Supporting Information

Palladium and Nickel Catalyzed Suzuki Cross-Coupling with Alkyl Fluorides

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1. General information

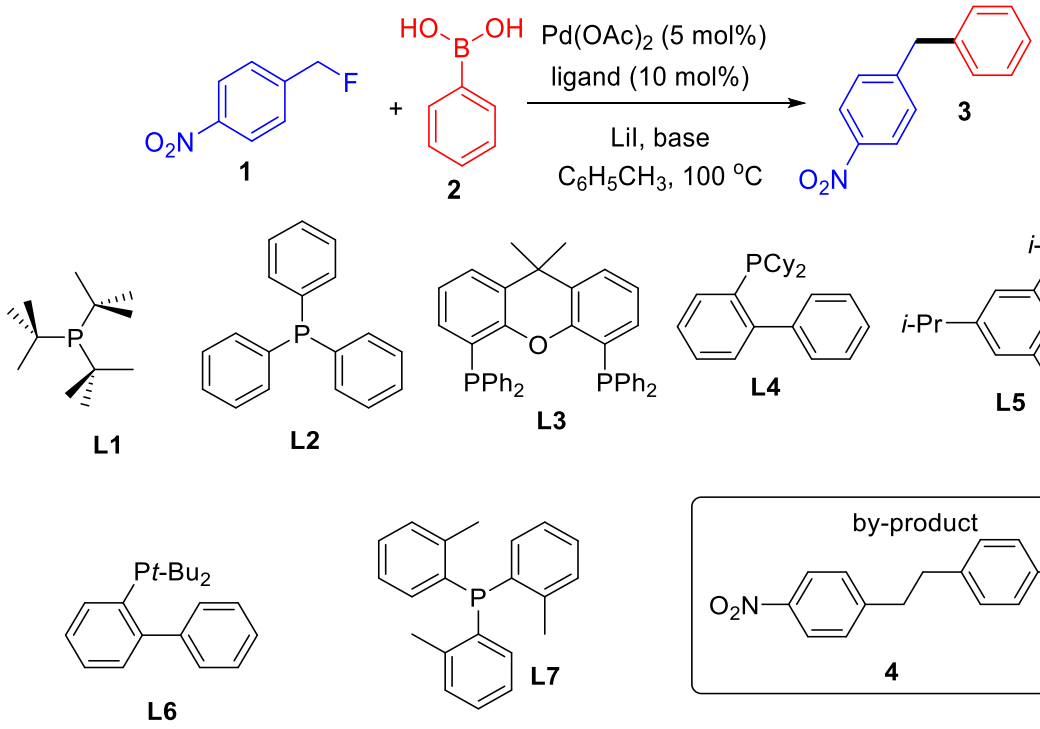
Commercially available organofluorines, ligands, catalysts, metal salts, boronic acids, reagents and solvents were used as purchased without further purification. The solvents were stored over 4Å molecular sieves prior to use.

NMR spectra were obtained at 400 MHz (^{1}H NMR), 376 MHz (^{19}F NMR) and 100 MHz (^{13}C NMR) in deuterated chloroform. Chemical shifts are reported in ppm relative to TMS. All reaction products were purified by column chromatography on silica gel (particle size 40-63 μm) as described below.

Single crystal X-ray analysis was performed at 100 K using a Siemens platform diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were integrated with the Bruker SAINT program. Structure solution and refinement were performed using the SHELXT/PC suite and ShelXle. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions.

2. Optimization of the Pd-catalyzed Suzuki cross-coupling

Screening of phosphine ligands, base, temperature and reaction time

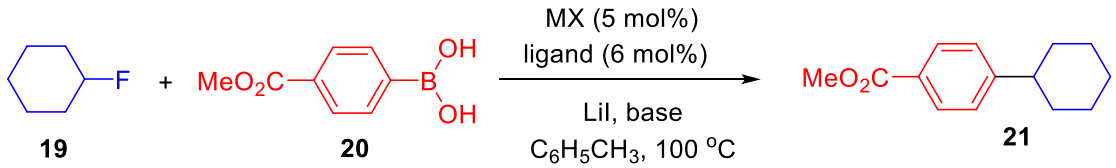


Entry	Ligand	Base	Time (h)	Temp. (°C)	Yield (%)
1	**L2**	Cs_2CO_3	36	100	68
2	**L2**	K_2CO_3	18	100	28
3	**L2**	K_3PO_4	18	100	42
4	**L1**	K_2CO_3	24	25	0
5	**L1**	K_2CO_3	18	80	33
6	**L1**	K_2CO_3	2	90	29[a]
7	**L1**	K_3PO_4	18	80	33
8	**L1**	K_3PO_4	18	100	40
9	**L1**	Cs_2CO_3	18	70	43
10	**L1**	Cs_2CO_3	18	100	60[b]
11	**L1**	Cs_2CO_3	18	100	54[c]
12	**L3**	Cs_2CO_3	18	100	54
13	**L4**	Cs_2CO_3	18	100	57
14	**L5**	Cs_2CO_3	18	100	29
15	**L6**	Cs_2CO_3	18	100	51
16	**L7**	Cs_2CO_3	18	100	92
17	**L7**	Cs_2CO_3	18	100	95[d]
18	**L7**	Cs_2CO_3	18	100	91[e]

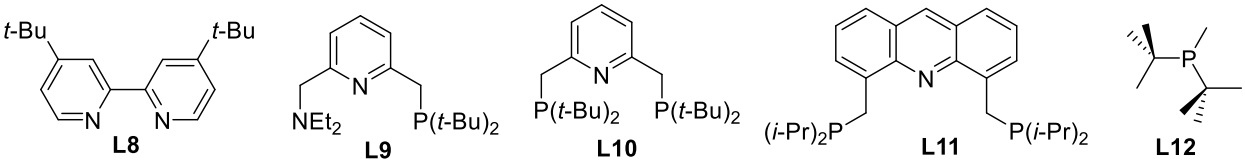
Conditions: **1** (0.2 mmol), **2** (0.6 mmol), LiI (0.3 mmol), $Pd(OAc)_2$ (5 mol%), ligand (10 mol%) in 2.0 mL solvent. [a]Microwave reaction, [b]28% of **4** isolated, [c]*m*-xylene used as a solvent, [d]0.4 mmol of **2** used, [e]0.3 mmol of **2** used.

3. Optimization of the Ni-catalyzed Suzuki cross-coupling

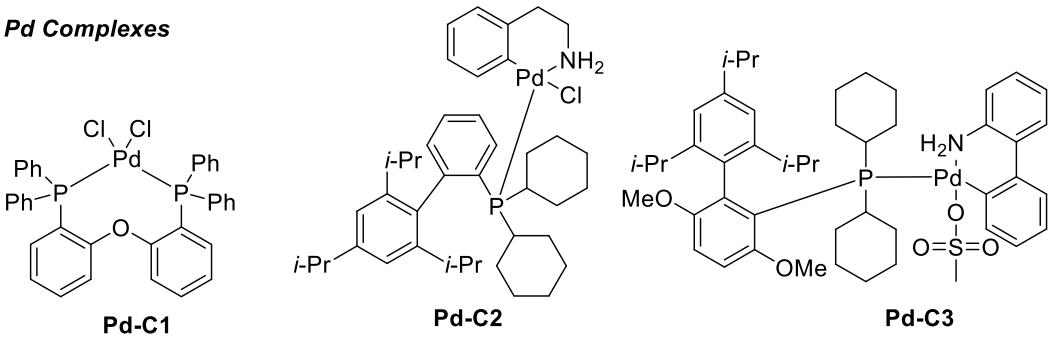
Screening of Ni complexes, base, solvent, temperature and reaction time



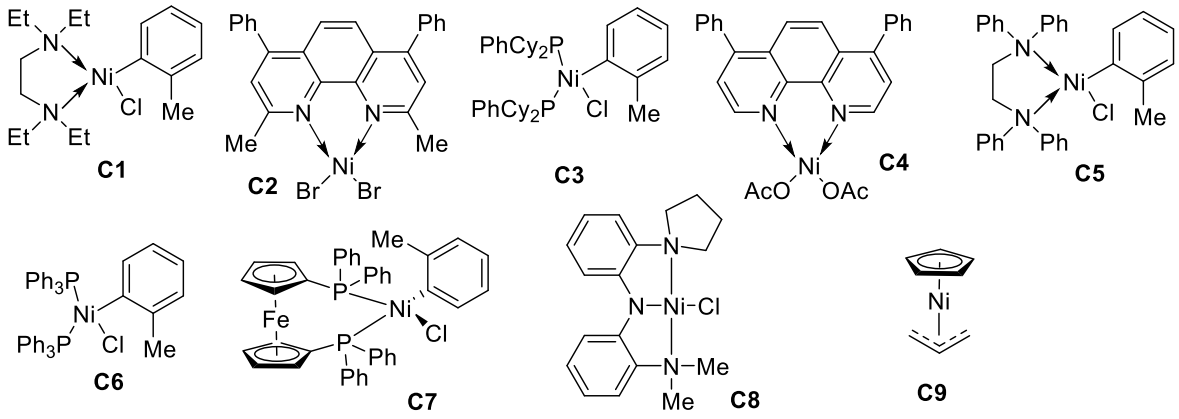
Ligands



Pd Complexes



Ni Complexes



Entry		Catalyst	Base	Solvent	Time (h)	Yield (%)
1	**L7**	$Pd(OAc)_2$	Cs_2CO_3	Toluene	24	0
2	-	$Pd(PPh_3)_4$	Cs_2CO_3	Toluene	24	<5
3	-	**Pd-C1**	Cs_2CO_3	Toluene	24	0
4	-	**Pd-C2**	Cs_2CO_3	Toluene	24	0
5	-	**Pd-C3**	Cs_2CO_3	Toluene	24	0
6	-	$Ni(PPh_3)_4$	Cs_2CO_3	Toluene	24	12
7	**L8**	$Ni(NO_3)_2{\cdot}6H_2O$	Cs_2CO_3	Toluene	24	24

8	**L8**	$NiCl_2$	Cs_2CO_3	Toluene	24	12
9	-	$NiCl_2(PCy_3)_2$	Cs_2CO_3	Toluene	24	<5
10	-	$NiCl_2(PPh_3)_2$	Cs_2CO_3	Toluene	24	<5
11	-	$Ni(dppe)Cl_2$	Cs_2CO_3	Toluene	24	<5
12	-	$Ni(dppf)Cl_2$	Cs_2CO_3	Toluene	24	<5
13	**L8**	$NiBr_2$	Cs_2CO_3	Toluene	24	15
14	**L8**	$NiBr_2$·DME	Cs_2CO_3	Toluene	24	12
15	**L8**	$NiBr_2$·Diglyme	Cs_2CO_3	Toluene	24	8
16	**L8**	NiI_2	Cs_2CO_3	Toluene	24	36
17	**L8**	$Ni(COD)_2$	Cs_2CO_3	Toluene	24	57
18	**L8**	$Ni(ClO_4)_2$	Cs_2CO_3	Toluene	24	30
19	**L8**	NiO	Cs_2CO_3	Toluene	24	0
20	**L9**	NiI_2	Cs_2CO_3	Toluene	24	30
21	**L9**	$Ni(COD)_2$	Cs_2CO_3	Toluene	24	48
22	**L8**	$Ni(COD)_2$	Cs_2CO_3	Toluene	48	71
23	**L8**	$Ni(COD)_2$	K_2CO_3	Toluene	48	56
24	**L8**	$Ni(COD)_2$	K_3PO_4	Toluene	48	45
25	**L8**	$Ni(COD)_2$	KO*t*-Bu	Toluene	48	54
26	**L8**	$Ni(COD)_2$	Cs_2CO_3	IPA	48	0
27	**L8**	$Ni(COD)_2$	Cs_2CO_3	Dioxane	48	0
28	**L8**	$Ni(COD)_2$	Cs_2CO_3	DMF	48	0
29	**L8**	$Ni(COD)_2$	Cs_2CO_3	*t*-BuOH	48	0
30	**L9**	$Ni(COD)_2$	Cs_2CO_3	Toluene	48	15
31	**L10**	$Ni(COD)_2$	Cs_2CO_3	Toluene	48	0
32	**L11**	$Ni(COD)_2$	Cs_2CO_3	Toluene	48	13
33	**L12**	$Pd(OAc)_2$	KO*t*-Bu	Toluene	24	0
34	-	**C1**	Cs_2CO_3	Toluene	48	36
35	-	**C2**	Cs_2CO_3	Toluene	48	28
36	-	**C3**	Cs_2CO_3	Toluene	48	38
37	-	**C4**	Cs_2CO_3	Toluene	48	0
38	-	**C5**	Cs_2CO_3	Toluene	48	30
39	-	**C6**	Cs_2CO_3	Toluene	48	35
40	-	**C7**	Cs_2CO_3	Toluene	48	25
41	-	**C8**	Cs_2CO_3	Toluene	48	12
42	-	**C9**	Cs_2CO_3	Toluene	48	<5

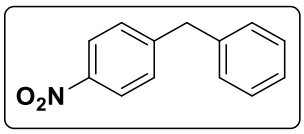
Conditions: **19** (0.2 mmol), **20** (0.4 mmol), LiI (0.3 mmol), **MX** (5 mol%) and ligand (6 mol%) or metal complex (5 mol%) in 2.0 mL solvent at 100 °C.

4. General procedure for the Pd-catalyzed Suzuki cross-coupling

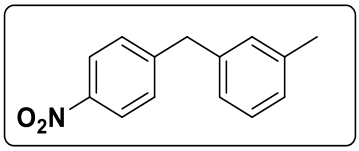
Method A: $Pd(OAc)_2$ (5 mol%), P(*o*-tolyl)$_3$ (10 mol%), alkyl fluoride (0.2 mmol, 1.0 eq), boronic acid (0.4 mmol, 2.0 eq), LiI (0.3 mmol, 1.5 eq) and Cs_2CO_3 (0.4 mmol, 2.0 eq) were added into 2 mL of dry toluene under nitrogen atmosphere. The reaction mixture was stirred at 100 ^oC in an oil bath and stirred at this temperature for 18 hours in the dark. The solvent was removed and the crude products were purified by silica flash column chromatography as described below.

Method B: $Pd(OAc)_2$ (5 mol%), P(*o*-tolyl)$_3$ (10 mol%), alkyl fluoride (0.4 mmol, 2.0 eq), boronic acid (0.2 mmol, 1.0 eq), LiI (0.6 mmol, 3.0 eq) and Cs_2CO_3 (0.4 mmol, 2 eq) were added into 2 mL of dry toluene under nitrogen atmosphere. The reaction mixture was stirred at 25 ^oC for 3 hours and then heated to 100 ^oC in an oil bath and stirred at this temperature for another 18 hours in the dark. The solvent was removed and the crude products were purified by silica flash column chromatography as described below.

4.1. Product purification and characterization

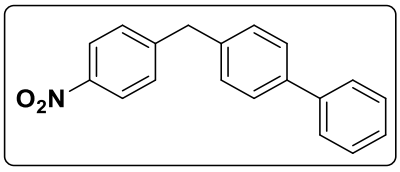


1-Benzyl-4-nitrobenzene (3). Compound **3** was obtained after column purification using hexanes/ethyl acetate (19:1) as mobile phase as a colorless oil in 95% yield (40 mg, 0.19 mmol) from 1-(fluoromethyl)-4-nitrobenzene (31 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.5 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.13 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.28 (m, 4H), 7.24 (m, 1H), 7.17 (d, *J* = 6.8 Hz, 2H), 4.07 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 149.0, 146.7, 139.3, 129.8, 129.1, 128.9, 126.9, 123.9, 41.9; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{13}H_{12}NO_2$ 214.0863, found 214.0866.

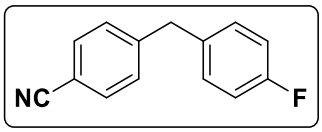


1-Methyl-3-(4-nitrobenzyl)benzene (5). Compound **5** was obtained after column purification using hexanes/ethyl acetate (49:1) as mobile phase as a colorless solid in 96% yield (43 mg, 0.192 mmol) from 1-(fluoromethyl)-4-nitrobenzene (31 mg, 0.2 mmol) and *m*-tolylboronic acid (54 mg,

0.4 mmol) by following the general procedure described above (Method A). R_f = 0.6 (hexanes/EtOAc, 19:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.14 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.30 (m, 2H), 7.21 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 2H), 4.04 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 149.1, 146.6, 139.2, 138.6, 129.8, 129.8, 128.8, 127.6, 126.1, 123.9, 41.8, 21.5; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1019, found 228.1024.

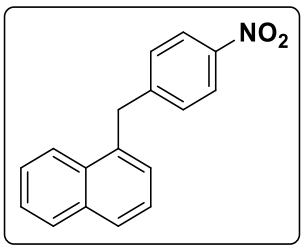


4-(4-Nitrobenzyl)-1,1'-biphenyl (6). Compound **6** was obtained after column purification using hexanes/ethyl acetate (49:1) as mobile phase as a colorless solid in 92% yield (53 mg, 0.184 mmol) from 1-(fluoromethyl)-4-nitrobenzene (31 mg, 0.2 mmol) and [1,1'-biphenyl]-4-ylboronic acid (80 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.6 (hexanes/EtOAc, 19:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.14 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.53 (m, 4H), 7.42 (dd, *J* = 7.6, 7.5 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 2H), 4.10 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 148.9, 146.7, 140.7, 139.9, 138.4, 129.8, 129.5, 128.9, 127.6, 127.4, 127.1, 123.9, 41.5; HRMS (ESI-TOF) *m*/*z*: $[M-H]^-$ calcd for $C_{19}H_{14}NO_2$ 288.1030, found 288.1025.

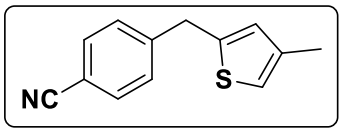


4-(4-Fluorobenzyl)benzonitrile (7). Compound **7** was obtained after column purification using hexanes/ethyl acetate (19:1) as mobile phase as a colorless solid in 86% yield (36 mg, 0.172 mmol) from 4-(fluoromethyl)benzonitrile (27 mg, 0.2 mmol) and (4-fluorophenyl)boronic acid (56 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.3 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.11 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.03 – 6.94 (m, 2H), 4.00 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 161.8 (d, J_{C-F} = 245.0 Hz), 146.6 (d, J_{C-F} = 1.0 Hz), 135.1 (d, J_{C-F} = 3.2 Hz), 132.5, 130.5 (d, J_{C-F} = 7.9 Hz), 129.7, 119.0, 115.7 (d, J_{C-F} = 21.4 Hz), 110.4, 41.2; ^{19}F NMR

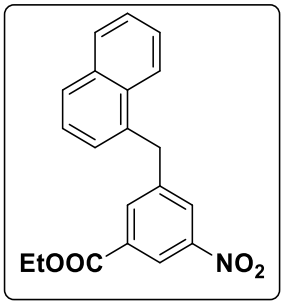
(376 MHz, chloroform-*d*) δ = -116.3 (m, 1F); HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{11}FN$ 212.0870, found 212.0873.



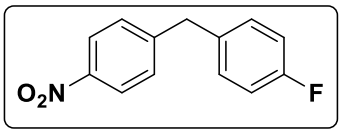
1-(4-Nitrobenzyl)naphthalene (8). Compound **8** was obtained after column purification using hexanes/ethyl acetate (32:1) as mobile phase as a colorless solid in 87% yield (46 mg, 0.174 mmol) from 1-(fluoromethyl)naphthalene (32 mg, 0.2 mmol) and (4-nitrophenyl)boronic acid (67 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.6 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.12 (d, *J* = 8.7 Hz, 2H), 7.90 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.84 (dd, *J* = 8.7, 8.7 Hz, 2H), 7.53 – 7.42 (m, 3H), 7.37 – 7.30 (m, 3H), 4.54 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 148.7, 146.7, 134.8, 134.2, 131.9, 129.5, 129.0, 128.1, 127.8, 126.5, 126.0, 125.7, 124.0, 123.9, 39.1; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{17}H_{14}NO_2$ 264.1019, found 264.1019.



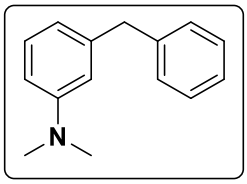
4-((4-Methylthiophen-2-yl)methyl)benzonitrile (9). Compound **9** was obtained after column purification using hexanes/ethyl acetate (19:1) as mobile phase as a colorless solid in 96% yield (41 mg, 0.192 mmol) from 4-(fluoromethyl)benzonitrile (27 mg, 0.2 mmol) and (4-methylthiophen-2-yl)boronic acid (57 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.4 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.59 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 6.61 (s, 1H), 4.14 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 146.0, 141.6, 137.8, 132.5, 129.4, 128.4, 119.8, 119.0, 110.6, 36.3, 15.8; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{13}H_{12}NS$ 214.0685, found 214.0685.



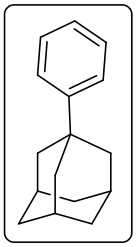
Ethyl 3-(naphthalen-1-ylmethyl)-5-nitrobenzoate (10). Compound **10** was obtained after column purification using hexanes/ethyl acetate (9:1) as mobile phase as a colorless oil in 89% yield (59 mg, 0.178 mmol) from 1-(fluoromethyl)naphthalene (32 mg, 0.2 mmol) and (3-(ethoxycarbonyl)-5-nitrophenyl)boronic acid (96 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.3 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.68 (dd, *J* = 1.7, 1.7 Hz, 1H), 8.27 (dd, *J* = 1.7, 1.7 Hz, 1H), 8.19 (dd, *J* = 1.7, 1.7 Hz, 1H), 7.93 – 7.79 (m, 3H), 7.53 – 7.43 (m, 3H), 7.33 (dd, *J* = 7.0, 1.4 Hz, 1H), 4.58 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 164.7, 148.7, 143.6, 135.6, 134.4, 134.3, 132.4, 131.7, 129.2, 128.3, 127.9, 127.4, 126.6, 126.1, 125.8, 123.7, 122.6, 62.1, 38.8, 14.4; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{18}NO_4$ 336.1230, found 336.1225.



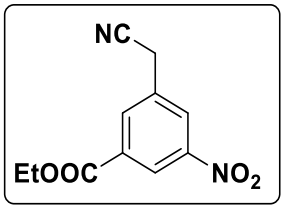
1-Fluoro-4-(4-nitrobenzyl)benzene (11). Compound **11** was obtained after column purification using hexanes/ethyl acetate (19:1) as mobile phase as a colorless solid in 97% yield (45 mg, 0.194 mmol) from 1-(fluoromethyl)-4-nitrobenzene (31 mg, 0.2 mmol) and (4-fluorophenyl)boronic acid (56 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.7 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.15 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.17 – 7.10 (m, 2H), 7.06 – 6.95 (m, 2H), 4.05 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 161.9 (d, J_{C-F} = 245.4 Hz), 148.7 (d, J_{C-F} = 1.0 Hz), 146.7, 135.0 (d, J_{C-F} = 3.3 Hz), 130.5 (d, J_{C-F} = 8.0 Hz), 129.7, 123.9, 115.8 (d, J_{C-F} = 21.4 Hz), 41.0; ^{19}F NMR (376 MHz, chloroform-*d*) δ = -116.1 (m, 1F); HRMS (ESI-TOF) *m*/*z*: $[M-H]^-$ calcd for $C_{13}H_9FNO_2$ 230.0623, found 230.0625.



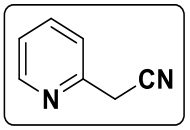
3-Benzyl-*N*,*N*-dimethylaniline (12). Compound **12** was obtained after column purification using hexanes/ethyl acetate (9:1) as mobile phase as a colorless oil in 89% yield (38 mg, 0.178 mmol) from 3-(fluoromethyl)-*N*,*N*-dimethylaniline (31 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.6 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.25 – 7.19 (m, 3H), 7.18 – 7.11 (m, 3H), 7.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.55 – 6.45 (d, *J* = 8.1 Hz, 2H), 4.07 (s, 2H), 2.86 (s, 6H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 149.9, 142.4, 141.0, 133.5, 129.3, 129.2, 128.3, 125.9, 114.8, 111.8, 40.7, 40.2. The spectroscopic data of 3-benzyl-*N*,*N*-dimethylaniline (**12**) are in accordance with the literature.[1]



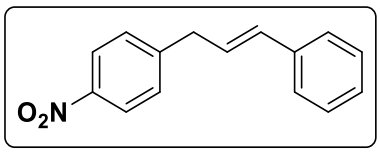
1-Phenyladamantane (13). Compound **13** was obtained after preparative TLC purification using hexanes as mobile phase as a colorless solid in 41% yield (17 mg, 0.082 mmol) from 1-fluoroadamantane (31 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.9 (hexanes); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.41 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 7.19 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.11 (bs, 3H), 1.93 (bs, 6H), 1.85 – 1.71 (m, 6H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 151.5, 128.2, 125.6, 125.0, 43.3, 37.0, 36.3, 29.1. The spectroscopic data of 1-phenyladamantane (**13**) are in accordance with the literature.[2]



Ethyl 3-(cyanomethyl)-5-nitrobenzoate (14). Compound **14** was obtained after column purification using hexanes/ethyl acetate (3:1) as mobile phase as a colorless solid in 91% yield (42 mg, 0.182 mmol) from 2-fluoroacetonitrile (24 mg, 0.4 mmol) and (3-(ethoxycarbonyl)-5-nitrophenyl)boronic acid (48 mg, 0.2 mmol) by following the general procedure described above (Method B). R_f = 0.3 (hexanes/EtOAc, 1:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.81 (dd, *J* = 1.7, 1.7 Hz, 1H), 8.41 (dd, *J* = 1.7, 1.7 Hz, 1H), 8.35 (dd, *J* = 1.7, 1.7 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 2H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 163.9, 148.9, 134.7, 133.5, 132.7, 126.8, 124.5, 116.2, 62.5, 23.6, 14.4; HRMS (ESI-TOF) *m*/*z*: $[M-H]^-$ calcd for $C_{11}H_9N_2O_4$ 233.0568, found 233.0566.

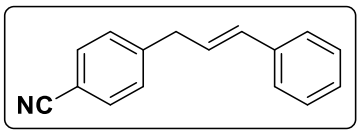


2-(Pyridin-2-yl)acetonitrile (15). Compound **15** was obtained after column purification using hexanes/ethyl acetate (4:1) as mobile phase as a colorless oil in 83% yield (20 mg, 0.166 mmol) from 2-fluoroacetonitrile (24 mg, 0.4 mmol) and pyridin-2-ylboronic acid (25 mg, 0.2 mmol) by following the general procedure described above (Method B). R_f = 0.4 (hexanes/EtOAc, 1:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.59 (d, *J* = 7.7 Hz, 1H), 7.74 (dd, *J* = 7.8, 7.7 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.27 (m, 1H), 3.95 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 150.6, 150.0, 137.5, 123.1, 122.3, 117.1, 26.7; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_7H_7N_2$ 119.0604, found 119.0601.

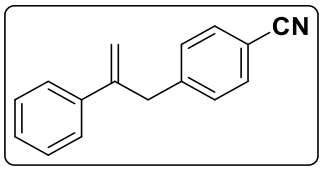


(*E*)-3-(4-Nitrophenyl)-1-phenylpropene (16). Compound **16** was obtained after column purification using hexanes/ethyl acetate (19:1) as mobile phase as a colorless solid in 81% yield (39 mg, 0.162 mmol) from 1-(fluoromethyl)-4-nitrobenzene (31 mg, 0.2 mmol) and (*E*)-phenylethenylboronic acid (59 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.5 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.17 (d, *J* = 8.7 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.31 (dd, *J* = 8.0, 7.3 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.8 Hz, 1H), 3.65 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz,

chloroform-*d*) δ = 148.1, 146.8, 137.0, 132.7, 129.6, 128.8, 127.7, 127.1, 126.3, 123.9, 39.2; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{15}H_{14}NO_2$ 240.1019, found 240.1021.



(*E*)-3-(4-Cyanophenyl)-1-phenylpropene (17). Compound **17** was obtained after column purification using hexanes/ethyl acetate (19:1) as mobile phase as a colorless solid in 89% yield (39 mg, 0.178 mmol) from 4-(fluoromethyl)benzonitrile (27 mg, 0.2 mmol) and (*E*)-phenylethenylboronic acid (59 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.4 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.57 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.24 (m, 6H), 7.22 (m, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.26 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.57 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 145.9, 137.0, 132.6, 132.4, 129.6, 128.7, 127.7, 127.3, 126.3, 119.1, 110.3, 39.4; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{16}H_{14}N$ 220.1121, found 220.1123.

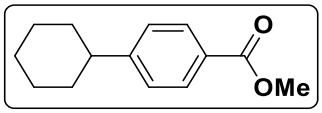


4-(2-Phenylallyl)benzonitrile (18). Compound **18** was obtained after column purification using hexanes/ethyl acetate (19:1) as mobile phase as a colorless oil in 88% yield (38 mg, 0.176 mmol) from 4-(fluoromethyl)benzonitrile (27 mg, 0.2 mmol) and (1-phenylvinyl)boronic acid (59 mg, 0.4 mmol) by following the general procedure described above (Method A). R_f = 0.4 (hexanes/EtOAc, 8:2); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.56 – 7.49 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.20 (m, 5H), 5.53 (d, *J* = 1.2 Hz, 1H), 5.05 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 145.8, 145.4, 140.1, 132.3, 129.7, 128.5, 127.9, 126.2, 119.1, 115.6, 110.2, 41.9; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{16}H_{14}N$ 220.1126, found 220.1125.

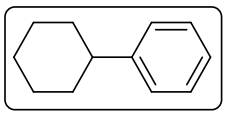
5. General procedure for the Ni-catalyzed Suzuki cross-coupling

$Ni(cod)_2$ (5 mol%), **L8** (6 mol%), alkyl fluoride (0.2 mmol, 1.0 eq), boronic acid (0.4 mmol, 2.0 eq), LiI (0.3 mmol, 1.5 eq) and Cs_2CO_3 (0.4 mmol, 2.0 eq) were added into 2 mL of dry toluene under nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 3 hours and then heated to 100 °C in an oil bath and stirred at this temperature for 48 hours in the dark. The solvent was removed and the crude products were purified by silica flash column chromatography as described below.

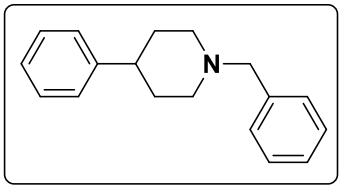
5.1. Product purification and characterization



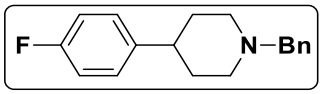
Methyl 4-cyclohexylbenzoate (21). Compound **21** was obtained after preparative TLC purification using hexanes/ethyl acetate (49:1) as mobile phase as a colorless oil in 71% yield (31 mg, 0.142 mmol) from fluorocyclohexane (17 mg, 0.2 mmol) and (4-(methoxycarbonyl)phenyl)boronic acid (72 mg, 0.4 mmol) by following the general procedure described above. R_f = 0.7 (hexanes/EtOAc, 19:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.98 – 7.92 (m, 2H), 7.30 – 7.23 (m, 2H), 3.89 (s, 3H), 2.56 (m, 1H), 1.93 – 1.80 (m, 4H), 1.76 (m, 1H), 1.52 – 1.33 (m, 4H), 1.27 (m, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 167.3, 153.6, 129.8, 127.9, 127.0, 52.1, 44.9, 34.3, 26.9, 26.2; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{19}O_2$ 219.1380, found 219.1379.



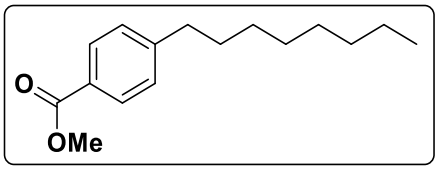
Cyclohexylbenzene (22). Compound **22** was obtained after preparative TLC purification using hexanes as mobile phase as a colorless oil in 63% yield (20 mg, 0.126 mmol) from fluorocyclohexane (17 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above. R_f = 0.8 (hexanes); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.31 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 2.49 (m, 1H), 1.92 – 1.82 (m, 4H), 1.74 (m, 1H), 1.51 – 1.34 (m, 4H), 1.25 (m, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 148.2, 128.4, 127.0, 125.9, 44.8, 34.6, 27.1, 26.3. The spectroscopic data of cyclohexylbenzene (**22**) are in accordance with the literature.[3]



1-Benzyl-4-phenylpiperidine (23). Compound **23** was obtained after column purification using hexanes/ethyl acetate (9:1) as mobile phase as a colorless solid in 69% yield (35 mg, 0.138 mmol) from 1-benzyl-4-fluoropiperidine (38 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above. R_f = 0.3 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.38 – 7.26 (m, 6H), 7.26 – 7.11 (m, 4H), 3.55 (s, 2H), 3.03 – 2.98 (m, 2H), 2.49 (m, 1H), 2.15 – 2.01 (m, 2H), 1.86 – 1.74 (m, 4H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 146.7, 138.6, 129.4, 128.5, 128.3, 127.1, 127.0, 126.2, 63.7, 54.4, 42.9, 33.7; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{18}H_{22}N$ 252.1747, found 252.1751.

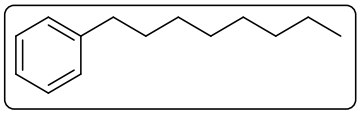


1-Benzyl-4-(4-fluorophenyl)piperidine (24). Compound **24** was obtained after column purification using hexanes/ethyl acetate (9:1) as mobile phase as a colorless solid in 65% yield (35 mg, 0.13 mmol) from 1-benzyl-4-fluoropiperidine (38 mg, 0.2 mmol) and (4-fluorophenyl)boronic acid (56 mg, 0.4 mmol) by following the general procedure described above. R_f = 0.3 (hexanes/EtOAc, 4:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.37 – 7.29 (m, 4H), 7.25 (m, 1H), 7.20 – 7.13 (m, 2H), 6.99 – 6.93 (m, 2H), 3.54 (s, 2H), 3.05 – 2.94 (m, 2H), 2.47 (tt, *J* = 10.5, 5.5 Hz, 1H), 2.07 (td, *J* = 11.1, 3.9 Hz, 2H), 1.83 – 1.67 (m, 4H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 161.4 (d, J_{C-F} = 243.5 Hz), 142.3 (d, J_{C-F} = 3.1 Hz), 138.5, 129.4, 128.3, 128.2, 127.1, 115.2 (d, J_{C-F} = 21.0 Hz), 63.6, 54.3, 42.1, 33.8; ^{19}F NMR (376 MHz, chloroform-*d*) δ = -117.5 (m, 1F); HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{18}H_{21}FN$ 270.1653, found 270.1653.

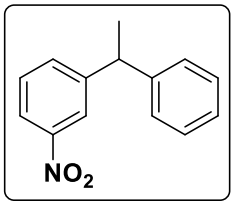


Methyl 4-octylbenzoate (25). Compound **25** was obtained after column purification using hexanes/ethyl acetate (49:1) as mobile phase as a colorless oil in 72% yield (36 mg, 0.144 mmol) from 1-fluorooctane (26 mg, 0.2 mmol) and (4-(methoxycarbonyl)phenyl)boronic acid (72 mg, 0.4

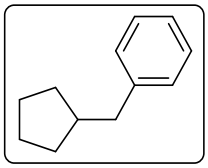
mmol) by following the general procedure described above. R_f = 0.8 (hexanes/EtOAc, 19:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.94 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.69 – 1.56 (m, 2H), 1.38 – 1.20 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 167.3, 148.6, 129.7, 128.5, 127.8, 52.0, 36.1, 32.0, 31.2, 29.5, 29.4, 29.3, 22.8, 14.2; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{16}H_{25}O_2$ 249.1849, found 249.1852.



Octylbenzene (26). Compound **26** was obtained after preparative TLC purification using hexanes as mobile phase as a colorless oil in 74% yield (28 mg, 0.148 mmol) from 1-fluorooctane (26 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above. R_f = 0.8 (hexanes); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.30 – 7.23 (m, 2H), 7.18 – 7.14 (m, 3H), 2.59 (t, *J* = 7.2 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.39 – 1.18 (m, 10H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 143.1, 128.5, 128.4, 125.7, 36.2, 32.0, 31.7, 29.6, 29.5, 29.4, 22.8, 14.3. The spectroscopic data of octylbenzene (**26**) are in accordance with the literature.[3]



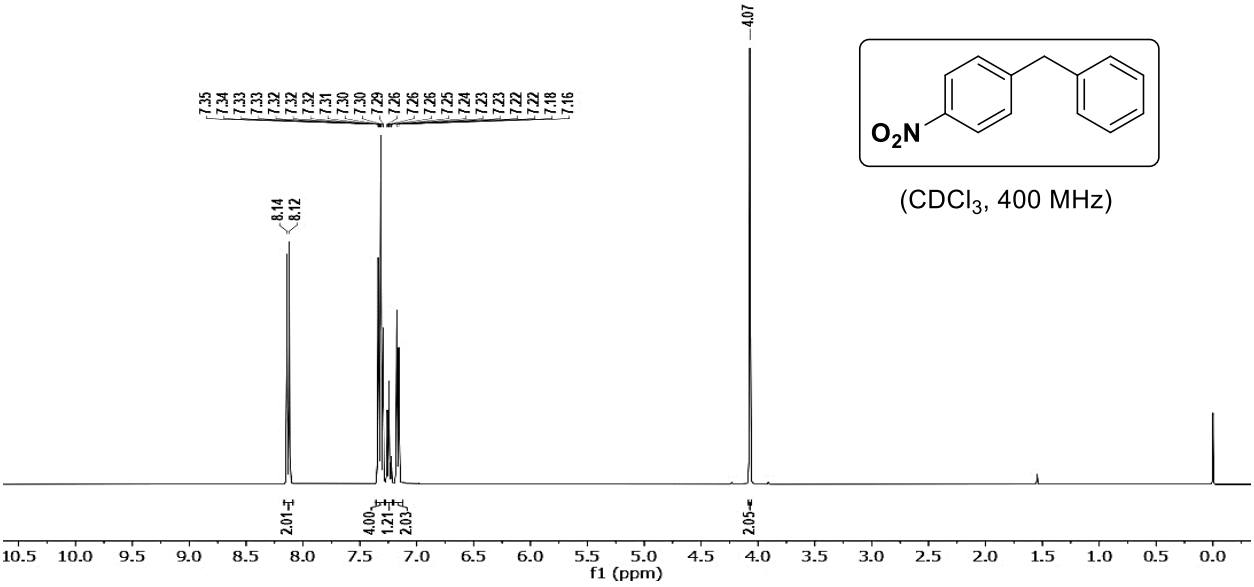
1-Nitro-3-(1-phenylethyl)benzene (27). Compound **27** was obtained after column purification using hexanes/ethyl acetate (9:1) as mobile phase as a colorless solid in 24% yield (11 mg, 0.048 mmol) from 1-(1-fluoroethyl)-3-nitrobenzene (34 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above. R_f = 0.4 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 8.10 (dd, *J* = 1.8, 1.6 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.53 (ddd, *J* = 7.8, 1.6, 0.8 Hz, 1H), 7.42 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 4.25 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 148.6, 148.6, 144.9, 134.1, 129.4, 128.9, 127.7, 126.8, 122.5, 121.4, 44.7, 21.7. The spectroscopic data of 1-nitro-3-(1-phenylethyl)benzene (**27**) are in accordance with the literature.[4]



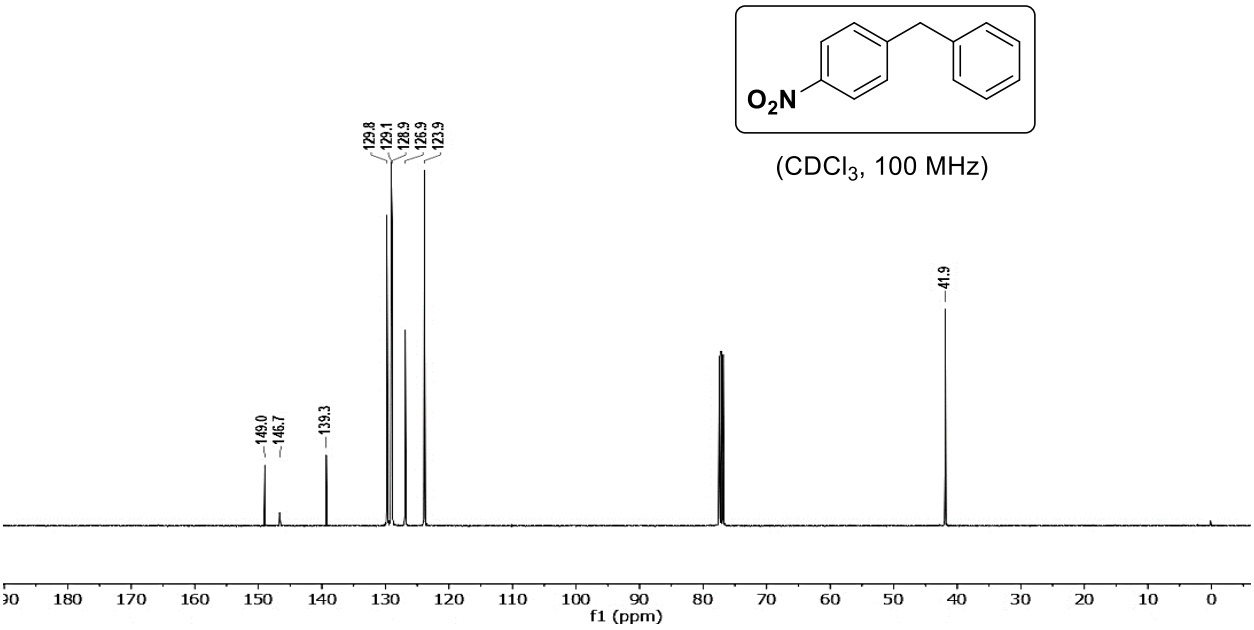
(Cyclopentylmethyl)benzene (29). Compound **29** was obtained after column purification using hexanes as mobile phase as a colorless oil in 68% yield (22 mg, 0.136 mmol) from 6-fluorohex-1-ene (20 mg, 0.2 mmol) and phenylboronic acid (49 mg, 0.4 mmol) by following the general procedure described above. R_f = 0.9 (hexanes); ^{1}H NMR (400 MHz, chloroform-*d*) δ = 7.32 – 7.21 (m, 2H), 7.19 – 7.11 (m, 3H), 2.59 (d, *J* = 7.4 Hz, 2H), 2.07 (m, 1H), 1.75 – 1.46 (m, 6H), 1.19 (m, 1H), 0.87 (m, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ = 142.5, 128.9, 128.3, 125.7, 42.3, 42.2, 32.6, 25.1. The spectroscopic data of (cyclopentylmethyl)benzene (**29**) are in accordance with the literature.[3]

6. ^{1}H, ^{13}C and ^{19}F NMR spectra

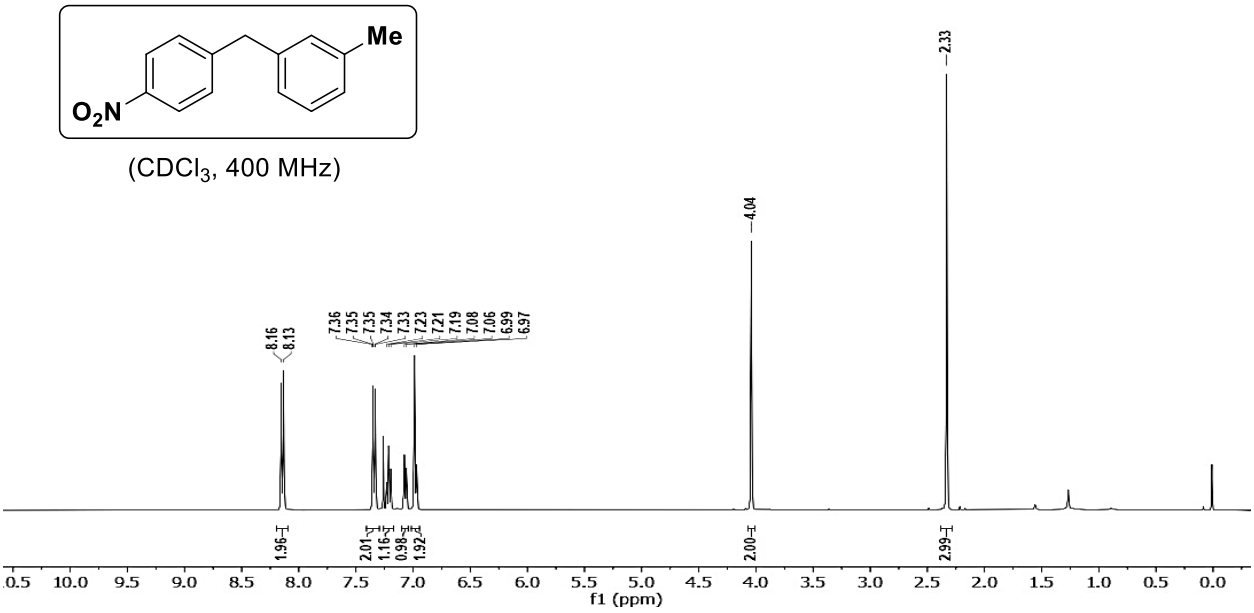
^{1}H NMR spectrum of 1-benzyl-4-nitrobenzene (3).



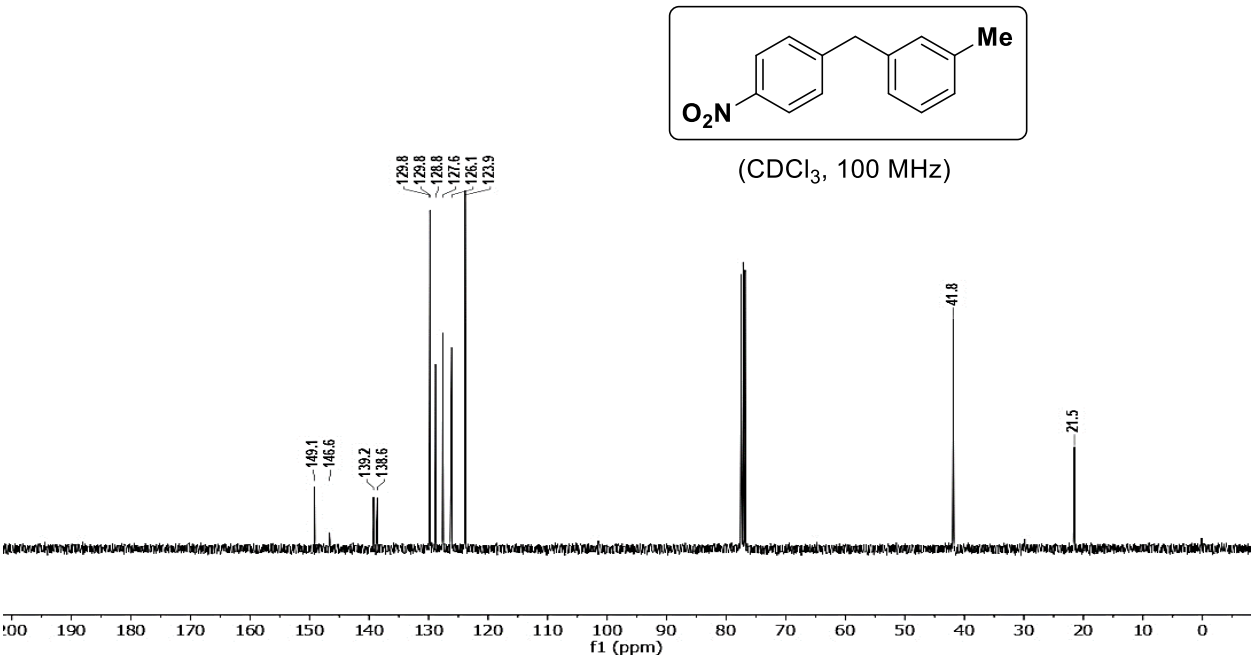
^{13}C NMR spectrum of 1-benzyl-4-nitrobenzene (3).



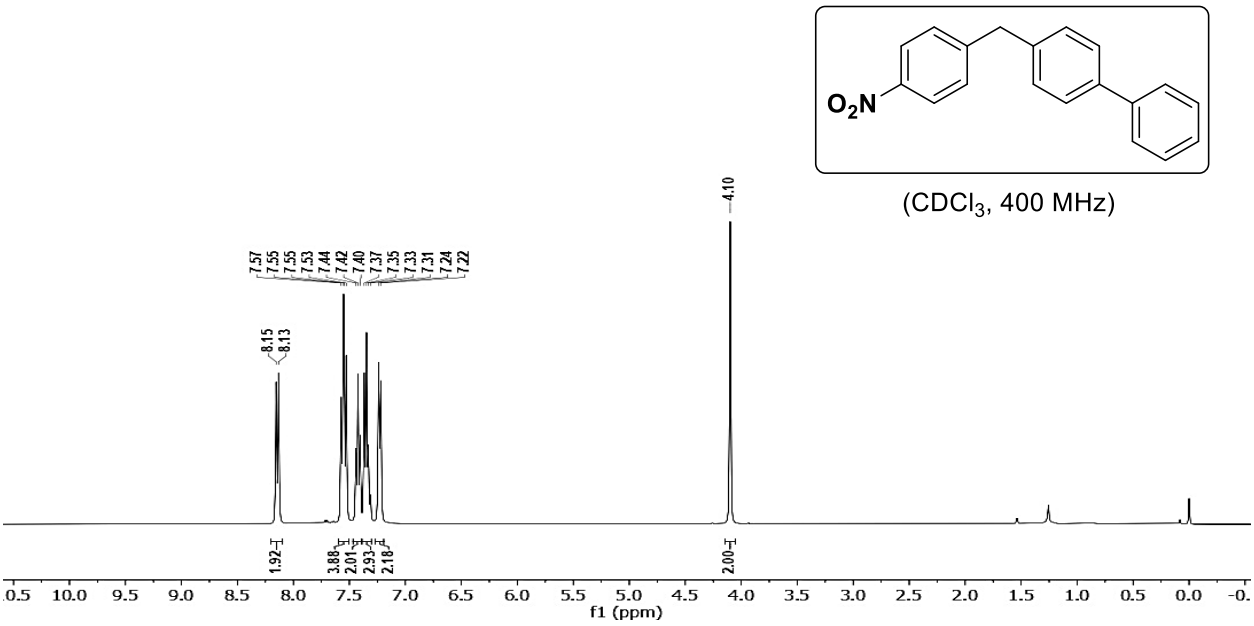
^{1}H NMR spectrum of 1-methyl-3-(4-nitrobenzyl)benzene (5).



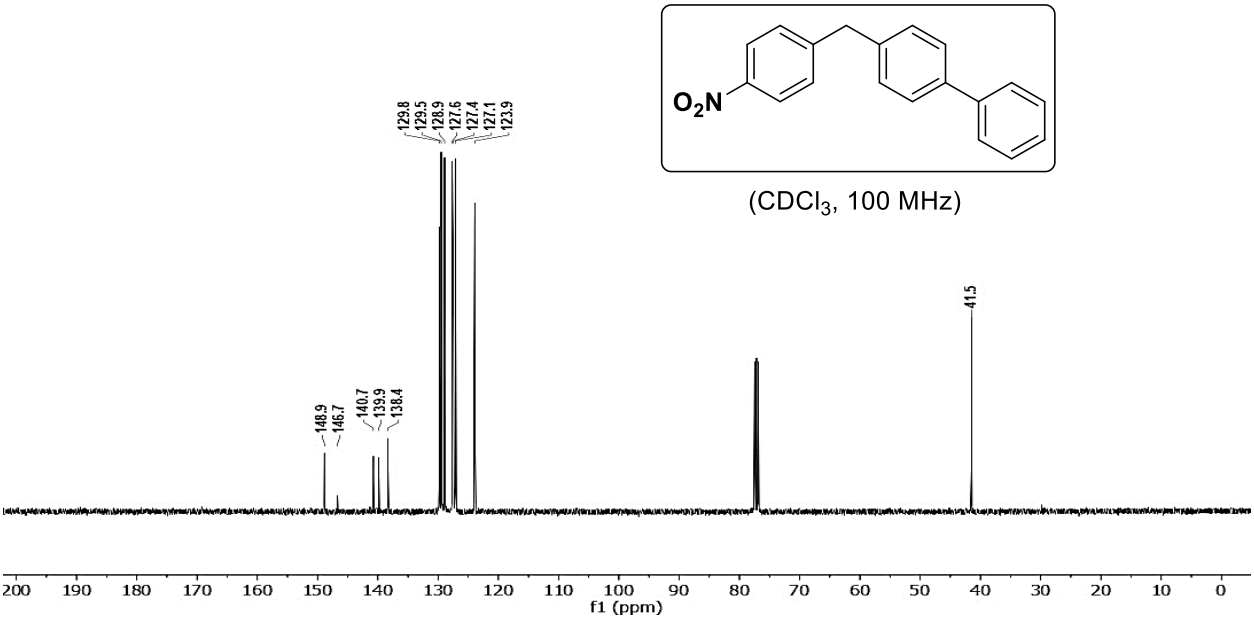
^{13}C NMR spectrum of 1-methyl-3-(4-nitrobenzyl)benzene (5).



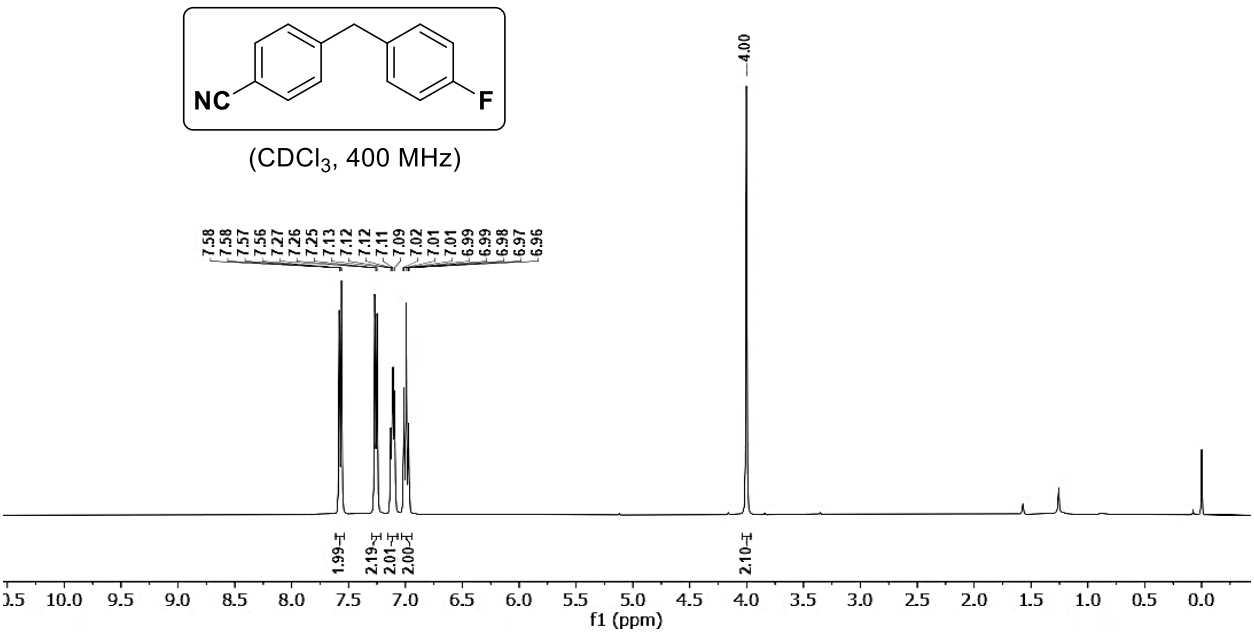
^{1}H NMR spectrum of 4-(4-nitrobenzyl)-1,1'-biphenyl (6).



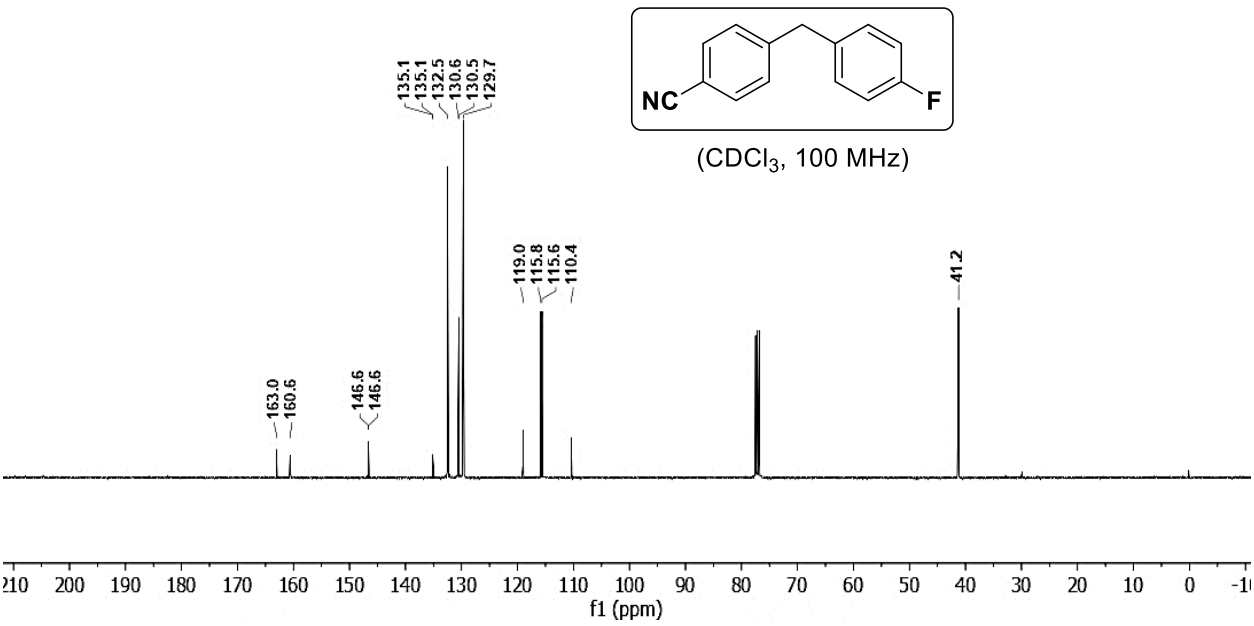
^{13}C NMR spectrum of 4-(4-nitrobenzyl)-1,1'-biphenyl (6).



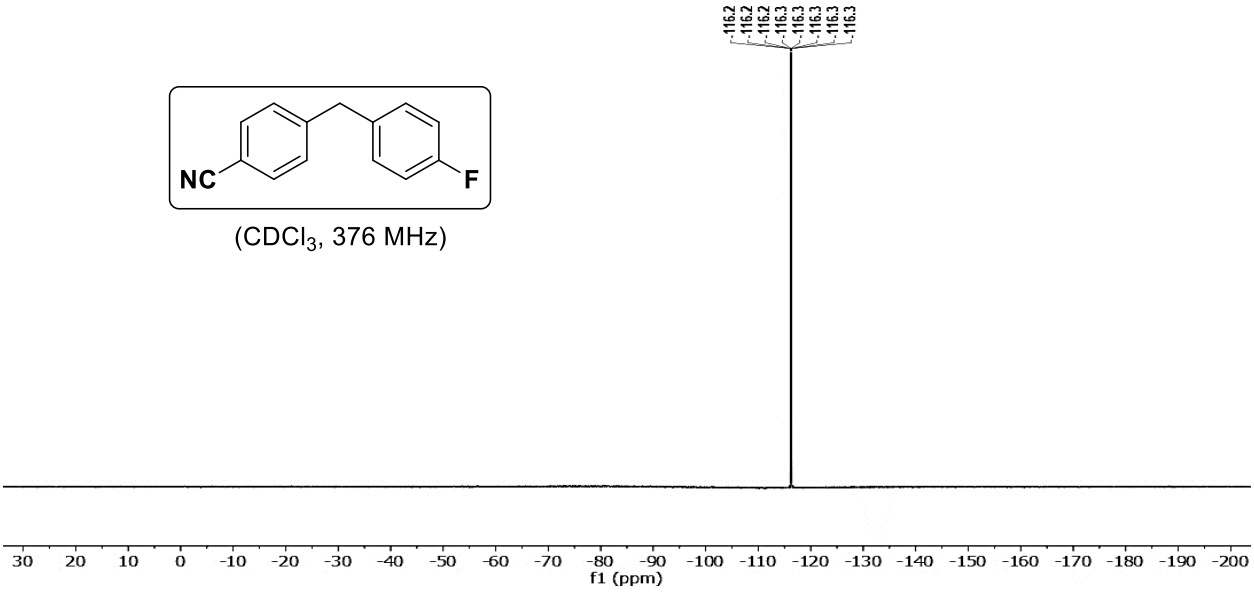
^{1}H NMR spectrum of 4-(4-fluorobenzyl)benzonitrile (7).



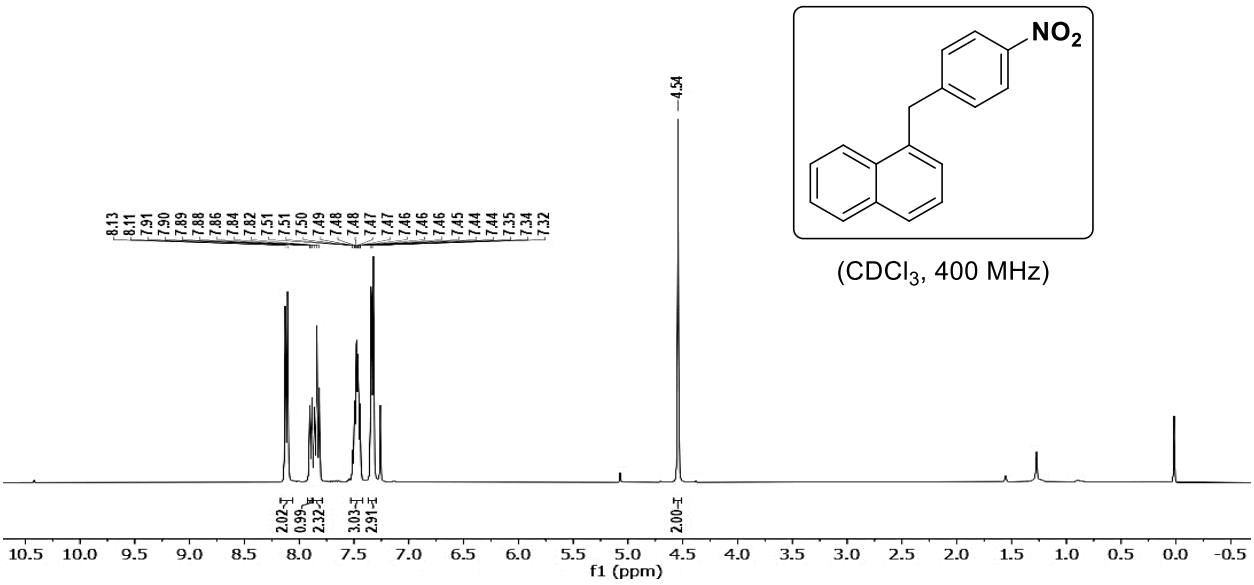
^{13}C NMR spectrum of 4-(4-fluorobenzyl)benzonitrile (7).



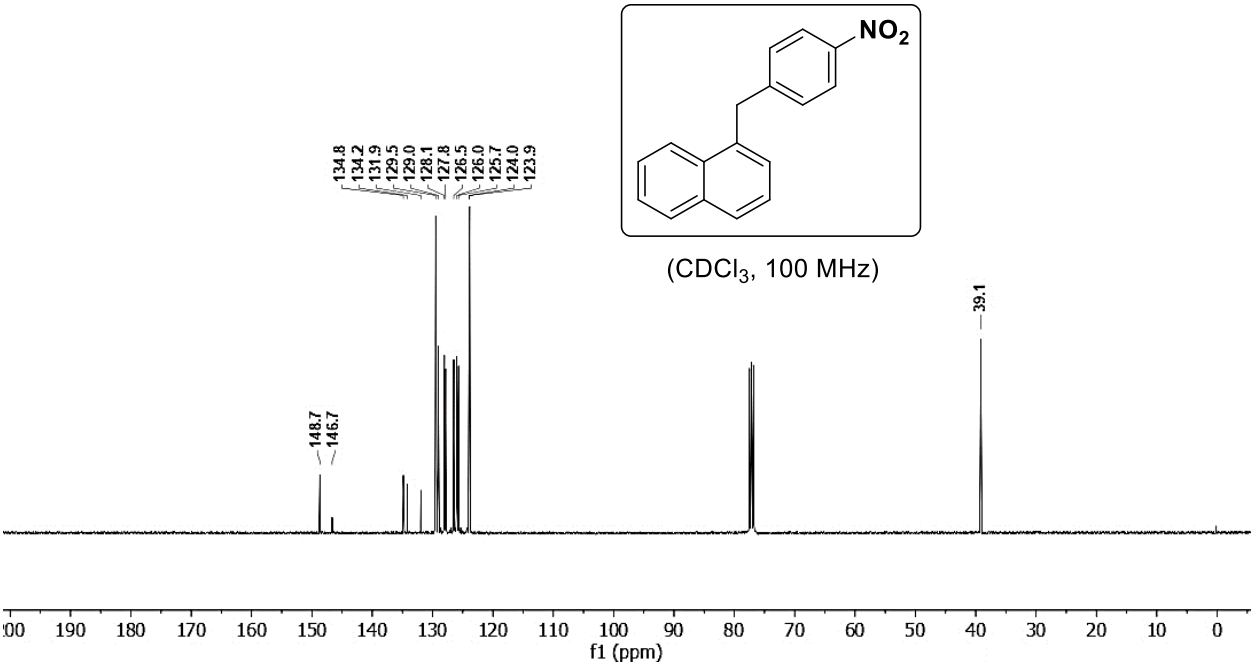
^{19}F NMR spectrum of 4-(4-fluorobenzyl)benzonitrile (7).



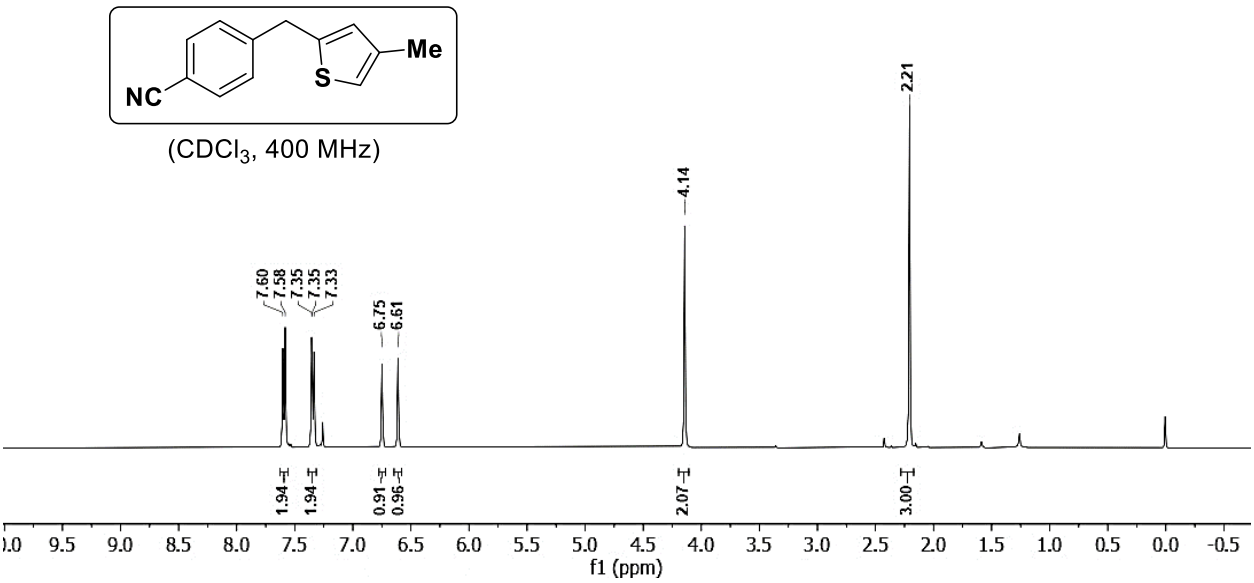
^{1}H NMR spectrum of 1-(4-nitrobenzyl)naphthalene (8).



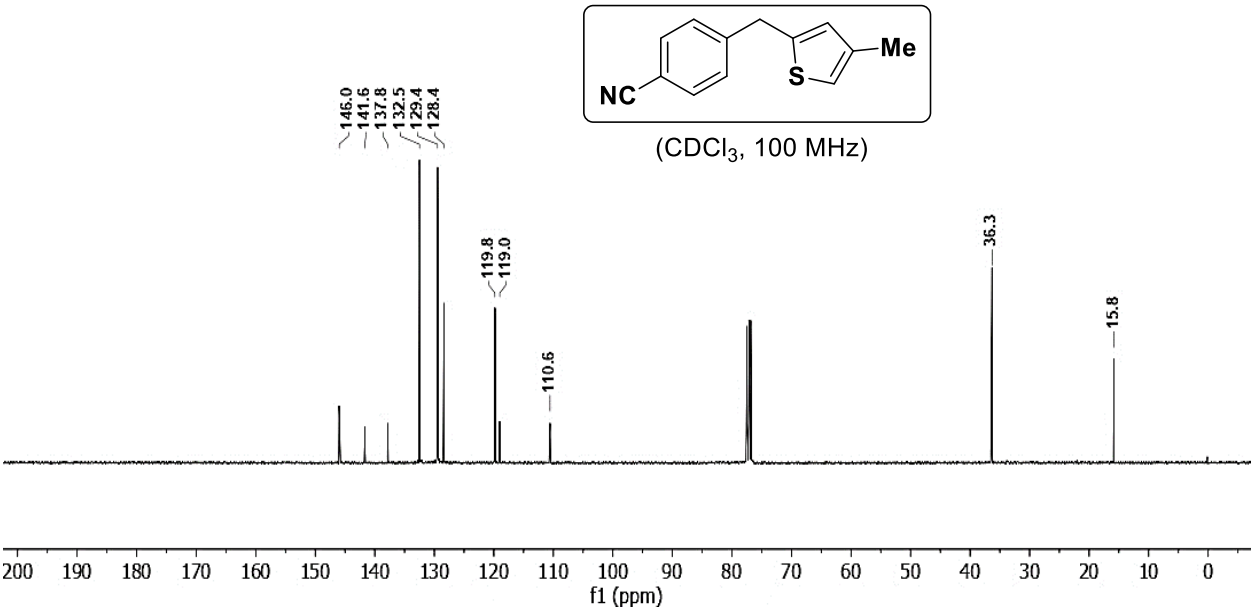
^{13}C NMR spectrum of 1-(4-nitrobenzyl)naphthalene (8).



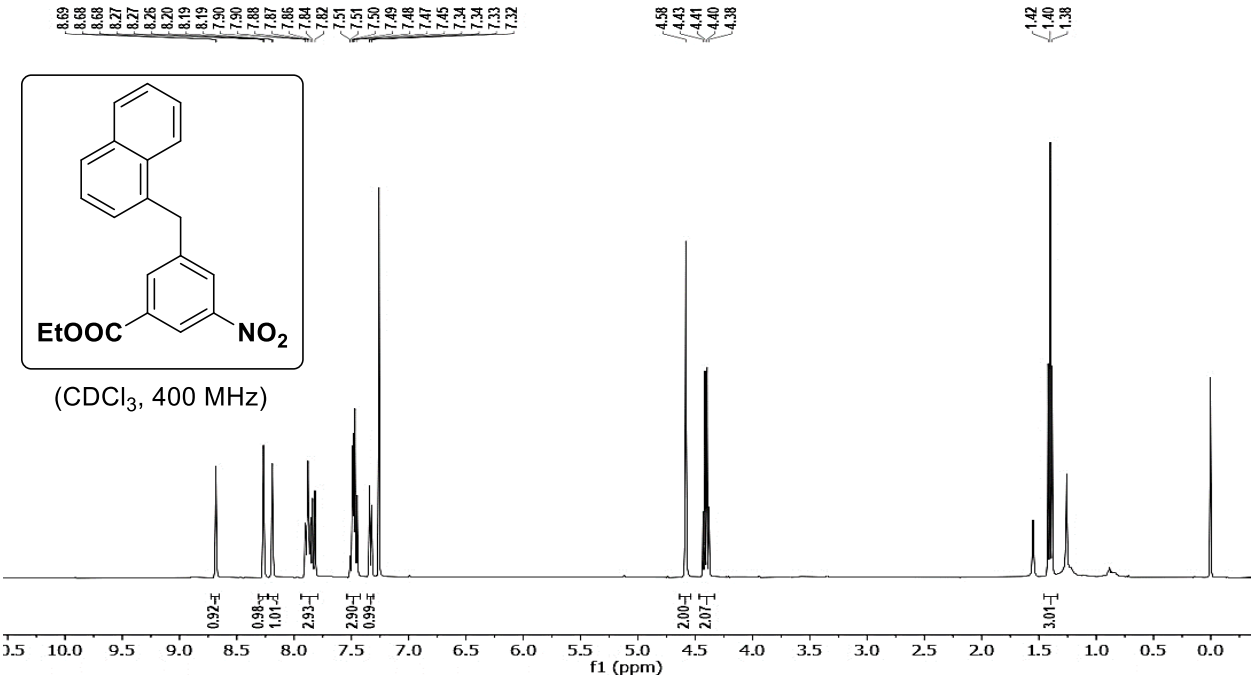
^{1}H NMR spectrum of 4-((4-methylthiophen-2-yl)methyl)benzonitrile (9).



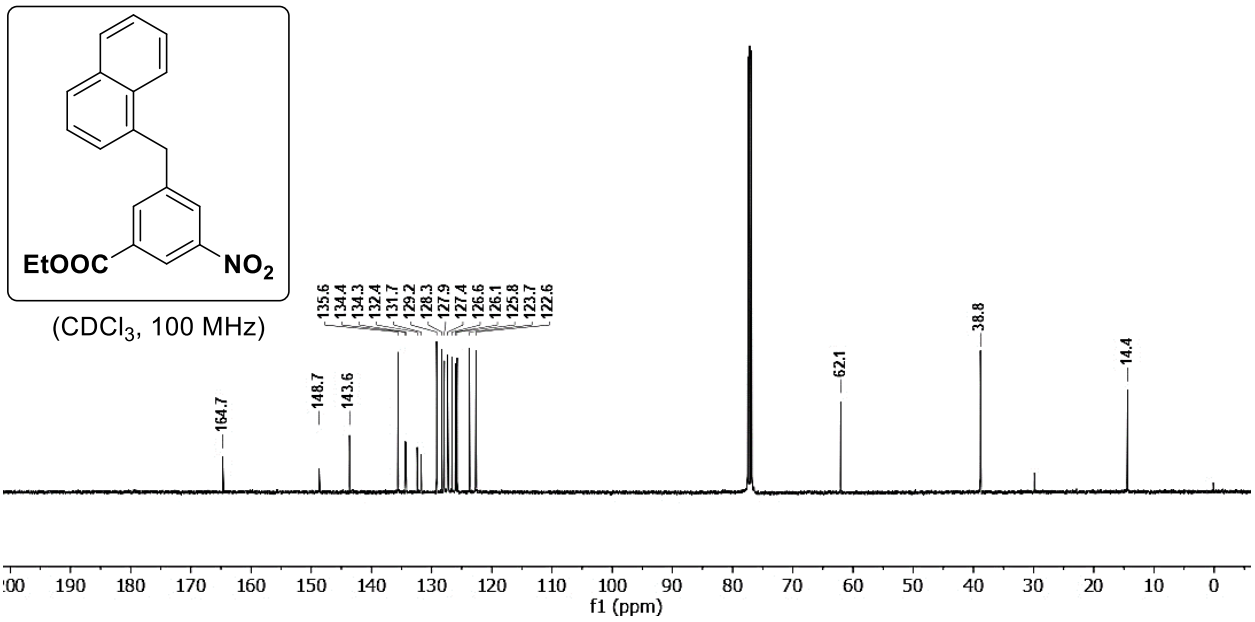
^{13}C NMR spectrum of 4-((4-methylthiophen-2-yl)methyl)benzonitrile (9).



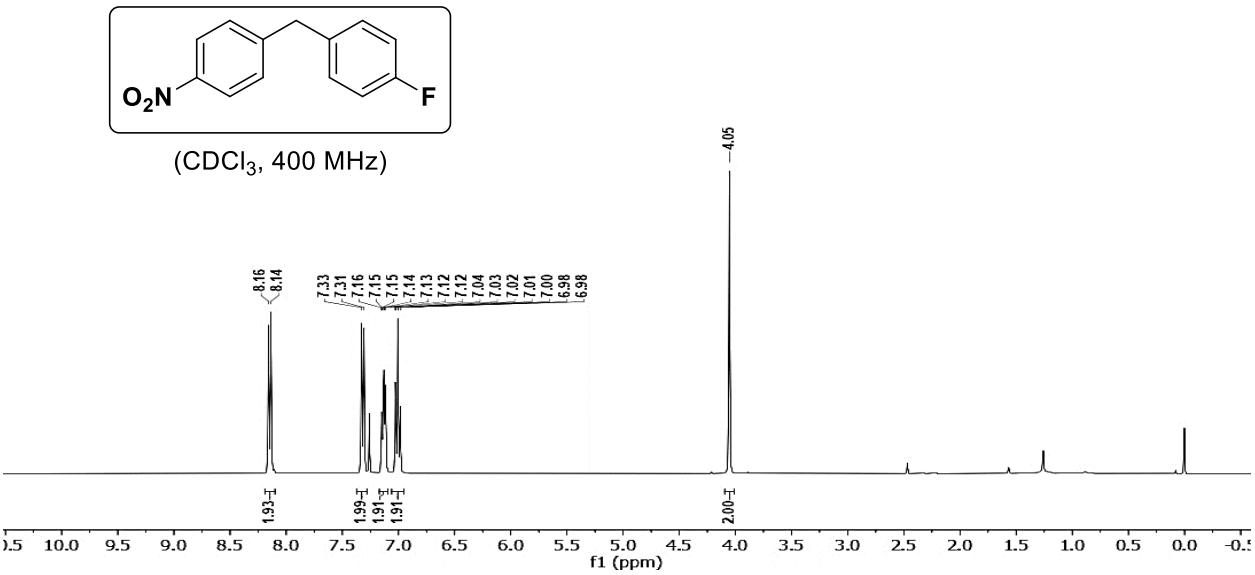
^{1}H NMR spectrum of ethyl 3-(naphthalen-1-ylmethyl)-5-nitrobenzoate (10).



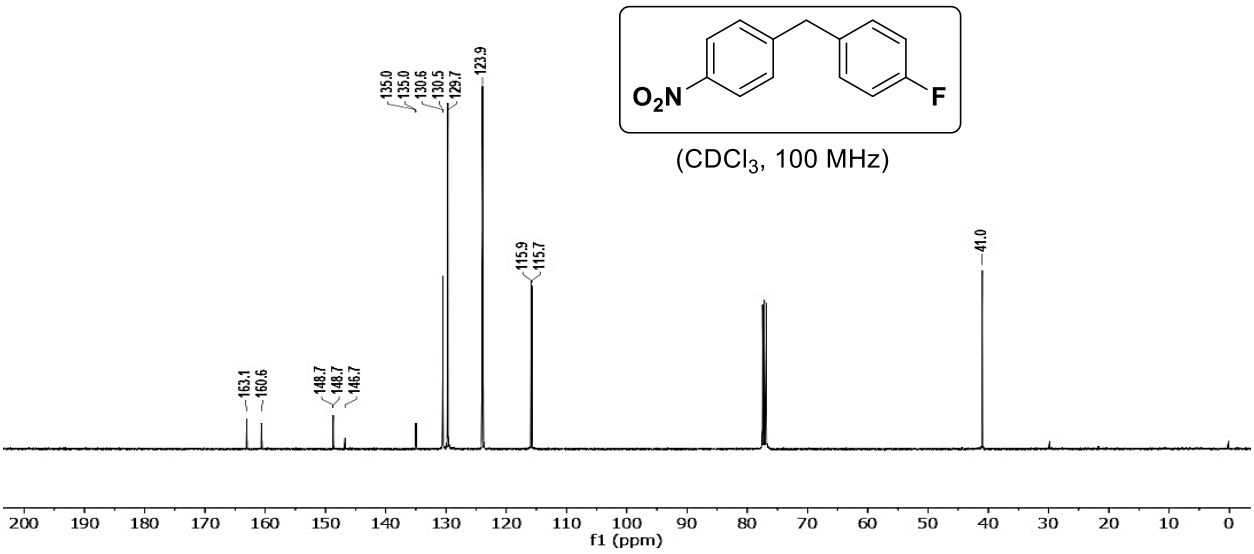
^{13}C NMR spectrum of ethyl 3-(naphthalen-1-ylmethyl)-5-nitrobenzoate (10).



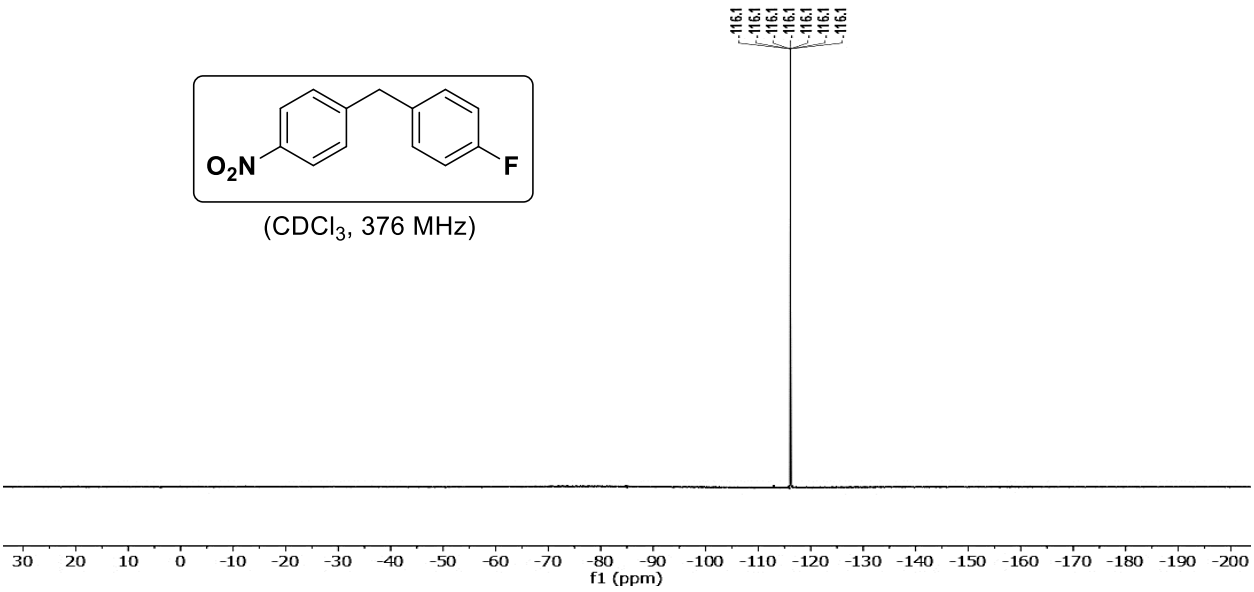
^{1}H NMR spectrum of 1-fluoro-4-(4-nitrobenzyl)benzene (11).



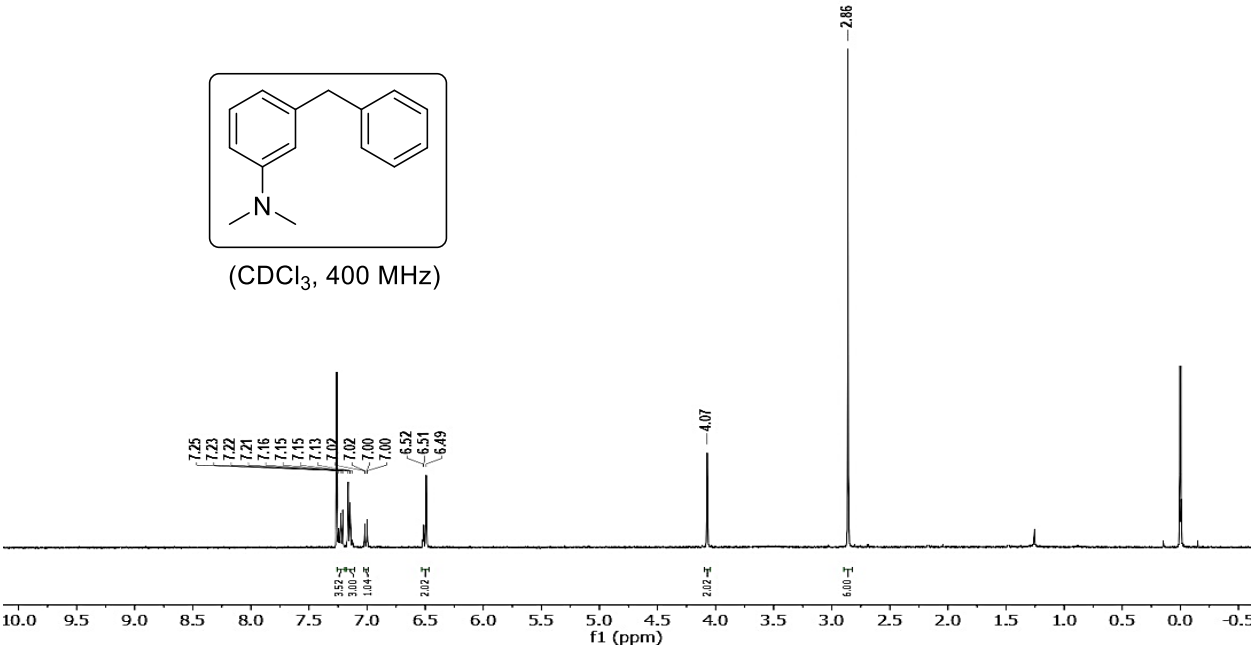
^{13}C NMR spectrum of 1-fluoro-4-(4-nitrobenzyl)benzene (11).



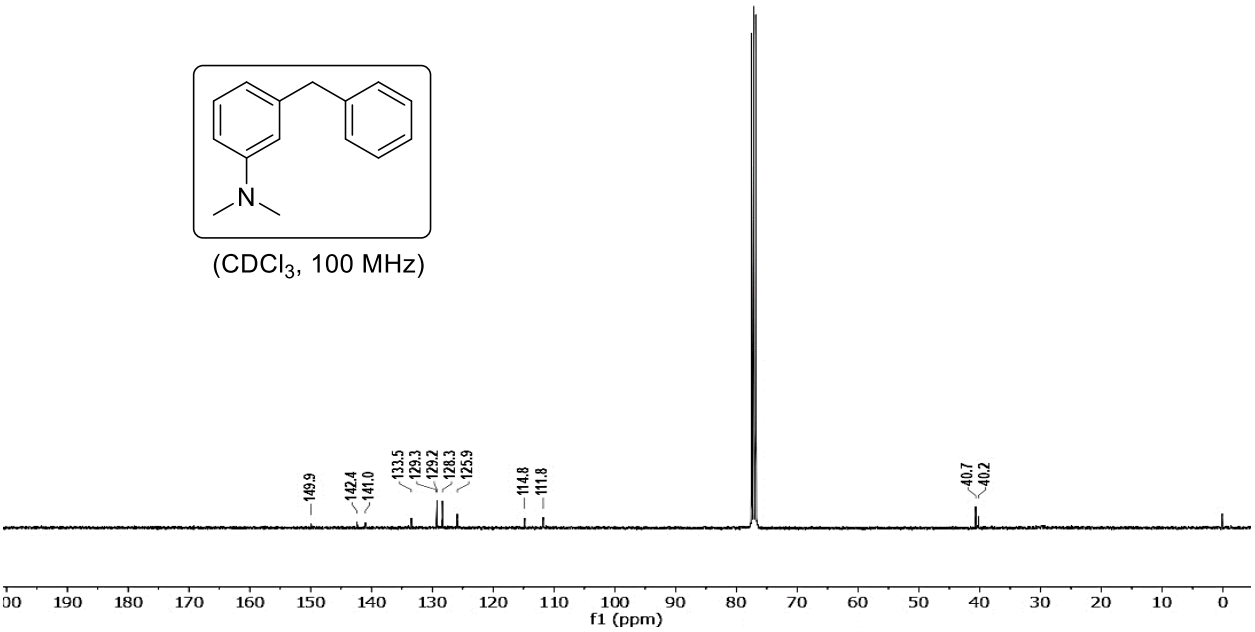
^{19}F NMR spectrum of 1-fluoro-4-(4-nitrobenzyl)benzene (11).



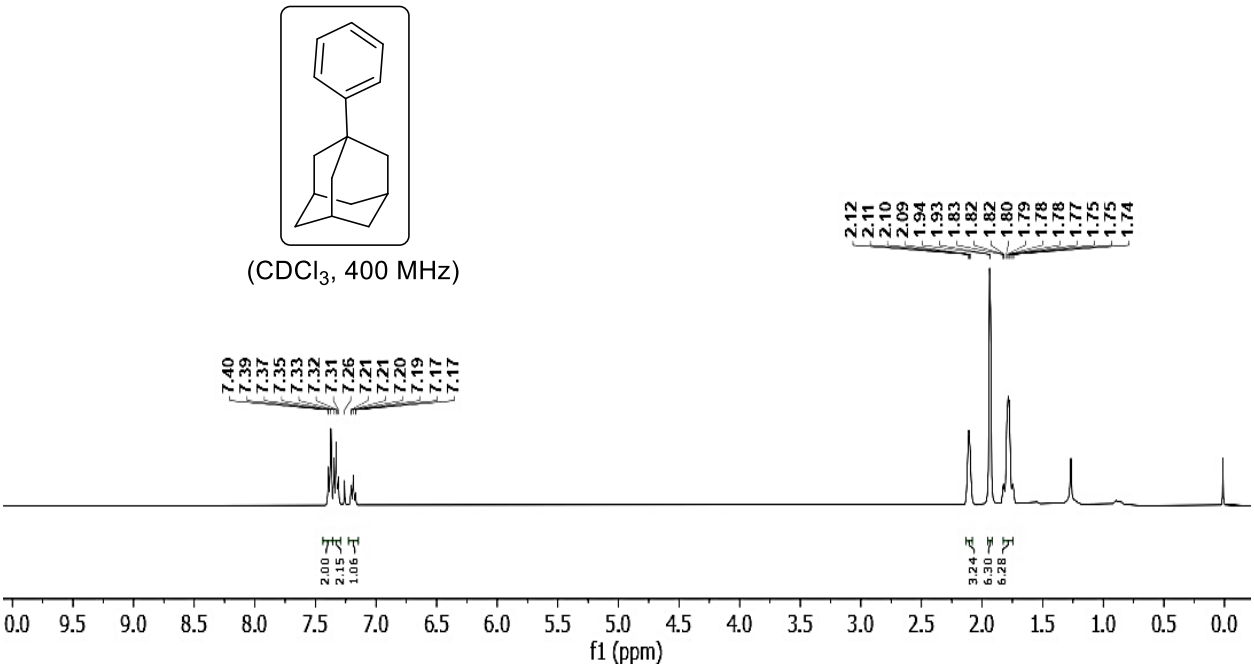
^{1}H NMR spectrum of 3-benzyl-*N*,*N*-dimethylaniline (12).



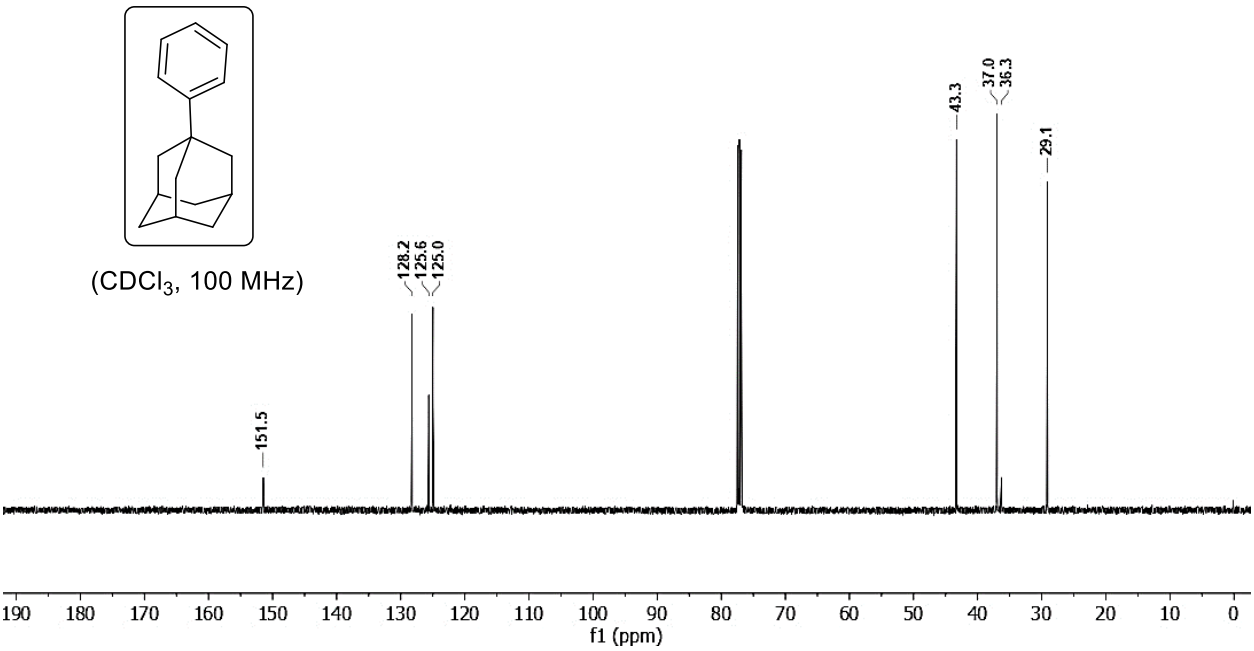
^{13}C NMR spectrum of 3-benzyl-*N*,*N*-dimethylaniline (12).



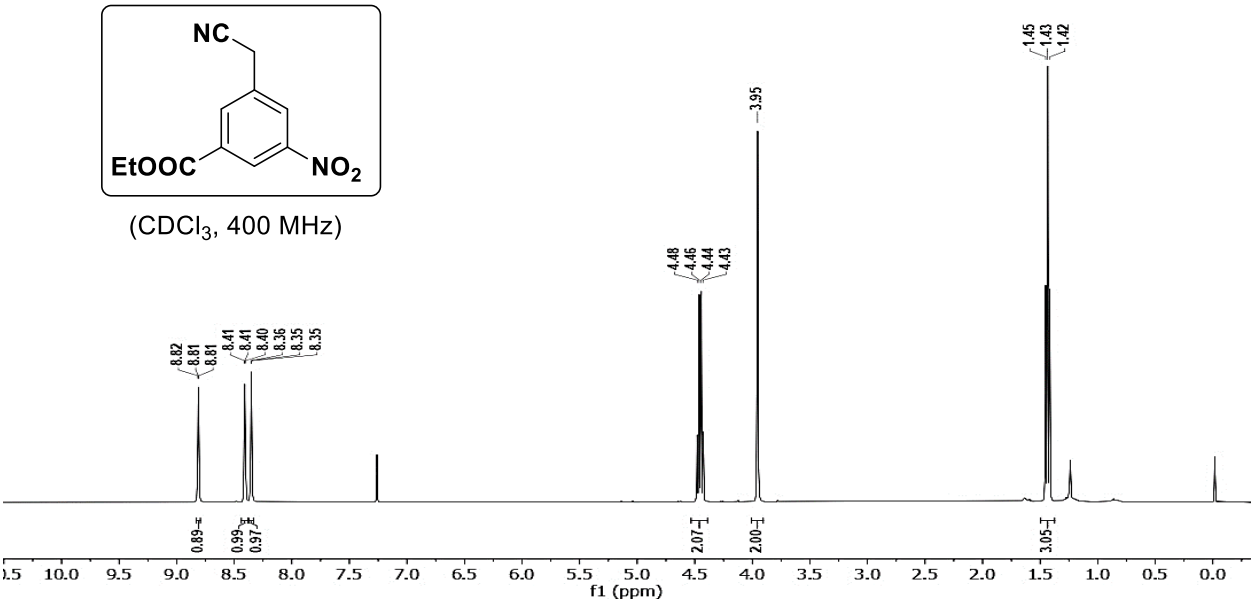
^{1}H NMR spectrum of 1-phenyladamantane (13).



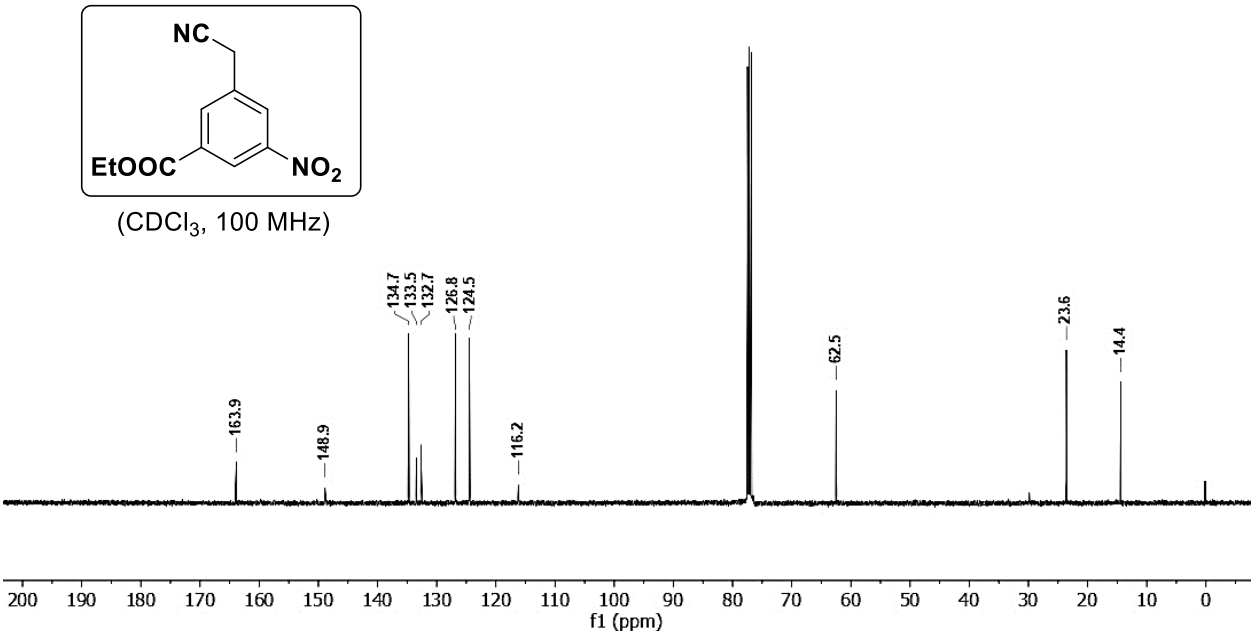
^{13}C NMR spectrum of 1-phenyladamantane (13).



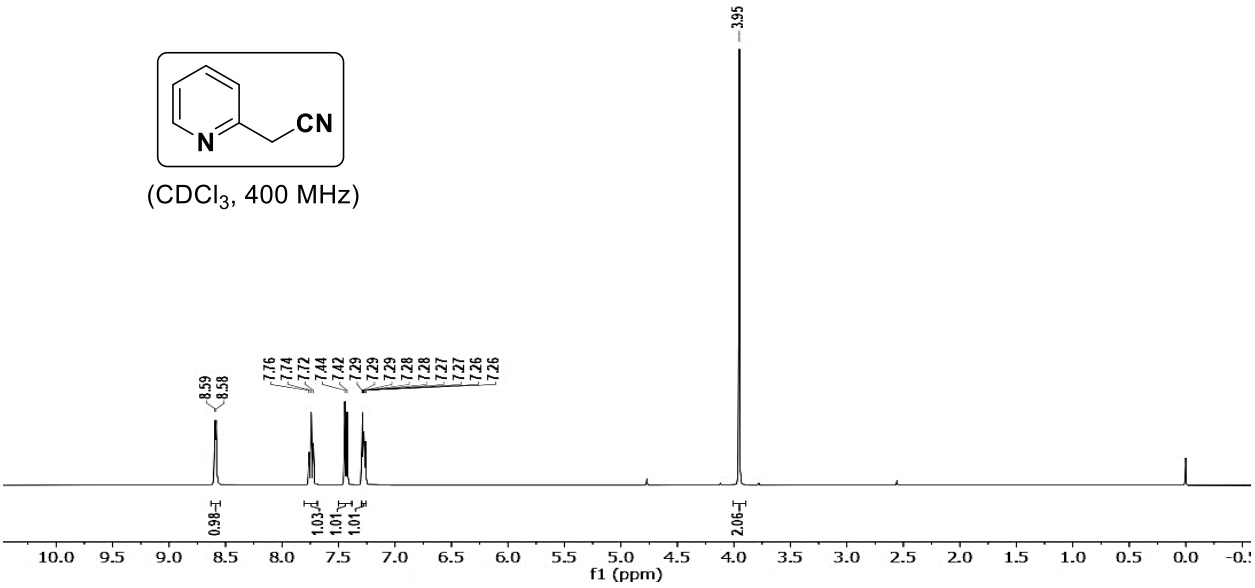
^{1}H NMR spectrum of ethyl 3-(cyanomethyl)-5-nitrobenzoate (14).



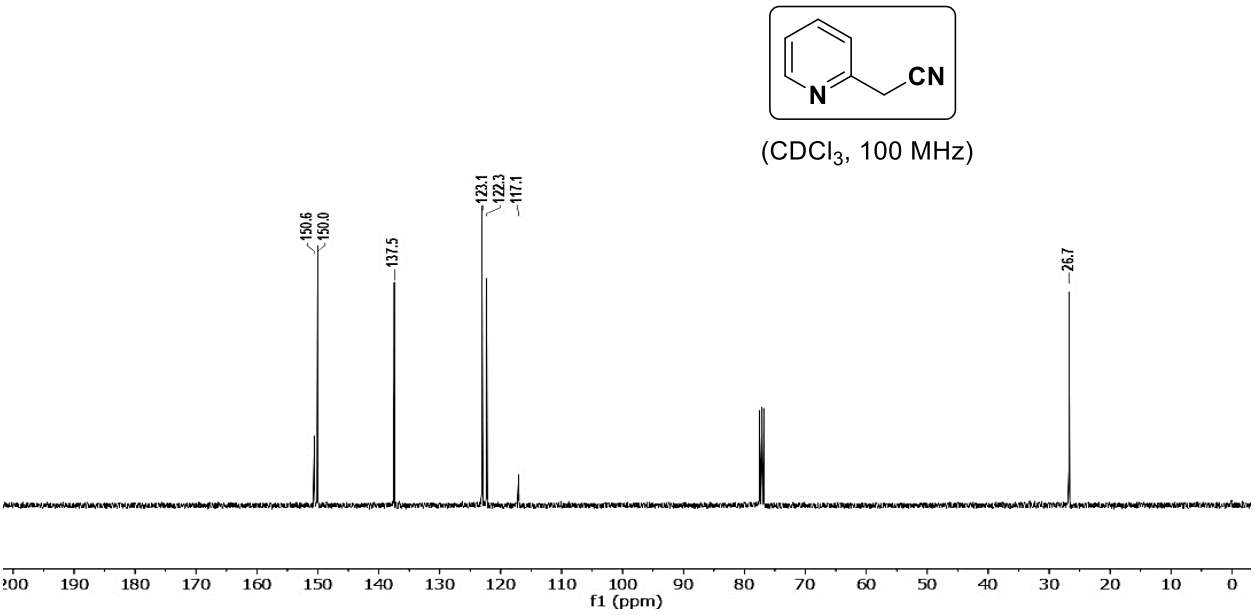
^{13}C NMR spectrum of ethyl 3-(cyanomethyl)-5-nitrobenzoate (14).



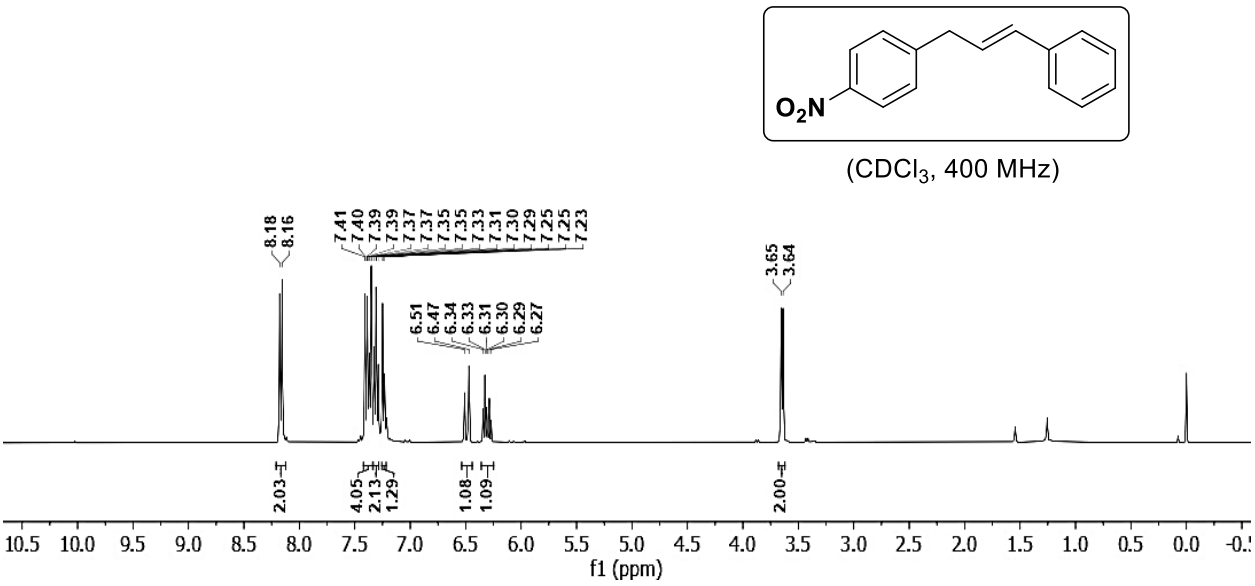
^{1}H NMR spectrum of 2-(pyridin-2-yl)acetonitrile (15).



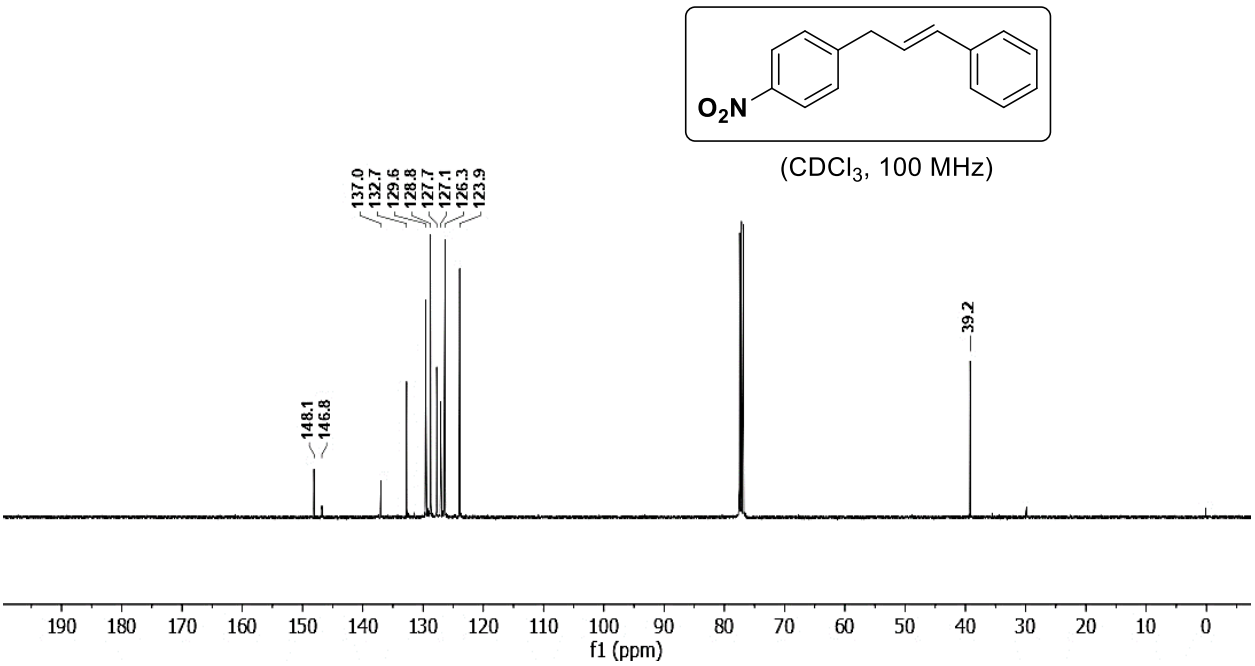
^{13}C NMR spectrum of 2-(pyridin-2-yl)acetonitrile (15).



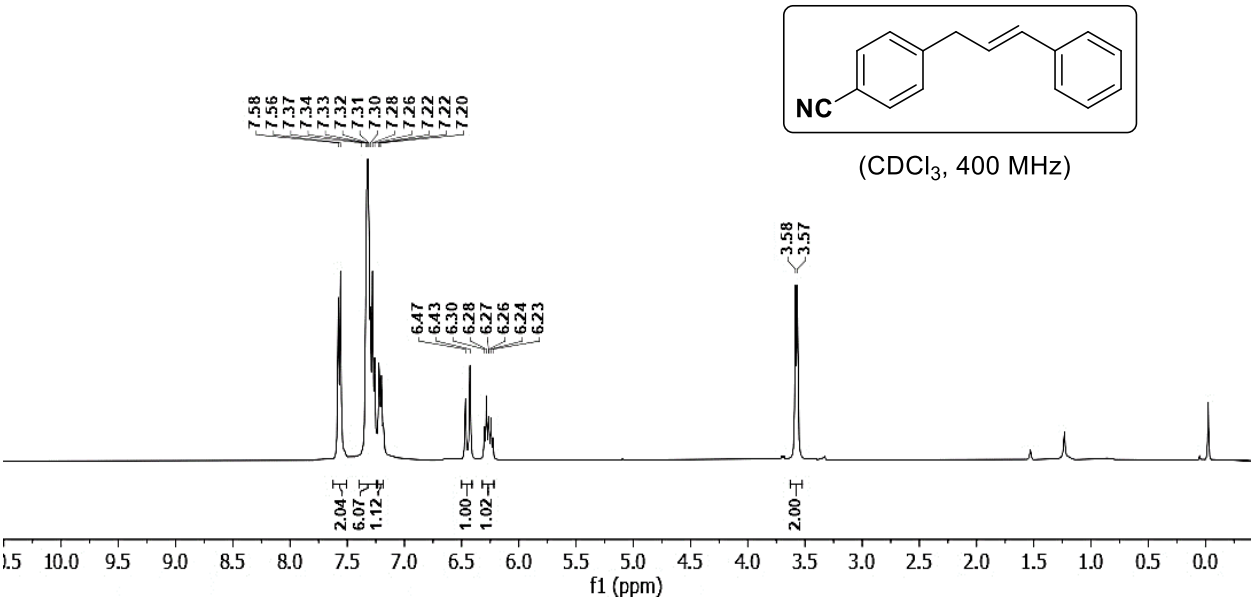
^{1}H NMR spectrum of (*E*)-3-(4-nitrophenyl)-1-phenylpropene (16).



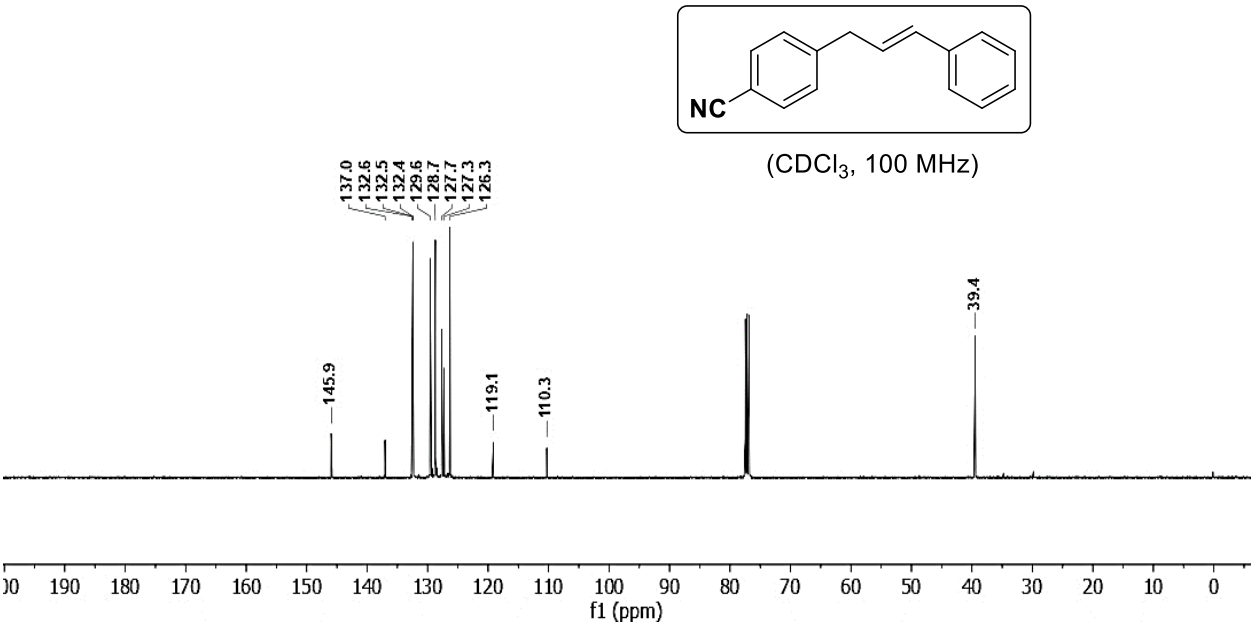
^{13}C NMR spectrum of (*E*)-3-(4-nitrophenyl)-1-phenylpropene (16).



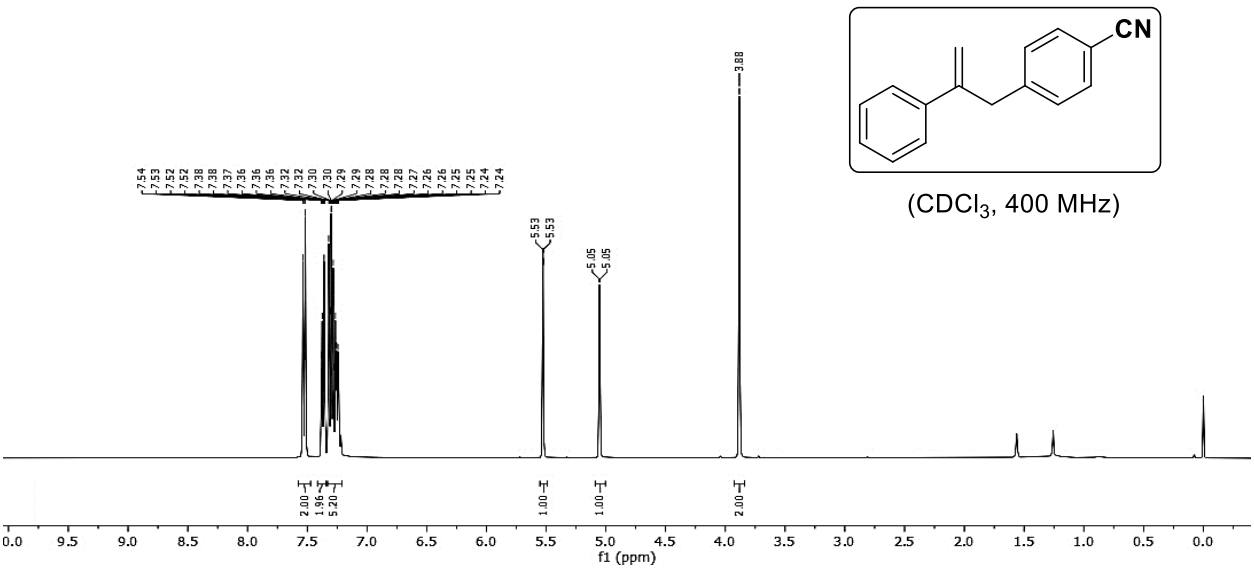
^{1}H NMR spectrum of (*E*)-3-(4-cyanophenyl)-1-phenylpropene (17).



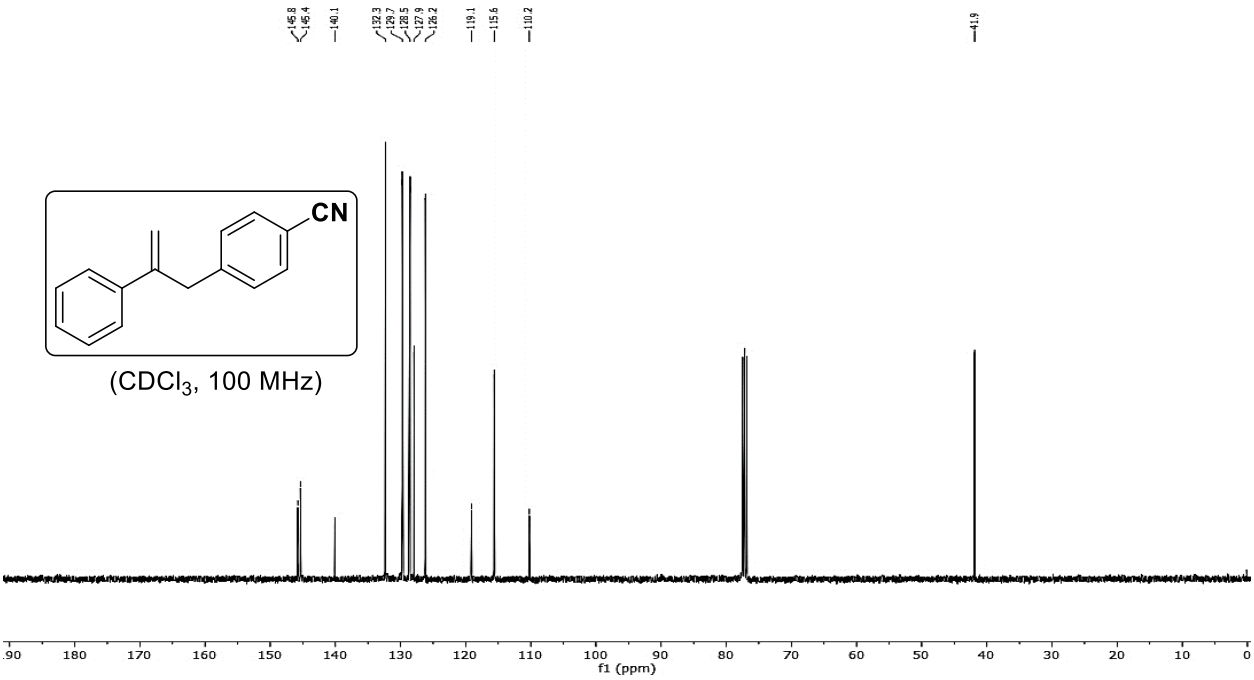
^{13}C NMR spectrum of (*E*)-3-(4-cyanophenyl)-1-phenylpropene (17).



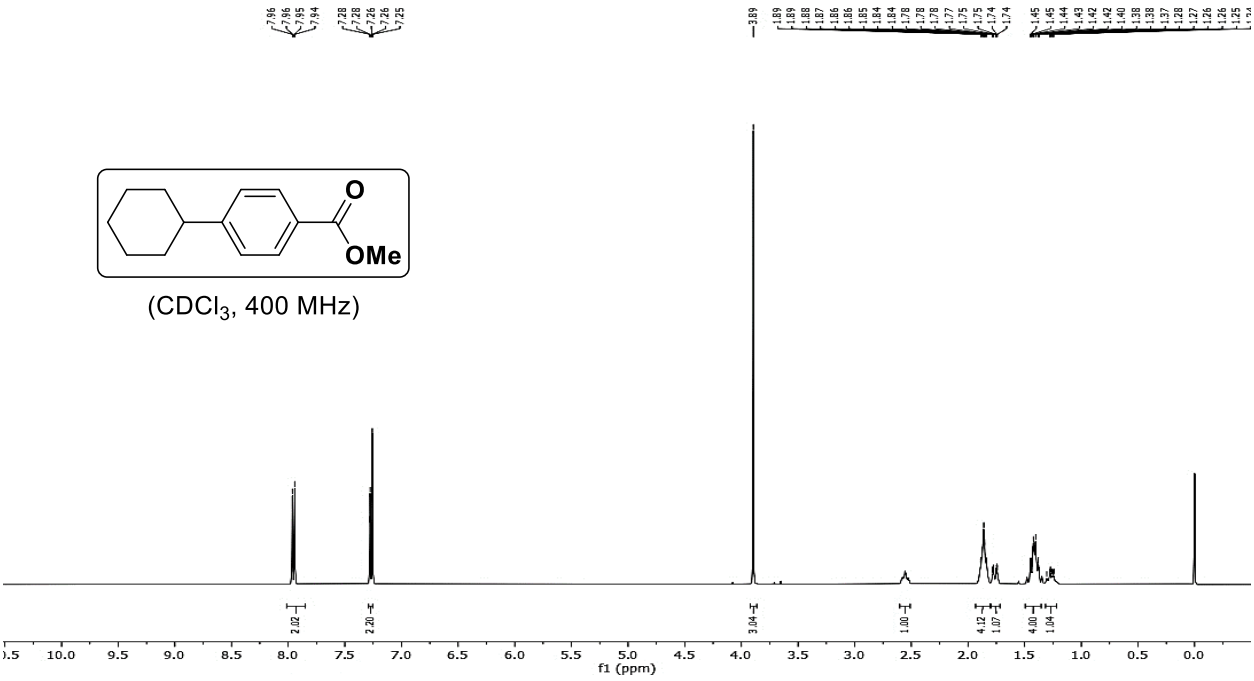
^{1}H NMR spectrum of 4-(2-phenylallyl)benzonitrile (18).



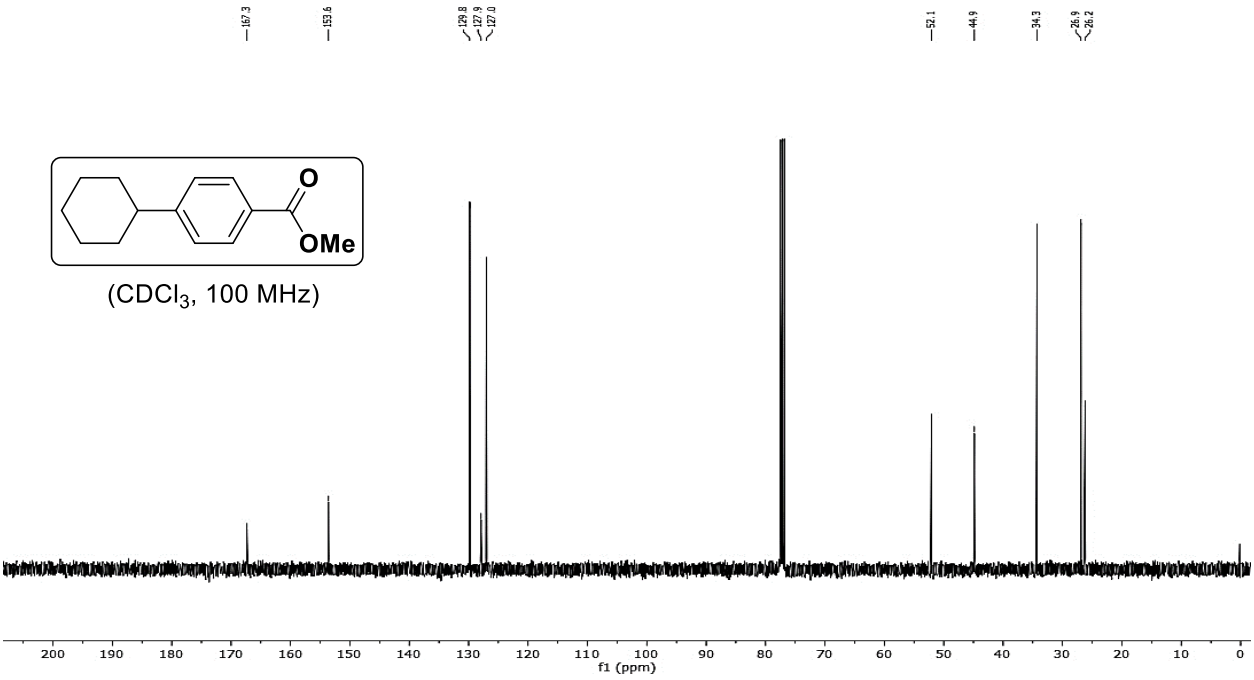
^{13}C NMR spectrum of 4-(2-phenylallyl)benzonitrile (18).



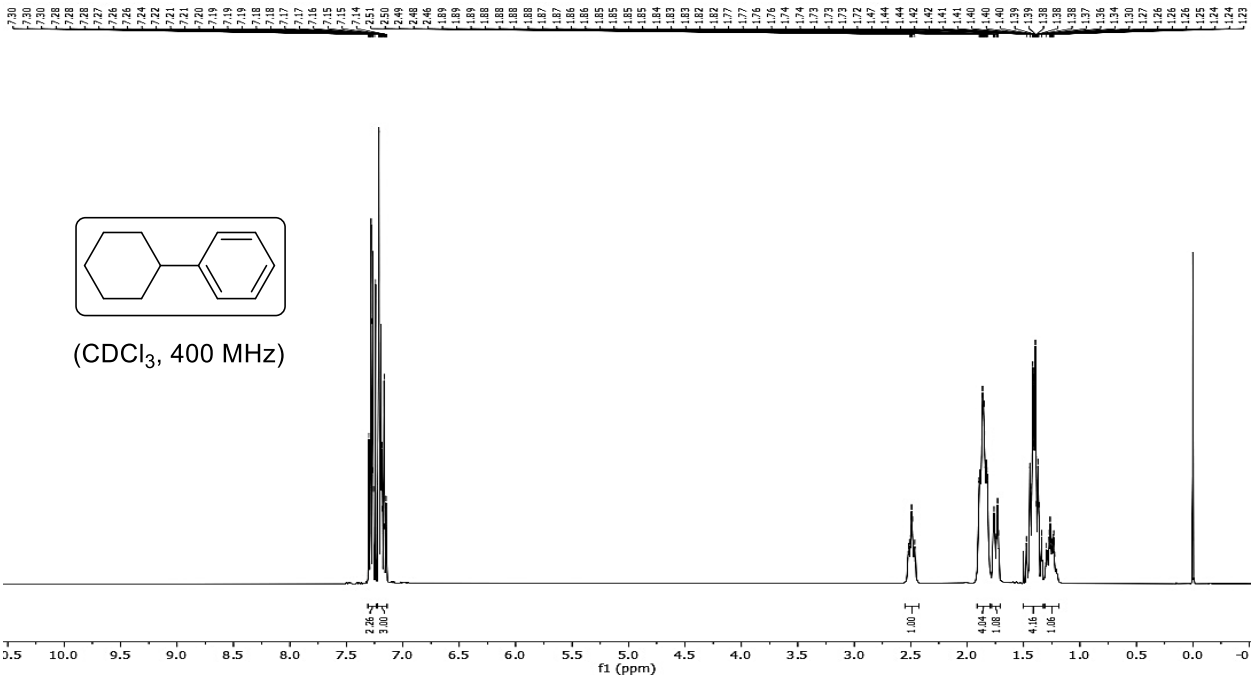
^{1}H NMR spectrum of methyl 4-cyclohexylbenzoate (21).



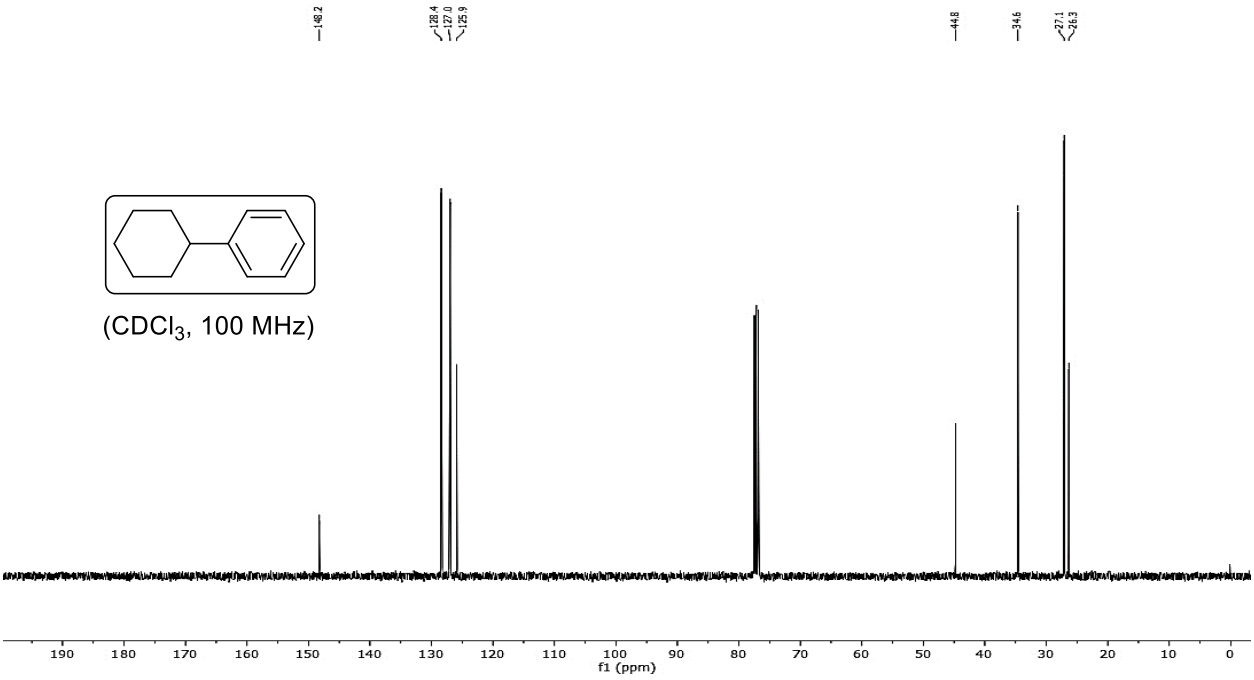
^{13}C NMR spectrum of methyl 4-cyclohexylbenzoate (21).



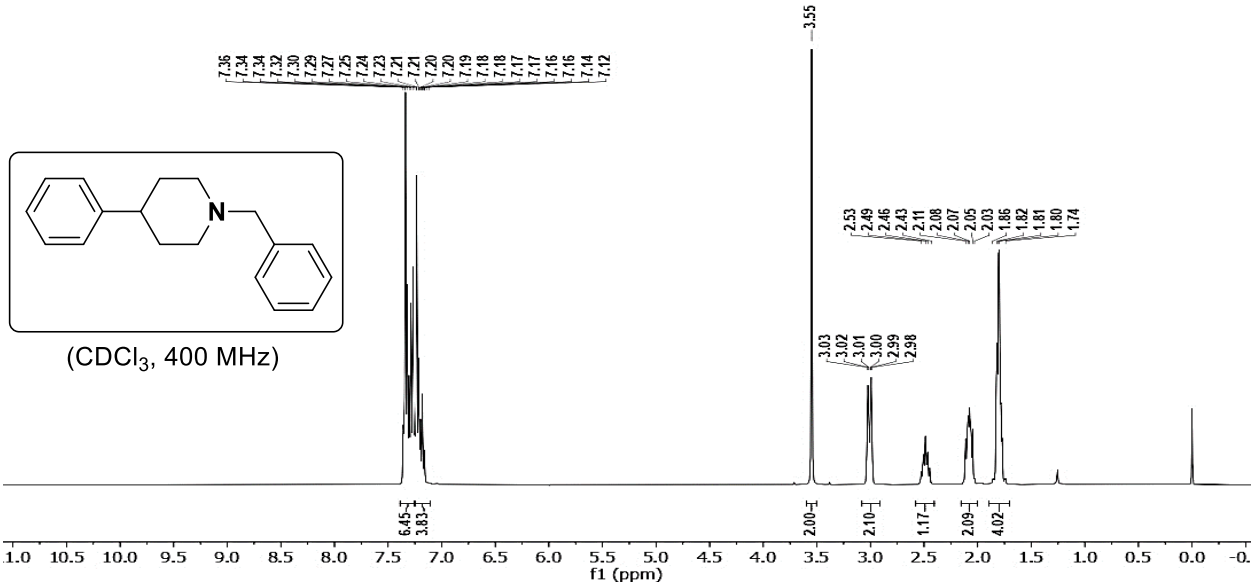
^{1}H NMR spectrum of cyclohexylbenzene (22).



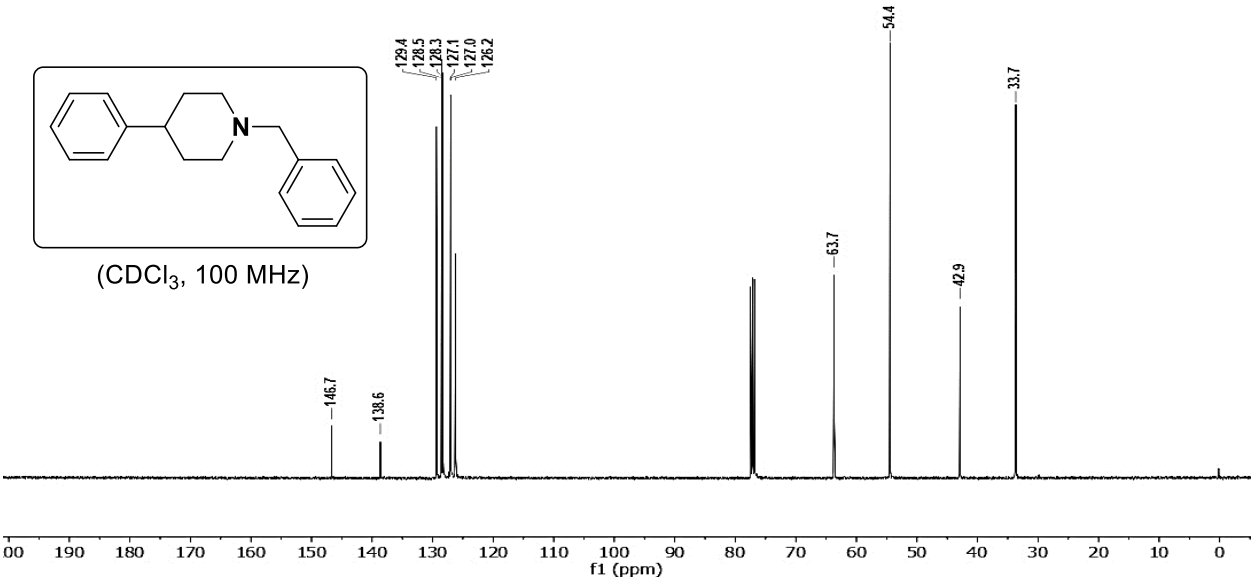
^{13}C NMR spectrum of cyclohexylbenzene (22).



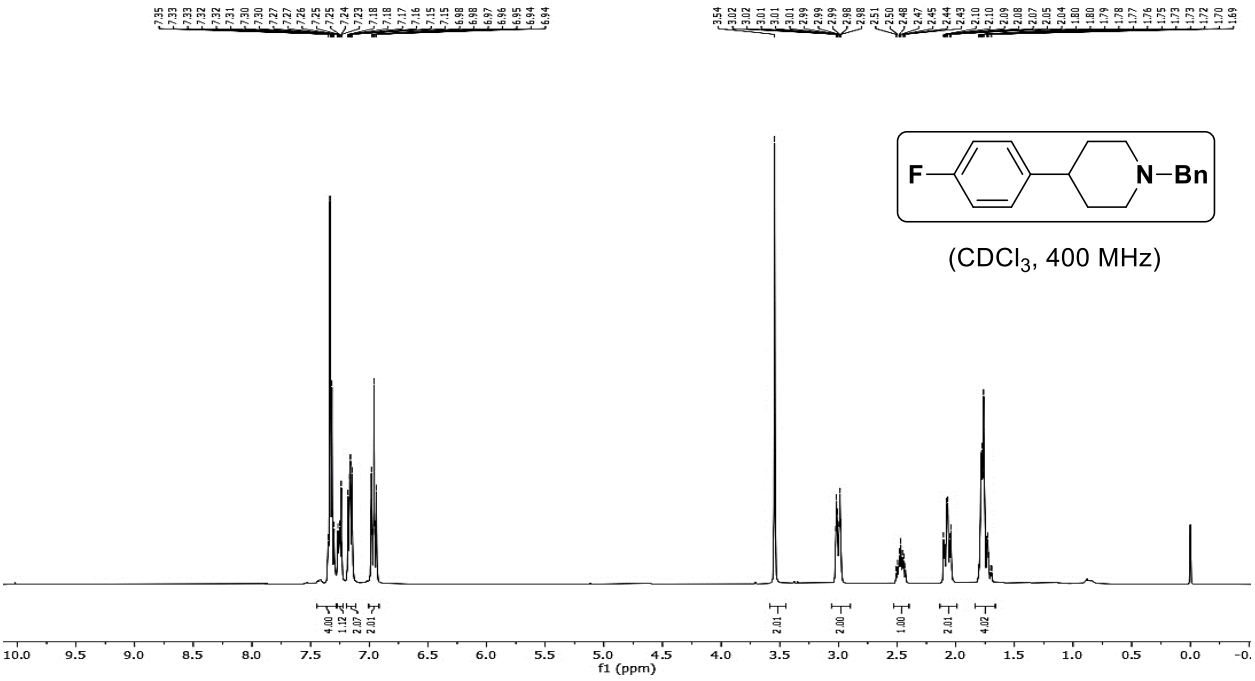
^{1}H NMR spectrum of 1-benzyl-4-phenylpiperidine (23).



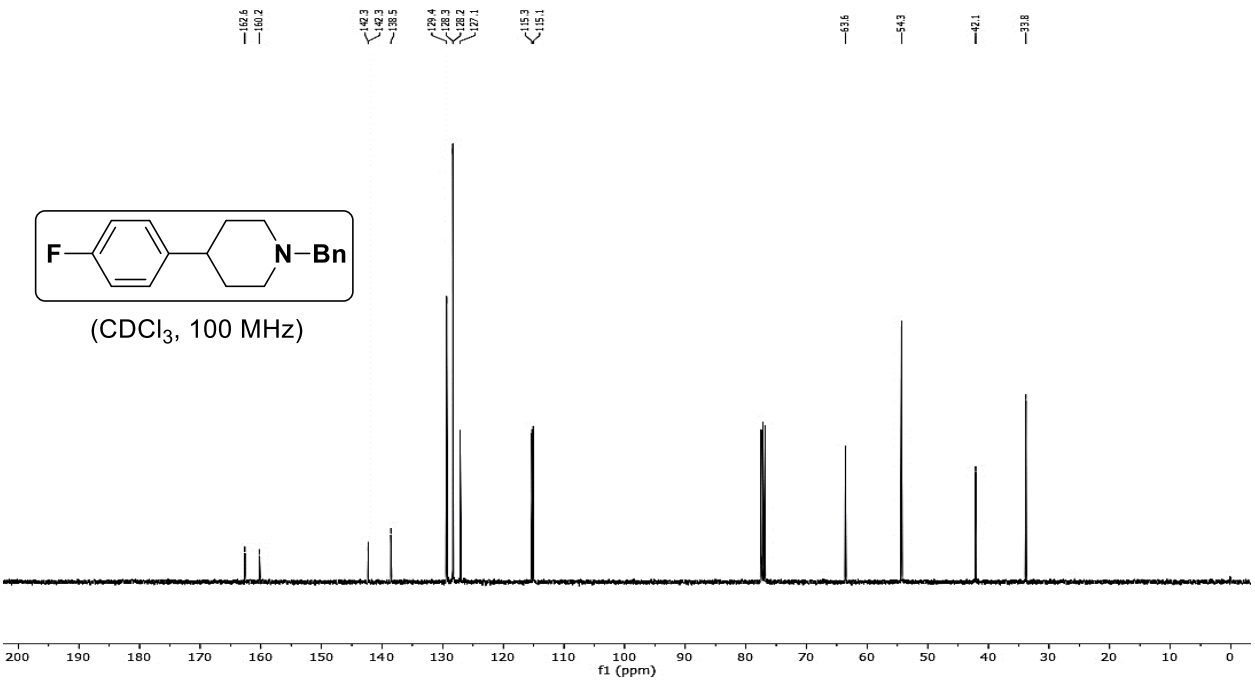
^{13}C NMR spectrum of 1-benzyl-4-phenylpiperidine (23).



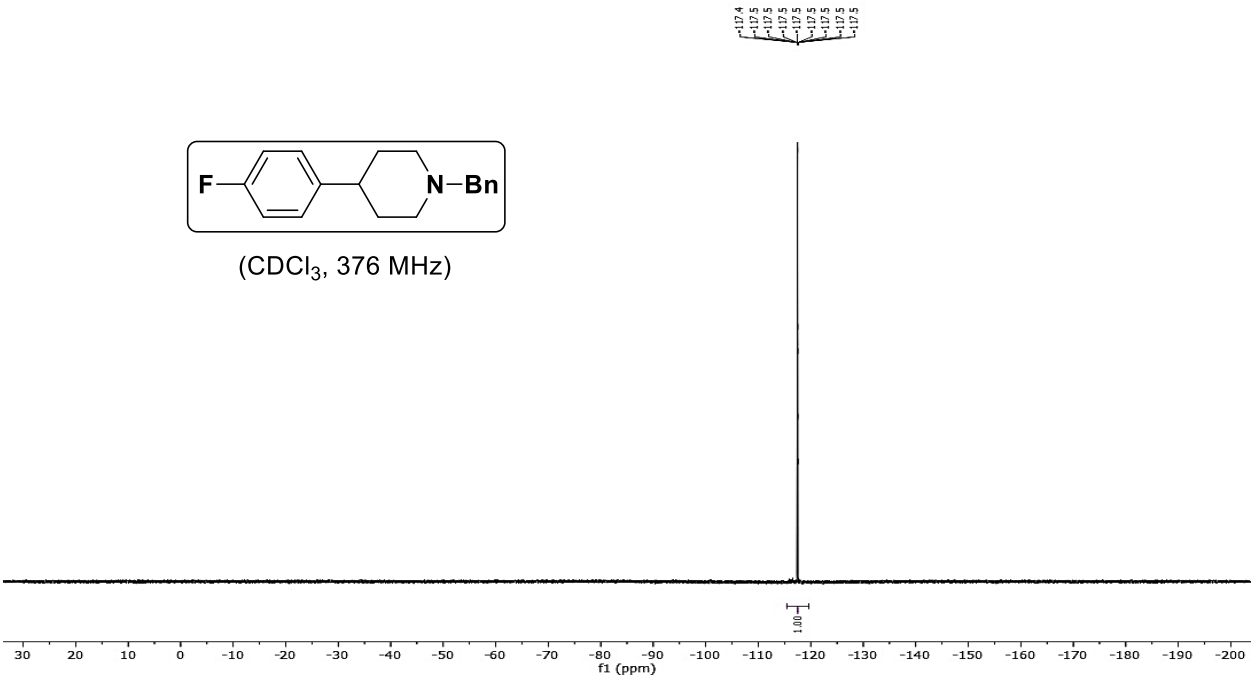
^{1}H NMR spectrum of 1-benzyl-4-(4-fluorophenyl)piperidine (24).



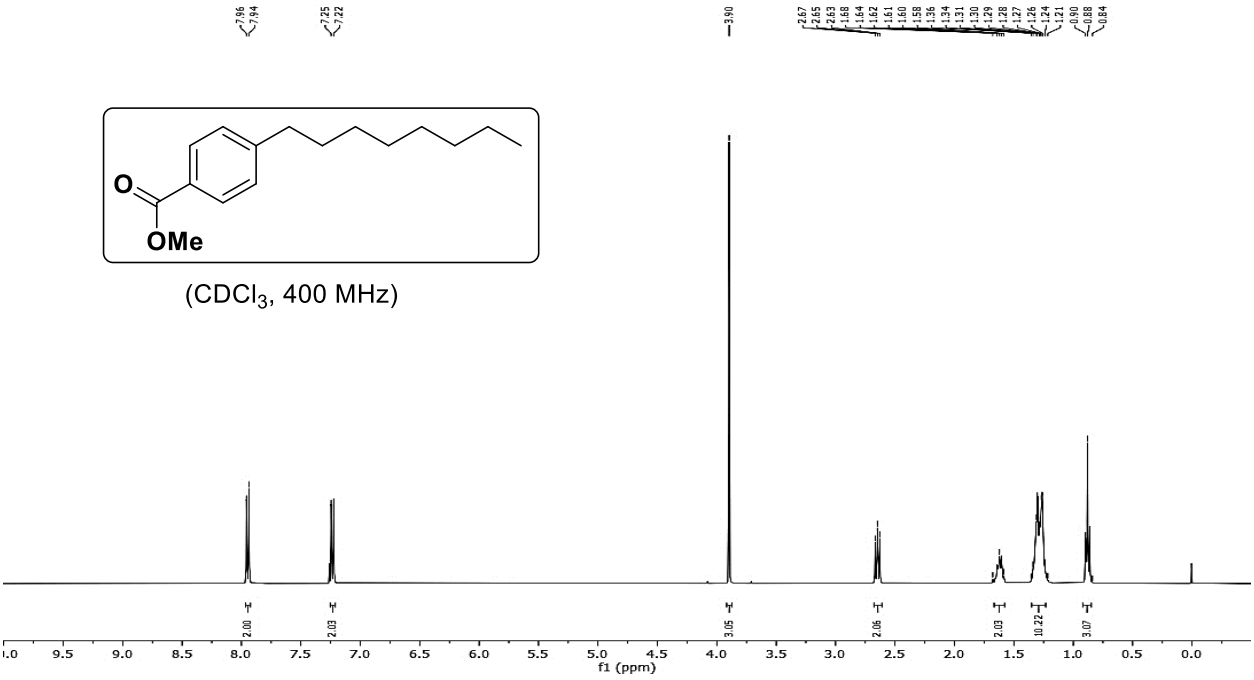
^{13}C NMR spectrum of 1-benzyl-4-(4-fluorophenyl)piperidine (24).



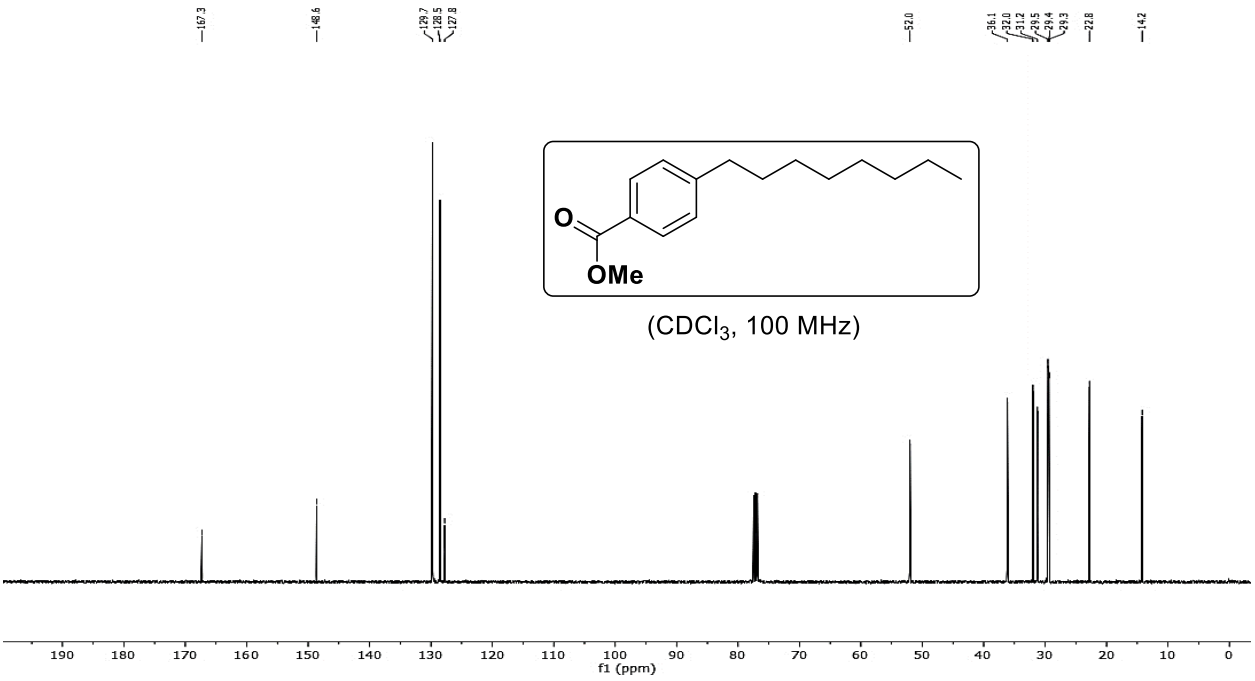
^{19}F NMR spectrum of 1-benzyl-4-(4-fluorophenyl)piperidine (24).



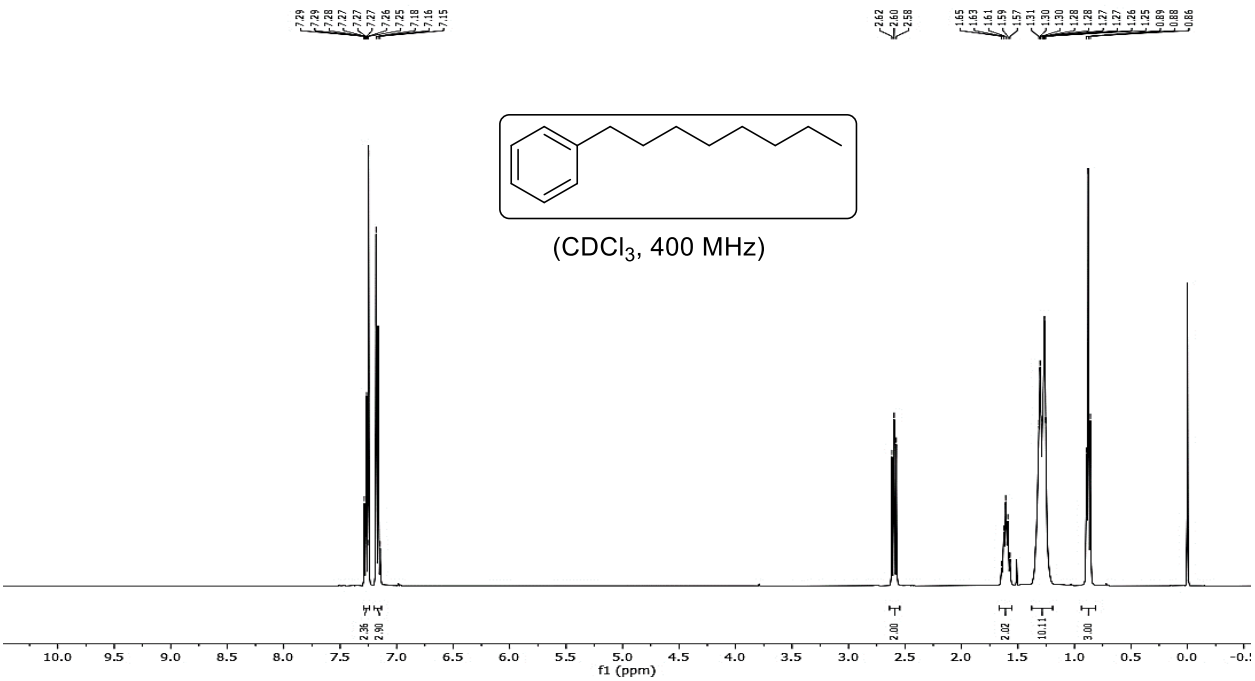
^{1}H NMR spectrum of methyl 4-octylbenzoate (25).



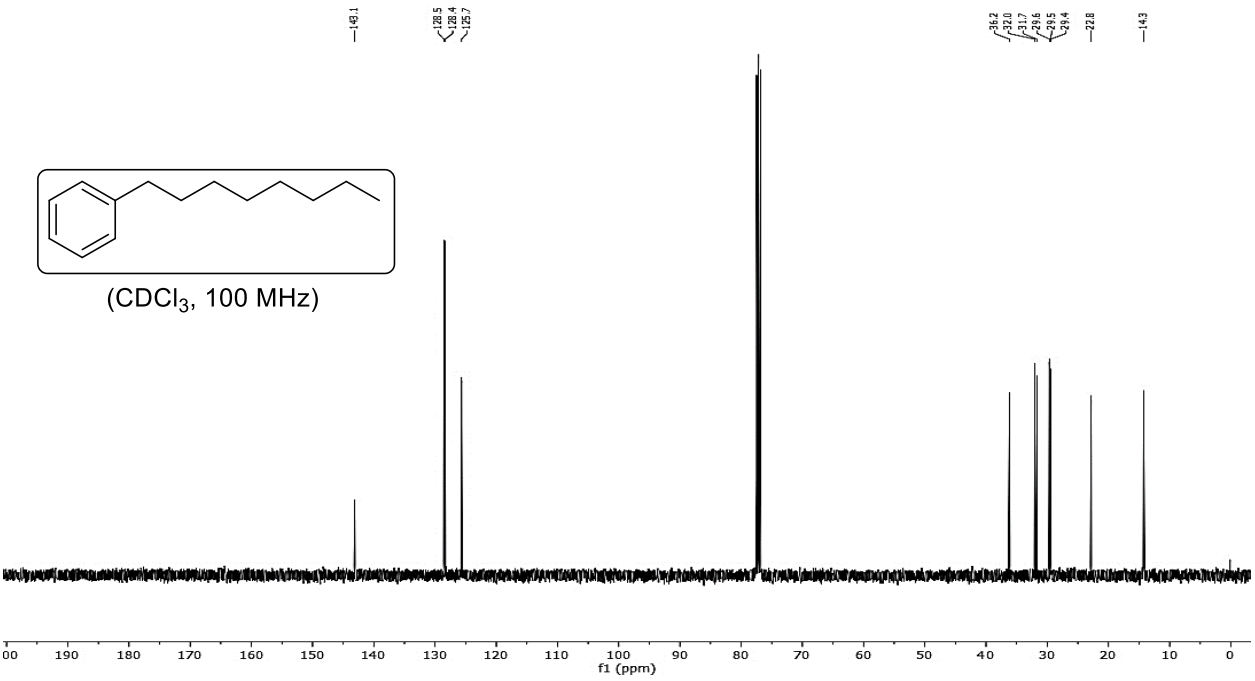
^{13}C NMR spectrum of methyl 4-octylbenzoate (25).



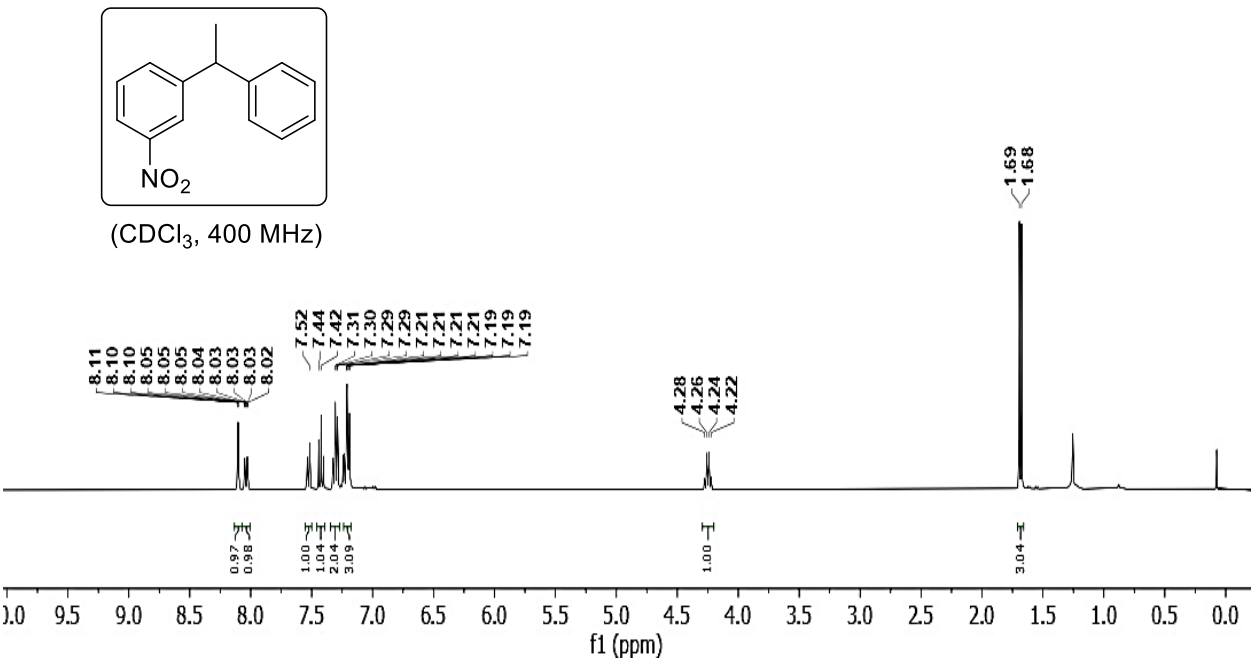
^{1}H NMR spectrum of octylbenzene (26).



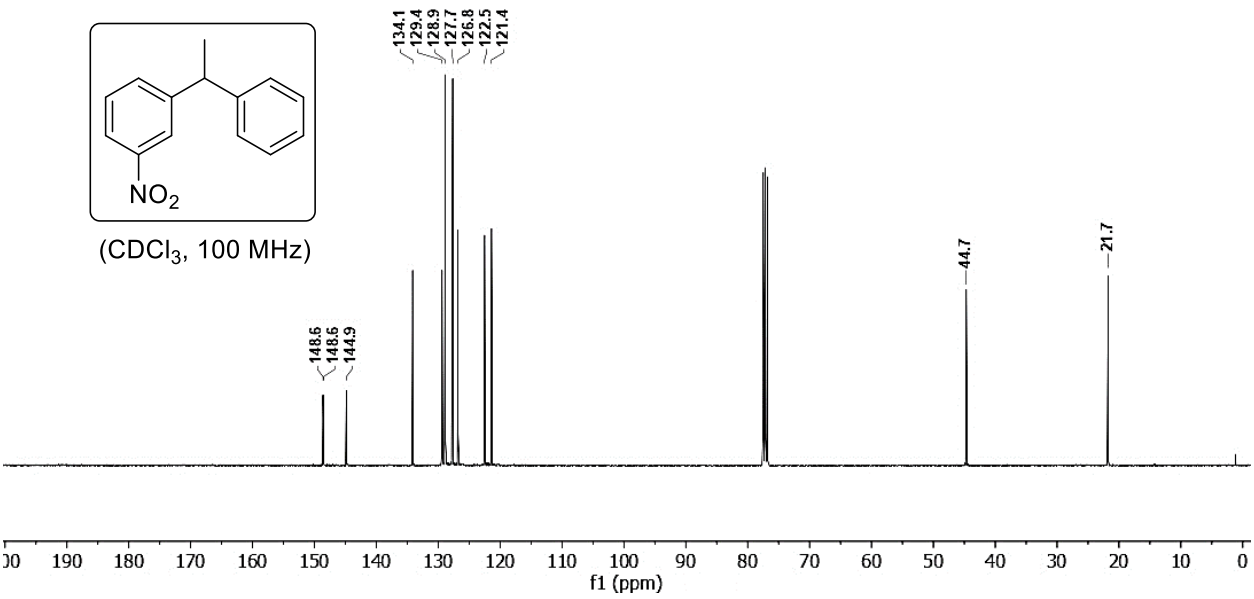
^{13}C NMR spectrum of octylbenzene (26).



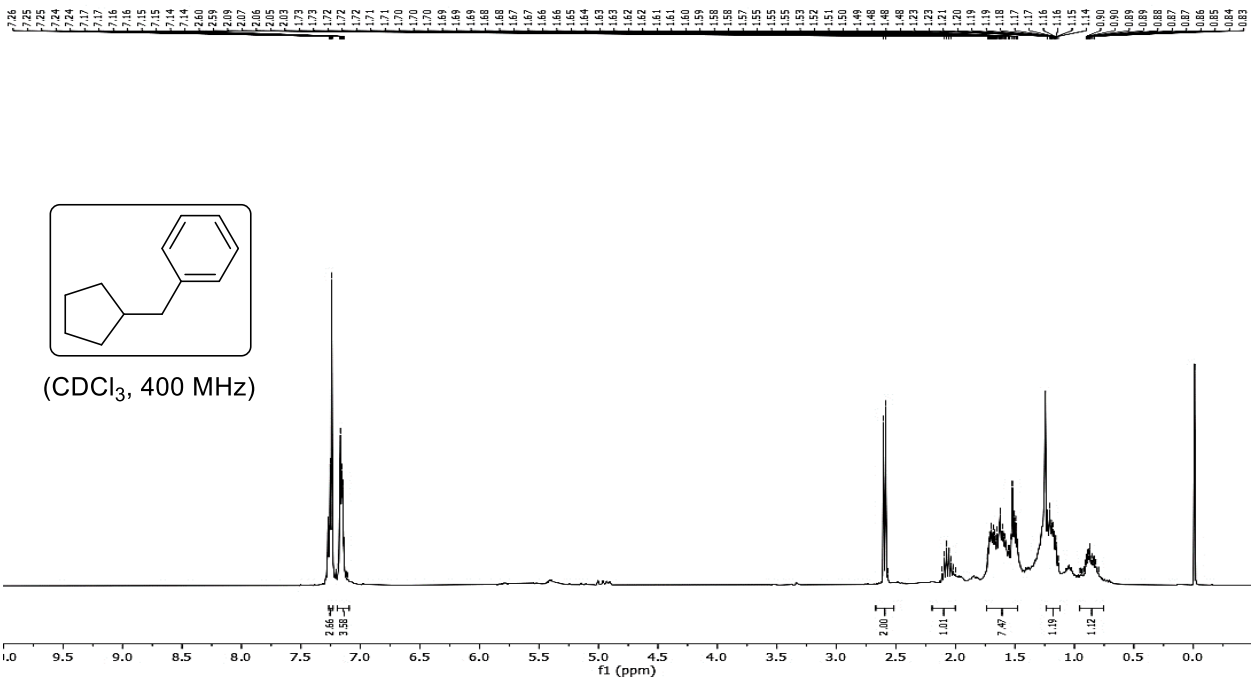
^{1}H NMR spectrum of 1-nitro-3-(1-phenylethyl)benzene (27).



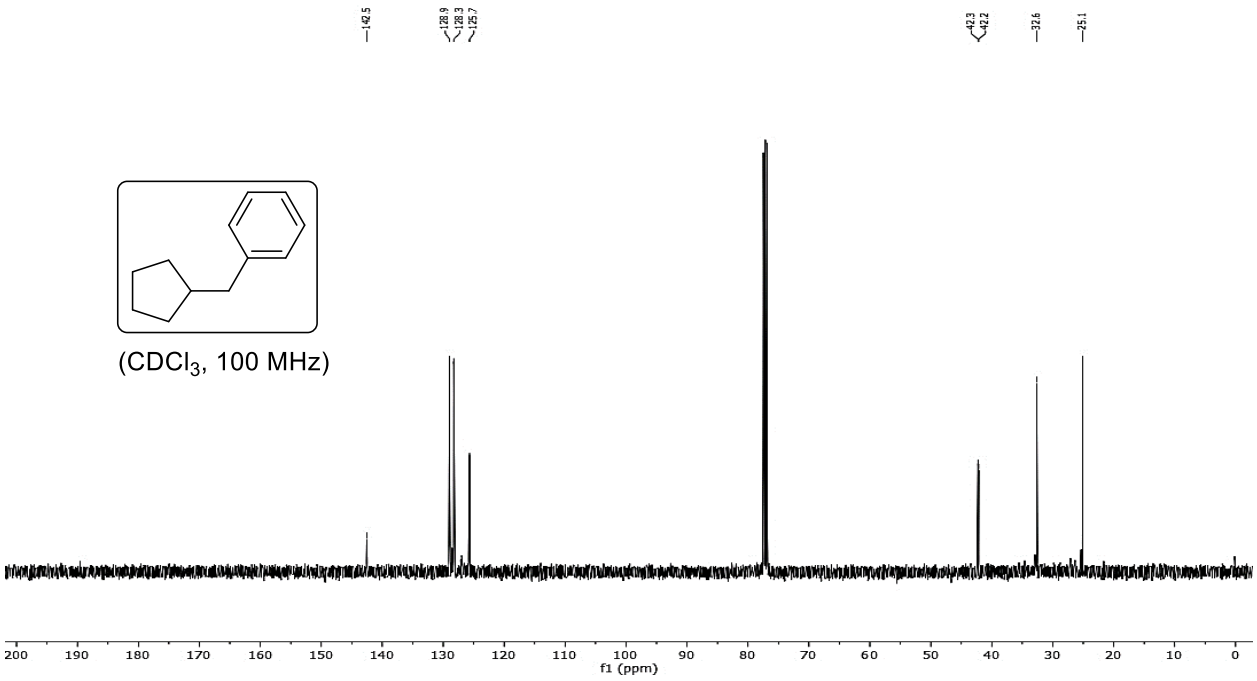
^{13}C NMR spectrum of 1-nitro-3-(1-phenylethyl)benzene (27).



^{1}H NMR spectrum of (cyclopentylmethyl)benzene (29).



^{13}C NMR spectrum of (cyclopentylmethyl)benzene (29).



7. Crystallographic analysis[5]

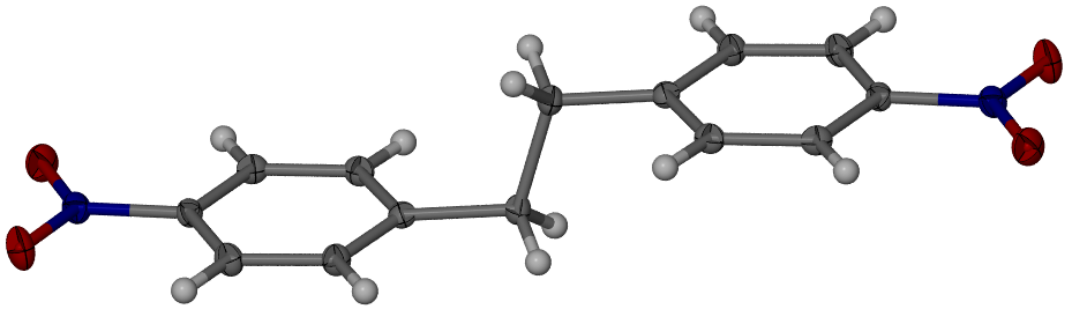


Figure S1. X-ray structure (ellipsoids are drawn at the 50% probability level) of 1,2-bis(4-nitrophenyl)ethane (**4**)

A single crystal was obtained by slow evaporation of a solution containing the homo-coupling product in a mixture of hexanes and ethyl acetate (4:1). Single crystal X-ray analysis was performed at 100 K using a Siemens platform diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were integrated with the Bruker SAINT program. Structure solution and refinement were performed using the SHELXT/PC suite and ShelXle. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions. Crystal data: $C_{14}H_{12}N_2O_4$, M = 272.26, pale yellow needle, 0.214 x 0.115 x 0.068 mm^3, monoclinic, space group $P2_1/c$, a = 4.4892(6), b = 13.2061(19), c = 10.6589(15) Å, α = 90, β = 98.845(2), γ = 90,V = 624.40(15) $Å^3$, Z = 2.

8. References

1. W-C. Dai, B. Yang, S-H. Xu, Z-X. Wang. *J. Org. Chem*. **2021**, *86*, 2235-2243.
2. Buden, M. E.; Bardagi, J. I.; Puiatti, M.; Rossi, R. A. *J. Org. Chem*. **2017**, *82*, 8325-8333.
3. R.B. Bedford, P.B. Brenner, E. Carter, T.W. Carvell, P.M. Cogswell, T. Gallagher, J.N. Harvey, D.M. Murphy, E.C. Neeve, J. Nunn, D.R. Pye. *Chem. Eur. J*. **2014**, *20*, 7935-7938.
4. V. Saini, L. Liao, Q. Wang, R. Jana, M.S. Sigman. *Org. Lett*. **2013**, *15*, 5008-5011.
5. CCDC 1992313 (compound **4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.