Supporting Information

Ni(II) source as a pre-catalyst for the cross-coupling of benzylic pivalates with arylboronic acids: facile access to tri- and diarylmethanes

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General remarks

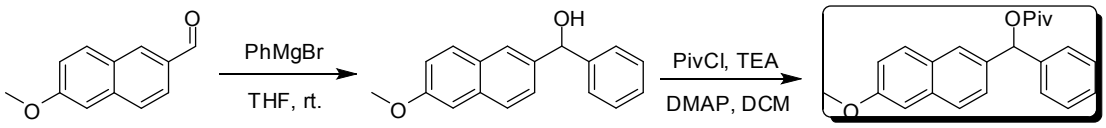
All reactions were carried out under nitrogen atmosphere with oven-dried glassware. *Trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel(II) was prepared according to the published procedures.[1] Toluene, THF and dioxane were distilled from sodium/benzophenone before use. Potassium carbonate, potassium phosphate, cesium fluoride were commercially available and used with finely-ground powder. All ligands were purchased commercially and used as received. 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 products are characterized by melting points, HRMS, ^{1}H and ^{13}C NMR. Melting points were measured with a X-4 micro melting point apparatus and uncorrected.

Synthesis of $Ni(PPh_3)_2$(1-naphthyl)Cl (C-1).

A stirred mixture of $NiCl_2 \cdot 6H_2O$ (4.8 g, 0.02 mol), triphenylphosphane (11.53 g, 0.044 mol) and 95% ethanol (90 mL) was heated until a gentle reflux started. 1-Chloronaphthalene (6.5 g, 0.04 mol, excess) was then added, followed by zinc dust (1.3 g, 0.02 mol) over 5 min. The dark-green mixture very soon turned yellow. After stirring and heating under reflux for 1.5 h (under nitrogen), the mixture was cooled to room temperature. Four 2-mL portions of 30% aqueous hydrochloric acid were added over 15 min. After stirring for 1.5 h, the solid was filtered off on a sintered-glass funnel and successively washed with 20 mL of ethanol, twice with 20 mL of 1 M aqueous hydrochloric acid, twice with 20 ml of ethanol and once with 20 ml of petroleum (30–60 °C). The yellow solid was dried in vacuo at a bath temperature of not higher than 45°C. The yield was above 80%.

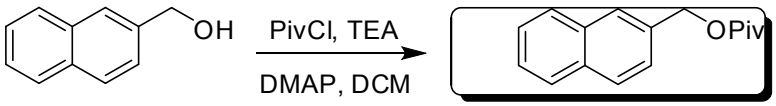
General procedure for the preparation of benzylic pivalates

A. Representative procedure for the synthesis of diarylmethyl pivalates.



In a flame-dried round-bottom flask, to a solution of 6-methoxy-2-naphthaldehyde (372mg, 2.0 mmol, 1.0 equiv) in THF (10 mL) was added phenylmagnesium bromide (1.0 M in THF, 3.0 mL, 1.5 equiv). After stirring at room temperature for 4 h, saturated ammonium chloride (10 mL) was added and the reaction was extracted with EtOAc (3 x 8 mL).The combined organic layers were washed with brine (3 x 5 mL), dried over $MgSO_4$, and concentrated in vacuo to afford the crude corresponding diarylmethyl alcohols, which was used without further purification. Then, the obtained crude diarylmethyl alcohols and 4-(dimethylamino)pyridine (24.4mg, 0.1 equiv) were added to a 25 mL round bottom flask , which was evacuated and backfilled with nitrogen before addition of methylene chloride (10 mL), triethylamine (0.33 mL, 1.2 equiv), and trimethylacetyl chloride (0.29 mL, 1.2 equiv). After stirring for 8 h, the reaction was quenched with 1M HCl (5 mL), and the product was extracted with methylene chloride (3 x 9 mL). The combined organics were washed with brine (2 x 5 mL), dried over $MgSO_4$, and concentrated in vacuo. The product was purified by flash column chromatography to afford the desired diarylmethyl pivalates as a white solid (494mg, 71%).

B. Representative procedure for the synthesis of primary benzylic pivalates.



To a 25 mL round bottom flask was added 2-naphthalenemethanol (158mg, 1.0 mmol, 1.0 equiv) and 4-(dimethylamino)pyridine (12.2 mg, 0.10 equiv). The flask was evacuated and backfilled with nitrogen before addition of methylene chloride (8 mL), triethylamine (0.16 mL, 1.2 equiv), and trimethylacetyl chloride (0.15 mL, 1.2 equiv). After stirring for 8 h, the reaction was quenched with 1M HCl (3 mL), and the product was extracted with methylene chloride (3 x 9 mL). The combined organics were washed with brine (2 x 5 mL), dried over $MgSO_4$, and concentrated in vacuo.

The product was purified by flash column chromatography to afford the desired primary benzylic pivalates as a colorless oil (201mg, 83%).

General procedure for Ni(II)-catalyzed cross-couplings of benzylic pivalates with arylboronic acids for the synthesis of di- and triarylmethanes.

An oven-dried 25-mL three-necked flask was charged with K_3PO_4 (2.5 mmol) and $Ni(PPh_3)_2$(1-naphthyl)Cl (0.05 mmol). Then the benzylic pivalate (1 mmol) (if solid) and the arylboronic acid (1.5 mmol) were added. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. The benzylic pivalate (if liquid), dried toluene (5 mL) were added via syringe at this time. The reaction mixture was heated in an oil bath of 70 °C 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 product.

Characterization data of the products

2-Methoxy-6-((4-methoxyphenyl)(phenyl)methyl)naphthalene (Table 2, **2** and **9**). White solid: mp 137–139 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 9.6 Hz, 1H), 7.39 (s, 1H), 7.32–7.19 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.12–7.03 (m, 4H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.63 (s, 1H), 3.90 (s, 3H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1, 157.6, 144.3, 139.6, 136.1, 133.2, 130.5, 129.5, 129.4, 128.9, 128.6, 128.4, 127.5, 126.8, 126.3, 118.7, 113.7, 105.7, 56.0, 55.3, 55.2; HRMS: calcd. for $C_{25}H_{22}O_2$: 354.1620 [M+]; found: 354.1625.

2-Methoxy-6-(phenyl(p-tolyl)methyl)naphthalene (Table 2, **3**). White solid: mp 131–133 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.39 (s, 1H), 7.31–7.18 (m, 4H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.12–7.06 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 3.90 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.6, 144.2, 141.0, 139.5, 135.9, 133.3, 129.6, 129.5, 129.4,

129.1, 128.9, 128.6, 128.4, 127.6, 126.8, 126.3, 118.7, 105.7, 56.5, 55.3, 21.1; HRMS: calcd. for $C_{25}H_{22}O$: 338.1671 [M+]; found: 338.1512.

2-Methoxy-6-(phenyl(m-tolyl)methyl)naphthalene (Table 2, **4**). White solid: mp 113–115 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 9.6 Hz, 1H), 7.40 (s, 1H), 7.32–7.18 (m, 4H), 7.16 (t, *J* = 7.0 Hz, 3H), 7.12–7.07 (m, 2H), 7.03 (d, *J* =7.6 Hz, 1H), 6.98 (s, 1H), 6.93 (d, *J* =7.6 Hz, 1H), 5.63 (s, 1H), 3.90 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.6, 144.1, 143.9, 139.4, 137.9, 133.3, 130.4, 129.6, 129.4, 128.9, 128.7, 128.4, 128.3, 127.7, 127.2, 126.8, 126.7, 126.4, 118.7, 105.7, 56.8, 55.3, 21.6; HRMS: calcd. for $C_{25}H_{22}O$: 338.1671 [M+]; found: 338.1667.

2-Benzhydryl-6-methoxynaphthalene (Table 2, **5**). White solid: mp 120–122 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 9.6 Hz, 1H), 7.40 (s, 1H), 7.32–7.19 (m, 7H), 7.15 (d, *J* = 7.6 Hz, 4H), 7.12–7.07 (m, 2H), 5.67 (s, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.7, 144.0, 139.3, 133.3, 129.7, 129.5, 129.0, 128.7, 128.4, 127.7, 126.9, 126.4, 118.8, 105.7, 56.9, 55.4; HRMS: calcd. for $C_{24}H_{20}O$: 324.1514 [M+]; found: 324.1518.

2-Methoxy-6-(naphthalen-1-yl(phenyl)methyl)naphthalene (Table 2, **6** and **14**). White solid: mp 80–81 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.46–7.33 (m, 4H), 7.32–7.20 (m, 4H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.13–7.06 (m, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.39 (s, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.6, 143.8, 140.0, 139.2, 134.0, 133.4, 132.1, 129.9, 129.5, 129.0, 128.9, 128.8, 128.5, 128.0, 127.8, 127.4, 126.9, 126.5, 126.2, 125.5, 125.3, 124.4, 118.8, 105.7, 55.4, 53.2; HRMS: calcd. for $C_{28}H_{22}O$: 374.1671 [M+]; found: 374.1676.

2-((4-Fluorophenyl)(phenyl)methyl)-6-methoxynaphthalene (Table 2, **8** and **10**). White solid: mp 117–119 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 9.6 Hz, 1H), 7.37 (s, 1H), 7.33–7.20 (m, 4H), 7.16–7.07 (m, 6H), 6.97 (t, *J* = 8.8 Hz, 2H), 5.65 (s, 1H), 3.90 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5 (d, *J* = 243 Hz), 157.7, 143.8, 139.7, 139.1, 133.4, 131.0 (d, *J* = 7.7 Hz), 129.5,

129.4, 128.9, 128.5, 127.6, 127.0, 126.5, 118.9, 115.2 (d, *J* = 21.0 Hz), 105.7, 56.1, 55.3; HRMS: calcd. for $C_{24}H_{19}FO$: 342.1420 [M+]; found: 342.1425.

1-(Bis(4-methoxyphenyl)methyl)naphthalene (Table 2, **11**). White solid: mp 145–146 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.6Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.46–7.33 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 4H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.17 (s, 1H), 3.78 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1, 140.6, 136.3, 134.0, 131.9, 130.5, 128.7, 127.4, 127.2, 126.1, 125.4, 125.3, 124.5, 113.8, 55.2, 51.6; HRMS: calcd. for $C_{24}H_{19}FO$: 354.1620 [M+]; found: 354.1625.

1-((4-Methoxyphenyl)(phenyl)methyl)naphthalene (Table 2, **12**). White solid: mp 128–131 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.46–7.33 (m, 3H), 7.32–7.18 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.22 (s, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1, 144.2, 140.3, 135.9, 134.0, 132.0, 130.7, 129.7, 128.8, 128.4, 127.6, 127.3, 126.4, 126.1, 125.5, 125.3, 124.4, 113.8, 55.2, 52.4; HRMS: calcd. for $C_{24}H_{20}O$: 324.1514 [M+]; found: 354.1518.

1-((4-Fluorophenyl)(4-methoxyphenyl)methyl)naphthalene (Table 2, **13**). White solid: mp 117–120 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.48–7.33 (m, 3H), 7.10–6.91 (m, 7H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5 (d, *J* = 243.4 Hz), 158.2, 140.1, 139.9, 135.7, 134.0, 131.9, 131.0 (d, *J* = 7.7 Hz), 130.5, 128.8, 127.4, 126.2, 125.6, 125.3, 124.3, 115.2 (d, *J* = 21.1 Hz), 113.9, 55.1, 51.6; HRMS: calcd. for $C_{24}H_{19}FO$: 342.1420 [M+]; found: 342.1424.

1,1'-((4-Methoxyphenyl)methylene)dinaphthalene (Table 2, **15**). White solid: mp 193–195 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.88 (s, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3,

140.3, 135.5, 134.1, 131.9, 130.8, 128.8, 127.7, 127.4, 126.3, 125.6, 125.4, 124.3, 114.0, 55.2, 48.8; HRMS: calcd. for $C_{28}H_{22}O$: 374.1641 [M+]; found: 374.1676.

2,2'-((6-Methoxynaphthalen-2-yl)methylene)dinaphthalene (Table 2, **16**). White solid: mp 85–87 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.77 (m, 4H), 7.73–7.67 (m, 3H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.55 (s, 2H), 7.49–7.33 (m, 8H), 7.15–7.09 (m, 2H), 6.00 (s, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ157.7, 141.4, 138.9, 133.6, 133.4, 132.3, 129.5, 129.0, 128.8, 128.4, 128.1, 128.1, 128.0, 127.7, 127.0, 126.1, 125.8, 118.9, 105.7, 57.1, 55.4; HRMS: calcd. for $C_{32}H_{24}O$: 424.1827 [M+]; found: 424.1832.

1,3'-((6-Methoxynaphthalen-2-yl)methylene)dinaphthalene (Table 2, **17** and **18**). White solid: mp 95–97 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.71–7.64 (m, 2H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.48 (s, 1H), 7.47–7.31 (m, 8H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.55 (s, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.7, 141.5, 139.8, 139.0, 134.1, 133.6, 133.4, 132.4, 132.1, 129.5, 129.0, 129.0, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.5, 127.0, 126.3, 126.0, 125.7, 125.6, 125.4, 124.5, 118.8, 105.7, 55.4, 53.3; HRMS: calcd. for $C_{32}H_{24}O$: 424.1827 [M+]; found: 424.1833.

1,1'-((6-Methoxynaphthalen-2-yl)methylene)dinaphthalene (Table 2, **19**). White solid: mp 89–91 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.47–7.40 (m, 3H), 7.38–7.28 (m, 5H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.10–7.05 (m, 2H), 6.95 (d, *J* = 7.2 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.7, 139.9, 138.8, 134.1, 133.5, 131.9, 129.5, 129.1, 129.0, 128.9, 128.3, 128.0, 127.5, 127.1, 126.4, 125.6, 125.5, 124.3, 118.8, 105.7, 55.4, 49.5; HRMS: calcd. for $C_{32}H_{24}O$: 424.1827 [M+]; found: 424.1832.

Trinaphthalen-1-ylmethane (Table 2, **20**). White solid: mp 266–268 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (t, *J* = 8.2 Hz, 6H), 7.76 (d, *J* = 8.0 Hz, 3H), 7.60 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.26 (t, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 7.2 Hz, 3H), 5.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.5, 134.2, 131.9,

128.9, 128.1, 127.6, 126.5, 125.6, 125.5, 124.0, 45.6; HRMS: calcd. for $C_{31}H_{22}$: 394.1722 [M+]; found: 394.1725.

2-Methoxy-6-(4-methoxybenzyl)naphthalene (Table 3, **27** and **40**). White solid: mp 101–102 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 8.4, 1H), 7.64 (d, *J* = 8.4, 1H), 7.53 (s, 1H), 7.26 (d, *J* = 8.4, 1H), 7.16–7.08 (m, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.04 (s, 1H), 3.90 (s, 3H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1, 157.4, 136.8, 133.4, 133.2, 130.0, 129.1, 128.2, 127.0, 126.9, 118.8, 114.0, 105.8, 55.3, 41.1; HRMS: calcd. for $C_{19}H_{18}O_2$: 278.1307 [M+]; found: 278.1310.

2-Methoxy-6-(4-methylbenzyl)naphthalene (Table 3, **28**). White solid: mp 98–100 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.13–7.07 (m, 6H), 4.06 (s, 2H), 3.90 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 138.3, 136.7, 135.6, 133.2, 129.2, 129.1, 129.0, 128.2, 127.0, 126.9, 118.8, 105.8, 55.4, 41.6, 21.1; HRMS: calcd. for $C_{19}H_{18}O$: 262.1358 [M+]; found: 262.1354.

2-Methoxy-6-(3-methylbenzyl)naphthalene (Table 3, **29**). White solid: mp 75–77 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.14–7.09 (m, 2H), 7.06–6.99 (m, 3H), 4.07 (s, 2H), 3.91 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 141.2, 138.1, 136.5, 133.2, 129.9, 129.1, 128.4, 128.3, 127.0, 126.9, 126.1, 118.8, 105.8, 55.4, 41.9, 21.5; HRMS: calcd. for $C_{19}H_{18}O$: 262.1358 [M+]; found: 262.1362.

2-Benzyl-6-methoxynaphthalene (Table 3, **30** and **41**). White solid: mp 86–88 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.4, 1H), 7.65 (d, *J* = 8.0, 1H), 7.56 (s, 1H), 7.32–7.18 (m, 6H), 7.13–7.09 (m, 2H), 4.11 (s, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 141.3, 136.3, 133.2, 129.1, 129.1, 128.5, 128.2, 127.0, 126.1, 118.8, 105.8, 55.3, 42.0; HRMS: calcd. for $C_{18}H_{16}O$: 248.1201 [M+]; found: 248.1205.

2-Methoxy-6-(naphthalen-1-ylmethyl)naphthalene (Table 3, **31** and **36**). White solid: mp 112–114 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J*

= 9.6 Hz, 1H), 7.53 (s, 1H), 7.48–7.40 (m, 3H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.11–7.07 (m, 2H), 4.57 (s, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 136.8, 135.9, 134.0, 133.2, 132.3, 129.1, 128.7, 127.5, 127.2, 127.0, 126.1, 125.6, 124.4, 118.8, 105.7, 55.3, 39.1; HRMS: calcd. for $C_{22}H_{18}O$: 298.1358 [M+]; found: 298.1361.

2-(4-Fluorobenzyl)-6-methoxynaphthalene (Table 3, **32**). White solid: mp 74–75 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.23 (d, *J* = 1.2 Hz, 1H), 7.20–7.09 (m, 4H), 6.97 (t, *J* = 8.6 Hz, 2H), 4.07 (s, 2H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.5 (d, *J* = 242.5 Hz), 157.5, 136.9, 136.2, 133.3, 130.4 (d, *J* = 7.7 Hz), 129.1, 128.0, 127.1 (d, *J* = 15.7 Hz), 118.9, 115.3 (d, *J* = 21.1 Hz), 105.8, 55.4, 41.1; HRMS: calcd. for $C_{18}H_{15}FO$: 266.1107 [M+]; found: 266.1111.

3-((6-Methoxynaphthalen-2-yl)methyl)thiophene (Table 3, **33**). White solid: mp 69–71 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 7.30 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.14–7.09 (m, 2H), 6.96–6.92 (m, 2H), 4.10 (s, 2H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 141.8, 135.8, 133.3, 129.1, 128.6, 128.1, 127.0, 126.8, 125.7, 121.4, 118.8, 105.8, 55.4, 36.6; HRMS: calcd. for $C_{16}H_{14}OS$: 254.0765 [M+]; found: 254.0770.

2-(4-Methoxybenzyl)naphthalene (Table 3, **34**). White solid: mp 56–58 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82–7.72 (m, 3H), 7.61 (s, 1H), 7.47–7.39 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.08 (s, 2H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1, 139.2, 133.7, 133.2, 132.1, 130.0, 128.1, 127.7, 127.6, 127.0, 126.0, 125.4, 114.0, 55.3, 41.3; HRMS: calcd. for $C_{18}H_{18}O$: 248.1201 [M+]; found: 248.1198.

1-(4-Methoxybenzyl)naphthalene (Table 3, **35** and **39**). White solid: mp 56–58 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02–7.98 (m, 1H), 7.89–7.83 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.49–7.38 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.39 (s, 2H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.0, 137.1, 134.0, 132.7, 132.2, 129.7, 128.7, 127.2, 127.1, 126.0, 125.6, 124.3, 114.4, 55.3, 38.2; HRMS: calcd. for $C_{18}H_{18}O$: 248.1201 [M+]; found: 248.1205.

2-(1-(4-Methoxyphenyl)ethyl)naphthalene (Table 3, **37**). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81–7.76 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.47–7.38 (m, 2H), 7.29 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 1.70 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.0, 144.2, 138.4, 133.6, 132.1, 128.7, 128.0, 127.8, 127.6, 126.9, 126.0, 125.4, 125.3, 113.8, 55.2, 44.1, 22.0; HRMS: calcd. for $C_{19}H_{18}O$: 262.1358 [M+]; found: 262.1362.

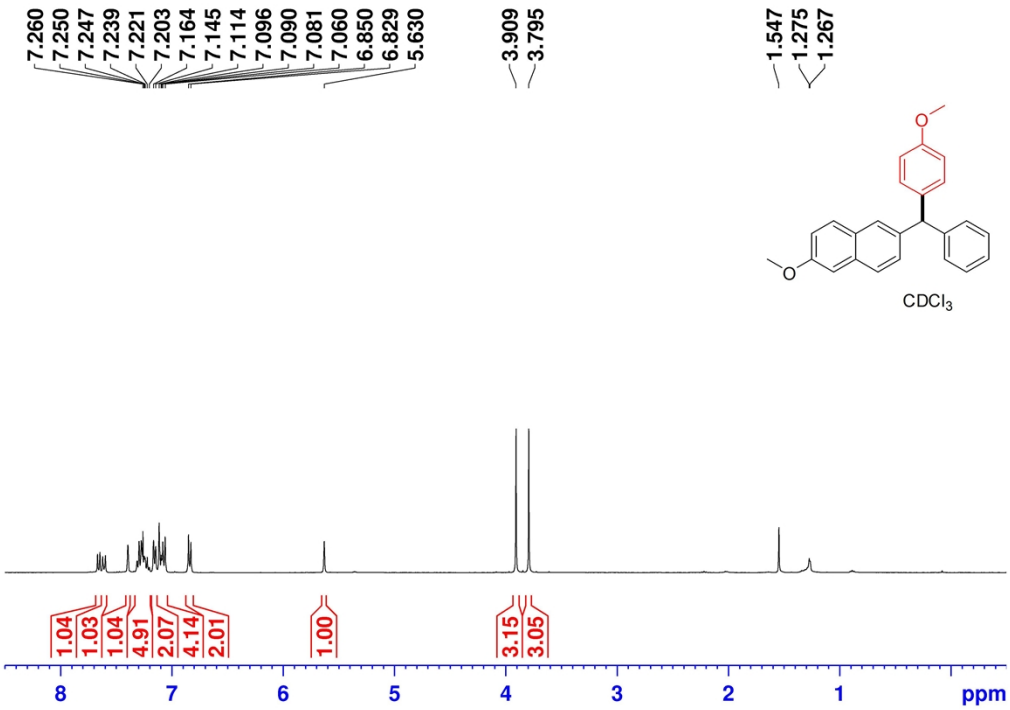
4-(4-Methoxybenzyl)biphenyl (Table 3, **38**). White solid: mp 89–91 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 2H), 3.79 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1, 141.0, 140.8, 139.0, 133.1, 129.9, 129.2, 128.8, 127.2, 127.1, 127.0, 114.0, 55.2, 40.7; HRMS: calcd. for $C_{20}H_{18}O$: 274.1358 [M+]; found: 274.1354.

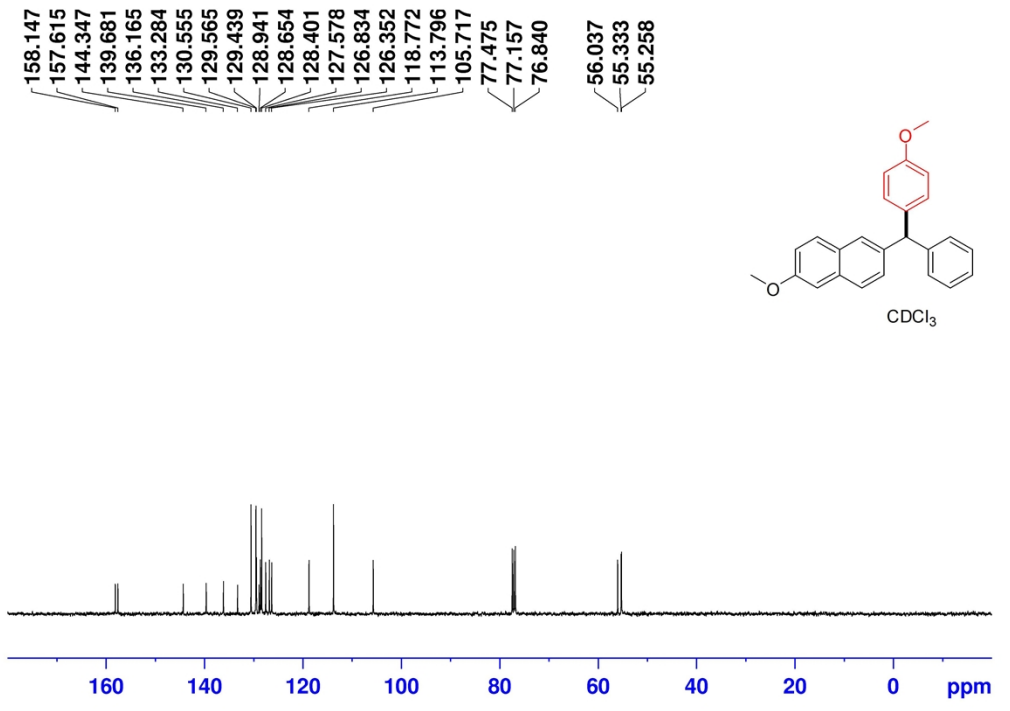
References

1. (a) J. van Soolingen, H. D. Verkruijsse, M. A. Keegstra and L. Brandsma, Synth. Commun., 1990, **20**, 3153; (b) L. Brandsma, S. F. Vasilevsky and H. D. Verkruijsse, in *Application of Transition Metal Catalysts in Organic Synthesis*, Springer, New York, 1998, 3–4.

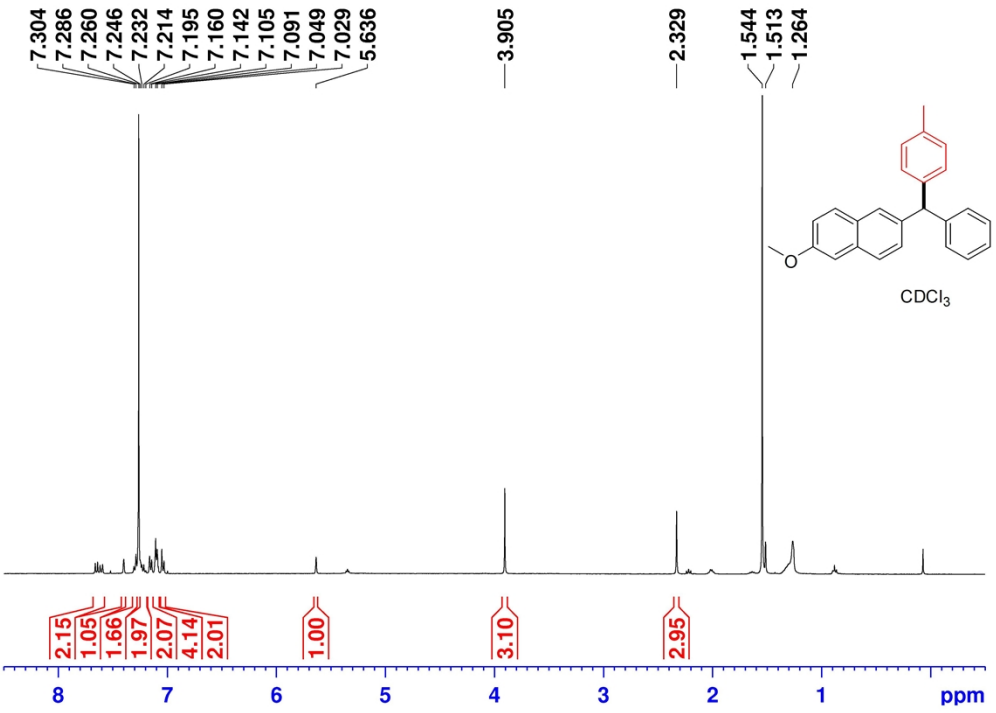
^{1}H NMR and ^{13}C NMR spectra of the products

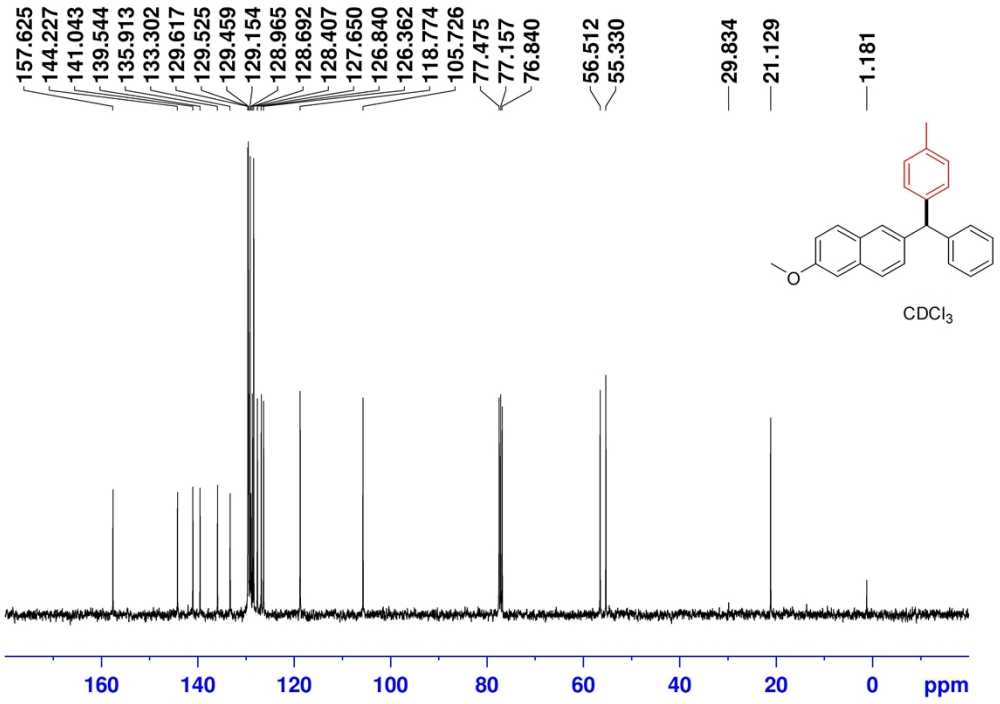
2-Methoxy-6-((4-methoxyphenyl)(phenyl)methyl)naphthalene (Table 2**, 2** and **9)**



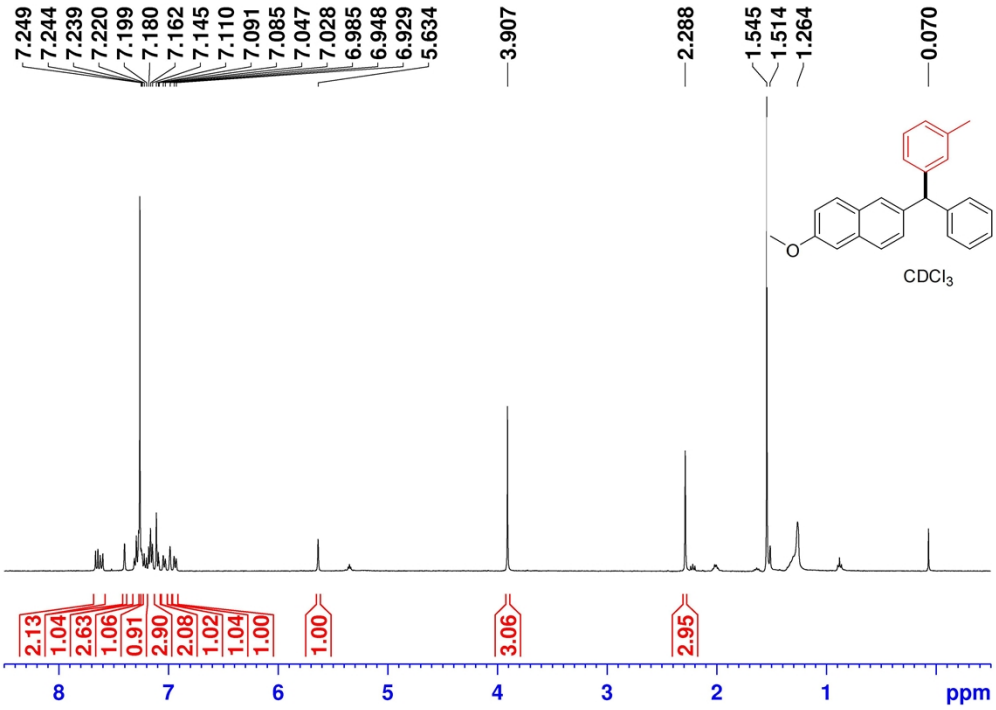


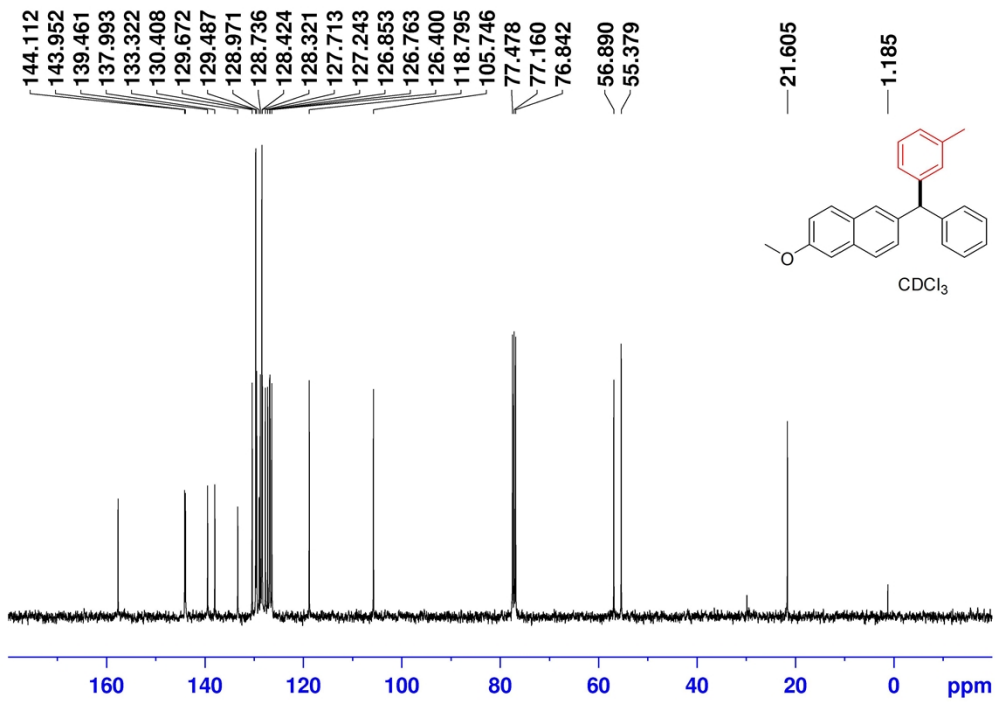
2-Methoxy-6-(phenyl(p-tolyl)methyl)naphthalene (Table 2, **3**)



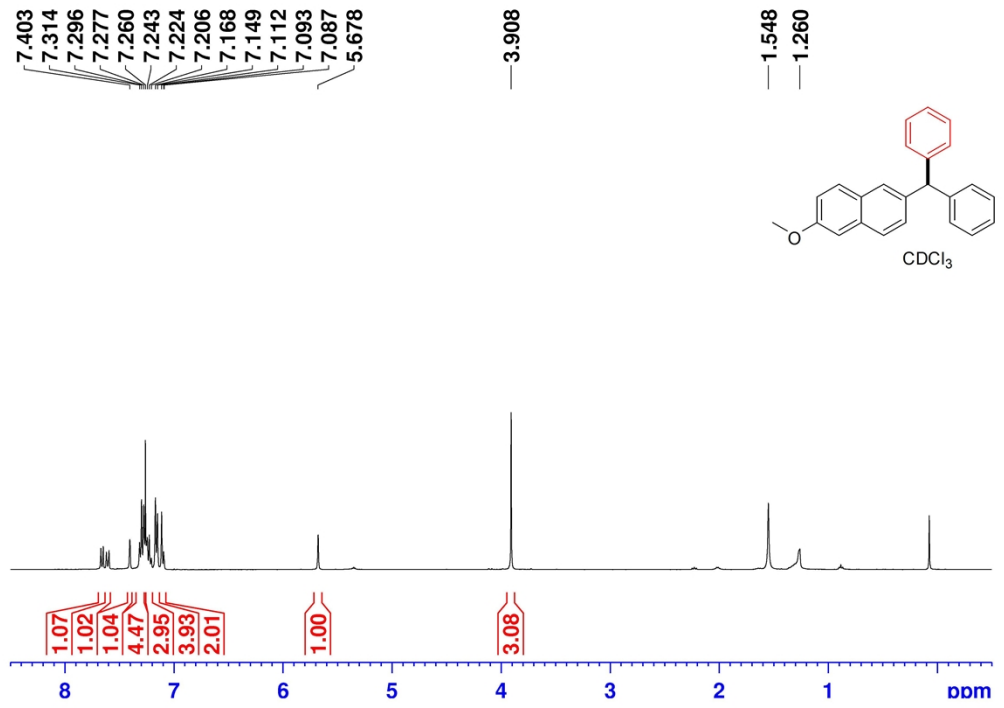


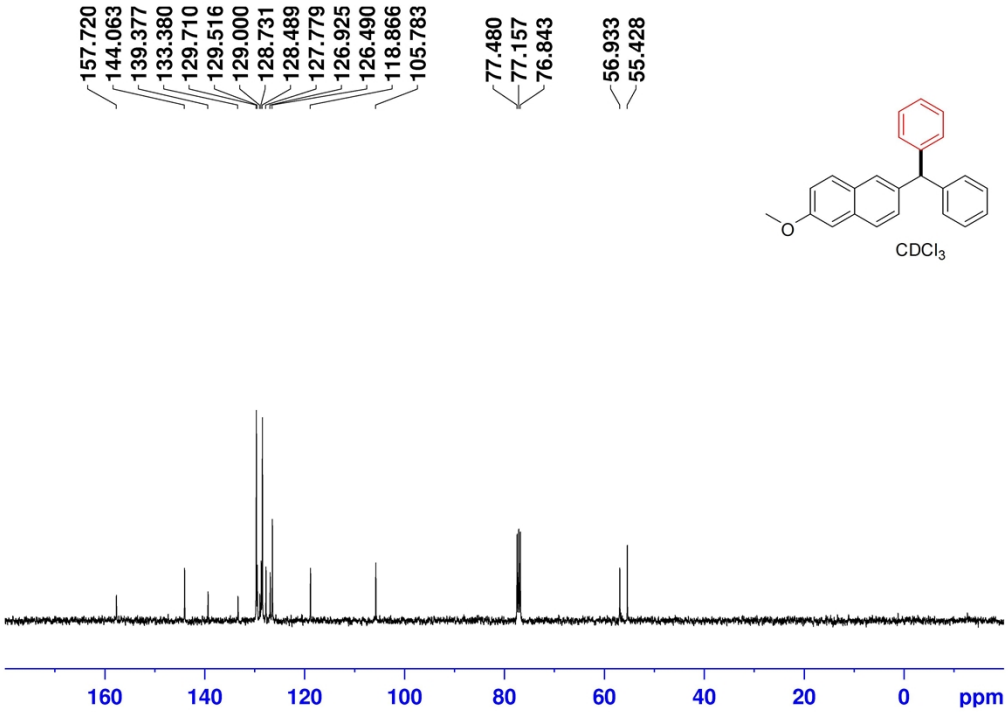
2-Methoxy-6-(phenyl(m-tolyl)methyl)naphthalene (Table 2, **4**).



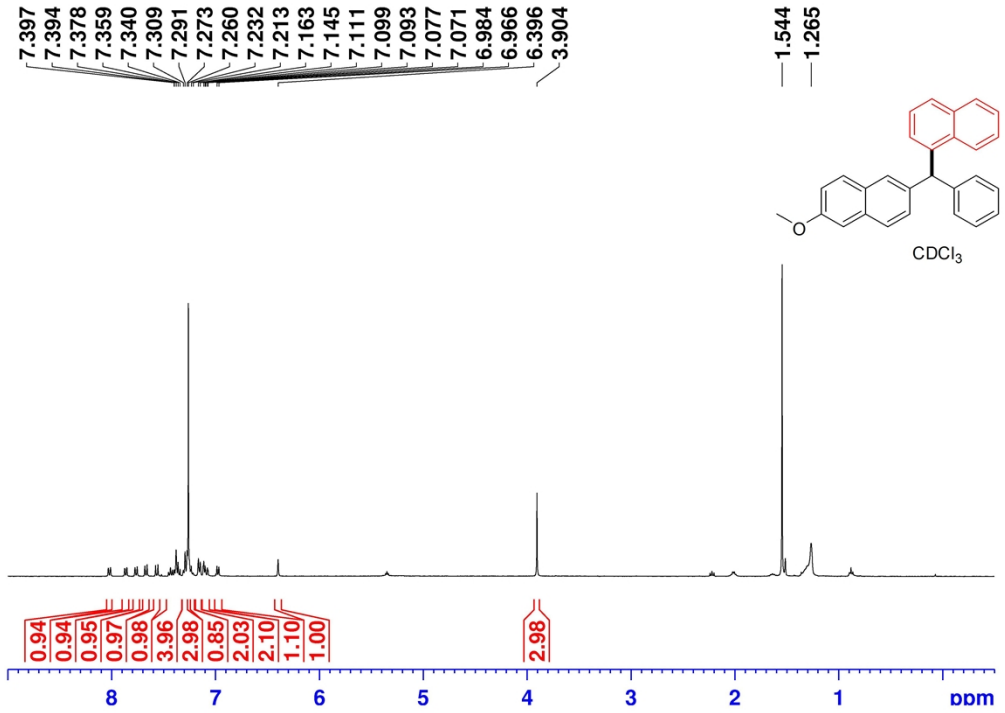


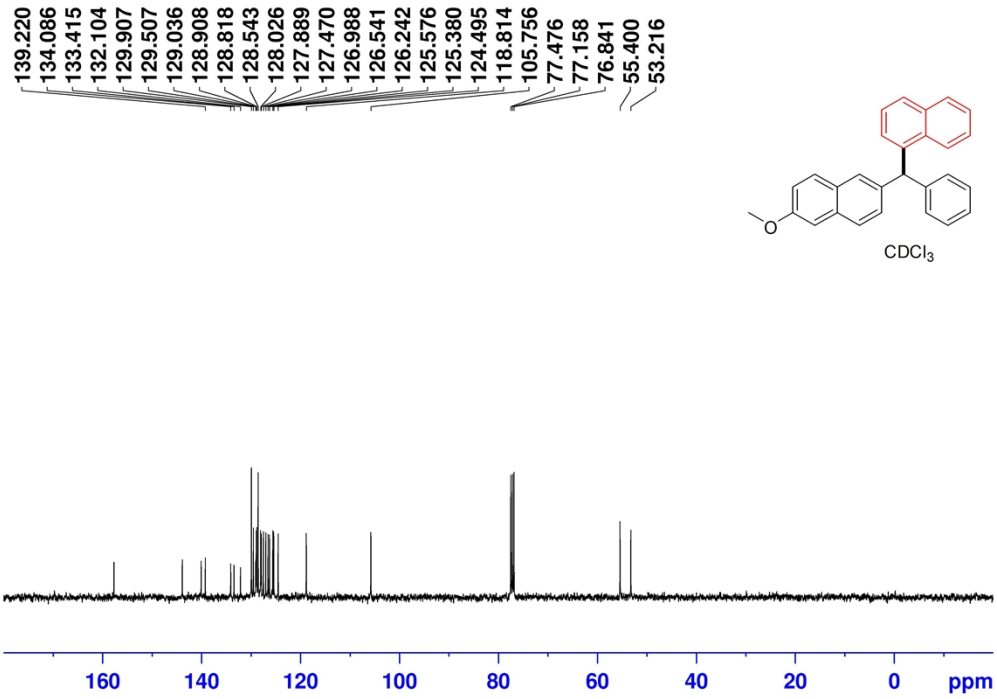
2-Benzhydryl-6-methoxynaphthalene (Table 2, **5**).



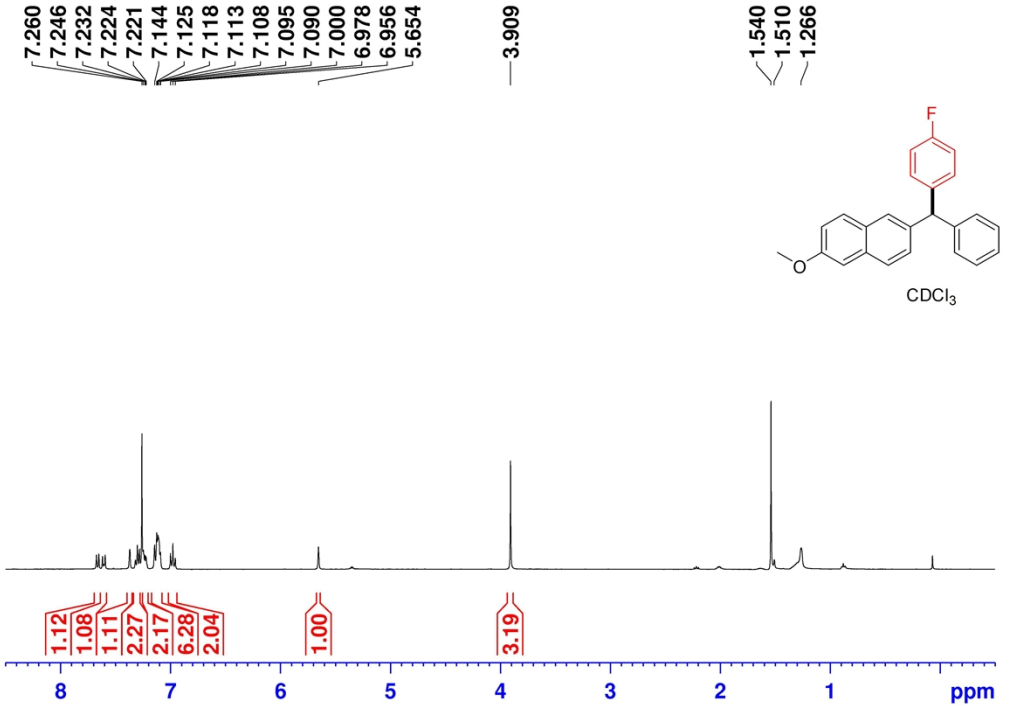


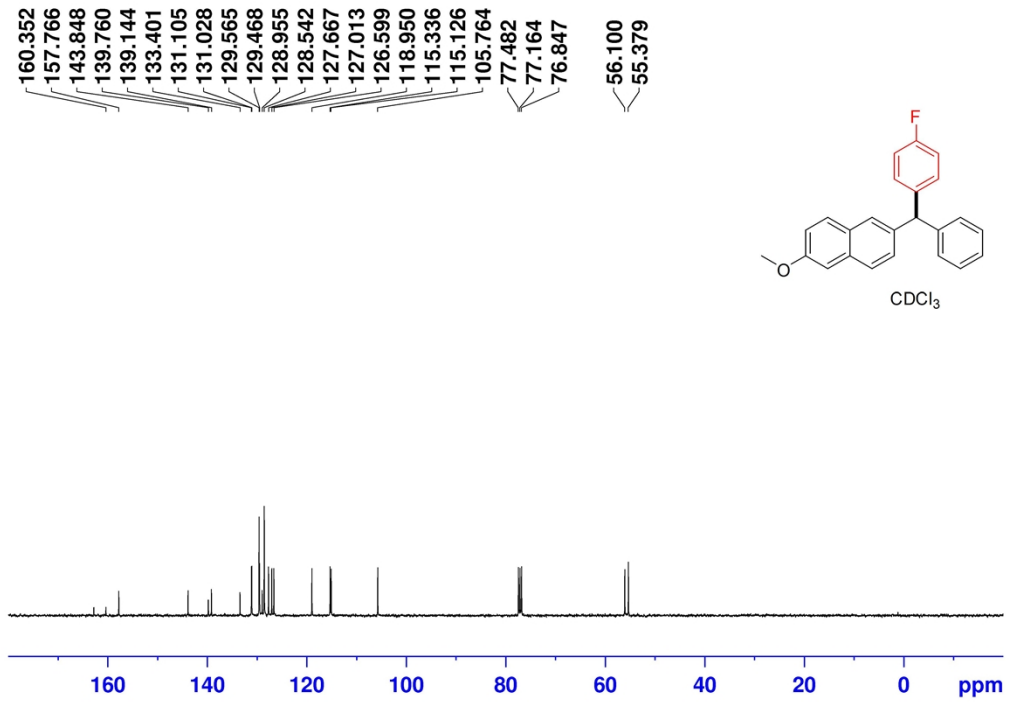
2-Methoxy-6-(naphthalen-1-yl(phenyl)methyl)naphthalene (Table 2, **6** and **14**).



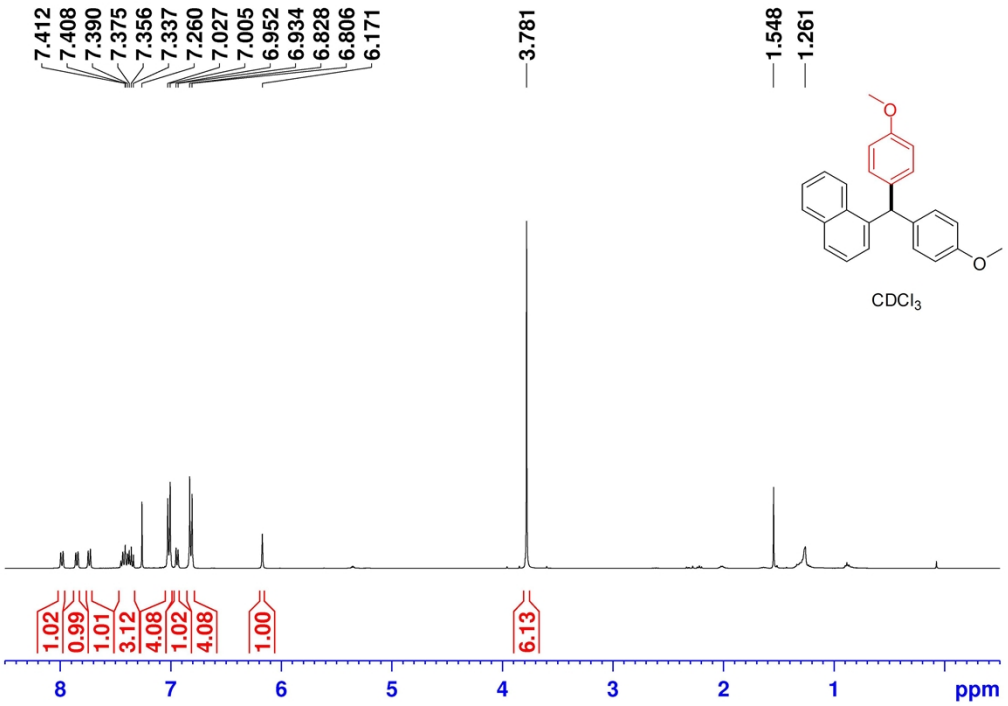


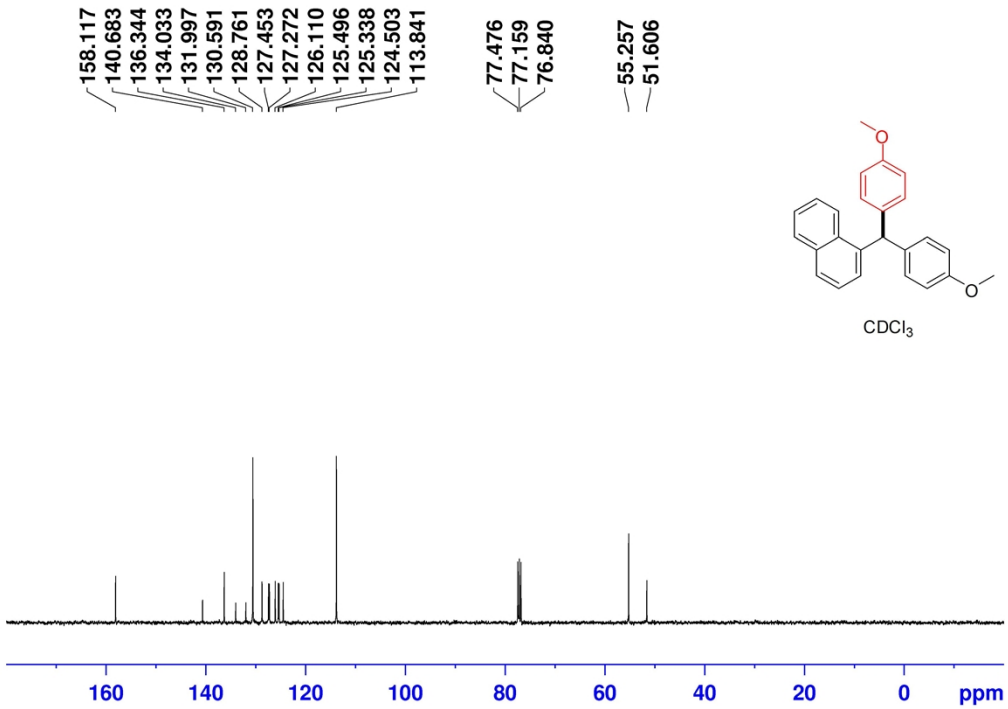
2-((4-Fluorophenyl)(phenyl)methyl)-6-methoxynaphthalene (Table 2, **8** and **10**).



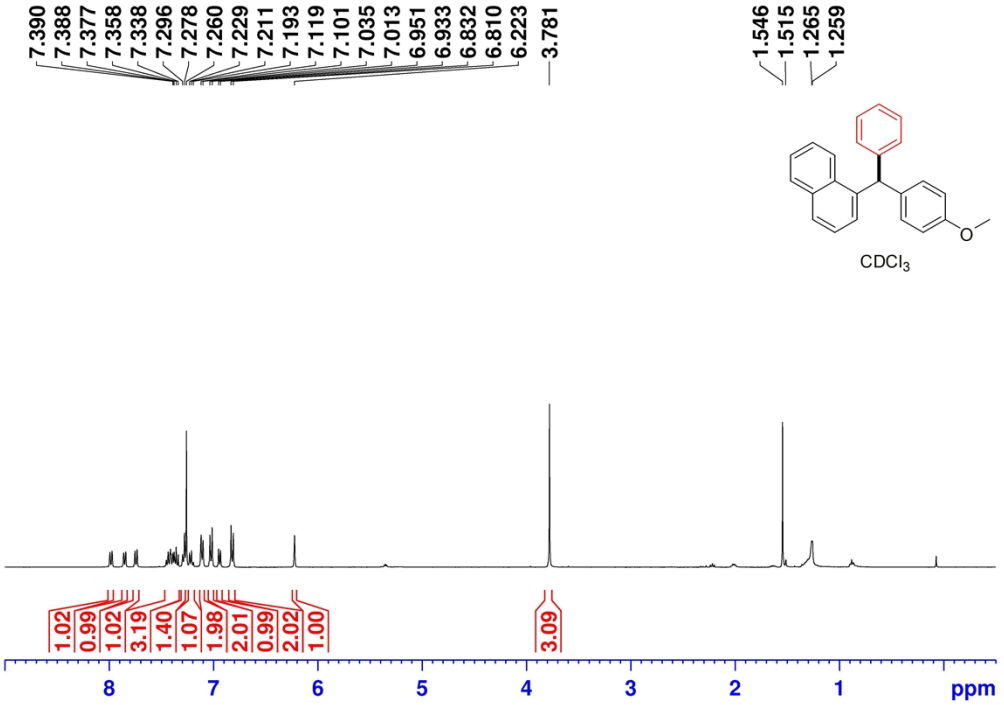


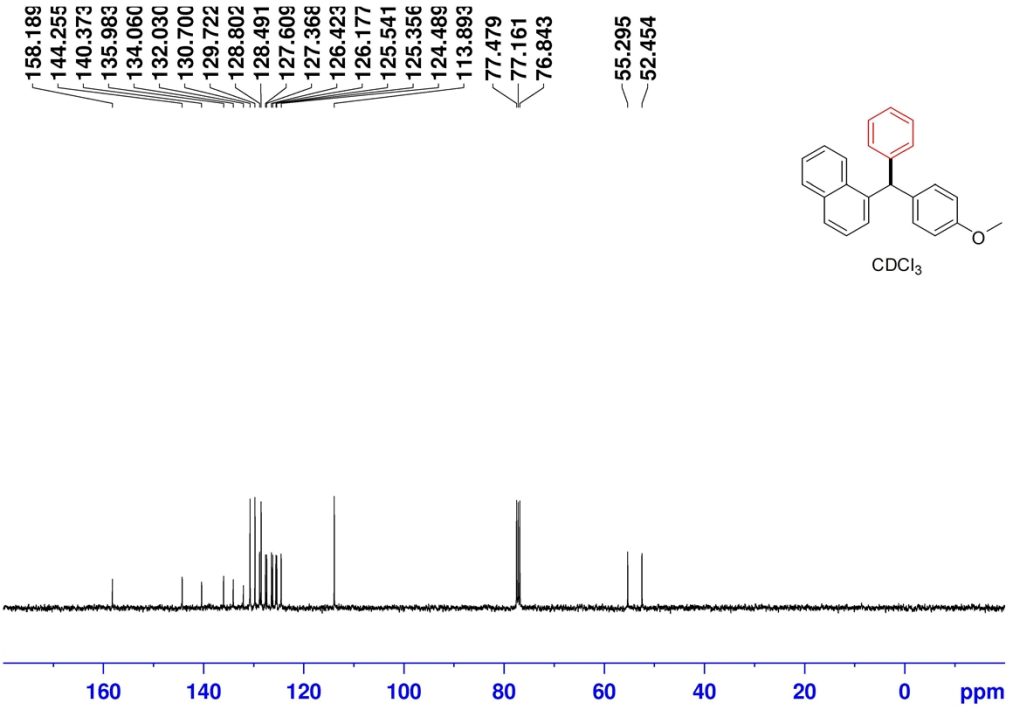
1-(Bis(4-methoxyphenyl)methyl)naphthalene (Table 2, **11**).



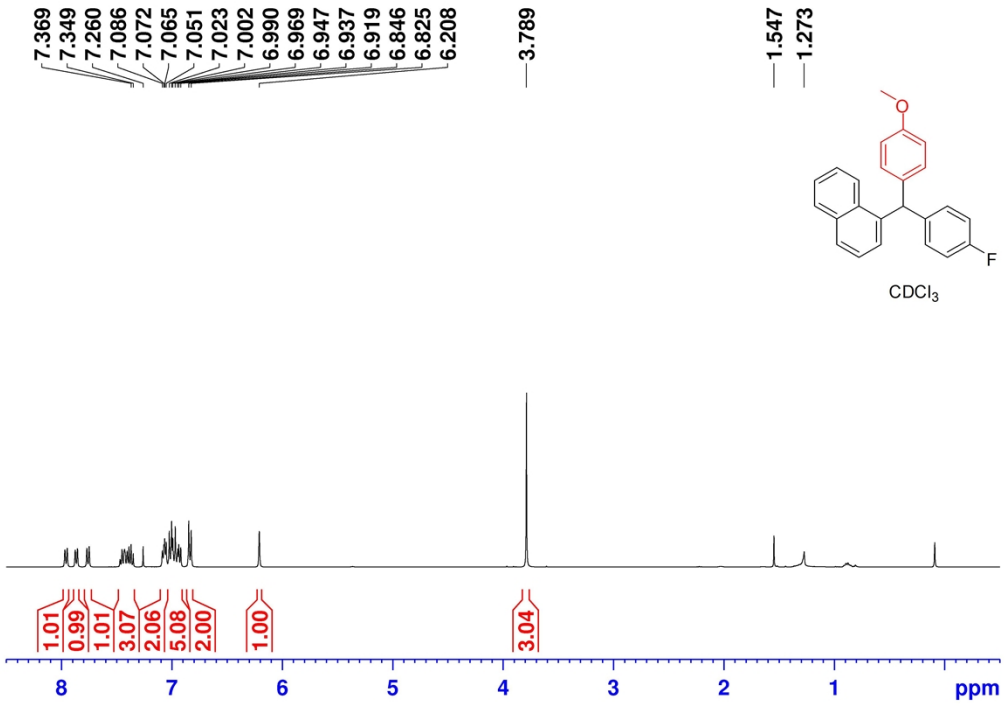


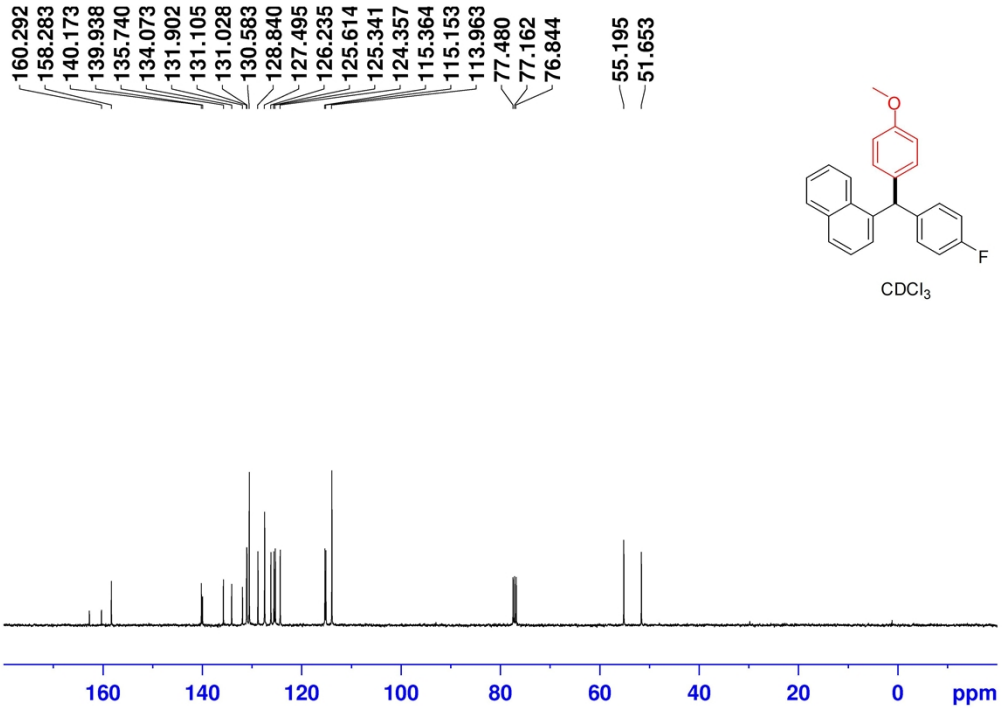
1-((4-Methoxyphenyl)(phenyl)methyl)naphthalene (Table 2, **12**).



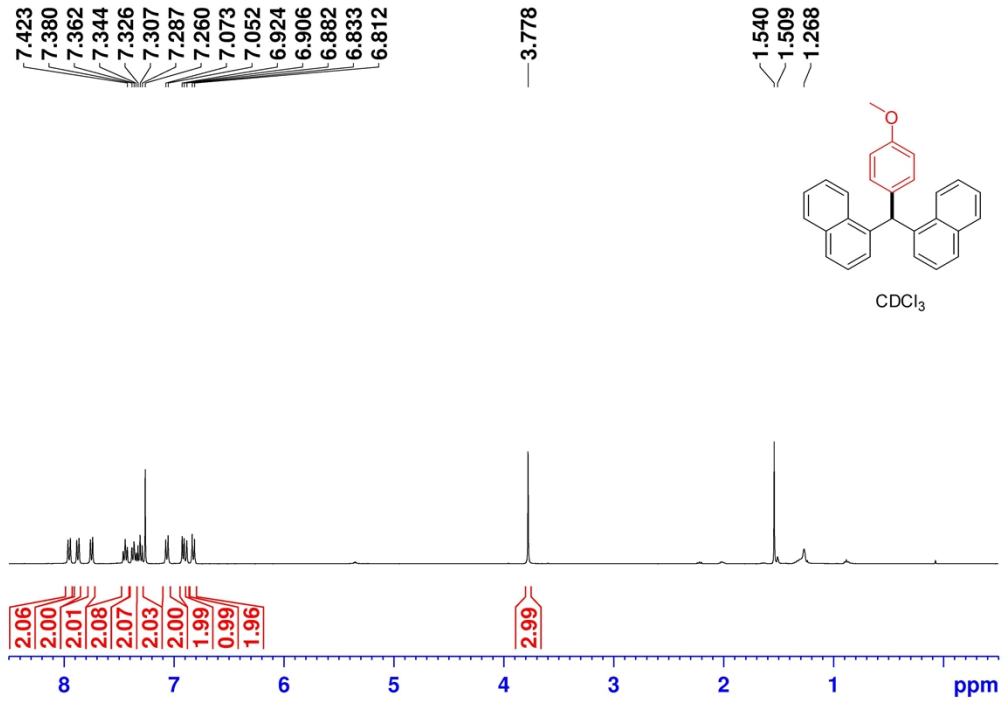


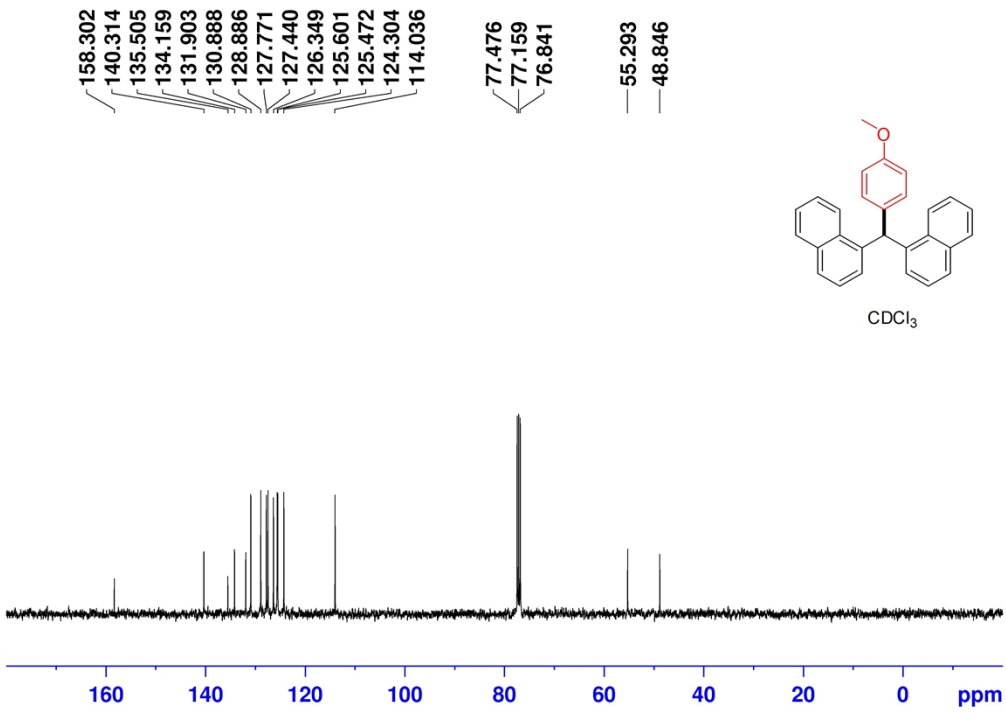
1-((4-Fluorophenyl)(4-methoxyphenyl)methyl)naphthalene (Table 2, **13**).



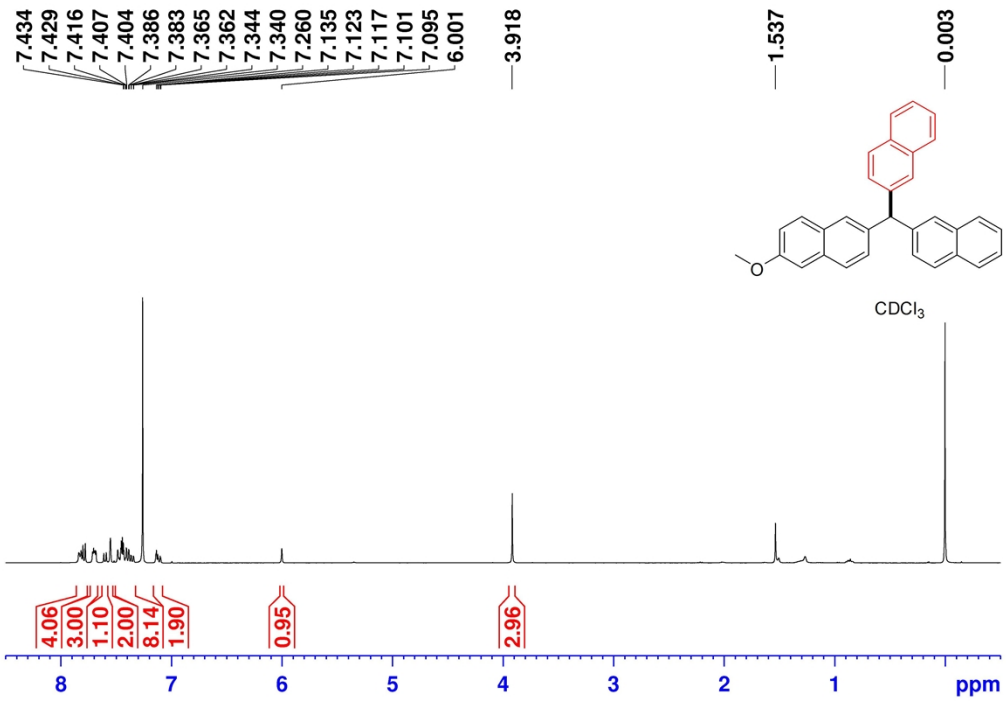


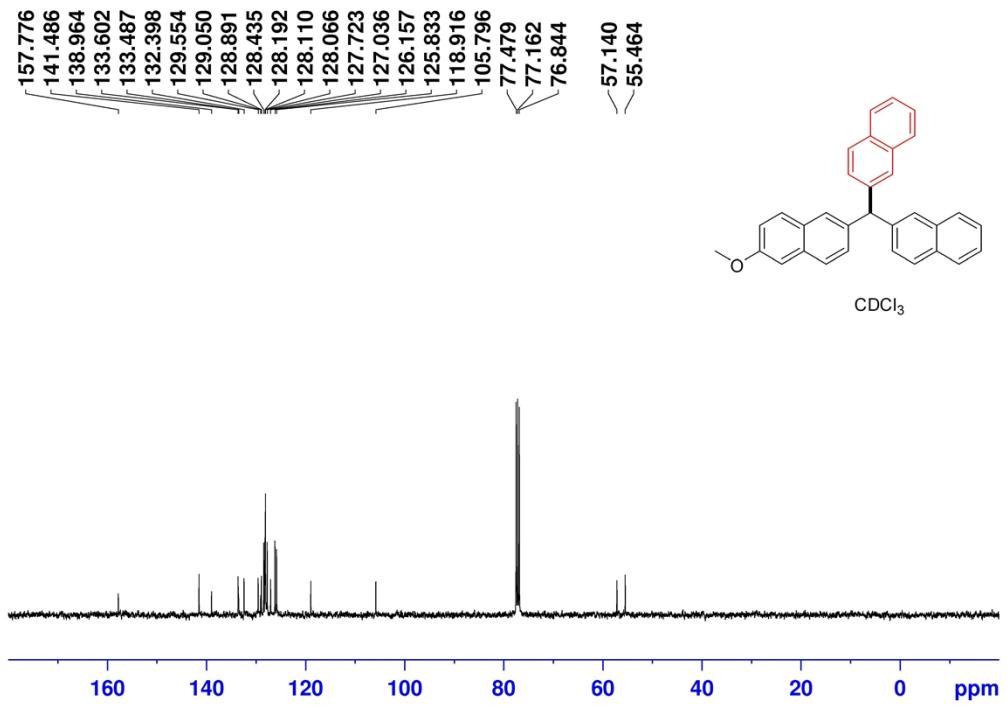
1,1'-((4-Methoxyphenyl)methylene)dinaphthalene (Table 2, **15**).



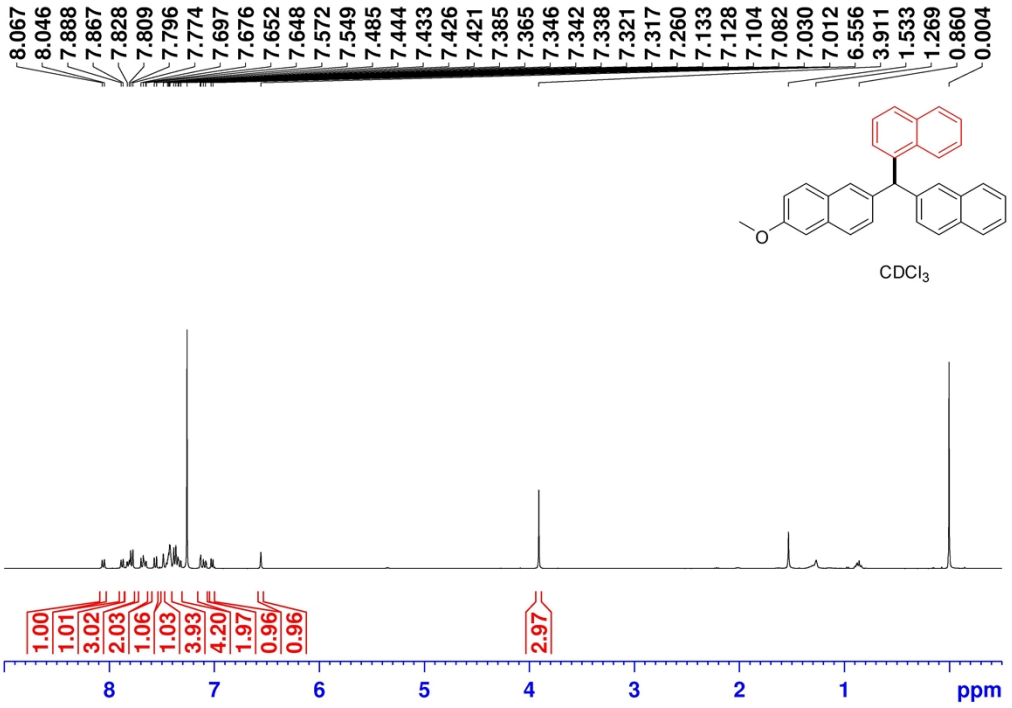


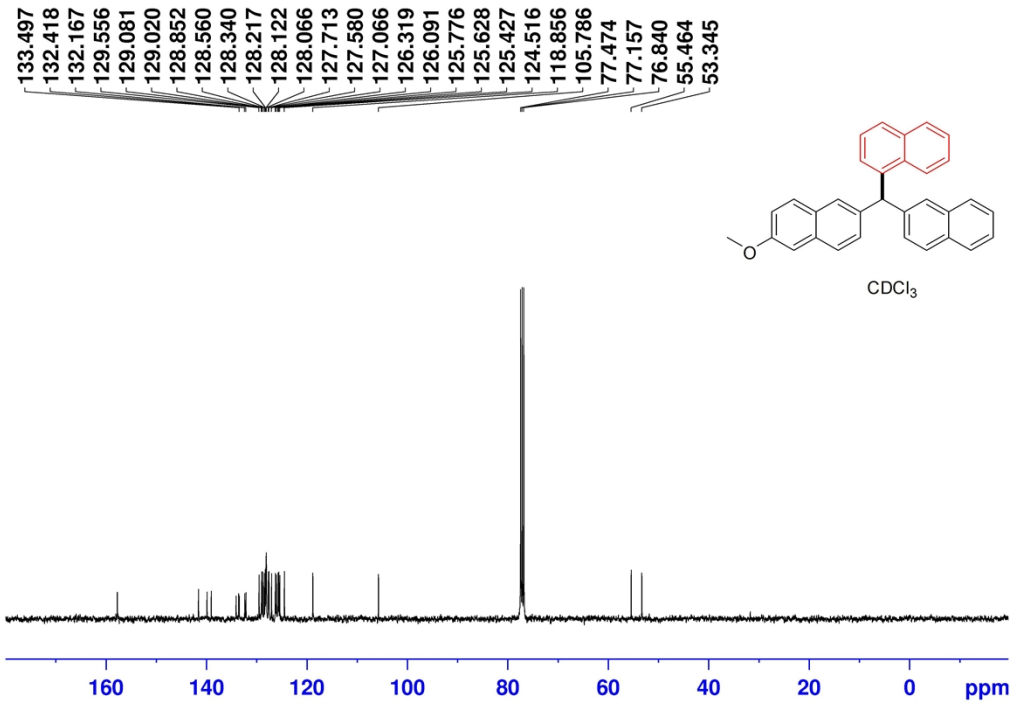
2,2'-((6-Methoxynaphthalen-2-yl)methylene)dinaphthalene (Table 2, **16**).



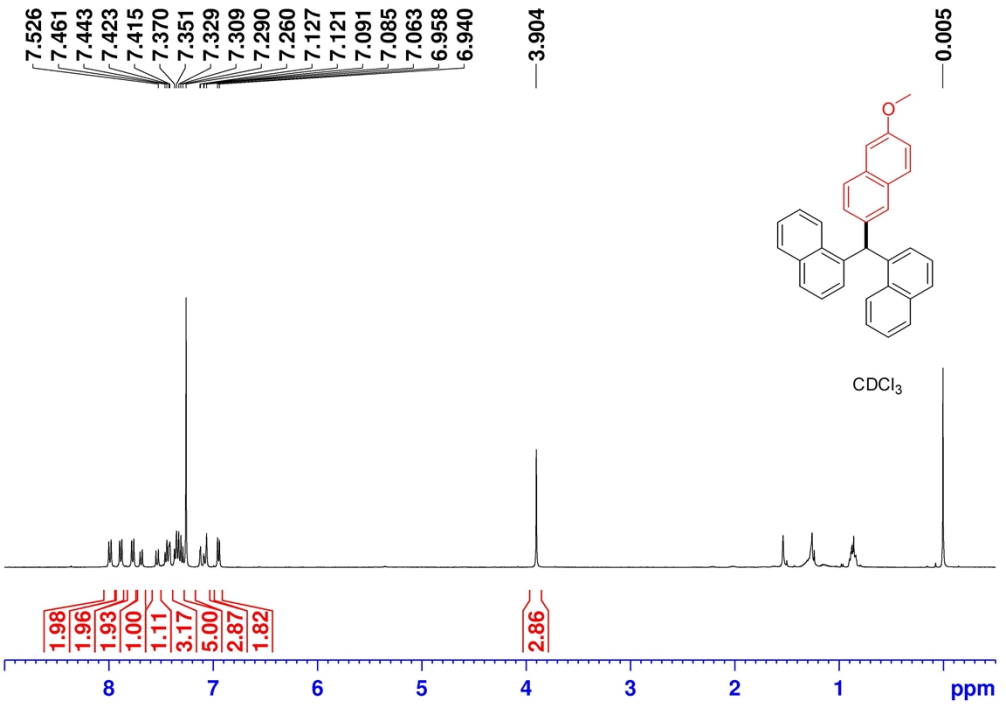


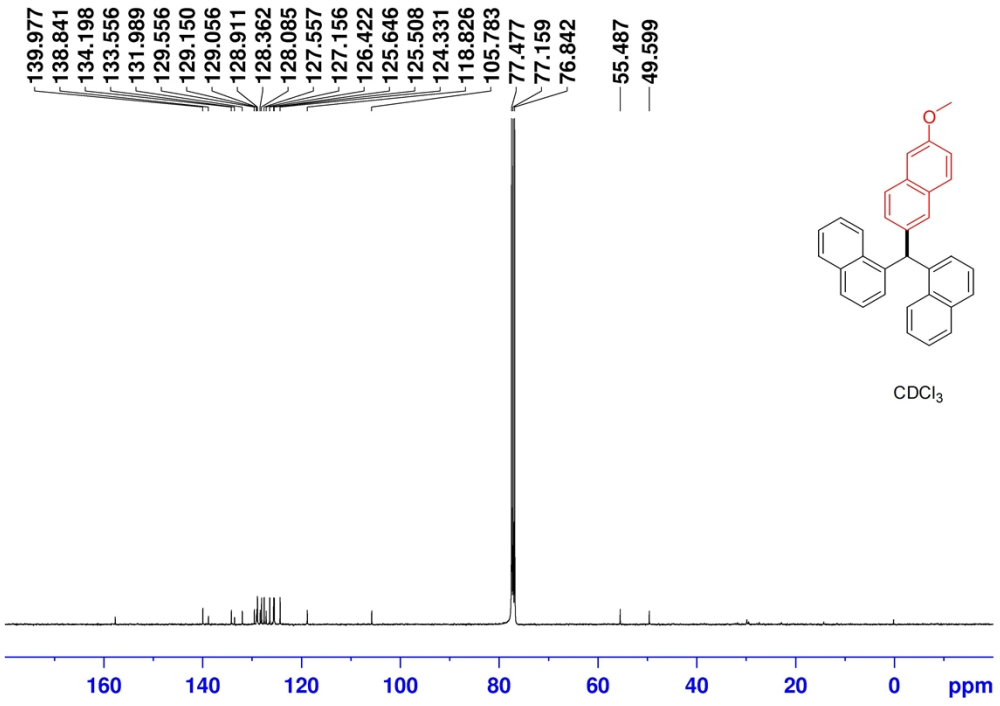
1,3'-((6-Methoxynaphthalen-2-yl)methylene)dinaphthalene (Table 2, **17** and **18**).



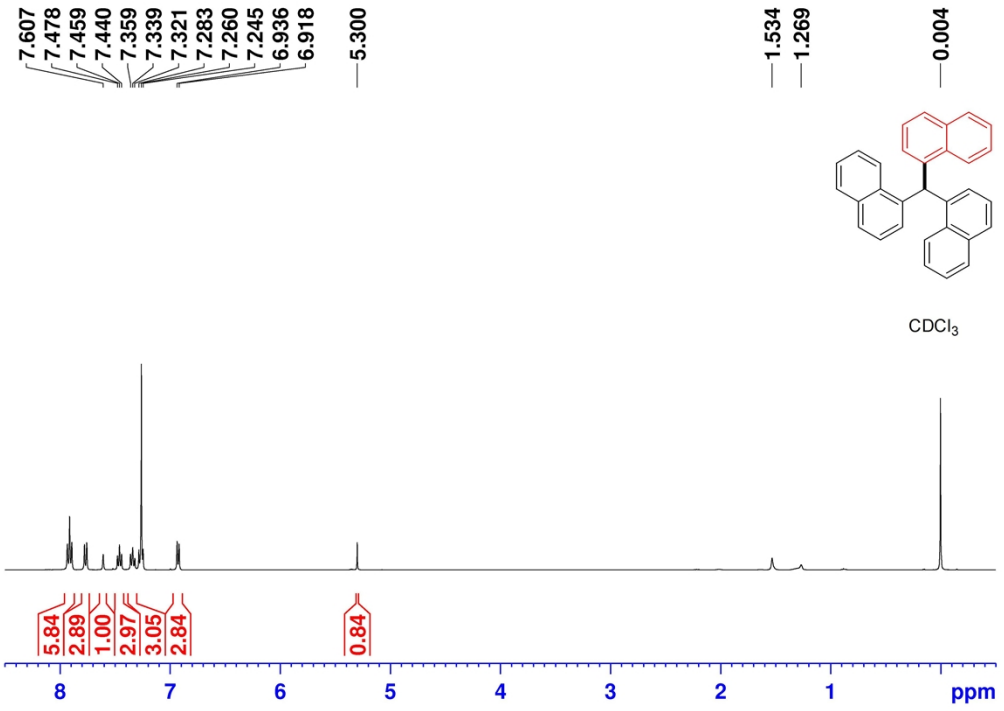


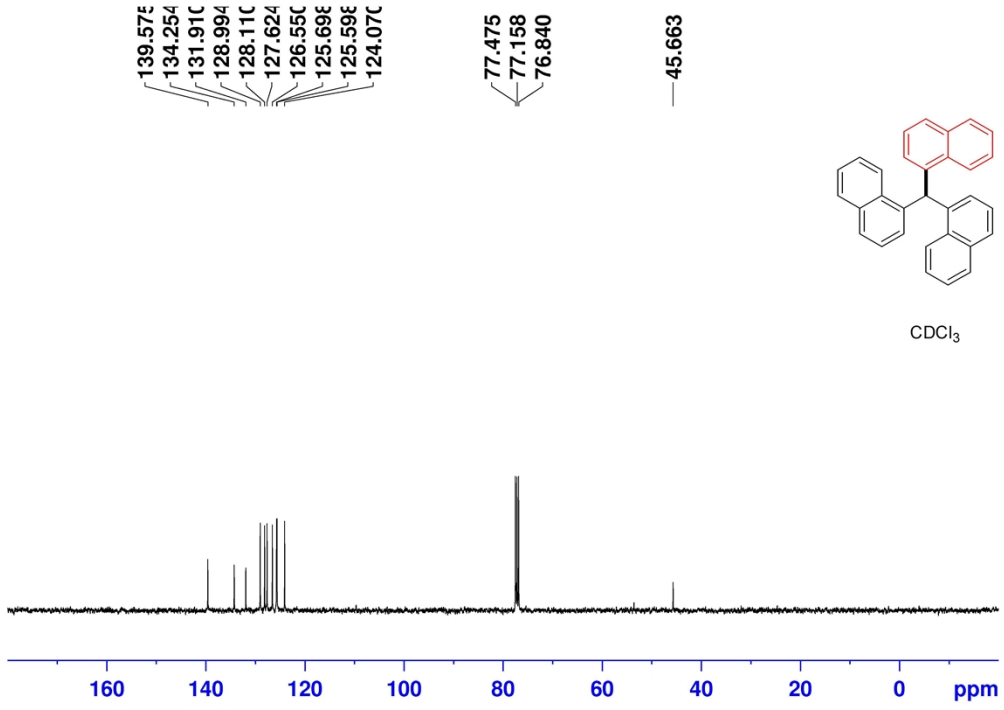
1,1'-((6-Methoxynaphthalen-2-yl)methylene)dinaphthalene (Table 2, **19**).



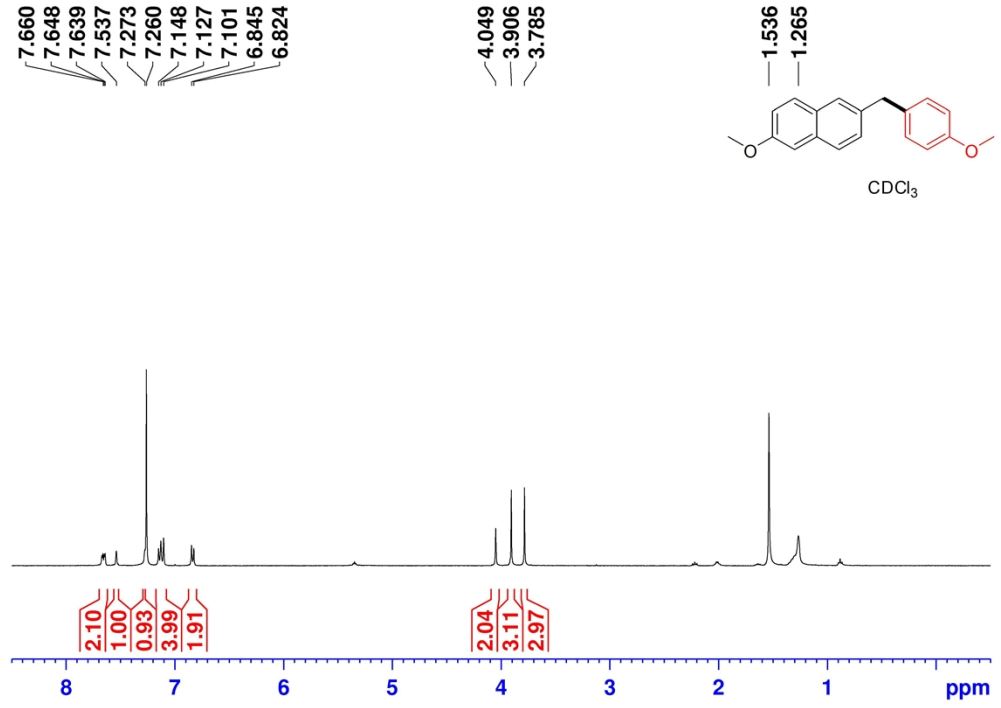


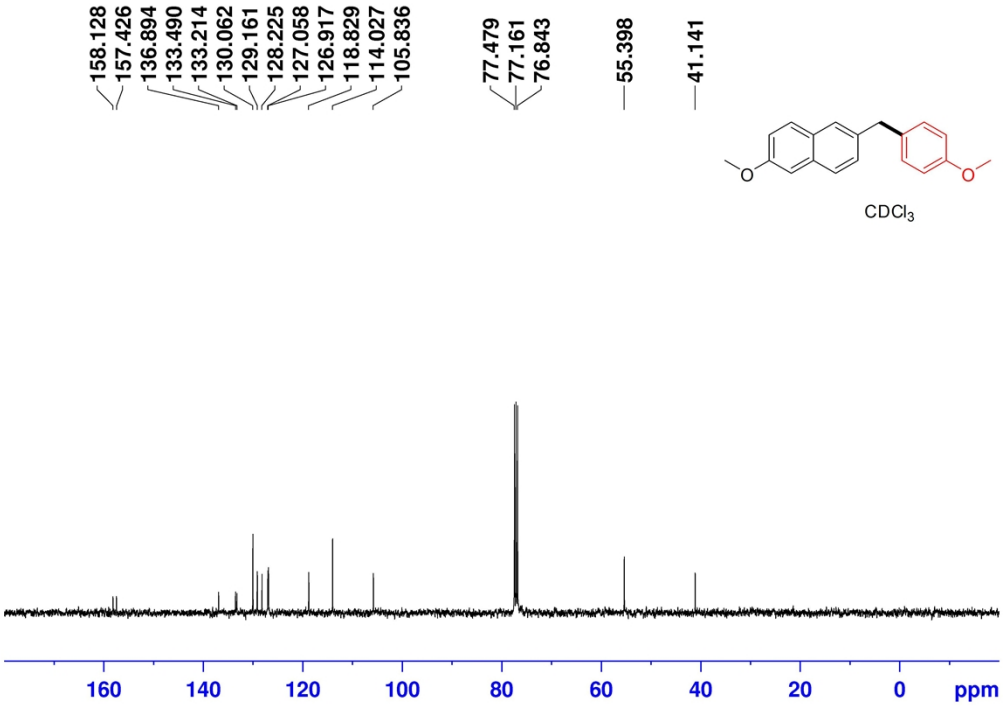
Trinaphthalen-1-ylmethane (Table 2, **20**).



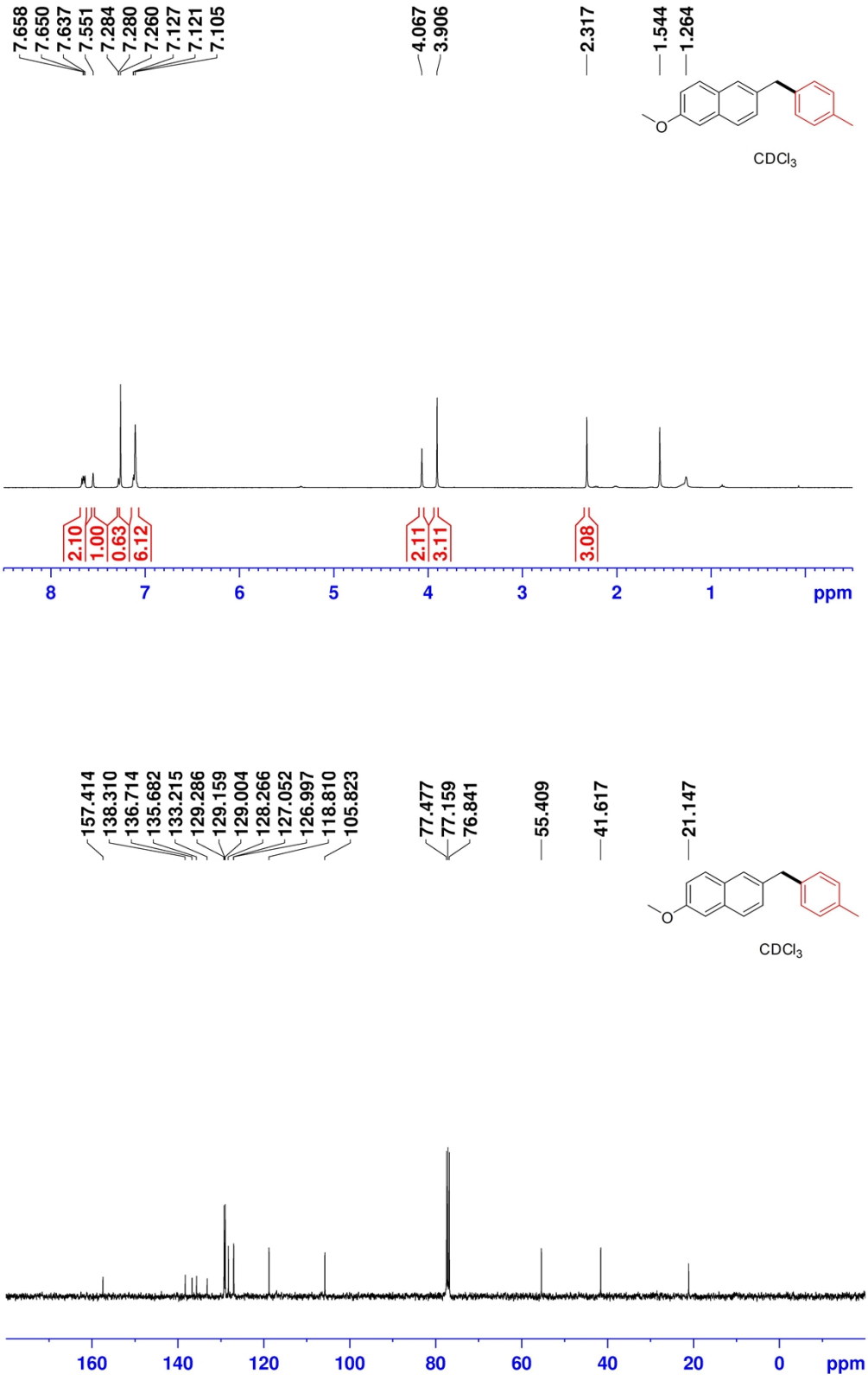


2-Methoxy-6-(4-methoxybenzyl)naphthalene (Table 3, **27** and **40**).

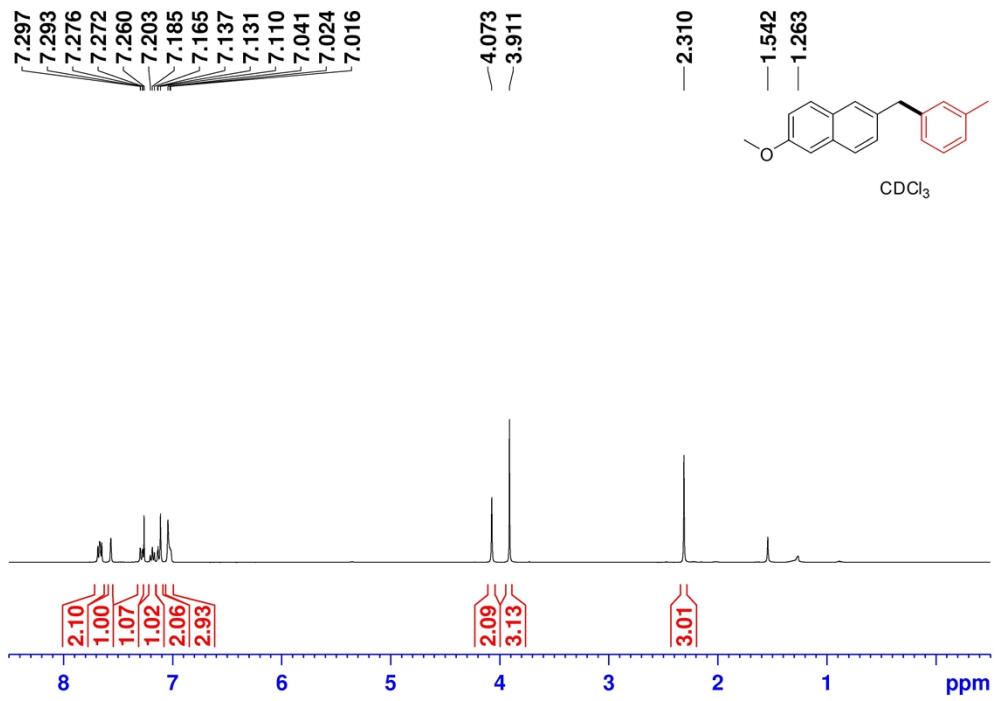


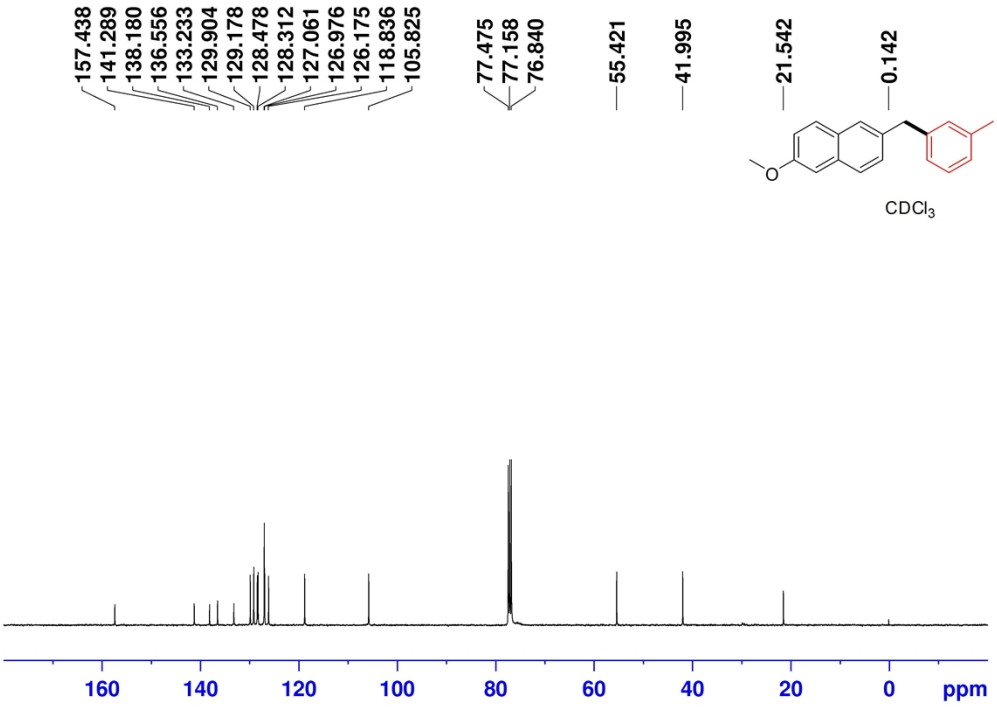


2-Methoxy-6-(4-methylbenzyl)naphthalene (Table 3, **28**).

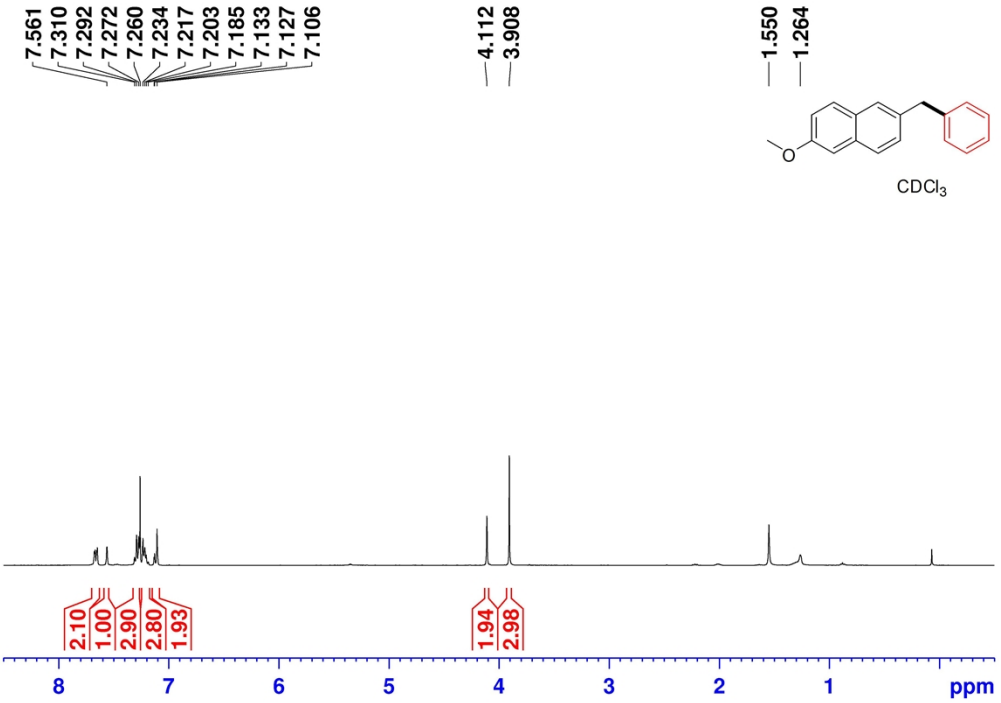


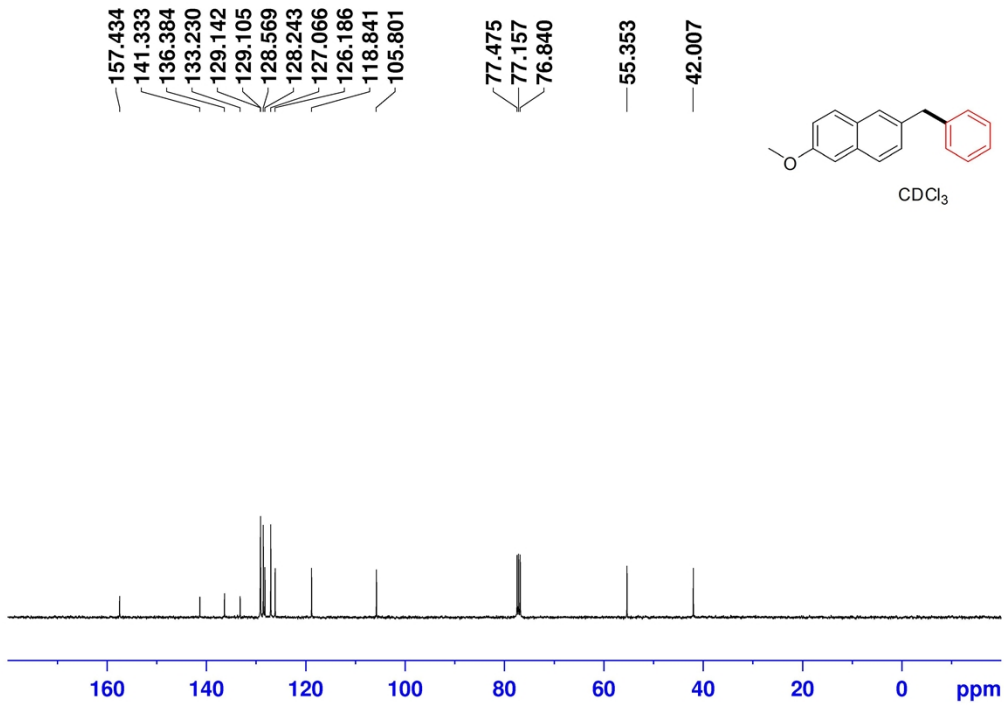
2-Methoxy-6-(3-methylbenzyl)naphthalene (Table 3, **29**).



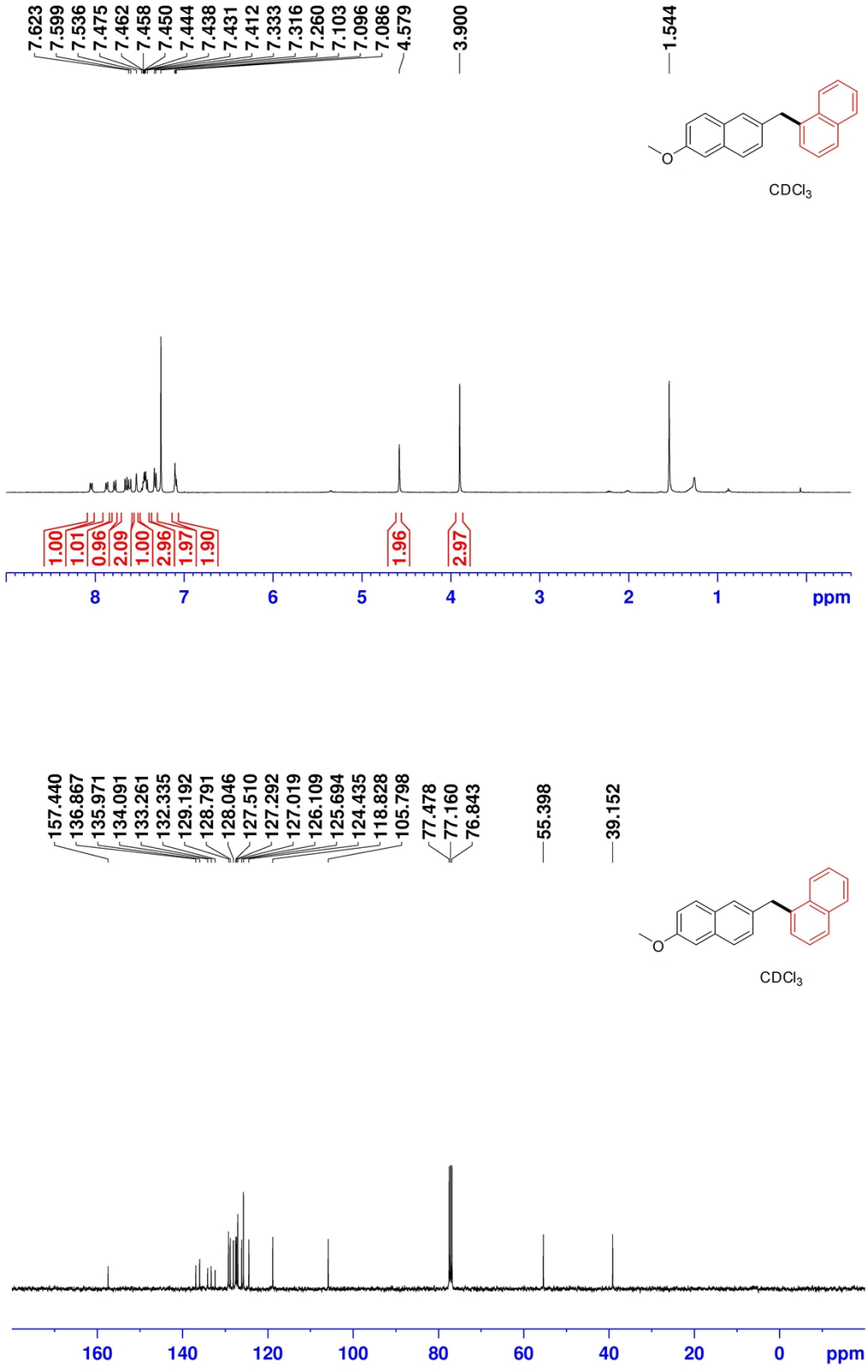


2-Benzyl-6-methoxynaphthalene (Table 3, **30** and **41**).

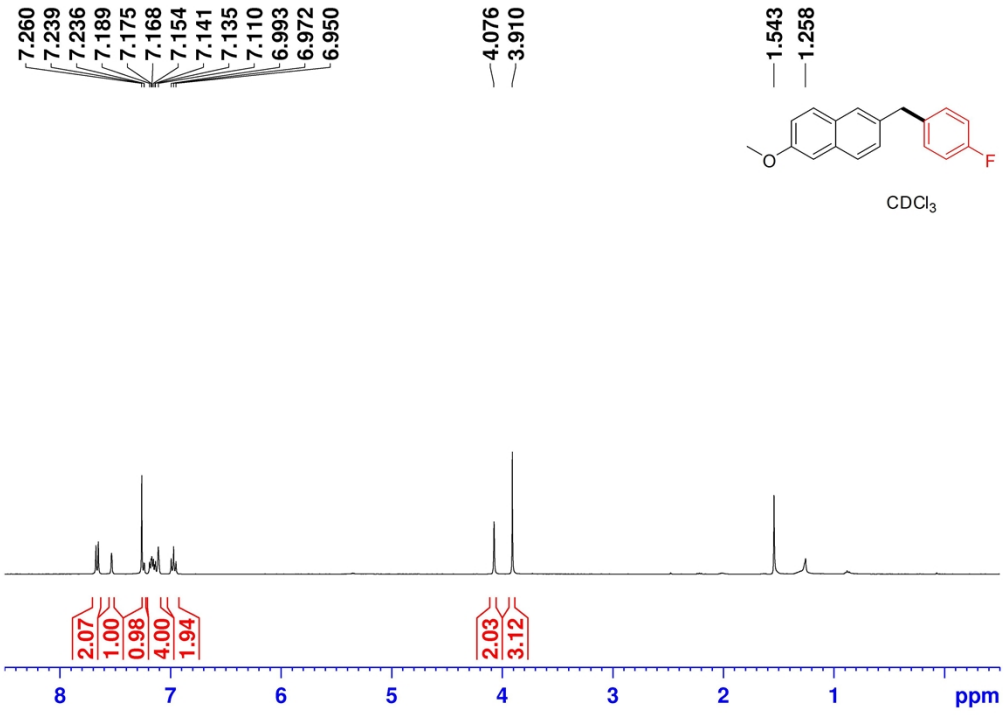


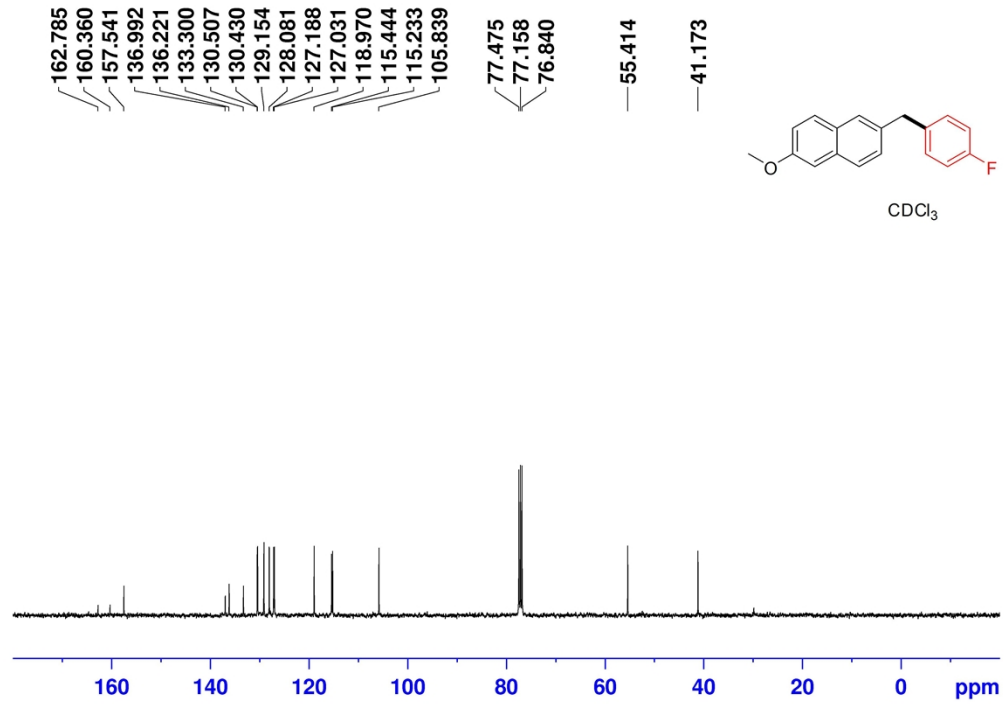


2-Methoxy-6-(naphthalen-1-ylmethyl)naphthalene (Table 3, **31** and **36**).

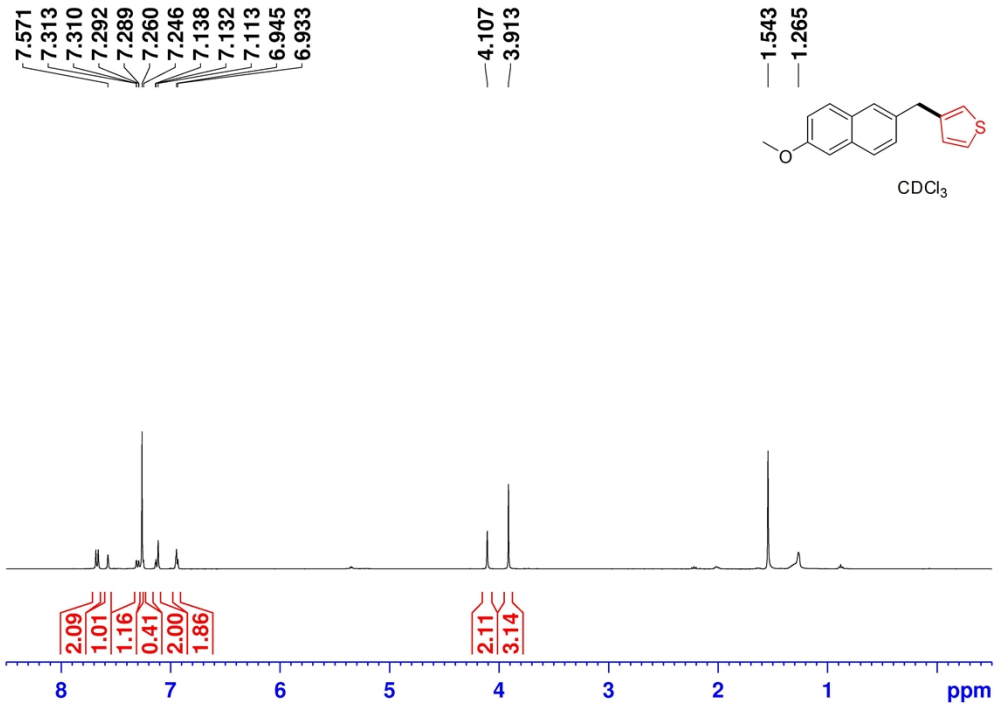


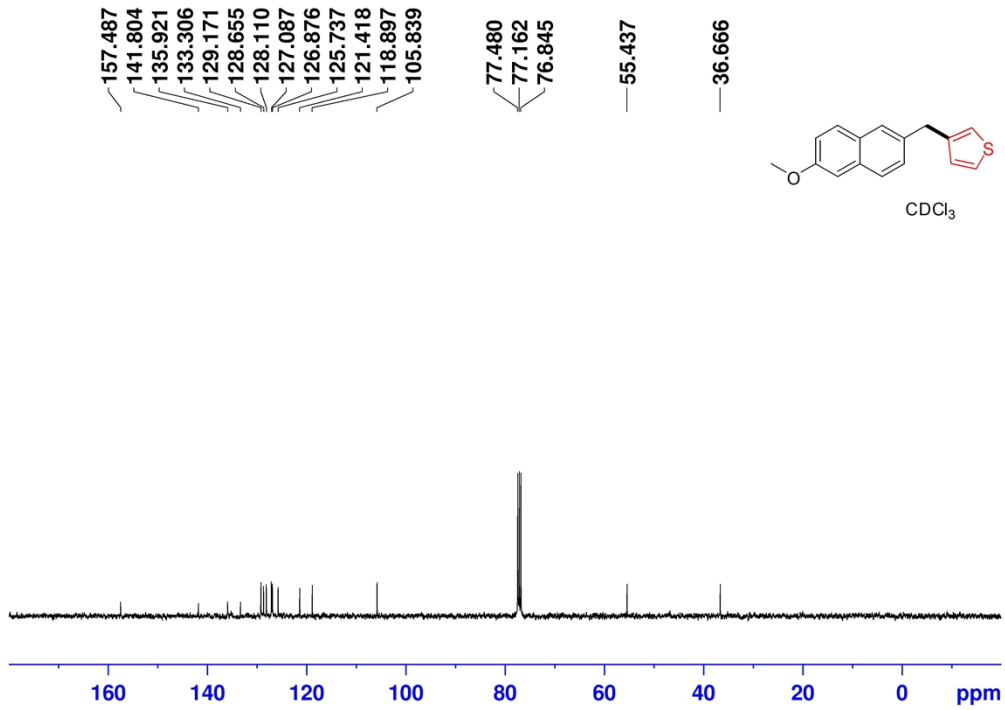
2-(4-Fluorobenzyl)-6-methoxynaphthalene (Table 3, **32**).



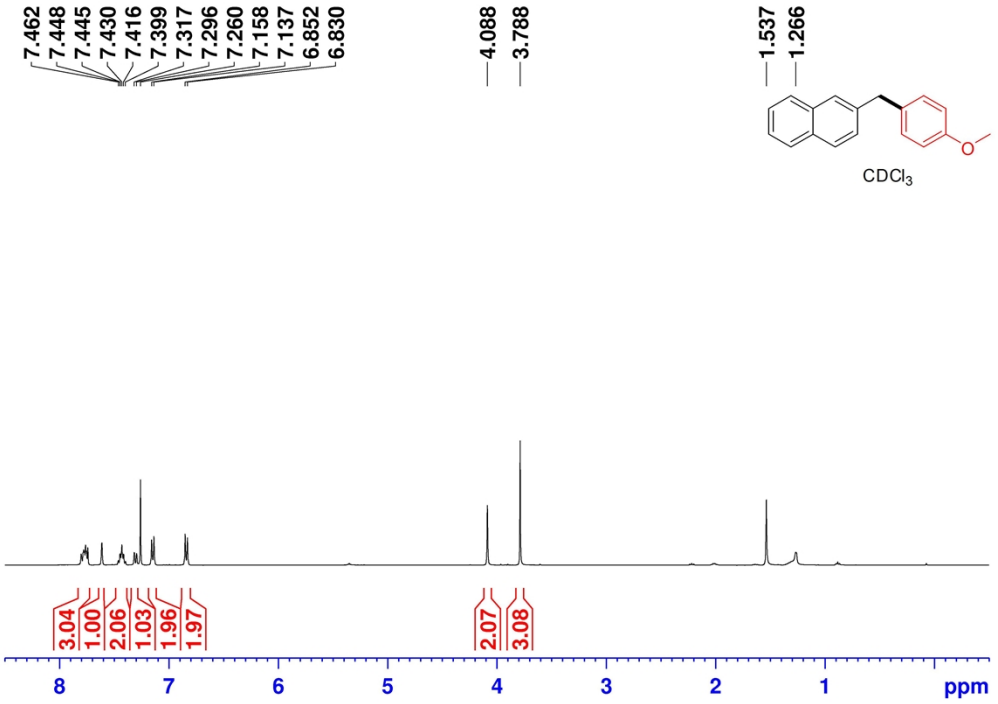


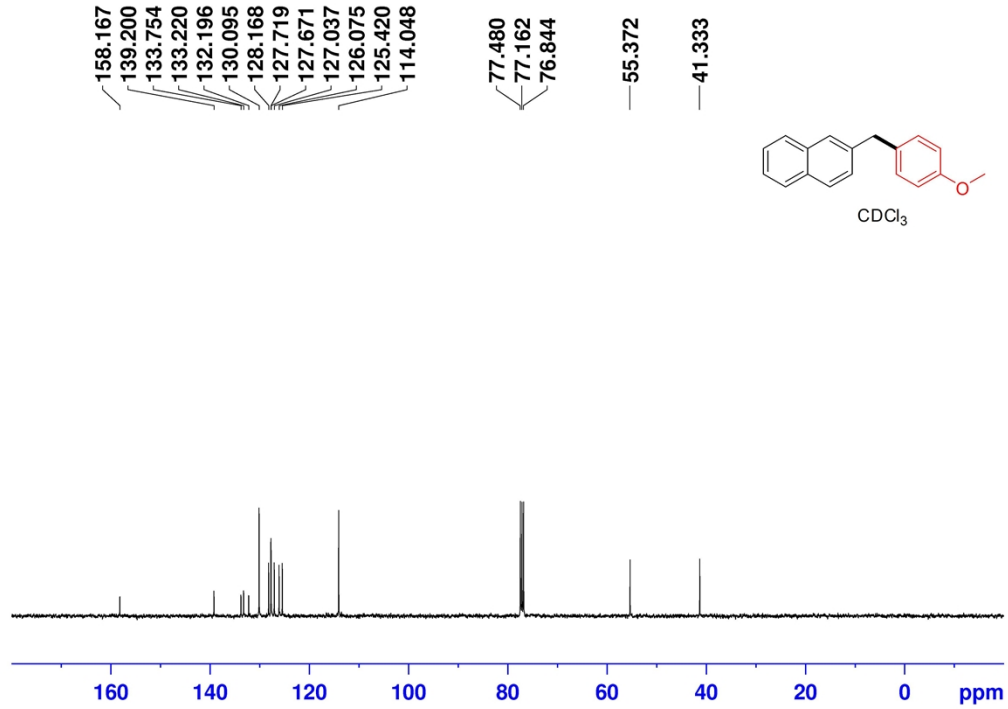
3-((6-Methoxynaphthalen-2-yl)methyl)thiophene (Table 3, **33**).



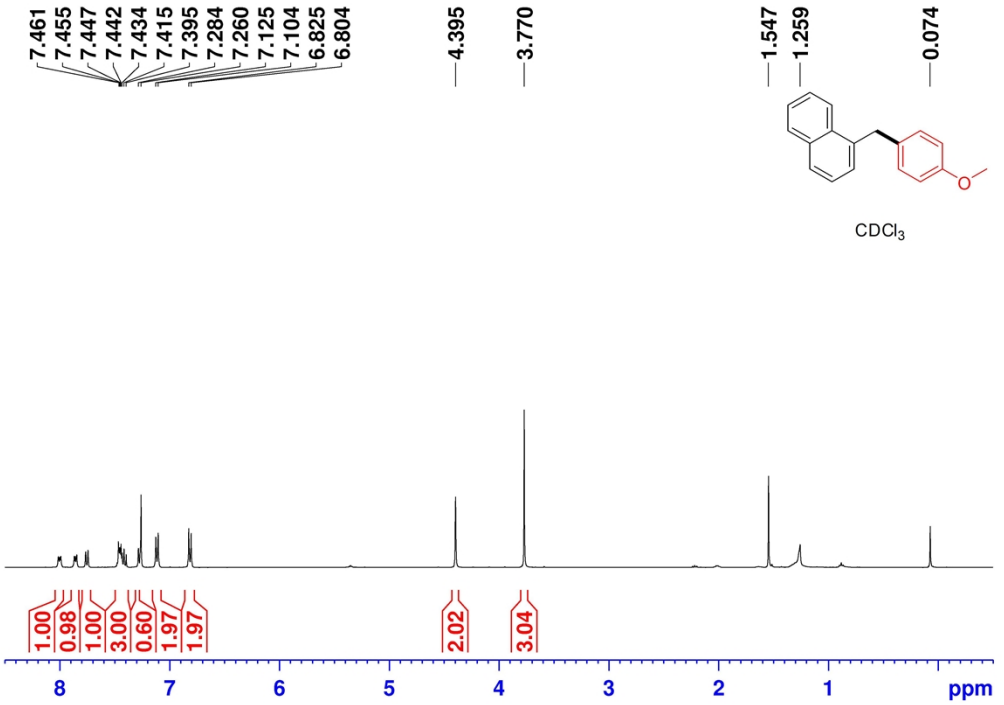


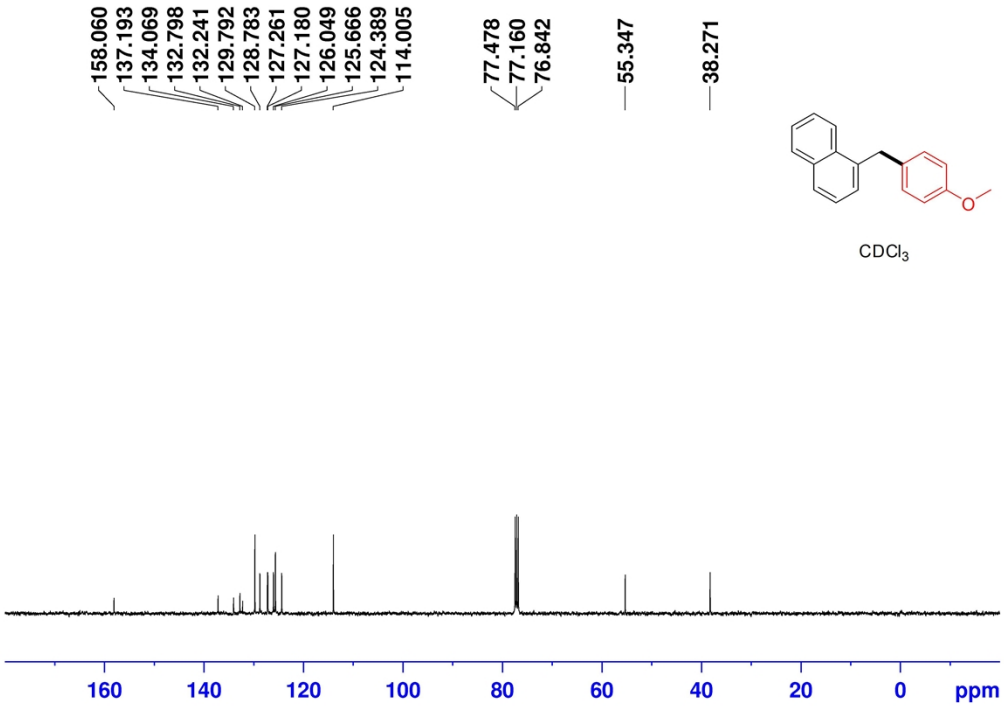
2-(4-Methoxybenzyl)naphthalene (Table 3, **34**).



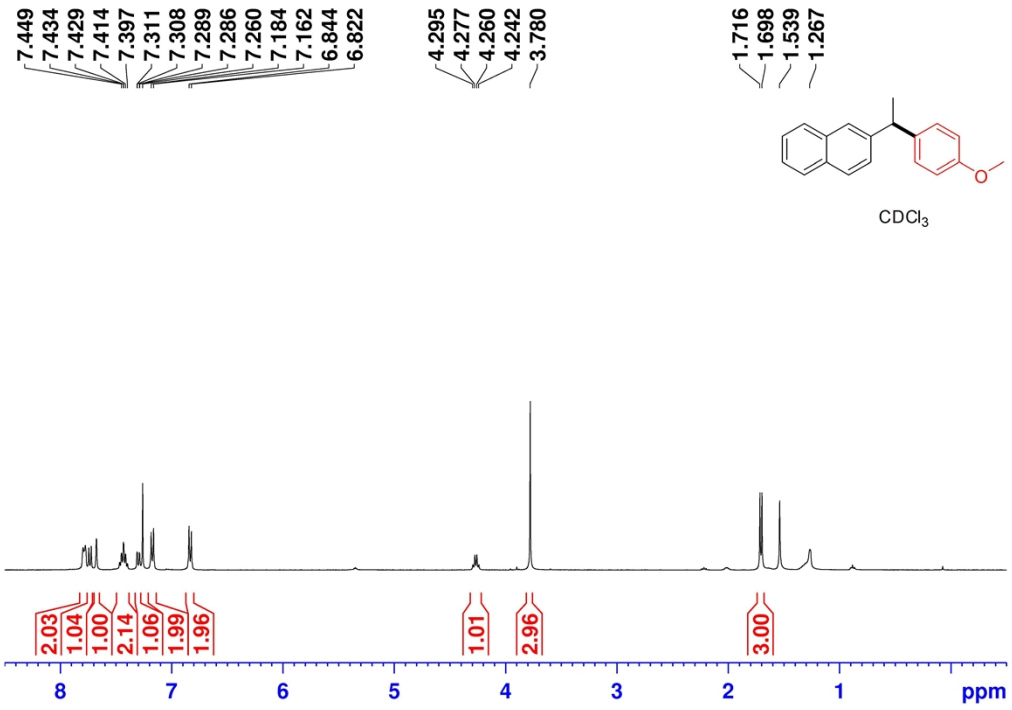


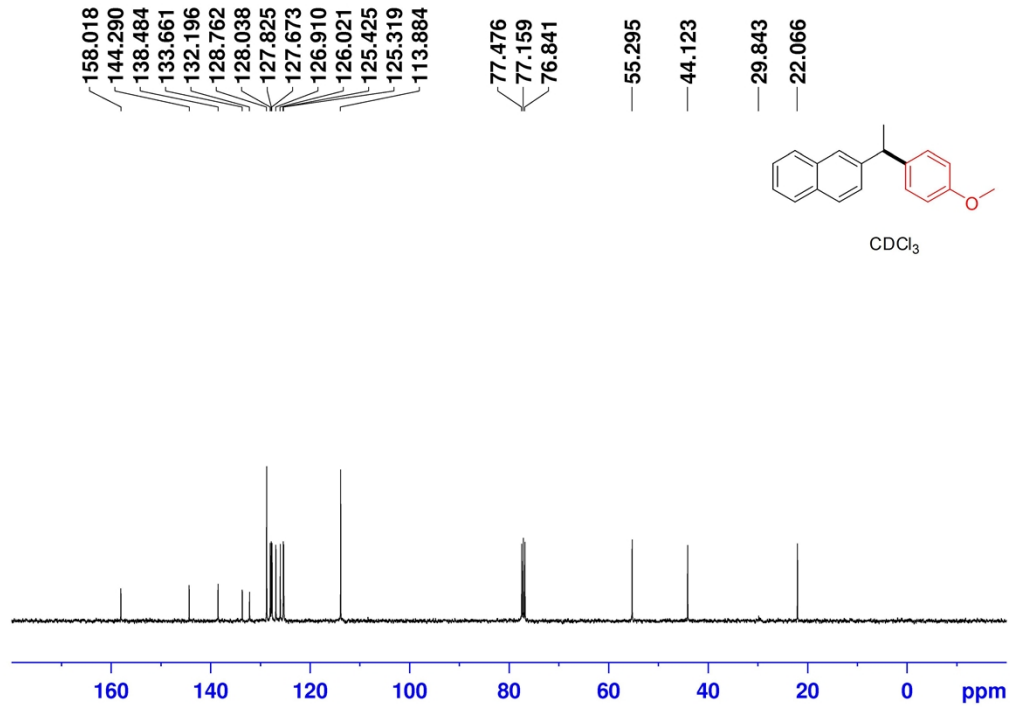
1-(4-Methoxybenzyl)naphthalene (Table 3, **35** and **39**).





2-(1-(4-Methoxyphenyl)ethyl)naphthalene (Table 3, **37**).





4-(4-Methoxybenzyl)biphenyl (Table 3, **38**).