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Carbanionic Route to Electroactive Carbon-Centered Anion and Radical Oligomers

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**Carbanionic Route to Electroactive Carbon-Centered Anion
and Radical Oligomers**

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Carbanionic Route to Electroactive Carbon-Centered Anion and Radical Oligomers

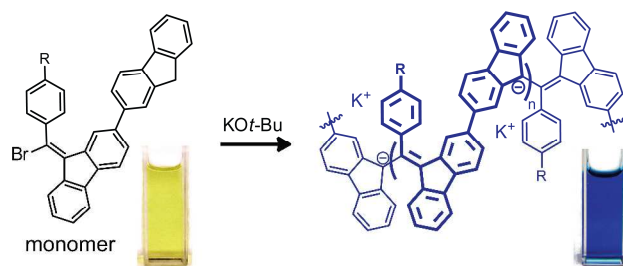
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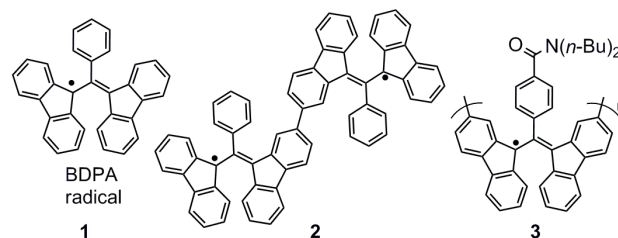
ABSTRACT



The synthesis of poly-1,3-allyl (BDPA) radicals via a strategy is reported. The material displays a reversible reduction from the orange-red radical to the blue carbanion in solution.

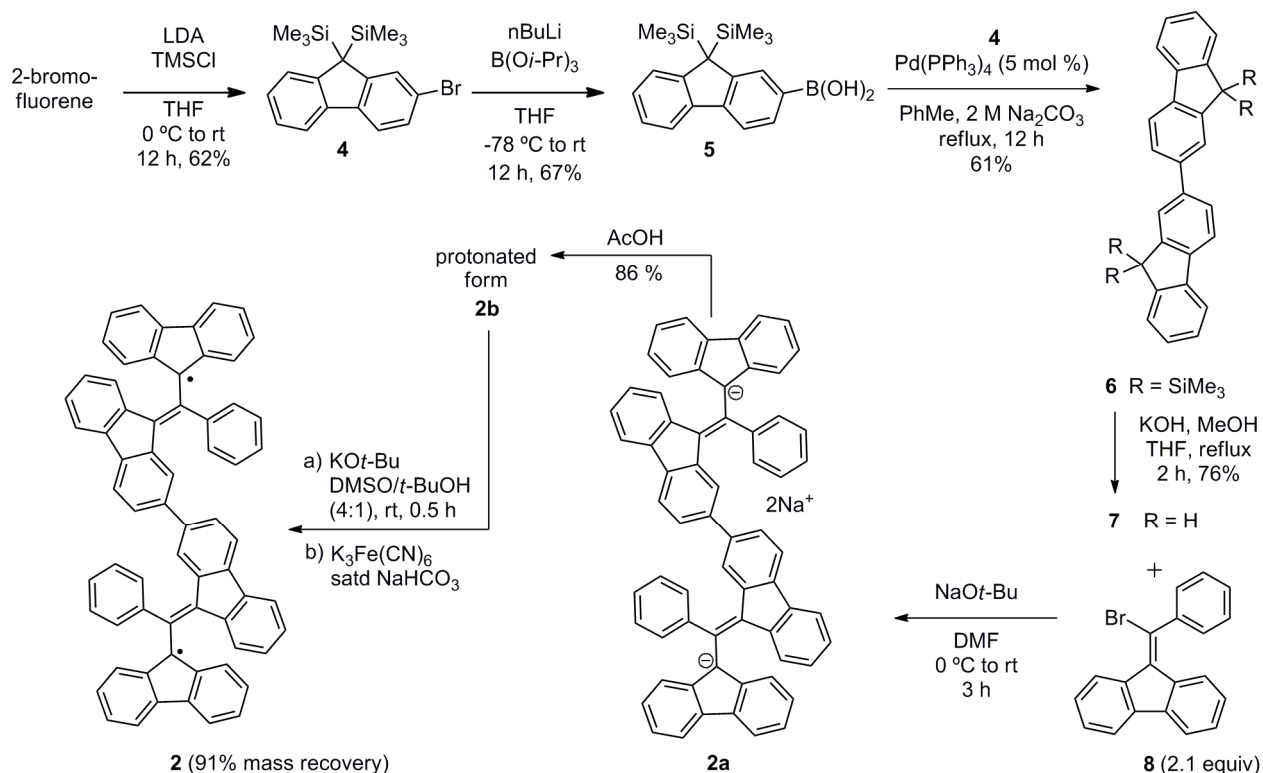
bisdiphenylene-2-phenyl new anionic oligomerization

We report electroactive conjugated materials containing a carbon-centered radical based on the 1,3-bisdiphenylene-2-phenylallyl (BDPA) radical (**1**)¹ that can be reversibly reduced to a delocalized carbanion.² Our synthesis of these materials is based on a new anionic oligomerization that produces a soluble carbanionic polymer. The ability of biradical-**2** and oligomer-**3** to be readily reduced to give anionic materials is critical to several applications, including battery anodes, in which polycarbanions with lithium counterions are used for charge storage.³ Additionally, *n*-dopable (electron-conducting) organic conjugated materials that become conductive upon reduction are essential elements of photovoltaic and field effect transistor devices.⁴ Conjugated polymer semiconductors that are *p*-dopable are abundant, but there remains a limited number of stable *n*-dopable materials.⁴ Finally, **2** and **3** are electrochromic because they can be switched between the orange-red colored radical and the deep blue carbanion.⁵



The BDPA carbanion is remarkably stable for a material containing no electronegative heteroatoms and can persist for days under 1 atm oxygen in polar aprotic solvents, such as DMF and DMSO, when generated electrochemically.^{2a} The predominant decomposition pathway of the BDPA carbanion under ambient conditions is via oxidation to the radical.^{2a} Previous electrochemical studies have found that the BDPA radical, and closely related derivatives with substitution at the 4-position of the phenyl ring, behave as semiconductors with energy gaps of 1.5-1.7 eV in the solid state.⁶

Scheme 1. Synthesis of **2**



Building on Kuhn and Neugebauer's synthesis of BDPA,^{1b} an anionic oligomerization method was pursued. In this approach, the BDPA oligomer is synthesized as a polycarbanion (**3a**), which can then be oxidized to the polyradical. The incorporation of the BDPA radical into the main chain of a conducting polymer or oligomer has not been previously investigated. However, polyacetylenes with a pendant BDPA connected through the 4-position of the phenyl ring have been previously studied.⁷ In addition, there have been extensive efforts reported in the literature to develop materials based on the related triphenylmethyl radical and its derivatives.⁸

To test the viability of an anionic oligomerization strategy and to study the effect of linking two BDPA radicals through the 2-position of a fluorene ring, dimer **2** was synthesized as a model system (Scheme 1). Previously reported bis-BDPA biradicals have been limited to those linked through the phenyl ring.⁹ Bifluorene **6**, synthesized by Pd-catalyzed coupling of **4** and **5** followed by deprotection of the 9-positions, was reacted with 2.1 equivalents of bromide **8** to obtain dianion **2a**. Protonation of **2a** resulted in a complex mixture of tautomers, *E/Z*-double bond isomers, and rotamers (¹H and ¹³C NMR spectra included in Supporting Information).¹⁰ However, **2a** offered a simplified ¹H and ¹³C NMR spectrum due to its increased symmetry.¹¹ Figure 1 (*top*) shows a portion of the ¹H NMR spectrum of the carbanion of a previously reported BDPA derivative with a bromide at the 4-position of the phenyl ring (Br-BDPA).^{1b} Figure 1 (*bottom*) shows a portion of the ¹H NMR spectrum of **2a** and the proton assignments, which were determined using gCOSY 2D NMR. Oxidation of **2a** with potassium ferricyanide produces biradical **2**, which shows an EPR signal very

similar to that of BDPA at room temperature in solution.¹² Biradial **2** was observed in HRMS, but could not be isolated as an analytically pure compound.

Based on the success of the dimer synthesis, monomer **9** was prepared, beginning with the condensation of 2-bromofluorene and 4-carboxybenzaldehyde (Scheme 2). The crude carboxylate salt was converted to a dibutylamide via the acid chloride, and the *E* and *Z* isomers were separated by chromatography for characterization. We have previously shown that amides are compatible with the polymerization conditions^{10a} and the *n*-butyl groups were chosen to provide greater solubility to both the monomer and the oligomer. After Pd-catalyzed coupling of **10-E/Z** with boronic acid **5**, the alkene of **11-E/Z** was dibrominated in acetic acid. Hydrogen bromide was eliminated with sodium hydroxide in refluxing ethanol with concurrent removal of the trimethylsilyl groups to provide **9-E** and **9-Z**, which could be separated by chromatography.

Several conditions for oligomerization were screened, but in all cases *tert*-butoxide was used as the base because it deprotonates fluorene at the 9-position without attacking the alkenyl bromide. The effects of solvent (THF, DMA) and counterion (Li, Na, K, Mg, Ba, Zn) were explored (see Table S1 in Supporting Information) and the extent of oligomerization was analyzed based on the *M_n*, as determined by GPC (DMF) of the crude polyanions. Potassium *tert*-butoxide in THF was chosen

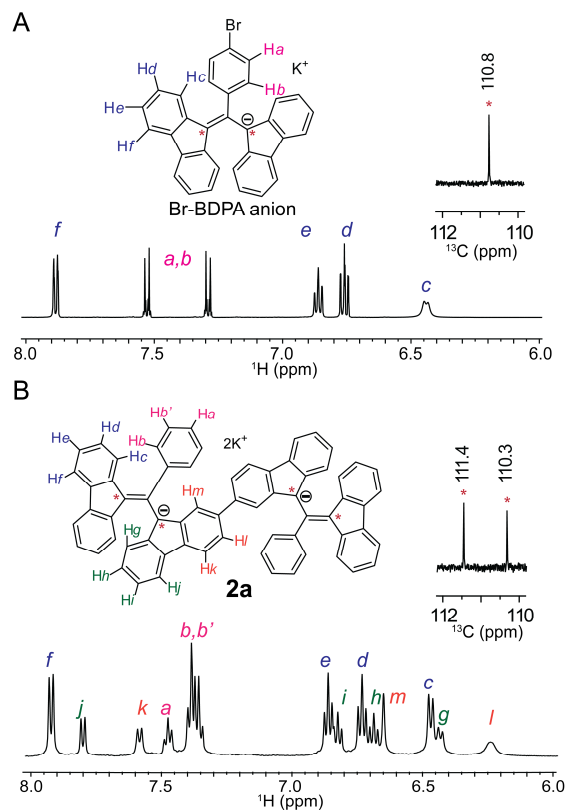
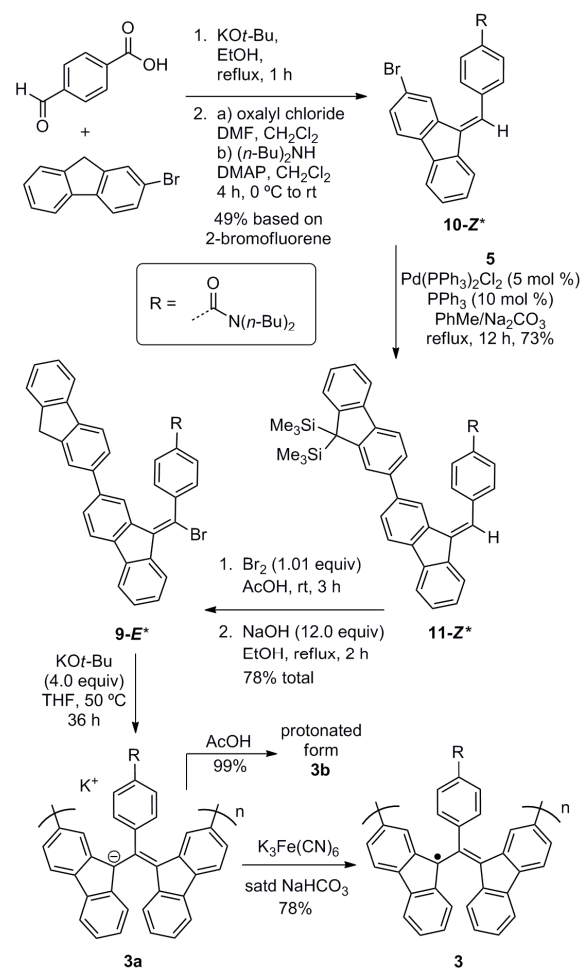


Figure 1. Selected regions of ¹H and ¹³C NMR of Br-BDPA anion (a) and **2a** (b) are shown. Spectra were collected in *d*₆-DMSO (a, 20 °C; b, 40 °C).

as the preferable method and was used to synthesize **3b**, which is a light yellow powder that is readily soluble in CH₂Cl₂, THF, and chloroform (GPC (THF): *M*_n = 6.5 kDa, degree of polymerization (DP) = 11). The ¹H and ¹³C NMR of **3b** showed broadened signals that are in agreement with the proposed structure. In the ¹³C spectrum, the resonance at 52.7 ppm, which is specific to the carbon attached to the acidic proton of BDPA precursors, supports the proposed structure (see Supporting Information). To isolate the radical form of the oligomer, **3a** was treated with potassium ferricyanide. After precipitation into methanol, a dark red powder (GPC (THF): *M*_n = 9.4 kDa, DP = 16) was isolated. The higher *M*_n may be a result of **3** having a larger persistence length in THF as compared to **3a**. Fractionation of the polymer during precipitation may also contribute to the discrepancy. In addition to the expected IR absorbances, the isolated oligomers **3** and **3b** display a weak ketone stretch at approximately 1720 cm⁻¹ that we attribute to 9-fluorenone end-groups (see Figure S2 in Supporting Information).¹³ Oligomer **3** showed a featureless EPR absorption in THF at room temperature (see Figure S1 in the Supporting Information).



* *E/Z* isomers were synthesized in a 1:1 ratio, but were isolated and characterized separately.

The UV-vis spectra of the protonated precursor, the carbanions, and the radicals are presented in Figure 2. Dianion **2a** shows a strong absorbance at 614 nm in DMSO similar to the BDPA anion absorbance at 600 nm in DMF. The polyanion **3a** is red-shifted and appears broadened. Biradical **2** and polyradical **3** show strong absorbances near 490 nm and weak absorbances at 865 nm in THF, which are comparable to the reported values for BDPA in dioxane (485 and 860 nm).^{1b}

Biradical **2** shows two closely-spaced, reversible one-electron reductions to form the dianion **2a** (Figure 3). Polyradical **3** displays a broad, reversible reduction peak, presumably attributable to multiple radicals undergoing 1-electron reduction. The electrode displays a visible change in color from reddish brown to deep blue upon reduction to the blue polyanion. In general, **3** did not

Scheme 2. Synthesis of **3**

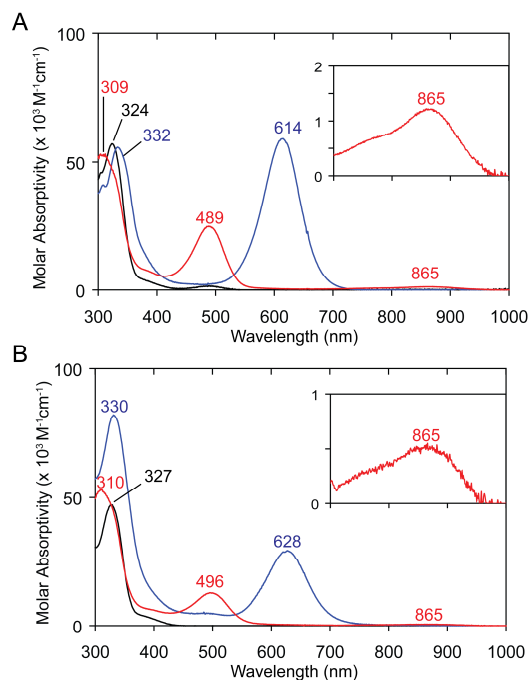
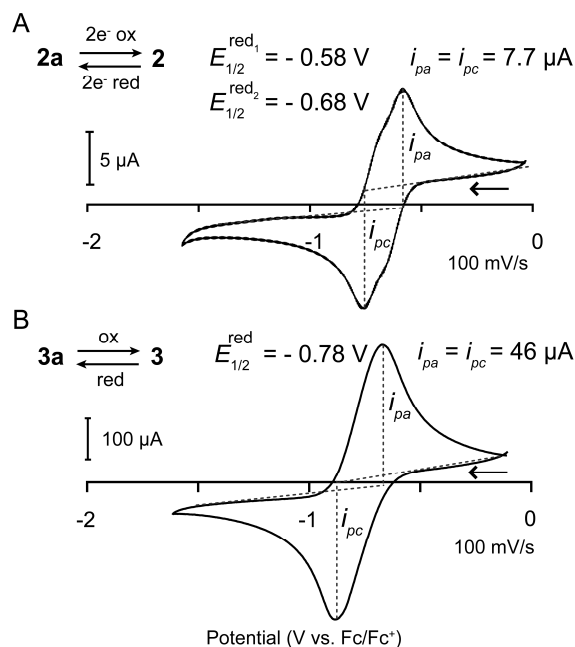


Figure 2. Absorption spectra of **2a**, **2b**, **2** (a) and **3a**, **3b**, **3** (b) are shown. All spectra were collected in THF except for **2a** and **3a**, which were collected in DMSO purged with nitrogen.

Figure 3. Cyclic voltammograms of **2** (a) and **3** (b) showing the reversible redox couple between the carbanion and the radical.



Conditions: (a) 0.10 M LiClO₄ in DMF, Pt-button electrode, [2a] \approx 1 mM, 2a formed by deprotonation with LiOt-Bu in DMF; (b) 0.10 M (*n*-Bu)₄NPF₆ in MeCN, Pt-wire electrode with 3 dropcast from a chloroform solution.

form quality films. Future work will examine how cross-linking through the solubilizing groups can aid in film formation.

In conclusion, materials that join BDPA radicals through the 2-position of the fluorene ring have been synthesized via a new anionic oligomerization strategy. The carbanions have been characterized with ¹H and ¹³C NMR. The absorption spectra of the protonated, anionic, and radical forms of **2** and **3** are reported, as is the ability to reversibly perform one-electron reductions to form the carbanions from the radicals. Further work will investigate how to improve the film forming abilities of **3** and investigate how changing the connectivity between the fluorene rings affects the electronic and magnetic properties of the materials.

Supporting Information Available. Experimental details and additional spectra are available free of charge via the Internet at <http://pubs.acs.org>.

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11 Carbanions for NMR study were generated by adding 2.0 equivalents of potassium *tert*-butoxide per acidic proton to a *d*₆-DMSO solution of the protonated precursor.

12 Solution EPR spectra and effective magnetic moment measurements are available in Figure S1 of the Supporting Information. Solid-state EPR and the magnetic properties of the materials will be a focus of future investigations.

13 The results of combustion analysis for **3** and **3b** are reported and discussed in the Supporting Information. Additionally, oligomer **3** showed no detectable level (< 0.1%) of bromide in combustion analysis.

Supporting Information for “Carbanionic Route to Electroactive Carbon-Centered Anion and Radical Oligomers”

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gCOSY	24
9-Z ^1H and ^{13}C	25
gCOSY	26
10-E ^1H and ^{13}C	27
gCOSY	28
10-Z ^1H and ^{13}C	29
gCOSY	30
11-E ^1H and ^{13}C	31
gCOSY	32
11-Z ^1H and ^{13}C	33
gCOSY	34

General Methods and Materials.

All air and water sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. All commercial chemicals were of reagent grade and used as received unless otherwise noted. Sublimed potassium *tert*-butoxide was purchased from Sigma-Aldrich and stored under nitrogen. Column chromatography was performed using ultra pure silica gel (SILIYCYCLE, 40~63 μm). Polymer molecular weights and polydispersity indexes were estimated by gel permeation chromatography (GPC) using a HP series 1100 GPC system. Polystyrene standards were used for calibration, and tetrahydrofuran (THF) or dimethylformamide (DMF) was used as the eluent at a flow rate of 1.0 mL/min. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer in quartz cuvettes and corrected for background signal. All electrochemical measurements were made with an AUTOLAB PGSTAT 20 potentiostat (Eco Chemie) using a quasi-internal Ag wire reference electrode (BioAnalytical Systems) submersed in 0.01 M AgNO_3 /0.1 M $n\text{-Bu}_4\text{NPF}_6$ in anhydrous acetonitrile. CVs were recorded using platinum button electrodes or platinum wire as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as an external reference. Combustion analysis was performed by Columbia Analytical Services, Tucson, Ar. Compound **8** was synthesized according to the literature.¹

Synthetic Procedures.

(2-bromo-9H-fluorene-9,9-diyl)bis(trimethylsilane) (4). To an oven-dried 1000 mL flask were added 30.00 g of 2-bromofluorene (0.1224 mol, 1.0 equiv) and 200 mL of dry THF. In a separate flask, an LDA solution was prepared by adding 196.0 mL of a 1.50 M *n*-butyllithium solution in hexane (0.294 mol, 2.4 equiv) to a solution of 50.0 mL of diisopropylamine in 50.0 mL of THF. Half of the LDA solution (approximately 150 mL) was slowly added to the flask containing 2-bromofluorene, which was maintained at 0 °C in an ice bath during the addition. The flask was allowed to warm to room temperature. The reaction was cooled with an ice bath to 0 °C and 20.2 mL of trimethylsilylchloride (17.3 g, 0.171 mol, 1.4 equiv) was added. After stirring for 0.5 h at 0 °C, the reaction was allowed to warm to room temperature. The reaction was cooled to 0 °C and the remaining LDA solution was added. The reaction was warmed to room temperature and then cooled to 0 °C before adding 20.2 mL of trimethylsilylchloride and stirring for 0.5 h at 0 °C. The reaction was allowed to warm to room temperature overnight and quenched with excess saturated ammonium chloride. The reaction mixture was extracted with diethyl ether (3 x 50 mL). The organic layers were combined and washed with 0.1 M HCl, saturated sodium bicarbonate, and brine. The diethyl ether solution was dried over sodium sulfate. After removal of solvent, the crude material was recrystallized from refluxing ethanol (approximately 500 mL). After filtration, 28.00 g (62%) of product was isolated as clear, rectangular prisms. ¹H NMR (500 MHz, CDCl_3 , δ) (all coupling constants (*J*) in Hz): 7.89 (multiplet with second-order splitting, 1H), 7.79 (dd, *J* = 8.0, 0.50, 1H), 7.70 (dd, *J* = 1.5, 0.50, 1H), 7.57 (multiplet with second-order splitting, 1H), 7.48 (dd, *J* = 8.0, 1.5, 1H), 7.36 (multiplet with second-order splitting, 2H), -0.07 (s, 16H); ¹³C NMR (126 MHz, CDCl_3 , δ) 149.8, 147.6, 139.4(2), 127.6, 127.5, 125.8, 124.7, 124.6, 121.2, 120.1, 119.7, 44.8, 0.7; HRMS (EI): calcd for $\text{C}_{19}\text{H}_{25}\text{BrSi}_2$ [$\text{M}]^+$: 388.0673; found, 388.0674. IR (KBr, thin film) ν_{max} (cm^{-1}):

3050, 2952, 2892, 1589, 1554, 1456, 1436, 1397, 1261, 1248, 1171, 1105, 1063, 941, 901, 873, 857, 821, 734, 684; mp 169-170 °C (ethanol).

(9,9-bis(trimethylsilyl)-9H-fluoren-2-yl)boronic acid (5). To an oven-dried 200 mL flask were added 5.00 g of (2-bromo-9H-fluorene-9,9-diyl)*bis*(trimethylsilane) (**4**) (0.0128 mol, 1.0 equiv) and 80 mL of dry THF. The solution was cooled to -78 °C with dry ice in acetone, and 12.0 mL of a 1.5 M solution of *n*-butyllithium in hexane (0.0167 mol, 1.3 equiv) was added. The solution was stirred at -78 °C for 1 h. To the reaction mixture was added 4.81 g (0.0256 mol, 2.0 equiv) of triisopropylborate. The solution was allowed to warm to room temperature and stir overnight. The reaction was quenched with 50 mL of 1 M HCl and then extracted into diethyl ether (3 X 30 mL). The combined organic layers were washed with brine and dried over sodium sulfate. After removal of the ether, the crude mixture was purified by recrystallization from refluxing hexane to yield 3.02 g (67 %) of a white powder. ¹H NMR (500 MHz, CDCl₃/CD₃OD, δ) (all coupling constants (*J*) in Hz): 7.99 (s, 1H), 7.90 (m, 2H), 7.71 (d, *J* = 7.5, 1H), 7.57 (m, 1H), 7.32 (m, 2H), -0.12 (s, 18H); ¹³C NMR (126 MHz, CDCl₃/CD₃OD, δ) 148.3, 146.9, 142.5, 140.2, 130.1, 129.6, 126.1, 124.6, 124.3, 120.2, 119.4, 119.1, 44.1, -0.9; HRMS (ESI): calcd for C₁₉H₂₇BO₂Si₂ [M - H]⁻: 352.1606; found, 352.1600. IR (KBr, thin film) ν_{max} (cm⁻¹): 3206, 3050, 2954, 2892, 1607, 1560, 1446, 1401, 1347, 1328, 1261, 1250, 926, 883, 840, 741; mp 85-90 °C (hexane).

9,9,9',9'-tetrakis(trimethylsilyl)-9H,9'H-2,2'-bifluorene (6). To an oven-dried 100 mL flask were added 1.00 g of (2-bromo-9H-fluorene-9,9-diyl)*bis*(trimethylsilane) (**4**) (0.00257 mol, 1.0 equiv), 1.09 g of (9,9-bis(trimethylsilyl)-9H-fluoren-2-yl)boronic acid (**5**) (0.00308 mol, 1.2 equiv), 0.150 g of Pd(PPh₃)₄ (5 mol%), 30 ml toluene, and 20 mL of aqueous 2M Na₂CO₃. The solution was degassed with bubbling argon and then heated to reflux for 12 h under argon. After cooling to room temperature, the reaction mixture was moved to a separatory funnel and 50 mL of diethyl ether was added. The organic layer was washed with brine. After drying over sodium sulfate, the organic layer was removed and the mixture was purified with silica gel chromatography eluting with 95:5 hexane/dichloromethane. A total of 0.975 g (61%) of product was isolated as a white powder. ¹H NMR (500 MHz, CDCl₃, δ) (all coupling constants (*J*) in Hz): 8.02 (d, *J* = 8.0, 2H), 7.97 (m, 4H), 7.76 (dd, *J* = 8.0, 1.5, 2H), 7.62 (d, *J* = 8.0), 7.38 (m, 4H), 0.00 (s, 36H); ¹³C NMR (126 MHz, CDCl₃, δ) 148.4, 148.1, 140.2, 139.6, 139.1, 125.8, 124.7, 124.6, 123.8, 123.1, 120.3, 120.1, 44.4, -0.6; HRMS (EI): calcd for C₃₈H₅₀Si₄ [M]⁺: 618.2984; found, 618.2998; IR (KBr, thin film) ν_{max} (cm⁻¹): 3058, 2954, 2899, 1609, 1442, 1396, 1249, 1173, 1124, 1105, 941, 905, 860, 821, 780, 752, 738, 685, 622; mp 243-245 °C (hexane).

9H,9'H-2,2'-bifluorene (7). To a 200 mL flask were added 0.500 g of 9,9,9',9'-tetrakis(trimethylsilyl)-9H,9'H-2,2'-bifluorene (**6**) (0.000807 mol, 1.00 equiv), 0.034 g KOH flake (0.00061 mol, 0.75 equiv), 50 mL of tetrahydrofuran, and 25 mL of methanol. The solution was degassed with bubbling argon for 5 minutes and then heated to reflux for 2 h under argon. The solution was cooled and filtered to isolated 0.202 g (76%) of product as a white crystal. ¹H NMR (500 MHz, CDCl₃, δ) (all coupling constants (*J*) in Hz): 7.88 (d, *J* = 8.0, 2H), 7.86 (m, 2H), 7.84 (d, *J* = 8.0, 2H), 7.70 (dd, *J* = 8.0, 2.0, 2H), 7.59 (d, *J* = 8.0, 2H), 7.41 (t, *J* = 8.0, 2H), 7.33 (td, *J* = 8.0, 2.0, 2H), 4.00 (s, 4H); ¹³C NMR (126 MHz, CDCl₃, δ)

144.1, 143.7, 141.7, 141.0, 140.3, 127.0, 126.9, 126.2, 125.3, 124.0, 120.4, 120.2, 127.0, 126.9, 126.2, 125.3, 124.0, 120.4, 120.2, 37.2; HRMS (EI): calcd for $C_{26}H_{18} [M]^+$: 330.1403 ; found, 330.1405; IR (KBr, thin film) ν_{\max} (cm^{-1}): 3064, 3014, 2921, 1590, 1146, 1403, 1234, 1180, 947, 817, 761, 728; mp 316-318 °C (tetrahydrofuran/methanol), lit. mp 316-318 °C (toluene).²

Protonated BDPA Dimer (2b). To an oven-dried 50 mL flask cooled in an ice bath were added 0.080 g of 9H,9'H-2,2'-bifluorene (**7**) (0.000240 mol, 1.0 equiv), 0.170 g of 9-(bromo(phenyl)methylene)-9H-fluorene (0.000510 mol, 2.10 equiv), 0.210 g of sodium *tert*-butoxide (0.00220 mol, 9.00 equiv), and 30 mL of anhydrous, degassed dimethylformamide. The solution was stirred at 0 °C for 30 minutes and at room temperature for 3.5 h. The reaction was quenched by adding 5.0 mL of glacial acetic acid followed by 50 mL of water. The quenched reaction mixture was extracted with diethyl ether (2 x 10 mL). The combined organic layers were washed several times with water and once with brine, before being dried over sodium sulfate. The crude product was purified by silica gel chromatography, eluting with 45:45:10 hexane/DCM/ethyl acetate. The isolated material (0.172 g, 86%) is a complex mixture of tautomers, E/Z-double bond isomers, and rotamers. NMR: see spectra. HRMS (EI): calcd for $C_{66}H_{42} [M]^+$: 834.3281; found, 834.3282; IR (KBr, thin film) ν_{\max} (cm^{-1}): 3059, 1615, 1593, 1572, 1146, 1342, 1268, 1155, 1024, 908, 825, 782, 731, 703, 674, 620; UV-Vis (THF) λ_{\max} , nm (ϵ): 324 (5.7×10^4).

BDPA dimer dianion (2a). To generate the dianion for NMR, 0.035 g of **2b**, 0.019 g of potassium *tert*-butoxide (4.0 equiv), and 1.0 mL of d_6 -DMSO were stirred under argon for 30 minutes and then transferred to an NMR tube, which was subsequently flushed with argon and capped. ¹H NMR (500 MHz, d_6 -DMSO, 40 °C, δ) (all coupling constants (*J*) in Hz): 7.92 (d, *J* = 7.5, 4H), 7.80 (d, *J* = 7.5, 2H), 7.58 (d, *J* = 7.5, 2H), 7.45 (m, 2H), 7.37 (m, 8H), 6.86 (t, *J* = 7.5, 4H), 6.82 (t, *J* = 7.5, 2H), 6.73 (t, *J* = 7.5, 4H), 6.69 (t, *J* = 7.5, 2H), 6.65 (s, 2H), 6.47 (d, *J* = 7.5, 4H), 6.43 (d, *J* = 7.5, 2H), 6.24 (br, 2H); ¹³C NMR (126 MHz, d_6 -DMSO, 40 °C, δ) 145.1, 143.5, 139.2, 138.9, 137.4, 132.5, 132.2, 132.1, 130.8, 127.6, 127.4, 122.8, 122.6, 120.7 (2), 119.6, 118.1, 117.9, 117.8 (2), 117.3, 117.2, 111.4, 110.3. UV-Vis (DMSO) λ_{\max} , nm (ϵ): 332 (5.5×10^4), 614 (5.9×10^4).

BDPA Dimer Biradical (2). To a 100 mL flask were added 0.055 g of **2b** (0.066 mmol, 1.0 equiv), 0.044 g (0.395 mmol, 6.0 equiv) of potassium *tert*-butoxide, and 12.0 mL of a degassed 4:1 DMSO/*t*-BuOH solution. The solution was stirred at room temperature under argon for 0.5 h. To the reaction mixture was added 0.087 g of $K_3Fe(CN)_6$ (0.26 mmol, 4.0 equiv) dissolved in the minimum amount of saturated aqueous sodium bicarbonate solution needed. The reaction was allowed to stir for 2 minutes. An additional 50 mL of water was added and the precipitate formed was collected by filtration and thoroughly washed with water, methanol, and hexane. After filtration, 0.050 g (91% yield based on mass recovery) of a dark-red powder was obtained. The material showed no resolved NMR signals other than those belonging to solvent at a concentration of 50 mM in $CDCl_3$. Thin-layer chromatography (SiO_2) with 1:1 hexane/dichloromethane showed a red-spot that coeluted with the starting material. Any benefits gained from further purification via recrystallization or chromatography appeared to be counteracted by loss of material due to reaction with oxygen to form alcohol and ketone decomposition

products. The decomposition products could be observed as significantly more polar spots on TLC, but were not isolated and characterized. HRMS (ESI): calcd for $C_{66}H_{40}$ $[M + H]^+$: 833.3210; found, 833.3275; IR (KBr, thin film) ν_{max} (cm^{-1}): 3057, 1611, 1569, 1145, 1350, 1268, 907, 731; UV-Vis (THF) λ_{max} , nm (ϵ): 309 (6.0×10^4), 489 (2.8×10^4), 865 (2.6×10^3); EPR: see Figure S1.

(E/Z)-4-((2-bromo-9H-fluoren-9-ylidene)methyl)-N,N-dibutylbenzamide (10). To a 500 mL flask equipped with a reflux condenser were added 3.68 g of 2-bromofluorene (0.0150 mol, 1.00 equiv), 2.70 g of 4-carboxybenzaldehyde (0.0180 mol, 1.2 equiv), 4.62 g potassium *tert*-butoxide (0.0413 mol, 2.75 equiv), and 150 mL of absolute ethanol. The reaction mixture was heated to reflux. After 1 h, a yellow precipitate formed, and the reaction was allowed to cool to room temperature overnight. The precipitate, which is the potassium salt of the condensation product, was filtered with vacuum and washed with ethanol and hexanes. After drying under high vacuum at 100 °C overnight, 5.15 g of yellow powder was isolated. A portion of this material was carried to the next step without further purification. To a 200 mL flask cooled in an ice bath were added 3.93 g of the potassium salt of the crude condensation product (assumed to be 0.0095 mol, 1.0 equiv), 30 mL of dry dichloromethane, 1.24 mL oxalyl chloride (1.80 g, 0.0140 mol, 1.5 equiv), and 1 drop of DMF. The reaction mixture was allowed to warm to room temperature until bubbling ceased. The solvent and excess reagent were distilled off, and the remaining solid was dissolved in 50 mL of dichloromethane. To this solution were added 6.40 mL of di-*n*-butylamine (4.91 g, 0.038 mol, 4.0 equiv) and catalytic 4-dimethylaminopyridine. The solution was stirred for 4 h and then moved to a separatory funnel where it was washed with 0.1 M HCl (3 X 20 mL), satd sodium bicarbonate (3 X 20 mL), and brine. The solution was dried over sodium sulfate. After removal of the solvent, the crude reaction product was purified with silica gel chromatography. The *E* and *Z* isomers could be eluted separately using a mixture of 80% hexane, 10% dichloromethane, and 10% ethyl acetate. The *E* isomer eluted before the *Z* isomer. In total, 3.61 g (49% based on 2-bromofluorene) of product was isolated (*E* isomer, 1.31 g; *Z* isomer, 1.53 g; mixed fractions, 0.770 g). The *E* isomer was isolated as an amorphous yellow solid and the *Z* isomer was isolated as a viscous yellow oil. Additionally, the reaction was performed on approximately 3-times this scale and the product was isolated as a 1:1 mixture of *E* and *Z* isomers with similar yields. *E* isomer: 1H NMR (500 MHz, $CDCl_3$, δ) (all coupling constants (*J*) in Hz): 7.91 (d, *J* = 2.0, 1H), 7.69 (d, *J* = 7.5, 1H), 7.6 (m, 5H), 7.51 (dd, *J* = 8.0, 2.0, 1H), 7.47 (d, *J* = 8.0, 2H), 7.33 (td, *J* = 7.5, 1.0, 1H), 7.08 (td, *J* = 7.5, 1.0, 1H), 3.54 (t, *J* = 7.5, 2H), 3.28 (t, *J* = 7.5, 2H), 1.69 (m, 2H), 1.56 (m, 2H), 1.45 (m, 2H), 1.21 (m, 2H), 1.01 (t, *J* = 7.5, 3H), 0.85 (t, *J* = 7.5); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 171.4, 141.4, 140.5, 138.2, 137.4, 137.3, 136.3, 136.2, 131.3, 129.4, 129.2, 127.6, 127.3, 127.0, 124.6, 123.8, 121.1, 121.0, 120.0, 49.1, 44.8, 31.0, 29.9, 20.5, 20.0, 14.2, 13.8; HRMS (ESI): calcd for $C_{29}H_{30}BrNO$ $[M + H]^+$: 488.1584; found, 488.1598; IR (KBr, thin film) ν_{max} (cm^{-1}): 3059, 2958, 2930, 2872, 1633, 1508, 1448, 1425, 1412, 1378, 1297, 1257, 1234, 1187, 1101, 1064, 955, 869, 820, 771, 728. *Z* isomer: 1H NMR (500 MHz, $CDCl_3$, δ) (all coupling constants (*J*) in Hz): 7.79 (d, *J* = 7.5, 1H), 7.69 (m, 3H), 7.61 (d, *J* = 8.0, 2H), 7.58 (d, *J* = 8.0, 1H), 7.49 (d, *J* = 8, 2H), 7.44 (dd, *J* = 8.0, 2.0, 1H), 7.40 (td, *J* = 7.5, 1.0, 1H), 7.37 (td, *J* = 7.5, 1.0, 1H), 3.54 (t, *J* = 7.5, 2H), 3.31 (t, *J* = 7.5, 2H), 1.69 (m, 2H), 1.56 (m, 2H), 1.43 (m, 2H), 1.23 (m, 2H), 1.01 (t, *J* = 7.5), 0.86 (t, *J* = 7.5); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 171.4, 140.4, 139.2, 138.5, 138.3,

137.5, 137.2, 136.3, 131.7, 129.5, 128.8, 127.9, 127.7, 127.5, 127.2, 121.3, 120.6(2), 119.9, 49.2, 44.8, 31.2, 29.9, 20.6, 20.1, 14.2, 14.1; HRMS (ESI): calcd for $C_{29}H_{30}BrNO$ $[M + H]^+$: 488.1584; found, 488.1569; IR (KBr, thin film) ν_{max} (cm^{-1}): 3050, 2958, 2930, 2872, 1633, 1508, 1464, 1440, 1421, 1378, 1296, 1268, 1186, 1101, 1064, 955, 831, 776, 734.

(*E/Z*)-4-((9',9'-bis(trimethylsilyl)-9H,9'H-[2,2'-bifluoren]-9-ylidene)methyl)-*N,N*-dibutylbenzamide (11). To an oven-dried 500 mL flask were added 8.40 g of a (*E/Z*)-4-((2bromo-9H-fluoren-9-ylidene)methyl)-*N,N*-dibutylbenzamide (**10**) (1:1 mixture of isomers) (0.00123 mol, 1.0 equiv), 6.70 g of (9,9-bis(trimethylsilyl)-9H-fluoren-2-yl)boronic acid (**2**) (0.00147 mol, 1.2 equiv), 0.604 g of $Pd(PPh_3)_2Cl_2$ (5 mol%), 0.450 g of triphenylphosphine (10 mol%), 100 ml toluene, and 50 mL of aqueous 2M Na_2CO_3 . The solution was degassed with bubbling argon and then heated to reflux for 12 h under argon. After cooling to room temperature, the reaction mixture was moved to a separatory funnel and 100 mL of diethyl ether were added. The organic layer was washed with satd sodium bicarbonate and brine. After drying over sodium sulfate, the organic layer was removed and the mixture was purified with silica gel chromatography using mixtures of hexane, dichloromethane, and ethyl acetate. The product was eluted with 10:9:1 hexane, dichloromethane, and ethyl acetate as a 1:1 mixture of *E* and *Z* isomers and obtained in 73% yield (8.96 g) as a yellow powder. The *E* and *Z* isomers could not be resolved in our hands using chromatography. In order to isolate pure samples of the *E* and *Z* isomers for characterization, the same reaction was performed twice on a smaller scale with pure samples of the *E* and *Z* isomers. *E* isomer: 1H NMR (500 MHz, $CDCl_3$, δ) (all coupling constants (*J*) in Hz): 8.08 (d, *J* = 1.0, 1H), 8.02 (d, *J* = 7.5, 1H), 7.97 (m, 1H), 7.89 (d, *J* = 1.0, 1H), 7.83 (d, *J* = 7.5, 1H), 7.77 (s, 1H), 7.76 (d, *J* = 7.5, 1H), 7.71 (ddd, *J* = 7.5, 2.5, 1.5, 2H), 7.66 (d, *J* = 7.5, 2H), 7.62 (d, *J* = 7.5, 1H), 7.58 (d, *J* = 7.5, 1H), 7.49 (d, *J* = 7.5, 1H), 7.37 (m, 3H), 7.07 (td, *J* = 7.5, 1.0, 1H), 3.55 (t, *J* = 7.5, 2H), 3.30 (t, *J* = 7.5, 2H), 1.70 (m, 2H), 1.57 (m, 2H), 1.45 (m, 2H), 1.22 (m, 2H), 1.02 (t, *J* = 7.5, 3H), 0.86 (t, *J* = 7.5, 3H), -0.01 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 171.5, 148.4, 148.1, 141.5, 141.4, 140.1 (2), 139.8, 139.1, 138.3, 138.0, 137.4, 137.1, 136.9, 129.5, 129.1, 128.0, 127.0, 126.9, 126.5, 125.9, 124.7(2), 124.6, 124.0, 123.3, 120.3, 120.2, 120.1 (2), 119.5, 49.1, 44.8, 44.5, 31.1, 29.9, 20.6, 20.0, 14.2, 13.9, -0.6; HRMS (ESI): calcd for $C_{48}H_{55}NOSi_2$ $[M + H]^+$: 718.3895; found, 718.3870; IR (KBr, thin film) ν_{max} (cm^{-1}): 3050, 2957, 2863, 1633, 1452, 1424, 1297, 1250, 1104, 915, 834, 822, 732. *Z* isomer: 1H NMR (500 MHz, $CDCl_3$, δ) (all coupling constants (*J*) in Hz): 8.10 (d, *J* = 1.0, 1H), 7.90 (d, *J* = 7.5, 1H), 7.87 (d, *J* = 8.0, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.5, 1H), 7.76 (m, 4H), 7.71 (s, 1H), 7.64 (dd, *J* = 8.0, 1.5, 1H), 7.59 (m, 1H), 7.51 (d, *J* = 8.0, 2H), 7.42 (td, *J* = 7.5, 1.0, 1H), 7.35 (m, 4H), 3.53 (t, *J* = 7.5, 2H), 3.29 (t, *J* = 7.5, 2H), 1.69 (m, 2H), 1.45 (m, 4H), 1.05 (m, 2H), 1.01 (t, *J* = 7.5, 3H), 0.68 (t, *J* = 7.5, 3H), -0.08 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 171.3, 148.4, 148.1, 140.9, 140.5, 140.1, 140.0, 139.7, 139.2, 138.8, 137.9, 137.2(2), 137.1, 129.7, 128.7, 128.2, 127.3, 127.2, 126.7, 125.9, 124.7, 124.5, 123.5, 123.4, 123.0, 120.5, 120.4, 120.2, 120.0, 119.9, 49.2, 44.9, 44.4, 31.0, 29.9, 20.6, 19.8, 14.2, 13.9, -0.06; HRMS (ESI): calcd for $C_{48}H_{55}NOSi_2$ $[M + H]^+$: 718.3895; found, 718.3890; IR (KBr, thin film) ν_{max} (cm^{-1}): 3050, 2957, 2871, 1633, 1457, 1443, 1424, 1296, 1250, 1104, 902, 884, 842, 822, 737.

(*E/Z*)-4-(9H,9'H-[2,2'-bifluoren]-9-ylidenebromomethyl)-N,N-dibutylbenzamide (9). To a 500 mL oven-dried flask were added 4.36 g (*E/Z*)-4-((9',9'-bis(trimethylsilyl)-9H,9'H-[2,2'-bifluoren]-9-ylidene)methyl)-N,N-dibutylbenzamide (**11**) (0.00607 mol, 1.00 equiv) and 280 mL of glacial acetic acid. To this solution, 0.32 mL of bromine (0.98 g, 0.0061 mol, 1.01 equiv) was added dropwise over 10 minutes. The reaction was stirred for 3 h at room temperature and then 200 mL of water were added. The crude dibromide was isolated by filtration and allowed to thoroughly dry on the filter pad. To a 1000 mL flask containing the dibromide (approx. 4.8 g, 0.0055 mol) was added 500 mL of absolute ethanol. To this flask was added a solution of 2.64 g of NaOH (pellet form) (0.066 mol, 12.0 equiv) in the minimum amount of water needed for dissolution. The reaction mixture was heated to reflux for 2 h and then cooled to room temperature. The yellow precipitate formed was isolated by filtration and then subsequently purified by silica gel chromatography eluting with mixtures of hexane, dichloromethane, and ethyl acetate. The elution solvent was ramped from 50:50 hexane/DCM to 45:45:10 hexane/DCM/ethyl acetate with the *E*-isomer eluting before the *Z*-isomer. A total of 3.08 g (78%) of pure material was isolated (*E*-isomer, 1.62 g; *Z*-isomer, 1.46 g). *E* isomer: ¹H NMR (500 MHz, CDCl₃, δ) (all coupling constants (*J*) in Hz): 8.88 (d, *J* = 7.5, 1H), 7.75 (m, 4H), 7.58 (s, 4H), 7.56 (d, *J* = 7.5, 1H), 7.55 (dd, *J* = 8.0, 2.0, 1H), 7.48 (td, *J* = 7.5, 1.5, 1H), 7.42 (td, *J* = 7.5, 1.5, 1H), 7.39 (m, 2H), 7.32 (td, *J* = 7.5, 1.5, 1H), 7.23 (dd, *J* = 7.5, 1.5, 1H), 6.61 (d, *J* = 1.5), 3.93 (s, 2H), 3.48 (t, *J* = 7.5, 2H), 3.02 (t, *J* = 7.5, 2H), 1.64 (m, 2H), 1.41 (m, 4H), 1.01 (t, *J* = 7.5, 3H), 0.88 (m, 2H), 0.64 (t, *J* = 7.5, 3H); ¹³C NMR (126 MHz, CDCl₃, δ) 170.6, 144.2, 143.8 (2), 141.5, 141.2, 141.1, 140.3, 139.7, 139.0, 138.8, 138.5, 138.3, 136.7, 129.6, 129.1, 127.9, 127.4, 127.3, 126.9 (2), 126.3, 125.7, 125.3, 124.0, 123.5 (2), 120.4, 120.1, 119.9, 119.8, 49.1, 44.8, 37.1, 30.9, 29.8, 20.6, 19.7, 14.2, 13.8; HRMS (ESI): calcd for C₄₂H₃₈BrNO [M + H]⁺: 652.2210; found, 652.2225; IR (KBr, thin film) ν_{max} (cm⁻¹): 3043, 2957, 2927, 2856, 1624, 1446, 1417, 1295, 1098, 822, 769, 733. *Z* isomer: ¹H NMR (500 MHz, CDCl₃, δ) (all coupling constants (*J*) in Hz): 9.21 (d, *J* = 1.5, 1H), 7.90 (m, 2H), 7.85 (d, *J* = 7.5, 1H), 7.81 (d, *J* = 8.0, 1H), 7.76 (td, *J* = 7.5, 1.5, 2H), 7.69 (d, *J* = 8.0, 1H), 7.59 (d, *J* = 7.5, 1H), 7.54 (multiplet with second-order splitting, 4H), 7.42 (td, *J* = 7.5, 1.5, 1H), 7.34 (td, *J* = 7.5, 1.5, 1H), 7.27 (td, *J* = 7.5, 1.5, 1H), 6.87 (td, *J* = 7.5, 1.5, 1H), 6.37 (d, *J* = 7.5, 1H), 4.02 (s, 2H), 3.56 (t, *J* = 7.5, 2H), 3.32 (t, *J* = 7.5, 2H), 1.70 (m, 2H), 1.58 (m, 2H), 1.45 (m, 2H), 1.24 (m, 2H), 1.02 (t, *J* = 7.5, 3H), 0.88 (t, *J* = 7.5, 3H); ¹³C NMR (126 MHz, CDCl₃, δ) 171.0, 144.2, 143.7, 143.6, 141.6, 141.2, 140.9, 140.4, 140.3, 139.9, 138.7, 138.5, 138.3, 136.6, 129.1, 128.7, 128.6, 127.7, 127.1, 127.0(2), 126.3, 125.3, 125.2, 125.0, 124.1, 123.8, 120.4, 120.2, 120.1, 119.6, 49.2, 44.9, 37.3, 31.1, 29.9, 20.6, 20.1, 14.2, 13.9; HRMS (ESI): calcd for C₄₂H₃₈BrNO [M + H]⁺: 652.2210; found, 652.2210; IR (KBr, thin film) ν_{max} (cm⁻¹): 3058, 2957, 2930, 2871, 1633, 1448, 1425, 1297, 1101, 825, 770, 734.

Oligomer 3b. To an oven-dried 100 mL flask was added 0.280 g of (*E*)-4-(9H,9'H-[2,2'-bifluoren]-9-ylidenebromomethyl)-N,N-dibutylbenzamide (**9-E**) (0.000429 mol, 1.00 equiv). The flask was flushed with argon and sealed under vacuum and then moved into a nitrogen glovebox. In the glovebox, 0.192 g of sublimed potassium *tert*-butoxide (0.00171 mol, 4.00 equiv) and 40 mL of anhydrous tetrahydrofuran were added. The reaction was heated to 50 °C in a sandbath for 36 h within the glovebox. After cooling, the reaction flask was removed from the glovebox and 5.0 mL of glacial acetic acid was added with stirring. Additional water was added and the precipitate was isolated by filtration, washing with

methanol and hexane. After drying under vacuum, 0.244 g (99%) of a light yellow material was isolated. NMR: see spectrum; GPC (THF) $M_n = 6.5$ kDa, PDI (M_n/M_w) = 2.1, DP (based on M_n) = 11; IR (KBr, thin film) ν_{\max} (cm^{-1}): 3060, 2957, 2930, 2871, 1720, 1634, 1506, 1447, 1424, 1378, 1297, 1265, 1184, 1101, 1020, 908, 824, 769, 735, 650; UV-Vis (THF) λ_{\max} , nm (ϵ based on repeat unit): 327 (4.7×10^4). Anal. Calcd for $\text{C}_{42}\text{H}_{37}\text{NO}$: C, 88.23; H, 6.52; N, 2.45. Found: C, 86.76; H, 6.54; N, 2.25. The elemental is in general agreement with the proposed structure. The carbon content is 1.5% below the predicted value, which may be partially accounted for by 9-fluorenone-like end groups.

Anionic form of Oligomer 3 (3a). To generate the polyanion for NMR, 0.035 g of **P1b**, 0.014 g of potassium *tert*-butoxide, and 1.0 mL of d_6 -DMSO were stirred under argon for 30 minutes and then transferred to an NMR tube, which was subsequently flushed with argon and capped. UV-Vis (DMSO) λ_{\max} , nm (ϵ): 330 (8.0×10^4), 628 (3.6×10^4).

Oligomer 3. To an oven-dried 100 mL flask was added 0.280 g of (*E*)-4-(9H,9'H-[2,2'-bifluoren]-9-ylidenebromomethyl)-*N,N*-dibutylbenzamide (**12-E**) (0.000429 mol, 1.00 equiv). The flask was flushed with argon and sealed under vacuum and then moved into a nitrogen glove box. In the glove box, 0.192 g of sublimed potassium *tert*-butoxide (0.00171 mol, 4.00 equiv) and 40 mL of anhydrous THF were added. The reaction was heated to 50 °C in a sandbath for 36 h within the glove box. After cooling, the reaction flask was removed from the glove box and 1.40 g of potassium ferricyanide (0.00429 mol, 10.0 equiv) dissolved in 10 mL of saturated aqueous sodium bicarbonate was added. The reaction mixture immediately turned brown. After stirring for 2 minutes, additional water was added and the reaction mixture was transferred to a separatory funnel where it was extracted with DCM (3 x 50 mL). The combined organic layers were washed with water and brine and then dried over sodium sulfate. After removal of the solvent the crude product was dissolve in the minimum amount of DCM needed (approximately 5 mL) and then added drop-wise to a beaker of rapidly stirring methanol (100 mL). The resulting precipitate was isolated by filtration and washed with hexane to obtain 0.190 g (78 %) of a dark red solid. The material (0.025 g in 0.5 mL CDCl_3) showed no resolved NMR signals other than those belonging to solvent. GPC (THF) $M_n = 9.4$ kDa, PDI (M_n/M_w) = 2.1, DP (based on M_n) = 16; IR (KBr, thin film) ν_{\max} (cm^{-1}): 3059, 2957, 2930, 2871, 1720, 1633, 1504, 1445, 1424, 1378, 1297, 1261, 1184, 1100, 1020, 953, 823, 779, 736; UV-Vis (THF) λ_{\max} , nm (ϵ based on repeat unit): 310 (5.3×10^4), 496 (1.5×10^4), 865 (6.0×10^2); EPR: see Figure S1. Anal. Calcd for $\text{C}_{42}\text{H}_{36}\text{NO}^{\cdot}$: C, 88.38; H, 6.36; N, 2.45. Found: C, 85.56; H, 6.39; N, 2.39. The elemental is in general agreement with the proposed structure, although the carbon content is 2.8% below the predicted value. The lower than expected carbon content may be partially accounted for by 9-fluorenone-like end groups and decomposition products formed by reaction of the radical with oxygen. Further combustion analysis found no detectable level of bromide (the limit of detection was estimated to be 0.1%).

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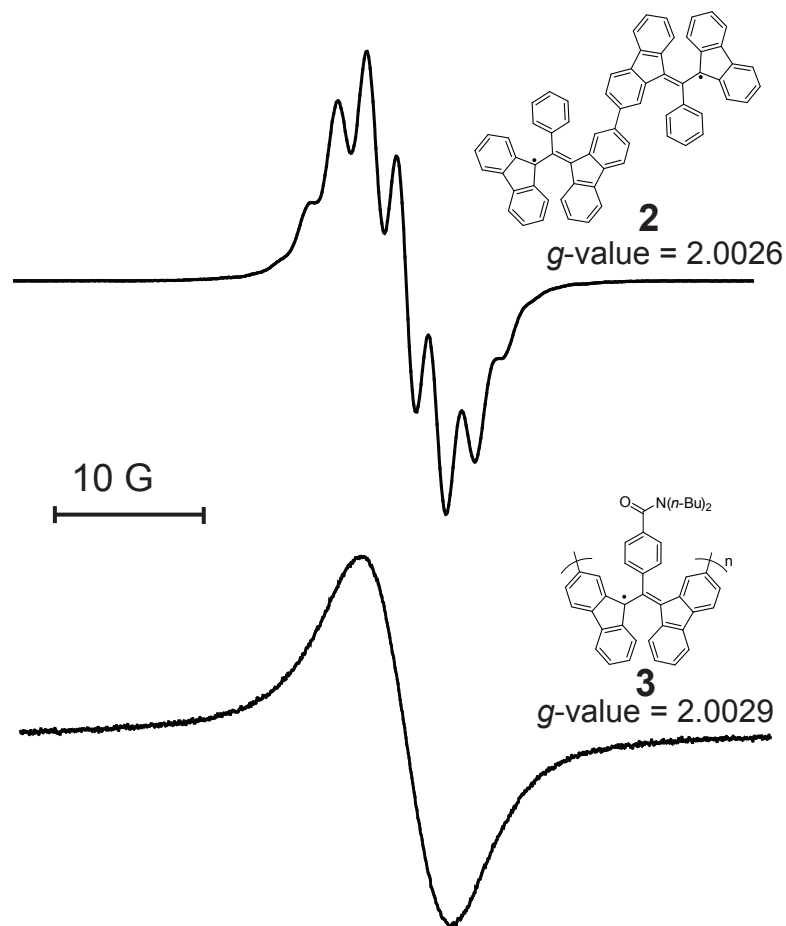


Figure S1.

The 9 GHz solution EPR spectrum of **2** (toluene, 0.01 mM) and **3** (THF, 0.05 mM) at room temperature is shown. The spectrum of **2** could be reasonably well simulated with hyperfine couplings ($A = 2.0$ G) to 8 protons, but further simulation to take into account the through-bond coupling between the radicals was not investigated. Additionally, the sample may contain monoradical impurities due to incomplete radical generation or decomposition from reaction with oxygen. Using the Evans NMR method corrected for superconducting magnets¹ to estimate paramagnetic susceptibility, we measured an effective magnetic moment of 1.18 BM on a per radical basis (2.36 per molecule). Comparing the measured value with the theoretical value of 1.73 BM for a monoradical, we estimate there are 68% of the unpaired electrons that would be expected for a pure sample of **2**. The spectrum of **3** appeared broad even at lower concentrations. Using the same method as above, we measured an effective magnetic moment of 1.36 BM per repeat unit, which results in an estimated 78% of the expected spins if the end groups of the oligomers are ignored. General parameters: power, 0.20 mW; modulation frequency, 100.00 kHz; modulation amplitude, 1.00 G.

1. (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, 42, 791.

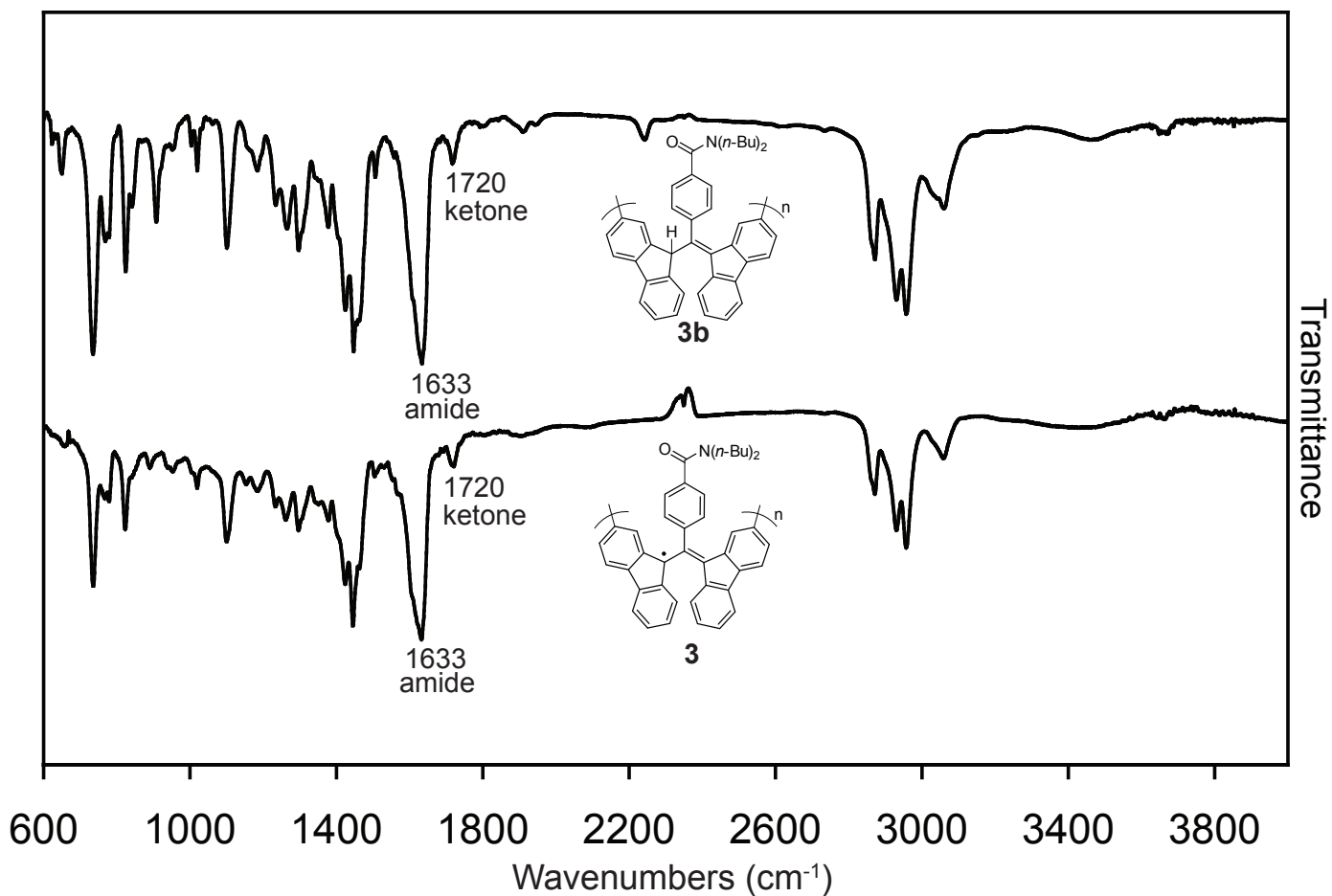


Figure S2.

IR spectra of **3b** (top) and **3** (bottom) showing the presence of ketone impurities that we ascribe to 9-fluorenone end-groups. Samples were prepared by drop-casting from a concentrated solution of the material onto KBr plates.

Table S1.

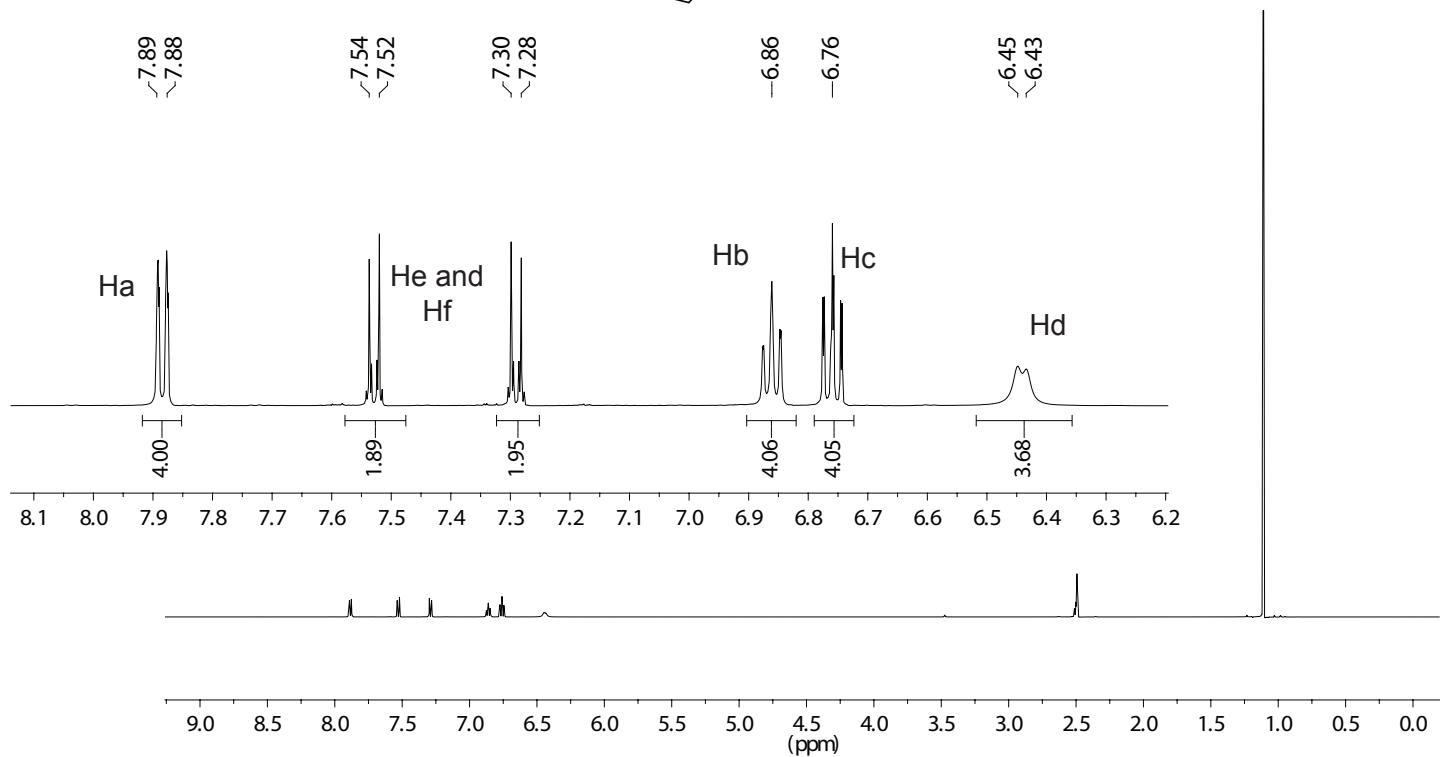
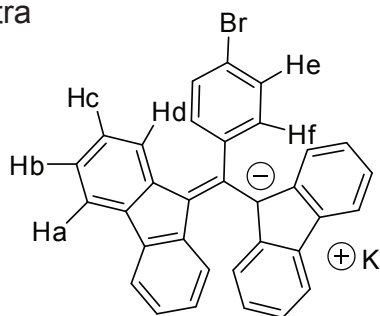
Monomer	Solvent^a	Base/Additive^b	<i>M_n</i> (kDa)^c	<i>M_w</i> (kDa)^c	<i>M_w</i> / <i>M_n</i>
12-<i>E</i>	THF	Li <i>Ot</i> -Bu	1.8	2.3	1.3
12-<i>E</i>	THF	Na <i>Ot</i> -Bu	3.9	4.9	1.3
12-<i>E</i>	THF	K <i>Ot</i> -Bu	4.7	6.2	1.3
12-<i>E</i>	THF	Mg(<i>Ot</i> -Bu) ₂	NR	****	****
12-<i>E</i>	THF	Ba(<i>Ot</i> -Bu) ₂	2.0	2.8	1.4
12-<i>E</i>	THF	K <i>Ot</i> -Bu/ZnCl ₂	3.2	4.6	1.4
12-<i>E</i>	DMA	Li <i>Ot</i> -Bu	3.3	4.3	1.3
12-<i>E</i>	DMA	Na <i>Ot</i> -Bu	4.4	6.0	1.4
12-<i>E</i>	DMA	K <i>Ot</i> -Bu	4.3	5.6	1.3
12-<i>E</i>	DMA	Mg(<i>Ot</i> -Bu) ₂	1.9	2.0	1.1
12-<i>E</i>	DMA	Ba(<i>Ot</i> -Bu) ₂	3.1	3.9	1.3
12-<i>E</i>	DMA	K <i>Ot</i> -Bu/ZnCl ₂	2.7	5.3	2.0
12-<i>Z</i>	DMA	K <i>Ot</i> -Bu	3.8	5.0	1.3
12-<i>E/Z</i> (1:1)	DMA	K <i>Ot</i> -Bu	4.3	6.1	1.4
12-<i>E</i>	DMF	Li <i>Ot</i> -Bu	4.3	6.4	1.5
12-<i>E</i>	DME	Na <i>Ot</i> -Bu	3.0	3.9	1.3

^aReactions were performed with a monomer concentration of 10 mM. ^b4.0 equivalents of base were used; 2.0 equivalents of ZnCl₂. ^cDetermined with GPC (DMF) against polystyrene standards. Note: GPC (DMF) analysis of polyanions generally gave smaller *M_n*'s compared to GPC (THF) analysis of the radical or protonated forms. The GPC (DMF) results were compared to each other for optimization of reaction conditions, but we cannot comment on the accuracy of the absolute values obtained. The anionic oligomers could not be analyzed using THF as the eluent due to instability in that solvent (air oxidation).

Br-BDPA anion NMR Spectra

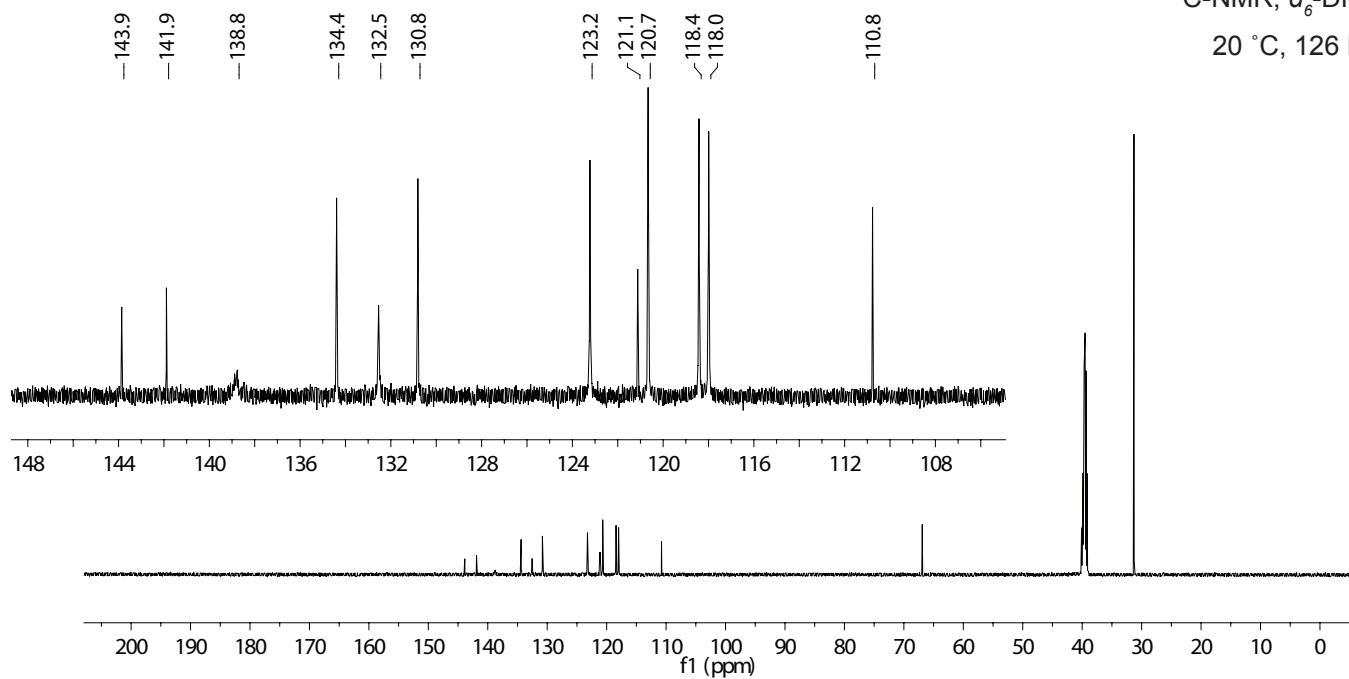
$^1\text{H-NMR}$, $d_6\text{-DMSO}$

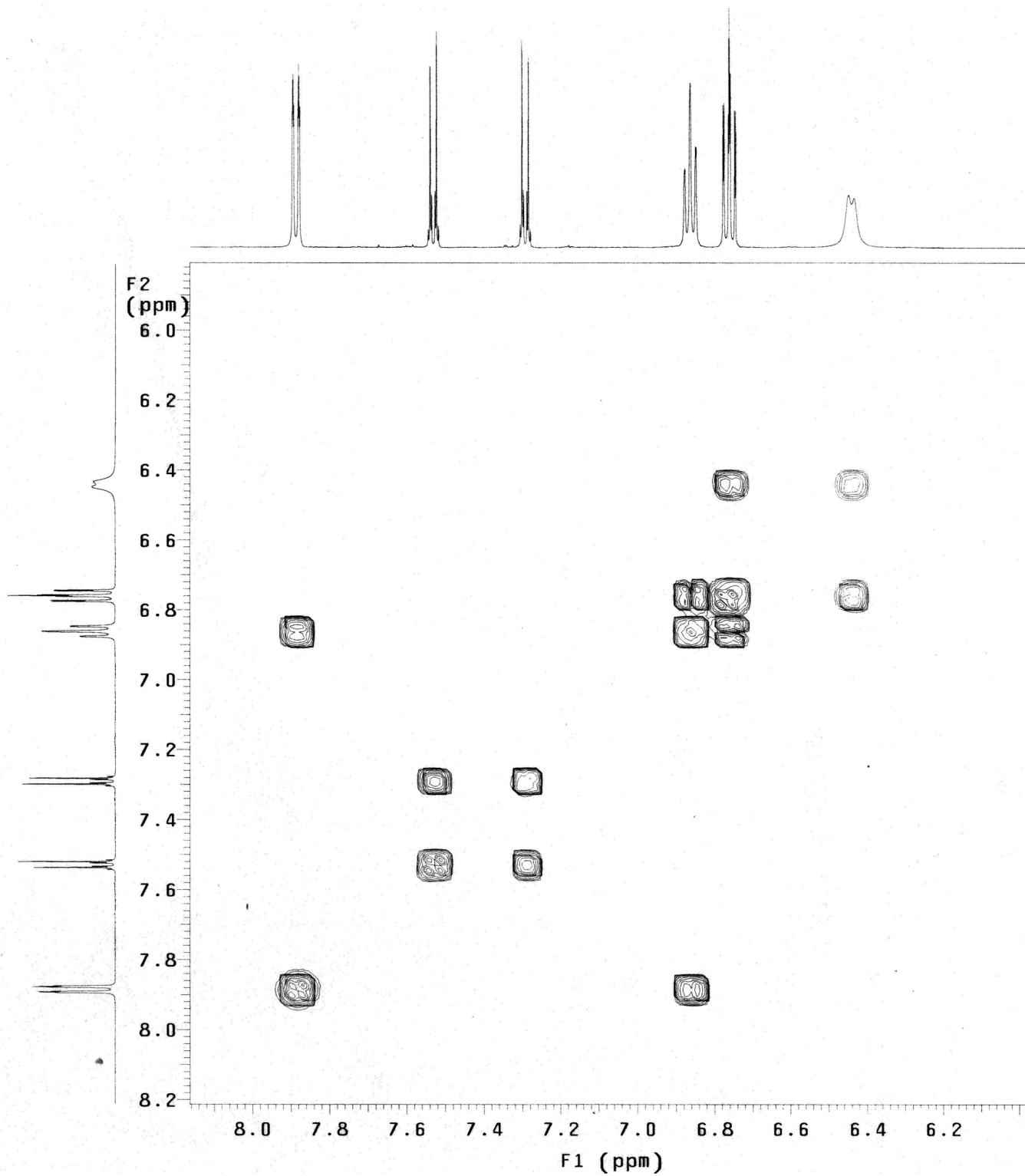
20 °C, 500 MHz



$^{13}\text{C-NMR}$, $d_6\text{-DMSO}$

20 °C, 126 MHz

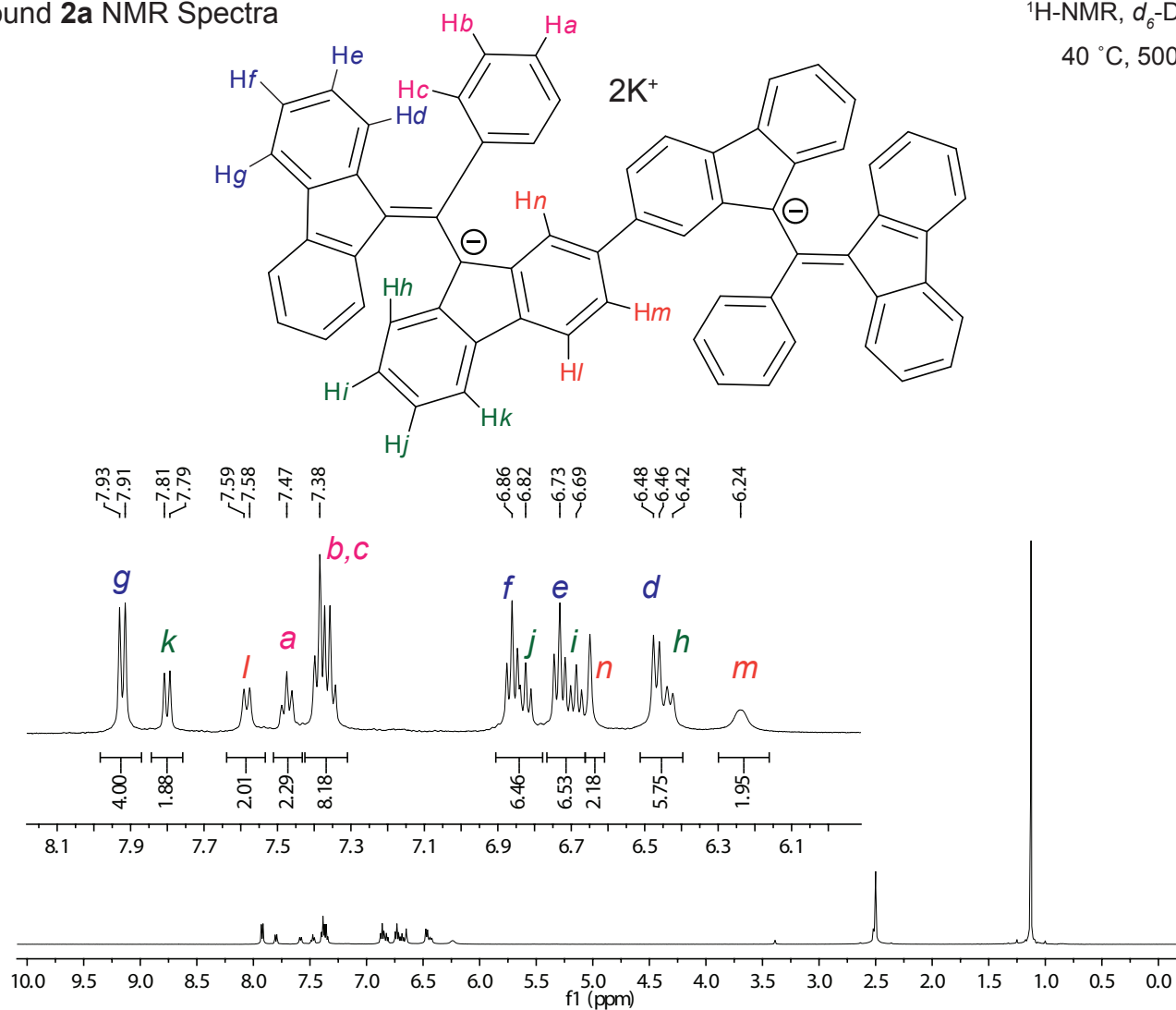




Compound **2a** NMR Spectra

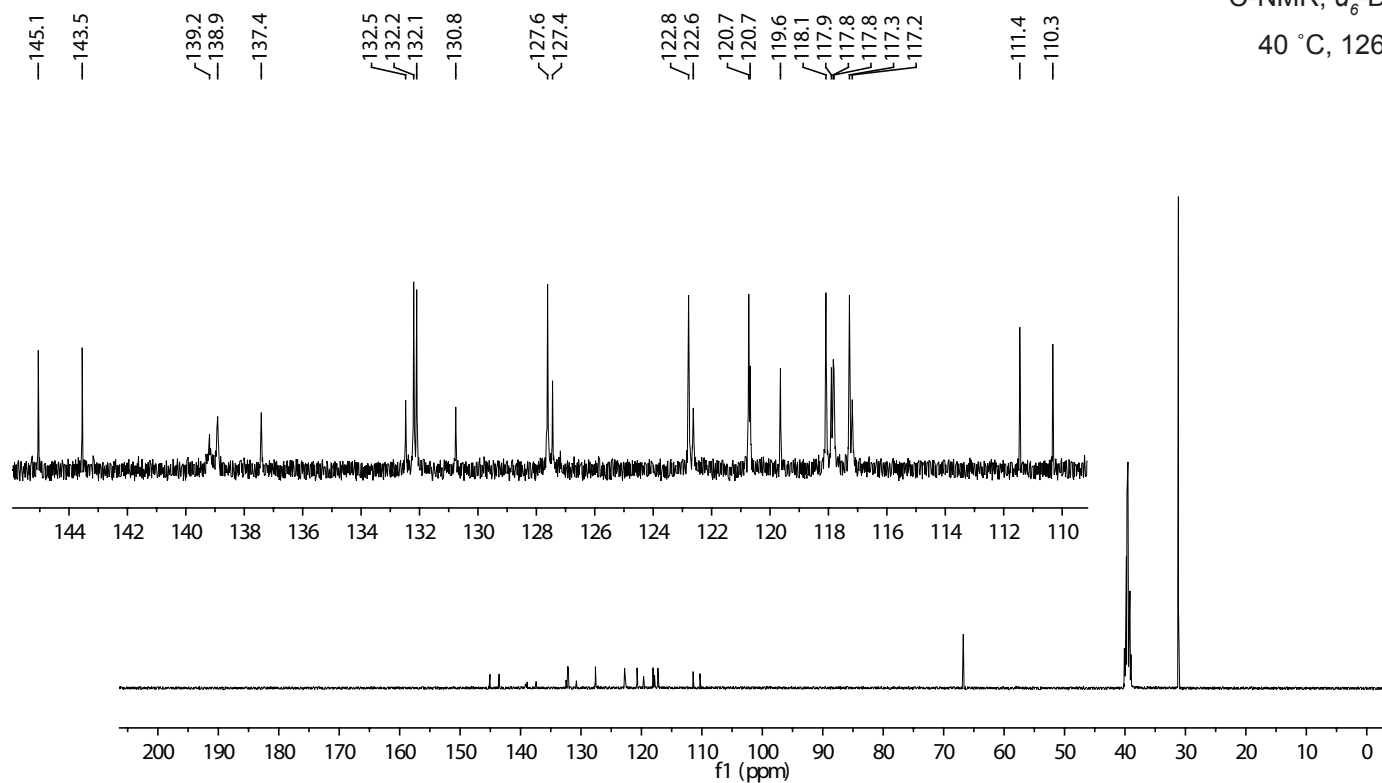
$^1\text{H-NMR}$, $d_6\text{-DMSO}$

40 °C, 500 MHz



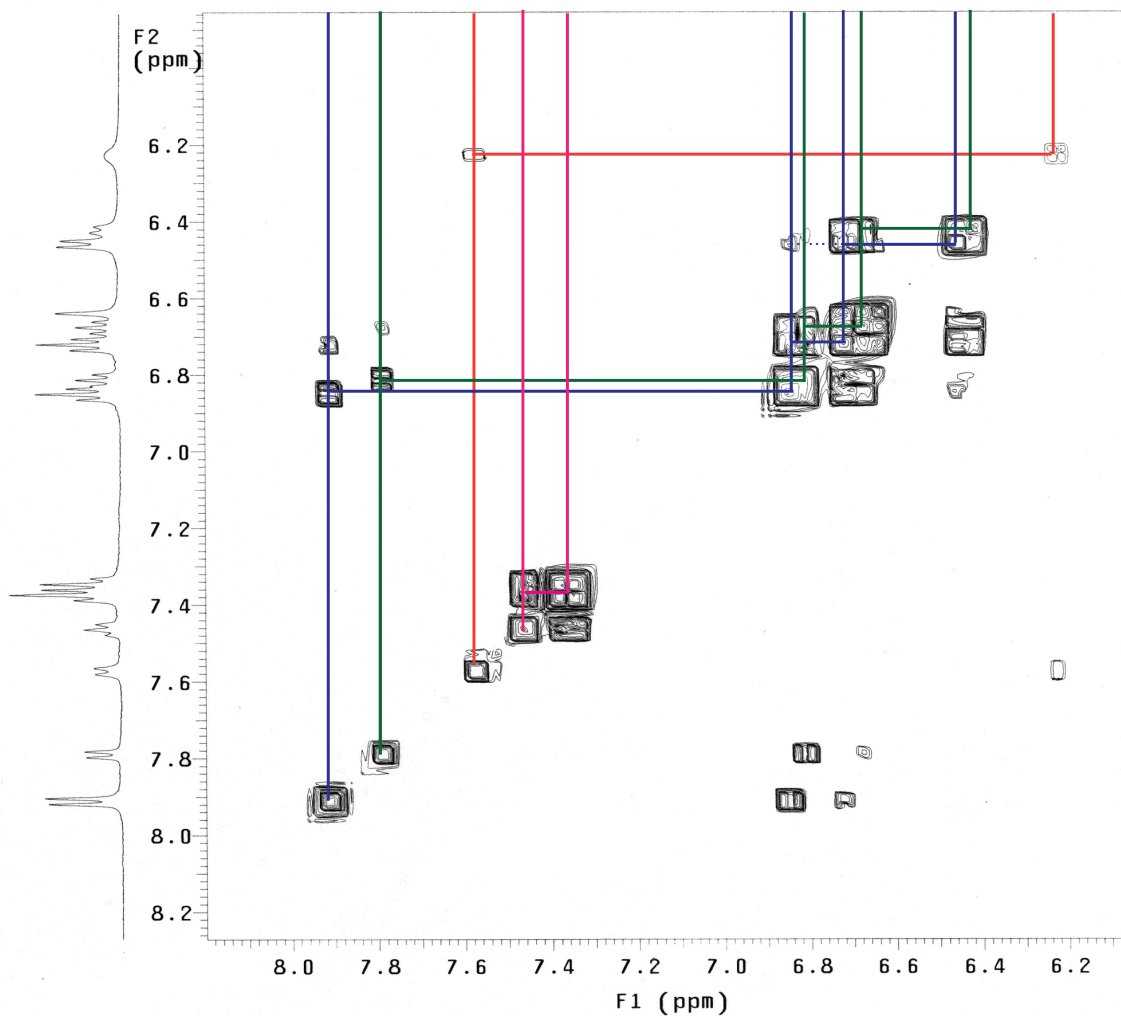
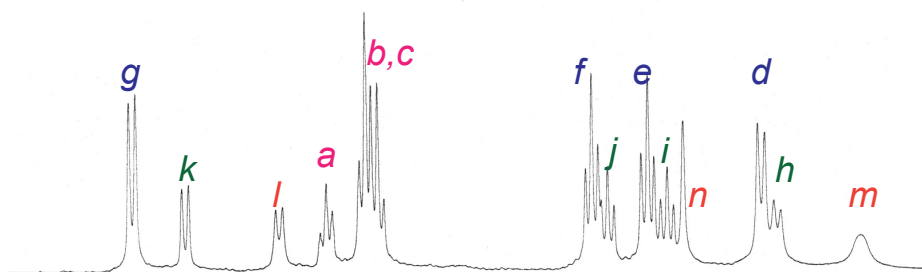
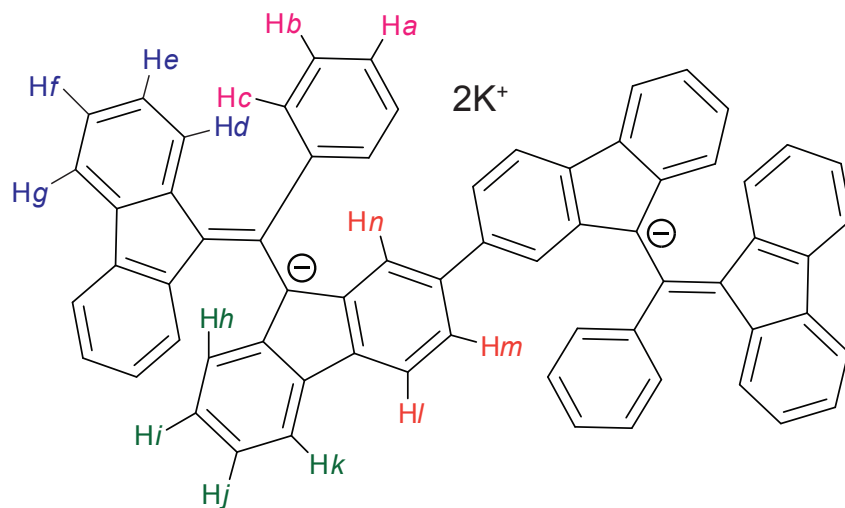
$^{13}\text{C-NMR}$, $d_6\text{-DMSO}$

40 °C, 126 MHz

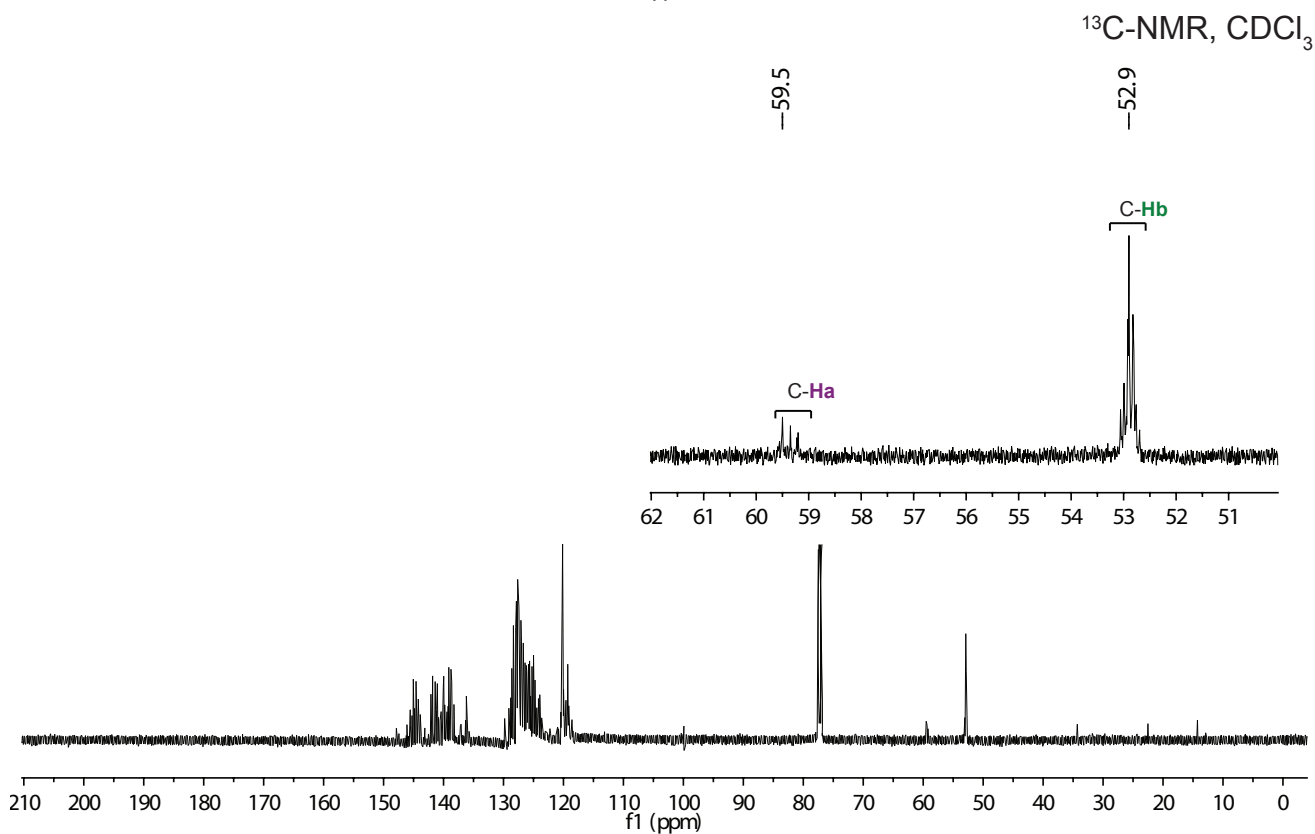
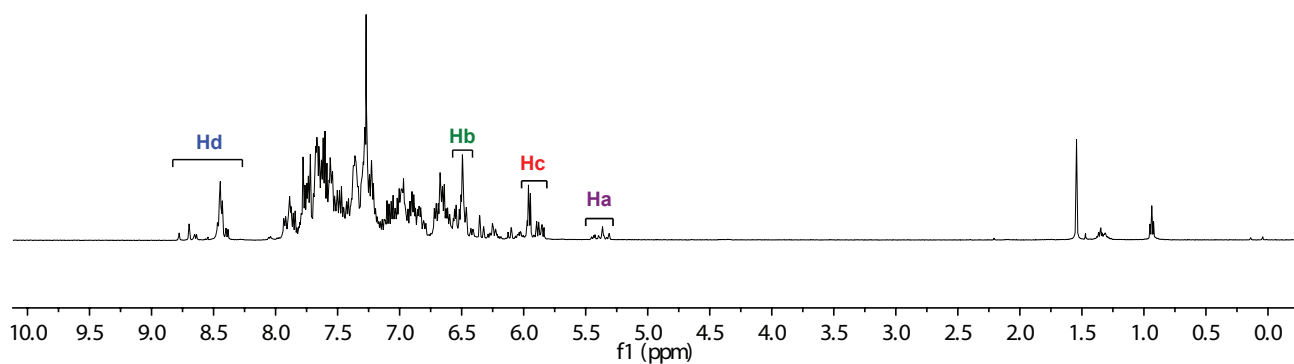
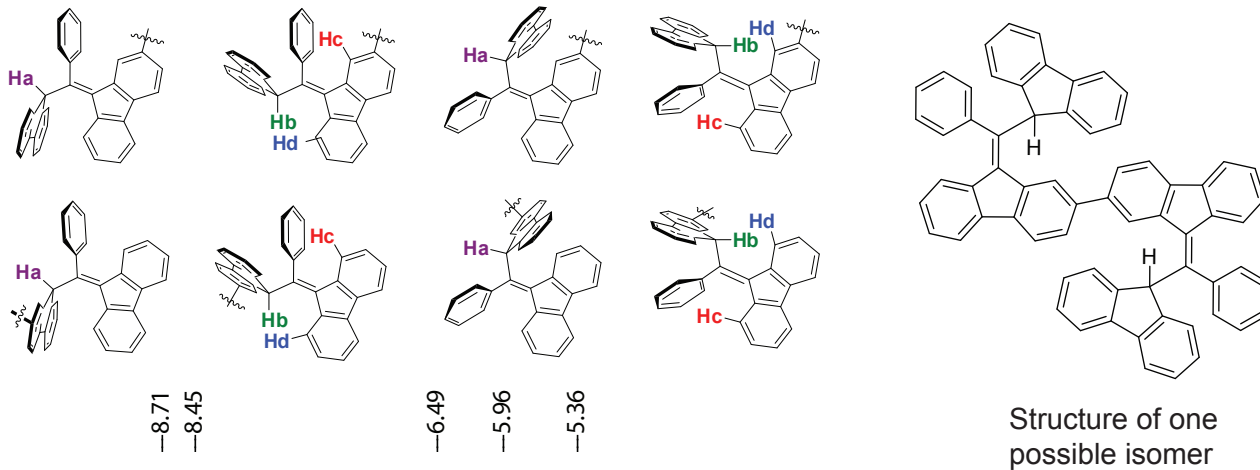


Compound **2a** 2D-NMR Spectra - gCOSY

$^1\text{H-NMR}$, $d_6\text{-DMSO}$
40 °C, 500 MHz

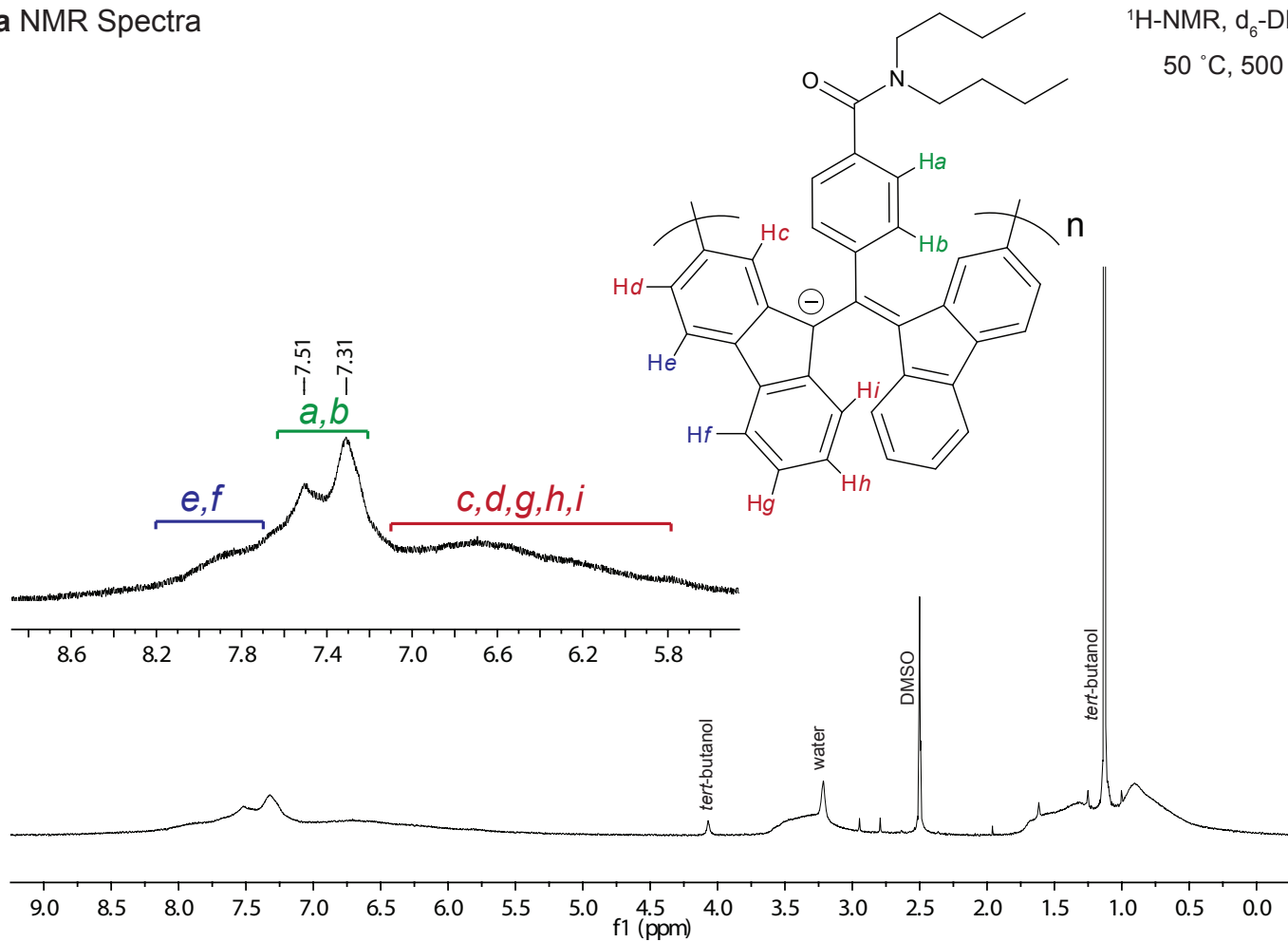


General proton chemical shifts for proposed tautomers, isomers, and rotamers

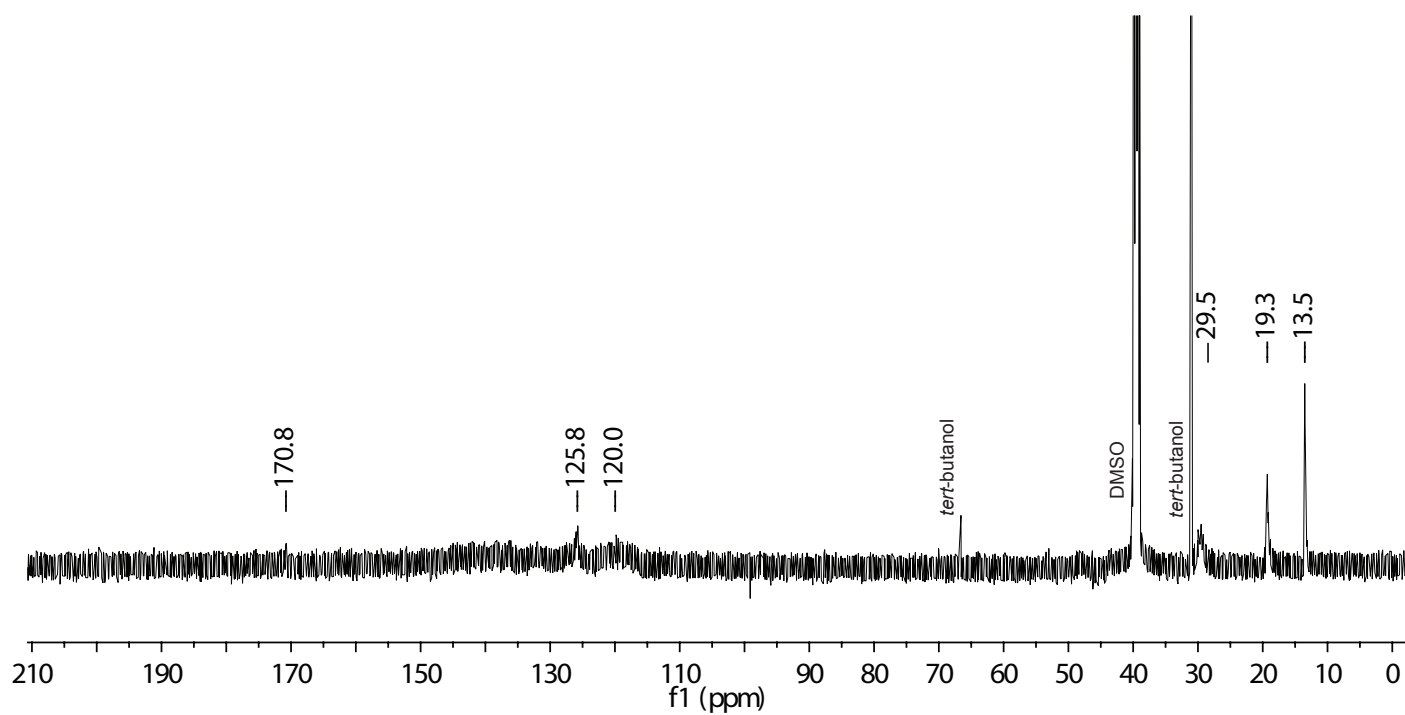


3a NMR Spectra

$^1\text{H-NMR}$, $\text{d}_6\text{-DMSO}$
 50 °C, 500 MHz

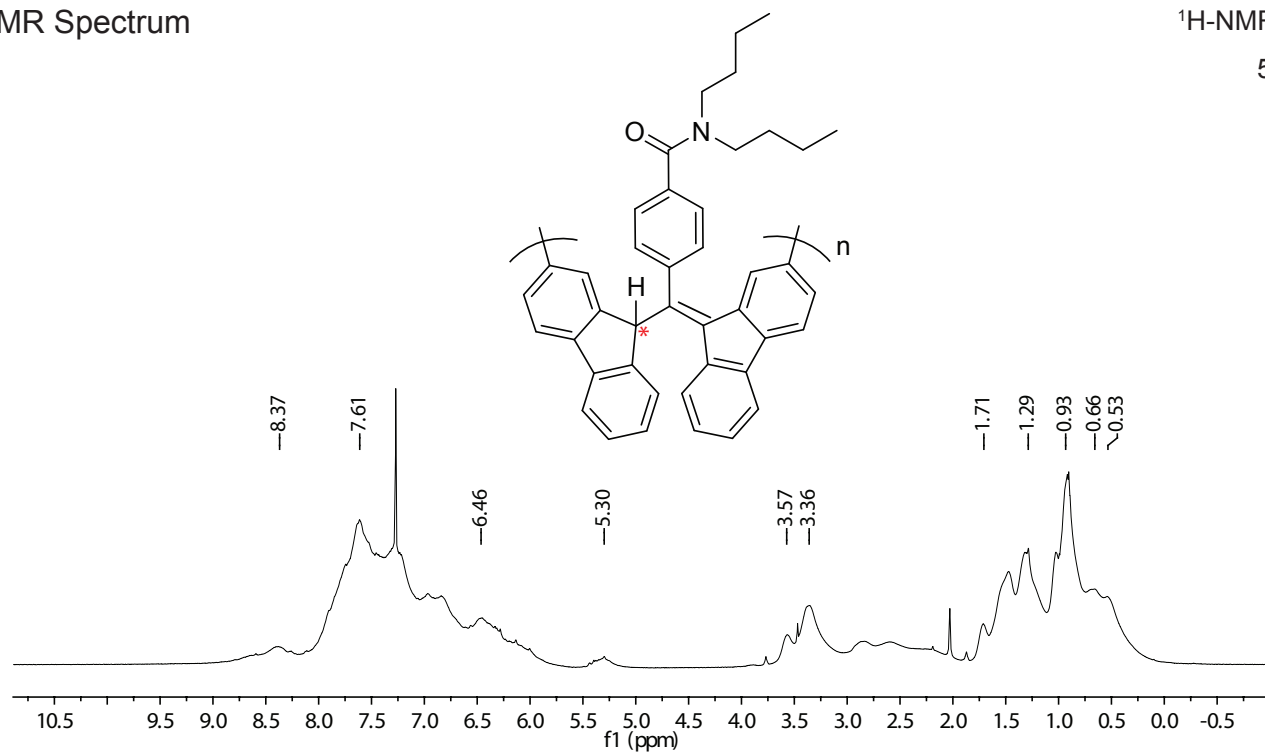


$^{13}\text{C-NMR}$, $\text{d}_6\text{-DMSO}$
 50 °C, 126 MHz

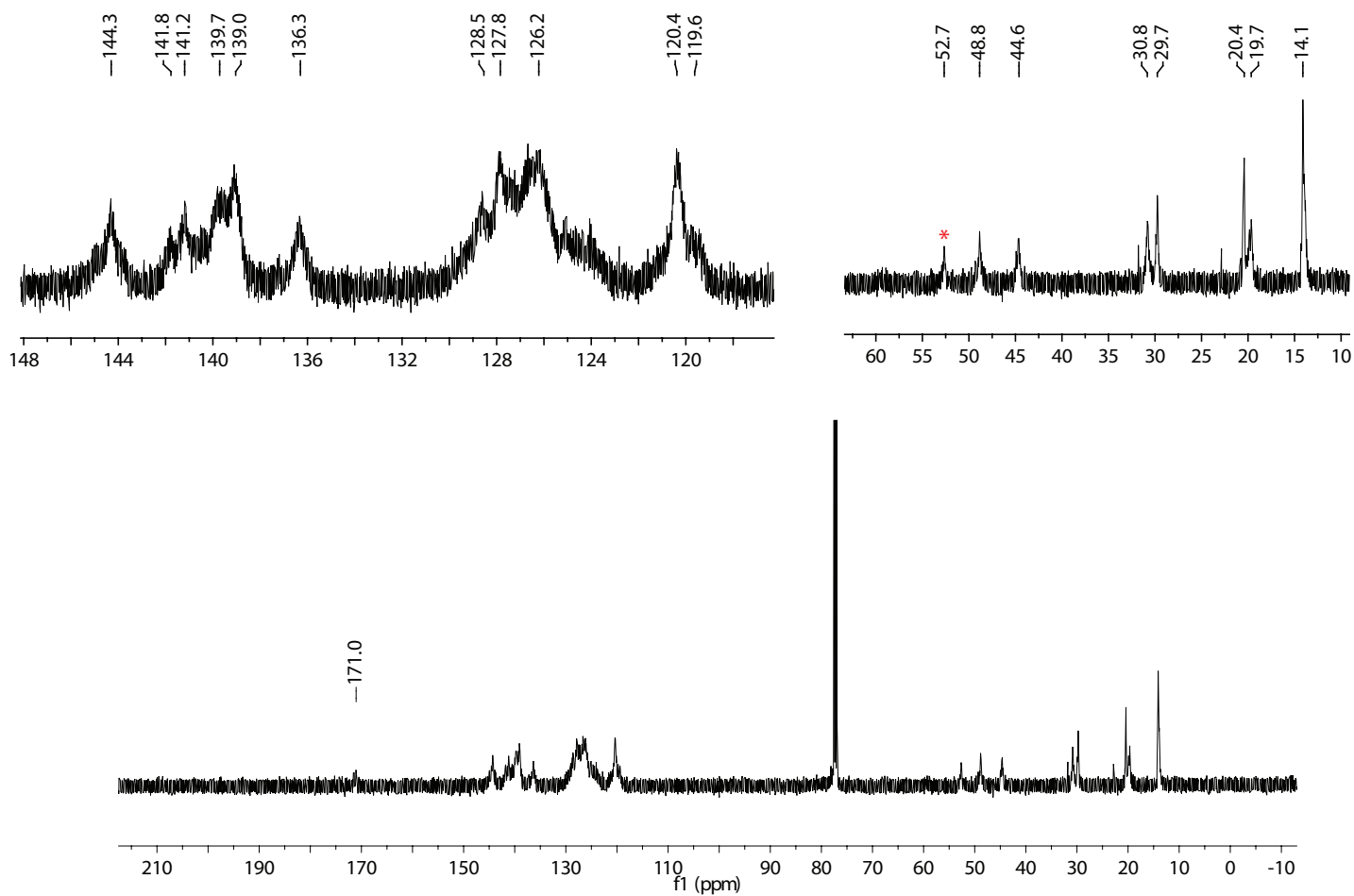


3b NMR Spectrum

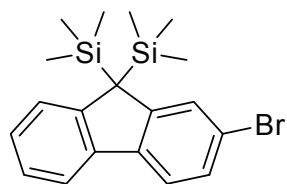
$^1\text{H-NMR}$, CDCl_3
500 MHz



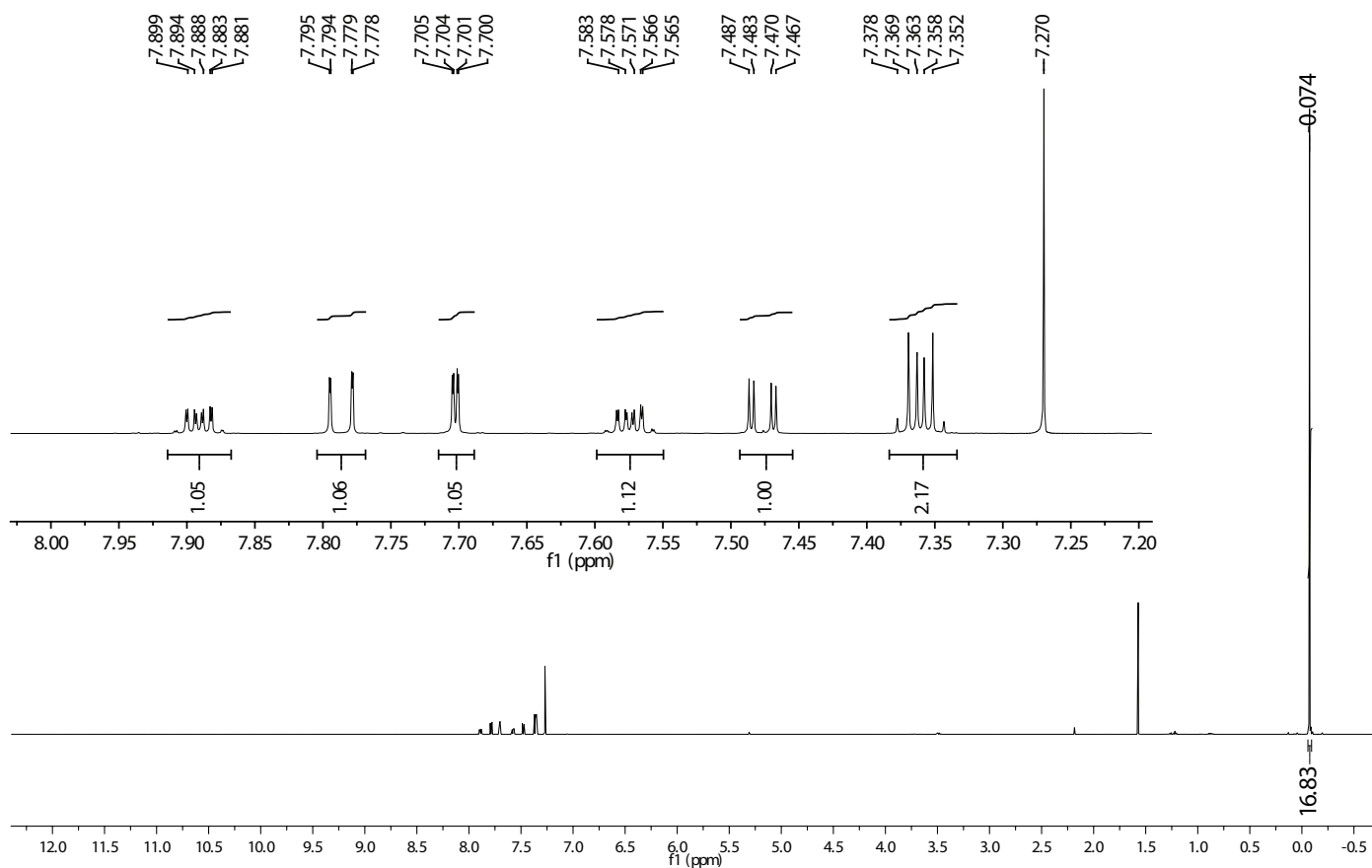
$^{13}\text{C-NMR}$, CDCl_3
126 MHz



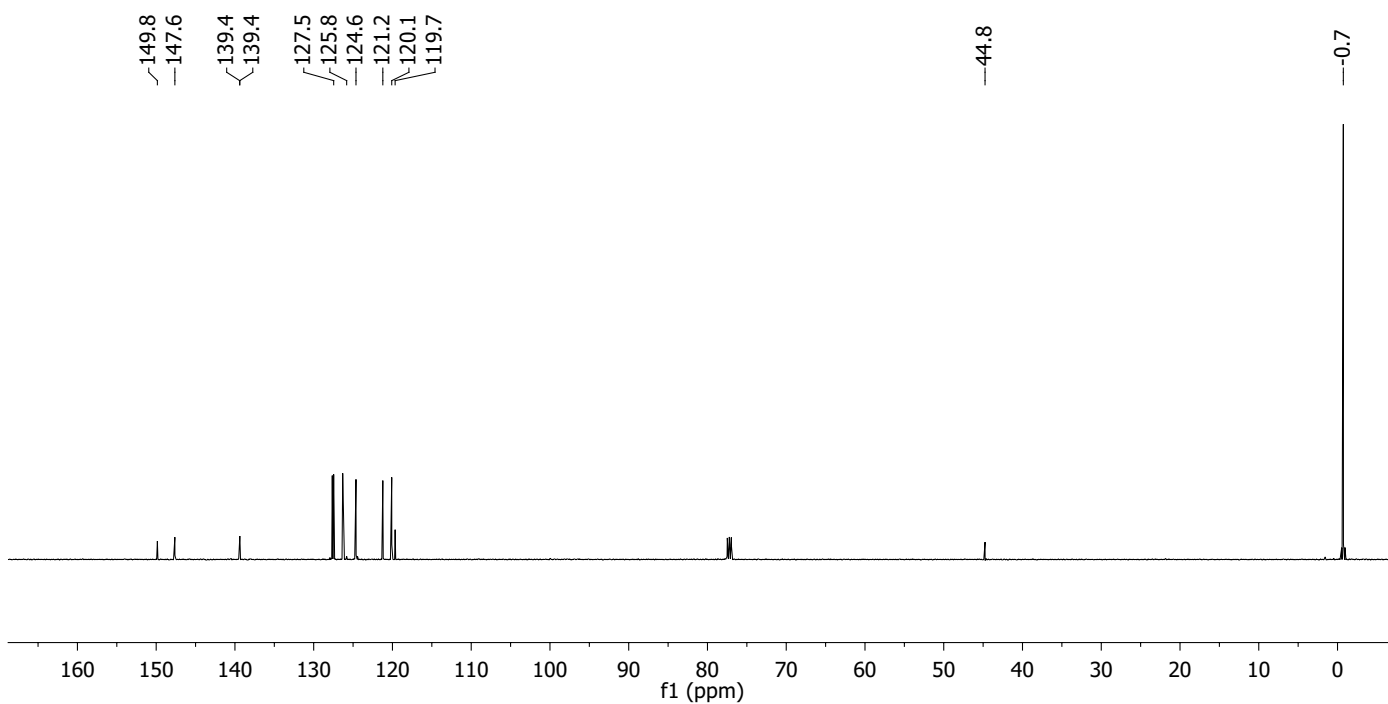
Compound 4 NMR Spectra



¹H-NMR, CDCl₃
500 MHz



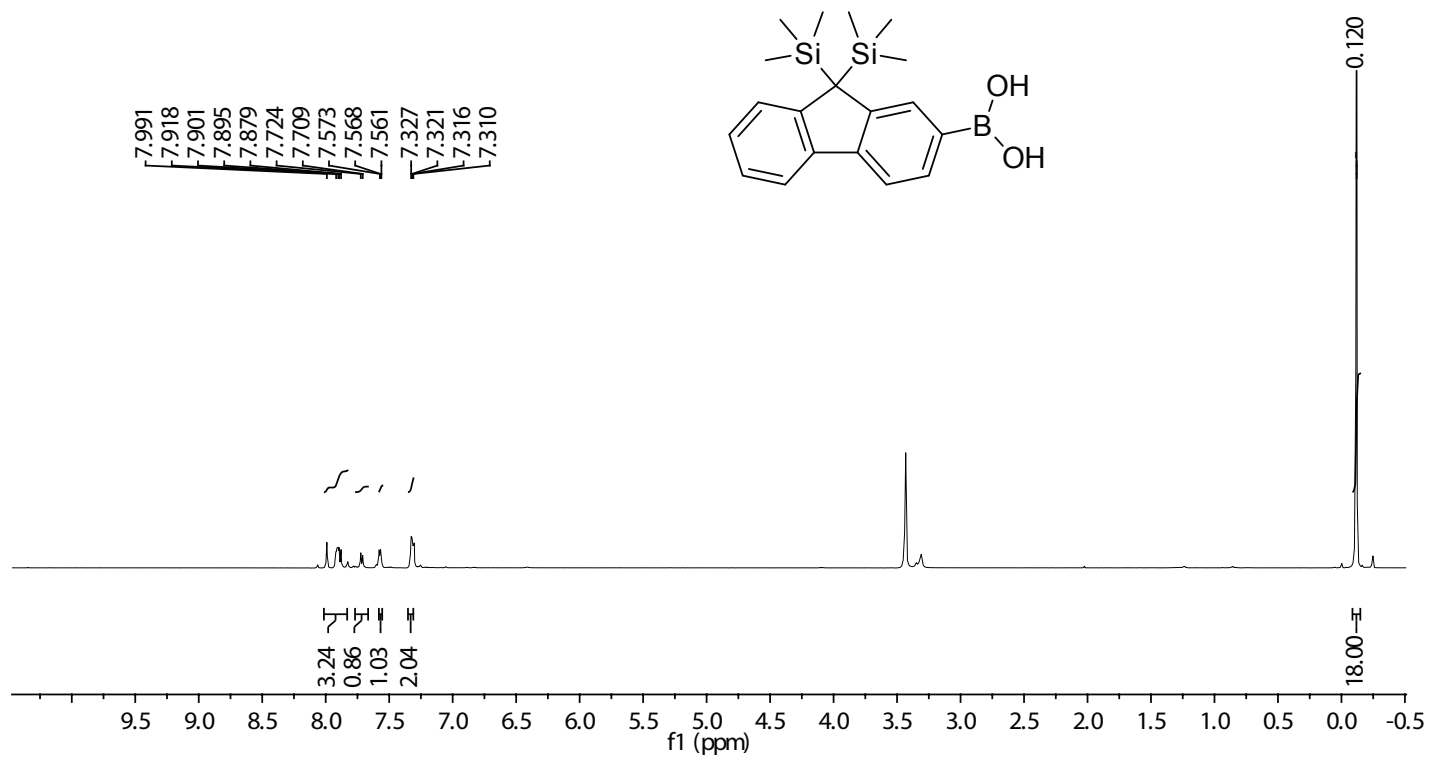
¹³C-NMR, CDCl₃
126 MHz



Compound **5** NMR Spectra

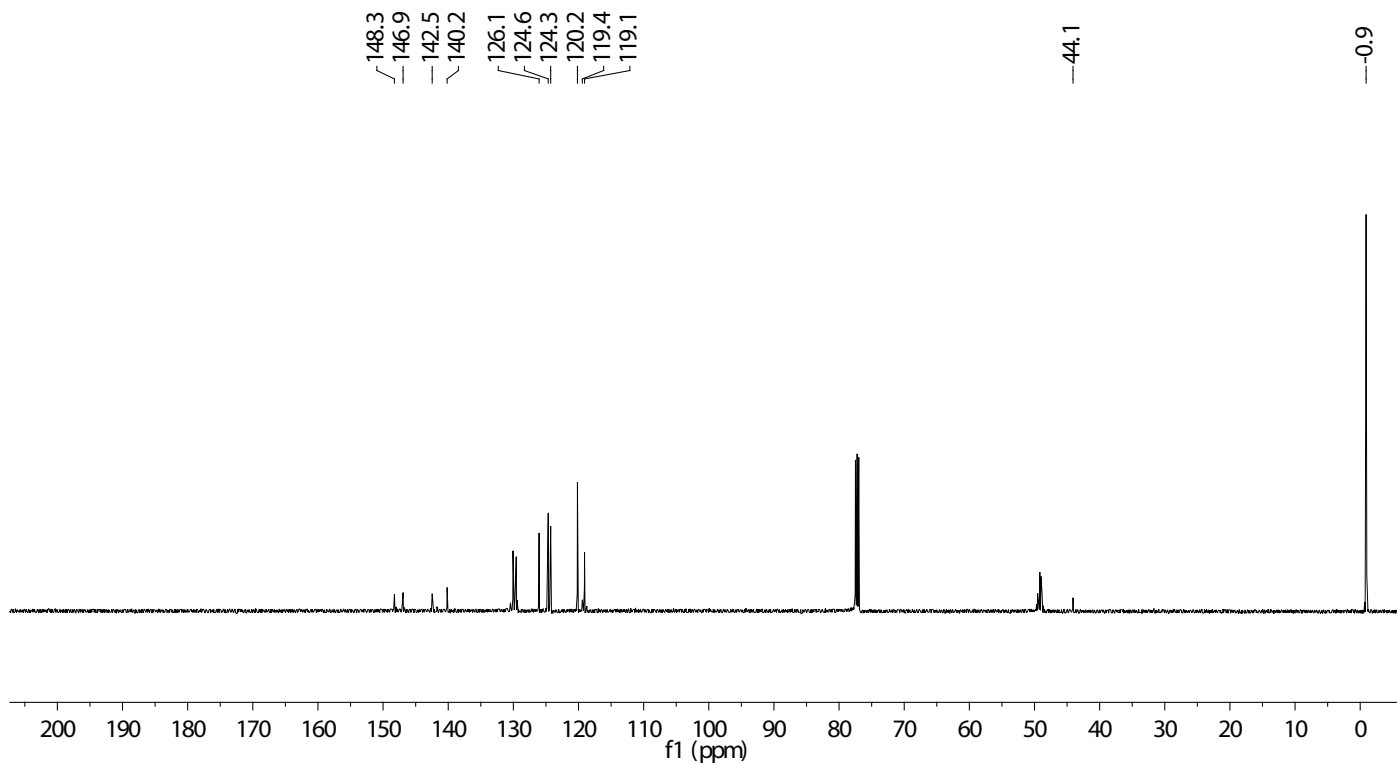
$^1\text{H-NMR}$, CD_3OD

500 MHz



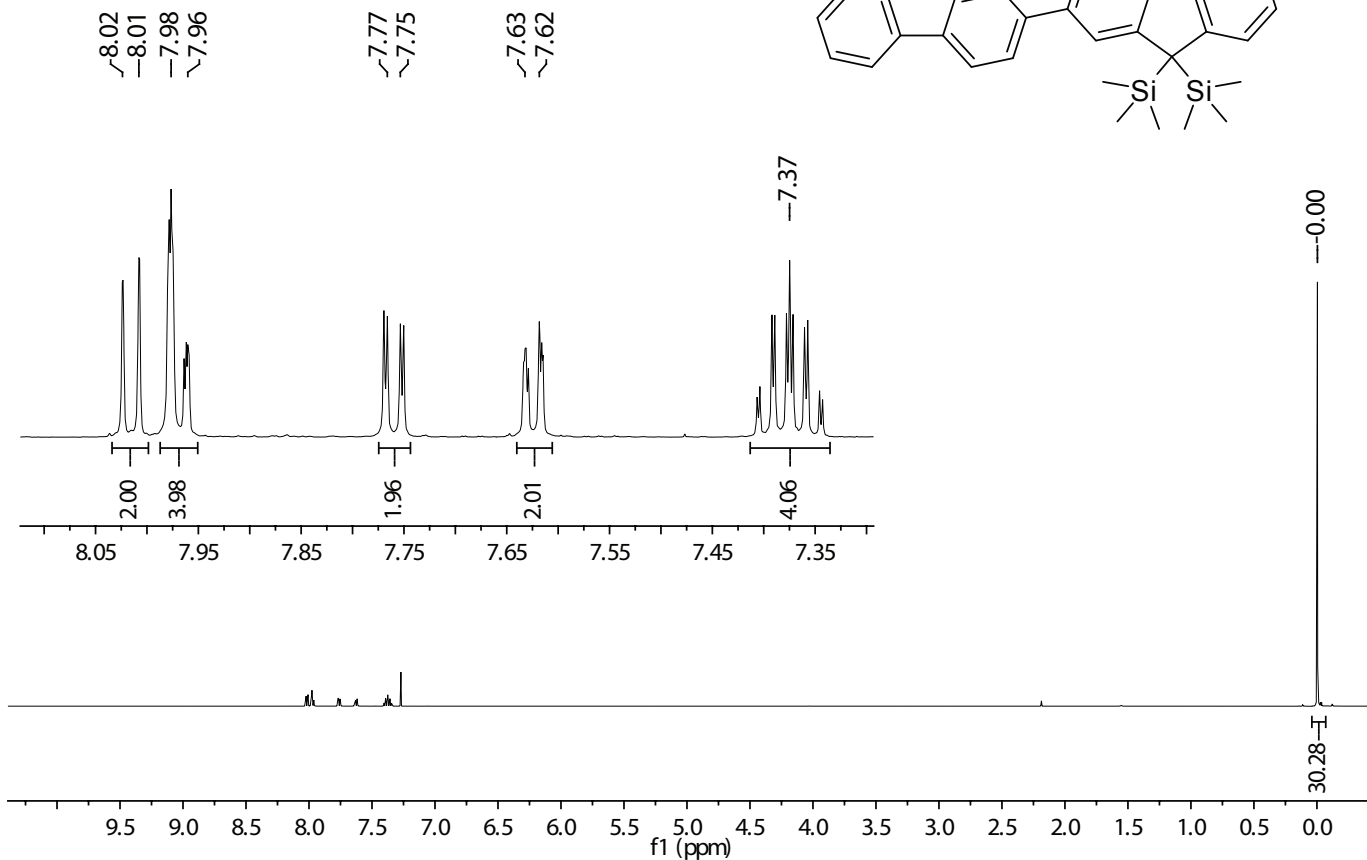
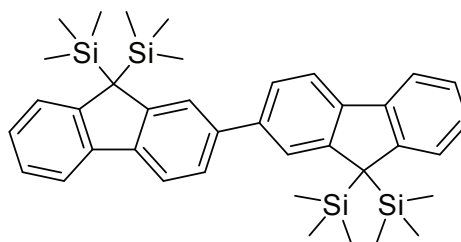
$^{13}\text{C-NMR}$, $\text{CD}_3\text{OD}/$

CDCl_3 126 MHz

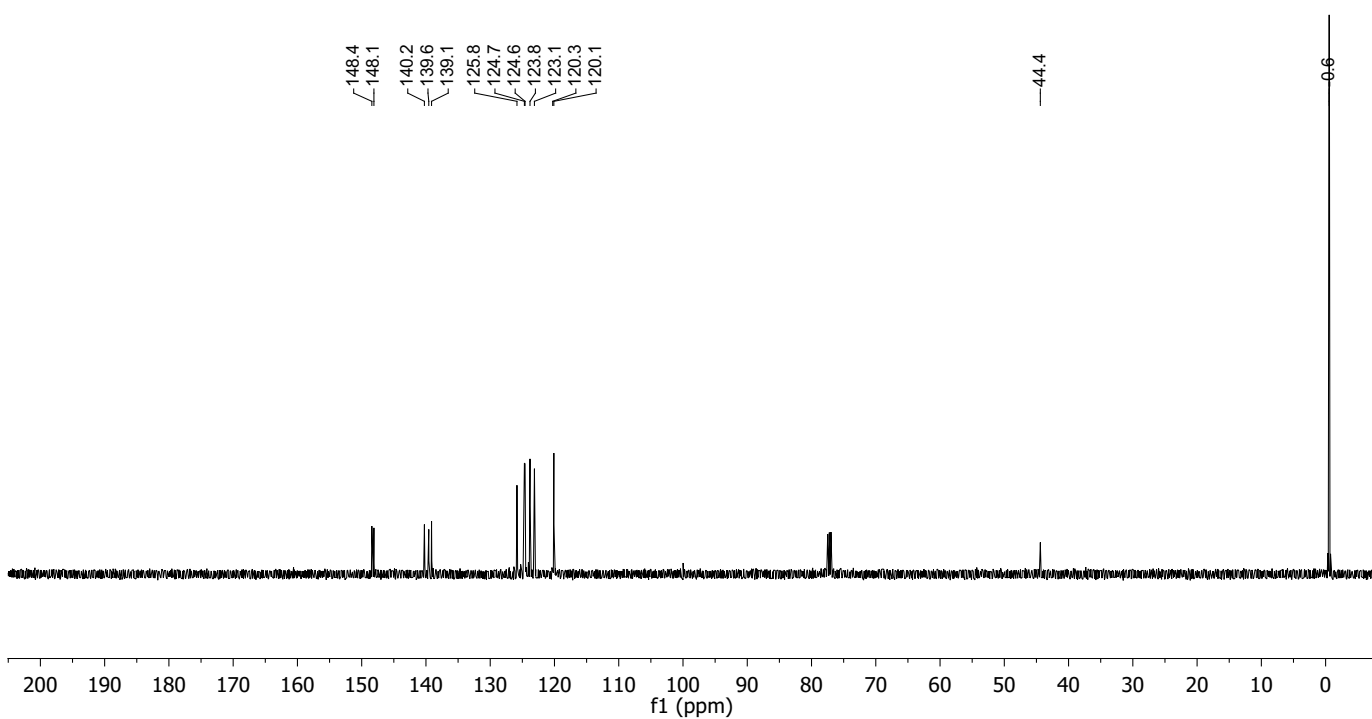


Compound **6** NMR Spectra

¹H-NMR, CDCl₃
500 MHz

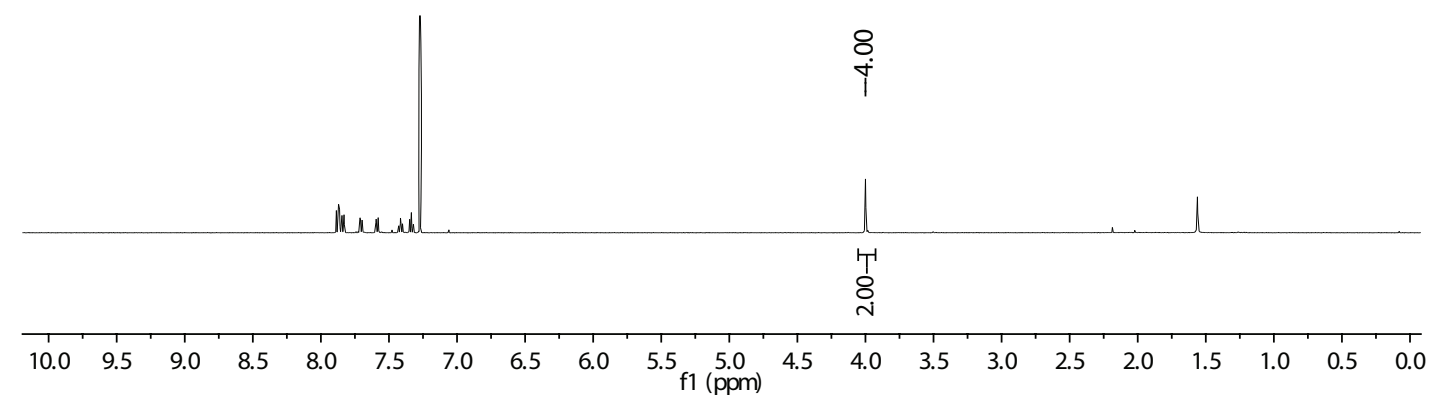
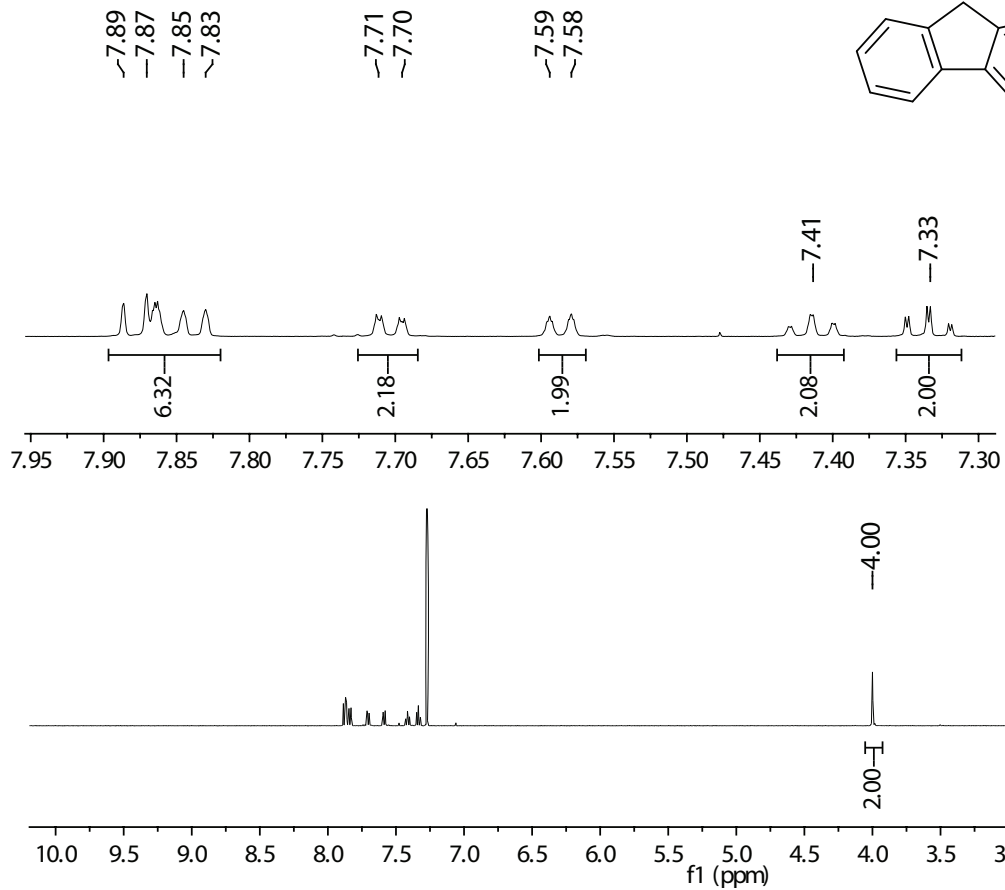
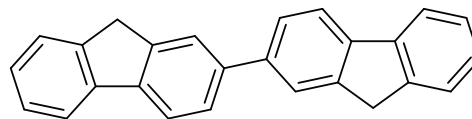


¹³C-NMR, CDCl₃
126 MHz

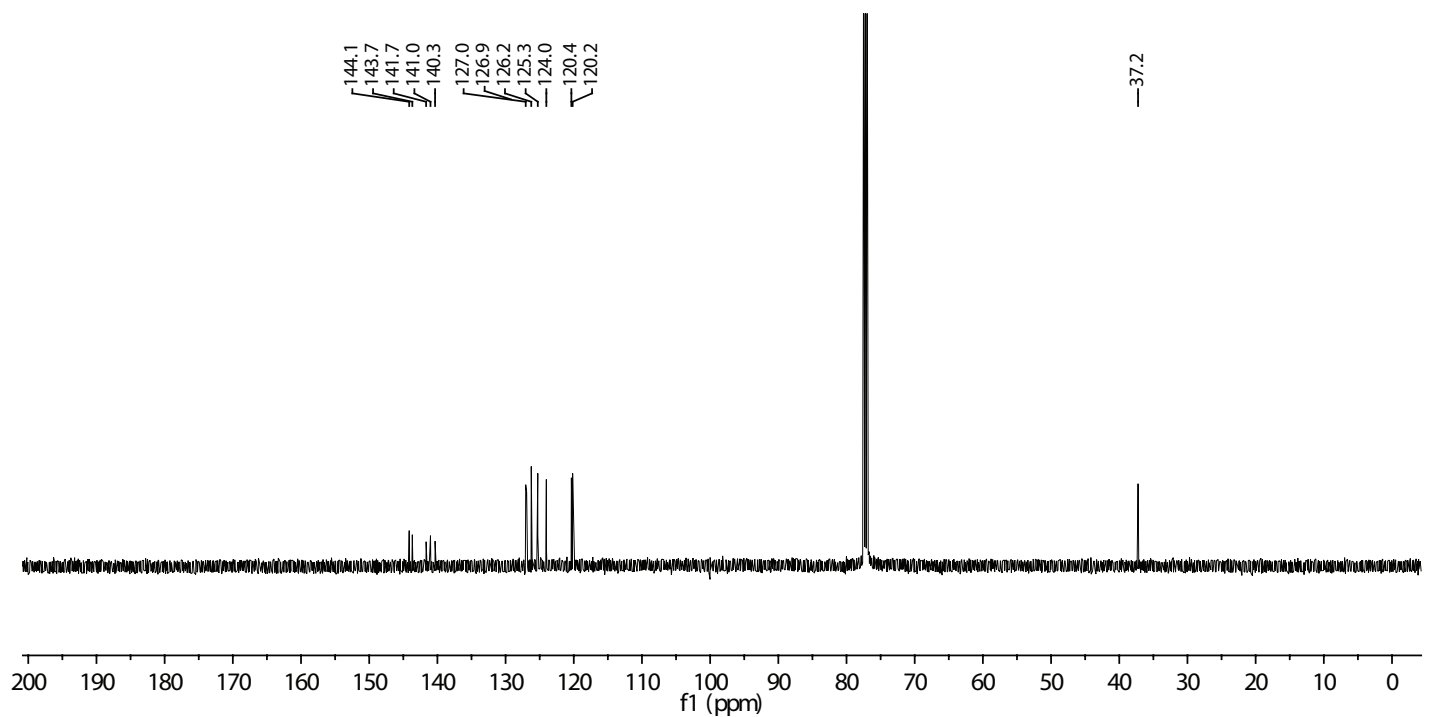


Compound 7 NMR Spectra

¹H-NMR, CDCl₃
500 MHz

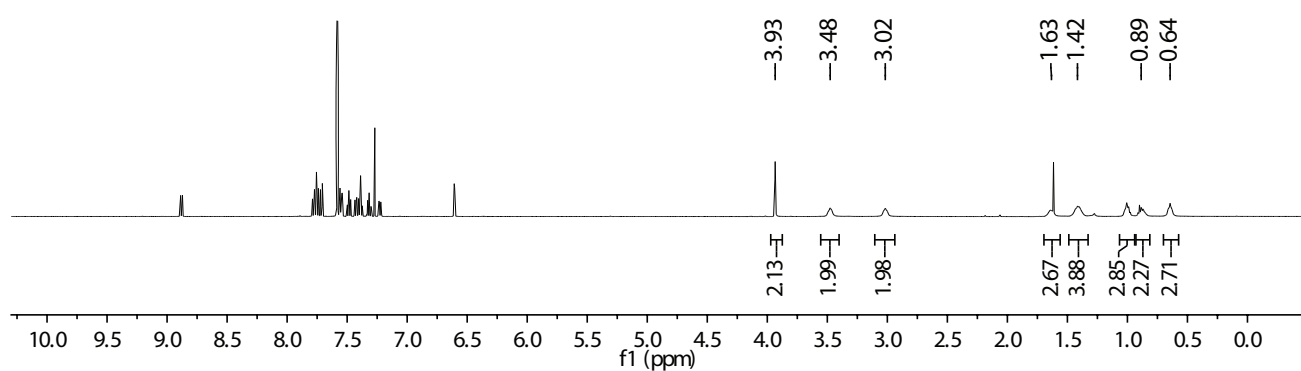
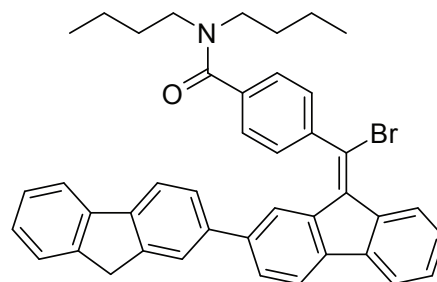
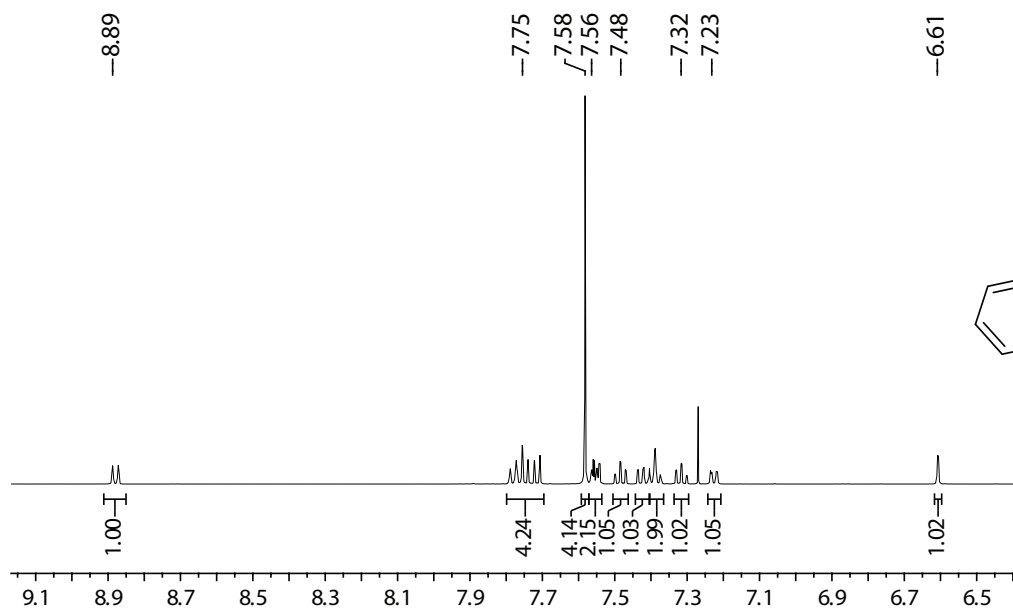


¹³C-NMR, CDCl₃
126 MHz

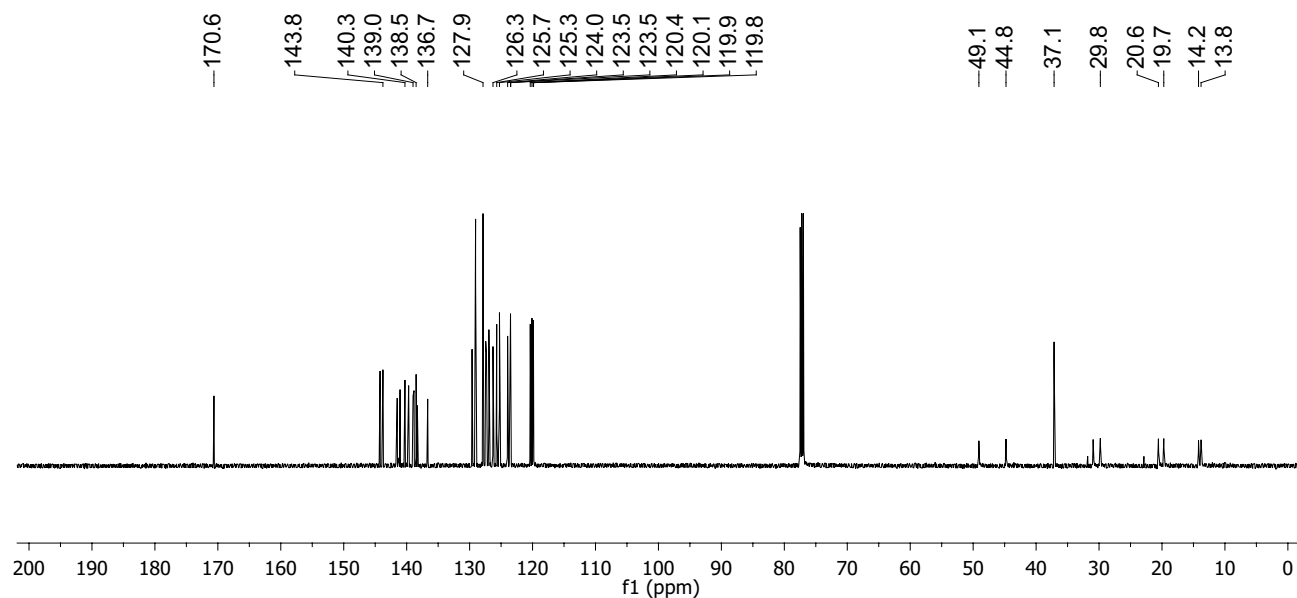


Compound **9-E** NMR Spectra

¹H-NMR, CDCl₃
500 MHz

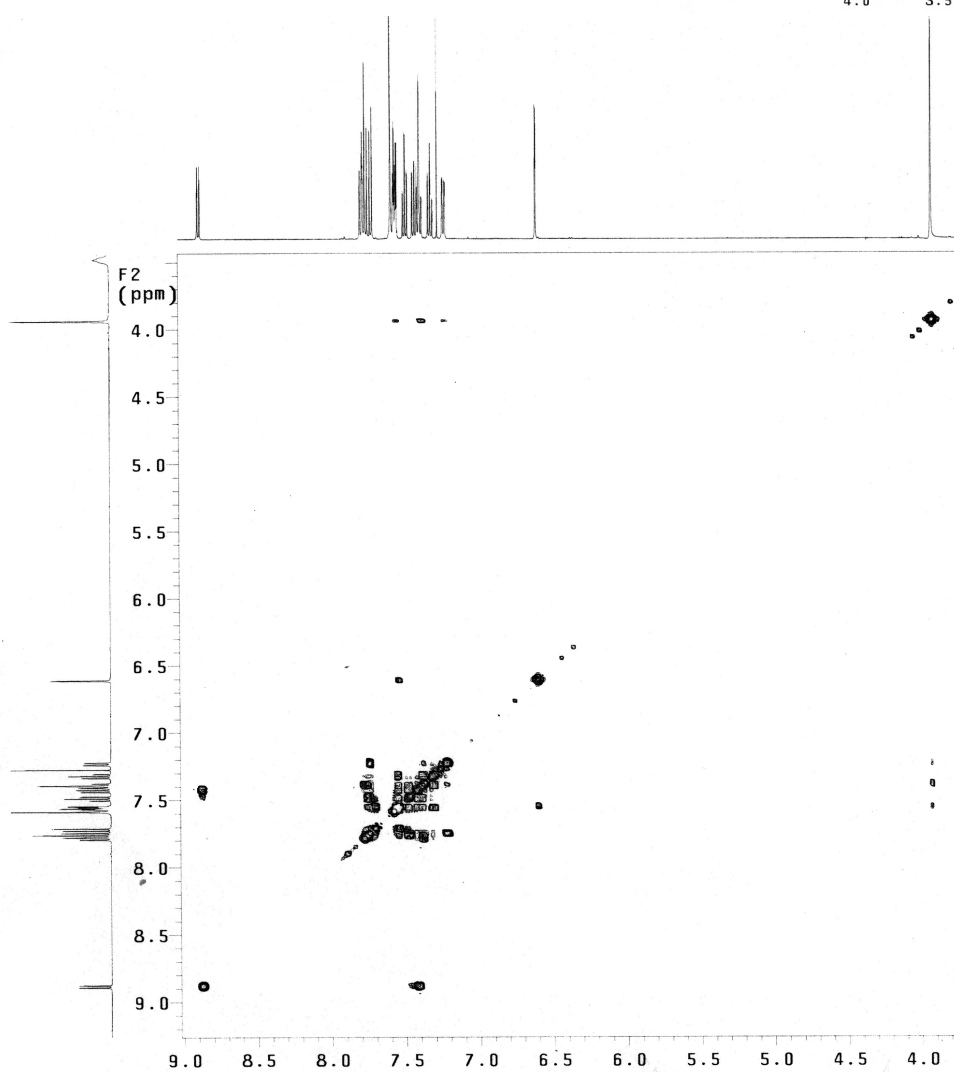
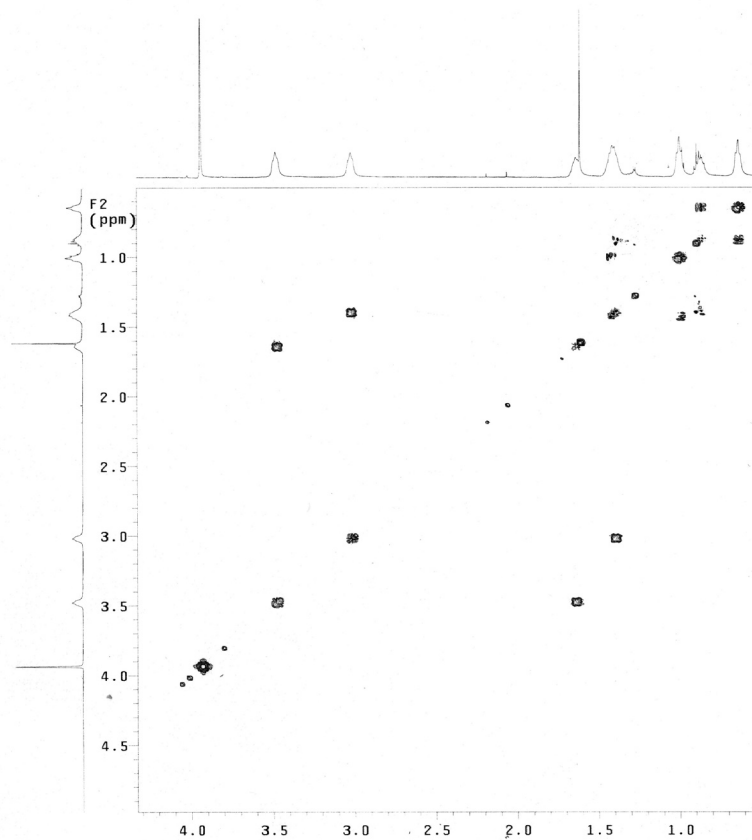


¹³C-NMR, CDCl₃
126 MHz



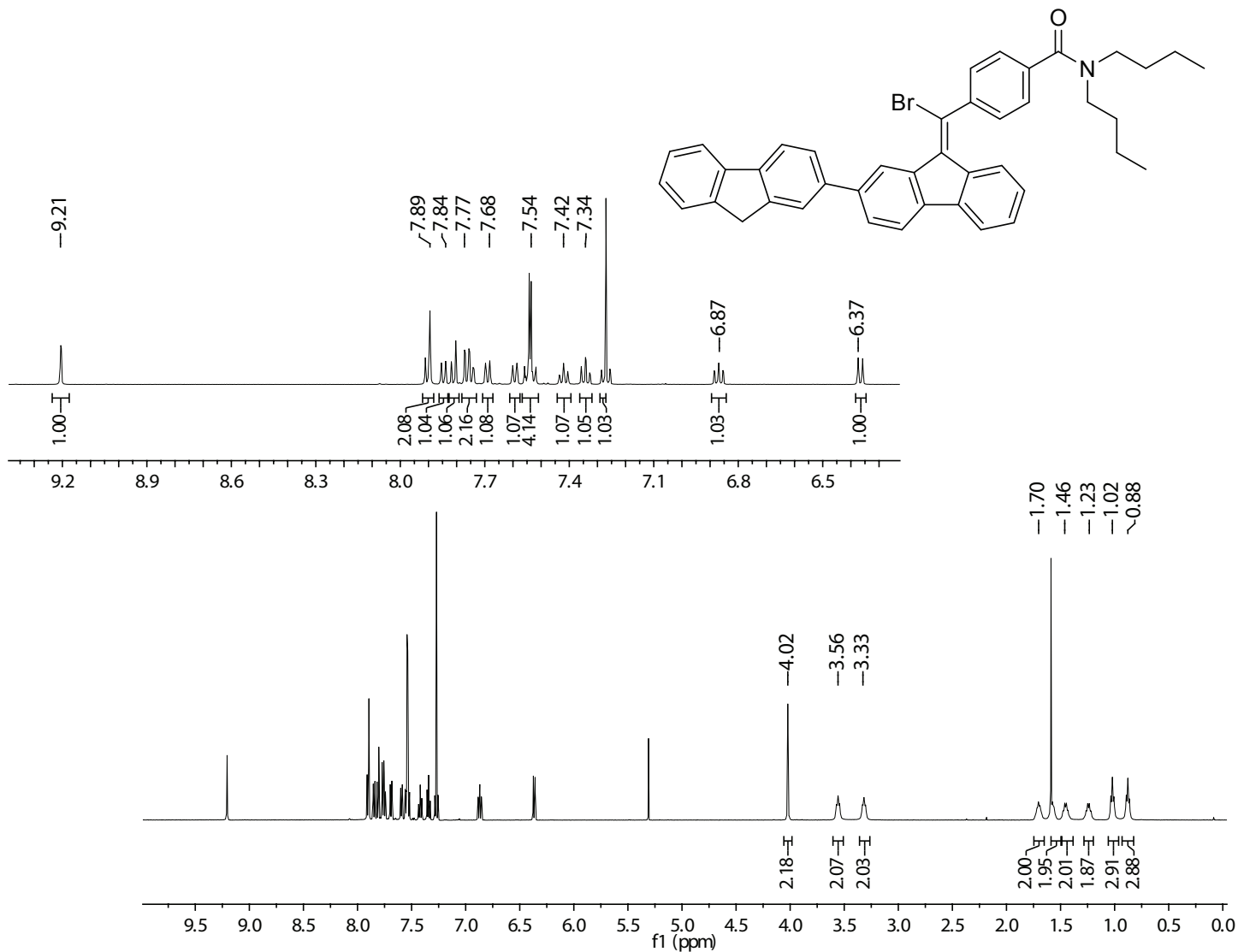
Compound **9-E** 2D-NMR Spectra - gCOSY

$^1\text{H-NMR}$, CDCl_3
500 MHz

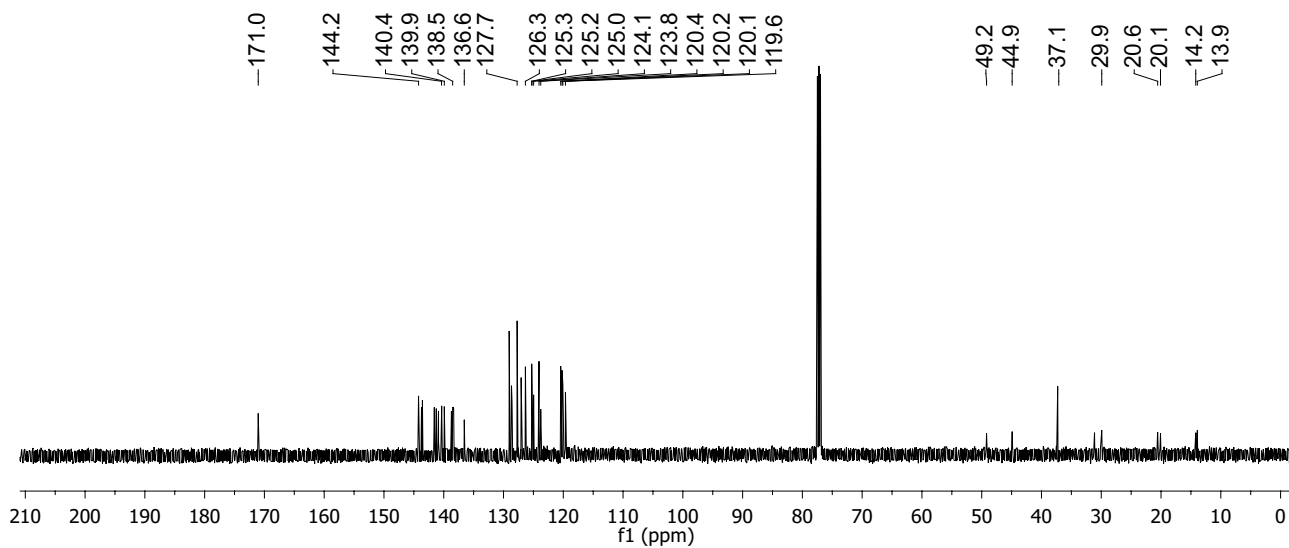


Compound **9-Z** NMR Spectra

¹H-NMR, CDCl₃
500 MHz

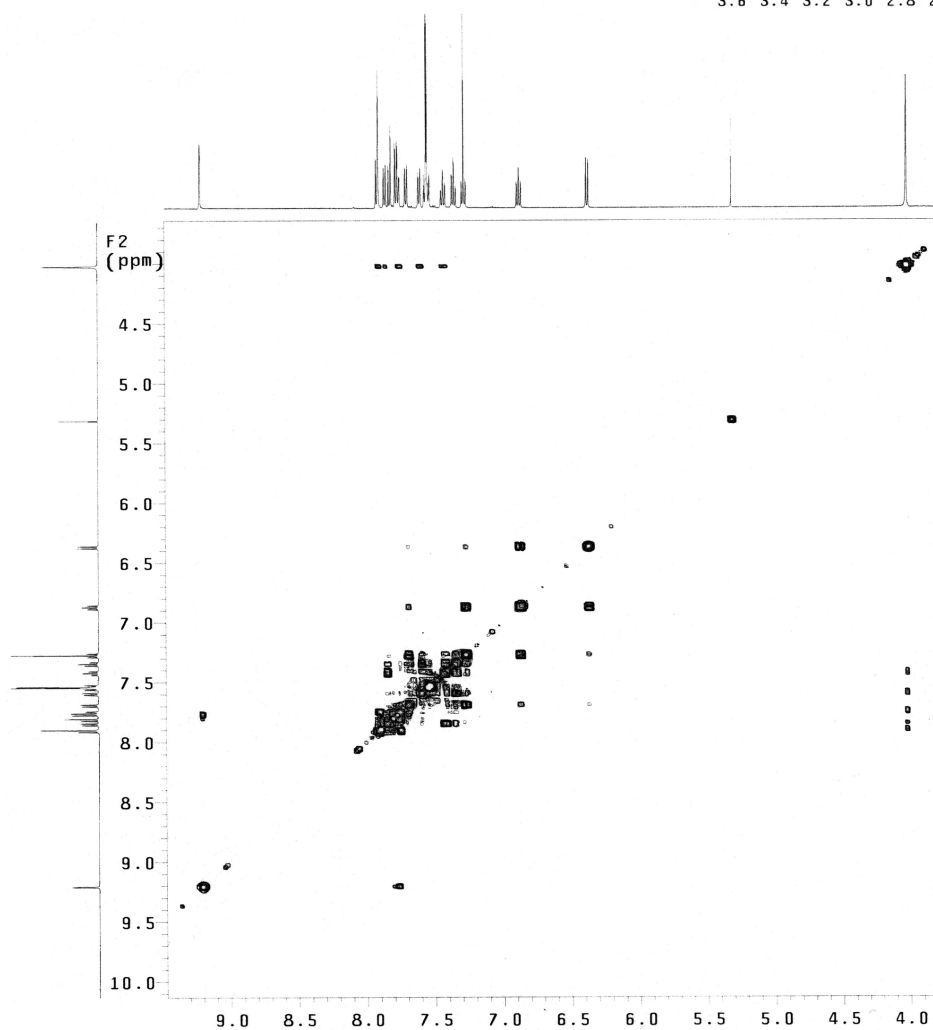
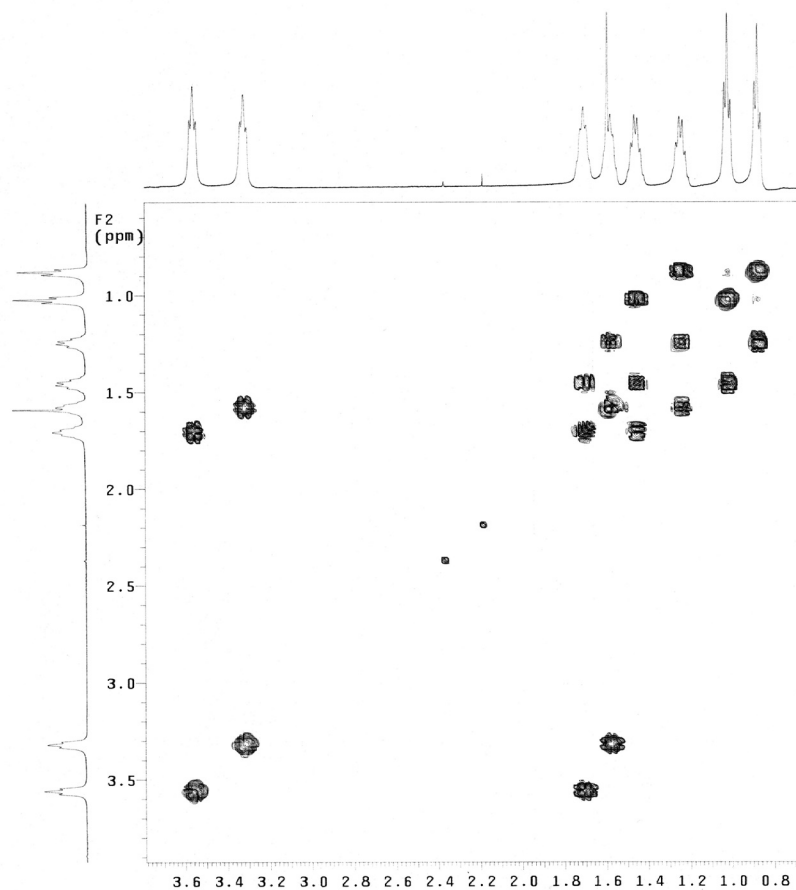


¹³C-NMR, CDCl₃
126 MHz



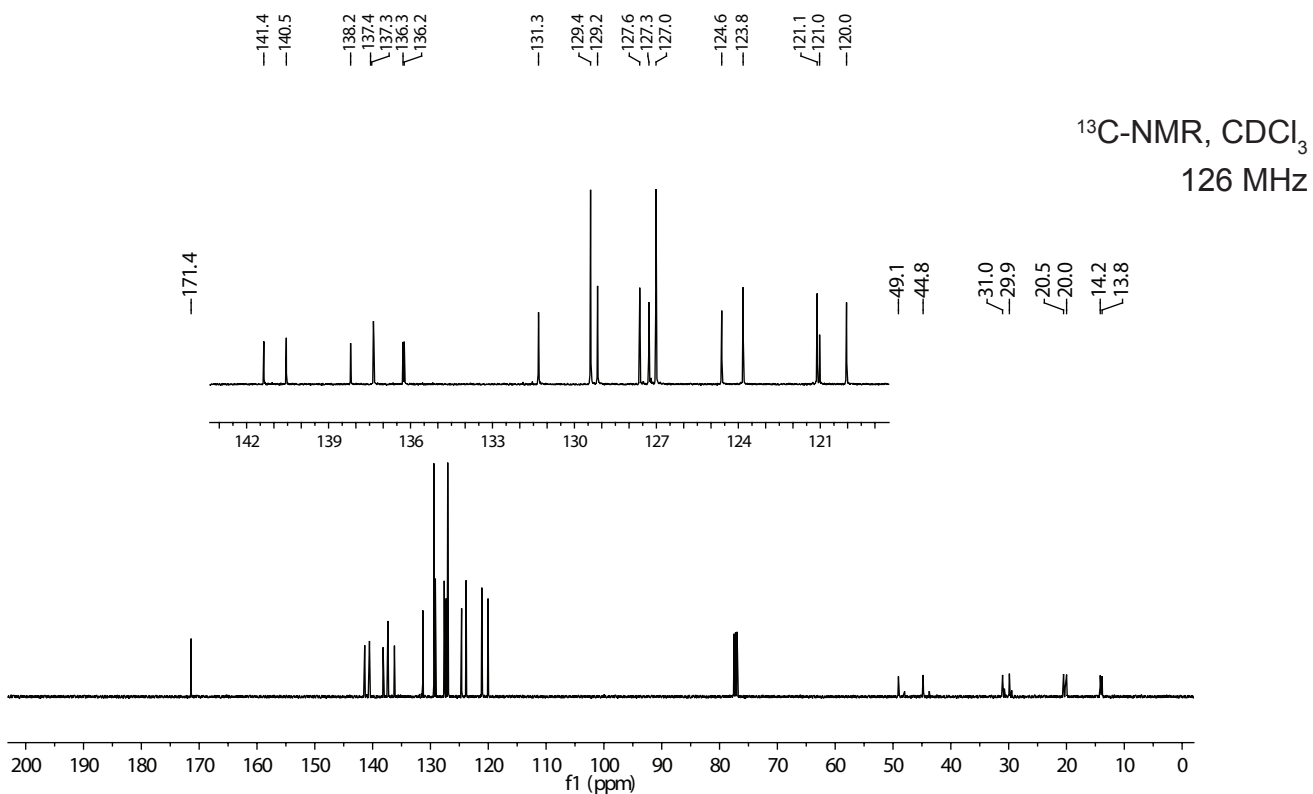
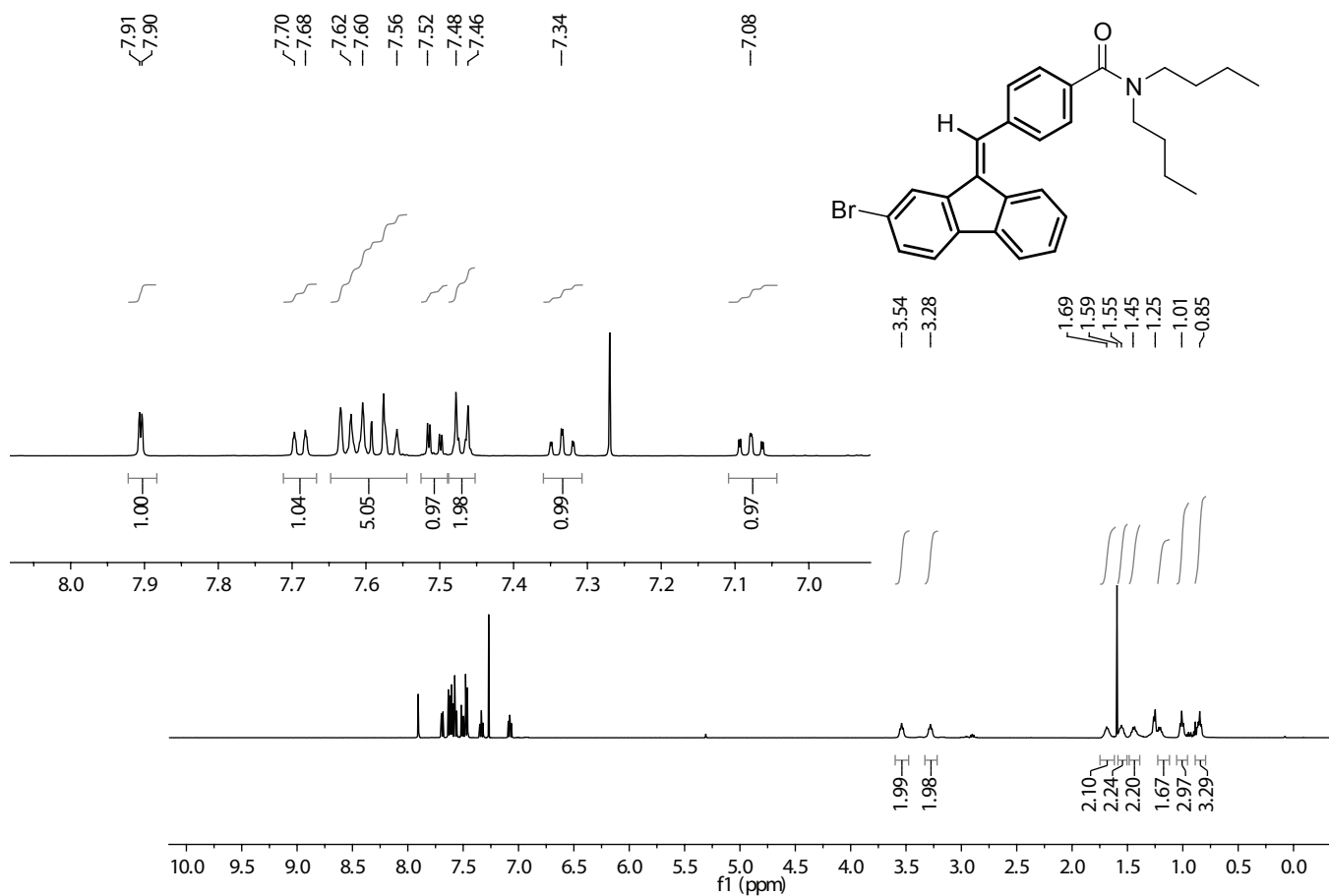
Compound **9-Z** 2D-NMR Spectra - gCOSY

$^1\text{H-NMR}$, CDCl_3
500 MHz



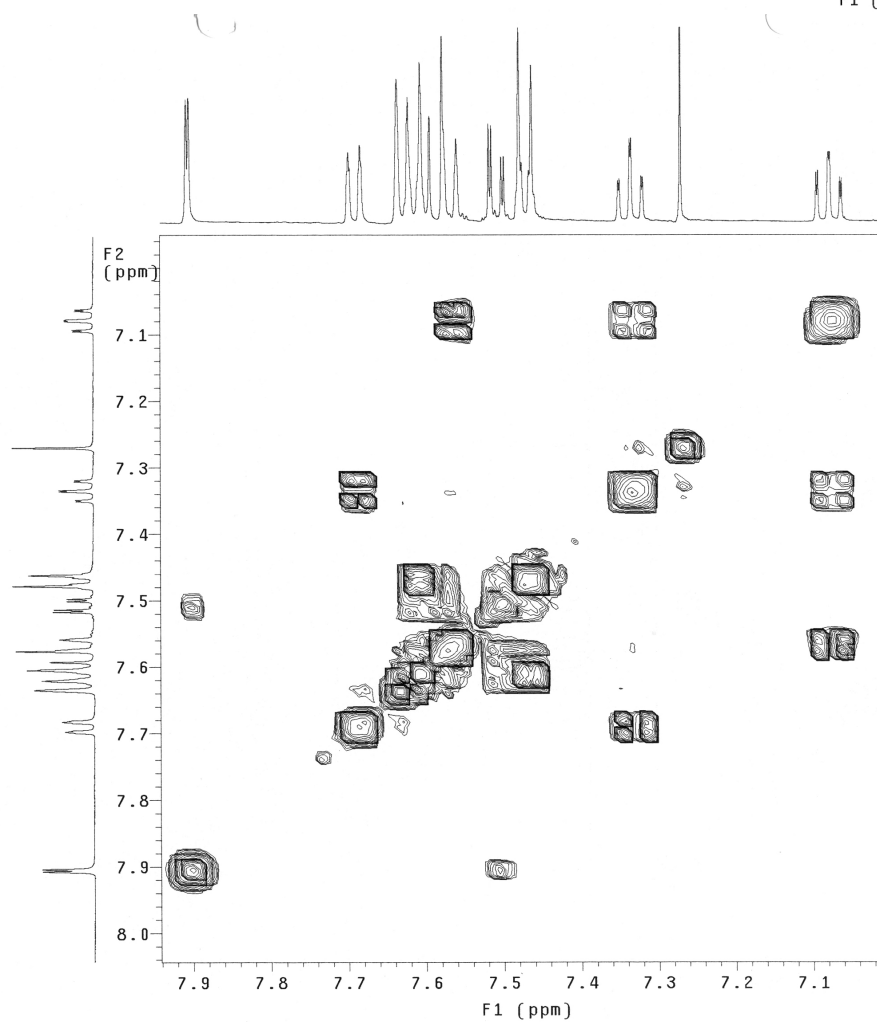
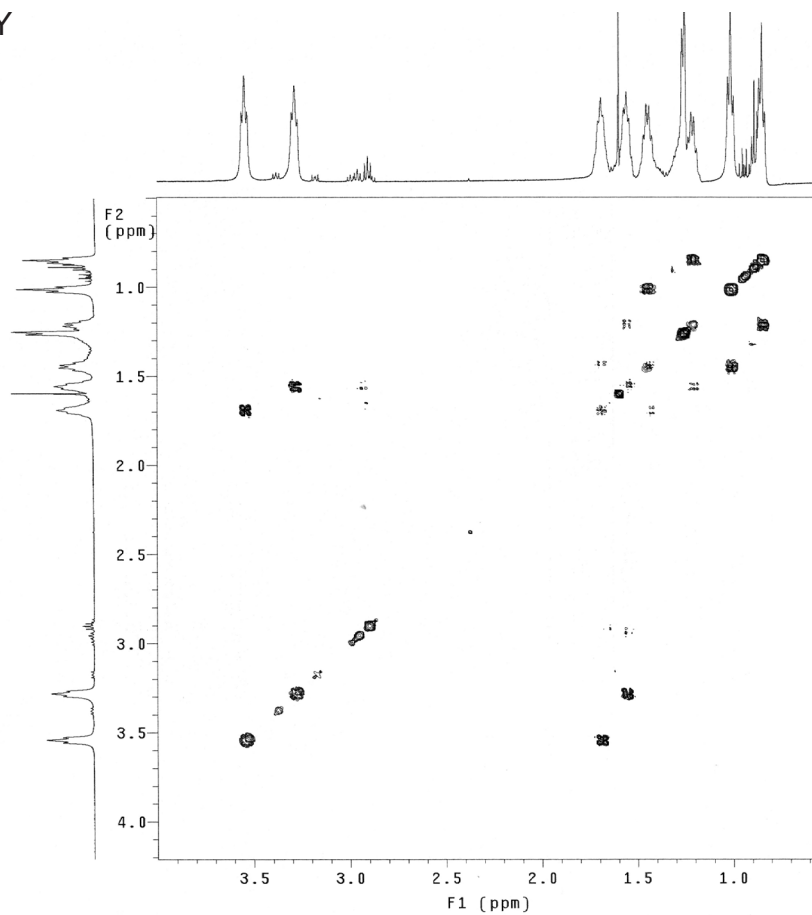
Compound **10-E** NMR Spectra

¹H-NMR, CDCl₃
500 MHz



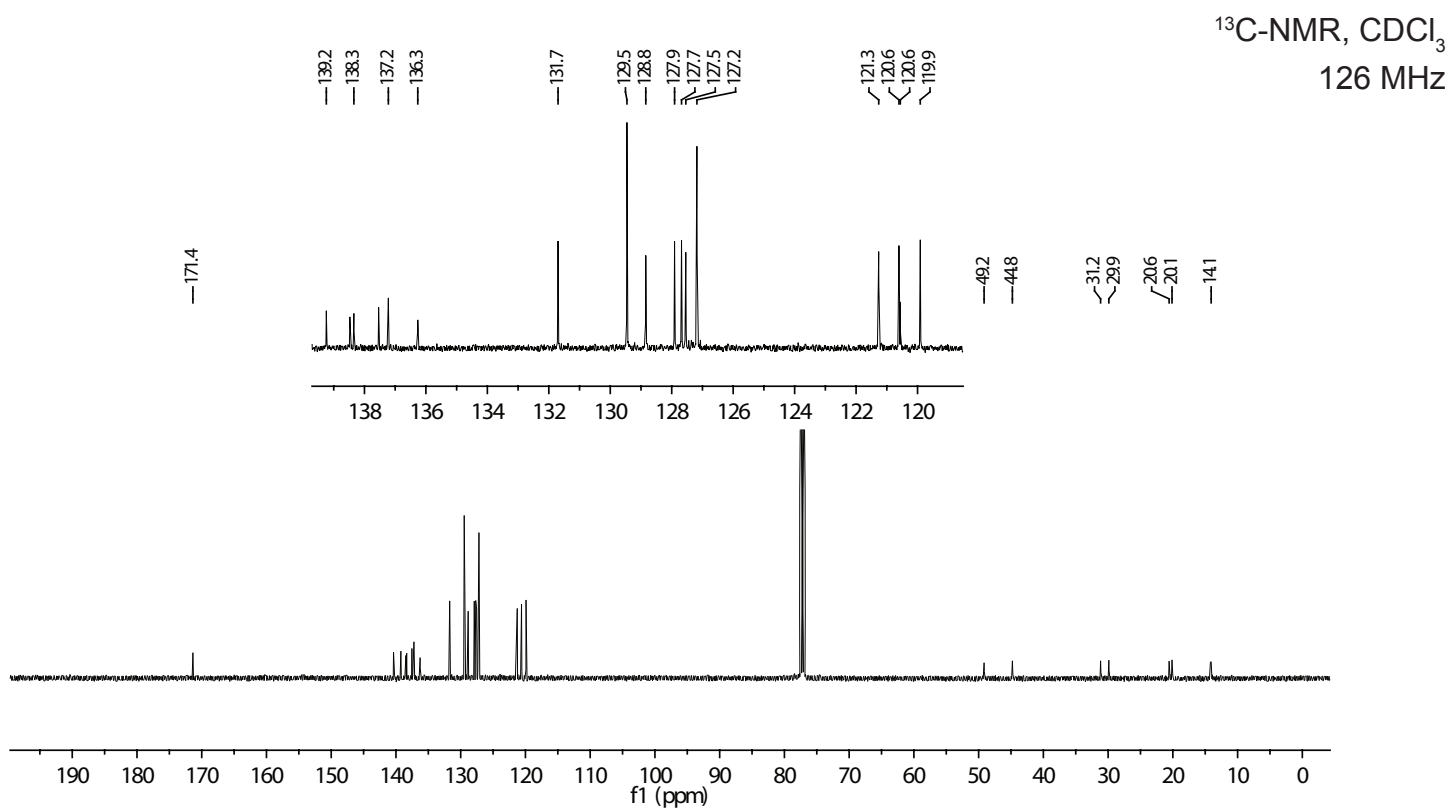
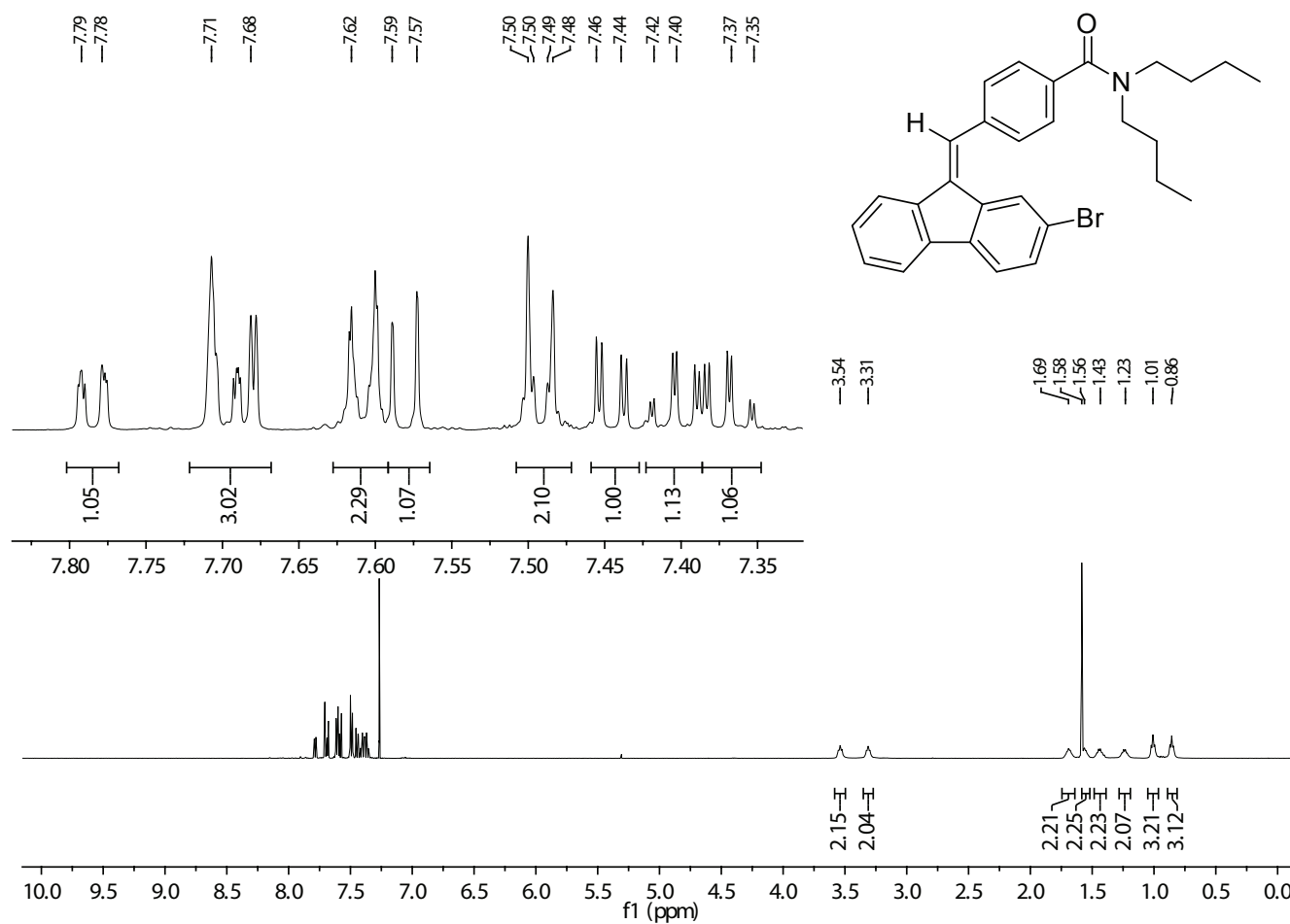
Compound **10-E** 2D-NMR Spectra - gCOSY

$^1\text{H-NMR}$, CDCl_3
500 MHz



Compound **10-Z** NMR Spectra

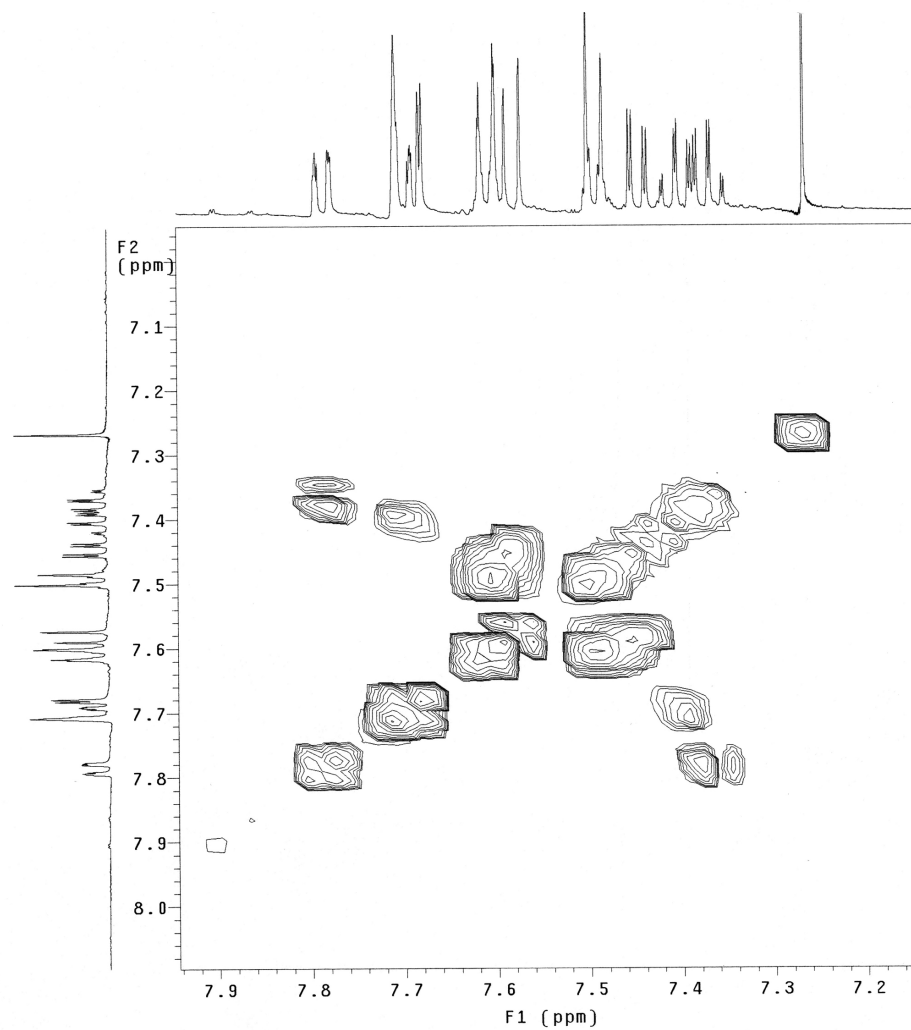
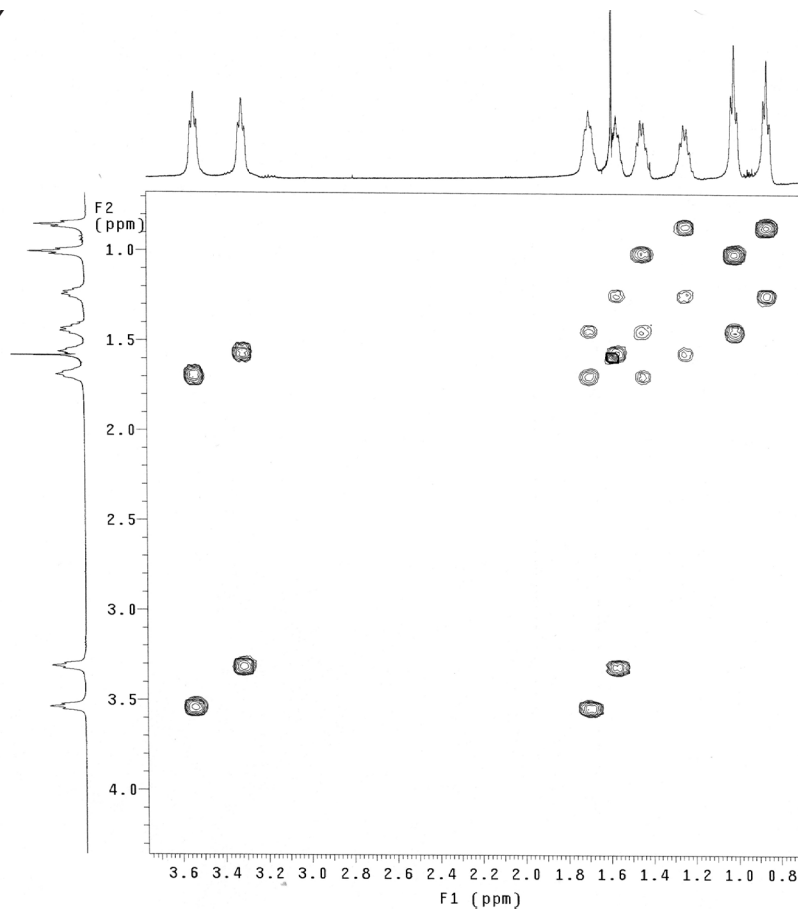
¹H-NMR, CDCl₃
500 MHz



Compound **10-Z** 2D-NMR Spectra - gCOSY

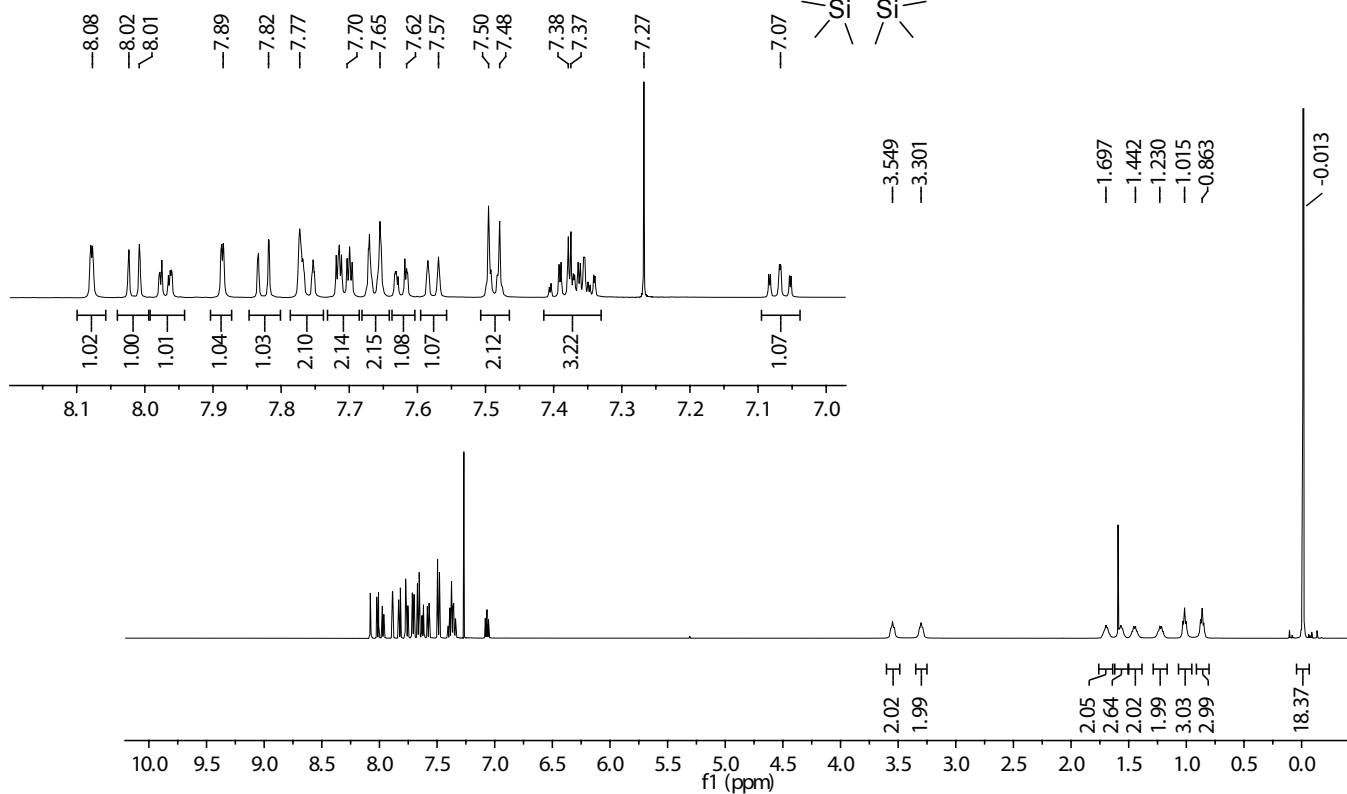
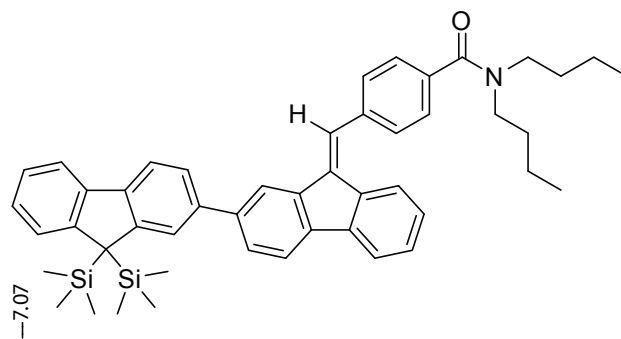
$^1\text{H-NMR}$, CDCl_3

500 MHz

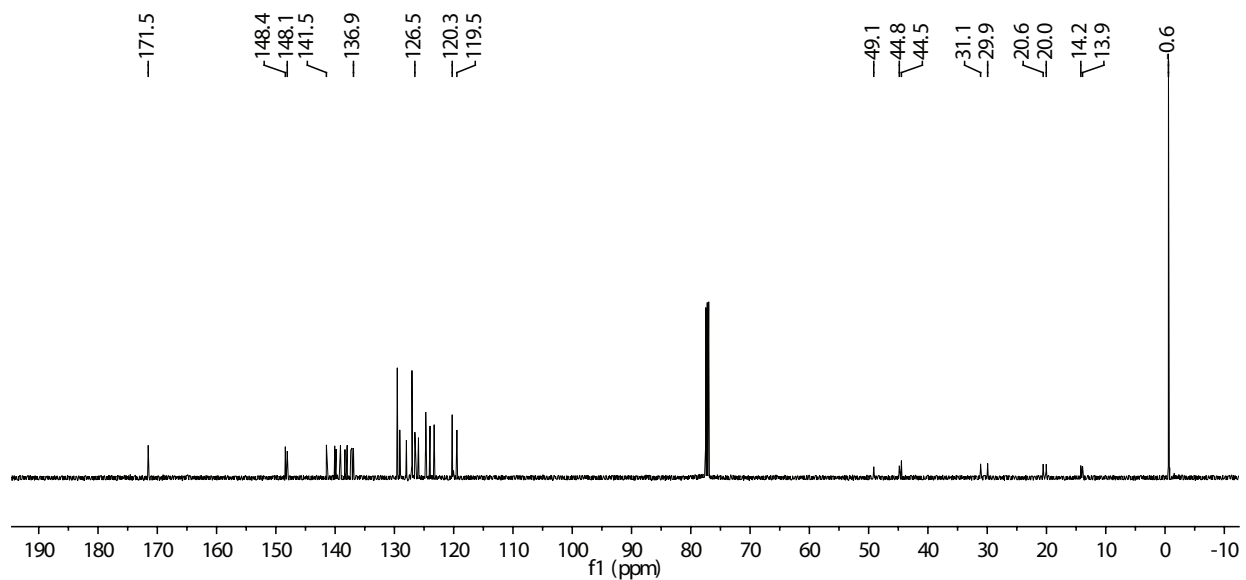


Compound **11-E** NMR Spectra

$^1\text{H-NMR}$, CDCl_3
500 MHz

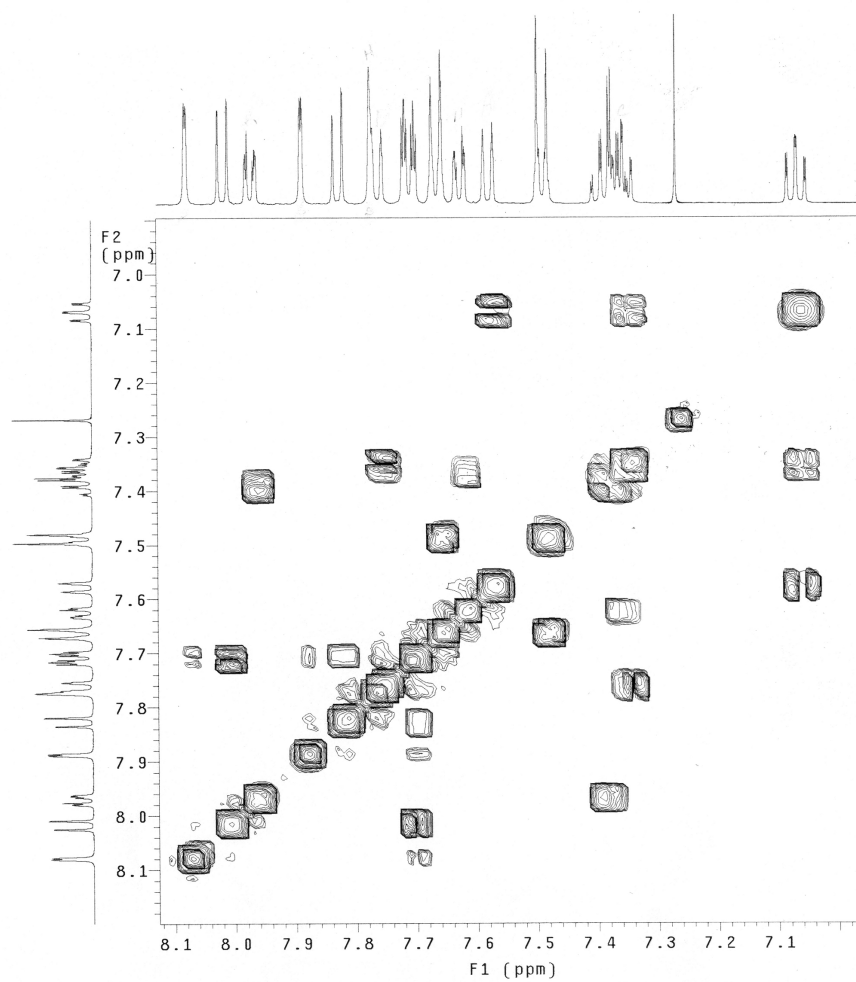
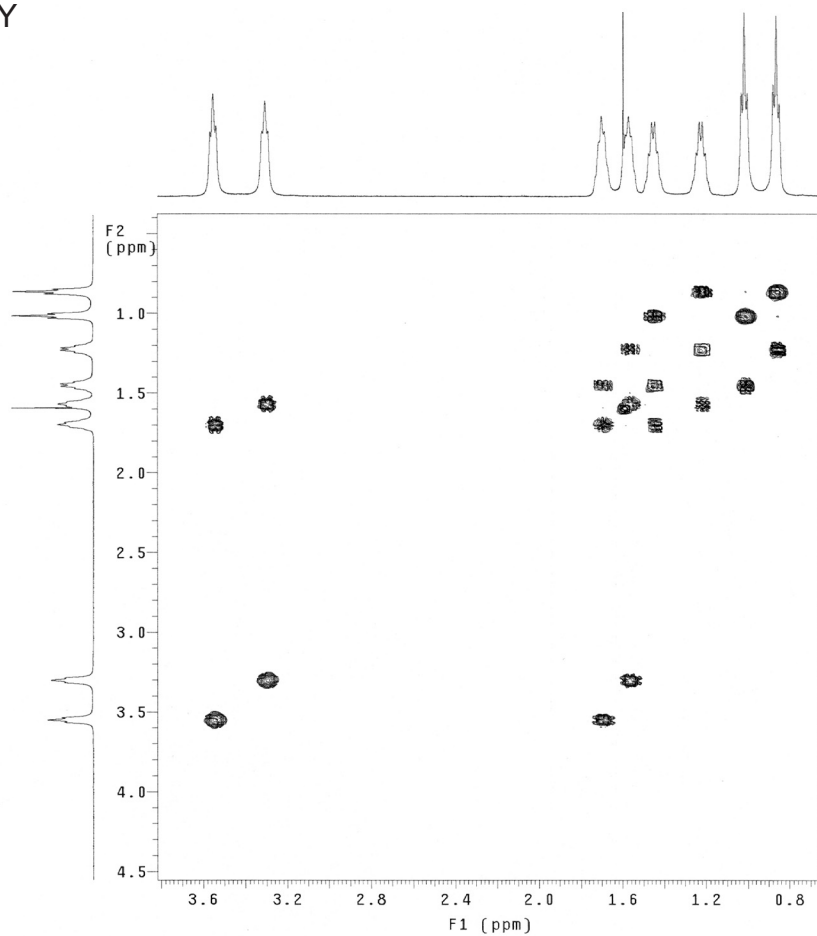


$^{13}\text{C-NMR}$, CDCl_3
126 MHz



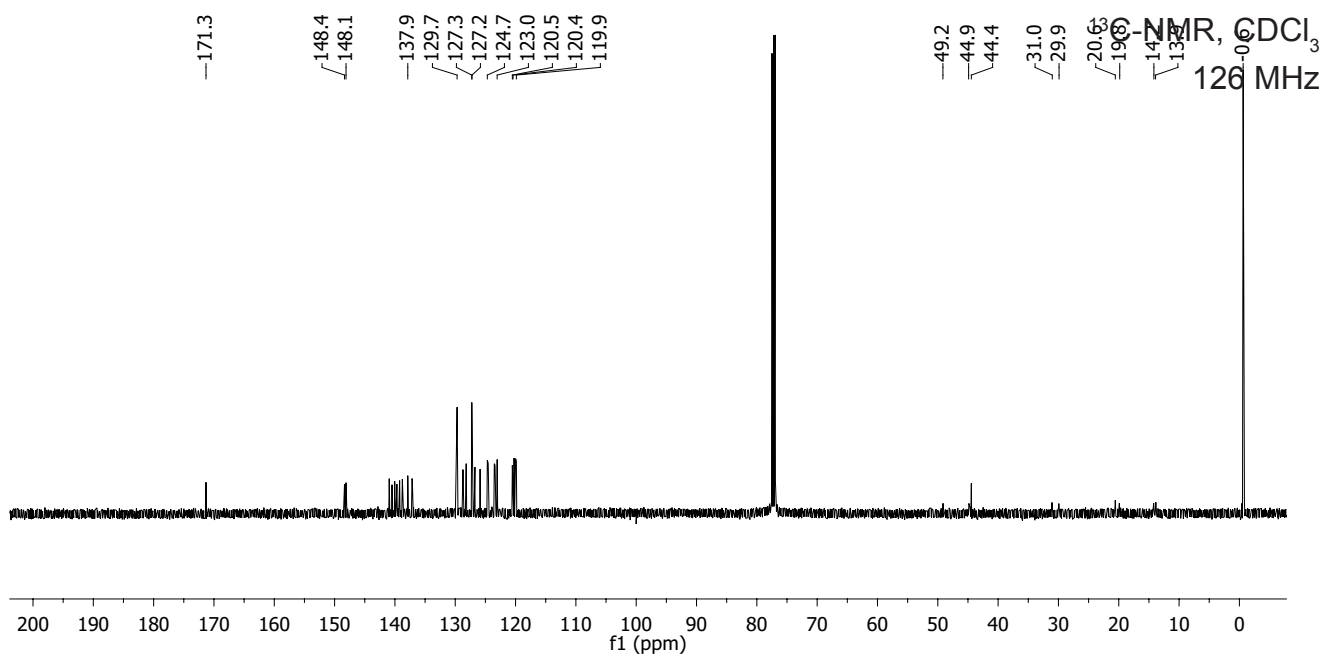
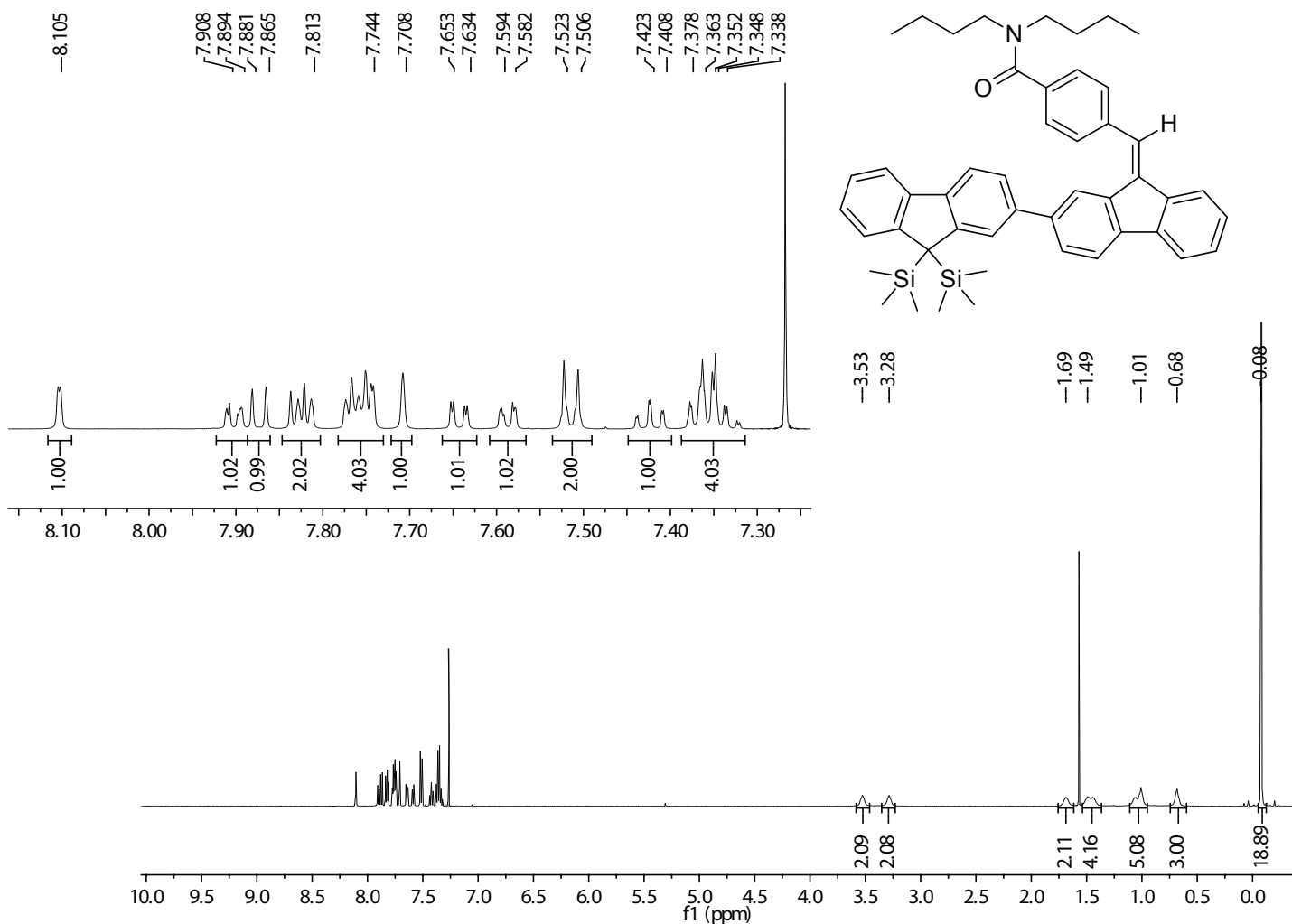
Compound **11-E** 2D-NMR Spectra - gCOSY

$^1\text{H-NMR}$, CDCl_3
500 MHz



Compound **11-Z** NMR Spectra

¹H-NMR, CDCl₃
500 MHz



Compound **11-Z** 2D-NMR Spectra - gCOSY

$^1\text{H-NMR}$, CDCl_3
500 MHz

