Supporting Information

t-BuOK-catalysed alkylation of fluorene with alcohols: a highly green route to 9-monoalkylfluorene derivatives

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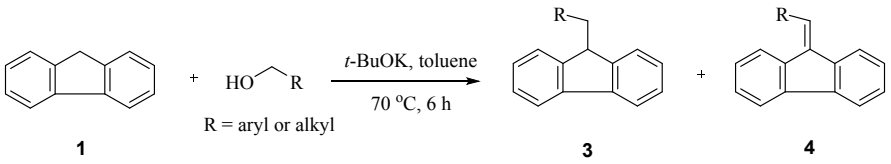
General remarks

All reactions were carried out under nitrogen atmosphere with oven-dried glassware. Toluene, THF and dioxane were distilled from sodium/benzophenone before use. Potassium carbonate, sodium hydroxide, potassium hydroxide, cesium hydroxide monohydrate, sodium tert-butoxide and potassium tert-butoxide were commercially available and used with finely-ground powder. Column chromatography was performed on silica gel (200–300 mesh). All yields were referred to isolated yields (average of two runs) of compounds estimated to be >95% pure as determined by ^{1}H NMR. All the products are characterized by MS, ^{1}H and ^{13}C NMR. The reaction was performed on WATTECS WP-TEC-1020 parallel reactor.

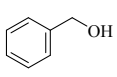
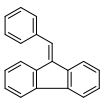
General procedure for *t*-BuOK-catalysed olefination of fluorene and alcohols

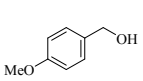
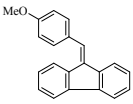
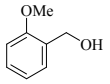
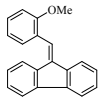
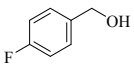
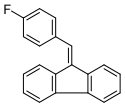
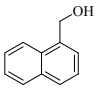
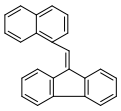
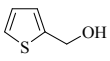
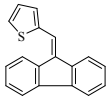
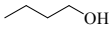
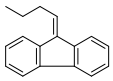
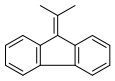
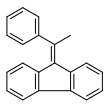
An oven-dried 25-mL flask was charged with *t*-BuOK (0.5 mmol), then the fluorene (0.5 mmol) and the alcohol (1.5 mmol) (if solid) were added. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. Dried toluene (4 mL) and the alcohol (1.5 mmol) (if liquid) were added via syringe at this time. The reaction mixture was performed on WATTECS WP-TEC-1020 parallel reactor of 70 ℃ for 6 h and then allowed to cool to room temperature; it was then filtered through a silica-gel pad that was washed with ethyl acetate. The combined organic phases were evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give the desired products.

Table S1. Base-catalyzed olefination of fluorene and alcohols[a]



1 **3** **4**

Entry	Alcohol	Product	**1** (%)[b]	**3** (%)[b]	**4** (%)[c]
1	 **2a**	 **4a**	25	3	63

2	 **2c**	 **4c**	12	3	81
3	 **2e**	 **4e**	26	trace	68
4	 **2g**	 **4g**	38	trace	57
5	 **2l**	 **4l**	10	3	84
6	 **2m**	 **4m**	44	trace	54
7	 **2o**	 **4o**	52	10	30
8	 **2q**	 **4q**	90	0	9
9	 **2r**	 **4r**	99	0	0

[a] Reaction conditions: fluorene (0.5 mmol), alcohols (1.5 mmol), *t*-BuOK (0.5 mmol), toluene (4 mL), in N_2. [b] NMR yields: determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yields.

General procedure for *t*-BuOK-catalysed alkylation of fluorene with alcohols

An oven-dried 25-mL flask was charged with *t*-BuOK (0.25 mmol), then the fluorene (0.5 mmol) and the alcohol (1.5 mmol) (if solid) were added. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. Dried toluene (4 mL) and the alcohol (1.5 mmol) (if liquid) were added via syringe at this time. The reaction mixture was performed on WATTECS WP-TEC-1020 parallel

reactor of 120 ℃ for 3 h and then allowed to cool to room temperature; it was then filtered through a silica-gel pad that was washed with ethyl acetate. The combined organic phases were evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give the desired products.

Characterization data of the products

9-benzyl-9H-fluorene[2], 3a (Table 2, entry 1). Yield: 98%. White solid, mp 133–134 ^{0}C (lit.[2] 132–134 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.45–6.96 (m, 11H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.11 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.8, 140.8, 139.8, 129.5, 128.3, 127.1, 126.7, 126.4, 124.9, 119.8, 48.7, 40.1; MS (EI, m/z, rel.%): 256 (M^+, 32%), 165 (M^+-91, 100%).

9-(4-methylbenzyl)-9H-fluorene[3], 3b (Table 2, entry 2). Yield: 99%. White solid, mp 136–137 ^{0}C (lit.[3] 137–138 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.25–7.17 (m, 4H), 7.12 (s, 4H), 4.20 (t, *J* = 7.6 Hz, 1H), 3.06 (d, *J* = 7.6 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.96, 140.82, 136.73, 135.80, 129.37, 128.98, 127.05, 126.62, 124.87, 119.78, 48.80, 39.67, 21.13; MS (EI, m/z, rel.%): 270 (M^+, 52%), 165 (M^+-105, 100%), 105 (M^+-165, 50%).

9-(4-methoxybenzyl)-9H-fluorene[4], 3c (Table 2, entry 3). Yield: 96%. White solid, mp 110–112 ^{0}C (lit.[4] 112 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.25–7.17 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.18 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.05 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.2, 146.9, 140.8, 131.9, 130.4, 127.1, 126.6, 124.9, 119.8, 113.7, 55.3, 48.9, 39.2; MS (EI, m/z, rel.%): 286 (M^+, 16%), 165 (M^+-121, 12%), 121 (M^+-165, 100%).

9-(3-methoxybenzyl)-9H-fluorene[2], 3d (Table 2, entry 4). Yield: 99%. White solid, mp 133–134 ^{0}C (lit.[2] 132–134 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.39–7.0 (m, 2H), 7.26–7.17 (m, 5H), 6.86–6.77 (m, 2H), 6.75 (s, 1H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.05 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.55, 146.79, 141.38, 140.85, 129.22, 127.13, 126.68, 124.87, 121.99, 119.82, 114.92, 112.04, 55.18, 48.59, 40.10; MS (EI, m/z, rel.%): 286 (M^+, 68%), 165

(M^+-121, 50%), 121 (M^+-165, 100%), 91 (M^+-195, 18%).

9-(2-methoxybenzyl)-9H-fluorene[5], 3e (Table 2, entry 5). Yield: 95%. White solid, mp 70–72 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, J = 7.5 Hz, 2H), 7.33–7.24 (m, 3H), 7.20–7.14 (m, 4H), 7.03 (d, J = 7.2 Hz, 1H), 6.92–6.86 (m, 2H), 4.34 (t, J = 7.5 Hz, 1H), 3.83 (s, 3H), 3.05 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.2, 147.9, 140.9, 131.7, 128.8, 127.9, 127.0, 126.7, 125.2, 120.4, 119.9, 110.5, 55.4, 46.9, 35.7; MS (EI, m/z, rel.%): 286 (M^+, 50%), 165 (M^+-121, 38%), 121 (M^+-165, 100%), 91 (M^+-195, 15%).

9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene, 3f (Table 2, entry 6). Yield: 99%. White solid, mp 184–185 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.36–7.31 (m, 3H), 7.27 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 4.1 Hz, 4H), 4.24 (t, J = 7.5 Hz, 1H), 3.13 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 140.94, 140.92, 139.2, 139.0, 130.0, 128.8, 127.2, 127.01, 126.96, 126.7, 124.9, 119.9, 48.7, 39.8; MS (EI, m/z, rel.%): 332 (M^+, 18%), 167 (M^+-165, 100%), 165 (M^+-167, 28%); HRMS (EI) calcd for $C_{26}H_{20}$ (M^+): 332.1569, Found: 332.1565.

9-(4-fluorobenzyl)-9H-fluorene[5], 3g (Table 2, entry 7). Yield: 99%. White solid, mp 131–132 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.22–7.15 (m, 4H), 7.09–7.06 (m, 2H), 6.94–6.90 (m, 2H), 4.15 (t, J = 7.2 Hz, 1H), 3.07 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.6 (d, $J_{C\text{-}F}$ = 242.7 Hz), 146.6, 140.9, 135.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 127.3, 126.7, 124.8, 119.9, 115.0 (d, $J_{C\text{-}F}$ = 21.1 Hz), 48.8, 39.2; ^{19}F NMR ($CDCl_3$, 565 MHz): δ -116.83; MS (EI, m/z, rel.%): 274 (M^+, 25%), 165 (M^+-109, 100%), 109 (M^+-165, 8%).

9-(4-chlorobenzyl)-9H-fluorene[6], 3h (Table 2, entry 8). Yield: 99%. White solid, mp 149–150 ^{0}C (lit.[6] 150–151 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.25–7.16 (m, 6H), 7.07 (d, J = 8.2 Hz, 2H), 4.18 (t, J = 7.3 Hz, 1H), 3.09 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.8, 140.8, 139.8, 129.5, 128.3, 127.1, 126.7, 126.4, 124.9, 119.8, 48.7, 40.1; MS (EI, m/z, rel.%): 292 ($[M+2]^+$, 5%), 290 (M^+, 18%), 165 (M^+-125, 100%).

9-(4-bromobenzyl)-9H-fluorene[7], 3i (Table 2, entry 9). Yield: 99%. White solid, mp 150–151 ^{0}C (lit.[7] 151 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.39–7.33 (m, 4H), 7.25–7.19 (m, 4H), 7.03 (d, *J* = 8.2 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 1H), 3.09 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.4, 140.9, 138.5, 131.3, 131.2, 127.3, 126.7, 124.7, 120.2, 119.9, 48.4, 39.3; MS (EI, m/z, rel.%): 336 ($[M+2]^+$, 13%), 334 (M^+, 12%), 165 (M^+-169, 100%).

9-(4-iodobenzyl)-9H-fluorene, 3j (Table 2, entry 10). Yield: 99%. White solid, mp 154–155 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.25–7.19 (m, 4H), 6.92 (d, *J* = 8.1 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 1H), 3.07 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.4, 140.9, 139.2, 137.2, 131.6, 127.2, 126.7, 124.7, 119.9, 48.4, 39.4; MS (EI, m/z, rel.%): 382 (M^+, 25%), 217 (M^+-165, 15%), 165 (M^+-217, 100%); HRMS (EI) calcd for $C_{20}H_{15}I$ (M^+): 382.0219, Found: 382.0215.

9-(naphthalen-2-ylmethyl)-9H-fluorene[6], 3k (Table 2, entry 11). Yield: 99%. White solid, mp 163–164 ^{0}C (lit.[6] 164 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87–7.78 (m, 2H), 7.76–7.72 (m, 3H), 7.62 (s, 1H), 7.48–7.43 (m, 3H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.22–7.14 (m, 4H), 4.33 (t, *J* = 7.6 Hz, 1H), 3.25 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 140.9, 137.5, 133.5, 132.3, 128.03, 127.95, 127.9, 127.70, 127.69, 127.2, 126.7, 126.0, 125.4, 124.9, 119.9, 48.6, 40.4; MS (EI, m/z, rel.%): 306 (M^+, 45%), 165 (M^+-141, 50%), 141 (M^+-165, 100%).

9-(naphthalen-1-ylmethyl)-9H-fluorene[6], 3l (Table 2, entry 12). Yield: 99%. White solid, mp 132–133 ^{0}C (lit.[6] 133–134 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.55–7.47 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 4.37 (t, *J* = 7.8 Hz, 1H), 3.43 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.2, 140.9, 136.1, 134.2, 132.2, 129.2, 128.4, 127.6, 127.3, 126.8, 126.2, 125.8, 125.5, 125.3, 123.9, 119.9, 47.7, 38.1; MS (EI, m/z, rel.%): 306 (M^+, 40%), 165 (M^+-141, 40%), 141 (M^+-165, 100%).

2-((9H-fluoren-9-yl)methyl)thiophene[5]**, 3m** (Table 2, entry 13). Yield: 97%. White solid, mp 97–98 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.29–7.22 (m, 4H), 7.11 (d, *J* = 5.1 Hz, 1H), 6.87 (t, *J* = 4.0 Hz, 1H), 6.70 (d, *J* = 2.8 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 3.38 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.8, 140.8, 139.8, 129.5, 128.3, 127.1, 126.7, 126.4, 124.9, 119.8, 48.7, 40.1; MS (EI, m/z, rel.%): 264 ($[M+2]^+$, 2%), 263 ($[M+1]^+$, 10%), 262 (M^+, 40%), 165 (M^+-97, 100%), 97 (M^+-165, 30%).

9-octyl-9H-fluorene[8]**, 3n** (Table 2, entry 14). Yield: 99%. White solid, mp 41–42 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.36–7.27 (m, 4H), 3.95 (t, *J* = 5.8 Hz, 1H), 2.00–1.97 (m, 2H), 1.24–1.20 (m, 12H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.7, 141.2, 126.9, 126.8, 124.4, 119.8, 48.6, 33.2, 31.9, 30.0, 29.4, 29.3, 25.8, 22.7, 14.1; MS (EI, m/z, rel.%): 278 (M^+, 84%), 179 (M^+-99, 17%), 165 (M^+-113, 100%).

9-butyl-9H-fluorene[9]**, 3o** (Table 2, entry 15). Yield: 99%. Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.35–7.26 (m, 4H), 3.95 (t, *J* = 5.8 Hz, 1H), 2.01–1.95 (m, 2H), 1.31–1.22 (m, 2H), 1.18–1.12 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.7, 141.2, 126.9, 126.8, 124.4, 119.8, 47.5, 32.9, 27.9, 23.1, 13.9; MS (EI, m/z, rel.%): 222 (M^+, 35%), 165 (M^+-57, 100%).

9-(2-ethylhexyl)-9H-fluorene[10]**, 3p** (Table 2, entry 16). Yield: 99%. Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 3.97 (t, *J* = 6.2 Hz, 1H), 1.77–1.71 (m, 3H), 1.45–1.25 (m, 8H), 0.90–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 148.3, 140.89, 140.86, 126.83, 126.76, 126.75, 124.7, 124.6, 119.8, 45.4, 38.3, 36.7, 32.9, 28.5, 25.9, 23.2, 14.2, 10.5; MS (EI, m/z, rel.%): 278 (M^+, 98%), 179 (M^+-99, 58%), 166 (M^+-112, 65%), 165 (M^+-113, 30%).

9-isopropyl-9H-fluorene[11]**, 3q** (Table 2, entry 17). Yield: 89%. White solid, mp 53–55 ^{0}C (lit.[11] 54–55 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 3.92 (d, *J* = 3.0 Hz, 1H), 2.61–2.53 (m, 1H), 0.85 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 146.3, 141.7, 126.9, 126.6, 124.8, 119.6, 53.8, 32.2, 19.1; MS (EI, m/z, rel.%): 208 (M^+, 35%), 165 (M^+-43, 100%).

9-(1-phenylethyl)-9H-fluorene[12]**, 3r** (Table 2, entry 18). Yield: 90%. White solid, mp 88–89 ^{0}C (lit.[12] 88–91 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.40–7.19 (m, 8H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.27 (d, *J* = 4.2 Hz, 1H), 3.70–3.60 (m, 1H), 0.91 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 144.68, 144.65, 141.9, 141.5, 128.24, 128.15, 127.2, 127.1, 126.9, 126.4, 126.3, 125.7, 124.4, 119.8, 119.7, 54.3, 42.0, 14.0; MS (EI, m/z, rel.%): 270 (M^+, 20%), 165 (M^+-105, 50%), 105 (M^+-165, 100%).

2-bromo-9-(4-methoxybenzyl)-9H-fluorene[4]**, 3s** (Table 2, entry 19). Yield: 99%. White solid, mp 121–122 ^{0}C (lit.[4] 122 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.14 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.06 (dd, *J* = 13.8, 7.3 Hz, 1H), 3.00 (dd, *J* = 13.8, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 148.9, 146.5, 139.9, 139.8, 131.2, 130.4, 130.2, 128.2, 127.3, 127.0, 124.9, 121.1, 120.4, 119.9, 113.7, 55.3, 48.9, 38.9; MS (EI, m/z, rel.%): 366 ($[M+2]^+$, 4%), 364 (M^+, 5%), 121 (M^+-243, 100%).

9-(4-(trifluoromethyl)benzyl)-9H-fluorene, 3t (Table 2, entry 20). Yield: 85%. White solid, mp 141–142 ^{0}C . ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.27–7.12 (m, 6H), 4.20 (t, *J* = 7.2 Hz, 1H), 3.15 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 143.7, 140.92, 129.8, 127.4, 126.8, 125.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.7, 120.0, 48.3, 39.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.00; MS (EI, m/z, rel.%): 324 (M^+, 46%), 165 (M^+-159, 100%), 159 (M^+-165, 4%).

5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole, 3u (Table 2, entry 21). Yield: 99%. White solid, mp 106–107 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.34–7.24 (m, 2H), 7.23–7.12 (m, 4H), 6.67 (d, *J* = 7.1 Hz, 2H), 6.56 (d, *J* = 7.9 Hz, 1H), 5.84 (s, 2H), 4.08 (t, *J* = 7.5 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.8, 146.2, 141.0, 133.7, 127.3, 126.8, 125.0, 122.7,

120.0, 109.8, 108.1, 100.9, 48.9, 39.8; MS (EI, m/z, rel.%): 300 (M^+, 51%), 165 (M^+-135, 49%), 135 (M^+-165, 100%), 77 (M^+-223, 35%).

9-cyclohexyl-9H-fluorene[18]**, 3v** (Table 2, entry 22). Yield: 81%. White solid, mp 113–114 ^{0}C (lit.[18] 113–116 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 3.87 (d, *J* = 1.9 Hz, 1H), 2.15 (td, *J* = 11.7, 2.7 Hz, 1H), 1.63 (t, *J* = 14.8 Hz, 3H), 1.45 (d, *J* = 12.2 Hz, 2H), 1.26–1.02 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 141.7, 126.8, 126.6, 124.9, 119.6, 53.6, 43.2, 29.7, 27.0, 26.5; MS (EI, m/z, rel.%): 248 (M^+, 75%), 166 (M^+-82, 100%), 165 (M^+-83, 89%), 83 (M^+-165, 34%), 55 (M^+-193, 48%).

9-benzylidene-9H-fluorene[13]**, 4a** (Table S1, entry 1). Yield: 63%. Yellow solid, mp 75–76 ^{0}C (lit.[13] 75–76 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.71–7.68 (m, 3H), 7.58–7.54 (m, 3H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.39–7.27 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 139.6, 139.3, 136.9, 136.62, 136.57, 129.3, 128.6, 128.2, 128.1, 127.3, 127.0, 126.7, 124.5, 120.3, 119.7, 119.6; MS (EI, m/z, rel.%): 256 ($[M+2]^+$, 5%), 255($[M+1]^+$, 15%), 254 (M^+, 90%), 253 (M^+-1, 100%), 252 (M^+-2, 70%).

9-(4-methoxybenzylidene)-9H-fluorene[13]**, 4c** (Table S1, entry 2). Yield: 81%. Yellow solid, mp 132–134 ^{0}C (lit.[13] 133–134 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.1 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 3H), 7.66 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.39–7.30 (m, 3H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6, 141.1, 139.7, 139.0, 136.7, 135.5, 130.9, 129.1, 128.3, 127.9, 127.4, 126.9, 126.6, 124.2, 120.1, 119.7, 119.6, 114.0, 55.4; MS (EI, m/z, rel.%): 284 (M^+, 100%), 269 (M^+-15, 20%), 253 (M^+-31, 20%), 239 (M^+-45, 40%).

9-(2-methoxybenzylidene)-9H-fluorene[14]**, 4e** (Table S1, entry 3). Yield: 68%. Yellow solid, mp 65–66 ^{0}C (lit.[14] 66 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 6.8 Hz, 1H), 7.68 (d, *J* = 4.4 Hz, 2H), 7.66 (s, 1H), 7.62 (t, *J* = 7.0 Hz, 2H), 7.36–7.24 (m, 4H), 7.05–7.01 (m, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.8, 141.3, 139.8, 139.2, 136.9, 136.2, 131.3,

130.0, 128.4, 128.0, 127.0, 126.6, 125.6, 124.4, 124.1, 120.6, 120.4, 119.7, 119.6, 110.9, 55.6; MS (EI, m/z, rel.%): 284 (M^+, 80%), 239 (M^+-45, 35%), 178 (M^+-106, 100%).

9-(4-fluorobenzylidene)-9H-fluorene[15]**, 4g** (Table S1, entry 4). Yield: 57%. Yellow solid, mp 121–122 ^{0}C (lit.[15] 120–121 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 7.4 Hz, 2H), 7.58 (s, 1H), 7.53–7.58 (m, 3H), 7.38–7.27 (m, 3H), 7.14–7.10 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.5 (d, J_{C-F} = 246.5 Hz), 141.4, 139.4, 139.2, 136.8, 136.4, 132.9 (d, J_{C-F} = 3.5 Hz), 131.1 (d, J_{C-F} = 8.0 Hz), 128.7, 128.4, 127.1, 126.8, 126.0, 124.3, 120.3, 119.9, 119.7, 115.6 (d, J_{C-F} = 21.5 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz): δ -113.17; MS (EI, m/z, rel.%): 272 (M^+, 90%), 271 (M^+-1, 100%), 135 (M^+-137, 10%).

9-(naphthalen-1-ylmethylene)-9H-fluorene[16]**, 4l** (Table S1, entry 5). Yield: 84%. Yellow solid, mp 99–100 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, J = 8.3 Hz, 2H), 7.93–7.89 (m, 3H), 7.74–7.67 (m, 3H), 7.55–7.50 (m, 2H), 7.47–7.34 (m, 3H), 7.25–7.21 (m, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 139.5, 139.3, 138.07, 136.8, 134.4, 133.7, 131.7, 128.58, 128.55, 128.52, 128.4, 127.2, 127.1, 126.8, 126.4, 126.3, 125.5, 125.4, 125.2, 124.8, 120.5, 119.73, 119.68; MS (EI, m/z, rel.%): 305 ($[M+1]^+$, 20%), 304 (M^+, 100%), 303 (M^+-1, 95%).

2-((9H-fluoren-9-ylidene)methyl)thiophene[17]**, 4m** (Table S1, entry 6). Yield: 54%. Yellow solid, mp 73–74 ^{0}C (lit.[17] 73–75 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 14.4, 7.3 Hz, 3H), 7.60 (s, 1H), 7.45–7.42 (m, 2H), 7.37–7.27 (m, 3H), 7.19–7.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 139.6, 139.2, 139.0, 136.7, 136.2, 129.3, 128.8, 128.3, 127.6, 127.4, 127.0, 126.9, 124.4, 120.2, 119.8, 119.6, 119.0; MS (EI, m/z, rel.%): 262 ($[M+2]^+$, 8%), 261 ($[M+1]^+$, 20%), 260 (M^+, 85%), 259 (M^+-1, 100%).

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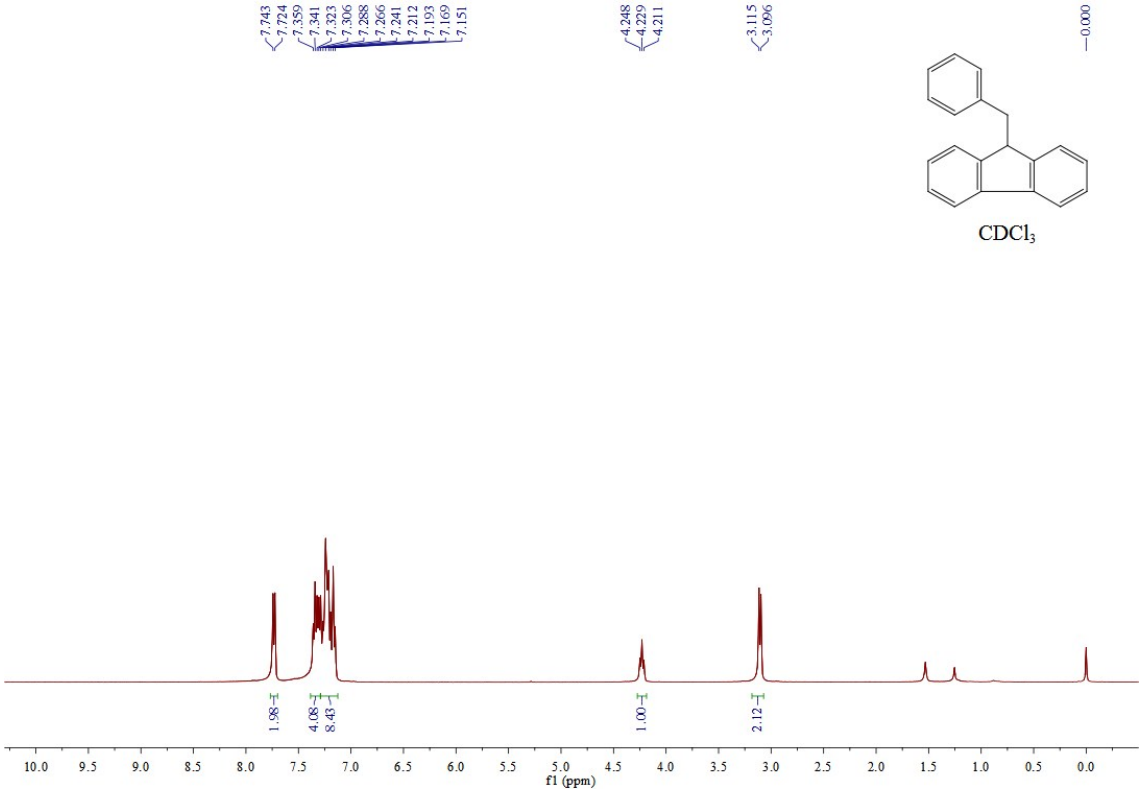
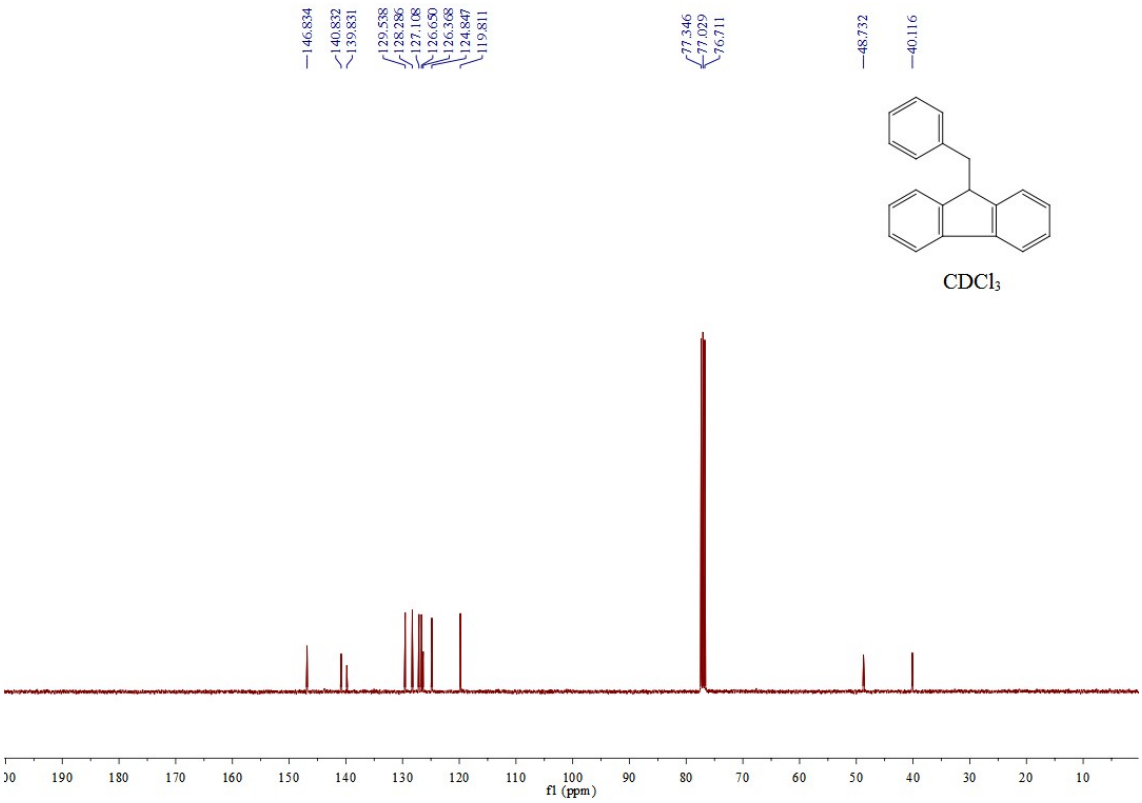
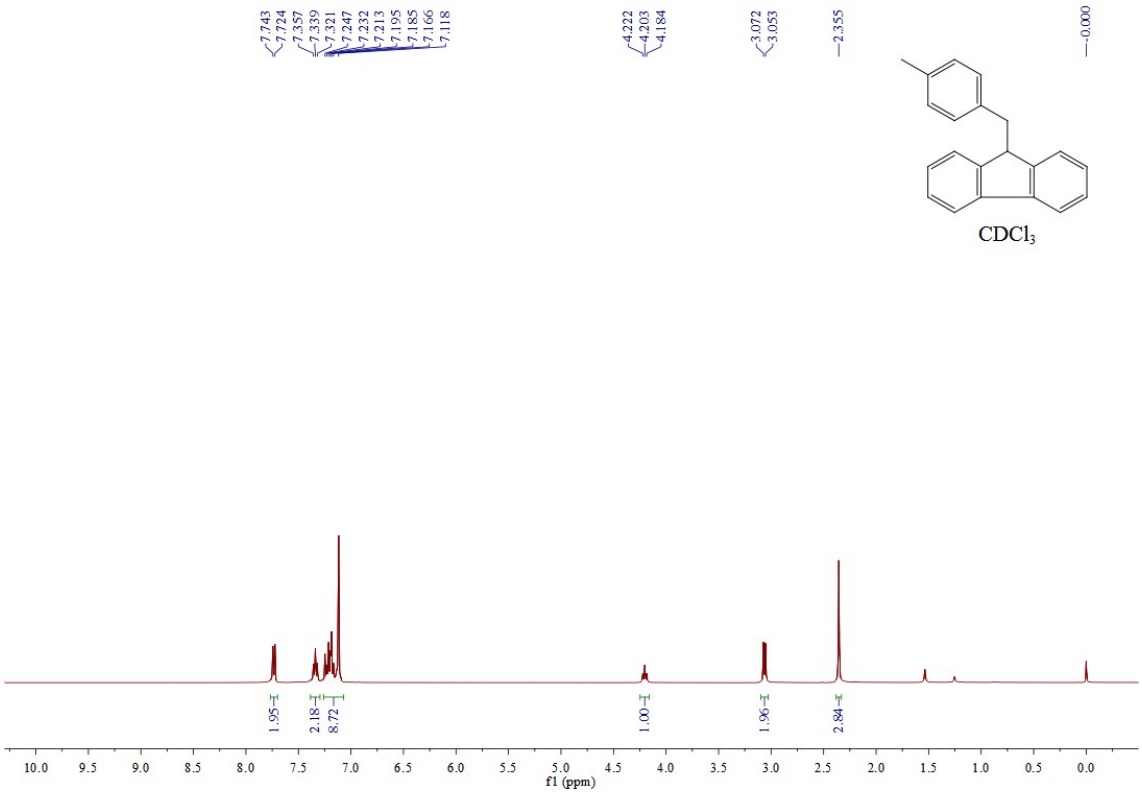
^{1}H NMR and ^{13}C NMR spectra of the products

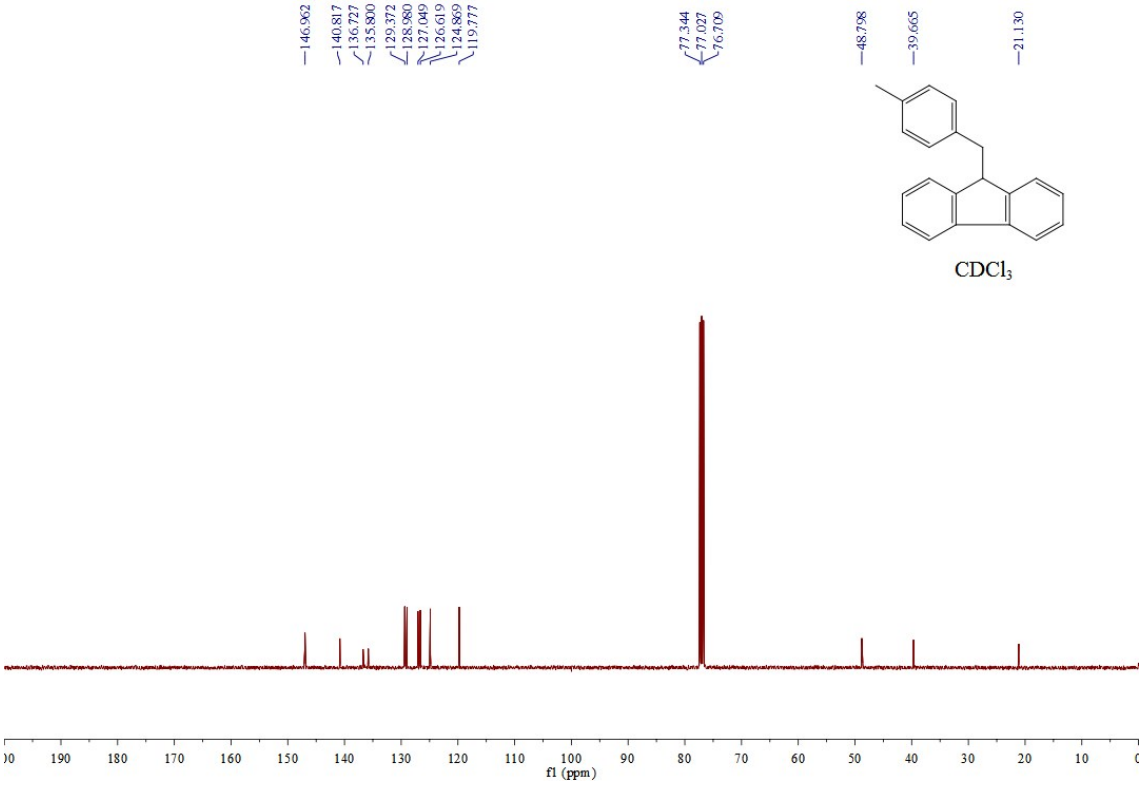
9-**benzyl-9H-fluorene, 3a** (Table 2, entry 1).



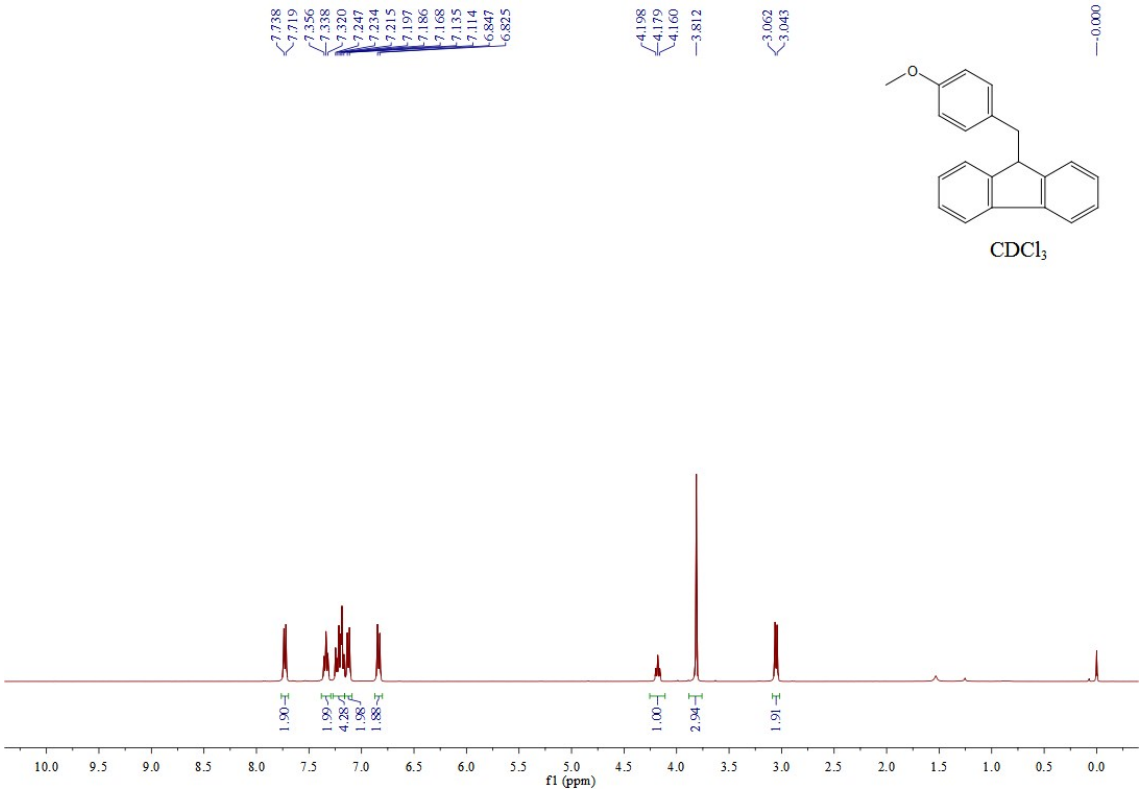


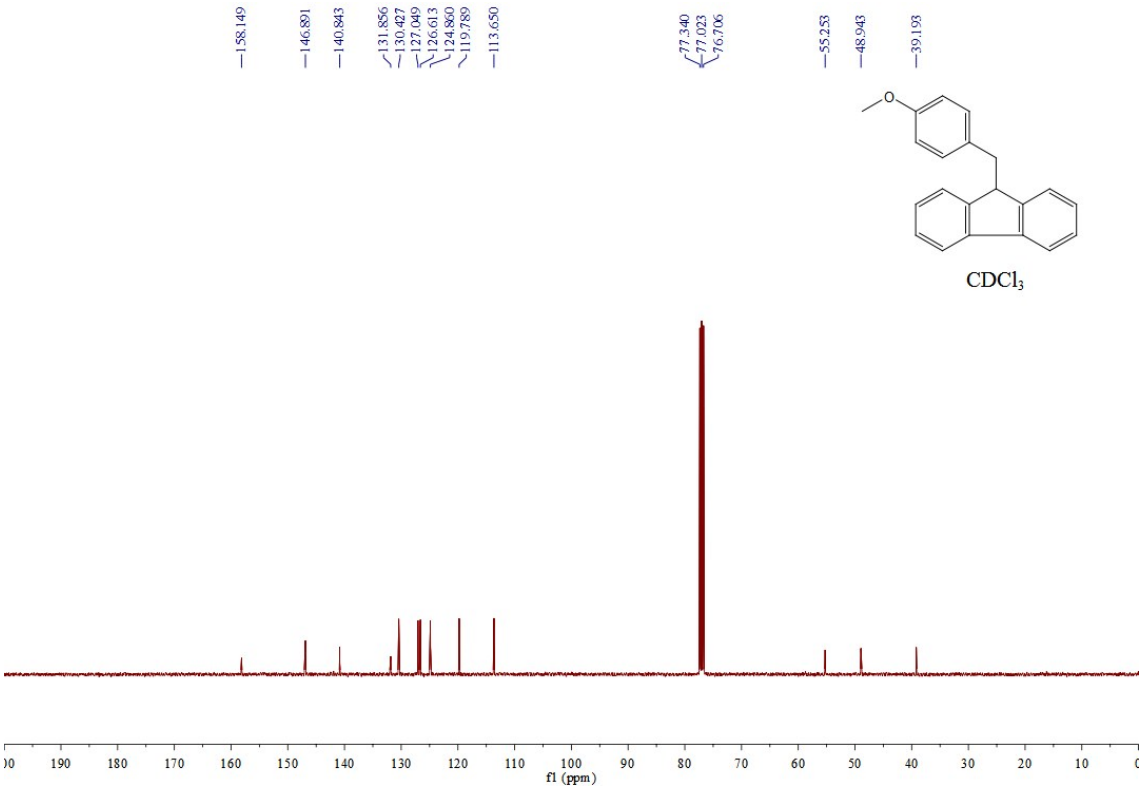
9-(4-methylbenzyl)-9H-fluorene, 3b (Table 2, entry 2).



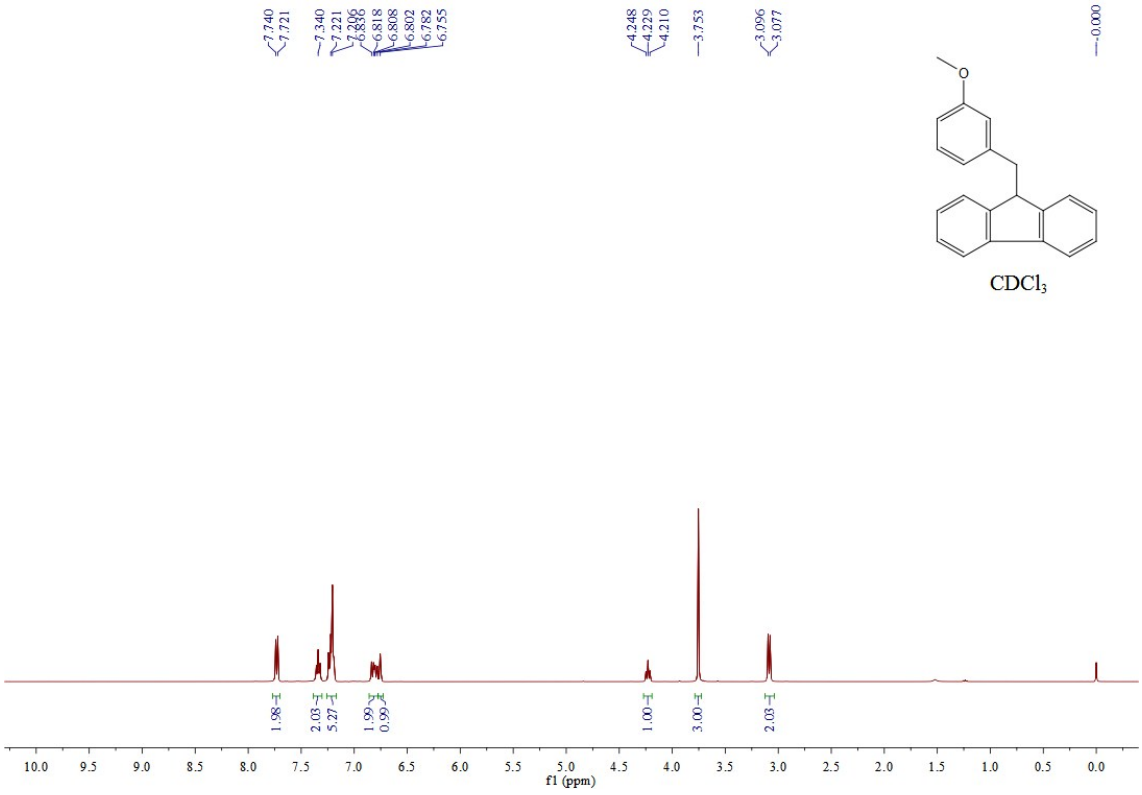


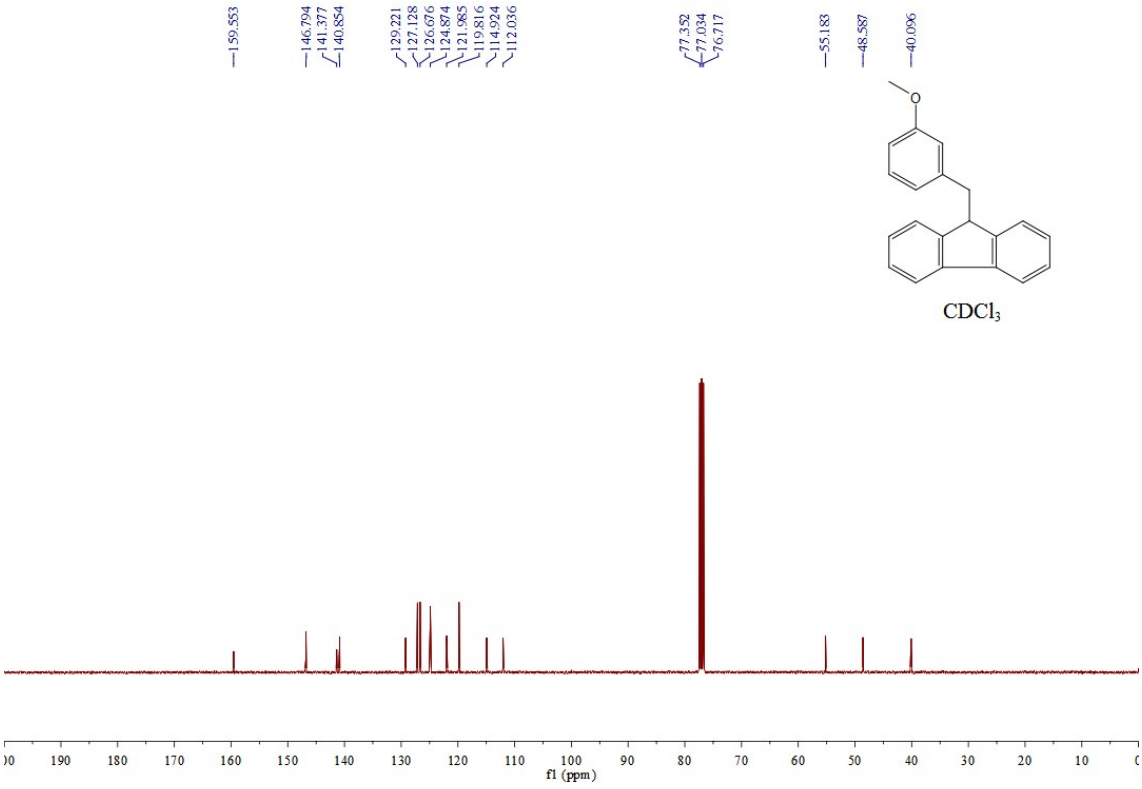
9-(4-methoxybenzyl)-9H-fluorene, 3c (Table 2, entry 3).



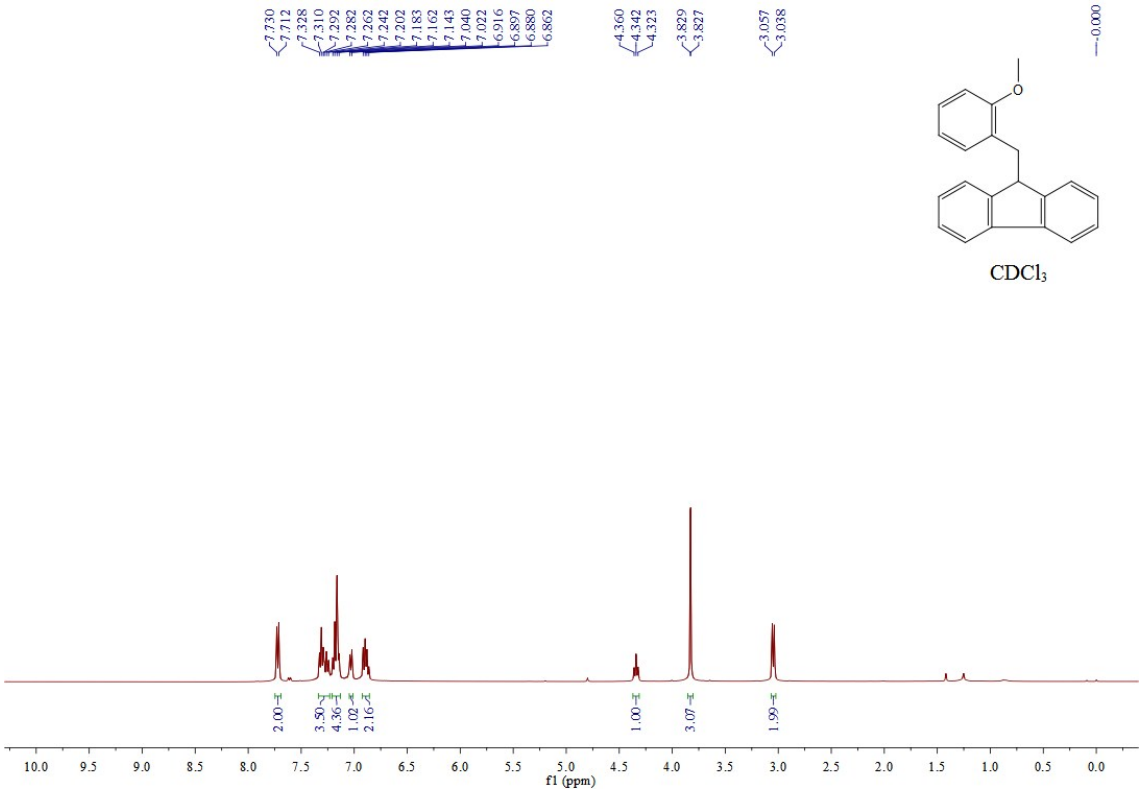


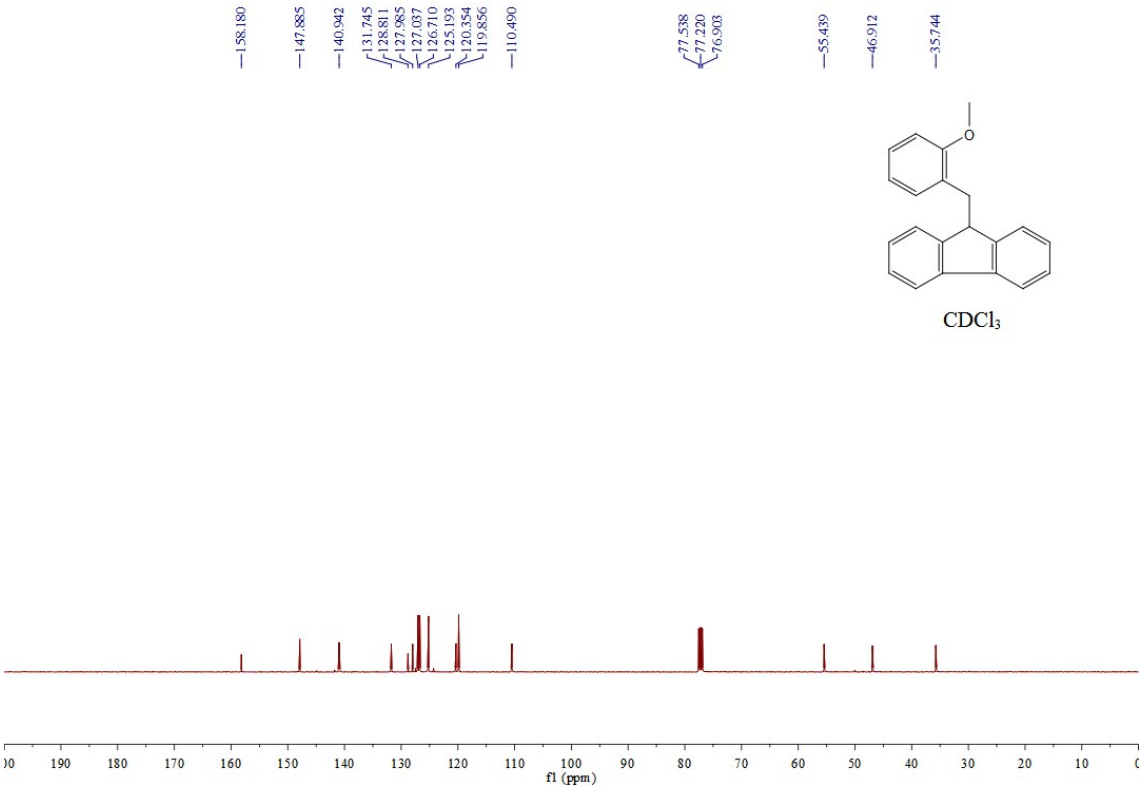
9-(3-methoxybenzyl)-9H-fluorene, 3d (Table 2, entry 4).



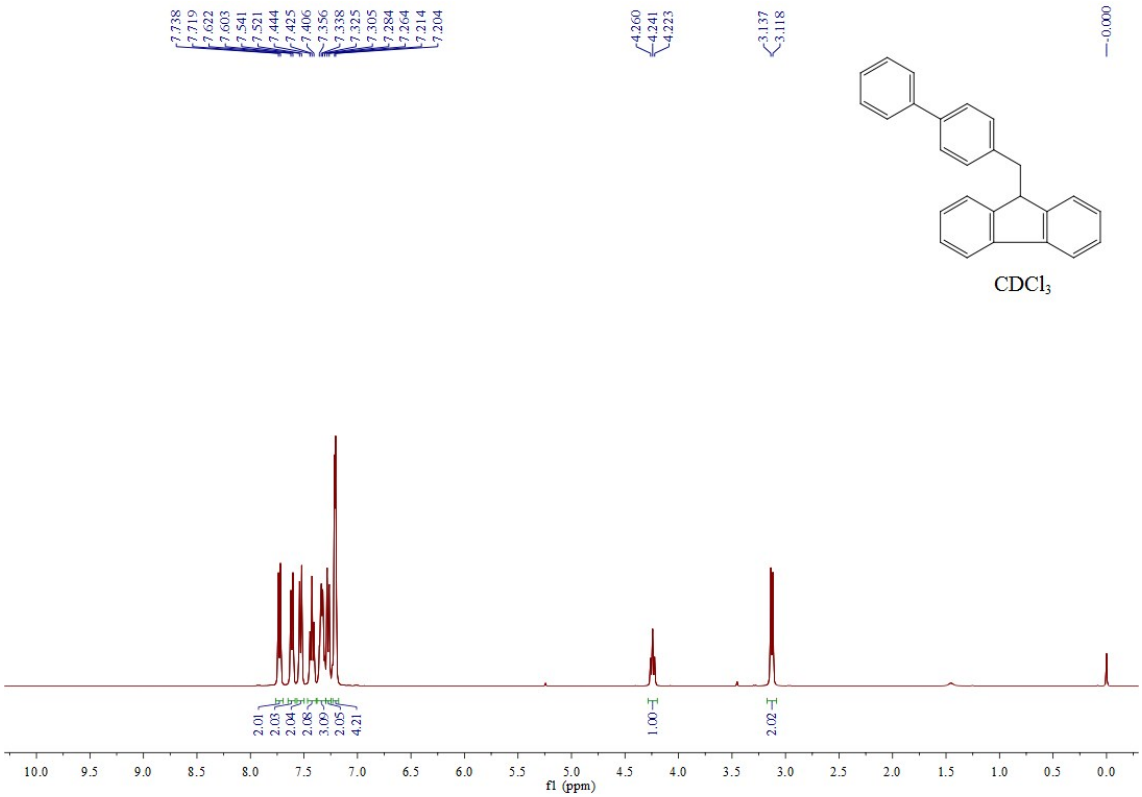


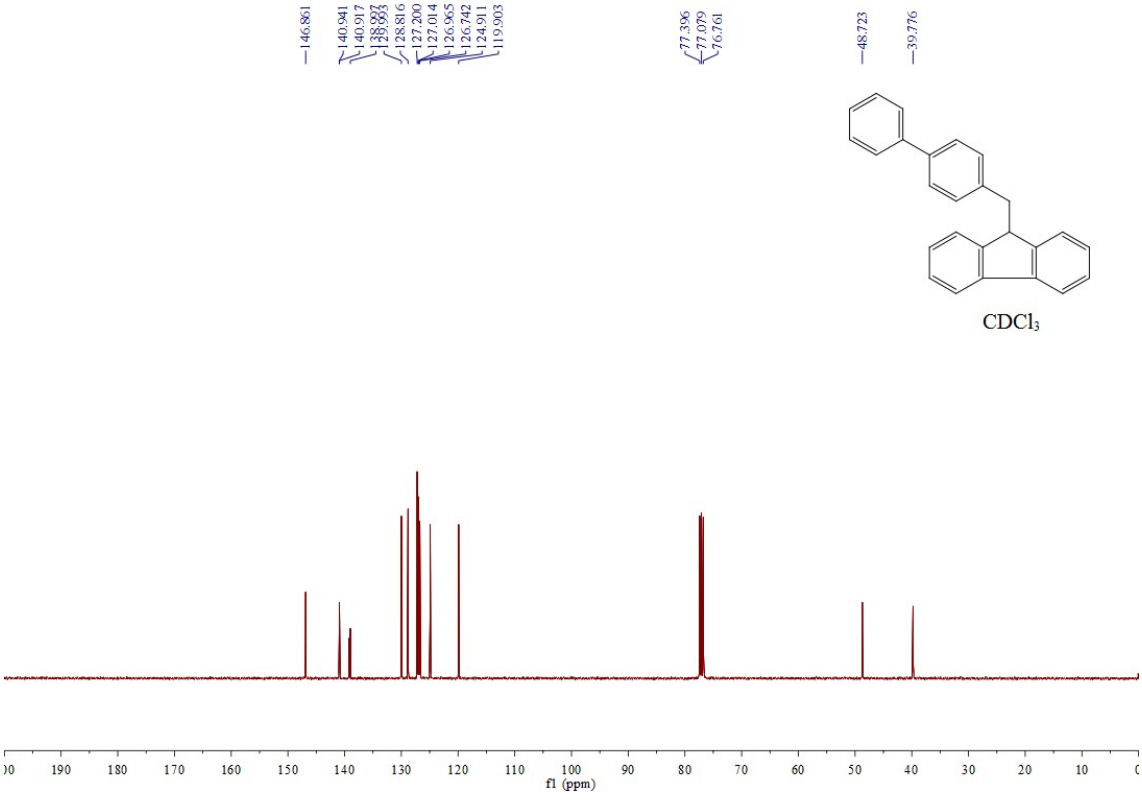
9-(2-methoxybenzyl)-9H-fluorene, 3e (Table 2, entry 5).



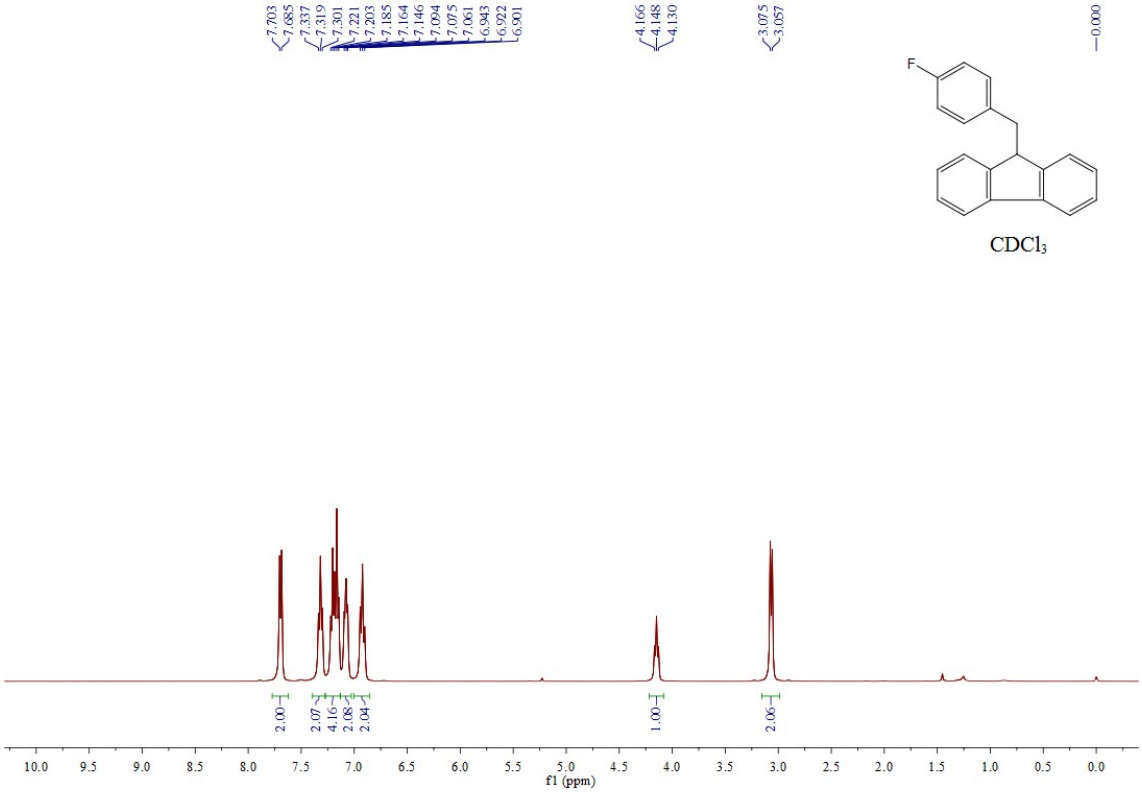


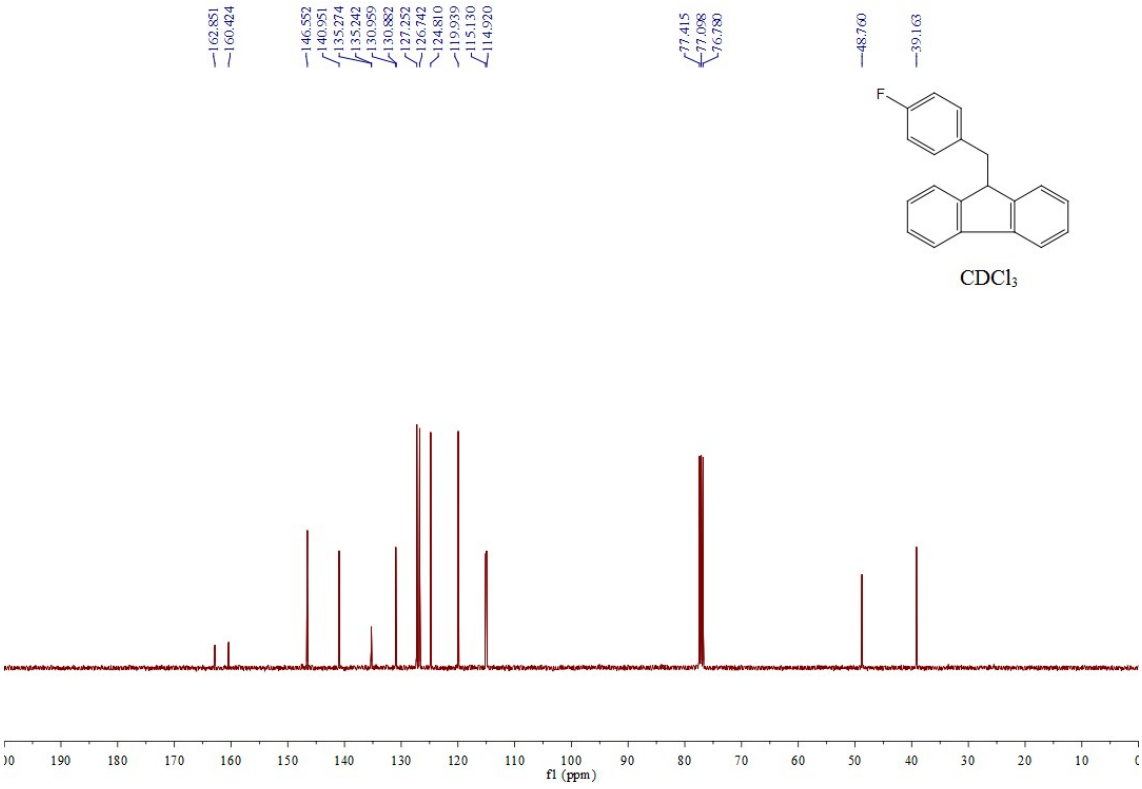
9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene, 3f (Table 2, entry 6).



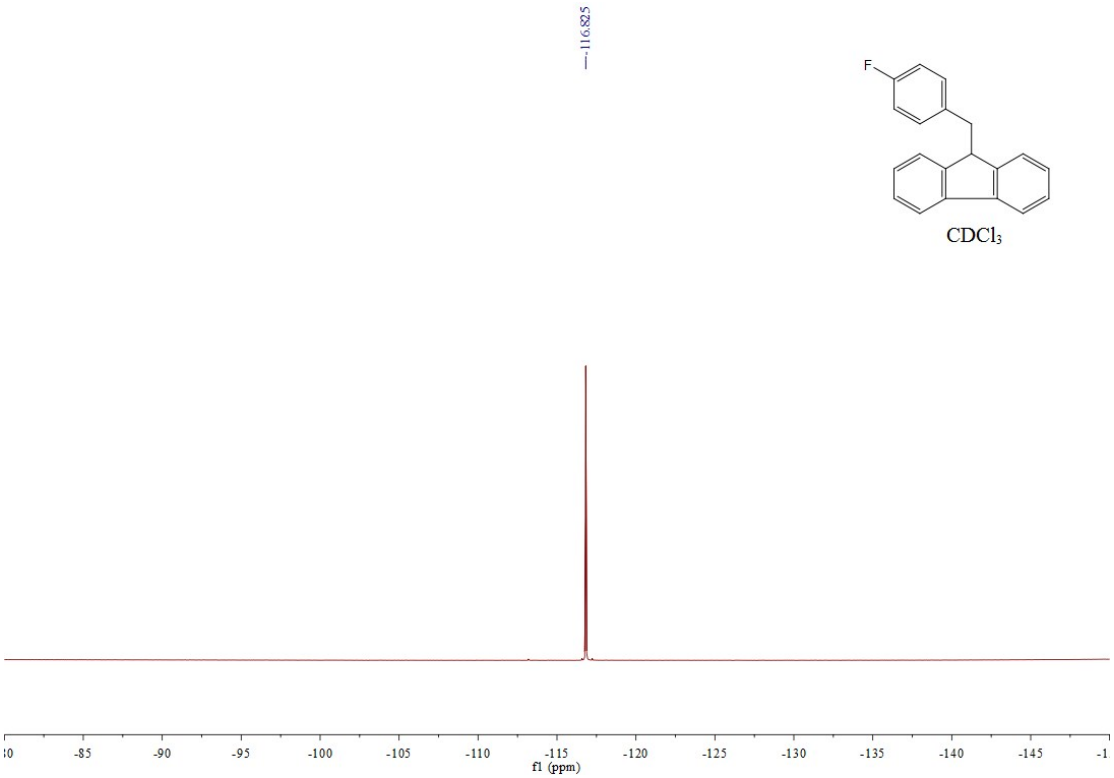


9-(4-fluorobenzyl)-9H-fluorene, 3g (Table 2, entry 7).

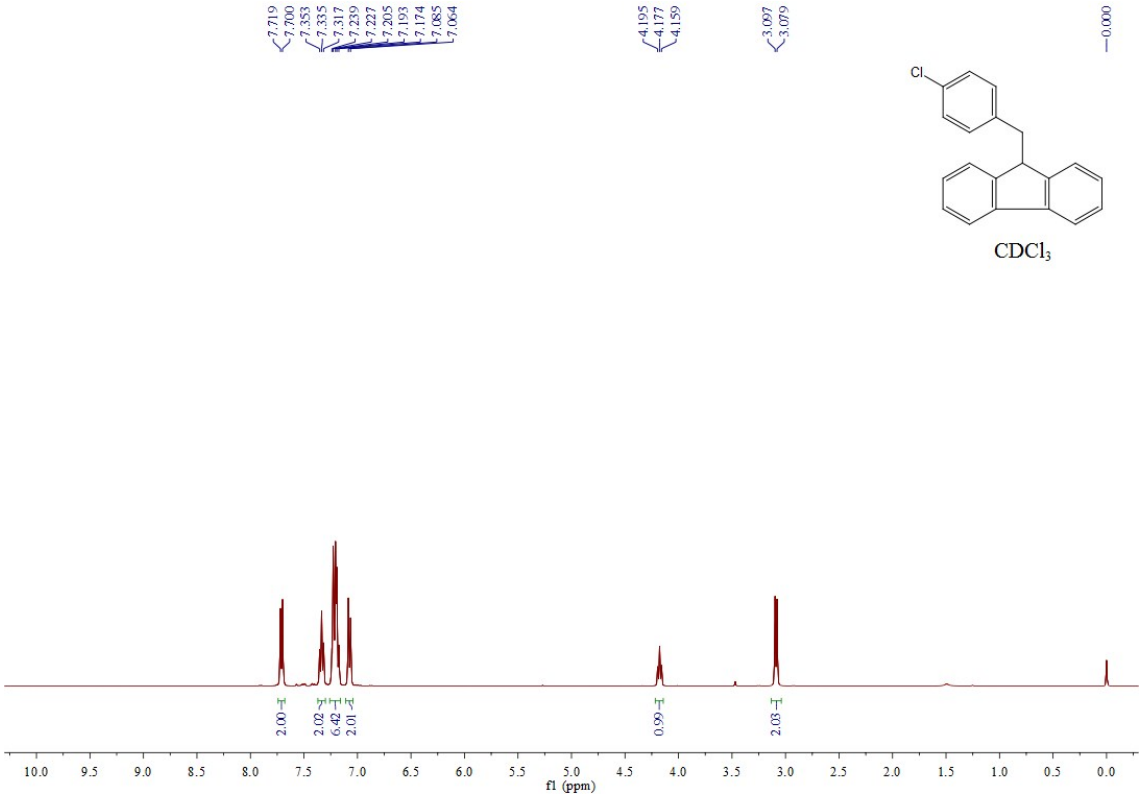


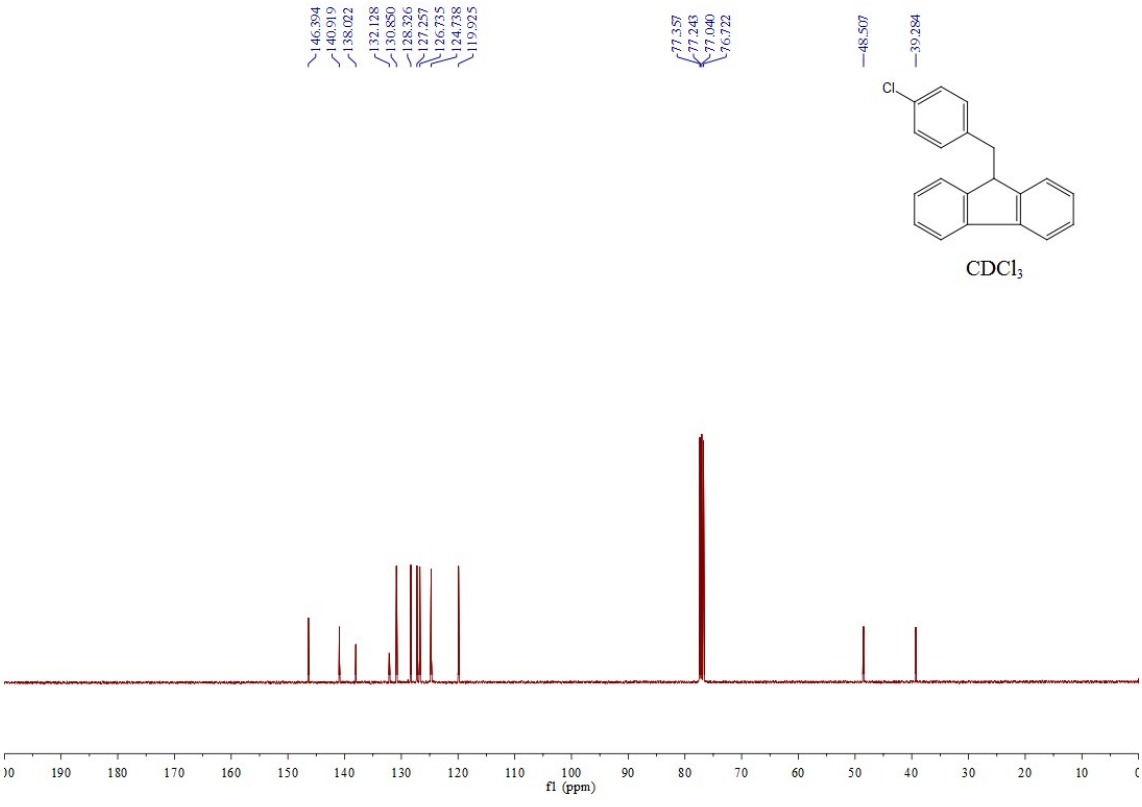


^{19}F NMR spectra of 9-(4-fluorobenzyl)-9H-fluorene, 3g (Table 2, entry 7).

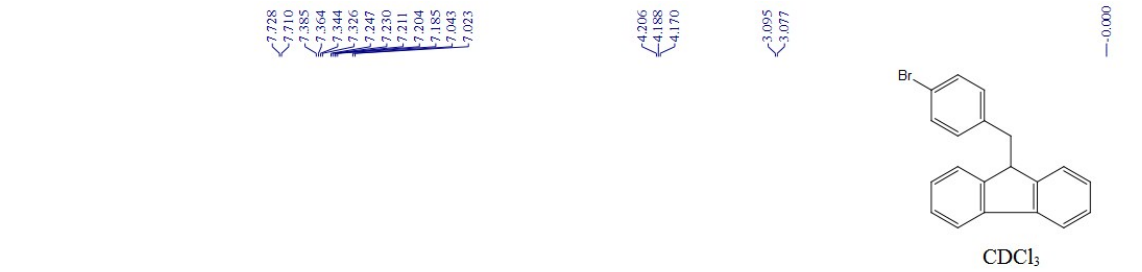


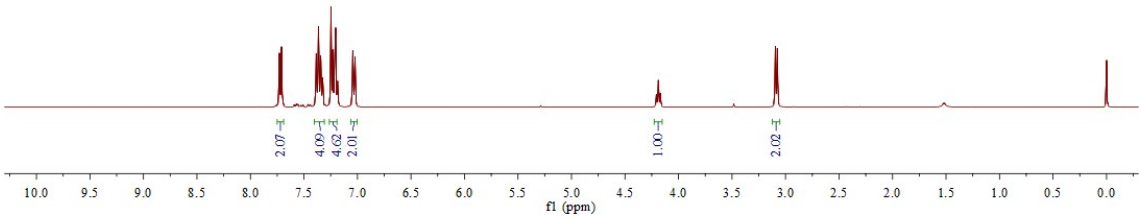
9-(4-chlorobenzyl)-9H-fluorene, 3h (Table 2, entry 8).

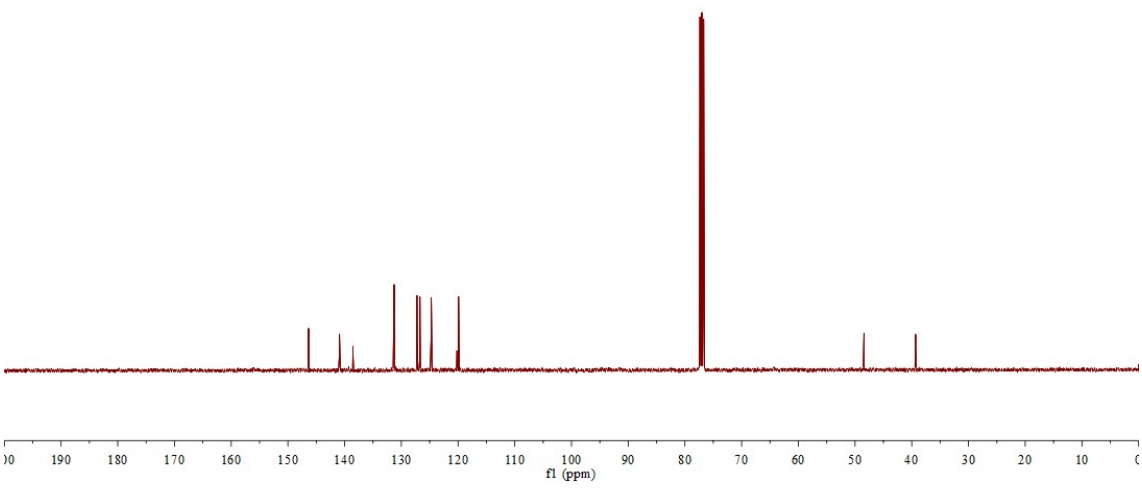




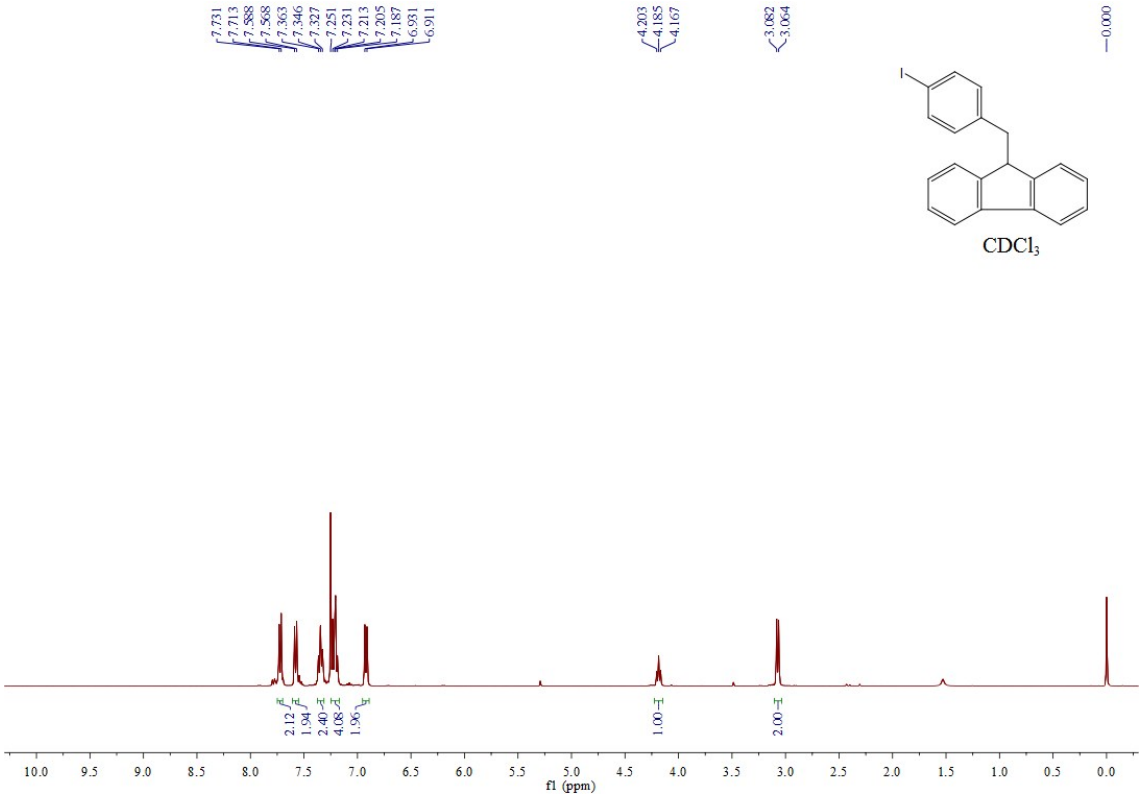
9-(4-bromobenzyl)-9H-fluorene, 3i (Table 2, entry 9).

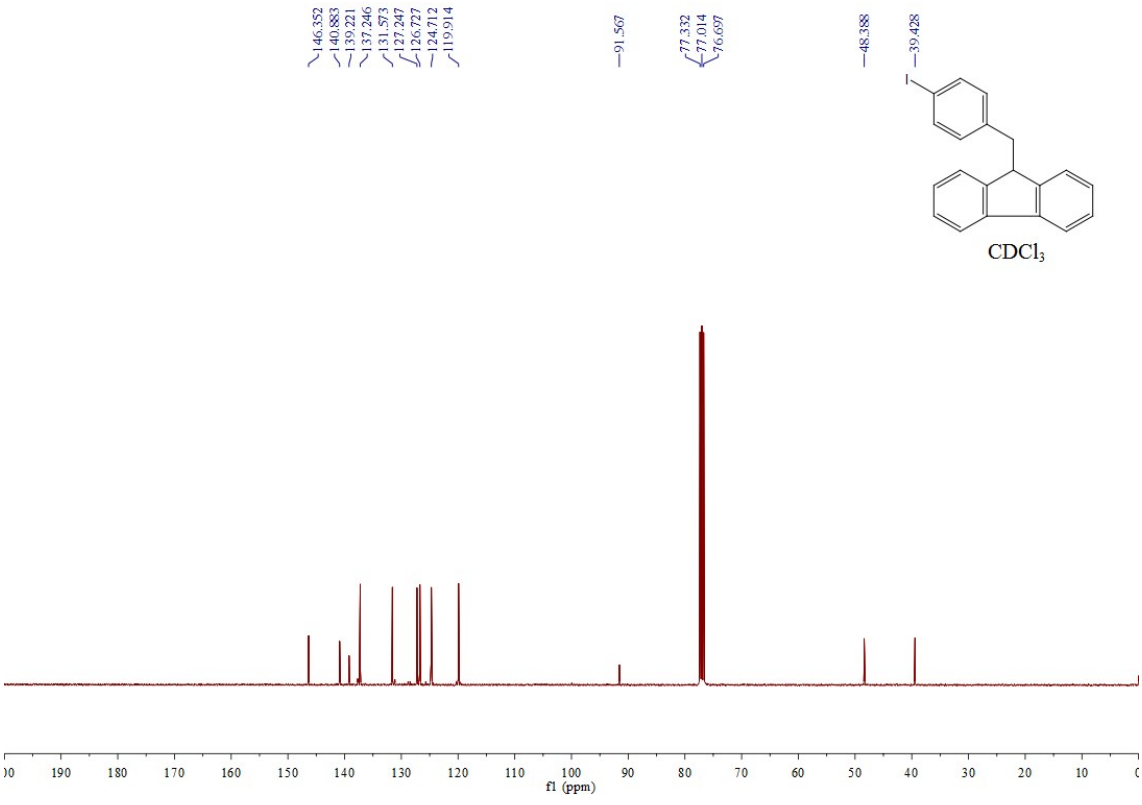




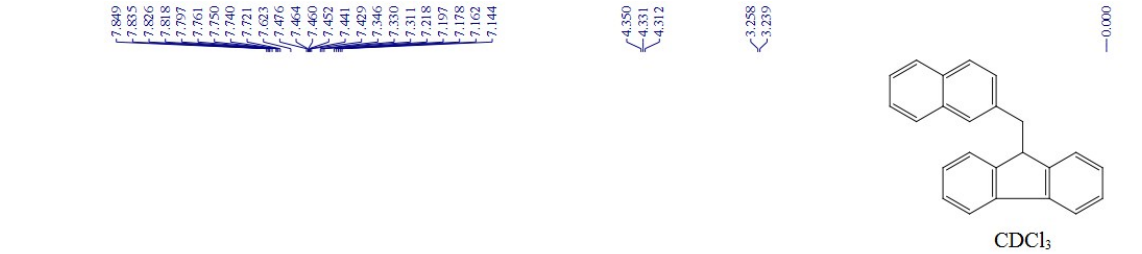


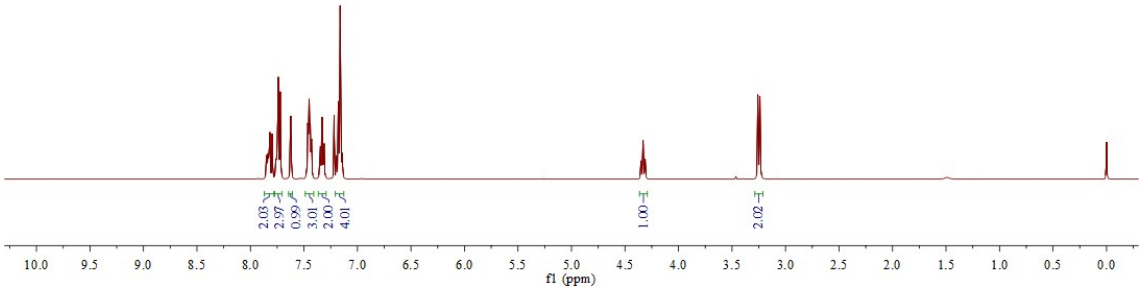
9-(4-iodobenzyl)-9H-fluorene, 3j (Table 2, entry 10).

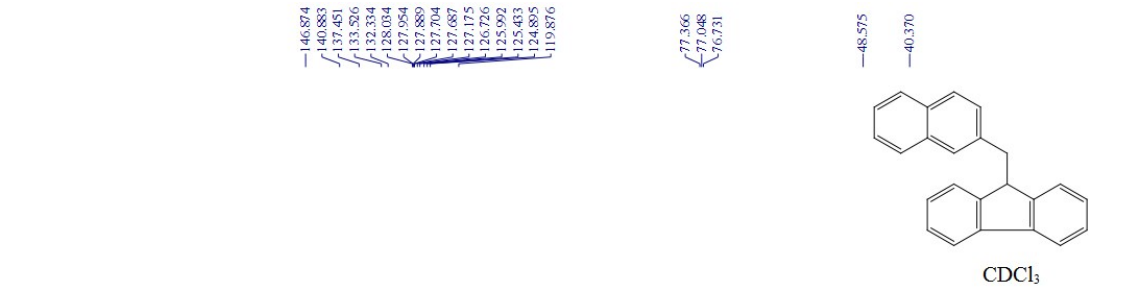




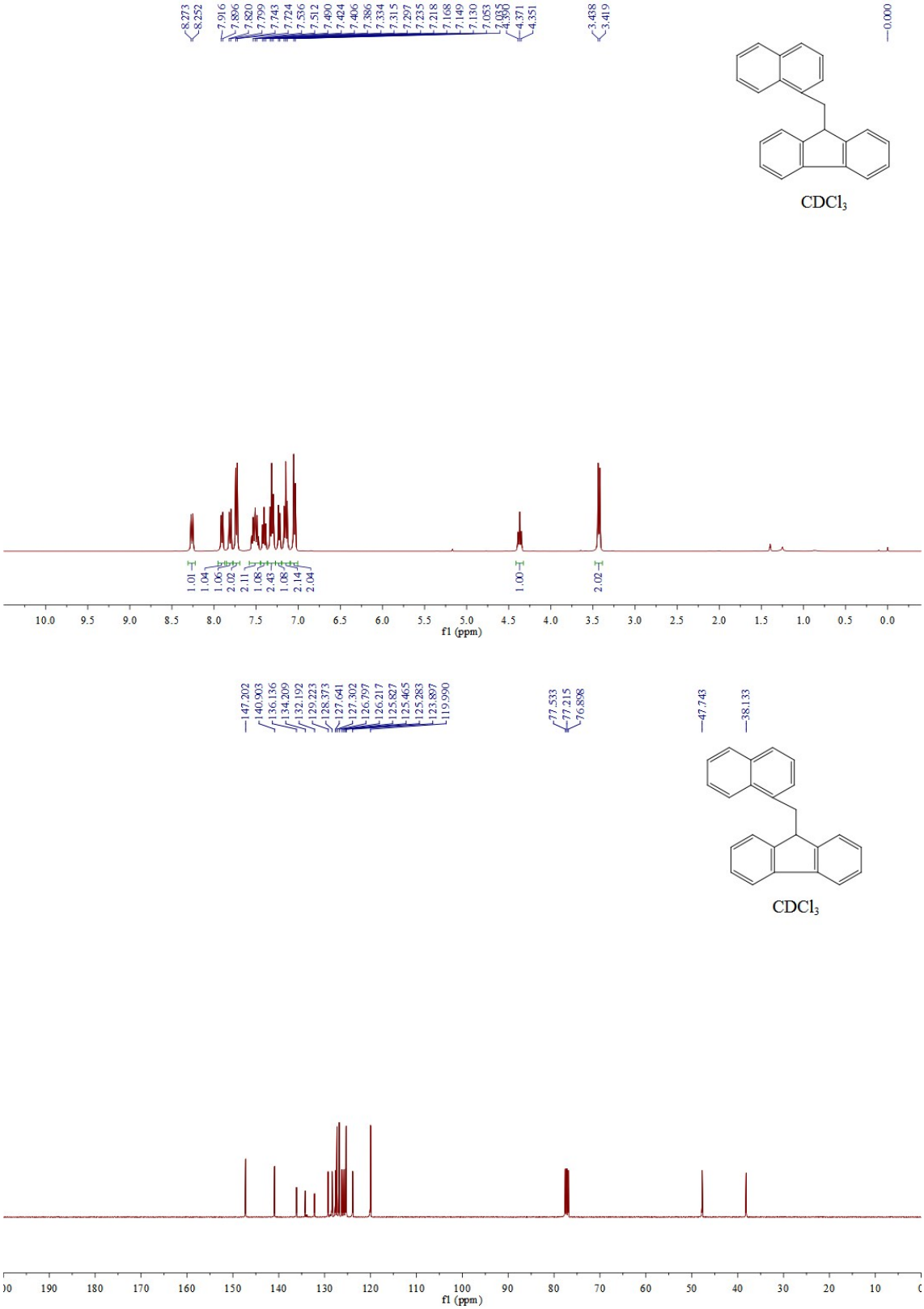
9-(naphthalen-2-ylmethyl)-9H-fluorene, 3k (Table 2, entry 11).



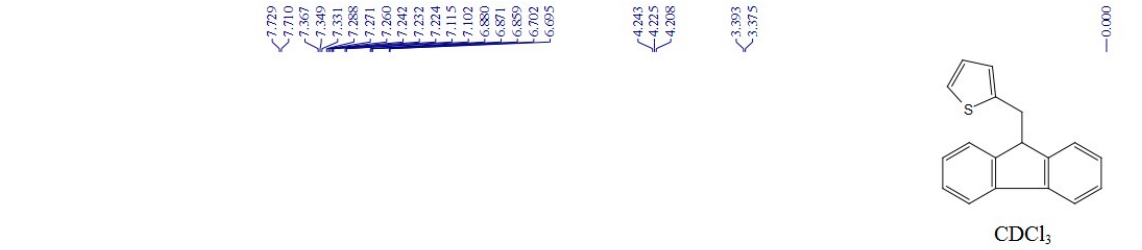


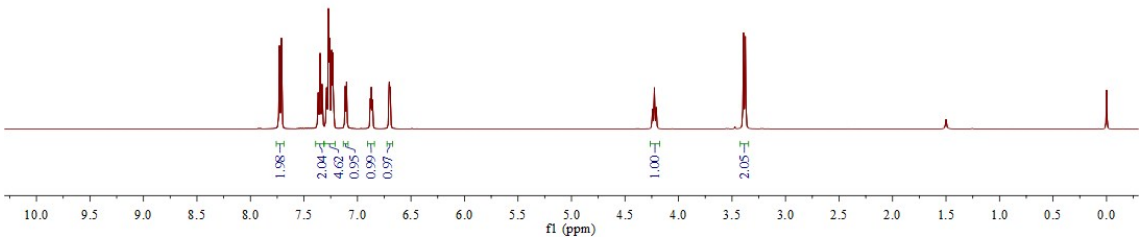


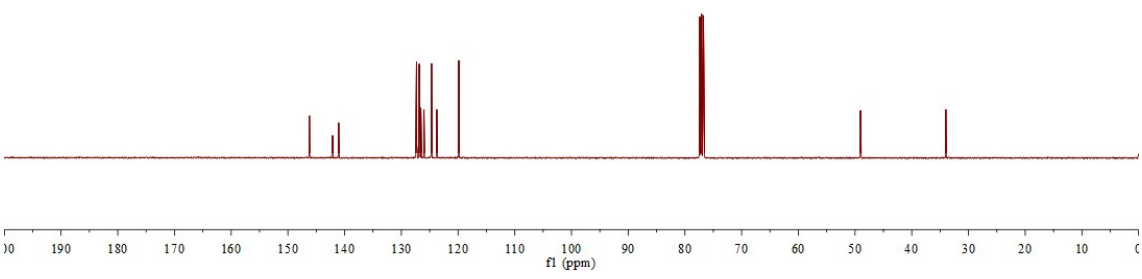
9-(naphthalen-1-ylmethyl)-9H-fluorene, 3l (Table 2, entry 12).



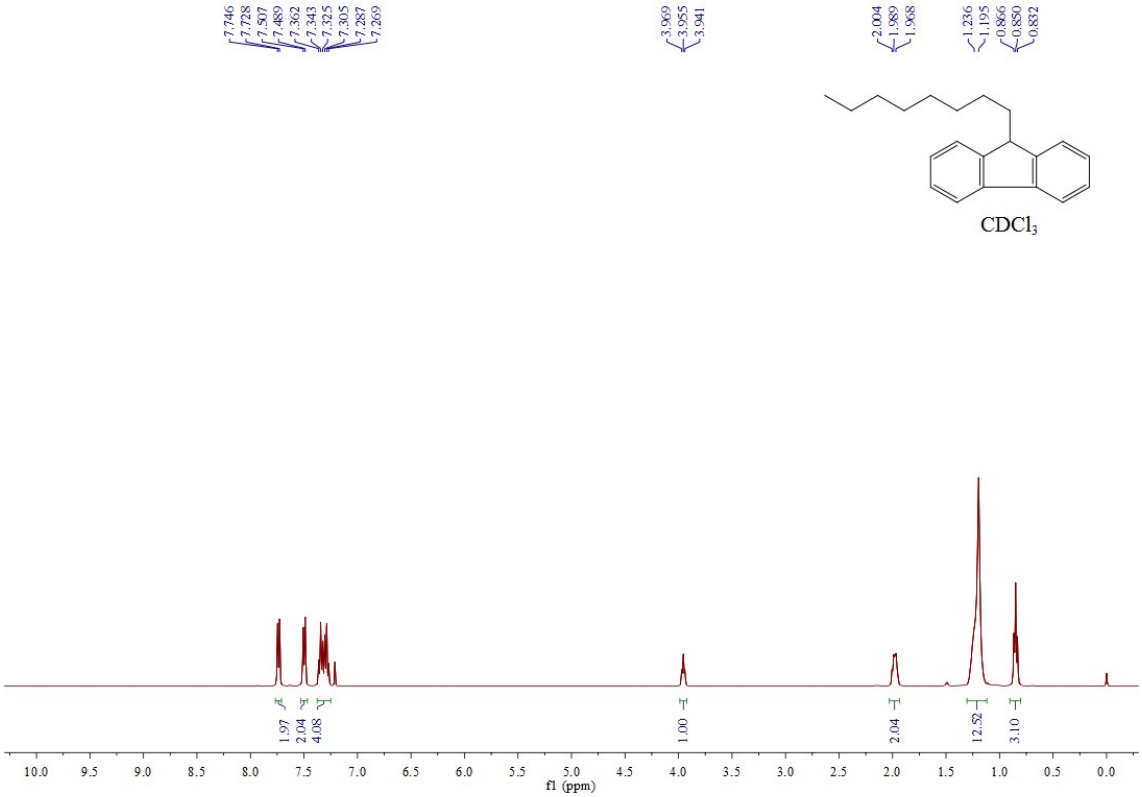
2-((9H-fluoren-9-yl)methyl)thiophene, 3m (Table 2, entry 13).

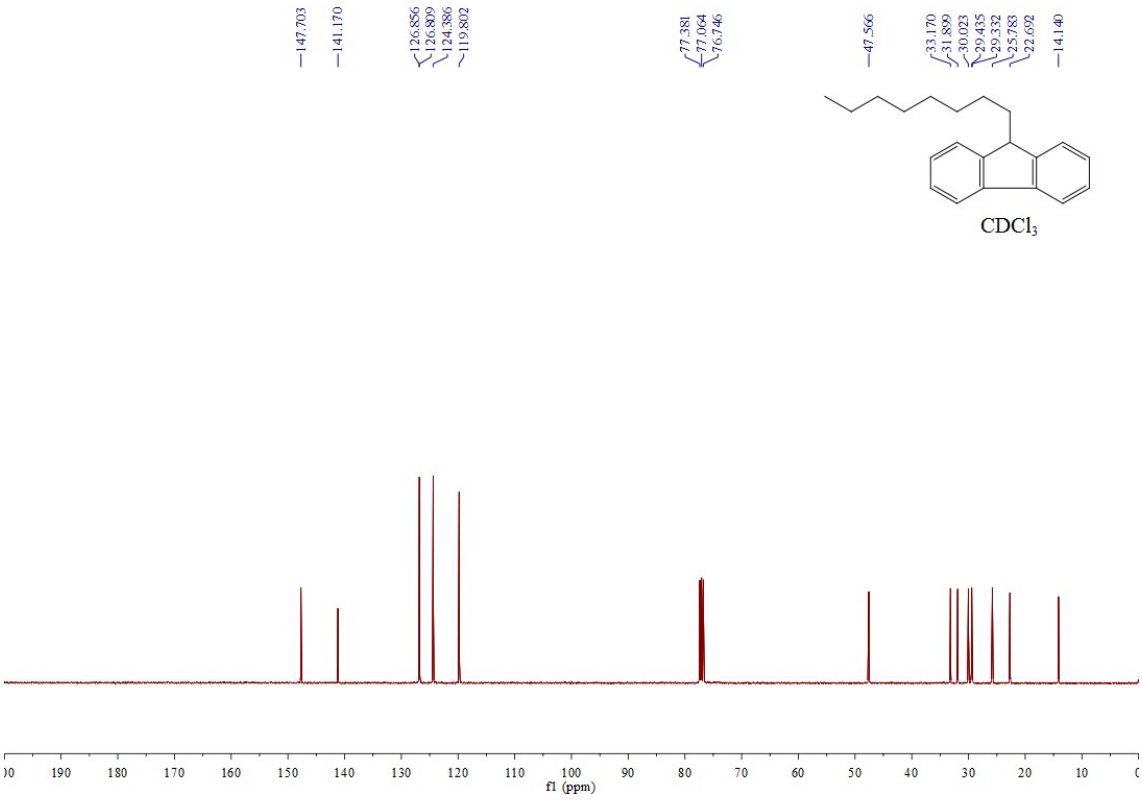




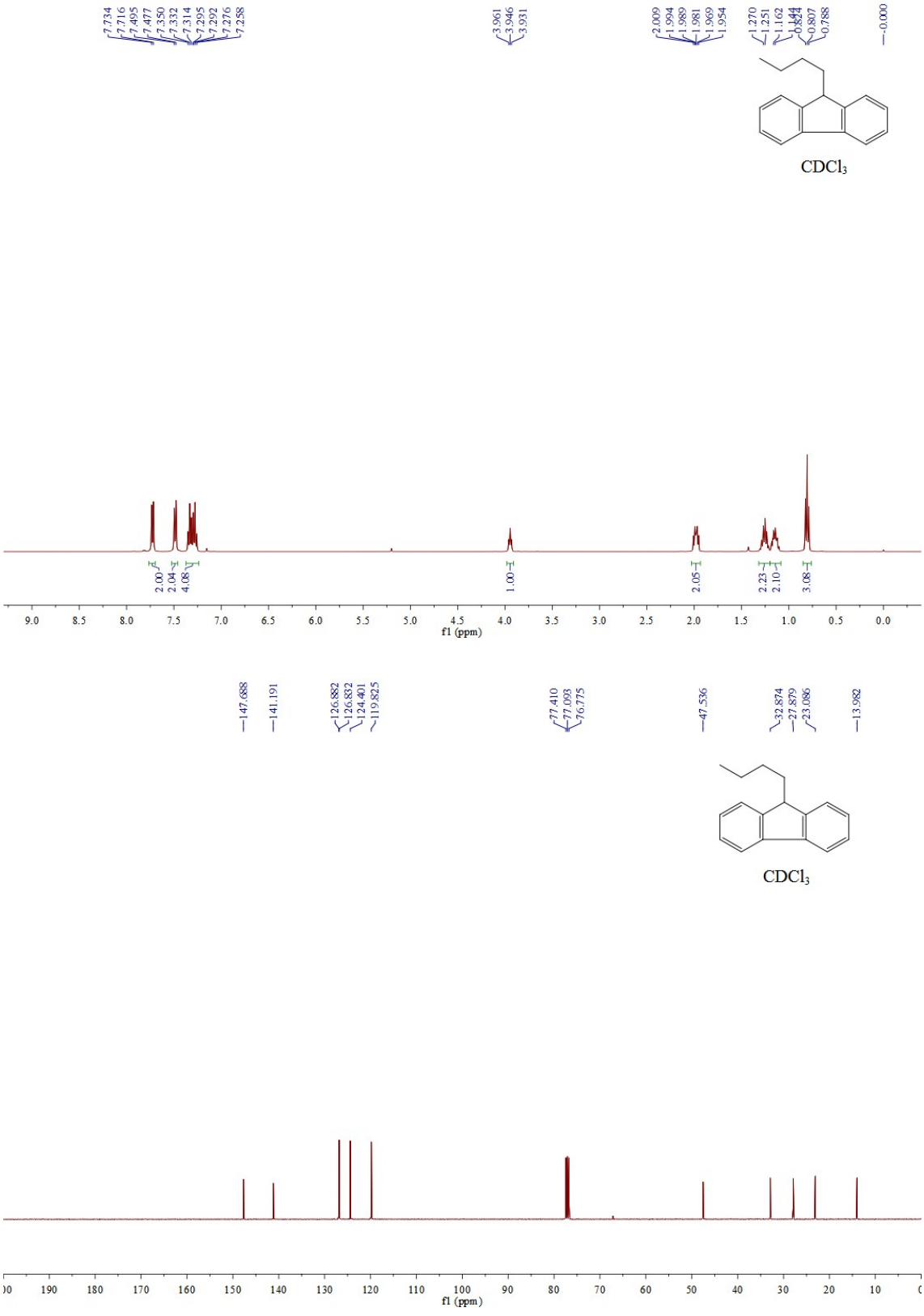


9-octyl-9H-fluorene, 3n (Table 2, entry 14).

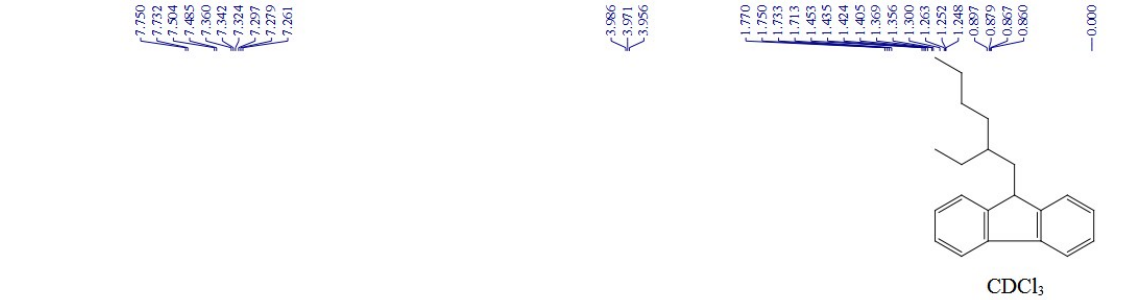


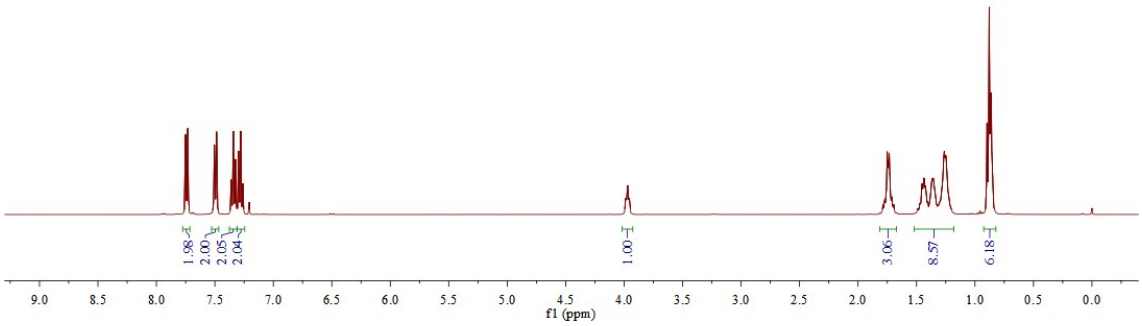


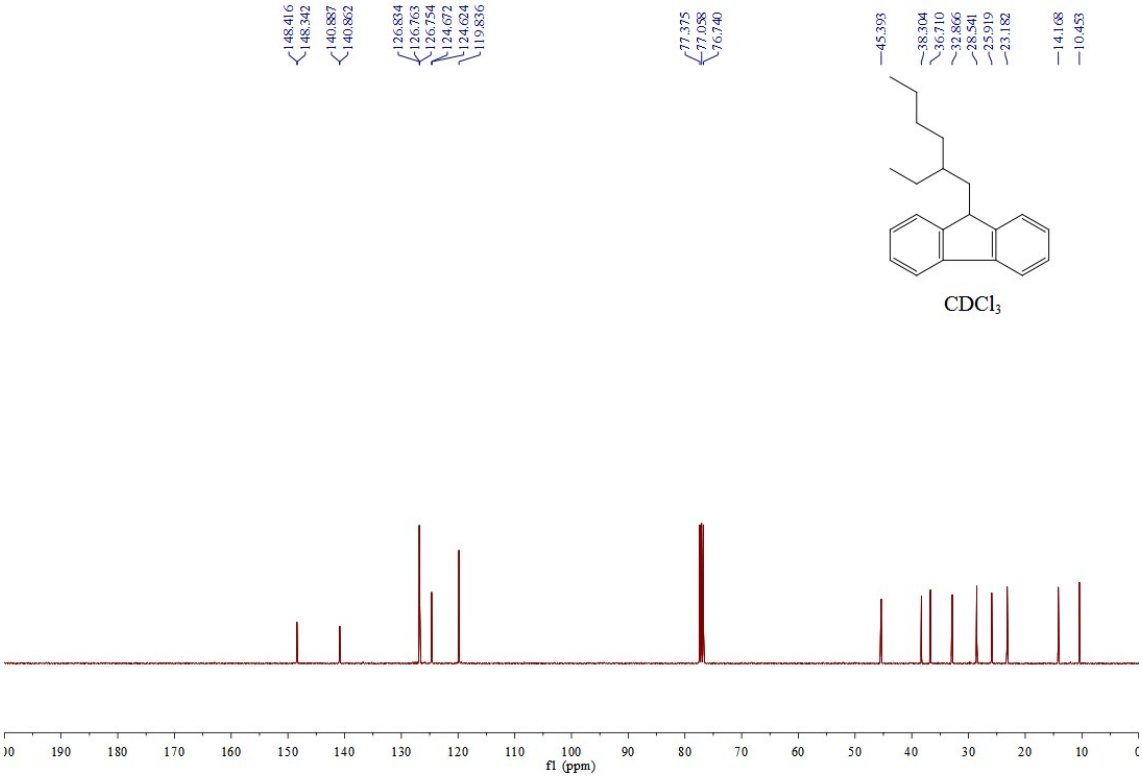
9-butyl-9H-fluorene, 3o (Table 2, entry 15).



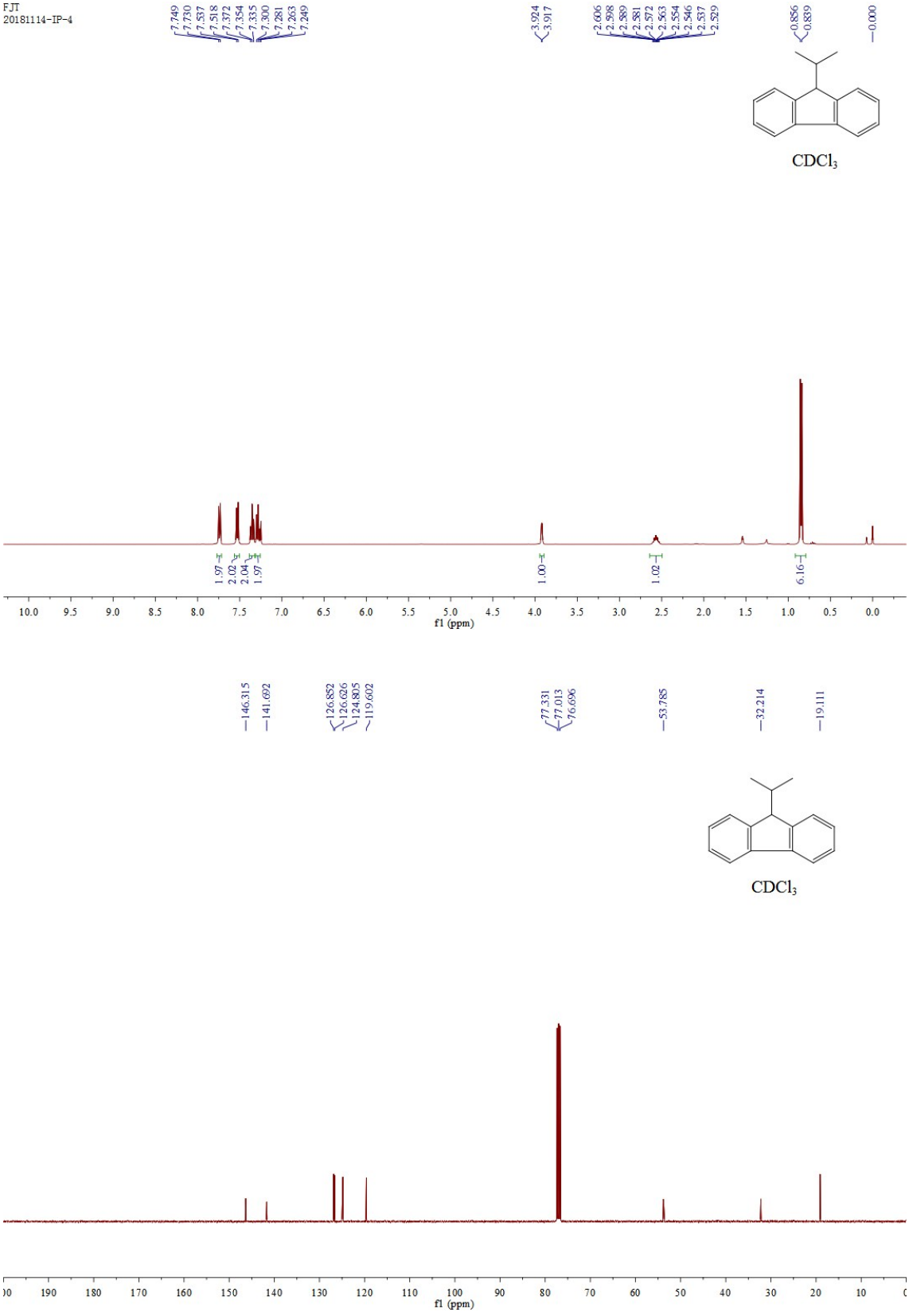
9-(2-ethylhexyl)-9H-fluorene, 3p (Table 2, entry 16).



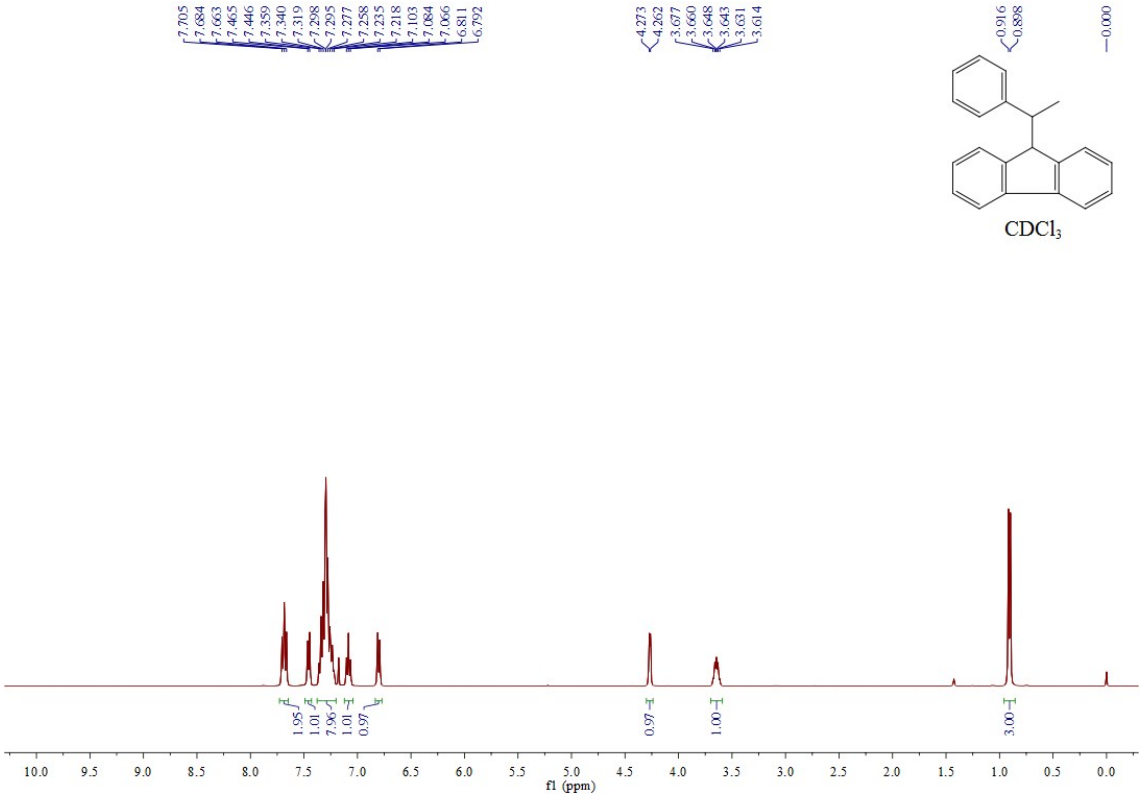


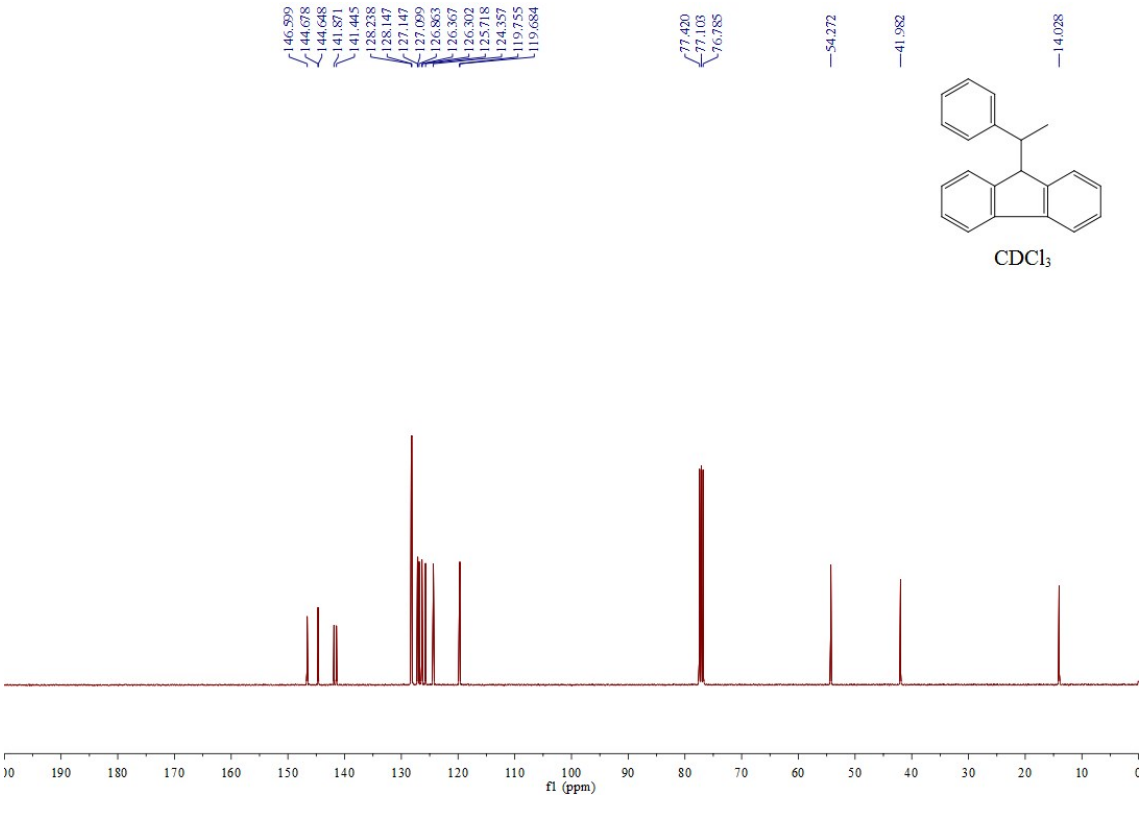


9-isopropyl-9H-fluorene, 3q (Table 2, entry 17).

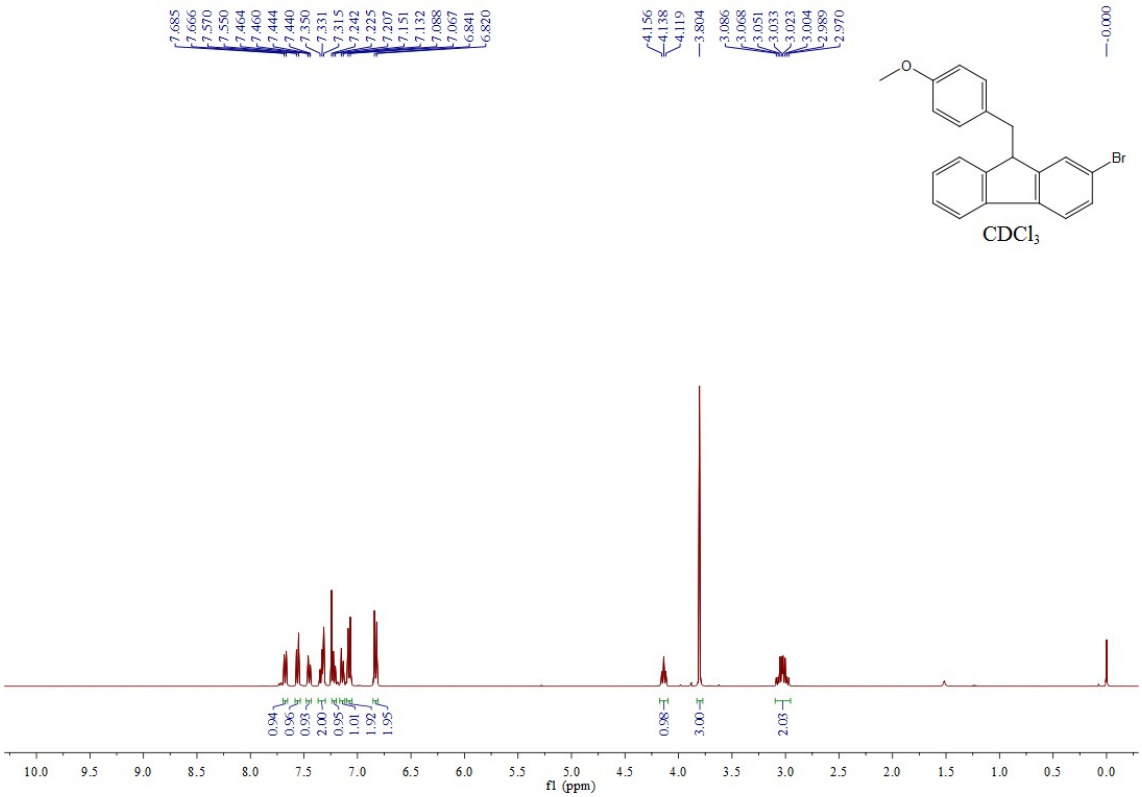


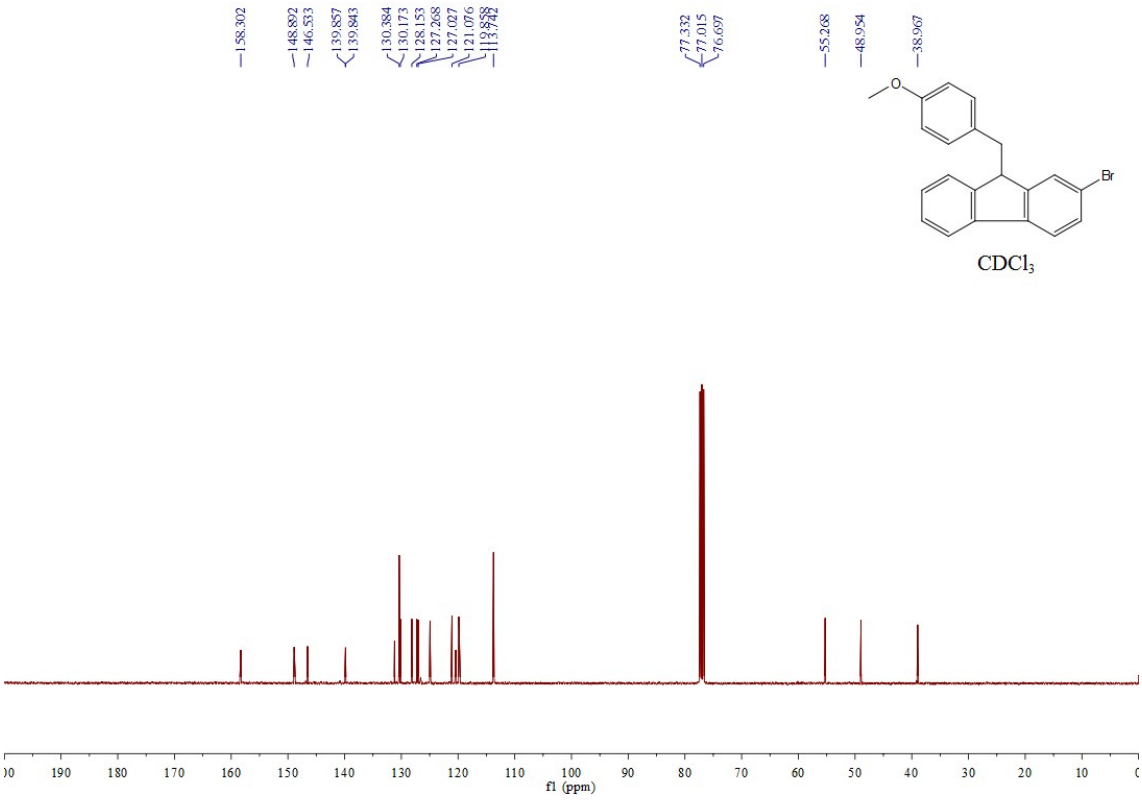
9-(1-phenylethyl)-9H-fluorene, 3r (Table 2, entry 18)





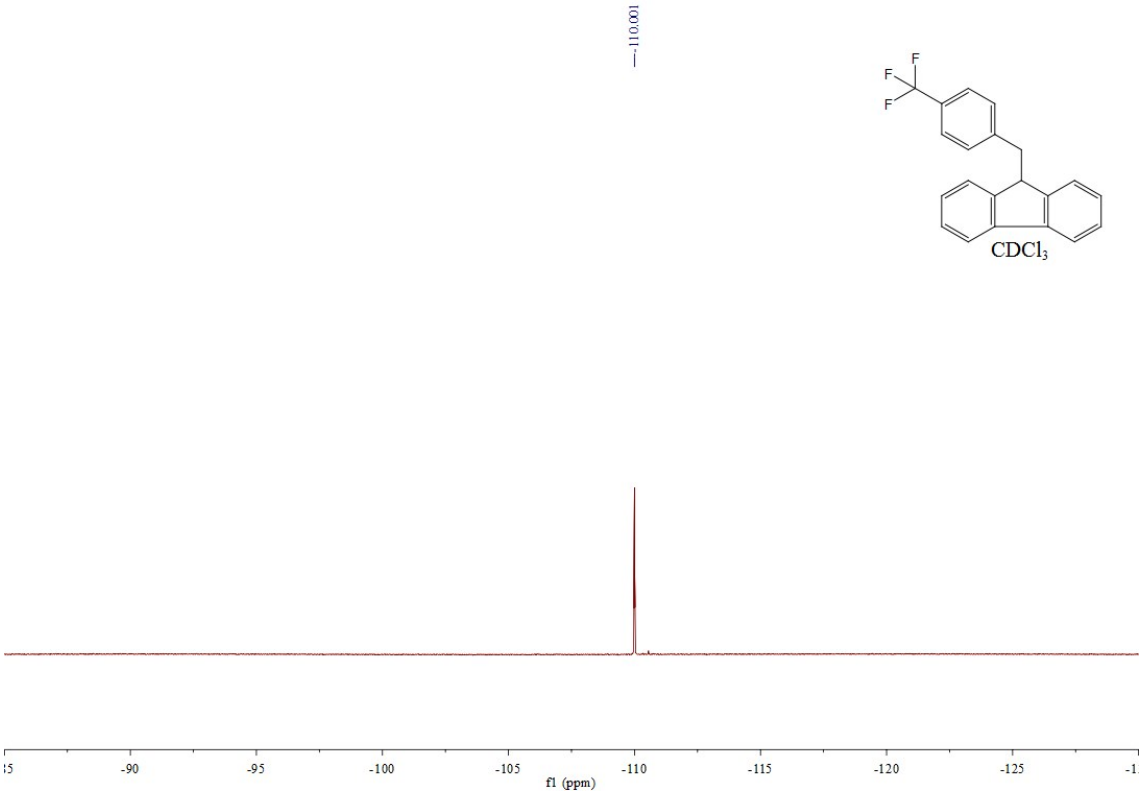
2-**bromo-9-(4-methoxybenzyl)-9H-fluorene, 3s** (Table 2, entry 19).



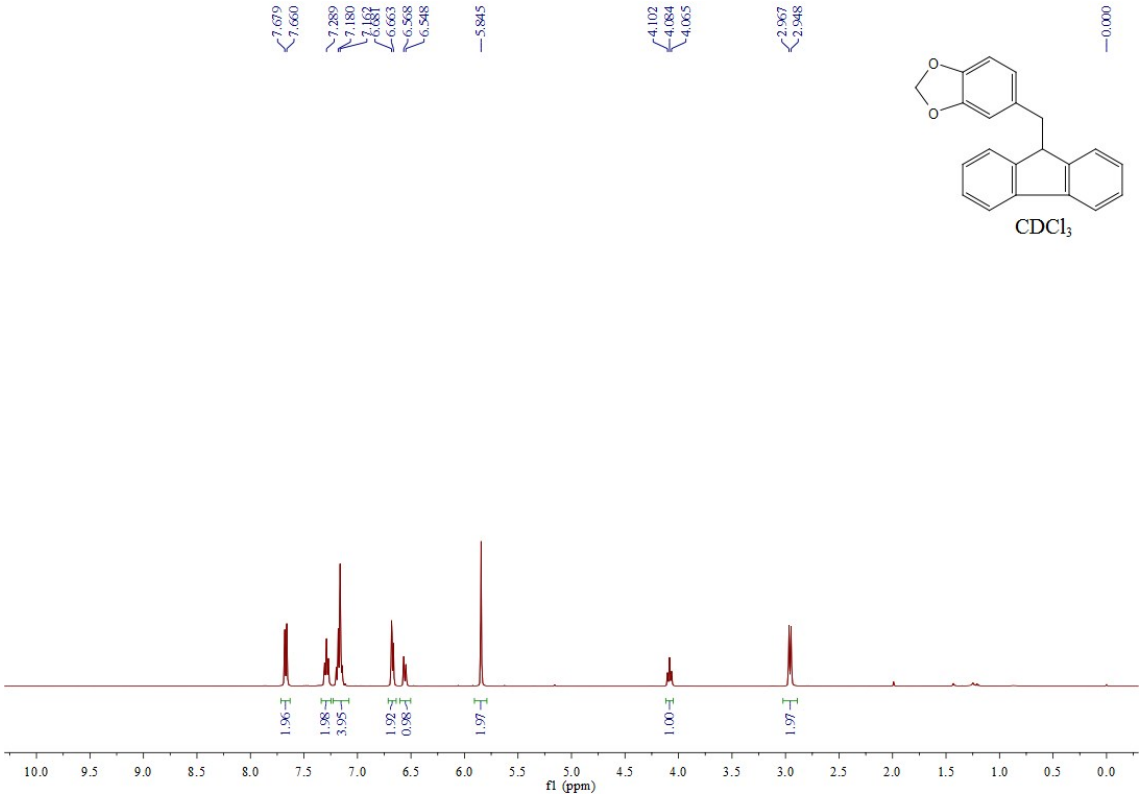


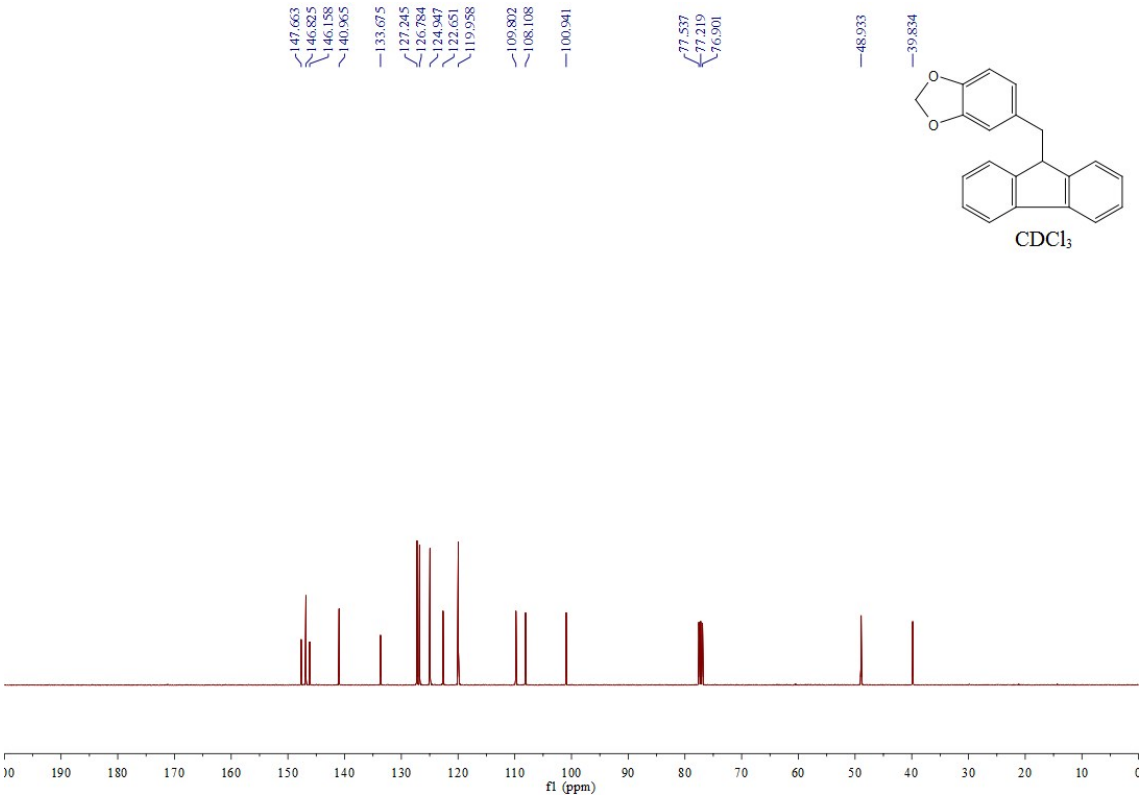
9-(4-(trifluoromethyl)benzyl)-9H-fluorene, 3t (Table 2, entry 20).

^{19}F NMR spectra of 9-(4-(trifluoromethyl)benzyl)-9H-fluorene, 3t (Table 2, entry 20).

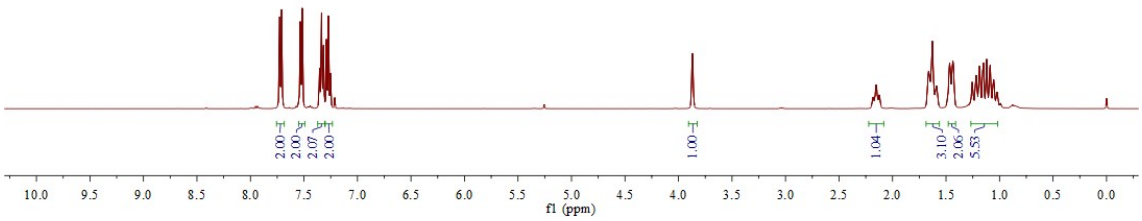


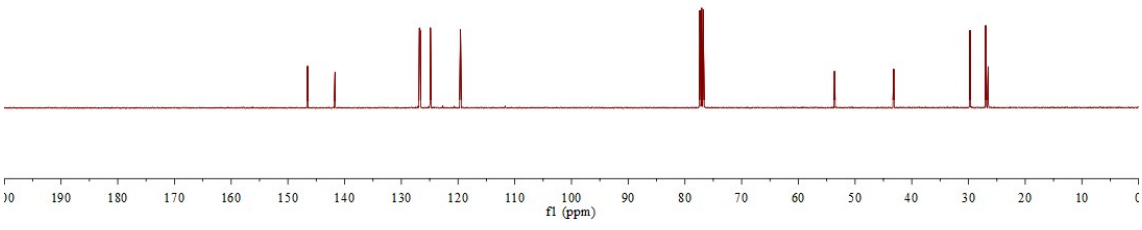
5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole, 3u (Table 2, entry 21).



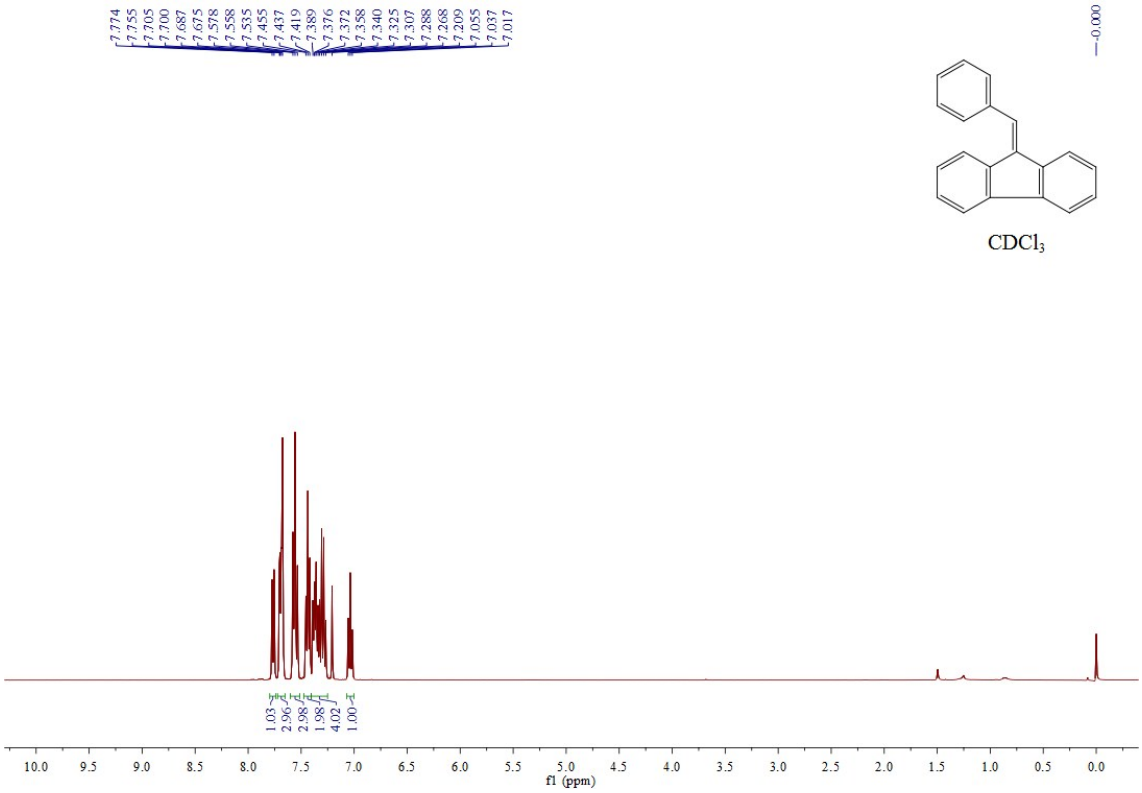


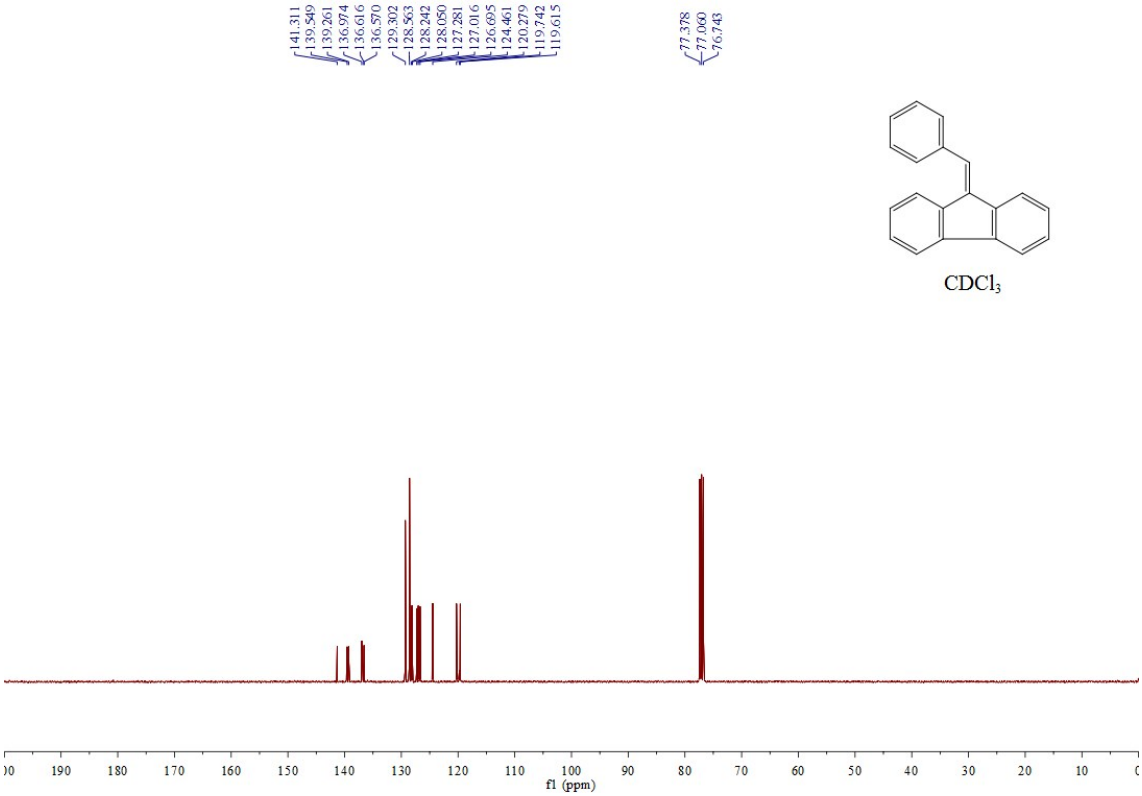
9-cyclohexyl-9H-fluorene, 3v (Table 2, entry 22).



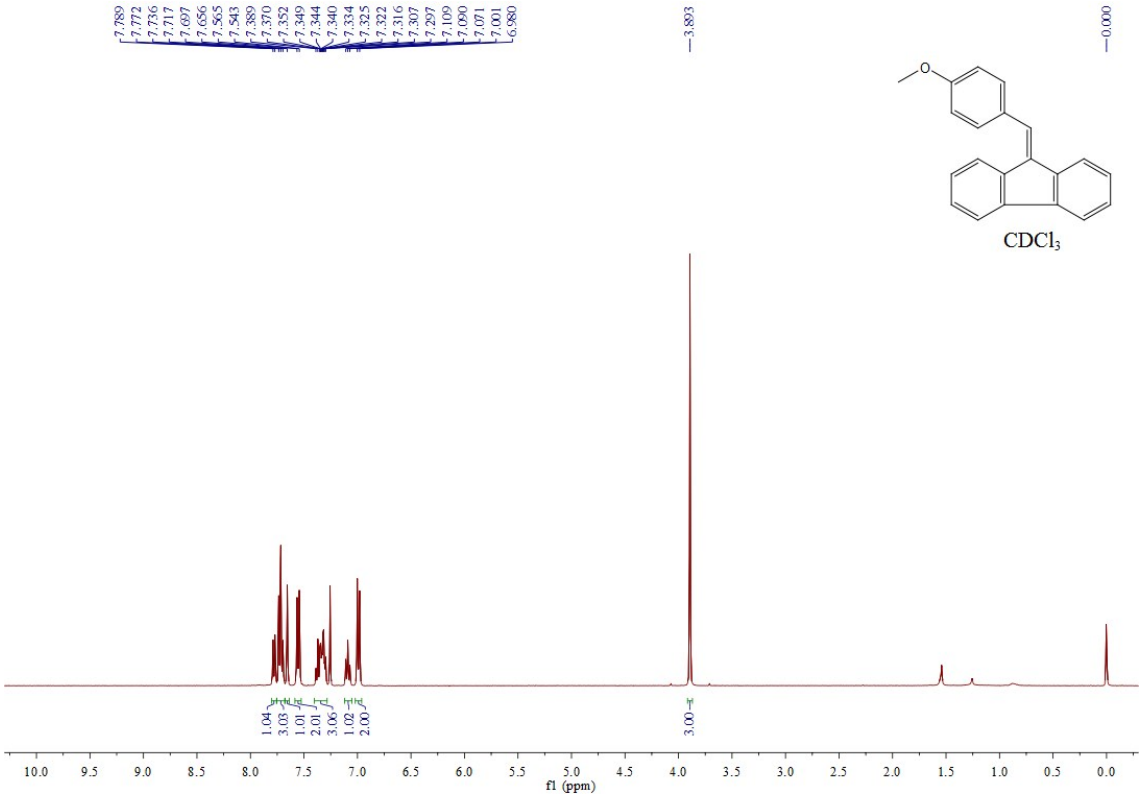


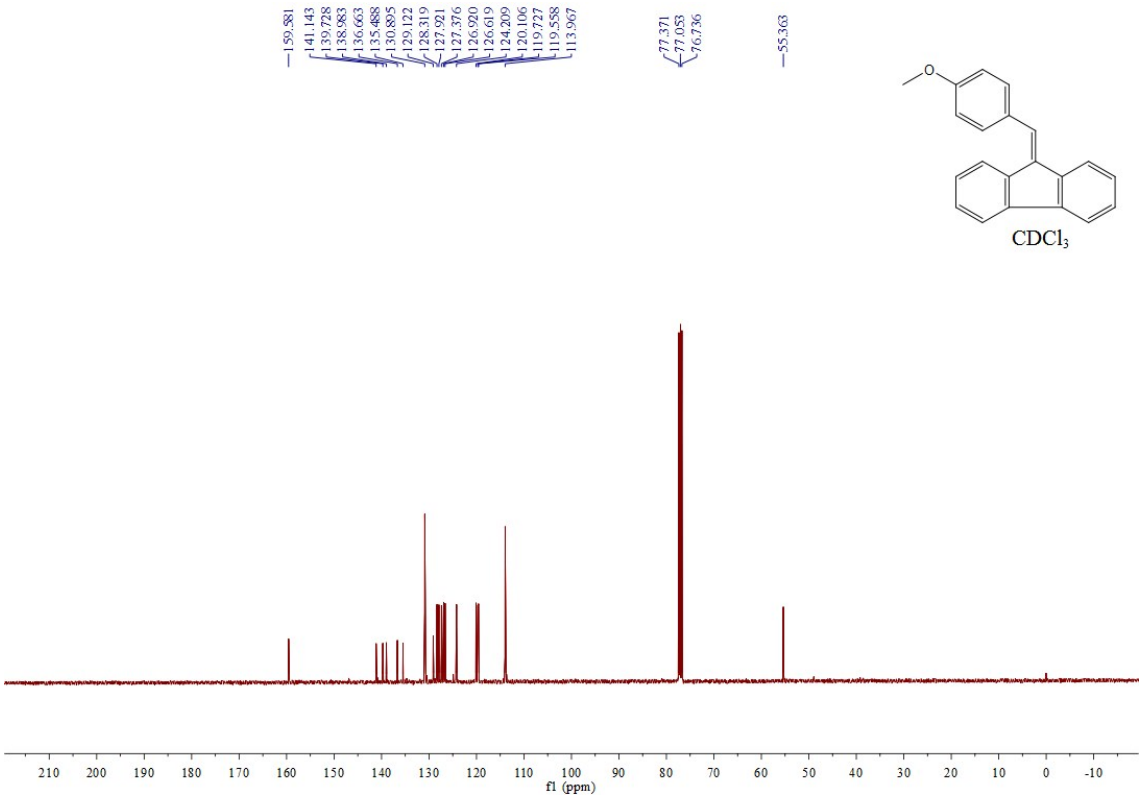
9-benzylidene-9H-fluorene, 4a (Table S1, entry 1).



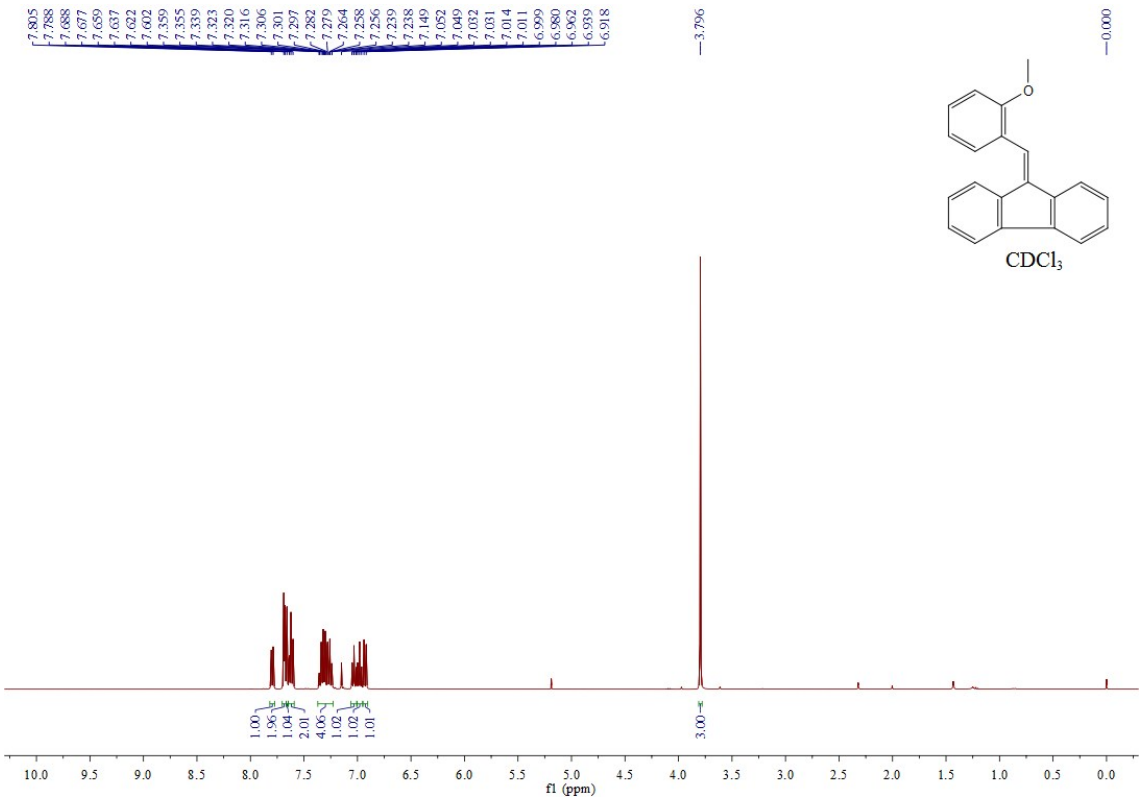


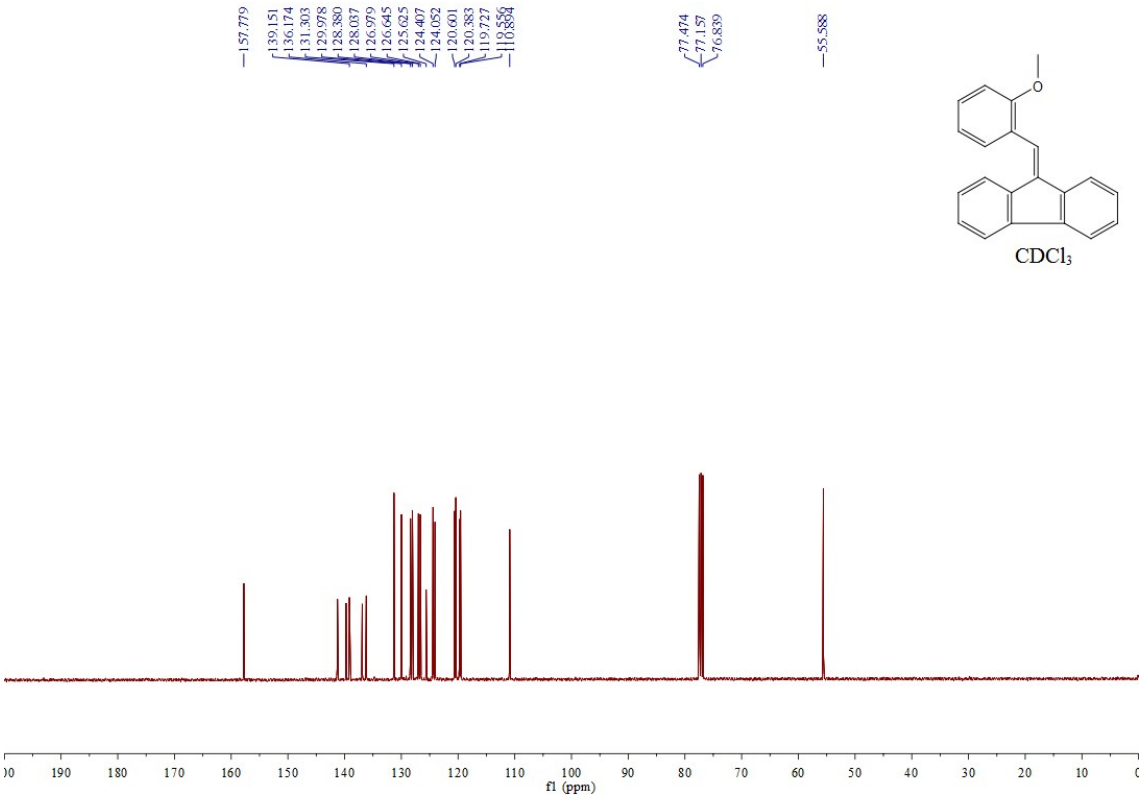
9-(4-methoxybenzylidene)-9H-fluorene, 4c (Table S1, entry 2).



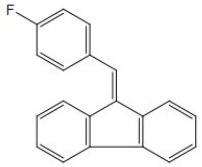


9-(2-methoxybenzylidene)-9H-fluorene, 4e (Table S1, entry 3).

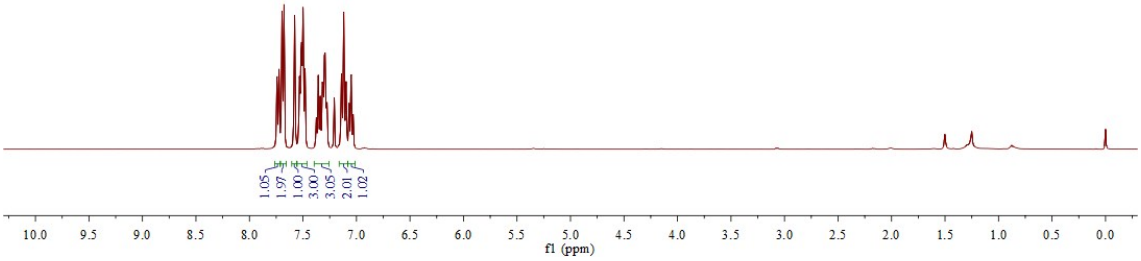


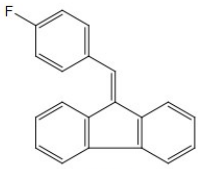


9-(4-fluorobenzylidene)-9H-fluorene, 4g (Table S1, entry 4).

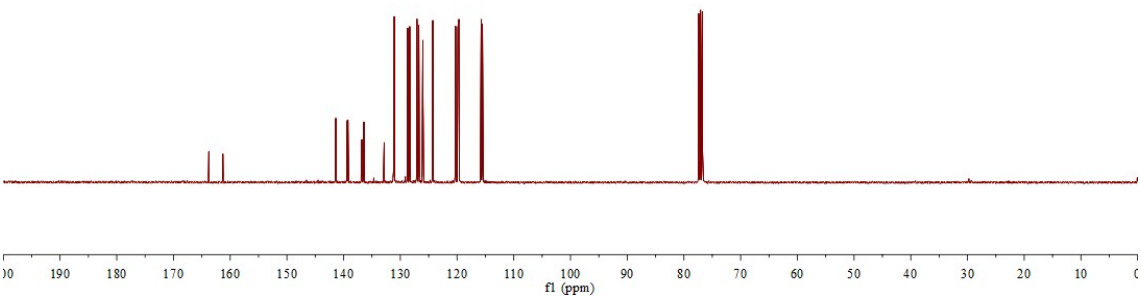


$CDCl_3$

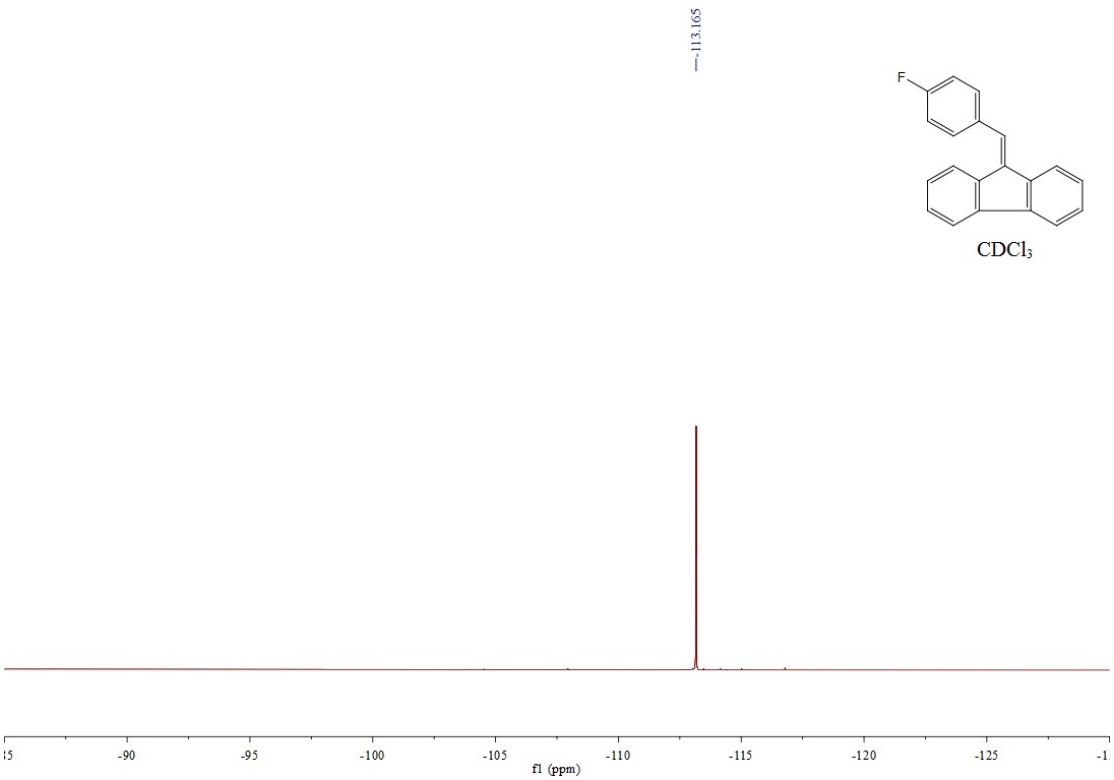




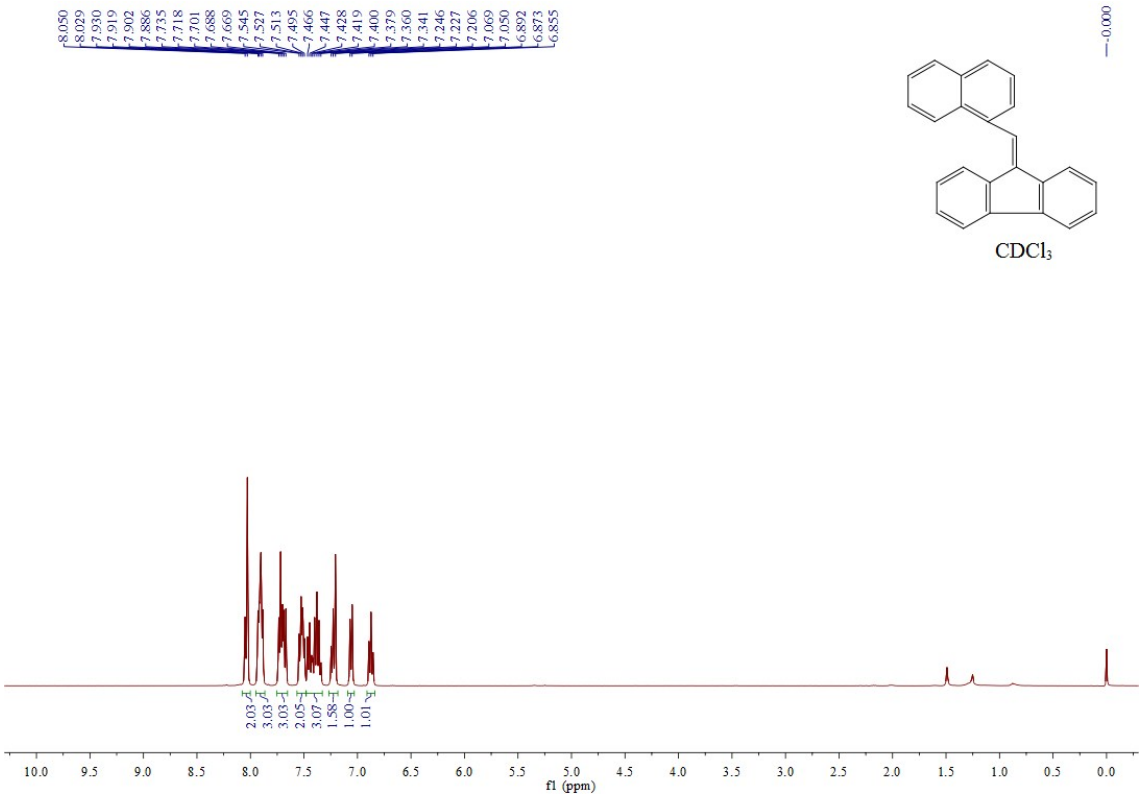
$CDCl_3$

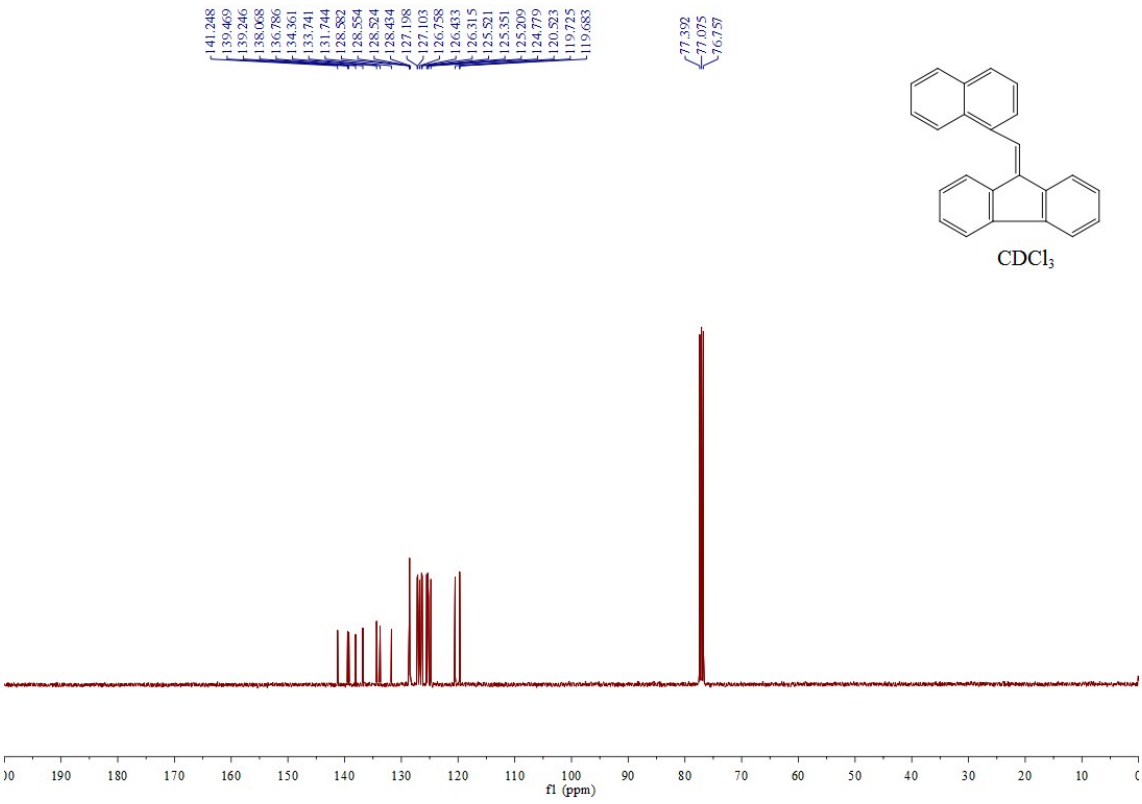


^{19}F NMR spectra of 9-(4-fluorobenzylidene)-9H-fluorene, 4g (Table S1, entry 4).



9-(naphthalen-1-ylmethylene)-9H-fluorene, 4l (Table S1, entry 5).





2-((9H-fluoren-9-ylidene)methyl)thiophene, 4m (Table S1, entry 6).