Ring-fused hexahydro-1,2,4,5-tetrazines: synthesis, structure, and mechanistic studies on isolable rotational isomers

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Experimental section

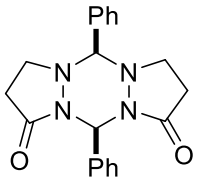
General.

Melting points were determined on a Yanaco MP-13 melting point apparatus and are uncorrected. IR spectra were taken with a JASCO FT/IR-4200 spectrophotometer and are reported in wavenumbers (cm^{-1}). ^{1}H NMR spectra were recorded on BRUKER AVANCE III Fourier 300 (300 MHz) and Ascend 500 (500 MHz) spectrometers. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. $^{13}C\{^{1}H\}$ NMR spectra were recorded on BRUKER AVANCE III Fourier 300 (75 MHz) and Ascend 500 (125 MHz) spectrometers using broadband proton decoupling. Chemical shifts are expressed in parts per million using the middle resonance of $CDCl_3$ (77.0 ppm) as an internal standard. Hydrogen multiplicity (C, CH, CH_2, CH_3) information was obtained from carbon DEPT spectra. High-resolution mass spectra were obtained on BRUKER micrOTOF II ESI-TOF spectrometer. Optical rotations were recorded with a JASCO P-1010 polarimeter. X-ray diffraction data were collected at 93 K using a Bruker SMART APEX2 diffractometer [Mo Kα radiation (λ = 0.71073 Å)]. Thin-layer chromatography (TLC) was performed using TLC aluminum sheets from Merck (silica gel 60 F254, 200 μm), and flash chromatography was performed using silica gel from Fuji Silysia Chemical (PSQ60B, 60 μm). Products were visualized by ultraviolet (UV) light and TLC stains. Unless otherwise noted, all reactions were carried out under an argon atmosphere in dried glassware.

Materials.

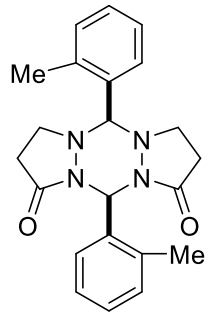
All reagents and solvents were commercial grade and purified prior to use when necessary. Azomethine imines **1a** and **1b** were prepared by the procedure reported previously.[1]

Synthesis of hexahydro-1,2,4,5-terrazine 2a. A solution of azomethine imine **1a** (34.8 mg, 0.20 mmol) and AgOTf (5.1 mg, 0.020 mmol, 10 mol%) in 1,2-dichloroethane (2.0 mL) was stirred at 85 ºC for 24 h. After cooling the mixture at room temperature, the reaction mixture was filtered through a plug of Celite and silica gel (2 g) with EtOAc/MeOH (10:1, v/v, 30 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (11 g) with EtOAc/Hexane (1:1 – 2:1, v/v) to provide hexahydro-1,2,4,5-terrazine **2a** (18.3 mg, 53%).



(5*s,11*s**)-5,11-diphenyltetrahydrodipyrazolo[1,2-*a*:1',2'-*d*][1,2,4,5]tetrazine-1,9(5*H*,11*H*)-dione (2a)**:[2] Colorless plates; mp 222-223 ºC; R_f = 0.30 (EtOAc:Hexane = 9:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 2925, 1718, 1686, 1380, 1256, 1079, 842, 756, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77-7.69 (m, 2H), 7.69-7.60 (m, 1H), 7.50-7.27 (m, 7H), 7.24 (s, 1H), 3.98 (s, 1H), 3.11 (ddd, *J* = 10.9, 9.3, 6.1 Hz), 2.82 (dt, *J* = 10.9, 8.6 Hz), 2.62 (ddd, *J* = 16.9, 8.6, 6.1 Hz), 2.45 (ddd, *J* = 16.9, 9.3, 8.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 169.6 (C), 135.9 (C), 133.8 (C), 130.3 (CH), 130.0 (CH), 129.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.3 (CH), 91.5 (CH), 62.3 (CH), 46.0 (CH_2), 29.7 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{20}N_4NaO_2$ $[M+Na]^+$ 371.1478, found 371.1481.

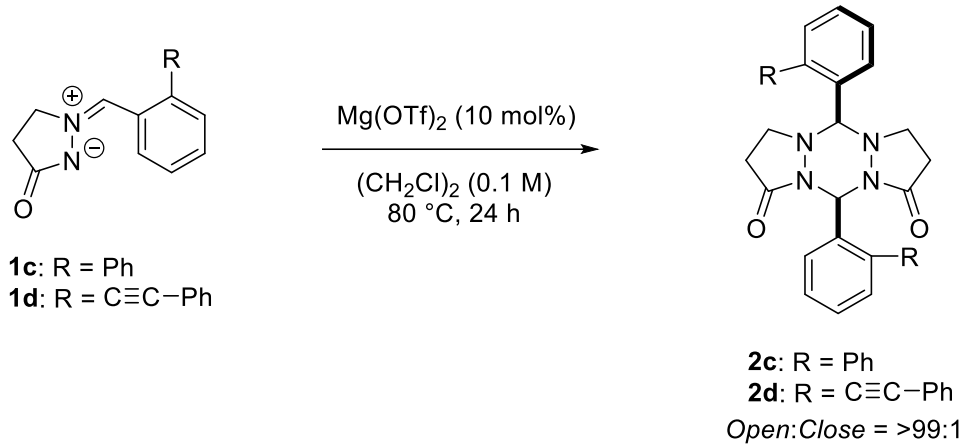
Synthesis of hexahydro-1,2,4,5-terrazine 2b. A solution of azomethine imine **1b** (37.6 mg, 0.20 mmol) and $Mg(OTf)_2$ (6.4 mg, 0.020 mmol, 10 mol%) in 1,2-dichloroethane (2.0 mL) was stirred at 80 ºC for 24 h. After cooling the mixture at room temperature, the reaction mixture was filtered through a plug of Celite and silica gel (0.1 g) with EtOAc/MeOH (4:1, v/v, 50 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (10 g) with EtOAc/Hexane (1:1 – 2:1, v/v) to provide hexahydro-1,2,4,5-terrazine **2b** (19.5 mg, 52%, *open*:*close* = 80:20).



(5*s,11*s**)-5,11-di-*o*-tolyltetrahydrodipyrazolo[1,2-*a*:1',2'-*d*][1,2,4,5]tetrazine-1,9(5*H*,11*H*)-dione**

(2b): White powder; mp 259-261 ºC; R_f = 0.34 (EtOAc:Hexane = 2:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 1718, 1685, 1460, 1365, 1284, 1260, 1076, 845, 762, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13-8.06 (m, 1H×80/100), 7.91-7.86 (m, 1H×20/100), 7.74-7.67 (m, 1H×80/100), 7.38 (s, 1H×80/100), 7.36-7.15 (m, 6H×80/100+8H×20/100), 4.51 (s, 1H×80/100), 4.20 (s, 1H×20/100), 3.16 (dt, *J* = 11.5, 8.7 Hz, 2H), 2.94-2.75 (m, 2H), 2.71-2.38 (m, 10H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 170.3 (C, *open*), 170.2 (C, *close*), 139.4 (C, *close*), 136.81 (C, *open*), 136.78 (C, *open*), 133.6 (C, *open*), 133.5 (C, *close*), 132.8 (CH, *close*), 132.7 (C, *open*), 132.1 (CH, *close*), 131.5 (C, *close*), 130.8 (CH, *open*), 130.3 (CH, *open*), 130.0 (CH, *close*), 129.59 (CH, *open*), 129.57 (CH, *open*), 128.6 (CH, *open*), 128.4 (CH, *close*), 127.8 (CH, *open*), 127.7 (CH, *close*), 127.1 (CH, *open*), 125.6 (CH, *open*), 125.4 (CH, *close*), 93.7 (CH, *close*), 84.6 (CH, *open*), 60.1 (CH, *close*), 59.7 (CH, *open*), 45.7 (CH_2, *close*), 45.3 (CH_2, *open*), 29.6 (CH_2, *open*), 29.1 (CH_2, *close*), 20.5 (CH_3, *close*), 19.9 (CH_3, *open*), 19.4 (CH_3, *open* and *close*). One aromatic tertiary carbon and two methine carbons of a *close* rotamer are overlapped; HRMS (ESI-TOF) m/z: calcd for $C_{22}H_{24}N_4NaO_2$ $[M+Na]^+$ 399.1791, found 399.1810.

Synthesis of hexahydro-1,2,4,5-terrazines 2c and 2d.



1c: R = Ph
1d: R = C≡C−Ph

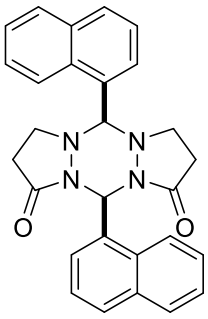
2c: R = Ph
2d: R = C≡C−Ph
Open:*Close* = >99:1

(5*s,11*s**)-5,11-di([1,1'-biphenyl]-2-yl)tetrahydrodipyrazolo[1,2-*a*:1',2'-*d*][1,2,4,5]tetrazine-1,9(5*H*,11*H*)-dione (2c).** Isolated as white powder (12.7 mg, 25%, *open*:*close* = >99:1) after silica gel column chromatography (10 g, Hexane:EtOAc = 10:1 – 1:1, v/v) following the procedure for synthesis of **2b** using azomethine imine **1c** (50.1 mg, 0.20 mmol). mp 211-213 ºC; R_f = 0.26 (EtOAc:Hexane = 1:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3024, 2944, 1726, 1478, 1362, 1276, 1251, 1181, 1069, 844, 759, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07-7.99 (m, 1H), 7.80-7.73 (m, 1H), 7.50-7.20 (m, 15H), 7.17-7.09 (m, 2H), 4.14 (s, 1H), 3.02 (dt, *J* = 11.7, 9.0 Hz, 2H), 2.81 (ddd, *J* = 11.7, 8.2, 5.7 Hz, 2H), 2.17-1.97 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 170.1 (C), 143.4 (C), 142.0 (C), 140.4 (C), 139.9 (C), 132.8 (C), 132.3 (C), 130.9 (CH), 129.7 (CH), 129.5 (CH), 129.2 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.13 (CH), 128.06 (CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 127.0 (CH), 83.6 (CH), 59.6 (CH), 45.3 (CH_2), 28.9 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{32}H_{28}N_4NaO_2$ $[M+Na]^+$ 523.2104, found 523.2100.

(5*s,11*s**)-5,11-di-*o*-(phenylethynyl)phenyltetrahydrodipyrazolo[1,2-*a*:1',2'-*d*][1,2,4,5]tetrazine-1,9(5*H*,11*H*)-dione (2d).** Isolated as white powder (27.6 mg, 50%, *open*:*close* = >99:1) after silica gel column chromatography (10 g, Hexane:EtOAc = 1:1, v/v) following the procedure for synthesis of **2b** using azomethine imine **1d** (54.9 mg, 0.20 mmol). mp 163-165 ºC; R_f = 0.47 (EtOAc:Hexane = 1:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 1726, 1495, 1443, 1360, 1254, 1179, 1072, 830, 758 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 8.47-8.41 (m, 1H), 8.43 (s, 1H), 8.09-8.03 (m, 2H), 7.83-7.77 (m,

1H), 7.64-7.58 (m, 1H), 7.52-7.46 (m, 2H), 7.43-7.37 (m, 1H), 7.27-7.19 (m, 1H), 7.14-6.91 (m, 9H), 5.03 (s, 1H), 2.54 (dt, *J* = 11.4, 9.0 Hz, 2H), 2.47-2.23 (m, 4H), 1.80 (ddd, *J* = 16.3, 8.3, 4.3 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ 171.1 (C), 138.8 (C), 136.9 (C), 133.5 (CH), 132.9 (CH), 132.0 (CH), 131.6 (CH), 129.7 (CH), 129.6 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 128.8 (CH), 128.47 (CH), 128.45 (CH), 128.4 (CH), 127.9 (CH), 124.9 (C), 124.1 (C), 123.7 (C), 122.5 (C), 96.9 (C), 96.1 (C), 87.3 (C), 86.7 (C), 85.8 (CH), 61.0 (CH), 45.6 (CH_2), 29.5 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{36}H_{28}NaO_2$ $[M+Na]^+$ 571.2104, found 571.2095.

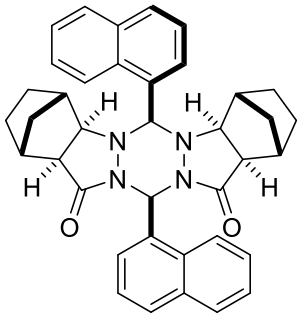
Synthesis of hexahydro-1,2,4,5-terrazine 2e. A solution of azomethine imine **1e** (44.8 mg, 0.20 mmol) and $Mg(OTf)_2$ (6.4 mg, 0.020 mmol, 10 mol%) in 1,2-dichloroethane (2.0 mL) was stirred at 80 ºC for 24 h. After cooling the mixture at room temperature, the reaction mixture was filtered through a plug of Celite and silica gel (0.1 g) with EtOAc/MeOH (4:1, v/v, 50 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (10 g) with Hexane/EtOAc (30:1 – 1:2, v/v) to provide hexahydro-1,2,4,5-terrazine **2e** (25.2 mg, 56%, *open*:*close* = 43:57).



(5*s,11*s**)-5,11-di(naphthalen-1-yl)tetrahydrodipyrazolo[1,2-*a*:1',2'-*d*][1,2,4,5]tetrazine-1,9(5*H*,11*H*)-dione (2e)**: White powder; mp 286-288 ºC; R_f (*open*) = 0.57 (EtOAc:Hexane = 2:1, v/v) visualized with phosphomolybdic acid, R_f (*close*) = 0.28 (EtOAc:Hexane = 2:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3049, 2924, 2853, 1717, 1686, 1511, 1372, 1278, 1263, 1090, 1077, 858, 791, 768 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03-8.95 (m, 1H×57/100), 8.40-8.30 (m, 1H), 8.29-8.24 (m, 1H×43/100), 8.23-8.15 (m, 1H), 8.06-7.80 (m, 5H×57/100+6H×43/100), 7.68-7.40 (m, 6H),

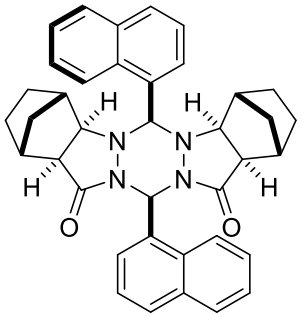
7.37-7.28 (m, 1H×57/100), 5.25 (s, 1H×43/100), 4.61 (s, 1H×57/100), 3.17-2.67 (m, 6H), 2.56-2.42 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 170.8 (C, *open*), 170.3 (C, *close*), 134.6 (C), 133.9 (C), 133.8 (C), 133.4 (C), 132.4 (C), 131.4 (CH), 131.2 (C), 131.1 (C), 131.0 (C), 130.9 (C), 130.8 (C), 130.3 (CH), 130.0 (C), 129.9 (C), 129.72 (CH), 129.66 (CH), 129.5 (CH), 128.72 (CH), 128.69 (CH), 128.4 (CH), 128.00 (CH), 127.95 (CH), 127.6 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 126.0 (CH), 125.93 (CH), 125.90 (CH), 125.8 (CH), 124.8 (CH), 124.6 (CH), 124.5 (CH), 123.4 (CH), 123.3 (CH), 120.7 (CH), 93.9 (CH, *close*), 83.0 (CH, *open*), 60.3 (CH, *close*), 59.7 (CH, *open*), 45.8 (CH_2, *close*), 45.5 (CH_2, *open*), 29.4 (CH_2, *open*), 29.1 (CH_2, *close*). Four aromatic methine carbons are overlapped; HRMS (ESI-TOF) m/z: calcd for $C_{28}H_{24}N_4NaO_2$ $[M+Na]^+$ 471.1791, found 471.1773.

Synthesis of hexahydro-1,2,4,5-terrazine 2f. A solution of azomethine imine **1f** (58.1 mg, 0.20 mmol), 4-oxo-2,3-diazatricyclo[4.3.1^{6,9}.0]decane[3] (6.0 mg, 0.040 mmol, 20 mol%), and AgOTf (5.1 mg, 0.020 mmol, 10 mol%) in chlorobenzene (2.0 mL) was stirred at 120 ºC for 48 h. After cooling the mixture at room temperature, the reaction mixture was filtered through a plug of Celite and silica gel (0.1 g) with EtOAc/MeOH (4:1, v/v, 50 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (7 g) with Hexane/EtOAc (7:3 – 1:2, v/v) to provide hexahydro-1,2,4,5-terrazines **2f**-*Open* (8.8 mg, 15%) and **2f**-*Close* (11.4 mg, 20%).



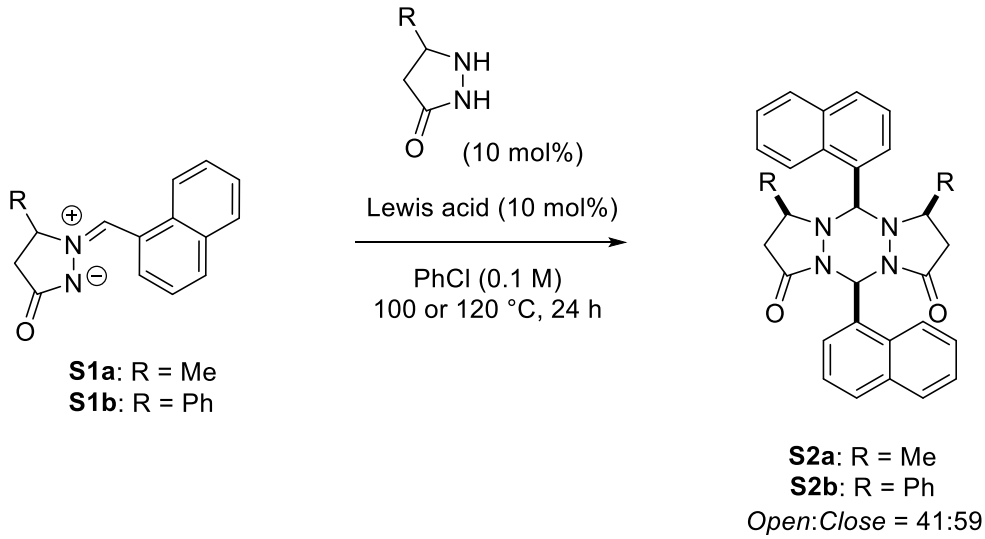
(1*R,4*S**,4a*R**,6*s**,7a*S**,8*R**,11*S**,11a*R**,14*s**,16a*S**)-6,14-di(naphthalen-1-yl)dodecahydro-1,4:8,11-dimethano[1,2,4,5]tetrazino[1,2-*a*:5,4-*a'*]bis(indazole)-12,16(6*H*,14*H*)-dione (2f-*Open*)**: White powder; mp 290-292 ºC; R_f = 0.25 (EtOAc:Hexane = 1:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3051, 2963, 2874, 1703, 1598, 1514, 1394, 1314, 1279, 1255, 1239, 1080, 865, 801, 778,

637, 555, 447 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 7.2 Hz, 1H), 8.58 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.16 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.01-7.84 (m, 4H), 7.96 (s, 1H), 7.71-7.55 (m, 5H), 7.53-7.46 (m, 1H), 5.16 (s, 1H), 2.80 (d, *J* = 8.1 Hz, 2H), 2.68 (d, *J* = 8.1 Hz, 2H), 2.53 (d, *J* = 3.8 Hz, 2H), 1.71-1.63 (m, 2H), 1.40-1.24 (m, 2H), 1.14 (d, *J* = 10.7 Hz, 2H), 1.07-0.92 (m, 4H), 0.82 (d, *J* = 10.7 Hz, 2H), 0.41-0.26 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 168.2 (C), 133.6 (C), 133.4 (C), 132.6 (C), 132.2 (C), 130.9 (C), 130.3 (CH), 130.0 (C), 129.7 (CH), 129.5 (CH), 129.3 (CH), 128.5 (CH), 127.5 (CH), 126.8 (CH), 126.5 (CH), 125.77 (CH), 125.76 (CH), 125.6 (CH), 124.6 (CH), 123.8 (CH), 121.3 (CH), 85.9 (CH), 64.3 (CH), 57.9 (CH), 49.6 (CH), 43.4 (CH), 39.8 (CH), 33.2 (CH_2), 27.7 (CH_2), 24.7 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{38}H_{36}N_4NaO_2$ $[M+Na]^+$ 603.2730, found 603.2726.



(1*R,4*S**,4a*R**,6*s**,7a*S**,8*R**,11*S**,11a*R**,14*s**,16a*S**)-6,14-di(naphthalen-1-yl)dodecahydro-1,4:8,11-dimethano[1,2,4,5]tetrazino[1,2-*a*:5,4-*a'*]bis(indazole)-12,16(6*H*,14*H*)-dione (2f-*Close*)**: White powder; mp 296-297 ºC; R_f = 0.25 (EtOAc:Hexane = 3:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3050, 2967, 2874, 1702, 1510, 1392, 1315, 1279, 1076, 866, 780, 736, 580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (d, *J* = 8.7 Hz, 1H), 8.61 (d, *J* = 7.3 Hz, 1H), 8.50 (d, *J* = 8.5 Hz, 1H), 8.00-7.82 (m, 4H), 7.94 (s, 1H), 7.69-7.43 (m, 6H), 7.42-7.34 (m, 1H), 4.50 (s, 1H), 3.04 (d, *J* = 8.2 Hz, 2H), 2.71 (d, *J* = 8.2 Hz, 2H), 2.56 (d, *J* = 3.7 Hz, 2H), 1.42-1.28 (m, 4H), 1.16 (d, *J* = 10.7 Hz, 2H), 1.11-0.87 (m, 4H), 0.76 (d, *J* = 10.7 Hz, 2H), 0.53-0.40 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 168.3 (C), 134.4 (C), 133.7 (C), 132.1 (C), 131.6 (C), 131.3 (CH), 130.91 (C), 130.89 (CH), 130.3 (C), 129.6 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 126.82 (CH), 126.75 (CH), 126.4 (CH), 125.9 (CH), 125.3 (CH), 124.31 (CH), 124.29 (CH), 123.9 (CH), 96.9 (CH), 64.4 (CH), 58.6 (CH), 49.6 (CH), 42.5

(CH), 39.7 (CH), 33.3 (CH_2), 27.7 (CH_2), 24.9 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{38}H_{36}N_4NaO_2$ $[M+Na]^+$ 603.2730, found 603.2758.



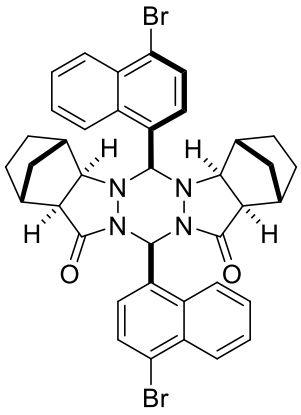
(3*R,5*s**,7*S**,11*s**)-3,7-dimethyl-5,11-di(naphthalen-1-yl)tetrahydrodipyrazolo[1,2-*a*:1',2'-*d*][1,2,4,5]tetrazine-1,9(5*H*,11*H*)-dione (S2a)**: Isolated as white powder (16.7 mg, 35%, *open*:*close* = 41:59) after silica gel column chromatography (6 g, Hexane:EtOAc = 30:1 – 1:3, v/v, CH_2Cl_2:MeOH = 100:0 – 50:1, v/v, and then Wakogel C-300HG 6 g, CH_2Cl_2:MeOH = 100:0 – 50:1, v/v) following the procedure for synthesis of **2e** using azomethinimine **S1a** (47.7 mg, 0.20 mmol), 5-methyl-3-pyrazolidinone (2.0 mg, 0.020 mmol, 10 mol%), $Mg(OTf)_2$ (6.4 mg, 0.020 mmol, 10 mol%) at 100 ºC in chlorobenzene (2.0 mL) for 24 h. mp 277-279 ºC; R_f (*open*) = 0.59 (EtOAc:Hexane = 3:1, v/v) visualized with phosphomolybdic acid, R_f (*close*) = 0.24 (EtOAc:Hexane = 3:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3051, 2977, 2927, 1717, 1599, 1512, 1377, 1302, 1265, 1196, 1080, 785, 767, 721, 647, 506 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.6 Hz, 1H×59/100), 8.40-8.21 (m, 2H), 8.14 (d, *J* = 8.4 Hz, 1H×41/100), 8.07 (s, 1H×41/100), 8.03 (s, 1H×59/100), 8.02-7.85 (m, 3H+2H×41/100), 7.81 (d, *J* = 8.1 Hz, 1H×59/100), 7.69-7.39 (m, 6H), 7.31-7.22 (m, 1H×59/100), 5.25 (s, 1H×41/100), 4.68 (s, 1H×59/100), 3.31-3.18 (m, 2H×59/100), 3.12-2.88 (m, 2H×41/100+2H), 2.20-2.09 (m, 2H), 0.77 (d, *J* = 6.5 Hz, 3H×41/100), 0.58 (d, *J* = 6.6 Hz, 3H×59/100); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 170.9 (C, *open*), 170.0 (C, *close*), 134.5 (C), 133.7 (C), 133.6 (C), 133.4 (C), 132.5 (C), 131.3 (CH), 131.2 (C), 131.02 (C), 130.99 (C), 130.9 (C), 130.7 (C), 130.1 (CH), 129.7 (CH), 129.5

(CH), 129.2 (CH), 128.7 (CH), 128.6 (CH), 128.38 (CH), 128.36 (CH), 127.8 (CH), 127.7 (CH), 126.8 (CH), 126.7 (CH), 126.5 (CH), 126.23 (CH), 126.20 (CH), 125.9 (CH), 125.81 (CH), 125.80 (CH), 125.7 (CH), 125.4 (CH), 124.7 (CH), 124.5 (CH), 124.4 (CH), 123.3 (CH), 123.2 (CH), 120.7 (CH), 93.4 (CH, *close*), 82.2 (CH, *open*), 59.2 (CH, *close*), 58.7 (CH, *open*), 51.9 (CH, *close*), 51.3 (CH, *open*), 36.1 (CH_2, *open*), 35.9 (CH_2, *close*), 21.3 (CH_3, *open*), 20.9 (CH_3, *close*). Two aromatic tertiary carbons and one methine carbon are overlapped; HRMS (ESI-TOF) m/z: calcd for $C_{30}H_{28}N_4NaO_2$ $[M+Na]^+$ 499.2104, found 499.2121.

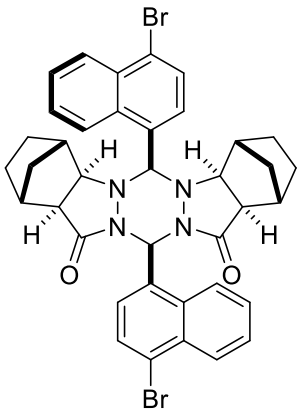
(3*R,5*s**,7*S**,11*s**)-3,7-diphenyl-5,11-di(naphthalen-1-yl)tetrahydrodipyrazolo[1,2-*a*:1',2'-*d*][1,2,4,5]tetrazine-1,9(5*H*,11*H*)-dione (S2b)**: Afforded as white solid (21.0 mg, NMR yield 22% using 1,1,2,2,-tetrachloroethane as an internal standard, *open*:*close* = 41:59) after silica gel column chromatography (6 g, Toluene:EtOAc = 15:1 – 3:1, v/v) following the procedure for synthesis of **2a** using azomethinimine **S1b** (60.1 mg, 0.20 mmol), 5-phenyl-3-pyrazolidinone (3.2 mg, 0.020 mmol, 10 mol%), AgOTf (5.1 mg, 0.020 mmol, 10 mol%) at 120 ºC in chlorobenzene (2 mL) for 24 h. The authentic sample (*open*:*close* = 42:58) of **S2b** was obtained by a GPC purification. mp 117-119 ºC; R_f (*open*) = 0.42 (Toluene:EtOAc = 2:1, v/v) visualized with phosphomolybdic acid, R_f (*close*) = 0.17 (Toluene:EtOAc = 2:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3051, 2977, 2927, 1717, 1599, 1512, 1377, 1302, 1265, 1196, 1080, 785, 767, 721, 647, 506 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.7 Hz, 1H×58/100), 8.37 (d, *J* = 8.5 Hz, 1H×42/100), 8.31-8.21 (m, 2H×42/100+1H×58/100), 8.19-8.10 (m, 1H×58/100), 8.17 (s, 1H×58/100), 8.12 (s, 1H×42/100), 8.03 (d, *J* = 8.2 Hz, 1H×58/100), 7.97-7.83 (m, 2H×42/100+1H×58/100), 7.76-7.37 (m, 8H×42/100+6H×58/100), 7.31-7.16 (m, 2H×58/100), 7.14-7.02 (m, 1H×42/100+1H×58/100), 6.97-6.89 (m, 2H×42/100), 6.84-6.69 (m, 4H×42/100+2H×58/100), 6.62-6.53 (m, 4H×58/100+4H×42/100), 6.49-6.42 (m, 4H×58/100), 5.63 (s, 1H×42/100), 4.93 (s, 1H×58/100), 4.24 (dd, *J* = 9.0, 5.5 Hz, 2H×58/100), 4.11 (dd, *J* = 9.3, 4.3 Hz, 2H×42/100), 3.26 (dd, *J* = 17.5, 9.3 Hz, 2H×42/100), 3.24 (dd, *J* = 17.4, 9.0 Hz, 2H×58/100), 2.67 (dd, *J* = 17.5, 4.3 Hz, 2H×42/100), 2.66 (dd, *J* = 17.4, 5.5 Hz, 2H×58/100); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 169.4 (C, *open*), 168.5 (C, *close*), 140.2 (C), 138.9 (C), 134.0 (C),

133.8 (C), 133.7 (C), 133.3 (C), 132.5 (C), 131.5 (CH), 131.3 (C), 131.1 (C), 131.0 (C), 130.4 (C), 130.3 (C), 130.2 (CH), 129.8 (CH), 129.6 (CH), 129.4 (CH), 129.32 (CH,), 129.28 (C), 128.7 (C), 128.5 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 127.3 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.6 (CH), 126.2 (CH), 126.1 (CH), 126.02 (CH), 125.96 (CH), 125.9 (CH), 125.79 (CH), 125.77 (CH), 125.6 (CH), 125.1 (CH), 124.6 (CH), 124.3 (CH), 123.9 (CH), 123.5 (CH), 123.4 (CH), 120.8 (CH), 95.0 (CH, *close*), 84.0 (CH, *open*), 60.5 (CH, *close*), 60.4 (CH, *close*), 59.7 (CH, *open*), 59.2 (CH, *open*), 37.9 (CH_2, *close*), 37.6 (CH_2, *open*). Four aromatic methine carbons are overlapped; HRMS (ESI-TOF) m/z: calcd for $C_{40}H_{32}N_4NaO_2$ $[M+Na]^+$ 623.2417, found 623.2425.

Synthesis of hexahydro-1,2,4,5-terrazine S2c. A solution of azomethine imine **S1c** (58.1 mg, 0.20 mmol), 4-oxo-2,3-diazatricyclo[4.3.1^{6,9}.0]decane[3] (6.0 mg, 0.040 mmol, 20 mol%), AgOTf (10.3 mg, 0.040 mmol, 20 mol%), and 4-bromo-1-naphthaldehyde (18.8 mg, 0.080 mmol, 40 mol%) in chlorobenzene (4.0 mL) was stirred at 120 ºC for 24 h. After cooling the mixture at room temperature, the reaction mixture was filtered through a plug of Celite and silica gel (0.1 g) with EtOAc/MeOH (4:1, v/v, 50 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (5 g) with Hexane/EtOAc (5:1 – 1:2, v/v) and then CH_2Cl_2:MeOH (200:1 – 100:1) to provide hexahydro-1,2,4,5-terrazines **S2c** (11.5 mg, 16%, *open*:*close* = 41:59). **S2c**-*Open* and **S2c**-*Close* could be partly isolated by careful silica gel column chromatography with Hexane/EtOAc (7:3 – 1:2, v/v) as an eluent, respectively.



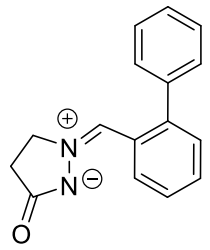
(1*R,4*S**,4a*R**,6*s**,7a*S**,8*R**,11*S**,11a*R**,14*s**,16a*S**)-6,14-di(4-bromonaphthalen-1-yl)dodecahydro-1,4:8,11-dimethano[1,2,4,5]tetrazino[1,2-*a*:5,4-*a'*]bis(indazole)-12,16(6*H*,14*H*)-dione (S2c-*Open*)**: White powder; mp 226-228 ºC; R_f = 0.41 (EtOAc:Hexane = 3:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3072, 2962, 2873, 1703, 1567, 1510, 1455, 1388, 1313, 1278, 1255, 1200, 1157, 1080, 992, 913, 897, 843, 820, 790, 758, 708, 647, 546 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.61-8.52 (m, 2H), 8.48-8.40 (m, 1H), 8.35-8.28 (m, 1H), 8.26-8.19 (m, 1H), 7.99-7.88 (m, 3H), 7.90 (s, 1H), 7.78-7.58 (m, 4H), 5.12 (s, 1H), 2.76 (d, *J* = 8.1 Hz, 2H), 2.68 (d, *J* = 8.1 Hz, 2H), 2.53 (d, *J* = 3.6 Hz, 2H), 1.69 (d, *J* = 3.9 Hz, 2H), 1.42-1.20 (m, 2H), 1.13-0.95 (m, 6H), 0.85 (d, *J* = 10.7 Hz, 2H), 0.42-0.29 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 168.3 (C), 133.7 (C), 132.3 (C), 132.1 (C), 131.9 (C), 131.8 (C), 130.1 (C), 130.0 (CH), 129.8 (CH), 129.0 (CH), 128.9 (CH), 128.5 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 126.8 (CH), 125.5 (C), 124.3 (C), 124.2 (CH), 121.7 (CH), 85.7 (CH), 64.4 (CH), 57.5 (CH), 49.5 (CH), 43.4 (CH), 39.9 (CH), 33.2 (CH_2), 27.6 (CH_2), 24.8 (CH_2). One aromatic methine carbon is overlapped; HRMS (ESI-TOF) m/z: calcd for $C_{38}H_{34}Br_2N_4NaO_2$ $[M+Na]^+$ 761.0924, found 761.0946.



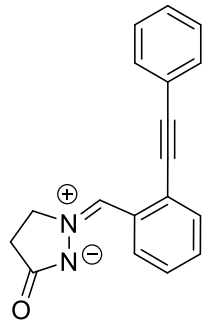
(1*R,4*S**,4a*R**,6*s**,7a*S**,8*R**,11*S**,11a*R**,14*s**,16a*S**)-6,14-di(4-bromonaphthalen-1-yl)dodecahydro-1,4:8,11-dimethano[1,2,4,5]tetrazino[1,2-*a*:5,4-*a'*]bis(indazole)-12,16(6*H*,14*H*)-dione (S2c-*Close*)**: White powder; mp 299-300 ºC; R_f = 0.28 (EtOAc:Hexane = 3:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3071, 3008, 2967, 2874, 1699, 1567, 1508, 1425, 1386, 1302, 1276, 1255, 1230, 1200, 1119, 1082, 929, 914, 895, 846, 758, 709, 589, 549 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.3 Hz, 1H), 8.53-8.47 (m, 1H), 8.44 (d, *J* = 7.8 Hz, 1H), 8.38-8.28 (m, 2H), 7.98

(d, *J* = 7.8 Hz, 1H), 7.89 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.70-7.60 (m, 3H), 7.52-7.44 (m, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 4.46 (s, 1H), 3.01 (d, *J* = 8.2 Hz, 2H), 2.71 (d, *J* = 8.2 Hz, 2H), 2.57 (d, *J* = 3.7 Hz, 2H), 1.44-1.27 (m, 4H), 1.13-0.84 (m, 4H), 1.09 (d, *J* = 10.7 Hz, 2H), 0.79 (d, *J* = 10.7 Hz, 2H), 0.57-0.43 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 168.3 (C), 132.7 (C), 132.5 (C), 132.4 (C), 132.2 (C), 132.1 (C), 131.0 (CH), 130.2 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 126.6 (C), 126.3 (CH), 124.7 (C), 124.3 (CH), 96.4 (CH), 64.5 (CH), 58.2 (CH), 49.5 (CH), 42.5 (CH), 39.7 (CH), 33.4 (CH_2), 27.6 (CH_2), 24.9 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{38}H_{34}Br_2N_4NaO_2$ $[M+Na]^+$ 761.0924, found 761.0935.

Synthesis of azomethine imines 1c and 1d. Azomethine imines **1c** and **1d** were synthesized according to the procedure for synthesis of **1e**.

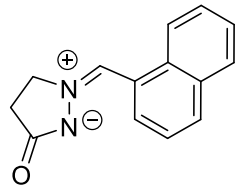


(2*Z*)-2-(biphenyl-2-ylmethylidene)-5-oxopyrazolidin-2-ium-1-ide (1c): Isolated as white powder (167.1 mg, 35%) after silica gel column chromatography (20 g, EtOAc:MeOH = 20:1 – 10:1, v/v) following the procedure for synthesis of **1e** using 3-pyrazolidinone[1] (406.7 mg, 4.7 mmol) and 2-phenylbenzaldehyde (350.5 mg, 1.9 mmol) in MeOH (2.4 mL, 2.0 M). mp 145-147 ºC; R_f = 0.28 (EtOAc:MeOH = 10:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3060, 3026, 2948, 1672, 1655, 1598, 1584, 1558, 1470, 1455, 1340, 1282, 1119, 1099, 959, 853, 759, 745, 707, 668 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39-9.31 (m, 1H), 7.57-7.42 (m, 5H), 7.42-7.30 (m, 3H), 7.01 (br s, 1H), 4.41-4.31 (m, 2H), 2.84-2.74 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 184.8 (C), 143.7 (C), 139.1 (C), 131.3 (CH), 131.1 (CH), 131.0 (CH), 130.0 (CH), 129.8 (CH), 128.5 (CH), 128.0 (CH), 127.8 (CH), 126.6 (C), 58.1 (CH_2), 29.1 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{16}H_{14}N_2NaO$ $[M+Na]^+$ 273.0998, found 273.1020.

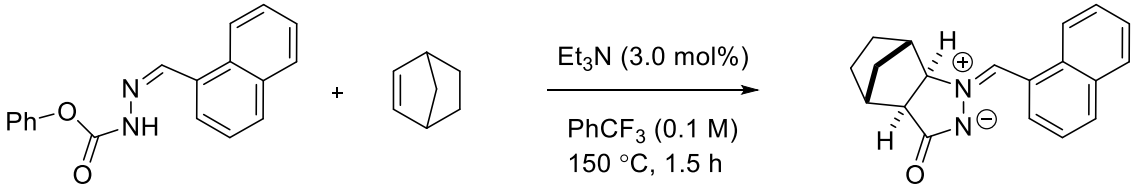


(2*Z*)-5-oxo-2-[2-(phenylethynyl)benzylidene]pyrazolidin-2-ium-1-ide (1d): Isolated as white powder (254.7 mg, 60%) following the procedure for synthesis of **1e** using 3-pyrazolidinone[1] (268.1 mg, 3.1 mmol) and 2-(phenylethynyl)benzaldehyde (321.1 mg, 1.5 mmol) in MeOH (1.6 mL, 2.0 M). mp 202-203 ºC; R_f = 0.43 (CH_2Cl_2:MeOH = 20:1, v/v) visualized with $KMnO_4$; IR (KBr) 3051, 2210, 1678, 1656, 1591, 1577, 1556, 1493, 1469, 1429, 1338, 1295, 1110, 1088, 957, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.37-9.28 (m, 1H), 7.79 (br s, 1H), 7.64--7.52 (m, 3H), 7.50-7.37 (m, 5H), 4.64-4.55 (m, 2H), 2.88-2.79 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 185.1 (C), 132.5 (CH), 131.43 (CH), 131.39 (CH), 130.9 (CH), 130.0 (CH), 129.5 (C), 129.0 (CH), 128.8 (CH), 128.5 (CH), 124.1 (C), 122.1 (C), 96.1 (C), 85.9 (C), 58.4 (CH_2), 29.1 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{18}H_{14}N_2NaO$ $[M+Na]^+$ 297.0998, found 297.0997.

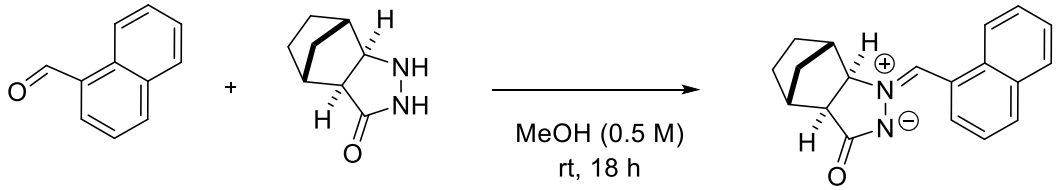
Synthesis of azomethine imine 1e. 1-Naphthaldehyde (312.3 mg, 0.28 mL, 2.0 mmol) was added to a solution of 3-pyrazolidinone[1] (289.9 mg, 3.4 mmol) in MeOH (1.6 mL, 2.0 M). The mixture was stirred for 24 h at room temperature and then diluted with Et_2O (10 mL). The precipitate was collected by filtration, washed with Et_2O, and dried under reduced pressure to afford azomethine imine **1e** (366.8 mg, 82%).



(2*Z*)-2-(naphthalen-1-ylmethylidene)-5-oxopyrazolidin-2-ium-1-ide (1e): Yellow powder; mp 184-186 ºC; R_f = 0.33 (EtOAc:MeOH = 4:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3055, 3011, 1673, 1645, 1580, 1518, 1440, 1356, 1335, 1308, 1293, 1262, 1115, 1102, 957, 807, 794, 783, 768 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.52-9.44 (m, 1H), 8.12-8.05 (m, 1H), 7.97-7.86 (m, 2H), 7.94 (br s, 1H), 7.66-7.50 (m, 3H), 4.72-4.61 (m, 2H), 2.91-2.80 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 185.3 (C), 133.2 (C), 132.4 (CH), 131.4 (CH), 131.0 (C), 129.4 (CH), 128.5 (CH), 127.5 (CH), 126.1 (CH), 125.5 (CH), 124.1 (C), 121.3 (CH), 58.5 (CH_2), 29.2 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{14}H_{12}N_2NaO$ $[M+Na]^+$ 247.0842, found 247.0830.



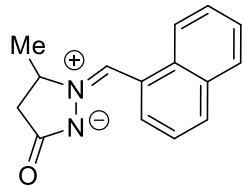
Synthesis of azomethine imine 1f.[4] Phenyl 2-(naphthalen-1-ylmethylene)hydrazinecarboxylate[4] (290.3 mg, 1.0 mmol), $PhCF_3$ (5.0 mL, 0.2 M), Et_3N (4.2 μL, 3.0 mol%), and 2-norbornene (470.8 mg, 5.0 mmol) were successively added to the sealed tube. The tube was purged with argon and then quickly sealed with a cap. The mixture was heated at 150 ºC for 1.5 h while stirring. After cooling the mixture at room temperature, the reaction mixture was concentrated and then filtered through a plug of silica gel (5 g) with CH_2Cl_2 (60 mL), EtOAc (15 mL), and EtOAc/MeOH (4:1, v/v, 50 mL) as an eluent. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (6 g) with EtOAc to provide azomethine imine **1f** (129.3 mg, 44%).



Alternative procedure for synthesis of azomethine imine 1f. 1-Naphthaldehyde (62.5 mg, 54 μL, 0.4 mmol) was added to a solution of 4-oxo-2,3-diazatricyclo[4.3.$1^{6,9}$.0]decane[3] (60.1 mg, 0.4 mmol) in MeOH (0.8 mL, 0.5 M). The mixture was stirred for 18 h at room temperature and then concentrated

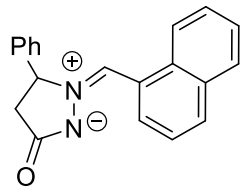
under reduce pressure. The residue was purified by silica gel column chromatography (7 g) with EtOAc to provide azomethine imine **1f** (84.9 mg, 73%).

***exo*-(*Z*)-2-(naphth-1-ylmethylene)-4-oxo-2,3-diazatricyclo[4,3,1^{6,9},0]decane-2-ium-3-ide (1f)**:[4] Yellow powder; mp 235-237 ºC; R_f = 0.25 (EtOAc:MeOH = 10:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3048, 2967, 2866, 1733, 1653, 1579, 1510, 1430, 1325, 1301, 1211, 1127, 1106, 1087, 1051, 996, 869, 797, 768, 687, 667, 623 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.52 (dd, *J* = 7.7, 0.8 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.98-7.88 (m, 2H), 7.66-7.52 (m, 3H), 4.60 (dd, *J* = 7.1, 0.7 Hz, 1H), 2.87-2.74 (m, 3H), 1.86-1.61 (m, 2H), 1.55-1.24 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 186.4 (C), 133.3 (C), 132.3 (CH), 131.4 (CH), 131.1 (C), 129.5 (CH), 127.5 (CH), 127.4 (CH), 126.1 (CH), 125.7 (CH), 124.4 (C), 121.3 (CH), 77.5 (CH), 49.9 (CH), 44.7 (CH), 39.2 (CH), 32.4 (CH_2), 27.5 (CH_2), 24.9 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{19}H_{19}N_2O$ $[M+H]^+$ 291.1492, found 291.1498.



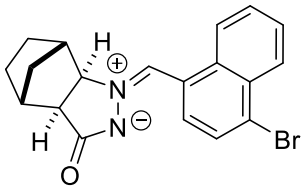
(2*Z*)-3-methyl-2-(naphthalen-1-ylmethylidene)-5-oxopyrazolidin-2-ium-1-ide (S1a): Isolated as yellow powder (4.68 g, 75%) following the procedure for synthesis of **1c** using 5-methyl-3-pyrazolidinone (2.68 g, 27.0 mmol) and 1-naphthaldehyde (4.53 g, 3.9 mL, 29.0 mmol) in MeOH (17.0 mL, 1.5 M). mp 156-158 ºC; R_f = 0.23 (EtOAc:MeOH = 4:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3057, 2978, 1663, 1581, 1510, 1433, 1330, 1314, 1293, 1252, 1102, 1084, 1017, 957, 803, 772, 667, 531 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (dd, *J* = 7.6, 0.7 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.00-7.90 (m, 3H), 7.67-7.53 (m, 3H), 4.93-4.80 (m, 1H), 3.10 (dd, *J* = 16.5, 9.1 Hz, 1H), 2.54 (dd, *J* = 16.5, 4.1 Hz, 1H), 1.79 (d, *J* = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 183.8 (C), 133.3 (C), 132.4 (CH), 131.4 (CH), 131.1 (C), 129.4 (CH), 127.6 (CH), 127.5 (CH), 126.1 (CH), 125.5 (CH),

124.2 (C), 121.2 (CH), 66.8 (CH), 37.3 (CH_2), 22.9 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{15}H_{14}N_2NaO$ $[M+Na]^+$ 261.0998, found 261.0991.



(2*Z*)-2-(naphthalen-1-ylmethylidene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide (S1b): Isolated as yellow powder (613.6 mg, 49%) after silica gel column chromatography (30 g, CH_2Cl_2:MeOH = 100:0 – 97:3, v/v) following the procedure for synthesis of **1c** using 5-phenyl-3-pyrazolidinone (675.7 mg, 4.2 mmol) and 1-naphthaldehyde (656.0 mg, 570 μL, 4.2 mmol) in MeOH (3.0 mL, 1.5 M) for 16 h, and then for additional 32 h after adding 5.0 mL of MeOH. mp 185-187 ºC; R_f = 0.30 (CH_2Cl_2:MeOH = 20:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3062, 2989, 1670, 1652, 1581, 1513, 1497, 1449, 1306, 1283, 1257, 1095, 1074, 974, 950, 804, 771, 735, 698, 683, 622, 485 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.54 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.90-7.83 (m, 1H), 7.71-7.65 (m, 1H), 7.69 (br s, 1H), 7.60 (t, *J* = 7.9 Hz, m, 1H), 7.53-7.41 (m, 7H), 5.71 (ddd, *J* = 9.8, 5.7, 0.9 Hz, 1H), 3.36 (dd, *J* = 16.9, 9.8 Hz, 1H), 2.92 (dd, *J* = 16.9, 5.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 183.5 (C), 138.4 (C), 133.3 (C), 132.6 (CH), 131.5 (CH), 131.2 (C), 129.8 (CH), 129.7 (CH), 129.4 (CH), 129.1 (CH), 127.5 (CH), 126.8 (CH), 126.1 (CH), 125.6 (CH), 124.1 (C), 121.0 (CH), 74.6 (CH), 38.9 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{16}N_2NaO$ $[M+Na]^+$ 323.1155, found 323.1161.

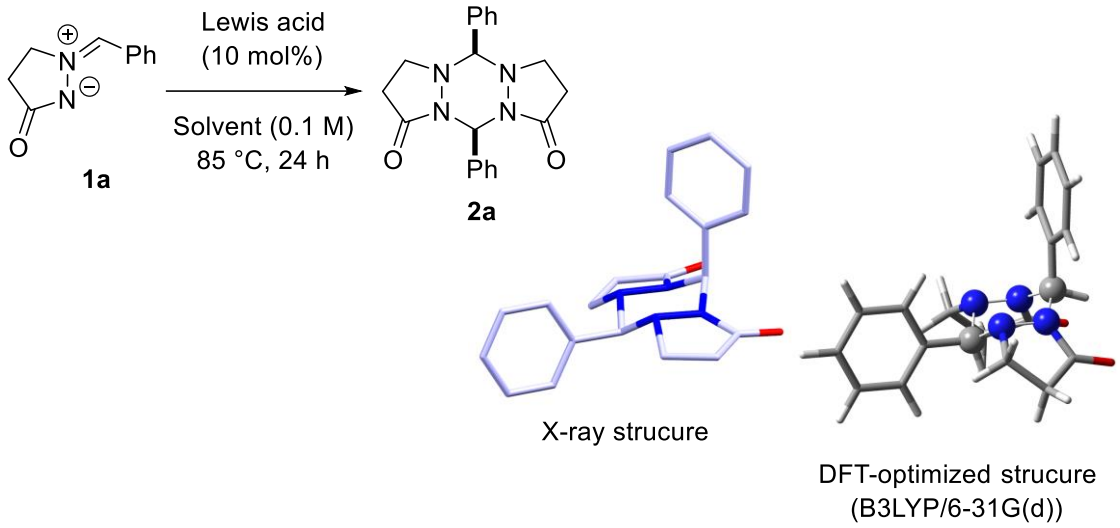
Synthesis of azomethine imine S1c. 4-Bromo-1-naphthaldehyde (150.2 mg, 1.0 mmol) was added to a solution of 4-oxo-2,3-diazatricyclo[4.3.1^{6,9}.0]decane[3] (235.1 mg, 1.0 mmol) in MeOH (2.0 mL, 0.5 M). The mixture was stirred for 18 h at room temperature and then concentrated under reduce pressure. The residue was washed with Et_2O/Hexane (1:1, v/v, 50 mL) to provide azomethine imine **S1c** (326.0 mg, 88%).



***exo*-(*Z*)-2-(4-bromonaphth-1-ylmethylene)-4-oxo-2,3-diazatricyclo[4,3,1^{6,9},0]decane-2-ium-3-ide (S1c)**: Yellow powder; mp 269-270 ºC (dec.); R_f = 0.29 (EtOAc:MeOH = 10:1, v/v) visualized with phosphomolybdic acid; IR (KBr) 3043, 2972, 2875, 1658, 1582, 1571, 1507, 1454, 1430, 1322, 1302, 1292, 1262, 1128, 1106, 1000, 907, 868, 763, 691, 671, 567 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (d, *J* = 8.2 Hz, 1H), 8.43-8.33 (m, 1H), 8.16-8.07 (m, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.88 (br s, 1H), 7.72-7.63 (m, 2H), 4.60 (d, *J* = 7.0 Hz, 1H), 2.88-2.75 (m, 3H), 1.86-1.63 (m, 2H), 1.55-1.22 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 186.4 (C), 132.1 (C), 132.0 (C), 131.3 (CH), 130.2 (CH), 128.8 (CH), 128.3 (CH), 127.7 (C), 127.5 (CH), 126.2 (CH), 124.3 (C), 121.6 (CH), 77.9 (CH), 49.9 (CH), 44.7 (CH), 39.3 (CH), 32.6 (CH_2), 27.6 (CH_2), 25.0 (CH_2); HRMS (ESI-TOF) m/z: calcd for $C_{19}H_{17}BrN_2NaO$ $[M+Na]^+$ 391.0416, found 391.0396.

Reaction optimization for the synthesis of hexahydro-1,2,4,5-terrazine 2a

Table S1. Dimerization reactions of azomethine imine **1a** in the presence of Lewis acids[a)]



Entry	Lewis acid	Solvent	Yield (%)[b)]
1	none	$(CH_2Cl)_2$	15
2	$Mg(OTf)_2$	$(CH_2Cl)_2$	52
3	$Zn(OTf)_2$	$(CH_2Cl)_2$	50
4	AgOTf	$(CH_2Cl)_2$	60 (53)[c)]
5	AgOTf	Toluene	49
6	AgOTf	PhCl	56
7	AgOTf	1,4-Dioxane	57
8	$Sc(OTf)_3$	$(CH_2Cl)_2$	40
9	$Yb(OTf)_3$	$(CH_2Cl)_2$	40

a) The reaction of azomethine imine **1a** (0.2 mmol) was performed in the solvent (0.1 M) in the presence of Lewis acid (10 mol%) at 85 ºC for 24 h. b) NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. c) Isolated yield.

Variable temperature ^{13}C NMR spectra of hexahydro-1,2,4,5-terrazine 2a

The C-C bond rotation of an equatorial phenyl group was hindered by the H atoms on a 3-pyrazolidinone ring. Thus, *ortho*- and *meta*-carbons of an equatorial phenyl group at the C_3-position were observed as non-equivalent signals in the ^{13}C NMR experiments.

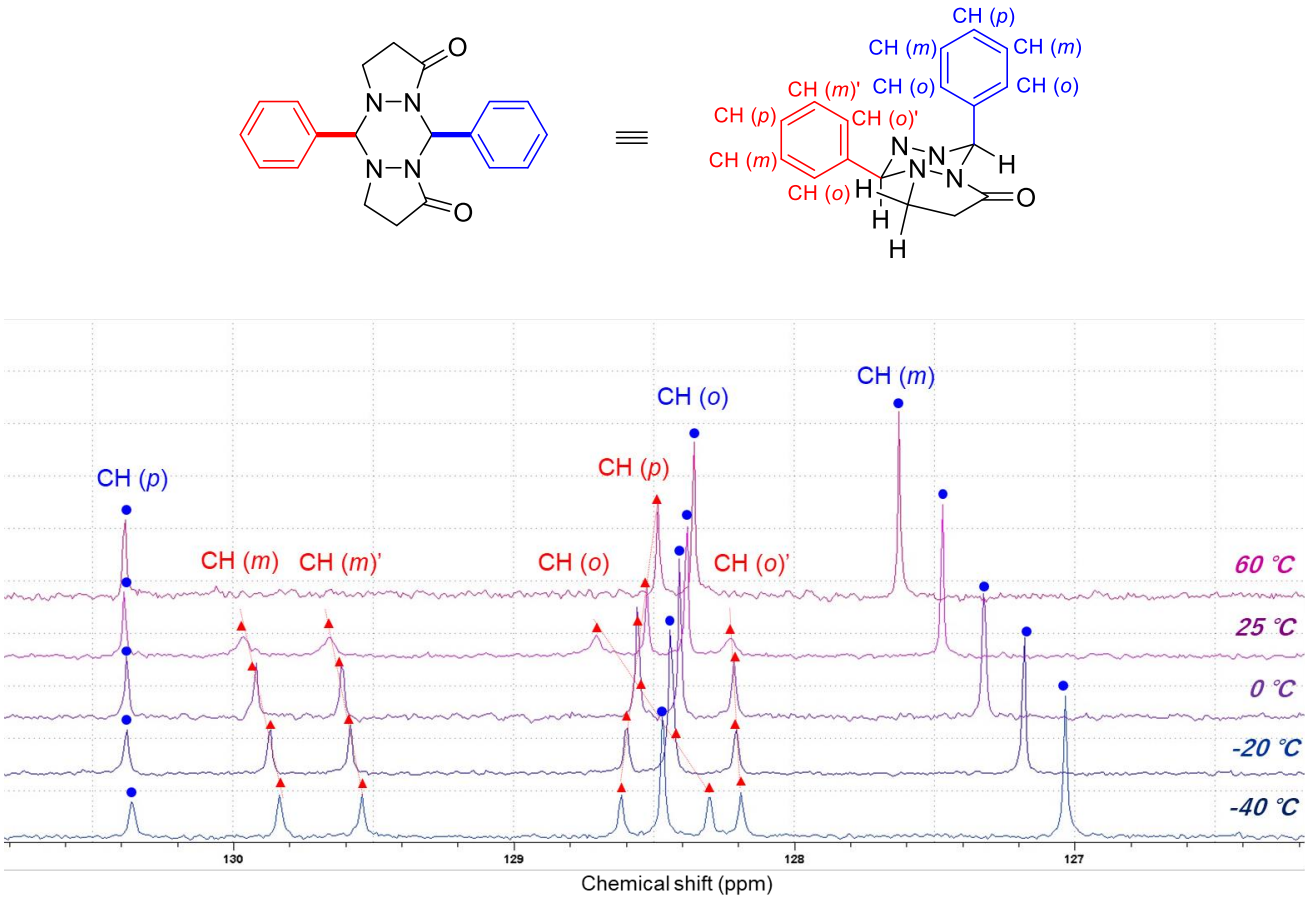


Figure S1. Variable temperature ^{13}C NMR spectra of **2a**

NOE experiments for hexahydro-1,2,4,5-terrazines 2b, 2e, and 2f

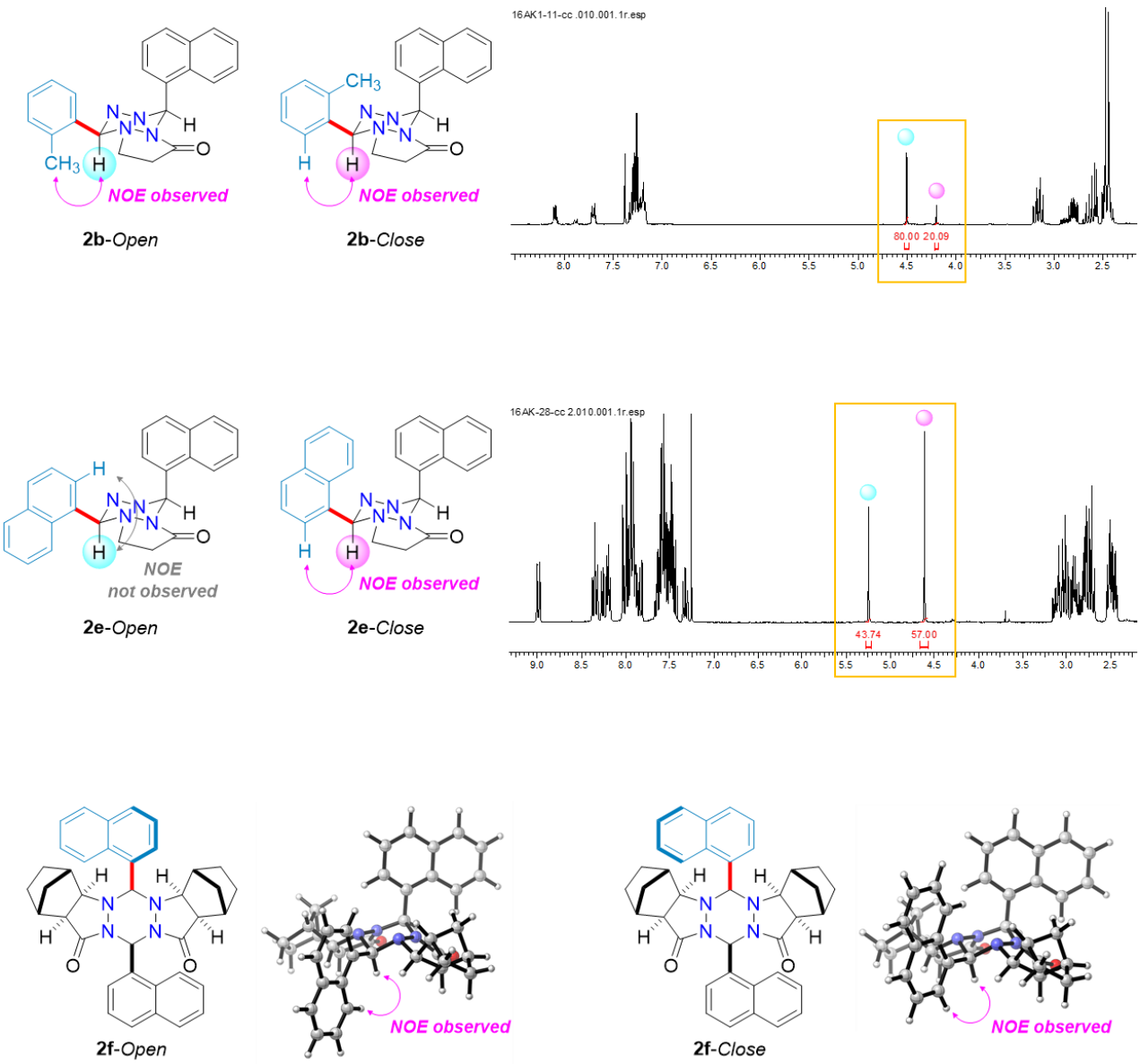
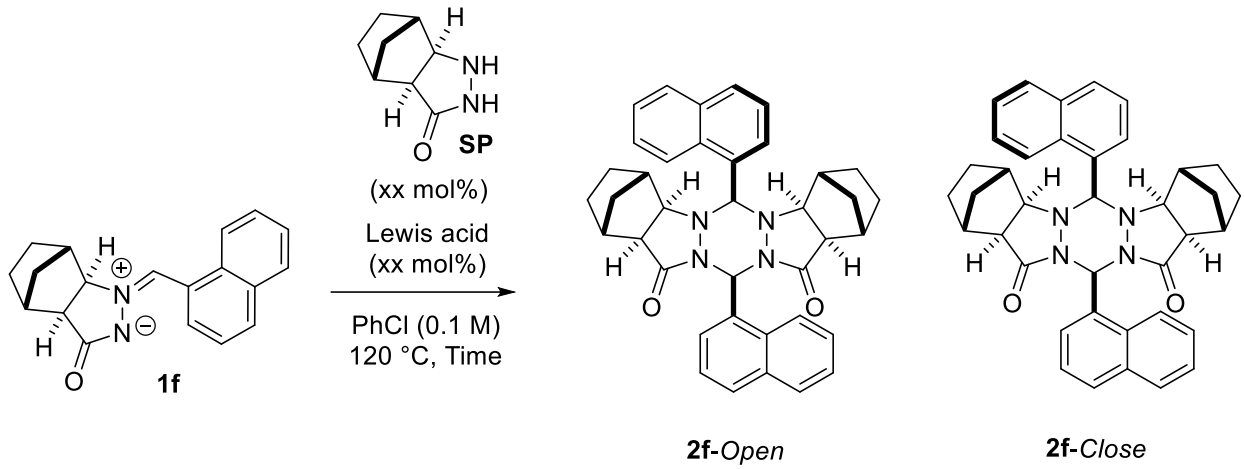


Figure S2. Summary of NOE experiments

Reaction optimization for the synthesis of hexahydro-1,2,4,5-terrazine 2f

Table S2. Dimerization reactions of azomethine imine **1f**[a)]



Entry	Lewis acid (mol%)	**SP** (mol%)	Time (h)	Yield (%)[b)]	*Open*:*Close*[c)]	Recovered **1f** (%)[d)]
1	$Mg(OTf)_2$ (10)	none	24	4[d)]	43:57	88
2	$Mg(OTf)_2$ (10)	10	24	3[d)]	39:61	93
3	AgOTf (10)	10	24	28[d)]	40:60	53
4[e)]	AgOTf (10)	10	24	28[f)]	40:60	56
5	AgOTf (10)	20	24	32	42:58	53
6	AgOTf (20)	10	24	29	42:58	41
7	AgOTf (20)	20	24	21	42:58	47
8[g)]	AgOTf (10)	10	24	18	43:57	45
9	AgOTf (10)	10	48	33[h)]	41:59	48
10	AgOTf (10)	20	48	35[i)]	42:58	50
11	AgOTf (10)	10	96	34	41:59	41

a) The reaction of azomethine imine **1f** (0.2 mmol) was performed in PhCl (0.1 M) in the presence of Lewis acid and 3-pyrazolidinone **SP** at 120 ºC. b) Combined yield. c) Determined by ^{1}H NMR. d) NMR

yield using 1,1,2,2-tetrachloroethane as an internal standard. e) 0.6 mmol scale. f) Isolated yield of **2f**-*Open*: 11%, **2f**-*Close*: 17%. g) 150 ºC. h) Isolated yield of **2f**-*Open*: 14%, **2f**-*Close*: 19%. i) Isolated yield of **2f**-*Open*: 15%, **2f**-*Close*: 20%.

HPLC tracking experiments for rotamers 2e-*Open* and 2e-*Close*

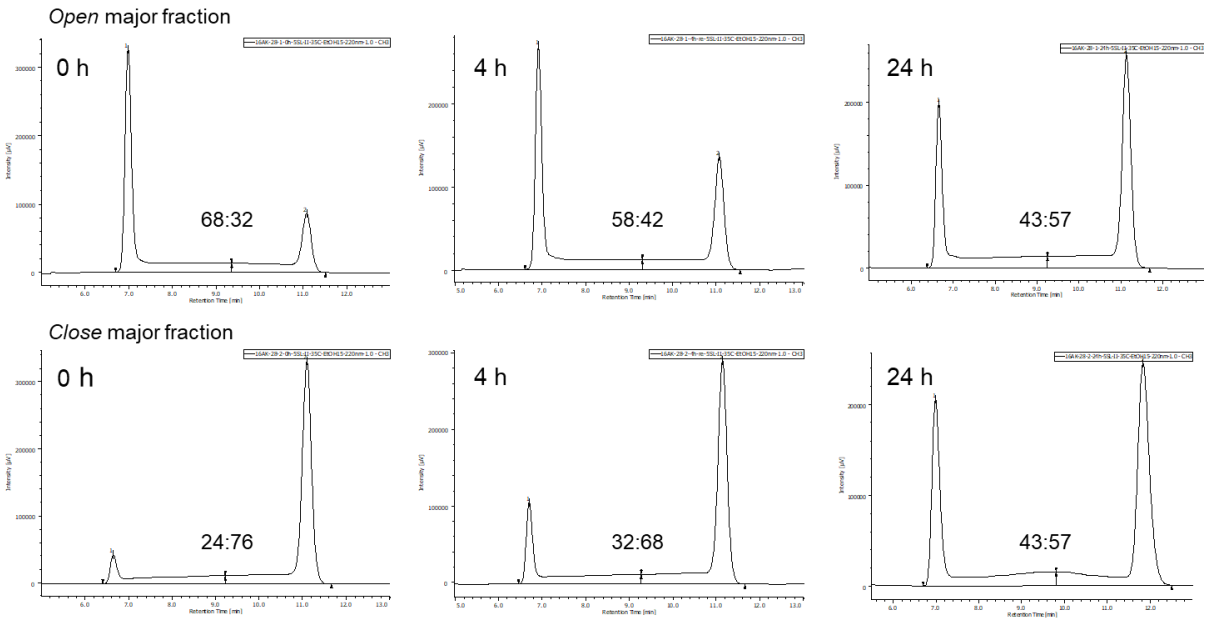


Figure S3. HPLC chromatograms for hexahydro-1,2,4,5-terrazine **2e**

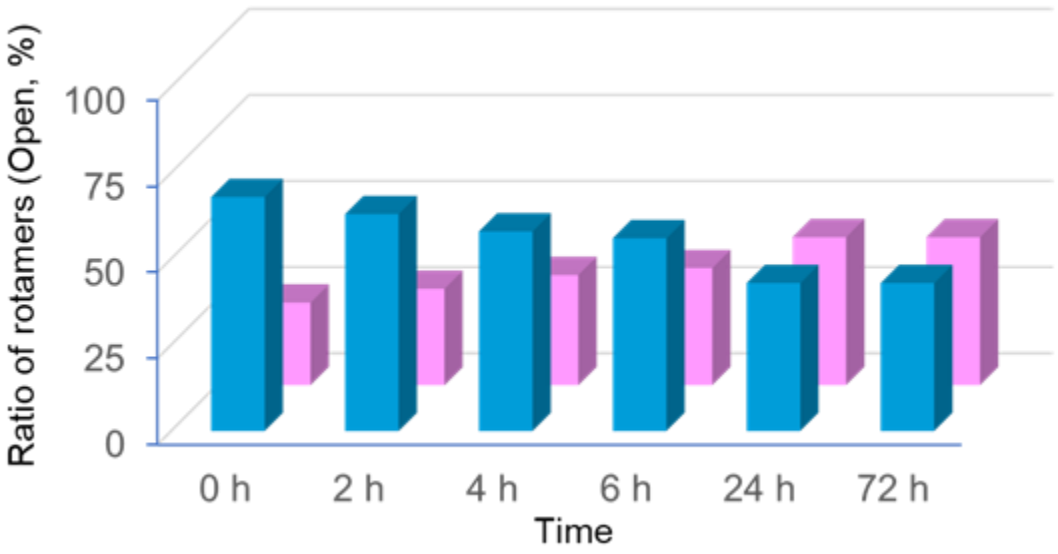


Figure S4. Results of HPLC tracking experiments

NMR tracking experiments for rotamers 2f-*Open* and 2f-*Close*

^{1}H NMR tracking experiments in $CDCl_3$ were performed. The spectra at 60 °C (15 min interval for both isomers) were shown in Figure S5.

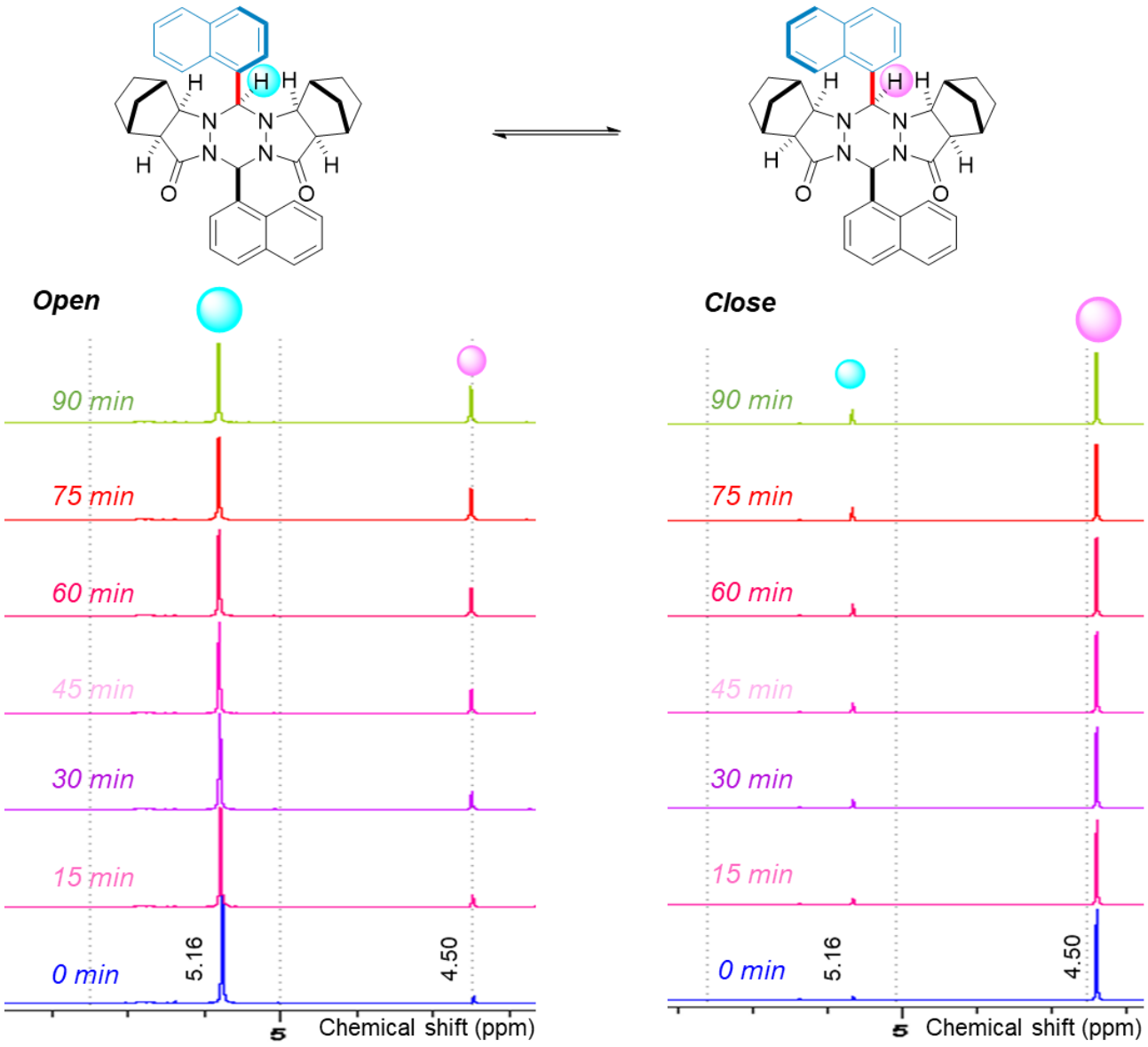
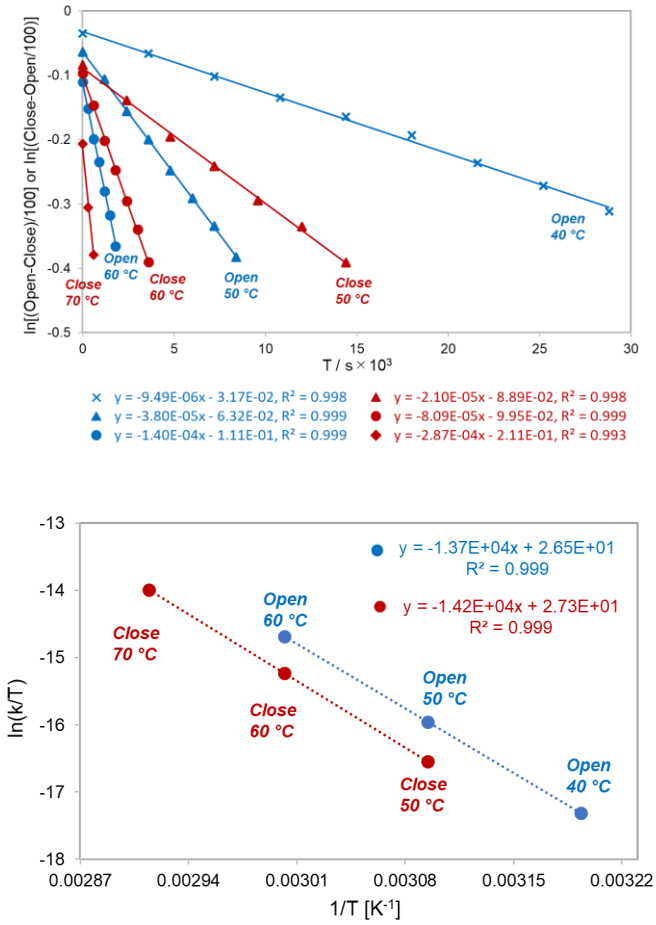


Figure S5. ^{1}H NMR (500 MHz) spectra in $CDCl_3$ (8.6 mM) at 60 ºC

By plotting logarithms of excess percentages for each rotamer with respect to elapsed times, a rate constant for each temperature could be determined from the slope. The rate constants (k) of the isomerization, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values were obtained from the Eyring equation. The isomerization rate for *Open* to *Close* is slightly faster than that for *Close* to *Open*. This reflects the difference in the thermodynamic stability of the two isomers.



	k [s^{-1}]	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [kcal mol^{-1} K^{-1}]	$\Delta G^{\ddagger}$ [kcal mol^{-1}]
Open	9.95 x 10^{-7}	27.3	5.48 x 10^{-3}	25.6
Close	4.90 x 10^{-7}	28.2	7.06 x 10^{-3}	26.1

Figure S6. Kinetic study by NMR experiments and Eyring plot for the isomerization

Long-term tracking experiments by ^{1}H NMR spectra

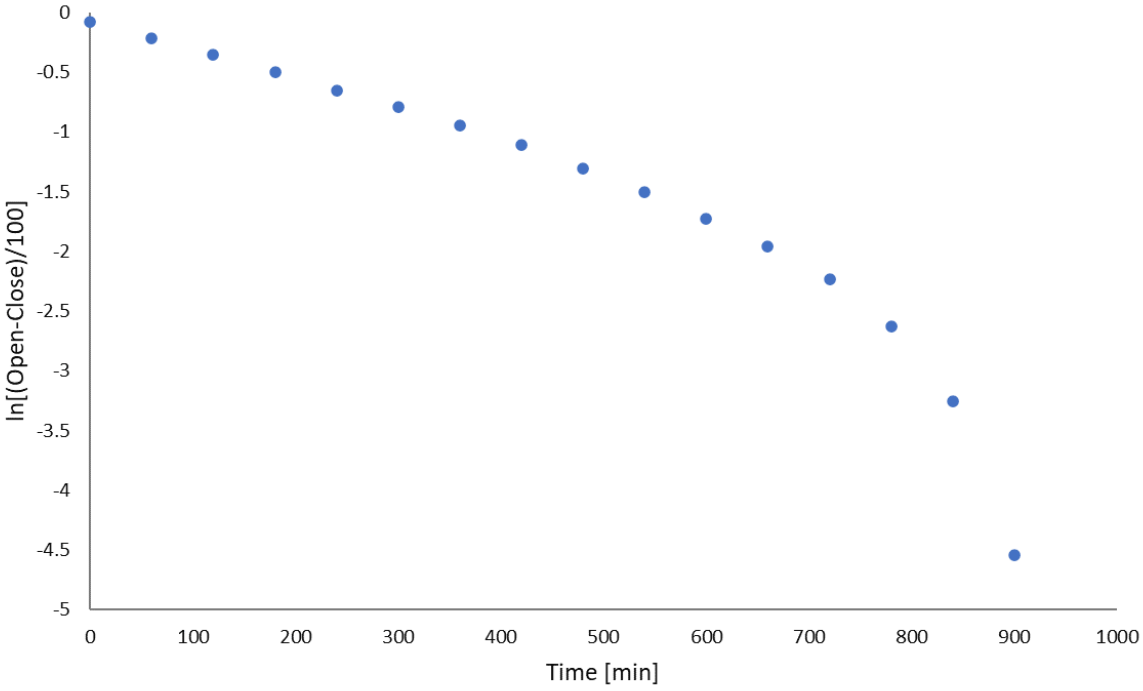


Figure S7. The isomerization rate for **2f**-*Open* to **2f**-*Close* at 60 ºC

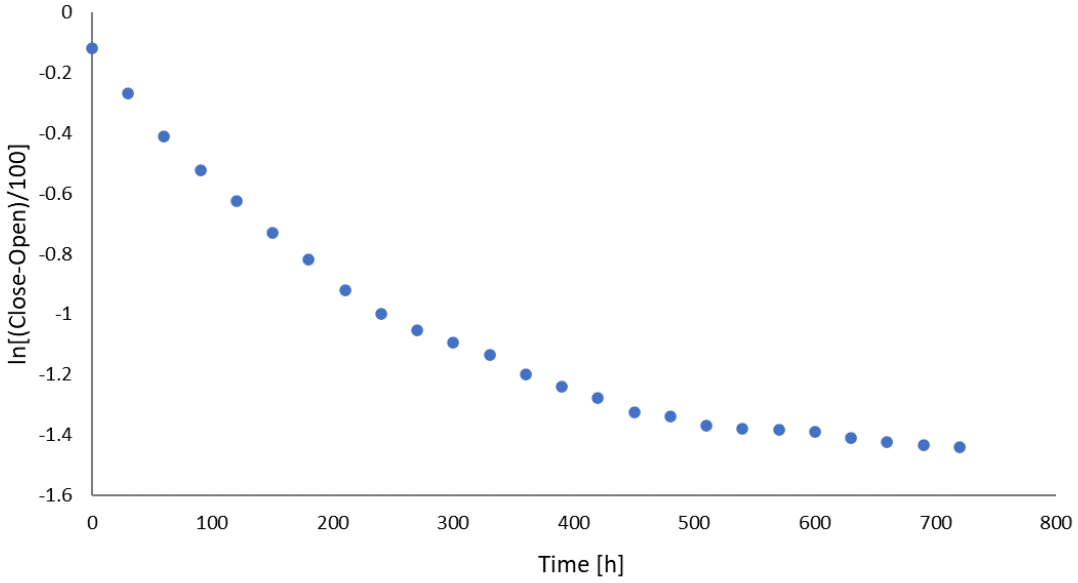


Figure S8. The isomerization rate for **2f**-*Close* to **2f**-*Open* at 50 ºC

X-ray crystallographic analysis

Hexahydro-1,2,4,5-terrazine ***2a***

X-ray analysis was carried out using the single crystal which was grown in EtOAc (Figure S9).

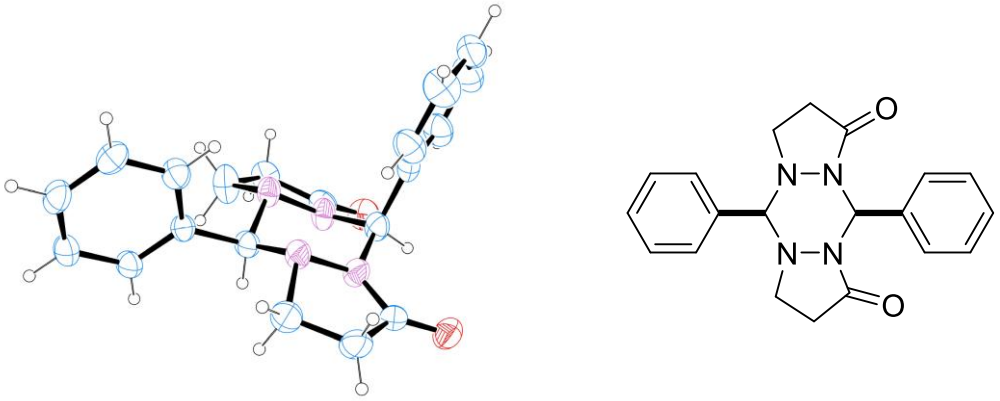


Figure S9. ORTEP drawing (30% probability ellipsoids) of **2a**

```
Bond precision:  C-C = 0.0048 A          Wavelength=0.71073

Cell:            a=21.28(2)     b=8.194(8)            c=22.20(2)
                 alpha=90       beta=115.876(12)      gamma=90
Temperature:     88 K

                 Calculated                Reported
Volume           3483(6)                   3483(6)
Space group      C 2/c                     C 1 2/c 1
Hall group       -C 2yc                    -C 2yc
Moiety formula   C20 H20 N4 O2             ?
Sum formula      C20 H20 N4 O2             C20 H20 N4 O2
Mr               348.40                    348.40
Dx,g cm-3        1.329                     1.329
Z                8                         8
Mu (mm-1)        0.089                     0.089
F000             1472.0                    1472.0
F000'            1472.57
h,k,lmax         27,10,28                  27,10,28
Nref             3877                      3758
Tmin,Tmax        0.974,0.980               0.974,0.980
Tmin'            0.972

Correction method= # Reported T Limits: Tmin=0.974 Tmax=0.980
AbsCorr = MULTI-SCAN

Data completeness= 0.969          Theta(max)= 27.140

R(reflections)= 0.0555( 1854)     wR2(reflections)= 0.1687( 3758)

S = 1.031                 Npar= 244
```

Hexahydro-1,2,4,5-terrazine ***2b****-Open*

X-ray analysis was carried out using the single crystal which was grown in MeOH (Figure S10).

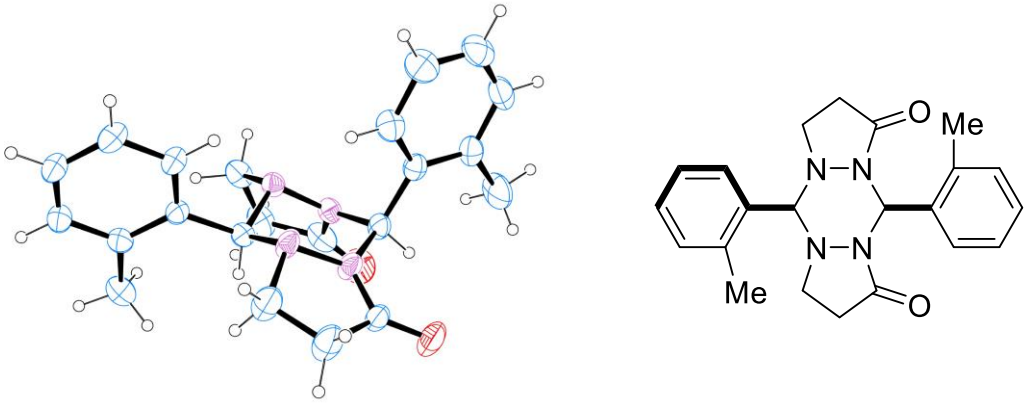


Figure S10. ORTEP drawing (30% probability ellipsoids) of **2b**

```
Bond precision:  C-C = 0.0040 A          Wavelength=0.71073

Cell:            a=18.660(2)     b=13.2963(15)      c=7.8585(9)
                 alpha=90        beta=90            gamma=90
Temperature:     296 K

                 Calculated                Reported
Volume           1949.8(4)                 1949.8(4)
Space group      P n a 21                  P n a 21
Hall group       P 2c -2n                  P 2c -2n
Moiety formula   C22 H24 N4 O2             ?
Sum formula      C22 H24 N4 O2             C22 H24 N4 O2
Mr               376.45                    376.45
Dx,g cm-3        1.282                     1.282
Z                4                         4
Mu (mm-1)        0.084                     0.084
F000             800.0                     800.0
F000'            800.31
h,k,lmax         22,15,9                   22,15,9
Nref             3469[ 1873]               3305
Tmin,Tmax        0.961,0.973               0.790,0.970
Tmin'            0.931

Correction method= # Reported T Limits: Tmin=0.790 Tmax=0.970
AbsCorr = MULTI-SCAN

Data completeness= 1.76/0.95      Theta(max)= 25.080

R(reflections)= 0.0418( 2686)     wR2(reflections)= 0.1136( 3305)

S = 1.253                 Npar= 255
```

Hexahydro-1,2,4,5-terrazine ***2f****-Open*

X-ray analysis was carried out using the single crystal which was grown in CH_2Cl_2-Hexane (Figure S11).

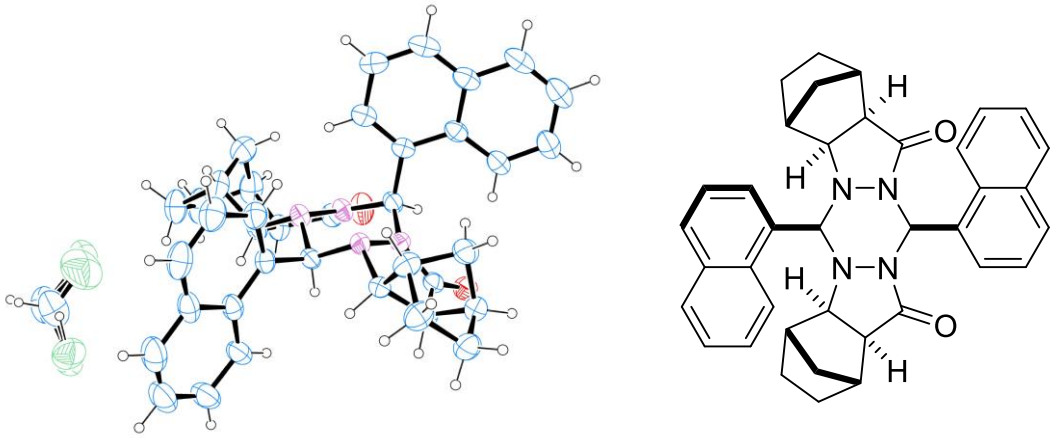


Figure S11. ORTEP drawing (30% probability ellipsoids) of **2f**-*Open*

```
Bond precision:   C-C = 0.0058 A          Wavelength=0.71073

Cell:           a=12.1570(17)      b=12.4397(18)     c=13.855(2)
                alpha=65.487(2)    beta=84.060(2)    gamma=62.571(2)
Temperature:    93 K

                 Calculated                 Reported
Volume           1682.1(4)                  1682.1(4)
Space group      P -1                       P -1
Hall group       -P 1                       -P 1
Moiety formula   C38 H36 N4 O2, C H2 Cl2    ?
Sum formula      C39 H38 Cl2 N4 O2          C39 H38 Cl2 N4 O2
Mr               665.63                     665.63
Dx,g cm-3        1.314                      1.314
Z                2                          2
Mu (mm-1)        0.234                      0.234
F000             700.0                      700.0
F000'            700.83
h,k,lmax         14,14,16                   14,14,16
Nref             5859                       5752
Tmin,Tmax        0.924,0.930                0.820,0.930
Tmin'            0.924

Correction method= # Reported T Limits: Tmin=0.820 Tmax=0.930
AbsCorr = MULTI-SCAN

Data completeness= 0.982           Theta(max)= 24.890

R(reflections)= 0.0456( 2449)                wR2(reflections)=
                                             0.1188( 5752)
S = 0.841                  Npar= 452
```

Hexahydro-1,2,4,5-terrazine ***2f****-Close*

X-ray analysis was carried out using the single crystal which was grown in $CDCl_3$-Hexane (Figure S12).

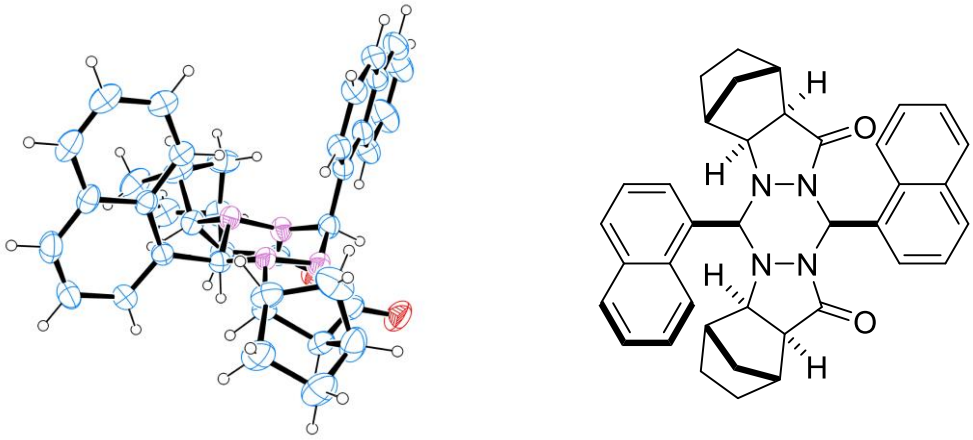


Figure S12. ORTEP drawing (30% probability ellipsoids) of **2f**-*Close*

```
Bond precision:   C-C = 0.0032 A          Wavelength=0.71073

Cell:             a=25.3011(11)     b=13.3310(5)        c=22.1748(9)
                  alpha=90          beta=110.356(3)     gamma=90
Temperature:      93 K

                  Calculated                  Reported
Volume            7012.2(5)                   7012.2(5)
Space group       C 2/c                       C 1 2/c 1
Hall group        -C 2yc                      -C 2yc
Moiety formula    C38 H36 N4 O2 [+ solvent]   ?
Sum formula       C38 H36 N4 O2 [+ solvent]   C76 H72 N8 O4
Mr                580.71                      1161.41
Dx,g cm-3         1.100                       1.100
Z                 8                           4
Mu (mm-1)         0.069                       0.069
F000              2464.0                      2464.0
F000'             2464.93
h,k,lmax          30,15,26                    30,15,26
Nref              6203                        6160
Tmin,Tmax         0.971,0.979                 0.920,0.980
Tmin'             0.971

Correction method= # Reported T Limits: Tmin=0.920 Tmax=0.980
AbsCorr = MULTI-SCAN

Data completeness= 0.993           Theta(max)= 25.050

R(reflections)= 0.0445( 3914)                wR2(reflections)=
                                             0.1509( 6160)
S = 0.933                  Npar= 397
```

DFT studies

As shown in Figure S13, there are four possible isomers of a chair conformation of **2** based on the direction of the two aromatic rings. Owing to DFT calculations, *Open* and *Close* isomers were satisfactorily found to explain the result of NMR experiments.

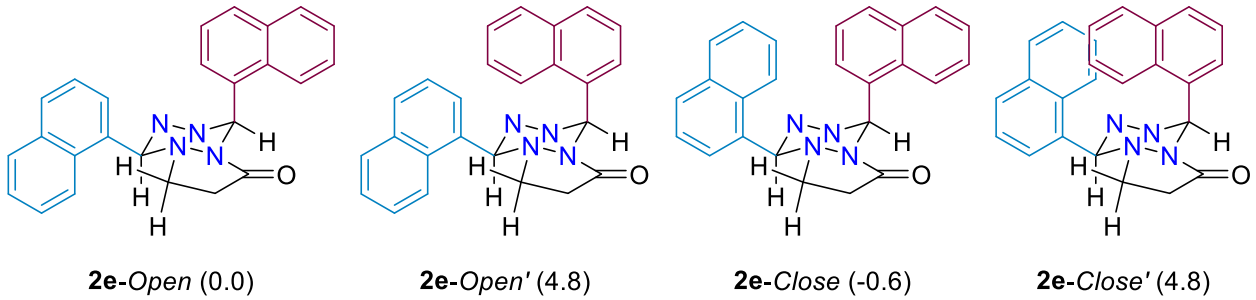
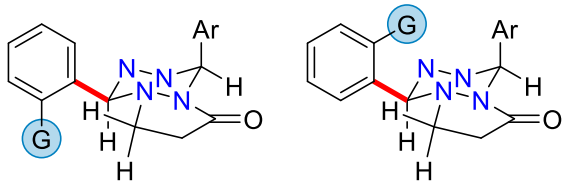


Figure S13. Relative Gibbs free energy (kcal mol^{-1}) of four possible isomers based on C-C bond rotation around two naphthyl groups. The calculations were performed at the PCM ($CHCl_3$)-B3LYP-D3(BJ)/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

One rotamer would be predominantly formed than the other if the isomers display large energy gap. The calculated ratios of rotamers based on the energy gaps are shown in Figure S14.



2 (G =)	ΔG kcal mol^{-1}	*Open*:*Close* *Calcd*	*Exp*
2b (Me)	0.7	3.2:1	4:1
2c (Ph)	1.8	19:1	>20:1
2d (CCPh)	2.9	>20:1	>20:1

Figure S14. Relative Gibbs free energy (kcal mol^{-1}) of the rotamers. The calculations were performed at the PCM ($CHCl_3$)-B3LYP-D3(BJ)/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

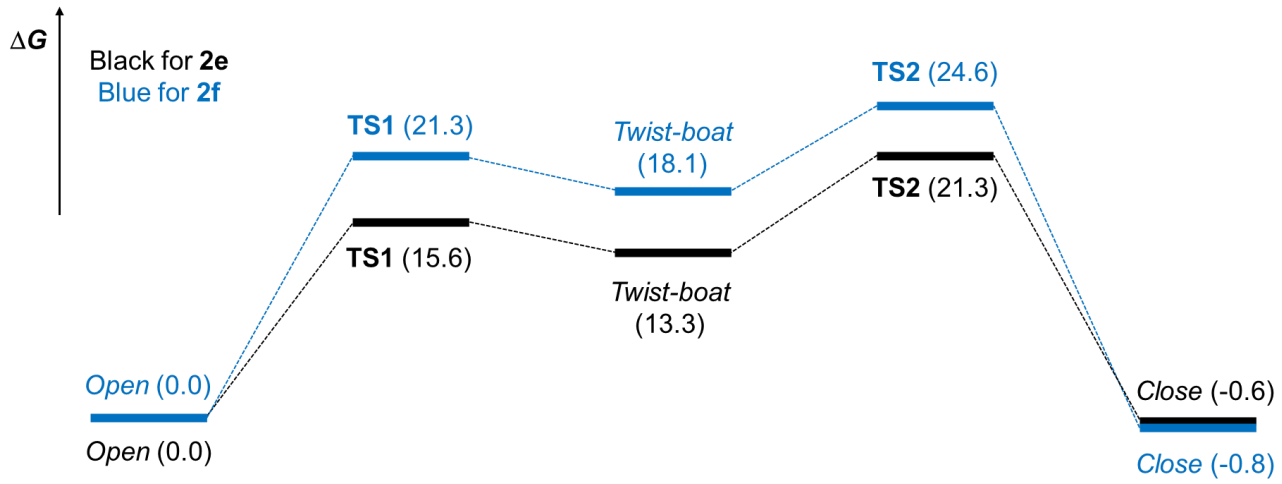


Figure S15. Computed energy profile for the isomerization. The calculations were performed at the PCM ($CHCl_3$)-B3LYP-D3(BJ)/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

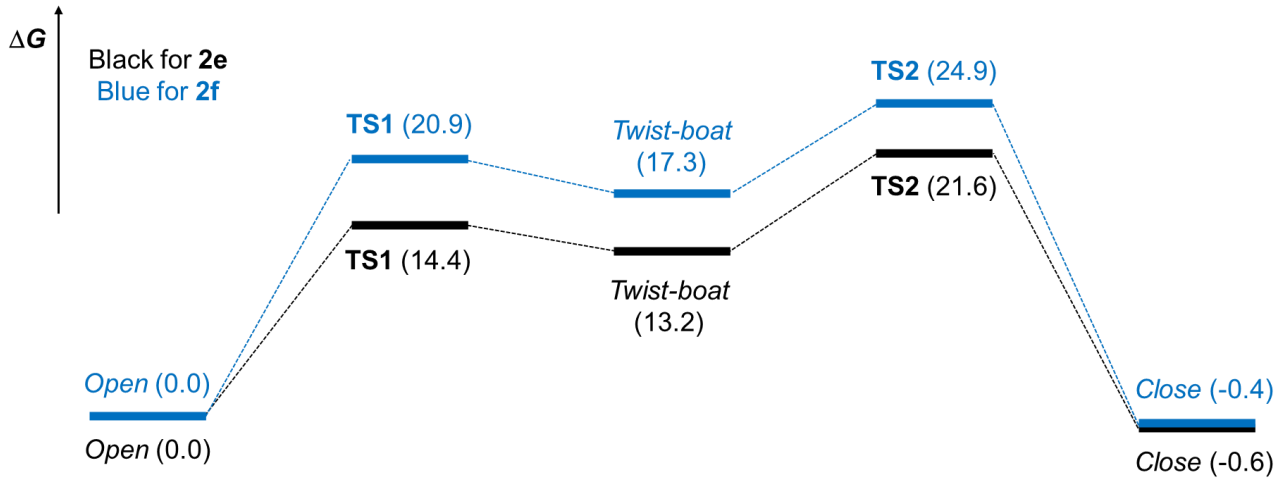
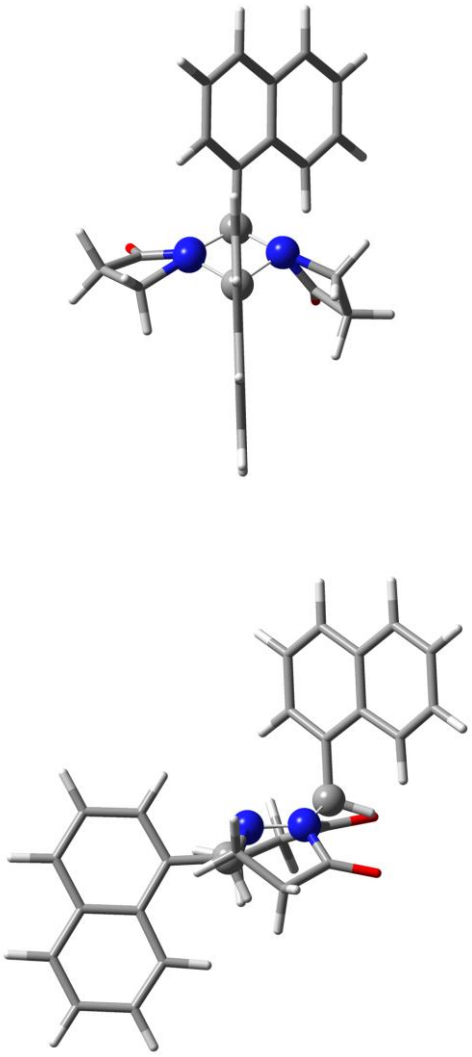


Figure S16. Computed energy profile for the isomerization. The calculations were performed at the SMD ($CHCl_3$)-ωB97X-D/6-311+G(d,p)// ωB97X-D/6-31G(d) level of theory.

Computational details

Quantum mechanical calculations were performed using Gaussian 16 (Revision C.01)[5] and Reaction plus Pro 2 (ver. 1.0)[6] software packages. The molecular geometries for the transition states were first estimated by Reaction plus based on the nudged elastic band (NEB) method[7] and were subsequently re-optimized using Gaussian. All geometries were optimized at the B3LYP/6-31G(d) level of theory with an ultrafine integration grid in the gas phase. For hexahydro-1,2,4,5-terrazine **2e**, the quasi-intrinsic reaction coordinate (qIRC) approach was used to search for reactants and products. In the qIRC calculations, the geometry of transition states was first shifted by perturbing the geometries very slightly along the reaction coordinate, and then released for equilibrium optimization. Single point energies were calculated using B3LYP-D3(BJ),[8] the 6-311+G(d,p) basis set, and an ultrafine integration grid with the PCM model ($CHCl_3$).[9] The refined energies were converted to zero-point energy-corrected free energies at 298.15 K and 1 atm with use of the B3LYP/6-31G(d) harmonic frequencies. In the case of hexahydro-1,2,4,5-terrazine **2f**, transition states, reactants, and products were directly calculated using the same level of theory on the basis of the results obtained by DFT calculations on hexahydro-1,2,4,5-terrazine **2e**.

2e-*Open*



Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1450.85461095 a.u.

Thermal correction to Gibbs Free Energy = 0.413834 a.u.

Sum of electronic and thermal Free Energies = -1450.440777 a.u.

The lowest frequency = 18.4691 cm^{-1}

Number of imaginary frequencies = 0

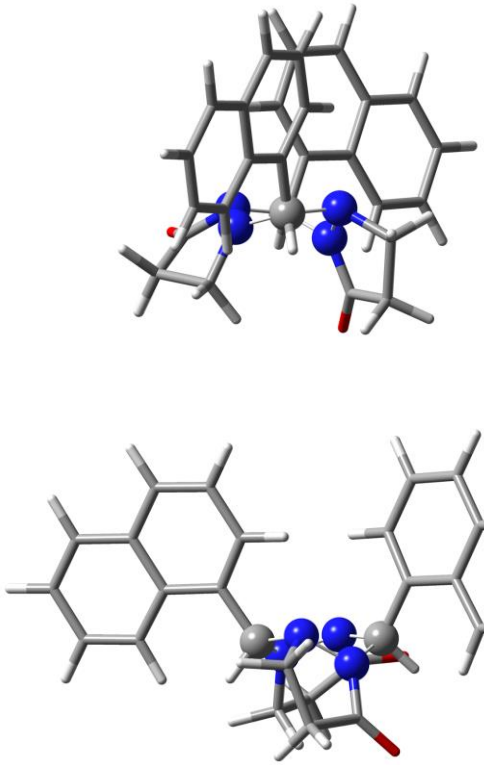
Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1451.38971433 a.u.

N	-2.6636687585	0.4426901419	0.0619323977
N	-2.1187923791	1.1627824295	-1.0721423888
C	-0.6649636502	1.3537364282	-0.8697732847
H	-0.5076906738	1.9151866718	0.0682171183
N	-0.0801605495	-0.0124829405	-0.7515114067
N	-0.6382414114	-0.6435899589	0.4076543082
C	-2.0763477016	-0.8471945928	0.3945987061
H	-2.3715521148	-1.0417116364	1.4284894208
C	1.3743916424	-0.0291851427	-0.4433429904
H	1.8699193779	0.7938502402	-0.9586640019
C	0.1397060129	-0.5467990221	1.5432060008
C	1.4858998707	0.0183534247	1.0893600431
H	1.5941365005	1.0341776321	1.488229849
O	-0.197180838	-0.9000529484	2.6609730724
C	-3.9482530765	0.8185613002	0.3716448543
C	-2.8758007863	2.440942396	-1.0264491833
H	-2.4093009834	3.1443978159	-0.3180315223
C	-4.2551756469	2.0277597608	-0.5101478019
H	-4.7717310186	2.8093629061	0.0503905396
O	-4.6719810789	0.256386841	1.1739069394
H	-0.7485472829	0.5017420925	-3.3474542814
C	-0.2341180778	1.4556404098	-3.3046306599
C	-0.0853649694	2.0700703462	-2.073576497
C	0.92780151	3.2478352718	-4.4269058566
C	0.5988708185	3.3277936579	-1.9783696737
C	0.2708073835	2.041302101	-4.4854459149
C	1.1096188935	3.9165938407	-3.1883327471
C	0.8109721664	4.0372539526	-0.7603545209
H	0.1372648389	1.5326554202	-5.4359953635
H	2.1691078336	5.5900772727	-4.0523977412

H	1.3208257867	3.7088958539	-5.3299150542
C	1.4777940392	5.2421814773	-0.7375738496
H	0.4425655591	3.6304413082	0.1749207713
H	1.6227338692	5.7577708153	0.2078795098
C	1.9749529484	5.8151797586	-1.9310722989
H	2.4986280021	6.7663925963	-1.89867634
C	1.7916904517	5.1619023543	-3.1267979947
H	-3.2009553976	-0.7822352775	-2.0868601857
C	-3.0677119834	-1.7982269724	-1.7334936097
C	-2.4943318771	-2.0155318472	-0.4984429775
C	-3.2909734528	-4.1709382238	-2.1362832009
C	-2.2935418668	-3.3570746057	-0.0297866041
C	-3.4679911841	-2.8760476412	-2.5575095925
C	-2.7049050961	-4.4454360157	-0.872030381
C	-1.7108846592	-3.6703783355	1.2317297297
H	-3.9170531937	-2.668737483	-3.525096846
H	-2.8414789595	-6.5930862456	-1.0737582589
H	-3.5979897009	-5.0056017192	-2.7622694992
C	-1.5501310269	-4.979122788	1.6330025148
H	-1.3770618075	-2.8792334764	1.8949408396
H	-1.1044248669	-5.1905164915	2.6012660882
C	-1.9574420214	-6.0473757173	0.8012613074
H	-1.8244258272	-7.0737478054	1.1326449508
C	-2.5223137737	-5.781028768	-0.4243264751
H	-4.9163765679	1.6944405074	-1.3196540683
H	-2.8780189263	2.8926503201	-2.0193658799
H	1.7749372736	-0.972271429	-0.827825793
H	2.3061254079	-0.5823372606	1.4893417843

$TS1_{2e}$



Optimization: B3LYP-D3/6-31G(d)

E(RB3LYP) = -1450.83106360 a.u.

Thermal correction to Gibbs Free Energy = 0.415199 a.u.

Sum of electronic and thermal Free Energies = -1450.415864 a.u.

The lowest frequency = -3.4524 cm^{-1}

Number of imaginary frequencies = 1

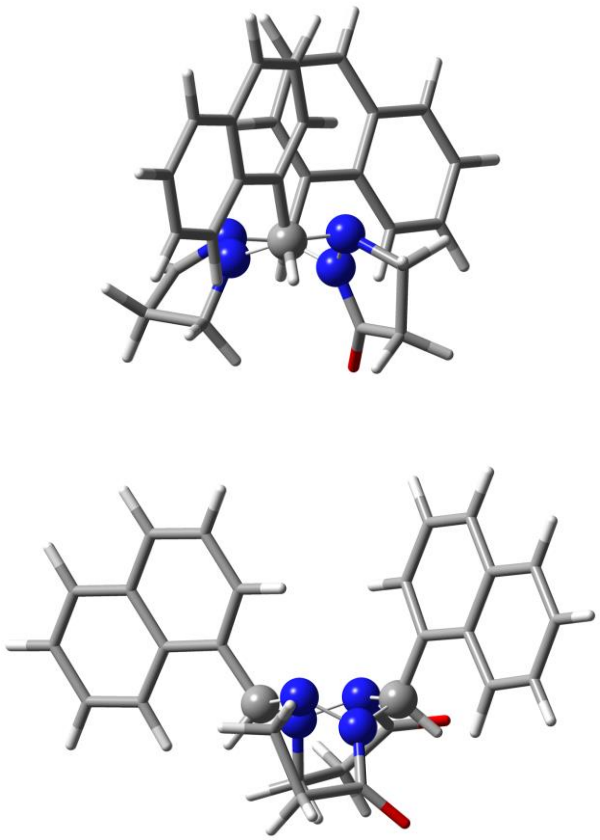
Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1451.36618929 a.u.

N	-2.5637874788	0.6482139763	-0.1233357607
N	-1.5688742357	1.6957827431	-0.0631529425
C	-0.2015534537	1.3716457127	-0.4607606763
H	0.427678066	1.9951466453	0.1897843619
N	0.1262950316	-0.0768251648	-0.2403671679
N	-0.7680666749	-0.624060436	0.7197820684

C	-2.1444930609	-0.7296680483	0.3022104689
H	-2.7197988734	-0.9993427662	1.1933999946
C	1.4512152916	-0.2994355412	0.3866843928
H	2.1577582669	0.4487517004	0.020957444
C	-0.2827539457	-0.6506899148	2.0078977963
C	1.196272224	-0.2598561761	1.9046922487
H	1.3298523064	0.7359235737	2.3449496922
O	-0.9180147103	-0.9707454891	2.9991662391
C	-3.7072027535	1.1325677483	0.5306882637
C	-1.8649505781	2.4777643738	1.1453102077
H	-1.5555417444	1.9856042321	2.0848284919
C	-3.3932920789	2.5402259759	1.04052075
H	-3.9171996362	2.7170159339	1.981451506
O	-4.7032481831	0.4690024552	0.7285581287
H	-0.0878679964	-0.2710624446	-2.5990540374
C	0.0850671448	0.7563968339	-2.8946763384
C	0.0844058253	1.7358424662	-1.9218836731
C	0.544196078	2.3622836638	-4.6418389338
C	0.3347999637	3.100914289	-2.294312323
C	0.3086485806	1.0659521714	-4.2570161875
C	0.568594068	3.4064434749	-3.6789768879
C	0.3766082771	4.1816856168	-1.3689854067
H	0.2941557606	0.2669233404	-4.9932335432
H	0.996200577	4.9577478476	-5.1205113303
H	0.7190645252	2.6104170521	-5.6860936285
C	0.6319726622	5.473153405	-1.7767549873
H	0.2081886762	3.9972255402	-0.3144051628
H	0.6594685406	6.2742083845	-1.0428117783
C	0.8552043932	5.7653518969	-3.1411419405
H	1.0517148066	6.7874920222	-3.4525281053
C	0.8236569127	4.7486946272	-4.0672769729
H	-2.8614577256	-0.3496663656	-2.2804369274
C	-2.724306832	-1.4021672373	-2.0605374926
C	-2.3614444895	-1.7754708273	-0.7848718025
C	-2.7676318697	-3.700962996	-2.8059528793
C	-2.2136107671	-3.1656840761	-0.4605603853
C	-2.9258747207	-2.3644515014	-3.0782748184
C	-2.4154663146	-4.1358102879	-1.4999095181
C	-1.8912129131	-3.6396671396	0.843322605
H	-3.2089903469	-2.0349556598	-4.0742187375
H	-2.4244107435	-6.2382792155	-2.0012528209
H	-2.9199171744	-4.4478036708	-3.5817306277
C	-1.7667377528	-4.9887190004	1.0977349872
H	-1.7477757165	-2.9416941619	1.6612182814
H	-1.5267651652	-5.3240324934	2.1031953993
C	-1.950955089	-5.9394130903	0.0677933597
H	-1.8465020409	-6.9993739355	0.283313166
C	-2.2706655449	-5.5169539821	-1.2018429935
H	-3.7041244114	3.2917427566	0.3054493505
H	-1.3850717423	3.4575361276	1.0813309895
H	1.8070236511	-1.2887369183	0.0815114713
H	1.8138101348	-0.9577610464	2.474611123

2e-*Twist-boat*



Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1450.83106407 a.u.

Thermal correction to Gibbs Free Energy = 0.411611 a.u.

Sum of electronic and thermal Free Energies = -1450.419453 a.u.

The lowest frequency = 4.1901 cm^{-1}

Number of imaginary frequencies = 0

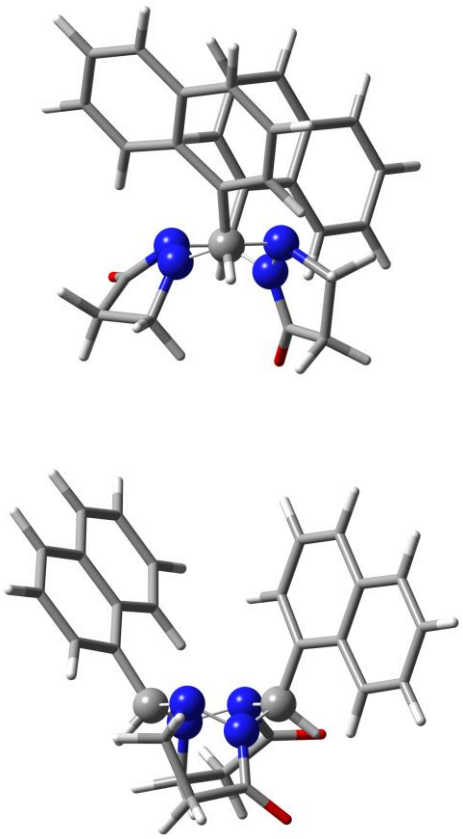
Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1451.36631605 a.u.

N	-0.100559727	1.5438489851	-0.0660613048
N	0.9071734896	2.577962799	0.0036028384
C	2.2614819926	2.2439549317	-0.4247953621
H	2.9092164287	2.8650370193	0.2097178829
N	2.5861938346	0.7930338937	-0.2086298881
N	1.6897233989	0.2437334763	0.7488435867
C	0.3098766748	0.155768886	0.3376156775
H	-0.2617857015	-0.1211366047	1.2289316494
C	3.9104472256	0.5610233565	0.4159178719
H	4.6196934101	1.3089354192	0.0548277512
C	2.1768228406	0.2064064441	2.0361382221
C	3.6573782732	0.5908913931	1.9343020312
H	3.7954421798	1.5831024952	2.3812820741
O	1.5407755787	-0.116215474	3.0261454599
C	-1.2305695144	2.0305888142	0.6106907559
C	0.6372670919	3.3369198265	1.2329266586
H	0.9497764739	2.8202327243	2.157868827
C	-0.8912638096	3.4226304385	1.1471273922
H	-1.4021879516	3.5858885828	2.0976035185
O	-2.2335490678	1.3770682886	0.8056588226
H	2.3718667724	0.5928806554	-2.5594804353
C	2.5234769839	1.6217716439	-2.8613361709
C	2.5172454688	2.6050459335	-1.8926359384
C	2.9326210391	3.2279071483	-4.6208088576
C	2.7390025922	3.9726755201	-2.2739802543
C	2.7247287012	1.9294222333	-4.2277423338
C	2.950436201	4.2764575827	-3.6624620906
C	2.7731069895	5.0575128155	-1.3533625748
H	2.7150191634	1.1270123491	-4.9603505117
H	3.3332131232	5.8290744035	-5.1151840986
H	3.0902473914	3.4745980936	-5.6681520704
C	3.0011882795	6.351549177	-1.7691424832
H	2.620126211	4.8739934249	-0.2963865757
H	3.0236429474	7.1559626724	-1.0386954396
C	3.2025850534	6.6420769543	-3.1372670638
H	3.3774900477	7.6662102563	-3.4549459242
C	3.1772741005	5.6213095584	-4.0591064846

H	-0.4276368652	0.5759242435	-2.23308432
C	-0.2959816497	-0.4803212008	-2.0285834028
C	0.0764955985	-0.8733117282	-0.7616578547
C	-0.361445491	-2.7684751286	-2.8046233356
C	0.2176451047	-2.2688093804	-0.4574620198
C	-0.5135177891	-1.4273966456	-3.0572562653
C	-0.000097678	-3.2233692016	-1.5079280902
C	0.5479970705	-2.7626362618	0.8370231975
H	-0.8036936712	-1.0824921661	-4.0459170163
H	-0.027460858	-5.3187155812	-2.0376230136
H	-0.5258051266	-3.5036875381	-3.5890011163
C	0.6655638826	-4.1158124752	1.0720870486
H	0.7026616322	-2.0767667073	1.6630486011
H	0.9117688713	-4.4663700285	2.0708215201
C	0.4661927399	-5.0511613138	0.030984755
H	0.5654845852	-6.1146171484	0.2311774173
C	0.1381713525	-4.6093552392	-1.2299225173
H	-1.1997605846	4.1941103272	0.432047648
H	1.1304558753	4.3110592874	1.1852108256
H	4.2625550647	-0.4274530893	0.1036846466
H	4.2724552091	-0.1135108218	2.4988621344

$TS2_{2e}$



Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1450.81864102 a.u.

Thermal correction to Gibbs Free Energy = 0.415051 a.u.

Sum of electronic and thermal Free Energies = -1450.403590 a.u.

The lowest frequency = -36.5112 cm^{-1}

Number of imaginary frequencies = 1

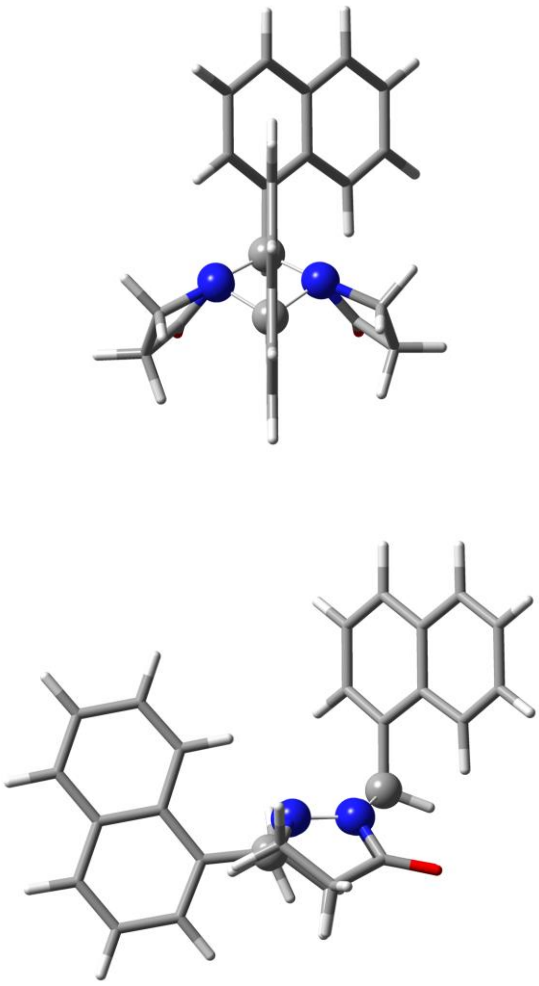
Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1451.35691425 a.u.

N	-0.0901711556	2.051823463	-0.2465296356
N	1.1679376936	2.7647209571	-0.1492228064
C	2.3487188679	2.2009123566	-0.7642281864
H	3.1718540654	2.5581499554	-0.1298112373
N	2.3357444526	0.6712088122	-0.737314716

N	1.3146606937	0.2188078772	0.1515879637
C	-0.040730801	0.5566223117	-0.2010526669
H	-0.6677200614	0.2440071347	0.6394538796
C	3.5440051821	0.0331693316	-0.1432963679
H	4.4345781302	0.6167291785	-0.371187605
C	1.741871977	-0.12553128	1.4153065262
C	3.2674752357	-0.1011903431	1.3624560906
H	3.6278794286	0.7524288556	1.9504377922
O	1.0150714676	-0.4233570083	2.3493447108
C	-0.9797306708	2.6528273159	0.654542163
C	1.2141447794	3.369576752	1.1880449507
H	1.4894857882	2.659198575	1.9875998225
C	-0.245814776	3.8096043542	1.3371063287
H	-0.5948231847	3.9090333616	2.3661958827
O	-2.0960922481	2.2367815814	0.8825953548
H	4.6076988316	1.7452123124	-1.9633556498
C	3.9571779546	2.2992559599	-2.6311397024
C	2.6934963157	2.671531163	-2.2014589986
C	3.6868929661	3.3208472286	-4.789279611
C	1.8790300708	3.4615730119	-3.0910811292
C	4.4603157268	2.6053505119	-3.9115293989
C	2.3997525469	3.7695072151	-4.4022949226
C	0.5916400156	3.9918234988	-2.7766912195
H	5.4566151457	2.2730097396	-4.1894526242
H	2.0427991467	4.7450400702	-6.2945608497
H	4.0507462156	3.5665809558	-5.7839294399
C	-0.1298646905	4.7378880661	-3.6824949822
H	0.1769431659	3.8070640481	-1.800344047
H	-1.1067794211	5.1201161416	-3.3979846668
C	0.3818806583	5.0142401899	-4.9699466263
H	-0.1993422776	5.601481311	-5.6755958932
C	1.6232930875	4.5378978422	-5.3127800061
H	-0.6001173416	1.6603518971	-2.6262373965
C	-0.7420904982	0.5868913803	-2.6283198466
C	-0.5110678374	-0.1284338009	-1.4753566636
C	-1.3706347582	-1.409785756	-3.8362312251
C	-0.7330875053	-1.5468048258	-1.4555785055
C	-1.1699811729	-0.0520027239	-3.8159900987
C	-1.1651091324	-2.188076027	-2.6652517929
C	-0.5623075623	-2.3547997324	-0.2951640662
H	-1.3350908465	0.5440235102	-4.7091502789
H	-1.7144607943	-4.06034679	-3.5944335703
H	-1.6976524779	-1.9098751424	-4.7449623507
C	-0.7974300292	-3.7125606972	-0.3334388452
H	-0.2508688761	-1.9083274397	0.6431129768
H	-0.6660946746	-4.3045990684	0.5683888416
C	-1.209503582	-4.3416434204	-1.5303635114
H	-1.3880733138	-5.4134594624	-1.5460478049
C	-1.3899373206	-3.590402858	-2.6687489331
H	-0.4335603878	4.7492676438	0.8037566774
H	1.9271614239	4.1987108606	1.1865620555
H	3.652283931	-0.953903832	-0.6042552096
H	3.6822228736	-1.0082233043	1.8082130708

2e-*Close*



Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1450.85588575 a.u.

Thermal correction to Gibbs Free Energy = 0.414572 a.u.

Sum of electronic and thermal Free Energies = -1450.441314 a.u.

The lowest frequency = 18.3841 cm^{-1}

Number of imaginary frequencies = 0

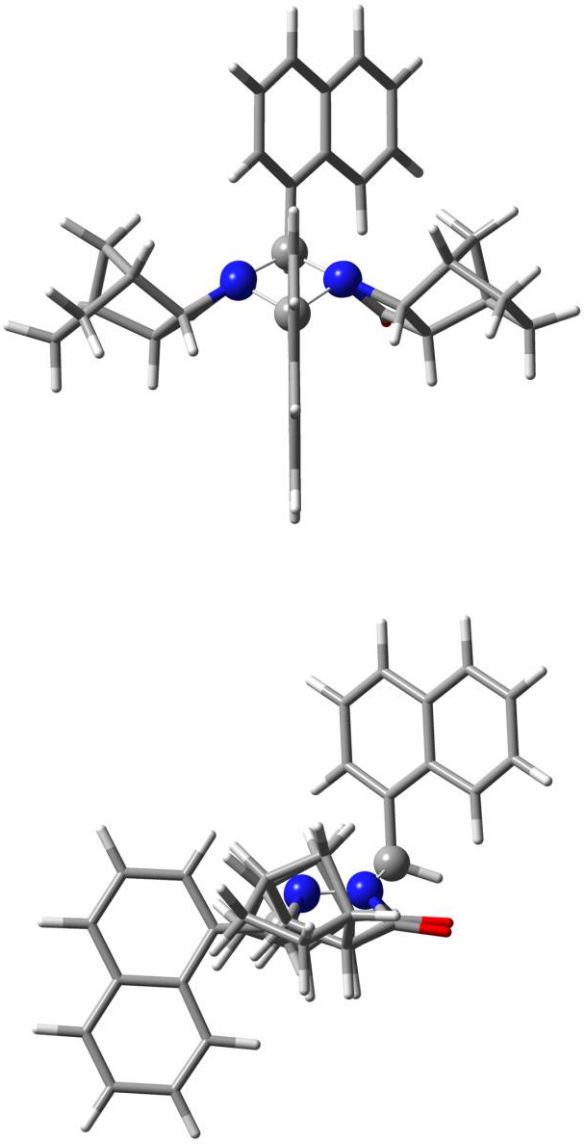
Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1451.39141009 a.u.

N	-0.1898609168	0.0109738271	0.2325689264
N	0.4500873923	0.9066514539	-0.6924133648
C	1.910246805	0.6092495094	-0.7374091755
H	2.3411708045	0.6791564242	0.2824663349
N	1.9999999163	-0.7947809043	-1.2290394554
N	1.377096125	-1.6551831378	-0.2668960312
C	-0.039420417	-1.4143524644	-0.0041431947
H	-0.2519687772	-1.8886936656	0.9589816472
C	3.3786091995	-1.3443299849	-1.2985658826
H	4.0728981127	-0.5582620415	-1.5953594111
C	2.2574479311	-2.2616904103	0.6068212312
C	3.6605573439	-1.9581149393	0.0813687644
H	4.1538457917	-1.2665431377	0.7750553834
O	1.9408726811	-2.9428964407	1.56773079
C	-0.4061624855	0.5541416062	1.4904893478
C	0.097155657	2.2393333522	-0.1368365642
H	0.8612341639	2.9653301214	-0.4142356279
C	-0.0772382508	2.0420709255	1.3761015432
H	0.8355260098	2.241485818	1.9504207515
O	-0.8118001048	-0.0599425156	2.4584254447
H	3.8617081495	2.2354284672	-0.0068181159
C	3.6422204099	2.3524764313	-1.0657179133
C	2.6485483921	1.5780545592	-1.6394637797
C	4.1140361021	3.4598652364	-3.1537098579
C	2.3547818056	1.7258795047	-3.0389400519
C	4.3801620807	3.2954871166	-1.8158516988
C	3.1075103964	2.6896079886	-3.794812086
C	1.3602008171	0.9670082193	-3.7190448722
H	5.1517597198	3.8843718103	-1.3282738724
H	3.4112639132	3.5905392193	-5.7371362471
H	4.6723534629	4.182916573	-3.7436109307
C	1.1249875408	1.1558967866	-5.0631820232
H	0.7967819197	0.2292458089	-3.1643047376
H	0.3627981475	0.5626120114	-5.5610823222

C	1.8636540808	2.1086538886	-5.8032155747
H	1.6642221823	2.2448673505	-6.8627229584
C	2.8340250099	2.8569687194	-5.1792574585
H	-1.514925612	-0.0590913471	-1.8402461115
C	-1.6377835287	-1.1305963837	-1.9424166008
C	-0.9508141234	-1.9733700635	-1.0935520007
C	-2.6540633047	-2.9915312443	-3.1022611182
C	-1.1146272609	-3.3943452058	-1.2140359722
C	-2.4908297235	-1.6365644124	-2.951222501
C	-1.9802460958	-3.8997935697	-2.243076631
C	-0.47633408	-4.3344485015	-0.3553128761
H	-3.0140973325	-0.9425831335	-3.6034778373
H	-2.8158142064	-5.6679501412	-3.163551204
H	-3.3066335415	-3.3899073663	-3.8757395693
C	-0.6770697032	-5.6889245006	-0.5133225369
H	0.1774789926	-3.9955317093	0.4412417205
H	-0.1808391588	-6.3843623571	0.158258631
C	-1.5206462994	-6.1827076865	-1.5347798994
H	-1.6669937902	-7.2536726916	-1.6470128272
C	-2.1580320685	-5.3026144473	-2.3781121548
H	-0.8781249819	2.6458814416	1.8089362959
H	-0.8498923844	2.5422822515	-0.595132756
H	3.378266142	-2.1195439615	-2.071098722
H	4.2586658092	-2.8714769774	0.0436677143

2f-*Open*



Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1839.14714592 a.u.

Thermal correction to Gibbs Free Energy = 0.607033 a.u.

Sum of electronic and thermal Free Energies = -1838.540113 a.u.

The lowest frequency = 16.2113 cm^{-1}

Number of imaginary frequencies = 0

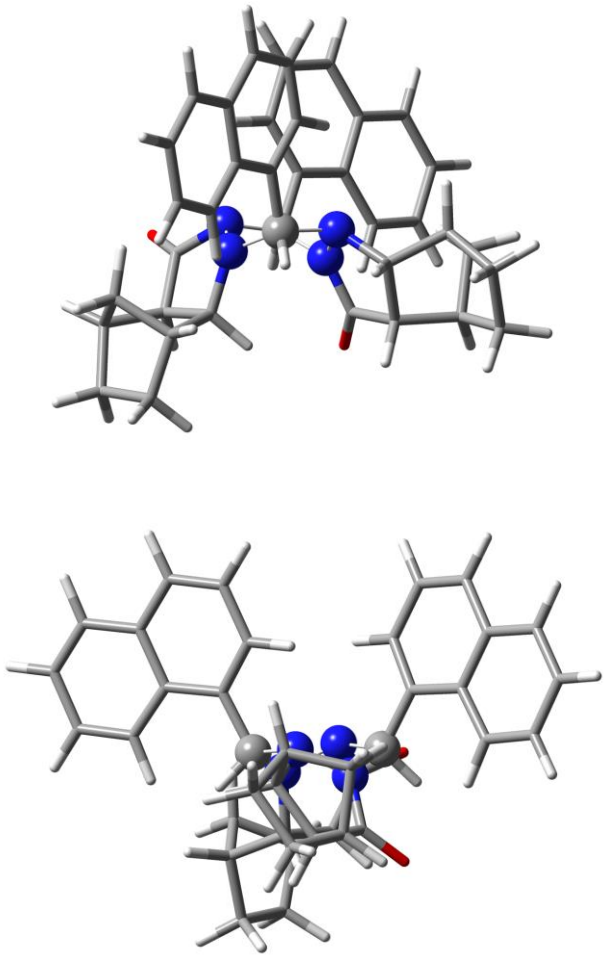
Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1839.836104 a.u.

N	0.4925107197	0.5673343143	0.0365715809
N	0.8238622712	1.3901262837	-1.0923788178
C	2.2994311547	1.3718580887	-1.3049956364
H	2.8064319822	1.7591409058	-0.403504779
N	2.6862872786	-0.0528935438	-1.5145628643
N	2.3535656802	-0.7844215624	-0.3303998229
C	0.9456758389	-0.8103542246	0.0397776417
H	0.9084484585	-1.1164594728	1.0886916021
C	4.1646209843	-0.2379180984	-1.6665366283
H	4.6165195056	0.738224344	-1.8511088763
C	3.4099987041	-1.1947135925	0.4389614967
C	4.6753649374	-0.920427323	-0.3605390424
H	5.365471185	-0.3214034658	0.2421211496
O	3.3231474072	-1.7589928191	1.5217343245
C	-0.0034700444	1.2246266336	1.1359407505
C	0.2991796683	2.7494008021	-0.7383145764
H	1.0970000735	3.478878962	-0.891882534
C	-0.1977536082	2.6801546744	0.7373729021
H	0.3473914065	3.3181736559	1.4403845287
O	-0.2895119556	0.6978764051	2.1993085472
H	1.4361972648	0.8814714784	-3.7330077877
C	2.0720718026	1.7599698127	-3.7405298495
C	2.6319282599	2.1788303452	-2.5463393463
C	3.1297425874	3.5536846045	-4.9600955625
C	3.4851245728	3.3325296476	-2.5239273234
C	2.3185069572	2.4436078647	-4.9508100134
C	3.728913741	4.0239518757	-3.7626654433
C	4.1125350176	3.8438719478	-1.3501388931
H	1.8637313728	2.0865446235	-5.8705465647
H	4.7397531121	5.6783725695	-4.7166485162
H	3.326177303	4.089026147	-5.8859883224
C	4.9211530836	4.9582252719	-1.3947699987
H	3.9577031762	3.3524657039	-0.3959303022
H	5.3846300958	5.3220199258	-0.4817728434
C	5.1545202929	5.6324613189	-2.6156186692
H	5.7943654232	6.5101184094	-2.6367090027
C	4.5686366684	5.1703558579	-3.770498406
H	-0.6675025404	-0.2155919232	-2.062244872
C	-0.6648918748	-1.2789751596	-1.8553822018
C	0.1164814768	-1.7618413032	-0.8251363078
C	-1.4481176119	-3.4961699623	-2.4138605478
C	0.1438818614	-3.1717013011	-0.5529764454
C	-1.448768768	-2.1441372845	-2.6535965501
C	-0.6606450111	-4.042353979	-1.3661728214
C	0.9215064458	-3.7592395533	0.4865760726
H	-2.0521571755	-1.7276928964	-3.4558182469
H	-1.2763878283	-6.0816050371	-1.7303339648
H	-2.0504942578	-4.1688767012	-3.02009431
C	0.898095747	-5.1197868384	0.7073320503
H	1.5587707734	-3.1426539621	1.111645108
H	1.5014580067	-5.5405906808	1.5071562905
C	0.1018332936	-5.971347975	-0.092070912
H	0.0932534656	-7.0415627182	0.0966285189
C	-0.6590600477	-5.4388728279	-1.106680029
C	5.3346076102	-2.2292725613	-0.8752317088
H	5.4624539285	-2.9740647855	-0.0861691208
C	4.557195304	-1.2481460224	-2.7680615759
H	3.9938130066	-1.1091756876	-3.6933095021
C	4.4052808301	-2.6076674946	-2.0506650032
H	3.3789071999	-2.8410165653	-1.754094922
H	4.794914076	-3.4434263311	-2.6427746772
C	6.6323528842	-1.8368778436	-1.6199674412
H	7.2660155589	-1.1692317549	-1.0256667891
H	7.2268727386	-2.7279216411	-1.8494619973

C	6.0964348139	-1.1606019817	-2.9269836818
H	6.445362275	-0.1281485515	-3.0437496792
H	6.4172468147	-1.7117591163	-3.8172080512
C	-1.6945108661	3.0767058724	0.6337285454
H	-2.2711450154	2.7743438625	1.511011406
C	-0.9747201603	3.1473221076	-1.5176471115
H	-0.9086129084	2.9245353573	-2.5850202419
C	-2.0925259016	2.4415329275	-0.7172233052
H	-3.0966446957	2.73536379	-1.0433316196
H	-2.028234132	1.349551228	-0.7300828466
C	-1.2589806287	4.6346159744	-1.1862600895
H	-0.3722738155	5.2657710295	-1.3148179572
H	-2.0342804936	5.0292815593	-1.8513282366
C	-1.7578894132	4.5849456281	0.2973011665
H	-1.1403964536	5.1867574301	0.9731671283
H	-2.7856864906	4.9543169015	0.3825363789

$TS1_{2f}$



Optimization: B3LYP-D3/6-31G(d)

E(RB3LYP) = -1839.11399215 a.u.

Thermal correction to Gibbs Free Energy = 0.609145 a.u.

Sum of electronic and thermal Free Energies = -1838.504847 a.u.

The lowest frequency = -11.9264 cm^{-1}

Number of imaginary frequencies = 1

Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

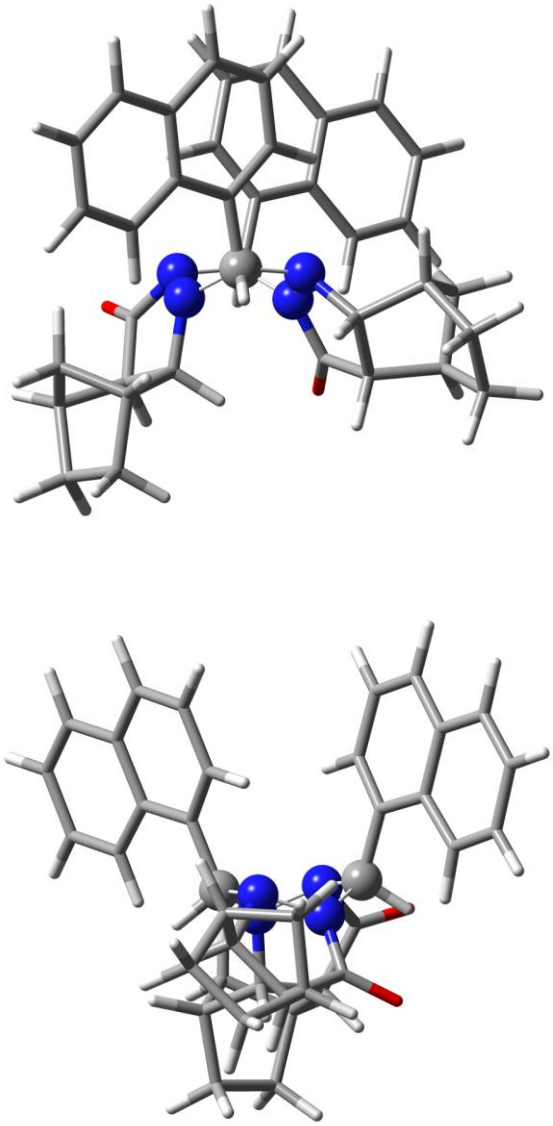
E(RB3LYP) = -1839.804311 a.u.

N	1.0492771437	1.1093686123	-0.3617422063
N	2.1000748318	2.083598539	-0.2274257063
C	3.2925396596	1.7755605672	-0.9996052161

H	4.0771012955	2.4027341867	-0.5583804624
N	3.6933232109	0.3226191911	-0.8656487748
N	2.9052948235	-0.2812520177	0.1577486625
C	1.4720944803	-0.3155429413	-0.0338700914
H	1.0734288443	-0.6046505572	0.9452525056
C	5.1059235451	0.1180423554	-0.442784328
H	5.6376273781	1.0648763624	-0.5746449662
C	3.5755152024	-0.5752315427	1.3163104435
C	5.0604162081	-0.3777336351	1.0375678664
H	5.4837763742	0.30780857	1.7789408214
O	3.0617105485	-1.0021841991	2.3439888565
C	0.0307566543	1.5355150706	0.5386373342
C	2.1451588246	2.5862496558	1.1718199033
H	2.8296038654	2.0220390656	1.821488594
C	0.6533726672	2.4503797183	1.5898456824
H	0.5217484426	1.9184188592	2.5387915529
O	-1.0962867063	1.0989813547	0.5345643254
H	2.8533400339	0.0884879403	-3.0514878157
C	2.9103778095	1.1084659159	-3.4066844389
C	3.1565564057	2.1150967649	-2.4940192764
C	2.8259685676	2.6580693342	-5.2587198818
C	3.2878545179	3.4657697936	-2.9694349659
C	2.7350856292	1.3736331051	-4.7847938627
C	3.1135076872	3.7291602929	-4.3723903079
C	3.6125477315	4.57090834	-2.1361972192
H	2.5286275959	0.5487561294	-5.4613707889
H	3.1026218247	5.2327829401	-5.9229815489
H	2.6926885778	2.8745124318	-6.3161276268
C	3.7432880041	5.8472210139	-2.639213512
H	3.7664263605	4.4121298104	-1.0782247264
H	3.9961329284	6.6659768565	-1.9706082509
C	3.5503766134	6.1000270698	-4.0157884575
H	3.6495949775	7.1104332325	-4.402741948
C	3.2445479937	5.0572707147	-4.8590489775
H	0.2635648463	0.2133477409	-2.3880825169
C	0.3787382937	-0.8534031284	-2.2433898305
C	0.9783813598	-1.305797033	-1.086973596
C	0.0362834786	-3.1056545106	-3.0498916379
C	1.0852725145	-2.7185324983	-0.8471769278
C	-0.0902964065	-1.7509450058	-3.2312143492
C	0.6144781383	-3.6228340278	-1.8598647875
C	1.6122284655	-3.2791027567	0.3518948939
H	-0.5525465337	-1.3558116984	-4.1316595233
H	0.3595938406	-5.6916453732	-2.4288717692
H	-0.3179733699	-3.8038629671	-3.8048037731
C	1.6866086776	-4.6453448053	0.5260656942
H	1.9497471325	-2.6358752843	1.1573115848
H	2.0861218548	-5.0440282595	1.4547844796
C	1.2445247397	-5.5300070428	-0.4832828783
H	1.3130743512	-6.6040226222	-0.3326668773
C	0.7170391713	-5.0234981603	-1.6485677966
C	5.82730053	-1.7273134855	0.9848513364
H	5.6280334461	-2.3586863158	1.8540726739
C	5.8484025616	-1.0247415966	-1.1729461499
H	5.6782500977	-1.0219744427	-2.2519993754
C	5.3994809899	-2.279799082	-0.3936967828
H	4.3321003791	-2.4998671722	-0.4789044536
H	5.9614586302	-3.1763279982	-0.6787781925
C	7.3206162206	-1.4058136489	0.7396632489
H	7.7019674369	-0.648584375	1.4337510044
H	7.9322829668	-2.3045391535	0.8737755516
C	7.3368268774	-0.9260367149	-0.7512241169
H	7.7372316043	0.0880243964	-0.8654864279
H	7.9511189163	-1.5862149707	-1.3722399987

C	0.1517763083	3.9133064417	1.7127968353
H	-0.9302010333	4.0110662738	1.5959905327
C	2.3662842392	4.1133936406	1.2732183813
H	3.2914870816	4.4685995273	0.8149444659
C	1.042935276	4.6579546994	0.6938160389
H	0.9551678733	5.7470090187	0.7761057811
H	0.879494323	4.3615397209	-0.3449683851
C	2.2523025423	4.5013877135	2.7732411358
H	2.816893143	3.8176114965	3.417767274
H	2.655383997	5.5056470256	2.9392201725
C	0.713471383	4.4517901066	3.0481846628
H	0.4525098311	3.8158616451	3.9008184968
H	0.3179868721	5.4528987816	3.2524457105

2f-*Twist-boat*



Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1839.11438147 a.u.

Thermal correction to Gibbs Free Energy = 0.607032 a.u.

Sum of electronic and thermal Free Energies = -1838.507349 a.u.

The lowest frequency = 9.6481 cm^{-1}

Number of imaginary frequencies = 0

Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1839.807246 a.u.

N	-0.4007960441	0.4082254293	-0.0000397924
N	0.7245061415	1.3210573397	0.0065718536
C	1.8509535605	0.895516351	-0.808871285
H	2.6666269874	1.570021434	-0.5158469
N	2.2840766835	-0.5161327025	-0.5085489839
N	1.3724477178	-1.1163332012	0.4155600081
C	-0.0462409854	-1.056010409	0.1306981689
H	-0.5213065452	-1.4446436723	1.0377397638
C	3.634762078	-0.674260383	0.0979314087
H	4.1273771041	0.3036203284	0.1094668766
C	1.9171190974	-1.4919158308	1.6138776601
C	3.4202887214	-1.2794973741	1.5193513209
H	3.7430226018	-0.644219554	2.3509884749
O	1.2928972112	-1.9786705106	2.5503575481
C	-1.2519752107	0.8218516204	1.0552022347
C	0.9499646168	1.8189834816	1.3922694457
H	1.7188836411	1.2505556401	1.9344281863
C	-0.4623044048	1.6955559413	2.0245706038
H	-0.4626498665	1.1332361827	2.9649508517
O	-2.3743846005	0.3984124556	1.2163220434
H	1.8878614139	-1.0146378927	-2.7131443896
C	1.7141837477	-0.04403773	-3.1572465491
C	1.6369340011	1.0578003394	-2.3286042379
C	1.3573077053	1.2815440963	-5.1454826574
C	1.4447994022	2.3550579769	-2.9208597335
C	1.566522888	0.0589679201	-4.5603192068
C	1.3010031671	2.4549179187	-4.3479730495
C	1.41666987	3.5659074335	-2.1773932303
H	1.6192064152	-0.8419747588	-5.1652441098
H	1.0070243992	3.7794352123	-6.0286381258
H	1.2441564548	1.3741008603	-6.223192278
C	1.2515899985	4.7896814468	-2.7898073916
H	1.5147606918	3.5258828502	-1.1037951878
H	1.2373647489	5.6945327894	-2.1876925773
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H	-1.7570904487	-3.969939602	-4.1290154685
C	0.1927121048	-5.4177176564	0.0650831563
H	0.4024549831	-3.5202042026	0.9938543546
H	0.5720555778	-5.9450868817	0.9363316611
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C	4.2158161374	-2.6118754462	1.4675376403
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H	4.5104905697	-1.6433094616	-1.6900357296
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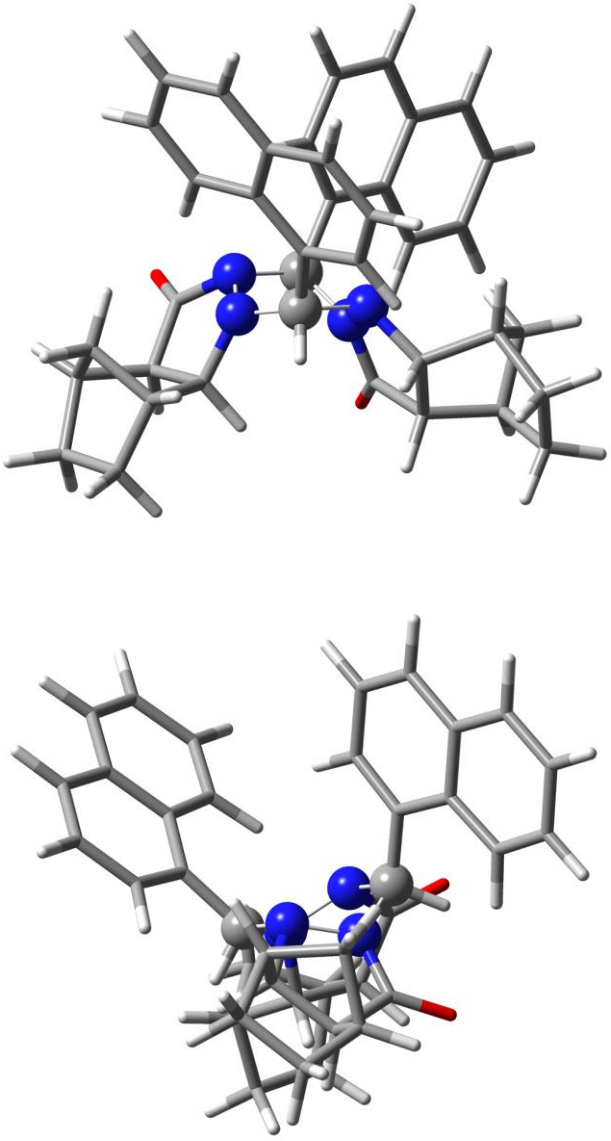

Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1839.10654542 a.u.

Thermal correction to Gibbs Free Energy = 0.609305 a.u.

Sum of electronic and thermal Free Energies = -1838.497241 a.u.

The lowest frequency = -14.6255 cm^{-1}

Number of imaginary frequencies = 1

Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1839.799173 a.u.

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N	0.9856111797	1.9450539796	-1.2335739057
N	0.0696038091	1.3891869196	-0.2911137465
C	-1.3358330869	1.5326065983	-0.577942087
H	-1.8580414782	1.1456762415	0.3015861733
C	2.3339378473	1.5452027641	-0.7173733584
H	2.9696009396	2.4335742921	-0.6803978861
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C	2.1195997269	0.9043048938	0.6891082854
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O	-0.0303024359	0.407156438	1.7912203377
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C	-0.2847090112	4.4713510367	0.7492090141
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C	-1.7307501948	4.4153687601	1.3036743362
H	-1.7972536454	3.9390736855	2.2876319277
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C	0.9373262708	3.9173352244	-2.7814957044
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C	-1.7907273586	0.7648142861	-1.8137783822
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C	-1.8939209711	-0.66718293	-1.7486719621
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C	-2.3109702045	-1.3774462656	-2.9258623015
C	-1.6213834062	-1.4272508533	-0.5744897607
H	-2.7724785579	1.268506478	-5.0356587187
H	-2.7385491312	-3.3123567367	-3.7868338776
H	-2.9292743851	-1.2083765019	-4.9933983918
C	-1.7465270744	-2.8008248922	-0.5708747488
H	-1.3149375739	-0.9344058306	0.3420963463
H	-1.5379014852	-3.353471433	0.3413236526
C	-2.1458410264	-3.4951317168	-1.7350145242
H	-2.2384748193	-4.5777422888	-1.7169596283
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C	3.008817134	0.4099503211	-1.5207382533
H	2.9305539143	0.5473351064	-2.6013482421
C	2.3495507223	-0.8557474612	-0.9306330912
H	1.274656358	-0.9237380825	-1.1179140006
H	2.8218840791	-1.7798719875	-1.2822085217
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C	4.456465485	0.2764292425	-0.9824062594
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C	-2.1607355638	5.9034275965	1.3886457013
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H	0.7095182023	5.8722382386	2.7744427923
H	0.4964397522	7.5157705261	2.1754643116
C	-1.4225361525	6.5025623309	2.610194536
H	-1.5835900315	5.9205984768	3.5238926728
H	-1.7759231203	7.5210395415	2.8047988993

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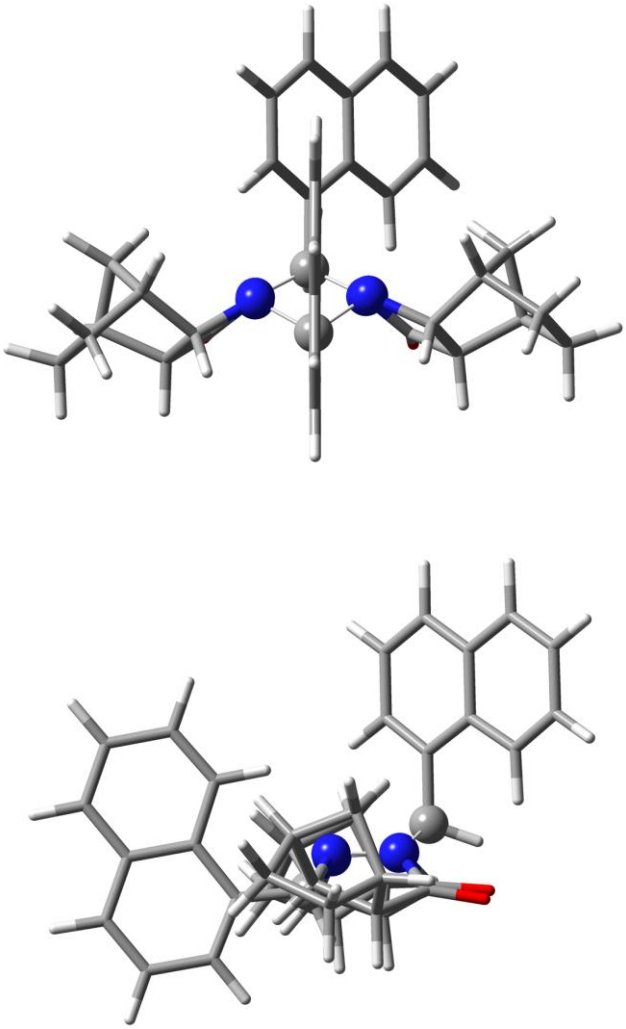

Optimization: B3LYP/6-31G(d)

E(RB3LYP) = -1839.14802752 a.u.

Thermal correction to Gibbs Free Energy = 0.607985 a.u.

Sum of electronic and thermal Free Energies = -1838.540042 a.u.

The lowest frequency = 16.3529 cm^{-1}

Number of imaginary frequencies = 0

Single-point calculation: PCM($CHCl_3$)- B3LYP-D3(BJ)/6-311+G(d,p)

E(RB3LYP) = -1839.838386 a.u.

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N	-1.4813387971	0.5960246383	-0.5315909121
C	-0.052225934	0.2041405903	-0.7045948488
H	0.4598195436	0.2405919527	0.2790742588
N	-0.0510347287	-1.200741596	-1.2055443115
N	-0.660280862	-2.0262055441	-0.2071124194
C	-2.044596174	-1.725349675	0.1308957928
H	-2.2351733941	-2.2039566155	1.0958336031
C	1.3243209239	-1.7662465577	-1.3702520706
H	2.0355123075	-0.9391360866	-1.3596623078
C	0.1914193798	-2.841605649	0.4923838733
C	1.5390646626	-2.7870544057	-0.2114290779
H	2.3178865231	-2.5211387801	0.510384177
O	-0.1229453975	-3.5472648684	1.4417830218
C	-2.4884991627	0.2448992106	1.6001794255
C	-1.6570760864	1.9527237337	0.0798401437
H	-0.6879850583	2.4541083177	0.0852489862
C	-2.2536081305	1.7448281475	1.5042274544
H	-1.6047566053	2.0573168106	2.3288360834
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C	0.6600352934	1.1475717478	-1.657705811
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C	0.2743740066	1.3162823288	-3.0317416647
C	2.4374394158	2.8024633486	-1.9518045884
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H	3.2636910117	3.3584283031	-1.518047542
H	1.1972128171	3.1662252174	-5.7886455408
H	2.6198385178	3.6971131902	-3.8899397369
C	-1.114195968	0.8019569662	-4.9681363826
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C	0.6367273525	2.4477215161	-5.1951759522
H	-3.3964198853	-0.2889083166	-1.7384876455
C	-3.6513238272	-1.3404538252	-1.7872933604
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C	-2.6184934806	4.2423681117	-0.0106807472
H	-1.5887797997	4.6176475543	-0.0064950282
H	-3.2170580946	4.9513569253	-0.5922083585
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H	-2.4870835446	4.3251890208	2.2162172548
H	-4.0933141735	4.6779769609	1.5799754215

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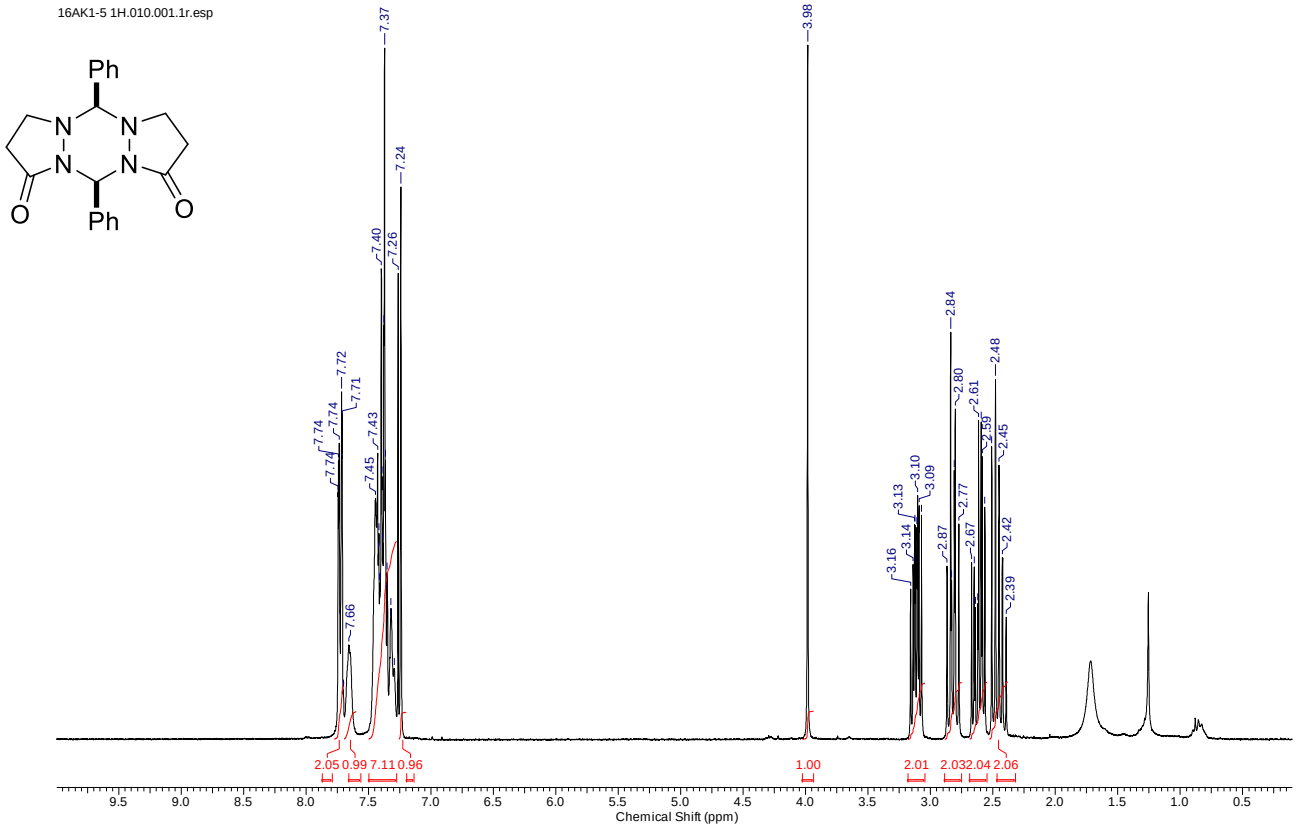
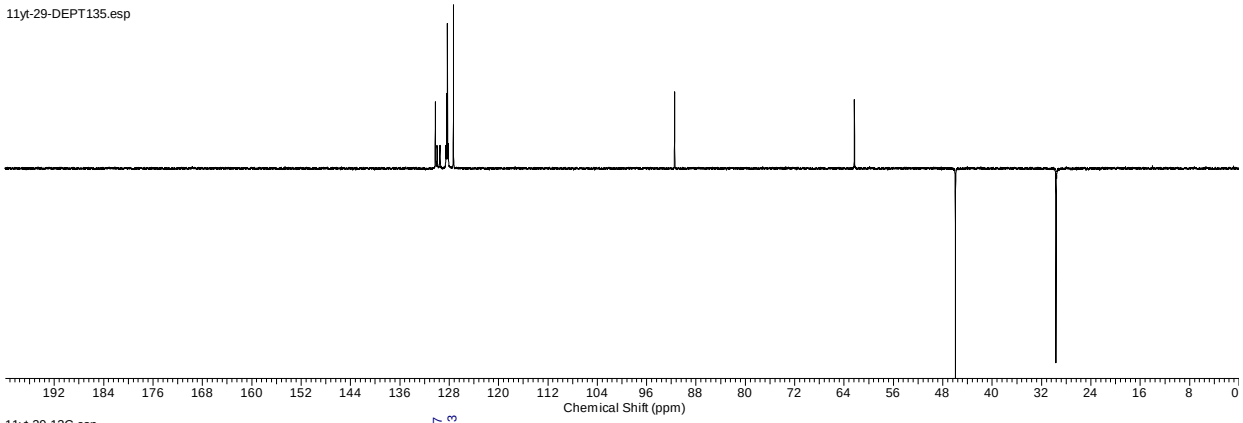
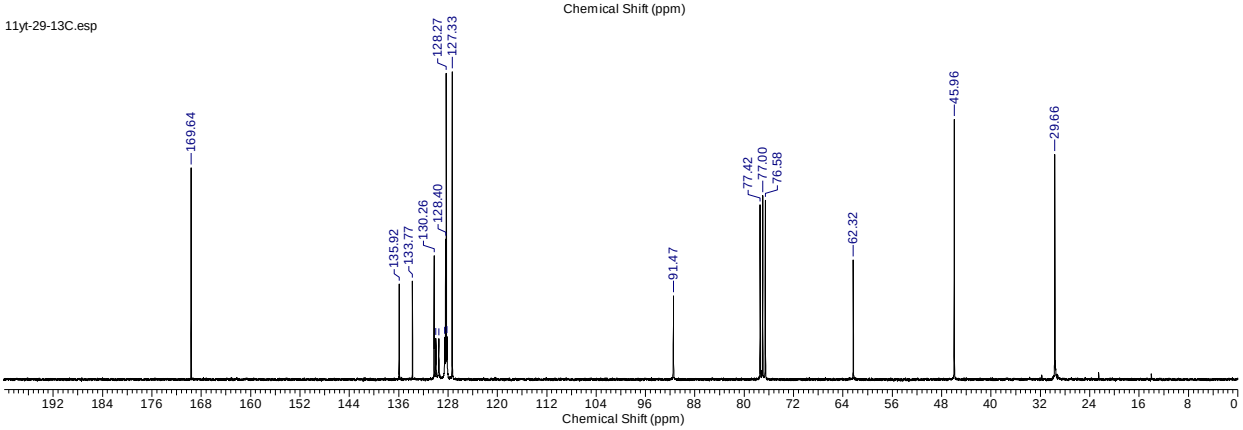
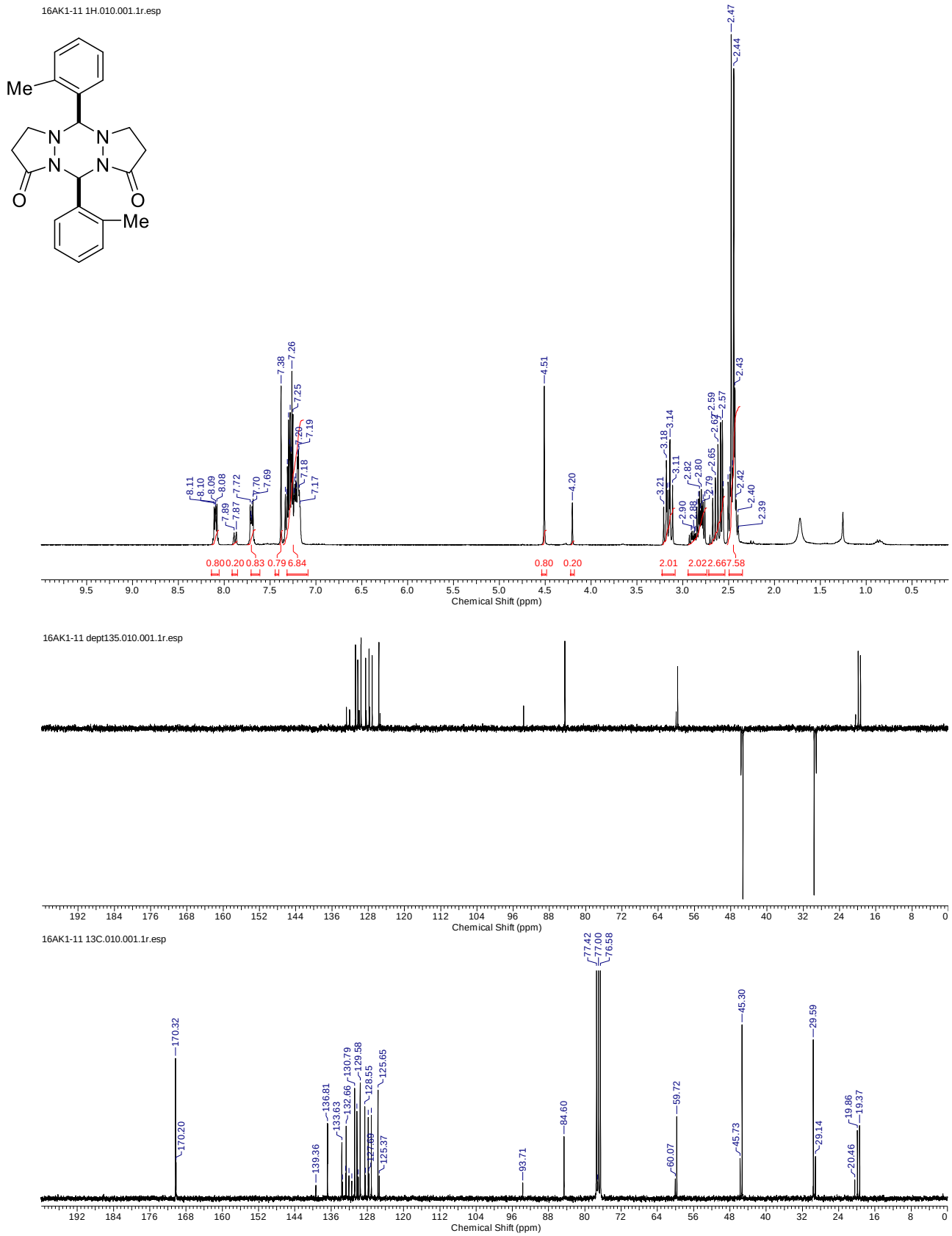
NMR spectra ^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **2a**



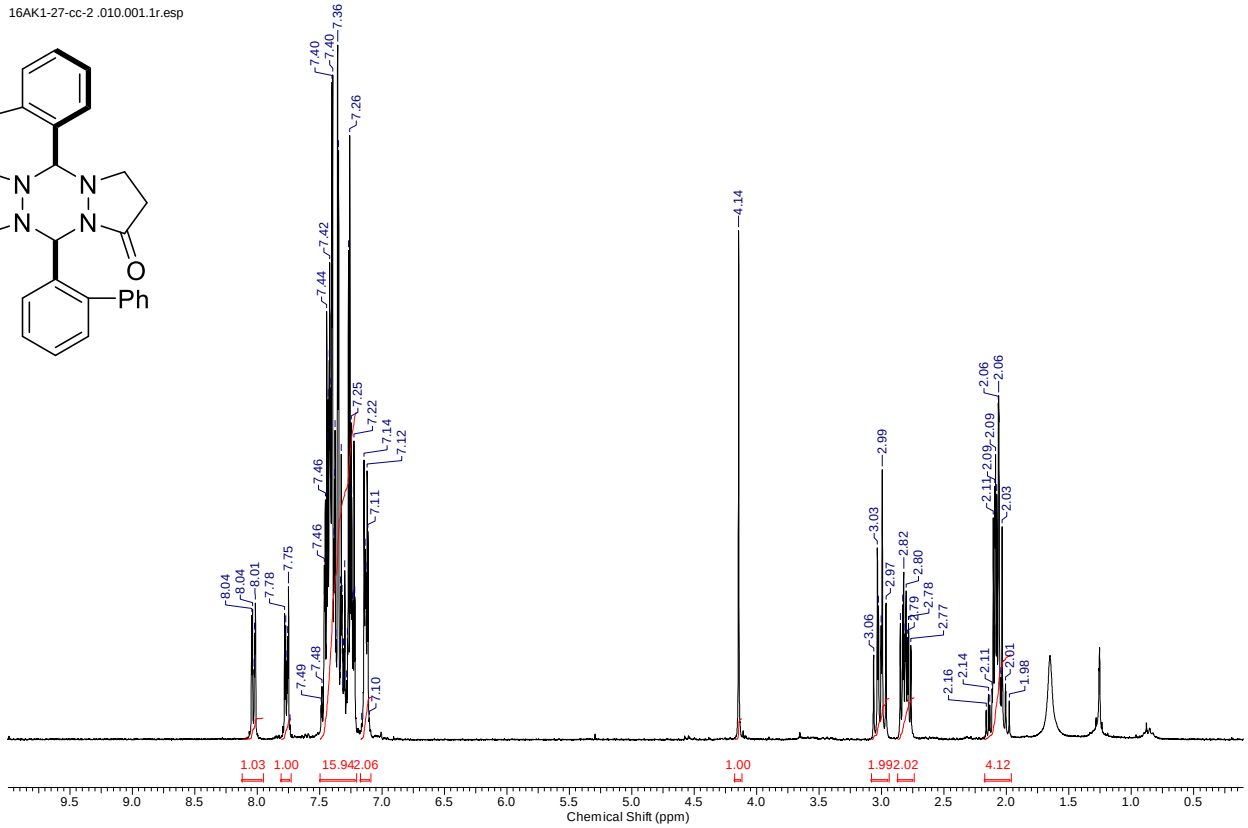


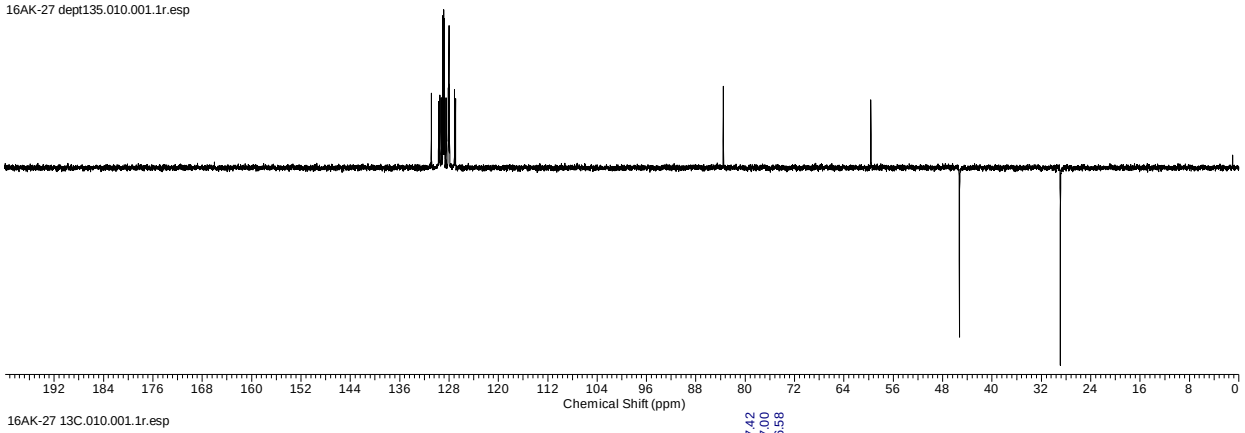


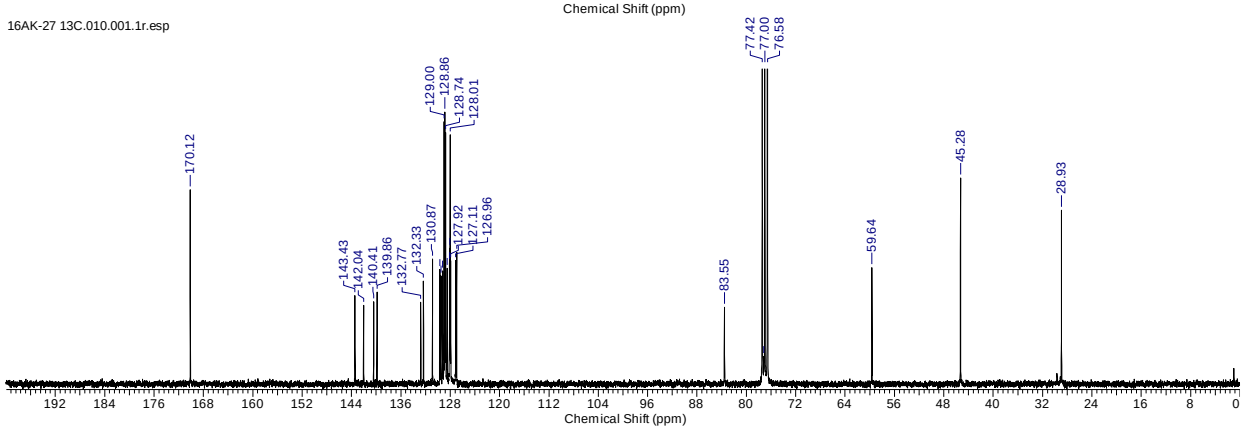
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **2b**



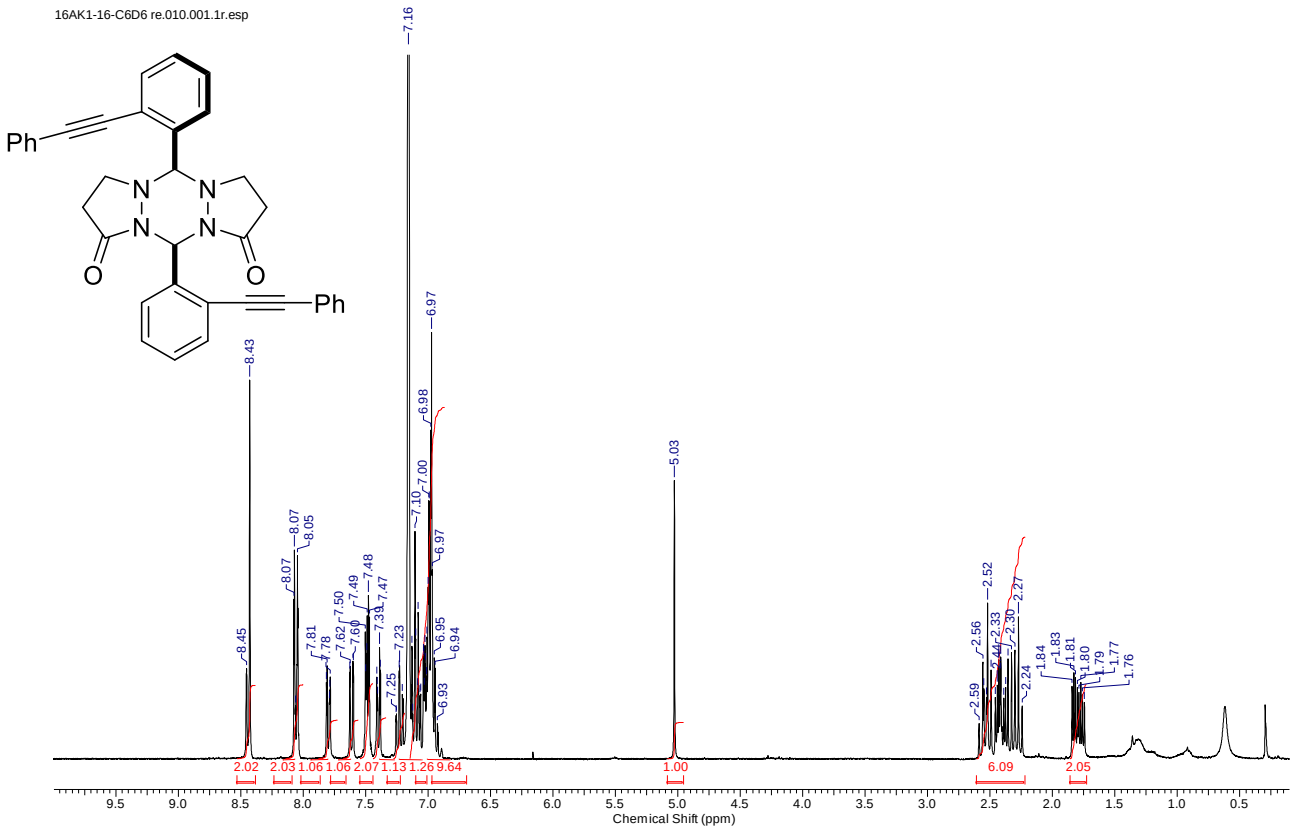
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **2c**

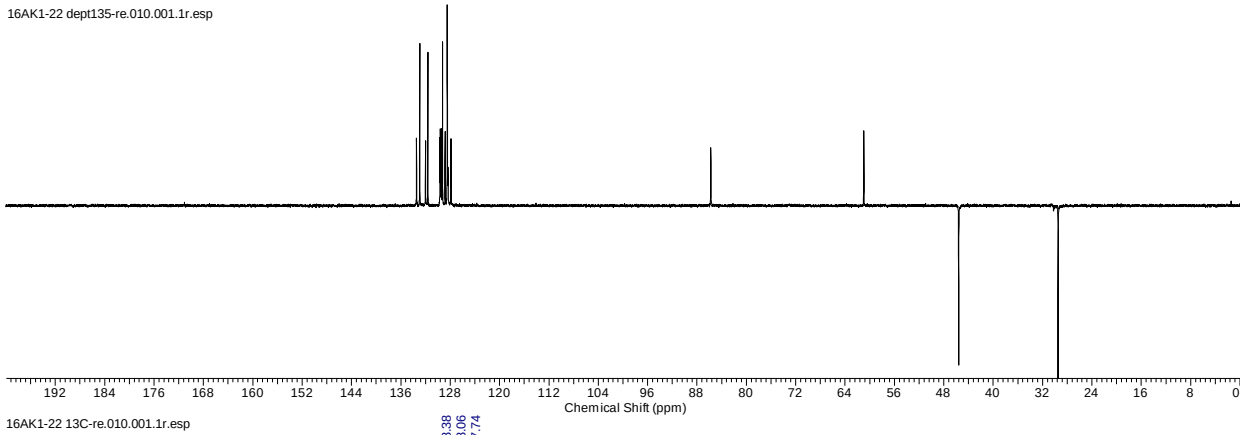


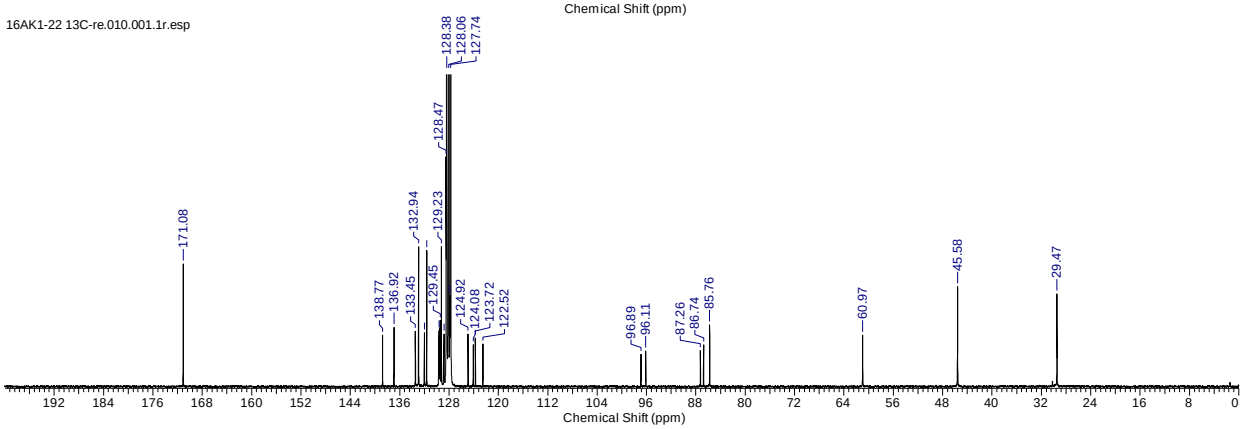




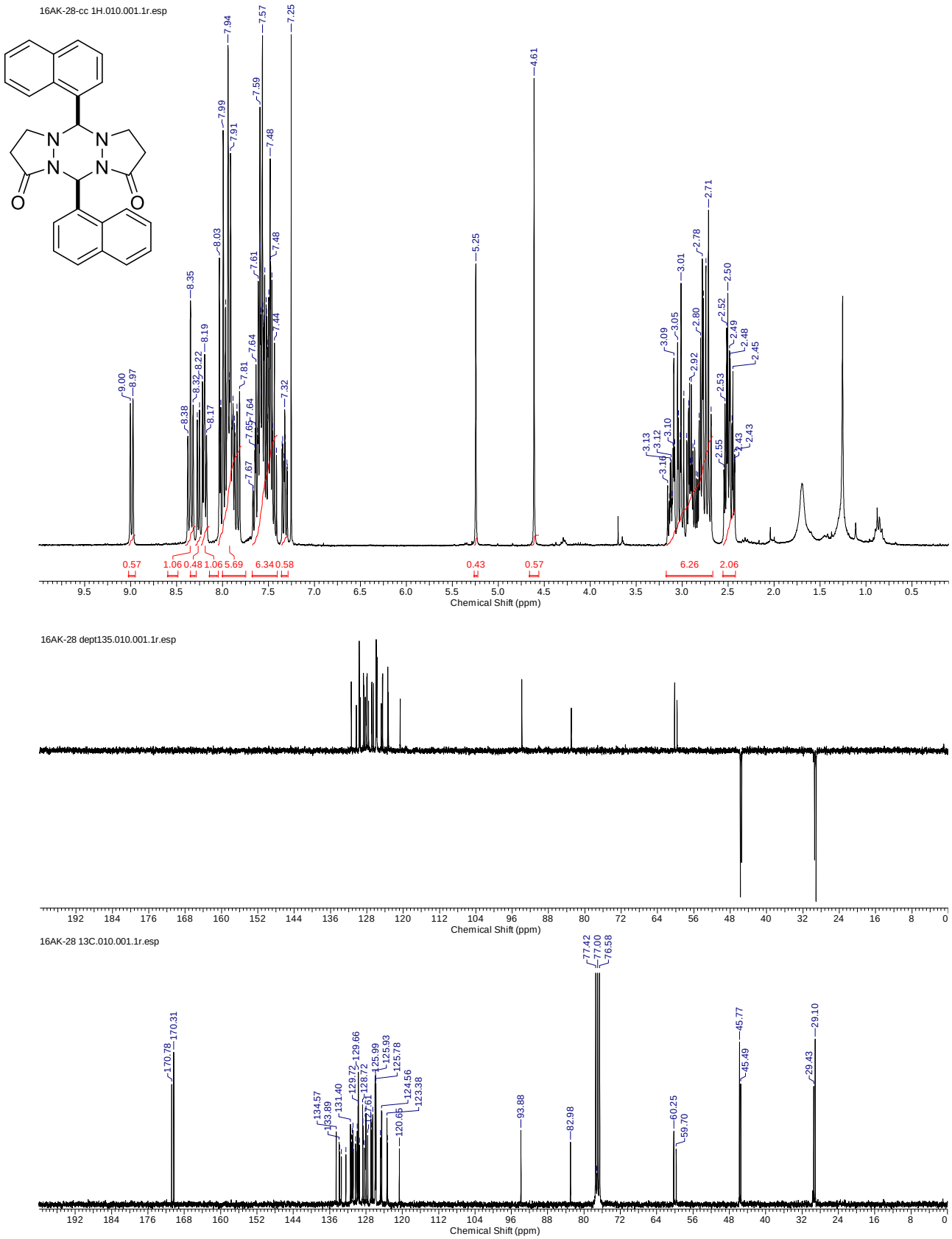
^{1}H NMR (300 MHz, C_6D_6) and ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) of **2d**



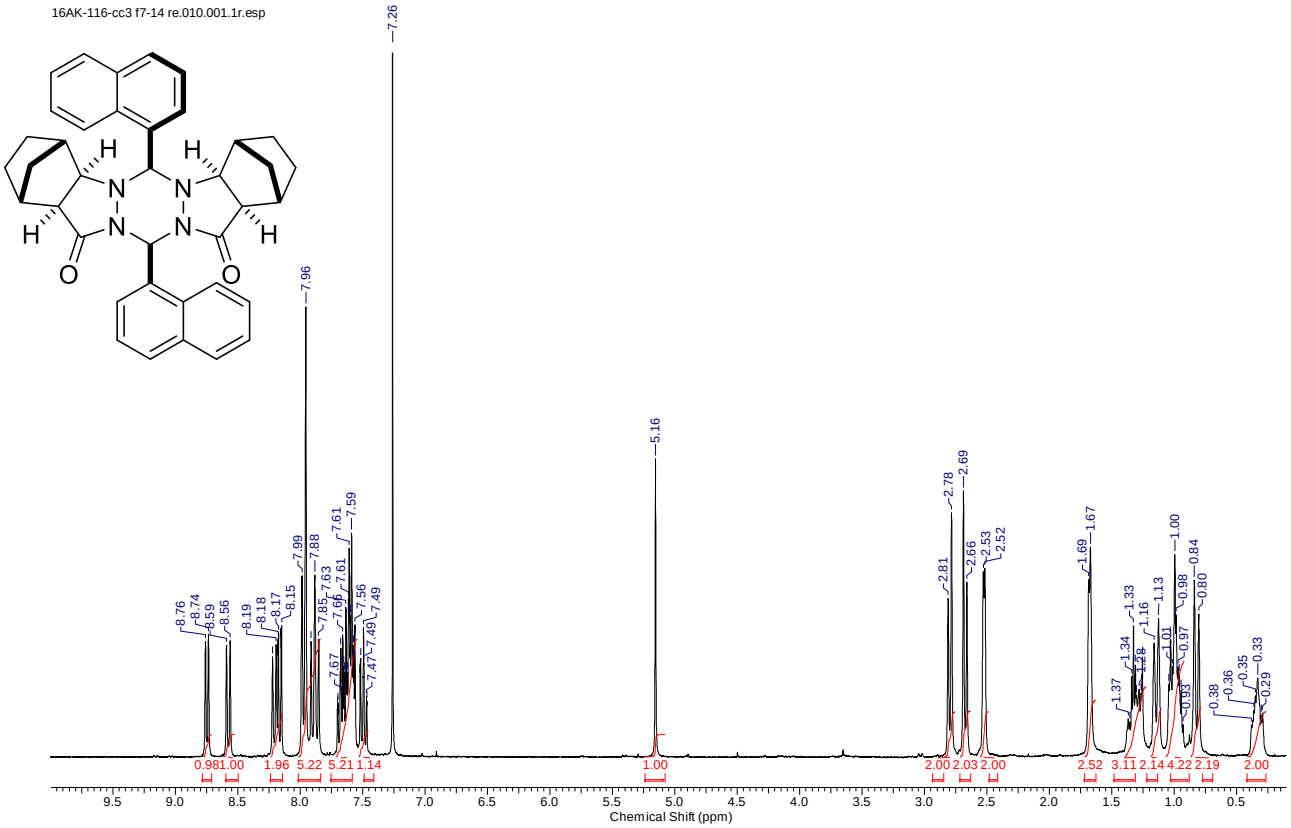


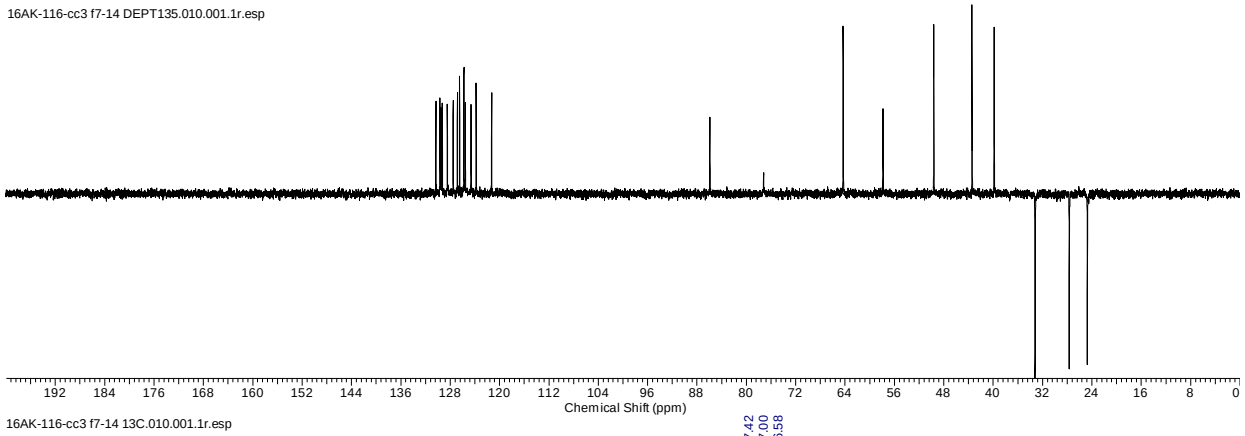


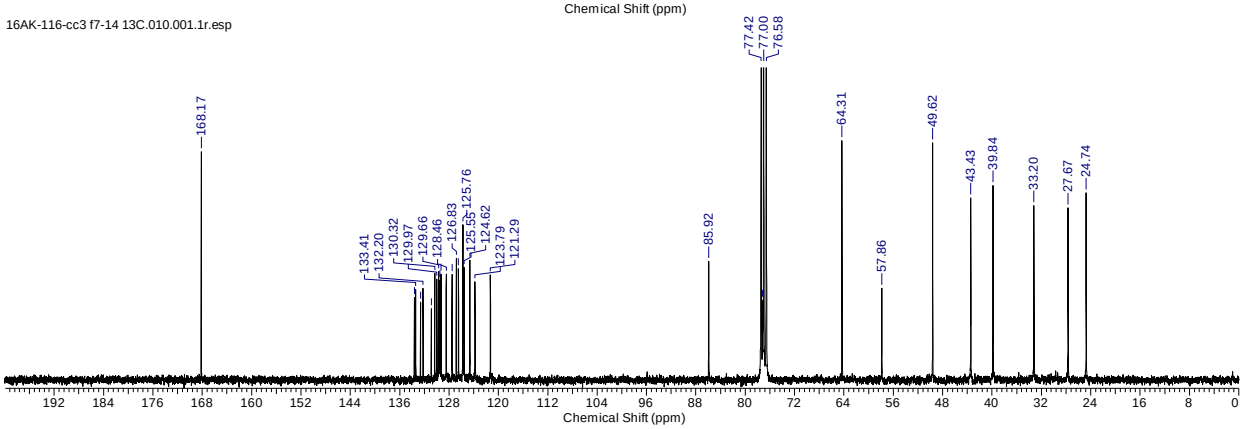
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **2e**



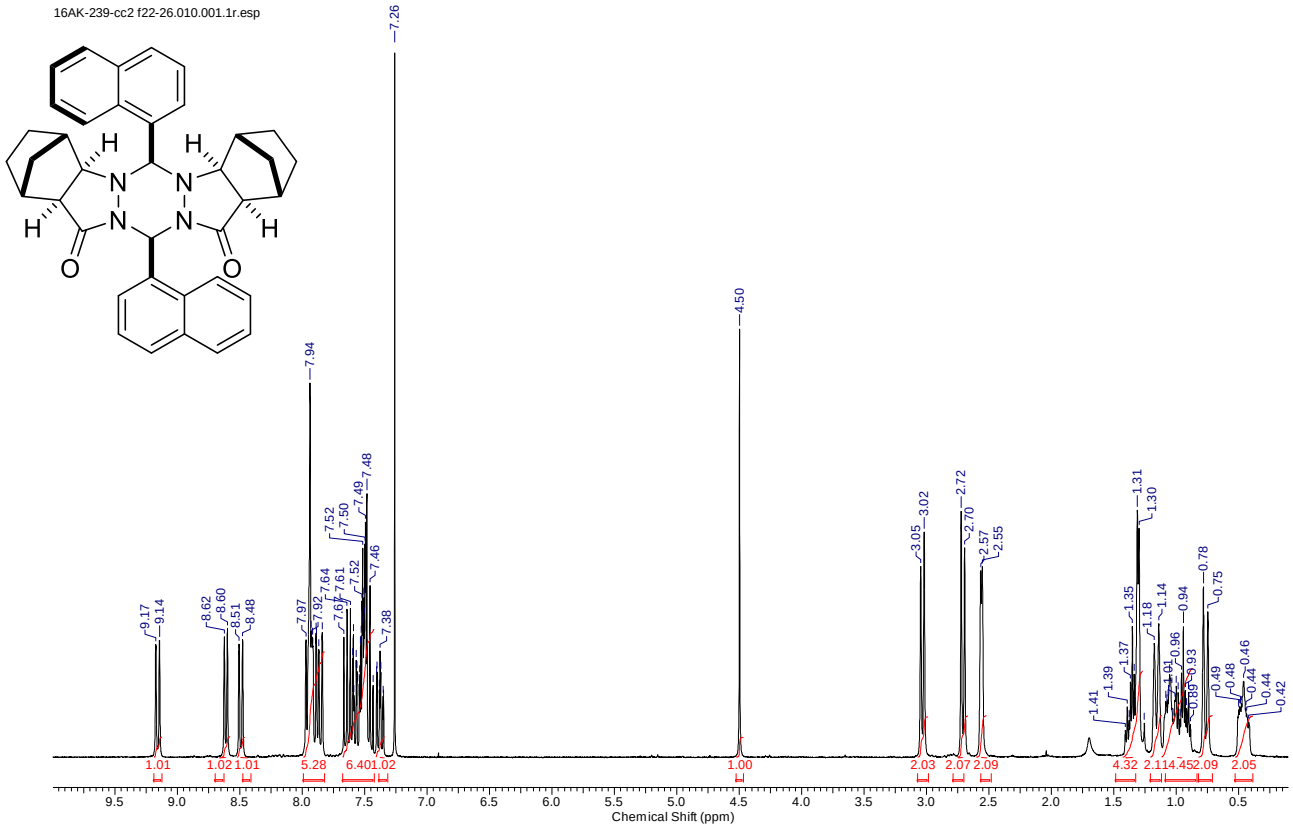
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **2f**-*Open*

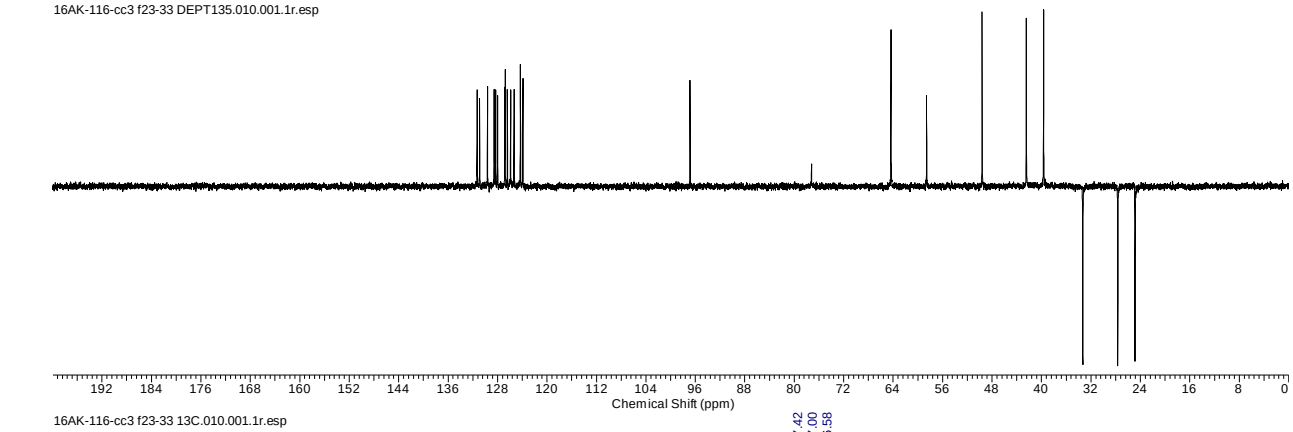


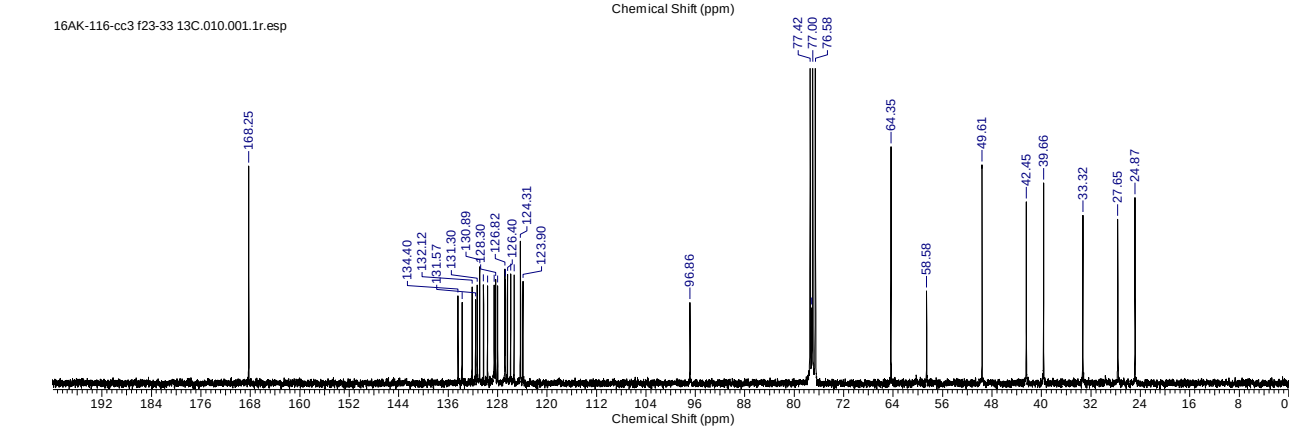




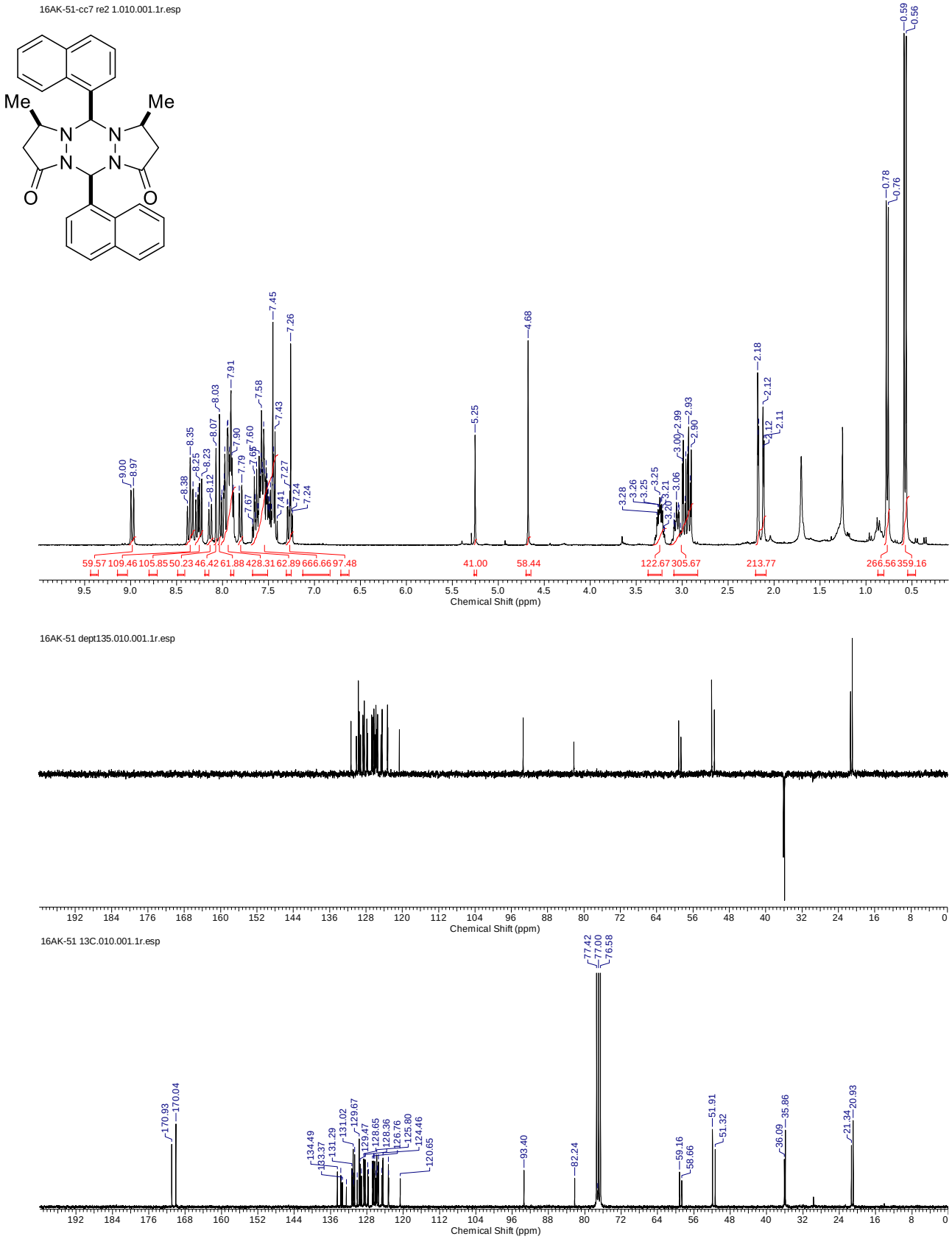
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **2f**-*Close*



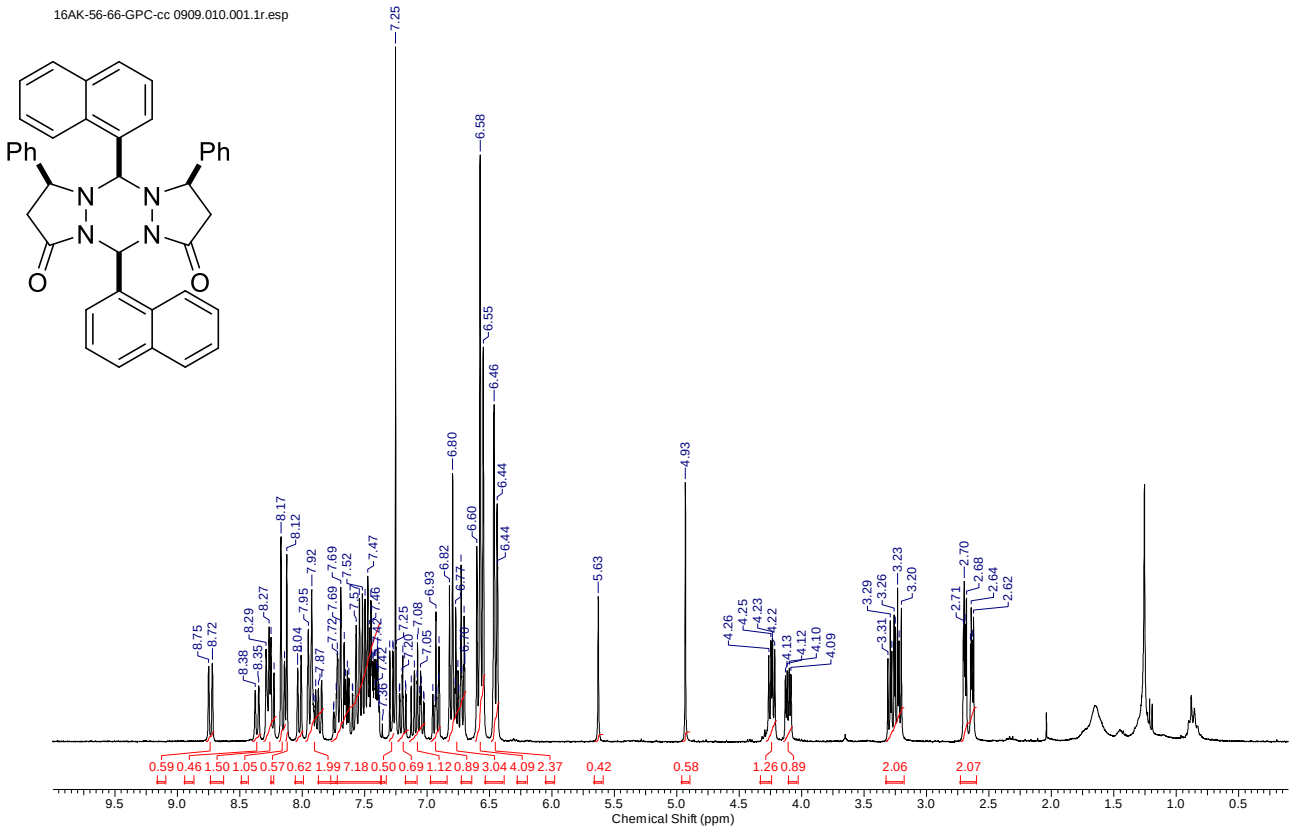


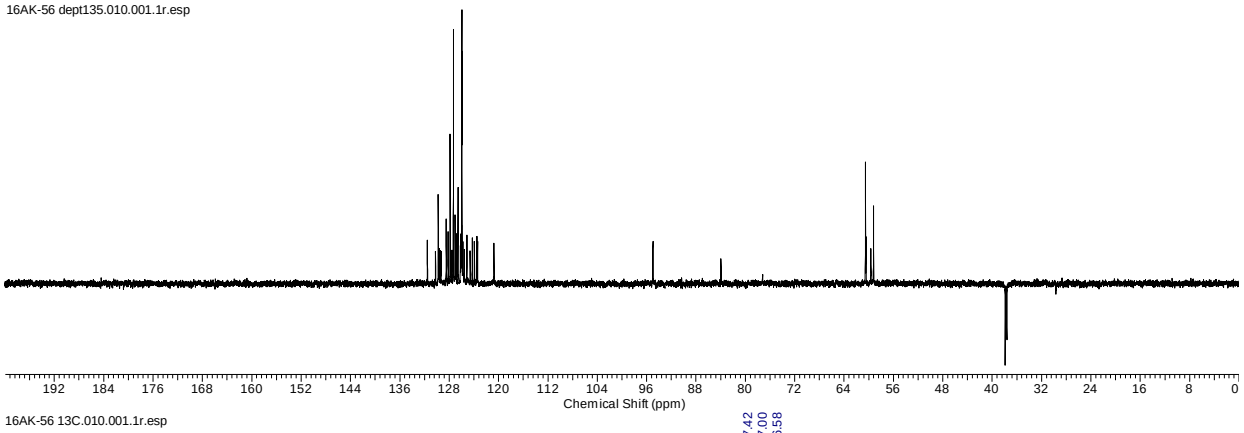


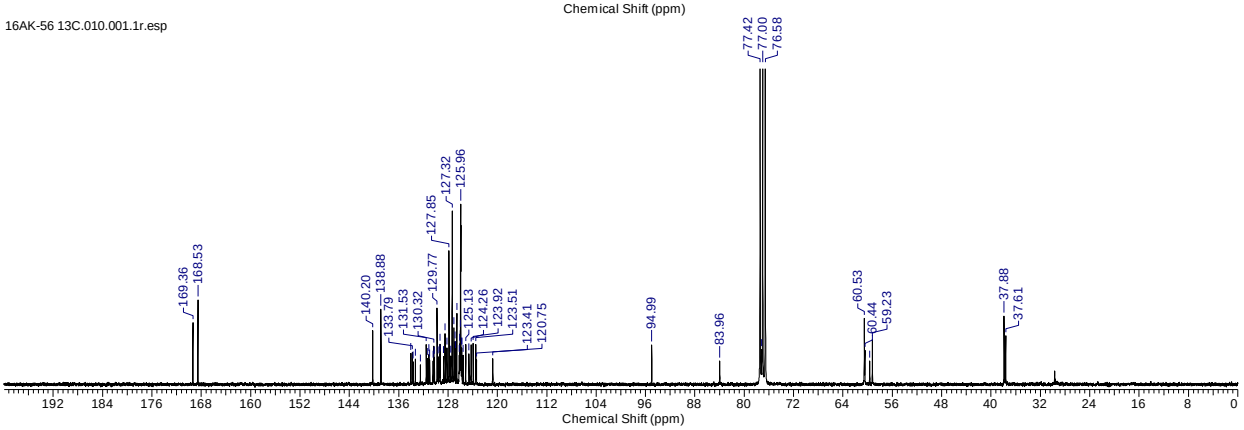
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of **S2a**



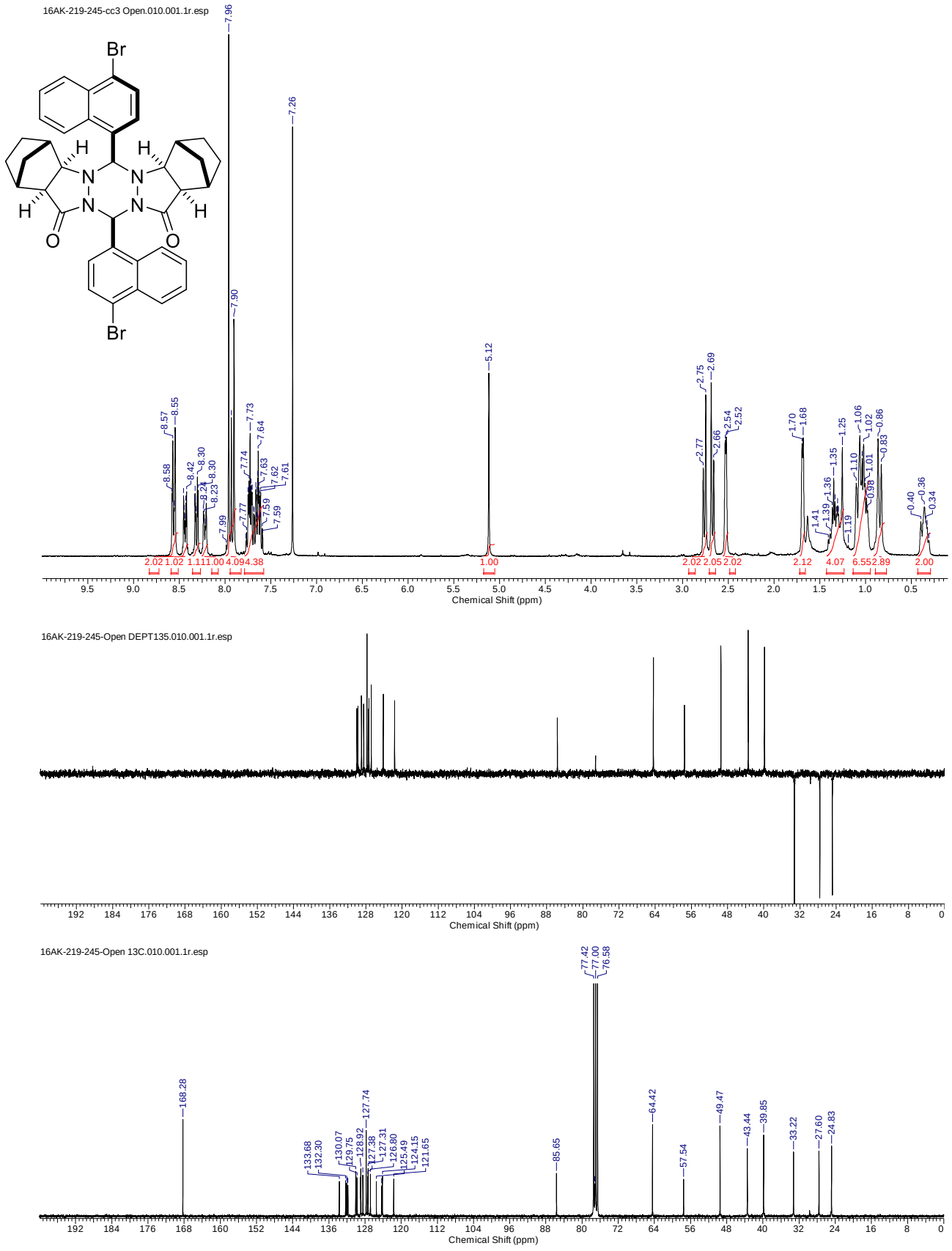
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **S2b**



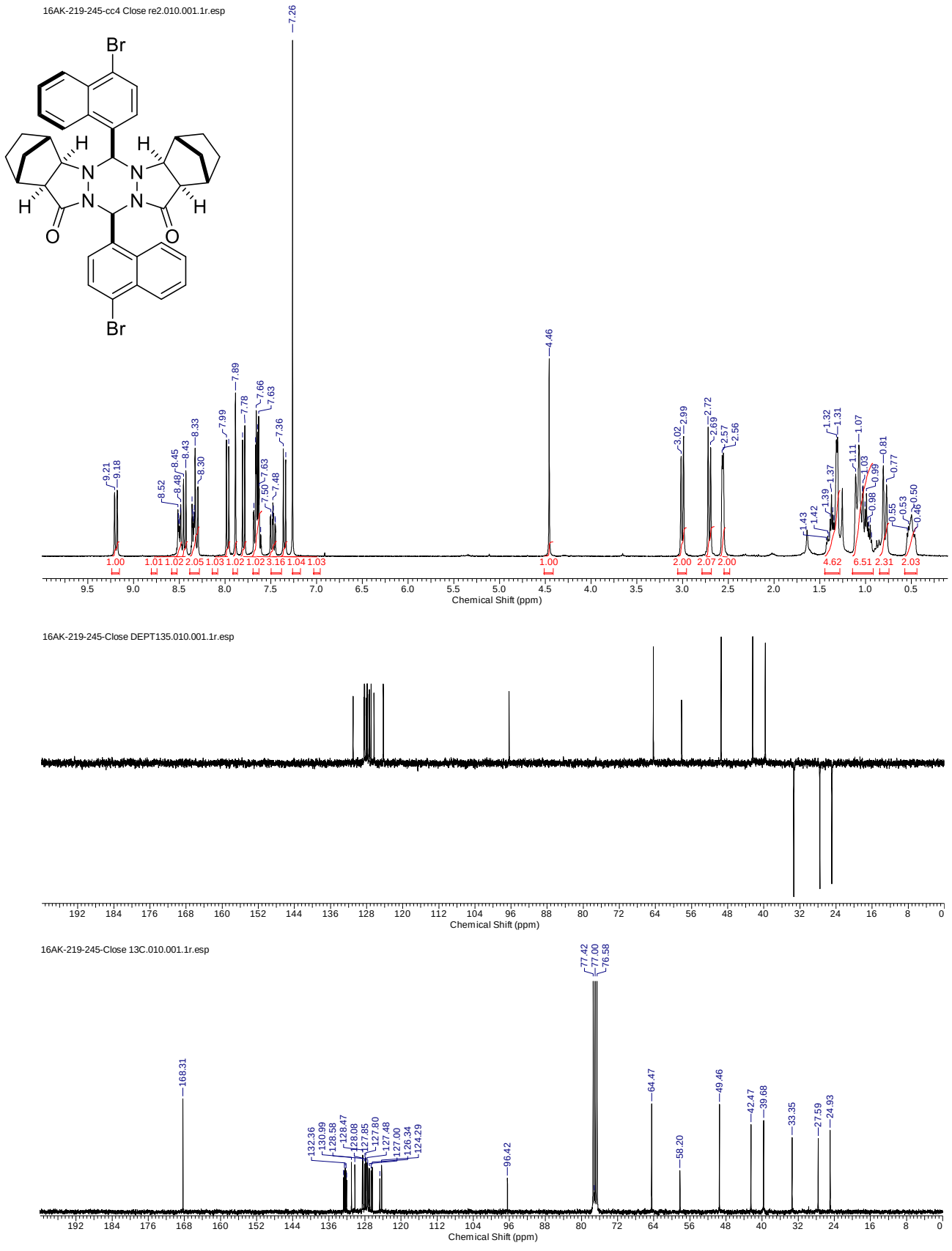




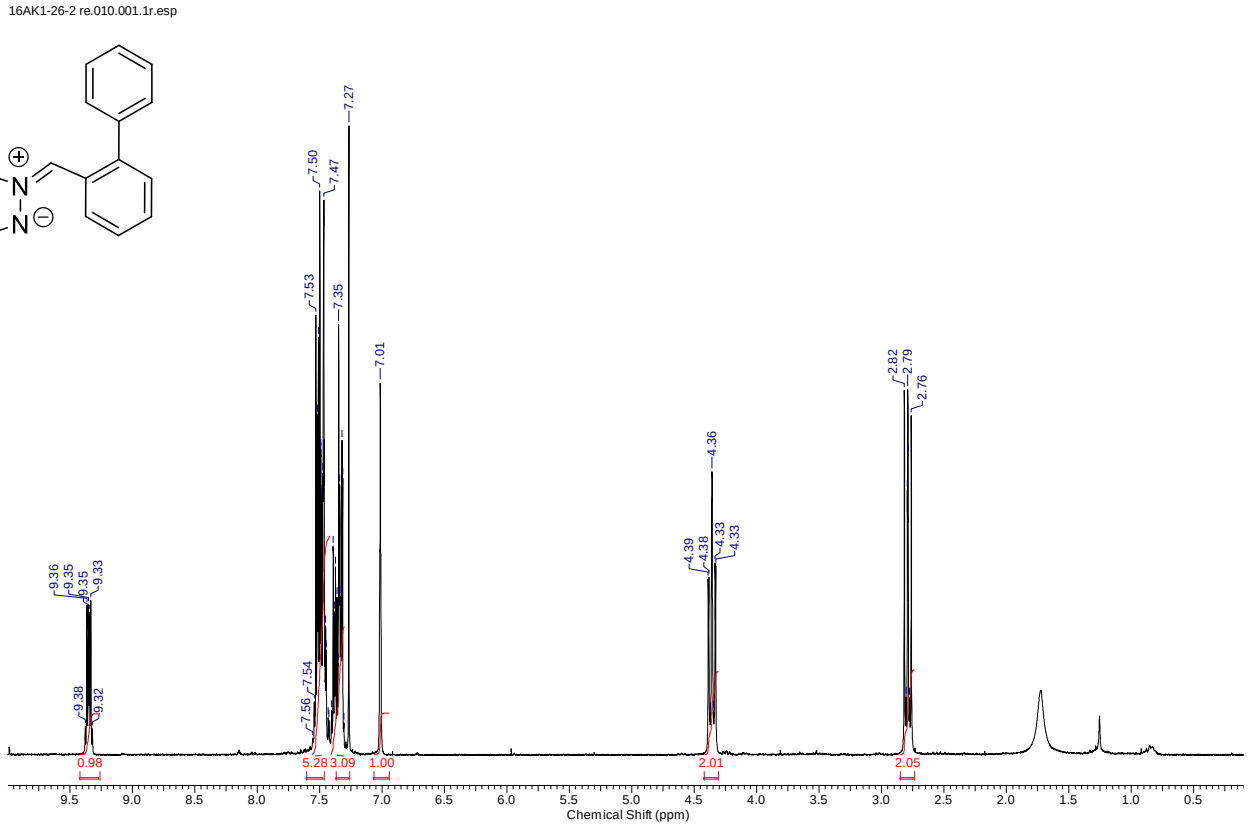
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **S2c**-*Open*

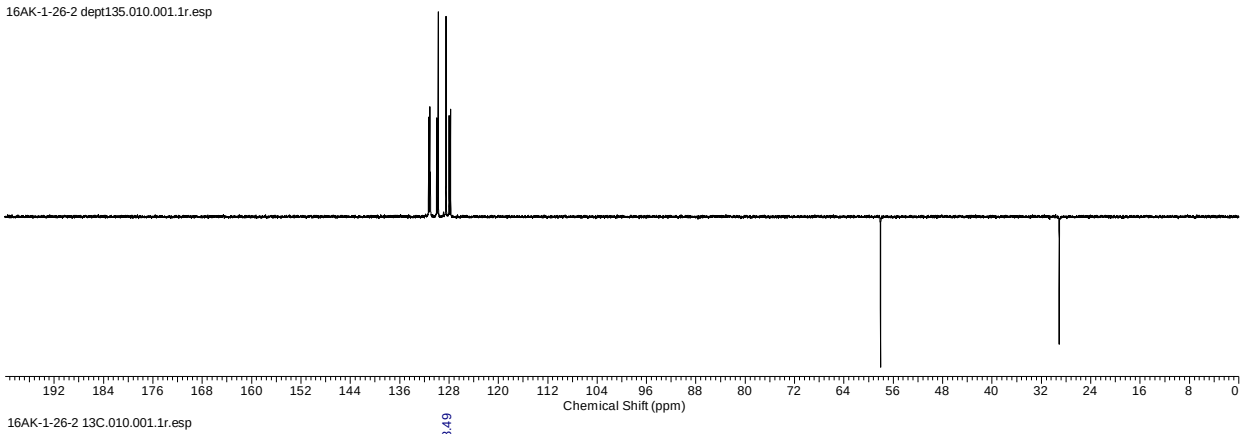


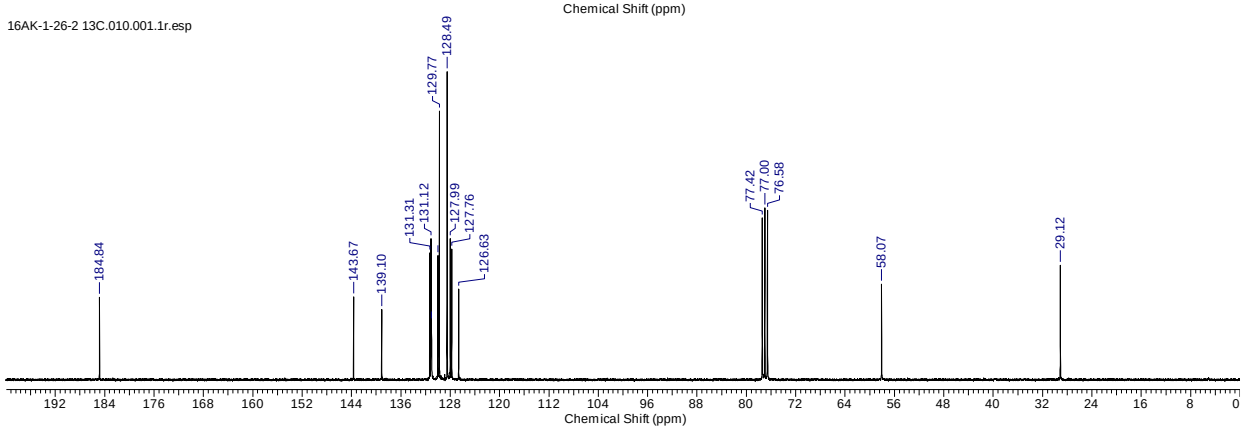
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **S2c**-*Close*



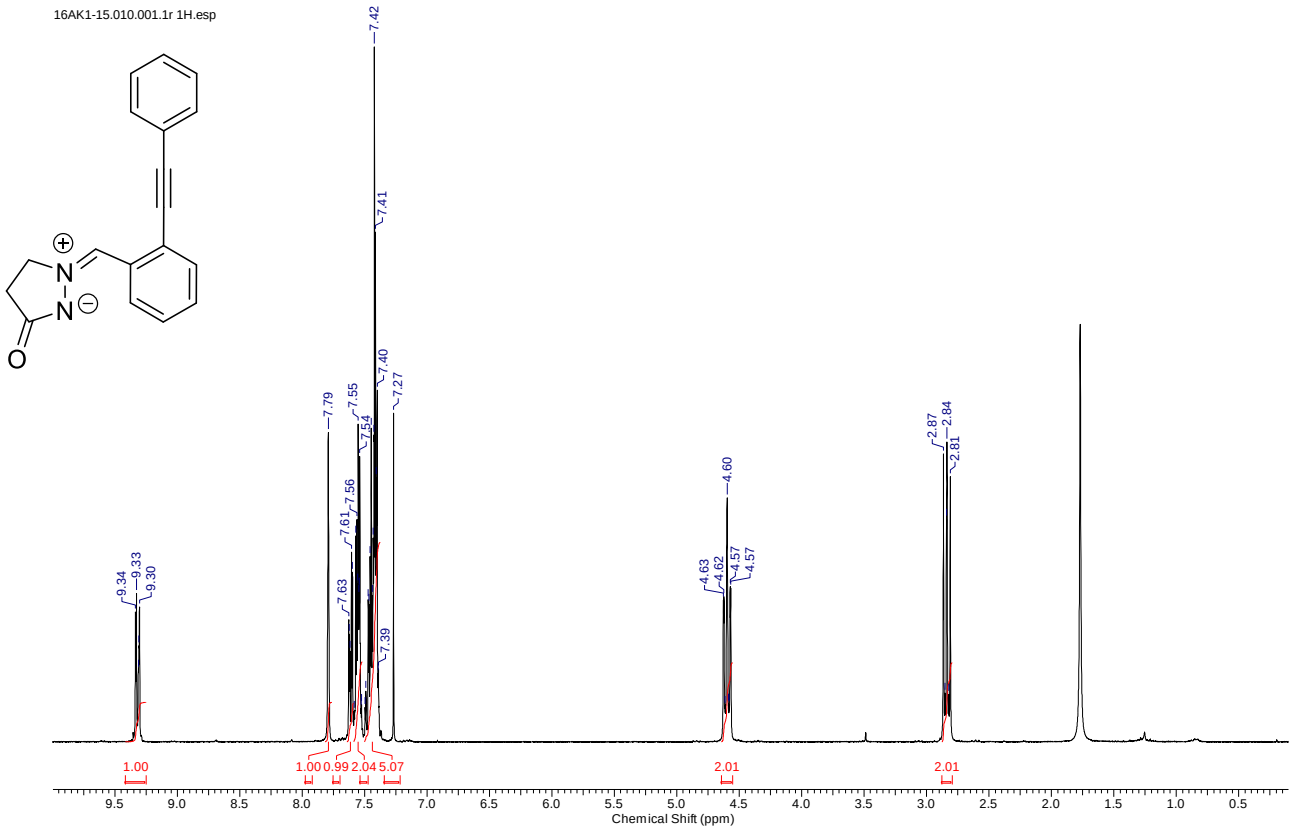
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **1c**

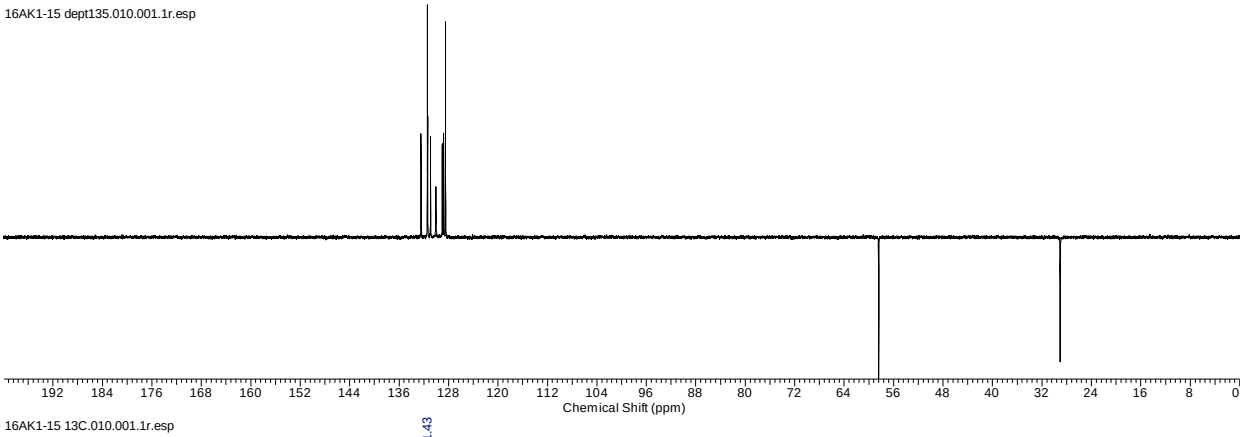


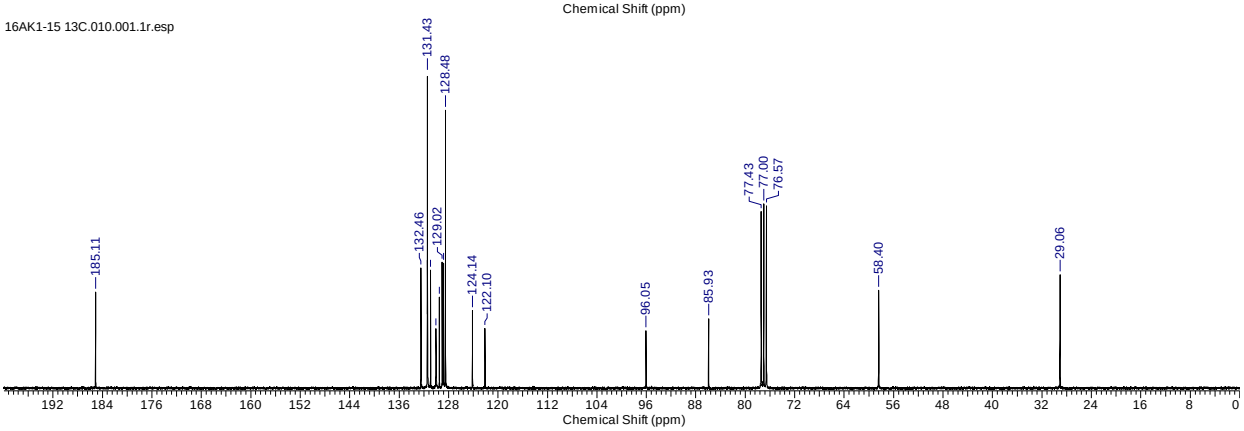




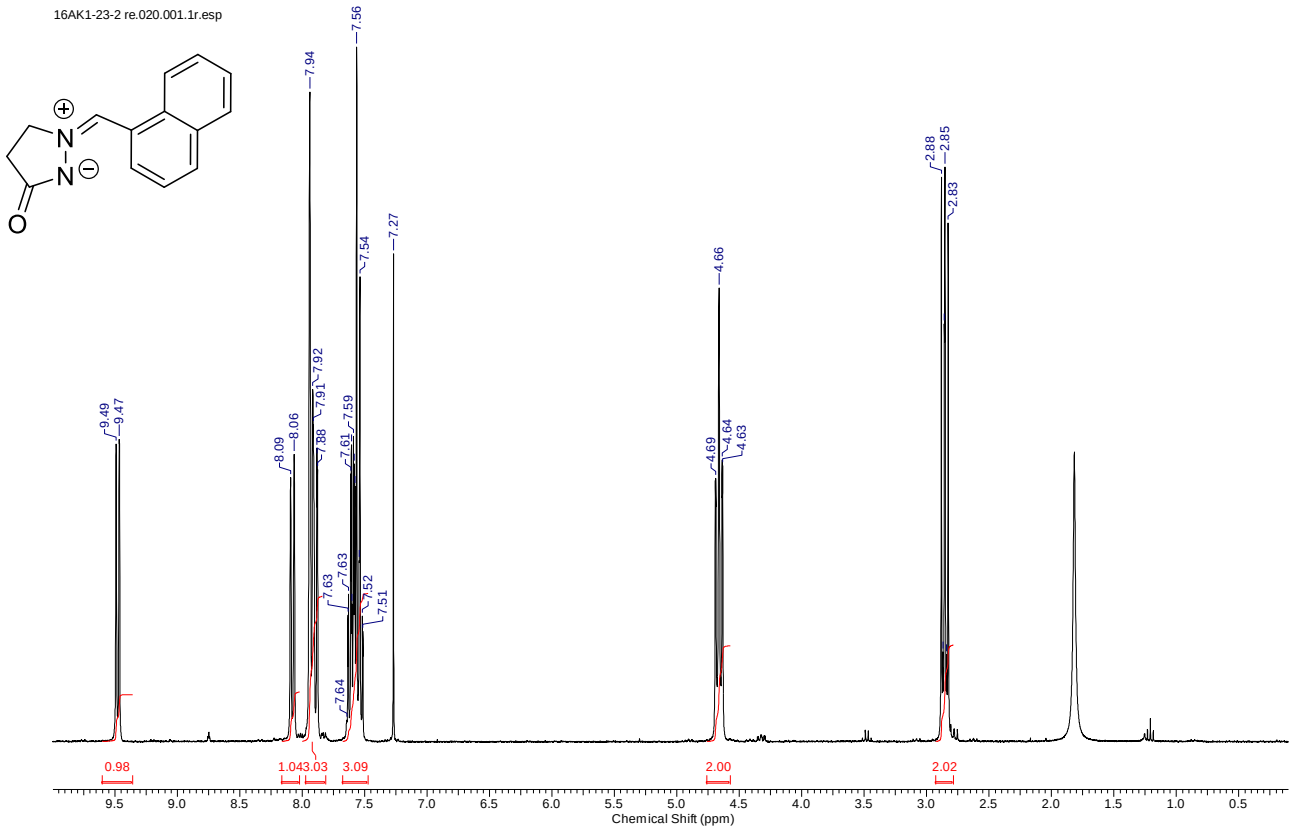
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **1d**

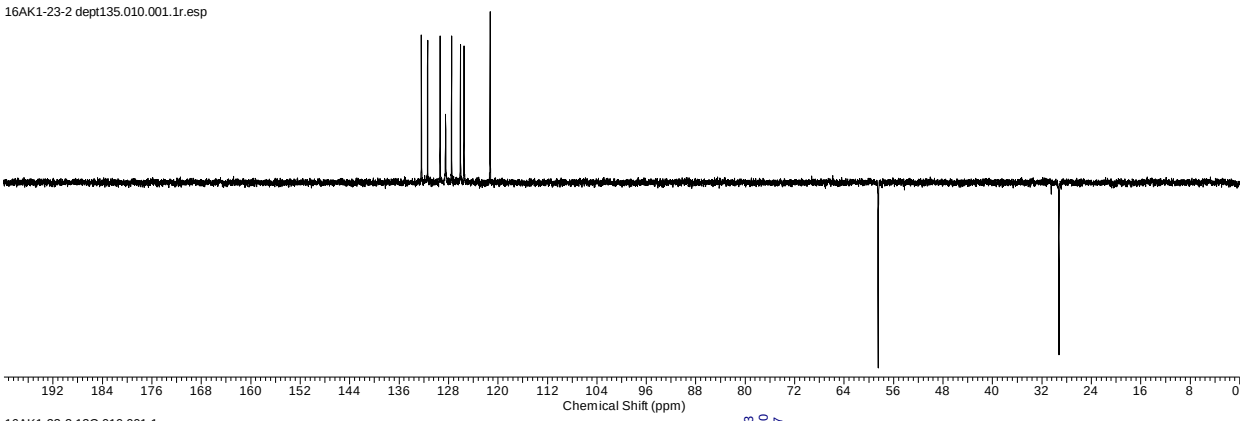


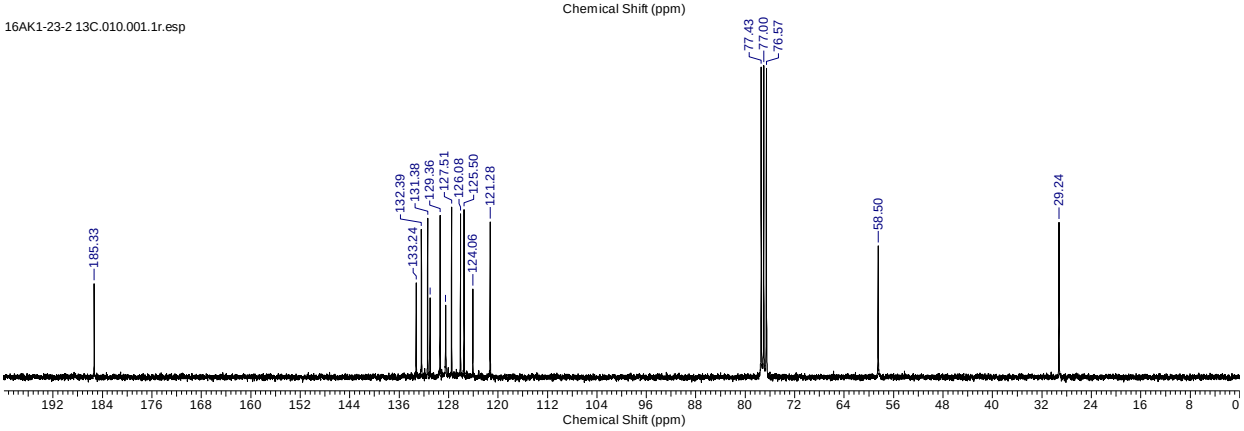




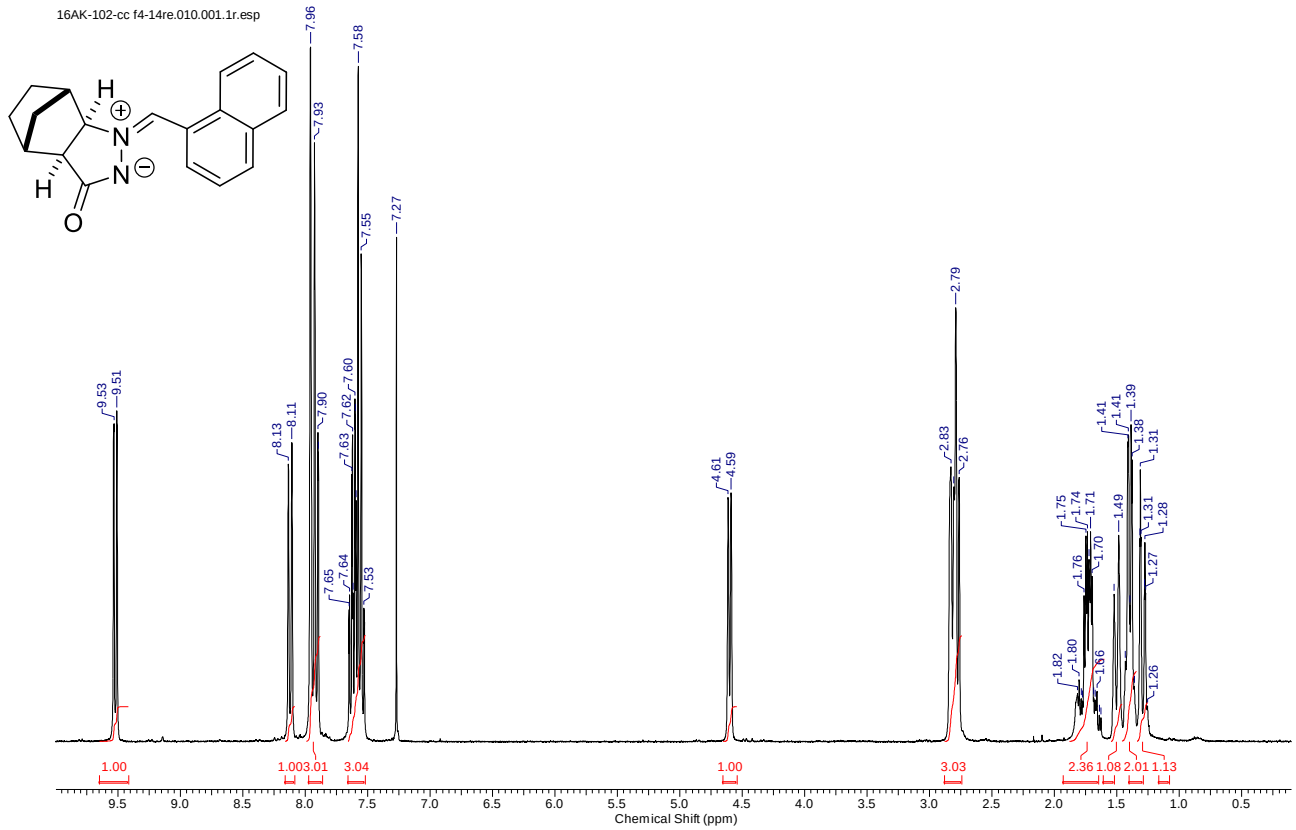
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **1e**

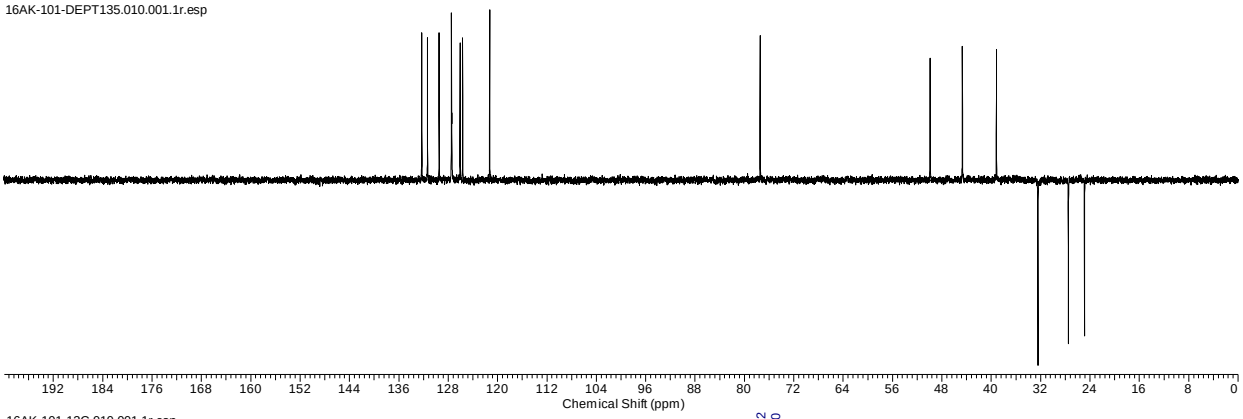


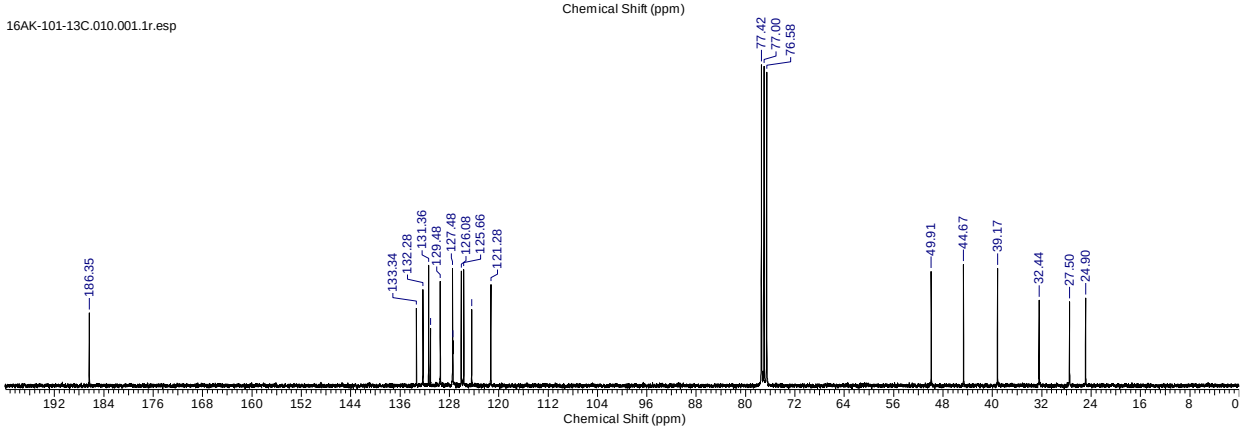




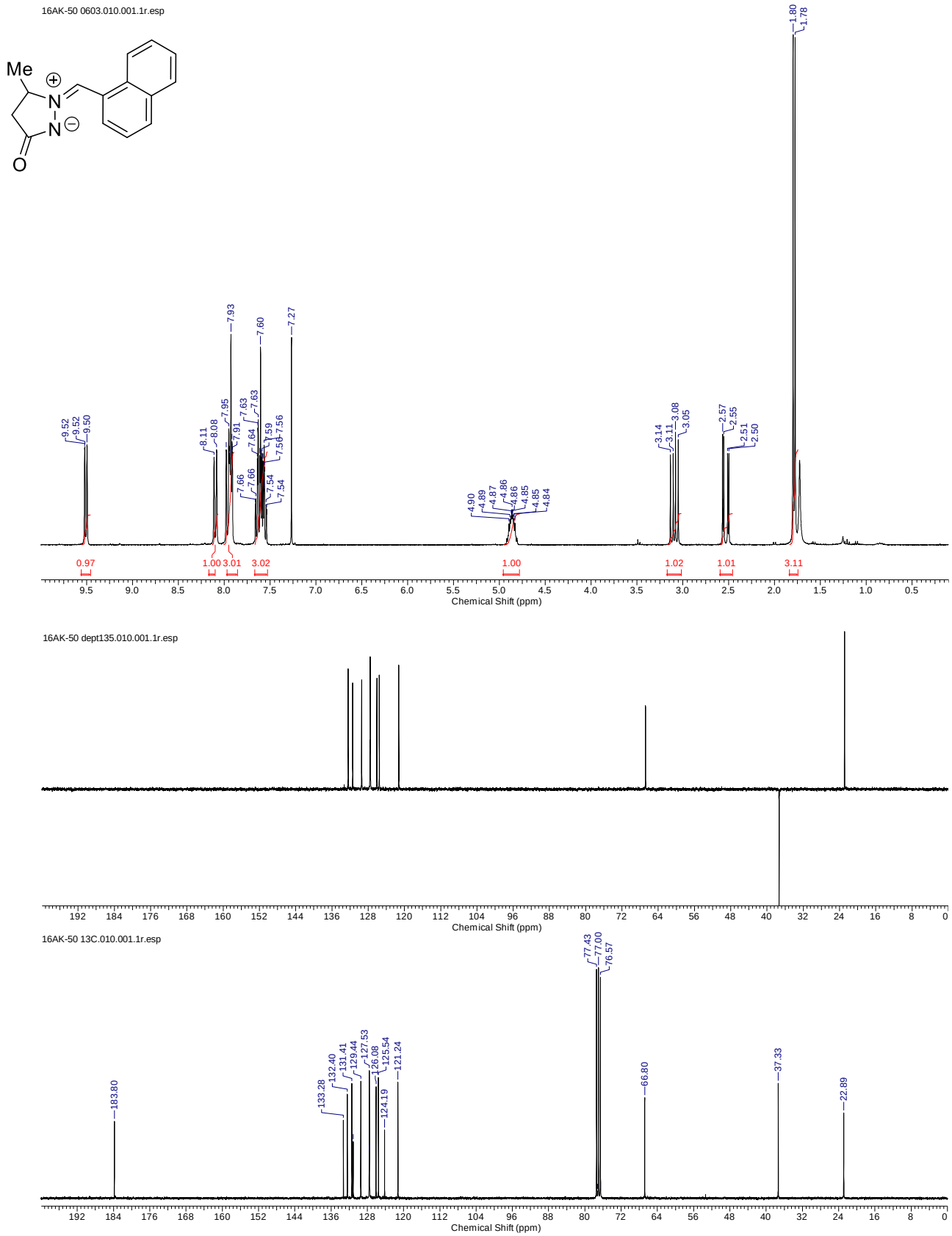
^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **1f**



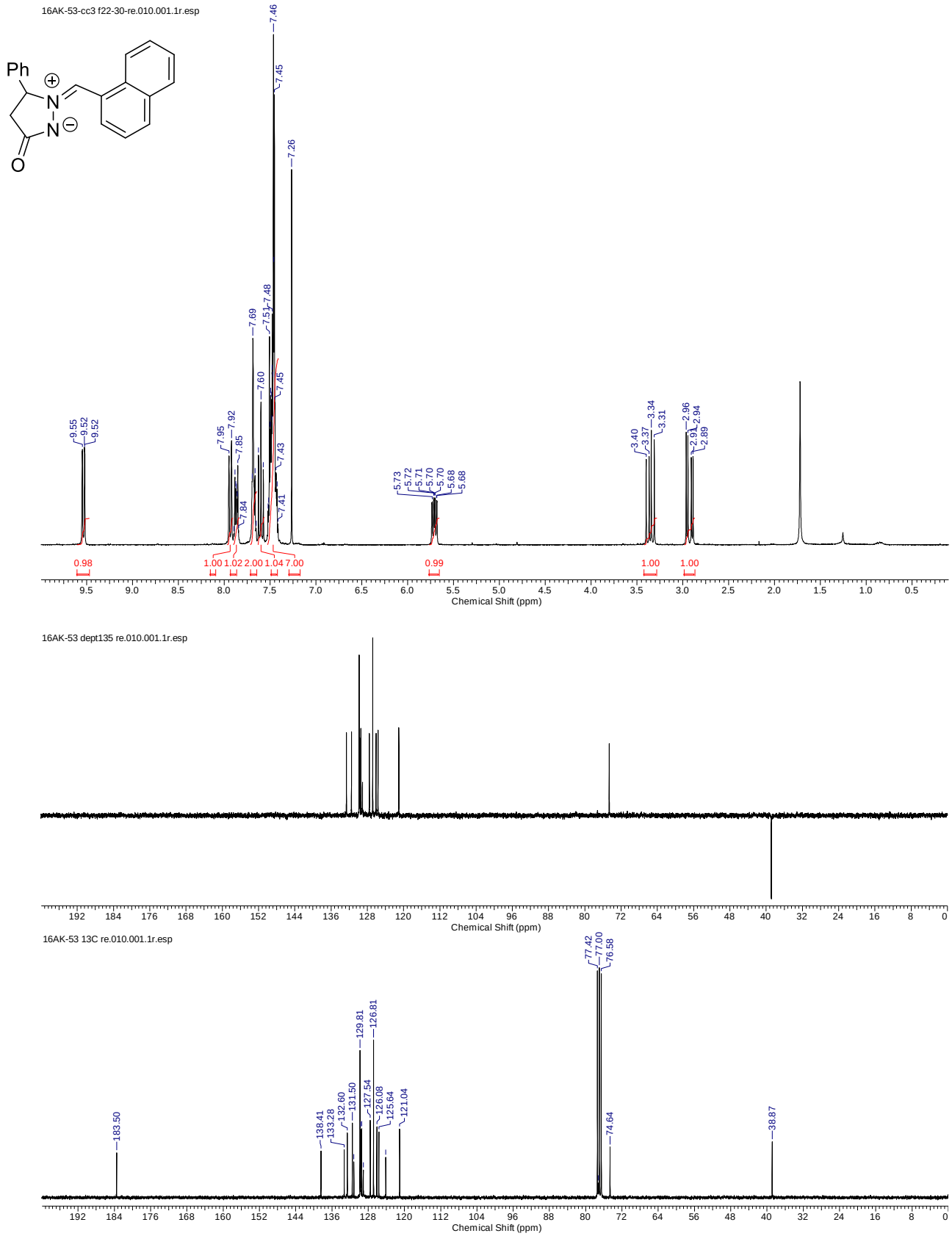




^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **S1a**



^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **S1b**



^{1}H NMR (300 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **S1c**