

Supporting Information for:

Synthesis and Optical Properties of Mono- and Diaminocorannulenes

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1. Materials and instrumentation.

All commercial reagents were used without further purification. Solvents were purified using standard procedures. All reactions involving anhydrous and inert conditions were carried under an argon atmosphere, and the glassware was performed using the oven (130 °C) dried. Anhydrous solvents were obtained by filtration of reagent-grade solvent through an Innovative Technologies solvent drying system.

Column chromatographic purification was carried out on Merck silica gel 60 (particle size 0.040 – 0.063 mm). Reactions were monitored by thin layer chromatography (TLC) and visualized by ultraviolet (UV) light ($\lambda = 254$ nm and $\lambda = 365$ nm). Analytical TLC was performed with Merck TLC silica gel 60 F254.

^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Ascend III 400 and Avance III 600 instruments at 298.6 K. ^1H NMR chemical shifts were recorded in parts per million (ppm) relative to CDCl_3 ($\delta = 7.26$ ppm) and CD_3OD ($\delta = 3.31$ ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet). ^{13}C NMR chemical shifts were recorded in parts per million (ppm) relative to CDCl_3 ($\delta = 77.00$ ppm), CD_3OD ($\delta = 48.8$ ppm), and DMSO-d_6 ($\delta = 49.7$ ppm).

MS data were obtained with Agilent Technologies TOF (6230B) in ESI^+ mode with TOF mass analyzer.

The UV absorption spectra were measured with Hitachi U-3900 spectrophotometer. Fluorescence measurements were carried out on Edinburgh FLS 980 and FLS 1000 spectrophotometer, using 450W Xenon lamp. Emission spectra were obtained by exciting at the longest wavelength excitation maximum. Absolute quantum yields were measured by using an integrating sphere detector from Edinburgh Instruments.

Abbreviations :

RT: Room Temperature

BINAP: (\pm)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl

$\text{Pd}(\text{dba})_2$: Bis(dibenzylidene-acetone) palladium

DCM: Dichloromethane

MeOH: Methanol

EtOAc: Ethylacetate

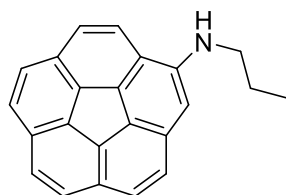
TEA: Triethylamine

THF: Tetrahydrofuran

DMF: *N,N*-Dimethylformamide

2. Synthetic procedures.

4a:



To a solution of monobromocorannulene (20 mg, 0.06 mmol) and KO^tBu (14 mg, 0.12 mmol) in toluene (5 mL), under an argon atmosphere, propylamine (0.5 mL) was added, and the mixture was degassed three times by evacuating the flask and backfilling with Ar. $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.006 mmol) and BINAP (3 mg, 0.006 mmol)

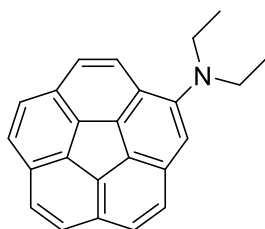
were added, and the mixture was heated to 50 °C. After 2 hours, the mixture was heated to 80 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (10 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH₄Cl (30 mL), and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phase was washed with saturated aqueous NaCl (30 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 60 : 1) to afford **4a** (2 mg, 0.007 mmol, 11%).

¹H NMR (600 MHz, CDCl₃) δ: 7.75-7.87 (m, 5H), 7.64-7.74 (m, 3H), 7.59 (d, *J* = 8.7 Hz, 1H), 3.37 (t, *J* = 7.2 Hz, 2H), 1.85-1.91 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ: 136.0, 135.8, 135.7, 135.3, 134.9, 130.7, 130.3, 127.9, 127.5, 127.3, 127.2, 127.1, 126.9, 126.5, 126.4, 126.3, 125.0, 122.9, 122.1, 55.4, 21.6, 11.5.

MS-ESI: calculated for C₂₃H₁₇N [M+H]⁺: 308.1361; found: 308.1187.

4b:



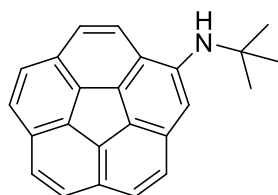
To a solution of monobromocorannulene (50 mg, 0.15 mmol) and KO^tBu (48 mg, 0.43 mmol) in toluene (5 mL), under an argon atmosphere, diethylamine (40 μL, 0.39 mmol) was added, and the mixture was degassed three times by evacuating the flask and backfilling with Ar. Pd(OAc)₂ (4 mg, 0.02 mmol) and BINAP (10 mg, 0.02 mmol) were added, and the mixture was heated to 55 °C. After 2 hours, the mixture was heated to 70 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (20 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH₄Cl (30 mL), and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 60 : 1) to afford **4b** (5 mg, 0.02 mmol, 11%).

¹H NMR (600 MHz, CDCl₃) δ: 7.89 (d, *J* = 8.7 Hz, 1H), 7.71-7.81 (m, 6H), 7.65 (d, *J* = 8.6 Hz, 1H), 6.85 (s, 1H), 3.70 (q, *J* = 6.9 Hz, 4H), 1.25 (t, *J* = 7.0 Hz, 6H).

¹³C NMR (150 MHz, CDCl₃) δ: 150.6, 137.6, 136.3, 136.0, 135.8, 132.4, 131.4, 130.8, 130.8, 130.4, 129.2, 127.2, 127.2, 127.0, 126.6, 126.2, 125.7, 108.2, 47.3, 12.1.

MS-ESI: calculated for C₂₄H₁₉N [M+H]⁺: 322.1571; found: 322.1361.

4c:



To a solution of monobromocorannulene (50 mg, 0.15 mmol) and KO^tBu (48 mg, 0.43 mmol) in toluene (5 mL), under an argon atmosphere, *tert*-Butylamine (3 mL) was added, and the mixture was degassed three times by evacuating the flask and backfilling with argon. Pd(OAc)₂ (4 mg, 0.02 mmol) and BINAP (10 mg, 0.02 mmol) were added, and the mixture was heated to 45 °C. After 2 hours, the mixture was heated to 60 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (30 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH₄Cl (30

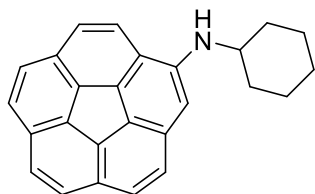
mL), and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 60 : 1) to afford **4c** (5 mg, 0.02 mmol, 11%).

¹H NMR (400 MHz, CDCl₃) δ: 7.55-7.86 (m, 8H), 6.87 (s, 1H), 1.57 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ: 137.9, 135.8, 130.9, 130.3, 129.0, 128.2, 127.4, 127.3, 127.0, 126.6, 126.5, 125.3, 125.0, 122.6, 103.9, 29.5, 21.5.

MS-ESI: calculated for C₂₄H₁₉N [M+H]⁺: 322.1517; found: 322.1261.

4d:



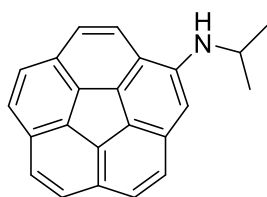
To a solution of monobromocorannulene (30 mg, 0.09 mmol) and KO^tBu (28 mg, 0.25 mmol) in toluene (5 mL), under an argon atmosphere, cyclohexylamine (2 mL) was added, and the mixture was degassed three times by evacuating the flask and backfilling with Ar. Pd(OAc)₂ (2 mg, 0.01 mmol) and BINAP (5 mg, 0.01 mmol) were added, and the mixture was heated to reflux. After 9 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (20 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH₄Cl (30 mL), and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 60 : 1) to afford **4d** (12 mg, 0.04 mmol, 39%).

¹H NMR (400 MHz, CDCl₃) δ: 7.64 -7.90 (m, 7H), 7.60 (d, *J* = 8.6 Hz, 1H), 6.71 (s, 1H), 3.60 (s, 1H), 2.24 (d, *J* = 9.4 Hz, 2H), 1.82 (s, 2H), 1.70 (d, *J* = 12.0 Hz, 1H), 1.60-1.19 (m, 5H).

¹³C NMR (100 MHz, CDCl₃) δ: 136.0, 135.8, 135.1, 130.9, 130.4, 127.4, 127.1, 126.5, 123.3, 122.4, 29.7, 25.8, 24.9.

MS-ESI: calculated for C₂₆H₂₁N [M+Na]⁺: 370.1647; found: 370.1817.

4e:



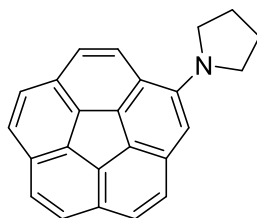
To a solution of monobromocorannulene (50 mg, 0.15 mmol) and KO^tBu (48 mg, 0.43 mmol) in toluene (5 mL), under an argon atmosphere, isopropylamine (2 mL) was added, and the mixture was degassed three times by evacuating the flask and backfilling with Ar. Pd(OAc)₂ (4 mg, 0.02 mmol) and BINAP (10 mg, 0.02 mmol) were added, and the mixture was heated to 30 °C. After 2 hours, the mixture was heated to 50 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (20 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH₄Cl (30 mL), and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 60 : 1) to afford **4e** (5 mg, 0.02 mmol, 11%).

^1H NMR (400 MHz, CDCl_3) δ : 7.55-7.88 (m, 8H), 6.69 (s, 1H), 3.95 (dt, $J = 12.4, 6.2$ Hz, 1H), 1.41 (d, $J = 5.7$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ : 136.4, 136.1, 135.9, 135.2, 131.0, 130.5, 128.7, 127.4, 127.1, 126.6, 126.5, 125.1, 123.3, 122.3, 53.9, 22.4.

MS-ESI: calculated for $\text{C}_{23}\text{H}_{17}\text{N}$ $[\text{M}+\text{H}]^+$: 308.1361; found: 308.1117.

4f:



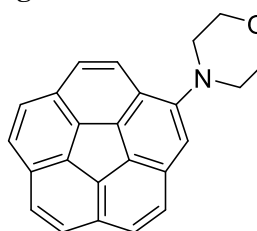
To a solution of monobromocorannulene (30 mg, 0.09 mmol) and Cs_2CO_3 (60 mg, 0.18 mmol) in toluene (5 mL), pyrrolidine (3 mL) was added under an argon atmosphere, and the mixture was degassed three times by evacuating the flask and backfilling with argon. $\text{Pd}(\text{OAc})_2$ (5 mg, 0.02 mmol) and BINAP (10 mg, 0.02 mmol) were added^[S1], and the mixture was heated to reflux. After 9 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (20 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH_4Cl (30 mL), and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether : EtOAc = 50 : 1) to afford **4f** (16 mg, 0.05 mmol, 56%).

^1H NMR (400 MHz, CDCl_3) δ : 8.02 (d, $J = 8.9$ Hz, 1H), 7.70-7.86 (m, 6H), 7.64 (d, $J = 8.7$ Hz, 1H), 6.56 (s, 1H), 3.83 (t, $J = 6.3$ Hz, 4H), 2.15 (t, $J = 6.4$ Hz, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ : 149.6, 136.8, 136.1, 135.6, 135.4, 133.8, 130.9, 130.8, 129.3, 128.2, 127.4, 127.3, 126.9, 126.8, 126.4, 126.2, 124.9, 124.7, 124.5, 101.0, 52.2, 26.1.

MS-ESI: calculated for $\text{C}_{27}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$: 320.1361; found: 320.1117.

4g:

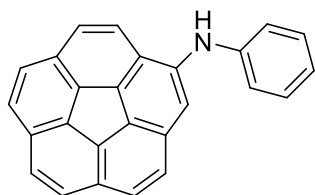


To a solution of monobromocorannulene (50 mg, 0.15 mmol) and KO^tBu (48 mg, 0.43 mmol) in toluene (4 mL), morpholine (40 μL , 0.46 mmol) was added under an argon atmosphere, and the mixture was degassed three times by evacuating the flask and backfilling with Ar. $\text{Pd}(\text{OAc})_2$ (4 mg, 0.02 mmol) and BINAP (10 mg, 0.02 mmol) were added, and the mixture was heated to reflux. After 9 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (20 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH_4Cl (30 mL), and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 20 : 1) to afford **4g** (36 mg, 0.11 mmol, 70%).

^1H NMR (400 MHz, CDCl_3) δ : 7.87 (d, $J = 8.8$ Hz, 1H), 7.72-7.81 (m, 6H), 7.67 (d, $J = 8.7$ Hz, 1H), 6.98 (s, 1H), 4.02-4.07 (m, 4H), 3.54 (s, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ : 151.9, 137.4, 136.3, 136.1, 135.6, 132.3, 131.9, 130.8, 129.6, 129.1, 127.3, 127.0, 126.8, 126.7, 126.1, 125.6, 108.1, 67.1, 53.5.

MS-ESI: calculated for $\text{C}_{27}\text{H}_{17}\text{NO}$ $[\text{M}+\text{Na}]^+$: 358.1310; found: 358.3291.

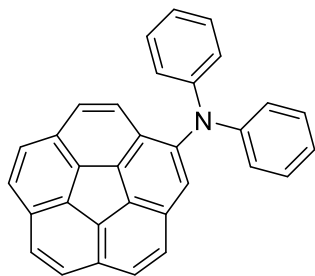
4h:

To a solution of monobromocorannulene (50 mg, 0.15 mmol) and KO^tBu (48 mg, 0.43 mmol) in toluene (5 mL), under an argon atmosphere, aniline (2 mL) was added, and the mixture was degassed three times by evacuating the flask and backfilling with Ar. Pd(OAc)₂ (4 mg, 0.02 mmol) and BINAP (10 mg, 0.02 mmol) were added, and the mixture was heated to reflux. After 9 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (20 mL), and filtered through celite. The filtrate was washed with aqueous HCl (1M, 30 mL), and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 20 : 1) to afford **4h** (20 mg, 0.06 mmol, 39%).

¹H NMR (400 MHz, CDCl₃) δ: 7.72-7.84 (m, 7H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.30-7.45 (m, 5H), 7.04 (dt, *J* = 8.4, 4.4 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃) δ: 144.7, 135.8, 130.9, 130.9, 129.5, 129.4, 128.9, 128.3, 127.9, 127.6, 127.5, 127.3, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 126.4, 126.1, 126.1, 125.7, 124.9, 124.1, 123.3, 121.9, 117.7.

MS-ESI: calculated for C₂₆H₁₅N [M+H]⁺: 342.1204; found: 342.1251.

4i:

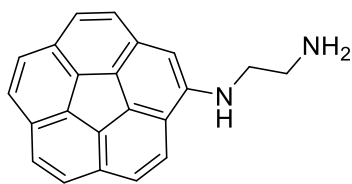
To a solution of monobromocorannulene (50 mg, 0.15 mmol) and KO^tBu (45 mg, 0.40 mmol) in toluene (5 mL), diphenylamine (6 mg, 0.04 mmol) was added under an argon atmosphere, and the mixture was degassed three times by evacuating the flask and backfilling with Ar. Pd(OAc)₂ (5 mg, 0.02 mmol) and BINAP (10 mg, 0.02 mmol) were added, and the mixture was heated to reflux. After 9 hours, the reaction mixture was allowed to cool to RT, diluted with EtOAc (20 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH₄Cl (30 mL), and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaCl (50 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 20 : 1) to afford **4i** (12 mg, 0.03 mmol, 78%).

¹H NMR (400 MHz, CDCl₃) δ: 7.69-7.86 (m, 6H), 7.59 (dd, *J* = 14.7, 8.8 Hz, 2H), 7.51 (d, *J* = 8.9 Hz, 1H), 7.16 – 7.32 (m, 8H), 7.04 (t, *J* = 7.3 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 149.0, 146.4, 137.5, 136.2, 135.9, 135.8, 133.2, 131.8, 131.7, 130.9, 130.8, 130.2, 129.3, 127.3, 127.1, 127.1, 126.9, 126.7, 125.7, 124.0, 122.8, 121.8, 120.4.

MS-ESI: calculated for C₂₃H₁₉N [M+H]⁺: 418.1517; found: 418.1823.

4j:



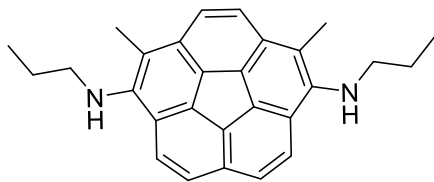
Monobromocorannulene (566mg, 1.7 mmol), Pd(dba)₂^[s21] (98 mg, 0.17 mmol), BINAP (105 mg, 1.7 mmol), and NaO^tBu (660 mg, 6.9 mmol) were added to a dried sealed tube, toluene (10 mL) was added. After stirring at RT for 30 minutes, ethylenediamine (1 mL) was added. Then, the mixture was heated to 110 °C. After 8 hours, the reaction mixture was allowed to cool to RT, diluted with DCM (50 mL), and washed with H₂O (3 x 100 mL), and the aqueous phase was extracted with DCM (3 x 100mL). The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: PE: TEA = 250: 1 to DCM: MeOH = 5:1) to afford brown oil, and then precipitate in the mixed solvent of DCM and *n*-Hexane to give **4j** (204 mg, 0.66 mmol, 39%).

¹H NMR (400 MHz, CD₃OD) δ: 8.05 (d, *J* = 8.8 Hz, 1H), 7.86-7.80 (m, 3H), 7.76-7.66 (m, 3H), 7.61 (d, *J* = 8.7 Hz, 1H), 6.66 (s, 1H), 3.64 (t, *J* = 6.1 Hz, 2H), 3.27 (t, *J* = 6.1 Hz, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ: 148.2, 137.4, 137.0, 136.8, 135.9, 135.4, 132.1, 131.7, 130.4, 129.6, 128.2, 128.2, 127.4, 127.4, 127.1, 125.7, 124.6, 124.2, 100.2, 43.6, 39.7.

MS-ESI: calculated for C₂₂H₁₆N₂ [M+H]⁺: 309.1313; found: 309.1391.

5a:

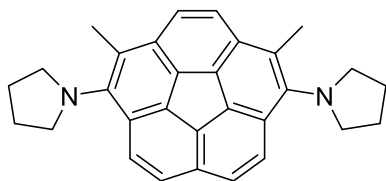


1,6-dibromo-2,5-dimethylcorannulene (70 mg, 0.16 mmol), Pd(OAc)₂ (11 mg, 0.05 mmol), BINAP (30 mg, 0.05 mmol), and KO^tBu (72 mg, 0.64 mmol) were added to a dried sealed tube, toluene (5 mL) and propylamine (2 mL) was added, and stirring at rt for 30 minutes. Then, the mixture was heated to 110 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with DCM (30 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH₄Cl (50 mL), and the aqueous phase was extracted with DCM (3 x 40 mL). The combined organic phase was washed with saturated aqueous NaCl (100 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 50 : 1) to afford **5a** (33 mg, 0.08 mmol, 53%).

¹H NMR (400 MHz, CDCl₃) δ: 7.94 (d, *J* = 8.8 Hz, 2H), 7.76 (s, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 4H), 2.61 (s, 6H), 1.82-1.93 (m, 4H), 1.13 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ: 143.6, 136.2, 135.4, 130.5, 130.4, 130.1, 127.3, 125.9, 125.4, 125.0, 116.1, 53.4, 24.7, 12.72, 11.7. MS-ESI: calculated for C₂₈H₂₈N₂ [M+H]⁺: 339.2252; found: 339.2040.

5b:



1,6-dibromo-2,5-dimethylcorannulene (70 mg, 0.16 mmol), Pd(OAc)₂ (11 mg, 0.05 mmol), BINAP (30 mg, 0.05 mmol), and KO^tBu (72 mg, 0.64 mmol) were added to a dried sealed tube, toluene (5 mL) and pyrrolidine (2 mL) was added, and stirring at RT for 30 minutes. Then, the mixture was heated to 110 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with DCM

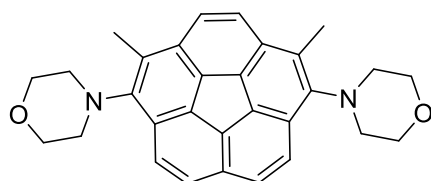
(30 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH_4Cl (50 mL), and the aqueous phase was extracted with DCM (3 x 40 mL). The combined organic phase was washed with saturated aqueous NaCl (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 50 : 1) to afford **5b** (37 mg, 0.09 mmol, 56%).

^1H NMR (400 MHz, CDCl_3) δ : 7.86 (s, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 3.56 (s, 8H), 2.76 (s, 6H), 2.18 (s, 8H).

^{13}C NMR (100 MHz, CDCl_3) δ : 144.4, 137.9, 136.0, 132.2, 131.9, 131.6, 131.3, 129.7, 125.7, 125.2, 125.0, 53.0, 26.7, 14.2.

MS-ESI: calculated for $\text{C}_{30}\text{H}_{28}\text{N}_2$ $[\text{M}+\text{H}]^+$: 417.2252; found: 417.2026.

5c:



1,6-dibromo-2,5-dimethylcorannulene (70 mg, 0.16 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.05 mmol), BINAP (30 mg, 0.05 mmol), and KO^tBu (72 mg, 0.64 mmol) were added to a dried sealed tube, toluene (5 mL) and morpholine (2 mL) was added, and stirring at RT for 30

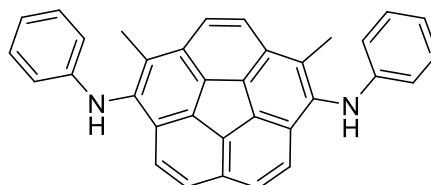
minutes. Then, the mixture was heated to 110 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with DCM (30 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH_4Cl (50 mL), and the aqueous phase was extracted with DCM (3 x 40 mL). The combined organic phase was washed with saturated aqueous NaCl (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 50 : 1) to afford **5c** (27 mg, 0.06 mmol, 38%).

^1H NMR (400 MHz, CDCl_3) δ : 8.06 (d, J = 8.9 Hz, 2H), 7.89 (s, 2H), 7.74 (d, J = 8.9 Hz, 2H), 4.01 (t, J = 4.5 Hz, 8H), 3.48 (s, 8H), 2.87 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ : 145.0, 136.9, 135.7, 132.4, 131.6, 131.5, 131.0, 129.5, 126.2, 125.5, 67.9, 52.5, 14.3.

MS-ESI: calculated for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 449.2152; found: 449.1959.

5d:



Dibromocorannulene (70 mg, 0.16 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.05 mmol), BINAP (30 mg, 0.05 mmol), and KO^tBu (72 mg, 0.64 mmol) were added to a dried sealed tube, toluene (5 mL) and aniline (2 mL) was added, and stirring at RT for 30 minutes.

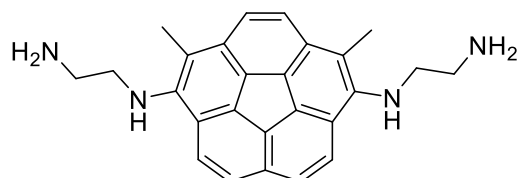
Then, the mixture was heated to 110 °C. After 10 hours, the reaction mixture was allowed to cool to RT, diluted with DCM (30 mL), and filtered through celite. The filtrate was washed with saturated aqueous NH_4Cl (50 mL), and the aqueous phase was extracted with DCM (3 x 40 mL). The combined organic phase was washed with saturated aqueous NaCl (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether to petroleum ether : EtOAc = 50 : 1) to afford **5d** (37 mg, 0.08 mmol, 50%).

^1H NMR (400 MHz, CDCl_3) δ : 7.83 (s, 2H), 7.56 (q, $J = 8.8$ Hz, 4H), 7.23-7.30 (m, 5H), 7.06 (s, 4H), 6.91 (s, 2H), 2.68 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ : 135.4, 132.6, 130.2, 129.4, 126.7, 125.4, 125.2, 115.8, 29.7.

MS-ESI: calculated for $\text{C}_{34}\text{H}_{24}\text{N}_2$ $[\text{M}+\text{H}]^+$: 461.1939; found: 461.1623.

5e:



1,6-dibromo-2,5-dimethylcorannulene (23 mg, 0.05 mmol), $\text{Pd}(\text{dba})_2$ (3 mg, 0.005 mmol), BINAP (3 mg, 0.005 mmol), and NaO^tBu (21 mg, 0.22 mmol) were added to a dried sealed tube, toluene (3 mL) was added. After stirring at

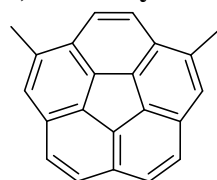
RT for 30 minutes, ethylenediamine (24 μL , 0.36 mmol) was added. Then, the mixture was heated to 110 $^\circ\text{C}$. After 12 hours, the reaction mixture was allowed to cool to RT, diluted with DCM (20 mL), and filtered through celite. The filtrate was washed with H_2O (3 x 50 mL), and the aqueous phase was extracted with DCM (3 x 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: DCM: MeOH: TEA = 150: 30: 1) to afford brown oil, and then precipitate in the mixed solvent of methanol and cyclopentane to give **5e** (3 mg, 0.008 mmol, 15%).

^1H NMR (400 MHz, CD_3OD) δ : 7.94 (d, $J = 8.8$ Hz, 2H), 7.81 (s, 2H), 7.76 (d, $J = 8.8$ Hz, 2H), 3.83 (t, $J = 6.4$ Hz, 4H), 3.17 (t, $J = 6.4$ Hz, 4H), 2.65 (s, 6H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 143.7, 134.6, 130.4, 129.8, 129.7, 127.3, 126.1, 125.8, 125.5, 117.1, 52.1, 48.8, 13.1.

MS-ESI: calculated for $\text{C}_{26}\text{H}_{26}\text{N}_4$ $[\text{M}+\text{H}]^+$: 395.2157; found: 395.2240.

2,5-dimethylcorannulene:



A solution of 1,6-dibromo-2,5-dimethylcorannulene (105 mg, 0.24 mmol) in anhydrous THF (5 mL) was cooled to -78 $^\circ\text{C}$ under argon atmosphere using an acetone dry-ice bath, $n\text{-BuLi}$ (3M, 0.1 mL) was added dropwise. Anhydrous DMF (0.03 mL) was added slowly to the reaction mixture after stirring at -78 $^\circ\text{C}$ for 1 hour. After 1h at -78 $^\circ\text{C}$, the mixture was brought back to RT and the reaction was quenched by carefully adding aqueous HCl (1M, 10 mL), and washed with saturated aqueous NaCl (100 mL), and the aqueous phase was extracted with DCM (3 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4 . Then the crude product was purified by chromatography on silica gel with petroleum ether to afford 2,5-dimethylcorannulene^[s3, s4] (30 mg, 0.11 mmol, 45%).

^1H NMR (400 MHz, CDCl_3) δ : 7.94 (s, 2H), 7.71 (dd, $J = 23.9, 8.7$ Hz, 4H), 7.56 (s, 2H), 2.84 (s, 6H);

^{13}C NMR (100 MHz, CDCl_3) δ : 136.6, 136.0, 135.4, 134.9, 131.5, 130.6, 129.9, 127.0, 126.2, 125.7, 124.8, 18.8.

3. Optical data and spectra

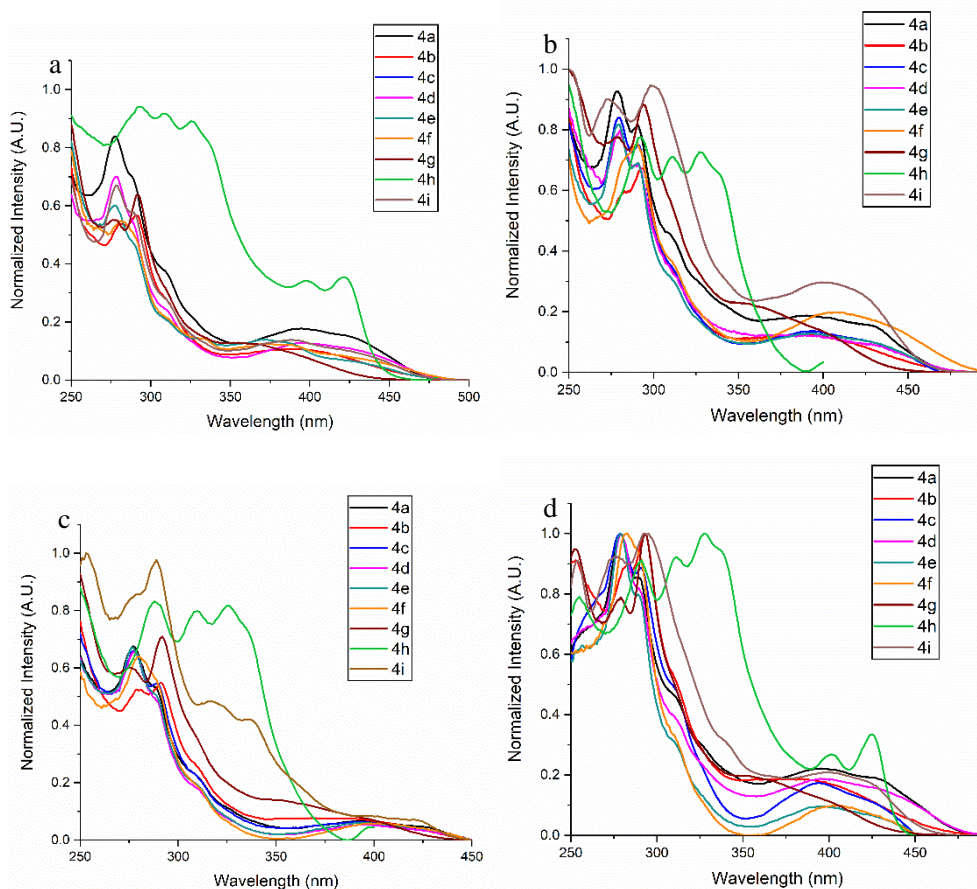


Fig. S1 Excitation spectra of **4a-i** in CH₃CN (a), DCM (b), MeOH (c), THF (d) at RT.

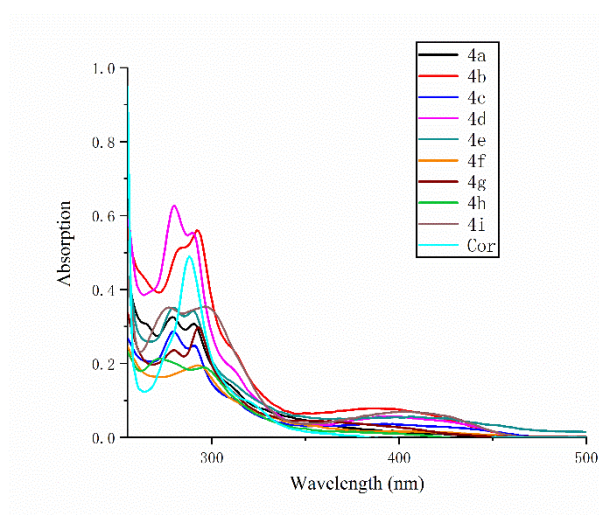


Fig. S2 UV spectra of **4a-i** and **Cor** in DCM at RT.

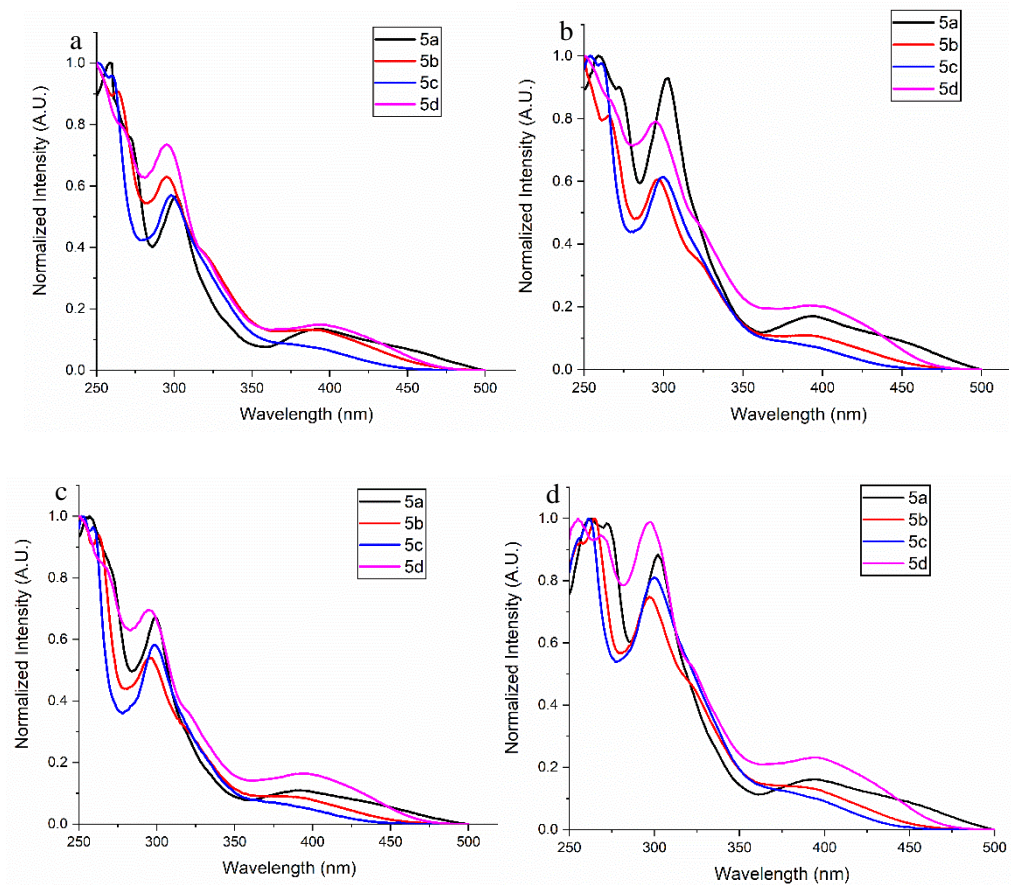


Fig. S3 Excitation spectra of **5a-d** in CH₃CN (a), DCM (b), MeOH (c), THF (d) at RT.

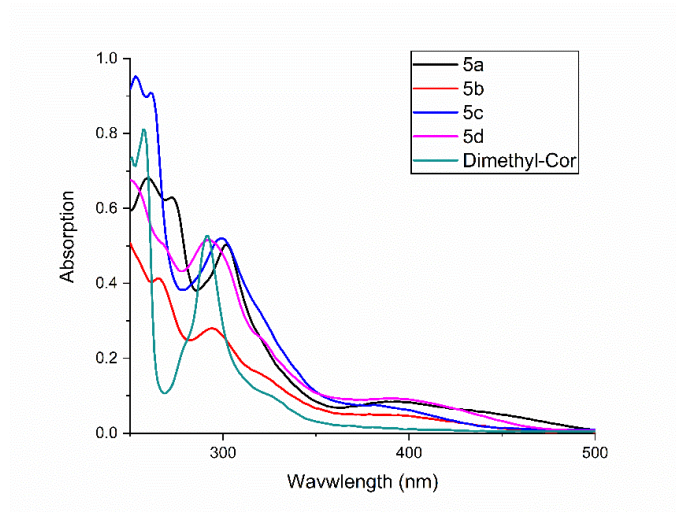


Fig. S4 UV spectra of **5a-d** and **2,5-dimethylcorannulene** in DCM at RT.

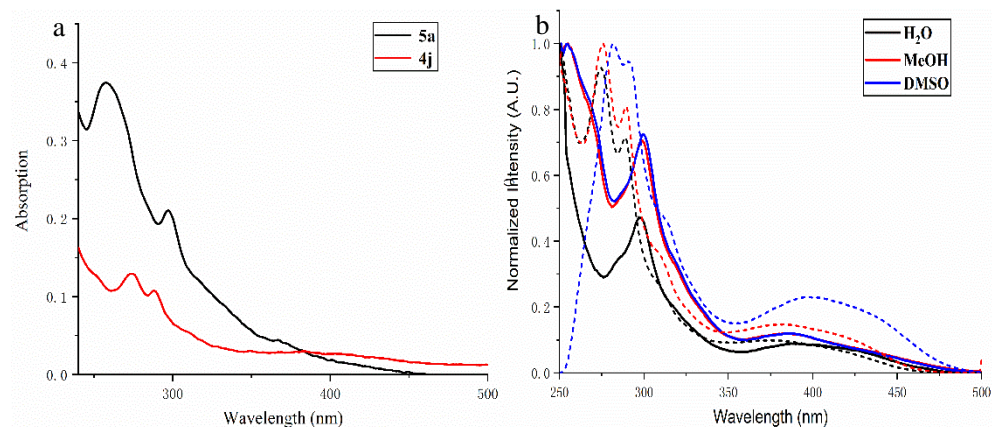


Fig. S5 (a) UV spectra of **4j** and **5a** in H₂O at $\sim 10^{-5}$ M. (b) Excitation spectra of **4j** (dashed lines) and **5e** (solid lines) at RT.

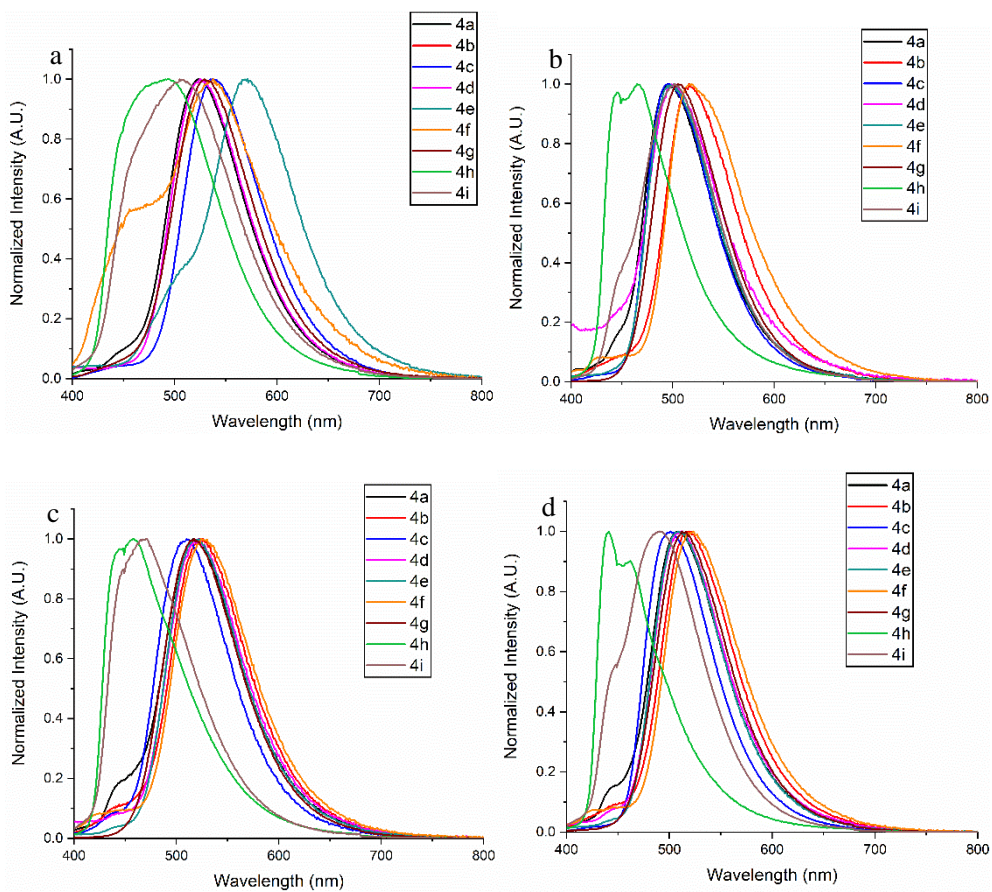


Fig. S6 Emission spectra of **4a-i** in CH₃CN (a), DCM (b), MeOH (c), THF (d) at RT.

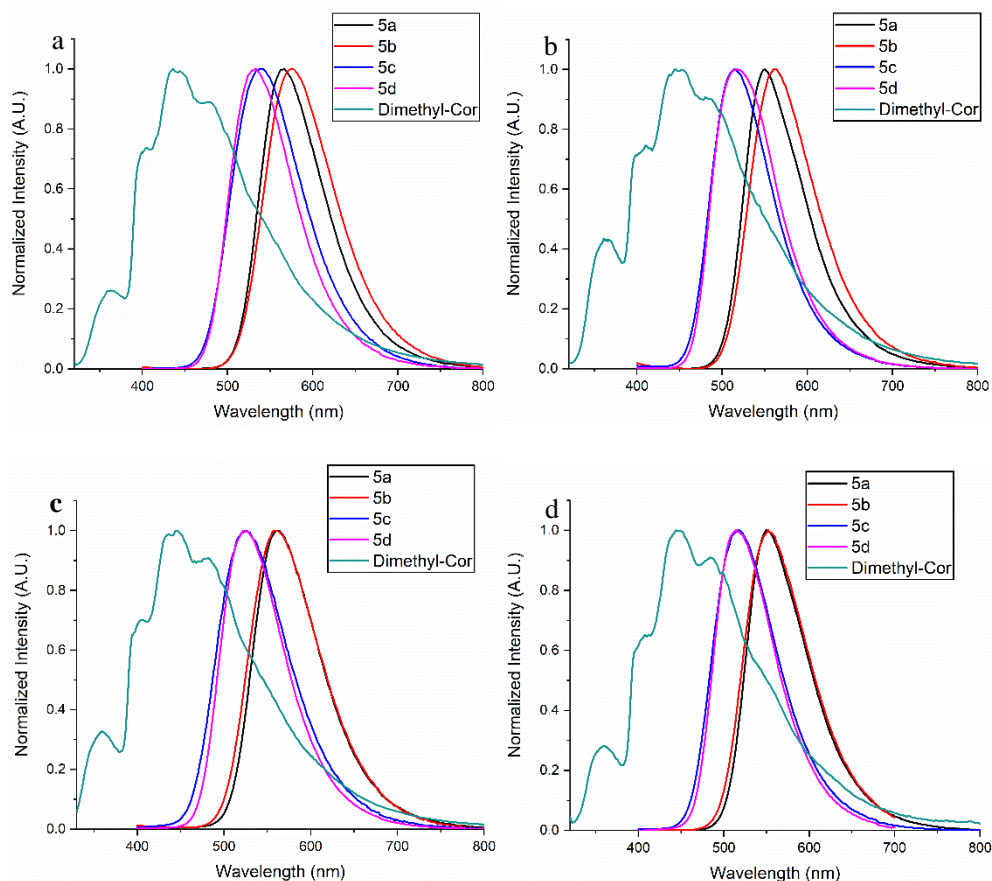


Fig. S7 Emission spectra of **5a-d** and **2,5-dimethylcorannulene** in CH_3CN (a), DCM (b), MeOH (c), THF (d) at RT.

Table S1. Optical properties of **4a-j**, **5a-e**.^{a-d}

	-NR ¹ R ²	$\lambda_{\text{max}}(\text{abs})^{\text{e}}$	$\epsilon_{\text{max}}^{\text{f}}$	$\lambda_{\text{max}}(\text{ex})$	$\lambda_{\text{max}}(\text{em})$	$\Phi(\%)$	Stokes shift
Cor	—	288	4.9	289	436	1	147
4a	NHPr	291	1.2	290	494	15	204
4b	NEt ₂	292	3.4	293	517	13	224
4c	NH ^t Bu	292	1.4	291	497	18	206
4d	NHCy	292	6.9	291	501	7	210
4e	NH ⁱ Pr	290	0.4	291	499	17	208
4f	pyr	293	2.4	290	518	17	228
4g	morph	294	2.1	294	502	18	208
4h	NHPh	295	0.2	295	465	18	170
4i	NPh ₂	296	2.4	298	502	25	204
4j	NH(CH ₂) ₂ NH ₂	288	1.3	289	517	9	228
CorMe₂	—	292	3.1	294	423	2	129
5a	NHPr	292	2.2	303	552	14	249
5b	pyr	294	1.6	297	562	6	265
5c	morph	299	1.7	299	516	8	217
5d	NHPh	292	6.4	295	518	17	223
5e	NH(CH ₂) ₂ NH ₂	297	1.5	297	560	11	263

^a All λ values in nm. ^b All measurements made at $\sim 10^{-5}$ M. ^c All measurements made in CH_2Cl_2 , except **4j** and **5e**, which was measured in H_2O for solubility reasons. ^d **Cor** = corannulene; **CorMe₂** = 2,5-dimethylcorannulene; **Cy** = cyclohexyl; pyr = pyrrolidiny; morph = morpholinyl. ^e $\lambda_{\text{max}}(\text{abs})$ are the longest λ well-resolved absorbances. ^f $(\text{M}^{-1}\text{cm}^{-1}) \times 10^4$.

Table S2. Lifetime of **4a-i**, **5a-d**, and **2,5-dimethylcorannulene**.^{a,b}

	4a	4b	4c	4d	4e	4f	4g	4h	4i	CorMe₂^c	5a	5b	5c	5d
τ_f	6.3	7.8	7.5	7.6	5.6	6.1	6.9	5.0	8.3	6.6	7.9	4.0	4.2	7.3
χ^2	1.11	1.12	1.05	1.11	0.92	1.15	0.96	1.08	0.96	1.09	0.97	1.01	1.03	1.10

^a Lifetime in ns. ^b All measurements made in CH₂Cl₂ at RT. ^c **CorMe₂** = 2,5-dimethylcorannulene.

Table S3. Photophysical parameters of **4j** and **5e**.^a

S^b	$\lambda_{\max}(\text{em})^c$		Φ (%)		τ_f^d		χ^2	
	4j	5e	4j	5e	4j	5e	4j	5e
MeOH	501	544	11	10	8.0	8.6	1.08	0.89
DMSO	533	571	23	17	12.8	12.7	1.13	0.93
H ₂ O	517	560	9	11	11.2	11.3	0.98	1.19

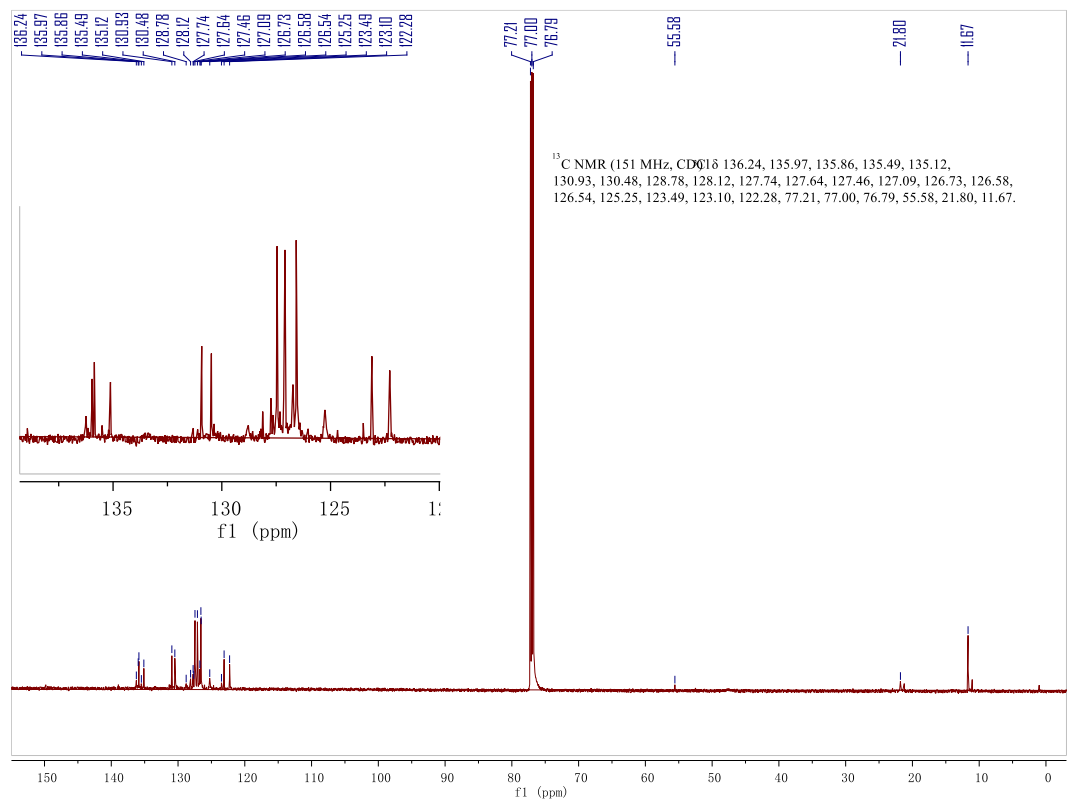
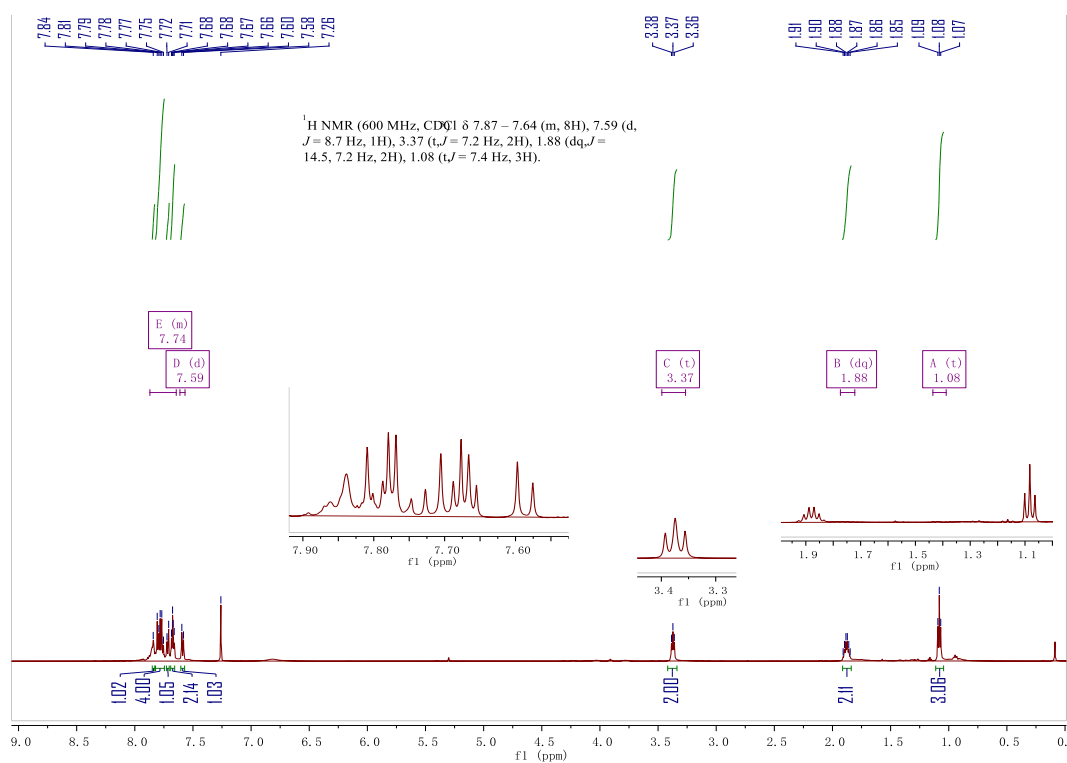
^a Room temperature. ^b S = solvent, ^c λ values in nm. ^d Lifetime in ns.

4. References

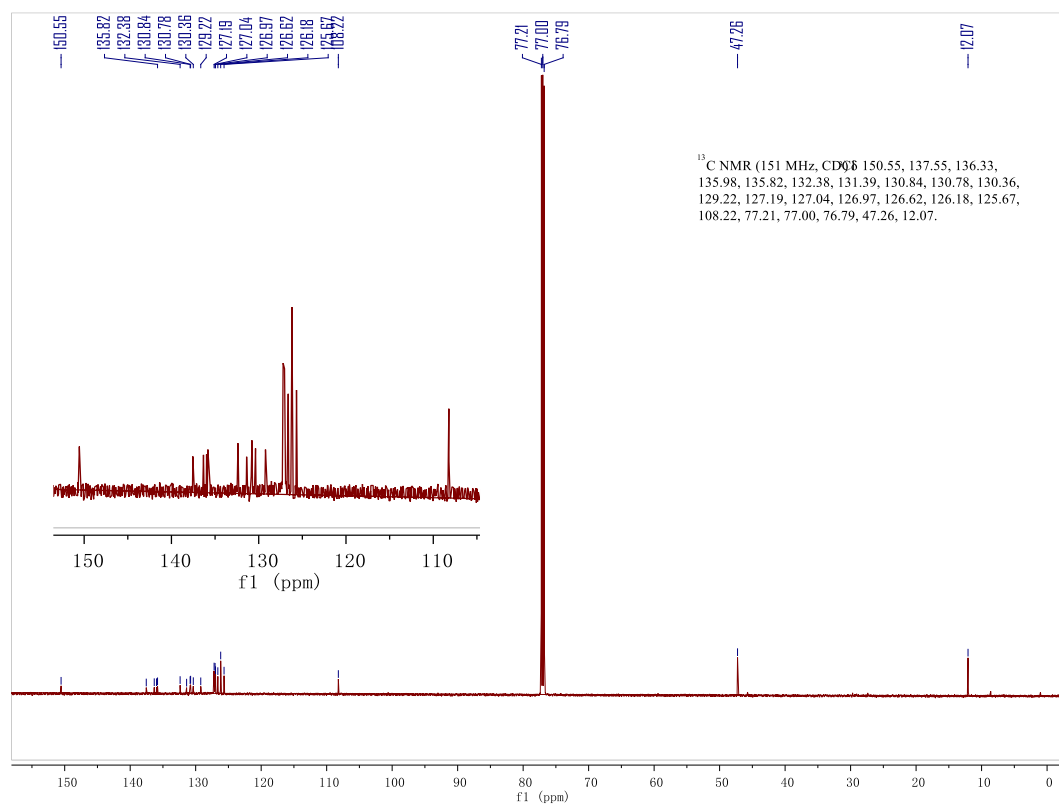
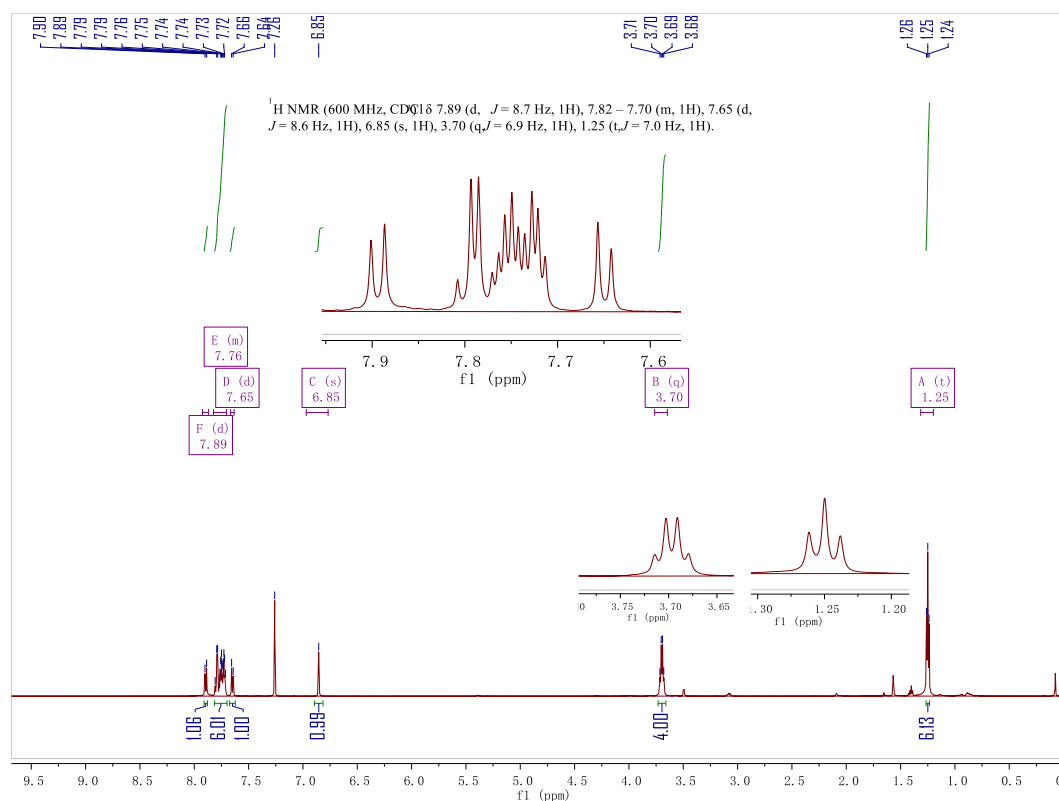
- S1. Sun, N.; Chen, H.; Li, X.; Xu, M.; Gan, Y.; Zhang, L.; Liu, Y. *J. Org. Chem.*, 2017, **82**, 10051.
- S2. Abel, A. S.; Averin, A. D.; Cheprakov, A. V.; Roznyatovsky, V. A.; Denat, F.; Bessmertnykh-Lemeune, A.; Beletskaya, I. P. *Org. Biomol. Chem.*, 2019, **17**, 4243.
- S3. Seiders, T. J.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.*, 1996, **118**, 2754.
- S4. Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.*, 1999, **121**, 7804.

5. ^1H NMR and ^{13}C NMR spectra

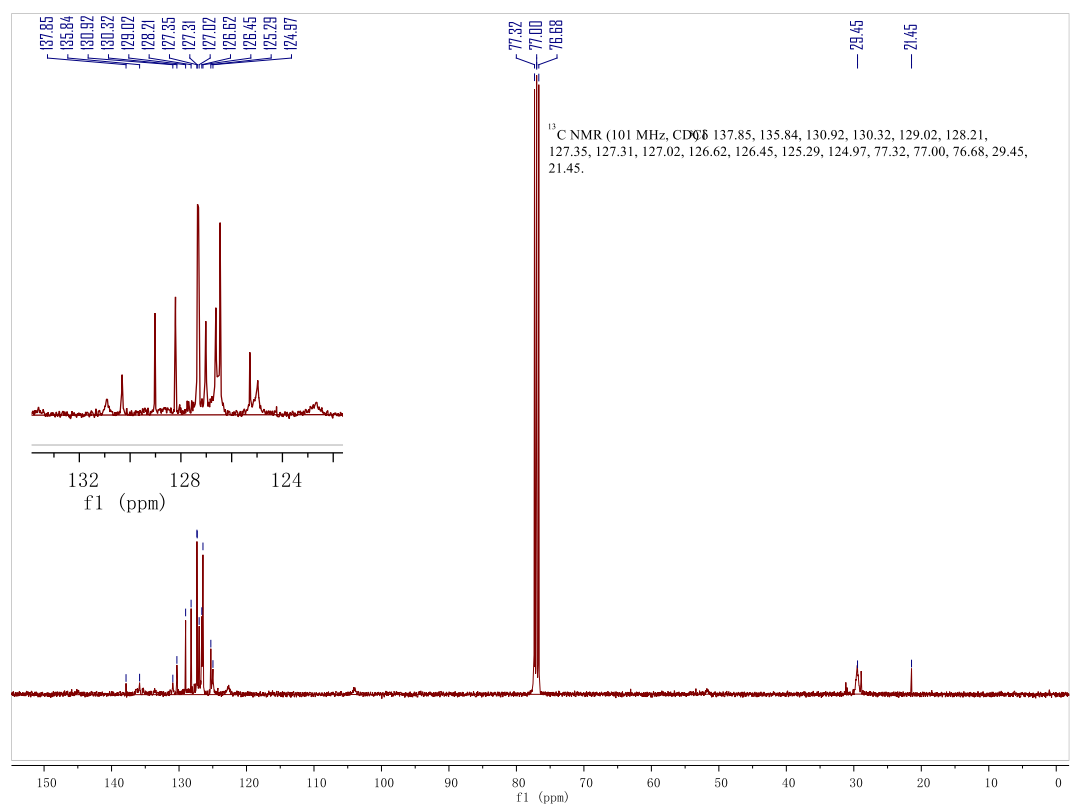
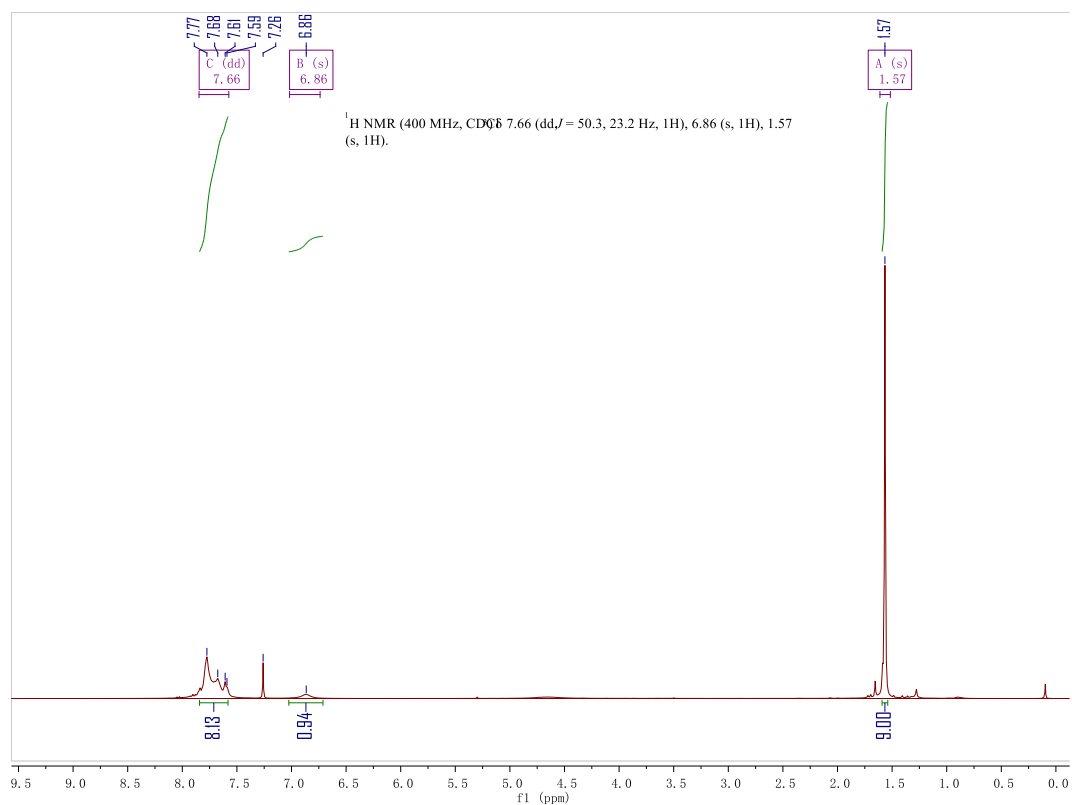
Compound **4a** (CDCl_3):



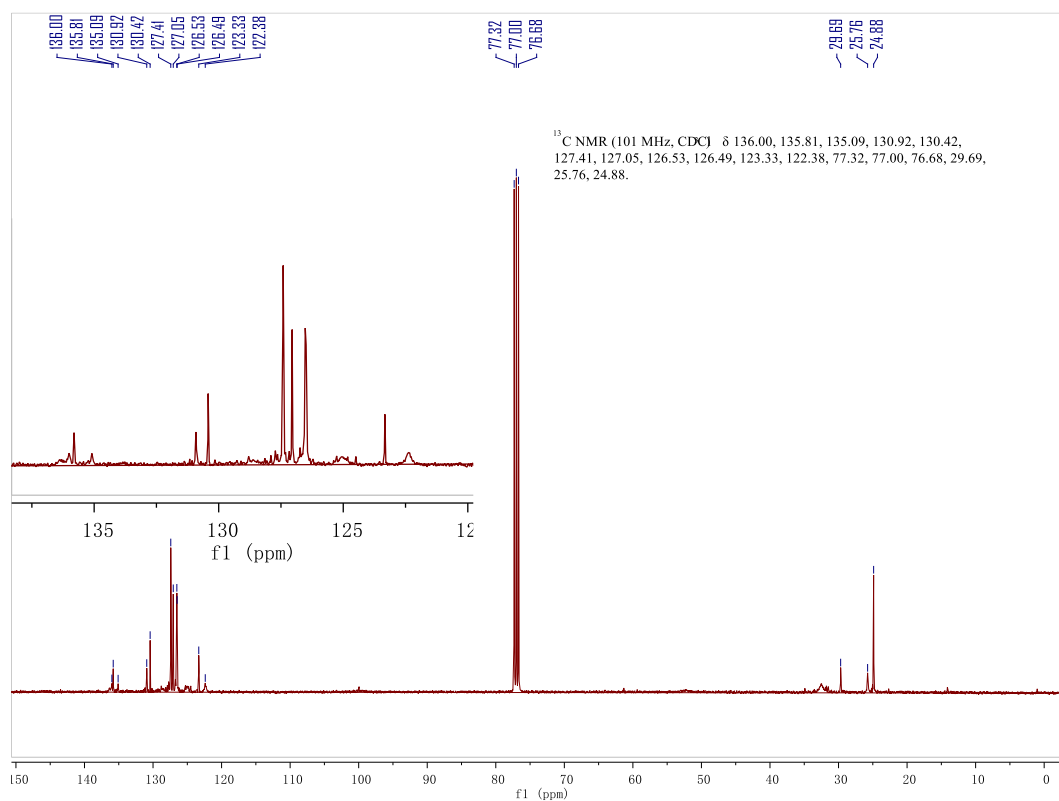
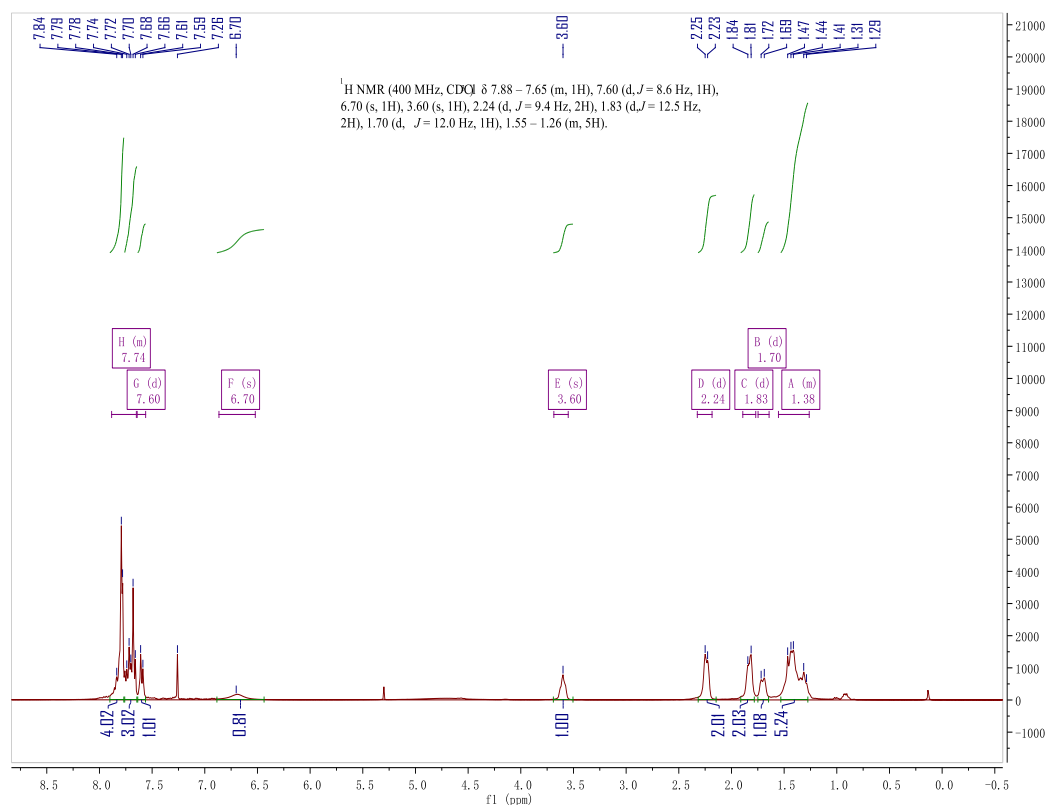
Compound **4b** (CDCl₃):



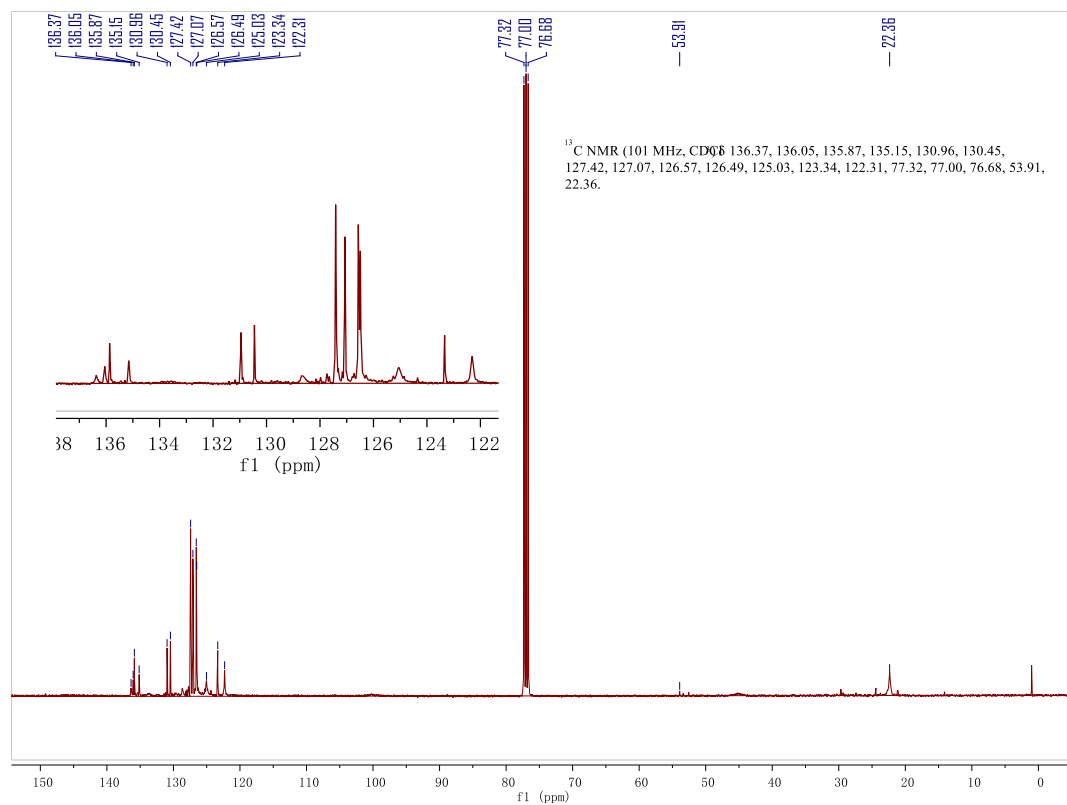
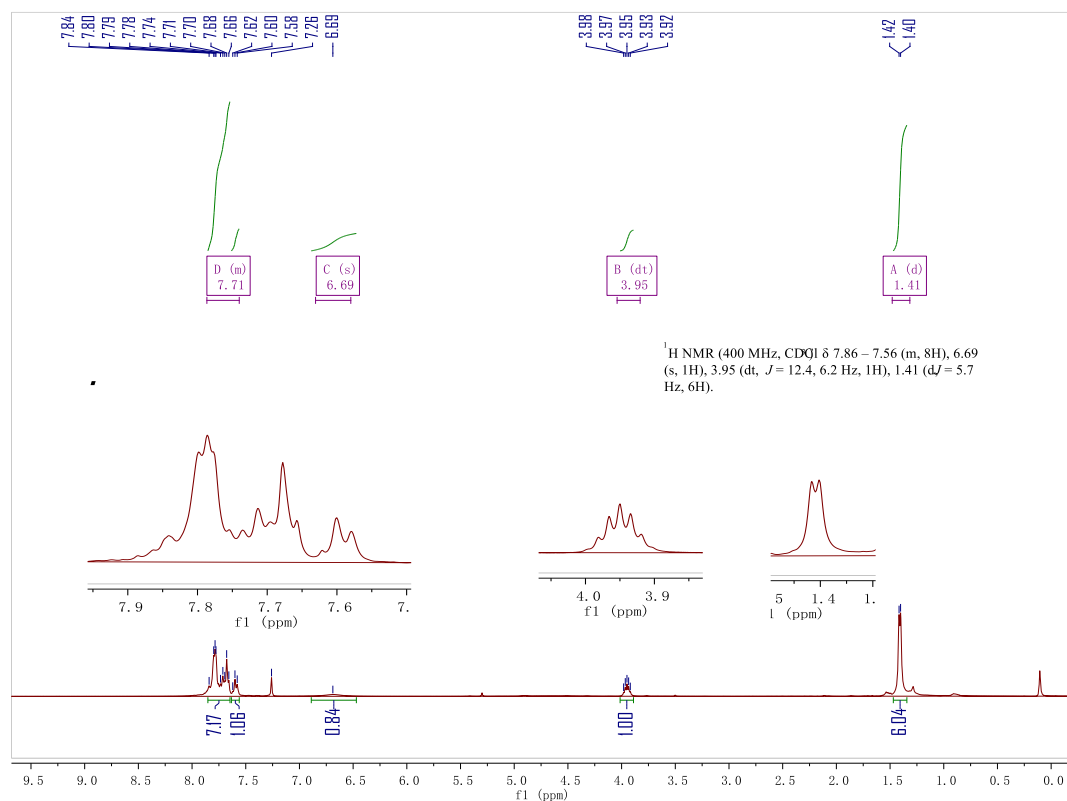
Compound **4c** (CDCl₃):



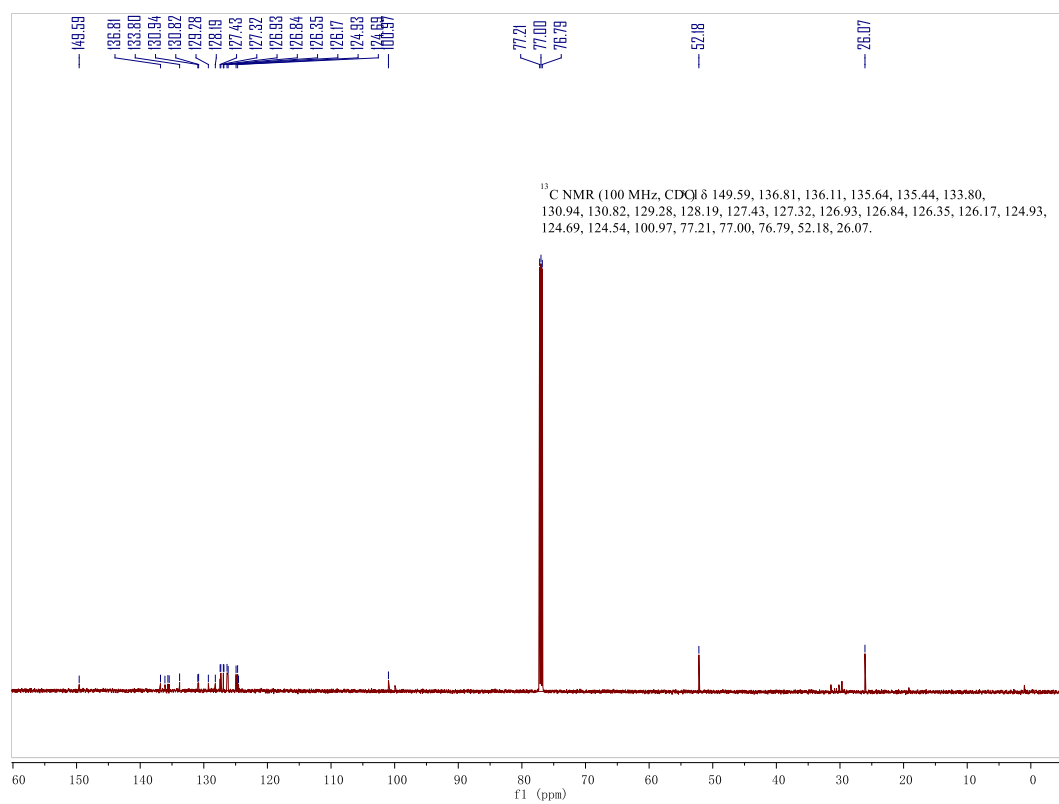
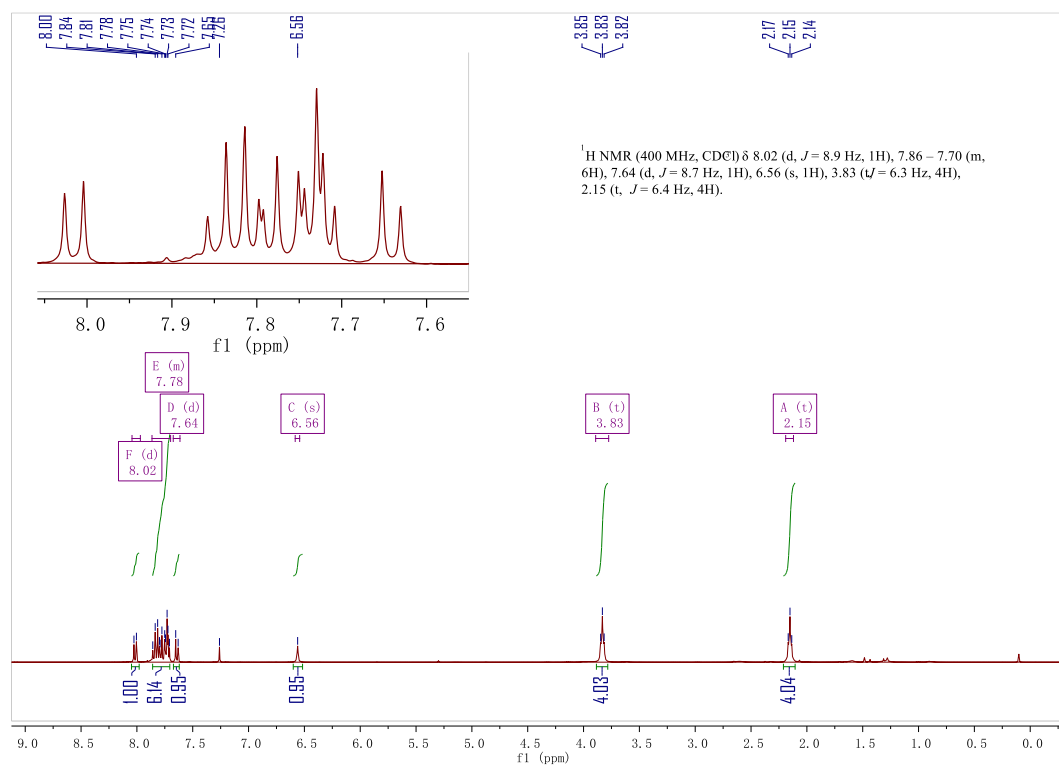
Compound **4d** (CDCl₃):



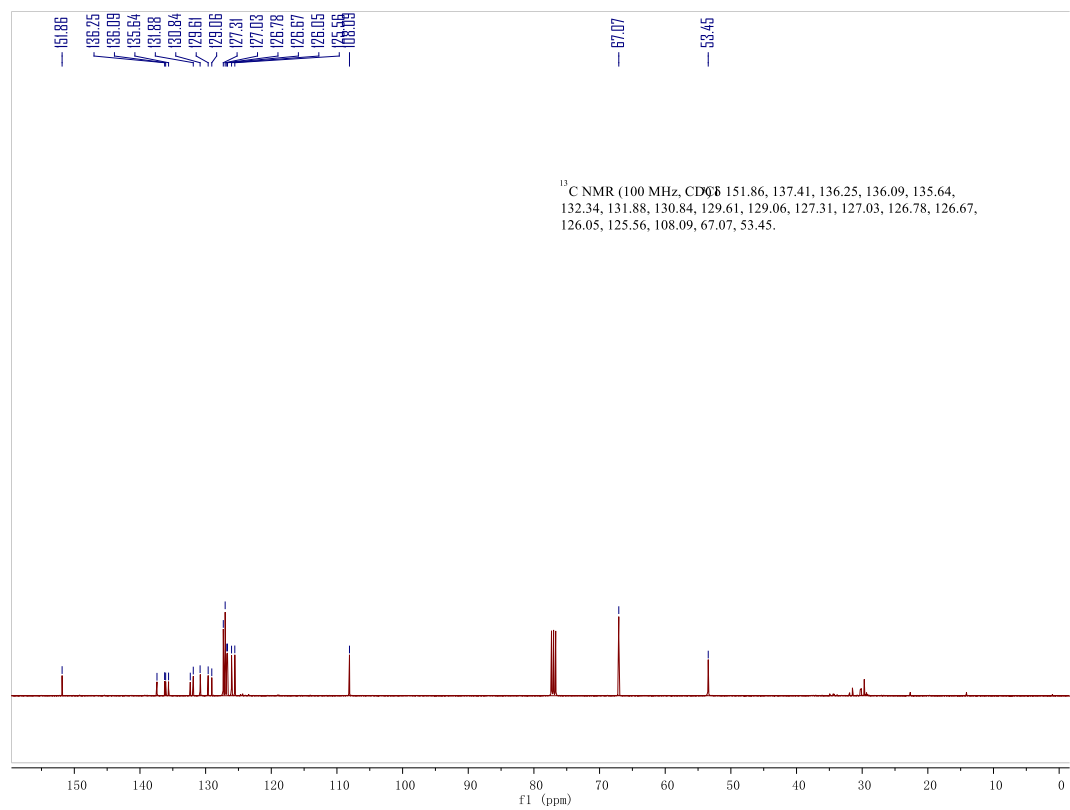
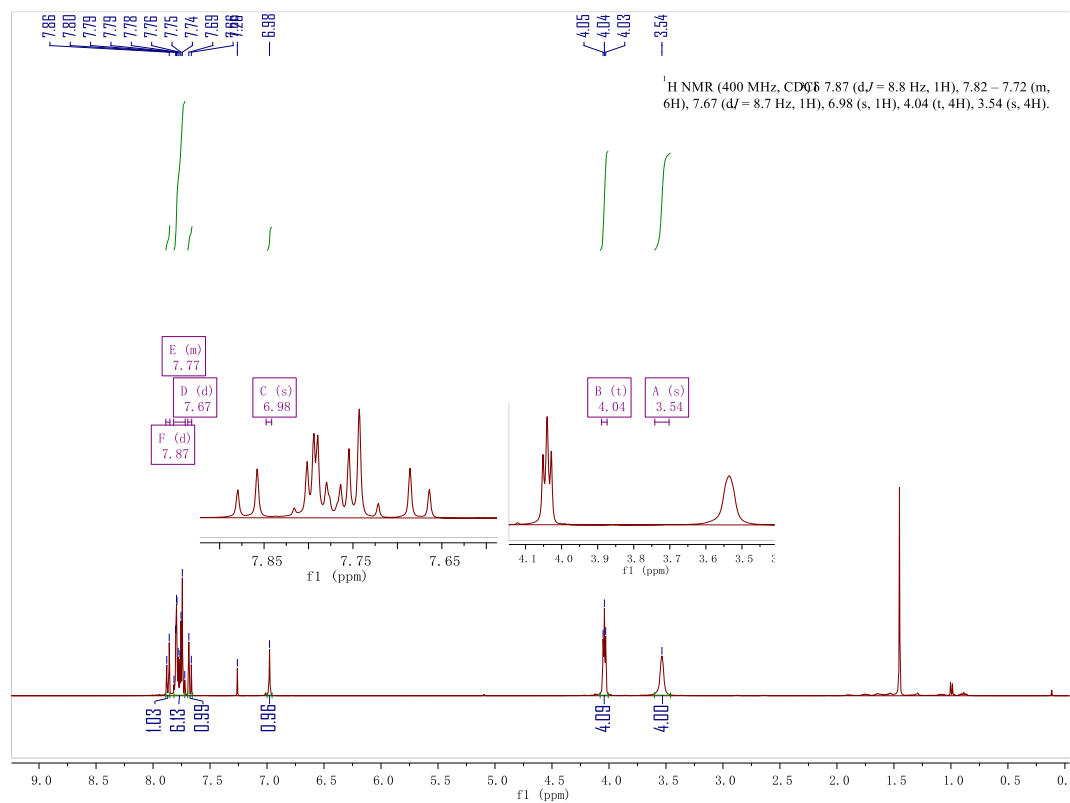
Compound 4e (CDCl₃):



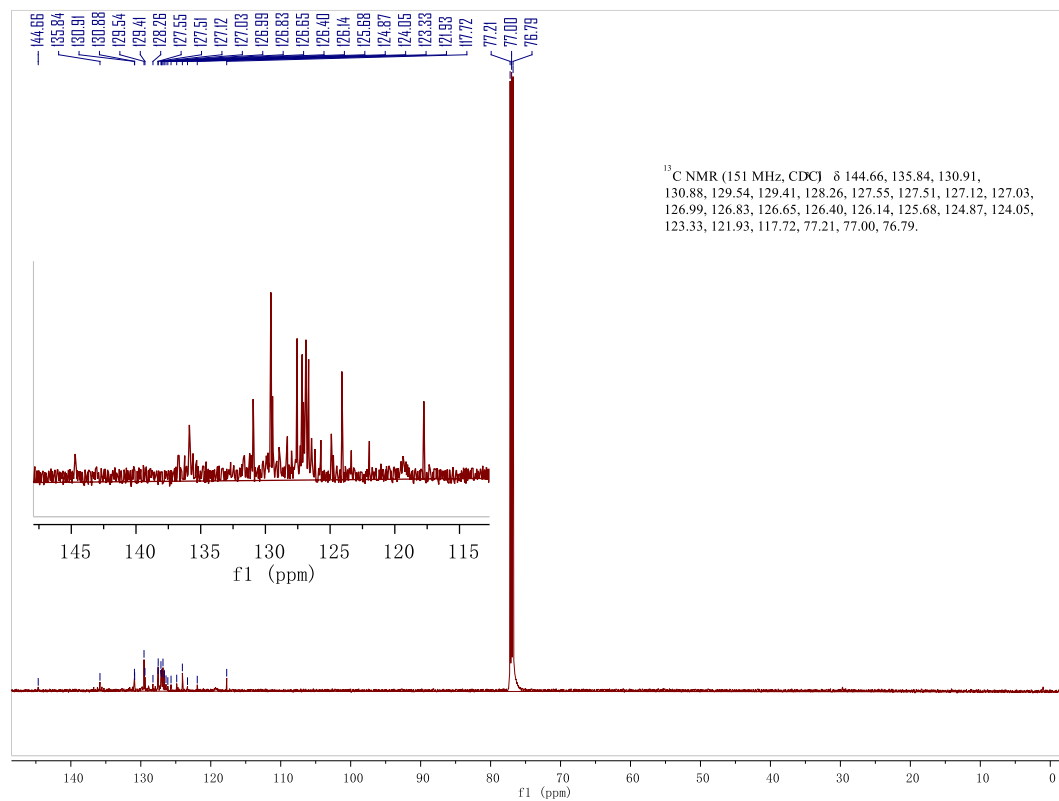
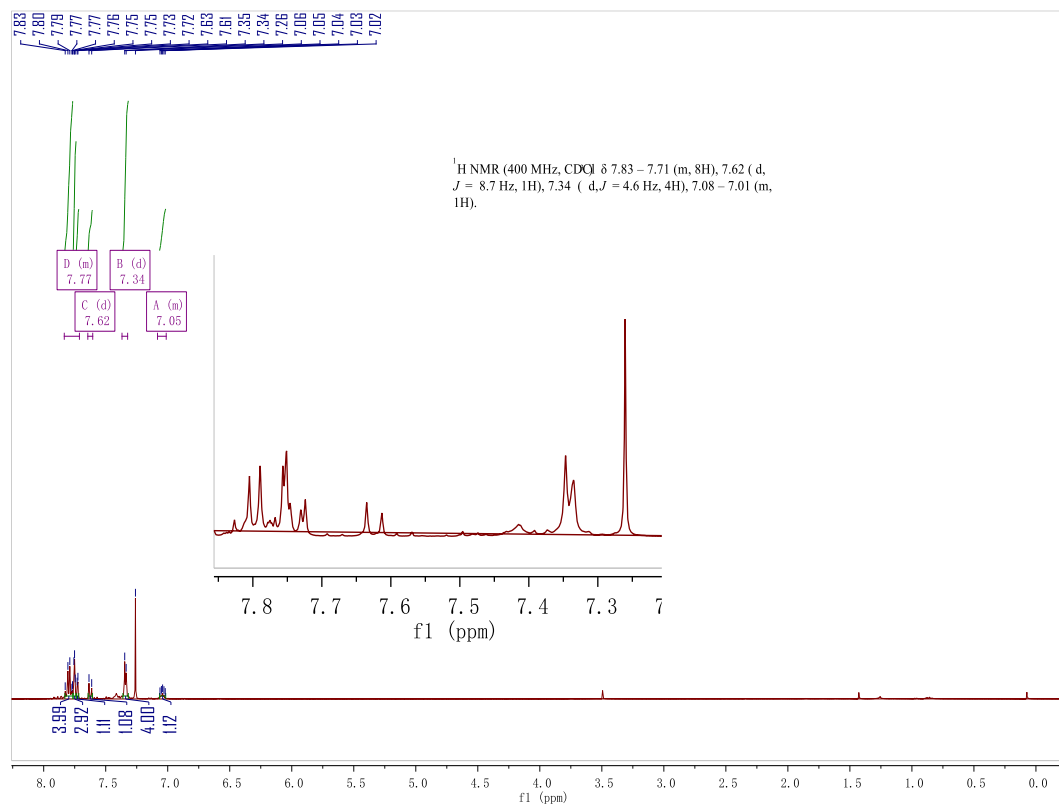
Compound **4f** (CDCl₃):



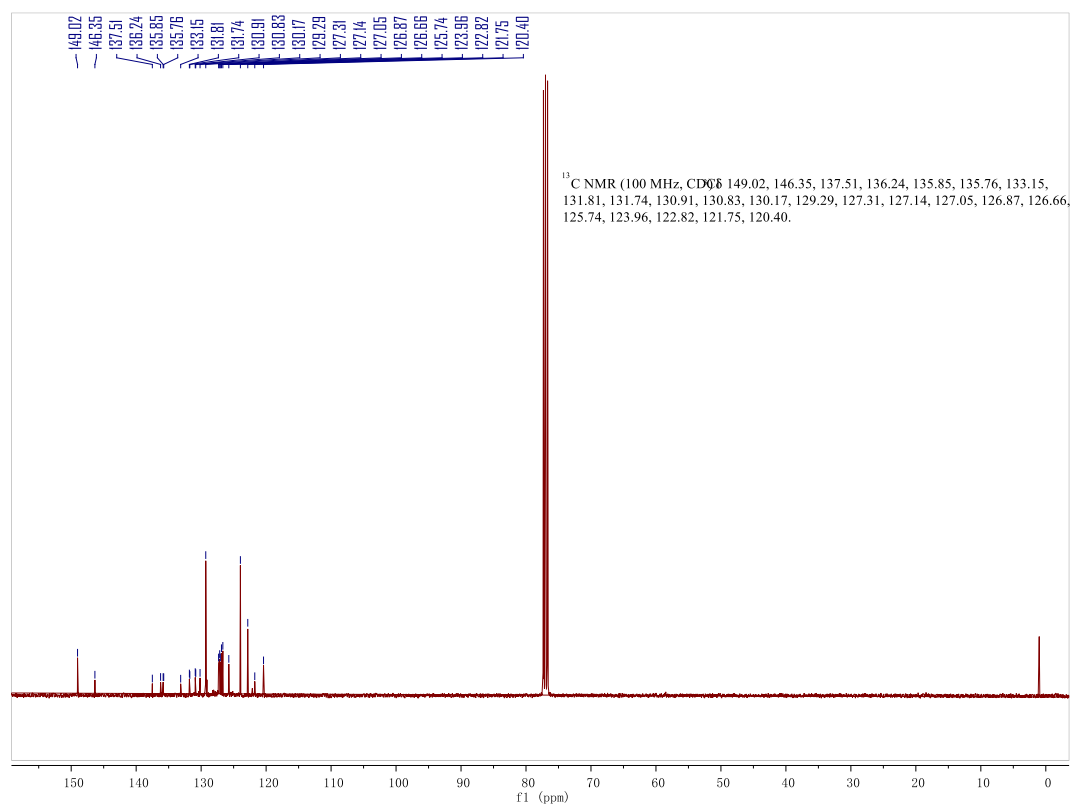
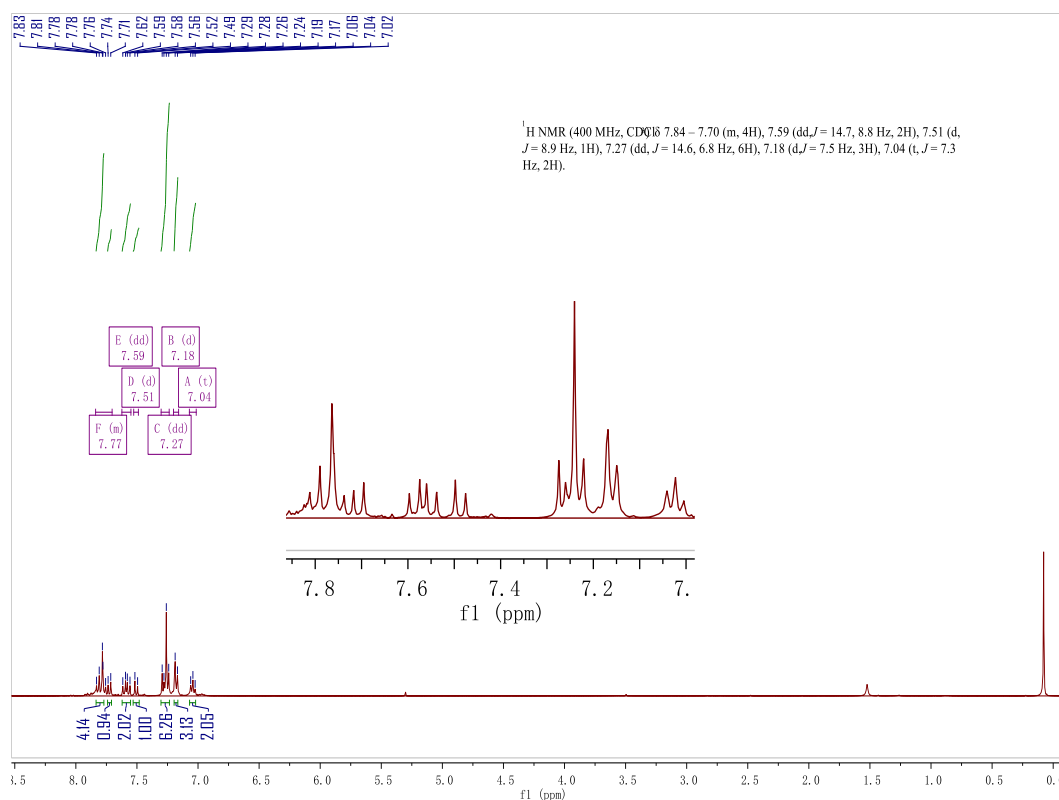
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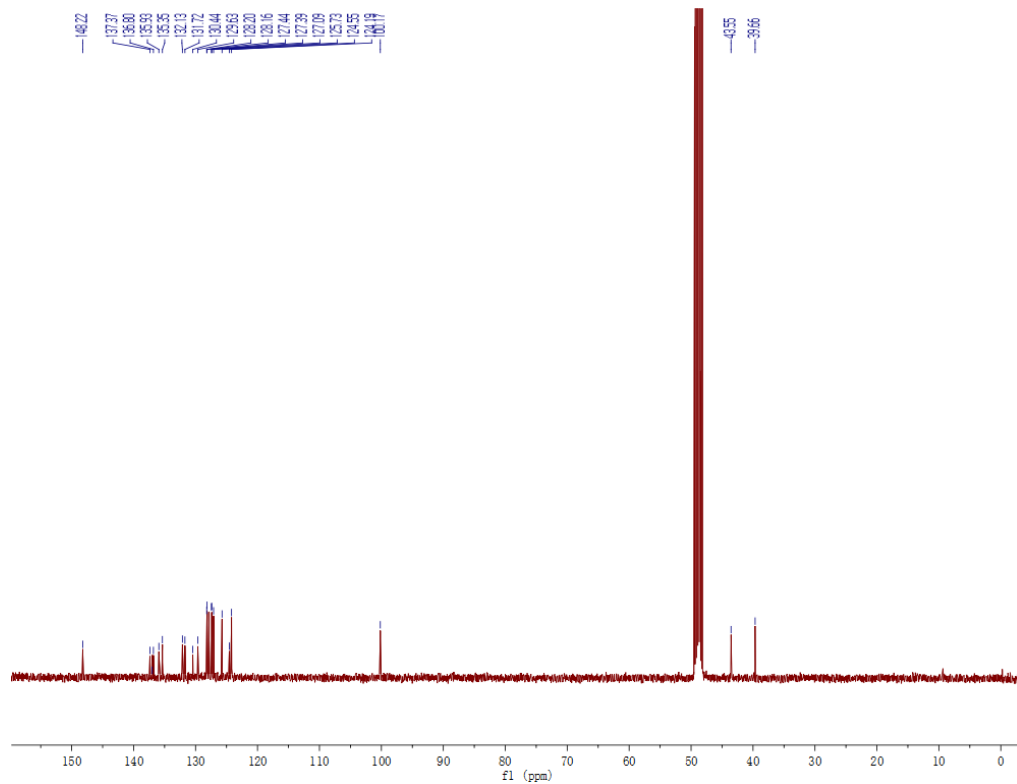
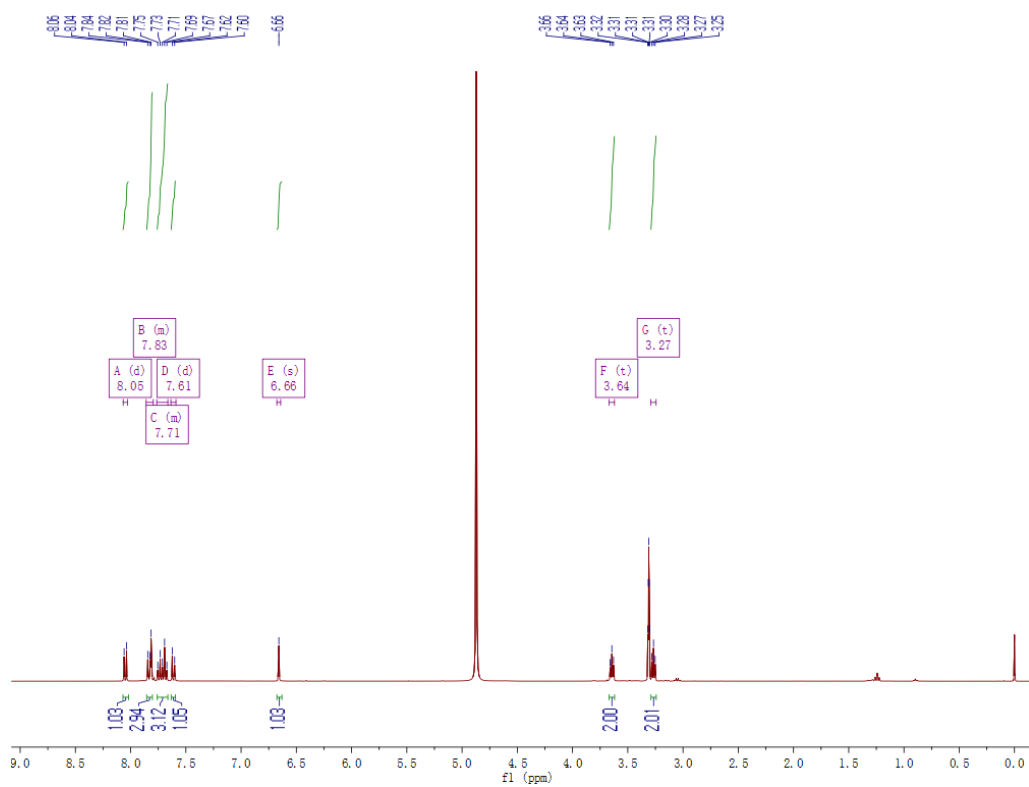
Compound **4h** (CDCl₃):



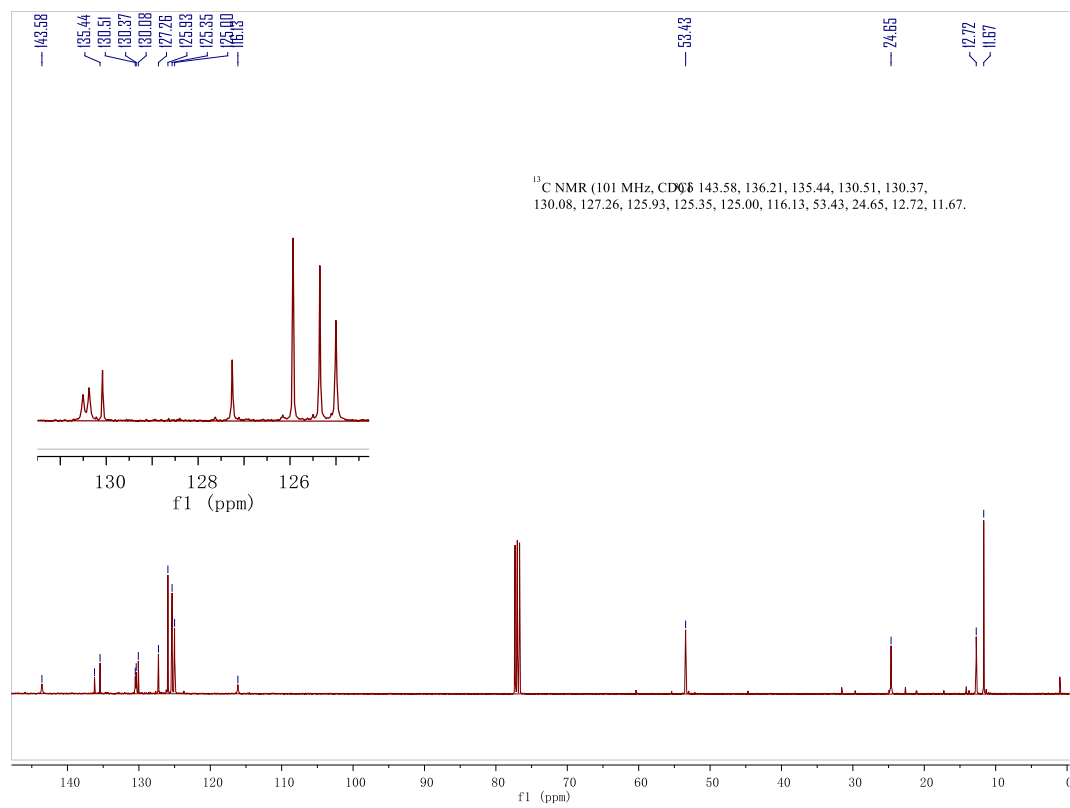
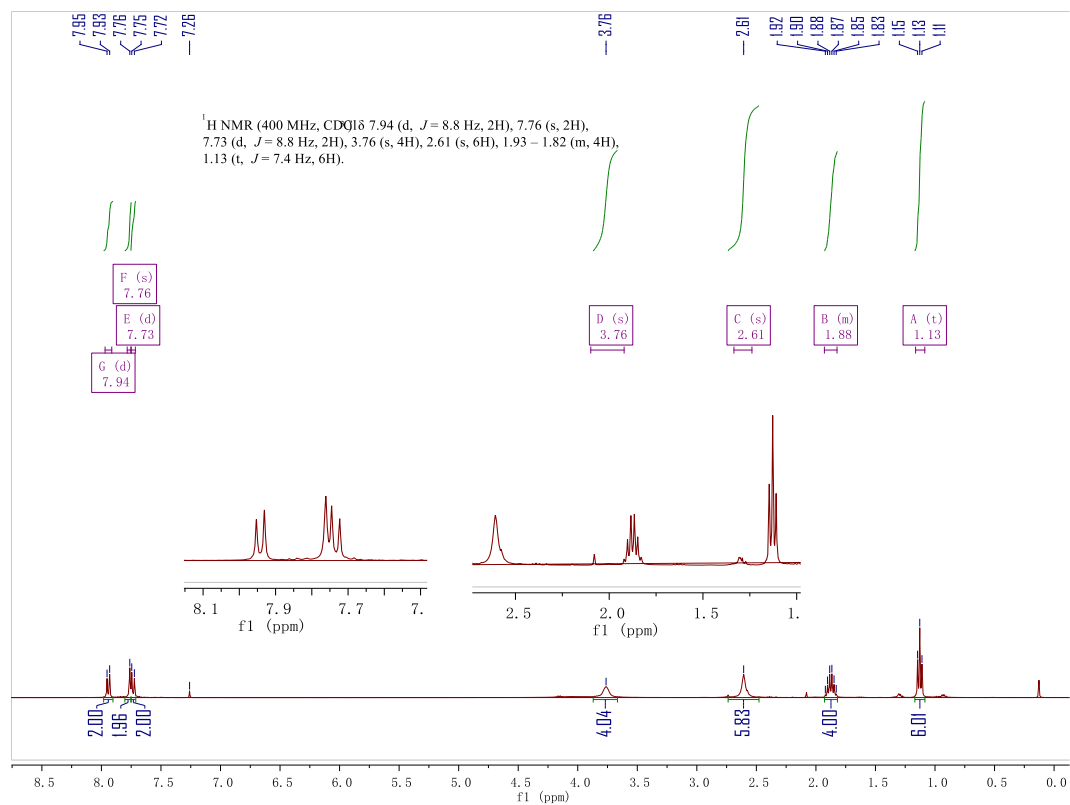
Compound **4i** (CDCl₃):



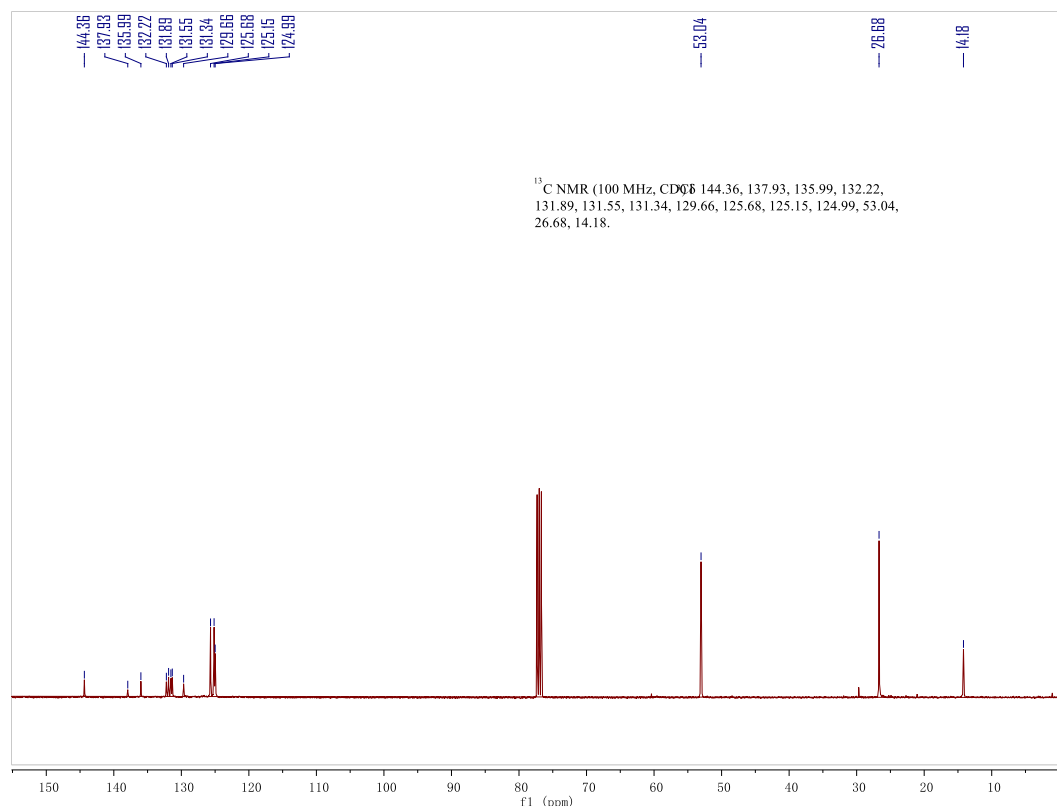
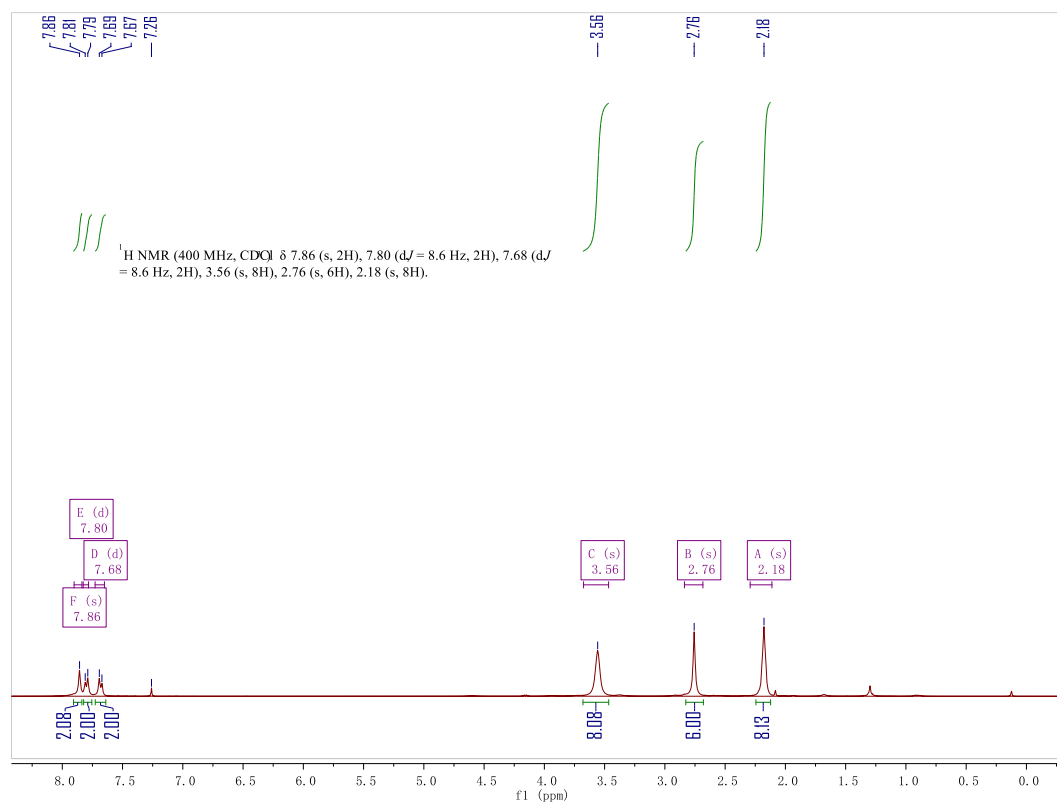
Compound **4j** (CD₃OD):



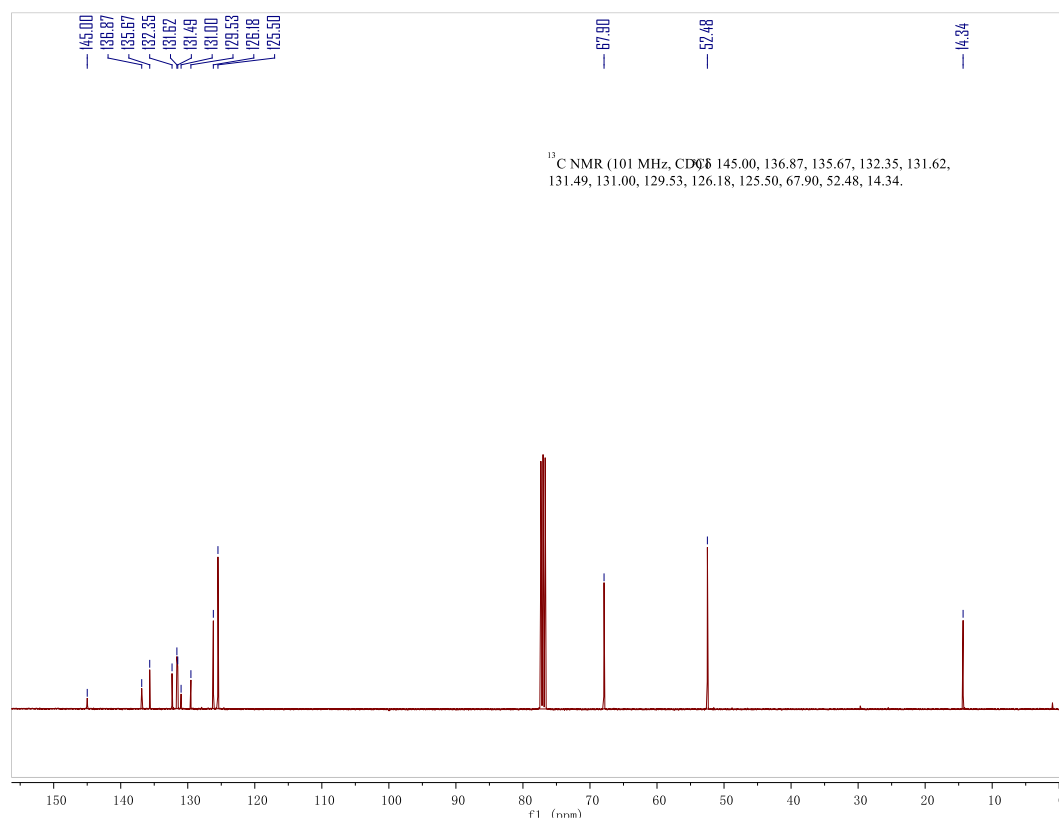
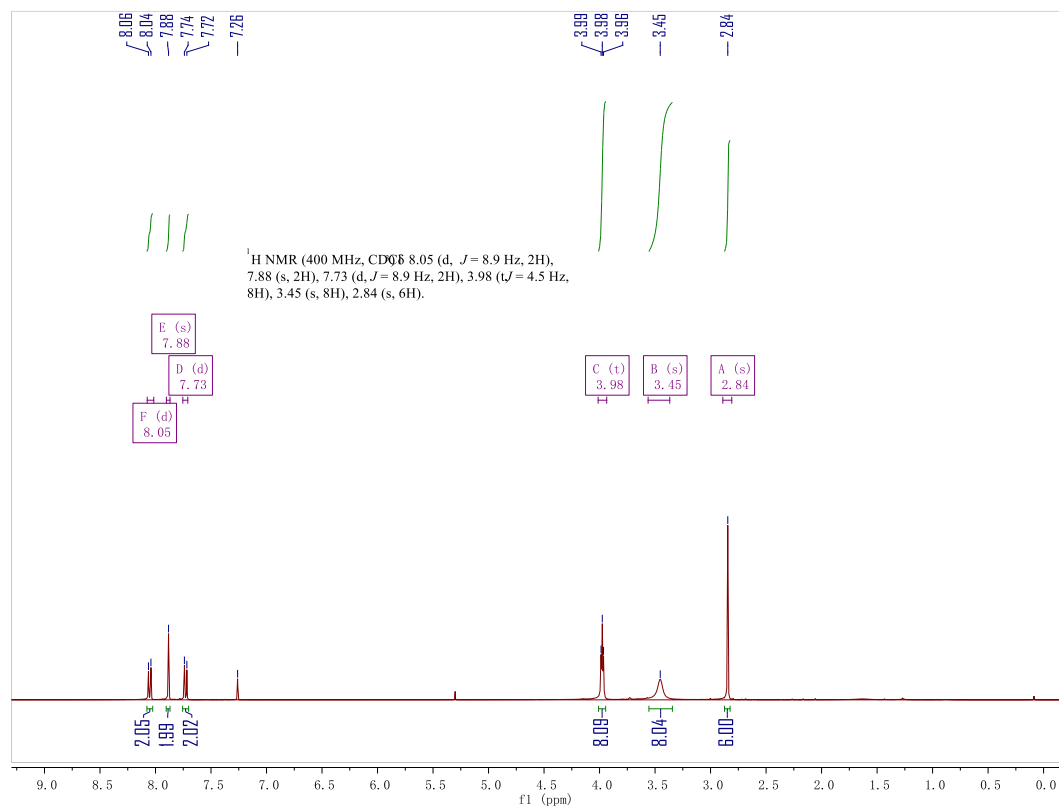
Compound **5a** (CDCl₃):



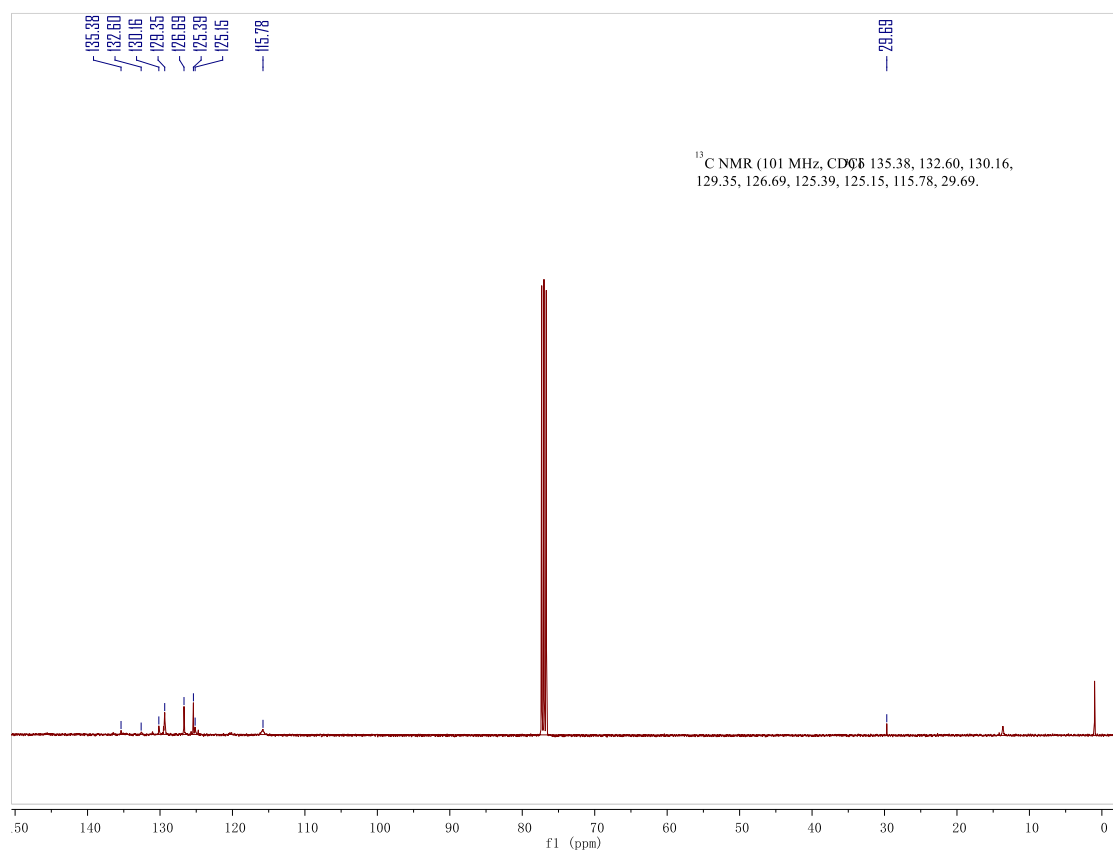
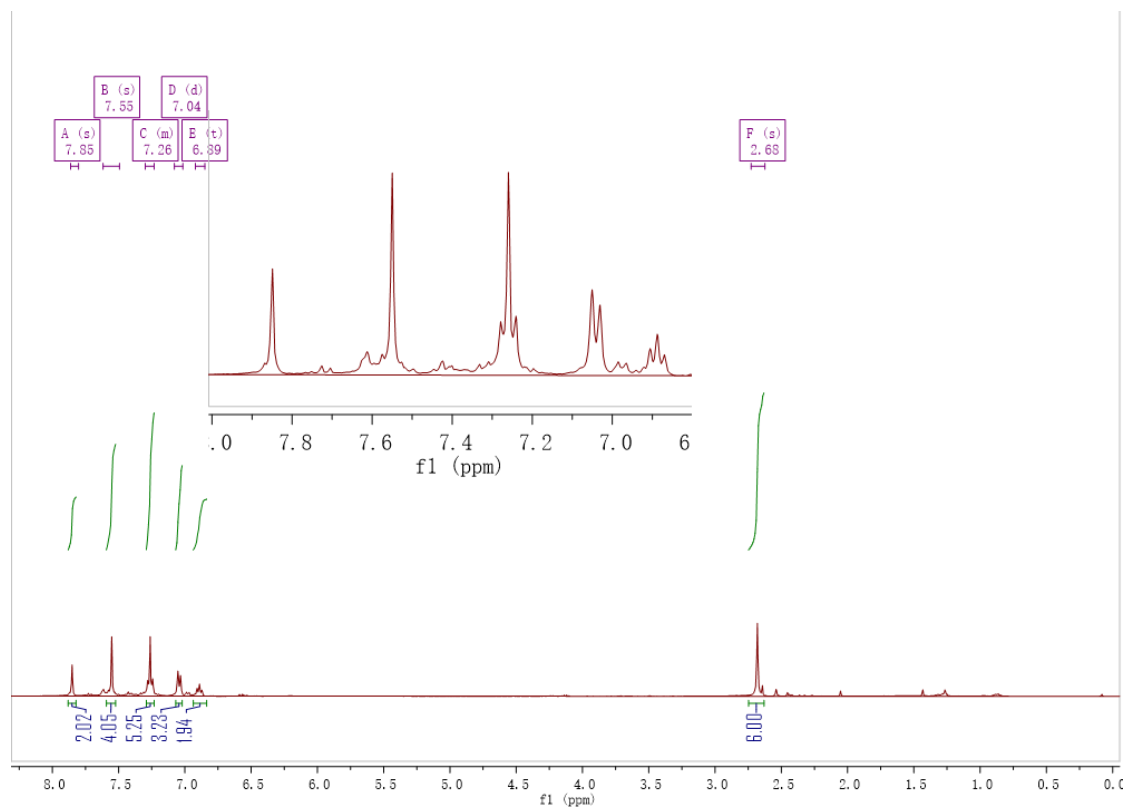
Compound **5b** (CDCl₃):



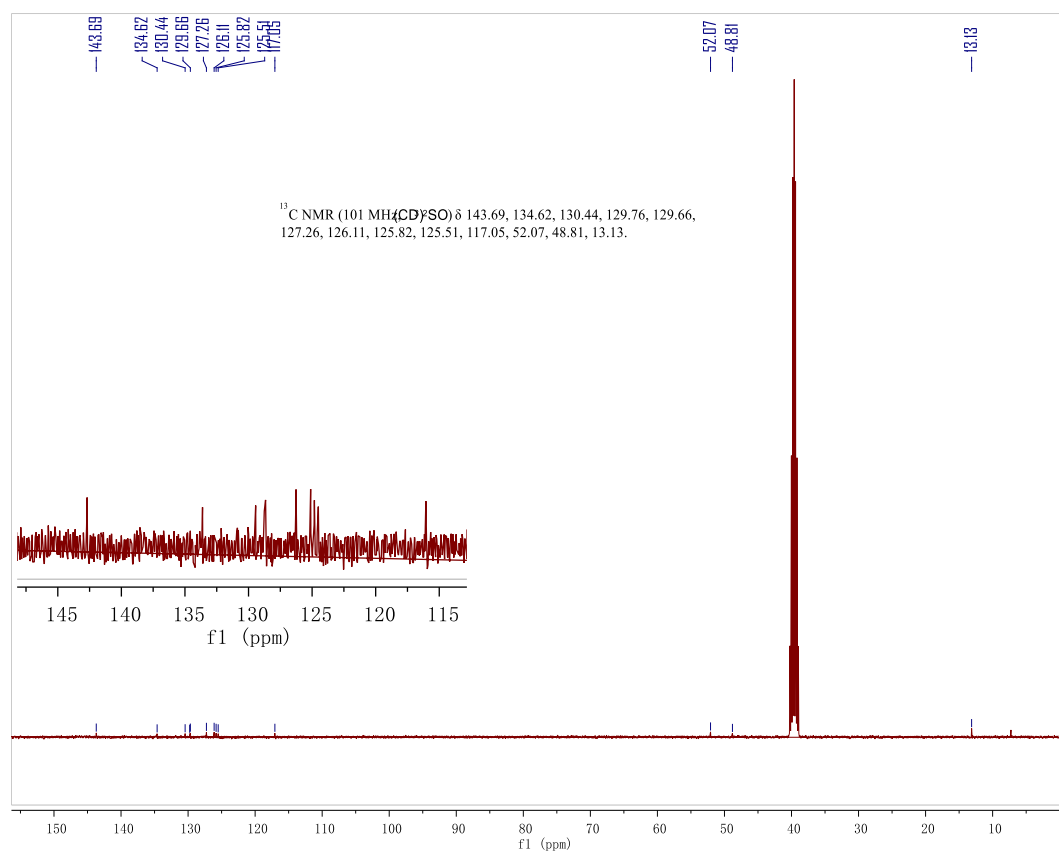
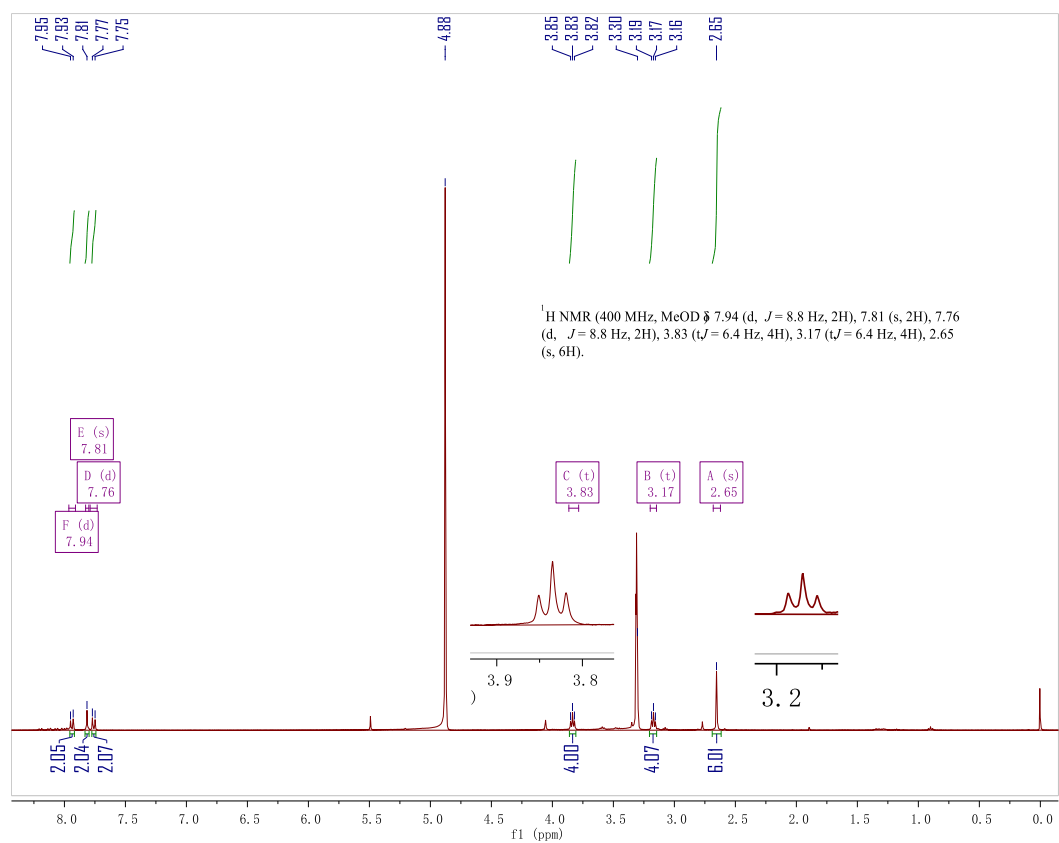
Compound **5c** (CDCl₃):



Compound **5d** (CDCl₃):



Compound **5e** (^1H NMR : CD_3OD ; ^{13}C NMR : DMSO-d_6):



2,5-dimethylcorannulene (CDCl₃):

