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**Electronic Supplementary Information**

# [4+1] Cyclization of α-Diazo Esters and Mesoionic *N*-Heterocyclic Olefins

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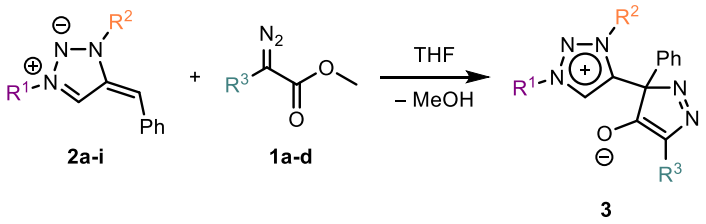
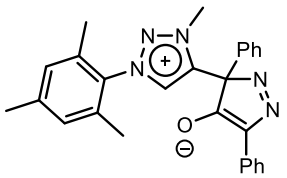
## 1. Experimental section

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 pentane solvents were dried by refluxing and distilling over sodium under dinitrogen. THF, benzene and toluene solvents were dried by refluxing and distilling over sodium benzophenone ketyl under dinitrogen. $C_6D_6$ and THF-$d_8$ 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 $^{1}$H-COSY, $^{1}$H-$^{13}$C-HSQC, and $^{1}$H-$^{13}$C-HMBC NMR spectroscopy. 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. Compounds **1a-d**,[1,2] **2a-i**,[3,4] **7**,[5] **I**,[6] **II**,[7] **III**,[8] **V**,[9] **9**,[9] 1,3-bis(2,6-diisopropylphenyl)-5-phenyl-1,2,3-triazolium hexafluorophosphate[10] and 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium tetrafluoroborate[11] were synthesized according to the literature procedures.



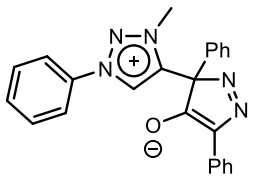

To a stirring solution of mNHO **2** (0.5 mmol) in THF (5 mL) was added α-diazo ester **1** (0.55 mmol) in THF (2 mL). The reaction mixture instantaneously turned dark red. The reaction mixture was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure. The residue was purified

by silica gel column chromatography eluted with acetone (0–20% gradient by volume) in DCM with 1% $Et_3N$ to afford the desired 3-(triazolium-4-yl)-(3*H*)-pyrazol-4-olates.



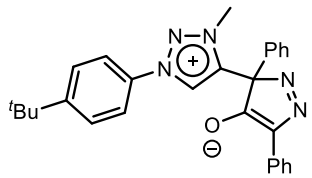
**3aa**

Yellow-orange solid. 169. mg, 77%. 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 8.34 (s, 1H, triazolium-*H*), 8.25–8.19 (m, 2H, Ph-*H*), 7.43–7.39 (m, 2H, Ph-*H*), 7.38–7.33 (m, 2H, Ph-*H*), 7.32–7.28 (m, 3H, Ph-*H*), 7.07–7.01 (m, 3H, overlapping, Ph-*H* and Mes-*H*), 4.44 (s, 3H, N-C$H_3$), 2.37 (s, 3H, Mes-C$H_3$), 2.02 (s, 6H, Mes-C$H_3$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 188.6 (*C*O$^-$), 144.6 (triazolium-*C*), 143.0 (Mes-*C*), 135.3 (Ph-*C*), 135.0 (Ph-*C*), 134.1 (Mes-*C*), 131.2 (Mes-*C*), 131.1 (N*C*(Ph)=CO$^-$), 131.0 (triazolium-*C*), 130.1 (Mes-*C*), 129.4 (Ph-*C*), 128.4 (Ph-*C*), 128.3 (Ph-*C*), 126.6 (Ph-*C*), 123.6 (Ph-*C*), 122.3 (Ph-*C*), 79.9 (quaternary *C*), 40.7 (N-*C*H$_3$), 21.4 (Mes-*C*H$_3$), 17.4 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{27}H_{26}N_5O$ $[M+H]^+$ 436.2133, found 436.2150.



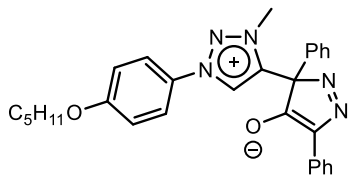
**3ab**

Yellow-orange solid. 158. mg, 81%. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H, triazolium-*H*), 8.16–8.10 (m, 2H, Ph-*H*), 7.78–7.70 (m, 2H, Ph-*H*), 7.62–7.55 (m, 1H, Ph-*H*), 7.57–7.50 (m, 2H, Ph-*H*), 7.44–7.38 (m, 2H, Ph-*H*), 7.34–7.25 (m, 5H, Ph-*H*), 7.06 (tt, *J* = 7.4, 1.3 Hz, 1H, Ph-*H*), 4.37 (s, 3H, N-C$H_3$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 189.19 (*C*O$^-$), 144.0 (triazolium-*C*), 134.7 (Ph-*C*), 134.5 (Ph-*C*), 134.3 (Ph-*C*), 132.3 (Ph-*C*), 131.8 (N*C*(Ph)=CO$^-$), 130.6 (Ph-*C*), 129.4 (Ph-*C*), 128.6 (Ph-*C*), 128.3 (Ph-*C*), 127.6 (triazolium-*C*), 127.0 (Ph-*C*), 124.3 (Ph-*C*), 122.7 (Ph-*C*), 121.3 (Ph-*C*), 79.1 (quaternary *C*), 40.8 (N-*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{24}H_{20}N_5O$ $[M+H]^+$ 394.1649, found 394.1659.



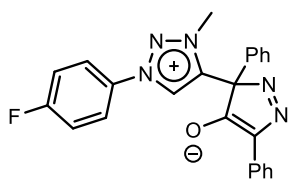
**3ac**

Yellow solid. 180. mg, 80%. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.87 (s, 1H, triazolium-*H*), 8.19–8.13 (m, 2H, Ph-*H*), 7.65–7.59 (m, 2H, $^{t}$Bu-$C_6H_4$), 7.53–7.46 (m, 2H, $^{t}$Bu-$C_6H_4$), 7.40–7.34 (m, 2H, Ph-*H*), 7.32–7.22 (m, 5H, Ph-*H*), 7.06–6.99 (m, 1H, Ph-*H*), 4.38 (s, 3H, N-C$H_3$), 1.32 (s, 9H, C(C$H_3$)$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 188.6 (*C*O$^-$), 156.1 ($^{t}$Bu-*C*$_6$H$_4$), 144.1 (triazolium-*C*), 135.1 (Ph-*C*), 134.9 (Ph-*C*), 132.3 ($^{t}$Bu-*C*$_6$H$_4$), 130.9 (N*C*(Ph)=CO$^-$), 129.3 (Ph-*C*), 128.3 (Ph-*C*), 128.2 (Ph-*C*), 127.5 ($^{t}$Bu-*C*$_6$H$_4$), 127.1 (triazolium-*C*), 127.0 (Ph-*C*), 123.6 (Ph-*C*), 122.3 (Ph-*C*), 120.9 ($^{t}$Bu-*C*$_6$H$_4$), 80.7 (quaternary *C*), 40.7 (N-*C*H$_3$), 35.3 (*C*(CH$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$). HRMS (ESI): *m/z* calcd. for $C_{28}H_{28}N_5O$ $[M+H]^+$ 450.2279, found 450.2288.



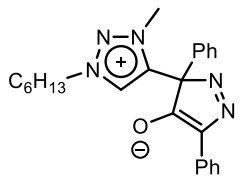
**3ad**

Yellow solid. 171. mg, 71%. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.90 (s, 1H, triazolium-*H*), 8.15–8.07 (m, 2H, Ph-*H*), 7.63–7.52 (m, 2H, pentoxy-$C_6H_4$), 7.35–7.30 (m, 2H, Ph-*H*), 7.28–7.19 (m, 5H, Ph-*H*), 7.01 (tt, *J* = 7.3, 1.3 Hz, 1H, Ph-*H*), 6.92–6.85 (m, 2H, pentoxy-$C_6H_4$), 4.34 (s, 3H, N-C$H_3$), 3.90 (td, *J* = 6.6, 2.0 Hz, 2H, C$H_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.83–1.70 (m, 2H, CH$_2$C$H_2$CH$_2$CH$_2$CH$_3$), 1.47–1.31 (m, 4H, CH$_2$CH$_2$C$H_2$C$H_2$CH$_3$), 0.93 (t, *J* = 7.1 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_2$C$H_3$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 188.7 (*C*O$^-$), 161.8 (pentoxy-*C*$_6$H$_4$), 143.6 (triazolium-*C*), 135.1 (Ph-*C*), 134.9 (Ph-*C*), 130.7 (N*C*(Ph)=CO$^-$), 129.2 (Ph-*C*), 128.20 (Ph-*C*), 128.19 (Ph-*C*), 127.5 (pentoxy-*C*$_6$H$_4$), 127.2 (triazolium-*C*), 127.0 (Ph-*C*), 123.57 (Ph-*C*), 122.8 (pentoxy-*C*$_6$H$_4$), 122.2 (Ph-*C*), 115.8 (pentoxy-*C*$_6$H$_4$), 80.7 (quaternary *C*), 68.8 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 40.6 (N-*C*H$_3$), 28.8 (CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.2 (CH$_2$CH$_2$*C*H$_2$CH$_2$C*H*$_3$), 22.5 (CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 14.1 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{29}H_{30}N_5O_2$ $[M+H]^+$ 480.2394, found 480.2392.



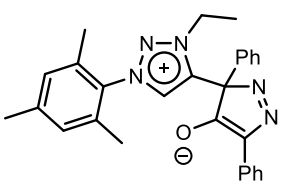
**3ae**

Yellow-orange solid. 155. mg, 75%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H, triazolium-*H*), 8.12–8.02 (m, 2H, Ph-*H*), 7.81–7.73 (m, 2H, F-$C_6H_4$), 7.40–7.33 (m, 2H, Ph-*H*), 7.31–7.24 (m, 5H, Ph-*H*), 7.20–7.13 (m, 2H, F-$C_6H_4$), 7.06 (tt, *J* = 7.4, 1.3 Hz, 1H), 4.36 (s, 3H, N-C$H_3$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 189.1 (*C*O$^-$), 164.3 (d, *J* = 255.0 Hz, F-*C*$_6$H$_4$), 143.7 (triazolium-*C*), 134.4, 134.3, 131.6, 130.9 (d, *J* = 3.4 Hz, F-*C*$_6$H$_4$), 129.4, 128.6, 128.3, 128.1 (triazolium-*C*), 127.1 (Ph-*C*), 124.4 (Ph-*C*), 123.8 (d, *J* = 9.2 Hz, F-*C*$_6$H$_4$), 122.6 (Ph-*C*), 117.7 (d, *J* = 23.8 Hz, F-*C*$_6$H$_4$), 79.6 (quaternary *C*), 40.9 (N-*C*H$_3$). $^{19}$F NMR (470 MHz, $CDCl_3$) δ −105.9 (tt, *J* = 8.0, 4.4 Hz). HRMS (ESI): *m/z* calcd. for $C_{24}H_{19}N_5OF$ $[M+H]^+$ 412.1568, found 412.1563.



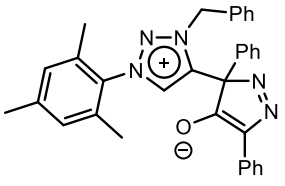
**3af**

Yellow solid. 132. mg, 66%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H, triazolium-*H*), 8.19–8.06 (m, 2H, Ph-*H*), 7.32–7.25 (m, 2H, Ph-*H*), 7.23–7.21 (m, 5H, Ph-*H*), 7.04 (tt, *J* = 7.3, 1.3 Hz, 1H, Ph-*H*), 4.48–4.34 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.21 (s, 3H, N-C$H_3$), 1.80–1.69 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.26–1.14 (m, 6H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.85–0.78 (m, 3H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 189.1 (*C*O$^-$), 142.7 (triazolium-*C*), 134.92 (Ph-*C*), 134.91 (Ph-*C*), 130.8 (N*C*(Ph)=CO$^-$), 129.7 (triazolium-*C*), 129.2 (Ph-*C*), 128.3 (Ph-*C*), 128.2 (Ph-*C*), 126.9 (Ph-*C*), 123.8 (Ph-*C*), 122.3 (Ph-*C*), 80.5 (quaternary *C*), 54.2 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 40.3 (N-*C*H$_3$), 30.9 (CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 29.3 (CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 25.9 (CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 22.3 (CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{24}H_{27}N_5O$ $[M+H]^+$ 402.2288, found 402.2296.



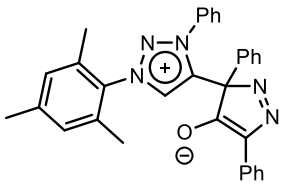
**3ag**

Yellow solid. 154. mg, 69%. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.36 (s, 1H, triazolium-*H*), 8.26–8.19 (m, 2H, Ph-*H*), 7.42–7.32 (m, 4H, Ph-*H*), 7.34–7.26 (m, 3H, Ph-*H*), 7.08–7.00 (m, 3H, overlapping, Ph-*H* and Mes-*H*), 4.98 (dq, *J* = 14.4, 7.2 Hz, 1H, C*H*$_2$CH$_3$), 4.89 (dq, *J* = 14.4, 7.2 Hz, 1H, C*H*$_2$CH$_3$), 2.37 (s, 3H, Mes-C*H*$_3$), 2.02 (s, 6H, Mes-C*H*$_3$), 1.45 (t, *J* = 7.3 Hz, 3H, CH$_2$C*H*$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 188.6 (*C*O$^-$), 144.1 (triazolium-*C*), 142.9 (Mes-*C*), 135.9 (Ph-*C*), 135.1 (Ph-*C*), 134.1 (Mes-*C*), 131.4 (Mes-*C*), 130.9 (N*C*(Ph)=CO$^-$), 130.7 (triazolium-*C*), 130.1 (Mes-*C*), 129.4 (Ph-*C*), 128.3 (Ph-*C*), 128.3 (Ph-*C*), 126.4 (Ph-*C*), 123.6 (Ph-*C*), 122.4 (Ph-*C*), 79.8 (quaternary *C*), 49.9 (*C*H$_2$CH$_3$), 21.4 (Mes-*C*H$_3$), 17.4 (Mes-*C*H$_3$), 14.3 (CH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{28}H_{28}N_5O$ $[M+H]^+$ 450.2292, found 450.2288.



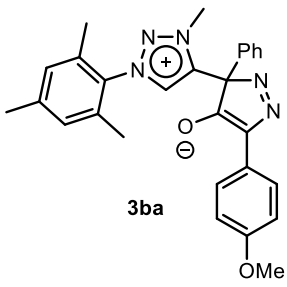
**3ah**

Yellow solid. 190. mg, 74%. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 1H, triazolium-*H*), 8.29–8.21 (m, 2H, Ph-*H*), 7.35–7.24 (m, 8H, Ph-*H*), 7.24–7.17 (m, 2H, Ph-*H*), 7.10–7.01 (m, 3H, Ph-*H*), 7.02 (q, *J* = 0.7 Hz, 2H, Mes-*H*), 6.16 (d, *J* = 14.5 Hz, 1H, C*H*$_2$), 6.08 (d, *J* = 14.5 Hz, 1H, C*H*$_2$), 2.35 (s, 3H, Mes-C*H*$_3$), 1.93 (s, 6H, Mes-C*H*$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 188.7 (*C*O$^-$), 144.2 (triazolium-*C*), 142.9 (Mes-*C*), 136.0 (Ph-*C*), 135.1 (Ph-*C*), 134.0 (Mes-*C*), 131.7 (Ph-*C*), 131.4 (Mes-*C*), 130.9 (N*C*(Ph)=CO$^-$), 130.7 (triazolium-*C*), 130.1 (Mes-*C*), 129.47 (Ph-*C*), 129.45 (Ph-*C*), 129.40 (Ph-*C*), 129.0 (Ph-*C*), 128.30, 128.28, 126.5 (Ph-*C*), 123.7 (Ph-*C*), 122.4 (Ph-*C*), 79.9 (quaternary *C*), 57.7 (*C*H$_2$), 21.3 (Mes-*C*H$_3$), 17.3 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{33}H_{30}N_5O$ $[M+H]^+$ 512.2445, found 512.2439.



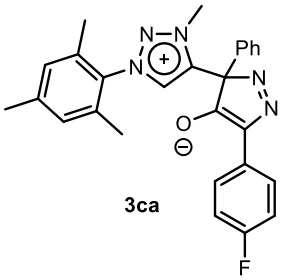
**3ai**

Yellow solid. 206. mg, 83%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H, triazolium-*H*), 8.16 (dq, *J* = 8.6, 1.6 Hz, 2H, Ph-*H*), 7.89–7.83 (m, 2H, Ph-*H*), 7.45–7.40 (m, 1H, Ph-*H*), 7.37–7.31 (m, 2H, Ph-*H*), 7.32–7.24 (m, 4H, Ph-*H*), 7.12–7.04 (m, 5H, Ph-*H* and Mes-*H*), 7.02 (tt, *J* = 7.3, 1.3 Hz, 1H, Ph-*H*), 2.37 (s, 3H, Mes-C*H*$_3$), 2.13 (s, 6H, Mes-C*H*$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 188.7 (*C*O$^-$), 145.1 (triazolium-*C*), 143.1 (Mes-*C*), 135.3, 134.9, 134.3, 134.1 (Mes-*C*), 132.0 (Ph-*C*), 131.4, 131.31, 131.28, 130.2 (Mes-*C*), 129.1 (Ph-*C*), 128.6 (Ph-*C*), 128.2, 127.9, 126.8 (Ph-*C*), 126.4 (Ph-*C*), 123.7 (Ph-*C*), 122.5 (Ph-*C*), 77.4 (quaternary *C*), 21.4 (Mes-*C*H$_3$), 17.5 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{32}H_{27}N_5O$ $[M+H]^+$ 498.2289, found 498.2288.



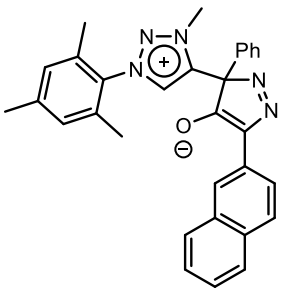
**3ba**

Yellow-orange solid. 175. mg, 75%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H, triazolium-*H*), 8.17–8.10 (m, 2H, MeO-C$_6$*H*$_4$-), 7.44–7.37 (m, 2H, Ph-*H*), 7.37–7.32 (m, 2H, Ph-*H*), 7.33–7.26 (m, 1H, Ph-*H*), 7.03 (s, 2H, Mes-*H*), 6.90–6.85 (m, 2H, MeO-C$_6$*H*$_4$-), 4.42 (s, 3H, N-C*H*$_3$), 3.78 (s, 3H, O-C*H*$_3$), 2.36 (s, 3H, Mes-C*H*$_3$), 2.01 (s, 6H, Mes-C*H*$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 188.0 (*C*O$^-$), 156.5 (MeO-*C*$_6$H$_4$-), 144.6 (triazolium-*C*), 142.9 (Mes-*C*), 135.4 (Ph-*C*), 134.1 (Mes-*C*), 131.2(Mes-*C*), 131.1 (N*C*(Ph)=CO$^-$), 131.0 (triazolium-*C*), 130.1 (Mes-*C*), 129.4 (Ph-*C*), 128.3 (Ph-*C*), 128.2 (MeO-*C*$_6$H$_4$-), 126.6 (Ph-*C*), 123.6 (MeO-*C*$_6$H$_4$-), 113.8 (MeO-*C*$_6$H$_4$-), 79.6 (quaternary *C*), 55.4 (O-*C*H$_3$), 40.6 (N-*C*H$_3$), 21.3 (Mes-*C*H$_3$), 17.4 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{28}H_{28}N_5O_2$ $[M+H]^+$ 466.2238, found 466.2235.



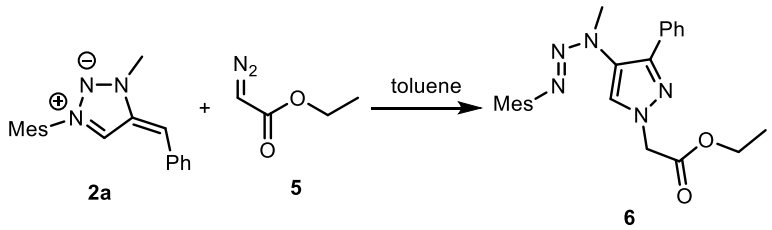

**3ca**

Yellow-orange solid. 180. mg, 79%. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H, triazolium-*H*), 8.17–8.08 (m, 2H, F-C$_6$*H*$_4$-), 7.52–7.47 (m, 2H, Ph-*H*), 7.42–7.36 (m, 2H, Ph-*H*), 7.36–7.31 (m, 1H, Ph-*H*), 7.05–7.02 (m, 2H, Mes-*H*), 7.02–6.97 (m, 2H, F-C$_6$*H*$_4$-), 4.37 (s, 3H, N-C*H*$_3$), 2.36 (s, 3H, Mes-C*H*$_3$), 2.05 (s, 6H, Mes-C*H*$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 189.6 (*C*O$^-$), 160.9 (d, *J* = 243.4 Hz, F-*C*$_6$H$_4$-), 143.8 (triazolium-*C*), 143.0 (Mes-*C*), 134.4 (Ph-*C*), 134.2 (Mes-*C*), 132.6 (N*C*(Ph)=CO$^-$), 131.6 (triazolium-*C*), 131.1 (Mes-*C*), 130.1 (Mes-*C*), 129.6 (Ph-*C*), 129.5 (d, *J* = 3.0 Hz, F-*C*$_6$H$_4$-), 129.0 (Ph-*C*), 126.8 (Ph-*C*), 124.7 (d, *J* = 7.5 Hz, F-*C*$_6$H$_4$-), 115.1 (d, *J* = 21.2 Hz, F-*C*$_6$H$_4$-), 76.4 (quaternary *C*), 40.9 (N-*C*H$_3$), 21.3 (Mes-*C*H$_3$), 17.6 (Mes-*C*H$_3$). $^{19}$F NMR (564 MHz, $CDCl_3$): δ −117.5. HRMS (ESI): *m/z* calcd. for $C_{27}H_{25}N_5OF$ $[M+H]^+$ 454.2038, found 454.2043.

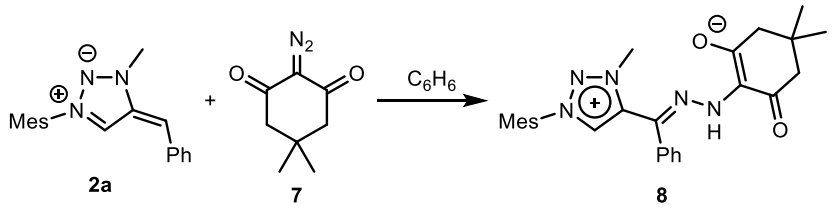



**3da**

Yellow-orange solid. 209. mg, 86%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H, nap-*H*), 8.45 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.38 (s, 1H, triazolium-*H*), 7.77 (dd, *J* = 8.2, 3.3 Hz, 2H), 7.71 (dd, *J* = 8.2, 1.2 Hz, 1H, nap-*H*), 7.45 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.41–7.23 (m, 5H), 7.01 (s, 2H, Mes-*H*), 4.44 (s, 3H, N-C*H*$_3$), 2.34 (s, 3H, Mes-C*H*$_3$), 2.01 (s, 6H, Mes-C*H*$_3$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 189.0 (*C*O$^-$), 144.4 (triazolium-*C*), 143.0 (Mes-*C*), 135.2, 134.3, 134.0 (Mes-*C*), 132.5 (nap-C), 131.4, 131.2, 131.2, 131.1, 130.1 (Mes-*C*), 129.4, 128.5, 127.9 (nap-*C*), 127.6, 126.6, 125.5, 123.8 (nap-*C*), 122.8, 119.0 (nap-*C*), 79.8 (quaternary *C*), 40.7 (N-*C*H$_3$), 21.3 (Mes-*C*H$_3$), 17.4 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{31}H_{28}N_5O$ $[M+H]^+$ 486.2288, found 486.2286.

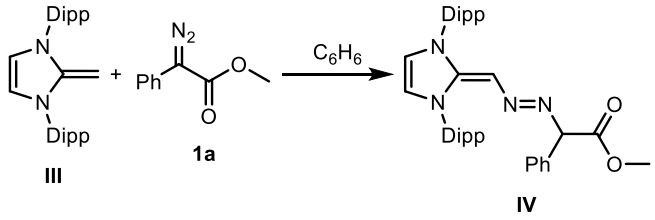



To a stirring solution of **2a** (140. mg, 0.48 mmol) in toluene (2 mL) was added **5** (365. mg, 15 wt% in toluene, 0.48 mmol). The reaction mixture was stirred for 24 h at room temperature. The mixture was passed through a short pad of alumina eluted with toluene. The filtrate was evaporated under vacuum to afford a light yellow oily residue. Yield: 104. mg, 53%. $^{1}$H NMR (500 MHz, $C_6D_6$) δ 8.06–7.91 (m, 2H, Ph-*H*), 7.23–7.15 (m, 2H, Ph-*H*), 7.09 (s, 1H, pyrazole-*H*), 7.08 (ddt, *J* = 8.0, 6.9, 1.3 Hz, 1H, Ph-*H*), 6.91–6.80 (br, 2H, Mes-*H*), 4.31 (s, 2H, N−C*H*$_2$−COOCH$_2$CH$_3$), 3.78 (q, *J* = 7.1 Hz, 2H, COOC*H*$_2$CH$_3$), 3.23 (s, 3H, N-C*H*$_3$), 2.39 (s, 6H, Mes-C*H*$_3$), 2.18 (s, 3H, Mes-C*H*$_3$), 0.81 (t, *J* = 7.1 Hz, 3H, COOCH$_2$C*H*$_3$). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 167.3 (*C*OOCH$_2$CH$_3$), 146.2 (Mes-*C*), 145.4, 134.7 (Mes-*C*), 133.2, 130.5 (Mes-*C*), 129.9 (Mes-*C*), 128.8 (Ph-*C*), 128.2, 127.72 (Ph-*C*), 127.71 (pyrazole-*C*), 61.5 (COO*C*H$_2$CH$_3$), 53.6 (N−*C*H$_2$−COOCH$_2$CH$_3$), 37.8 (N-*C*H$_3$), 21.0 (Mes-*C*H$_3$), 19.4 (Mes-*C*H$_3$), 13.9 (COOCH$_2$*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{23}H_{28}N_5O_2$ $[M+H]^+$ 406.2238, found 406.2230.



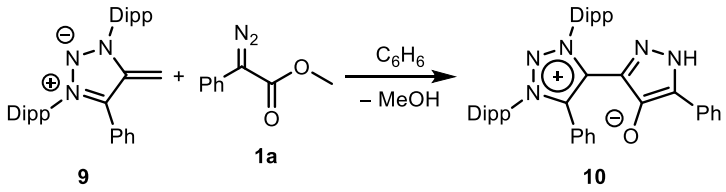

To a stirring solution of **2a** (146. mg, 0.50 mmol) in benzene (2 mL) was added **7** (83. mg, 0.50 mmol) in benzene (2 mL). The reaction mixture instantaneously turned from dark purple to red. The reaction mixture was stirred for 30 min at room temperature and an orange precipitate gradually formed. Diethyl

ether (10 mL) was added to the mixture. The solid was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried under vacuum. Orange solid. Yield: 209. mg, 91%. Crystals suitable for X-ray crystallography were obtained by top-layering a benzene solution of **2a** with a benzene solution of **7** and letting the reagents diffuse undisturbed at room temperature. $^{1}$H NMR (500 MHz, $CD_3OD$) δ 7.64 (d, *J* = 7.4 Hz, 2H, Ph-*H*), 7.59 (t, *J* = 7.6 Hz, 2H, Ph-*H*), 7.50 (t, *J* = 7.4 Hz, 1H, Ph-*H*), 7.12 (s, 2H, Mes-*H*), 4.52 (s, 3H, N-C*H*$_3$), 2.36 (s, 3H, Mes-C*H*$_3$), 2.28 (s, 4H, C*H*$_2$), 2.07 (s, 6H, Mes-C*H*$_3$), 1.09 (s, 6H, C(C*H*$_3$)$_2$). $^{13}$C NMR (126 MHz, $CD_3OD$) δ 189.3 (*C*O), 143.9 (triazolium-*C*), 143.6 (Mes-*C*), 135.8 (Mes-*C*), 133.0 (Mes-*C*), 131.5, 131.1, 130.7 (Mes-*C*), 130.3, 129.3, 125.8, 119.2, 50.6 (*C*H$_2$), 42.5 (N-*C*H$_3$), 32.6 (*C*(CH$_3$)$_2$), 28.9 (C(*C*H$_3$)$_2$), 21.2 (Mes-*C*H$_3$), 17.0 (Mes-*C*H$_3$). HRMS (ESI): *m/z* calcd. for $C_{27}H_{32}N_5O_2$ $[M+H]^+$ 458.2549, found 458.2551.



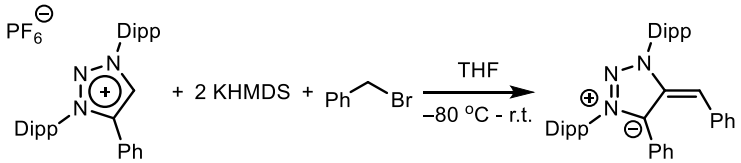

To a stirring solution of **III** (183. mg, 0.46 mmol) in benzene (2 mL) was added **1a** (80. mg, 0.46 mmol) in benzene (2 mL). The reaction mixture was stirred for 3 hours at room temperature. All volatiles were then removed under vacuum. The residue was stirred with diethyl ether (5 mL) for 30 min at room temperature to afford a yellow suspension. The yellow solid of **IV** was collected by filtration, washed with cold diethyl ether (−35 °C, 3 × 1 mL) and *n*-pentane (3 × 1 mL), and dried under vacuum. Yield: 148. mg, 56%. 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 7.62–7.51 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 1H, Ph-*H*), 7.23–7.17 (m, 2H), 7.12–7.09 (m, *J* = 7.6 Hz, 3H), 7.05–6.98 (m, 3H), 6.71 (s, 1H, im=C*H*–N), 5.92 (d, *J* = 2.3 Hz, 1H, im-*H*), 5.89 (d, *J* = 2.3 Hz, 1H, im-*H*), 4.54 (s, 1H, Ph–C*H*(N)–COOCH$_3$), 3.22

(s, 3H, COOC*H*$_3$), 3.10 (hept, *J* = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.96–2.87 (m, 2H, C*H*(CH$_3$)$_2$), 2.82 (hept, *J* = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 1.41 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.24 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.14 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.11 (d, J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.03 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.01 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 0.97 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 172.4 (*C*OOCH$_3$), 149.1 (im-*C*$^2$), 147.4 (Dipp-*C*), 147.3 (Dipp-*C*), 146.3 (Dipp-*C*), 145.9 (Dipp-*C*), 140.5 (Ph-*C*), 136.5 (Dipp-*C*), 132.2 (Dipp-*C*), 130.5 (Ph-*C*), 129.4 (Ph-*C*), 129.2 (Ph-*C*), 128.1 (Dipp-*C*), 127.1 (Dipp-*C*), 124.9 (Dipp-*C*), 124.8 (Dipp-*C*), 124.11 (Dipp-*C*), 124.09 (Dipp-*C*), 119.0 (im-*C*), 116.6 (im-*C*), 102.0 (im=*C*H–N), 81.6 (Ph–*C*H(N)–COOCH$_3$), 50.9 (COO*C*H$_3$), 29.3 (*C*H(CH$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 24.22 (CH(*C*H$_3$)$_2$), 24.18 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$). HRMS (ESI): *m/z* calcd for $C_{37}H_{47}N_4O_2$ $[M+H]^+$ 579.3694, found 579.3694.




To a stirring solution of **9** (240. mg, 0.50 mmol) in $C_6H_6$ (1 mL) was added **1a** (88. mg, 0.50 mmol) in $C_6H_6$ (1 mL). The reaction mixture turned from dark purple to brown. The reaction mixture was stirred for 30 min at room temperature and a brown precipitate gradually formed. Diethyl ether (5 mL) was added to the mixture. The brown solid of **10** was collected by filtration, washed with diethyl ether (3 × 1 mL) and *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 274. mg, 88%. Crystals suitable for X-ray crystallography were obtained by letting a concentrated THF/toluene solution stand at room temperature. $^1$H NMR (500 MHz, $CD_3OD$) δ 7.83–7.76 (m, 2H, Ph-*H*), 7.69 (t, *J* = 7.9 Hz, 1H, Dipp-*H*),

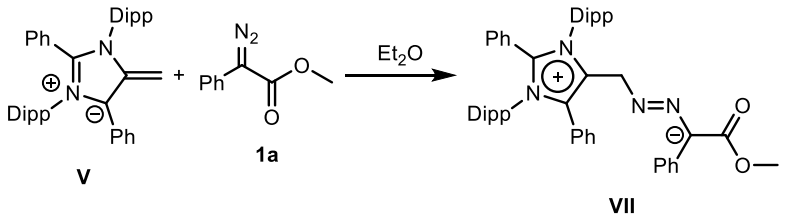
7.57 (t, *J* = 7.8 Hz, 1H, Dipp-*H*), 7.47 (d, *J* = 7.8 Hz, 2H, Dipp-*H*), 7.41–7.34 (m, 5H, Dipp-*H* and Ph-*H*), 7.31–7.27 (m, 2H, Ph-*H*), 7.27–7.22 (m, 2H, Ph-*H*), 7.10–7.02 (m, 1H, Ph-*H*), 2.78–2.58 (m, 4H, C*H*($CH_3$)$_2$), 1.24 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.9 Hz, 6H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.01 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR (126 MHz, $CD_3OD$) δ 153.3, 147.2 (Dipp-*C*), 147.1 (Dipp-*C*), 143.3, 140.4, 134.2 (Dipp-*C*), 133.2 (Dipp-*C*), 132.8, 132.10, 132.09, 131.3, 130.7, 129.9, 129.2, 126.3 (Dipp-*C*), 126.1 (Ph-*C*), 125.5 (Dipp-*C*), 125.0, 124.9 (Ph-*C*), 30.5 (*C*H($CH_3$)$_2$), 30.4 (*C*H($CH_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$). HRMS (ESI): *m/z* calcd. for $C_{41}H_{46}N_5O$ $[M+H]^+$ 624.3697, found 624.3697.




**11**

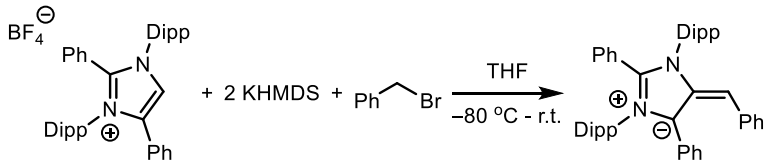
To a solid mixture of 1,3-bis(2,6-diisopropylphenyl)-5-phenyl-1,2,3-triazolium hexafluorophosphate (612. mg, 1.0 mmol) and KHMDS (399. mg, 2.0 mmol) was added THF (5 mL). The mixture was stirred for 1 h at room temperature and then cooled to −80 °C, followed by the addition of benzyl bromide (119. µL, 1.00 mmol). The mixture was slowly warmed to room temperature and stirred for 3 h. All volatiles were removed under reduced pressure. The residue was extracted with diethyl ether and filtered through Celite. The filtrate was concentrated to dryness under vacuum to afford a dark green crystalline solid. The solid of **11** was washed with cold diethyl ether (−35 °C, 3 × 1 mL) and *n*-pentane (3 × 1 mL), and dried under vacuum (479. mg, 86%). Crystals suitable for X-ray crystallography were obtained by cooling a saturated diethyl ether solution to −35 °C. $^1$H NMR (500 MHz, $C_6D_6$) δ 7.31 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.01 (dd, *J* = 7.6, 2.3 Hz, 2H), 6.98 – 6.90 (m, 4H), 6.79 (dd, *J* = 5.1, 2.0 Hz, 3H), 6.71–6.64 (m, 3H), 4.59 (s, 1H, C*H*), 3.38 (hept, *J* =

6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.02 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.38 (d, *J* = 6.8 Hz, 7H, CH(C*H*$_3$)$_2$), 1.25 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.85 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 148.3 (Dipp-*C*), 146.2 (Dipp-*C*), 142.0, 140.1, 132.8 (Dipp-*C*), 132.4 (Dipp-*C*), 131.5, 131.0, 127.8, 127.61, 127.59, 127.3, 126.8, 125.0, 124.49, 124.47, 121.8, 118.4, 68.6 (*C*H), 29.4 (*C*H(CH$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 22.6 (CH(*C*H$_3$)$_2$). Anal. Calcd. for $C_{39}H_{45}N_3$: C, 84.28; H, 8.16; N, 7.56. Found: C, 83.86; H, 8.45; N, 7.83.




To a stirring solution of **V** (306. mg, 0.55 mmol) in diethyl ether (1 mL) was added **1a** (97. mg, 0.55 mmol) in diethyl ether (1 mL). The reaction mixture turned from green to red orange. The reaction mixture was stirred for 3 h at room temperature and an orange brown precipitate gradually formed. The solid was collected by filtration, washed with cold diethyl ether (−35 °C, 1 mL) and *n*-pentane (3 × 1 mL). The solid was then dissolved in 10 mL of toluene, filtered. The filtrate was concentrated to ~1 mL and cooled to −35 °C to afford light yellow crystals of **VII** that were suitable for X-ray crystallography. The supernatant was decanted off and the crystals were washed with cold diethyl ether (−35 °C, 1 mL) and *n*-pentane (3 × 1 mL) and dried under vacuum (256. mg, 63%). $^1$H NMR (500 MHz, $C_6D_6$) δ 8.47–8.30 (m, 2H, Ph-*H*), 7.83–7.73 (m, 2H, Ph-*H*), 7.55–7.37 (m, 2H, Ph-*H*), 7.08–7.05 (m, 2H, Dipp-*H*), 6.97 (d, *J* = 7.8 Hz, 2H, Dipp-*H*), 6.95–6.92 (m, 2H), 6.90–6.84 (m, 3H), 6.59–6.55 (m, 1H), 6.55–6.50 (m, 2H), 4.96 (s, 1H, im−C*H*$_2$−N), 4.94 (s, 1H, im−C*H*$_2$−N), 3.84 (s, 3H, COOC*H*$_3$), 3.16–3.11 (m, 2H, C*H*(CH$_3$)$_2$), 3.05 (hept, *J* = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 1.13 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.95–0.92 (m, 6H, CH(C*H*$_3$)$_2$), 0.84 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.72–0.70 (m, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR (126

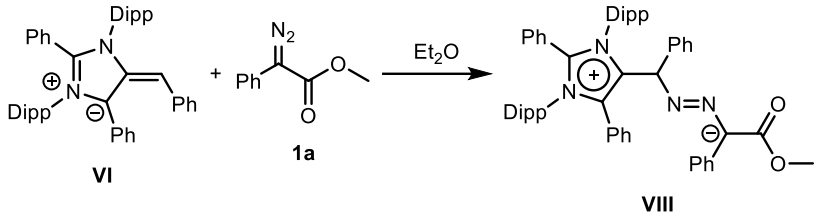
MHz, $C_6D_6$) δ 167.3 (*C*OOCH$_3$), 147.1 (Dipp-*C*), 147.0 (Dipp-*C*), 146.34 (Dipp-*C*), 146.31 (Dipp-*C*), 146.29 (Dipp-*C*), 143.2, 139.8, 139.3, 139.2, 134.1, 131.8, 131.7, 131.6 (Ph-*C*), 131.2, 130.9 (Ph-*C*), 130.7, 130.4, 129.6, 129.2, 128.7, 128.4, 126.9 (Ph-*C*), 126.5, 125.64, 125.61, 123.18, 123.17, 117.1, 54.3 (im−*C*H$_2$−N), 49.5 (COO*C*H$_3$), 28.81 (*C*H(CH$_3$)$_2$), 28.76 (*C*H(CH$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$). HRMS (ESI): *m/z* calcd. for $C_{49}H_{55}N_4O_2$ $[M+H]^+$ 731.4320, found 731.4308.




**VI**

To a solid mixture of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium tetrafluoroborate (629. mg, 1.0 mmol) and KHMDS (399. mg, 2.0 mmol) was added THF (5 mL). The mixture was stirred for 1 h at room temperature and then cooled to −80 °C, followed by the addition of benzyl bromide (119 μL, 1.0 mmol). The mixture was slowly warmed to room temperature and stirred for 3 h. All volatiles were removed under reduced pressure. The residue was extracted with diethyl ether and filtered through Celite. The filtrate was concentrated to dryness under vacuum to afford a dark green crystalline solid. The solid of **VI** was washed with cold diethyl ether (−35 °C, 3 × 1 mL) and *n*-pentane (3 × 1 mL), and dried under vacuum (515. mg, 82%). $^1$H NMR (600 MHz, $C_6D_6$) δ 7.24–7.17 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 2H, Dipp-*H*), 7.08–7.02 (m, 2H), 6.99–6.93 (m, 6H), 6.91–6.89 (m, 2H), 6.79–6.74 (m, 1H), 6.70–6.66 (m, 2H), 6.64 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.62–6.57 (m, 2H), 6.56–6.52 (m, 1H), 4.45 (s, 1H, C*H*Ph), 3.32 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.14 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.40 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.89 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.85 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR (151 MHz, $C_6D_6$) δ 147.4 (Dipp-*C*), 146.4 (Dipp-*C*), 141.0 (Ph-*C*), 140.5 (Ph-*C*), 134.1, 133.0 (Dipp-*C*), 132.6 (Dipp-*C*), 131.1, 130.7, 130.5, 128.4, 128.1, 127.5, 127.4, 127.0,

125.5 (Dipp-*C*), 125.2 (Dipp-*C*), 124.7, 123.6, 123.3, 116.1, 109.9, 70.7, 29.5 (*C*H(CH$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$). Anal. Calcd. for $C_{46}H_{50}N_2$: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.01; H, 8.46; N, 4.06.




To a stirring solution of **VI** (329. mg, 0.52 mmol) in diethyl ether (1 mL) was added **1a** (92. mg, 0.52 mmol) in diethyl ether (1 mL). The reaction mixture was stirred for 3 h at room temperature and a yellow precipitate gradually formed. The solid was collected by filtration, washed with cold diethyl ether (−35 °C, 1 mL) and *n*-pentane (3 × 1 mL). Yellow solid. Yield: 325. mg, 77%. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of *n*-pentane into a toluene solution at room temperature. The partial dissociation of **VIII** into **VI** and **1a** was observed when **VIII** was dissolved in $C_6D_6$ (see Figure S49). $^1$H NMR (500 MHz, $C_6D_6$) δ 8.47–8.40 (m, 2H), 7.77–7.64 (m, 2H), 7.60–7.53 (m, 2H), 7.55–7.48 (m, 2H), 6.81–6.78 (m, 1H), 6.76–6.74 (dd, *J* = 7.7, 1.5 Hz, 1H, Dipp-*H*), 6.72–6.70 (m, 2H), 6.25 (s, 1H, im–C*H*(Ph)–N), 3.84 (s, 3H, COOC*H*$_3$), 3.74 (hept, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 3.64 (hept, *J* = 6.5 Hz, 1H, C*H*(CH$_3$)$_2$), 3.09 (hept, *J* = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 2.56 (hept, *J* = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 1.46 (d, *J* = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.16 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 0.98 (d, *J* = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$), 0.56 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)$_2$), 0.40 (d, *J* = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$), 0.40 (d, *J* = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$). HRMS (ESI): *m/z* calcd. for $C_{55}H_{59}N_4O_2$ $[M+H]^+$ 807.4633, found 807.4639.

## 2. NMR spectra

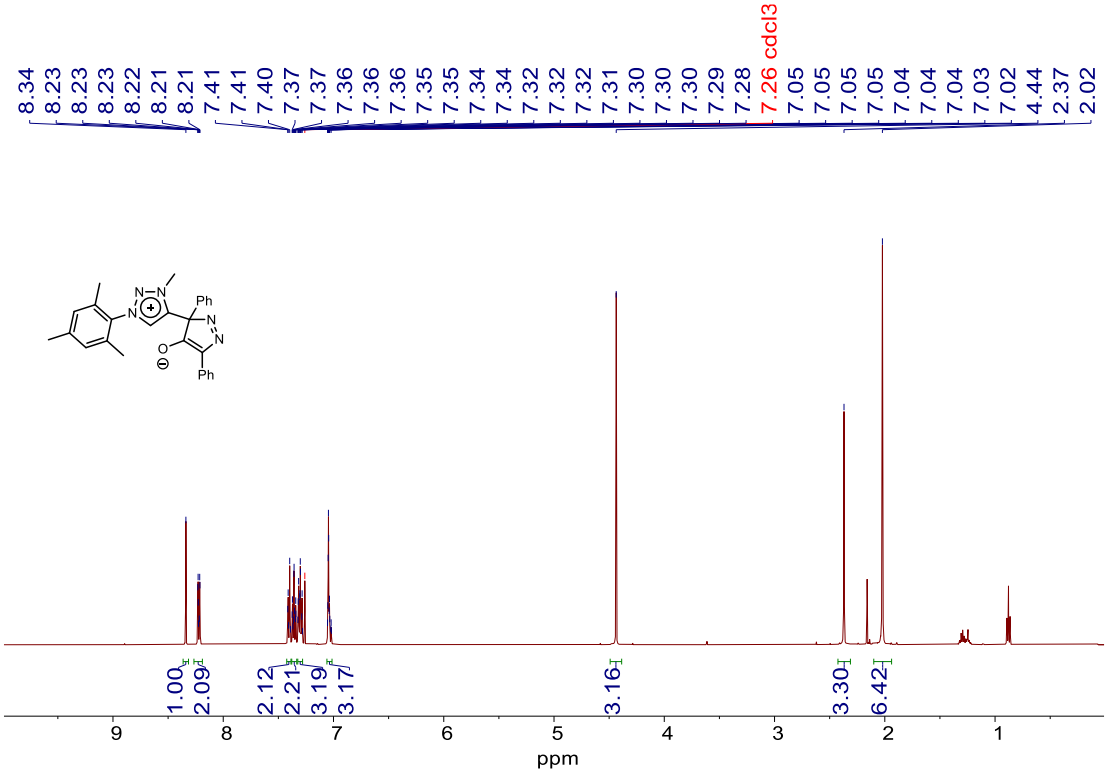



**Figure S1.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **3aa**.

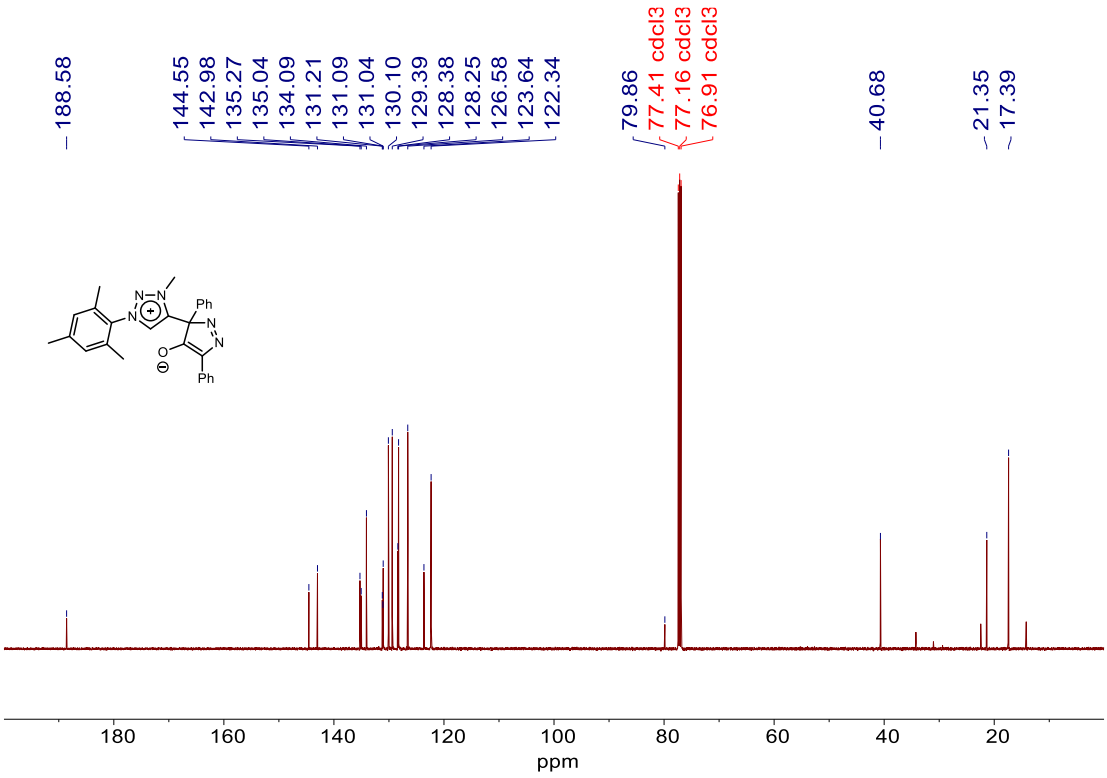



**Figure S2.** $^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **3aa**.

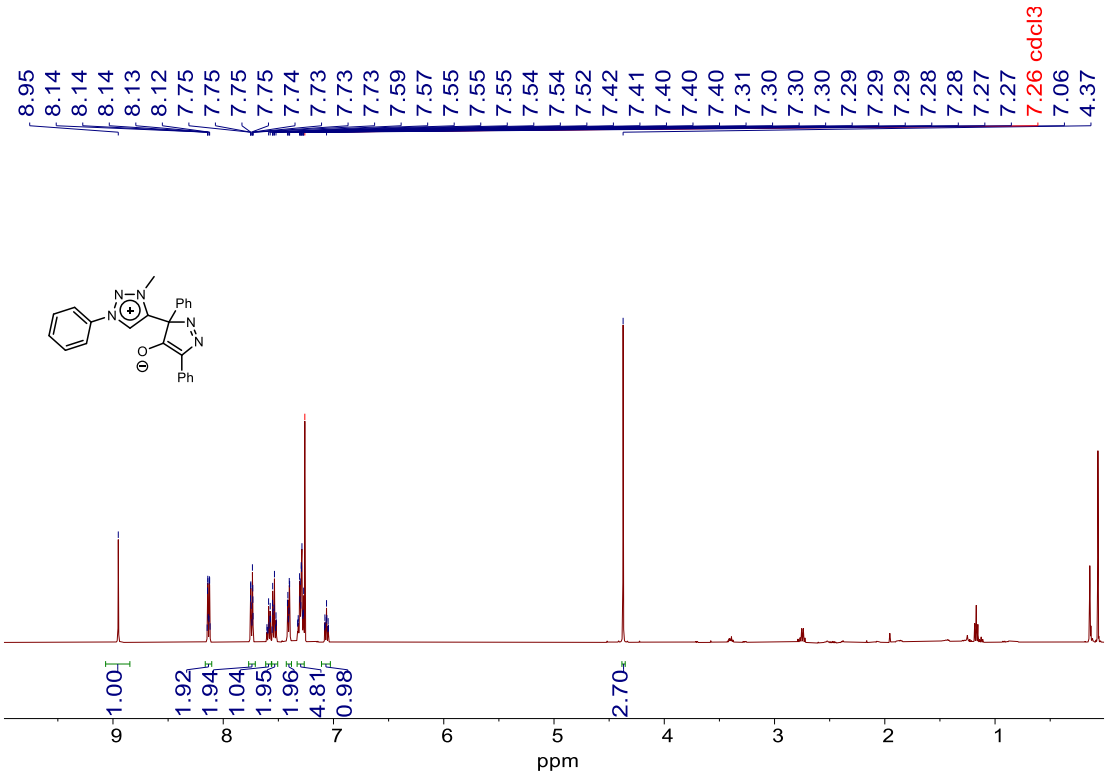



**Figure S3.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **3ab**.

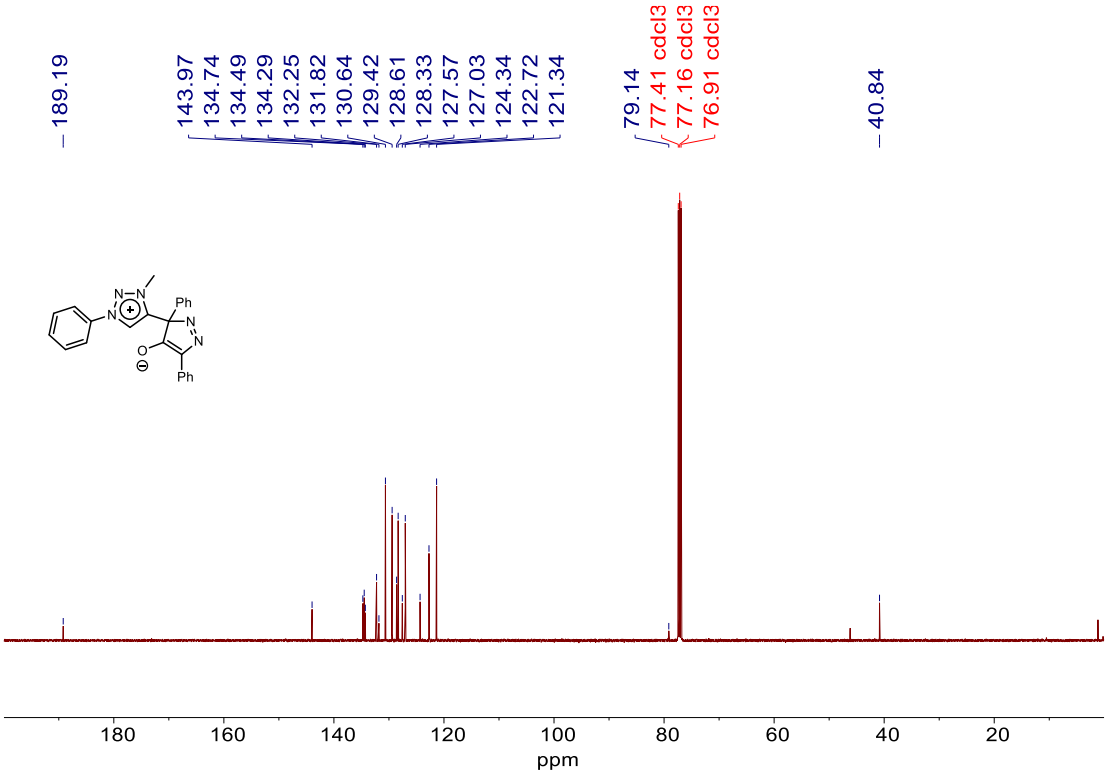



**Figure S4.** $^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **3ab**.

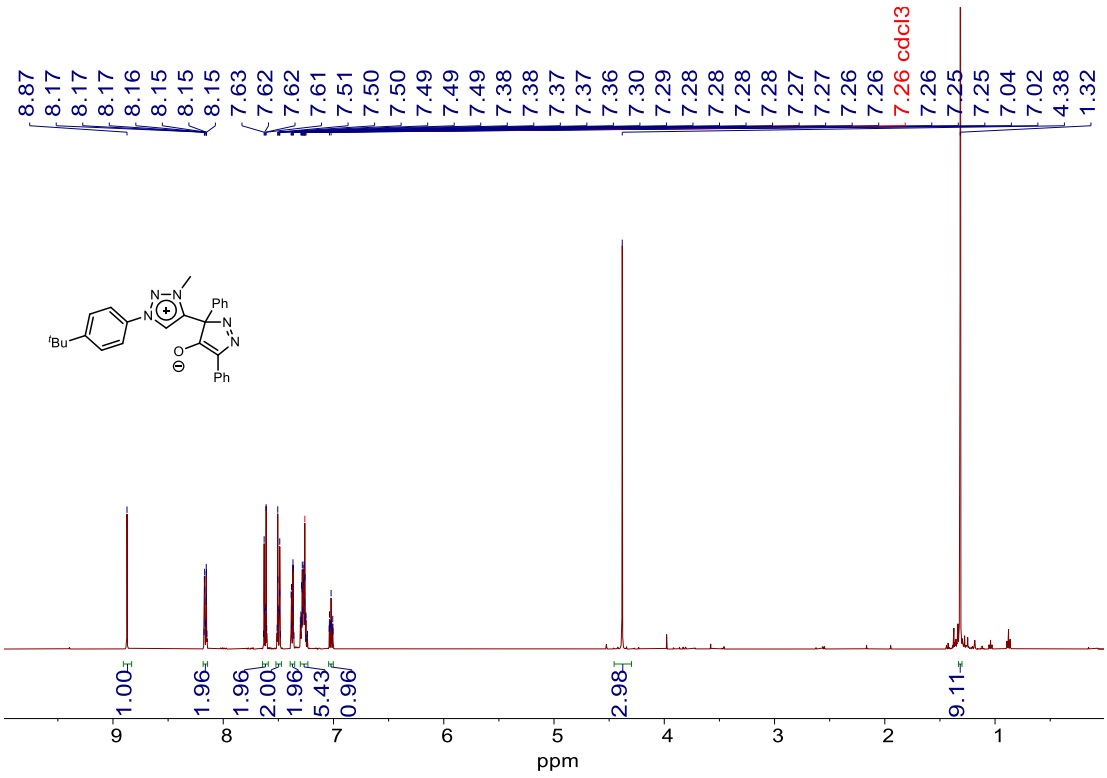



**Figure S5.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **3ac**.

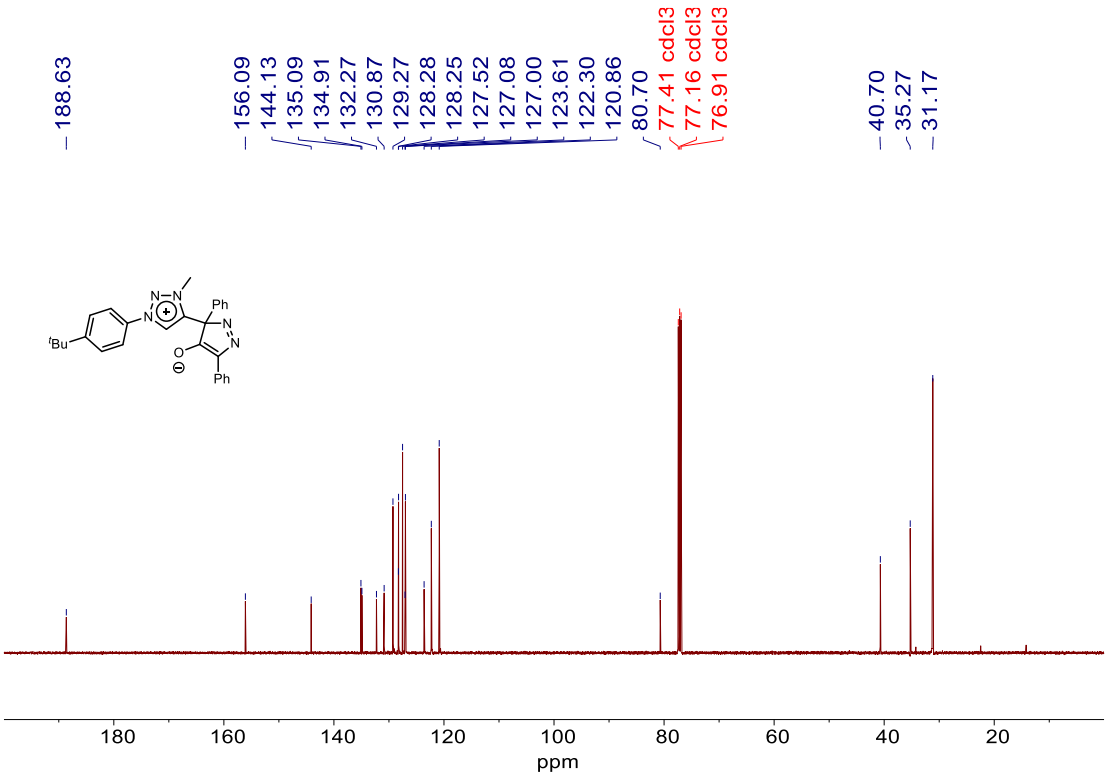



**Figure S6.** $^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **3ac**.

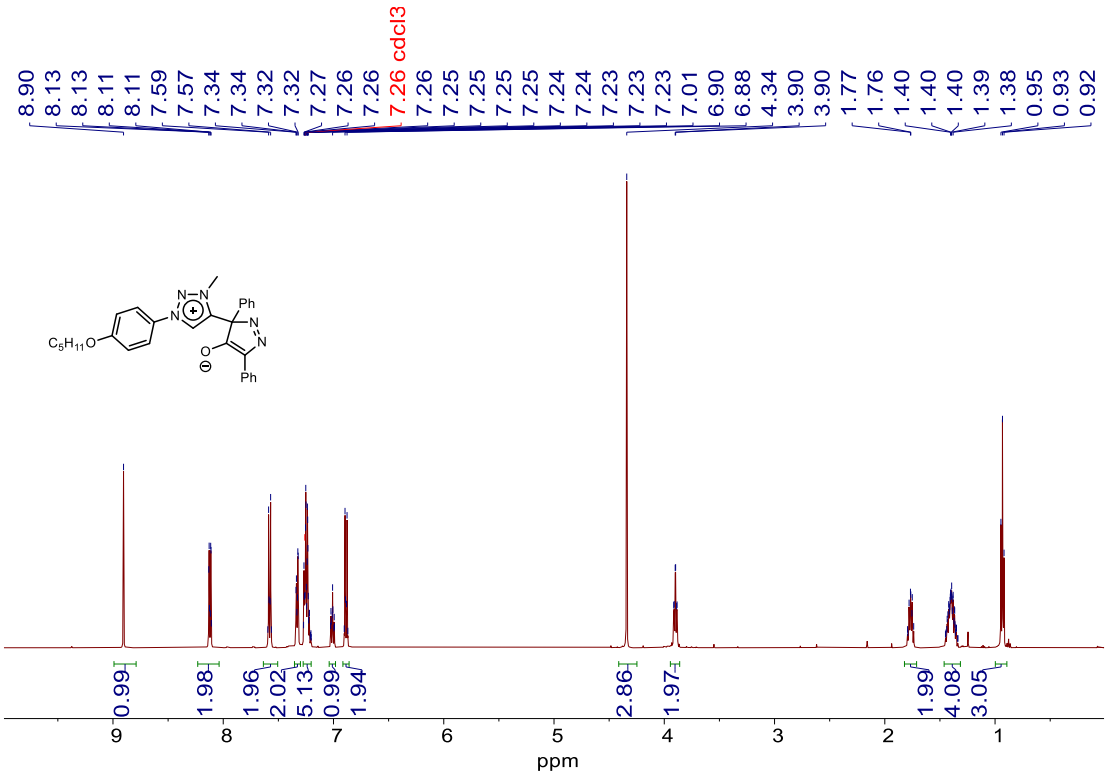



**Figure S7.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **3ad**.

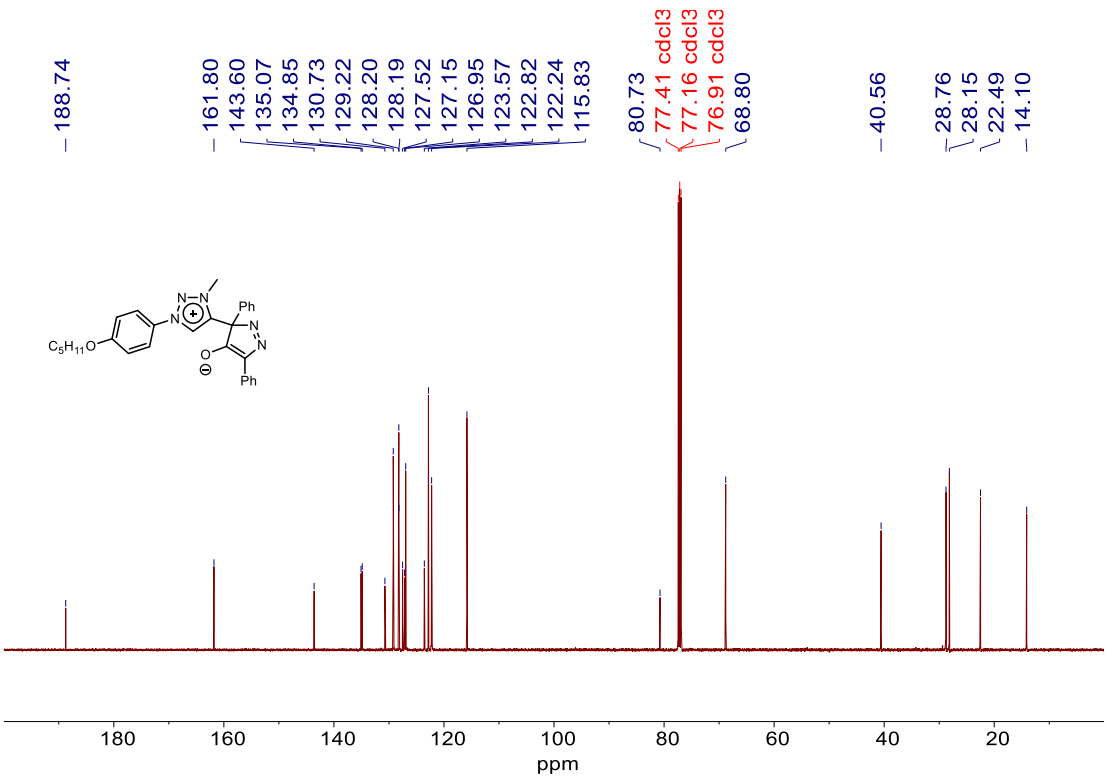



**Figure S8.** $^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **3ad**.

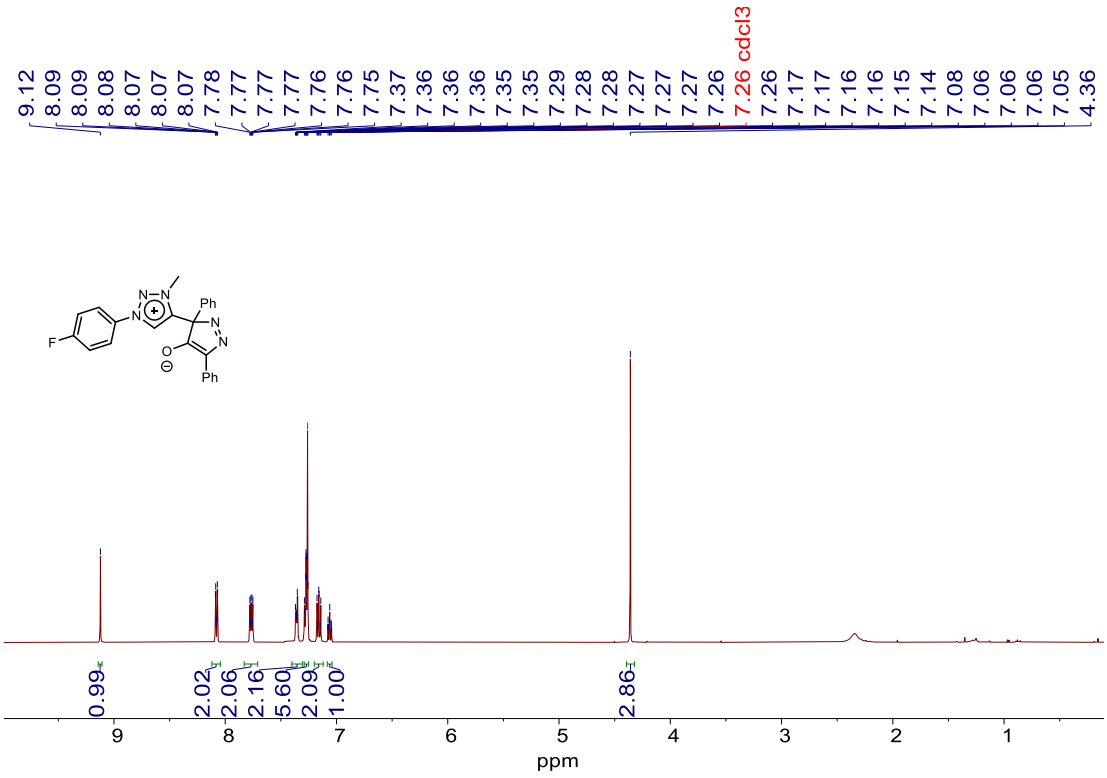



**Figure S9.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **3ae**.

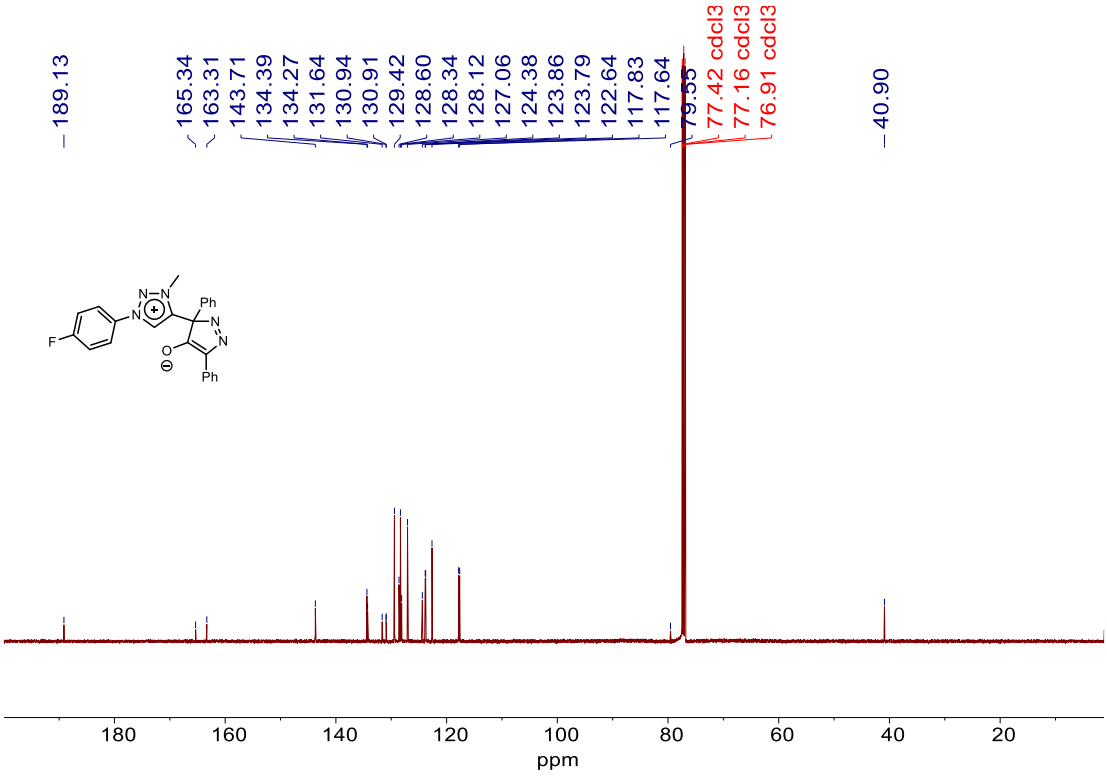



**Figure S10.** $^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **3ae**.

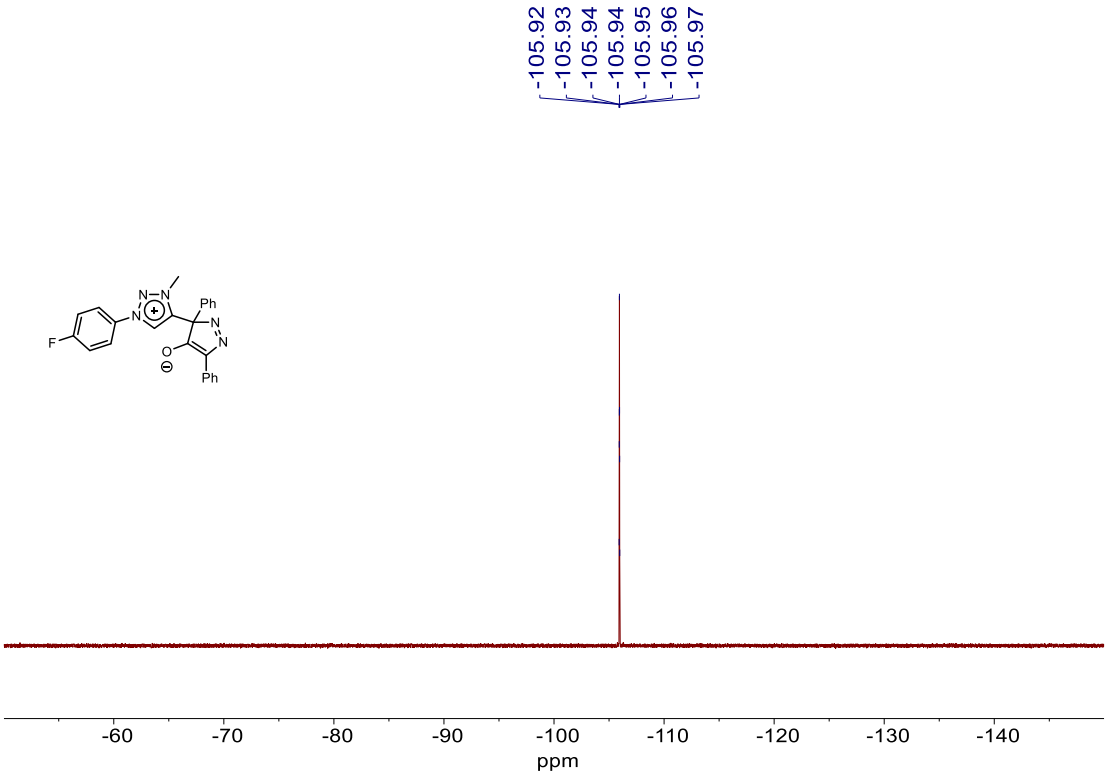



**Figure S11.** $^{19}F$ NMR (470 MHz, $CDCl_3$) spectrum of **3ae**.

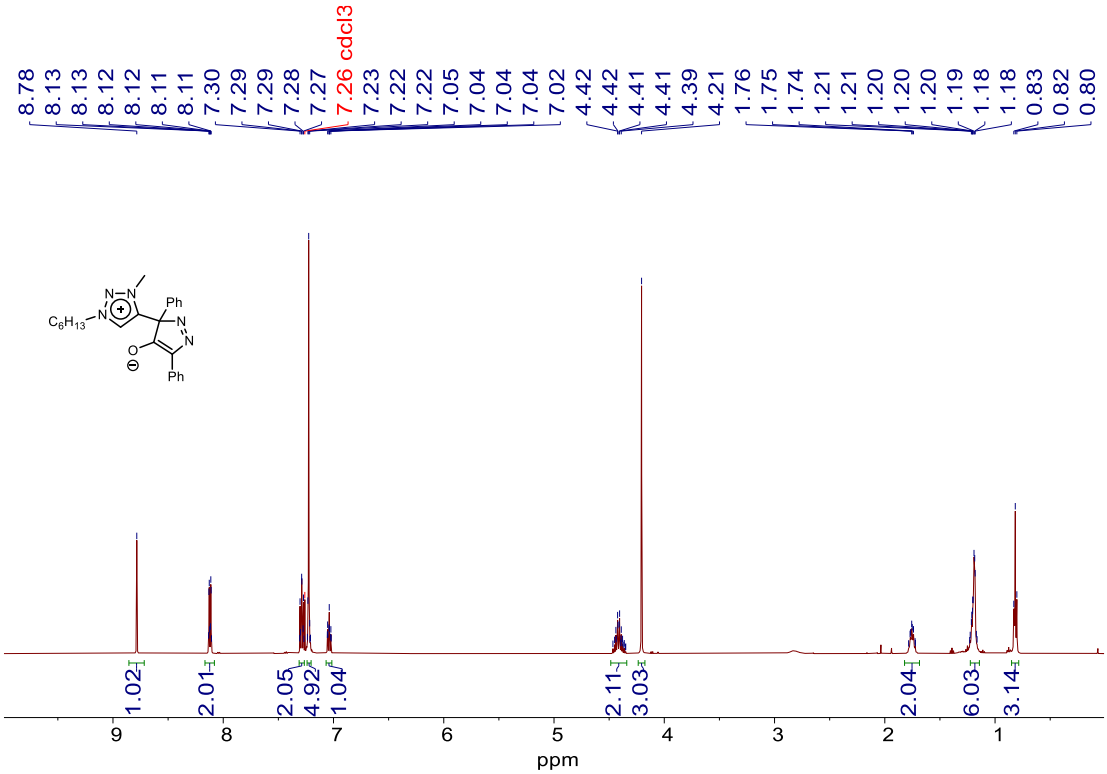



**Figure S12.** $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **3af**.

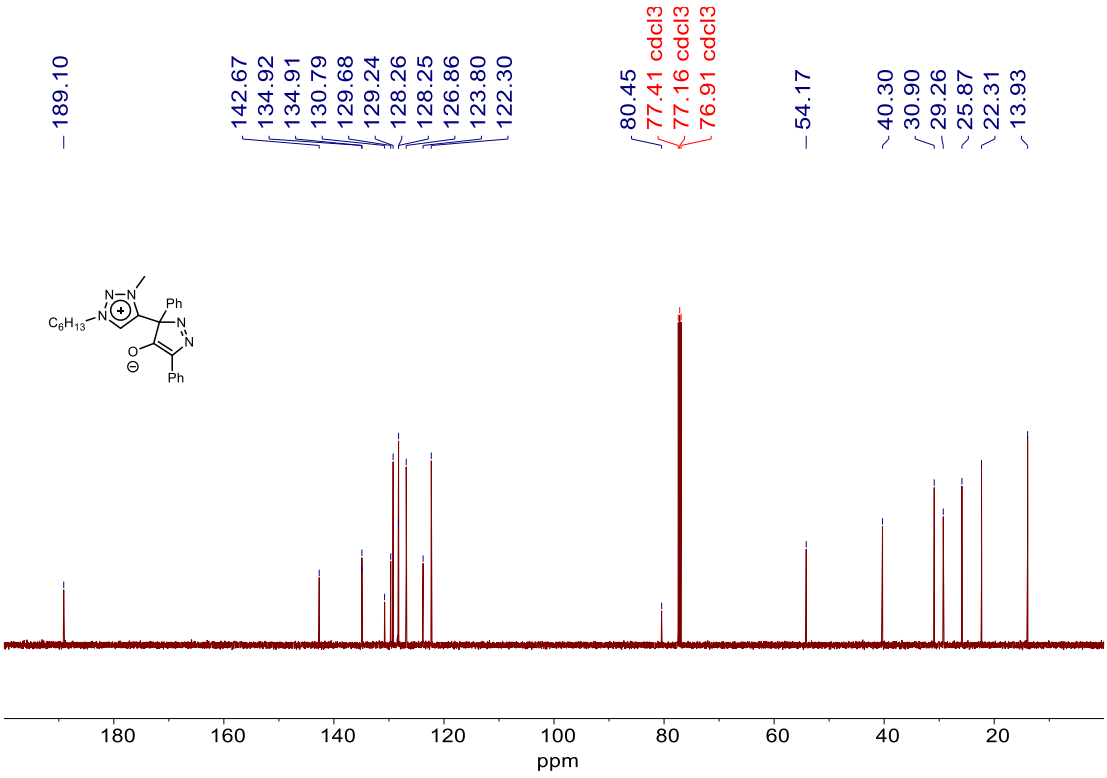



**Figure S13.** $^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **3af**.

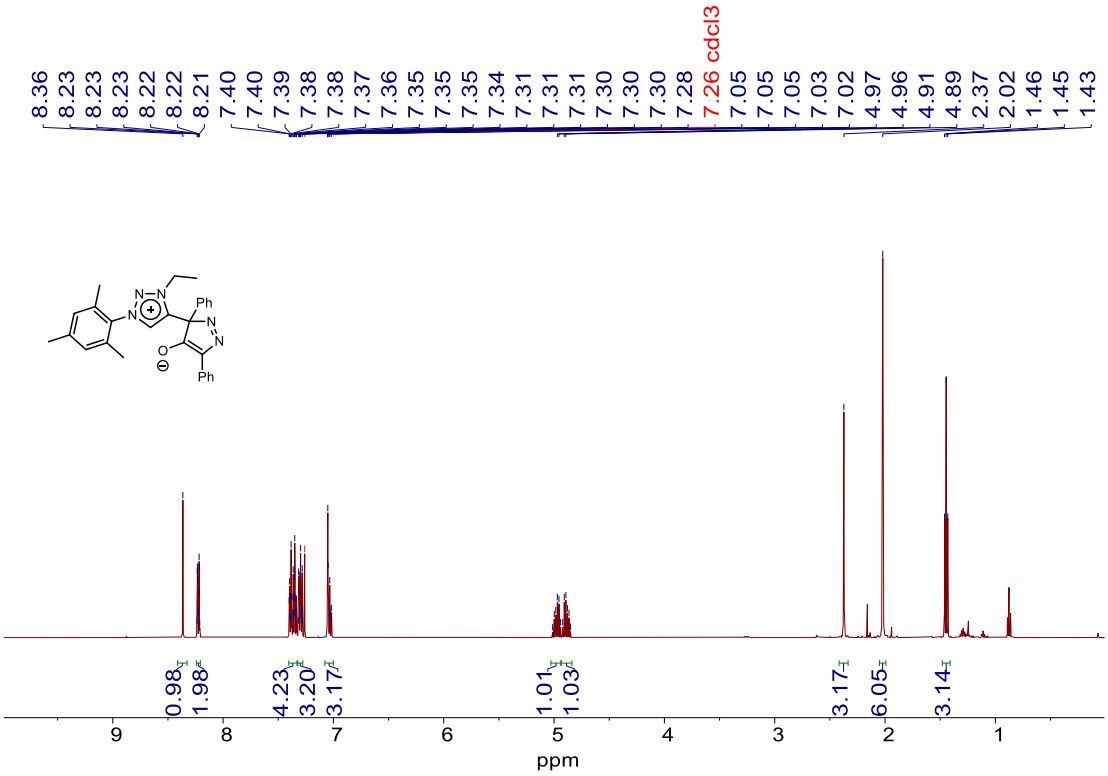



**Figure S14.** $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **3ag**.

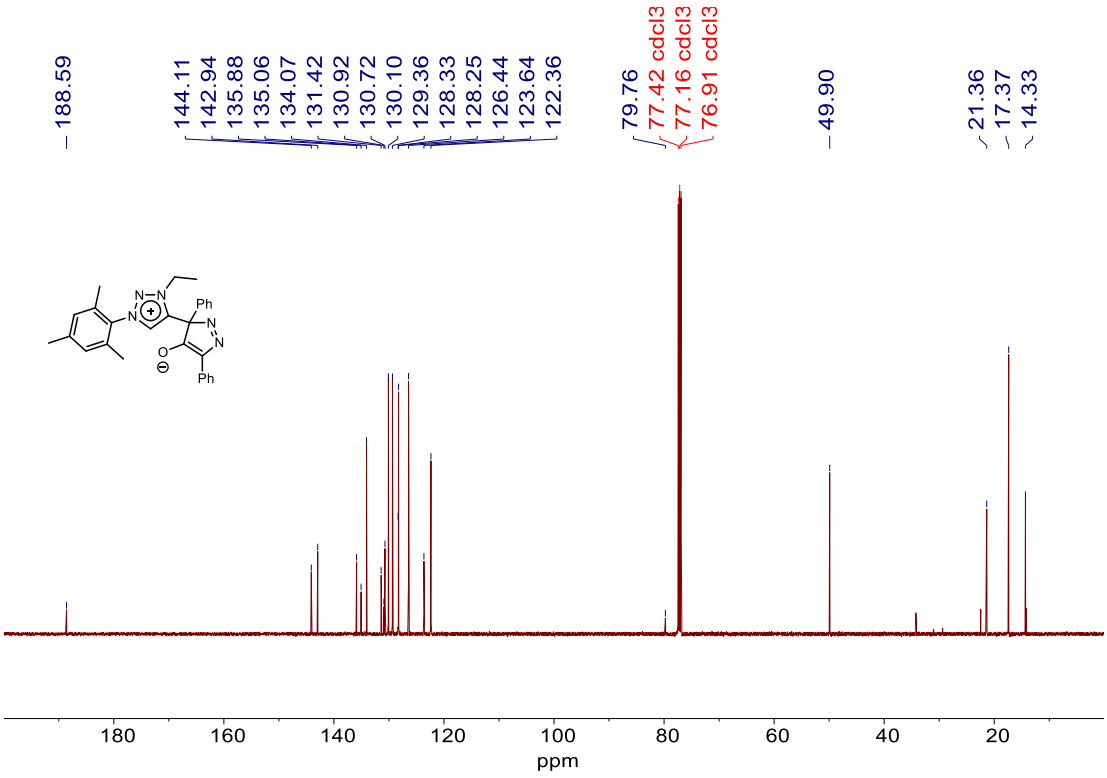



**Figure S15.** $^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **3ag**.

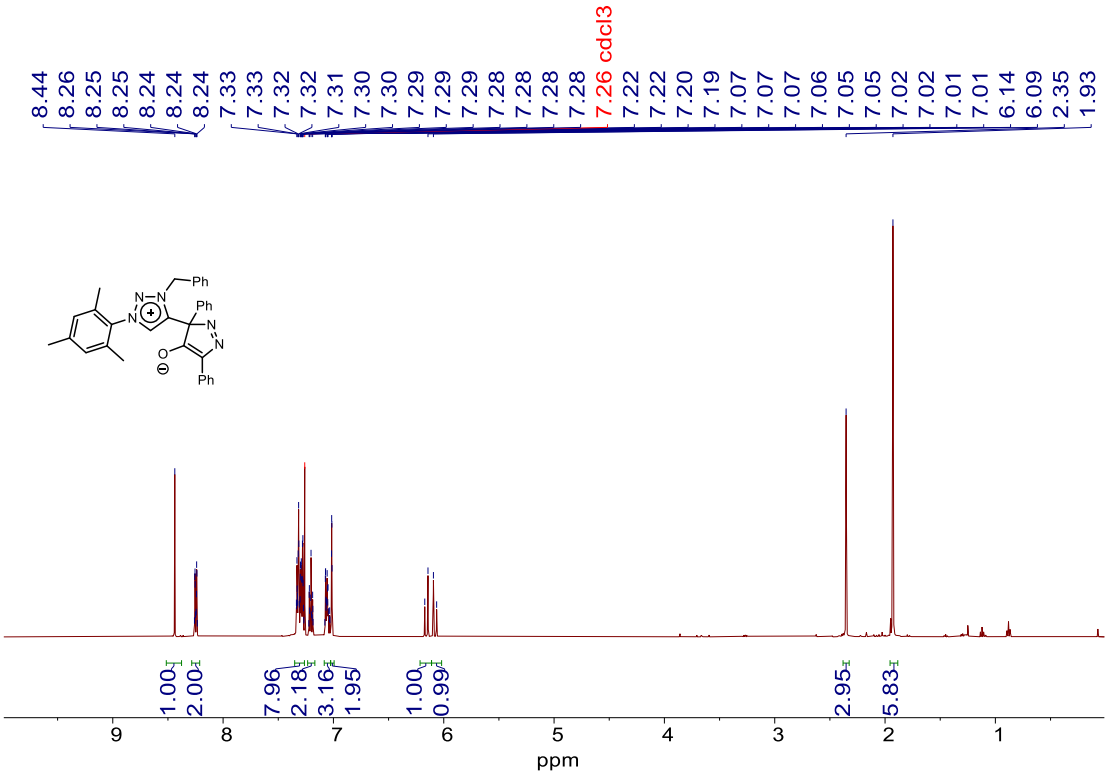



**Figure S16.** $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **3ah**.

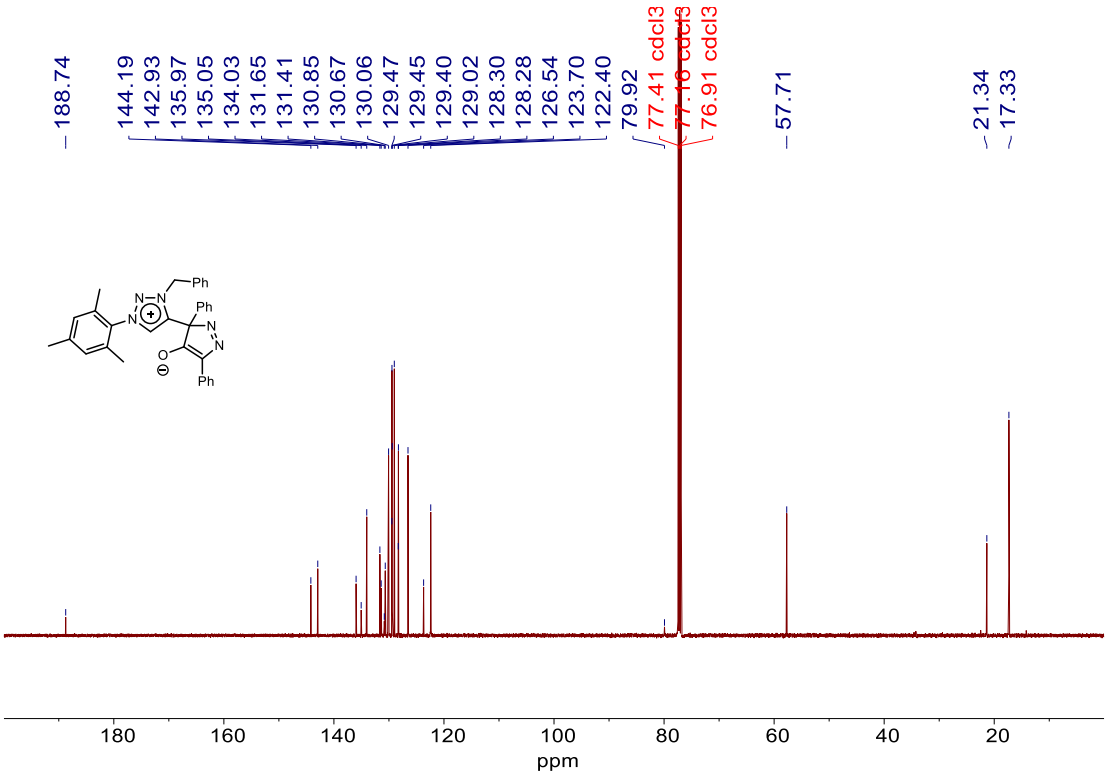



**Figure S17.** $^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **3ah**.

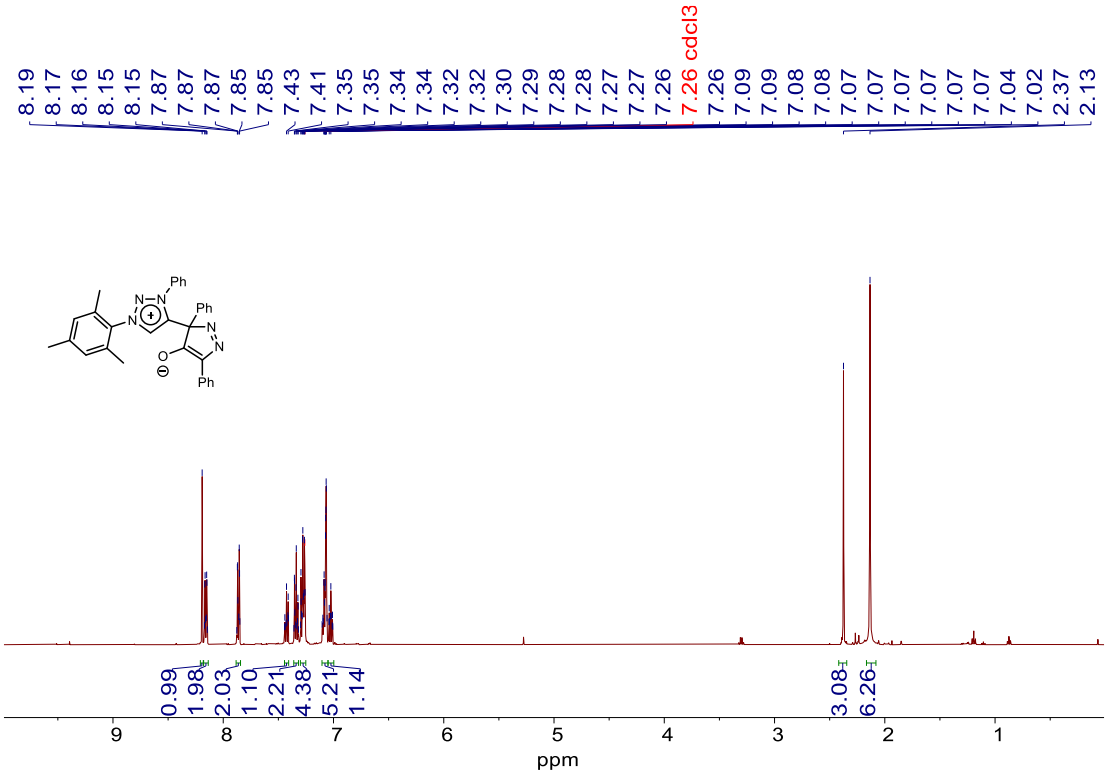



**Figure S18.** $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **3ai**.

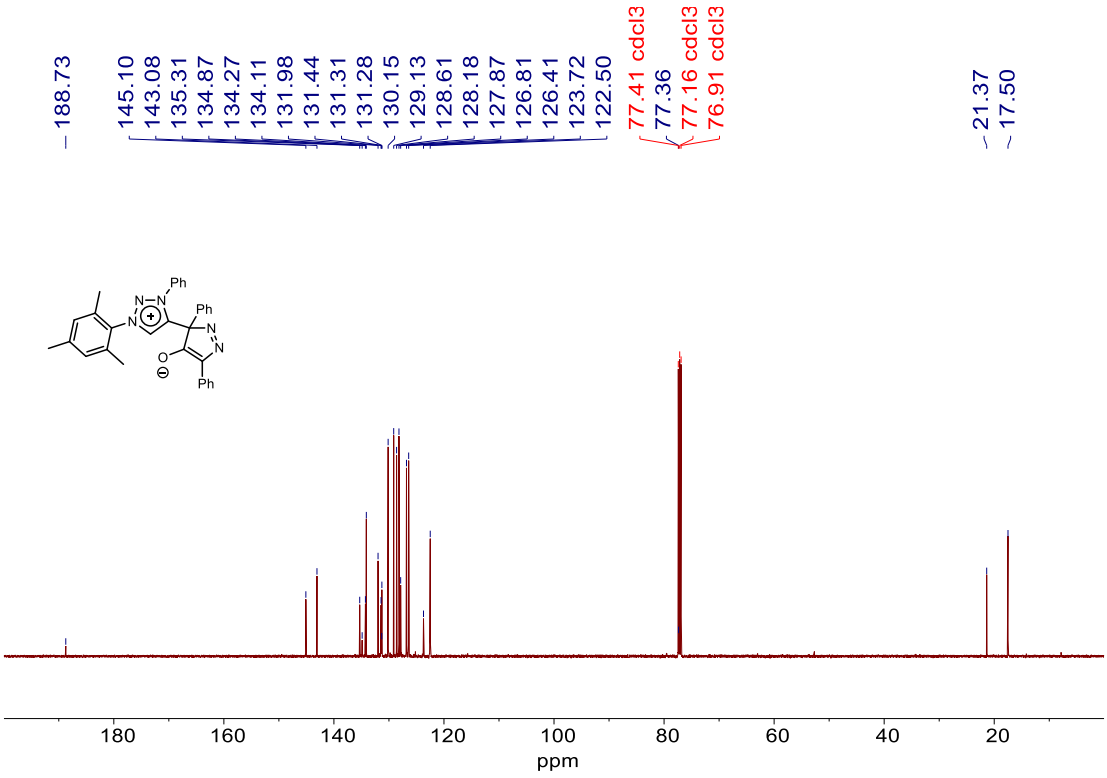



**Figure S19.** $^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **3ai**.

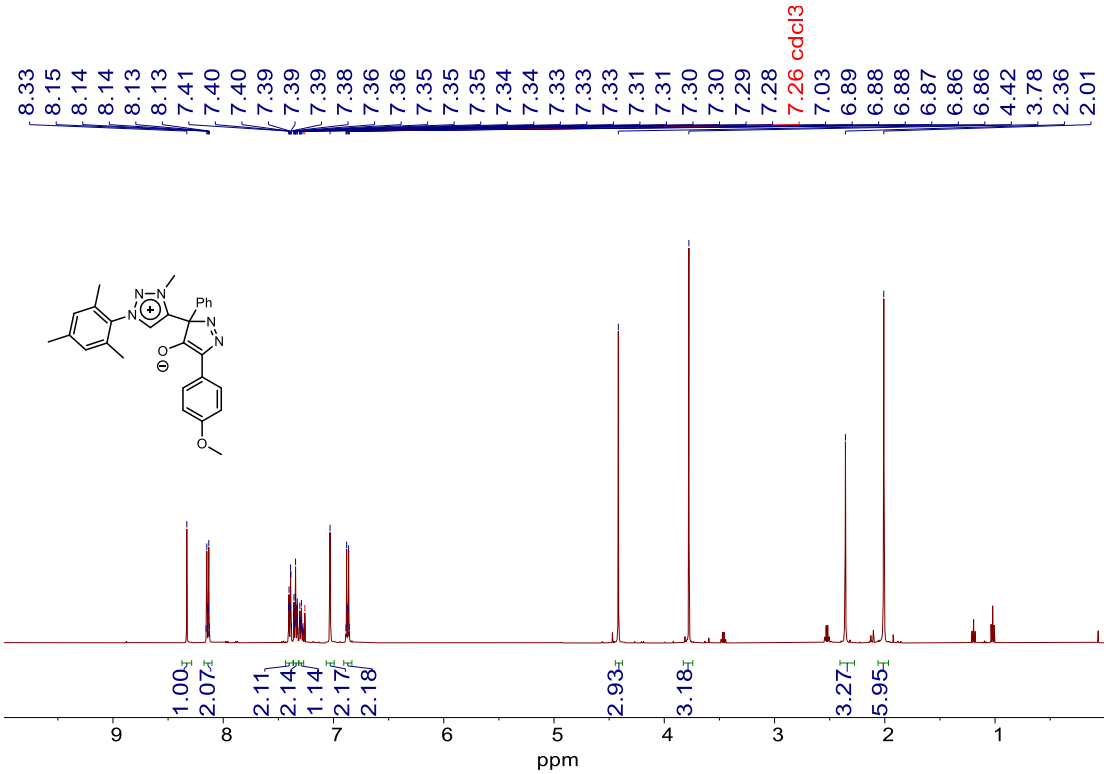



**Figure S20.** $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **3ba**.

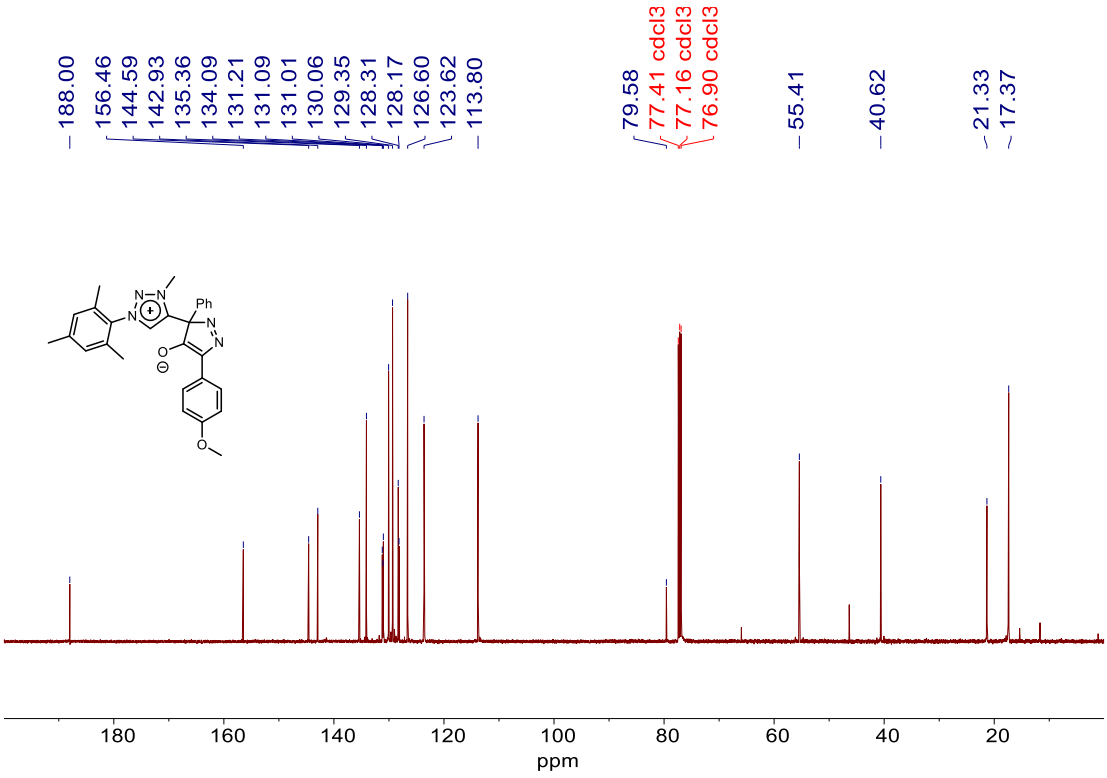



**Figure S21.** $^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **3ba**.

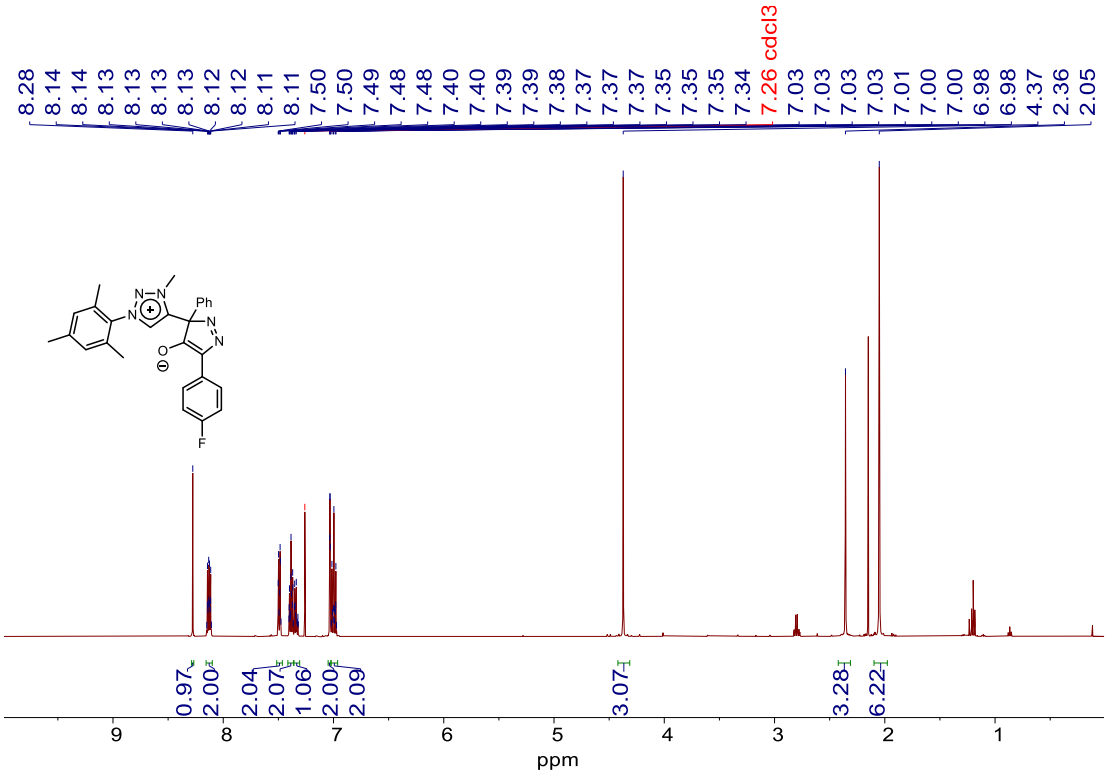



**Figure S22.** $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **3ca**.

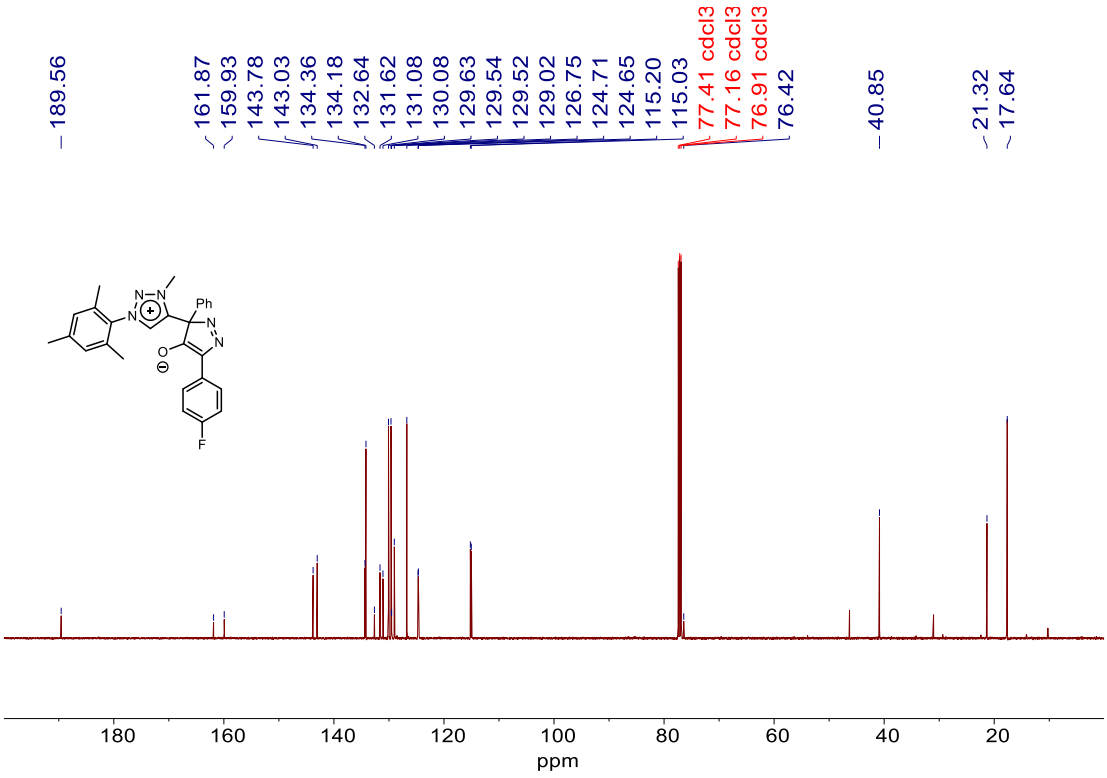



**Figure S23.** $^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **3ca**.

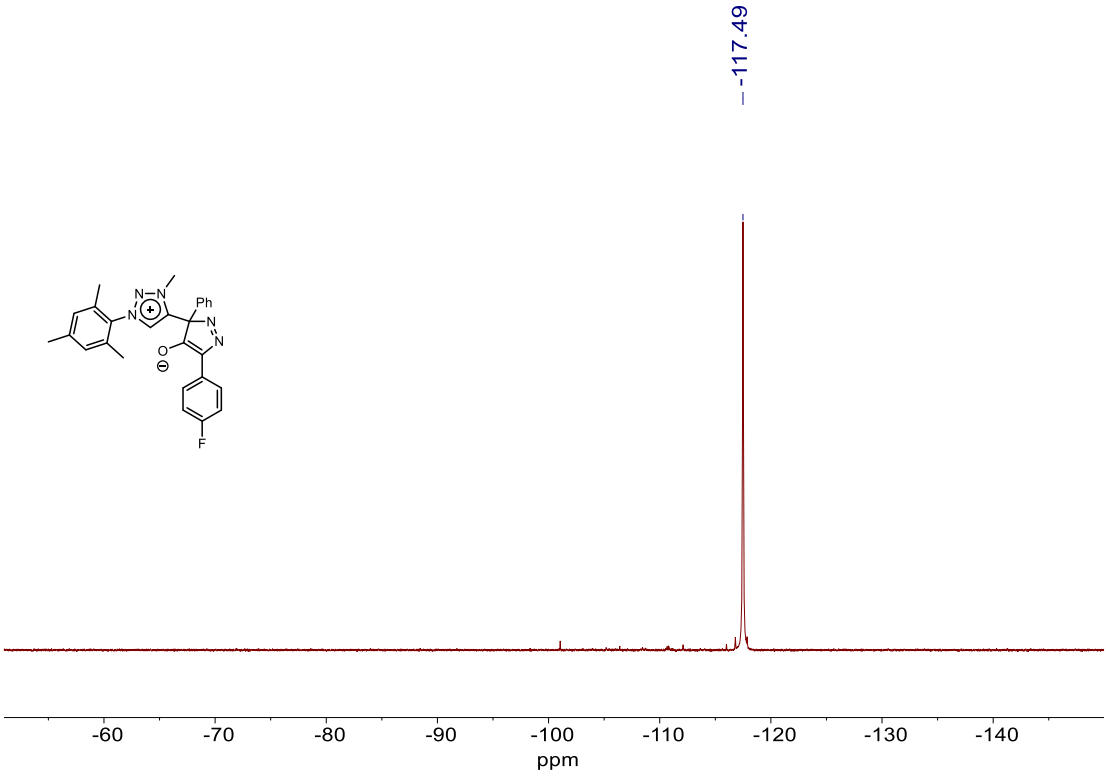



**Figure S24.** $^{19}F$ NMR (470 MHz, $CDCl_3$) spectrum of **3ca**.

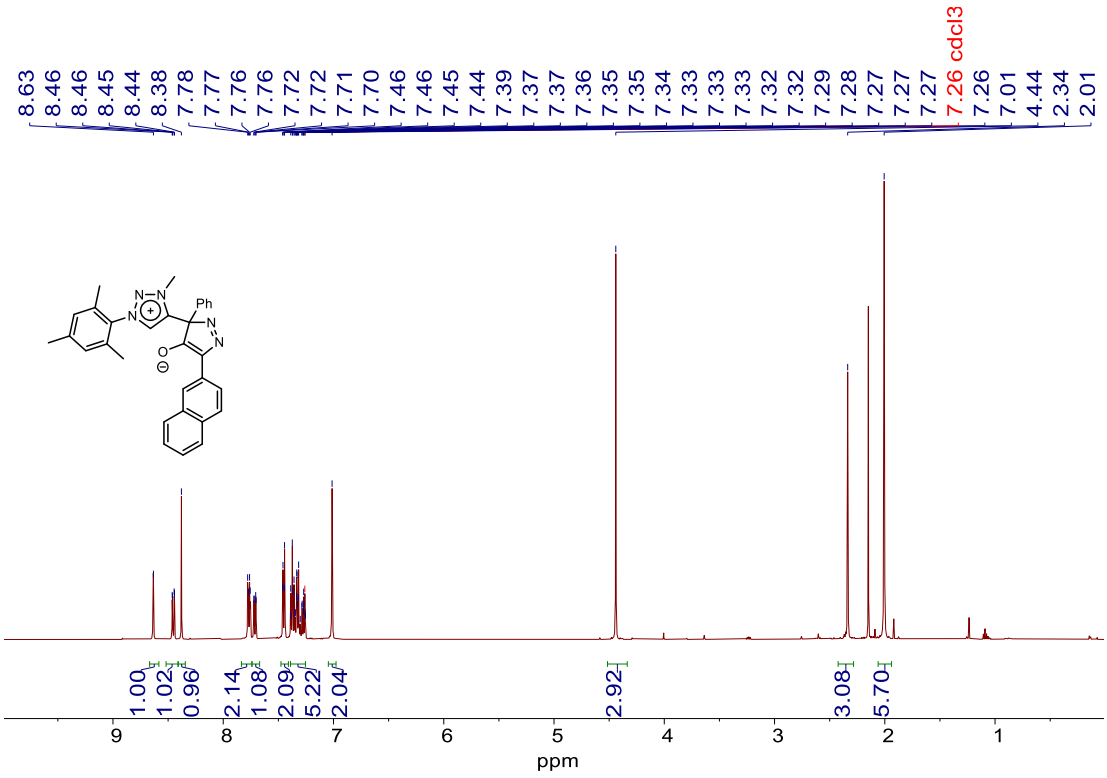



**Figure S25.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **3da**.

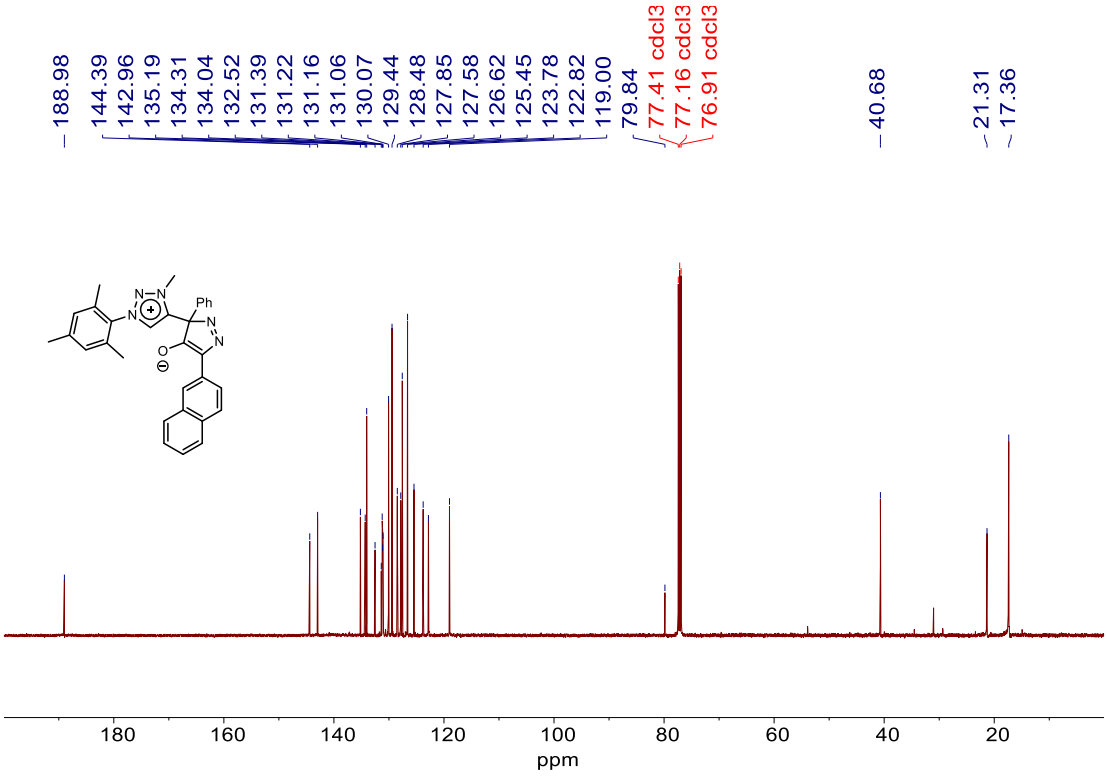



**Figure S26.** $^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **3da**.

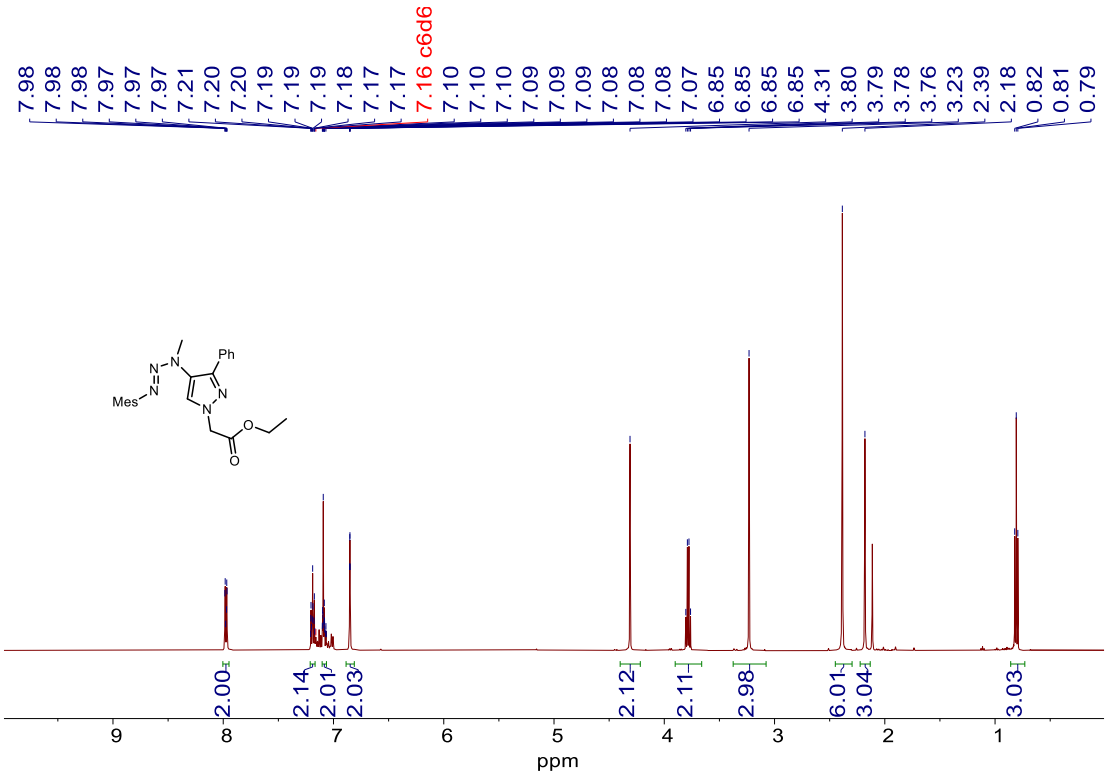



**Figure S27.** $^{1}$H NMR (500 MHz, $C_6D_6$) spectrum of **6**.

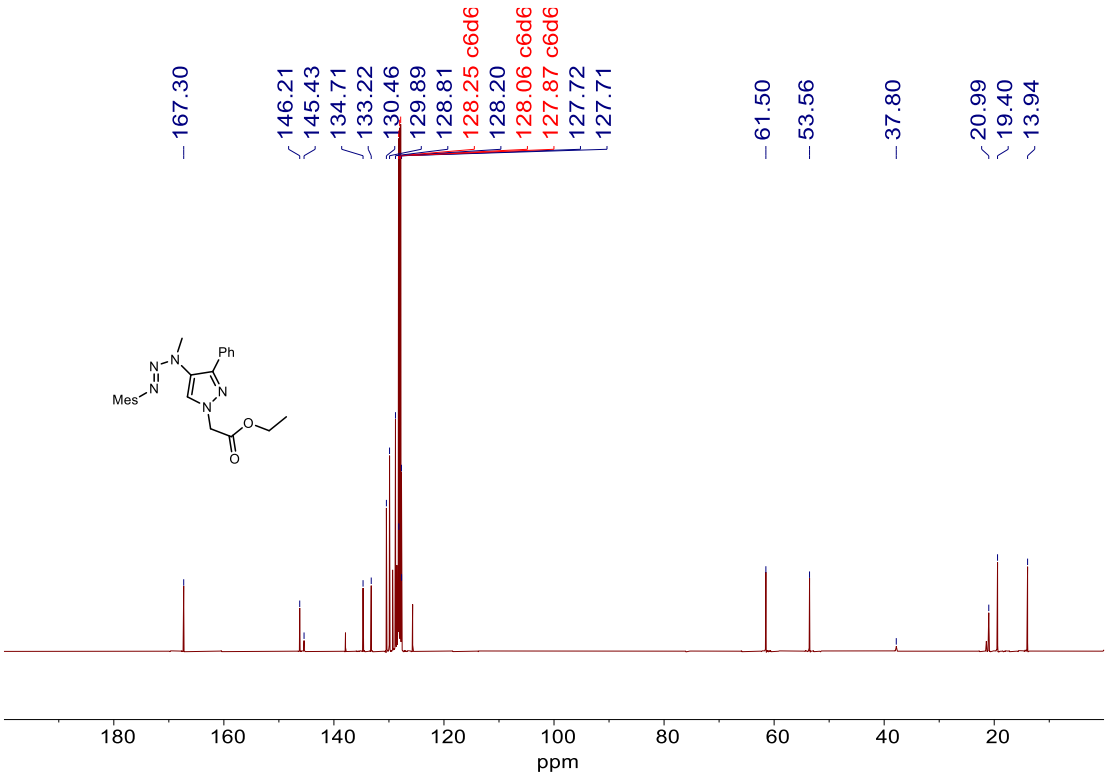



**Figure S28.** $^{13}$C NMR (126 MHz, $C_6D_6$) spectrum of **6**.

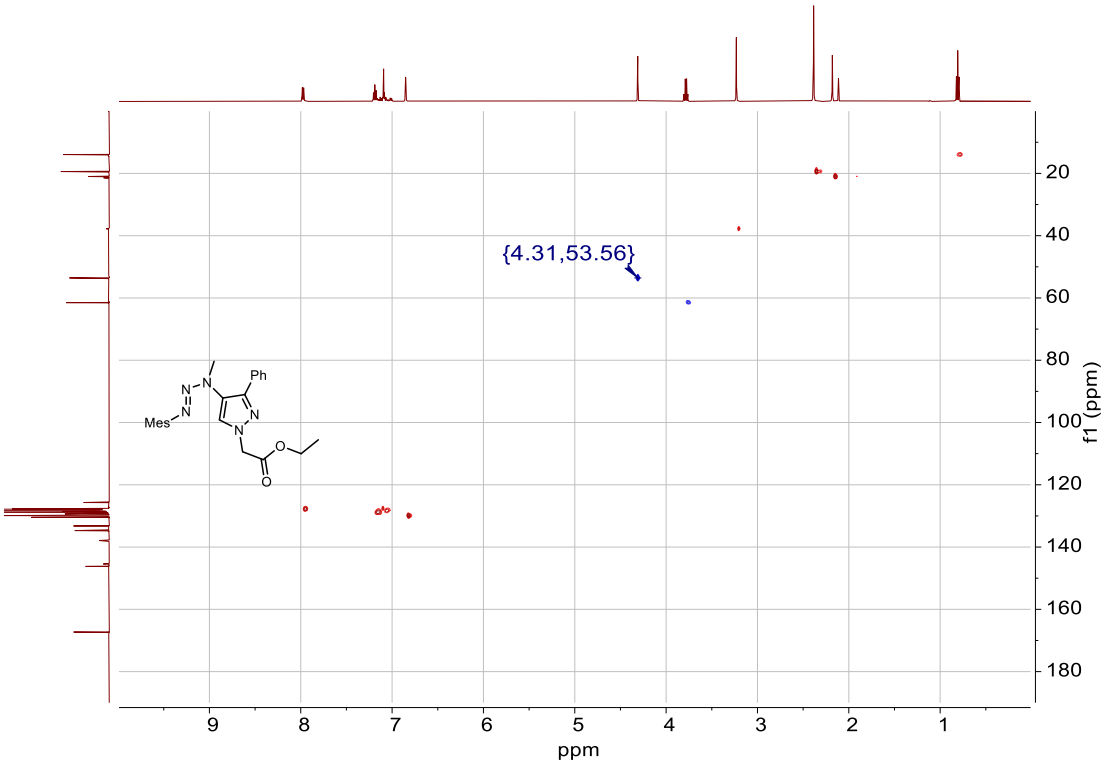



**Figure S29.** $^{1}H$-$^{13}C$-HSQC NMR (500 MHz, $C_6D_6$) of **6**.

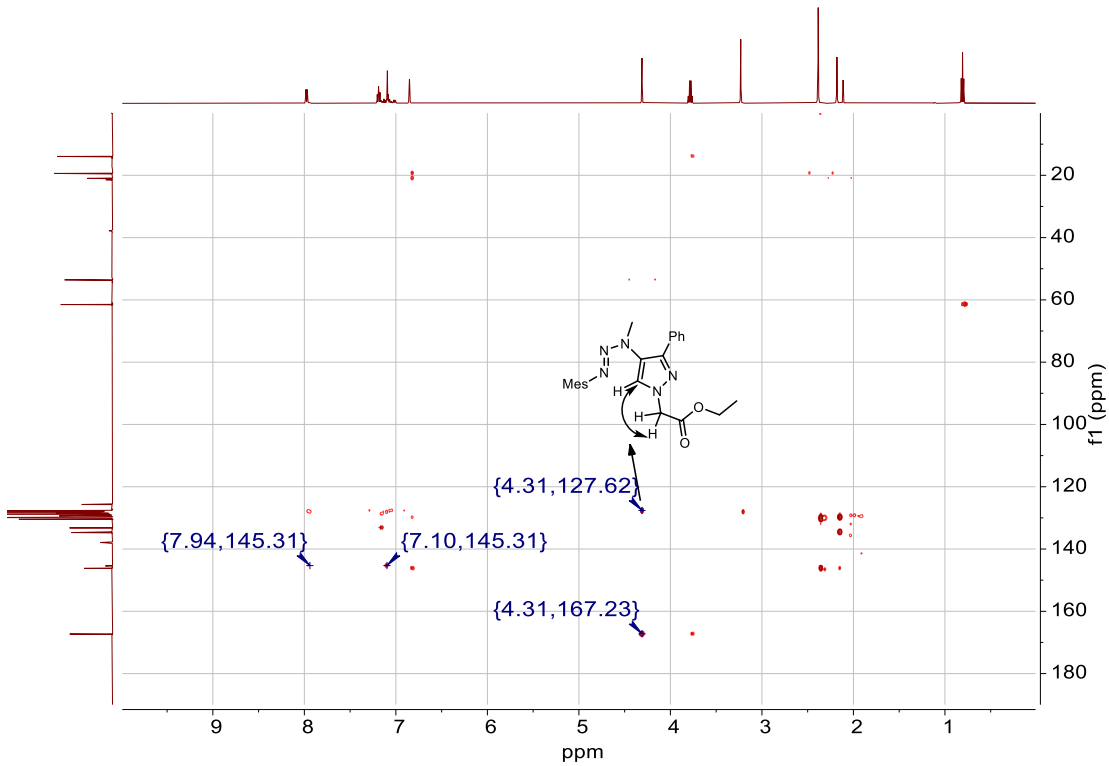



**Figure S30.** $^{1}H$-$^{13}C$-HMBC NMR (500 MHz, $C_6D_6$) of **6**.

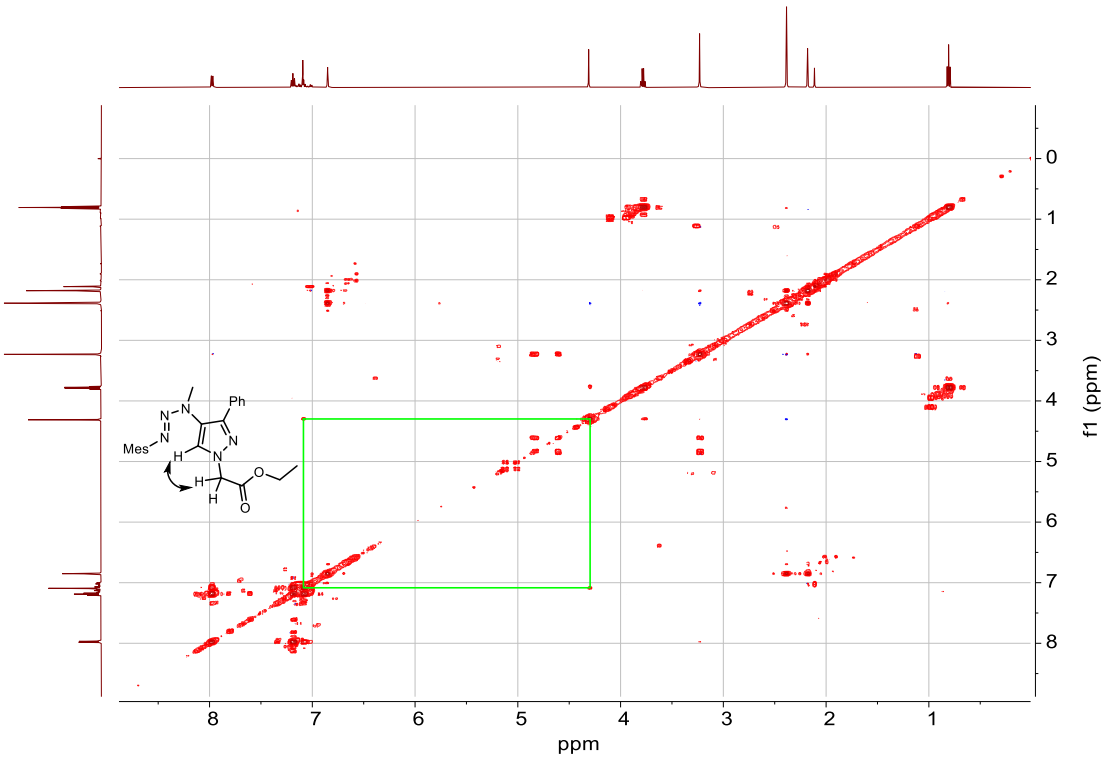



**Figure S31.** $^{1}$H-$^{1}$H-COSY NMR (500 MHz, $C_6D_6$) of **6**.

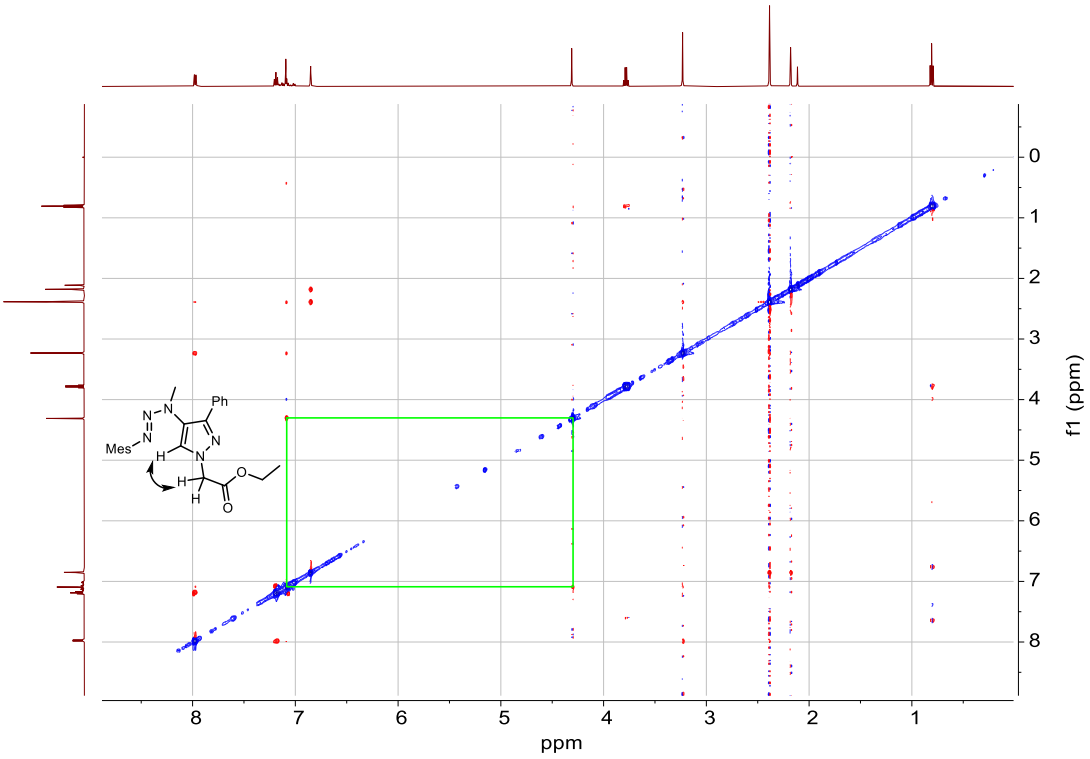



**Figure S32.** 2d-NOESY NMR (500 MHz, $C_6D_6$) of **6**.

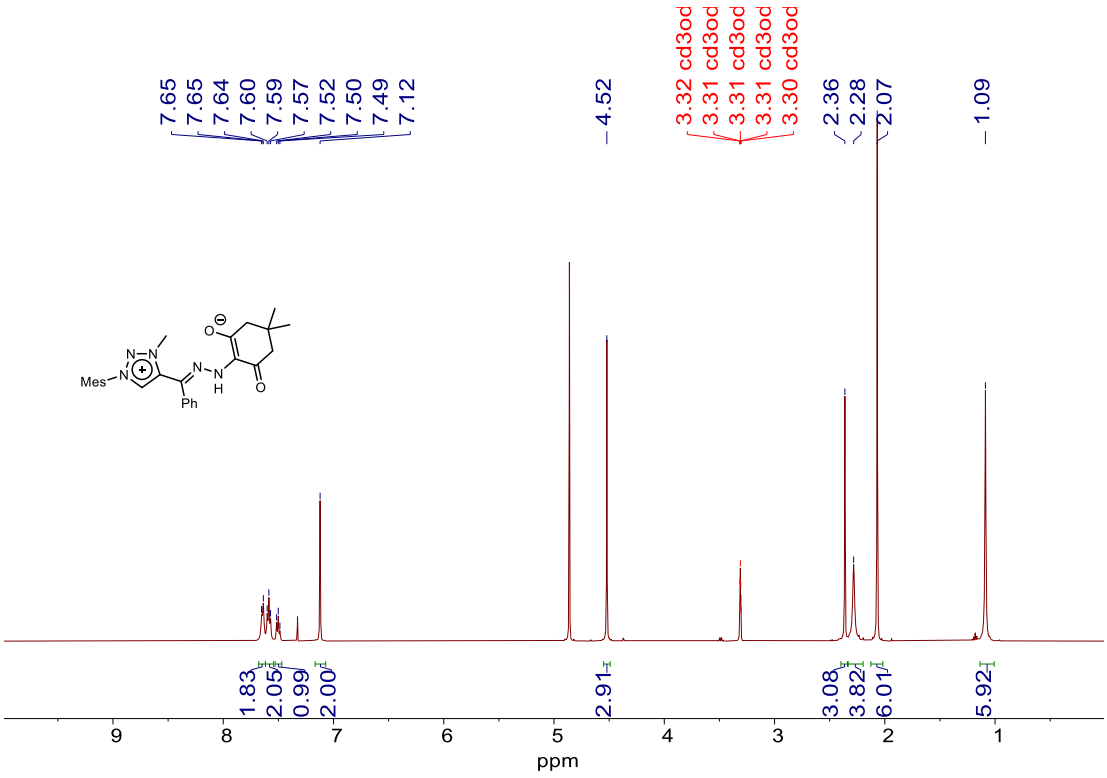



**Figure S33.** $^{1}$H NMR (500 MHz, $CD_3OD$) spectrum of **8**.

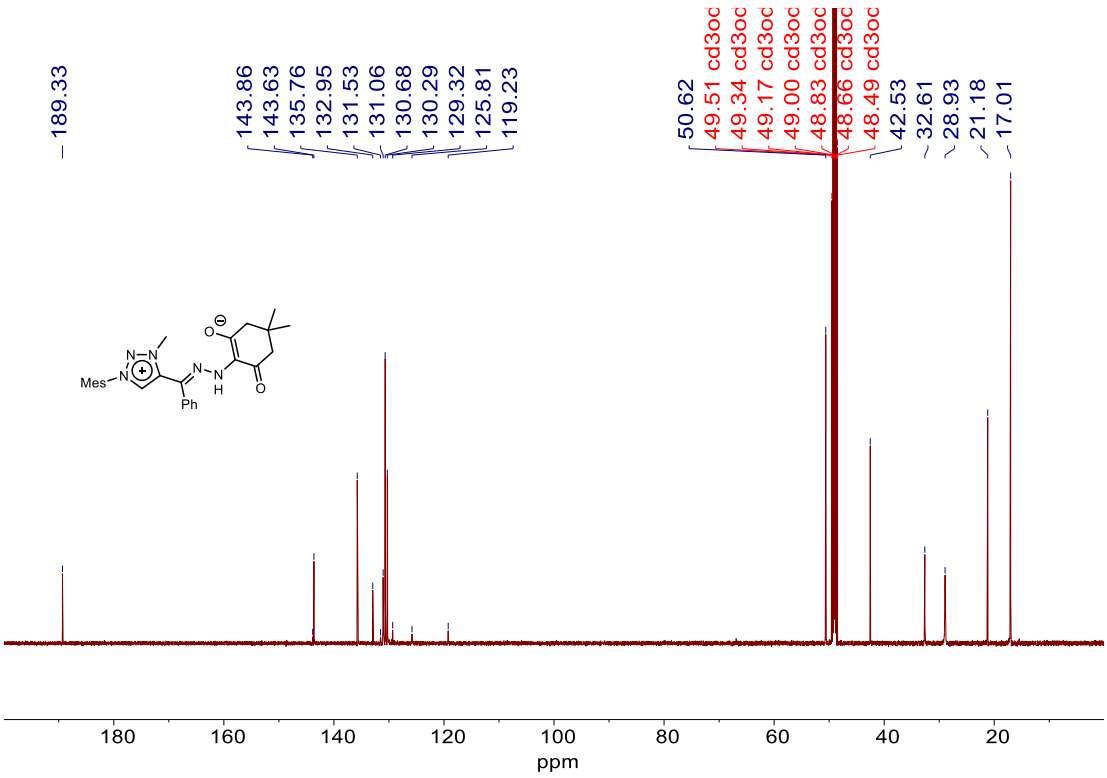



**Figure S34.** $^{13}$C NMR (126 MHz, $CD_3OD$) spectrum of **8**.

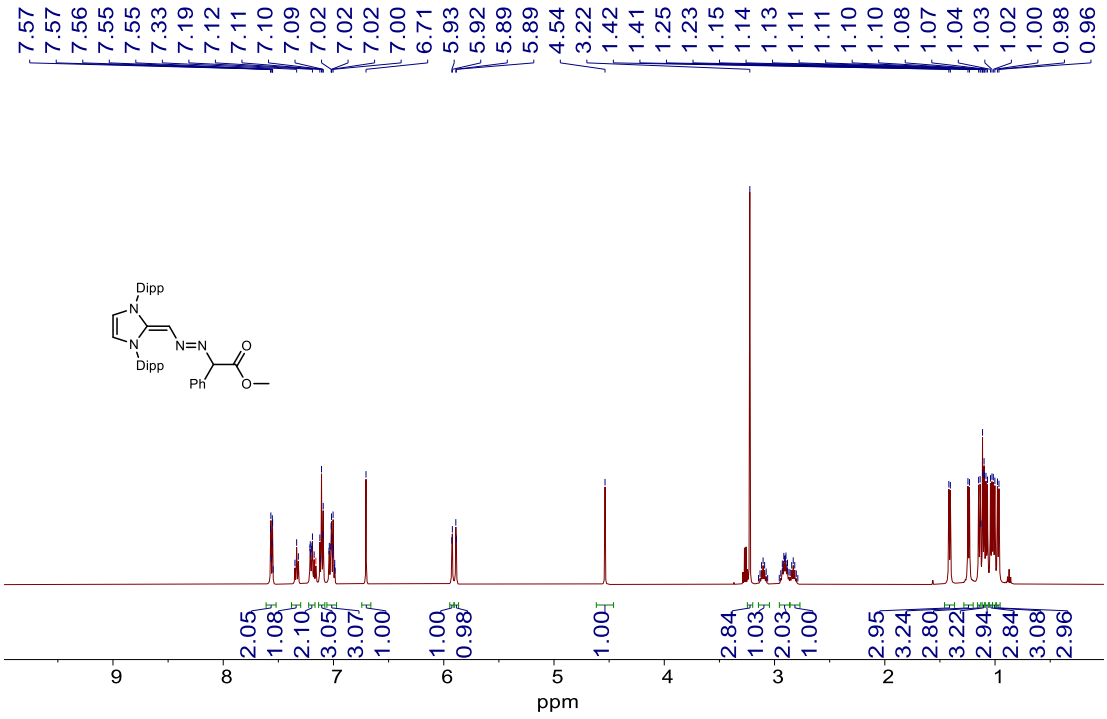



**Figure S35.** $^{1}$H NMR (500 MHz, $C_6D_6$) spectrum of **IV**.

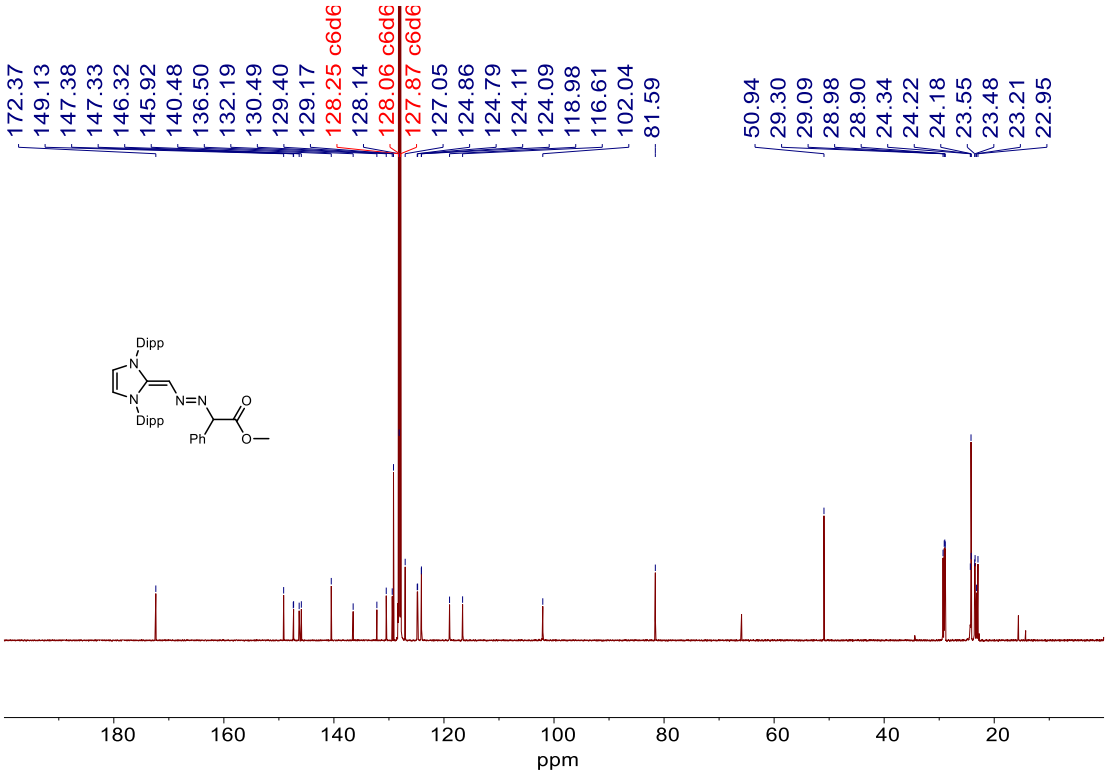



**Figure S36.** $^{13}$C NMR (126 MHz, $C_6D_6$) spectrum of **IV**.

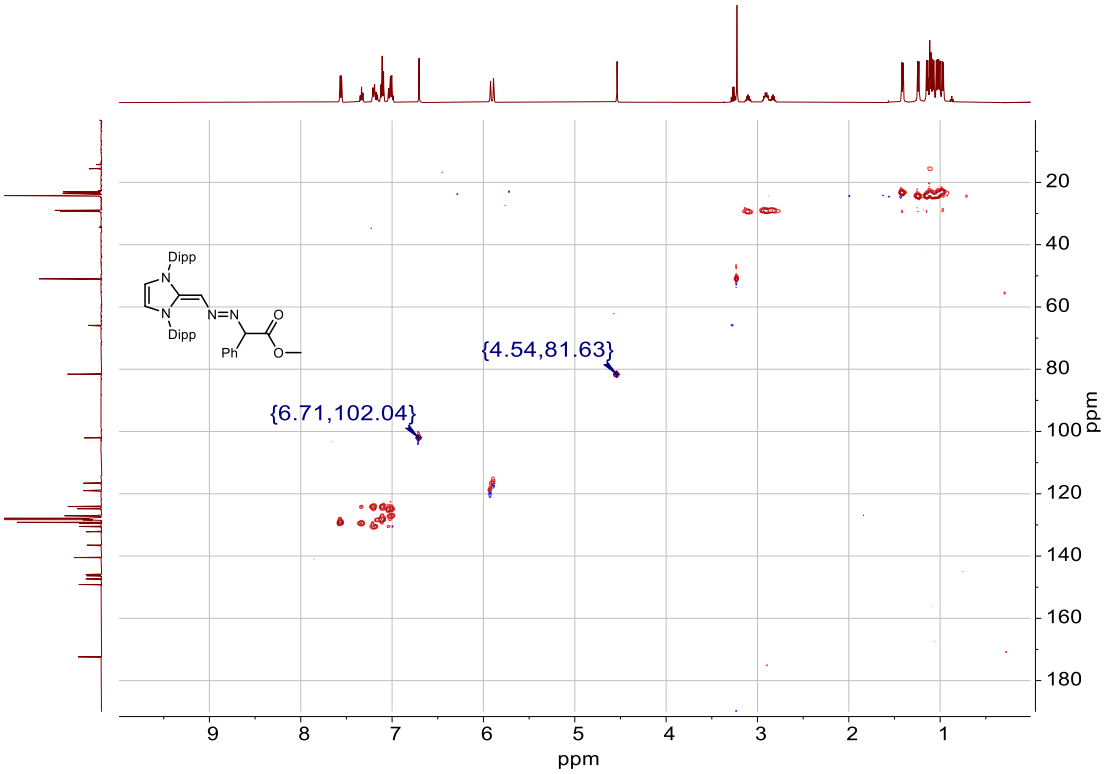



**Figure S37.** $^{1}H$-$^{13}C$-HSQC NMR (400 MHz, $C_6D_6$) of **IV**.

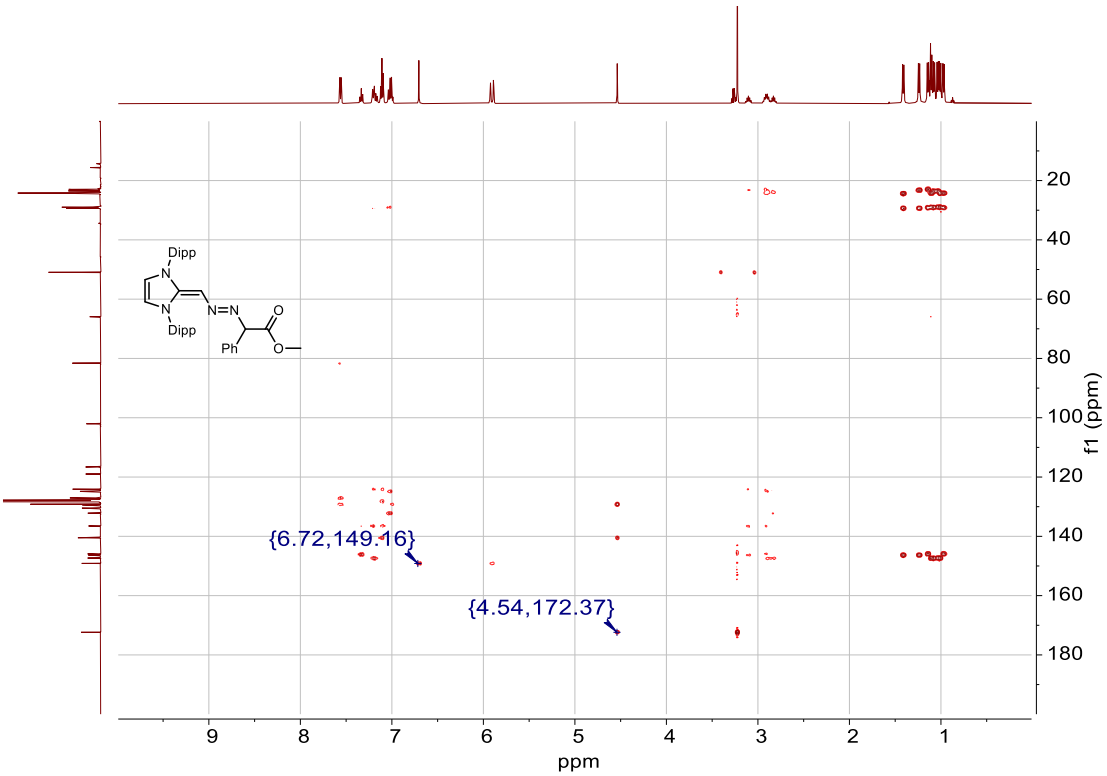



**Figure S38.** $^{1}H$-$^{13}C$-HMBC NMR (400 MHz, $C_6D_6$) of **IV**.

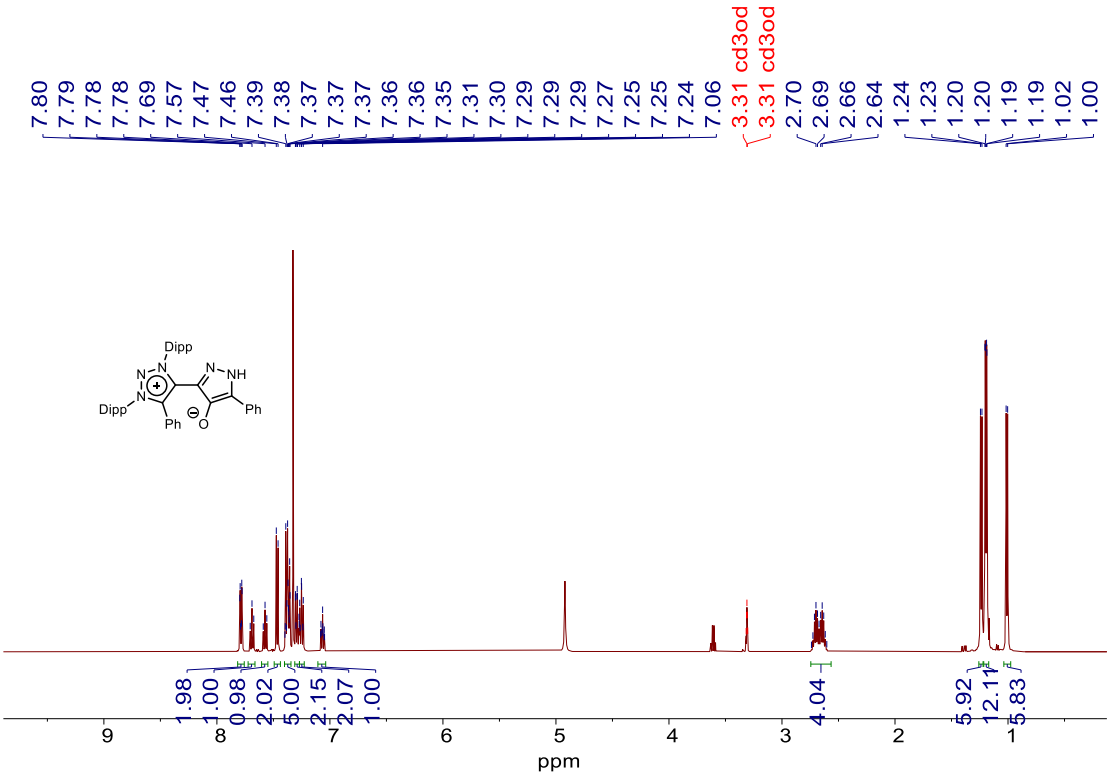



**Figure S39.** $^{1}$H NMR (500 MHz, $CD_3OD$) spectrum of **10**.

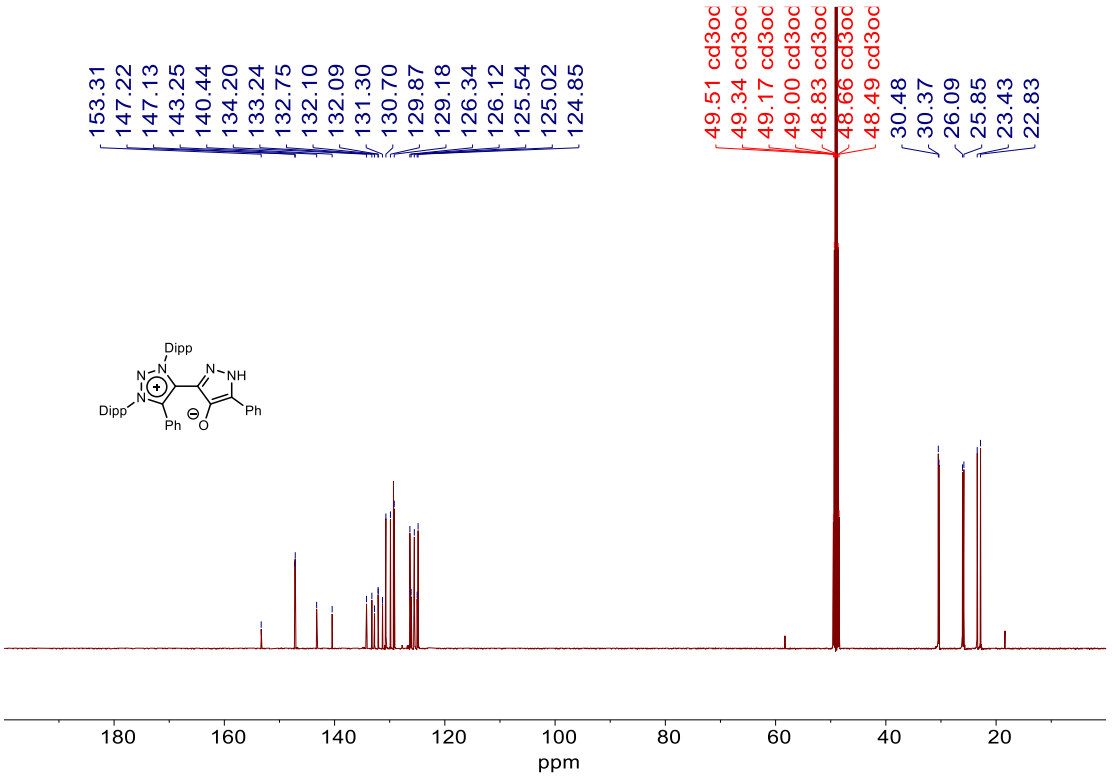



**Figure S40.** $^{13}$C NMR (126 MHz, $CD_3OD$) spectrum of **10**.

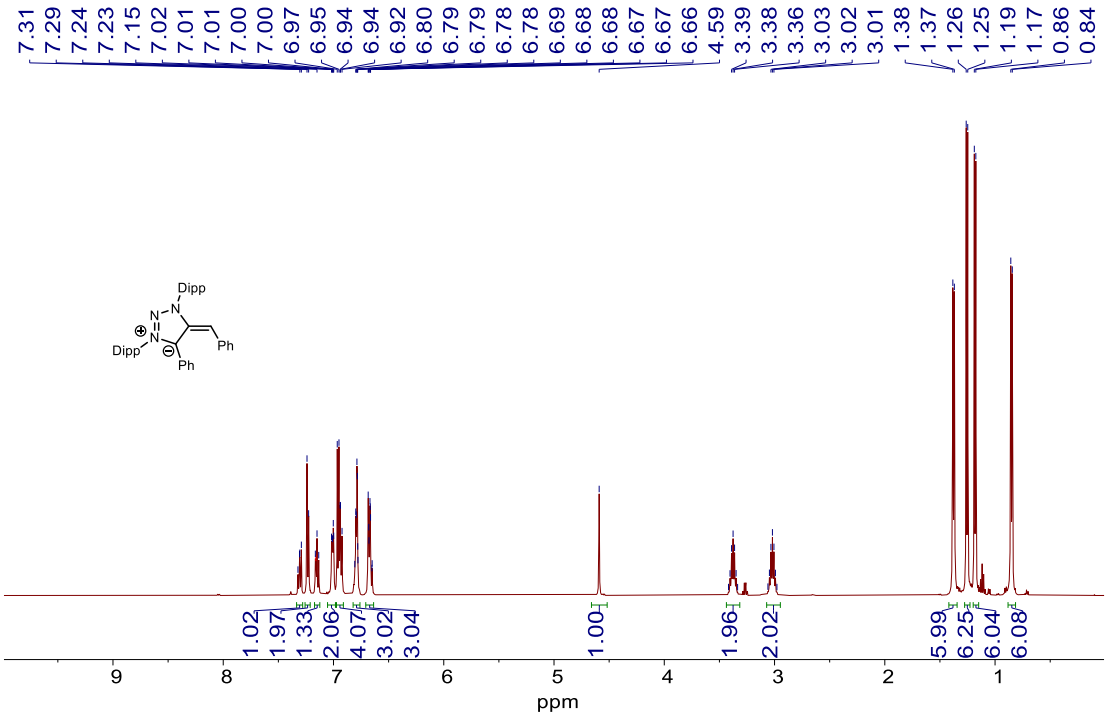



**Figure S41.** $^{1}$H NMR (500 MHz, $C_6D_6$) spectrum of **11**.

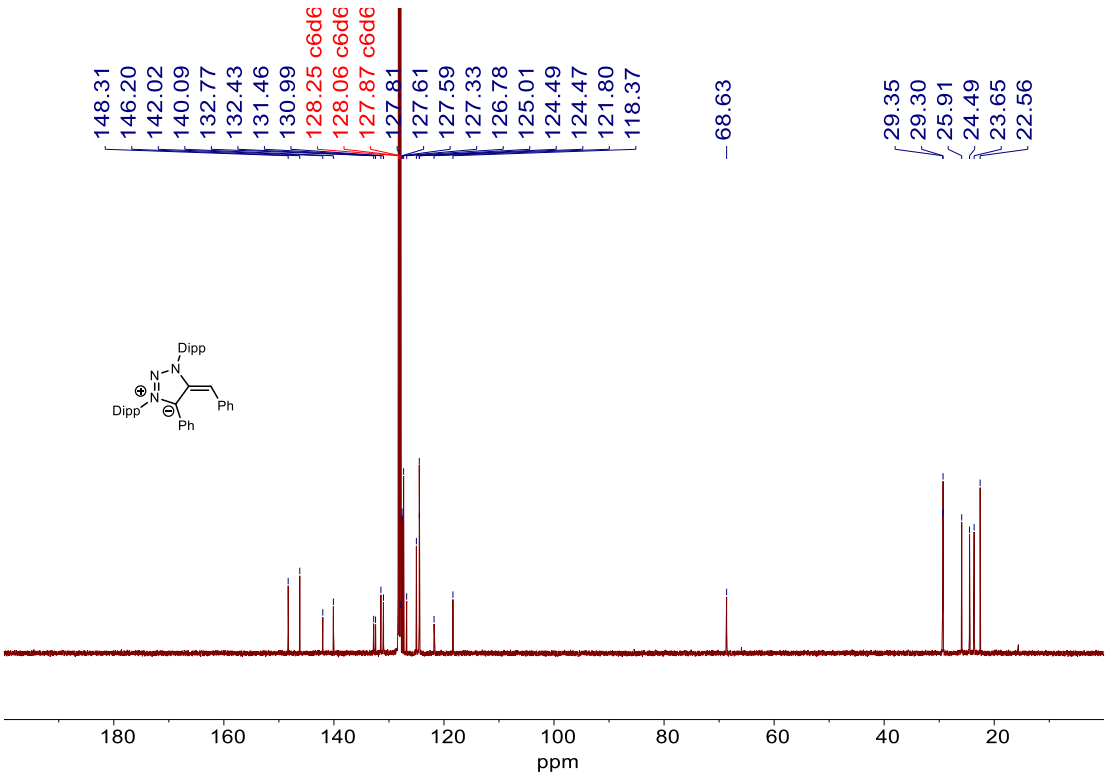



**Figure S42.** $^{13}$C NMR (126 MHz, $C_6D_6$) spectrum of **11**.

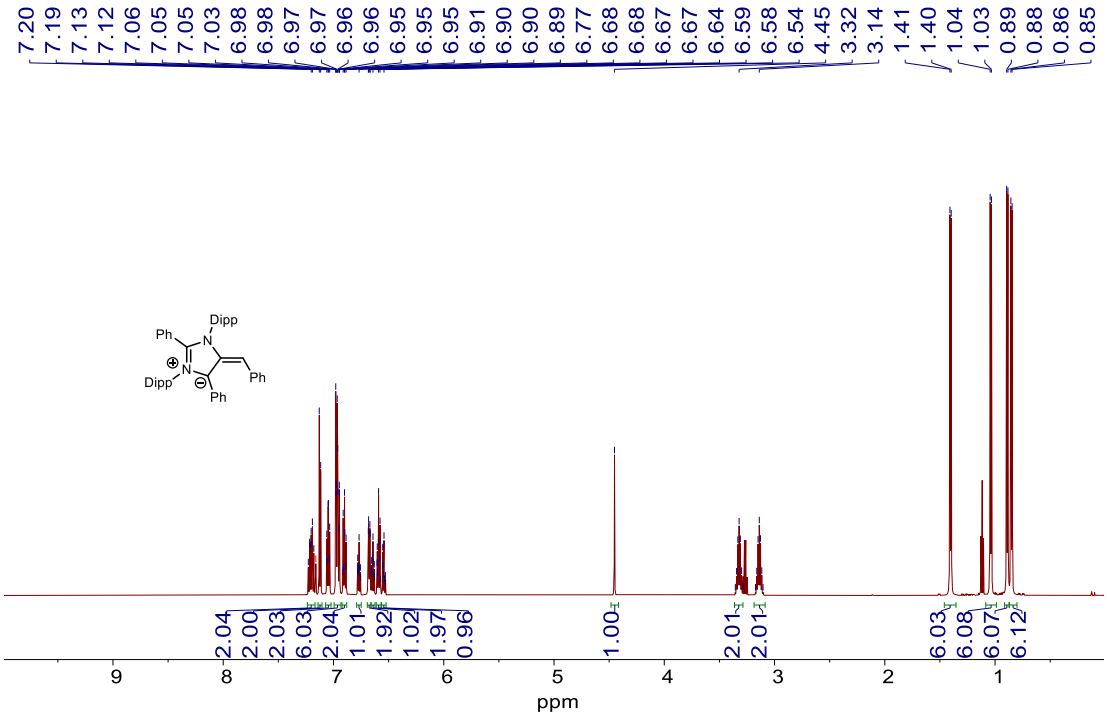



**Figure S43.** $^{1}$H NMR (600 MHz, $C_6D_6$) spectrum of **VI**.

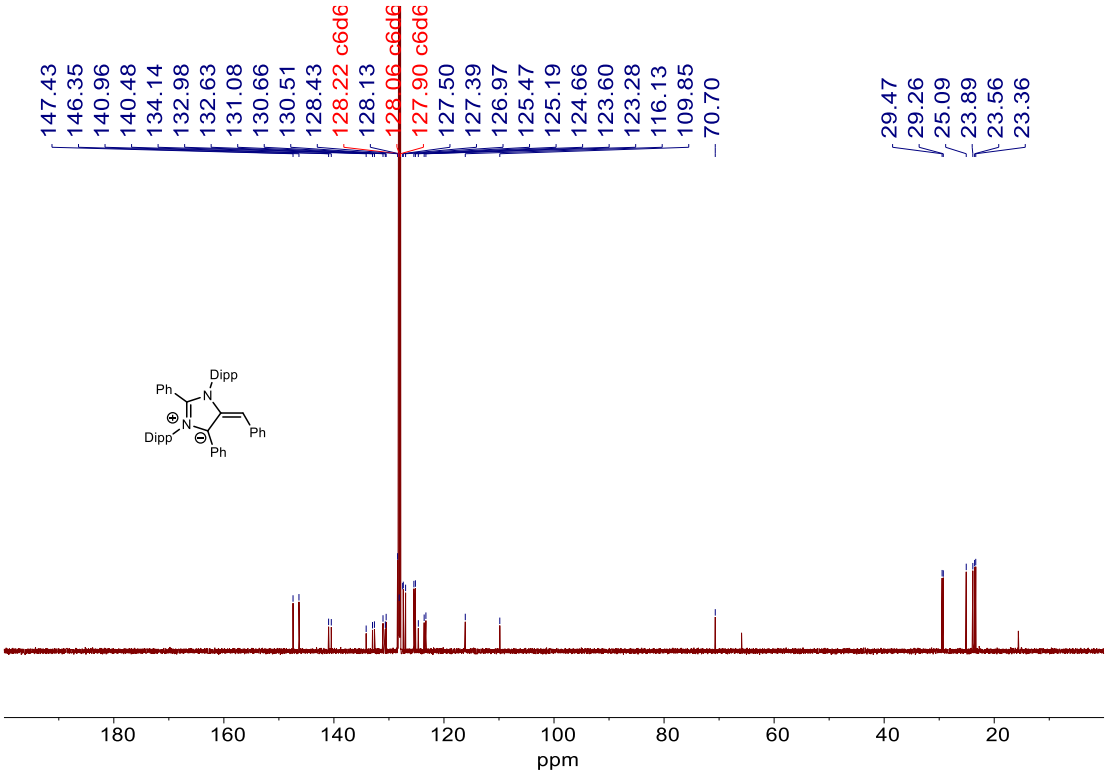



**Figure S44.** $^{13}$C NMR (151 MHz, $C_6D_6$) spectrum of **VI**.

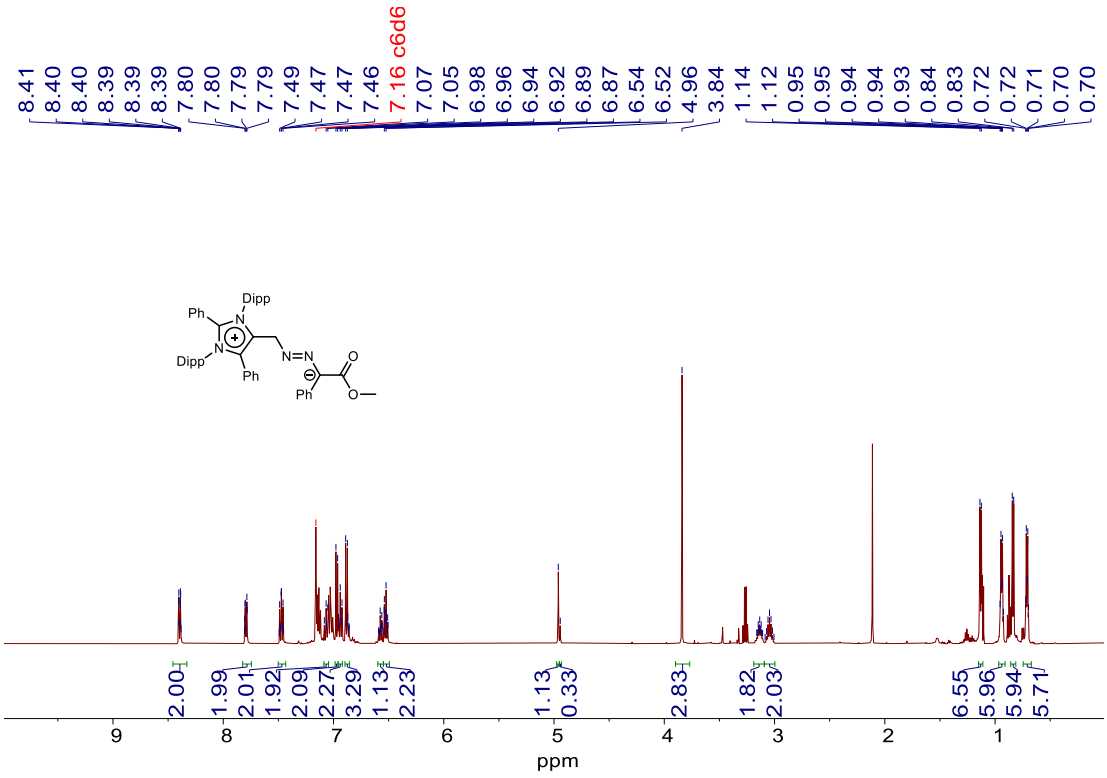



**Figure S45.** $^{1}$H NMR (500 MHz, $C_6D_6$) spectrum of **VII**.

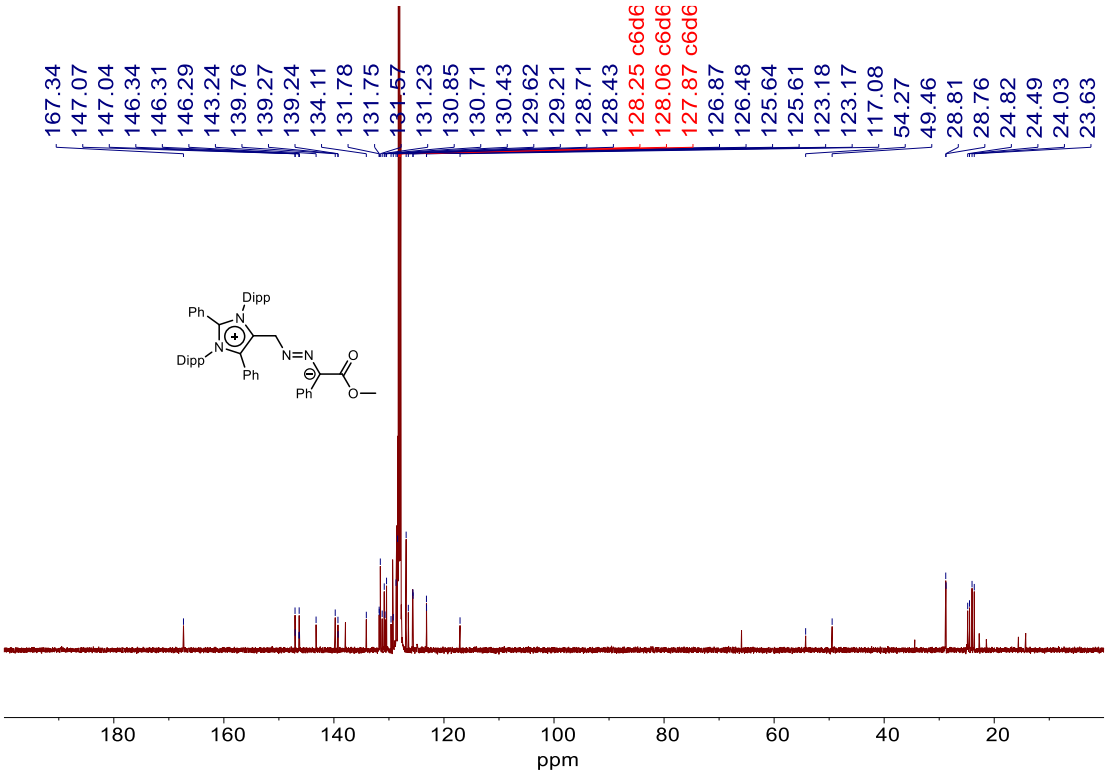



**Figure S46.** $^{13}$C NMR (126 MHz, $C_6D_6$) spectrum of **VII**.

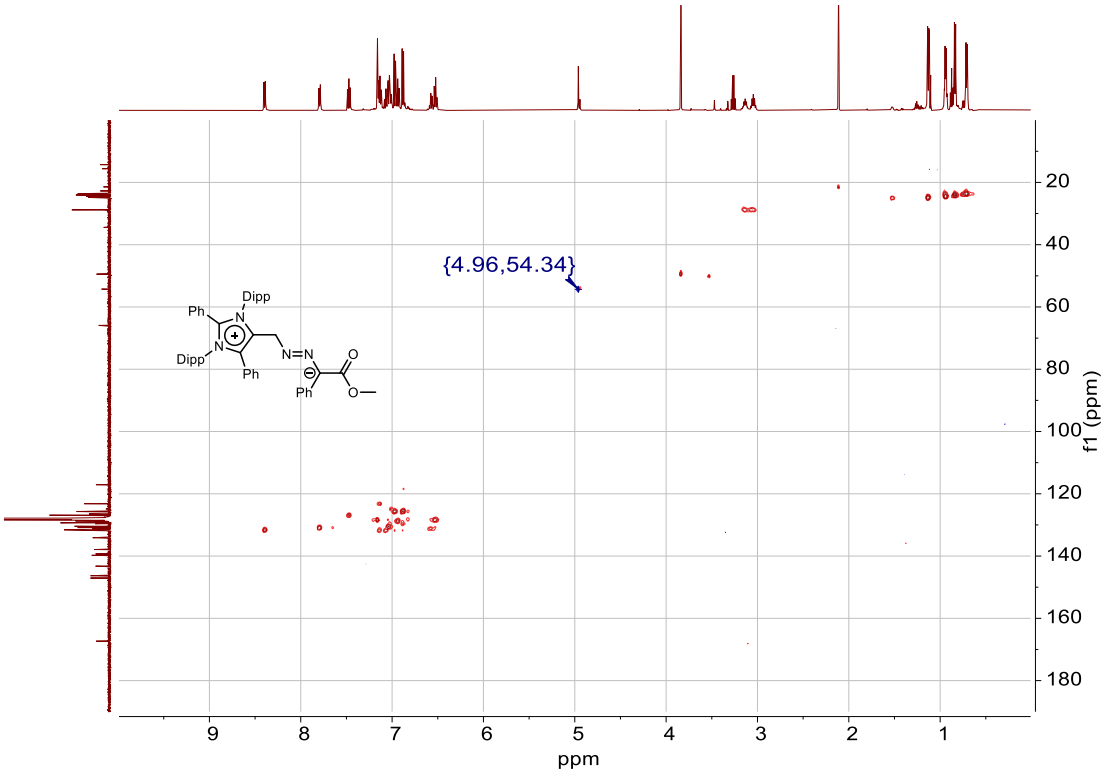



**Figure S47.** $^{1}H$-$^{13}C$-HSQC NMR (500 MHz, $C_6D_6$) of **VII**.

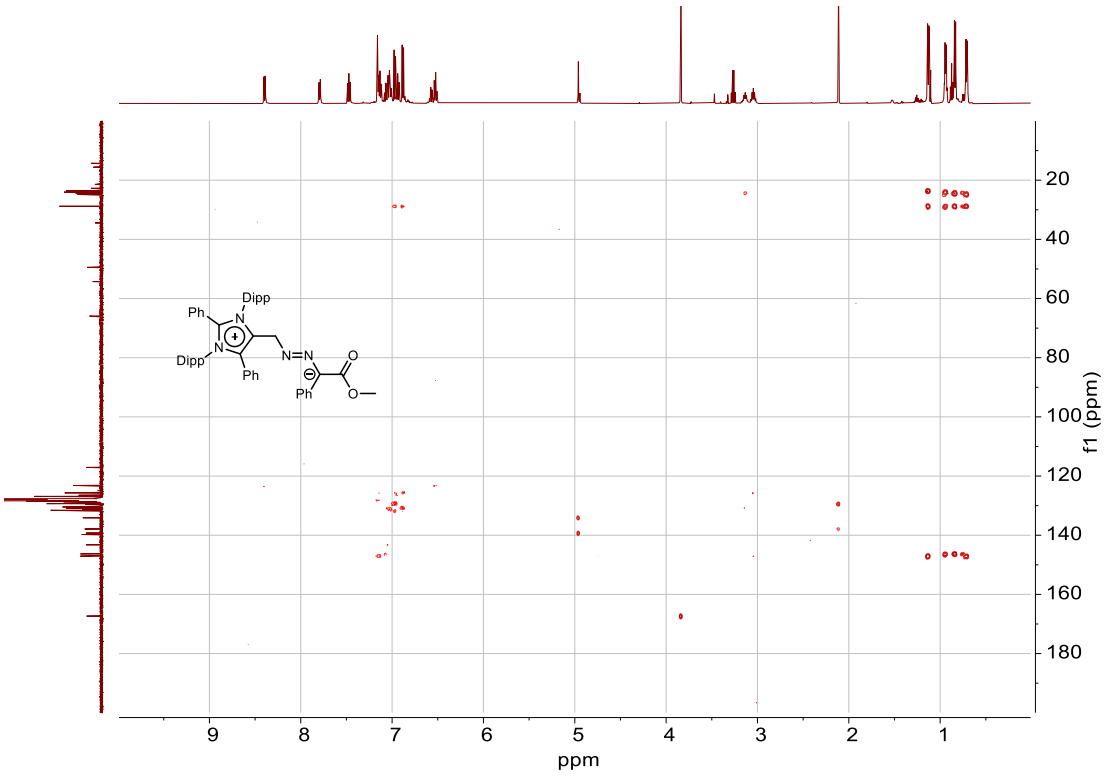



**Figure S48.** $^{1}H$-$^{13}C$-HMBC NMR (500 MHz, $C_6D_6$) of **VII**.

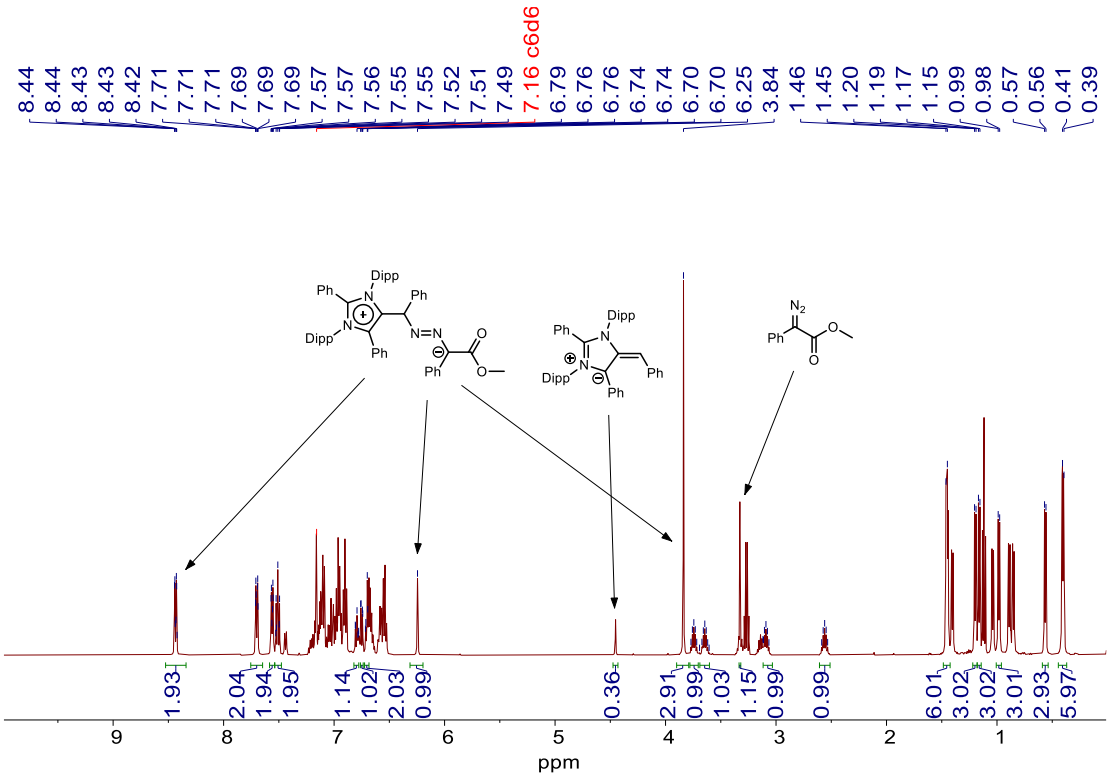



**Figure S49.** $^{1}$H NMR (500 MHz, $C_6D_6$) spectrum of **VIII** (significant dissociation into **1a** and **VI** is evident).

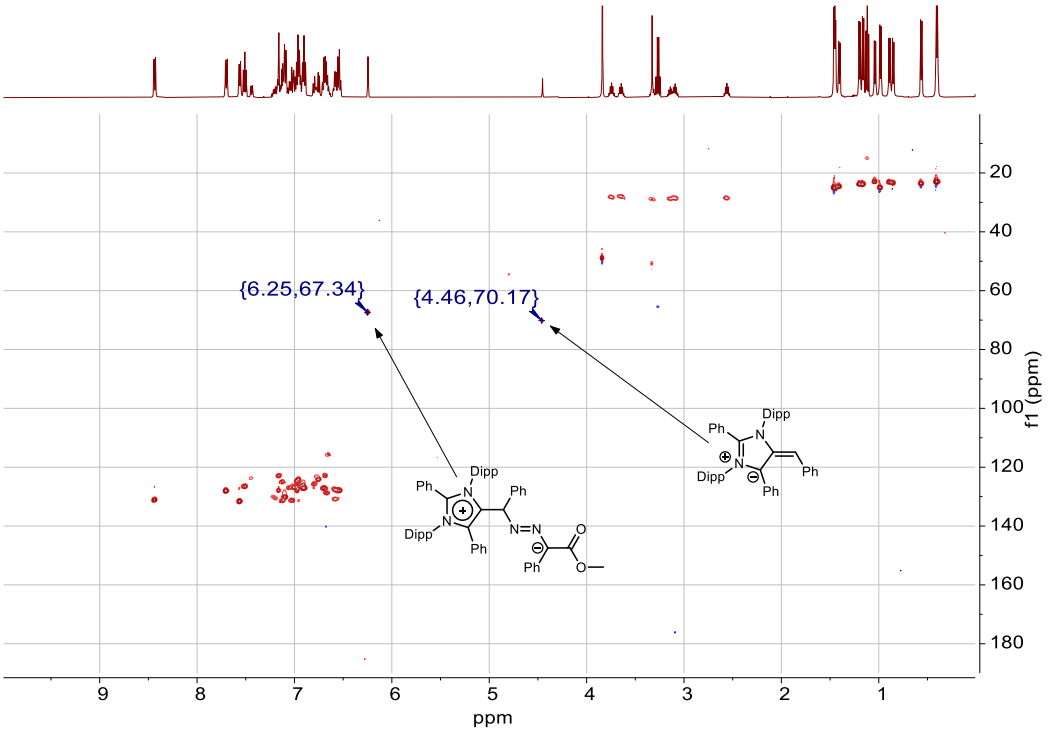



**Figure S50.** $^{1}$H-$^{13}$C-HSQC NMR (500 MHz, $C_6D_6$) of **VIII** (significant dissociation into **1a** and **VI** is evident).

## 3. NMR spectra of reaction between 1a and 2a at low temperature

A THF-$d_8$ solution of **2a** (400. μL, 48.0 mM of **2a** with 53.3 mM of $SiEt_4$) was transferred to an NMR tube. The NMR tube was then sealed with a septum, immersed into a dry ice/isopropanol bath (−78 °C). To the sample was added a THF-$d_8$ solution of **1a** (602 mM, 32.0 μL). The sample was then inserted into the probe of a 600 MHz NMR spectrometer, which was pre-cooled to −40 °C and calibrated. $^1$H NMR and $^1$H-$^{13}$C-HSQC spectra were recorded at −40 °C. The formation of mNHO−diazo ester adduct **4** was observed.

$^1$H NMR (600 MHz, THF-$d_8$) δ 8.39 (s, 1H, triazolium-*H*), 7.95 (d, $J$ = 8.0 Hz, 2H), 7.57 (d, $J$ = 7.8 Hz, 2H), 7.33 (t, $J$ = 7.5 Hz, 2H), 7.24 (t, $J$ = 7.3 Hz, 1H), 7.12 (s, 1H, Mes-*H*), 7.07 (s, 1H, Mes-*H*), 6.94 (t, $J$ = 7.6 Hz, 2H), 6.70 (t, $J$ = 7.3 Hz, 1H), 6.47 (s, 1H, C*H*), 4.42 (s, 3H, N-C$H_3$), 3.38 (s, 3H, COOC$H_3$), 2.35 (s, 3H, Mes-C$H_3$), 1.99 (s, 3H, Mes-C$H_3$), 1.83 (s, 3H, Mes-C$H_3$).

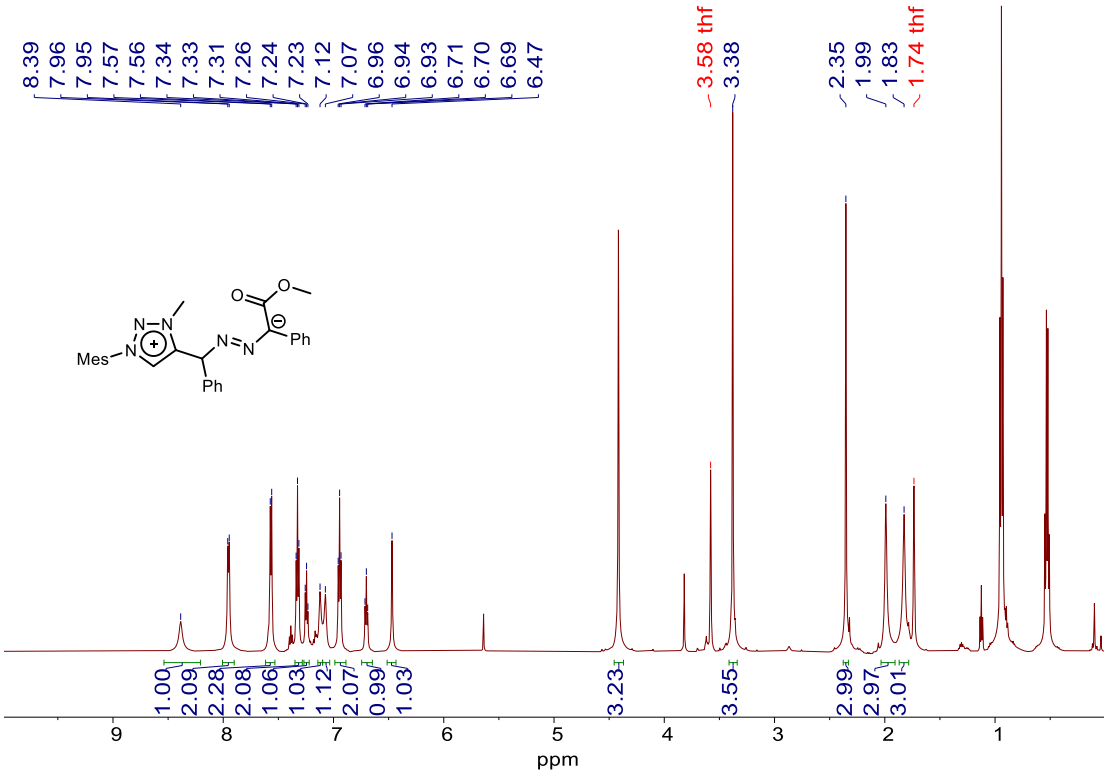



**Figure S51.** $^1$H NMR (600 MHz, THF-$d_8$) of the reaction mixture of **1a** and **2a** in THF-$d_8$ at −40 °C.

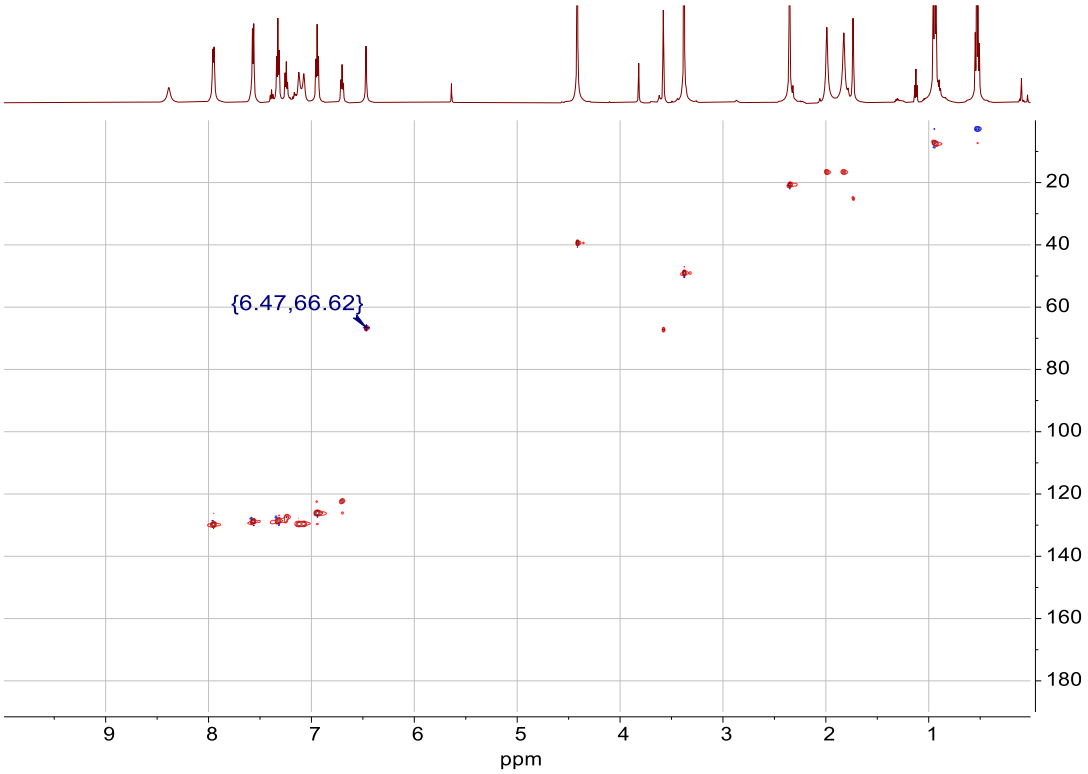



**Figure S52.** $^{1}$H-$^{13}$C-HSQC NMR (600 MHz, THF-$d_8$) of the reaction mixture of **1a** and **2a** in THF-$d_8$ at −40 °C.

## Reaction Kinetic

A THF-$d_8$ solution of **1a** (400. µL, 48.0 mM of **2a** with 53.3 mM of $SiEt_4$) in was transferred to an NMR tube. The NMR tube was then sealed with a septum, immersed into a dry ice/isopropanol bath (−78 °C). To the sample was added a THF-$d_8$ solution of **1a** (602 mM, 32.0 µL). The sample was then inserted into the probe of a 600 MHz NMR spectrometer, which was pre-cooled to −20 °C and calibrated. $^{1}$H NMR spectra were recorded at −20 °C every 9.3 minutes over a 5.6-hour period.

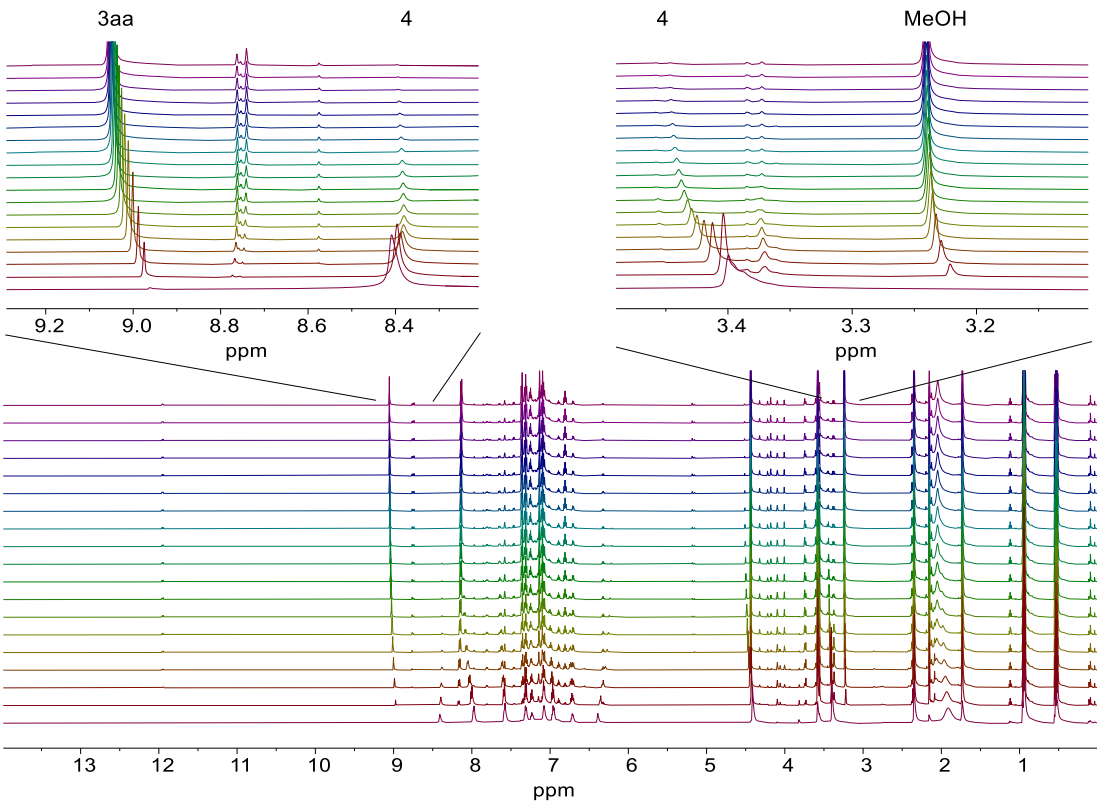



**Figure S53.** Partial $^{1}$H NMR spectra (600 MHz, THF-$d_8$) demonstrating the conversion of intermediate **4** to **3aa** and MeOH at −20 °C. Bottom to top: t = 2 min. for the first spectrum, with 18.6 min. intervals.

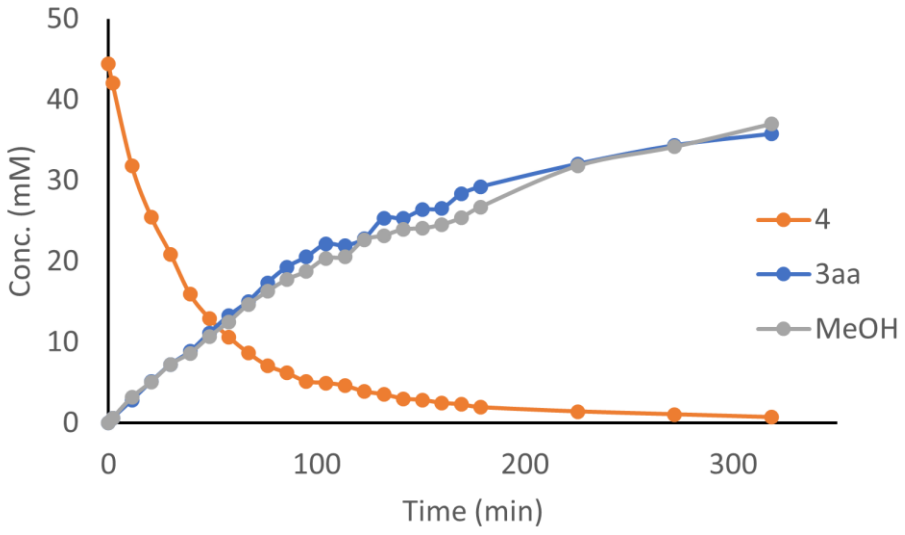



**Figure S54.** Experimentally measured concentrations for **4** → **3aa** + MeOH in at −20 °C ($SiEt_4$ was used as the internal standard).

## 4. 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.[12] The structures were solved by direct methods and refined using SHELX-2016 software package.[13,14] All non-hydrogen atoms were refined anisotropically except for some of the atoms of the disordered isopropyl group in **10**. All hydrogen atoms bonded to heteroatoms were located and their coordinates were refined, whereas those bonded to carbon atoms were calculated using the riding model. The diffuse residual electron density, Solvent Accessible Volume = 844 Å$^3$, # Electrons Found in S.A.V. = 309 in the lattice of **3aa**; Solvent Accessible Volume = 1479 Å$^3$, # Electrons Found in S.A.V. = 328 in the lattice of **10**; Solvent Accessible Volume = 1848 Å$^3$, # Electrons Found in S.A.V. = 463 in the lattice of **VI**; Solvent Accessible Volume = 1984 Å$^3$, # Electrons Found in S.A.V. = 516 in the lattice of **VII** were removed with the SQUEEZE function of PLATON[15] and was not included in the formula or the refinement. Selected crystallographic data are summarized in Tables S1−2.

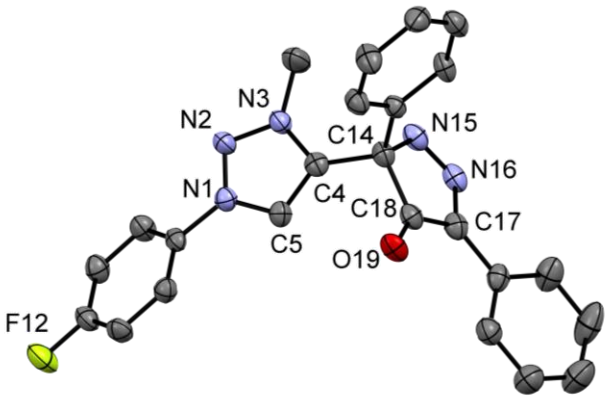



**Figure S55.** Intermolecular hydrogen bond of **3ae**.

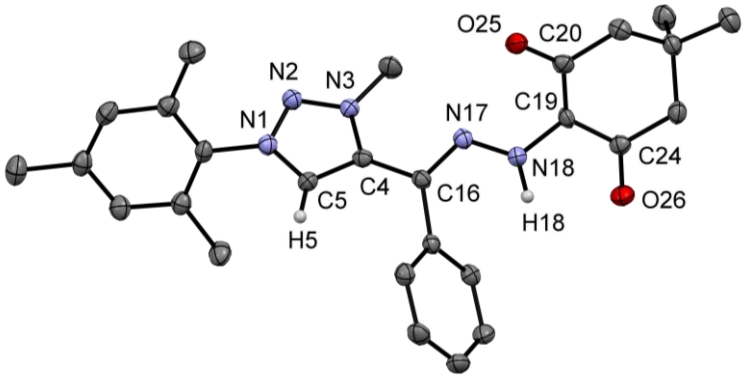



**Figure S56.** X-ray structures of **8** with thermal ellipsoids set to 50% probability level. All hydrogen atoms, except for H5 and H18, are omitted for clarity.

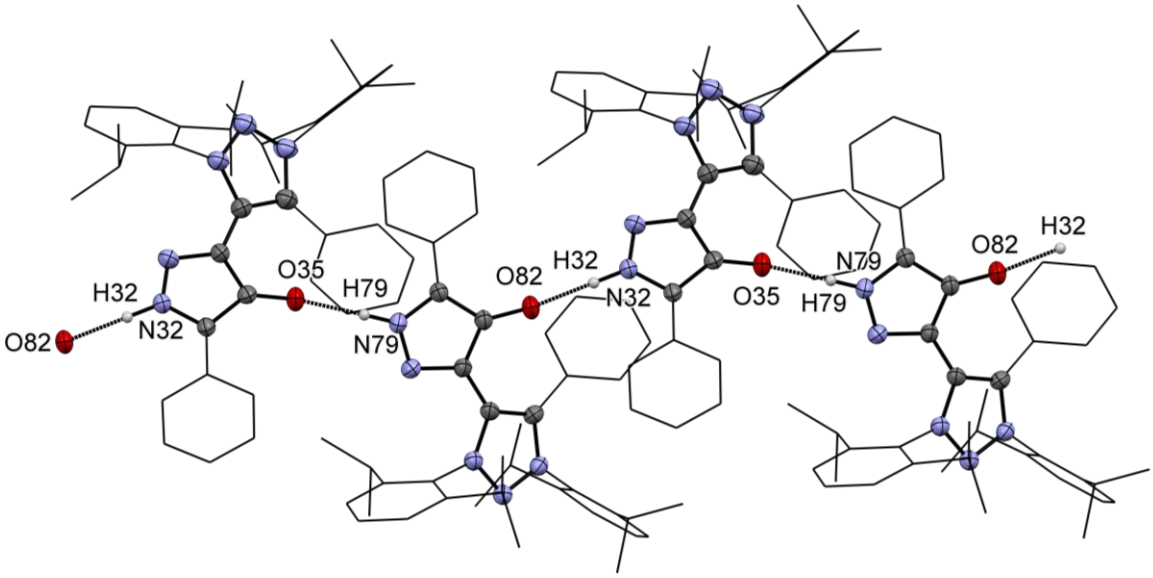



**Figure S57.** Intermolecular hydrogen bond of **10** to form a 1D chain.

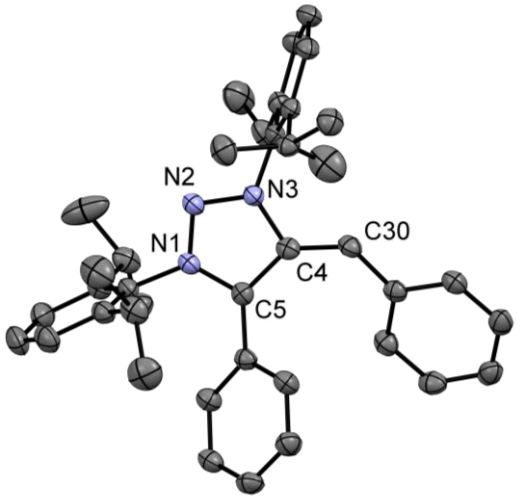



**Figure S58.** X-ray structure of **11**. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are omitted for clarity.

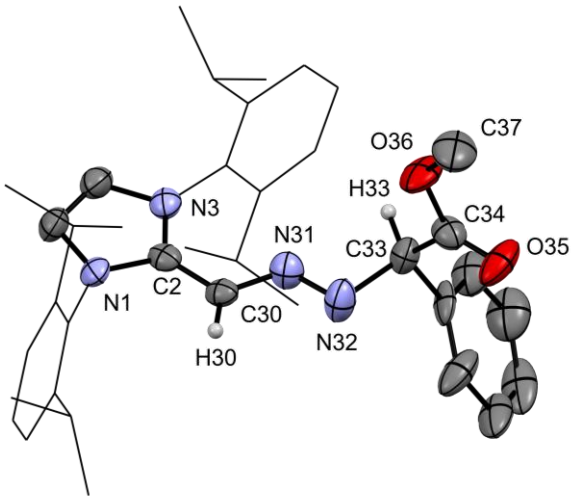



**Figure S59.** X-ray structures of **IV** with thermal ellipsoids shown at 50% probability level. All hydrogen atoms except for H30 and H33 are omitted and the aryl substituents on imidazole are drawn as wireframe for clarity.

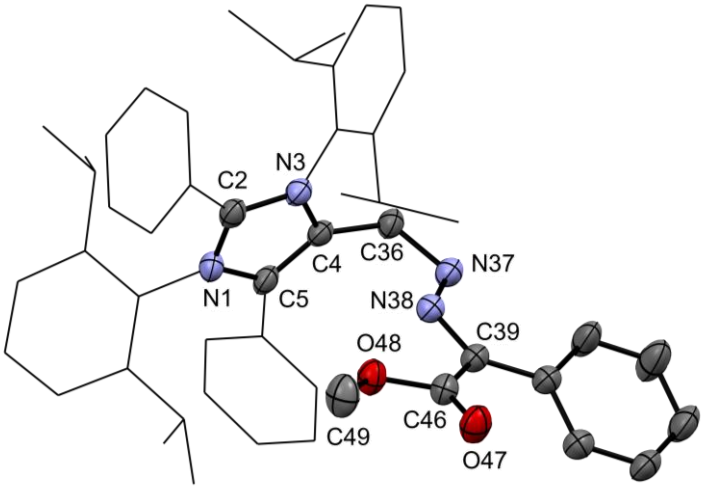



**Figure S60.** X-ray structures of **VII** with thermal ellipsoids shown at 50% probability level. All hydrogen atoms are omitted and the aryl substituents on imidazole are drawn as wireframe for clarity.

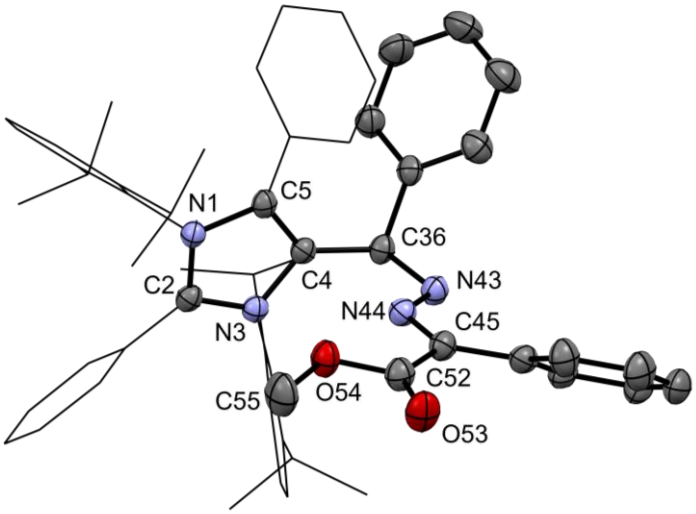



**Figure S61.** X-ray structures of **VIII** with thermal ellipsoids shown at 50% probability level. All hydrogen atoms are omitted and the aryl substituents on imidazole are drawn as wireframe for clarity.

**Table S1.** Selected crystallographic data for compounds **3aa**, **3ae**, **8**•0.5$C_6H_6$, **10**, and **11**.

| | **3aa** | **3ae** | **8•0.5$C_6H_6$** | **10** | **11** |
|---|---|---|---|---|---|
| Empirical formula | $C_{27}H_{25}N_5O$ | $C_{24}H_{18}N_5OF$ | $C_{30}H_{34}N_5O_2$ | $C_{41}H_{45}N_5O$ | $C_{39}H_{45}N_3$ |
| FW ($g \cdot mol^{-1}$) | 435.52 | 411.43 | 496.62 | 623.82 | 555.78 |
| Crystal system | Orthorhombic | Orthorhombic | Triclinic | Monoclinic | Monoclinic |
| Space Group | Pbcn | $P2_12_12_1$ | P-1 | $P2_1/n$ | $P2_1/n$ |
| $Z$ | 8 | 4 | 2 | 8 | 4 |
| $a$ (Å) | 26.084(7) | 8.4361(5) | 9.4016(11) | 12.217(3) | 9.797(3) |
| $b$ (Å) | 17.067(5) | 10.9609(6) | 9.7932(8) | 22.188(5) | 10.878(3) |
| $c$ (Å) | 11.802(3) | 21.3387(12) | 14.9499(17) | 29.927(8) | 30.575(8) |
| $\alpha$ (deg) | 90 | 90 | 100.871(3) | 90 | 90 |
| $\beta$ (deg) | 90 | 90 | 101.457(3) | 97.789(9) | 96.548(17) |
| $\gamma$ (deg) | 90 | 90 | 92.165(3) | 90 | 90 |
| $V$ ($Å^3$) | 5254(3) | 1973.13(19) | 1320.8(2) | 8037(3) | 3237.5(15) |
| $D_{calcd}$, ($g \cdot cm^{-3}$) | 1.101 | 1.385 | 1.249 | 1.031 | 1.140 |
| $\mu$ ($mm^{-1}$) | 0.070 | 0.095 | 0.080 | 0.063 | 0.066 |
| $F$(000) | 1840 | 856 | 530 | 2672 | 1200 |
| no. of obsd reflns | 3854 | 3245 | 3989 | 10429 | 4328 |
| no. of params refnd | 307 | 286 | 349 | 869 | 397 |
| goodness of fit | 1.031 | 1.028 | 1.025 | 1.040 | 1.039 |
| $R_1$ ($I>2\sigma$) | 0.0635 | 0.0516 | 0.0602 | 0.0769 | 0.0636 |
| $wR_2$ | 0.1826 | 0.1195 | 0.1408 | 0.2070 | 0.1553 |

**Table S2.** Selected crystallographic data for compounds **IV**, **VII** and **VIII**.

| | **IV** | **VII** | **VIII** |
|---|---|---|---|
| Empirical formula | $C_{37}H_{46}N_4O_2$ | $C_{49}H_{54}N_4O_2$ | $C_{55}H_{58}N_4O_2$ |
| FW ($g \cdot mol^{-1}$) | 578.78 | 730.96 | 807.05 |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space Group | P-1 | $P2_1/n$ | P-1 |
| $Z$ | 2 | 4 | 4 |
| $a$ (Å) | 10.384(8) | 12.713(5) | 17.399(7) |
| $b$ (Å) | 75.72(3) | 27.880(12) | 18.549(7) |
| $c$ (Å) | 16.438(12) | 15.682(7) | 20.435(7) |
| $\alpha$ (deg) | 72.09(3) | 90 | 87.920(11) |
| $\beta$ (deg) | 75.72(3) | 98.665(13) | 76.584(11) |
| $\gamma$ (deg) | 82.68(2) | 90 | 68.008(10) |
| $V$ ($Å^3$) | 1692(2) | 5495(4) | 5939(4) |
| $D_{calcd}$, ($g \cdot cm^{-3}$) | 1.136 | 0.884 | 0.903 |
| $\mu$ ($mm^{-1}$) | 0.071 | 0.054 | 0.055 |
| $F$(000) | 624 | 1568 | 1728 |
| no. of obsd reflns | 7844 | 12762 | 27800 |
| no. of params refnd | 463 | 506 | 1117 |
| goodness of fit | 0.995 | 1.050 | 1.059 |
| $R_1$ ($I>2\sigma$) | 0.1143 | 0.0777 | 0.0609 |
| $wR_2$ | 0.3231 | 0.1967 | 0.1544 |

## 5. Computation

All DFT calculations are performed with the TURBOMOLE 7.4 suite of programs.[16] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(THF) level, which combines the TPSS meta-GGA density functional[17] with the BJ-damped DFT-D3 dispersion correction[18] and the def2-TZVP basis set,[19] using the Conductor-like Screening Model (COSMO)[20] for THF solvent (dielectric constant $\varepsilon$ = 7.58 and diameter $R_{solv}$ = 3.18 Å). The well-established density-fitting RI-J approach[21] is used, which speeds up semi-local DFT functional calculations by a factor of 5-20 at practically no loss of accuracy. Chemically reasonable reaction paths are generated manually and tested in DFT calculations. Useful initial guesses of transition structures are obtained from interpolation between optimized intermediate structures as well as constrained optimizations with appropriate reaction coordinates. The optimized structures are characterized by frequency analysis (no imaginary frequency for true minima and only one imaginary frequency for transition states) to provide thermal free-energy corrections (at 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model.[22] The connection of the transition state with reactants and products is checked visually by careful examining the vibrational transition mode.

More accurate solvation free energies in THF solution are computed with the COSMO-RS model[23] (parameter file: BP_TZVP_16.ctd) using the COSMOtherm package[24] based on the TPSS-D3 optimized structures, corrected by +1.89 kcal/mol to account for the 1 mol/L reference concentration in solution. To check the effects of the chosen density functional on the reaction energies and barriers, single-point calculations at both TPSS-D3[17] and hybrid-meta-GGA PW6B95-D3[25] levels are performed using the large def2-QZVP[19] basis set. Final reaction free energies ($\Delta G$) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. Both DFT functionals are in good mutual agreement of 0.1 ± 2.9 (average ± standard deviation) kcal/mol with the

meta-GGA TPSS-D3 functional tends to predict 2.1 ± 2.9 kcal/mol too lower reaction barriers, as also observed in our recent DFT studies.[26] In the discussion, more reliable PW6B95-D3 + COSMO-RS free energies (in kcal/mol, at 298.15 K and 1 mol/L concentration) are used unless specified otherwise. The applied DFT methods in combination with the large AO basis sets provide usually accurate electronic energies with typical absolute errors of 1-2 kcal/mol for chemical energies (including barriers), which has been tested thoroughly for the huge data base GMTKN55[27] that is the common standard in the field of DFT benchmarking. To help NMR assignment, nuclear magnetic shielding constants are also computed using the GIAO (Gauge Including Atomic Orbital) method[28] at the TPSS/def2-QZVP level; final $^{13}$C-NMR chemical shifts are computed using the experimental NMR signal of the compound **3aa** observed at 188.6 ppm in THF as reference.

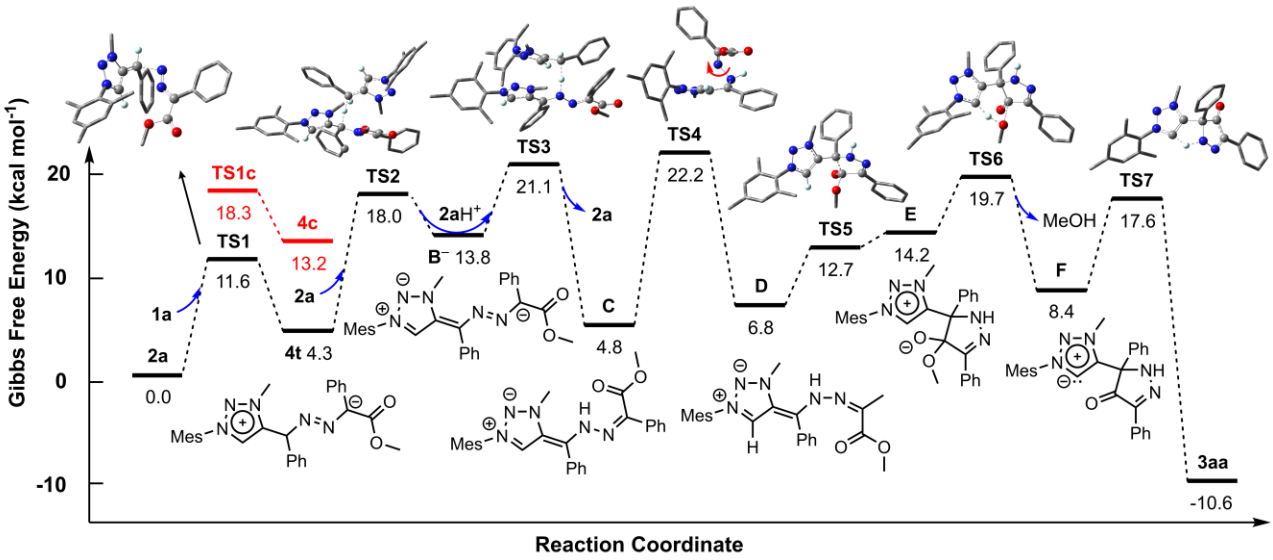
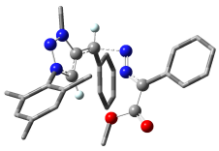
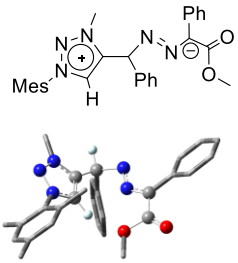
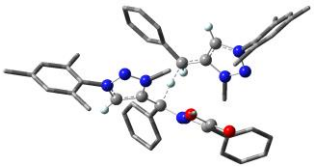
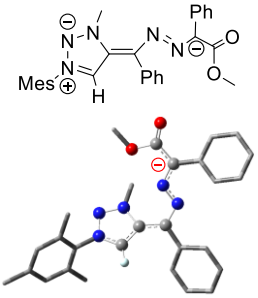
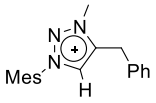
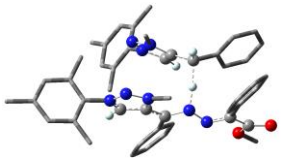
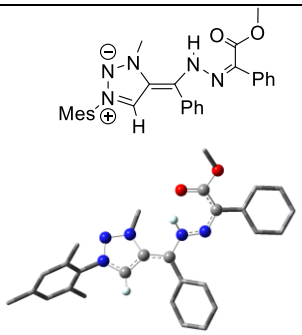
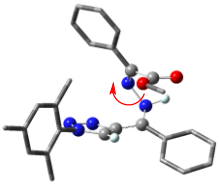
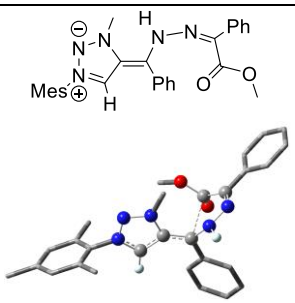
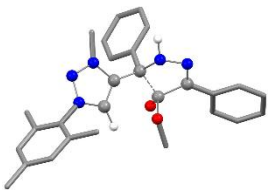
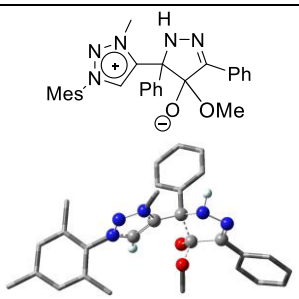
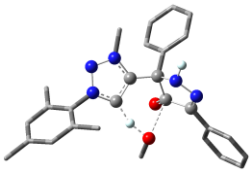
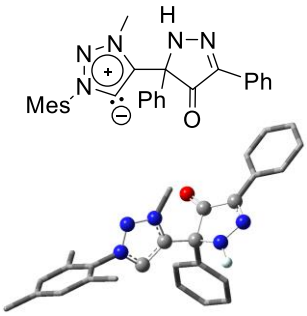
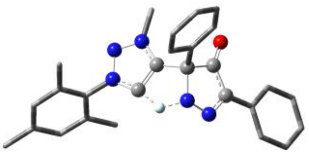



**Figure S62.** DFT computed free energy profile (in kcal mol$^{-1}$, at 298 K and 1 M concentration) for the reaction of **1a** and **2a** at the PW6B95-D3/def2-QZVP + COSMO-RS level using TPSS-D3/def2-TZVP + COSMO optimized geometries in THF solution.

**Table S3**. Computed intermediates and transition states.

| TS1 | 4t | TS2 | B⁻ |
|---|---|---|---|
|  |  |  |  |
| **2aH⁺** | **TS3** | **C** | **TS4** |
|  |  |  |  |
| **D** | **TS5** | **E** | **TS6** |
|  |  |  |  |
| **F** | **TS7** | | |
|  |  | | |

**Computed Mechanism:** As shown in Figure S62, the nucleophilic addition of the ylidic carbon of **2a** to the terminal nitrogen of **1a** leads to the selective formation of the meta-stable, zwitterionic adduct **4** in the *trans*-configuration (i.e., labelled as **4t**) with respect to the N–N double bond. This process is endergonic by 4.3 kcal $mol^{-1}$ via a low-lying transition state **TS1** (11.6 kcal $mol^{-1}$). The formation of the *cis*-adduct **4c** via **TS1c** (color-coded in red) is both kinetically and thermodynamically disfavored. The zwitterionic intermediate **4t** can undergo a **2a**-catalyzed proton transfer from the benzylic position to the adjacent diazo site to form intermediate **C**, which is 0.5 kcal $mol^{-1}$ less stable than **4t**. Such a proton transfer process involves the deprotonation of **4t** by **2a** to form **2a**$H^+$ and $\mathbf{B^-}$ (13.8 kcal $mol^{-1}$) via **TS2** (18.0 kcal $mol^{-1}$) followed by the protonation of $\mathbf{B^-}$ by **2a**$H^+$ via **TS3** (21.1 kcal $mol^{-1}$) to form **C** (4.8 kcal $mol^{-1}$). The related *N*-protonation of $\mathbf{B^-}$ at the other N-site of the diazo moiety to form the adduct **Cn** is 2.5 kcal/mol less favorable in free energy. The proton migration reduces the bond order of the diazo group, enabling the N–N rotation of intermediate **C** via **TS4** (22.2 kcal $mol^{-1}$) to afford **D** (6.8 kcal $mol^{-1}$), where the ylidic carbon and the carbonyl carbon are already in close contact with each other (i.e., 2.65 Å apart). The subsequent bond formation between the aforementioned two carbon atoms via **TS5** (12.7 kcal $mol^{-1}$) closes the new five-membered ring to form **E** (14.2 kcal $mol^{-1}$), which then eliminates MeOH via **TS6** (19.7 kcal $mol^{-1}$) to give a free carbene **F** (8.4 kcal $mol^{-1}$) and MeOH. The final intramolecular proton transfer from the N–H bond to the highly basic carbene site within **F** via **TS7** (17.6 kcal $mol^{-1}$) affords the product **3aa**. Consistent with the variable temperature experiments, all intermediates after **4t** are higher in free energy than **4t** and thus are not observed. The transition state, **TS4**, for the conversion of **C** into **D** through N–N rotation is the rate-limiting transition state of the overall reaction sequence due to the existence of a partial N–N π-bond, evidenced by the 1.31 Å bond length, comparable to that in compound **8** (1.331(3) Å). When the electron-deficient diazo compound **7** instead of **1a** is reacted with the mNHO **2a**, similar *N*-protonation of the $\mathbf{B^-}$-like anion can be expected but now with reversed regioselectivity, leading to the **Cn**-like product **8** that is indeed exergonic by 5.3 kcal $mol^{-1}$ (i.e., isolable experimentally). The formation of the **C**-like **8a** is now endergonic by 3.1 kcal $mol^{-1}$ and thus is thermodynamically disfavored.

**Table S4.** DFT computed energies for the reaction of mNHO **2a** and diazo **1a** in THF solution.
TPSS-D3/def2-TZVP + COSMO computed imaginary frequency (ImF), zero-point energies (ZPE), enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in THF; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95 ($E_P$)); total PW6B95-D3 Gibbs free energies ($G_P = E_P + Gc + Gsol$), relative electronic energies ($\Delta E_T$ and $\Delta E_P$) and final Gibbs free-energies ($\Delta G_T$ and $\Delta G_P$) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name, with singly charged cation and anion species indicated by the + and – superscripts, respectively. Transition structures (with only one imaginary frequency) are indicated by the "**TS**" prefix. See also **Figure S62** for structural labelings. The final PW6B95-D3 Gibbs free energies are used in our discussion.

| Reactions | ImF | ZPE | Hc | Gc | Hsol | Gsol | TPSS-D3 | PW6B95 | $G_P$ | $\Delta E_T$ | $\Delta E_P$ | $\Delta G_P$ | $\Delta G_T$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | kcal | kcal | kcal | kcal | kcal | | | | kcal | kcal | kcal | kcal |
| (1 mol/L in THF) | $cm^{-1}$ | /mol | /mol | /mol | /mol | /mol | $E_h$ | $E_h$ | $E_h$ | /mol | /mol | /mol | /mol |
| *Diazo with C=O tans to NN is 0.9 kcal/mol more stable than C=O cis to NN* | | | | | | | | | | | | | |
| Diazo **1a** | 0 | 97.73 | 105.51 | 74.58 | -13.64 | -9.27 | -608.08674 | -608.71879 | -608.61170 | 0.00 | 0.00 | *0.00* | 0.00 |
| diazo_cis | 0 | 97.53 | 105.41 | 74.20 | -14.10 | -9.67 | -608.08308 | -608.71607 | -608.61022 | 2.30 | 1.71 | *0.93* | 1.52 |
| *Nucleophilic addition of mNHO (**2a**) to terminal N of diazo (**1a**) is 4.3 kcal/mol endergonic to form meta-stable trans-adduct **4t*** | | | | | | | | | | | | | |
| **1a** + **2a** | 0 | 320.66 | 341.58 | 269.11 | -41.48 | -29.42 | -1509.55026 | -1511.14686 | -1510.75886 | 0.00 | 0.00 | *0.00* | 0.00 |
| **3aa** + $CH_3OH$ | 0 | 320.02 | 341.54 | 271.31 | -56.49 | -38.29 | -1509.55103 | -1511.15310 | -1510.77574 | -0.49 | -3.92 | *-10.59* | -7.16 |
| **3aa**$H^+$ + $CH_3O^-$ | 0 | 319.59 | 340.71 | 272.30 | -140.47 | -118.39 | -1509.35461 | -1510.95628 | -1510.70499 | 122.77 | 119.59 | *33.80* | 36.98 |
| **TS1** | 185i | 319.02 | 340.97 | 280.48 | -40.74 | -30.45 | -1509.55424 | -1511.14187 | -1510.74042 | -2.50 | 3.13 | *11.57* | 5.94 |
| **4t** | 0 | 322.53 | 343.43 | 286.37 | -44.96 | -33.88 | -1509.56056 | -1511.15735 | -1510.75198 | -6.47 | -6.58 | *4.32* | 4.43 |
| *..with disfavored Ph-trans-to-N=N orientation (3.9 kcal/mol less stable **Aa** than **A**, 1.8 kcal/mol higher **TS1a** than **TS1**)* | | | | | | | | | | | | | |
| **TS1a** | 273i | 319.09 | 340.93 | 281.14 | -40.06 | -30.23 | -1509.55101 | -1511.14037 | -1510.73751 | -0.47 | 4.07 | *13.40* | 8.85 |
| **Aa** | 0 | 321.73 | 343.04 | 284.82 | -43.95 | -32.63 | -1509.55373 | -1511.15070 | -1510.74581 | -2.18 | -2.41 | *8.19* | 8.41 |
| *..The cis adduct formation is kinetically 6.7 kcal/mol less favorable* | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1a** + **2a** | 0 | 320.66 | 341.58 | 269.11 | -41.48 | -29.42 | -1509.55026 | -1511.14686 | -1510.75886 | 0.00 | 0.00 | *0.00* | 0.00 |
| **TS1c** | 218i | 318.92 | 340.65 | 281.34 | -40.00 | -29.32 | -1509.54610 | -1511.13430 | -1510.72967 | 2.61 | 7.88 | *18.31* | 13.04 |
| **4c** | 0 | 322.50 | 343.25 | 286.76 | -42.30 | -31.60 | -1509.55135 | -1511.14755 | -1510.73791 | -0.69 | -0.43 | *13.15* | 12.89 |
| *..followed by mNHO **2a** catalyzed 1,2- H-shift to the next N site* | | | | | | | | | | | | | |
| **4t** + **2a** | 0 | 545.46 | 579.50 | 480.90 | -72.80 | -54.03 | -2411.02408 | -2413.58542 | -2412.89913 | 0.00 | 0.00 | *4.32* | 0.00 |
| **TS2** | 1618i | 539.19 | 575.22 | 487.78 | -57.19 | -43.17 | -2411.03289 | -2413.58879 | -2412.87726 | -5.53 | -2.12 | *18.04* | 10.32 |
| **B**$^{-}$ + **2a**H$^{+}$ | 0 | 545.40 | 579.44 | 480.71 | -139.86 | -116.17 | -2410.91151 | -2413.47101 | -2412.88404 | 70.64 | 71.79 | *13.79* | 8.32 |
| **TS3** | 1411i | 538.67 | 575.11 | 486.85 | -58.19 | -44.81 | -2411.02563 | -2413.57986 | -2412.87241 | -0.97 | 3.49 | *21.09* | 12.31 |
| **C** + **2a** | 0 | 545.86 | 579.67 | 481.51 | -67.45 | -49.38 | -2411.03344 | -2413.59299 | -2412.89833 | -5.87 | -4.76 | *4.82* | -0.61 |
| *....with Ph trans to the pro-carbenic C–H: **C0** is kinetically 0.5 kcal/mol and thermodynamically 0.7 kcal/mol less favorable than **C*** | | | | | | | | | | | | | |
| **TS20** | 1561i | 539.56 | 575.41 | 489.14 | -54.58 | -42.19 | -2411.03505 | -2413.59189 | -2412.87664 | -6.88 | -4.06 | *18.44* | 11.30 |
| **B0**$^{-}$ + **2a**H$^{+}$ | 0 | 545.13 | 579.24 | 480.43 | -137.99 | -115.15 | -2410.91823 | -2413.47831 | -2412.89018 | 66.43 | 67.21 | *9.94* | 4.84 |
| **TS30** | 1314i | 539.37 | 575.38 | 488.50 | -55.29 | -42.81 | -2411.03046 | -2413.58486 | -2412.87160 | -4.00 | 0.35 | *21.60* | 12.92 |
| **C0** + **2a** | 0 | 546.09 | 579.81 | 482.00 | -67.13 | -49.27 | -2411.03324 | -2413.59283 | -2412.89720 | -5.75 | -4.65 | *5.53* | 0.12 |
| *..H-shift to terminal C=O is possible but 11.2 kcal/mol less stable* | | | | | | | | | | | | | |
| **TS3a** | 857i | 539.38 | 575.11 | 488.71 | -52.53 | -39.99 | -2411.03175 | -2413.59107 | -2412.87299 | -4.81 | -3.55 | *20.72* | 15.14 |
| **Ca** + **2a** | 0 | 545.44 | 579.33 | 480.90 | -65.46 | -47.79 | -2411.01527 | -2413.57670 | -2412.88049 | -0.94 | -1.11 | *16.02* | 16.19 |
| **Bc**$^{-}$ + **2a**H$^{+}$ | 0 | 544.06 | 578.49 | 479.12 | -134.49 | -112.61 | -2410.89621 | -2413.45396 | -2412.86387 | 80.24 | 82.49 | *26.45* | 19.89 |
| *..folowed by N-N rotation via **TS4** rather than N inversion via **TS4a** ; The Cn with N-protonation at the other N-site is 2.5 kcal/mol less stable* | | | | | | | | | | | | | |
| **C** | 0 | 322.93 | 343.60 | 286.97 | -39.61 | -29.23 | -1509.56992 | -1511.16493 | -1510.75118 | -12.34 | -11.34 | *4.82* | 3.82 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cn** | 0 | 322.87 | 343.82 | 286.65 | -41.29 | -31.09 | -1509.56402 | -1511.15746 | -1510.74720 | -8.64 | -6.65 | *7.32* | 5.33 |
| **TS4** (rotation) | 34i | 320.06 | 341.48 | 283.13 | -35.49 | -26.22 | -1509.53893 | -1511.13592 | -1510.72349 | 7.11 | 6.87 | *22.20* | 22.44 |
| **TS4a** (inversion) | 385i | 319.00 | 341.19 | 279.96 | -41.38 | -29.65 | -1509.51462 | -1511.11539 | -1510.71348 | 22.36 | 19.75 | *28.47* | 31.09 |
| **D** | 0 | 322.59 | 343.52 | 286.60 | -41.00 | -29.86 | -1509.56026 | -1511.16016 | -1510.74801 | -6.28 | -8.35 | *6.81* | 8.88 |
| *..and further $CH_3OH$ elimination* | | | | | | | | | | | | | |
| **TS5** | 29i | 320.76 | 341.66 | 283.85 | -48.84 | -36.27 | -1509.53412 | -1511.13621 | -1510.73866 | 10.13 | 6.68 | *12.68* | 16.12 |
| **E** | 0 | 322.68 | 343.26 | 287.13 | -47.27 | -35.04 | -1509.53887 | -1511.14098 | -1510.73625 | 7.14 | 3.69 | *14.19* | 17.64 |
| **TS6** | 1105i | 316.79 | 338.47 | 278.91 | -44.20 | -31.94 | -1509.52859 | -1511.12399 | -1510.72740 | 13.60 | 14.35 | *19.74* | 18.98 |
| **E** + $CH_3OH$ | 0 | 320.11 | 341.60 | 271.64 | -54.44 | -34.32 | -1509.52313 | -1511.12967 | -1510.74546 | 17.02 | 10.79 | *8.41* | 14.64 |
| *..and final intramolecular H-shift from N-H bond to the carbene carbon site* | | | | | | | | | | | | | |
| **1a** + **2a** - $CH_3OH$ | 0 | 289.02 | 307.28 | 251.73 | -29.64 | -24.64 | -1393.75239 | -1395.23520 | -1394.87031 | 0.00 | 0.00 | *0.00* | 0.00 |
| **F** | 0 | 288.47 | 307.30 | 254.25 | -42.59 | -29.55 | -1393.72526 | -1395.21801 | -1394.85691 | 17.02 | 10.79 | *8.41* | 14.64 |
| **TS7** | 1498i | 284.26 | 303.43 | 248.76 | -36.51 | -27.32 | -1393.71323 | -1395.19816 | -1394.84226 | 24.57 | 23.25 | *17.60* | 18.93 |
| **3aa** | 0 | 288.37 | 307.24 | 253.92 | -44.64 | -33.51 | -1393.75316 | -1395.24144 | -1394.88719 | -0.49 | -3.92 | *-10.59* | -7.16 |
| Some high-lying intermediates: *direct MeOH elimination to form ketene C=C=O unit is unlikely* | | | | | | | | | | | | | |
| **G** | 0 | 287.30 | 306.61 | 252.52 | -36.60 | -26.92 | -1393.72221 | -1395.20468 | -1394.84216 | 18.93 | 19.15 | *17.66* | 17.44 |
| **TS8** (rotation) | 20i | 284.36 | 304.54 | 248.14 | -42.99 | -31.15 | -1393.68723 | -1395.16359 | -1394.81478 | 40.89 | 44.94 | *34.84* | 30.80 |
| **Gc** | 0 | 286.66 | 306.03 | 251.89 | -36.05 | -27.13 | -1393.71021 | -1395.18985 | -1394.82867 | 26.47 | 28.46 | *26.13* | 24.14 |
| *..also, acylic and cyclic intermediates with OH group are also highlying in free energy* | | | | | | | | | | | | | |
| **Ca** | 0 | 322.51 | 343.26 | 286.36 | -37.62 | -27.65 | -1509.55175 | -1511.14863 | -1510.73333 | -0.94 | -1.11 | *16.02* | 16.19 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cb** | 0 | 322.02 | 342.72 | 286.23 | -36.57 | -27.15 | -1509.54116 | -1511.13655 | -1510.72067 | 5.71 | 6.47 | *23.96* | 23.19 |
| **TS9** | 390i | 317.74 | 339.12 | 280.44 | -44.49 | -33.36 | -1509.49986 | -1511.09273 | -1510.69596 | 31.62 | 33.97 | *39.47* | 37.12 |
| **Cc** | 0 | 322.12 | 342.66 | 286.47 | -41.62 | -29.93 | -1509.53511 | -1511.14171 | -1510.72987 | 9.51 | 3.23 | *18.19* | 24.46 |

*When more electron-deficient diazo **7** is used in reaction with mNHO **2a** : reversed N-protonation site.*

*The formation of **Cn**-like adduct **8** is now -5.3 kcal/mol exergonic while that of C-like adduct **6a** is 3.1 kcal/mol endergonic.*

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **2a** + **7** | 0 | 329.83 | 350.83 | 278.69 | -41.96 | -30.02 | -1472.63320 | -1474.18751 | -1473.78520 | 0.00 | 0.00 | *0.00* | 0.00 |
| **8** (**Cn**-like) | 0 | 333.29 | 353.93 | 297.75 | -42.03 | -31.57 | -1472.66638 | -1474.22086 | -1473.79366 | -20.82 | -20.92 | *-5.31* | -5.20 |
| **8a** (**C**-like) | 0 | 333.12 | 353.53 | 297.84 | -43.05 | -31.93 | -1472.65698 | -1474.20697 | -1473.78020 | -14.92 | -12.21 | *3.14* | 0.42 |

**Table S5.** TPSS-D3/def2-TZVP + COSMO optimized Cartesian coordinates (in Å) in THF.
Each structure is labeled by the specific name (See also Table S4 and Figure S62), followed by the number of atoms, the total energy, and the detailed atomic coordinates (in double-column text list). Abbreviations for substituents: Mes = mesityl $C_6H_2Me_3$, E = $CO_2Me$ and Ph = $C_6H_5$.

**Aa** : higher cis C..N adduct with Ph trans to N=N
64
Energy = -1509.493497778

| | | | |
|---|---|---|---|
| N | -2.1639228 | -0.5787630 | 1.4323531 |
| N | -0.8729949 | -0.3074845 | 1.3072135 |
| N | -2.7523493 | 0.2028684 | 0.5326996 |
| C | -0.6116179 | 0.6403045 | 0.3501675 |
| C | 0.0824062 | -1.0560501 | 2.1399632 |
| C | -4.1860460 | 0.1455826 | 0.3490704 |
| C | -1.8540710 | 0.9634022 | -0.1524983 |
| C | 0.7720952 | 1.0864186 | -0.0422856 |
| H | 0.8278574 | -0.3621118 | 2.5267853 |
| H | 0.5767388 | -1.7993090 | 1.5133942 |
| H | -0.4901599 | -1.5179820 | 2.9425628 |
| C | -4.7134735 | -0.9380245 | -0.3667627 |
| C | -4.9633022 | 1.1796712 | 0.8800542 |
| H | -2.1508777 | 1.6471041 | -0.9303154 |
| C | 0.7003197 | 1.9247186 | -1.3049301 |
| H | 1.1921796 | 1.6881297 | 0.7782420 |
| C | -6.0971565 | -0.9613895 | -0.5462339 |
| C | -3.8320665 | -2.0287532 | -0.9194430 |
| C | -6.3439763 | 1.1028026 | 0.6712603 |
| C | -4.3494601 | 2.3223348 | 1.6479455 |
| C | 0.8604580 | 3.3118412 | -1.2531050 |
| C | 0.4757579 | 1.3055019 | -2.5414558 |
| C | -6.9260177 | 0.0465541 | -0.0361128 |
| H | -6.5358606 | -1.7873348 | -1.1011235 |
| H | -2.9936786 | -1.6152009 | -1.4912593 |
| H | -3.4104938 | -2.6403647 | -0.1142741 |
| H | -4.4069223 | -2.6815770 | -1.5791703 |
| H | -6.9769143 | 1.8881837 | 1.0770814 |
| H | -3.6768247 | 1.9603382 | 2.4327892 |
| H | -3.7661695 | 2.9774017 | 0.9903469 |
| H | -5.1302315 | 2.9259548 | 2.1150241 |
| C | 0.7963115 | 4.0753265 | -2.4215839 |
| H | 1.0411327 | 3.7960369 | -0.2962266 |
| C | 0.4105235 | 2.0661675 | -3.7079024 |
| H | 0.3730727 | 0.2246732 | -2.5784558 |
| C | -8.4175523 | -0.0114226 | -0.2504594 |
| C | 0.5691065 | 3.4541965 | -3.6505312 |
| H | 0.9272429 | 5.1527338 | -2.3707668 |
| H | 0.2403267 | 1.5781835 | -4.6637800 |
| H | -8.9176470 | 0.8369843 | 0.2234002 |
| H | -8.8345684 | -0.9355925 | 0.1652214 |
| H | -8.6564581 | 0.0002919 | -1.3200501 |
| H | 0.5200296 | 4.0463361 | -4.5600546 |
| N | 1.5847256 | -0.1324308 | -0.2309774 |
| N | 2.5804660 | -0.1176302 | 0.6050329 |
| C | 3.3743722 | -1.1996690 | 0.7188544 |
| C | 3.1691111 | -2.4800148 | 0.0100402 |
| C | 4.4645157 | -1.0728797 | 1.6699078 |
| C | 3.4087953 | -3.7139550 | 0.6515239 |
| C | 2.6795440 | -2.5229988 | -1.3122376 |
| O | 5.3368358 | -1.9242250 | 1.8850160 |
| O | 4.4884791 | 0.1250338 | 2.3494074 |
| C | 3.1752067 | -4.9254059 | 0.0048699 |
| H | 3.7861774 | -3.7132433 | 1.6676412 |
| C | 2.4513146 | -3.7377704 | -1.9589031 |
| H | 2.4738917 | -1.5937825 | -1.8270288 |
| C | 5.6151761 | 0.2710490 | 3.2358510 |
| C | 2.6945790 | -4.9482663 | -1.3077252 |
| H | 3.3675850 | -5.8580632 | 0.5304397 |
| H | 2.0796480 | -3.7363062 | -2.9811849 |
| H | 5.5289162 | 1.2807011 | 3.6384870 |
| H | 5.5765630 | -0.4680426 | 4.0418523 |
| H | 6.5569003 | 0.1557224 | 2.6916570 |
| H | 2.5118326 | -5.8937053 | -1.8120599 |

**4c** : cis C..N adduct of **1a** and **2a**
64
Energy = -1509.490903398

| | | | |
|---|---|---|---|
| N | 0.1359182 | -1.5492807 | -1.5796180 |
| N | 1.2122745 | -0.7687829 | -1.5202769 |
| N | -0.4322282 | -1.3907705 | -0.3838874 |
| C | 1.3474363 | -0.1157596 | -0.3270480 |
| C | 2.1074450 | -0.6918654 | -2.6792425 |
| C | -1.6277706 | -2.1367103 | -0.0513994 |
| C | 0.2591173 | -0.5348527 | 0.4117649 |
| C | 2.5104148 | 0.7735352 | 0.0105216 |
| H | 3.0800914 | -1.0998652 | -2.3983586 |
| H | 2.2059236 | 0.3552412 | -2.9687152 |
| H | 1.6593665 | -1.2815879 | -3.4762933 |
| C | -2.8679821 | -1.4964545 | -0.1325438 |
| C | -1.4627328 | -3.4715475 | 0.3489838 |
| H | -0.0684340 | -0.2774454 | 1.4045746 |
| C | 3.6841035 | -0.0749719 | 0.4631897 |
| H | 2.7789228 | 1.3202412 | -0.9039769 |
| C | -3.9909423 | -2.2610869 | 0.2082161 |
| C | -3.0125402 | -0.0546647 | -0.5409998 |
| C | -2.6164618 | -4.1811742 | 0.6794277 |
| C | -0.0999196 | -4.1121527 | 0.4206810 |
| C | 4.8845188 | -0.0533716 | -0.2521901 |
| C | 3.5819432 | -0.8787537 | 1.6045223 |
| C | -3.8875359 | -3.5933953 | 0.6132465 |
| H | -4.9719002 | -1.7954463 | 0.1493026 |
| H | -4.0103305 | 0.1203268 | -0.9505816 |
| H | -2.8875615 | 0.6092721 | 0.3221637 |
| H | -2.2706628 | 0.2485724 | -1.2833844 |
| H | -2.5189214 | -5.2169926 | 0.9962762 |
| H | 0.5880703 | -3.5197374 | 1.0349150 |
| H | -0.1737800 | -5.1105416 | 0.8564542 |

| | | | |
|---|---|---|---|
| H | 0.3464512 | -4.2042872 | -0.5755923 |
| C | 5.9710318 | -0.8261260 | 0.1643811 |
| H | 4.9721053 | 0.5796311 | -1.1322049 |
| C | 4.6647452 | -1.6500671 | 2.0234245 |
| H | 2.6548993 | -0.8894516 | 2.1717361 |
| C | -5.1167266 | -4.3923395 | 0.9674663 |
| C | 5.8617271 | -1.6276750 | 1.3016849 |
| H | 6.9006170 | -0.7987298 | -0.3972711 |
| H | 4.5773985 | -2.2683067 | 2.9126267 |
| H | -5.0304728 | -4.8149704 | 1.9746644 |
| H | -5.2475850 | -5.2308421 | 0.2734722 |
| H | -6.0153739 | -3.7714112 | 0.9281807 |
| H | 6.7049625 | -2.2305198 | 1.6269151 |
| N | 2.1633839 | 1.7180731 | 1.1200030 |
| N | 1.0680410 | 2.3948461 | 1.0872749 |
| C | 0.1368540 | 2.4855321 | 0.0867904 |
| C | -1.2120801 | 2.8279844 | 0.5771646 |
| C | 0.4448124 | 2.3957179 | -1.3225263 |
| C | -1.5744291 | 2.4402364 | 1.8852128 |
| C | -2.1749480 | 3.5321811 | -0.1745375 |
| O | 1.5518715 | 2.5764499 | -1.8561170 |
| O | -0.6548765 | 2.1122550 | -2.1062800 |
| C | -2.8320041 | 2.7298568 | 2.4117769 |
| H | -0.8472375 | 1.9026623 | 2.4864182 |
| C | -3.4347983 | 3.8115175 | 0.3484435 |
| H | -1.9358324 | 3.8618950 | -1.1786457 |
| C | -0.4560176 | 2.2607916 | -3.5280569 |
| C | -3.7786557 | 3.4097690 | 1.6430454 |
| H | -3.0775419 | 2.4077264 | 3.4207862 |
| H | -4.1538839 | 4.3561146 | -0.2587559 |
| H | 0.2362194 | 1.5035063 | -3.9059298 |
| H | -1.4429960 | 2.1231223 | -3.9702575 |
| H | -0.0624433 | 3.2539524 | -3.7589175 |
| H | -4.7657655 | 3.6237705 | 2.0433644 |

**4t** : trans C..N adduct of **1a** and **2a**
64
Energy = -1509.499719369

| | | | |
|---|---|---|---|
| N | -0.7430011 | -1.9043421 | 0.5699938 |
| N | -1.9507042 | -1.3565551 | 0.6737596 |
| N | 0.0414916 | -0.8739866 | 0.2590392 |
| C | -1.9583782 | -0.0052137 | 0.4509639 |
| C | -3.0874217 | -2.2176499 | 1.0146438 |
| C | 1.4660168 | -1.0504271 | 0.0991326 |
| C | -0.6382279 | 0.3016873 | 0.1685631 |
| C | -3.1304660 | 0.8904402 | 0.6663750 |
| H | -2.7097664 | -3.2347165 | 1.0980097 |
| H | -3.8353319 | -2.1507301 | 0.2235598 |
| H | -3.5109511 | -1.8914306 | 1.9656466 |
| C | 2.3008102 | -0.5365794 | 1.0999705 |
| C | 1.9377112 | -1.6724222 | -1.0632019 |
| H | -0.1529883 | 1.2448743 | -0.0289832 |
| C | -3.6073587 | 1.5312671 | -0.6273003 |
| H | -3.9534053 | 0.2993783 | 1.0769444 |
| C | 3.6778677 | -0.6682589 | 0.9021577 |
| C | 1.7471071 | 0.1247415 | 2.3366161 |
| C | 3.3231952 | -1.7780845 | -1.2059294 |
| C | 0.9995458 | -2.1907545 | -2.1229891 |
| C | -4.9043429 | 1.2835807 | -1.0886497 |
| C | -2.7783212 | 2.3973658 | -1.3530072 |
| C | 4.2054752 | -1.2846881 | -0.2375292 |
| H | 4.3520360 | -0.2791463 | 1.6614631 |
| H | 0.9900760 | -0.5041659 | 2.8176093 |
| H | 2.5487853 | 0.3082032 | 3.0550910 |
| H | 1.2711204 | 1.0822616 | 2.0989753 |
| H | 3.7201304 | -2.2482692 | -2.1026170 |
| H | 1.5609730 | -2.4920120 | -3.0098452 |
| H | 0.4347381 | -3.0571410 | -1.7623608 |
| H | 0.2720746 | -1.4264602 | -2.4191101 |
| C | -5.3693816 | 1.8845089 | -2.2604153 |
| H | -5.5563245 | 0.6200093 | -0.5246368 |
| C | -3.2427743 | 2.9986898 | -2.5211788 |
| H | -1.7826061 | 2.6207513 | -0.9800214 |
| C | 5.6960767 | -1.4353229 | -0.4100016 |
| C | -4.5378351 | 2.7420605 | -2.9817657 |
| H | -6.3799104 | 1.6841819 | -2.6061811 |
| H | -2.5942950 | 3.6729960 | -3.0742382 |
| H | 5.9772691 | -1.3960148 | -1.4665318 |
| H | 6.0311022 | -2.4026502 | -0.0148550 |
| H | 6.2374173 | -0.6523350 | 0.1284967 |
| H | -4.8959284 | 3.2115141 | -3.8937695 |
| N | -2.8072565 | 1.9248826 | 1.7203244 |
| N | -1.6537938 | 2.4346511 | 1.4685697 |
| C | -1.0789669 | 3.3971911 | 2.2131174 |
| C | -1.6565969 | 4.0134609 | 3.4204950 |
| C | 0.2139301 | 3.8246955 | 1.7134397 |
| C | -0.8431430 | 4.5453041 | 4.4462095 |
| C | -3.0545999 | 4.0673833 | 3.6121032 |
| O | 0.9187772 | 4.7352011 | 2.1579808 |
| O | 0.6556469 | 3.1077169 | 0.6014227 |
| C | -1.3990039 | 5.1061181 | 5.5938290 |
| H | 0.2335406 | 4.5192450 | 4.3315325 |
| C | -3.6057296 | 4.6356340 | 4.7605173 |
| H | -3.7008059 | 3.6492493 | 2.8515921 |
| C | 1.9360039 | 3.5363477 | 0.0948227 |
| C | -2.7859373 | 5.1595654 | 5.7620478 |
| H | -0.7421749 | 5.5023504 | 6.3648857 |
| H | -4.6872863 | 4.6676713 | 4.8718415 |
| H | 1.8967119 | 4.5800300 | -0.2277461 |
| H | 2.7122301 | 3.4247296 | 0.8571255 |
| H | 2.1392690 | 2.8818827 | -0.7543775 |
| H | -3.2176188 | 5.5981100 | 6.6579086 |

**Bc**$^{-}$ : C-H bond deprotonated adduct **4c**
63
Energy = -1508.972460762

| | | | |
|---|---|---|---|
| N | -0.5435407 | -1.3356277 | -1.1590749 |
| N | -1.6727398 | -0.6301192 | -0.8773355 |
| N | 0.3741702 | -0.7487135 | -0.4033395 |
| C | -1.4812555 | 0.3725216 | 0.1075749 |

| | | | |
|---|---|---|---|
| C | -2.7740792 | -0.7735902 | -1.8152419 |
| C | 1.7257228 | -1.2516132 | -0.3667483 |
| C | -0.0856338 | 0.2739013 | 0.3455464 |
| C | -2.4269258 | 1.3034225 | 0.5599943 |
| H | -2.3926864 | -1.3140621 | -2.6817567 |
| H | -3.1164564 | 0.2229440 | -2.1070671 |
| H | -3.6156158 | -1.3113221 | -1.3713009 |
| C | 2.0914372 | -2.0692424 | 0.7096838 |
| C | 2.6150106 | -0.8591580 | -1.3728840 |
| H | 0.5831332 | 0.8360308 | 0.9700230 |
| C | -3.8697769 | 1.1586629 | 0.3742888 |
| C | 3.4170353 | -2.5114477 | 0.7499563 |
| C | 1.1040667 | -2.4464795 | 1.7832394 |
| C | 3.9280327 | -1.3299942 | -1.2845195 |
| C | 2.1863864 | 0.0605533 | -2.4879220 |
| C | -4.5126234 | -0.0884514 | 0.5421117 |
| C | -4.7002290 | 2.2808852 | 0.1453602 |
| C | 4.3462972 | -2.1502025 | -0.2308943 |
| H | 3.7276743 | -3.1535343 | 1.5713914 |
| H | 0.1735233 | -2.8260443 | 1.3469735 |
| H | 1.5269277 | -3.2224596 | 2.4266331 |
| H | 0.8368616 | -1.5866368 | 2.4098164 |
| H | 4.6392995 | -1.0438284 | -2.0564718 |
| H | 2.9564221 | 0.1058647 | -3.2617877 |
| H | 1.2485552 | -0.2716698 | -2.9429465 |
| H | 2.0230540 | 1.0764994 | -2.1081864 |
| C | -5.8961993 | -0.2174085 | 0.4379439 |
| H | -3.9140400 | -0.9571521 | 0.8024788 |
| C | -6.0803923 | 2.1495998 | 0.0407371 |
| H | -4.2332910 | 3.2565074 | 0.0537688 |
| C | 5.7803235 | -2.6112033 | -0.1379520 |
| C | -6.6966131 | 0.8976119 | 0.1775999 |
| H | -6.3533030 | -1.1940714 | 0.5830561 |
| H | -6.6870120 | 3.0321967 | -0.1523942 |
| H | 6.2312521 | -2.7072803 | -1.1303390 |
| H | 5.8540191 | -3.5742456 | 0.3761318 |
| H | 6.3802011 | -1.8876216 | 0.4288098 |
| H | -7.7762345 | 0.7997363 | 0.1003923 |
| N | -2.0561743 | 2.5372740 | 1.1242937 |
| N | -1.1102580 | 2.7314028 | 1.9853398 |
| C | -0.4491881 | 1.7310771 | 2.7268287 |
| C | 0.9652234 | 1.9897985 | 2.9475298 |
| C | -1.1087257 | 0.6164128 | 3.3308928 |
| C | 1.7876536 | 1.2818421 | 3.8650649 |
| C | 1.6161620 | 2.9750773 | 2.1538976 |
| O | -0.5948990 | -0.3239031 | 3.9736924 |
| O | -2.4920674 | 0.6722089 | 3.2182808 |
| C | 3.1452898 | 1.5588007 | 3.9855146 |
| H | 1.3384797 | 0.5009517 | 4.4653089 |
| C | 2.9732292 | 3.2546693 | 2.2941470 |
| H | 1.0228714 | 3.5146030 | 1.4221600 |
| C | -3.1840462 | -0.4503719 | 3.7811971 |
| C | 3.7596267 | 2.5505367 | 3.2099750 |
| H | 3.7378659 | 0.9858672 | 4.6966397 |
| H | 3.4250733 | 4.0200081 | 1.6654314 |
| H | -2.8530682 | -1.3849152 | 3.3168011 |
| H | -3.0182945 | -0.5147561 | 4.8616122 |
| H | -4.2384598 | -0.2732531 | 3.5636889 |
| H | 4.8235472 | 2.7528335 | 3.3035609 |

**B0**$^{-}$ : anion with Ph trans to pro-carbenic C-H

63

Energy = -1508.995135910

| | | | |
|---|---|---|---|
| N | -0.5445013 | -1.2943520 | -1.0248011 |
| N | -1.6973423 | -0.6117387 | -0.8137231 |
| N | 0.2936473 | -0.7383292 | -0.1488199 |
| C | -1.6045871 | 0.3488314 | 0.2088649 |
| C | -2.7554114 | -0.7469907 | -1.7972214 |
| C | 1.6641483 | -1.1754157 | -0.0852587 |
| C | -0.2544474 | 0.2414480 | 0.6023081 |
| C | -2.5927286 | 1.2842585 | 0.5996155 |
| H | -2.3211119 | -1.1876961 | -2.6946807 |
| H | -3.1478635 | 0.2524522 | -2.0056042 |
| H | -3.5755005 | -1.3676209 | -1.4245061 |
| C | 1.9557017 | -2.4029142 | 0.5206716 |
| C | 2.6473201 | -0.3228672 | -0.6051413 |
| H | 0.3161180 | 0.8091550 | 1.3171450 |
| C | -4.0173377 | 1.0187808 | 0.5467054 |
| C | 3.3013930 | -2.7742157 | 0.5993616 |
| C | 0.8675889 | -3.2889479 | 1.0716741 |
| C | 3.9767112 | -0.7406535 | -0.4968987 |
| C | 2.2882918 | 0.9866549 | -1.2603688 |
| C | -4.5513126 | -0.2930311 | 0.6332587 |
| C | -4.9575557 | 2.0828368 | 0.5065324 |
| C | 4.3224196 | -1.9562969 | 0.1038612 |
| H | 3.5548026 | -3.7225686 | 1.0685040 |
| H | 0.3028998 | -3.7664332 | 0.2636596 |
| H | 1.2978662 | -4.0713261 | 1.7016024 |
| H | 0.1531388 | -2.7128186 | 1.6694125 |
| H | 4.7591639 | -0.0987136 | -0.8956884 |
| H | 3.1791680 | 1.4489404 | -1.6920711 |
| H | 1.5530065 | 0.8357224 | -2.0587605 |
| H | 1.8459435 | 1.6829988 | -0.5396124 |
| C | -5.9231098 | -0.5280344 | 0.6250776 |
| H | -3.8721267 | -1.1336388 | 0.7557737 |
| C | -6.3265745 | 1.8419605 | 0.5092359 |
| H | -4.5803465 | 3.0999038 | 0.4786700 |
| C | 5.7693466 | -2.3623818 | 0.2414786 |
| C | -6.8317363 | 0.5346062 | 0.5547297 |
| H | -6.2876051 | -1.5507850 | 0.6987780 |
| H | -7.0143084 | 2.6846061 | 0.4686917 |
| H | 6.3755094 | -1.9469115 | -0.5691201 |
| H | 5.8771727 | -3.4512103 | 0.2381812 |
| H | 6.1846249 | -1.9920848 | 1.1875387 |
| H | -7.9027468 | 0.3512545 | 0.5520495 |
| N | -2.2335033 | 2.5283078 | 1.1348503 |
| N | -0.9632779 | 2.7221343 | 1.2905879 |
| C | -0.4929629 | 3.8974185 | 1.8325354 |
| C | -1.2862155 | 5.0922578 | 2.1376022 |
| C | 0.9216339 | 3.8835514 | 2.0835276 |

| | | | |
|---|---|---|---|
| C | -0.8649563 | 6.0561529 | 3.0909473 |
| C | -2.5250534 | 5.3495982 | 1.4942886 |
| O | 1.6496701 | 4.8239149 | 2.4544049 |
| O | 1.5183258 | 2.6276742 | 1.8736848 |
| C | -1.6191277 | 7.1928977 | 3.3683722 |
| H | 0.0740785 | 5.9007964 | 3.6077217 |
| C | -3.2710352 | 6.4937512 | 1.7721157 |
| H | -2.8962682 | 4.6298012 | 0.7779355 |
| C | 2.9408626 | 2.6161295 | 2.0693265 |
| C | -2.8326356 | 7.4308705 | 2.7119931 |
| H | -1.2563188 | 7.9007497 | 4.1115193 |
| H | -4.2108270 | 6.6520521 | 1.2461506 |
| H | 3.4418006 | 3.3011470 | 1.3773152 |
| H | 3.2018129 | 2.8973564 | 3.0943133 |
| H | 3.2485325 | 1.5874182 | 1.8684089 |
| H | -3.4206845 | 8.3184310 | 2.9315614 |

**B**$^{-}$ : anion from C-H deprotonation of **4t**

63

Energy = -1508.990022908

| | | | |
|---|---|---|---|
| N | -1.8930689 | -1.0832919 | 1.2205524 |
| N | -0.6577595 | -0.5570450 | 1.3351534 |
| N | -2.5208566 | -0.2155025 | 0.4210997 |
| C | -0.4733726 | 0.6130986 | 0.5942753 |
| C | 0.2652893 | -1.1527327 | 2.2879053 |
| C | -3.8736713 | -0.4852655 | 0.0126315 |
| C | -1.7340459 | 0.8093362 | 0.0230072 |
| C | 0.7486323 | 1.3355909 | 0.4344299 |
| H | 0.8709809 | -1.9089286 | 1.7845322 |
| H | -0.3260027 | -1.5727044 | 3.1044816 |
| H | 0.9108892 | -0.3514567 | 2.6540437 |
| C | -4.1051524 | -1.5633084 | -0.8516045 |
| C | -4.8937448 | 0.3521957 | 0.4841710 |
| H | -2.0854980 | 1.5586494 | -0.6663336 |
| C | 0.7288820 | 2.7749294 | 0.3206363 |
| N | 1.9713484 | 0.7029252 | 0.2104367 |
| C | -5.4276709 | -1.7934455 | -1.2446999 |
| C | -2.9843456 | -2.4414148 | -1.3479009 |
| C | -6.1962843 | 0.0762797 | 0.0608009 |
| C | -4.6078787 | 1.5062072 | 1.4125103 |
| C | -0.3877489 | 3.5706005 | 0.7023166 |
| C | 1.8666970 | 3.4864987 | -0.1596400 |
| N | 1.9207854 | -0.5858214 | 0.0742904 |
| C | -6.4824165 | -0.9909616 | -0.7986705 |
| H | -5.6335544 | -2.6174650 | -1.9244290 |
| H | -2.6965249 | -3.1744515 | -0.5866796 |
| H | -3.2981290 | -2.9816596 | -2.2446730 |
| H | -2.0892624 | -1.8573502 | -1.5836325 |
| H | -7.0057460 | 0.7101828 | 0.4164251 |
| H | -5.5320639 | 1.8486057 | 1.8842644 |
| H | -3.8991827 | 1.2221883 | 2.1967361 |
| H | -4.1735336 | 2.3547753 | 0.8707248 |
| C | -0.3800851 | 4.9555956 | 0.5801492 |
| H | -1.2631651 | 3.0893452 | 1.1313226 |
| C | 1.8699016 | 4.8726501 | -0.2623805 |
| H | 2.7439888 | 2.9138692 | -0.4408133 |
| C | 3.0832877 | -1.2756332 | -0.1980056 |
| C | -7.9031506 | -1.2811488 | -1.2163473 |
| C | 0.7467089 | 5.6328235 | 0.0932391 |
| H | -1.2601892 | 5.5184415 | 0.8860727 |
| H | 2.7621188 | 5.3722207 | -0.6361531 |
| C | 4.3823499 | -0.6707694 | -0.5163462 |
| C | 2.9458229 | -2.7029180 | -0.1963773 |
| H | -8.4612749 | -0.3557588 | -1.3901698 |
| H | -8.4291475 | -1.8388933 | -0.4311860 |
| H | -7.9308007 | -1.8838465 | -2.1285881 |
| H | 0.7519210 | 6.7155172 | 0.0029354 |
| C | 5.6067123 | -1.3223846 | -0.2236639 |
| C | 4.4811990 | 0.5997313 | -1.1375701 |
| O | 3.8121130 | -3.5588302 | -0.4716622 |
| O | 1.6629138 | -3.1415842 | 0.1506159 |
| C | 6.8368864 | -0.7472018 | -0.5330374 |
| H | 5.5766983 | -2.2976095 | 0.2475064 |
| C | 5.7143098 | 1.1684031 | -1.4509909 |
| H | 3.5718264 | 1.1350249 | -1.3752877 |
| C | 1.4950823 | -4.5647308 | 0.1063367 |
| C | 6.9090310 | 0.5069143 | -1.1505690 |
| H | 5.7403686 | 2.1418279 | -1.9374809 |
| H | 1.6767919 | -4.9538326 | -0.9012183 |
| H | 2.1724519 | -5.0690013 | 0.8036375 |
| H | 0.4560578 | -4.7384033 | 0.3954679 |
| H | 7.8699074 | 0.9562160 | -1.3887120 |
| H | 7.7512095 | -1.2827566 | -0.2838126 |

**Ca** : C=O protonation of anion **B**$^{-}$

64

Energy = -1509.480004971

| | | | |
|---|---|---|---|
| N | -2.2091521 | -1.5451039 | -0.7060658 |
| N | -0.9196047 | -1.1380045 | -0.6849084 |
| N | -2.8739613 | -0.4961741 | -0.2377638 |
| C | -0.7574753 | 0.1558541 | -0.1854518 |
| C | 0.0831151 | -2.0592314 | -1.2092326 |
| C | -4.3110053 | -0.5584845 | -0.1122374 |
| C | -2.0784019 | 0.5464581 | 0.0885967 |
| C | 0.4603828 | 0.8557020 | 0.0075688 |
| H | -0.4583013 | -2.8556919 | -1.7211072 |
| H | 0.7016071 | -2.4558974 | -0.4025183 |
| H | 0.7317919 | -1.5167486 | -1.8978255 |
| C | -5.0869733 | 0.1307325 | -1.0507398 |
| C | -4.8556778 | -1.2890071 | 0.9517315 |
| H | -2.4755123 | 1.4547913 | 0.5081138 |
| C | 0.4142843 | 2.3083561 | 0.2660170 |
| H | 3.7994458 | 2.0827017 | 0.0041957 |
| C | -6.4756587 | 0.0678558 | -0.8985820 |
| C | -4.4617757 | 0.9115217 | -2.1791930 |
| C | -6.2480858 | -1.3164021 | 1.0577691 |
| C | -3.9812605 | -2.0110838 | 1.9446801 |
| C | -0.4431450 | 3.1473084 | -0.4723220 |
| C | 1.2207156 | 2.9089771 | 1.2545273 |
| C | -7.0721520 | -0.6489850 | 0.1434237 |

| | | | |
|---|---|---|---|
| H | -7.1032371 | 0.5921597 | -1.6155971 |
| H | -4.0057266 | 1.8395090 | -1.8145423 |
| H | -3.6764513 | 0.3340262 | -2.6774902 |
| H | -5.2195615 | 1.1783654 | -2.9191982 |
| H | -6.6973374 | -1.8692567 | 1.8797299 |
| H | -3.5005582 | -2.8805195 | 1.4836888 |
| H | -3.1848043 | -1.3598248 | 2.3211870 |
| H | -4.5765423 | -2.3557580 | 2.7931437 |
| C | -0.5099445 | 4.5180373 | -0.2260134 |
| H | -1.0519454 | 2.7171472 | -1.2641189 |
| C | 1.1595863 | 4.2794371 | 1.4954815 |
| H | 1.8909451 | 2.2893115 | 1.8393412 |
| C | -8.5736184 | -0.7204944 | 0.2704709 |
| C | 0.2937118 | 5.0950275 | 0.7596845 |
| H | -1.1803285 | 5.1386035 | -0.8154968 |
| H | 1.7879689 | 4.7148980 | 2.2685557 |
| H | -8.9471165 | -1.6761581 | -0.1180177 |
| H | -9.0565624 | 0.0819747 | -0.2938177 |
| H | -8.8844430 | -0.6497076 | 1.3176179 |
| H | 0.2511040 | 6.1640324 | 0.9488238 |
| N | 1.5868879 | 0.0931801 | -0.0413434 |
| N | 2.7296728 | 0.6852440 | 0.0685034 |
| C | 3.8850652 | -0.1084416 | -0.0084701 |
| C | 3.9303848 | -1.5742342 | 0.0307482 |
| C | 4.9937477 | 0.7151835 | -0.0666778 |
| C | 4.8661582 | -2.3054002 | -0.7273881 |
| C | 3.0360071 | -2.3017433 | 0.8434210 |
| O | 4.8150341 | 2.0510900 | -0.0533110 |
| O | 6.2595997 | 0.2754107 | -0.1091337 |
| C | 4.9127306 | -3.6972696 | -0.6685132 |
| H | 5.5602510 | -1.7728823 | -1.3694326 |
| C | 3.0833544 | -3.6932088 | 0.8982524 |
| H | 2.3070148 | -1.7623471 | 1.4372735 |
| C | 7.3065229 | 1.2784874 | -0.1096454 |
| C | 4.0198696 | -4.4033685 | 0.1418161 |
| H | 5.6452954 | -4.2337274 | -1.2667199 |
| H | 2.3867071 | -4.2274307 | 1.5400353 |
| H | 8.2335434 | 0.7081873 | -0.1504577 |
| H | 7.2137311 | 1.9251913 | -0.9853248 |
| H | 7.2625679 | 1.8753993 | 0.8045239 |
| H | 4.0526266 | -5.4886674 | 0.1829882 |

**Cb** : C=O protonation of anion **Bc**$^{-}$

64

Energy = -1509.471874855

| | | | |
|---|---|---|---|
| N | -2.1847460 | -1.6361719 | -0.4929895 |
| N | -0.9236460 | -1.1574126 | -0.5008863 |
| N | -2.9202999 | -0.5710208 | -0.1960429 |
| C | -0.8461640 | 0.1994050 | -0.1942414 |
| C | 0.1415402 | -2.0851240 | -0.8756528 |
| C | -4.3558345 | -0.6951030 | -0.1016424 |
| C | -2.1902584 | 0.5509837 | -0.0072698 |
| C | 0.3372602 | 0.9822068 | -0.0959332 |
| H | -0.3323704 | -2.9191017 | -1.3951286 |
| H | 0.6788562 | -2.4300516 | 0.0076624 |
| H | 0.8385461 | -1.5593085 | -1.5276473 |
| C | -5.1331790 | -0.1677672 | -1.1385808 |
| C | -4.8980318 | -1.3177116 | 1.0305060 |
| H | -2.6447535 | 1.4876625 | 0.2660170 |
| C | 0.1792358 | 2.4453476 | 0.0115919 |
| H | 4.1073999 | 0.9498052 | 1.0301657 |
| C | -6.5215241 | -0.2855310 | -1.0164855 |
| C | -4.5123498 | 0.5027297 | -2.3383757 |
| C | -6.2897523 | -1.4056327 | 1.1017917 |
| C | -4.0225580 | -1.8630156 | 2.1296200 |
| C | -0.7128903 | 3.1541124 | -0.8135677 |
| C | 0.9155214 | 3.1720909 | 0.9675386 |
| C | -7.1155175 | -0.8997552 | 0.0900293 |
| H | -7.1504350 | 0.1117519 | -1.8098316 |
| H | -4.1481351 | 1.5059181 | -2.0871329 |
| H | -3.6615868 | -0.0695472 | -2.7218745 |
| H | -5.2500962 | 0.6049810 | -3.1373447 |
| H | -6.7377796 | -1.8769883 | 1.9736695 |
| H | -3.4721132 | -2.7474065 | 1.7915801 |
| H | -3.2824369 | -1.1226882 | 2.4528139 |
| H | -4.6302074 | -2.1440478 | 2.9926075 |
| C | -0.8627952 | 4.5320629 | -0.6966374 |
| H | -1.2519681 | 2.6197055 | -1.5908287 |
| C | 0.7740662 | 4.5541478 | 1.0756645 |
| H | 1.5967767 | 2.6436718 | 1.6263509 |
| C | -8.6149372 | -1.0329526 | 0.1873729 |
| C | -0.1119432 | 5.2429993 | 0.2443007 |
| H | -1.5415771 | 5.0584604 | -1.3624706 |
| H | 1.3594116 | 5.0969748 | 1.8136425 |
| H | -8.9246568 | -2.0630894 | -0.0278672 |
| H | -9.1171326 | -0.3744800 | -0.5264395 |
| H | -8.9669419 | -0.7907025 | 1.1953559 |
| H | -0.2126863 | 6.3219462 | 0.3247170 |
| N | 1.4755111 | 0.2652238 | 0.1344901 |
| N | 2.6916463 | 0.7322121 | 0.0293577 |
| C | 3.0384949 | 1.9662377 | -0.5782109 |
| C | 2.4086005 | 2.5097505 | -1.7816049 |
| C | 4.2189667 | 2.4216689 | -0.0260339 |
| C | 2.4228437 | 3.8847012 | -2.0851608 |
| C | 1.7334565 | 1.6452072 | -2.6676228 |
| O | 4.7534920 | 1.7379192 | 1.0022621 |
| O | 4.9111632 | 3.4780082 | -0.4749639 |
| C | 1.7791431 | 4.3729283 | -3.2178892 |
| H | 2.9137185 | 4.5720798 | -1.4062939 |
| C | 1.0816101 | 2.1391928 | -3.7951271 |
| H | 1.7265608 | 0.5800993 | -2.4610270 |
| C | 6.1592377 | 3.7841497 | 0.1970508 |
| C | 1.0934781 | 3.5071461 | -4.0754210 |
| H | 1.7905783 | 5.4409494 | -3.4204485 |
| H | 0.5589109 | 1.4526917 | -4.4568161 |
| H | 6.5271032 | 4.6806189 | -0.3001448 |
| H | 5.9825002 | 3.9773165 | 1.2578565 |
| H | 6.8672767 | 2.9606106 | 0.0785932 |
| H | 0.5754056 | 3.8939717 | -4.9487414 |

**Cc** : $C_3N_2$ cyclic intermediate with OH
64
Energy = -1509.467417461

| | | | |
|---|---|---|---|
| N | -2.3954230 | -0.5044354 | -0.5592375 |
| N | -1.4928805 | 0.3983838 | -0.9076391 |
| N | -1.7512118 | -1.2273099 | 0.3760815 |
| C | -0.3107563 | 0.2363663 | -0.2170578 |
| C | -1.8807476 | 1.4100755 | -1.8973006 |
| C | -2.4630845 | -2.3161104 | 0.9962797 |
| C | -0.4625869 | -0.8452179 | 0.6524413 |
| C | 0.9186185 | 1.0771485 | -0.4593487 |
| H | -1.9065955 | 2.3893355 | -1.4173905 |
| H | -2.8647911 | 1.1374143 | -2.2738576 |
| H | -1.1585076 | 1.4216951 | -2.7146250 |
| C | -3.5196722 | -2.0231723 | 1.8661891 |
| C | -2.0401565 | -3.6249074 | 0.7250963 |
| C | 0.6226461 | 2.5568588 | -0.3439271 |
| N | 1.5338671 | 0.6943426 | -1.7596037 |
| C | 2.1045470 | 0.6136861 | 0.5444235 |
| C | -4.1747689 | -3.1021127 | 2.4698272 |
| C | -3.9286877 | -0.6030908 | 2.1660092 |
| C | -2.7273652 | -4.6656873 | 1.3541029 |
| C | -0.8887238 | -3.9024909 | -0.2068713 |
| C | -0.0416498 | 3.0177045 | 0.8003605 |
| C | 0.9843047 | 3.4693852 | -1.3375972 |
| N | 2.4134857 | -0.3713314 | -1.5795949 |
| H | 0.8805431 | 0.4654015 | -2.5048316 |
| C | 2.7774292 | -0.4443884 | -0.3397847 |
| O | 1.6664884 | 0.1780428 | 1.7818393 |
| O | 2.9737295 | 1.6897802 | 0.8589701 |
| C | -3.7978472 | -4.4256374 | 2.2242976 |
| H | -4.9926481 | -2.8976445 | 3.1574445 |
| H | -4.4420828 | -0.1490940 | 1.3115850 |
| H | -4.6029823 | -0.5769466 | 3.0253829 |
| H | -3.0552983 | 0.0196700 | 2.3891920 |
| H | -2.4156293 | -5.6894544 | 1.1579777 |
| H | -0.7500071 | -4.9794215 | -0.3283589 |
| H | -1.0655557 | -3.4615073 | -1.1947790 |
| H | 0.0374642 | -3.4621344 | 0.1776293 |
| C | -0.3352519 | 4.3714052 | 0.9486689 |
| H | -0.3193488 | 2.3097755 | 1.5767095 |
| C | 0.6857248 | 4.8256119 | -1.1912125 |
| H | 1.4918440 | 3.1127512 | -2.2283945 |
| C | 3.7739873 | -1.4043565 | 0.1282823 |
| H | 0.8898788 | -0.4734386 | 1.6015727 |
| C | 3.9267966 | 2.0732981 | -0.1494282 |
| C | -4.5352947 | -5.5728175 | 2.8703782 |
| C | 0.0260607 | 5.2809389 | -0.0492801 |
| H | -0.8467379 | 4.7178773 | 1.8423694 |
| H | 0.9666217 | 5.5250185 | -1.9738709 |
| C | 4.1533592 | -2.4950192 | -0.6769239 |
| C | 4.3769169 | -1.2488315 | 1.3886434 |
| H | 4.6980718 | 1.3037915 | -0.2718260 |
| H | 3.4419754 | 2.2663907 | -1.1107266 |
| H | 4.3829610 | 2.9917805 | 0.2219278 |
| H | -5.2252461 | -6.0400094 | 2.1564081 |
| H | -5.1220261 | -5.2317015 | 3.7279505 |
| H | -3.8407294 | -6.3487714 | 3.2081160 |
| H | -0.2089497 | 6.3356872 | 0.0624199 |
| C | 5.1124331 | -3.3991571 | -0.2343790 |
| H | 3.6829980 | -2.6218447 | -1.6471702 |
| C | 5.3397359 | -2.1578658 | 1.8261674 |
| H | 4.0862021 | -0.4150585 | 2.0177863 |
| C | 5.7112411 | -3.2350299 | 1.0200459 |
| H | 5.3933898 | -4.2383725 | -0.8649665 |
| H | 5.8000262 | -2.0236734 | 2.8012587 |
| H | 6.4586417 | -3.9441500 | 1.3649035 |

$CH_3OH$ : methanol by-product
6
Energy = -115.7944689170

| | | | |
|---|---|---|---|
| C | 0.6808174 | -0.0362630 | -0.0002187 |
| H | 1.0175904 | -0.5772159 | -0.8940509 |
| H | 1.1229499 | 0.9624205 | -0.0015822 |
| H | 1.0163308 | -0.5741602 | 0.8959157 |
| O | -0.7457639 | 0.1497562 | -0.0015407 |
| H | -1.1570716 | -0.7289677 | 0.0016188 |

$CH_3O^-$ : methoxy anion
5
Energy = -115.2609229215

| | | | |
|---|---|---|---|
| C | 0.6035869 | -0.0136214 | -0.0003097 |
| H | 1.0302051 | -0.5713100 | -0.8851201 |
| H | 1.1806007 | 0.9574190 | -0.0015466 |
| H | 1.0289459 | -0.5683035 | 0.8869905 |
| O | -0.7514139 | 0.1203534 | -0.0014908 |

**C0** : **C**-like with Ph trans to pro-carbenic C-H
64
Energy = -1509.500528530

| | | | |
|---|---|---|---|
| N | 2.4428388 | -1.7427951 | -0.6228161 |
| N | 1.1201688 | -1.4668052 | -0.6634385 |
| N | 2.9860815 | -0.6048825 | -0.2093349 |
| C | 0.8147985 | -0.1669171 | -0.2469966 |
| C | 0.2235711 | -2.4465075 | -1.2553285 |
| C | 4.4172518 | -0.5118496 | -0.0428128 |
| C | 2.0841161 | 0.3703523 | 0.0384058 |
| C | -0.4445982 | 0.4652373 | -0.2440051 |
| H | -0.3664937 | -2.9523105 | -0.4865567 |
| H | 0.8344053 | -3.1634118 | -1.8024775 |
| H | -0.4551459 | -1.9204762 | -1.9313957 |
| C | 5.0159110 | -1.2174260 | 1.0084801 |
| C | 5.1320461 | 0.2963230 | -0.9366902 |
| H | 2.3762039 | 1.3324718 | 0.4249725 |
| C | -1.7194643 | -0.1916311 | -0.0102140 |
| N | -0.3422089 | 1.8513613 | -0.3738009 |
| C | 6.4007456 | -1.0928006 | 1.1492574 |
| C | 4.2128275 | -2.0725346 | 1.9553329 |
| C | 6.5142659 | 0.3821203 | -0.7493097 |
| C | 4.4559320 | 1.0383390 | -2.0628218 |

| | | | |
|---|---|---|---|
| C | -1.8000220 | -1.3152427 | 0.8426812 |
| C | -2.9210854 | 0.2666914 | -0.5979701 |
| N | -1.2693739 | 2.6975169 | -0.0186029 |
| C | 7.1638360 | -0.2991886 | 0.2858610 |
| H | 6.8918031 | -1.6274795 | 1.9591068 |
| H | 3.9007574 | -3.0057539 | 1.4749150 |
| H | 4.8099507 | -2.3216142 | 2.8355338 |
| H | 3.3052502 | -1.5564708 | 2.2866838 |
| H | 7.0956791 | 0.9927989 | -1.4362112 |
| H | 5.1990586 | 1.3726797 | -2.7902609 |
| H | 3.7252390 | 0.4067415 | -2.5781742 |
| H | 3.9216895 | 1.9230205 | -1.6966967 |
| C | -3.0071540 | -1.9766148 | 1.0586081 |
| H | -0.9062268 | -1.6498610 | 1.3639165 |
| C | -4.1241057 | -0.3901840 | -0.3709671 |
| H | -2.8983207 | 1.1378876 | -1.2432632 |
| C | -1.0988250 | 4.0240805 | -0.2380647 |
| C | 8.6528836 | -0.1604544 | 0.4821963 |
| C | -4.1802691 | -1.5221566 | 0.4525686 |
| H | -3.0335388 | -2.8378308 | 1.7214980 |
| H | -5.0300520 | -0.0201175 | -0.8445782 |
| C | -2.2719836 | 4.8454509 | 0.1168327 |
| C | 0.1181323 | 4.5345930 | -0.8201749 |
| H | 8.8746529 | 0.6892459 | 1.1402747 |
| H | 9.1618233 | 0.0180240 | -0.4695321 |
| H | 9.0758679 | -1.0565069 | 0.9454440 |
| H | -5.1244199 | -2.0297031 | 0.6278536 |
| C | -2.1876591 | 6.1939787 | 0.5191916 |
| C | -3.5527541 | 4.2512203 | 0.1047583 |
| O | 1.1302631 | 3.8403983 | -1.0758887 |
| O | 0.1068741 | 5.8632772 | -1.1373562 |
| C | -3.3288006 | 6.9100368 | 0.8790096 |
| H | -1.2216625 | 6.6823666 | 0.5585492 |
| C | -4.6888698 | 4.9679783 | 0.4700089 |
| H | -3.6382848 | 3.2106868 | -0.1910967 |
| C | 1.3303437 | 6.3605278 | -1.7274320 |
| C | -4.5889167 | 6.3076938 | 0.8568000 |
| H | -3.2284378 | 7.9476182 | 1.1883482 |
| H | -5.6604857 | 4.4804480 | 0.4440177 |
| H | 2.1728747 | 6.1998836 | -1.0503515 |
| H | 1.5263062 | 5.8570750 | -2.6773442 |
| H | 1.1547981 | 7.4247675 | -1.8831762 |
| H | -5.4755140 | 6.8704831 | 1.1354719 |
| H | 0.5143060 | 2.2732294 | -0.7831381 |

**C** : mNHO-like with an N-H bond

64

Energy = -1509.501327036

| | | | |
|---|---|---|---|
| N | 2.4362270 | -1.7337976 | -0.4469405 |
| N | 1.1303944 | -1.3790924 | -0.5380025 |
| N | 3.0464778 | -0.5857388 | -0.1753199 |
| C | 0.9084535 | -0.0175532 | -0.2907720 |
| C | 0.1859641 | -2.3891198 | -1.0059950 |
| C | 4.4798527 | -0.5681977 | 0.0036216 |
| C | 2.2108609 | 0.4678119 | -0.0705022 |
| C | -0.3373865 | 0.6380043 | -0.2269909 |
| H | -0.4191769 | -2.7836513 | -0.1847766 |
| H | 0.7707086 | -3.1895124 | -1.4580142 |
| H | -0.4675463 | -1.9326306 | -1.7525741 |
| C | 5.0079943 | -1.0813203 | 1.1943483 |
| C | 5.2668637 | -0.0345729 | -1.0240401 |
| H | 2.5652866 | 1.4515100 | 0.1853475 |
| C | -0.4580557 | 2.0799371 | -0.3760073 |
| N | -1.4293359 | -0.1611304 | 0.1068426 |
| C | 6.3973713 | -1.0435610 | 1.3407385 |
| C | 4.1246602 | -1.6535200 | 2.2734113 |
| C | 6.6501724 | -0.0240223 | -0.8255330 |
| C | 4.6582071 | 0.5014310 | -2.2953026 |
| C | 0.4537365 | 2.8041942 | -1.1773387 |
| C | -1.4666681 | 2.8210360 | 0.2836583 |
| N | -2.6683214 | 0.1360710 | -0.1886028 |
| C | 7.2314029 | -0.5186524 | 0.3473092 |
| H | 6.8355715 | -1.4343008 | 2.2562547 |
| H | 3.7201335 | -2.6263313 | 1.9740463 |
| H | 4.6934035 | -1.7866733 | 3.1963924 |
| H | 3.2735142 | -0.9964433 | 2.4822316 |
| H | 7.2867390 | 0.3745933 | -1.6121554 |
| H | 5.4297421 | 0.6314144 | -3.0574681 |
| H | 3.8913476 | -0.1738391 | -2.6882816 |
| H | 4.1840391 | 1.4756659 | -2.1277237 |
| C | 0.3872045 | 4.1908353 | -1.2833019 |
| H | 1.2076347 | 2.2646504 | -1.7446539 |
| C | -1.5326632 | 4.2048895 | 0.1686098 |
| H | -2.1958945 | 2.3017624 | 0.8946881 |
| C | -3.6803722 | -0.6429128 | 0.2554307 |
| C | 8.7255757 | -0.4646416 | 0.5468426 |
| C | -0.6057640 | 4.9074827 | -0.6102876 |
| H | 1.1047639 | 4.7127753 | -1.9115752 |
| H | -2.3150087 | 4.7440516 | 0.6971831 |
| C | -5.0238463 | -0.1360533 | -0.0900342 |
| C | -3.4306647 | -1.8190739 | 1.0520669 |
| H | 9.0154868 | 0.4850453 | 1.0140487 |
| H | 9.2544709 | -0.5374489 | -0.4079585 |
| H | 9.0664960 | -1.2723211 | 1.2009578 |
| H | -0.6660272 | 5.9881032 | -0.7007981 |
| C | -6.1408938 | -0.9707008 | -0.2913593 |
| C | -5.2042574 | 1.2503544 | -0.2802526 |
| O | -2.2891392 | -2.2615944 | 1.3250513 |
| O | -4.5387581 | -2.4311773 | 1.5598325 |
| C | -7.3778888 | -0.4396260 | -0.6553898 |
| H | -6.0386150 | -2.0423766 | -0.1708556 |
| C | -6.4395698 | 1.7766247 | -0.6480468 |
| H | -4.3530097 | 1.9086524 | -0.1390029 |
| C | -4.2778495 | -3.6027174 | 2.3680399 |
| C | -7.5406044 | 0.9358755 | -0.8351970 |
| H | -8.2196831 | -1.1106186 | -0.8080447 |
| H | -6.5461681 | 2.8505156 | -0.7808160 |
| H | -3.7405578 | -4.3546741 | 1.7849314 |
| H | -3.6898506 | -3.3339253 | 3.2491172 |
| H | -5.2626020 | -3.9682426 | 2.6578952 |

| | | | |
|---|---|---|---|
| H | -8.5068318 | 1.3454643 | -1.1162997 |
| H | -1.3052254 | -1.0256391 | 0.6658925 |

**Cn** : **C**-like but with N-H bond to the other N

64

Energy = -1509.499145624

| | | | |
|---|---|---|---|
| N | -0.3575821 | -1.5469328 | -0.6399583 |
| N | -1.6242670 | -1.1313151 | -0.4249468 |
| N | 0.3759132 | -0.6780568 | 0.0450076 |
| C | -1.6997714 | 0.0059026 | 0.3731811 |
| C | -2.7090454 | -1.9476508 | -0.9574933 |
| C | 1.8163202 | -0.7951815 | 0.0410293 |
| C | -0.3550933 | 0.2720170 | 0.6685232 |
| C | -2.8620529 | 0.6859092 | 0.8266556 |
| H | -2.2862457 | -2.9159590 | -1.2217429 |
| H | -3.1532318 | -1.4726606 | -1.8351616 |
| H | -3.4710310 | -2.0600526 | -0.1843606 |
| C | 2.4459592 | -1.2466619 | 1.2081279 |
| C | 2.5085964 | -0.4278269 | -1.1189739 |
| H | 0.0937986 | 1.0569060 | 1.2515765 |
| C | -4.1569226 | 0.6327863 | 0.1209913 |
| H | -4.4530698 | 2.2763620 | 1.8713374 |
| C | 3.8400971 | -1.3312864 | 1.1843997 |
| C | 1.6647056 | -1.6277548 | 2.4404410 |
| C | 3.9021726 | -0.5302833 | -1.0850262 |
| C | 1.7930728 | 0.0651189 | -2.3507200 |
| C | -5.3649521 | 0.4144626 | 0.8131089 |
| C | -4.2208017 | 0.8554198 | -1.2682830 |
| C | 4.5826853 | -0.9810087 | 0.0508615 |
| H | 4.3554292 | -1.6817670 | 2.0756618 |
| H | 0.7987435 | -2.2490159 | 2.1903740 |
| H | 2.3014373 | -2.1829638 | 3.1326041 |
| H | 1.2901940 | -0.7419032 | 2.9670152 |
| H | 4.4674000 | -0.2423696 | -1.9683739 |
| H | 2.5053162 | 0.5140711 | -3.0464689 |
| H | 1.2818646 | -0.7565954 | -2.8635544 |
| H | 1.0351743 | 0.8153668 | -2.0998018 |
| C | -6.5839678 | 0.4099326 | 0.1383097 |
| H | -5.3452489 | 0.2241719 | 1.8828535 |
| C | -5.4389767 | 0.8322663 | -1.9440595 |
| H | -3.3034109 | 1.0608031 | -1.8146594 |
| C | 6.0855723 | -1.1078263 | 0.0490309 |
| C | -6.6276177 | 0.6127983 | -1.2433373 |
| H | -7.5020356 | 0.2340259 | 0.6920466 |
| H | -5.4623945 | 1.0022093 | -3.0170115 |
| H | 6.5345126 | -0.4718624 | -0.7189232 |
| H | 6.3823204 | -2.1435199 | -0.1588799 |
| H | 6.5060004 | -0.8353784 | 1.0218982 |
| H | -7.5786264 | 0.6049252 | -1.7677868 |
| N | -2.6017558 | 1.4806546 | 1.8960617 |
| N | -3.5281100 | 2.2948709 | 2.3161207 |
| C | -3.4552001 | 3.1589180 | 3.4079099 |
| C | -2.1974797 | 3.5264723 | 4.0344631 |
| C | -4.7266114 | 3.6819850 | 3.8083211 |
| C | -2.1681087 | 4.1087070 | 5.3280754 |
| C | -0.9461690 | 3.3421532 | 3.3930013 |
| O | -4.9672900 | 4.5422469 | 4.6661064 |
| O | -5.7762664 | 3.1111704 | 3.0807132 |
| C | -0.9702001 | 4.4828438 | 5.9277290 |
| H | -3.1030468 | 4.2687396 | 5.8497111 |
| C | 0.2465531 | 3.7264331 | 4.0004704 |
| H | -0.9199097 | 2.8989746 | 2.4069955 |
| C | -7.0738802 | 3.6796156 | 3.3389787 |
| C | 0.2533018 | 4.2979044 | 5.2747744 |
| H | -0.9933982 | 4.9218741 | 6.9224769 |
| H | 1.1835030 | 3.5771013 | 3.4681597 |
| H | -7.3488583 | 3.5452430 | 4.3883659 |
| H | -7.0845331 | 4.7456095 | 3.0949036 |
| H | -7.7587188 | 3.1322756 | 2.6900570 |
| H | 1.1864857 | 4.5883204 | 5.7491142 |

**1a** : diazo N=N=CPhE reactant

21

Energy = -608.0606453889

| | | | |
|---|---|---|---|
| C | -3.7123415 | -0.4677389 | -0.0366591 |
| C | -2.7894039 | -1.5106218 | -0.1220552 |
| C | -3.2467282 | 0.8429878 | 0.0899063 |
| H | -3.1342963 | -2.5362565 | -0.2207195 |
| H | -3.9487840 | 1.6691223 | 0.1578778 |
| C | -1.4182754 | -1.2604762 | -0.0827265 |
| C | -1.8807455 | 1.1058600 | 0.1297258 |
| H | -0.7119724 | -2.0774899 | -0.1497256 |
| H | -1.5484143 | 2.1354251 | 0.2274702 |
| C | -0.9436005 | 0.0580308 | 0.0439316 |
| H | -4.7785315 | -0.6713994 | -0.0679841 |
| C | 0.4999317 | 0.3458371 | 0.0871448 |
| C | 1.6071948 | -0.6080887 | -0.0099115 |
| O | 1.4852902 | -1.8170552 | -0.1453481 |
| O | 2.8082248 | 0.0200097 | 0.0691635 |
| C | 3.9657566 | -0.8536792 | -0.0206454 |
| H | 3.9645175 | -1.3752575 | -0.9799026 |
| H | 4.8234324 | -0.1879193 | 0.0605237 |
| H | 3.9514958 | -1.5754037 | 0.7985403 |
| N | 0.8655004 | 1.6071566 | 0.2284977 |
| N | 1.1542149 | 2.6977017 | 0.3503636 |

**7** : more electron-deficient diazo

22

Energy = -571.1478019652

| | | | |
|---|---|---|---|
| C | -0.2984736 | 0.4255446 | 1.3117803 |
| C | -0.3364632 | 1.0851734 | -0.0000528 |
| O | -0.2844211 | 1.0575993 | 2.3666157 |
| C | -0.2982185 | -1.0877813 | 1.2539403 |
| C | -0.2983962 | 0.4255057 | -1.3118451 |
| N | -0.3709655 | 2.4113501 | -0.0000178 |
| H | -1.3518656 | -1.4027229 | 1.2834150 |
| H | 0.1754689 | -1.4513537 | 2.1710542 |
| C | 0.3762926 | -1.6817735 | 0.0000023 |
| O | -0.2841736 | 1.0575103 | -2.3667132 |
| C | -0.2982663 | -1.0878160 | -1.2539303 |

| | | | |
|---|---|---|---|
| N | -0.4079894 | 3.5350706 | 0.0002009 |
| C | 1.8815284 | -1.3602150 | -0.0000357 |
| C | 0.1765871 | -3.2041893 | 0.0000271 |
| H | -1.3519506 | -1.4026503 | -1.2833391 |
| H | 0.1753034 | -1.4515092 | -2.1710562 |
| H | 2.3616168 | -1.7858141 | 0.8874958 |
| H | 2.3615221 | -1.7855980 | -0.8877222 |
| H | 2.0688561 | -0.2802684 | 0.0000992 |
| H | -0.8890941 | -3.4593583 | -0.0001076 |
| H | 0.6381899 | -3.6517733 | -0.8871333 |
| H | 0.6379629 | -3.6517357 | 0.8873228 |

**8** : stable **Cn**-like adduct of mNHO **2a** and **7**

65

Energy = -1472.604921759

| | | | |
|---|---|---|---|
| N | -3.1484700 | 1.5709838 | 0.6710580 |
| N | -1.9200064 | 2.1008271 | 0.7456784 |
| N | -2.9454076 | 0.3397600 | 0.2226953 |
| C | -0.9264697 | 1.2179742 | 0.3455298 |
| C | -1.8103429 | 3.5066747 | 1.1522031 |
| C | -4.0686736 | -0.5471759 | 0.0206691 |
| C | -1.6366173 | 0.0651930 | 0.0028126 |
| C | 0.4815576 | 1.4607185 | 0.3071710 |
| H | -2.7666987 | 3.7775374 | 1.5987401 |
| H | -1.6124894 | 4.1139895 | 0.2660635 |
| H | -0.9729744 | 3.6329961 | 1.8386484 |
| C | -4.2706462 | -1.5790564 | 0.9457684 |
| C | -4.8849693 | -0.3377779 | -1.0968979 |
| H | -1.3065313 | -0.8860058 | -0.3782169 |
| C | 1.3948792 | 0.3437023 | -0.0459998 |
| H | 2.8608748 | 2.3380729 | 0.3798003 |
| C | -5.3554958 | -2.4295038 | 0.7199388 |
| C | -3.3650345 | -1.7696797 | 2.1362832 |
| C | -5.9539214 | -1.2204391 | -1.2746575 |
| C | -4.6273464 | 0.7833316 | -2.0706752 |
| C | 2.3221547 | 0.4797361 | -1.0931560 |
| C | 1.3692917 | -0.8605109 | 0.6771065 |
| C | -6.2064534 | -2.2651444 | -0.3792220 |
| H | -5.5390520 | -3.2378706 | 1.4239181 |
| H | -3.1847139 | -0.8241035 | 2.6580549 |
| H | -3.8127112 | -2.4731184 | 2.8414619 |
| H | -2.3902598 | -2.1710257 | 1.8350874 |
| H | -6.6005501 | -1.0880295 | -2.1388989 |
| H | -5.2380355 | 0.6531947 | -2.9666681 |
| H | -4.8721930 | 1.7538812 | -1.6256706 |
| H | -3.5745847 | 0.8180451 | -2.3717208 |
| C | 3.1970223 | -0.5599310 | -1.4065859 |
| H | 2.3489351 | 1.3982093 | -1.6734278 |
| C | 2.2362293 | -1.9034675 | 0.3554312 |
| H | 0.6740225 | -0.9709139 | 1.5055412 |
| C | -7.3866589 | -3.1824231 | -0.5797583 |
| C | 3.1544570 | -1.7554265 | -0.6868520 |
| H | 3.9070662 | -0.4378803 | -2.2194483 |
| H | 2.2035851 | -2.8276047 | 0.9256983 |
| H | -7.6986545 | -3.2010982 | -1.6276513 |
| H | -8.2417888 | -2.8410298 | 0.0170861 |
| H | -7.1522033 | -4.2032563 | -0.2633653 |
| H | 3.8346865 | -2.5653579 | -0.9337186 |
| N | 0.8661575 | 2.6918974 | 0.6345525 |
| N | 2.1308301 | 2.9893058 | 0.7009749 |
| C | 1.9376500 | 5.1741271 | 1.8785634 |
| C | 2.6440771 | 4.2423393 | 1.0651591 |
| O | 0.8061958 | 4.9740257 | 2.3850224 |
| C | 2.6541811 | 6.4876285 | 2.1886500 |
| C | 3.9993072 | 4.4123334 | 0.6553771 |
| H | 3.0939931 | 6.3839845 | 3.1924908 |
| H | 1.8854845 | 7.2662584 | 2.2625644 |
| C | 3.7574254 | 6.8993728 | 1.1978263 |
| O | 4.6110827 | 3.5067659 | 0.0246966 |
| C | 4.7079986 | 5.7005015 | 1.0273393 |
| C | 3.1421553 | 7.2915135 | -0.1579216 |
| C | 4.5346368 | 8.0983943 | 1.7613366 |
| H | 5.2464605 | 5.5298415 | 1.9721192 |
| H | 5.4656557 | 5.9000584 | 0.2606012 |
| H | 2.4655349 | 8.1453345 | -0.0363963 |
| H | 3.9280621 | 7.5763919 | -0.8671231 |
| H | 2.5730858 | 6.4627267 | -0.5913506 |
| H | 4.9894517 | 7.8498591 | 2.7274559 |
| H | 5.3340757 | 8.4004307 | 1.0739657 |
| H | 3.8691135 | 8.9577715 | 1.9070545 |

**8a** : less stable **C**-like adduct of **2a** and **7**

65

Energy = -1472.595698912

| | | | |
|---|---|---|---|
| N | -2.8510031 | 1.1428160 | 1.5857170 |
| N | -1.5790991 | 1.4599475 | 1.8795444 |
| N | -2.7326006 | 0.2273299 | 0.6277112 |
| C | -0.6488958 | 0.7845011 | 1.0924515 |
| C | -1.3335672 | 2.3665071 | 3.0002864 |
| C | -3.9195528 | -0.3570803 | 0.0463501 |
| C | -1.4503352 | -0.0311256 | 0.2896188 |
| C | 0.7682154 | 0.9594792 | 1.1209175 |
| H | -2.2270381 | 2.3596158 | 3.6225506 |
| H | -1.1194360 | 3.3780813 | 2.6427713 |
| H | -0.4758429 | 1.9845102 | 3.5576922 |
| C | -4.2104918 | -1.6936356 | 0.3483963 |
| C | -4.7051826 | 0.4355084 | -0.7989754 |
| H | -1.1938349 | -0.7174368 | -0.4994491 |
| C | 1.6685927 | -0.1462137 | 0.8209266 |
| H | 0.4826773 | 3.0530402 | 1.3007696 |
| C | -5.3565628 | -2.2399589 | -0.2338575 |
| C | -3.3344414 | -2.5157005 | 1.2601979 |
| C | -5.8384332 | -0.1645350 | -1.3551683 |
| C | -4.3507676 | 1.8676084 | -1.1079578 |
| C | 2.9970455 | 0.0439437 | 0.3714988 |
| C | 1.2162394 | -1.4797440 | 0.9634774 |
| C | -6.1815199 | -1.4930751 | -1.0828342 |
| H | -5.6096691 | -3.2744711 | -0.0137739 |
| H | -3.0442599 | -1.9539374 | 2.1538897 |
| H | -3.8622227 | -3.4181341 | 1.5760062 |

| | | | |
|---|---|---|---|
| H | -2.4143649 | -2.8280291 | 0.7518372 |
| H | -6.4632770 | 0.4231004 | -2.0235861 |
| H | -4.9478009 | 2.2304341 | -1.9474012 |
| H | -4.5413131 | 2.5147595 | -0.2452900 |
| H | -3.2914493 | 1.9706751 | -1.3672600 |
| C | 3.7972483 | -1.0463801 | 0.0390803 |
| H | 3.3990771 | 1.0467982 | 0.3088916 |
| C | 2.0238446 | -2.5613618 | 0.6311883 |
| H | 0.2258314 | -1.6684468 | 1.3678617 |
| C | -7.4282326 | -2.1031221 | -1.6727007 |
| C | 3.3223846 | -2.3550685 | 0.1564451 |
| H | 4.8106756 | -0.8680167 | -0.3111804 |
| H | 1.6428204 | -3.5712334 | 0.7584952 |
| H | -7.7436584 | -1.5658371 | -2.5712902 |
| H | -8.2532245 | -2.0601818 | -0.9505900 |
| H | -7.2704416 | -3.1552926 | -1.9282541 |
| H | 3.9578644 | -3.1986912 | -0.0964875 |
| N | 1.1750972 | 2.2514001 | 1.3443331 |
| N | 2.4028278 | 2.6434224 | 1.5315547 |
| C | 1.5392221 | 4.9710262 | 1.5696323 |
| C | 2.5849941 | 4.0085150 | 1.6495885 |
| O | 0.3142321 | 4.6399695 | 1.3985569 |
| C | 1.8548436 | 6.4473394 | 1.6936732 |
| C | 3.9728830 | 4.4191990 | 1.8170402 |
| H | 1.7193897 | 6.7286975 | 2.7497540 |
| H | 1.0982599 | 6.9962301 | 1.1206846 |
| C | 3.2774061 | 6.8310074 | 1.2530361 |
| O | 4.9180399 | 3.6133535 | 1.8353528 |
| C | 4.2510001 | 5.9053077 | 2.0015491 |
| C | 3.4341538 | 6.6540264 | -0.2677175 |
| C | 3.5576475 | 8.2937201 | 1.6260198 |
| H | 4.1880132 | 6.1204003 | 3.0796144 |
| H | 5.2874888 | 6.0867649 | 1.6972160 |
| H | 2.7376082 | 7.3091735 | -0.8033641 |
| H | 4.4532672 | 6.9100752 | -0.5787883 |
| H | 3.2347246 | 5.6210657 | -0.5727394 |
| H | 3.4571289 | 8.4473128 | 2.7068401 |
| H | 4.5744772 | 8.5793523 | 1.3322536 |
| H | 2.8553764 | 8.9650009 | 1.1173291 |

**D** : mNHO-like via N-N rotation of **C**

64

Energy = -1509.493769271

| | | | |
|---|---|---|---|
| N | 1.9247031 | -1.5404413 | 1.1754653 |
| N | 0.6681441 | -1.0650781 | 1.3138373 |
| N | 2.5565121 | -0.5729935 | 0.5348801 |
| C | 0.4926668 | 0.2201886 | 0.7835708 |
| C | -0.2798018 | -1.9210329 | 2.0248970 |
| C | 3.9611472 | -0.7160790 | 0.2266260 |
| C | 1.7760785 | 0.5005389 | 0.2658839 |
| C | -0.6931236 | 0.9779866 | 0.8132386 |
| H | -0.5053015 | -1.5019034 | 3.0062561 |
| H | 0.2003930 | -2.8940174 | 2.1298774 |
| H | -1.1930838 | -2.0098215 | 1.4378574 |
| C | 4.8881666 | -0.4576411 | 1.2413225 |
| C | 4.3250199 | -1.0946609 | -1.0724189 |
| H | 2.1833607 | 1.3830252 | -0.1940566 |
| C | -0.8453847 | 2.2700138 | 0.1635926 |
| N | -1.6644413 | 0.5973922 | 1.7908022 |
| C | 6.2424810 | -0.5893759 | 0.9156219 |
| C | 4.4528195 | -0.0579843 | 2.6279194 |
| C | 5.6893728 | -1.2125053 | -1.3430292 |
| C | 3.2906152 | -1.3814472 | -2.1304911 |
| C | -1.8277543 | 3.1848118 | 0.6117361 |
| C | -0.0911285 | 2.6591652 | -0.9690153 |
| N | -2.9230207 | 0.1961549 | 1.4920004 |
| C | 6.6606089 | -0.9638349 | -0.3644001 |
| H | 6.9856805 | -0.3900066 | 1.6841529 |
| H | 3.9885014 | -0.9016100 | 3.1503366 |
| H | 5.3116813 | 0.2779844 | 3.2130726 |
| H | 3.7158907 | 0.7518933 | 2.5968718 |
| H | 5.9984824 | -1.5078236 | -2.3432004 |
| H | 3.7742791 | -1.6651412 | -3.0674377 |
| H | 2.6307982 | -2.1992320 | -1.8204460 |
| H | 2.6594007 | -0.5069976 | -2.3220065 |
| C | -2.0046265 | 4.4226692 | 0.0016696 |
| H | -2.4670206 | 2.9125330 | 1.4461854 |
| C | -0.2698398 | 3.8990342 | -1.5745240 |
| H | 0.6062723 | 1.9608574 | -1.4189988 |
| C | -3.2248863 | -0.2320009 | 0.3055769 |
| C | 8.1272132 | -1.0972357 | -0.6917005 |
| C | -1.2195629 | 4.8031898 | -1.0907366 |
| H | -2.7673416 | 5.0974779 | 0.3835581 |
| H | 0.3287045 | 4.1541399 | -2.4461236 |
| C | -4.6022398 | -0.7002645 | 0.0631305 |
| C | -2.2848381 | -0.2884854 | -0.8799471 |
| H | 8.4096139 | -0.4147970 | -1.5015020 |
| H | 8.3605570 | -2.1140273 | -1.0277627 |
| H | 8.7475604 | -0.8721677 | 0.1797184 |
| H | -1.3579499 | 5.7704553 | -1.5651512 |
| C | -4.9907619 | -1.1927915 | -1.1954080 |
| C | -5.5629936 | -0.6773709 | 1.0935667 |
| O | -2.3292567 | 0.4605889 | -1.8416169 |
| O | -1.5573992 | -1.4459137 | -0.8738377 |
| C | -6.2916661 | -1.6461209 | -1.4164155 |
| H | -4.2768324 | -1.2148084 | -2.0132294 |
| C | -6.8581984 | -1.1296394 | 0.8693509 |
| H | -5.2718341 | -0.2983080 | 2.0673334 |
| C | -0.7034506 | -1.6258924 | -2.0306349 |
| C | -7.2334578 | -1.6181497 | -0.3879123 |
| H | -6.5672392 | -2.0206730 | -2.3985533 |
| H | -7.5828501 | -1.1015986 | 1.6790190 |
| H | -1.3079299 | -1.7205611 | -2.9356646 |
| H | -0.0298408 | -0.7718247 | -2.1286199 |
| H | -0.1491375 | -2.5433263 | -1.8364314 |
| H | -8.2465616 | -1.9702212 | -0.5601660 |
| H | -1.6622655 | 1.0787439 | 2.6843699 |

**E**: contact ion pair of $OMe^-$ anion

64

Energy = -1509.480166836

| | | | |
|---|---|---|---|
| N | 2.4190047 | 1.2034485 | -1.5465088 |
| N | 1.1115325 | 1.4342794 | -1.6446944 |
| N | 2.5193459 | 0.4115866 | -0.4774093 |
| C | 0.3755960 | 0.7971906 | -0.6864160 |
| C | 0.6411720 | 2.3123770 | -2.7223332 |
| C | 3.8206418 | -0.0417726 | -0.0406163 |
| C | 1.3136907 | 0.1320637 | 0.0775813 |
| C | -1.0988212 | 0.8606430 | -0.5054609 |
| H | 0.0353988 | 1.7299275 | -3.4156008 |
| H | 1.5228670 | 2.7168262 | -3.2153449 |
| H | 0.0497345 | 3.1165764 | -2.2812913 |
| C | 4.1825725 | -1.3692045 | -0.3056099 |
| C | 4.6425204 | 0.8673649 | 0.6339173 |
| H | 1.1827884 | -0.4997910 | 0.9401227 |
| C | -1.5039558 | 1.9780143 | 0.4427556 |
| N | -1.8331446 | 0.8740100 | -1.7760183 |
| C | -1.5930281 | -0.5870114 | 0.1276227 |
| C | 5.4418945 | -1.7804544 | 0.1344581 |
| C | 3.2579742 | -2.3156772 | -1.0274248 |
| C | 5.8919081 | 0.3999442 | 1.0532965 |
| C | 4.2068798 | 2.2847374 | 0.9045481 |
| C | -0.7071200 | 2.3087110 | 1.5474020 |
| C | -2.7192721 | 2.6544419 | 0.2717298 |
| N | -3.0331397 | 0.1332490 | -1.6291383 |
| H | -2.0947604 | 1.8072522 | -2.0899187 |
| C | -2.9404125 | -0.6711768 | -0.6215262 |
| O | -1.4700322 | -0.7427078 | 1.3856373 |
| C | 6.3078430 | -0.9131292 | 0.8126763 |
| H | 5.7527157 | -2.8039828 | -0.0619956 |
| H | 2.8255249 | -1.8546097 | -1.9210943 |
| H | 3.7986940 | -3.2155186 | -1.3279914 |
| H | 2.4255156 | -2.6205351 | -0.3835180 |
| H | 6.5519493 | 1.0814058 | 1.5846457 |
| H | 4.8999609 | 2.7674328 | 1.5966564 |
| H | 4.1785968 | 2.8728138 | -0.0192837 |
| H | 3.2036475 | 2.3167224 | 1.3441239 |
| C | -1.0991216 | 3.3040696 | 2.4411402 |
| H | 0.2261685 | 1.7829042 | 1.7193613 |
| C | -3.1147097 | 3.6482959 | 1.1676638 |
| H | -3.3791864 | 2.3908826 | -0.5492842 |
| C | -4.0150322 | -1.6151275 | -0.3092901 |
| C | 7.6626097 | -1.3913718 | 1.2717182 |
| C | -2.3044973 | 3.9828250 | 2.2536207 |
| H | -0.4625069 | 3.5464503 | 3.2878073 |
| H | -4.0623643 | 4.1578641 | 1.0159986 |
| C | -5.0568536 | -1.8547815 | -1.2265609 |
| C | -4.0221810 | -2.3022174 | 0.9171820 |
| H | 8.2729990 | -1.7061466 | 0.4174507 |
| H | 7.5655848 | -2.2560927 | 1.9377464 |
| H | 8.1991713 | -0.6028009 | 1.8055017 |
| H | -2.6108321 | 4.7597411 | 2.9483932 |
| C | -6.0769751 | -2.7493209 | -0.9204730 |
| H | -5.0480545 | -1.3349729 | -2.1797828 |
| C | -5.0465773 | -3.2000322 | 1.2174145 |
| H | -3.2157302 | -2.1074314 | 1.6171185 |
| C | -6.0778194 | -3.4272909 | 0.3043397 |
| H | -6.8726237 | -2.9265061 | -1.6395968 |
| H | -5.0399714 | -3.7235168 | 2.1700838 |
| H | -6.8743643 | -4.1280387 | 0.5397654 |
| O | -0.7329792 | -1.5676046 | -0.7320936 |
| C | -0.7172528 | -2.8807701 | -0.1866954 |
| H | -0.5684594 | -2.8482208 | 0.8995631 |
| H | -1.6521899 | -3.4210656 | -0.3990711 |
| H | 0.1134997 | -3.4155817 | -0.6591153 |

**F** : MIC-like via C5 C-H proton transfer to N 58

Energy = -1393.666006623

| | | | |
|---|---|---|---|
| N | 1.8820519 | -1.6460887 | 0.6402155 |
| N | 0.6177481 | -1.2715525 | 0.6698367 |
| N | 2.5187145 | -0.4942207 | 0.3386706 |
| C | 0.4750635 | 0.0714748 | 0.3885693 |
| C | -0.3977435 | -2.2742698 | 1.0064167 |
| C | 3.9559423 | -0.5407191 | 0.2363862 |
| C | 1.7387905 | 0.6285715 | 0.1657597 |
| C | -0.8701665 | 0.7323166 | 0.4121508 |
| H | -1.0514760 | -1.8649329 | 1.7786691 |
| H | 0.1190082 | -3.1545799 | 1.3838293 |
| H | -0.9725848 | -2.5285297 | 0.1145241 |
| C | 4.7141130 | -0.6196029 | 1.4096394 |
| C | 4.5345438 | -0.4757531 | -1.0377806 |
| C | -0.8741731 | 2.1085696 | -0.2697242 |
| N | -1.4266610 | 0.7774028 | 1.7668468 |
| C | 6.1068469 | -0.6412291 | 1.2787262 |
| C | 4.0593726 | -0.6592088 | 2.7670494 |
| C | 5.9291649 | -0.5001077 | -1.1156043 |
| C | 3.6828894 | -0.3766578 | -2.2767558 |
| C | -1.5296733 | 3.2043358 | 0.2945272 |
| C | -0.2803172 | 2.2324464 | -1.5315621 |
| N | -2.7205356 | 0.4441839 | 1.8144433 |
| C | 6.7309477 | -0.5868337 | 0.0289089 |
| H | 6.7157420 | -0.6924149 | 2.1790196 |
| H | 3.5457293 | -1.6128737 | 2.9315212 |
| H | 4.8065765 | -0.5311230 | 3.5540270 |
| H | 3.3097785 | 0.1341549 | 2.8636920 |
| H | 6.3985188 | -0.4482337 | -2.0959049 |
| H | 4.3097371 | -0.3584863 | -3.1714611 |
| H | 2.9946162 | -1.2265729 | -2.3518068 |
| H | 3.0694591 | 0.5307616 | -2.2497770 |
| C | -1.5640190 | 4.4262639 | -0.3820664 |
| H | -2.0216044 | 3.1198425 | 1.2583882 |
| C | -0.3189863 | 3.4508466 | -2.2041935 |
| H | 0.2147172 | 1.3782623 | -1.9780784 |
| C | -3.1178937 | -0.0747855 | 0.6636325 |
| C | 8.2349421 | -0.6368140 | -0.0875226 |
| C | -0.9562484 | 4.5542668 | -1.6299983 |
| H | -2.0705584 | 5.2736271 | 0.0707970 |
| H | 0.1519572 | 3.5396298 | -3.1790558 |
| C | -4.4623521 | -0.6213991 | 0.4868866 |

| | | | |
|---|---|---|---|
| C | -2.0156008 | -0.0593426 | -0.3083368 |
| H | 8.5941918 | 0.0435122 | -0.8663547 |
| H | 8.5690040 | -1.6470357 | -0.3560035 |
| H | 8.7131785 | -0.3681211 | 0.8587700 |
| H | -0.9816412 | 5.5046462 | -2.1553843 |
| C | -4.9030972 | -1.0474315 | -0.7786754 |
| C | -5.3412692 | -0.7224070 | 1.5824807 |
| O | -1.9377539 | -0.5242967 | -1.4354553 |
| C | -6.1912878 | -1.5570350 | -0.9404896 |
| H | -4.2325175 | -0.9786954 | -1.6275965 |
| C | -6.6249750 | -1.2291857 | 1.4121860 |
| H | -5.0058912 | -0.4005565 | 2.5634223 |
| C | -7.0572547 | -1.6499301 | 0.1496670 |
| H | -6.5178345 | -1.8817238 | -1.9244824 |
| H | -7.2919045 | -1.3005673 | 2.2669326 |
| H | -8.0595583 | -2.0482105 | 0.0205127 |
| H | -1.1048980 | 1.4354614 | 2.4673650 |

**Gc** : ketene-like with a cis N=N bond
58
Energy = -1393.651126372

| | | | |
|---|---|---|---|
| N | -0.5969350 | -1.9002582 | 0.4811346 |
| N | -1.7644580 | -1.9468458 | 1.1429166 |
| N | -0.1188208 | -0.6958189 | 0.7645581 |
| C | -2.0367246 | -0.7878051 | 1.8573686 |
| C | -2.5721638 | -3.1586074 | 0.9966815 |
| C | 1.1427179 | -0.2698377 | 0.2047369 |
| C | -0.9274938 | 0.0185015 | 1.5826739 |
| C | -3.1889708 | -0.5106083 | 2.6579604 |
| H | -2.1430734 | -3.7238264 | 0.1692090 |
| H | -3.6000629 | -2.8661988 | 0.7839643 |
| H | -2.5526435 | -3.7353501 | 1.9208925 |
| C | 2.3206092 | -0.8363942 | 0.7065561 |
| C | 1.1205820 | 0.7082712 | -0.7979113 |
| H | -0.6709084 | 1.0073529 | 1.9214298 |
| C | -3.3455308 | 0.8966501 | 3.1082002 |
| C | 3.5245154 | -0.3858974 | 0.1578684 |
| C | 2.3017601 | -1.8792609 | 1.7946027 |
| C | 2.3531747 | 1.1191399 | -1.3114066 |
| C | -0.1692268 | 1.3004267 | -1.3085094 |
| C | -3.3033023 | 1.9527338 | 2.1830811 |
| C | -3.5019177 | 1.2074768 | 4.4684619 |
| C | 3.5611440 | 0.5843376 | -0.8494559 |
| H | 4.4561958 | -0.8008232 | 0.5353568 |
| H | 1.9541766 | -2.8434981 | 1.4084627 |
| H | 3.3051921 | -2.0152466 | 2.2039434 |
| H | 1.6300855 | -1.5933753 | 2.6112735 |
| H | 2.3658064 | 1.8748506 | -2.0933692 |
| H | 0.0058391 | 1.8314783 | -2.2466199 |
| H | -0.9244334 | 0.5273631 | -1.4839889 |
| H | -0.5890664 | 2.0161319 | -0.5917656 |
| C | -3.4231158 | 3.2764424 | 2.5986847 |
| H | -3.2185772 | 1.7247742 | 1.1240029 |
| C | -3.6358130 | 2.5311340 | 4.8848976 |
| H | -3.5154184 | 0.4044908 | 5.1990861 |
| C | 4.8745087 | 1.0289780 | -1.4427780 |
| C | -3.5980442 | 3.5708844 | 3.9526730 |
| H | -3.4083799 | 4.0763866 | 1.8635324 |
| H | -3.7673903 | 2.7510559 | 5.9409953 |
| H | 4.8388707 | 2.0820786 | -1.7370989 |
| H | 5.1064011 | 0.4429049 | -2.3410353 |
| H | 5.6955971 | 0.8886935 | -0.7341116 |
| H | -3.7072168 | 4.6013701 | 4.2792644 |
| N | -3.9032746 | -1.5963009 | 3.0135635 |
| N | -5.0723147 | -1.6777600 | 3.5703062 |
| C | -5.8755538 | -0.4367625 | 3.6636739 |
| C | -6.1967090 | 0.3884610 | 2.4974910 |
| C | -6.3061184 | -0.1811140 | 4.8869669 |
| C | -6.7233958 | 1.6854237 | 2.6425536 |
| C | -5.9564745 | -0.0947861 | 1.1990541 |
| O | -6.6550403 | -0.0660500 | 6.0086903 |
| C | -6.9967561 | 2.4717453 | 1.5294761 |
| H | -6.8869307 | 2.0865865 | 3.6398789 |
| C | -6.2188301 | 0.7036203 | 0.0866824 |
| H | -5.5617615 | -1.0971556 | 1.0715603 |
| C | -6.7363653 | 1.9909229 | 0.2418462 |
| H | -7.3966131 | 3.4730199 | 1.6660241 |
| H | -6.0162721 | 0.3157740 | -0.9085307 |
| H | -6.9338450 | 2.6124677 | -0.6269354 |

**G** : ketene-like with a trans N=N bond
58
Energy = -1393.659430062

| | | | |
|---|---|---|---|
| N | -0.2595110 | -1.7978094 | 0.1003714 |
| N | -1.5804097 | -1.5934832 | 0.2699264 |
| N | 0.2807729 | -0.6225616 | 0.3944308 |
| C | -1.8915897 | -0.2918831 | 0.6549650 |
| C | -2.4663161 | -2.7364688 | 0.0624424 |
| C | 1.7137099 | -0.4549731 | 0.3255074 |
| C | -0.6311321 | 0.3171871 | 0.7320531 |
| C | -3.1840851 | 0.2613668 | 0.8829551 |
| H | -1.8346344 | -3.6246651 | 0.0368829 |
| H | -3.0179856 | -2.6205278 | -0.8704301 |
| H | -3.1772952 | -2.7805632 | 0.8876421 |
| C | 2.4253845 | -0.3566721 | 1.5270038 |
| C | 2.3154373 | -0.3809323 | -0.9373514 |
| H | -0.3471484 | 1.3288156 | 0.9653885 |
| C | -3.2856774 | 1.5442693 | 1.6104230 |
| C | 3.8092119 | -0.1810998 | 1.4338123 |
| C | 1.7406979 | -0.4353368 | 2.8683399 |
| C | 3.7005375 | -0.2026308 | -0.9710226 |
| C | 1.5106260 | -0.4816680 | -2.2077959 |
| C | -4.1948061 | 2.5481467 | 1.2214250 |
| C | -2.4717225 | 1.7981219 | 2.7317507 |
| C | 4.4623404 | -0.1046492 | 0.1993509 |
| H | 4.3880338 | -0.1057472 | 2.3514583 |
| H | 1.0137437 | -1.2532283 | 2.9004182 |
| H | 2.4773858 | -0.5952326 | 3.6587434 |
| H | 1.2023521 | 0.4927172 | 3.0943378 |
| H | 4.1931145 | -0.1324625 | -1.9381403 |

| | | | |
|---|---|---|---|
| H | 2.1187098 | -0.1827312 | -3.0644254 |
| H | 1.1637249 | -1.5073936 | -2.3725329 |
| H | 0.6240035 | 0.1606442 | -2.1708791 |
| C | -4.2660667 | 3.7550236 | 1.9134643 |
| H | -4.8460153 | 2.3733442 | 0.3737967 |
| C | -2.5421979 | 3.0068613 | 3.4222023 |
| H | -1.7892251 | 1.0260852 | 3.0789143 |
| C | 5.9603391 | 0.0567827 | 0.1286213 |
| C | -3.4408372 | 3.9957337 | 3.0158551 |
| H | -4.9709864 | 4.5159839 | 1.5881458 |
| H | -1.9042049 | 3.1706253 | 4.2869491 |
| H | 6.2499525 | 0.6847514 | -0.7194293 |
| H | 6.4448603 | -0.9187345 | -0.0040299 |
| H | 6.3538358 | 0.5019268 | 1.0466897 |
| H | -3.5037959 | 4.9367356 | 3.5552020 |
| N | -4.2216735 | -0.4465330 | 0.3774359 |
| N | -5.4208445 | 0.0053750 | 0.5797451 |
| C | -6.4625005 | -0.7794864 | 0.0120563 |
| C | -7.8501981 | -0.3955420 | 0.2888834 |
| C | -6.1434245 | -1.8086605 | -0.7762072 |
| C | -8.9397880 | -1.1297527 | -0.2158457 |
| C | -8.1111668 | 0.7392675 | 1.0775802 |
| O | -5.7465032 | -2.6702171 | -1.4708641 |
| C | -10.2472406 | -0.7407520 | 0.0574199 |
| H | -8.7604619 | -2.0131919 | -0.8261135 |
| C | -9.4252341 | 1.1224098 | 1.3480613 |
| H | -7.2725970 | 1.3058143 | 1.4685947 |
| C | -10.5009397 | 0.3898355 | 0.8426567 |
| H | -11.0732009 | -1.3228867 | -0.3425729 |
| H | -9.6082894 | 2.0023768 | 1.9596992 |
| H | -11.5222553 | 0.6921291 | 1.0557228 |

**2a**$H^+$ : ylidic carbon protonated mNHO **2a**
44
Energy = -901.9075346309

| | | | |
|---|---|---|---|
| N | 0.3172789 | 1.3505084 | 0.3096209 |
| N | -0.9566004 | 1.3702623 | -0.0500703 |
| N | 0.8360872 | 0.3418403 | -0.3808902 |
| C | -1.2761027 | 0.3919154 | -0.9561198 |
| C | -1.8543436 | 2.3674821 | 0.5455378 |
| C | 2.2368186 | 0.0039088 | -0.2335032 |
| C | -0.0900441 | -0.2749041 | -1.1665023 |
| C | -2.6540300 | 0.1674150 | -1.4840953 |
| H | -1.2380145 | 3.0667843 | 1.1064183 |
| H | -2.5594242 | 1.8559910 | 1.2027395 |
| H | -2.3881899 | 2.8791508 | -0.2554066 |
| C | 3.1840531 | 0.8144993 | -0.8696090 |
| C | 2.5590937 | -1.1255768 | 0.5295742 |
| H | 0.1583024 | -1.1083958 | -1.8029020 |
| C | -3.6397529 | -0.2080699 | -0.3857687 |
| H | -2.9996911 | 1.0715575 | -1.9969813 |
| C | 4.5244622 | 0.4506854 | -0.7183371 |
| C | 2.7854904 | 2.0203268 | -1.6806968 |
| C | 3.9148309 | -1.4381315 | 0.6478733 |
| C | 1.5009684 | -1.9660056 | 1.1988876 |
| C | -4.8725065 | 0.4451975 | -0.2977593 |
| C | -3.3265096 | -1.2066836 | 0.5442311 |
| C | 4.9080008 | -0.6641843 | 0.0355698 |
| H | 5.2854595 | 1.0540310 | -1.2071081 |
| H | 2.4213677 | 2.8265360 | -1.0340953 |
| H | 3.6422668 | 2.3966239 | -2.2430468 |
| H | 1.9866834 | 1.7806648 | -2.3912681 |
| H | 4.1990131 | -2.3070779 | 1.2363731 |
| H | 1.9640749 | -2.6784066 | 1.8842843 |
| H | 0.8003622 | -1.3472677 | 1.7703494 |
| H | 0.9198048 | -2.5371589 | 0.4653158 |
| C | -5.7835819 | 0.1025373 | 0.7029860 |
| H | -5.1202484 | 1.2249403 | -1.0138270 |
| C | -4.2342929 | -1.5476032 | 1.5464130 |
| H | -2.3715909 | -1.7243681 | 0.4846026 |
| C | 6.3646848 | -1.0118599 | 0.2071945 |
| C | -5.4654896 | -0.8928048 | 1.6280315 |
| H | -6.7385496 | 0.6165558 | 0.7608560 |
| H | -3.9818280 | -2.3244850 | 2.2620973 |
| H | 6.7562277 | -0.5630970 | 1.1287247 |
| H | 6.9623268 | -0.6332867 | -0.6264895 |
| H | 6.5064790 | -2.0938833 | 0.2819670 |
| H | -6.1717559 | -1.1568659 | 2.4094869 |
| H | -2.5939856 | -0.6227736 | -2.2390814 |

**2a** : mNHO
43
Energy = -901.4240576117

| | | | |
|---|---|---|---|
| N | 0.7346772 | 2.0311123 | 0.0227195 |
| N | -0.6029641 | 2.2200933 | 0.0231192 |
| N | 0.8511412 | 0.7147898 | 0.0092983 |
| C | -1.3567153 | 1.0340553 | 0.0057808 |
| C | -1.1337838 | 3.5685662 | 0.0336478 |
| C | 2.1657343 | 0.1174508 | -0.0035322 |
| C | -0.3328737 | 0.0517580 | 0.0000708 |
| C | -2.7469696 | 1.0294055 | -0.0093788 |
| H | -0.2934538 | 4.2604937 | 0.0710129 |
| H | -1.7736514 | 3.7050894 | 0.9113844 |
| H | -1.7244659 | 3.7430751 | -0.8716304 |
| C | 2.8403468 | 0.0249641 | -1.2264483 |
| C | 2.6928300 | -0.3562061 | 1.2038497 |
| H | -0.3545730 | -1.0219873 | -0.0407960 |
| C | -3.6296509 | -0.1019541 | 0.0087989 |
| H | -3.2256378 | 2.0042017 | -0.0464208 |
| C | 4.1030518 | -0.5746007 | -1.2149367 |
| C | 2.2344584 | 0.5503233 | -2.5026794 |
| C | 3.9599921 | -0.9440861 | 1.1597283 |
| C | 1.9296995 | -0.2398675 | 2.4988440 |
| C | -5.0325098 | 0.1248692 | -0.0787934 |
| C | -3.2284478 | -1.4612589 | 0.1166102 |
| C | 4.6784730 | -1.0601465 | -0.0356205 |
| H | 4.6457653 | -0.6668076 | -2.1530784 |
| H | 2.2126890 | 1.6456858 | -2.5023479 |
| H | 2.8171764 | 0.2181624 | -3.3648191 |
| H | 1.2023962 | 0.2046291 | -2.6256854 |

| | | | |
|---|---|---|---|
| H | 4.3936636 | -1.3192487 | 2.0839983 |
| H | 2.5722140 | -0.5028412 | 3.3421014 |
| H | 1.5567106 | 0.7786712 | 2.6490110 |
| H | 1.0620598 | -0.9094434 | 2.5093309 |
| C | -5.9527879 | -0.9144703 | -0.0671500 |
| H | -5.3861788 | 1.1513738 | -0.1592871 |
| C | -4.1577256 | -2.4995081 | 0.1280541 |
| H | -2.1794178 | -1.7163753 | 0.2107718 |
| C | 6.0565257 | -1.6741178 | -0.0476951 |
| C | -5.5292275 | -2.2471786 | 0.0340379 |
| H | -7.0141098 | -0.6861232 | -0.1381597 |
| H | -3.8007214 | -3.5236655 | 0.2146369 |
| H | 6.1536476 | -2.4431105 | 0.7244121 |
| H | 6.8187727 | -0.9096854 | 0.1496000 |
| H | 6.2811505 | -2.1216372 | -1.0202192 |
| H | -6.2477068 | -3.0616049 | 0.0419587 |

**3aa**$H^+$ : N-protonated **3aa**

59

Energy = -1394.157601927

| | | | |
|---|---|---|---|
| N | 1.8652150 | -1.6143609 | 0.8716809 |
| N | 0.5949294 | -1.2509076 | 0.9239342 |
| N | 2.5045704 | -0.5283345 | 0.4484120 |
| C | 0.3995032 | 0.0505877 | 0.5359077 |
| C | -0.4084381 | -2.2263969 | 1.3735658 |
| C | 3.9391106 | -0.5499102 | 0.2611064 |
| C | 1.6586860 | 0.5146038 | 0.2305656 |
| C | -0.9312895 | 0.7270425 | 0.4945985 |
| H | -1.0320938 | -1.7489002 | 2.1298895 |
| H | 0.1295452 | -3.0721702 | 1.7960537 |
| H | -1.0024306 | -2.5442798 | 0.5154983 |
| C | 4.7543459 | -0.6786957 | 1.3931226 |
| C | 4.4281405 | -0.4228467 | -1.0461125 |
| H | 2.0035120 | 1.4801659 | -0.0990419 |
| C | -0.8529766 | 2.0868110 | -0.2175872 |
| N | -1.5406494 | 0.7766035 | 1.8199412 |
| C | 6.1336439 | -0.6789553 | 1.1745577 |
| C | 4.1882955 | -0.8006081 | 2.7845184 |
| C | 5.8158443 | -0.4345930 | -1.2006540 |
| C | 3.5174100 | -0.2860165 | -2.2406426 |
| C | -1.2842991 | 3.2646915 | 0.3941636 |
| C | -0.3632319 | 2.1212787 | -1.5301275 |
| N | -2.8519664 | 0.4578261 | 1.7881368 |
| C | 6.6812592 | -0.5633659 | -0.1082317 |
| H | 6.7951440 | -0.7648898 | 2.0329939 |
| H | 3.7777196 | -1.8013593 | 2.9568923 |
| H | 4.9717785 | -0.6231574 | 3.5239307 |
| H | 3.3830633 | -0.0784323 | 2.9581372 |
| H | 6.2276359 | -0.3452694 | -2.2028342 |
| H | 4.0705417 | -0.4956980 | -3.1581684 |
| H | 2.6697131 | -0.9769774 | -2.1873545 |
| H | 3.1163391 | 0.7313674 | -2.3233367 |
| C | -1.1996741 | 4.4765512 | -0.2944533 |
| H | -1.6934654 | 3.2567137 | 1.3988409 |
| C | -0.2762018 | 3.3336276 | -2.2103094 |
| H | -0.0695675 | 1.2005134 | -2.0255922 |
| C | -3.1844366 | -0.0844666 | 0.6337702 |
| C | 8.1738896 | -0.6013305 | -0.3123462 |
| C | -0.6908381 | 4.5154825 | -1.5918546 |
| H | -1.5344100 | 5.3885460 | 0.1899203 |
| H | 0.1059118 | 3.3524720 | -3.2263066 |
| C | -4.5190337 | -0.6231497 | 0.3763781 |
| C | -2.0241520 | -0.1089965 | -0.2715465 |
| H | 8.4699164 | -0.0017599 | -1.1777404 |
| H | 8.5055894 | -1.6313333 | -0.4940335 |
| H | 8.7028649 | -0.2339675 | 0.5713209 |
| H | -0.6247907 | 5.4599448 | -2.1231056 |
| C | -4.9003417 | -1.0006376 | -0.9227787 |
| C | -5.4431555 | -0.7573588 | 1.4295167 |
| O | -1.8565067 | -0.6349494 | -1.3566045 |
| C | -6.1815988 | -1.4967252 | -1.1600927 |
| H | -4.1954127 | -0.9049347 | -1.7406719 |
| C | -6.7192572 | -1.2509769 | 1.1834498 |
| H | -5.1498778 | -0.4735483 | 2.4352552 |
| C | -7.0941114 | -1.6230746 | -0.1121834 |
| H | -6.4660720 | -1.7835858 | -2.1681605 |
| H | -7.4243375 | -1.3507251 | 2.0035235 |
| H | -8.0908324 | -2.0111832 | -0.3001572 |
| H | -1.2888468 | 1.4896915 | 2.4954476 |

**3aa** : 3-triazolium-(3*H*-)pyrazol-4-olate

58

Energy = -1393.701029554

| | | | |
|---|---|---|---|
| N | 0.9232247 | -1.5639984 | 1.3605293 |
| N | 2.1988850 | -1.2114411 | 1.3297055 |
| O | -1.5398835 | 0.2182906 | -1.7794372 |
| N | -2.6661148 | 0.4163871 | 1.5454114 |
| C | 5.8993283 | 1.6555880 | -0.4887122 |
| N | 2.2439830 | -0.2284535 | 0.4334671 |
| C | 4.9273185 | 2.3177816 | 0.2677576 |
| C | -3.5441741 | 2.5659827 | -1.3988415 |
| C | -1.7406367 | -2.3659749 | -0.0872822 |
| C | 1.0198106 | 0.0446566 | -0.0982942 |
| C | -2.8955033 | -2.9727358 | 0.4185757 |
| C | -5.0431012 | 3.8516007 | 0.5700520 |
| C | -0.9966846 | -3.0197420 | -1.0776471 |
| C | -1.3939449 | -4.2726444 | -1.5454487 |
| C | -4.2733874 | 2.7402245 | 0.9012245 |
| C | 3.5024409 | 0.4134097 | 0.1258270 |
| C | 4.4371731 | -0.2973378 | -0.6388239 |
| N | -1.9269846 | -0.6283269 | 1.7161327 |
| C | 3.7077455 | 1.7165973 | 0.5925753 |
| C | 0.1408322 | -0.8264843 | 0.5087781 |
| C | -2.5422457 | -4.8793385 | -1.0331914 |
| C | -5.0730071 | 4.3313995 | -0.7438046 |
| C | -2.7052720 | 0.9067475 | 0.2619492 |
| C | -1.8685027 | 0.1265576 | -0.5815023 |
| C | -3.2925339 | -4.2234582 | -0.0540749 |
| C | -1.3300944 | -0.9839757 | 0.3796828 |
| C | -3.5071083 | 2.0726537 | -0.0777916 |

| | | | |
|---|---|---|---|
| C | -4.3181287 | 3.6792906 | -1.7221276 |
| C | 5.6355678 | 0.3542963 | -0.9345131 |
| H | 6.3774665 | -0.1679151 | -1.5339817 |
| H | 5.1191704 | 3.3284616 | 0.6195820 |
| H | 0.8627333 | 0.7921039 | -0.8578233 |
| H | -3.4688981 | -2.4648510 | 1.1871213 |
| H | -4.1891229 | -4.6882154 | 0.3466790 |
| H | -2.8507348 | -5.8561565 | -1.3946477 |
| H | -0.8077408 | -4.7725040 | -2.3114957 |
| H | -0.1115603 | -2.5439944 | -1.4916636 |
| H | -2.9589399 | 2.0629536 | -2.1617165 |
| H | -4.3317830 | 4.0400531 | -2.7478854 |
| H | -5.6755478 | 5.1987181 | -0.9993734 |
| H | -5.6259560 | 4.3479800 | 1.3423087 |
| H | -4.2557396 | 2.3723184 | 1.9225150 |
| C | 0.4933375 | -2.6589323 | 2.2415919 |
| H | 0.3291154 | -3.5513000 | 1.6348394 |
| H | 1.2854463 | -2.8236110 | 2.9692409 |
| H | -0.4340926 | -2.3469358 | 2.7212322 |
| C | 4.1648063 | -1.6959398 | -1.1303918 |
| H | 4.9239873 | -1.9948518 | -1.8559017 |
| H | 4.1782992 | -2.4148425 | -0.3041008 |
| H | 3.1831401 | -1.7657698 | -1.6125435 |
| C | 2.6714798 | 2.4465912 | 1.4088757 |
| H | 1.8267080 | 2.7652055 | 0.7869021 |
| H | 2.2724819 | 1.8159705 | 2.2102220 |
| H | 3.1082352 | 3.3400567 | 1.8594489 |
| C | 7.2153934 | 2.3200351 | -0.8049724 |
| H | 7.1611243 | 3.4001308 | -0.6456481 |
| H | 8.0093288 | 1.9231584 | -0.1602924 |
| H | 7.5119092 | 2.1316557 | -1.8416445 |

**TS1a** : nucleophilic addition with trans-Ph
64
Energy = -1509.485506662

| | | | |
|---|---|---|---|
| N | -0.5402432 | 1.7848188 | 2.4321131 |
| N | 0.7889124 | 1.8018934 | 2.3959925 |
| N | -0.8894492 | 1.5376390 | 1.1751667 |
| C | 1.3152454 | 1.5688478 | 1.1384992 |
| C | 1.5307558 | 1.9952861 | 3.6406960 |
| C | -2.2671242 | 1.3062517 | 0.8097541 |
| C | 0.1792969 | 1.3942676 | 0.3456901 |
| C | 2.6672931 | 1.1645839 | 0.9009100 |
| H | 2.2865114 | 2.7666166 | 3.4864916 |
| H | 2.0075249 | 1.0549398 | 3.9266982 |
| H | 0.8187648 | 2.3050903 | 4.4034521 |
| C | -2.8583994 | 0.1043317 | 1.2218157 |
| C | -2.9080093 | 2.2445052 | -0.0060309 |
| H | 0.0397821 | 1.1561307 | -0.6920080 |
| C | 3.3653885 | 1.4412319 | -0.3625034 |
| H | 3.3089373 | 1.2230798 | 1.7758636 |
| C | -4.1610736 | -0.1399526 | 0.7854382 |
| C | -2.1190130 | -0.8969229 | 2.0702734 |
| C | -4.2118729 | 1.9476967 | -0.4113338 |
| C | -2.2261895 | 3.5129144 | -0.4523593 |
| C | 2.7252068 | 1.8839728 | -1.5326162 |
| C | 4.7464868 | 1.1704257 | -0.4293316 |
| C | -4.8476906 | 0.7607141 | -0.0354799 |
| H | -4.6399851 | -1.0718153 | 1.0761675 |
| H | -1.1171210 | -1.0889168 | 1.6711016 |
| H | -2.0069662 | -0.5395241 | 3.0997078 |
| H | -2.6639396 | -1.8429086 | 2.0914489 |
| H | -4.7374453 | 2.6610049 | -1.0419804 |
| H | -1.6342524 | 3.9610382 | 0.3514867 |
| H | -1.5480028 | 3.3197071 | -1.2927421 |
| H | -2.9671775 | 4.2427728 | -0.7863944 |
| C | 3.4346671 | 2.0374038 | -2.7242186 |
| H | 1.6734398 | 2.1478816 | -1.5160185 |
| C | 5.4535882 | 1.3254931 | -1.6168314 |
| H | 5.2592286 | 0.8271741 | 0.4657973 |
| C | -6.2294405 | 0.4332709 | -0.5419285 |
| C | 4.7999879 | 1.7554064 | -2.7768956 |
| H | 2.9163209 | 2.3857329 | -3.6136659 |
| H | 6.5184499 | 1.1095970 | -1.6406798 |
| H | -6.1634782 | -0.1986485 | -1.4369894 |
| H | -6.7784260 | 1.3391116 | -0.8141749 |
| H | -6.8068905 | -0.1178462 | 0.2063931 |
| H | 5.3504006 | 1.8752950 | -3.7055259 |
| N | 2.4140610 | -0.7089972 | 0.8546827 |
| N | 1.4561829 | -0.9379257 | 0.1371470 |
| C | 0.7742018 | -2.0503366 | -0.2186901 |
| C | -0.3626169 | -1.8210176 | -1.1256829 |
| C | 1.0881608 | -3.3607790 | 0.3065449 |
| C | -1.5670184 | -2.5455387 | -1.0408760 |
| C | -0.2902841 | -0.7930811 | -2.0894070 |
| O | 0.4761250 | -4.4070994 | 0.0580301 |
| O | 2.1637947 | -3.3469135 | 1.1523602 |
| C | -2.6606159 | -2.2127587 | -1.8386176 |
| H | -1.6456911 | -3.3550694 | -0.3246118 |
| C | -1.3880573 | -0.4554426 | -2.8781346 |
| H | 0.6525559 | -0.2650754 | -2.2128549 |
| C | 2.4994026 | -4.6274879 | 1.7230689 |
| C | -2.5887727 | -1.1579156 | -2.7510101 |
| H | -3.5868765 | -2.7716133 | -1.7294942 |
| H | -1.3014201 | 0.3495079 | -3.6042123 |
| H | 3.3540748 | -4.4334032 | 2.3715214 |
| H | 1.6588601 | -5.0240036 | 2.2996549 |
| H | 2.7654026 | -5.3408168 | 0.9378560 |
| H | -3.4498058 | -0.8933277 | -3.3581967 |

**TS1c** : nucleophilic addition with cis N=N
64
Energy = -1509.480238710

| | | | |
|---|---|---|---|
| N | -0.2119767 | -1.5750389 | -1.7890841 |
| N | 0.9893669 | -1.0045658 | -1.8300042 |
| N | -0.5277746 | -1.5565065 | -0.4967693 |
| C | 1.4465207 | -0.5836197 | -0.5963579 |
| C | 1.6927579 | -0.9031277 | -3.1093180 |
| C | -1.7628671 | -2.1644610 | -0.0517163 |

| | | | |
|---|---|---|---|
| C | 0.4308019 | -0.9727623 | 0.2681995 |
| C | 2.6856921 | 0.1342838 | -0.3857114 |
| H | 2.6977320 | -1.3083671 | -2.9774959 |
| H | 1.7448070 | 0.1472540 | -3.3989837 |
| H | 1.1340472 | -1.4902549 | -3.8361705 |
| C | -2.8290798 | -1.3351212 | 0.3112272 |
| C | -1.8119189 | -3.5649870 | 0.0093309 |
| H | 0.3174867 | -0.8494422 | 1.3319939 |
| C | 3.7677730 | -0.4968242 | 0.3803517 |
| H | 3.0097542 | 0.6783457 | -1.2685280 |
| C | -3.9975715 | -1.9678739 | 0.7514891 |
| C | -2.7366250 | 0.1660776 | 0.2500316 |
| C | -3.0012750 | -4.1396478 | 0.4581889 |
| C | -0.6329539 | -4.4176382 | -0.3849179 |
| C | 5.0729575 | 0.0182703 | 0.2578569 |
| C | 3.5597259 | -1.5456603 | 1.2939479 |
| C | -4.1035337 | -3.3587326 | 0.8305456 |
| H | -4.8462062 | -1.3500174 | 1.0354904 |
| H | -3.7357193 | 0.6075746 | 0.2571057 |
| H | -2.1966953 | 0.5659816 | 1.1156650 |
| H | -2.2103599 | 0.5145077 | -0.6423582 |
| H | -3.0646626 | -5.2235503 | 0.5220193 |
| H | 0.2878897 | -4.0768613 | 0.1020265 |
| H | -0.8066637 | -5.4574650 | -0.1001932 |
| H | -0.4631018 | -4.3810868 | -1.4664837 |
| C | 6.1252681 | -0.4995487 | 1.0075358 |
| H | 5.2532436 | 0.8350721 | -0.4370289 |
| C | 4.6137642 | -2.0643343 | 2.0453596 |
| H | 2.5677909 | -1.9731198 | 1.4130244 |
| C | -5.3808008 | -4.0123538 | 1.2955824 |
| C | 5.9035236 | -1.5466014 | 1.9082599 |
| H | 7.1233160 | -0.0852754 | 0.8900393 |
| H | 4.4257677 | -2.8784267 | 2.7407400 |
| H | -5.1787658 | -4.7627026 | 2.0674743 |
| H | -5.8764522 | -4.5267229 | 0.4634321 |
| H | -6.0770168 | -3.2737186 | 1.7012201 |
| H | 6.7241763 | -1.9525803 | 2.4927698 |
| N | 2.2024281 | 1.5342351 | 0.8685049 |
| N | 1.2093741 | 2.2103309 | 0.7171366 |
| C | 0.1664119 | 2.4516593 | -0.1180976 |
| C | -0.9719663 | 3.1371775 | 0.5171671 |
| C | 0.2954622 | 2.1683249 | -1.5298809 |
| C | -1.1160684 | 3.0618970 | 1.9202596 |
| C | -1.9374862 | 3.8843088 | -0.1879464 |
| O | 1.3532672 | 2.0247623 | -2.1541843 |
| O | -0.9166800 | 2.1015463 | -2.1755429 |
| C | -2.1609373 | 3.7005205 | 2.5823738 |
| H | -0.3920031 | 2.4859527 | 2.4893993 |
| C | -2.9887750 | 4.5125254 | 0.4770655 |
| H | -1.8657946 | 3.9743990 | -1.2646515 |
| C | -0.8563710 | 2.0023140 | -3.6157461 |
| C | -3.1140853 | 4.4282119 | 1.8658448 |
| H | -2.2381707 | 3.6162425 | 3.6636828 |
| H | -3.7137786 | 5.0823627 | -0.0993304 |
| H | -0.6073586 | 0.9802628 | -3.9144295 |
| H | -1.8570773 | 2.2584997 | -3.9641962 |
| H | -0.1123945 | 2.6930074 | -4.0173773 |
| H | -3.9374042 | 4.9180459 | 2.3782371 |

**TS1** : nucleophilic addition, trans N=N cis-Ph 64

Energy = -1509.489504639

| | | | |
|---|---|---|---|
| N | 0.9410366 | -2.2252211 | -2.2283596 |
| N | 1.8565034 | -1.2578746 | -2.2218988 |
| N | 0.4394898 | -2.1917452 | -1.0006451 |
| C | 1.9557624 | -0.5953078 | -1.0101788 |
| C | 2.6064096 | -0.9799529 | -3.4449391 |
| C | -0.6380892 | -3.0747526 | -0.6142853 |
| C | 1.0048217 | -1.2363046 | -0.2160426 |
| C | 2.6894292 | 0.6115176 | -0.8218948 |
| H | 2.3504052 | -1.7510036 | -4.1691981 |
| H | 3.6743048 | -1.0047543 | -3.2212475 |
| H | 2.3269725 | 0.0044798 | -3.8265031 |
| C | -1.9480899 | -2.5935076 | -0.7264502 |
| C | -0.3141214 | -4.3331214 | -0.0950607 |
| H | 0.6456951 | -1.0447019 | 0.7790470 |
| C | 3.3087337 | 0.9976362 | 0.4457305 |
| H | 3.2427129 | 0.9373503 | -1.6985807 |
| C | -2.9709019 | -3.4387106 | -0.2879678 |
| C | -2.2418042 | -1.2289079 | -1.2932787 |
| C | -1.3762785 | -5.1375735 | 0.3250614 |
| C | 1.1154685 | -4.7993223 | 0.0082045 |
| C | 4.4771675 | 1.7860793 | 0.4087832 |
| C | 2.7539992 | 0.7010143 | 1.7060744 |
| C | -2.7057466 | -4.7084949 | 0.2367634 |
| H | -3.9990629 | -3.0914511 | -0.3572153 |
| H | -1.8646848 | -1.1402036 | -2.3182856 |
| H | -3.3183981 | -1.0476651 | -1.3068445 |
| H | -1.7660131 | -0.4382266 | -0.7032471 |
| H | -1.1557506 | -6.1189299 | 0.7386774 |
| H | 1.1667222 | -5.7529458 | 0.5376762 |
| H | 1.5577636 | -4.9336643 | -0.9854637 |
| H | 1.7357787 | -4.0730481 | 0.5451589 |
| C | 5.0783719 | 2.2414327 | 1.5778355 |
| H | 4.9135480 | 2.0359150 | -0.5556767 |
| C | 3.3565565 | 1.1635965 | 2.8753487 |
| H | 1.8287765 | 0.1451252 | 1.7845769 |
| C | -3.8329280 | -5.6079451 | 0.6785084 |
| C | 4.5226333 | 1.9290573 | 2.8228925 |
| H | 5.9825534 | 2.8416342 | 1.5192215 |
| H | 2.9059584 | 0.9266373 | 3.8357221 |
| H | -3.5263848 | -6.2445995 | 1.5137170 |
| H | -4.1412572 | -6.2668393 | -0.1429903 |
| H | -4.7075137 | -5.0254208 | 0.9816491 |
| H | 4.9902257 | 2.2820618 | 3.7376189 |
| N | 1.1364696 | 1.8551002 | -0.9036711 |
| N | 0.3398275 | 1.5022236 | -0.0641035 |
| C | -0.8563346 | 1.9720556 | 0.3682958 |
| C | -1.4832816 | 3.1536675 | -0.2414137 |
| C | -1.4502722 | 1.2335891 | 1.4646484 |

| | | | |
|---|---|---|---|
| C | -2.7795841 | 3.6028119 | 0.1096836 |
| C | -0.8002478 | 3.8900398 | -1.2356703 |
| O | -2.5177654 | 1.4831439 | 2.0277574 |
| O | -0.7009839 | 0.1445172 | 1.8868580 |
| C | -3.3436113 | 4.7212519 | -0.4984201 |
| H | -3.3337502 | 3.0634155 | 0.8655470 |
| C | -1.3723357 | 5.0094909 | -1.8378609 |
| H | 0.1942524 | 3.5768171 | -1.5359122 |
| C | -1.3083076 | -0.6073249 | 2.9601866 |
| C | -2.6497449 | 5.4389317 | -1.4762890 |
| H | -4.3420930 | 5.0341245 | -0.2018521 |
| H | -0.8095840 | 5.5486387 | -2.5961786 |
| H | -1.4323409 | 0.0180997 | 3.8473599 |
| H | -2.2811143 | -0.9992010 | 2.6522152 |
| H | -0.6139987 | -1.4240254 | 3.1629625 |
| H | -3.0954423 | 6.3118123 | -1.9454424 |

**TS20** : **TS2** but Ph trans to pro-carbenic C-H

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Energy = -2410.924240826

| | | | |
|---|---|---|---|
| N | -3.9577075 | -0.0925610 | -2.2602234 |
| N | -2.6806602 | -0.4446179 | -2.4439753 |
| N | -4.1520147 | -0.3126629 | -0.9632116 |
| C | -2.0531898 | -0.9028125 | -1.2922642 |
| C | -2.1017326 | -0.2458597 | -3.7697094 |
| C | -5.4265437 | -0.0151993 | -0.3536343 |
| C | -3.0535951 | -0.7901346 | -0.3251141 |
| C | -0.6286420 | -1.1897253 | -1.1892167 |
| H | -1.0206308 | -0.2184791 | -3.6536378 |
| H | -2.4739639 | 0.6989272 | -4.1655770 |
| H | -2.3766442 | -1.0677484 | -4.4340047 |
| C | -5.5219909 | 1.1481317 | 0.4181465 |
| C | -6.4822664 | -0.9183139 | -0.5297718 |
| H | -3.0336620 | -0.9681837 | 0.7358766 |
| C | -0.0199721 | -2.2106641 | -2.0746641 |
| N | 0.0005300 | -1.1542616 | 0.1132706 |
| C | -6.7496951 | 1.3953630 | 1.0410435 |
| C | -4.3592755 | 2.0937434 | 0.5602489 |
| C | -7.6862243 | -0.6195899 | 0.1116404 |
| C | -6.3260998 | -2.1611630 | -1.3683150 |
| C | -0.7493343 | -2.9895020 | -2.9912679 |
| C | 1.3749234 | -2.4145263 | -2.0104485 |
| N | -0.7741374 | -0.7366004 | 1.0532292 |
| C | -7.8363430 | 0.5263158 | 0.9031958 |
| H | -6.8560891 | 2.2940314 | 1.6442812 |
| H | -3.9768172 | 2.4033273 | -0.4175238 |
| H | -4.6614276 | 2.9880996 | 1.1093659 |
| H | -3.5230213 | 1.6285145 | 1.0919340 |
| H | -8.5235669 | -1.3038606 | -0.0060501 |
| H | -7.2133524 | -2.7920704 | -1.2807142 |
| H | -6.1846184 | -1.9091369 | -2.4248713 |
| H | -5.4543909 | -2.7451294 | -1.0520020 |
| C | -0.1124766 | -3.9014069 | -3.8337167 |
| H | -1.8327907 | -2.9083306 | -3.0256374 |
| C | 2.0085285 | -3.3267537 | -2.8490624 |
| H | 1.9365933 | -1.8501094 | -1.2739548 |
| C | -0.2674497 | -0.3878272 | 2.2645846 |
| C | -9.1416625 | 0.8049177 | 1.6063752 |
| C | 1.2725342 | -4.0721060 | -3.7765429 |
| H | -0.7056018 | -4.4923993 | -4.5271469 |
| H | 3.0854784 | -3.4595182 | -2.7806832 |
| C | 1.1689052 | -0.3691471 | 2.5815933 |
| C | -1.2301386 | 0.0884900 | 3.2186230 |
| H | -9.2746136 | 0.1247913 | 2.4567544 |
| H | -9.9922459 | 0.6540749 | 0.9334743 |
| H | -9.1741087 | 1.8295651 | 1.9863429 |
| H | 1.7682360 | -4.7818890 | -4.4325862 |
| C | 1.7589051 | 0.7049707 | 3.2817430 |
| C | 2.0233012 | -1.4025518 | 2.1385557 |
| O | -0.9967016 | 0.5629190 | 4.3405751 |
| O | -2.5539462 | -0.0526593 | 2.7982075 |
| C | 3.1318560 | 0.7445773 | 3.5247868 |
| H | 1.1244210 | 1.5112906 | 3.6325583 |
| C | 3.3904407 | -1.3702447 | 2.4046662 |
| H | 1.6011768 | -2.2319678 | 1.5850462 |
| C | -3.5251634 | 0.4180432 | 3.7497843 |
| C | 3.9588682 | -0.2952143 | 3.0917306 |
| H | 3.5578035 | 1.5932808 | 4.0551266 |
| H | 4.0206781 | -2.1891630 | 2.0685901 |
| H | -3.4455039 | -0.1279368 | 4.6942103 |
| H | -3.3958992 | 1.4871283 | 3.9442448 |
| H | -4.4948381 | 0.2332441 | 3.2837498 |
| H | 5.0288142 | -0.2628528 | 3.2728155 |
| H | -0.0560527 | 0.0174088 | -1.6655386 |
| C | 0.6319123 | 1.2775608 | -1.9050822 |
| C | 2.0131088 | 0.9827781 | -1.6330067 |
| C | -0.1012250 | 2.2724131 | -1.0921785 |
| H | 0.4708847 | 1.4403748 | -2.9726951 |
| N | 2.8978330 | 0.6002729 | -2.6310794 |
| C | 2.7995037 | 0.9137687 | -0.4784460 |
| C | -0.9918159 | 3.1562736 | -1.7351516 |
| C | 0.0017882 | 2.3614410 | 0.3082643 |
| N | 4.1321695 | 0.3192304 | -2.1876857 |
| C | 2.5878101 | 0.3773161 | -4.0346898 |
| N | 4.0396284 | 0.5287403 | -0.8781498 |
| H | 2.5694520 | 1.0525370 | 0.5639681 |
| C | -1.7162642 | 4.1059993 | -1.0186467 |
| H | -1.0987681 | 3.1038567 | -2.8172074 |
| C | -0.7231039 | 3.3105177 | 1.0242051 |
| H | 0.6154836 | 1.6579405 | 0.8567249 |
| H | 3.5201150 | 0.1446093 | -4.5463144 |
| H | 2.1421191 | 1.2796203 | -4.4586917 |
| H | 1.8918883 | -0.4636292 | -4.1188286 |
| C | 5.2135574 | 0.3608750 | -0.0572039 |
| C | -1.5801740 | 4.1976022 | 0.3693793 |
| H | -2.3887788 | 4.7779128 | -1.5464592 |
| H | -0.6293759 | 3.3405851 | 2.1066736 |
| C | 5.7985168 | -0.9119575 | 0.0220755 |
| C | 5.7066880 | 1.4738877 | 0.6328293 |
| H | -2.1478901 | 4.9336684 | 0.9314510 |

| | | | |
|---|---|---|---|
| C | 6.9242244 | -1.0466726 | 0.8345864 |
| C | 5.2269651 | -2.1046317 | -0.7002531 |
| C | 6.8404974 | 1.2806795 | 1.4291705 |
| C | 5.0573364 | 2.8322627 | 0.5570404 |
| C | 7.4605219 | 0.0350931 | 1.5442369 |
| H | 7.3851054 | -2.0278193 | 0.9242711 |
| H | 5.4025708 | -2.0402253 | -1.7785523 |
| H | 5.6871052 | -3.0229851 | -0.3281779 |
| H | 4.1451361 | -2.1728210 | -0.5474459 |
| H | 7.2436186 | 2.1311976 | 1.9738501 |
| H | 5.7705350 | 3.6045810 | 0.8548041 |
| H | 4.6982798 | 3.0592275 | -0.4511470 |
| H | 4.1977756 | 2.8918309 | 1.2353801 |
| C | 8.6796805 | -0.1474079 | 2.4131457 |
| H | 8.9035517 | 0.7633385 | 2.9747975 |
| H | 9.5568748 | -0.3992787 | 1.8054171 |
| H | 8.5329308 | -0.9669557 | 3.1254807 |

**TS2** : benzylic site C-H deprotonation by **2a**

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Energy = -2410.921402640

| | | | |
|---|---|---|---|
| N | -2.7460482 | -0.7433038 | -1.6216998 |
| N | -1.6601588 | -0.2580340 | -1.0081718 |
| N | -3.7585264 | -0.2344593 | -0.9262816 |
| C | -1.9567593 | 0.5500465 | 0.0791488 |
| C | -0.3632570 | -0.6878821 | -1.5250890 |
| C | -5.1149817 | -0.5731637 | -1.2799938 |
| C | -3.3482923 | 0.5539301 | 0.0948929 |
| C | -1.0165535 | 1.1470345 | 1.0167036 |
| H | -0.0230941 | 0.0214523 | -2.2808753 |
| H | -0.4953950 | -1.6922163 | -1.9307556 |
| H | 0.3433119 | -0.6956606 | -0.6978448 |
| C | -5.6631040 | -0.0150953 | -2.4401146 |
| C | -5.8172730 | -1.4384449 | -0.4293601 |
| H | -4.0447755 | 1.0545862 | 0.7454903 |
| C | -1.6260473 | 1.6798828 | 2.2670749 |
| N | 0.0945414 | 1.9255134 | 0.5599506 |
| C | -6.9856026 | -0.3542697 | -2.7432364 |
| C | -4.8713125 | 0.9119686 | -3.3266452 |
| C | -7.1331189 | -1.7448484 | -0.7827118 |
| C | -5.1887953 | -2.0176281 | 0.8137085 |
| C | -2.5008184 | 0.8902039 | 3.0395013 |
| C | -1.2597839 | 2.9387824 | 2.7749376 |
| N | 0.2646910 | 1.9426109 | -0.7220430 |
| C | -7.7321821 | -1.2148384 | -1.9323323 |
| H | -7.4420166 | 0.0712680 | -3.6339187 |
| H | -4.1246717 | 0.3570149 | -3.9050478 |
| H | -5.5352602 | 1.4250918 | -4.0259049 |
| H | -4.3339468 | 1.6648942 | -2.7403960 |
| H | -7.7007063 | -2.4179357 | -0.1439604 |
| H | -5.7742691 | -2.8683688 | 1.1696943 |
| H | -4.1633659 | -2.3547667 | 0.6357939 |
| H | -5.1527794 | -1.2770235 | 1.6215964 |
| C | -3.0156338 | 1.3526335 | 4.2470728 |
| H | -2.7587257 | -0.1089330 | 2.6978027 |
| C | -1.7659546 | 3.3965640 | 3.9921270 |
| H | -0.5668585 | 3.5447788 | 2.2018451 |
| C | 1.3894397 | 2.5326023 | -1.2160458 |
| C | -9.1504108 | -1.5803394 | -2.2938689 |
| C | -2.6520441 | 2.6127839 | 4.7342962 |
| H | -3.6897416 | 0.7209358 | 4.8205463 |
| H | -1.4699252 | 4.3760836 | 4.3603366 |
| C | 2.4109460 | 3.1811911 | -0.3692816 |
| C | 1.5971938 | 2.4542789 | -2.6325840 |
| H | -9.8108955 | -1.5026377 | -1.4239455 |
| H | -9.2022900 | -2.6160418 | -2.6512835 |
| H | -9.5359089 | -0.9307236 | -3.0841707 |
| H | -3.0467073 | 2.9717166 | 5.6808513 |
| C | 3.7830350 | 2.9177201 | -0.5383619 |
| C | 2.0412769 | 4.0556720 | 0.6722969 |
| O | 2.5637000 | 2.9095960 | -3.2653315 |
| O | 0.5825557 | 1.7882630 | -3.3189728 |
| C | 4.7390804 | 3.4884860 | 0.3004119 |
| H | 4.0954379 | 2.2510819 | -1.3345679 |
| C | 2.9956867 | 4.6324518 | 1.5077332 |
| H | 0.9918245 | 4.2845274 | 0.8180177 |
| C | 0.7825995 | 1.7159718 | -4.7410502 |
| C | 4.3533562 | 4.3473798 | 1.3331800 |
| H | 5.7905546 | 3.2535127 | 0.1529071 |
| H | 2.6791353 | 5.3065705 | 2.3003983 |
| H | 0.8468378 | 2.7165669 | -5.1783358 |
| H | 1.6964424 | 1.1641615 | -4.9825719 |
| H | -0.0919033 | 1.1882250 | -5.1262510 |
| H | 5.0980906 | 4.7889224 | 1.9903408 |
| H | -0.3350779 | 0.0045064 | 1.5703304 |
| C | 0.3895409 | -1.0112380 | 2.2681393 |
| C | 1.6832991 | -1.0422432 | 1.6428848 |
| C | -0.5007619 | -2.1873886 | 2.2663198 |
| H | 0.4123167 | -0.5061046 | 3.2360067 |
| N | 2.6261816 | -0.0374243 | 1.8329694 |
| C | 2.3060338 | -1.8759795 | 0.7099781 |
| C | -1.3158791 | -2.4289143 | 3.3920674 |
| C | -0.6771623 | -3.0361322 | 1.1546988 |
| N | 3.7373437 | -0.1977801 | 1.1097551 |
| C | 2.4663208 | 1.1704377 | 2.6345965 |
| N | 3.5164855 | -1.3163644 | 0.4378109 |
| H | 2.0074963 | -2.8049119 | 0.2577127 |
| C | -2.2486020 | -3.4614814 | 3.4103593 |
| H | -1.2128000 | -1.7821527 | 4.2602054 |
| C | -1.6094739 | -4.0728464 | 1.1734350 |
| H | -0.1036258 | -2.8765373 | 0.2480638 |
| H | 3.3888763 | 1.7416880 | 2.5475457 |
| H | 2.2778106 | 0.8921379 | 3.6743132 |
| H | 1.6270643 | 1.7402385 | 2.2127378 |
| C | 4.5172879 | -1.8051082 | -0.4825584 |
| C | -2.4029041 | -4.2973434 | 2.2998730 |
| H | -2.8580044 | -3.6165895 | 4.2971350 |
| H | -1.7211622 | -4.7029183 | 0.2946482 |
| C | 4.3870850 | -1.4862864 | -1.8370601 |
| C | 5.5688691 | -2.5758929 | 0.0341167 |

| | | | |
|---|---|---|---|
| H | -3.1322133 | -5.1019541 | 2.3103080 |
| C | 5.3716668 | -1.9811880 | -2.7016702 |
| C | 3.2431883 | -0.6608784 | -2.3668104 |
| C | 6.5191974 | -3.0452248 | -0.8721836 |
| C | 5.6699362 | -2.8780408 | 1.5073952 |
| C | 6.4364675 | -2.7585879 | -2.2422448 |
| H | 5.3024626 | -1.7425750 | -3.7605517 |
| H | 2.8353963 | 0.0188842 | -1.6155042 |
| H | 3.5693486 | -0.0609019 | -3.2197666 |
| H | 2.4289563 | -1.3099442 | -2.7115496 |
| H | 7.3454960 | -3.6457220 | -0.4982338 |
| H | 6.5234515 | -3.5304876 | 1.7034094 |
| H | 5.7959580 | -1.9584848 | 2.0892241 |
| H | 4.7647798 | -3.3748994 | 1.8748852 |
| C | 7.4840300 | -3.2779239 | -3.1954906 |
| H | 7.5192045 | -4.3733060 | -3.1767430 |
| H | 8.4799011 | -2.9162779 | -2.9150827 |
| H | 7.2776569 | -2.9580015 | -4.2201524 |

**TS3a** : $H^+$ transfer from **2a**$H^+$ to O=C of $\mathbf{B}^-$

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Energy = -2410.914370879

| | | | |
|---|---|---|---|
| N | 3.9159647 | -2.2759167 | 0.2837325 |
| N | 2.6086355 | -2.0550230 | 0.5683809 |
| N | 4.4513291 | -1.0640775 | 0.3157965 |
| C | 2.3110012 | -0.7013333 | 0.7811370 |
| C | 1.7642222 | -3.2337467 | 0.7332371 |
| C | 5.8551201 | -0.8940423 | 0.0246719 |
| C | 3.5659652 | -0.0857638 | 0.6089641 |
| C | 1.0496662 | -0.1403511 | 1.0936953 |
| H | 1.4918425 | -3.3425636 | 1.7860377 |
| H | 2.3552548 | -4.0878304 | 0.3983133 |
| H | 0.8352344 | -3.1241177 | 0.1718121 |
| C | 6.7799209 | -1.1217152 | 1.0498955 |
| C | 6.2187343 | -0.4899995 | -1.2653734 |
| H | 3.8704149 | 0.9425007 | 0.6957191 |
| C | 0.9470399 | 1.3200366 | 1.3213022 |
| N | 0.0310279 | -1.0401191 | 1.2136941 |
| C | 8.1300471 | -0.9273834 | 0.7440754 |
| C | 6.3414534 | -1.5578665 | 2.4243684 |
| C | 7.5813889 | -0.3130334 | -1.5187116 |
| C | 5.1862318 | -0.2521706 | -2.3385205 |
| C | 1.5566468 | 2.2554731 | 0.4654347 |
| C | 0.2305716 | 1.8234837 | 2.4240184 |
| N | -1.1577974 | -0.5826849 | 1.4481018 |
| C | 8.5484915 | -0.5278006 | -0.5299202 |
| H | 8.8703662 | -1.0896552 | 1.5242034 |
| H | 5.9473960 | -2.5798078 | 2.4026338 |
| H | 7.1835969 | -1.5278681 | 3.1192004 |
| H | 5.5471285 | -0.9114207 | 2.8131349 |
| H | 7.8918028 | -0.0007882 | -2.5132857 |
| H | 5.6678199 | -0.1490267 | -3.3133072 |
| H | 4.4721913 | -1.0807394 | -2.3904057 |
| H | 4.6167440 | 0.6644170 | -2.1438407 |
| C | 1.4623087 | 3.6265531 | 0.6982588 |
| H | 2.0690210 | 1.9053704 | -0.4248889 |
| C | 0.1316930 | 3.1924989 | 2.6565654 |
| H | -0.2493311 | 1.1254738 | 3.0986503 |
| C | -2.1853804 | -1.5392409 | 1.5430673 |
| C | 10.0149327 | -0.3563415 | -0.8397060 |
| C | 0.7458294 | 4.1054386 | 1.7952782 |
| H | 1.9252674 | 4.3224207 | 0.0034752 |
| H | -0.4352876 | 3.5503102 | 3.5126291 |
| C | -3.3305983 | -1.0672359 | 2.3454226 |
| C | -2.1718009 | -2.7728562 | 0.9056666 |
| H | 10.1728164 | 0.4324663 | -1.5812565 |
| H | 10.4307674 | -1.2845833 | -1.2515152 |
| H | 10.5829981 | -0.1104936 | 0.0620468 |
| H | 0.6505432 | 5.1739077 | 1.9662957 |
| C | -4.6559894 | -1.5251701 | 2.1771308 |
| C | -3.1301971 | -0.0320487 | 3.2839859 |
| O | -1.3765659 | -3.1410090 | -0.0841614 |
| O | -3.0542550 | -3.7310468 | 1.3465392 |
| C | -5.7099095 | -0.9783452 | 2.9037819 |
| H | -4.8609963 | -2.3090326 | 1.4596261 |
| C | -4.1858529 | 0.5157505 | 4.0097778 |
| H | -2.1248391 | 0.3491771 | 3.4186824 |
| C | -3.4066546 | -4.7679112 | 0.4038470 |
| C | -5.4888322 | 0.0473584 | 3.8294244 |
| H | -6.7183097 | -1.3518852 | 2.7390297 |
| H | -3.9874865 | 1.3122101 | 4.7237678 |
| H | -3.9179369 | -4.3370079 | -0.4629424 |
| H | -2.5189850 | -5.3127136 | 0.0760860 |
| H | -4.0796604 | -5.4288014 | 0.9516101 |
| H | -6.3146972 | 0.4703302 | 4.3952820 |
| H | -1.6482354 | -2.5901153 | -1.0337747 |
| C | -2.1464065 | -1.9099325 | -2.3272328 |
| C | -1.6922141 | -0.5693821 | -2.1255277 |
| C | -3.5745231 | -2.2397838 | -2.3115493 |
| H | -1.5678103 | -2.4569687 | -3.0743572 |
| N | -0.3482374 | -0.2376004 | -2.1467585 |
| C | -2.3003656 | 0.6470903 | -1.8136036 |
| C | -4.0722623 | -3.2643424 | -3.1452602 |
| C | -4.4831549 | -1.6512274 | -1.4047675 |
| N | -0.0970658 | 1.0468818 | -1.8794376 |
| C | 0.7586022 | -1.1409606 | -2.4108869 |
| N | -1.3001229 | 1.5605513 | -1.6712943 |
| H | -3.3342086 | 0.9200363 | -1.7087755 |
| C | -5.4030082 | -3.6712426 | -3.0844654 |
| H | -3.3930888 | -3.7487952 | -3.8439547 |
| C | -5.8163179 | -2.0521394 | -1.3533302 |
| H | -4.1293376 | -0.9119556 | -0.6929603 |
| H | 0.7730368 | -1.4227221 | -3.4672019 |
| H | 0.6281630 | -2.0317992 | -1.7941322 |
| H | 1.6770704 | -0.6227416 | -2.1422162 |
| C | -1.4301193 | 2.9549695 | -1.3343298 |
| C | -6.2916759 | -3.0636363 | -2.1921851 |
| H | -5.7497407 | -4.4664252 | -3.7401820 |
| H | -6.4838327 | -1.5816836 | -0.6356473 |
| C | -2.1677972 | 3.3018657 | -0.1927228 |

| | | | |
|---|---|---|---|
| C | -0.8079084 | 3.9065606 | -2.1610577 |
| H | -7.3299371 | -3.3792756 | -2.1447490 |
| C | -2.2543288 | 4.6644669 | 0.1143876 |
| C | -2.8225602 | 2.2913179 | 0.7111588 |
| C | -0.9308663 | 5.2480032 | -1.7991254 |
| C | -0.0365210 | 3.5362860 | -3.4035631 |
| C | -1.6434459 | 5.6474832 | -0.6629641 |
| H | -2.7999396 | 4.9548034 | 1.0091343 |
| H | -2.1941591 | 1.4076888 | 0.8770198 |
| H | -3.0243366 | 2.7486439 | 1.6823876 |
| H | -3.7844917 | 1.9523037 | 0.3072110 |
| H | -0.4567586 | 5.9992099 | -2.4273377 |
| H | 0.0702560 | 4.4142868 | -4.0459028 |
| H | 0.9632773 | 3.1676379 | -3.1524923 |
| H | -0.5379967 | 2.7468964 | -3.9725055 |
| C | -1.7388911 | 7.1053300 | -0.2883783 |
| H | -2.2463237 | 7.6807630 | -1.0716345 |
| H | -0.7412505 | 7.5414522 | -0.1610737 |
| H | -2.2927259 | 7.2360989 | 0.6451571 |

**TS30** : **TS3** but Ph trans to pro-carbenic C-H

107

Energy = -2410.920609864

| | | | |
|---|---|---|---|
| N | 2.9797583 | -0.4134659 | -2.8793538 |
| N | 1.6722425 | -0.0323301 | -2.8043448 |
| N | 3.4851124 | 0.0156552 | -1.7240679 |
| C | 1.3675701 | 0.6700047 | -1.6303711 |
| C | 0.7452616 | -0.5647381 | -3.7850469 |
| C | 4.8919072 | -0.1673823 | -1.4465466 |
| C | 2.5953023 | 0.6578785 | -0.9407882 |
| C | 0.1189136 | 1.1560015 | -1.1836671 |
| H | -0.1621609 | -0.8739007 | -3.2590774 |
| H | 1.2228158 | -1.4172730 | -4.2678843 |
| H | 0.4697548 | 0.1866230 | -4.5297497 |
| C | 5.3112427 | -1.3778139 | -0.8855331 |
| C | 5.7643013 | 0.8886960 | -1.7403862 |
| H | 2.8656878 | 1.0692493 | 0.0172350 |
| C | -0.9252911 | 1.6663795 | -2.0583516 |
| N | 0.1138684 | 1.2373824 | 0.2166419 |
| C | 6.6745081 | -1.5132621 | -0.6061753 |
| C | 4.3408514 | -2.4930736 | -0.5936111 |
| C | 7.1154813 | 0.7006453 | -1.4420179 |
| C | 5.2686735 | 2.1753411 | -2.3503932 |
| C | -2.2893163 | 1.7707794 | -1.6777024 |
| C | -0.5843012 | 2.1668095 | -3.3417907 |
| N | -0.9450093 | 1.6999708 | 0.8291106 |
| C | 7.5872924 | -0.4879139 | -0.8718611 |
| H | 7.0275908 | -2.4441317 | -0.1686513 |
| H | 3.8588675 | -2.8452159 | -1.5118581 |
| H | 4.8564624 | -3.3362278 | -0.1295659 |
| H | 3.5500189 | -2.1595178 | 0.0875543 |
| H | 7.8147473 | 1.5033468 | -1.6650837 |
| H | 6.1112598 | 2.7926658 | -2.6692358 |
| H | 4.6298371 | 1.9833782 | -3.2186915 |
| H | 4.6781802 | 2.7540022 | -1.6305453 |
| C | -3.2398162 | 2.2891968 | -2.5533780 |
| H | -2.5892909 | 1.4647603 | -0.6859569 |
| C | -1.5434040 | 2.6680201 | -4.2141987 |
| H | 0.4617210 | 2.1969823 | -3.6359701 |
| C | -0.9363602 | 1.7448337 | 2.1873405 |
| C | 9.0496704 | -0.6496491 | -0.5393098 |
| C | -2.8887133 | 2.7267679 | -3.8324318 |
| H | -4.2769428 | 2.3375426 | -2.2302533 |
| H | -1.2356060 | 3.0384315 | -5.1891727 |
| C | 0.2619567 | 1.7629842 | 3.0407561 |
| C | -2.2560343 | 1.8766303 | 2.7662102 |
| H | 9.3199396 | -0.0252161 | 0.3209483 |
| H | 9.6809000 | -0.3384466 | -1.3782893 |
| H | 9.2858653 | -1.6877557 | -0.2909951 |
| H | -3.6393153 | 3.1221001 | -4.5109804 |
| C | 1.5094853 | 2.2068738 | 2.5435855 |
| C | 0.2143333 | 1.3893808 | 4.4000156 |
| O | -2.5509671 | 2.1638572 | 3.9323484 |
| O | -3.2661070 | 1.6004680 | 1.8455448 |
| C | 2.6342714 | 2.2805653 | 3.3593694 |
| H | 1.5867007 | 2.5139148 | 1.5069324 |
| C | 1.3435519 | 1.4596205 | 5.2112408 |
| H | -0.7198070 | 1.0354377 | 4.8152360 |
| C | -4.5995001 | 1.8421416 | 2.3321287 |
| C | 2.5651557 | 1.9040720 | 4.7035723 |
| H | 3.5735262 | 2.6373586 | 2.9419956 |
| H | 1.2699503 | 1.1432952 | 6.2486955 |
| H | -4.8082445 | 1.2377020 | 3.2194346 |
| H | -4.7357232 | 2.8989648 | 2.5802635 |
| H | -5.2578501 | 1.5574270 | 1.5095715 |
| H | 3.4473710 | 1.9459734 | 5.3366056 |
| H | 0.5529071 | 0.1444709 | 0.7239109 |
| C | 0.5565605 | -1.3016439 | 1.0000200 |
| C | -0.6291536 | -1.6419129 | 0.2487611 |
| C | 0.5887773 | -1.5408596 | 2.4634105 |
| H | 1.4605833 | -1.6713263 | 0.5125871 |
| N | -0.6759690 | -2.5317035 | -0.8071684 |
| C | -1.9184204 | -1.1184070 | 0.2795497 |
| C | 1.8267314 | -1.5016808 | 3.1316543 |
| C | -0.5543297 | -1.8190706 | 3.2331457 |
| N | -1.8613061 | -2.5795736 | -1.4219494 |
| C | 0.4127859 | -3.3721164 | -1.2947532 |
| N | -2.6010570 | -1.7127534 | -0.7356538 |
| H | -2.3464235 | -0.3266247 | 0.8760867 |
| C | 1.9217858 | -1.7529698 | 4.4968243 |
| H | 2.7247745 | -1.2627363 | 2.5660715 |
| C | -0.4601580 | -2.0658676 | 4.6015978 |
| H | -1.5307298 | -1.8515565 | 2.7571561 |
| H | 0.8378490 | -3.9177759 | -0.4506145 |
| H | 1.1839509 | -2.7535180 | -1.7590297 |
| H | -0.0031429 | -4.0632096 | -2.0254642 |
| C | -3.9696235 | -1.4555558 | -1.1058505 |
| C | 0.7786952 | -2.0446086 | 5.2447157 |
| H | 2.8930570 | -1.7073019 | 4.9821246 |
| H | -1.3634981 | -2.2784072 | 5.1682638 |

| | | | |
|---|---|---|---|
| C | -4.2656903 | -1.0978500 | -2.4332440 |
| C | -4.9444039 | -1.5309348 | -0.0997061 |
| H | 0.8499458 | -2.2325529 | 6.3121732 |
| C | -5.5940481 | -0.7849620 | -2.7232619 |
| C | -3.2242027 | -1.0176229 | -3.5191552 |
| C | -6.2572602 | -1.2042277 | -0.4543453 |
| C | -4.6414637 | -1.9601667 | 1.3157377 |
| C | -6.6010712 | -0.8222482 | -1.7521787 |
| H | -5.8414483 | -0.4871014 | -3.7395274 |
| H | -2.8865747 | -2.0132881 | -3.8222755 |
| H | -3.6420187 | -0.5083035 | -4.3899853 |
| H | -2.3531414 | -0.4482623 | -3.1826219 |
| H | -7.0290474 | -1.2593854 | 0.3097404 |
| H | -5.5526874 | -2.3333767 | 1.7890587 |
| H | -3.8856912 | -2.7504518 | 1.3497879 |
| H | -4.2737358 | -1.1228140 | 1.9191137 |
| C | -8.0235022 | -0.4697925 | -2.1073400 |
| H | -8.6572985 | -0.4429155 | -1.2171164 |
| H | -8.4440210 | -1.2041192 | -2.8046597 |
| H | -8.0727463 | 0.5084037 | -2.5982623 |

**TS3** : $H^+$ transfer from **2a**$H^+$ to N=N of **B**$^-$

107

Energy = -2410.914786269

| | | | |
|---|---|---|---|
| N | 2.0727194 | -2.9832121 | -0.8170013 |
| N | 0.8198298 | -2.6071647 | -0.3927964 |
| N | 2.8775350 | -2.2152275 | -0.0914713 |
| C | 0.8462249 | -1.6239875 | 0.6198508 |
| C | -0.2774282 | -3.4621781 | -0.8233230 |
| C | 4.3093756 | -2.4055036 | -0.1682527 |
| C | 2.2373301 | -1.3921720 | 0.7584972 |
| C | -0.2363491 | -1.0224253 | 1.2761441 |
| H | -0.6031213 | -4.1036338 | 0.0020289 |
| H | 0.1024899 | -4.0786749 | -1.6388029 |
| H | -1.1206727 | -2.8637762 | -1.1594947 |
| C | 4.8680376 | -3.3932963 | 0.6530792 |
| C | 5.0712149 | -1.5993824 | -1.0222990 |
| H | 2.7819327 | -0.7252907 | 1.4015850 |
| C | 0.0029573 | -0.0922687 | 2.3820841 |
| N | -1.5268741 | -1.2963708 | 0.7867498 |
| C | 6.2543645 | -3.5639175 | 0.5986747 |
| C | 4.0132728 | -4.2329173 | 1.5674533 |
| C | 6.4533031 | -1.8074279 | -1.0326997 |
| C | 4.4431845 | -0.5685473 | -1.9226235 |
| C | -0.8009931 | 1.0557404 | 2.5775550 |
| C | 1.0587540 | -0.2887988 | 3.3004746 |
| N | -2.5341290 | -0.9933537 | 1.5861662 |
| C | 7.0614757 | -2.7816451 | -0.2334398 |
| H | 6.7116980 | -4.3255421 | 1.2260398 |
| H | 3.2128065 | -4.7318785 | 1.0114660 |
| H | 4.6202894 | -4.9926891 | 2.0641582 |
| H | 3.5375873 | -3.6164937 | 2.3394939 |
| H | 7.0665538 | -1.1898560 | -1.6854034 |
| H | 5.1871284 | 0.1673805 | -2.2368336 |
| H | 4.0406618 | -1.0432311 | -2.8249210 |
| H | 3.6195101 | -0.0393591 | -1.4372548 |
| C | -0.5055935 | 1.9854868 | 3.5682490 |
| H | -1.6749992 | 1.2020220 | 1.9561899 |
| C | 1.3540209 | 0.6439547 | 4.2923807 |
| H | 1.6414398 | -1.2043489 | 3.2484582 |
| C | -3.7854830 | -1.2363736 | 1.1734734 |
| C | 8.5573062 | -2.9760231 | -0.2664347 |
| C | 0.5849328 | 1.8022136 | 4.4258522 |
| H | -1.1361355 | 2.8650616 | 3.6743299 |
| H | 2.1809478 | 0.4561940 | 4.9732258 |
| C | -4.1663565 | -2.1319450 | 0.0625797 |
| C | -4.8390137 | -0.5780864 | 1.9250830 |
| H | 9.0746484 | -2.0726508 | 0.0772196 |
| H | 8.9029326 | -3.1800930 | -1.2860475 |
| H | 8.8606023 | -3.8084752 | 0.3738754 |
| H | 0.8128058 | 2.5335383 | 5.1960098 |
| C | -3.5337043 | -3.3813298 | -0.0830989 |
| C | -5.1891976 | -1.8033099 | -0.8422967 |
| O | -6.0518997 | -0.7881723 | 1.8082036 |
| O | -4.3699888 | 0.3804415 | 2.7946794 |
| C | -3.8930555 | -4.2574389 | -1.1032822 |
| H | -2.7637097 | -3.6639097 | 0.6272849 |
| C | -5.5491552 | -2.6792030 | -1.8651312 |
| H | -5.6901078 | -0.8470210 | -0.7466263 |
| C | -5.3975613 | 1.0447073 | 3.5536835 |
| C | -4.9019776 | -3.9082334 | -2.0077693 |
| H | -3.3940013 | -5.2199434 | -1.1884420 |
| H | -6.3331805 | -2.3937874 | -2.5623251 |
| H | -6.0861519 | 1.5737956 | 2.8880656 |
| H | -5.9639815 | 0.3294162 | 4.1574545 |
| H | -4.8669184 | 1.7501399 | 4.1947608 |
| H | -5.1827374 | -4.5893105 | -2.8069356 |
| H | -1.6767422 | -0.9248864 | -0.4411150 |
| C | -1.7171889 | -0.1629894 | -1.6843395 |
| C | -0.5633529 | 0.6991556 | -1.6045440 |
| C | -3.0346944 | 0.5380160 | -1.7449191 |
| H | -1.6180720 | -0.8996188 | -2.4848895 |
| N | 0.6353022 | 0.5017942 | -2.2702535 |
| C | -0.3315047 | 1.8843505 | -0.9010935 |
| C | -3.8710279 | 0.3633401 | -2.8592626 |
| C | -3.4929858 | 1.3691537 | -0.7086951 |
| N | 1.5563069 | 1.4511809 | -2.0250770 |
| C | 0.9656430 | -0.5564213 | -3.2183298 |
| N | 0.9313381 | 2.2757770 | -1.1944945 |
| H | -0.9560803 | 2.4535308 | -0.2366716 |
| C | -5.1088489 | 0.9997729 | -2.9427370 |
| H | -3.5464627 | -0.2905710 | -3.6652289 |
| C | -4.7300439 | 2.0045855 | -0.7873305 |
| H | -2.9077348 | 1.4699203 | 0.1998654 |
| H | 0.0579843 | -0.8232174 | -3.7610448 |
| H | 1.3583407 | -1.4324715 | -2.6968691 |
| H | 1.7100207 | -0.1638774 | -3.9095166 |
| C | 1.5714077 | 3.5043862 | -0.7750946 |
| C | -5.5456616 | 1.8286018 | -1.9079882 |
| H | -5.7370229 | 0.8401216 | -3.8154813 |

| | | | |
|---|---|---|---|
| H | -5.0672576 | 2.6220629 | 0.0409341 |
| C | 2.3784551 | 3.4938975 | 0.3655191 |
| C | 1.3227693 | 4.6547756 | -1.5368084 |
| H | -6.5133823 | 2.3188025 | -1.9661017 |
| C | 2.9521390 | 4.7109378 | 0.7483037 |
| C | 2.6311126 | 2.2317398 | 1.1435547 |
| C | 1.9236592 | 5.8407157 | -1.1120254 |
| C | 0.4412289 | 4.6164128 | -2.7591199 |
| C | 2.7381746 | 5.8883625 | 0.0268543 |
| H | 3.5799883 | 4.7332999 | 1.6358479 |
| H | 3.2366753 | 1.5341358 | 0.5534445 |
| H | 3.1660583 | 2.4535248 | 2.0686326 |
| H | 1.6972912 | 1.7240932 | 1.4032180 |
| H | 1.7471334 | 6.7484186 | -1.6846860 |
| H | 0.4473477 | 5.5860482 | -3.2612750 |
| H | 0.7811912 | 3.8555234 | -3.4699447 |
| H | -0.5951075 | 4.3770926 | -2.4936470 |
| C | 3.3773435 | 7.1856117 | 0.4558063 |
| H | 2.6327586 | 7.9861910 | 0.5230111 |
| H | 4.1327821 | 7.5043773 | -0.2723672 |
| H | 3.8650913 | 7.0820959 | 1.4286183 |

**TS4a** : N-inversion of mNHO-like **C**

64

Energy = -1509.447272084

| | | | |
|---|---|---|---|
| N | -2.3992938 | -1.6596570 | 0.5828905 |
| N | -1.1062736 | -1.4240076 | 0.2558534 |
| N | -3.0196583 | -0.5601603 | 0.1826917 |
| C | -0.9034504 | -0.1973743 | -0.3940925 |
| C | -0.1005812 | -2.3729827 | 0.7182976 |
| C | -4.4490088 | -0.4426469 | 0.3636969 |
| C | -2.2063267 | 0.3505023 | -0.3983691 |
| C | 0.3124555 | 0.2684934 | -0.9069612 |
| H | 0.2915178 | -2.9694800 | -0.1078667 |
| H | -0.5815544 | -3.0212848 | 1.4501781 |
| H | 0.7163287 | -1.8160666 | 1.1838517 |
| C | -5.2890931 | -0.9459013 | -0.6380420 |
| C | -4.9191390 | 0.1791322 | 1.5243820 |
| H | -2.5918538 | 1.2672916 | -0.8094819 |
| C | 0.6006751 | 1.6417354 | -1.2405170 |
| N | 1.2833369 | -0.7355079 | -1.2727592 |
| C | -6.6647174 | -0.8063130 | -0.4439473 |
| C | -4.7322537 | -1.6090088 | -1.8719993 |
| C | -6.3060456 | 0.2936885 | 1.6680334 |
| C | -3.9755314 | 0.6973515 | 2.5794194 |
| C | -0.1183211 | 2.7283197 | -0.6799601 |
| C | 1.6675663 | 1.9726960 | -2.1159507 |
| N | 2.4580812 | -0.8254482 | -0.8013496 |
| C | -7.1903099 | -0.1907088 | 0.6994362 |
| H | -7.3401592 | -1.1877292 | -1.2065420 |
| H | -4.1246457 | -2.4817152 | -1.6096453 |
| H | -5.5432868 | -1.9357387 | -2.5263137 |
| H | -4.0908938 | -0.9220537 | -2.4357305 |
| H | -6.7006107 | 0.7730694 | 2.5609108 |
| H | -4.5348463 | 1.1518262 | 3.3998397 |
| H | -3.3588142 | -0.1116047 | 2.9863181 |
| H | -3.2939986 | 1.4508991 | 2.1690550 |
| C | 0.1893406 | 4.0468100 | -0.9968300 |
| H | -0.9009750 | 2.5326520 | 0.0474335 |
| C | 1.9730124 | 3.2946828 | -2.4215959 |
| H | 2.2636927 | 1.1769751 | -2.5521852 |
| C | 3.6356760 | -0.8914534 | -0.3166959 |
| C | -8.6824667 | -0.0600896 | 0.8797864 |
| C | 1.2355141 | 4.3499367 | -1.8751370 |
| H | -0.3841996 | 4.8494521 | -0.5385562 |
| H | 2.7986209 | 3.5035043 | -3.0981207 |
| C | 4.0681783 | -0.0397537 | 0.8350824 |
| C | 4.5483095 | -1.8769448 | -0.9905714 |
| H | -9.1356875 | 0.4566680 | 0.0264235 |
| H | -8.9223230 | 0.4977724 | 1.7887422 |
| H | -9.1534966 | -1.0476478 | 0.9489161 |
| H | 1.4776638 | 5.3809595 | -2.1157026 |
| C | 5.0396058 | -0.4420526 | 1.7671553 |
| C | 3.4190733 | 1.1888351 | 1.0435199 |
| O | 4.1690249 | -2.7343047 | -1.7779019 |
| O | 5.8619528 | -1.6940956 | -0.6955764 |
| C | 5.3538642 | 0.3634296 | 2.8632713 |
| H | 5.5495242 | -1.3904623 | 1.6411306 |
| C | 3.7386902 | 1.9956726 | 2.1316573 |
| H | 2.6577291 | 1.5039679 | 0.3367748 |
| C | 6.7740016 | -2.6067853 | -1.3580137 |
| C | 4.7112478 | 1.5884306 | 3.0504562 |
| H | 6.1033452 | 0.0279333 | 3.5758489 |
| H | 3.2291176 | 2.9470744 | 2.2626259 |
| H | 6.7093835 | -2.4798442 | -2.4412580 |
| H | 7.7637366 | -2.3342713 | -0.9931309 |
| H | 6.5300580 | -3.6384125 | -1.0941389 |
| H | 4.9621200 | 2.2162374 | 3.9012050 |
| H | 1.0468182 | -1.3569151 | -2.0524422 |

**TS4** : N-N rotation of mNHO-like **C**

64

Energy = -1509.469031662

| | | | |
|---|---|---|---|
| N | 1.3900119 | -0.9762112 | -1.7615903 |
| N | 0.3173220 | -0.2673091 | -2.1941496 |
| N | 1.8201011 | -0.2677061 | -0.7198811 |
| C | 0.0381643 | 0.8543490 | -1.4032163 |
| C | -0.2124608 | -0.5905307 | -3.5143478 |
| C | 2.8979720 | -0.7807950 | 0.0932380 |
| C | 1.0866104 | 0.8361093 | -0.4671771 |
| C | -1.1503632 | 1.6156945 | -1.4533265 |
| H | -1.2211403 | -0.1885578 | -3.5896847 |
| H | -0.2236471 | -1.6752980 | -3.6271079 |
| H | 0.4303275 | -0.1438446 | -4.2803361 |
| C | 2.5701108 | -1.6523950 | 1.1412508 |
| C | 4.2043691 | -0.3779882 | -0.1962034 |
| H | 1.2819475 | 1.4534133 | 0.3920277 |
| C | -1.2231117 | 2.9968068 | -1.0702722 |
| N | -2.3141767 | 0.9567193 | -2.0204641 |
| C | 3.6238537 | -2.1268692 | 1.9244366 |

| | | | |
|---|---|---|---|
| C | 1.1445453 | -2.0616105 | 1.4073498 |
| C | 5.2220869 | -0.8834834 | 0.6202919 |
| C | 4.5047343 | 0.5611278 | -1.3364643 |
| C | -2.4584706 | 3.6987743 | -1.0024621 |
| C | -0.0601385 | 3.7447858 | -0.7284612 |
| N | -2.3865039 | -0.4370657 | -1.5459885 |
| C | 4.9519325 | -1.7541944 | 1.6801906 |
| H | 3.3988698 | -2.8042192 | 2.7454788 |
| H | 0.7192316 | -2.5929272 | 0.5495785 |
| H | 1.0935201 | -2.7187229 | 2.2780990 |
| H | 0.5032090 | -1.1933560 | 1.5908474 |
| H | 6.2493048 | -0.5889556 | 0.4179945 |
| H | 5.5836232 | 0.6822013 | -1.4556772 |
| H | 4.0903115 | 0.1847330 | -2.2777226 |
| H | 4.0669369 | 1.5505484 | -1.1603020 |
| C | -2.5258295 | 5.0091112 | -0.5384705 |
| H | -3.3838636 | 3.2215009 | -1.3070235 |
| C | -0.1394909 | 5.0479136 | -0.2603137 |
| H | 0.9196679 | 3.2941683 | -0.8517794 |
| C | -2.4091127 | -0.5706778 | -0.2596100 |
| C | 6.0655005 | -2.2892996 | 2.5460069 |
| C | -1.3766846 | 5.6975879 | -0.1426493 |
| H | -3.4952177 | 5.4996188 | -0.4900800 |
| H | 0.7767377 | 5.5732974 | -0.0003563 |
| C | -2.3916928 | -1.9332025 | 0.3093530 |
| C | -2.4515688 | 0.6151306 | 0.6719617 |
| H | 7.0325591 | -1.8788781 | 2.2436755 |
| H | 6.1196827 | -3.3821475 | 2.4791145 |
| H | 5.8969117 | -2.0368630 | 3.5990838 |
| H | -1.4364064 | 6.7201099 | 0.2183226 |
| C | -2.6177746 | -2.1569501 | 1.6761874 |
| C | -2.1126939 | -3.0315458 | -0.5242457 |
| O | -3.3877129 | 1.4067343 | 0.6722912 |
| O | -1.4440239 | 0.6275068 | 1.5773811 |
| C | -2.5601735 | -3.4475420 | 2.1998620 |
| H | -2.8322996 | -1.3224155 | 2.3354977 |
| C | -2.0538386 | -4.3166549 | 0.0015764 |
| H | -1.9317780 | -2.8520304 | -1.5785104 |
| C | -1.4423831 | 1.7835819 | 2.4610922 |
| C | -2.2749572 | -4.5295970 | 1.3667841 |
| H | -2.7354042 | -3.6060061 | 3.2599303 |
| H | -1.8277953 | -5.1563582 | -0.6494084 |
| H | -2.3847746 | 1.8360628 | 3.0098306 |
| H | -0.6061314 | 1.6200010 | 3.1390776 |
| H | -1.3005295 | 2.6904327 | 1.8698140 |
| H | -2.2211787 | -5.5339913 | 1.7770720 |
| H | -3.1329194 | 1.4318779 | -1.6286949 |

**TS5** : C-C ring-closing via $MeO^-$ elimination

64

Energy = -1509.475536847

| | | | |
|---|---|---|---|
| N | 2.4893510 | 1.5523889 | -1.0301535 |
| N | 1.1787472 | 1.7253701 | -1.1264739 |
| N | 2.6134686 | 0.3795650 | -0.4154613 |
| C | 0.4472020 | 0.6830918 | -0.5971862 |
| C | 0.7013644 | 2.9651053 | -1.7537085 |
| C | 3.9236056 | -0.1588365 | -0.1323991 |
| C | 1.4111815 | -0.1894394 | -0.1347511 |
| C | -1.0462283 | 0.6542258 | -0.5552653 |
| H | -0.1200238 | 2.7261238 | -2.4265101 |
| H | 1.5383899 | 3.3852299 | -2.3081412 |
| H | 0.3598642 | 3.6501457 | -0.9769747 |
| C | 4.3308639 | -1.3016041 | -0.8360898 |
| C | 4.7073898 | 0.4760346 | 0.8373273 |
| H | 1.2975632 | -1.1433247 | 0.3445603 |
| C | -1.5915967 | 1.9582030 | -0.0001196 |
| N | -1.5963449 | 0.2739173 | -1.8654909 |
| C | -1.6555386 | -0.5580319 | 0.3930371 |
| C | 5.5951227 | -1.8104942 | -0.5360470 |
| C | 3.4588506 | -1.9530482 | -1.8800741 |
| C | 5.9636290 | -0.0804514 | 1.0975962 |
| C | 4.2298063 | 1.6973169 | 1.5807196 |
| C | -1.0169952 | 2.4924184 | 1.1623461 |
| C | -2.6791176 | 2.6172581 | -0.5797646 |
| N | -2.8381361 | -0.3754417 | -1.6741965 |
| H | -1.7493838 | 1.0572851 | -2.4986180 |
| C | -2.9064270 | -0.8492759 | -0.4740117 |
| O | -1.7163819 | -0.3487881 | 1.6448847 |
| C | 6.4233325 | -1.2160849 | 0.4246366 |
| H | 5.9411293 | -2.6911932 | -1.0719311 |
| H | 3.0384793 | -1.2147840 | -2.5708982 |
| H | 4.0417346 | -2.6731259 | -2.4579094 |
| H | 2.6190361 | -2.4914430 | -1.4258044 |
| H | 6.5930526 | 0.3858600 | 1.8515397 |
| H | 4.8617012 | 1.8771126 | 2.4529183 |
| H | 4.2657541 | 2.5868419 | 0.9425824 |
| H | 3.1960019 | 1.5798559 | 1.9234503 |
| C | -1.4922857 | 3.6834617 | 1.7068330 |
| H | -0.2022915 | 1.9616853 | 1.6458569 |
| C | -3.1614954 | 3.8070915 | -0.0307334 |
| H | -3.1682611 | 2.1986799 | -1.4544579 |
| C | -4.0478585 | -1.6611945 | -0.0481127 |
| C | 7.7838272 | -1.7944960 | 0.7222970 |
| C | -2.5651427 | 4.3495812 | 1.1082440 |
| H | -1.0314006 | 4.0886339 | 2.6036053 |
| H | -4.0063814 | 4.3078259 | -0.4954947 |
| C | -4.9645303 | -2.1687871 | -0.9897561 |
| C | -4.2478677 | -1.9499693 | 1.3131269 |
| H | 8.4149163 | -1.7820002 | -0.1737244 |
| H | 7.7007777 | -2.8379666 | 1.0463313 |
| H | 8.2901660 | -1.2279882 | 1.5078327 |
| H | -2.9363610 | 5.2791471 | 1.5305161 |
| C | -6.0512599 | -2.9336689 | -0.5789998 |
| H | -4.8061128 | -1.9589587 | -2.0432564 |
| C | -5.3377593 | -2.7202790 | 1.7187293 |
| H | -3.5366601 | -1.5514246 | 2.0294101 |
| C | -6.2445332 | -3.2137544 | 0.7789407 |
| H | -6.7483644 | -3.3206886 | -1.3178076 |
| H | -5.4805373 | -2.9344213 | 2.7748992 |
| H | -7.0922198 | -3.8146092 | 1.0972782 |

| | | | |
|---|---|---|---|
| O | -0.7506696 | -1.7683210 | -0.0203216 |
| C | -0.8596068 | -2.8519921 | 0.8964249 |
| H | -0.9752070 | -2.4745073 | 1.9191292 |
| H | -1.7130673 | -3.5025588 | 0.6535313 |
| H | 0.0628087 | -3.4413592 | 0.8236714 |

**TS6** : C-C ring-closing via MeOH elimination
64
Energy = -1509.464557193

| | | | |
|---|---|---|---|
| N | 2.5319975 | 1.6941936 | -0.7639996 |
| N | 1.2588226 | 2.0416387 | -0.8856691 |
| N | 2.4662984 | 0.4254224 | -0.3271093 |
| C | 0.4097398 | 1.0194807 | -0.5286487 |
| C | 0.9732916 | 3.3954987 | -1.3817915 |
| C | 3.6925875 | -0.2931572 | -0.0817846 |
| C | 1.2021354 | -0.0613395 | -0.1736300 |
| C | -1.0871174 | 1.0357122 | -0.5886193 |
| H | 0.1611408 | 3.3423970 | -2.1063928 |
| H | 1.8824600 | 3.7623929 | -1.8547194 |
| H | 0.6822920 | 4.0373348 | -0.5492799 |
| C | 4.0002995 | -1.3774056 | -0.9162916 |
| C | 4.4945725 | 0.0955498 | 0.9967098 |
| H | 0.5409789 | -1.2202811 | -0.0289700 |
| C | -1.7166210 | 2.3799693 | -0.2208890 |
| N | -1.5524705 | 0.4752401 | -1.8621915 |
| C | 5.1779082 | -2.0768377 | -0.6453994 |
| C | 3.1005648 | -1.7820978 | -2.0561175 |
| C | 5.6617949 | -0.6416636 | 1.2238218 |
| C | 4.1136103 | 1.2423690 | 1.8988633 |
| C | -1.2684456 | 3.0283690 | 0.9389572 |
| C | -2.7586288 | 2.9441255 | -0.9605803 |
| N | -2.6435049 | -0.3447809 | -1.6780693 |
| C | 6.0196163 | -1.7256866 | 0.4173770 |
| H | 5.4404664 | -2.9191894 | -1.2819074 |
| H | 2.8648825 | -0.9264500 | -2.6985466 |
| H | 3.5846808 | -2.5502636 | -2.6637872 |
| H | 2.1488511 | -2.1810447 | -1.6871572 |
| H | 6.2993802 | -0.3639392 | 2.0601106 |
| H | 4.7747479 | 1.2743347 | 2.7670299 |
| H | 4.1833887 | 2.2018891 | 1.3763827 |
| H | 3.0818731 | 1.1386208 | 2.2535563 |
| C | -1.8278264 | 4.2435930 | 1.3276448 |
| H | -0.4859888 | 2.5720792 | 1.5388590 |
| C | -3.3213445 | 4.1607471 | -0.5672835 |
| H | -3.1486382 | 2.4380402 | -1.8387281 |
| C | -2.7475472 | -0.6992465 | -0.4245302 |
| C | 7.2803785 | -2.5095246 | 0.6868901 |
| C | -2.8539418 | 4.8172512 | 0.5715446 |
| H | -1.4663222 | 4.7406811 | 2.2235880 |
| H | -4.1287983 | 4.5907049 | -1.1532591 |
| C | -3.7244270 | -1.6924242 | 0.0213474 |
| C | -1.7486235 | -0.0012340 | 0.4217590 |
| H | 7.9340822 | -2.5143429 | -0.1928152 |
| H | 7.0462893 | -3.5542009 | 0.9228832 |
| H | 7.8364073 | -2.0848794 | 1.5269997 |
| H | -3.2889066 | 5.7652316 | 0.8757473 |
| C | -4.4431388 | -2.4520640 | -0.9207760 |
| C | -3.9615631 | -1.9097308 | 1.3895156 |
| O | -1.6219577 | 0.0473587 | 1.6338283 |
| O | -0.3848253 | -2.0551238 | -0.0220619 |
| C | -5.3774493 | -3.3949831 | -0.5040611 |
| H | -4.2524660 | -2.2970332 | -1.9784048 |
| C | -4.8975761 | -2.8591259 | 1.8010518 |
| H | -3.4043705 | -1.3351953 | 2.1201874 |
| C | -0.3225333 | -2.7076974 | 1.2262403 |
| C | -5.6097393 | -3.6042732 | 0.8602701 |
| H | -5.9224465 | -3.9759549 | -1.2434054 |
| H | -5.0691043 | -3.0173195 | 2.8626405 |
| H | -0.8431908 | -2.1203358 | 2.0114236 |
| H | -0.8018235 | -3.7026145 | 1.1672785 |
| H | 0.7257595 | -2.8506077 | 1.5698779 |
| H | -6.3367406 | -4.3449731 | 1.1835286 |
| H | -1.6900525 | 1.1159494 | -2.6385350 |

**TS7** : intramolecular $H^+$ transfer from N-H
58
Energy = -1393.651977531

| | | | |
|---|---|---|---|
| N | 0.8050028 | 1.0701249 | 1.5624720 |
| N | 2.0708156 | 0.6661362 | 1.5947621 |
| O | -2.6354492 | 0.3452513 | 1.7631728 |
| N | -1.9141436 | -0.8377134 | -1.4468728 |
| C | 6.0037490 | -1.6361776 | -0.4920745 |
| N | 2.2406949 | 0.0455933 | 0.4119122 |
| C | 5.8358925 | -0.2492452 | -0.4498414 |
| C | -4.4668936 | -2.0058230 | 1.0008576 |
| C | -1.5136009 | 2.3868781 | -0.3695134 |
| C | 1.1250913 | 0.0360745 | -0.3808714 |
| C | -2.6316560 | 2.9972353 | 0.2041320 |
| C | -5.0197655 | -3.7496834 | -1.1065634 |
| C | -0.6610855 | 3.1408338 | -1.1880259 |
| C | -0.9242330 | 4.4866216 | -1.4303771 |
| C | -4.0247936 | -2.7875456 | -1.2472191 |
| C | 3.5326903 | -0.5247770 | 0.1155329 |
| C | 3.6450119 | -1.9218852 | 0.0823908 |
| N | -1.0623164 | 0.1706320 | -1.4542424 |
| C | 4.6024925 | 0.3377314 | -0.1469662 |
| C | 0.2017692 | 0.7043774 | 0.4004653 |
| C | -2.0432496 | 5.0954785 | -0.8546963 |
| C | -5.7468320 | -3.8489414 | 0.0846477 |
| C | -2.6828902 | -0.8909389 | -0.3459942 |
| C | -2.2656717 | 0.1172700 | 0.6043296 |
| C | -2.8927725 | 4.3484945 | -0.0396765 |
| C | -1.1746022 | 0.9167703 | -0.1453391 |
| C | -3.7284971 | -1.8999336 | -0.1933943 |
| C | -5.4645524 | -2.9714795 | 1.1330500 |
| C | 4.8987526 | -2.4541168 | -0.2236760 |
| H | 5.0131565 | -3.5356054 | -0.2482028 |
| H | 6.6830730 | 0.3985583 | -0.6630735 |
| H | 0.2102987 | -0.1557808 | -1.4295578 |
| H | -3.2933684 | 2.4274020 | 0.8469196 |

| | | | |
|---|---|---|---|
| H | -3.7653283 | 4.8135022 | 0.4103208 |
| H | -2.2496558 | 6.1453097 | -1.0424037 |
| H | -0.2583994 | 5.0601676 | -2.0689742 |
| H | 0.2059147 | 2.6659088 | -1.6396395 |
| H | -4.2488561 | -1.3282508 | 1.8189072 |
| H | -6.0236367 | -3.0376685 | 2.0627520 |
| H | -6.5245135 | -4.6000413 | 0.1910922 |
| H | -5.2328047 | -4.4251554 | -1.9309909 |
| H | -3.4661812 | -2.7090368 | -2.1745476 |
| C | 0.2565212 | 1.8537459 | 2.6772232 |
| H | 0.4012192 | 2.9159167 | 2.4683039 |
| H | -0.8054416 | 1.6188927 | 2.7520218 |
| H | 0.7846527 | 1.5693880 | 3.5856120 |
| C | 2.4668300 | -2.8174977 | 0.3687930 |
| H | 2.7926608 | -3.8569720 | 0.4484516 |
| H | 1.9706733 | -2.5366515 | 1.3041623 |
| H | 1.7183067 | -2.7495106 | -0.4284505 |
| C | 4.4419545 | 1.8365895 | -0.1207360 |
| H | 4.3157293 | 2.2038932 | 0.9033498 |
| H | 5.3225673 | 2.3181699 | -0.5516121 |
| H | 3.5611710 | 2.1506955 | -0.6919188 |
| C | 7.3429550 | -2.2445846 | -0.8273735 |
| H | 8.1087516 | -1.4729582 | -0.9421339 |
| H | 7.6649608 | -2.9381511 | -0.0425902 |
| H | 7.2879858 | -2.8148198 | -1.7621298 |

**TS8** : ring-closing via ketene-like

58

Energy = -1393.647204638

| | | | |
|---|---|---|---|
| N | 2.4642302 | -1.7102647 | 0.6894767 |
| N | 1.1250773 | -1.6753621 | 0.5993315 |
| N | 2.8466373 | -0.5723697 | 0.1208325 |
| C | 0.6425539 | -0.5332663 | -0.0309929 |
| C | 0.3695130 | -2.7504639 | 1.2428756 |
| C | 4.2519377 | -0.2513473 | 0.0279225 |
| C | 1.8116069 | 0.1745044 | -0.3290861 |
| C | -0.7376074 | -0.2634985 | -0.2790959 |
| H | 1.0648125 | -3.2820070 | 1.8926016 |
| H | -0.0581275 | -3.4161377 | 0.4951441 |
| H | -0.4349454 | -2.2960799 | 1.8244813 |
| C | 4.7541914 | 0.7557139 | 0.8612523 |
| C | 5.0338344 | -0.9459331 | -0.9033765 |
| H | 1.9663653 | 1.1060488 | -0.8454603 |
| C | -1.1283022 | 1.0897564 | -0.7049965 |
| C | 6.1122696 | 1.0620117 | 0.7402960 |
| C | 3.8782284 | 1.4844004 | 1.8491656 |
| C | 6.3846716 | -0.5973964 | -0.9826551 |
| C | 4.4501041 | -2.0157564 | -1.7902611 |
| C | -2.1667495 | 1.2948560 | -1.6383232 |
| C | -0.4563463 | 2.2330749 | -0.2214251 |
| C | 6.9408216 | 0.3973757 | -0.1704517 |
| H | 6.5301208 | 1.8379026 | 1.3776216 |
| H | 3.2350531 | 0.7924366 | 2.4024151 |
| H | 4.4937874 | 2.0324309 | 2.5658067 |
| H | 3.2272239 | 2.2085651 | 1.3449946 |
| H | 7.0142035 | -1.1138492 | -1.7035708 |
| H | 5.1680153 | -2.2979610 | -2.5633743 |
| H | 4.1960856 | -2.9106117 | -1.2122872 |
| H | 3.5319675 | -1.6715061 | -2.2790917 |
| C | -2.4974652 | 2.5753836 | -2.0759335 |
| H | -2.7066937 | 0.4399677 | -2.0312785 |
| C | -0.7816274 | 3.5089006 | -0.6678927 |
| H | 0.3043536 | 2.1196514 | 0.5459187 |
| C | 8.4096622 | 0.7289438 | -0.2569924 |
| C | -1.8079041 | 3.6924540 | -1.6003557 |
| H | -3.3012314 | 2.6988750 | -2.7972272 |
| H | -0.2450366 | 4.3674506 | -0.2720917 |
| H | 8.7991685 | 0.5391202 | -1.2613881 |
| H | 8.9832631 | 0.1089523 | 0.4435775 |
| H | 8.5945540 | 1.7757863 | 0.0007904 |
| H | -2.0715513 | 4.6897042 | -1.9406293 |
| N | -1.4914104 | -1.3996596 | -0.4875512 |
| N | -2.7603081 | -1.4786363 | -0.3359449 |
| C | -3.5379941 | -0.4805595 | 0.3236677 |
| C | -5.0050756 | -0.6676336 | 0.2717264 |
| C | -3.0545678 | 0.4704359 | 1.1340641 |
| C | -5.8868142 | 0.2274821 | 0.9041045 |
| C | -5.5483752 | -1.7443640 | -0.4502996 |
| O | -2.7654497 | 1.3651912 | 1.8407446 |
| C | -7.2650100 | 0.0458352 | 0.8267232 |
| H | -5.4936200 | 1.0769198 | 1.4581204 |
| C | -6.9301940 | -1.9168785 | -0.5286179 |
| H | -4.8748102 | -2.4347348 | -0.9449719 |
| C | -7.7985647 | -1.0289404 | 0.1094592 |
| H | -7.9251874 | 0.7506168 | 1.3253598 |
| H | -7.3293068 | -2.7551079 | -1.0943831 |
| H | -8.8740521 | -1.1683082 | 0.0463767 |

**TS9** : C=N cleavage

58

Energy = -1393.631619572

| | | | |
|---|---|---|---|
| N | 1.1767076 | -0.7554393 | 1.1536234 |
| N | 0.0829881 | -0.0089719 | 1.1036423 |
| N | 2.0049925 | -0.1755405 | 0.2879018 |
| C | 0.1664353 | 1.0143675 | 0.1853260 |
| C | -1.0493419 | -0.3156562 | 1.9843145 |
| C | 3.3381084 | -0.7070517 | 0.1034964 |
| C | 1.4495946 | 0.9014480 | -0.3234711 |
| C | -0.9131443 | 1.9351014 | -0.1053823 |
| H | -0.6912477 | -1.0068512 | 2.7447241 |
| H | -1.3809748 | 0.6217073 | 2.4346843 |
| H | -1.8479516 | -0.7676672 | 1.3850008 |
| C | 3.6483946 | -1.3336049 | -1.1098619 |
| C | 4.2546922 | -0.5495177 | 1.1536471 |
| H | 1.9778181 | 1.4798903 | -1.0624661 |
| C | -0.7298285 | 3.3829960 | -0.2436136 |
| C | 4.9511044 | -1.8244023 | -1.2490417 |
| C | 2.6469629 | -1.4759734 | -2.2270196 |
| C | 5.5399143 | -1.0550536 | 0.9541977 |
| C | 3.8826695 | 0.1423338 | 2.4402587 |

| | | | |
|---|---|---|---|
| C | -1.7328171 | 4.1863647 | -0.8203171 |
| C | 0.4486956 | 4.0074003 | 0.2052758 |
| C | 5.9049063 | -1.6979732 | -0.2353740 |
| H | 5.2202813 | -2.3219338 | -2.1777941 |
| H | 1.6377082 | -1.6694824 | -1.8556812 |
| H | 2.9424653 | -2.2901875 | -2.8930252 |
| H | 2.6027030 | -0.5587586 | -2.8279176 |
| H | 6.2745221 | -0.9374400 | 1.7474085 |
| H | 4.7759216 | 0.3272003 | 3.0405098 |
| H | 3.1916305 | -0.4677750 | 3.0314627 |
| H | 3.3906039 | 1.1031670 | 2.2509214 |
| C | -1.5587310 | 5.5616101 | -0.9408122 |
| H | -2.6509957 | 3.7286981 | -1.1775978 |
| C | 0.6198955 | 5.3838752 | 0.0720976 |
| H | 1.2299116 | 3.4174936 | 0.6762789 |
| C | 7.2934456 | -2.2599358 | -0.4079933 |
| C | -0.3802061 | 6.1716199 | -0.5007848 |
| H | -2.3468268 | 6.1600657 | -1.3893803 |

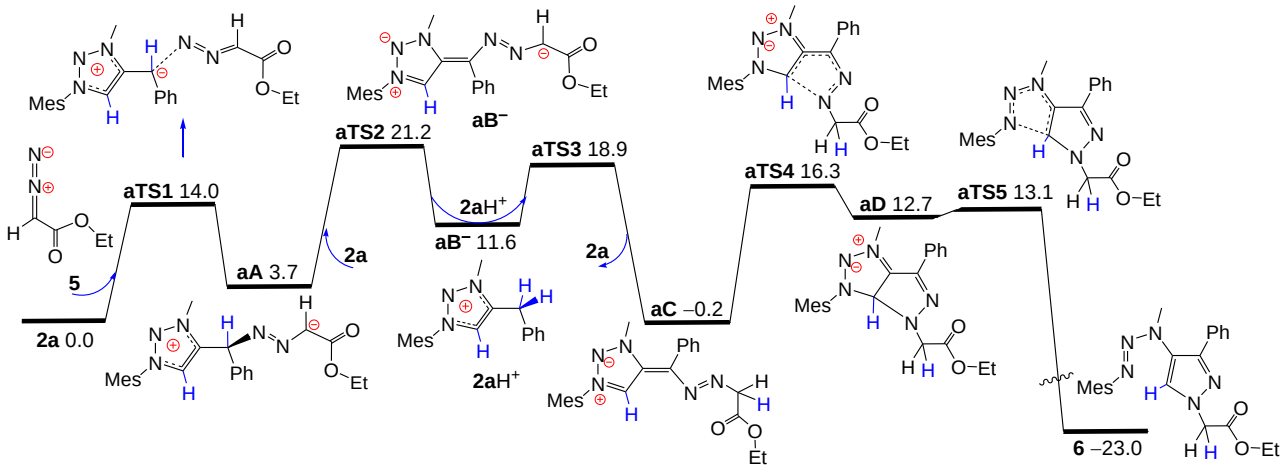


**Figure S63**. DFT computed free energy profile (in kcal/mol, at 298 K and 1 M in THF solution) for the formation of **6** from **5** and **2a** at the PW6B95-D3/def2-QZVP + COSMO-RS level using TPSS-D3/def2-TZVP + COSMO optimized geometries in THF solution.

**Table S6.** DFT computed energies for the reaction of diazo **5** and mNHO **2a** for the formation of **6** in THF solution.
TPSS-D3/def2-TZVP + COSMO computed imaginary frequency (ImF), zero-point energies (ZPE), enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in THF; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95 ($E_P$)); total PW6B95-D3 Gibbs free energies ($G_P = E_P + Gc + Gsol$), relative electronic energies ($\Delta E_T$ and $\Delta E_P$) and final Gibbs free-energies ($\Delta G_T$ and $\Delta G_P$) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name, with singly charged cation and anion species indicated by the + and – superscripts, respectively. Transition structures (with only one imaginary frequency) are indicated by the "**TS**" prefix. See **Figure S63** for structural labelings. The final PW6B95-D3 Gibbs free energies are used in our discussion.

| Reactions | ImF | ZPE | Hc | Gc | Hsol | Gsol | TPSS-D3 | PW6B95 | GP | ΔET | ΔEP | *ΔGP* | ΔGT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | kcal | kcal | kcal | kcal | kcal | | | | kcal | kcal | *kcal* | kcal |
| (1 mol/L in THF) | cm-1 | /mol | /mol | /mol | /mol | /mol | Eh | Eh | Eh | /mol | /mol | */mol* | /mol |

*Nucleophilic addition of mNHO (**2a**) to terminal N of diazo (**5**) is 3.7 kcal/mol endergonic to form meta-stable trans-adduct **aA***

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **5** + **2a** | 0 | 287.61 | 306.59 | 238.50 | -38.79 | -26.64 | -1317.68314 | -1319.06543 | -1318.72179 | 0.00 | 0.00 | *0.00* | 0.00 |
| **aTS1** | 219i | 286.72 | 306.47 | 251.16 | -34.92 | -26.18 | -1317.68636 | -1319.06110 | -1318.69955 | -2.02 | 2.72 | *13.96* | 9.22 |
| **aA** | 0 | 289.71 | 308.62 | 255.45 | -40.30 | -30.30 | -1317.69544 | -1319.07776 | -1318.71595 | -7.72 | -7.74 | *3.67* | 3.68 |
| *..followed by mNHO **2a** catalyzed proton transfer (formal 1,4-H-shift)* | | | | | | | | | | | | | |
| **5** + **2a** + **2a** | 0 | 510.53 | 542.66 | 433.04 | -66.63 | -46.79 | -2219.14666 | -2221.49350 | -2220.86895 | 0.00 | 0.00 | *0.00* | 0.00 |
| **aTS2** | 1626i | 506.83 | 540.68 | 457.76 | -47.71 | -36.60 | -2219.16962 | -2221.50941 | -2220.83524 | -14.41 | -9.99 | *21.15* | 16.73 |
| **aB**$^{-}$ + **2a**H$^{+}$ | 0 | 512.41 | 544.52 | 449.57 | -135.35 | -113.36 | -2219.04738 | -2221.39233 | -2220.85052 | 62.30 | 63.48 | *11.56* | 10.38 |
| **aTS3** | 1548i | 506.04 | 540.28 | 455.18 | -51.25 | -38.68 | -2219.16700 | -2221.50562 | -2220.83887 | -12.76 | -7.60 | *18.87* | 13.71 |
| **aC** + **2a** | 0 | 512.69 | 544.68 | 450.11 | -60.46 | -44.62 | -2219.17297 | -2221.52147 | -2220.86925 | -16.51 | -17.55 | *-0.19* | 0.85 |
| *..and kinetically even more facile nucleophilic addition and 5-ring opening to reach **6*** | | | | | | | | | | | | | |
| **5** + **2a** | 0 | 287.61 | 306.59 | 238.50 | -38.79 | -26.64 | -1317.68314 | -1319.06543 | -1318.72179 | 0.00 | 0.00 | *0.00* | 0.00 |
| **aC** | 0 | 289.76 | 308.61 | 255.58 | -32.62 | -24.47 | -1317.70945 | -1319.09340 | -1318.72209 | -16.51 | -17.55 | *-0.19* | 0.85 |
| **aTS4** | 166i | 288.00 | 307.15 | 253.17 | -30.27 | -22.64 | -1317.68643 | -1319.06614 | -1318.69576 | -2.06 | -0.44 | *16.34* | 14.71 |
| **aD** | 0 | 290.68 | 309.10 | 256.92 | -31.23 | -23.26 | -1317.69338 | -1319.07695 | -1318.70158 | -6.43 | -7.23 | *12.69* | 13.48 |
| **aTS5** | 225i | 288.08 | 307.30 | 252.91 | -30.03 | -22.46 | -1317.68996 | -1319.07119 | -1318.70093 | -4.28 | -3.61 | *13.09* | 12.43 |
| **6** | 0 | 290.01 | 308.93 | 255.46 | -34.34 | -24.41 | -1317.74015 | -1319.12972 | -1318.75850 | -35.77 | -40.34 | *-23.03* | -18.47 |

**Table S7.** TPSS-D3/def2-TZVP + COSMO optimized Cartesian coordinates (in Å) in THF. Each structure is labeled by the specific name (See also **Table S6** and Figure S63), followed by the number of atoms, the total energy, and the detailed atomic coordinates (in double-column text list). Abbreviations for substituents: Mes = mesityl $C_6H_2Me_3$, E = $CO_2Et$ and Ph = $C_6H_5$.

**5** : diazo N=N=CHE
14
Energy = -416.2040736493

| | | | |
|---|---|---|---|
| C | -1.7250106 | 0.6071144 | 0.0003414 |
| N | -2.0978127 | -0.6489439 | -0.0010531 |
| H | -2.5073161 | 1.3526924 | 0.0007524 |
| N | -2.4004995 | -1.7422386 | -0.0022176 |
| C | -0.3152255 | 0.9484167 | 0.0006747 |
| O | 0.0985143 | 2.1019822 | 0.0013431 |
| O | 0.4793308 | -0.1496993 | 0.0001237 |
| C | 1.9193638 | 0.1118693 | 0.0004303 |
| H | 2.1580724 | 0.7019888 | 0.8894912 |
| H | 2.1583153 | 0.7026143 | -0.8881500 |
| C | 2.6128801 | -1.2342668 | 0.0000500 |
| H | 2.3456768 | -1.8114370 | -0.8902545 |
| H | 3.6968298 | -1.0800282 | 0.0003831 |
| H | 2.3452620 | -1.8121294 | 0.8897883 |

**6** : final product of diazo **5** and mNHO **2a**
57
Energy = -1317.678632770

| | | | |
|---|---|---|---|
| N | 0.0018257 | -0.8246669 | -2.0379734 |
| N | 1.1863700 | -0.2310070 | -1.7750008 |
| N | -0.8895173 | -0.6297575 | -1.1542117 |
| C | 1.4130506 | 0.6011381 | -0.6551759 |
| C | 2.1232886 | -0.2140131 | -2.8969384 |
| C | -2.0981234 | -1.3322168 | -1.3300733 |
| C | 0.6133478 | 1.6370818 | -0.1995836 |
| C | 2.5412551 | 0.5802054 | 0.2161529 |
| H | 1.8503604 | -1.0295239 | -3.5674887 |
| H | 3.1401567 | -0.3644772 | -2.5277162 |
| H | 2.0708351 | 0.7413267 | -3.4331848 |
| C | -2.2502295 | -2.5783527 | -1.9878085 |
| C | -3.2087863 | -0.7316568 | -0.6862828 |
| H | -0.3441787 | 2.0020022 | -0.5328364 |
| C | 3.6974276 | -0.3233103 | 0.2251625 |
| H | 0.2847669 | 4.0000587 | 1.1688195 |
| C | -3.5220966 | -3.1627663 | -2.0076926 |
| C | -1.1074062 | -3.3343159 | -2.6220679 |
| C | -4.4545823 | -1.3528361 | -0.7463731 |
| C | -3.0438451 | 0.5751520 | 0.0498146 |
| C | 4.9412276 | 0.1198681 | 0.7056110 |
| C | 3.5787520 | -1.6503110 | -0.2204357 |
| C | -4.6386089 | -2.5710143 | -1.4111972 |
| H | -3.6358290 | -4.1277808 | -2.4996670 |
| H | -0.8042923 | -2.8911999 | -3.5755787 |
| H | -0.2187469 | -3.3274193 | -1.9822124 |
| H | -1.4082548 | -4.3716990 | -2.8000784 |
| H | -5.3010051 | -0.8780538 | -0.2526083 |
| H | -3.9641536 | 0.8279705 | 0.5852400 |
| H | -2.2126839 | 0.5249146 | 0.7604677 |
| H | -2.8179442 | 1.3941868 | -0.6442040 |
| C | 6.0363892 | -0.7403939 | 0.7339010 |
| H | 5.0372450 | 1.1450687 | 1.0496576 |
| C | 4.6777788 | -2.5074643 | -0.1951593 |
| H | 2.6166752 | -2.0120803 | -0.5704859 |
| C | -5.9985352 | -3.2208297 | -1.4840312 |
| C | 5.9109253 | -2.0564276 | 0.2800514 |
| H | 6.9927230 | -0.3819482 | 1.1047379 |
| H | 4.5688039 | -3.5321176 | -0.5396067 |
| H | -5.9148470 | -4.2879654 | -1.7109230 |
| H | -6.6103425 | -2.7607660 | -2.2711288 |
| H | -6.5437812 | -3.1072007 | -0.5410227 |
| H | 6.7669705 | -2.7249008 | 0.2983328 |
| N | 2.4367022 | 1.5600158 | 1.1326383 |
| N | 1.2662669 | 2.1854965 | 0.8542696 |
| C | 0.7670734 | 3.2072809 | 1.7462940 |
| C | -0.2279128 | 2.6449083 | 2.7624521 |
| O | -0.4880902 | 1.4694368 | 2.9085558 |
| O | -0.7666446 | 3.6580015 | 3.4650822 |
| C | -1.7676398 | 3.2845332 | 4.4771548 |
| H | -1.4352185 | 2.3616171 | 4.9562673 |
| H | -1.7318595 | 4.1095658 | 5.1894922 |
| H | 1.6180722 | 3.6401945 | 2.2764306 |
| C | -3.1389009 | 3.1358076 | 3.8432759 |
| H | -3.4342944 | 4.0583839 | 3.3346277 |
| H | -3.1487662 | 2.3107950 | 3.1259305 |
| H | -3.8743634 | 2.9217048 | 4.6261980 |

**aA** : initial N..C adduct of **5** and **2a**
57
Energy = -1317.646931960

| | | | |
|---|---|---|---|
| N | -0.7912538 | -1.9067930 | 0.5434481 |
| N | -1.9902258 | -1.3429697 | 0.6592813 |
| N | -0.0003859 | -0.8907777 | 0.2033025 |
| C | -1.9871743 | 0.0047081 | 0.4185739 |
| C | -3.1304557 | -2.1858597 | 1.0336819 |
| C | 1.4216745 | -1.0832471 | 0.0350925 |
| C | -0.6679906 | 0.2911456 | 0.1068704 |
| C | -3.1526889 | 0.9130483 | 0.6458556 |
| H | -2.7640688 | -3.2069252 | 1.1180971 |
| H | -3.8945342 | -2.1162211 | 0.2585591 |
| H | -3.5281124 | -1.8447624 | 1.9905058 |
| C | 2.2633400 | -0.6328540 | 1.0600934 |
| C | 1.8834623 | -1.6504102 | -1.1581903 |
| H | -0.1700931 | 1.2199457 | -0.1171115 |

| | | | |
|---|---|---|---|
| C | -3.6560028 | 1.5232495 | -0.6549635 |
| H | -3.9697912 | 0.3295220 | 1.0800532 |
| C | 3.6381171 | -0.7787952 | 0.8569952 |
| C | 1.7168006 | -0.0064114 | 2.3172516 |
| C | 3.2671959 | -1.7693800 | -1.3074632 |
| C | 0.9347562 | -2.1007944 | -2.2390619 |
| C | -4.9587607 | 1.2589396 | -1.0898042 |
| C | -2.8432513 | 2.3752714 | -1.4146269 |
| C | 4.1562243 | -1.3426038 | -0.3139845 |
| H | 4.3180778 | -0.4360067 | 1.6331751 |
| H | 0.9726212 | -0.6545920 | 2.7929169 |
| H | 2.5238279 | 0.1716181 | 3.0309858 |
| H | 1.2289499 | 0.9510800 | 2.1025979 |
| H | 3.6572834 | -2.1970269 | -2.2280647 |
| H | 1.4882917 | -2.3703109 | -3.1408623 |
| H | 0.3554307 | -2.9731908 | -1.9173371 |
| H | 0.2200224 | -1.3110849 | -2.4968175 |
| C | -5.4452501 | 1.8300887 | -2.2678965 |
| H | -5.5986876 | 0.6065037 | -0.4996029 |
| C | -3.3278841 | 2.9461302 | -2.5899466 |
| H | -1.8421196 | 2.6105914 | -1.0642590 |
| C | 5.6443507 | -1.5050013 | -0.4955752 |
| C | -4.6292161 | 2.6733310 | -3.0228944 |
| H | -6.4603247 | 1.6176815 | -2.5923538 |
| H | -2.6911772 | 3.6089559 | -3.1697713 |
| H | 5.9260162 | -1.4126001 | -1.5486411 |
| H | 5.9655365 | -2.4969968 | -0.1537858 |
| H | 6.1967814 | -0.7601987 | 0.0841918 |
| H | -5.0040744 | 3.1196361 | -3.9396895 |
| N | -2.8003097 | 1.9595787 | 1.6681916 |
| N | -1.6222288 | 2.4246435 | 1.4068986 |
| C | -1.0804128 | 3.4034503 | 2.1187953 |
| C | 0.2405495 | 3.8481172 | 1.7938463 |
| O | 0.8576108 | 4.7533290 | 2.3723112 |
| O | 0.8214363 | 3.1632324 | 0.7339079 |
| C | 2.1532404 | 3.6026001 | 0.3708882 |
| H | 2.1293696 | 4.6749524 | 0.1530774 |
| H | 2.8269766 | 3.4450751 | 1.2203509 |
| H | -1.5943584 | 3.8906446 | 2.9499802 |
| C | 2.5768200 | 2.7917466 | -0.8403994 |
| H | 2.6129386 | 1.7228057 | -0.6081873 |
| H | 1.8839492 | 2.9478457 | -1.6737984 |
| H | 3.5761038 | 3.1048475 | -1.1609989 |

**aB⁻** : C-H deprotonated adduct **aA**

56

Energy = -1317.135528065

| | | | |
|---|---|---|---|
| N | -2.7015300 | -0.6795320 | -1.6940931 |
| N | -1.6024211 | -0.1079133 | -1.1222477 |
| N | -3.6824428 | -0.3198938 | -0.8576103 |
| C | -1.8937007 | 0.6423111 | 0.0320089 |
| C | -0.2957714 | -0.5549237 | -1.5583348 |
| C | -5.0315071 | -0.7556764 | -1.1064593 |
| C | -3.2786442 | 0.4341201 | 0.1834492 |
| C | -0.9748865 | 1.3248960 | 0.8627261 |
| H | 0.1879599 | 0.1766074 | -2.2141829 |
| H | -0.4221584 | -1.5053043 | -2.0783182 |
| H | 0.3278306 | -0.6785003 | -0.6674134 |
| C | -5.7648073 | -0.1361883 | -2.1235218 |
| C | -5.5581868 | -1.7615332 | -0.2831726 |
| H | -3.9576281 | 0.7625344 | 0.9487117 |
| C | 0.2379399 | 1.9422943 | 0.3658312 |
| N | -1.2488109 | 1.5275908 | 2.2253042 |
| C | -7.0854742 | -0.5601246 | -2.3103480 |
| C | -5.1659714 | 0.9513733 | -2.9785321 |
| C | -6.8820320 | -2.1443328 | -0.5097468 |
| C | -4.7288530 | -2.4050032 | 0.7989029 |
| C | 0.3913728 | 2.3638522 | -0.9817650 |
| C | 1.3079314 | 2.2517961 | 1.2490319 |
| N | -2.3258270 | 0.9440422 | 2.6635309 |
| C | -7.6592928 | -1.5568757 | -1.5160364 |
| H | -7.6806351 | -0.0881837 | -3.0891525 |
| H | -4.4402608 | 0.5381837 | -3.6871298 |
| H | -5.9482536 | 1.4642588 | -3.5435079 |
| H | -4.6359557 | 1.6889115 | -2.3663888 |
| H | -7.3139689 | -2.9222586 | 0.1164170 |
| H | -5.2748231 | -3.2402689 | 1.2444295 |
| H | -3.7846134 | -2.7843901 | 0.3923578 |
| H | -4.4770219 | -1.6905996 | 1.5902012 |
| C | 1.5460602 | 3.0018643 | -1.4231105 |
| H | -0.4334448 | 2.2261493 | -1.6770347 |
| C | 2.4556144 | 2.8968046 | 0.8029843 |
| H | 1.2027549 | 1.9719124 | 2.2924128 |
| C | -2.6645829 | 1.1539043 | 3.9542141 |
| C | -9.0858027 | -1.9973719 | -1.7378535 |
| C | 2.6004213 | 3.2713123 | -0.5407832 |
| H | 1.6158282 | 3.3129628 | -2.4637327 |
| H | 3.2560277 | 3.1064975 | 1.5104425 |
| C | -3.8422609 | 0.6089434 | 4.5104194 |
| H | -2.0477620 | 1.7840716 | 4.6008411 |
| H | -9.6574307 | -1.9638201 | -0.8037224 |
| H | -9.1223651 | -3.0304754 | -2.1040757 |
| H | -9.5853400 | -1.3589689 | -2.4717709 |
| H | 3.5014310 | 3.7708030 | -0.8864065 |
| O | -4.2285436 | 0.7441967 | 5.6955061 |
| O | -4.6268407 | -0.1217143 | 3.6021070 |
| C | -5.7960747 | -0.7483191 | 4.1634636 |
| H | -6.2595181 | -0.0723189 | 4.8882553 |
| H | -6.4708776 | -0.8837533 | 3.3116553 |
| C | -5.4655127 | -2.0868703 | 4.8137096 |
| H | -4.9802969 | -2.7565641 | 4.0958496 |
| H | -4.7959437 | -1.9363561 | 5.6650502 |
| H | -6.3835406 | -2.5693090 | 5.1715704 |

**aC** : C-protonated **aB⁻**, formal 1,4-H-shift

57

Energy = -1317.650730855

| | | | |
|---|---|---|---|
| N | -0.0708790 | -2.3442058 | -0.9201433 |
| N | 1.1835289 | -1.8587637 | -0.9051211 |
| N | -0.7959425 | -1.3215185 | -0.4613255 |

| | | | |
|---|---|---|---|
| C | 1.2735996 | -0.5632734 | -0.4200152 |
| C | 2.2481248 | -2.6713255 | -1.4836435 |
| C | -2.2283526 | -1.4312998 | -0.3325972 |
| C | -0.0594203 | -0.2291601 | -0.1650712 |
| C | 2.4496743 | 0.2417235 | -0.2697968 |
| H | 1.7869903 | -3.3772423 | -2.1730457 |
| H | 2.7974559 | -3.2002133 | -0.7017080 |
| H | 2.9298523 | -2.0020395 | -2.0105366 |
| C | -3.0234557 | -0.6705797 | -1.1999350 |
| C | -2.7508724 | -2.2367529 | 0.6868312 |
| H | -0.4922188 | 0.6858434 | 0.1996088 |
| C | 3.7377917 | -0.2947145 | 0.1570431 |
| H | 1.0635714 | 3.9523345 | -1.7276288 |
| C | -4.4076931 | -0.7446801 | -1.0220951 |
| C | -2.4227120 | 0.1956543 | -2.2787157 |
| C | -4.1413989 | -2.2735688 | 0.8179020 |
| C | -1.8597062 | -3.0178415 | 1.6184479 |
| C | 4.9384661 | 0.3800145 | -0.1570235 |
| C | 3.8371577 | -1.4643669 | 0.9419392 |
| C | -4.9831731 | -1.5387774 | -0.0244780 |
| H | -5.0492225 | -0.1646856 | -1.6814809 |
| H | -1.6896568 | -0.3605305 | -2.8725089 |
| H | -3.2060994 | 0.5594607 | -2.9471717 |
| H | -1.9017195 | 1.0631913 | -1.8569249 |
| H | -4.5739445 | -2.8826223 | 1.6084094 |
| H | -2.4359652 | -3.3897682 | 2.4685894 |
| H | -1.4077730 | -3.8739928 | 1.1066058 |
| H | -1.0408022 | -2.3978427 | 1.9998970 |
| C | 6.1685954 | -0.0966740 | 0.2854032 |
| H | 4.8825293 | 1.2850706 | -0.7541018 |
| C | 5.0720601 | -1.9482816 | 1.3688416 |
| H | 2.9300960 | -1.9773607 | 1.2539861 |
| C | -6.4816158 | -1.6170825 | 0.1284952 |
| C | 6.2500915 | -1.2707107 | 1.0435455 |
| H | 7.0757039 | 0.4440200 | 0.0258090 |
| H | 5.1120724 | -2.8492770 | 1.9761329 |
| H | -6.7645173 | -1.7649312 | 1.1750059 |
| H | -6.8820667 | -2.4634027 | -0.4438194 |
| H | -6.9649899 | -0.7086048 | -0.2420741 |
| H | 7.2129256 | -1.6465641 | 1.3777734 |
| N | 2.3412119 | 1.5998509 | -0.3740255 |
| N | 1.2174199 | 2.0746084 | -0.7931029 |
| C | 1.1734522 | 3.5214266 | -0.7203403 |
| C | -0.0227279 | 4.0415387 | 0.0692053 |
| O | -0.2447456 | 5.2280779 | 0.2489472 |
| O | -0.8210057 | 3.0598851 | 0.5373889 |
| C | -1.9984243 | 3.4989554 | 1.2894831 |
| H | -1.6550472 | 4.0644275 | 2.1599170 |
| H | -2.5832372 | 4.1647589 | 0.6490901 |
| H | 2.0813133 | 3.9496211 | -0.2708387 |
| C | -2.7660719 | 2.2519665 | 1.6796149 |
| H | -3.0958977 | 1.6964254 | 0.7963661 |
| H | -2.1529114 | 1.5933156 | 2.3026271 |
| H | -3.6526083 | 2.5387268 | 2.2542330 |

**aD** : C..N nucleophilic addition within **aC**

57

Energy = -1317.630501651

| | | | |
|---|---|---|---|
| N | 0.0080296 | -2.6418450 | -0.6395303 |
| N | 1.2335926 | -2.3612323 | -0.2987378 |
| N | -0.7673740 | -1.6870578 | -0.0434811 |
| C | 1.4222332 | -1.2349416 | 0.5017894 |
| C | 2.2920940 | -3.2398142 | -0.7903212 |
| C | -2.0726361 | -1.4431437 | -0.5773394 |
| C | 0.0527936 | -0.6053305 | 0.5727338 |
| C | 2.3002564 | -0.1464363 | 0.0333948 |
| H | 1.8367659 | -3.9586866 | -1.4694052 |
| H | 2.7655283 | -3.7497290 | 0.0510717 |
| H | 3.0351330 | -2.6356997 | -1.3149922 |
| C | -2.2702628 | -1.2370806 | -1.9566299 |
| C | -3.1378631 | -1.3606026 | 0.3361396 |
| H | -0.3668240 | -0.3687633 | 1.5574359 |
| C | 3.7567460 | -0.1781712 | -0.0747493 |
| H | -1.6374378 | 1.5057834 | -0.2570334 |
| C | -3.5699779 | -0.9796421 | -2.4002650 |
| C | -1.1240885 | -1.2355359 | -2.9373993 |
| C | -4.4168165 | -1.0851862 | -0.1565527 |
| C | -2.9124151 | -1.5521219 | 1.8138108 |
| C | 4.4427425 | 0.7146363 | -0.9190217 |
| C | 4.5008943 | -1.1024726 | 0.6785791 |
| C | -4.6561070 | -0.9020028 | -1.5208480 |
| H | -3.7321473 | -0.8094429 | -3.4631549 |
| H | -0.2746631 | -0.6735338 | -2.5348128 |
| H | -0.7758779 | -2.2503925 | -3.1545802 |
| H | -1.4378568 | -0.7707347 | -3.8761564 |
| H | -5.2457890 | -1.0213373 | 0.5455114 |
| H | -3.8555798 | -1.7696456 | 2.3216400 |
| H | -2.2067062 | -2.3666189 | 2.0025064 |
| H | -2.4911252 | -0.6476812 | 2.2730301 |
| C | 5.8313350 | 0.6826019 | -1.0004679 |
| H | 3.8684526 | 1.4233583 | -1.5076672 |
| C | 5.8914953 | -1.1350731 | 0.5905864 |
| H | 3.9745882 | -1.7809501 | 1.3447819 |
| C | -6.0494273 | -0.6392353 | -2.0372850 |
| C | 6.5634502 | -0.2436573 | -0.2487943 |
| H | 6.3480628 | 1.3764728 | -1.6581617 |
| H | 6.4521943 | -1.8534373 | 1.1824837 |
| H | -6.7053659 | -0.2790977 | -1.2394333 |
| H | -6.4920637 | -1.5570089 | -2.4449064 |
| H | -6.0390225 | 0.1026665 | -2.8424893 |
| H | 7.6471997 | -0.2698667 | -0.3194152 |
| N | 1.6113589 | 0.9111375 | -0.3192776 |
| N | 0.2474455 | 0.6386489 | -0.1986563 |
| C | -0.6101528 | 1.7778237 | 0.0064123 |
| C | -0.6061760 | 2.3235856 | 1.4368753 |
| O | 0.1449980 | 1.9666378 | 2.3239762 |
| O | -1.5697898 | 3.2577872 | 1.5740573 |
| C | -1.7214617 | 3.8488331 | 2.9100533 |
| H | -0.7270954 | 3.9682879 | 3.3448180 |
| H | -2.1627171 | 4.8268447 | 2.7131496 |

| | | | |
|---|---|---|---|
| H | -0.3035110 | 2.5812013 | -0.6699153 |
| C | -2.6199037 | 2.9830673 | 3.7755751 |
| H | -3.5951431 | 2.8400869 | 3.3003911 |
| H | -2.1623886 | 2.0064781 | 3.9569128 |
| H | -2.7748133 | 3.4755127 | 4.7416350 |

**aTS1** : electrophilic **5** N-to-C **2a** addition

57

Energy = -1317.632547302

| | | | |
|---|---|---|---|
| N | 0.9183715 | -2.4266125 | 1.1301166 |
| N | -0.3986463 | -2.5994006 | 1.2067890 |
| N | 1.0529683 | -1.3710274 | 0.3389829 |
| C | -1.1245882 | -1.6743941 | 0.4756375 |
| C | -0.9284431 | -3.6780843 | 2.0378198 |
| C | 2.3562626 | -0.8288337 | 0.0299397 |
| C | -0.1362003 | -0.8645858 | -0.0855546 |
| C | -2.5328464 | -1.5054887 | 0.5839376 |
| H | -0.0837000 | -4.2692514 | 2.3862230 |
| H | -1.6014301 | -4.2923565 | 1.4371246 |
| H | -1.4683185 | -3.2499216 | 2.8848719 |
| C | 2.8932340 | 0.1271094 | 0.8998992 |
| C | 2.9720166 | -1.2272941 | -1.1623927 |
| H | -0.1718063 | 0.0144455 | -0.7004673 |
| C | -3.3547288 | -0.9172099 | -0.4760568 |
| H | -3.0378440 | -2.2740823 | 1.1621335 |
| C | 4.1104737 | 0.7049417 | 0.5288786 |
| C | 2.1933054 | 0.5178382 | 2.1745610 |
| C | 4.1902089 | -0.6223883 | -1.4798826 |
| C | 2.3392225 | -2.2459533 | -2.0752883 |
| C | -4.6697735 | -1.3942357 | -0.6496733 |
| C | -2.9319216 | 0.1550080 | -1.2875507 |
| C | 4.7695911 | 0.3459044 | -0.6516533 |
| H | 4.5459298 | 1.4621812 | 1.1764277 |
| H | 2.3036277 | -0.2662247 | 2.9328479 |
| H | 2.6199884 | 1.4401544 | 2.5742524 |
| H | 1.1225415 | 0.6758690 | 2.0137239 |
| H | 4.6891384 | -0.9065685 | -2.4032971 |
| H | 3.0231013 | -2.5044449 | -2.8862869 |
| H | 2.0828551 | -3.1620606 | -1.5329602 |
| H | 1.4142498 | -1.8597621 | -2.5199544 |
| C | -5.5180722 | -0.8449359 | -1.6064330 |
| H | -5.0197924 | -2.2114857 | -0.0232597 |
| C | -3.7866254 | 0.7066013 | -2.2409579 |
| H | -1.9557158 | 0.6015624 | -1.1460025 |
| C | 6.0895853 | 0.9768108 | -1.0176424 |
| C | -5.0787236 | 0.2078843 | -2.4150203 |
| H | -6.5240816 | -1.2389016 | -1.7227431 |
| H | -3.4398626 | 1.5379031 | -2.8491221 |
| H | 6.2184814 | 1.0195771 | -2.1030119 |
| H | 6.9220501 | 0.3907179 | -0.6082511 |
| H | 6.1687602 | 1.9898077 | -0.6129031 |
| H | -5.7366739 | 0.6369942 | -3.1650907 |
| N | -2.4742766 | -0.0167390 | 1.9226981 |
| N | -1.7216734 | 0.8228417 | 1.4782186 |
| C | -1.3539876 | 2.0412005 | 1.8889478 |
| C | -0.4486159 | 2.8422846 | 1.1296653 |
| O | -0.0741706 | 3.9744983 | 1.4627194 |
| O | 0.0070865 | 2.2611644 | -0.0392691 |
| C | 0.9390419 | 3.0743922 | -0.7991075 |
| H | 0.4530787 | 4.0192613 | -1.0608289 |
| H | 1.8059856 | 3.2997777 | -0.1703359 |
| H | -1.7522245 | 2.4587434 | 2.8117251 |
| C | 1.3301929 | 2.2807701 | -2.0310037 |
| H | 1.8527650 | 1.3596874 | -1.7565139 |
| H | 0.4485272 | 2.0265221 | -2.6290811 |
| H | 2.0038540 | 2.8796461 | -2.6526619 |

**aTS2** : deprotonation of **aA** with base **2a**

100

Energy = -2219.063933615

| | | | |
|---|---|---|---|
| N | -2.0126169 | 1.6179888 | -3.5542745 |
| N | -2.3803081 | 1.8608615 | -2.2869884 |
| N | -1.0409666 | 0.7137491 | -3.4228388 |
| C | -1.6889817 | 1.1041459 | -1.3540380 |
| C | -3.3823385 | 2.9000607 | -2.0622796 |
| C | -0.3171790 | 0.2294253 | -4.5732083 |
| C | -0.7975163 | 0.3703126 | -2.1378768 |
| C | -1.7690176 | 1.1364847 | 0.0957648 |
| H | -4.3548470 | 2.4510490 | -1.8498937 |
| H | -3.4279295 | 3.5056765 | -2.9661711 |
| H | -3.0700649 | 3.5000882 | -1.2077762 |
| C | -0.8802542 | -0.7897641 | -5.3458175 |
| C | 0.9525486 | 0.7725245 | -4.8101648 |
| H | -0.0465406 | -0.3496426 | -1.8664196 |
| C | -2.9783932 | 1.6402199 | 0.7710393 |
| N | -0.5302250 | 1.4073811 | 0.8043236 |
| C | -0.1124528 | -1.2773050 | -6.4083127 |
| C | -2.2481365 | -1.3434511 | -5.0433236 |
| C | 1.6763568 | 0.2482851 | -5.8825458 |
| C | 1.5089183 | 1.8678464 | -3.9374916 |
| C | -4.2513313 | 1.1515501 | 0.4041444 |
| C | -2.9028937 | 2.4830911 | 1.8977480 |
| N | 0.5122729 | 0.9585547 | 0.1783824 |
| C | 1.1620685 | -0.7752403 | -6.6886082 |
| H | -0.5192372 | -2.0773930 | -7.0224880 |
| H | -3.0291007 | -0.6127077 | -5.2818252 |
| H | -2.4310937 | -2.2456500 | -5.6314055 |
| H | -2.3441319 | -1.5967318 | -3.9825010 |
| H | 2.6659696 | 0.6492825 | -6.0901183 |
| H | 2.4288351 | 2.2658878 | -4.3719351 |
| H | 0.7930884 | 2.6906771 | -3.8343380 |
| H | 1.7312094 | 1.4955482 | -2.9305449 |
| C | -5.3999391 | 1.5295467 | 1.0959974 |
| H | -4.3309806 | 0.4500782 | -0.4245866 |
| C | -4.0520291 | 2.8465693 | 2.5976756 |
| H | -1.9268073 | 2.8358926 | 2.2113304 |
| C | 1.7021724 | 1.0207796 | 0.7924041 |
| C | 1.9671406 | -1.3145100 | -7.8451205 |
| C | -5.3107240 | 2.3838927 | 2.1998514 |
| H | -6.3659442 | 1.1390624 | 0.7855188 |

| | | | |
|---|---|---|---|
| H | -3.9657885 | 3.5017686 | 3.4614251 |
| C | 2.8768857 | 0.4869692 | 0.1896433 |
| H | 1.8121157 | 1.4387930 | 1.7949896 |
| H | 2.9979679 | -1.5265067 | -7.5420586 |
| H | 2.0122142 | -0.5824692 | -8.6607526 |
| H | 1.5245754 | -2.2329998 | -8.2399591 |
| H | -6.2034316 | 2.6697512 | 2.7488389 |
| O | 3.9898235 | 0.4127794 | 0.7396918 |
| O | 2.6928506 | 0.0157719 | -1.1081819 |
| C | 3.8501682 | -0.6036949 | -1.7126787 |
| H | 4.3641643 | -1.2115499 | -0.9622110 |
| H | 3.4315903 | -1.2553861 | -2.4852918 |
| C | 4.8029809 | 0.4166496 | -2.3219266 |
| H | 4.2893424 | 1.0324146 | -3.0663125 |
| H | 5.2124803 | 1.0660419 | -1.5441786 |
| H | 5.6321025 | -0.1022752 | -2.8178318 |
| H | -1.8764615 | -0.2509240 | 0.3789067 |
| C | -1.7841734 | -1.5830157 | 0.8711417 |
| C | -1.1739754 | -1.3272245 | 2.1471398 |
| C | -1.1349778 | -2.3596943 | -0.1999136 |
| H | -2.8445371 | -1.8236599 | 0.9655610 |
| N | -1.9274934 | -0.9817299 | 3.2607945 |
| C | 0.1373405 | -1.1562531 | 2.5961678 |
| C | -1.9600005 | -3.0278281 | -1.1303918 |
| C | 0.2555681 | -2.4009161 | -0.4273898 |
| N | -1.1918754 | -0.5992970 | 4.3154075 |
| C | -3.3794640 | -0.9187542 | 3.3543769 |
| N | 0.0542342 | -0.7161913 | 3.8750141 |
| H | 1.0859879 | -1.1896130 | 2.0897978 |
| C | -1.4294320 | -3.6913003 | -2.2328800 |
| H | -3.0378420 | -3.0107764 | -0.9820602 |
| C | 0.7847348 | -3.0675425 | -1.5308004 |
| H | 0.9330369 | -1.8494319 | 0.2122581 |
| H | -3.6292146 | -0.6494153 | 4.3790512 |
| H | -3.8015424 | -1.8961713 | 3.1089467 |
| H | -3.7568641 | -0.1628292 | 2.6590931 |
| C | 1.1550037 | -0.2889764 | 4.7038121 |
| C | -0.0482097 | -3.7145429 | -2.4466173 |
| H | -2.0975058 | -4.1896312 | -2.9308006 |
| H | 1.8600448 | -3.0622380 | -1.6842273 |
| C | 1.3022668 | 1.0830614 | 4.9398891 |
| C | 2.0388470 | -1.2583820 | 5.1961354 |
| H | 0.3691444 | -4.2207859 | -3.3119373 |
| C | 2.4018072 | 1.4771366 | 5.7097437 |
| C | 0.3335014 | 2.0969821 | 4.3872607 |
| C | 3.1150105 | -0.8077496 | 5.9623382 |
| C | 1.8457127 | -2.7280018 | 4.9173339 |
| C | 3.3146313 | 0.5531687 | 6.2254819 |
| H | 2.5494509 | 2.5375806 | 5.9009152 |
| H | -0.5974869 | 2.1002444 | 4.9653046 |
| H | 0.7712647 | 3.0972636 | 4.4386670 |
| H | 0.0689380 | 1.8797094 | 3.3453596 |
| H | 3.8132679 | -1.5400632 | 6.3615835 |
| H | 2.4821465 | -3.3226930 | 5.5766197 |
| H | 0.8050441 | -3.0320005 | 5.0701832 |
| H | 2.1099446 | -2.9760069 | 3.8828248 |
| C | 4.4967621 | 1.0079045 | 7.0450859 |
| H | 5.4383624 | 0.7229542 | 6.5615740 |
| H | 4.4875343 | 0.5421248 | 8.0371550 |
| H | 4.4925777 | 2.0934248 | 7.1739995 |

**aTS3** : rotonation of **aB**$^{-}$ with base **2a**H$^{+}$

100

Energy = -2219.061450369

| | | | |
|---|---|---|---|
| N | -5.2599099 | 0.2583664 | 1.6582987 |
| N | -4.2338148 | 0.4294126 | 2.5184426 |
| N | -4.6511111 | 0.1644822 | 0.4771386 |
| C | -2.9779008 | 0.4187010 | 1.9037359 |
| C | -4.5463602 | 0.7887581 | 3.8929166 |
| C | -5.4244674 | 0.0248653 | -0.7315108 |
| C | -3.3053271 | 0.2642936 | 0.5441824 |
| C | -1.7184339 | 0.6451784 | 2.5198361 |
| H | -4.4261669 | -0.0666359 | 4.5625455 |
| H | -5.5741958 | 1.1494773 | 3.9142808 |
| H | -3.8520720 | 1.5745662 | 4.1994243 |
| C | -6.0327592 | -1.2038406 | -1.0064857 |
| C | -5.4864541 | 1.1274953 | -1.5961821 |
| H | -2.6793848 | 0.2378901 | -0.3288057 |
| C | -1.3868460 | 0.2323337 | 3.8748317 |
| N | -0.6650738 | 1.1577426 | 1.7787811 |
| C | -6.7365110 | -1.3113442 | -2.2107544 |
| C | -5.9285168 | -2.3706780 | -0.0577907 |
| C | -6.2001999 | 0.9635906 | -2.7848522 |
| C | -4.8129913 | 2.4354001 | -1.2635879 |
| C | -2.0062802 | -0.8768793 | 4.4979107 |
| C | -0.3432594 | 0.8688688 | 4.5898552 |
| N | -0.9017914 | 1.4492412 | 0.5432722 |
| C | -6.8295540 | -0.2446824 | -3.1090043 |
| H | -7.2124407 | -2.2585596 | -2.4542975 |
| H | -6.5454833 | -2.2108562 | 0.8328649 |
| H | -6.2630003 | -3.2880869 | -0.5478268 |
| H | -4.8975457 | -2.5144210 | 0.2836905 |
| H | -6.2655175 | 1.8037185 | -3.4727230 |
| H | -5.1460964 | 3.2143664 | -1.9535609 |
| H | -5.0483464 | 2.7529392 | -0.2420802 |
| H | -3.7221346 | 2.3542785 | -1.3339964 |
| C | -1.6293337 | -1.3019169 | 5.7690363 |
| H | -2.7599701 | -1.4400271 | 3.9523484 |
| C | 0.0419975 | 0.4296067 | 5.8518191 |
| H | 0.1584010 | 1.7123113 | 4.1255858 |
| C | 0.2393675 | 1.8048384 | -0.1839282 |
| C | -7.5951555 | -0.3858224 | -4.4013244 |
| C | -0.6021922 | -0.6535686 | 6.4626381 |
| H | -2.1251181 | -2.1628397 | 6.2119865 |
| H | 0.8466267 | 0.9440919 | 6.3728647 |
| C | 0.0742868 | 2.2839964 | -1.5431232 |
| H | 1.0723980 | 2.2677500 | 0.3577243 |
| H | -6.9804835 | -0.0831848 | -5.2562332 |
| H | -8.4850519 | 0.2549757 | -4.3984642 |
| H | -7.9199171 | -1.4181463 | -4.5564393 |

| | | | |
|---|---|---|---|
| H | -0.3046487 | -0.9894056 | 7.4520880 |
| O | 0.9434832 | 2.8817360 | -2.1900961 |
| O | -1.1204905 | 1.9040269 | -2.1074672 |
| C | -1.2384703 | 2.0943246 | -3.5399621 |
| H | -1.5652096 | 3.1237223 | -3.7311700 |
| H | -0.2531340 | 1.9570278 | -3.9925758 |
| C | -2.2405719 | 1.0768814 | -4.0540404 |
| H | -1.8895925 | 0.0615858 | -3.8506824 |
| H | -3.2213648 | 1.2089903 | -3.5879225 |
| H | -2.3573624 | 1.1935029 | -5.1375196 |
| H | 0.8047639 | 0.5140438 | -0.4150154 |
| C | 1.2303974 | -0.8228420 | -0.4571340 |
| C | 2.5930703 | -0.7479724 | -0.0211108 |
| C | 0.8891877 | -1.2637983 | -1.8243059 |
| H | 0.5713289 | -1.2438830 | 0.3040735 |
| N | 2.9349802 | -0.5837205 | 1.3147830 |
| C | 3.8246136 | -0.6510616 | -0.6726628 |
| C | -0.1740352 | -2.1648610 | -2.0212143 |
| C | 1.5182327 | -0.7376438 | -2.9688513 |
| N | 4.2502194 | -0.4051001 | 1.5168078 |
| C | 2.0216031 | -0.6056948 | 2.4517099 |
| N | 4.7582717 | -0.4470093 | 0.2911595 |
| H | 4.0944585 | -0.7131939 | -1.7124881 |
| C | -0.5711320 | -2.5488170 | -3.2996058 |
| H | -0.6911235 | -2.5657033 | -1.1519962 |
| C | 1.1255066 | -1.1265266 | -4.2480948 |
| H | 2.2878101 | 0.0210133 | -2.8606415 |
| H | 2.6025265 | -0.3847871 | 3.3453913 |
| H | 1.5710364 | -1.5991191 | 2.5340689 |
| H | 1.2283546 | 0.1415694 | 2.3005021 |
| C | 6.1742904 | -0.2362141 | 0.0949622 |
| C | 0.0831639 | -2.0394209 | -4.4247167 |
| H | -1.3962711 | -3.2463470 | -3.4194724 |
| H | 1.6250408 | -0.6981469 | -5.1134063 |
| C | 6.6190155 | 1.0753164 | -0.1068617 |
| C | 7.0222403 | -1.3496822 | 0.0991257 |
| H | -0.2273325 | -2.3343598 | -5.4229530 |
| C | 7.9898230 | 1.2559736 | -0.3125635 |
| C | 5.6635859 | 2.2414289 | -0.0974120 |
| C | 8.3830240 | -1.1119858 | -0.1094965 |
| C | 6.4903911 | -2.7438812 | 0.3127315 |
| C | 8.8835788 | 0.1795510 | -0.3133083 |
| H | 8.3649725 | 2.2638443 | -0.4743327 |
| H | 5.1654167 | 2.3320442 | 0.8742000 |
| H | 6.1979904 | 3.1721458 | -0.2984089 |
| H | 4.8801059 | 2.1241382 | -0.8546768 |
| H | 9.0661656 | -1.9583408 | -0.1118612 |
| H | 7.3137052 | -3.4584121 | 0.3776981 |
| H | 5.9026636 | -2.8069233 | 1.2345573 |
| H | 5.8373468 | -3.0489422 | -0.5131750 |
| C | 10.3623898 | 0.4069730 | -0.5054713 |
| H | 10.8138834 | -0.4009375 | -1.0893937 |
| H | 10.8744683 | 0.4371328 | 0.4645251 |
| H | 10.5534390 | 1.3567308 | -1.0126555 |

**aTS4** : ring-closing N-to-C addition of **aC**

57

Energy = -1317.624708427

| | | | |
|---|---|---|---|
| N | 0.1127821 | -2.0688654 | -0.8154933 |
| N | 1.3712533 | -1.8669370 | -0.5104010 |
| N | -0.5646667 | -1.1631127 | -0.0628708 |
| C | 1.6078218 | -0.8493205 | 0.4030657 |
| C | 2.3776286 | -2.6678683 | -1.2024547 |
| C | -1.9897561 | -1.0810580 | -0.1751425 |
| C | 0.2886933 | -0.2487666 | 0.6275633 |
| C | 2.6203662 | 0.1783487 | 0.1562508 |
| H | 1.8664813 | -3.2453638 | -1.9707288 |
| H | 2.8732766 | -3.3301191 | -0.4901443 |
| H | 3.1134636 | -1.9977634 | -1.6508237 |
| C | -2.5810951 | -0.6682083 | -1.3779238 |
| C | -2.7566899 | -1.4208480 | 0.9528823 |
| H | -0.1031899 | 0.0177874 | 1.6034009 |
| C | 4.0647921 | -0.0154368 | 0.0948664 |
| H | 0.0608120 | 2.0255300 | -1.7674710 |
| C | -3.9763079 | -0.5670065 | -1.4180371 |
| C | -1.7652076 | -0.3645105 | -2.6077231 |
| C | -4.1446109 | -1.3046847 | 0.8623539 |
| C | -2.1078143 | -1.9221224 | 2.2176012 |
| C | 4.9034624 | 0.9171247 | -0.5478559 |
| C | 4.6555864 | -1.1449141 | 0.6903941 |
| C | -4.7725697 | -0.8693017 | -0.3109184 |
| H | -4.4479833 | -0.2334000 | -2.3398032 |
| H | -1.5828640 | -1.2792015 | -3.1835555 |
| H | -2.2942422 | 0.3442951 | -3.2493362 |
| H | -0.7876095 | 0.0513146 | -2.3553759 |
| H | -4.7494889 | -1.5661661 | 1.7280953 |
| H | -2.8668482 | -2.2786317 | 2.9180914 |
| H | -1.4133055 | -2.7415706 | 2.0049161 |
| H | -1.5316452 | -1.1356224 | 2.7189201 |
| C | 6.2781710 | 0.7151045 | -0.6003143 |
| H | 4.4551544 | 1.7923161 | -1.0079790 |
| C | 6.0336267 | -1.3471048 | 0.6303086 |
| H | 4.0216716 | -1.8533214 | 1.2174879 |
| C | -6.2713454 | -0.7063020 | -0.3667155 |
| C | 6.8534855 | -0.4201912 | -0.0160646 |
| H | 6.9084741 | 1.4429919 | -1.1045894 |
| H | 6.4687544 | -2.2261829 | 1.0982702 |
| H | -6.5674768 | 0.2732610 | 0.0303416 |
| H | -6.7751594 | -1.4688703 | 0.2353078 |
| H | -6.6388428 | -0.7709548 | -1.3948037 |
| H | 7.9276522 | -0.5753050 | -0.0619402 |
| N | 2.0675290 | 1.3537853 | -0.0981558 |
| N | 0.7502560 | 1.4002550 | 0.1664620 |
| C | 0.0307086 | 2.3172646 | -0.7087502 |
| C | -1.4301767 | 2.4948467 | -0.3469157 |
| O | -2.2528366 | 2.9269702 | -1.1365966 |
| O | -1.7119469 | 2.1613745 | 0.9240307 |
| C | -3.1199026 | 2.3105434 | 1.3078471 |
| H | -3.4163959 | 3.3442060 | 1.1128704 |
| H | -3.7066776 | 1.6468265 | 0.6678327 |

| | | | |
|---|---|---|---|
| H | 0.5069090 | 3.3049040 | -0.6412097 |
| C | -3.2293014 | 1.9461485 | 2.7722204 |
| H | -2.9066659 | 0.9162200 | 2.9449269 |
| H | -2.6246244 | 2.6161366 | 3.3904703 |
| H | -4.2744282 | 2.0348767 | 3.0864342 |

**aTS5** : N..C ring-opening of **aD**

57

Energy = -1317.628128766

| | | | |
|---|---|---|---|
| N | 0.6162687 | -1.9568175 | 1.1997892 |
| N | 1.7527490 | -1.3449241 | 1.4169499 |
| N | -0.3431041 | -1.0553132 | 1.0835359 |
| C | 1.7548598 | 0.0564001 | 1.2336792 |
| C | 2.9301864 | -2.1854303 | 1.6096618 |
| C | -1.5276668 | -1.4295232 | 0.3806014 |
| C | 0.3498569 | 0.5032182 | 1.0713746 |
| C | 2.4642434 | 0.6142874 | 0.0862789 |
| H | 2.5905629 | -3.2190999 | 1.6574811 |
| H | 3.4300984 | -1.9025889 | 2.5380838 |
| H | 3.6176440 | -2.0519707 | 0.7713577 |
| C | -1.4698313 | -1.9341632 | -0.9344226 |
| C | -2.7541105 | -1.1724948 | 1.0153330 |
| H | -0.2448566 | 0.9522362 | 1.8609800 |
| C | 3.8852035 | 0.4768164 | -0.2440891 |
| H | -1.1122813 | 0.8820061 | -1.4675274 |
| C | -2.6755789 | -2.1861446 | -1.5922445 |
| C | -0.1575430 | -2.1575687 | -1.6468010 |
| C | -3.9327543 | -1.4494426 | 0.3178338 |
| C | -2.7964646 | -0.6123980 | 2.4143565 |
| C | 4.3126930 | 0.4711544 | -1.5834005 |
| C | 4.8490207 | 0.3680248 | 0.7727723 |
| C | -3.9160587 | -1.9525401 | -0.9854244 |
| H | -2.6435226 | -2.5609633 | -2.6137357 |
| H | 0.5186480 | -1.3050635 | -1.5193670 |
| H | 0.3635669 | -3.0402747 | -1.2622922 |
| H | -0.3322690 | -2.3022016 | -2.7162593 |
| H | -4.8870829 | -1.2614728 | 0.8051860 |
| H | -3.8141856 | -0.6522515 | 2.8116573 |
| H | -2.1333575 | -1.1700329 | 3.0830545 |
| H | -2.4679443 | 0.4337162 | 2.4315082 |
| C | 5.6650934 | 0.3545332 | -1.8939126 |
| H | 3.5686262 | 0.5507291 | -2.3699760 |
| C | 6.2015484 | 0.2462159 | 0.4591410 |
| H | 4.5266578 | 0.3964976 | 1.8099830 |
| C | -5.2005228 | -2.2337065 | -1.7255665 |
| C | 6.6158188 | 0.2375919 | -0.8749081 |
| H | 5.9798917 | 0.3462543 | -2.9339734 |
| H | 6.9344776 | 0.1667248 | 1.2574192 |
| H | -6.0682739 | -1.9060192 | -1.1463021 |
| H | -5.3110780 | -3.3060612 | -1.9267898 |
| H | -5.2171964 | -1.7196698 | -2.6933211 |
| H | 7.6699263 | 0.1416132 | -1.1193723 |
| N | 1.6662229 | 1.3296412 | -0.6831177 |
| N | 0.4205237 | 1.3674747 | -0.0694617 |
| C | -0.6948476 | 1.7344323 | -0.9147818 |
| C | -1.8232978 | 2.4002116 | -0.1447466 |
| O | -1.7840431 | 2.7512307 | 1.0195537 |
| O | -2.8829690 | 2.5572981 | -0.9600636 |
| C | -4.0654074 | 3.2110764 | -0.3855514 |
| H | -3.7254569 | 3.9690481 | 0.3228099 |
| H | -4.5387346 | 3.6891638 | -1.2443739 |
| H | -0.3190560 | 2.4462005 | -1.6556265 |
| C | -4.9770456 | 2.1890882 | 0.2682968 |
| H | -5.2577893 | 1.4081509 | -0.4440747 |
| H | -4.4889095 | 1.7248002 | 1.1285954 |
| H | -5.8877076 | 2.6898785 | 0.6142597 |

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