

Catalytic Enantioselective Tautomerization of Metastable Enamines

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Supporting Information

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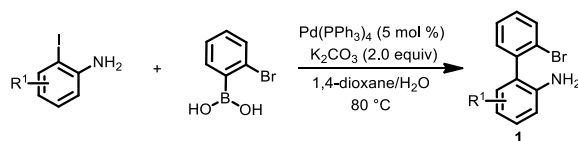
A. General information:

All reactions were carried out under an argon atmosphere using Standard Schlenk-Lines or a glovebox (Innovative Technology). All reagents were used as received unless otherwise noted. DMF, DCM, DCE, CHCl₃ and DMSO were dried over CaH₂. Toluene, (trifluoromethyl)benzene, *m*-xylene, *o*-xylene, *n*-hexane and THF were dried over sodium. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F₂₅₄); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh) or basic alumina (200-300 mesh, pH ≈ 9.0). Proton nuclear magnetic

resonance (^1H NMR) data were acquired on a Varian Unity Inova-400 (400 MHz) or Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q = quartet; m, multiplet, coupling constants J are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Varian Unity Inova-400 or Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform- d . Fluorine nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported relative to inter standard CFCl_3 at 0.0 ppm. Infrared spectra were recorded on a TENSOR 27 FT-IR spectrophotometer and reported in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. HPLC analyses were performed on an Agilent Technologies 1260. Optical rotations were measured on a Rudolph Research Analytical Autopol II automatic polarimeter. **1a**¹ and **2b**-**1**²⁻⁵ were prepared according to literature methods.

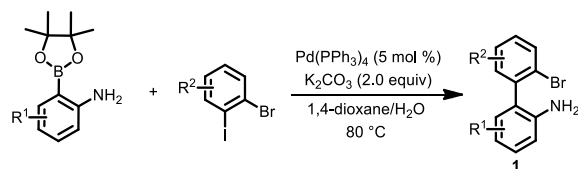
B. Preparation of the biaryl coupling partner **1b-u**:

(I) General method A:



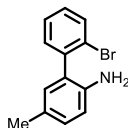
A 50 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $\text{Pd}(\text{PPh}_3)_4$ (0.15 g, 0.13 mmol), K_2CO_3 (0.69 g, 5.0 mmol), (2-bromophenyl)boronic acid (0.60 g, 3.0 mmol), *ortho*-iodoaniline derivatives (2.5 mmol), deoxygenated 1,4-dioxane (13.0 mL) and deoxygenated water (2.5 mL). The mixture was stirred at 80 °C until the reaction was judged to be completed by TLC analysis. Water was added and extracted with EtOAc. The organic phase was dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was then chromatographed on silica gel (petroleum ether/ethyl acetate) to afford the 2'-bromo-[1,1'-biphenyl]-2-amine derivative **1**.

(II) General method B:



A 50 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $\text{Pd}(\text{PPh}_3)_4$ (0.17 g, 0.15 mmol), K_2CO_3 (0.83 g, 6.0 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)aniline derivative (3.0 mmol), the corresponding dihalogenated aryl derivatives (3.6 mmol), deoxygenated 1,4-dioxane (15.0 mL) and deoxygenated water (3.0 mL). The mixture was stirred at 80 °C until the reaction was judged to be

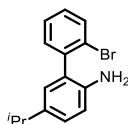
completed by TLC analysis. Water was added and extracted with EtOAc. The organic phase was dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was then chromatographed on silica gel (petroleum ether/ethyl acetate) to afford the 2'-bromo-[1,1'-biphenyl]-2-amine derivative **1**.



2'-Bromo-5-methyl-[1,1'-biphenyl]-2-amine (**1b**)

Compound **1b** was prepared from 2-iodo-4-methylaniline by using Method A.

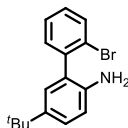
1b (Red solid, 0.56 g, 85% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.60 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.31 – 7.27 (m, 1H), 7.23 (dd, $J = 7.6, 1.9$ Hz, 1H), 7.18 – 7.11 (m, 1H), 6.94 (dd, $J = 8.1, 1.8$ Hz, 1H), 6.77 (d, $J = 1.5$ Hz, 1H), 6.62 (d, $J = 8.1$ Hz, 1H), 3.31 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.0, 140.2, 133.0, 131.9, 130.6, 129.7, 129.2, 127.8, 127.6, 127.4, 124.2, 115.8, 20.5. IR (KBr): 3457, 3371, 3017, 2919, 1618, 1432, 1257, 751 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{13}\text{BrN}$ $[\text{M}+\text{H}]^+$ 262.0231, found 262.0231.



2'-Bromo-5-isopropyl-[1,1'-biphenyl]-2-amine (**1c**)

Compound **1c** was prepared from 2-iodo-4-isopropylaniline by using Method A.

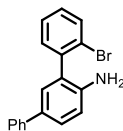
1c (Red solid, 0.50 g, 69% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, $J = 8.0$ Hz, 1H), 7.42 – 7.32 (m, 2H), 7.26 – 7.20 (m, 1H), 7.08 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.90 (d, $J = 1.8$ Hz, 1H), 6.73 (d, $J = 8.2$ Hz, 1H), 3.43 (s, 2H), 2.93 – 2.79 (m, 1H), 1.23 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.4, 140.4, 138.8, 133.1, 131.9, 129.2, 128.3, 127.8, 127.1, 127.0, 124.4, 115.6, 33.2, 24.3, 24.2. IR (KBr): 3450, 3054, 2957, 1617, 1463, 1420, 1260, 746 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$ 290.0544, found 290.0544.



2'-Bromo-5-(*tert*-butyl)-[1,1'-biphenyl]-2-amine (**1d**)

Compound **1d** was prepared from 2-iodo-4-(*tert*-butyl)aniline by using Method A.

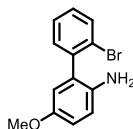
1d (Red solid, 0.57 g, 75% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 7.8$ Hz, 1H), 7.39 – 7.37 (m, 2H), 7.25 – 7.22 (m, 2H), 7.05 (d, $J = 2.3$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 3.44 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.0, 139.9, 139.4, 132.1, 130.8, 128.0, 126.7, 126.4, 125.6, 124.8, 123.3, 114.2, 32.9, 30.5. IR (KBr): 3460, 3375, 3055, 2958, 1618, 1467, 1363, 1261, 753 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{18}\text{BrN}$ $[\text{M}+\text{Na}]^+$ 326.0520, found 326.0508.



2''-Bromo-[1,1':3',1''-terphenyl]-4'-amine (**1e**)

Compound **1e** was prepared from 3-(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)-[1,1'-biphenyl]-4-amine by using Method B.

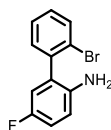
1e (White solid, 0.75 g, 77% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.74 – 7.70 (m, 1H), 7.59 – 7.55 (m, 2H), 7.48 (dd, J = 8.3, 2.2 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.32 (d, J = 2.2 Hz, 1H), 7.28 – 7.24 (m, 2H), 6.86 (d, J = 8.3 Hz, 1H), 3.62 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 140.9, 139.9, 133.3, 132.0, 131.2, 129.5, 129.0, 128.8, 128.0, 127.8, 127.4, 126.5, 126.4, 124.3, 116.0. IR (KBr): 3468, 3379, 3033, 2923, 1615, 1478, 1263, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{14}\text{BrNNa}$ $[\text{M}+\text{Na}]^+$ 346.0207, found 346.0222.



2'-Bromo-5-methoxy-[1,1'-biphenyl]-2-amine (**1f**)

Compound **1f** was prepared from 2-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline by using Method B.

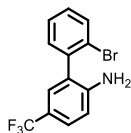
1f (Yellow solid, 0.50 g, 60% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.32 (dd, J = 7.6, 1.8 Hz, 1H), 7.23 (td, J = 7.7, 2.0 Hz, 1H), 6.81 (dd, J = 8.7, 2.9 Hz, 1H), 6.72 (d, J = 8.7 Hz, 1H), 6.62 (d, J = 2.9 Hz, 1H), 3.75 (s, 3H), 3.28 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.4, 140.0, 137.3, 133.1, 131.7, 129.3, 128.3, 127.9, 124.0, 117.0, 115.4, 115.1, 55.8. IR (KBr): 3443, 3361, 3052, 2939, 1611, 1503, 1273, 752 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{13}\text{BrNO}$ $[\text{M}+\text{H}]^+$ 278.0181, found 278.0174.



2'-Bromo-5-fluoro-[1,1'-biphenyl]-2-amine (**1g**)

Compound **1g** was prepared from 4-fluoro-2-iodoaniline by using Method A.

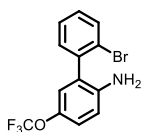
1g (Red oil, 0.47 g, 70% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.27 (dd, J = 7.6, 1.7 Hz, 1H), 7.26 – 7.19 (m, 1H), 6.90 (td, J = 8.5, 2.9 Hz, 1H), 6.76 (dd, J = 8.9, 2.9 Hz, 1H), 6.67 (dd, J = 8.8, 4.8 Hz, 1H), 3.39 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.4 (d, J = 236.3 Hz), 139.6 (d, J = 1.9 Hz), 138.6 (d, J = 1.2 Hz), 132.9, 131.3, 129.4, 127.7, 127.6 (d, J = 7.6 Hz), 123.6, 116.3 (d, J = 29.8 Hz), 116.2, 115.4 (d, J = 22.1 Hz). ^{19}F NMR (376 MHz, CDCl_3): δ -126.86. IR (KBr): 3459, 3375, 3059, 2922, 1617, 1500, 1423, 1265, 752 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_9\text{BrFNNa}$ $[\text{M}+\text{Na}]^+$ 287.9800, found 287.9796.



2'-Bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (**1h**)

Compound **1h** was prepared from 2-iodo-4-(trifluoromethyl)aniline by using Method A.

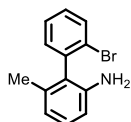
1h (Red oil, 0.62 g, 78% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 15.2, 7.7 Hz, 2H), 7.32 – 7.22 (m, 3H), 6.77 (d, J = 8.4 Hz, 1H), 3.83 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.7, 138.5, 133.4, 131.8, 129.9, 128.1, 127.7 (q, J = 3.8 Hz), 126.3 (q, J = 3.8 Hz), 126.2, 124.8 (q, J = 270.5 Hz), 124.1, 119.9 (q, J = 32.5 Hz), 114.8. ^{19}F NMR (376 MHz, CDCl_3): δ -60.94. IR (KBr): 3484, 3398, 3060, 2924, 1623, 1512, 1331, 1270, 751 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_9\text{BrF}_3\text{NNa}$ $[\text{M}+\text{Na}]^+$ 337.9768, found 337.9754.



2'-Bromo-5-(trifluoromethoxy)-[1,1'-biphenyl]-2-amine (**1i**)

Compound **1i** was prepared from 2-(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)-4-(trifluoromethoxy)aniline by using Method B.

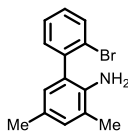
1i (Colorless oil, 0.55 g, 55% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.31 (dd, J = 7.6, 1.5 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.06 (d, J = 8.7 Hz, 1H), 6.93 (s, 1H), 6.72 (d, J = 8.7 Hz, 1H), 3.57 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.6, 140.9, 140.8, 138.6, 133.3, 131.6, 129.8, 128.0, 127.4, 124.0, 123.4, 120.7 (q, J = 255.9 Hz), 115.9. ^{19}F NMR (376 MHz, CDCl_3): δ -58.35. IR (KBr): 3475, 3388, 3060, 2924, 1619, 1471, 1256, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{10}\text{BrF}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 331.9898, found 331.9892.



2'-Bromo-6-methyl-[1,1'-biphenyl]-2-amine (**1j**)

Compound **1j** was prepared from 3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline by using Method B.

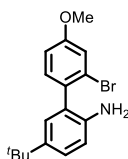
1j (White solid, 0.64 g, 81% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.69 – 7.63 (m, 1H), 7.34 (td, J = 7.6, 1.2 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.04 (t, J = 7.8 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 3.25 (s, 2H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 139.0, 137.0, 133.3, 131.7, 129.3, 128.6, 128.3, 127.1, 124.9, 120.0, 113.0, 20.2. IR (KBr): 3465, 3375, 3056, 2960, 1613, 1462, 1301, 767 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{12}\text{BrNNa}$ $[\text{M}+\text{Na}]^+$ 284.0051, found 284.0048.



2'-Bromo-3,5-dimethyl-[1,1'-biphenyl]-2-amine (**1k**)

Compound **1k** was prepared from 2-iodo-4,6-dimethylaniline by using Method A.

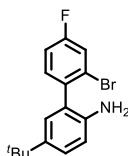
1k (White solid, 0.46 g, 66% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.66 (dd, $J = 8.0, 3.0$ Hz, 1H), 7.39 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.24 – 7.16 (m, 1H), 6.93 (s, 1H), 6.72 (d, $J = 2.9$ Hz, 1H), 3.32 (s, 2H), 2.24 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.5, 139.3, 133.1, 132.0, 131.1, 129.2, 128.4, 127.9, 127.1, 127.0, 124.3, 122.7, 20.5, 17.9. IR (KBr): 3463, 3379, 3009, 2918, 1615, 1475, 1260, 753 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{15}\text{BrN}$ $[\text{M}+\text{H}]^+$ 276.0388, found 276.0381.



2'-Bromo-5-(*tert*-butyl)-4'-methoxy-[1,1'-biphenyl]-2-amine (**1l**)

Compound **1l** was prepared from 2-bromo-1-iodo-4-methoxybenzene by using Method B.

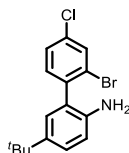
1l (Red solid, 0.49 g, 49% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.26 (t, $J = 5.6$ Hz, 2H), 7.21 (dd, $J = 8.3, 2.3$ Hz, 1H), 7.04 (d, $J = 2.2$ Hz, 1H), 6.94 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.72 (d, $J = 8.3$ Hz, 1H), 3.84 (s, 3H), 3.44 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.5, 141.3, 141.1, 132.5, 132.2, 127.9, 126.4, 125.7, 124.6, 118.2, 115.1, 113.9, 55.6, 34.0, 31.6. IR (KBr): 3454, 3377, 3009, 2956, 1606, 1491, 1221, 752 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{20}\text{BrNNaO}$ $[\text{M}+\text{Na}]^+$ 356.0626, found 356.0624.



2'-Bromo-5-(*tert*-butyl)-4'-fluoro-[1,1'-biphenyl]-2-amine (**1m**)

Compound **1m** was prepared from 2-bromo-4-fluoro-1-iodobenzene by using Method B.

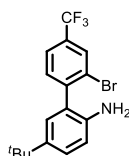
1m (Red oil, 0.56 g, 58% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.45 (dd, $J = 8.3, 2.6$ Hz, 1H), 7.33 (dd, $J = 8.5, 6.1$ Hz, 1H), 7.24 (dd, $J = 8.2, 2.2$ Hz, 1H), 7.11 (td, $J = 8.3, 2.6$ Hz, 1H), 7.01 (d, $J = 2.3$ Hz, 1H), 6.73 (d, $J = 8.4$ Hz, 1H), 3.42 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.8 (d, $J = 250.8$ Hz), 141.2, 141.1, 136.5 (d, $J = 3.6$ Hz), 132.7 (d, $J = 8.3$ Hz), 127.6, 126.1, 125.7, 124.6 (d, $J = 9.5$ Hz), 120.3 (d, $J = 24.2$ Hz), 115.3, 115.0 (d, $J = 20.9$ Hz), 34.0, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -112.76. IR (KBr): 3455, 3062, 2958, 1609, 1480, 1259, 753 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{17}\text{BrFNNa}$ $[\text{M}+\text{Na}]^+$ 344.0426, found 344.0416.



2'-Bromo-5-(*tert*-butyl)-4'-chloro-[1,1'-biphenyl]-2-amine (**1n**)

Compound **1n** was prepared from 2-bromo-4-chloro-1-iodobenzene by using Method B.

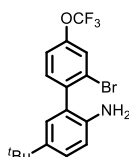
1n (Red oil, 0.65 g, 64% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.71 (d, J = 1.5 Hz, 1H), 7.35 (dd, J = 8.2, 1.4 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.23 (dd, J = 8.4, 2.0 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 3.40 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.1, 140.8, 138.9, 133.9, 132.7, 132.5, 127.9, 127.2, 126.1, 125.3, 124.7, 115.3, 33.9, 31.4. IR (KBr): 3460, 3374, 2961, 1620, 1502, 1468, 872, 819, 766 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{17}\text{BrClINa}$ $[\text{M}+\text{Na}]^+$ 360.0131, found 360.0120.



2'-Bromo-5-(*tert*-butyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (**1o**)

Compound **1o** was prepared from 2-bromo-1-iodo-4-(trifluoromethyl)benzene by using Method B.

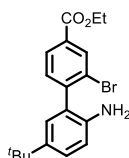
1o (White solid, 0.64 g, 57% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.97 (s, 1H), 7.65 (dd, J = 8.0, 1.1 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.27 (dd, J = 8.3, 2.5 Hz, 1H), 7.02 (d, J = 2.3 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 3.43 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.5, 141.4, 140.7, 132.3, 131.3 (q, J = 33.1 Hz), 130.2 (q, J = 3.9 Hz), 127.0, 126.5, 125.3, 124.8, 124.6 (q, J = 3.5 Hz), 120.5 (q, J = 272.6 Hz), 115.6, 34.0, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -62.65. IR (KBr): 3462, 3383, 3053, 2959, 1618, 1383, 1264, 743 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{17}\text{BrF}_3\text{NNa}$ $[\text{M}+\text{Na}]^+$ 394.0394, found 394.0394.



2'-Bromo-5-(*tert*-butyl)-4'-(trifluoromethoxy)-[1,1'-biphenyl]-2-amine (**1p**)

Compound **1p** was prepared from 2-bromo-1-iodo-4-(trifluoromethoxy)benzene by using Method B.

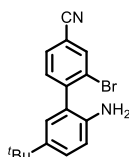
1p (White solid, 0.80 g, 69% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, J = 1.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.02 (d, J = 2.3 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 3.42 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.6, 141.3, 140.9, 139.4, 132.7, 127.4, 126.3, 125.7, 125.3, 124.7, 120.4 (q, J = 258.5 Hz), 120.3, 115.5, 34.0, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -57.84. IR (KBr): 3461, 3375, 3058, 2960, 1618, 1478, 1399, 1370, 1265, 744 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{18}\text{BrF}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 388.0524, found 388.0524.



Ethyl 2'-amino-2-bromo-5'-(*tert*-butyl)-[1,1'-biphenyl]-4-carboxylate (**1q**)

Compound **1q** was prepared from ethyl 3-bromo-4-iodobenzoate by using Method B.

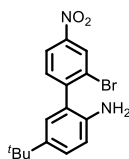
1q (Brown solid, 0.50 g, 44% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.37 (d, J = 1.2 Hz, 1H), 8.05 (dd, J = 7.9, 1.4 Hz, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.25 (dd, J = 7.9, 2.7 Hz, 1H), 7.03 (d, J = 2.2 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 3.43 (s, 2H), 1.42 (t, J = 7.1 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.2, 145.2, 141.2, 140.7, 134.3, 131.9, 131.3, 128.8, 127.0, 126.4, 125.8, 124.4, 115.5, 61.5, 34.0, 31.5, 14.4. IR (KBr): 3462, 3376, 2959, 1717, 1619, 1472, 1373, 1267, 869 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{22}\text{BrNNaO}_2$ [$\text{M}+\text{Na}$] $^+$ 398.0732, found 398.0714.



2'-Amino-2-bromo-5'-(*tert*-butyl)-[1,1'-biphenyl]-4-carbonitrile (**1r**)

Compound **1r** was prepared from 3-bromo-4-iodobenzonitrile by using Method B.

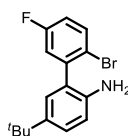
1r (White solid, 0.52 g, 53% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.00 (d, J = 1.5 Hz, 1H), 7.68 (dd, J = 7.9, 1.6 Hz, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.27 (dd, J = 8.3, 2.2 Hz, 1H), 6.99 (d, J = 2.3 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 3.42 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.9, 141.5, 140.5, 136.5, 132.6, 131.2, 126.9, 126.8, 125.0, 124.9, 117.3, 115.8, 112.9, 38.3, 31.8. IR (KBr): 3456, 3377, 3054, 2959, 2232, 1623, 1501, 1437, 1264, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{17}\text{BrN}_2\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 351.0473, found 351.0461.



2'-Bromo-5-(*tert*-butyl)-4'-nitro-[1,1'-biphenyl]-2-amine (**1s**)

Compound **1s** was prepared from 2-bromo-1-iodo-4-nitrobenzene by using Method B.

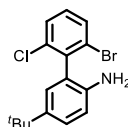
1s (Yellow solid, 0.62 g, 59% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, J = 2.3 Hz, 1H), 8.24 (dd, J = 8.4, 2.3 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.28 (dd, J = 8.4, 2.3 Hz, 1H), 7.01 (d, J = 2.3 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 3.44 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.6, 147.5, 141.5, 140.5, 132.5, 128.4, 127.0, 126.8, 124.9, 124.6, 122.6, 115.8, 34.1, 31.5. IR (KBr): 3446, 3367, 3105, 2954, 1626, 1512, 1349, 1267, 751 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{17}\text{BrN}_2\text{NaO}_2$ [$\text{M}+\text{Na}$] $^+$ 371.0371, found 371.0361.



2'-Bromo-5-(*tert*-butyl)-5'-fluoro-[1,1'-biphenyl]-2-amine (**1t**)

Compound **1t** was prepared from 1-bromo-4-fluoro-2-iodobenzene by using Method B.

1t (Red oil, 0.77 g, 80% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.64 (dd, $J = 8.8, 5.4$ Hz, 1H), 7.27 – 7.21 (m, 1H), 7.10 (dd, $J = 8.9, 3.1$ Hz, 1H), 7.02 (d, $J = 2.3$ Hz, 1H), 6.99 – 6.94 (m, 1H), 6.73 (d, $J = 8.4$ Hz, 1H), 3.45 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.0 (d, $J = 248.4$ Hz), 142.4 (d, $J = 7.9$ Hz), 141.3, 140.7, 134.4 (d, $J = 8.3$ Hz), 127.1, 126.3, 125.7 (d, $J = 1.3$ Hz), 118.9 (d, $J = 22.1$ Hz), 118.6 (d, $J = 3.2$ Hz), 116.3 (d, $J = 22.3$ Hz), 115.5, 34.0, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -114.48. IR (KBr): 3446, 3051, 2970, 1617, 1461, 1266, 760 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{18}\text{BrFN}$ $[\text{M}+\text{H}]^+$ 322.0607, found 322.0606.



2'-Bromo-5-(*tert*-butyl)-6'-chloro-[1,1'-biphenyl]-2-amine (**1u**)

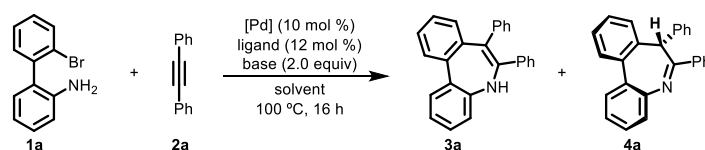
Compound **1u** was prepared from 2-bromo-3-chlore-2-iodobenzene by using Method B.

1u (Red oil, 0.63 g, 62% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.58 (d, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 9.0$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 1H), 7.11 (t, $J = 8.0$ Hz, 1H), 6.97 (s, 1H), 6.72 (d, $J = 8.4$ Hz, 1H), 3.34 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.4, 140.9, 139.2, 135.9, 131.7, 130.0, 129.1, 127.2, 126.4, 126.3, 124.8, 115.6, 34.2, 31.7. IR (KBr): 3460, 3375, 3037, 2960, 1621, 1425, 1291, 765 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{18}\text{BrClN}$ $[\text{M}+\text{H}]^+$ 338.0311, found 338.0310.

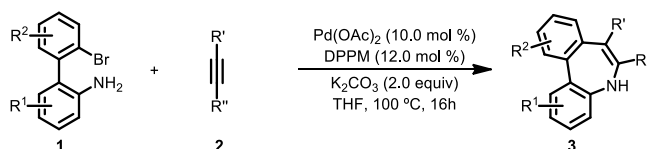
C. Preparation of the enamines **3**:

(I) Optimization of the reaction conditions for the preparation of **3a**:

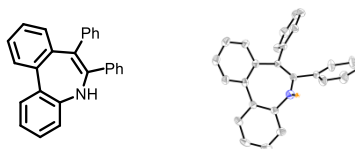
2'-Bromo-[1,1'-biphenyl]-2-amine (**1a**) and diphenylacetylene (**2a**) were chosen as the model substrates to optimize the reaction conditions for the synthesis of enamine **3a**. Several solvents, ligands, palladium sources and bases were surveyed. The optimization details are shown in Table S1, and the optimized reaction conditions were obtained as the following: 10 mol % of $\text{Pd}(\text{OAc})_2$, 12 mol % of DPPM and 2.0 equivalents of K_2CO_3 in THF at 100 $^\circ\text{C}$ for 16 h.

Table S1. Optimization of the reaction conditions for the synthesis of enamine **3a**.^a

entry	[Pd]	ligand	base	solvent	yield (%) ^b	
					3a	4a
1	Pd(OAc) ₂	PPh ₃	K ₂ CO ₃	DMF	61	19
2	Pd(OAc) ₂	PPh ₃	K ₂ CO ₃	DMSO	0	13
3	Pd(OAc) ₂	PPh ₃	K ₂ CO ₃	THF	74	trace
4	Pd(OAc) ₂	—	K ₂ CO ₃	THF	0	0
5	Pd(OAc) ₂	PCy ₃	K ₂ CO ₃	THF	0	0
6	Pd(OAc) ₂	Xphos	K ₂ CO ₃	THF	45	trace
7	Pd(OAc)₂	DPPM	K₂CO₃	THF	92	trace
8	Pd(OAc) ₂	DPPE	K ₂ CO ₃	THF	42	trace
9	Pd(OAc) ₂	DPPP	K ₂ CO ₃	THF	86	trace
10	Pd(OAc) ₂	DPPF	K ₂ CO ₃	THF	71	trace
11	Pd(OAc) ₂	BINAP	K ₂ CO ₃	THF	68	trace
12	Pd(OAc) ₂	Xantphos	K ₂ CO ₃	THF	84	trace
13	PdCl ₂	DPPM	K ₂ CO ₃	THF	8	0
14	[Pd(allyl)Cl] ₂	DPPM	K ₂ CO ₃	THF	0	0
15	Pd ₂ (dba) ₃	DPPM	K ₂ CO ₃	THF	0	0
16	Pd(OAc) ₂	DPPM	Na ₂ CO ₃	THF	59	trace
17	Pd(OAc) ₂	DPPM	Cs ₂ CO ₃	THF	0	13
18	Pd(OAc) ₂	DPPM	K ₃ PO ₄	THF	0	30

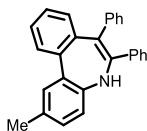
^a0.2 mmol scale. ^bIsolated yield.**(II) General procedure for the preparation of enamines 3:**

In a glovebox, a 25.0 mL vial equipped with a stir bar was charged with Pd(OAc)₂ (22.4 mg, 0.1 mmol), DPPM (46.1 mg, 0.12 mmol) and THF (5.0 mL) was then added. After the catalyst mixture was stirred at room temperature for 10 min, **1** (1.0 mmol), **2** (1.5 mmol) and K₂CO₃ (276.4 mg, 2.0 mmol) were sequentially added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 100 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was concentrated under reduced pressure. The residue was then quickly chromatographed on basic alumina (petroleum ether/THF) to afford the desired product **3**.

**6,7-Diphenyl-5H-dibenzo[b,d]azepine (3a)**

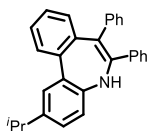
Yellow solid (317.4 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.55 – 7.51 (m, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.28 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.22 – 7.11 (m, 8H), 7.09 – 7.06 (m, 3H), 7.03 – 7.98 (m,

2H), 6.89 (dd, $J = 7.9, 0.9$ Hz, 1H), 6.60 (dd, $J = 5.7, 3.4$ Hz, 1H), 4.76 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.3, 148.0, 141.1, 140.9, 140.7, 140.0, 133.3, 131.7, 130.4, 130.2, 129.7, 128.3, 128.2, 128.1, 127.6, 127.4, 127.0, 126.9, 126.1, 125.8, 124.2, 119.8. IR (KBr): 3366, 3055, 1641, 1593, 1477, 1261, 739 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 346.1596, found 346.1596.



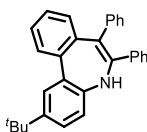
2-Methyl-6,7-diphenyl-5H-dibenzo[b,d]azepine (3b)

Yellow solid (266.0 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, $J = 7.2$ Hz, 1H), 7.35 (s, 1H), 7.29 (dd, $J = 9.6, 2.3$ Hz, 1H), 7.23 – 7.11 (m, 6H), 7.09 (dd, $J = 5.1, 1.6$ Hz, 3H), 7.03 – 6.97 (m, 3H), 6.90 (d, $J = 7.9$ Hz, 1H), 6.52 (d, $J = 7.9$ Hz, 1H), 4.72 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 148.3, 141.2, 140.9, 140.7, 140.0, 133.5, 133.1, 131.7, 130.7, 130.4, 129.6, 128.7, 128.3, 128.1, 127.6, 127.3, 126.9, 126.8, 126.1, 125.6, 119.6, 20.9. IR (KBr): 3373, 3053, 2924, 1604, 1456, 1264, 739 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 360.1752, found 360.1758.



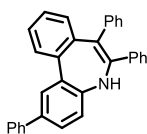
2-Isopropyl-6,7-diphenyl-5H-dibenzo[b,d]azepine (3c)

Yellow solid (243.8 mg, 63% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, $J = 7.8$ Hz, 1H), 7.38 (s, 1H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.18 – 7.13 (m, 6H), 7.11 – 7.08 (m, 3H), 7.03 (t, $J = 5.5$ Hz, 3H), 6.90 (d, $J = 7.9$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 4.73 (s, 1H), 2.96 (dt, $J = 13.6, 6.8$ Hz, 1H), 1.32 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.9, 148.3, 144.5, 141.2, 140.9, 140.8, 140.3, 133.0, 131.8, 130.4, 129.6, 128.3, 128.2, 128.1, 127.5, 127.3, 126.9, 126.8, 126.1, 126.0, 125.4, 119.6, 33.6, 24.2. IR (KBr): 3437, 3058, 2959, 1635, 1431, 1325, 1255, 736 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ 388.2065, found 388.2065.



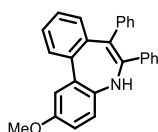
2-(*Tert* -butyl)-6,7-diphenyl-5H-dibenzo[b,d]azepine (3d)

Yellow solid (337.7 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, $J = 1.9$ Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.23 – 7.13 (m, 7H), 7.13 – 7.07 (m, 3H), 7.07 – 7.01 (m, 2H), 6.90 (d, $J = 7.9$ Hz, 1H), 6.54 (d, $J = 8.2$ Hz, 1H), 4.74 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.7, 148.2, 146.7, 141.2, 141.0, 140.7, 140.5, 132.5, 131.7, 130.3, 129.6, 128.2, 128.1, 127.5, 127.3, 127.2, 126.9, 126.7, 126.0, 125.3, 124.9, 119.2, 34.4, 31.5. IR (KBr): 3372, 3055, 2960, 1601, 1494, 1263, 737 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{27}\text{NNa}$ $[\text{M}+\text{Na}]^+$ 424.2041, found 424.2020.



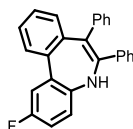
2,6,7-Triphenyl-6,7-diphenyl-5H-dibenzo[b,d]azepine (3e)

Yellow solid (227.3 mg, 54% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, J = 2.0 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.43 (d, J = 6.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.32 (dd, J = 8.1, 2.1 Hz, 1H), 7.28 (d, J = 7.3 Hz, 1H), 7.22 (dd, J = 7.5, 1.1 Hz, 1H), 7.13 – 7.06 (m, 7H), 7.04 – 7.00 (m, 3H), 6.98 – 6.93 (m, 2H), 6.84 (d, J = 7.9 Hz, 1H), 6.60 (d, J = 8.1 Hz, 1H), 4.76 (s, 1H). ^{13}C NMR: (100 MHz, CDCl_3): δ 151.7, 148.0, 141.1, 141.0, 140.8, 140.7, 139.9, 137.2, 133.5, 131.7, 130.4, 129.8, 129.0, 128.8, 128.4, 128.1, 127.6, 127.4, 127.2, 127.1, 127.0, 126.8, 126.7, 126.2, 125.7, 120.1. IR (KBr): 3370, 3023, 2970, 1603, 1265, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 422.1909, found 422.1900.



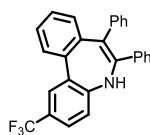
2-Methoxy-6,7-diphenyl-5H-dibenzo[b,d]azepine (3f)

Yellow solid (228.8 mg, 61% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.49 (dd, J = 7.8, 1.1 Hz, 1H), 7.29 (td, J = 7.7, 1.3 Hz, 1H), 7.21 – 7.13 (m, 6H), 7.09 (dd, J = 6.6, 2.3 Hz, 4H), 7.00 (dd, J = 7.0, 2.7 Hz, 2H), 6.92 (dd, J = 7.9, 1.0 Hz, 1H), 6.74 (dd, J = 8.5, 2.9 Hz, 1H), 6.55 (d, J = 8.5 Hz, 1H), 4.63 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.6, 148.6, 145.5, 141.1, 141.0, 140.6, 139.8, 134.4, 131.7, 130.5, 129.4, 128.3, 128.1, 127.6, 127.3, 127.0, 126.9, 126.1, 125.6, 120.5, 115.3, 113.3, 55.7. IR (KBr): 3444, 3031, 2924, 2856, 1622, 1459, 1263, 749 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$ 376.1701, found 376.1669.



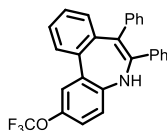
2-Fluoro-6,7-diphenyl-5H-dibenzo[b,d]azepine (3g)

Yellow solid (250.5 mg, 69% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.43 (dd, J = 7.8, 0.9 Hz, 1H), 7.30 (td, J = 7.7, 1.1 Hz, 1H), 7.25 – 7.16 (m, 5H), 7.15 – 7.11 (m, 2H), 7.09 (dd, J = 5.0, 1.8 Hz, 3H), 6.99 (dd, J = 6.6, 3.0 Hz, 2H), 6.92 (d, J = 6.9 Hz, 1H), 6.87 (td, J = 8.3, 2.9 Hz, 1H), 6.55 (dd, J = 8.6, 4.9 Hz, 1H), 4.69 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.0 (d, J = 240.7 Hz), 148.1, 148.0, 147.9, 140.9 (d, J = 2.5 Hz), 140.4, 138.9, 134.9 (d, J = 7.7 Hz), 131.7, 130.5, 129.5, 128.4, 128.1, 127.7, 127.5, 127.4, 127.2, 126.3, 126.0, 120.6 (d, J = 8.3 Hz), 116.3 (d, J = 23.2 Hz), 114.4 (d, J = 22.6 Hz). ^{19}F NMR (376 MHz, CDCl_3): δ -120.43. IR (KBr): 3369, 3057, 2923, 1638, 1599, 1258, 766 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{19}\text{FN}$ $[\text{M}+\text{H}]^+$ 364.1502, found 364.1500.



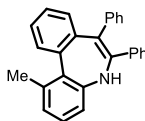
6,7-Diphenyl-2-(trifluoromethyl)-5H-dibenzo[b,d]azepine (3h)

Yellow solid (335.3 mg, 81% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.78 (s, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.23 – 7.18 (m, 4H), 7.16 – 7.09 (m, 5H), 7.04 – 7.00 (m, 2H), 6.92 (d, J = 7.9 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 4.93 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.5, 147.2, 140.9, 140.6, 140.3, 138.7, 133.5, 131.6, 130.6, 129.9, 128.5, 128.1, 127.8, 127.7, 127.6, 127.5, 127.3 (q, J = 3.8 Hz), 126.4, 126.3, 126.2 (q, J = 32.4 Hz), 125.1 (q, J = 3.7 Hz), 124.5 (q, J = 271.7 Hz), 119.7. ^{19}F NMR (376 MHz, CDCl_3): δ -61.69. IR (KBr): 3366, 3059, 2925, 1606, 1484, 1260, 737 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{18}\text{F}_3\text{NNa}$ $[\text{M}+\text{Na}]^+$ 436.1289, found 436.1274.



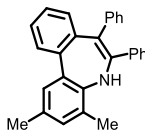
6,7-Diphenyl-2-(trifluoromethoxy)-5H-dibenzo[b,d]azepine (3i)

Yellow solid (343.6 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.43 – 7.37 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.22 – 7.07 (m, 9H), 7.06 – 6.99 (m, 3H), 6.92 (dd, J = 7.8, 3.7 Hz, 1H), 6.59 (d, J = 8.5 Hz, 1H), 4.78 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.8, 147.8, 145.9, 145.8, 140.9, 140.7, 140.3, 138.6, 134.6, 131.6, 130.5, 129.6, 128.4, 128.1, 127.7, 127.6, 127.3, 126.3, 126.0, 122.7, 120.7 (q, J = 256.8 Hz), 120.6, 120.4. ^{19}F NMR (376 MHz, CDCl_3): δ -57.96. IR (KBr): 3436, 3064, 2960, 1637, 1474, 1256, 743 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{18}\text{F}_3\text{NNaO}$ $[\text{M}+\text{Na}]^+$ 452.1238, found 452.1210.



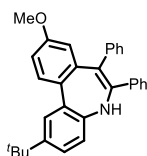
1-Methyl-6,7-diphenyl-5H-dibenzo[b,d]azepine (3j)

Yellow solid (212.2 mg, 59% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.37 (d, J = 7.2 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 4H), 7.14 – 7.09 (m, 5H), 7.07 (d, J = 4.7 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.98 (d, J = 7.8 Hz, 1H), 6.49 (d, J = 7.0 Hz, 1H), 4.71 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 154.5, 148.2, 141.9, 140.6, 140.4, 138.9, 137.5, 132.2, 131.6, 131.2, 129.8, 128.4, 128.1, 127.6, 127.4, 127.1, 127.0, 126.5, 126.3, 126.2, 125.7, 117.5, 21.6. IR (KBr): 3361, 3056, 2923, 1656, 1463, 1265, 735 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 360.1752, found 360.1752.



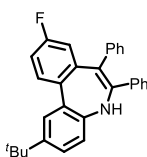
2,4-Dimethyl-6,7-diphenyl-5H-dibenzo[b,d]azepine (3k)

Yellow solid (340.0 mg, 91% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.3 Hz, 1H), 7.21 – 7.13 (m, 7H), 7.11 – 7.07 (m, 3H), 7.00 (dd, J = 6.5, 2.9 Hz, 2H), 6.92 – 6.87 (m, 2H), 4.84 (s, 1H), 2.36 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.5, 147.8, 141.2, 141.0, 140.9, 140.6, 133.5, 132.8, 131.7, 130.3, 130.2, 129.7, 128.7, 128.4, 127.7, 127.6, 127.2, 126.9, 126.6, 126.5, 126.1, 20.8, 17.4. IR (KBr): 3438, 3059, 2924, 1615, 1429, 1256, 737 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{28}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 374.1909, found 374.1905.



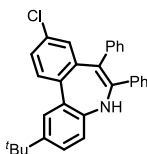
2-(*Tert*-butyl)-9-methoxy-6,7-diphenyl-5*H*-dibenzo[*b,d*]azepine (3l)

Yellow solid (207.2 mg, 48% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.50 – 7.47 (m, 1H), 7.40 (d, J = 8.6 Hz, 1H), 7.20 – 7.13 (m, 6H), 7.11 – 7.06 (m, 3H), 7.06 – 7.01 (m, 2H), 6.87 (dd, J = 8.6, 2.6 Hz, 1H), 6.53 (d, J = 8.2 Hz, 1H), 6.45 (d, J = 2.6 Hz, 1H), 4.75 (s, 1H), 3.65 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.3, 148.9, 148.2, 146.7, 142.2, 141.0, 140.8, 133.2, 132.3, 131.7, 130.8, 128.3, 128.1, 127.6, 127.3, 126.8, 126.1, 125.1, 124.4, 119.1, 115.7, 113.0, 55.2, 34.4, 31.6. IR (KBr): 3434, 3053, 2925, 1615, 1455, 1398, 1267, 753 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{29}\text{NNaO}$ $[\text{M}+\text{Na}]^+$ 454.2147, found 454.2140.



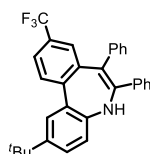
2-(*Tert*-butyl)-9-fluoro-6,7-diphenyl-5*H*-dibenzo[*b,d*]azepine (3m)

Yellow solid (310.2 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, J = 1.7 Hz, 1H), 7.44 (dd, J = 8.5, 6.1 Hz, 1H), 7.25 – 7.16 (m, 6H), 7.15 – 7.09 (m, 3H), 7.07 – 6.99 (m, 3H), 6.63 (dd, J = 10.9, 2.5 Hz, 1H), 6.56 (d, J = 8.2 Hz, 1H), 4.80 (s, 1H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.8 (d, J = 244.0 Hz), 149.3, 149.2, 147.0, 143.2 (d, J = 7.4 Hz), 140.6, 140.5, 136.6 (d, J = 2.7 Hz), 131.7, 131.4, 131.3, 128.4, 128.1, 127.8, 127.5, 127.1, 126.4, 125.1, 124.4, 119.4, 116.7 (d, J = 22.0 Hz), 114.1 (d, J = 22.0 Hz), 34.5, 31.6. ^{19}F NMR (376 MHz, CDCl_3): δ -116.13. IR (KBr): 3370, 3054, 2960, 1491, 1261, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{27}\text{FN}$ $[\text{M}+\text{H}]^+$ 420.2128, found 420.2120.



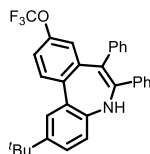
2-(*Tert*-butyl)-9-chloro-6,7-diphenyl-5*H*-dibenzo[*b,d*]azepine (3n)

Yellow solid (292.2 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, J = 2.2 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.24 (dd, J = 8.4, 2.2 Hz, 1H), 7.21 – 7.16 (m, 4H), 7.15 – 7.07 (m, 5H), 7.00 (dd, J = 6.7, 2.8 Hz, 2H), 6.86 (d, J = 2.2 Hz, 1H), 6.53 (d, J = 8.2 Hz, 1H), 4.75 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.5, 147.1, 142.8, 140.5, 140.4, 139.0, 132.9, 131.7, 131.6, 131.0, 130.0, 128.4, 128.0, 127.8, 127.5, 127.0, 126.4, 125.4, 124.2, 119.4, 34.4, 31.6. IR (KBr): 3372, 3056, 2960, 1640, 1593, 1482, 1261, 749 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{27}\text{ClN}$ $[\text{M}+\text{H}]^+$ 436.1832, found 436.1813.



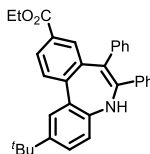
2-(*Tert*-butyl-6,7-diphenyl-9-(trifluoromethyl)-5*H*-dibenzo[*b,d*]azepine (3o)

Yellow solid (249.1 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, $J = 8.2$ Hz, 1H), 7.53 (d, $J = 2.2$ Hz, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.19 (m, 3H), 7.19 – 7.15 (m, 3H), 7.12 (dd, $J = 6.9, 3.6$ Hz, 3H), 7.03 (dd, $J = 6.6, 2.9$ Hz, 2H), 6.57 (d, $J = 8.2$ Hz, 1H), 4.79 (s, 1H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.1, 149.9, 147.3, 144.1, 141.8, 140.5, 140.2, 131.7, 131.4, 130.1, 128.8 (q, $J = 32.3$ Hz), 128.4, 128.0, 127.8, 127.6, 127.3, 127.0 (q, $J = 3.8$ Hz), 126.6, 126.0, 124.4, 124.2 (q, $J = 272.4$ Hz), 123.3 (q, $J = 4.0$ Hz), 119.6, 34.5, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -62.69. IR (KBr): 3367, 3056, 2961, 1605, 1495, 1331, 1260, 747 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{26}\text{F}_3\text{NNa}$ $[\text{M}+\text{Na}]^+$ 492.1915, found 492.1912.



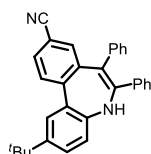
2-(*Tert*-butyl-6,7-diphenyl-9-(trifluoromethoxy)-5*H*-dibenzo[*b,d*]azepine (3p)

Yellow solid (329.8 mg, 68% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.48 – 7.43 (m, 2H), 7.23 – 7.12 (m, 7H), 7.10 (dd, $J = 5.0, 1.9$ Hz, 3H), 7.00 (dd, $J = 6.6, 3.1$ Hz, 2H), 6.71 (d, $J = 2.1$ Hz, 1H), 6.54 (d, $J = 8.2$ Hz, 1H), 4.78 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.6, 149.5, 148.1, 147.1, 143.0, 140.5, 140.3, 139.2, 131.6, 131.4, 131.0, 128.4, 128.0, 127.8, 127.6, 127.2, 126.5, 125.5, 124.3, 122.5, 120.4 (q, $J = 257.0$ Hz), 119.5, 119.0, 34.4, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -57.69. IR (KBr): 3433, 3057, 2964, 1663, 1363, 1262, 748 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{27}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 486.2045, found 486.2043.



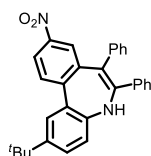
Ethyl 2-(*tert*-butyl)-6,7-diphenyl-5*H*-dibenzo[*b,d*]azepine-9-carboxylate (3q)

Yellow solid (407.6 mg, 86% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.61 (d, $J = 1.6$ Hz, 1H), 7.53 (d, $J = 2.1$ Hz, 1H), 7.50 (d, $J = 8.2$ Hz, 1H), 7.23 (dd, $J = 8.2, 2.2$ Hz, 1H), 7.21 – 7.14 (m, 5H), 7.13 – 7.07 (m, 3H), 7.07 – 7.01 (m, 2H), 6.56 (d, $J = 8.2$ Hz, 1H), 4.75 (s, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.40 (s, 9H), 1.30 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.5, 150.1, 149.1, 147.0, 145.1, 141.3, 140.6, 140.5, 131.7, 131.5, 129.8, 128.7, 128.3, 128.1, 127.7, 127.5, 127.4, 127.2, 126.4, 125.9, 124.8, 119.5, 60.8, 34.4, 31.5, 14.3. IR (KBr): 3360, 3056, 2962, 1713, 1602, 1459, 1390, 1255, 745 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{33}\text{H}_{31}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 496.2252, found 496.2247.



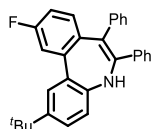
2-(Tert-butyl)-6,7-diphenyl-5H-dibenzo[b,d]azepine-9-carbonitrile (3r)

Yellow solid (269.0 mg, 63% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.51 (s, 2H), 7.47 (d, J = 2.2 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.22 – 7.18 (m, 3H), 7.18 – 7.08 (m, 6H), 7.04 – 6.97 (m, 2H), 6.55 (d, J = 8.2 Hz, 1H), 4.81 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.5, 150.1, 147.4, 145.3, 142.5, 140.2, 139.9, 133.9, 131.6, 130.9, 130.4, 129.6, 128.4, 128.0, 127.9, 127.7, 127.2, 126.8, 126.4, 123.5, 119.7, 119.1, 110.4, 34.5, 31.5. IR (KBr): 3368, 3055, 2961, 2228, 1601, 1265, 753 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{26}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 449.1994, found 449.1994.



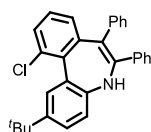
2-(Tert-butyl)-9-nitro-6,7-diphenyl-5H-dibenzo[b,d]azepine (3s)

Yellow solid (307.7 mg, 69% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.08 (dd, J = 8.6, 2.3 Hz, 1H), 7.73 (d, J = 2.3 Hz, 1H), 7.55 (d, J = 8.7 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.28 (m, 1H), 7.23 – 7.18 (m, 3H), 7.17 – 7.10 (m, 5H), 7.07 – 7.00 (m, 2H), 6.59 – 6.56 (d, J = 8.3 Hz, 1H), 4.81 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.6, 150.2, 147.5, 147.2, 146.6, 142.7, 140.2, 139.8, 131.6, 130.6, 130.5, 128.4, 128.1, 127.9, 127.8, 127.3, 126.8, 126.7, 125.0, 123.7, 121.2, 119.8, 34.5, 31.5. IR (KBr): 3368, 3059, 2961, 1640, 1515, 1344, 1260, 745 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 469.1892, found 469.1896.



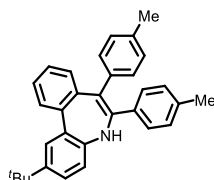
2-(Tert-butyl)-10-fluoro-6,7-diphenyl-5H-dibenzo[b,d]azepine (3t)

Yellow solid (301.7 mg, 72% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, J = 1.9 Hz, 1H), 7.23 – 7.13 (m, 7H), 7.12 – 7.06 (m, 3H), 7.04 – 6.98 (m, 2H), 6.89 – 6.83 (m, 2H), 6.55 (d, J = 8.2 Hz, 1H), 4.74 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.4 (d, J = 246.1 Hz), 149.4, 147.8, 147.0, 142.6 (d, J = 7.5 Hz), 141.1, 140.6, 137.0 (d, J = 2.8 Hz), 132.3 (d, J = 8.3 Hz), 131.7, 128.6 (d, J = 12.6 Hz), 128.3, 128.1, 127.7, 127.4, 127.0, 126.2, 125.7, 124.7, 119.5, 115.7 (d, J = 21.9 Hz), 113.7 (d, J = 21.2 Hz), 34.5, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -115.86. IR (KBr): 3435, 3050, 2958, 1604, 1491, 1265, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{27}\text{FN}$ $[\text{M}+\text{H}]^+$ 420.2128, found 420.2125.



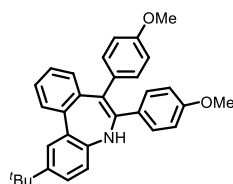
2-(Tert-butyl)-11-chloro-6,7-diphenyl-5H-dibenzo[b,d]azepine (3u)

Yellow solid (392.4 mg, 90% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.74 (d, J = 2.2 Hz, 1H), 7.39 (dd, J = 7.9, 1.1 Hz, 1H), 7.23 – 7.17 (m, 4H), 7.12 – 7.07 (m, 5H), 7.05 (d, J = 7.9 Hz, 1H), 6.99 (dd, J = 6.5, 3.1 Hz, 2H), 6.84 (dd, J = 8.0, 1.1 Hz, 1H), 6.59 (d, J = 8.2 Hz, 1H), 4.75 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.3, 150.0, 145.5, 143.8, 140.6, 140.3, 138.1, 132.4, 131.6, 130.8, 128.7, 128.6, 128.3, 128.2, 127.9, 127.6, 127.4, 127.1, 126.2, 125.0, 124.5, 119.5, 34.4, 31.4. IR (KBr): 3362, 3055, 2961, 1420, 1387, 1262, 738 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{ClNNa}$ $[\text{M}+\text{Na}]^+$ 458.1651, found 458.1651.



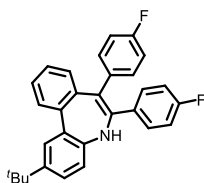
2-(*Tert*-butyl-6,7-di-*p*-toyl-5*H*-dibenzo[*b,d*]azepine (3a')

Yellow solid (364.7 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, J = 2.1 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.19 (dd, J = 8.2, 2.2 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.94 – 6.87 (m, 5H), 6.54 (d, J = 8.2 Hz, 1H), 4.72 (s, 1H), 2.29 (s, 3H), 2.25 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 148.0, 146.7, 141.3, 140.5, 138.4, 138.1, 136.9, 135.5, 132.6, 131.6, 130.4, 129.6, 129.0, 128.3, 128.0, 127.2, 126.8, 126.7, 125.1, 125.0, 119.2, 34.5, 31.6, 21.3, 21.2. IR (KBr): 3455, 3020, 2958, 1641, 1501, 1461, 1394, 1265, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{32}\text{N}$ $[\text{M}+\text{H}]^+$ 430.2535, found 430.2526.



2-(*Tert*-butyl-6,7-bis(4-methoxyphenyl)-5*H*-dibenzo[*b,d*]azepine (3b')

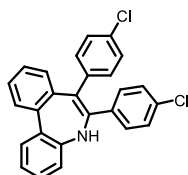
Yellow solid (382.6 mg, 83% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.55 (s, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.00 – 6.90 (m, 3H), 6.74 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 6.56 (d, J = 8.2 Hz, 1H), 4.73 (s, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.4, 157.7, 149.9, 147.6, 146.7, 141.4, 140.4, 133.9, 133.6, 132.8, 132.6, 130.4, 129.6, 129.5, 127.2, 126.8, 126.7, 125.0, 124.8, 119.2, 113.6, 113.0, 55.2, 55.1, 34.5, 31.6. IR (KBr): 3374, 3055, 2959, 1639, 1504, 1460, 1226, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{32}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 462.2433, found 462.2427.



2-(*Tert*-butyl-6,7-bis(4-fluorophenyl)-5*H*-dibenzo[*b,d*]azepine (3c')

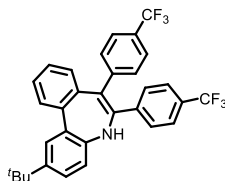
Yellow solid (402.0 mg, 92% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.22 (dd, J = 8.2, 2.1 Hz, 1H), 7.18 (d, J = 7.3 Hz, 1H), 7.14

(dd, $J = 8.5, 5.5$ Hz, 2H), 6.99 (dd, $J = 8.4, 5.6$ Hz, 2H), 6.93 – 6.86 (m, 3H), 6.82 (t, $J = 8.7$ Hz, 2H), 6.55 (d, $J = 8.2$ Hz, 1H), 4.67 (s, 1H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.7 (d, $J = 247.4$ Hz), 161.3 (d, $J = 245.7$ Hz), 149.6, 147.5, 147.1, 140.7, 140.5, 137.1 (d, $J = 2.7$ Hz), 136.8 (d, $J = 3.2$ Hz), 133.3 (d, $J = 7.9$ Hz), 132.5, 130.3, 130.0 (d, $J = 8.0$ Hz), 129.9, 127.4, 127.2, 126.9, 125.2, 124.8, 119.4, 115.5 (d, $J = 21.4$ Hz), 114.7 (d, $J = 21.2$ Hz), 34.5, 31.6. ^{19}F NMR (376 MHz, CDCl_3): δ -113.28, -115.81. IR (KBr): 3433, 3016, 2960, 1603, 1502, 1395, 1266, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$ 438.2033, found 438.2032.



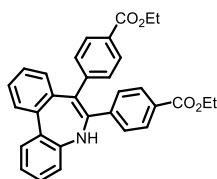
6,7-Bis(4-chlorophenyl)-5H-dibenzo[b,d]azepine (3d')

Yellow solid (272.6 mg, 66% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.54 – 7.49 (m, 1H), 7.44 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.30 (td, $J = 7.6, 1.3$ Hz, 1H), 7.21 – 7.14 (m, 5H), 7.11 – 7.04 (m, 4H), 6.95 – 6.89 (m, 2H), 6.84 (dd, $J = 7.9, 1.1$ Hz, 1H), 6.63 – 6.56 (m, 1H), 4.66 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.9, 147.1, 140.2, 140.0, 139.3, 138.7, 133.5, 133.1, 132.9, 132.3, 130.3, 130.2, 129.9, 129.5, 128.8, 128.3, 128.1, 127.4, 127.0, 125.2, 124.5, 119.8. IR (KBr): 3366, 2918, 1588, 1478, 1262, 827, 750 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{N}$ $[\text{M}+\text{H}]^+$ 414.0816, found 414.0814.



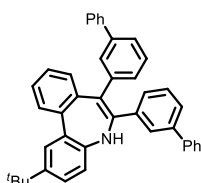
2-(tert-butyl-6,7-bis(4-(trifluoromethyl)phenyl)-5H-dibenzo[b,d]azepine (3e')

Yellow solid (424.2 mg, 79% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.53 (d, $J = 1.6$ Hz, 1H), 7.49 (d, $J = 8.2$ Hz, 3H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.28 (s, 1H), 7.26 – 7.25 (m, 1H), 7.21 (dd, $J = 8.4, 2.2$ Hz, 1H), 7.16 (d, $J = 8.3$ Hz, 1H), 7.12 (d, $J = 8.1$ Hz, 2H), 6.76 (d, $J = 7.9$ Hz, 1H), 6.53 (d, $J = 8.2$ Hz, 1H), 4.68 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.9, 146.5, 146.4, 143.5, 142.3, 139.6, 138.7, 131.2, 130.9, 129.3, 128.8, 128.6 (q, $J = 32.6$ Hz), 127.5 (q, $J = 32.6$ Hz), 127.3, 126.5, 126.3, 125.9, 124.6 (q, $J = 7.2$ Hz), 124.3, 124.0, 123.7 (q, $J = 3.5$ Hz), 123.0 (q, $J = 271.9$ Hz), 122.8 (q, $J = 272.2$ Hz), 118.4, 33.4, 30.4. ^{19}F NMR (376 MHz, CDCl_3): δ -62.35, -62.60. IR (KBr): 3364, 3059, 2962, 1613, 1325, 1260, 745 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{26}\text{F}_6\text{N}$ $[\text{M}+\text{H}]^+$ 538.1969, found 538.1969.



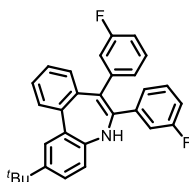
Diethyl 4,4'-(5H-dibenzo[b,d]azepine-6,7-diyl)dibenzoate (3f')

Yellow solid (410.8 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.88 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.21 – 7.13 (m, 5H), 7.07 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 7.8 Hz, 1H), 6.60 – 6.56 (m, 1H), 4.77 (s, 1H), 4.33 (dq, J = 12.3, 7.1 Hz, 4H), 1.36 (dt, J = 8.9, 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.4, 166.0, 151.7, 147.7, 145.7, 144.3, 140.2, 139.9, 133.1, 131.6, 130.4, 130.3, 129.9, 129.6, 129.1, 128.5, 128.3, 128.1, 127.6, 127.1, 125.8, 124.6, 119.9, 61.1, 60.9, 14.3. IR (KBr): 3346, 3057, 2982, 1715, 1606, 1275, 761, 709 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{28}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 490.2018, found 490.2009.



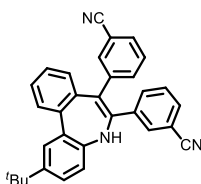
6,7-Di([1,1'-biphenyl]-3-yl)-2-(tert-butyl)-5H-dibenzo[b,d]azepine (3g')

Yellow solid (431.3 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, J = 2.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.43 (d, J = 7.8 Hz, 2H), 7.37 – 7.28 (m, 14H), 7.24 – 7.15 (m, 4H), 7.07 (d, J = 7.7 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 6.58 (d, J = 8.2 Hz, 1H), 4.86 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.7, 148.5, 147.0, 141.8, 141.2, 141.1, 140.9, 140.7, 140.6, 132.6, 131.1, 130.8, 130.5, 129.8, 129.0, 128.8, 128.6, 128.2, 127.8, 127.5, 127.4, 127.2, 127.1, 126.9, 126.6, 126.5, 126.1, 126.0, 125.6, 125.5, 125.4, 125.1, 125.0, 119.4, 34.5, 31.6. IR (KBr): 3436, 3032, 2958, 1632, 1470, 1313, 1267, 756 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{42}\text{H}_{36}\text{N}$ $[\text{M}+\text{H}]^+$ 554.2848, found 554.2836.



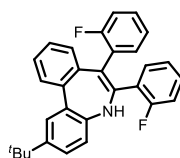
2-(Tert-butyl)-6,7-bis(3-fluorophenyl)-5H-dibenzo[b,d]azepine (3h')

Yellow solid (380.2 mg, 87% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, J = 2.2 Hz, 1H), 7.48 (dd, J = 7.8, 0.9 Hz, 1H), 7.32 (td, J = 7.7, 1.2 Hz, 1H), 7.25 – 7.14 (m, 3H), 7.08 (dd, J = 14.0, 8.0 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.94 – 6.85 (m, 3H), 6.82 (dd, J = 8.0, 1.9 Hz, 2H), 6.80 – 6.73 (m, 1H), 6.55 (d, J = 8.2 Hz, 1H), 4.69 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.4 (d, J = 247.3 Hz), 162.3 (d, J = 245.8 Hz), 149.2, 147.3 (d, J = 1.8 Hz), 147.1, 143.0 (d, J = 7.8 Hz), 142.1 (d, J = 7.5 Hz), 140.5, 140.0, 132.3, 130.3, 130.2, 130.1, 129.8, 129.1 (d, J = 8.5 Hz), 127.5 (d, J = 2.7 Hz), 127.3, 126.9, 125.2, 124.7 (d, J = 1.8 Hz), 123.8 (d, J = 2.9 Hz), 119.3, 118.4 (d, J = 21.1 Hz), 115.1 (d, J = 21.8 Hz), 114.6 (d, J = 21.0 Hz), 113.4 (d, J = 20.9 Hz), 34.4, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -111.96, -113.81. IR (KBr): 3373, 3059, 2961, 1643, 1476, 1393, 1265, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$ 438.2033, found 438.2033.



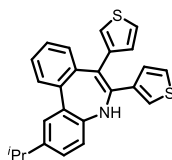
3,3'-(2-(*Tert*-butyl)-5*H*-dibenzo[*b,d*]azepine-6,7-diyl)dibenzonitrile (3i')

Yellow solid (207.5 mg, 46% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.54 – 7.42 (m, 3H), 7.40 – 7.28 (m, 5H), 7.24 – 7.11 (m, 5H), 6.70 (d, J = 7.2 Hz, 1H), 6.50 (d, J = 8.2 Hz, 1H), 4.62 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.7, 147.6, 146.9, 141.8, 140.8, 140.6, 139.0, 136.0, 134.9, 132.6, 132.1, 131.6, 131.5, 130.4, 130.1, 130.0, 129.7, 128.8, 127.9, 127.5, 127.1, 125.5, 124.8, 119.5, 118.4, 118.0, 112.9, 112.1, 34.5, 31.4. IR (KBr): 3354, 3061, 2959, 2230, 1606, 1475, 1264, 752 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{26}\text{N}_3$ $[\text{M}+\text{H}]^+$ 452.2127, found 452.2126.



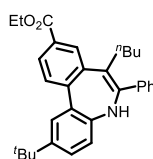
2-(*Tert*-butyl)-6,7-bis(3-fluorophenyl)-5*H*-dibenzo[*b,d*]azepine (3j')

Yellow solid (384.6 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.21 – 7.14 (m, 3H), 7.13 – 7.07 (m, 3H), 6.99 (t, J = 8.7 Hz, 1H), 6.92 – 6.83 (m, 4H), 6.54 (d, J = 8.2 Hz, 1H), 4.71 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.5 (d, J = 245.8 Hz), 159.2 (d, J = 247.0 Hz), 149.5, 146.9, 144.4, 140.4, 139.6, 133.2 (d, J = 3.0 Hz), 132.4, 130.4 (d, J = 3.5 Hz), 129.9, 129.7 (d, J = 7.9 Hz), 129.2, 128.8 (d, J = 8.1 Hz), 128.4 (d, J = 16.2 Hz), 127.5 (d, J = 17.1 Hz), 127.4, 127.3, 126.9, 125.0, 123.8 (d, J = 3.1 Hz), 123.5 (d, J = 3.4 Hz), 121.3, 119.3, 115.6 (d, J = 21.7 Hz), 115.2 (d, J = 22.4 Hz), 34.4, 31.5. ^{19}F NMR (376 MHz, CDCl_3): δ -112.72, -112.83. IR (KBr): 3435, 3062, 2959, 1615, 1486, 1394, 1265, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$ 438.2033, found 438.2032.



2-Isopropyl-6,7-di(thiophen-3-yl)-5*H*-dibenzo[*b,d*]azepine (3k')

Yellow solid (259.4 mg, 65% yield). ^1H NMR (400 MHz, C_6D_6): δ 7.46 – 7.39 (m, 2H), 7.19 (dd, J = 7.9, 1.3 Hz, 1H), 7.09 (td, J = 7.5, 1.4 Hz, 1H), 7.00 (td, J = 7.7, 1.4 Hz, 1H), 6.89 (dd, J = 8.0, 2.0 Hz, 1H), 6.69 – 6.62 (m, 3H), 6.62 – 6.58 (m, 2H), 6.55 (dd, J = 5.0, 1.3 Hz, 1H), 6.19 (d, J = 8.0 Hz, 1H), 4.43 (s, 1H), 2.75 (dt, J = 13.7, 6.9 Hz, 1H), 1.18 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.9, 144.7, 143.6, 141.1, 141.0, 140.6, 139.9, 133.1, 130.5, 129.9, 129.7, 128.1, 127.4, 127.0, 126.8, 126.1, 125.3, 124.6, 124.1, 123.4, 120.8, 119.6, 33.6, 24.2. IR (KBr): 3366, 3101, 2958, 1638, 1462, 1263, 735 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{22}\text{NS}_2$ $[\text{M}+\text{H}]^+$ 400.1194, found 400.1206.



Ethyl 2-(*tert*-butyl)-7-butyl-6-phenyl-5*H*-dibenzo[*b,d*]azepine-9-carboxylate (3l')

One regioisomer was isolated, and the other possible isomer was not found in the crude ^1H NMR. Yellow solid (263.1 mg, 58% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.12 (s, 1H), 7.95 (d, J = 8.0 Hz,

1H), 7.53 – 7.34 (m, 7H), 7.28 (s, 1H), 6.74 (d, $J = 8.2$ Hz, 1H), 4.56 (s, 1H), 4.42 (dd, $J = 14.2, 7.1$ Hz, 2H), 2.56 – 2.40 (m, 2H), 1.43 (t, $J = 6.8$ Hz, 3H), 1.38 (s, 9H), 1.15 – 1.09 (m, 2H), 1.03 – 0.92 (m, 2H), 0.58 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.8, 151.5, 147.6, 146.6, 145.9, 141.2, 141.1, 132.1, 130.0, 129.1, 128.7, 128.6, 128.0, 127.3, 126.9, 125.5, 122.2, 118.6, 60.9, 34.4, 31.5, 31.4, 31.3, 21.8, 14.4, 13.7. IR (KBr): 3449, 3059, 2960, 1709, 1630, 1461, 1389, 1288, 748 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{36}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 454.2746, found 454.2757.

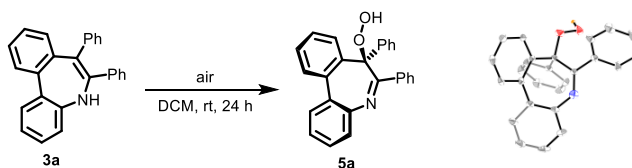
D. Preliminary studies on the stability of enamine 3a:

(I) Stability of enamine 3a towards silica gel:



To a solution of **3a** (103.6 mg, 0.30 mmol) in DCM (3.0 mL), silica gel (518 mg) was added. The resulting mixture was stirred at room temperature for 24 h, filtered, and concentrated *in vacuo*. The residue was purified by basic alumina chromatography (petroleum ether/ethyl acetate = 50:1) to afford the imine product **4a** in 14% yield (14.6 mg). The spectral data of **4a** are in accordance with the literature values.⁶

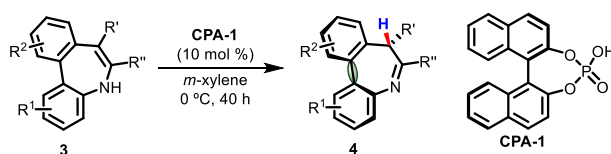
(II) Stability of enamine 3a towards the air:



The solution of **3a** (103.6 mg, 0.30 mmol) in DCM (3.0 mL) was stirred under the air at room temperature for 24 h. The mixture was then purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford peroxide **5a** in 22% yield (24.9 mg). ^1H NMR (400 MHz, CDCl_3): δ 8.18 – 8.10 (m, 1H), 7.90 – 7.82 (m, 2H), 7.74 – 7.70 (m, 1H), 7.70 – 7.62 (m, 1H), 7.55 (td, $J = 7.6, 1.2$ Hz, 1H), 7.49 – 7.41 (m, 3H), 7.38 (d, $J = 7.5$ Hz, 1H), 7.21 (s, 1H), 7.13 (qd, $J = 8.0, 1.5$ Hz, 2H), 7.04 – 6.81 (m, 5H), 6.79 – 6.49 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.7, 145.3, 139.5, 138.9, 135.6, 134.6, 131.0, 129.8, 129.3, 129.0, 128.6, 128.3, 128.1, 128.0, 127.7, 127.1, 125.3, 124.3, 123.9, 91.7. IR (KBr): 3059, 2851, 1620, 1475, 1265, 733 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 378.1494, found 378.1490.

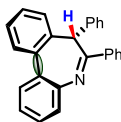
E. Catalytic results:

The chiral phosphoric acids catalyzed enantioselective tautomerization of enamines 3:



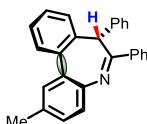
In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with **CPA-1** (7.2 mg, 0.02 mmol)

and *m*-xylene (0.34 mL), stirred for 10 min, and a *m*-xylene (0.34 mL) solution of enamine **3** (0.2 mmol) was added. The vial was immediately sealed with a Teflon screw cap and stirred at 0 °C for 40 h. The mixture was then directly chromatographed on basic (petroleum ether/ethyl acetate) to afford the desired product **4**.



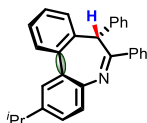
6,7-Diphenyl-7H-dibenzo[*b,d*]azepine (**4a**)

White solid (61.4 mg, 89% yield). 93% ee, $[\alpha]_D^{17} = 474.00$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.08 (dd, $J = 6.3, 2.9$ Hz, 2H), 7.80 – 7.72 (m, 1H), 7.46 – 7.40 (m, 7H), 7.24 (d, $J = 3.7$ Hz, 1H), 7.14 (t, $J = 7.5$ Hz, 1H), 6.97 (t, $J = 7.5$ Hz, 1H), 6.94 – 6.86 (m, 3H), 6.79 – 6.71 (m, 2H), 6.03 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.2, 146.2, 140.4, 138.9, 137.4, 136.8, 130.9, 130.4, 129.8, 129.8, 128.7, 128.6, 128.2, 127.9, 127.8, 127.6, 127.5, 126.7, 126.3, 126.1, 124.2, 53.8. The ee of **4a** was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{minor}} = 12.6$ min, $t_{\text{major}} = 16.8$ min). The spectral data are in accordance with the literature values.⁶



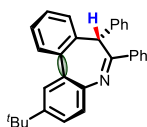
2-Methyl-6,7-diphenyl-7H-dibenzo[*b,d*]azepine (**4b**)

White solid (68.2 mg, 95% yield). 87% ee, $[\alpha]_D^{17} = 436.86$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.06 (dd, $J = 6.6, 2.4$ Hz, 2H), 7.82 – 7.70 (m, 1H), 7.55 – 7.31 (m, 5H), 7.25 (d, $J = 0.6$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 1H), 7.02 – 6.86 (m, 4H), 6.83 – 6.72 (m, 2H), 6.00 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.3, 144.1, 140.6, 138.8, 137.6, 136.9, 133.6, 130.6, 130.2, 129.8, 128.8, 128.7, 128.5, 128.2, 127.9, 127.8, 127.5, 126.7, 126.4, 126.2, 53.8, 21.1. The ee of compound **4b** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, $t_{\text{minor}} = 9.1$ min, $t_{\text{major}} = 10.8$ min). The spectral data are in accordance with the literature values.⁶



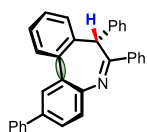
2-Isopropyl-6,7-diphenyl-7H-dibenzo[*b,d*]azepine (**4c**)

White solid (74.4 mg, 96% yield). 93% ee, $[\alpha]_D^{17} = 475.66$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.09 (dd, $J = 6.7, 2.9$ Hz, 2H), 7.77 (d, $J = 7.0$ Hz, 1H), 7.52 – 7.36 (m, 6H), 7.30 – 7.26 (m, 1H), 7.14 (d, $J = 8.2$ Hz, 1H), 7.00 (dd, $J = 8.2, 1.9$ Hz, 1H), 6.92 – 6.86 (m, 3H), 6.80 – 6.70 (m, 2H), 6.02 (s, 1H), 2.90 – 2.78 (m, 1H), 1.17 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.8, 144.7, 144.5, 140.5, 138.9, 137.5, 137.3, 130.9, 130.2, 129.7, 129.6, 128.7, 128.1, 127.9, 127.8, 127.4, 126.7, 126.4, 126.2, 125.9, 125.7, 53.7, 33.8, 24.2, 23.8. IR (KBr): 3056, 2923, 1615, 1450, 1333, 1267, 747 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ 388.2065, found 388.2047. The ee of compound **4c** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{minor}} = 9.6$ min, $t_{\text{major}} = 12.8$ min).



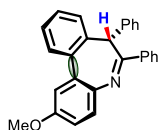
2-(*Tert*-butyl)-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (4d)

White solid (76.2 mg, 95% yield). 97% ee, $[\alpha]_D^{17} = 842.86$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.07 – 7.93 (m, 2H), 7.66 (d, $J = 7.4$ Hz, 1H), 7.42 – 7.30 (m, 7H), 7.05 (s, 2H), 6.78 (d, $J = 5.2$ Hz, 3H), 6.72 – 6.59 (m, 2H), 5.92 (s, 1H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.9, 145.8, 143.0, 139.4, 137.9, 136.4, 136.3, 129.5, 129.2, 128.6, 128.5, 127.6, 126.9, 126.8, 126.7, 126.3, 125.6, 124.8, 124.7, 124.3, 123.5, 52.6, 33.3, 30.2. The ee of compound **4d** was determined by HPLC using an IC column (n -hexane/ i -PrOH = 95/5, flow rate = 0.5 mL/min, $t_{\text{minor}} = 9.4$ min, $t_{\text{major}} = 11.3$ min). The spectral data are in accordance with the literature values.⁶



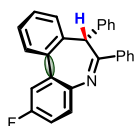
2,6,7-Triphenyl-7*H*-dibenzo[*b,d*]azepine (4e)

White solid (79.2 mg, 94% yield). 93% ee, $[\alpha]_D^{17} = 523.80$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.09 (dd, $J = 3.7, 2.3$ Hz, 2H), 7.86 – 7.78 (m, 1H), 7.71 – 7.65 (m, 1H), 7.55 – 7.52 (m, 2H), 7.51 – 7.42 (m, 6H), 7.42 – 7.35 (m, 3H), 7.33 – 7.25 (m, 2H), 6.91 – 6.83 (m, 3H), 6.83 – 6.73 (m, 2H), 6.05 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.3, 145.6, 140.8, 140.4, 138.9, 137.4, 136.9, 136.7, 131.3, 130.5, 129.9, 128.8, 128.5, 128.0, 127.6, 127.2, 127.1, 127.0, 126.9, 126.7, 126.3, 126.2, 53.9. The ee of compound **4e** was determined by HPLC using an IB column (n -hexane/ i -PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{major}} = 16.2$ min, $t_{\text{minor}} = 18.8$ min). The spectral data are in accordance with the literature values.⁶



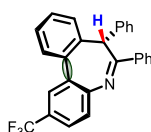
2-Methoxy-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (4f)

White solid (69.8 mg, 93% yield). 80% ee, $[\alpha]_D^{17} = 481.74$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.84 (dd, $J = 6.1, 2.5$ Hz, 2H), 7.77 – 7.65 (m, 1H), 7.40 – 7.37 (m, 2H), 7.32 – 7.24 (m, 6H), 6.95 (d, $J = 2.8$ Hz, 1H), 6.86 – 6.80 (m, 2H), 6.69 – 6.58 (m, 3H), 6.01 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.9, 155.6, 140.7, 140.3, 138.7, 138.5, 137.4, 137.3, 137.1, 132.8, 130.3, 130.0, 129.9, 129.6, 128.7, 128.6, 127.9, 127.8, 127.7, 127.4, 126.9, 126.7, 126.3, 115.6, 112.4, 55.6, 52.7. IR (KBr): 3058, 3019, 2926, 1614, 1269, 755. HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$ 376.1701, found 376.1695. The ee of compound **4f** was determined by HPLC using an IC column (n -hexane/ i -PrOH = 95/5, flow rate = 0.5 mL/min, $t_{\text{minor}} = 12.6$ min, $t_{\text{major}} = 17.5$ min).



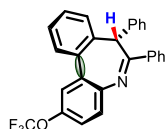
2-Fluoro-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (4g)

White solid (68.2 mg, 94% yield). 78% ee, $[\alpha]_D^{17} = 146.34$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.01 – 7.95 (m, 2H), 7.63 – 7.58 (m, 1H), 7.41 – 7.32 (m, 6H), 7.14 – 7.09 (m, 1H), 7.05 (dd, $J = 10.0, 2.9$ Hz, 1H), 6.84 (dd, $J = 4.3, 2.3$ Hz, 3H), 6.79 – 6.73 (m, 1H), 6.69 – 6.63 (m, 2H), 5.95 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.1, 158.8 (d, $J = 244.1$ Hz), 142.8 (d, $J = 2.5$ Hz), 140.2, 138.8, 137.2, 135.9 (d, $J = 2.0$ Hz), 132.4 (d, $J = 8.0$ Hz), 130.5, 130.0, 129.8, 128.9, 128.8, 128.4 (d, $J = 8.6$ Hz), 128.0, 127.9, 127.7, 126.6, 126.3, 114.9 (d, $J = 22.6$ Hz), 114.2 (d, $J = 22.8$ Hz), 53.6. ^{19}F NMR (376 MHz, CDCl_3): δ -118.07. IR (KBr): 3059, 3023, 2925, 1615, 1265, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{19}\text{FN}$ $[\text{M}+\text{H}]^+$ 364.1502, found 364.1495. The ee of compound **4g** was determined by HPLC using an IA column (n -hexane/ i -PrOH = 98/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 9.5$ min, $t_{\text{minor}} = 11.7$ min).



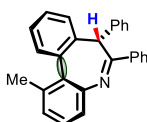
6,7-Diphenyl-2-(trifluoromethyl)-7H-dibenzo[*b,d*]azepine (**4h**)

White solid (43.0 mg, 52% yield). 72% ee, $[\alpha]_D^{17} = 127.46$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.13 – 7.93 (m, 2H), 7.69 (dd, $J = 5.8, 3.2$ Hz, 1H), 7.64 (s, 1H), 7.50 – 7.32 (m, 6H), 7.27 – 7.16 (m, 2H), 6.82 (dd, $J = 6.6, 3.6$ Hz, 3H), 6.70 – 6.59 (m, 2H), 6.02 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 147.5, 138.6, 138.0, 135.7, 134.7, 129.9, 129.8, 128.9, 128.6, 127.9, 127.8, 127.1, 127.0, 126.7 (q, $J = 268.0$ Hz), 125.5, 125.4, 124.8 (q, $J = 12.0$ Hz), 124.4, 122.8 (q, $J = 12.0$ Hz), 52.7. The ee of compound **4h** was determined by HPLC using an IA column (n -hexane/ i -PrOH = 98/2, flow rate = 1.0 mL/min, $t_{\text{minor}} = 7.9$ min, $t_{\text{major}} = 8.5$ min). The spectral data are in accordance with the literature values.⁶



6,7-Diphenyl-2-(trifluoromethoxy)-7H-dibenzo[*b,d*]azepine (**4i**)

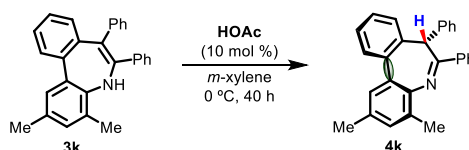
White solid (79.0 mg, 92% yield). 81% ee, $[\alpha]_D^{17} = 615.20$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.14 – 8.06 (m, 2H), 7.71 (d, $J = 3.4$ Hz, 1H), 7.54 – 7.42 (m, 6H), 7.30 (s, 1H), 7.22 (d, $J = 8.8$ Hz, 1H), 6.97 (d, $J = 8.7$ Hz, 1H), 6.92 (d, $J = 2.9$ Hz, 3H), 6.73 (s, 2H), 6.08 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 145.0, 144.8, 139.9, 139.0, 137.0, 135.7, 132.3, 130.7, 129.9, 129.7, 129.0, 128.8, 128.1, 128.0, 127.8, 127.7, 126.7, 126.3, 120.8, 120.5 (q, $J = 256.8$ Hz), 120.2, 53.6. ^{19}F NMR (376 MHz, CDCl_3): δ -58.01. IR (KBr): 3061, 3028, 1619, 1444, 1254, 736 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{19}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 430.1419, found 430.1419. The ee of compound **4i** was determined by HPLC using an IA column (n -hexane/ i -PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{major}} = 17.0$ min, $t_{\text{minor}} = 18.0$ min).



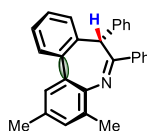
1-Methyl-6,7-diphenyl-7H-dibenzo[*b,d*]azepine (**4j**)

White solid (36.0 mg, 50% yield). 72% ee, $[\alpha]_D^{17} = 423.60$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.03 (dd, $J = 6.6, 3.0$ Hz, 2H), 7.62 – 7.50 (m, 1H), 7.53 – 7.43 (m, 3H), 7.45 – 7.32 (m, 3H), 7.07 (d, $J = 7.4$ Hz, 1H), 6.99 (t, $J = 7.7$ Hz, 1H), 6.96 – 6.83 (m, 3H), 6.76 (dd, $J = 10.9, 4.6$ Hz, 3H), 5.93 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.4, 146.9, 140.8, 140.4, 137.4, 135.1, 134.3, 132.3, 130.9, 130.3, 129.0, 128.7, 127.8, 127.7, 127.5, 126.9, 126.6, 126.2, 126.1, 126.0, 123.0, 53.8, 22.1. HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 360.1752, found 360.1752. The ee of compound **4j** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, $t_{\text{minor}} = 9.5$ min, $t_{\text{major}} = 12.0$ min). The spectral data are in accordance with the literature values.⁶

Tautomerization of enamines **3k** by using catalytic amount of HOAc:

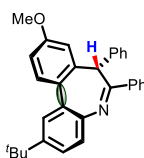


A 5.0 mL vial equipped with a stir bar was charged with HOAc (1.2 mg, 0.02 mmol) and *m*-xylene (0.34 mL), stirred for 10 min, and a *m*-xylene (0.34 mL) solution of enamine **3k** (74.6 mg, 0.2 mmol) was added. The vial was immediately sealed with a Teflon screw cap and stirred at 0 °C for 40 h. The mixture was then directly chromatographed on basic (petroleum ether/ethyl acetate = 50:1) to afford the desired product **4k**.



2,4-Dimethyl-6,7-diphenyl-7H-dibenzo[b,d]azepine (**4k**)

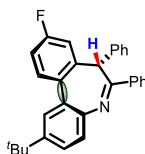
Colorless solid (70.9 mg, 95% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.18 – 8.02 (m, 2H), 7.77 – 7.60 (m, 1H), 7.53 – 7.31 (m, 6H), 7.04 (s, 1H), 6.95 – 6.79 (m, 3H), 6.66 (dd, $J = 14.9, 11.7$ Hz, 3H), 5.96 (s, 1H), 2.24 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.1, 141.4, 139.1, 137.6, 136.7, 136.1, 132.0, 131.8, 129.1, 129.0, 128.8, 128.6, 128.5, 127.5, 126.9, 126.7, 126.5, 126.3, 125.5, 125.0, 124.9, 52.0, 20.0, 17.7. The spectral data are in accordance with the literature values.⁶



2-(*Tert*-butyl)-9-methoxy-6,7-diphenyl-7H-dibenzo[b,d]azepine (**4l**)

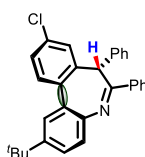
White solid (82.0 mg, 95% yield). 90% ee, $[\alpha]_D^{17} = 411.80$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.06 (dd, $J = 6.5, 2.8$ Hz, 2H), 7.67 (d, $J = 8.6$ Hz, 1H), 7.53 – 7.45 (m, 3H), 7.34 (s, 1H), 7.11 (s, 2H), 7.04 (dd, $J = 8.6, 2.5$ Hz, 1H), 6.94 (d, $J = 2.5$ Hz, 1H), 6.87 (d, $J = 6.8$ Hz, 3H), 6.78 – 6.74 (m, 2H), 5.93 (s, 1H), 3.88 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.3, 159.9, 146.9, 143.8, 140.6, 140.1, 137.3, 130.8, 130.4, 130.3, 130.2, 128.7, 127.9, 127.4, 126.7, 125.9, 125.8, 125.1, 124.0, 114.7, 113.3, 55.5, 53.8, 34.4, 31.3. IR (KBr): 3006, 2955, 1609, 1456, 1322, 813, 753

cm⁻¹. HRMS (ESI) *m/z* calculated for C₃₁H₃₀NO [M+H]⁺ 432.2327, found 432.2321. IR (KBr): 3059, 2955, 1615, 1456, 1265, 755 cm⁻¹. HRMS (ESI) *m/z* calculated for C₃₁H₃₀NO [M+H]⁺ 432.2327, found 432.2321. The ee of compound **4l** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, *t*_{minor} = 14.3 min, *t*_{major} = 25.6 min).



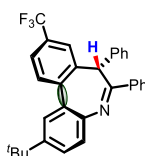
2-(*Tert*-butyl)-9-fluoro-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (**4m**)

White solid (72.2 mg, 86% yield). 90% ee, [α]_D¹⁷ = 722.26 (*c* = 1, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.07 (dd, *J* = 3.7, 2.0 Hz, 2H), 7.74 – 7.69 (m, 1H), 7.57 – 7.44 (m, 3H), 7.36 – 7.33 (m, 1H), 7.23 – 7.10 (m, 4H), 6.89 (t, *J* = 3.3 Hz, 3H), 6.80 – 6.68 (m, 2H), 5.96 (s, 1H), 1.24 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 165.3, 163.0 (d, *J* = 248.0 Hz), 147.0, 143.9, 140.6 (d, *J* = 7.2 Hz), 140.2, 136.7, 133.7 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 8.3 Hz), 130.4, 129.6, 128.8, 127.9, 127.5, 126.6, 126.1, 125.9, 125.2, 124.7, 116.0 (d, *J* = 21.4 Hz), 114.9 (d, *J* = 21.2 Hz), 53.5, 34.4, 31.3. ¹⁹F NMR (376 MHz, CDCl₃): δ -115.52. IR (KBr): 3058, 2958, 1607, 1492, 1353, 1265, 753 cm⁻¹. HRMS (ESI) *m/z* calculated for C₃₀H₂₇FN [M+H]⁺ 420.2128, found 420.2115. The ee of compound **4m** was determined by HPLC using an IA column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, *t*_{minor} = 11.2 min, *t*_{major} = 13.2 min).



2-(*Tert*-butyl)-9-chloro-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (**4n**)

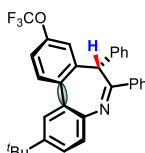
White solid (75.8 mg, 87% yield). 92% ee, [α]_D¹⁷ = 577.80 (*c* = 1, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.07 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.46 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.91 – 6.84 (m, 3H), 6.77 – 6.72 (m, 2H), 5.96 (s, 1H), 1.24 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 165.5, 147.1, 144.1, 140.2, 140.7, 136.6, 136.0, 134.1, 130.9, 130.5, 129.5, 129.2, 128.8, 128.0, 127.9, 127.5, 126.6, 126.1, 126.0, 125.2, 125.0, 53.3, 34.4, 31.2. IR (KBr): 3058, 2924, 1616, 1475, 1397, 1267, 755 cm⁻¹. HRMS (ESI) *m/z* calculated for C₃₀H₂₇ClN [M+H]⁺ 436.1832, found 436.1822. The ee of compound **4n** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, *t*_{minor} = 9.0 min, *t*_{major} = 11.0 min).



2-(*Tert*-butyl)-6,7-diphenyl-9-(trifluoromethyl)-7*H*-dibenzo[*b,d*]azepine (**4o**)

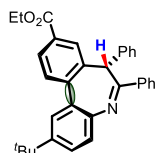
White solid (77.0 mg, 82% yield). 87% ee, [α]_D¹⁷ = 428.80 (*c* = 1, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 2.7 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.68 (s, 1H), 7.56

– 7.48 (m, 3H), 7.39 (s, 1H), 7.26 – 7.20 (m, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 6.93 – 6.86 (m, 3H), 6.72 (d, $J = 3.9$ Hz, 2H), 6.09 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.8, 147.3, 144.4, 140.9, 140.0, 139.3, 136.5, 130.6, 130.2, 130.0 (q, $J = 32.4$ Hz), 129.3, 128.8, 127.9, 127.6, 126.6, 126.2 (q, $J = 2.6$ Hz), 126.0, 125.6, 125.5, 124.6 (q, $J = 3.5$ Hz), 124.3 (q, $J = 272.5$ Hz), 53.5, 34.5, 31.2. ^{19}F NMR (376 MHz, CDCl_3): δ -61.90. IR (KBr): 3019, 2957, 1617, 1480, 1321, 1266, 747 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{26}\text{F}_3\text{NNa}$ $[\text{M}+\text{Na}]^+$ 492.1915, found 492.1910. The ee of compound **4o** was determined by HPLC using an IC column (n -hexane/ i -PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{minor}} = 7.8$ min, $t_{\text{major}} = 9.3$ min).



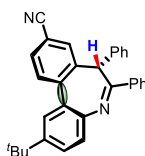
2-(*Tert*-butyl)-6,7-diphenyl-9-(trifluoromethoxy)-7H-dibenzo[*b,d*]azepine (**4p**)

White solid (87.4 mg, 90% yield). 91% ee, $[\alpha]_{\text{D}}^{17} = 501.46$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.08 – 8.05 (m, 2H), 7.75 (d, $J = 8.6$ Hz, 1H), 7.51 – 7.49 (m, 3H), 7.37 – 7.33 (m, 2H), 7.29 (d, $J = 1.7$ Hz, 1H), 7.17 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.12 (d, $J = 8.4$ Hz, 1H), 6.90 – 6.87 (m, 3H), 6.74 – 6.70 (m, 2H), 5.99 (s, 1H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.4, 149.2, 147.2, 144.1, 140.4, 140.1, 136.5, 136.2, 131.0, 130.5, 129.3, 128.8, 127.8, 127.5, 126.6, 126.3, 126.0, 125.3, 125.1, 121.6, 120.6 (d, $J = 257.6$ Hz), 120.0, 53.4, 34.4, 31.2. ^{19}F NMR (376 MHz, CDCl_3): δ -57.64. IR (KBr): 3045, 2956, 1615, 1490, 1258, 756 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{27}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 486.2045, found 486.2051. The ee of compound **4p** was determined by HPLC using an IC column (n -hexane/ i -PrOH = 95/5, flow rate = 0.5 mL/min, $t_{\text{minor}} = 7.5$ min, $t_{\text{major}} = 8.4$ min).



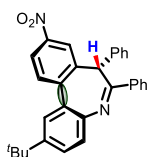
Ethyl 2-(*tert*-butyl)-6,7-diphenyl-7H-dibenzo[*b,d*]azepine-9-carboxylate (**4q**)

White solid (87.0 mg, 92% yield). 85% ee, $[\alpha]_{\text{D}}^{17} = 587.00$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.16 (dd, $J = 8.1, 1.7$ Hz, 1H), 8.14 – 8.05 (m, 3H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.55 – 7.47 (m, 3H), 7.41 (d, $J = 2.0$ Hz, 1H), 7.21 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 6.91 – 6.81 (m, 3H), 6.76 – 6.68 (m, 2H), 6.12 (s, 1H), 4.44 (q, $J = 7.1$ Hz, 2H), 1.44 (t, $J = 7.1$ Hz, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.5, 166.1, 147.2, 144.5, 141.8, 140.2, 139.0, 136.8, 130.8, 130.5, 129.9, 129.8, 129.7, 128.8, 128.0, 127.5, 126.7, 126.1, 126.0, 125.5, 125.4, 61.2, 53.5, 34.5, 31.3. IR (KBr): 3056, 2959, 1714, 1615, 1398, 1266, 742 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{33}\text{H}_{32}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 474.2433, found 474.2416. The ee of compound **4q** was determined by HPLC using an IC column (n -hexane/ i -PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{minor}} = 7.5$ min, $t_{\text{major}} = 8.6$ min).



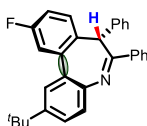
2-(*Tert*-butyl)-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine-9-carbonitrile (**4r**)

White solid (75.8 mg, 89% yield). 95% ee, $[\alpha]_{\text{D}}^{17} = 577.06$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.08 (dd, $J = 6.7, 2.9$ Hz, 2H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.78 – 7.69 (m, 2H), 7.57 – 7.47 (m, 3H), 7.36 (d, $J = 2.1$ Hz, 1H), 7.23 (dd, $J = 8.4, 2.2$ Hz, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 6.93 – 6.85 (m, 3H), 6.75 – 6.62 (m, 2H), 6.07 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.6, 147.4, 144.5, 142.0, 139.7, 139.5, 136.0, 133.0, 131.2, 130.8, 130.5, 129.0, 128.9, 127.9, 127.7, 126.5, 126.4, 126.2, 126.1, 125.3, 118.8, 111.6, 53.2, 34.5, 31.2. IR (KBr): 3059, 2957, 2227, 1616, 1484, 1265, 759 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{27}\text{N}_2$ $[\text{M}+\text{H}]^+$ 427.2174, found 427.2169. The ee of compound **4r** was determined by HPLC using an IA column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, $t_{\text{minor}} = 12.4$ min, $t_{\text{major}} = 14.5$ min).



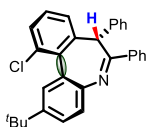
2-(*Tert*-butyl)-9-nitro-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (**4s**)

White solid (82.2 mg, 92% yield). 84% ee, $[\alpha]_{\text{D}}^{17} = 421.86$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.40 – 8.28 (m, 2H), 8.11 (dd, $J = 6.5, 2.8$ Hz, 2H), 7.91 (d, $J = 9.2$ Hz, 1H), 7.58 – 7.48 (m, 3H), 7.40 (d, $J = 1.9$ Hz, 1H), 7.31 – 7.24 (m, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 6.95 – 6.89 (m, 3H), 6.81 – 6.63 (m, 2H), 6.18 (s, 1H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.6, 147.5, 147.4, 144.6, 143.9, 139.7, 139.6, 135.9, 130.9, 130.6, 129.0, 128.6, 128.0, 127.7, 126.5, 126.4, 126.2, 125.5, 124.5, 122.8, 53.3, 34.5, 31.2. IR (KBr): 3060, 2960, 1607, 1520, 1394, 1260, 769 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 447.2073, found 447.2074. The ee of compound **4s** was determined by HPLC using an IA column (*n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, $t_{\text{minor}} = 5.9$ min, $t_{\text{major}} = 8.0$ min).



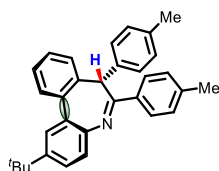
2-(*Tert*-butyl)-10-fluoro-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (**4t**)

White solid (76.2 mg, 91% yield). 94% ee, $[\alpha]_{\text{D}}^{17} = 625.54$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.07 (dd, $J = 6.5, 3.0$ Hz, 2H), 7.52 – 7.48 (m, 3H), 7.44 (dd, $J = 10.0, 2.6$ Hz, 1H), 7.37 (dd, $J = 8.6, 5.8$ Hz, 2H), 7.18 – 7.08 (m, 3H), 6.91 – 6.83 (m, 3H), 6.76 – 6.70 (m, 2H), 6.00 (s, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.2, 162.3 (d, $J = 245.2$ Hz), 144.1, 140.2, 139.4 (d, $J = 8.0$ Hz), 137.2, 134.9 (d, $J = 2.6$ Hz), 131.1 (d, $J = 8.5$ Hz), 130.4, 129.6, 129.5, 128.7, 127.9, 127.4, 126.6, 126.0, 125.9, 125.3, 125.2, 116.0 (d, $J = 22.2$ Hz), 114.9 (d, $J = 21.7$ Hz), 52.8, 34.4, 31.2. ^{19}F NMR (376 MHz, CDCl_3): δ -114.96. IR (KBr): 3056, 3013, 2958, 1613, 1487, 1265, 757 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{27}\text{FN}$ $[\text{M}+\text{H}]^+$ 420.2128, found 420.2120. The ee of compound **4t** was determined by HPLC using an IA column (*n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{minor}} = 6.2$ min, $t_{\text{major}} = 12.8$ min).



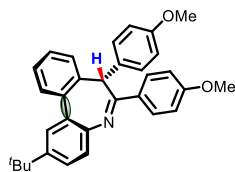
2-(*Tert*-butyl)-11-chloro-6,7-diphenyl-7*H*-dibenzo[*b,d*]azepine (**4u**)

White solid (81.8 mg, 94% yield). 94% ee, $[\alpha]_{\text{D}}^{17} = 765.20$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.06 (dd, $J = 6.6, 2.9$ Hz, 2H), 7.57 – 7.47 (m, 5H), 7.31 (d, $J = 4.8$ Hz, 2H), 7.12 – 7.05 (m, 2H), 6.90 – 6.85 (m, 3H), 6.76 – 6.71 (m, 2H), 5.94 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.5, 145.5, 144.9, 142.8, 140.1, 136.7, 134.7, 134.3, 130.5, 130.2, 128.7, 128.5, 128.1, 127.8, 127.5, 127.0, 126.4, 125.9, 124.9, 124.6, 53.7, 34.3, 31.1. IR (KBr): 3059, 2960, 1618, 1493, 1262, 750 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{27}\text{ClN}$ $[\text{M}+\text{H}]^+$ 436.1832, found 436.1820. The ee of compound **4u** was determined by HPLC using an IC column (n -hexane/ i -PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{minor}} = 9.3$ min, $t_{\text{major}} = 12.0$ min).



2-(*Tert*-butyl)-6,7-di-*p*-tolyl-7*H*-dibenzo[*b,d*]azepine (**4a'**)

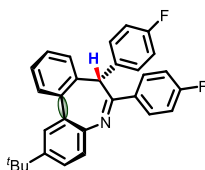
White solid (80.8 mg, 94% yield). 93% ee, $[\alpha]_{\text{D}}^{17} = 600.40$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 8.1$ Hz, 2H), 7.75 (d, $J = 7.2$ Hz, 1H), 7.53 – 7.37 (m, 4H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.15 (dt, $J = 14.3, 5.2$ Hz, 2H), 6.68 (d, $J = 8.0$ Hz, 2H), 6.62 (d, $J = 7.9$ Hz, 2H), 5.97 (s, 1H), 2.43 (s, 3H), 2.08 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.1, 146.6, 144.3, 140.5, 139.3, 137.8, 137.5, 135.2, 134.4, 130.7, 129.6, 129.5, 129.4, 128.0, 127.9, 127.8, 127.6, 126.6, 125.7, 125.4, 124.6, 53.3, 34.4, 31.3, 21.5, 20.7. IR (KBr): 3041, 2959, 1610, 1467, 1325, 1267, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{32}\text{N}$ $[\text{M}+\text{H}]^+$ 430.2535, found 430.2517. The ee of compound **4a'** was determined by HPLC using an IC column (n -hexane/ i -PrOH = 95/5, flow rate = 0.5 mL/min, $t_{\text{major}} = 9.5$ min, $t_{\text{minor}} = 12.5$ min).



2-(*Tert*-butyl)-6,7-bis(4-methoxyphenyl)-7*H*-dibenzo[*b,d*]azepine (**4b'**)

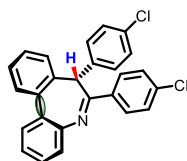
White solid (87.6 mg, 95% yield). 95% ee, $[\alpha]_{\text{D}}^{17} = 497.86$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.07 – 8.02 (m, 2H), 7.74 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.50 – 7.41 (m, 2H), 7.41 – 7.36 (m, 2H), 7.15 (dd, $J = 8.4, 2.2$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 7.02 – 6.95 (m, 2H), 6.63 (d, $J = 8.0$ Hz, 2H), 6.43 – 6.35 (m, 2H), 5.94 (s, 1H), 3.87 (s, 3H), 3.58 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.4, 161.4, 157.6, 146.4, 144.2, 139.2, 137.5, 133.1, 130.6, 129.7, 129.6, 129.5, 129.4, 127.9, 127.8, 127.6, 125.7, 125.3, 124.6, 113.9, 112.7, 55.4, 55.1, 52.7, 34.4, 31.3. IR (KBr): 3051, 2924, 1606, 1509, 1460, 1251, 738 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{32}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 462.2433, found 462.2420.

The ee of compound **4b'** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{minor}} = 11.2$ min, $t_{\text{major}} = 12.5$ min).



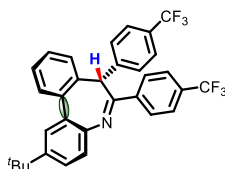
2-(Tert-butyl)-6,7-bis(4-fluorophenyl)-7H-dibenzo[b,d]azepine (4c')

White solid (77.8 mg, 89% yield). 94% ee, $[\alpha]_{\text{D}}^{17} = 489.54$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.13 – 8.00 (m, 2H), 7.77 – 7.72 (m, 1H), 7.52 – 7.42 (m, 2H), 7.39 (dd, $J = 4.1, 1.9$ Hz, 2H), 7.20 – 7.06 (m, 4H), 6.67 (dd, $J = 7.9, 5.5$ Hz, 2H), 6.55 (t, $J = 8.7$ Hz, 2H), 5.90 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.5, 164.2 (d, $J = 251.1$ Hz), 161.1 (d, $J = 244.5$ Hz), 147.2, 143.8, 138.6, 137.3, 136.4 (d, $J = 3.1$ Hz), 132.9 (d, $J = 3.2$ Hz), 130.5, 130.0 (d, $J = 8.6$ Hz), 129.8, 129.4, 128.2, 128.1, 128.0, 125.7, 125.4, 124.8, 115.7 (d, $J = 21.7$ Hz), 114.1 (d, $J = 21.4$ Hz), 52.8, 34.5, 31.3. ^{19}F NMR (376 MHz, CDCl_3): δ -110.22, -117.21. IR (KBr): 3066, 2924, 1608, 1504, 1224, 727 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$ 438.2033, found 438.2028. The ee of compound **4c'** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{major}} = 11.2$ min, $t_{\text{minor}} = 12.5$ min).



6,7-Bis(4-chlorophenyl)-7H-dibenzo[b,d]azepine (4d')

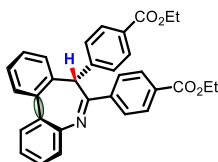
White solid (70.2 mg, 85% yield). 80% ee, $[\alpha]_{\text{D}}^{17} = 415.00$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.00 (dd, $J = 14.6, 12.7$ Hz, 2H), 7.75 (dd, $J = 7.2, 1.8$ Hz, 1H), 7.55 – 7.44 (m, 5H), 7.42 – 7.38 (m, 1H), 7.27 – 7.15 (m, 2H), 7.06 – 6.99 (m, 1H), 6.91 – 6.85 (m, 2H), 6.66 (dd, $J = 8.5, 1.0$ Hz, 2H), 5.90 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.1, 145.8, 138.4, 138.3, 136.8, 136.7, 135.7, 131.9, 130.7, 130.0, 129.6, 129.2, 129.0, 128.6, 128.5, 128.2, 127.9, 127.8, 127.7, 126.3, 124.7, 52.8. IR (KBr): 3061, 2923, 1617, 1432, 1091, 762 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{N}$ $[\text{M}+\text{H}]^+$ 414.0816, found 414.0816. The ee of compound **4d'** was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, $t_{\text{minor}} = 11.9$ min, $t_{\text{major}} = 15.7$ min).



2-(Tert-butyl)-6,7-bis(4-(trifluoromethyl)phenyl)-7H-dibenzo[b,d]azepine (4e')

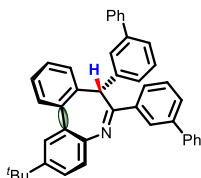
White solid (88.0 mg, 82% yield). 95% ee, $[\alpha]_{\text{D}}^{17} = 534.74$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.19 (d, $J = 8.2$ Hz, 2H), 7.76 (d, $J = 8.3$ Hz, 3H), 7.57 – 7.48 (m, 2H), 7.48 – 7.43 (m, 1H), 7.36 (d, $J = 2.0$ Hz, 1H), 7.19 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.12 (dd, $J = 8.4, 2.3$ Hz, 3H), 6.83 (d, $J = 8.1$

Hz, 2H), 5.96 (s, 1H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 147.9, 143.8, 143.1, 141.3, 138.3, 137.2, 132.1 (q, $J = 32.7$ Hz), 130.5, 129.9, 129.2, 128.5, 128.4 (q $J = 32.4$ Hz), 128.3, 128.1, 127.0, 125.8, 125.7 (q, $J = 3.8$ Hz), 125.4, 125.1, 124.3 (q, $J = 3.4$ Hz), 124.0 (q, $J = 272.2$ Hz), 123.9 (q, $J = 271.9$ Hz), 53.1, 34.5, 31.1. ^{19}F NMR (376 MHz, CDCl_3): δ -62.74. IR (KBr): 3055, 2925, 1618, 1462, 1322, 1266, 756 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{26}\text{F}_6\text{N}$ $[\text{M}+\text{H}]^+$ 538.1969, found 538.1968. The ee of compound **4e'** was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, $t_{\text{major}} = 11.2$ min, $t_{\text{minor}} = 12.5$ min).



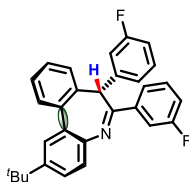
Diethyl 4,4'-(7H-dibenzo[b,d]azepine-6,7-diyl)-dibenzoate (**4f'**)

White solid (88.0 mg, 90% yield). 82% ee, $[\alpha]_{\text{D}}^{17} = 434.94$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.18 – 8.12 (m, 4H), 7.76 (dd, $J = 5.9, 3.0$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.55 – 7.41 (m, 4H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.19 – 7.13 (m, 1H), 7.03 – 6.95 (m, 1H), 6.81 (d, $J = 8.1$ Hz, 2H), 6.01 (s, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.3, 166.1, 164.4, 145.8, 143.8, 142.6, 138.2, 136.7, 132.1, 130.7, 130.1, 130.0, 129.6, 128.9, 128.7, 128.6, 128.4, 128.3, 127.9, 127.8, 126.5, 126.4, 124.9, 61.3, 60.8, 53.6, 14.3, 14.2. IR (KBr): 3061, 2981, 1716, 1610, 1446, 1276, 734 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{28}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 490.2018, found 490.2012. The ee of compound **4f'** was determined by HPLC using an IA column (*n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, $t_{\text{minor}} = 9.0$ min, $t_{\text{major}} = 34.9$ min).



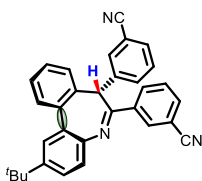
6,7-Di([1,1'-biphenyl]-3-yl)-2-(tert-butyl)-7H-dibenzo[b,d]azepine (**4g'**)

White solid (100.6 mg, 91% yield). 93% ee, $[\alpha]_{\text{D}}^{17} = 595.14$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.21 (d, $J = 1.6$ Hz, 1H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.62 (d, $J = 7.7$ Hz, 1H), 7.58 (dd, $J = 5.3, 4.2$ Hz, 2H), 7.47 (td, $J = 7.7, 2.2$ Hz, 1H), 7.43 – 7.32 (m, 6H), 7.31 – 7.21 (m, 3H), 7.20 – 7.14 (m, 3H), 7.13 – 7.05 (m, 2H), 6.99 (d, $J = 6.9$ Hz, 1H), 6.90 (td, $J = 7.6, 2.1$ Hz, 1H), 6.82 (s, 1H), 6.74 (d, $J = 7.6$ Hz, 1H), 6.03 (s, 1H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.7, 147.0, 144.2, 141.8, 141.3, 140.9, 140.8, 140.4, 138.8, 138.0, 137.5, 130.7, 129.7, 129.6, 129.2, 129.1, 128.9, 128.5, 128.2, 127.9, 127.8, 127.6, 127.4, 127.1, 127.0, 126.9, 126.8, 126.0, 125.9, 125.8, 125.2, 124.9, 124.8, 53.8, 34.5, 31.3. IR (KBr): 3056, 2960, 1607, 1479, 1266, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{42}\text{H}_{36}\text{N}$ $[\text{M}+\text{H}]^+$ 554.2848, found 554.2838. The ee of compound **4g'** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{minor}} = 9.5$ min, $t_{\text{major}} = 11.8$ min).



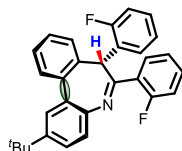
2-(*Tert*-butyl)-6,7-bis(3-fluorophenyl)-7H-dibenzo[*b,d*]azepine (**4h'**)

White solid (77.0 mg, 88% yield). 90% ee, $[\alpha]_{\text{D}}^{17} = 677.60$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.87 (d, $J = 7.8$ Hz, 1H), 7.78 (t, $J = 9.4$ Hz, 2H), 7.55 – 7.37 (m, 5H), 7.19 (td, $J = 8.6$, 2.1 Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 1H), 6.85 (dd, $J = 14.1$, 7.9 Hz, 1H), 6.56 (dd, $J = 12.8$, 7.8 Hz, 2H), 6.39 (d, $J = 10.4$ Hz, 1H), 5.91 (s, 1H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.8, 163.7, 163.1 (d, $J = 246.5$ Hz), 162.3 (d, $J = 245.1$ Hz), 147.5, 143.7, 142.3 (d, $J = 7.1$ Hz), 139.8 (d, $J = 7.2$ Hz), 138.2, 137.3, 130.6, 130.2 (d, $J = 8.1$ Hz), 129.8, 129.4, 128.8 (d, $J = 8.3$ Hz), 128.3, 128.2, 125.8, 125.4, 124.9, 123.3 (d, $J = 2.8$ Hz), 122.4 (d, $J = 2.7$ Hz), 117.3 (d, $J = 21.4$ Hz), 114.9 (d, $J = 22.9$ Hz), 113.9 (d, $J = 22.6$ Hz), 112.8 (d, $J = 21.2$ Hz), 53.1, 34.5, 31.3. ^{19}F NMR (376 MHz, CDCl_3): δ -112.17, -114.40. IR (KBr): 3063, 2960, 1611, 1482, 1323, 1263, 757 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$ 438.2033, found 438.2033. The ee of **4h'** was determined by HPLC using an IA column (n -hexane/ i -PrOH = 98/2, flow rate = 0.5 mL/min, $t_{\text{minor}} = 14.8$ min, $t_{\text{major}} = 19.5$ min).



3,3'-(2-(*Tert*-butyl)-7H-dibenzo[*b,d*]azepine-6,7-diyl)dibenzonitrile (**4i'**)

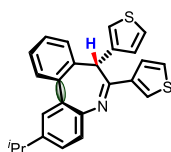
White solid (48.8 mg, 54% yield). 80% ee, $[\alpha]_{\text{D}}^{17} = 370.26$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.39 (s, 1H), 8.33 (d, $J = 8.1$ Hz, 1H), 7.80 – 7.75 (m, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.57 – 7.52 (m, 2H), 7.47 – 7.44 (m, 1H), 7.42 (d, $J = 2.1$ Hz, 1H), 7.22 – 7.16 (m, 2H), 7.11 (d, $J = 8.4$ Hz, 1H), 7.03 – 6.99 (m, 2H), 6.91 (s, 1H), 5.89 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.9, 148.4, 143.3, 140.7, 138.5, 137.2, 137.0, 133.6, 131.8, 131.5, 130.9, 130.6, 130.3, 130.1, 129.9, 129.7, 129.2, 128.8, 128.7, 128.4, 125.8, 125.5, 125.3, 118.5, 118.4, 113.3, 111.6, 52.3, 34.6, 31.2. IR (KBr): 3062, 2959, 2229, 1613, 1474, 1324, 1267, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{26}\text{N}_3$ $[\text{M}+\text{H}]^+$ 452.2127, found 452.2117. The ee of compound **4i'** was determined by HPLC using an IA column (n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $t_{\text{minor}} = 11.3$ min, $t_{\text{major}} = 14.8$ min).



2-(*Tert*-butyl)-6,7-bis(2-fluorophenyl)-7H-dibenzo[*b,d*]azepine (**4j'**)

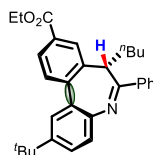
White solid (45.4 mg, 52% yield). 85% ee, $[\alpha]_{\text{D}}^{17} = 678.94$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.86 (t, $J = 7.2$ Hz, 1H), 7.77 (d, $J = 6.8$ Hz, 1H), 7.54 – 7.48 (m, 3H), 7.47 – 7.38 (m, 2H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.19 – 7.12 (m, 3H), 6.85 (dd, $J = 13.4$, 6.5 Hz, 1H), 6.74 – 6.68 (m, 1H), 6.51

(t, $J = 7.5$ Hz, 1H), 6.37 (t, $J = 7.9$ Hz, 1H), 5.81 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.0, 162.9, 161.0 (d, $J = 250.2$ Hz), 160.3 (d, $J = 246.9$ Hz), 147.3, 143.3, 137.8, 137.5, 132.2 (d, $J = 2.8$ Hz), 131.4 (d, $J = 8.5$ Hz), 130.6, 130.2 (d, $J = 2.4$ Hz), 129.6 (d, $J = 3.9$ Hz), 129.4, 128.0, 127.9, 127.8 (d, $J = 8.3$ Hz), 125.6, 125.3, 124.7, 124.4 (d, $J = 3.3$ Hz), 123.6 (d, $J = 13.5$ Hz), 122.5 (d, $J = 3.3$ Hz), 116.2 (d, $J = 22.8$ Hz), 114.9 (d, $J = 22.2$ Hz), 51.8 (d, $J = 5.0$ Hz), 34.5, 31.3. ^{19}F NMR (376 MHz, CDCl_3): δ -110.05, -111.34. IR (KBr): 3059, 2959, 1618, 1481, 1326, 1267, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{26}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$ 438.2033, found 438.2033. The ee of compound **4j'** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, t_{minor} = 10.9 min, t_{major} = 13.0 min).



2-Isopropyl-6,7-di(thiophen-3-yl)-7H-dibenzo[b,d]azepine (**4k'**)

White solid (69.4 mg, 87% yield). 71% ee, $[\alpha]_{\text{D}}^{17} = 284.54$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, $J = 1.7$ Hz, 1H), 7.77 (dd, $J = 5.1$, 1.2 Hz, 1H), 7.73 (dd, $J = 6.1$, 2.6 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.36 (dd, $J = 5.1$, 2.9 Hz, 1H), 7.29 (d, $J = 1.9$ Hz, 1H), 7.15 (d, $J = 8.2$ Hz, 1H), 7.06 (dd, $J = 8.2$, 1.9 Hz, 1H), 6.85 (dd, $J = 5.0$, 3.0 Hz, 1H), 6.48 (dd, $J = 5.0$, 1.0 Hz, 1H), 6.35 (dd, $J = 2.9$, 1.4 Hz, 1H), 5.77 (s, 1H), 2.87 (dt, $J = 13.8$, 6.9 Hz, 1H), 1.20 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.0, 144.7, 144.1, 143.4, 139.1, 137.2, 137.0, 131.1, 129.8, 128.8, 128.1, 127.9, 127.8, 127.0, 126.7, 126.5, 126.4, 126.3, 125.7, 124.2, 121.6, 51.1, 33.8, 24.1, 23.9. IR (KBr): 3056, 2957, 1732, 1616, 1261, 736 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{22}\text{NS}_2$ $[\text{M}+\text{H}]^+$ 400.1194, found 400.1197. The ee of compound **4k'** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, t_{minor} = 11.4 min, t_{major} = 17.9 min).



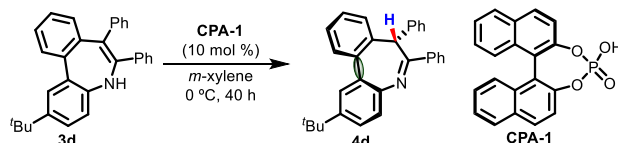
Ethyl 2-(tert-butyl)-7-butyl-6-phenyl-7H-dibenzo[b,d]azepine-9-carboxylate (**4l'**)

Compound **4l'** was isolated as an inseparable diastereomeric mixture (dr = 4:1) in 56% yield (50.7 mg).

Yellow oil. 50% ee for the major diastereomer. $[\alpha]_{\text{D}}^{17} = 47.66$ ($c = 1$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, $J = 8.2$ Hz, 1H), 7.87 (dd, $J = 9.9$, 8.0 Hz, 3H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.60 (s, 1H), 7.43 (d, $J = 8.6$ Hz, 1H), 7.40 – 7.29 (m, 4H), 4.60 (t, $J = 7.9$ Hz, 0.79H), 4.32 (q, $J = 7.1$ Hz, 2H), 2.98 – 2.93 (m, 0.21 H), 2.12 (s, 1H), 1.40 – 1.31 (m, 12H), 0.99 (d, $J = 4.2$ Hz, 2H), 0.56 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.6, 165.5, 146.5, 143.0, 139.9, 139.4, 139.2, 129.2, 129.0, 128.7, 128.5, 128.2, 127.5, 127.1, 126.9, 125.5, 124.9, 124.8, 60.0, 49.8, 33.7, 30.5, 29.3, 25.2, 21.2, 13.4, 12.5. IR (KBr): 3060, 2959, 1716, 1619, 1454, 1364, 1254, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{36}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 454.2746, found 454.2739. The ee of **4l'** was determined by HPLC using an IA column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, t_{minor} = 9.8 min, t_{major} = 11.0 min).

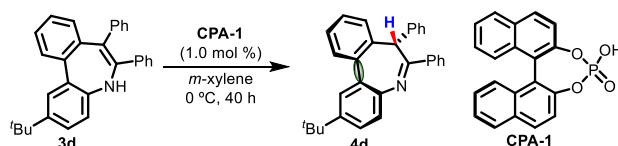
F. Further studies on the catalytic enantioselective tautomerization of enamine **3d**:

(I) Gram-scale studies:



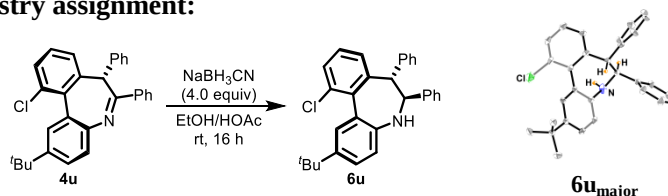
In a glovebox, a 25.0 mL vial equipped with a stir bar was charged with **CPA-1** (104.4 mg, 0.3 mmol) and *m*-xylene (5.1 mL), stirred for 10 min, and a *m*-xylene (5.1 mL) solution of **3d** (1.20 g, 3.0 mmol) was added. The vial was immediately sealed with a Teflon screw cap and stirred at 0 °C for 40 h. The mixture was then directly chromatographed on basic alumina (petroleum ether/ethyl acetate = 50:1) to afford the desired product **4d** in 94% yield (1.13 g, 95% ee).

(II) Low catalyst loading studies:



In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with **CPA-1** (0.7 mg, 0.002 mmol) and *m*-xylene (0.34 mL), stirred for 10 min, and a *m*-xylene (0.34 mL) solution of enamine **3d** (80.2 mg, 0.2 mmol) was added. The vial was immediately sealed with a Teflon screw cap and stirred at 0 °C for 40 h. The mixture was then directly chromatographed on basic alumina (petroleum ether/ethyl acetate = 50:1) to afford the desired product **4d** in 27% yield (21.6 mg, 96% ee).

G. Absolute stereochemistry assignment:



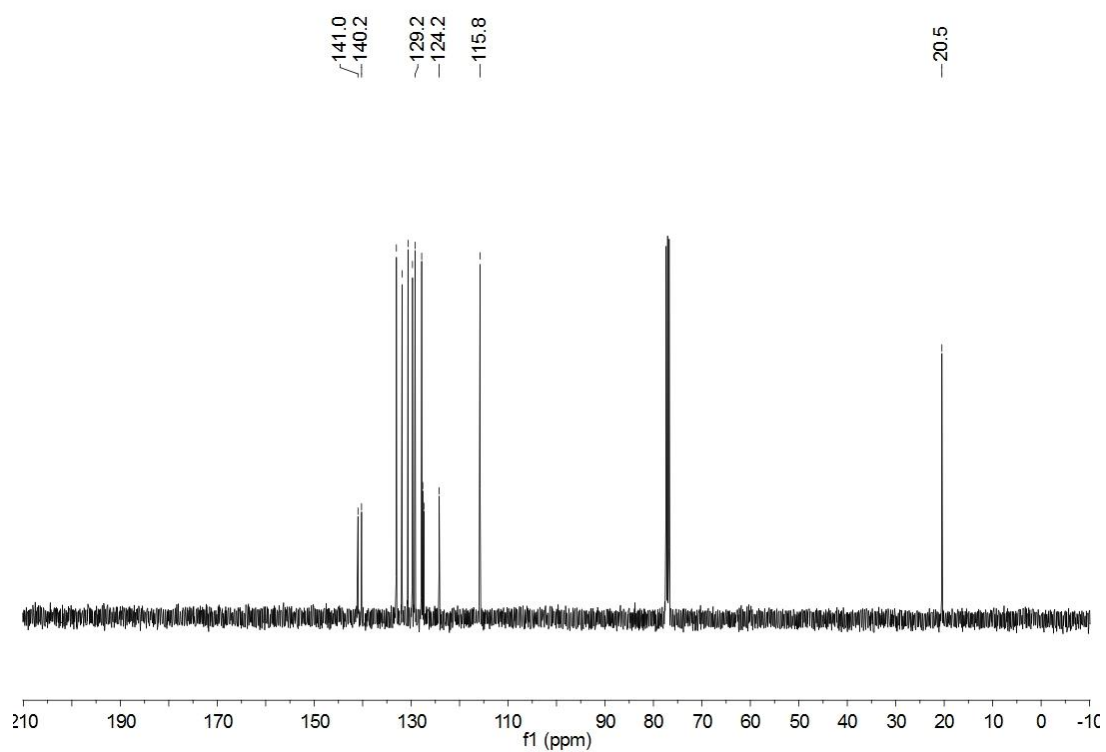
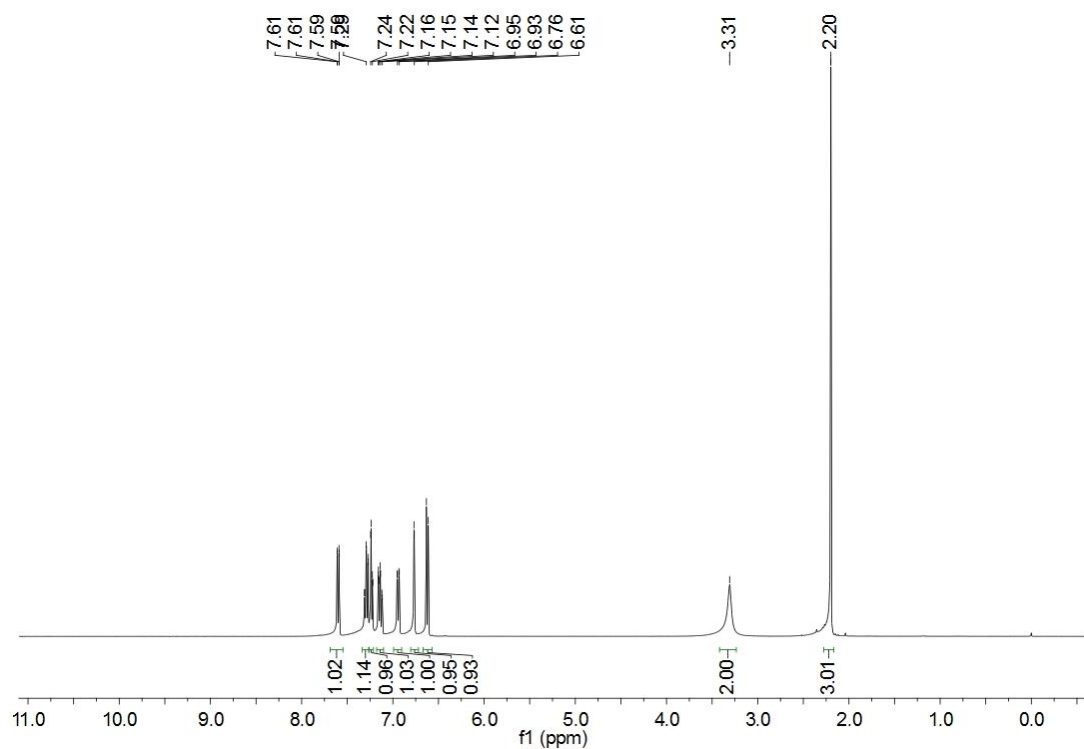
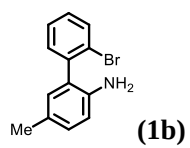
To an ethanol (10 mL) solution of **4u** (218.0 mg, 0.50 mmol), cooled at 0 °C, was sequentially added NaBH₃CN (125.6 mg, 2.0 mmol) and HOAc (180.0 mg, 3.0 mmol). The reaction mixture was then stirred at room temperature for 24 h. After the reaction completed, EtOAc (10 mL) and H₂O (20 mL) were added, the organic layer was washed several times with 1N NaOH and finally with brine and dried over Na₂SO₄, and the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford product **6u** in 95% yield (208.1 mg, 8:1 *dr*). The analytical sample of the major regioisomer **6u_{major}** was collected by preparative thin-layer chromatography (92% ee). $[\alpha]_D^{17} = -40.06$ (*c* = 1, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.22 – 7.06 (m, 11H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 5.11 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 3.31 (s, 1H), 1.43 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 144.8, 143.6, 143.0, 140.3, 138.7, 137.3, 131.9, 130.1, 129.6, 129.3, 128.8, 128.5, 128.3, 128.0, 127.3, 126.8, 126.7, 125.8, 125.5, 123.0, 72.6, 50.9, 34.5, 31.6. IR (KBr): 3360, 3061, 2962, 1602, 1394, 1260, 734 cm⁻¹. HRMS (ESI) *m/z* calculated for

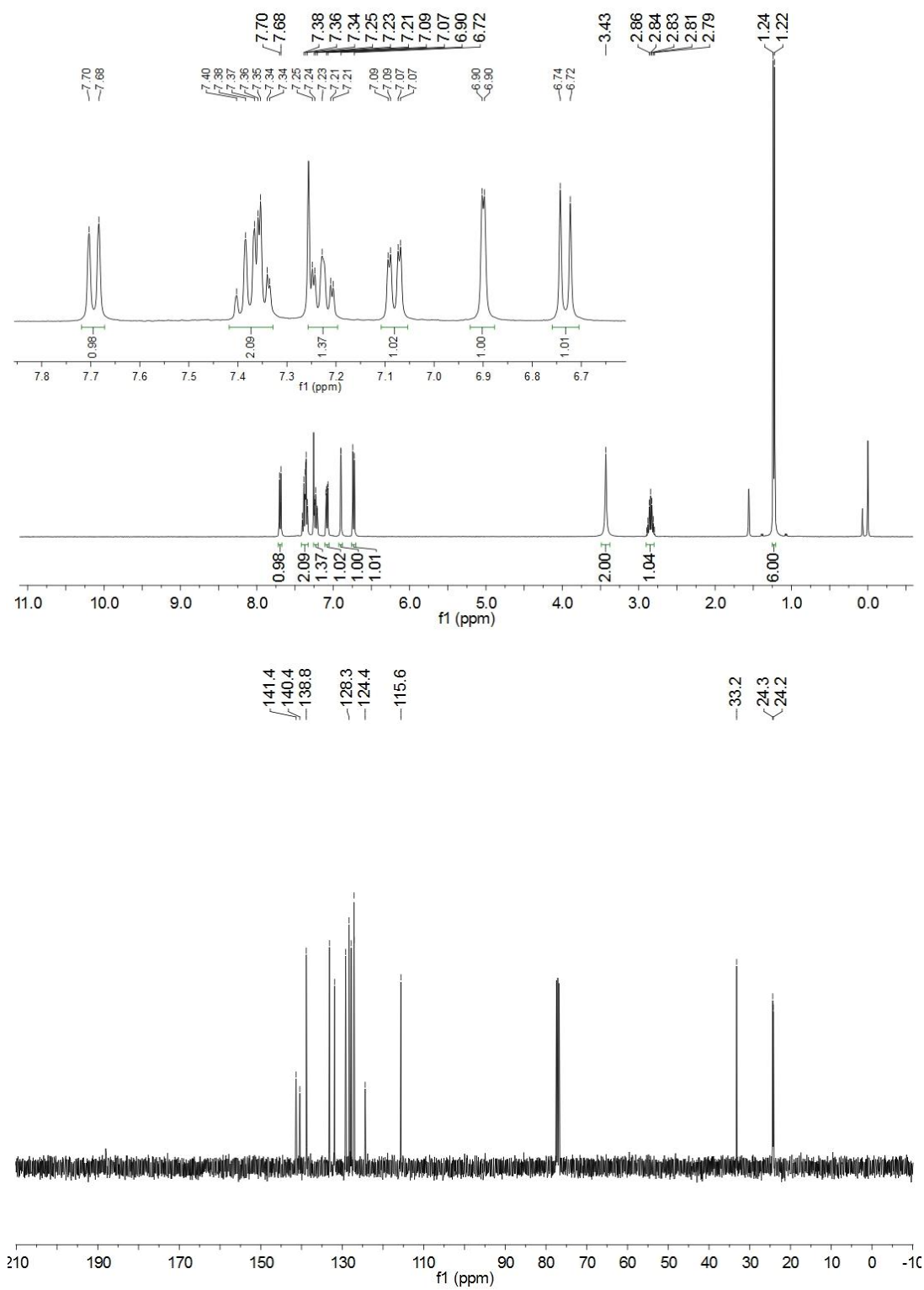
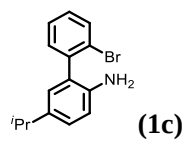
C₃₀H₂₉ClN [M+H]⁺ 438.1989, found 438.1987. The ee of compound **6u_{major}** was determined by HPLC using an IC column (*n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, *t*_{minor} = 11.2 min, *t*_{major} = 12.7 min).

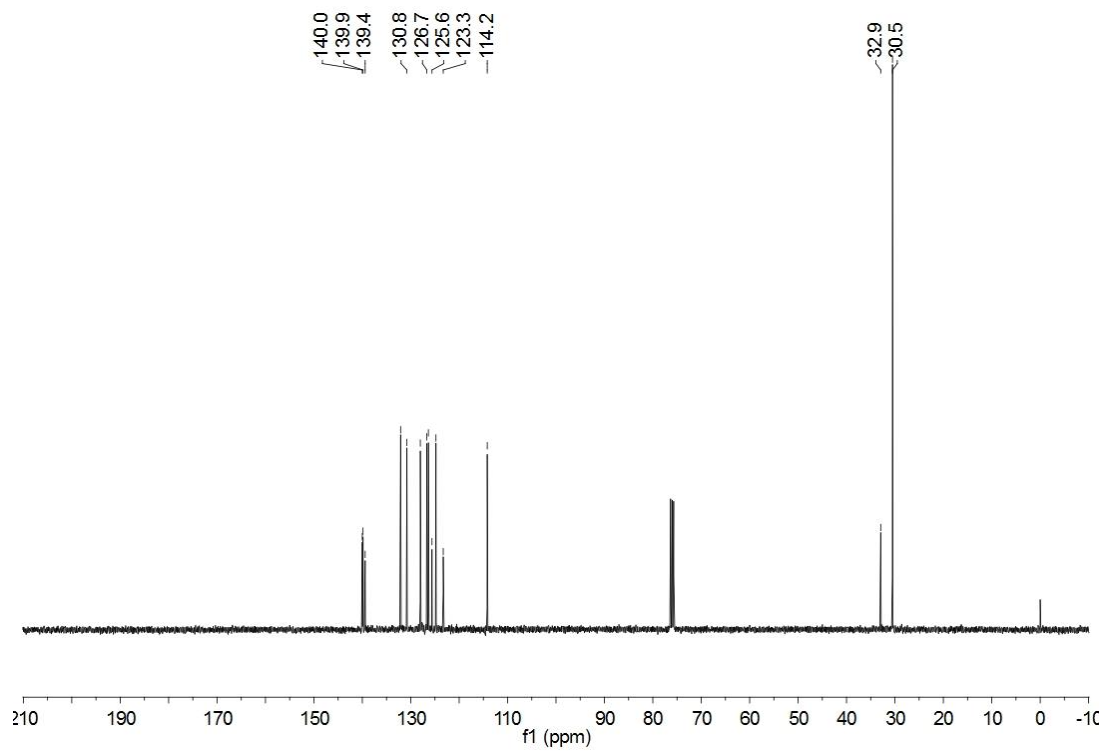
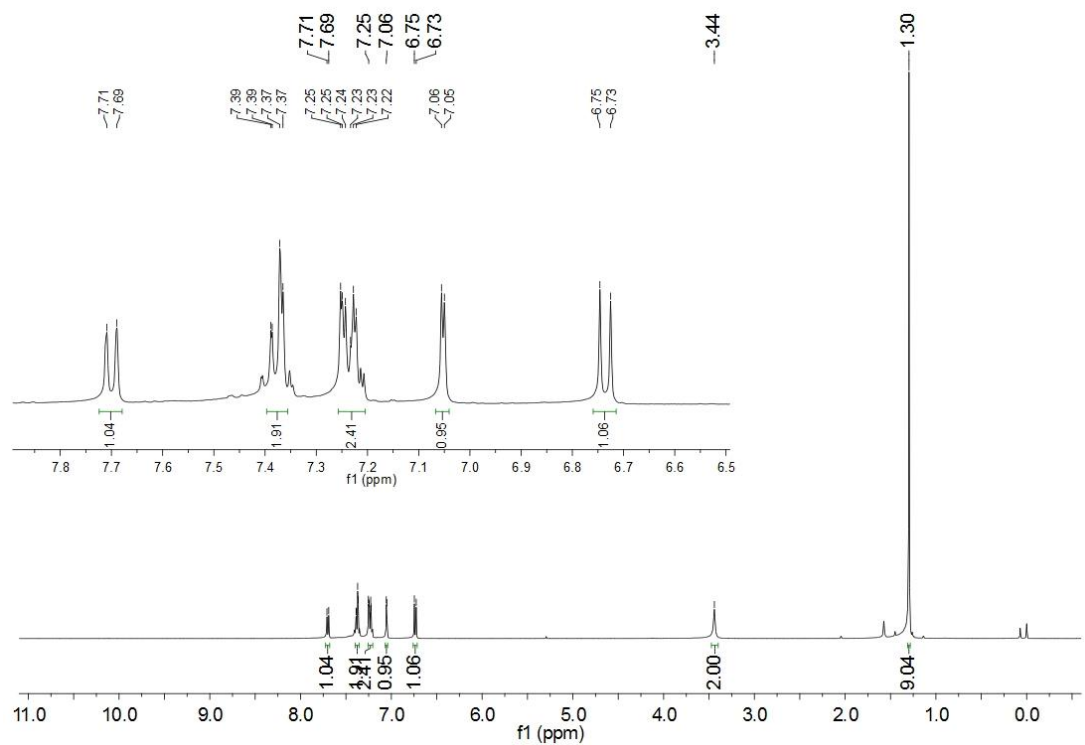
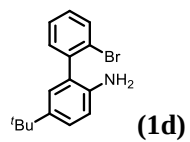
H. References:

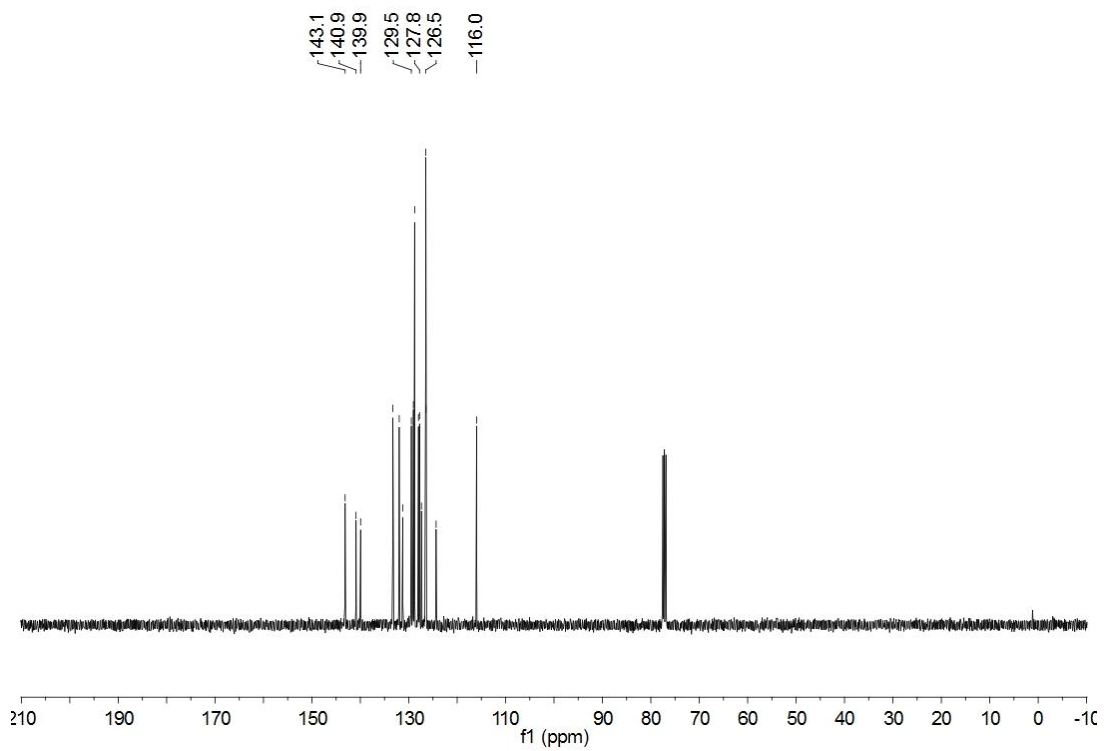
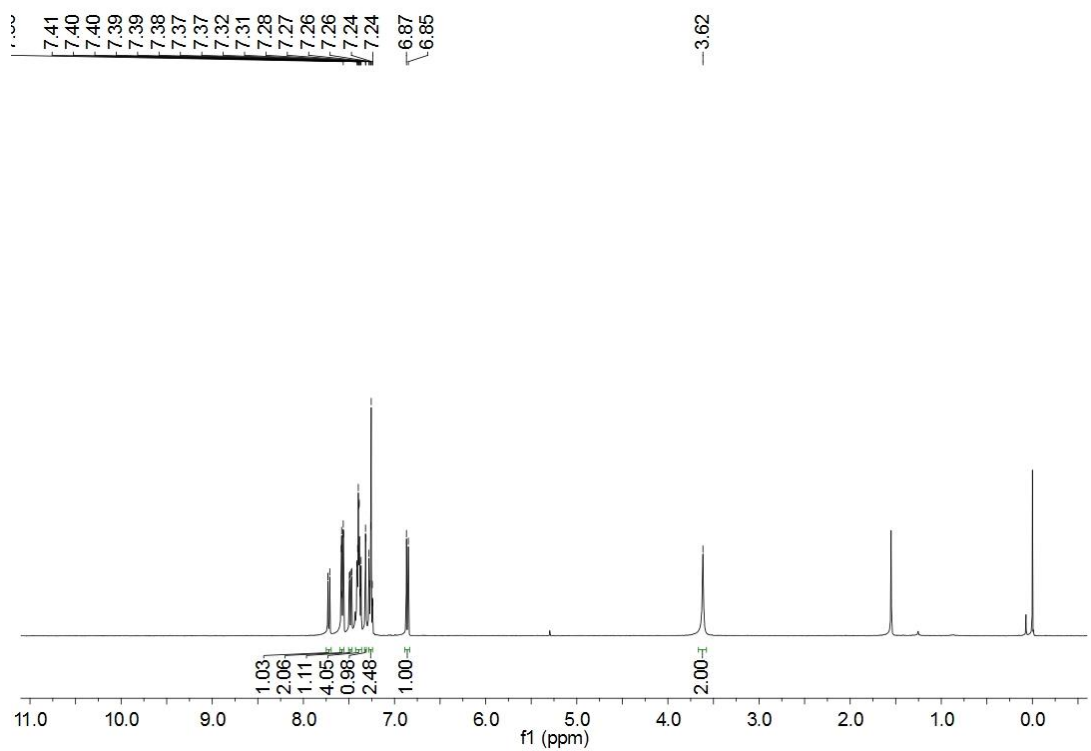
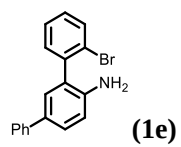
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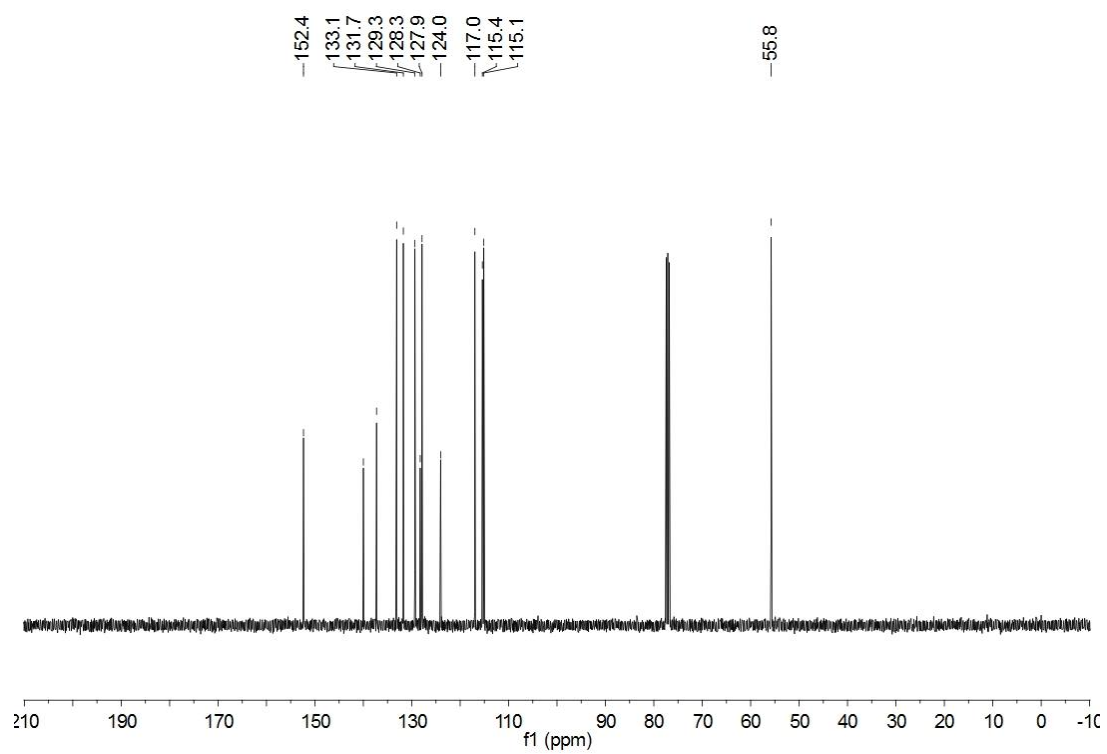
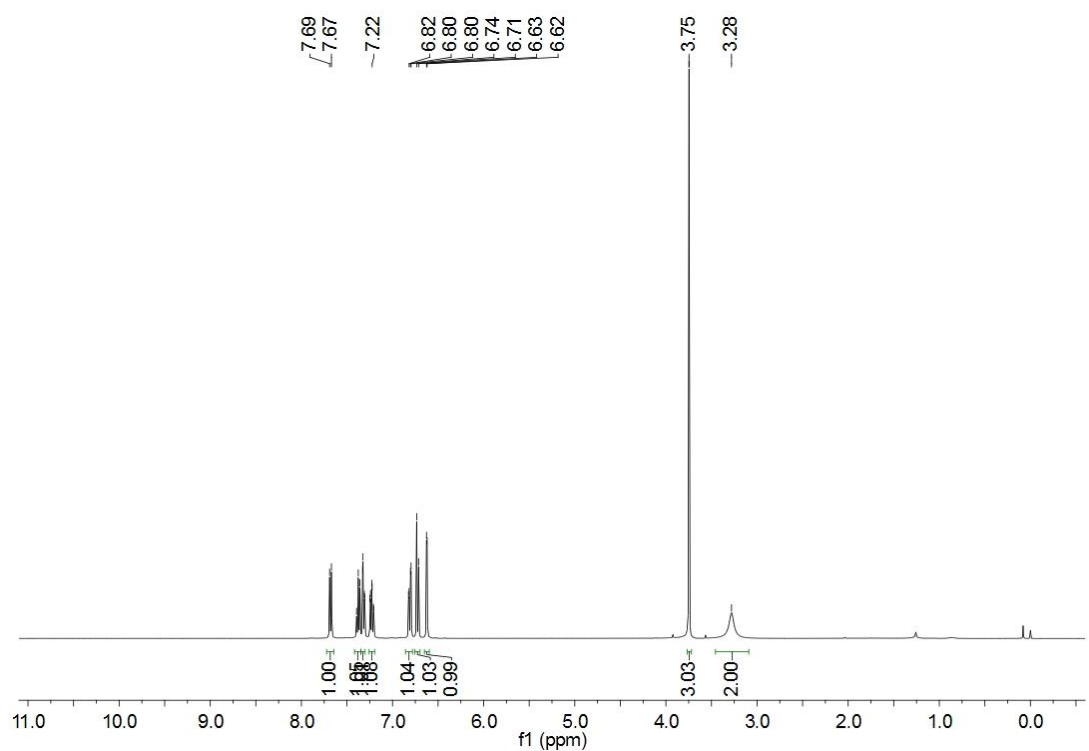
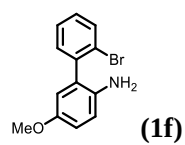
I. NMR Spectra and HPLC:

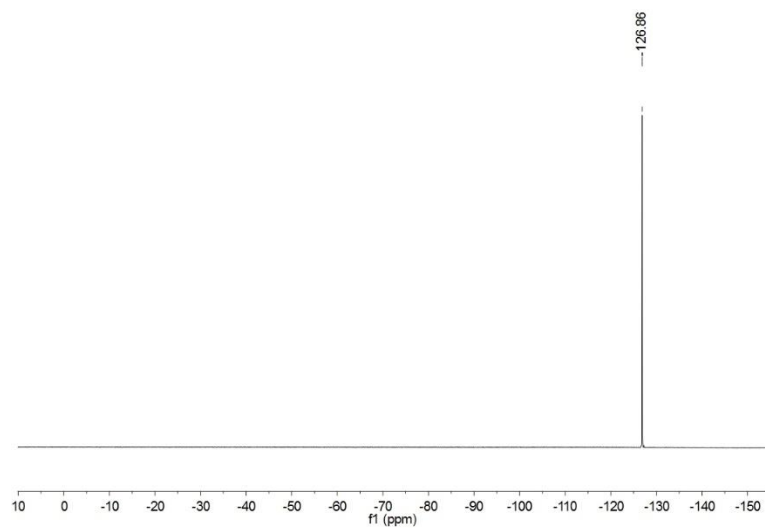
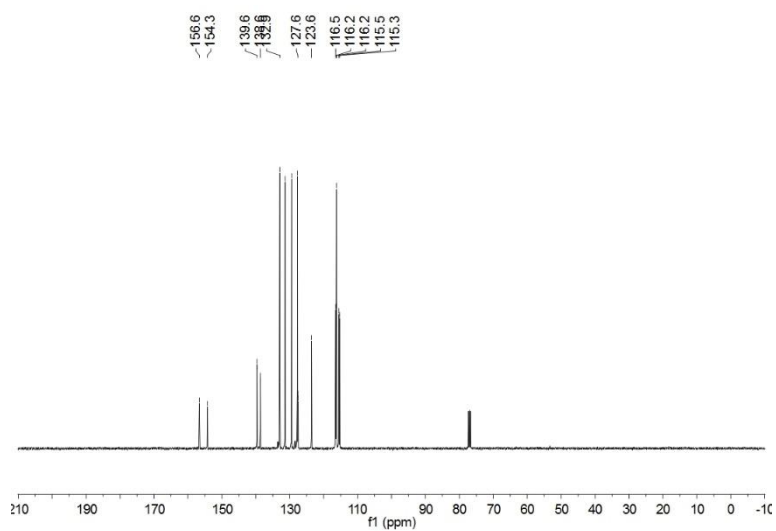
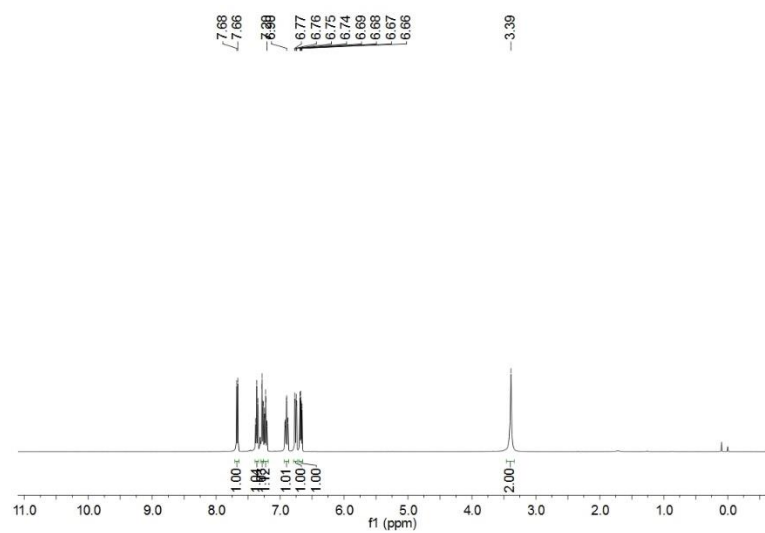
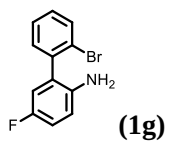


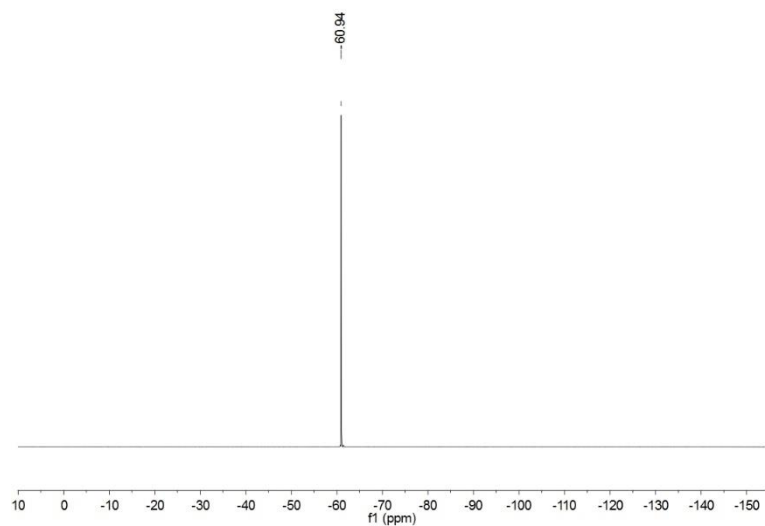
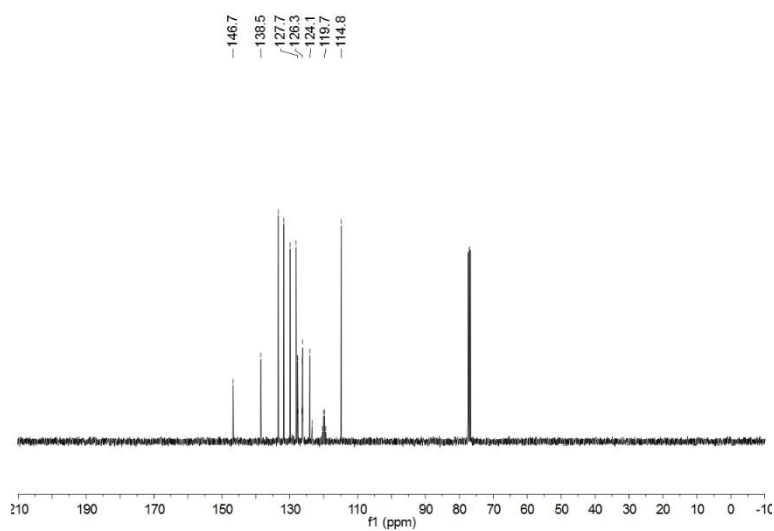
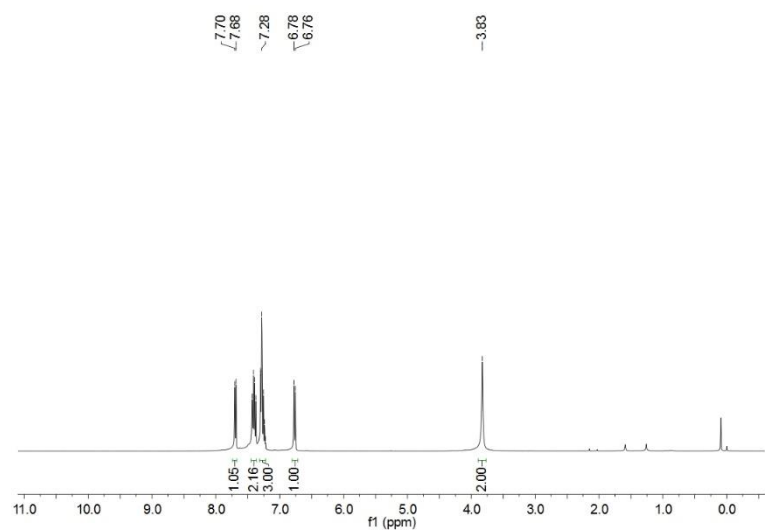
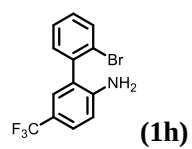


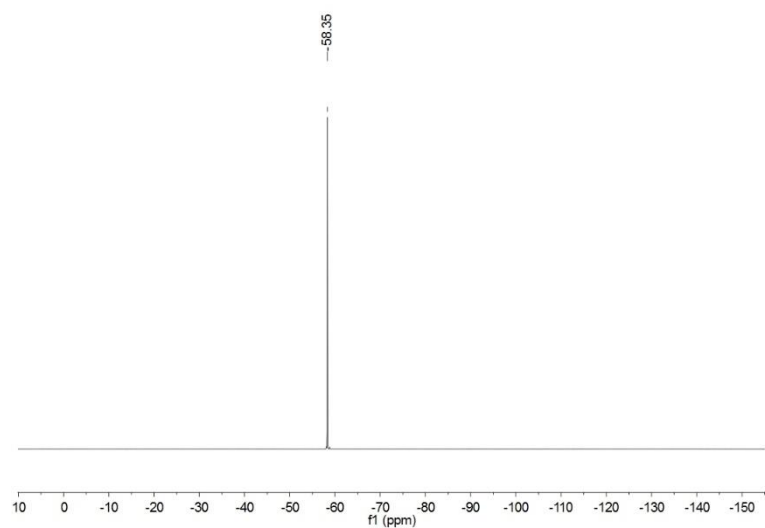
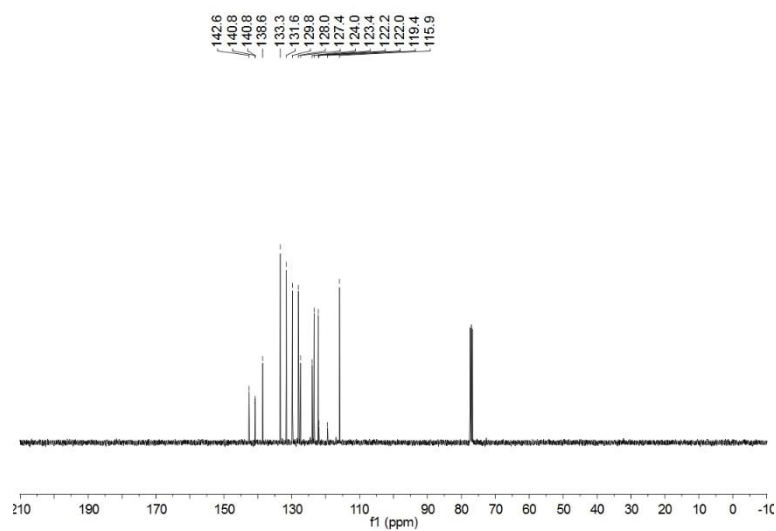
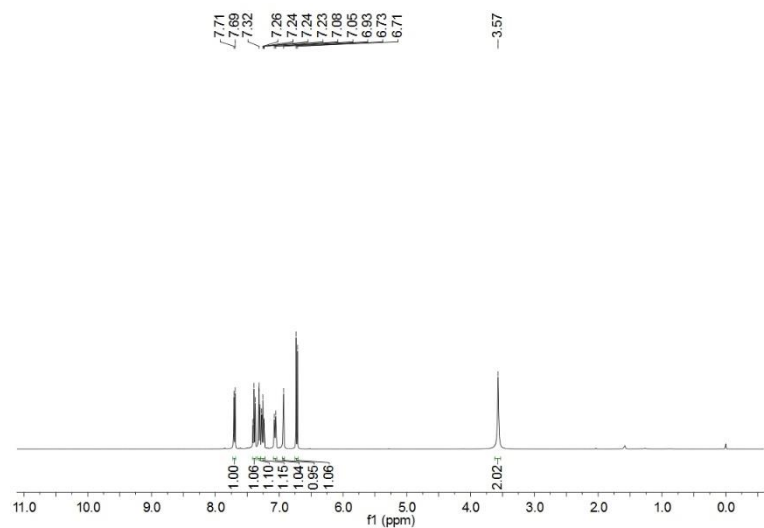
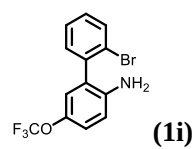


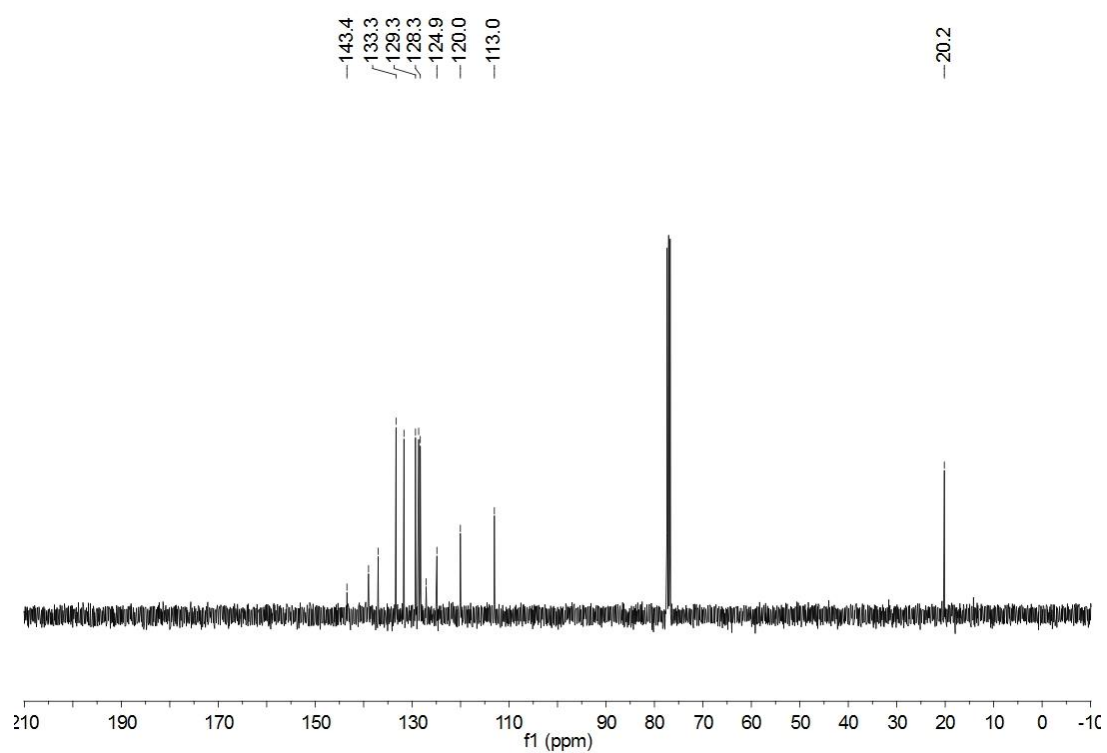
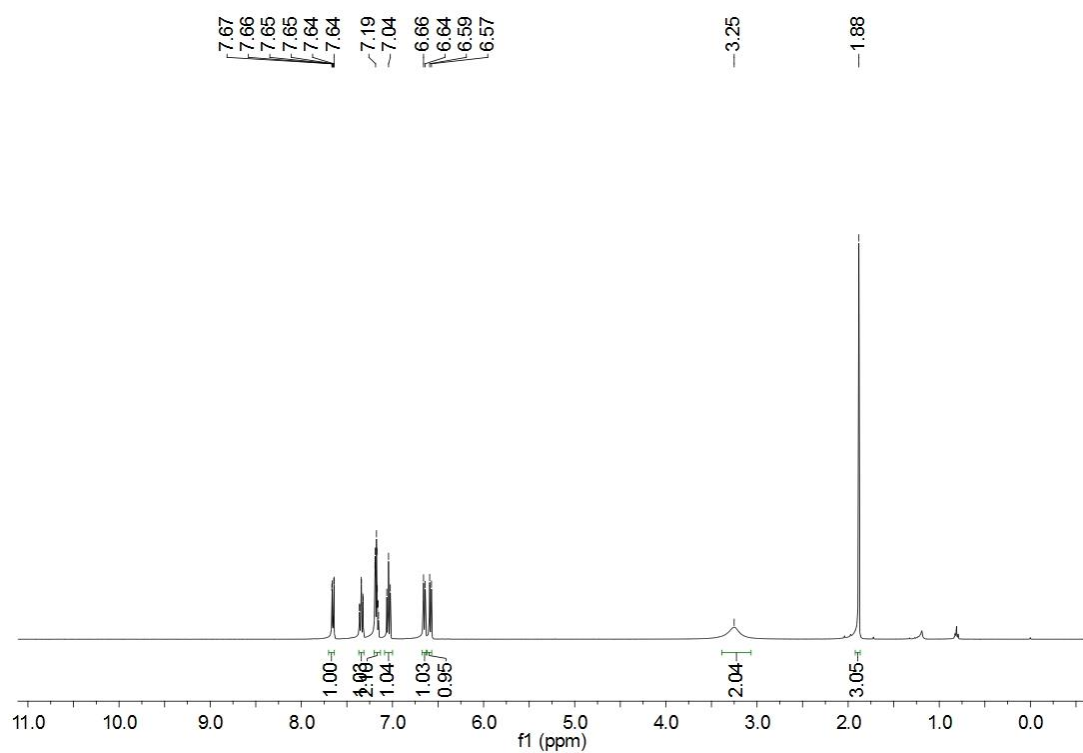
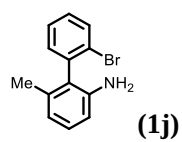


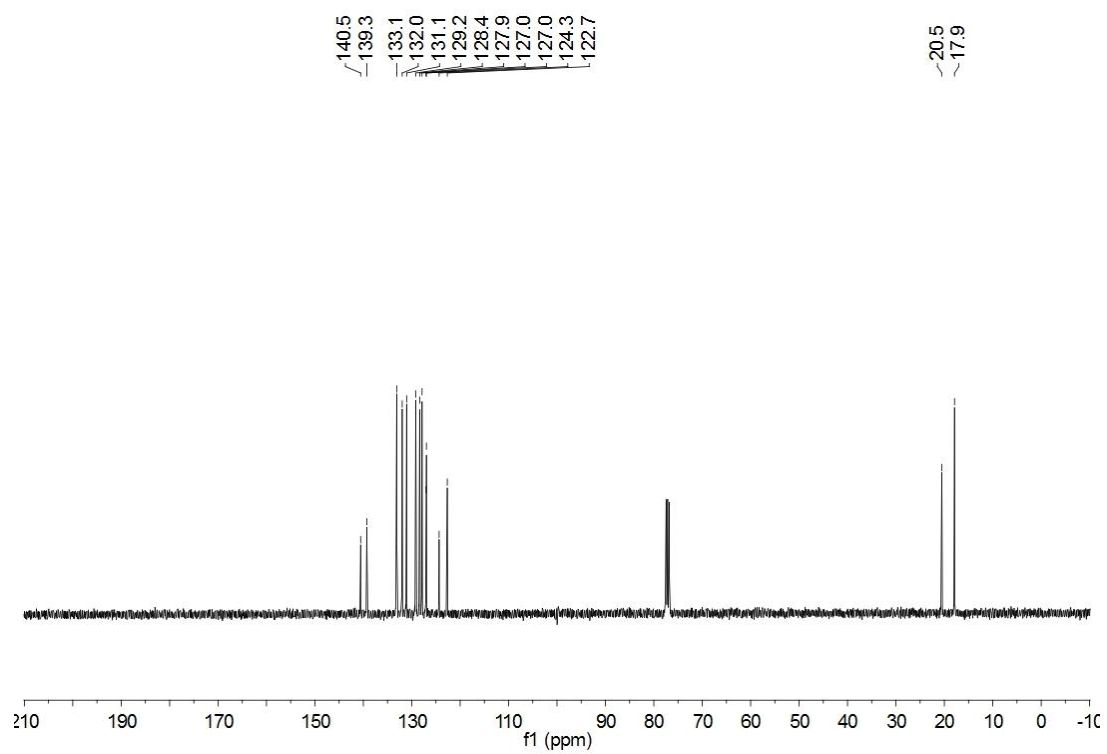
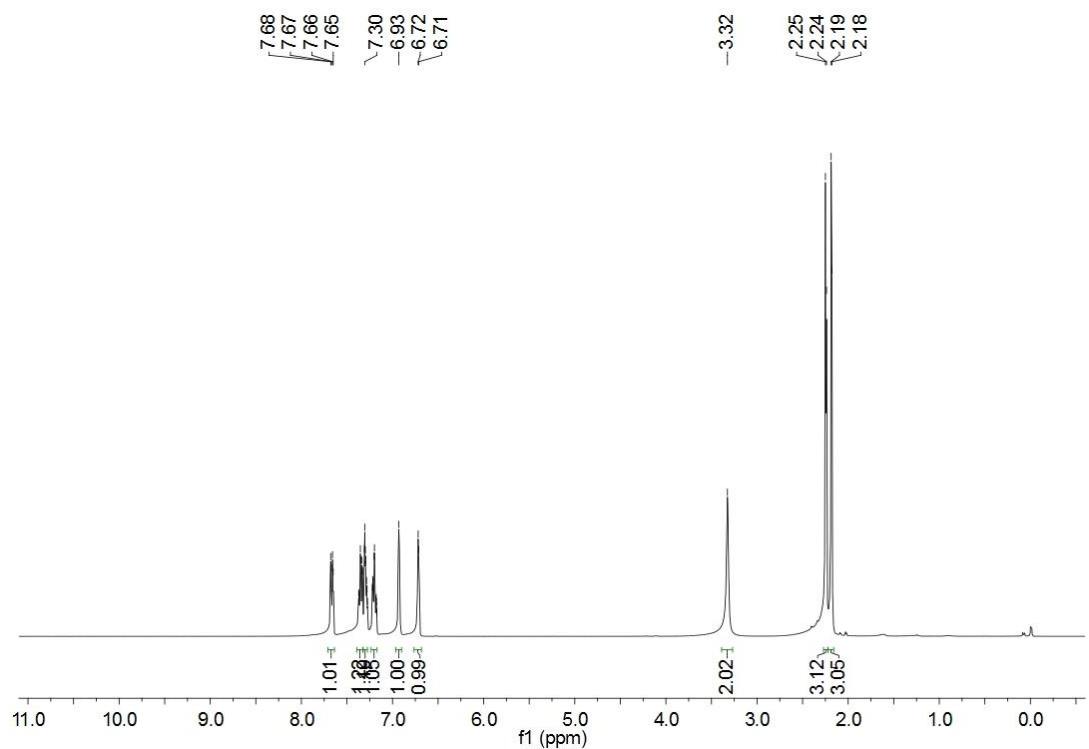
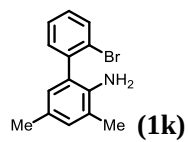


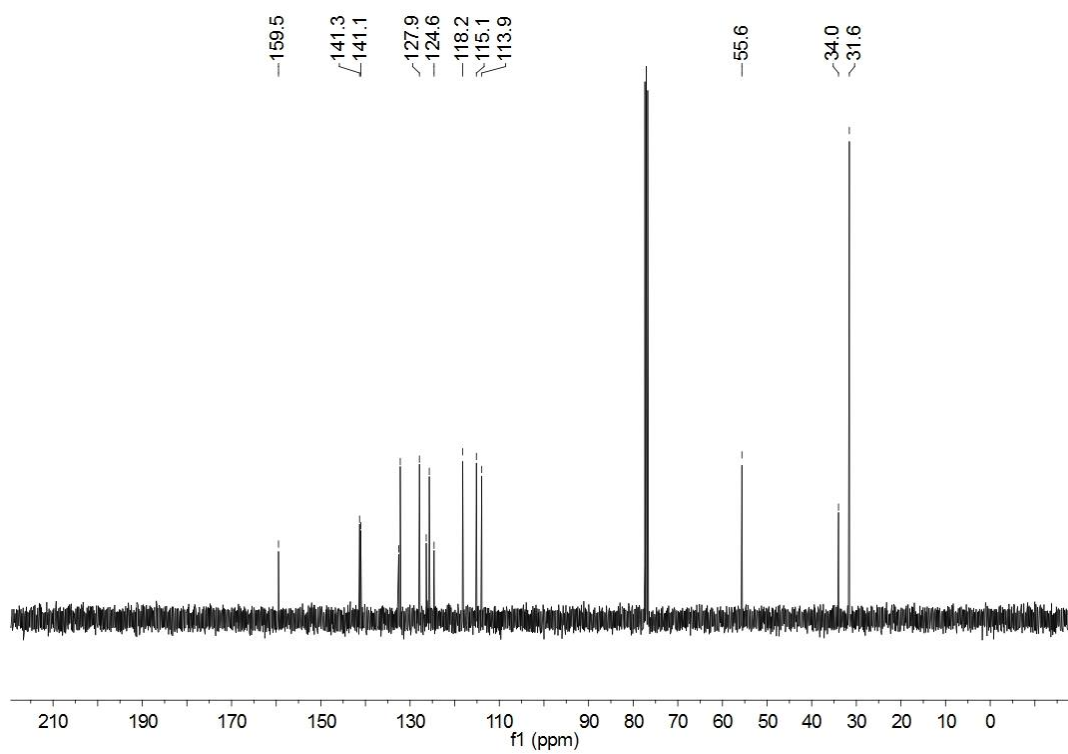
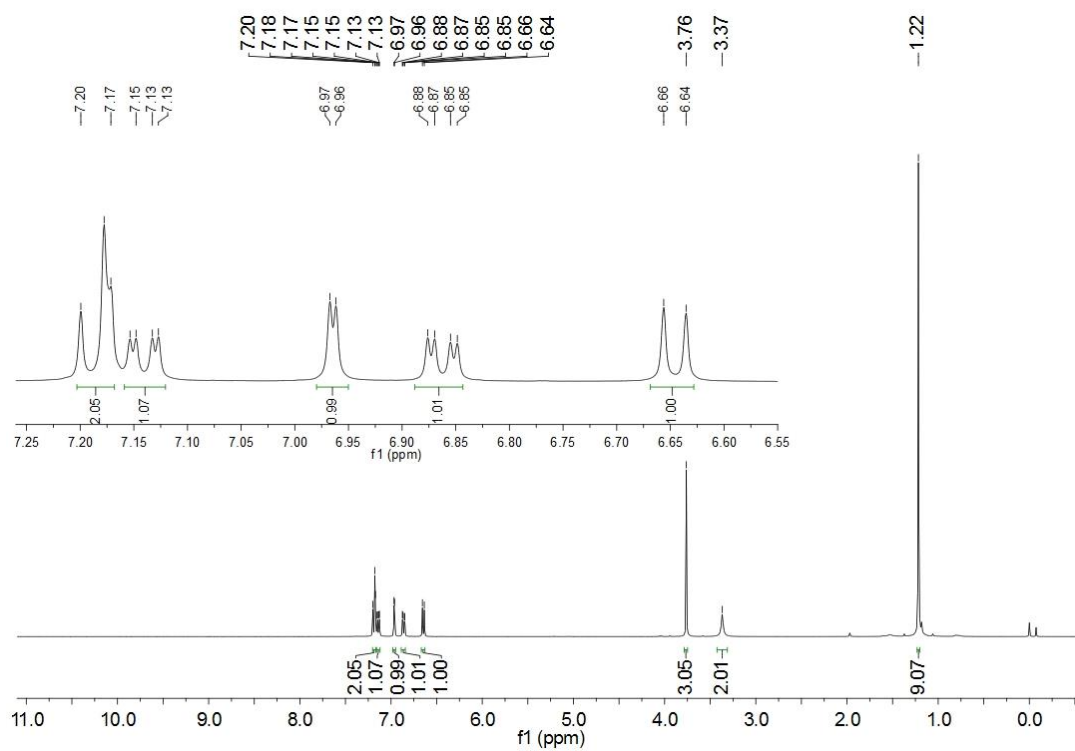
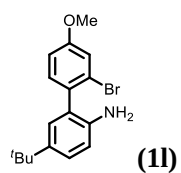


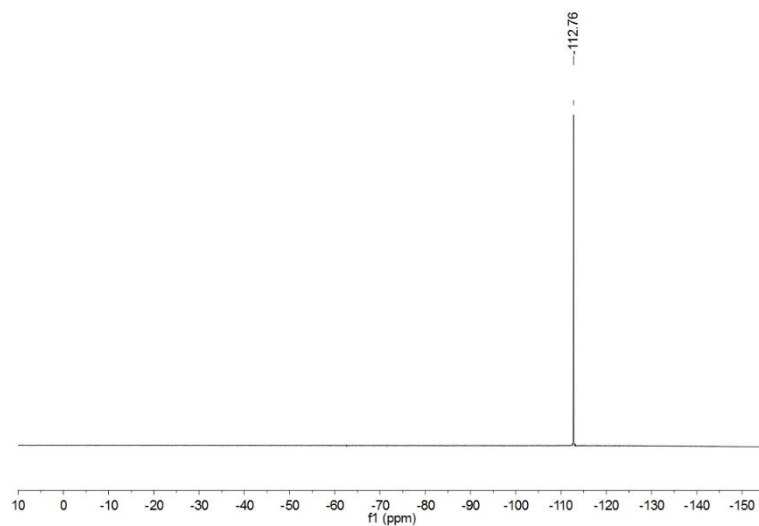
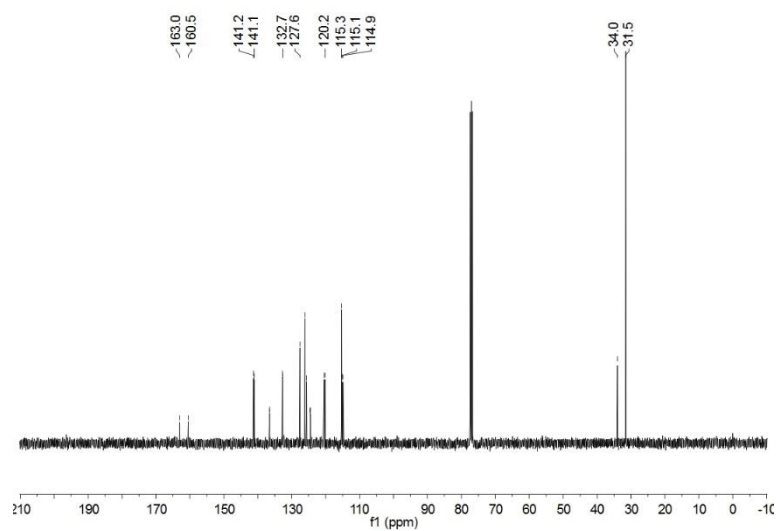
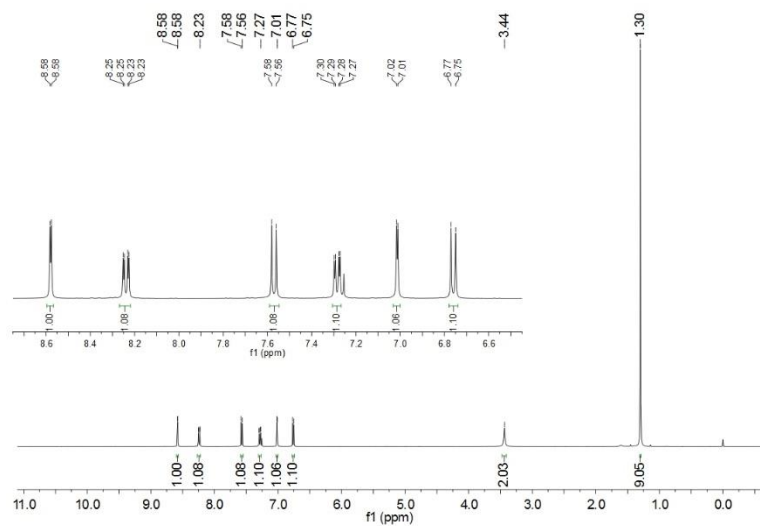
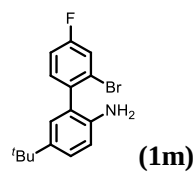


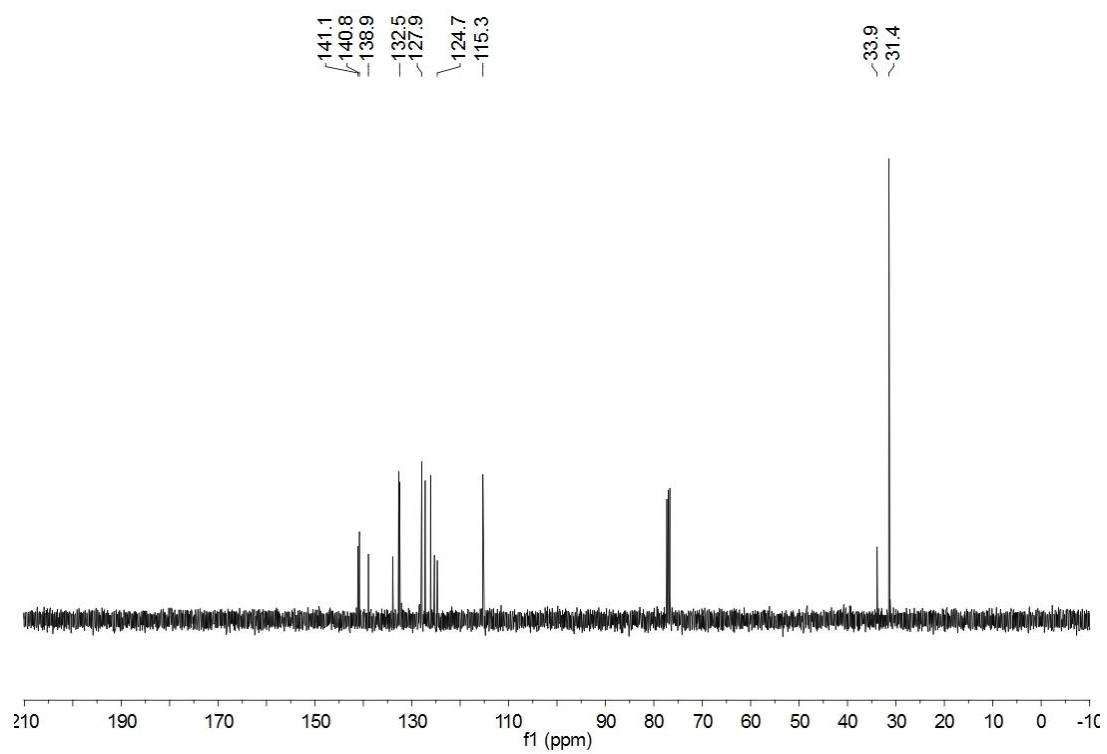
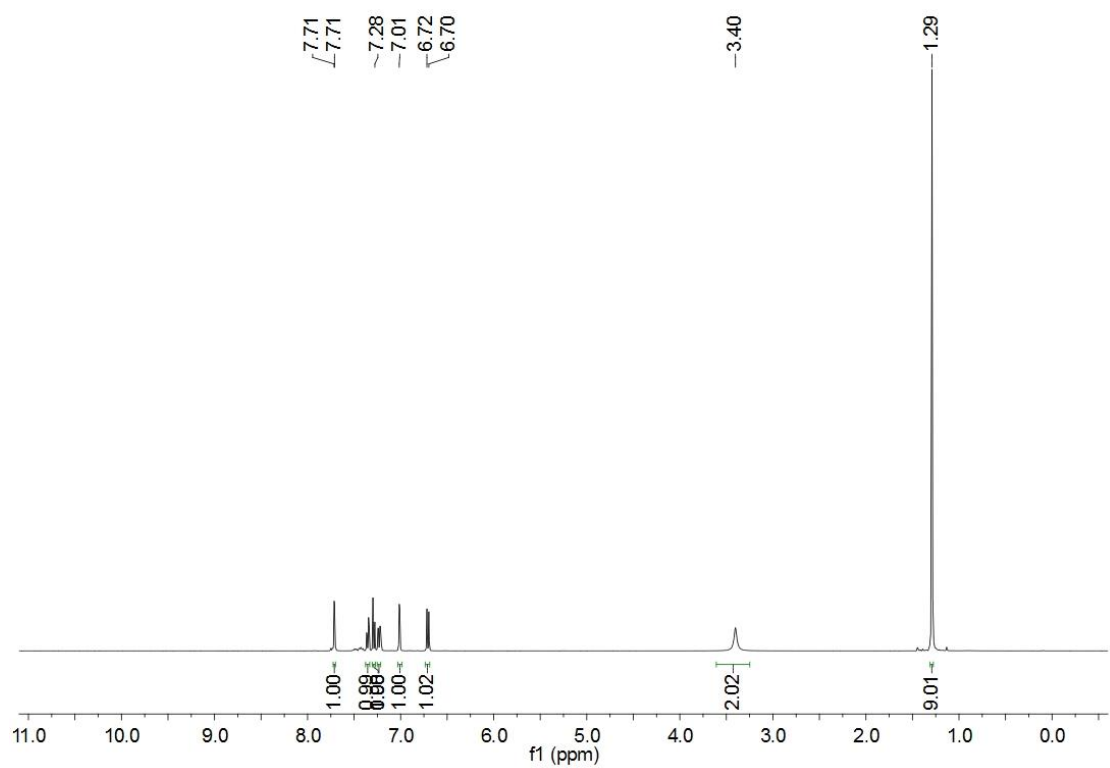
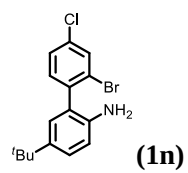


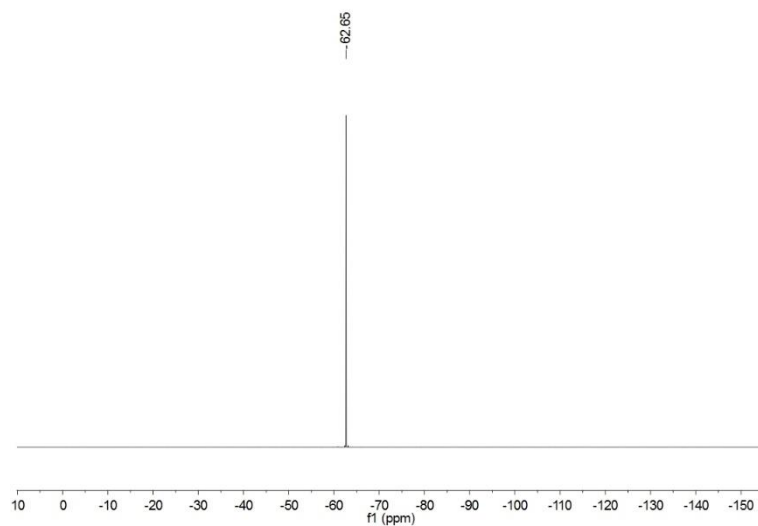
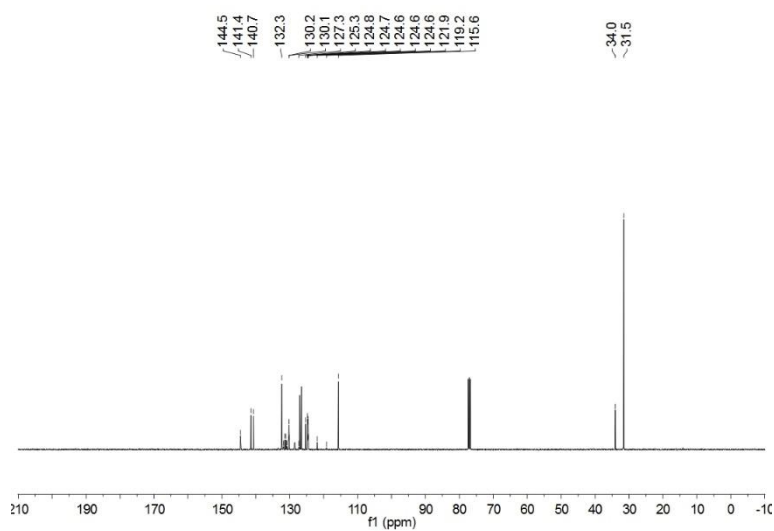
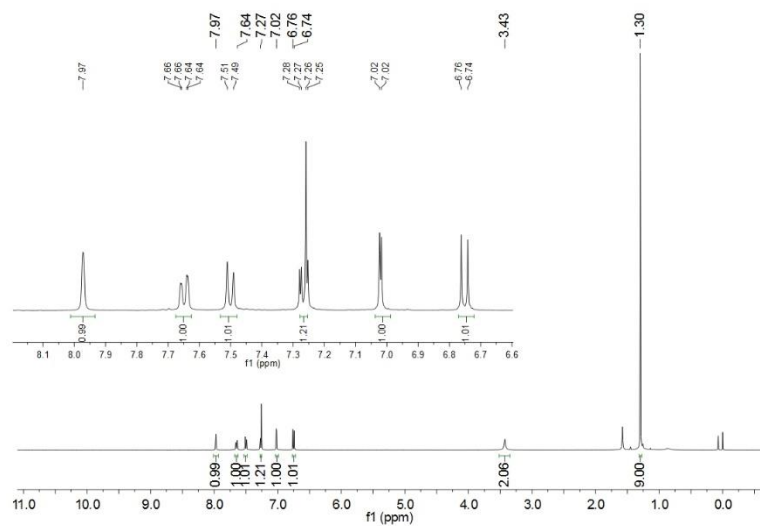
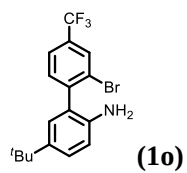


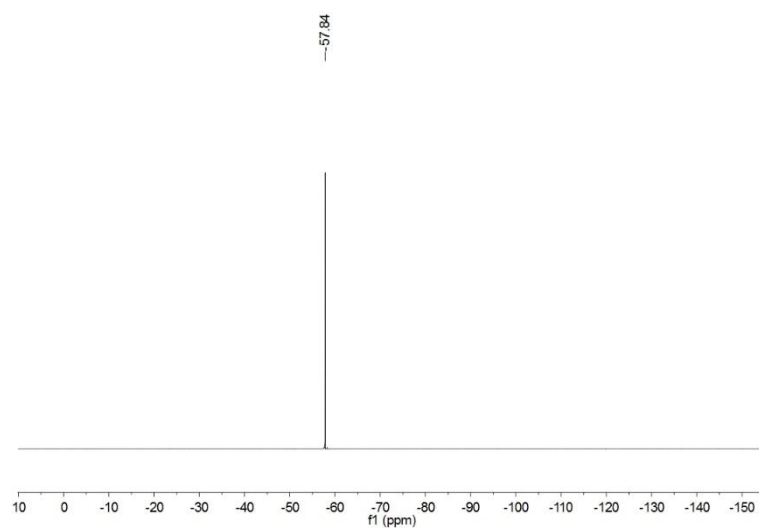
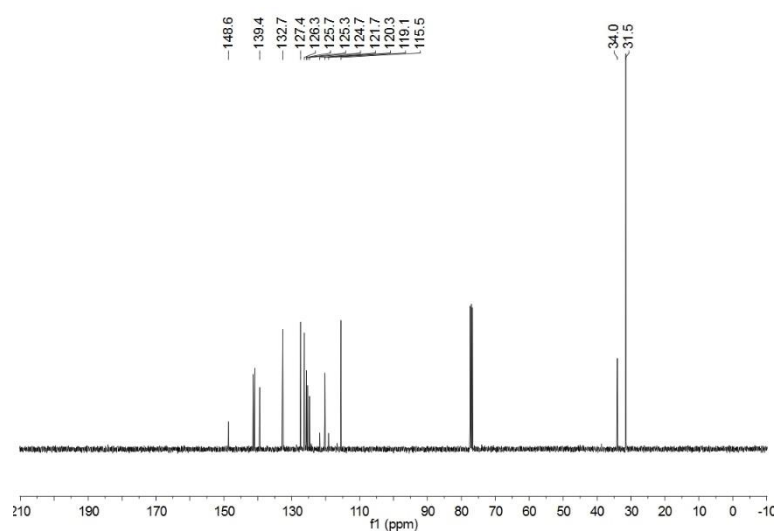
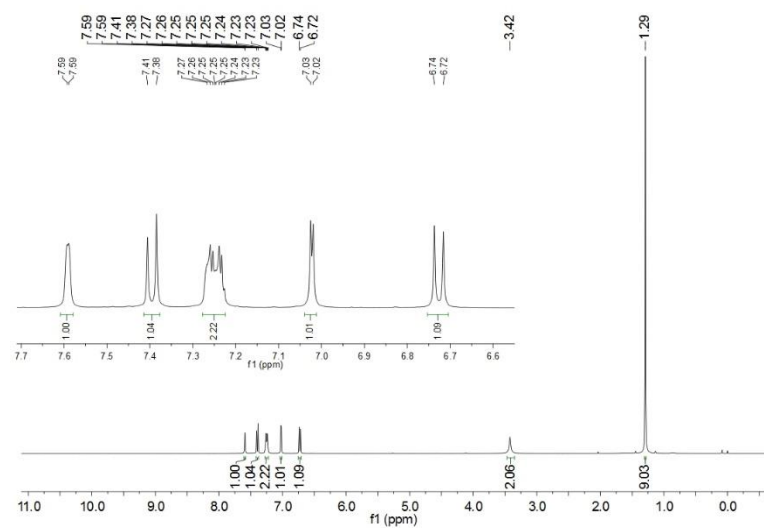
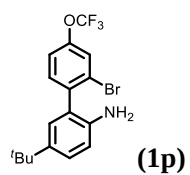


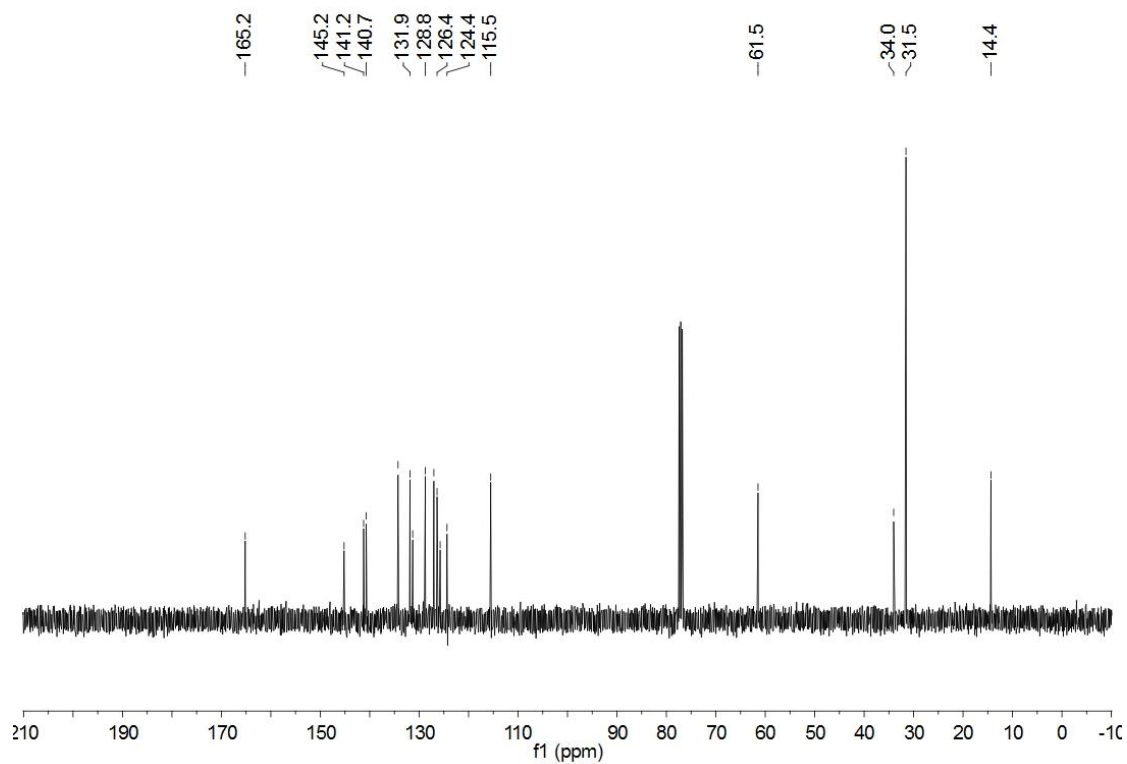
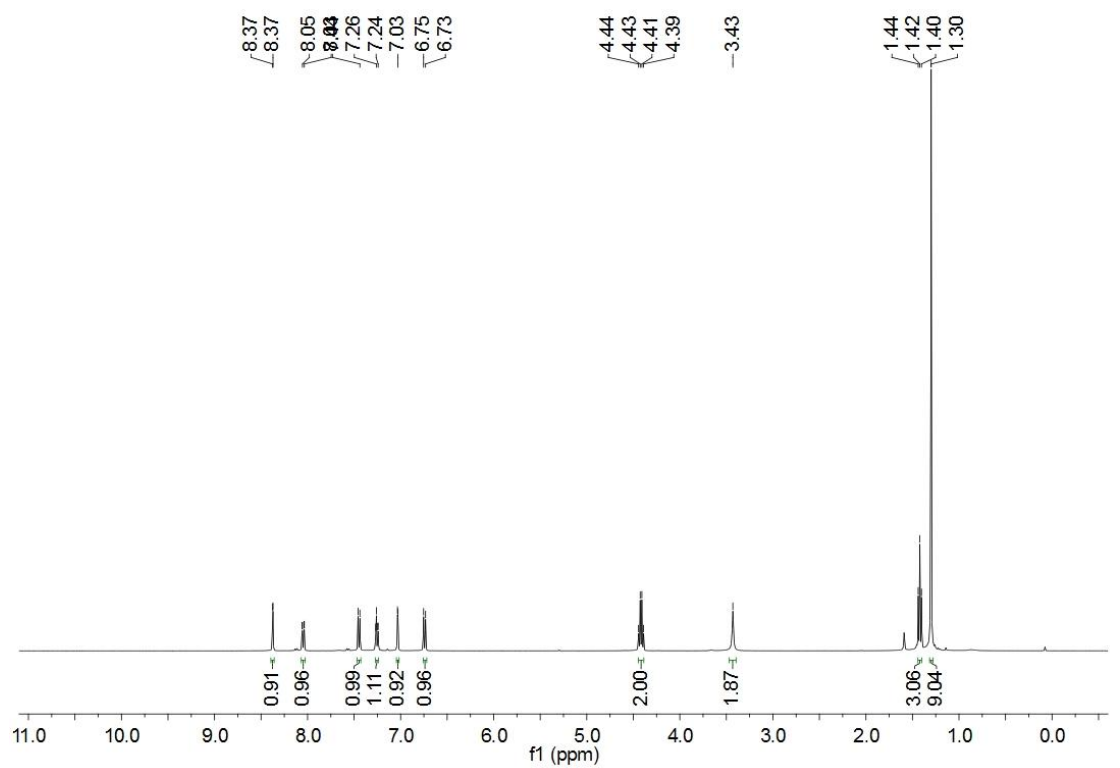
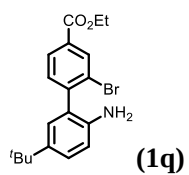


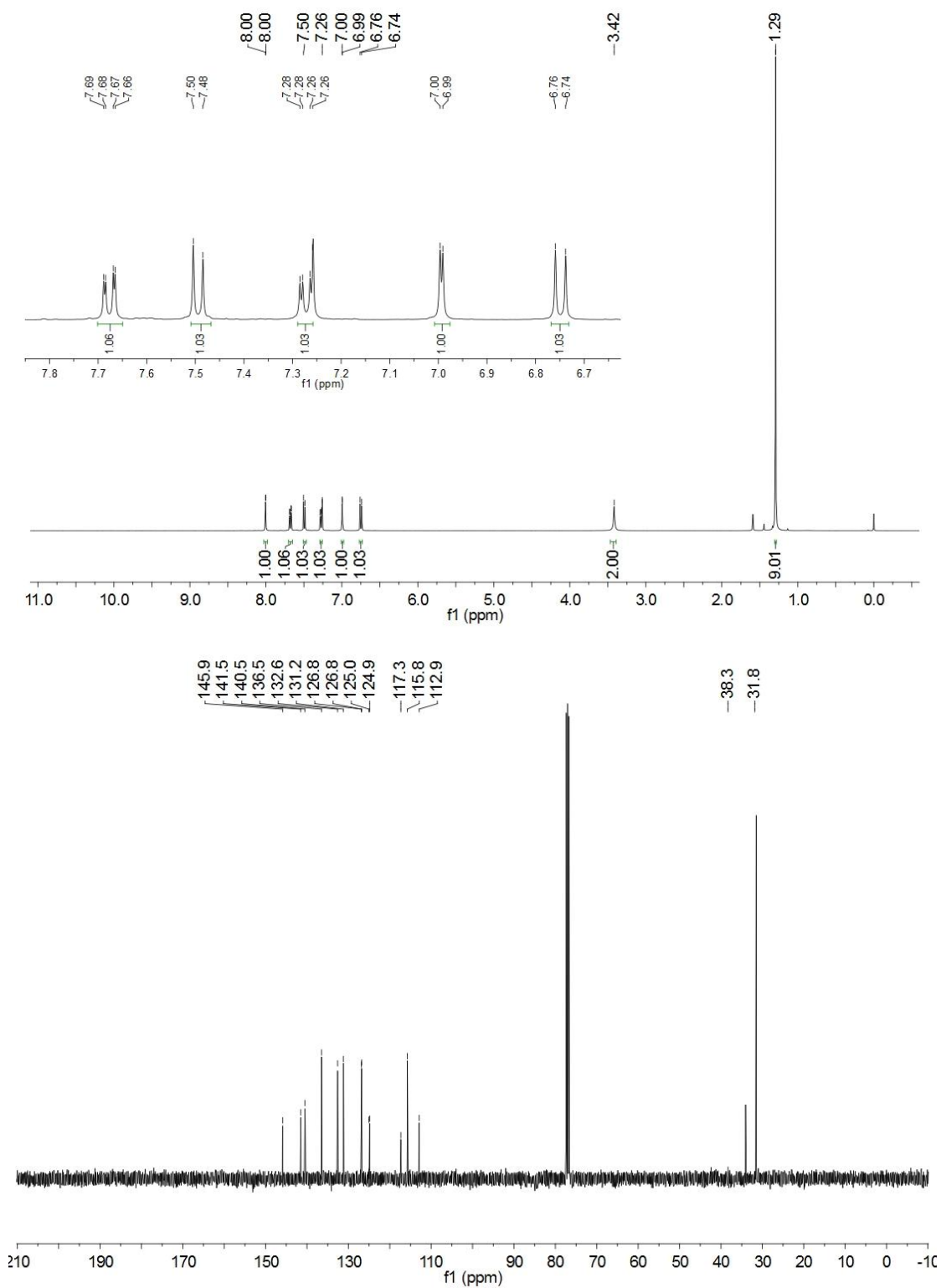
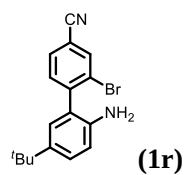


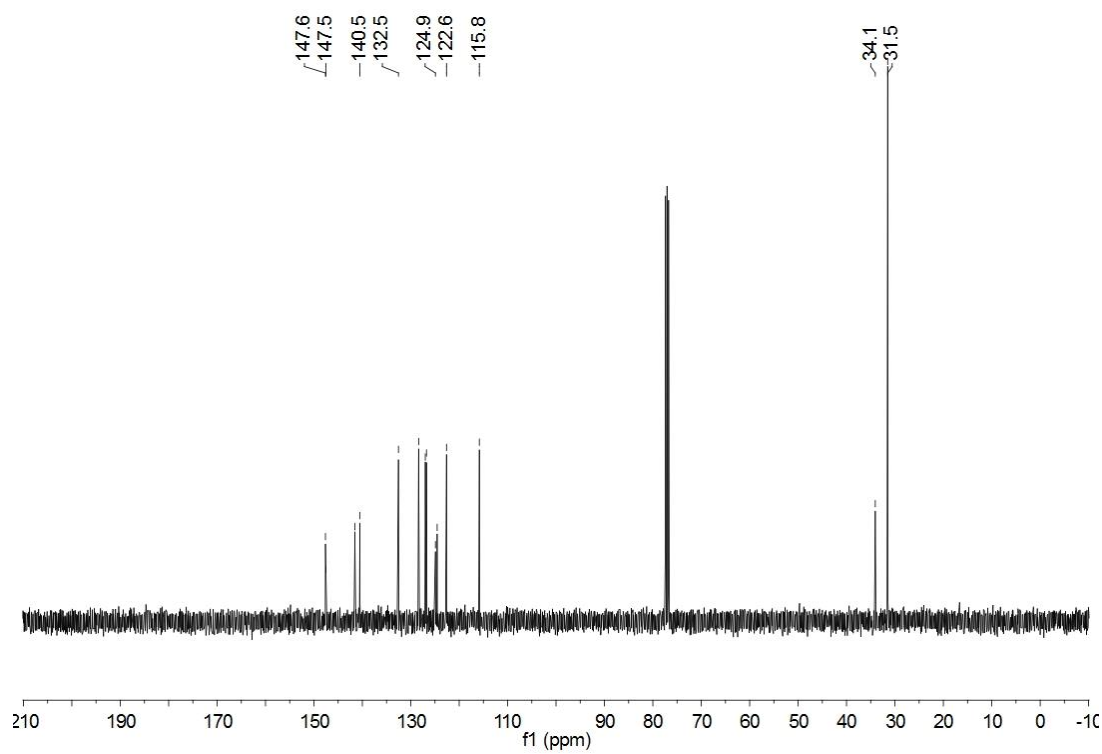
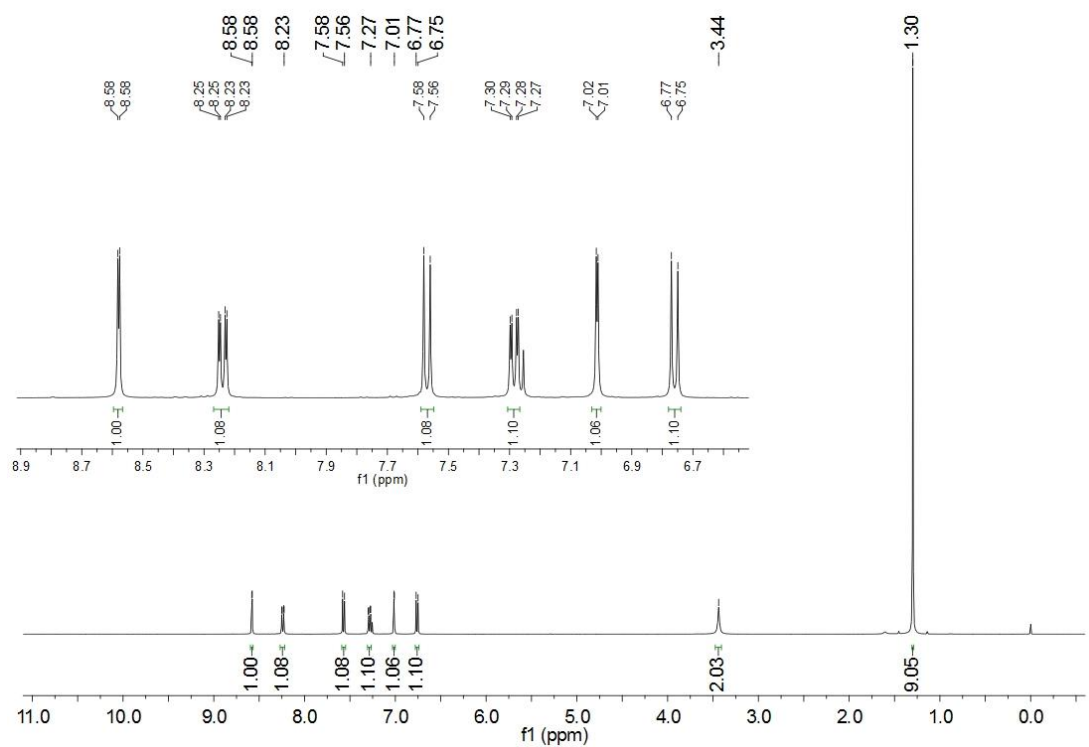
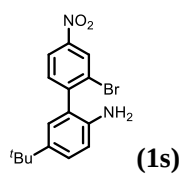


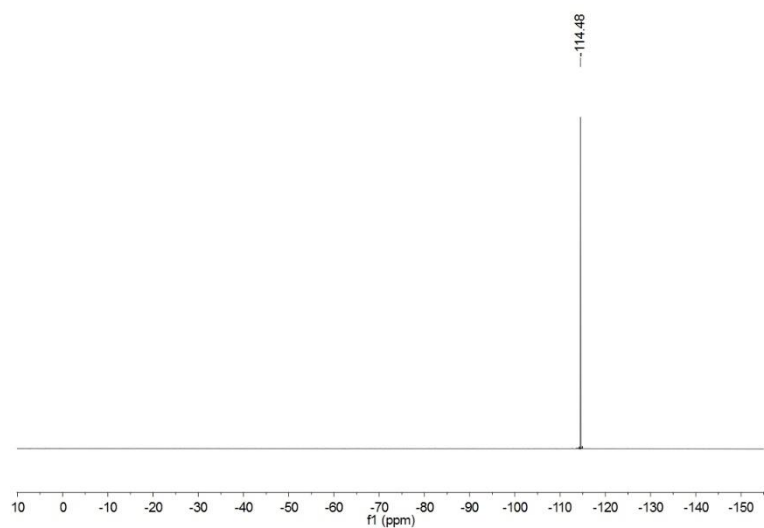
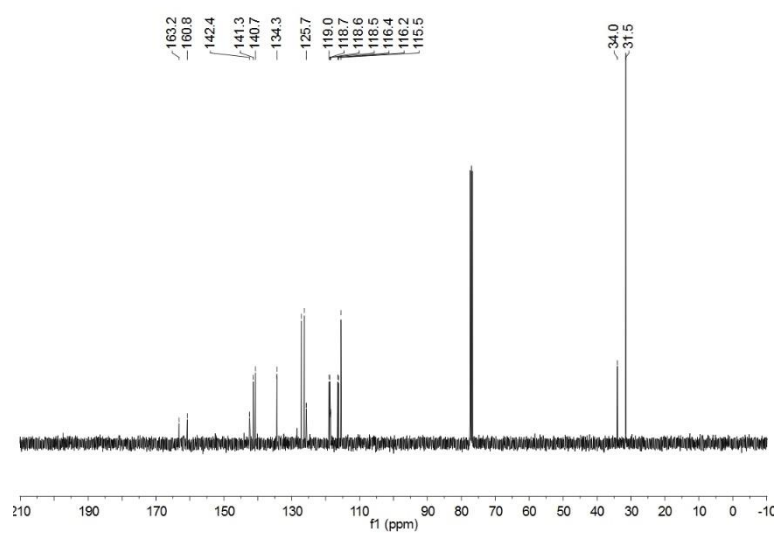
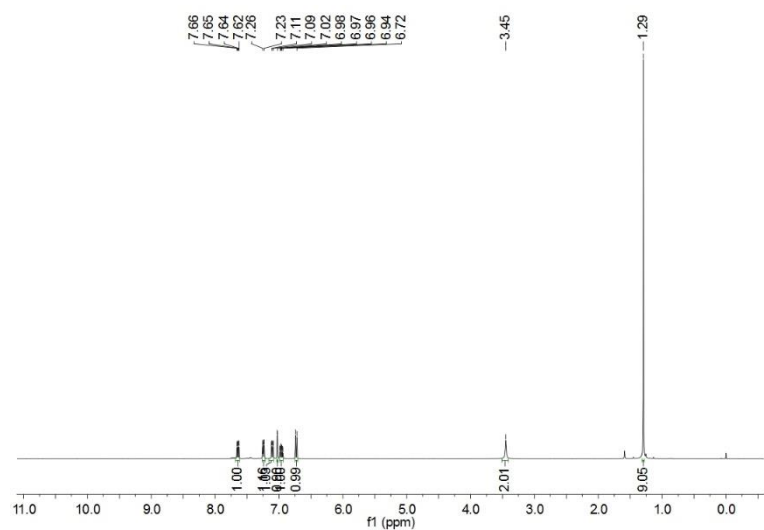
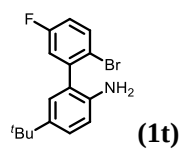


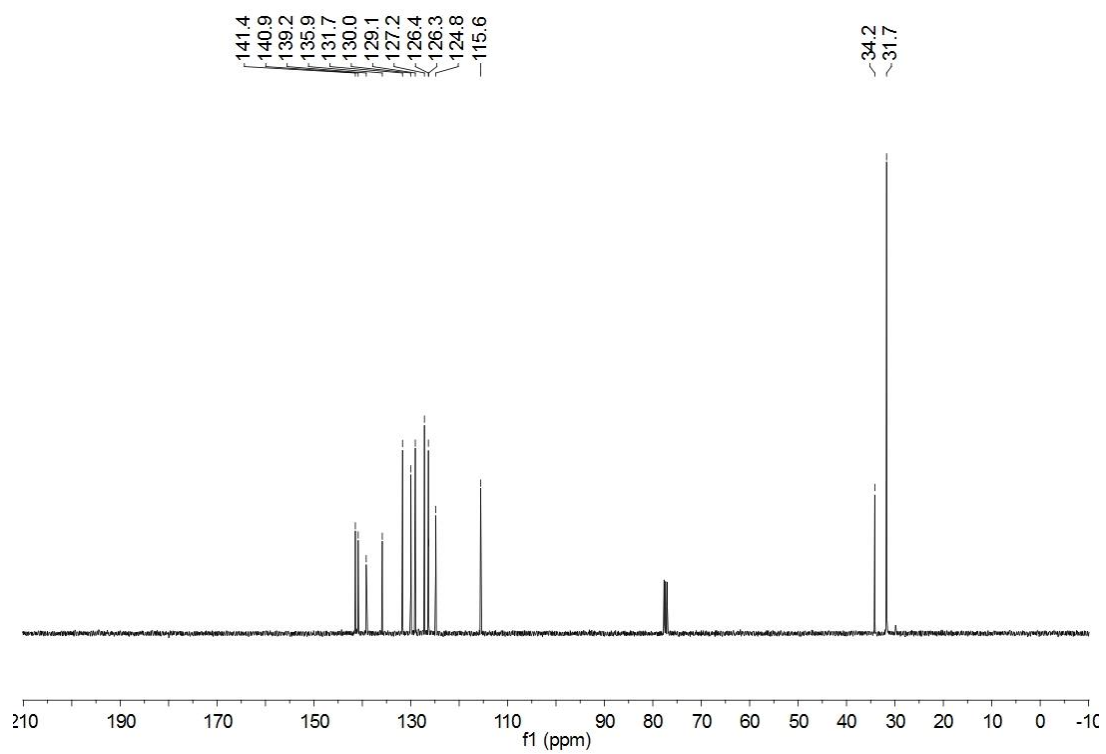
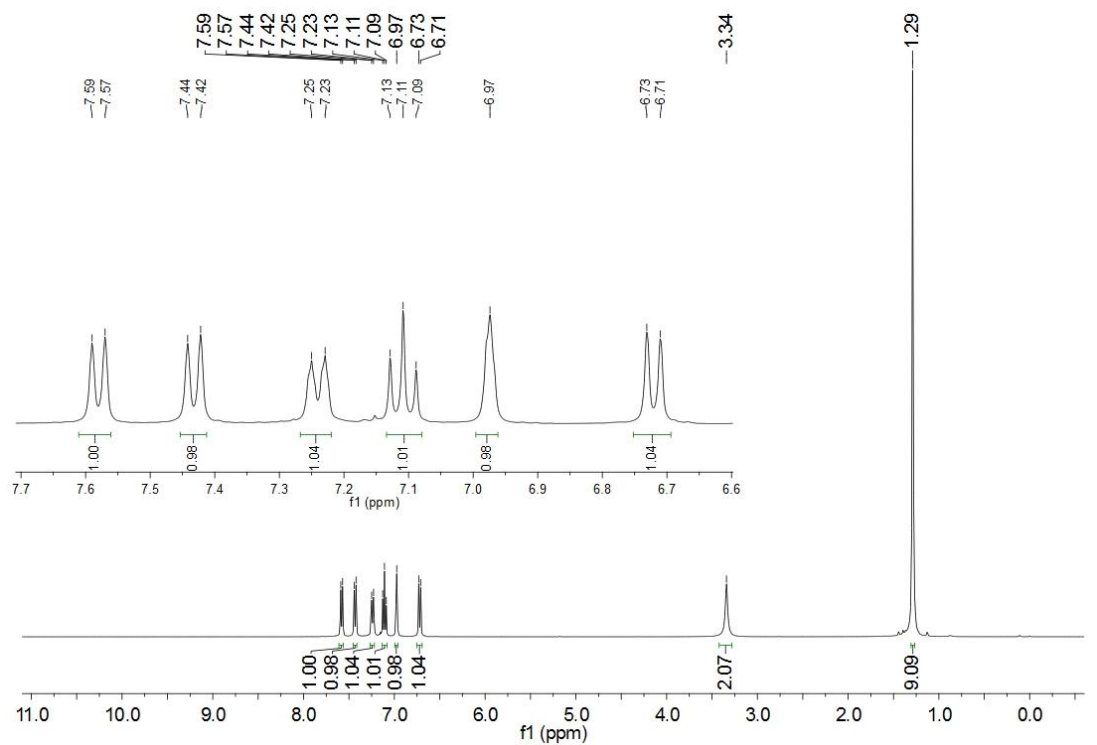
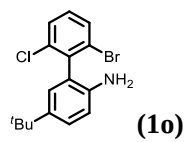


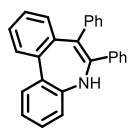




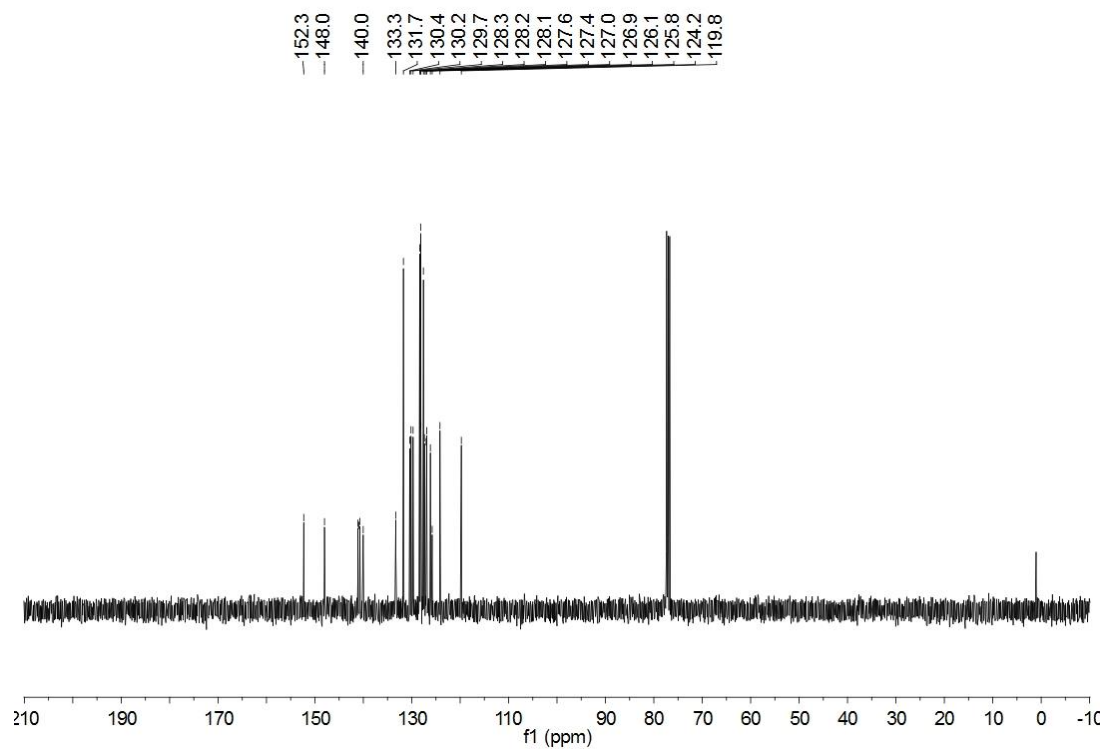
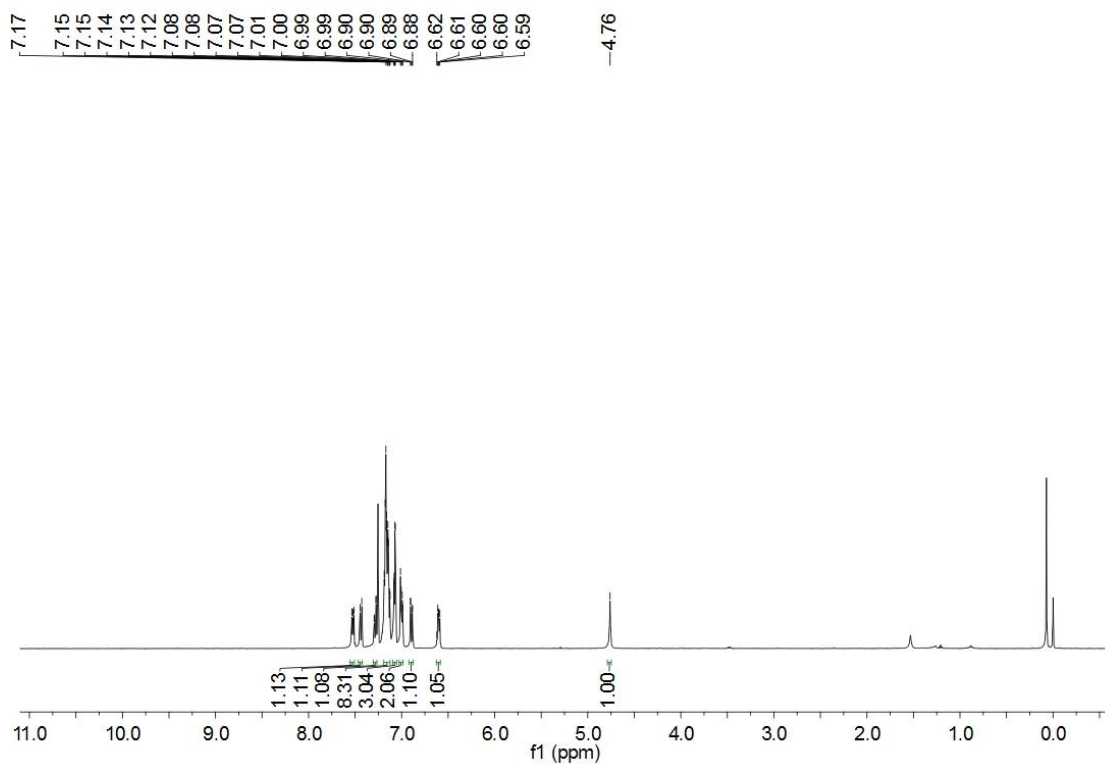


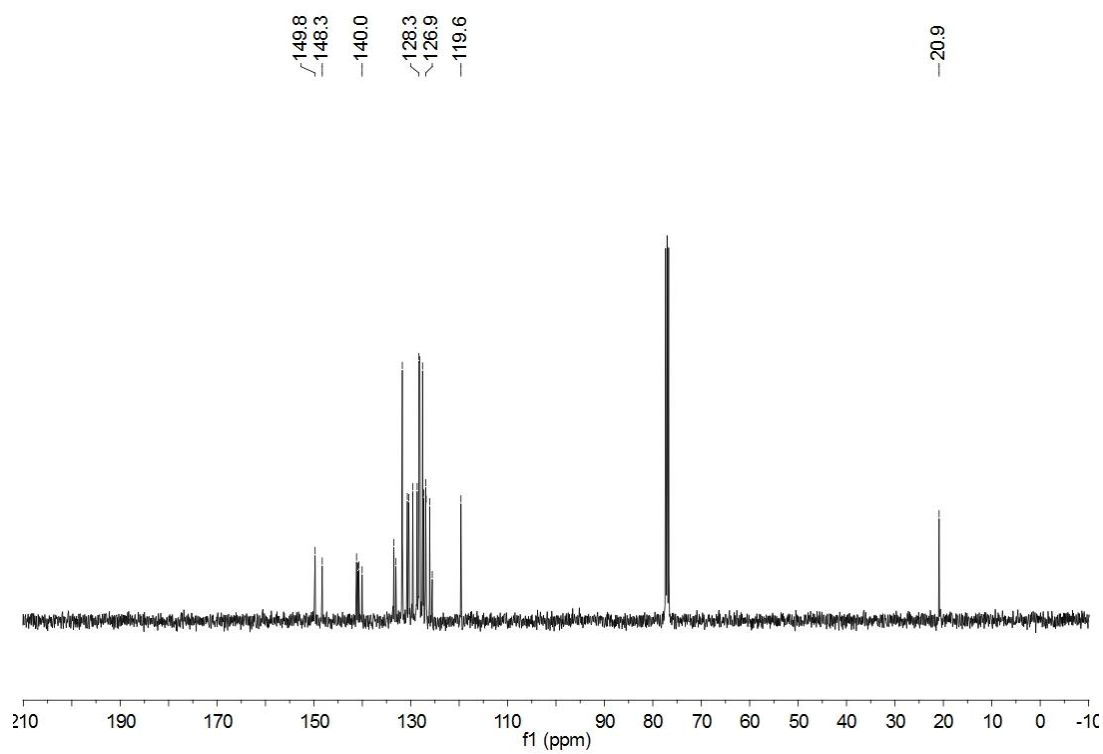
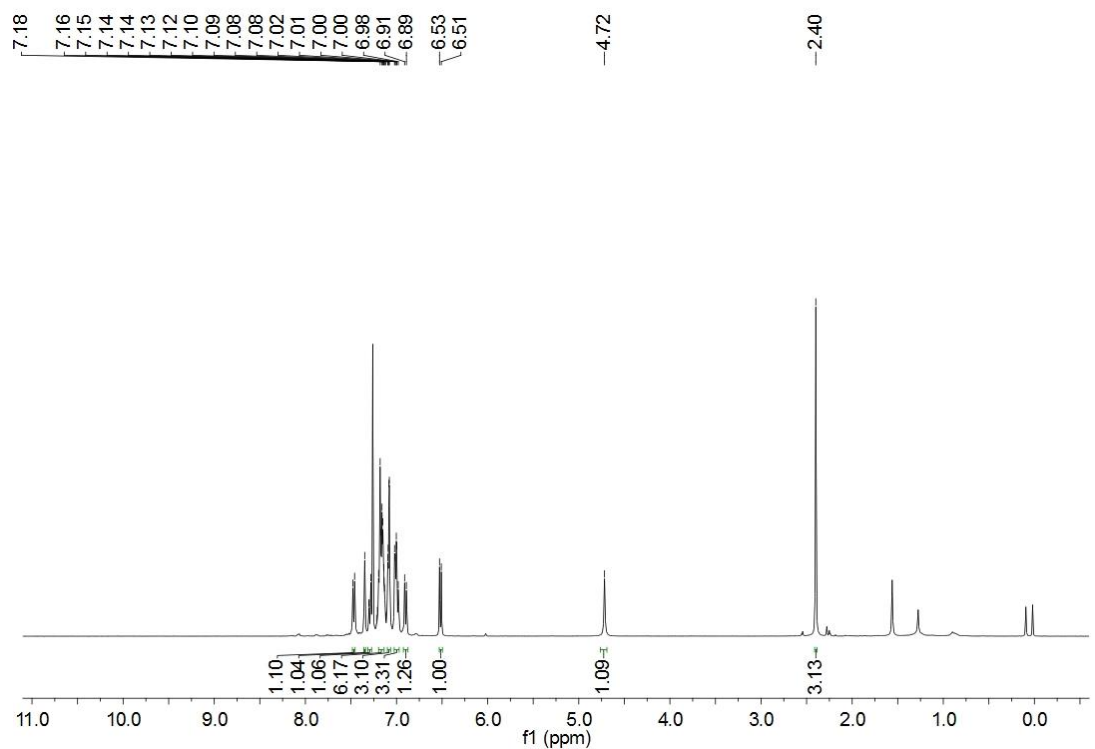
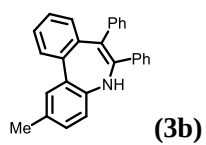


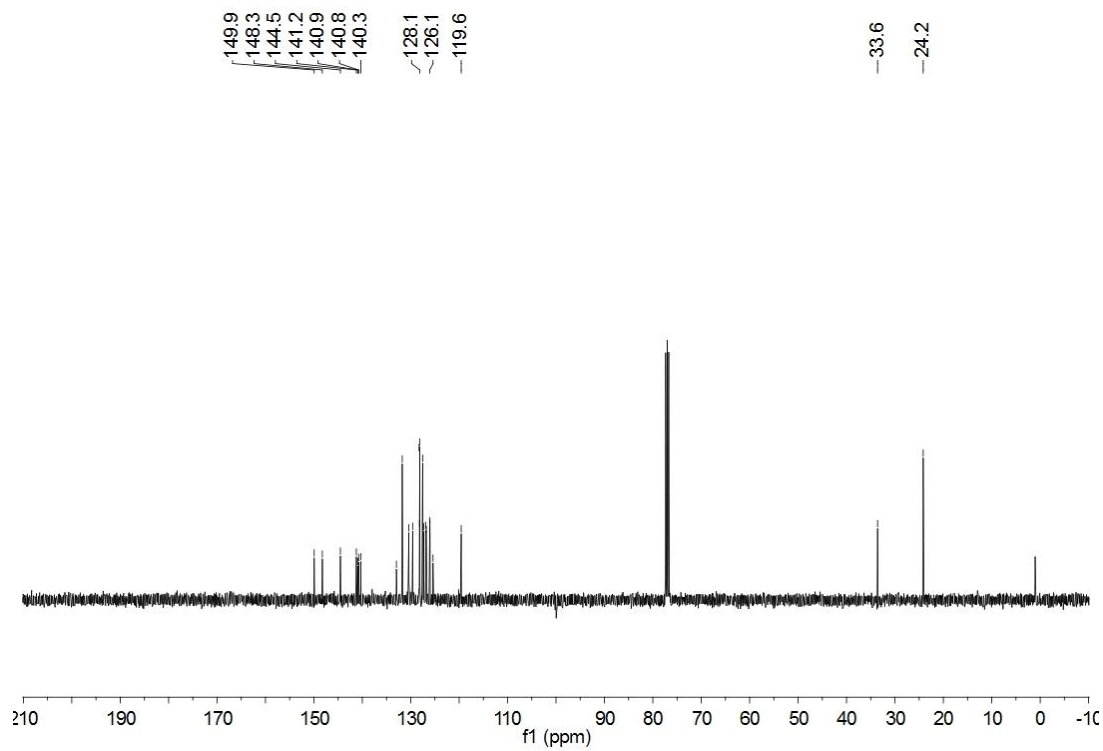
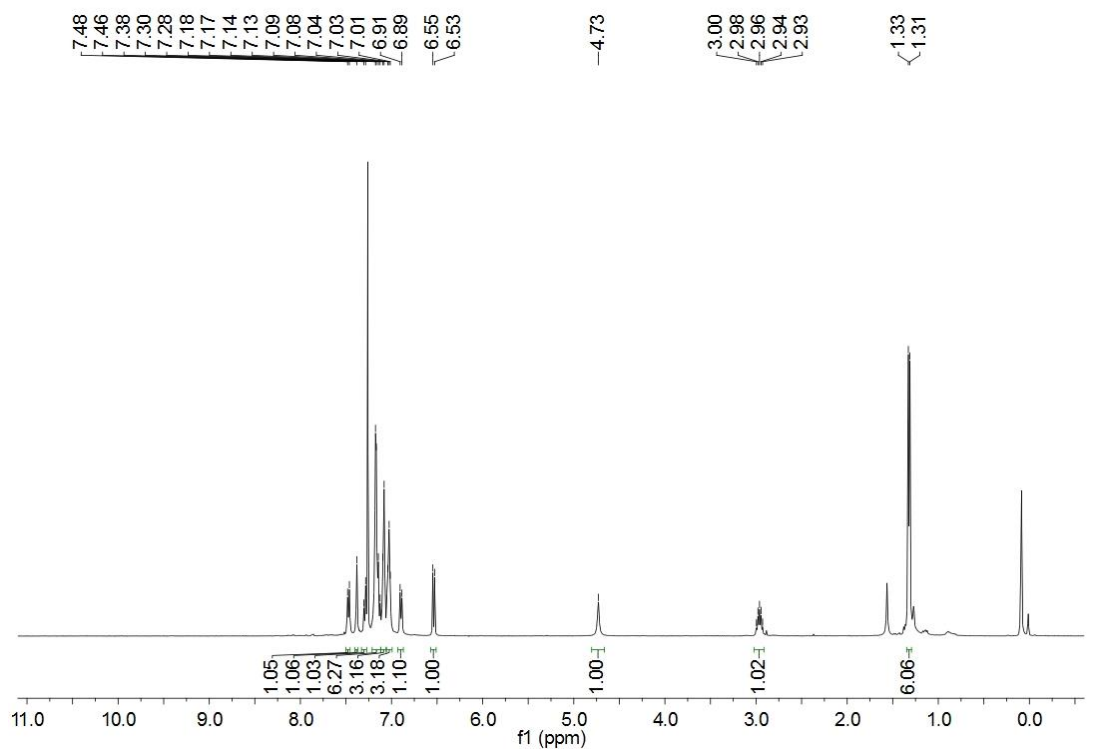
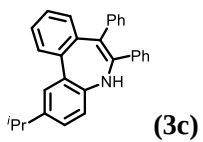


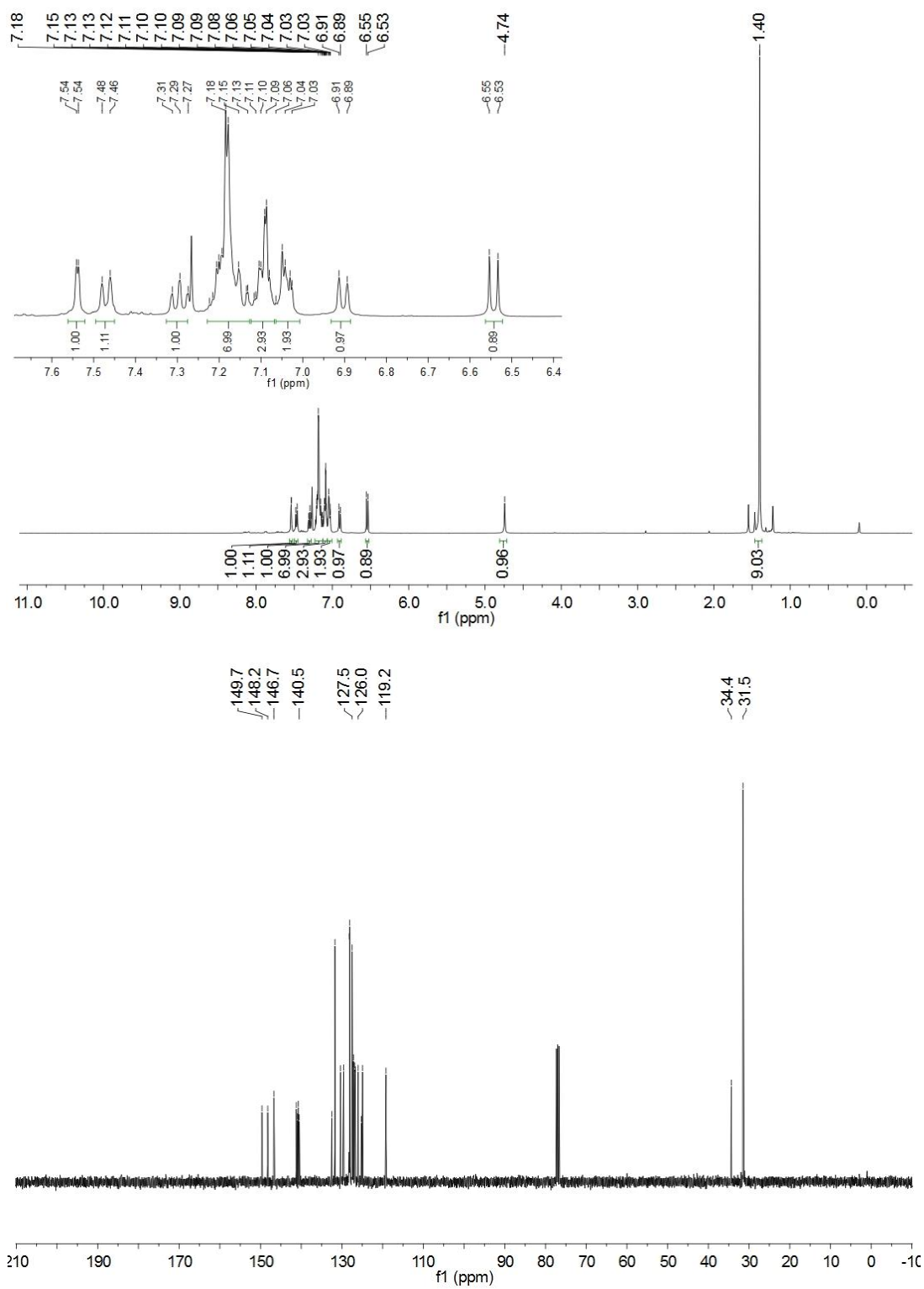
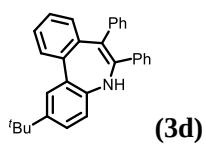


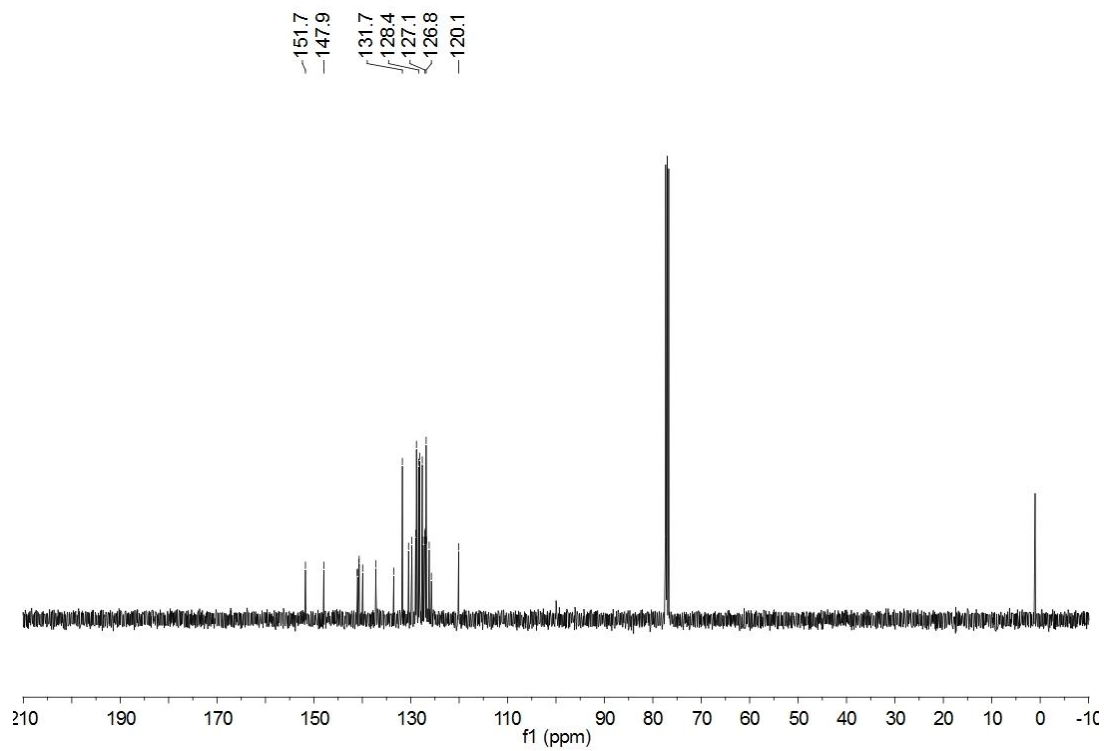
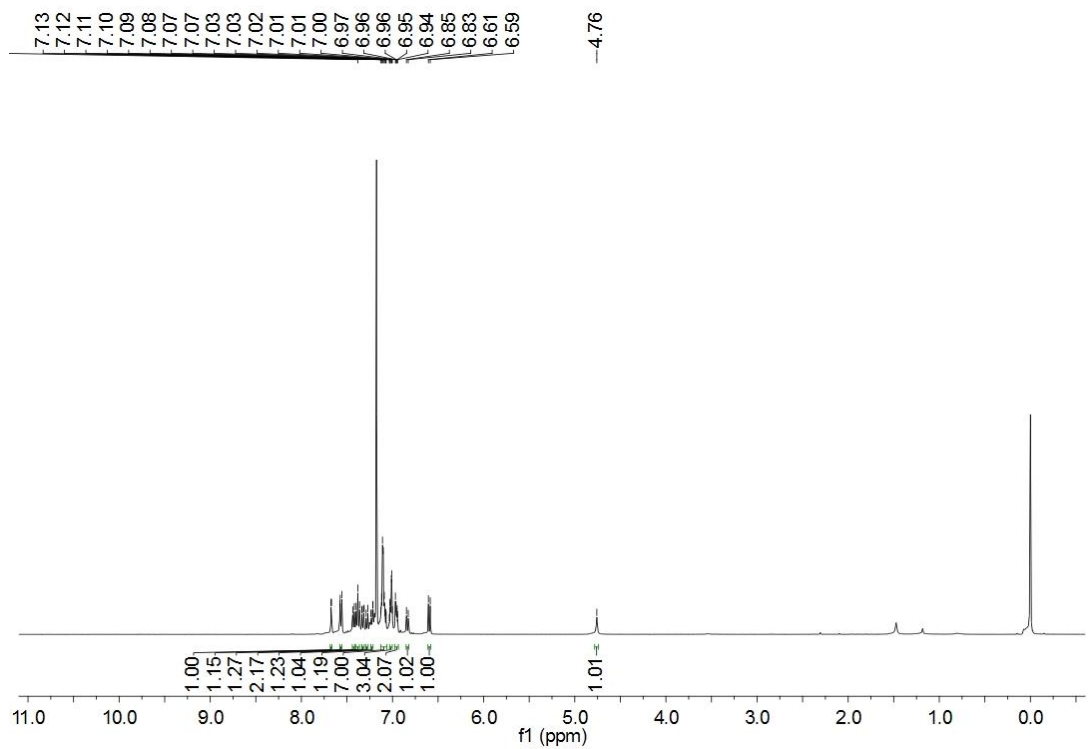
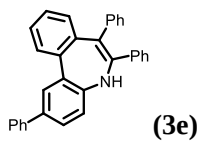
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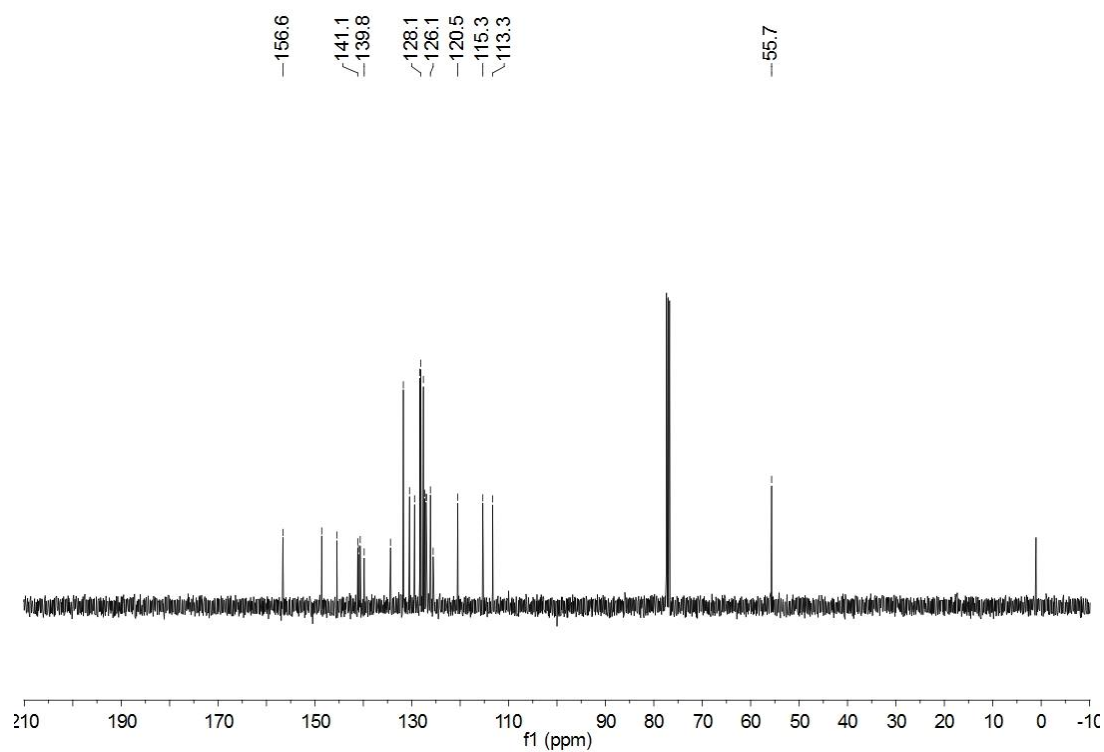
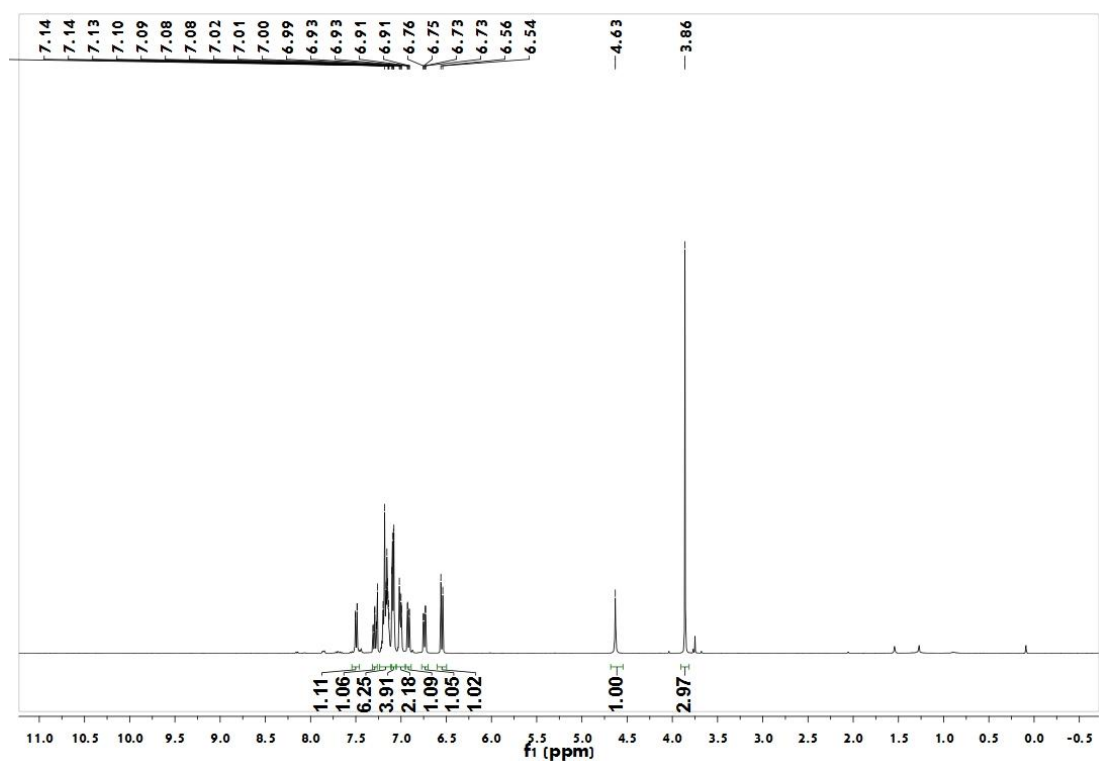
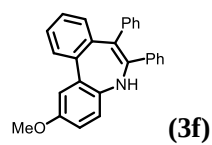


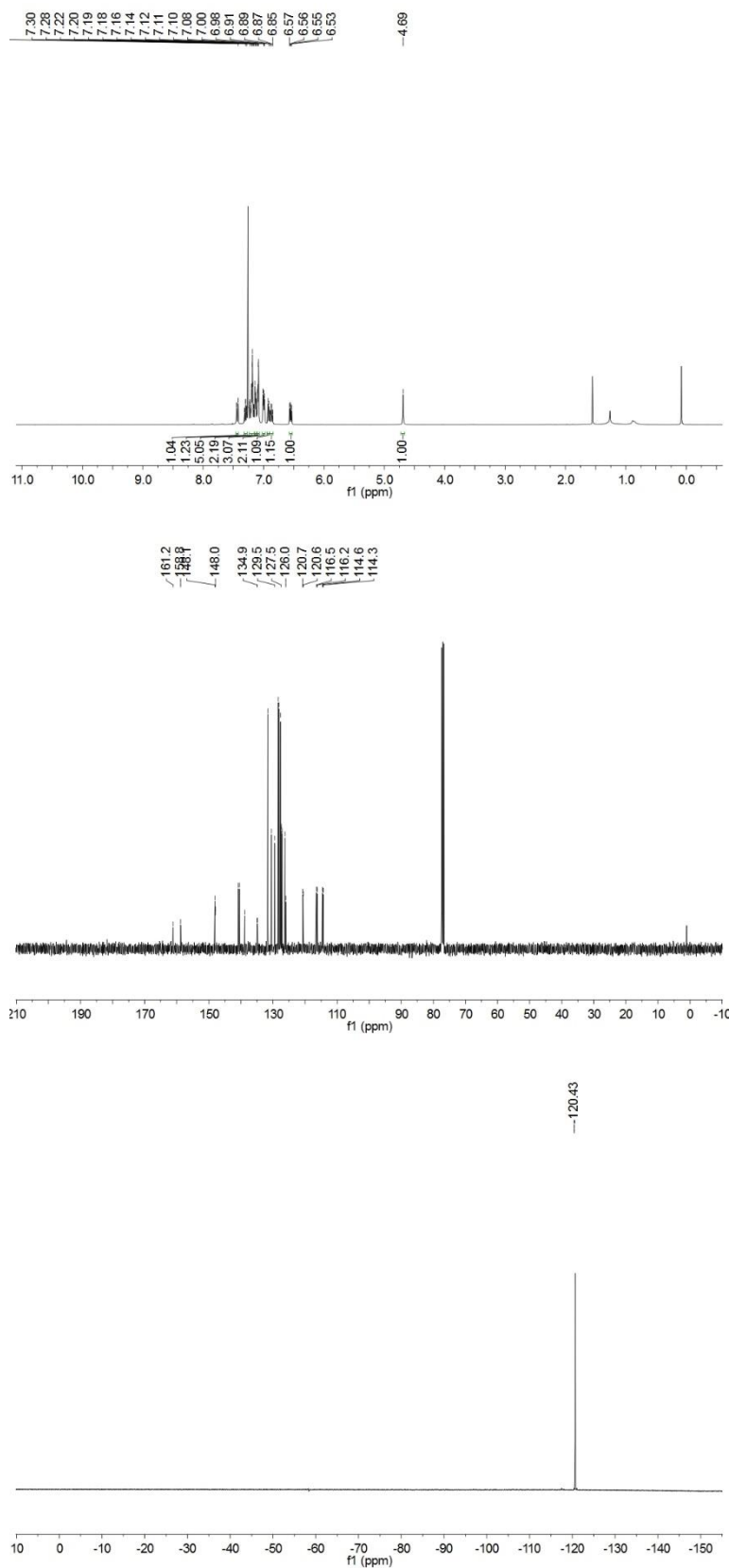
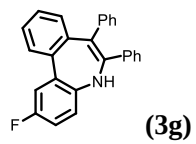


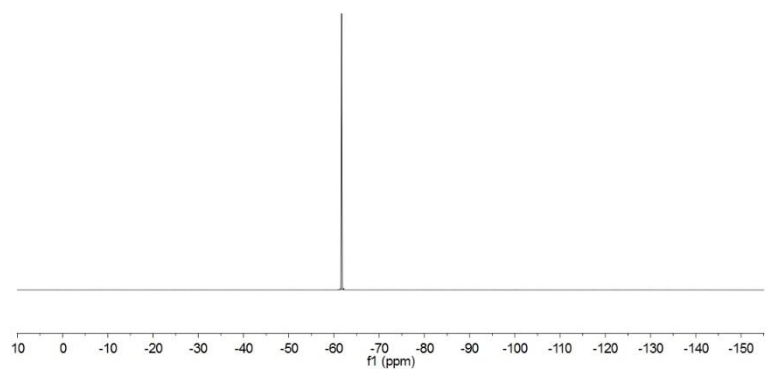
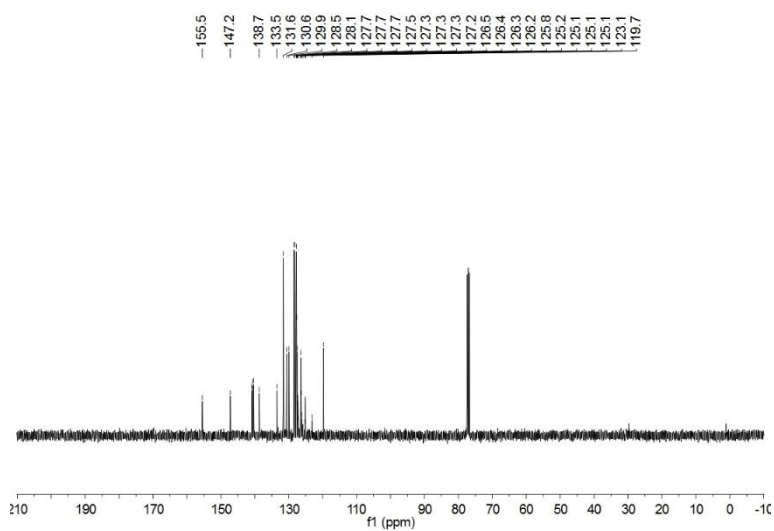
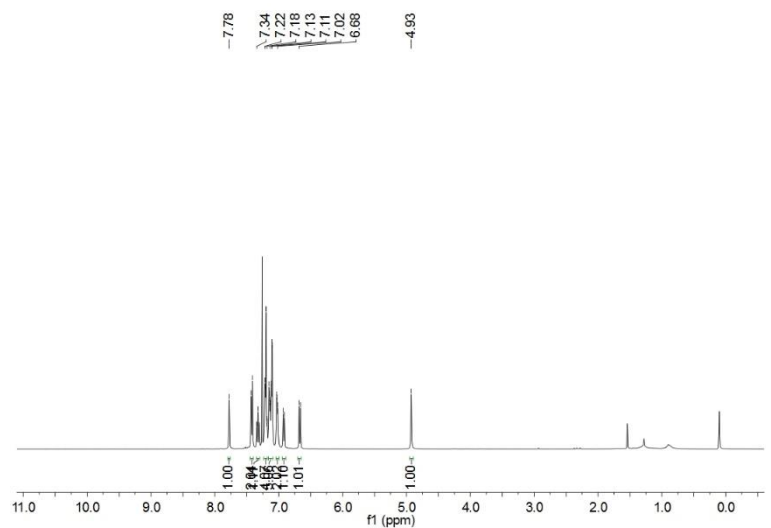
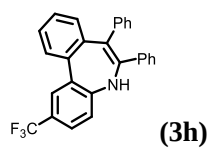


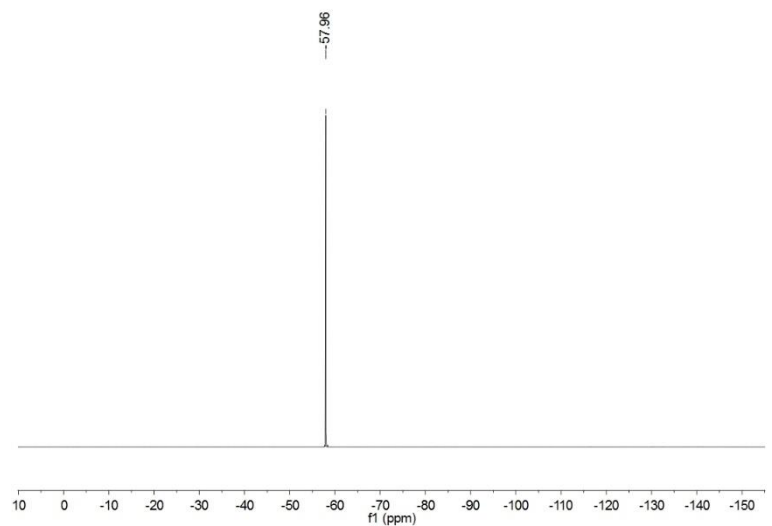
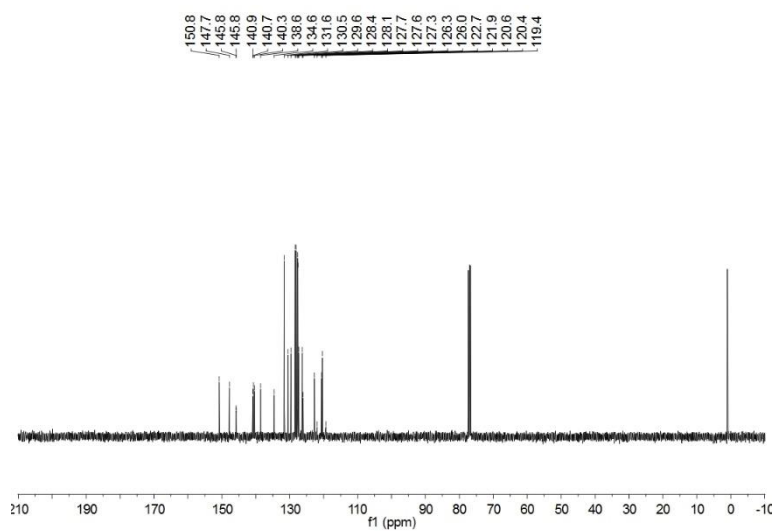
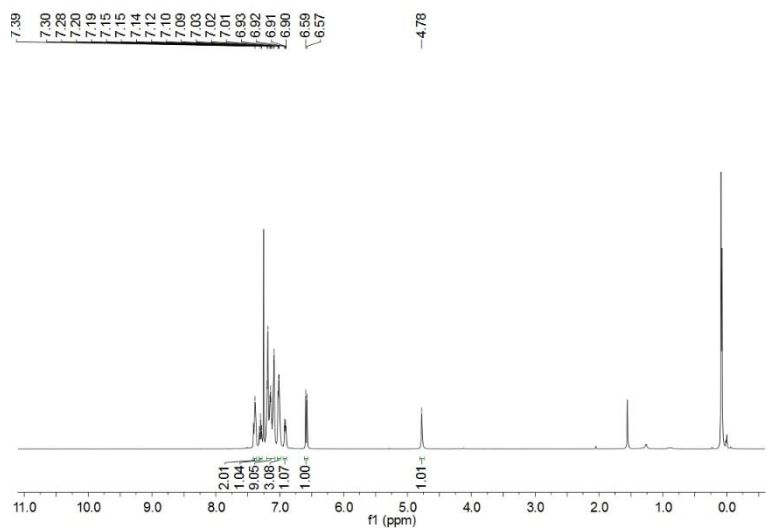
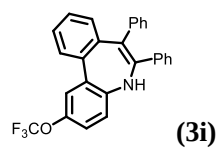


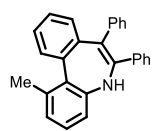




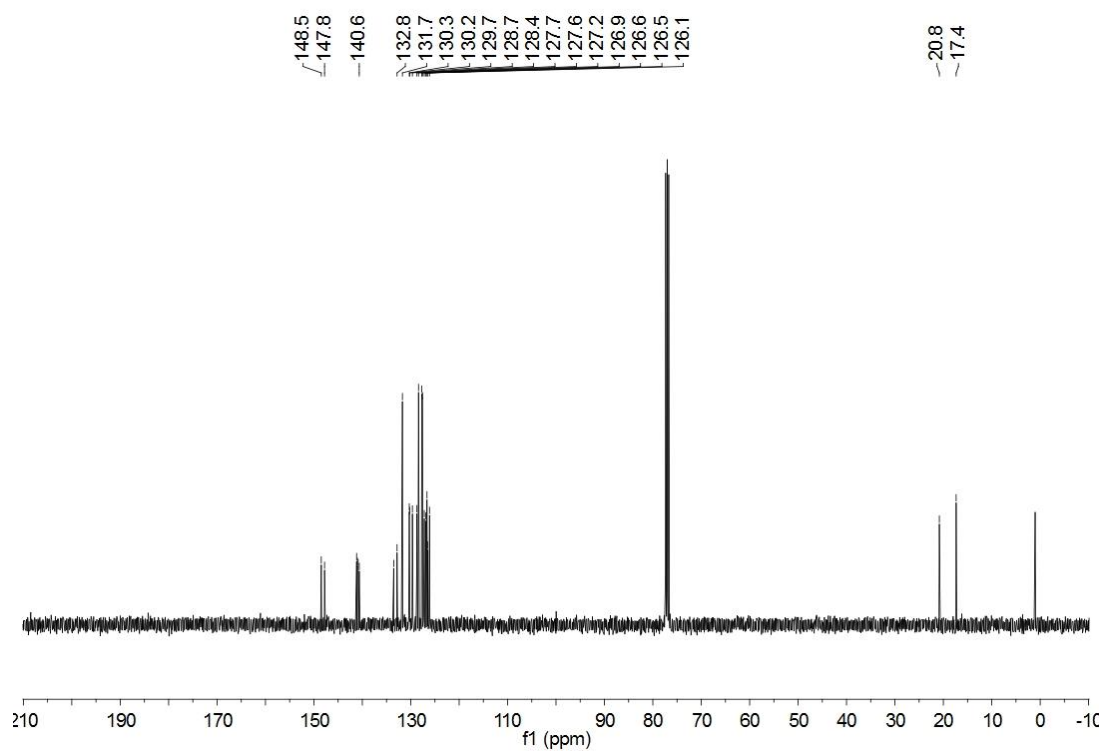
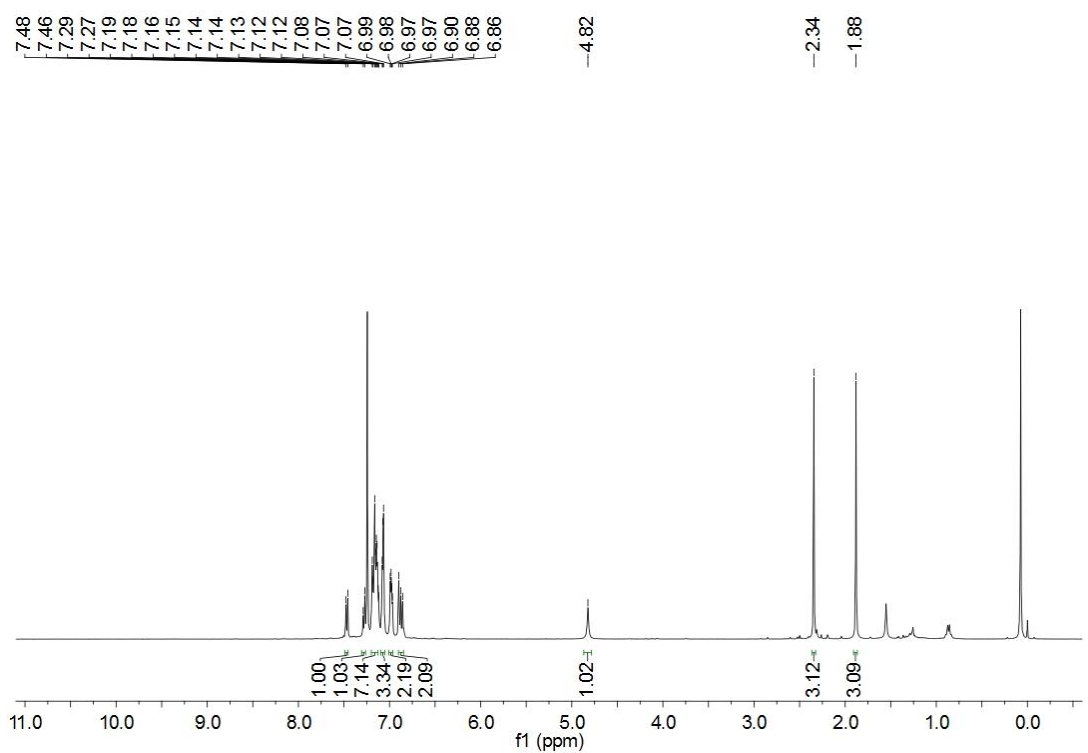


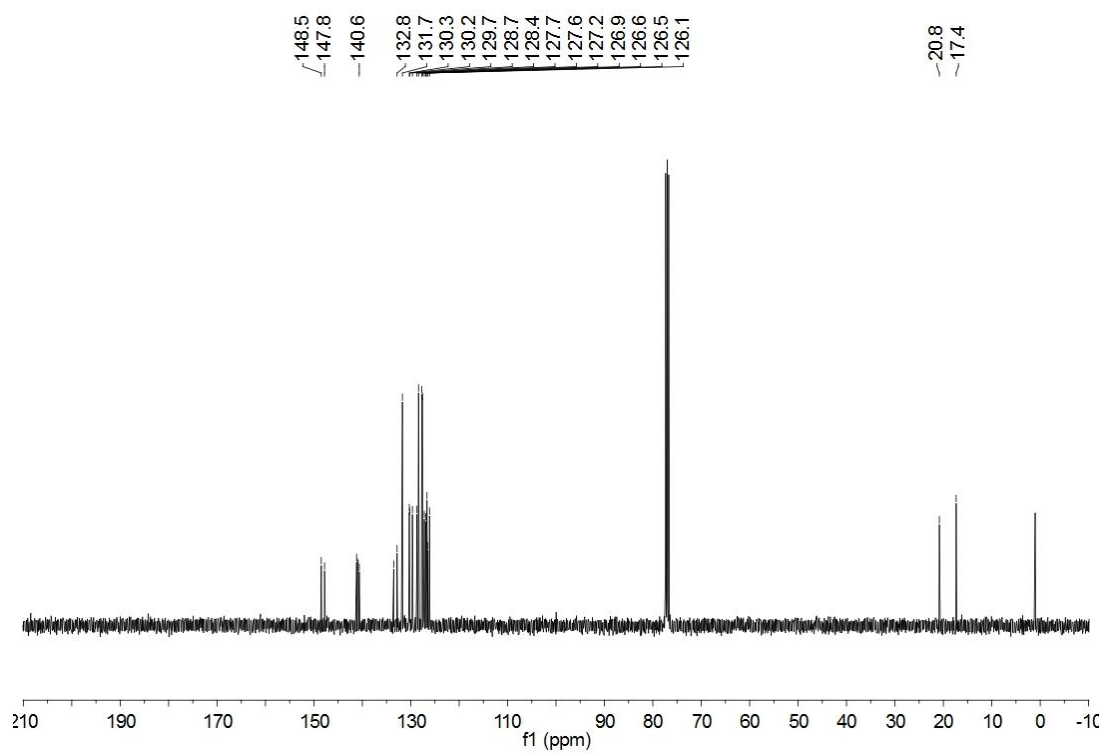
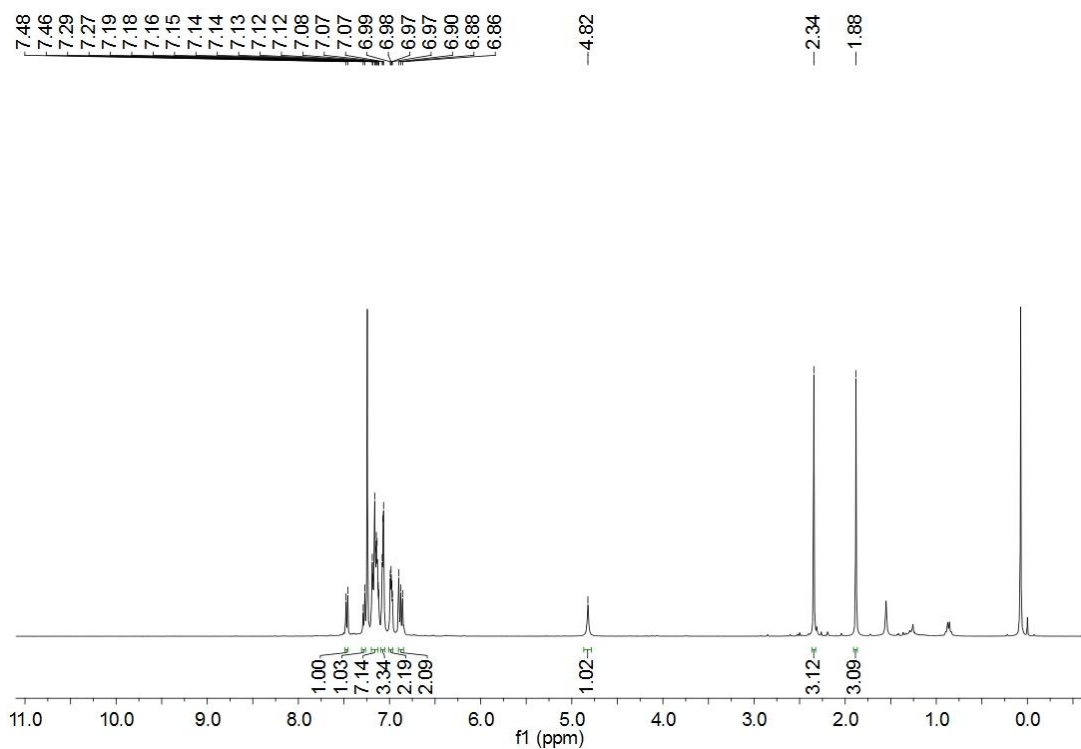
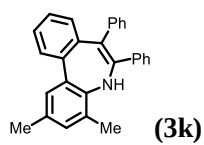


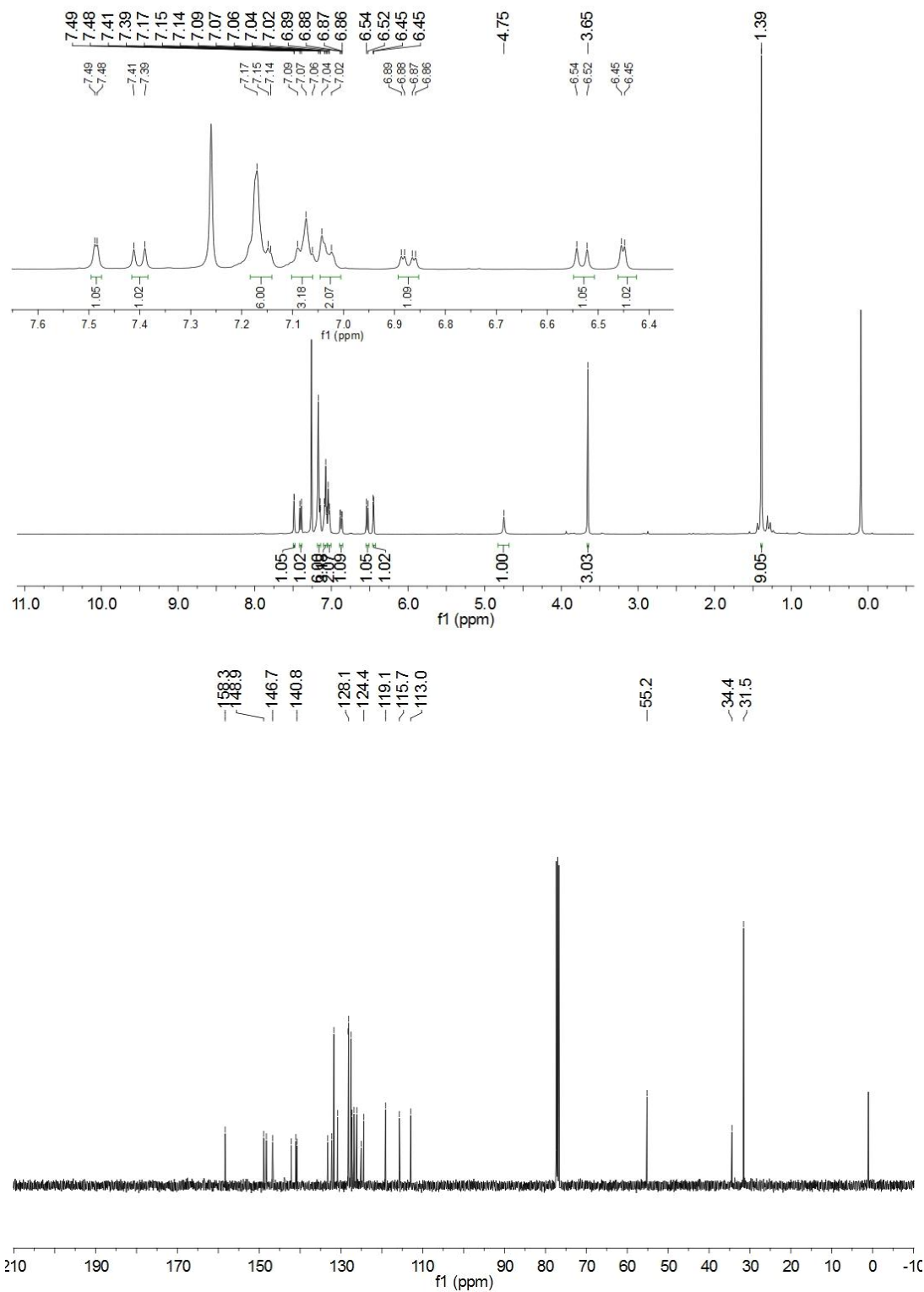
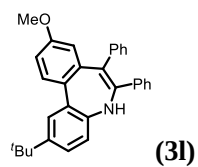




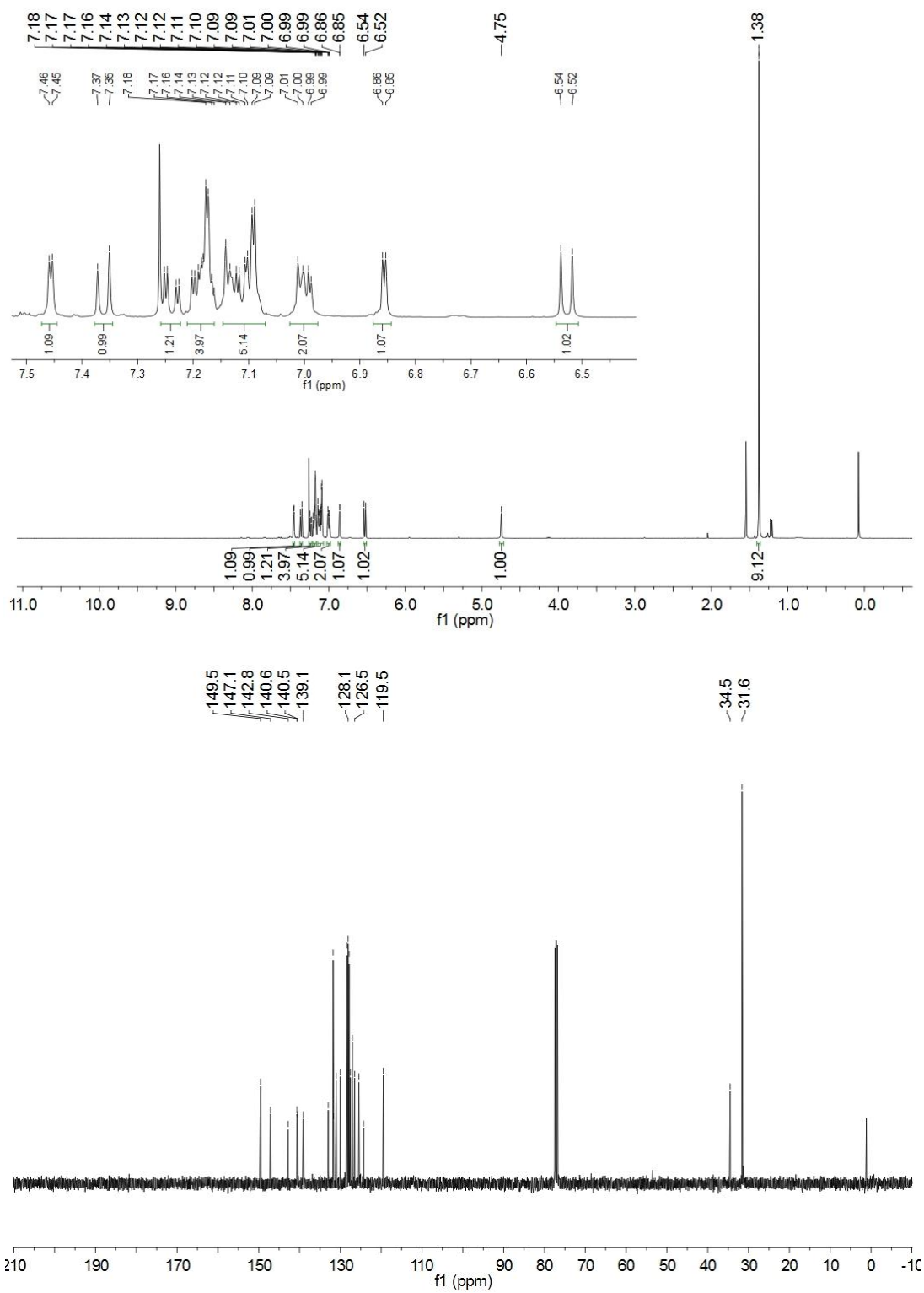
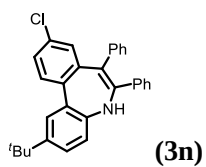
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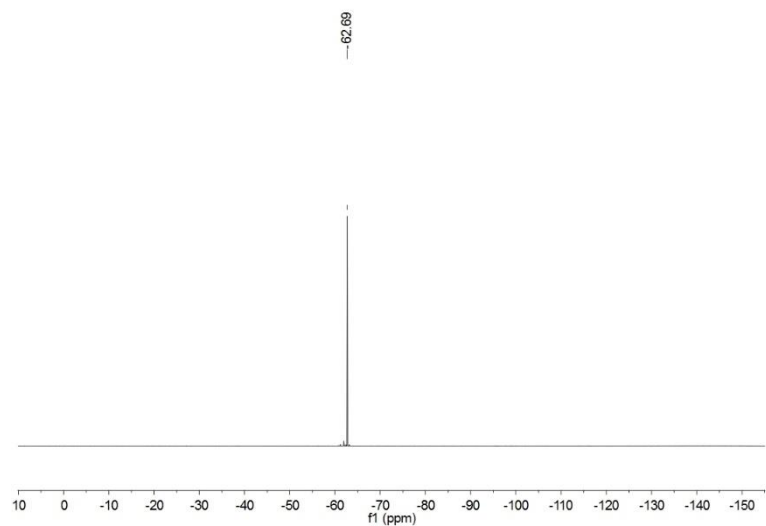
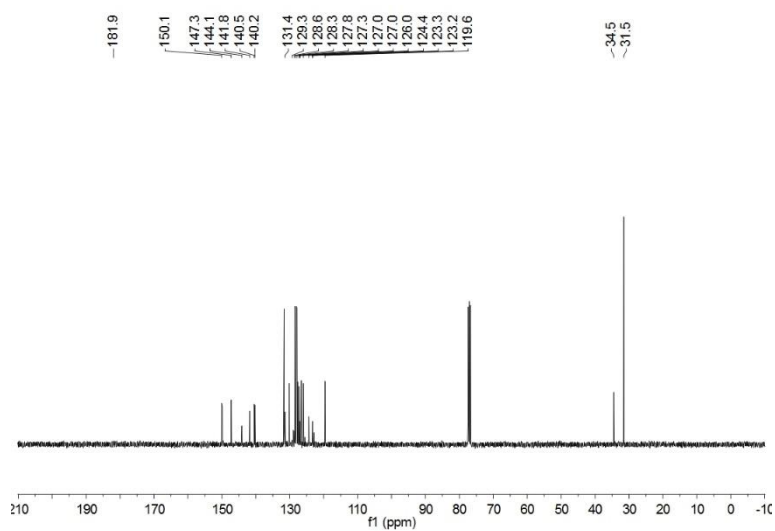
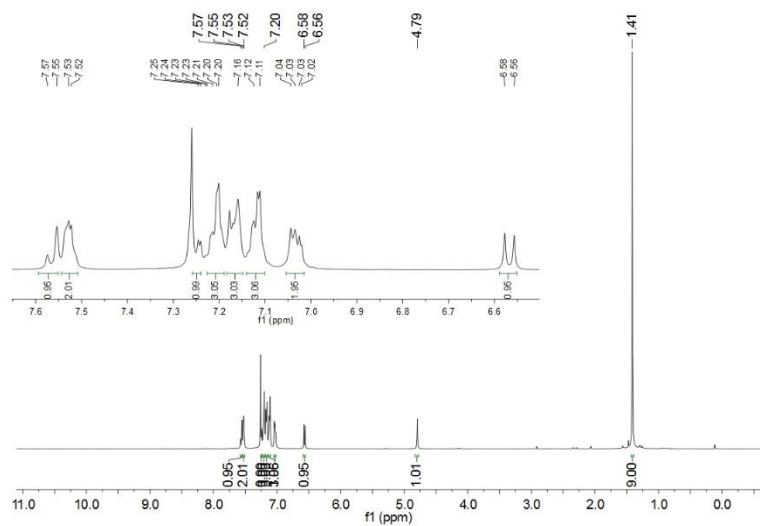
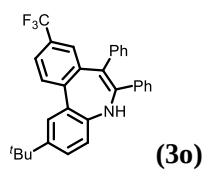


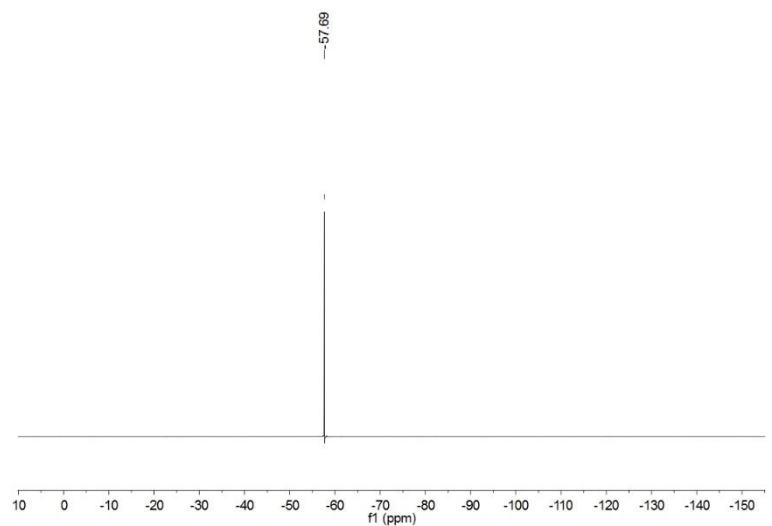
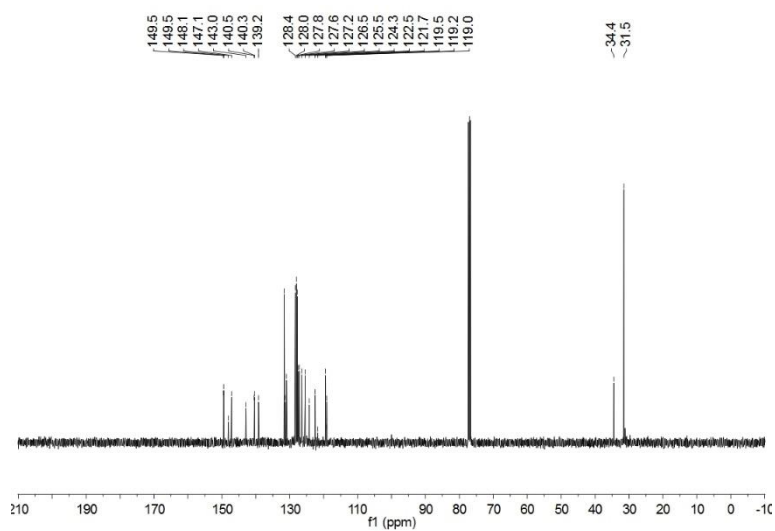
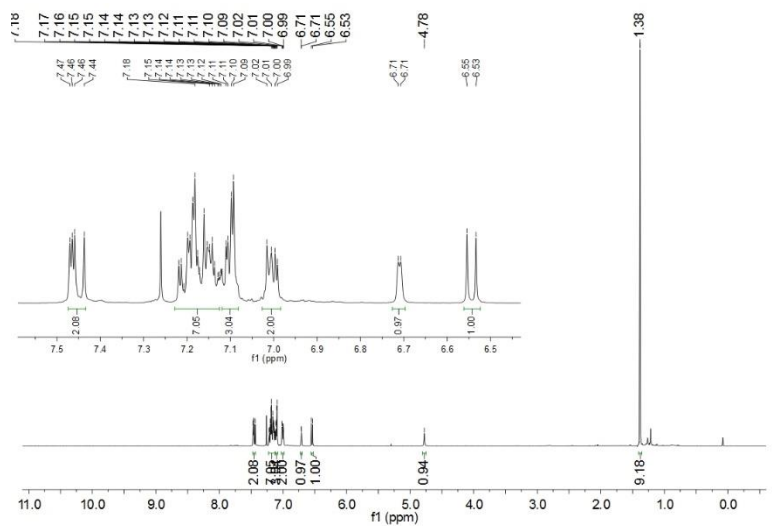
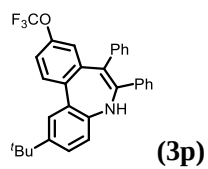


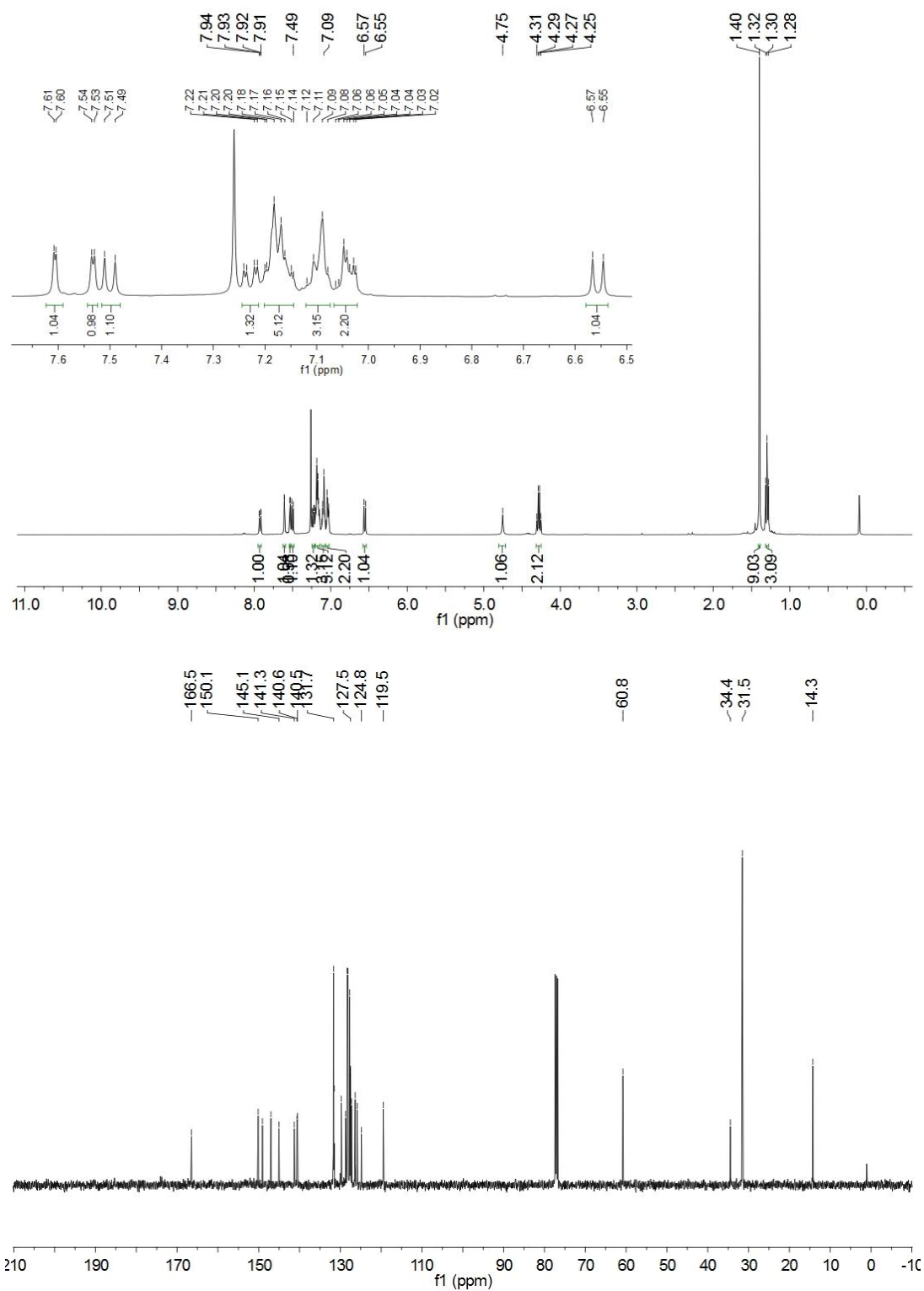
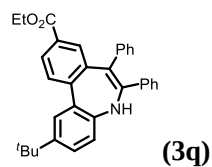


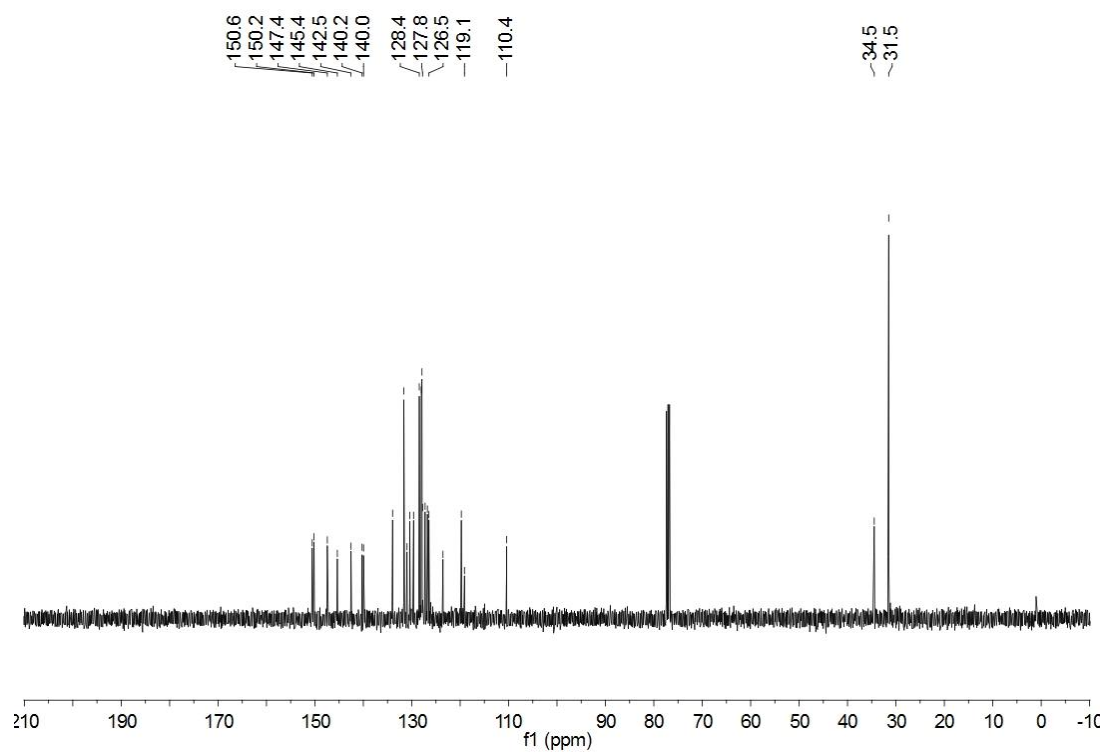
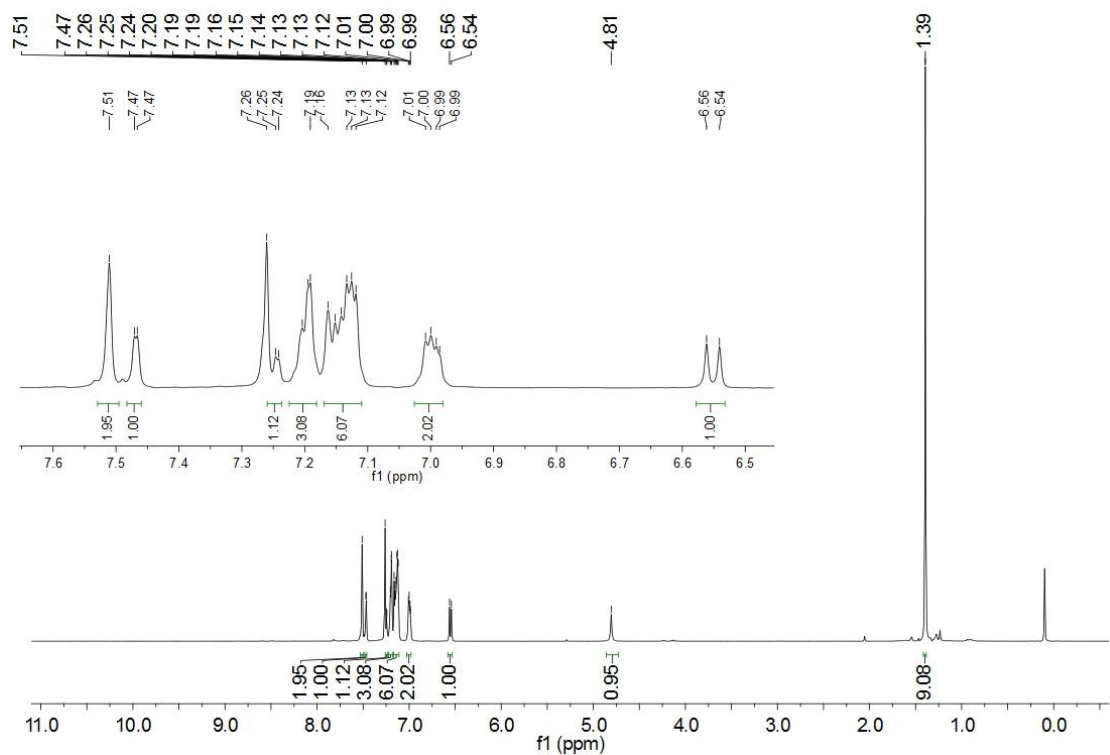
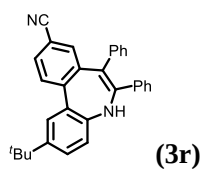


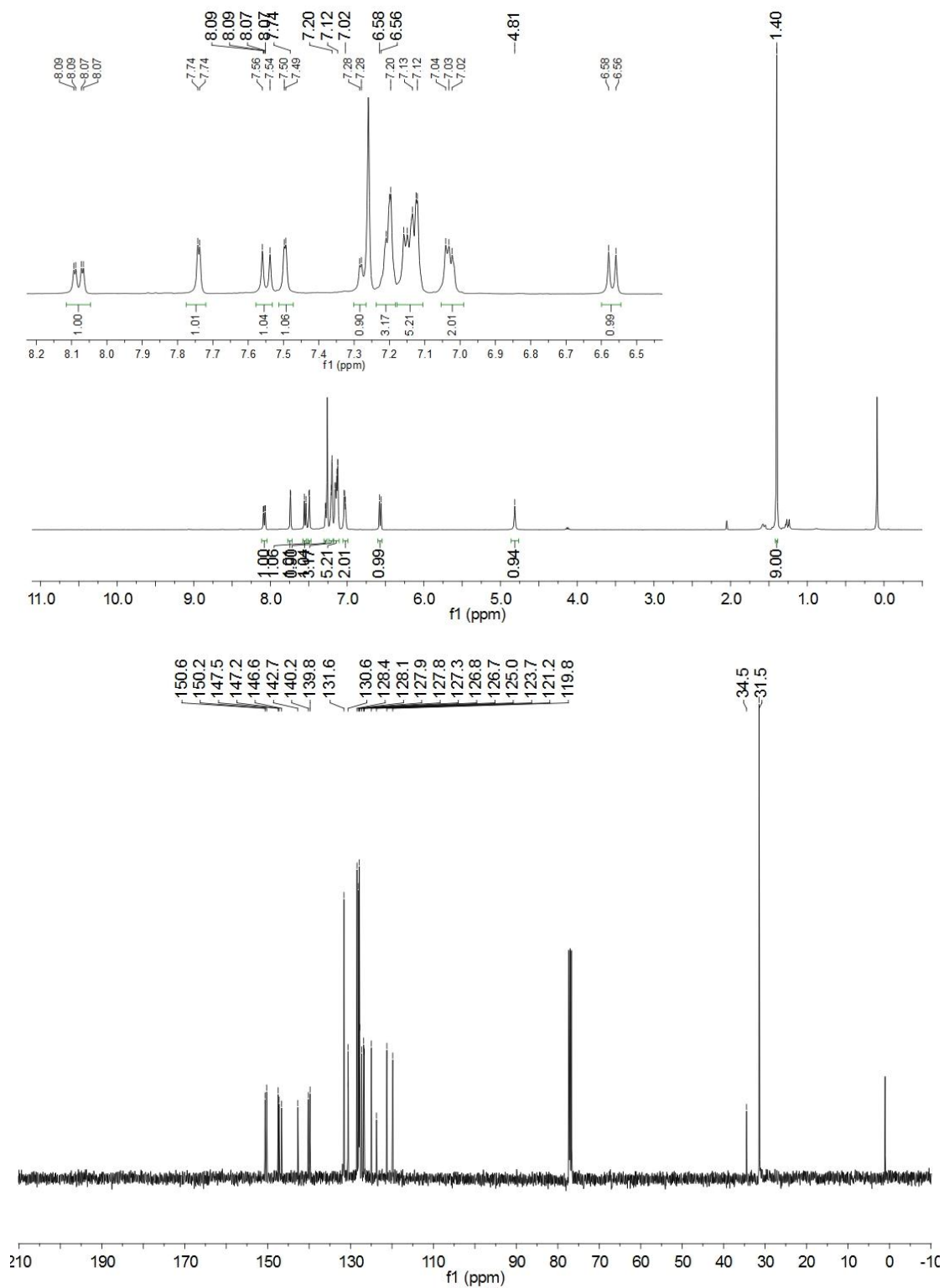
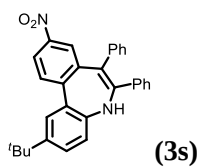


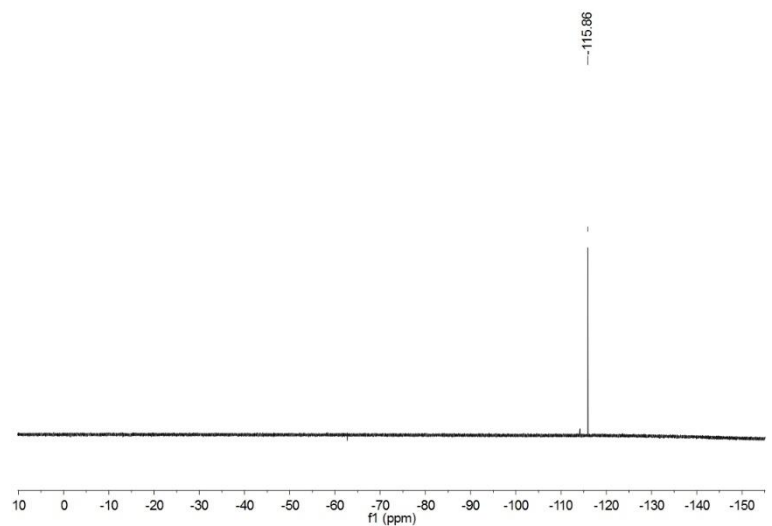
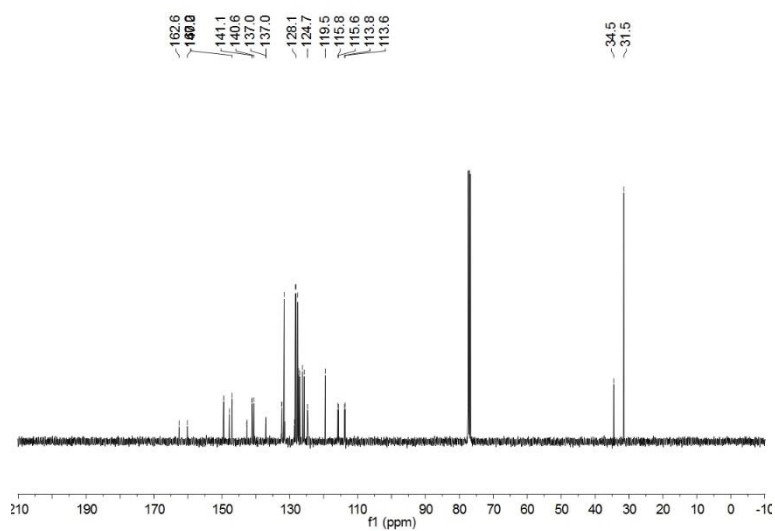
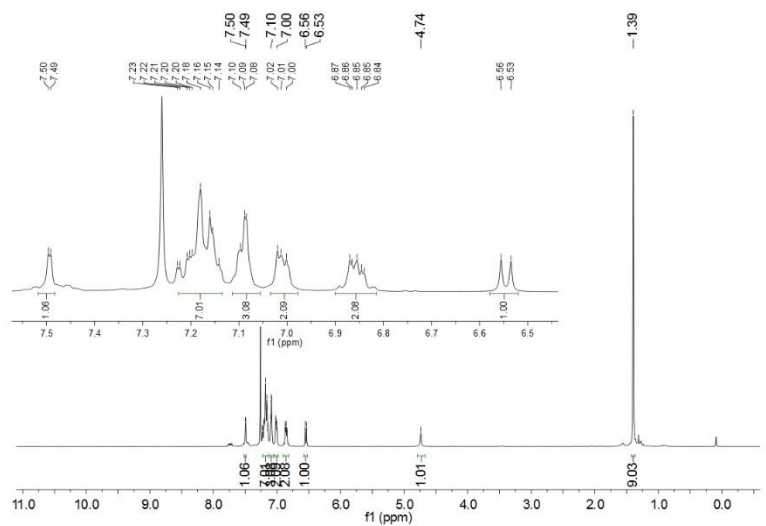
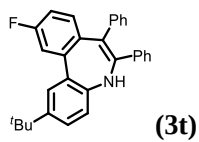




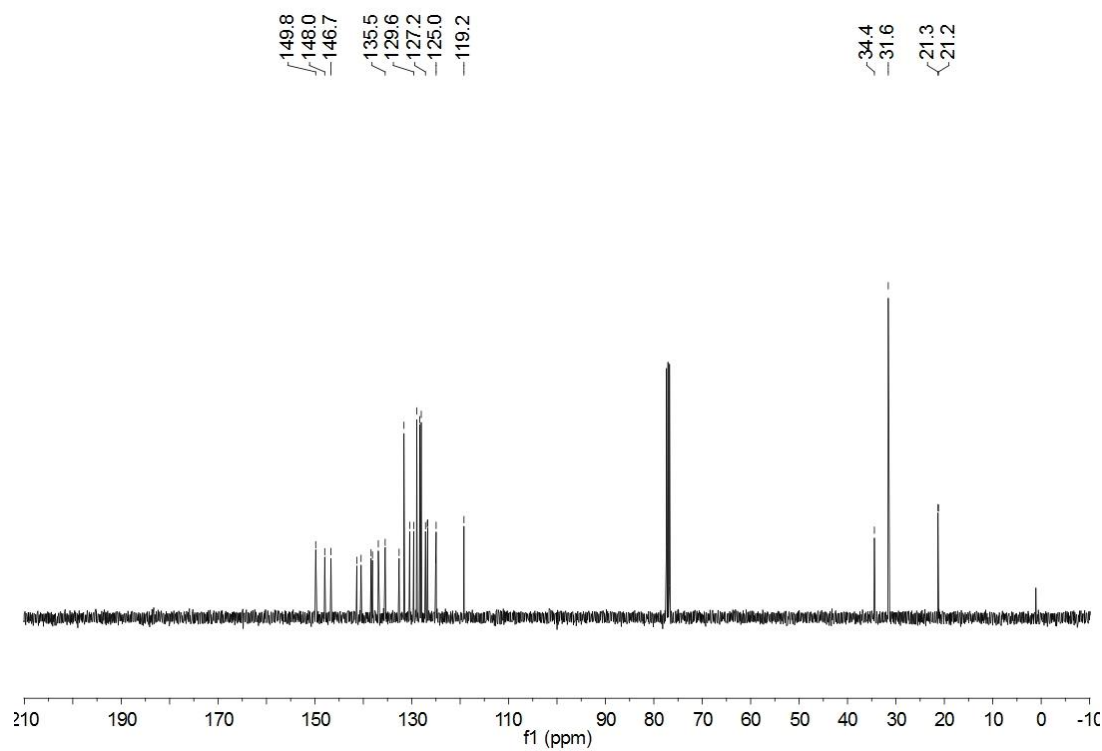
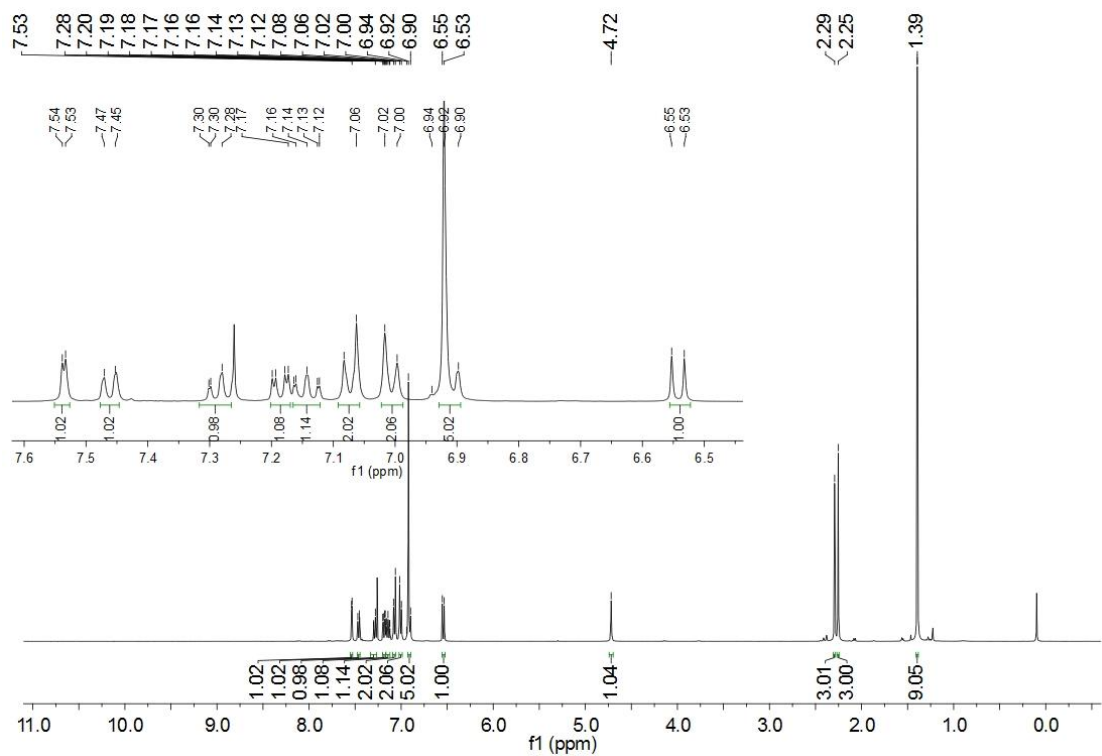
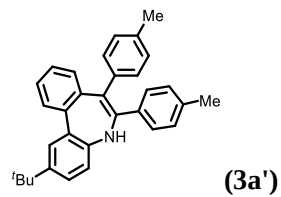


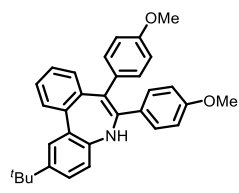




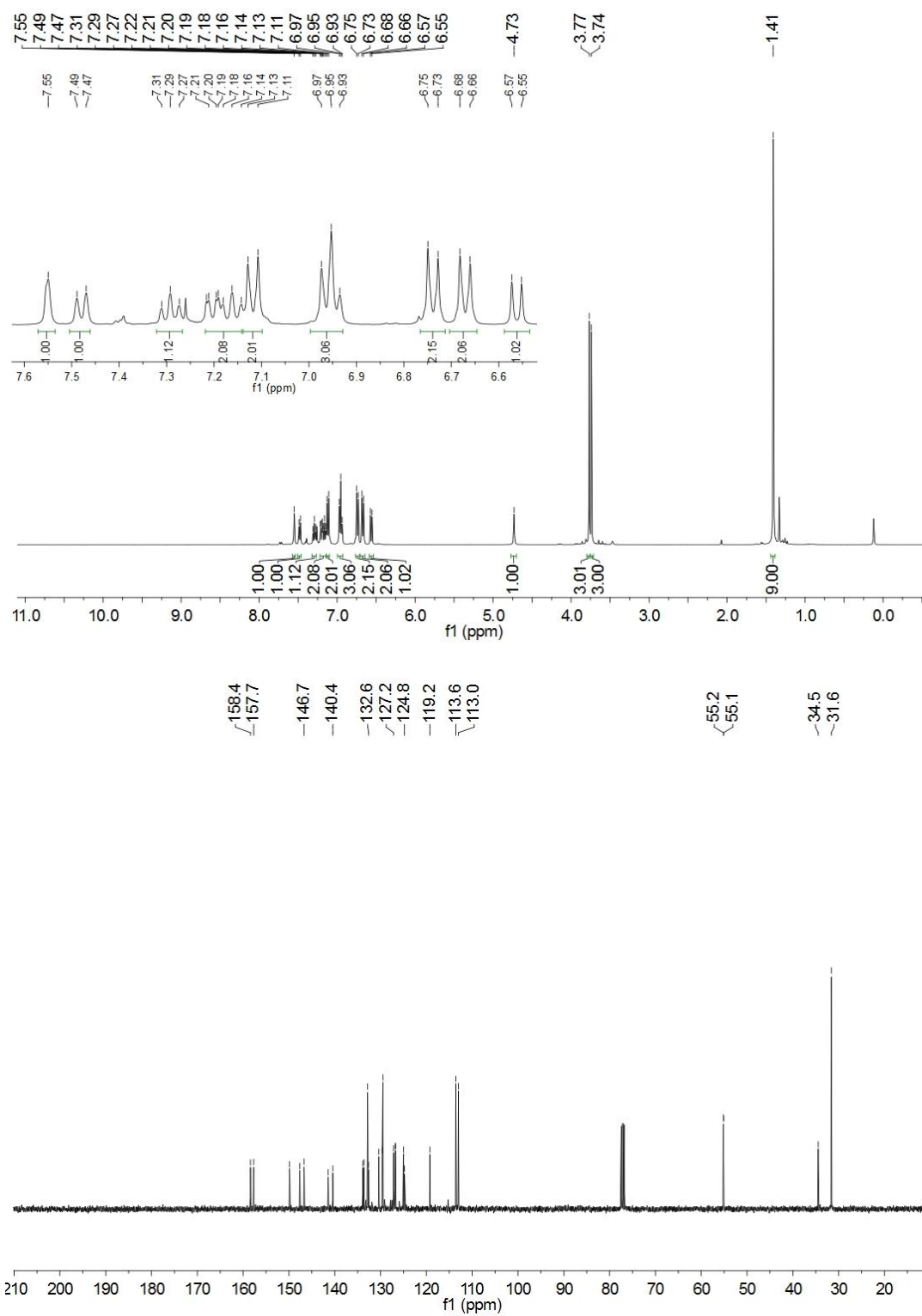


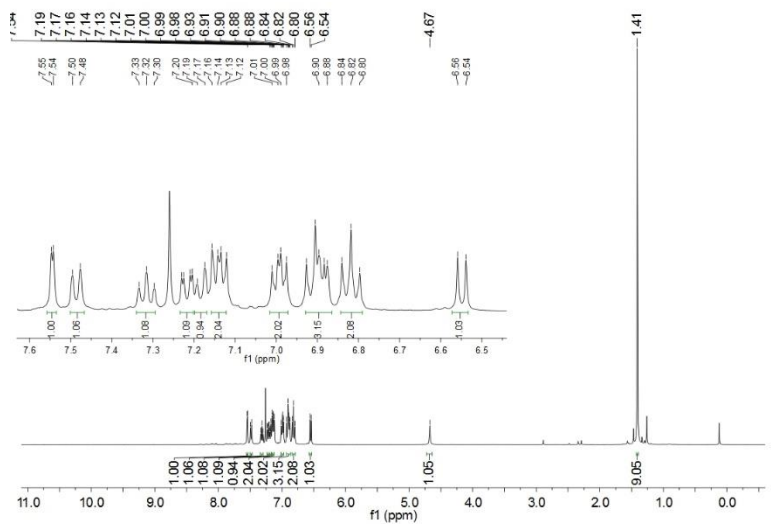
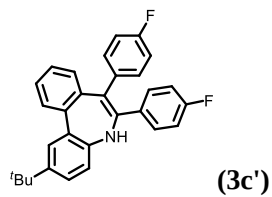


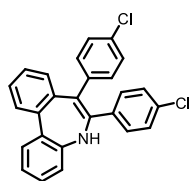




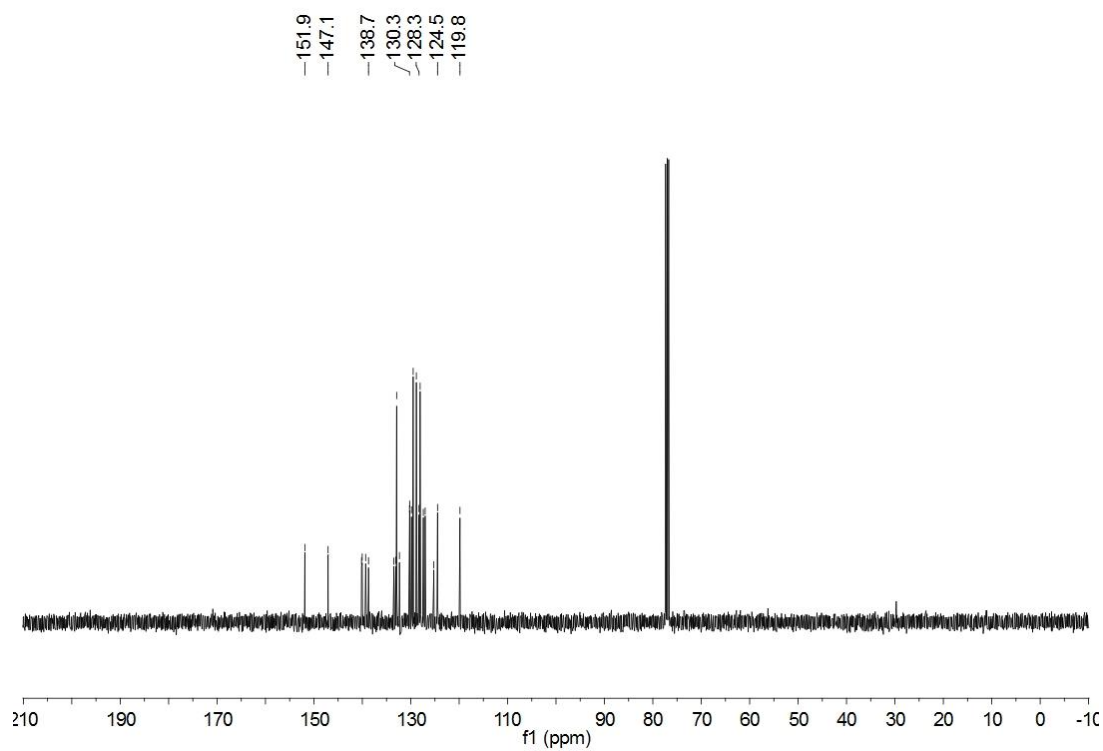
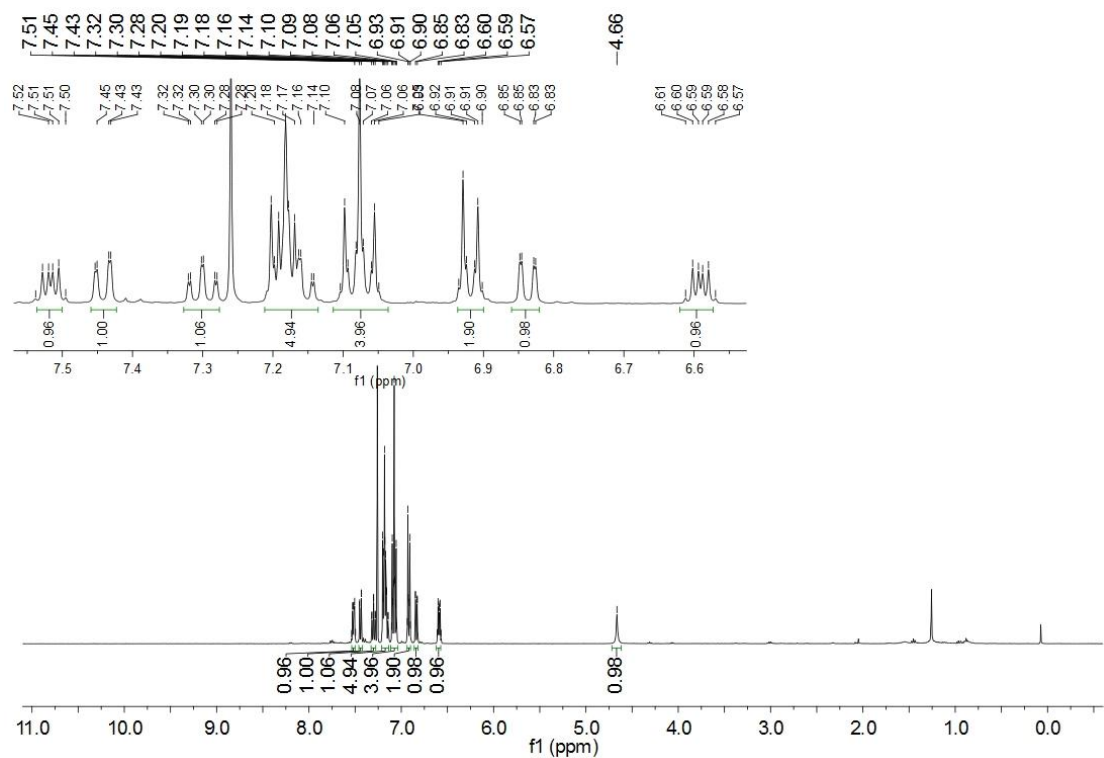
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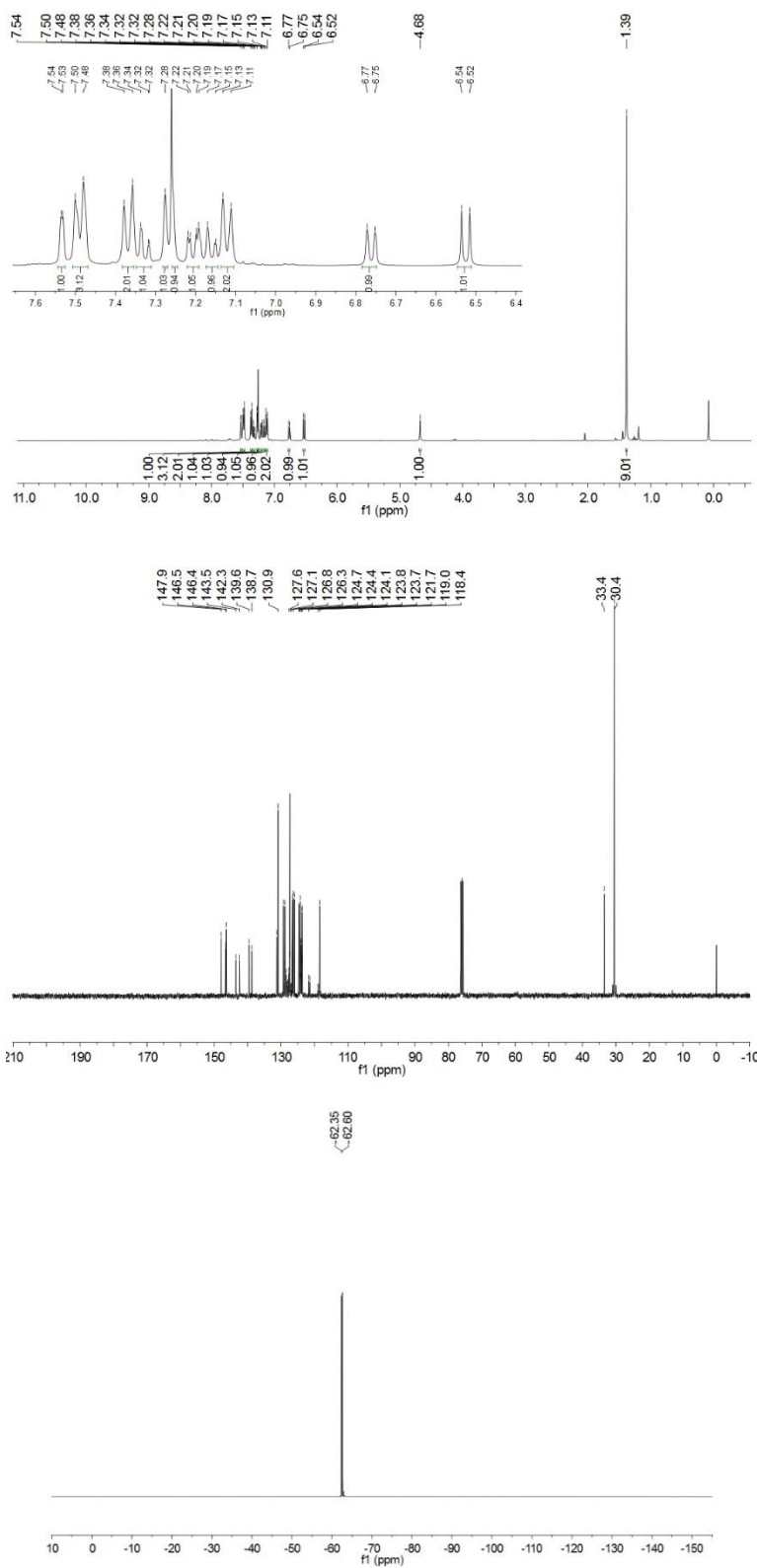
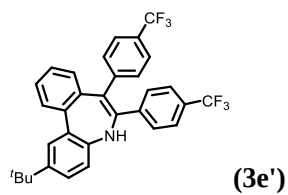


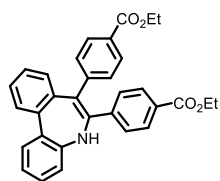




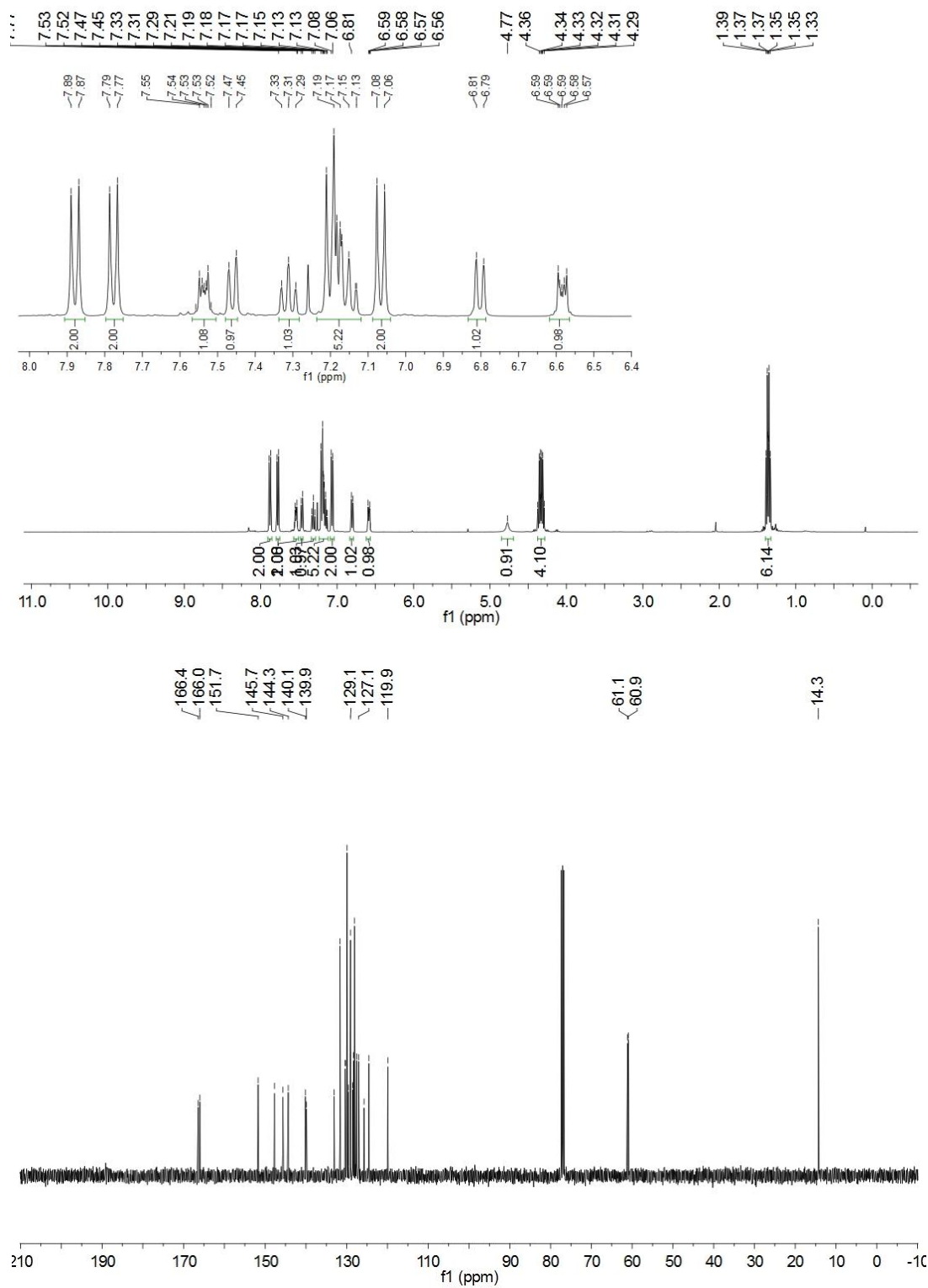
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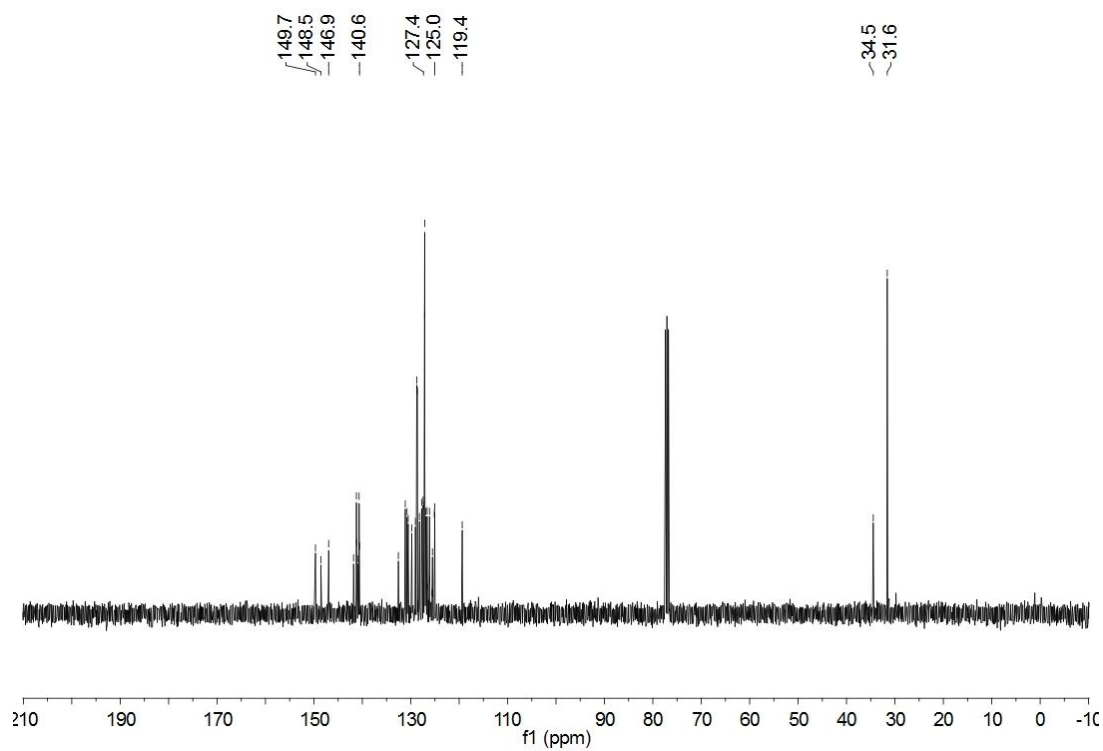
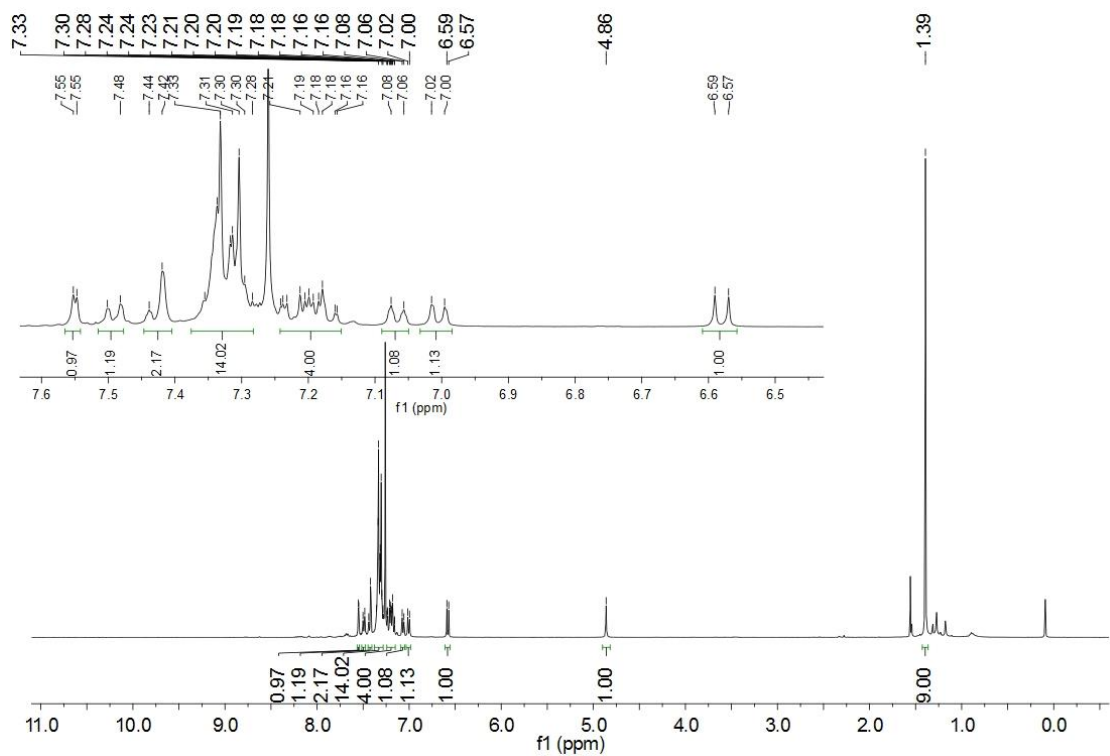
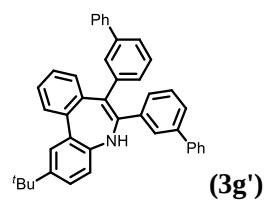


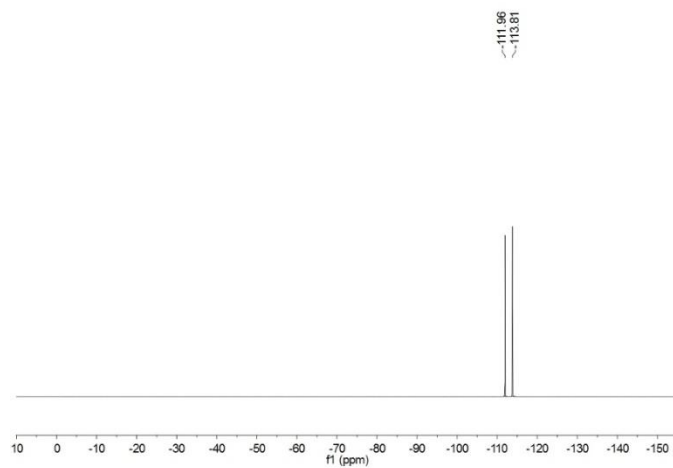
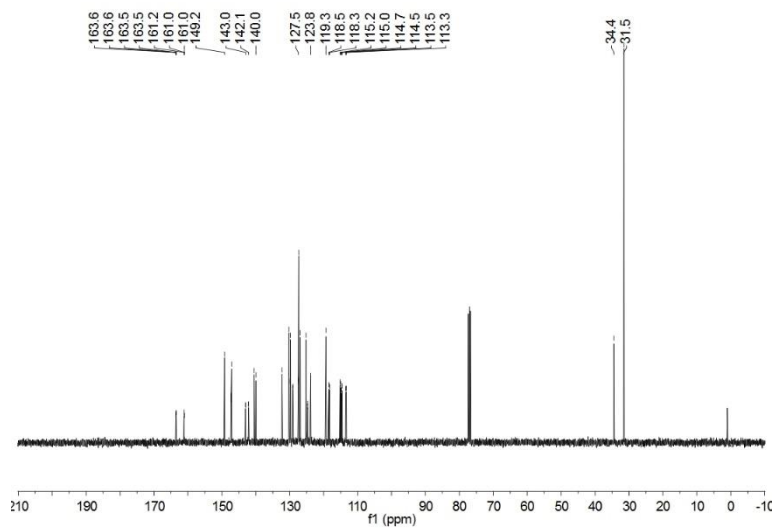
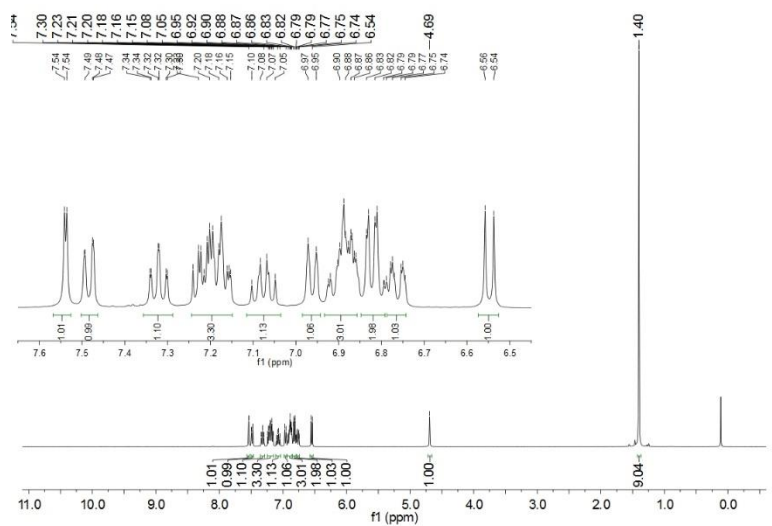
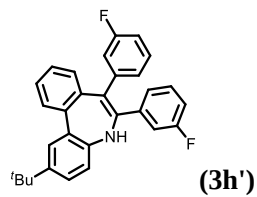


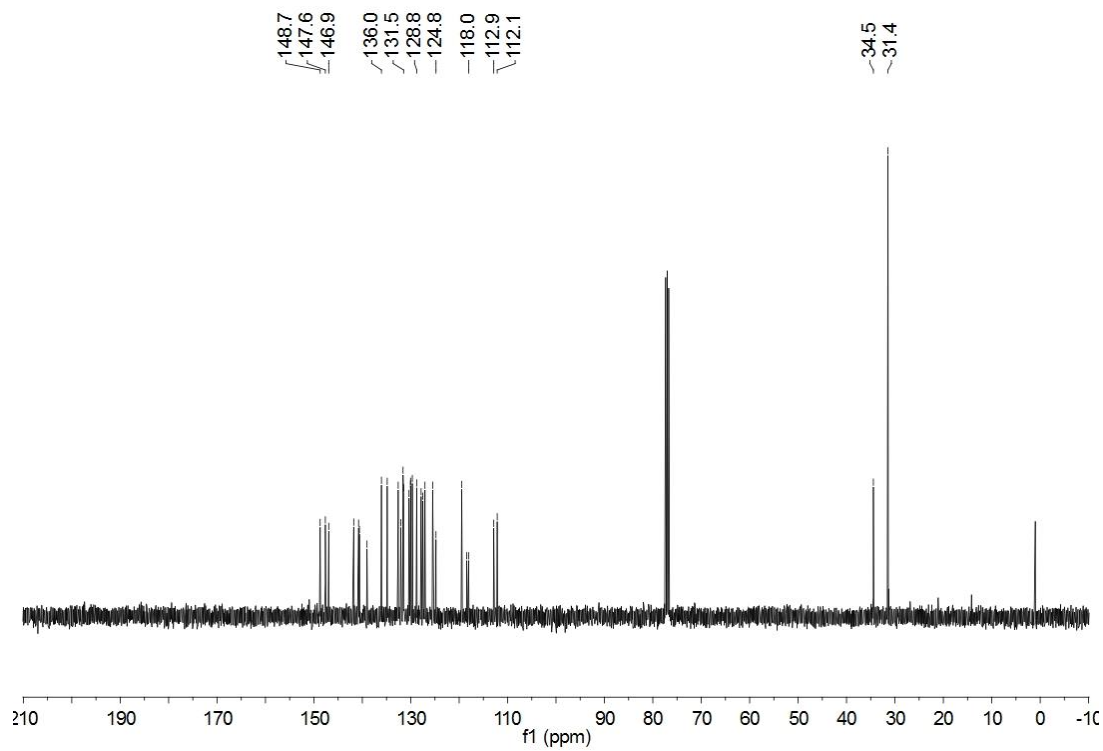
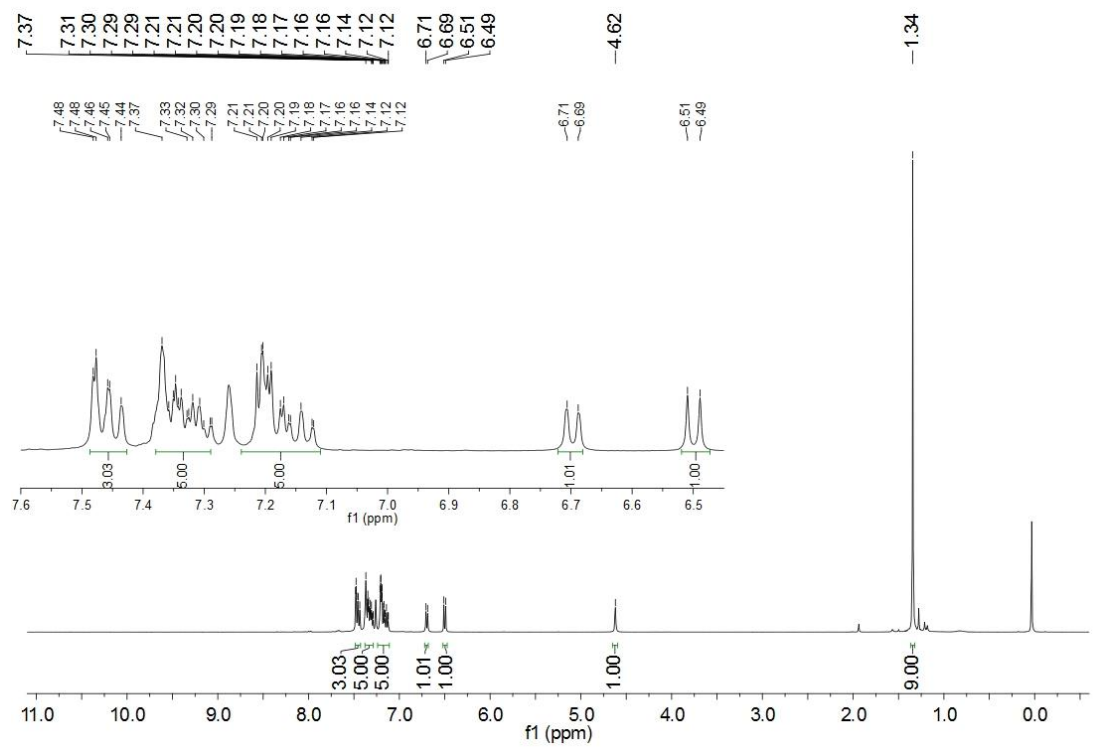
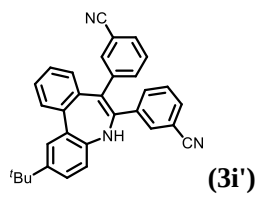


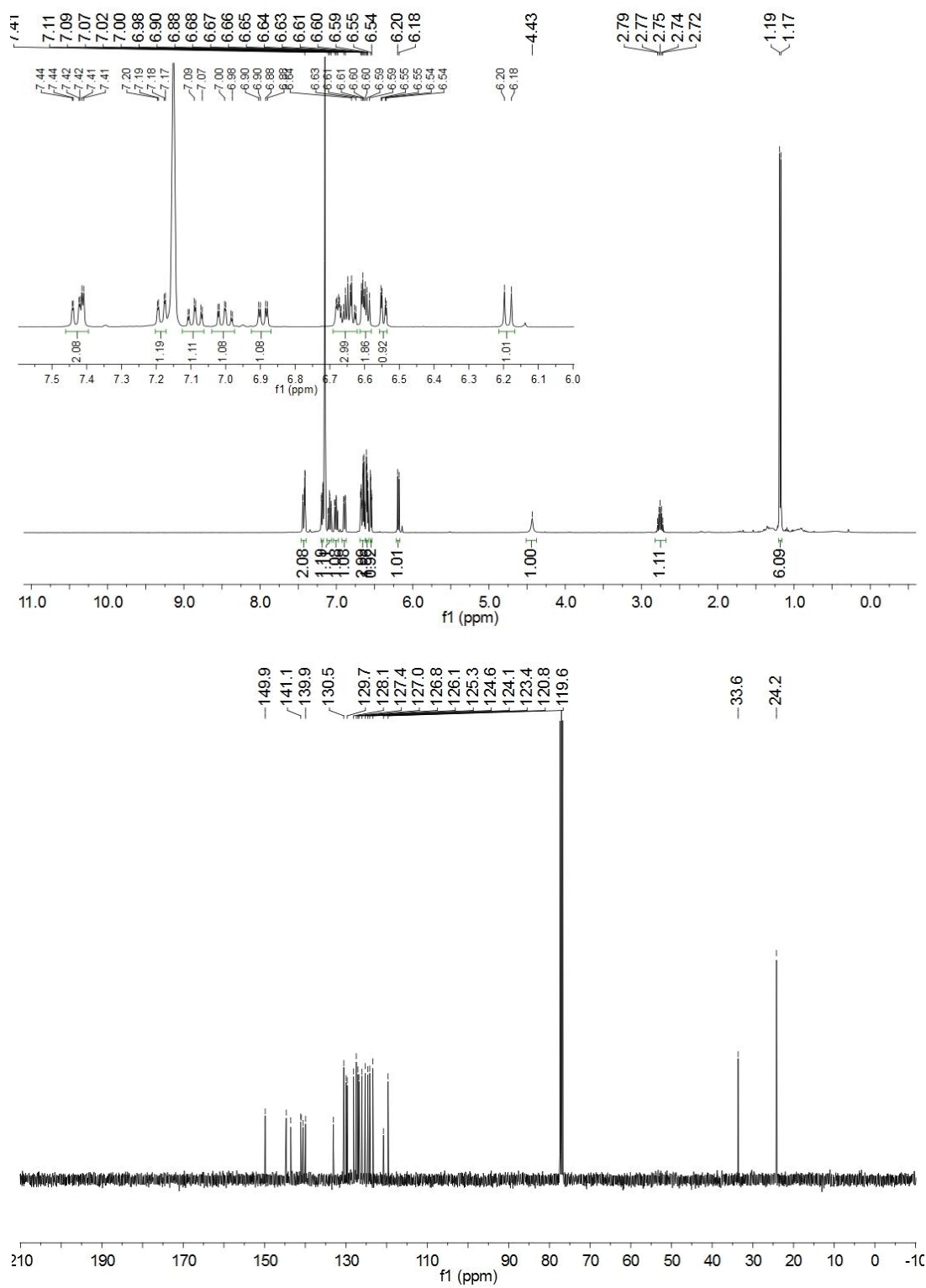
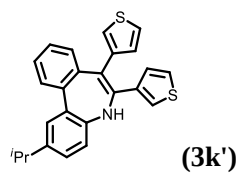
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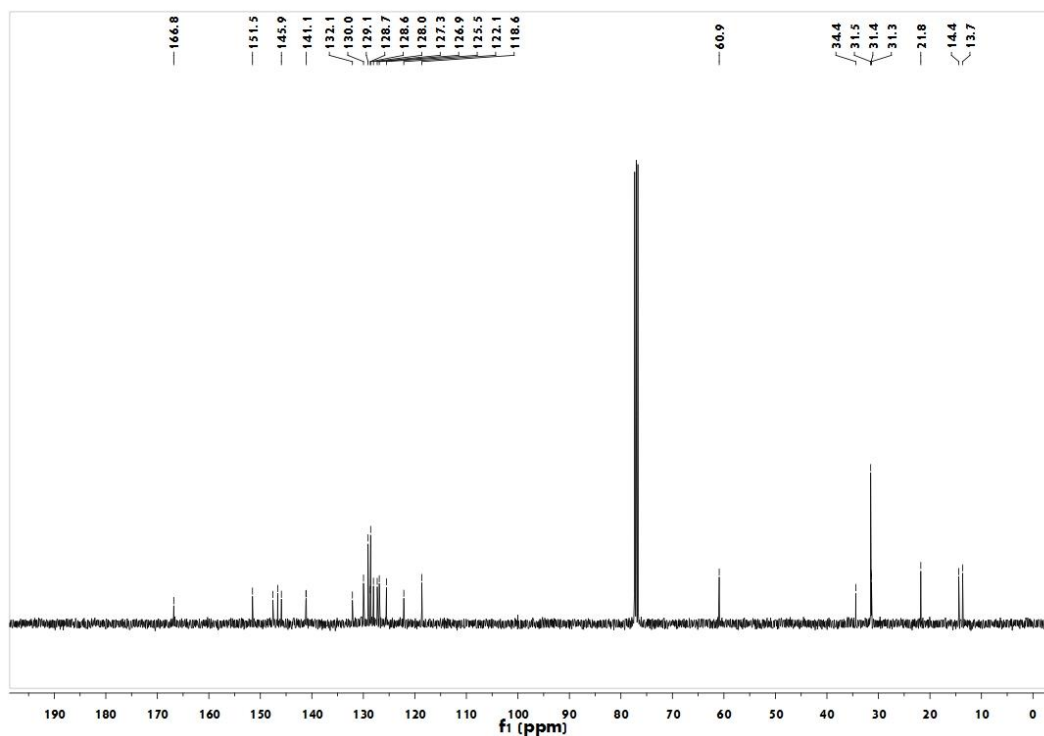
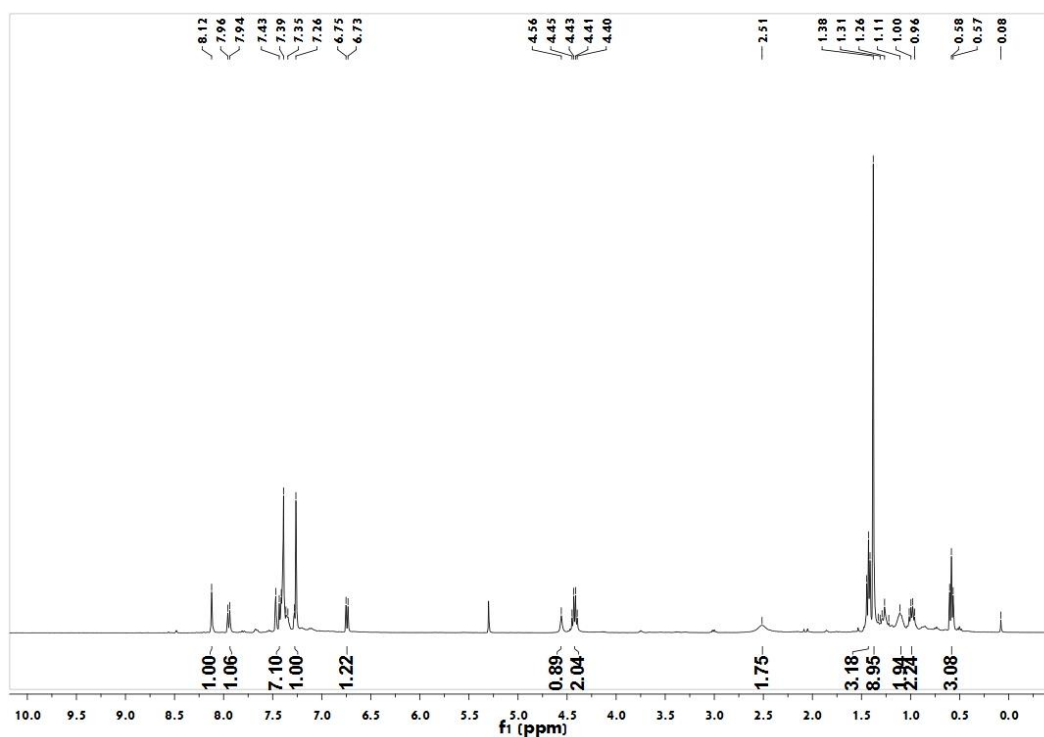
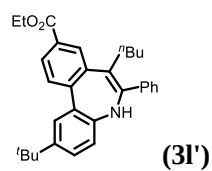


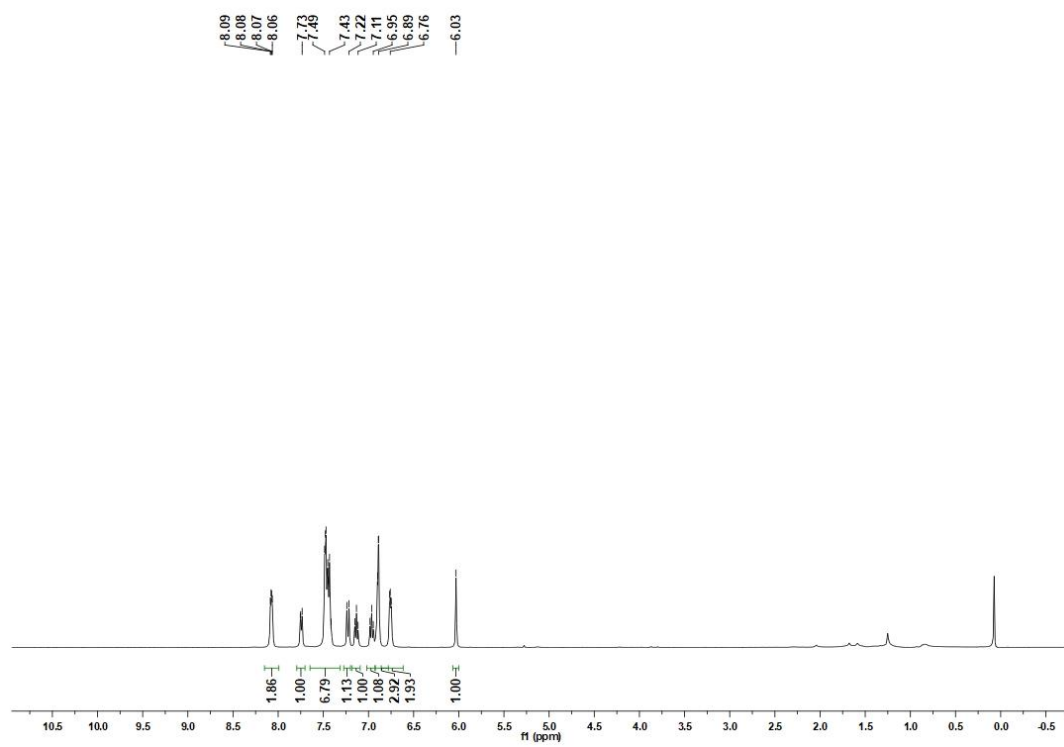
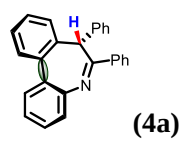


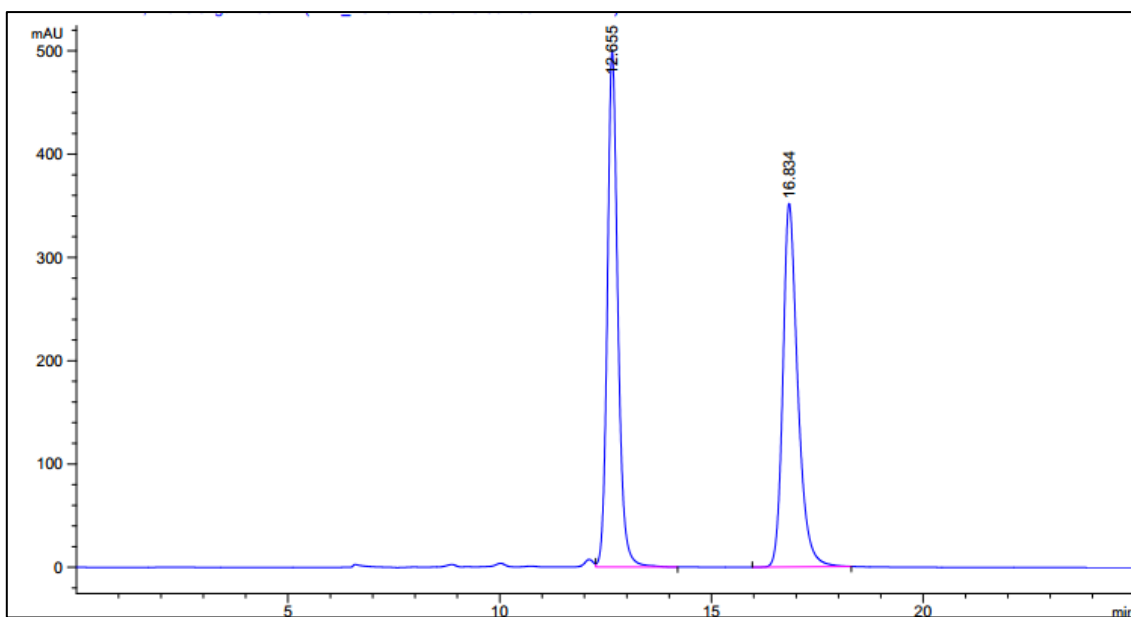




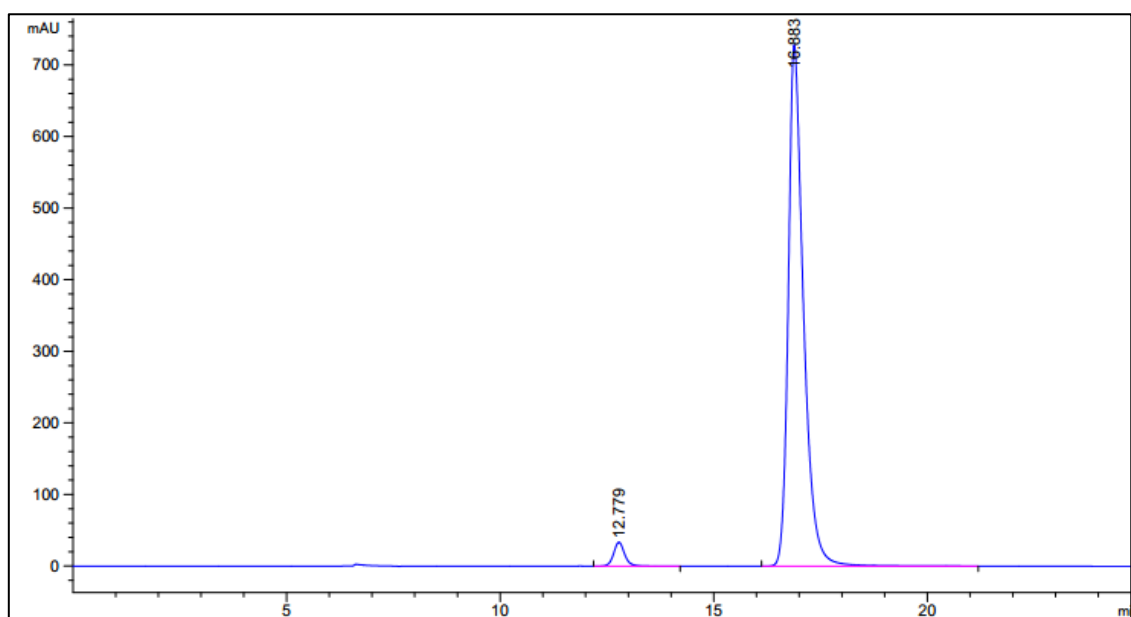




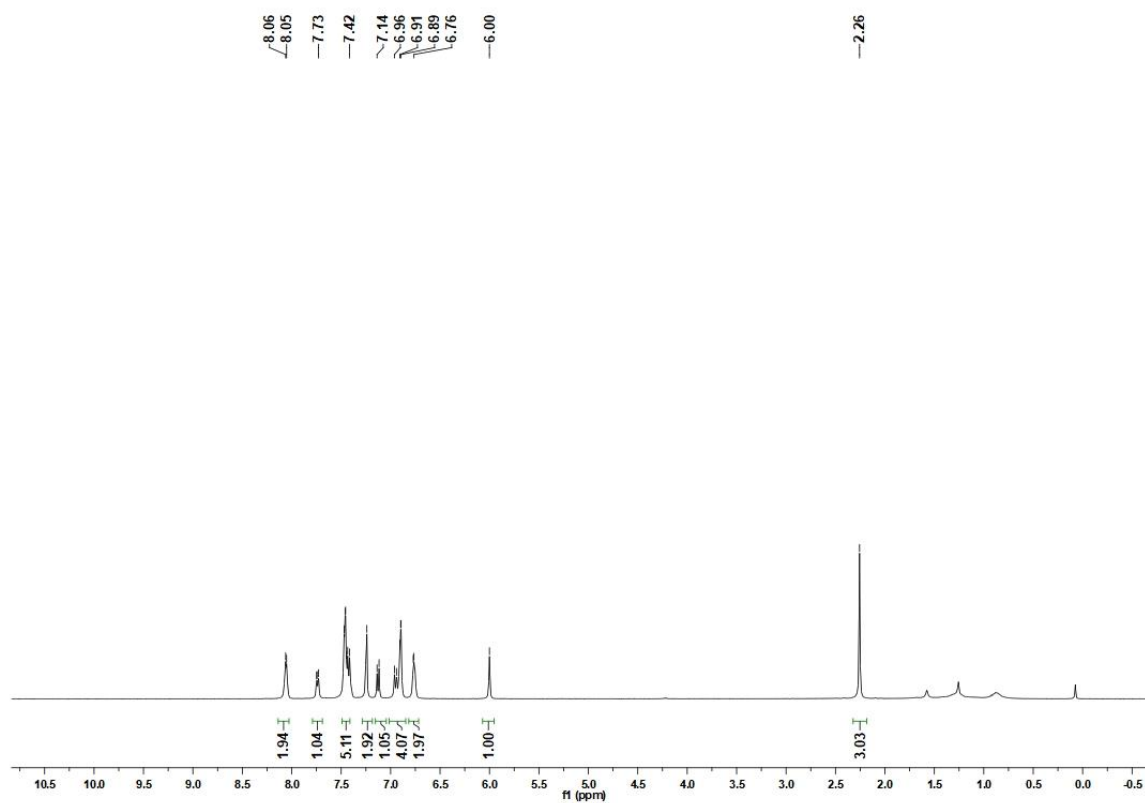
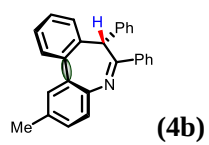


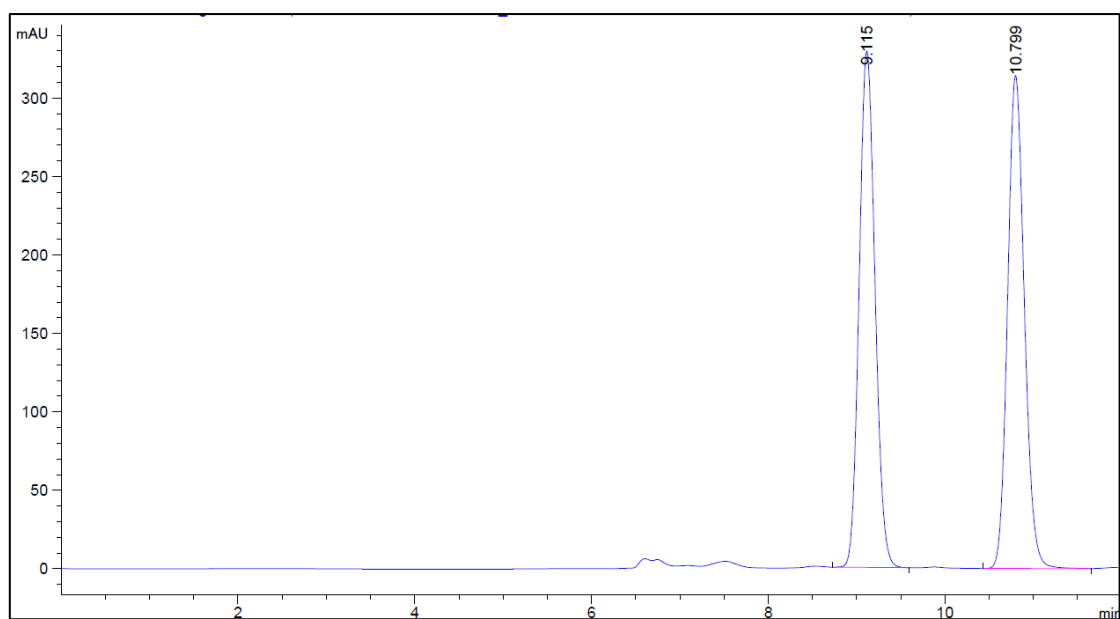


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.655	VB	0.2619	8641.50000	499.26428	50.1072
2	16.834	BBA	0.3632	8604.53320	352.04340	49.8928

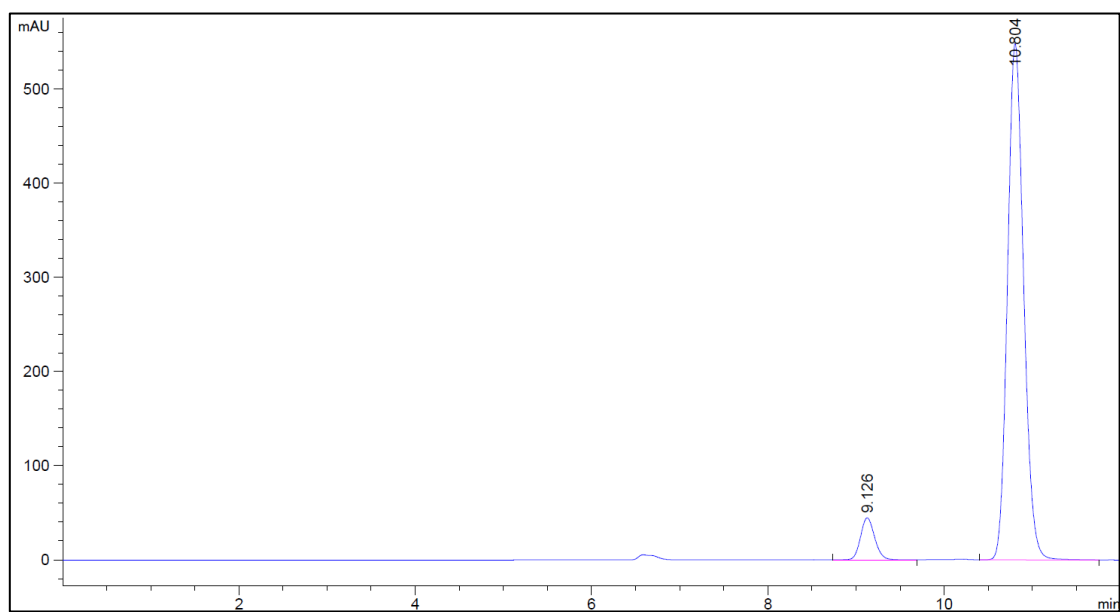


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.779	BB	0.2729	606.77435	33.56808	3.2645
2	16.883	BB	0.3631	1.79805e4	728.22675	96.7355

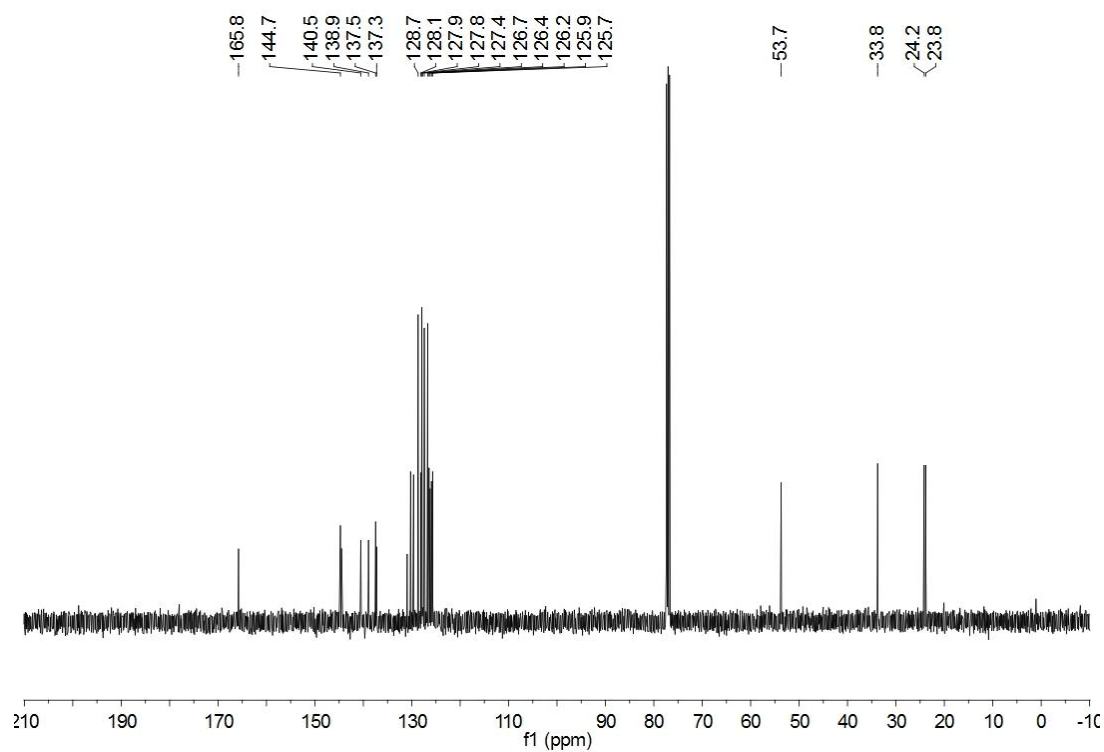
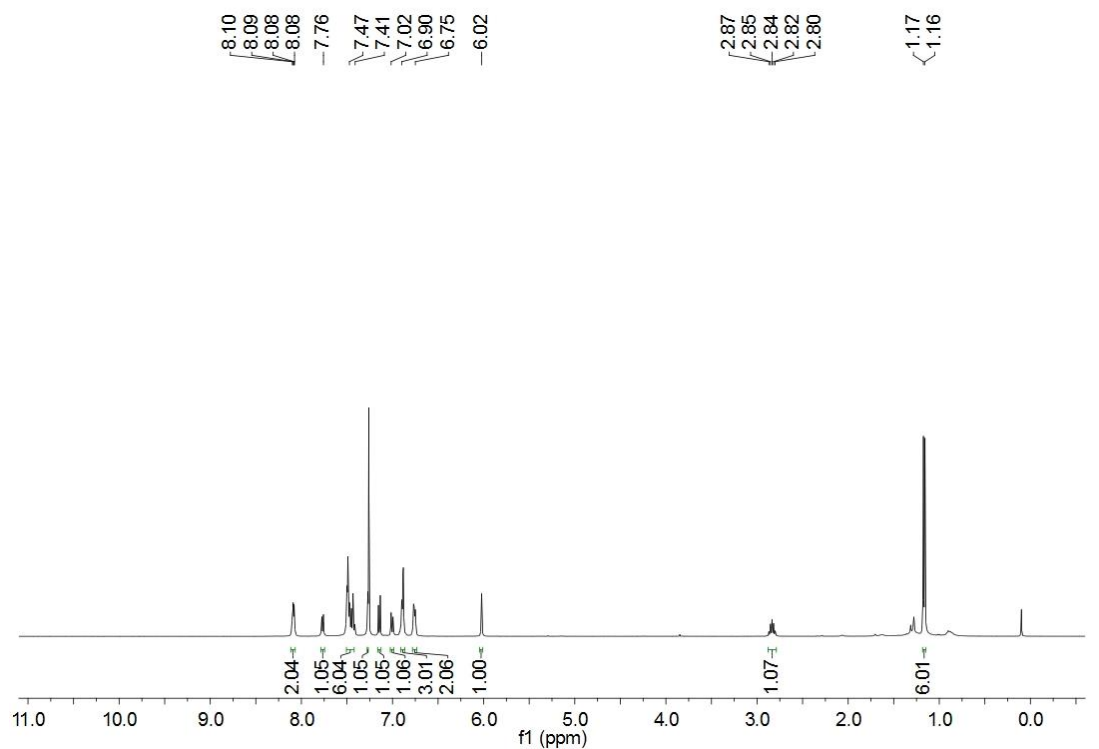
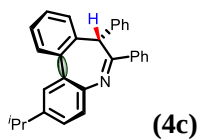


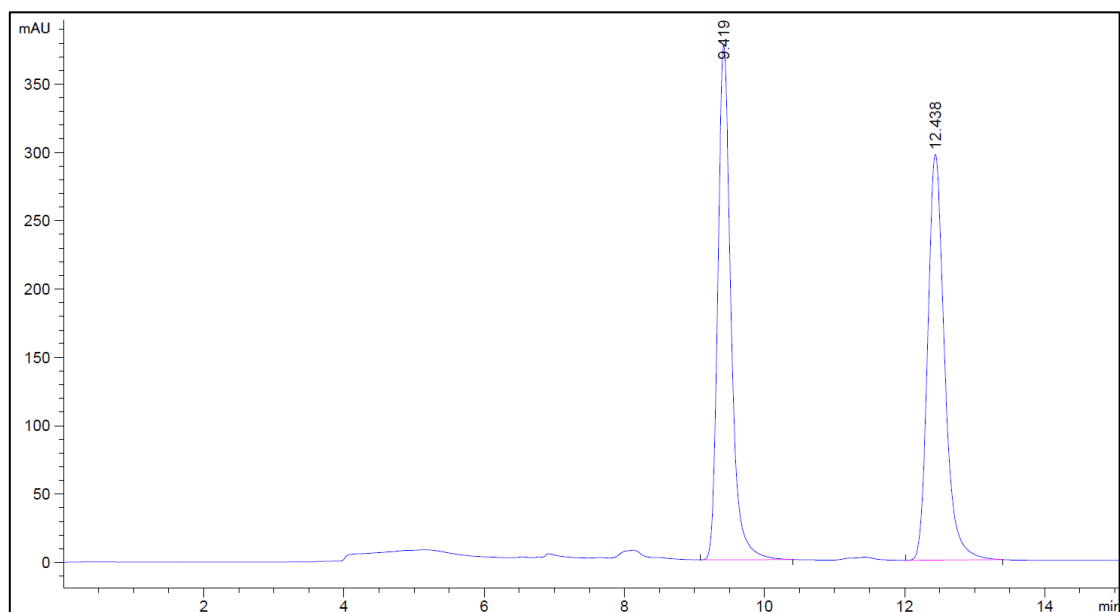


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.115	BB	0.1942	4096.98389	329.15689	49.7976
2	10.799	BB	0.2033	4130.28027	314.30936	50.2024

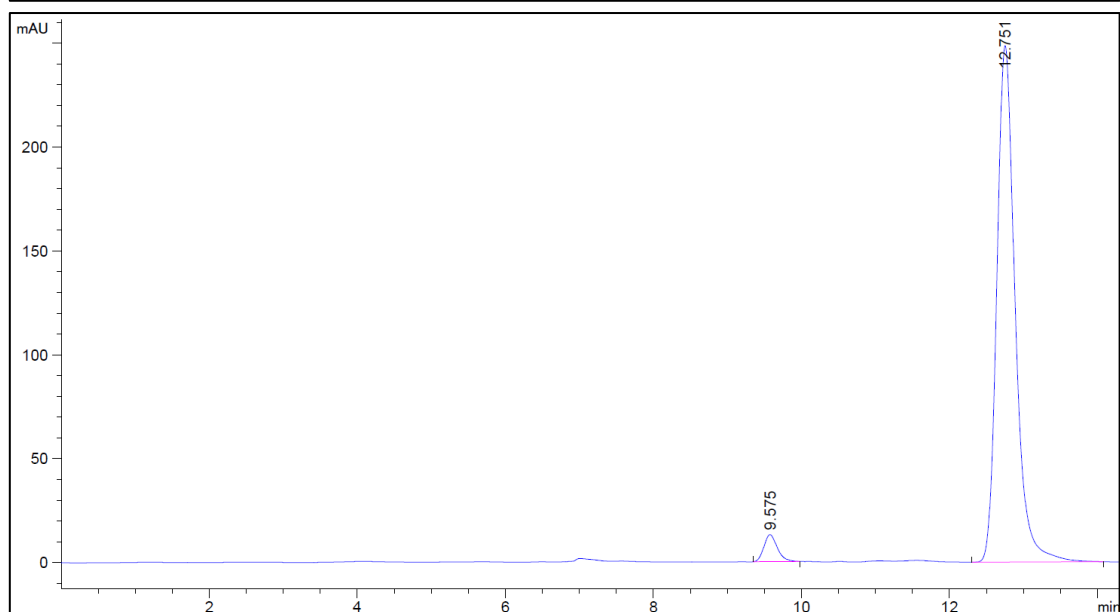


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.126	BB	0.1712	493.39417	44.57006	6.6265
2	10.804	BB	0.1959	6952.33545	548.52753	93.3735

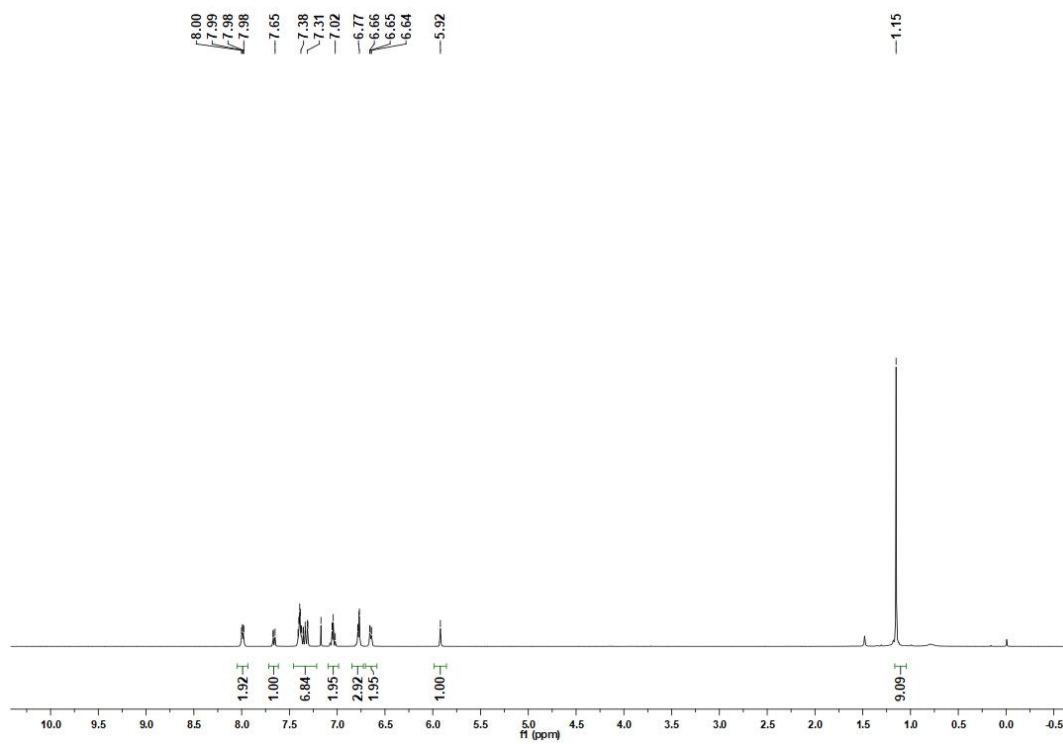
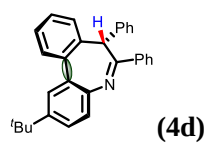


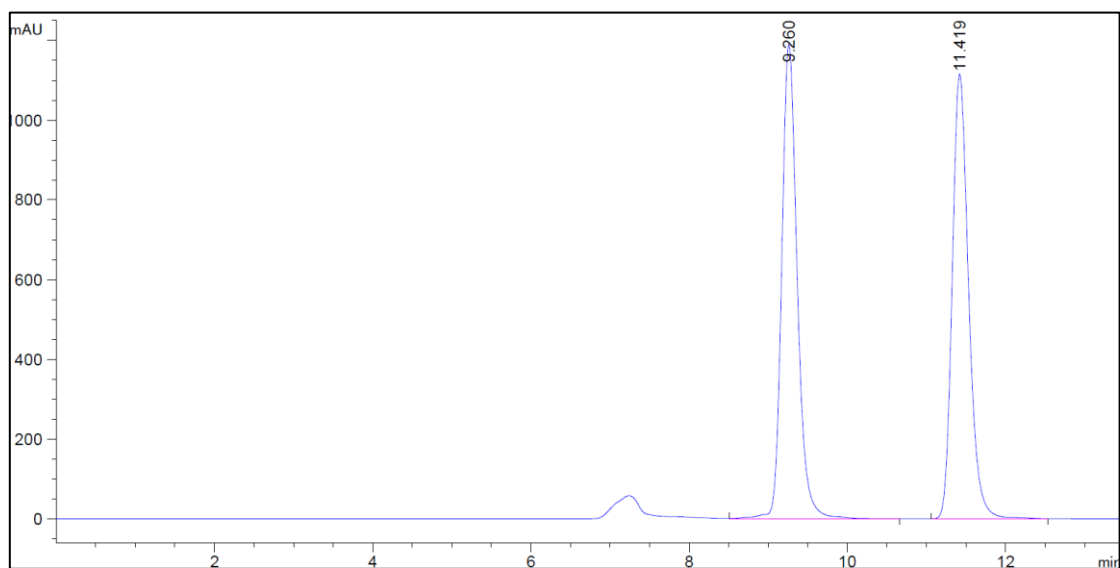


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.419	BBA	0.1978	4896.48438	376.39325	49.7082
2	12.438	BBA	0.2546	4953.97314	297.02237	50.2918

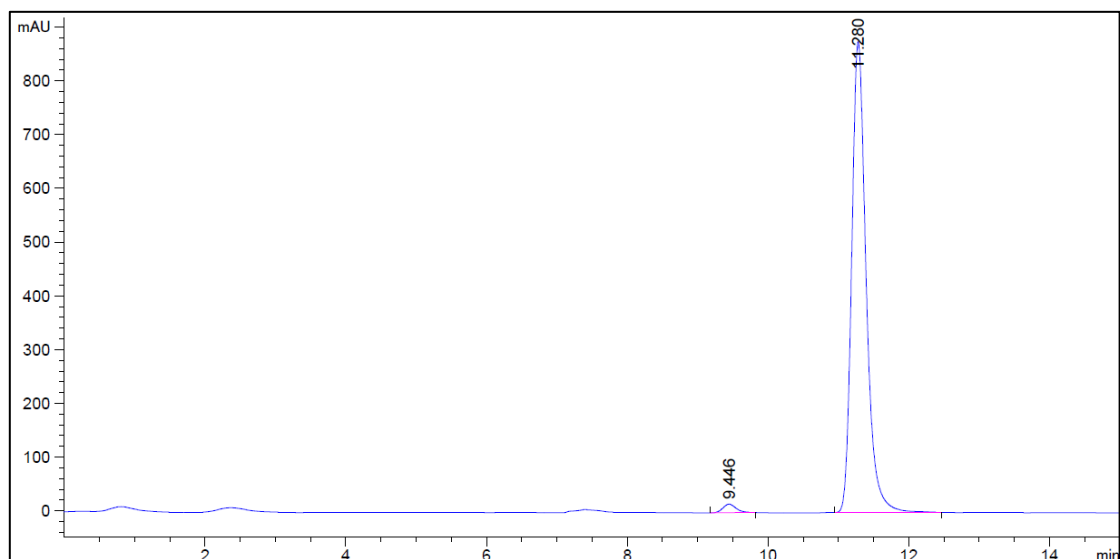


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.575	BBA	0.1932	164.11179	13.00341	3.6995
2	12.751	BBA	0.2616	4271.95703	248.48421	96.3005

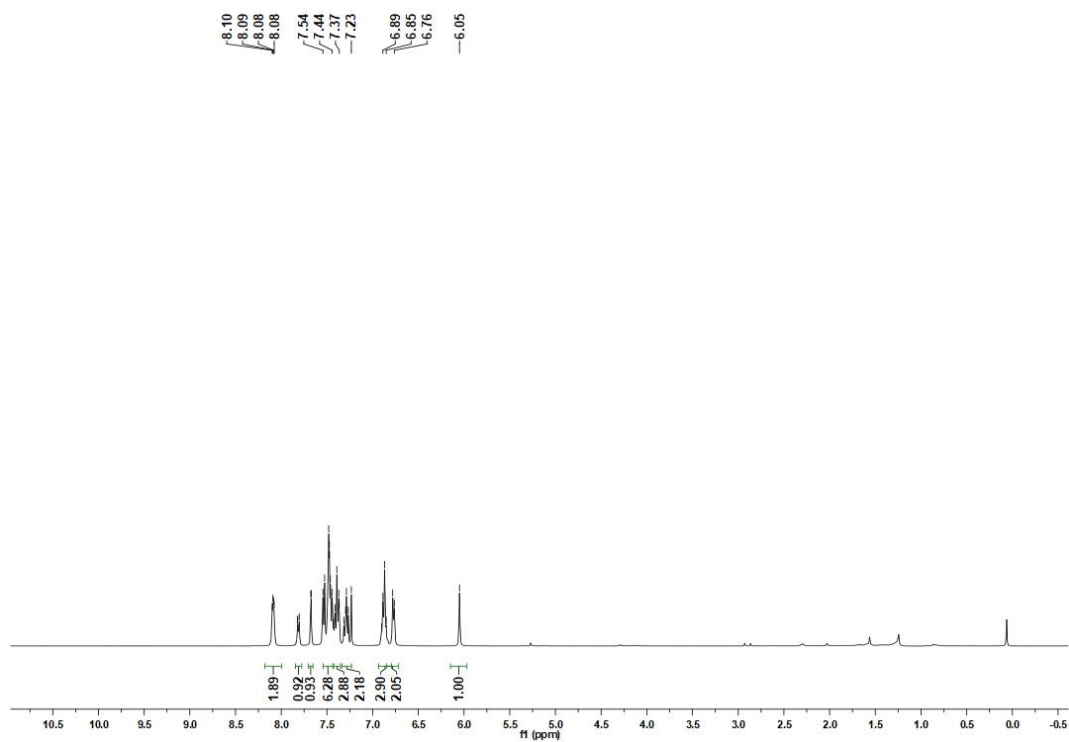
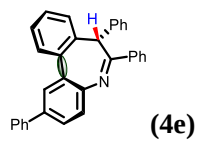


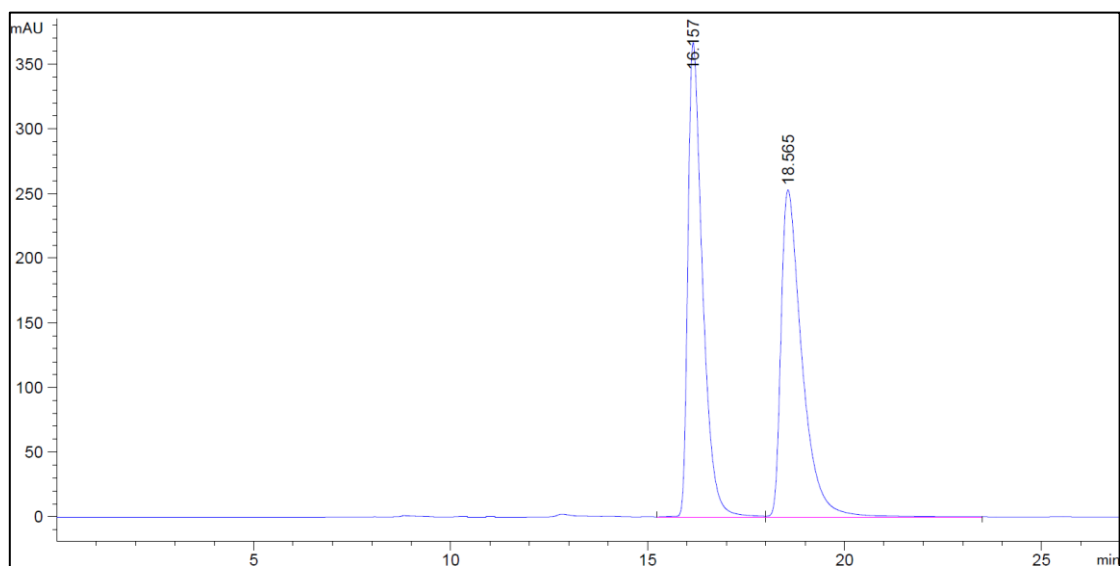


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.260	VV	0.2093	1.63167e4	1191.41980	50.3804
2	11.419	VV	0.2215	1.60703e4	1115.78687	49.6196

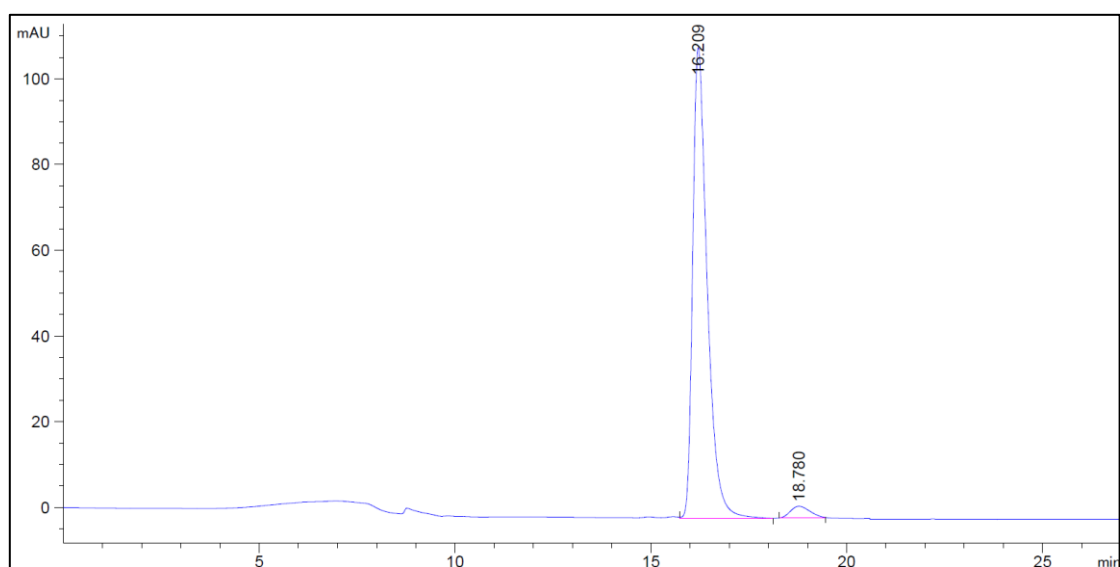


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.446	BBA	0.1967	201.27455	15.68499	1.5934
2	11.280	BBA	0.2161	1.24305e4	875.97247	98.4066

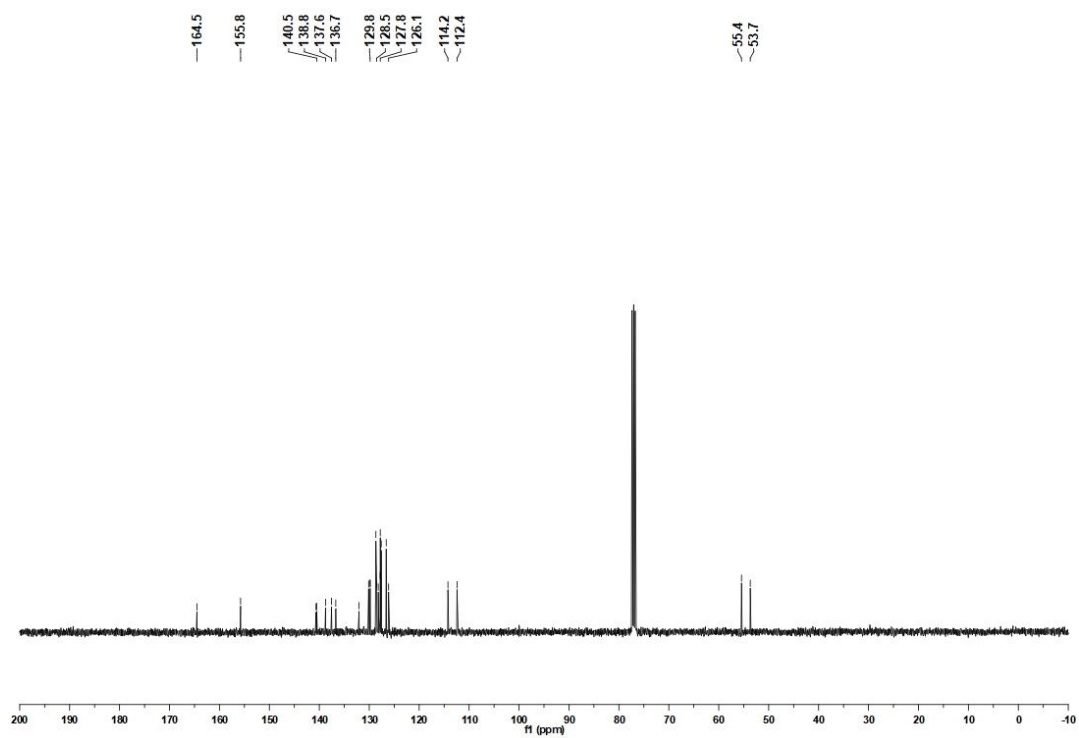
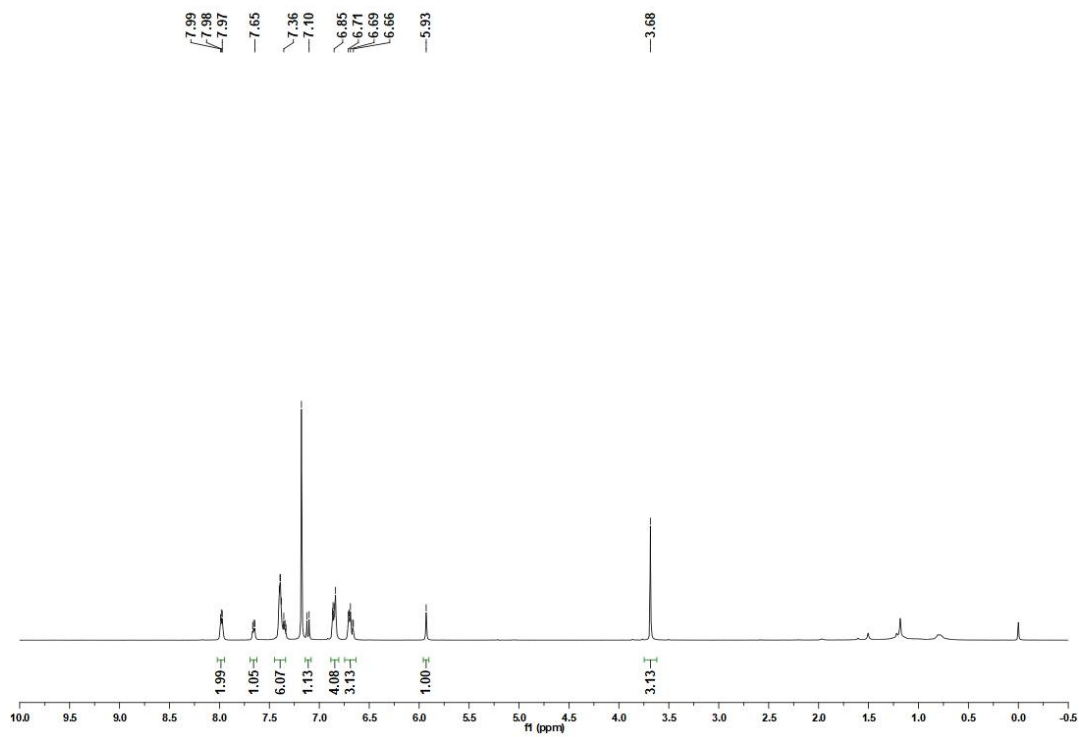
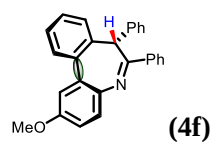


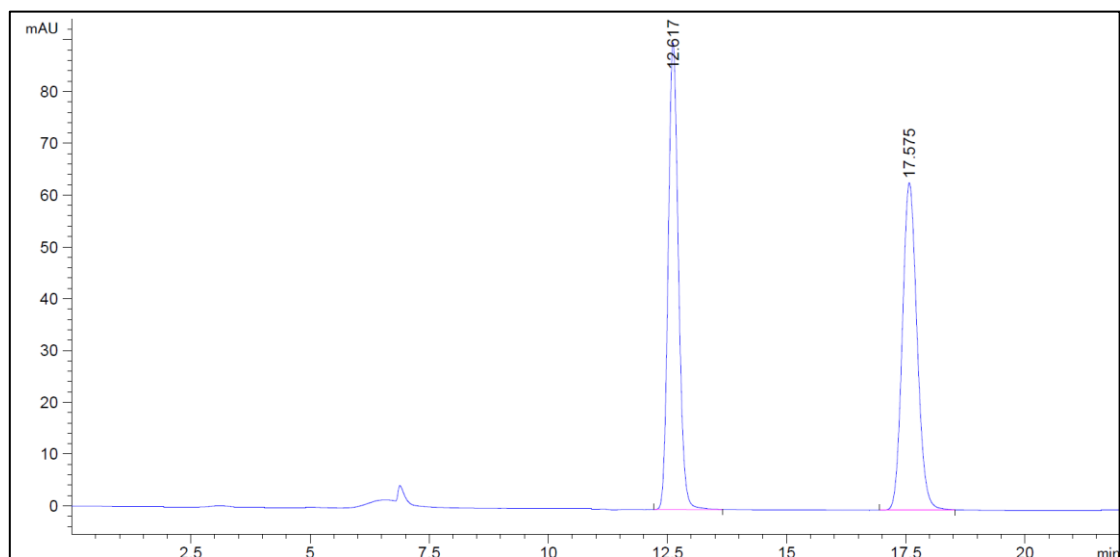


#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.157	VV	0.3879	9493.50098	366.89404	50.2609
2	18.565	VV	0.5533	9394.92969	252.96281	49.7391

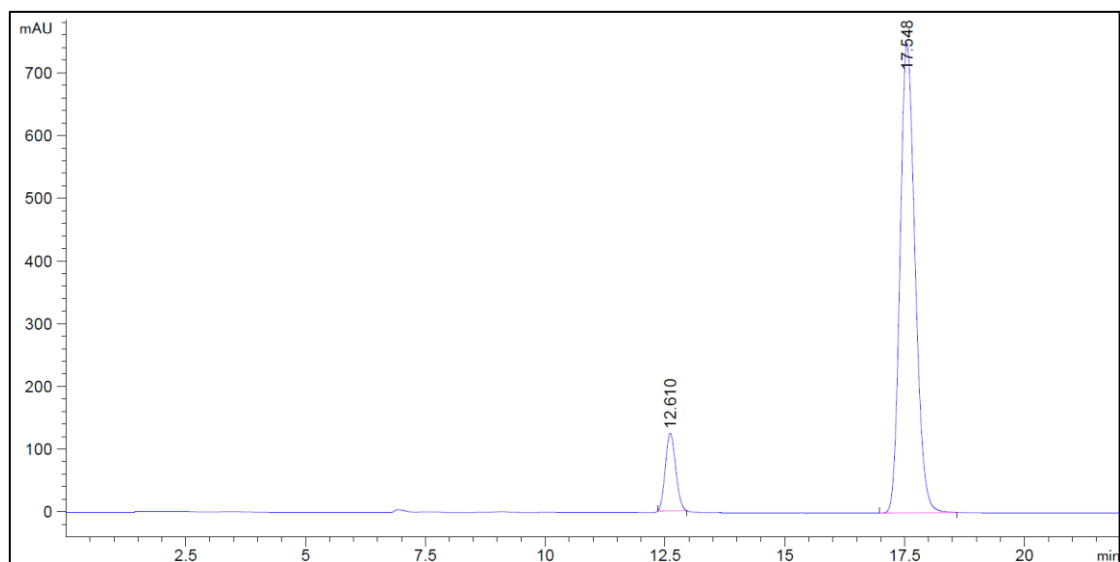


#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.209	VV	0.3870	2826.18481	109.91087	96.7249
2	18.780	BBA	0.5340	95.69595	2.74282	3.2751

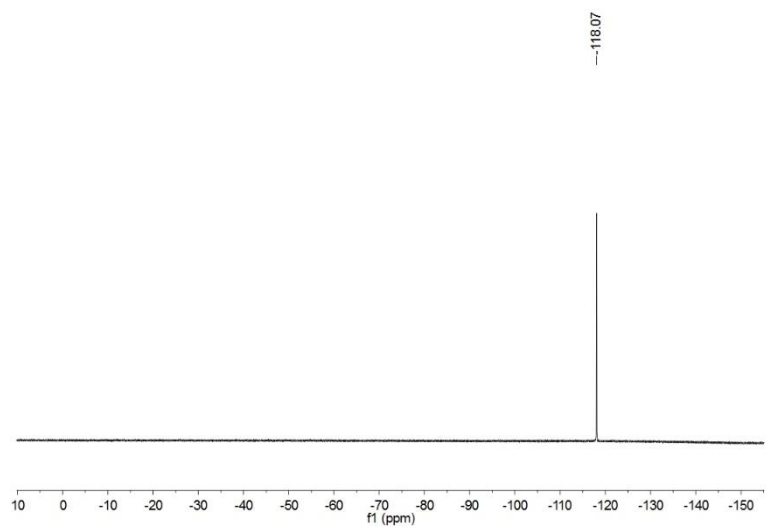
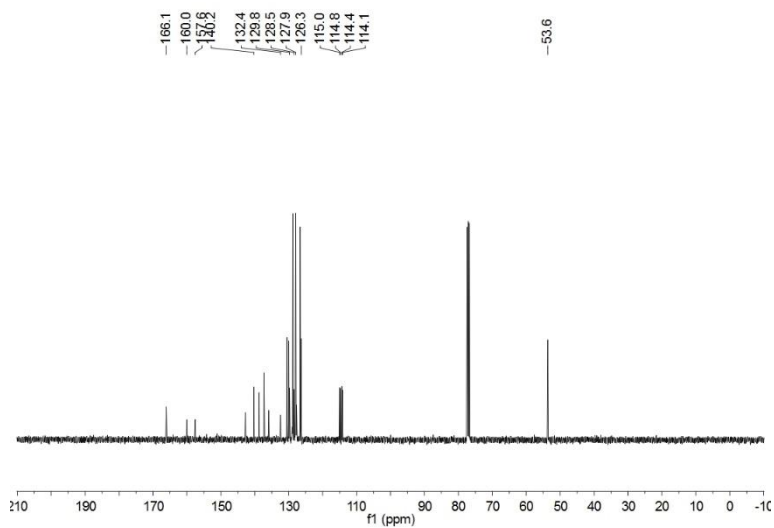
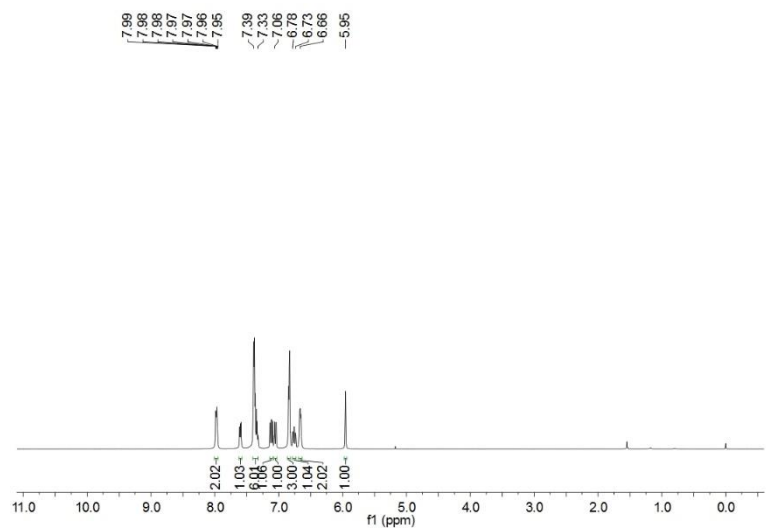
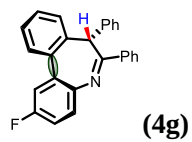


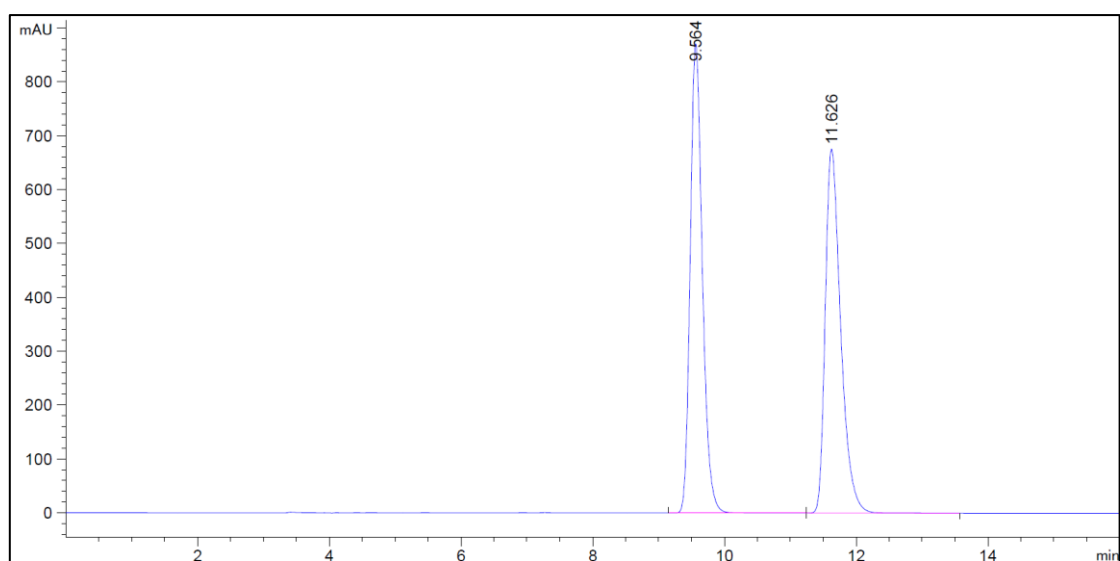


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.617	BV	0.2304	1347.14111	90.13447	49.8233
2	17.575	VV	0.3324	1356.69507	63.22003	50.1767

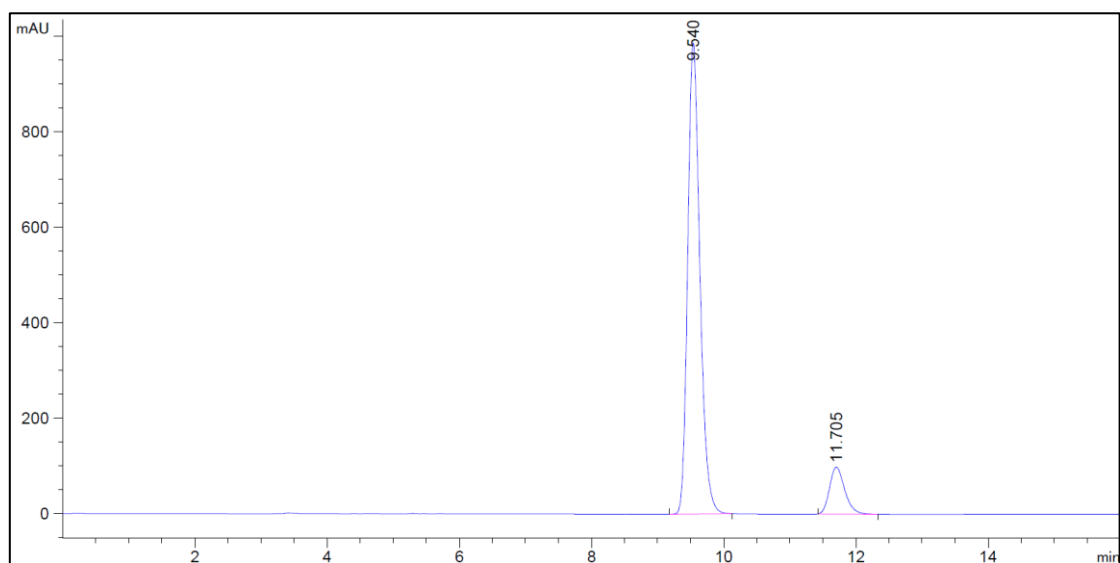


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.610	BBA	0.2337	1842.66882	123.38950	10.1448
2	17.548	BBA	0.3382	1.63210e4	748.97626	89.8552

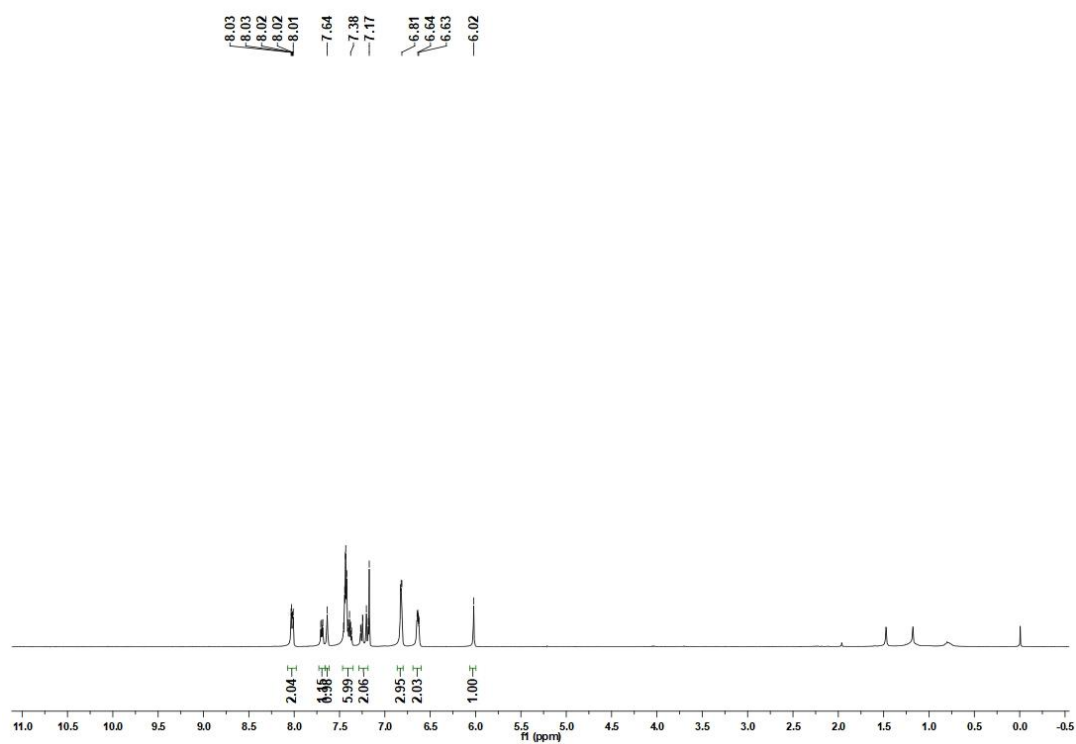
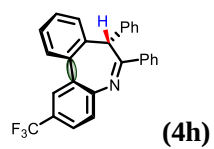


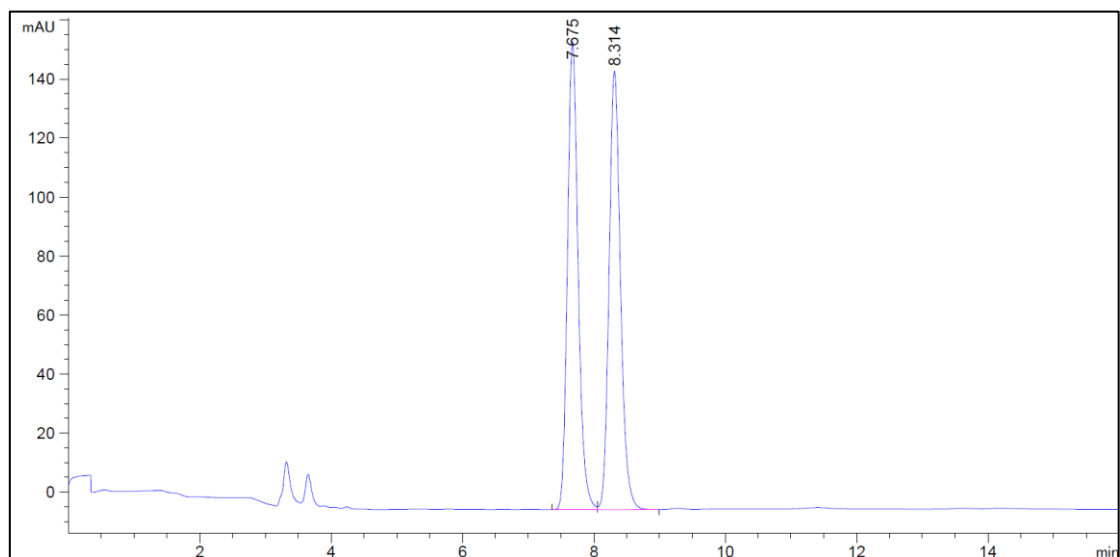


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.564	BB	0.1976	1.11751e4	871.34161	50.3874
2	11.626	BB	0.2479	1.10033e4	675.93262	49.6126

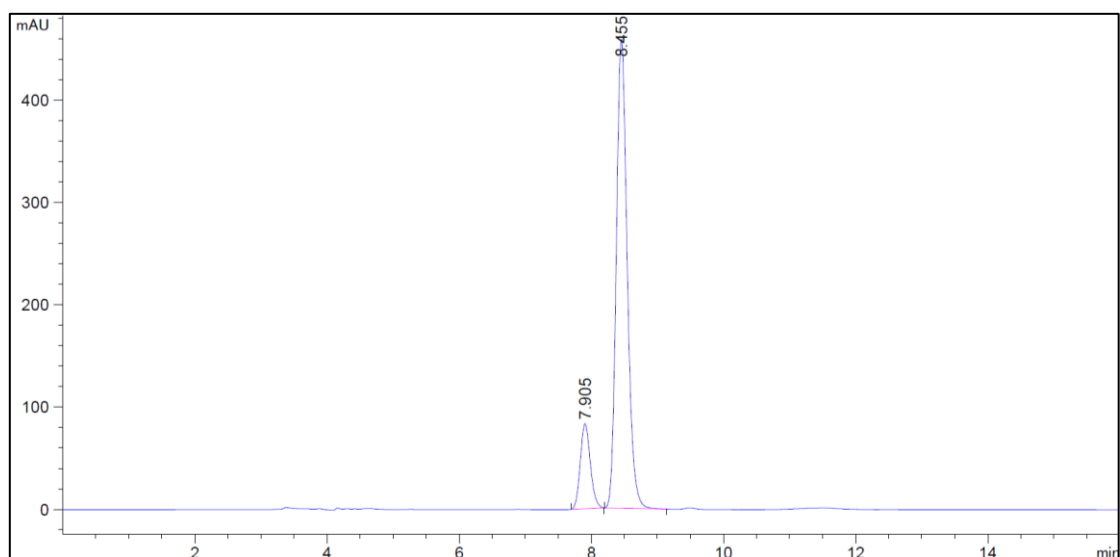


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.540	BBA	0.1960	1.26017e4	986.59607	89.0025
2	11.705	BBA	0.2442	1557.11682	98.10758	10.9975

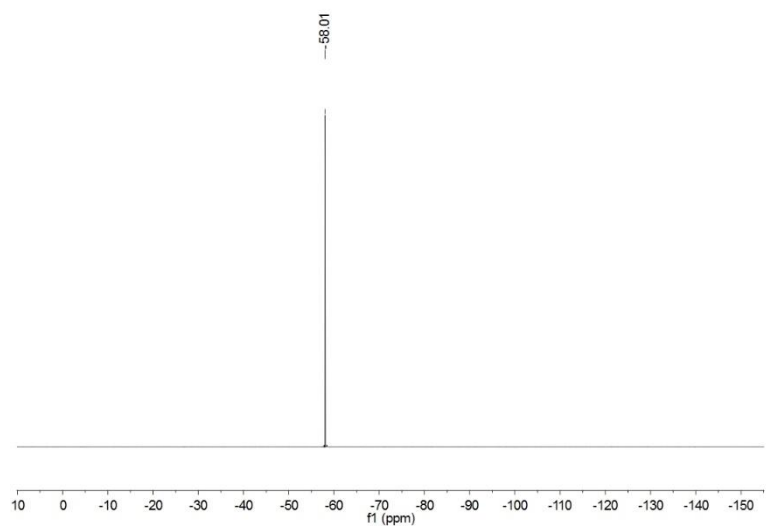
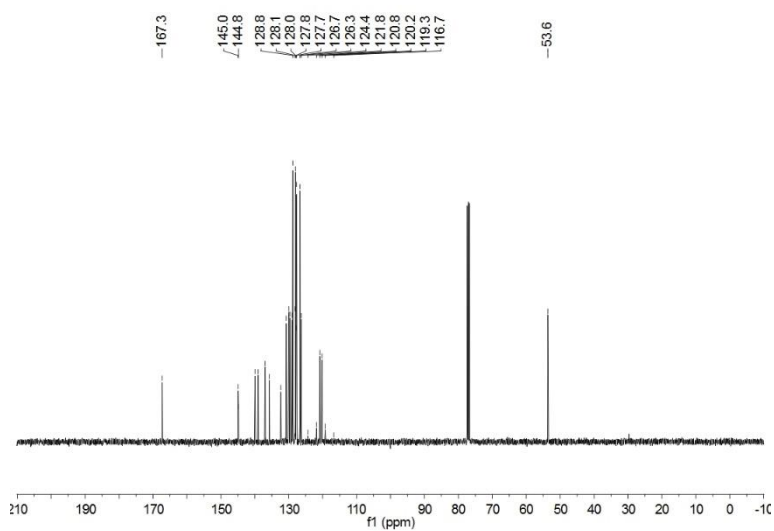
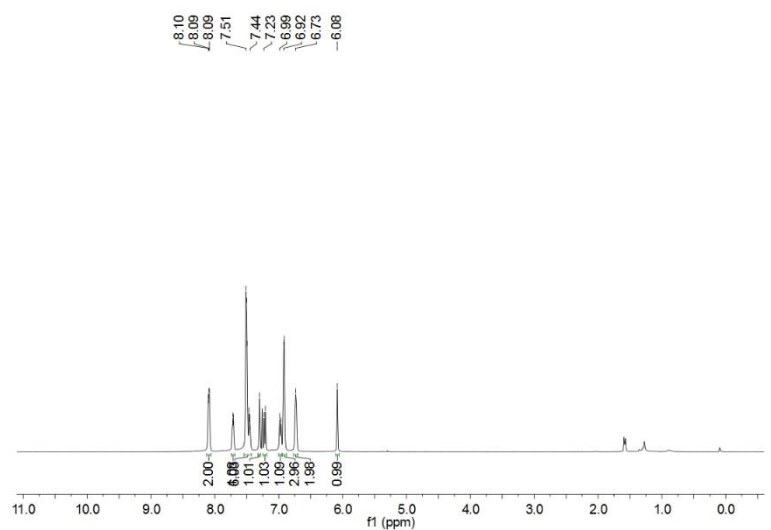
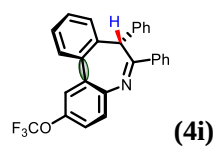


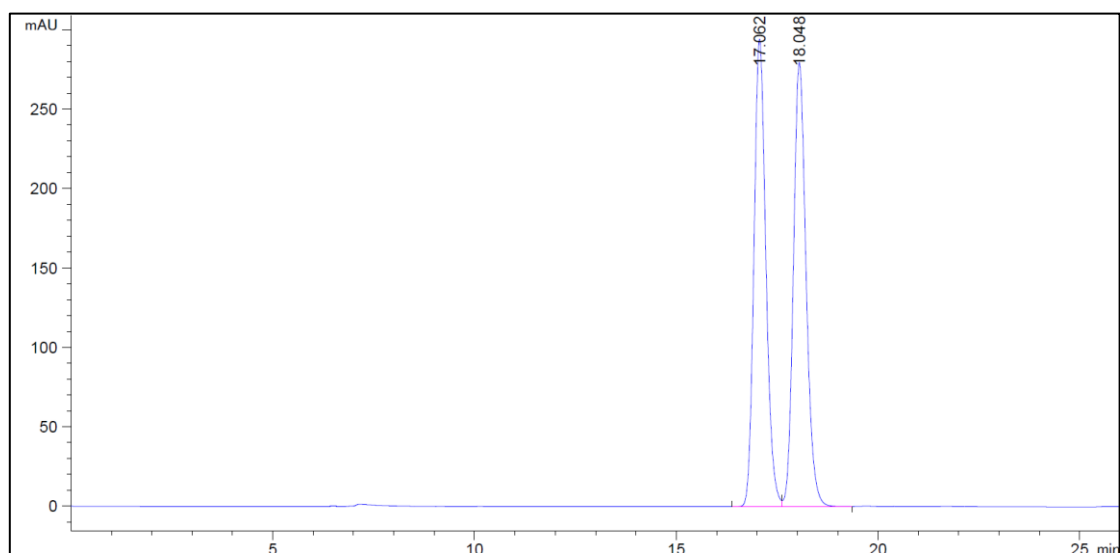


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.675	BV	0.1736	1790.70508	158.70277	49.9647
2	8.314	VB	0.1857	1793.23608	148.70023	50.0353

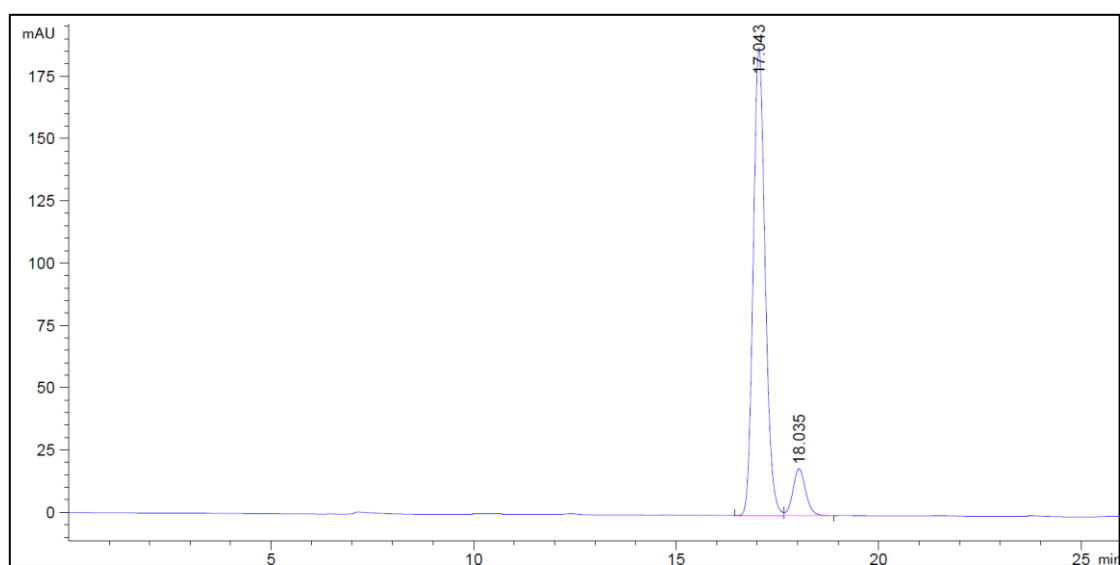


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.905	BBA	0.1628	872.74231	82.93486	14.2473
2	8.455	BBA	0.1767	5252.93604	458.36237	85.7527



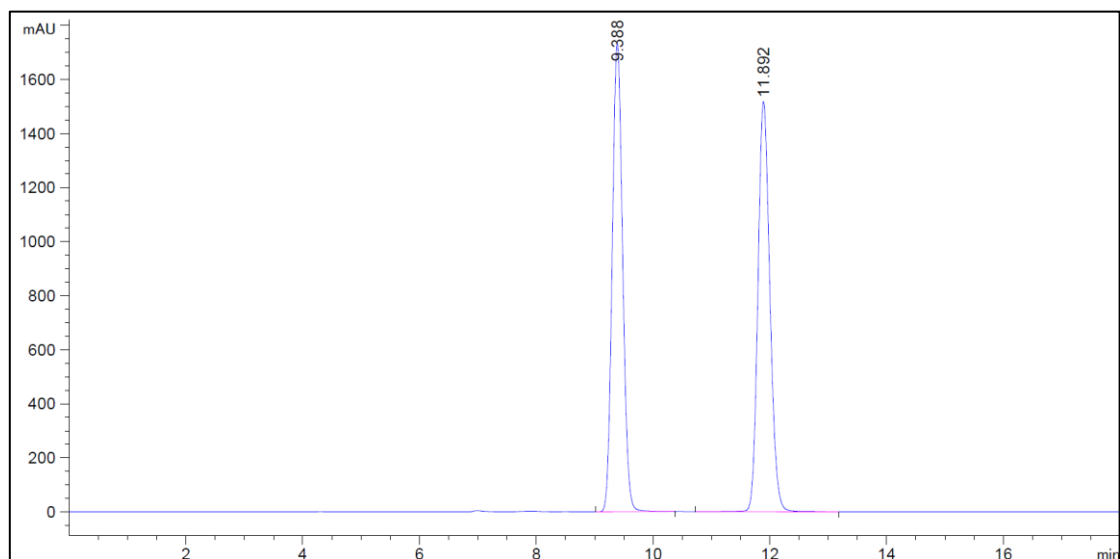


#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.062	BV	0.3165	6044.71143	294.40063	49.8423
2	18.048	VB	0.3348	6082.97314	279.62564	50.1577

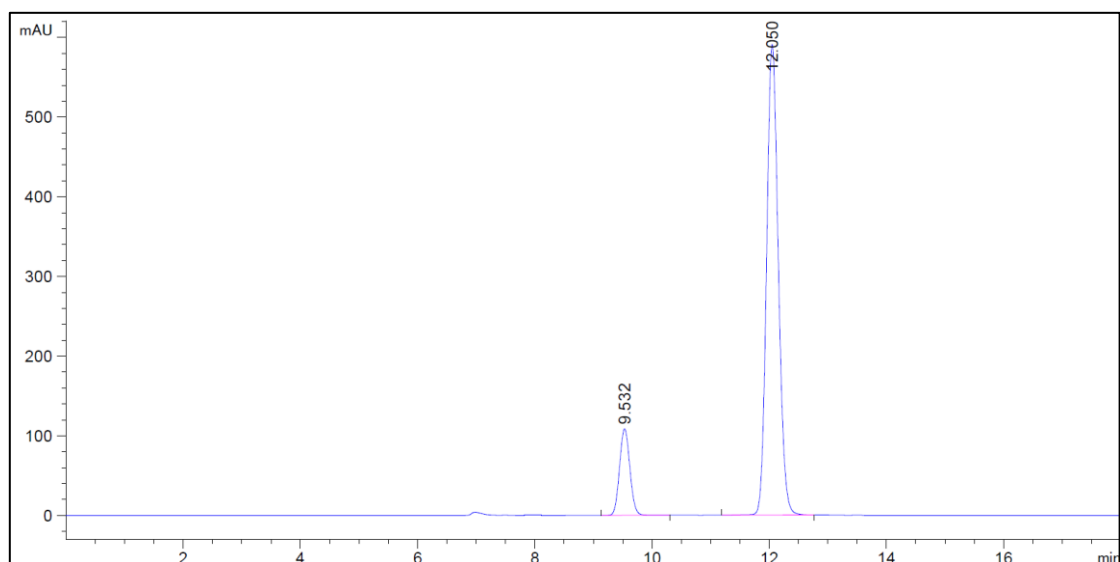


#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.043	BV	0.3165	3838.41797	187.76039	90.3620
2	18.035	VB	0.3362	409.40625	18.79168	9.6380

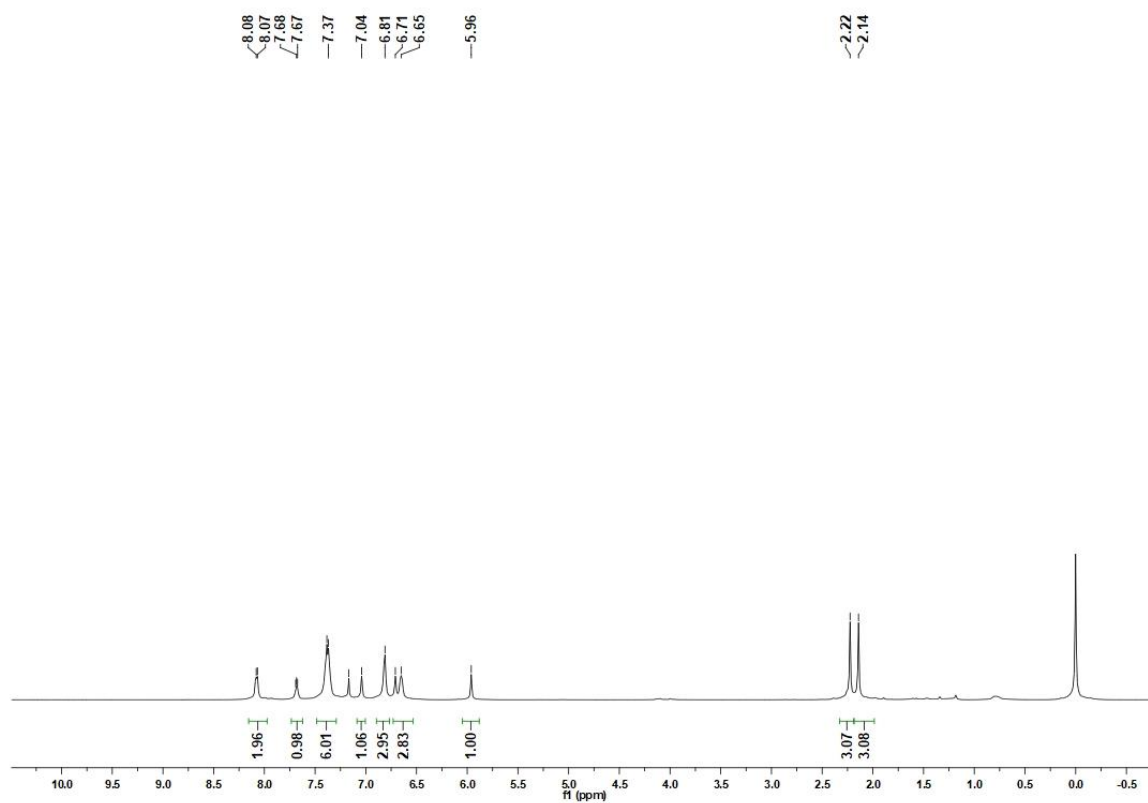
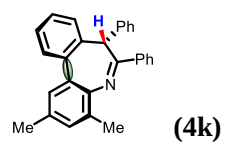


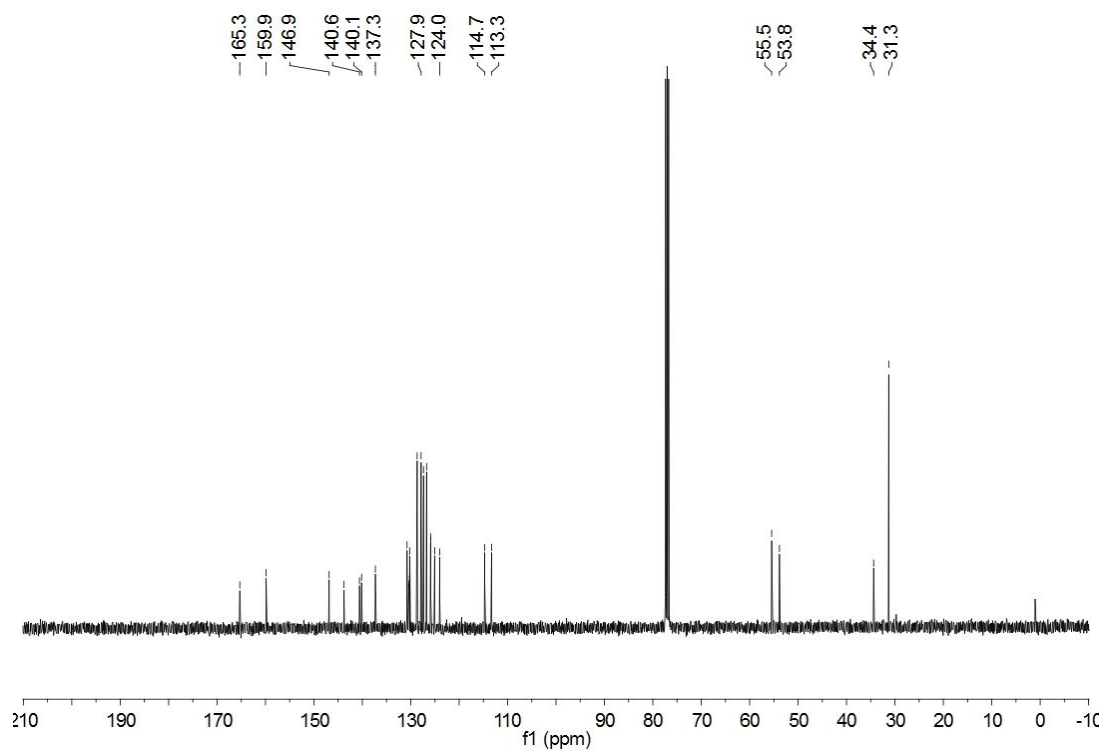
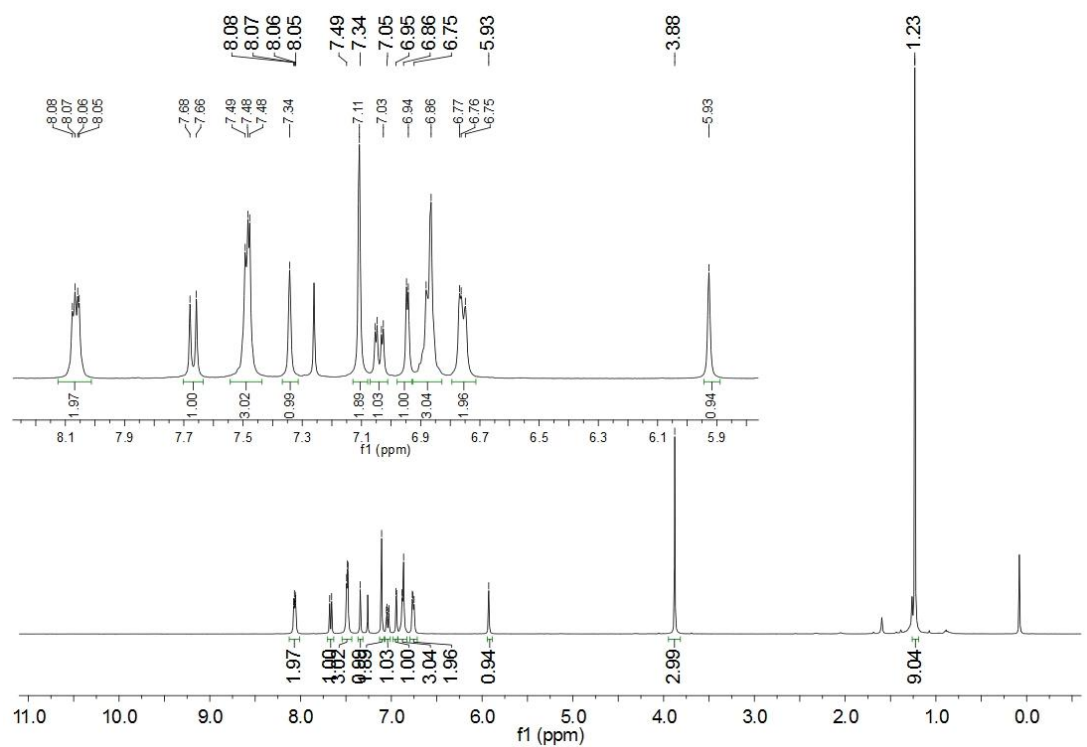
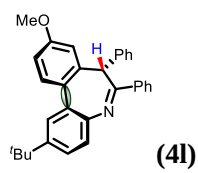


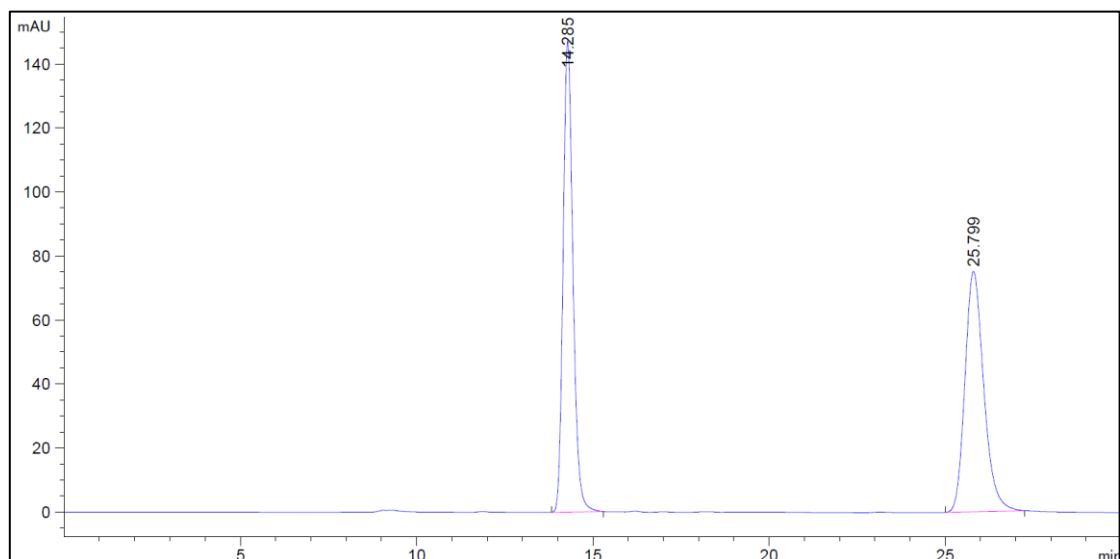
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.388	BB	0.1940	2.14577e4	1732.31067	49.8929
2	11.892	BB	0.2203	2.15498e4	1516.58887	50.1071



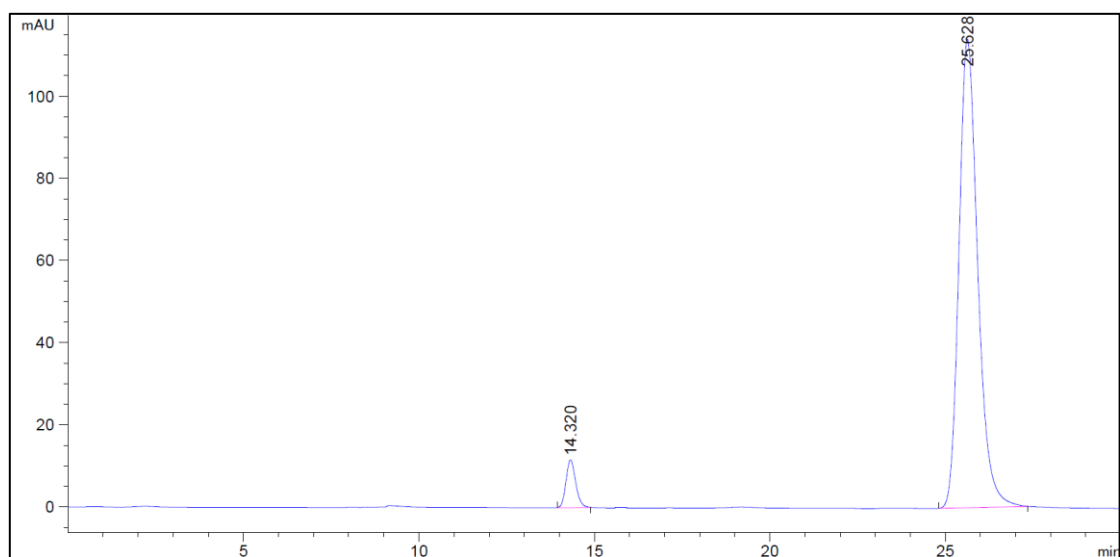
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.532	BB	0.1919	1329.39453	108.56033	13.9481
2	12.050	BB	0.2159	8201.58691	590.96320	86.0519



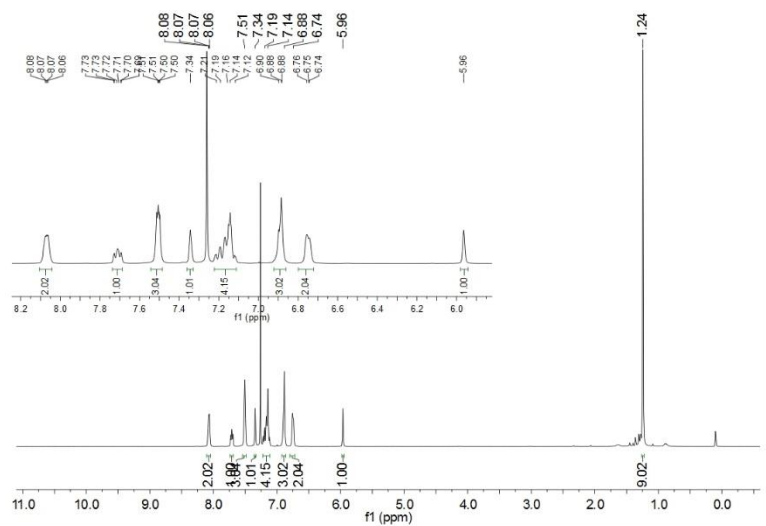
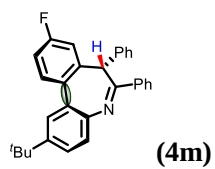


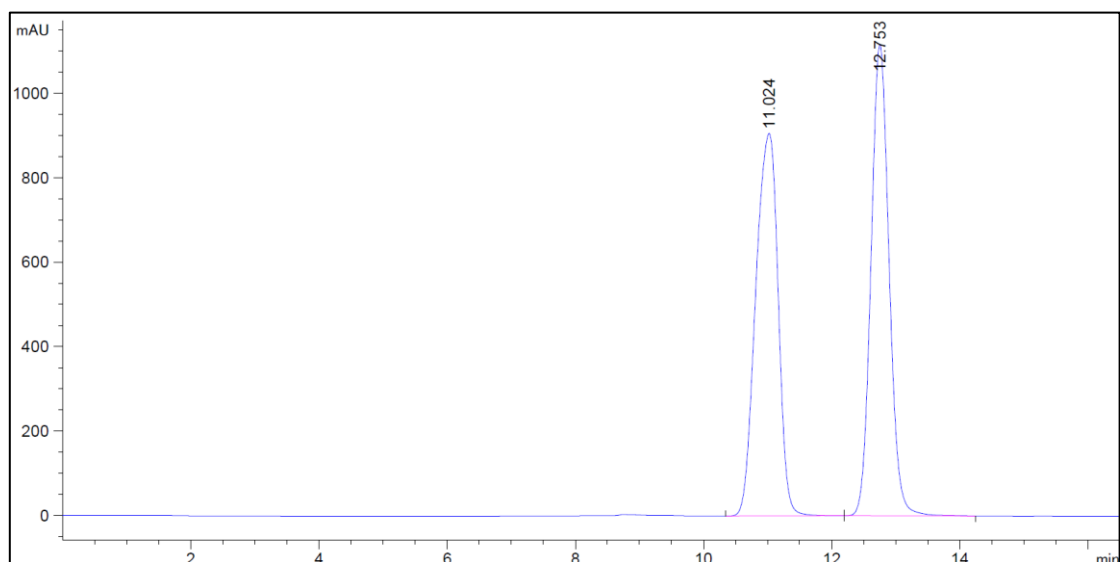


#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.285	BB	0.2976	2861.00757	147.27937	50.6156
2	25.799	BB	0.5694	2791.41846	75.14096	49.3844

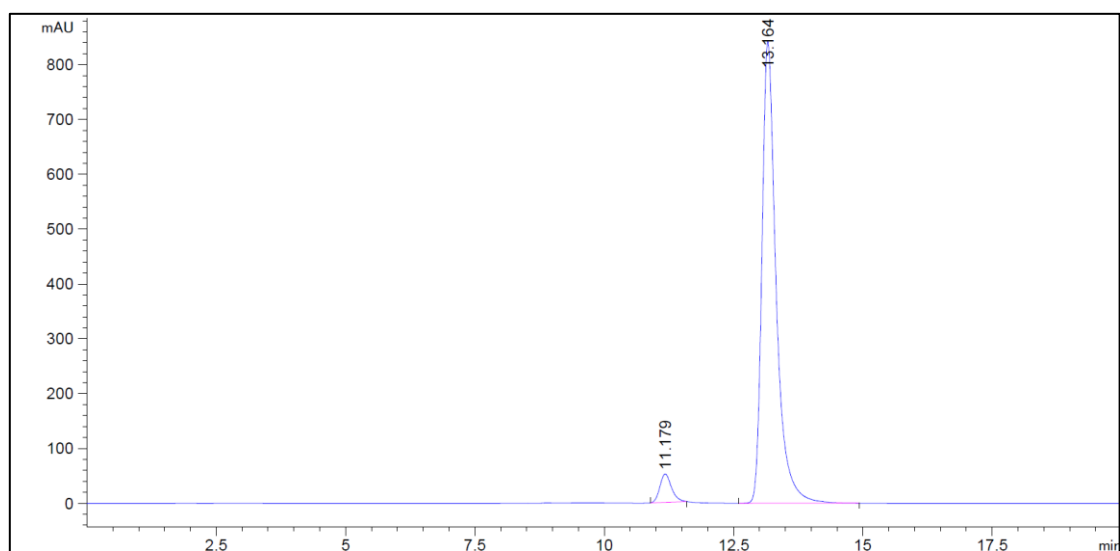


#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.320	BB	0.2972	223.56891	11.63281	5.0060
2	25.628	BB	0.5699	4242.44385	114.07462	94.9940

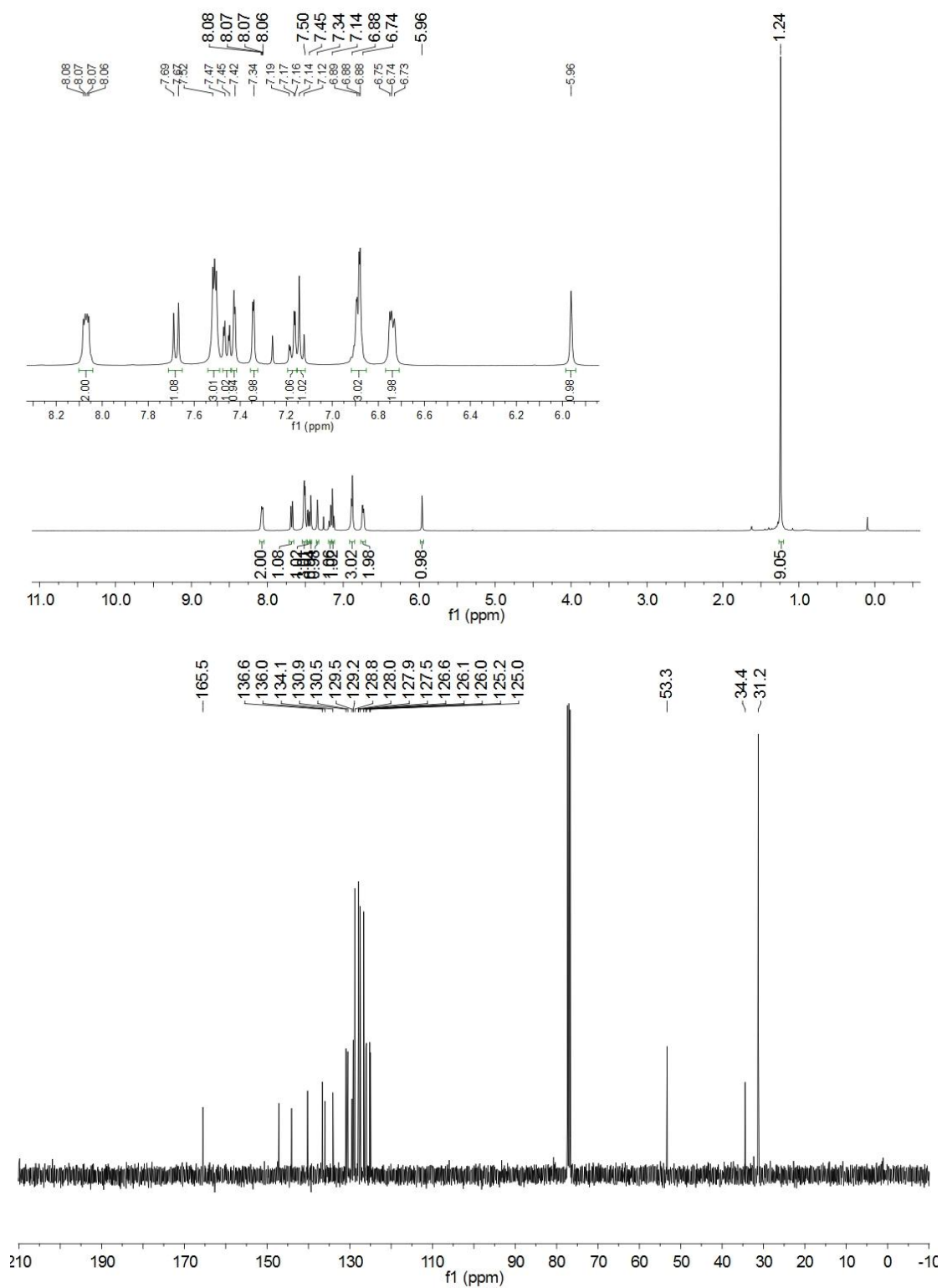
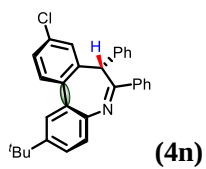


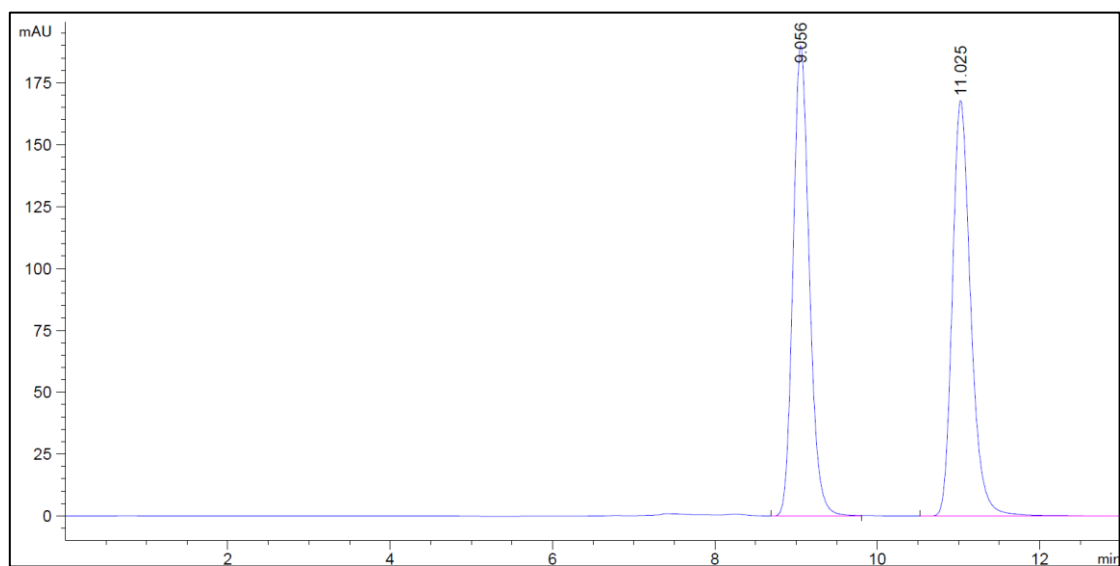


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.024	BB	0.3970	2.19504e4	904.92871	50.1082
2	12.753	BV	0.3046	2.18556e4	1115.19934	49.8918

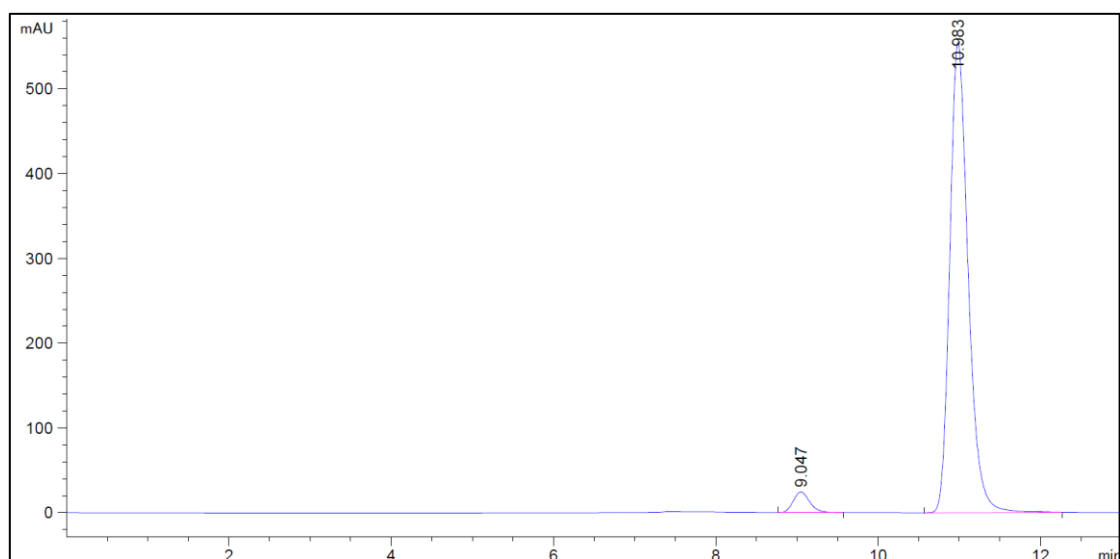


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.179	BBA	0.2372	803.66656	51.75016	4.7706
2	13.164	BBA	0.2852	1.60427e4	842.20593	95.2294

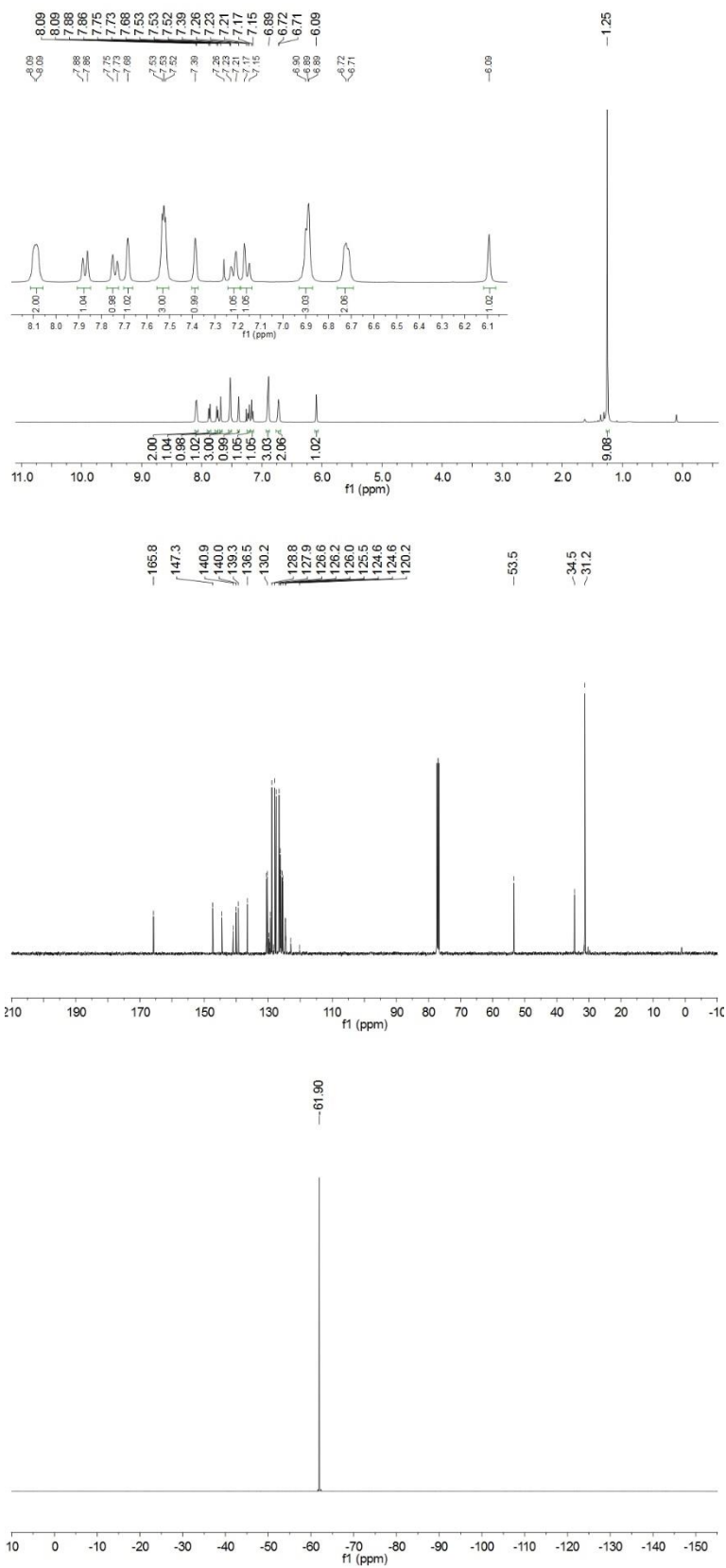
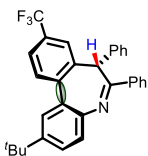


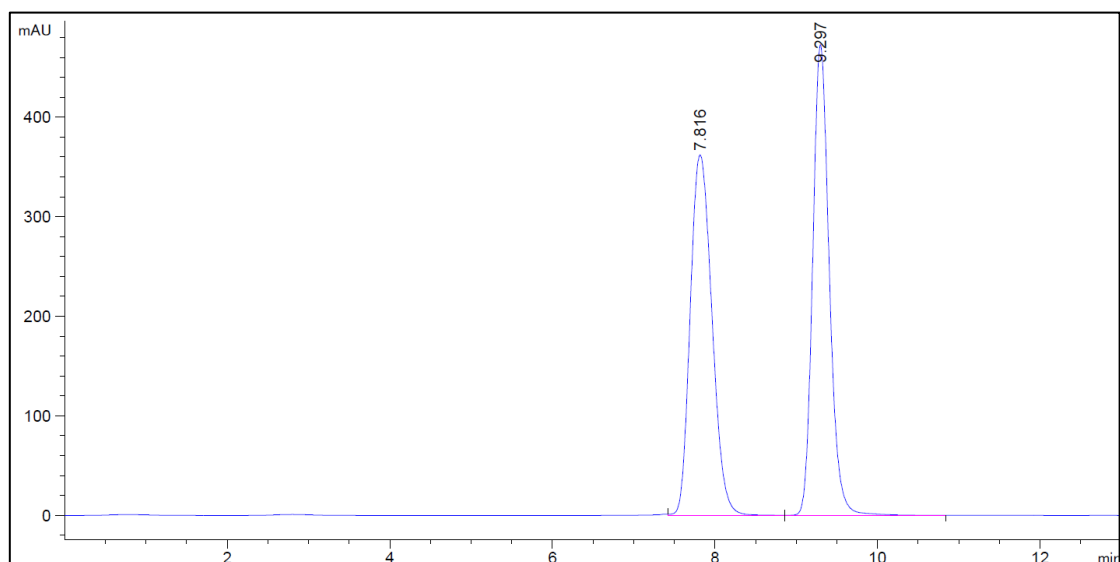


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.056	BV	0.2143	2643.10449	189.96155	49.9996
2	11.025	VBA	0.2408	2643.14697	167.74509	50.0004

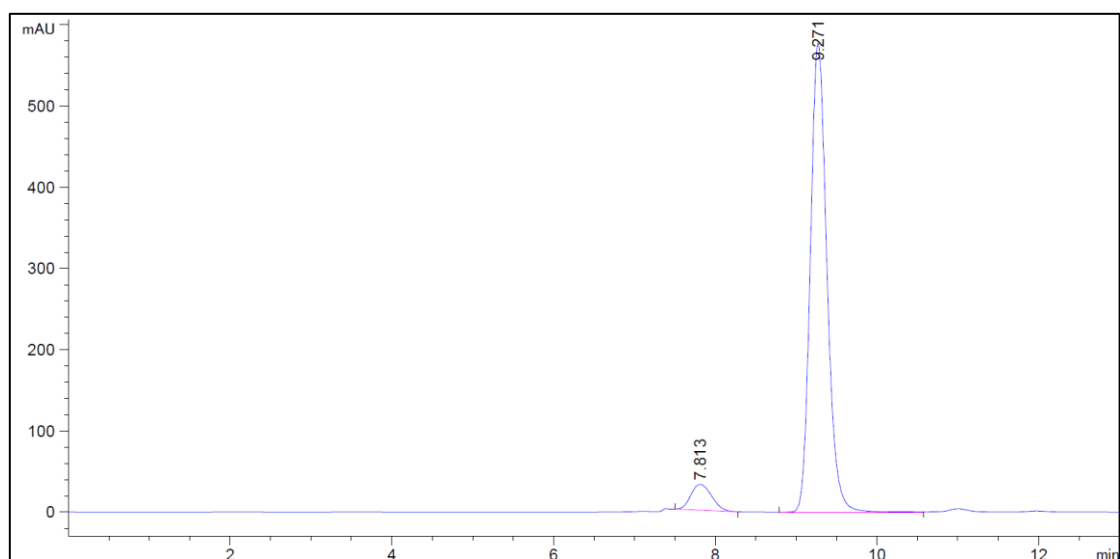


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.047	BBA	0.2193	346.69611	24.47344	3.8298
2	10.983	BBA	0.2402	8705.78223	554.51855	96.1702

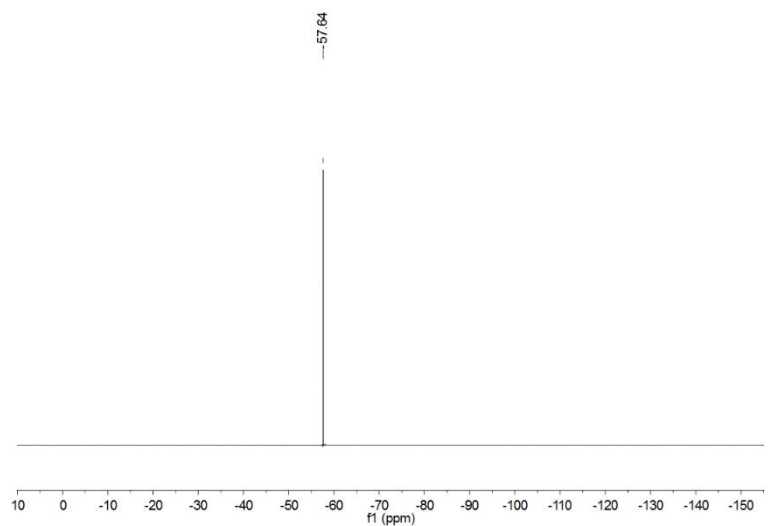
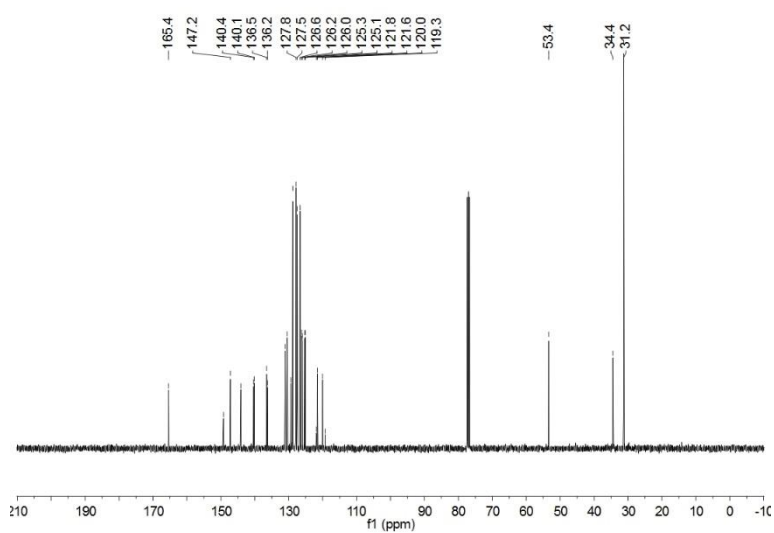
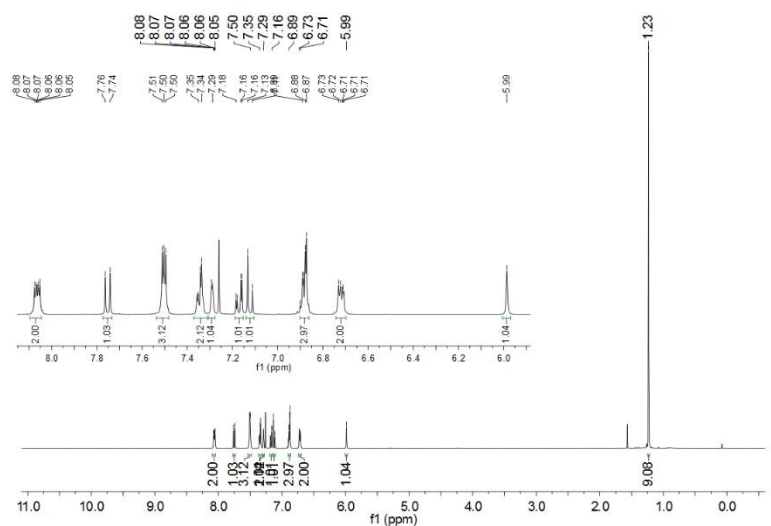
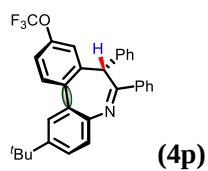


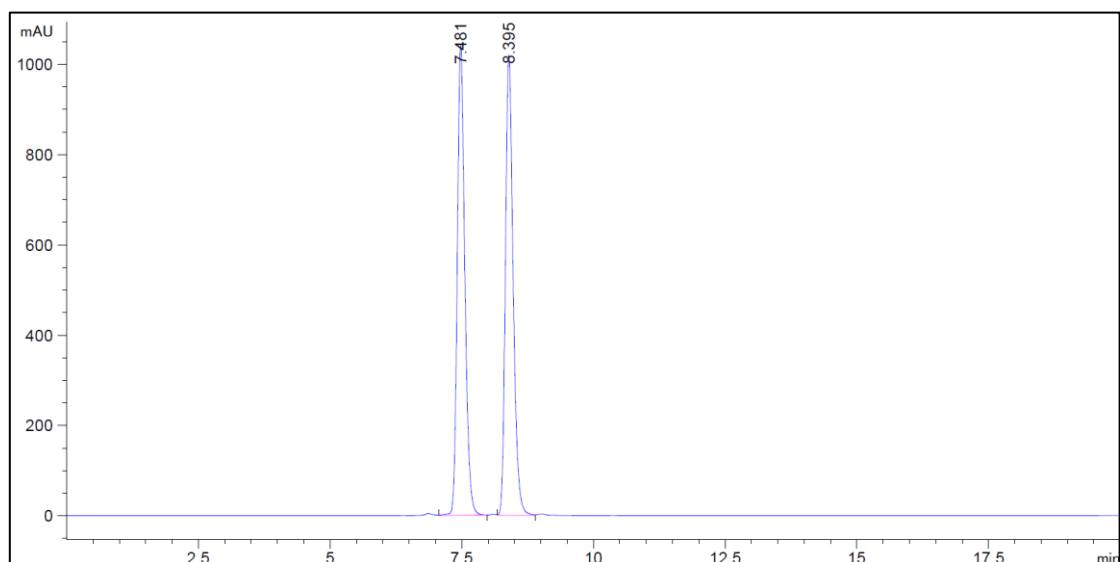


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.816	VB	0.2951	6705.67236	362.08527	50.0586
2	9.297	BV	0.2181	6689.97119	472.78369	49.9414

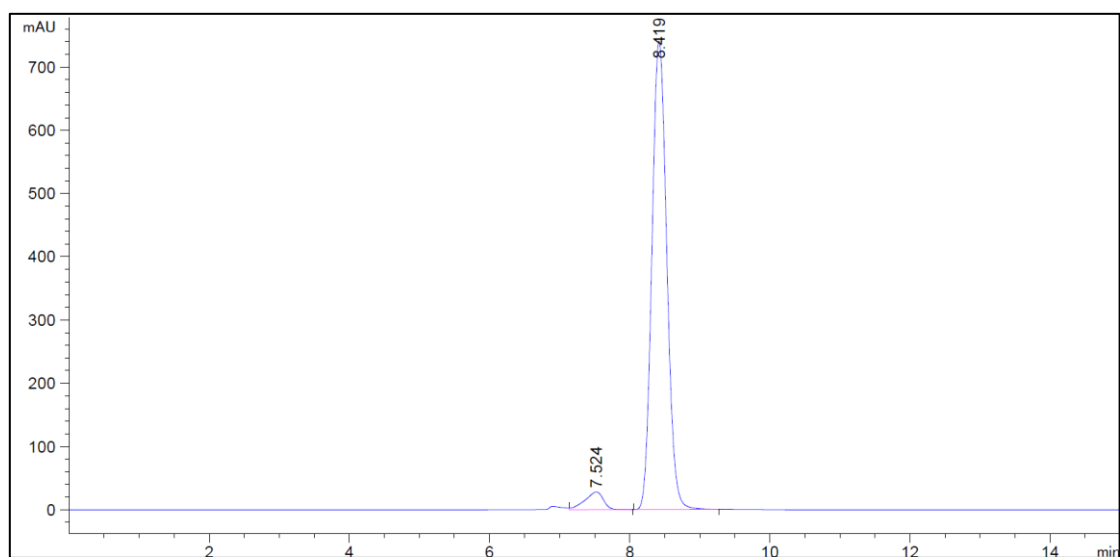


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.813	BB	0.2851	562.97852	31.71809	6.4055
2	9.271	BV	0.2192	8225.97949	577.51050	93.5945

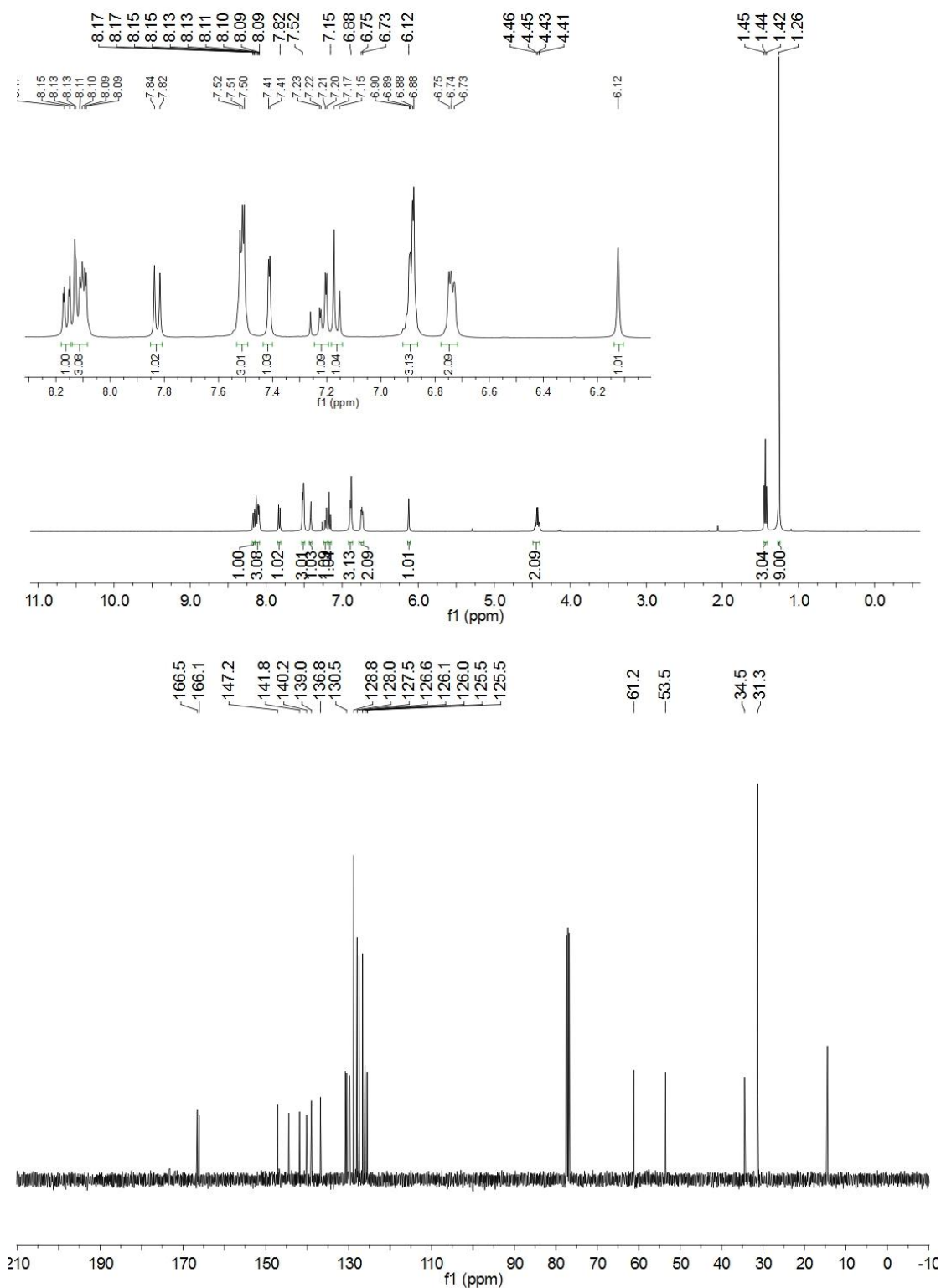
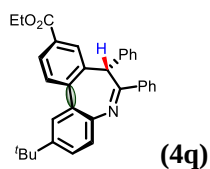


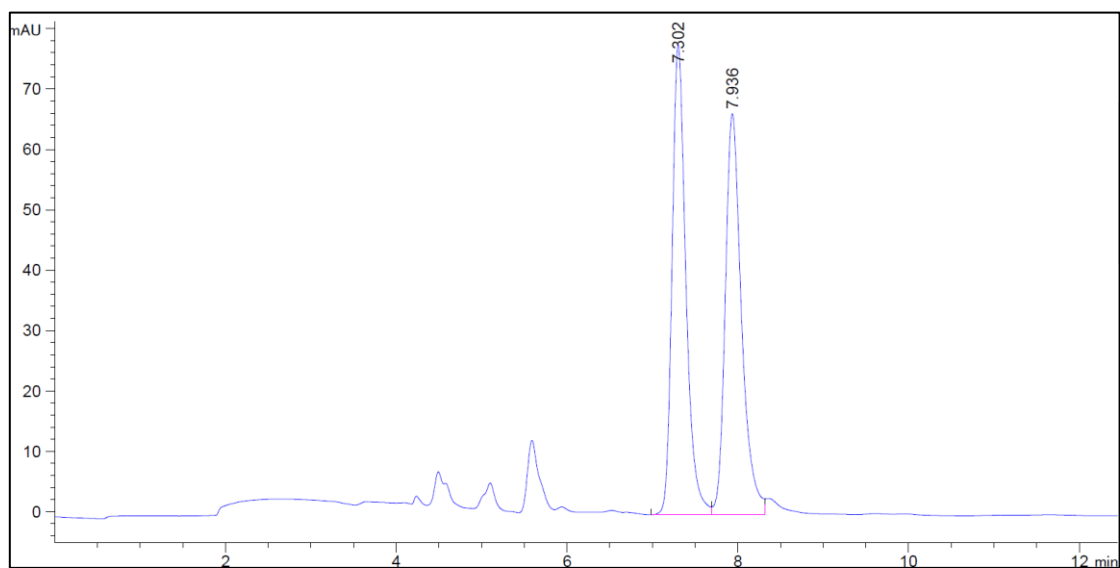


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.481	VB	0.1507	1.03558e4	1040.02014	49.9775
2	8.395	VV	0.1547	1.03651e4	1018.37793	50.0225

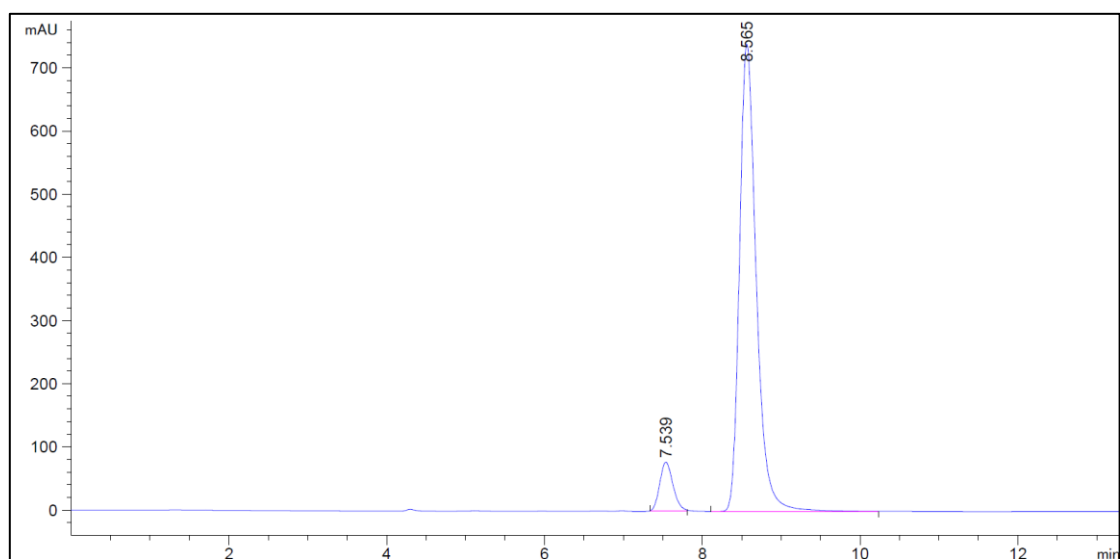


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.524	VB	0.2721	511.33356	27.85810	4.4736
2	8.419	BB	0.2310	1.09188e4	740.51282	95.5264

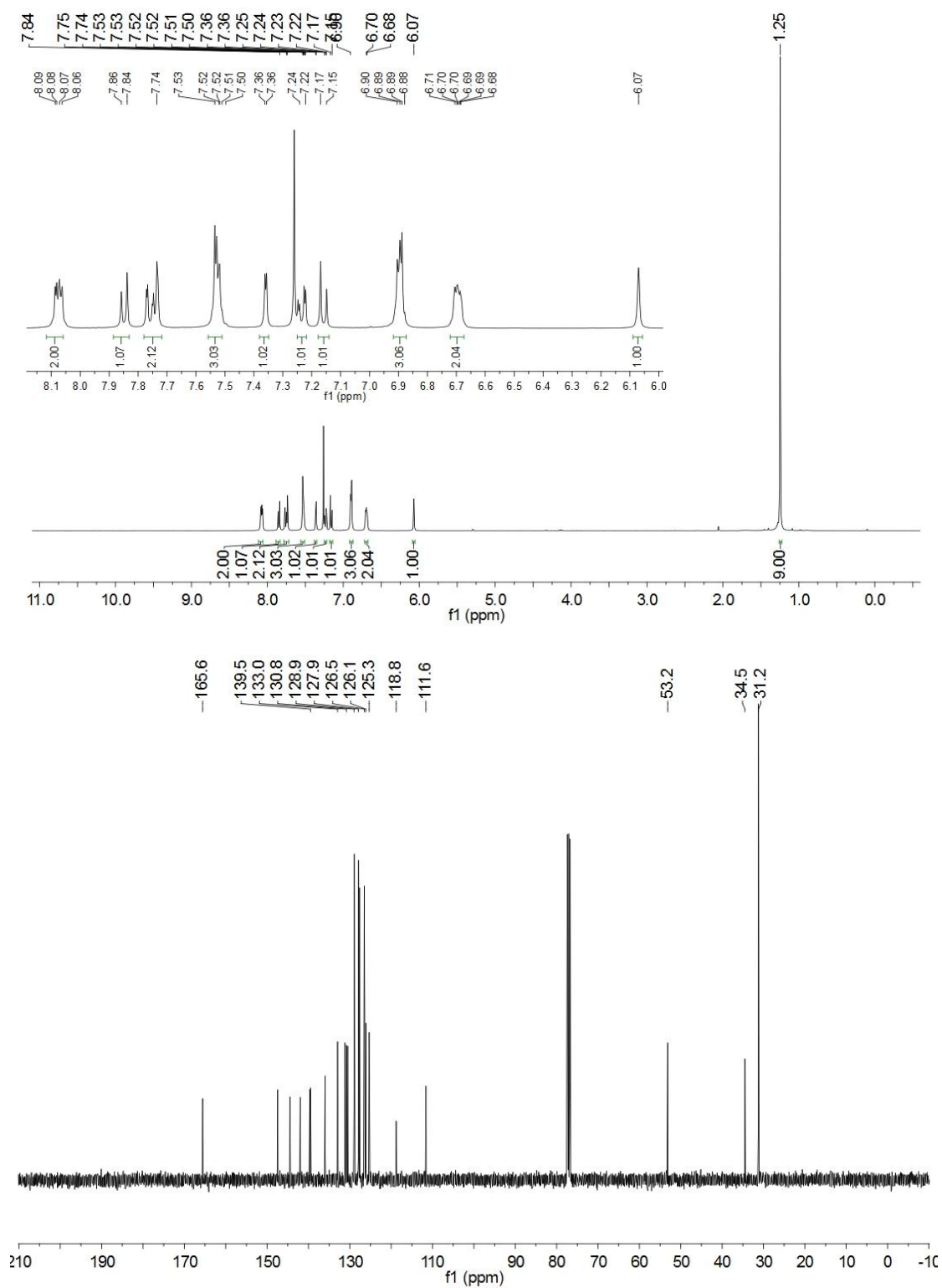
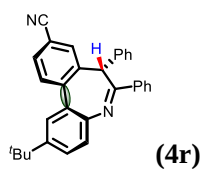


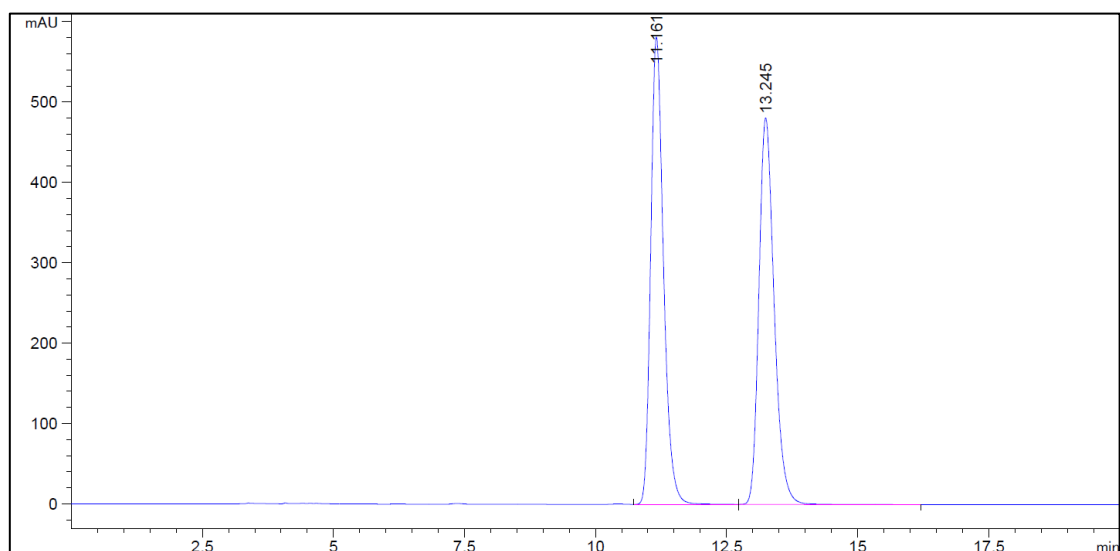


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.302	BV	0.1708	875.48889	77.80673	49.8618
2	7.936	VV	0.1998	880.34100	66.36287	50.1382

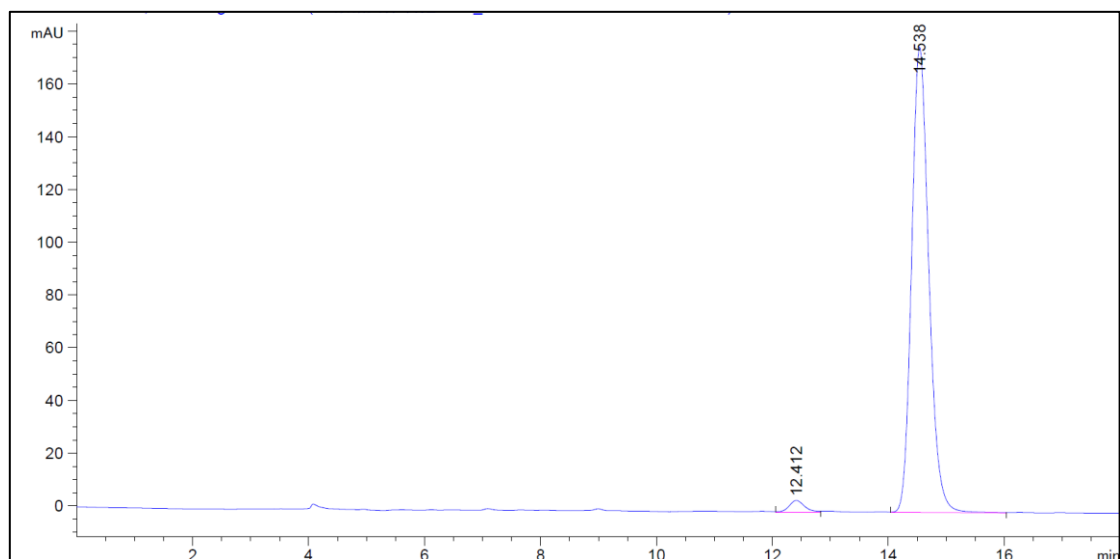


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.539	BBA	0.1801	892.58276	77.06824	7.5668
2	8.565	BV	0.2250	1.09035e4	739.57208	92.4332

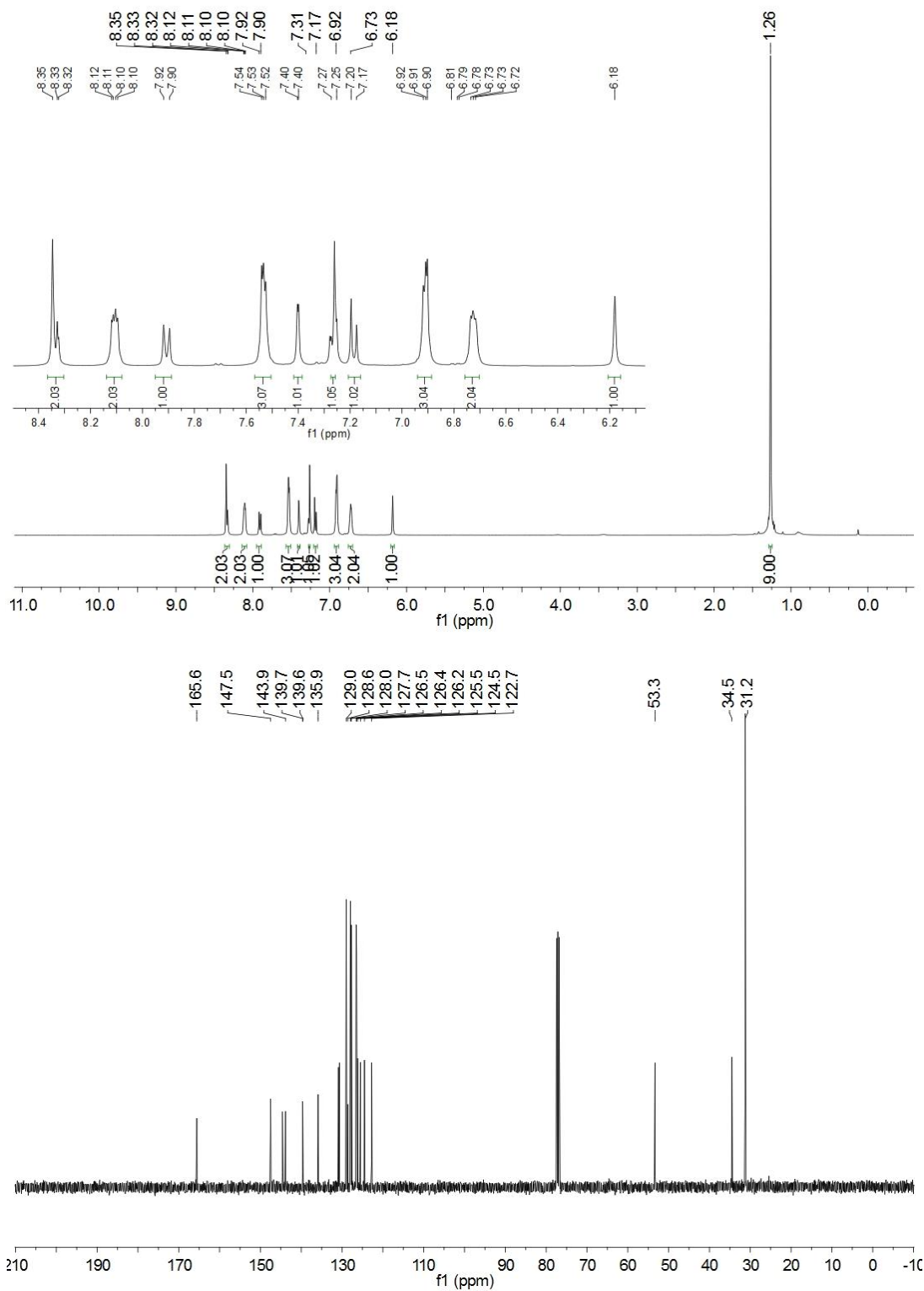
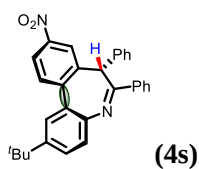


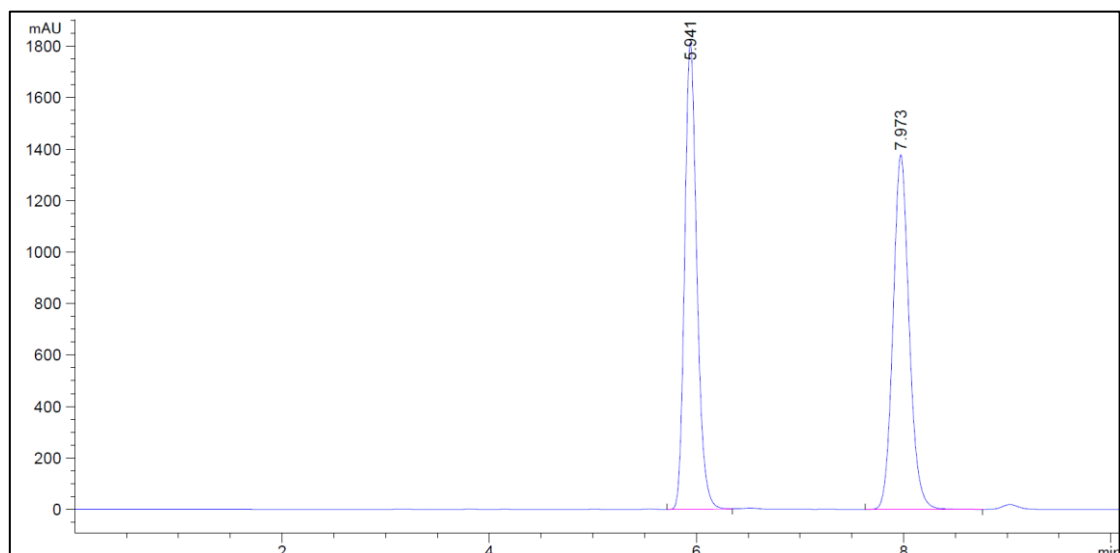


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.161	VV	0.2599	9875.41211	582.04071	50.3775
2	13.245	VV	0.3108	9727.41992	481.32559	49.6225

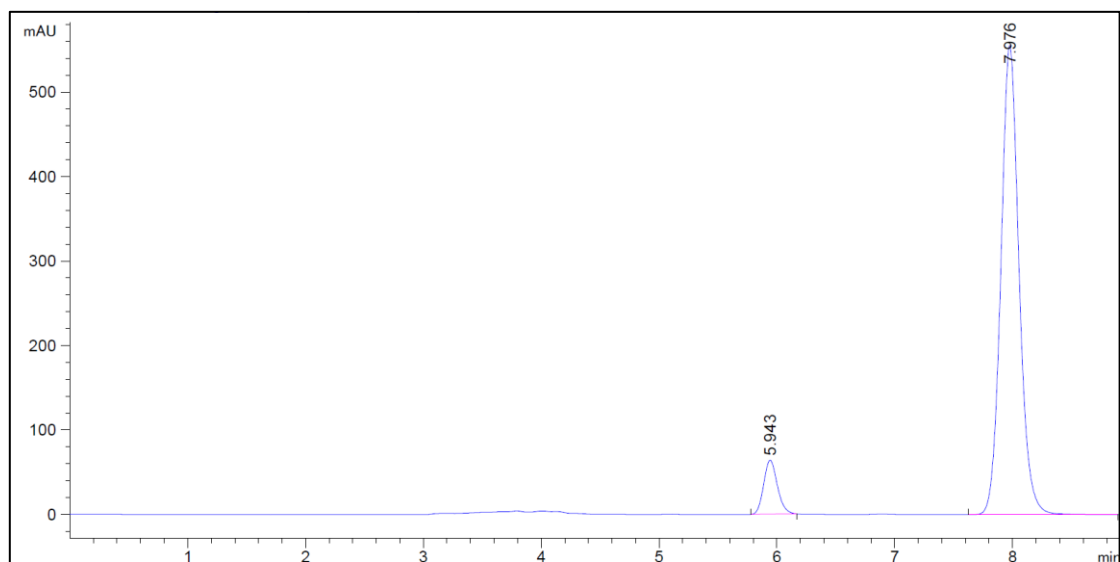


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.412	VV	0.2832	83.15584	4.44556	2.2372
2	14.538	VV	0.3183	3633.79785	176.45589	97.7628

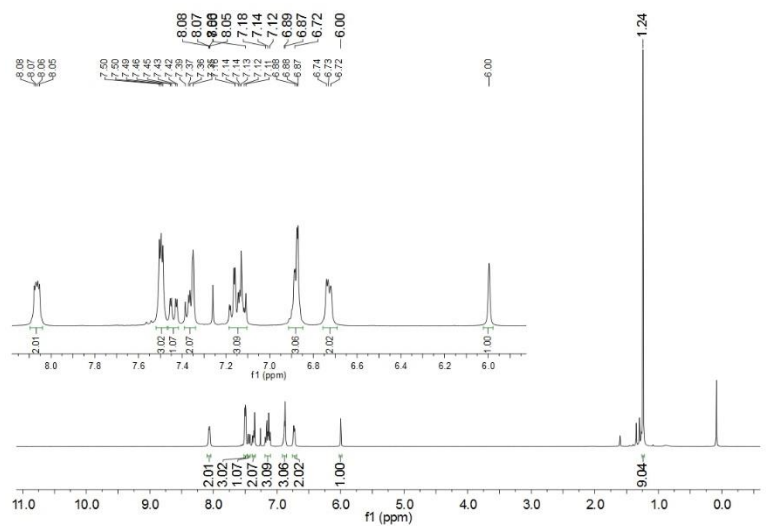
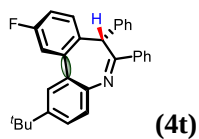


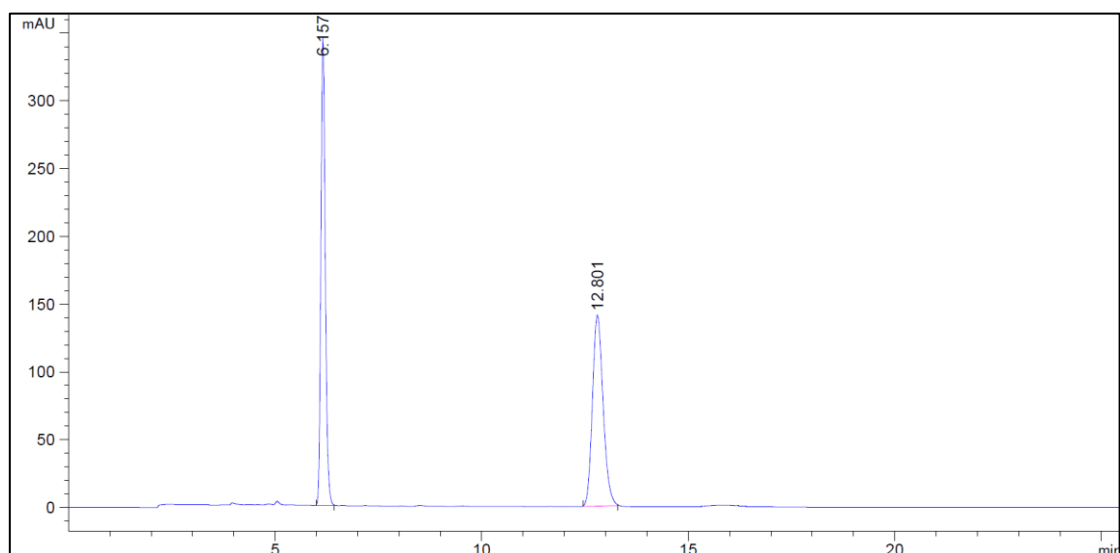


#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.941	BV	0.1258	1.48829e4	1813.22375	49.9503
2	7.973	BB	0.1653	1.49125e4	1377.44031	50.0497

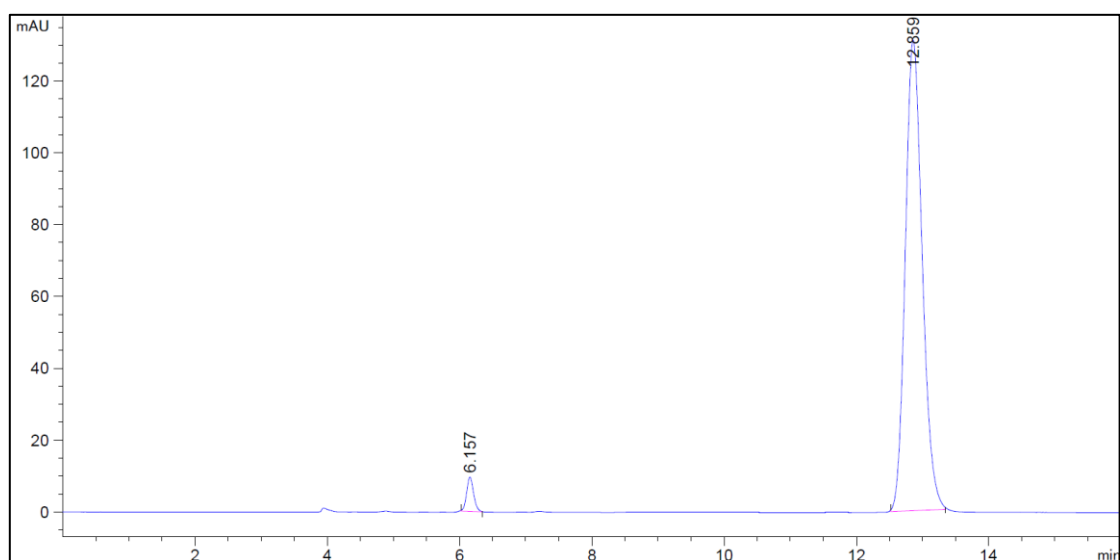


#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.943	BBA	0.1241	515.94440	63.99943	7.9933
2	7.976	BBA	0.1627	5938.74756	555.55316	92.0067

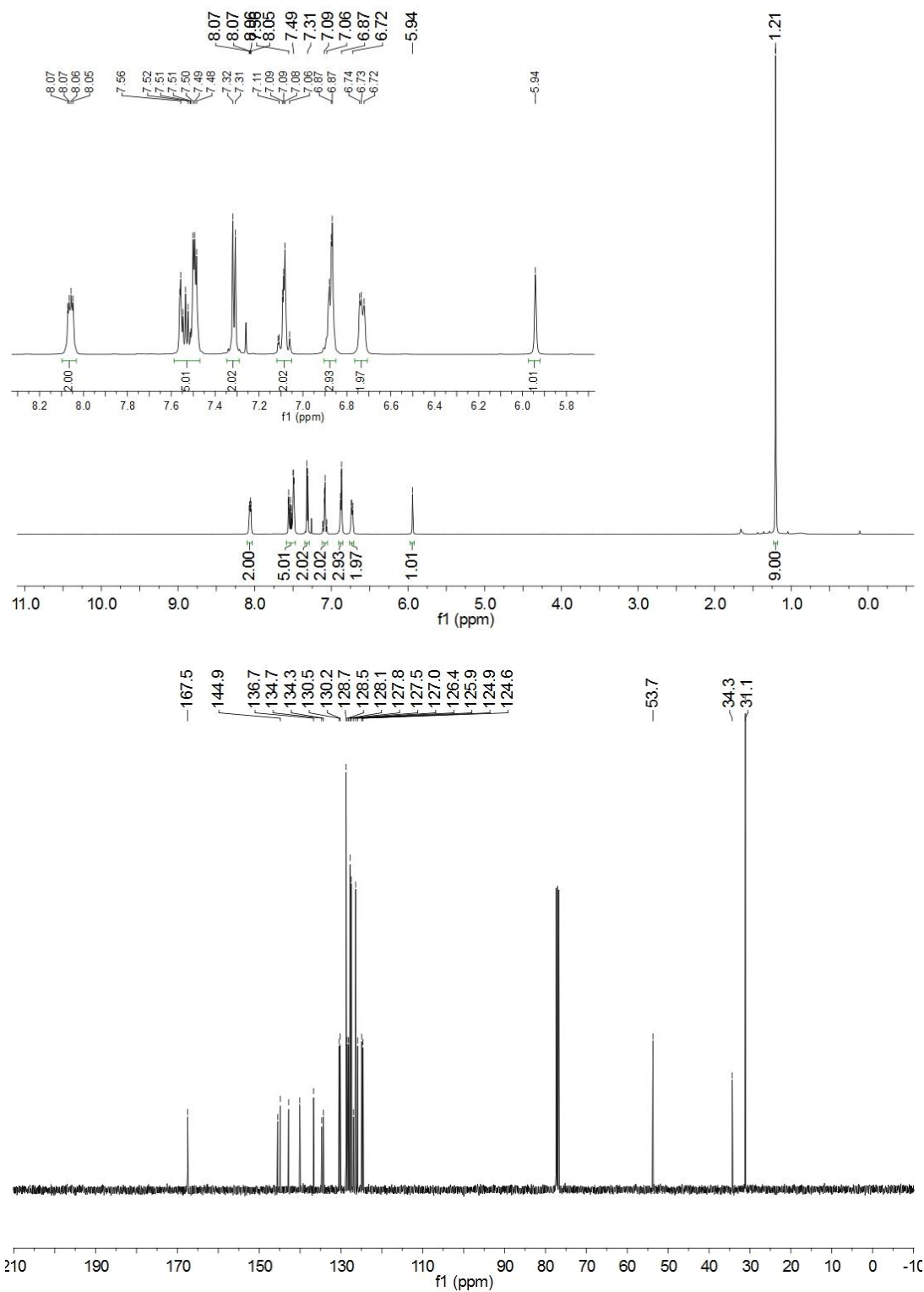
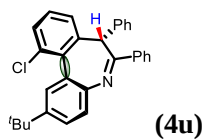


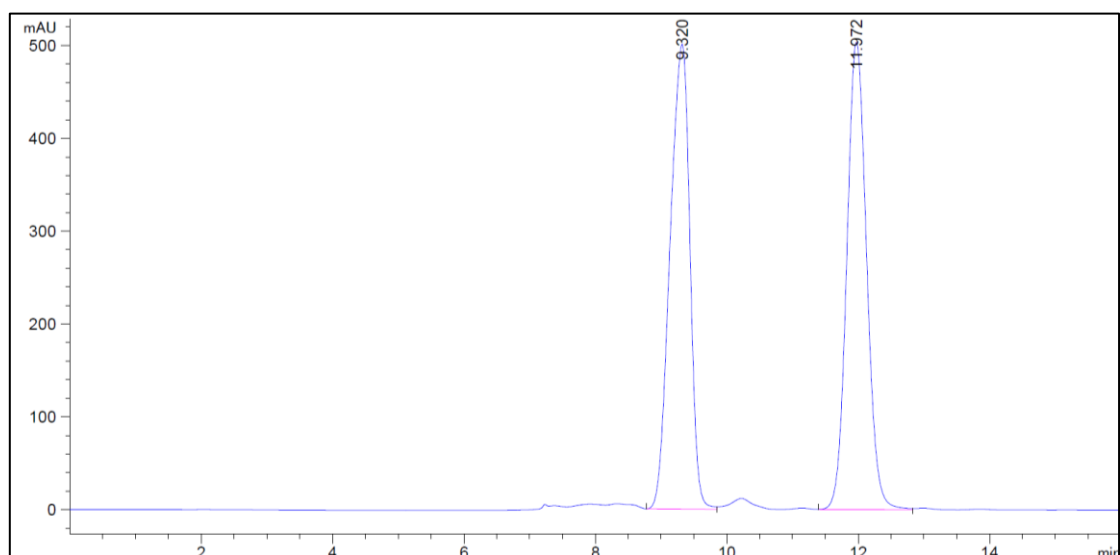


#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.157	BB	0.1137	2560.65503	344.67841	50.2940
2	12.801	BB	0.2782	2530.71875	140.81192	49.7060

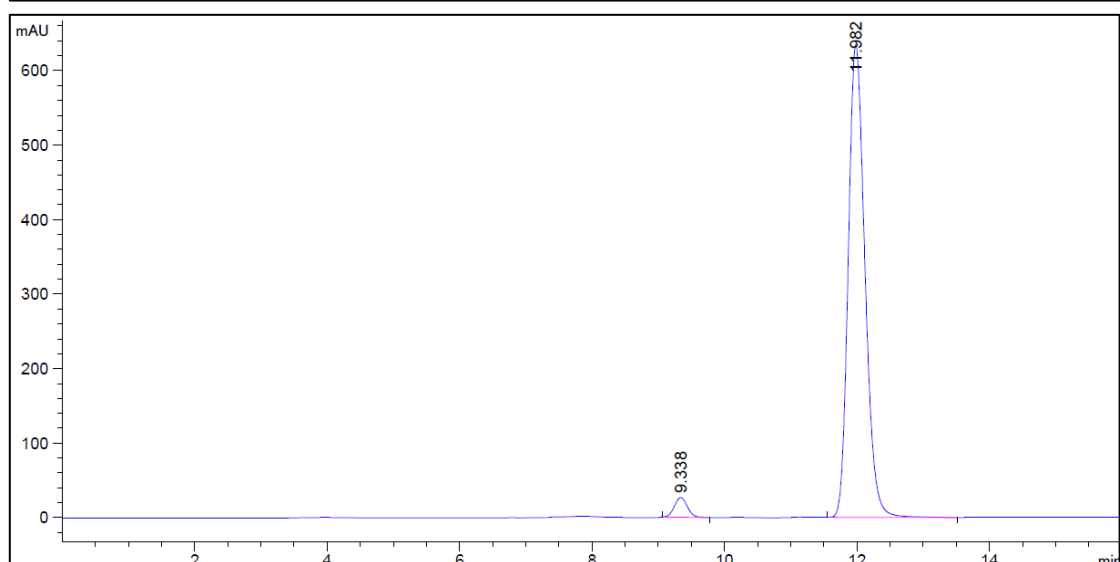


#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.157	BB	0.1124	69.71935	9.52990	2.9026
2	12.859	BB	0.2747	2332.28271	131.01860	97.0974

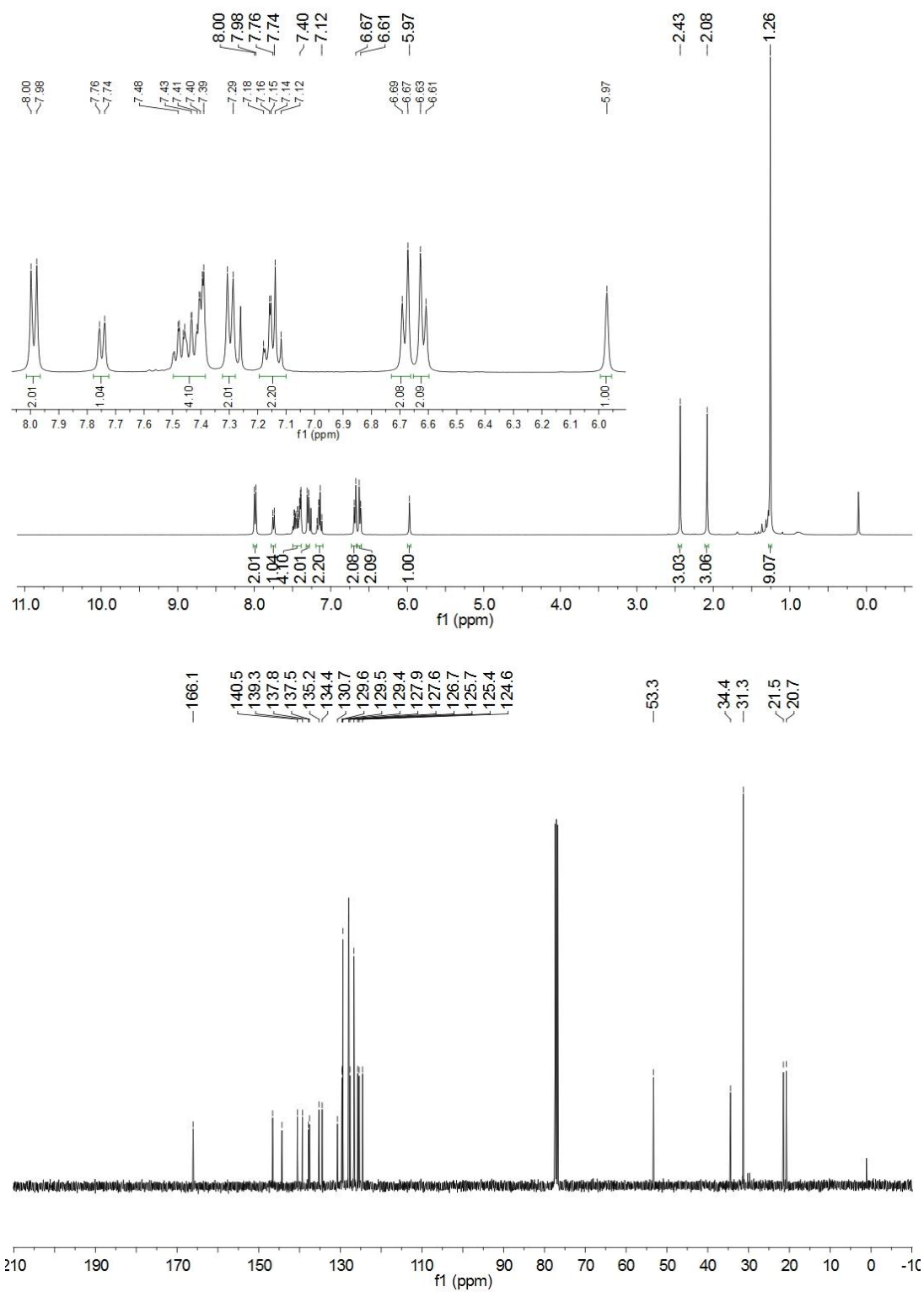
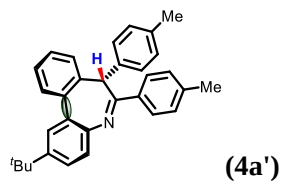


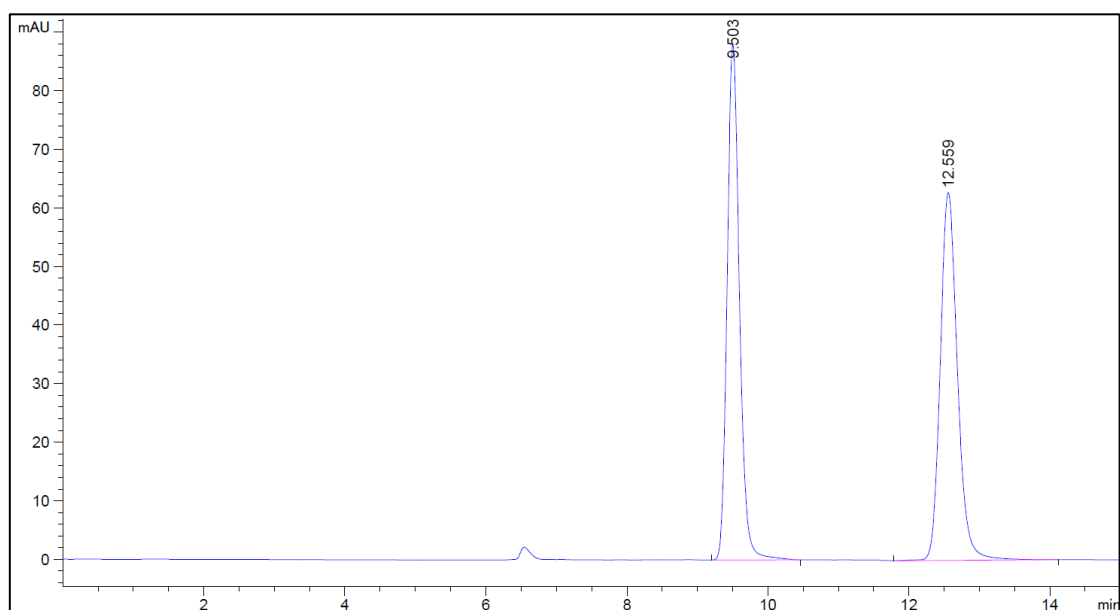


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.320	BV	0.3429	1.04671e4	500.59225	49.8746
2	11.972	BV	0.3258	1.05198e4	503.37442	50.1254

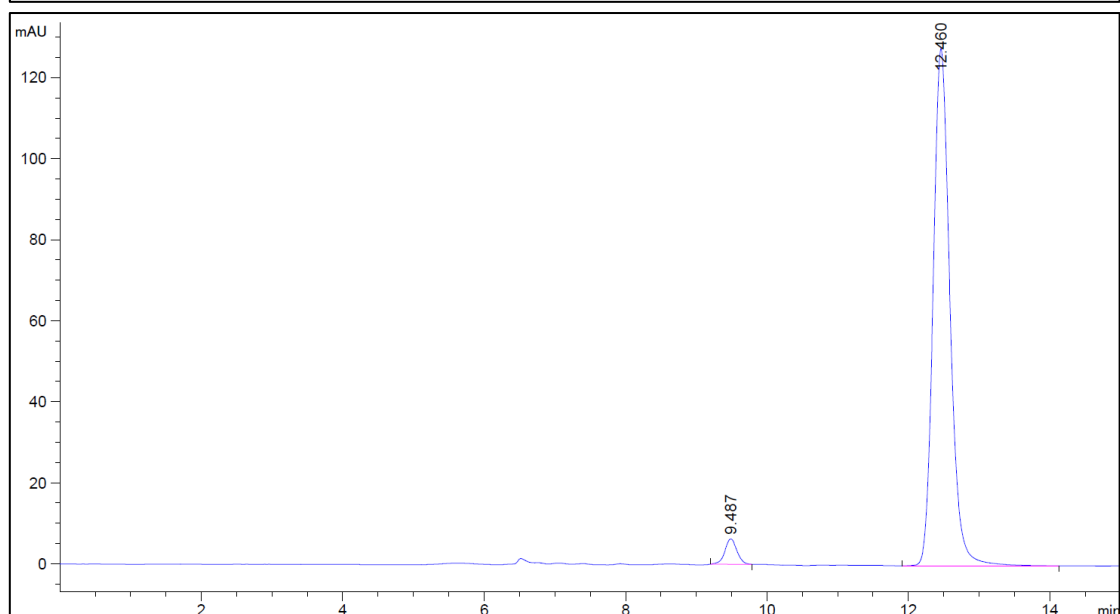


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.338	BBA	0.2124	360.21011	26.53753	3.1568
2	11.982	BB	0.2703	1.10505e4	634.21344	96.8432

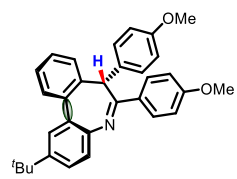




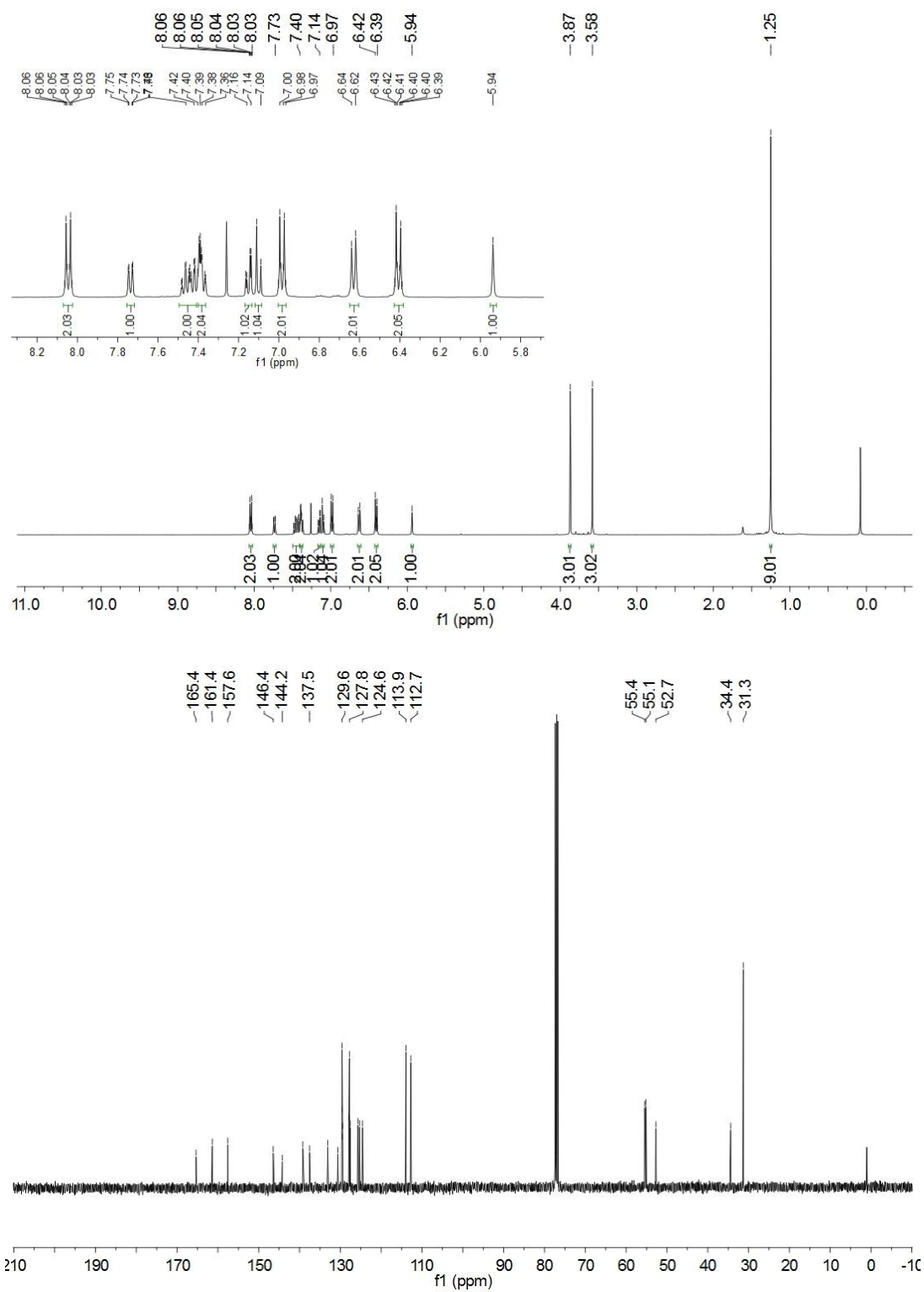
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.503	BB	0.1861	1065.08154	88.03826	50.0636
2	12.559	BB	0.2594	1062.37378	62.77296	49.9364

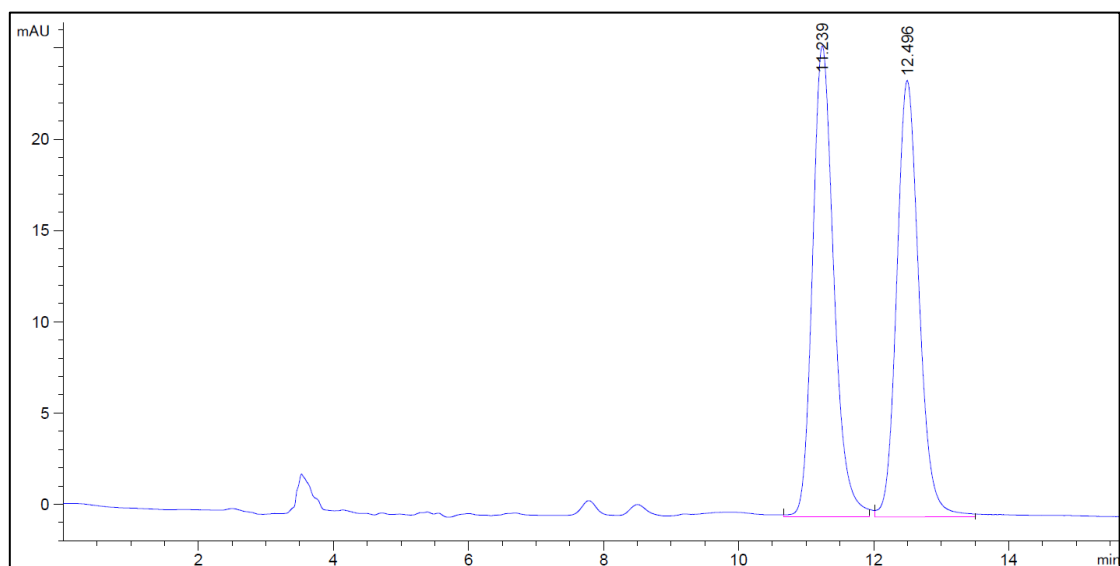


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.487	BBA	0.1813	73.65261	6.25917	3.3849
2	12.460	BB	0.2520	2102.25659	127.76471	96.6151

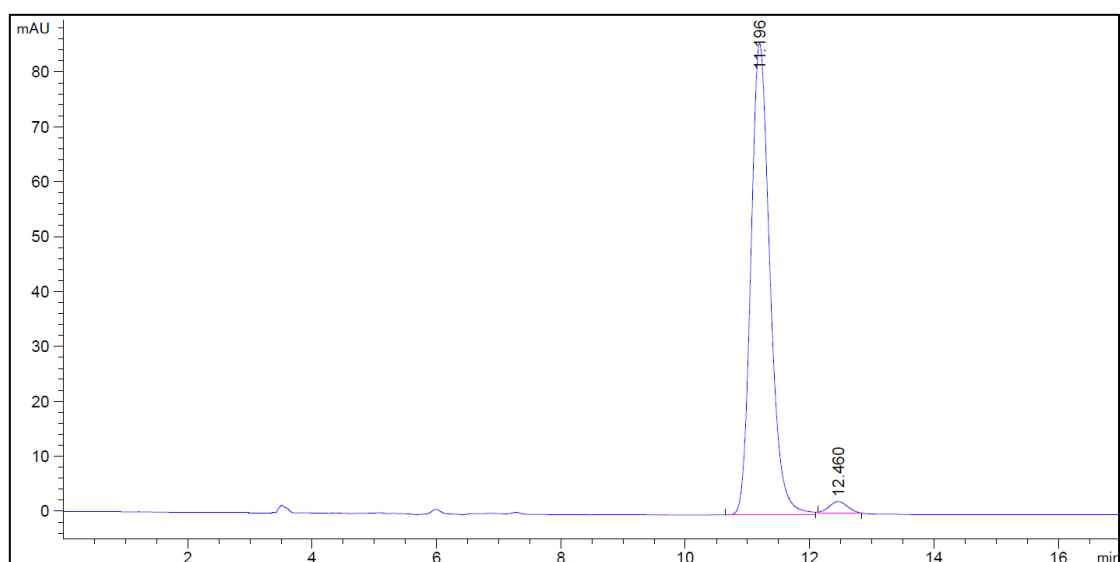


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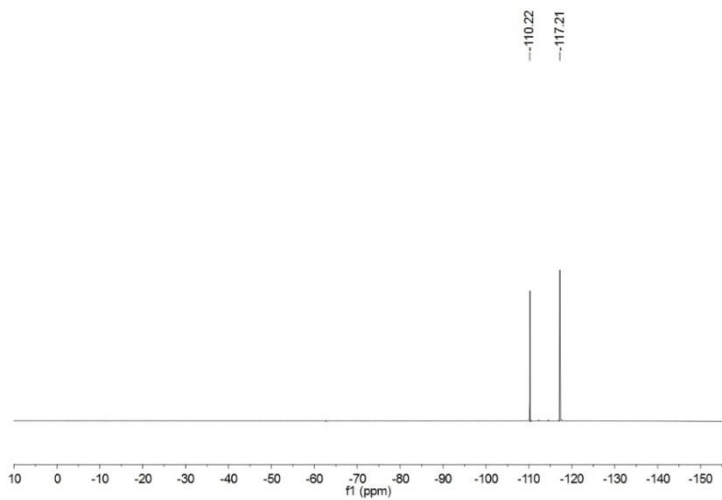
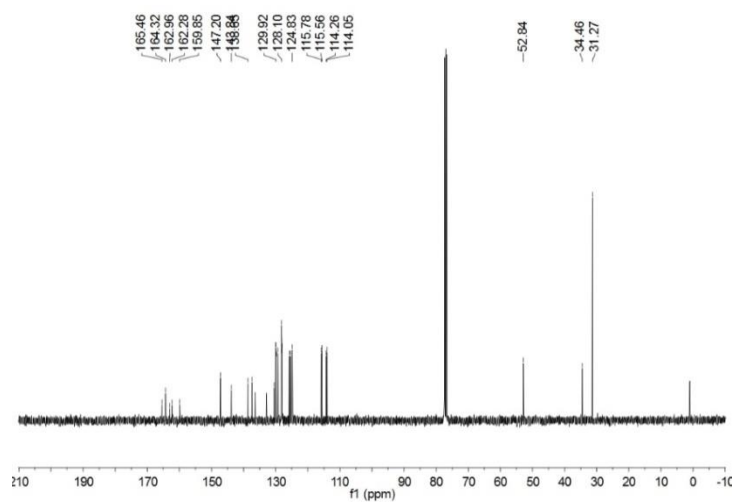
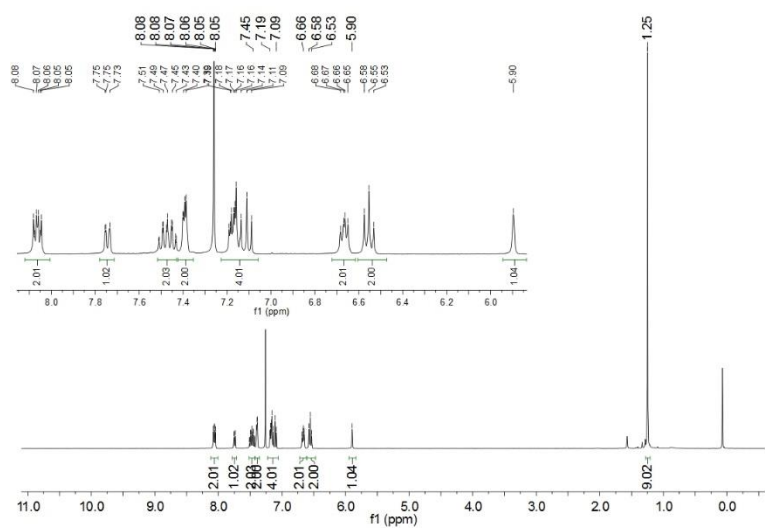
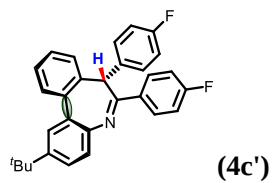


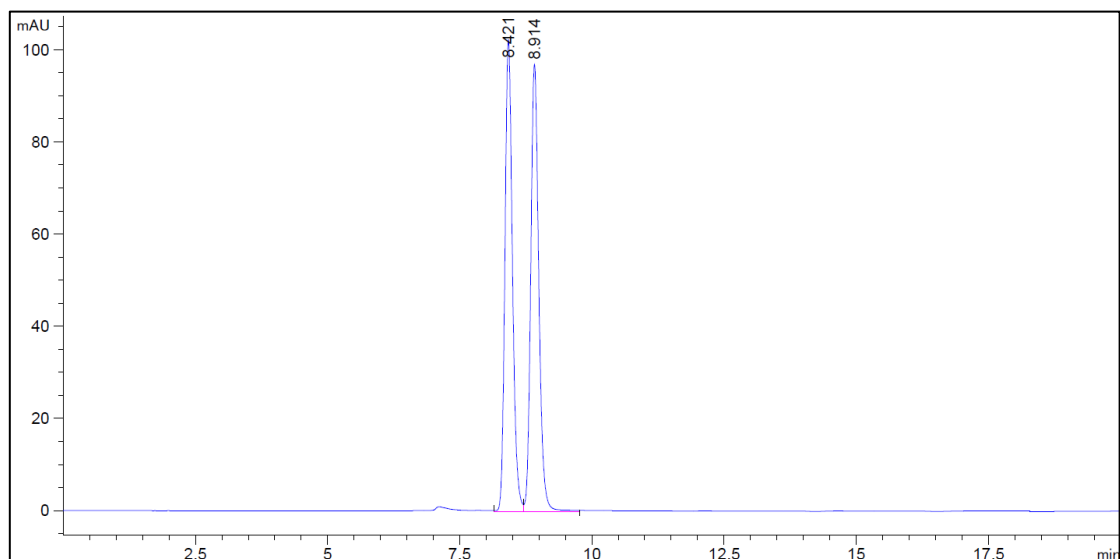


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.239	VV	0.3351	565.20880	25.80225	50.8124
2	12.496	VV	0.3521	547.13477	23.89867	49.1876

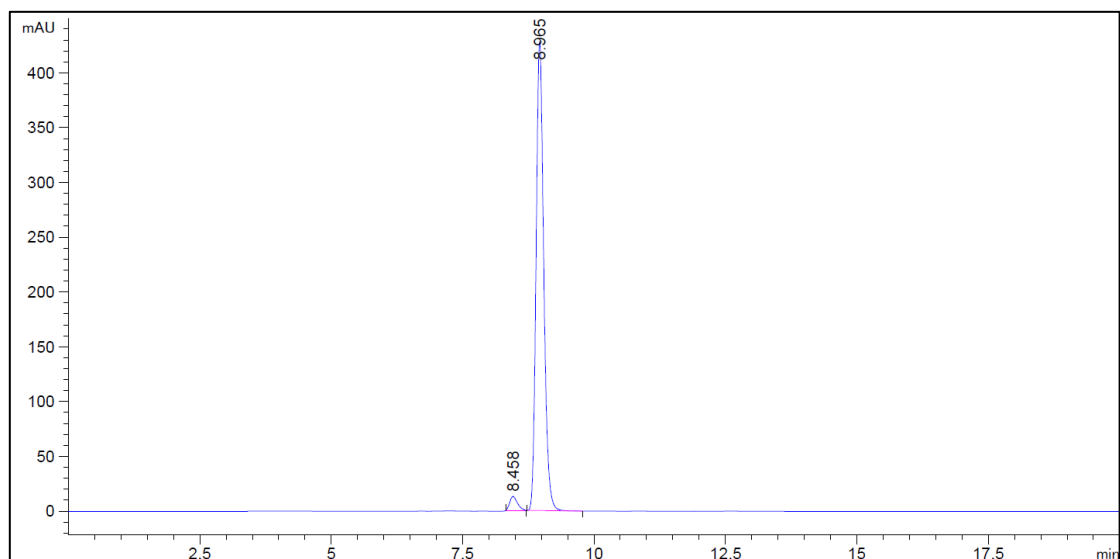


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.196	VBA	0.3256	1822.82947	85.89575	97.6566
2	12.460	BBA	0.2924	43.74052	2.10917	2.3434

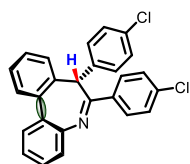




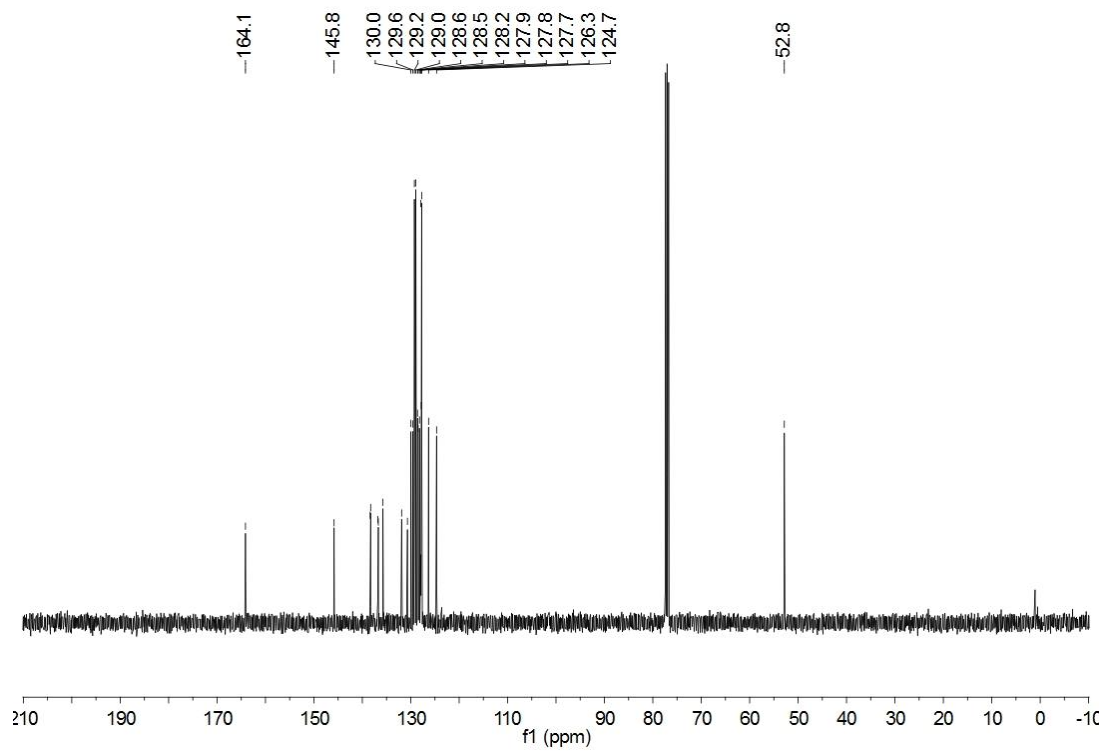
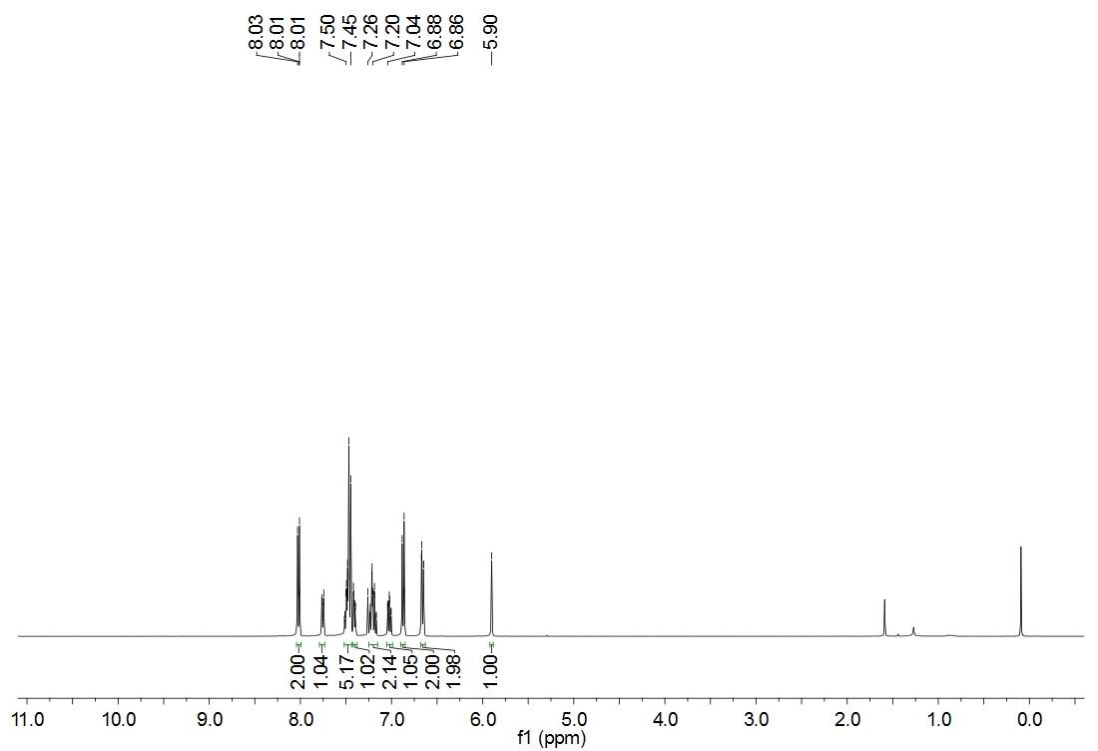
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.421	VV	0.1513	1011.26593	102.34654	49.6434
2	8.914	VV	0.1624	1025.79504	96.97514	50.3566

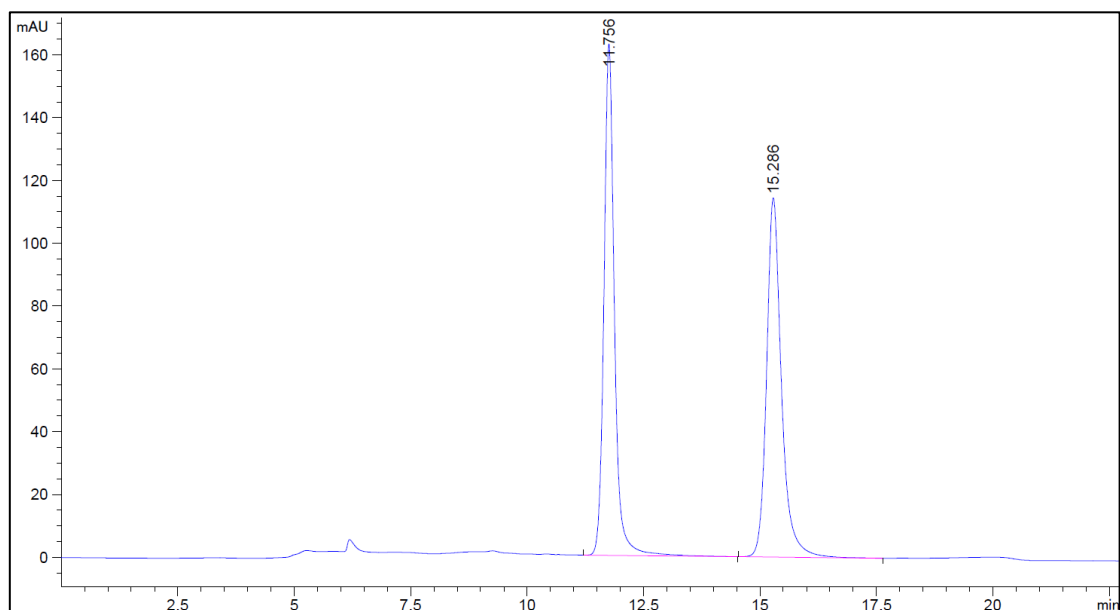


#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.458	BBA	0.1555	125.90249	12.50379	2.8299
2	8.965	BBA	0.1549	4323.13281	427.74899	97.1701

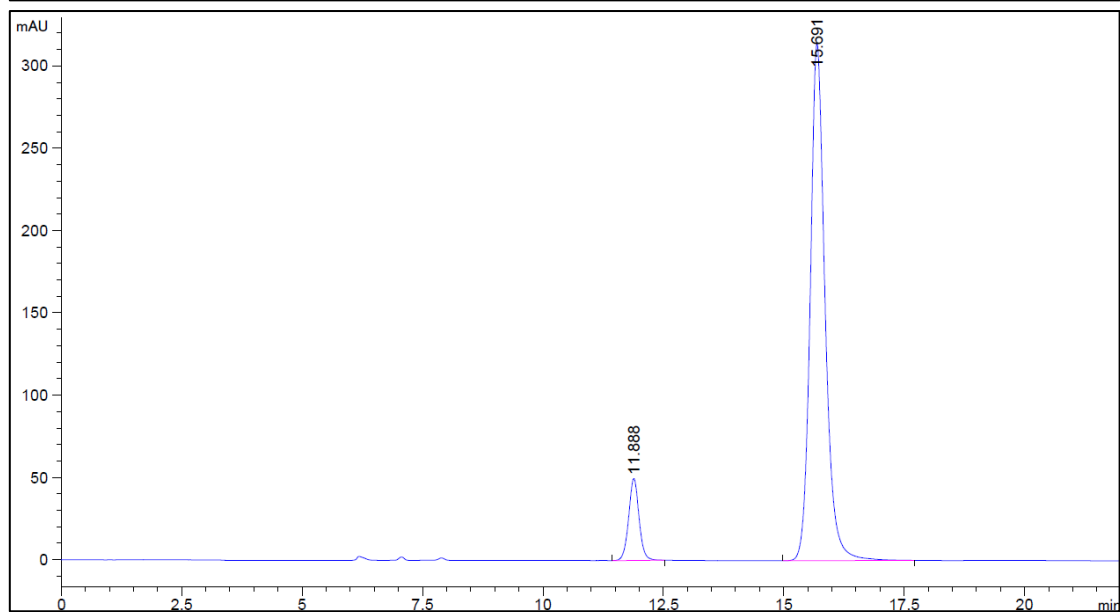


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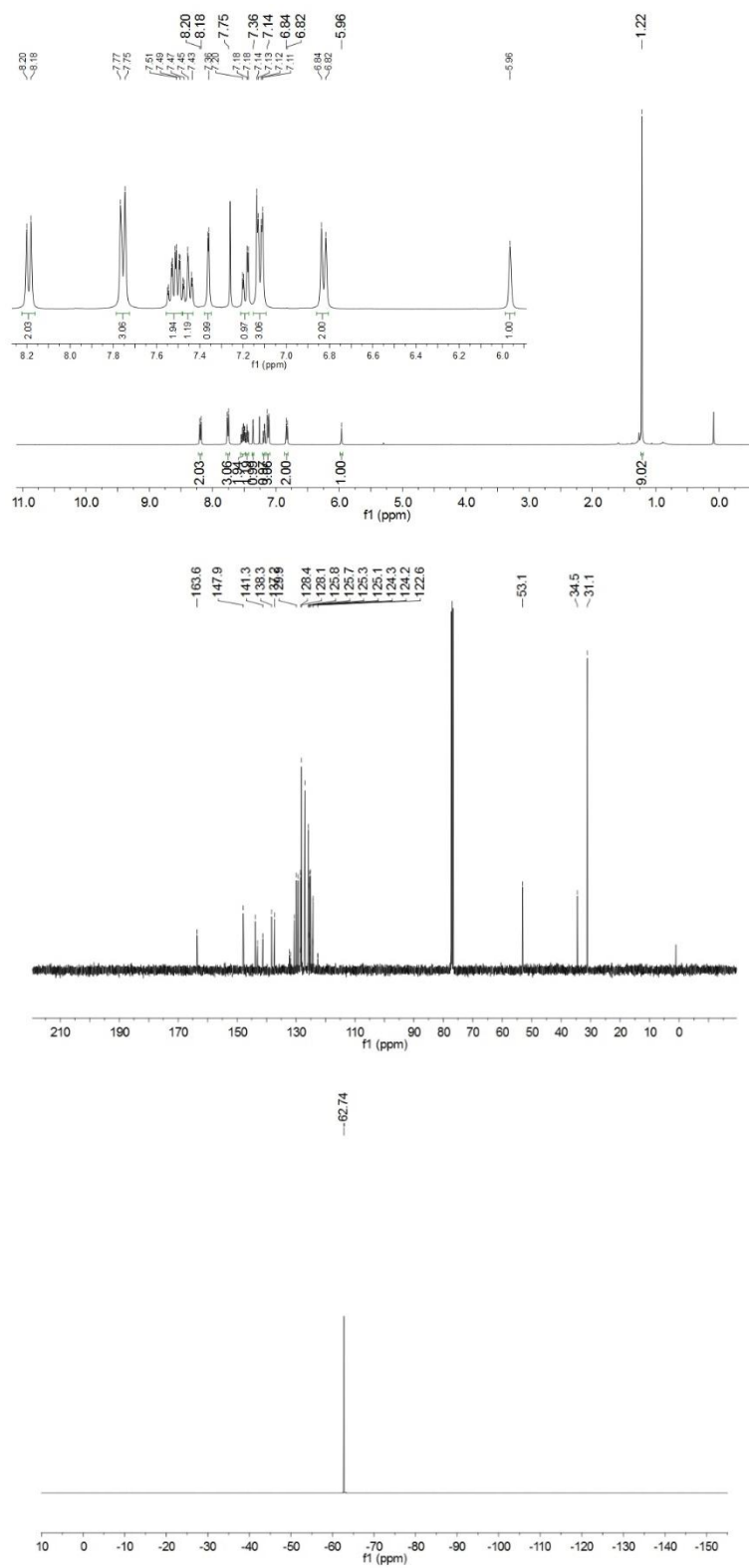
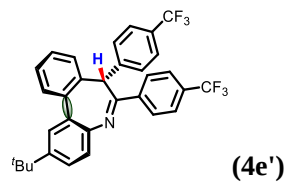


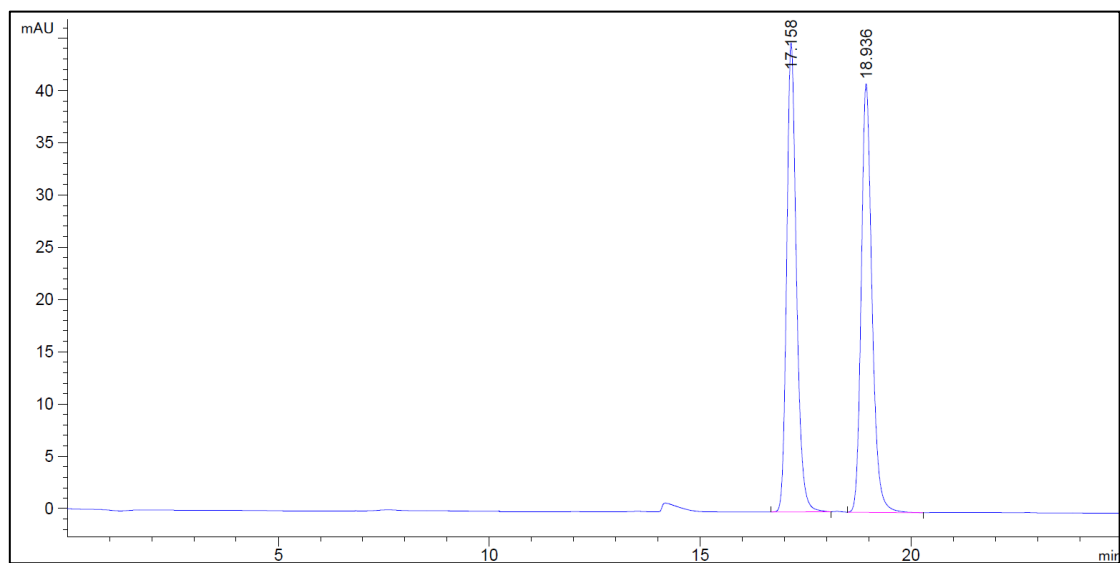


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.756	BB	0.2345	2547.20215	162.87585	50.0772
2	15.286	BB	0.3309	2539.34644	114.41748	49.9228

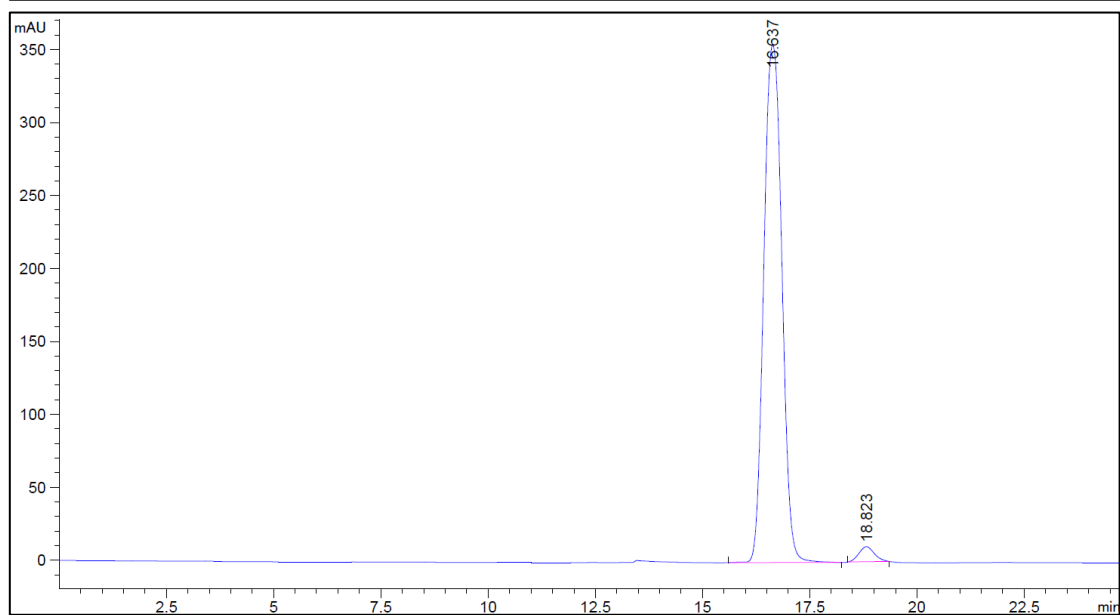


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.888	BBA	0.2287	744.00757	49.68361	9.9764
2	15.691	BBA	0.3184	6713.68652	314.00278	90.0236

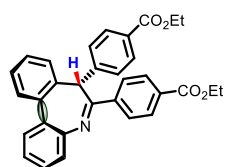




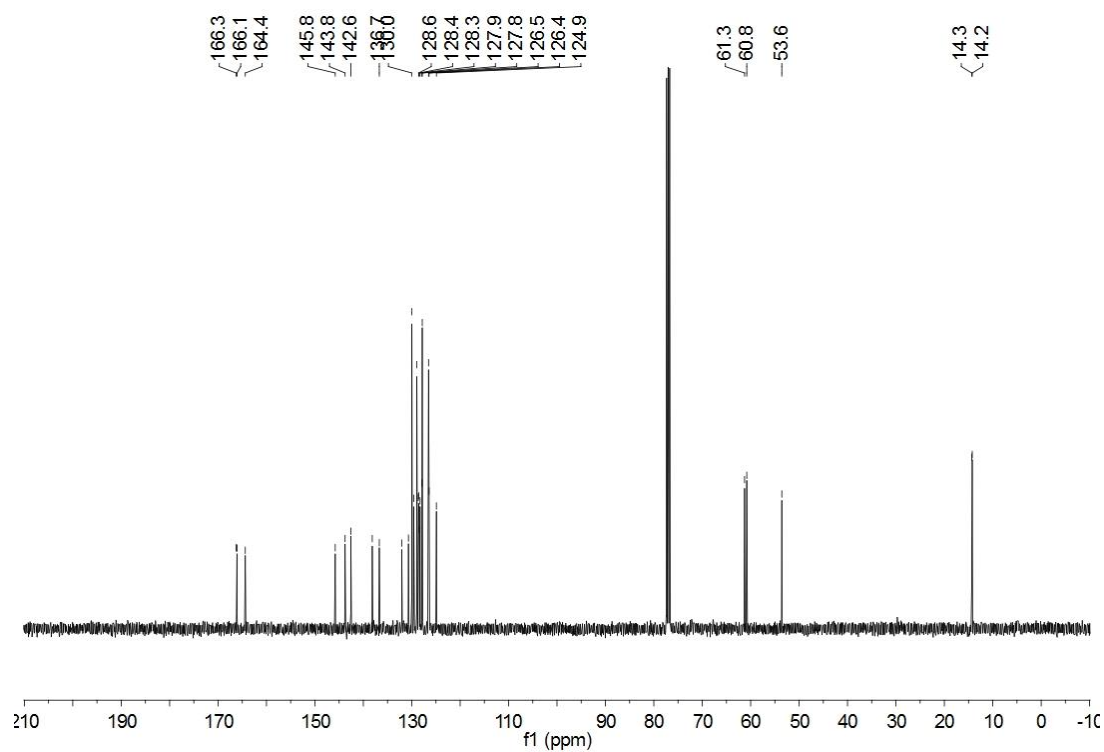
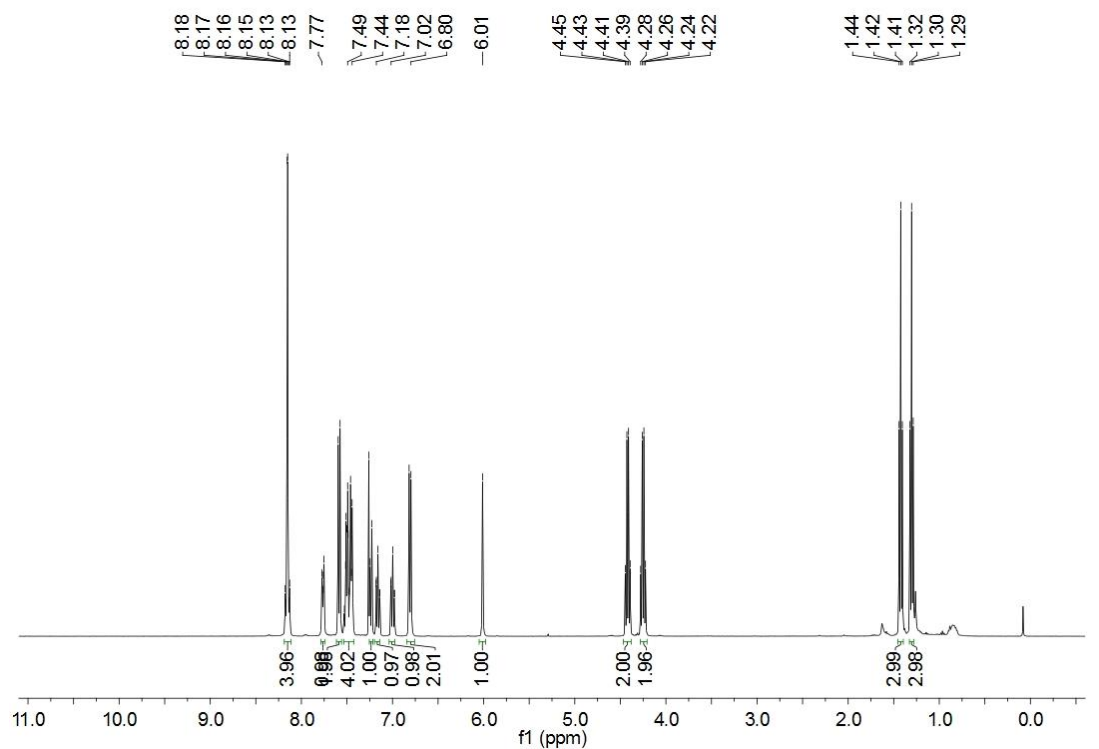
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.158	BB	0.2429	719.04529	44.87556	49.8099
2	18.936	BB	0.2683	724.53406	40.98320	50.1901

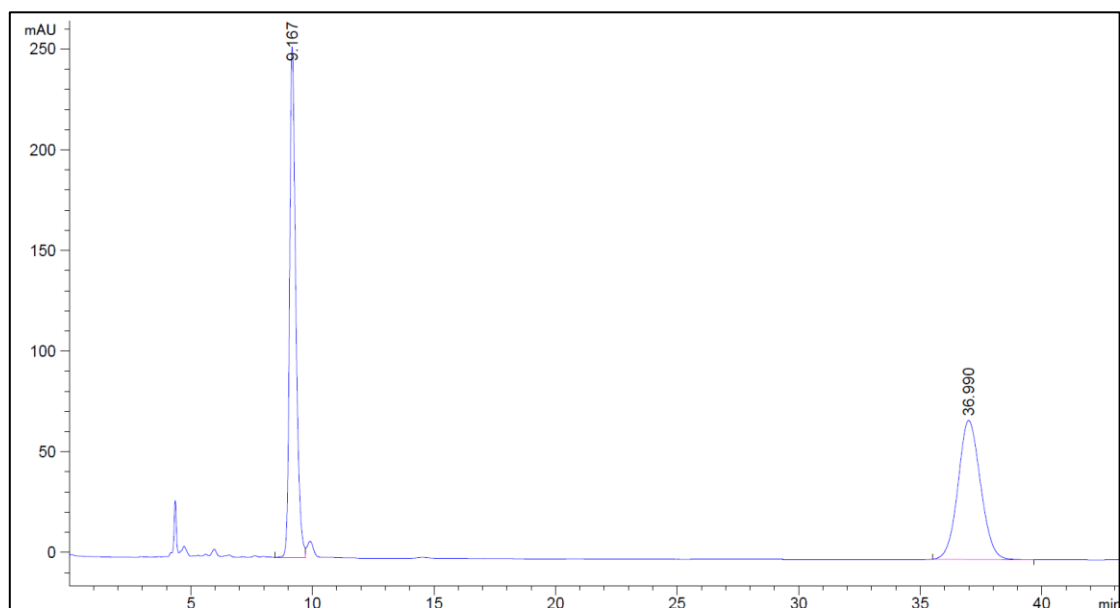


#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.637	BBA	0.4676	1.03591e4	354.80176	97.5593
2	18.823	BBA	0.3848	259.15976	10.36248	2.4407

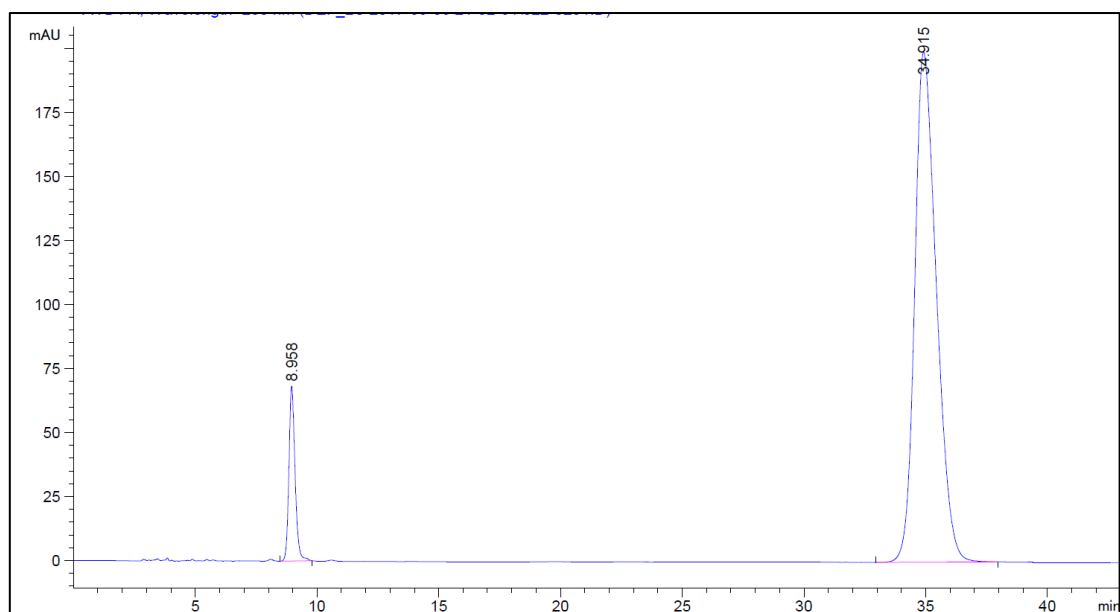


(4f')

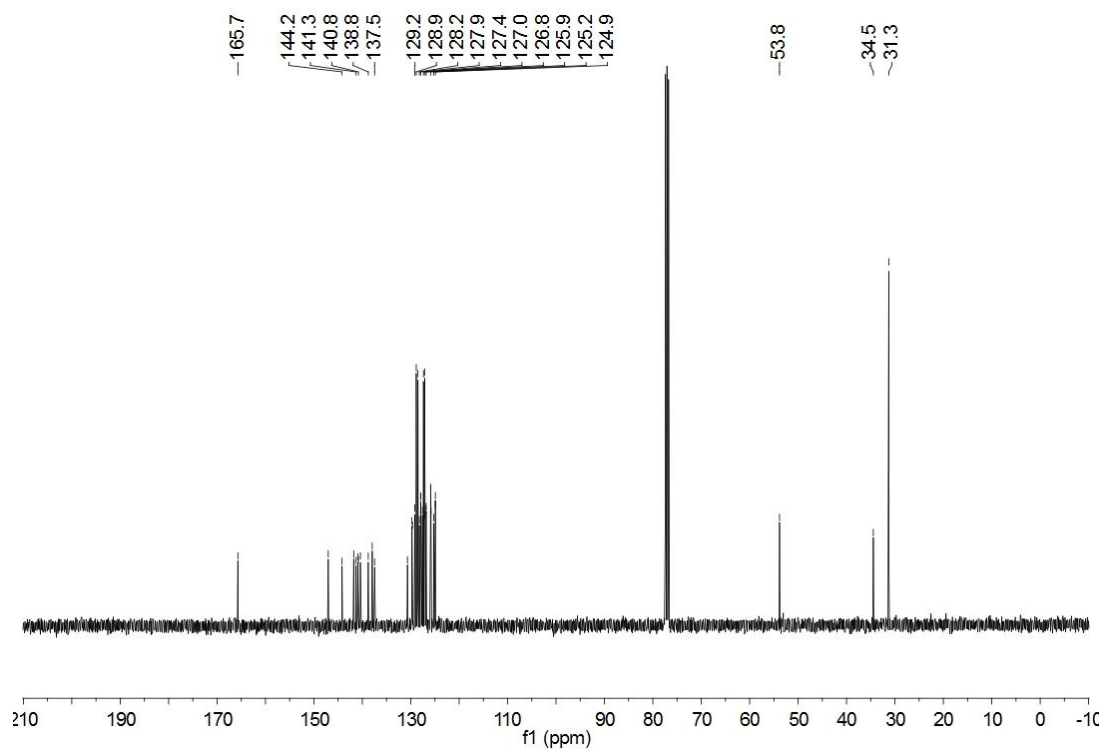
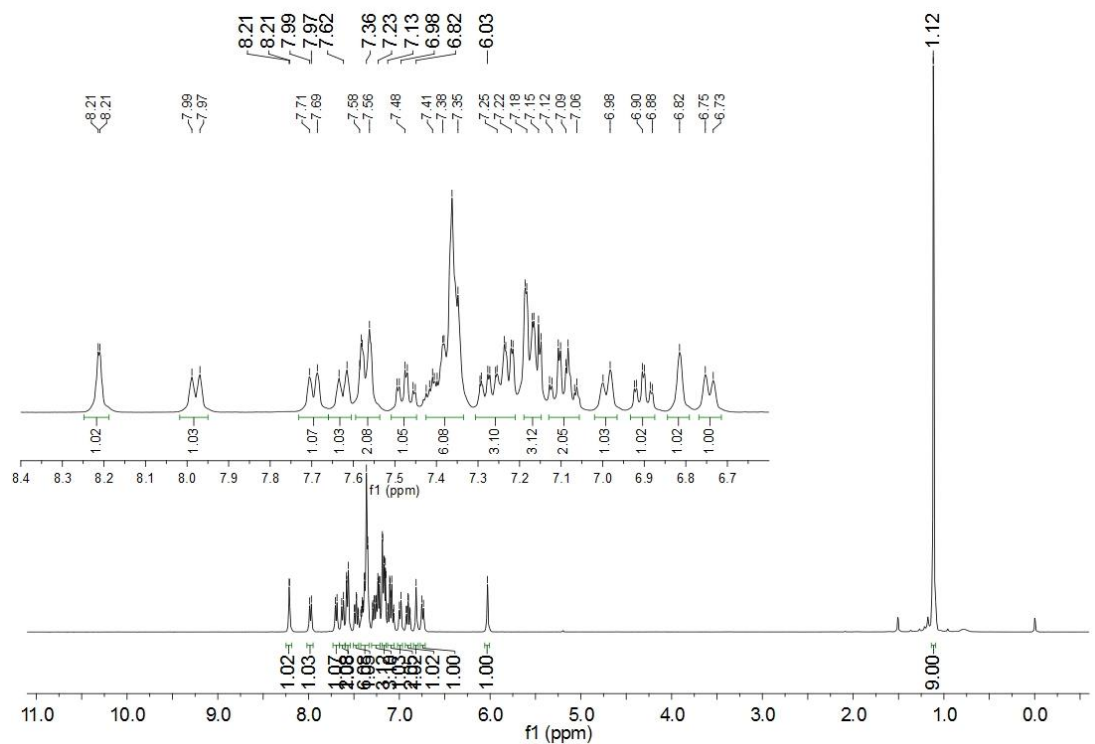
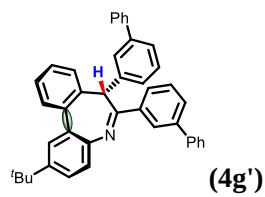


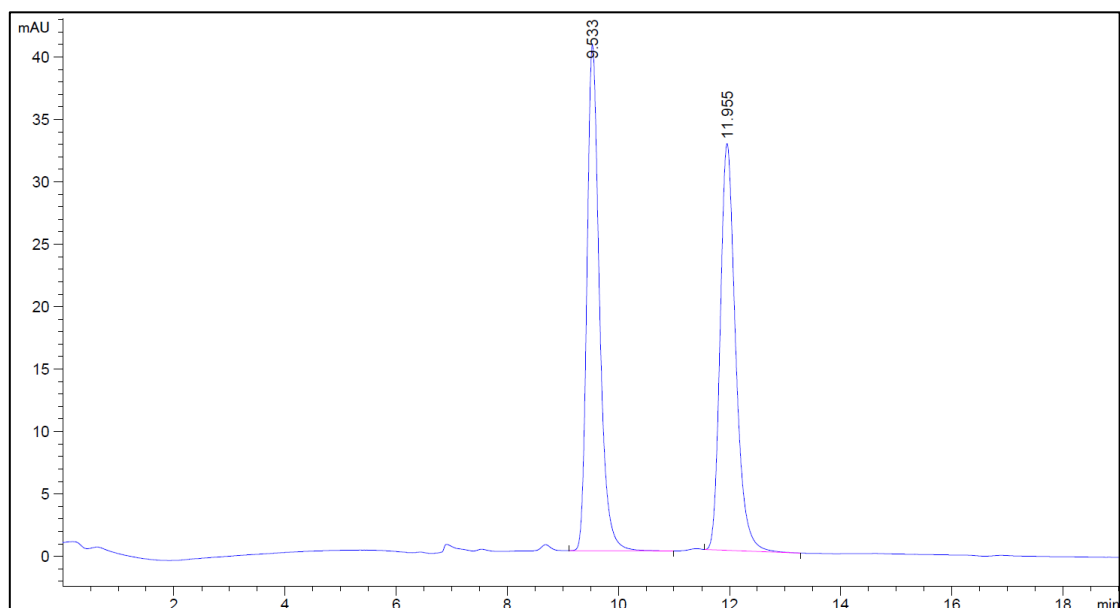


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.167	BV	0.2660	4502.98730	253.77095	50.3357
2	36.990	BV	0.9630	4442.92480	69.01980	49.6643

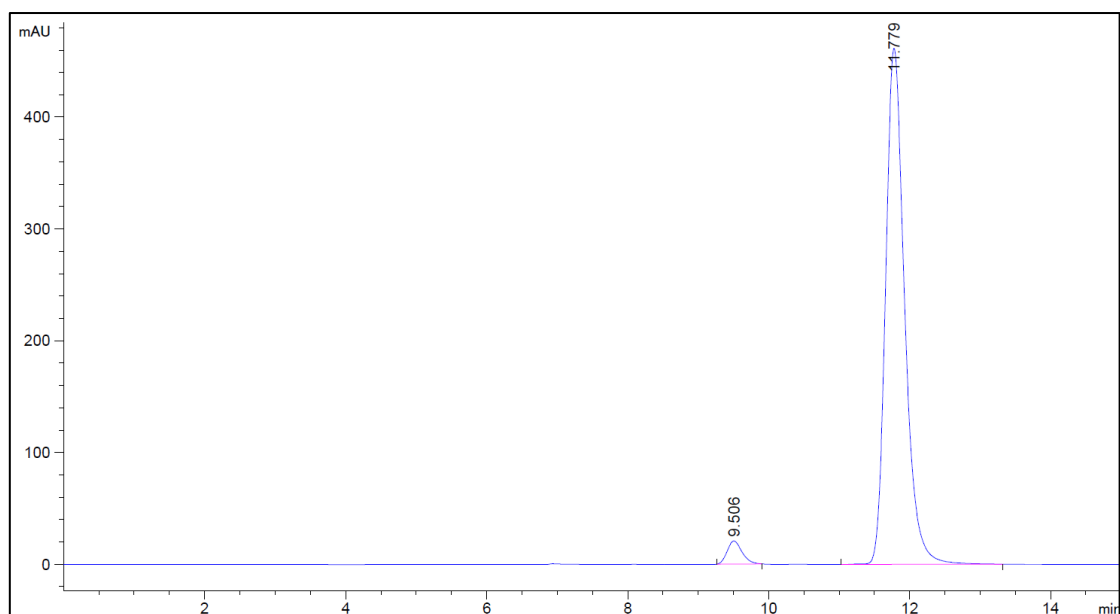


#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.958	BBA	0.2650	1195.07861	68.35365	8.8275
2	34.915	BBA	0.9458	1.23431e4	199.22371	91.1725

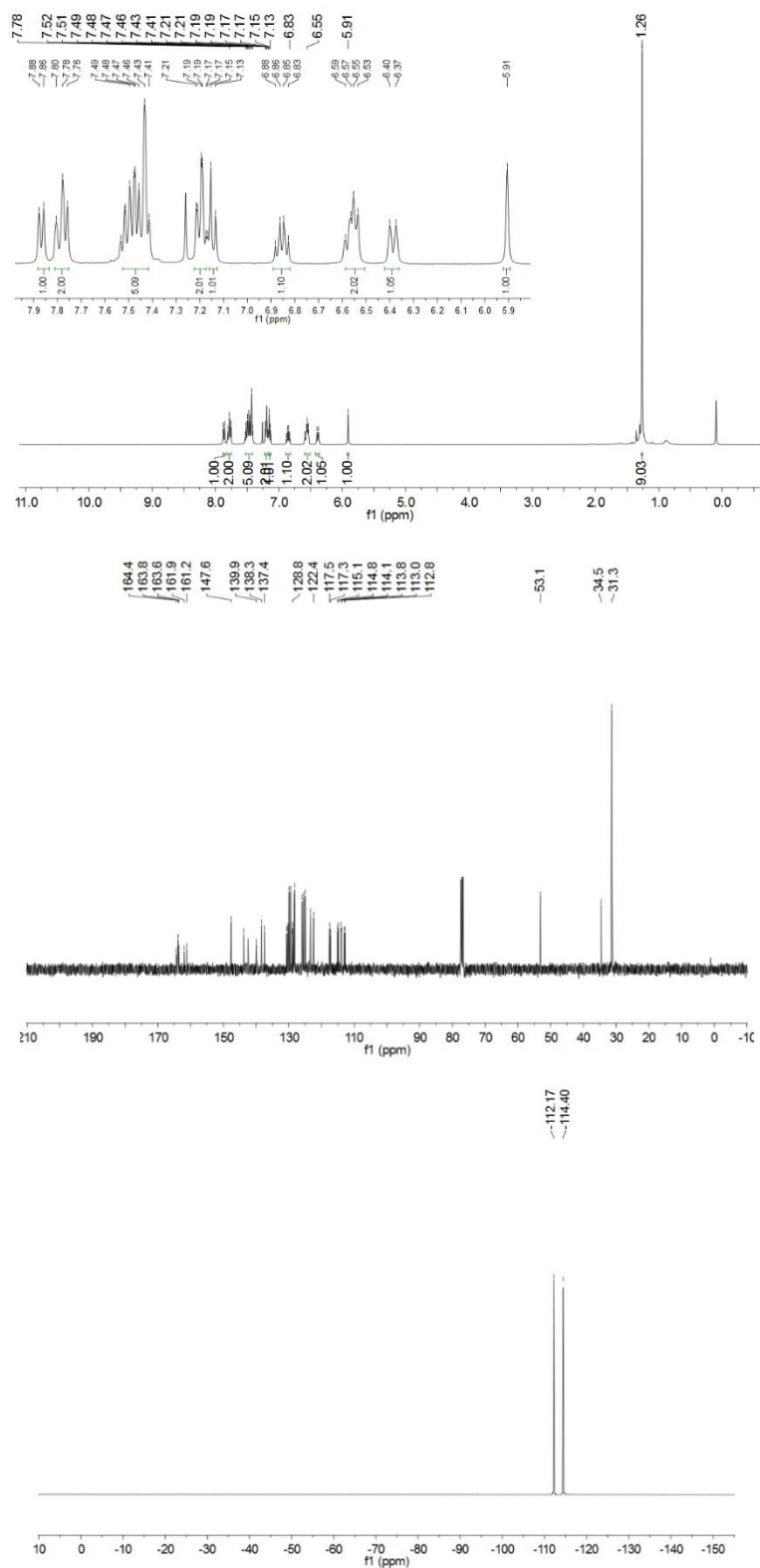
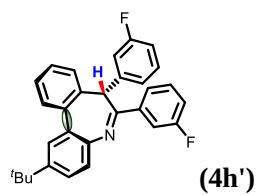


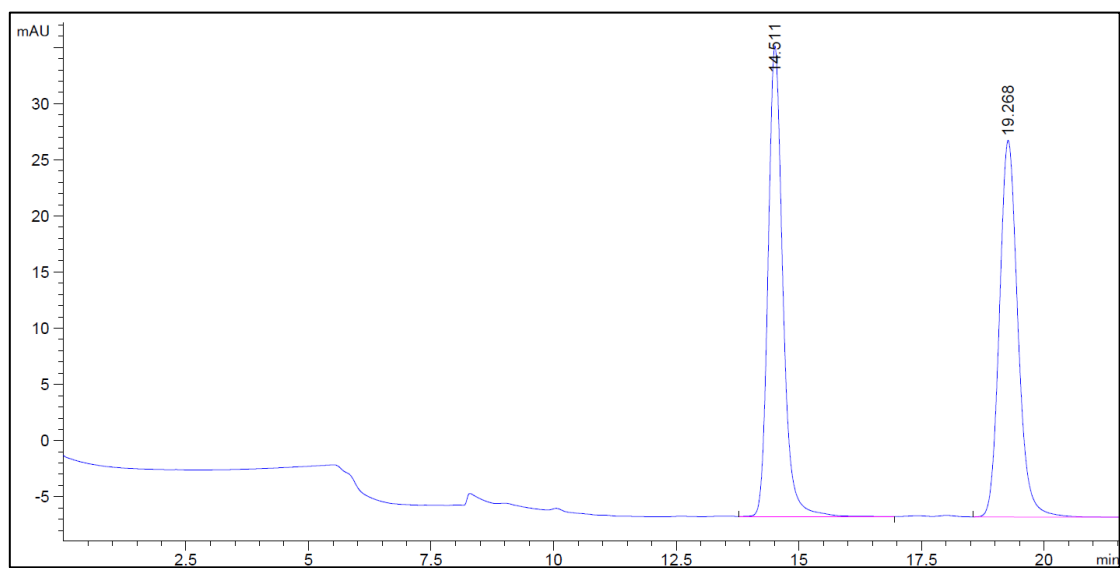


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.533	BB	0.2384	633.50085	40.52577	50.3211
2	11.955	BB	0.2940	625.41541	32.57364	49.6789

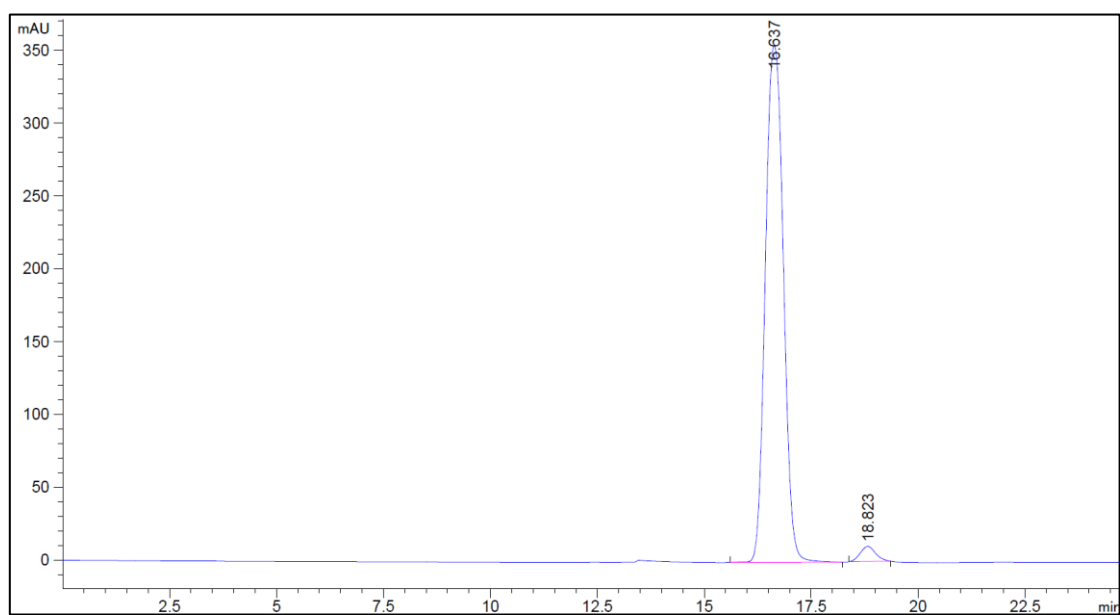


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.506	BBA	0.2254	300.88522	20.60564	3.3754
2	11.779	BB	0.2847	8613.16504	461.61801	96.6246

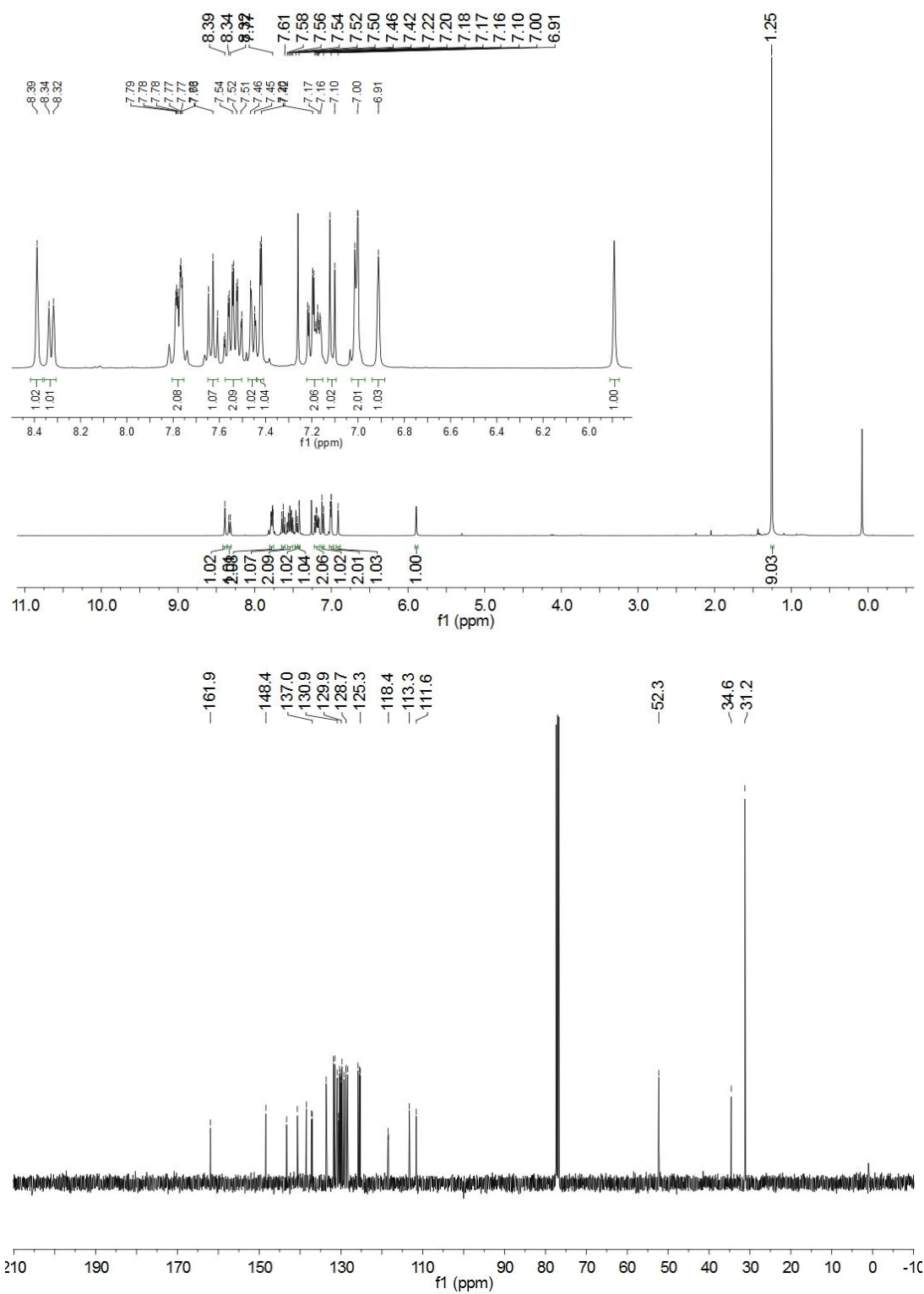
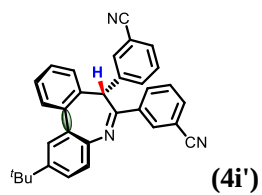


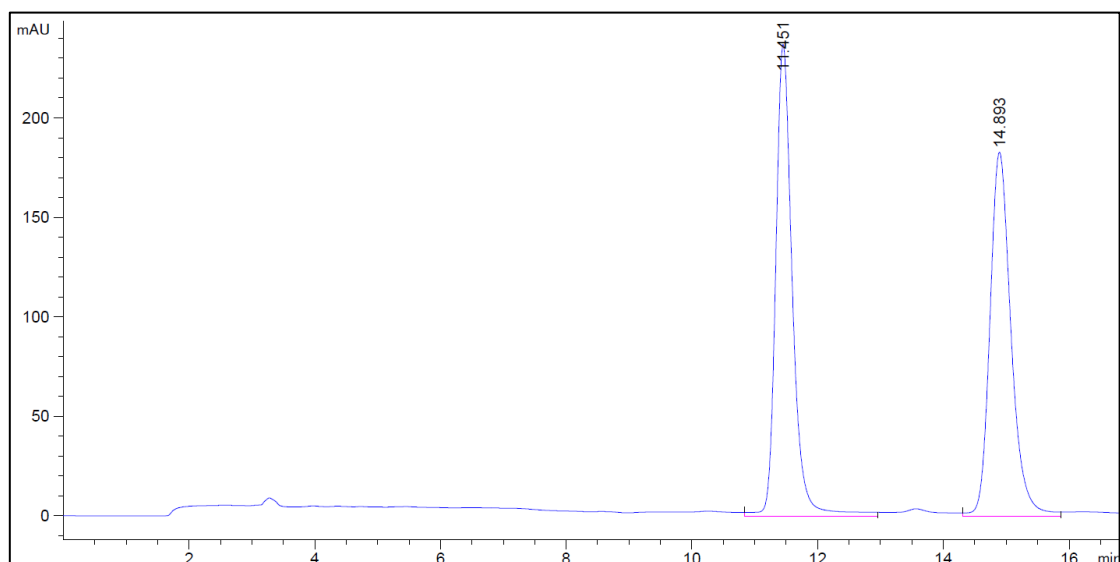


#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.511	VV	0.3210	879.59326	41.88810	50.0953
2	19.268	BBA	0.4009	876.24554	33.52683	49.9047

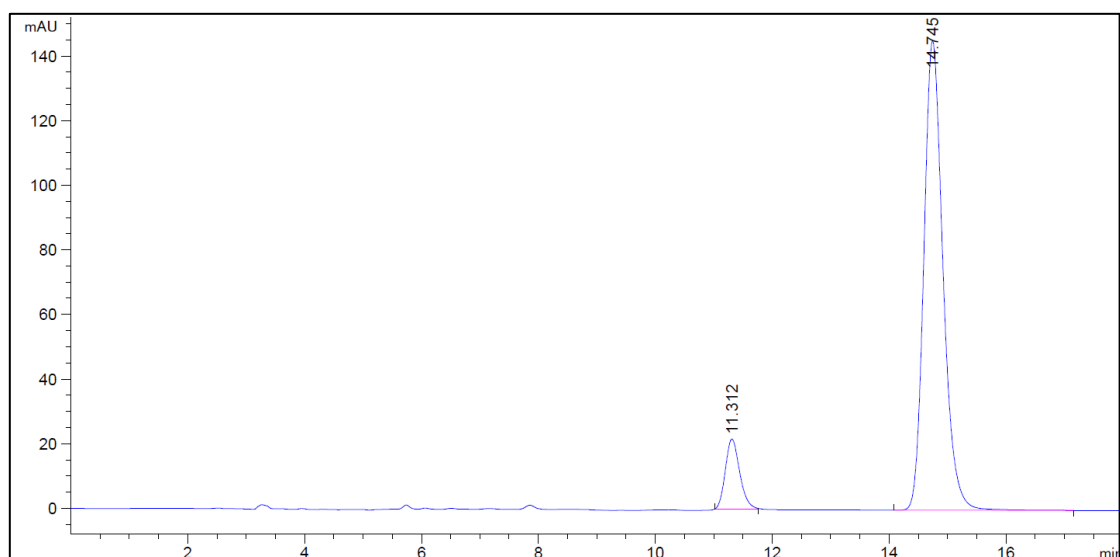


#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.772	BV	0.2191	28.26594	1.57745	4.8141
2	19.492	VV	0.3994	558.88184	21.42288	95.1859

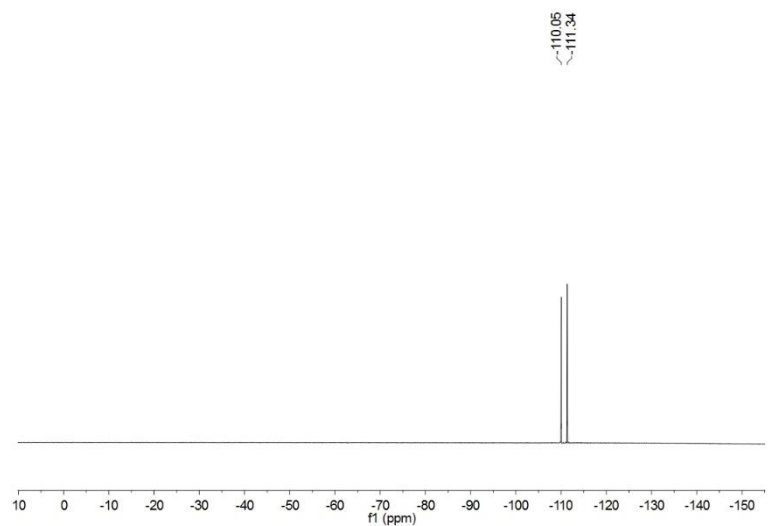
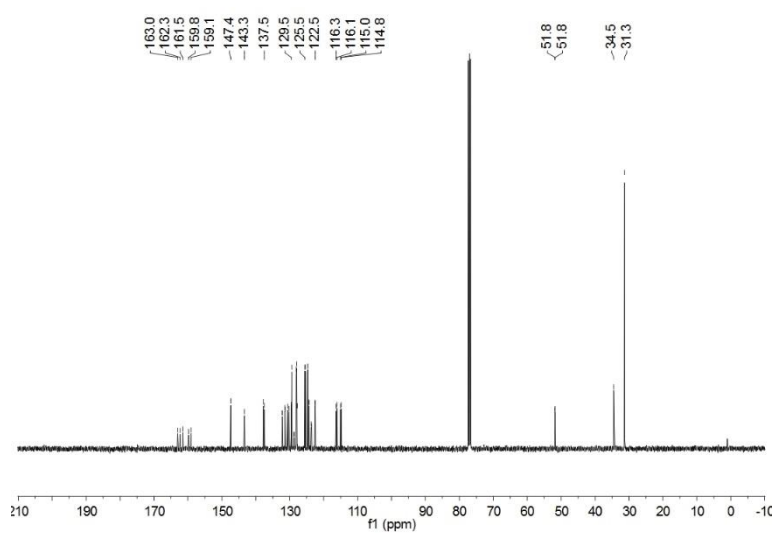
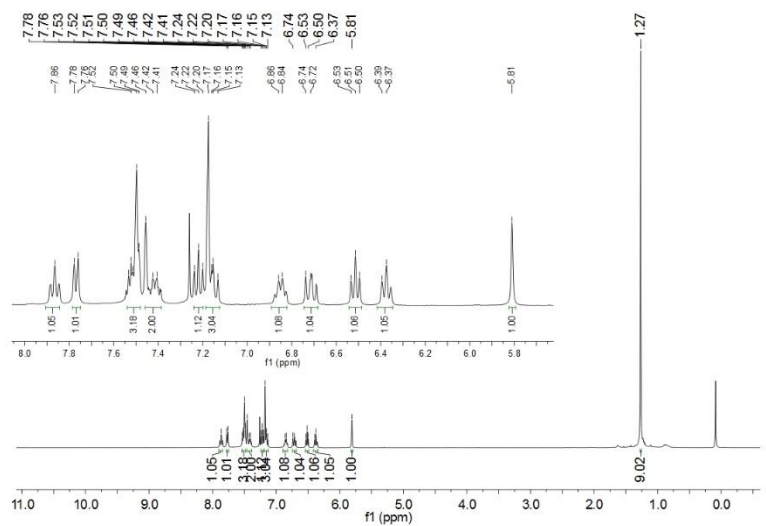
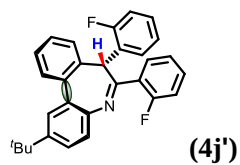


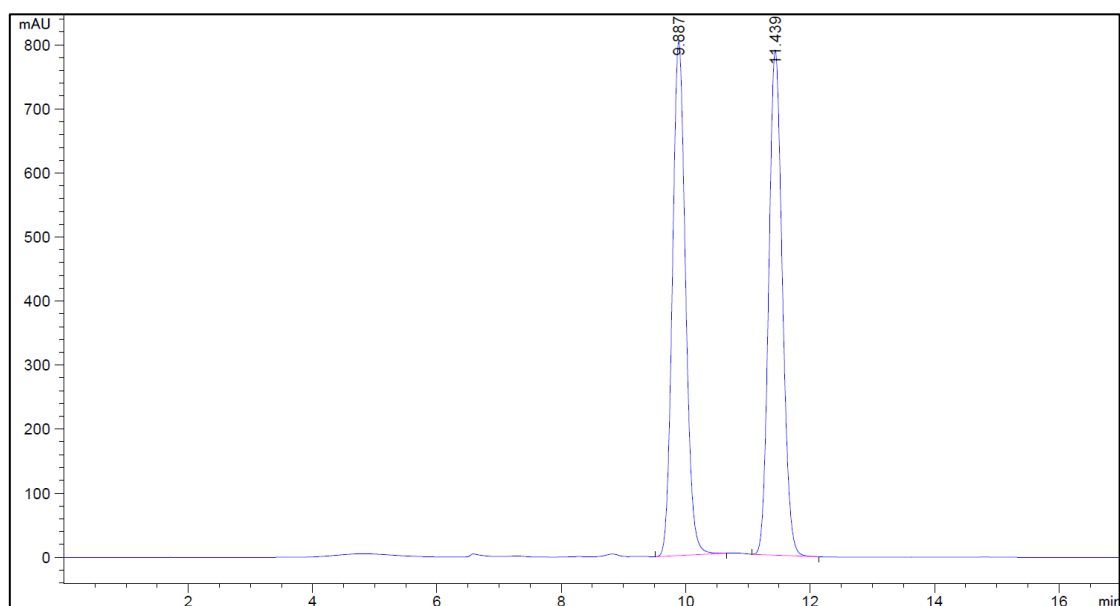


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.451	VV	0.2795	4379.94043	237.12959	50.6399
2	14.893	VV	0.3553	4269.24561	182.91077	49.3601

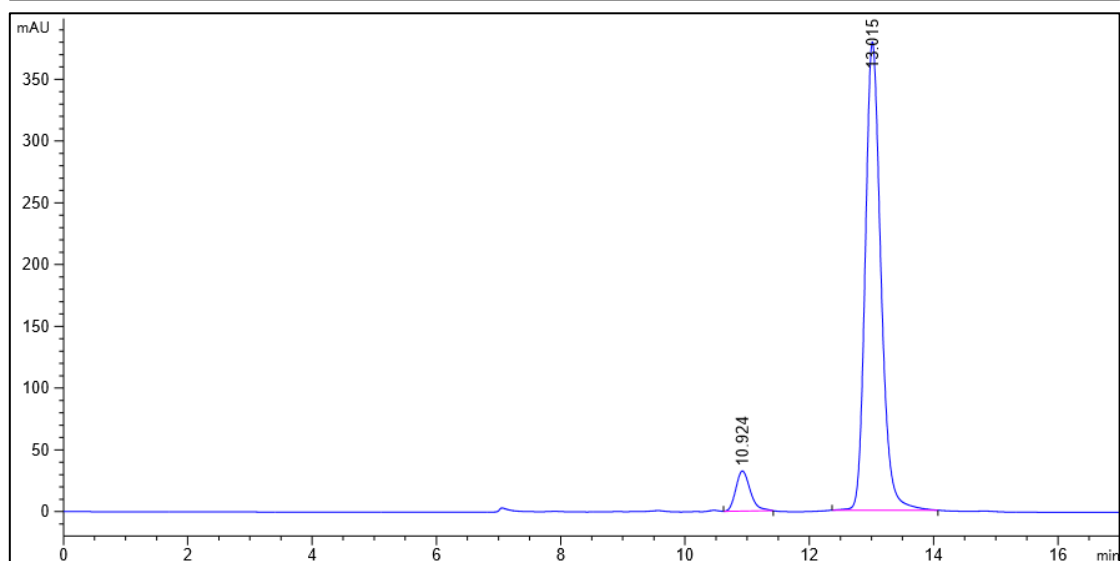


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.312	BBA	0.2618	369.37769	21.67614	10.0713
2	14.745	VV	0.3478	3298.23291	145.32513	89.9287

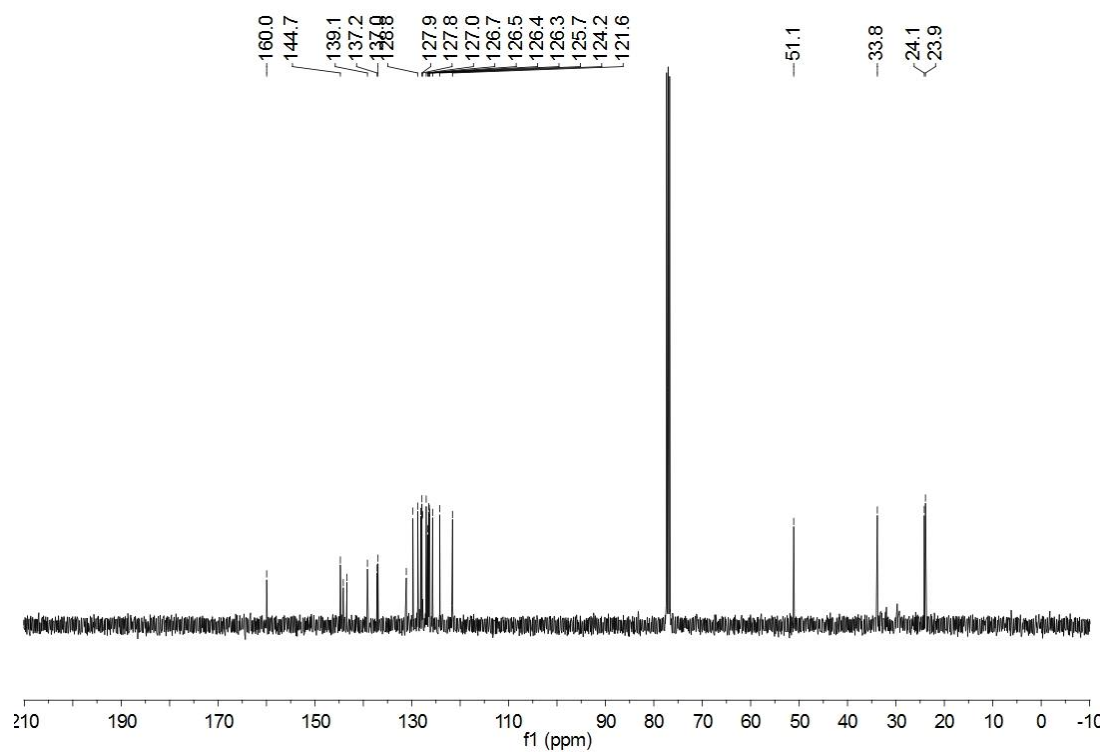
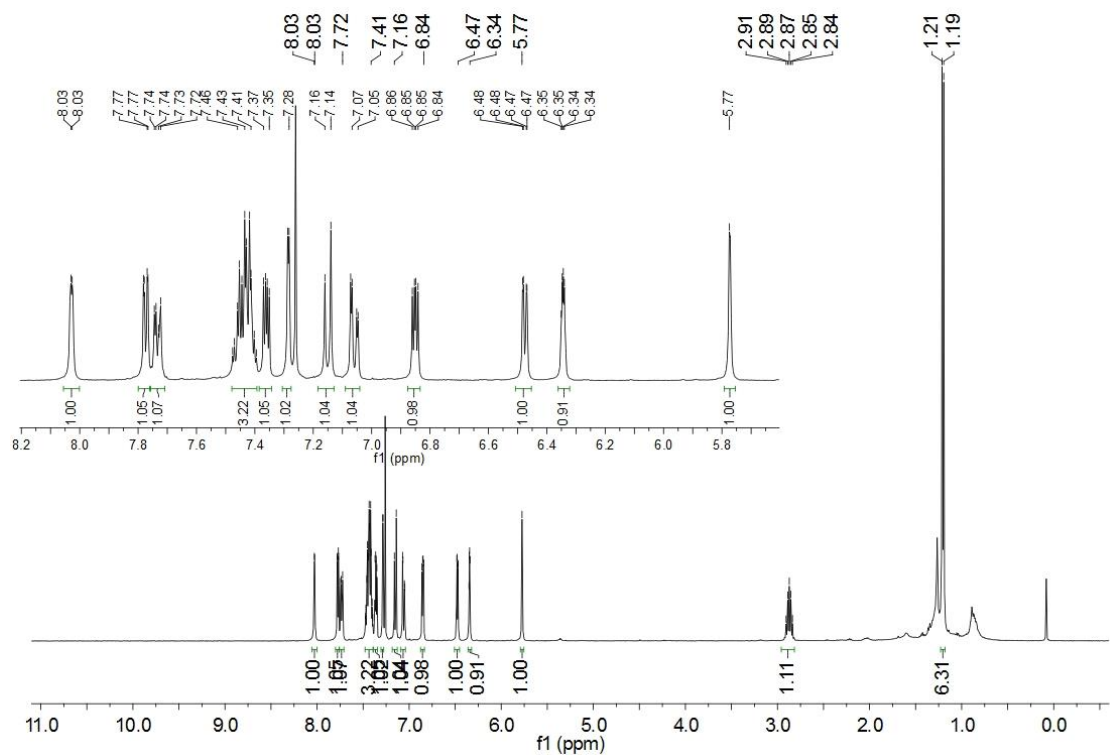
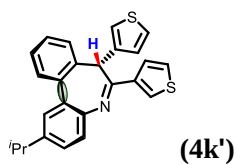


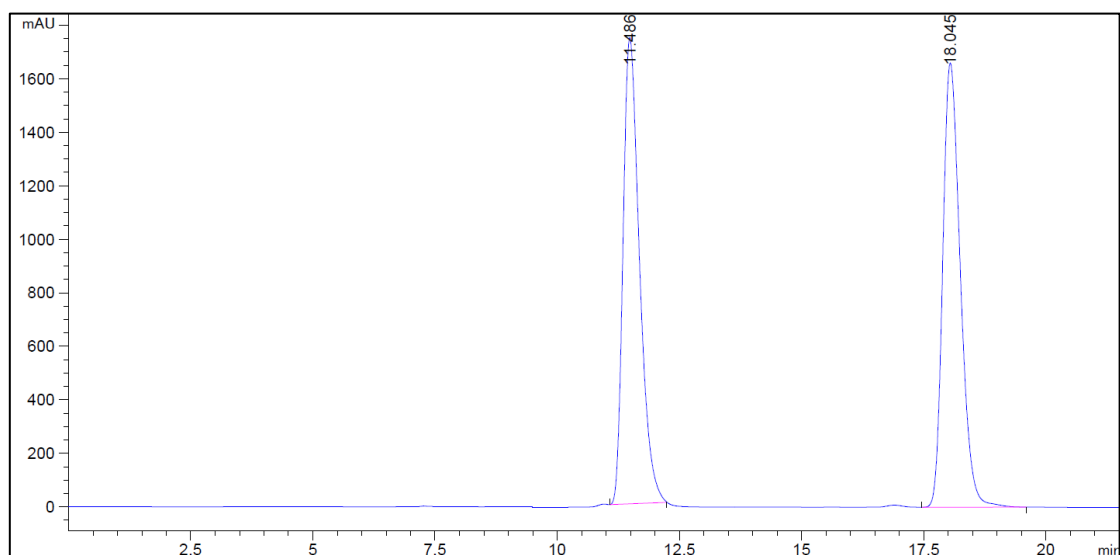


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.887	BB	0.2269	1.17660e4	802.99066	49.6733
2	11.439	BB	0.2353	1.19208e4	788.82898	50.3267

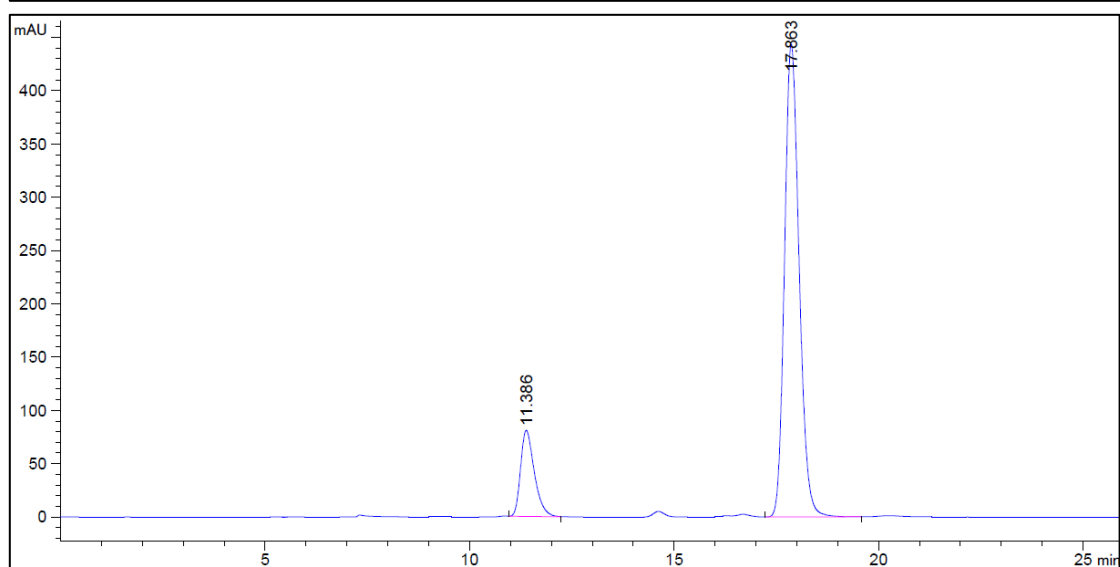


#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.924	BBA	0.2511	531.06781	32.59730	7.2811
2	13.015	BBA	0.2715	6762.72900	380.31223	92.7189

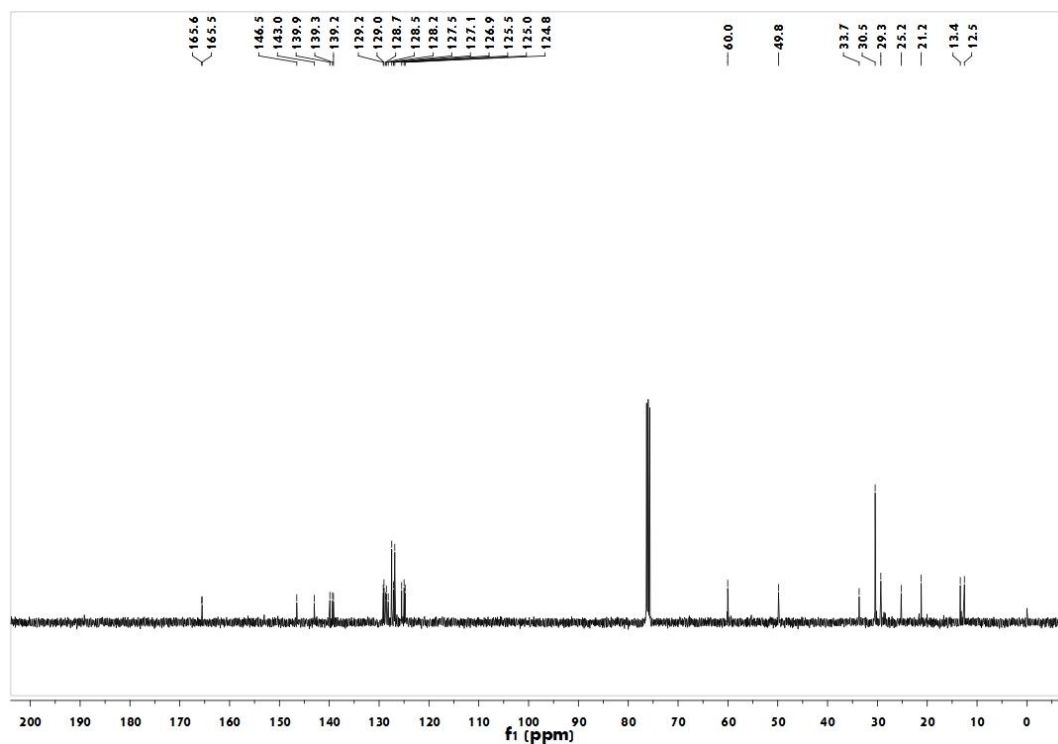
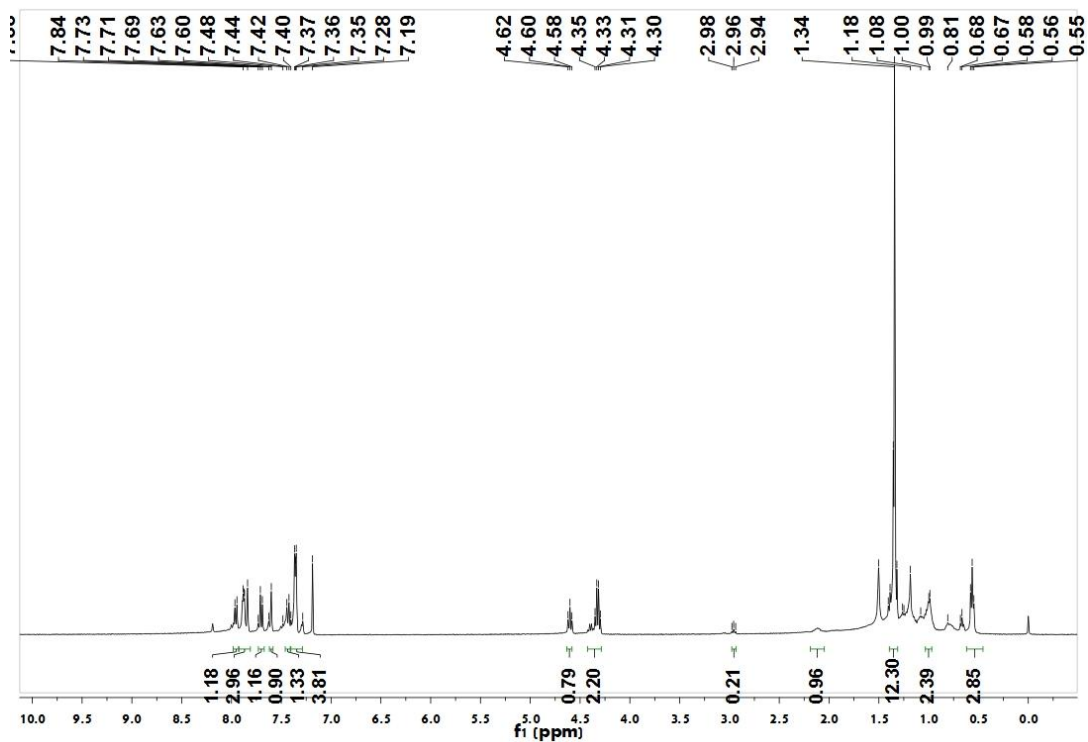
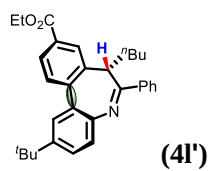


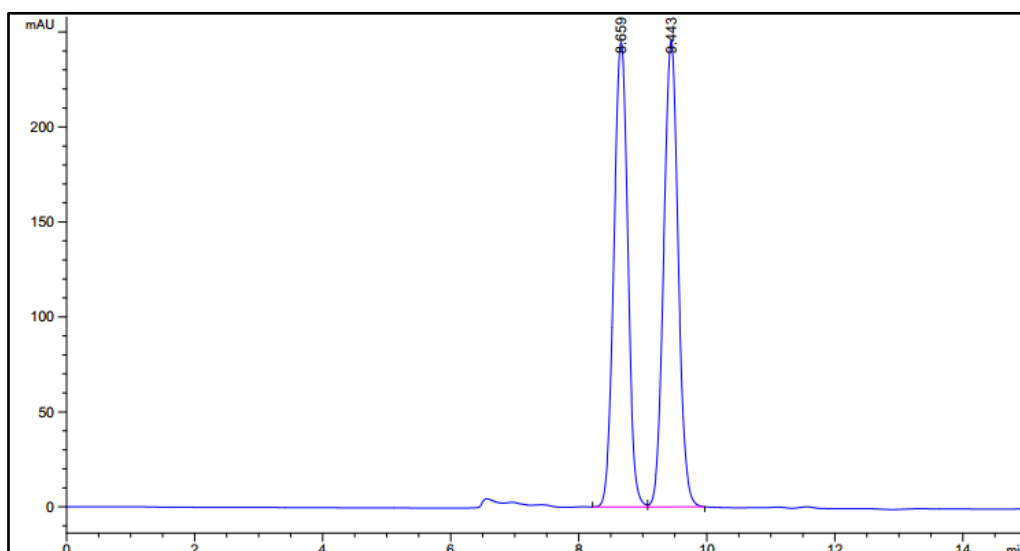


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.486	BBA	0.3565	4.06972e4	1742.07471	49.4689
2	18.045	BBA	0.3882	4.15710e4	1659.87964	50.5311

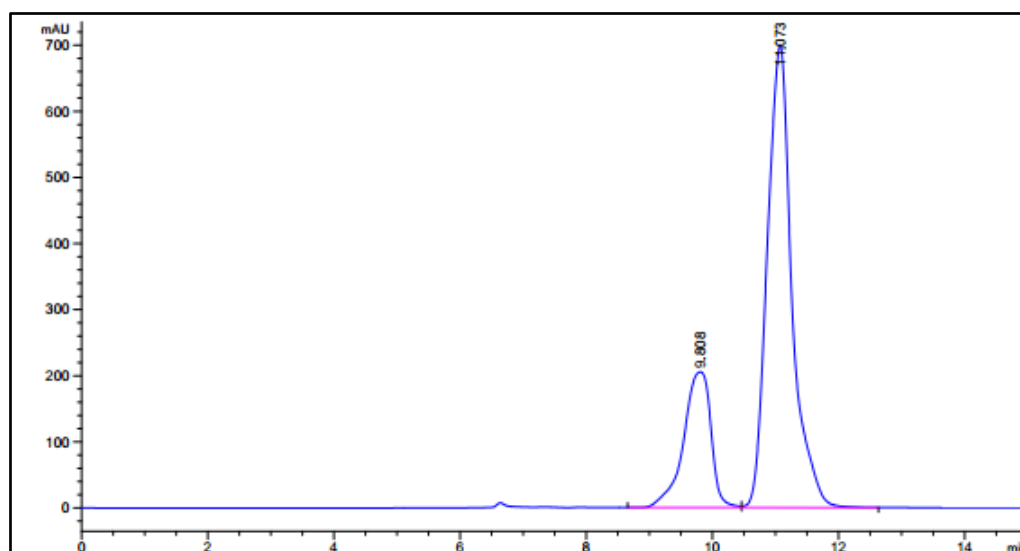


#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.386	BBA	0.3562	1883.48755	80.72688	14.6318
2	17.863	BBA	0.3851	1.09891e4	443.46741	85.3682

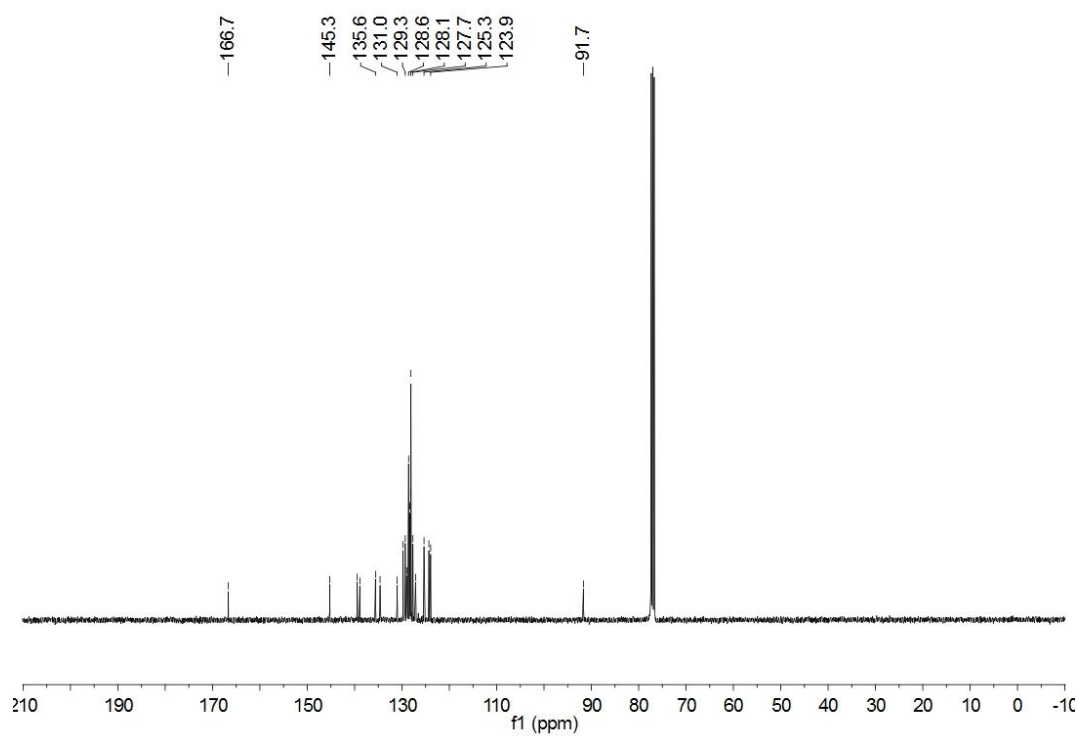
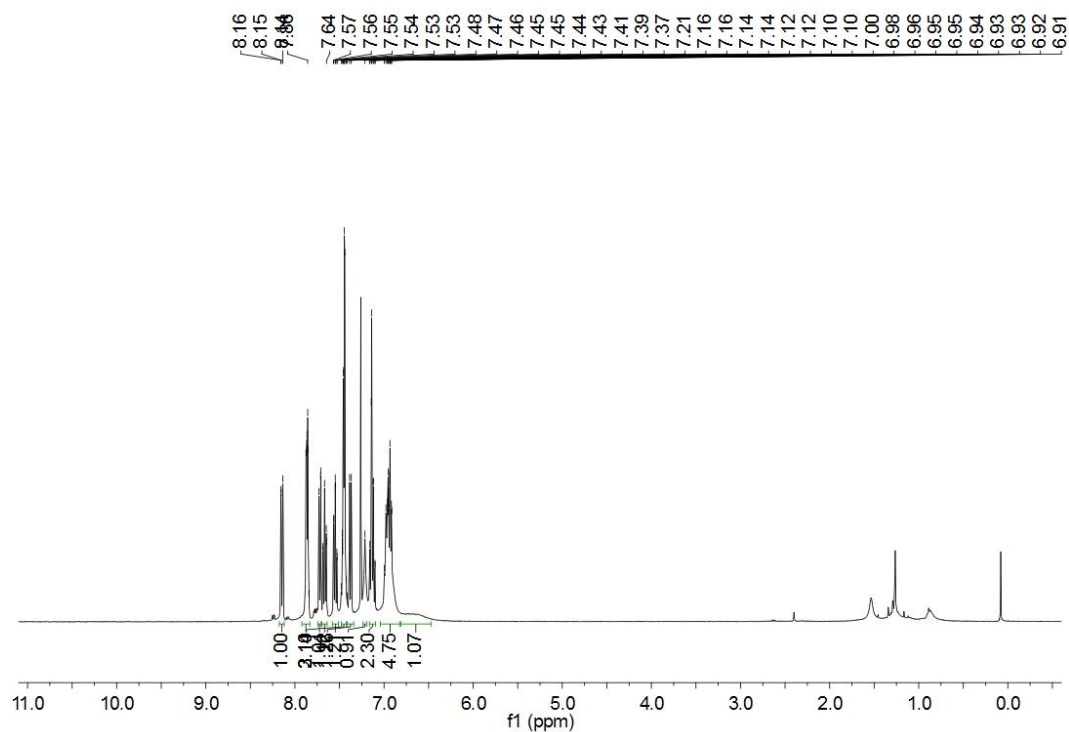
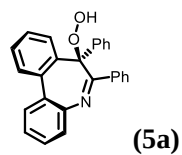


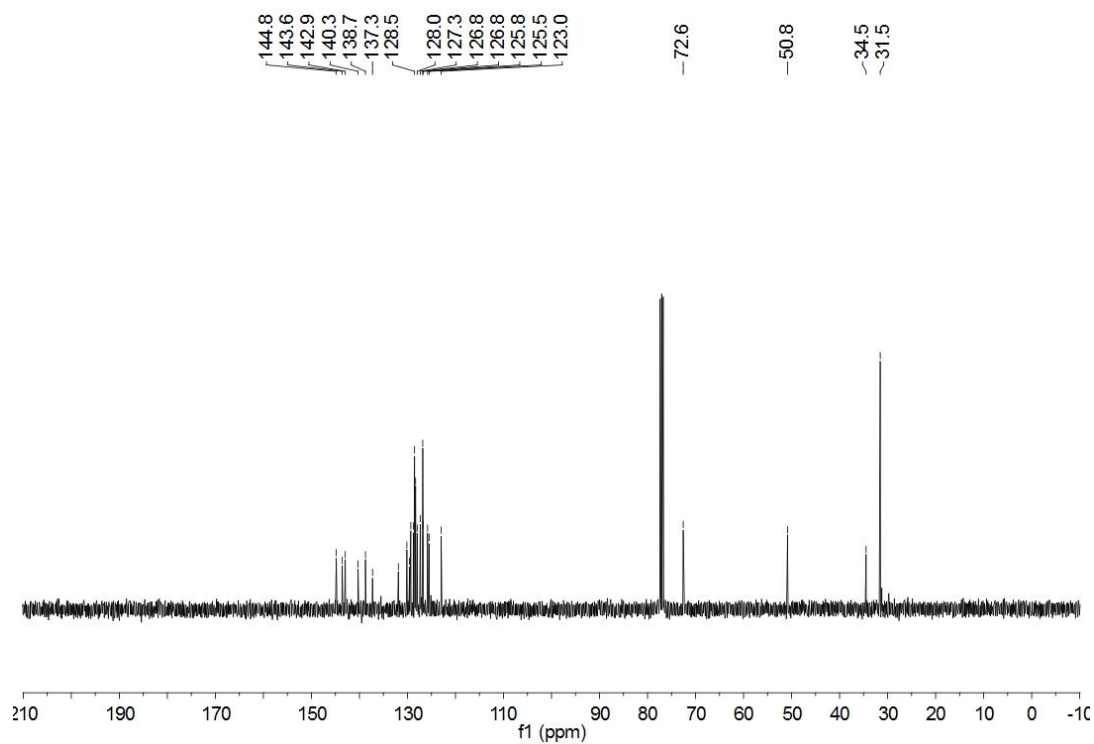
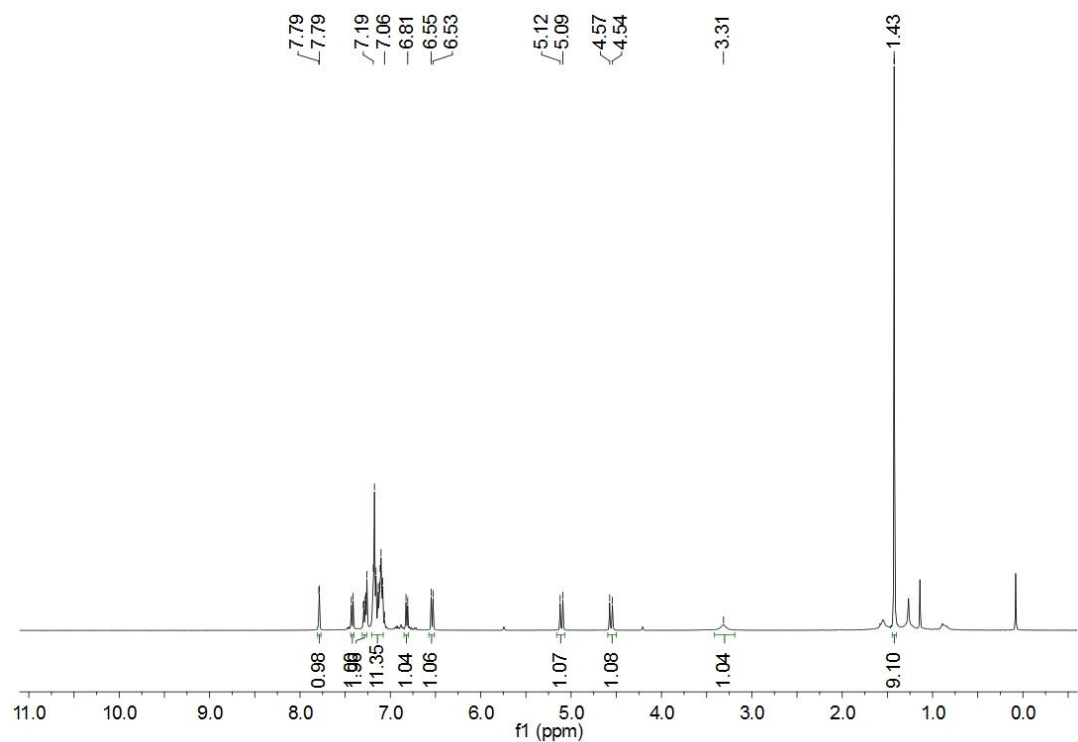
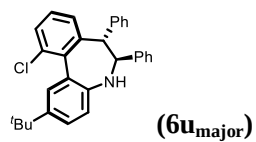


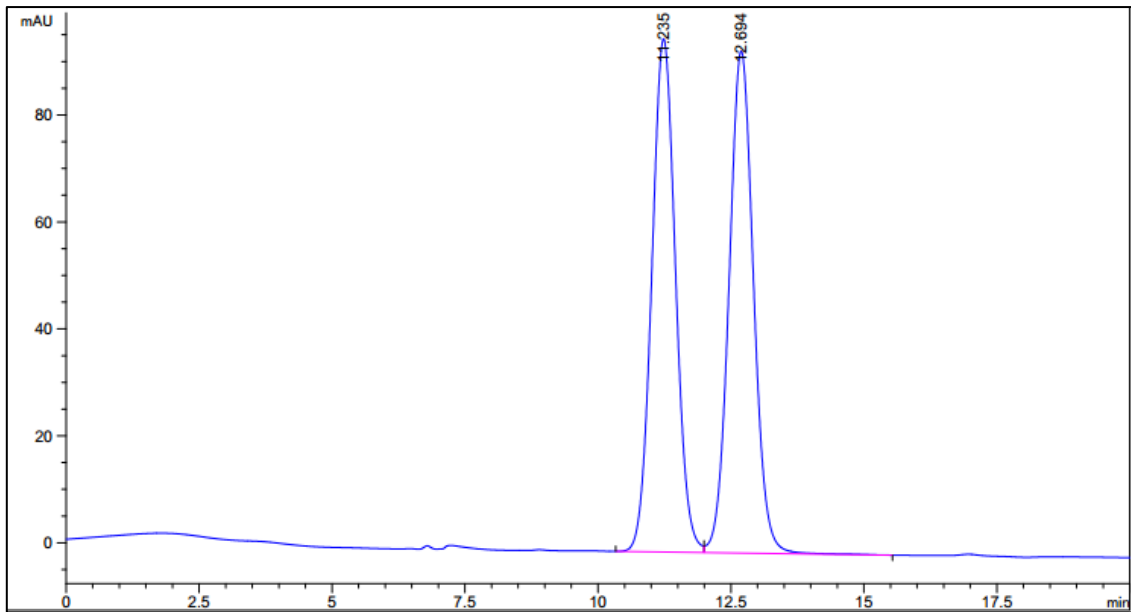
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.659	BV	0.2408	3707.14111	244.67029	49.0084
2	9.443	VBA	0.2452	3857.15332	245.61423	50.9916



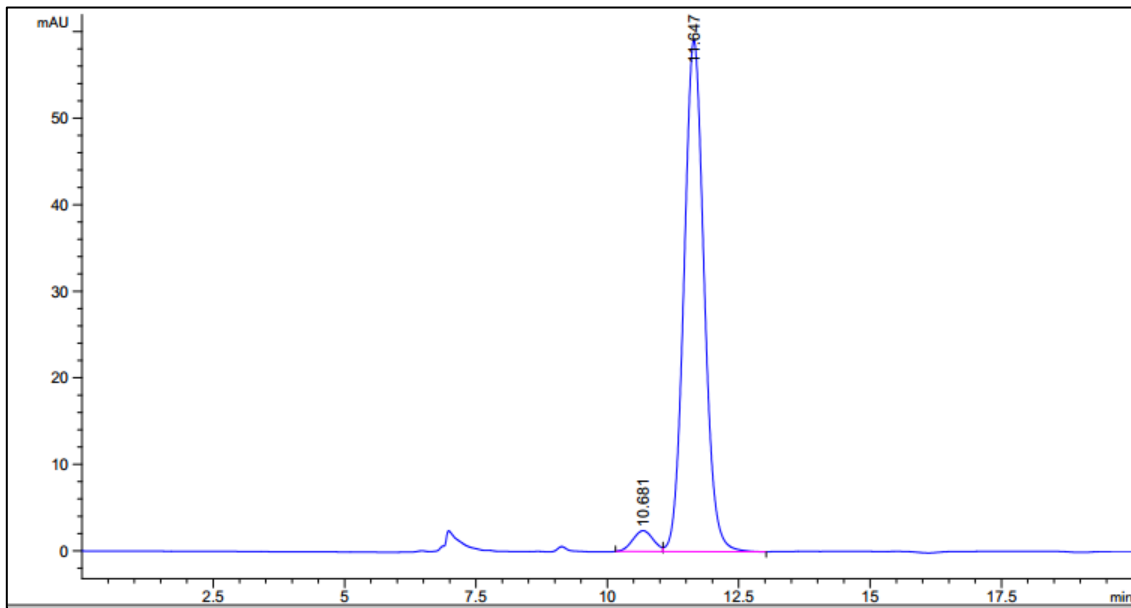
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.808	BV	0.4749	6220.49268	205.08487	24.6950
2	11.073	VV	0.4233	1.89688e4	699.73987	75.3050



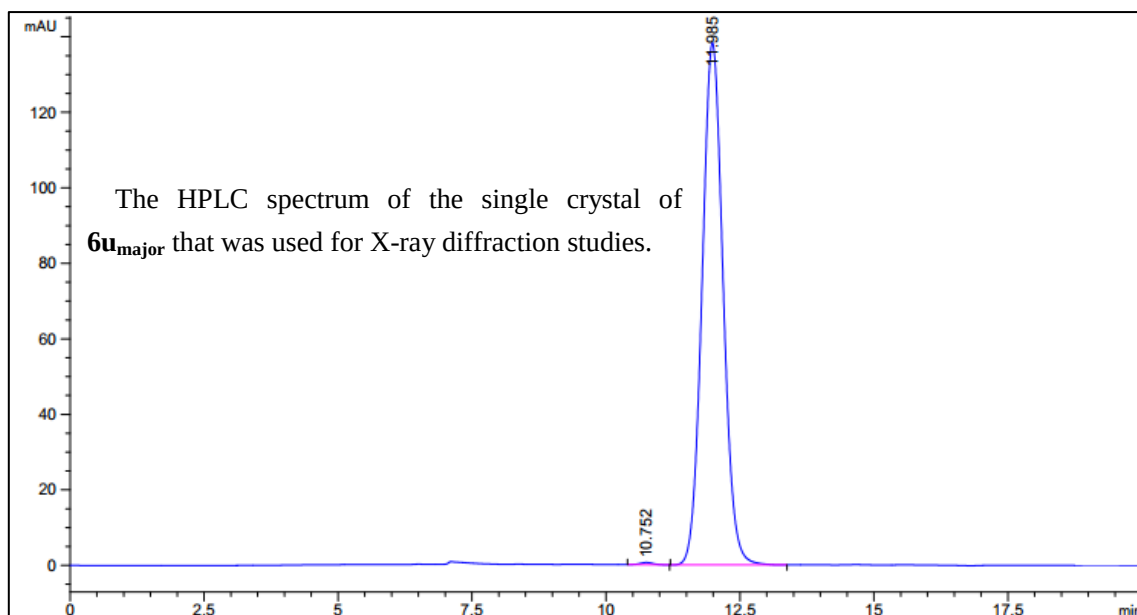




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.235	BV	0.4804	2974.23047	96.00435	49.7625
2	12.694	VB	0.4930	3002.61597	93.91580	50.2375



#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.681	BV	0.4199	65.05103	2.40238	3.9765
2	11.647	VB	0.4100	1570.84863	59.11199	96.0235



#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.752	BB	0.2481	9.74523	5.91773e-1	0.2587
2	11.985	BB	0.4201	3757.54761	138.26041	99.7413