Electronic Supplementary Information for

Azide-alkyne cycloadditions with an electronically activated alkyne: indole formation via 1-aryl-1,2,3-triazole-derived imino carbenes

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1. Experimental Details

1.1 General comments

All syntheses were carried out in an argon-filled glovebox or with standard Schlenk techniques unless otherwise stated. All non-deuterated solvents were dried by distillation over appropriate drying agents and stored over activated molecular sieves under argon atmosphere. Deuterated solvents were dried under an argon atmosphere over activated molecular sieves and degassed by three *freeze-pump-thaw* cycles. All solution NMR spectra were acquired on a Bruker Avance 400 NMR spectrometer (^{1}H: 400.1 MHz, ^{13}C: 101 MHz) or a Bruker Avance I 500 spectrometer (^{1}H: 500.1 MHz, ^{13}C: 125.8 MHz, ^{19}F: 470.6 MHz). ^{1}H NMR and ^{13}C NMR spectra were referenced to external TMS via residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{19}F NMR spectra were referenced to external CCl_3F. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR signals were assigned with assistance from DEPT135 and HSQC experiments. High-resolution mass spectrometry data was obtained from a Thermo Scientific Exactive Plus spectrometer in LIFDI mode. 1,2-Bis(piperidyl)acetylene **1**,[1] azidobenzene,[2] 2´-azido-1,1´:3,1´´-terphenyl,[2] 1-azido-2-methylbenzene,[2] 1-azido-4-fluorobenzene,[2] 1-azido-4-(trifluoromethyl)benzene,[2] 1-azido-4-fluoro-6-(trifluoromethyl)benzene,[2] 1-azido-4-cyanobenzene,[2] 1-azido-4-nitrobenzene,[2] 1-azido-4-methoxybenzene,[2] and 1-azido-4-(dimethylamino)benzene[2] were synthesised according to literature procedures. We note that product isolation was achieved without using any extensive purification techniques due to the thermal instability of some of the products. Thus, in their ^{1}H NMR spectra, we observe minor signals for impurities in < 3 %.

1.2 General procedures for the synthesis of 3*H*-indoles

2,3-Dipiperidyl-3H-indole (2)

A benzene solution (1.5 mL) of alkyne **1** (30.0 mg, 156 μmol) was added to a benzene solution of azidobenzene (19.0 mg, 156 μmol) at room temperature. The solution was stirred for 2 d at 80 °C. During this time the reaction mixture changed colour to red-orange. The solvent was removed under dynamic vacuum, the residue washed with pentane (7 x 2 mL) at room temperature and dried under reduced pressure to afford **2** as a beige solid (yield: 35.4 mg, 125 μmol, 80%). Colourless crystals were obtained by slow evaporation of a saturated toluene solution of **2** at −30 °C. ^{1}H NMR (C_6D_6): δ 7.51 (dd, $^{3}J_{H\text{-}H}$ = 7.46 Hz, $^{4}J_{H\text{-}H}$ = 1.01 Hz, 1H, 7-CH_{Aryl}), 7.25 (t, $^{3}J_{H\text{-}H}$ = 7.46 Hz, 2H, 6,5-CH_{Aryl}), 6.91 (td, $^{3}J_{H\text{-}H}$ = 7.46 Hz, $^{4}J_{H\text{-}H}$ = 1.01 Hz, 1H, 4-CH_{Aryl}), 4.07 (s, 1H, 3-CH_{indole}), 3.75- 3.40 (m, 2H, 2,6-NC$_5H_{10}$), 3.40-2.95 (m, 2H, 2,6-NC$_5H_{10}$), 2.60-2.50 (m, 2H, 2,6-NC$_5H_{10}$), 2.29- 2.15 (br s, 2H, 2,6-NC$_5H_{10}$), 1.43-1.26 (m, 10H, 3,4,5-NC$_5H_{10}$), 1.20-1.12 (m, 2H, 3,4,5- NC$_5H_{10}$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 171.5 (C_q, N=*C*), 158.5 (C_q, *C*−N=C), 131.9 (C_q, *C*−C−N=C), 129.4, 124.3 (CH, 5,6-C_6H_4), 120.1 (CH, 4-C_6H_4), 117.2 (CH, 7-C_6H_4), 70.8 (CH, 3*H*-indole), 54.2, 51.7 (CH_2, 2,6-NC_5H_{10}), 49.9

(br s, CH_2, 2,6-NC_5H_{10}), 47.7 (CH_2, 2,6-NC_5H_{10}), 26.9, 24.9, 24.6 (CH_2, 3,4,5-NC_5H_{10}) ppm. LIFDI-MS *(m/z)* calculated for [$C_{18}H_{25}N_3$] = 282.2043; found: 283.2032.

2,3-Dipiperidyl-3,7-diphenyl-3H-indole (3)

3*H*-Indole **3** was prepared according to the general procedure starting from **1** (30.0 mg, 156 μmol) and 2´-azido-1,1´:3,1´´-terphenyl (42.0 mg, 156 μmol) in benzene (2 mL). Volatiles were removed under reduced pressure and the residue was washed with pentane (7 x 2 mL) to obtain a beige solid of **3** (yield: 50.9 mg, 117 μmol, 75%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated toluene solution at −30 °C. ^{1}H NMR (C_6D_6): δ 8.31 (dd, $^3J_{H\text{-}H}$ = 7.87 Hz, $^4J_{H\text{-}H}$ = 1.28 Hz, 2H, 3´´,5´´-CH_{Aryl}), 7.57 (dd, $^3J_{H\text{-}H}$ = 7.87 Hz, $^4J_{H\text{-}H}$ = 1.28 Hz, 1H, 4´´-CH_{Aryl}), 7.42 (t, $^3J_{H\text{-}H}$ = 7.87 Hz, 2H, 2´´,6´´-CH_{Aryl}), 7.37 (d, $^3J_{H\text{-}H}$ = 7.28 Hz, 4,6-CH_{Aryl}), 7.21 (t, $^3J_{H\text{-}H}$ = 7.34 Hz, 1H, 2´,3´,4´,5´,6´-CH_{Aryl}), 7.07 (t, $^3J_{H\text{-}H}$ = 7.34 Hz, 2H, 2´,3´,4´,5´,6´-CH_{Aryl}), 7.00 (t, $^3J_{H\text{-}H}$ = 7.34 Hz, 1H, 2´,3´,4´,5´,6´-CH_{Aryl}), 6.93 (t, $^3J_{H\text{-}H}$ = 7.34 Hz, 1H, 2´,3´,4´,5´,6´-CH_{Aryl}), 6.80 (d, $^3J_{H\text{-}H}$ = 7.28 Hz, 1H, 5-CH_{Aryl}), 3.64 (br s, 3H, 2,6-NC_5H_{10}), 2.63 (br s, 3H, 2,6-NC_5H_{10}), 1.56-1.48 (m, 4H, 2,3,5,6-NC_5H_{10}), 1.40-1.12 (m, 3H, 3,4,5-NC_5H_{10}), 1.11-0.93 (m, 5H, 3,4,5-NC_5H_{10}), 0.91-0.77 (m, 2H, 3,4,5-NC_5H_{10}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 173.8 (C_q, N=*C*), 155.2 (C_q, *C*−N=C), 140.6, 140.1 (C_q, 1´,1´´-$C_{18}H_{13}$), 138.4 (C_q, *C*−C−N=C), 130.0, 129.6, 129.1, 128.6 (CH, $C_{18}H_{13}$), 128.3 (br, C_q, 3-$C_{18}H_{13}$), 127.0, 126.7, 124.2, 120.9 (CH, $C_{18}H_{13}$), 81.3 (C_q, N=C−*C*), 50.2, 46.5 (CH_2, 2,6-NC_5H_{10}), 27.1, 25.9, 24.9, 24.5 (CH_2, 3,4,5-NC_5H_{10}) ppm. LIFDI-MS *(m/z)* calculated for [$C_{30}H_{33}N_3$] = 435.2669; found: 435.2668.

2,3-Dipiperidyl-7-methyl-3*H*-indole (4)

3*H*-Indole **4** was prepared according to the general procedure starting from a benzene solution of **1** (30.0 mg, 156 μmol) and 1-azido-2-methylbenzene (20 mg, 156 μmol). Volatiles were removed under dynamic vacuum and the residue was washed with pentane (7 x 2 mL) to afford **4** as a beige solid (yield: 29.2 mg, 98.3 μmol, 63%). Crystals suitable for X-ray diffraction were grown by pentane diffusion into a saturated THF solution of compound **4** at −30 °C. ^{1}H NMR (CD_2Cl_2): δ 7.13 (d, $^3J_{H\text{-}H}$ = 7.21 Hz, 1H, 4-CH_{Aryl}), 6.98 (dq, $^3J_{H\text{-}H}$ = 7.60 Hz, $^4J_{H\text{-}H}$ = 0.60 Hz, 1H, 6-CH_{Aryl}), 6.72 (t, $^3J_{H\text{-}H}$ = 7.39 Hz, 1H, 5-CH_{Aryl}), 4.47 (s, 1H, 3- CH_{indole}), 4.25-3.75 (br m, 2H, equatorial 2,6-NC_5H_{10} of 2-piperidyl), 3.58-3.22 (br m, 2H, axial 2,6-NC_5H_{10} of 2-piperidyl), 2.70-2.55 (m, 2H, equatorial 2,6-NC_5H_{10} of 3-piperidyl), 2.50-2.35 (m, 2H, axial 2,6-NC_5H_{10} of 3-piperidyl), 2.32 (s, 3H,7-CH_3), 1.71-1.65 (m, 4H, 3,4,5-NC_5H_{10}), 1.60-1.48 (m, 6H, 3,4,5-NC_5H_{10}), 1.43-1.37 (m, 2H, 3,4,5-NC_5H_{10}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 171.4 (C_q, N=*C*), 155.9 (C_q, *C*−N=C), 131.3 (C_q, *C*−C−N=C), 130.2 (C_q, 7-*C*CH_3), 125.3 (CH, 6-*C*$_6H_3(CH_3)$), 121.9 (CH, 4-*C*$_6H_3(CH_3)$), 119.7 (CH, 5-*C*$_6H_3(CH_3)$), 71.1 (CH, 3*H*-indole), 50.1 (br, CH_2, 2,6-NC_5H_{10}), 27.1, 25.0, 24.8 (CH_2, 3,4,5-NC_5H_{10}), 16.8 (CH_3, 7-C*C*H_3) ppm. LIFDI-MS *(m/z)* calculated for [$C_{19}H_{27}N_3$] = 297.2199; found: 297.2184.

2,3-Dipiperidyl-5-fluoro-3*H*-indole (5)

3*H*-Indole **5** was prepared according to the general procedure starting from a benzene solution of **1** (40.0 mg, 208 μmol) and 1-azido-4-fluorobenzene (29 mg, 208 μmol). All volatiles were removed under reduced pressure and the residue was washed with pentane (7 x 2 mL) to obtain **5** as an orange solid (yield: 53.3 mg, 177 μmol, 85%). Crystals of **5** suitable for X-ray diffraction analysis were grown by evaporation of a saturated toluene solution at −30 °C. ^{1}H NMR (C_6D_6): δ 7.22 (dd, $^{3}J_{H\text{-}H}$ = 7.93 Hz, $^{4}J_{H\text{-}H}$ = 4.63 Hz, 1H, 6-CH_{Aryl}), 7.03 (d, $^{3}J_{H\text{-}H}$ = 7.93 Hz, 1H, 7-CH_{Aryl}), 6.92-6.87 (m, 1H, 4-CH_{Aryl}), 3.94 (s, 1H, 3-CH_{indole}), 3.59-3.31 (br m, 2H, equatorial 2,6-NC$_5H_{10}$ of 2-piperidyl), 3.23 (t, geminal $^{2}J_{H\text{-}H}$ = 5.33 Hz, 1H, axial 2,6-NC$_5H_{10}$ of 2-piperidyl), 3.14 (t, geminal $^{2}J_{H\text{-}H}$ = 5.33 Hz, 1H, axial 2,6-NC$_5H_{10}$ of 2-piperidyl), 2.46-2.36 (m, 2H, 2,6-NC$_5H_{10}$), 2.15-2.02 (m, 2H, 2,6-NC$_5H_{10}$), 1.59-1.49 (m, 1H, 3,4,5-NC$_5H_{10}$), 1.44-1.34 (m, 3H, 3,4,5-NC$_5H_{10}$), 1.33-1.23 (m, 6H, 3,4,5-NC$_5H_{10}$), 1.18-1.09 (m, 2H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 171.4 (d, $^{5}J_{C\text{-}F}$ = 2.10 Hz, C_q, N=*C*), 158.3 (d, $^{1}J_{C\text{-}F}$ = 236.7 Hz, CF, 5-C(*C*F)), 154.2 (d, $^{4}J_{C\text{-}F}$ = 1.77 Hz, C_q, *C*–N=C), 133.2 (d, $^{3}J_{C\text{-}F}$ = 7.60 Hz, C_q, *C*–C–N=C), 116.9 (d, $^{3}J_{C\text{-}F}$ = 7.89 Hz, CH, 7-*C*$_6H_3$F), 115.2 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz, CH, 6-*C*$_6H_3$F), 112.2 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz, CH, 4-*C*$_6H_3$F), 70.9 (d, $^{4}J_{C\text{-}F}$ = 2.17 Hz, CH, 3*H*-indole), 53.8, 51.1 (CH_2, 2,6-N*C*$_5H_{10}$), 49.8 (br, CH_2, 2,6-N*C*$_5H_{10}$), 26.8, 24.8, 24.4 (CH_2, 3,4,5-N*C*$_5H_{10}$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ −124.5 (m, 1F, 5-C*F*) ppm. LIFDI-MS *(m/z)* calculated for [$C_{18}H_{24}FN_3$] = 301.1949; found: 301.1940.

2,3-Dipiperidyl-5-trifluoromethyl-3*H*-indole (6)

3*H*-Indole **6** was prepared according to the general procedure starting from a benzene solution of **1** (30.0 mg, 156 μmol) and 1-azido-4-(trifluoromethyl)benzene (29 mg, 156 μmol). Volatiles were removed under dynamic vacuum and the residue was washed with pentane (7 x 2 mL) to yield **6** as an orange solid (yield: 50.9 mg, 145 μmol, 93%). Crystals suitable for X-ray diffraction were grown by a saturated benzene solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.48 (s, 1H, 4-CH_{Aryl}), 7.42 (d, $^{3}J_{H\text{-}H}$ = 8.28 Hz, 1H, 6-CH_{Aryl}), 7.01 (d, $^{3}J_{H\text{-}H}$ = 8.28 Hz, 1H, 7-CH_{Aryl}), 4.52 (s, 1H, 3-CH_{indole}), 4.11 (d, geminal $^{2}J_{H\text{-}H}$ = 12.4 Hz, 1H, equatorial 2,6-NC$_5H_{10}$ of 2-piperidyl), 4.03 (d, geminal $^{2}J_{H\text{-}H}$ = 12.4 Hz, 1H, equatorial 2,6-NC$_5H_{10}$ of 2-piperidyl), 3.44-3.40 (m, 2H, axial 2,6-NC$_5H_{10}$ of 2-piperidyl), 2.60 (br s, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 2.44 (br s, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 1.80-1.49 (m, 10H, 3,4,5-NC$_5H_{10}$), 1.44-1.37 (m, 2H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 173.5 (C_q, N=*C*), 161.4 (d, $^{2}J_{C\text{-}F}$ = 1.14 Hz, C_q, *C*CF_3), 132.1 (C_q, *C*–N=C), 126.9 (d, $^{3}J_{C\text{-}F}$ = 4.02 Hz, CH, 6-*C*$_7H_3F_3$), 124.7 (C_q, *C*–C–N=C), 121.2 (d, $^{1}J_{C\text{-}F}$ = 95.0 Hz, CF, *C*F_3), 121.0 (d, $^{3}J_{C\text{-}F}$ = 4.02 Hz, CH, 4-*C*$_7H_3F_3$), 115.5 (CH, 7-*C*$_7H_3F_3$), 70.5 (CH, 3*H*-indole), 51.1 (CH_2, 2,6-N*C*$_5H_{10}$), 50.2 (br s, CH_2, 2,6-N*C*$_5H_{10}$), 48.7, 46.8 (CH_2, 2,6-N*C*$_5H_{10}$), 26.9, 24.8, 24.6 (CH_2, 3,4,5-N*C*$_5H_{10}$) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −60.9 (s, 3F, 5-C*F*$_3$) ppm. LIFDI-MS *(m/z)* calculated for [$C_{19}H_{24}F_3N_3$] = 351.1917; found: 351.1903.

2,3-Dipiperidyl-7-fluoro-5-trifluoromethyl-3H-indole (7)

3*H*-Indole **7** was prepared according to the general procedure starting from a benzene solution of **1** (40.0 mg, 208 μmol) and 1-azido-4-fluoro-6-(trifluoromethyl)benzene (36 mg, 208 μmol). Volatiles were removed under dynamic vacuum and the residue was washed with pentane (7 x 2 mL) to afford **7** as a red solid (yield: 69.1 mg, 187 μmol, 90%). Crystals suitable for X-ray diffraction were grown by a saturated benzene solution at room temperature. ^{1}H NMR (C_6D_6): δ 7.28 (dd, $^{3}J_{H\text{-}F}$ = 9.62 Hz, $^{4}J_{H\text{-}H}$ = 2.56 Hz, 1H, 6-CH_{Aryl}), 6.92 (dd, $^{3}J_{H\text{-}F}$ = 7.58 Hz, $^{4}J_{H\text{-}H}$ = 2.56 Hz, 1H, 4-CH_{Aryl}), 4.14 (br s, 1H, equatorial 2,6-NC$_5H_{10}$), 3.69 (s, 1H, 3-CH_{indole}), 3.51 (br s, 1H, equatorial 2,6-NC$_5H_{10}$), 3.19 (br s, 1H, axial 2,6-NC$_5H_{10}$), 2.89 (br s, 1H, axial 2,6-NC$_5H_{10}$), 2.27-2.23 (m, 2H, 2,6-NC$_5H_{10}$), 1.95 (br s, 2H, 2,6-NC$_5H_{10}$), 1.32-1.04 (m, 12H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 172.2 (d, $^{5}J_{C\text{-}F}$ = 1.58 Hz, C_q, N=*C*), 156.7 (d, $^{1}J_{C\text{-}F}$ = 238.4 Hz, CF, 5-*C*$_6H_2F(CF_3)$), 152.4 (C_q, *C*–N=C), 135.3 (d, $^{3}J_{C\text{-}F}$ = 7.28 Hz, C_q, *C*–C–N=C), 124.7 (d, $^{2}J_{C\text{-}F}$ = 272.7 Hz, C_q, *C*CF_3), 117.3 (d, $^{1}J_{C\text{-}F}$ = 32.3 Hz, CF, *C*F_3), 115.3 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz, CH, 4- *C*$_6H_2F(CF_3)$), 112.2 (d, $^{2}J_{C\text{-}F}$ = 25.7 Hz, CH, 6-*C*$_6H_2F(CF_3)$), 69.9 (d, $^{4}J_{C\text{-}F}$ = 2.10 Hz, CH, 3*H*-indole), 53.3, 49.7, 47.9, 46.5 (CH_2, 2,6-N*C*$_5H_{10}$), 26.9, 24.5, 24.3 (CH_2, 3,4,5-N*C*$_5H_{10}$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ –60.8 (s, 3F, 7-C*F*$_3$), –124.2 (t, $^{5}J_{F\text{-}F}$ = 8.39 Hz, 1F, 5-C*F*) ppm. LIFDI-MS *(m/z)* calculated for [$C_{19}H_{23}F_4N_3$] = 369.1813; found: 369.1823.

2,3-Dipiperidyl-5-cyano-3*H*-indole (8)

3*H*-Indole **8** was prepared according to the general procedure starting from **1** (40.0 mg, 208 μmol) and 1-azido-4-cyanobenzene (30.0 mg, 208 μmol) in benzene. Volatiles were removed under reduced pressure and the residue was washed with pentane (7 x 2 mL) to afford **8** as a red solid (yield: 44.9 mg, 145 μmol, 70%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated pentane solution at –30 °C. ^{1}H NMR (C_6D_6): δ 7.27-7.26 (m, 1H, 4-CH_{Aryl}), 7.21 (dd, $^{3}J_{H\text{-}H}$ = 8.17 Hz, $^{4}J_{H\text{-}H}$ = 1.66 Hz, 1H, 6-CH_{Aryl}), 7.08 (d, $^{3}J_{H\text{-}H}$ = 8.17 Hz, 1H, 7-CH_{Aryl}), 4.10 (d, geminal $^{2}J_{H\text{-}H}$ = 12.53 Hz, 1H, equatorial 2,6-NC$_5H_{10}$ of 2-piperidyl), 3.73 (s, 1H, 3-CH_{indole}), 3.52 (d, geminal $^{2}J_{H\text{-}H}$ = 12.53 Hz, 1H, equatorial 2,6-NC$_5H_{10}$ of 2-piperidyl), 3.27-3.17 (m, 1H, axial 2,6-NC$_5H_{10}$ of 2-piperidyl), 2.97-2.89 (m, 1H, axial 2,6-NC$_5H_{10}$ of 2-piperidyl), 2.26-2.16 (m, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 1.95 (br s, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 1.35-1.04 (m, 12H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 173.3 (C_q, N=*C*), 162.4 (C_q, *C*–N=C), 134.6 (CH, 6-*C*$_6H_3$(CN)), 132.2 (C_q, *C*–C–N=C), 127.1 (CH, 4-*C*$_6H_3$(CN)), 120.7 (C_q, N≡*C*), 116.9 (CH, 7-*C*$_6H_3$(CN)), 102.7 (C_q, *C*(CN)), 69.9 (CH, 3*H*-indole), 53.8, 50.6, 48.0, 46.6 (CH_2, 2,6-N*C*$_5H_{10}$), 26.7, 24.5, 24.1 (CH_2, 3,4,5-N*C*$_5H_{10}$) ppm. LIFDI-MS *(m/z)* calculated for [$C_{19}H_{24}N_4$] = 308.1995; found: 308.1984.

2,3-Dipiperidyl-5-nitro-3*H*-indole (9)

3*H*-Indole **9** was prepared according to the general procedure starting from **1** (40.0 mg, 208 μmol) and 1-azido-4-nitrobenzene (34.0 mg, 208 μmol) in benzene. The reaction solution was heated at 80 °C for 16 h, whereupon a red colouration developed. After cooling the reaction solution to room temperature, a beige solid formed, which was washed with pentane (2 x 2 mL). Compound **9** was obtained in analytically pure form (49.9 mg, 151.8 μmol, 73%) and crystals suitable for X-ray diffraction were grown from a saturated benzene solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 8.13-8.10 (m, 2H, 4,6-CH_{Aryl}), 6.95 (d, $^{3}J_{H-H}$ = 9.32 Hz, 1H, 7-CH_{Aryl}), 4.55 (s, 1H, 3-CH_{indole}), 4.19-4.10 (m, 1H, equatorial 2,6-NC$_5H_{10}$ of 2-piperidyl), 4.10-4.01 (m, 1H, equatorial 2,6-NC$_5H_{10}$ of 2-piperidyl), 3.55-3.38 (m, 2H, axial 2,6-NC$_5H_{10}$ of 2-piperidyl), 2.62 (br s, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 2.48 (br s, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 1.84-1.48 (m, 10H, 3,4,5-NC$_5H_{10}$), 1.46-1.34 (m, 2H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 175.3 (C_q, N=*C*), 165.1 (C_q, *C*–N=C), 140.9 (C_q, *C*(NO_2)) 131.8 (C_q, *C*–C–N=C), 127.1, 119.9 (CH, 4,6-*C*$_6H_3$(NO_2)), 114.9 (CH, 7-*C*$_6H_3$(NO_2)), 70.1 (CH, 3*H*-indole), 48.9, 47.3 (CH_2, 2,6-N*C*$_5H_{10}$), 27.1, 26.9, 26.2, 24.7, 24.5 (CH_2, 3,4,5-N*C*$_5H_{10}$) ppm. LIFDI-MS *(m/z)* calculated for [$C_{18}H_{24}N_4O_2$] = 328.1894; found: 328.1882.

2,3-Dipiperidyl-5-methoxy-3*H*-indole (10)

3*H*-Indole **10** was prepared according to the general procedure starting from a benzene solution of **1** (40.0 mg, 208 μmol) and 1-azido-4-methoxybenzene (31 mg, 208 μmol). Volatiles were removed under dynamic vacuum and the residue was washed with pentane (7 x 2 mL) to afford **10** as an amorphous beige solid (yield: 44.4 mg, 141 μmol, 68%). Crystals suitable for X-ray diffraction were grown by a saturated toluene solution at –30 °C. ^{1}H NMR (C_6D_6): δ 7.59 (d, $^{3}J_{H-H}$ = 9.07 Hz, 1H, 7-CH_{Aryl}), 6.68 (d, $^{3}J_{H-H}$ = 9.07 Hz, 2H, 4,6-CH_{Aryl}), 3.47 (s, 1H, 3-CH_{indole}), 3.29 (t, geminal $^{2}J_{H-H}$ = 5.34 Hz, 4H, 2,6-NC$_5H_{10}$ of 2-piperidyl), 3.22 (s, 3H, OCH_3), 2.88 (t, geminal $^{2}J_{H-H}$ = 5.34 Hz, 4H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 1,66-1.58 (m, 4H, 3,4,5-NC$_5H_{10}$), 1.47-1.41 (m, 2H, 3,4,5-NC$_5H_{10}$), 1.35-1,27 (m, 6H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 159.7 (C_q, N=*C*), 148.4 (C_q, *C*–N=C), 135.9 (C_q, *C*(OCH_3)), 131.4 (C_q, *C*–C–N=C), 125.6 (CH, 7-*C*$_6H_3$(OCH_3)), 114.3 (CH, 4,6-*C*$_6H_3$(OCH_3)), 71.1 (CH, 3*H*-indole), 54.9 (CH_3, O*C*H_3), 54.2, 51.4 (CH_2, 2,6-N*C*$_5H_{10}$), 26.9, 26.6, 26.3, 24.9, 24.6, 24.2 (CH_2, 3,4,5-N*C*$_5H_{10}$) ppm. LIFDI-MS *(m/z)* calculated for [$C_{19}H_{27}N_3O$] = 313.2149; found: 313.2142.

2,3-Dipiperidyl-5-dimethylamino-3*H*-indole (11)

To a toluene solution of **1** (30 mg, 156 μmol) was added a toluene solution of 1-azido-4-(dimethylamino)benzene (25 mg, 156 μmol). The reaction solution was heated at 100 °C for 16 h, upon which a red colouration developed. All volatiles were removed in vacuo and the residue was washed with pentane (7 x 2 mL) to obtain compound **11** as an orange solid (yield: 42.3 mg, 129 μmol,

83%). Single crystals of **11** suitable for X-ray structural analysis were obtained from a saturated benzene solution at room temperature within two days. ^{1}H NMR (C_6D_6): δ 7.47 (d, $^{3}J_{H\text{-}H}$ = 8.34 Hz, 7-CH_{Aryl}), 6.99 (d, $^{4}J_{H\text{-}H}$ = 2.53 Hz, 1H, 4-CH_{Aryl}), 6.68 (dd, $^{3}J_{H\text{-}H}$ = 8.34 Hz, $^{4}J_{H\text{-}H}$ = 2.53 Hz, 1H, 6-CH_{Aryl}), 4.19 (s, 1H, 3-CH_{indole}), 3.79-3.48 (m, 4H, 2,6-NC$_5H_{10}$ of 2-piperidyl), 2.73-2.69 (m, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 2.68 (s, 6H, N(CH_3)$_2$), 2.35-2.28 (m, 2H, 2,6-NC$_5H_{10}$ of 3-piperidyl), 1.53-1.28 (m, 12H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 169.9 (C_q, N=*C*), 150.0 (C_q, *C*–N=C), 146.5 (C_q, *C*(N(CH$_3$)$_2$)), 133.0 (C_q, *C*–C–N=C), 117.2 (CH, 7-*C*$_6$H$_3$(N(CH$_3$)$_2$)), 114.6 (CH, 6-*C*$_6$H$_3$(N(CH$_3$)$_2$)), 112.2 (CH, 4-*C*$_6$H$_3$(N(CH$_3$)$_2$)), 71.3 (CH, 3*H*-indole), 50.1, 47.3 (br, CH_2, 2,6-NC$_5$H$_{10}$), 42.2 (CH_3, N(*C*H$_3$)$_2$), 27.0, 24.9, 24.7 (CH_2, 3,4,5-NC$_5$H$_{10}$) ppm. LIFDI-MS *(m/z)* calculated for [$C_{20}H_{30}N_4$] = 326.2465; found: 326.2464.

1-(4-Dimethylaminophenyl)-4,5-dipiperidyl-1,2,3-triazole (12)

A benzene solution (6 mL) of **1** (100 mg, 520 μmol) was added to a benzene solution of 1-azido-4-(dimethylamino)benzene (84.0 mg, 520 μmol) at room temperature. The solution was stirred for 16 h at 60 °C upon which a colour change to orange was observed. The solvent was removed under dynamic vacuum. The residue was washed three times with pentane (3 x 3 mL) and dried under reduced pressure to afford **12** as a beige solid (yield: 128 mg, 364 μmol, 70%). Single crystals suitable for X-ray structural analysis were obtained from a THF/pentane mixture at –30 °C. ^{1}H NMR (C_6D_6): δ 7.62 (d, $^{3}J_{H\text{-}H}$ = 9.22 Hz, 2H, 2,6-CH_{Aryl}), 6.44 (d, $^{3}J_{H\text{-}H}$ = 9.22 Hz, 2H, 3,5-CH_{Aryl}), 3.32 (t, $^{3}J_{H\text{-}H}$ = 5.36 Hz, 4H, equatorial 2,6-NC$_5H_{10}$ of 4,5-dipiperidyl), 2.95 2.95 (t, $^{3}J_{H\text{-}H}$ = 5.36 Hz, 4H, axial 2,6-NC$_5H_{10}$ of 4,5-dipiperidyl), 2.42 (s, 6H, N(CH_3)$_2$), 1.67-1.59 (m, 4H, 3,4,5-NC$_5H_{10}$), 1.49-1.39 (m, 2H, 3,4,5-NC$_5H_{10}$), 1.39-1.31 (m, 4H, 3,4,5-NC$_5H_{10}$), 1.28-1.21 (m, 2H, 3,4,5-NC$_5H_{10}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 150.3 (C_q, 4-*C*(N(CH$_3$)$_2$)), 148.2 (C_q, 1-*C*$_6$H$_4$(N(CH$_3$)$_2$)), 135.8 (Cq, C···C$_{triazole}$), 125.4, 112.2 (CH, 2,3,5,6-*C*$_6$H$_4$(N(CH$_3$)$_2$)), 54.1, 51.4 (CH_2, 2,6-N*C*$_5$H$_{10}$), 39.9 (CH_3, N(*C*H$_3$)$_2$), 26.7, 26.5, 24.7, 24.3 (CH_2, 3,4,5-N*C*$_5$H$_{10}$) ppm. LIFDI-MS *(m/z)* calculated for [$C_{20}H_{30}N_6$] = 354.2526; found: 354.2529.

2. NMR Spectra

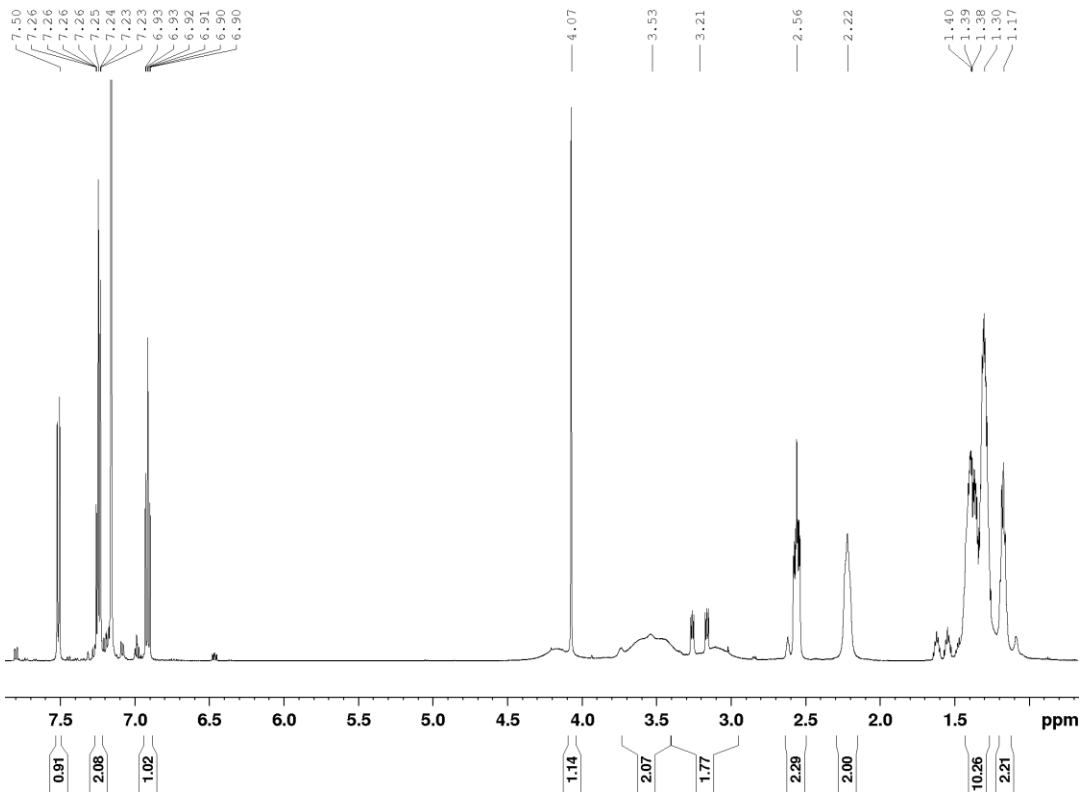


Figure S1. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **2**.

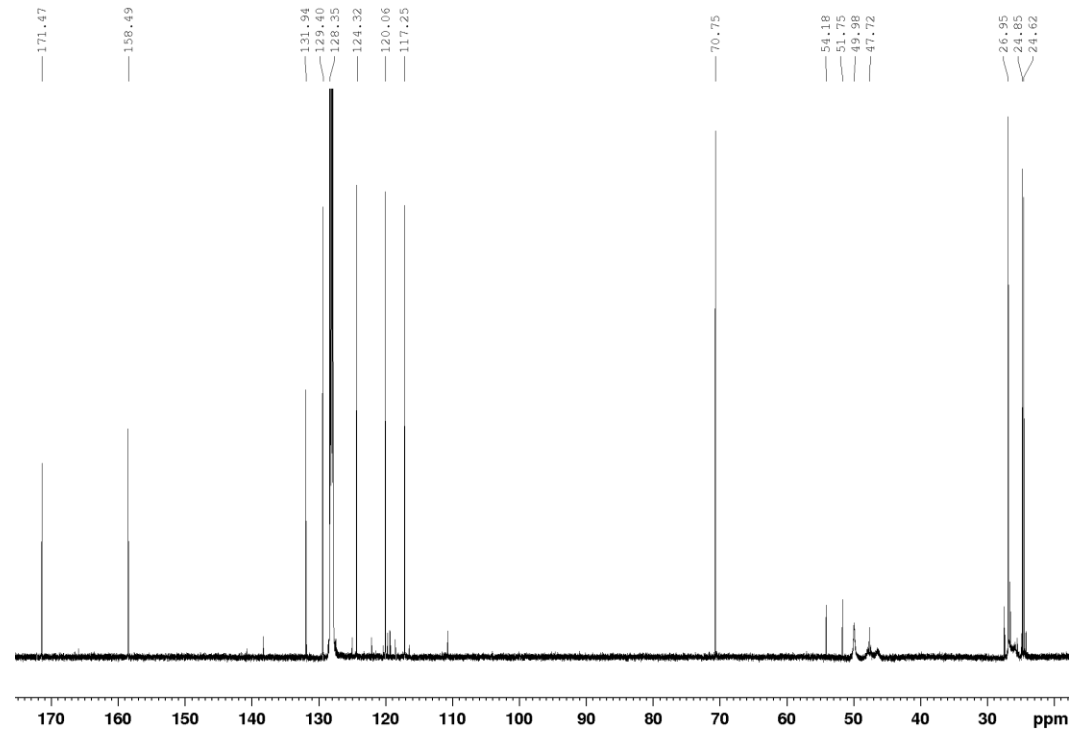


Figure S2. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6) spectrum of **2**.

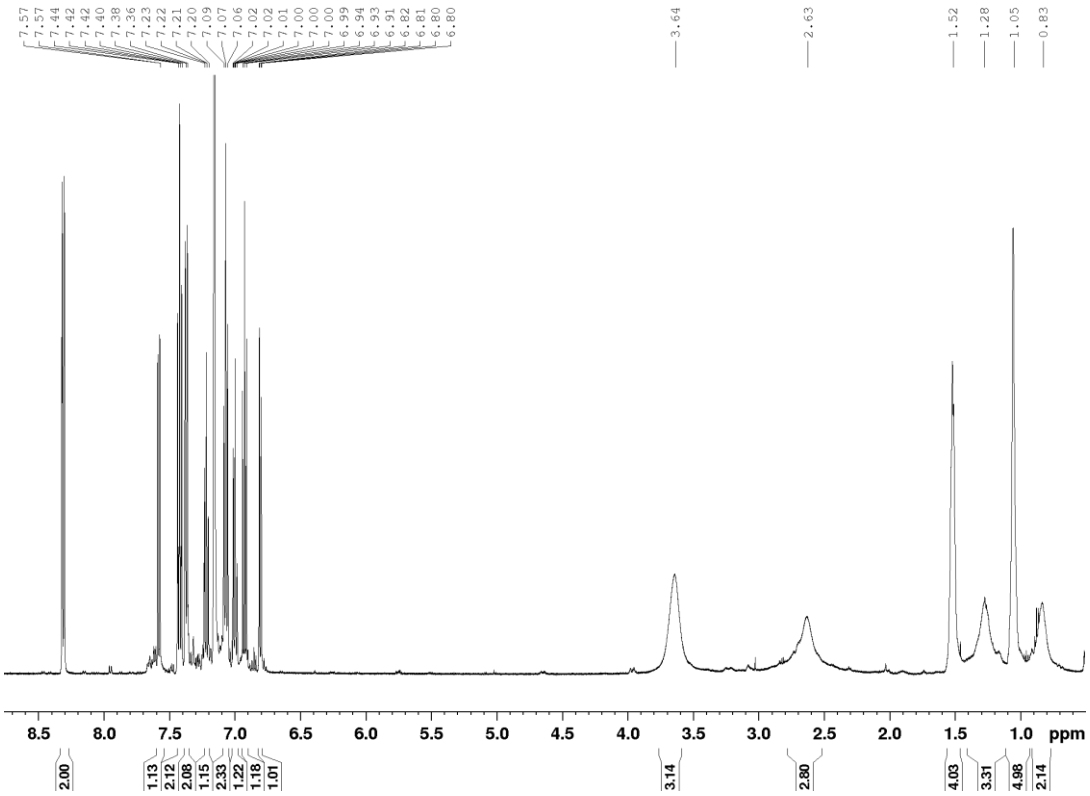


Figure S3a. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **3**.

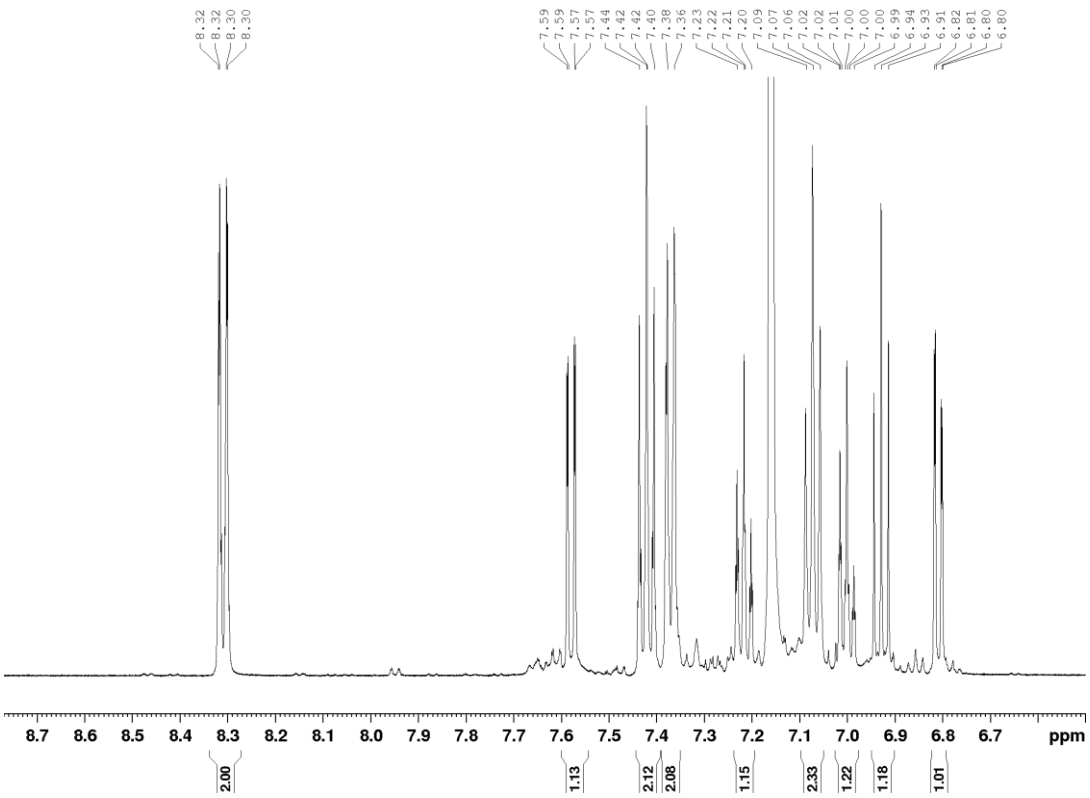


Figure S3b. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **3** in the range of 8.77 to 6.50 ppm.

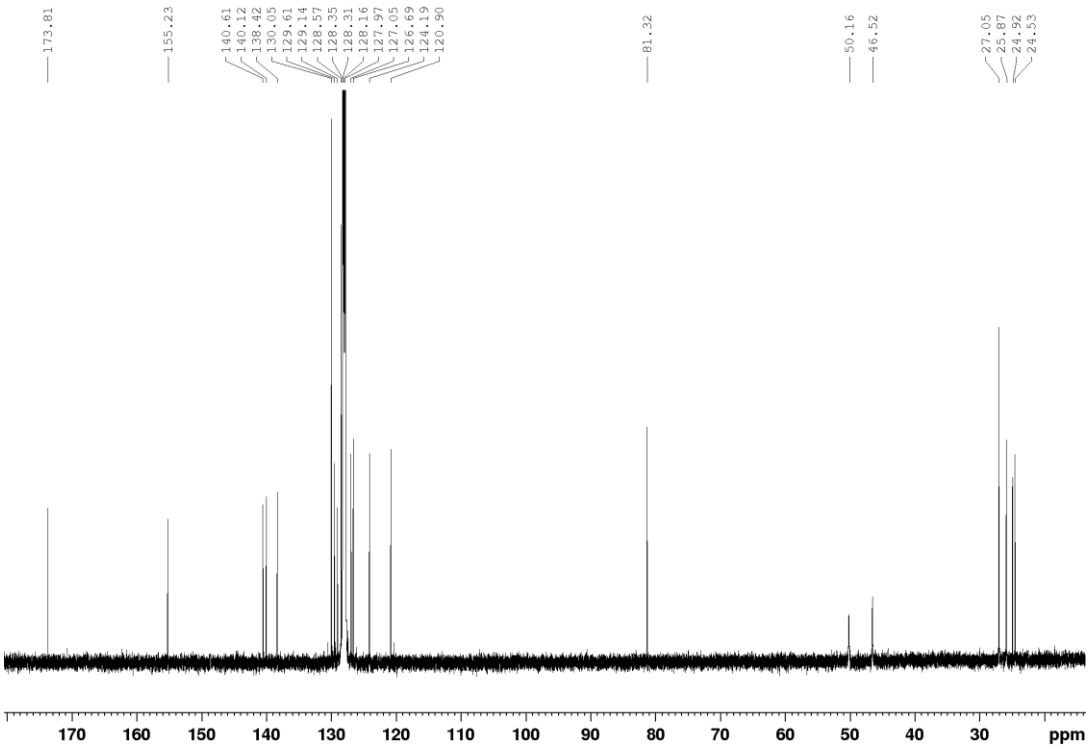


Figure S4. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6) spectrum of **3**.

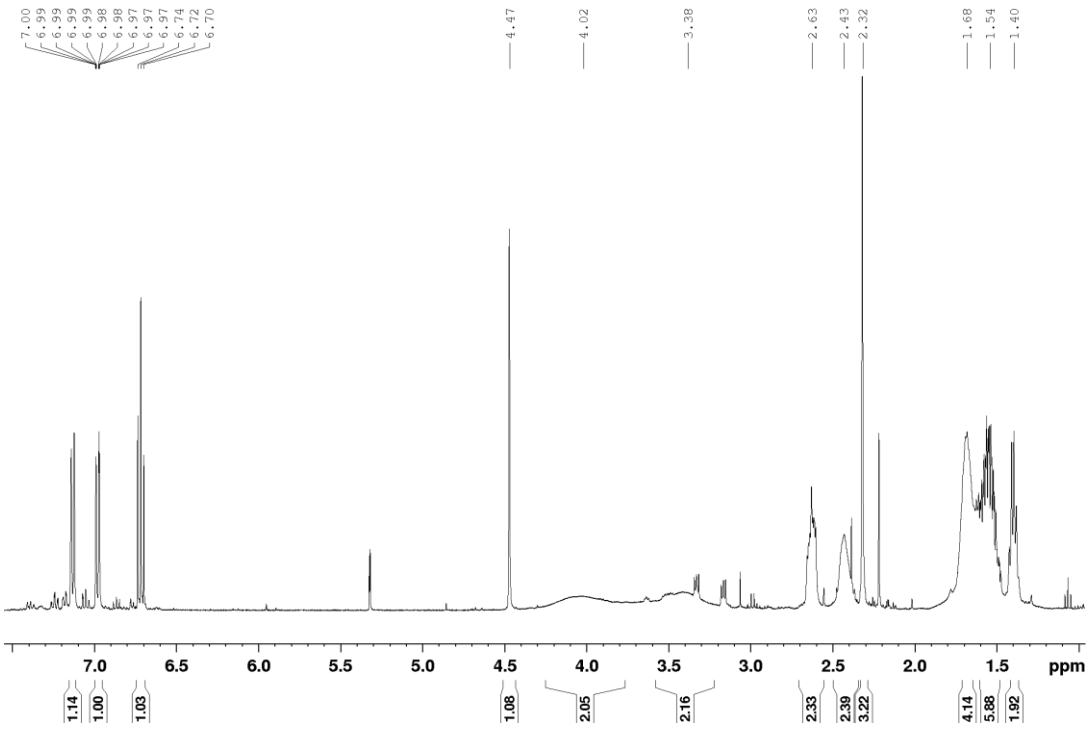


Figure S5. ^{1}H NMR (400.6 MHz, CD_2Cl_2) spectrum of **4**.

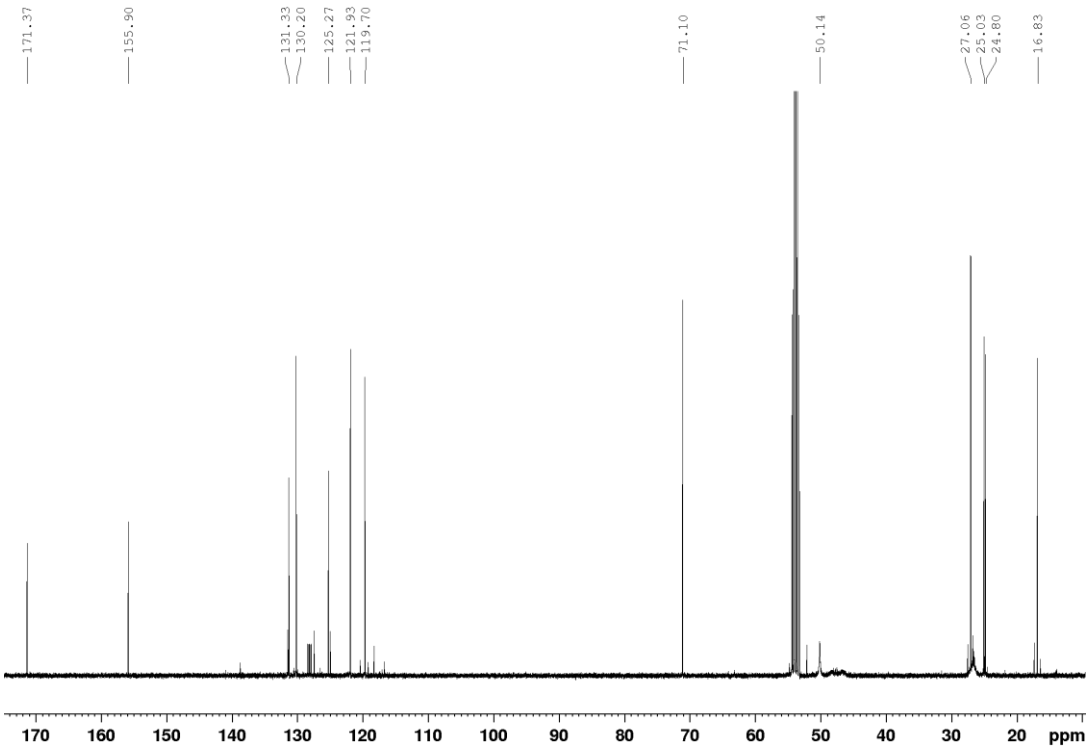


Figure S6. $^{13}C\{^{1}H\}$ NMR (100.7 MHz, CD_2Cl_2) spectrum of **4**.

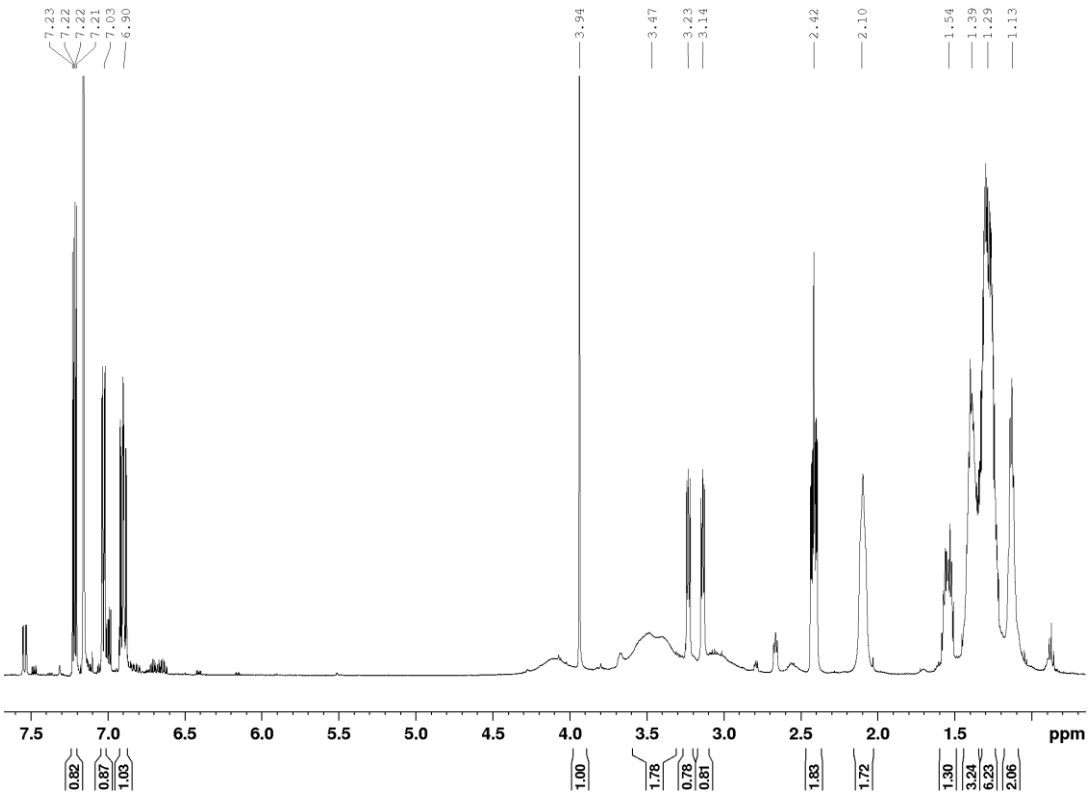


Figure S7. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **5**.

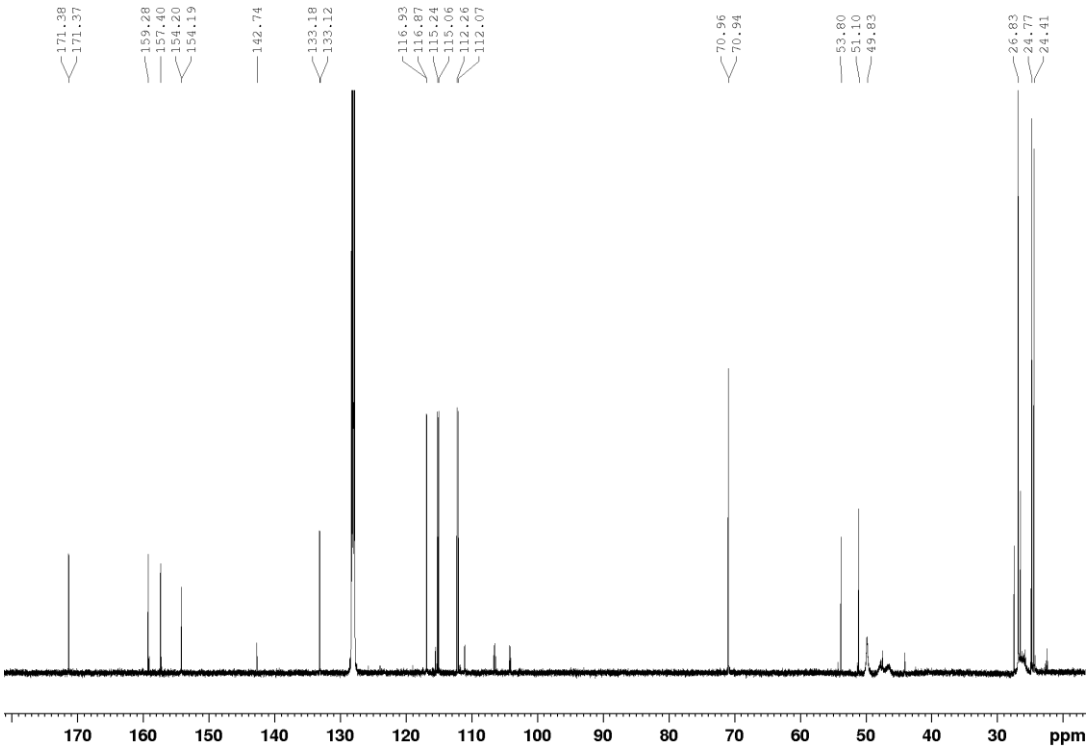


Figure S8. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6) spectrum of **5.**

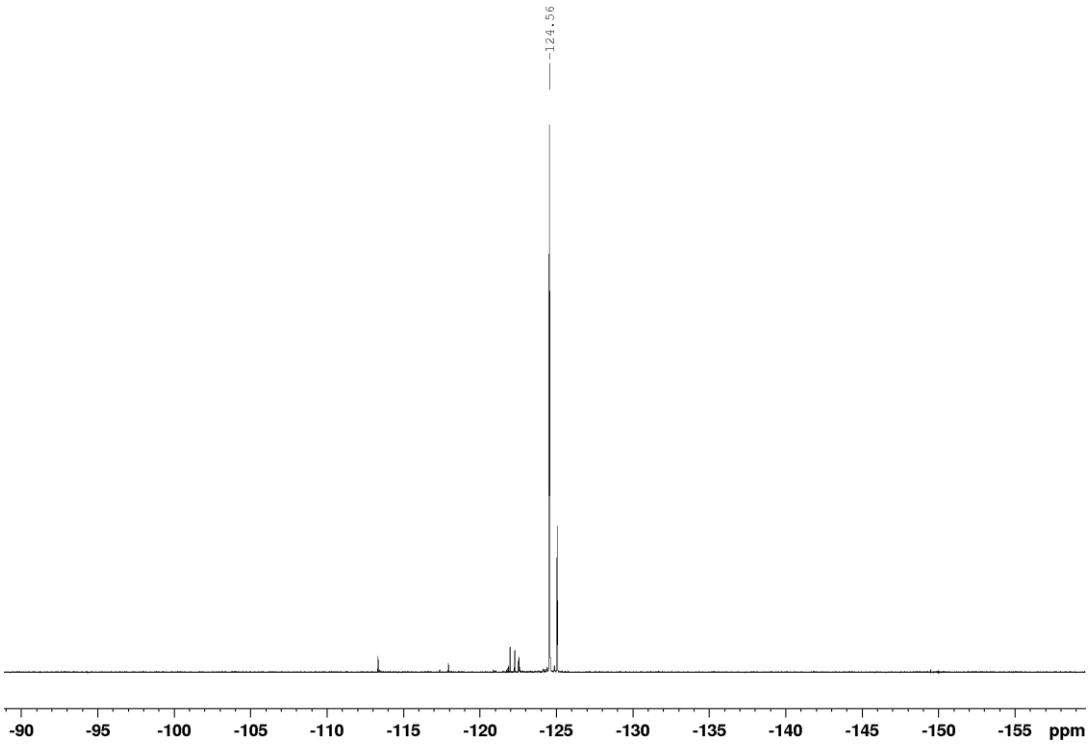


Figure S9. $^{19}F\{^{1}H\}$ NMR (470.6 MHz, C_6D_6) spectrum of **5**.

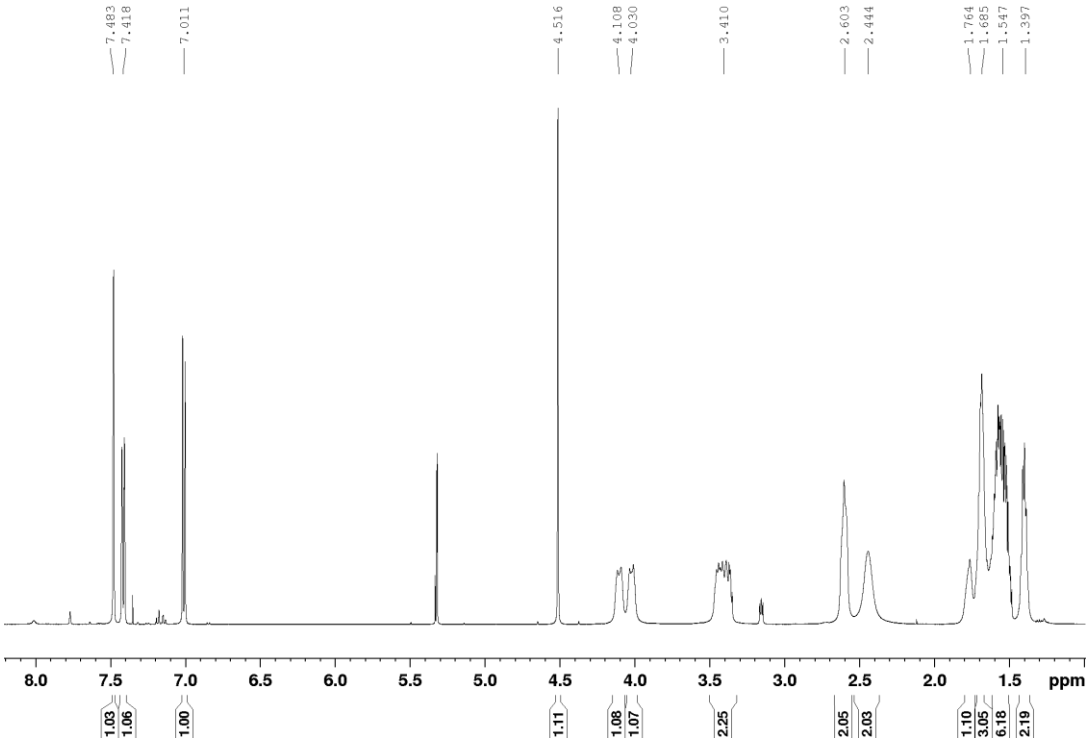


Figure S10. ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum of **6**.

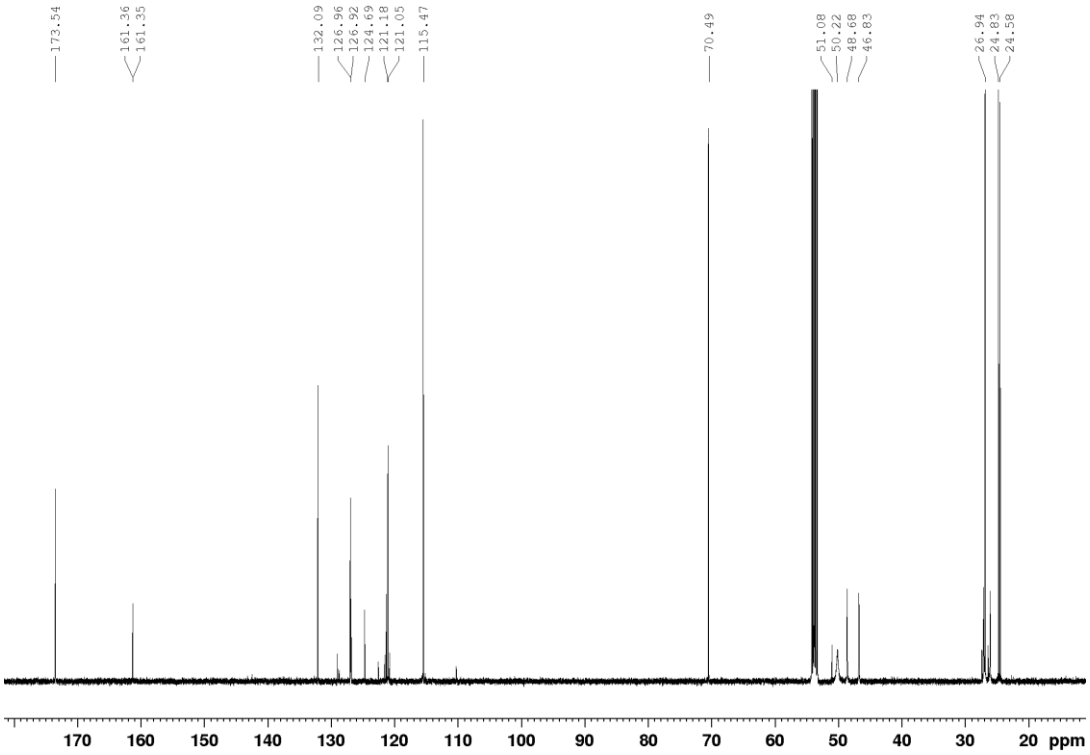


Figure S11. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2) spectrum of **6**.

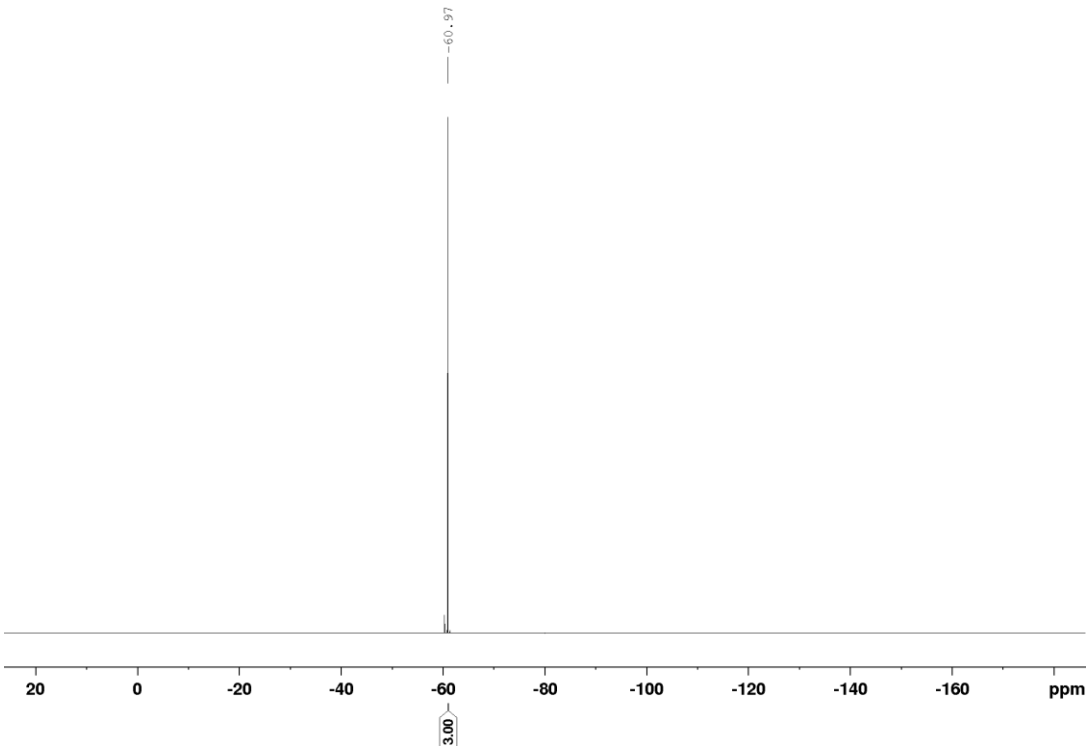


Figure S12. ^{19}F NMR (470.6 MHz, CD_2Cl_2) spectrum of **6**.

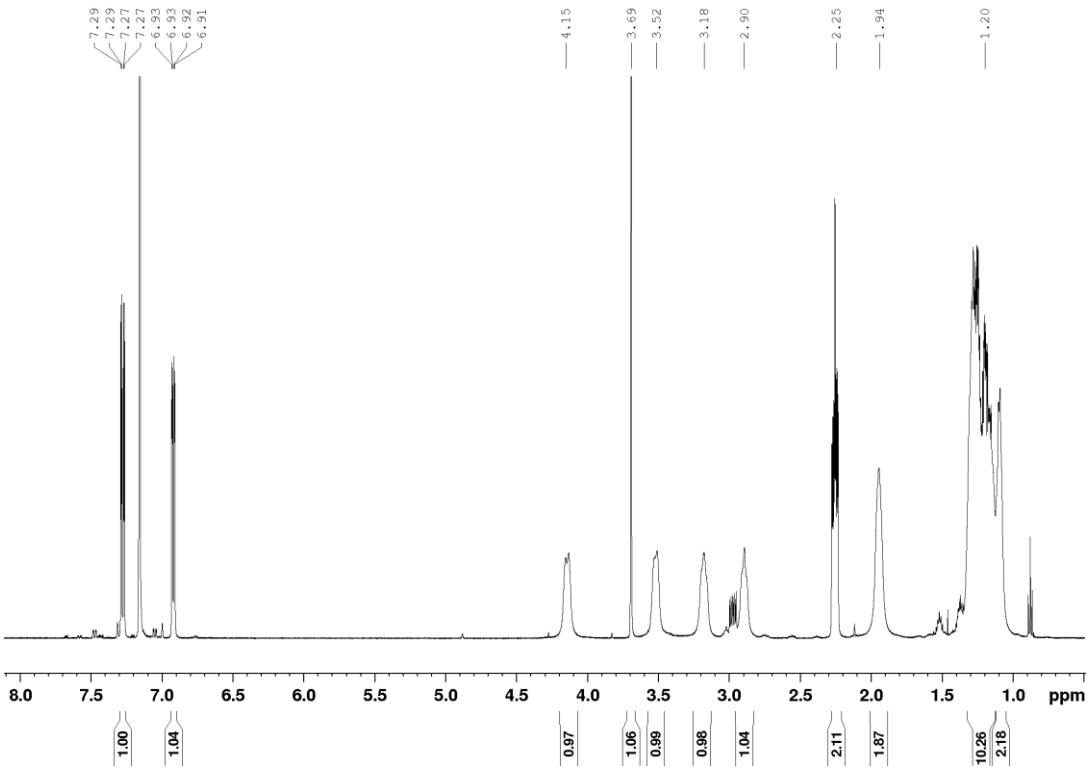


Figure S13. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **7**.

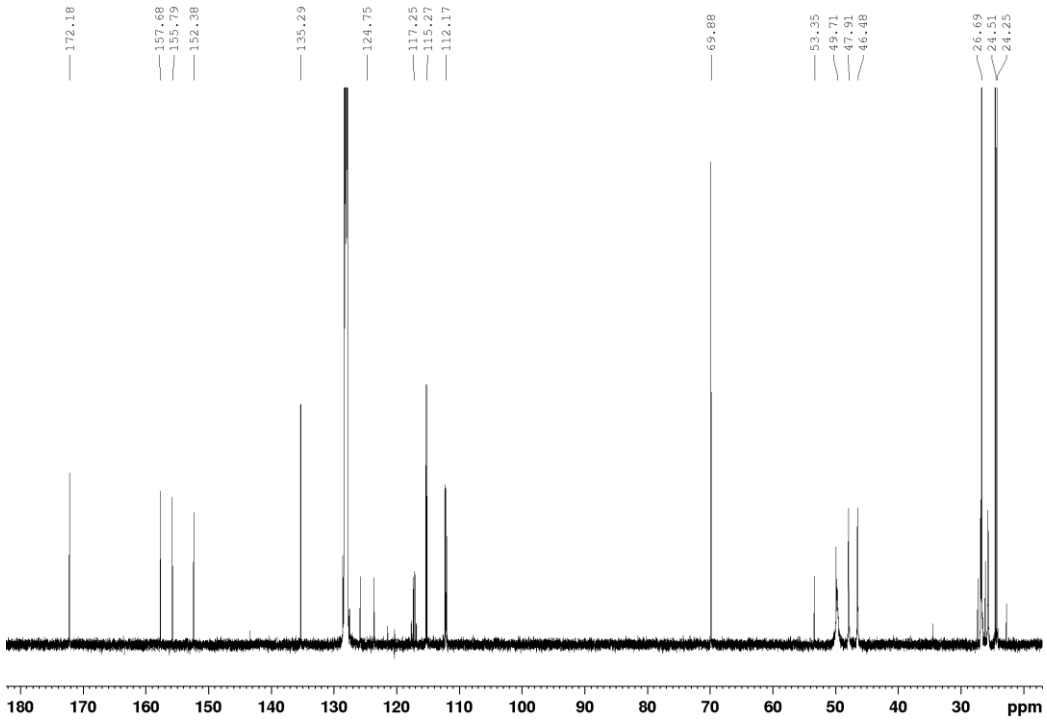


Figure S14. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6) spectrum of **7**.

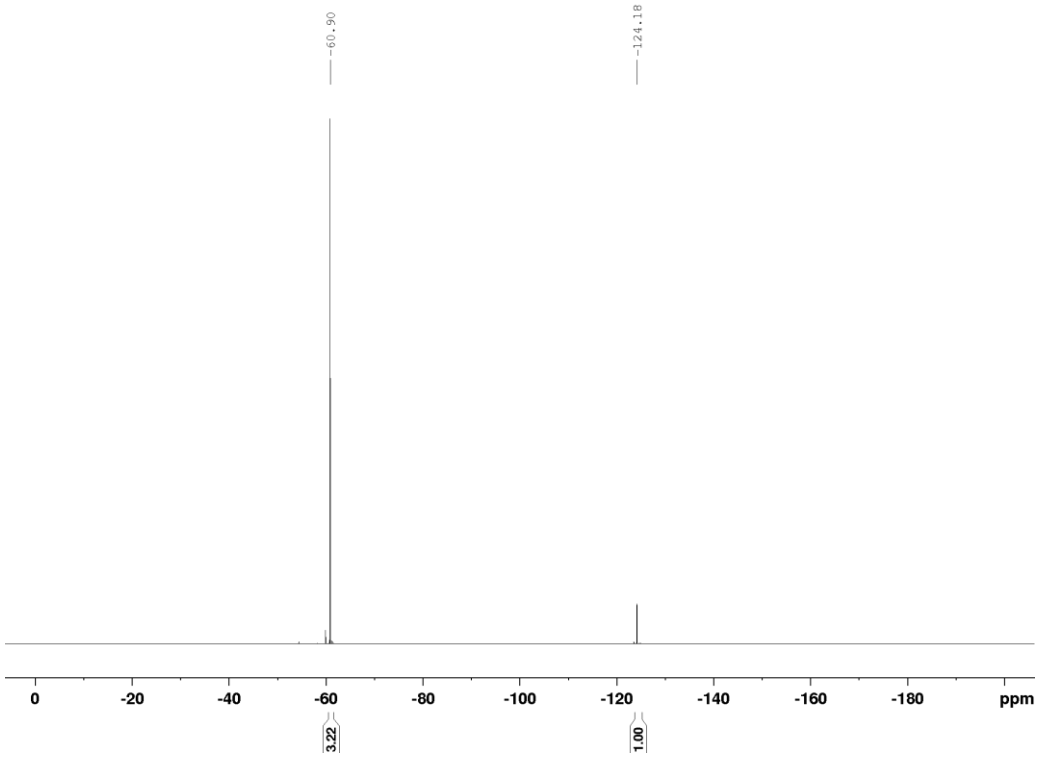


Figure S15. ^{19}F NMR (470.6 MHz, C_6D_6) spectrum of **7** (2,3-dipiperidyl-5-fluor-7-trifluormethyl-3*H*-indole).

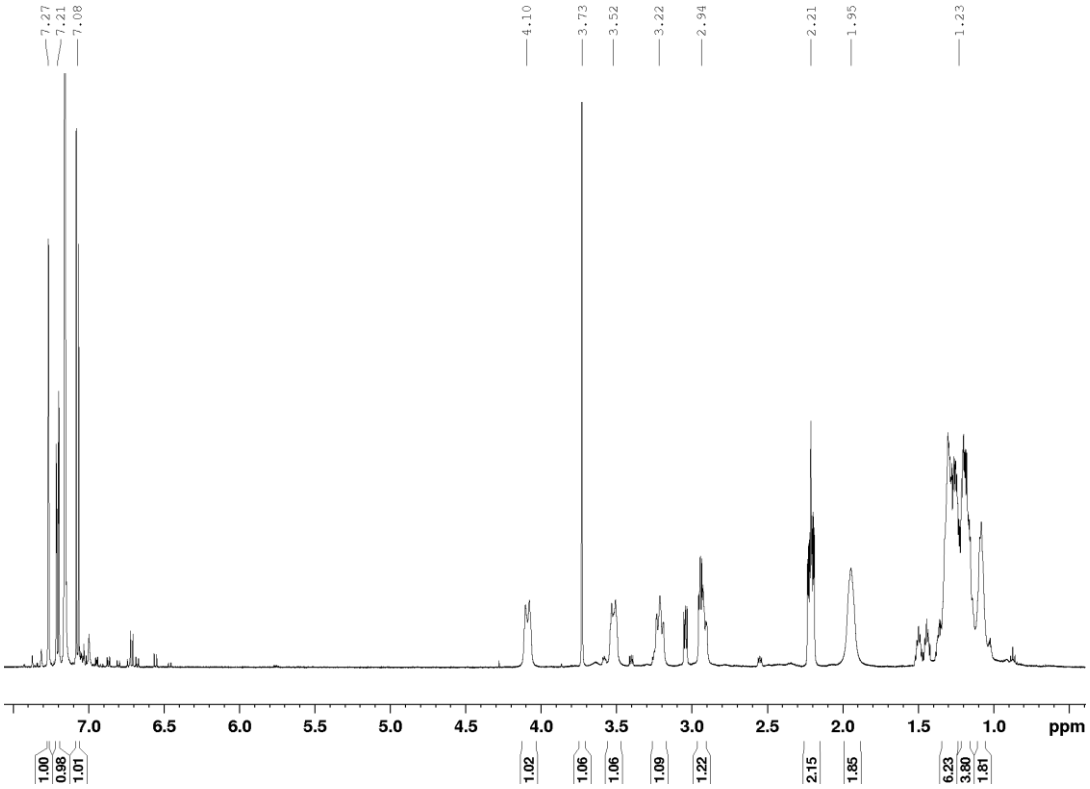


Figure S16. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **8**.

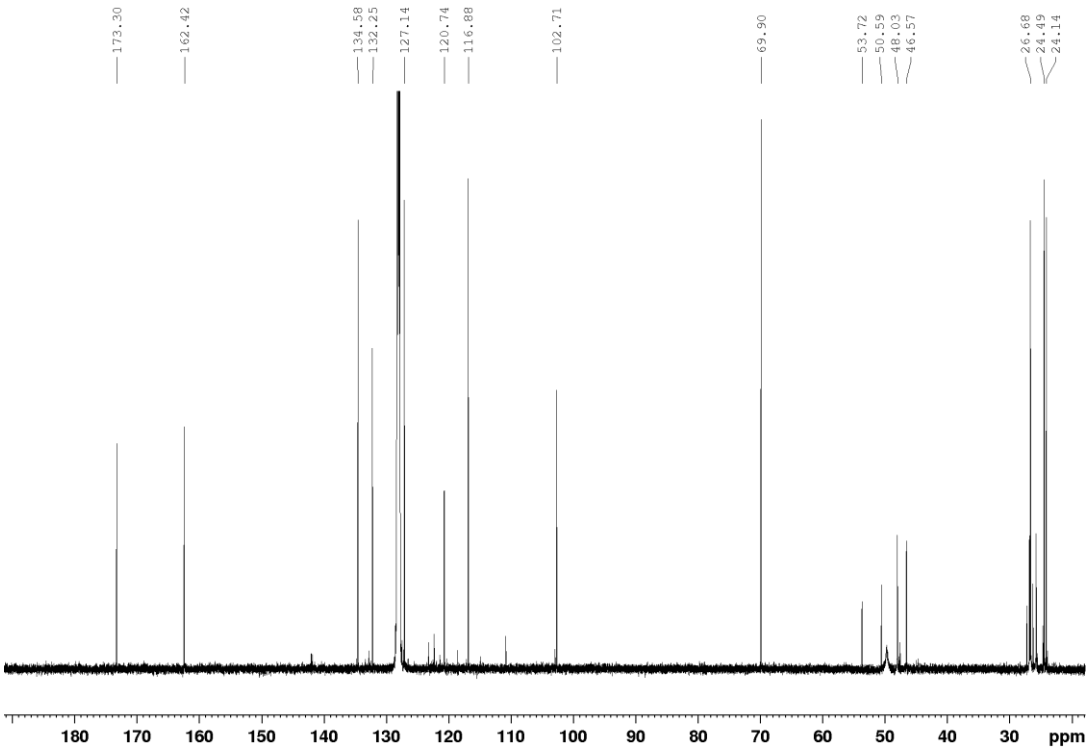


Figure S17. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6) spectrum of **8**.

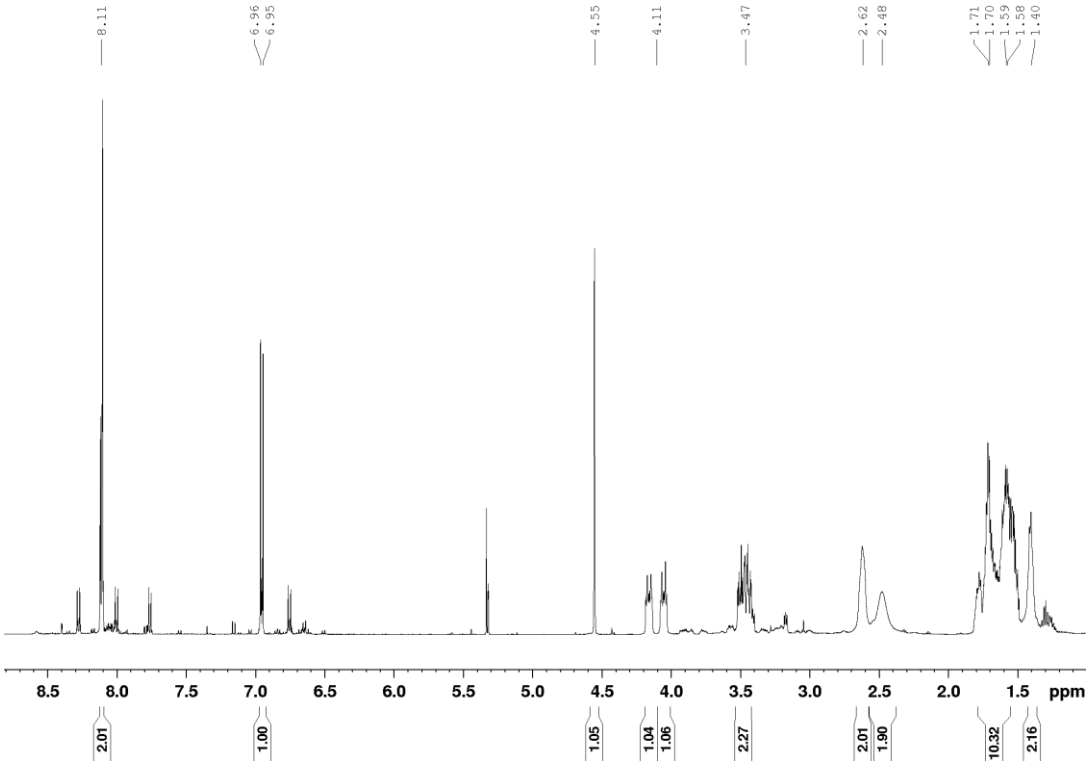


Figure S18. ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum of **9**.

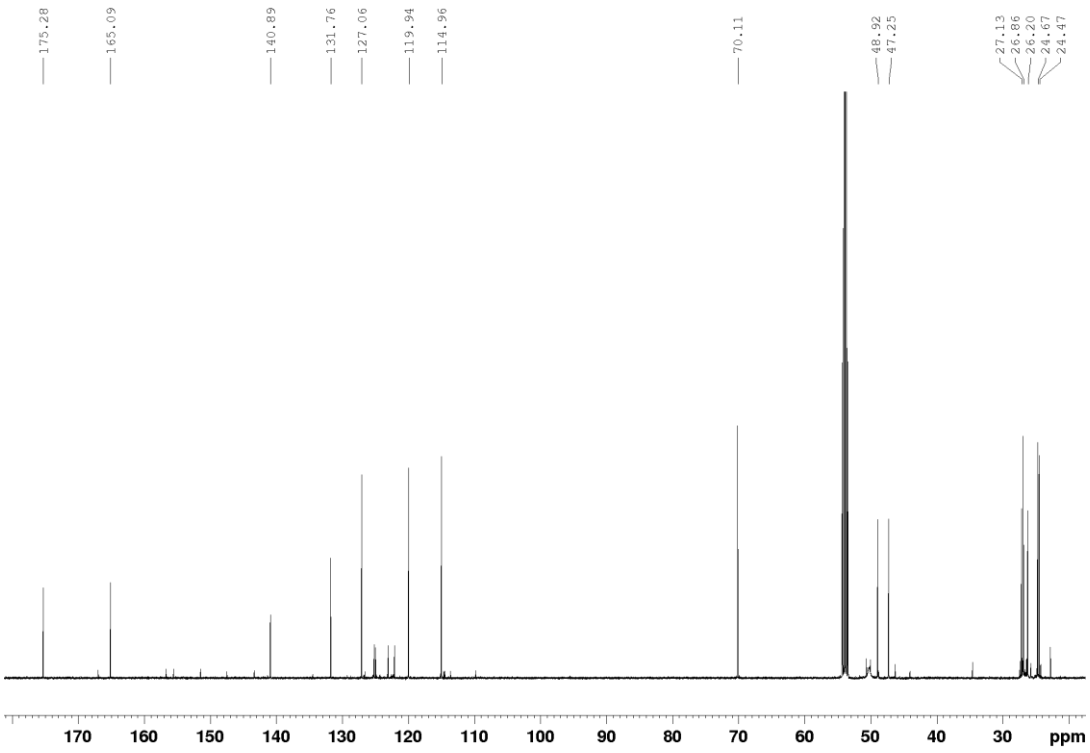


Figure S19. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2) spectrum of **9**.

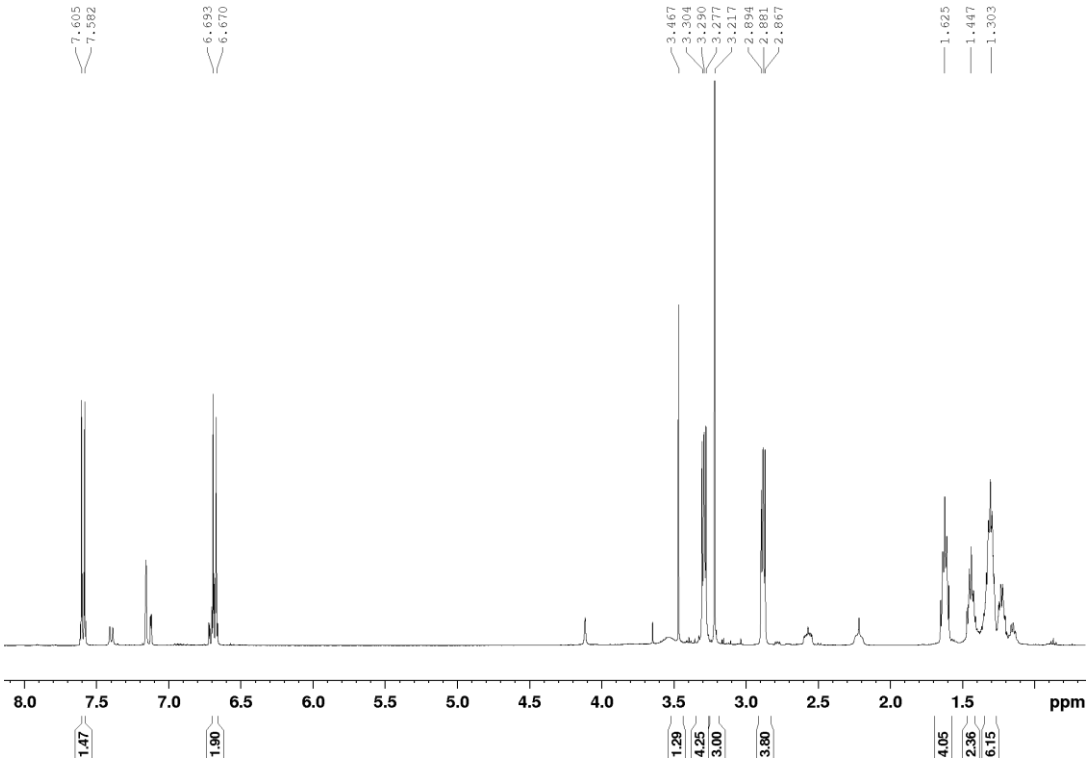


Figure S20. ^{1}H NMR (400.3 MHz, C_6D_6) spectrum of **10**.

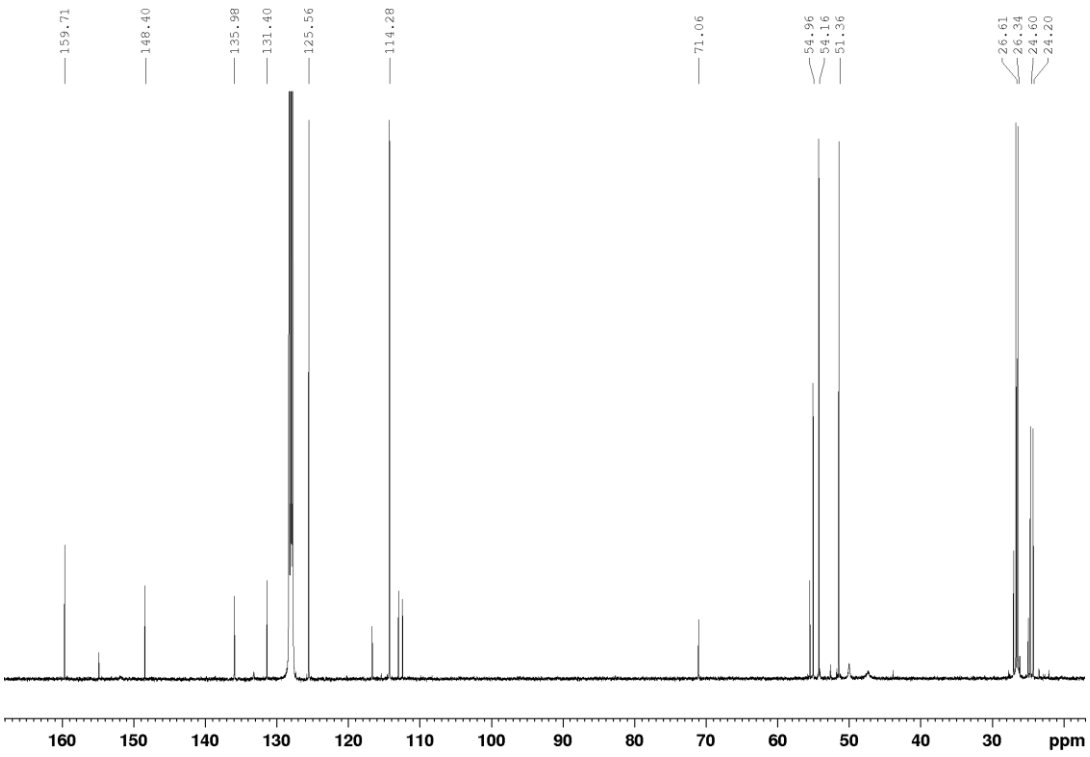


Figure S21. $^{13}C\{^{1}H\}$ NMR (100.7 MHz, C_6D_6) spectrum of **10**.

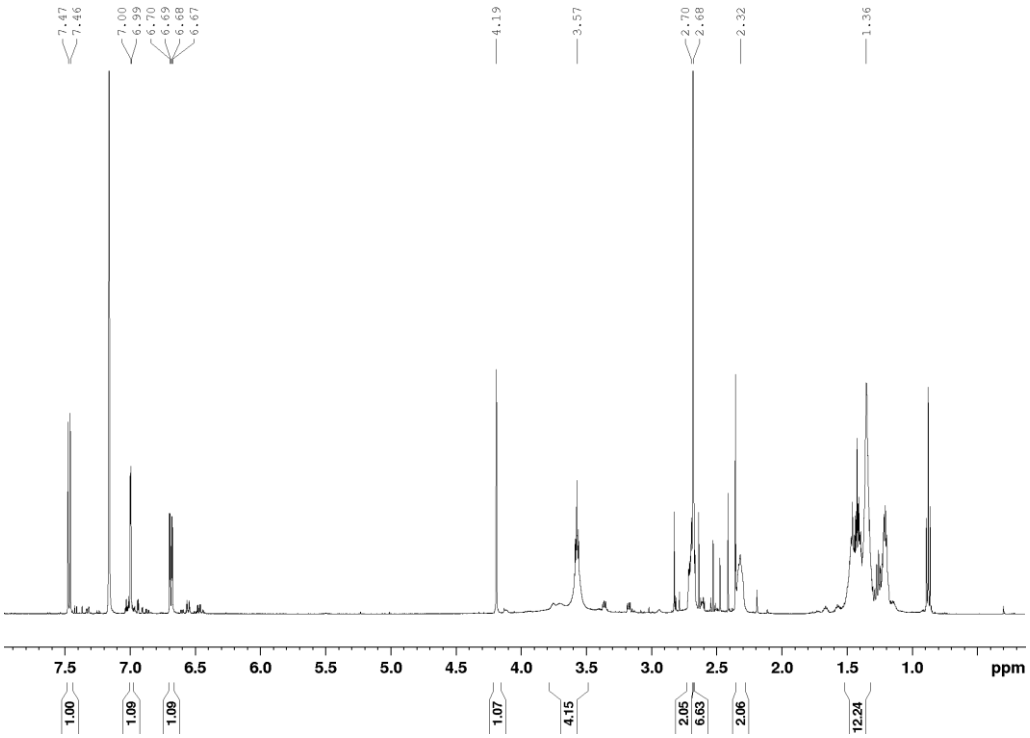


Figure S22. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **11**. The triplet at 0.87 ppm and the corresponding multiplet at 1.23 ppm are due to residual pentane.

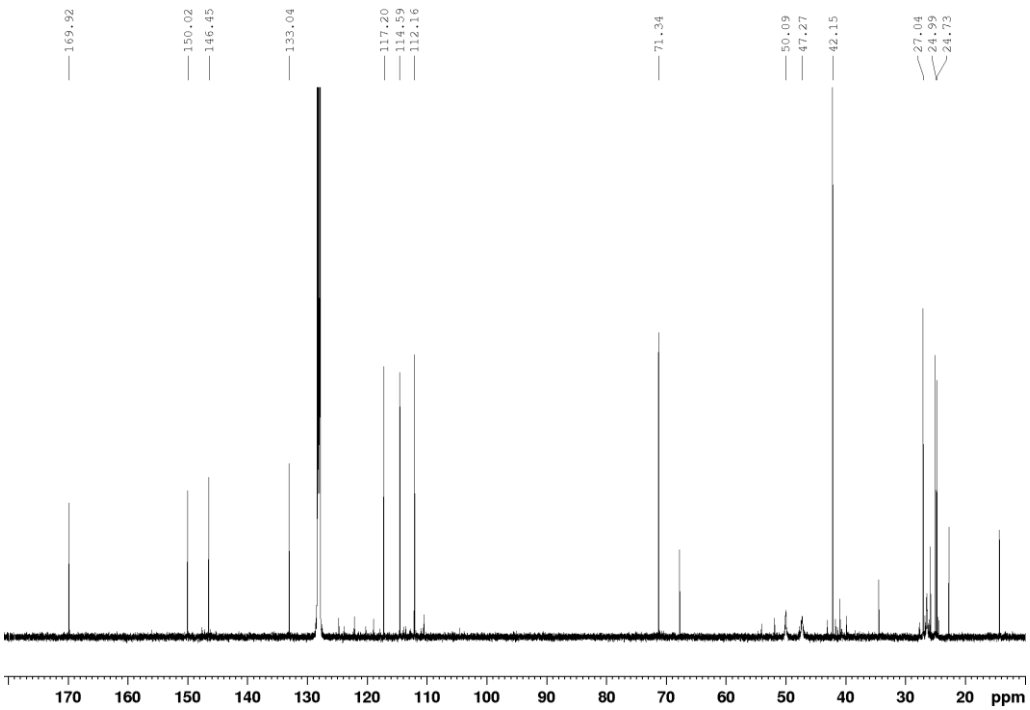


Figure S23. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6) spectrum of **11**. The singlets at 34.45, 22.72 and 14.10 ppm are due to residual pentane.

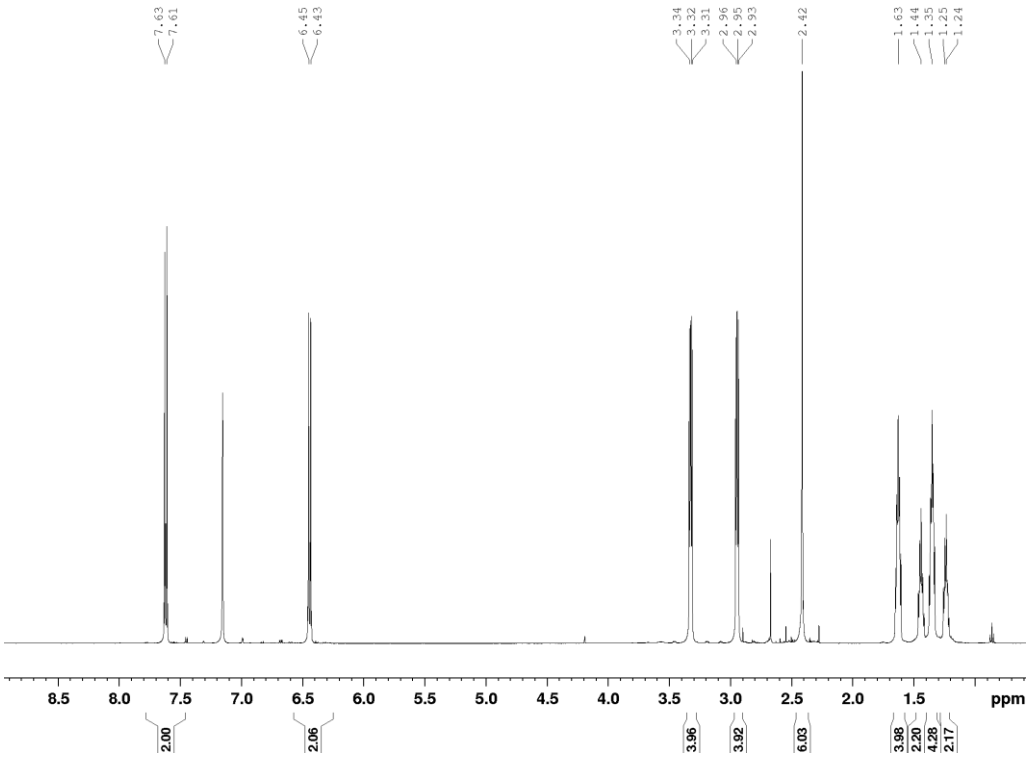


Figure S24. ^{1}H NMR (500.1 MHz, C_6D_6) spectrum of **12**.

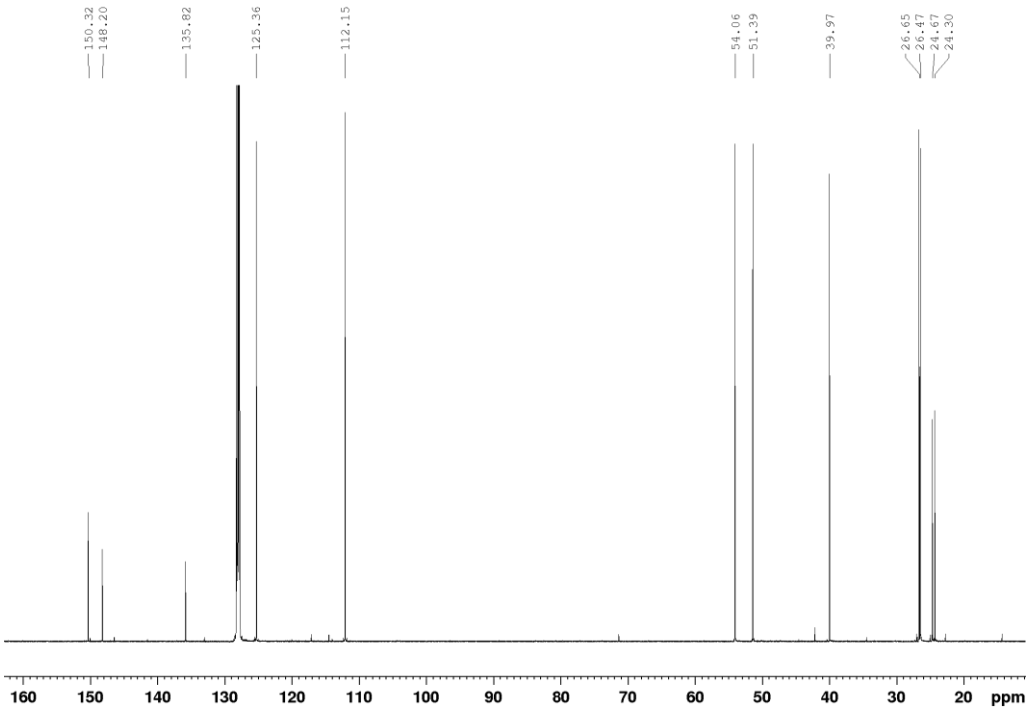


Figure S25. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6) spectrum of **12**.

3. Crystallographic Details

X-ray crystal data of **2** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Due to the Mo radiation and the presence of only C, H and N atoms in the structure, the absolute configuration could not be reliably determined. The Flack parameter is therefore meaningless. Crystal data for **2**: $C_{18}H_{25}N_3$, M_r = 283.41, colourless needle, 0.4×0.15×0.05 mm^3, monoclinic space group $P2_1$, a = 6.071(3) Å, b = 13.890(5) Å, c = 9.126(4) Å, β = 95.97(3)°, V = 765.4(6) Å^3, Z = 2, ρ_{calcd} = 1.230 g·cm^{-3}, μ = 0.074 mm^{-1}, F(000) = 308, T = 100(2) K, R_1 = 0.0331, wR^2 = 0.0815, 2958 independent reflections [2θ≤52.038°] and 190 parameters. CCDC-2103235.

The crystallographic data of **3** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. The unit cell contains one toluene molecule which has been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[5] The displacement parameters of atoms C1_1 > C5_20 of the residues RESI 1, RESI 2, RESI 10 and RESI 20 were restrained to the same value with the similarity restraint SIMU. The Uii displacement parameters of the atoms C1_1 > C5_20 were restrained with the ISOR keyword to approximate isotropic behaviour. The atomic displacement parameters of the atoms C1_1 > C5_20 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.005 for both parameters s1 and s2 were used). Crystal data for **3**: $C_{30}H_{33}N_3$, M_r = 435.59, colourless plate, 0.299×0.252×0.216 mm^3, triclinic space group P 1, a = 8.7901(17) Å, b = 9.3624(14) Å, c = 16.873(4) Å, α = 93.673(5)°, β = 91.942(8)°, γ = 109.928(4)°, V = 1300.4(4) Å^3, Z = 2, ρ_{calcd} = 1.112 g·cm^{-3}, μ = 0.065 mm^{-1}, F(000) = 468, T = 100(2) K, R_1 = 0.0453, wR^2 = 0.1017, 5302 independent reflections [2θ≤52.744°] and 407 parameters. CCDC-2103238.

The crystallographic data of **4** were collected on a BRUKER SMART-APEX diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in

the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **4**: $C_{19}H_{27}N_3$, M_r = 297.43, colourless block, 0.21×0.204×0.093 mm^3, monoclinic space group $P2_1/n$, a = 5.617(3) Å, b = 9.249(4) Å, c = 32.279(13) Å, β = 94.18(2)°, V = 1672.5(13) Å^3, Z = 4, ρ_{calcd} = 1.181 g·cm^{-3}, μ = 0.070 mm^{-1}, F(000) = 648, T = 103(2) K, R_1 = 0.0968, wR^2 = 0.1654, 3289 independent reflections [2θ≤52.04°] and 200 parameters. CCDC-2103234.

The crystallographic data of **5** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **5**: $C_{18}H_{24}FN_3$, M_r = 301.40, colourless block, 0.187×0.167×0.159 mm^3, triclinic space group $P\bar{1}$, a = 6.3289(19) Å, b = 11.536(4) Å, c = 11.603(4) Å, α = 108.626(9)°, β = 102.536(7)°, γ = 92.226(7)°, V = 778.2(5) Å^3, Z = 2, ρ_{calcd} = 1.286 g·cm^{-3}, μ = 0.085 mm^{-1}, F(000) = 324, T = 103(2) K, R_1 = 0.0731, wR^2 = 0.1356, 3053 independent reflections [2θ≤52.038°] and 199 parameters. CCDC-2103233.

The crystallographic data of **6** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **6**: $C_{19}H_{24}F_3N_3$, M_r = 351.41, colourless block, 0.374×0.298×0.16 mm^3, triclinic space group $P\bar{1}$, a = 6.2027(18) Å, b = 11.891(4) Å, c = 12.512(4) Å, α = 68.122(8)°, β = 76.813(8)°, γ = 86.440(8)°, V = 833.5(4) Å^3, Z = 2, ρ_{calcd} = 1.400 g·cm^{-3}, μ = 0.107 mm^{-1}, F(000) = 372, T = 296(2) K, R_1 = 0.1416, wR^2 = 0.1948, 3408 independent reflections [2θ≤52.746°] and 226 parameters. CCDC-2103232.

The crystal data of **7** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **7**: $C_{19}H_{23}F_4N_3$, M_r = 369.40, white block, 0.253×0.201×0.156 mm^3, monoclinic space group $C2/c$, a = 25.7461(8) Å, b = 9.7101(3) Å, c = 16.6172(5) Å, β = 121.8730(10)°, V = 3527.88(19) Å^3, Z = 8,

ρ_{calcd} = 1.391 g·cm^{-3}, μ = 0.113 mm^{-1}, F(000) = 1552, T = 100(2) K, R_1 = 0.0347, wR^2 = 0.0935, 3604 independent reflections [2θ≤52.74°] and 235 parameters. CCDC-2103242.

The crystalllographic data of **8** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **8**: $C_{25}H_{30}N_4$, M_r = 386.53, colourless block, 0.227×0.135×0.085 mm^3, monoclinic space group $P2_1/c$, a = 6.249(9) Å, b = 29.67(4) Å, c = 11.62(4) Å, β = 99.92(2)°, V = 2122(9) Å^3, Z = 4, ρ_{calcd} = 1.210 g·cm^{-3}, μ = 0.072 mm^{-1}, F(000) = 832, T = 103(2) K, R_1 = 0.0605, wR^2 = 0.1171, 4507 independent reflections [2θ≤53.464°] and 262 parameters. CCDC-2103239.

The crystallographic data of **9** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **9**: $C_{2.21}H_{2.84}N_{0.42}O_{0.21}$, M_r = 38.68, yellow block, 0.351×0.168×0.145 mm^3, triclinic space group $P\bar{1}$, a = 6.3974(18) Å, b = 12.354(4) Å, c = 12.818(4) Å, α = 105.132(12)°, β = 102.567(9)°, γ = 91.995(10)°, V = 950.0(5) Å^3, Z = 19, ρ_{calcd} = 1.285 g·cm^{-3}, μ = 0.085 mm^{-1}, F(000) = 394, T = 175(2) K, R_1 = 0.0567, wR^2 = 0.1100, 3743 independent reflections [2θ≤52.29°] and 244 parameters. CCDC-2103236.

The crystallographic data of **10** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **10**: $C_{19}H_{27}N_3O$, M_r = 313.43, colourless needle, 0.781×0.28×0.119 mm^3, triclinic space group $P\bar{1}$, a = 6.133(2) Å, b = 11.723(4) Å, c = 12.936(6) Å, α = 114.651(15)°, β = 96.357(16)°, γ = 95.980(14)°, V = 828.4(6) Å^3, Z = 2, ρ_{calcd} = 1.257 g·cm^{-3}, μ = 0.079 mm^{-1}, F(000) = 340, T = 100(2) K, R_1 = 0.0517, wR^2 = 0.1362, 3247 independent reflections [2θ≤52.044°] and 209 parameters. CCDC-2103237.

The crystallographic data of **11** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **11**: $C_{20}H_{30}N_4$, M_r = 326.48, orange block, 0.22×0.215×0.196 mm^3, orthorhombic space group *Pbca*, *a* = 8.002(9) Å, *b* = 12.763(13) Å, *c* = 34.89(3) Å, *V* = 3563(6) Å^3, *Z* = 8, ρ_{calcd} = 1.217 g·cm^{-3}, μ = 0.073 mm^{-1}, *F*(000) = 1424, *T* = 103(2) K, R_1 = 0.1295, wR^2 = 0.1213, 3623 independent reflections [2θ≤52.74°] and 219 parameters. CCDC-2103241.

The crystallographic data of **12** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **12**: $C_{20}H_{30}N_6$, M_r = 354.50, colourless block, 0.314×0.204×0.16 mm^3, triclinic space group $P\ \bar{1}$, *a* = 9.1184(16) Å, *b* = 10.4276(18) Å, *c* = 10.849(2) Å, α = 88.78(2)°, β = 72.367(9)°, γ = 76.798(9)°, *V* = 955.9(3) Å^3, *Z* = 2, ρ_{calcd} = 1.232 g·cm^{-3}, μ = 0.077 mm^{-1}, *F*(000) = 384, *T* = 100(2) K, R_1 = 0.0483, wR^2 = 0.1039, 3892 independent reflections [2θ≤52.742°] and 237 parameters. CCDC-2103240.

4. Computational Details

Geometry optimisations and vibrational frequency calculations were performed using the DFT functional B97D3,[6] the basis set 6-311+g(d,p), and the CPCM solvation model for benzene[7] as implemented the Gaussian 16 (Revision B.01) software.[8] Calculations at the B3LYP-D3[9,10]/6-311G++(d,p)/SMD(benzene)[11]//B3LYP-D3/6-31G+(d,p) level of theory were also performed and found that the results obtained were very similar to that obtained at the B97D3 level. Therefore, only the results of the former level of theory are discussed. Both levels of theories have been employed previously for studying the mechanism of azide-alkyne cycloadditions.[12] Geometry optimisation of all stationary points was performed without any symmetry constraints. Stability tests were performed on the single-determinant wavefunctions of the optimised geometries of carbenes **A4**, **A4'** and **B4**.[13] No internal instability was found for **A4** and **A4'**, suggestive of closed-shell singlet systems. However, for compound **B4**, a restricted Hartree-Fock (RHF) to unrestricted Hartree-Fock (UHF) instability was observed, indicating that **B4** has an open-shell structure. Optimisations and frequency calculations performed at the UB97D3/6-311G+(d,p)/CPCM(benzene) demonstrated that the ground state for **B4** is a triplet (**B4'**). Transition state geometries were obtained using opt = (ts, noeigentest, calcfc) algorithms.[14] All optimised transition state structures were confirmed as maxima with only one imaginary frequency, and the magnitudes of all frequencies were greater than the residual frequencies related to rotations and translations. Additionally, each transition state located was ensured to be on the preferred reaction path by performing "plus-and-minus-displacement" minimisation calculations, which involves the displacement of transition state structure by ca. 0.05 Å or 5° to 10° on the imaginary frequency normal mode in both directions,[15] and the displaced geometries were subsequently optimised to the nearest minimum. Zero-point vibrational energies and thermal corrections were computed from frequency calculations with a standard state of 298 K and 1 atm. The energies (ΔG) given are corrected for zero-point vibrational energies (ZPVEs).

Bonding analyses on the 1,3- dipolar cycloaddition transition states were done using the energy decomposition analysis based on natural orbitals for the chemical valence (EDA-NOCV) method.[16] The analyses were performed at the B3LYP-D3/TZVP level using the ADF 2019.304 package.[17]

Optimised structures, Cartesian coordinates, and energies

4.1 For the reaction between phenyl azide and diamino acetylene

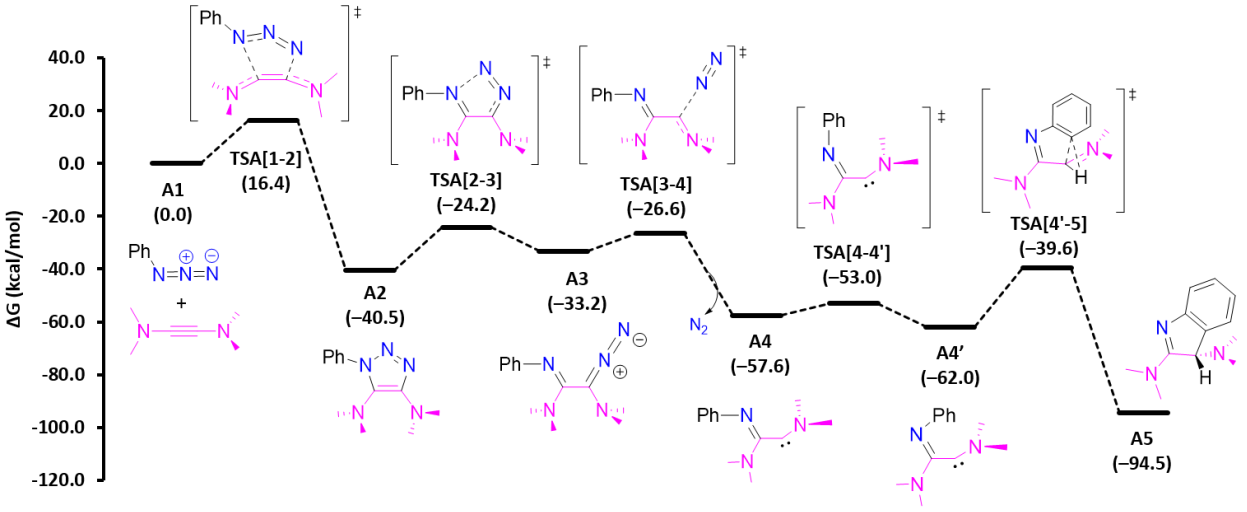
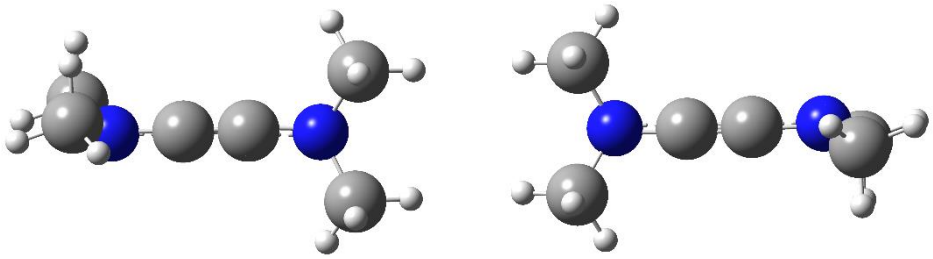


Figure S25. Computed mechanism for the formation of N_2,N_2,N_3,N_3-tetramethyl-3*H*-indole-2,3-diamine from the reaction of phenyl azide with N_1,N_1,N_2,N_2-tetramethylethyne-1,2-diamine.

1) Bis(dimethylamino acetylene) **A1**

side view *top view*



Number of imaginary frequencies = 0

E_{total} = -345.146767 a.u

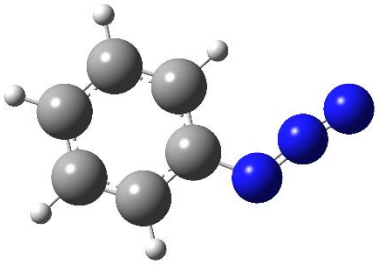
$G_{correction}$ = 0.133101 a.u

Cartesian coordinates:

C	0.60570100	-0.08245400	-0.09324400
C	-0.60571000	-0.08258200	0.09337300
N	-1.94171600	-0.17472800	0.20137900
N	1.94169200	-0.17446900	-0.20155200
C	-2.66413600	-0.80055500	-0.91611000
H	-3.67300200	-1.07654200	-0.58566300
H	-2.74845700	-0.12035100	-1.78198600
H	-2.12993500	-1.70301800	-1.22566900
C	-2.64796100	0.95190300	0.82694100

H	-2.09554600	1.27103000	1.71502100
H	-2.74409800	1.81025000	0.13861300
H	-3.65221500	0.62815500	1.12671400
C	2.66428200	-0.80156700	0.91511400
H	3.67309900	-1.07717100	0.58420200
H	2.74872800	-0.12234800	1.78175100
H	2.13013200	-1.70438500	1.22372500
C	2.64783500	0.95288700	-0.82592400
H	2.74407500	1.81044000	-0.13662100
H	3.65204300	0.62949100	-1.12622800
H	2.09527800	1.27303600	-1.71354800

2) **Phenyl azide**



Number of imaginary frequencies = 0

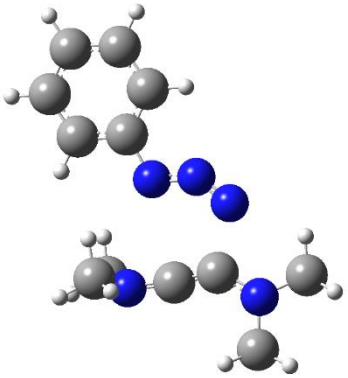
E_{total} = -395.697653 a.u

$G_{correction}$ = 0.068953 a.u

Cartesian coordinates:

C	0.88424000	-1.31460100	0.00003600
C	-0.14655300	-0.36184500	0.00000400
C	0.15510400	1.01039600	-0.00001300
C	1.49135400	1.41919800	0.00000200
C	2.52535800	0.47507600	0.00003300
C	2.21459100	-0.89080200	0.00005000
N	-1.47528100	-0.87350500	-0.00000800
N	-2.42257600	-0.08583600	-0.00003900
N	-3.39183100	0.52301400	-0.00006500
H	-0.64286200	1.74991600	-0.00003700
H	1.72245300	2.48240100	-0.00001200
H	3.56288900	0.80076500	0.00004400
H	3.01097300	-1.63197300	0.00007400
H	0.62979900	-2.37136400	0.00004800

3) **TSA[1-2]**



Number of imaginary frequencies = 1 (240.6 cm^{-1})

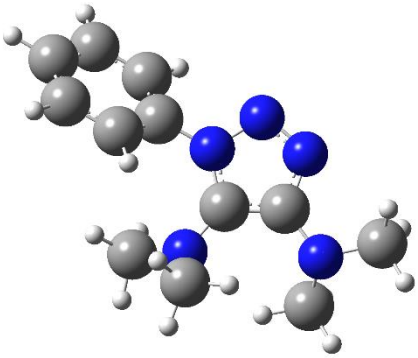
E_{total} = -740.839620 a.u

$G_{correction}$ = 0.223417 a.u

Cartesian coordinates:

N	-0.78244200	-0.28400500	0.28377300
N	-0.12253000	-1.18254500	-0.35101500
N	1.00992300	-1.47797100	-0.57563100
C	1.94049500	0.97390600	0.26143400
C	2.38837200	-0.22986900	0.09802000
N	3.56034100	-0.88189000	0.10673000
N	1.32606200	2.00667300	-0.25916500
C	0.48189600	2.84981900	0.59316900
H	0.42237200	3.86028000	0.17495200
H	-0.52473300	2.40670000	0.64087800
H	0.90841600	2.88445200	1.59734300
C	0.98939600	2.03549100	-1.69434600
H	-0.00527200	1.58698300	-1.83742500
H	0.97753000	3.07094400	-2.05188500
H	1.73317800	1.45841300	-2.24651500
C	4.78413900	-0.08447000	0.23413000
H	5.64535400	-0.69010600	-0.06950400
H	4.71590700	0.79165200	-0.41656900
H	4.93126500	0.25114500	1.27432700
C	3.64366100	-2.24958300	0.63190300
H	3.81926200	-2.24078000	1.72004300
H	2.70998000	-2.77233400	0.42281800
H	4.47254300	-2.77466600	0.14384400
C	-2.18614400	-0.37029400	0.18342800
C	-2.92902500	0.50472300	1.00209000
C	-2.87996900	-1.23980600	-0.68601000
C	-4.32464400	0.51068100	0.95140500
C	-4.27546300	-1.22736900	-0.72659600
C	-5.00979100	-0.35377600	0.08762300
H	-2.39514500	1.16654300	1.68082100
H	-4.88002300	1.19184400	1.59406300
H	-2.31609400	-1.91683000	-1.32378100
H	-4.79463100	-1.90461100	-1.40326400
H	-6.09693700	-0.34818900	0.04951500

4) Intermediate **A2**



Number of imaginary frequencies = 0

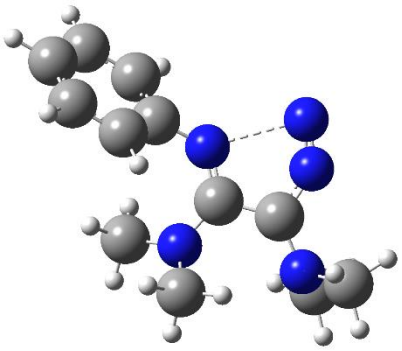
E_{total} = -740.939731 a.u

$G_{correction}$ = 0.232901 a.u

Cartesian coordinates:

N	-0.30411000	-0.72970900	-0.04815400
N	0.18206800	-1.99762800	-0.21311800
N	1.49523500	-1.90278200	-0.26480300
C	0.72468600	0.19074200	0.03114900
C	1.87629600	-0.59937700	-0.12208200
N	3.20684100	-0.17272900	-0.17442700
N	0.60708400	1.55361500	0.24028500
C	-0.40382800	2.09323500	1.14368100
H	-0.00546600	3.00263100	1.61415900
H	-1.34824800	2.35037300	0.63782900
H	-0.62023600	1.36213400	1.92825100
C	1.05840800	2.44062900	-0.83042900
H	0.27166300	2.62091700	-1.58503900
H	1.35394300	3.40639500	-0.40113900
H	1.92790900	1.99745100	-1.32606200
C	3.63566800	0.66138700	0.95678400
H	4.59245800	1.13464400	0.70821000
H	2.89181700	1.44047500	1.14456000
H	3.76431300	0.06600300	1.87945800
C	4.18117900	-1.20977800	-0.51951400
H	4.30863400	-1.95588100	0.28463100
H	3.85918000	-1.73316600	-1.42395100
H	5.14593900	-0.72499500	-0.70737100
C	-1.71002600	-0.50167700	-0.05985200
C	-2.53009500	-1.21415300	0.82179800
C	-2.25496600	0.40991800	-0.97184200
C	-3.91157000	-1.00252600	0.79271800
C	-3.63551400	0.62606100	-0.98258300
C	-4.46556800	-0.07861800	-0.10197800
H	-1.60201400	0.93263400	-1.66531700
H	-4.06297800	1.33562500	-1.68759300
H	-5.54039800	0.08818400	-0.11646700
H	-4.55395000	-1.55418600	1.47556600
H	-2.08040300	-1.91967100	1.51469400

5) **TSA[2-3]**



Number of imaginary frequencies = 1 (158.6 cm^{-1})

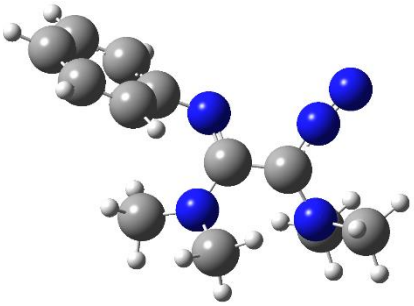
E_{total} = -740.909295 a.u

$G_{correction}$ = 0.228429 a.u

Cartesian coordinates:

N	-0.45887600	-0.79821700	0.32890700
N	0.96889500	-2.73302300	-0.43113600
N	1.76121800	-1.89410100	-0.32549500
C	0.53959500	0.02561500	0.11436100
C	1.86548800	-0.54721900	-0.17464500
N	3.08277900	0.10570600	-0.00120500
N	0.46934400	1.39717000	0.22187600
C	-0.51638300	2.03575600	1.08742800
H	-0.03068400	2.87052500	1.61035000
H	-1.37544500	2.42359300	0.52087600
H	-0.88328500	1.32151600	1.82679400
C	1.27720400	2.30861200	-0.58437000
H	0.61230500	3.08356500	-0.99312500
H	2.06683300	2.79329000	0.00603000
H	1.73832100	1.77488300	-1.41542500
C	3.63122300	0.03151300	1.35905100
H	4.46230400	0.74071100	1.45956700
H	2.84857700	0.30303300	2.07492800
H	3.99827400	-0.98301800	1.60494100
C	4.07048700	-0.13761000	-1.05003000
H	4.44159100	-1.18112900	-1.04279800
H	3.61979900	0.06122500	-2.02834200
H	4.92781600	0.53178300	-0.91041600
C	-1.79229500	-0.47311000	0.10274400
C	-2.78002400	-0.98855100	0.96984400
C	-2.21184300	0.28926200	-1.01345600
C	-4.13317000	-0.72704300	0.74615300
C	-3.56688100	0.54141900	-1.23300100
C	-4.53784900	0.04141600	-0.35390300
H	-2.46049700	-1.59009900	1.81834200
H	-4.87740000	-1.12897600	1.43188500
H	-5.59307500	0.23953000	-0.52944900
H	-3.86892000	1.12700700	-2.10023100
H	-1.46336000	0.66946100	-1.70560400

6) Intermediate **A3**



Number of imaginary frequencies = 0

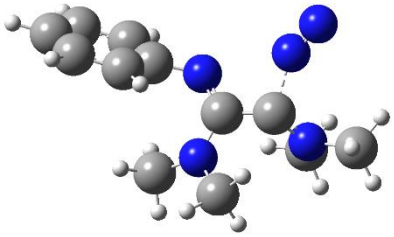
E_{total} = -740.923379 a.u

$G_{correction}$ = 0.228045 a.u

Cartesian coordinates:

C	-2.77670600	-1.01756000	1.07174500
C	-1.82590600	-0.52930600	0.14861800
C	-2.30309700	0.11331800	-1.01888500
C	-3.67299200	0.27442800	-1.23732100
C	-4.60539200	-0.19557800	-0.30251700
C	-4.14474900	-0.84393600	0.85185300
N	-0.47149200	-0.79067000	0.36574400
N	1.89824000	-1.72195700	-0.47242100
N	2.22997800	-2.76434700	-0.81251200
C	0.46362700	0.08799200	0.08812500
C	1.80415900	-0.42329000	-0.17246600
N	3.01129400	0.21284800	0.19052000
N	0.32923000	1.46179900	0.10137200
C	3.40007700	0.03810500	1.59786400
H	3.77085300	-0.98137100	1.80709700
H	4.19235900	0.75544000	1.84347200
H	2.53174100	0.23638300	2.23357600
C	4.11697800	0.06297400	-0.75380300
H	4.92141300	0.75291400	-0.47481000
H	4.53437800	-0.96224400	-0.76722200
H	3.76957800	0.30934100	-1.76256800
C	1.08931900	2.33698200	-0.78542600
H	1.70811600	1.74525300	-1.46047800
H	0.38860200	2.93408800	-1.38921400
H	1.73511700	3.02073800	-0.21720100
C	-0.71829800	2.11556100	0.87323900
H	-0.30110900	3.02768100	1.32073200
H	-1.58516600	2.38764900	0.25254300
H	-1.06109100	1.45295600	1.67031000
H	-1.58604000	0.47065400	-1.75577900
H	-4.01565300	0.76687400	-2.14656600
H	-2.41688200	-1.52861900	1.96277800
H	-4.85720700	-1.22222500	1.58358600
H	-5.67186800	-0.06737200	-0.47533500

7) **TSA[3-4]**



Number of imaginary frequencies = 1 (391.4 cm^{-1})

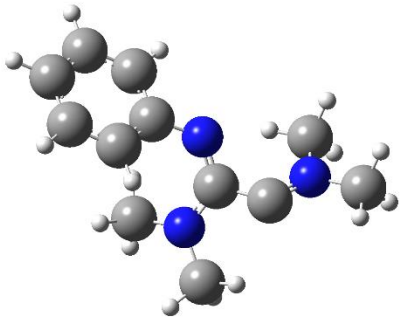
E_{total} = -740.909812 a.u

$G_{correction}$ = 0.225076 a.u

Cartesian coordinates:

C	-2.67434800	-0.89313200	1.18439400
C	-1.76189900	-0.48976600	0.18378700
C	-2.28951700	0.00410300	-1.03382700
C	-3.66847400	0.10541600	-1.22729500
C	-4.56236600	-0.27866600	-0.21792600
C	-4.05220300	-0.78024600	0.98766900
N	-0.39641300	-0.69793500	0.38511100
N	1.73238800	-1.98561500	-0.45490400
N	2.24530800	-2.91007900	-0.84609800
C	0.51316100	0.16120700	-0.01904000
C	1.84803300	-0.27886000	-0.41459700
N	2.94920400	0.10121400	0.24410900
N	0.32324300	1.52856400	-0.13701400
C	2.97598000	0.30426000	1.70321800
H	3.30852300	-0.61358200	2.21180100
H	3.66721800	1.11779700	1.95251300
H	1.97142800	0.55917200	2.04715100
C	4.25428100	-0.12517600	-0.37704200
H	4.96561500	0.63825600	-0.04053000
H	4.65148800	-1.11624300	-0.10239800
H	4.14153700	-0.07346200	-1.46227600
C	1.18954900	2.37915400	-0.94791000
H	1.70948300	1.77402900	-1.69464300
H	0.57133300	3.12589600	-1.46429800
H	1.93791200	2.90763400	-0.33694800
C	-0.71622400	2.22461200	0.61070600
H	-0.29408200	3.15517800	1.01323700
H	-1.58501400	2.46939900	-0.01791300
H	-1.05941100	1.60516700	1.44122600
H	-1.60208600	0.29649700	-1.82546900
H	-4.04952900	0.48341400	-2.17536200
H	-5.63633800	-0.19725000	-0.37185600
H	-4.73367000	-1.09112500	1.77843800
H	-2.27635000	-1.29124600	2.11609100

8) Intermediate **A4** (singlet species)



Number of imaginary frequencies = 0

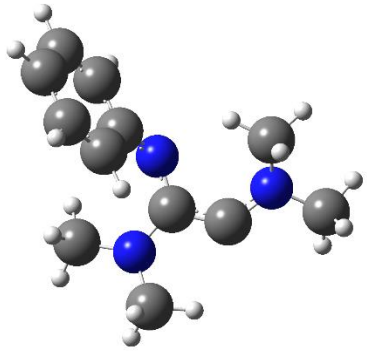
E_{total} = -631.451537 a.u

$G_{correction}$ = 0.221618 a.u

Cartesian coordinates:

C	-2.20731600	-1.38432900	0.73768400
C	-1.37239000	-0.54895100	-0.04104800
C	-1.98933800	0.29852300	-0.99451900
C	-3.37791600	0.32130200	-1.13922200
C	-4.19531000	-0.49327300	-0.34367900
C	-3.59518500	-1.34682600	0.59344500
N	0.00833800	-0.66846400	0.08020700
C	0.85586500	0.32882300	-0.05282200
C	2.08827800	-0.00020800	-0.76616000
N	2.94065900	-0.82007500	-0.21629500
N	0.65839100	1.64201200	0.30009900
C	2.85939400	-1.40537500	1.14576400
H	2.61045100	-2.46992100	1.07141100
H	3.83337000	-1.29791100	1.63638100
H	2.08386400	-0.89576100	1.71640300
C	4.09777100	-1.30886800	-0.98763800
H	5.02743100	-1.05407900	-0.46364100
H	4.03690700	-2.40010600	-1.08757400
H	4.07553700	-0.84029000	-1.97187700
C	1.65205700	2.66558400	-0.01061000
H	2.34041600	2.27914900	-0.76882100
H	1.14970400	3.55799100	-0.40717200
H	2.22413000	2.95250800	0.88455900
C	-0.47149800	2.06861800	1.11499400
H	-0.12246700	2.82399000	1.82955900
H	-1.27959400	2.49683800	0.50429800
H	-0.87656300	1.21886700	1.66819800
H	-1.74157400	-2.05396600	1.45859200
H	-4.21466500	-1.99344800	1.21376900
H	-5.27694100	-0.47090700	-0.45839500
H	-3.82597500	0.97893200	-1.88342300
H	-1.36221500	0.92368200	-1.62749200

9) Intermediate **A4** (triplet species)



Number of imaginary frequencies = 0

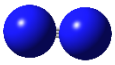
E_{total} = -631.404006 a.u

$G_{correction}$ = 0.217583 a.u

Cartesian coordinates:

C	-2.23723500	-0.95189700	1.17951900
C	-1.23158400	-0.32528600	0.39483200
C	-1.58055100	0.06829500	-0.92780900
C	-2.86823600	-0.14096900	-1.42089300
C	-3.85536200	-0.73691800	-0.62251100
C	-3.52453500	-1.13951500	0.68149300
N	0.03156800	-0.20324800	0.92909800
C	0.95863500	0.60955100	0.38813100
C	2.21303100	0.06568900	0.04660300
N	2.62713900	-1.21999300	0.04182300
N	0.75329800	1.96764100	0.19849800
C	1.80562200	-2.31375200	-0.50237800
H	1.90892600	-2.36900400	-1.59817500
H	2.14761100	-3.26019400	-0.06804100
H	0.76310500	-2.14396800	-0.23522100
C	4.07329100	-1.45353500	-0.01717500
H	4.31113300	-2.38349600	0.51324600
H	4.42021800	-1.54246800	-1.05964500
H	4.59313300	-0.62036000	0.46218700
C	1.64980200	2.76060100	-0.62702400
H	2.59978600	2.22751500	-0.73713700
H	1.22440600	2.93133800	-1.62939800
H	1.83101200	3.73304100	-0.15181400
C	-0.45848500	2.61614900	0.66800500
H	-0.21360500	3.63900100	0.97910300
H	-1.23739700	2.65911500	-0.10995300
H	-0.86152100	2.06559700	1.52176400
H	-1.97545300	-1.27115000	2.18649900
H	-4.27821100	-1.61088000	1.31089400
H	-4.85933400	-0.89320900	-1.01101700
H	-3.10520500	0.16168100	-2.44034300
H	-0.81900300	0.51614200	-1.56364300

10) **Dinitrogen**



Number of imaginary frequencies = 0

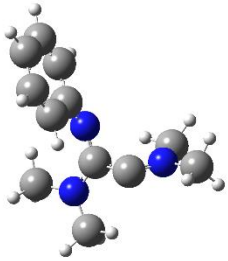
E_{total} = -109.491188 a.u

$G_{correction}$ = -0.013057 a.u

Cartesian coordinates:

N	0.00000000	0.00000000	0.55178800
N	0.00000000	0.00000000	-0.55178800

11) **TSA[4-4']**



Number of imaginary frequencies = 1 (83.5 cm^{-1})

E_{total} = -631.442979 a.u

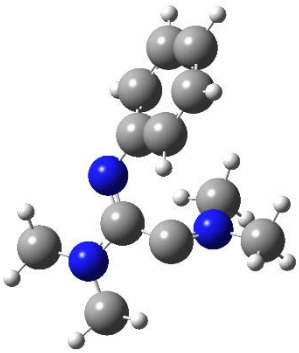
$G_{correction}$ = 0.220360 a.u

Cartesian coordinates:

N	-0.19192700	0.12351200	0.77003400
C	0.86508800	0.48503100	0.05480500
C	1.47718100	-0.57604200	-0.69329800
N	2.32828500	-1.40176700	-0.14750300
N	1.31658100	1.76352700	-0.01203500
C	2.88601000	-1.29292300	1.22164400
H	3.98039400	-1.25285600	1.16597500
H	2.49992000	-0.39293300	1.70078500
H	2.59229300	-2.17242100	1.80621900
C	2.77568600	-2.60317600	-0.87292700
H	3.87036100	-2.60616100	-0.94668700
H	2.45582400	-3.50153700	-0.32933900
H	2.32923100	-2.58957300	-1.86751800
C	2.60172000	2.08243700	-0.62188700
H	2.95284400	1.22465900	-1.20408400
H	2.48850100	2.94095500	-1.29508200
H	3.35199500	2.32996900	0.14281100
C	0.53970400	2.87026300	0.53503900
H	1.14169300	3.42722700	1.26502300
H	0.23477300	3.55320000	-0.26961700
H	-0.34539000	2.46384900	1.02830400
C	-1.47348300	-0.09304800	0.33572800
C	-2.43850200	-0.60327300	1.24469900
C	-1.91234500	0.20697600	-0.98425000
C	-3.76254200	-0.79996400	0.85232100

H	-2.12021200	-0.83711400	2.25926300
C	-3.23920500	0.00075400	-1.36221400
H	-1.19079000	0.58848500	-1.70465500
C	-4.18218000	-0.50316900	-0.45345700
H	-4.47719200	-1.19316200	1.57506800
H	-3.54227900	0.23838000	-2.38200400
H	-5.21533200	-0.66106600	-0.75514200

12) Intermediate **A4'** (singlet species)



Number of imaginary frequencies = 0

E_{total} = -631.458655 a.u

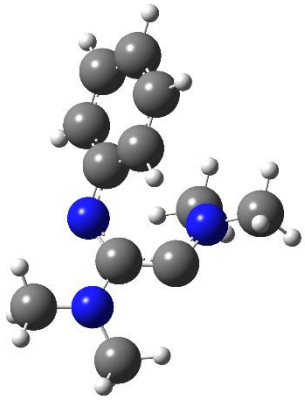
$G_{correction}$ = 0.221797 a.u

Cartesian coordinates:

C	1.91213200	-1.38532200	0.86742700
C	1.03897300	-0.88733500	-0.12791600
C	1.60358400	-0.11817000	-1.17366400
C	2.97140300	0.16276200	-1.19844900
C	3.82006300	-0.31304000	-0.18912800
C	3.27756400	-1.09357100	0.84082600
N	-0.30652400	-1.24728100	-0.05136700
C	-1.28526900	-0.40020700	-0.27744200
C	-1.10370400	1.01200600	-0.65900100
N	-0.60352300	1.81686600	0.23711000
N	-2.57880900	-0.86873100	-0.31134900
H	1.49059100	-1.99752800	1.66264400
H	3.92318600	-1.48171100	1.62757000
H	4.88456300	-0.08908600	-0.21138200
H	3.37910400	0.75512400	-2.01684600
H	0.95584400	0.25343600	-1.96464500
C	-0.23329800	3.19351900	-0.13689700
H	-0.76208300	3.90888200	0.50459100
H	0.84737100	3.32595200	0.00016000
H	-0.50198300	3.34684600	-1.18227300
C	-0.24664700	1.48290900	1.64101500
H	0.84249200	1.38961600	1.71997000
H	-0.59391700	2.28523100	2.30077000
H	-0.70857300	0.53547600	1.91875500
C	-3.68220100	0.07136800	-0.16215600
H	-3.92651500	0.26172800	0.89633700
H	-3.41011800	1.02155100	-0.63724000

H	-4.57264900	-0.32895300	-0.66012900
C	-2.84901400	-2.26296300	0.01475300
H	-3.83511600	-2.52757600	-0.38302600
H	-2.08491900	-2.89916900	-0.43561600
H	-2.84680000	-2.43752400	1.10340200

13) Intermediate **A4'** (triplet species)



Number of imaginary frequencies = 0

E_{total} = -631.412910 a.u

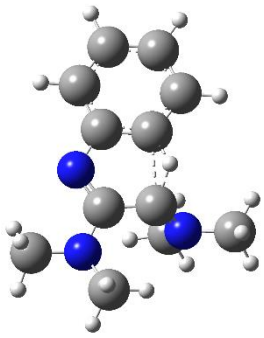
$G_{correction}$ = 0.218219 a.u

Cartesian coordinates:

C	1.81163300	-1.39556400	0.99892200
C	0.84712800	-0.91129000	0.07860300
C	1.31718700	-0.34743100	-1.13811100
C	2.68272300	-0.23915200	-1.39450100
C	3.62416800	-0.69472900	-0.45905400
C	3.17531600	-1.27879500	0.73570900
N	-0.48689500	-1.06497700	0.38426500
C	-1.42420900	-0.20808900	-0.04395100
C	-1.23361100	1.19841000	-0.12423800
N	-0.10797500	1.86890900	0.23684200
N	-2.69229300	-0.70829000	-0.29600500
H	1.45762500	-1.84314500	1.92564400
H	3.89628900	-1.64597400	1.46461900
H	4.68928400	-0.61040400	-0.66449600
H	3.01888300	0.19640300	-2.33469600
H	0.59016700	-0.01025200	-1.87349100
C	0.33184100	2.99828600	-0.57551200
H	-0.07074200	3.95177600	-0.19509600
H	1.42816300	3.04565300	-0.56083400
H	-0.00631200	2.85466000	-1.60492800
C	0.35261300	1.86967100	1.62867600
H	1.44678800	1.94010400	1.64363500
H	-0.07053300	2.72318800	2.18294800
H	0.05065800	0.93793100	2.11036800
C	-3.86056200	0.15915100	-0.21415700
H	-4.28058800	0.17779800	0.80619200
H	-3.57552500	1.17726700	-0.49284500
H	-4.63088400	-0.20485800	-0.90429400

C	-2.94215900	-2.12890800	-0.09750900
H	-3.82497700	-2.41483300	-0.68074300
H	-2.07496400	-2.70389200	-0.43026600
H	-3.12559600	-2.37026800	0.96330400

14) **TSA[4'-5]**



Number of imaginary frequencies = 1 (1041.0 cm^{-1})

E_{total} = -631.420393 a.u

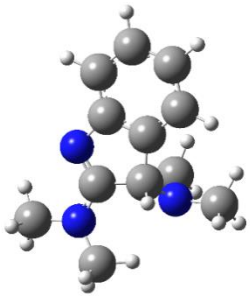
$G_{correction}$ = 0.219204 a.u

Cartesian coordinates:

C	2.52986800	-1.62245600	0.21827900
C	1.32762800	-0.91747200	-0.01284800
C	1.42354400	0.45157900	-0.31377900
C	2.62876500	1.13464000	-0.41569100
C	3.81252200	0.42964200	-0.13071300
C	3.74984500	-0.94043700	0.17452500
N	0.08295200	-1.52935200	0.03202700
C	-0.92512300	-0.69023400	-0.15819000
C	-0.74159900	0.70822900	-0.54269600
N	-1.24594900	1.74142600	0.16276800
N	-2.21824900	-1.15891200	-0.01648300
H	2.49162600	-2.69147400	0.42132100
H	4.67138200	-1.48517800	0.37399500
H	4.77075300	0.94626400	-0.14296800
H	2.66575500	2.18798300	-0.69153500
H	0.34551600	0.86983900	-1.08899900
C	-1.14904500	3.07824800	-0.42221100
H	-1.91031700	3.73414800	0.01560900
H	-0.15605900	3.51718100	-0.22738300
H	-1.30294100	3.00734600	-1.50199400
C	-1.24480700	1.71386600	1.63230300
H	-0.25716300	2.02106700	2.01398600
H	-2.01082900	2.39528200	2.01932300
H	-1.45849800	0.69848600	1.97396400
C	-3.33241100	-0.53013900	-0.72662200
H	-4.25933100	-0.72002000	-0.17353900
H	-3.18333400	0.54706600	-0.79640400
H	-3.44005600	-0.94547600	-1.74289400
C	-2.40213900	-2.58454600	0.25247800
H	-2.27324500	-3.19177500	-0.65807600

H	-1.66997200	-2.91622800	0.99037000
H	-3.41684600	-2.73216200	0.63803000

15) Product **A5**



Number of imaginary frequencies = 0

E_{total} = -631.516026 a.u

$G_{correction}$ = 0.227257 a.u

Cartesian coordinates:

C	2.28962300	-1.84013200	0.31061200
C	1.09903200	-1.15263600	0.05753100
C	1.12161300	0.18851600	-0.39128100
C	2.32644700	0.84547900	-0.61160400
C	3.53011600	0.15969600	-0.35054300
C	3.50442600	-1.16416500	0.10744300
N	-0.21043600	-1.66961500	0.17370100
C	-1.03632600	-0.69650400	-0.14923800
C	-0.33049500	0.62797200	-0.53539700
N	-0.79605800	1.75662400	0.28614000
N	-2.38449500	-0.82059200	-0.10626000
H	2.26890200	-2.87362500	0.65028200
H	4.44219200	-1.68213500	0.30211200
H	4.48285600	0.65996100	-0.51159500
H	2.35471100	1.86622200	-0.98650000
H	-0.55979700	0.87244000	-1.58304800
C	-0.33006600	3.05339100	-0.20307400
H	-0.86839000	3.84814600	0.32859800
H	0.75242900	3.21852500	-0.05001000
H	-0.54786300	3.14411100	-1.27419100
C	-0.51280800	1.58423500	1.71300500
H	0.56799600	1.61601400	1.94421200
H	-1.01142300	2.38534500	2.27121800
H	-0.91179900	0.62365200	2.05610700
C	-3.26430300	0.13338300	-0.78013600
H	-4.21968300	0.17244800	-0.24512100
H	-2.81297500	1.12619800	-0.75417500
H	-3.45924500	-0.17311200	-1.82058600
C	-2.96439800	-2.12408000	0.21610600
H	-3.03373800	-2.76192100	-0.67869100
H	-2.33508000	-2.62726700	0.95244600
H	-3.96932600	-1.97084600	0.62333300

4.2 For the reaction between phenyl azide and phenyl acetylene

Because our interest is on comparing the free energy profile of the reaction between phenyl azide and diamino acetylene and that of the reaction between phenyl azide and phenylacetylene up to the stage of carbene generation, the free energy profile with phenylacetylene was computed only up to this stage.

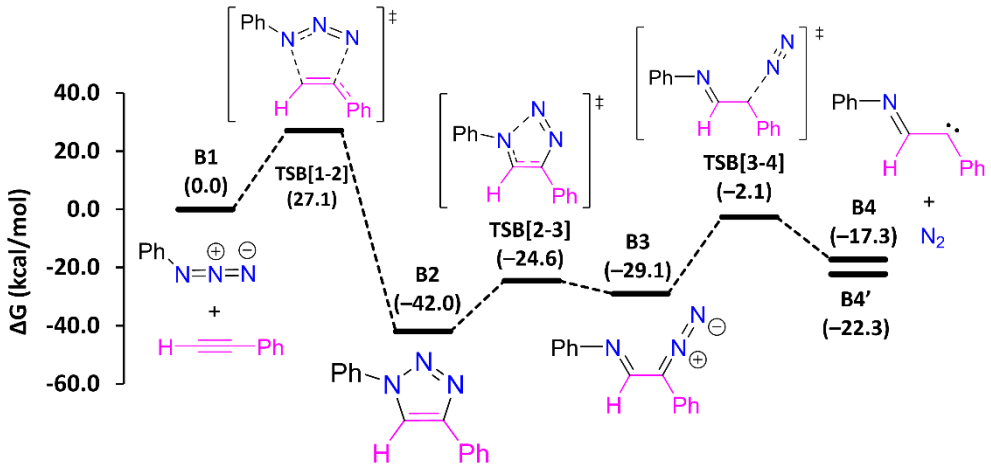
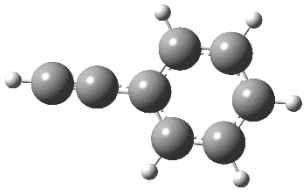


Figure S26. The computed mechanism for the generation of carbene from the reaction between phenyl azide and phenylacetylene. **B4'** is a triplet species.

Note: Details of phenyl azide and N_2 are provided above in the mechanism computed for the reaction between phenyl azide and diaminoacetylene.

16) **Phenylacetylene**



Number of imaginary frequencies = 0

E_{total} = -308.265546 a.u

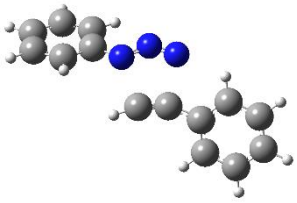
$G_{correction}$ = 0.076166 a.u

Cartesian coordinates:

C	2.02346500	-0.00003200	-0.00013600
C	3.23840400	0.00005000	0.00000200
H	4.30547900	-0.00014000	0.00036000
C	0.59680000	-0.00001500	-0.00005800
C	-0.11880800	-1.21744200	-0.00001700
C	-0.11878200	1.21742700	-0.00003000
C	-1.51461000	-1.21198300	0.00004700
H	0.43007200	-2.15588100	-0.00003900
C	-1.51458400	1.21199900	0.00003400

H	0.43011800	2.15585400	-0.00006100
C	-2.21677100	0.00001600	0.00007300
H	-2.05584500	-2.15584500	0.00007600
H	-2.05579700	2.15587300	0.00005400
H	-3.30470800	0.00002700	0.00012400

17) **TSB[1-2]**



Number of imaginary frequencies = 1 (353.3 cm^{-1})

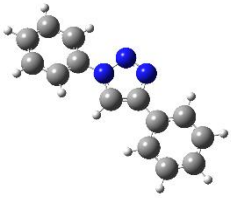
E_{total} = -703.939479 a.u

$G_{correction}$ = 0.164626 a.u

Cartesian coordinates:

N	-1.35967700	-0.36902900	-0.66944400
N	-0.66148800	-1.34403800	-0.26715900
N	0.47272700	-1.58099200	-0.08133600
C	0.23271400	1.10634700	-0.66257600
C	1.27153800	0.47346300	-0.39893500
C	-2.68734200	-0.17712000	-0.23810700
C	-3.43306800	0.80747700	-0.91036800
C	-3.25926100	-0.87947500	0.83964300
C	-4.73622200	1.09279000	-0.49770700
C	-4.56973500	-0.59706200	1.22807900
C	-5.31253200	0.39151200	0.56865900
H	-2.98539200	1.33322400	-1.75019700
H	-5.30700100	1.85775600	-1.01993900
H	-2.67859800	-1.64128600	1.35433900
H	-5.01093600	-1.14945800	2.05531900
H	-6.33129700	0.60932900	0.88065900
C	2.67178900	0.29977400	-0.11506700
C	3.33077600	1.24034500	0.70667100
C	3.41117200	-0.77218200	-0.65470000
C	4.69438200	1.10860400	0.97611100
H	2.76203700	2.06550300	1.12850800
C	4.77718900	-0.88887300	-0.39102500
H	2.90518500	-1.50572000	-1.27557200
C	5.42365800	0.04679500	0.42640200
H	5.18868200	1.83796000	1.61482400
H	5.33751700	-1.71769400	-0.81903500
H	6.48667700	-0.05236500	0.63592800
H	-0.41814900	1.90679800	-0.94173400

18) **B2**



Number of imaginary frequencies = 0

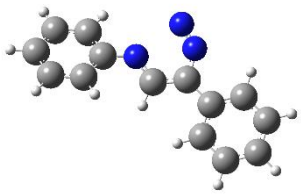
E_{total} = -704.058289 a.u

$G_{correction}$ = 0.173256 a.u

Cartesian coordinates:

N	-1.10116700	-0.35822000	-0.09421600
N	-0.68291900	-1.62212600	-0.41161900
N	0.62122300	-1.61122300	-0.41081500
C	-0.02797500	0.45911400	0.10761500
C	1.08163400	-0.34966600	-0.09818900
C	-2.48799600	-0.04073000	-0.01710600
C	-2.93002600	1.23528300	-0.38906700
C	-3.39099900	-1.01532200	0.42657300
C	-4.29107700	1.54010700	-0.29899100
C	-4.75042800	-0.70164100	0.49575100
C	-5.20419800	0.57452300	0.14008400
H	-2.22389800	1.97217100	-0.76237800
H	-4.63718000	2.53007800	-0.58723600
H	-3.02303400	-1.99577500	0.71178200
H	-5.45499300	-1.45567800	0.83919600
H	-6.26316300	0.81427700	0.20250500
C	2.50993700	-0.03029600	-0.00979000
C	2.94994700	1.30310700	0.10422400
C	3.47058200	-1.06025700	-0.03610400
C	4.31210600	1.59735300	0.19660700
H	2.22631000	2.11566600	0.11180800
C	4.83199300	-0.76151400	0.05182600
H	3.13694700	-2.09052700	-0.12397500
C	5.25991800	0.56665400	0.17045800
H	4.63446600	2.63315800	0.28327900
H	5.56156500	-1.56876600	0.03045800
H	6.32102100	0.79696000	0.24002500
H	-0.13851500	1.48912900	0.40773600

19) **TSB[2-3]**



Number of imaginary frequencies = 1 (146.4 cm^{-1})

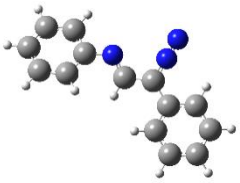
E_{total} = -704.025569 a.u

$G_{correction}$ = 0.168347 a.u

Cartesian coordinates:

N	1.25192400	0.65164900	-0.00701500
N	-0.02654500	2.66916600	-0.35049500
N	-0.90788000	1.92514100	-0.24551000
C	0.15924300	-0.03632700	0.06186200
C	-1.12330400	0.60740900	-0.05836900
C	2.53483400	0.09699100	0.00035800
C	3.57835800	0.85116600	0.57369800
C	2.83331300	-1.15419300	-0.58216100
C	4.88022200	0.34859500	0.59823700
C	4.13986900	-1.64614000	-0.55669000
C	5.16843800	-0.90239700	0.03644800
H	3.34318400	1.82289900	1.00150300
H	5.67440000	0.93747400	1.05301900
H	6.18530400	-1.28841800	0.04959300
H	4.35794100	-2.61024200	-1.01255800
H	2.04537800	-1.72171400	-1.07281200
C	-2.46280000	0.03844300	0.01589600
C	-3.60081400	0.86051800	-0.13895000
C	-2.66242900	-1.34037500	0.23991500
C	-4.88582800	0.32270800	-0.07278900
H	-3.47052300	1.92717000	-0.31272000
C	-3.95244500	-1.87205300	0.30455000
H	-1.81235900	-2.00619800	0.36615000
C	-5.07296800	-1.04793400	0.14924600
H	-5.74596200	0.97804700	-0.19559700
H	-4.08010200	-2.93870900	0.47862500
H	-6.07572700	-1.46590900	0.20050800
H	0.15384500	-1.11455900	0.23790900

20) **B3**



Number of imaginary frequencies = 0

E_{total} = -704.032961 a.u

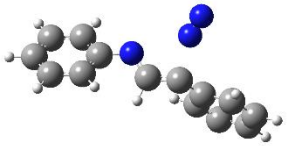
$G_{correction}$ = 0.168555 a.u

Cartesian coordinates:

N	1.32602200	0.85066800	-0.15014300
N	-1.12216300	3.15285900	-0.61710000
N	-1.12750700	2.03492400	-0.39879200
C	0.24122400	0.16746600	0.00371300
C	-1.08226000	0.73899700	-0.14111500
C	2.56691300	0.20102900	-0.04132200
C	3.63416600	0.90585400	0.55163200
C	2.80555000	-1.09546700	-0.54688200
C	4.89093700	0.31178000	0.67855000

C	4.07017500	-1.67798900	-0.42789800
C	5.11651200	-0.98315500	0.19150900
H	3.45157400	1.91347300	0.91859800
H	5.70080800	0.86402300	1.15172700
H	6.10051200	-1.43868500	0.27922800
H	4.24210700	-2.67405900	-0.83227700
H	2.00807300	-1.62698200	-1.06241800
C	-2.35721600	0.01230000	-0.00133900
C	-3.54813400	0.68502100	0.34124000
C	-2.40522300	-1.38113000	-0.21111000
C	-4.74787600	-0.01621700	0.47223900
H	-3.53528700	1.75858600	0.51776300
C	-3.60684400	-2.07813000	-0.06211700
H	-1.51035700	-1.92165800	-0.50791800
C	-4.78440200	-1.40244000	0.27760500
H	-5.65524300	0.52224400	0.73805700
H	-3.62259400	-3.15356000	-0.22720300
H	-5.71901800	-1.94800400	0.38596100
H	0.24382000	-0.89204200	0.29250300

21) **TSB[3-4]**



Number of imaginary frequencies = 1 (-275.3 cm^{-1})

E_{total} = -703.984999 a.u

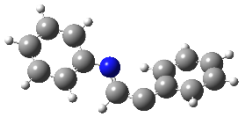
$G_{correction}$ = 0.162652 a.u

Cartesian coordinates:

C	-3.37735500	-0.01363900	-1.23612800
C	-2.50341400	0.07381800	-0.13060100
C	-3.00967900	-0.23613000	1.15228600
C	-4.33354100	-0.65305000	1.31231900
C	-5.18486700	-0.75943600	0.20464400
C	-4.69799800	-0.43334700	-1.06903300
N	-1.19599000	0.52106800	-0.36018400
N	0.97407600	2.24444800	-0.42964300
N	1.23744100	3.32561000	-0.44009400
C	-0.21725100	0.06260100	0.36894900
C	1.07594700	0.54516100	0.58365900
H	-2.36715400	-0.12171100	2.02363300
H	-4.70664300	-0.88323100	2.30917500
H	-6.21654400	-1.07976800	0.33373500
H	-5.35287000	-0.50373300	-1.93596100
H	-2.99346900	0.24524100	-2.22081700
C	2.32573500	-0.09806100	0.27065400
C	2.38725300	-1.27636400	-0.51942700
C	3.53321400	0.43808600	0.78573500
C	3.60613200	-1.90837800	-0.75361000
H	1.46607900	-1.68098000	-0.93253000

C	4.75367600	-0.17604900	0.51799500
H	3.48417400	1.33982400	1.39199800
C	4.78977200	-1.35448200	-0.24308000
H	3.64358900	-2.82053300	-1.34522900
H	5.67599500	0.24634000	0.91014500
H	5.74261000	-1.84208900	-0.43924000
H	-0.37020900	-0.80161500	1.04836000

22) **B4** (singlet species)



Number of imaginary frequencies = 0

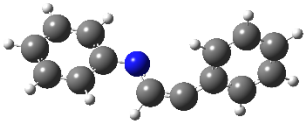
E_{total} = -594.501661 a.u

$G_{correction}$ = 0.160210 a.u

Cartesian coordinates:

C	2.67856400	1.30731100	-0.36636500
C	2.08068800	0.05764900	-0.05201800
C	2.92929700	-1.06839100	0.12133400
C	4.31558600	-0.92637100	0.05081900
C	4.89193600	0.32472100	-0.20696600
C	4.06266300	1.43905600	-0.41748300
N	0.70220400	0.03034600	0.05355800
C	0.12573100	-0.96328000	0.73605400
C	-1.12999900	-1.37000300	0.32516100
H	2.49174400	-2.05376800	0.26180200
H	4.95157500	-1.80081300	0.17806600
H	5.97319900	0.42736100	-0.26807400
H	4.50336700	2.41044900	-0.63438300
H	2.02485600	2.16068200	-0.53277800
C	-2.29440000	-0.59314300	0.13243800
C	-2.50328900	0.63363700	0.83523000
C	-3.32136700	-1.05828000	-0.74103100
C	-3.68537500	1.34609200	0.67416100
H	-1.72182000	0.99048500	1.50058300
C	-4.47933100	-0.31425100	-0.93190300
H	-3.16589100	-2.00077400	-1.26062500
C	-4.66757600	0.88029100	-0.21610500
H	-3.84673000	2.27144300	1.22302700
H	-5.24949800	-0.66362400	-1.61573000
H	-5.58693400	1.44756300	-0.34791700
H	0.69194800	-1.57164000	1.46115900

23) **B4'** (triplet species)



Number of imaginary frequencies = 0

E_{total} = -594.506408 a.u

$G_{correction}$ = 0.157045 a.u

Cartesian coordinates:

C	2.82760900	1.12935900	0.75306400
C	2.18311600	0.03258700	0.12450400
C	2.98015000	-0.87585900	-0.62298800
C	4.36052500	-0.70268600	-0.70286300
C	4.98565000	0.36813800	-0.04579700
C	4.20973300	1.28336300	0.68134200
N	0.80483600	-0.03353500	0.25940800
C	0.17488100	-1.19890500	0.05388200
C	-1.19351300	-1.28728200	0.07148300
H	2.51160400	-1.69060200	-1.16911000
H	4.95569100	-1.39912700	-1.29084400
H	6.06386400	0.49571700	-0.11350600
H	4.68652700	2.12245700	1.18422200
H	2.21037700	1.83386700	1.30588200
C	-2.38750000	-0.55076800	0.01020200
C	-3.47866300	-0.84202900	0.87884500
C	-2.55077200	0.48257500	-0.96125000
C	-4.66482200	-0.12053000	0.78799500
H	-3.36611800	-1.63207300	1.61756000
C	-3.74501100	1.19163600	-1.03890500
H	-1.72432100	0.70897400	-1.62956800
C	-4.80683200	0.89690900	-0.16883700
H	-5.48657000	-0.34861600	1.46381200
H	-3.85295900	1.98198500	-1.77926900
H	-5.73802100	1.45499400	-0.23690700
H	0.73876700	-2.13189800	-0.09219500

4.3 For the reaction between 4-azido-*N,N*-dimethylaniline and diamino acetylene

The mechanism for forming an indole derivative from the reaction between 4-azido-N,N-dimethylaniline and diamino acetylene was computed (Figure S27) to compare its free energy profile with that of the reaction between phenyl azide and diamino acetylene.

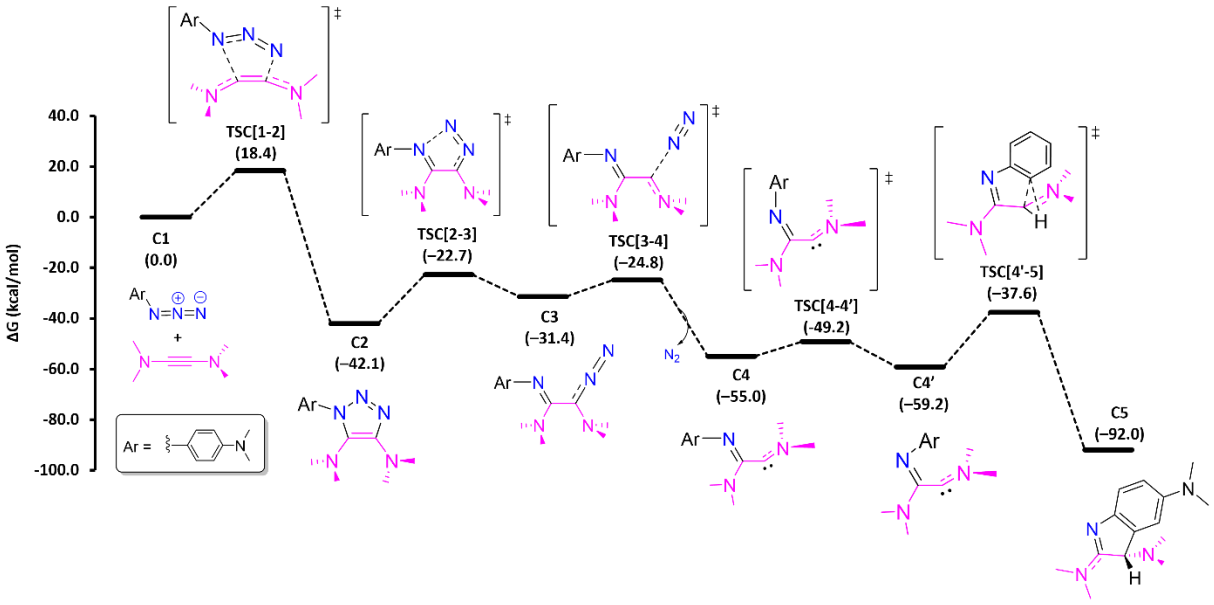
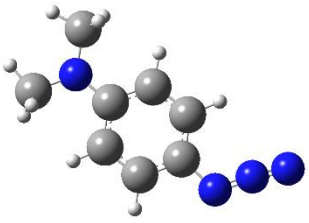


Figure S27. Computed mechanism for the formation of N^2,N^2,N^3,N^3,N^5,N^5-hexamethyl-3*H*-indole-2,3,5-triamine from the reaction of phenyl azide with N^1,N^1,N^2,N^2-tetramethylethyne-1,2-diamine.

Note: Details of diaminoacetylene and N_2 are provided above in the mechanism computed for the reaction between phenyl azide and diaminoacetylene.

24) **4-Azido-*N,N*-dimethylaniline**



Number of imaginary frequencies = 0

E_{total} = -529.621289 a.u

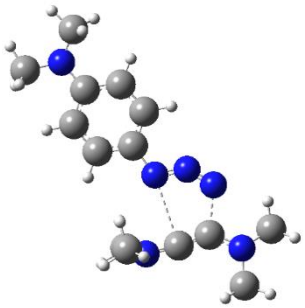
$G_{correction}$ = 0.133975 a.u

Cartesian coordinates:

C	-0.59406000	1.53428300	-0.00936300
C	-1.48306300	0.45071800	-0.00846400
C	-0.96568600	-0.85321900	-0.03009100
C	0.41064100	-1.06795200	-0.06027500

C	1.32785300	0.01485100	-0.08250100
C	0.78179400	1.32444700	-0.03957800
N	-2.87477900	0.75596700	0.02705700
N	-3.69544400	-0.15947300	0.03190900
N	-4.56329500	-0.91068800	0.03929900
H	-1.63510700	-1.71133300	-0.01637400
H	0.76749000	-2.09206700	-0.06738000
H	1.43242200	2.19196200	-0.03021600
H	-0.99006500	2.54662500	0.02067400
N	2.69878800	-0.19771500	-0.15797400
C	3.60229600	0.91911300	0.09617400
H	4.63160800	0.57823200	-0.03878000
H	3.42562900	1.73272800	-0.61744400
H	3.49714800	1.32369000	1.11790100
C	3.22099500	-1.53942600	0.07732500
H	2.80759600	-2.25068900	-0.64770000
H	4.30547200	-1.52449600	-0.05537400
H	2.99630000	-1.90819100	1.09328900

25) **TSC[1-2]**



Number of imaginary frequencies = 1 (279.5 cm^{-1})

E_{total} = -874.760526 a.u

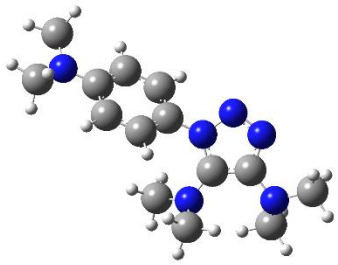
$G_{correction}$ = 0.288806 a.u

Cartesian coordinates:

N	-0.36756400	-0.23718000	-0.34530400
N	-1.01244400	-1.19908900	0.19597100
N	-2.14332700	-1.52737900	0.40423300
C	-3.09692000	0.98413700	-0.17621700
C	-3.52890300	-0.23590500	-0.10546000
N	-4.70084800	-0.88858300	-0.14008200
N	-2.47479900	1.96752700	0.42865100
C	-1.65346600	2.88993900	-0.36081700
H	-1.56913600	3.85110700	0.15761500
H	-0.65368500	2.44685300	-0.49069100
H	-2.11465500	3.03203600	-1.34005300
C	-2.08537400	1.84683500	1.84519400
H	-1.08829500	1.38434700	1.90290100
H	-2.05573600	2.83938900	2.30816100
H	-2.81074700	1.21565900	2.36167500
C	-5.92778100	-0.08719000	-0.15894500
H	-6.78056300	-0.72141700	0.10836400

H	-5.84322000	0.72394200	0.56950700
H	-6.10289000	0.34530400	-1.15844900
C	-4.79882500	-2.20386100	-0.78273200
H	-5.01178700	-2.09812300	-1.85920600
H	-3.85649300	-2.73662500	-0.65296900
H	-5.60924000	-2.77571600	-0.31642800
C	1.04193400	-0.30855700	-0.25889100
C	1.78003500	0.62567500	-1.00617000
C	1.76100100	-1.21028300	0.54896900
C	3.17345900	0.65885600	-0.96015700
C	3.15383100	-1.18550500	0.59686700
C	3.90631900	-0.25923500	-0.16846600
H	1.24616400	1.33550000	-1.63529100
H	3.68775500	1.40555000	-1.55614300
H	1.21881800	-1.93480100	1.15318600
H	3.65502300	-1.89945500	1.24261000
N	5.30634200	-0.26780100	-0.15955200
C	5.98536700	-0.98167200	0.91626000
H	7.06531900	-0.90662000	0.76297800
H	5.74270800	-0.57774700	1.91616600
H	5.72305300	-2.04574100	0.90249800
C	6.00572100	0.89750300	-0.68874300
H	5.75360500	1.05530800	-1.74368400
H	5.77117300	1.82462800	-0.13412600
H	7.08293300	0.71971400	-0.63018600

26) Intermediate **C2**



Number of imaginary frequencies = 0

E_{total} = -874.866244 a.u

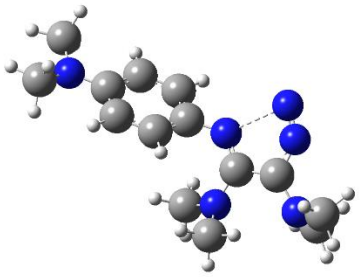
$G_{correction}$ = 0.298165 a.u

Cartesian coordinates:

N	0.77428900	-0.75065200	-0.13733700
N	1.29072100	-1.97422600	-0.44900900
N	2.60454100	-1.84505400	-0.48061800
C	1.78001600	0.17784300	0.05564200
C	2.95147600	-0.55809900	-0.18660800
N	4.27165500	-0.09471500	-0.19306500
N	1.62768700	1.51027900	0.41130000
C	0.58825800	1.90726700	1.35778300
H	0.92084700	2.81464700	1.88003800
H	-0.38267200	2.11621000	0.88058100
H	0.44569100	1.11284500	2.09640500

C	1.97660000	2.50576500	-0.60234900
H	1.15393500	2.68273300	-1.31893200
H	2.21681800	3.45606000	-0.10868600
H	2.85872900	2.16580700	-1.15432000
C	4.67614300	0.64414600	1.01028200
H	5.62349400	1.15839100	0.81135800
H	3.91294100	1.38608000	1.26080900
H	4.81422500	-0.02807100	1.87756200
C	5.27253400	-1.07148600	-0.62532200
H	5.41354000	-1.88638000	0.10700100
H	4.96844200	-1.51650100	-1.57666200
H	6.22652700	-0.54883700	-0.75951500
C	-0.63575000	-0.54814400	-0.09896300
C	-1.42717000	-1.25823800	0.80807500
C	-1.23925500	0.34923300	-0.98527000
C	-2.80557700	-1.06389500	0.84412600
C	-2.61473500	0.56127900	-0.94929500
C	-3.43831100	-0.13035400	-0.02035500
H	-0.62776300	0.87921600	-1.71149500
H	-3.04818400	1.25912200	-1.65699900
H	-3.38910300	-1.63929000	1.55417200
H	-0.95715500	-1.96779700	1.48433300
N	-4.80164800	0.10184100	0.04470100
C	-5.64325000	-0.79160200	0.83381800
H	-5.33329800	-0.79150100	1.88602900
H	-6.67477600	-0.43466000	0.79127900
H	-5.61567300	-1.83013100	0.46323100
C	-5.44500500	0.88823300	-1.00217700
H	-5.01105500	1.89431400	-1.05640700
H	-5.35693200	0.41742400	-1.99591000
H	-6.50514500	0.99632800	-0.76199200

27) **TSC[2-3]**



Number of imaginary frequencies = 1 (163.6 cm^{-1})

E_{total} = -874.830156 a.u

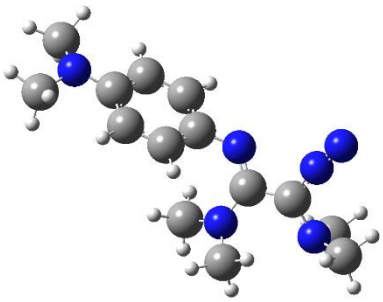
$G_{correction}$ = 0.292990 a.u

Cartesian coordinates:

N	0.64614300	-0.90870600	0.24637200
N	2.19040600	-2.68384400	-0.84792800
N	2.91170200	-1.80635800	-0.61261200
C	1.60528700	-0.02527400	0.11817600
C	2.94286900	-0.49078600	-0.29144900

N	4.13243100	0.20590800	-0.07529100
N	1.49975900	1.31746900	0.42711300
C	0.56262700	1.78441000	1.44108200
H	1.05958100	2.55633600	2.04502300
H	-0.34975000	2.21292800	1.00007300
H	0.27427000	0.95730600	2.09249600
C	2.18168900	2.36631700	-0.32378000
H	1.43638800	3.11692500	-0.62986300
H	2.95701300	2.86328800	0.27637300
H	2.64560300	1.95217200	-1.21889000
C	4.70322300	0.04114200	1.26744300
H	5.50393000	0.77591700	1.41948400
H	3.91966000	0.21657900	2.01177500
H	5.11757600	-0.97330000	1.42285000
C	5.11452000	0.09226300	-1.15014400
H	5.53187300	-0.93060700	-1.23395600
H	4.64199600	0.35102200	-2.10397200
H	5.94394200	0.78540000	-0.96457500
C	-0.70632900	-0.58338800	0.16364900
C	-1.63606600	-1.26172200	0.97638100
C	-1.22622000	0.33518900	-0.77470400
C	-3.00381800	-1.01008500	0.89449200
C	-2.59253300	0.58710300	-0.87134100
C	-3.52474200	-0.06050500	-0.02067400
H	-1.26441000	-2.00035900	1.68419700
H	-3.66837700	-1.56519200	1.54843900
H	-2.93254200	1.29135400	-1.62383700
H	-0.54346000	0.84535400	-1.45149500
N	-4.88973100	0.23220900	-0.07461600
C	-5.82389800	-0.68209100	0.57307900
H	-5.61257800	-0.75690100	1.64598700
H	-6.83762300	-0.28810300	0.46235300
H	-5.79183000	-1.69869300	0.14173100
C	-5.40114200	0.95919000	-1.23105900
H	-4.91571300	1.93803100	-1.31949000
H	-5.25146600	0.41103300	-2.17868200
H	-6.47185200	1.13220000	-1.09419000

28) Intermediate **C3**



Number of imaginary frequencies = 0

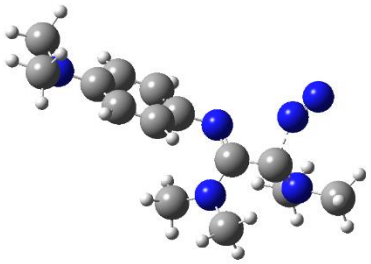
E_{total} = -874.844072 a.u

$G_{correction}$ = 0.293069 a.u

Cartesian coordinates:

C	-1.64525400	-1.27945600	1.00426500
C	-0.73280400	-0.62343300	0.15539600
C	-1.28076200	0.19898500	-0.85255700
C	-2.65761100	0.36747200	-0.99572900
C	-3.57450800	-0.28668900	-0.13626100
C	-3.02320000	-1.10689600	0.87930500
N	0.63813200	-0.88647500	0.27587400
N	3.00612000	-1.60759100	-0.74615700
N	3.36115100	-2.57238200	-1.25491500
C	1.54067400	0.05220500	0.11850100
C	2.88632700	-0.37333700	-0.25018300
N	4.08631800	0.24282700	0.16954500
N	1.37687600	1.40863200	0.34388600
C	4.51864100	-0.11451200	1.52860400
H	4.92243900	-1.14149900	1.58405200
H	5.29775400	0.58529900	1.85448300
H	3.66288400	-0.03365000	2.20578900
C	5.16855700	0.25602000	-0.81245600
H	5.96418200	0.92203200	-0.45950600
H	5.60961300	-0.74568500	-0.97980000
H	4.78772700	0.63086300	-1.76830700
C	2.03954400	2.42283400	-0.46746600
H	2.68432700	1.94980800	-1.20871400
H	1.28246000	3.02382100	-0.99700800
H	2.64735800	3.09518400	0.15430500
C	0.34836600	1.90577900	1.24526900
H	0.75707800	2.76197200	1.79941100
H	-0.55838000	2.22808100	0.71077200
H	0.06737100	1.12427800	1.95416400
H	-0.61124000	0.70897400	-1.54330200
H	-3.01519500	1.01004800	-1.79417300
H	-1.25301800	-1.92644500	1.78716600
H	-3.67084900	-1.62801900	1.57700600
N	-4.95924500	-0.15559600	-0.30444900
C	-5.82800900	-0.57226900	0.79052700
H	-5.64622100	-0.00283500	1.72060600
H	-6.86925800	-0.42604800	0.49051800
H	-5.69352900	-1.63784900	1.00870200
C	-5.45163500	0.95051400	-1.11757400
H	-5.16066500	1.93848000	-0.71544900
H	-5.07723900	0.87453300	-2.14492300
H	-6.54300900	0.89944800	-1.16014000

29) **TSC[3-4]**



Number of imaginary frequencies = 1 (380.2 cm^{-1})

E_{total} = -874.830464 a.u

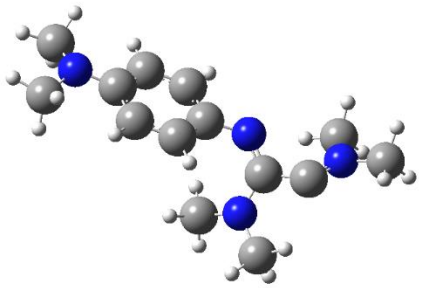
$G_{correction}$ = 0.289961 a.u

Cartesian coordinates:

C	-1.57536400	-0.98522300	1.20513900
C	-0.69299400	-0.46731800	0.23645400
C	-1.27818900	0.19837700	-0.86271400
C	-2.65828400	0.36011500	-0.97427300
C	-3.54150500	-0.12100400	0.02422700
C	-2.95647600	-0.81745800	1.11049600
N	0.67782100	-0.73842100	0.33504700
N	2.75651100	-1.95734800	-0.69351600
N	3.25389000	-2.84059100	-1.18854200
C	1.58754700	0.14939000	0.00062700
C	2.90425300	-0.25749700	-0.48265000
N	4.02696000	0.04237600	0.18182700
N	1.41342600	1.52737700	0.02979600
C	4.09653500	0.09949100	1.65219600
H	4.45687200	-0.85894600	2.05656600
H	4.78483400	0.89489300	1.96214900
H	3.09987600	0.30239400	2.04934800
C	5.31315600	-0.12589700	-0.49383800
H	6.03742600	0.60103300	-0.10683900
H	5.71384800	-1.13915400	-0.32574600
H	5.17050000	0.02873800	-1.56569200
C	2.25620400	2.44528900	-0.72782900
H	2.71774200	1.91777100	-1.56646700
H	1.63248800	3.26022500	-1.12078200
H	3.05339100	2.88598100	-0.10756300
C	0.45247600	2.15549400	0.92679600
H	0.93655300	3.01051900	1.41921300
H	-0.44096000	2.51164400	0.39262700
H	0.13123800	1.44527600	1.69060000
H	-0.63449100	0.58026300	-1.65324400
H	-3.04560000	0.86511700	-1.85366500
H	-3.57958800	-1.24131300	1.89150200
H	-1.15657000	-1.53304400	2.04788700
N	-4.92449900	0.09662600	-0.05106900
C	-5.79420900	-0.71292600	0.79528900
H	-5.56063600	-0.55502200	1.85432900
H	-6.83057700	-0.40249300	0.63606500
H	-5.71310300	-1.79432400	0.58046200

C	-5.48898900	0.49334000	-1.33625800
H	-5.05729100	1.44281500	-1.67294500
H	-5.32413500	-0.26167400	-2.12685300
H	-6.56555100	0.64413600	-1.21772600

30) Intermediate **C4**



Number of imaginary frequencies = 0

E_{total} = -765.371115 a.u

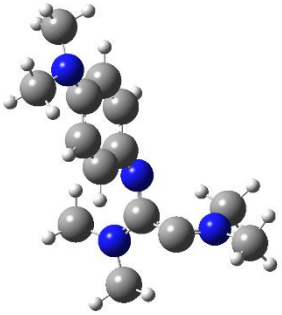
$G_{correction}$ = 0.286653 a.u

Cartesian coordinates:

C	-1.09487500	-1.39089000	0.65568900
C	-0.26062500	-0.48800100	-0.03437900
C	-0.90247500	0.48481400	-0.83164500
C	-2.29262900	0.56154100	-0.92051500
C	-3.12989800	-0.33932300	-0.21918800
C	-2.48552700	-1.31157500	0.58445500
N	1.12688000	-0.65550900	0.01218300
C	1.98972200	0.33403200	-0.01824300
C	3.20899900	0.06431600	-0.78110800
N	4.03473600	-0.84995900	-0.34787200
N	1.82007400	1.61252600	0.47009200
C	3.93396800	-1.60852600	0.92410300
H	3.60820400	-2.63369300	0.71455800
H	4.92055400	-1.63468300	1.40051400
H	3.20478100	-1.13024400	1.57718300
C	5.16792000	-1.27780100	-1.18692100
H	6.10973600	-1.13336000	-0.64256900
H	5.06253300	-2.34281700	-1.43145700
H	5.16184000	-0.68186200	-2.10003000
C	2.81116100	2.65559000	0.22825600
H	3.47120700	2.34139100	-0.58603300
H	2.30455600	3.58657700	-0.06156100
H	3.41564000	2.85177100	1.12741000
C	0.74141500	1.95574600	1.38610700
H	1.14262200	2.60696200	2.17319600
H	-0.08240300	2.47665600	0.87612600
H	0.33806000	1.05188300	1.84664000
H	-0.63152900	-2.15971300	1.27218600
H	-3.06891300	-2.02678500	1.15573100
H	-2.72207900	1.33138100	-1.55412200
H	-0.29598100	1.18803600	-1.39984600
N	-4.52892600	-0.29579500	-0.34431600

C	-5.32407800	-0.98832000	0.66352400
H	-6.38356000	-0.87340600	0.41782700
H	-5.10011700	-2.06103900	0.66475700
H	-5.15482200	-0.59853700	1.68479000
C	-5.12657400	0.92227000	-0.87947500
H	-6.21130200	0.79159900	-0.92851000
H	-4.90654400	1.81413900	-0.26316200
H	-4.77084900	1.11366600	-1.89819600

31) **TSC[4-4']**



Number of imaginary frequencies = 1 (91.3 cm^{-1})

E_{total} = -765.360426 a.u

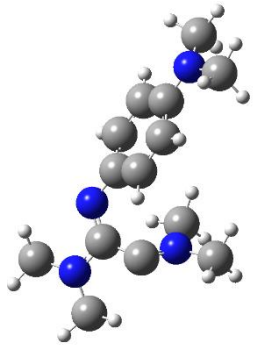
$G_{correction}$ = 0.285312 a.u

Cartesian coordinates:

N	-1.00083100	0.11972900	-0.87131700
C	-2.01096800	0.45745400	-0.08363600
C	-2.47843900	-0.60505800	0.75571500
N	-3.35528100	-1.48357600	0.34002100
N	-2.53786600	1.71077600	-0.03878600
C	-4.08078100	-1.43729400	-0.95029400
H	-5.16138000	-1.45958500	-0.76341900
H	-3.81200600	-0.52650800	-1.48629400
H	-3.80835700	-2.31006100	-1.55575800
C	-3.64222300	-2.68876000	1.13445600
H	-4.71831200	-2.75222400	1.34042100
H	-3.33761600	-3.58251900	0.57371800
H	-3.08187700	-2.62640100	2.06778100
C	-3.78311300	1.98758200	0.66562900
H	-4.04939800	1.12807700	1.28818900
H	-3.65725600	2.86448400	1.31311200
H	-4.60150800	2.18698400	-0.04136300
C	-1.87722400	2.83006700	-0.69979700
H	-2.56249100	3.30512900	-1.41453300
H	-1.56389900	3.57772300	0.04200600
H	-1.00349200	2.44966200	-1.23292000
C	0.33012500	-0.00213100	-0.53634400
C	1.24543700	-0.54705800	-1.46656600
C	0.87513400	0.44540700	0.69259000
C	2.60896800	-0.64673200	-1.18787500
H	0.86813600	-0.88812600	-2.42943600

C	2.23741300	0.33938800	0.97480000
H	0.21119600	0.87701500	1.44001900
C	3.14828300	-0.22352600	0.04983100
H	3.25344100	-1.07030400	-1.95218000
H	2.58508400	0.70314300	1.93719500
N	4.51753800	-0.38893100	0.36099600
C	5.43522300	-0.58352700	-0.75599600
H	6.44956900	-0.70237500	-0.36341600
H	5.18656200	-1.49699100	-1.30754300
H	5.43017800	0.26283400	-1.46974800
C	5.05597000	0.42042100	1.44840800
H	4.96178600	1.50797200	1.26335000
H	4.54845900	0.18928700	2.39161100
H	6.11543000	0.17939900	1.57728700

32) Intermediate **C4'**



Number of imaginary frequencies = 0

E_{total} = -765.378872 a.u

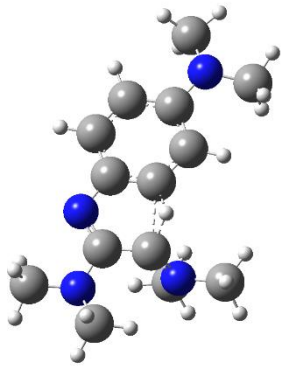
$G_{correction}$ = 0.287848 a.u

Cartesian coordinates:

C	0.82763600	-1.57226900	0.70214000
C	-0.03134100	-0.93254800	-0.21506500
C	0.57514100	-0.05612500	-1.13997900
C	1.94839700	0.18993400	-1.12954200
C	2.80724000	-0.44142000	-0.19681000
C	2.20045500	-1.32595500	0.72772600
N	-1.39493900	-1.25302700	-0.18041100
C	-2.33516500	-0.34905300	-0.31787400
C	-2.10233500	1.08749000	-0.57038400
N	-1.57006900	1.78261000	0.39799300
N	-3.65198700	-0.75934000	-0.39353900
H	0.39310500	-2.26529200	1.42087300
H	2.79924100	-1.83927300	1.47340700
H	2.34935700	0.87560200	-1.86953800
H	-0.04457300	0.44605000	-1.88007400
C	-1.14863400	3.17360000	0.15738700
H	-1.63786500	3.84225800	0.87626100
H	-0.06131000	3.24830200	0.28711200
H	-1.42476600	3.44168700	-0.86268900
C	-1.21263900	1.29719500	1.75630600

H	-0.12778700	1.14932200	1.80797800
H	-1.51739200	2.04352900	2.49794500
H	-1.71200200	0.34681400	1.94524000
C	-4.70882300	0.20463500	-0.11548100
H	-4.91798500	0.29647500	0.96427600
H	-4.40902800	1.18676600	-0.50017400
H	-5.62909600	-0.10571800	-0.62367800
C	-3.97409200	-2.16330900	-0.17635100
H	-4.98034500	-2.35296600	-0.56692600
H	-3.24913800	-2.79049700	-0.69872300
H	-3.95248800	-2.43079100	0.89369100
N	4.19463000	-0.22940500	-0.21289900
C	4.95848200	-0.61776900	0.96733700
H	4.86385900	-1.69347400	1.15393800
H	6.01643500	-0.40596300	0.78920600
H	4.64010200	-0.07930700	1.87954100
C	4.69922000	0.93583600	-0.93034500
H	4.43911000	0.88040200	-1.99346900
H	4.30753500	1.88885600	-0.52794200
H	5.79033500	0.94989500	-0.85866300

33) **TSC[4'-5]**



Number of imaginary frequencies = 1 (1089.3 cm^{-1})

E_{total} = -765.340552 a.u

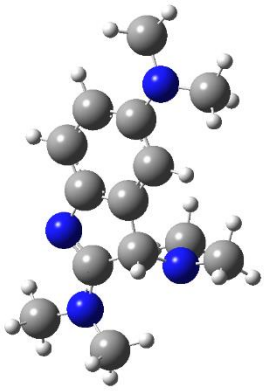
$G_{correction}$ = 0.283866 a.u

Cartesian coordinates:

C	1.20767800	-2.09084300	0.16192900
C	0.13834000	-1.19022500	-0.02211200
C	0.48043800	0.14528000	-0.26537400
C	1.78237300	0.61053000	-0.38458600
C	2.86017000	-0.29643100	-0.18430500
C	2.52916200	-1.64914300	0.09477700
N	-1.19570500	-1.58950100	0.00103700
C	-2.05483900	-0.60213600	-0.16756400
C	-1.65318100	0.76338600	-0.51023200
N	-2.00969600	1.83275300	0.22878900
N	-3.41568500	-0.85796200	-0.03312800
H	0.99587400	-3.14553800	0.33362100
H	3.31945000	-2.37780900	0.24506900

H	1.96968500	1.65984600	-0.59296200
H	-0.54053000	0.78098700	-1.01056800
C	-1.66067400	3.15748300	-0.28159300
H	-2.32233900	3.91428200	0.15528500
H	-0.61918300	3.41056600	-0.02033400
H	-1.76711800	3.16064700	-1.36934400
C	-2.09636000	1.74441700	1.69335900
H	-1.09402700	1.86804600	2.13574200
H	-2.76028400	2.52771500	2.07632500
H	-2.49287800	0.76591400	1.97240500
C	-4.38818400	-0.08504300	-0.80770100
H	-5.36521800	-0.14810700	-0.31506600
H	-4.09140200	0.96293400	-0.85738100
H	-4.48811800	-0.47817200	-1.83448000
C	-3.81421800	-2.24386200	0.20576900
H	-3.73871100	-2.85786200	-0.70715700
H	-3.16787800	-2.68622000	0.96596400
H	-4.85405600	-2.24643800	0.55120400
N	4.19840000	0.12147600	-0.26002300
C	5.19601100	-0.63685600	0.49315100
H	6.17619100	-0.17538600	0.34353300
H	4.97799400	-0.66197100	1.57600600
H	5.26071100	-1.66838400	0.13082600
C	4.46194100	1.55020100	-0.37401100
H	3.97106000	1.96110900	-1.26341500
H	4.11887000	2.12327000	0.50822800
H	5.53875700	1.70266800	-0.48928200

34) Product **C5**



Number of imaginary frequencies = 0

E_{total} = -765.436090 a.u

$G_{correction}$ = 0.292743 a.u

Cartesian coordinates:

C	1.01831200	-2.23151100	0.32983100
C	-0.05991700	-1.38781600	0.06845200
C	0.18040100	-0.05168400	-0.31125500
C	1.46645700	0.44722500	-0.45664100
C	2.58287700	-0.40027900	-0.19962400

C	2.32449100	-1.73210400	0.20854400
N	-1.44030000	-1.70659400	0.11707000
C	-2.09563000	-0.60786000	-0.17856200
C	-1.18392200	0.61014500	-0.47783100
N	-1.50423000	1.75845100	0.38525500
N	-3.45325200	-0.51832600	-0.17234200
H	0.85506700	-3.26504900	0.62975000
H	3.14854900	-2.40222100	0.42910400
H	1.61851200	1.47151900	-0.77607700
H	-1.33345600	0.93438200	-1.51819400
C	-0.83696900	2.99282400	-0.02420300
H	-1.27464400	3.83409500	0.52830700
H	0.25159300	2.99172900	0.17173200
H	-0.99731100	3.16154900	-1.09608000
C	-1.29882700	1.48077200	1.80848600
H	-0.23319100	1.34247200	2.07004600
H	-1.69473600	2.31961800	2.39326900
H	-1.84444200	0.57385300	2.08998600
C	-4.13973800	0.56451400	-0.87468600
H	-5.12042800	0.72043800	-0.41160800
H	-3.56170200	1.48495200	-0.77689100
H	-4.29202600	0.32113700	-1.93964200
C	-4.22884600	-1.73580600	0.05670400
H	-4.31382600	-2.33877900	-0.86161500
H	-3.73524500	-2.34059400	0.82027900
H	-5.23255900	-1.45537700	0.39326900
N	3.89374100	0.07066400	-0.37503000
C	4.10543400	1.51426900	-0.39999400
H	3.58284200	1.97197200	-1.24805100
H	3.76329900	2.01141300	0.52645000
H	5.17302000	1.71241300	-0.52779700
C	4.98512900	-0.71483400	0.18971100
H	4.91173200	-0.82186900	1.28782500
H	5.00834900	-1.71782900	-0.25165400
H	5.93337600	-0.22630900	-0.05066200

4.3 EDA-NOCV analysis on the cycloaddition transition state TSA[1-2]

Table S1. EDA-NOCV computations at the B3LYP-D3/TZ2P level of theory on transition states **TSA[1-2]** and **TSB[1-2]** using alkyne and azide as interacting fragments. Energy values are given in kcal/mol.

	TSA[1-2]	**TSB[1-2]**
$\Delta E_{\text{distortion (alkyne)}}$	6.2	9.8
$\Delta E_{\text{distortion (azide)}}$	19.7	20.6
$\Delta E_{\text{interaction}}$[a]	-15.7	-11.2
$\Delta E_{\text{Pauli repulsion}}$	98.9	76.7
$\Delta E_{\text{electrostatic interaction}}$	-49.4	-40.3
$\Delta E_{\text{dispersion}}$	-7.2	-5.9
$\Delta E_{\text{orbital interaction}}$	-58.0	-41.7
$\Delta E^{\ddagger}$	10.1	19.1

[a] $\Delta E_{\text{interaction}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{disp}} + \Delta E_{\text{orb}}$.

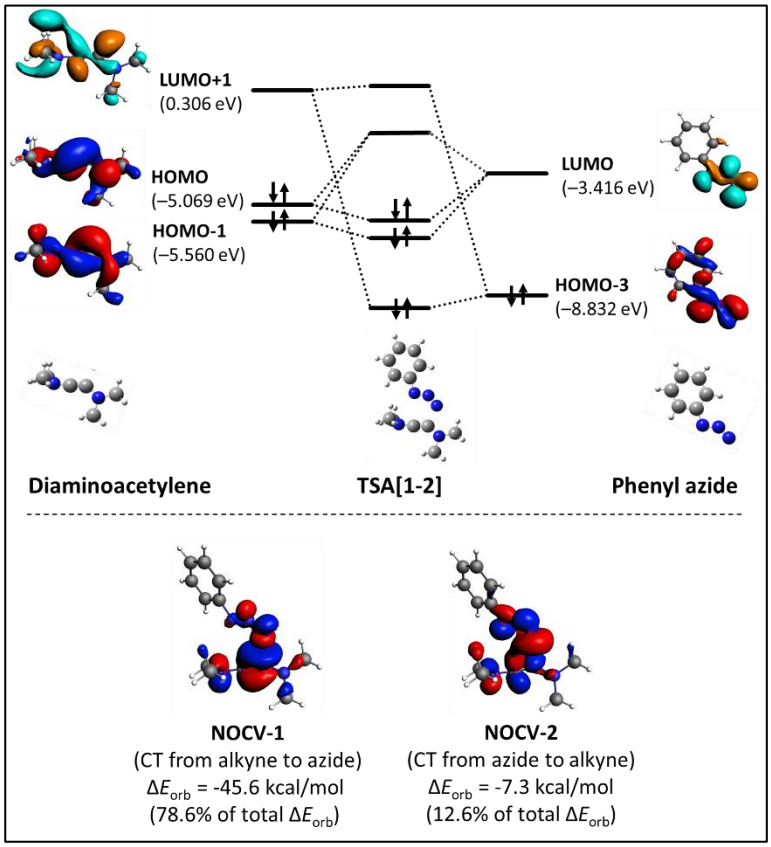


Figure S28. Frontier molecular orbital interaction diagram (top) and their two main deformation density plots (isovalue: 0.0015 a.u.) derived from the EDA-NOCV analysis for the interaction between bis(dimethylamino)acetylene and phenyl azide in **TSA[1-2]**. Charge flow in the deformation density plots occurs from red to blue.

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