

Supporting information

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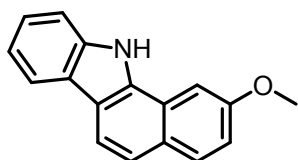
GENERAL METHODS FOR SYNTHESIS

All reactions were carried out under argon. Dichloromethane was distilled from P_2O_5 , THF and toluene were distilled over Na/benzophenone. Dichloromethane and toluene were kept over activated 3Å molecular sieves. 1,2-Dichloroethane was dried over activated 3Å molecular sieves. All commercial reagents were used without further purification. 1H and ^{13}C NMR spectra were recorded at room temperature on Bruker Avance-300 MHz NMR spectrometer. 1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz. Chloroform residual peak was taken as internal reference at 7.26 ppm for 1H NMR and 77 ppm for ^{13}C NMR. Acetone residual peak was taken as internal reference at 2.09 ppm for 1H NMR and 205.87 ppm for ^{13}C NMR. DMSO residual peak was taken as internal reference at 2.54 ppm for 1H NMR and 40.45 ppm for ^{13}C NMR. High-resolution mass spectra were obtained by using Waters Xevo Q-ToF using positive mode. Infrared spectra were recorded from Nicolet 6700 FT-IR spectrometer.

SYNTHESIS

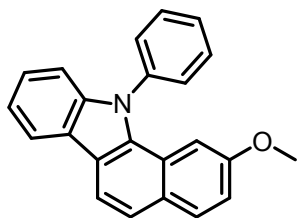
Compound 1 (2-methoxy-11H-benzo[a]carbazole)

Compound 1 was prepared in two steps from 7-methoxy-1-tetralone according to a published procedure.¹



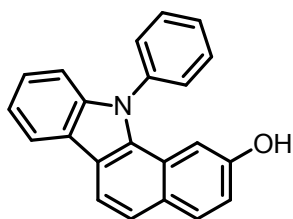
¹H NMR (300 MHz, Acetone) δ 11.23 (s, 0.5H), 8.22 – 8.16 (m, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.97 (t, J = 6.2 Hz, 2H), 7.65 (dd, J = 8.1, 7.2 Hz, 2H), 7.44 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.28 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 7.22 (dd, J = 8.9, 2.6 Hz, 1H), 4.03 (s, 3H). ¹³C NMR (75 MHz, Acetone) δ 158.38, 139.69, 135.67, 130.72, 128.08, 125.08, 124.52, 123.07, 120.19, 119.93, 119.75, 118.92, 117.43, 117.20, 111.66, 111.60, 101.43, 55.39.

Compound 2 (2-methoxy-11-phenyl-11H-benzo[a]carbazole)



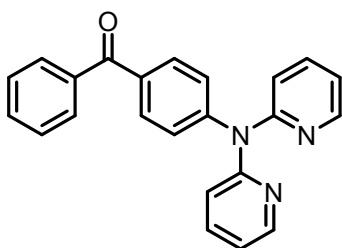
2-methoxy-11H-benzo[a]carbazole (0.2g, 0.8mmol), iodobenzene (0.198g, 0.97mmol), K₃PO₄ (0.36g, 1.70mmol) and toluene (3mL) were added to a monocol flask. The resulting mixture was degassed for 30 min then racemic cyclohexane-1,2-diamine (40 μ L, 0.35mmol) and CuI (18.5mg, 0.097mmol) were added. After 24 hours of heating at 110°C under argon, the reaction mixture was cooled to ambient temperature, diluted with dichloromethane and filtered through a plug of silica gel. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (Petroleum ether/CH₂Cl₂: 50/50) to provide the desired product (0.210 g, 80%). M.p.: 130-131 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.21 (dd, J = 6.9, 1.4 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.74 – 7.55 (m, 6H), 7.44 – 7.33 (m, 2H), 7.25 – 7.19 (m, 1H), 7.09 (dd, J = 8.9, 2.5 Hz, 1H), 6.79 (d, J = 2.5 Hz, 1H), 3.42 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 156.72, 142.01, 140.07, 134.89, 130.44, 129.90, 129.60, 128.70, 128.43, 124.98, 123.38, 122.61, 120.88, 120.13, 119.86, 119.63, 116.83, 116.63, 110.20, 101.65, 54.44; HRMS (ESI): m/z calcd for C₂₃H₁₈NO+H⁺: 324.1388 [M +H⁺]; found: 324.1401.

Compound 3 (11-phenyl-11H-benzo[a]carbazol-2-ol)



2-methoxy-11-phenyl-11H-benzo[*a*]carbazole (2.1g, 6.49mmol) and CH₂Cl₂ (60mL) were added to a monocol flask. Then, BBr₃ (19.48mL, 1M in hexane) was added at room temperature. After 2 hours of stirring under argon, the reaction mixture was cooled down by an icy bath then quenched carefully with water. The aqueous phase was extracted twice with CH₂Cl₂ then the combined organic phase was washed twice with water. After drying over MgSO₄, filtered and concentrated under vacuum, the crude product was purified by column chromatography on silica gel (100% CH₂Cl₂) to provide the desired product (1.91 g, 95%). M.p.: 159.5-160.5 °C; ¹H NMR (300 MHz, DMSO) δ 9.61 (s, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.85 – 7.71 (m, 3H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.48 – 7.28 (m, 2H), 7.16 – 7.02 (m, 2H), 6.68 (d, *J* = 2.1 Hz, 1H); ¹³C NMR (75 MHz, DMSO) δ 154.67, 141.57, 139.18, 133.88, 130.53, 130.28, 129.01, 128.62, 127.30, 125.12, 122.89, 122.87, 121.17, 120.17, 119.73, 119.09, 116.75, 115.78, 110.06, 104.88; HRMS (ESI): *m/z* calcd for C₂₂H₁₅NO+H⁺: 310.1232 [*M*+H⁺]; found: 310.1238.

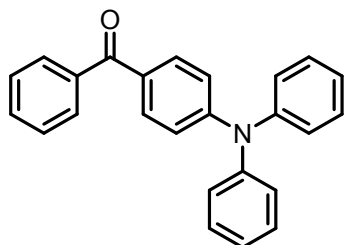
Compound 4 (4-(dipyridin-2-ylamino)benzophenone)



2,2'-dipyridylamine (1.57g, 9.19mmol) and 4-bromobenzophenone (2g, 7.65mmol) were dissolved in 50 mL of dichloromethane in a monocol flask. Then, K₂CO₃ (2.11g, 15.26mmol) dissolved in water (20mL) and CuSO₄ (0.132g, 8.27mmol) in water (10mL) were added. After drying under vacuum, the reaction mixture was heated at 225°C for 8h under argon. The reaction mixture was cooled to ambient temperature, diluted with dichloromethane and the resulting mixture was washed with water, dried over MgSO₄ and concentrated. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/ Et₂O, 80 / 20) to provide the desired product (2.20g, 82%). M.p. 111.5-112.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.38 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 2H), 7.86 – 7.77 (m, 4H), 7.67 – 7.52 (m, 3H), 7.50 – 7.42 (m, 2H), 7.24 – 7.17 (m, 2H), 7.09 – 6.98 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 195.41, 157.54, 148.96, 148.86,

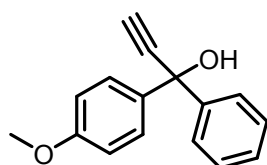
137.99, 137.84, 133.12, 132.04, 131.73, 129.77, 128.17, 124.60, 119.29, 118.03; HRMS (ESI): m/z calcd for $C_{23}H_{17}N_3O+H^+$: 352.1450 [$M+H^+$]; found: 352.1440.

Compound 5 (4-(diphenylamino)benzophenone)



Diphenylamine (1.62g, 9.57mmol) and 4-bromobenzophenone (2g, 7.65mmol) were dissolved in 50 mL of dichloromethane in a monocol flask. Then, K_2CO_3 (2.11g, 15.26mmol) dissolved in water (20mL) and $CuSO_4$ (0.132g, 8.27mmol) in water (10mL) were added. Then, the reaction mixture was heated at 225°C for 24h under argon. The reaction mixture was cooled to ambient temperature, diluted with dichloromethane and the resulting mixture was washed with water, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 / Et_2O , 50 / 50) to provide the desired product (0.90g, 33%). 1H NMR (300 MHz, $CDCl_3$) δ 7.74 (m, 4H), 7.55 (m, 1H), 7.46 (m, 2H), 7.33 (m, 4H), 7.16 (m, 6H), 7.05 – 6.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.20, 151.90, 146.47, 138.44, 131.95, 131.67, 129.62, 129.59, 129.50, 128.10, 125.96, 124.61, 119.50.

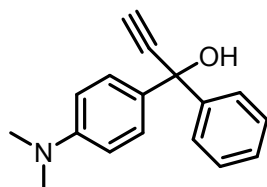
Compound 6 (1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol)



Ethynyltrimethylsilane (2.77g, 28mmol) and THF (45mL) were added to a three-necked flask. The resulting mixture was cooled at -20°C. Then, *n*-BuLi (15.90mL, 1.6M in Hexane) was added dropwise. After 1hour of stirring between -10°C and 0°C, 4-methoxy-benzophenone (3g, 14.1mmol) was added in powder. The reaction was stirred for 30 min. Then the reaction was quenched with a saturated ammonium sulphate aqueous solution and diluted with diethyl ether (200mL). The organic phase was washed three times with water, dried over $MgSO_4$ and concentrated under vacuum. Then, the resulting product was dissolved in methanol and K_2CO_3 (11.72g, 84.8mmol) was added. After 1h of stirring, water and diethyl ether was added. The organic phase was washed three times with water, dried over $MgSO_4$ and concentrated under vacuum to provide the desired compound (3.22g, 96%) that was used without further purification. Viscous oil; 1H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.56 – 7.47 (m, 2H),

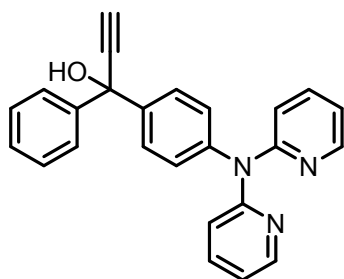
7.39 – 7.26 (m, 3H), 6.91 – 6.81 (m, 2H), 3.79 (s, 3H), 2.87 (s, 1H), 2.83 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.15, 144.55, 136.69, 128.24, 127.75, 127.35, 125.90, 113.56, 86.53, 73.92, 55.26; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2 + \text{H}^+$: 239.1072 [$M + \text{H}^+$]; found: 239.1095

Compound 7 (1-(4-(dimethylamino)phenyl)-1-phenylprop-2-yn-1-ol)



Ethynyltrimethylsilane (2.61g, 26.6mmol) and THF (45mL) were added to a three-necked flask. The resulting mixture was cooled at -20°C . Then, *n*-BuLi (16.64mL, 1.6M in Hexane) was added dropwise. After 1hour of stirring between -10°C and 0°C , 4-(dimethylamino)-benzophenone (3g, 13.3mmol) was added in powder. The reaction was stirred for 30 min. Then the reaction was quenched with a saturated ammonium sulphate aqueous solution and diluted with diethylether (200mL). The organic phase was washed three times with water, dried over MgSO_4 and concentrated under vacuum. Then, the resulting product was dissolved in methanol and K_2CO_3 (11.03mmol, 79.8mmol) was added. After 1hour of stirring, water and diethyl ether were added. The organic phase was washed three times with water, dried over MgSO_4 and concentrated under vacuum to provide the desired compound (3.18g, 95%) that was used without further purification. M.p. $121\text{--}123^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.67 – 7.56 (m, 2H), 7.48 – 7.39 (m, 2H), 7.39 – 7.23 (m, 3H), 6.72 – 6.64 (m, 2H), 2.94 (s, 6H), 2.85 (s, 1H), 2.78 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.11, 144.82, 132.30, 128.12, 127.51, 127.01, 125.95, 112.00, 86.89, 74.88, 74.02, 40.48.

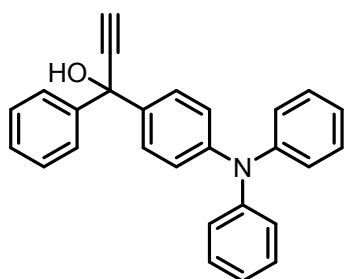
Compound 8 (1-(4-(dipyridin-2-ylamino)phenyl)-1-phenylprop-2-yn-1-ol)



Ethynyltrimethylsilane (1.5g, 15. mmol) and THF (30mL) were added to a three-necked flask. The resulting mixture was cooled at -20°C . Then, *n*-BuLi (9.56mL, 1.6M in Hexane) was added dropwise. After 1hour of stirring between -10°C and 0°C , the lithium acetylide was transferred via cannula to another flask pre-cooled at 0°C containing **compound 4** (1.8g, 5.12mmol) and THF (20mL). The reaction was stirred for 30 min. Then the reaction was quenched with a

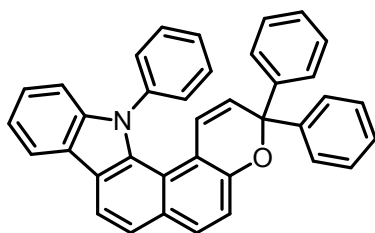
saturated ammonium sulphate aqueous solution and diluted with diethylether. The organic phase was washed three times with water, dried over MgSO_4 and concentrated under vacuum. Then, the resulting product was dissolved in methanol/THF (50/50) and K_2CO_3 (4.24g, 30.72mmol) was added. After 1 hour of stirring, water and diethyl ether were added. The organic phase was washed three times with water, dried over MgSO_4 and concentrated under vacuum to provide the desired compound in quantitative yield that was used without further purification. M.p. 182.-182.5 °C; ^1H NMR (300 MHz, Acetone) δ 8.27 – 8.18 (m, 2H), 7.74 (ddd, $J = 4.4, 3.5, 1.9$ Hz, 2H), 7.71 – 7.61 (m, 4H), 7.42 – 7.35 (m, 2H), 7.34 – 7.26 (m, 1H), 7.16 – 7.11 (m, 2H), 7.04 – 6.98 (m, 4H), 3.43 (s, 1H); ^{13}C NMR (75 MHz, Acetone) δ 158.65, 148.60, 146.40, 144.92, 143.34, 137.86, 128.53, 127.79, 127.52, 127.25, 126.42, 118.64, 117.37, 75.92; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{20}\text{N}_3\text{O}+\text{H}^+$: 378.1606 [$M+\text{H}^+$]; found: 378.1608

Compound 9 (1-(4-(diphenylamino)phenyl)-1-phenylprop-2-yn-1-ol)



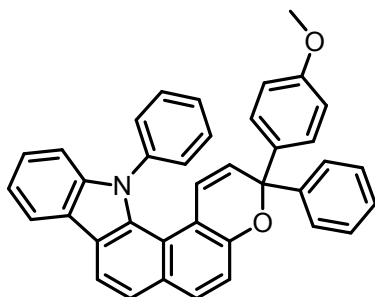
Ethynyltrimethylsilane (0.42g, 4.30mmol) and THF (10mL) were added to a three-necked flask under argon. The resulting mixture was cooled at -20°C . Then, $n\text{-BuLi}$ (2.65mL, 1.6M in Hexane) was added dropwise. After 1hour of stirring between -10°C and 0°C , the lithium acetylide was transferred via cannula to another flask pre-cooled at 0°C containing **compound 5** (0.75g, 2.15mmol) and THF (20mL). The reaction was stirred for 1hour. Then the reaction was quenched with a saturated ammonium sulfate aqueous solution and diluted with diethylether. The organic phase was washed three times with water, dried over MgSO_4 and concentrated under vacuum. Then, the resulting product was dissolved in methanol/THF (50/50) and K_2CO_3 (1.78g, 12.9mmol) was added. After 1hour of stirring, water and diethyl ether were added. The organic phase was washed three times with water, dried over MgSO_4 and concentrated under vacuum to provide the desired compound in quantitative yield that was used without further purification.

CN-Ph-H (3,13-dihydro-3,3,13-triphenyl-benzopyrano[5,6-a]carbazole)



Compound 3 (0.2g, 0.65mmol), 1,1-diphenylprop-2-yn-1-ol (0.148g, 0.71mmol) and 1,2-dichloroethane (15mL) were added to a monocol flask. Then, trimethyl orthoformate (0.274g, 2.58mmol) and PPTS (16mg, 0.065mmol) were added. The resulting mixture was heated at 80°C for 2hours, then left to return to room temperature diluted with dichloromethane and filtered through a plug of silica gel. After concentration of the filtrate under vacuum, the crude product was purified by column chromatography on silica gel (petroleum ether /CH₂Cl₂ :80 / 20) to provide the desired product (0.15g, 33%). M.p. 196.2-197.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.17 – 8.12 (m, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.42 – 7.27 (m, 5H), 7.26 – 7.08 (m, 12H), 7.04 (d, *J* = 9.9 Hz, 1H), 5.49 (d, *J* = 9.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 151.35, 144.90, 143.91, 142.35, 136.01, 131.34, 129.80, 129.62, 127.85, 127.25, 127.16, 126.52, 125.98, 125.62, 124.99, 124.49, 124.46, 123.33, 121.76, 121.41, 120.38, 119.75, 116.91, 116.61, 113.45, 111.78, 81.40; HRMS (ESI): *m/z* calcd for C₃₇H₂₆NO+H⁺: 500.2014 [*M*+H⁺]; found: 500.2025.

CN-Ph-OMe (3,13-dihydro 3-(4-methoxyphenyl)-3,13-diphenyl-benzopyrano[5,6-a]carbazole)

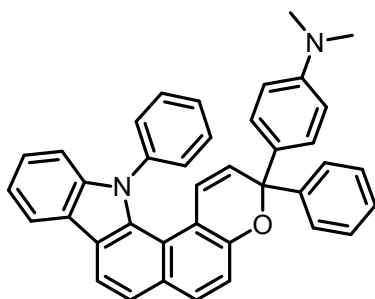


Compound 3 (0.2g, 0.65mmol), **compound 6** (0.308g, 1.29mmol) and 1,2-dichloroethane (15mL) were added to a monocol flask. Then, trimethyl orthoformate (0.274g, 2.58mmol) and PPTS (16mg, 0.065mmol) were also added. The resulting mixture was heated at 80°C for 2 hours, then left to return to room temperature, diluted with dichloromethane and filtered through a plug of silica gel. After concentration of the filtrate under vacuum, the crude product was purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂ : 80/20) to provide the desired product (167mg, 52%). M.p. 144-146 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.18

– 8.11 (m, 1H), 8.04 (d, $J = 8.3$ Hz, 1H), 7.87 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.58 (d, $J = 7.2$ Hz, 1H), 7.43 – 7.16 (m, 13H), 7.15 – 7.08 (m, 4H), 7.03 (d, $J = 9.8$ Hz, 1H), 6.80 (d, $J = 8.8$ Hz, 2H), 5.46 (d, $J = 9.9$ Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.86, 151.43, 145.21, 144.01, 142.47, 137.21, 136.11, 131.39, 129.86, 129.70, 128.76, 127.89, 127.21, 127.10, 126.57, 126.08, 125.69, 125.09, 124.54, 124.43, 123.43, 122.03, 121.49, 120.47, 119.83, 117.01, 116.65, 113.52, 113.24, 111.88, 81.31, 55.32; HRMS (ESI): m/z calcd for $\text{C}_{38}\text{H}_{27}\text{NO}_2 + \text{H}^+$: 530.2120 [$M + \text{H}^+$]; found: 530.2155.

CN-Ph-N(Me)₂

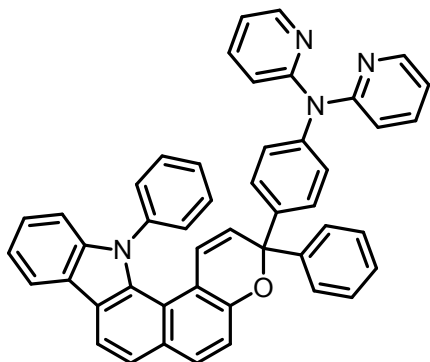
(4-(3,13-diphenyl-3,13-dihydrochromeno[5,6-a]carbazol-3-yl)-N,N-dimethylaniline)



Compound 3 (0.2g, 0.65mmol), **compound 7** (0.324g, 1.29mmol) and 1,2-dichloroethane (15mL) were added to a monocol flask. Then, trimethyl orthoformate (0.274g, 2.58mmol) and PPTS (16mg, 0.065mmol) were added. The resulting mixture was heated at 80°C for 2 hours, then left to return to room temperature diluted with dichloromethane and filtered through a plug of silica gel. After concentration of the filtrate under vacuum, the crude product was purified by column chromatography on silica gel (CH_2Cl_2) to provide the desired product (70mg, 20%). M.p. 195-196 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.19 – 8.12 (m, 1H), 8.03 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.60 (dd, $J = 6.9, 1.7$ Hz, 1H), 7.45 – 7.26 (m, 6H), 7.26 – 7.12 (m, 7H), 7.06 (d, $J = 8.9$ Hz, 2H), 7.00 (d, $J = 9.9$ Hz, 1H), 6.65 (d, $J = 8.3$ Hz, 2H), 5.47 (d, $J = 9.9$ Hz, 1H), 2.94 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.55, 145.30, 143.82, 142.31, 136.00, 131.14, 129.69, 129.55, 128.44, 127.68, 127.01, 126.90, 126.46, 125.94, 125.52, 125.00, 124.31, 124.08, 123.30, 122.17, 121.33, 120.38, 119.71, 117.00, 116.42, 113.42, 111.75, 81.44, 40.60; HRMS (ESI): m/z calcd for $\text{C}_{39}\text{H}_{30}\text{N}_2\text{O} + \text{H}^+$: 543.2436 [$M + \text{H}^+$]; found: 543.2421.

CN-Ph-N(Py)₂

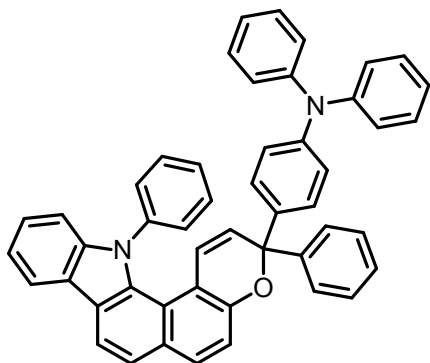
(N-(4-(3,13-diphenyl-3,13-dihydrochromeno[5,6-a]carbazol-3-yl)phenyl)-N-(pyridin-2-yl)pyridin-2-amine



Compound 3 (0.2g, 0.65mmol), **compound 8** (0.487g, 1.29mmol) and 1,2-dichloroethane (15mL) were added to a monocol flask. Then, trimethyl orthoformate (0.274g, 2.58mmol) and PPTS (30mg, 0.122mmol) were added. The resulting mixture was heated at 80°C for 2 hours, then left to return to room temperature diluted with dichloromethane and filtered through a plug of silica gel. After concentration of the filtrate under vacuum, the crude product was purified by column chromatography on silica gel (CH₂Cl₂/MeOH: 95/5) to provide the desired product (194mg, 45%). M.p. 184-186 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.30 (d, *J* = 4.4 Hz, 2H), 8.15 – 8.08 (m, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 16.5, 7.9 Hz, 3H), 7.33 (dt, *J* = 12.6, 6.4 Hz, 3H), 7.24 – 7.14 (m, 7H), 7.06 (t, *J* = 9.5 Hz, 4H), 6.98 (d, *J* = 9.9 Hz, 1H), 6.91 (dd, *J* = 12.5, 7.6 Hz, 4H), 5.47 (d, *J* = 9.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 157.85, 151.28, 148.34, 144.56, 143.81, 143.72, 142.23, 142.10, 137.70, 135.92, 131.35, 129.76, 129.68, 128.54, 127.84, 127.27, 127.13, 126.56, 126.08, 125.92, 125.61, 124.94, 124.44, 123.29, 121.60, 121.38, 120.33, 119.73, 118.30, 117.11, 116.86, 116.63, 113.37, 111.74, 81.19; HRMS (ESI): *m/z* calcd for C₄₇H₃₂N₄O+H⁺: 669.2654[*M*+H⁺]; found: 669.2676.

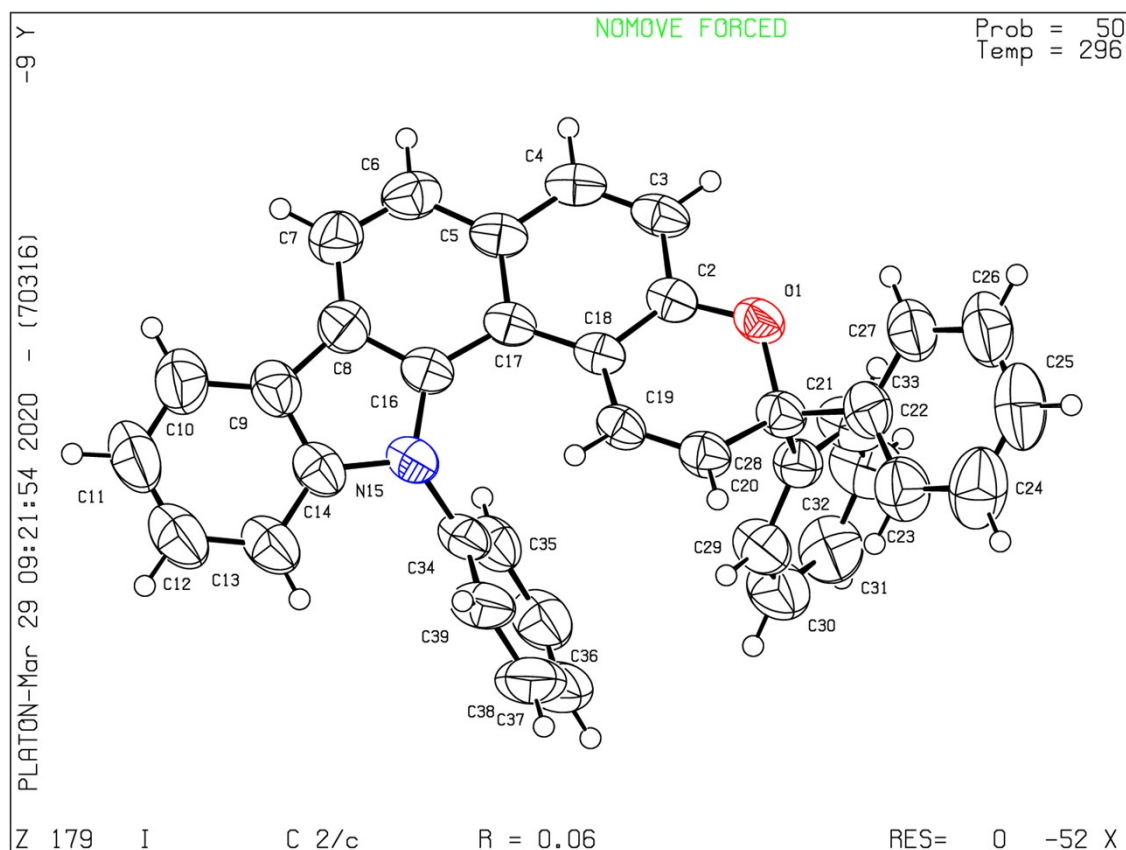
CN-Ph-N(Ph)₂

(4-(3,13-diphenyl-3,13-dihydrochromeno[5,6-a]carbazol-3-yl)-N,N-diphenylaniline)



Compound 3 (0.1g, 0.32mmol), **compound 9** (0.242g, 0.46mmol) and 1,2-dichloroethane (15mL) were added to a monocol flask. Then, trimethyl orthoformate (0.274g, 2.58mmol) and PPTS (15mg, 0.065mmol) were added. The resulting mixture was heated at 80°C for 2 hours, then left to return to room temperature diluted with dichloromethane and filtered through a plug of silica gel. After concentration of the filtrate under vacuum, the crude product was purified by column chromatography on silica gel (CH₂Cl₂) to provide the desired product (160mg, 74%). M.p. 185-187 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.17 – 8.12 (m, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.58 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.42 – 7.27 (m, 5H), 7.25 – 6.91 (m, 23H), 5.47 (d, *J* = 9.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 151.39, 147.60, 146.88, 144.84, 143.89, 142.34, 138.88, 136.00, 131.28, 129.77, 129.60, 129.19, 128.17, 127.79, 127.14, 127.06, 126.51, 125.99, 125.61, 124.99, 124.43, 124.32, 123.33, 122.91, 122.60, 121.91, 121.40, 120.39, 119.74, 116.95, 116.59, 113.45, 111.77, 81.27; HRMS (ESI): *m/z* calcd for C₄₉H₃₄N₂O+H⁺: 667.2754[*M*+H⁺]; found: 667.2756.

X-RAY STRUCTURE OF CN-Ph-H (CCDC = 1998515)



Crystal data for CN-Ph-H : $C_{37}H_{25}NO$, $M_w = 499.58$, monoclinic, space group $C2/c$; dimensions: $a = 31.8763(12)$ Å, $b = 6.7502(2)$ Å, $c = 27.2595(10)$ Å, $\beta = 114.087(2)^\circ$, $V = 5354.7(3)$ Å³; $Z = 8$; $\mu = 0.07$ mm⁻¹; 185603 reflections measured at room temperature; independent reflections: 4721 [4329 $F_o > 4\sigma(F_o)$]; data were collected up to a $2\theta_{max}$ value of 50.1° (99.6 % coverage). Number of variables: 352; $R_1 = 0.057$, $wR_2 = 0.135$, $S = 1.17$; highest residual electron density 0.14 e.Å⁻³; CCDC = 1998515.

THEORETICAL CALCULATIONS

The computations were performed using the computer facilities at the Research Institute for Information Technology, Kyushu University. Molecular orbital calculations were performed using the program Gaussian 16.

The geometries were optimized at the CAM-B3LYP/6-31G(d,p) level and M06-2X/6-31G(d,p). The presence of energy minima for the geometry optimization was confirmed by the absence of imaginary modes (no imaginary frequencies). To numerically achieve accurate values, we have used tightened convergence thresholds for the self-consistent field (10^{-10} a.u.) and geometry optimization (10^{-5} a.u.) and a fine grid. The solvation effect in a solvent of toluene was considered by using the polarizable continuum model (PCM).

The time-dependent density functional theory (TD-DFT) calculations were conducted at the B3LYP/6-31G(d,p) level using the optimized structures at the CAM-B3LYP/6-31G(d,p).

Table S1. Gibbs free energies [kcal mol⁻¹] calculated at the CAM-B3LYP/6-31G(d,p) level

	RN	CN-Ph-H	
CF	-651263.94	-974957.75	
TC	-651255.54	-974951.01	
TT	-651254.39	-974949.47	
	CN-Ph-N(pyridyl) ₂ -A ^a	CN-Ph-N(pyridyl) ₂ -B ^a	
CF1	-1319534.71	-1319534.93	
CF2	-1319535.83	-1319535.00	
TTC	-1319528.39	-1319528.76	
CTC	-1319527.88	-1319528.28	
TTT	-1319527.10	-1319526.87	
CTT	-1319526.70	-1319527.50	
	CN-Ph-N(phenyl) ₂	CN-Ph-OMe	CN-Ph-N(methyl) ₂
CF1	-1299385.76	-1046777.23	-1058939.92
CF2	-1299385.31	-1046777.23	-1058940.05
TTC	-1299379.35	-1046770.73	-1058934.39
CTC	-1299378.82	-1046770.05	-1058934.55
TTT	-1299377.58	-1046768.97	-1058932.97
CTT	-1299377.68	-1046769.23	-1058932.75

^aDifferent conformation for the 2-pyridyl moiety.

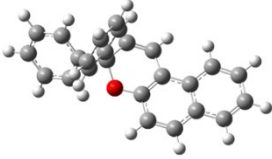
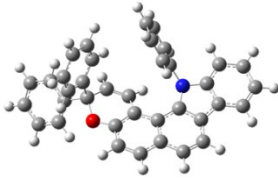
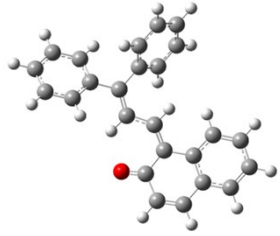
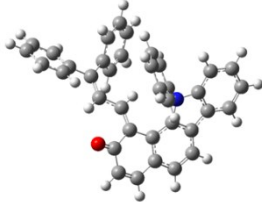
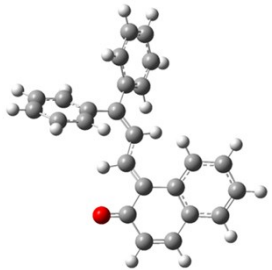
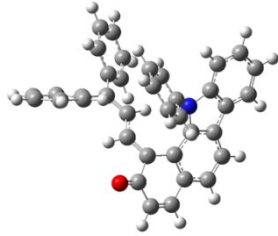
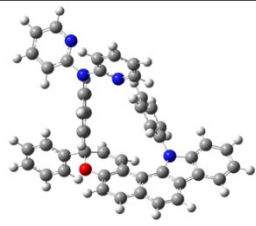
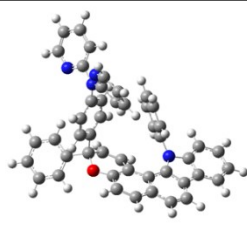
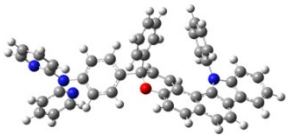
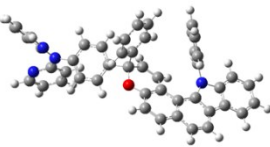
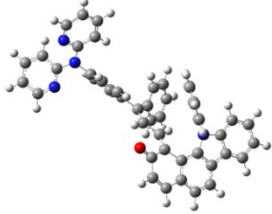
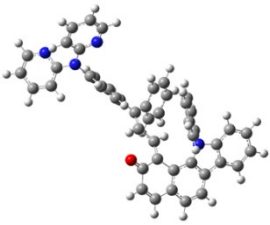
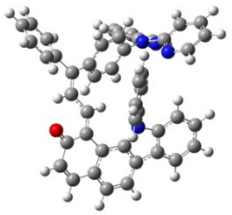
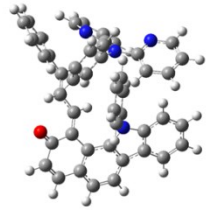
Table S2. Gibbs free energies [kcal mol⁻¹] calculated at the M06-2X/6-31G(d,p) level

	RN	CN-Ph-H	
CF	-651361.60	-975112.99	
TC	-651350.20	-975103.32	
TT	-651349.40	-975102.37	
	CN-Ph-N(pyridyl) ₂ -A ^a	CN-Ph-N(pyridyl) ₂ -B ^a	
CF1	-1319738.93	-1319736.56	
CF2	-1319738.05	-1319737.53	
TTC	-1319727.64	-1319727.81	
CTC	-1319729.60	-1319728.70	
TTT	-1319727.26	-1319727.14	
CTT	-1319726.62	-1319727.49	
	CN-Ph-N(phenyl) ₂	CN-Ph-OMe	CN-Ph-N(methyl) ₂
CF1	-1299592.44	-1046932.31	-1059101.39
CF2	-1299593.05	-1046932.28	-1059101.08
TTC	-1299583.38	-1046922.90	-1059093.15
CTC	-1299583.28	-1046923.15	-1059094.11
TTT	-1299582.45	-1046922.37	-1059092.15
CTT	-1299582.52	-1046922.13	-1059092.34

^aDifferent conformation for the 2-pyridyl moiety.

Table S3. Dipole moment [debye] calculated at the CAM-B3LYP/6-31G(d,p) level

	RN		CN-Ph-H	
CF	0.88		2.01	
TC	3.85		3.55	
TT	4.13		3.73	
	CN-Ph-N(pyridyl) ₂	CN-Ph-N(phenyl) ₂	CN-Ph-OMe	CN-Ph-N(methyl) ₂
CF1	2.72–3.82	2.17	2.37	4.30
CF2	2.49–3.26	2.00	0.82	3.14
TTC	1.63–5.44	3.53	4.63	4.90
CTC	4.08–5.78	3.96	5.12	6.87
TTT	4.41–5.14	4.75	5.11	7.30
CTT	2.06–5.06	3.35	4.17	3.80

	RN	CN-Ph-H
CF		
TC		
TT		
	CN-Ph-N(pyridyl) ₂ -A ^a	CN-Ph-N(pyridyl) ₂ -B ^a
CF1		
CF2		
TTC		
CTC		

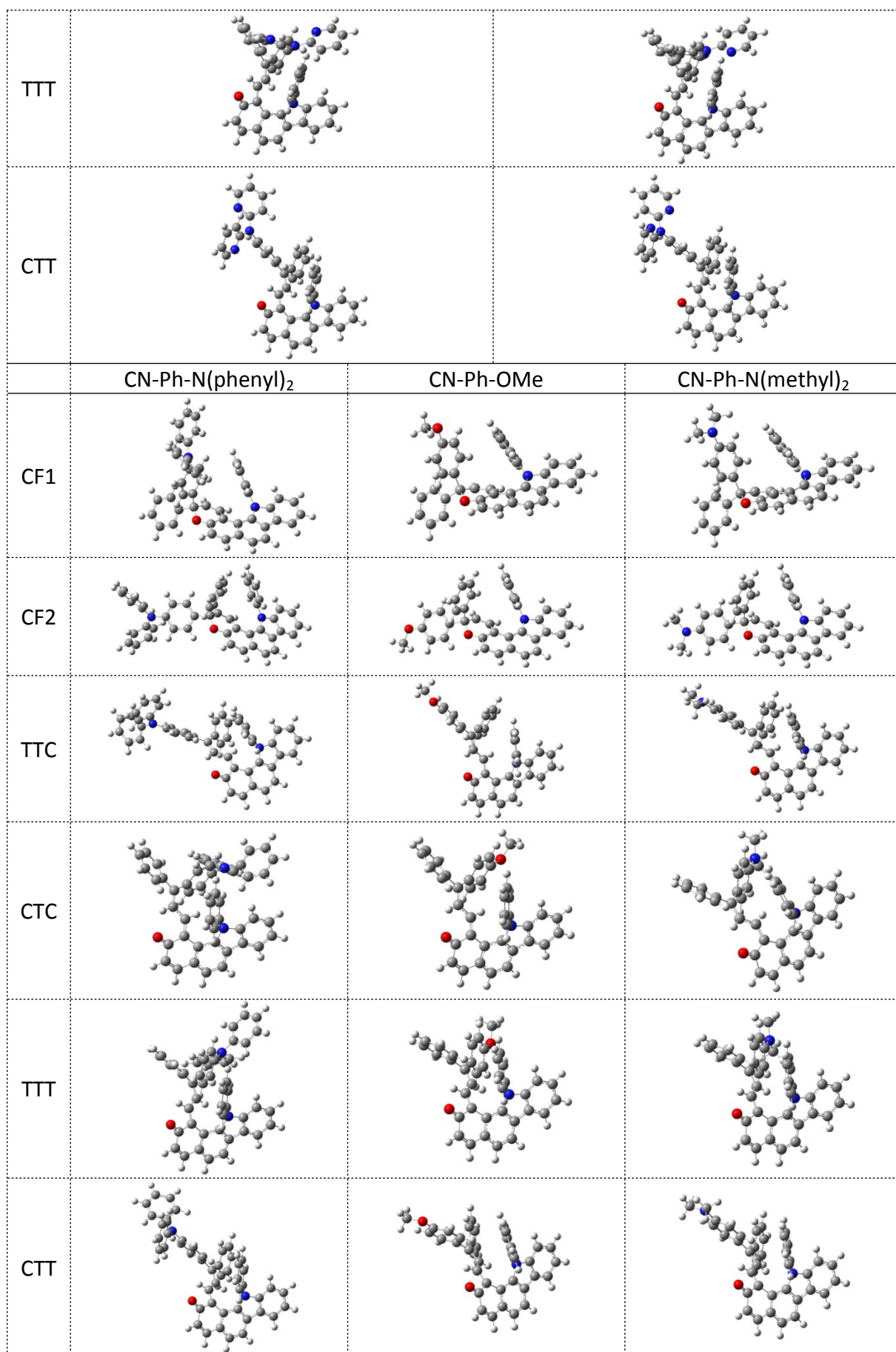


Figure S1. Optimized geometry at the CAM-B3LYP/6-31G(d,p)

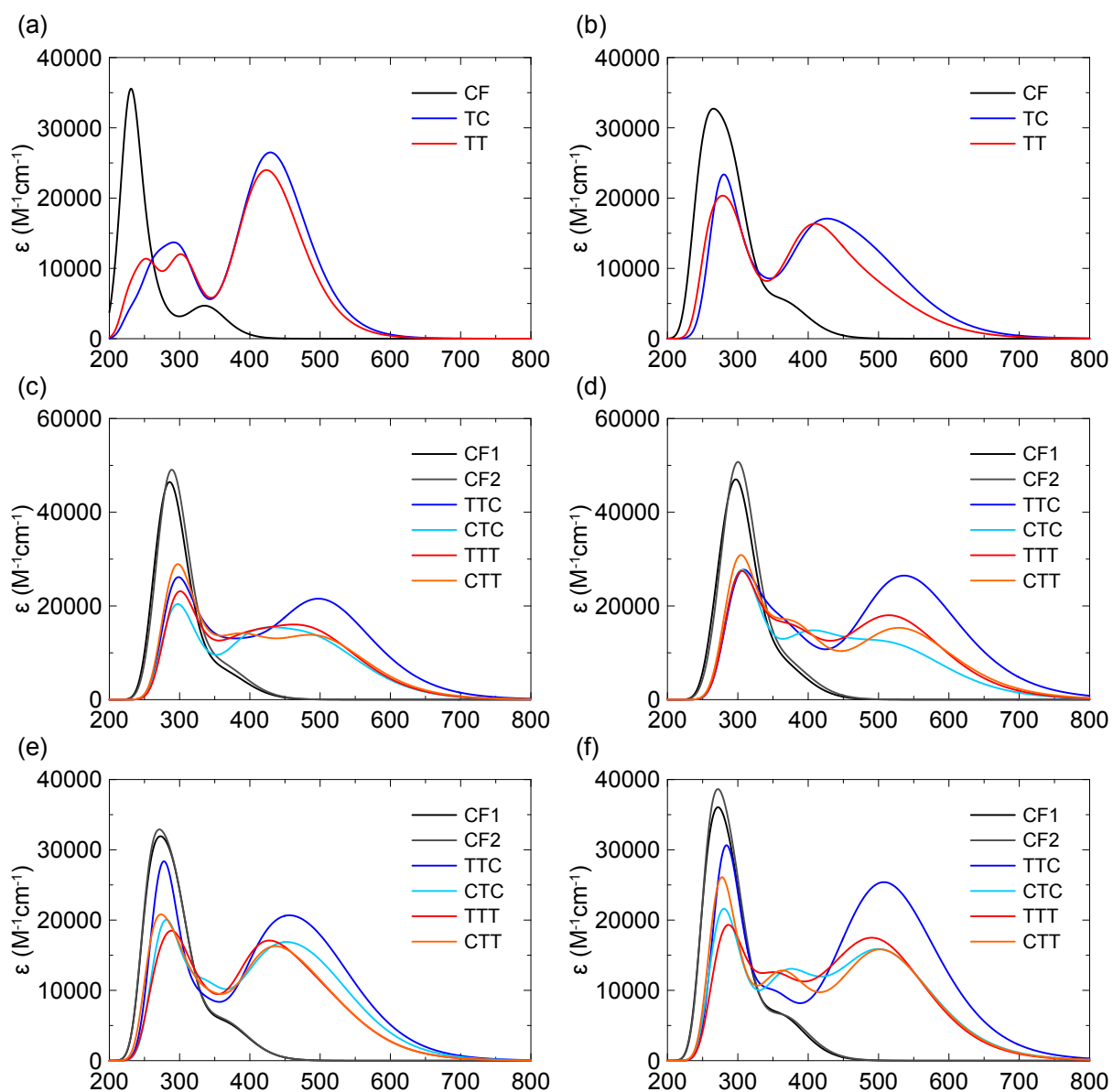


Figure S2. Calculated absorption spectra at the B3LYP/6-31G(d,p) level for (a) RN, (b) CN-Ph-H, (c) CN-Ph-N(pyridyl)₂, (d) CN-Ph-N(phenyl)₂, (e) CN-Ph-OMe, and (f) CN-Ph-N(methyl)₂.

Table S4. Calculated vertical excitation energies (VEE), wavelength, and oscillator strength (f) of the singlet excited states for RN at the B3LYP/6-31G(d,p) level

S_n	CF			TC			TT		
	VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]
1	3.6650	338.15	0.1109	2.6358	470.38	0.0264	2.7314	453.93	0.0953
2	4.2550	291.39	0.0368	2.8610	433.36	0.5802	2.9396	421.78	0.4969
3	4.5171	274.48	0.0092	3.2309	383.75	0.1229	3.3315	372.16	0.0576
4	4.6146	268.68	0.0285	3.8421	322.70	0.0045	3.8691	320.45	0.0110
5	4.6463	266.85	0.0041	3.9012	317.81	0.0076	3.9922	310.57	0.0217
6	4.6692	265.53	0.0068	3.9678	312.48	0.0395	4.0368	307.14	0.0634
7	4.8952	253.28	0.0990	4.0925	302.96	0.0196	4.0905	303.10	0.1471
8	4.9205	251.97	0.0426	4.1202	300.92	0.2058	4.1445	299.15	0.0393
9	4.9611	249.91	0.0072	4.4257	280.14	0.0085	4.4828	276.58	0.0084
10	4.9829	248.82	0.0389	4.5341	273.45	0.1109	4.6139	268.72	0.0294
11	5.0401	246.00	0.0018	4.5656	271.56	0.0222	4.6171	268.53	0.0164
12	5.0843	243.86	0.0051	4.7659	260.15	0.0856	4.7298	262.13	0.0577
13	5.3345	232.42	0.6198	4.8664	254.77	0.0480	4.8189	257.29	0.0407
14	5.4045	229.41	0.0062	4.9186	252.07	0.0056	4.9421	250.88	0.0530
15	5.4836	226.10	0.0016	4.9877	248.58	0.0039	5.0122	247.37	0.0752
16	5.5637	222.84	0.1990	5.1179	242.26	0.0228	5.1544	240.54	0.0200
17	5.6090	221.04	0.0084	5.2397	236.62	0.0053	5.2392	236.65	0.0115
18	5.6892	217.93	0.0021	5.3233	232.91	0.0144	5.2970	234.06	0.0022
19	5.7518	215.56	0.0286	5.3755	230.65	0.0266	5.3758	230.64	0.0131
20	5.7956	213.93	0.0090	5.3920	229.94	0.0052	5.4107	229.15	0.0109
21	5.8832	210.74	0.0772	5.4455	227.68	0.0017	5.4438	227.75	0.0151
22	5.9197	209.44	0.0087	5.4640	226.91	0.0007	5.4776	226.35	0.0520
23	5.9657	207.83	0.0115	5.4884	225.90	0.0147	5.4981	225.51	0.0248
24	5.9871	207.09	0.0032	5.5090	225.06	0.0095	5.5402	223.79	0.0069

Table S5. Calculated vertical excitation energies (VEE), wavelength, and oscillator strength (f) of the singlet excited states for CN-Ph-H at the B3LYP/6-31G(d,p) level

S_n	CF			TC			TT		
	VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]
1	3.3652	368.43	0.1150	2.4545	505.14	0.1928	2.4731	501.33	0.1312
2	3.7589	329.84	0.0224	2.7813	445.77	0.1171	2.8542	434.40	0.0930
3	3.9572	313.31	0.0241	2.8450	435.80	0.0589	3.0039	412.74	0.0430
4	4.0779	304.04	0.0748	3.0983	400.17	0.2541	3.0988	400.11	0.2608
5	4.1209	300.87	0.0753	3.6950	335.54	0.1224	3.6018	344.23	0.0933
6	4.2703	290.34	0.3286	3.9108	317.03	0.0049	3.9267	315.75	0.0071
7	4.4349	279.56	0.0017	3.9302	315.47	0.0145	3.9780	311.67	0.0045
8	4.4653	277.66	0.0141	3.9444	314.33	0.0079	4.0563	305.66	0.0207
9	4.5357	273.35	0.1344	4.0233	308.16	0.0081	4.0731	304.40	0.0128
10	4.5887	270.19	0.0027	4.0558	305.70	0.0202	4.1062	301.94	0.1115
11	4.6185	268.45	0.1146	4.1566	298.28	0.0331	4.1748	296.99	0.0068
12	4.6749	265.21	0.0379	4.1992	295.26	0.0137	4.1864	296.16	0.0067
13	4.7571	260.63	0.0015	4.2145	294.18	0.0449	4.1965	295.45	0.0224
14	4.7858	259.07	0.0467	4.2260	293.39	0.0236	4.2645	290.74	0.0059
15	4.8278	256.81	0.1549	4.2836	289.44	0.0018	4.3121	287.52	0.1497
16	4.8465	255.82	0.0510	4.3524	284.86	0.0386	4.3539	284.77	0.0172
17	4.8521	255.53	0.0010	4.3747	283.41	0.0391	4.4131	280.94	0.0159
18	4.9034	252.85	0.1173	4.3962	282.02	0.0342	4.4920	276.01	0.0599
19	4.9094	252.55	0.0179	4.4595	278.02	0.1475	4.4940	275.89	0.0151
20	4.9629	249.82	0.0192	4.5279	273.82	0.1842	4.5514	272.41	0.0199
21	5.0035	247.80	0.0026	4.6923	264.23	0.0388	4.7216	262.59	0.0605
22	5.0366	246.17	0.0222	4.7699	259.93	0.0200	4.7422	261.45	0.0415
23	5.0750	244.3	0.0076	4.7923	258.72	0.0120	4.8112	257.70	0.1796
24	5.1784	239.43	0.2021	4.8129	257.61	0.0046	4.8410	256.11	0.0118

Table S6. Calculated vertical excitation energies (VEE), wavelength, and oscillator strength (f) of the singlet excited states for CN-Ph-N(pyridyl)₂ at the B3LYP/6-31G(d,p) level

S_n	CF1-A			TTC-A			TTT-A		
	VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]
1	3.3074	374.87	0.1158	2.3954	517.60	0.4164	2.4426	507.59	0.2455
2	3.7102	334.17	0.0151	2.6501	467.85	0.1377	2.7132	456.97	0.1110
3	3.8435	322.58	0.0190	2.8257	438.77	0.0121	2.8967	428.01	0.0785
4	3.8864	319.02	0.0146	2.8441	435.94	0.0579	3.0119	411.64	0.0447
5	3.9478	314.06	0.0059	3.1983	387.66	0.1909	3.2069	386.62	0.1773
6	4.0128	308.97	0.0775	3.6206	342.44	0.1930	3.5428	349.96	0.1015
7	4.0218	308.28	0.0981	3.8636	320.90	0.0265	3.8745	320.00	0.1229
8	4.0424	306.71	0.0290	3.9309	315.41	0.0412	3.8914	318.61	0.0113
9	4.1649	297.69	0.0188	3.9349	315.09	0.0051	3.9140	316.77	0.0063
10	4.2049	294.86	0.1662	3.9530	313.65	0.0020	3.9887	310.84	0.0016
11	4.2605	291.01	0.1014	4.0200	308.42	0.0605	4.0741	304.32	0.0081
12	4.2620	290.90	0.1839	4.0409	306.82	0.0208	4.0873	303.34	0.0419
13	4.3244	286.71	0.0256	4.0476	306.32	0.0067	4.0990	302.47	0.0501
14	4.3497	285.04	0.1797	4.1057	301.98	0.0315	4.1019	302.26	0.0221
15	4.3583	284.48	0.0469	4.1308	300.15	0.1014	4.1557	298.35	0.1158
16	4.4069	281.34	0.0294	4.1475	298.94	0.0010	4.1701	297.31	0.0591
17	4.5058	275.17	0.0238	4.1778	296.77	0.1189	4.2077	294.66	0.0343
18	4.5370	273.27	0.0703	4.1874	296.09	0.0254	4.2473	291.92	0.0136
19	4.5478	272.63	0.0568	4.2010	295.13	0.0071	4.2705	290.33	0.0094
20	4.5877	270.25	0.0128	4.2636	290.80	0.0021	4.3015	288.24	0.0489
21	4.6305	267.76	0.0704	4.2719	290.23	0.0362	4.3088	287.74	0.0495
22	4.6470	266.81	0.0467	4.2868	289.22	0.0083	4.3333	286.12	0.0150
23	4.6833	264.74	0.0014	4.3207	286.95	0.0153	4.3643	284.08	0.0082
24	4.7049	263.52	0.0159	4.3331	286.13	0.1352	4.3833	282.86	0.0228
S_n	CF1-B			TTC-B			TTT-B		
VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]
1	3.3627	368.70	0.1132	2.3917	518.39	0.3962	2.4224	511.82	0.2331
2	3.6968	335.38	0.0366	2.6511	467.67	0.1345	2.7221	455.47	0.1346
3	3.7646	329.34	0.0125	2.8146	440.50	0.0189	2.8677	432.34	0.0935
4	3.9493	313.94	0.0196	2.8361	437.16	0.0516	2.9886	414.86	0.0334
5	4.0304	307.62	0.0694	3.1792	389.99	0.2036	3.2263	384.29	0.1782
6	4.0388	306.98	0.0299	3.6301	341.54	0.1885	3.5322	351.02	0.1009
7	4.0915	303.03	0.0495	3.8807	319.49	0.0084	3.8636	320.90	0.0515
8	4.1202	300.92	0.0842	3.9173	316.50	0.0330	3.9005	317.87	0.0761
9	4.2489	291.80	0.2735	3.9253	315.86	0.0090	3.9518	313.74	0.0021
10	4.2859	289.29	0.1005	3.9728	312.08	0.0015	3.9717	312.17	0.0010
11	4.3128	287.48	0.1499	4.0001	309.95	0.0443	4.0451	306.51	0.0331
12	4.3212	286.92	0.1288	4.0282	307.79	0.0127	4.0582	305.51	0.0167
13	4.3346	286.03	0.0127	4.0339	307.35	0.0519	4.0755	304.22	0.0963
14	4.4515	278.52	0.0027	4.1215	300.82	0.0418	4.1134	301.41	0.0839
15	4.4609	277.93	0.0217	4.1231	300.71	0.0113	4.1332	299.97	0.0280
16	4.5362	273.32	0.0549	4.1564	298.30	0.0818	4.1858	296.20	0.0772
17	4.5456	272.76	0.1013	4.1882	296.03	0.0259	4.2075	294.67	0.0118
18	4.5587	271.97	0.0790	4.1941	295.61	0.0844	4.2305	293.07	0.0096
19	4.5877	270.25	0.0006	4.1979	295.35	0.0164	4.2412	292.33	0.0120
20	4.6030	269.35	0.0391	4.2547	291.41	0.0089	4.2775	289.85	0.0638
21	4.6224	268.22	0.0658	4.2795	289.72	0.0271	4.3042	288.06	0.0305
22	4.6402	267.20	0.0821	4.3048	288.02	0.0452	4.3334	286.12	0.0102

23	4.6651	265.77	0.0171	4.3299	286.34	0.0563	4.3766	283.29	0.0236
24	4.6958	264.03	0.0264	4.3388	285.76	0.1230	4.3835	282.84	0.0099
S_n	CF2-A			CTC-A			CTT-A		
VEE	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$
1	3.3606	368.94	0.1397	2.4056	515.39	0.2041	2.4402	508.08	0.2206
2	3.6996	335.13	0.0321	2.7051	458.33	0.0809	2.6507	467.74	0.0870
3	3.7597	329.77	0.0184	2.8132	440.72	0.1095	2.8742	431.36	0.0458
4	3.9524	313.70	0.0288	2.8389	436.74	0.0139	3.0020	413.01	0.0352
5	3.9993	310.01	0.0702	3.1530	393.22	0.2336	3.1770	390.26	0.2194
6	4.0791	303.95	0.0881	3.6287	341.68	0.0432	3.5568	348.59	0.1261
7	4.1219	300.79	0.1077	3.8177	324.76	0.0298	3.8408	322.81	0.0785
8	4.1632	297.81	0.0029	3.8250	324.14	0.0036	3.9099	317.10	0.0078
9	4.2657	290.65	0.2189	3.8711	320.28	0.0024	3.9409	314.61	0.0123
10	4.2697	290.38	0.1916	3.9306	315.43	0.0416	3.9806	311.47	0.0125
11	4.2825	289.52	0.2978	3.9749	311.92	0.0090	4.0338	307.36	0.0121
12	4.3448	285.36	0.0248	3.9772	311.74	0.0642	4.0768	304.12	0.0324
13	4.3829	282.88	0.0215	4.0375	307.09	0.0585	4.0947	302.79	0.0841
14	4.4405	279.21	0.0476	4.0579	305.53	0.0475	4.1301	300.20	0.0065
15	4.4635	277.77	0.0006	4.1025	302.22	0.0248	4.1604	298.01	0.0293
16	4.5139	274.67	0.0787	4.1142	301.36	0.0305	4.2049	294.86	0.0568
17	4.5378	273.23	0.0604	4.1453	299.1	0.1016	4.2189	293.88	0.0246
18	4.5504	272.47	0.0505	4.1626	297.86	0.0306	4.2416	292.31	0.1107
19	4.5912	270.05	0.0003	4.2500	291.72	0.0822	4.2606	291.00	0.0118
20	4.6108	268.90	0.0648	4.2762	289.94	0.0375	4.2697	290.38	0.0000
21	4.6178	268.49	0.0235	4.2857	289.30	0.0778	4.2985	288.44	0.0548
22	4.6739	265.27	0.0127	4.3071	287.86	0.0229	4.3207	286.96	0.0913
23	4.6892	264.40	0.0134	4.3333	286.12	0.0019	4.3355	285.97	0.0873
24	4.7546	260.76	0.0305	4.3610	284.30	0.0080	4.3411	285.61	0.0430
S_n	CF2-B			CTC-B			CTT-B		
VEE	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$
1	3.3586	369.15	0.1380	2.4423	507.65	0.2375	2.4216	511.99	0.2456
2	3.6903	335.97	0.0252	2.6485	468.12	0.0186	2.6214	472.97	0.0682
3	3.7592	329.81	0.0216	2.8183	439.93	0.0727	2.8684	432.24	0.0495
4	3.9472	314.11	0.0282	2.8831	430.03	0.0859	3.0067	412.36	0.0301
5	4.0032	309.72	0.0628	3.1490	393.73	0.2161	3.1718	390.89	0.2188
6	4.0741	304.32	0.0843	3.6482	339.85	0.0721	3.5478	349.47	0.1277
7	4.1243	300.62	0.1108	3.8744	320.01	0.0034	3.8266	324.00	0.0725
8	4.1666	297.57	0.0011	3.9105	317.05	0.0652	3.8831	319.29	0.0021
9	4.2567	291.27	0.2639	3.9337	315.19	0.0122	3.9492	313.95	0.0587
10	4.2731	290.15	0.1771	3.9617	312.96	0.0530	3.9819	311.37	0.0038
11	4.2842	289.40	0.2728	3.9922	310.56	0.0116	4.0342	307.33	0.0060
12	4.3599	284.38	0.0553	3.9999	309.97	0.0046	4.0575	305.57	0.0079
13	4.4023	281.64	0.0069	4.0348	307.29	0.0197	4.0926	302.95	0.0994
14	4.4551	278.30	0.0092	4.1055	301.99	0.0077	4.1247	300.59	0.0166
15	4.4716	277.27	0.0271	4.1460	299.04	0.0577	4.1388	299.57	0.0522
16	4.5098	274.92	0.0893	4.1680	297.46	0.0076	4.1561	298.32	0.0760
17	4.5382	273.20	0.1128	4.1907	295.85	0.0125	4.1963	295.46	0.0641
18	4.5672	271.46	0.0026	4.2296	293.14	0.0123	4.2133	294.27	0.0632
19	4.5878	270.25	0.0012	4.2403	292.39	0.0388	4.2593	291.09	0.0109
20	4.6118	268.84	0.0634	4.2555	291.35	0.0188	4.2891	289.07	0.0251
21	4.6195	268.39	0.0288	4.2833	289.46	0.0818	4.3095	287.70	0.1263
22	4.6745	265.23	0.0118	4.3078	287.81	0.0136	4.3253	286.65	0.0072
23	4.6897	264.37	0.0027	4.3110	287.60	0.0675	4.3418	285.56	0.0567
24	4.7428	261.42	0.0045	4.3474	285.19	0.0801	4.3603	284.35	0.0538

Table S7. Calculated vertical excitation energies (VEE), wavelength, and oscillator strength (f) of the singlet excited states for CN-Ph-N(phenyl)₂ at the B3LYP/6-31G(d,p) level

S _n	CF1			TTC			TTT		
VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]
1	3.3516	369.92	0.0268	2.2873	542.05	0.6160	2.3576	525.89	0.3949
2	3.3676	368.17	0.1287	2.5873	479.20	0.0416	2.6173	473.72	0.0424
3	3.7608	329.68	0.0199	2.8234	439.13	0.0163	2.8989	427.70	0.0763
4	3.9042	317.57	0.0187	2.8529	434.60	0.0634	3.0155	411.16	0.0481
5	3.9491	313.95	0.0186	3.2374	382.97	0.1724	3.2521	381.24	0.1675
6	3.9879	310.90	0.3169	3.5149	352.74	0.2273	3.4366	360.77	0.1449
7	4.0709	304.56	0.0442	3.7931	326.86	0.0085	3.7753	328.41	0.1064
8	4.1063	301.93	0.0632	3.9081	317.25	0.0667	3.8134	325.13	0.0214
9	4.1146	301.33	0.1228	3.9505	313.85	0.0262	3.9652	312.68	0.0023
10	4.1197	300.95	0.0951	3.9610	313.01	0.0029	3.9971	310.18	0.0221
11	4.1441	299.18	0.0961	3.9854	311.09	0.1415	4.0270	307.89	0.1239
12	4.2357	292.71	0.0993	4.0070	309.42	0.0309	4.0292	307.71	0.0452
13	4.2599	291.05	0.0413	4.0134	308.93	0.1447	4.0937	302.87	0.0053
14	4.2774	289.86	0.0893	4.0361	307.19	0.0134	4.0974	302.59	0.2335
15	4.3113	287.58	0.1169	4.0658	304.95	0.0031	4.1229	300.72	0.0138
16	4.4387	279.33	0.0179	4.1093	301.72	0.0360	4.1440	299.19	0.0104
17	4.4636	277.77	0.0182	4.1358	299.78	0.0168	4.1961	295.48	0.0447
18	4.4847	276.46	0.0341	4.1685	297.43	0.0219	4.2080	294.64	0.0324
19	4.5264	273.91	0.1228	4.1789	296.69	0.0082	4.2523	291.57	0.0153
20	4.5490	272.55	0.0016	4.2145	294.19	0.0420	4.2911	288.94	0.0056
21	4.5924	269.98	0.0031	4.2220	293.66	0.0026	4.3160	287.27	0.0106
22	4.6186	268.45	0.1099	4.2881	289.14	0.1403	4.3304	286.31	0.0108
23	4.6659	265.72	0.0156	4.3447	285.37	0.0099	4.3469	285.22	0.0484
24	4.7426	261.43	0.0053	4.3860	282.68	0.0020	4.3898	282.44	0.0090
S _n	CF2			CTC			CTT		
VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]
1	3.3042	375.24	0.1261	2.3087	537.02	0.2109	2.3121	536.25	0.3499
2	3.3981	364.87	0.0438	2.5301	490.04	0.0561	2.5550	485.25	0.0248
3	3.7575	329.97	0.0334	2.8064	441.79	0.0749	2.8843	429.86	0.0493
4	3.8934	318.44	0.0083	2.8678	432.33	0.0809	3.0132	411.46	0.0354
5	3.9380	314.84	0.1017	3.1694	391.20	0.2367	3.2068	386.63	0.2081
6	4.0238	308.13	0.4689	3.5600	348.27	0.0503	3.4400	360.41	0.1629
7	4.0616	305.26	0.0313	3.8186	324.69	0.1114	3.7267	332.69	0.0505
8	4.1035	302.14	0.0413	3.8534	321.75	0.0148	3.8399	322.89	0.0126
9	4.1131	301.44	0.2242	3.9316	315.35	0.0989	3.9578	313.27	0.0553
10	4.1348	299.86	0.0127	3.9507	313.83	0.0339	4.0020	309.80	0.1726
11	4.1798	296.63	0.0305	3.9662	312.60	0.0697	4.0288	307.74	0.0365
12	4.2598	291.06	0.2061	3.9786	311.63	0.0030	4.0505	306.09	0.0498
13	4.2835	289.45	0.0595	4.0369	307.13	0.0096	4.0833	303.64	0.1116
14	4.3318	286.22	0.0069	4.0773	304.08	0.0429	4.0913	303.04	0.0232
15	4.3588	284.45	0.0553	4.0891	303.21	0.0049	4.1115	301.55	0.0465
16	4.4260	280.12	0.0393	4.1373	299.68	0.1869	4.1269	300.43	0.0731
17	4.4311	279.81	0.0384	4.1569	298.26	0.0010	4.1567	298.28	0.0253
18	4.4803	276.73	0.0395	4.1936	295.65	0.0176	4.1994	295.25	0.0242

19	4.5009	275.47	0.0087	4.2213	293.71	0.0296	4.2162	294.07	0.0039
20	4.5791	270.76	0.0056	4.2339	292.84	0.0716	4.2764	289.92	0.0305
21	4.5855	270.38	0.0080	4.2649	290.71	0.0041	4.2874	289.18	0.0033
22	4.6079	269.07	0.0570	4.2798	289.70	0.0058	4.3351	286.00	0.1036
23	4.6375	267.35	0.0269	4.3197	287.02	0.0468	4.3492	285.07	0.0072
24	4.7034	263.61	0.0193	4.3320	286.20	0.0270	4.3555	284.66	0.0169

Table S8. Calculated vertical excitation energies (VEE), wavelength, and oscillator strength (f) of the singlet excited states for CN-Ph-OMe at the B3LYP/6-31G(d,p) level

S_n	CF1			TTC			TTT		
VEE	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$
1	3.3650	368.45	0.1155	2.4462	506.85	0.2879	2.4769	500.56	0.1856
2	3.7605	329.70	0.0234	2.7680	447.92	0.1647	2.8541	434.41	0.1323
3	3.9602	313.08	0.0237	2.8661	432.59	0.0690	3.0180	410.82	0.2123
4	4.0793	303.94	0.0074	3.0155	411.15	0.1847	3.0314	409.01	0.0335
5	4.0901	303.13	0.0820	3.6554	339.18	0.1173	3.5809	346.24	0.0996
6	4.1505	298.72	0.1677	3.6972	335.34	0.0509	3.7859	327.49	0.0828
7	4.2986	288.43	0.2360	3.9719	312.15	0.0045	4.0159	308.73	0.0093
8	4.4036	281.55	0.0008	4.0025	309.77	0.0076	4.0250	308.04	0.0034
9	4.5245	274.03	0.1667	4.0506	306.09	0.0077	4.0897	303.16	0.0265
10	4.5952	269.81	0.0050	4.0837	303.61	0.0051	4.1167	301.17	0.0610
11	4.6204	268.34	0.0857	4.1195	300.97	0.0137	4.1215	300.82	0.0324
12	4.6724	265.36	0.0477	4.1754	296.94	0.0259	4.1741	297.03	0.0113
13	4.7626	260.33	0.0047	4.2054	294.82	0.0153	4.2130	294.29	0.0520
14	4.7770	259.54	0.0025	4.2216	293.69	0.0035	4.2526	291.55	0.0635
15	4.8052	258.02	0.0191	4.2333	292.88	0.0246	4.2673	290.55	0.0343
16	4.8135	257.57	0.2110	4.2856	289.31	0.0306	4.3331	286.13	0.0065
17	4.8309	256.65	0.0729	4.2938	288.75	0.0207	4.3870	282.62	0.0188
18	4.8884	253.63	0.0004	4.3437	285.43	0.0510	4.3953	282.08	0.0274
19	4.9199	252.01	0.0279	4.4268	280.08	0.1580	4.4505	278.59	0.0460
20	4.9316	251.41	0.0267	4.5176	274.45	0.3036	4.5633	271.70	0.0484
21	4.9427	250.84	0.0267	4.6342	267.54	0.0140	4.6648	265.78	0.0199
22	4.9502	250.46	0.0249	4.6764	265.13	0.0568	4.7058	263.47	0.0727
23	5.0038	247.78	0.0001	4.7204	262.66	0.0083	4.7210	262.62	0.0468
24	5.0142	247.27	0.0040	4.7699	259.93	0.0602	4.7375	261.71	0.0156
S_n	CF2			CTC			CTT		
VEE	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$	[eV]	[nm]	$f[-]$
1	3.3669	368.25	0.1199	2.4539	505.26	0.2333	2.4713	501.69	0.1754
2	3.7614	329.62	0.0227	2.7725	447.20	0.1218	2.8364	437.11	0.1617
3	3.9519	313.73	0.0236	2.8592	433.63	0.0628	2.9894	414.74	0.1589
4	4.0644	305.05	0.1171	3.0301	409.17	0.1641	3.0195	410.62	0.0277
5	4.0840	303.59	0.0071	3.5764	346.68	0.0858	3.5787	346.45	0.0843
6	4.1617	297.92	0.0385	3.6788	337.02	0.1323	3.6201	342.48	0.0910
7	4.2713	290.28	0.3506	3.9557	313.44	0.0206	4.0129	308.96	0.0134
8	4.4472	278.79	0.0115	3.9855	311.09	0.0042	4.0418	306.76	0.0203
9	4.4627	277.82	0.0202	3.9946	310.38	0.0129	4.0903	303.12	0.0568
10	4.5799	270.71	0.0441	4.0841	303.58	0.0057	4.1160	301.22	0.0448
11	4.5978	269.66	0.0287	4.1226	300.74	0.0389	4.1233	300.69	0.0217
12	4.6737	265.28	0.3059	4.1979	295.35	0.0098	4.1664	297.58	0.0160
13	4.7547	260.76	0.0006	4.2121	294.36	0.0032	4.1901	295.90	0.0142
14	4.7755	259.63	0.0140	4.2298	293.12	0.0403	4.2666	290.59	0.0251
15	4.8110	257.71	0.0149	4.2580	291.18	0.0008	4.2850	289.34	0.0904
16	4.8236	257.04	0.1089	4.3144	287.38	0.0242	4.3379	285.82	0.0123

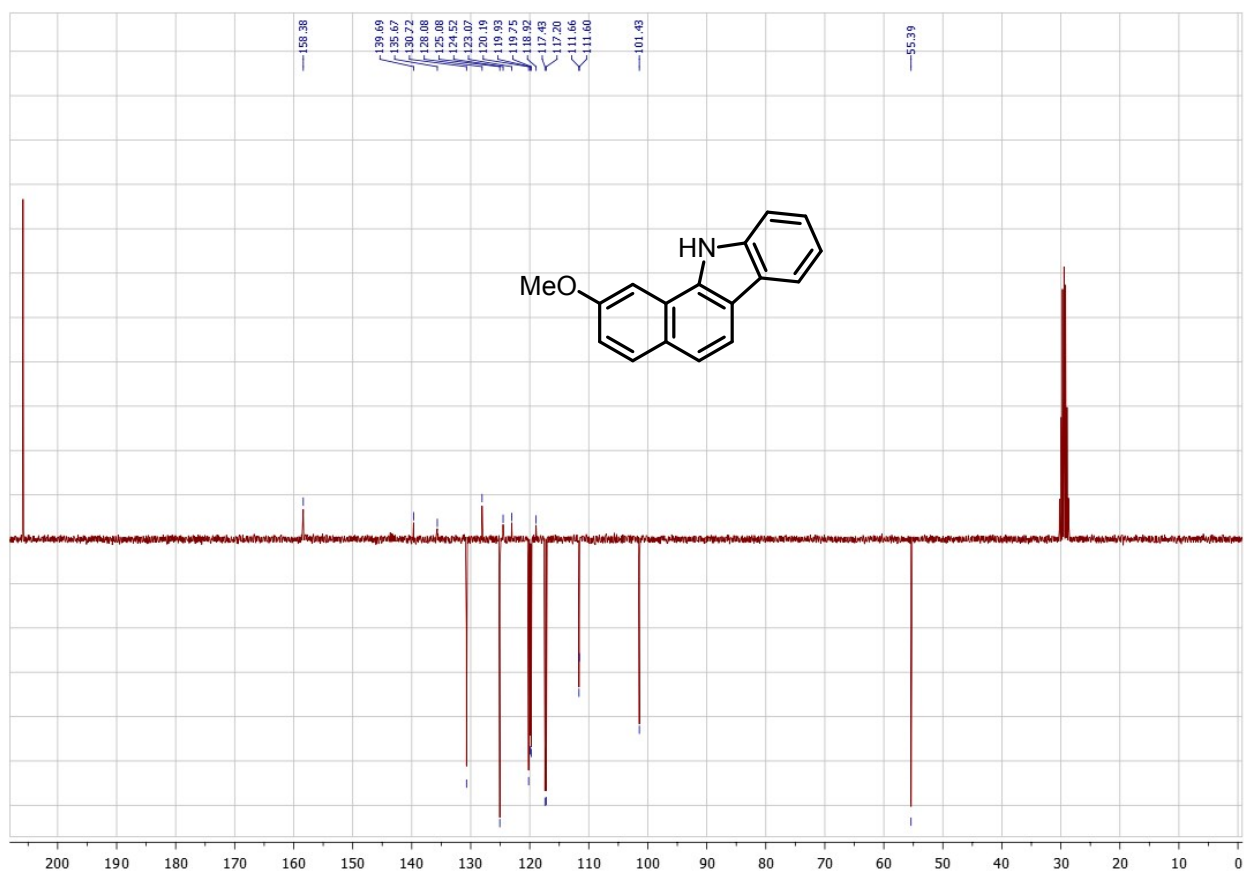
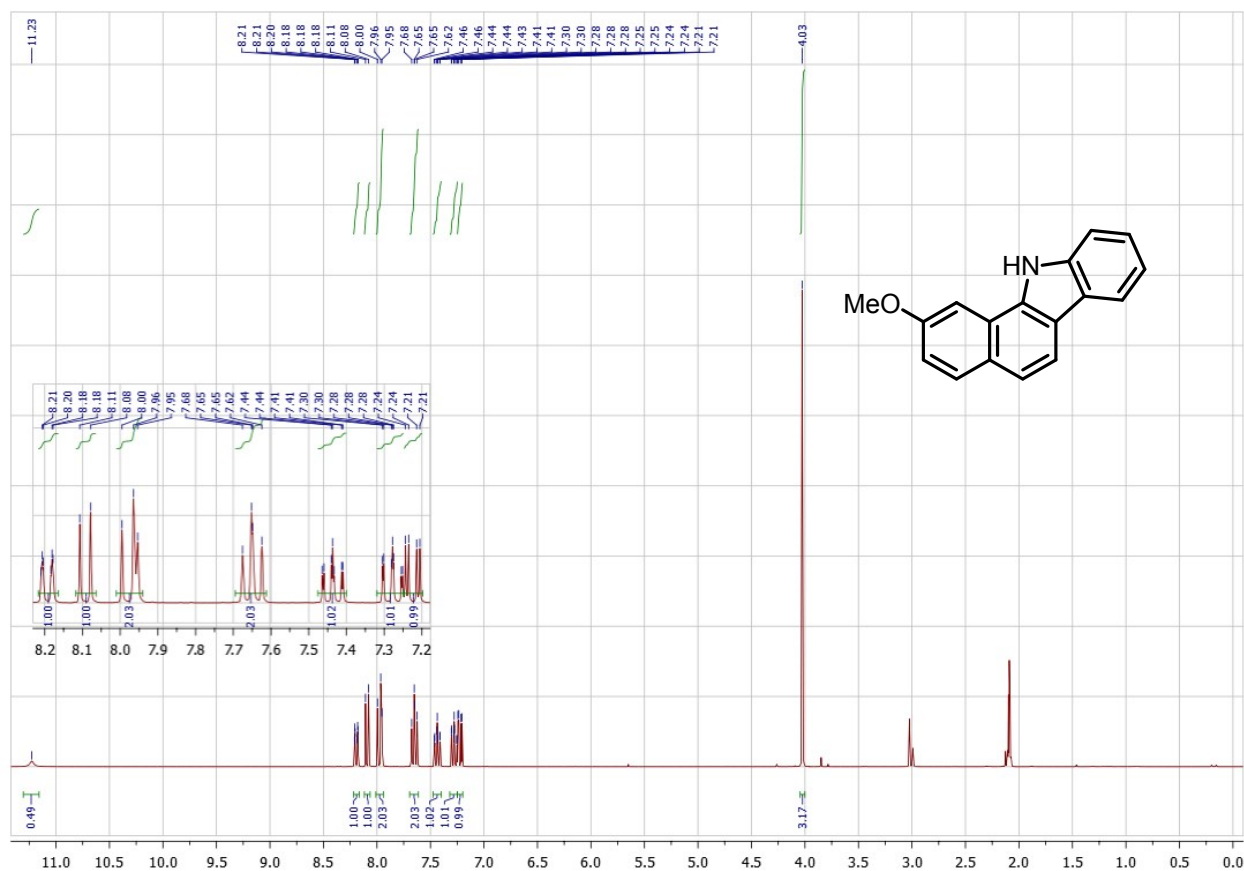
17	4.8470	255.79	0.0545	4.3563	284.61	0.0929	4.3885	282.52	0.0071
18	4.8916	253.46	0.0122	4.3711	283.65	0.0899	4.4077	281.29	0.0169
19	4.9066	252.69	0.0322	4.4820	276.63	0.0367	4.4824	276.60	0.0414
20	4.9429	250.83	0.0393	4.5682	271.41	0.1482	4.6283	267.88	0.1018
21	4.9604	249.95	0.0132	4.6753	265.19	0.0355	4.6800	264.93	0.0038
22	4.9673	249.60	0.0114	4.7113	263.16	0.0141	4.7201	262.67	0.0525
23	5.0208	246.94	0.0170	4.7546	260.77	0.0067	4.7270	262.29	0.0952
24	5.0268	246.65	0.0047	4.7949	258.57	0.0218	4.7646	260.22	0.1208

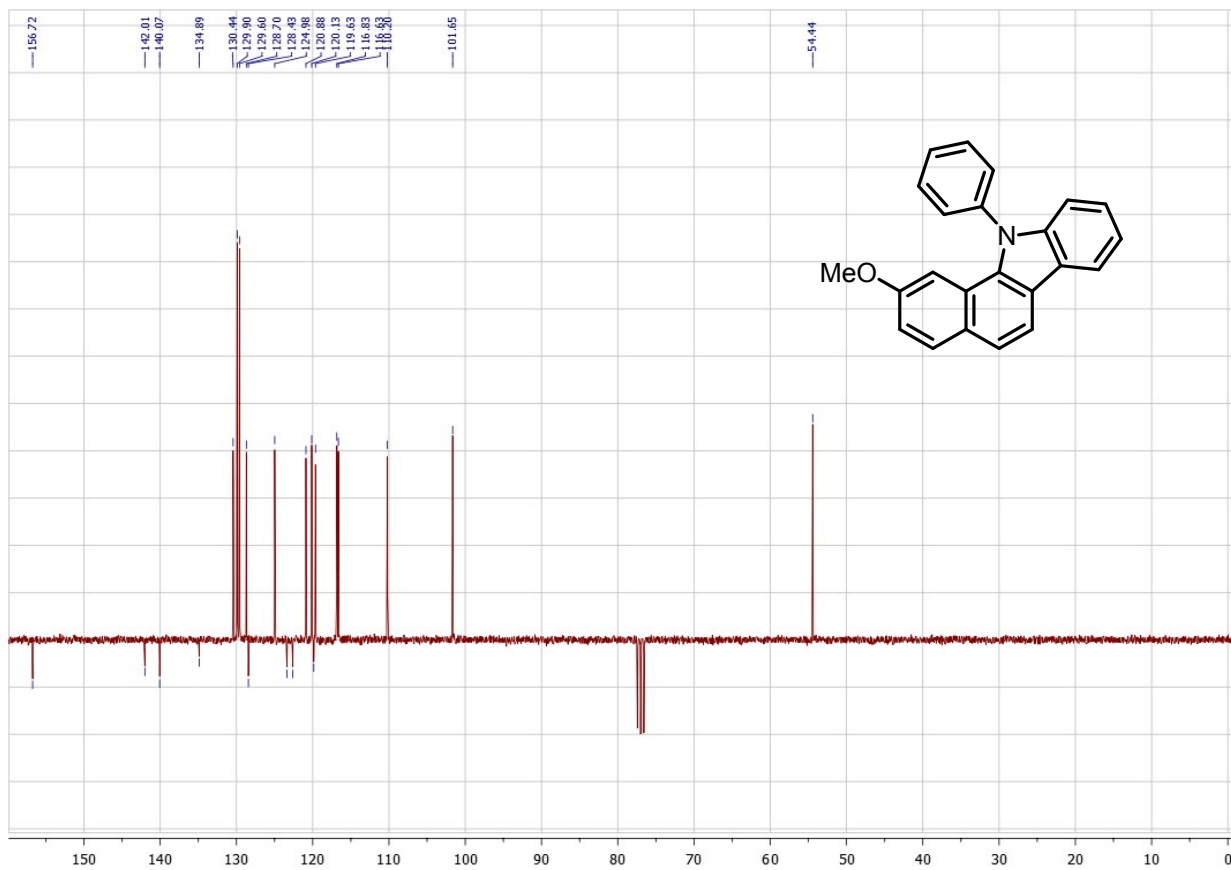
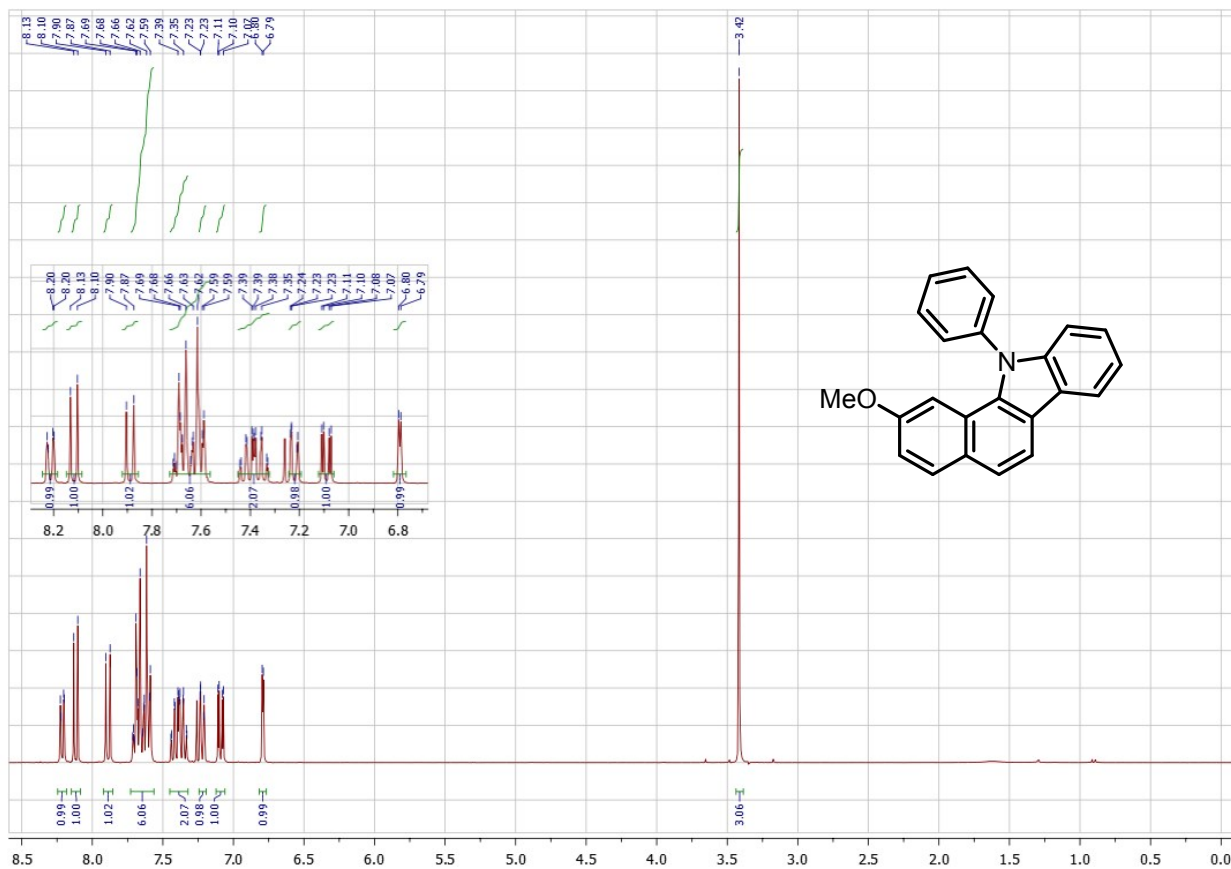
Table S9. Calculated vertical excitation energies (VEE), wavelength, and oscillator strength (f) of the singlet excited states for CN-Ph- N(methyl)₂ at the B3LYP/6-31G(d,p) level

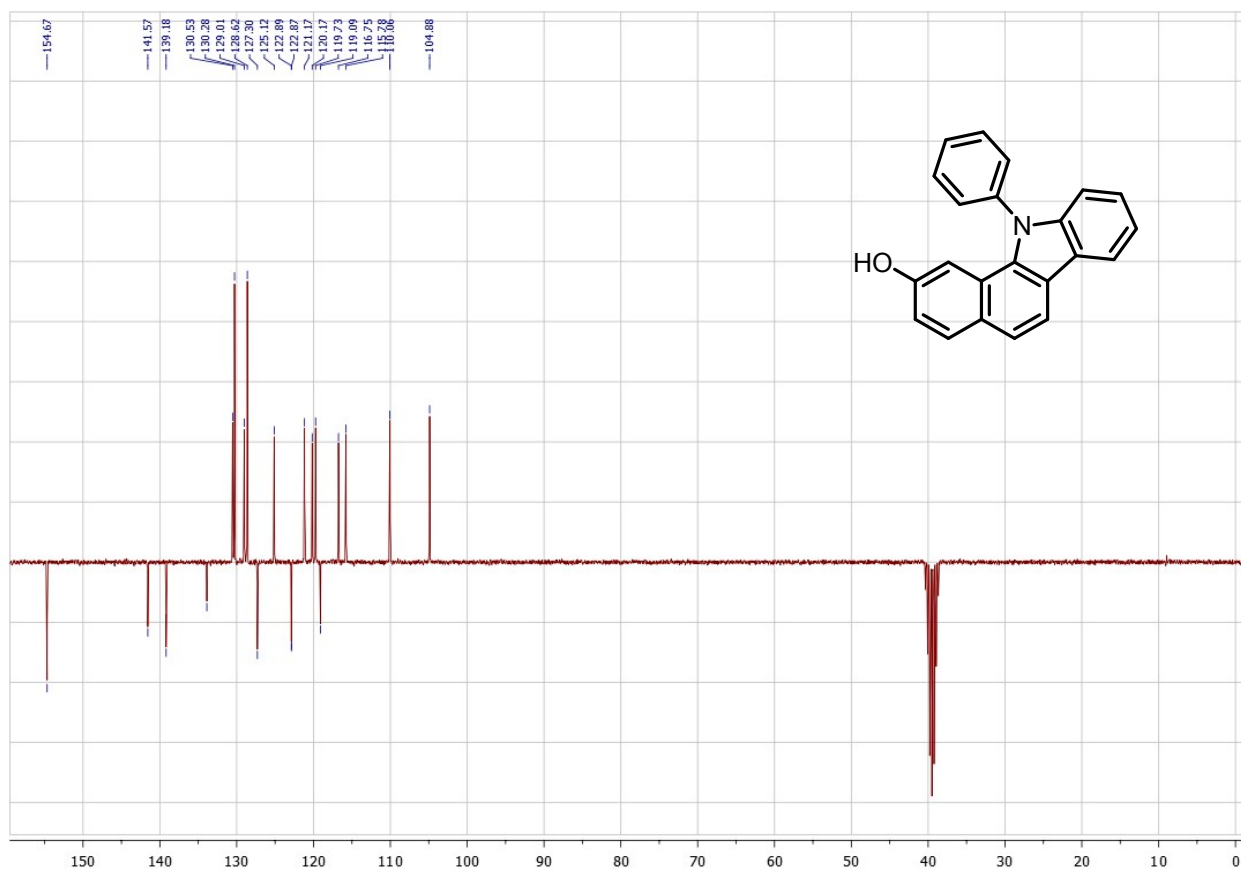
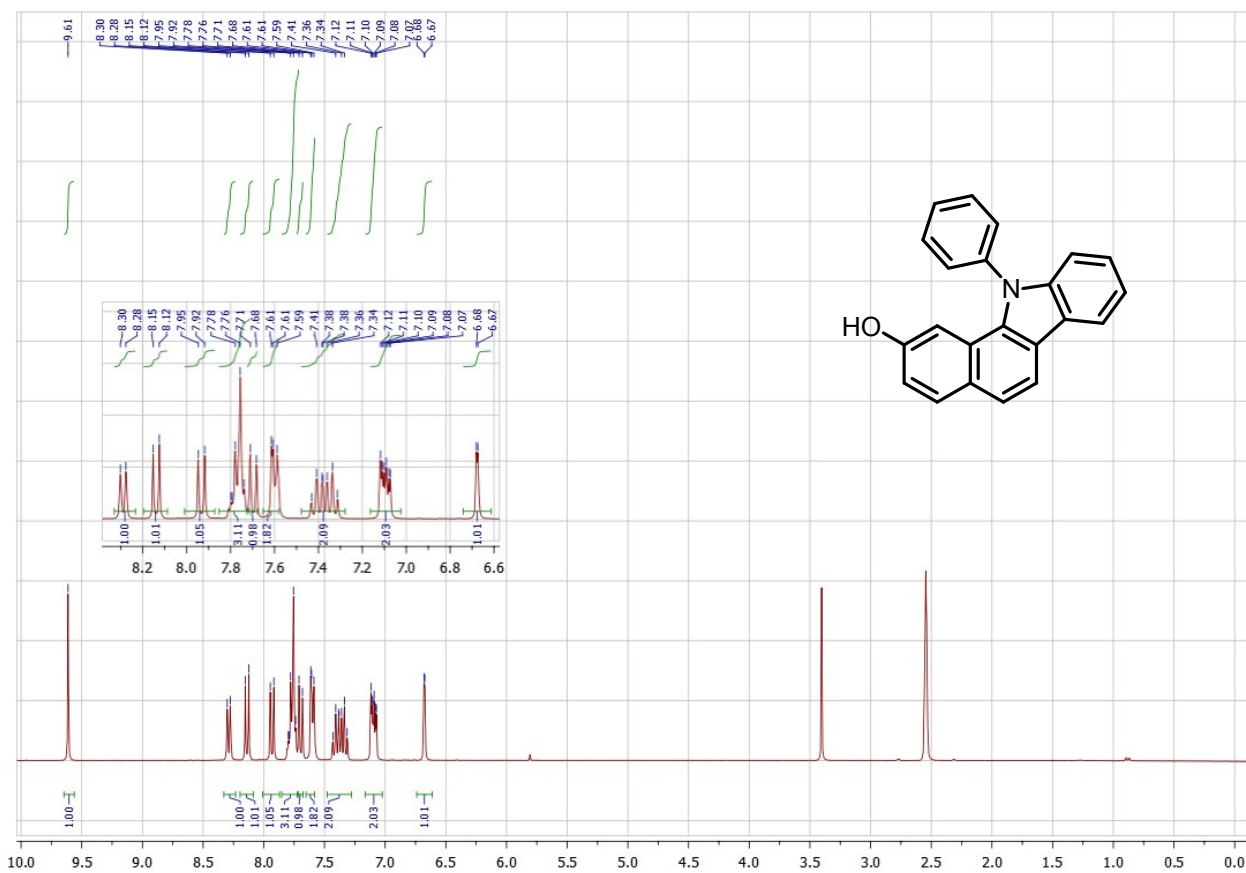
S _n	CF1			TTC			TTT		
VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]
1	3.3625	368.73	0.1029	2.3727	522.55	0.5216	2.4243	511.42	0.3378
2	3.4918	355.08	0.0424	2.6938	460.26	0.1432	2.7380	452.82	0.1088
3	3.7726	328.64	0.0137	2.8808	430.38	0.0595	2.9683	417.70	0.0803
4	3.9240	315.96	0.0218	2.9169	425.05	0.0262	3.0471	406.89	0.0471
5	4.0539	305.84	0.0333	3.4472	359.67	0.0734	3.4667	357.64	0.0610
6	4.1370	299.69	0.1311	3.5442	349.82	0.1405	3.5013	354.11	0.1811
7	4.1879	296.06	0.0112	3.9144	316.74	0.0082	3.9298	315.49	0.0807
8	4.2255	293.42	0.0157	3.9872	310.95	0.0008	4.0017	309.83	0.0086
9	4.2821	289.54	0.2691	4.0168	308.67	0.0120	4.0161	308.72	0.0008
10	4.3457	285.31	0.0185	4.0376	307.08	0.0140	4.0560	305.68	0.0074
11	4.4888	276.21	0.0313	4.0771	304.10	0.0150	4.1179	301.09	0.0058
12	4.5222	274.17	0.1642	4.0822	303.72	0.0062	4.1330	299.99	0.0143
13	4.5607	271.85	0.0344	4.1214	300.83	0.0407	4.1599	298.05	0.0073
14	4.5845	270.44	0.0022	4.1352	299.83	0.0109	4.1961	295.47	0.0900
15	4.6164	268.58	0.0781	4.1483	298.88	0.0196	4.2234	293.56	0.0272
16	4.6661	265.71	0.0321	4.2427	292.23	0.0379	4.2817	289.57	0.0897
17	4.7393	261.61	0.0924	4.2608	290.99	0.0104	4.3145	287.36	0.0126
18	4.7496	261.04	0.0105	4.2636	290.80	0.0531	4.3475	285.18	0.0153
19	4.7623	260.34	0.0150	4.3759	283.34	0.3269	4.3983	281.89	0.0140
20	4.7945	258.60	0.0364	4.4416	279.14	0.1848	4.4517	278.51	0.0697
21	4.8249	256.97	0.1348	4.4851	276.44	0.0193	4.5200	274.30	0.0305
22	4.8402	256.16	0.0623	4.5514	272.41	0.0072	4.5503	272.47	0.0027
23	4.8710	254.54	0.0896	4.6154	268.63	0.0638	4.5787	270.79	0.0642
24	4.8846	253.83	0.0281	4.6415	267.12	0.0167	4.6303	267.77	0.0774
S _n	CF2			CTC			CTT		
VEE	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]	[eV]	[nm]	f [-]
1	3.3543	369.63	0.1361	2.4005	516.49	0.3288	2.4089	514.69	0.3278
2	3.4936	354.89	0.0066	2.6788	462.84	0.0453	2.6642	465.37	0.0704
3	3.7696	328.90	0.0149	2.8590	433.66	0.0057	2.9356	422.35	0.0306
4	3.9353	315.06	0.0246	2.9079	426.37	0.1122	3.0374	408.19	0.0433
5	4.0522	305.96	0.0439	3.3152	373.98	0.2165	3.3466	370.48	0.1438
6	4.1325	300.02	0.1082	3.5934	345.03	0.0883	3.5002	354.22	0.1359
7	4.2236	293.55	0.0168	3.9521	313.71	0.0186	3.8711	320.28	0.0481
8	4.2691	290.42	0.3262	3.9967	310.22	0.0012	3.9611	313.00	0.0033
9	4.2974	288.51	0.0252	4.0165	308.69	0.0131	4.0200	308.42	0.0173
10	4.3953	282.08	0.0027	4.0477	306.30	0.0244	4.0822	303.72	0.0053
11	4.4330	279.68	0.0270	4.0775	304.07	0.0033	4.1229	300.72	0.0290
12	4.4794	276.79	0.0131	4.0923	302.97	0.0445	4.1446	299.15	0.0077
13	4.5552	272.18	0.0449	4.1407	299.43	0.0115	4.1710	297.26	0.0153
14	4.5827	270.55	0.0503	4.1857	296.21	0.0093	4.2014	295.10	0.0610

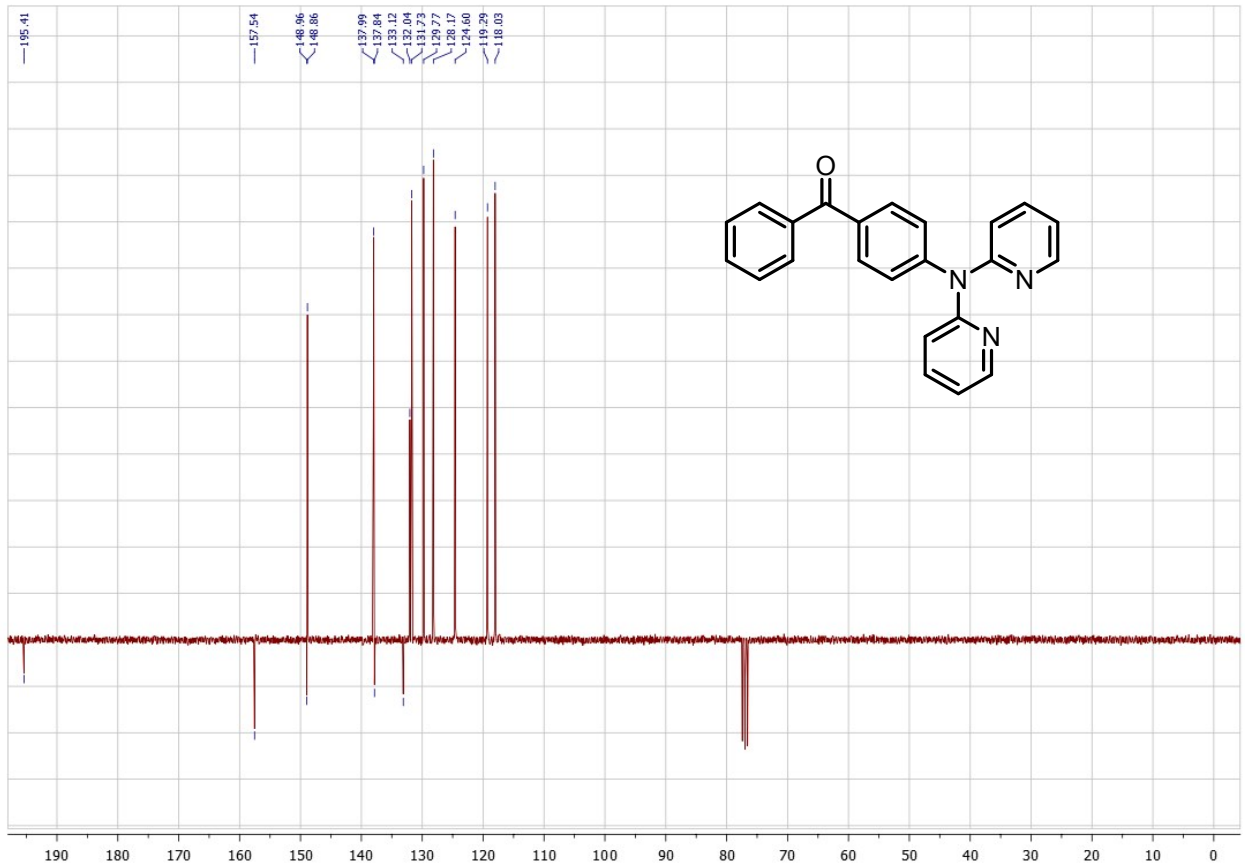
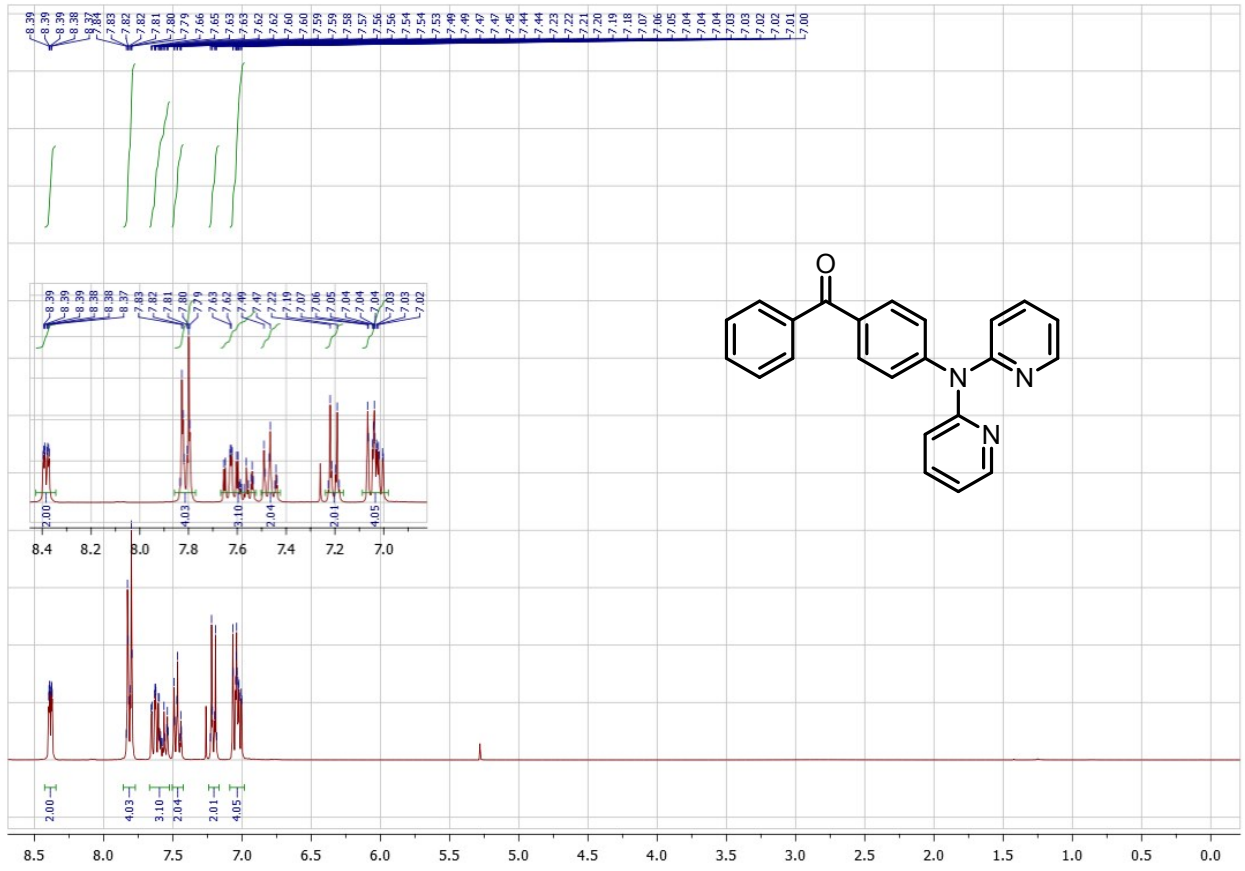
15	4.5956	269.79	0.0056	4.1975	295.38	0.0163	4.2622	290.89	0.0156
16	4.6060	269.18	0.0296	4.2632	290.82	0.0445	4.2726	290.18	0.0135
17	4.6774	265.07	0.3991	4.2884	289.11	0.0203	4.3042	288.06	0.0126
18	4.7573	260.62	0.0039	4.3431	285.48	0.1128	4.3706	283.68	0.0170
19	4.7906	258.81	0.0185	4.4265	280.09	0.0399	4.4231	280.31	0.0232
20	4.7991	258.35	0.0359	4.5052	275.2	0.0605	4.4652	277.67	0.0818
21	4.8217	257.14	0.0408	4.5718	271.19	0.0492	4.4784	276.85	0.0379
22	4.8444	255.93	0.0422	4.5883	270.22	0.1099	4.5534	272.29	0.3042
23	4.8701	254.58	0.0765	4.6176	268.50	0.0641	4.5845	270.44	0.0869
24	4.9044	252.80	0.0435	4.6733	265.30	0.0218	4.6087	269.02	0.0036

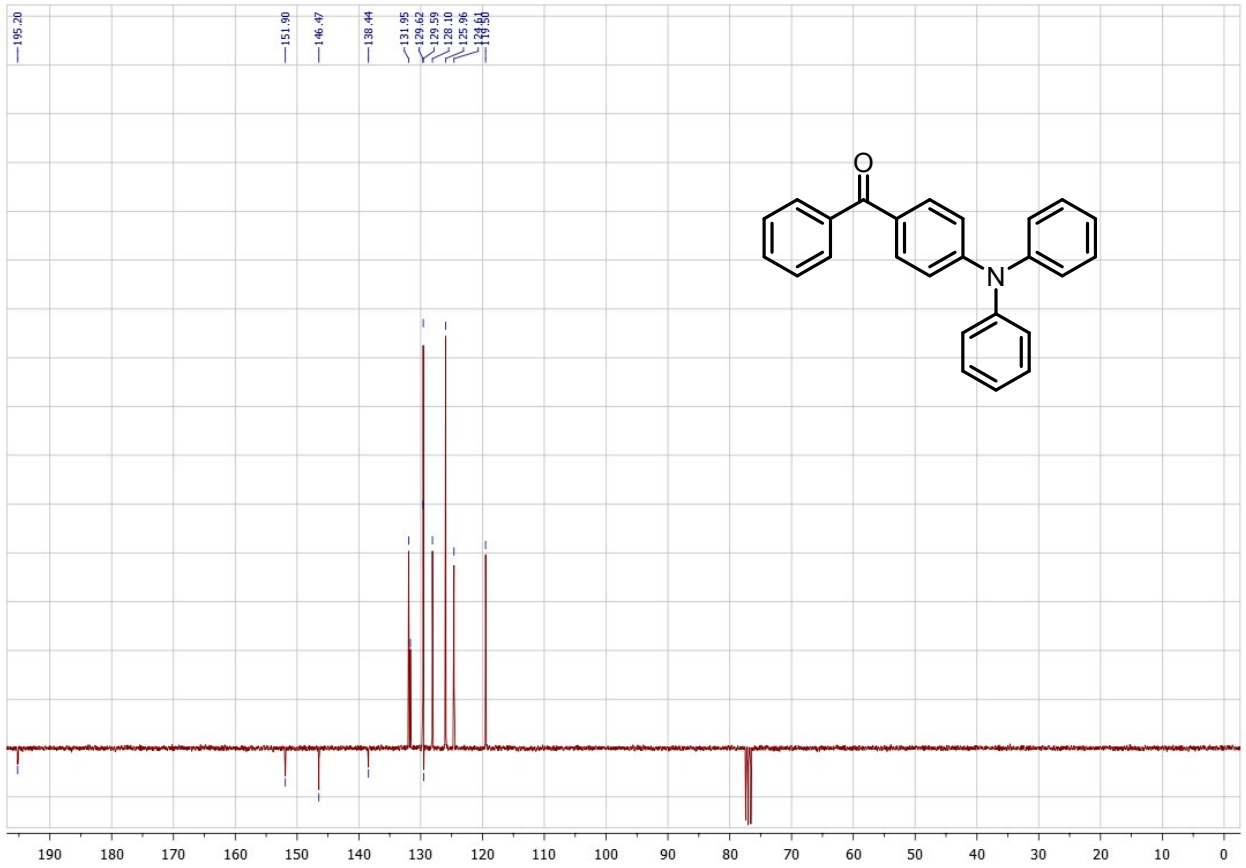
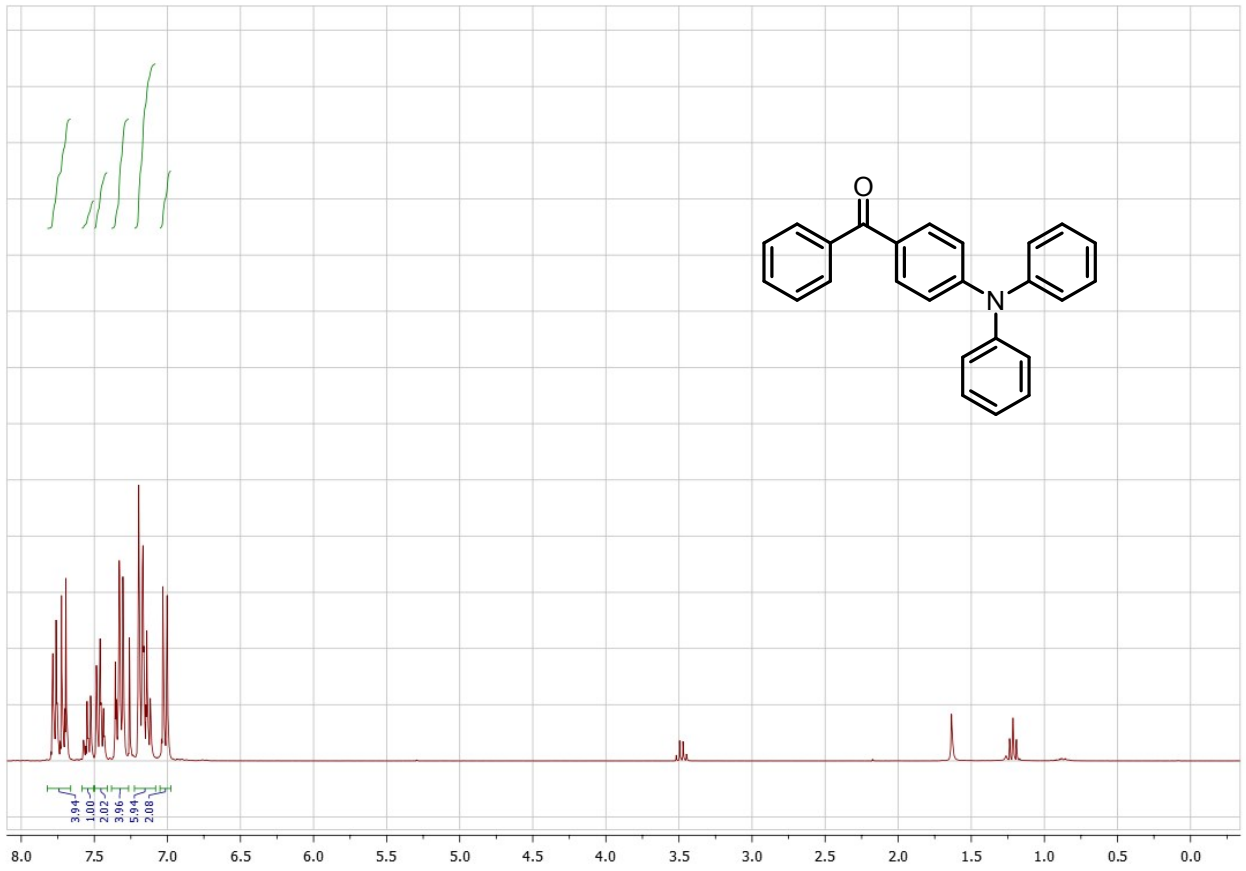
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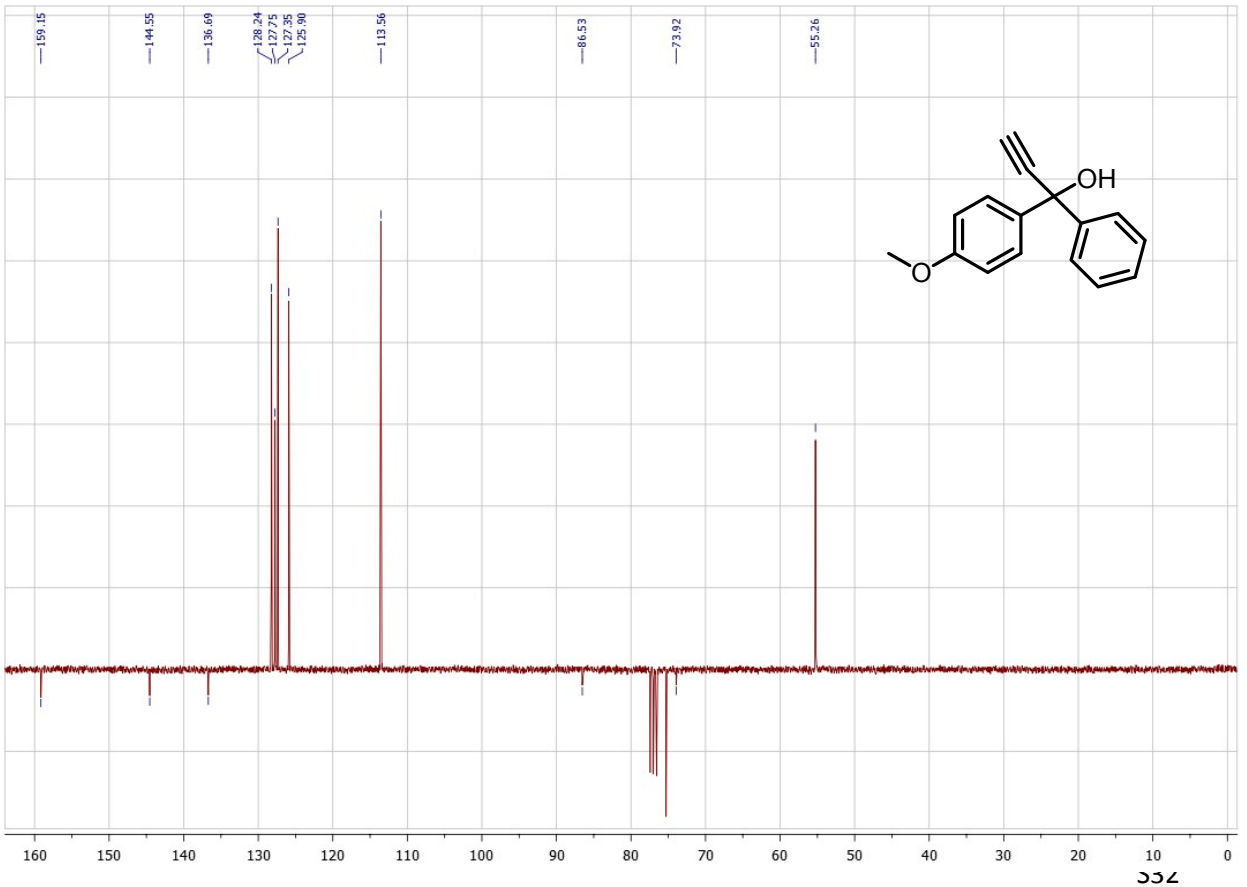
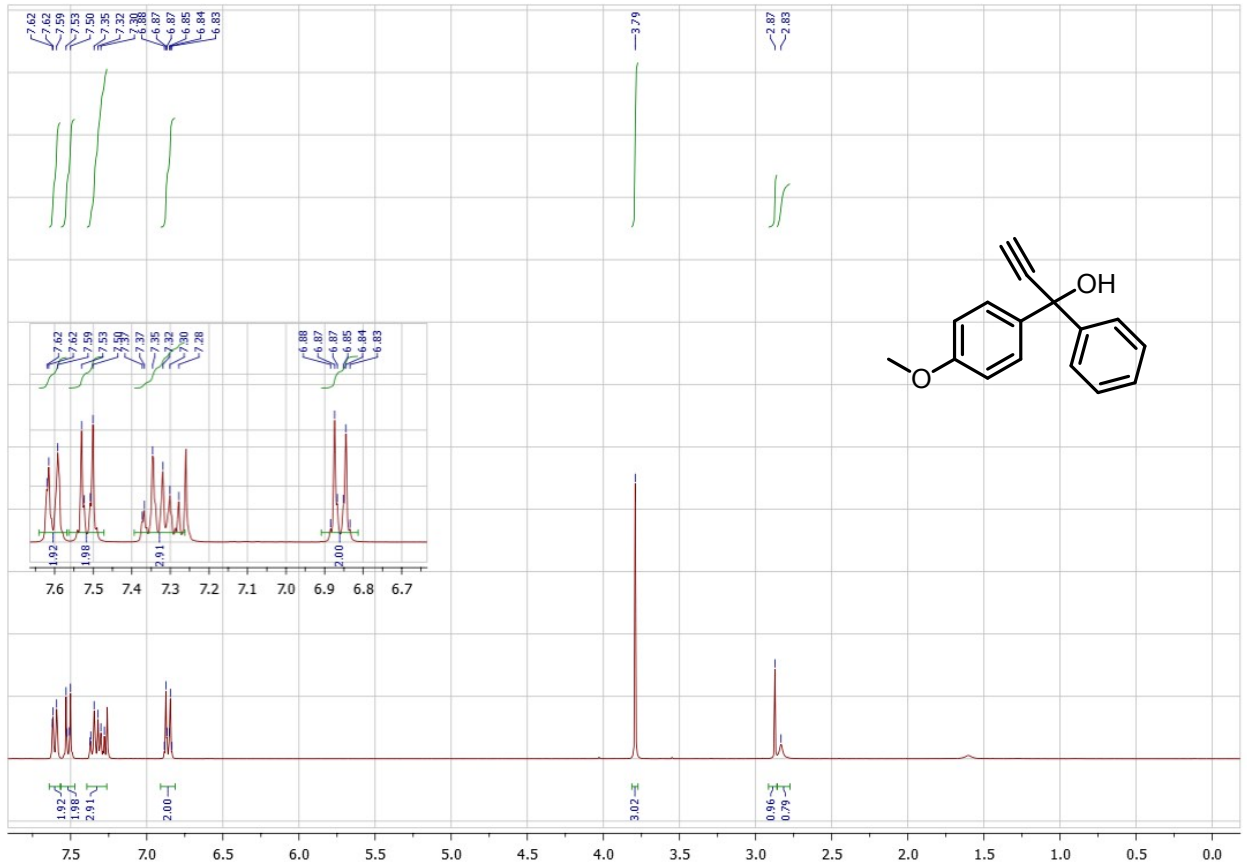


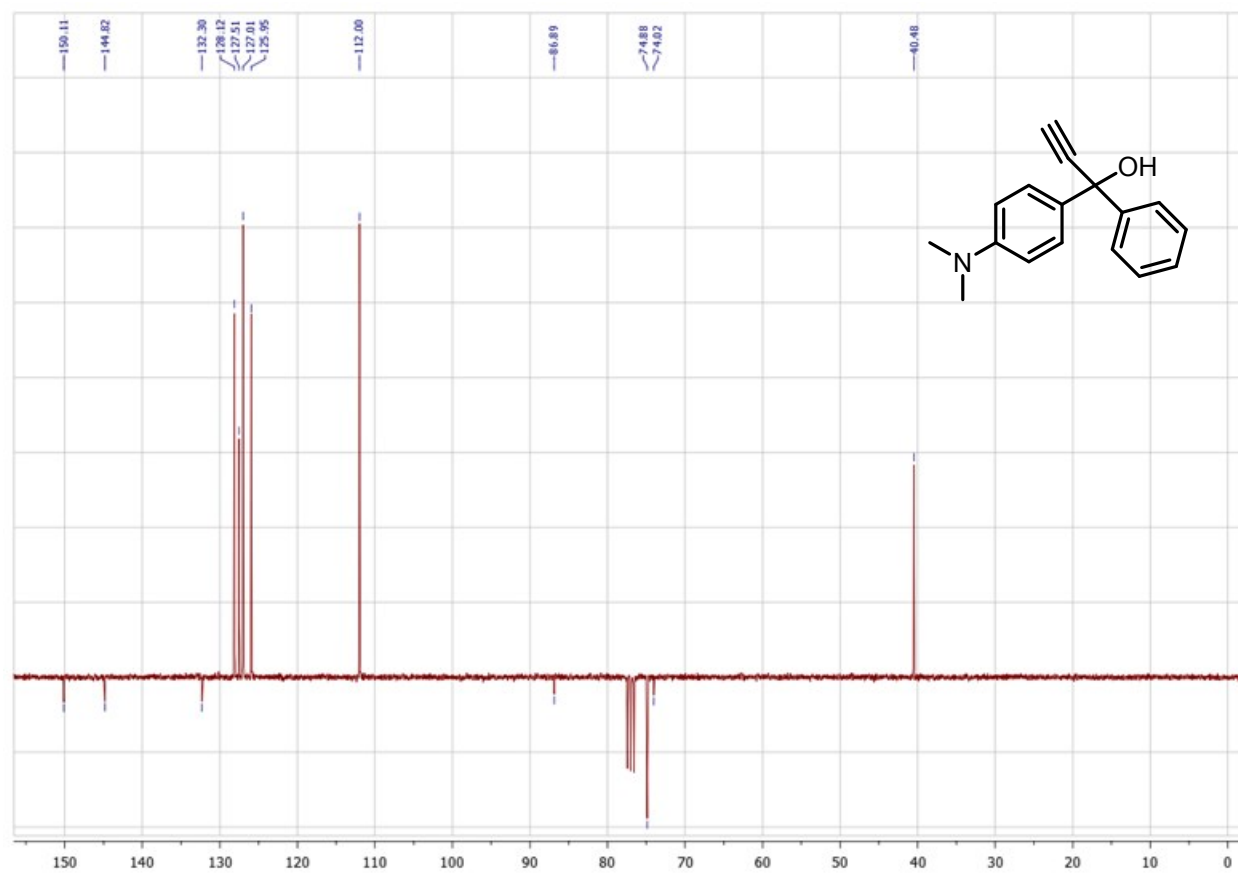
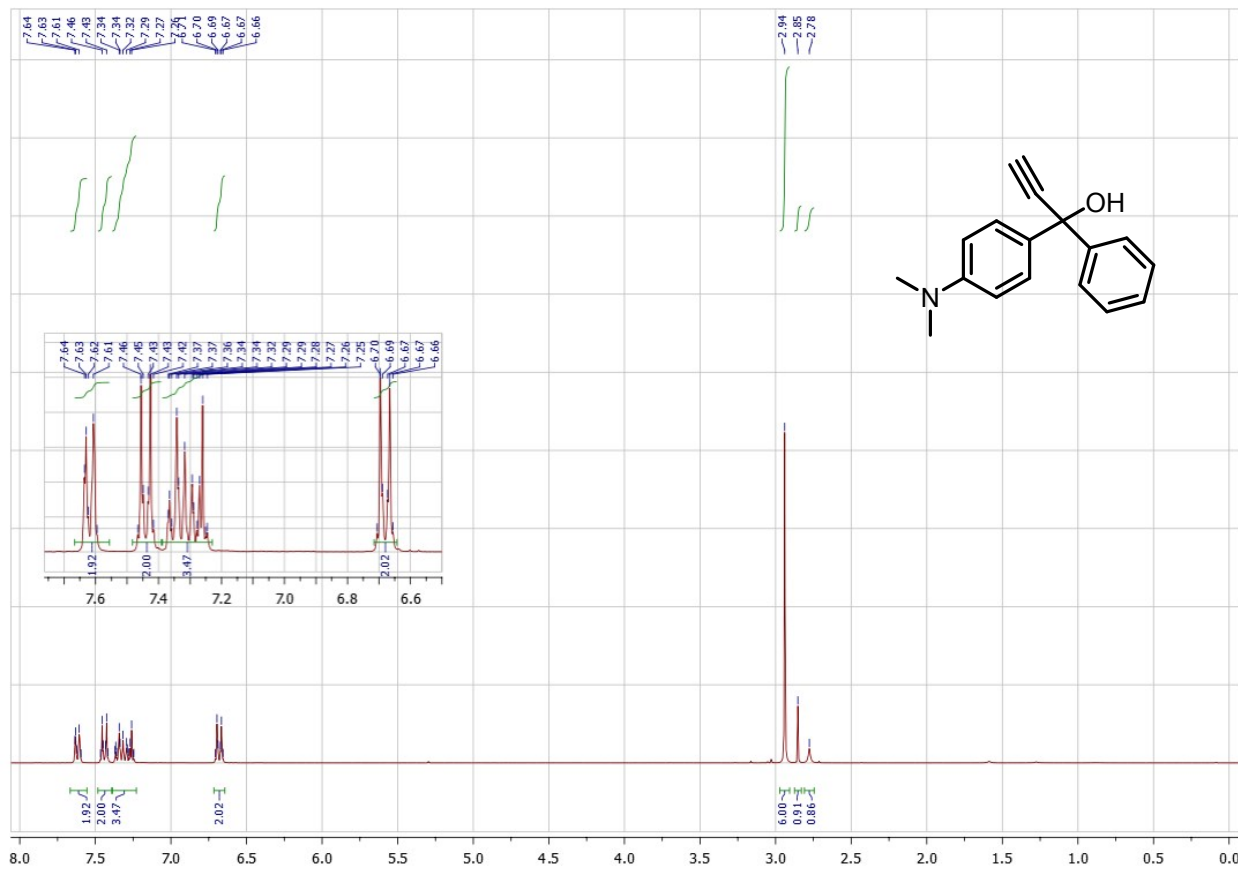


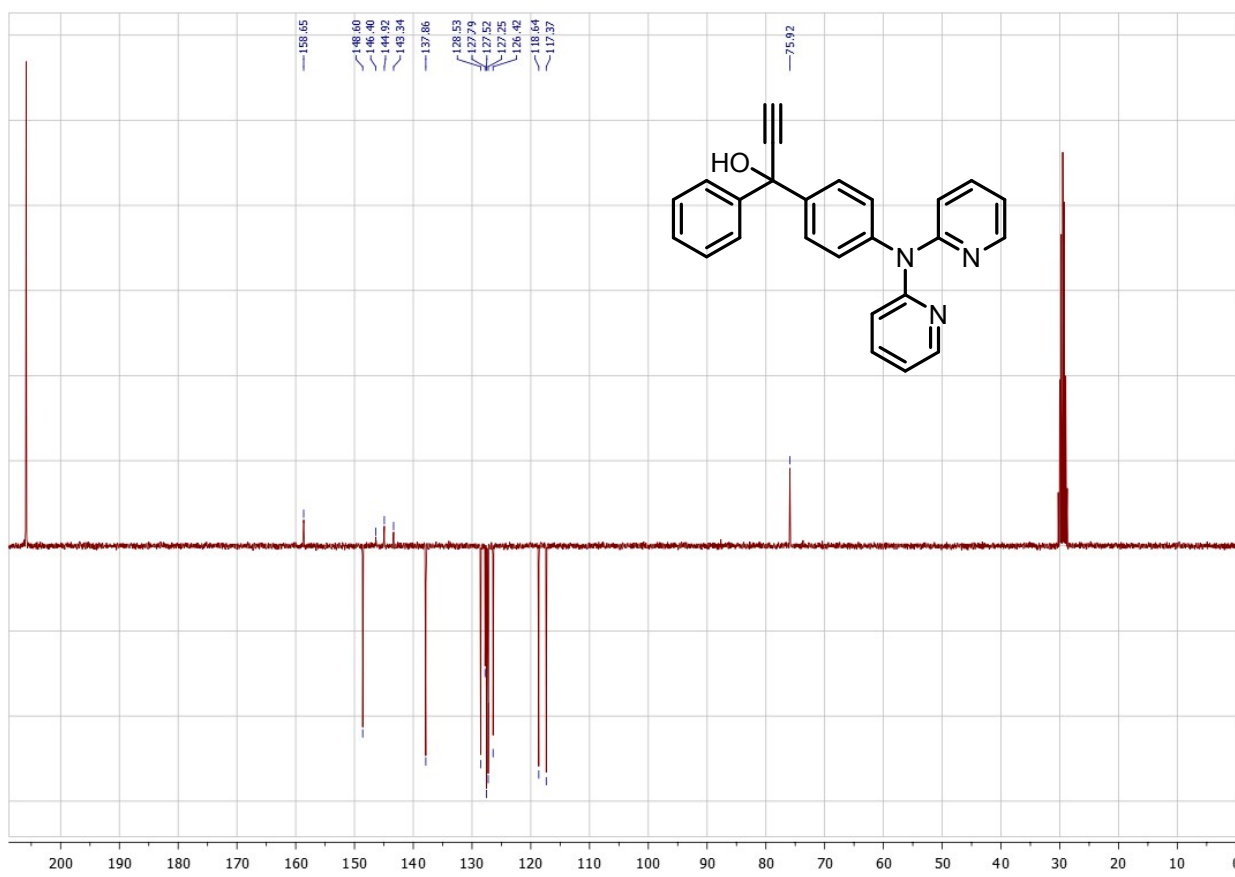
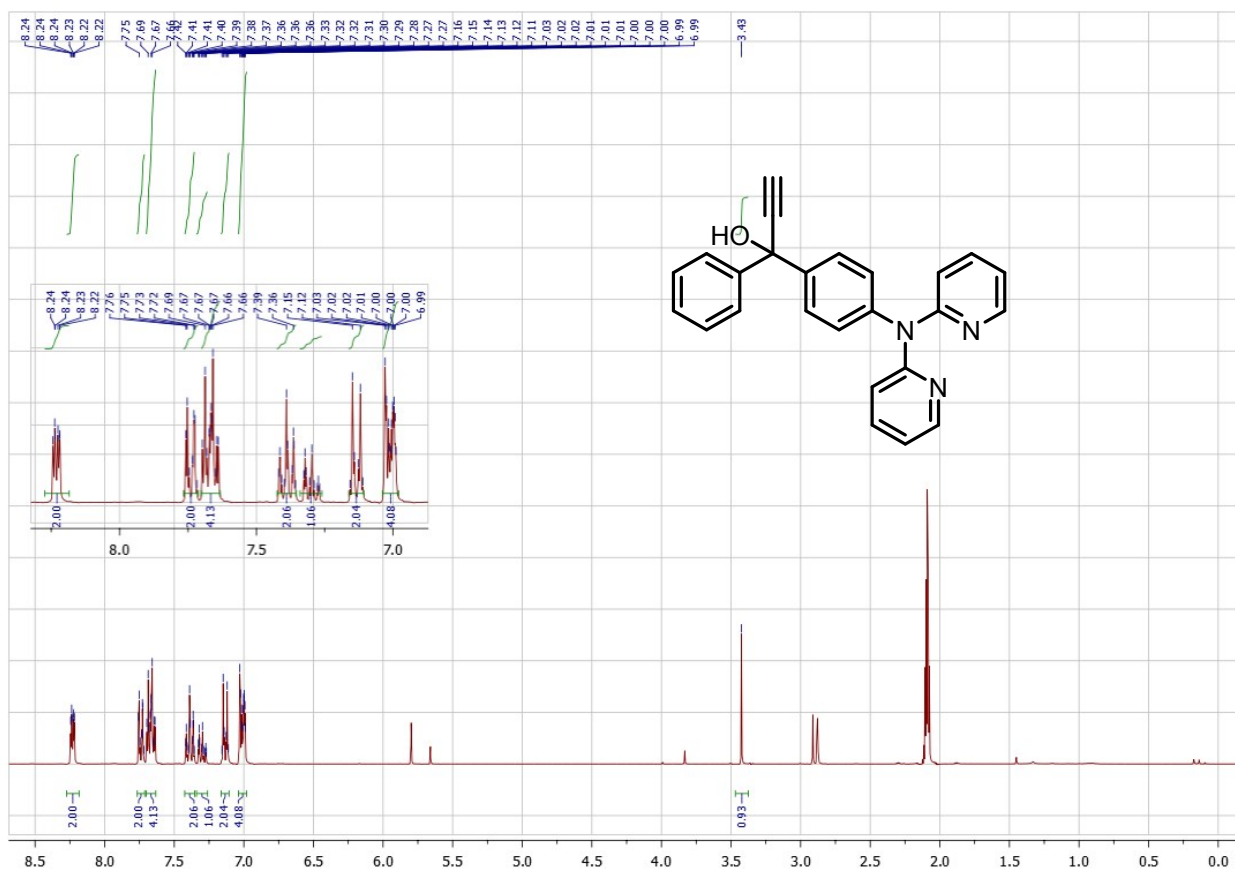


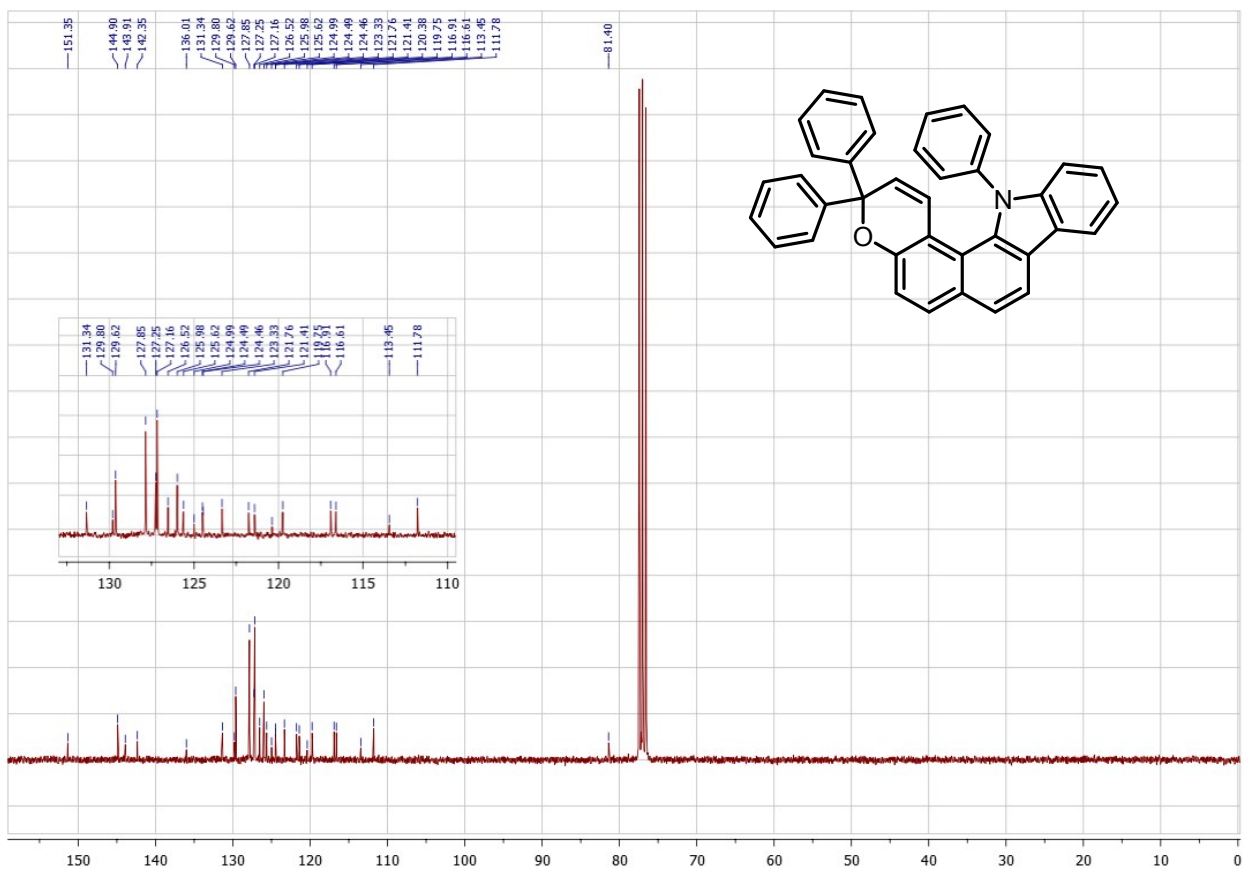
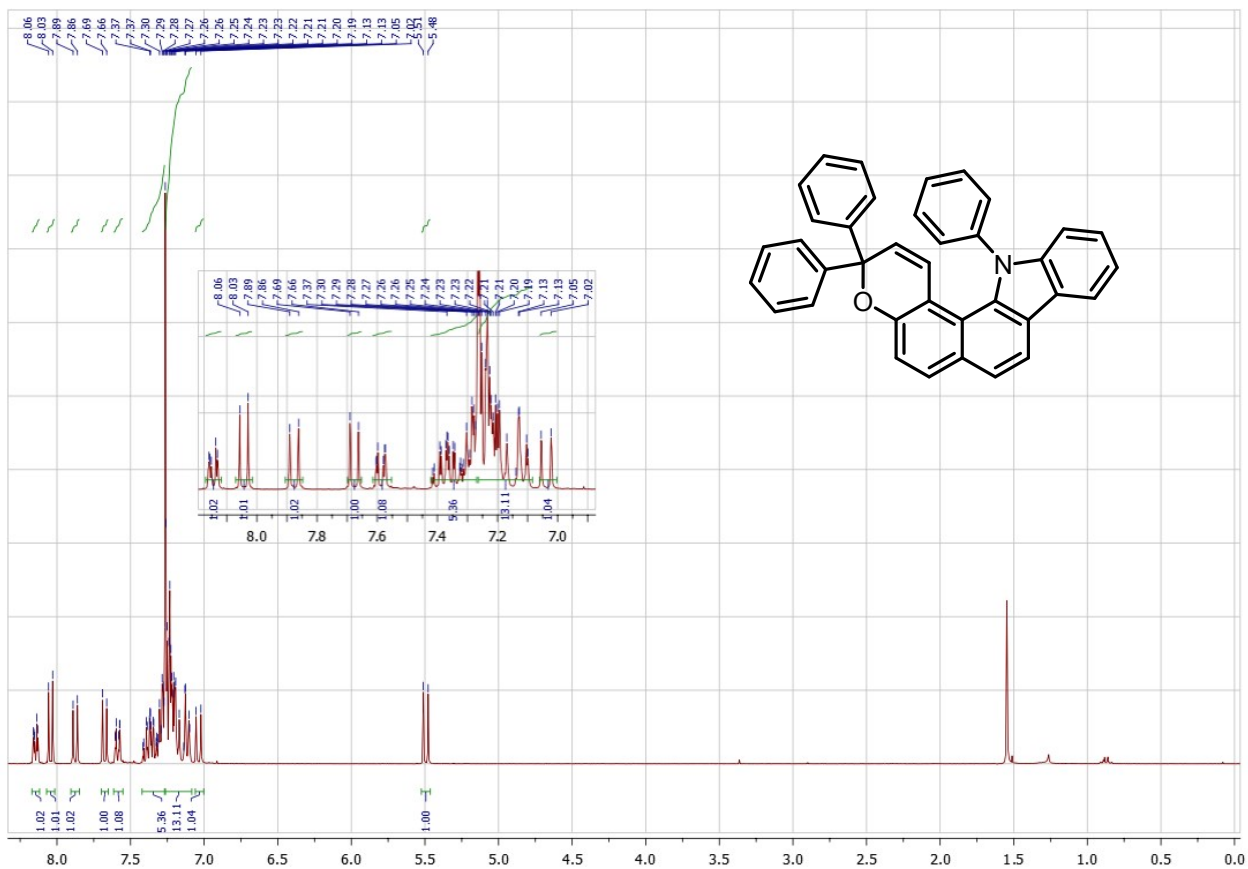


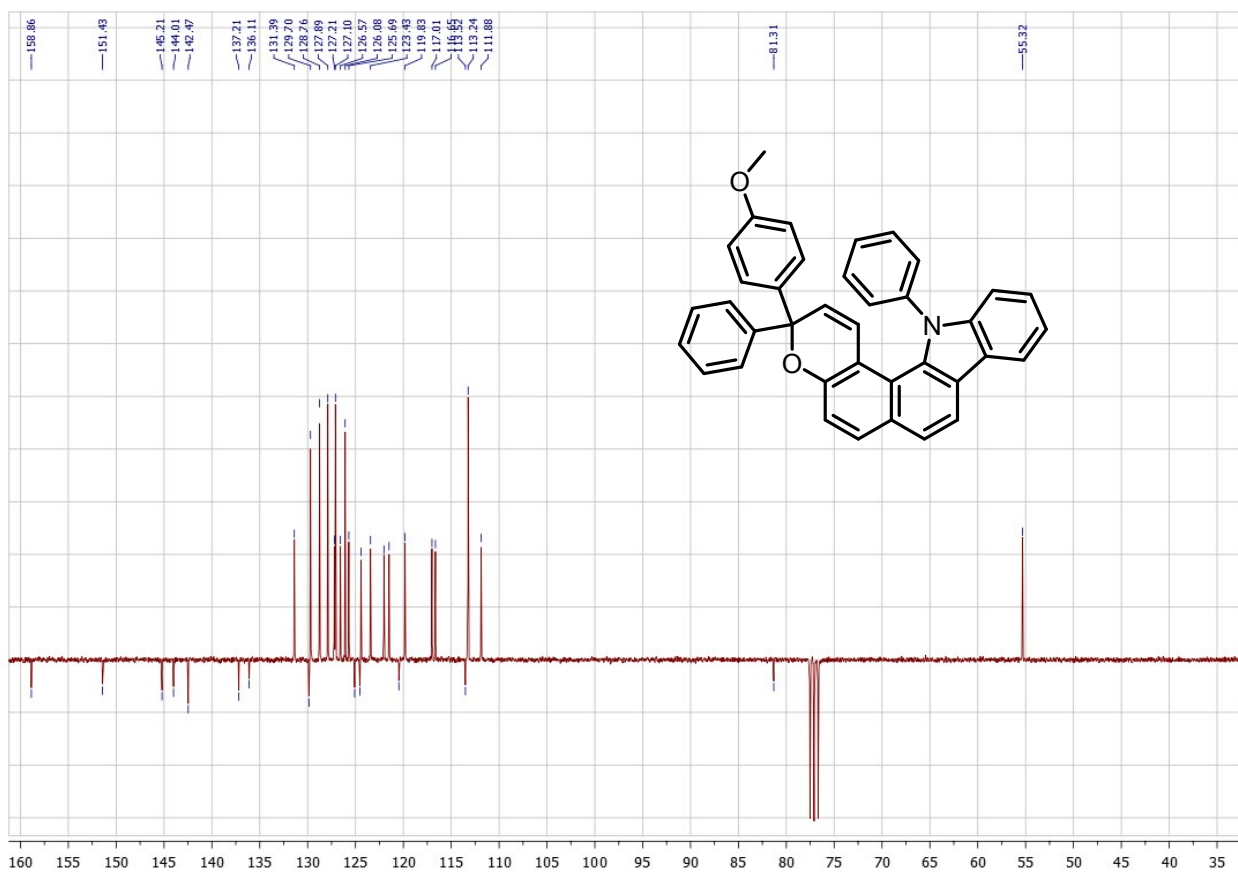
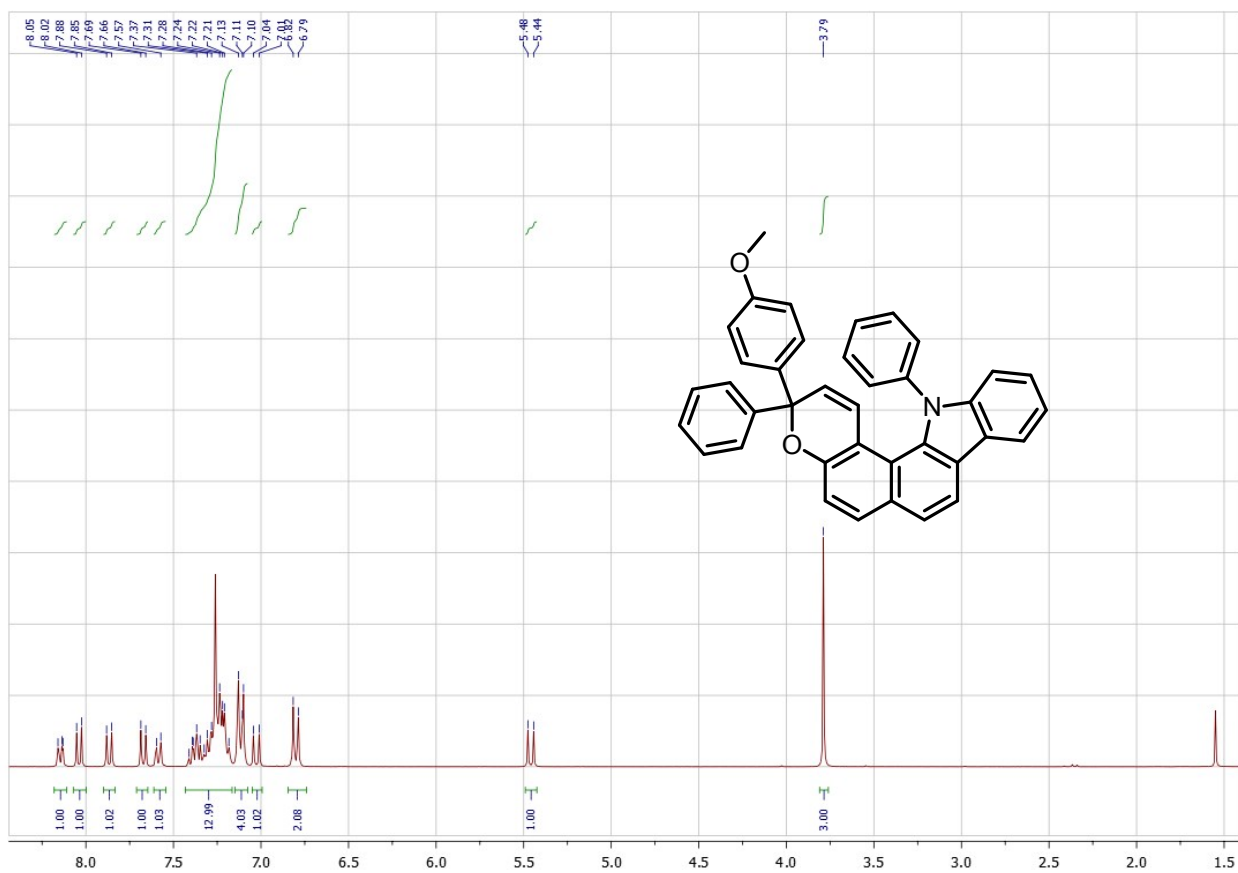


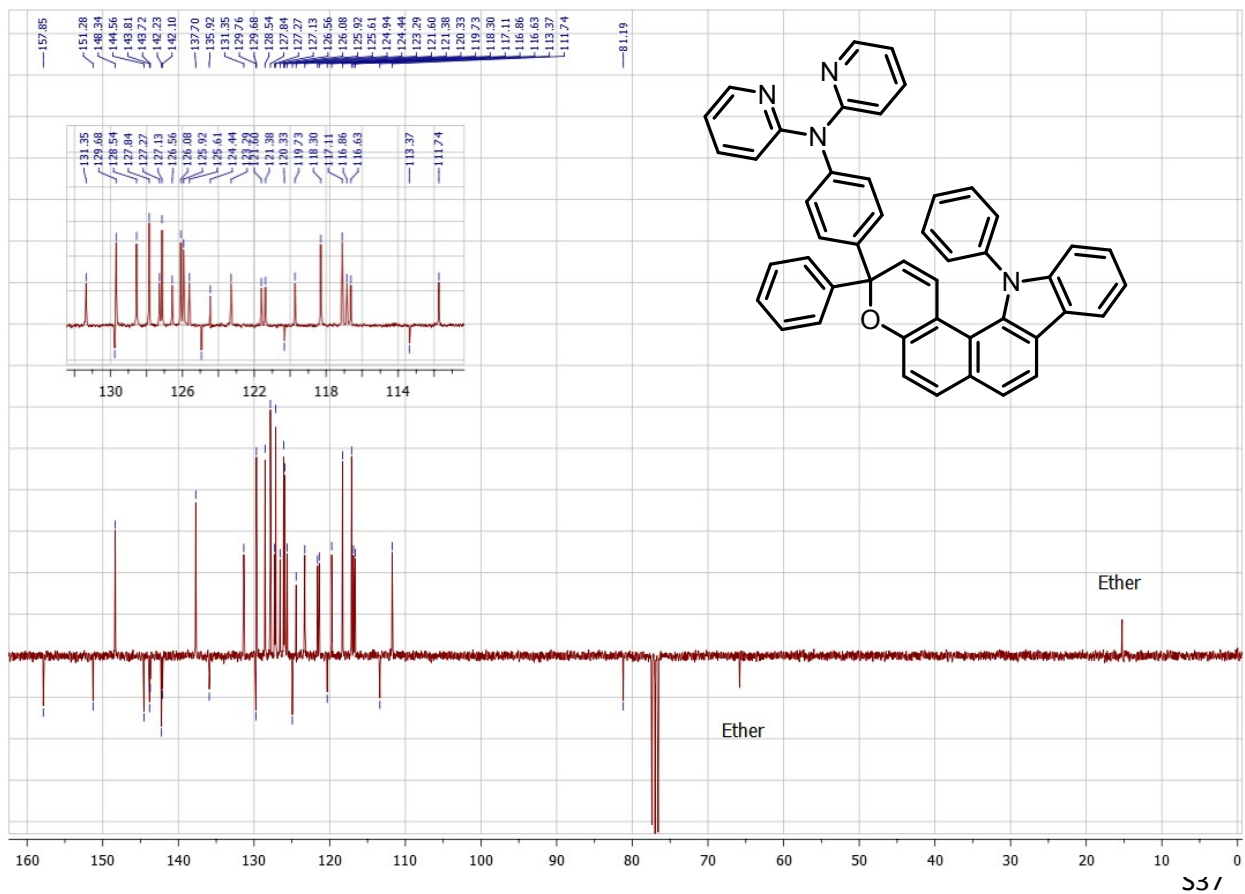
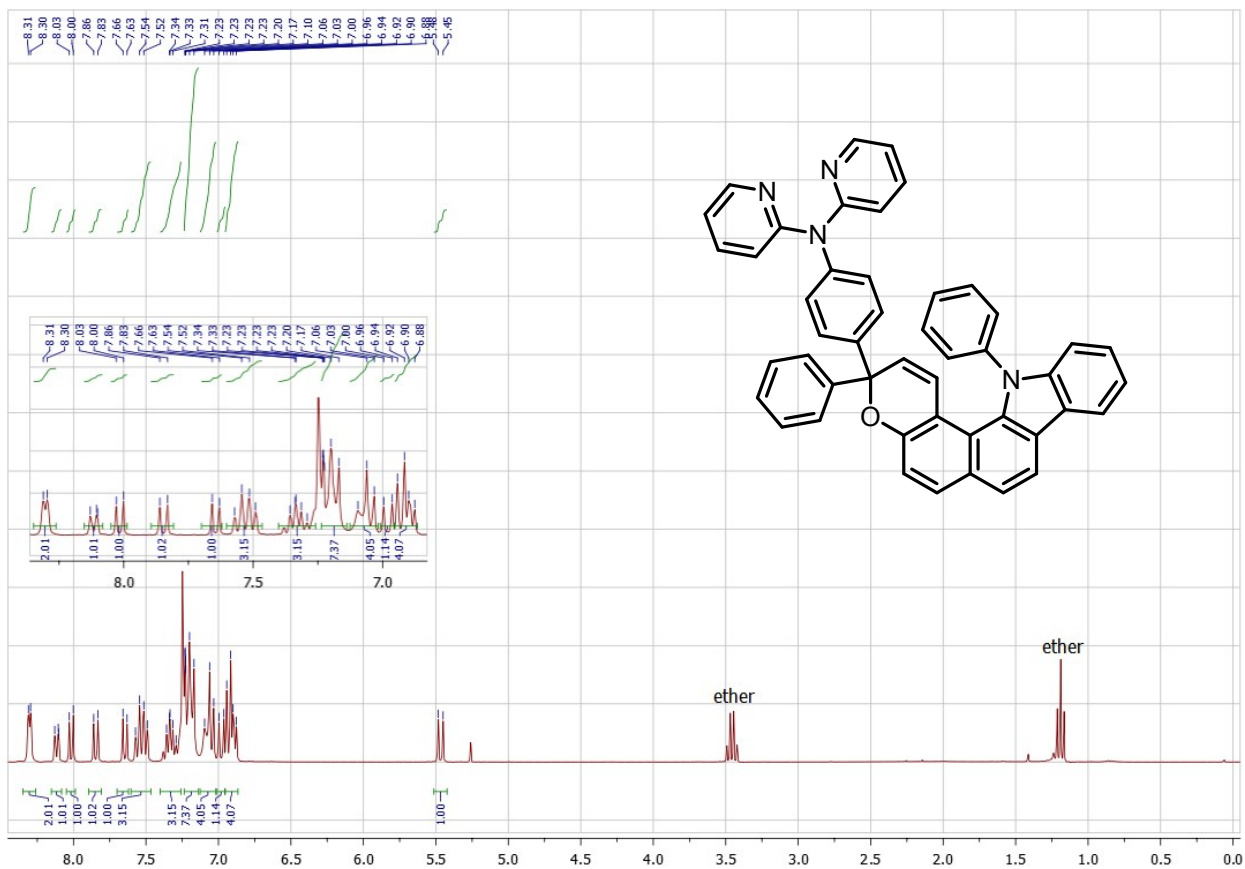


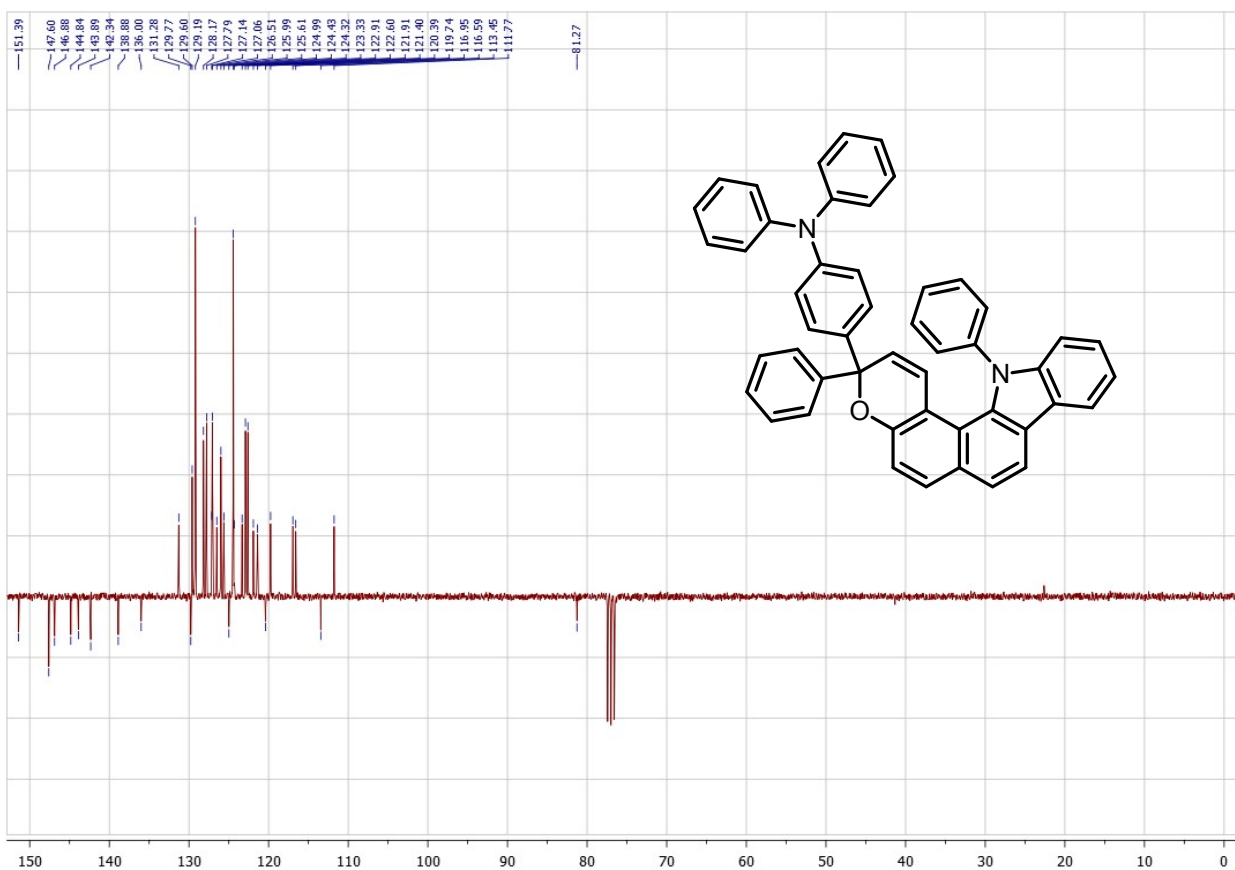
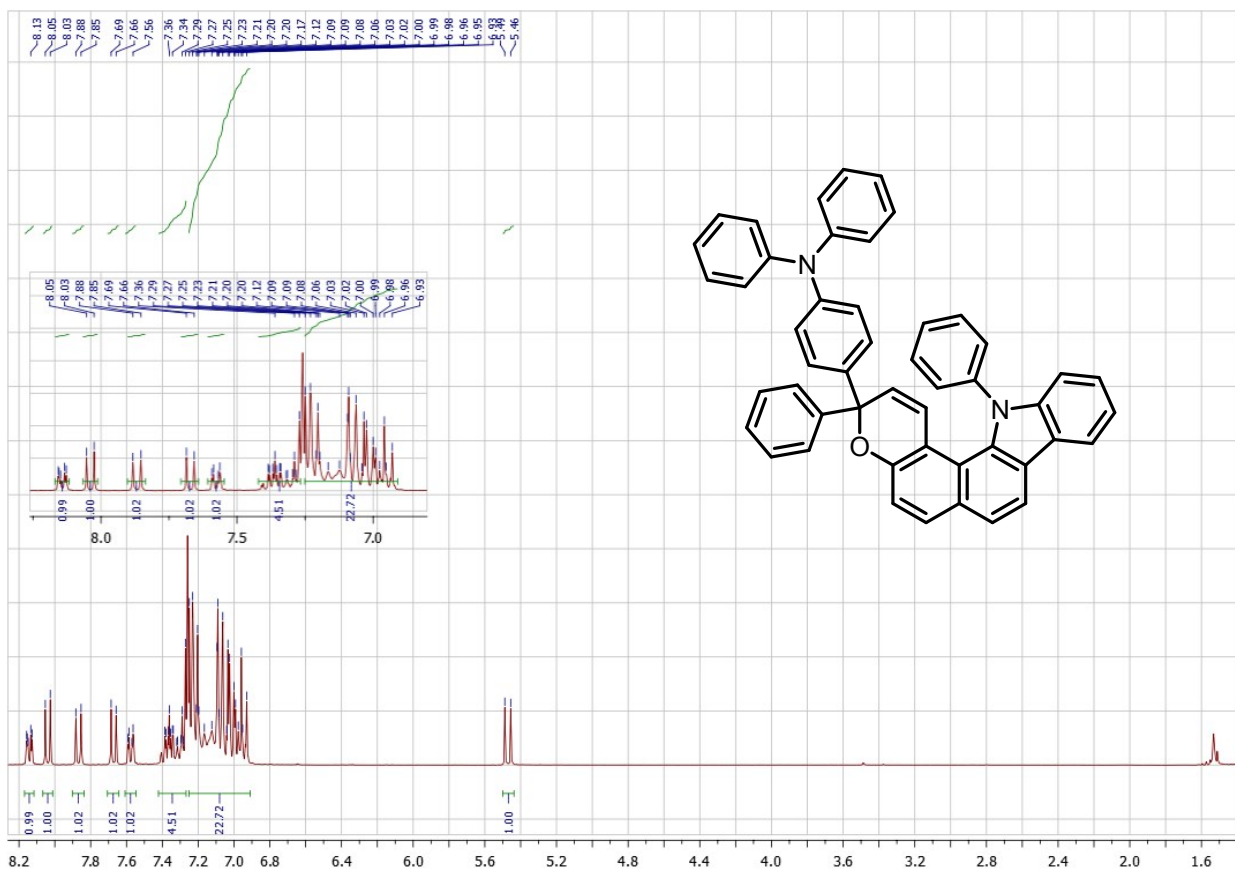


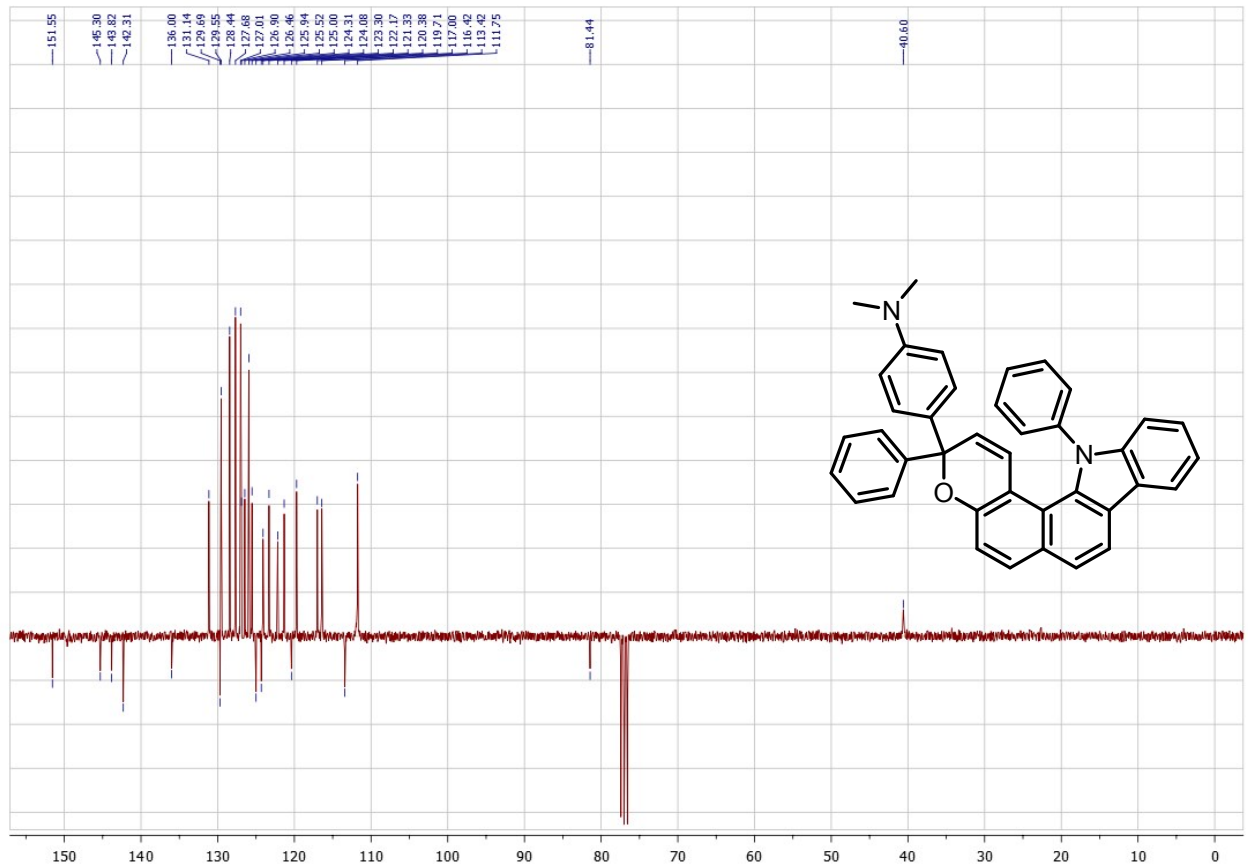
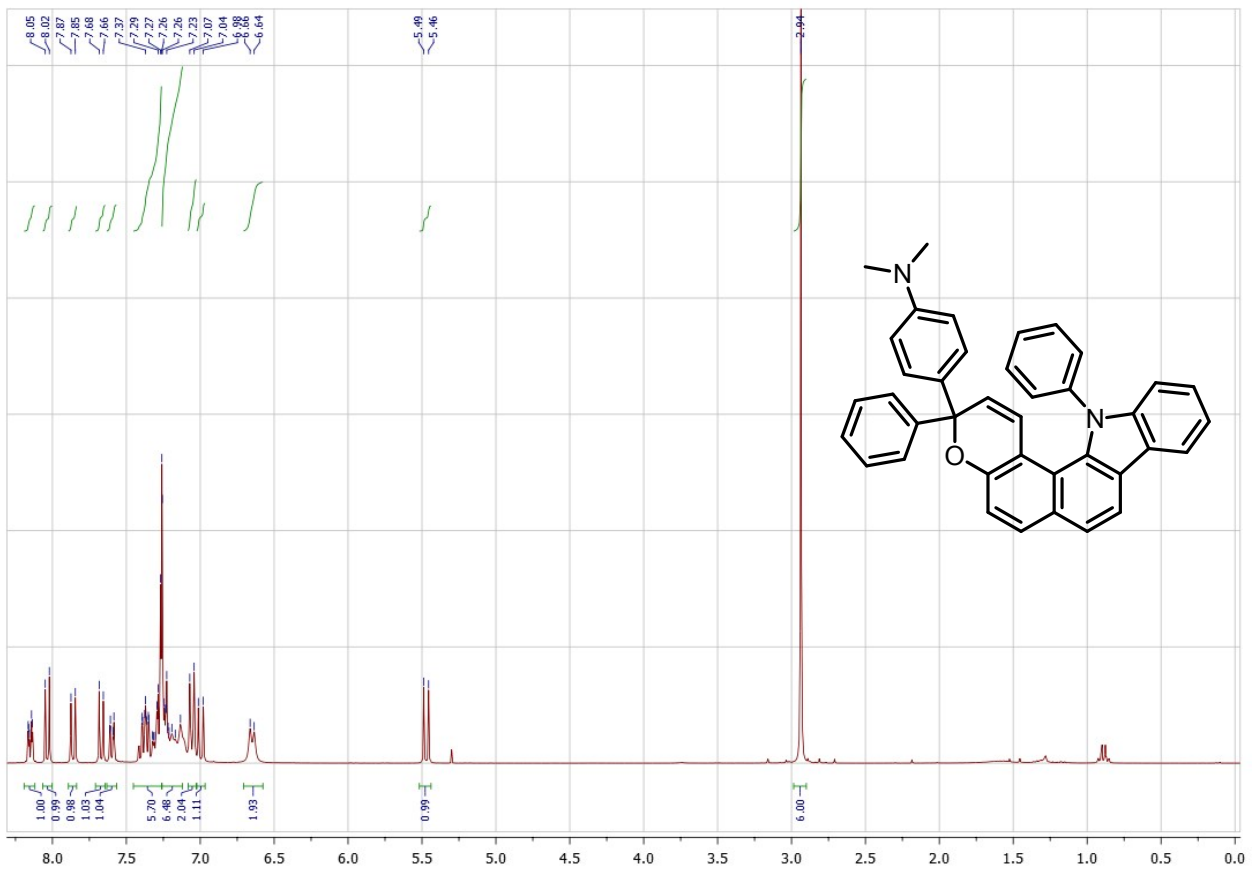












UV-VIS MEASUREMENTS

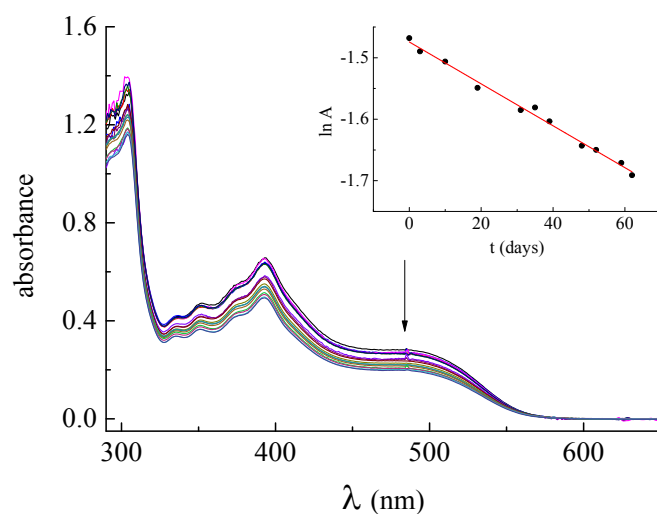


Figure S3. Absorption spectra recorded over a period of five months during the thermal decolouration of CN-Ph-H in toluene. Inset: linear interpolation using the absorbance data at 500 nm.

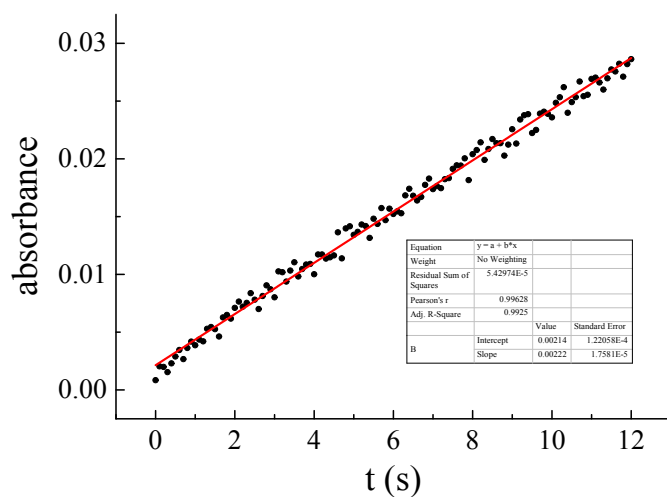


Figure S4. Linear interpolation of the first seconds of the UV photocoloration kinetics of CN-Ph-H in toluene, according to equation 5.

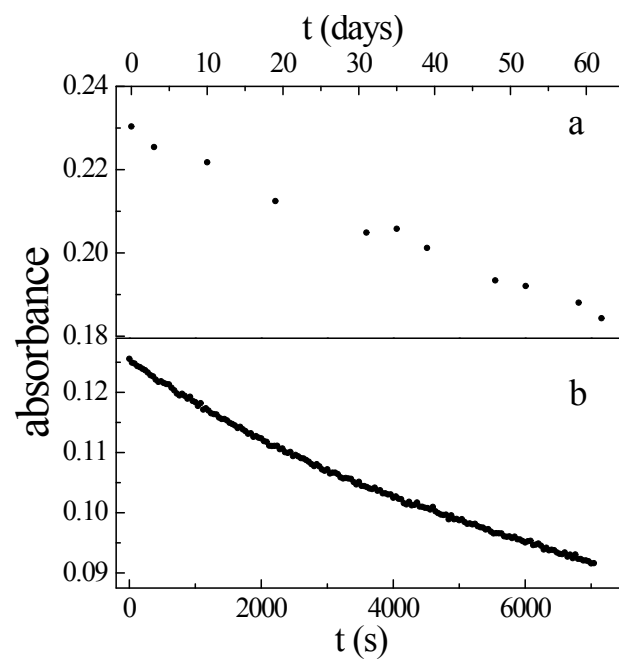


Figure S5. Decay plots of the TT isomers of CN-Ph-H (a) and CN-Ph-N(methyl)₂ (b) in toluene at room temperature in the dark.

REFERENCES

1. M.M. Oliveira, M.A. Salvador, P.J. Coelho and L.M. Carvalho, New benzopyranocarbazoles: synthesis and photochromic behavior, *Tetrahedron*, 2005, **61**, 1681–1691.