Supplementary Information (SI) for ChemComm.

Copper-Catalyzed C(sp^3)–H Alkylation of Fluorene with Primary and Secondary Alcohols using Borrowing Hydrogen Method

Ratnakar Saha,‡ Suraj Kumar Maharana,‡ Narayan Ch. Jana and Bidraha Bagh*

School of Chemical Sciences, National Institute of Science Education and Research (NISER), An OCC of Homi Bhabha National Institute, Bhubaneswar, PO Bhimpur-Padanpur, Via Jatni, District Khurda, Odisha, PIN 752050, India

E-mail: bidraha@niser.ac.in

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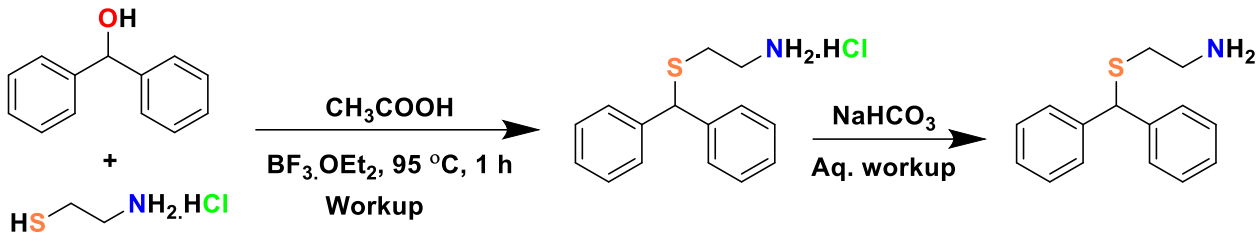
General experimental

All catalytic sp^3 C-H alkylation of fluorene were performed under dry nitrogen atmosphere using standard Schlenk or glovebox (MBraun) techniques. Catalytic α-alkylation of fluorene were performed in Ace pressure tubes purchased from Sigma-Aldrich. Analysis and purification of the products of alkylations were carried out in air. Solvents were purchased from Merck and Spectrochem. For the air-sensitive experiments, solvents (1,4 dioxane, toluene, *p*-xylene and benzene) were distilled, degassed and stored over 3 Å molecular sieves. Deuterated solvents ($CDCl_3$ and CD_3CN) were purchased from Sigma-Aldrich. TLC was performed on Merck Kiesel gel 60, F254 plates with the layer thickness of 0.25 mm. Column chromatography was performed using silica gel (100-200 mesh) as stationary phase. For reaction optimization GC was done by SHIMADZU GC-2010 Plus (Cat#: 221-75954-30, Serial#: 1562016). CuCl, diphenylmethanol, acetic acid, cysteamine hydrochlorid, pyridine-2-carboxaldehyde, $NaBH_4$, diethyl ether, n-dodecane, boronic acid, $Pd(OAc)_2$, butylated hydroxytoluene (BHT), TEMPO, $BF_3.OEt_2$, $NaHCO_3$, Na_2SO_4, KO*t*Bu, NaO*t*Bu, Cs_2CO_3, all fluorene substrate and all primary secondary alcohols were purchased from Sigma Aldrich, Alfa Aesar and TCI Chemicals and used without further purification.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at Bruker AV-400, AV-700 and JEOL-400 (^1H at 400 MHz and $^{13}C\{^1H\}$ at 101 MHz). ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are referenced in parts per million (ppm) with respect to residual solvent peaks ($CDCl_3$: δ 7.26 and 77.16 ppm; CD_3CN: 1.94 and 1.32, 118.26 ppm). The coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to describe multiplicity: s = singlet, bs = broad signal, d = doublet, t = triplet, q = quadtrate, m = multiplate. GC was recorded using Shimadzu GC-2010 instrument. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-Q II Spectrometer.

Synthesis and characterization of ligand (L_1) and Complex 1

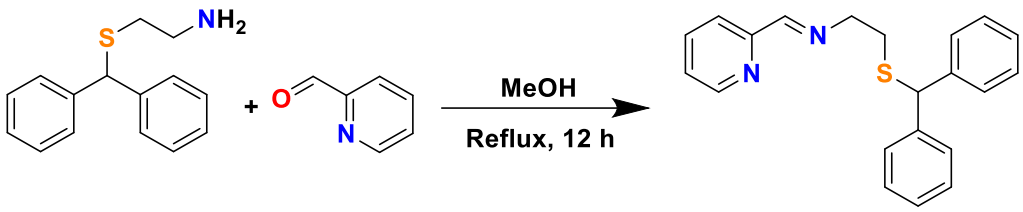
Synthesis of 2-(benzhydrylthio)-ethanamine: 2-(benzhydrylthio)-ethanamine was synthesized by our previous report.[1]



Diphenylmethanol (1.842 g, 10.00 mmol) was dissolved in acetic acid (40 mL) under N_2 atmosphere. Cysteamine hydrochloride (1.128 g, 10.00 mmol) and $BF_3.OEt_2$ (1.402 g, 12.00 mmol) were added separately to the above solution under N_2 atmosphere. The resultant mixture was then stirred at 95°C for 1 hour on a preheated oil bath under N_2 atmosphere. The following manipulations were done in air. The reaction mixture was cooled down to r.t. and diethyl ether was added which yielded white precipitate. The white solid was filtered, dried and kept over NaOH pellets for three days yielded 2-(benzhydrylthio)-ethanamine hydrochloride (2.744 g, 98%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 4H), 7.25–7.22 (m, 4H), 7.15 (t, J = 7.3 Hz, 2H), 5.23 (s, 1H), 2.94 (t, J = 6.2 Hz, 2H), 2.53 (t, J = 6.2 Hz, 2H).

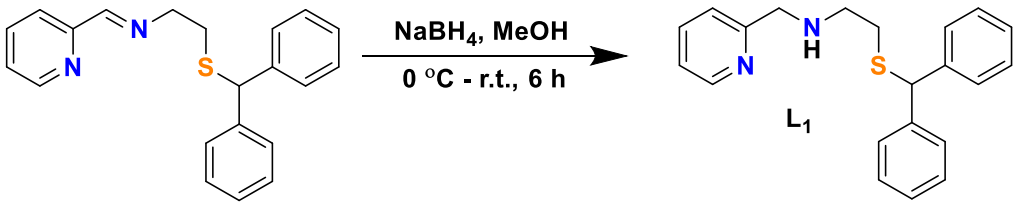
In the following step, HCl was removed from 2-(benzhydrylthio)-ethanamine hydrochloride. 2-(Benzhydrylthio)-ethanamine hydrochloride (2.798 g) was dissolve in saturated $NaHCO_3$ solution (100 mL) and extracted with chloroform (3 x 20 mL). The organic phase was dried over Na_2SO_4. All volatiles were evaporated under high vacuum to yield 2-(benzhydrylthio)-ethanamine (2.381 g, 98%) as light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.40 (m, 4H), 7.35–7.27 (m, 4H), 7.26–7.18 (m, 2H), 5.16 (s, 1H), 2.81 (t, J = 6.3 Hz, 2H), 2.51 (t, J = 6.3 Hz, 2H), 1.64 (bs, 2H).

Synthesis of N-(2-(benzhydrylthio) ethyl)-1-(pyridine-2-yl) methanimine:



A solution of 2-(benzhydrylthio)-ethanamine (0.972 g, 4.00 mmol) in methanol (20 mL) was added to a solution of pyridine-2-carboxaldehyde (0.428 g, 4.00 mmol) in methanol (10 mL) with continuous stirring. The resultant mixture was refluxed for 12 hours in a preheated oil bath. The solution was then cooled down to r.t. and all volatiles were removed under high vacuum to yield (1.297 g, 98%) as a reddish brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.4 Hz, 1H), 8.35 (s, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.75–7.71 (m, 1H), 7.44–7.42 (m, 4H), 7.33–7.27 (m, 5H), 7.24–7.19 (m, 2H), 5.26 (s, 1H), 3.83 (t, J = 6.3 Hz, 2H), 2.79 (t, J = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.05, 154.36, 149.59, 141.41, 136.64, 128.63, 128.44, 127.28, 124.91, 121.52, 60.95, 54.48, 32.91.

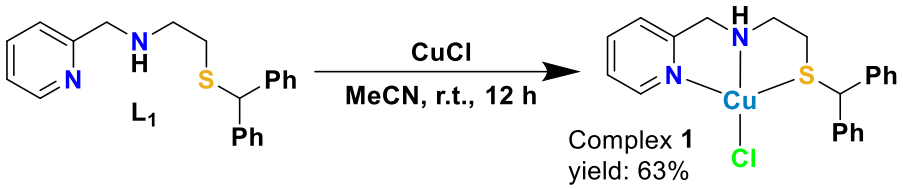
Synthesis of 2-(benzhydrylthio)-N-(pyridine-2-ylmethyl) ethan-1-amine (L_1):



A solution of **L_1** (1.328 g, 4.00 mmol) in methanol (30 mL) was cooled down to 0 °C in an ice-bath. Solid $NaBH_4$ (0.341 g, 9.00 mmol) was then added in small quantity to the solution at 0 °C under vigorous stirring. The resultant reaction mixture was stirred at 0 °C for another 10 minutes. Then the reaction mixture was warmed up to r.t. and stirred at r.t. for another 6 hours. Water (20 mL) was added to the reaction mixture and the mixture was extracted with

dichloromethane (3 x 20 mL). Combined organic phase was dried over Na_2SO_4 and dried under high vacuum to get **L₁** (1.321 g, 99%) as brown oil. ^{1}H NMR (400 MHz, CD_3CN) δ 8.50 (d, *J* = 4.5 Hz, 1H), 7.68 (t, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 4H), 7.37 – 7.30 (m, 5H), 7.27 – 7.18 (m, 3H), 5.26 (s, 1H), 3.78 (s, 2H), 2.71 (t, *J* = 6.6 Hz, 2H), 2.52 (t, *J* = 6.6 Hz, 2H), 2.23 (brs, 1H). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 161.4, 150.0, 143.0, 137.4, 129.6, 129.0, 128.1, 122.9, 122.8, 118.3, 55.2, 54.0, 48.6, 33.2.

Synthesis of complex 1:

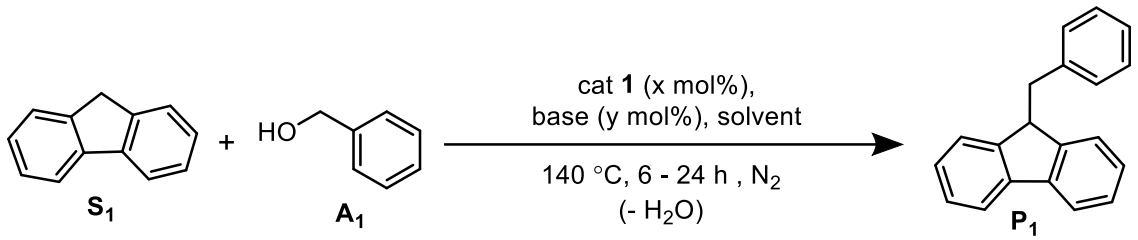


A solution of the ligand (**L₂**) (0.334 g 1.00 mmol) in dry acetonitrile (10 mL) was added dropwise to a suspension of CuCl (0.099 g, 1.00 mmol) in dry acetonitrile (10 mL) at r.t. Then the reaction mixture was stirred at r.t. for 12 hours. The brownish solution was then filtered and dried under high vacuum to afford a floppy solid with good yields (85%). The crude solid was then dissolved in minimum volume of dry acetonitrile in a 100 mL round bottom flux and then each diethyl ether and hexane were added in equal proportion to the solution. The mixture solution is then allowed to stand at r.t for couple of days. Light white crystals of complex **1** were grown at the bottom of the RB. Remaining solution were decanted and single crystals were washed with cold diethyl ether. Yield: 63% (0.272 g). ^{1}H NMR (400 MHz, CD_3CN) δ 8.15 (d, *J* = 4.7 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 4H), 7.33 – 7.23 (m, 8H), 5.03 (s, 1H), 3.93 (s, 2H), 3.55 (bs, 1H), 2.65 (t, *J* = 5.7 Hz, 2H), 2.46 (t, *J* = 5.8 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 158.5, 149.8, 141.9, 138.5, 129.7, 129.0, 128.5, 124.5, 124.2, 55.0, 54.2, 47.9, 34.7. HRMS (ESI-TOF) *m/z*: Calcd. for $[C_{21}H_{22}CuClN_2S]^+$ $[M]^+$

432.0488, Found 432.0479. Anal. Calcd for $C_{21}H_{22}CuClN_2S$ (433.47): C, 58.19; H, 5.12; N, 6.46; S, 7.40 Found: C, 58.24; H, 5.10; N, 6.45; S, 7.43.

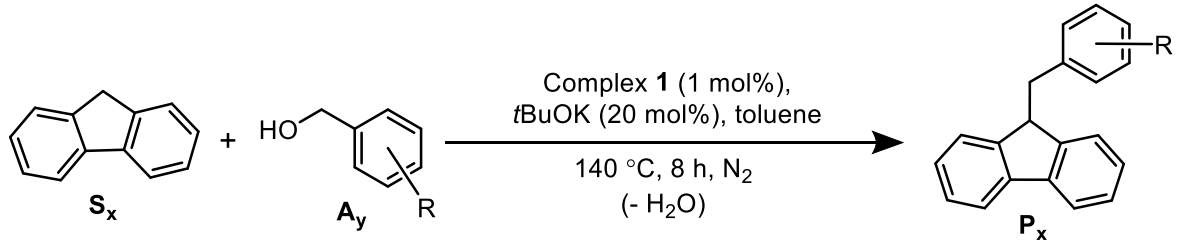
General experimental procedure for the C-9 alkylation of fluorene:

General condition for reaction optimization:



In a 15 mL dried pressure tube fitted with a magnetic stir bar, an appropriate amount of fluorene (**S1**) (0.083g, 0.50 mmol), benzyl alcohol (**A1**) (0.060 g, 0.55 mmol), complex **1** (1 to 5 mol%), base (10 to 50 mol%) and solvent (2 mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at appropriate temperature in a preheated oil bath for appropriate time. Thereafter the reaction mixture was cooled down to r.t. *n*-dodecane (0.085 g, 0.5 mmol) was added to the resultant mixture, and the product mixture was analyzed by GC. Occasionally the crude product was purified by column chromatography using silica as stationary phase and hexane as eluent.

General condition for substrate screening:



In a 15 mL dried pressure tube fitted with a magnetic stir bar, a mixture of fluorene (0.083 g, 0.50 mmol), primary alcohols (0.55 mmol), KO*t*Bu (0.011 g, 20 mol%), complex **1** (0.002 g, 1 mol%) and toluene (2 mL) was successively added under a nitrogen atmosphere. Then the reaction mixture was heated at 140 °C in a preheated oil bath for 8 h. Thereafter, the reaction mixture was cooled down to r.t. and the crude product was purified by column chromatography

(silica as stationary phase and a mixture of hexanes and ethyl acetate or petroleum ether and ethyl acetate as eluent) to give pure product.

General condition for gram scale synthesis of 9-benzyl-9H-fluorene (P_1): In a 50 mL dried pressure tube fitted with a magnetic stir bar, a mixture of fluorene (0.830 g, 5.0 mmol), benzyl alcohol (0.595 g, 5.5 mmol), KO*t*Bu (0.112 g, 1 mmol), complex **1** (0.022 g, 1 mol%) and toluene (15 mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 140 °C in a preheated oil bath for 8 h. Thereafter, the reaction mixture was cooled down to r.t. and the crude product was purified by column chromatography (hexanes as eluent) to give a white solid as pure product (1.22 g, 95%).

Post-functionalization:

Synthesis of 9-benzyl-9-(4-nitrophenyl)-9H-fluorene (P_{1a}):[6] In a Schlenk tube (25 mL), a mixture of 9-benzyl-9H-fluorene **P_1** (0.3 mmol), 4-chloronitrobenzene (0.45 mmol), CsOH (0.45 mmol), and acetonitrile (1.5 mL) was heated at 80 °C for 24 h. After completion of the reaction, the mixture was successively washed with brine solution, followed by extraction with ethyl acetate. The combined organic layer was concentrated under vacuum and then purified through column chromatography to give the pure product **P_{1a}**.

Hydroxylation of C-9 alkylated 9H-fluorene:[5] In a RB, a mixture of C-9 alkylated fluorene (0.20 mmol) and *t*-BuOK (0.023 g, 0.20 mmol) in DMSO (2.0 mL) was stirred at room temperature for 24 h in open air. After complete conversion of starting material (confirmed with TLC), 10 mL water and 2.0 mL brine solution were added to the reaction mixture and the mixture was extracted with diethyl ether (3 x 15 mL). The combined organic phase was dried over Na_2SO_4 and all volatiles were evaporated under reduced pressure to give the pure products.

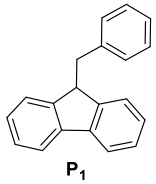
Synthesis of 9–(3,7–dimethyloct–6–en–1–yl)–9H–fluorene (P_{41}):[2] In a 15 mL dried pressure tube fitted with a magnetic stir bar, a mixture of fluorene (0.083 g, 0.5 mmol), β-citronellol (0.086 g, 0.55 mmol), KO*t*Bu (0.011 g, 20 mol%), complex **1** (0.002 g, 1 mol%) and toluene (2 mL) was successively added under a nitrogen atmosphere. Then the reaction mixture was heated at 140 °C in a preheated oil bath for 8 h. Thereafter, the reaction mixture was cooled down to r.t. and the crude product was purified by column chromatography to give the pure product.

Synthesis of 2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol (P_{42}):[3] In a dried pressure tube fitted with a magnetic stir bar, a mixture of 2-(dibutylamino)-1-(2,7-dichloro-9H-fluoren-4-yl)ethan-1-ol (0.175 g, 0.5 mmol), 4-chlorobenzyl alcohols (0.079 g, 0.55 mmol), complex **1** (0.002 g, 1 mol%), KO*t*Bu (0.011 g, 20 mol%), and toluene (2 mL) was successively added under a nitrogen atmosphere. Then the reaction mixture was heated at 140 °C in a preheated oil bath for 8 h. Thereafter, the reaction mixture was cooled down to r.t. and the crude product was purified by column chromatography to give the pure product.

Suzuki-Miyaura cross coupling: Synthesis of 9-([1,1'-biphenyl]-2-ylmethyl)-9H-fluorene (P_{43}):[4] In a dried pressure tube fitted with a magnetic stir bar, a mixture of 9-(2-bromobenzyl)-9H-fluorene (0.067 g, 0.2 mmol), (3-formylphenyl)boronic acid (0.027 g, 0.22 mmol), $Pd(OAc)_2$ (1.5 mg, 3 mol%), $K_3PO_4 \cdot 7H_2O$ (0.135 g, 0.4 mmol), isopropanol (2.5 mL) and water (2.5 mL) was stirred at 90 °C for 24 h under N_2 atmosphere. The following workup was performed in air. The mixture was added to brine (4.0 mL) and extracted with ethyl acetate (3 x 15 mL). The solvent was evaporated under reduced pressure and the product was purified by column chromatography to give the pure product.

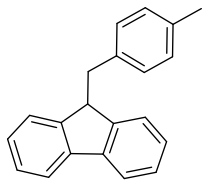
NMR data of pure alkylated products:

The following products are obtained by α-alkylation of fluorene with primary and secondary alcohols using the standard catalytic protocol. Known compounds are characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopies and new compounds are characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopies and HRMS:



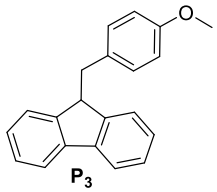
P_1

9-(3-methylbenzyl)-9H-fluorene (P_1):[5] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_1** as white solid (0.120 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.26 (m, 11H), 4.23 (t, *J* = 7.6 Hz, 1H), 3.11 (d, *J* = 7.6 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.0, 140.9, 140.0, 129.7, 128.4, 127.2, 126.8, 126.5, 125.0, 119.9, 48.8, 40.2.



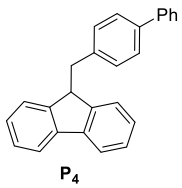
P_2

9-(3-methylbenzyl)-9H-fluorene (P_2):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_2** as white solid (0.125 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.14 (m, 6H), 4.22 (t, *J* = 7.6 Hz, 1H), 3.08 (d, *J* = 7.6 Hz, 2H), 2.38 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.1, 140.9, 136.8, 135.9, 129.5, 129.1, 127.2, 126.8, 125.0, 119.9, 48.9, 39.8, 21.3.



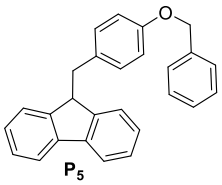
P_3

9-(4-methoxybenzyl)-9H-fluorene (P_3):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_3** as white solid (0.121 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.17 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.20 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.08 (d, *J* = 7.6 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.26, 147.01, 140.96, 131.96, 130.54, 127.17, 126.73, 124.98, 119.91, 113.76, 55.33, 49.03, 39.27.



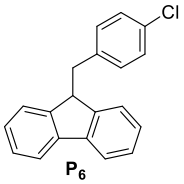
P_4

9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene (P_4):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_4** as white solid (0.128 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 4.2 Hz, 4H), 4.27 (t, *J* = 7.5 Hz, 1H), 3.16 (d, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.9, 141.0, 140.0, 139.3, 139.1, 130.1, 130.0, 128.9, 127.3, 127.1, 127.0, 126.8, 125.0, 120.0, 48.8, 39.9.



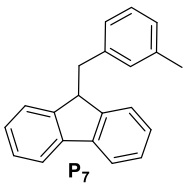
P_5

9-(4-(benzyloxy)benzyl)-9H-fluorene (P_5): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_5** as colorless oily liquid (0.138 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 3H), 7.29 – 7.22 (m, 4H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 5.11 (s, 2H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.10 (d, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.5, 147.0, 141.0, 137.2, 132.3, 130.6, 128.7, 128.1, 127.7, 127.2, 126.7, 125.0, 119.9, 114.8, 70.2, 49.0, 39.3. HRMS (ESI) *m/z*: [$(M + H)^+$] calcd for $C_{27}H_{23}O$: 363.1749, found 363.1759.

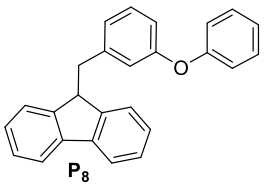


P_6

9-(4-chlorobenzyl)-9H-fluorene (P_6):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_6** as white solid (0.122 g, 84%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.22 – 7.19 (m, 6H), 7.08 (d, *J* = 8.2 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 1H), 3.11 (d, *J* = 7.3 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.5, 141.0, 138.1, 132.2, 131.0, 128.4, 127.4, 126.8 124.9, 120.0, 48.6, 39.4.

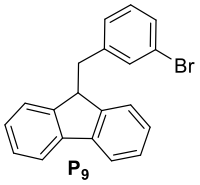

P_7

9-(3-methylbenzyl)-9H-fluorene (P_7):[9] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_7** as white solid (0.123 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 3H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.10 – 7.02 (m, 3H), 4.23 (t, *J* = 7.7 Hz, 1H), 3.06 (d, *J* = 7.7 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.1, 140.9, 140.0, 138.0, 130.4, 128.3, 127.2, 126.7, 126.7, 125.0, 119.9, 48.8, 40.2, 21.6.



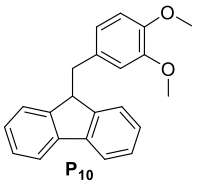
P_8

9-(3-phenoxybenzyl)-9H-fluorene (P_8):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_8** as yellow solid (0.136 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.27 (m, 4H), 7.27 – 7.16 (m, 5H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.84 (m, 5H), 4.19 (t, *J* = 7.4 Hz, 1H), 3.09 (d, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.5, 157.0, 146.6, 141.8, 140.9, 129.8, 129.6, 127.3, 126.8, 124.9, 124.7, 123.1, 120.3, 120.0, 118.7, 117.3, 48.6, 39.8.



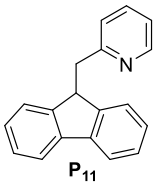
P_9

9-(3-bromobenzyl)-9H-fluorene (P_9):[8] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_9** as white solid (0.106 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.20 – 7.10 (m, 4H), 4.20 (t, *J* = 7.1 Hz, 1H), 3.08 (d, *J* = 7.3 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.4, 142.2, 140.9, 132.6, 129.9, 129.6, 128.3, 127.4, 126.8, 124.8, 122.4, 120.0, 48.4, 39.7.



P_{10}

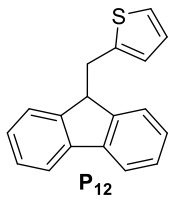
9-(3,4-dimethoxybenzyl)-9H-fluorene (P_{10}):[9] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{10}** as white solid. (0.139 g, 88%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.29 – 7.26 (m, 4H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.76 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 4.25 (t, *J* = 7.4 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.14 (d, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 148.6, 147.5, 146.8, 141.0, 132.1, 127.2, 126.7, 125.0, 121.6, 119.9, 112.7, 111.0, 55.9, 48.9, 39.5.



P_{11}

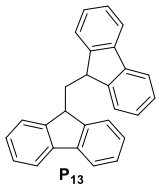
2-((9H-fluoren-9-yl)methyl)pyridine (P_{11}):[9] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{11}** as white solid (0.103 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.69 (m, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.59 (m, 1H),

7.36 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.19 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 4.65 (t, *J* = 7.7 Hz, 1H), 3.25 (d, *J* = 7.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.9, 149.5, 147.1, 140.9, 136.5, 127.2, 126.8, 124.8, 124.5, 121.8, 119.9, 47.3, 42.52.

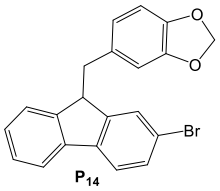


P12

9-(3-methylbenzyl)-9H-fluorene (P12):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P12** as yellow solid (0.106 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.11 (d, *J* = 4.1 Hz, 1H), 6.89 – 6.87 (m, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 3.38 (d, *J* = 7.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.2, 142.1, 141.1, 127.4, 126.9, 126.6, 126.0, 124.7, 123.8, 119.9, 49.0, 34.0.

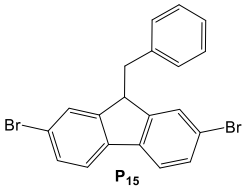

P13

di(9H-fluoren-9-yl)methane (P13):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P13** as yellow solid. (0.155 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 4H), 7.54 (d, *J* = 7.5 Hz, 4H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.28 (t, *J* = 7.4 Hz, 4H), 4.40 (t, *J* = 7.6 Hz, 2H), 2.23 (t, *J* = 7.6 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.6, 141.1, 127.4, 127.1, 125.1, 120.2, 46.0, 39.0.



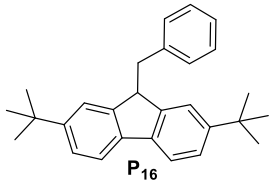
P14

5-((2-bromo-9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole (P14): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P14** as white solid (0.144 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.26 – 7.22 (m, 2H), 7.15 – 7.12 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.61 (dd, *J* = 16.0, 4.6 Hz, 2H), 6.48 (dd, J = 7.9, 1.5 Hz, 1H), 5.84 (dd, *J* = 3.6, 1.3 Hz, 2H), 4.00 (t, *J* = 7.5 Hz, 1H), 2.95 – 2.82 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.8, 147.7, 146.4, 146.3, 139.9, 133.0, 130.3, 128.2, 127.4, 127.2, 125.0, 122.6, 121.2, 120.6, 120.0, 109.7, 108.7, 108.2, 101.0, 48.9, 39.6. HRMS (ESI) *m/z*: $[(M + H)^{+}]$ calcd for $C_{21}H_{16}BrO_2$: 379.0334, found 379.0353.



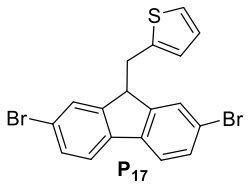
P_{15}

9-benzyl-2,7-dibromo-9H-fluorene (P_{15}):[9] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{15}** as yellow solid (0.174 g, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.54 (m, 2H), 7.43 – 7.36 (m, 3H), 7.34 (s, 2H), 7.25 (d, *J* = 6.6 Hz, 2H), 4.24 (t, *J* = 7.5 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.5, 139.0, 138.7, 130.6, 129.6, 128.6, 128.4, 127.0, 121.3, 121.0, 48.8, 39.8.



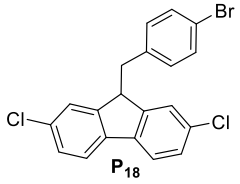
P_{16}

9-benzyl-2,7-di-tert-butyl-9H-fluorene (P_{16}):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{16}** as white solid (0.149 g, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.30 – 7.26 (m, 3H), 7.11 (s, 2H), 4.15 (t, *J* = 7.9 Hz, 1H), 3.07 (d, *J* = 8.0 Hz, 2H), 1.29 (s, 18H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.4, 147.0, 140.5, 138.3, 129.9, 128.4, 126.4, 124.2, 122.0, 119.1, 49.1, 40.8, 34.9, 31.6.



P_{17}

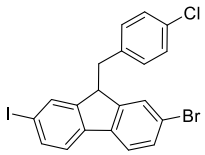
2-((2,7-dibromo-9H-fluoren-9-yl)methyl)thiophene (P_{17}): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{17}** as yellowish oil (0.166 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 – 7.46 (m, 4H), 7.38 (s, 2H), 7.17 – 7.14 (m, 1H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.69 (d, *J* = 3.2 Hz, 1H), 4.15 (t, *J* = 6.9 Hz, 1H), 3.35 (d, *J* = 6.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 140.7, 139.1, 130.8, 128.1, 126.8, 126.5, 124.3, 121.3, 121.2, 49.0, 33.6. HRMS (ESI) *m/z*: [$(M + Na)^+$] calcd for $C_{18}H_{12}Br_2SNa$: 440.8924, found 440.8926.



P_{18}

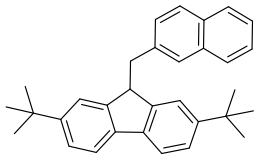
9-(4-bromobenzyl)-2,7-dichloro-9H-fluorene (P_{18}): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{18}** as white solid (0.152 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.18 (d, *J* = 1.5 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 4.11 (t, *J* = 7.2 Hz, 1H), 3.06

(d, *J* = 7.1 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 138.6, 137.4, 132.9, 131.6, 131.2, 127.9, 125.2, 121.0, 120.7, 48.4, 38.9. HRMS (ESI) *m/z*: [$(M + Na)^+$] calcd for $C_{20}H_{13}BrCl_2Na$: 424.9475, found 424.9478.



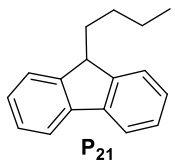
P19

2-bromo-9-(4-chlorobenzyl)-7-iodo-9H-fluorene (P19): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P19** as yellow oil (0.201 g, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.59 – 7.46 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 0.5 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.05 (dd, *J* = 16.9, 8.4 Hz, 2H), 4.10 (t, *J* = 7.1 Hz, 1H), 3.38 – 2.87 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.2, 147.8, 139.5, 139.0, 136.8, 136.5, 134.0, 132.6, 130.8, 130.6, 128.5, 128.1, 121.6, 121.4, 121.1, 92.3, 48.3, 38.8. HRMS (ESI) *m/z*: [$(M + H)^+$] calcd for $C_{20}H_{14}BrClI$: 494.9012, found 494.9022.



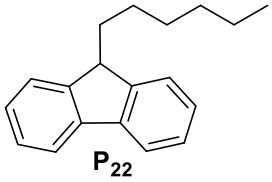
P20

2,7-di-tert-butyl-9-(naphthalen-2-ylmethyl)-9H-fluorene (P20):[9] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P20** as white solid (0.176 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.47 (m, 1H), 7.42 – 7.35 (m, 1H), 7.05 (s, 1H), 4.37 (t, *J* = 8.1 Hz, 1H), 3.51 (d, *J* = 8.1 Hz, 1H), 1.28 (s, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3) δ 149.4, 147.1, 138.2, 136.5, 134.2, 132.4, 129.1, 128.6, 127.5, 126.1, 125.7, 125.5, 124.3, 124.1, 122.2, 119.1, 48.2, 38.3, 34.9, 31.6.

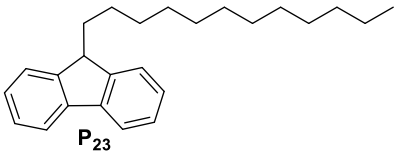


P21

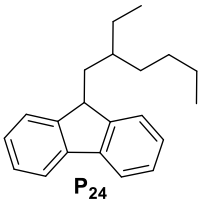
9-butyl-9H-fluorene (P21):[9] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P21** as colorless oil. (0.098 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.43 – 7.34 (m, 4H), 4.03 (t, *J* = 5.8 Hz, 1H), 2.09 – 2.03 (m, 2H), 1.35 – 1.29 (m, 2H), 1.26 – 1.18 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.7, 141.2, 126.9, 126.9, 124.5, 119.9, 47.6, 32.9, 27.9, 23.2, 14.1.



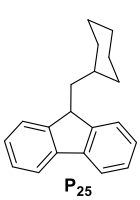
9-hexyl-9H-fluorene (P22):[8] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P22** as yellow sticky oil (0.108 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.37 – 7.26 (m, 4H), 3.95 (t, *J* = 5.8 Hz, 1H), 1.98 (dd, *J* = 15.2, 6.0 Hz, 1H), 1.26 – 1.12 (m, 3H), 0.84 (t, *J* = 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.7, 141.2, 126.9, 126.9, 124.4, 119.9, 47.6, 33.2, 31.8, 29.8, 25.8, 22.8, 14.2.



9-dodecyl-9H-fluorene (P23):[6] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P23** as colourless oil (0.139 g, 83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.39 (m, 4H), 4.08 (t, *J* = 5.9 Hz, 1H), 2.13 – 2.08 (m, 2H), 1.45 – 1.33 (m, 20H), 1.01 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.8, 141.2, 126.9, 126.9, 124.4, 119.9, 47.6, 33.2, 32.1, 30.1, 29.8, 29.8, 29.6, 29.5, 25.8, 22.9, 14.3.

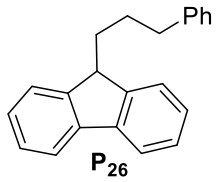


9-(2-ethylhexyl)-9H-fluorene (P24): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P24** as colorless oil. (0.108 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 6.8 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 1H), 1.84 – 1.70 (m, 3H), 1.51 – 1.24 (m, 8H), 0.930 – 0.88 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.50 (s), 148.43 (s), 141.0, 140.9, 126.9, 126.9, 126.8, 124.8, 124.7, 119.9, 45.4, 38.4, 36.8, 32.9, 28.6, 26.0, 23.3, 14.3, 10.5. HRMS (ESI) *m/z*: [(M + H)$^{+}$] calcd for $C_{21}H_{27}$: 279.2113, found 279.2131.



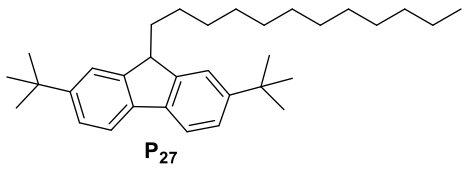
9-(cyclohexylmethyl)-9H-fluorene (P25): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P25** as colorless oil. (0.110 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.55 (d, J = 7.3 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 4.07 (t, *J* = 6.8 Hz, 1H), 1.87 (d, *J* = 12.3 Hz, 2H), 1.81

– 1.73 (m, 6H), 1.56 – 1.20 (m, 4H), 1.11 – 1.03 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.4, 140.9, 126.9, 126.8, 124.7, 119.9, 44.9, 41.9, 35.7, 33.8, 26.8, 26.4. HRMS (ESI) *m/z*: [$(M + H)^+$] calcd for $C_{20}H_{23}$: 263.1800, found 263.1802.

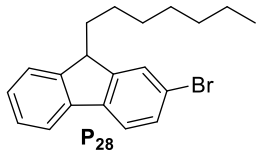


P26

9-(3-phenylpropyl)-9H-fluorene (P26):[8] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P26** as colorless oil. (0.111 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 2H), 7.27 – 7.11 (m, 6H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.1 Hz, 2H), 3.89 (t, *J* = 5.8 Hz, 1H), 2.45 (t, *J* = 7.7 Hz, 2H), 1.98 – 1.93 (m, 2H), 1.43 – 1.35 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.4, 142.3, 141.3, 128.5, 128.4, 127.0, 127.0, 125.8, 124.4, 119.9, 47.4, 36.3, 32.7, 27.3.

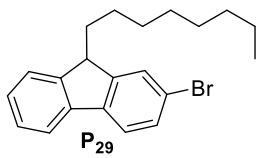

P27

2,7-di-tert-butyl-9-dodecyl-9H-fluorene (P27): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P27** as colourless oil (0.170 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.60 (s, 2H), 7.46 – 7.43 (m, 2H), 3.98 (t, *J* = 6.1 Hz, 1H), 2.15 – 2.04 (m, 2H), 1.47 (s, 18H), 1.42 – 1.32 (m, 20H), 0.96 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.5, 147.8, 138.6, 123.9, 121.3, 119.0, 47.7, 34.9, 33.4, 32.0, 31.8, 29.9, 29.8, 29.8, 29.7, 29.5, 26.1, 22.8, 14.2. HRMS(ESI) *m/z*: [$(M + Na)^+$] calcd for $C_{33}H_{50}Na$: 469.3810, found 469.3788.



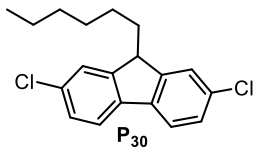
P28

2-bromo-9-heptyl-9H-fluorene (P28):[6] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P28** as colorless oil (0.131 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.8 Hz, 1H), 7.64 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.1 Hz, 2H), 7.39 – 7.31 (m, 2H), 3.96 (t, *J* = 5.8 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.32 – 1.12 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.9, 147.4, 140.2, 140.2, 130.1, 127.7, 127.3, 127.2, 124.5, 121.2, 120.8, 120.0, 47.6, 33.0, 32.0, 30.0, 29.4, 25.6, 22.8, 14.2.



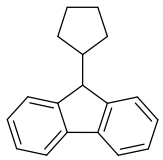
P29

2-bromo-9-octyl-9H-fluorene (P29):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P29** as colorless oil (0.129 g, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.64 – 7.48 (m, 4H), 7.39 – 7.26 (m, 2H), 3.96 (t, *J* = 5.7 Hz, 1H), 2.03 – 1.94 (m, 2H), 1.26 – 1.08 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 150.0, 147.5, 141.3, 140.4, 130.5, 127.9, 127.4, 127.3, 124.6, 121.3, 120.9, 120.1, 47.7, 33.1, 32.1, 30.1, 29.6, 29.5, 25.8, 22.9, 14.4.

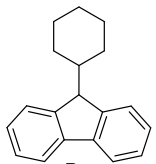


P30

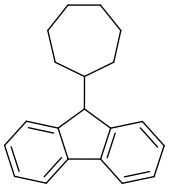
2,7-dichloro-9-hexyl-9H-fluorene (P30): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P30** as colorless oil (0.126 g, 79%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.46 (s, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.94 (t, *J* = 5.8 Hz, 1H), 2.00 – 1.94 (m, 2H), 1.29 – 1.18 (m, 6H), 1.16 – 1.08 (m, 2H), 0.85 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.2, 138.8, 133.0, 127.5, 124.9, 120.9, 47.6, 32.8, 31.7, 29.7, 25.5, 22.8, 14.2. HRMS (ESI) *m/z*: [$(M + Na)^+$] calcd for $C_{19}H_{20}Cl_2Na$: 341.0840, found 341.0824.


P31

9-cyclopentyl-9H-fluorene (P31):[8] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P31** as colorless oil (0.108 g, 92%). ^{1}H NMR (400 MHz, CDCl3) δ 7.73 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.4 Hz, 2H), 3.99 (d, J = 5.8 Hz, 1H), 2.39 – 2.34 (m, 1H), 1.78 – 1.73 (m, 2H), 1.58 – 1.54 (m, 2H), 1.49 – 1.45 (m, 2H), 1.38 – 1.33 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.2, 141.4, 126.9, 126.6, 125.2, 119.7, 51.3, 44.4, 30.1, 25.3.

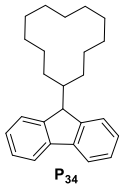

P32

9-cyclohexyl-9H-fluorene (P32):[8] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P32** as white solid (0.115 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 3.86 (d, *J* = 2.8 Hz, 1H), 2.15 (td, *J* = 11.7, 3.0 Hz, 1H), 1.63 (t, *J* = 14.1 Hz, 3H), 1.46 (d, *J* = 12.5 Hz, 2H), 1.27 – 0.99 (m, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.5, 141.7, 126.8, 126.7, 124.9, 119.6, 53.6, 43.2, 29.7, 27.0, 26.6.



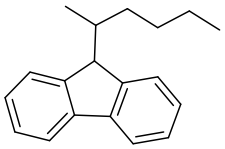
P_{33}

9-cycloheptyl-9H-fluorene (P_{33}):[8] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{33}** as colorless oil (0.114 g, 87%). 1H NMR (400 MHz, CDCl3) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 3.93 (d, *J* = 2.7 Hz, 1H), 2.37 – 2.31 (m, *J* = 10.2, 3.0 Hz, 1H), 1.62 – 1.25 (m, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.7, 141.8, 126.9, 126.8, 124.8, 119.6, 54.8, 44.1, 31.8, 27.8, 27.7.



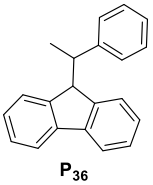
P_{34}

9-cyclododecyl-9H-fluorene (P_{34}): The crude product was purified by column chromatography (hexane as eluent) to give pure product **S_4** as pale yellow oil (0.137 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 4.10 (d, *J* = 1.5 Hz, 1H), 2.54 – 2.52 (m, 1H), 1.57 – 1.33 (m, 18H), 1.30 – 1.16 (m, 4H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.0, 141.8, 126.8, 126.7, 124.8, 119.7, 50.6, 36.2, 27.5, 24.4, 24.2, 23.2, 23.1, 22.7. HRMS (ESI) *m/z*: $[(M - H)^+]$ calcd for $C_{25}H_{31}$: 331.2426, found 331.2426.



P_{35}

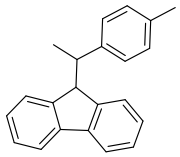
9-(hexan-2-yl)-9H-fluorene (P_{35}): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{35}** as colourless oil (0.104 g, 83%). ^{1}H NMR (400 MHz, CDCl3) δ 7.88 – 7.85 (m, 2H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 8.1 Hz, 2H), 7.43 – 7.38 (m, 2H), 4.12 (d, *J* = 2.7 Hz, 1H), 2.54 – 2.48 (m, 1H), 1.56 – 1.44 (m, 6H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3) δ 147.2, 145.9, 142.0, 141.6, 126.9, 126.9, 126.8, 126.6, 125.2, 124.5, 119.8, 119.7, 52.6, 37.3, 34.3, 30.3, 23.0, 15.8, 14.3. HRMS (ESI) *m/z*: $[(M + H)^+]$ calcd for $C_{19}H_{23}$: 251.1800, found 251.1798.



P_{36}

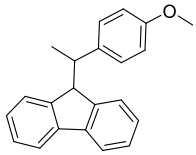
9-(1-phenylethyl)-9H-fluorene (P_{36}): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{36}** as white solid (0.103 g, 76%). ^{1}H

NMR (400 MHz,) δ 7.71 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.27 (m, 8H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.29 (d, *J* = 4.5 Hz, 1H), 3.71 – 3.63 (m, 1H), 0.94 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR 146.6, 144.7, 144.7, 141.9, 141.5, 128.3, 128.2, 127.2, 127.1, 126.9, 126.4, 126.4, 125.8, 124.4, 119.8, 119.7, 54.3, 42.0, 14.0 .



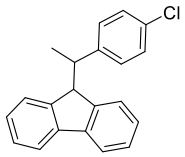
P37

9-(1-(p-tolyl)ethyl)-9H-fluorene (P37): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P37** as white solid. (0.114 g, 80%). ^{1}H NMR (400 MHz, CDCl3) δ 7.77 – 7.62 (m, 2H), 7.56 (d, J = 11.0 Hz, 1H), 7.44 – 7.42 (m, 1.4 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.27 – 7.20 (m, 4H), 6.87 (d, J = 0.7 Hz, 1H), 4.28 (d, J = 4.3 Hz, 1H), 3.73 – 3.65 (m, 1H), 2.47 (s, 3H), 0.99 (d, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.2, 146.3, 140.6, 139.4, 139.0, 136.4, 133.0, 132.4, 129.2, 128.0, 127.9, 127.7, 127.6, 126.1, 124.9, 120.8, 120.6, 54.4, 41.5, 21.2, 14.0.



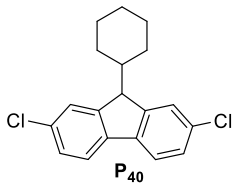
P38

9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene (P38):[7] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P38** as white solid. (0.116 g, 77%). ^{1}H NMR (400 MHz, CDCl3) δ 7.77 (t, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 3H), 4.31 (d, *J* = 4.5 Hz, 1H), 3.84 (s, 3H), 3.84 – 3.66 (m, 1H), 0.98 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3) δ 158.0, 146.6, 144.7, 141.8, 141.4, 136.6, 129.0, 127.1, 127.0, 126.8, 126.3, 125.7, 124.3, 119.7, 119.7, 113.5, 55.2, 54.4, 41.1, 14.2.



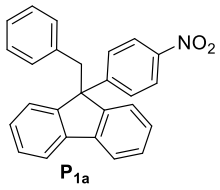
P39

9-(1-(4-chlorophenyl)ethyl)-9H-fluorene (P39):[8] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P39** as white solid. (0.125g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.23 (m, 6H), 7.13 – 7.08 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 4.17 (d, *J* = 4.4 Hz, 1H), 3.62 – 3.55 (m, 1H), 0.94 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.1, 144.4, 142.9, 141.8, 141.4, 132.0, 129.5, 128.2, 127.3, 127.2, 126.9, 126.4, 125.4, 124.4, 119.9, 119.8, 54.0, 41.6, 14.5.



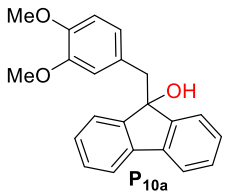
P40

2,7-dichloro-9-cyclohexyl-9H-fluorene (P40): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P40** as white solid. (0.127 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.50 (m, 4H), 7.34 – 7.32(m, 2H), 3.81 (d, *J* = 2.4 Hz, 1H), 2.12 (t, *J* = 10.6 Hz, 1H), 1.67 (t, *J* = 14.5 Hz, 3H), 1.45 (d, *J* = 11.3 Hz, 2H), 1.29 – 1.19 (m, 2H), 1.13 – 1.04 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.1, 139.2, 132.8, 127.4, 125.3, 120.6, 53.6, 43.1, 29.6, 26.8, 26.4. HRMS (ESI) *m/z*: [(M - H)$^{+}$] calcd for $C_{22}H_{17}Cl_2$: 316.0786, found 316.0784.



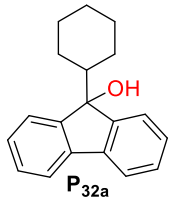
P1a

9-benzyl-9-(4-nitrophenyl)-9H-fluorene (P1a):[6] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P1a** as colourless oil (0.093 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.45 (d, *J* = 8.9 Hz, 2H), 7.33 – 7.28 (m, 6H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.80 (t, *J* = 7.7 Hz, 2H), 6.45 – 6.42 (m, 2H), 3.82 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.8, 149.5, 146.8, 141.0, 135.6, 130.1, 128.0, 128.0, 127.6, 127.1, 126.2, 125.0, 123.8, 120.2, 60.1, 43.7.



P10a

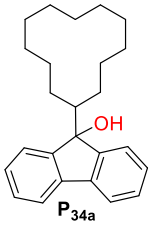
9-(3,4-dimethoxybenzyl)-9H-fluoren-9-ol (P10a): The crude product was isolated by the treatment with H_2O and DEE to give **P10a** (0.059 g, 88%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 6.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 6.52 (d, *J* = 8.2 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 1H), 6.29 (s, 1H), 3.71 (s, 3H), 3.52 (s, 3H), 3.19 (s, 2H), 2.17 (bs, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.3, 147.9, 147.6, 139.6, 129.0, 128.8, 127.6, 124.3, 123.0, 120.1, 113.7, 110.3, 82.6, 55.8, 55.6, 45.6. HRMS (ESI) *m/z*: [(M – H_2O)$^{+}$] calcd for $C_{22}H_{19}O_2$: 315.1385, found 315.1378.



P32a

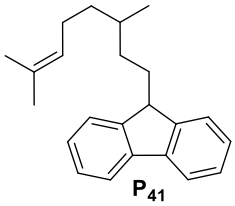
9-cyclohexyl-9H-fluoren-9-ol (P32a): The crude product was isolated by the treatment with H_2O and DEE to give **P32a** (0.045 g, 86%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52

(d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 2H), 2.09 – 2.01 (m, 1H), 1.97 (bs, 1H), 1.64 – 1.48 (m, 4H), 1.21 – 1.05 (m, 3H), 0.96 – 0.75 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.8, 140.2, 128.8, 127.8, 124.2, 119.8, 85.1, 47.6, 27.3, 26.6, 26.5. HRMS (ESI) *m/z*: $[(M - H_2O)^+]$ calcd for $C_{19}H_{19}$: 247.1487, found 247.1488.

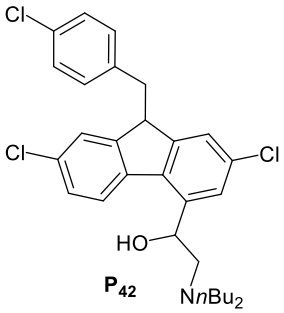


P34a

9-cyclododecyl-9H-fluoren-9-ol (P34a): The crude product was isolated by the treatment with H_2O and DEE to give **P34a** (0.054 g, 78%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 6.0 Hz, 2H), 2.39 – 2.27 (m, 1H), 1.96 (bs, 1H), 1.51 – 1.39 (m, 2H), 1.37 – 1.02 (m, 20H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.2, 140.2, 128.9, 127.7, 124.5, 119.9, 85.4, 42.8, 26.4, 24.7, 24.1, 24.0, 23.7. HRMS (ESI) *m/z*: $[(M - H_2O)^+]$ calcd for $C_{25}H_{31}$: 331.2426, found 331.2434.


P41

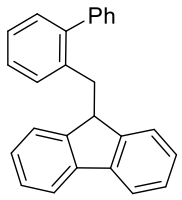
9–(3,7–dimethyloct–6–en–1–yl)–9H–fluorene(P41):[2] The crude product was purified by column chromatography (hexane as eluent) to give pure product **P41** as colourless oil (0.131 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.34 (m, 4H), 5.14 – 5.10 (m, 1H), 4.03 (t, *J* = 5.7 Hz, 1H), 2.14 – 2.05 (m, 2H), 2.02 – 1.89 (m, 2H), 1.74 (s, 3H), 1.63 (s, 3H), 1.47 – 1.03 (m, 5H), 0.89 (d, *J* = 6.6 Hz,3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.7, 147.7, 141.3, 131.1, 127.0, 126.9, 125.0, 124.4, 124.4, 119.9, 47.7, 36.8, 32.7, 32.5, 30.4, 25.8, 25.6, 19.6, 17.8.



P42

2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol(P42):[3] The crude product was purified by column chromatography (hexane/EtOAc mixture 9:1 as eluent) to give pure product **P42** as colourless oil (0.196 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.62 – 7.52 (m, 1H), 7.32 – 7.28 (m, 1H), 7.22 – 7.13 (m, 4H), 6.99 – 6.90 (m, 2H), 5.35 – 5.29 (m, 1H), 4.11 (q, *J* = 6.6 Hz, 1H), 3.14 – 3.03 (m, 2H), 2.84 – 2.62 (m, 3H), 2.53 – 2.31 (m, 3H), 1.52 – 1.25 (m, 9H), 0.98 – 0.94 (m, 6H). $^{13}C\{^{1}H\}$ NMR (101

MHz, $CDCl_3$) δ 148.7, 148.7, 140.1, 138.6, 136.5, 134.8, 133.4, 132.5, 130.8, 128.6, 128.4, 127.7, 125.3, 125.0, 124.0, 123.8, 65.6, 60.0, 53.5, 48.3, 39.5, 29.2, 20.7, 14.2.



P_{43}

9-([1,1'-biphenyl]-2-ylmethyl)-9H-fluorene (P_{43}): The crude product was purified by column chromatography (hexane as eluent) to give pure product **P_{43}** as colourless oil (0.051 g, 76%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.32 (m, 11H), 7.19 (t, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 3.90 (t, *J* = 7.9 Hz, 1H), 3.15 (d, *J* = 7.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.2, 142.8, 141.9, 140.7, 137.7, 131.0, 130.5, 129.4, 128.4, 127.4, 127.2, 127.1, 126.7, 126.6, 124.9, 119.8, 47.5, 38.2. HRMS (ESI) *m/z*: $[(M + H)^+]$ calcd for $C_{26}H_{21}$: 333.1643, found 333.1639.

^{1}H and ^{13}C NMR spectrum:

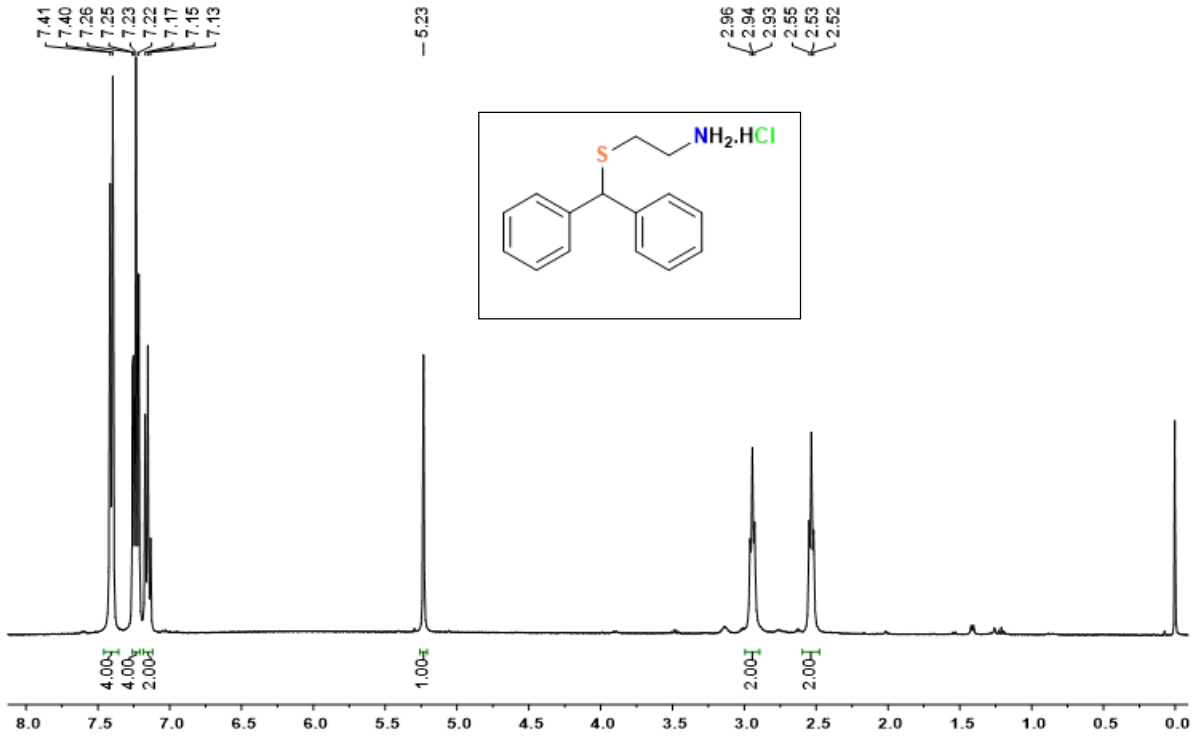


Figure S01. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-(benzhydrylthio)-ethanamine hydrochloride.

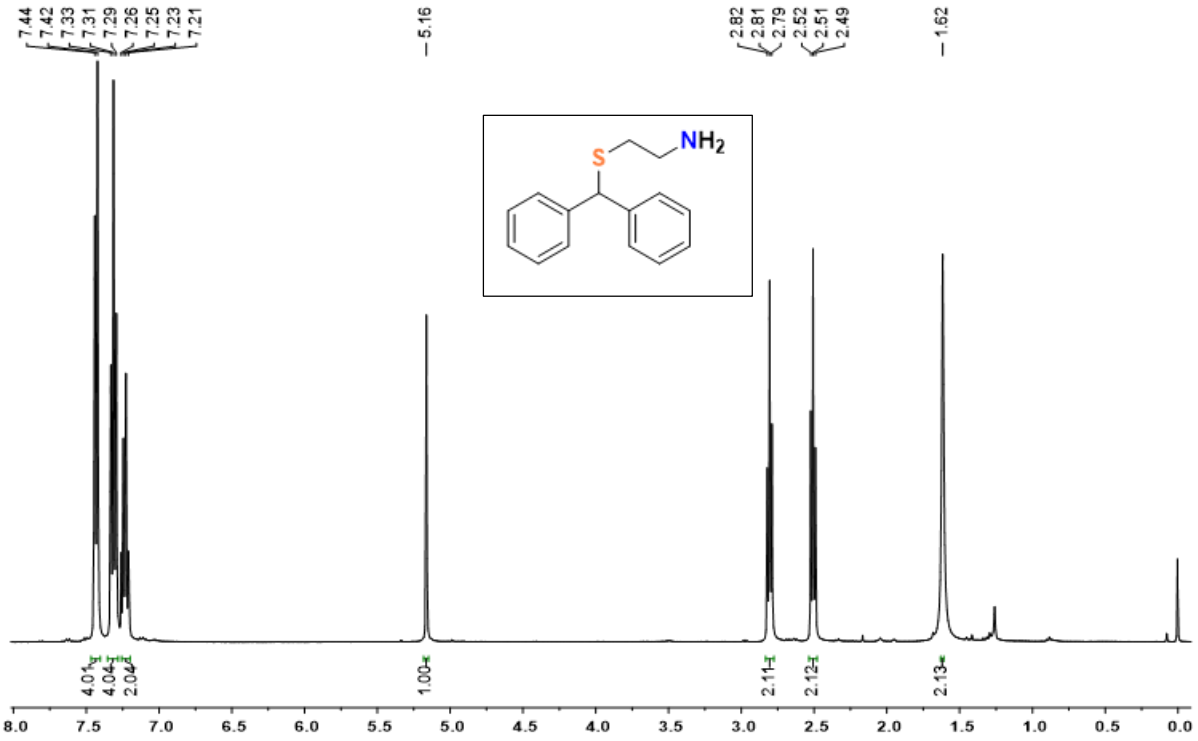


Figure S02. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-(benzhydrylthio)-ethanamine.

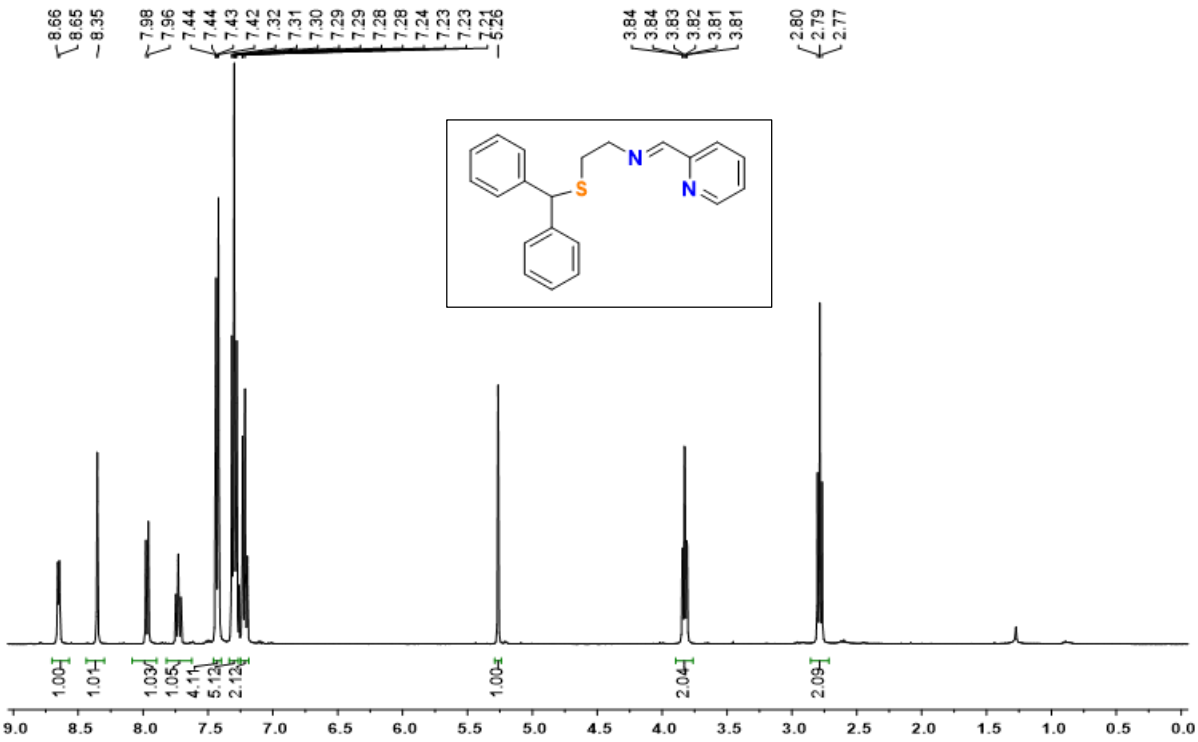


Figure S03. ^{1}H NMR (400 MHz, $CDCl_3$) of N-(2-(benzhydrlthio) ethyl)-1-(pyridine-2-yl) methanimine.

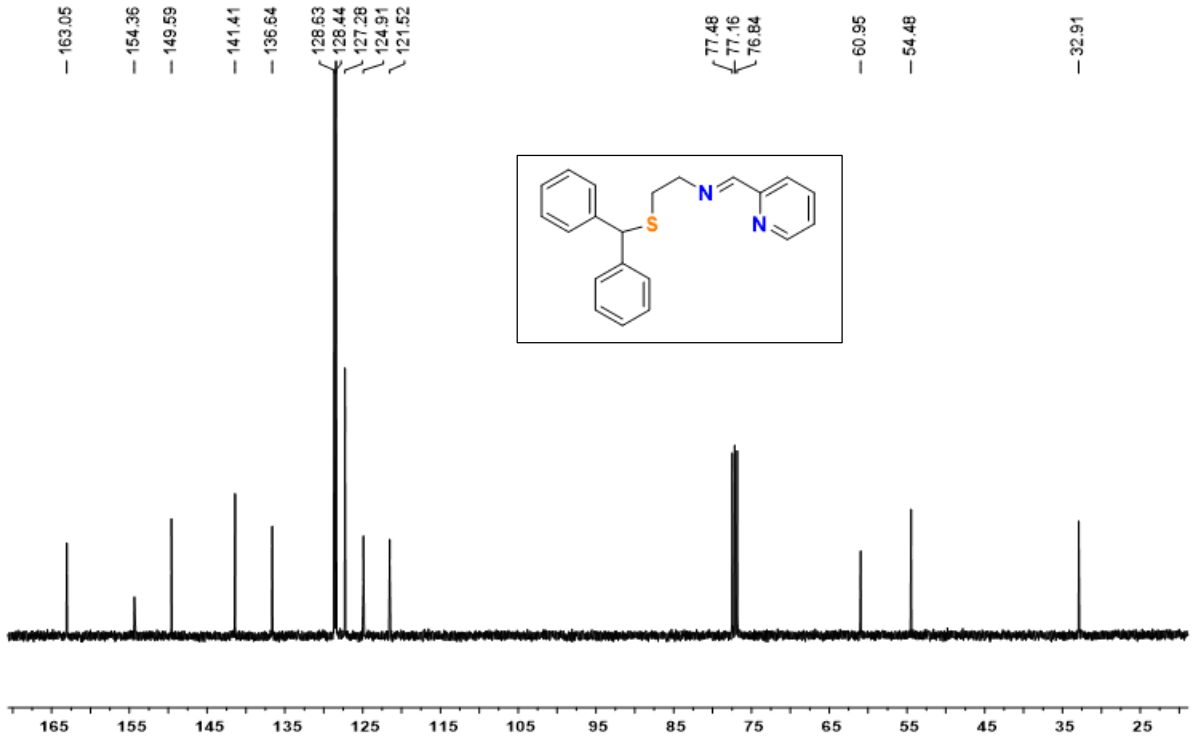


Figure S04. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of N-(2-(benzhydrlthio) ethyl)-1-(pyridine-2-yl) methanimine.

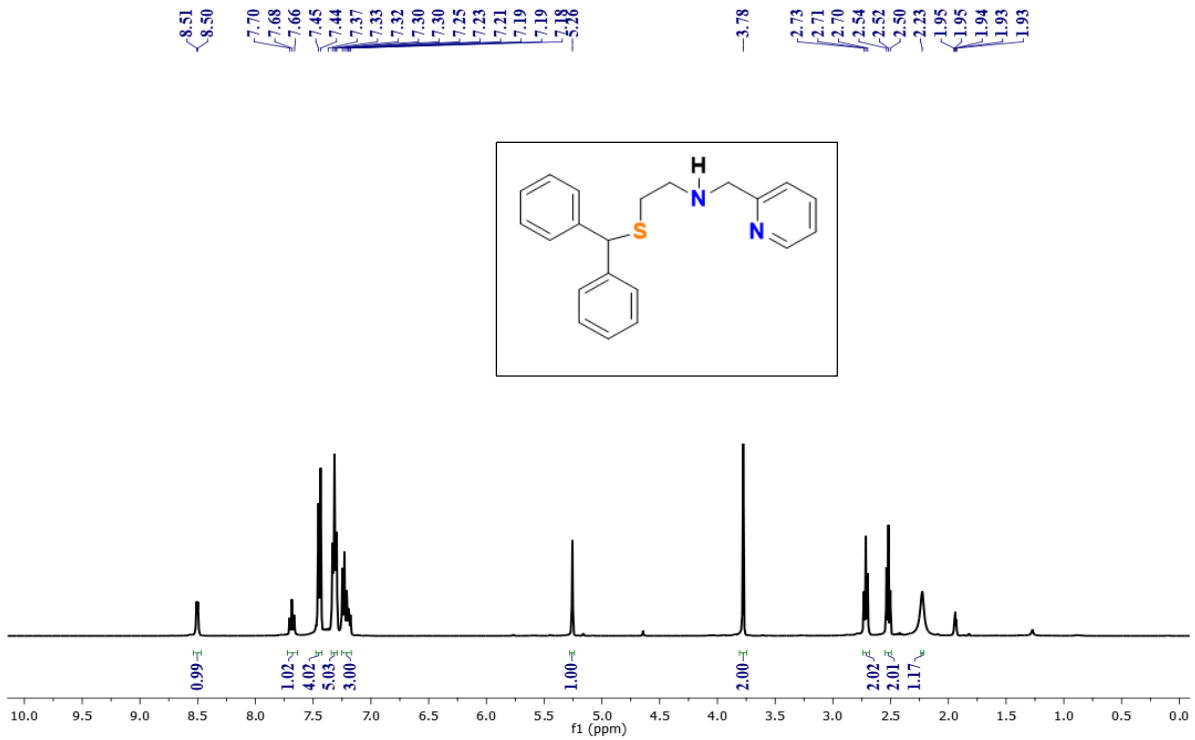


Figure S05. ^{1}H NMR (400 MHz, CD_3CN) of 2-(benzhydrylthio)-N-(pyridine-2-ylmethyl) ethan-1-amine (**L_1**)

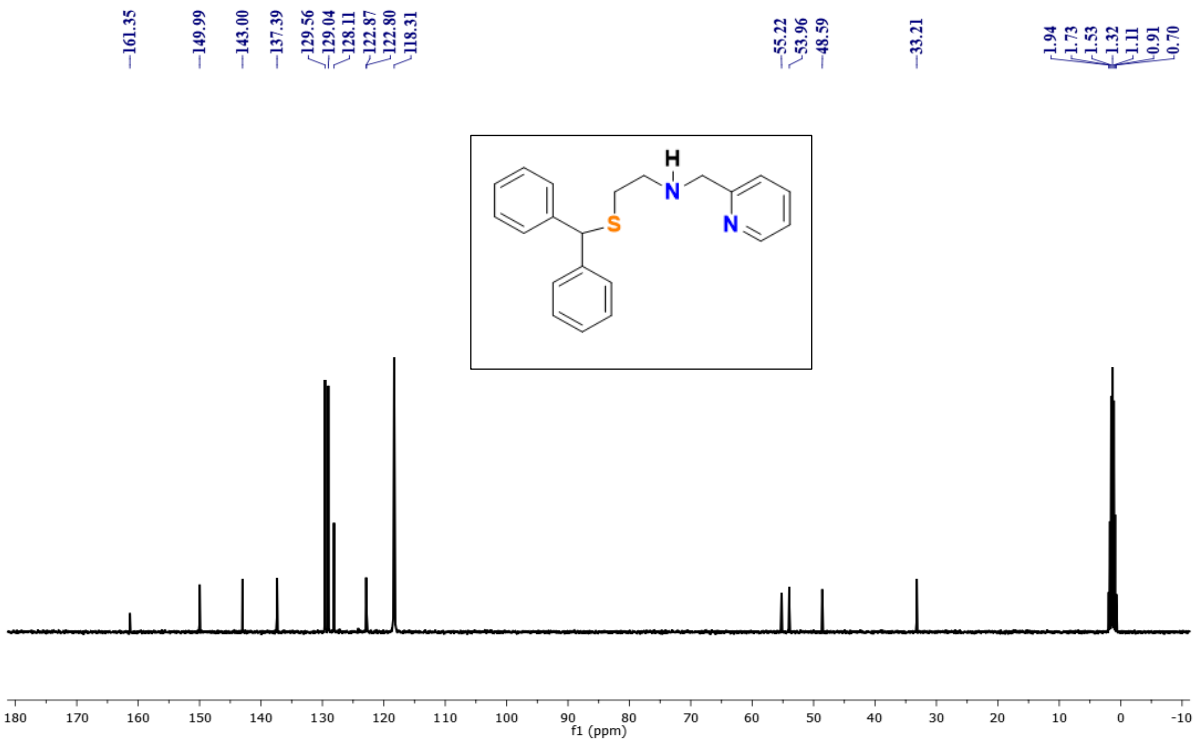


Figure S06. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) of 2-(benzhydrylthio)-N-(pyridine-2-ylmethyl) ethan-1-amine (**L_1**)

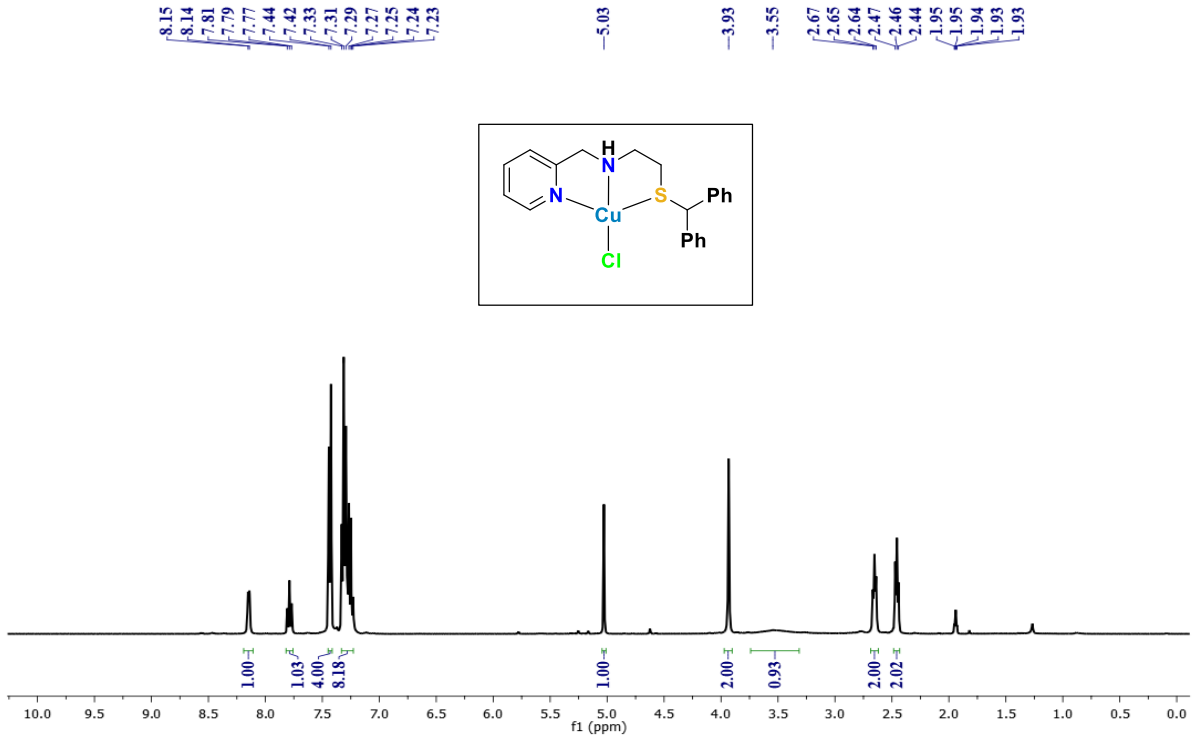


Figure S07. ^{1}H NMR (400 MHz, CD_3CN) of Complex **1**.

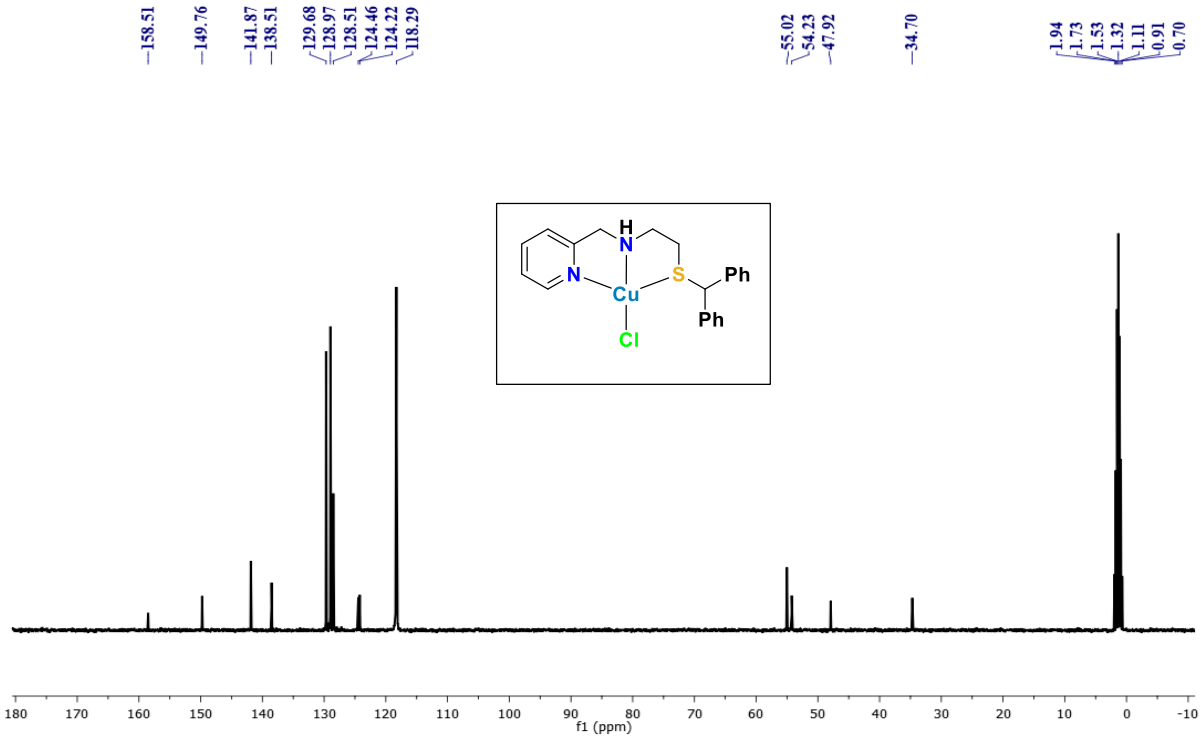


Figure S08. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN) of Complex **1**.

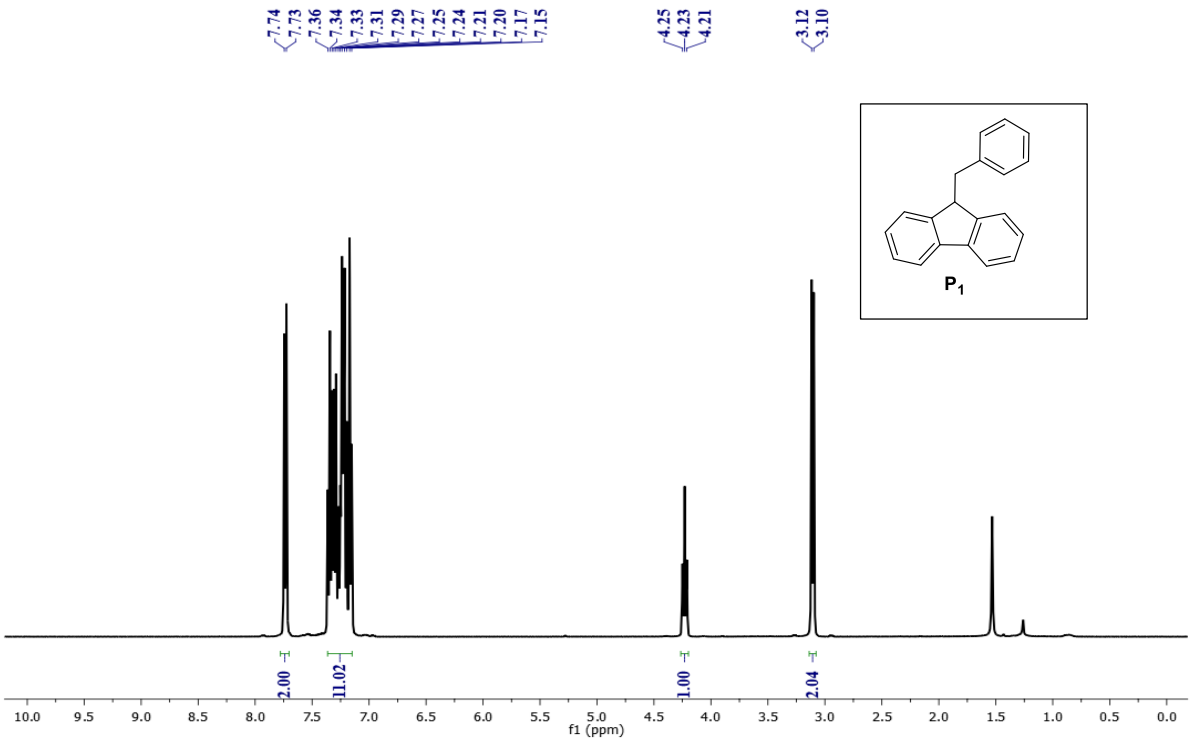


Figure S09. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-Benzyl)-9H-fluorene **(P_1)**.

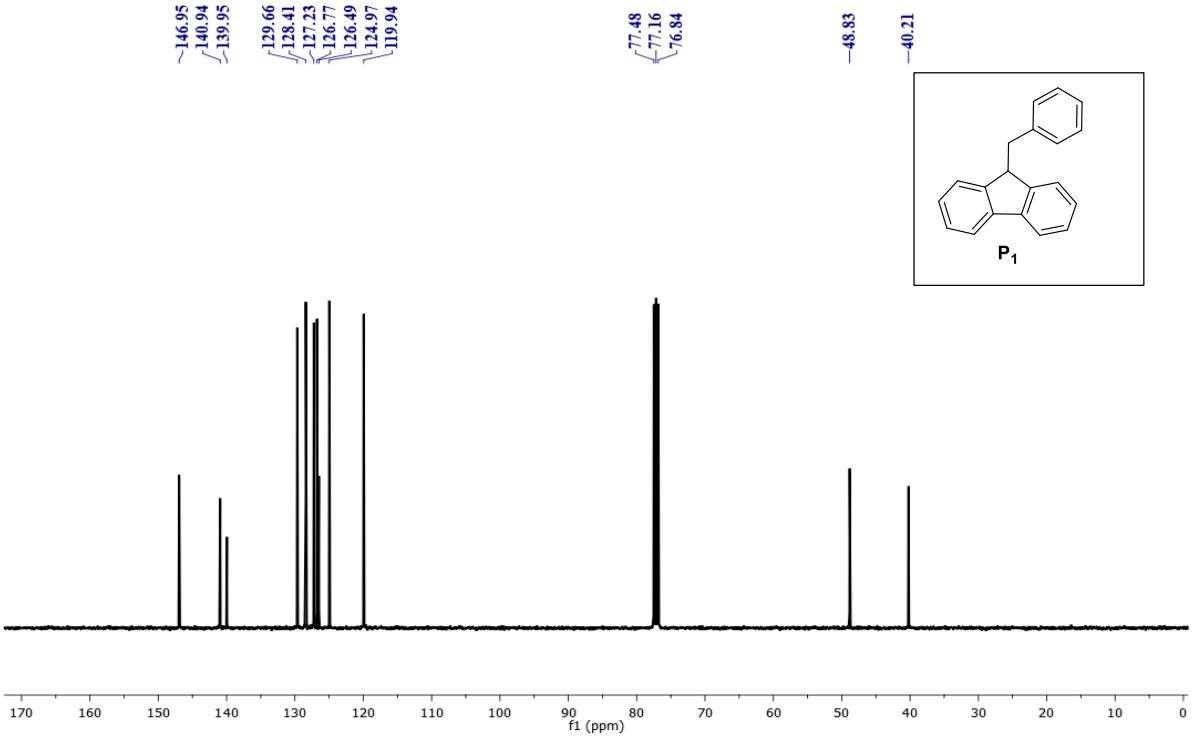


Figure S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-Benzyl)-9H-fluorene **(P_1)**.

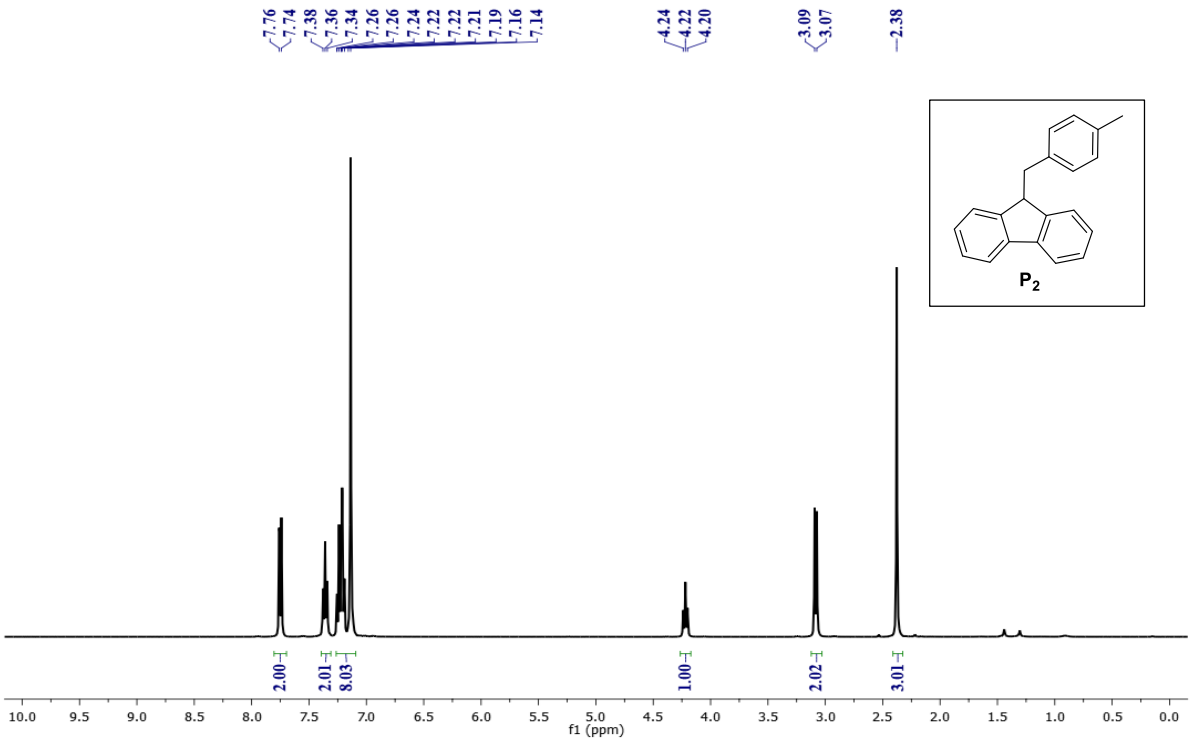


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(4-methylbenzyl)-9H-fluorene **(P_2)**.

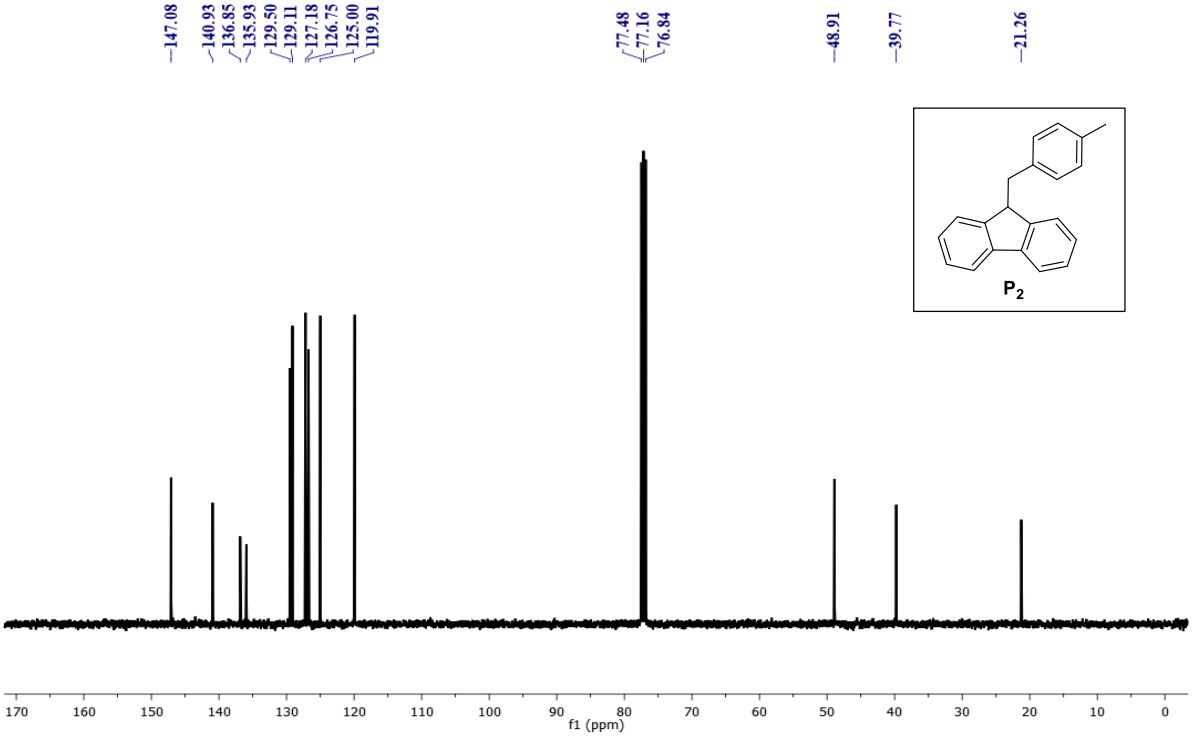


Figure S12. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-methylbenzyl)-9H-fluorene **(P_2)**.

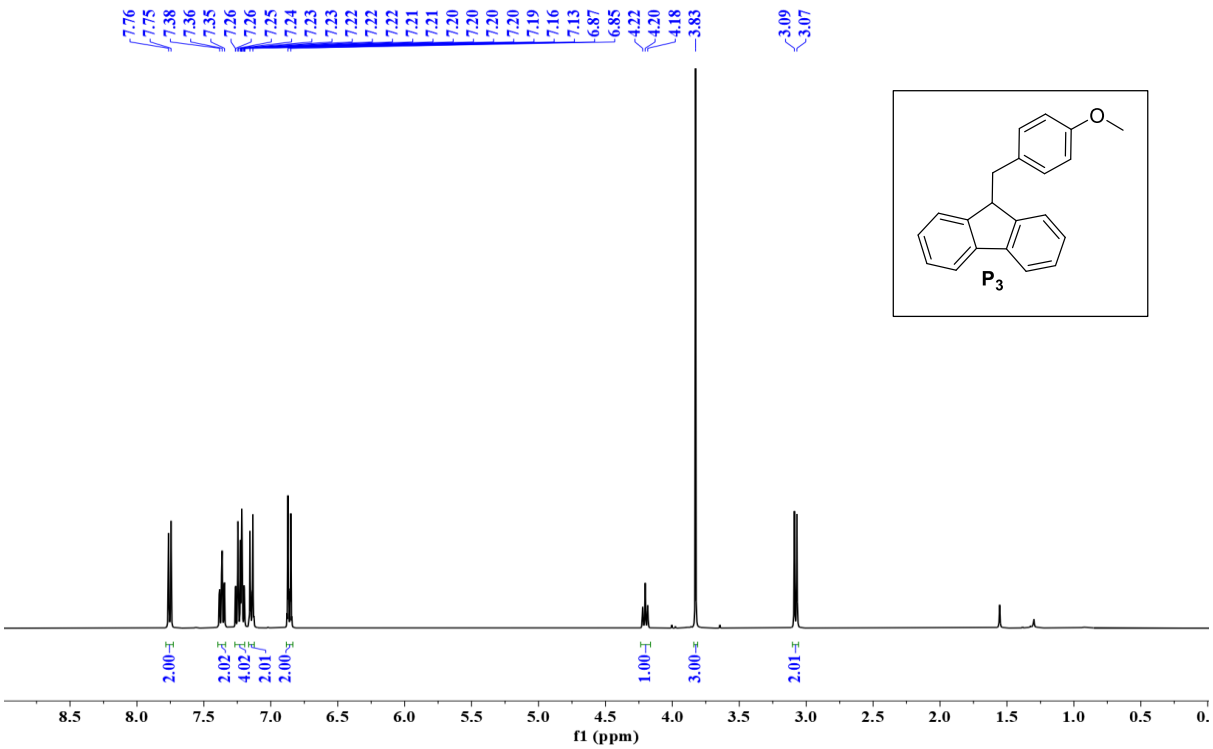


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(4-methoxybenzyl)-9H-fluorene **(P_3)**.

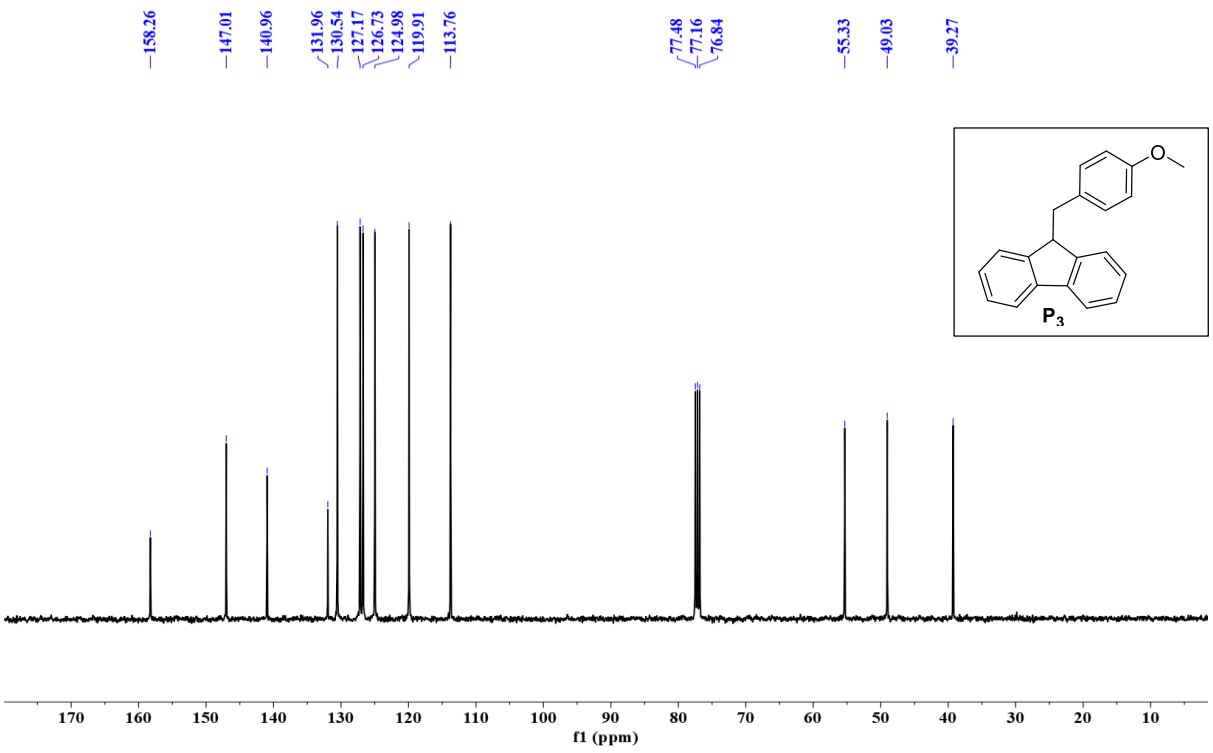


Figure S14. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-methoxybenzyl)-9H-fluorene **(P_3)**.

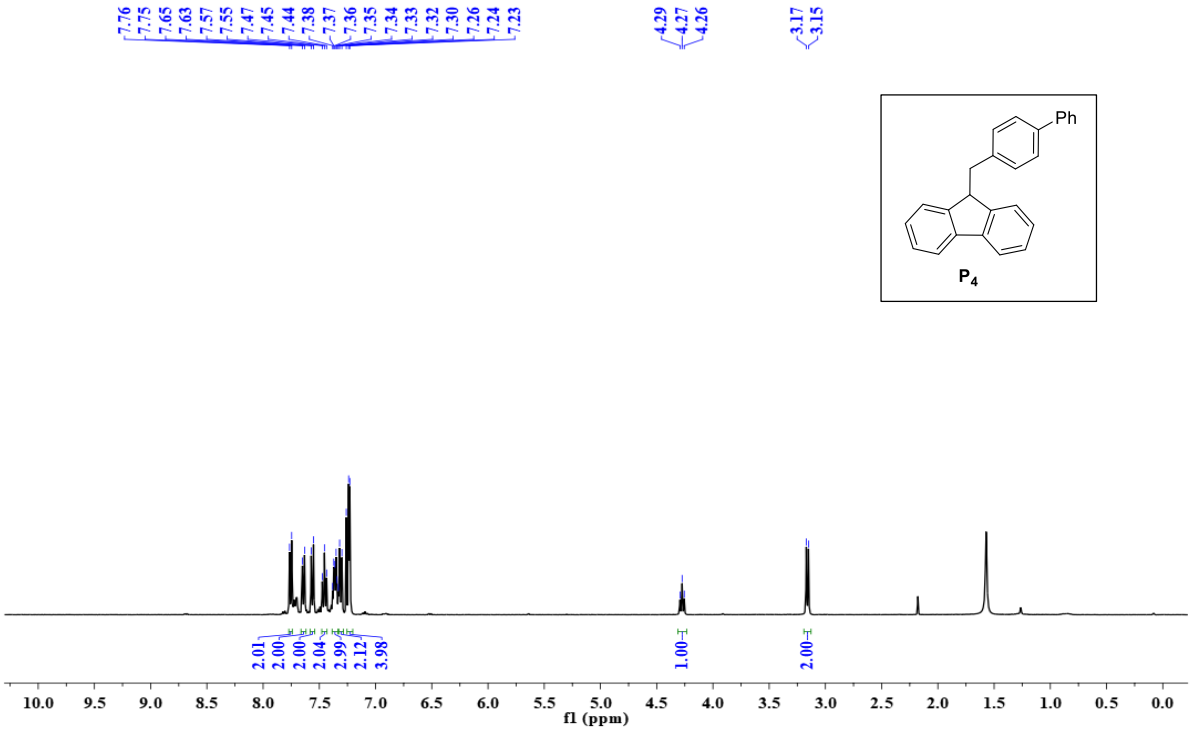


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene **(P_4)**.

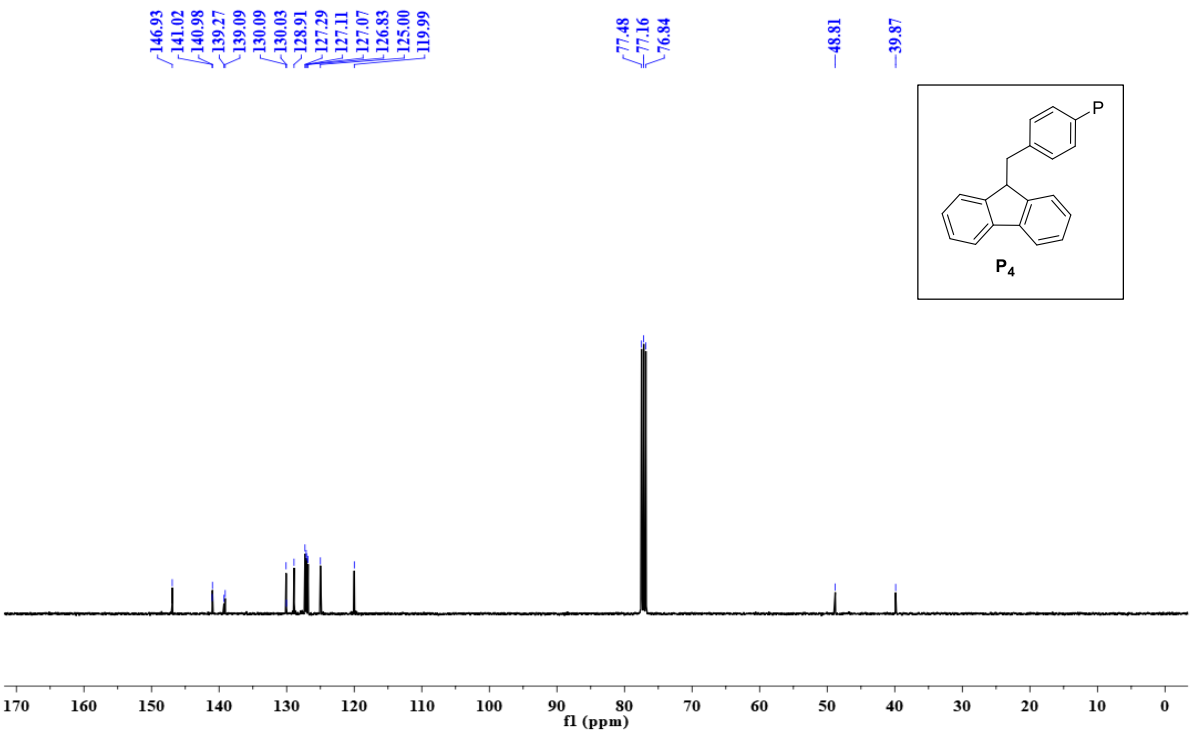


Figure S16. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene **(P_4)**.

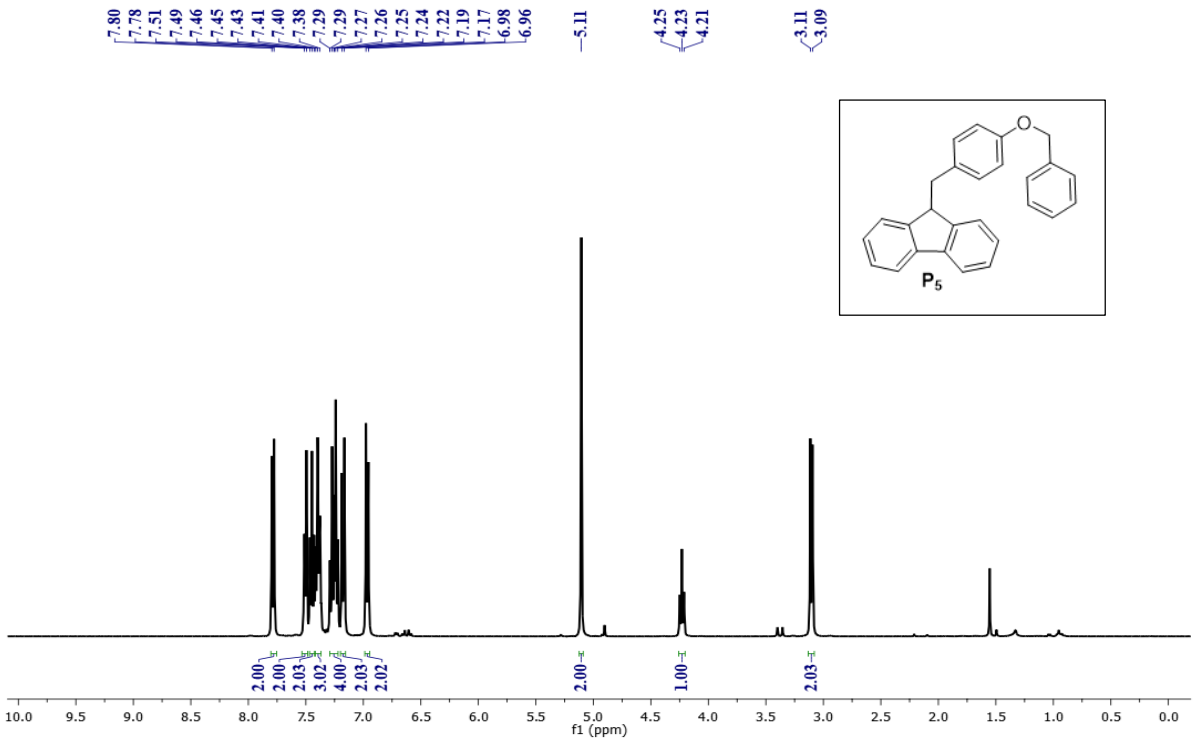


Figure S17. ^{1}H NMR (700 MHz, $CDCl_3$) of 9-(4-(benzyloxy)benzyl)-9H-fluorene **(P_5)**.

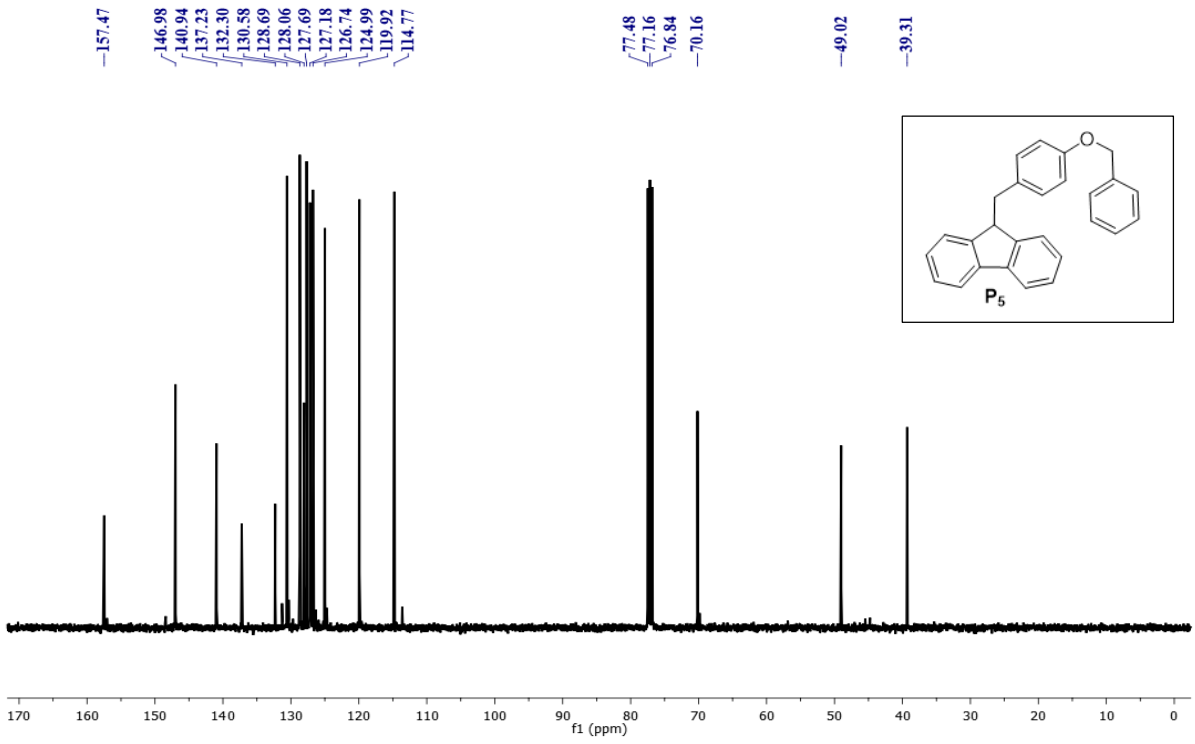


Figure S18. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-(benzyloxy)benzyl)-9H-fluorene **(P_5)**.

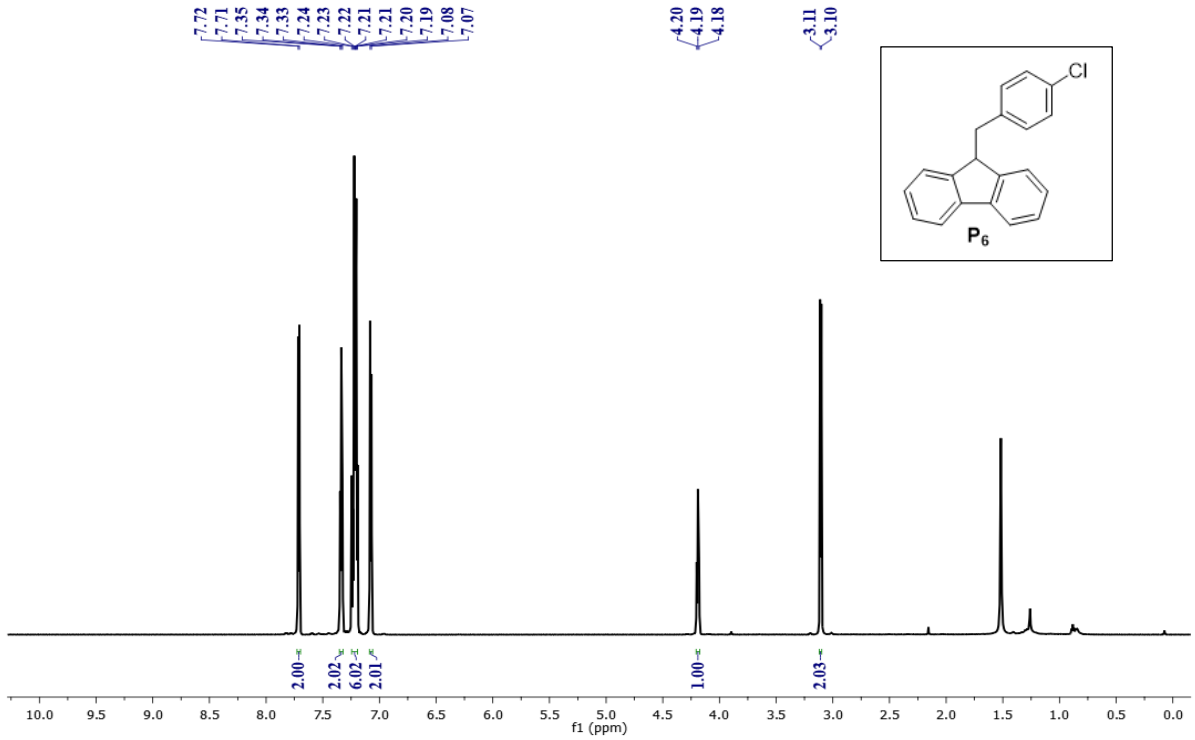


Figure S19. ^{1}H NMR (700 MHz, $CDCl_3$) of 9-(4-chlorobenzyl)-9H-fluorene **(P_6)**.

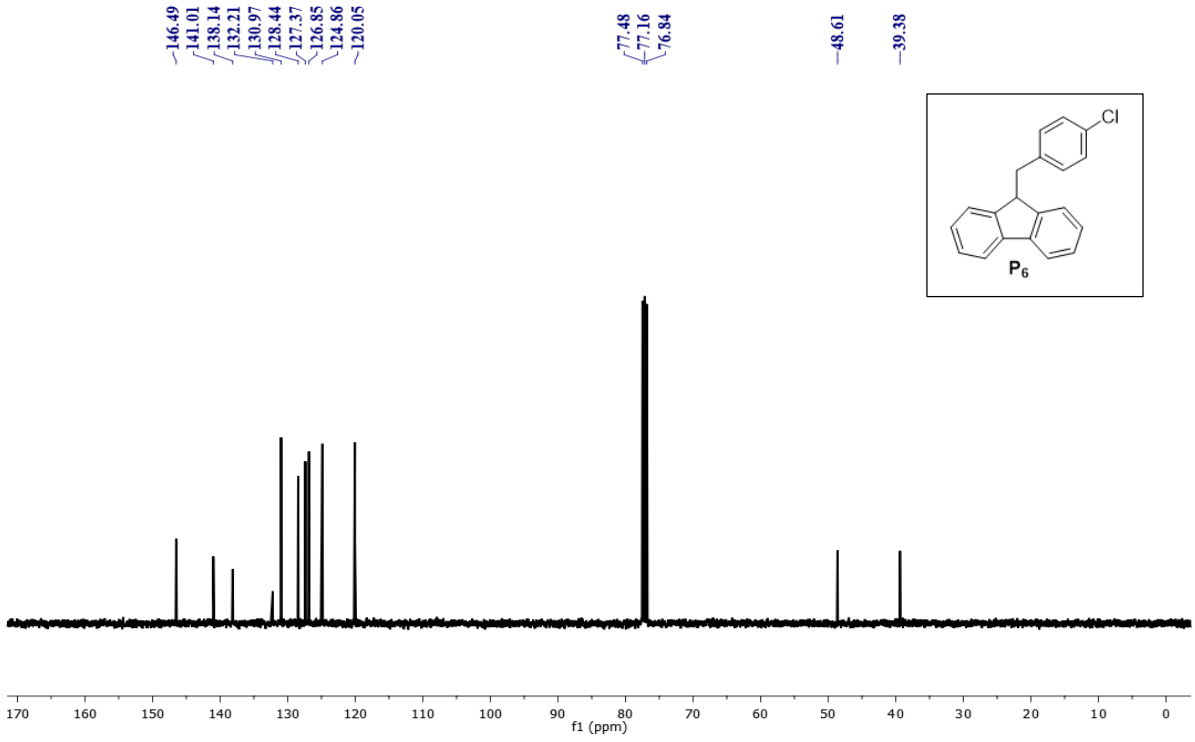


Figure S20. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-chlorobenzyl)-9H-fluorene **(P_6)**.

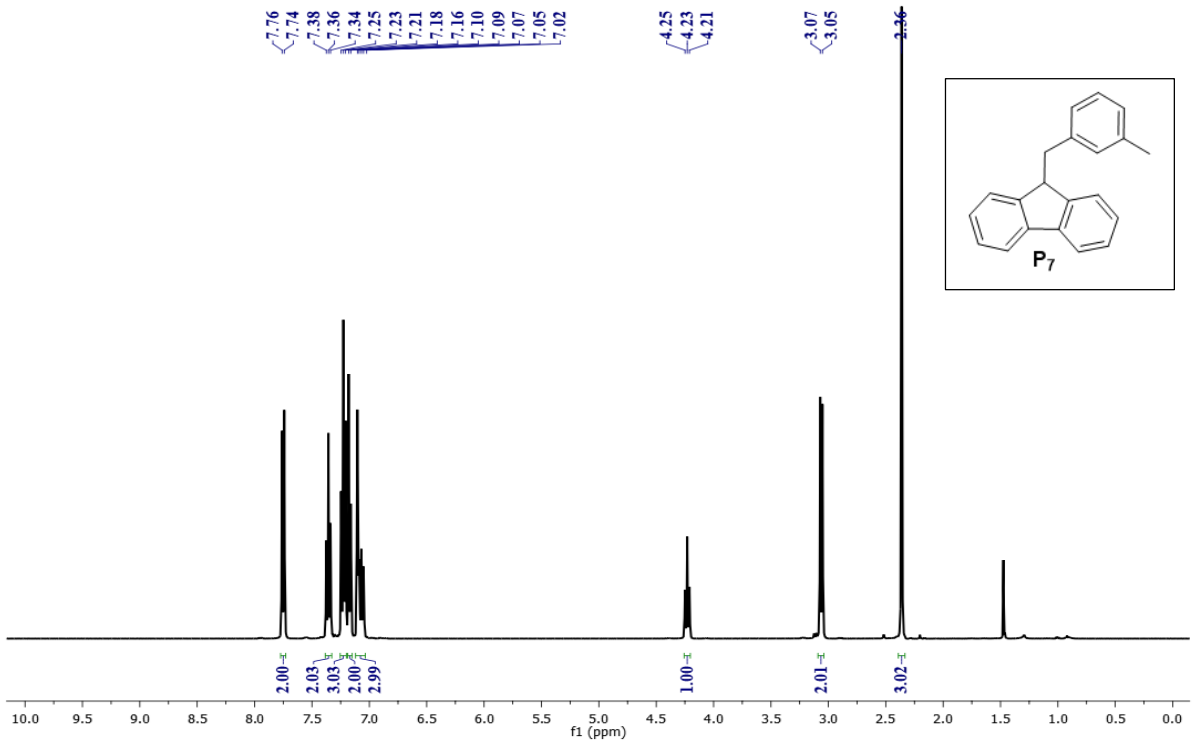


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(3-methylbenzyl)-9H-fluorene **(P_7)**.

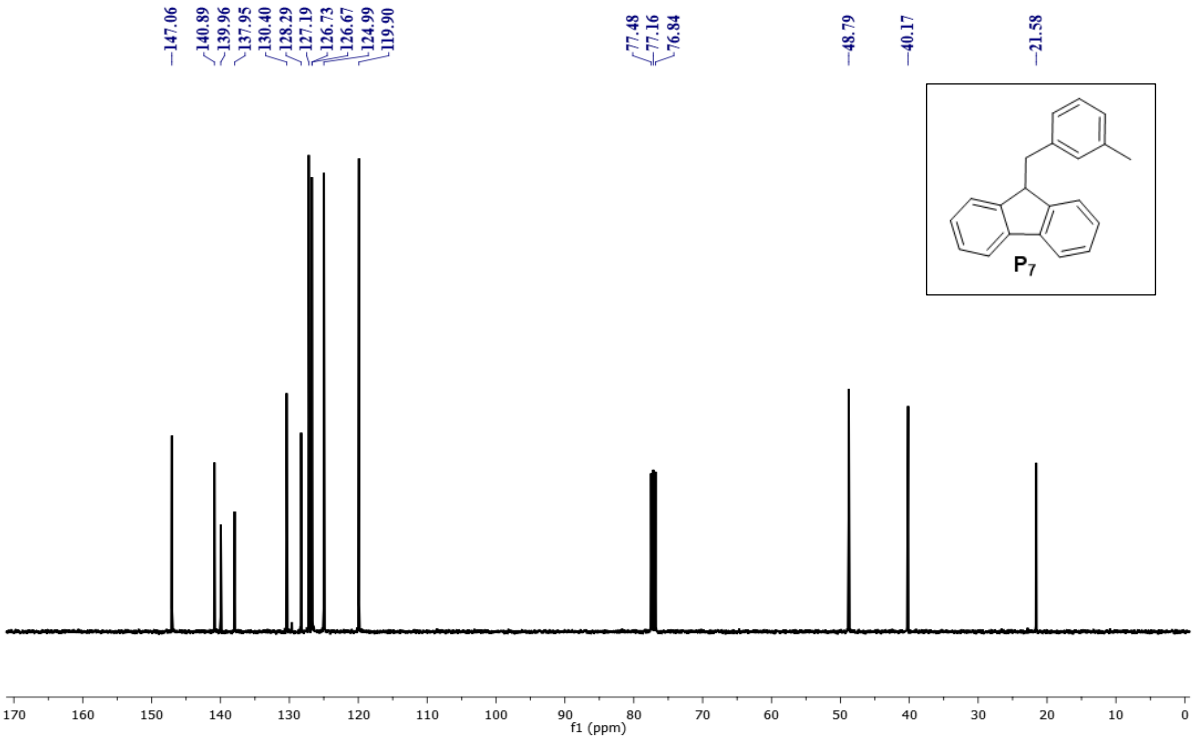


Figure S22. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(3-methylbenzyl)-9H-fluorene **(P_7)**.

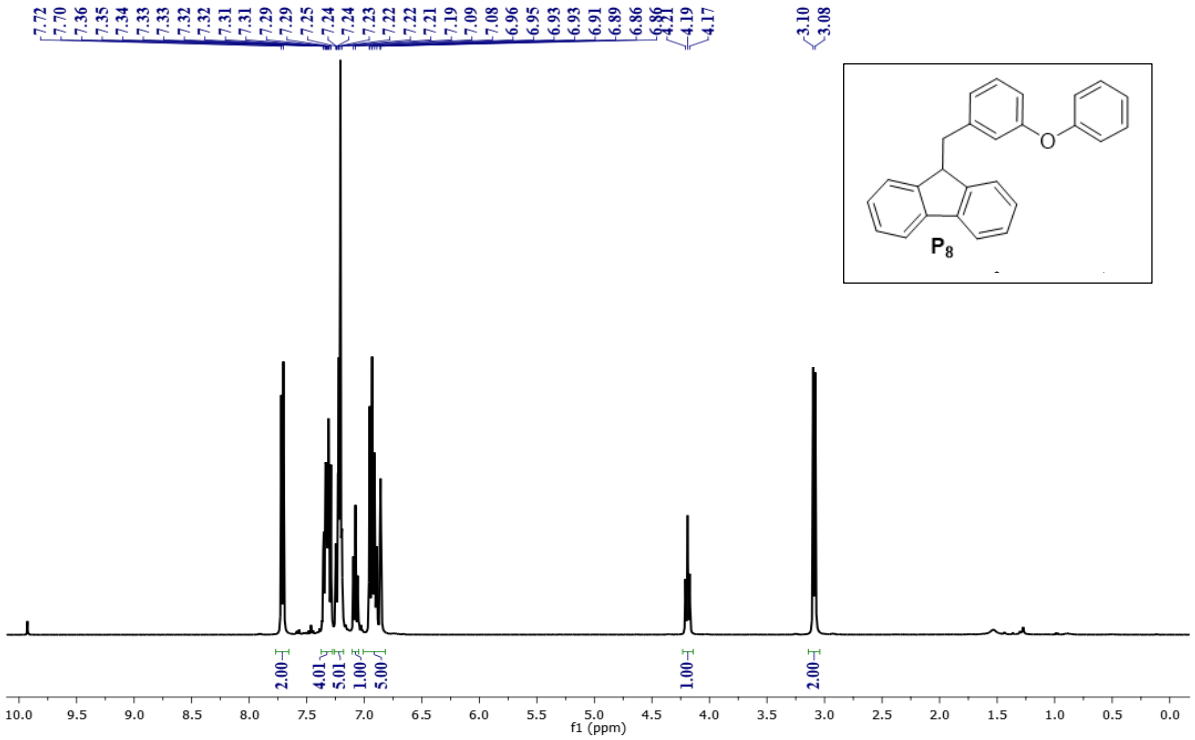


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(3-phenoxybenzyl)-9H-fluorene**(P8)**.

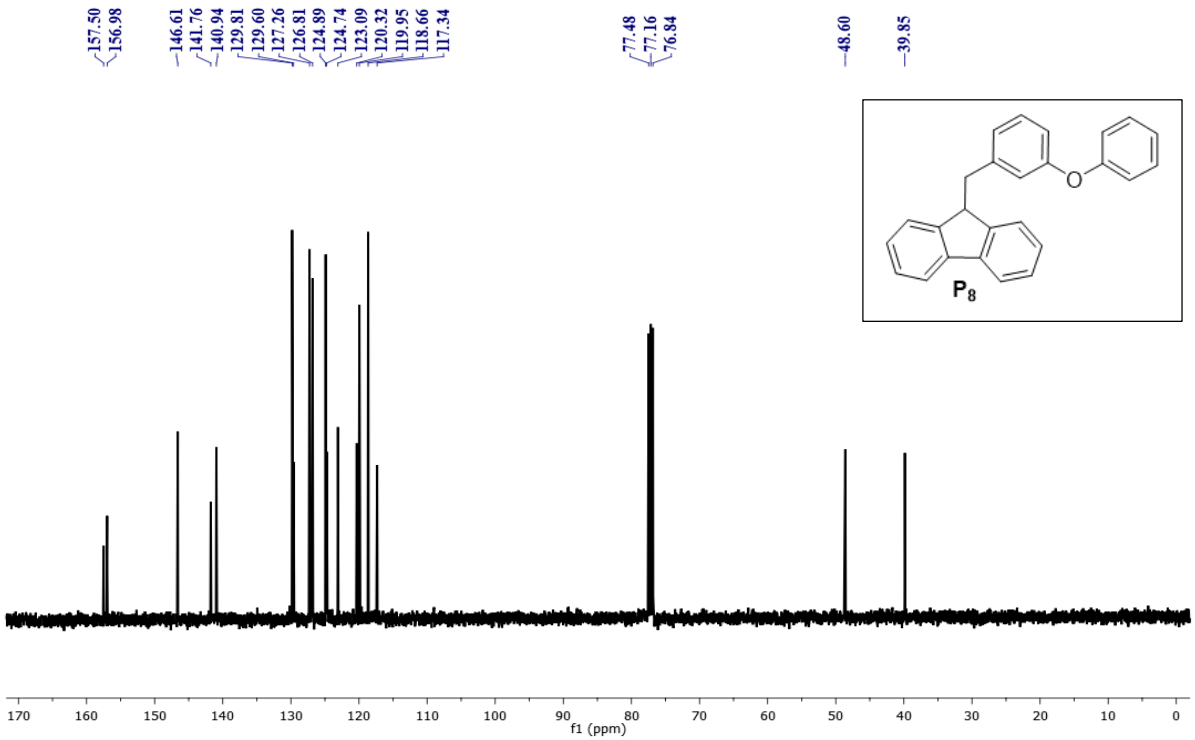


Figure S24. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(3-phenoxybenzyl)-9H-fluorene **(P8)**.

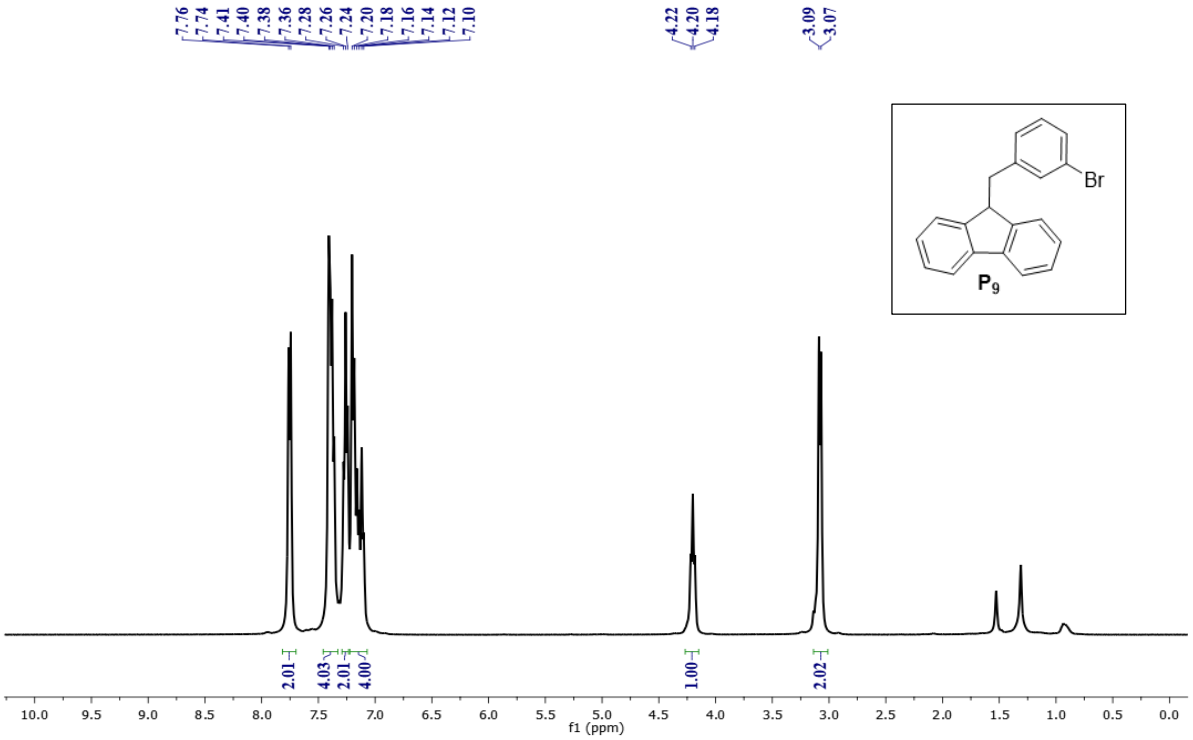


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(3-bromobenzyl)-9H-fluorene **(P9)**.

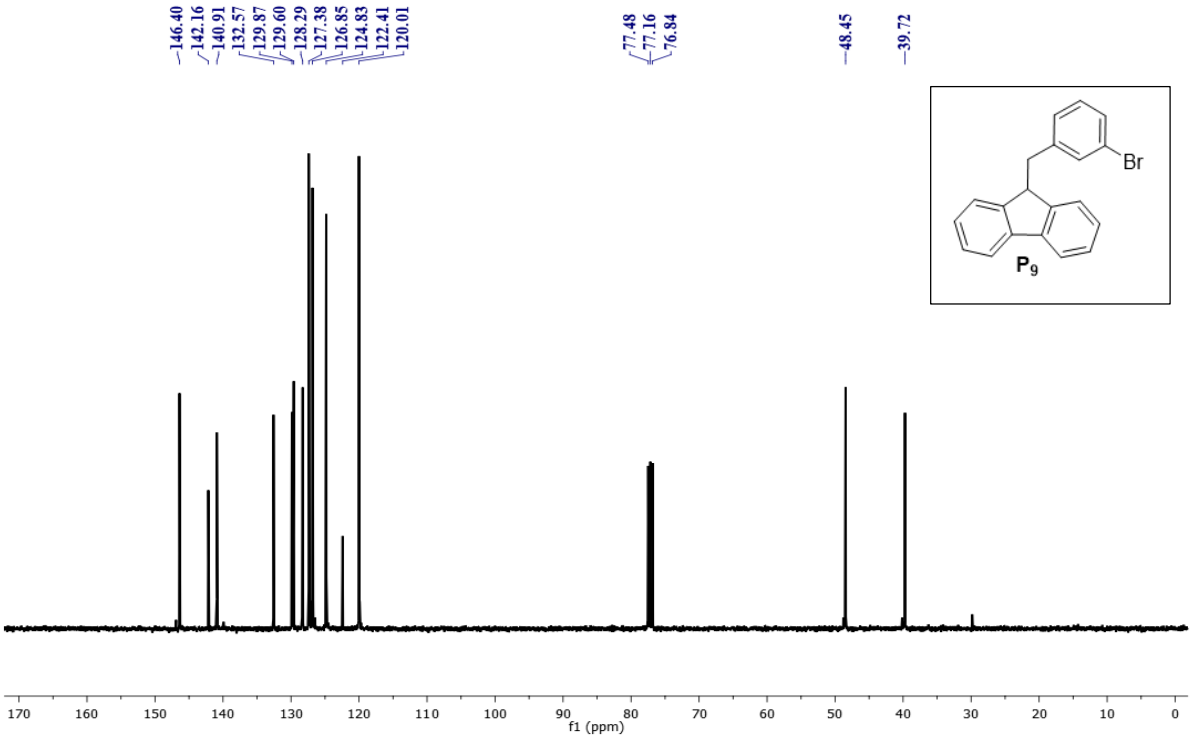


Figure S26. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(3-bromobenzyl)-9H-fluorene **(P9)**.

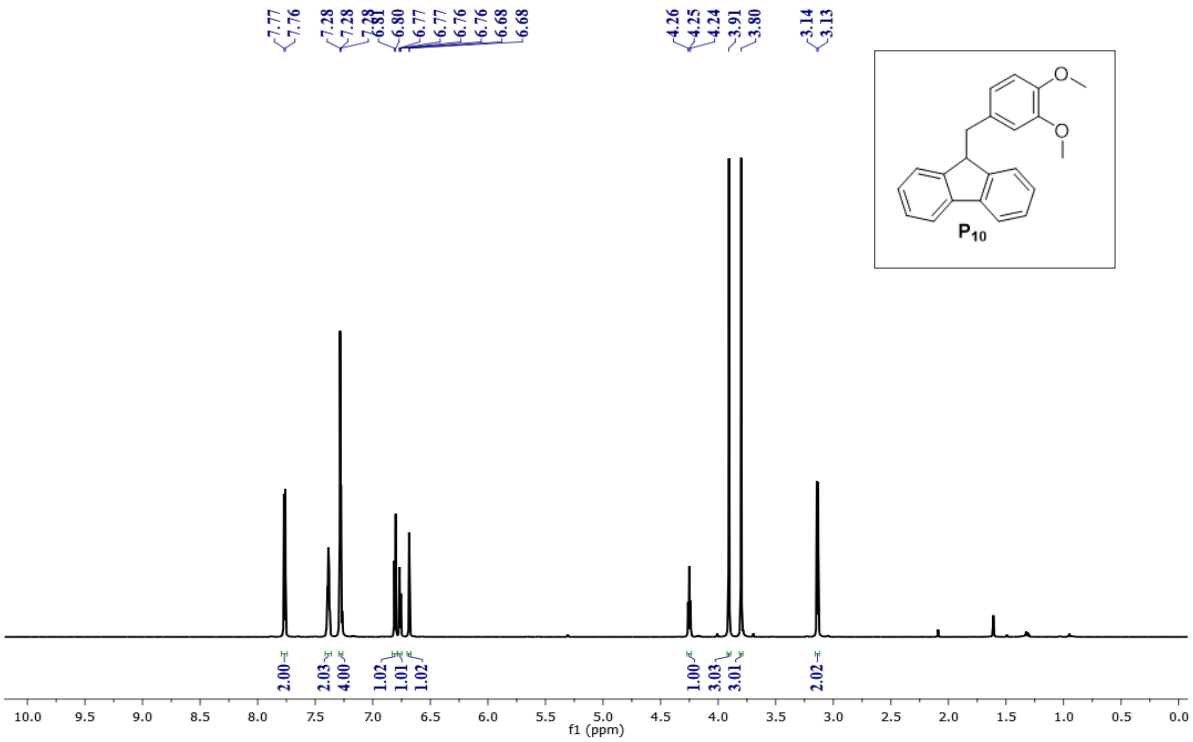


Figure S27. ^{1}H NMR (700 MHz, $CDCl_3$) of 9-(3,4-dimethoxybenzyl)-9H-fluorene **(P_{10})**.

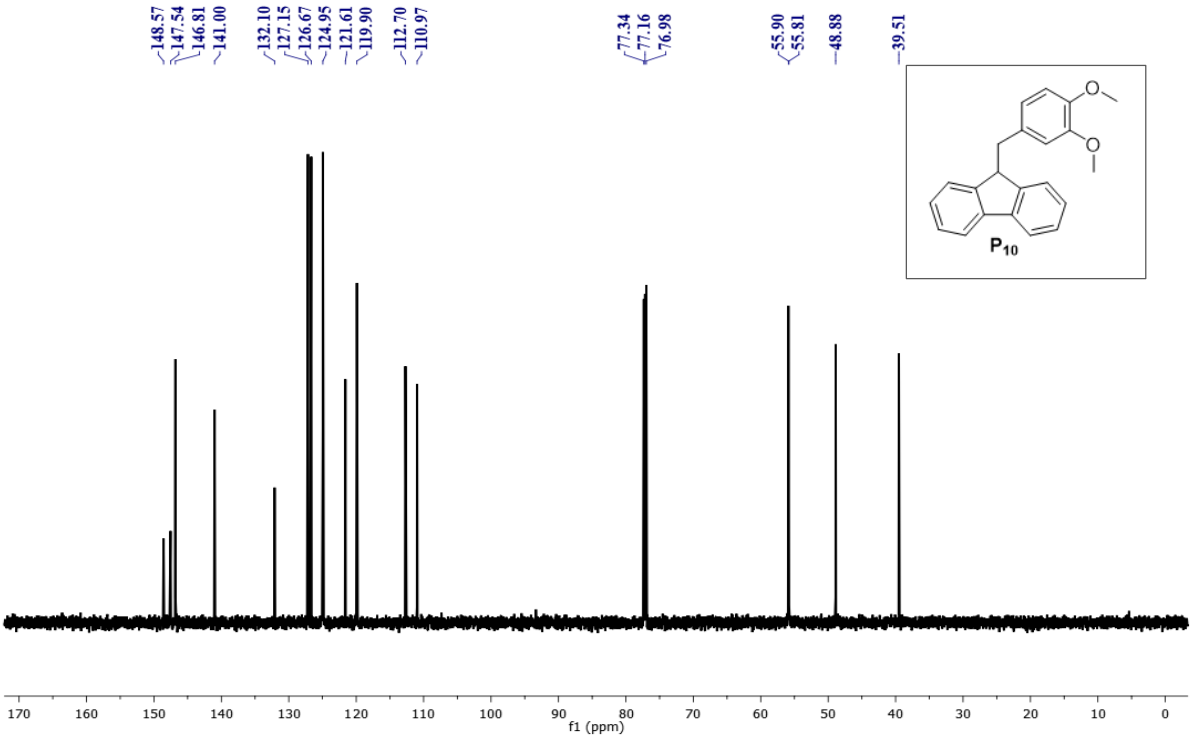


Figure S28. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) of 9-(3,4-dimethoxybenzyl)-9H-fluorene **(P_{10})**.

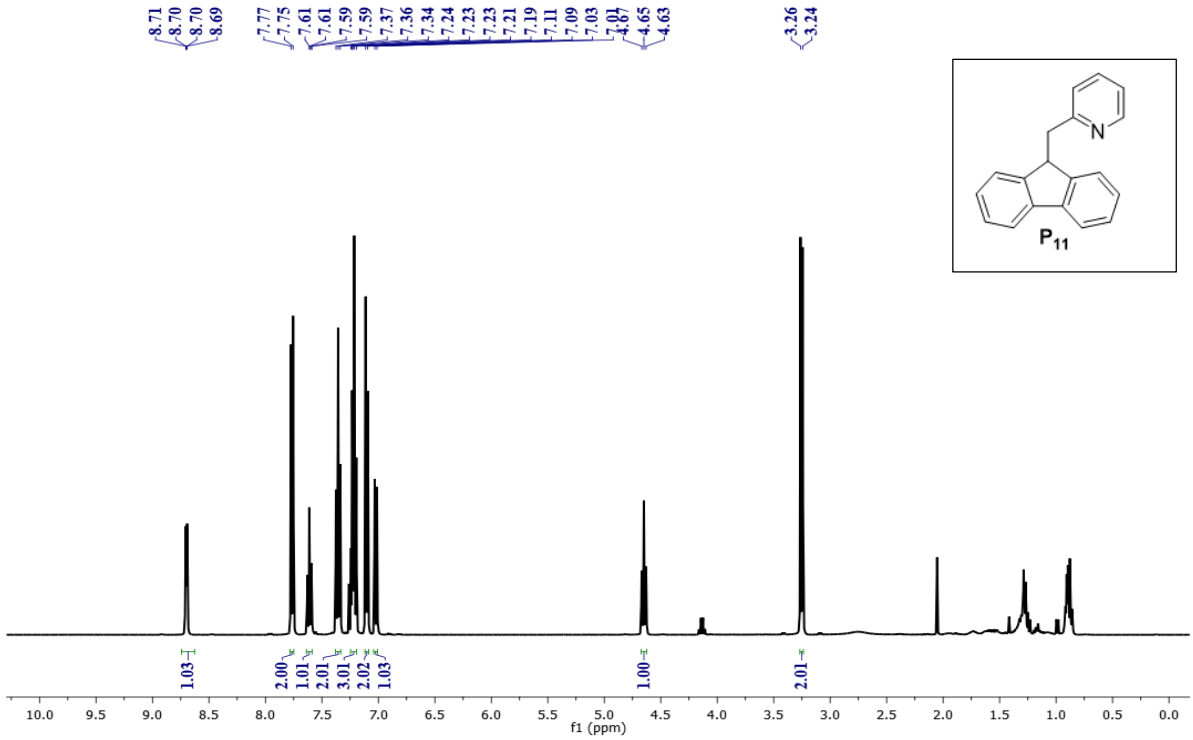


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-((9H-fluoren-9-yl)methyl)pyridine**(P_{11})**.

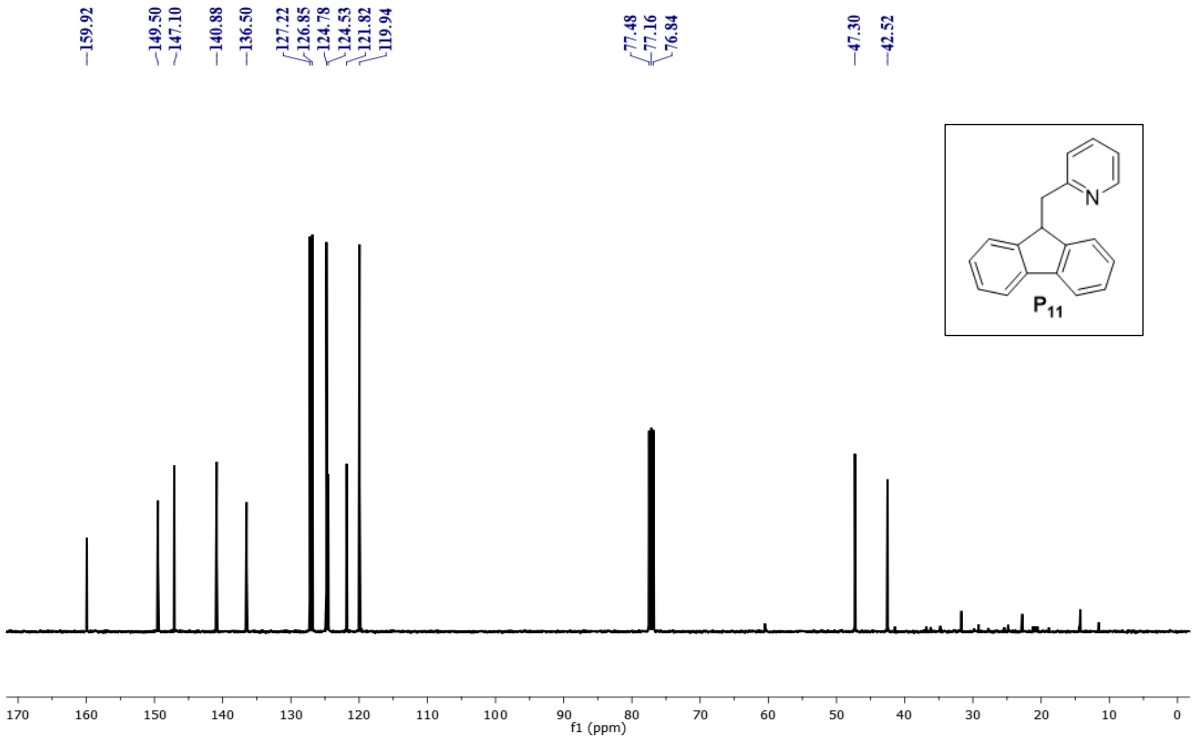


Figure S30. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-((9H-fluoren-9-yl)methyl)pyridine**(P_{11})**.

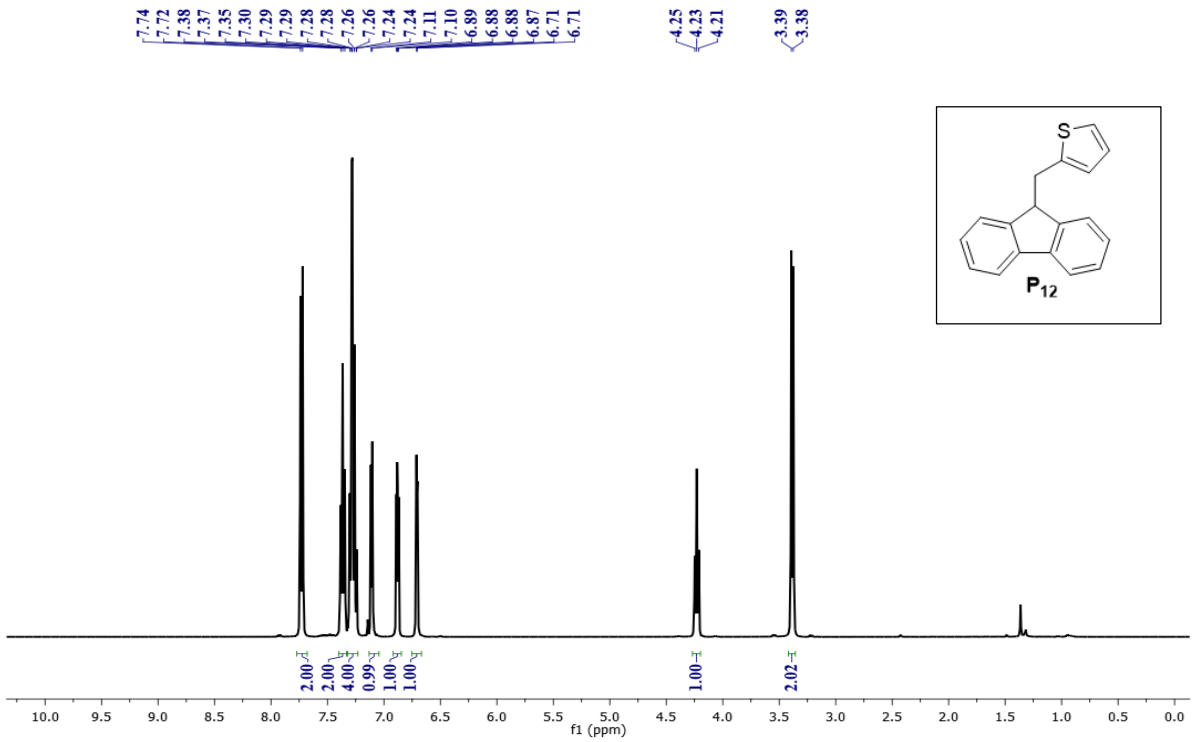


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-((9H-fluoren-9-yl)methyl)thiophene **(P_{12})**.

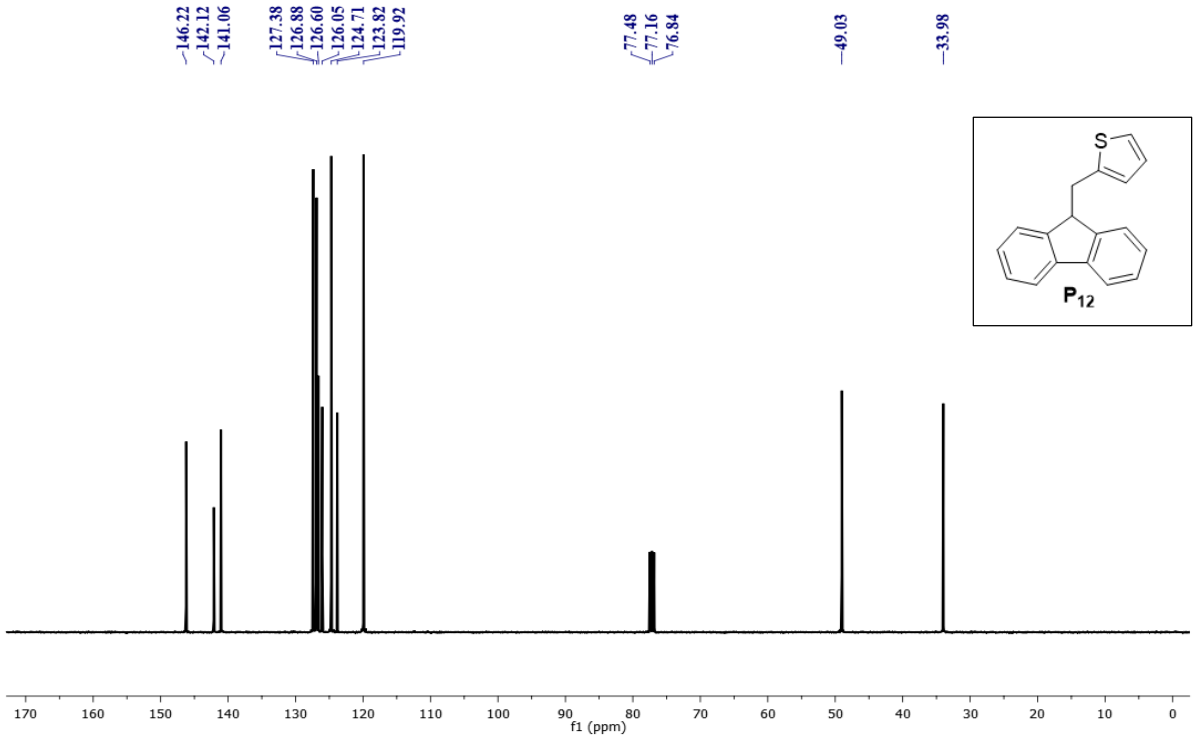


Figure S32. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-((9H-fluoren-9-yl)methyl)thiophene **(P_{12})**.

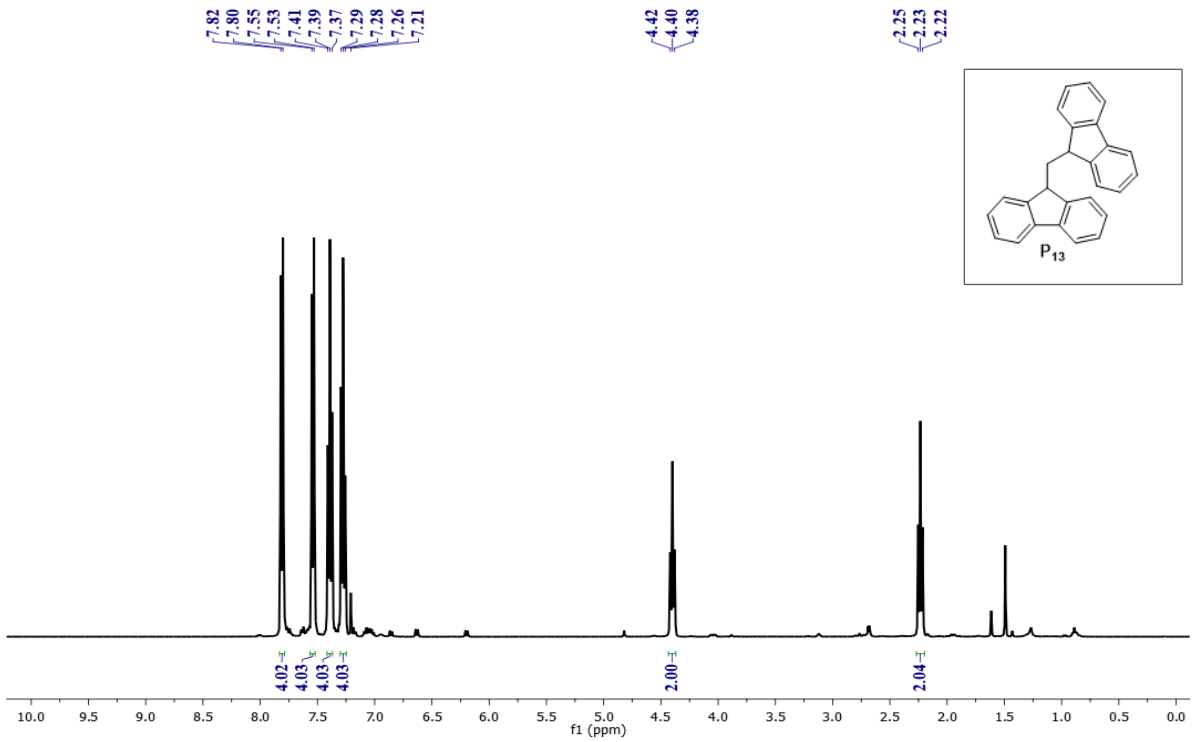


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of di(9H-fluoren-9-yl)methane **(P_{13})**.

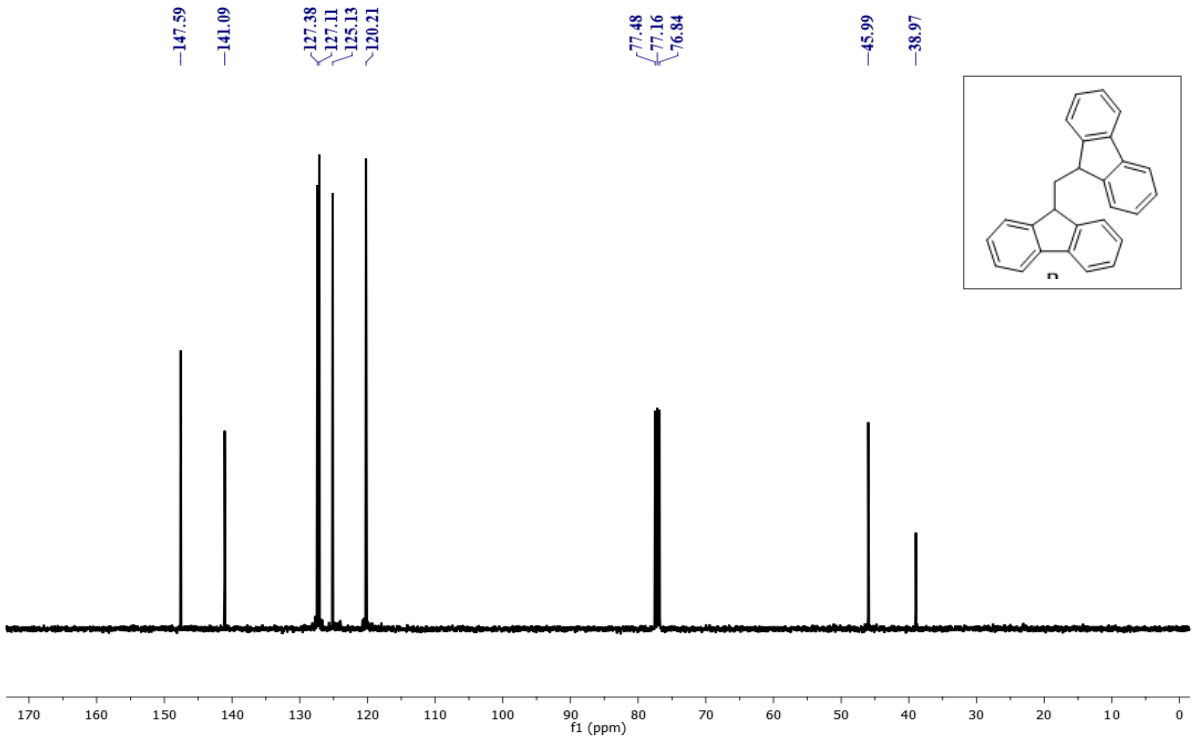


Figure S34. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of di(9H-fluoren-9-yl)methane **(P_{13})**.

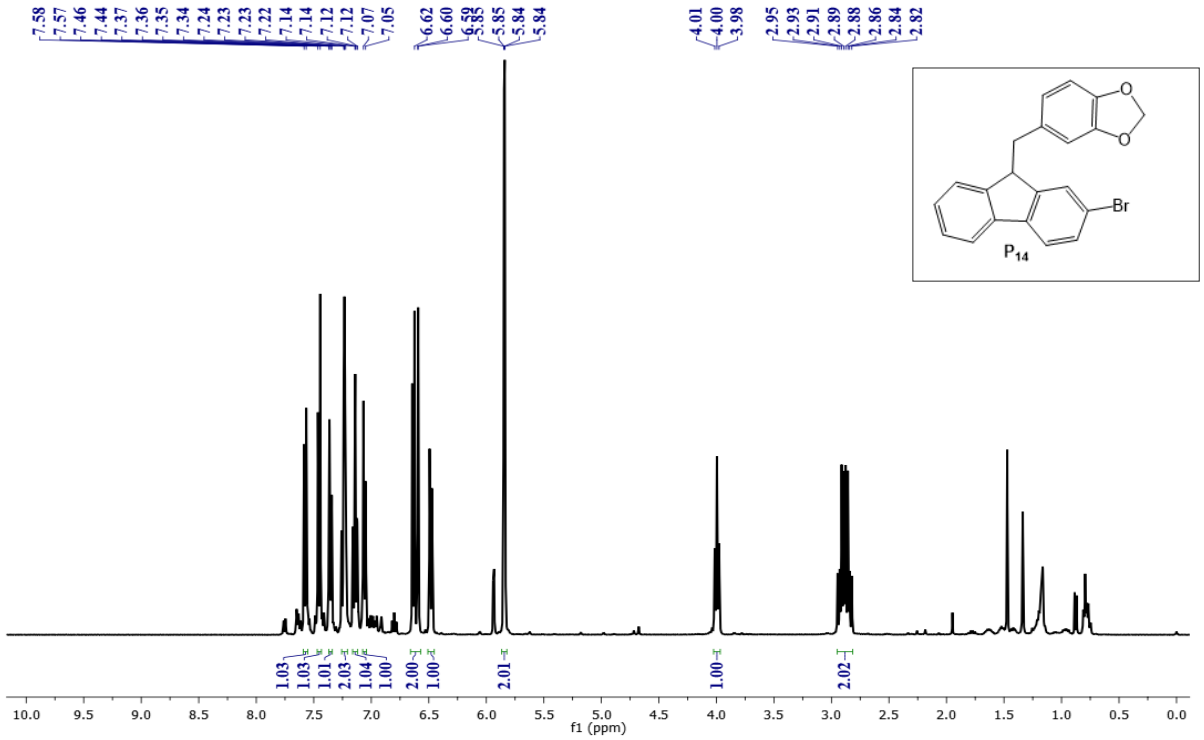


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-((2-bromo-9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole **(P_{14})**.

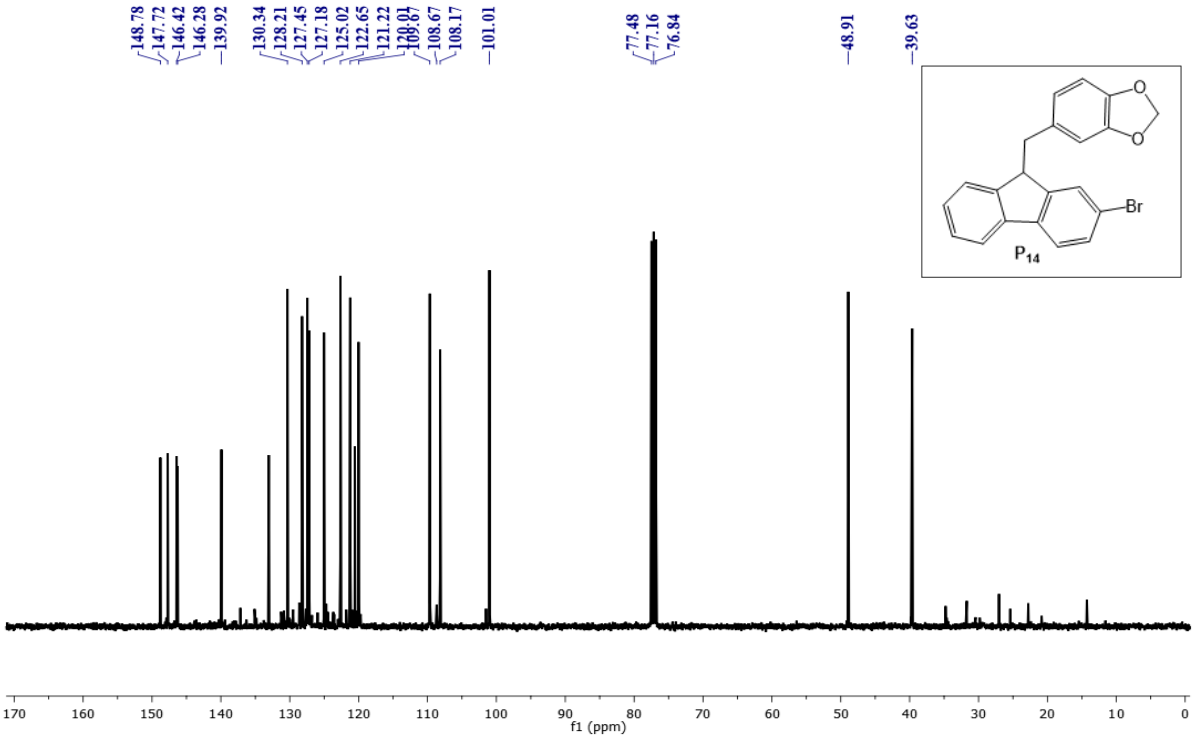


Figure S36. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 5-((2-bromo-9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole **(P_{14})**.

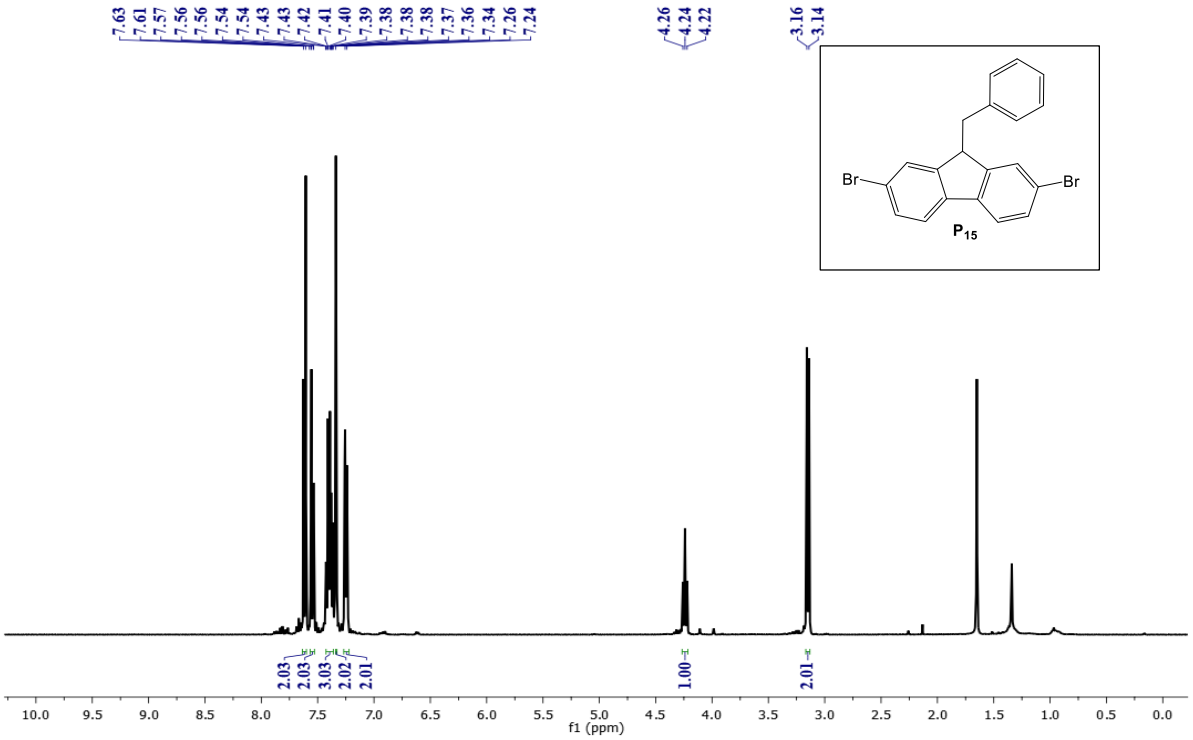


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-2,7-dibromo-9H-fluorene **(P_{15})**.

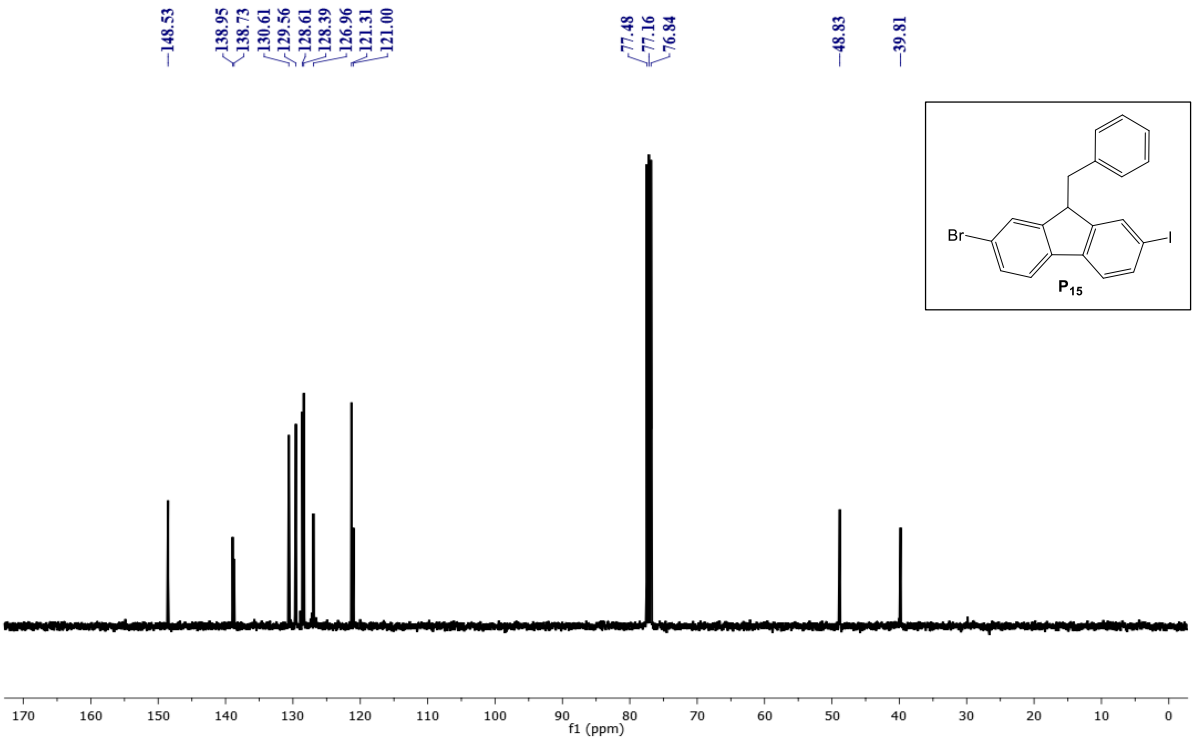


Figure S38. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-2,7-dibromo-9H-fluorene **(P_{15})**.

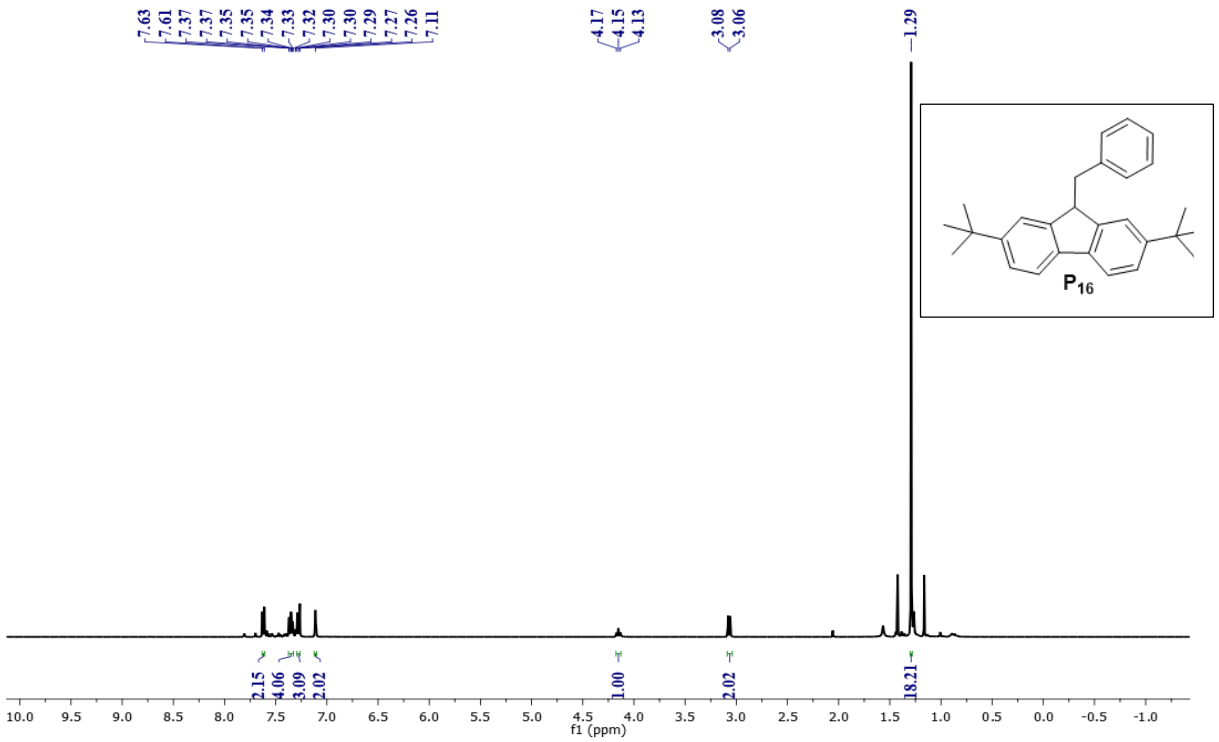


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-2,7-di-tert-butyl-9H-fluorene **(P_{16})**

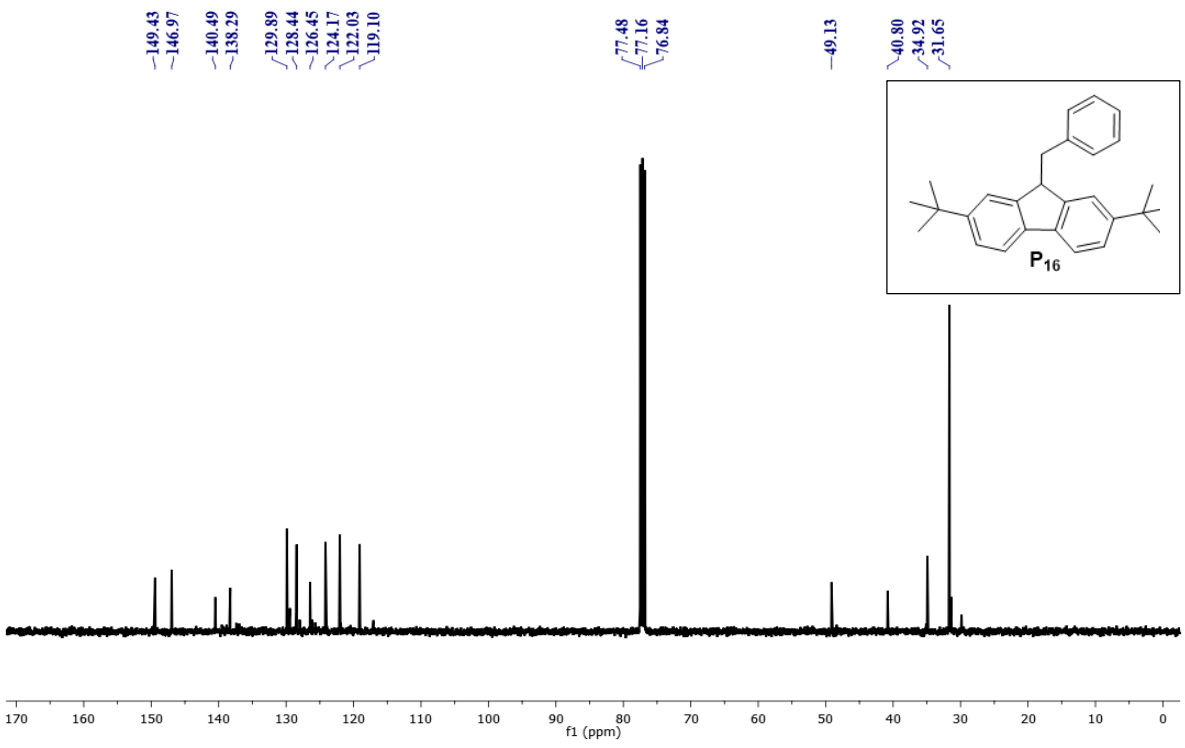


Figure S40. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-2,7-di-tert-butyl-9H-fluorene **(P_{16})**.

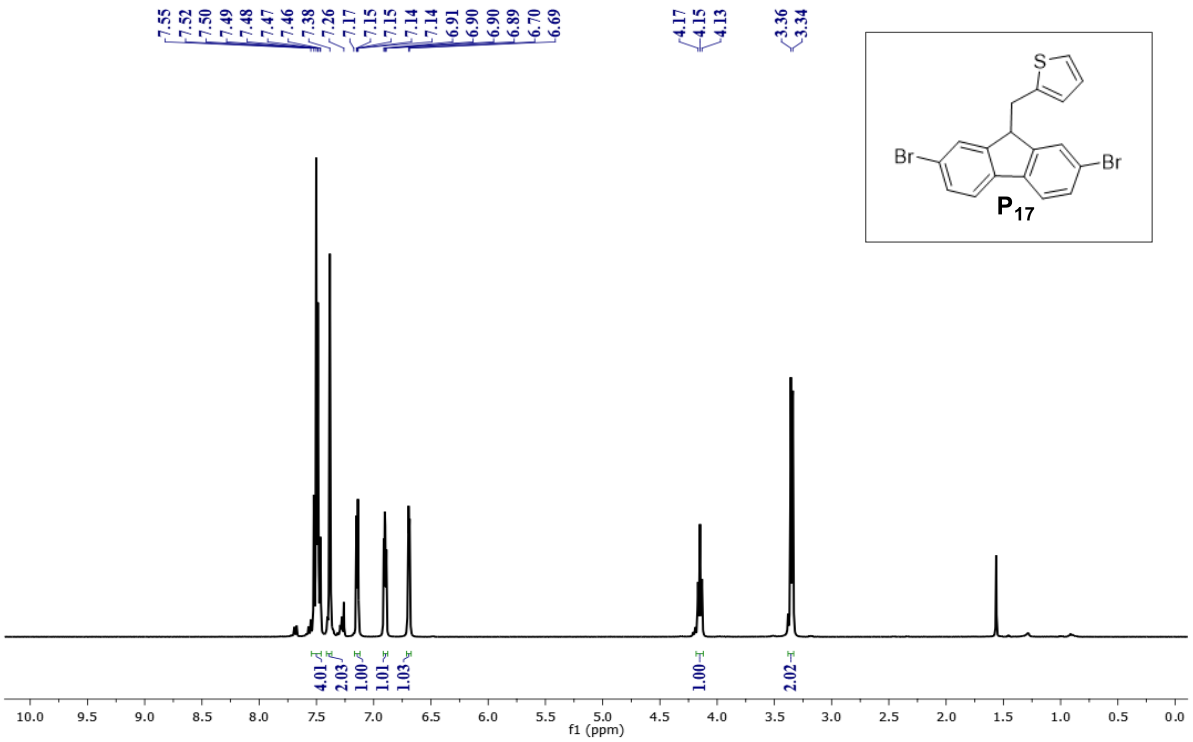


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-((2,7-dibromo-9H-fluoren-9-yl)methyl)thiophene **(P_{17})**.

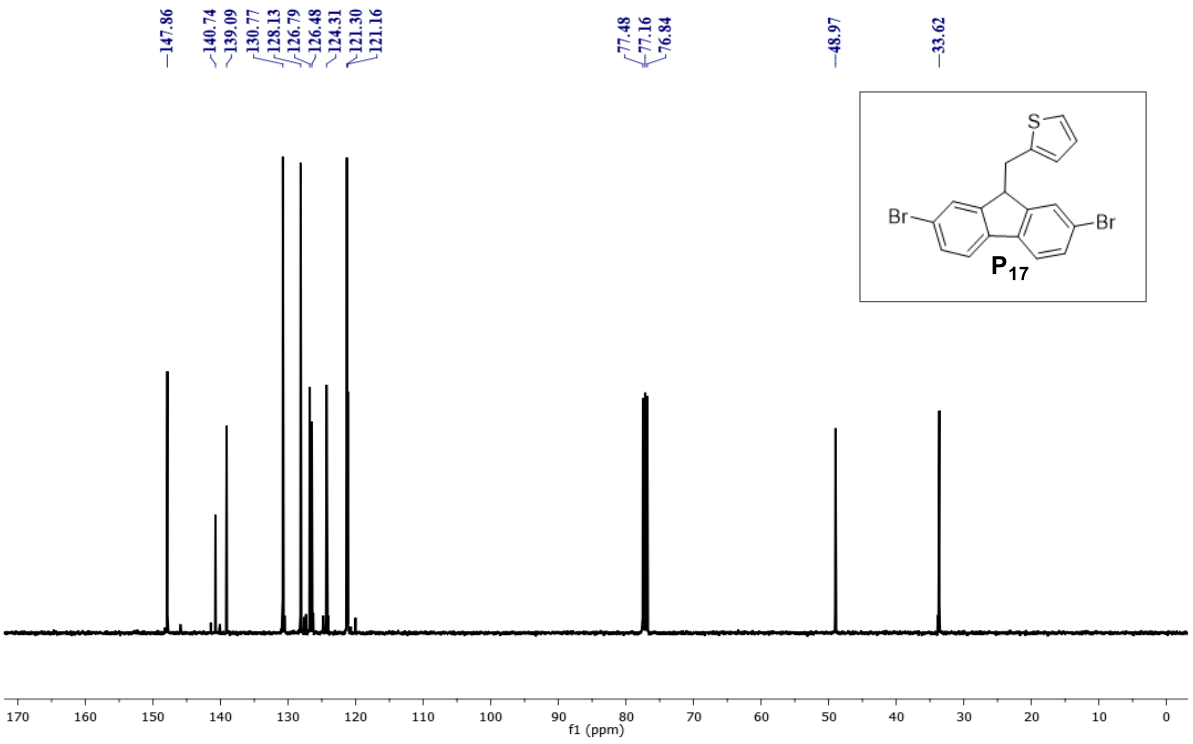


Figure S42. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-((2,7-dibromo-9H-fluoren-9-yl)methyl)thiophene **(P_{17})**.

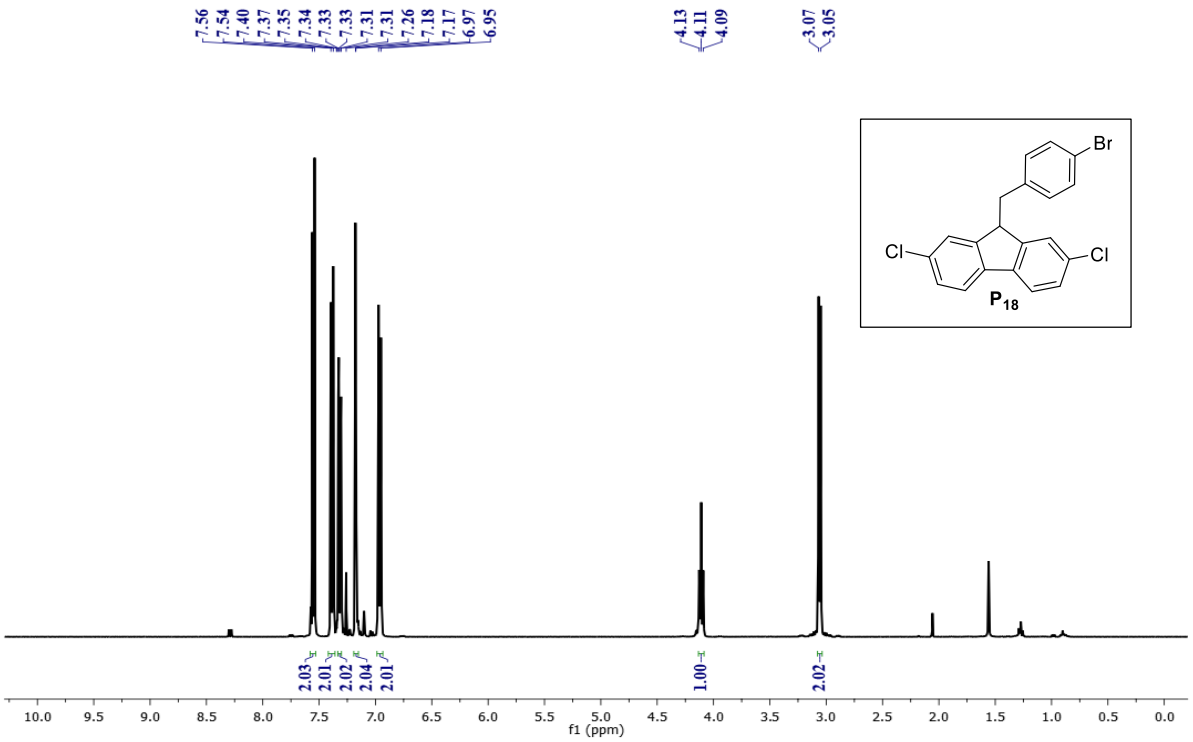


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(4-bromobenzyl)-2,7-dichloro-9H-fluorene **(P_{18})**.

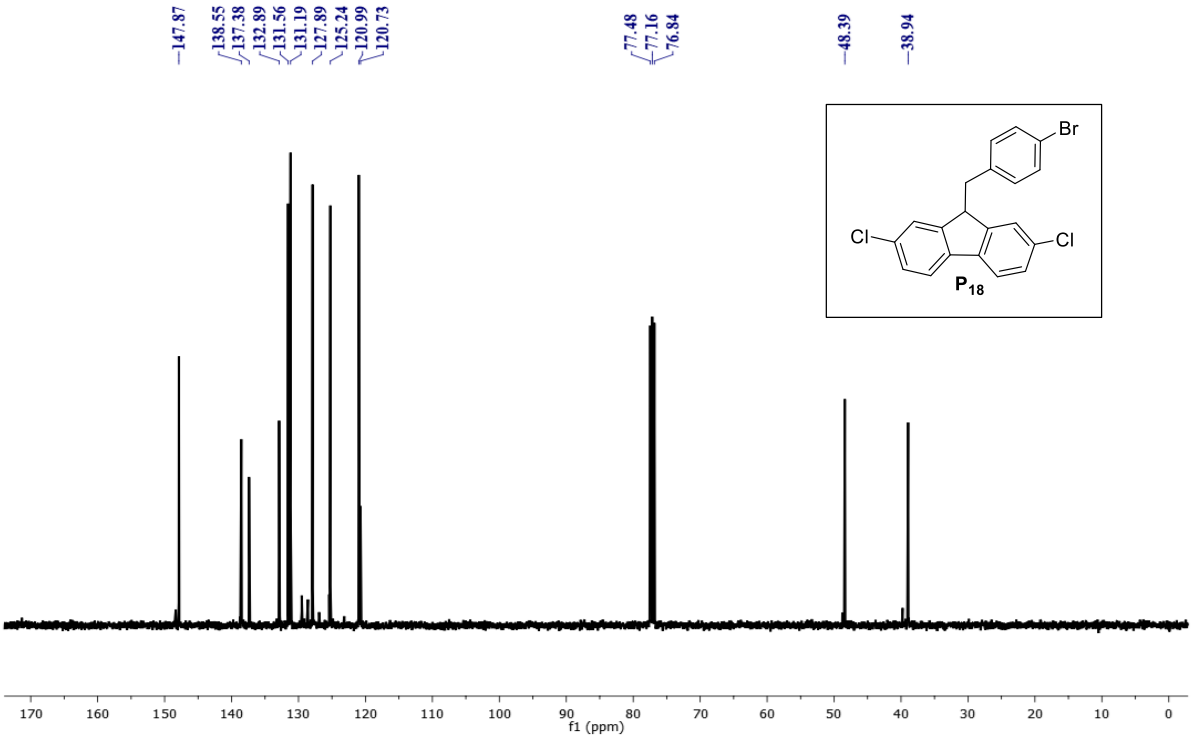


Figure S44. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(4-bromobenzyl)-2,7-dichloro-9H-fluorene **(P_{18})**.

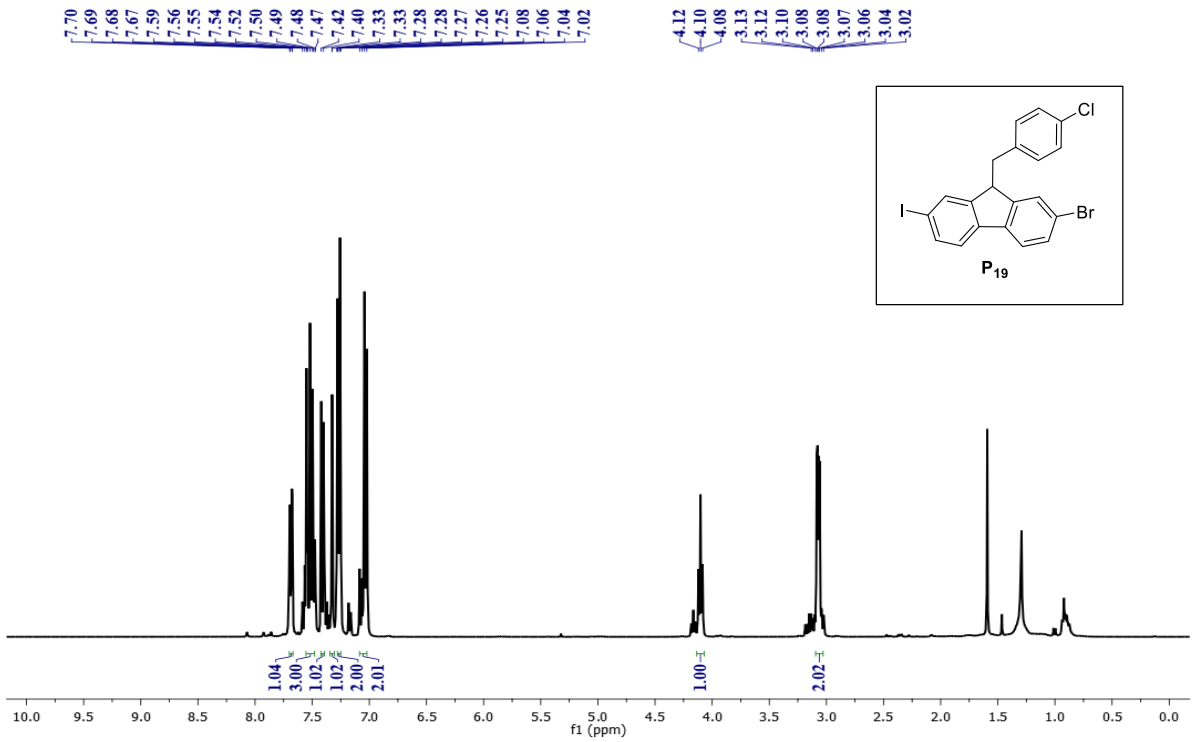


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-bromo-9-(4-chlorobenzyl)-7-iodo-9H-fluorene**(P19)**.

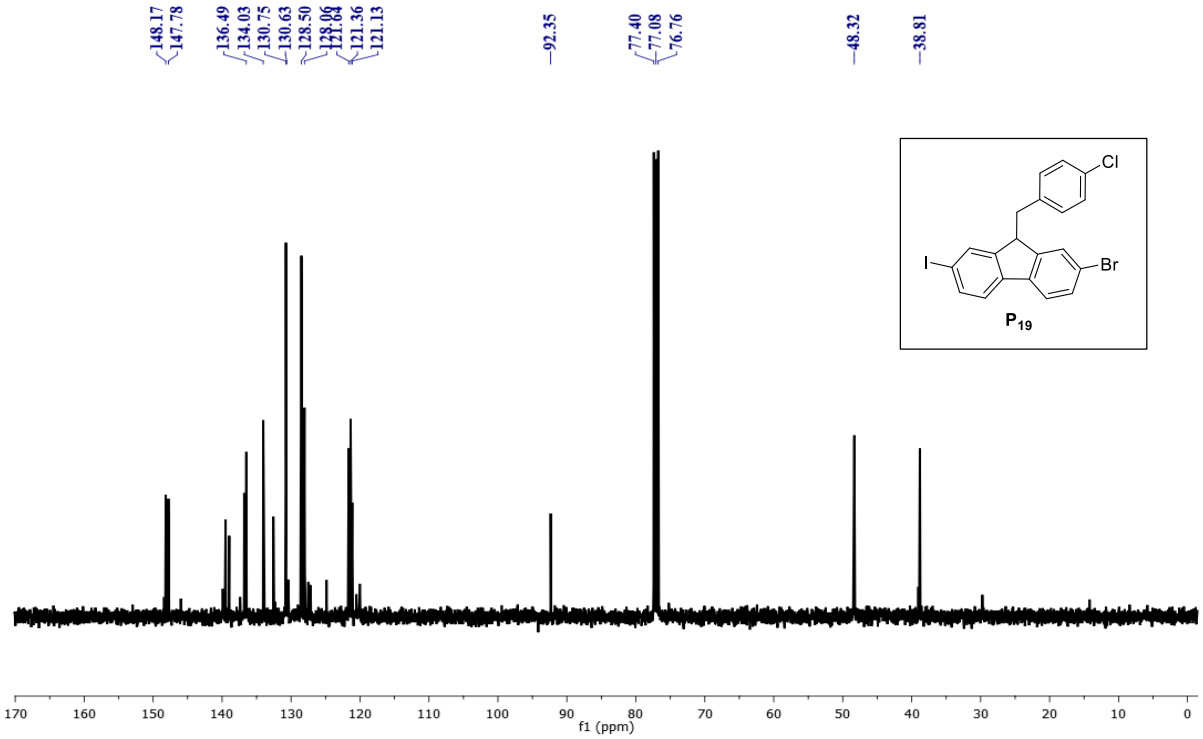


Figure S46. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-bromo-9-(4-chlorobenzyl)-7-iodo-9H-fluorene**(P19)**.

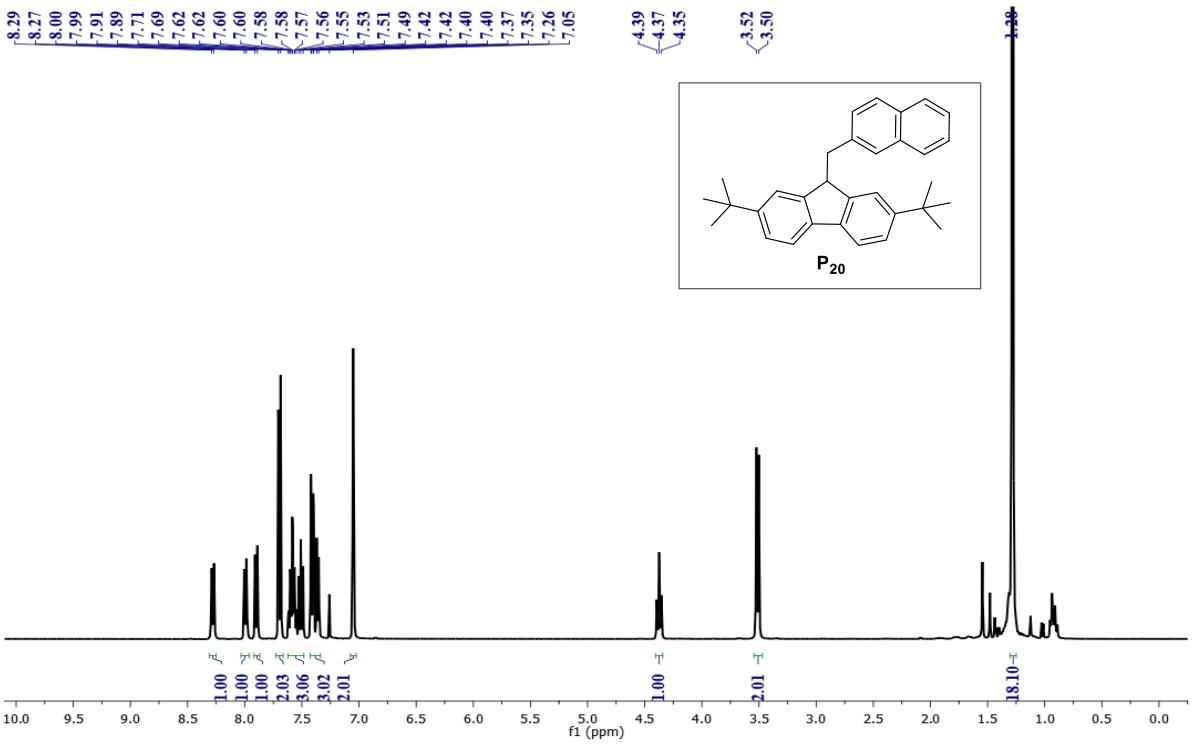


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-di-tert-butyl-9-(naphthalen-2-ylmethyl)-9H-fluorene **(P_{20})**.

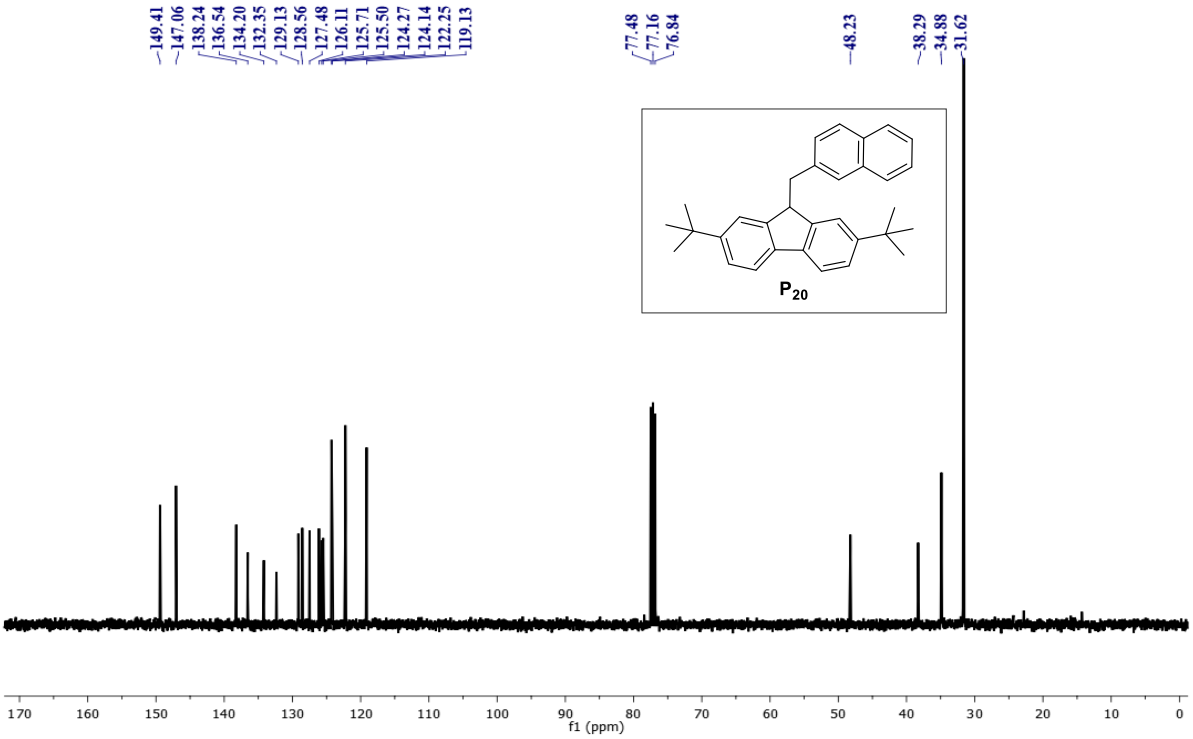


Figure S48. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-di-tert-butyl-9-(naphthalen-2-ylmethyl)-9H-fluorene **(P_{20})**

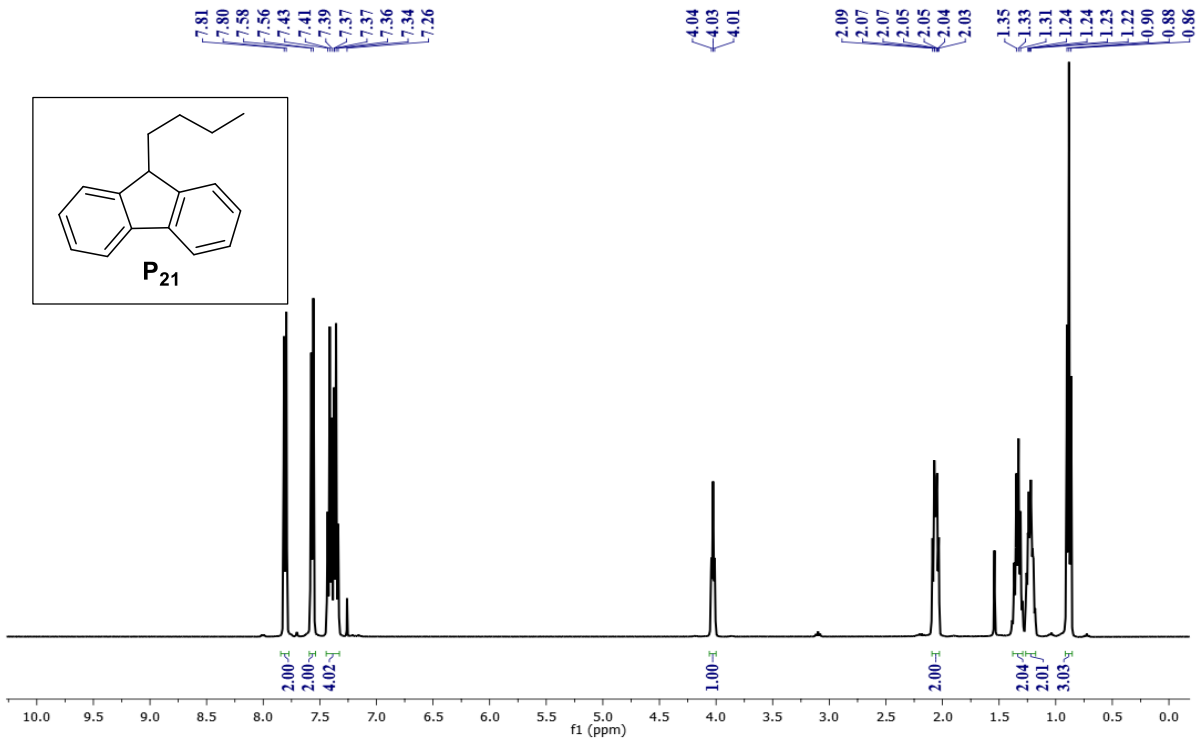


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-butyl-9H-fluorene**(P_{21})**.

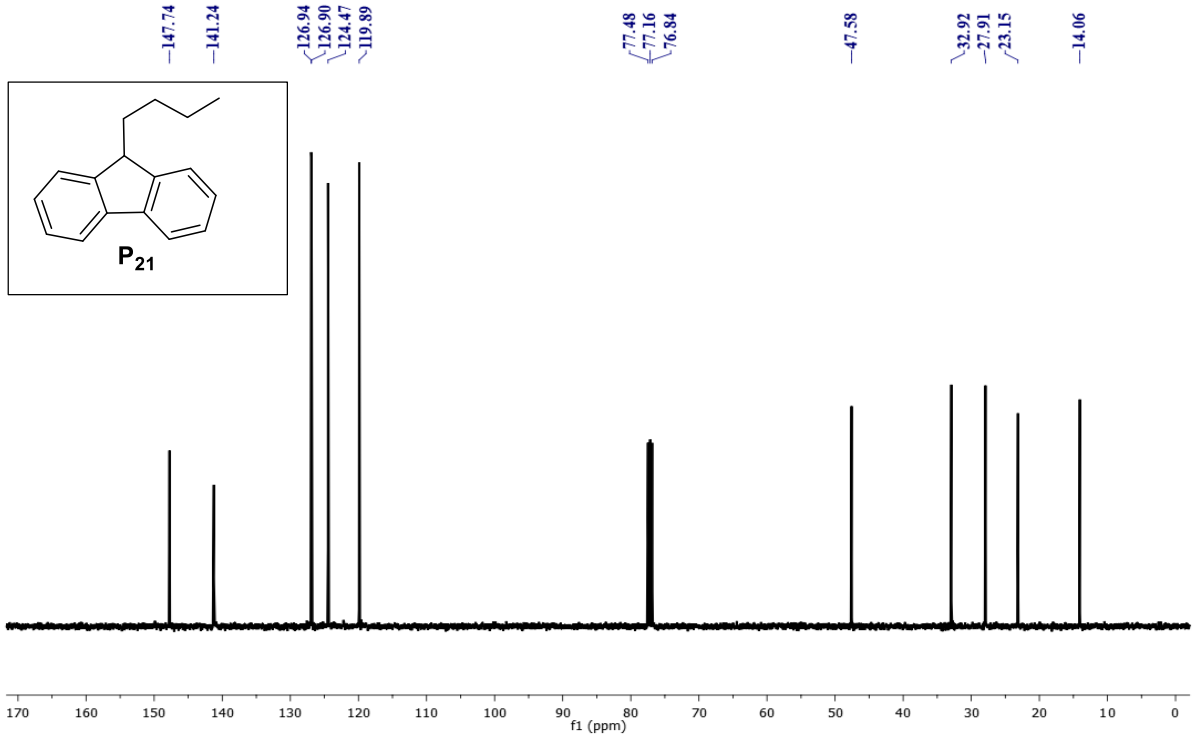


Figure S50. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-butyl-9H-fluorene**(P_{21})**.

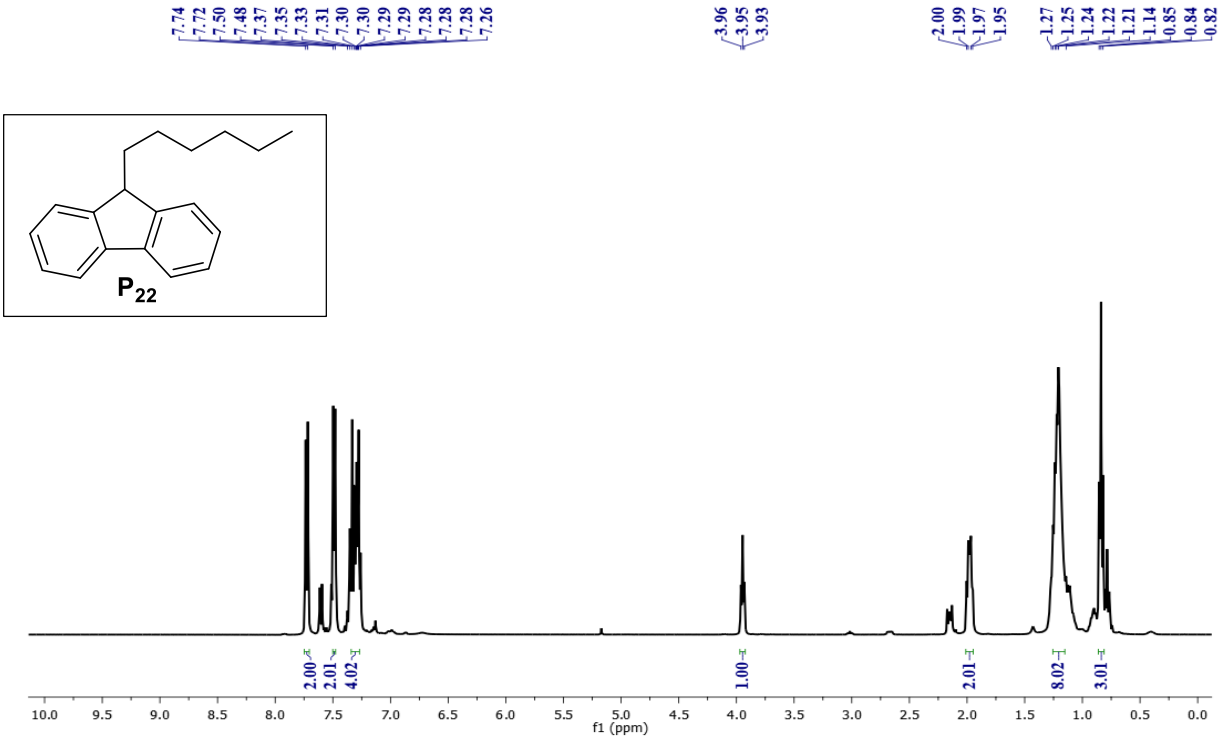


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-hexyl-9H-fluorene **(P_{22})**.

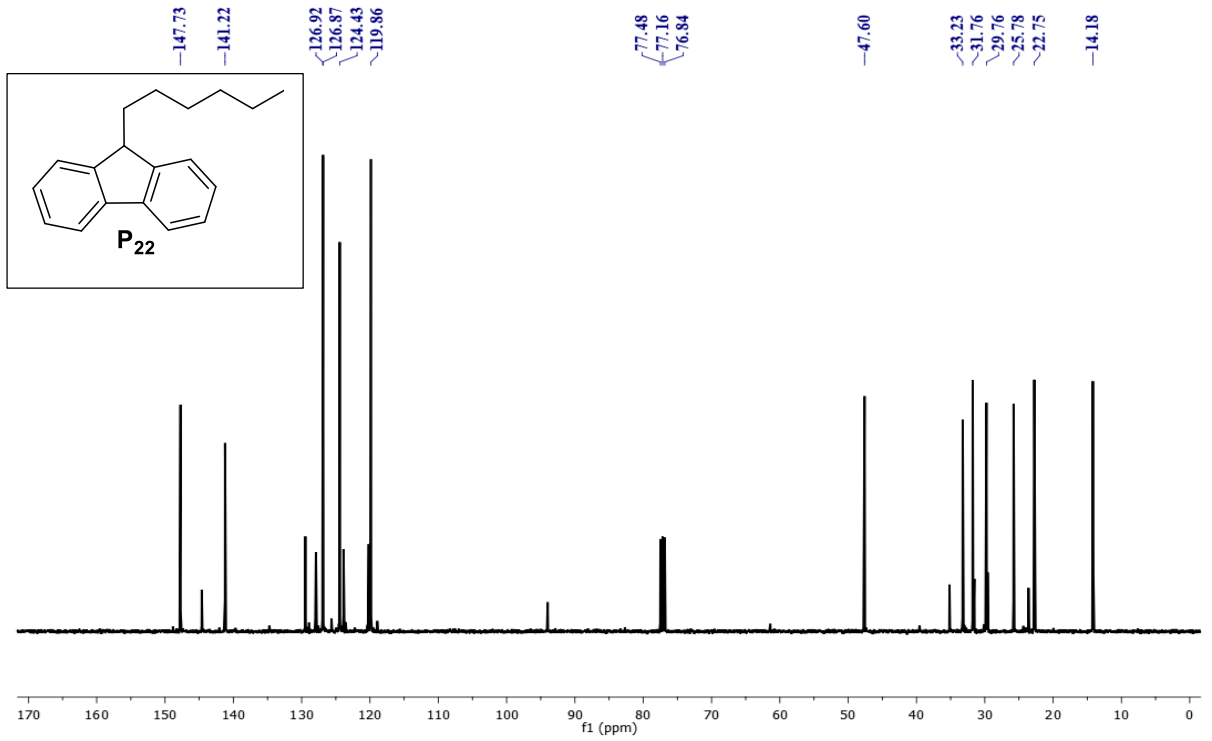


Figure S52. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-hexyl-9H-fluorene **(P_{22})**.

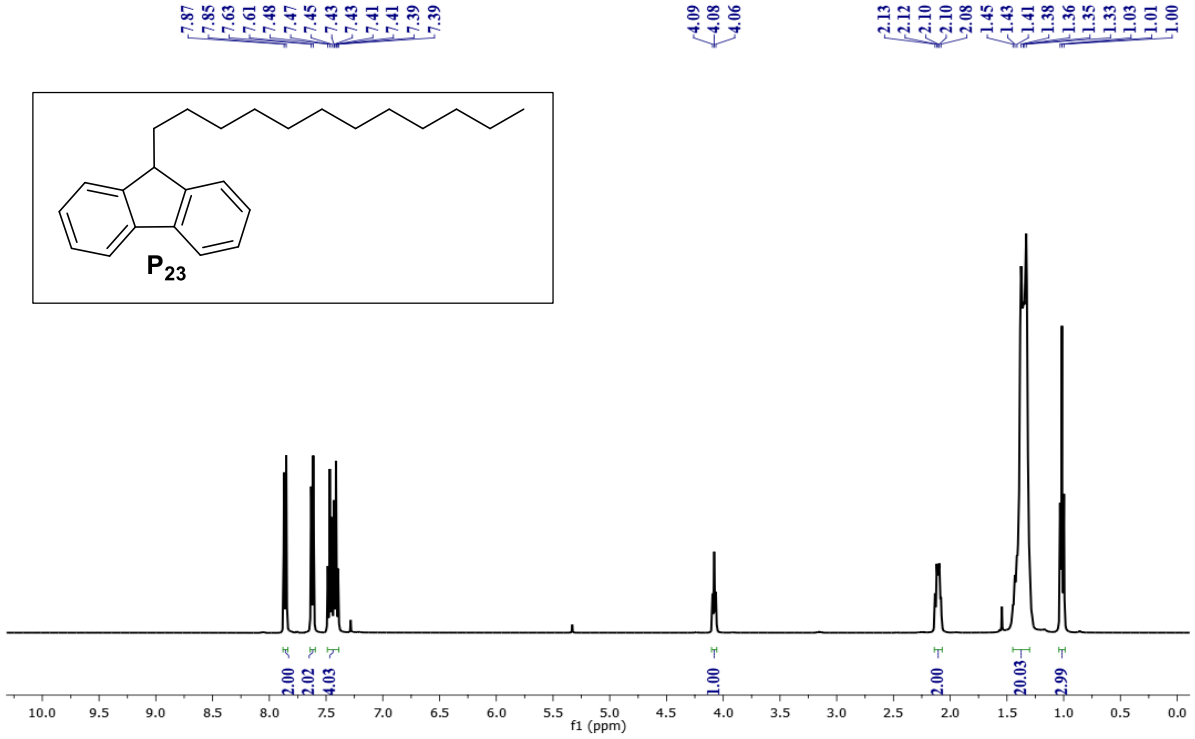


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-dodecyl-9H-fluorene **(P_{23})**.

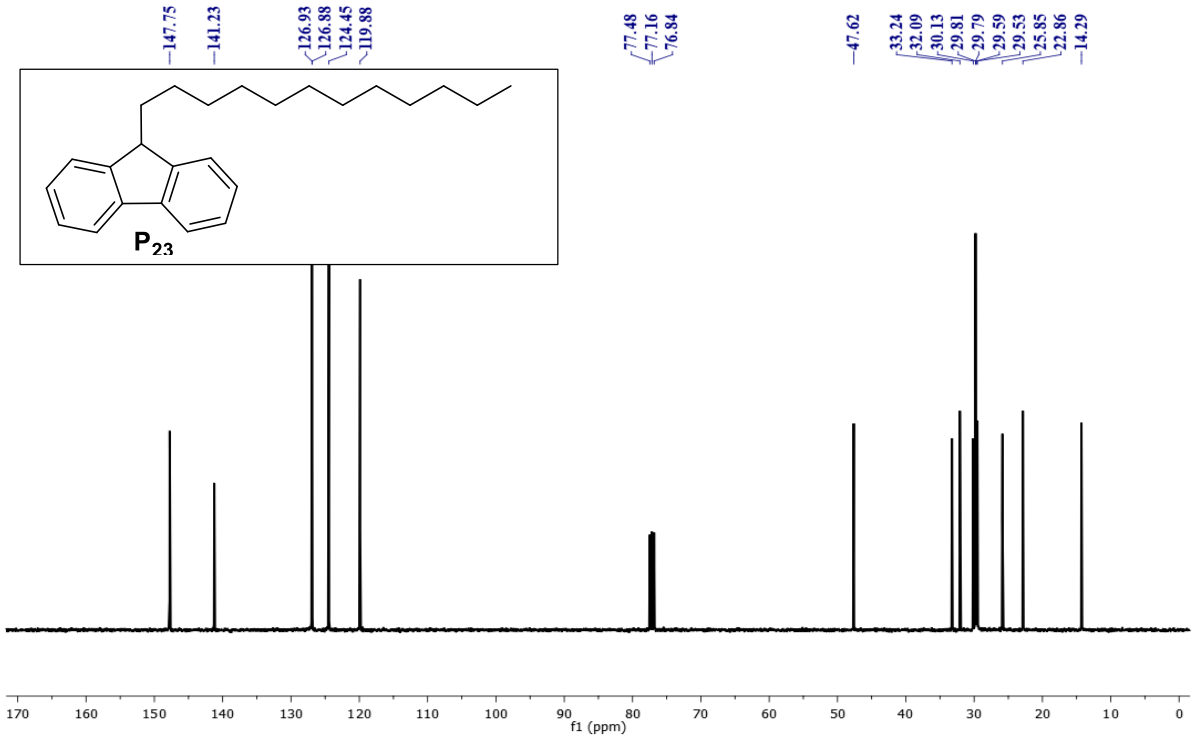


Figure S54. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-dodecyl-9H-fluorene **(P_{23})**.

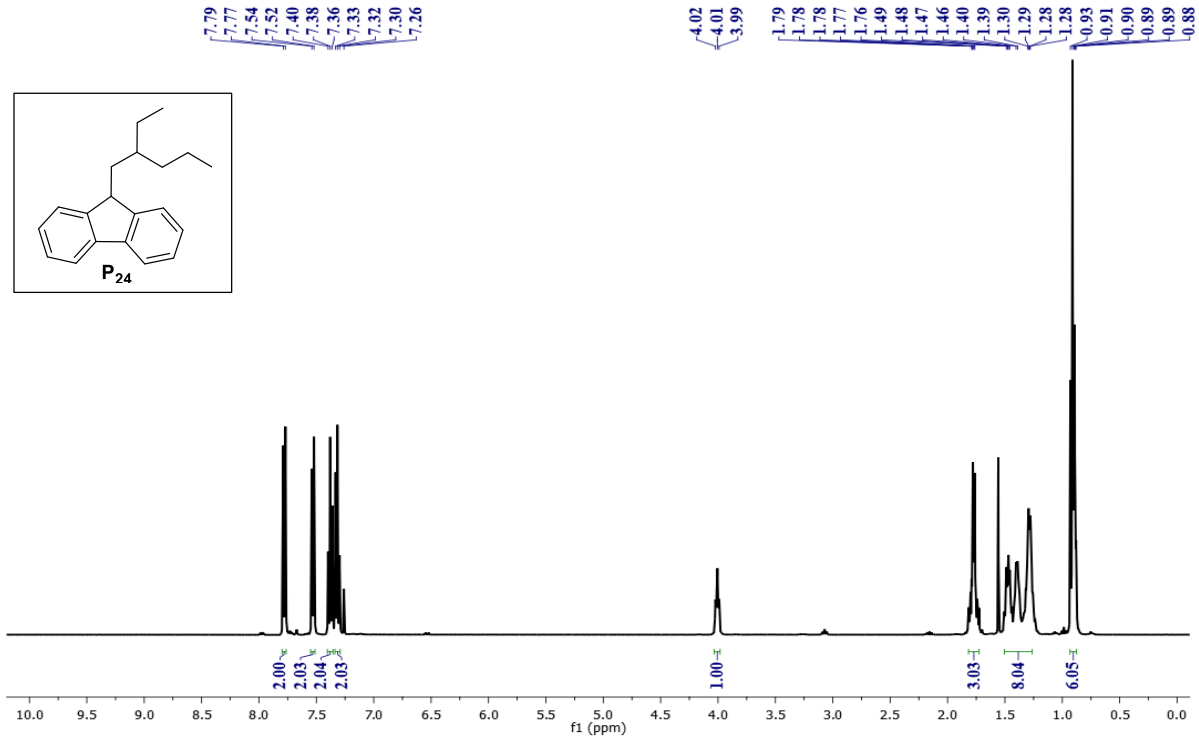


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(2-ethylhexyl)-9H-fluorene**(P_{24})**.

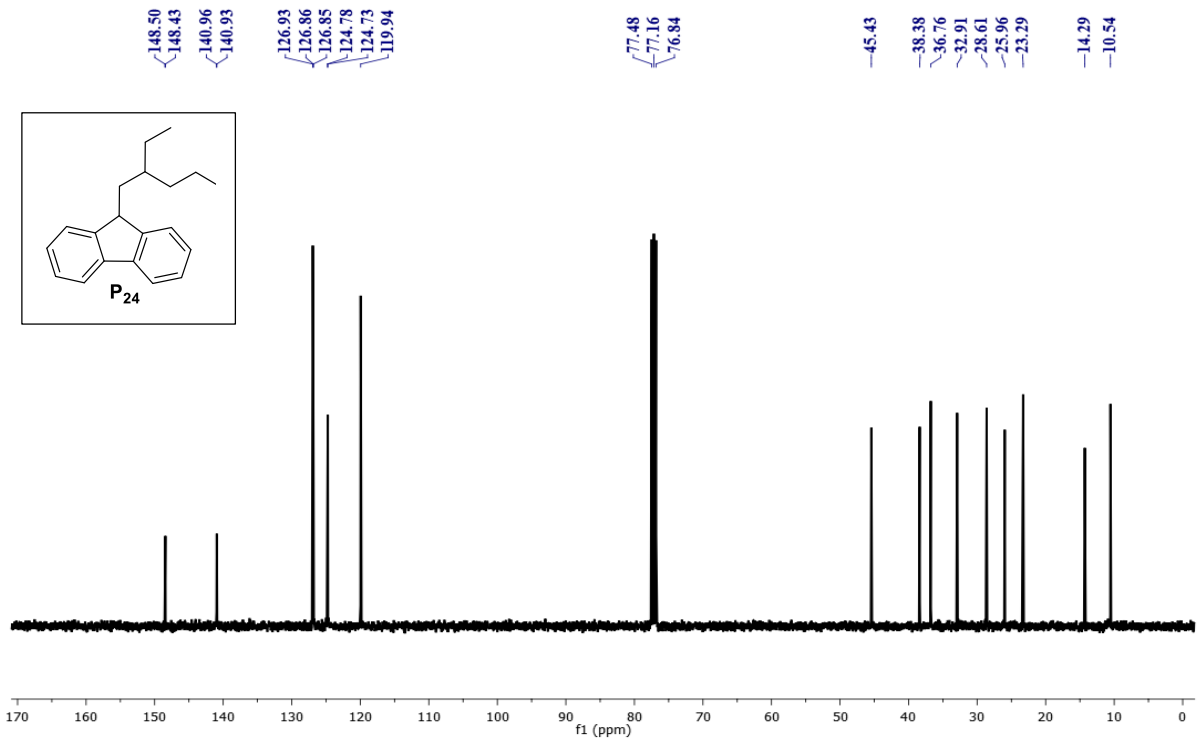


Figure S56. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(2-ethylhexyl)-9H-fluorene**(P_{24})**.

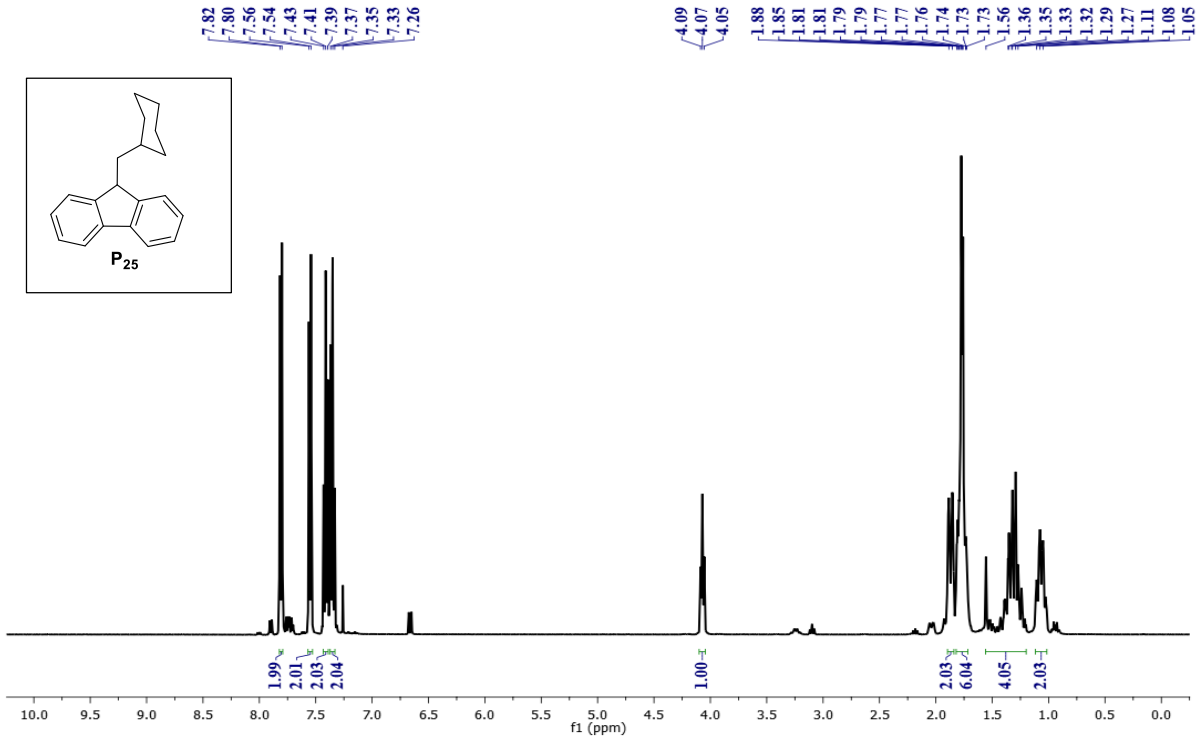


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(cyclohexylmethyl)-9H-fluorene**(P_{25})**.

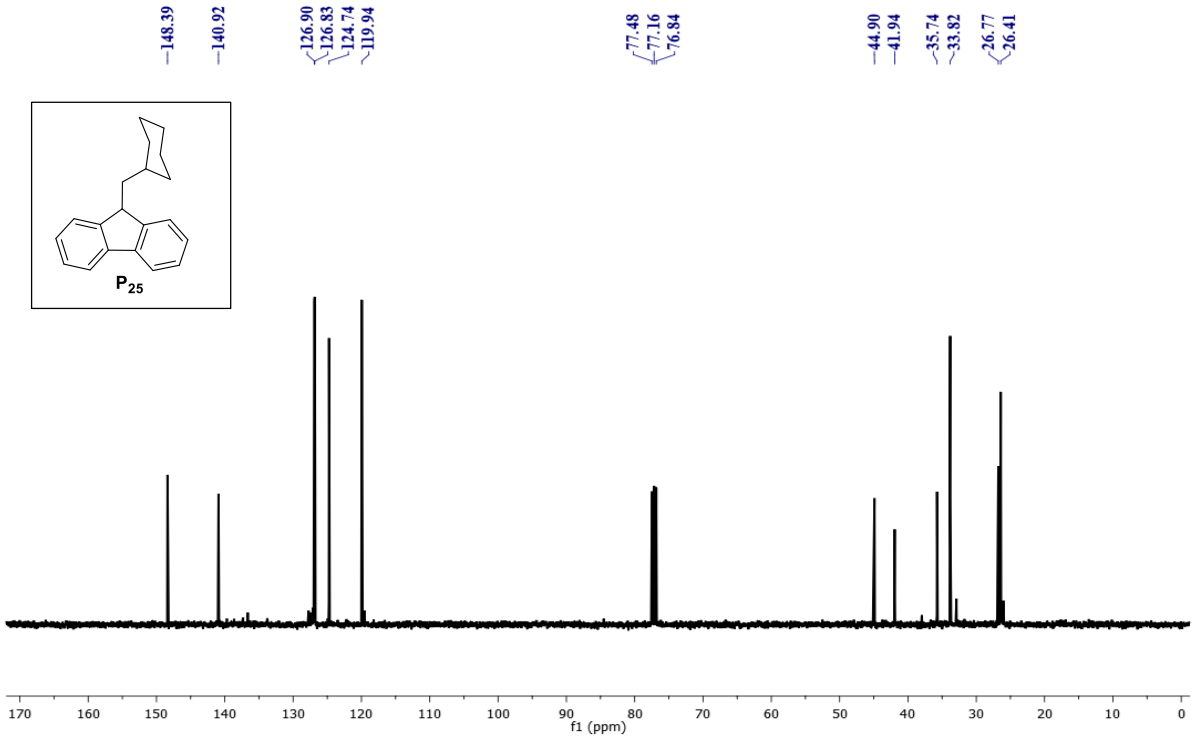


Figure S58. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(cyclohexylmethyl)-9H-fluorene**(P_{25})**.

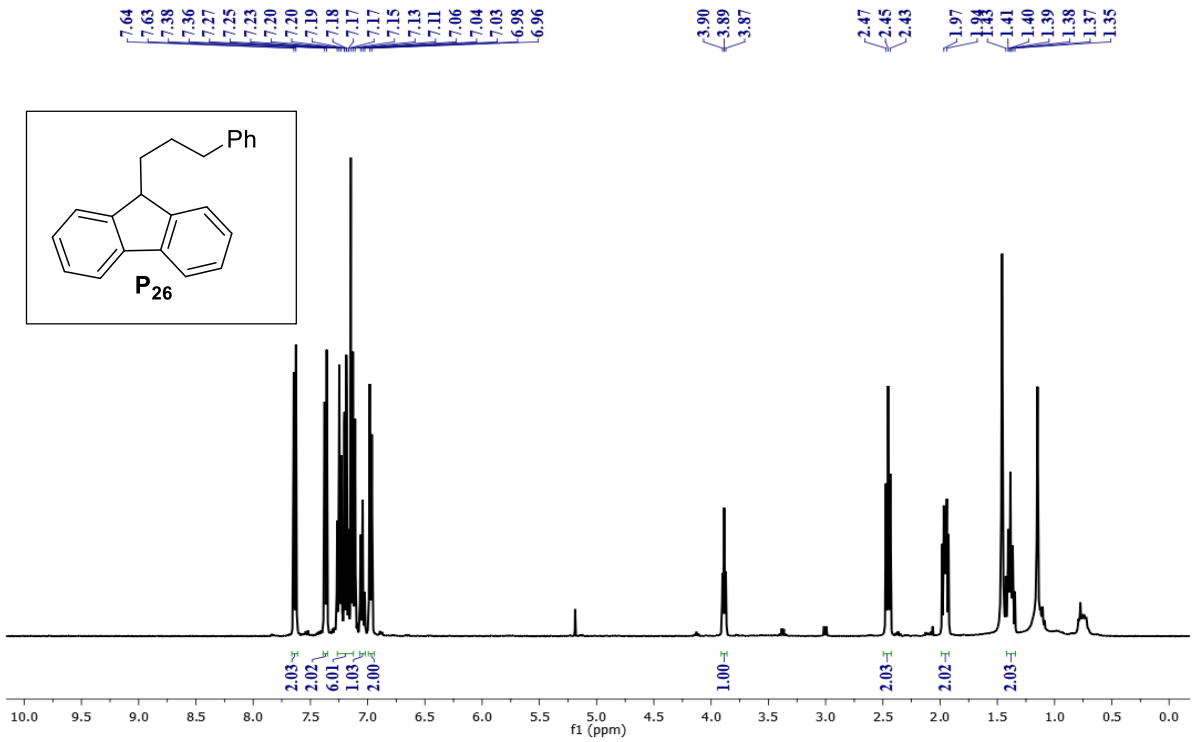


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(3-phenylpropyl)-9H-fluorene**(P26)**.

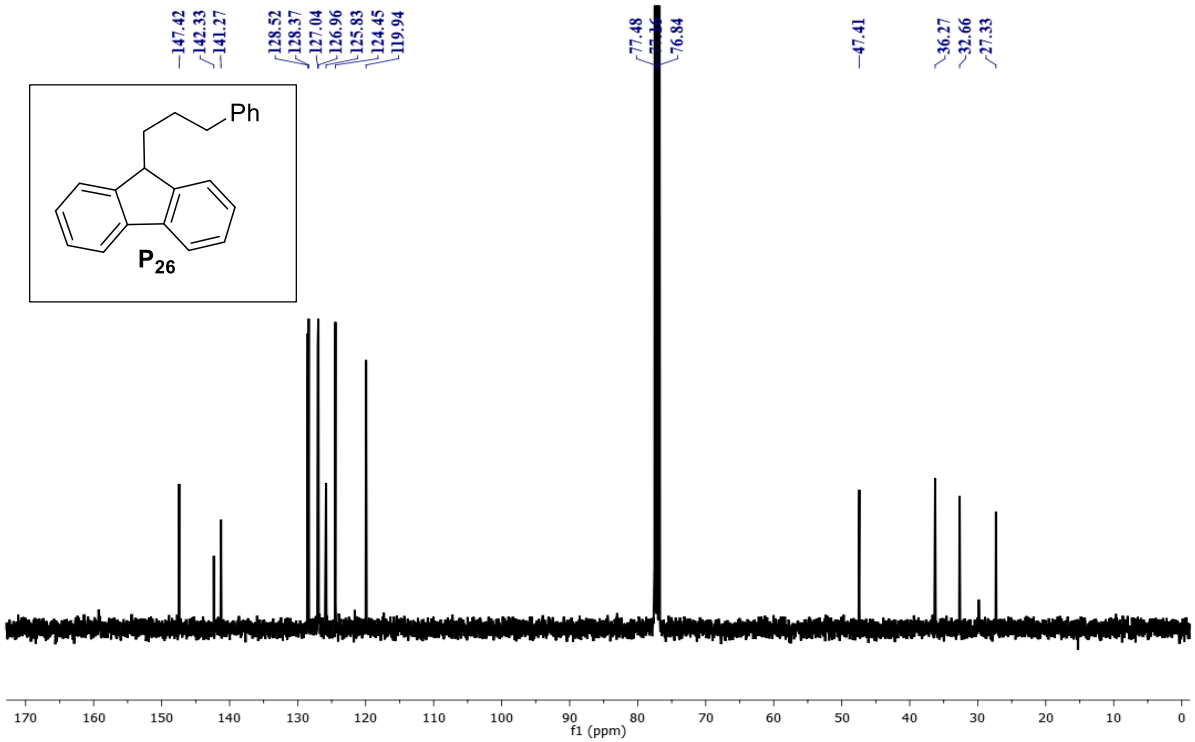


Figure S60. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(3-phenylpropyl)-9H-fluorene**(P26)**.

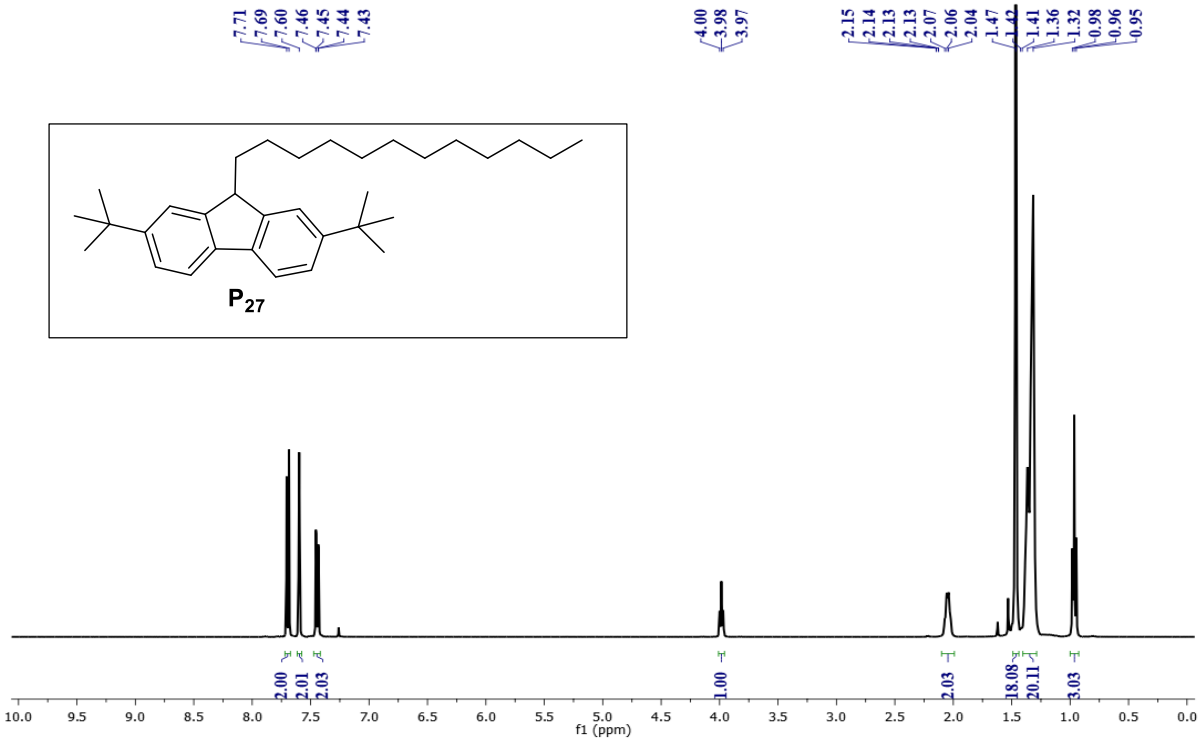


Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-di-tert-butyl-9-dodecyl-9H-fluorene**(P_{27})**.

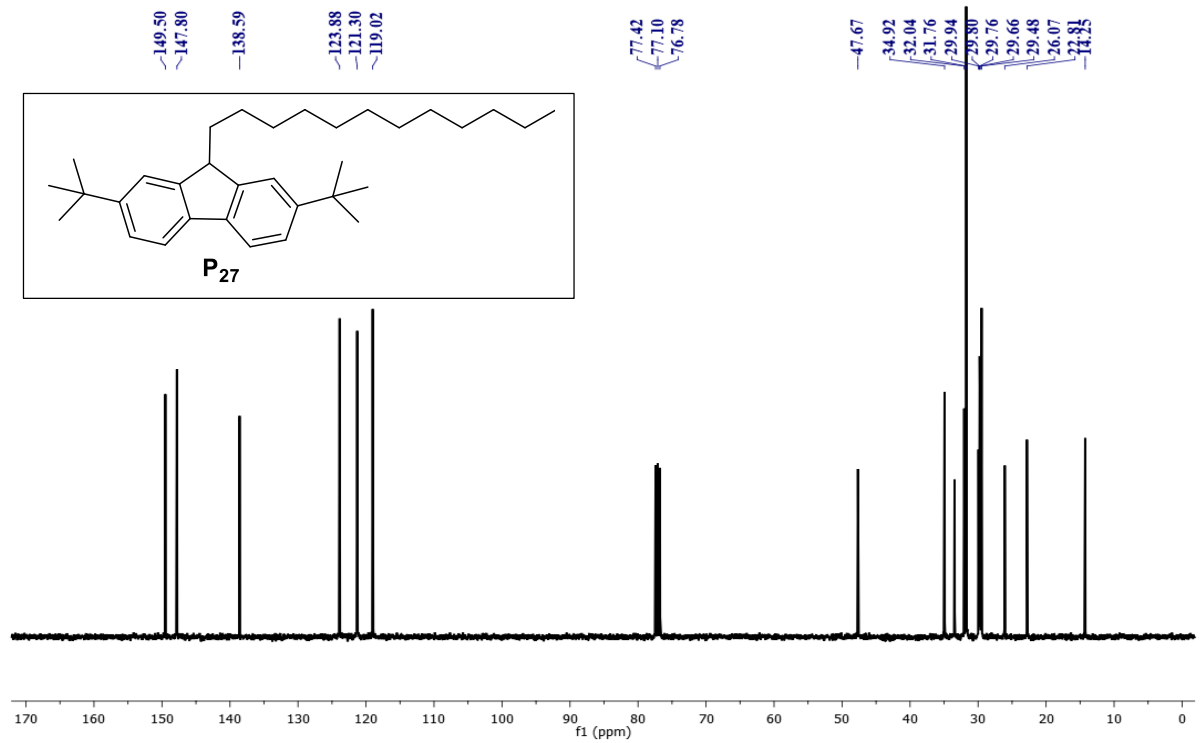


Figure S62. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-di-tert-butyl-9-dodecyl-9H-fluorene**(P_{27})**.

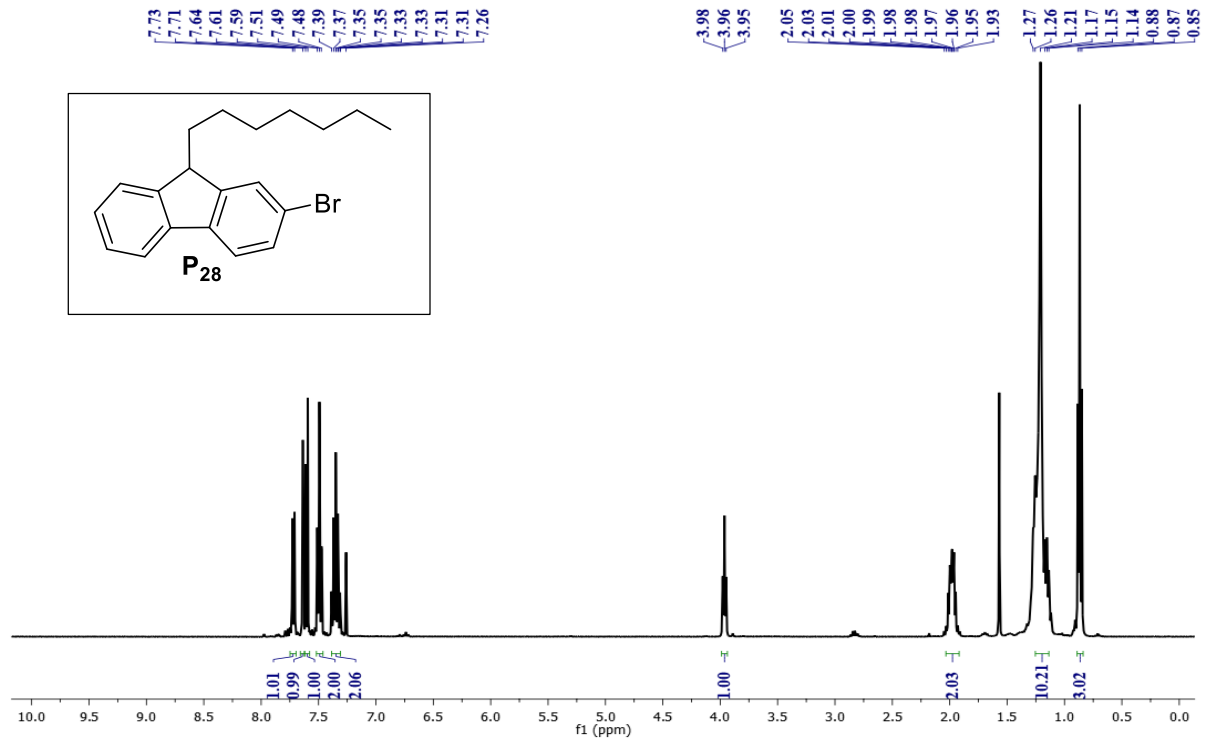


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-bromo-9-heptyl-9H-fluorene**(P_{28})**.

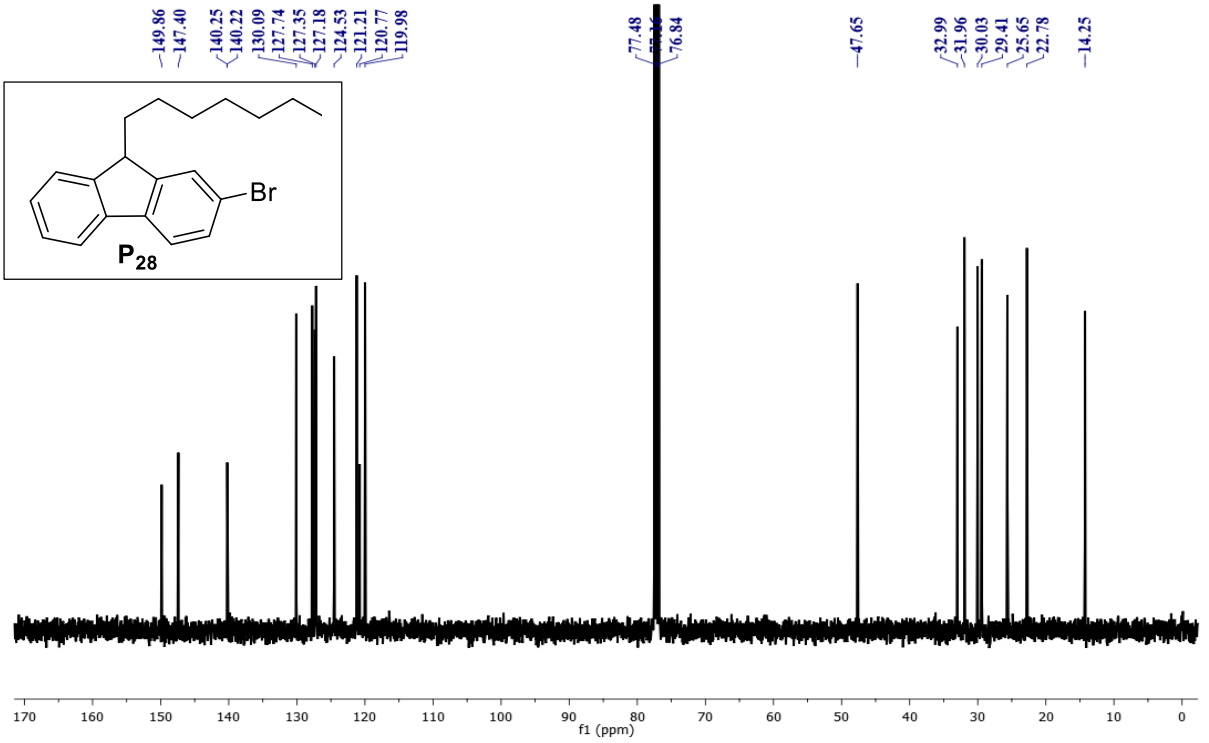


Figure S64. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-bromo-9-heptyl-9H-fluorene**(P_{28})**.

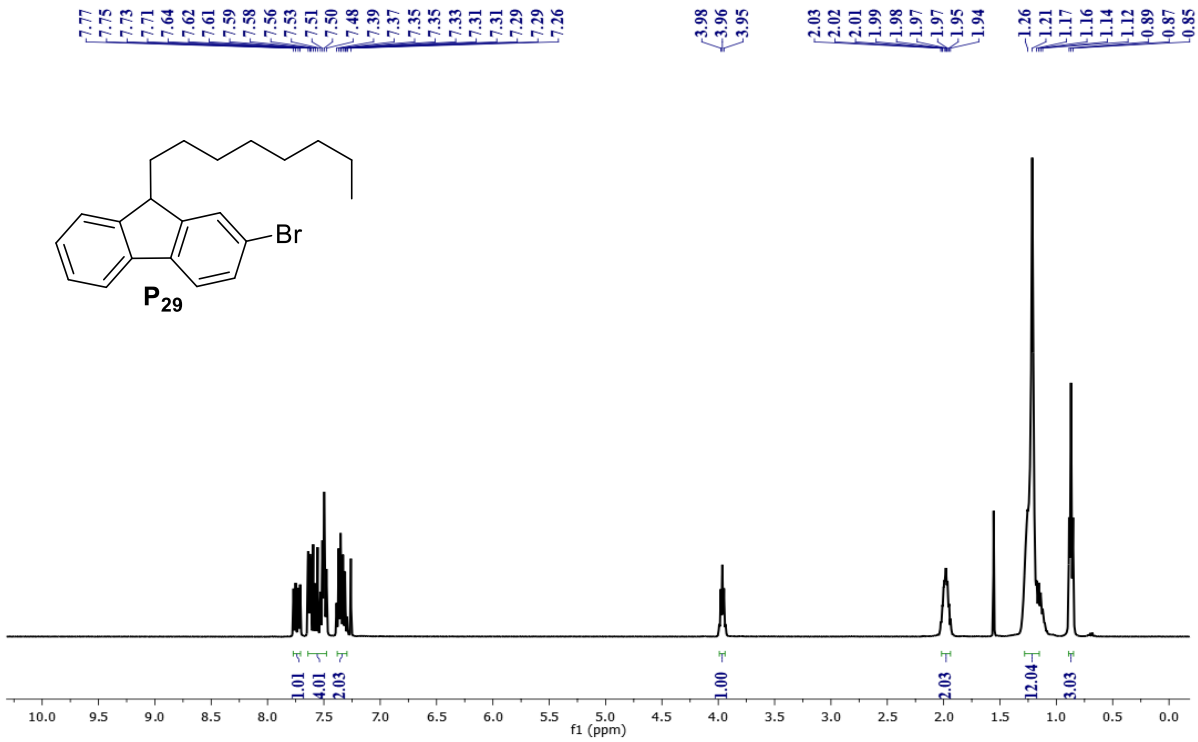


Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-Bromo-9-octyl-9H-fluorene **(P_{29})**.

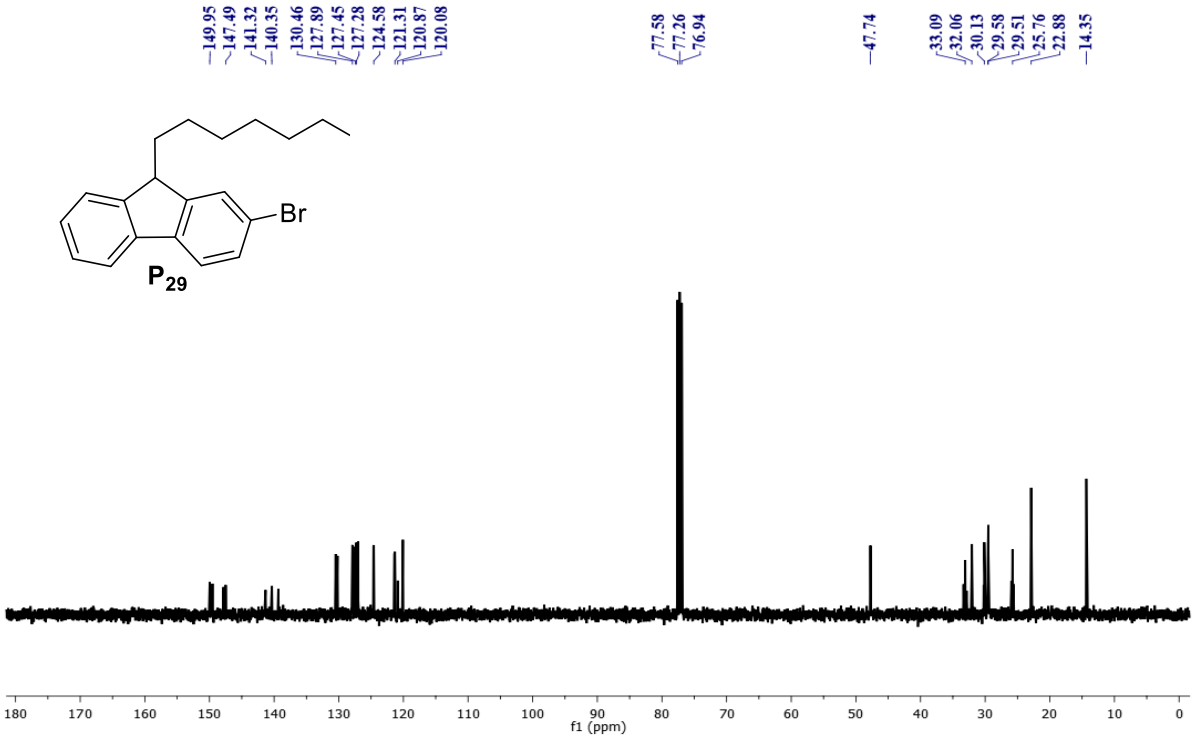


Figure S66. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-Bromo-9-octyl-9H-fluorene **(P_{29})**.

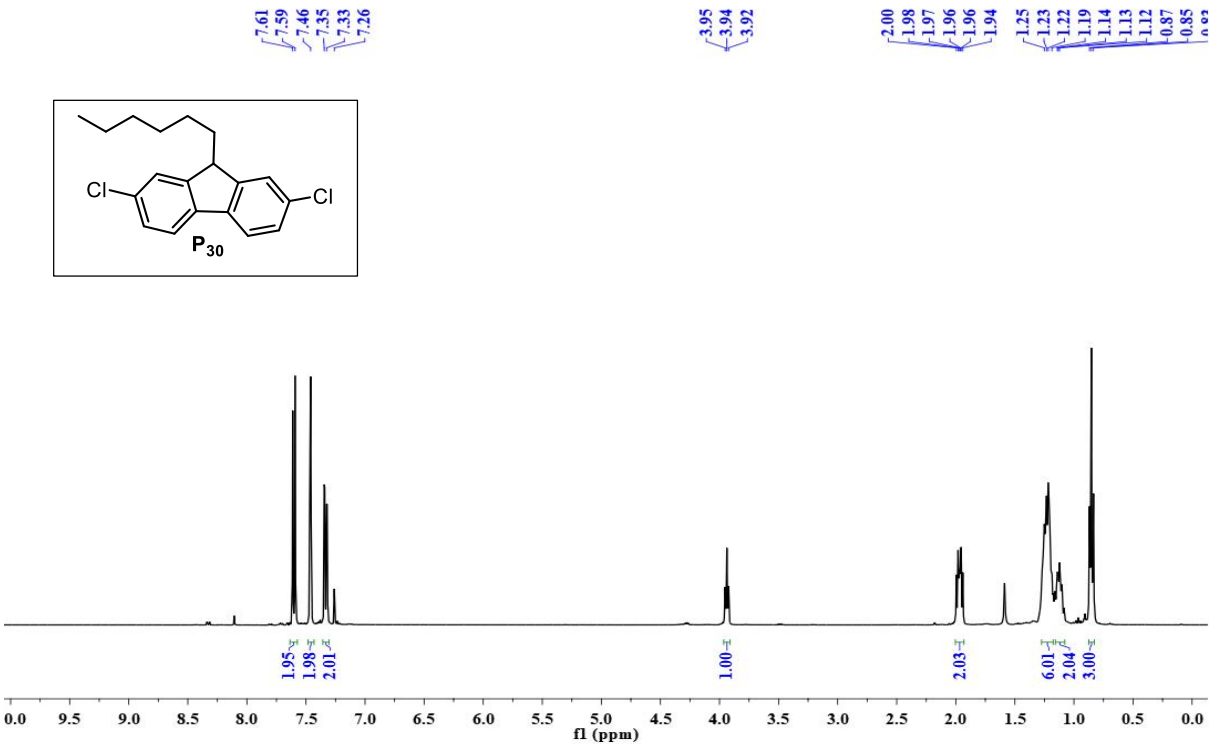


Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-dichloro-9-hexyl-9H-fluorene **(P_{30})**.

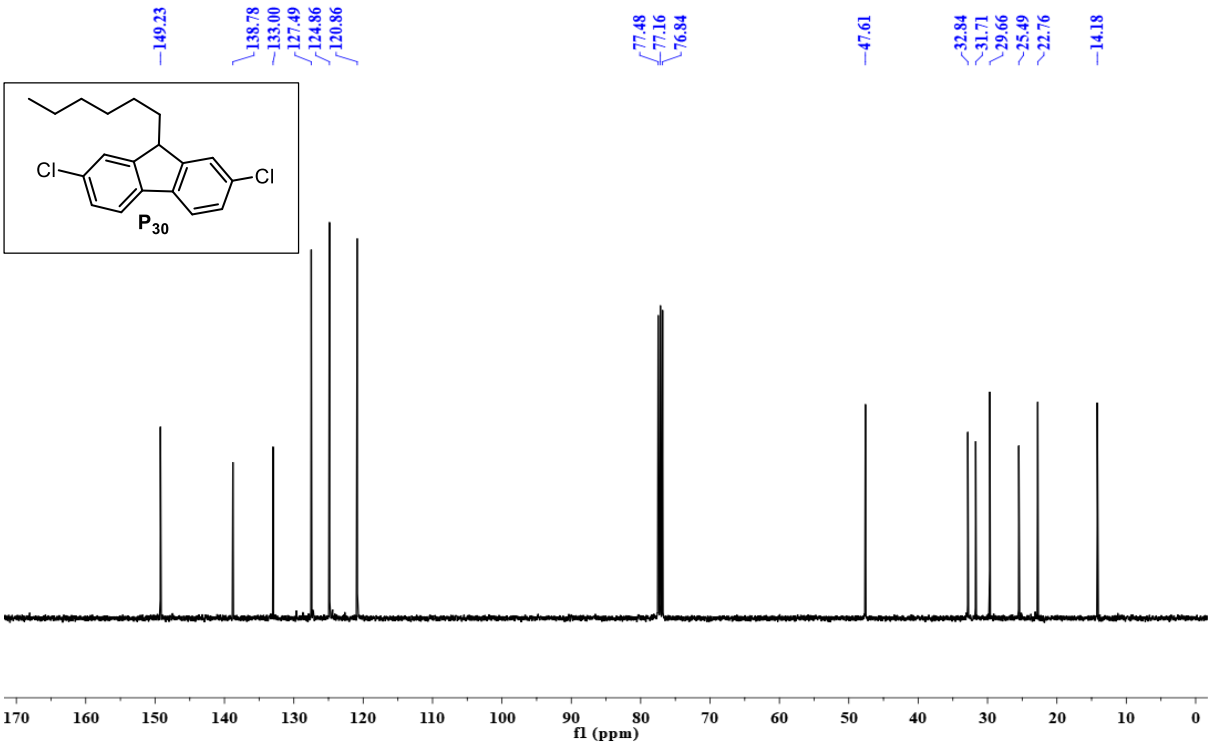


Figure S68. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-dichloro-9-hexyl-9H-fluorene **(P_{30})**.

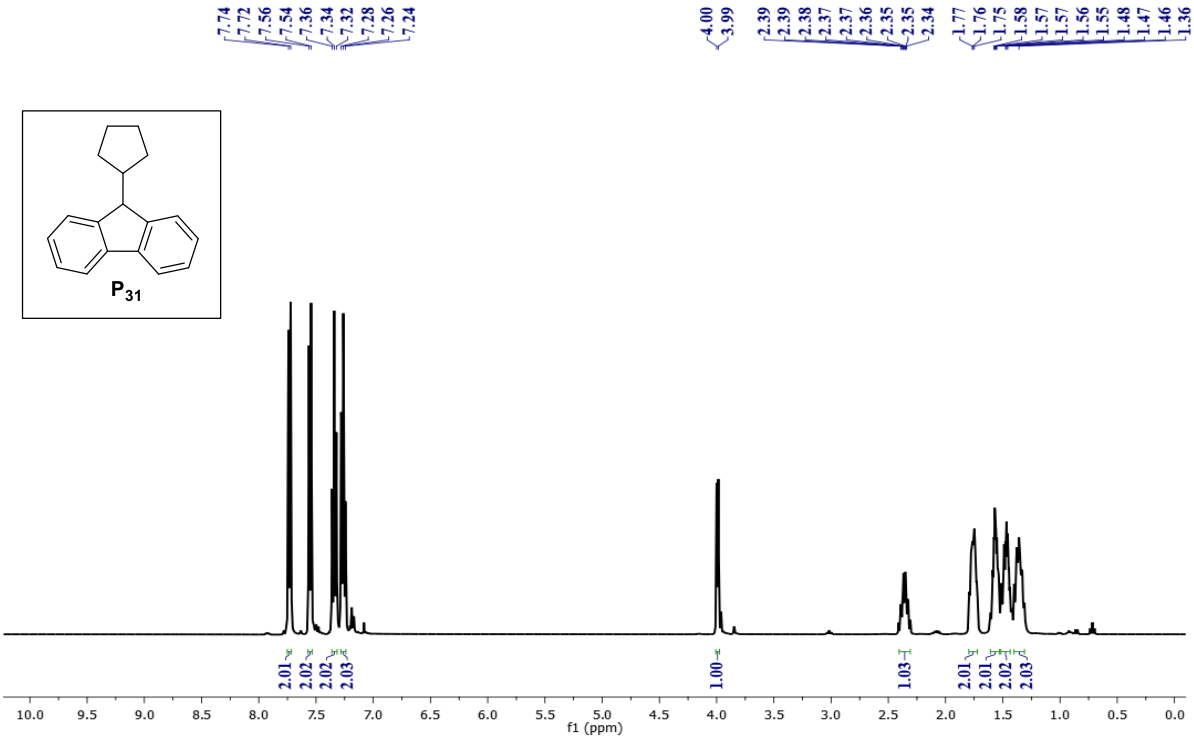


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-cyclopentyl-9H-fluorene **(P_{31})**.

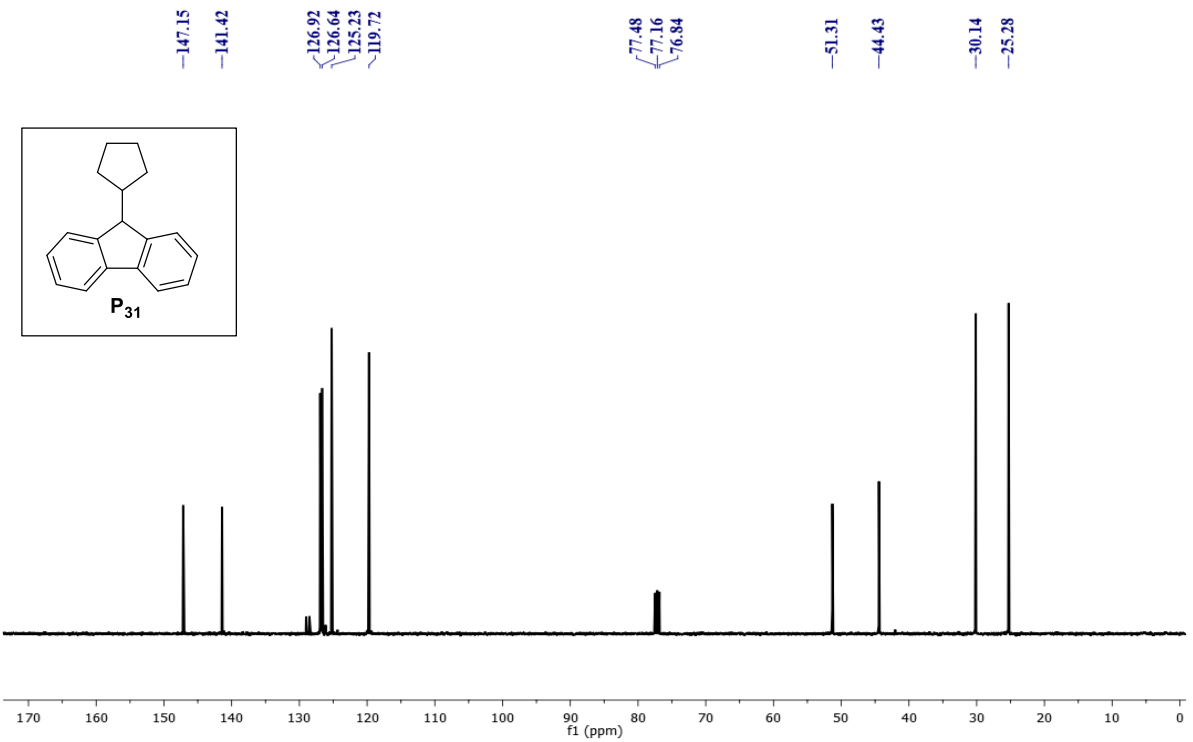


Figure S70. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-cyclopentyl-9H-fluorene **(P_{31})**.

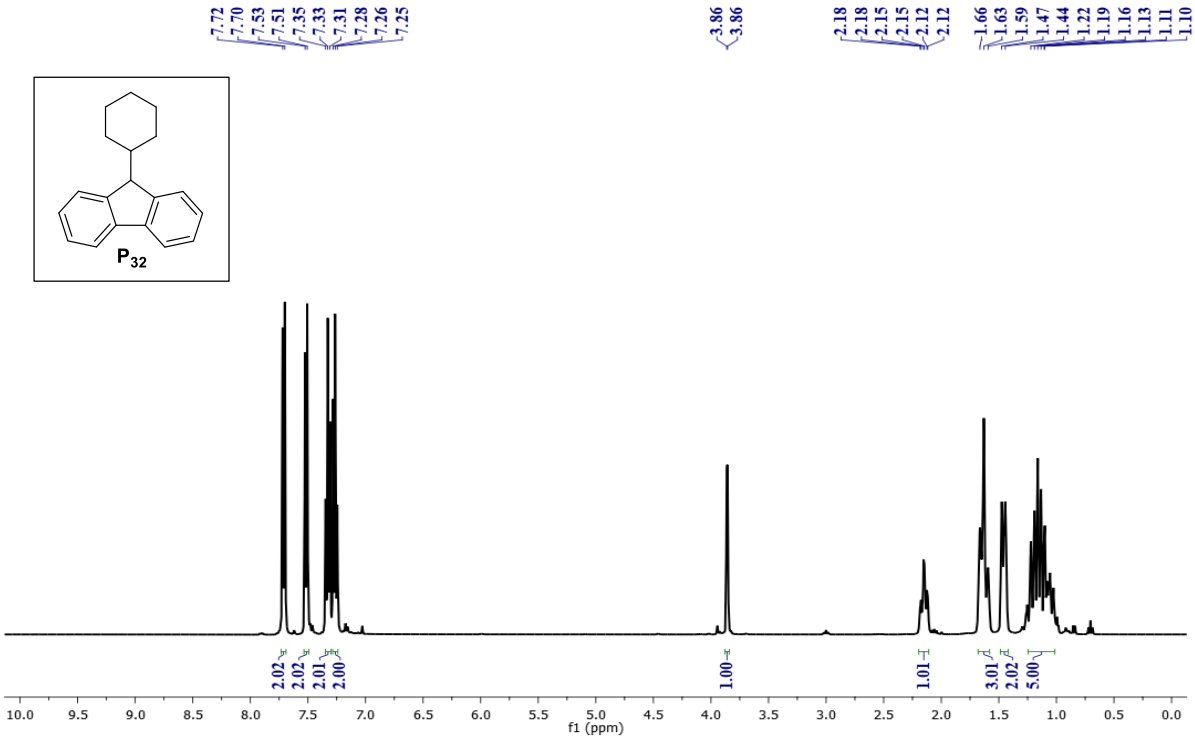


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-cyclohexyl-9H-fluorene **(P_{32})**.

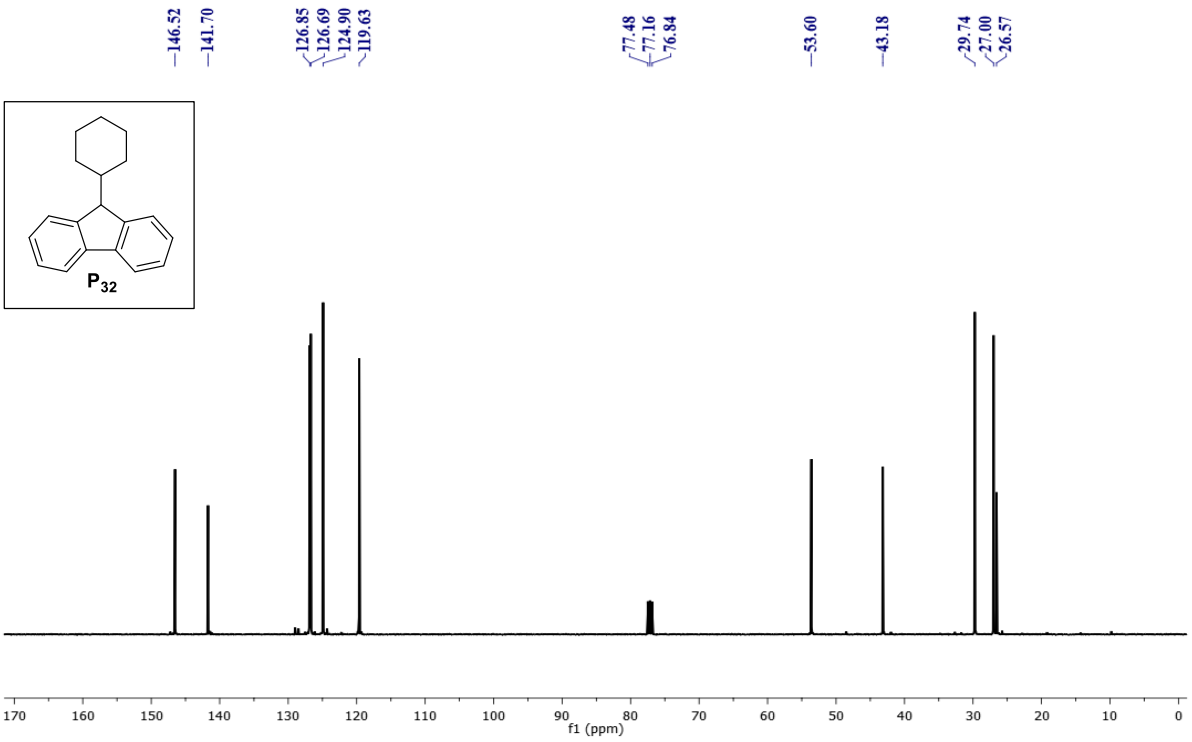


Figure S72. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-cyclohexyl-9H-fluorene **(P_{32})**.

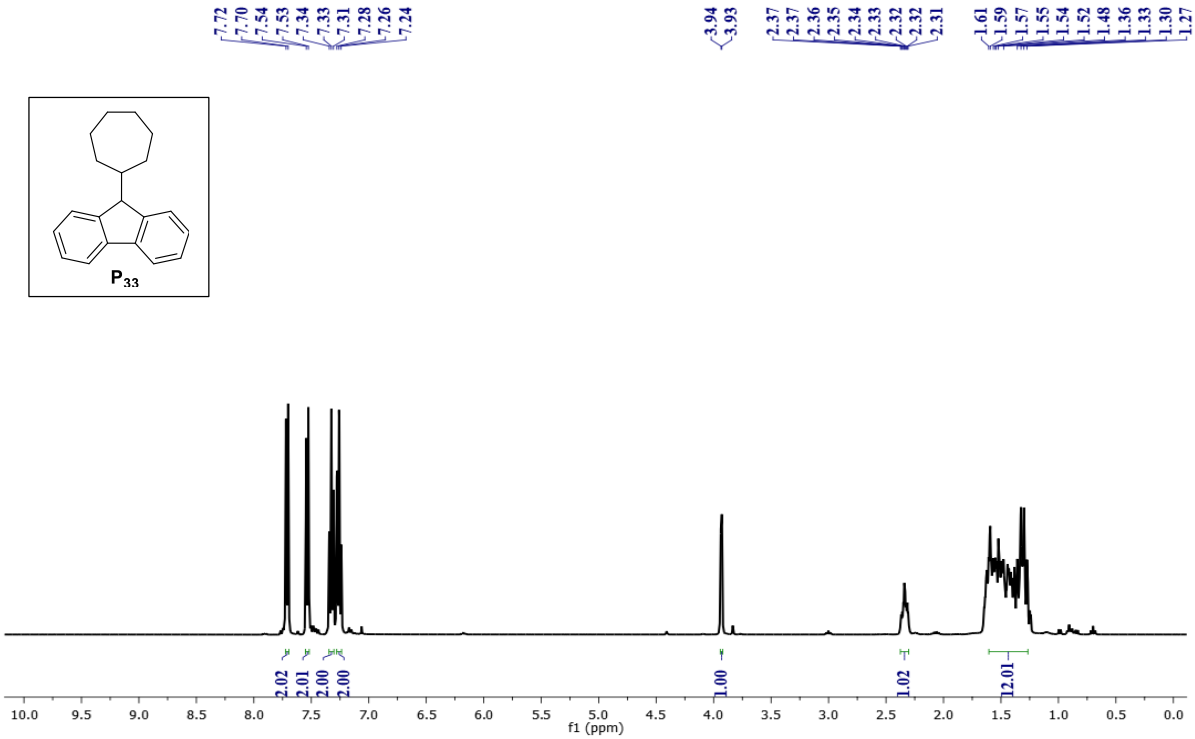


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-cycloheptyl-9H-fluorene **(P_{33})**.

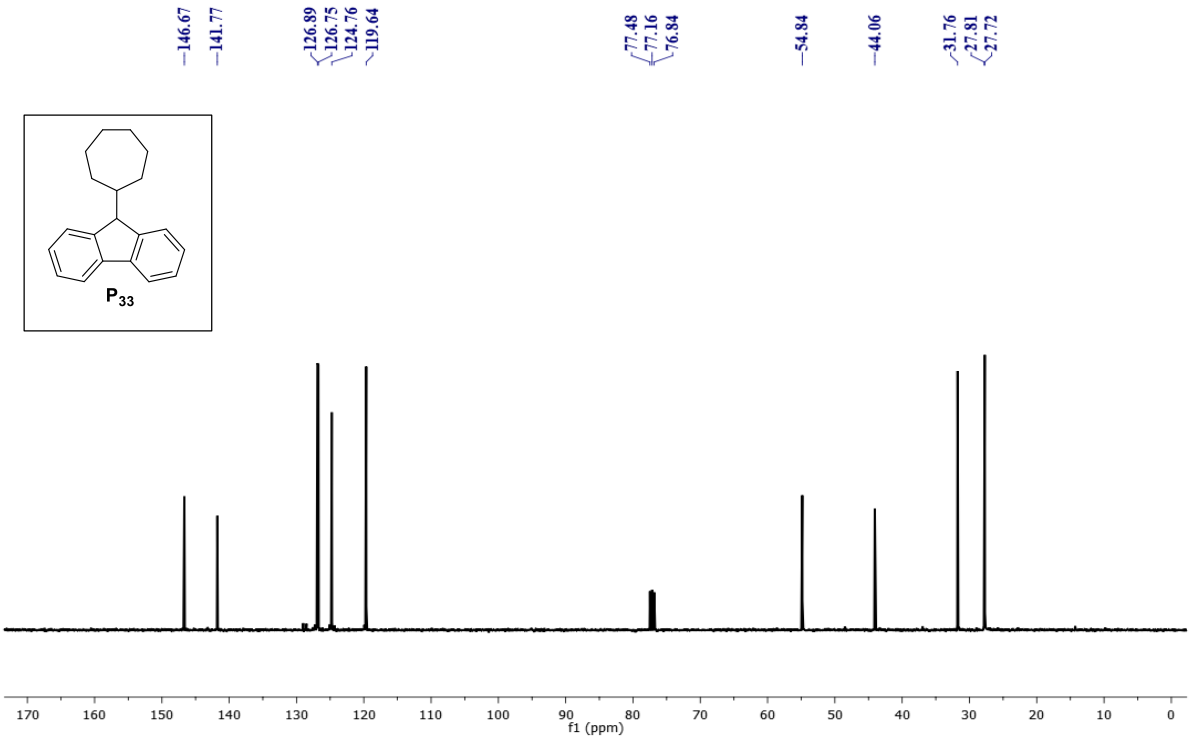


Figure S74. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-cycloheptyl-9H-fluorene **(P_{33})**.

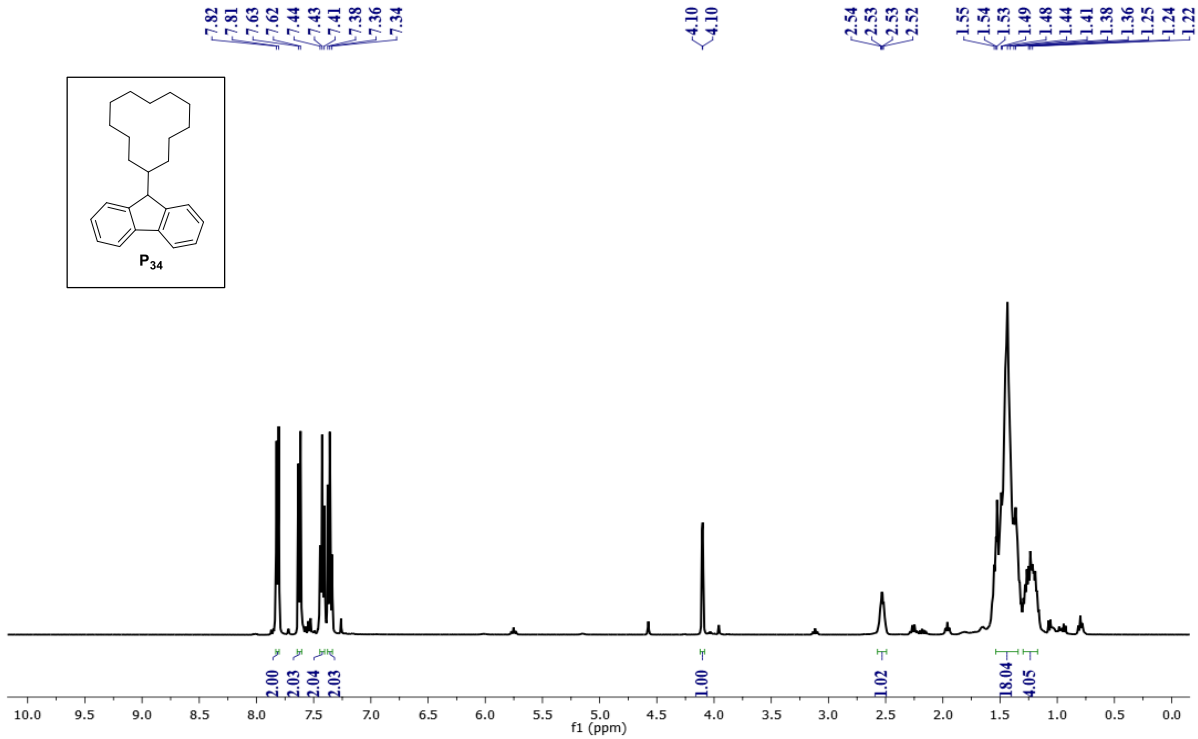


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-cyclododecyl-9H-fluorene **(P_{34})**.

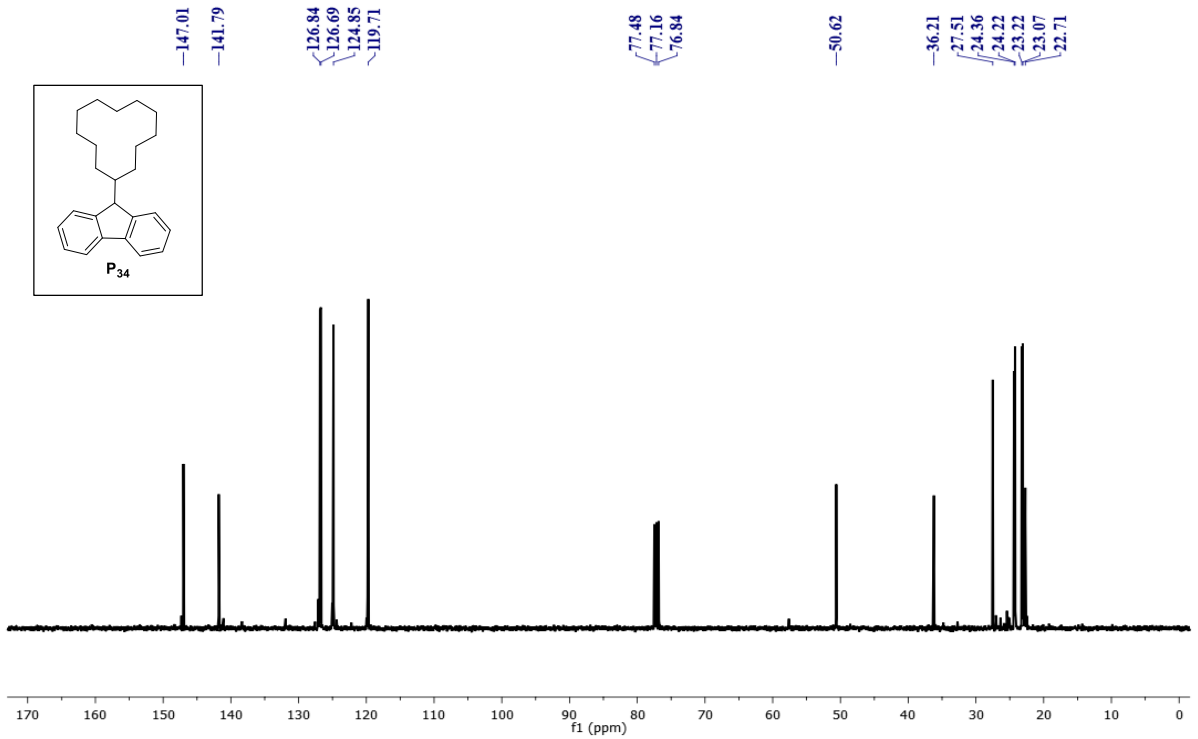


Figure S76. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-cyclododecyl-9H-fluorene **(P_{34})**.

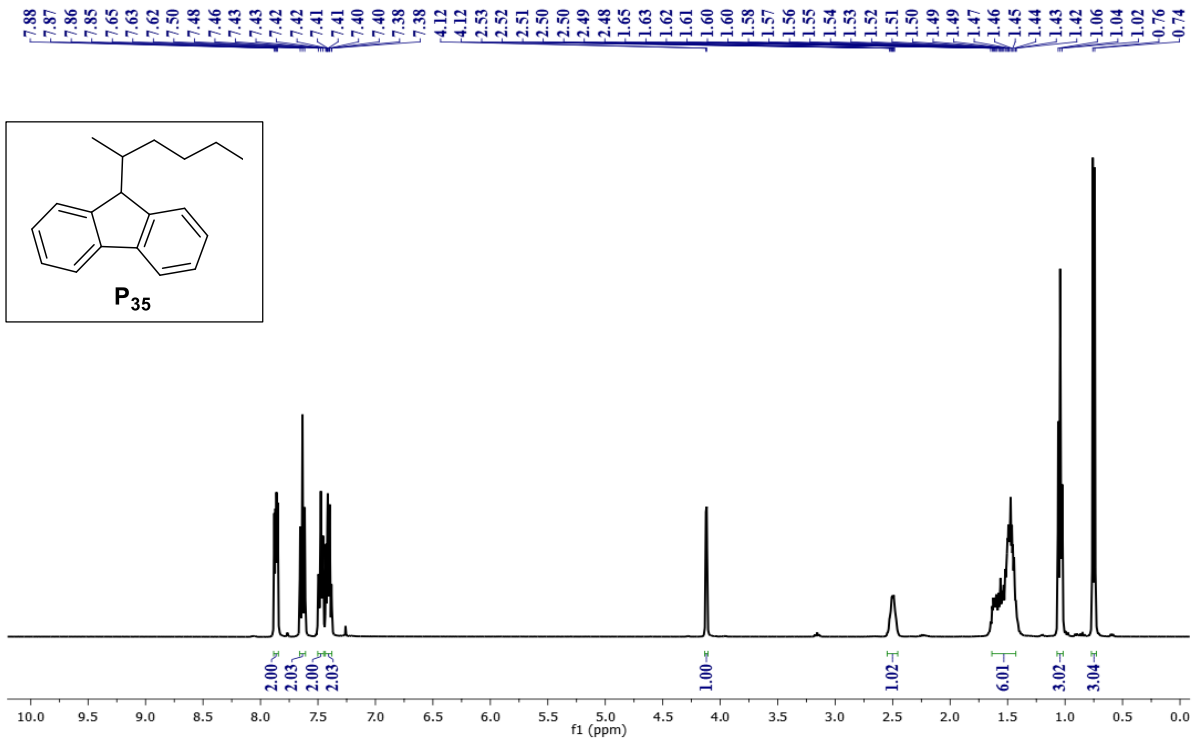


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(hexan-2-yl)-9H-fluorene **(P_{35})**.

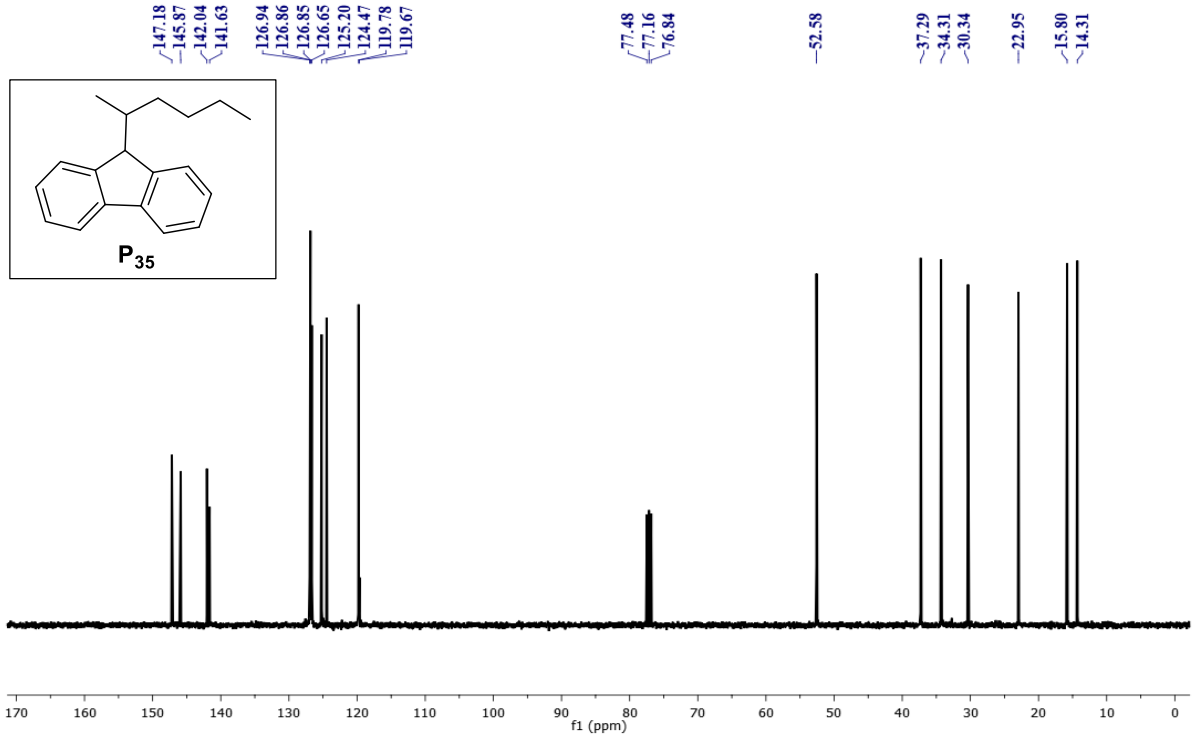


Figure S78. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(hexan-2-yl)-9H-fluorene **(P_{35})**

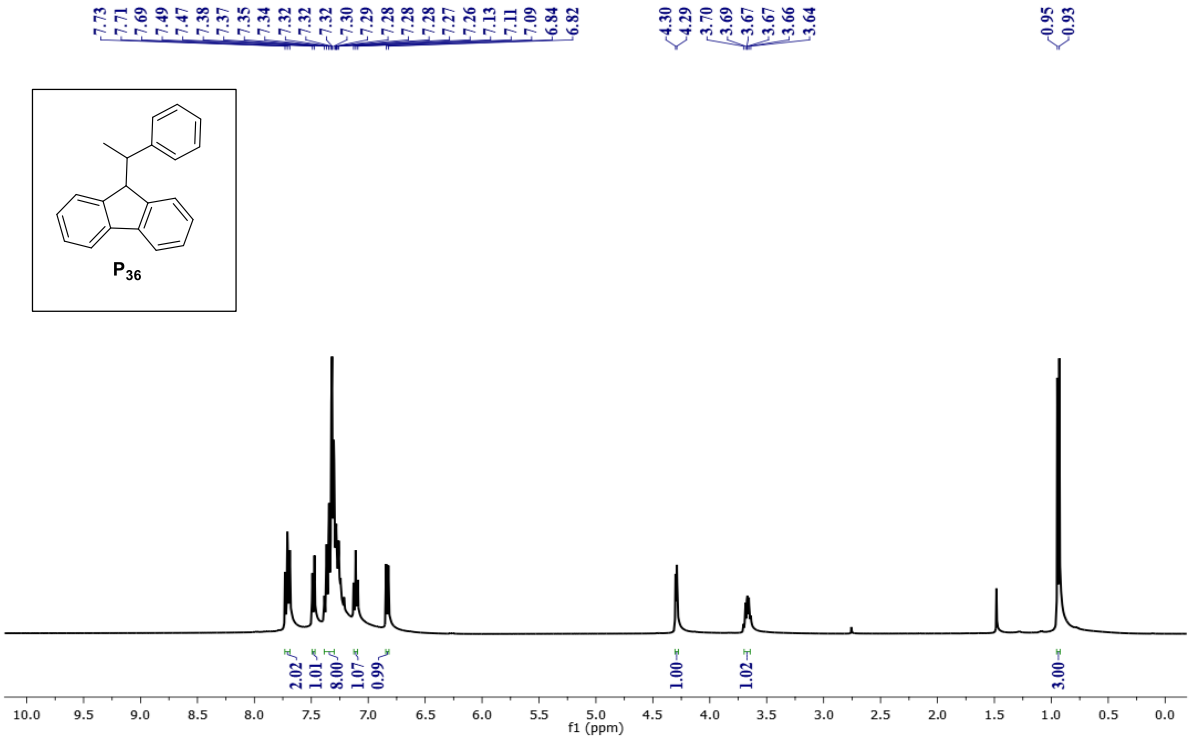


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(1-phenylethyl)-9H-fluorene **(P_{36})**.

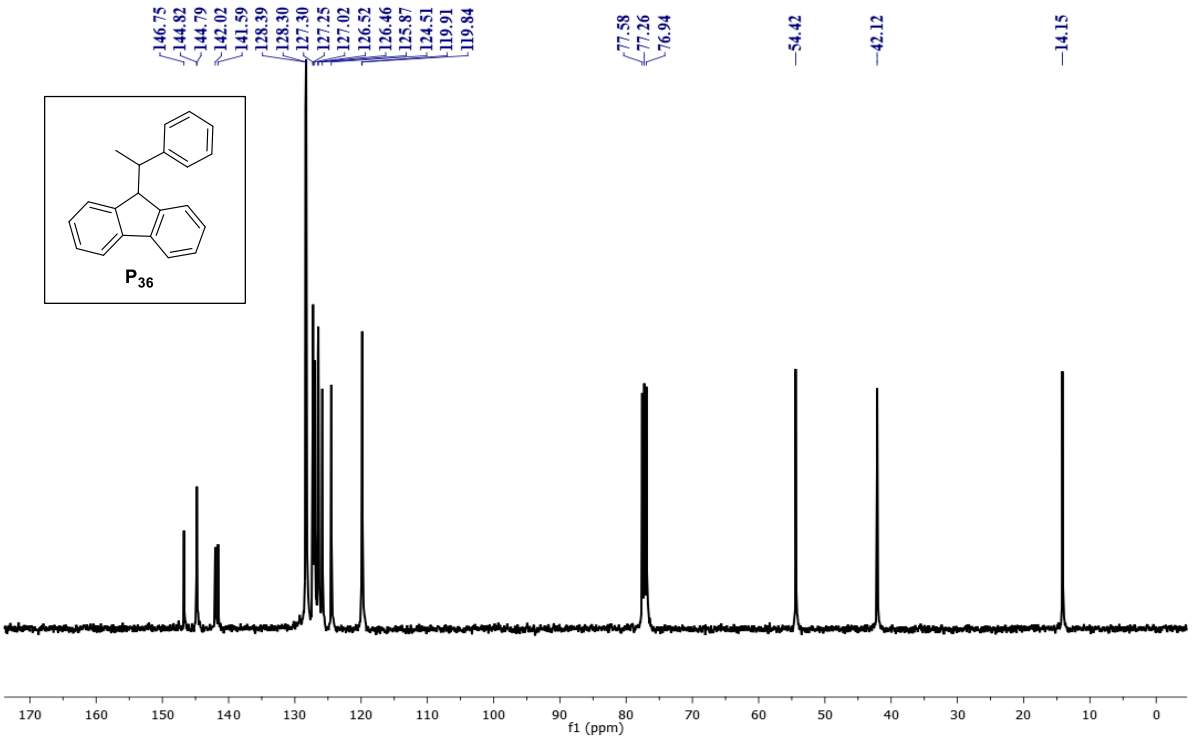


Figure S80. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(1-phenylethyl)-9H-fluorene **(P_{36})**.

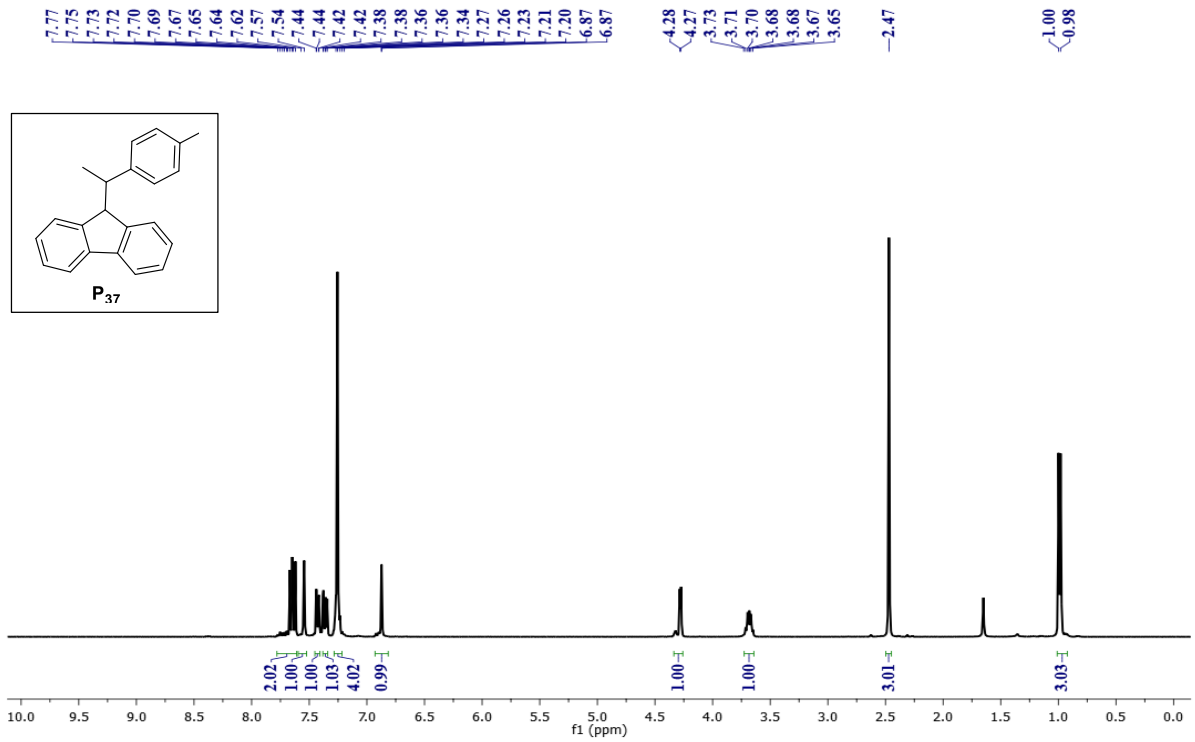


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(1-(p-tolyl)ethyl)-9H-fluorene **(P_{37})**.

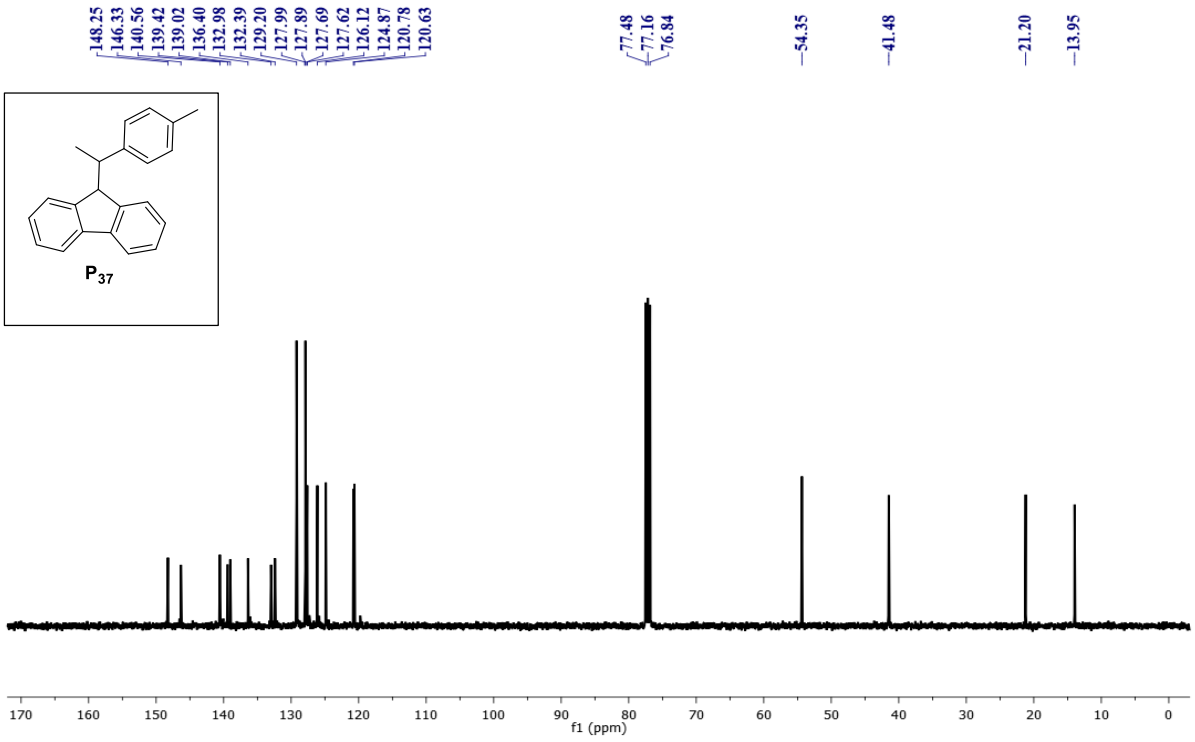


Figure S82. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(1-(p-tolyl)ethyl)-9H-fluorene **(P_{37})**.

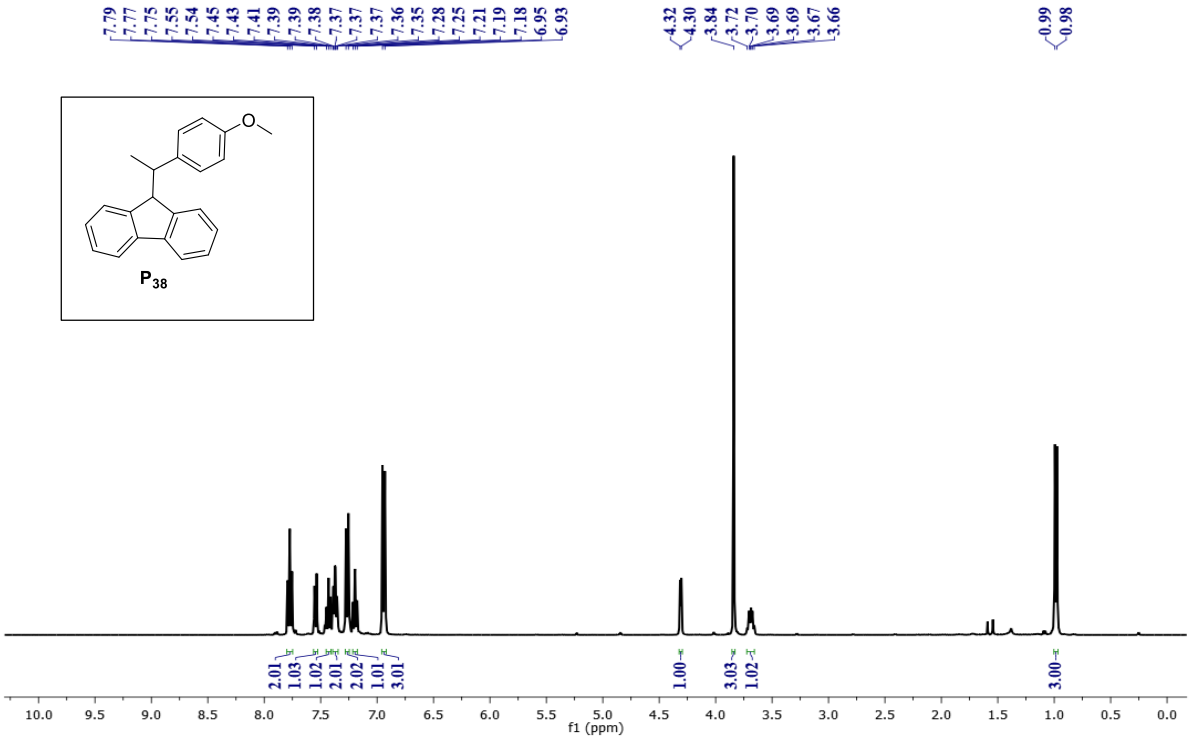


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene **(P38)**.

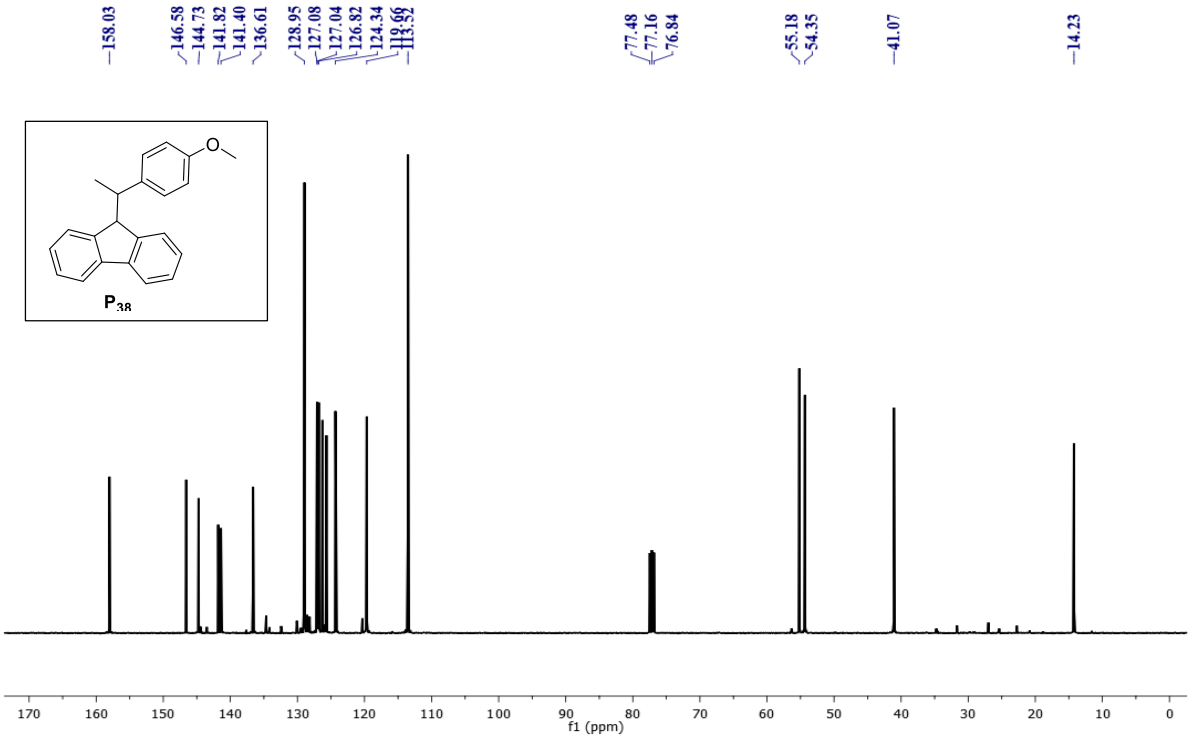


Figure S84. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene **(P38)**.

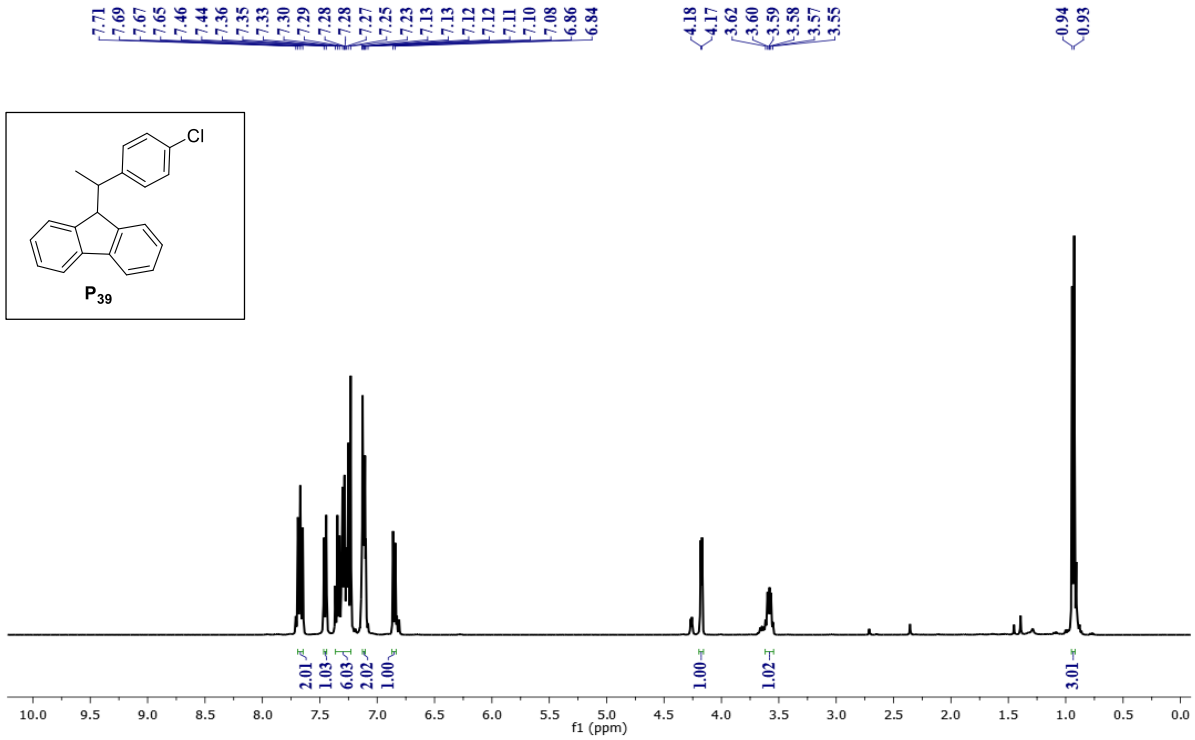


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(1-(4-chlorophenyl)ethyl)-9H-fluorene **(P_{39})**.

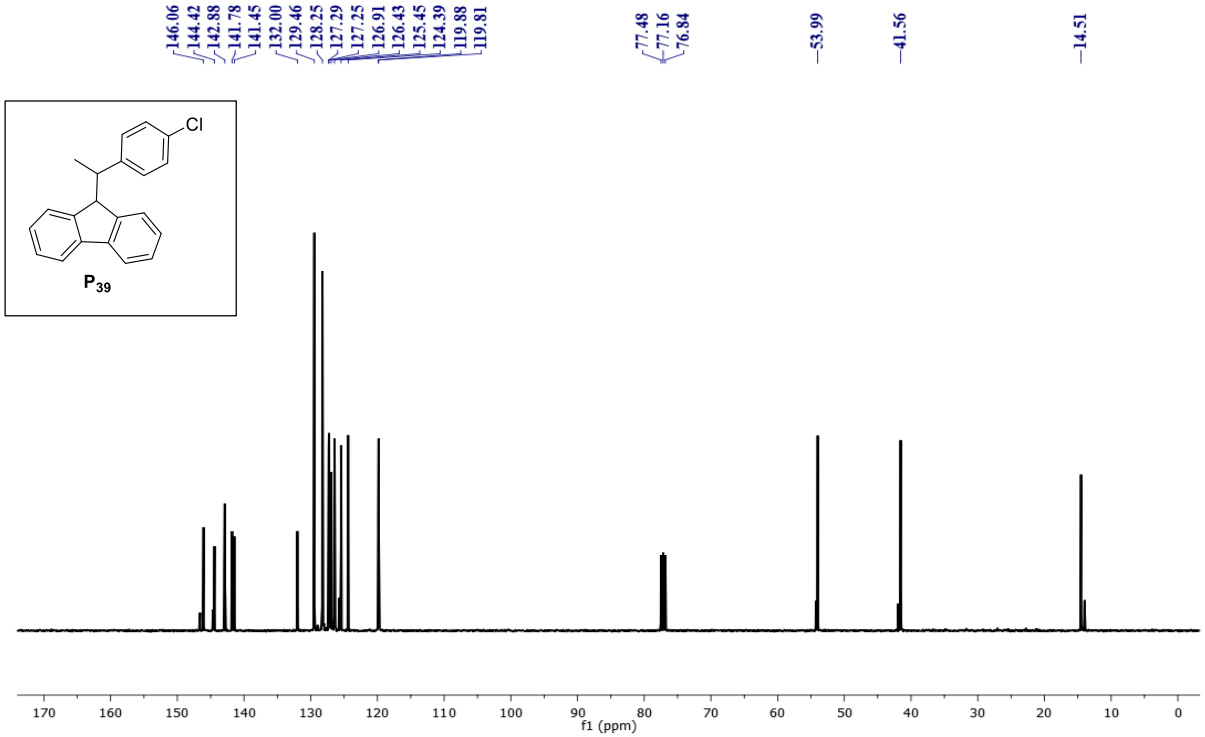


Figure S86. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(1-(4-chlorophenyl)ethyl)-9H-fluorene **(P_{39})**.

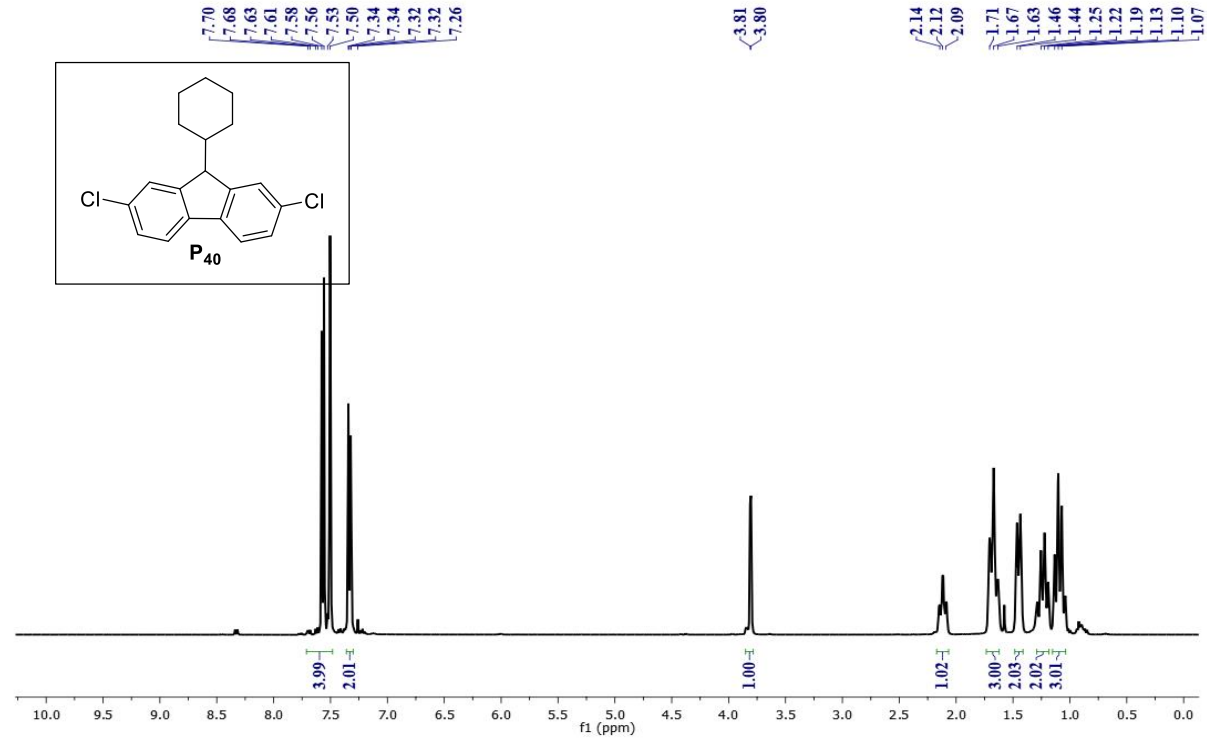


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-dichloro-9-cyclohexyl-9H-fluorene **(P_{40})**.

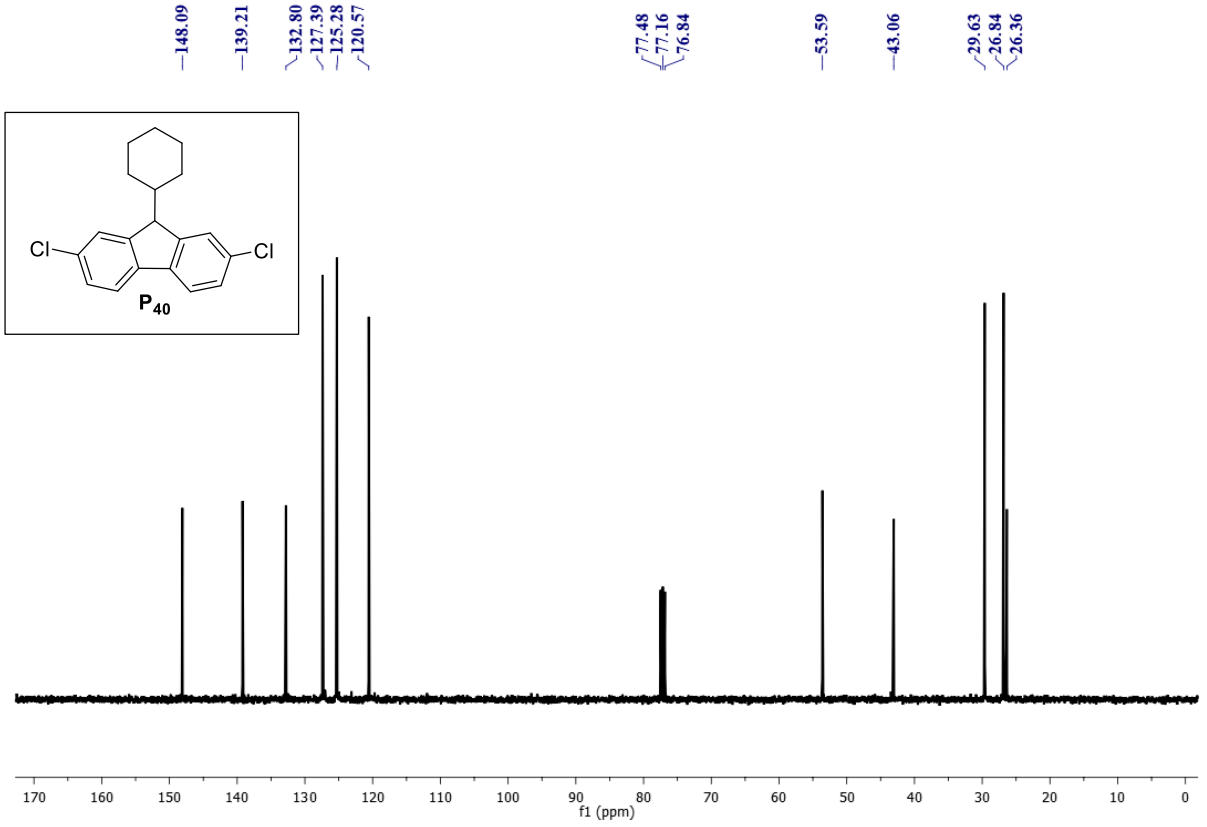


Figure S88. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2,7-dichloro-9-cyclohexyl-9H-fluorene **(P_{40})**.

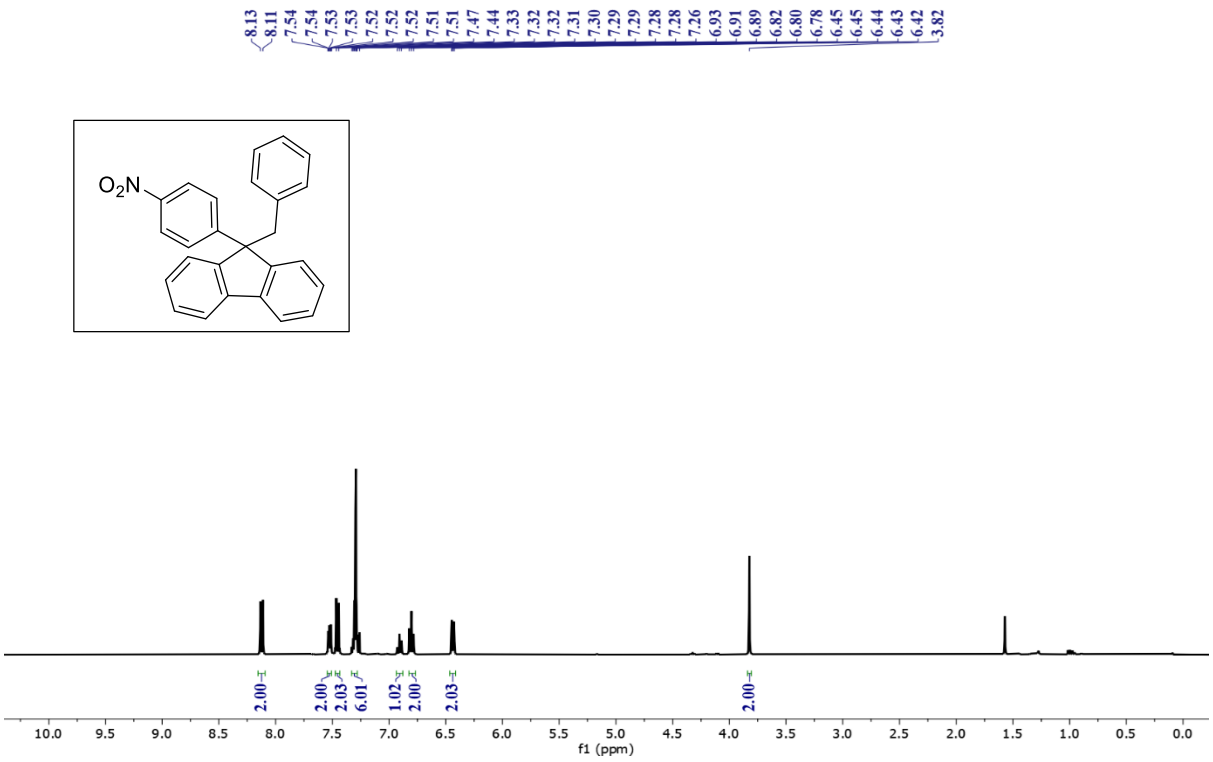


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzyl-9-(4-nitrophenyl)-9H-fluorene **(P_{1a}).**

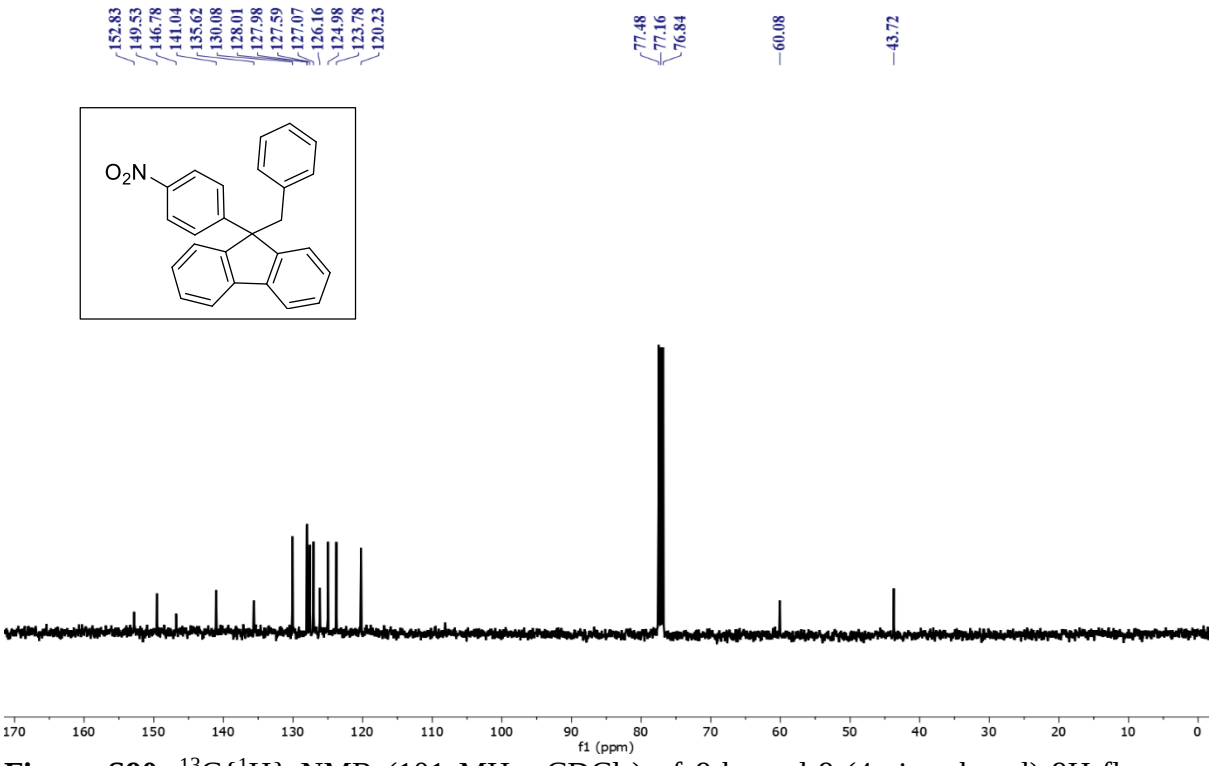


Figure S90. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzyl-9-(4-nitrophenyl)-9H-fluorene **(P_{1a}).**

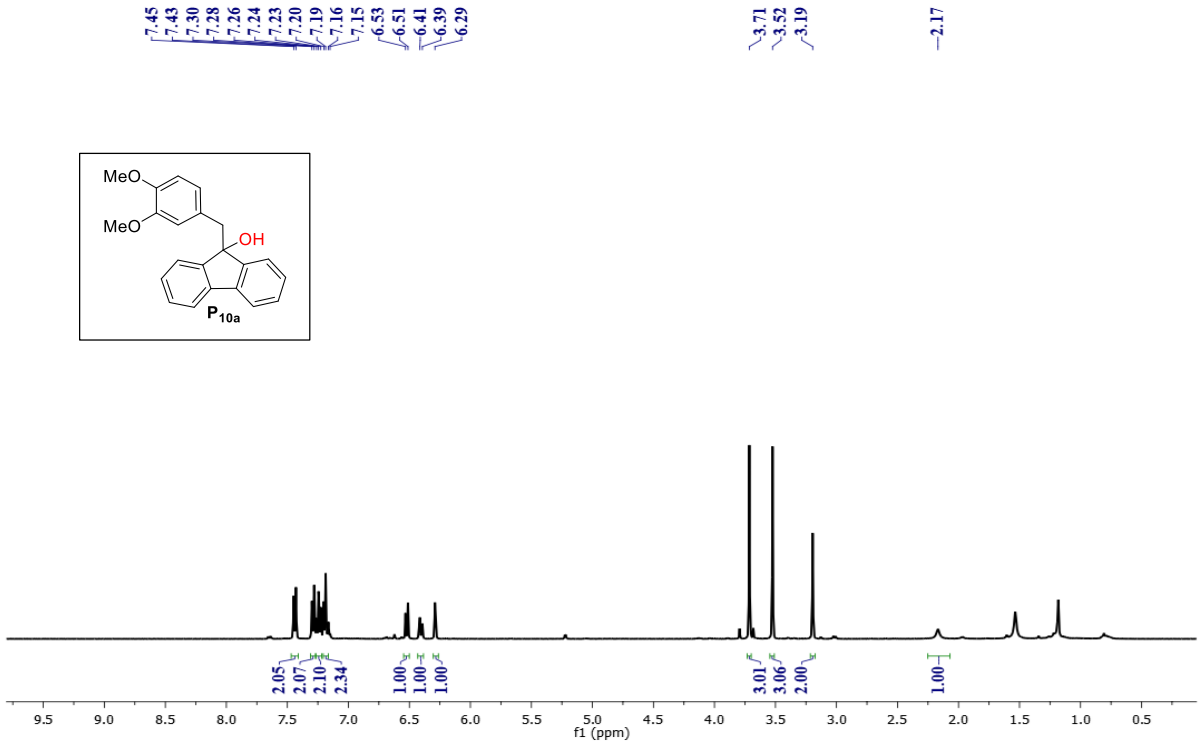


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-(3,4-dimethoxybenzyl)-9H-fluoren-9-ol **(P_{10a})**.

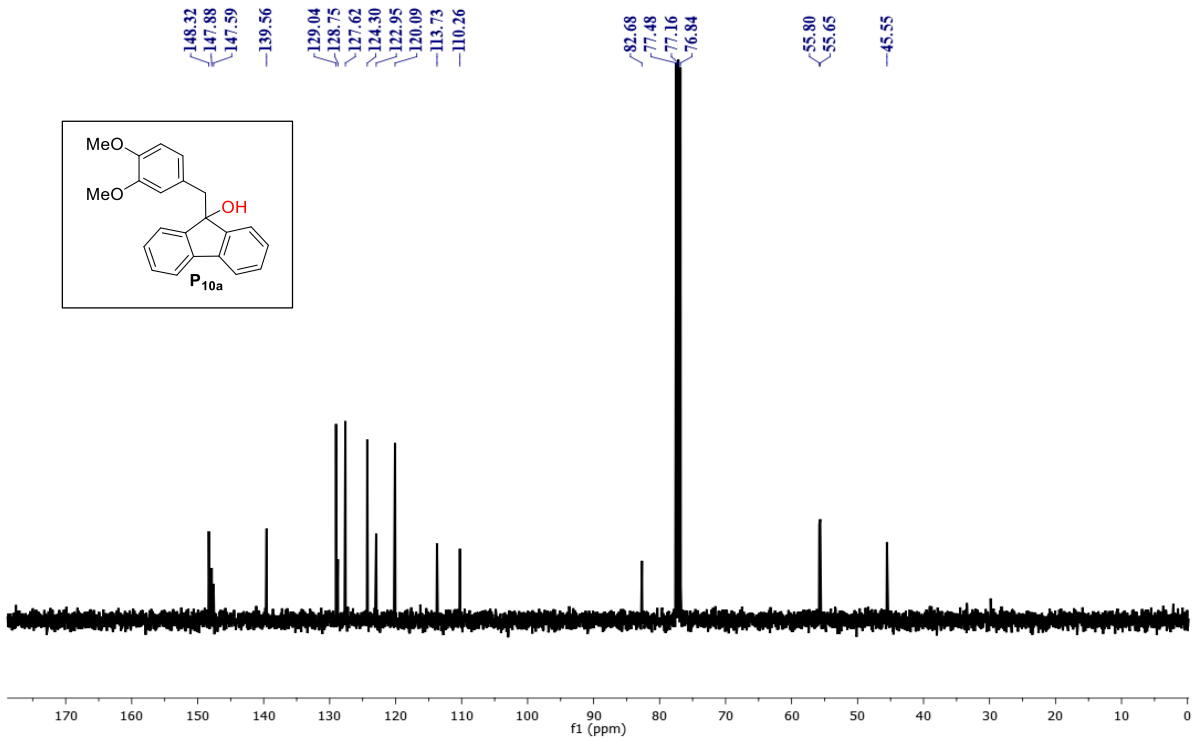


Figure S92. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-(3,4-dimethoxybenzyl)-9H-fluoren-9-ol **(P_{10a})**.

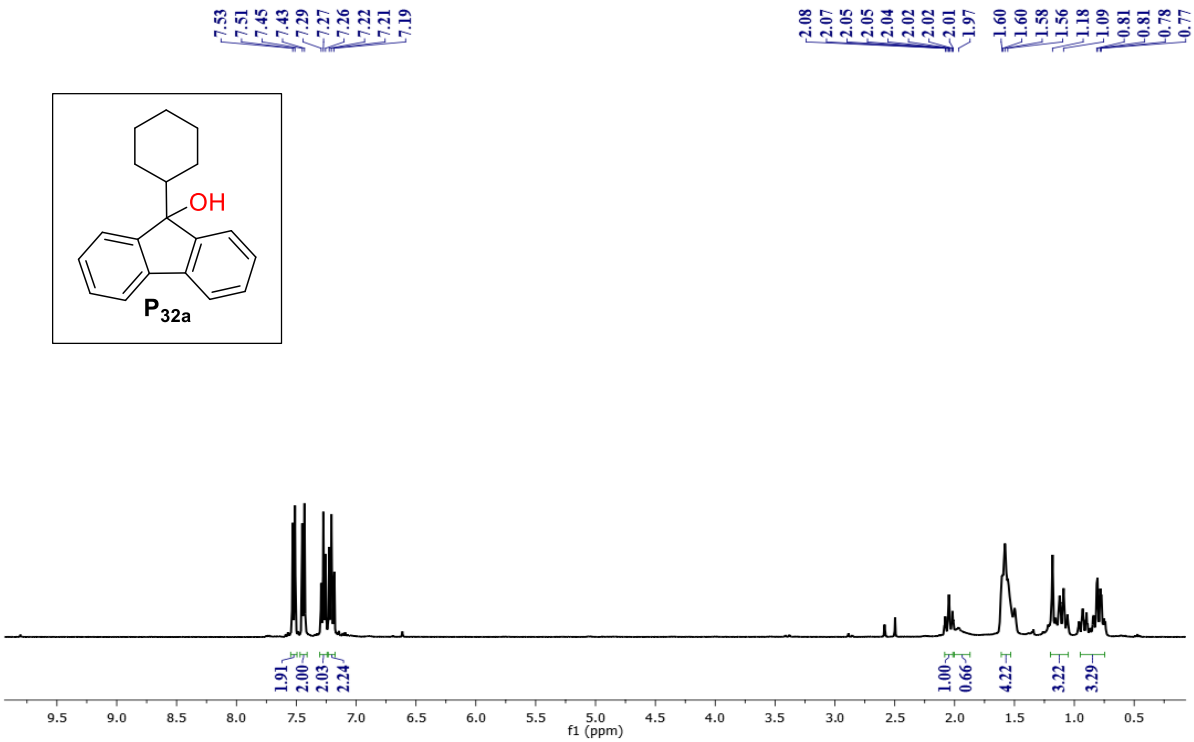


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-cyclohexyl-9H-fluoren-9-ol **(P_{32a})**.

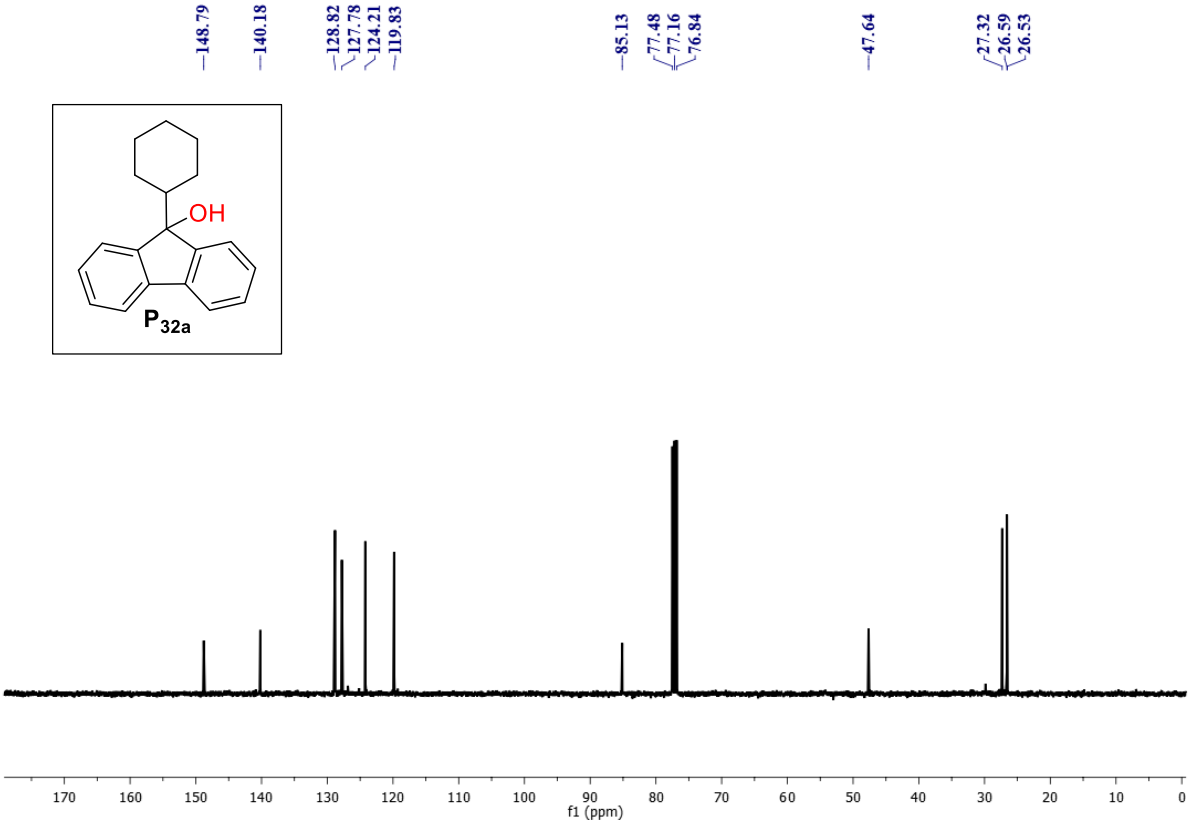


Figure S94. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-cyclohexyl-9H-fluoren-9-ol **(P_{32a})**.

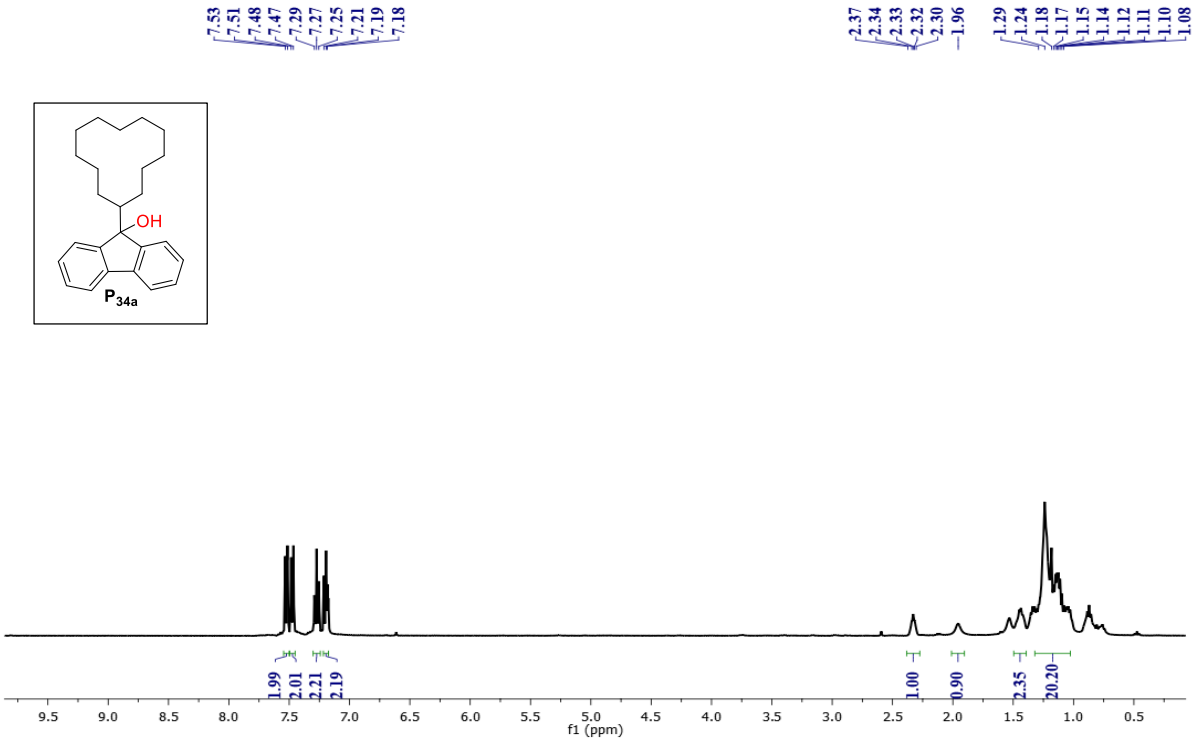


Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-cyclododecyl-9H-fluoren-9-ol **(P_{34a})**.

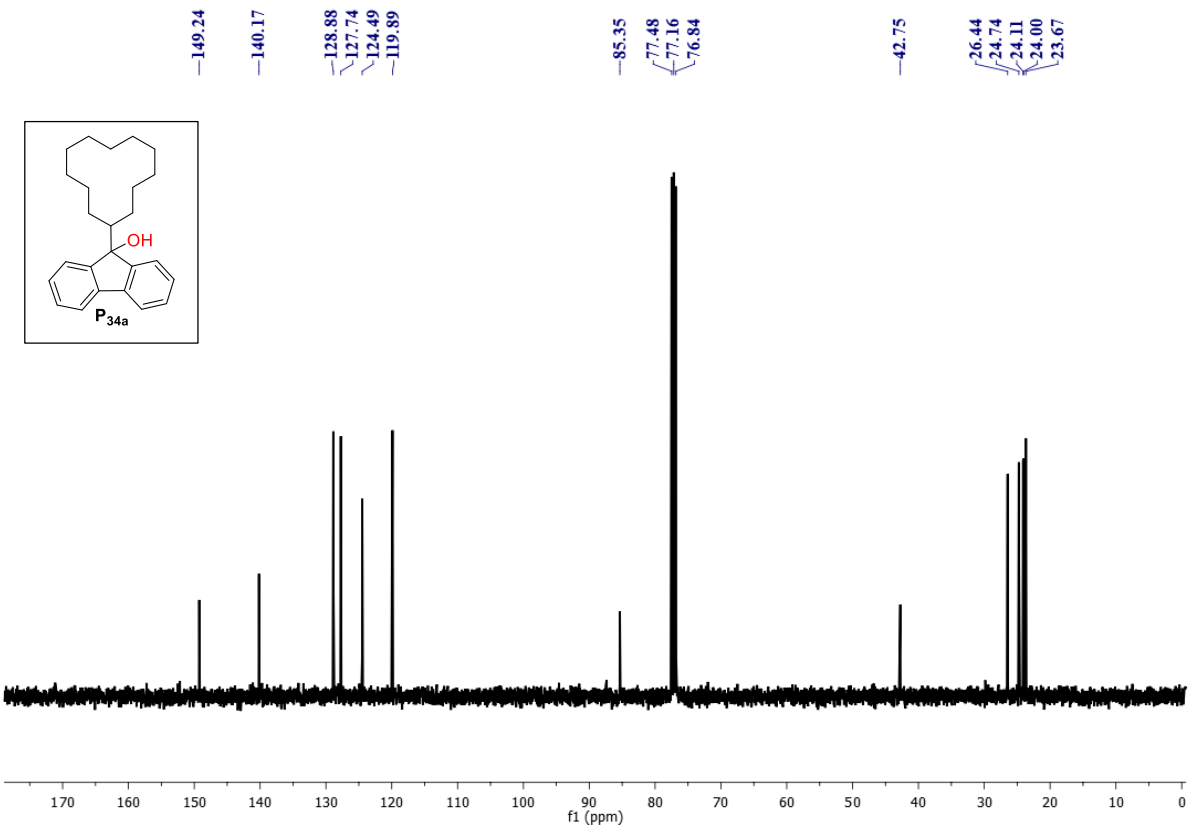


Figure S96. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-cyclododecyl-9H-fluoren-9-ol **(P_{34a})**.

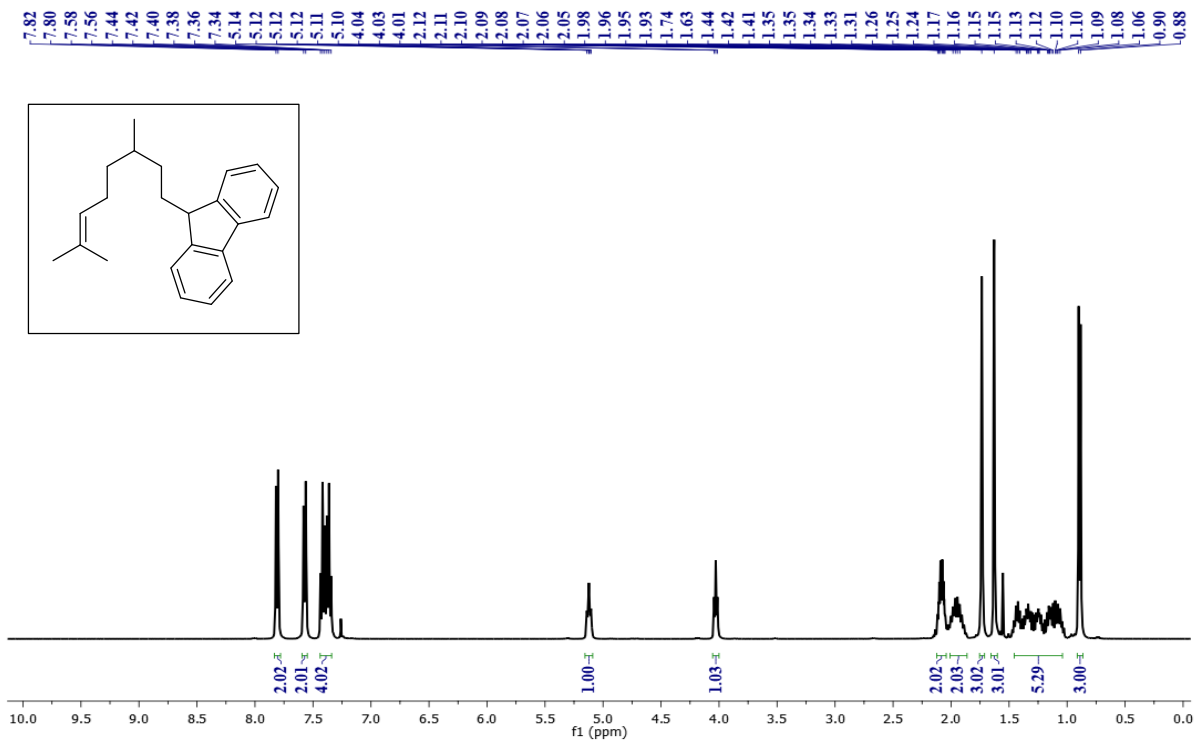


Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) of 9–(3,7–dimethyloct–6–en–1–yl)–9H–fluorene **(P_{41}).**

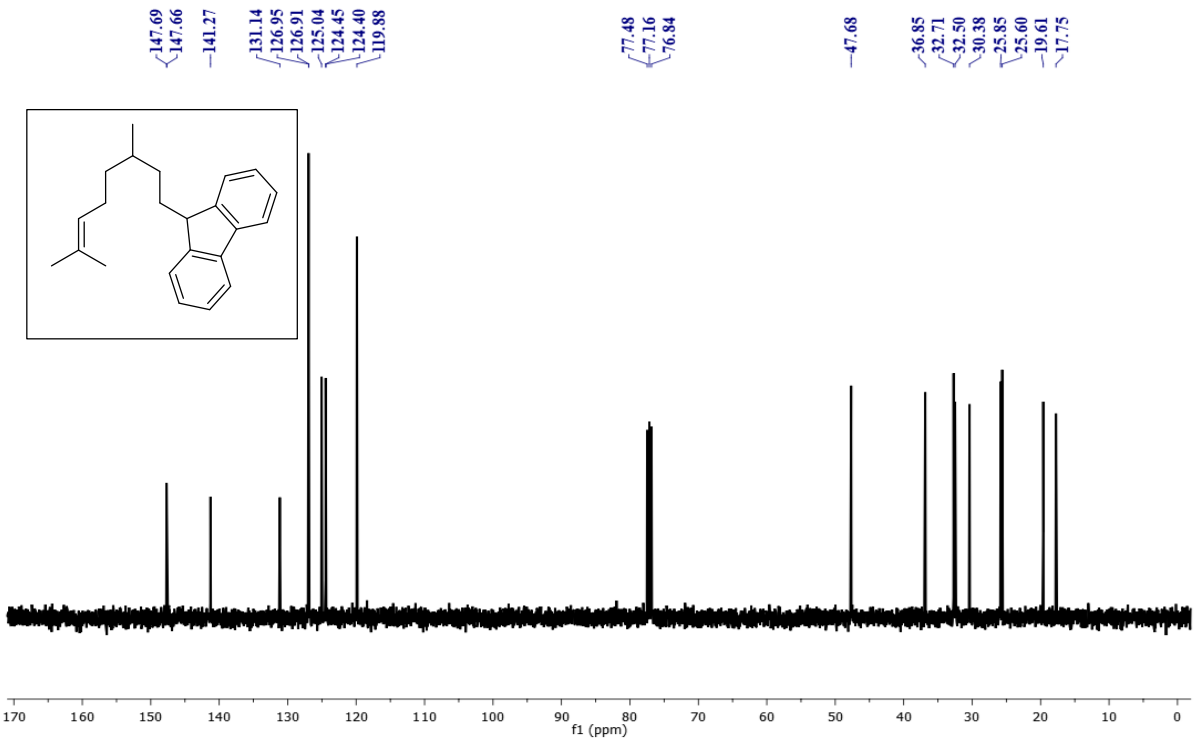


Figure S98. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9–(3,7–dimethyloct–6–en–1–yl)–9H–fluorene **(P_{41}).**

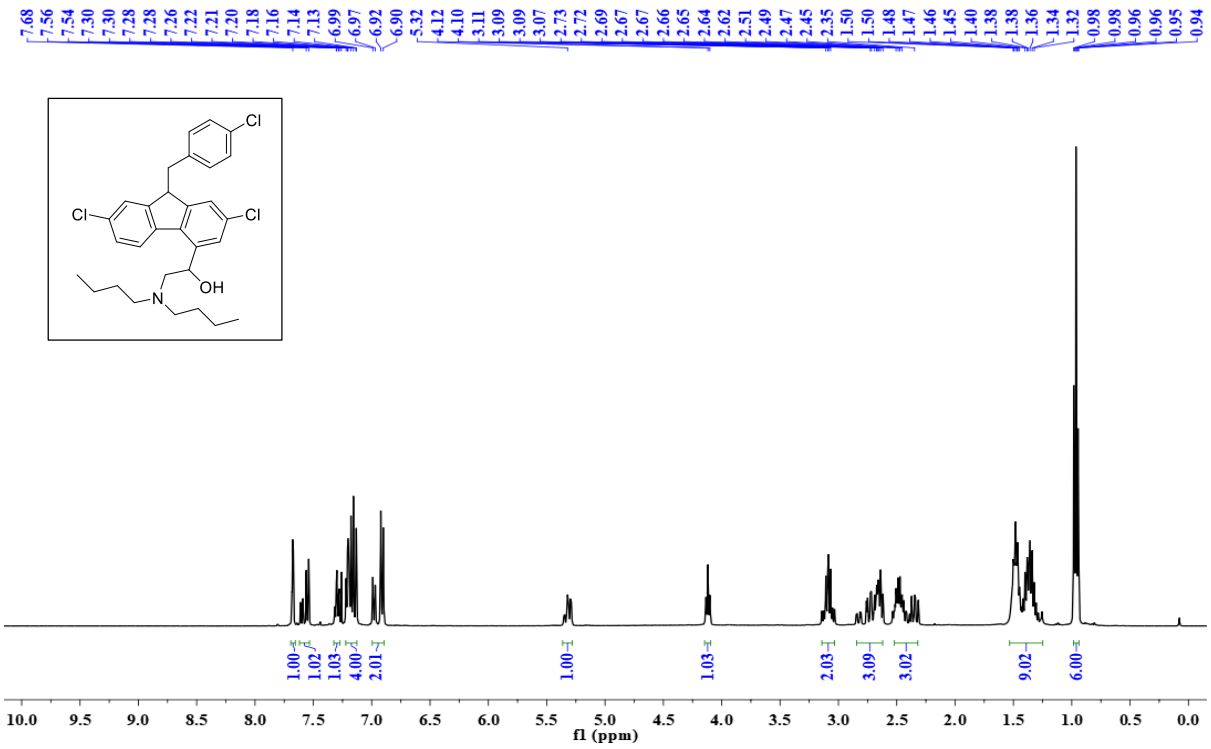


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol **(P_{42})**.

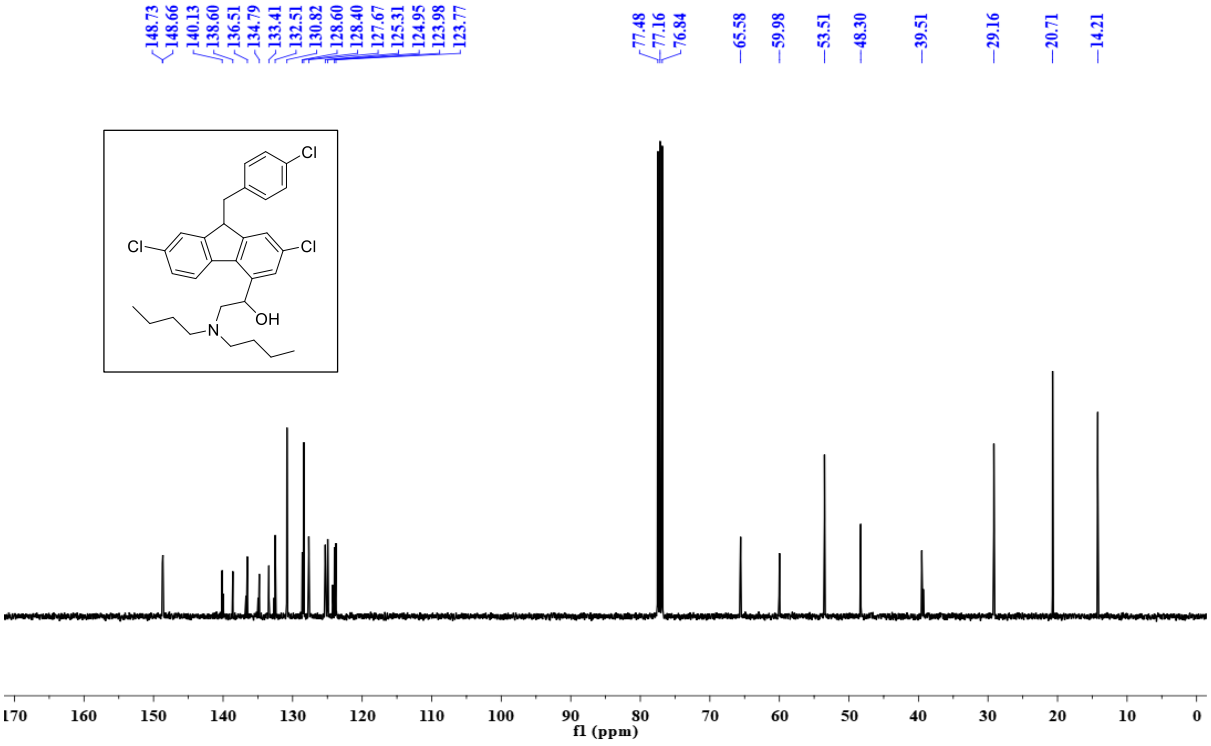


Figure S100. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol **(P_{42})**.

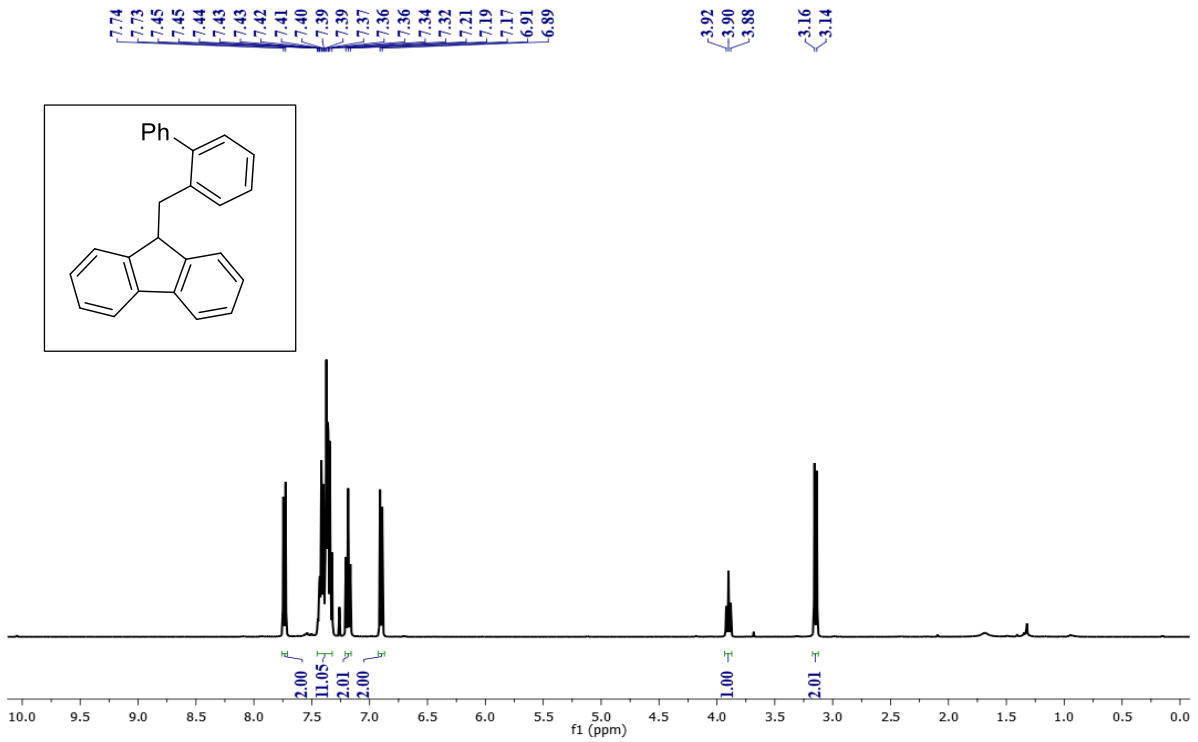


Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-2-ylmethyl)-9H-fluorene **(P_{43})**.

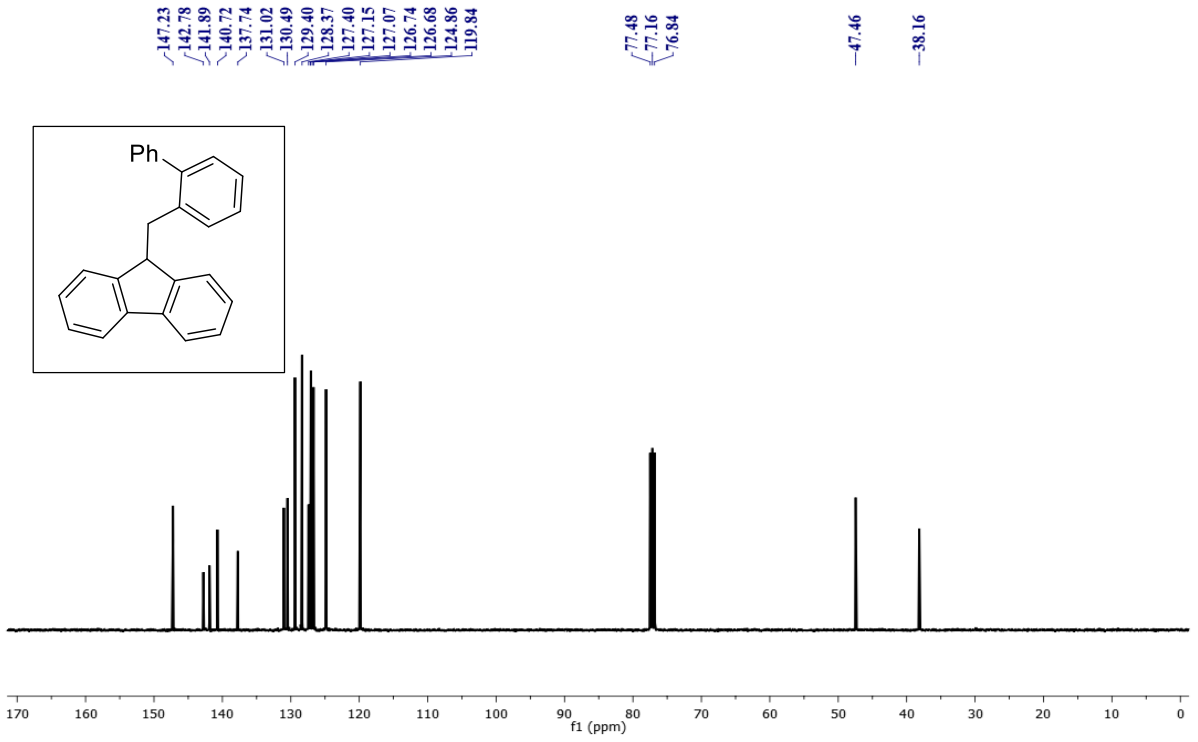
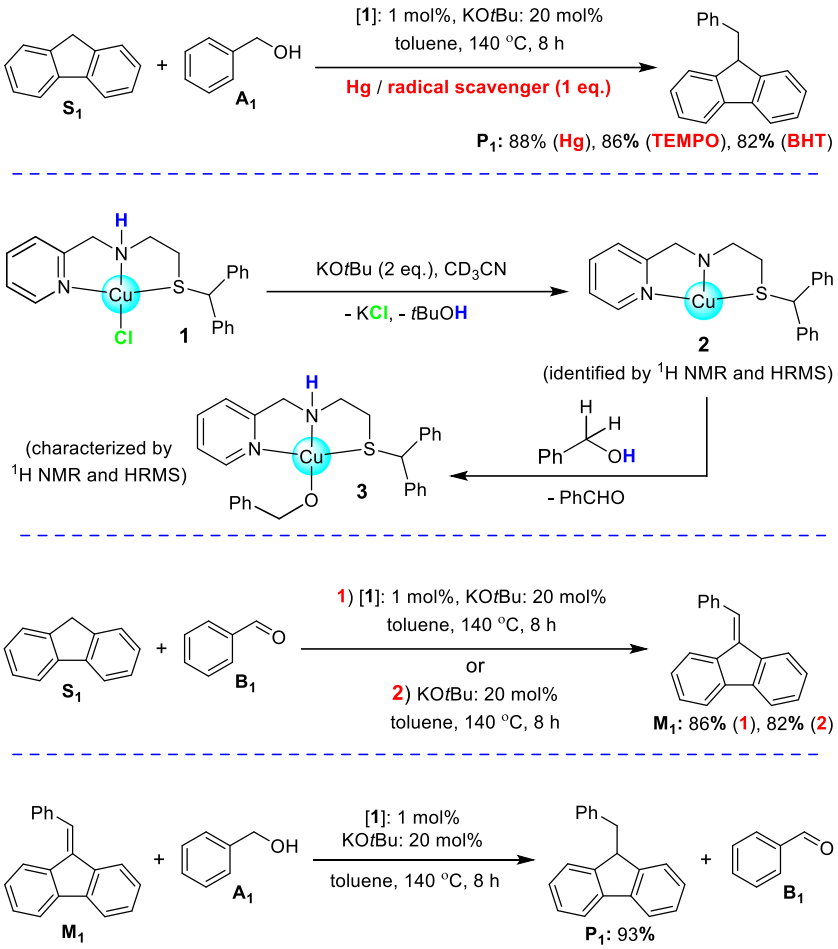


Figure 102. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-([1,1'-biphenyl]-2-ylmethyl)-9H-fluorene **(P_{43})**.

Mechanistic studies:



We focused to understand the identity of the active catalyst in the possible mechanistic pathway for the copper catalyzed C-alkylation of fluorenes with alcohols and thus, we carried out several control experiments (above Scheme). At first, a mercury poisoning test was performed and radical scavenging tests were performed. A drop of mercury was added in the alkylation reaction of fluoerene with benzyl alcohol using standard reaction condition. The expected C-alkylated fluorene **P1** was isolated in good yield, which indicated a homogeneous catalytic pathway. Successful alkylations also in the presence of radical scavengers such as TEMPO and BHT suggested that radical reactions were not involved. Then we performed a stoichiometric reaction of complex **1** and base in CD_3CN and the reaction was monitored by ^1H NMR spectroscopy. Dehydrochlorinated product (**2**) was identified by GCMS and ^1H NMR; NH resonance was absent in the respective ^1H NMR spectrum. Addition of benzyl alcohol to the

above reaction mixture resulted in the formation of copper(I)-benzoxy complex (**3**) with rehydrogenated ligand backbone. The NH and benzoxy-CH_2 resonance were observed at 3.46 and 4.57 ppm, respectively. Hence, the hydrogen transfer from alcohol to dehydrochlorinated copper species **2** was established. Both species **2** (397.0810) and **3** (545.1053) were also identified by HRMS. Thereafter, a reaction of fluorene with benzaldehyde was done under standard reaction condition for alkylation, which yielded olefinated species $\mathbf{M_1}$ in good yield. This aldol-type condensation reaction was also done in the absence of copper complex. The formation of expected olefinated species $\mathbf{M_1}$ suggested that it was a base-catalyzed condensation with no active role of copper complex. In the following reaction, olefinated species $\mathbf{M_1}$ was hydrogenated to C-alkyl fluorene $\mathbf{P_1}$ using benzyl alcohol as the hydrogen source; dehydrogenated product benzaldehyde was also identified.

Experimental procedure:

Mercury poisoning test: In a dried pressure tube fitted with a magnetic stir bar, a mixture of fluorene (0.083 g, 0.50 mmol), benzyl alcohol (0.06 g, 0.55 mmol), complex **1** (0.002 g, 1 mol%), KO*t*Bu (0.011 g, 20 mol%) and toluene (2 mL) was added under a nitrogen atmosphere. To this reaction mixture, a drop of mercury was added. Then the reaction mixture was heated at 140 °C in a preheated oil bath for 8 h. The reaction mixture was cooled down to room temperature upon completion and concentrated in vacuum. The purification of product was done by using column chromatography and hexane as eluent and the isolation of the expected product $\mathbf{P_1}$ in high yield (0.112 g, 88%) suggested the homogeneous behaviour of the catalyst.

Note: A heterogeneous reaction path may be considered if copper complex (**1**) degrades during the reaction and forms nanoparticles. During mercury poisoning test, mercury is supposed to form copper amalgam with the copper nanoparticles and this should inhibit the catalytic

reaction. Adding mercury to the copper complex (**1**) catalyzed alkylation reaction did not have any negative impact and this suggests homogeneous catalytic path.

Radical scavenging test: In a dried pressure tube fitted with a magnetic stir bar, a mixture of fluorene (0.083 g, 0.50 mmol), benzyl alcohol (0.06 g, 0.55 mmol), complex **1** (0.002 g, 1 mol%), KO*t*Bu (0.011 g, 20 mol%), radical scavenger (1 equiv.) and toluene (2 mL) was successively added under a nitrogen atmosphere. Then the reaction mixture was heated at 140 °C in a preheated oil bath for 8 h. The reaction mixture was cooled down to room temperature upon completion and concentrated in vacuum. The isolation of the expected product in $\mathbf{P_1}$ in high yields with TEMPO (0.110 g, 86%) and BHT (0.105 g, 82%) suggested a mechanistic path which does not follow radical pathway.

Synthesis of dehydrochlorinated intermediate (2): Under inert atmosphere, in a 5 ml vial, complex **1** (0.022 g, 0.05 mmol), KO*t*Bu (0.011 g, 0.1 mmol) was stirred for 30 minutes in CD_3CN (1 ml) at room temperature. After filtration, the reaction mixture was analysed by ^1H NMR spectroscopy. NH resonance was absent in the respective ^1H NMR spectrum, which clearly indicated the formation of dehydrochlorinated intermediate **2**. ^1H NMR (400 MHz, CD_3CN) δ 8.50 (d, J = 4.5 Hz, 1H), 7.68 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 7.5 Hz, 4H), 7.35 – 7.17 (m, 8H), 5.25 (s, 1H), 3.76 (s, 2H), 2.70 (t, J = 6.6 Hz, 2H), 2.52 (t, J = 6.6 Hz, 2H). HRMS (ESI) *m/z*: $[(M + H)^+]$ calcd for $C_{21}H_{22}CuN_2S$: 397.0800, found 397.0810.

Synthesis of Cu(I)-benzoxy complex (3): Under inert atmosphere, in a 5 ml vial complex **1** (0.022 g, 0.05 mmol), KO*t*Bu (0.011 g, 0.1 mmol) was stirred for 30 minutes in CH_3CN (1 ml). Then benzyl alcohol (0.006 g, 0.05 mmol) was added to the reaction mixture and the mixture was again stirred for 30 minutes at room temp. Then, the reaction mixture was dried under high vacuum to remove all the volatilities. CD_3CN (1 mL) was added and the solution was collected after filtration. The solution was analysed by ^1H NMR spectroscopy and HRMS.

Rehydrogenation of the ligand backbone was noted. The benzoxy-CH_2 resonance in the respective ^{1}H NMR spectrum indicated the formation of copper(I)-benzoxy complex **3**. ^{1}H NMR (400 MHz, CD_3CN) δ 8.14 (d, *J* = 4.5 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 4H), 7.37 – 7.22 (m, 13H), 5.02 (s, 1H), 4.57 (s, 3H), 3.94 (s, 2H), 3.46 (bs, 1H), 2.65 (t, *J* = 5.6 Hz, 2H), 2.45 (t, *J* = 5.8 Hz, 2H). HRMS (ESI) *m/z*: [(M + MeCN)$^+$] calcd for $C_{30}H_{32}CuN_3OS$: 545.1562, found 545.1053.

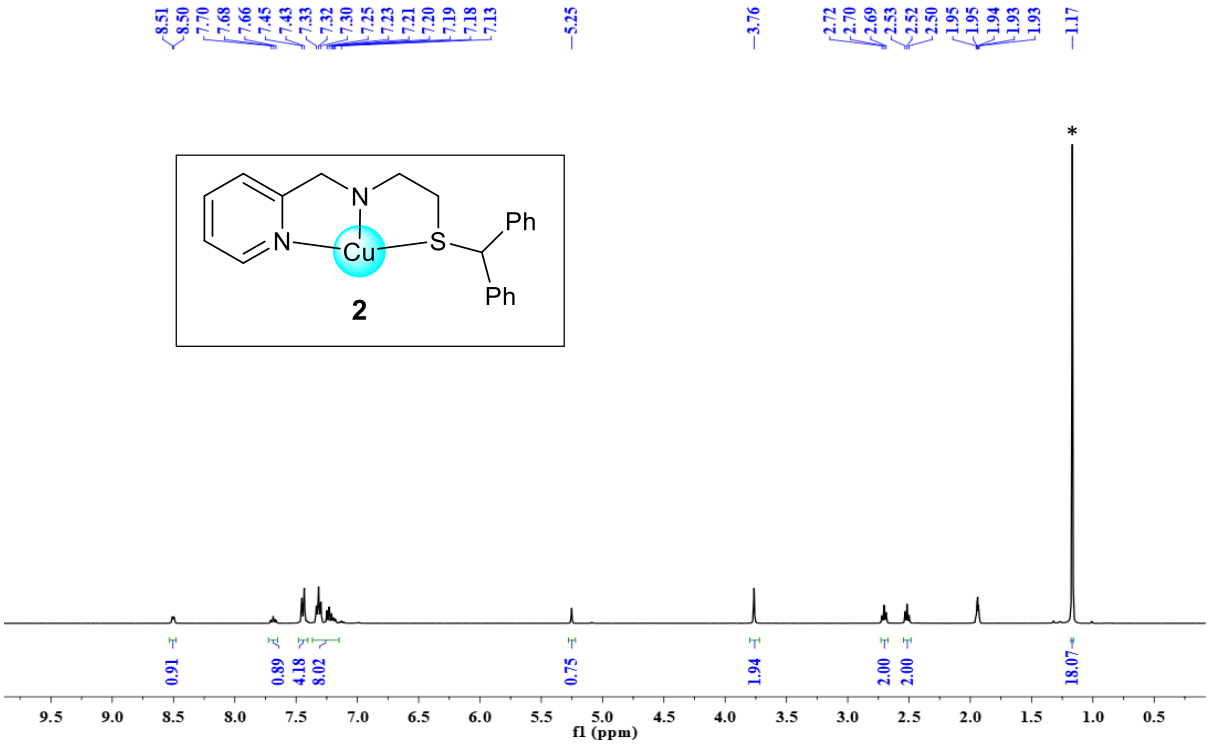


Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$) of dehydrochlorinated intermediate **(2)**. (‘*’ indicate t-BuOH)

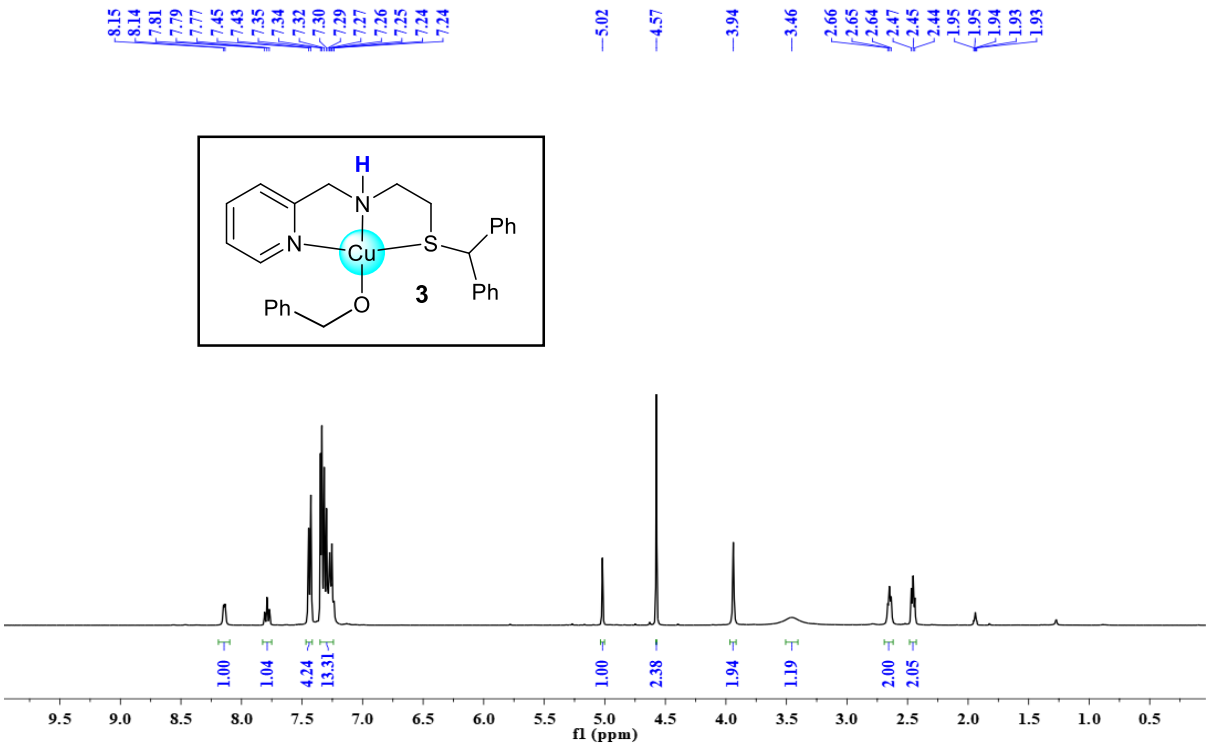


Figure 104. ^{1}H NMR (400 MHz, $CDCl_3$) of Cu(I)-benzoxy complex **(3)**.

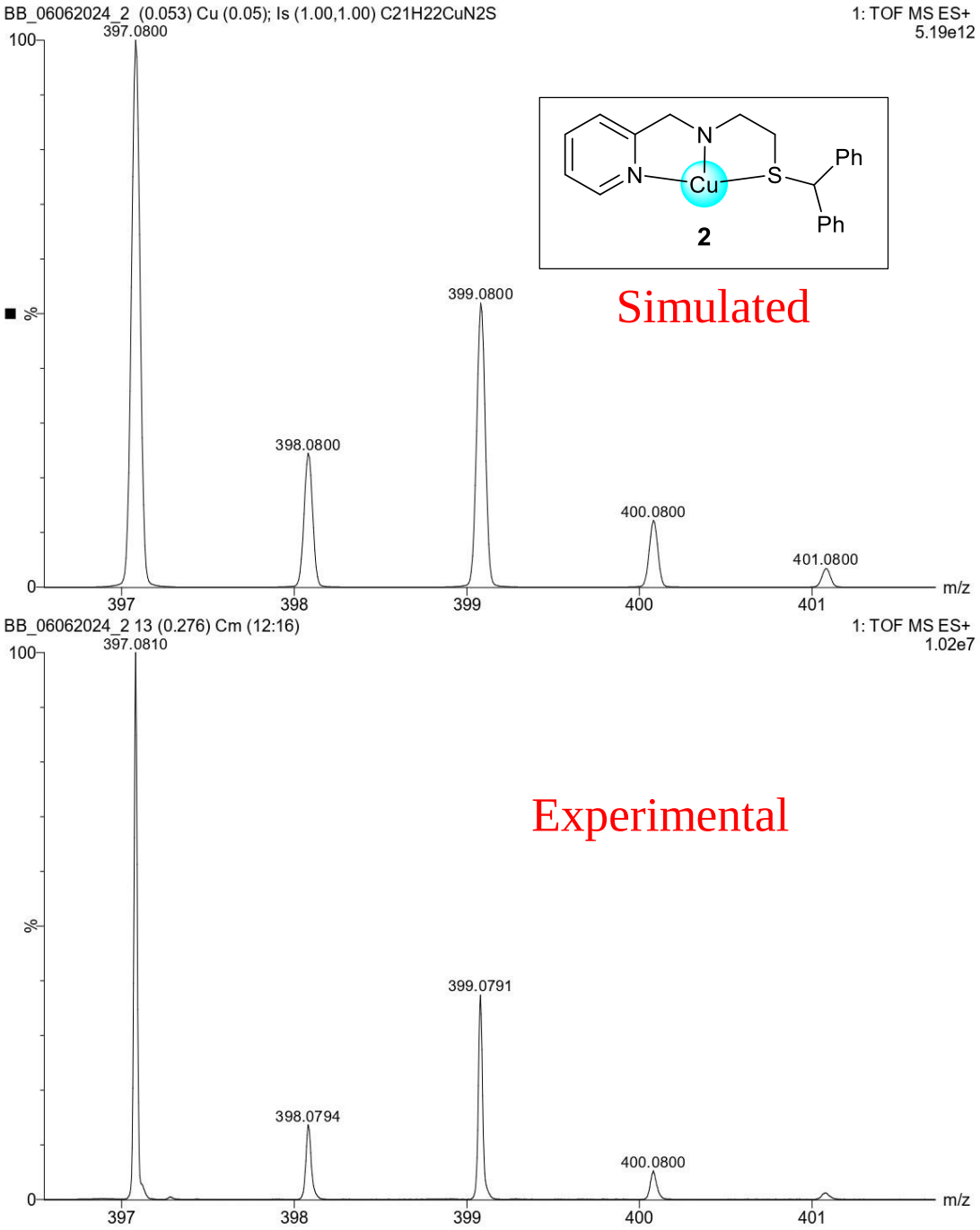


Figure S105: HRMS of dehydrochlorinated intermediate **(2)** $[(M + H)^+$: $C_{21}H_{22}CuN_2S]$.

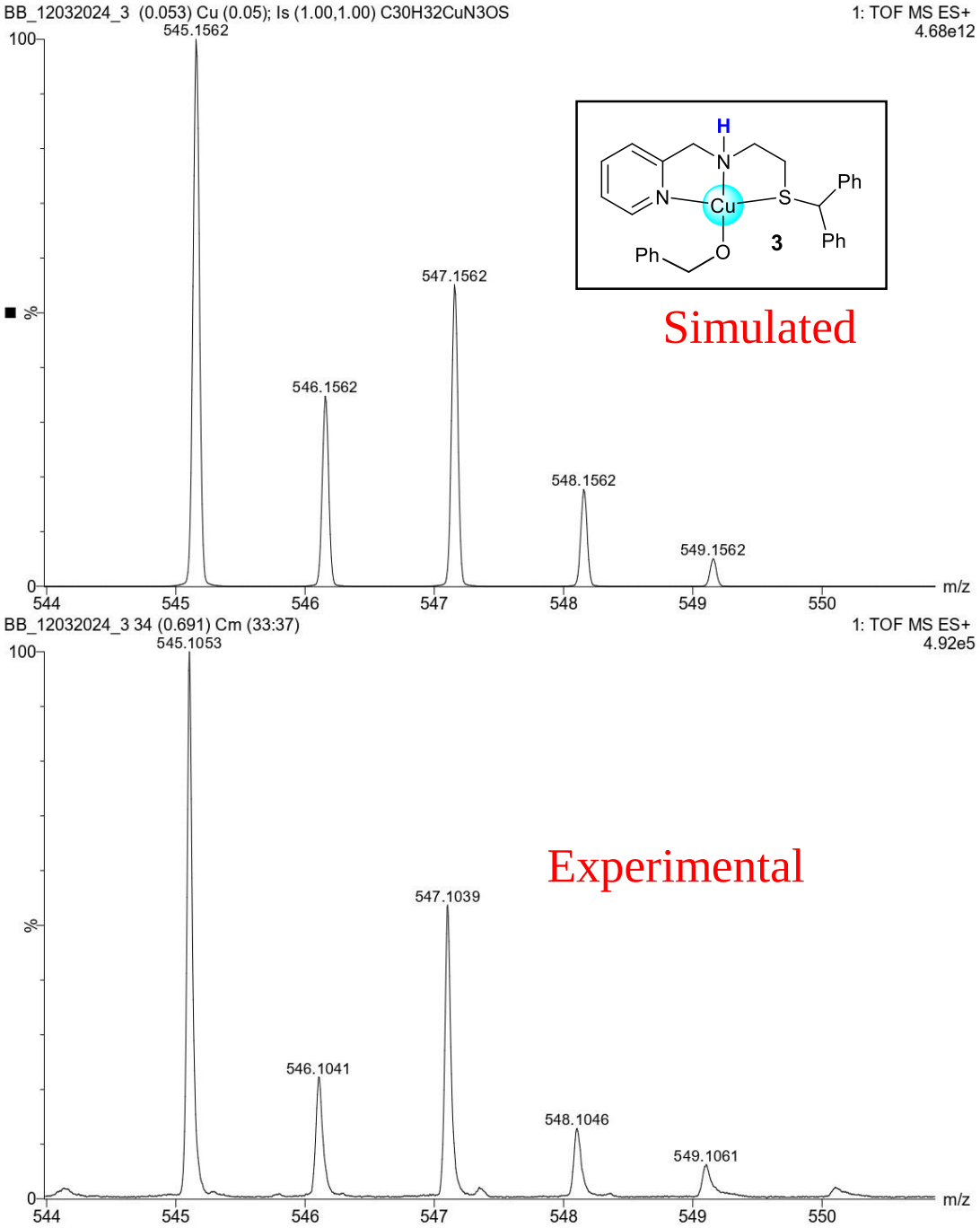


Figure S106: HRMS of Cu(I)-benzoxy complex **(3)** [(M + MeCN)$^+$: $C_{30}H_{32}CuN_3OS$].

Alkenylation of fluorene:

Procedure 1: In dried pressure tube fitted with a magnetic stir bar, a mixture of fluorene (0.083 g, 0.50 mmol), benzaldehyde (0.059 g, 0.55 mmol), complex **1** (0.002 g, 1 mol%), KO*t*Bu (0.011 g, 20 mol%) in toluene (2 mL) was added under a nitrogen atmosphere. Then the reaction mixture was stirred at 140 ^{o}C for 8 h. The reaction mixture was cooled down to room temperature upon completion and concentrated in vacuum. The residue was purified by column chromatography using hexane as an eluent to afford pure product 9-benzylidene-9H-fluorene (**M$_1$**) as a white solid (0.109 g, 86%). The desired product **M$_1$** was characterized by ^{1}H and ^{13}C NMR spectroscopies.

Procedure 2: In dried pressure tube fitted with a magnetic stir bar, a mixture of fluorene (0.083 g, 0.50 mmol), benzaldehyde (0.059 g, 0.55 mmol) and KO*t*Bu (0.011 g, 20 mol%) in toluene (2 mL) was added under a nitrogen atmosphere. Then the reaction mixture was stirred at 140 ^{o}C for 8 h. The reaction mixture was cooled down to room temperature upon completion and concentrated in vacuum. The residue was purified by column chromatography using hexane as an eluent to afford pure product 9-benzylidene-9H-fluorene (**M$_1$**) as a white solid (0.105 g, 82%). The desired product **M$_{11}$** was characterized by ^{1}H and ^{13}C NMR spectroscopies. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 1H), 7.75 – 7.72 (m, 3H), 7.62 – 7.56 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.50 – 7.33 (m, 4H), 7.08 (t, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 139.6, 139.3, 137.0, 136.7, 136.6, 129.4, 128.7, 128.3, 128.2, 127.4, 127.1, 126.8, 124.5, 120.4, 119.8, 119.7.

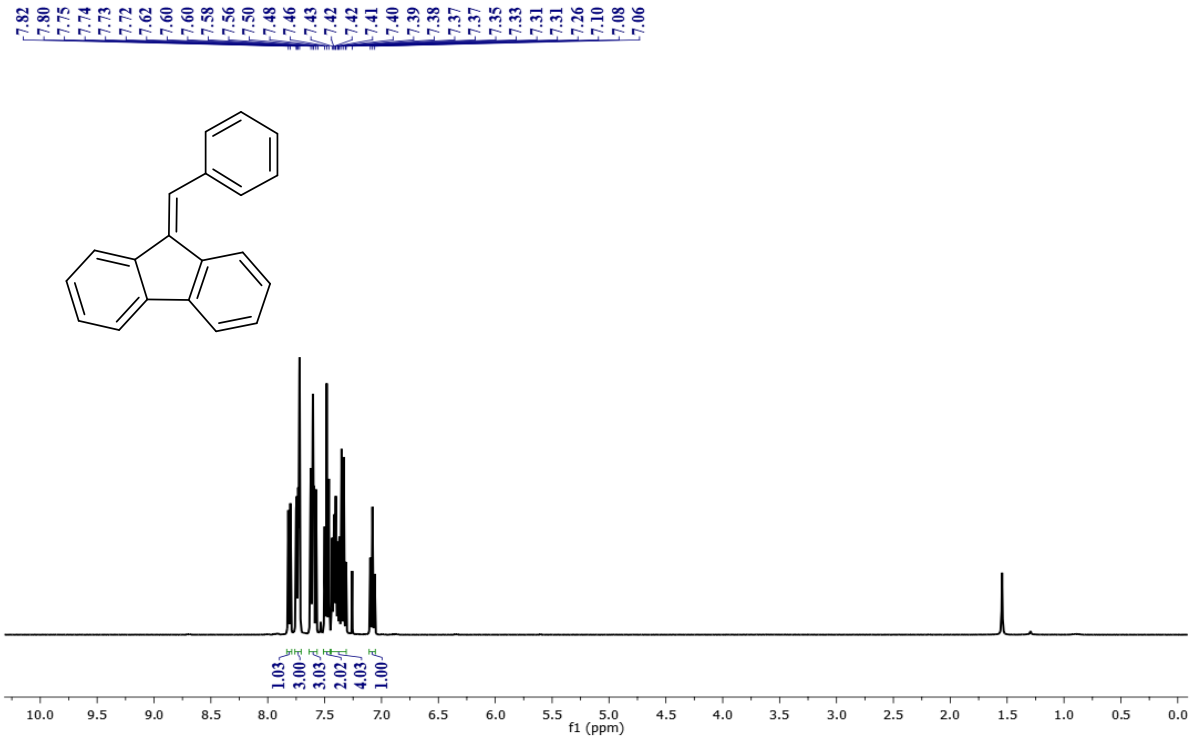


Figure S107. ^{1}H NMR (400 MHz, $CDCl_3$) of 9-benzylidene-9H-fluorene **(M_1)**

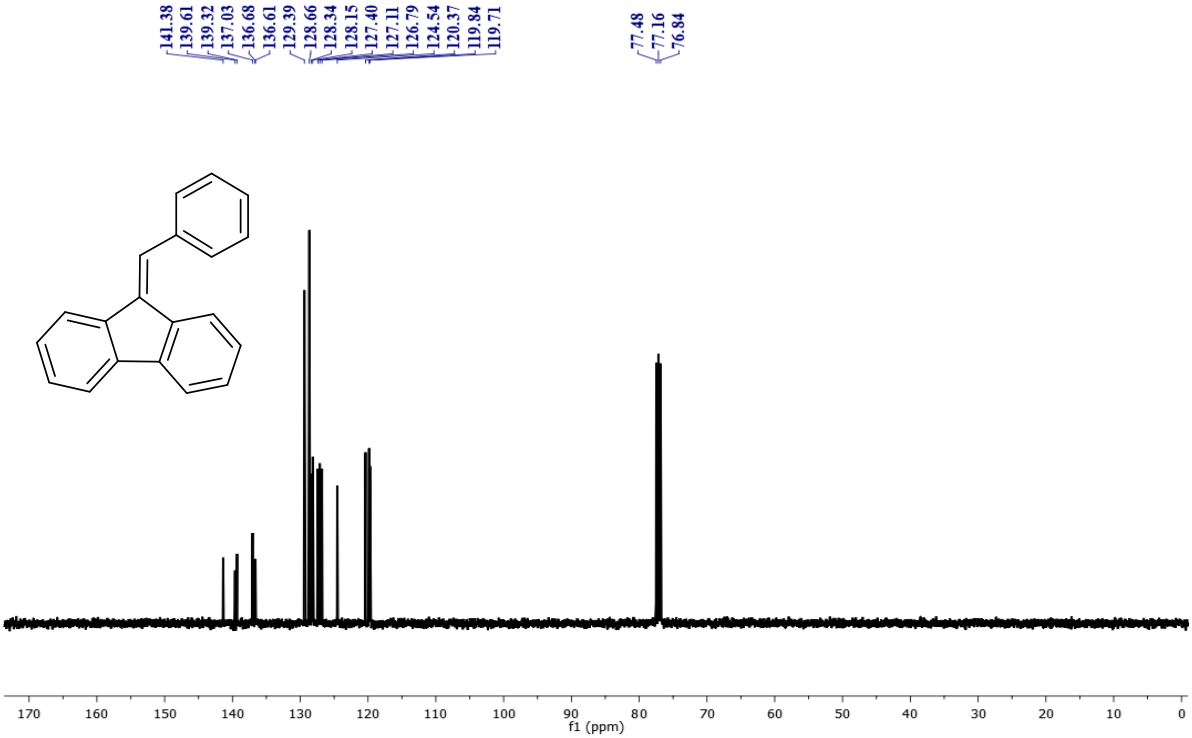


Figure S108. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 9-benzylidene-9H-fluorene **(M_1)**.

Hydrogenation of alkenylated compound: In a dried pressure tube fitted with a magnetic stir bar, a mixture of **M₁** (0.127 g, 0.50 mmol), complex **1** (0.002 g, 1 mol%), KO*t*Bu (0.011 g, 20 mol%) in toluene (2 mL) was added under a nitrogen atmosphere. Then the reaction mixture was stirred at 140 °C for 8 h. The reaction mixture was cooled down to room temperature upon completion and concentrated in vacuum. The residue was purified by column chromatography using hexane as an eluent to afford pure product **P₁** as a white solid (0.118 g, 93%).

Temperature stability test of the Cu-NNS catalyst: A solution of complex **1** in dry CD_3CN (0.6 mL) was taken in a dried NMR pressure tube under a nitrogen atmosphere. Then the reaction mixture was heated at 140 °C in a preheated oil bath for appropriate time. After 4 h and 8 h, the pressure NMR tube was taken out from oil bath, cooled down to r.t. and ^1H NMR spectra were measured. The result suggested that the copper catalyst did not decompose at 140 °C.

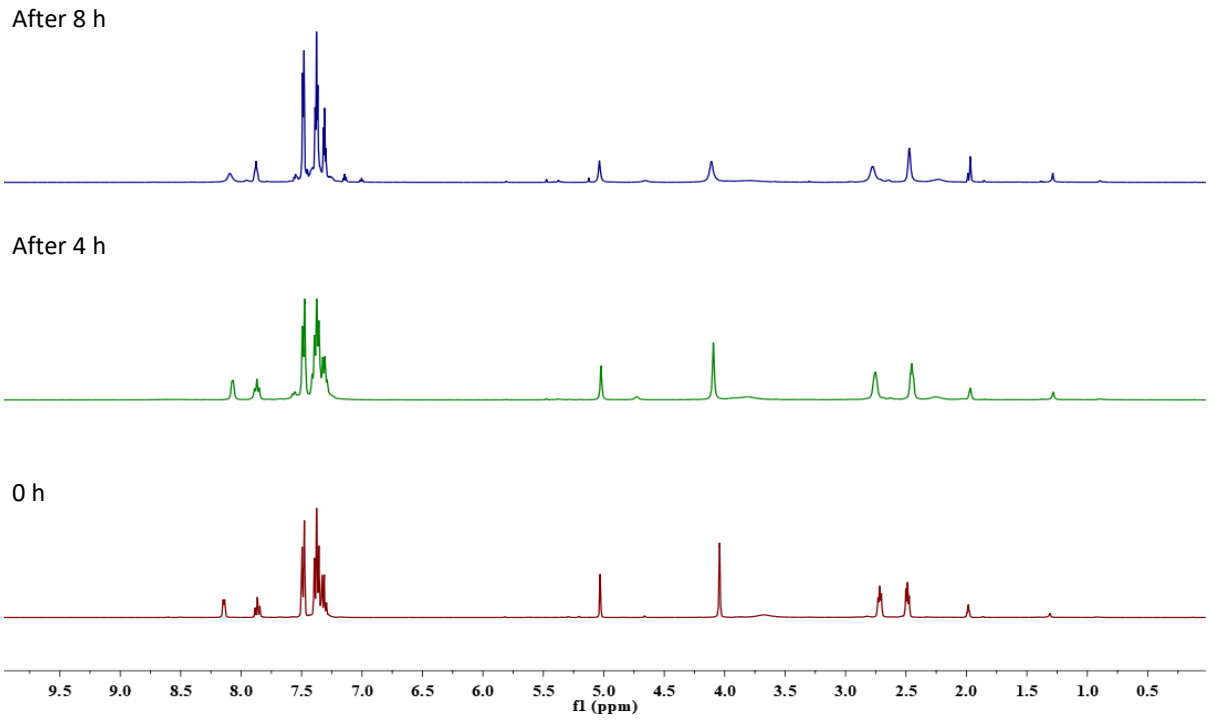


Figure S109. ^1H NMR (400 MHz, $CDCl_3$) of complex **1** (temperature stability test).

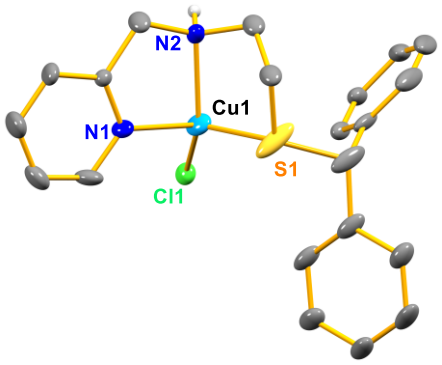
X-ray structure determination

Crystallographic data and structure determinations details are compiled in Table **S6**. The crystals were obtained by diffusion technique of **C₁** in MeCN and DEE at r.t. The crystals were coated with silicon oil on a glass slide and a suitable single crystal was mounted on a glass fibre. Crystal data were collected with a Rigaku Oxford diffractometer and with an INCOATEC micro source (Cu-Kα radiation, λ = 1.54184 Å, multilayer optics) at 100 K. The structure was determined using direct methods employed in ShelXT,[11] OleX,[12] and refinement was carried out using least-square minimization implemented in ShelXL.[13] All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were fixed geometrically in idealized positions and were refined using a riding model. CCDC 2362778 (for Complex **1**) contains the supplementary crystallographic data for this paper.

Table S1. Crystallographic Data and Refinement Parameters for Complex **1.**

	Complex **1**
Empirical formula	$C_{21}H_{22}ClCuN_2S$
CCDC	2362778
Formula weight (g mol^{-1})	433.45
Temperature (K)	100.00(10)
Wavelength (Å)	1.54184
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.56440(10)
b (Å)	9.69930(10)
c (Å)	23.7155(2)
α (deg)	90
β (deg)	90
γ (deg)	90
volume ($Å^3$)	1970.02(3)
Z	4
ρ_{calc} (g/cm^3)	1.461
μ (mm^{-1})	3.843
F(000)	896.0
Crystal Size	0.2 × 0.2 × 0.1 mm^3
2θ Range (deg)	7.456 to 136.492
Index Ranges	$-10 \le h \le 10$, $-11 \le k \le 11$, $-28 \le l \le 28$
Reflections collected	55581
Independent reflections (R_{int})	3620(0.0600)
Completeness to theta = 25.07^0	99.8
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/parameters	3620/0/233
Goodness-of-fit on *F*2	1.113
Final *R* indices [I>2σ(I)]	R_1 = 0.0537, wR_2 = 0.1294
R indices (all data)	R_1 = 0.0541, wR_2 = 0. 0.1298
Largest diff. peak/hole (e $Å^{-3}$)	0.87/-0.89
Flack parameter	0.024(8)

Figure S109. Molecular Structure of complex Complex **1** showing 30% Ellipsoids



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