Supporting Information

Dioxygenation of unprotected mesoionic N-heterocyclic olefins

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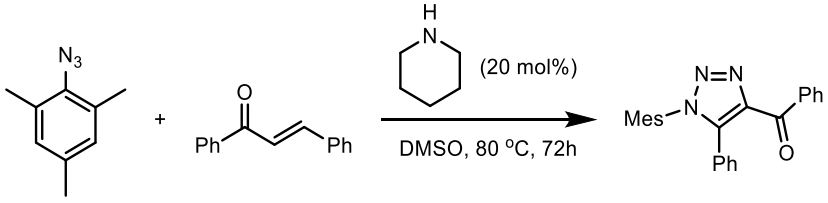
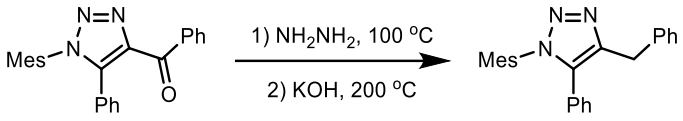
1. Experimental section

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 *n*-pentane solvent were dried by refluxing and distilling over sodium under dinitrogen. THF and toluene solvent were dried by refluxing and distilling over sodium benzophenone ketyl under dinitrogen. C_6D_6, toluene-d_8 and $CDCl_3$ 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 spectrometer or an Agilent DD2 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 ^1H-COSY, ^1H-^{13}C-HSQC, and ^1H-^{13}C-HMBC NMR spectroscopy. IR spectra were recorded on a Bruker ALPHA spectrometer equipped with a diamond ATR sampling unit. 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.



Benzalacetophenone[1] (10.4 g, 50 mmol), mesityl azide[2] (16.1 g, 100 mmol) and piperidine (1.0 mL, 10 mmol, 20 mol %) were dissolved in 50 mL of DMSO. The reaction mixture was stirred at 80 °C for 72 h. After cooling to room temperature, the mixture was partitioned with diethyl ether (100 mL) and water (100 mL). The aqueous layer was extracted with diethyl ether (2 × 100 mL). The combined ether fractions were washed with brine, dried over $MgSO_4$, filtered, and concentrated to dryness under reduced pressure.

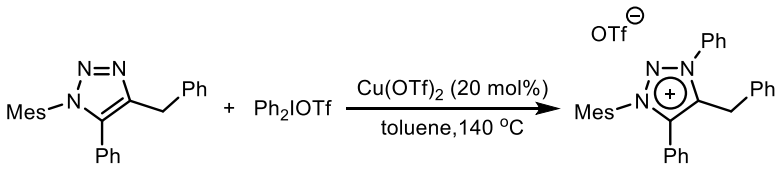
The residue was recrystallized from dichloromethane / hexanes to afford (1-mesityl-5-phenyl-1,2,3-triazol-4-yl)(phenyl)methanone as a white solid. Yield: 10.6 g, 58%. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 8.34 – 8.28 (m, 2H, Ph-*H*), 7.65 – 7.57 (m, 1H, Ph-*H*), 7.54 – 7.47 (m, 2H, Ph-*H*), 7.37 – 7.32 (m, 1H, Ph-*H*), 7.33 – 7.24 (m, 4H, Ph-*H*), 6.94 – 6.90 (m, 2H, Mes-*H*), 2.31 (s, 3H, Mes-CH_3), 1.95 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) δ 187.13 (*C*=O), 142.93, 142.54, 140.48 (Mes-*C*), 137.50 (Ph-*C*), 135.42 (Mes-*C*), 133.21 (Ph-*C*), 131.85 (Mes-*C*), 130.89 (Ph-*C*), 129.97 (Ph-*C*), 129.51 (Ph-*C*), 129.42 (Mes-*C*), 128.43 (Ph-*C*), 128.40 (Ph-*C*), 125.92 , 21.30 (Mes-*C*H_3), 17.87 (Mes-*C*H_3). HRMS (ESI): *m/z* calcd for $C_{24}H_{21}N_3ONa$ $[M+Na]^+$ 390.1577, found 390.1572.



A mixture of (1-mesityl-5-phenyl-1,2,3-triazol-4-yl)(phenyl)methanone (7.4 g, 20 mmol), 85% hydrazine hydrate (10 ml) and diethylene glycol (100 ml) was heated at 100 °C for 1 h. To the reaction mixture was then added of KOH pellets (10 g) and the resulting mixture was heated to 200 °C for 4 h. After cooling to room temperature, the mixture was partitioned with diethyl ether (100 mL) and water (100 mL). The aqueous layer was extracted with diethyl ether (2 × 100 mL). The combined ether fractions were washed with brine, dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography eluted with ethyl acetate (0–10% gradient by volume) in hexanes. The product 4-benzyl-1-mesityl-5-phenyl-1,2,3-triazole was isolated as a colorless oil. Yield: 5.2 g, 74%. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 7.32 – 7.21 (m, 7H, overlapping, Ph-*H*), 7.22 – 7.18 (m, 1H, Ph-*H*), 7.04 – 7.00 (m, 2H, Ph-*H*), 6.89 (s, 2H, Mes-*H*), 4.20 (s, 2H, CH_2), 2.29 (s, 3H, Mes-CH_3), 1.90 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) δ 143.53 (triazole-*C*), 139.84 (Mes-*C*), 139.75, 135.80, 135.53 (Mes-*C*), 132.84 (Mes-*C*), 129.22 (Mes-*C*), 128.98, 128.76, 128.67, 128.66, 128.57, 127.17,

126.37 (Ph-*C*), 31.61 (*C*H_2), 21.26 (Mes-*C*H_3), 17.78 (Mes-*C*H_3). HRMS (ESI): *m/z* calcd for $C_{24}H_{24}N_3$ $[M+H]^+$ 354.1965, found 354.1969.

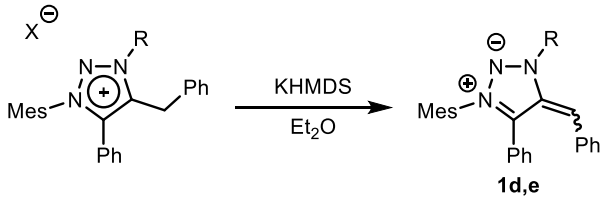
Trimethyloxonium tetrafluoroborate (1.1 g, 7.5 mmol, 1.3 equiv.) was added as solid to a stirring solution of 4-benzyl-1-mesityl-5-phenyl-1,2,3-triazole (2.1 g, 5.9 mmol) in DCM (20 mL). The mixture was stirred at room temperature overnight. It was then filtered, concentrated under vacuum to ~5 mL and dropwise added into rapid stirring diethyl ether (20 mL). The white precipitate was collected by filtration, washed with diethyl ether (3 × 5 mL) and *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 2.4 g, 89%. X-ray quality crystals were obtained by vapor diffusion of *n*-pentane into its concentrated DCM solution at room temperature. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 7.49 – 7.42 (m, 1H, Ph-*H*), 7.41 – 7.34 (m, 2H, Ph-*H*), 7.36 – 7.24 (m, 5H, Ph-*H*), 7.08 – 7.03 (m, 2H, Ph-*H*), 6.96 (q, *J* = 0.8 Hz, 2H, Mes-*H*), 4.55 (s, 2H, C*H*$_2$), 4.27 (s, 3H, N-C*H*$_3$), 2.32 (s, 3H, Mes-C*H*$_3$), 2.03 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) δ 142.47 (Mes-*C*), 142.08 (Ph-*C*), 141.56 (triazolium-*C*), 135.21 (Mes-*C*), 134.02 (Ph-*C*), 131.68 (Ph-*C*), 129.96, 129.92 (Mes-*C*), 129.64, 129.64, 129.41 (Ph-*C*), 128.27 (Ph-*C*), 128.00 (Ph-*C*), 122.39, 39.08 (N-*C*H_3), 29.08 (*C*H_2), 21.33 (Mes-*C*H_3), 17.59 (Mes-*C*H_3). HRMS (ESI): *m/z* calcd for $C_{25}H_{26}N_3$ $[M-BF_4]^+$ 368.2121, found 368.2121.



4-benzyl-1-mesityl-5-phenyl-1,2,3-triazole (1.8 g, 5.1 mmol), diphenyliodonium triflate[3] 430.179 (3.3 g, 7.7 mmol, 1.5 equiv.), $Cu(OTf)_2$ (368.9 mg, 1.02 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 dichloromethane to afford a pale brown sticky foam. Yield: 1.9 g, 64%. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 7.77 (dd, *J* = 7.2, 1.6 Hz, 2H, Ph-*H*), 7.65 – 7.58 (m, 1H, Ph-*H*), 7.57 – 7.54 (m, 2H, Ph-*H*), 7.49 – 7.41 (m, 3H, Ph-*H*), 7.41 – 7.35 (m, 2H, Ph-*H*), 7.12 – 7.05 (m, 3H, Ph-*H*), 6.96 (s, 2H, Mes-*H*), 6.67 (dd, *J* = 7.2, 2.2 Hz, 2H, Ph-*H*), 4.50 (s, 2H, C*H*$_2$), 2.31 (s, 3H, Mes-C*H*$_3$), 2.11 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) δ 143.01, 142.60 (Mes-*C*), 142.05, 135.03 (Mes-*C*), 134.30, 133.87, 132.33 (Ph-*C*), 131.69 (Ph-*C*), 130.16 (Ph-*C*), 129.95 (Mes-*C*), 129.88 (Mes-*C*), 129.61 (Ph-*C*), 129.57 (Ph-*C*), 129.02 (Ph-*C*), 128.21 (Ph-*C*), 127.52 (Ph-*C*), 126.35 (Ph-*C*), 124.79, 120.97 (q, *J* = 320.7 Hz, *C*$F_3SO_3^-$), 29.95 (*C*H_2), 21.28 (Mes-*C*H_3), 17.70 (Mes-*C*H_3). HRMS (ESI): *m/z* calcd for $C_{30}H_{28}N_3$ $[M-OTf]^+$ 430.2278, found 430.2280.

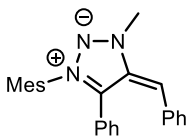
Syntheses of mNHOs:

mNHO **1a**[4], **1b**[5] and **1c**[5] were synthesized according to literatures.



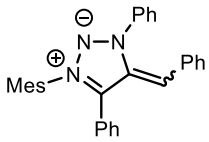
1d,e

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 **1d,e** The solid was washed with *n*-pentane (3 × 5 mL) and dried under vacuum.



1d

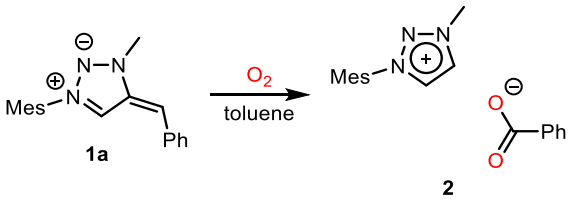
Dark green crystalline solid. Yield: 550.3 mg, 75%. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution to −35 °C. ^{1}H NMR (500 MHz, 25 °C, C_6D_6) δ 7.15 – 7.08 (m, 2H, Ph-*H*), 7.02 (dt, *J* = 6.1, 1.4 Hz, 2H, Ph-*H*), 6.92 (dd, *J* = 8.3, 1.3 Hz, 2H, Ph-*H*), 6.88 – 6.83 (m, 2H, Ph-*H*), 6.83 – 6.74 (m, 2H, Ph-*H*), 6.45 (s, 2H, Mes-*H*), 4.67 (s, 1H, C*H*), 3.12 (s, 3H, N-CH_3), 1.90 (s, 3H, Mes-CH_3), 1.84 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, 25 °C, C_6D_6) δ 141.00 (Ph-*C*), 140.63 (triazole-*C*), 140.27 (Mes-*C*), 135.42 (Mes-*C*), 133.21 (Mes-*C*), 129.41 (Mes-*C*), 127.85 (Ph-*C*), 127.77 (Ph-*C*), 127.66 (Ph-*C*), 127.29 (Ph-*C*), 126.89 (Ph-*C*), 123.97 (Ph-*C*), 121.11 (triazole-*C*), 117.80 (Ph-*C*), 66.11 (*C*H), 34.39 (N-*C*H_3), 20.94 (Mes-*C*H_3), 17.11 (Mes-*C*H_3). Anal. Calcd for $C_{25}H_{25}N_3$: C, 81.71; H, 6.86; N, 11.43. Found: C, 81.44; H, 7.23; N, 11.53.



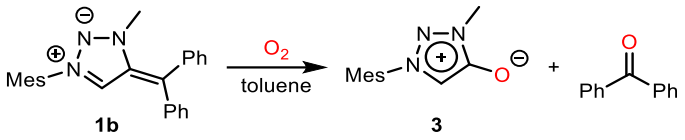
1e

Dark green crystalline solid. Yield: 608.8 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, 25 °C, C_6D_6) δ 7.80 (s, 2H, Ph-*H*), 7.11 – 6.99 (m, 5H, Ph-*H*), 6.96 – 6.80 (m, 7H, Ph-*H*), 6.76 (t, *J* = 7.2 Hz, 1H, Ph-*H*), 6.45 (s, 2H, Mes-*H*), 5.68 (s, 1H, C*H*), 1.95 (s, 6H, Mes-CH_3), 1.88 (s, 3H, Mes-CH_3). ^{13}C NMR (126 MHz, 25 °C, C_6D_6) δ 140.22 (Mes-*C*), 140.04 (Ph-*C*), 138.81, 135.24 (Mes-*C*), 133.01 (Mes-*C*), 129.40 (Mes-*C*), 127.54 (Ph-*C*), 124.74 (Ph-*C*), 20.93 (Mes-*C*H_3), 17.28 (Mes-*C*H_3). Although the X-ray structure shows the Z isomer, the toluene solution of compound **1e** contains a dynamic mixture of *E* and *Z* isomers. The ratio of two isomers is ~1:1.1 at 10 °C and has negligible change by cooling to −35 °C; at 25 °C the signals of the two isomers coalesce into one broad set (see Figure S23). Anal. Calcd for $C_{30}H_{27}N_3$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.24; H, 6.55; N, 9.58.

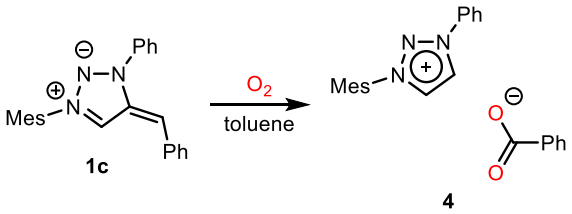
Reaction of mNHOs with O_2:



A solution of **1a**[4] (145.7 mg, 0.50 mmol) in 5 mL of toluene under nitrogen was subjected to a freeze−pump−thaw cycle before 1 atm of O_2 was introduced into the flask. The mixture was kept under O_2 for 15 min at room temperature. Top-layering the mixture with 5 mL of *n*-pentane and cooling to −35 °C afforded crystals of **2** that are suitable for X-ray crystallography. The supernatant was decanted off and the crystals were washed with *n*-pentane (3 × 5 mL) and dried under vacuum (134.5 mg, 83%). ^{1}H NMR (600 MHz, 25 °C, $CDCl_3$): δ 11.47 and 11.46 (s and d, J = 1.4 Hz, 1H, triazolium-*H*), 9.30 and 9.28 (s and d, J = 1.4 Hz, 1H, triazolium-*H*), 7.97 – 7.93 (m, 2H, Ph-*H*), 7.30 – 7.19 (m, 3H, Ph-*H*), 6.94 (s, 2H, Mes-*H*), 4.69 (s, 3H, N-CH_3), 2.31 (s, 3H, Mes-CH_3), 1.93 (s, 6H, Mes-CH_3). ^{13}C NMR (151 MHz, 25 °C, $CDCl_3$) δ 172.70 (Ph-CO_2^-), 142.43 (Mes-*C*), 139.86 (Ph-*C*), 135.87 (triazolium-*C*), 134.21 (Mes-*C*), 133.53 (triazolium-*C*), 131.41 (Mes-*C*), 129.90 (Mes-*C*), 129.27 (Ph-*C*), 128.99 (Ph-*C*), 127.32 (Ph-*C*), 40.63 (N-*C*H$_3$), 21.28 (Mes-*C*H$_3$), 17.27 (Mes-*C*H$_3$). IR (neat solid) for **2-$^{16}O_2$**: ν ($C^{16}O_2^-$) 1558 and 1357 cm^{-1}. IR (neat solid) for **2-$^{18}O_2$**: ν ($C^{18}O_2^-$) 1592 and 1338 cm^{-1}. HRMS (ESI) for **2-$^{16}O_2$**: *m/z* calcd for $C_7H_5{}^{16}O_2$ [M−$C_{12}H_{16}N_3$]$^-$ 121.0295, found 121.0295. HRMS (ESI) for **2-$^{18}O_2$**: *m/z* calcd for $C_7H_5{}^{18}O_2$ [M−$C_{12}H_{16}N_3$]$^-$ 125.0380, found 125.0381. Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.57; H, 6.55; N, 12.99. Found: C, 70.35; H, 6.45; N, 12.95.

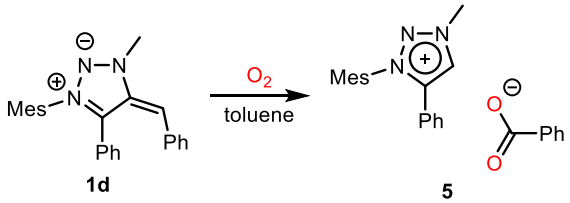


A solution of **1b**[5] (183.8 mg, 0.50 mmol) in 5 mL of toluene under nitrogen was subjected to a freeze−pump−thaw cycle before 1 atm of O_2 was introduced into the flask. The mixture was stirred for 15 min at room temperature. All volatiles were removed under vacuum. The residue was purified by flash chromatography eluted with dichloromethane. Compound **3** was isolated as a white solid. Yield: 95.4 mg, 82%. Crystals suitable for X-ray crystallography were obtained by slow evaporation of an acetone solution to at room temperature. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 6.97 (q, J = 0.7 Hz, 2H, Mes-*H*), 6.62 (s, 1H, triazole-*H*), 3.78 (s, 3H, N-C*H*$_3$), 2.33 (s, 3H, Mes-C*H*$_3$), 2.06 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) δ 158.60 (triazole-*C*), 140.96 (Mes-*C*), 134.60 (Mes-*C*), 133.65 (Mes-*C*), 129.38 (Mes-*C*), 108.55 (triazole-*C*), 31.39 (N-*C*H$_3$), 21.24 (Mes-*C*H$_3$), 16.91 (Mes-*C*H$_3$). Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.70; H, 6.95; N, 18.87.

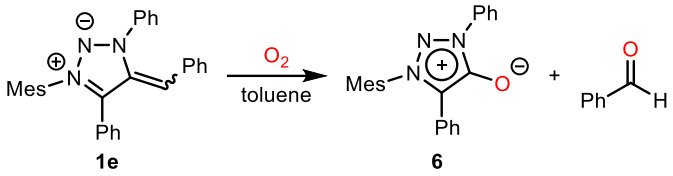


A solution of **1c**[5] (176.7 mg, 0.50 mmol) in 5 mL of toluene under nitrogen was subjected to a freeze−pump−thaw cycle before 1 atm of O_2 was introduced into the flask. The mixture was kept under O_2 for 15 min at room temperature. Top-layering the mixture with 5 mL of *n*-pentane and cooling to −35 °C afforded crystals of **4** that are suitable for X-ray crystallography. The supernatant was decanted off and the crystals were washed with *n*-pentane (3 × 5 mL) and dried under vacuum (171.2 mg, 89%). ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 11.68 and 11.67 (s and d, J = 1.6 Hz, 1H, triazolium-*H*), 9.51 and 9.49 (s and d, J = 1.5 Hz, 1H, triazolium-*H*), 8.27 – 8.22 (m, 2H, Ph-*H*), 8.06 – 8.02 (m, 2H, Ph-*H*), 7.59 – 7.55

(m, 3H, Ph-*H*), 7.30 – 7.24 (m, 3H, Ph-*H*), 7.01 (s, 2H, Mes-*H*), 2.35 (s, 3H, Mes-CH_3), 2.05 (s, 6H, Mes-CH_3). ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) δ 172.93 (Ph-CO_2^-), 142.70 and 142.69 (Mes-*C*), 139.81 (Ph-*C*), 135.68 and 135.61 (triazolium-*C*), 135.12 and 135.08 (Ph-*C*), 134.27 (Mes-*C*), 133.02 and 132.94 (triazolium-*C*),, 132.04 (Ph-*C*), 131.49 and 131.46 (Mes-*C*), 130.65 (Ph-*C*), 130.03 (Mes-*C*), 129.45 (Ph-*C*), 129.07 (Ph-*C*), 127.35 (Ph-*C*), 121.28 (Ph-*C*), 21.33 (Mes-*C*H_3), 17.44 (Mes-*C*H_3). Anal. Calcd for $C_{24}H_{23}N_3O_2$: C, 74.78; H, 6.01; N, 10.90. Found: C, 75.01; H, 6.05; N, 10.72.



A solution of **1d** (183.8 mg, 0.50 mmol) in 5 mL of toluene under nitrogen was subjected to a freeze−pump−thaw cycle before 1 atm of O_2 was introduced into the flask. The mixture was kept under O_2 for 15 min at room temperature. Top-layering the mixture with 5 mL of *n*-pentane and cooling to −35 °C afforded crystals of **5** that are suitable for X-ray crystallography. The supernatant was decanted off and the crystals were washed with *n*-pentane (3 × 5 mL) and dried under vacuum (152.7 mg, 76%). ^{1}H NMR (600 MHz, 25 °C, $CDCl_3$) δ 11.86 (s, 1H, triazolium-*H*), 8.19 – 8.15 (m, 2H), 7.44 – 7.38 (m, 1H), 7.40 – 7.35 (m, 2H), 7.36 – 7.30 (m, 5H), 7.06 (s, 2H), 4.79 (s, 3H, N-CH_3), 2.39 (s, 3H, Mes-CH_3), 1.90 (s, 6H, Mes-CH_3). ^{13}C NMR (151 MHz, 25 °C, $CDCl_3$) δ 173.14 (Ph-CO_2^-), 143.59 (triazolium-*C*), 142.91 (Mes-*C*), 140.13 (Ph-*C*), 134.71 (Mes-*C*), 133.41 (triazolium-*C*), 131.80 (Ph-*C*), 130.67 (Mes-*C*), 130.34 (Mes-*C*), 129.79 (Ph-*C*), 129.52 (Ph-*C*), 129.12 (Ph-*C*), 127.70 (Ph-*C*), 127.47 (Ph-*C*), 122.57 (Ph-*C*), 41.01 (N-*C*H_3), 21.42 (Mes-*C*H_3), 17.48 (Mes-*C*H_3). Anal. Calcd for $C_{25}H_{25}N_3O_2$: C, 75.16; H, 6.31; N, 10.52. Found: C, 75.56; H, 6.64; N, 10.56.



A solution of **1e** (214.8 mg, 0.50 mmol) in 5 mL of toluene under nitrogen was subjected to a freeze−pump−thaw cycle before 1 atm of O_2 was introduced into the flask. The mixture was stirred for 15 min at room temperature. All volatiles were removed under vacuum. The residue was purified by flash chromatography eluted with dichloromethane. Compound **6** was isolated as a white solid. Yield: 137.8 mg, 78%. Crystals suitable for X-ray crystallography were obtained by slow evaporation of an acetone solution to at room temperature. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ 8.26 – 8.17 (m, 2H, Ph-*H*), 7.56 – 7.46 (m, 4H, Ph-*H*), 7.41 – 7.35 (m, 1H, Ph-*H*), 7.29 – 7.21 (m, 2H, Ph-*H*), 7.22 – 7.17 (m, 1H, Ph-*H*), 7.03 (q, *J* = 0.8 Hz, 2H, Mes-*H*), 2.39 (s, 3H, Mes-C*H*$_3$), 2.06 (s, 6H, Mes-C*H*$_3$). ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) δ 155.59 (triazole-*C*), 141.18 (Mes-*C*), 136.31 (Ph-*C*), 134.86 (Mes-*C*), 133.64 (Mes-*C*), 129.78 (Mes-*C*), 129.21 (Ph-*C*), 128.64 (Ph-*C*), 127.97 (Ph-*C*), 127.68 (Ph-*C*), 127.24, 125.35 (Ph-*C*), 121.32 (Ph-*C*), 118.94, 21.36 (Mes-*C*H$_3$), 17.36 (Mes-*C*H$_3$). Anal. Calcd for $C_{23}H_{21}N_3O$: C, 77.72; H, 5.96; N, 11.82. Found: C, 77.53; H, 6.17; N, 11.62.

2. NMR spectra

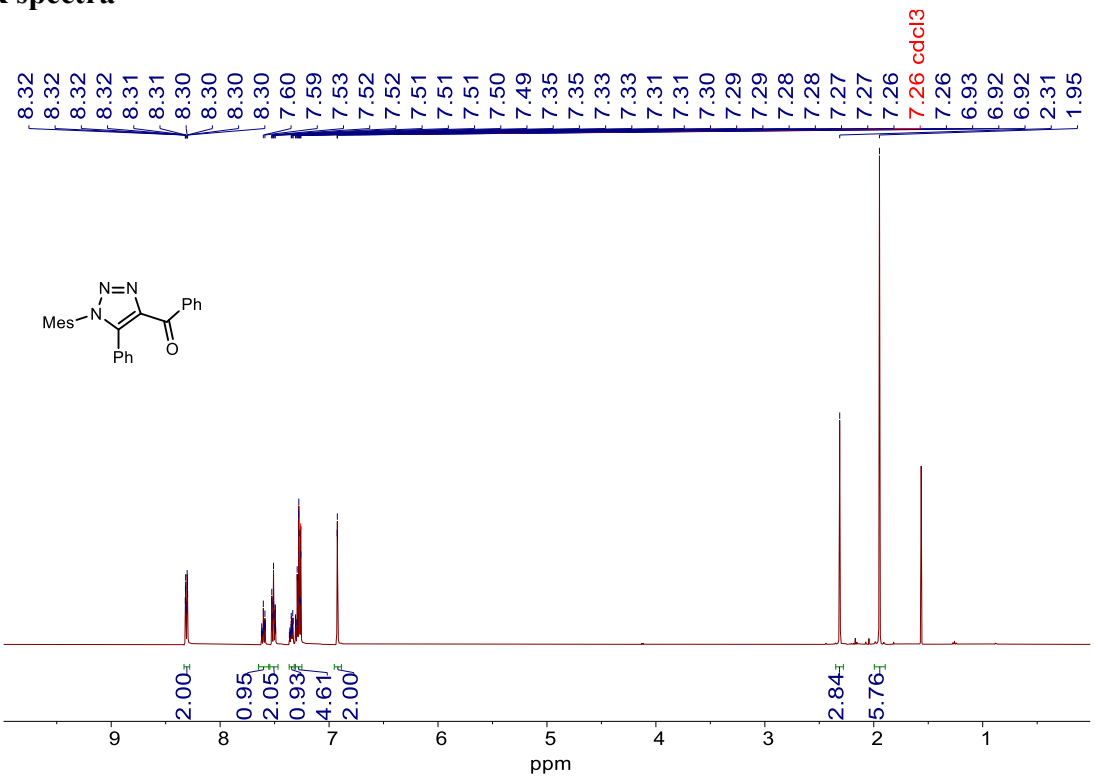


Figure S1. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of (1-mesityl-5-phenyl-1,2,3-triazol-4-yl)(phenyl)-methanone.

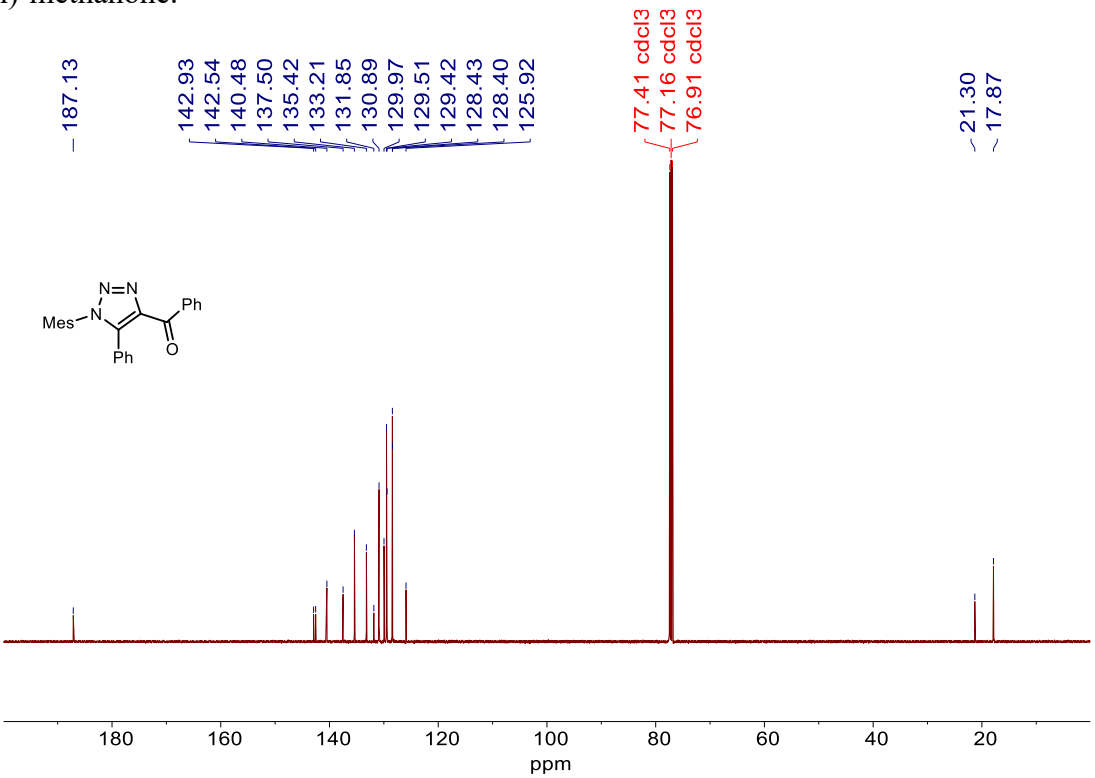


Figure S2. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of (1-mesityl-5-phenyl-1,2,3-triazol-4-yl)(phenyl)-methanone.

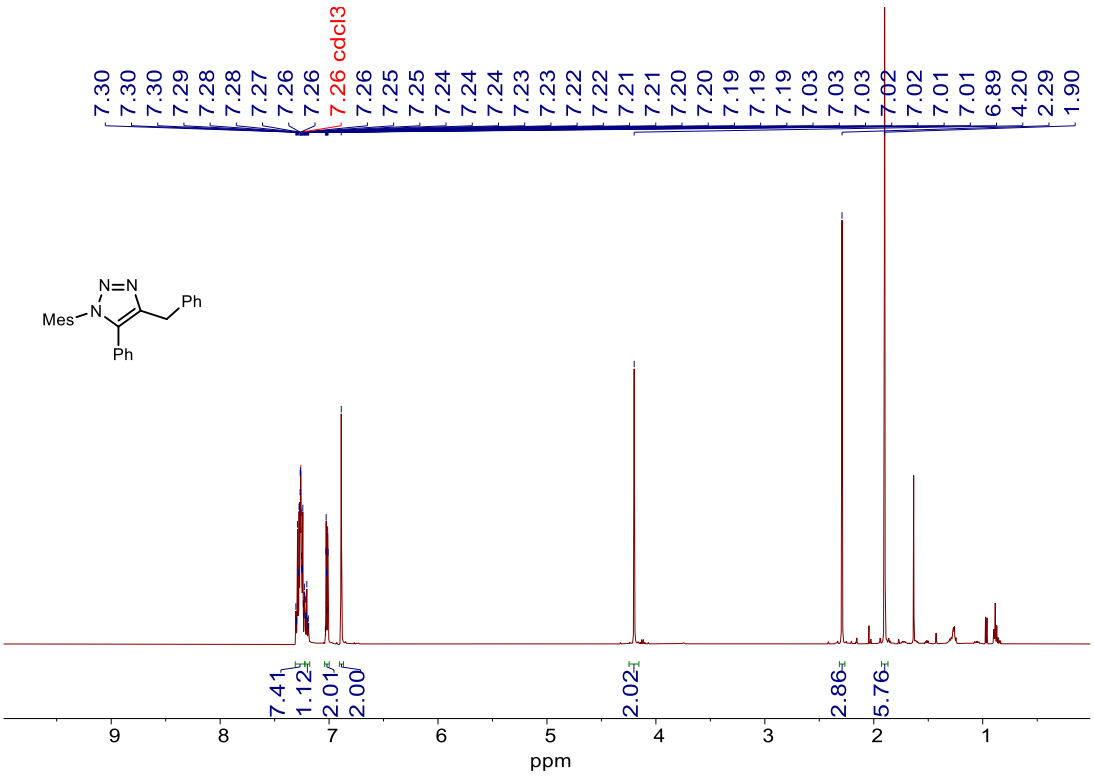


Figure S3. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-5-phenyl-1,2,3-triazole.

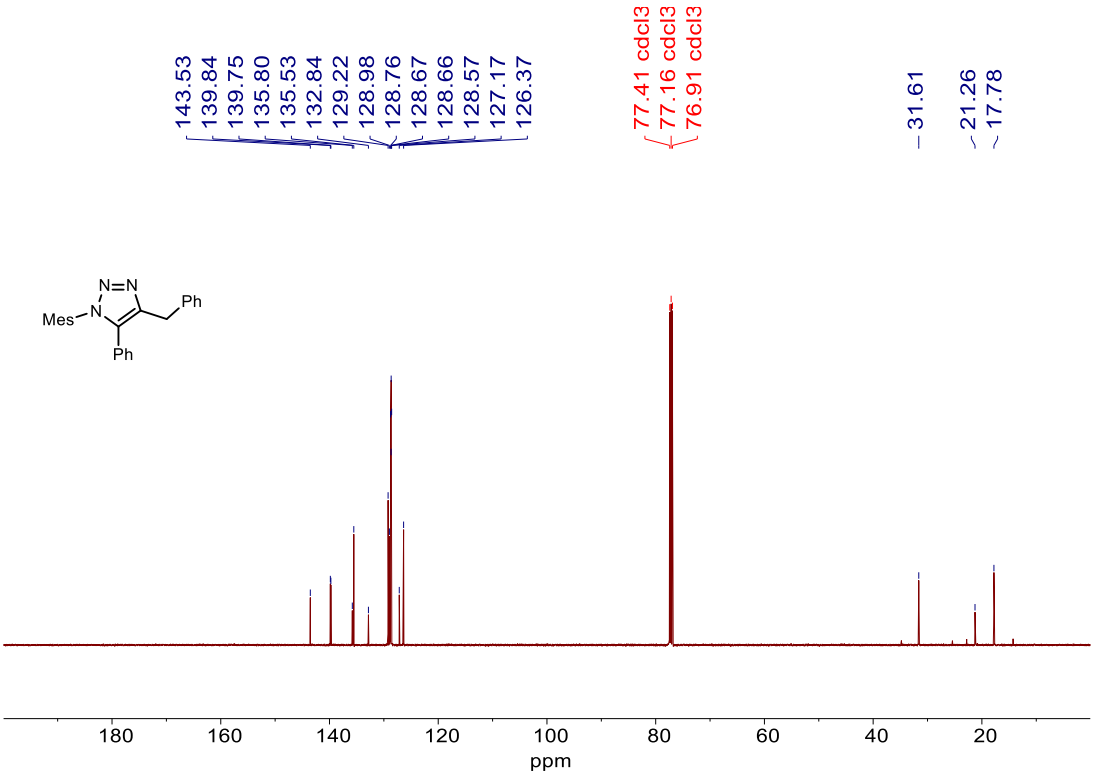


Figure S4. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-5-phenyl-1,2,3-triazole.

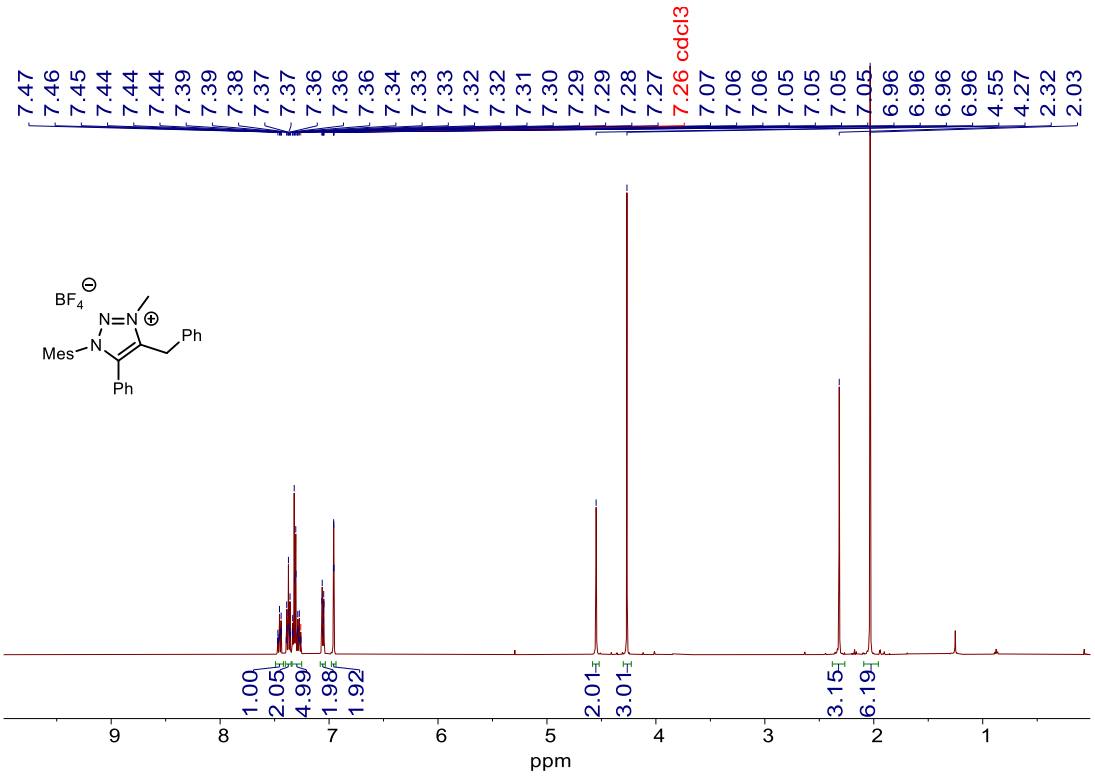


Figure S5. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-3-methyl-5-phenyl-1,2,3-triazolium tetrafluoroborate.

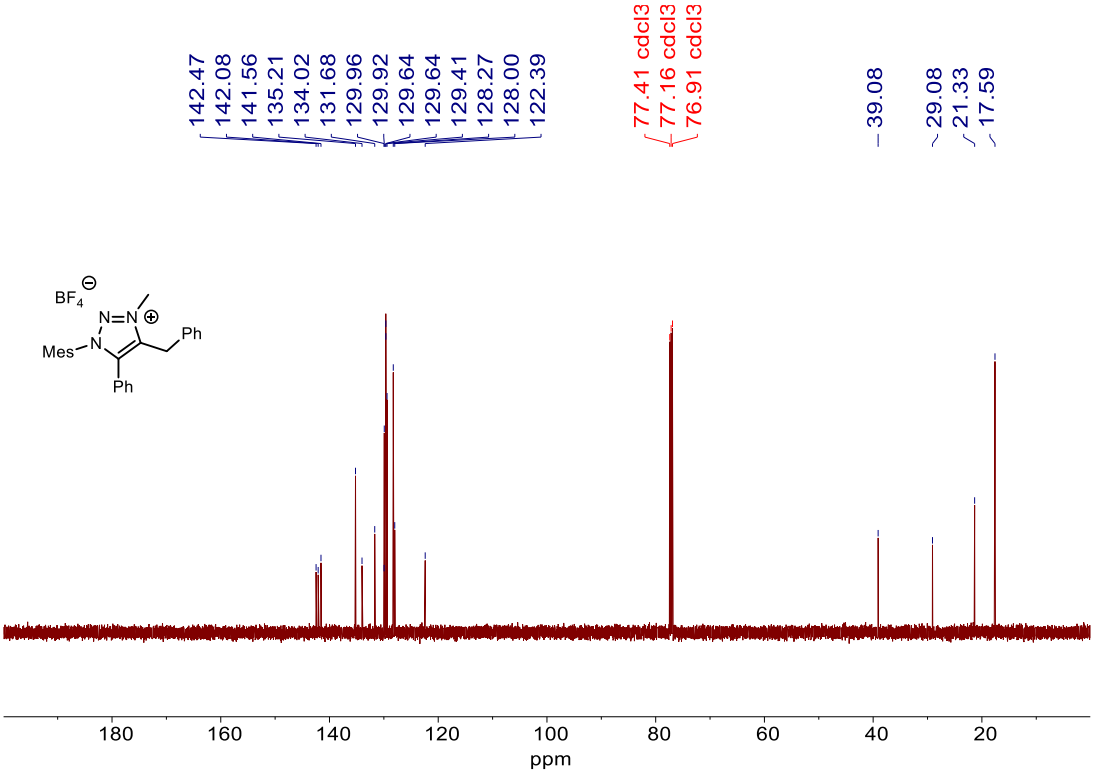


Figure S6. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-3-methyl-5-phenyl-1,2,3-triazolium tetrafluoroborate.

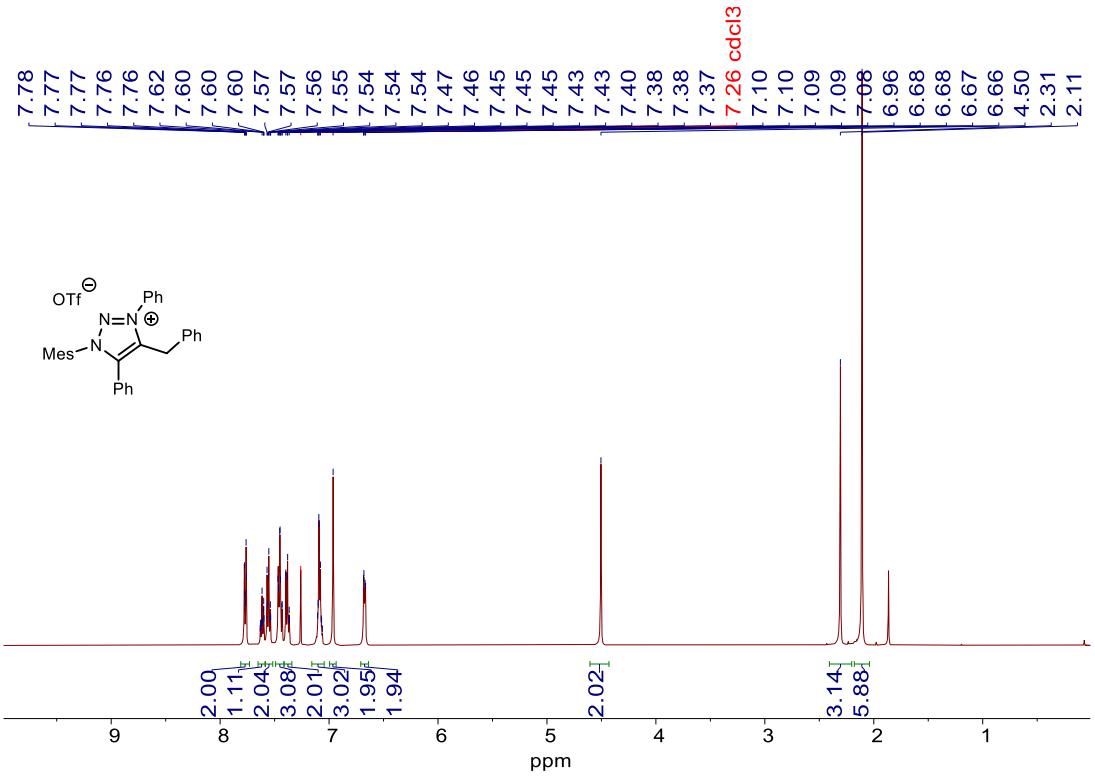


Figure S7. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-3,5-diphenyl-1,2,3-triazolium triflate.

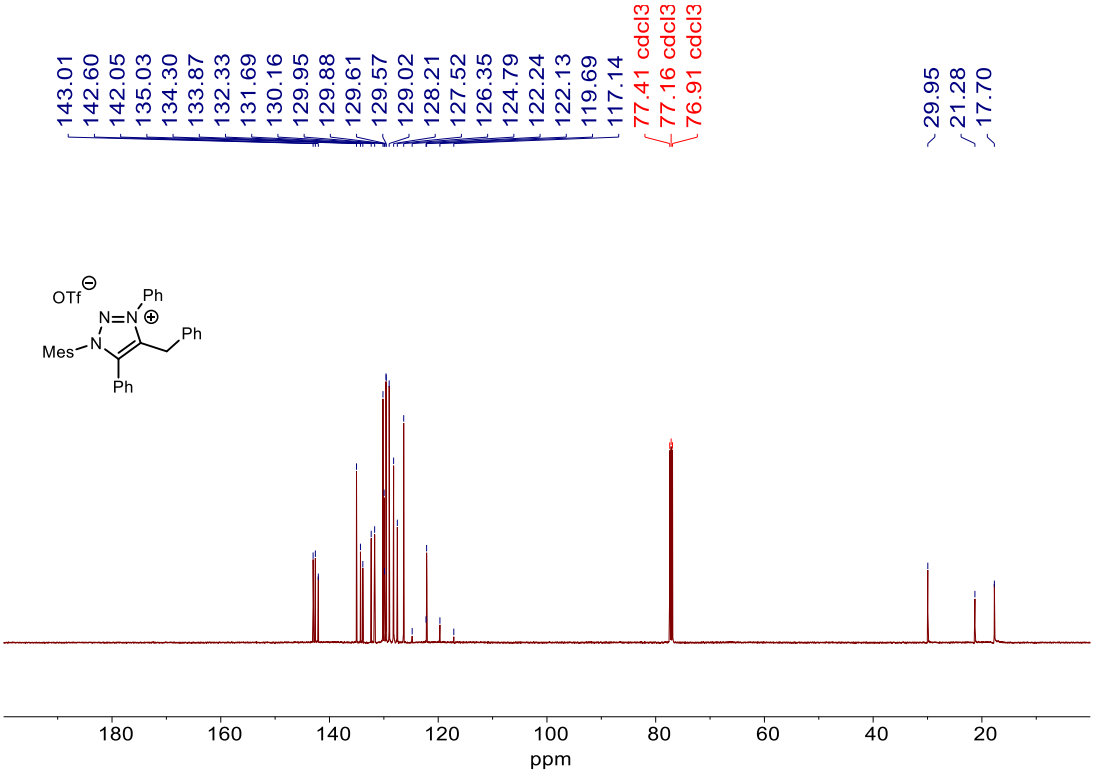


Figure S8. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of 4-benzyl-1-mesityl-3,5-diphenyl-1,2,3-triazolium triflate.

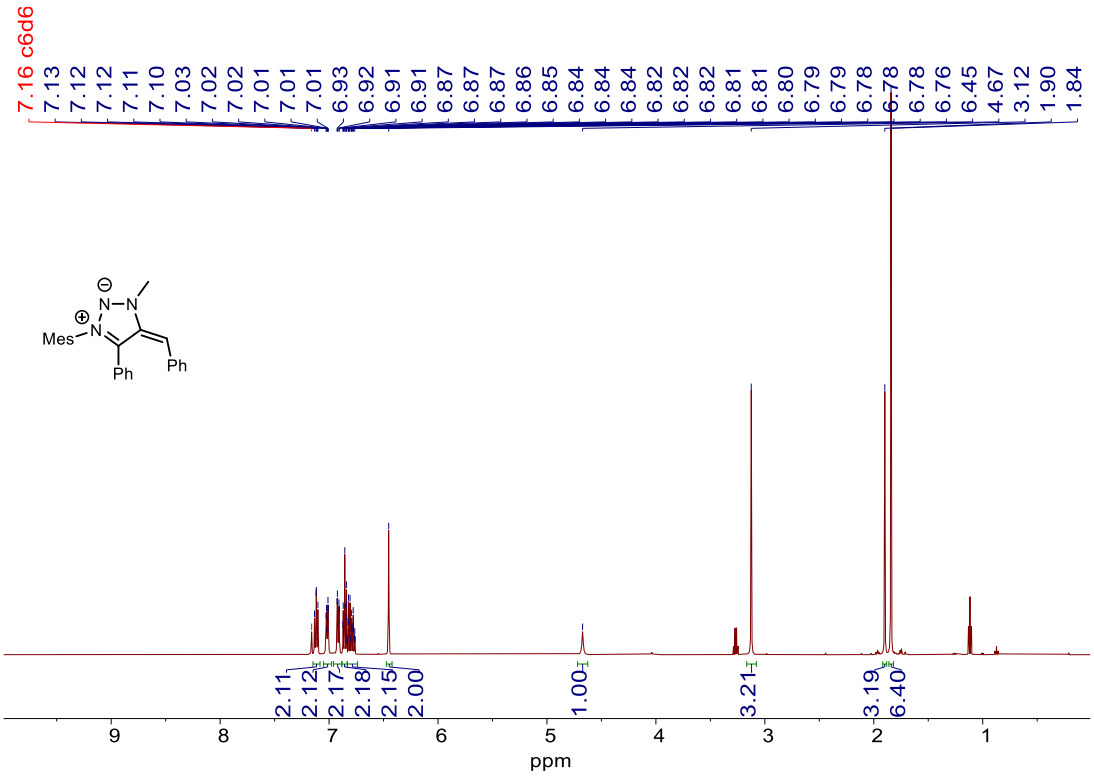


Figure S9. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of **1d**.

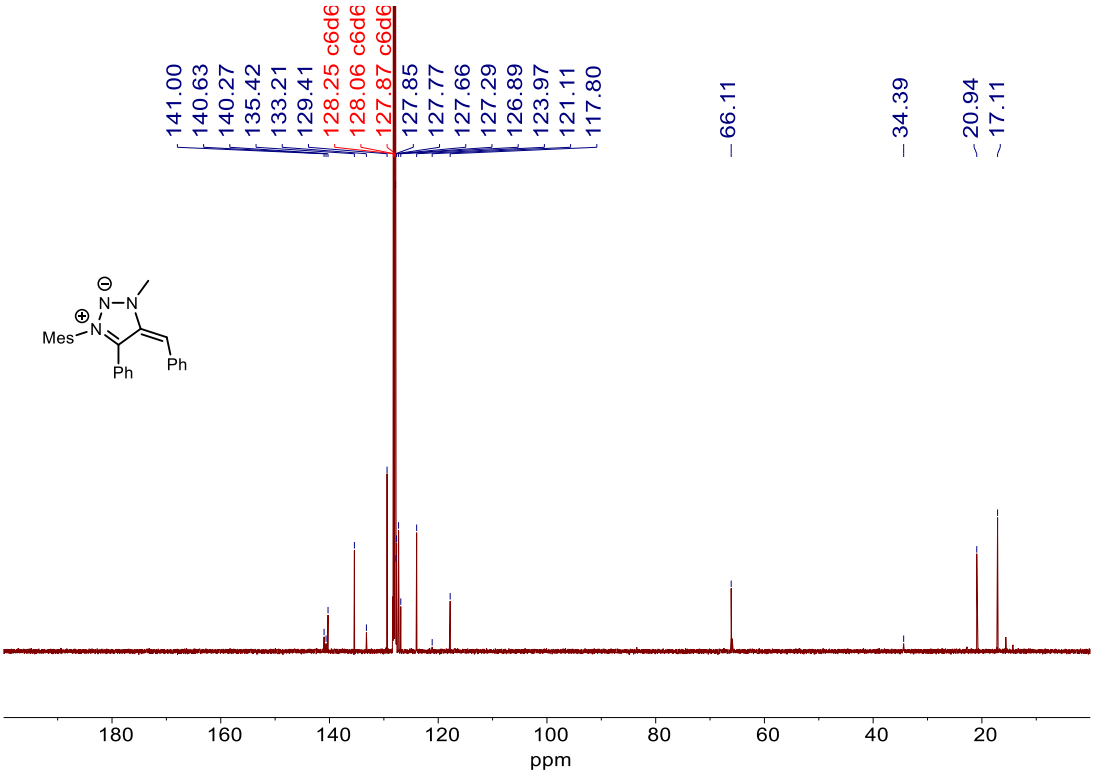


Figure S10. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of **1d**.

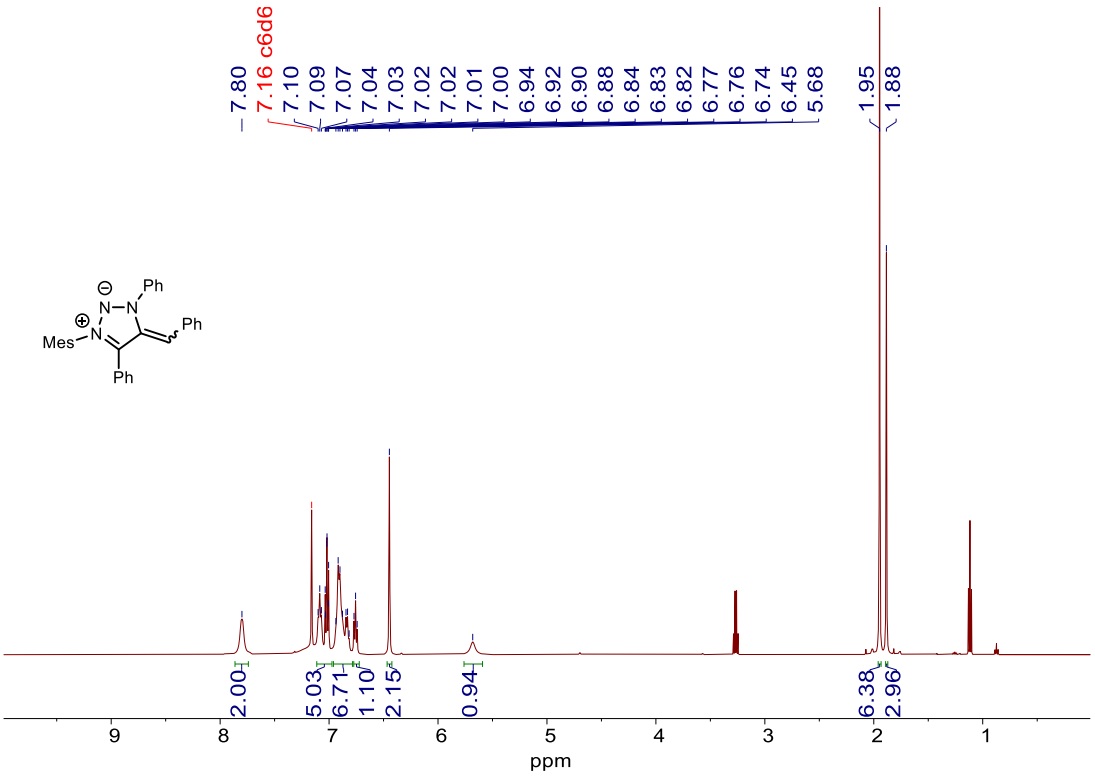


Figure S11. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of **1e**.

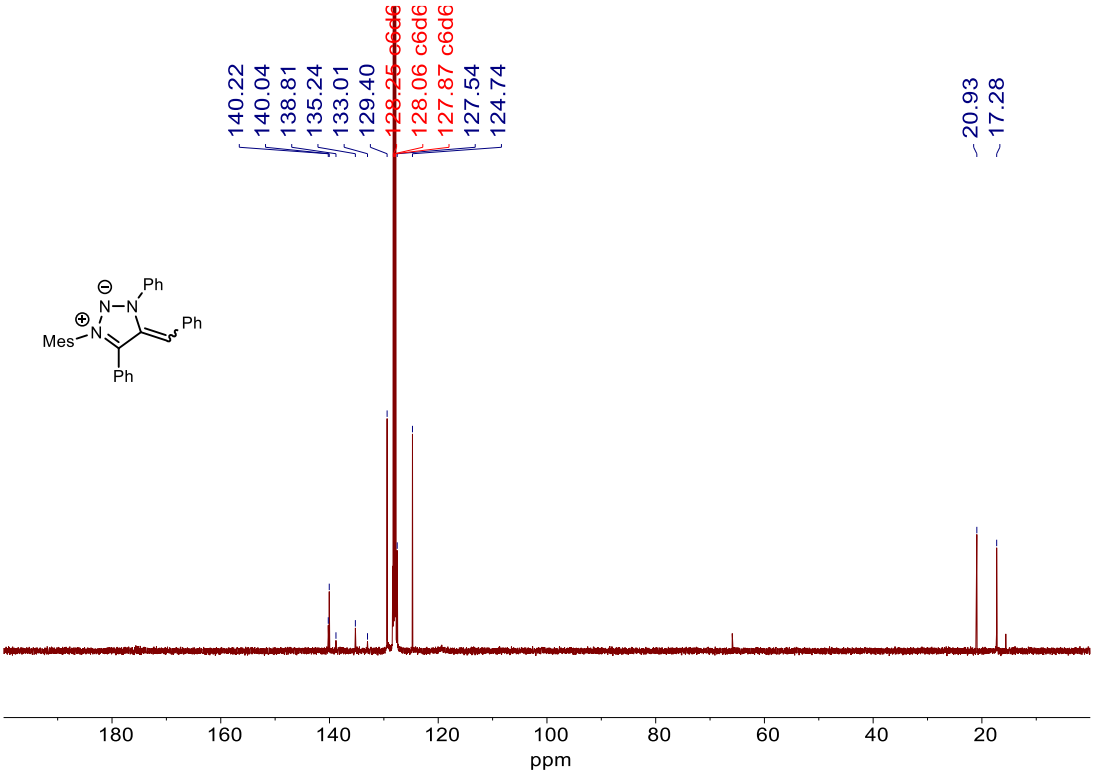


Figure S12. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of **1e**.

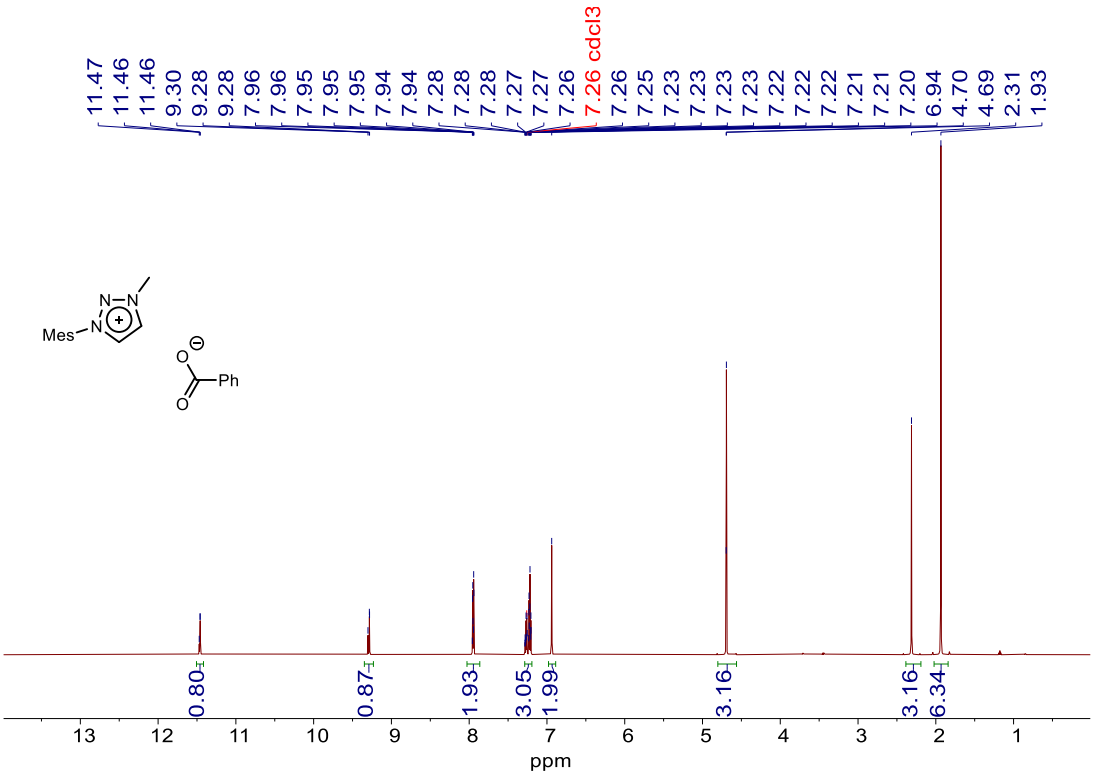


Figure S13. ^{1}H NMR (600 MHz, 25 °C, $CDCl_3$) spectrum of **2**.

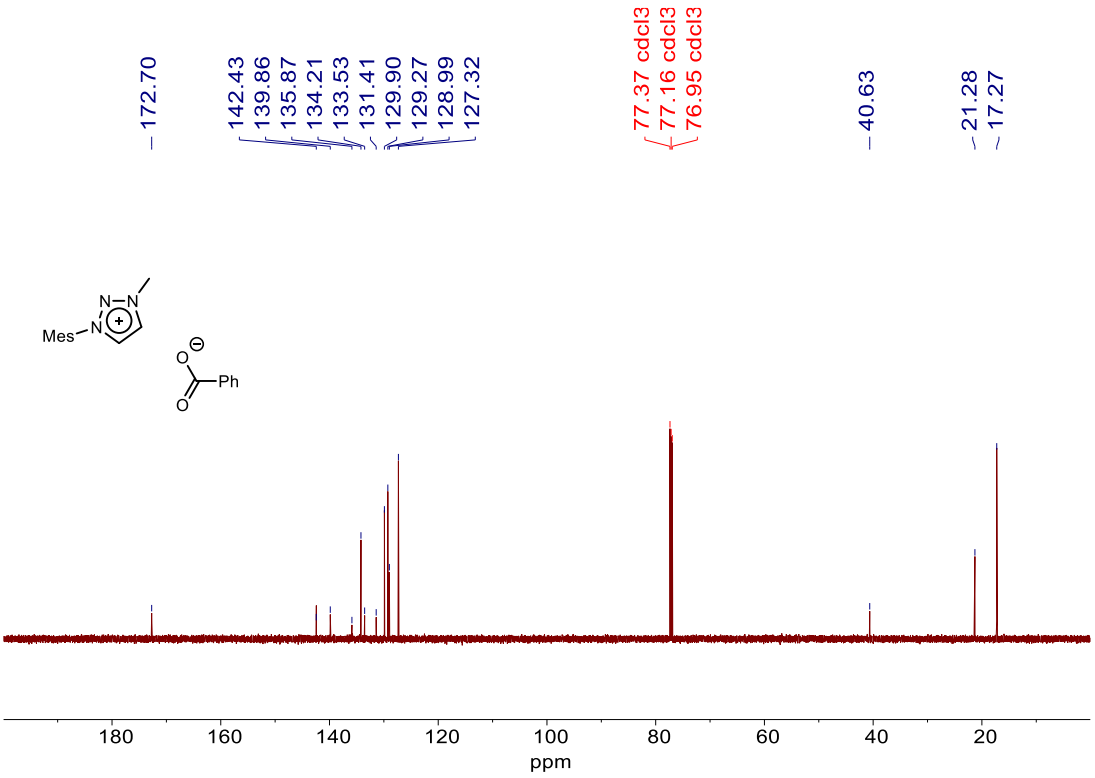


Figure S14. ^{13}C NMR (151 MHz, 25 °C, $CDCl_3$) spectrum of **2**.

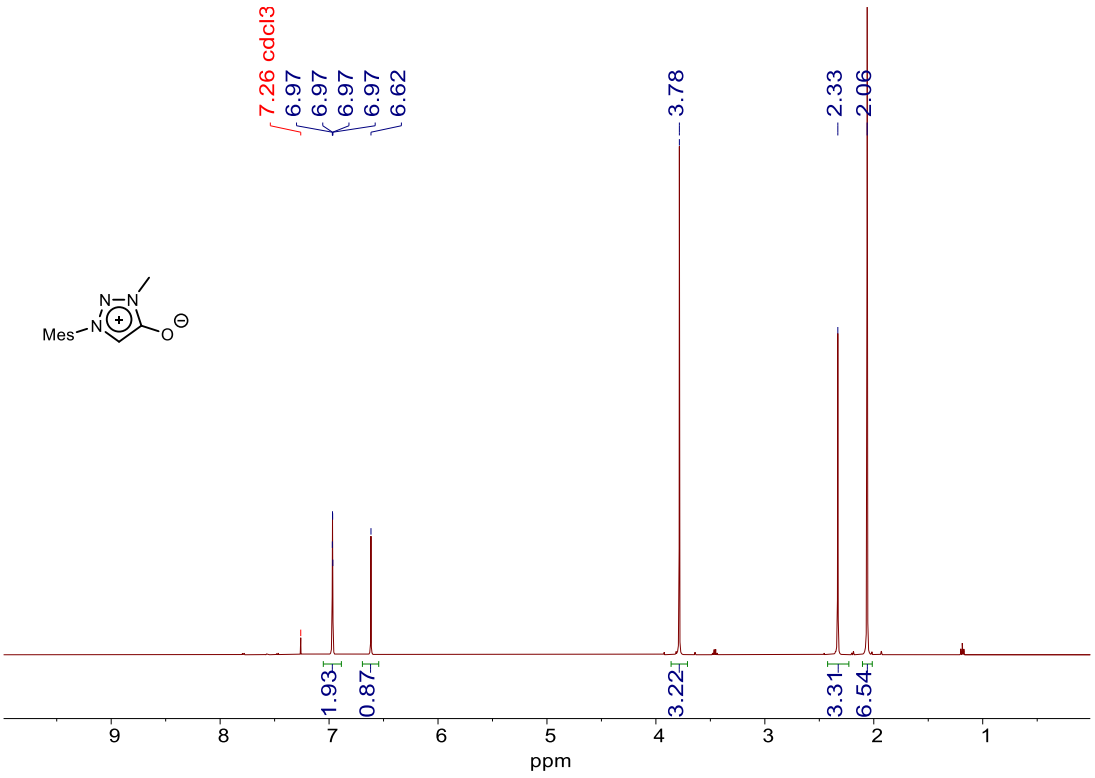


Figure S15. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of **3**.

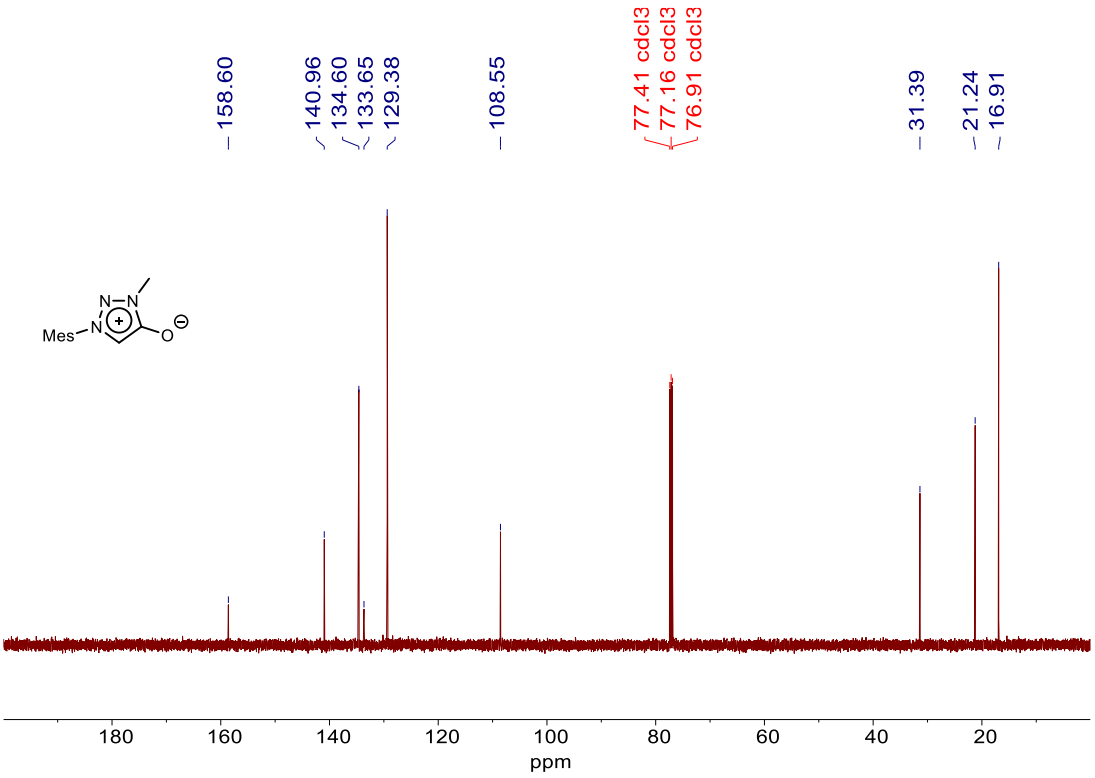


Figure S16. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of **3**.

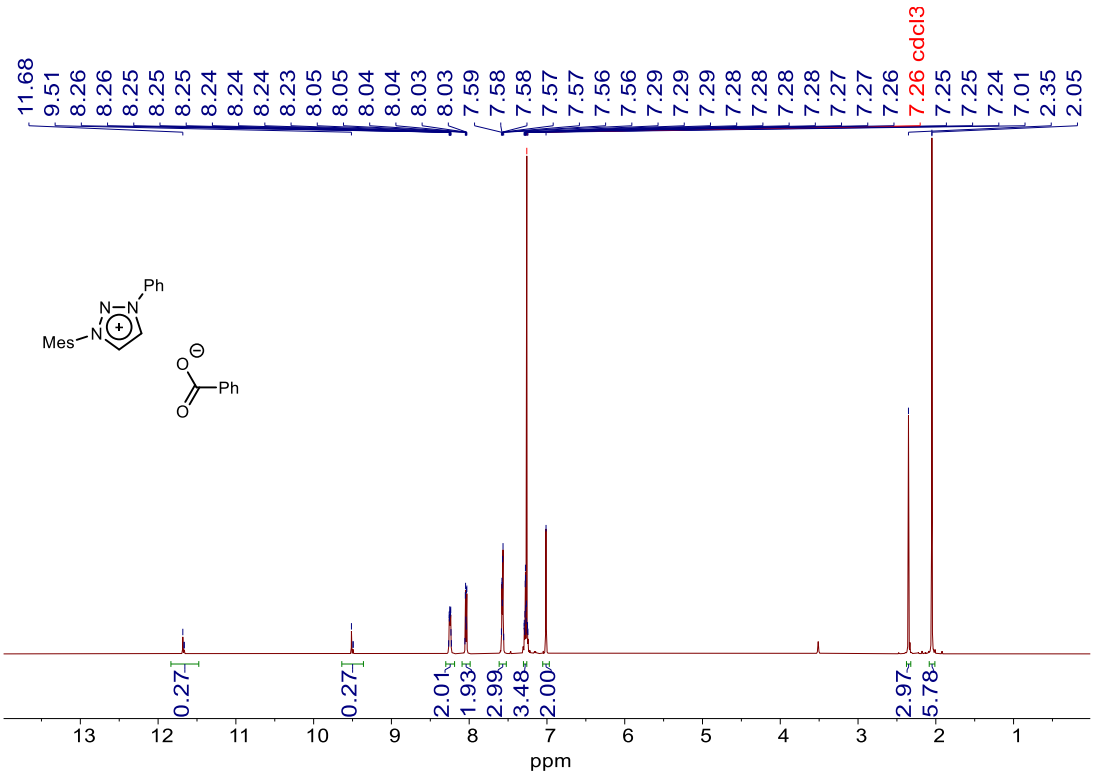


Figure S17. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of **4**.

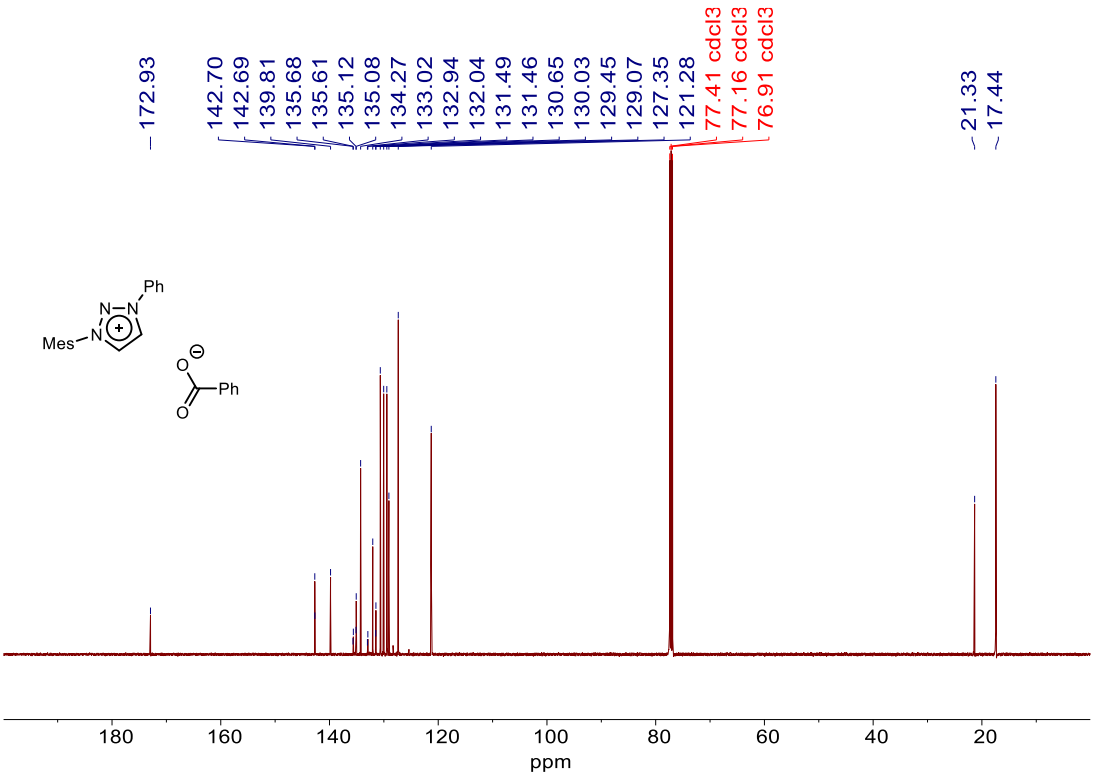


Figure S18. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of **4**.

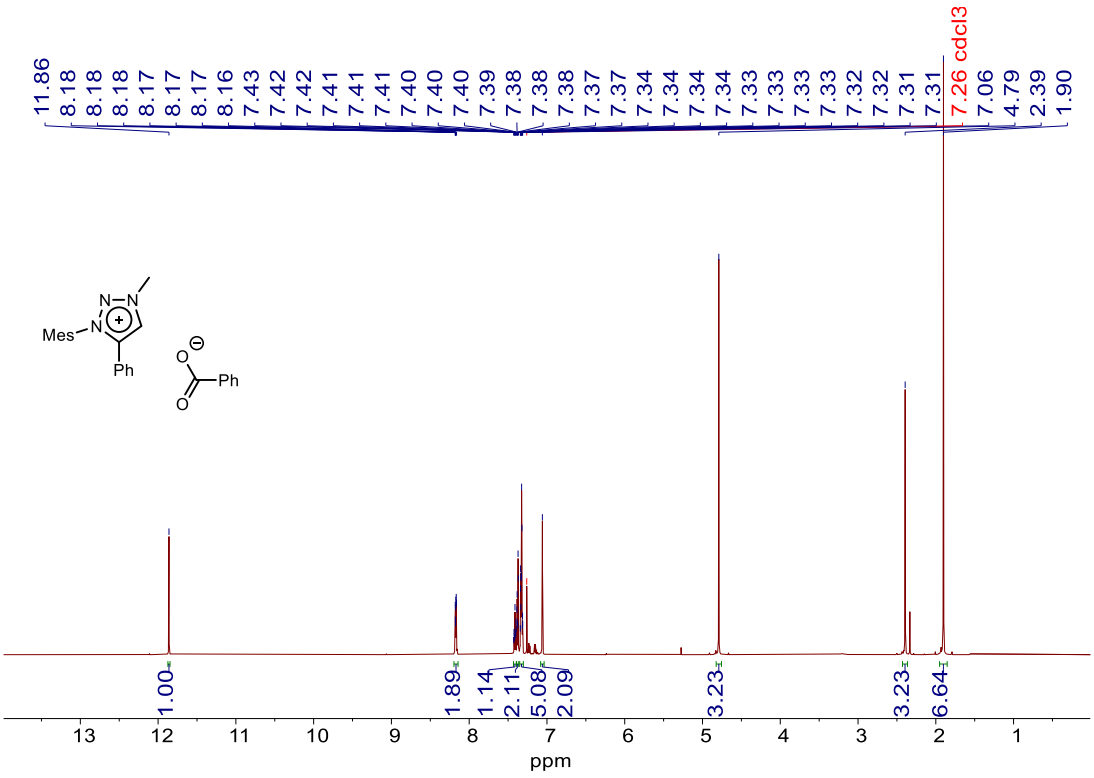


Figure S19. ^{1}H NMR (600 MHz, 25 °C, $CDCl_3$) spectrum of **5**.

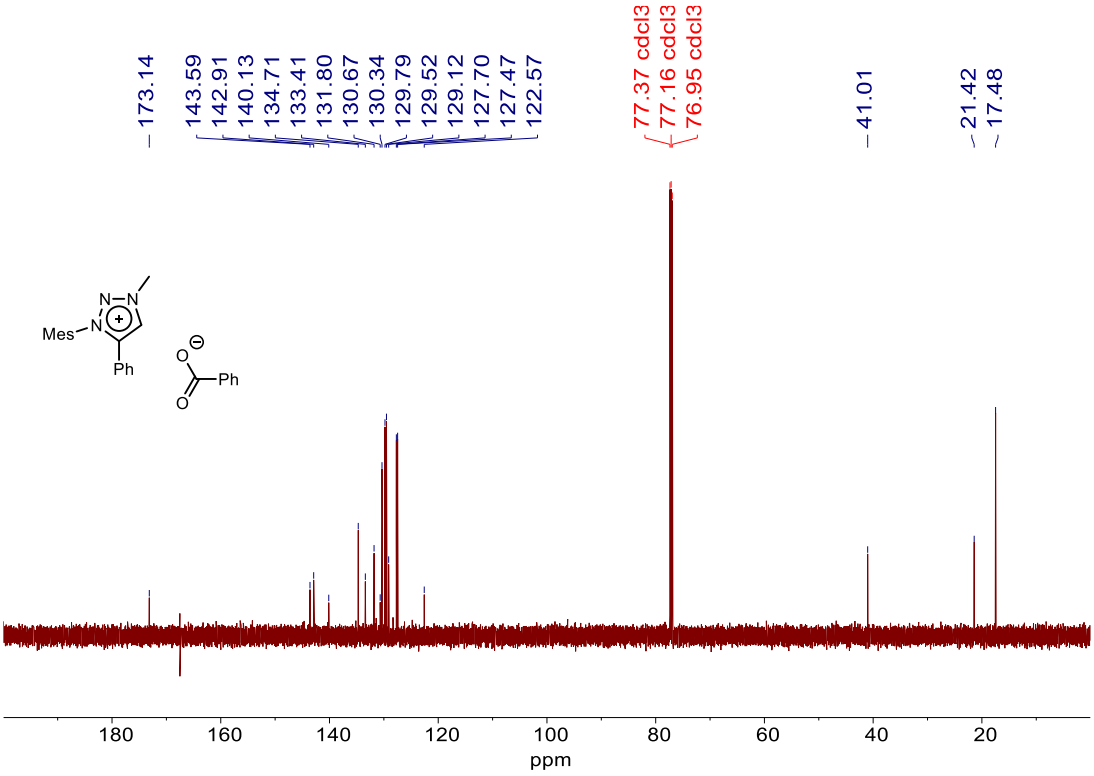


Figure S20. ^{13}C NMR (151 MHz, 25 °C, $CDCl_3$) spectrum of **5**.

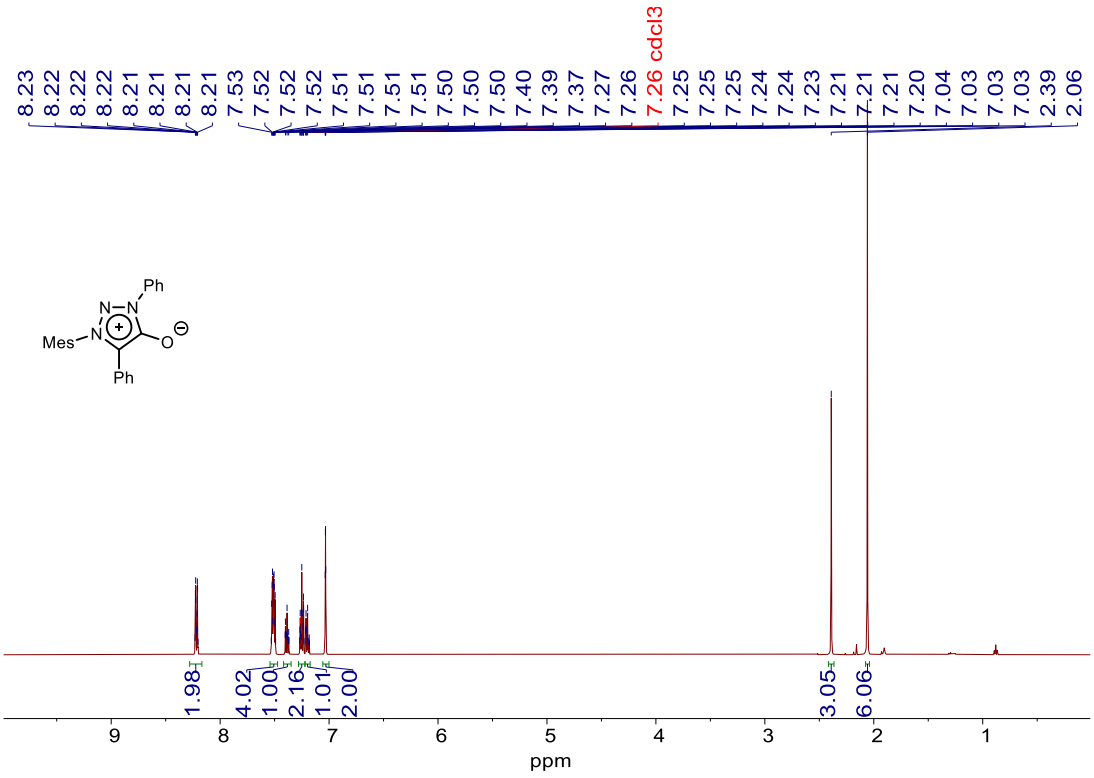


Figure S21. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) spectrum of **6**.

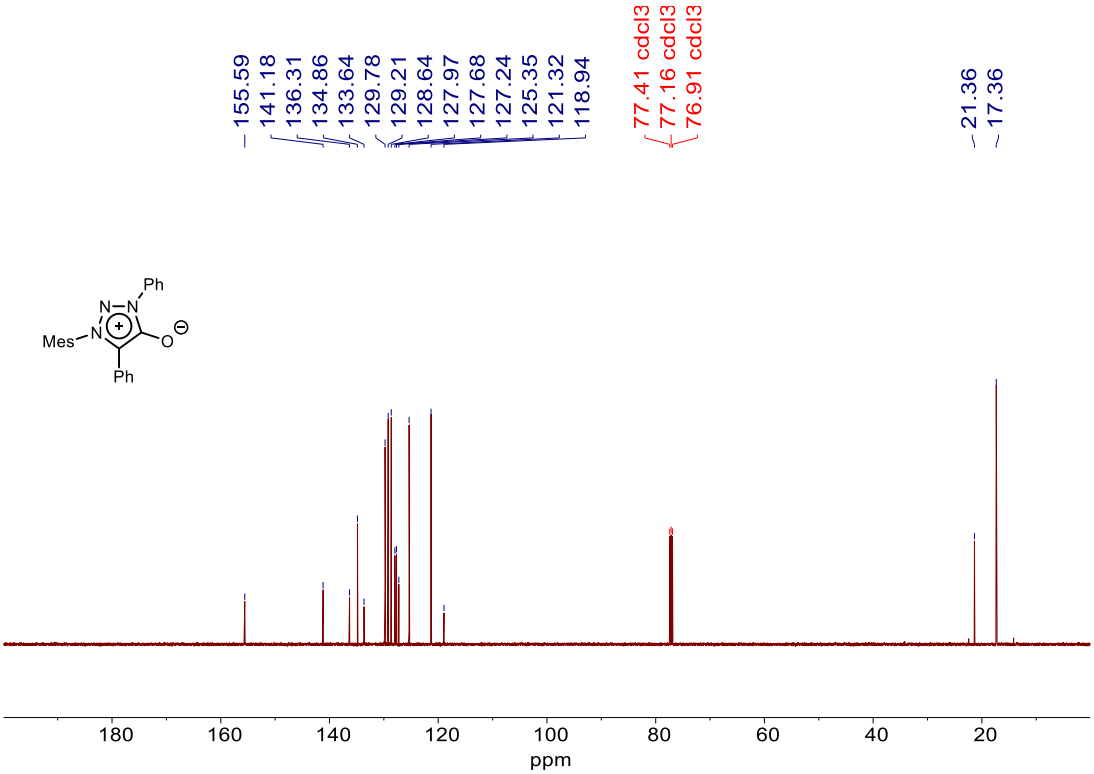


Figure S22. ^{13}C NMR (126 MHz, 25 °C, $CDCl_3$) spectrum of **6**.

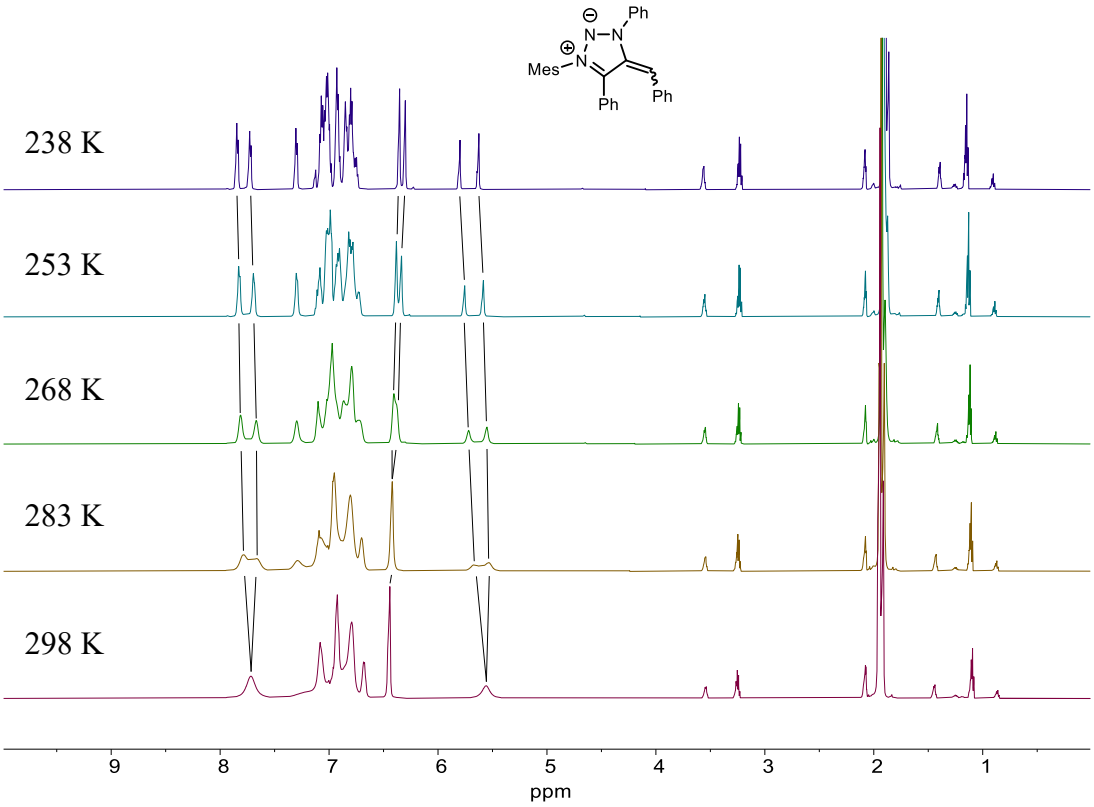


Figure S23. The ^{1}H NMR spectra (600 MHz, toluene-d_8) of compound **1e** at 298, 283, 268, 253 and 238 K.

3. IR spectra

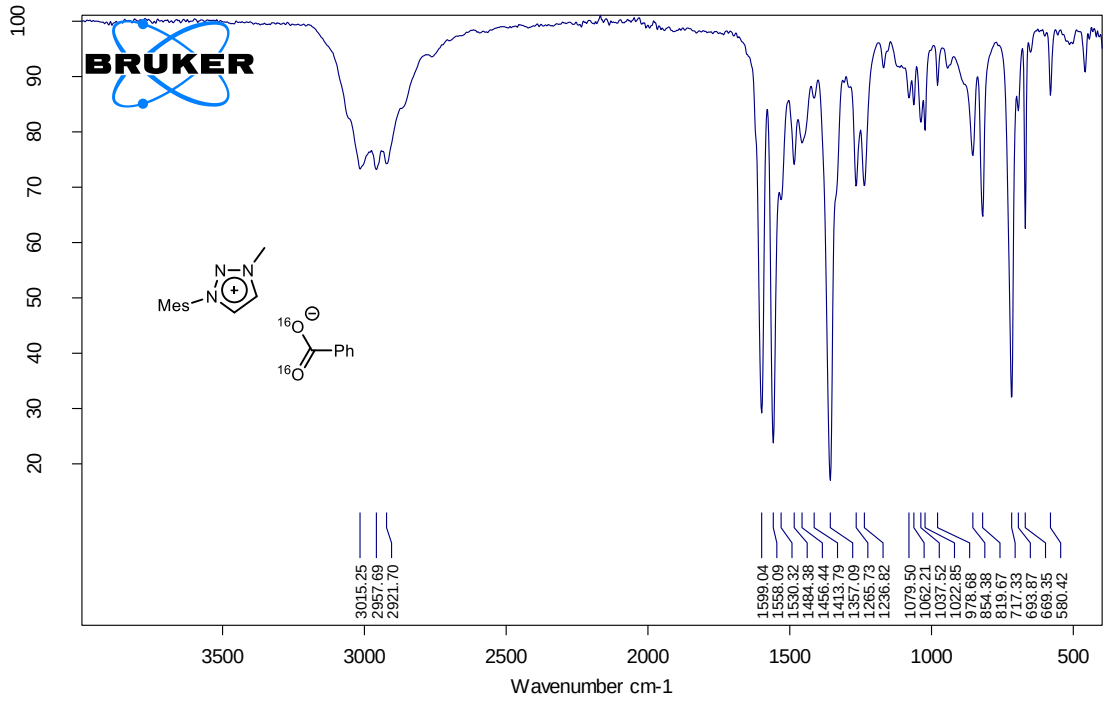


Figure S24. IR spectrum of **2-$^{16}O_2$**.

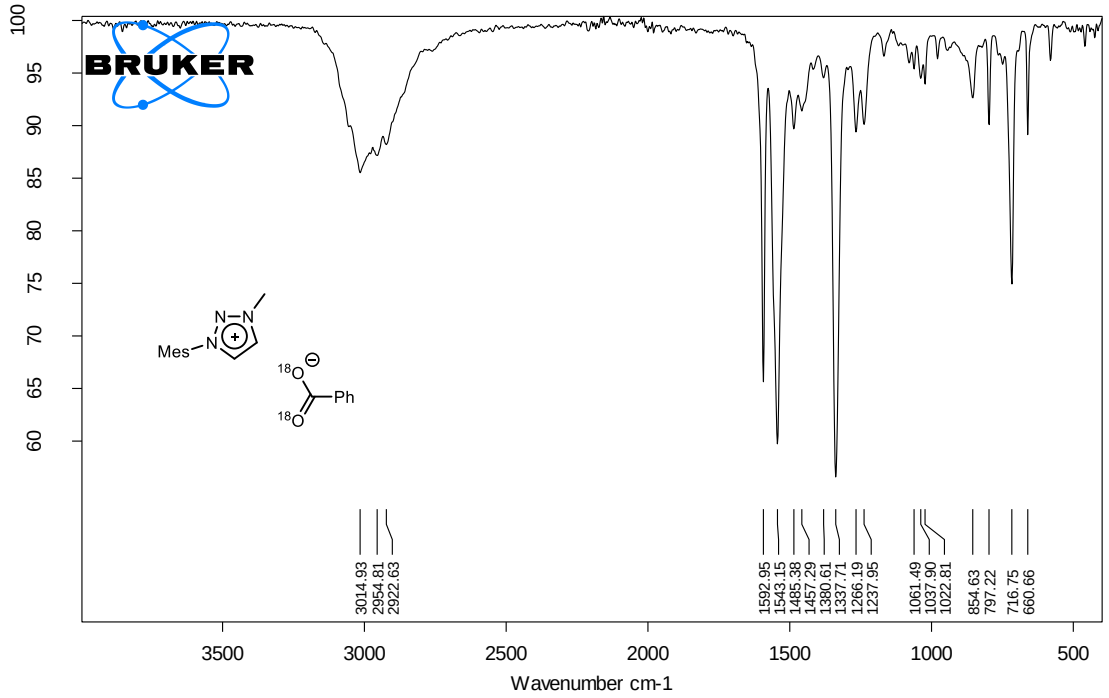
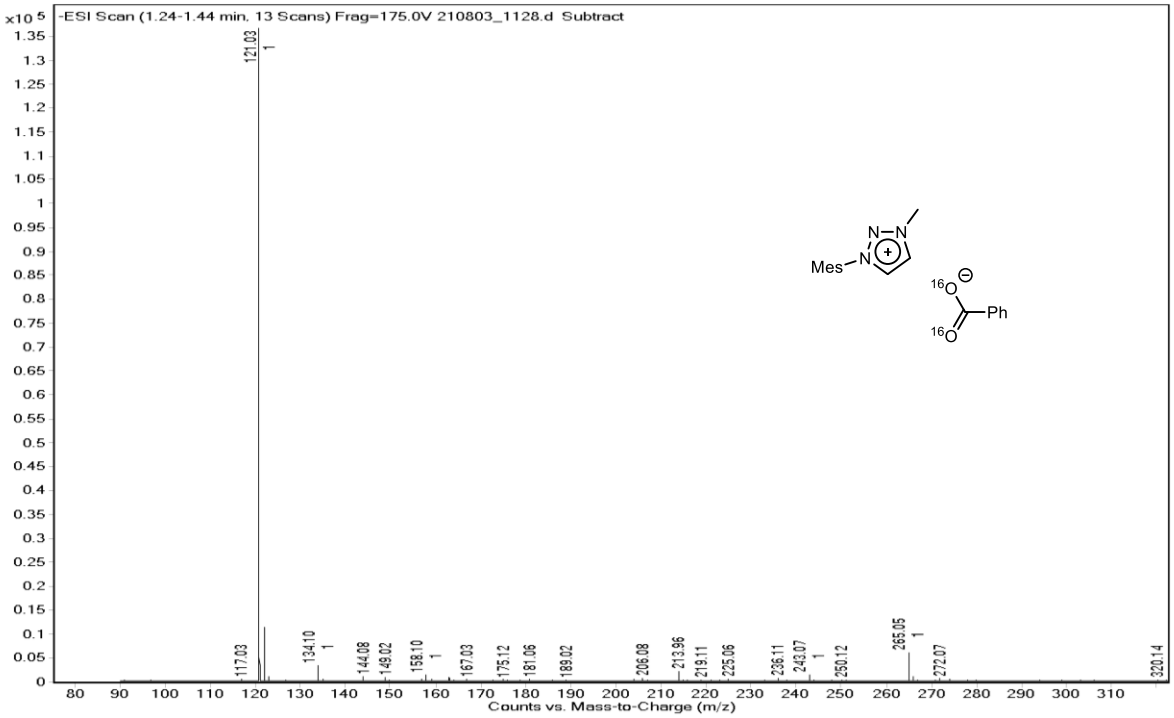


Figure S25. IR spectrum of **2-$^{18}O_2$**.

4. HRMS

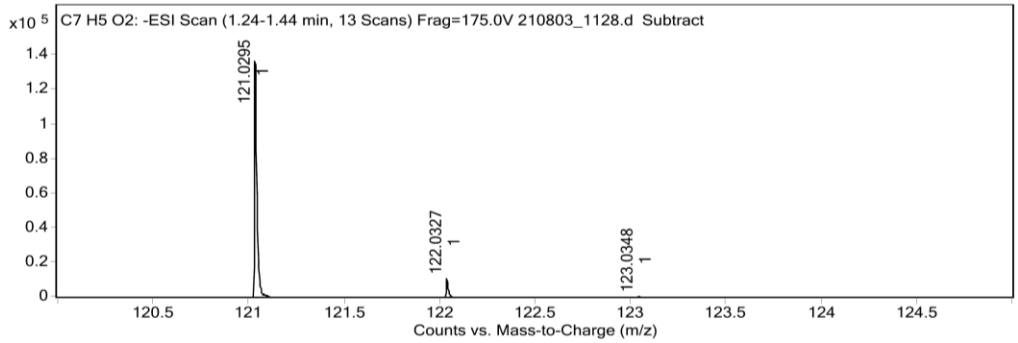


Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	121.0295	C7 H5 O2

MFG Calculator Results

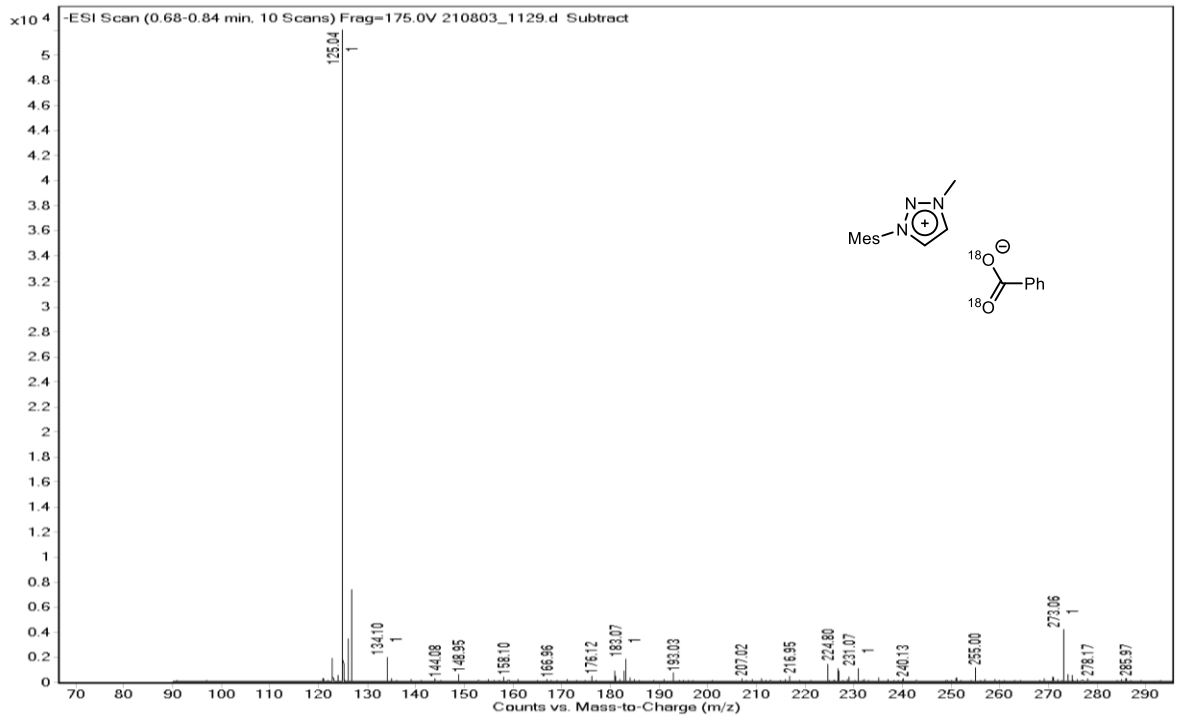
Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
121.0295	C7 H5 O2	121.0295	0.0	0.0	5.5	87.83



Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	121.0295	121.0295	0.0	100.0	100.0	0.0
2	122.0327	122.0329	-0.2	7.7	7.7	0.0

Figure S26. HRMS result of **2-$^{16}O_2$**.

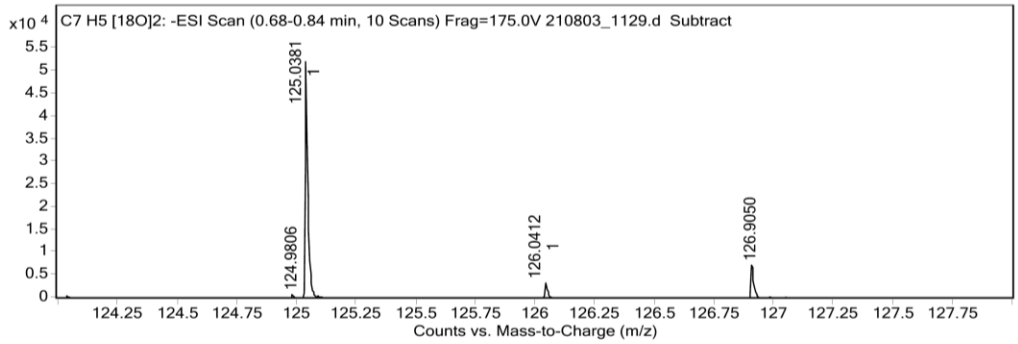


Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	125.0381	C7 H5 [18O]2

MFG Calculator Results

Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
125.0381	C7 H5 [18O]2	125.0380	0.1	0.8	5.5	87.81
125.0381	C10 H5	125.0397	-1.6	-12.8	8.5	69.82
125.0381	C5 H5 N2 O2	125.0357	2.4	19.2	4.5	59.95
125.0381	C4 H3 N4 [18O]	125.0355	2.6	20.8	5.5	54.81



Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	125.0381	125.0380	0.1	100.0	100.0	0.0
2	126.0412	126.0414	-0.2	7.2	7.6	0.4

Figure S27. HRMS result of **2-$^{18}O_2$**.

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 controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex 3 software package.[6] The structures were solved by direct methods and refined using SHELX-2016 software package.[7,8] All non-hydrogen atoms were refined anisotropically except for some of the atoms of the disordered BF_4^- in $C_{25}H_{26}N_3BF_4$. Selected crystallographic data are summarized in Tables S1−S2.

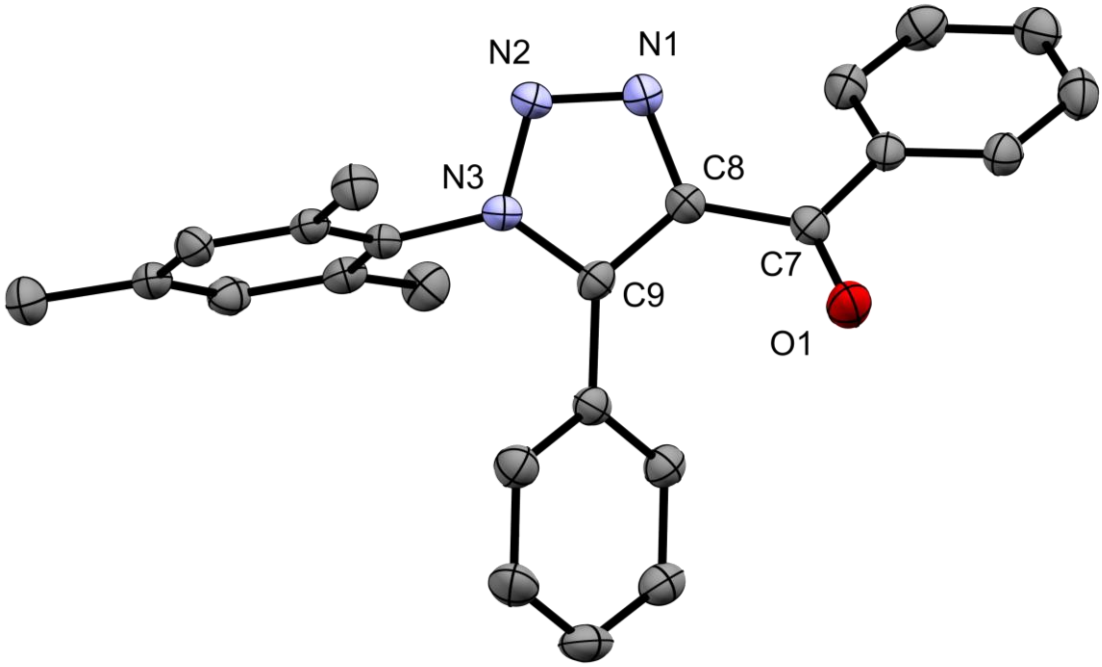


Figure S28. X-ray structure of **$C_{24}H_{21}N_3O$**. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are omitted for clarity.

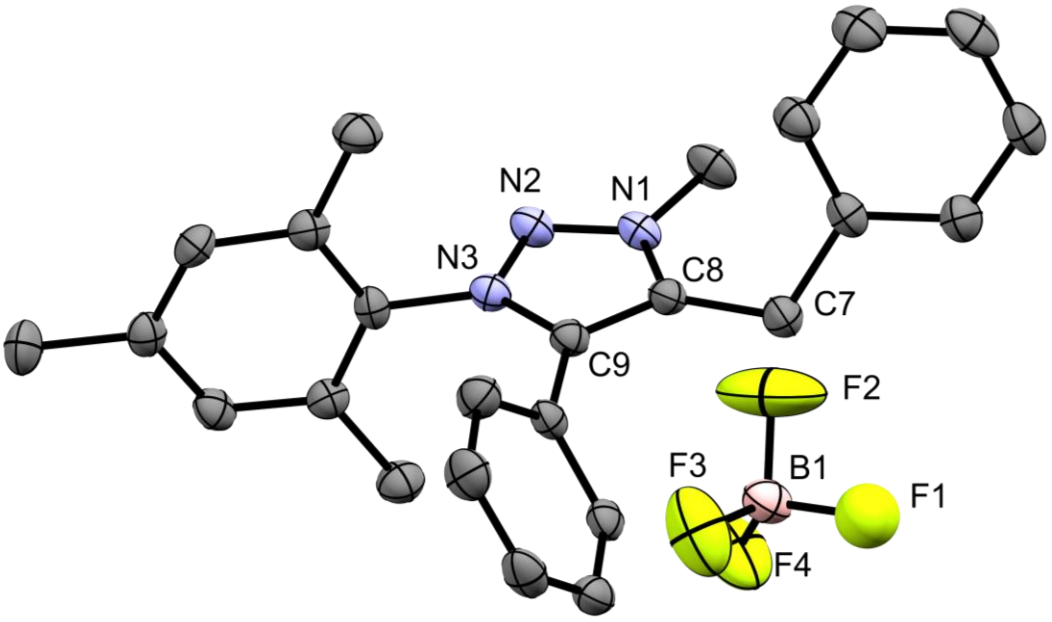


Figure S29. X-ray structure of $C_{25}H_{26}N_3BF_4$. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are omitted for clarity.

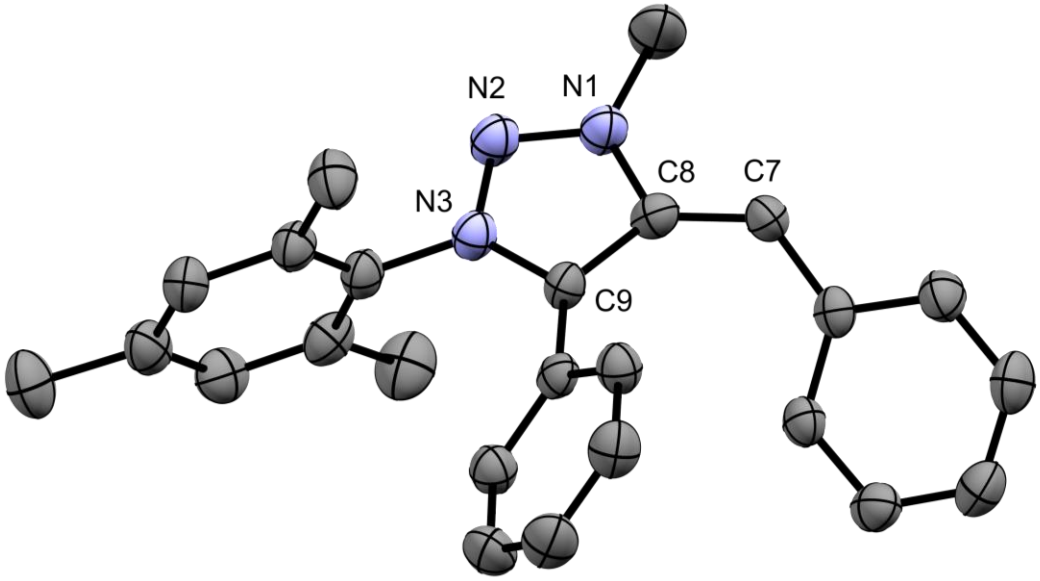


Figure S30. X-ray structure of **1d**. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are omitted for clarity.

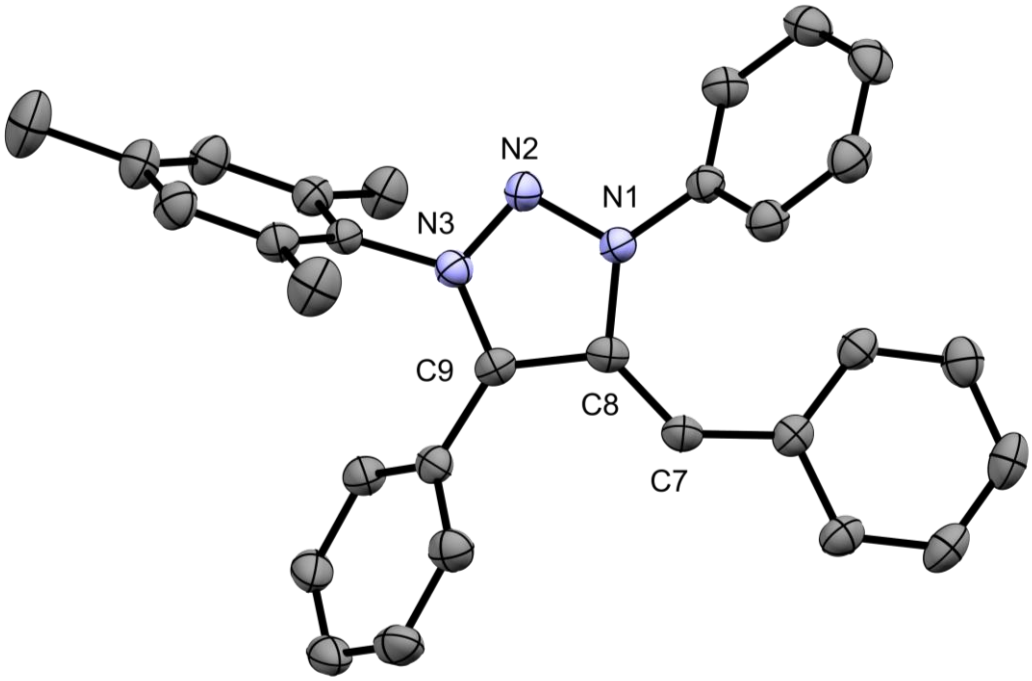


Figure S31. X-ray structure of **1e**. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are omitted for clarity.

Table S1. Selected crystallographic data for compounds **2**, **3**, **4•CH_2Cl_2**, **5**, and **6**.

	2	**3**	**4•CH_2Cl_2**	**5**	**6**
Empirical formula	$C_{19}H_{21}N_3O_2$	$C_{12}H_{15}N_3O$	$C_{25}H_{25}N_3O_2Cl_2$	$C_{25}H_{25}N_3O_2$	$C_{23}H_{21}N_3O$
FW ($g \cdot mol^{-1}$)	323.39	217.27	470.38	399.48	355.43
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	$P2_1/n$	P-1	$P2_1/n$	C2/c
Z	2	12	2	4	8
a (Å)	7.554(5)	10.765(4)	11.279(3)	16.149(5)	21.598(6)
b (Å)	7.800(5)	8.899(3)	11.539(4)	6.597(2)	10.343(3)
c (Å)	15.305(10)	37.044(15)	11.879(4)	21.350(7)	18.170(5)
α (deg)	96.293(19)	90	93.664(11)	90	90
β (deg)	90.202(18)	94.947(13)	116.197(9)	104.183(10)	109.301(7)
γ (deg)	99.553(18)	90	115.492(9)	90	90
V ($Å^3$)	883.7(10)	3536(2)	1189.0(7)	2205.3(12)	3830.7(17)
D_{calcd}, ($g \cdot cm^{-3}$)	1.215	1.225	1.314	1.203	1.233
μ (mm^{-1})	0.080	0.081	0.300	0.077	0.077
F(000)	344	1392	492	848	1504
no. of obsd reflns	2090	6287	4429	3396	3377
no. of params refnd	232	446	292	275	248
goodness of fit	1.006	1.027	1.048	1.031	1.032
R_1 ($I>2\sigma$)	0.0607	0.0582	0.0428	0.0599	0.0418
wR_2	0.1583	0.1529	0.1239	0.1734	0.1155

Table S2. Selected crystallographic data for compounds **$C_{24}H_{21}N_3O$**, **$C_{25}H_{26}N_3BF_4$**, **1d**, and **1e**.

	$C_{24}H_{21}N_3O$	**$C_{25}H_{26}N_3BF_4$**	**1d**	**1e**
Empirical formula	$C_{24}H_{21}N_3O$	$C_{25}H_{26}N_3BF_4$	$C_{25}H_{25}N_3$	$C_{30}H_{27}N_3$
FW ($g \cdot mol^{-1}$)	367.44	455.30	367.48	429.54
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space Group	Pbca	$P2_1/n$	Fdd2	$P2_1/c$
Z	8	4	16	4
a (Å)	19.077(7)	11.045(6)	25.226(9)	8.500(2)
b (Å)	8.652(3)	13.979(6)	45.845(16)	24.610(8)
c (Å)	23.320(8)	14.811(6)	7.020(3)	12.044(3)
α (deg)	90	90	90	90
β (deg)	90	93.520(13)	90	110.619(15)
γ (deg)	90	90	90	90
V ($Å^3$)	3849(2)	2282.4(18)	8119(5)	2358.1(12)
D_{calcd}, ($g \cdot cm^{-3}$)	1.268	1.325	1.203	1.210
μ (mm^{-1})	0.079	0.101	0.071	0.071
F(000)	1552	952	3136	912
no. of obsd reflns	3104	2849	3419	3265
no. of params refnd	257	301	262	306
goodness of fit	1.049	1.022	1.045	1.032
R_1 ($I>2\sigma$)	0.0610	0.0670	0.0447	0.0552
wR_2	0.1456	0.1823	0.0988	0.1372

6. Computation

All calculations were performed using Gaussian 16, Revision B.01[9] with M11L[10] functionals. The TZVP[11] basis set was used for all elements. Structures were optimized with PCM solvent correction (solvent = toluene). 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 for O_2 reaction

1a + O_2

M11L/TZVP (solvent = toluene)

G = -1050.961241 Hartree

N	-0.815354000	-1.493231000	-1.112512000
N	0.492410000	-1.590993000	-1.231438000
C	4.808964000	0.265205000	-0.142004000
C	3.426707000	0.506349000	-0.190350000
N	-0.968643000	-0.395375000	-0.446718000
C	1.203571000	-0.560574000	-0.663877000
C	-2.278948000	0.060508000	-0.146774000
C	-4.798102000	0.974225000	0.434500000
C	2.577882000	-0.517015000	-0.684122000
C	0.171870000	0.220506000	-0.130408000
C	-4.119538000	0.161447000	1.323675000
C	-4.184934000	1.309847000	-0.758629000
C	-2.917183000	0.864256000	-1.075377000
C	3.004078000	1.770949000	0.243295000
C	5.251773000	2.438060000	0.757831000
C	-2.849555000	-0.311844000	1.057688000
C	5.694973000	1.202902000	0.320049000
C	-6.148082000	1.496440000	0.765006000
C	3.899617000	2.707015000	0.705119000
C	1.043047000	-2.715594000	-1.888701000
C	-2.134861000	-1.193388000	2.012218000
C	-2.272294000	1.213546000	-2.364990000
H	-4.712336000	1.941467000	-1.474796000
H	3.076246000	-1.387343000	-1.104117000
H	6.759005000	0.966991000	0.343747000
H	0.223173000	-3.338951000	-2.247109000
H	5.174395000	-0.706515000	-0.477927000
H	-4.596252000	-0.120672000	2.263486000
H	1.669746000	-3.291410000	-1.195325000
H	5.952960000	3.182972000	1.127940000
H	-2.754045000	-1.394857000	2.889746000
H	-2.133269000	0.326898000	-2.995318000
H	-2.881497000	1.929438000	-2.922127000
H	1.955408000	2.050499000	0.181211000
H	-1.868996000	-2.153047000	1.553332000
H	-6.691667000	0.817698000	1.429266000
H	-6.750842000	1.655659000	-0.134408000
H	1.663499000	-2.394148000	-2.734551000
H	0.161744000	1.124073000	0.456055000
H	-1.192882000	-0.749113000	2.355492000
H	-6.079646000	2.463110000	1.280092000
H	-1.278493000	1.653714000	-2.219677000
H	3.528572000	3.680128000	1.028073000
O	2.067737000	-2.591621000	1.449178000
O	0.875062000	-2.565434000	1.636660000

Int 1

M11L/TZVP (solvent = toluene)

G = -1050.964938 Hartree

N	-4.632529000	1.759696000	-2.771780000
N	-3.828441000	2.322501000	-3.647950000
N	-4.584349000	3.261723000	-4.169217000
C	-2.818023000	-2.418075000	0.555198000
H	-2.174977000	-2.052974000	1.362231000
H	-2.271043000	-3.184461000	-0.002071000
H	-3.674671000	-2.912934000	1.030141000
C	-3.266073000	-1.312846000	-0.328966000
C	-3.525505000	-0.057374000	0.189933000
H	-3.367503000	0.127415000	1.253352000
C	-3.973067000	0.981215000	-0.601235000
C	-4.151801000	0.713958000	-1.949738000
C	-5.840253000	2.325571000	-2.719136000
H	-6.625033000	2.058916000	-2.027098000
C	-5.808147000	3.324159000	-3.646270000
C	-6.911148000	4.261788000	-4.001033000
H	-6.519571000	5.300215000	-3.890895000
C	-7.393392000	4.059991000	-5.410529000
C	-7.743378000	2.797909000	-5.857676000
H	-7.649303000	1.946868000	-5.181121000
C	-8.224390000	2.620264000	-7.136094000
H	-8.504269000	1.625102000	-7.478983000
C	-8.352778000	3.703197000	-7.982232000
H	-8.730914000	3.562326000	-8.993782000
C	-3.456578000	-1.523750000	-1.681781000
H	-3.255363000	-2.509017000	-2.104732000
C	-3.904126000	-0.522104000	-2.520378000
C	-4.225451000	2.330628000	-0.037575000
H	-3.706703000	3.110876000	-0.607560000

H	-3.880696000	2.383105000	0.998095000
H	-5.289003000	2.602261000	-0.049250000
C	-7.531902000	5.139628000	-6.260840000
H	-7.268109000	6.135553000	-5.901802000
C	-8.006841000	4.963595000	-7.543535000
H	-8.113979000	5.820964000	-8.206389000
C	-4.035114000	4.094086000	-5.190468000
H	-2.968184000	3.881962000	-5.262462000
H	-4.188640000	5.144723000	-4.928145000
H	-4.525292000	3.888490000	-6.147514000
C	-4.109571000	-0.765503000	-3.969043000
H	-5.048303000	-0.327143000	-4.328275000
H	-4.132618000	-1.837694000	-4.180454000
H	-3.306503000	-0.322276000	-4.569691000
O	-7.914703000	4.029447000	-3.111083000
O	-7.305478000	4.281707000	-1.843483000

TS1

M11L/TZVP (solvent = toluene)

G = -1050.956399 Hartree

Imaginary Frequency -1362.0147

N	-4.767714000	1.642491000	-2.441104000
N	-4.506147000	1.679018000	-3.733407000
N	-5.299041000	2.605452000	-4.202220000
C	-1.765136000	-1.746768000	0.926719000
H	-1.008011000	-1.195518000	1.492864000
H	-1.233535000	-2.498662000	0.329669000
H	-2.398572000	-2.289375000	1.635022000
C	-2.562255000	-0.845302000	0.057203000
C	-2.000287000	0.301447000	-0.473500000
H	-0.969834000	0.558912000	-0.224014000
C	-2.708074000	1.139880000	-1.311143000
C	-4.017994000	0.791483000	-1.598591000
C	-5.712189000	2.513672000	-2.091697000
H	-5.173090000	4.458194000	-5.203113000
C	-6.064417000	3.166397000	-3.232132000
C	-7.086800000	4.241823000	-3.423874000
H	-8.081052000	3.764387000	-3.530354000
C	-7.145881000	5.130900000	-2.209915000
C	-5.999670000	5.704077000	-1.685997000
H	-5.039558000	5.485646000	-2.152264000
C	-6.084119000	6.562340000	-0.611967000
H	-5.180269000	7.020118000	-0.211980000
C	-7.309182000	6.846092000	-0.042926000
H	-7.371207000	7.521389000	0.809367000
C	-3.873391000	-1.148459000	-0.259492000
H	-4.329251000	-2.050617000	0.150899000
C	-4.626566000	-0.344100000	-1.091318000
C	-2.094216000	2.365327000	-1.877257000
H	-1.849803000	2.236722000	-2.938209000
H	-1.171368000	2.616729000	-1.348310000
H	-2.768941000	3.228043000	-1.816890000
C	-8.368694000	5.423003000	-1.637498000
H	-9.273058000	4.976766000	-2.054914000
C	-8.453295000	6.273873000	-0.555790000
H	-9.422228000	6.492780000	-0.109367000
C	-5.149823000	3.092148000	-5.510501000
H	-6.088377000	2.959985000	-6.059660000
H	-4.330428000	2.545816000	-5.982183000
C	-6.030722000	-0.686823000	-1.428490000
H	-6.748077000	-0.037798000	-0.910408000
H	-6.256029000	-1.716346000	-1.138597000
H	-6.229338000	-0.583167000	-2.501300000
O	-6.934916000	4.918860000	-4.615145000
O	-5.602202000	5.406175000	-4.659305000
H	-6.034408000	2.640871000	-1.067810000

Int 2

M11L/TZVP (solvent = toluene)

G = -1050.963013 Hartree

N	-4.769319000	1.561353000	-2.213413000
N	-4.349389000	1.973753000	-3.424915000
N	-5.282184000	2.831495000	-3.808639000
C	-1.567346000	-2.049263000	0.717149000
H	-0.776700000	-2.464945000	0.079473000
H	-2.148946000	-2.891381000	1.104150000
H	-1.067403000	-1.561842000	1.561075000
C	-2.420132000	-1.096149000	-0.037813000
C	-1.978745000	0.188572000	-0.301448000
H	-1.006564000	0.509209000	0.077264000
C	-2.735730000	1.088652000	-1.022073000
C	-3.976763000	0.665554000	-1.481710000
C	-5.943885000	2.081705000	-1.880056000
H	-7.579210000	5.471360000	-0.899638000
C	-6.303679000	2.901530000	-2.895100000
C	-7.411104000	3.859086000	-3.049825000
H	-6.972190000	4.840986000	-3.337790000
C	-8.435109000	3.480200000	-4.082672000
C	-8.773377000	2.158525000	-4.298626000
H	-8.255861000	1.377223000	-3.740403000
C	-9.748535000	1.833972000	-5.216417000
H	-10.009795000	0.790374000	-5.384831000
C	-10.387423000	2.828599000	-5.926063000
H	-11.152789000	2.570543000	-6.656551000
C	-3.659649000	-1.475244000	-0.513596000
H	-4.020412000	-2.487298000	-0.322389000
C	-4.454474000	-0.615111000	-1.247754000
C	-2.249708000	2.466273000	-1.275360000
H	-1.928852000	2.594628000	-2.315162000
H	-1.403153000	2.701866000	-0.624354000
H	-3.037098000	3.209823000	-1.104344000
C	-9.080001000	4.473246000	-4.795841000
H	-8.803359000	5.515301000	-4.628133000
C	-10.051672000	4.150321000	-5.716163000
H	-10.550312000	4.936904000	-6.280303000
C	-5.179061000	3.570641000	-4.920077000
H	-6.123616000	3.855969000	-5.366633000
H	-4.347819000	3.304133000	-5.560319000
C	-5.769956000	-1.060623000	-1.773231000
H	-6.605832000	-0.703912000	-1.157497000
H	-5.826974000	-2.152721000	-1.790508000
H	-5.946194000	-0.690547000	-2.789872000
O	-8.136240000	3.988074000	-1.857132000

O	-7.266031000	4.564404000	-0.896849000
H	-6.424710000	1.882544000	-0.932989000

TS2
M11L/TZVP (solvent = toluene)
G = -1050.935981 Hartree
Imaginary Frequency -1969.6414

N	-4.750541000	1.378354000	-2.059563000
N	-4.527779000	1.740875000	-3.310233000
N	-5.541365000	2.514572000	-3.581351000
C	-1.075390000	-2.005456000	0.567870000
H	-0.927245000	-1.688449000	1.607115000
H	-0.090013000	-1.980597000	0.088886000
H	-1.417979000	-3.043927000	0.582238000
C	-2.041722000	-1.121535000	-0.131803000
C	-1.748516000	0.215771000	-0.336821000
H	-0.797922000	0.617608000	0.017260000
C	-2.626637000	1.064294000	-0.977294000
C	-3.829203000	0.525979000	-1.410041000
C	-5.889287000	1.869631000	-1.560649000
H	-9.081054000	4.023043000	-0.856105000
C	-6.427089000	2.630967000	-2.554087000
C	-7.382691000	3.712600000	-2.750158000
H	-6.590900000	4.155949000	-3.782581000
C	-8.678218000	3.395498000	-3.383309000
C	-9.698747000	4.339202000	-3.352981000
H	-9.524621000	5.288198000	-2.844389000
C	-10.906457000	4.092516000	-3.965729000
H	-11.694975000	4.843408000	-3.921633000
C	-11.118309000	2.910192000	-4.645499000
H	-12.071548000	2.718977000	-5.134877000
C	-3.249994000	-1.610935000	-0.587295000
H	-3.489505000	-2.665335000	-0.442847000
C	-4.167148000	-0.804185000	-1.234280000
C	-2.299540000	2.493970000	-1.196913000
H	-2.087897000	2.698550000	-2.253069000
H	-1.420253000	2.783093000	-0.615767000
H	-3.128856000	3.152068000	-0.911813000
C	-8.906002000	2.208875000	-4.065102000
H	-8.126871000	1.444477000	-4.090141000
C	-10.107614000	1.973129000	-4.696019000
H	-10.262354000	1.033248000	-5.225228000
C	-5.685907000	3.399105000	-4.653776000
H	-6.399858000	3.018254000	-5.392888000
H	-4.715495000	3.613472000	-5.108427000
C	-5.456580000	-1.349438000	-1.727246000
H	-6.300976000	-1.038776000	-1.099334000
H	-5.437066000	-2.442377000	-1.728894000
H	-5.680129000	-1.011074000	-2.745650000
O	-7.459089000	4.564085000	-1.704230000
O	-8.171505000	3.900920000	-0.570281000
H	-6.208321000	1.673164000	-0.547650000

Int3
M11L/TZVP (solvent = toluene)
G = -975.114590 Hartree

N	-4.390082000	1.779427000	-3.235979000
N	-4.296702000	2.441342000	-2.116946000
N	-5.200352000	3.360305000	-2.204465000
C	-1.042581000	-2.637970000	-4.279907000
H	-0.886553000	-3.256599000	-3.391435000
H	-0.066411000	-2.333455000	-4.667318000
H	-1.505517000	-3.279921000	-5.039642000
C	-1.904692000	-1.467740000	-3.986368000
C	-2.908465000	-1.553404000	-3.038154000
H	-3.047216000	-2.483869000	-2.486975000
C	-3.745150000	-0.492684000	-2.759967000
C	-3.533702000	0.669940000	-3.482088000
C	-5.348833000	2.257540000	-4.031340000
C	-5.899234000	3.307334000	-3.356545000
C	-6.891949000	4.355027000	-3.741727000
C	-7.926598000	3.991695000	-4.708653000
C	-8.535351000	5.023573000	-5.411791000
H	-8.201268000	6.045267000	-5.238546000
C	-9.529596000	4.742899000	-6.314576000
H	-9.997385000	5.548328000	-6.876894000
C	-9.938097000	3.436485000	-6.507059000
H	-10.731981000	3.216528000	-7.219093000
C	-1.735117000	-0.276336000	-4.668722000
H	-0.936067000	-0.188225000	-5.405236000
C	-2.542631000	0.817824000	-4.437647000
C	-4.808768000	-0.601491000	-1.731780000
H	-4.530472000	-0.080552000	-0.807823000
H	-4.989553000	-1.648242000	-1.476684000
H	-5.760024000	-0.172157000	-2.068077000
C	-8.344850000	2.682085000	-4.901830000
H	-7.917183000	1.871433000	-4.312964000
C	-9.354813000	2.409225000	-5.794281000
H	-9.696566000	1.385721000	-5.932889000
C	-5.347105000	4.270047000	-1.101874000
H	-4.738273000	3.883964000	-0.284344000
H	-6.397674000	4.320999000	-0.809803000
H	-5.013181000	5.264500000	-1.402699000
C	-2.336533000	2.095455000	-5.164194000
H	-3.125102000	2.285642000	-5.903344000
H	-1.388327000	2.077868000	-5.706222000
H	-2.316023000	2.956312000	-4.485631000
O	-6.766500000	5.444786000	-3.266029000
H	-5.556996000	1.833623000	-5.004377000

OH^- M11L/TZVP (solvent = toluene)
-75.863277 Hartree

O	-0.788783000	1.554898000	-2.500697000
H	-1.599991000	1.045401000	-2.501313000

Int4
M11L/TZVP (solvent = toluene)
G = -1051.090481 Hartree

N	-5.344236000	2.595509000	-5.203937000
N	-4.494572000	3.466325000	-4.741553000
N	-4.916024000	4.595760000	-5.232342000
C	-4.803320000	-2.858305000	-3.856027000

H	-4.875632000	-3.506621000	-4.734248000
H	-5.556086000	-3.176514000	-3.128089000
H	-3.821730000	-3.040483000	-3.400408000
C	-4.962605000	-1.427247000	-4.216657000
C	-5.407691000	-0.510716000	-3.281340000
H	-5.672071000	-0.851461000	-2.279363000
C	-5.534789000	0.831048000	-3.578135000
C	-5.201910000	1.226943000	-4.862937000
C	-6.287148000	3.154104000	-5.975250000
C	-6.008648000	4.489635000	-6.004286000
C	-6.529488000	5.680169000	-6.851092000
H	-6.795285000	7.435847000	-6.235774000
C	-7.763111000	5.154535000	-7.604417000
C	-7.650915000	4.890377000	-8.953840000
H	-6.695541000	5.107716000	-9.431914000
C	-8.727539000	4.397041000	-9.662279000
H	-8.634880000	4.199916000	-10.730521000
C	-9.924897000	4.155003000	-9.021003000
H	-10.777147000	3.768994000	-9.579359000
C	-4.646461000	-0.978999000	-5.485499000
H	-4.294889000	-1.690258000	-6.234030000
C	-4.758636000	0.351057000	-5.839203000
C	-6.009780000	1.803345000	-2.563445000
H	-5.189810000	2.430114000	-2.193403000
H	-6.444114000	1.283410000	-1.705918000
H	-6.768674000	2.483517000	-2.967853000
C	-8.965140000	4.909632000	-6.965799000
H	-9.057907000	5.138050000	-5.903312000
C	-10.043135000	4.414813000	-7.670010000
H	-10.991681000	4.235824000	-7.163330000
C	-4.192343000	5.796041000	-4.946916000
H	-3.196363000	5.517226000	-4.600743000
H	-4.721397000	6.367907000	-4.180062000
H	-4.167209000	6.373909000	-5.876692000
C	-4.412695000	0.814882000	-7.205727000
H	-5.305792000	1.048281000	-7.798699000
H	-3.858755000	0.041586000	-7.743831000
H	-3.800077000	1.723380000	-7.190591000
O	-5.597884000	6.148363000	-7.580700000
O	-6.987632000	6.589605000	-5.832549000
H	-7.076224000	2.577435000	-6.435916000

TS3

M11L/TZVP (solvent = toluene)

G = -1051.078473 Hartree

Imaginary Frequency -242.1396

N	-0.907893000	-0.477132000	-2.331387000
N	-0.064228000	0.494126000	-2.519943000
N	-0.854291000	1.519675000	-2.735597000
C	0.908638000	-5.672092000	-1.068285000
H	0.089665000	-6.256752000	-0.630199000
H	1.719787000	-5.660369000	-0.333483000
H	1.253403000	-6.215182000	-1.953334000
C	0.458656000	-4.298913000	-1.409470000
C	0.454123000	-3.300646000	-0.452223000
H	0.807913000	-3.521857000	0.555867000
C	0.014062000	-2.022908000	-0.733474000
C	-0.426867000	-1.773099000	-2.022694000
C	-2.185786000	-0.067531000	-2.426068000
C	-2.176692000	1.277663000	-2.702773000
C	-3.533858000	2.754882000	-2.450564000
H	-4.504735000	2.046490000	-1.052134000
C	-3.743425000	3.098710000	-3.899301000
C	-4.470978000	2.290440000	-4.754222000
H	-4.915107000	1.372735000	-4.370943000
C	-4.631964000	2.645609000	-6.074524000
H	-5.210718000	2.007765000	-6.742137000
C	-4.064847000	3.809817000	-6.555251000
H	-4.192474000	4.088321000	-7.600527000
C	0.013661000	-3.996938000	-2.682909000
H	0.024369000	-4.770254000	-3.452310000
C	-0.440972000	-2.736293000	-3.016879000
C	0.027549000	-0.956598000	0.297473000
H	0.833676000	-0.235786000	0.115453000
H	0.178694000	-1.381980000	1.292840000
H	-0.907003000	-0.383500000	0.309067000
C	-3.186289000	4.266120000	-4.380850000
H	-2.639097000	4.901495000	-3.684407000
C	-3.343216000	4.620041000	-5.704829000
H	-2.903941000	5.545282000	-6.076956000
C	-0.248494000	2.787933000	-2.995575000
H	0.790485000	2.757229000	-2.664901000
H	-0.817160000	3.547865000	-2.452217000
H	-0.290379000	3.007558000	-4.067335000
C	-0.910760000	-2.425271000	-4.389786000
H	-1.998598000	-2.289055000	-4.429341000
H	-0.656456000	-3.236315000	-5.076953000
H	-0.465943000	-1.500337000	-4.774325000
O	-3.005328000	3.540805000	-1.679214000
O	-4.567737000	1.981528000	-2.004838000
H	-3.000434000	-0.763073000	-2.277041000

Int5

M11L/TZVP (solvent = toluene)

G = -1051.117477 Hartree

N	-5.613948000	1.329117000	-5.237049000
N	-4.887374000	2.120357000	-5.967825000
N	-5.794205000	2.838595000	-6.590001000
C	-3.179573000	-2.606501000	-1.999792000
H	-2.096542000	-2.438116000	-1.943064000
H	-3.324635000	-3.614108000	-2.401896000
H	-3.561314000	-2.586652000	-0.974441000
C	-3.834162000	-1.578681000	-2.848368000
C	-4.337175000	-0.418106000	-2.290807000
H	-4.270247000	-0.267994000	-1.212241000
C	-4.924210000	0.566307000	-3.061423000
C	-4.989307000	0.350209000	-4.427334000
C	-6.929404000	1.554960000	-5.404734000
C	-7.093322000	2.576745000	-6.317688000
C	-9.195519000	4.231274000	-8.691661000
H	-8.545522000	3.350086000	-7.143247000
C	-10.436728000	4.755669000	-9.314162000

C	-10.351573000	5.323009000	-10.572926000
H	-9.377554000	5.362732000	-11.058668000
C	-11.478457000	5.820414000	-11.185603000
H	-11.409178000	6.266206000	-12.176707000
C	-12.697754000	5.754425000	-10.541855000
H	-13.590711000	6.148479000	-11.025739000
C	-3.929668000	-1.750609000	-4.217140000
H	-3.544594000	-2.665186000	-4.670661000
C	-4.502922000	-0.796377000	-5.033670000
C	-5.458913000	1.807485000	-2.448056000
H	-5.139778000	2.702443000	-2.994202000
H	-5.122120000	1.901634000	-1.412389000
H	-6.555910000	1.820186000	-2.441000000
C	-11.661037000	4.690089000	-8.671796000
H	-11.719661000	4.241368000	-7.682318000
C	-12.787798000	5.189813000	-9.286034000
H	-13.750936000	5.138580000	-8.780276000
C	-5.318679000	3.860159000	-7.471227000
H	-6.115719000	4.086990000	-8.182705000
H	-4.425230000	3.507226000	-7.990764000
H	-5.067135000	4.761665000	-6.902749000
C	-4.591427000	-0.988040000	-6.501854000
H	-5.584355000	-0.731771000	-6.890036000
H	-4.376969000	-2.025590000	-6.770677000
H	-3.874693000	-0.348970000	-7.031282000
O	-8.127749000	4.297953000	-9.235591000
O	-9.401073000	3.708602000	-7.522159000
H	-7.650757000	0.955340000	-4.865012000

TS4

G = -1051.118142 Hartree

Imaginary Frequency -218.0105

N	-5.559040000	1.460406000	-5.395700000
N	-4.726899000	2.188353000	-6.080896000
N	-5.531694000	2.986578000	-6.743028000
C	-3.692661000	-2.649722000	-2.003639000
H	-3.267271000	-2.257793000	-1.074692000
H	-2.940418000	-3.279206000	-2.488996000
H	-4.526400000	-3.305973000	-1.723132000
C	-4.153350000	-1.557630000	-2.897856000
C	-4.581805000	-0.351387000	-2.375709000
H	-4.549460000	-0.191979000	-1.296942000
C	-5.048540000	0.667576000	-3.182114000
C	-5.063809000	0.439513000	-4.547485000
C	-6.838867000	1.797568000	-5.626418000
C	-6.854689000	2.829880000	-6.535371000
C	-10.063946000	3.280125000	-6.761032000
H	-8.157614000	3.494101000	-7.041061000
C	-11.416409000	3.795823000	-7.119240000
C	-12.528144000	3.176304000	-6.577855000
H	-12.372400000	2.331693000	-5.907646000
C	-13.792156000	3.625161000	-6.885889000
H	-14.665601000	3.134222000	-6.458562000
C	-13.952744000	4.699701000	-7.737576000
H	-14.952833000	5.056347000	-7.981800000
C	-4.186590000	-1.734837000	-4.268657000
H	-3.846906000	-2.679330000	-4.696128000
C	-4.640218000	-0.747635000	-5.120509000
C	-5.502969000	1.958531000	-2.608643000
H	-5.048874000	2.814615000	-3.121139000
H	-5.245354000	2.021200000	-1.548284000
H	-6.589401000	2.083236000	-2.693173000
C	-11.582139000	4.872015000	-7.973154000
H	-10.700674000	5.352256000	-8.393838000
C	-12.847315000	5.322703000	-8.279679000
H	-12.976156000	6.170695000	-8.951167000
C	-4.924899000	3.943787000	-7.613478000
H	-3.842235000	3.816562000	-7.574173000
H	-5.191897000	4.954575000	-7.294970000
H	-5.281016000	3.790618000	-8.635207000
C	-4.664114000	-0.946747000	-6.590213000
H	-5.619329000	-0.635812000	-7.029740000
H	-4.500806000	-1.998005000	-6.840850000
H	-3.883366000	-0.358182000	-7.086809000
O	-9.929293000	2.359290000	-5.995365000
O	-9.104406000	3.909305000	-7.342160000
H	-7.656667000	1.282842000	-5.139503000

2

M11L/TZVP (solvent = toluene)

G = -1051.123235 Hartree

N	1.331686000	7.189524000	12.776067000
N	1.075086000	8.161455000	13.613397000
N	0.048442000	7.723144000	14.276864000
C	2.140548000	7.269794000	10.513304000
C	3.214269000	7.395721000	9.654759000
C	2.414747000	7.319967000	11.871831000
C	3.692515000	7.468316000	12.386437000
C	4.725620000	7.585657000	11.478530000
C	4.508502000	7.551521000	10.114285000
C	0.491489000	6.151626000	12.883845000
H	0.477196000	5.241634000	12.239433000
C	5.643160000	7.647655000	9.162291000
H	5.363552000	8.194168000	8.256070000
H	5.972009000	6.650514000	8.843491000
H	6.507272000	8.144649000	9.613072000
C	-0.359168000	6.514686000	13.879620000
H	-1.206196000	5.981404000	14.287036000
C	0.764687000	7.092790000	9.986985000
H	0.037361000	7.725236000	10.509196000
H	0.418278000	6.055157000	10.091879000
H	0.731203000	7.348278000	8.924824000
C	3.964100000	7.483922000	13.845484000
H	3.390856000	6.716266000	14.378279000
H	3.704451000	8.447065000	14.299251000
H	5.025218000	7.302127000	14.034888000
C	-0.492734000	8.532464000	15.324081000
H	-0.121699000	9.549568000	15.198344000

H	-0.180991000	8.142833000	16.297126000
H	-1.582240000	8.521443000	15.259456000
H	5.742190000	7.698252000	11.857579000
H	3.025341000	7.370270000	8.580888000
C	-1.840526000	2.344505000	11.365211000
C	-3.234531000	0.154687000	10.389770000
C	-2.097499000	0.595865000	9.743084000
C	-1.405763000	1.684336000	10.229901000
C	-2.980618000	1.894486000	12.006607000
C	-1.085423000	3.539808000	11.905365000
C	-3.675187000	0.806675000	11.524043000
O	-0.067281000	3.875535000	11.276342000
O	-1.536058000	4.076654000	12.917775000
H	-3.782233000	-0.706176000	10.006874000
H	-4.572133000	0.458308000	12.036459000
H	-0.505124000	2.050057000	9.738065000
H	-1.748275000	0.080530000	8.848141000
H	-3.307233000	2.426157000	12.899905000

MECP for the formation of **Int1**
M11L/TZVP (solvent = toluene)
G = -1050.926712 Hartree

N	-1.068074000	0.426648000	0.112292000
N	-0.476051000	0.602437000	1.257252000
N	0.790680000	0.691351000	0.945975000
C	-6.631689000	-0.511396000	0.040179000
H	-7.198173000	0.416859000	-0.073371000
H	-6.965608000	-1.005867000	0.958692000
H	-6.904645000	-1.172566000	-0.791164000
C	-5.169736000	-0.257133000	0.064493000
C	-4.663783000	0.993523000	-0.234261000
H	-5.350691000	1.804125000	-0.479012000
C	-3.306121000	1.250364000	-0.229937000
C	-2.468573000	0.199978000	0.092686000
C	-0.230212000	0.385749000	-0.922387000
H	-0.563289000	0.239683000	-1.936992000
C	1.039739000	0.566826000	-0.390219000
C	2.255858000	0.452204000	-1.054366000
H	2.250224000	0.832707000	-2.073408000
C	3.541360000	0.216745000	-0.450287000
C	3.711550000	-0.776383000	0.513283000
H	2.854793000	-1.397327000	0.776691000
C	4.945979000	-1.014273000	1.070445000
H	5.054331000	-1.799935000	1.818343000
C	6.048579000	-0.288065000	0.666335000
H	7.024822000	-0.482993000	1.106694000
C	-4.285829000	-1.274473000	0.378731000
H	-4.673398000	-2.265796000	0.616684000
C	-2.920539000	-1.073822000	0.401601000
C	-2.776561000	2.597692000	-0.554055000
H	-2.065236000	2.950359000	0.201614000
H	-3.590335000	3.323924000	-0.619915000
H	-2.247825000	2.608016000	-1.514916000
C	4.671235000	0.909132000	-0.879005000
H	4.563125000	1.665444000	-1.657551000
C	5.904905000	0.665736000	-0.321257000
H	6.771305000	1.230158000	-0.664318000
C	1.697439000	1.039120000	1.988561000
H	1.136723000	1.570980000	2.758831000
H	2.477826000	1.682322000	1.576547000
H	2.171140000	0.152555000	2.420597000
C	-1.975212000	-2.161686000	0.749073000
H	-1.133707000	-2.219131000	0.044133000
H	-2.486406000	-3.127156000	0.758879000
H	-1.543615000	-2.003256000	1.745609000
O	1.828605000	-1.530355000	-1.630022000
O	0.591696000	-1.790293000	-1.714850000

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