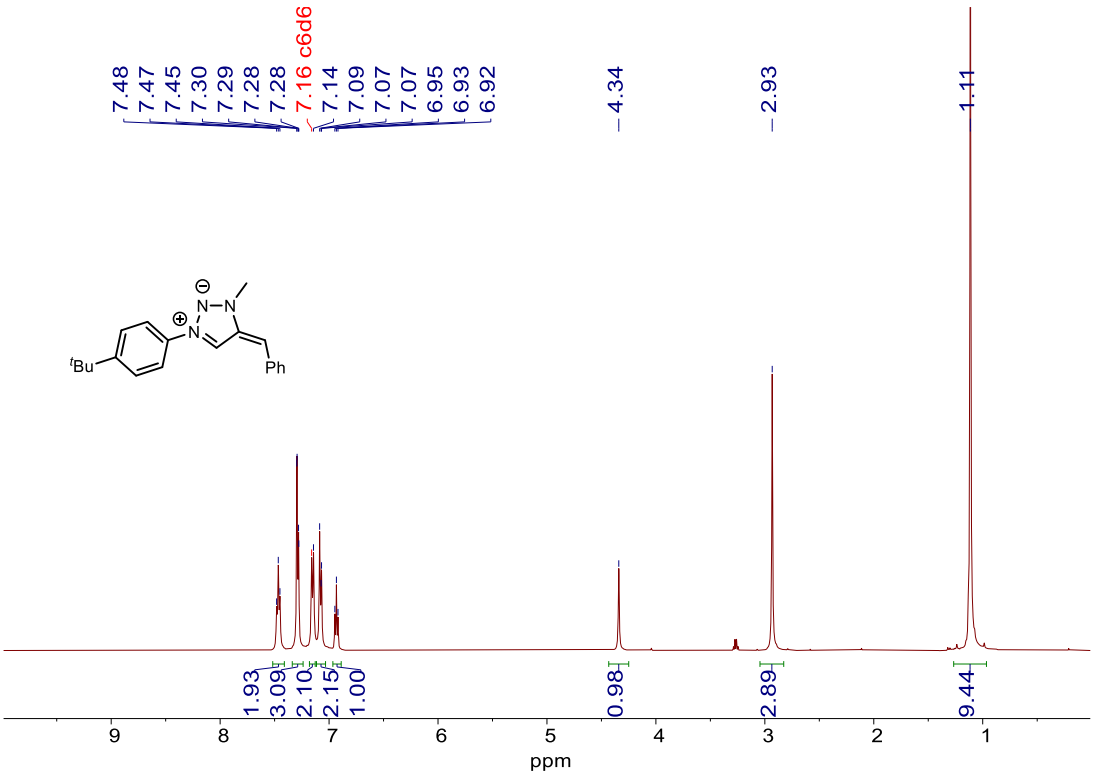


Figure S41. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1c**.

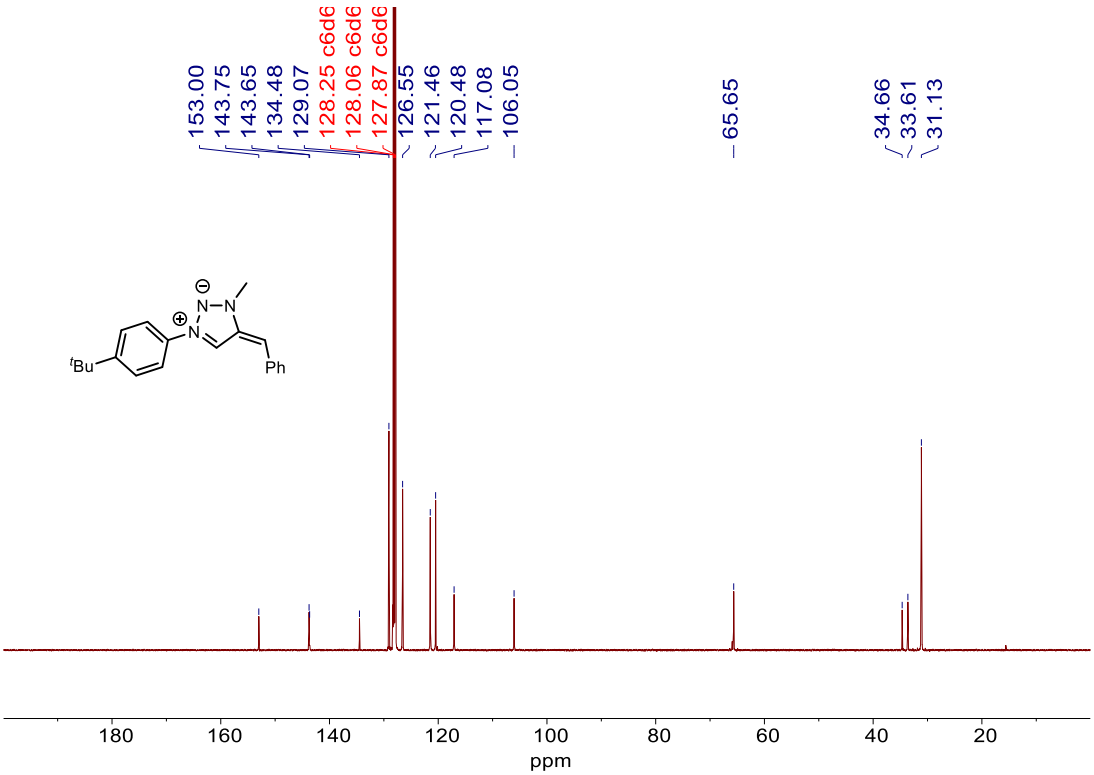


Figure S42. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1c**.

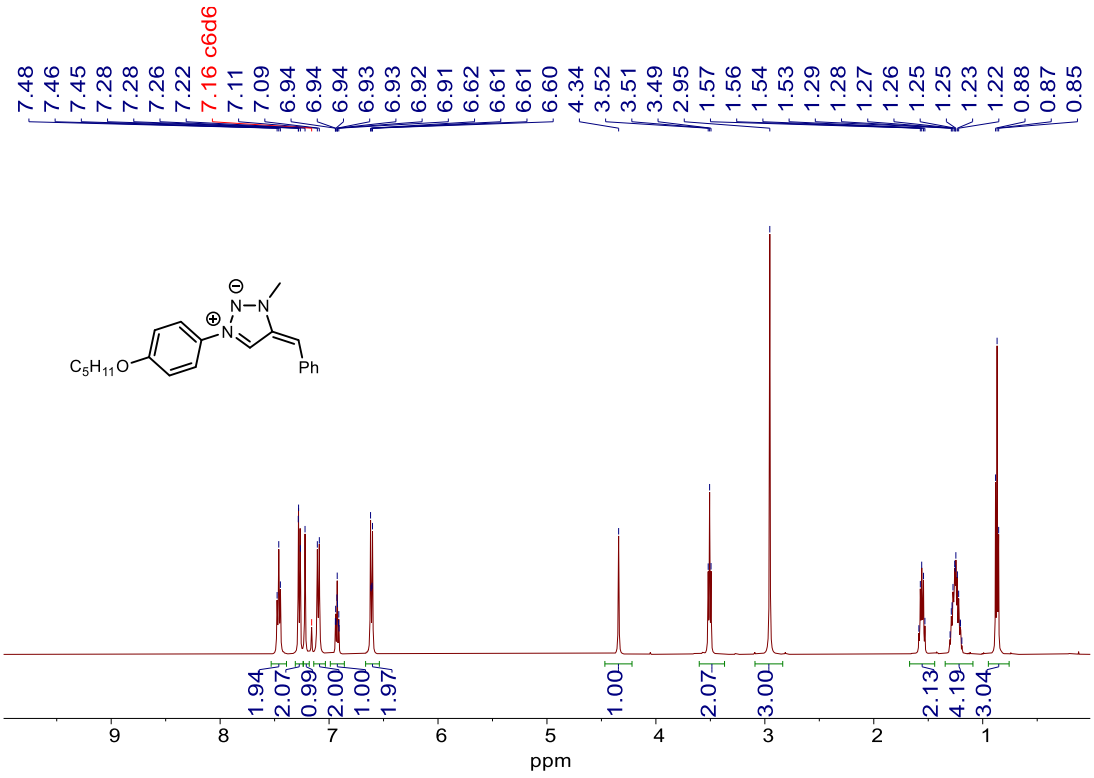


Figure S43. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1d**.

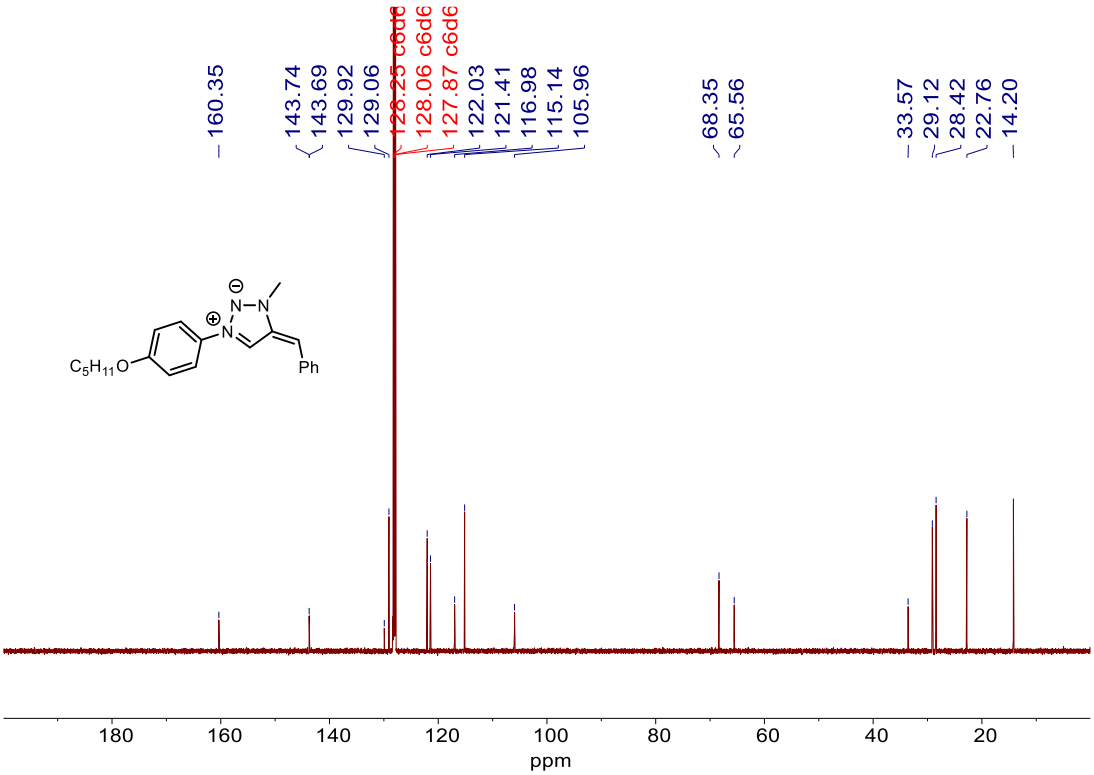


Figure S44. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1d**.

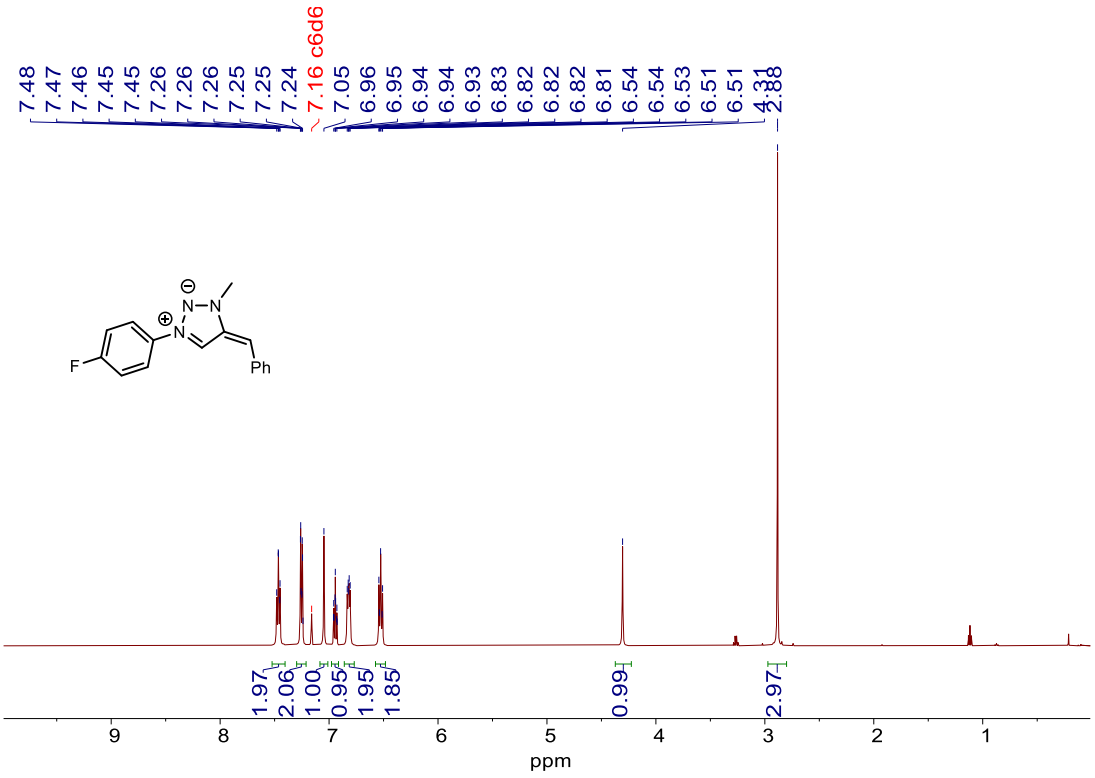


Figure S45. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1e**.

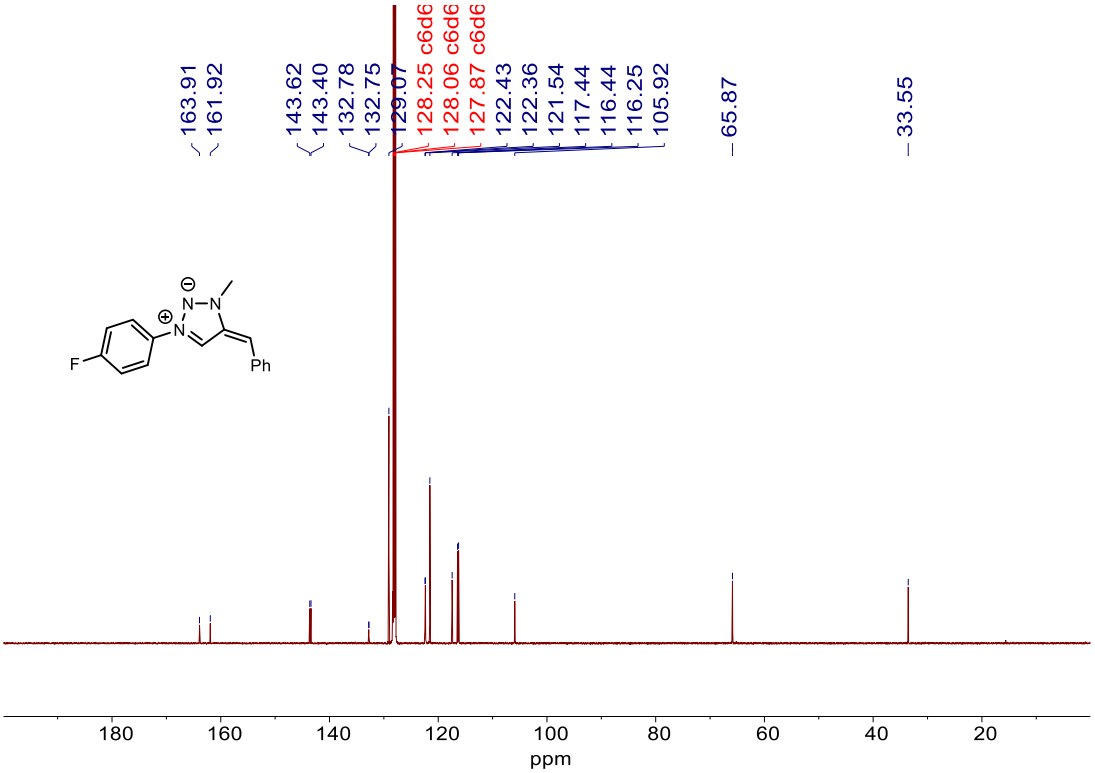


Figure S46. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1e**.

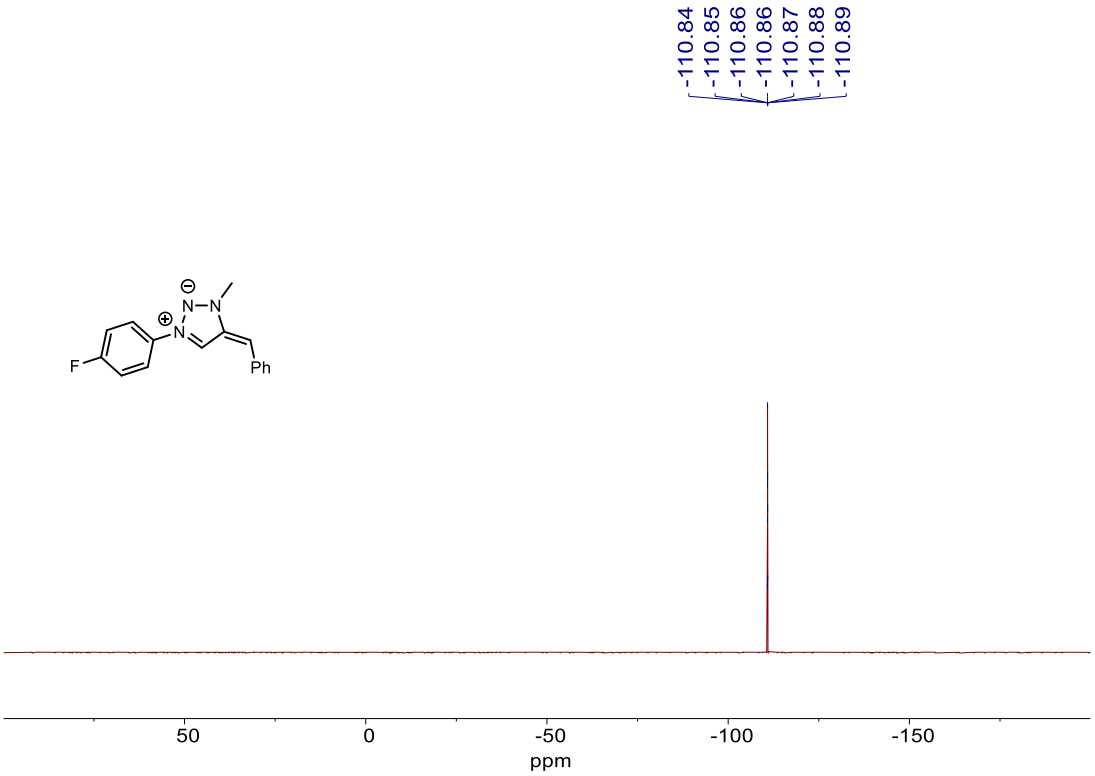


Figure S47. ^{19}F NMR (470 MHz, C_6D_6) spectrum of **1e**.

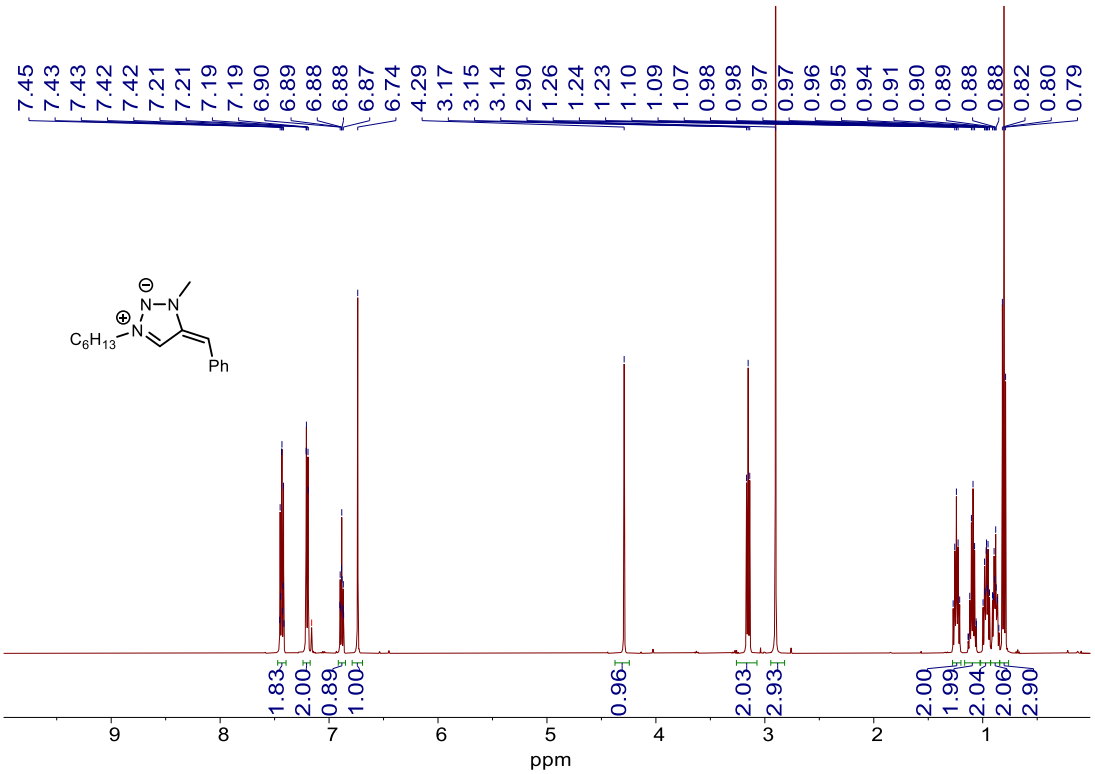


Figure S48. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1h**.

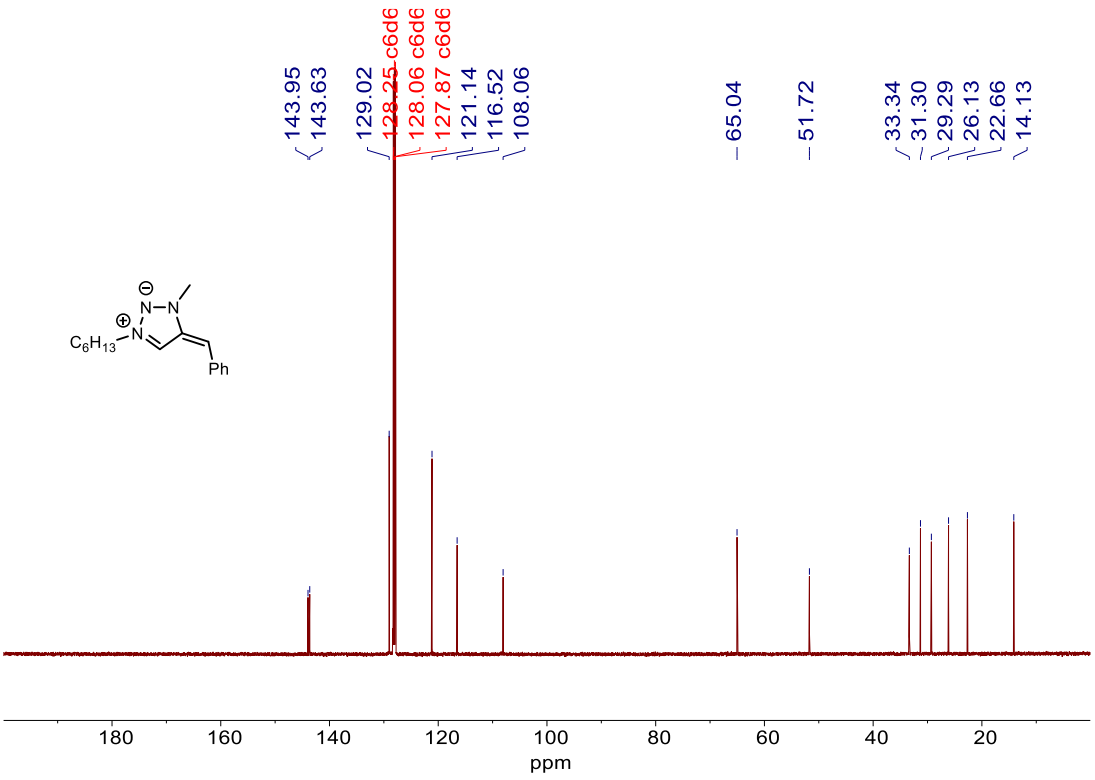


Figure S49. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1h**.

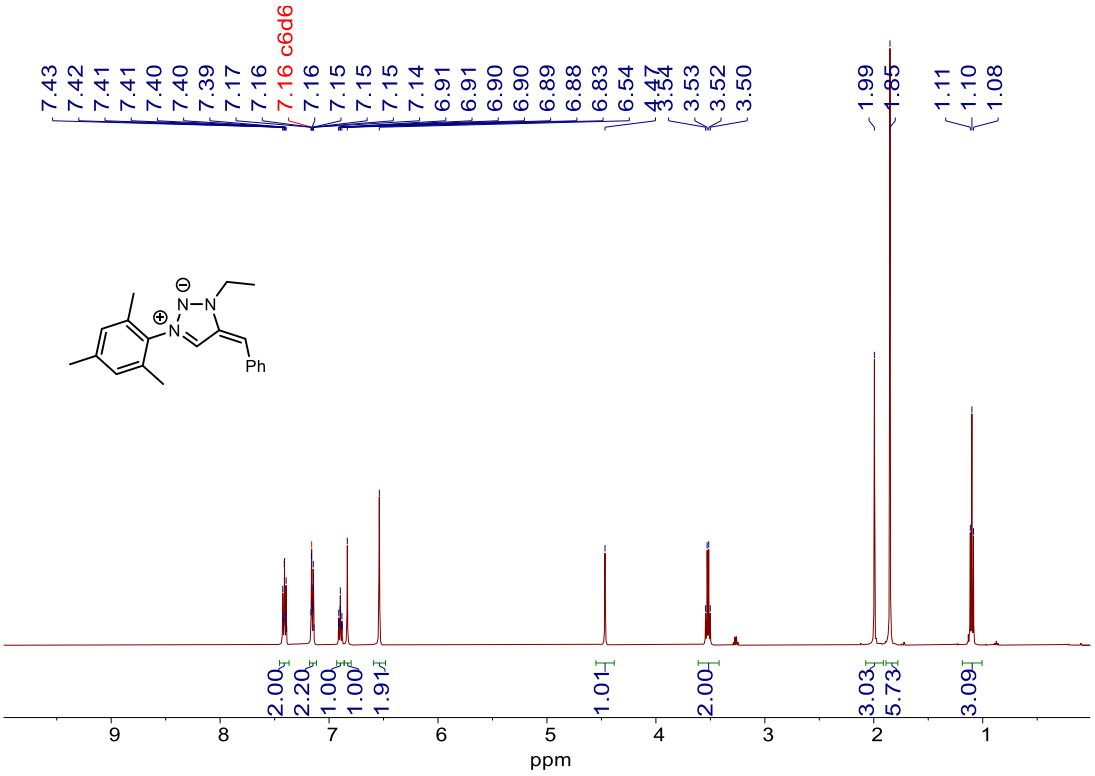


Figure S50. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1i**.

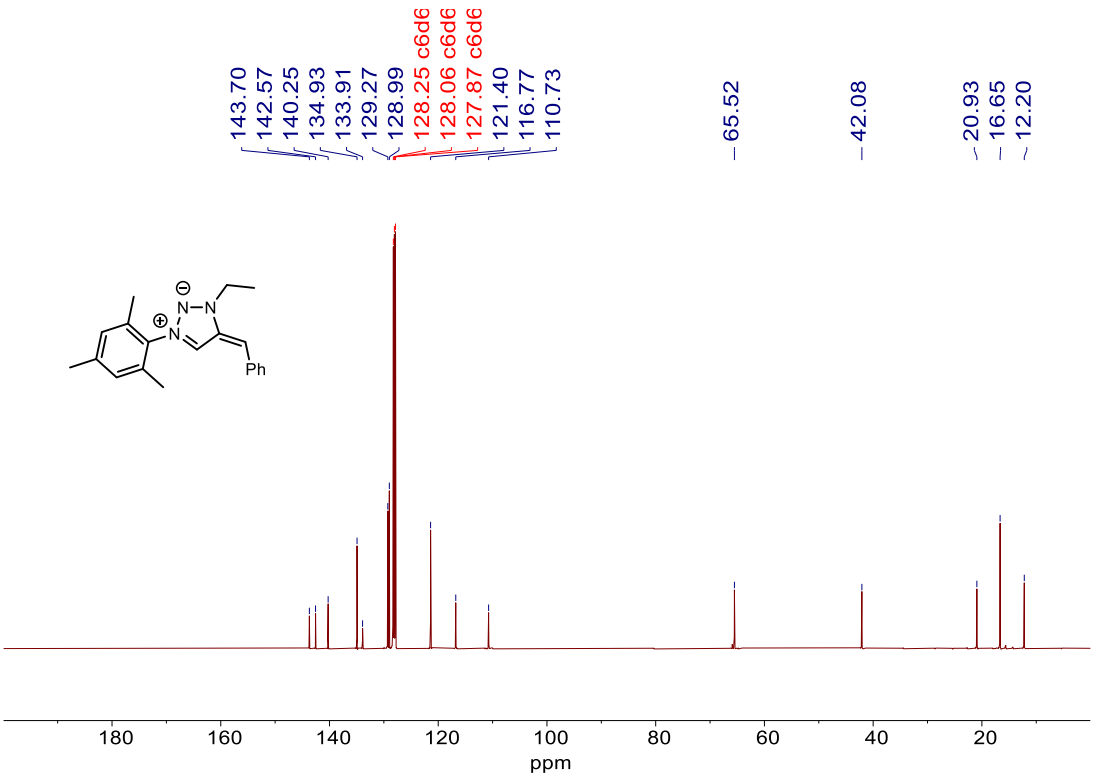


Figure S51. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1i**.

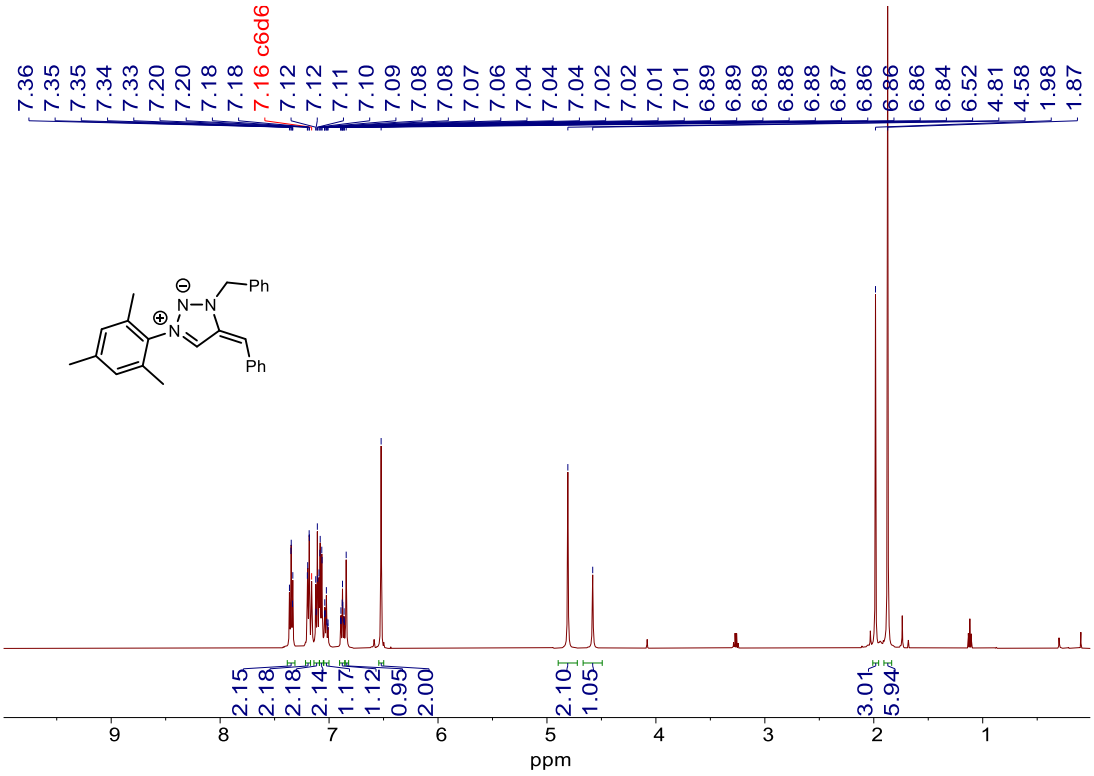


Figure S52. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1j**.

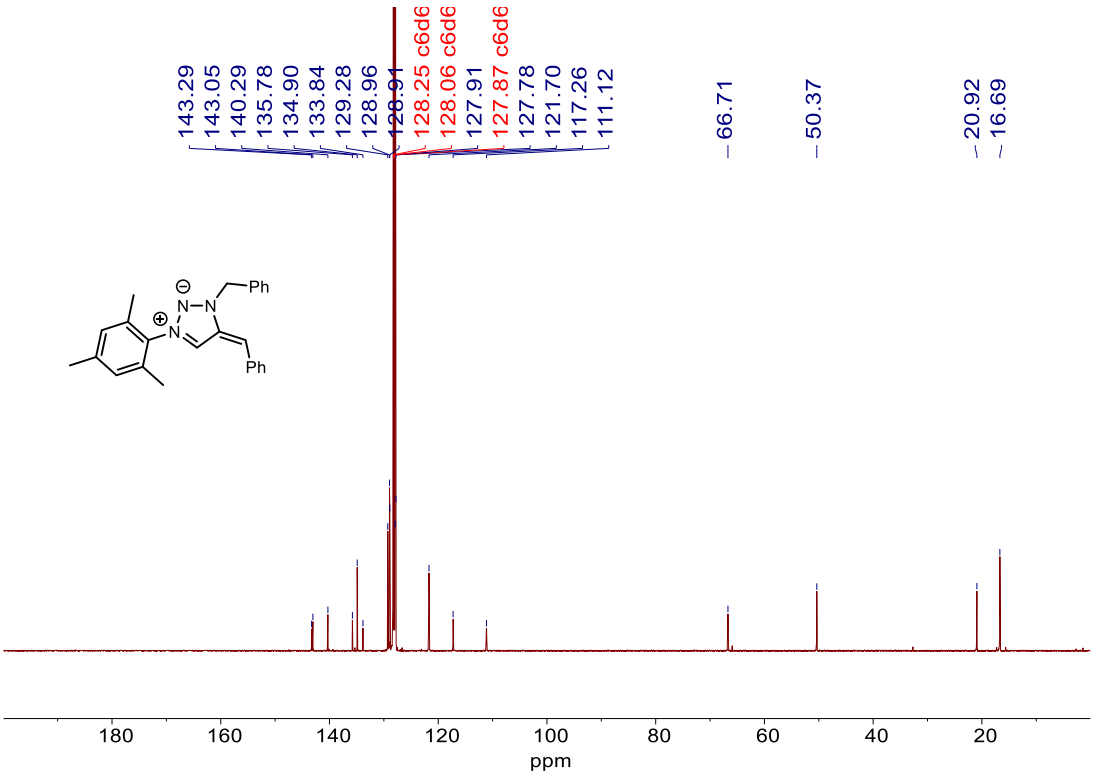


Figure S53. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1j**.

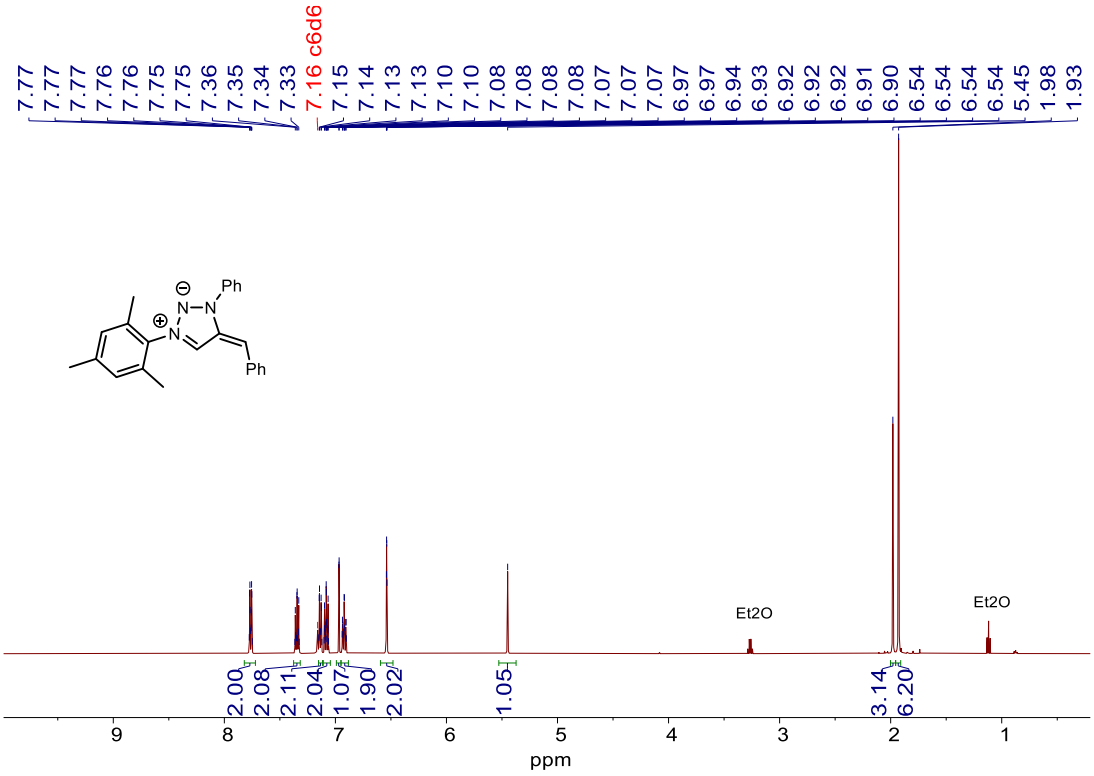


Figure S54. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1k**.

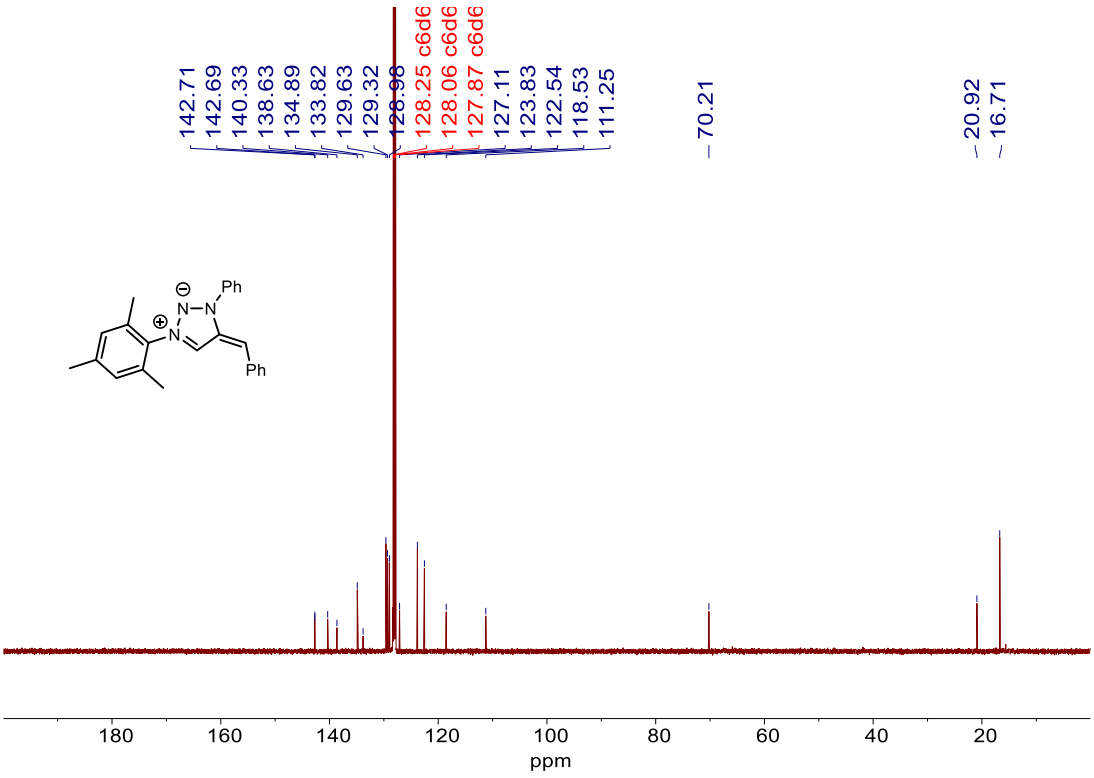


Figure S55. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1k**.

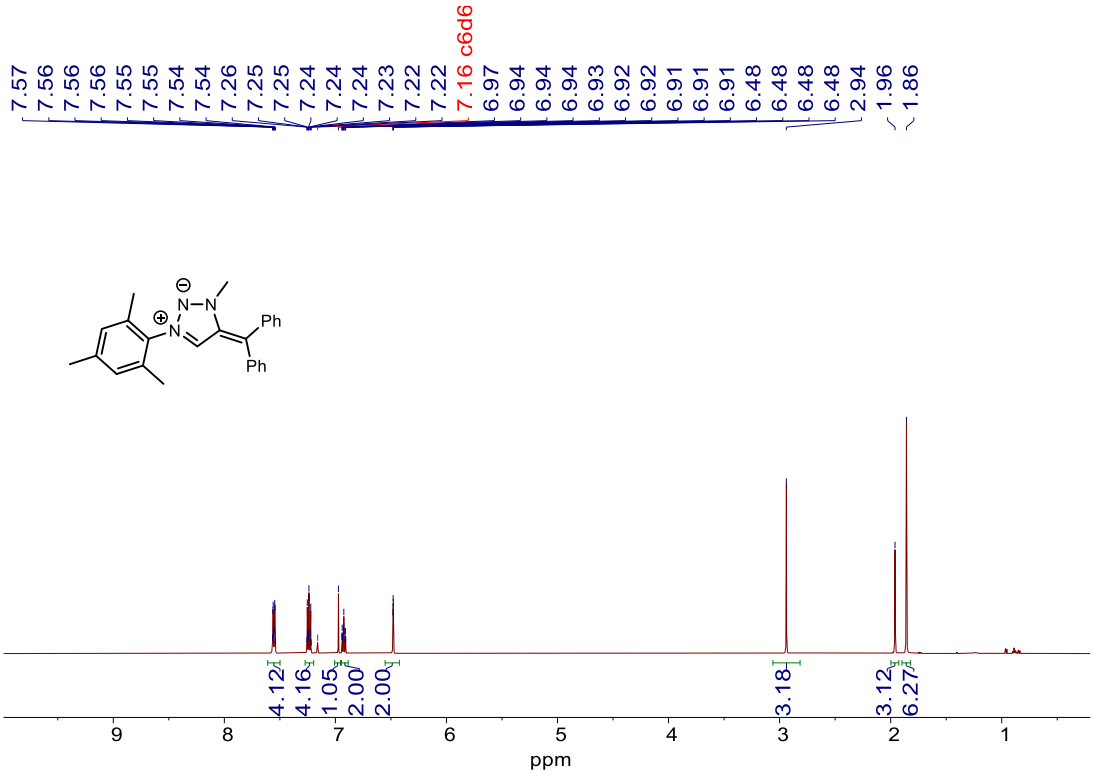


Figure S56. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **1l**.

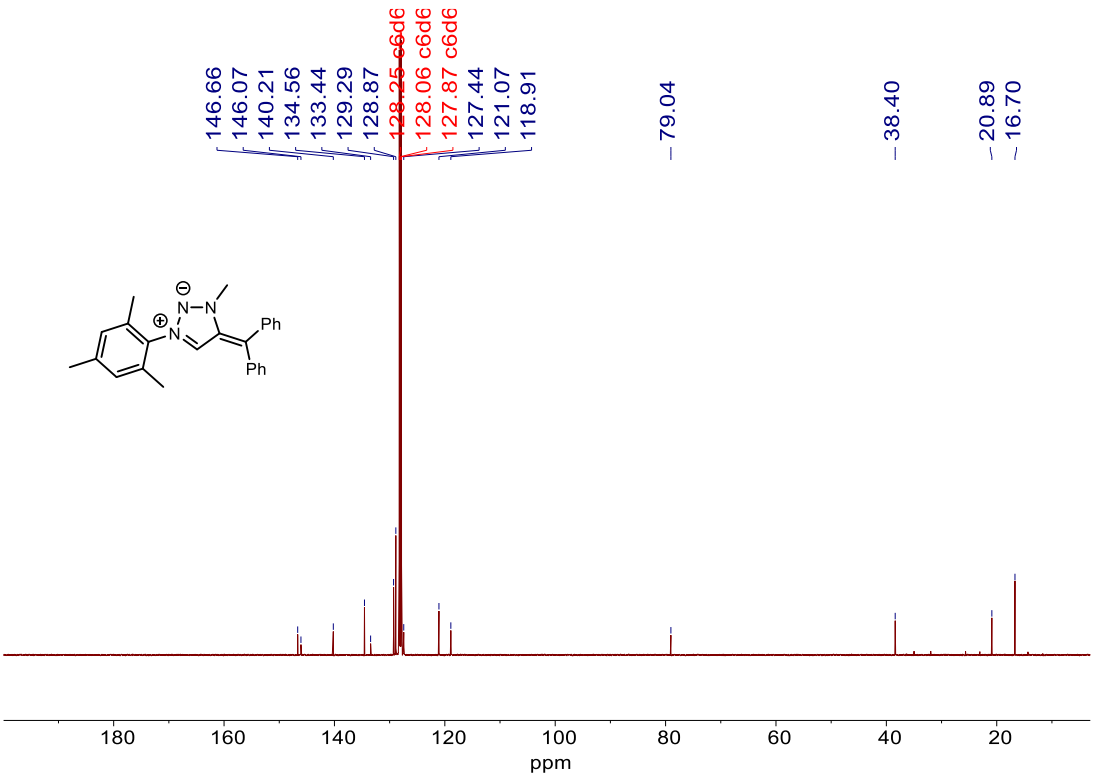


Figure S57. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **1l**.

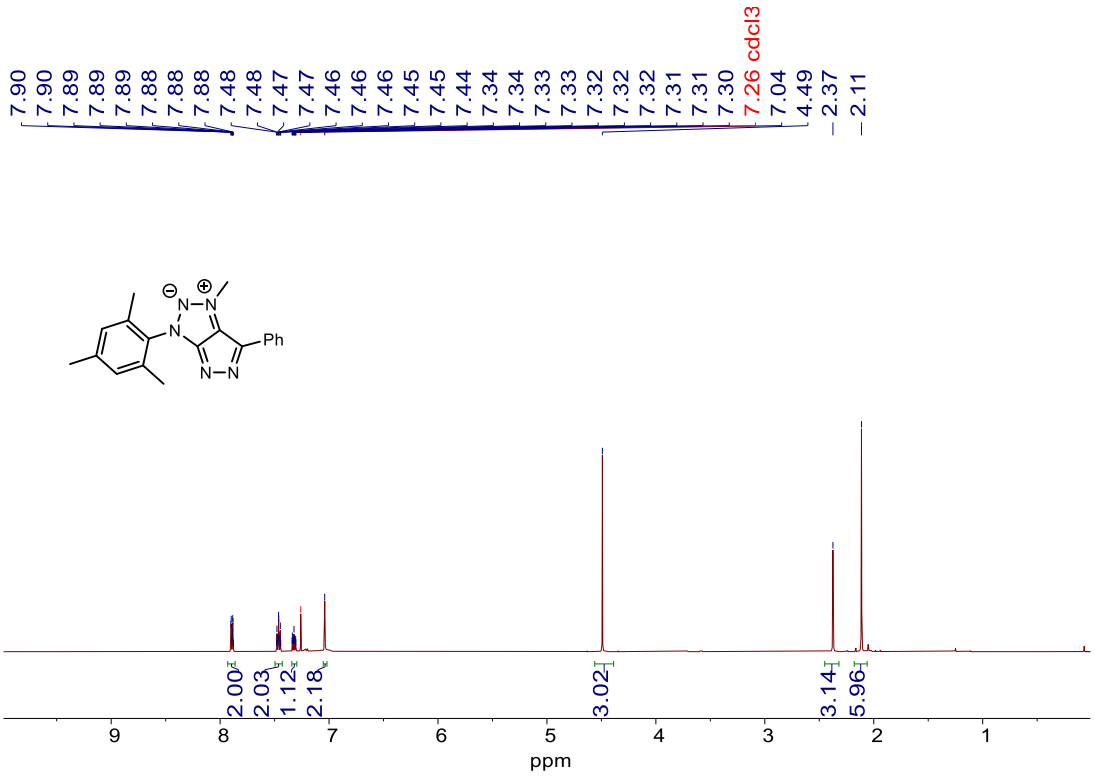


Figure S58. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2a**.

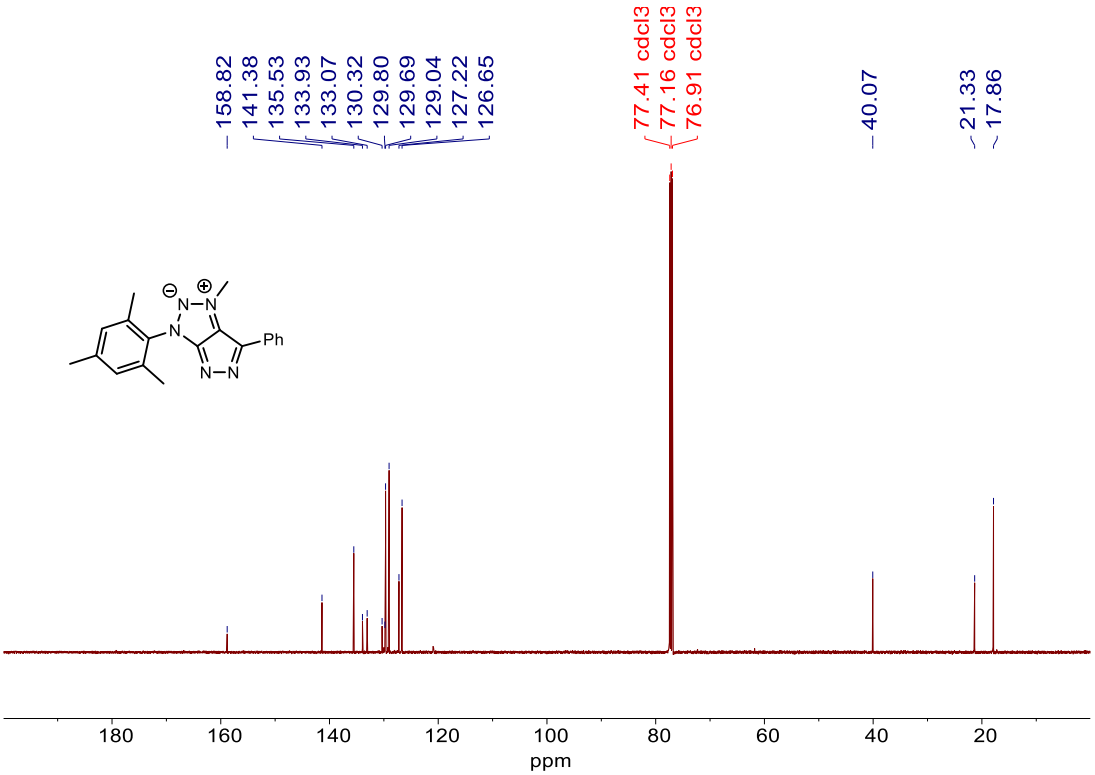


Figure S59. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2a**.

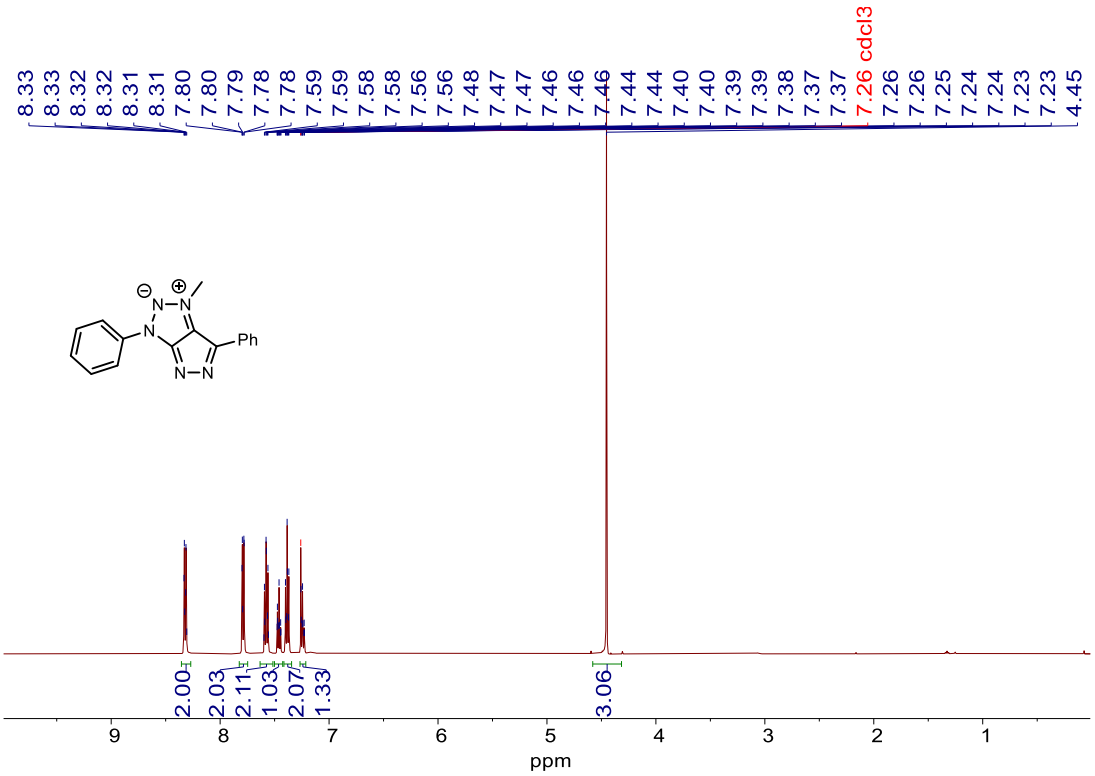


Figure S60. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2b**.

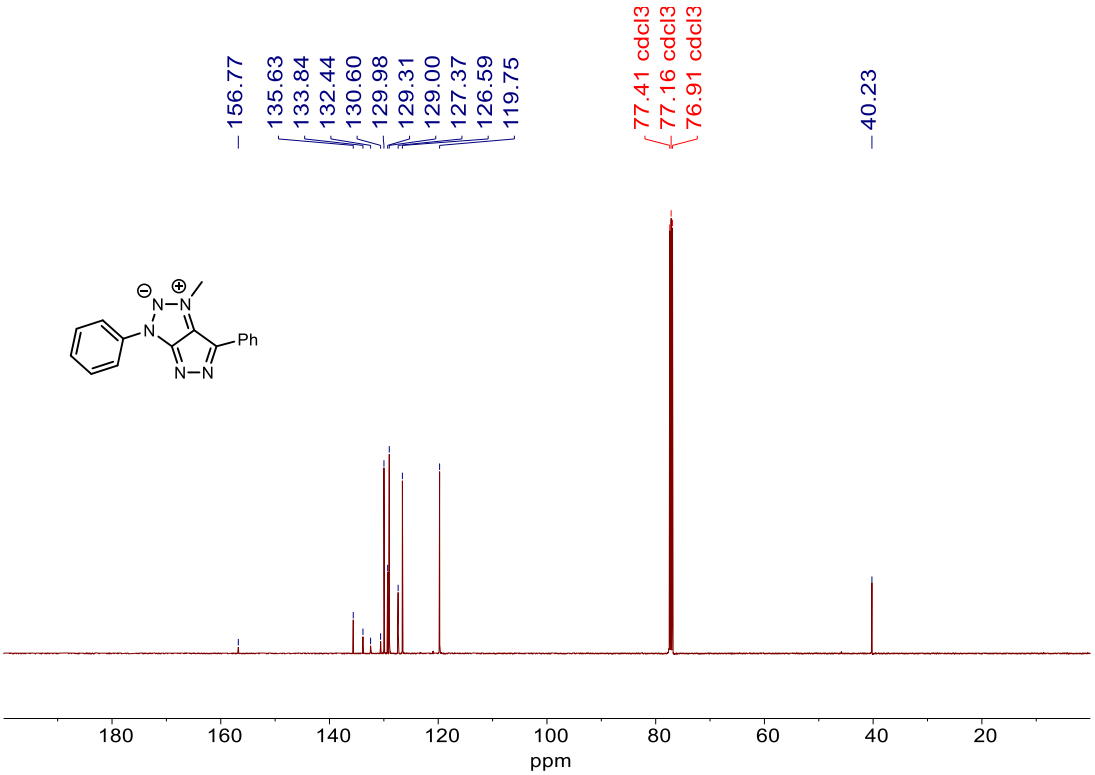


Figure S61. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2b**.

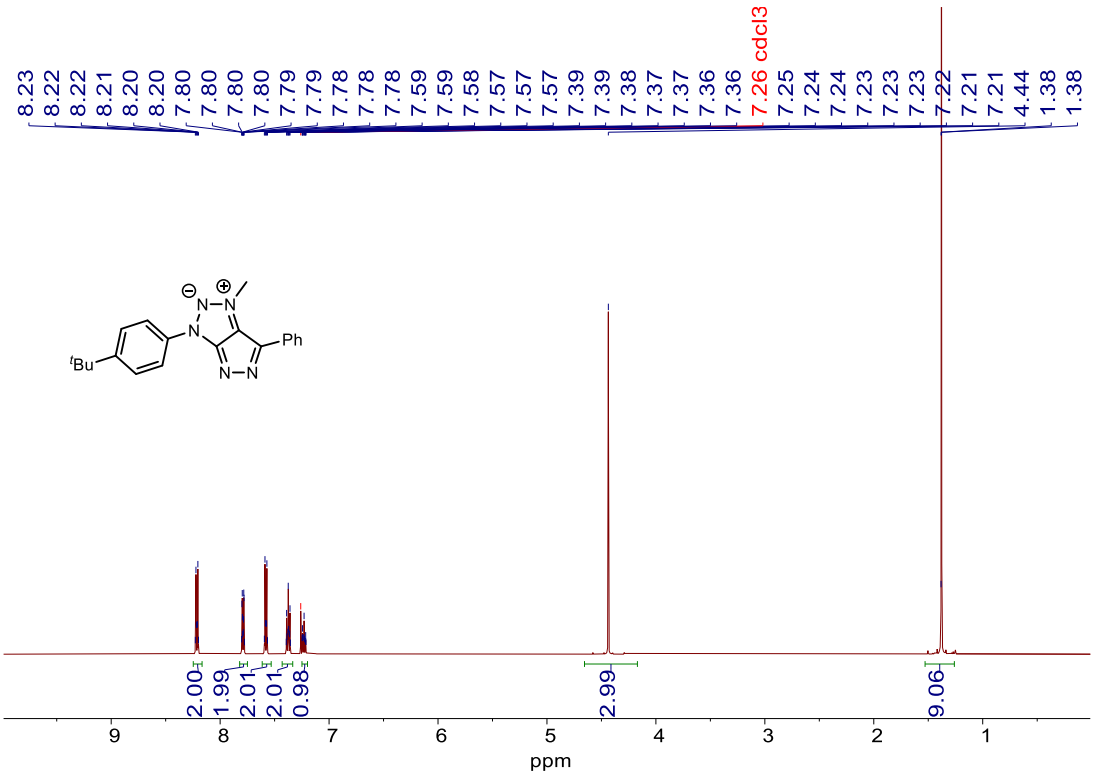


Figure S62. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2c**.

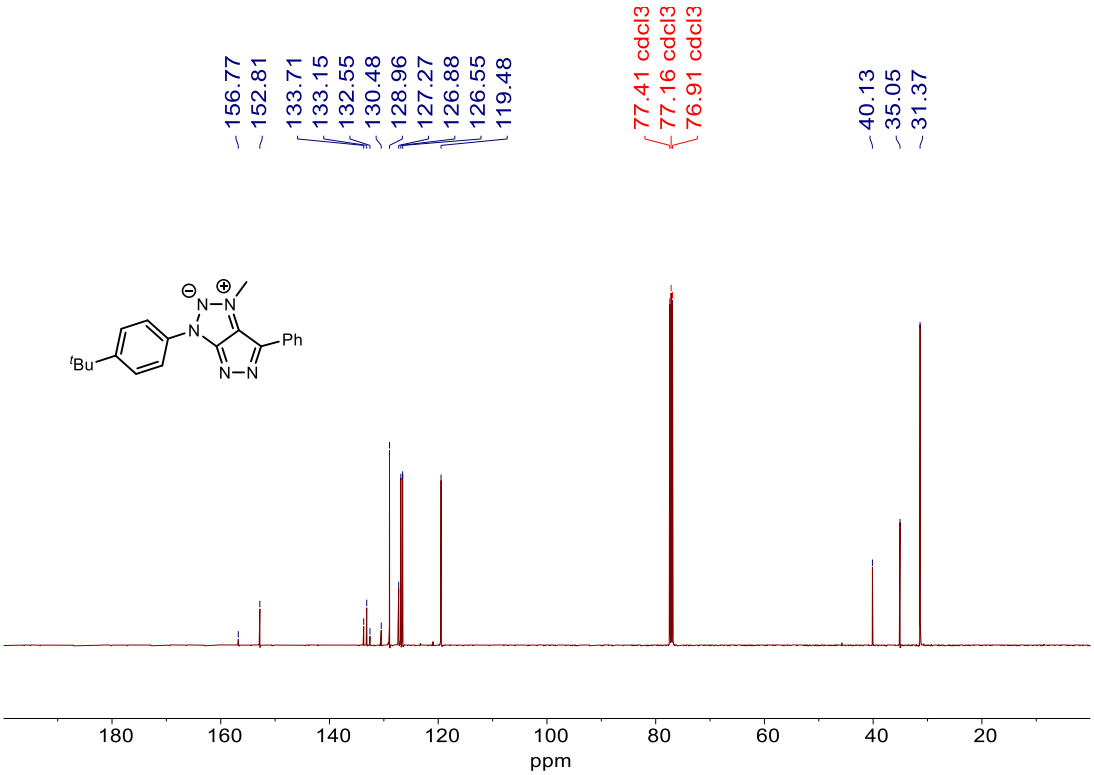


Figure S63. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2c**.

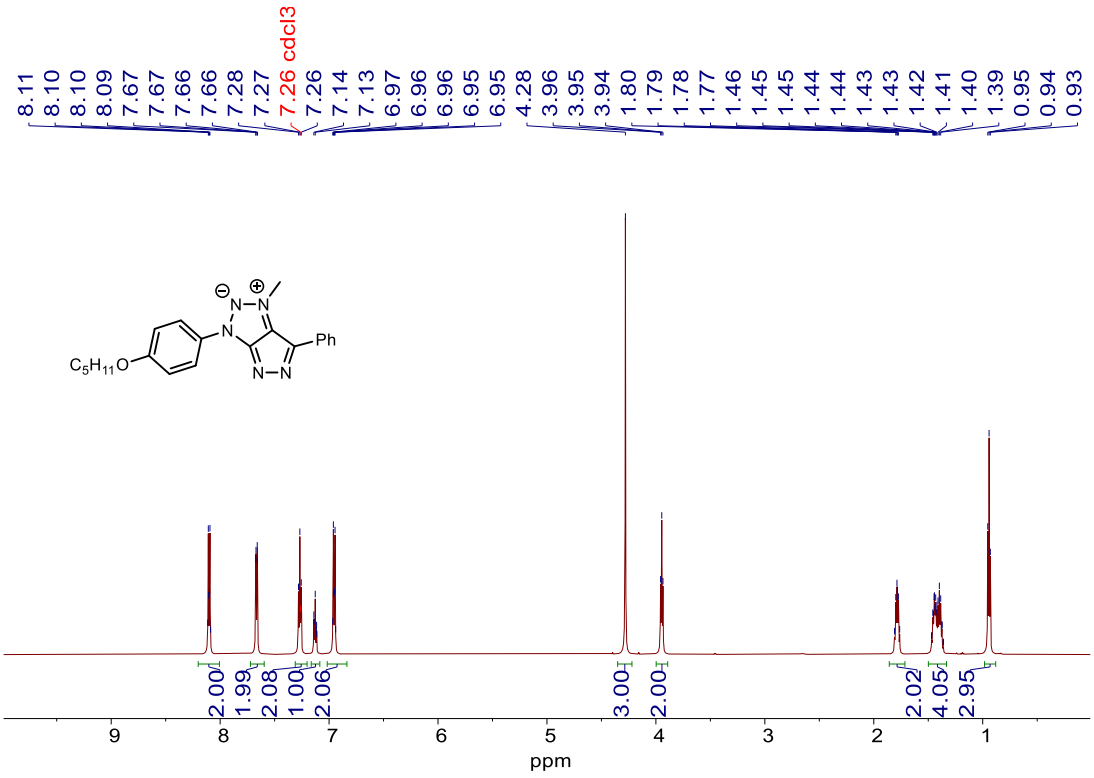


Figure S64. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2d**.

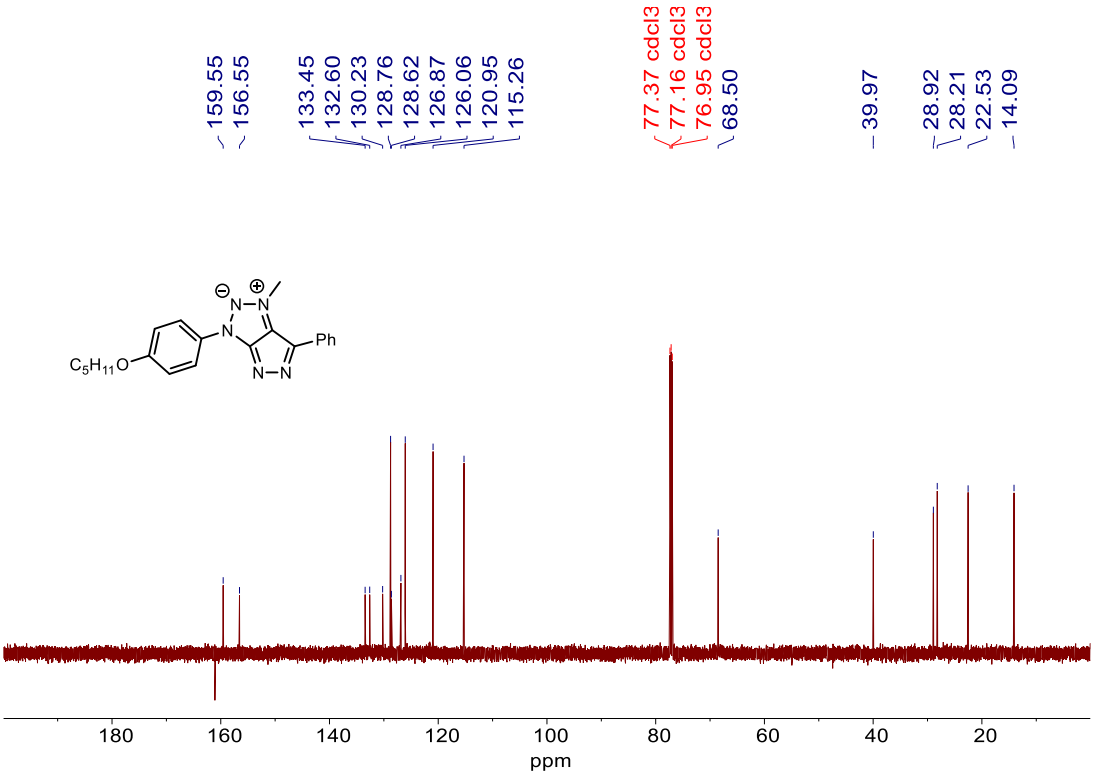


Figure S65. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2d**.

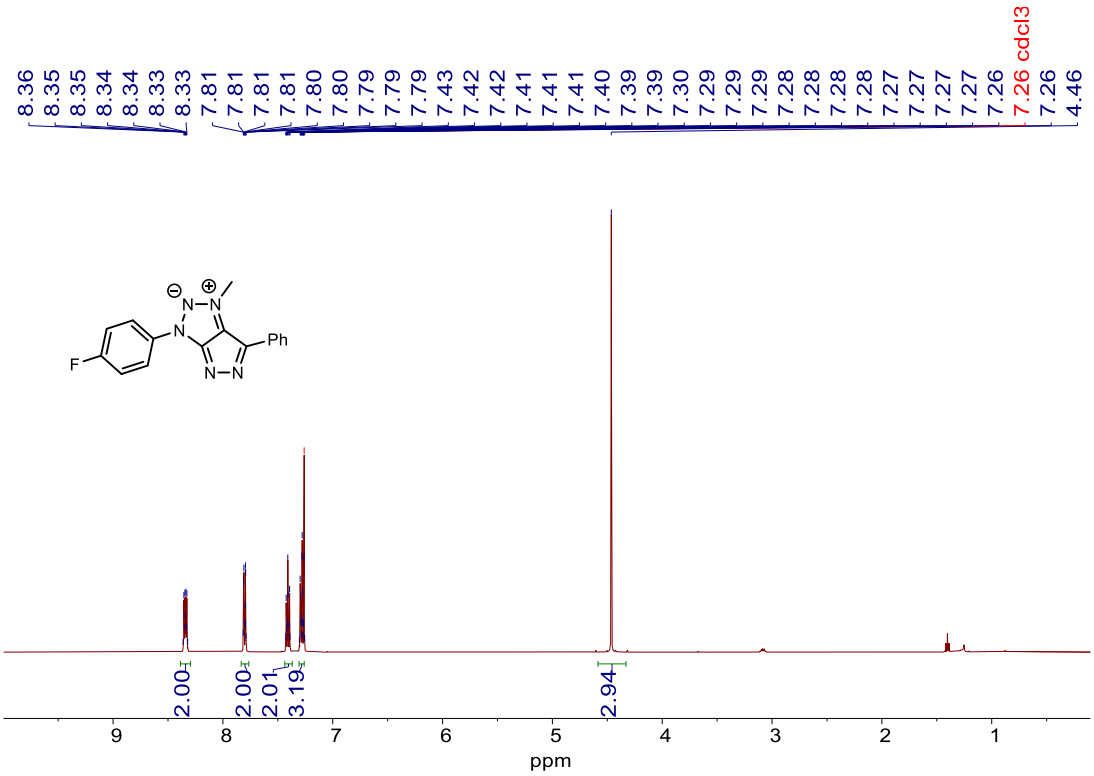


Figure S66. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2e**.

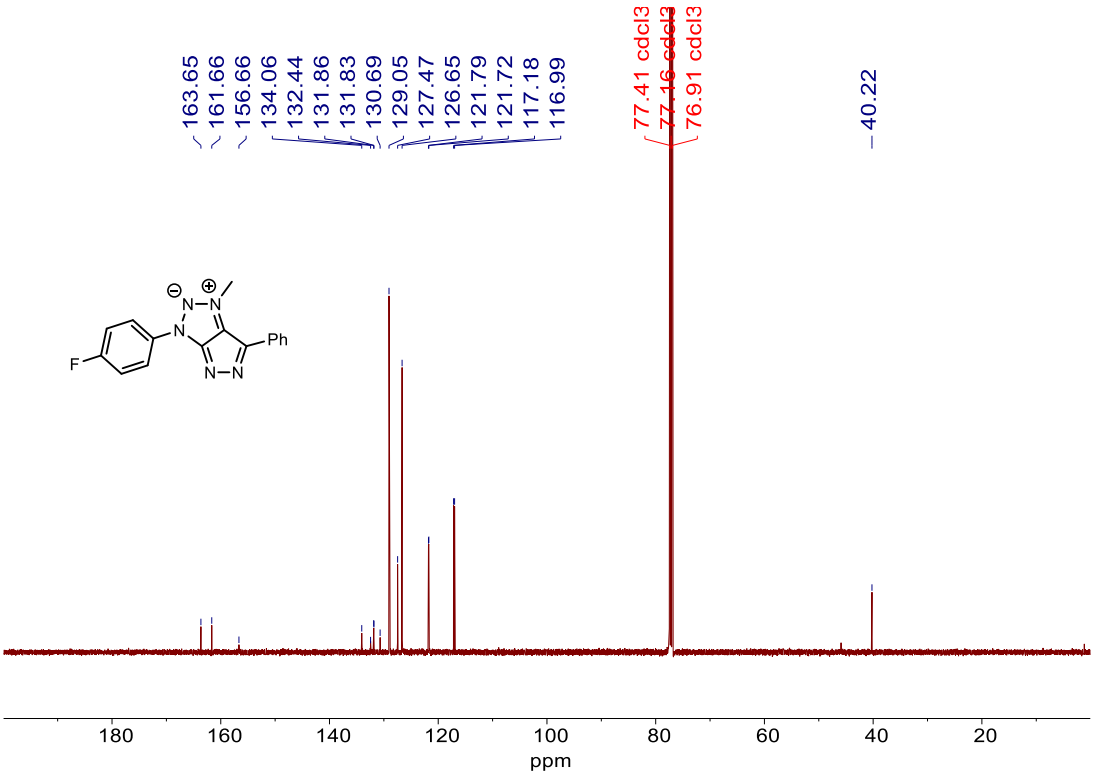


Figure S67. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2e**.

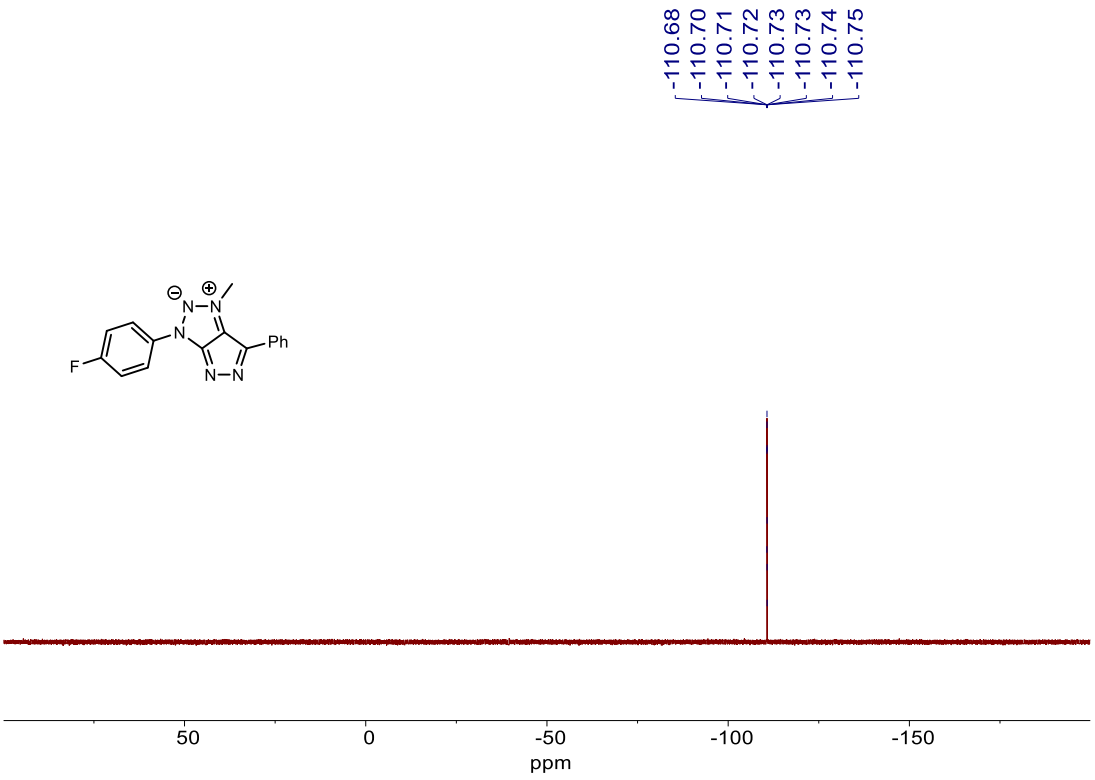


Figure S68. ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2e**.

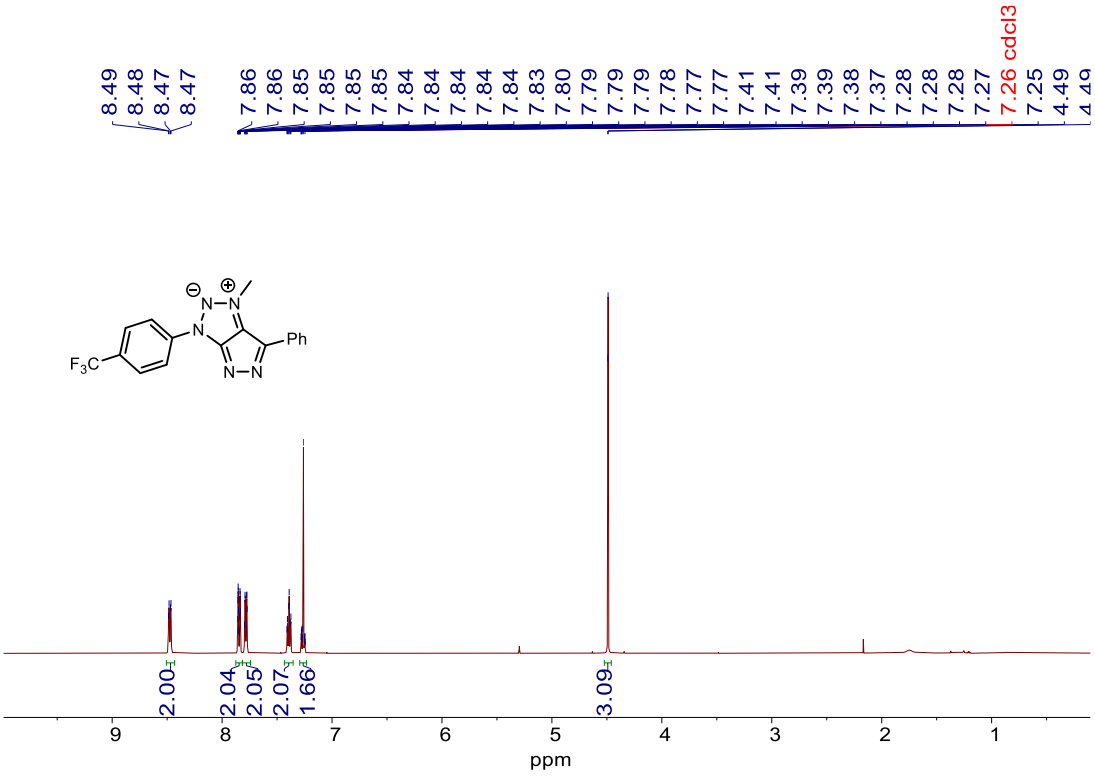


Figure S69. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2f**.

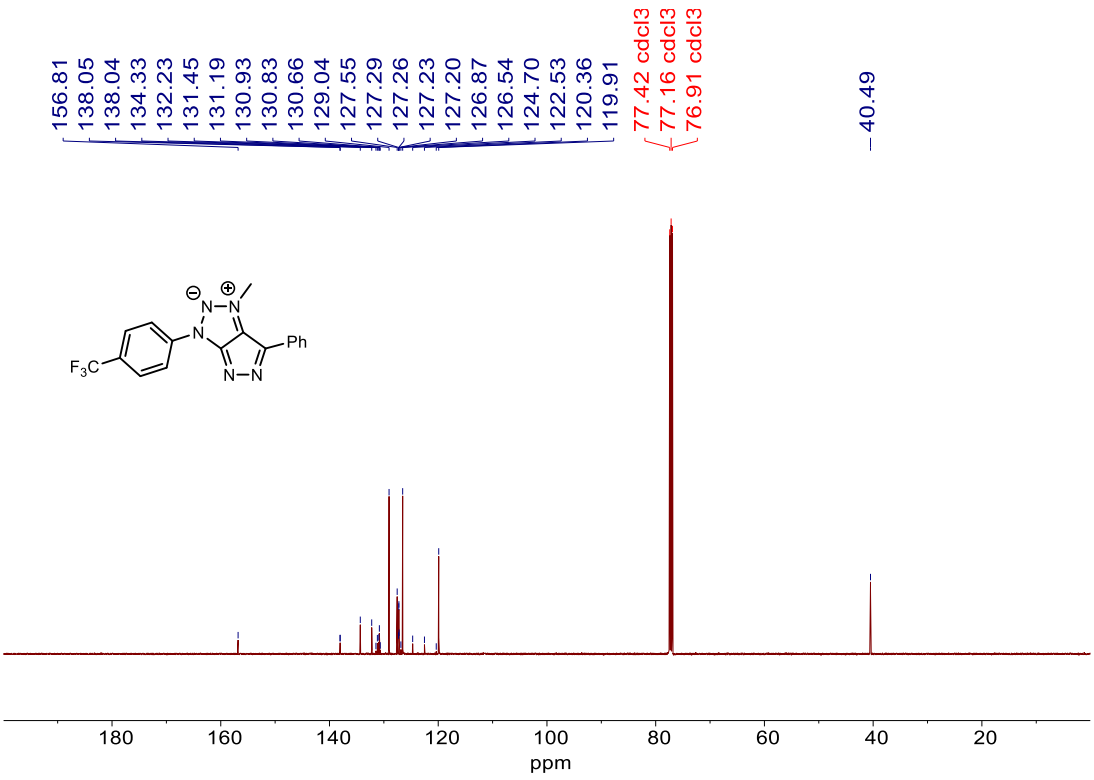


Figure S70. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2f**.

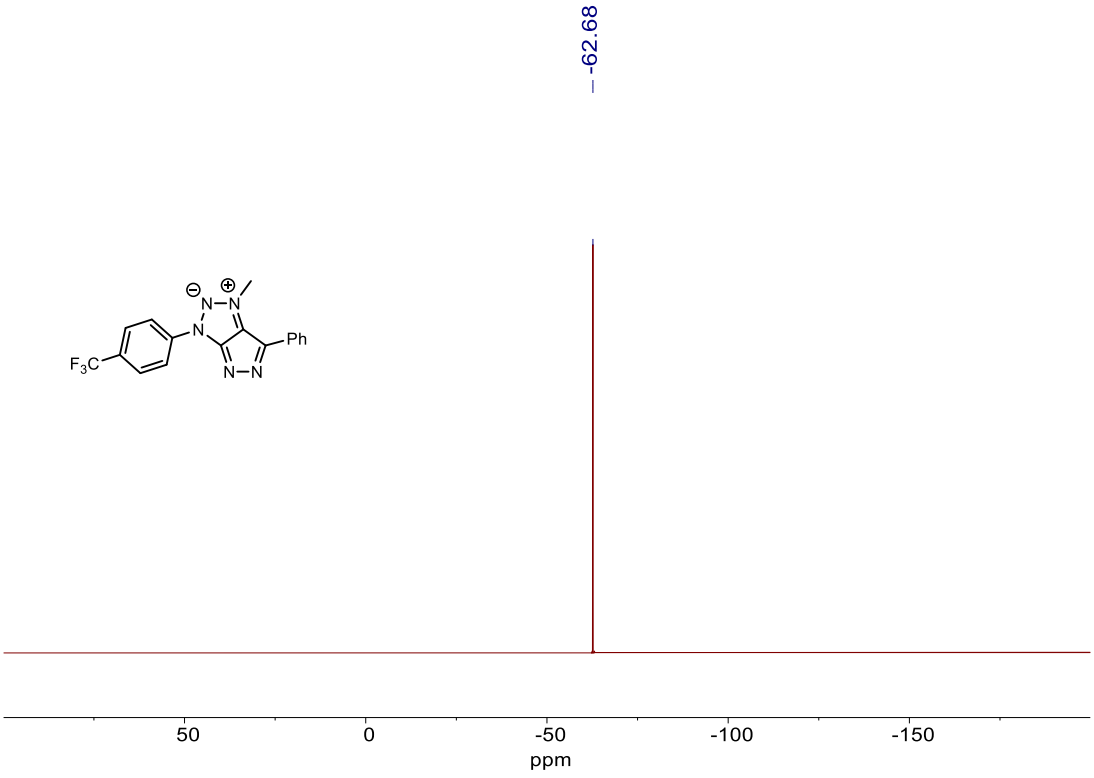


Figure S71. ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2f**.

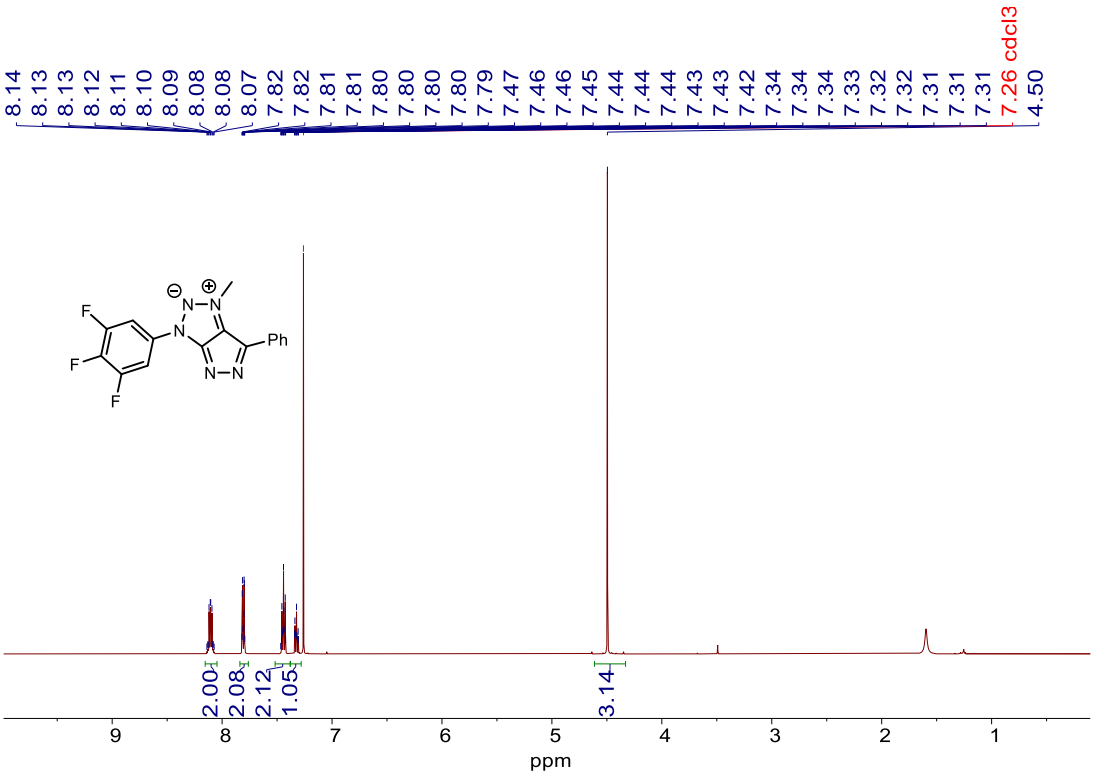


Figure S72. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2g**.

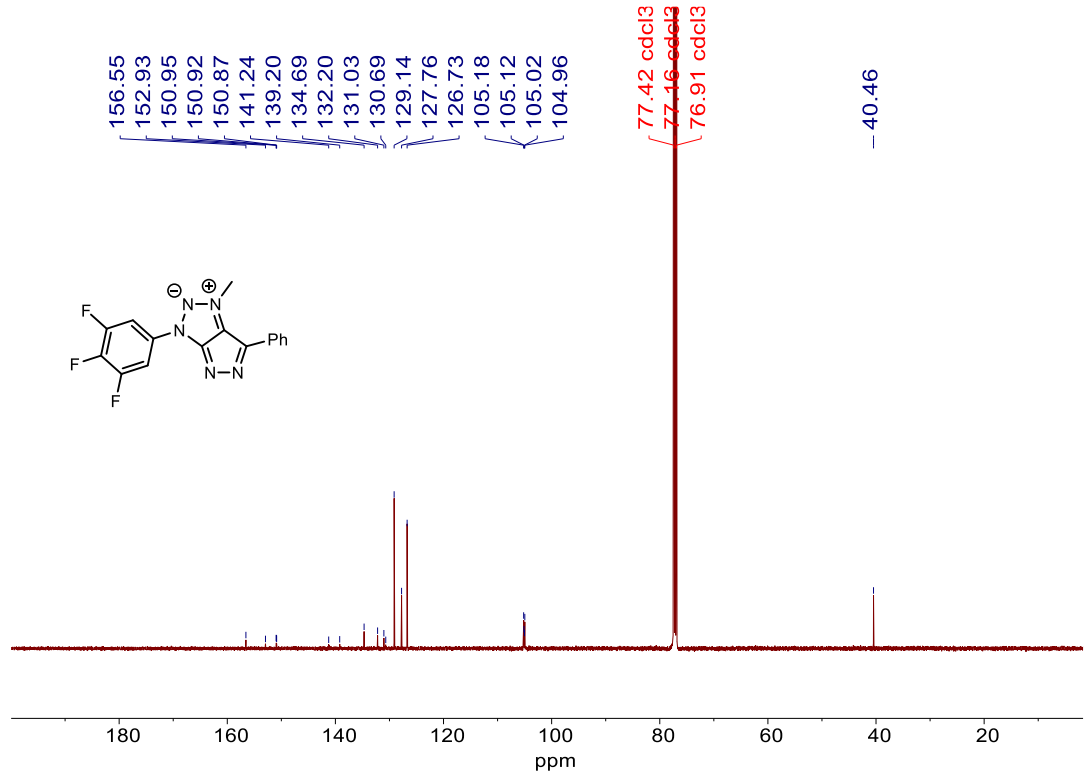


Figure S73. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2g**.

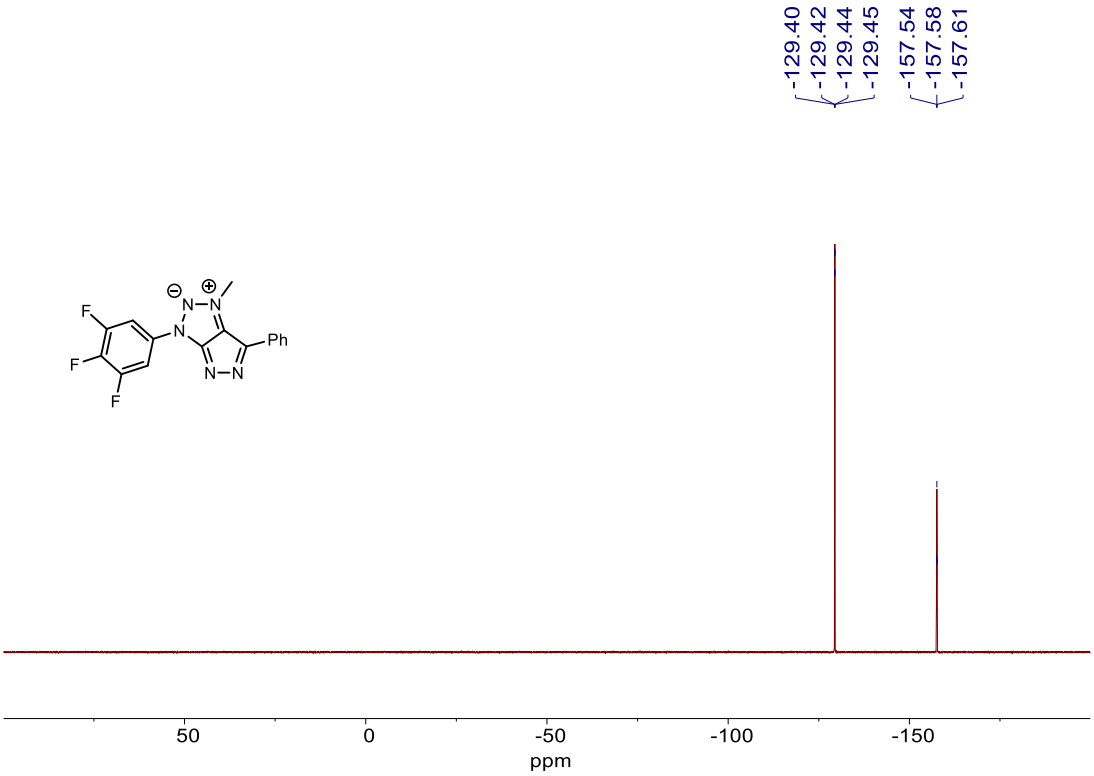


Figure S74. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2g**.

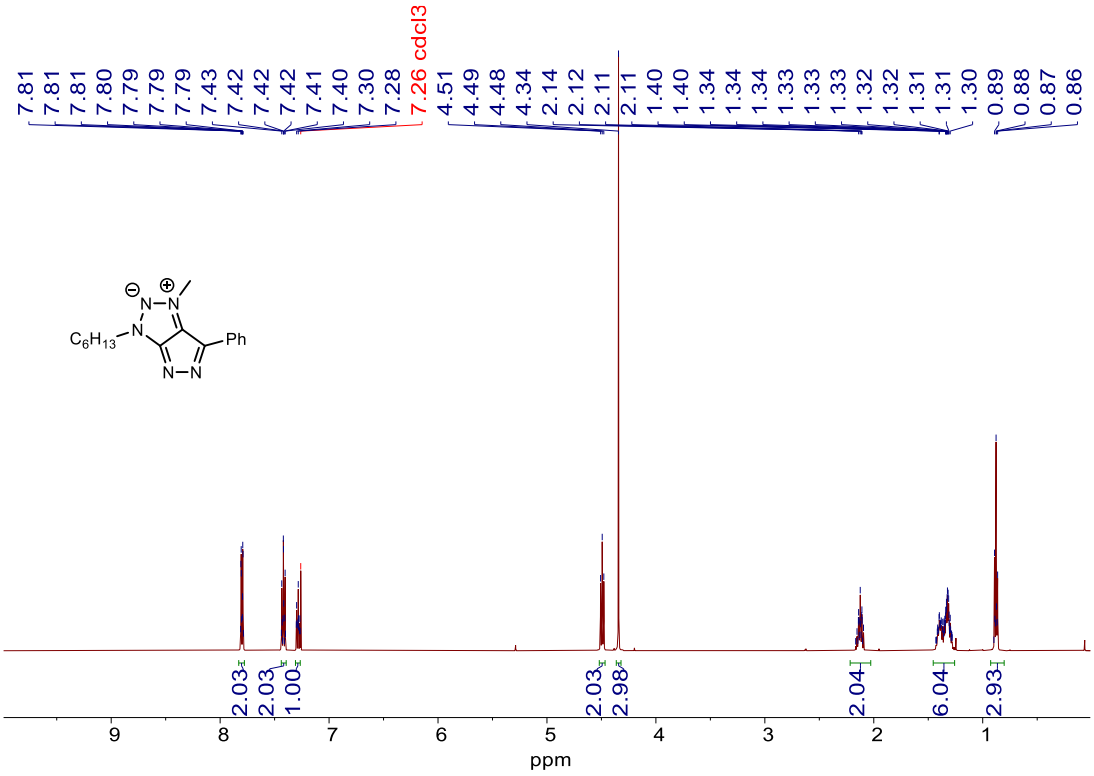


Figure S75. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2h**.

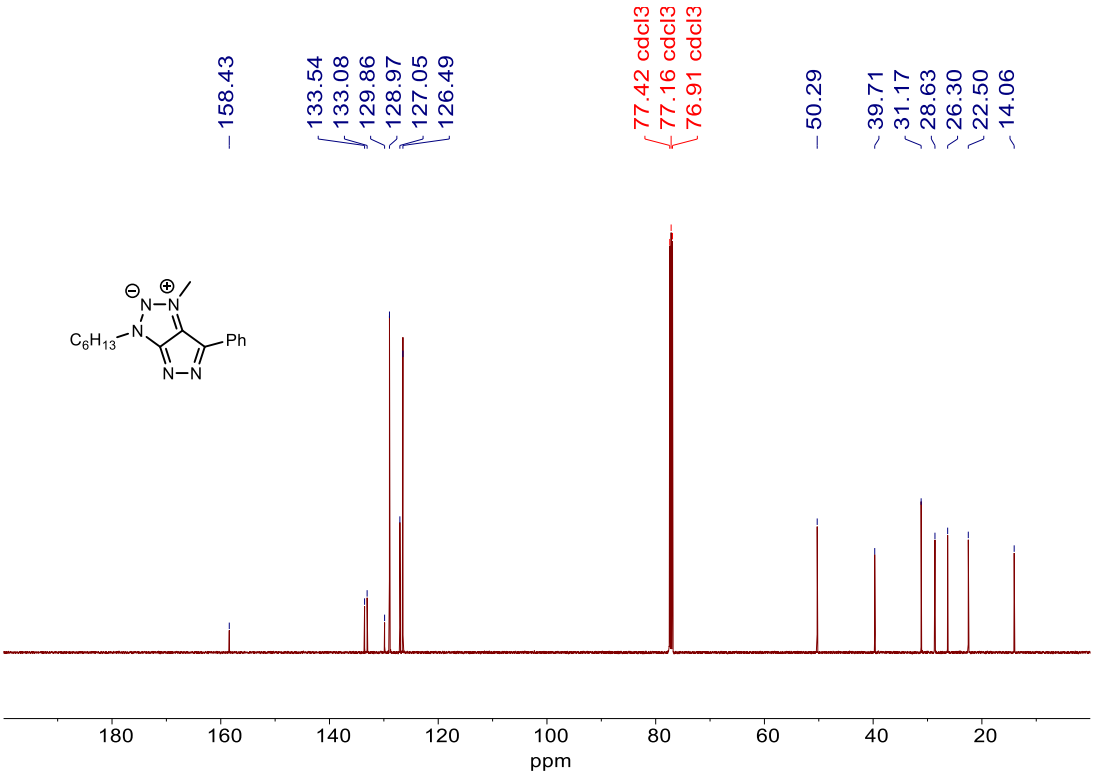


Figure S76. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2h**

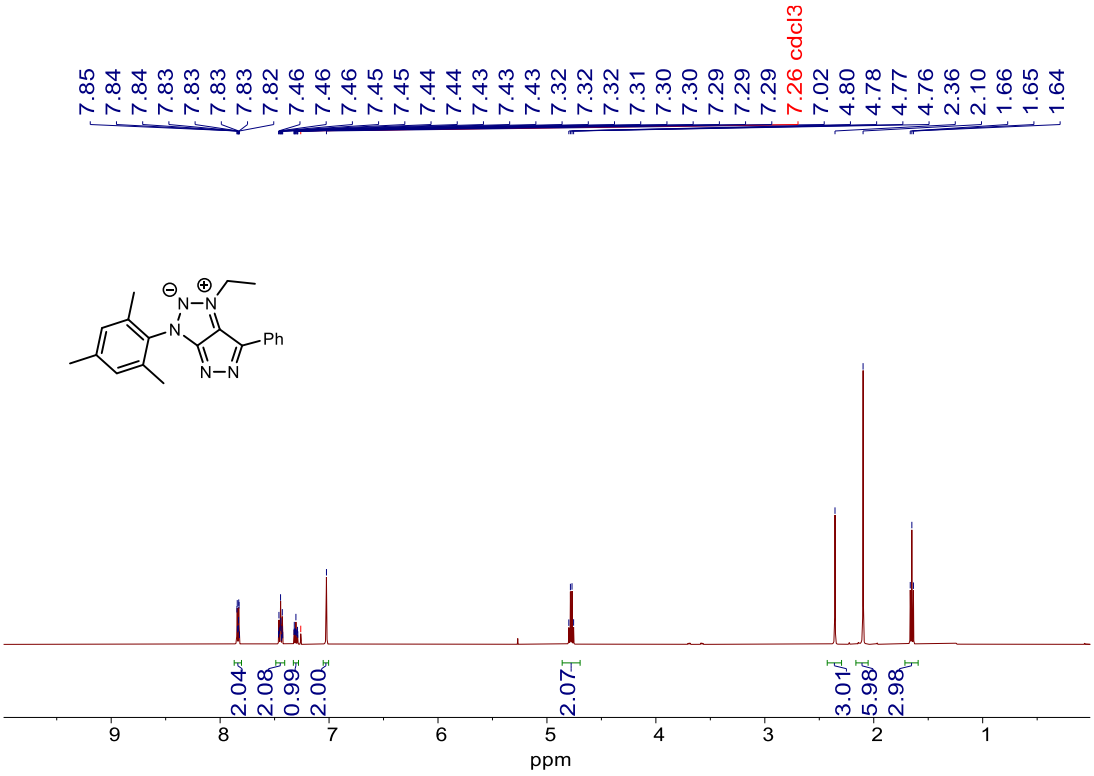


Figure S77. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2i**.

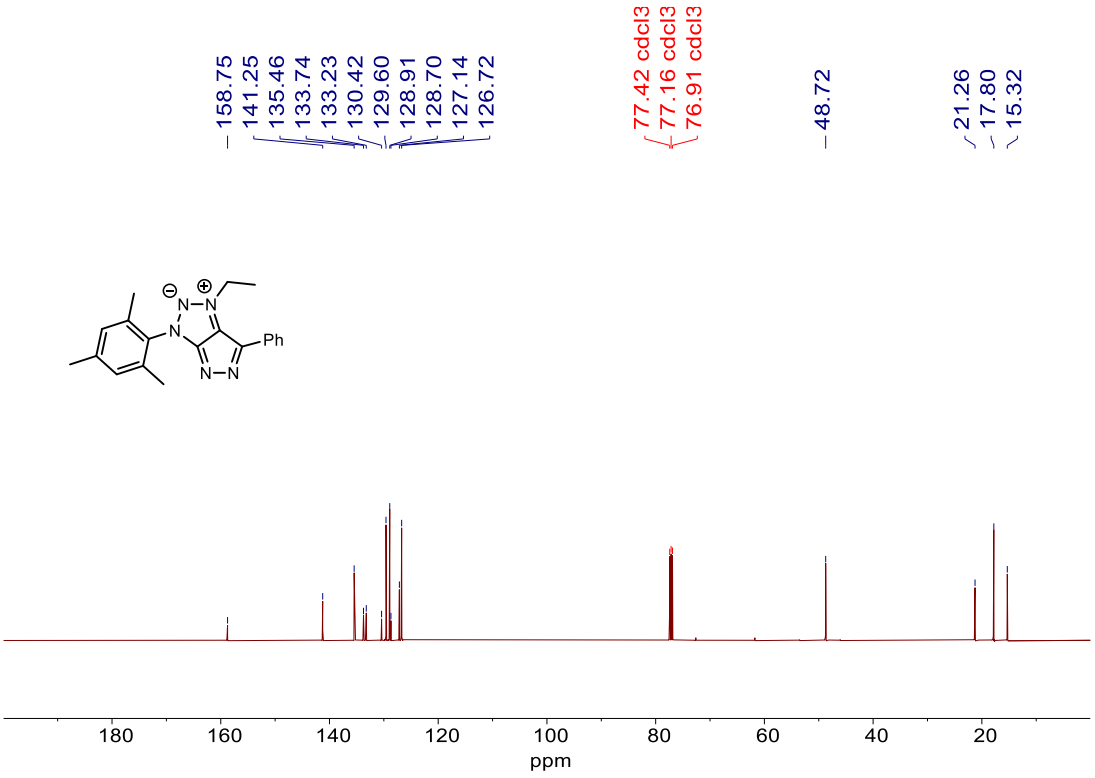


Figure S78. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2i**.

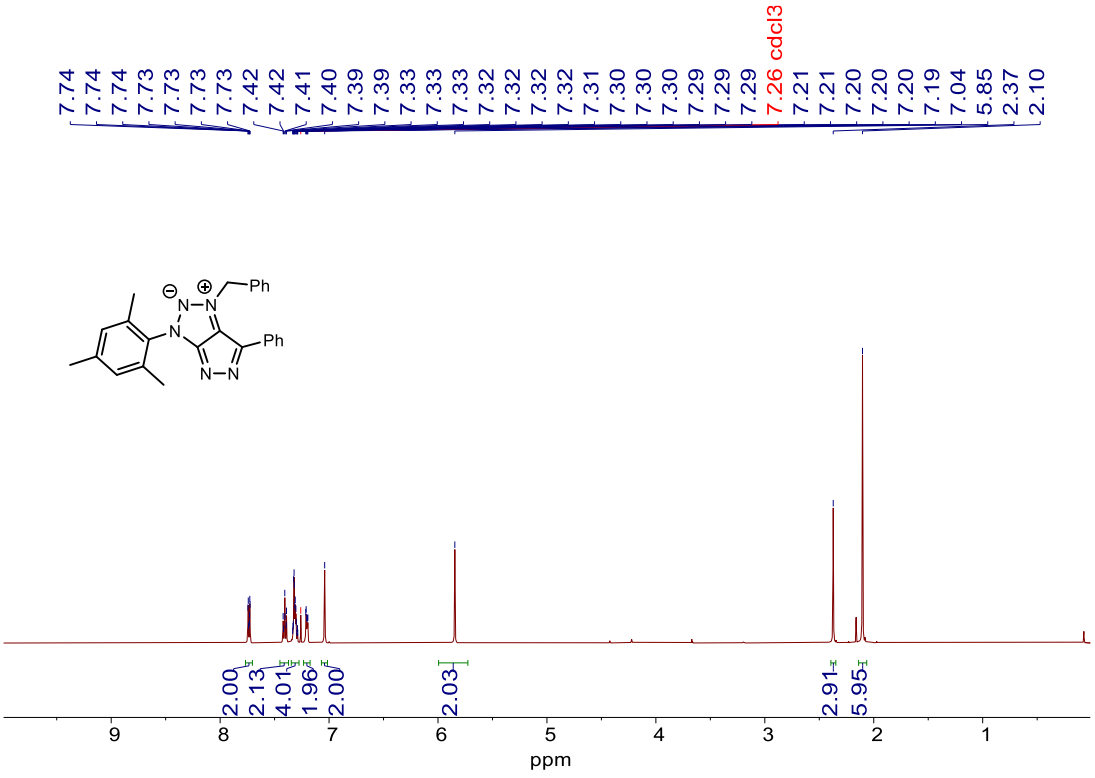


Figure S79. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2j**.

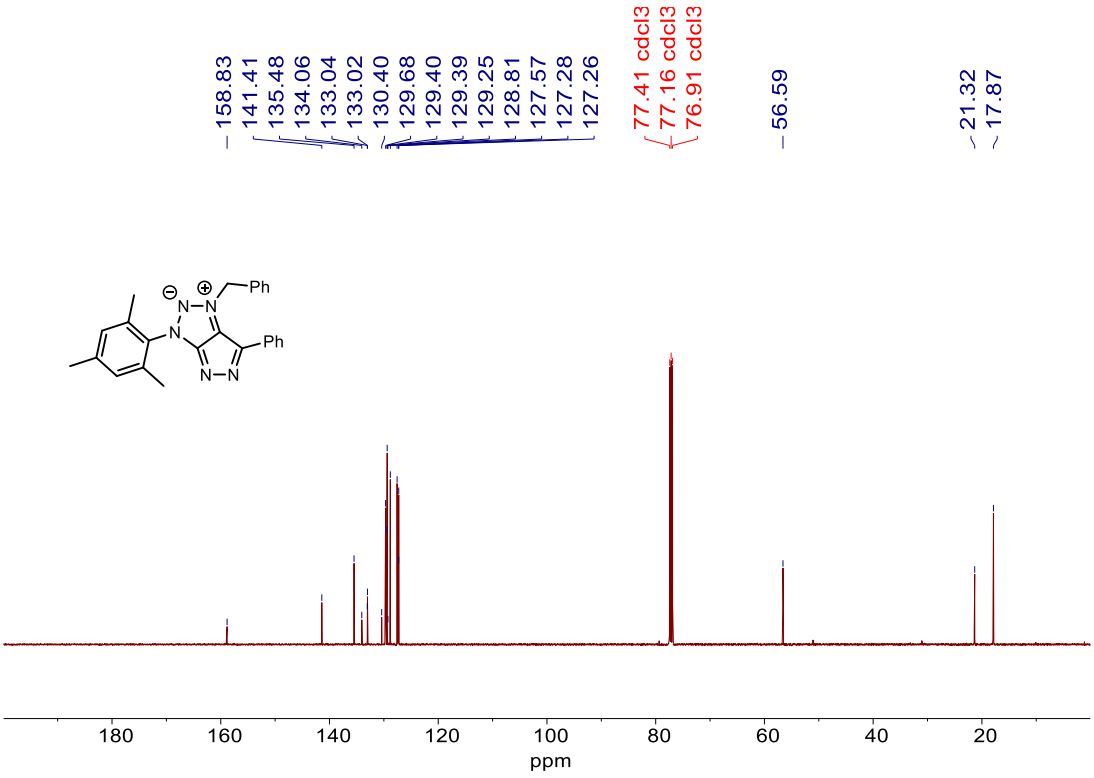


Figure S80. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2j**.

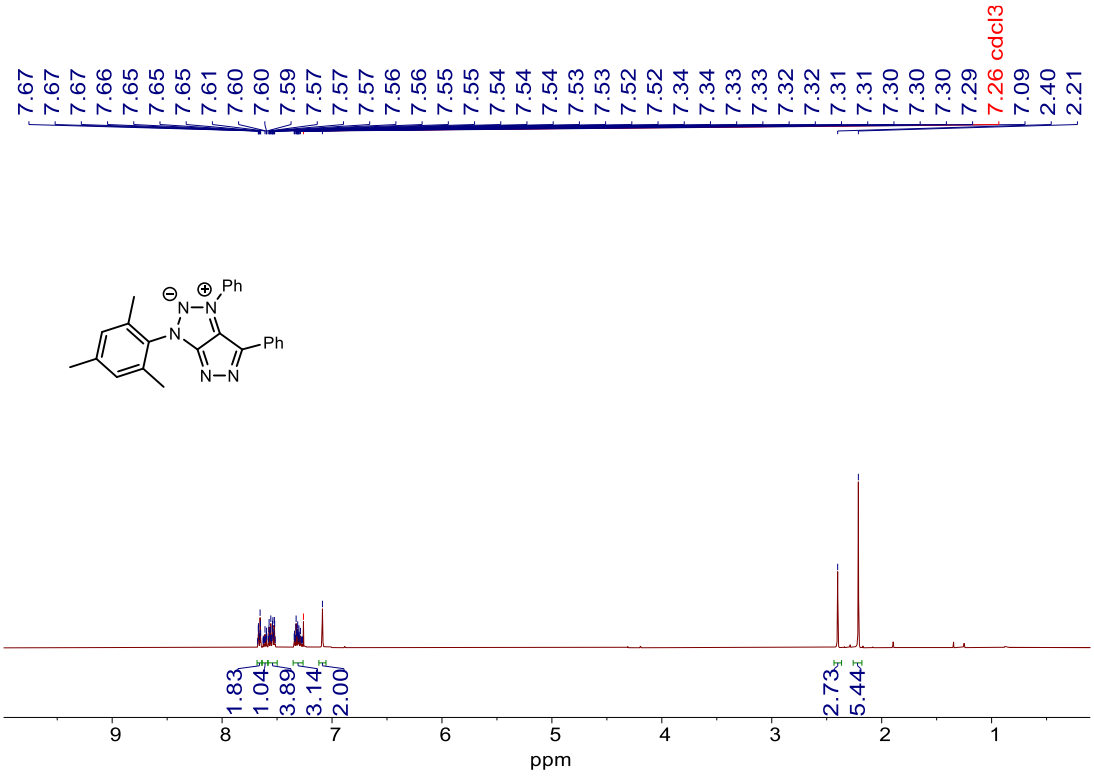


Figure S81. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2k**.

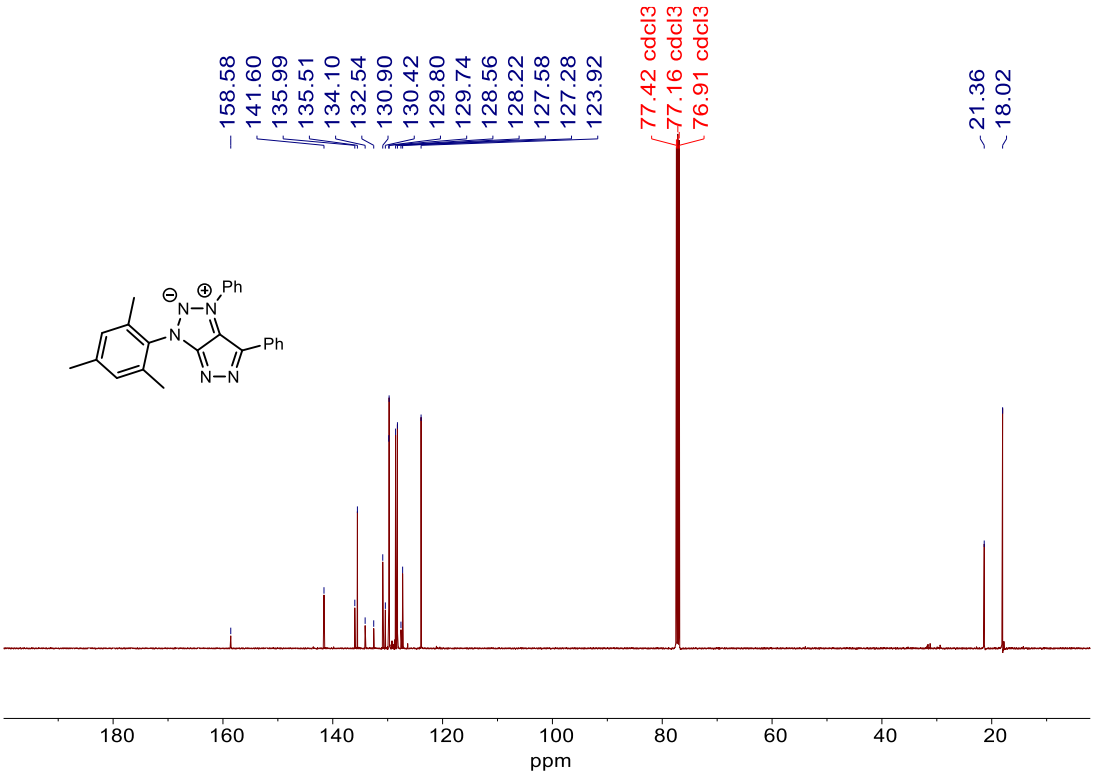


Figure S82. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2k**.

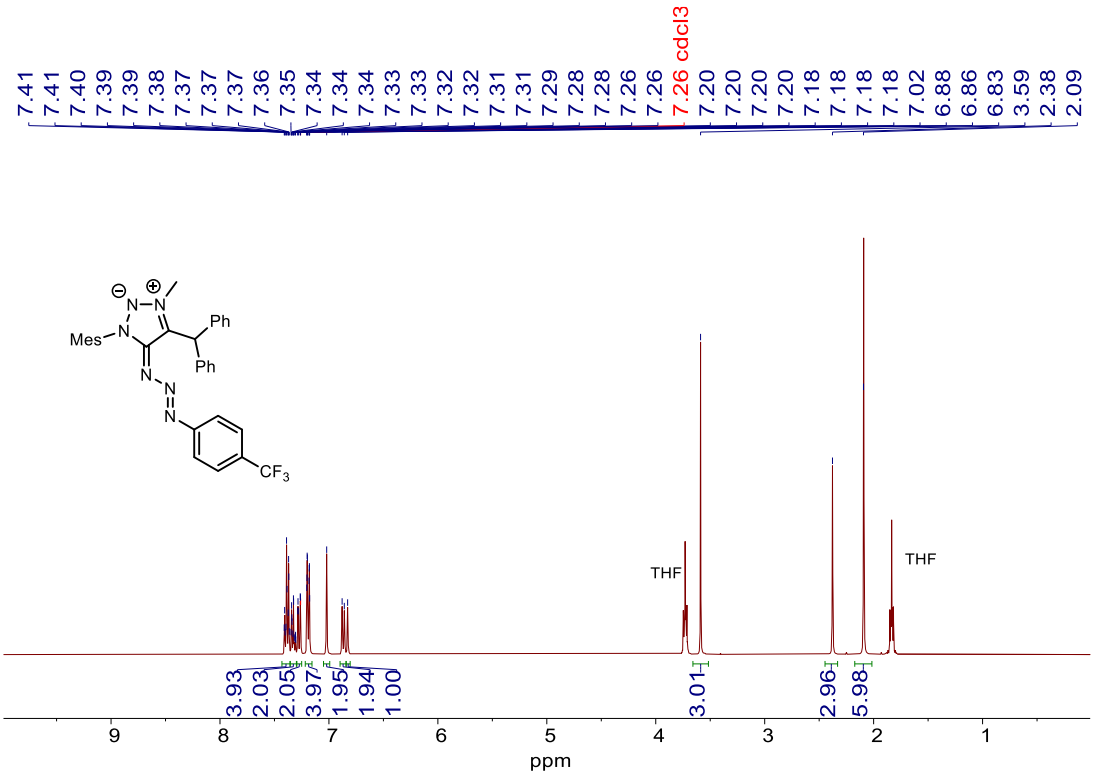


Figure S83. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4**.

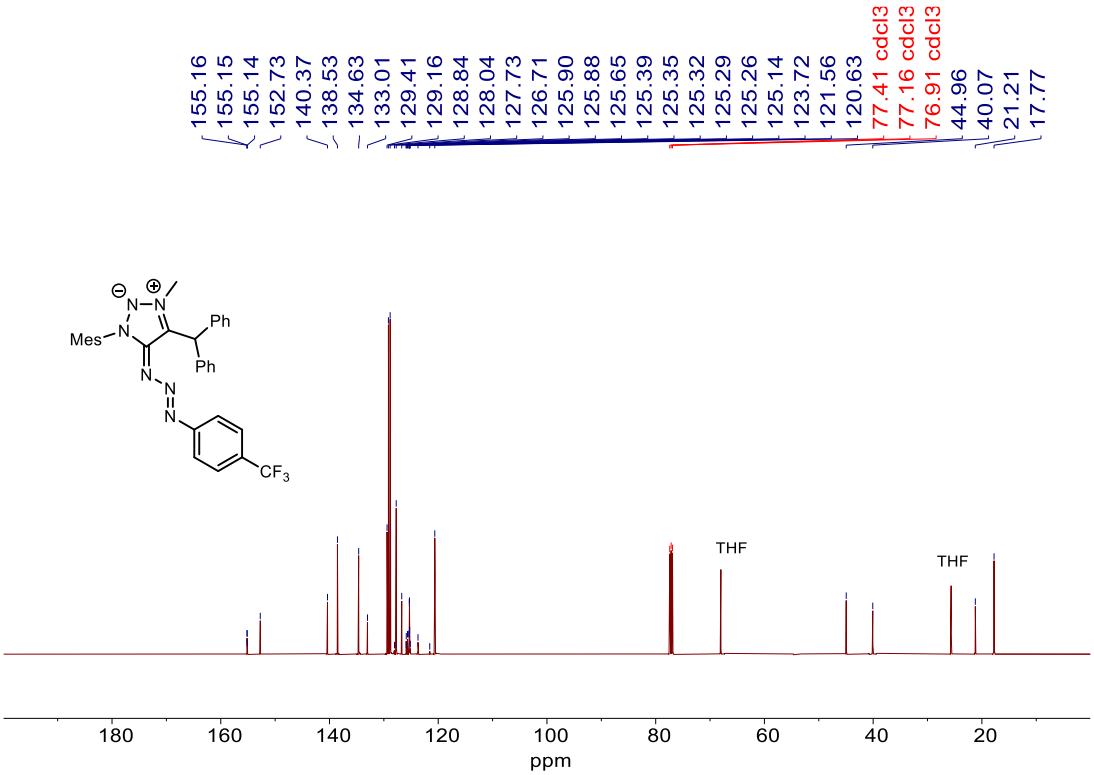


Figure S84. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4**.

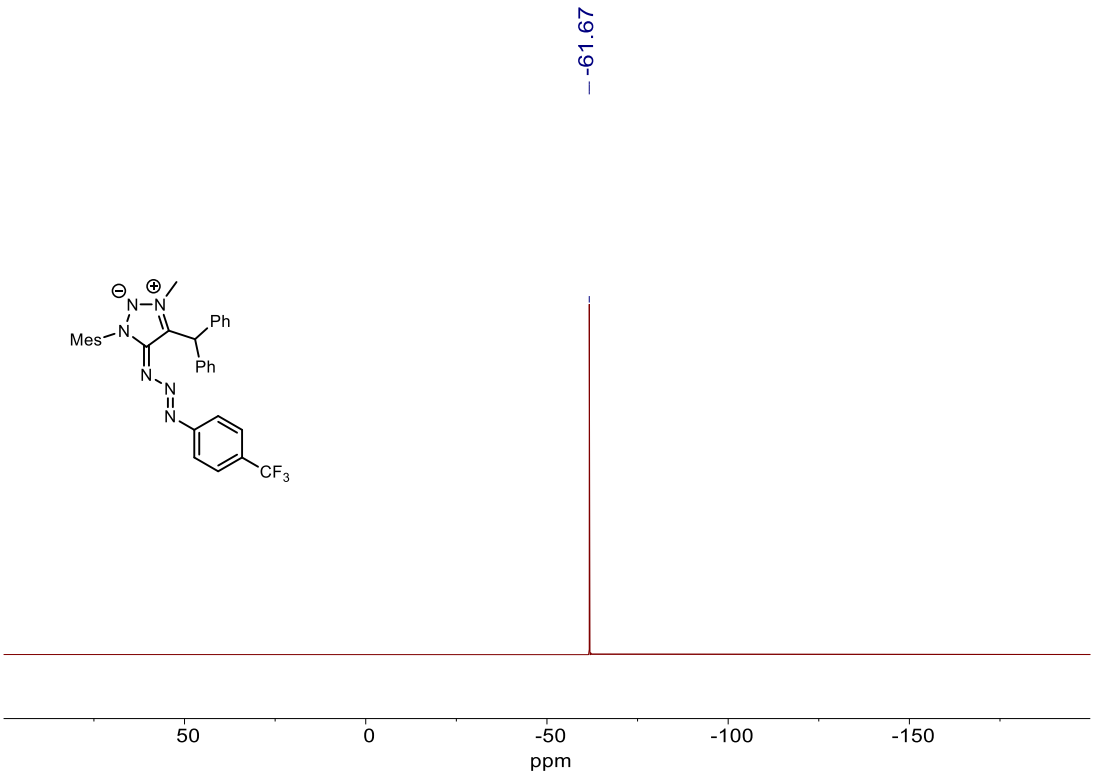


Figure S85. ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **4**.

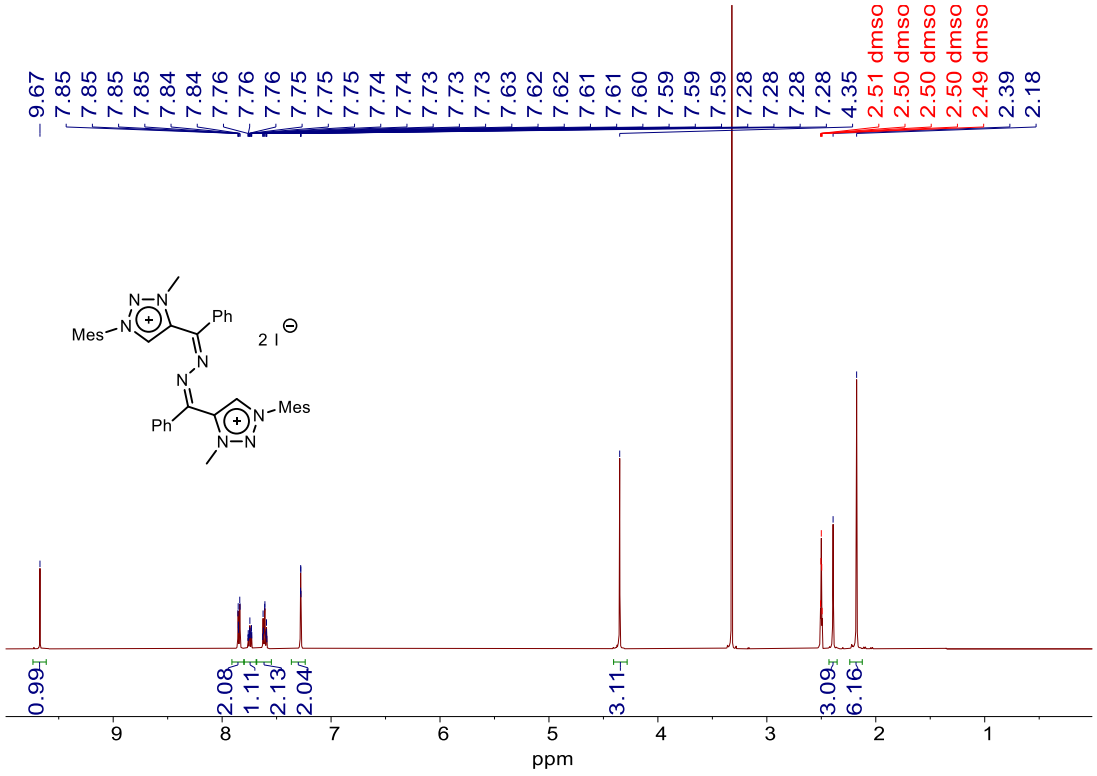


Figure S86. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **6**.

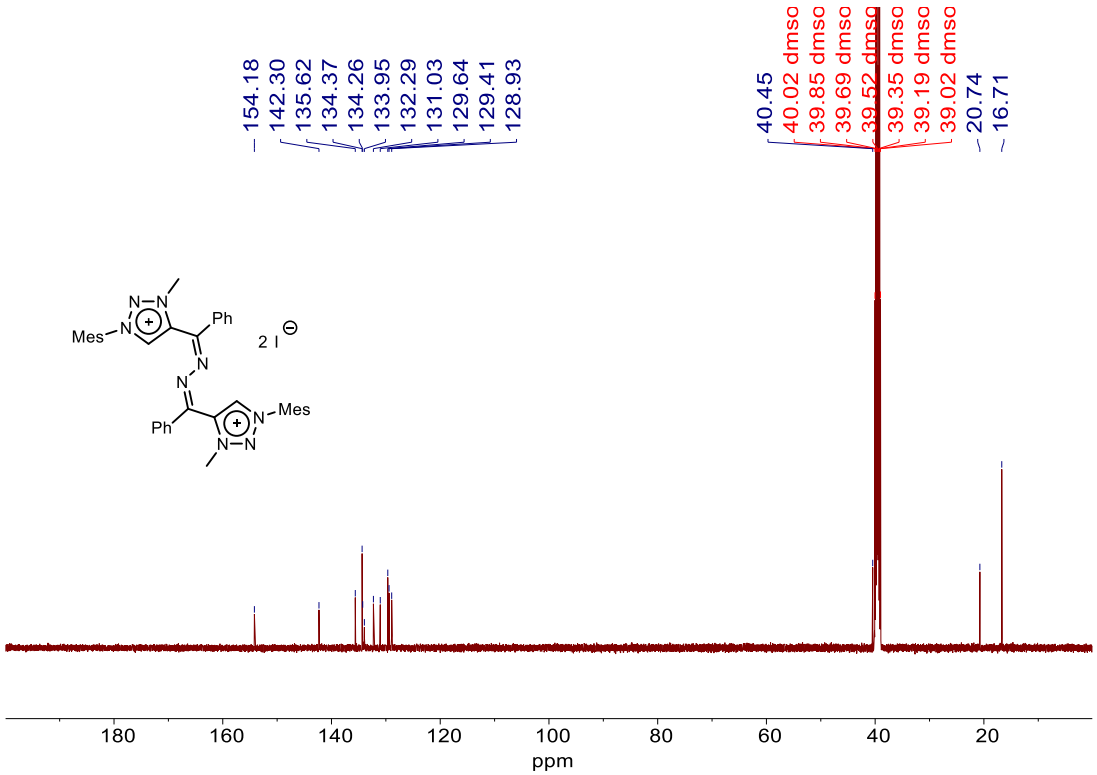


Figure S87. ^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **6**.

3. NMR spectra of the reaction mixtures of 2a and different organic azides

To a THF-d_8 solution of **1a** (74.2 μM, 500 μL, 37.1 μmol) in was added a THF-d_8 solution of azide (291.8 mM, 117 μL, 34.0 μmol) at room temperature. The solution was transferred to an NMR tube and NMR spectra were collected.

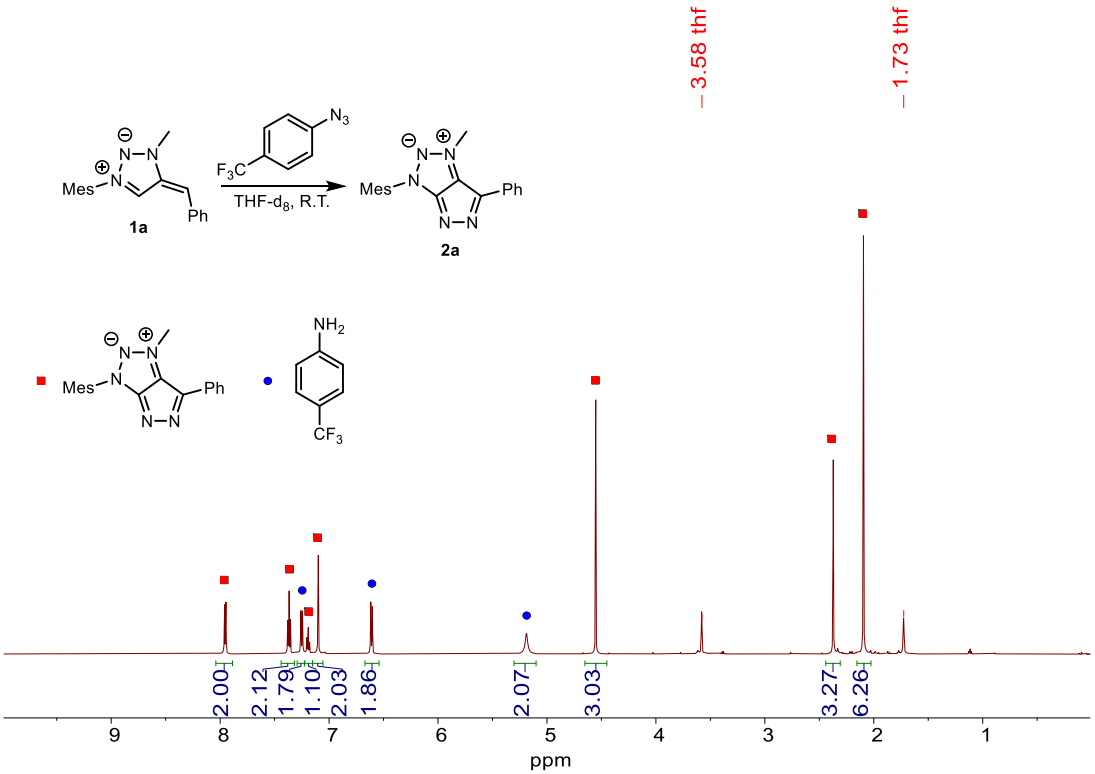


Figure S88. ^{1}H NMR spectrum (600 MHz, THF-d_8) of the reaction mixture of **1a** and 1-azido-4-(trifluoromethyl)benzene at room temperature in THF-d_8.

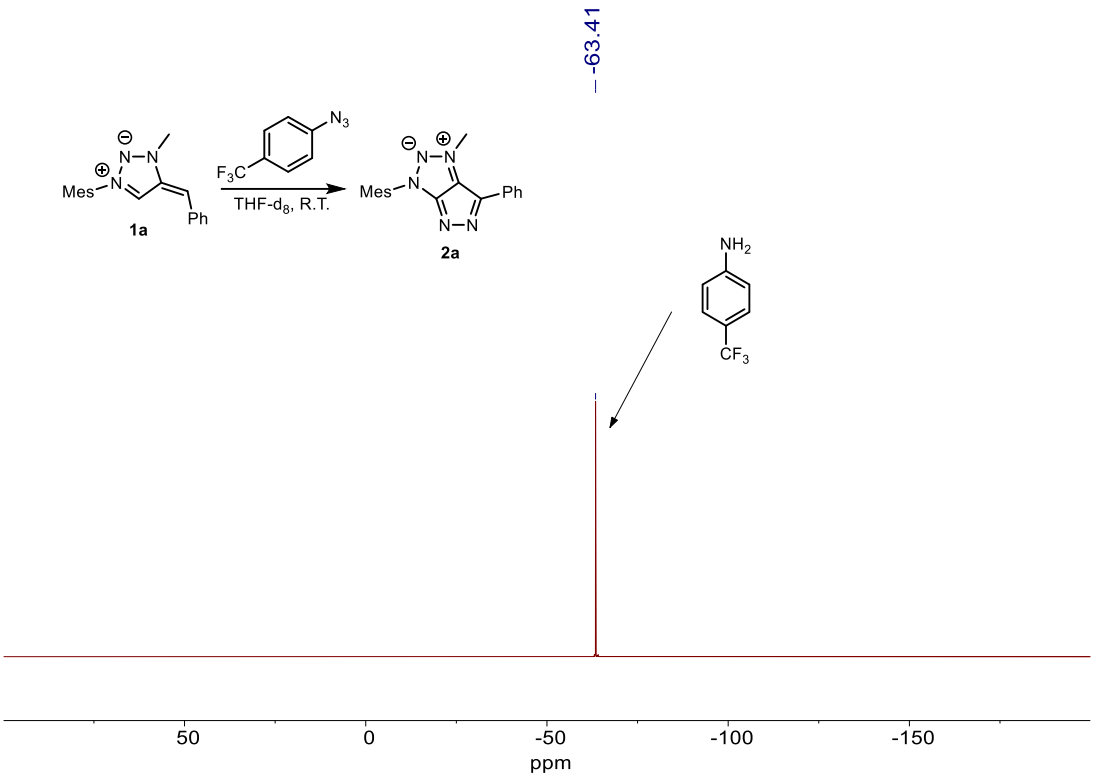


Figure S89. ^{19}F NMR spectrum (564 MHz, THF-d_8) of the reaction mixture of **1a** and 1-azido-4-(trifluoromethyl)benzene at room temperature in THF-d_8.

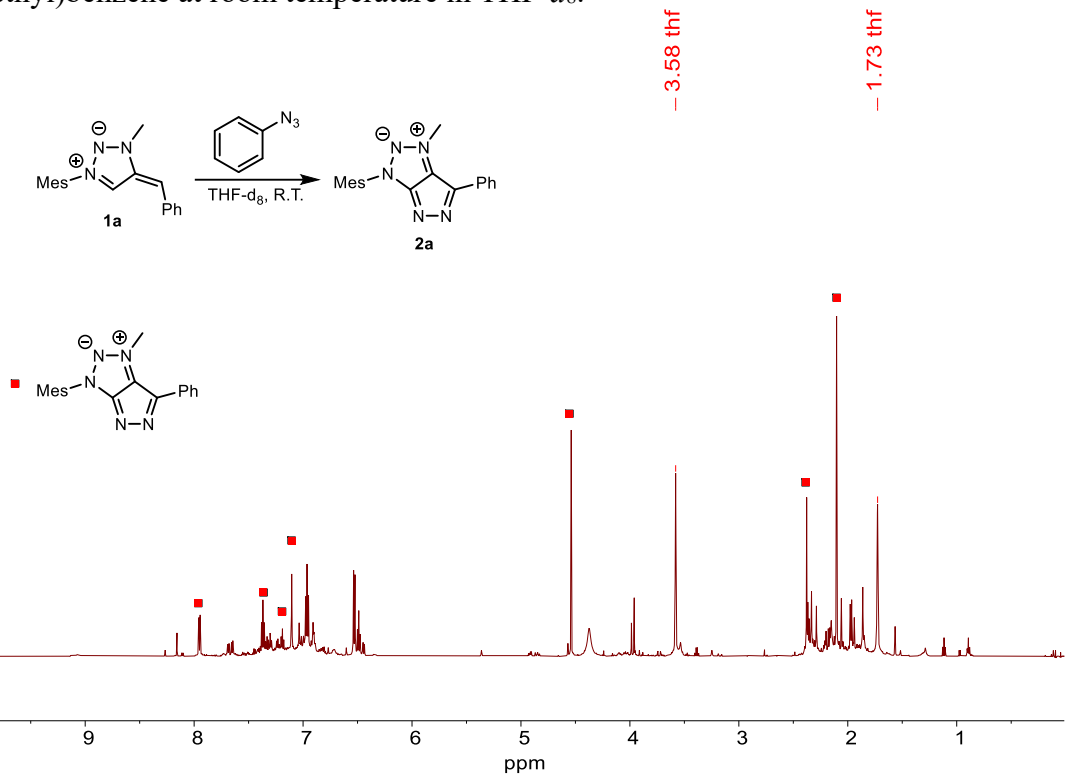


Figure S90. ^{1}H NMR spectrum (600 MHz, THF-d_8) of the reaction mixture of **1a** and azidobenzene at room temperature in THF-d_8.

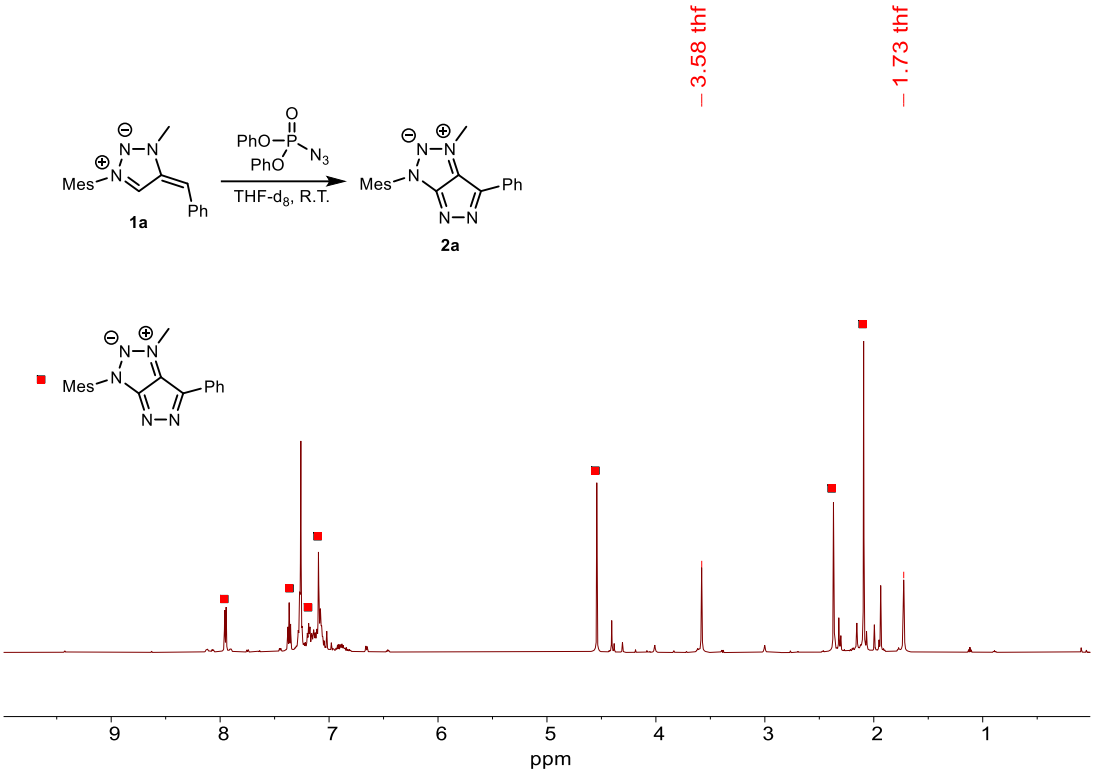


Figure S91. [1]H NMR spectrum (600 MHz, THF-d_8) of the reaction mixture of **1a** and diphenylphosphoryl azide at room temperature in THF-d_8.

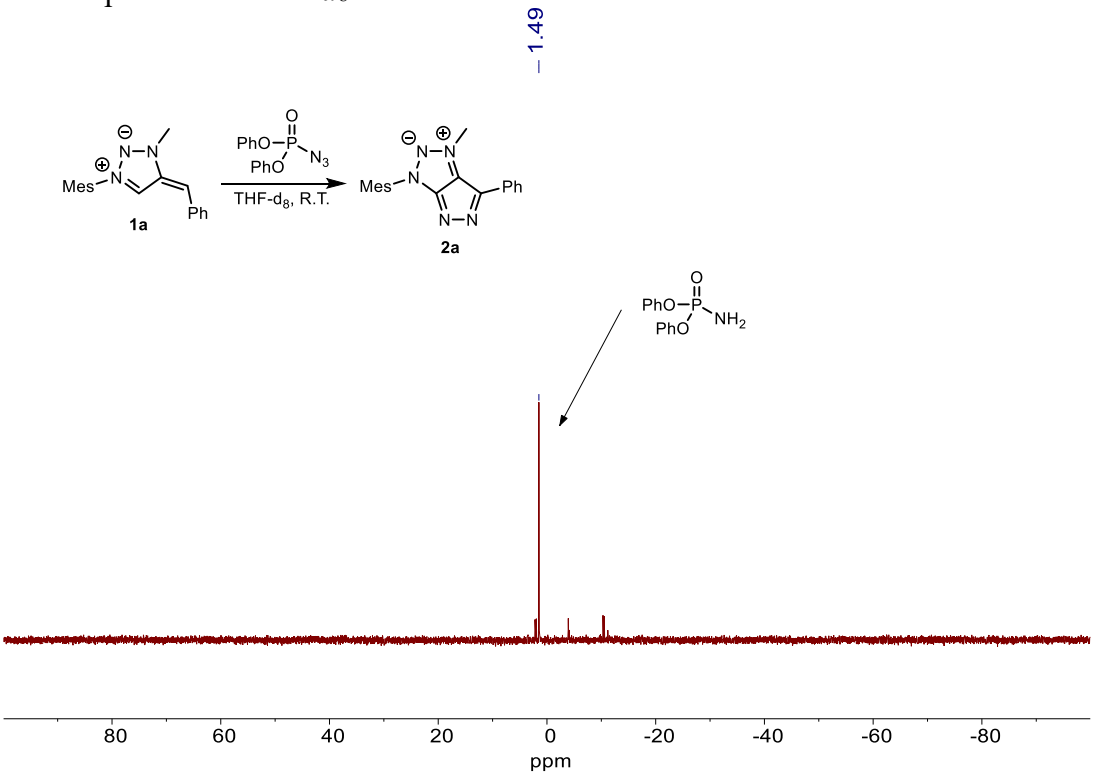


Figure S92. [31]H NMR spectrum (243 MHz, THF-d_8) of the reaction mixture of **1a** and diphenylphosphoryl azide at room temperature in THF-d_8.

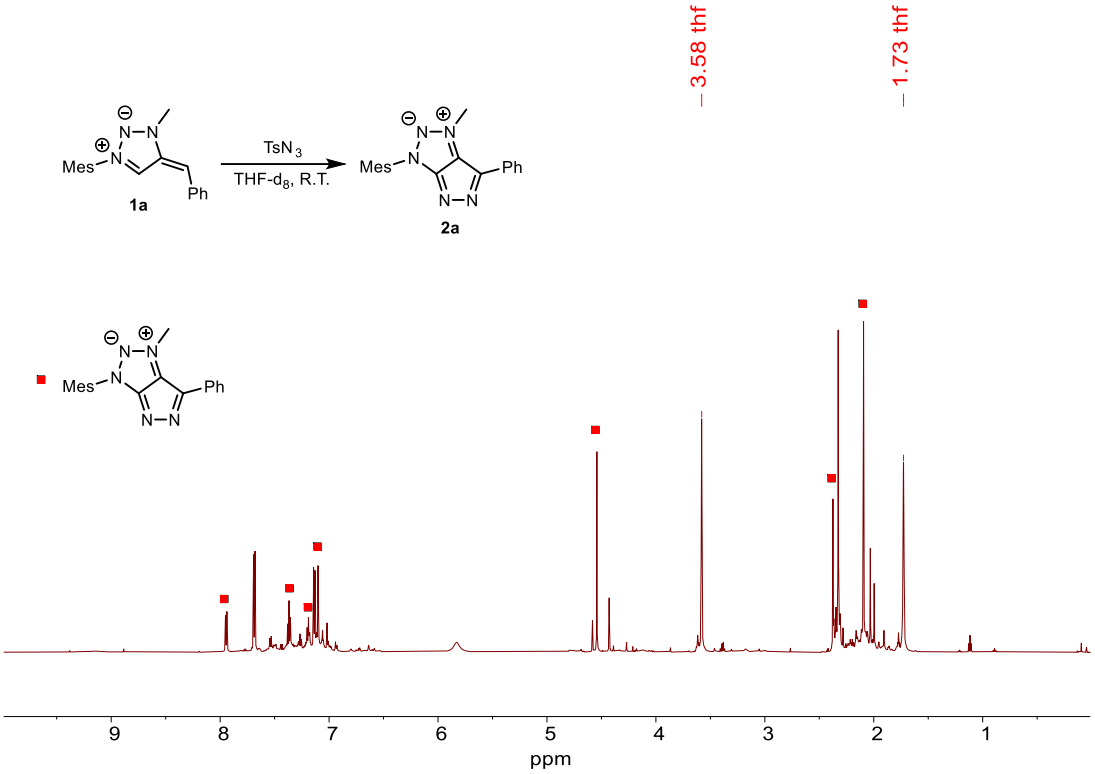


Figure S93. ^{1}H NMR spectrum (600 MHz, THF-d_8) of the reaction mixture of **1a** and tosyl azide at room temperature in THF-d_8.

4. Detecting 3 at low temperature

A THF-d_8 solution of **1a** (74.2 μM, 500 μL, 37.1 μmol) in was transferred to an NMR tube. The NMR tube was then sealed with septum, immersed into a dry ice / isopropanol bath (−78 °C). To the sample was added a THF-d_8 solution of 1-azido-4-(trifluoromethyl)benzene (291.8 mM, 117 μL, 34.0 μmol). The sample was then inserted into a 600 MHz NMR spectrometer which had been pre-cooled to −30 °C and calibrated. ^{1}H and ^{19}F NMR spectra were collected at −30 °C.

^{1}H NMR (600 MHz, THF-d_8, 223 K): δ 10.28 (s, 1H, triazolium-*H*), 7.63 – 7.61 (m, 2H, CF_3-C_6H_4-), 7.21 (d, *J* = 8.4 Hz, 2H, CF_3-C_6H_4-), 7.13 – 7.01 (m, 5H, Ph-*H*), 7.01 (s, 1H, Mes-*H*), 6.90 (s, 1H, Mes-*H*), 6.27 (s, 1H, C*H*), 4.53 (s, 3H, N-CH_3), 2.26 (s, 3H, Mes-CH_3), 2.04 (s, 3H, Mes-CH_3), 1.60 (s, 3H, Mes-CH_3). ^{19}F NMR (564 MHz, THF-d_8, 223 K): δ −62.70.

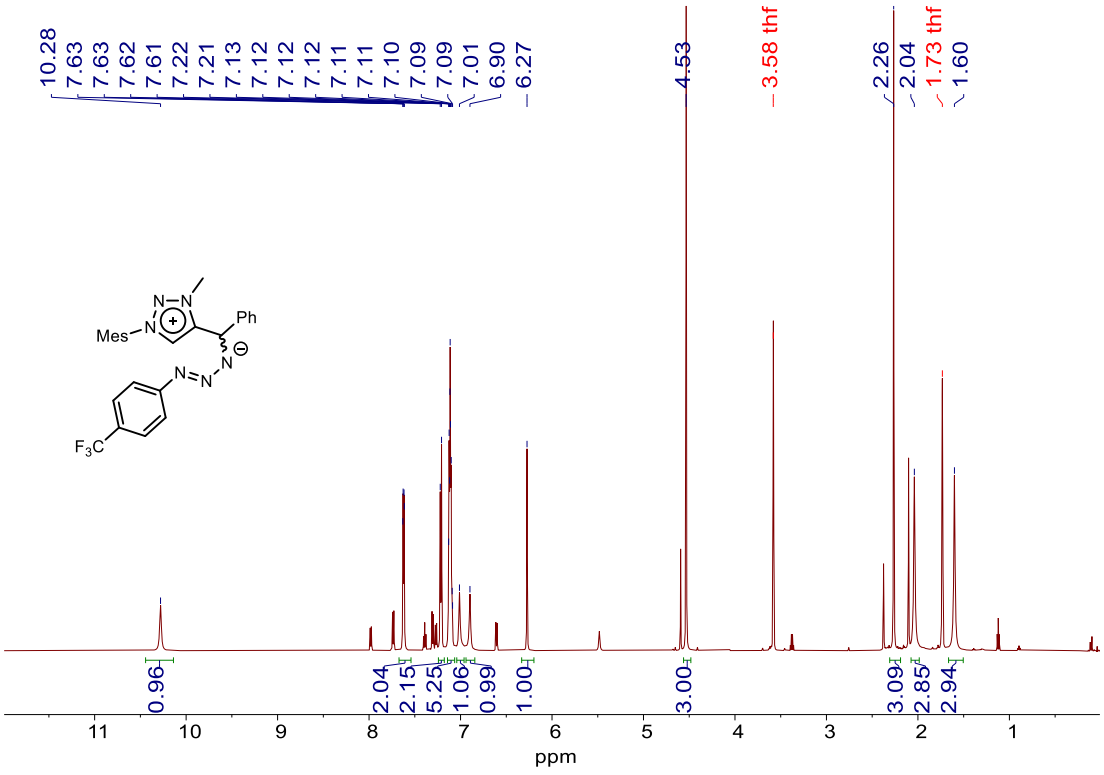


Figure S94. ^{1}H NMR (600 MHz, THF-d_8) of the reaction mixture of **1a** and 1-azido-4-(trifluoromethyl)-benzene in THF-d_8 at −30 °C. Peaks with integrations are from compound **3**.

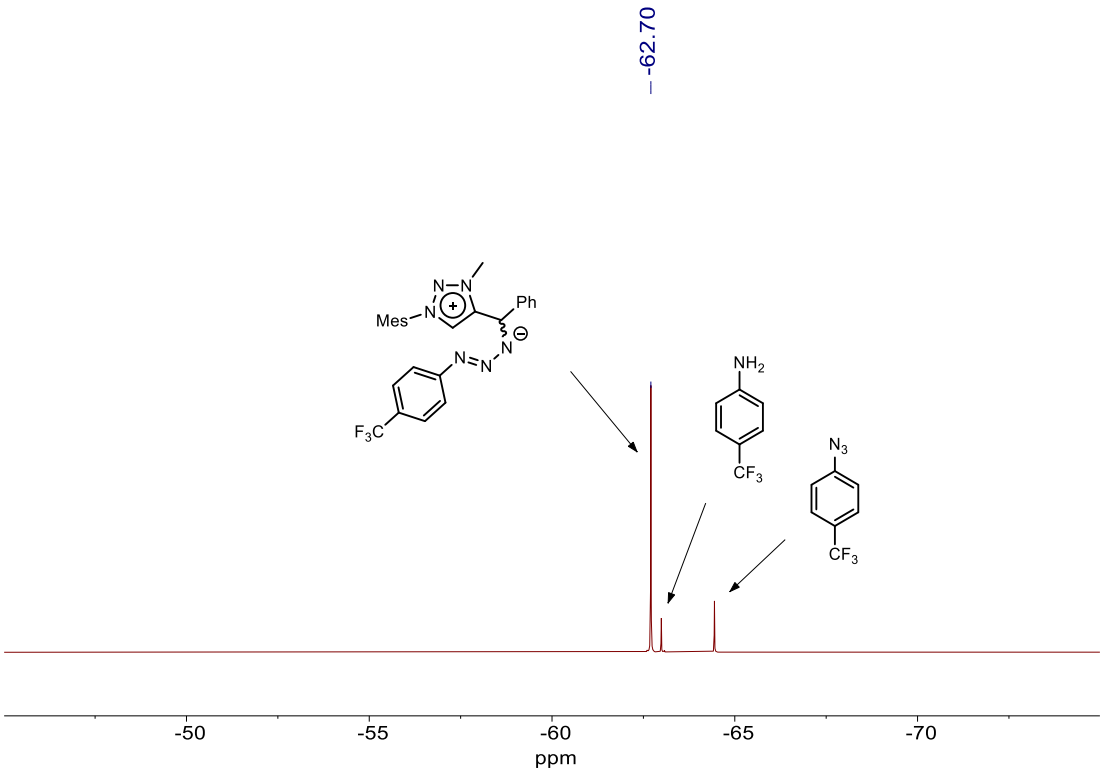


Figure S95. ^{19}F NMR (564 MHz, THF-d_8) spectrum of the reaction mixture of **1a** and 1-azido-4-(trifluoromethyl)-benzene in THF-d_8 at −30 °C.

5. X-ray crystallography

The X-ray diffraction data were collected on a Bruker Kappa Apex II / Photon II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K or 220 K (for **2d**) controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex 3 software package.[10] The structures were solved by direct methods and refined using SHELX-2016 software package.[11,12] All non-hydrogen atoms were refined anisotropically except for some of the atoms of the disordered phenyl group in **1b**. The diffuse residual electron density, Solvent Accessible Volume = 211 Å^3, # Electrons Found in S.A.V. = 82 in the lattice of **2k**, Solvent Accessible Volume = 1489 Å^3, # Electrons Found in S.A.V. = 546 in the lattice of **3**, Solvent Accessible Volume = 397 Å^3, # Electrons Found in S.A.V. = 122 in the lattice of **6** were removed with the SQUEEZE function of PLATON[13] and was not included in the formula or the refinement. Selected crystallographic data are summarized in Tables S1−S5.

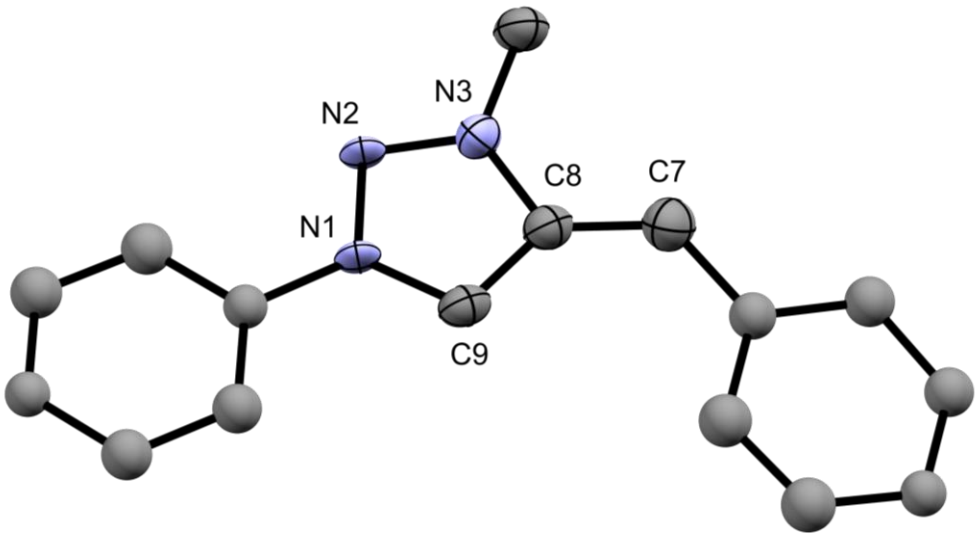


Figure S96. X-ray structure of **1b**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity. Only one orientation of the disordered molecule is shown.

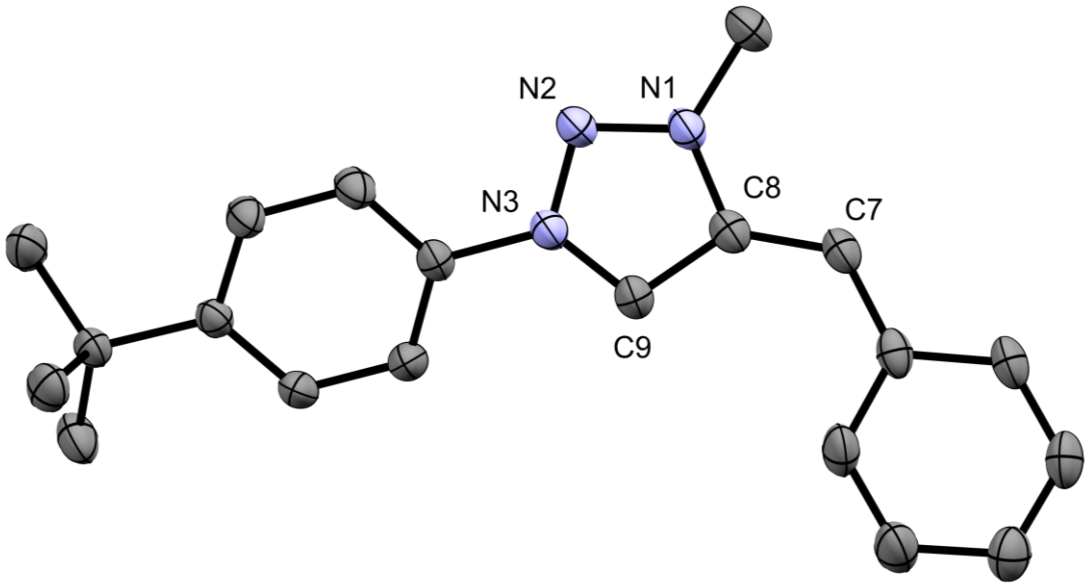


Figure S97. X-ray structure of **1c**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

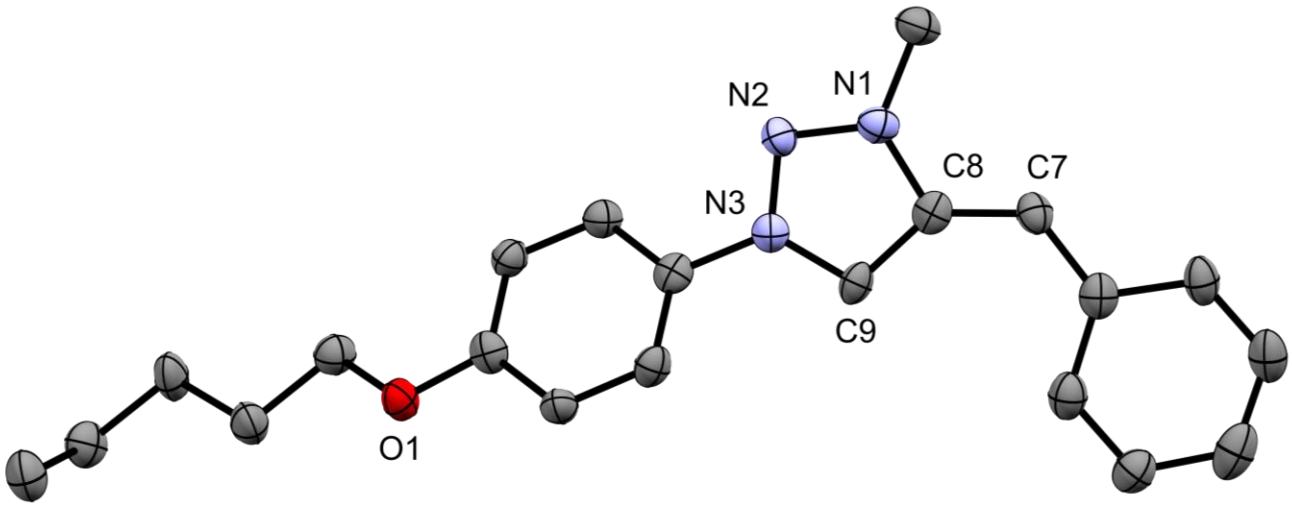


Figure S98. X-ray structure of **1d**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

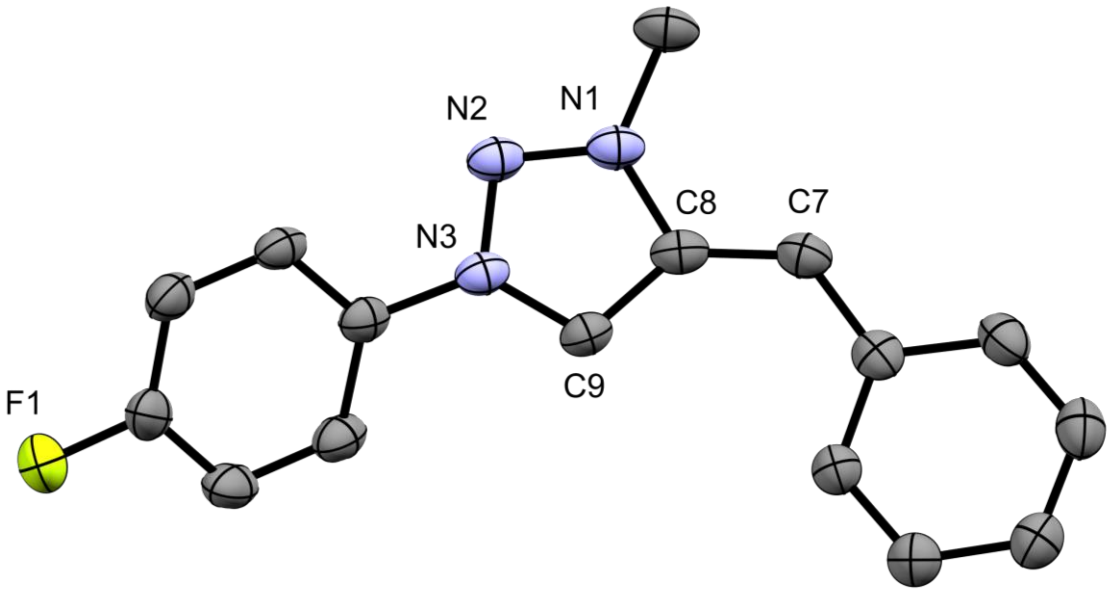


Figure S99. X-ray structure of **1e**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

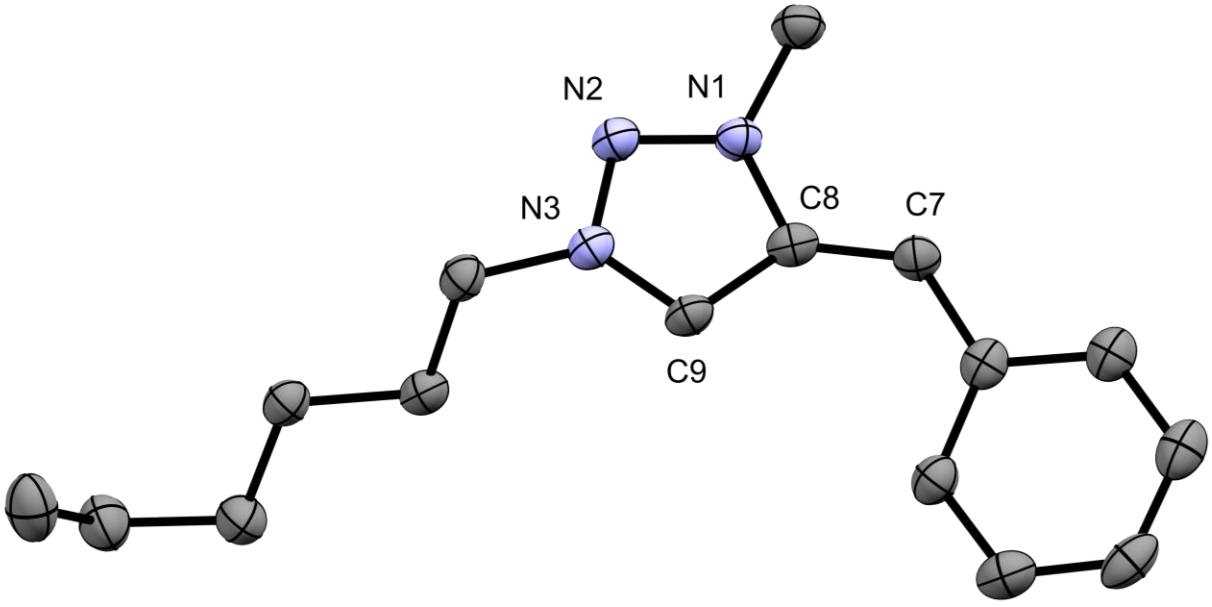


Figure S100. X-ray structure of **1h**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

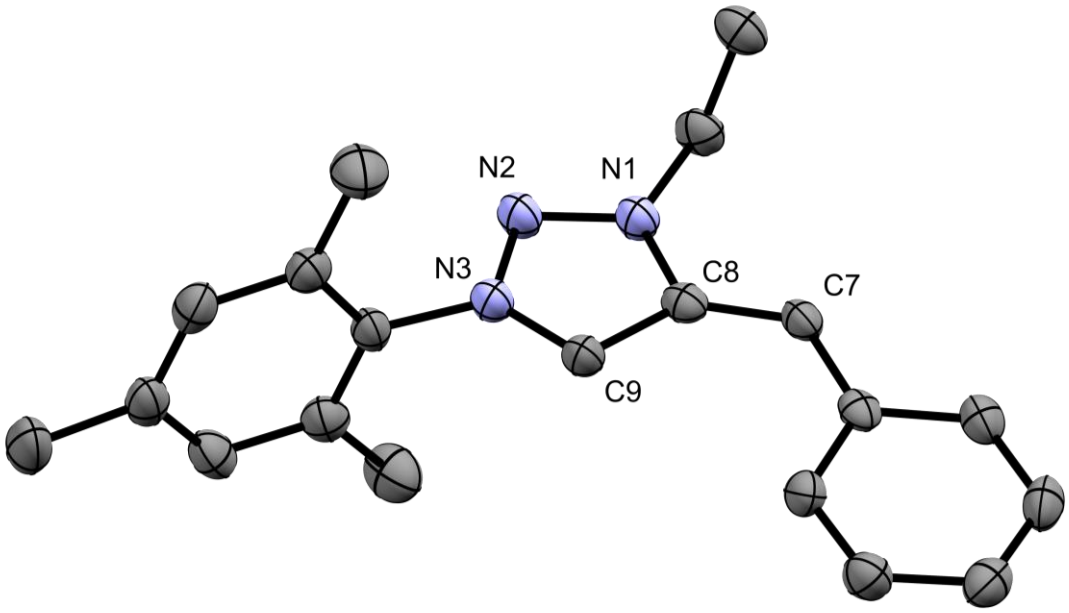


Figure S101. X-ray structure of **1i**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

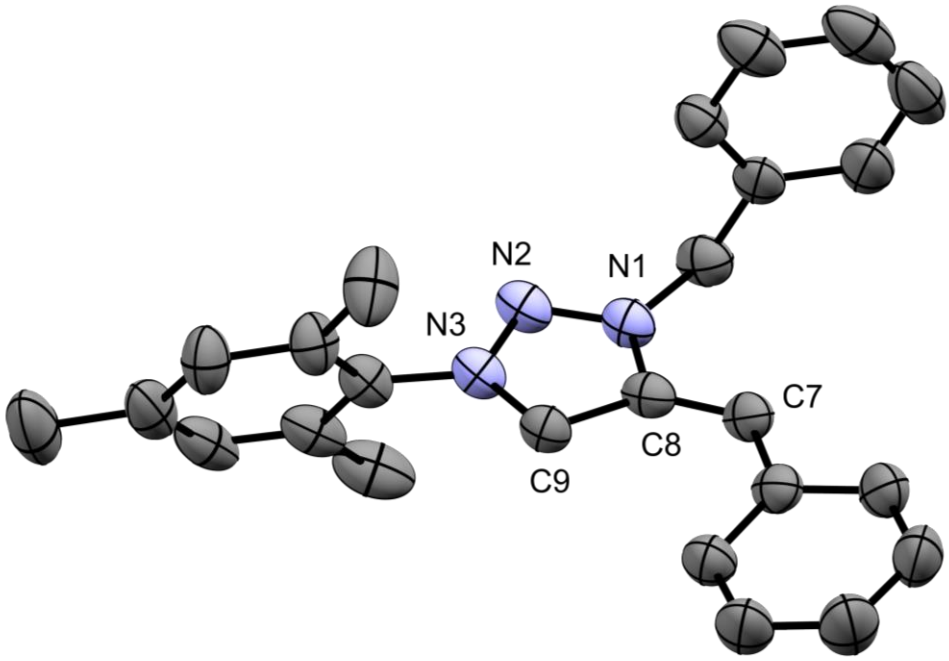


Figure S102. X-ray structure of **1j**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

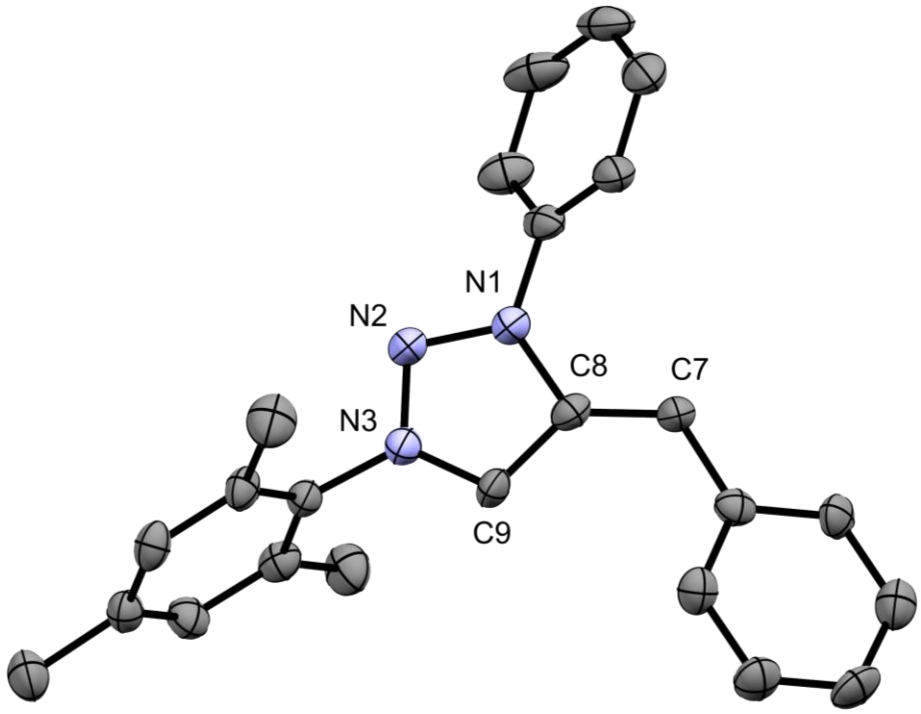


Figure S103. X-ray structure of **1k**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

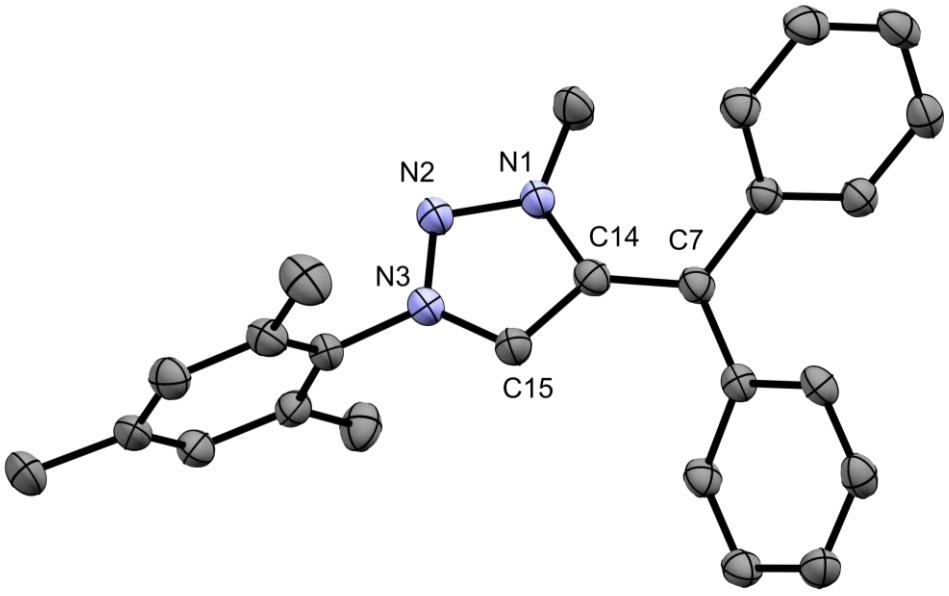


Figure S104. X-ray structure of **1l**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for clarity.

Table S1. Selected crystallographic data for compounds **1a**, **1c**, **1d**, **1e**, and **1h**.

	1b	**1c**	**1d**	**1e**	**1h**
Empirical formula	$C_{16}H_{15}N_3$	$C_{20}H_{23}N_3$	$C_{21}H_{25}N_3O$	$C_{16}H_{14}N_3F$	$C_{16}H_{26}N_3$
FW ($g \cdot mol^{-1}$)	249.31	305.41	335.44	267.30	257.37
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space Group	Fdd2	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
Z	16	4	8	8	4
a (Å)	23.99(2)	12.944(4)	8.327(7)	11.0959(5)	13.300(7)
b (Å)	38.69(4)	9.040(4)	14.46(1)	15.0897(7)	7.486(4)
c (Å)	5.573(6)	14.465(5)	29.68(2)	16.0556(6)	14.731(7)
α (deg)	90	90	90	90	90
β (deg)	90	100.393(12)	93.26(3)	90	93.762(17)
γ (deg)	90	90	90	90	90
V ($Å^3$)	5172(9)	1664.8(10)	3568(5)	2688.2(2)	1463.5(13)
D_{calcd}, ($g \cdot cm^{-3}$)	1.281	1.218	1.249	1.321	1.168
μ (mm^{-1})	0.078	0.073	0.078	0.090	0.070
F(000)	2112	656	1440	1120	560
no. of obsd reflns	1510	3647	3804	5227	2039
no. of params refnd	176	212	456	363	175
goodness of fit	1.047	1.100	1.152	1.033	1.008
R_1 ($I>2\sigma$)	0.0710	0.0462	0.1096	0.0335	0.0603
wR_2	0.1794	0.1448	0.2983	0.0805	0.1515

Table S2. Selected crystallographic data for compounds **1i**, **1j**, **1k** and **1l**.

	1i	**1j**	**1k**	**1l**
Empirical formula	$C_{20}H_{23}N_3$	$C_{25}H_{25}N3$	$C_{24}H_{23}N_3$	$C_{25}H_{25}N_3$
FW ($g \cdot mol^{-1}$)	305.41	367.48	353.45	367.48
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1$	C2/c	P-1	$P2_1/c$
Z	2	16	4	4
a (Å)	9.464(3)	22.126(7)	11.110(7)	7.9028(7)
b (Å)	7.518(2)	22.131(6)	12.493(9)	12.5696(8)
c (Å)	12.116(3)	17.067(5)	14.899(12)	20.7598(18)
α (deg)	90	90	75.149(18)	90
β (deg)	92.972(13)	91.565(13)	73.50(2)	95.571(3)
γ (deg)	90	90	87.94(4)	90
V ($Å^3$)	860.9(4)	8354(4)	1915(2)	2052.4(3)
D_{calcd}, ($g \cdot cm^{-3}$)	1.178	1.169	1.226	1.189
μ (mm^{-1})	0.070	0.069	0.073	0.071
F(000)	328	3136	752	784
no. of obsd reflns	2861	5312	3711	3740
no. of params refnd	213	512	495	257
goodness of fit	0.967	1.054	0.895	1.052
R_1 ($I>2\sigma$)	0.0369	0.0840	0.0704	0.0452
wR_2	0.0822	0.2441	0.1326	0.1291

Table S3. Selected crystallographic data for compounds **2a**, **2b•(CH_2Cl_2)**, **2c**, **2d** and **2e**.

	2a	**2b•(CH_2Cl_2)**	**2c**	**2d**	**2e**
Empirical formula	$C_{19}H_{19}N_5$	$C_{17}H_{15}N_5Cl_2$	$C_{20}H_{21}N_5$	$C_{21}H_{23}N_5O$	$C_{16}H_{12}N_5F$
FW ($g \cdot mol^{-1}$)	317.39	360.24	331.42	361.44	293.31
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	P-1	P-1	$P2_1/c$	$P2_1$
Z	4	2	4	4	4
a (Å)	8.704(3)	6.907(3)	6.858(2)	14.645(5)	7.2146(14)
b (Å)	15.441(5)	10.401(4)	15.868(5)	12.306(3)	11.816(2)
c (Å)	12.626(4)	12.709(4)	17.842(5)	10.398(3)	16.161(4)
α (deg)	90	102.837(12)	66.888(9)	90	90
β (deg)	91.212(17)	102.334(13)	89.896(10)	96.185(10)	102.558(7)
γ (deg)	90	99.423(14)	82.855(10)	90	90
V ($Å^3$)	1696.5(10)	848.0(5)	1769.5(9)	1862.9(10)	1344.7(5)
D_{calcd}, ($g \cdot cm^{-3}$)	1.243	1.411	1.244	1.289	1.449
μ (mm^{-1})	0.077	0.391	0.077	0.083	0.101
F(000)	672	372	704	768	608
no. of obsd reflns	2386	2807	4582	2237	6835
no. of params refnd	222	218	454	254	399
goodness of fit	1.038	1.079	1.043	1.012	0.988
R_1 ($I>2\sigma$)	0.0574	0.0452	0.0726	0.0636	0.0348
wR_2	0.1509	0.1261	0.1983	0.1867	0.0827

Table S4. Selected crystallographic data for compounds **2f**, **2g**, **2h**, **2i** and **2j**.

	2f	**2g**	**2h**	**2i**	**2j**
Empirical formula	$C_{17}H_{12}N_5F_3$	$C_{16}H_{10}N_5F_3$	$C_{16}H_{21}N_5$	$C_{20}H_{21}N_5$	$C_{25}H_{23}N_5$
FW ($g \cdot mol^{-1}$)	343.32	329.29	283.38	331.42	393.48
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	P-1	P-1	$P2_1/c$	$P2_1/c$	Pbca
Z	4	2	4	4	8
a (Å)	11.812(6)	7.229(2)	13.043(4)	8.6431(16)	19.342(7)
b (Å)	11.965(6)	7.692(2)	16.924(5)	15.692(2)	7.811(3)
c (Å)	13.312(6)	13.893(4)	7.147(2)	13.006(2)	27.328(3)
α (deg)	115.153(14)	100.422(10)	90	90	90
β (deg)	99.218(15)	93.394(11)	97.239(17)	91.965(6)	90
γ (deg)	109.557(14)	101.959(11)	90	90	90
V ($Å^3$)	1500.4(12)	739.5(4)	1564.9(8)	1762.9(5)	4129(3)
D_{calcd}, ($g \cdot cm^{-3}$)	1.520	1.479	1.203	1.249	1.266
μ (mm^{-1})	0.121	0.120	0.075	0.077	0.077
F(000)	704	336	608	704	1664
no. of obsd reflns	4525	2403	2228	3547	3822
no. of params refnd	453	219	211	231	275
goodness of fit	1.049	0.999	1.046	1.038	1.065
R_1 ($I>2\sigma$)	0.0614	0.0371	0.0609	0.0407	0.0432
wR_2	0.1561	0.1044	0.1883	0.1196	0.1220

Table S5. Selected crystallographic data for compounds **2k**, **3**, **4•(C_4H_8O)** and **6**.

	2k	**3**	**4•(C_4H_8O)**	**6**
Empirical formula	$C_{24}H_{21}N_5$	$C_{26}H_{25}N_6F_3$	$C_{36}H_{37}N_6F_3O$	$C_{38}H_{40}N_8I_2$
FW ($g \cdot mol^{-1}$)	379.46	478.52	626.71	862.58
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	C2/c	$P2_1/c$	$P2_1/c$
Z	4	8	4	2
a (Å)	12.612(7)	32.987(16)	14.323(6)	14.919(6)
b (Å)	19.074(12)	16.616(7)	15.575(7)	16.322(6)
c (Å)	8.914(5)	11.427(5)	14.988(7)	8.526(3)
α (deg)	90	90	90	90
β (deg)	99.301(19)	105.17(2)	103.939(15)	92.459(14)
γ (deg)	90	90	90	90
V ($Å^3$)	2116(2)	6045(5)	3245(3)	2075.6(14)
D_{calcd}, ($g \cdot cm^{-3}$)	1.191	1.052	1.283	1.380
μ (mm^{-1})	0.073	0.078	0.091	1.549
F(000)	800	2000	1320	860
no. of obsd reflns	2822	3214	4273	3093
no. of params refnd	266	325	439	222
goodness of fit	1.054	1.052	1.042	1.027
R_1 ($I>2\sigma$)	0.0797	0.0967	0.0859	0.0536
wR_2	0.2595	0.3110	0.2667	0.1374

6. Computation

All calculations were performed using Gaussian 16, Revision B.01[14] with B3LYP[15,16] functionals. The 6-31G* basis set was used for all elements. Structures were optimized with PCM solvent correction (solvent = tetrahydrofuran) and the D3 version of Grimme's dispersion correction with the original D3 damping function.[17] Frequency analysis was then performed to confirm that the structure is a ground state or a transition state as appropriate and to obtain the thermodynamic data.

Optimized x,y,z-coordinates

ArN_3

G = -732.861144 Hartree

7	-0.384440000	0.055198000	-0.323176000
7	-0.733053000	-0.237601000	0.720969000
7	0.139697000	0.340512000	-1.408640000
6	-0.697603000	0.774105000	-2.466877000
6	-0.050847000	1.077358000	-3.673670000
6	-2.091418000	0.904331000	-2.359620000
6	-0.793799000	1.507103000	-4.768650000
6	-2.829082000	1.334616000	-3.459566000
6	-2.184528000	1.633179000	-4.665172000
1	1.026865000	0.970473000	-3.742550000
1	-2.600999000	0.670585000	-1.429508000
1	-0.291735000	1.737872000	-5.702389000
1	-3.906744000	1.431483000	-3.376927000
6	-2.980145000	2.145023000	-5.829496000
9	-3.108812000	3.506183000	-5.807502000
9	-2.410945000	1.840326000	-7.024714000
9	-4.245170000	1.649017000	-5.854460000

$ArNH_2$

G = -624.613424 Hartree

7	1.819439000	6.757829000	1.612137000
6	1.999893000	5.432537000	1.244756000
6	2.092442000	4.420215000	2.223560000
1	1.980813000	4.676634000	3.274034000
6	2.332114000	3.101142000	1.857333000
1	2.399999000	2.336711000	2.625494000
6	2.489550000	2.756691000	0.507648000
6	2.156577000	5.075025000	-0.110856000
1	2.094397000	5.841302000	-0.879423000
6	2.396033000	3.753918000	-0.472155000
1	2.513244000	3.499084000	-1.520868000
1	1.405299000	6.925273000	2.521358000
1	1.455866000	7.381363000	0.901334000
6	2.686120000	1.328951000	0.118702000
9	3.334809000	1.188442000	-1.069327000
9	3.398774000	0.624571000	1.042064000
9	1.501490000	0.649826000	-0.024432000

1a

G = -900.629524 Hartree

7	0.902919000	2.366267000	2.819806000
7	1.425909000	2.472116000	1.581842000
6	2.129264000	5.394927000	-2.304799000
6	1.415340000	5.213762000	-1.084384000
7	0.290742000	3.517770000	2.993541000
6	1.168365000	3.698885000	0.950362000
6	-0.406249000	3.771789000	4.231208000
6	-1.755140000	4.277493000	6.607526000
6	1.649729000	4.016080000	-0.316726000
6	0.391569000	4.362491000	1.939148000
6	-0.425936000	4.688850000	6.439031000
6	-2.391889000	3.609708000	5.553007000
6	-1.735005000	3.340831000	4.346652000
6	0.506608000	6.252523000	-0.740143000
6	1.064696000	7.537312000	-2.734119000
6	0.276483000	4.446159000	5.253372000
6	1.960308000	6.521045000	-3.103846000
6	-2.476381000	4.523909000	7.912347000
6	0.341744000	7.381303000	-1.546331000
6	2.196485000	1.375746000	1.035482000
6	1.707781000	4.893800000	5.076961000
6	-2.423069000	2.613611000	3.216552000
1	-3.424968000	3.289817000	5.669665000
1	2.301351000	3.279776000	-0.778036000
1	2.533207000	6.610636000	-4.025026000
1	2.182995000	0.555433000	1.753376000
1	2.832548000	4.623551000	-2.615091000

1	0.078271000	5.210527000	7.249573000
1	3.229212000	1.694927000	0.855133000
1	0.933370000	8.418880000	-3.355984000
1	2.103355000	5.306711000	6.009084000
1	-1.938653000	1.650949000	3.015591000
1	-3.472693000	2.424228000	3.457789000
1	-0.103043000	6.173038000	0.151999000
1	2.349556000	4.059909000	4.770536000
1	-2.141109000	5.452997000	8.385751000
1	-2.283641000	3.707329000	8.620852000
1	1.753607000	1.049893000	0.088001000
1	-0.046073000	5.343754000	1.981689000
1	1.790599000	5.664987000	4.301823000
1	-3.560077000	4.583070000	7.766545000
1	-2.384256000	3.192787000	2.286553000
1	-0.369129000	8.146776000	-1.240078000

3

G = -1633.494042 Hartree

7	1.996035000	3.033658000	3.119786000
7	2.120309000	2.906063000	1.806698000
6	2.732116000	6.331655000	-0.494400000
6	1.742380000	5.455708000	-0.963000000
7	1.495981000	4.254610000	3.275744000
6	1.703518000	4.007264000	1.113395000
6	1.183788000	4.747741000	4.597499000
6	0.577302000	5.718487000	7.122746000
6	1.640017000	4.040794000	-0.389042000
6	1.293515000	4.886079000	2.094964000
6	1.866296000	5.866846000	6.592622000
6	-0.397076000	5.063858000	6.356736000
6	-0.120520000	4.564379000	5.079482000
6	0.923234000	5.869063000	-2.019890000
6	2.056252000	8.013923000	-2.101046000
6	2.198972000	5.387629000	5.321189000
6	2.886497000	7.604419000	-1.053427000
6	0.235332000	6.277441000	8.483787000
6	1.077691000	7.138200000	-2.583981000
6	2.642586000	1.653060000	1.253744000
6	3.589621000	5.541379000	4.753723000
6	-1.174758000	3.863174000	4.257697000
1	-1.397747000	4.935076000	6.762735000
1	2.522522000	3.498631000	-0.750935000
1	3.656742000	8.270574000	-0.672433000
1	2.731392000	0.940539000	2.072425000
1	3.392095000	6.022390000	0.313620000
1	2.632464000	6.365368000	7.181789000
1	3.621373000	1.838821000	0.806007000
1	2.171606000	9.002681000	-2.537620000
1	4.227765000	6.106983000	5.437890000
1	-0.826257000	2.884360000	3.908841000
1	-2.084745000	3.711604000	4.844187000
1	0.154171000	5.199835000	-2.390231000
1	4.057286000	4.564739000	4.581264000
1	1.119202000	6.334801000	9.127500000
1	-0.520912000	5.666763000	8.988268000
1	1.944037000	1.291591000	0.498256000
1	0.863932000	5.870709000	2.026651000
1	3.574784000	6.067276000	3.791588000
1	-0.172030000	7.292976000	8.391481000
1	-1.443804000	4.445023000	3.369013000
1	0.425835000	7.445563000	-3.398013000
7	-0.685927000	3.492876000	-0.498805000
7	0.507601000	3.178133000	-0.872363000
7	-0.859009000	4.586766000	0.206262000
6	-2.143999000	4.755275000	0.703210000
6	-2.438981000	6.019718000	1.267682000
6	-3.149409000	3.756628000	0.757529000
6	-3.667557000	6.277832000	1.862210000
6	-4.379153000	4.018802000	1.348891000
6	-4.651202000	5.278212000	1.906676000
1	-1.676019000	6.792684000	1.228697000
1	-2.943525000	2.776058000	0.343459000
1	-3.866903000	7.256291000	2.289401000
1	-5.133995000	3.238082000	1.385220000
6	-5.942041000	5.524030000	2.610024000
9	-6.322138000	6.832339000	2.583057000
9	-6.976623000	4.804752000	2.091184000
9	-5.897456000	5.185797000	3.943392000

TS1

G = -1633.464203 Hartree

Frequency -1579.8571

7	-1.358272000	-1.759709000	-1.686904000
7	-0.971729000	-1.695928000	-2.959767000
6	-1.939515000	-2.589203000	-5.984378000
6	-1.346308000	-1.319086000	-6.122753000
7	-2.229920000	-0.775798000	-1.564988000
6	-1.603454000	-0.695628000	-3.675641000
6	-2.860489000	-0.527417000	-0.289493000
6	-4.077290000	-0.033148000	2.154176000
6	-1.299385000	-0.311435000	-5.035879000
6	-2.426053000	-0.097649000	-2.723944000
6	-2.947301000	0.696041000	1.759069000
6	-4.577564000	-1.020546000	1.294530000
6	-3.984561000	-1.289716000	0.056230000
6	-0.800582000	-0.984975000	-7.380147000
6	-1.395055000	-3.158484000	-8.279742000
6	-2.314693000	0.468800000	0.532205000
6	-1.952509000	-3.501409000	-7.044081000
6	-4.759648000	0.260676000	3.469634000
6	-0.826776000	-1.887845000	-8.442915000
6	0.090919000	-2.580655000	-3.425495000
6	-1.097744000	1.257048000	0.110243000
6	-4.522841000	-2.357967000	-0.864960000
1	-5.450562000	-1.596444000	1.592951000
1	-0.098271000	0.472958000	-4.826290000
1	-2.415641000	-4.475869000	-6.906338000
1	0.657993000	-2.914734000	-2.557079000
1	-2.416346000	-2.862617000	-5.045791000
1	-2.545015000	1.458406000	2.422238000
1	0.725696000	-2.008973000	-4.106127000

1	-1.409798000	-3.865058000	-9.105487000
1	-0.269560000	0.595031000	-0.168144000
1	-3.803685000	-3.176878000	-0.983865000
1	-5.452681000	-2.777173000	-0.471314000
1	-0.349226000	-0.004636000	-7.513571000
1	-1.312462000	1.888651000	-0.760184000
1	-4.044882000	0.611333000	4.221615000
1	-5.269152000	-0.624790000	3.863885000
1	-0.329827000	-3.434020000	-3.960694000
1	-3.112732000	0.728980000	-2.803034000
1	-0.756821000	1.906713000	0.920767000
1	-5.515925000	1.046853000	3.344000000
1	-4.726676000	-1.958448000	-1.865419000
1	-0.397115000	-1.603158000	-9.400585000
7	-1.264988000	1.994177000	-5.228233000
7	-1.999232000	0.958425000	-5.408266000
7	-0.053308000	1.730657000	-4.733555000
6	0.911144000	2.721457000	-4.682943000
6	2.223488000	2.334365000	-4.335217000
6	0.648837000	4.088263000	-4.929805000
6	3.239924000	3.277006000	-4.237282000
6	1.670186000	5.025925000	-4.826794000
6	2.971587000	4.630455000	-4.485218000
1	2.431821000	1.284492000	-4.148029000
1	-0.353120000	4.399435000	-5.201605000
1	4.244100000	2.960085000	-3.973101000
1	1.455163000	6.072921000	-5.019692000
6	4.045938000	5.654834000	-4.323181000
9	3.897599000	6.713583000	-5.167158000
9	4.078155000	6.194311000	-3.060887000
9	5.292810000	5.152722000	-4.538371000

Int1

G = -1633.486859 Hartree

7	2.394966000	4.281699000	2.703136000
7	2.770628000	4.145359000	1.445109000
6	1.165099000	1.385876000	-0.544413000
6	1.389826000	2.493270000	-1.394514000
7	1.070293000	4.210467000	2.657523000
6	1.717658000	4.028640000	0.564695000
6	0.299892000	4.245191000	3.879158000
6	-1.204145000	4.292655000	6.210074000
6	1.848256000	3.794399000	-0.875304000
6	0.607316000	4.055197000	1.391199000
6	-1.032244000	5.455868000	5.447438000
6	-0.598289000	3.105588000	5.775998000
6	0.163207000	3.052444000	4.603704000
6	1.158897000	2.299853000	-2.777281000
6	0.512110000	-0.016329000	-2.416860000
6	-0.279916000	5.460375000	4.268069000
6	0.729277000	0.156982000	-1.046491000
6	-2.051977000	4.312610000	7.460159000
6	0.736890000	1.068500000	-3.275815000
6	4.188730000	4.166866000	1.102514000
6	-0.093598000	6.711987000	3.448922000
6	0.811017000	1.770579000	4.137992000
1	-0.721696000	2.197613000	6.361685000
1	3.330566000	7.105505000	-0.155557000
1	0.570061000	-0.671600000	-0.359701000
1	4.755037000	3.791755000	1.954360000
1	1.346750000	1.475540000	0.523441000
1	-1.492359000	6.384272000	5.777774000
1	4.485447000	5.187955000	0.858556000
1	0.175199000	-0.972627000	-2.808304000
1	-0.575084000	7.568645000	3.927173000
1	1.903719000	1.857587000	4.128333000
1	0.542463000	0.939147000	4.795114000
1	1.314805000	3.134089000	-3.453557000
1	0.967399000	6.948145000	3.313638000
1	-1.997387000	5.282980000	7.964957000
1	-1.741751000	3.536874000	8.167925000
1	4.326872000	3.527538000	0.229308000
1	-0.444157000	3.973252000	1.167679000
1	-0.522435000	6.607353000	2.446854000
1	-3.106357000	4.130764000	7.213132000
1	0.497928000	1.510927000	3.119308000
1	0.569289000	0.957460000	-4.345045000
7	2.707339000	5.888819000	-1.655111000
7	2.359571000	4.663953000	-1.756186000
7	2.517258000	6.514230000	-0.304966000
6	1.334103000	7.214638000	-0.094212000
6	1.334354000	8.391279000	0.689092000
6	0.104665000	6.749754000	-0.609896000
6	0.152257000	9.064663000	0.962621000
6	-1.077745000	7.429326000	-0.331081000
6	-1.066060000	8.587341000	0.456032000
1	2.273890000	8.771543000	1.083431000
1	0.082368000	5.860210000	-1.229011000
1	0.174943000	9.965575000	1.568355000
1	-2.014419000	7.056030000	-0.733791000
6	-2.342321000	9.268968000	0.819738000
9	-3.329988000	9.072998000	-0.095131000
9	-2.854892000	8.826728000	2.016167000
9	-2.199895000	10.616255000	0.963921000

TS2

G = -1633.476264 Hartree

Frequency -98.1401

7	2.418427000	4.301350000	2.683672000
7	2.801770000	4.085406000	1.444308000
6	1.066685000	1.158583000	-0.698887000
6	1.419651000	2.283810000	-1.469937000
7	1.105144000	4.109111000	2.664588000
6	1.758647000	3.786693000	0.601819000
6	0.337398000	4.215744000	3.884955000
6	-1.147068000	4.395432000	6.219294000
6	1.900453000	3.512100000	-0.824080000
6	0.649459000	3.797766000	1.426275000
6	-0.817811000	5.546363000	5.491748000
6	-0.705865000	3.149966000	5.749750000
6	0.043406000	3.030548000	4.575488000
6	1.303243000	2.197191000	-2.872409000

6	0.499198000	-0.087169000	-2.703321000
6	-0.070525000	5.487846000	4.309431000
6	0.607011000	-0.008962000	-1.311297000
6	-1.984107000	4.488712000	7.473224000
6	0.854844000	1.023655000	-3.477723000
6	4.204345000	4.247296000	1.069761000
6	0.277358000	6.731121000	3.530502000
6	0.518403000	1.687728000	4.072885000
1	-0.946696000	2.250716000	6.312117000
1	3.322615000	7.485452000	0.407416000
1	0.340476000	-0.863427000	-0.694333000
1	4.795648000	4.277297000	1.983755000
1	1.159416000	1.189115000	0.383262000
1	-1.149780000	6.517867000	5.850163000
1	4.290580000	5.181183000	0.510671000
1	0.144305000	-0.997746000	-3.177853000
1	-0.131206000	7.620042000	4.017462000
1	1.602889000	1.680409000	3.911450000
1	0.277228000	0.898761000	4.790135000
1	1.560355000	3.053610000	-3.490451000
1	1.361745000	6.857930000	3.440867000
1	-1.890803000	5.472045000	7.945417000
1	-1.695878000	3.725429000	8.203982000
1	4.492950000	3.396008000	0.450306000
1	-0.394335000	3.623680000	1.219513000
1	-0.118345000	6.694912000	2.510317000
1	-3.045865000	4.334298000	7.239653000
1	0.046660000	1.426953000	3.117351000
1	0.774378000	0.981218000	-4.560915000
7	2.872559000	5.478965000	-1.912797000
7	2.436444000	4.480725000	-1.543750000
7	2.577044000	6.836726000	0.138733000
6	1.391711000	7.461462000	0.204419000
6	1.194546000	8.792193000	0.724238000
6	0.189228000	6.792747000	-0.225023000
6	-0.062023000	9.348670000	0.873736000
6	-1.063271000	7.361633000	-0.080603000
6	-1.219787000	8.645531000	0.479933000
1	2.071105000	9.358125000	1.036705000
1	0.273984000	5.809287000	-0.675817000
1	-0.158194000	10.345513000	1.297774000
1	-1.940518000	6.809785000	-0.410061000
6	-2.562745000	9.204935000	0.726115000
9	-3.507554000	8.762791000	-0.158973000
9	-3.085510000	8.886624000	1.973410000
9	-2.599796000	10.571802000	0.683683000

Int2

G = -1633.482918 Hartree

7	1.460985000	2.561174000	3.094393000
7	2.062549000	2.528996000	1.921450000
6	1.384638000	3.831402000	-1.083588000
6	2.786064000	3.855247000	-0.963025000
7	1.743707000	3.765278000	3.578413000
6	2.698238000	3.713189000	1.622877000
6	1.252009000	4.151646000	4.880725000
6	0.313915000	4.902905000	7.383734000
6	3.398376000	3.963042000	0.372061000
6	2.484838000	4.519795000	2.726644000
6	1.258594000	3.876189000	7.253867000
6	-0.144787000	5.544555000	6.226373000
6	0.311451000	5.191308000	4.951615000
6	3.569599000	3.813752000	-2.129438000
6	1.569196000	3.723739000	-3.498341000
6	1.751381000	3.478793000	6.006784000
6	0.784679000	3.758723000	-2.341156000
6	-0.174553000	5.333666000	8.746637000
6	2.963114000	3.756250000	-3.383992000
6	1.986208000	1.318196000	1.101582000
6	2.779541000	2.378127000	5.891525000
6	-0.173761000	5.920163000	3.722207000
1	-0.878753000	6.342296000	6.313936000
1	3.789113000	7.877411000	3.366954000
1	-0.299537000	3.747672000	-2.414603000
1	1.762518000	0.480727000	1.760792000
1	0.760148000	3.905062000	-0.197331000
1	1.627892000	3.374431000	8.145343000
1	2.950957000	1.178283000	0.612493000
1	1.100634000	3.679618000	-4.477370000
1	3.214291000	2.156749000	6.870082000
1	-0.416820000	5.228794000	2.906969000
1	-1.070405000	6.502844000	3.951293000
1	4.653789000	3.839186000	-2.061172000
1	2.334228000	1.455494000	5.502154000
1	-0.128204000	4.511107000	9.467999000
1	-1.206207000	5.698852000	8.704636000
1	1.205260000	1.434943000	0.347685000
1	2.755451000	5.577453000	2.928060000
1	3.594588000	2.656797000	5.213378000
1	0.446523000	6.150496000	9.137541000
1	0.599808000	6.608832000	3.357013000
1	3.584456000	3.739677000	-4.275142000
7	5.651320000	4.915612000	0.554763000
7	4.600152000	4.481717000	0.486914000
7	3.019014000	7.463367000	2.834633000
6	3.231071000	7.643433000	1.520516000
6	4.385934000	8.289800000	0.942946000
6	2.276851000	7.139026000	0.565604000
6	4.577163000	8.373670000	-0.422770000
6	2.480576000	7.221860000	-0.800148000
6	3.633935000	7.835981000	-1.325866000
1	5.134957000	8.705515000	1.615857000
1	1.374094000	6.665768000	0.945067000
1	5.472993000	8.856899000	-0.808226000
1	1.744607000	6.795504000	-1.475760000
6	3.903723000	7.869792000	-2.774660000
9	4.343125000	9.095320000	-3.222677000
9	4.903880000	6.997302000	-3.181102000
9	2.822522000	7.549745000	-3.541013000

TS3

G = -1633.480695 Hartree

Frequency -1379.5634

7	1.369439000	2.674843000	3.141125000
7	1.965121000	2.576990000	1.971199000
6	1.346303000	3.980406000	-1.018134000
6	2.749854000	3.928675000	-0.927530000
7	1.748954000	3.874358000	3.591781000
6	2.685427000	3.708496000	1.661372000
6	1.274876000	4.317099000	4.880501000
6	0.380088000	5.194404000	7.363537000
6	3.392640000	3.890380000	0.395448000
6	2.551397000	4.573607000	2.740882000
6	1.305116000	4.146180000	7.266461000
6	-0.075399000	5.798234000	6.184948000
6	0.358150000	5.378188000	4.921953000
6	3.505479000	3.965423000	-2.113867000
6	1.476893000	4.110044000	-3.436610000
6	1.772403000	3.685984000	6.030902000
6	0.719442000	4.065299000	-2.261985000
6	-0.131043000	5.647005000	8.711415000
6	2.872825000	4.062332000	-3.352677000
6	1.792434000	1.366256000	1.167402000
6	2.781365000	2.565217000	5.945456000
6	-0.127092000	6.060752000	3.665421000
1	-0.786243000	6.619232000	6.246286000
1	4.200238000	7.381820000	3.275943000
1	-0.365405000	4.112426000	-2.308911000
1	1.527875000	0.548362000	1.836300000
1	0.741120000	3.991050000	-0.115874000
1	1.679726000	3.679258000	8.174759000
1	2.735123000	1.157804000	0.659797000
1	0.987519000	4.187916000	-4.403292000
1	3.203708000	2.350795000	6.931218000
1	-0.424353000	5.335492000	2.899306000
1	-0.987694000	6.699987000	3.882177000
1	4.590984000	3.935468000	-2.071963000
1	2.323374000	1.645016000	5.564799000
1	-0.994130000	5.042601000	9.020965000
1	-0.454100000	6.693013000	8.687088000
1	1.005233000	1.524762000	0.427305000
1	2.963629000	5.834978000	2.849280000
1	3.605670000	2.819716000	5.268815000
1	0.636209000	5.541267000	9.486024000
1	0.664058000	6.686609000	3.234972000
1	3.475651000	4.105051000	-4.255739000
7	5.752485000	4.538843000	0.560469000
7	4.653000000	4.238738000	0.499199000
7	3.389174000	7.126122000	2.711502000
6	3.551422000	7.468529000	1.406231000
6	4.689875000	8.159596000	0.883277000
6	2.549113000	7.099607000	0.456234000
6	4.828018000	8.412425000	-0.472019000
6	2.701439000	7.338371000	-0.899920000
6	3.841705000	7.998347000	-1.387852000
1	5.472949000	8.473419000	1.571122000
1	1.656914000	6.592641000	0.813204000
1	5.715118000	8.928328000	-0.832231000
1	1.934537000	6.999875000	-1.590252000
6	4.054957000	8.196501000	-2.840155000
9	4.553756000	9.436259000	-3.149098000
9	4.969487000	7.316248000	-3.387035000
9	2.922130000	8.041488000	-3.580954000

Int3

G = -1633.493879 Hartree

7	1.334605000	2.543607000	3.214732000
7	1.960510000	2.503970000	2.059139000
6	1.390977000	3.963409000	-0.904394000
6	2.792449000	3.928471000	-0.772856000
7	1.678334000	3.747122000	3.704212000
6	2.656441000	3.669745000	1.816836000
6	1.147264000	4.114447000	4.992992000
6	0.135785000	4.852336000	7.480344000
6	3.393557000	3.886196000	0.568786000
6	2.488625000	4.524030000	2.915396000
6	1.290697000	4.065289000	7.382868000
6	-0.495762000	5.266312000	6.299630000
6	-0.007613000	4.908041000	5.037989000
6	3.579830000	3.991586000	-1.938046000
6	1.588345000	4.136405000	-3.316261000
6	1.818413000	3.681216000	6.144196000
6	0.798787000	4.063031000	-2.164212000
6	-0.433703000	5.226211000	8.829693000
6	2.981786000	4.101039000	-3.192781000
6	1.842203000	1.316985000	1.213273000
6	3.068692000	2.841009000	6.044274000
6	-0.686669000	5.363906000	3.769165000
1	-1.389203000	5.884302000	6.360723000
1	4.646488000	7.477850000	2.973138000
1	-0.284892000	4.098078000	-2.241456000
1	1.592626000	0.466629000	1.847062000
1	0.762445000	3.947889000	-0.018388000
1	1.796652000	3.744530000	8.291168000
1	2.799356000	1.153933000	0.715812000
1	1.125856000	4.226290000	-4.295085000
1	3.495694000	2.656374000	7.034247000
1	-0.969734000	4.510560000	3.140977000
1	-1.590586000	5.937477000	3.993591000
1	4.664115000	3.973796000	-1.865774000
1	2.859472000	1.871578000	5.576438000
1	-0.917388000	6.208757000	8.801636000
1	0.343733000	5.248114000	9.600816000
1	1.064269000	1.471862000	0.462208000
1	3.285112000	6.469925000	2.803334000
1	3.828461000	3.337112000	5.428463000
1	-1.191590000	4.497577000	9.147395000
1	-0.016815000	5.993227000	3.171489000
1	3.609445000	4.166460000	-4.077341000
7	5.739757000	4.561596000	0.806964000
7	4.646850000	4.241530000	0.706566000
7	3.760473000	7.335742000	2.500713000
6	3.775603000	7.556688000	1.136135000
6	4.817002000	8.279617000	0.509515000

6	2.716842000	7.082133000	0.330336000
6	4.807485000	8.493814000	-0.863126000
6	2.718456000	7.285114000	-1.043516000
6	3.760962000	7.994627000	-1.653727000
1	5.640623000	8.659068000	1.109637000
1	1.910830000	6.521240000	0.793081000
1	5.622638000	9.043994000	-1.325005000
1	1.914161000	6.872771000	-1.643985000
6	3.811086000	8.159380000	-3.133634000
9	4.241061000	9.399759000	-3.513946000
9	4.677336000	7.281351000	-3.740738000
9	2.607317000	7.962997000	-3.735331000

TS4

G = -1008.860487 Hartree

Frequency -199.384

7	-0.262136000	-0.048506000	-0.046129000
7	-0.397553000	1.196853000	0.413012000
6	-0.191385000	4.746225000	3.179509000
6	-0.909057000	3.780063000	2.448402000
7	-0.334345000	-0.787938000	1.068020000
6	-0.565994000	1.224604000	1.769486000
6	-0.207490000	-2.218453000	0.927474000
6	0.035445000	-4.979672000	0.673701000
6	-0.681170000	2.347680000	2.680752000
6	-0.503037000	-0.102779000	2.232354000
6	1.165685000	-4.178591000	0.883315000
6	-1.219252000	-4.361338000	0.588972000
6	-1.367679000	-2.975247000	0.714735000
6	-1.876113000	4.219602000	1.525051000
6	-1.379130000	6.533911000	2.050294000
6	1.069775000	-2.788216000	1.015071000
6	-0.432417000	6.108072000	2.989298000
6	0.162312000	-6.482415000	0.571493000
6	-2.098627000	5.582567000	1.318886000
6	-0.298185000	2.290904000	-0.552665000
6	2.289742000	-1.929183000	1.243244000
6	-2.721041000	-2.312662000	0.624116000
1	-2.104568000	-4.971158000	0.421045000
1	0.130640000	6.838191000	3.565157000
1	0.240763000	3.120140000	-0.095192000
1	0.562228000	4.421382000	3.892486000
1	2.146656000	-4.645051000	0.945600000
1	-1.293384000	2.622803000	-0.855973000
1	-1.558006000	7.594420000	1.894702000
1	3.196021000	-2.540247000	1.284532000
1	-2.758905000	-1.601207000	-0.209513000
1	-3.510857000	-3.054734000	0.475864000
1	-2.474133000	3.489694000	0.986888000
1	2.410371000	-1.190839000	0.441470000
1	0.046278000	-6.949705000	1.558574000
1	1.143355000	-6.776589000	0.183208000
1	0.248780000	1.920837000	-1.419656000
1	2.206034000	-1.371108000	2.183238000
1	-0.607457000	-6.905924000	-0.082822000
1	-2.944483000	-1.748847000	1.537519000
1	-2.849511000	5.900737000	0.600088000
7	-0.507747000	0.819649000	4.458138000
7	-0.603960000	1.855463000	3.916732000

2a

G = -1008.933037 Hartree

7	2.898917000	-5.574957000	-4.534171000
7	2.711311000	-4.322990000	-4.132852000
6	2.633292000	-1.106161000	-2.262124000
6	2.093255000	-2.058160000	-1.378514000
7	2.855431000	-6.335261000	-3.433893000
6	2.562760000	-4.238410000	-2.775085000
6	2.984082000	-7.764055000	-3.536422000
6	3.231263000	-10.528892000	-3.698954000
6	2.299167000	-3.495250000	-1.592901000
6	2.641812000	-5.562766000	-2.320275000
6	4.263205000	-9.750085000	-3.158836000
6	2.072223000	-9.886896000	-4.155239000
6	1.919169000	-8.498262000	-4.080657000
6	1.350341000	-1.599514000	-0.273548000
6	1.687257000	0.704522000	-0.957992000
6	4.164279000	-8.357794000	-3.064254000
6	2.428162000	0.260386000	-2.057917000
6	3.350457000	-12.033969000	-3.756675000
6	1.154416000	-0.233685000	-0.065294000
6	2.711459000	-3.263011000	-5.139446000
6	5.279040000	-7.525714000	-2.477905000
6	0.659607000	-7.820360000	-4.564340000
1	1.262617000	-10.481333000	-4.573018000
1	2.857395000	0.977466000	-2.753247000
1	3.642146000	-2.694409000	-5.072816000
1	3.239369000	-1.432461000	-3.102004000
1	5.169679000	-10.235938000	-2.804725000
1	1.857809000	-2.607430000	-4.961176000
1	1.528553000	1.767498000	-0.796501000
1	6.156832000	-8.143852000	-2.269917000
1	0.839307000	-7.262676000	-5.490817000
1	-0.125424000	-8.556696000	-4.758156000
1	0.925995000	-2.324959000	0.413451000
1	5.579596000	-6.722805000	-3.161608000
1	2.932761000	-12.489254000	-2.848826000
1	4.396173000	-12.350648000	-3.830827000
1	2.630069000	-3.730150000	-6.120457000
1	4.964556000	-7.051681000	-1.540440000
1	2.803489000	-12.446695000	-4.611149000
1	0.282028000	-7.104863000	-3.824652000
1	0.576173000	0.099857000	0.792892000
7	2.462778000	-5.684667000	-1.000651000
7	2.254018000	-4.395380000	-0.577663000

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