Supporting Information

For

Direct Access to Multi-functionalized Benzenes via [4+2] Annulation of α-Cyano-β-methylenones and α,β-Unsaturated aldehydes

Qianfa Jia[a], Yunfei Lan [b], Xin Ye [b], Yinhe Lin*[a] and Qiao Ren *[b]

[a.] Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Fuling, Chongqing 408100, P. R. China.

[b.] College of Pharmaceutical Science, Southwest University, Chongqing 400715, P. R. China.

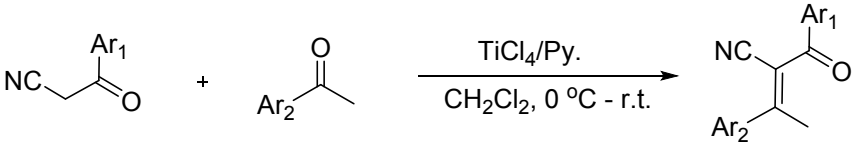
Email: 20170168@yznu.edu.cn

I: General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF400 (400 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Melting point was measured on a X-4 digital display microscopic melting point meter. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

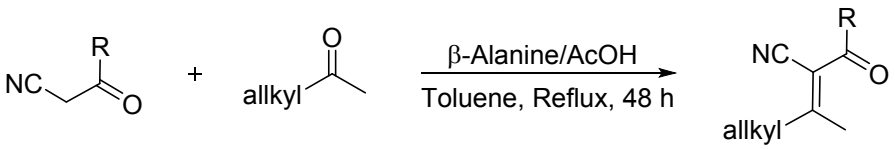
II: General procedure for the preparation of substrates 1

The substrates **1** were synthesized following the reported method.[1]



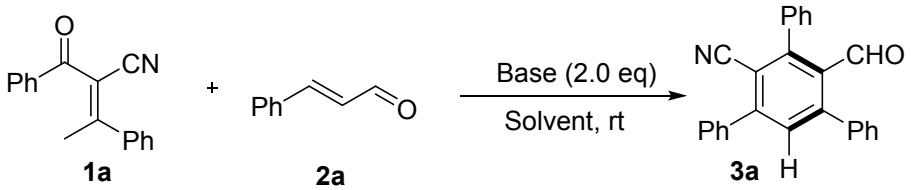
The appropriate 3-oxo-3-aryl-propanenitrile (2.0 mmol) and aromatic ketone (2.2 mmol) were dissolved in dry DCM (10 mL) under Ar atmosphere. The resulted reaction mixture was cooled to 0 °C with an ice bath. $TiCl_4$ (5.5 mmol, 0.6 mL) was slowly added within 10 minutes with vigorous stirring. After 0.5 hour, pyridine (18.7 mmol, 1.5 mL) was added via syringe pump over 30 mins. Then the ice bath was removed and the reaction mixture was stirred at room temperature. Upon completion (monitored by TLC), the reaction mixture was treated with 2 mol/L HCl (10 mL) and methylene dichloride (20 mL). The aqueous phase was extracted with methylene

dichloride (20 mL × 3). The combined organic phase was washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was further purified via careful column chromatography (Petroleum ether/Ethyl acetate = 15:1 to 5:1, v/v) to give product as an E/Z mixture (E/Z = 1:1.2 ~ 1:1.5, The products was stored in freezer at -28 °C for more than 3 months without decomposition).



A mixture of 3-oxo-propanenitrile (2.0 mmol), ketone (2.0 mmol), β-alanine (0.4 mmol), acetic acid (0.4 mmol) and toluene (20 mL) was heated to reflux under Dean-Stark conditions for 24 h. Then, the reaction mixture was cooled to room temperature and diluted with EtOAc (20 mL). The organic solvent was washed with 5% $NaHCO_3$ (20 mL × 3), water (20 mL), brine (20 mL), and dried with anhydrous $NaSO_4$. After concentration in vacuo, the residue was further purified via careful column chromatography (Petroleum ether/Ethyl acetate =15:1 to 5:1, v/v) to give product as E/Z mixture (E/Z = 1:1.2 ~ 1:1.5, The products was stored in freezer at -28 °C for more than 3 months without decomposition).

III: Optimization of reaction conditions[a]



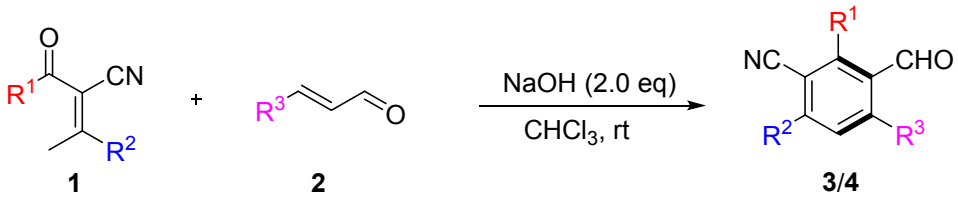
1a **2a** **3a**

Entry	Base	Solvent	Time (h)	Yield(%)[b]
1	Cs_2CO_3	Toluene	24	70
2	Na_2CO_3	Toluene	24	42
3	K_2CO_3	Toluene	24	38
4	NaOH	Toluene	12	78
5	NaOAc	Toluene	24	52
6	$NaHCO_3$	Toluene	24	36
7	NaOEt	Toluene	24	34
8	KO^{t}Bu	Toluene	24	23
9	KOH	Toluene	12	74
10	K_3PO_4	Toluene	24	58
11	DBU	Toluene	24	33
12	Et_3N	Toluene	48	46
13	NaOH	THF	24	38
14	NaOH	Et_2O	24	40
15	NaOH	CH_3CN	24	46
16	NaOH	MeOH	24	41
17	NaOH	1,4-dioxane	24	72
18	NaOH	DMF	48	34
19	NaOH	Acetone	24	52
20	NaOH	DCM	12	88
21	**NaOH**	**$CHCl_3$**	**12**	**94**
22	NaOH	DCE	12	84
23	NaOH	H_2O	48	0
24[c]	NaOH	$CHCl_3$	12	85
25[d]	NaOH	$CHCl_3$	12	80
26[e]	NaOH	$CHCl_3$	12	84
27	Cs_2CO_3	$CHCl_3$	12	76
28	K_2CO_3	$CHCl_3$	24	28
29	Na_2CO_3	$CHCl_3$	48	8
30	DBU	$CHCl_3$	12	36
31	Et_3N	$CHCl_3$	24	10
32	$NaHCO_3$	$CHCl_3$	48	5
33	KOH	$CHCl_3$	12	80
34	NaOMe	$CHCl_3$	12	62

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), base (0.2 mmol, 2.0 equiv), and solvent (1 mL) for 12 h. [b] Isolated yields.

[c] **1a**:**2a** = 1:1.2. [d] NaOH used 1.2 equiv. [e] 50°C.

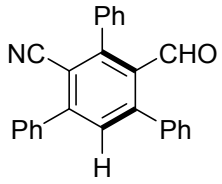
IV: General procedure



To a 10 mL sealed tube, a solution of $CHCl_3$ (1 mL) were added **1** (0.1 mmol), unsaturated aldehydes **2** (0.15 mmol), and NaOH (0.2 mmol, 8 mg). The reaction mixture was stirred at room temperature for 12 h. Then the mixture was concentrated, and purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate from 20:1 to 10:1 to afford the corresponding product **3** or **4**.

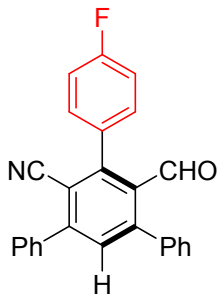
V: Characterization of products

4'-Formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3a)



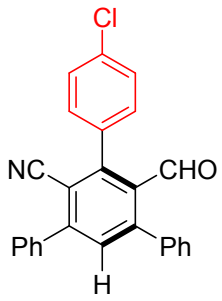
Light yellow solid, 33.7 mg, 94% yield (purification eluent: hexane/ethyl acetate = 10:1), m.p. 132-134 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.64 (dd, J = 7.8, 1.6 Hz, 2H), 7.54 (s, 1H), 7.52-7.46 (m, 6H), 7.46-7.40 (m, 5H), 7.38-7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 149.0, 148.7, 147.6, 138.0, 137.4, 135.7, 133.0, 132.2, 129.7 (2C), 129.6, 129.4 (2C), 129.2, 129.0 (2C), 128.9 (2C), 128.7, 128.6 (2C), 128.6 (2C), 116.6, 112.7. HRMS (EI): exact mass calculated for $C_{26}H_{17}NO$ $(M+H)^+$ required m/z 360.1383, found m/z 360.1384.

4-Fluoro-6'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3b)



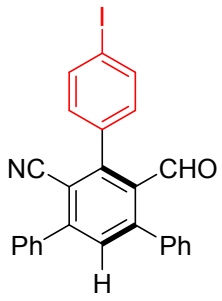
Light yellow solid, 33.9 mg, 90% yield (purification eluent: hexane/ ethyl acetate = 10:1), m.p. 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.64 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.58 (s, 1H), 7.53-7.45 (m, 7H), 7.42-7.36 (m, 4H), 7.23-7.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 164.4 (d, *J* = 248 Hz) 148.8, 148.0, 147.6, 137.6 (d, *J* = 32 Hz), 133.0, 132.2, 131.8 (d, *J* = 3 Hz), 131.4 (d, *J* = 9 Hz), 129.6, 129.4 (2C), 128.9 (3C), 128.9 (4C), 128.8, 128.7 (2C), 116.5, 115.9 (d, *J* = 21 Hz), 112.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.88. HRMS (EI): exact mass calculated for $C_{26}H_{17}FNO$ $(M+H)^+$ required m/z 378.1289, found m/z 378.1286.

4-Chloro-6'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3c)



Yellow solid, 36.5 mg, 93% yield (purification eluent: hexane/ ethyl acetate = 15:1), m.p. 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.64 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.59 (s, 1H), 7.53-7.46 (m, 8H), 7.38 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 148.9, 148.1, 147.3, 137.5, 137.2, 135.3, 134.4, 132.8, 132.3 (2C), 130.8 (2C), 129.6, 129.5 (2C), 129.0, 128.9 (3C), 128.9 (2C), 128.7 (2C), 116.4, 112.7. HRMS (EI): exact mass calculated for $C_{26}H_{17}ClNO$ $(M+H)^+$ required m/z 394.0993, found m/z 394.0991.

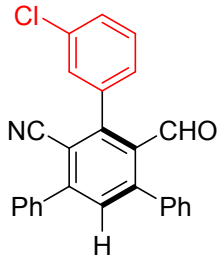
6'-Formyl-4-iodo-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3d)



Light yellow solid, 41.2 mg, 85% yield (purification eluent: hexane/ ethyl acetate = 10:1), m.p. 243-245 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H),

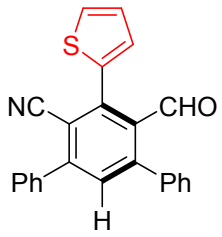
7.84 (d, J = 8.4 Hz, 2H), 7.63 (dd, J = 7.7, 1.8 Hz, 2H), 7.58 (s, 1H), 7.52-7.46 (m, 6H), 7.38 (dd, J = 6.7, 2.9 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 148.9, 148.1, 147.4, 137.7 (2C), 137.5, 137.2, 135.5, 132.7, 132.3, 131.2 (2C), 129.6, 129.4 (2C), 129.0 (2C), 128.9 (3C), 128.7 (2C), 116.4, 112.6, 95.5. HRMS (EI): exact mass calculated for $C_{26}H_{17}INO$ $(M+H)^+$ required m/z 486.3319, found m/z 486.3318.

3-Chloro-6'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3e)



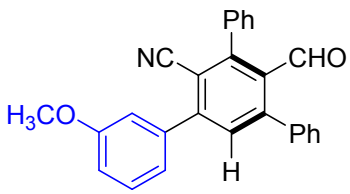
Yellow solid, 36.1 mg, 92% yield (purification eluent: hexane/ ethyl acetate = 15:1), m.p. 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.67-7.62 (m, 2H), 7.60 (s, 1H), 7.54-7.44 (m, 8H), 7.40-7.38 (m, 3H), 7.33-7.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 148.9, 148.2, 147.0, 137.8, 137.4, 137.2, 134.5, 132.6, 132.4 (2C), 129.8, 129.6, 129.4 (3C), 129.3, 129.0, 128.9 (3C), 128.7 (2C), 127.6, 116.3, 112.7. HRMS (EI): exact mass calculated for $C_{26}H_{17}ClNO$ $(M+H)^+$ required m/z 394.0993, found m/z 394.0989.

6'-formyl-5'-(thiophen-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3f)



Brown oil, 31.4 mg, 86% yield (purification eluent: hexane/ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.63 (dd, J = 7.7, 1.7 Hz, 1H), 7.57-7.54 (m, 1H), 7.52-7.43 (m, 3H), 7.36 (dd, J = 6.6, 3.1 Hz, 1H), 7.25 (dd, J = 3.5, 1.1 Hz, 1H), 7.19 (dd, J = 5.1, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 148.7, 147.3, 141.4, 137.9, 137.2, 134.9, 134.4, 133.0, 130.5, 129.6, 129.3 (2C), 129.0 (2C), 128.9 (2C), 128.7, 128.6 (3C), 127.6, 116.3, 113.8. HRMS (EI): exact mass calculated for $C_{24}H_{16}NSO$ $(M+H)^+$ required m/z 366.0947, found m/z 366.0946.

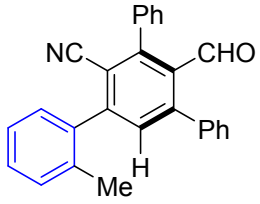
4'-Formyl-3-methoxy-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3g)



White solid, 34.2 mg, 88% yield (purification eluent: hexane/ethyl acetate = 10:1), m.p. 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s,

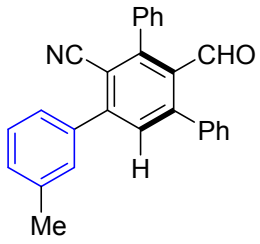
1H), 7.56 (s, 1H), 7.53-7.49 (m, 3H), 7.48-7.41 (m, 6H), 7.40-7.36 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.18-7.15 (m, 1H), 7.02 (dd, *J* = 8.2, 2.1 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 159.8, 149.0, 148.6, 147.5, 138.7, 138.0, 135.6, 133.0, 132.1, 130.0, 129.6 (2C), 129.3 (2C), 129.2, 128.7, 128.6 (2C), 128.5 (2C), 121.3, 116.5, 115.3, 114.4, 112.6, 55.5. HRMS (EI): exact mass calculated for $C_{27}H_{20}NO_2$ $(M+H)^+$ required m/z 390.1489, found m/z 390.1496.

4'-Formyl-2-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3h)



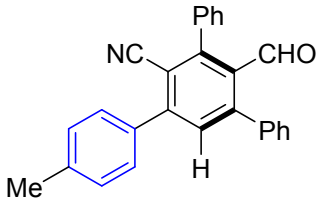
Light yellow solid, 30.9 mg, 83% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.52-7.50 (m, 3H), 7.45-7.42 (m, 6H), 7.40-7.29 (m, 6H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 149.3, 148.1, 147.3, 137.9, 137.3, 135.5, 135.5, 133.1, 132.4, 130.7, 129.6 (2C), 129.4 (2C), 129.3, 129.3, 129.2, 128.7, 128.6 (2C), 128.5 (2C), 126.1, 116.1, 114.1, 20.0. HRMS (EI): exact mass calculated for $C_{27}H_{20}NO(M+H)^+$ required m/z 374.1539, found m/z 374.1543.

4'-Formyl-3-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3i)



Light yellow solid, 31.7 mg, 85% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.54 (s, 1H), 7.53-7.50 (m, 3H), 7.48-7.35 (m, 10H), 7.29 (d, *J* = 7.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 149.0, 148.9, 147.5, 138.6, 138.1, 137.4, 135.7, 132.9, 132.1, 130.3, 129.6 (3C), 129.3 (2C), 129.2, 128.8, 128.7, 128.6 (2C), 128.5 (2C), 126.1, 116.6, 112.6, 21.5. HRMS (EI): exact mass calculated for $C_{27}H_{20}NO(M+H)^+$ required m/z 374.1539, found m/z 374.1537.

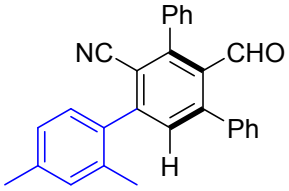
4'-Formyl-4-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3j)



Light yellow solid, 32.8 mg, 88% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s,

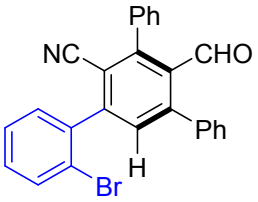
1H), 7.56 (s, 1H), 7.54 (s, 2H), 7.52-7.48 (m, 3H), 7.47-7.40 (m, 5H), 7.38-7.36(m, 2H), 7.31 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 149.1, 148.8, 147.5, 139.7, 138.1, 135.7, 134.5, 132.7, 132.1 (2C), 129.6 (3C), 129.3 (2C), 129.1, 128.9 (2C), 128.6, 128.5 (2C), 128.4 (2C), 116.7, 112.5, 21.3. HRMS (EI): exact mass calculated for $C_{27}H_{20}NO(M+H)^+$ required m/z 374.1539, found m/z 374.1538.

4'-Formyl-2,4-dimethyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3k)



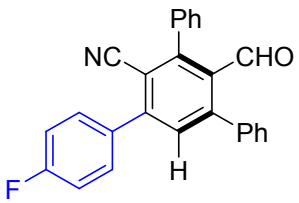
White solid, 32.9 mg, 85% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.53-7.48 (m, 3H), 7.47-7.40 (m, 6H), 7.38-7.36 (m, 2H), 7.19 (d, J = 7.7 Hz, 1H), 7.15 (s, 1H), 7.11 (d, J = 7.8 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 149.5, 148.1, 147.2, 139.2, 138.0, 135.6, 135.3, 134.5, 132.9, 132.6, 131.4, 129.6 (2C), 129.4 (2C), 129.2, 129.1, 128.7, 128.6 (2C), 128.5 (2C), 126.8, 116.2, 114.3, 21.3, 20.0. HRMS (EI): exact mass calculated for $C_{28}H_{22}NO$ $(M+H)^+$ required m/z 388.1696, found m/z 388.1696.

2-Bromo-4'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3l)



Light yellow solid, 36.7 mg, 84% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.54-7.49 (m, 4H), 7.47-7.37 (m, 9H), 7.36-7.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 148.0, 147.8, 147.1, 138.4, 137.7, 135.3, 133.6, 133.3 (2C), 132.6 (2C), 130.8, 130.7, 129.6, 129.4 (2C), 129.2, 128.8, 128.6 (3C), 127.7, 122.5, 115.8, 114.2. HRMS (EI): exact mass calculated for $C_{26}H_{17}BrNO$ $(M+H)^+$ required m/z 438.0488, found m/z 438.0485.

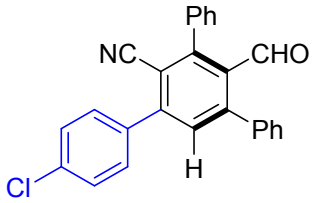
4-Fluoro-4'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3m)



Light yellow solid, 32.8 mg, 84% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.68-7.60 (m, 2H), 7.54-7.44 (m, 7H), 7.42-7.38 (m, 4H), 7.20 (t, J = 7.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.31. ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4,

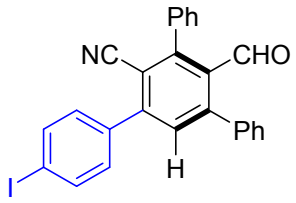
163.5 (d, J = 248 Hz), 149.0, 147.63 (d, J = 8.8 Hz), 137.9, 135.5, 133.43 (d, J = 3.4 Hz), 133.1, 132.0, 130.92 (d, J = 8.5 Hz), 129.6 (3C), 129.3 (3C), 129.2, 128.7, 128.6 (3C), 128.5 (3C), 116.3 (d, J = 30 Hz), 112.6. HRMS (EI): exact mass calculated for $C_{26}H_{17}FNO$ $(M+H)^+$ required m/z 378.1289, found m/z 378.1285.

4-Chloro-4'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3n)



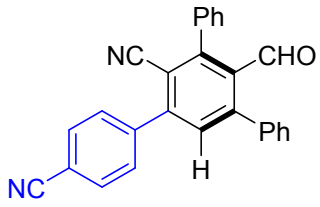
White solid, 35.3 mg, 90% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.54-7.45 (m, 9H), 7.41 (dd, J = 6.4, 2.9 Hz, 2H), 7.37 (dd, J = 6.4, 2.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 149.1, 147.7, 147.3, 137.8, 135.9, 135.7, 135.4, 133.2, 131.9 (2C), 130.3 (2C), 129.5 (2C), 129.3 (2C), 129.1 (2C), 128.8, 128.6 (2C), 128.5 (2C), 116.4, 112.5. HRMS (EI): exact mass calculated for $C_{26}H_{17}ClNO$ $(M+H)^+$ required m/z 394.0993, found m/z 394.0991.

4'-Formyl-4-iodo-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3o)



Light yellow solid, 42.1 mg, 87% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.54-7.49 (m, 4H), 7.48-7.45 (m, 3H), 7.42-7.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 149.1, 147.7, 147.5, 138.1 (2C), 137.8, 136.8, 135.4, 133.3, 131.8 (2C), 130.6 (2C), 129.5 (2C), 129.3 (2C), 128.8, 128.6 (2C), 128.5 (2C), 116.4, 112.4, 96.1. HRMS (EI): exact mass calculated for $C_{26}H_{17}INO$ $(M+H)^+$ required m/z 486.0349, found m/z 486.0352.

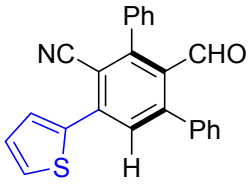
4'-Formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2',4-dicarbonitrile (3p)



Light yellow solid, 33.1 mg, 86% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 197-199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.56-7.51 (m, 4H), 7.50-7.46 (m, 3H), 7.41 (dd, J = 6.6, 2.9 Hz, 2H), 7.37 (dd, J = 6.6, 2.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 149.0, 147.9, 146.3, 141.7, 137.4, 135.1, 134.0, 132.6 (2C),

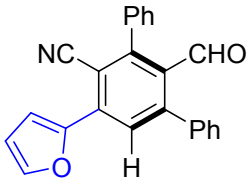
131.8 (2C), 129.8 (2C), 129.5 (2C), 129.4, 129.3 (2C), 128.9, 128.7 (3C), 118.1, 116.0, 113.4, 112.5. HRMS (EI): exact mass calculated for $C_{27}H_{17}N_2O$ $(M+H)^+$ required m/z 385.1335, found m/z 385.1335.

2'-Formyl-5'-(thiophen-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3q)



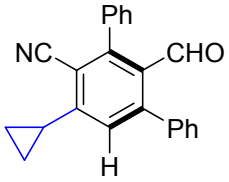
Yellow soild, 31.3 mg, 86% yield (purification eluent: hexane/ethyl acetate = 10:1), m.p. 174-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.82 (dd, *J* = 3.7, 0.6 Hz, 1H), 7.66 (s, 1H), 7.54-7.50 (m, 4H), 7.50-7.45 (m, 3H), 7.41 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.37 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.19 (dd, *J* = 5.0, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 149.8, 147.8, 140.6, 138.4, 137.9, 135.6, 132.7, 131.5 (2C), 129.5 (2C), 129.3, 129.2 (2C), 129.1, 128.8, 128.7, 128.6 (2C), 128.5 (2C), 116.8, 111.1. HRMS (EI): exact mass calculated for $C_{24}H_{16}NOS$ $(M+H)^+$ required m/z 366.0947, found m/z 366.0948.

2'-Formyl-5'-(furan-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3r)



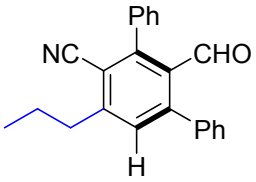
white solid, 24.7 mg, 71% yield. (purification eluent: hexane/ethyl acetate = 15:1), m.p. 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.97 (s, 1H), 7.61 (m, 2H), 7.54-7.45 (m, 6H), 7.42-7.37 (m, 4H), 6.61 (dd, *J* = 3.6, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 149.8, 148.9, 147.9, 144.6 (2C), 138.2, 135.6, 135.6, 132.0, 129.4 (2C), 129.2 (2C), 128.7, 128.6 (2C), 128.5 (2C), 127.6, 117.0, 113.5, 112.8, 107.6. HRMS (EI): exact mass calculated for $C_{24}H_{16}NO_2$ $(M+H)^+$ required m/z 350.1176, found m/z 350.1174.

5'-Cyclopropyl-2'-formyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3s)



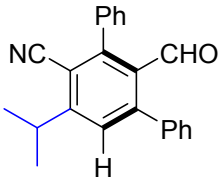
Light Yellow solid, 26.4 mg, 82% yield (purification eluent: hexane/ethyl acetate = 20:1), m.p. 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.54-7.48 (m, 3H), 7.46-7.41 (m, 3H), 7.37 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.29 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.88 (s, 1H), 2.50-2.41 (m, 1H), 1.30-1.25 (m, 2H), 0.98-0.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 152.3, 148.3, 148.0, 138.5, 135.8, 131.5, 129.5 (2C), 129.1 (2C), 129.0, 128.6 (2C), 128.5, 128.4 (2C), 125.7, 116.4, 114.5, 14.9, 11.1 (2C). HRMS (EI): exact mass calculated for $C_{23}H_{18}NO$ $(M+H)^+$ required m/z 324.1383, found m/z 324.1382.

2'-Formyl-5'-propyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3t)



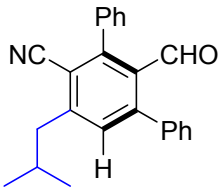
Light yellow solid, 26.9 mg, 83% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 92-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.52-7.47 (m, 3H), 7.47-7.42 (m, 3H), 7.38-7.31 (m, 5H), 2.99-2.92 (m, 2H), 1.86-1.75 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 150.5, 148.3, 147.6, 138.3, 135.8, 132.1, 131.5, 129.5 (2C), 129.2 (2C), 129.0, 128.6, 128.5 (2C), 128.4(2C), 116.1, 114.0, 37.1, 23.8, 13.9. HRMS (EI): exact mass calculated for $C_{23}H_{20}NO$ $(M+H)^+$ required m/z 326.1539, found m/z 326.1535.

2'-Formyl-5'-isopropyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3u)



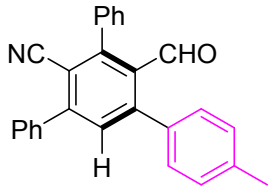
White solid, 25.3 mg, 78% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.51-7.47 (m, 3H), 7.47-7.45 (m, 3H), 7.42 (s, 1H), 7.38-7.33 (m, 4H), 3.54 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 156.3, 148.3, 148.0, 138.6, 135.9, 132.2, 129.5 (2C), 129.3 (2C), 129.0, 128.6, 128.5 (4C), 128.1, 116.0, 113.4, 33.0, 23.1 (2C). HRMS (EI): exact mass calculated for $C_{23}H_{20}NO$ $(M+H)^+$ required m/z 326.1539, found m/z 326.1540.

2'-Formyl-5'-isobutyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3v)



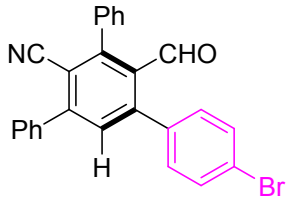
Light yellow solid, 27.1 mg, 80% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.51-7.47 (m, 3H), 7.46-7.42 (m, 3H), 7.39-7.32 (m, 5H), 2.85 (d, *J* = 7.2 Hz, 2H), 2.10 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.02 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 149.7, 148.2, 147.3, 138.3, 135.8, 132.2, 132.1, 129.5 (2C), 129.3 (2C), 129.0, 128.6, 128.5 (2C), 128.4 (2C), 116.3, 114.4, 44.2, 30.1, 22.4 (2C). HRMS (EI): exact mass calculated for $C_{24}H_{22}NO$ $(M+H)^+$ required m/z 340.1696, found m/z 340.1694.

4'-Formyl-5'-(p-tolyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4a)



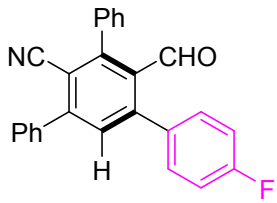
Light yellow solid, 33.5 mg, 90% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.64 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.54 (s, 1H), 7.52-7.47 (m, 6H), 7.42-7.39 (m, 2H), 7.28-7.23 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 148.9, 148.6, 147.7, 138.8, 137.5, 135.8, 135.0, 133.0, 132.1, 129.6 (2C), 129.4, 129.3 (2C), 129.2 (2C), 129.1, 128.9 (2C), 128.8 (2C), 128.5 (2C), 116.6, 112.4, 21.3. HRMS (EI): exact mass calculated for $C_{27}H_{20}NO$ $(M+H)^+$ required m/z 374.1539, found m/z 374.1538.

5'-(4-Bromophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile（4b）



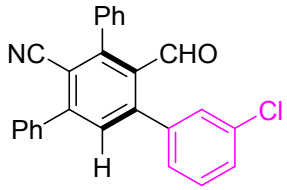
Light yellow solid, 37.1 mg, 85% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.64 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.48 (m, 7H), 7.45 – 7.41 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 149.7, 149.0, 146.0, 137.3, 137.2, 135.1, 132.7, 132.1, 131.7 (2C), 130.7 (2C), 129.7 (2C), 129.6, 129.4, 128.9 (4C), 128.7 (2C), 123.1, 116.4, 112.8. HRMS (EI): exact mass calculated for $C_{26}H_{17}BrNO$ $(M+H)^+$ required m/z 439.3315, found m/z 435.3313.

5'-(4-Fluorophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4c)



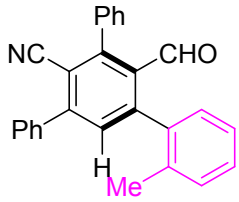
Light yellow solid, 33.1 mg, 88% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.64 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.55-7.48 (m, 7H), 7.45-7.41 (m, 2H), 7.38-7.32 (m, 2H), 7.18-7.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 164.2 (d, *J* = 247 Hz), 149.5, 148.9, 146.2, 137.3, 135.3, 134.2 (d, *J* = 3 Hz), 132.9, 132.3 (2C), 131.1 (d, *J* = 8 Hz), 129.7 (2C), 129.6, 129.4, 128.9 (3C),128.8 (2C), 128.7 (2C), 116.5, 115.7 (d, *J* = 22 Hz), 112.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.72. HRMS (EI): exact mass calculated for $C_{26}H_{17}FNO$ $(M+H)^+$ required m/z 378.1289, found m/z 378.1286.

5'-(3-Chlorophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4d)



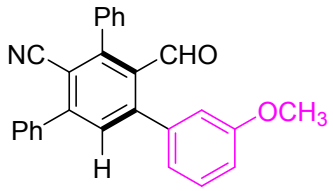
Light yellow solid, 36.1 mg, 92% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.66-7.62 (m, 2H), 7.55-7.49 (m, 7H), 7.45-7.35 (m, 5H), 7.25-7.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 149.6, 149.0, 145.7, 140.2, 137.1, 135.1, 134.4, 132.7, 132.2 (2C), 129.7 (2C), 129.6 (2C), 129.4, 129.0, 128.9 (3C), 128.7 (2C), 128.6, 127.4, 116.4, 113.0. HRMS (EI): exact mass calculated for $C_{26}H_{17}ClNO$ $(M+H)^+$ required m/z 394.0993, found m/z 394.0995.

4'-Formyl-5'-(o-tolyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4e)



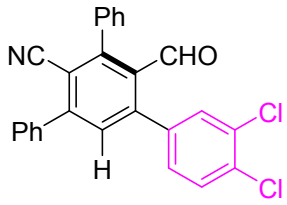
Light yellow solid, 30.9 mg, 83% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 172-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.66 (dd, J = 7.7, 1.7 Hz, 2H), 7.55-7.44 (m, 9H), 7.36-7.24 (m, 4H), 7.16 (d, J = 6.9 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 149.5, 149.0, 147.3, 138.3, 137.3, 135.4, 135.2, 132.8, 132.1 (2C), 130.1, 129.8, 129.6, 129.5, 129.3, 129.0 (2C), 128.9 (2C), 128.6 (2C), 128.5, 125.8, 116.6, 112.6, 20.3. HRMS (EI): exact mass calculated for $C_{27}H_{20}NO$ $(M+H)^+$ required m/z 374.1539, found m/z 374.1537.

4'-Formyl-5'-(3-methoxyphenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4f)



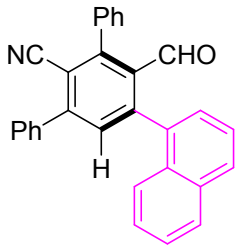
Light yellow solid, 31.8 mg, 82% yield (purification eluent: hexane/ethyl acetate = 10:1), m.p. 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.65 (dd, J = 7.8, 1.7 Hz, 2H), 7.56 (s, 1H), 7.54-7.48 (m, 6H), 7.43-7.35 (m, 3H), 7.01-6.90 (m, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 159.6, 148.8, 148.7, 147.5, 139.3, 137.4, 135.7, 133.0, 131.9, 129.6, 129.5 (2C), 129.4, 129.1, 128.9 (2C), 128.8 (2C), 128.5 (2C), 121.8, 116.5, 115.0, 114.2, 112.7, 55.4. HRMS (EI): exact mass calculated for $C_{27}H_{20}NO_2$ $(M+H)^+$ required m/z 390.1489, found m/z 390.1485.

5'-(3,4-Dichlorophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4g)



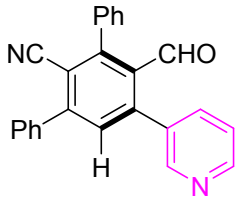
Yellow solid, 37.5 mg, 88% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.64-7.63 (m, 2H), 7.57-7.49 (m, 7H), 7.48-7.44 (m, 4H), 7.18 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 150.1, 149.2, 144.4, 138.6, 137.0, 134.7, 132.9, 132.7, 132.5, 132.2, 130.7, 130.3, 129.8 (2C), 129.7, 129.6, 129.0 (2C), 128.9 (2C), 128.8 (2C), 128.5, 116.3, 113.2. HRMS (EI): exact mass calculated for $C_{26}H_{16}Cl_2NO$ $(M+H)^+$ required m/z 428.0603, found m/z 428.0601.

4'-Formyl-5'-(naphthalen-1-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4h)



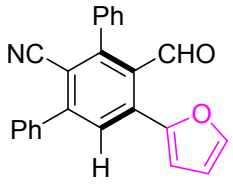
Yellow solid, 34.3 mg, 84% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 236-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.94 (dd, *J* = 8.2, 3.0 Hz, 2H), 7.67 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.60 (s, 1H), 7.57-7.46 (m, 12H), 7.41 (dd, *J* = 7.0, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 149.2, 148.9, 146.2, 137.2, 136.0, 135.5, 133.7, 133.4, 132.9 (2C), 131.6, 129.7, 129.6, 129.3, 129.0 (2C), 128.9, 128.8 (2C), 128.6 (3C), 127.1, 126.9, 126.2, 125.2, 125.1, 116.6, 113.0. HRMS (EI): exact mass calculated for $C_{30}H_{20}NO$ $(M+H)^+$ required m/z 410.1539, found m/z 410.1536.

4'-formyl-5'-(pyridin-3-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4i)



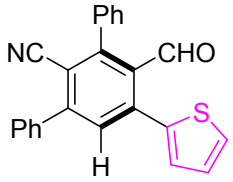
Light yellow solid, 30.9 mg, 86% yield (purification eluent: hexane/ethyl acetate = 10:1), m.p. 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.67 (d, *J* = 4.3 Hz, 1H), 8.62 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.58-7.45 (m, 9H), 7.39 (dd, *J* = 7.6, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 150.4, 149.5, 149.3, 149.1, 143.2, 137.0, 136.5, 134.7, 134.6, 132.7, 132.5, 129.9 (2C), 129.7, 129.6, 129.0 (2C), 128.9 (2C), 128.8 (2C), 122.9, 116.3, 113.2. HRMS (EI): exact mass calculated for $C_{25}H_{17}N_2O$ $(M+H)^+$ required m/z 361.1335, found m/z 361.1336.

4'-Formyl-5'-(furan-2-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4j)



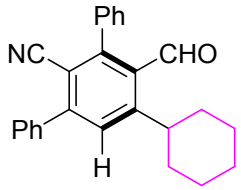
Brow oil, 27.2 mg, 78% yield (purification eluent: hexane/ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.86 (s, 1H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.56 (d, *J* = 0.6 Hz, 1H), 7.52-7.45 (m, 6H), 7.41-7.35 (m, 2H), 6.85 (d, *J* = 3.3 Hz, 1H), 6.53 (dd, *J* = 2.9, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 149.7, 148.5, 148.4, 144.8, 137.5, 135.4, 133.8, 132.3, 129.7 (2C), 129.5, 129.3, 128.9 (3C), 128.8, 128.6 (3C), 116.6, 113.6, 112.4, 112.0. HRMS (EI): exact mass calculated for $C_{24}H_{16}NO_2$ $(M+H)^+$ required m/z 350.1176, found m/z 350.1177.

4'-Formyl-5'-(thiophen-2-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4k)



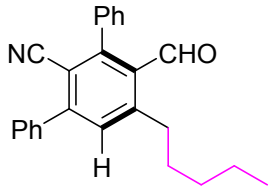
Yellow solid, 31.0 mg, 85% yield (purification eluent: hexane/ethyl acetate = 15:1). m.p. 174-176 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.67 (s, 1H), 7.63 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.53-7.47 (m, 7H), 7.42-7.38 (m, 2H), 7.18-7.15 (m, 1H), 7.15-7.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 148.5, 139.5, 138.3, 137.2, 135.6, 133.6, 132.1 (2C), 130.4, 129.6, 129.5 (2C), 129.2, 129.0 (2C), 128.9 (2C), 128.6, 128.5 (2C), 128.1, 116.5, 112.8. HRMS (EI): exact mass calculated for $C_{24}H_{16}NOS$ $(M+H)^+$ required m/z 366.0947, found m/z 366.0946.

5'-Cyclohexyl-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4l)



White solid, 29.9 mg, 82% yield (purification eluent: hexane/ethyl acetate = 15:1), m.p. 186-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.61 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.58 (s, 1H), 7.54-7.48 (m, 6H), 7.41 (dd, *J* = 6.5, 3.0 Hz, 2H), 3.59-3.53(m, 1H), 1.95-1.83 (m, 4H), 1.79 (d, *J* = 14.0 Hz, 1H), 1.51-1.43 (m, 4H), 1.30-1.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 153.9, 150.6, 149.1, 138.0, 135.3, 132.5, 130.1 (2C), 129.4, 129.3, 128.9 (2C), 128.8 (2C), 128.7 (2C), 128.3, 116.8, 110.5, 39.5, 34.3 (2C), 26.7 (2C), 26.1. HRMS (EI): exact mass calculated for $C_{26}H_{24}NO$ $(M+H)^+$ required m/z 366.1852, found m/z 366.1855.

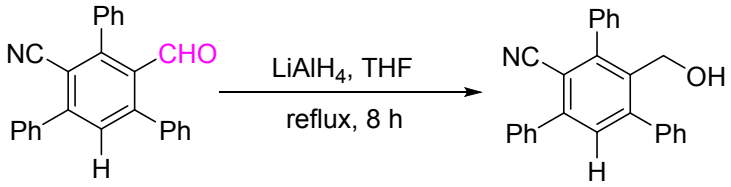
4'-Formyl-5'-pentyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4m)



Yellow oil, 28.2 mg, 80% yield (purification eluent: hexane/ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.51-7.50 (m, 6H), 7.45-7.38 (m, 3H), 3.12-3.01 (m, 2H), 1.70-1.55 (m, 2H), 1.47-1.31 (m, 4H), 0.94-0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 151.5, 149.6, 149.1, 137.7, 135.1, 132.3, 132.1, 130.1 (2C), 129.4, 129.4, 128.9 (2C), 128.8 (2C), 128.7 (2C), 116.7, 110.9, 34.3, 32.0, 31.3, 22.5, 14.0. HRMS (EI): exact mass calculated for $C_{25}H_{24}NO$ $(M+H)^+$ required m/z 354.1852, found m/z 354.1856.

VI: Synthetic transformations

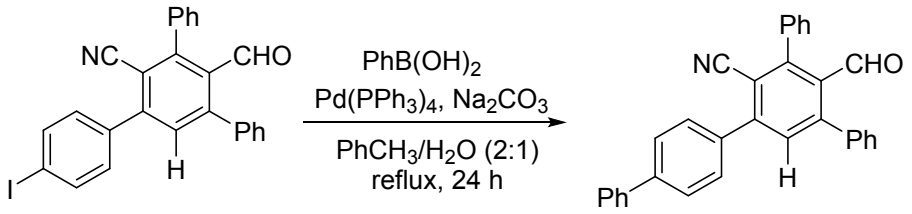
a) Synthesis of 4'-(Hydroxymethyl)-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile[2] (5)



3a **5**, 95% yield

To a solution of 4'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (**3a**, 35.9 mg, 0.1 mmol) in dry THF (2.0 mL) was added lithium aluminum hydride (11.4 mg, 0.3 mmol) under ice-cooling in an argon gas atmosphere. Then the solution was heated and refluxed with stirring for 8 h. After cooling to room temperature, the reaction mixture was quenched with water and diluted with DCM. Thereafter, the aqueous solution was extracted with DCM, and the combined organic layers was dried with Na_2SO4, filtered and concentrated in vacuo. The residue was purified by column chromatography to affored **5** as white solid. (34.2 mg, 95%). m.p. 205-207 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.52 (m, 7H), 7.51-7.38 (m, 9H), 4.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 147.5, 145.1, 139.6, 138.1, 137.5, 135.9, 131.3, 129.3 (2C), 129.1 (2C), 129.0 (2C), 128.9, 128.8, 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.2, 117.4, 111.7, 59.5. HRMS (EI): exact mass calculated for $C_{26}H_{20}NO$ $(M+H)^+$ required m/z 362.1539, found m/z 362.1539.

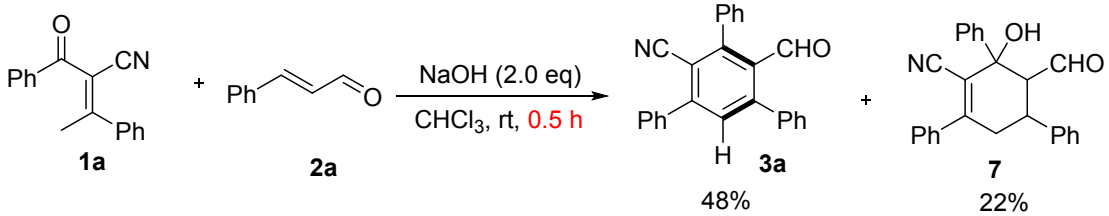
Synthesis of 6'-formyl-5'-phenyl-[1,1':3',1'':4'',1'''-quaterphenyl]-2'-carbonitrile[3] (6)



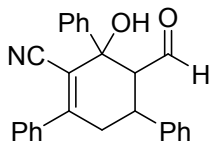
3o **6**, 90% yield

Under Ar atmosphere, to a solution of 4'-formyl-4-iodo-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (48.5 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in toluene (1.0 mL) and H_2O (0.5 mL) was added Na_2CO_3 (31.8 mg, 0.3 mmol), $PhB(OH)_2$ (15.2 mg, 0.125 mmol). The vigorously stirred mixture was heated to 100 °C for 2 h (monitored by TLC), After cooling to room temperature, the mixture was filtered through a pad of celite, the filter cake was washed with EtOAc. The organic solvent was removed and the residue was purified by column chromatography (EtOAc : Hexane = 1:15) to afford **6** as white solid (39.1 mg, 90% yield). m.p. 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.74 (s, 4H), 7.65 (d, J = 7.3 Hz, 2H), 7.61 (s, 1H), 7.55-7.50 (m, 3H), 7.50-7.43 (m, 7H), 7.42-7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 149.1, 148.3, 147.6, 142.4, 140.1, 138.1, 136.2, 135.6, 132.9, 132.1 (2C), 129.6 (2C), 129.4 (2C), 129.3 (2C), 129.2, 128.9 (2C), 128.7, 128.6 (2C), 128.5 (2C), 127.8, 127.6 (2C), 127.2 (2C), 112.4. HRMS (EI): exact mass calculated for $C_{32}H_{22}NO$ $(M+H)^+$ required m/z 436.5335, found m/z 436.5334.

VII: Synthesis of 6'-Formyl-1'-hydroxy-5'-phenyl-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-2'-carbonitrile (7)



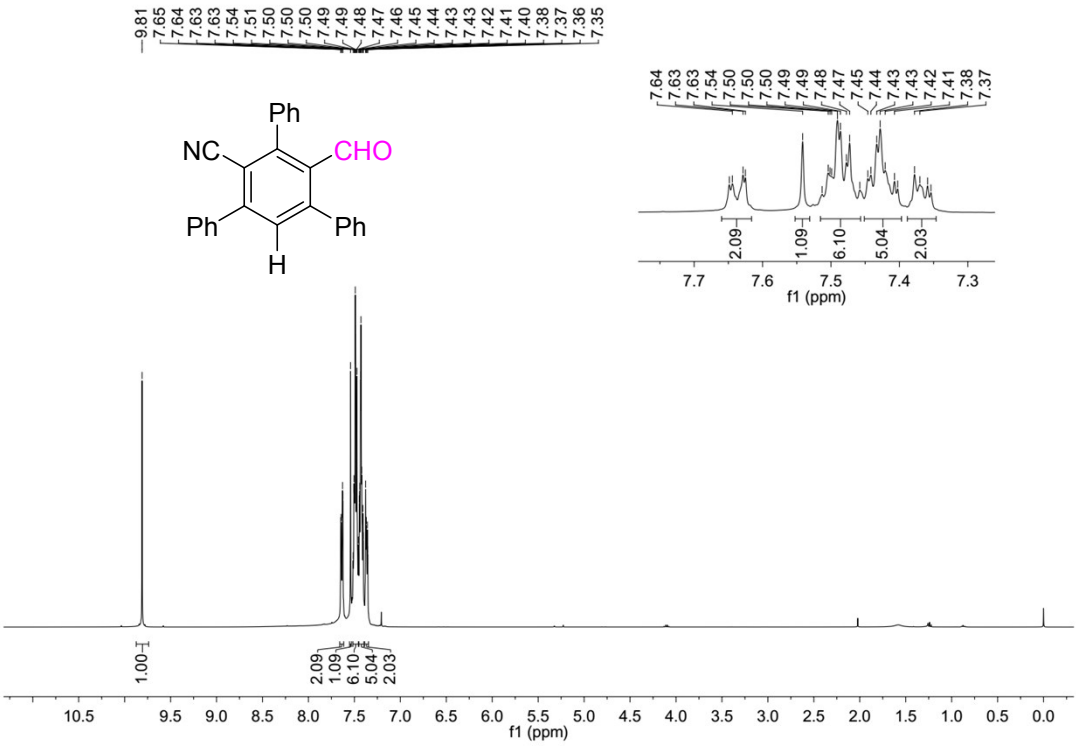
To a solution of $CHCl_3$ (1 mL) were added **1a** (0.2 mmol), cinnamyl aldehyde **2a** (0.3 mmol), and NaOH (0.4 mmol, 16 mg). The reaction mixture was stirred at room temperature for 0.5 h. Then the mixture was concentrated, and purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate from 20:1 to 5:1 to afford the corresponding product **3a** in 48% yield and product **7** in 22% yield individually.

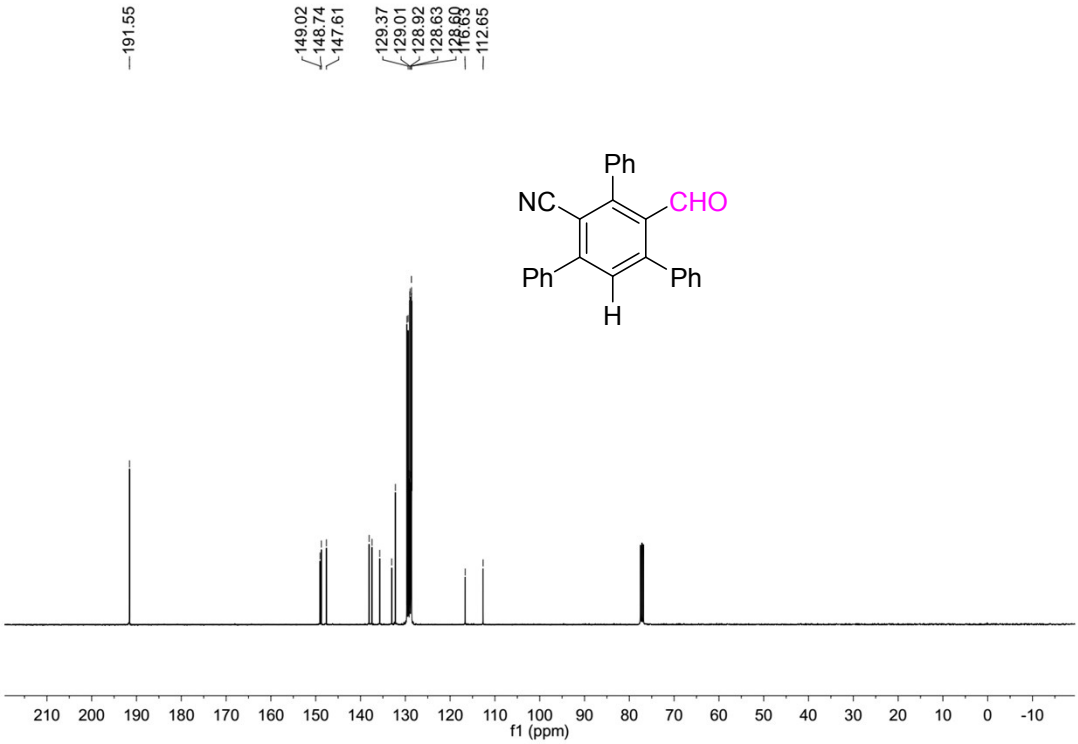


White solid, 12.1 mg, 32% yield (purification eluent: hexane/ethyl acetate = 5:1), m.p. 116-118 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 7.57 (dd, *J* = 19.1, 6.8 Hz, 4H), 7.50-7.35 (m, 7H), 7.34-7.26 (m, 3H), 7.21 (d, *J* = 6.8 Hz, 1H), 6.96 (s, 1H), 3.95 (dd, *J* = 10.7, 7.1 Hz, 1H), 3.22 (dd, *J* = 12.0, 3.3 Hz, 1H), 3.05 (dd, *J* = 18.8, 11.4 Hz, 1H), 2.92 (dd, *J* = 18.7, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 202.8, 157.4, 144.1, 142.1, 139.2, 129.8, 129.1 (2C), 128.9 (2C), 128.6 (2C), 128.4 (2C), 127.9 (3C), 127.8, 127.4, 126.4 (2C), 117.8, 115.8, 75.5, 62.4, 37.3. HRMS (EI): exact mass calculated for $C_{26}H_{22}NO_2$ $(M+H)^+$ required m/z 380.1645, found m/z 380.1647.

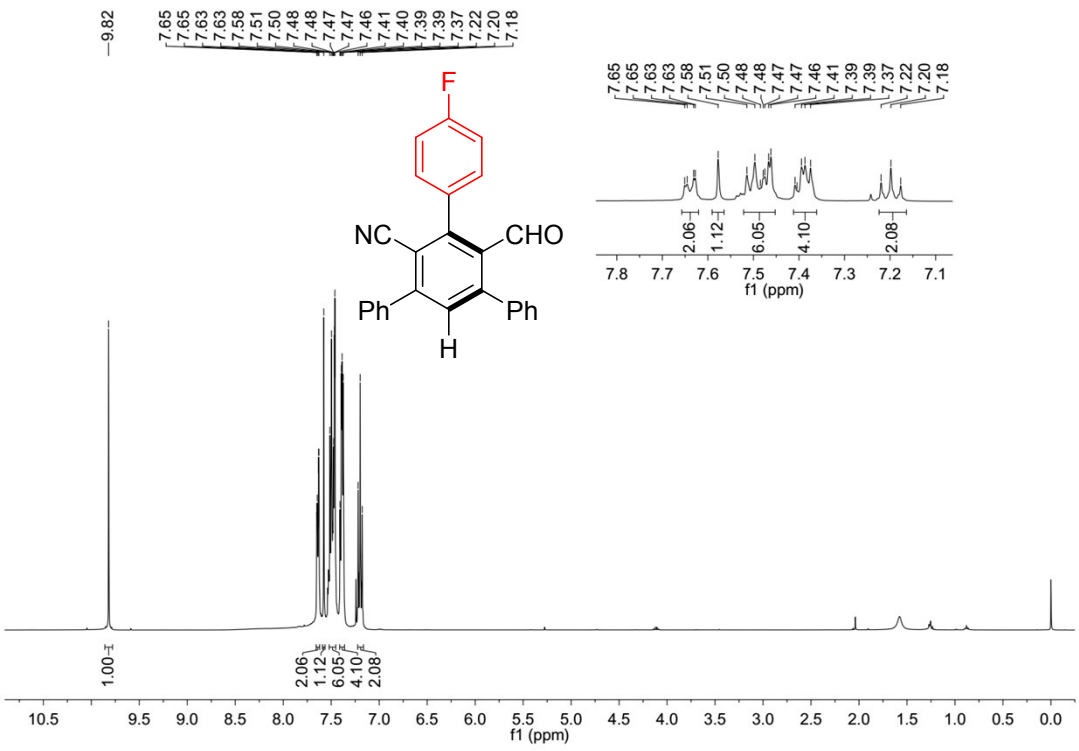
VIII: NMR Spectra

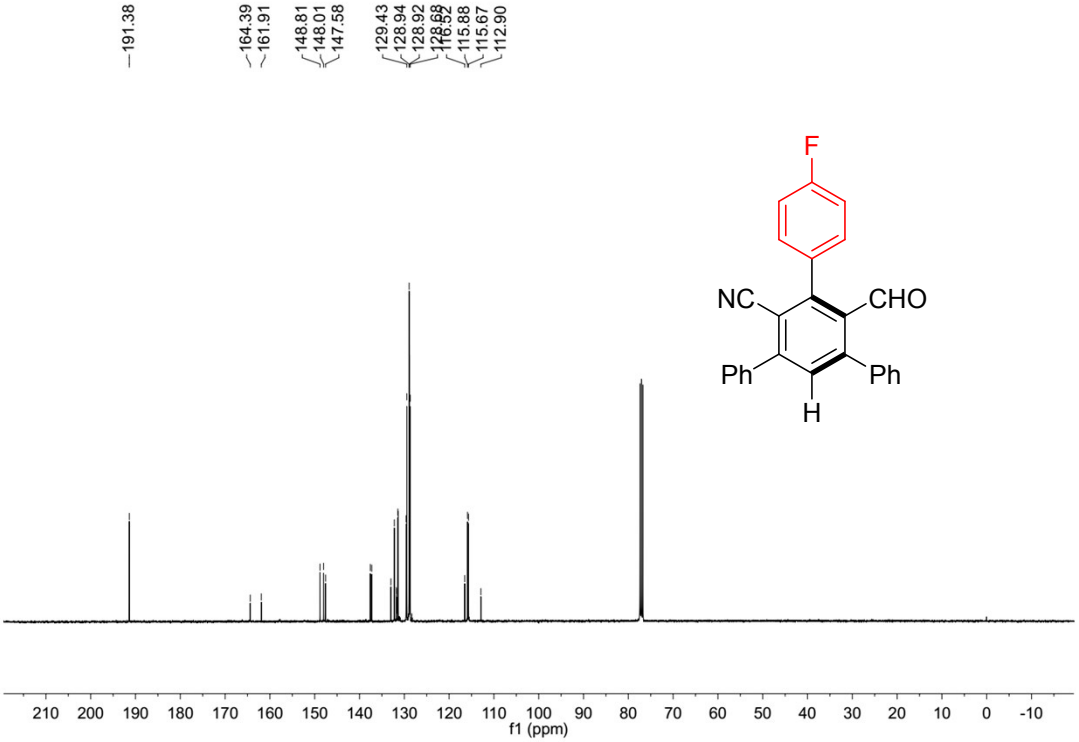
4'-Formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3a)

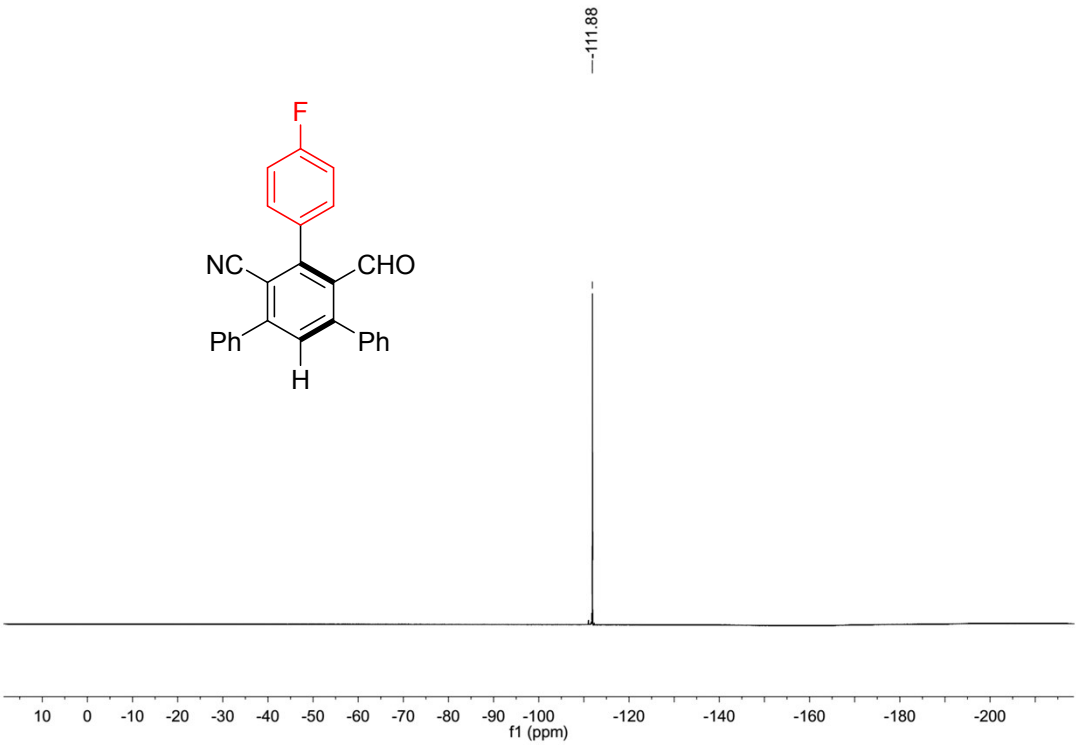




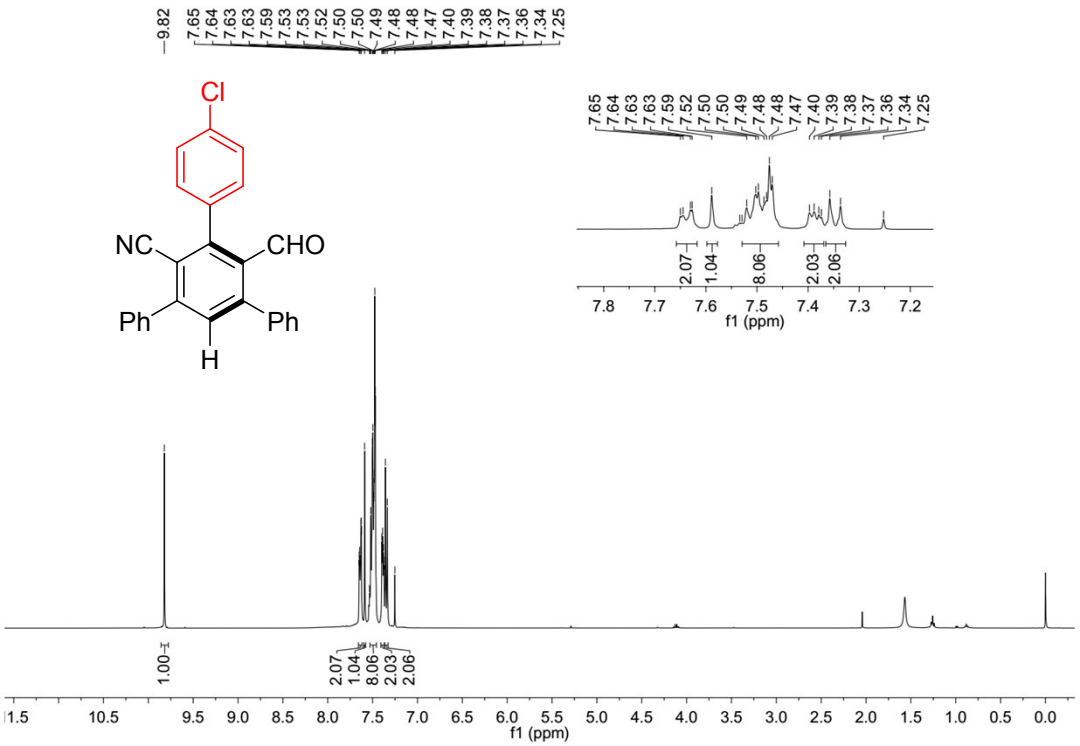
4-Fluoro-6'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3b)

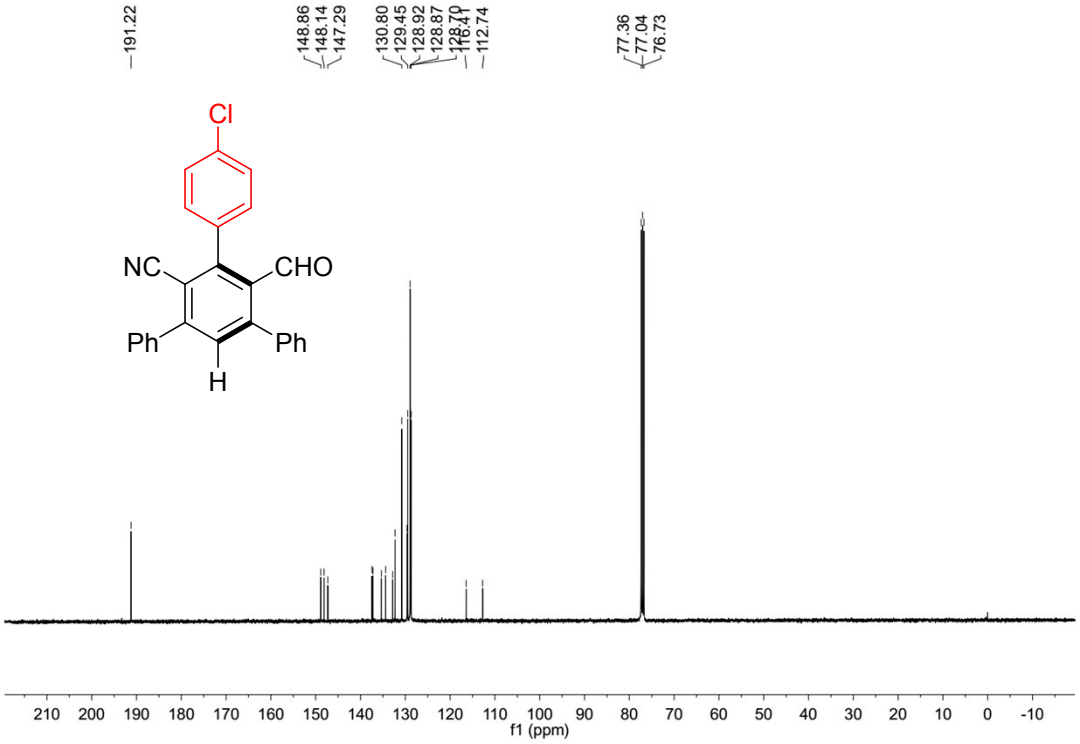



191.38
164.39
161.91
148.81
148.01
147.58
129.43
128.94
128.92
116.52
115.88
115.67
112.90
F
NC
CHO
Ph
Ph
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

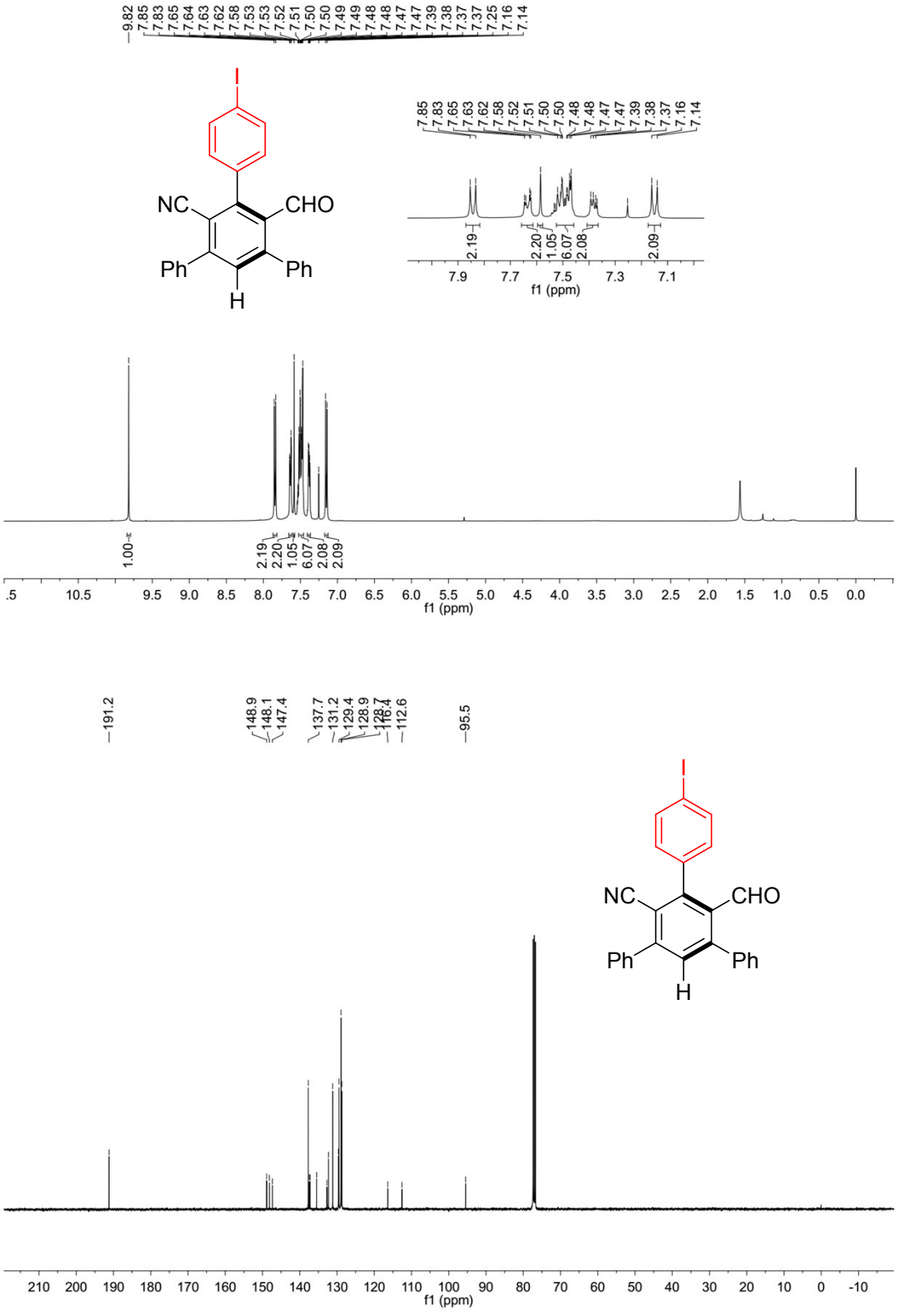

-111.88
F
NC
CHO
Ph
Ph
H
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

4-Chloro-6'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3c)

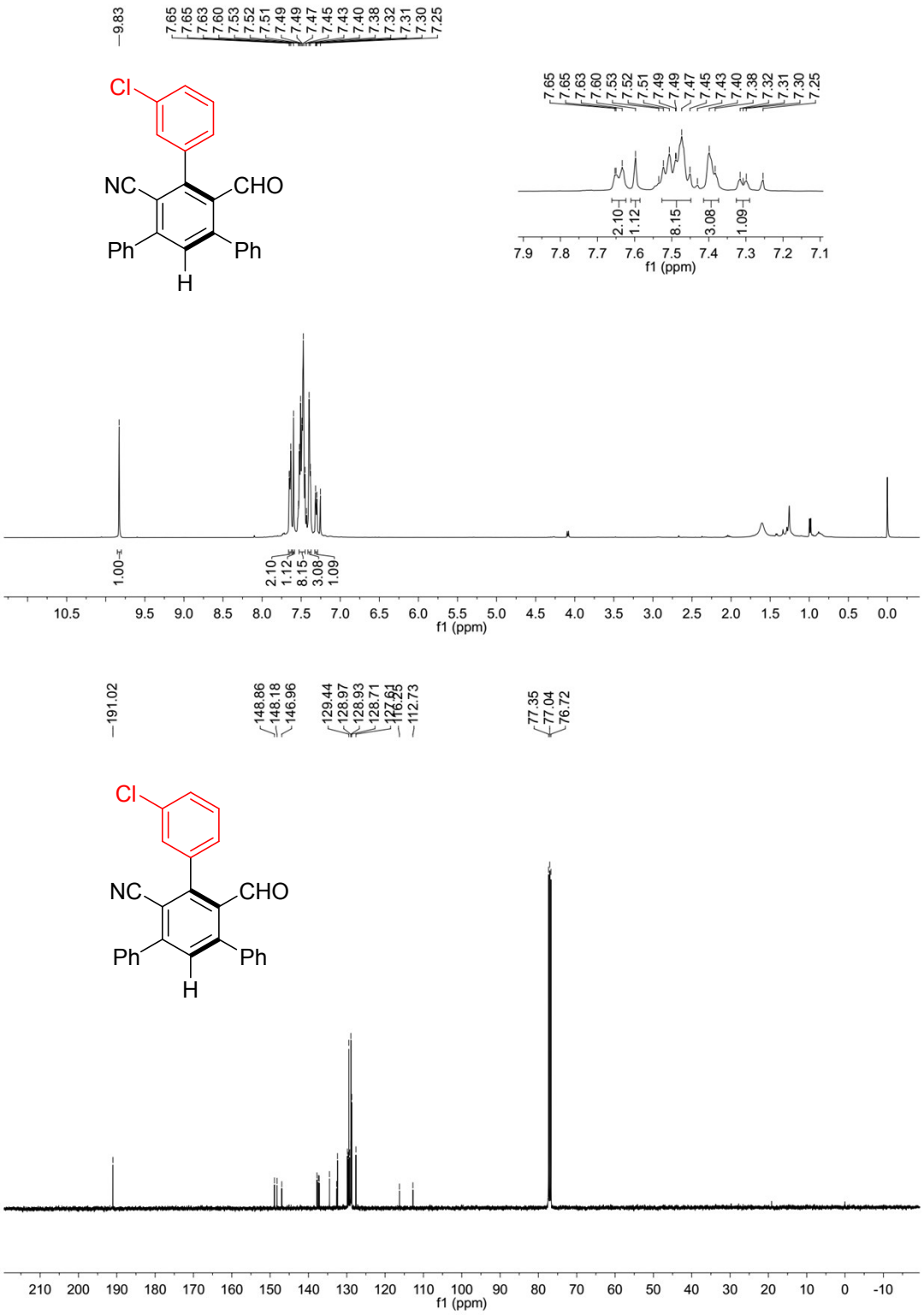




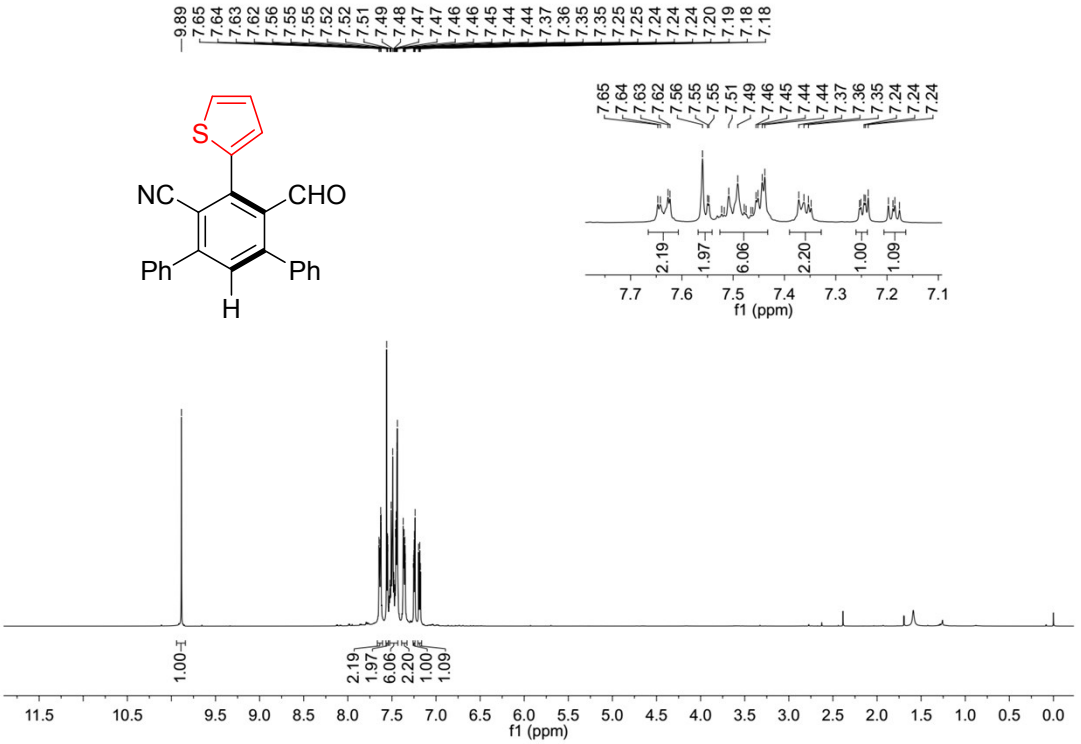
6'-Formyl-4-iodo-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3d)

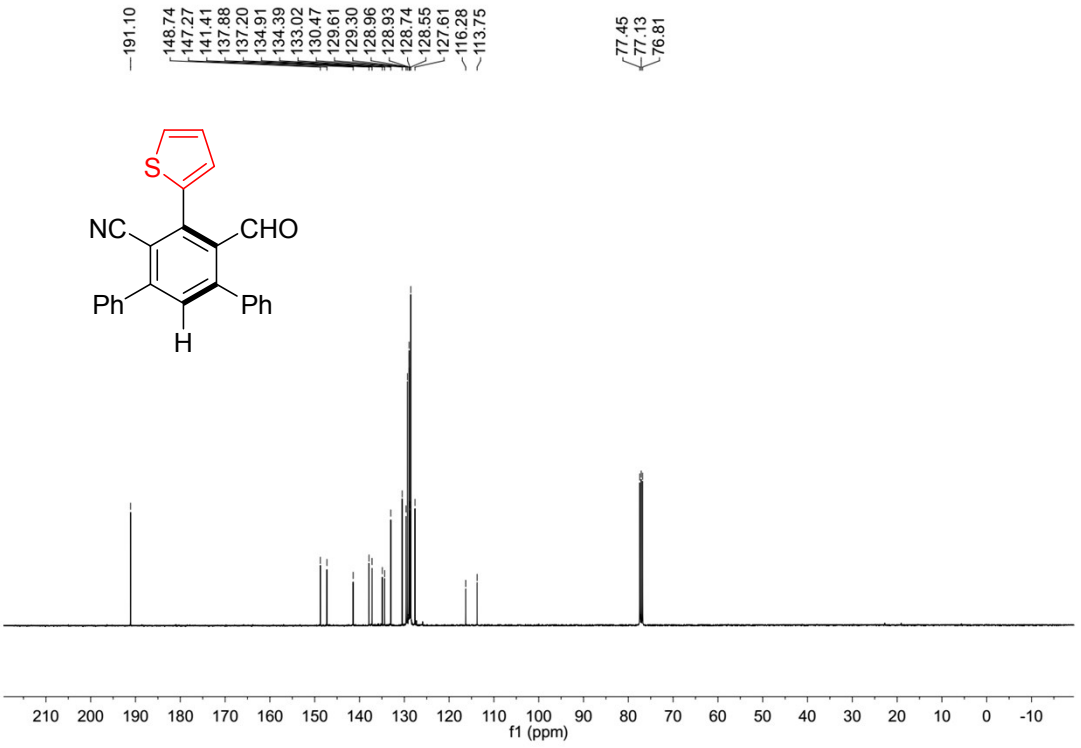


3-Chloro-6'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3e)

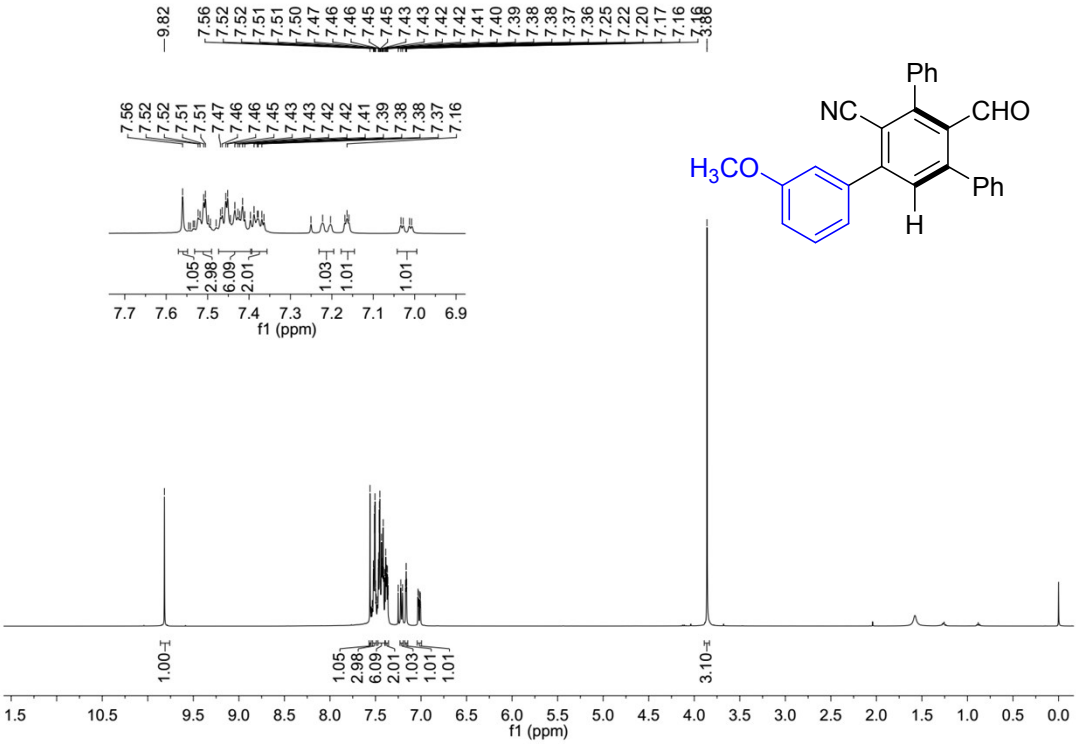


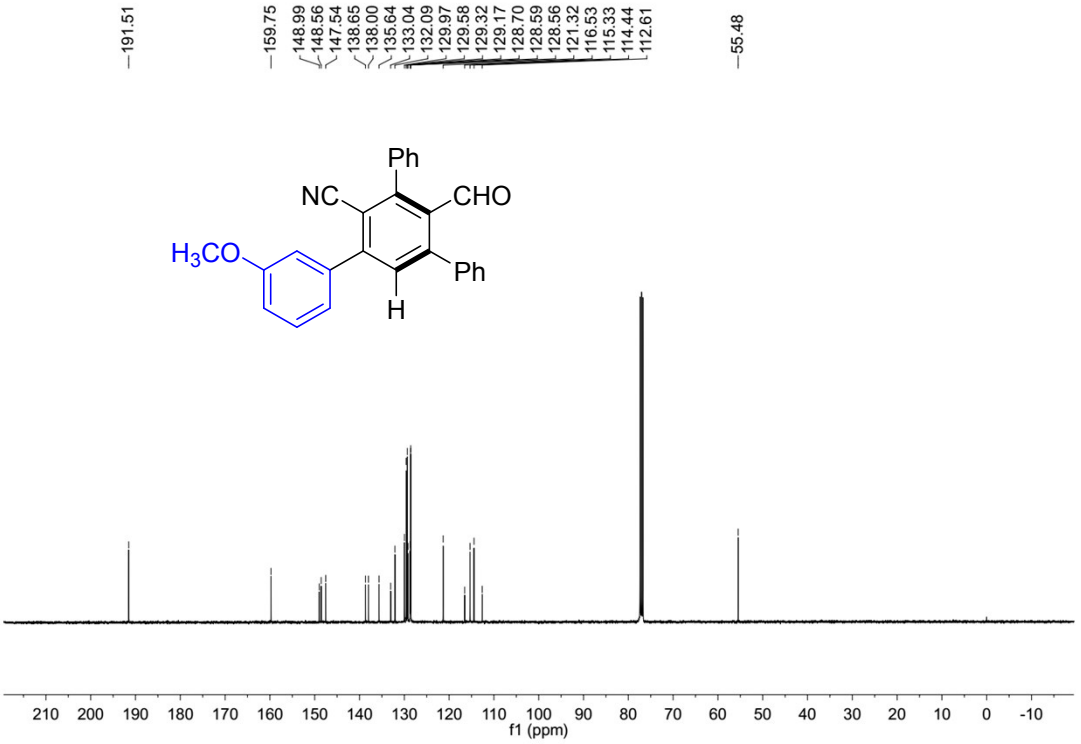
6'-Formyl-5'-(thiophen-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3f)



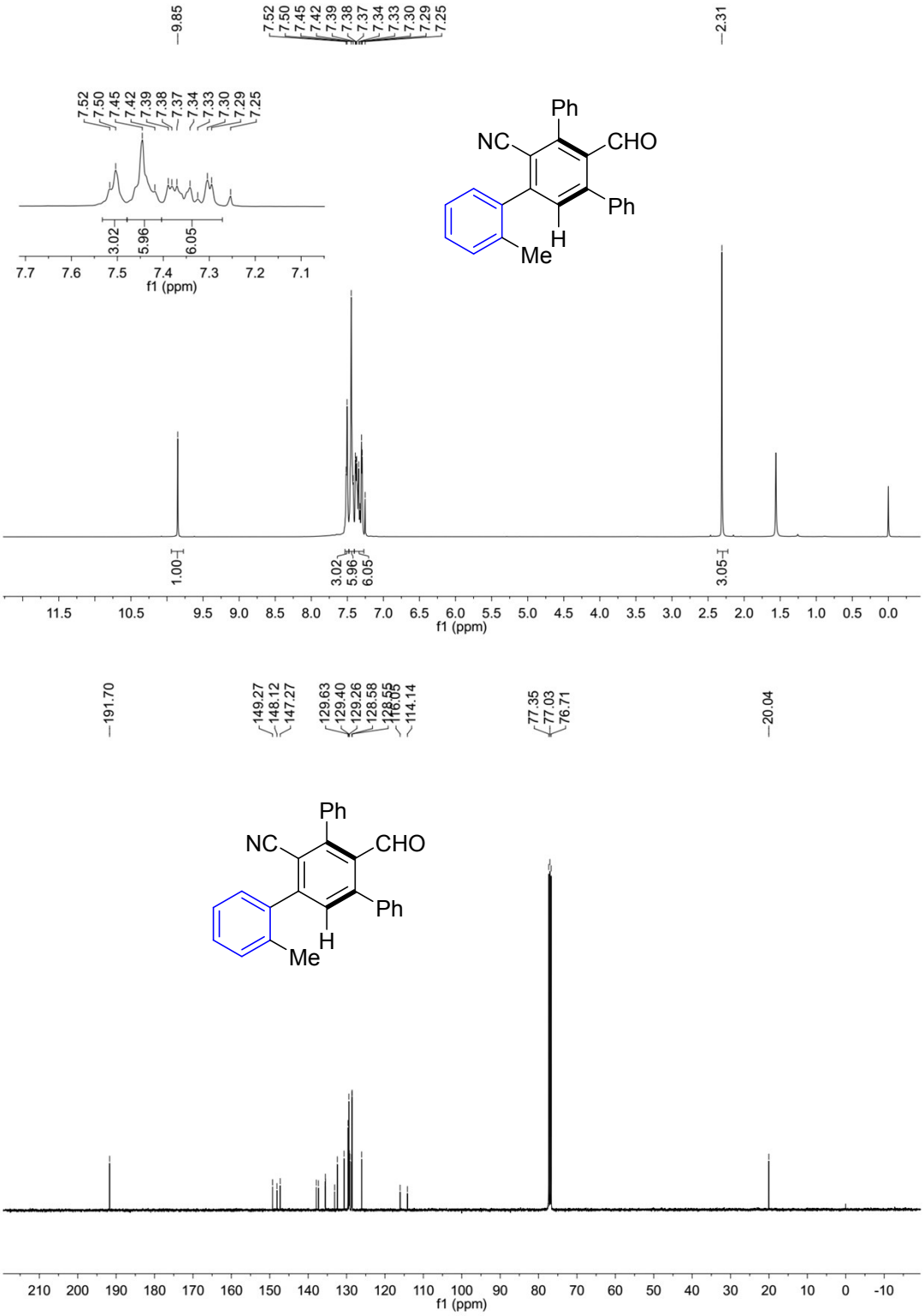


4'-Formyl-3-methoxy-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3g)

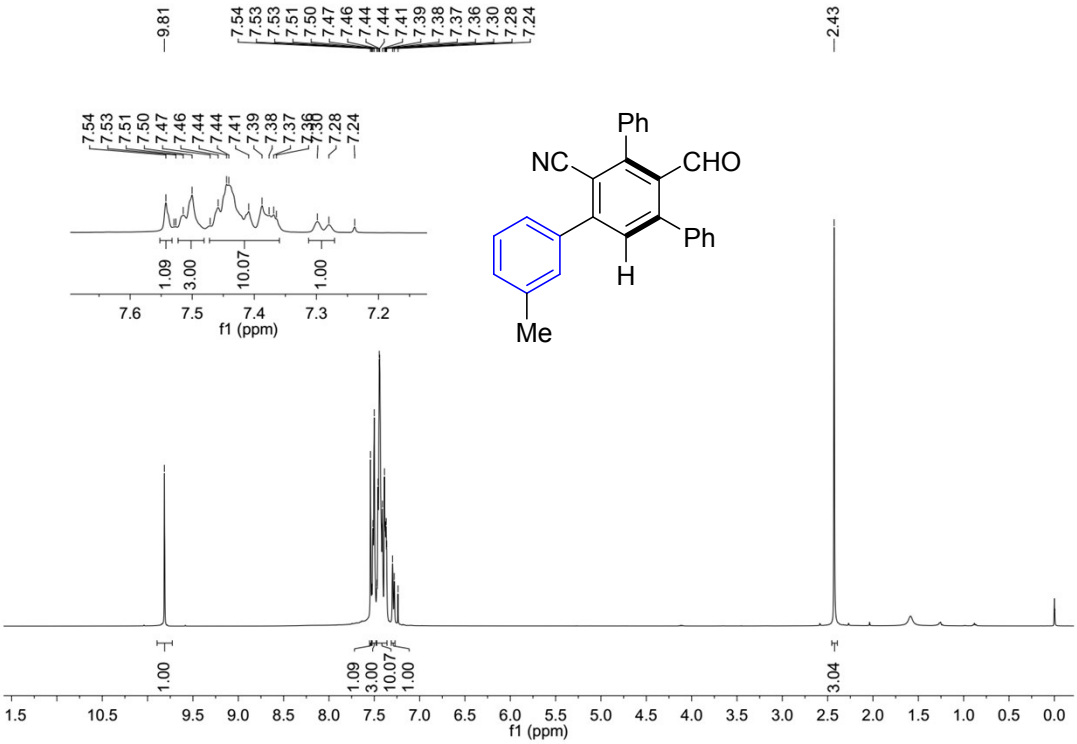


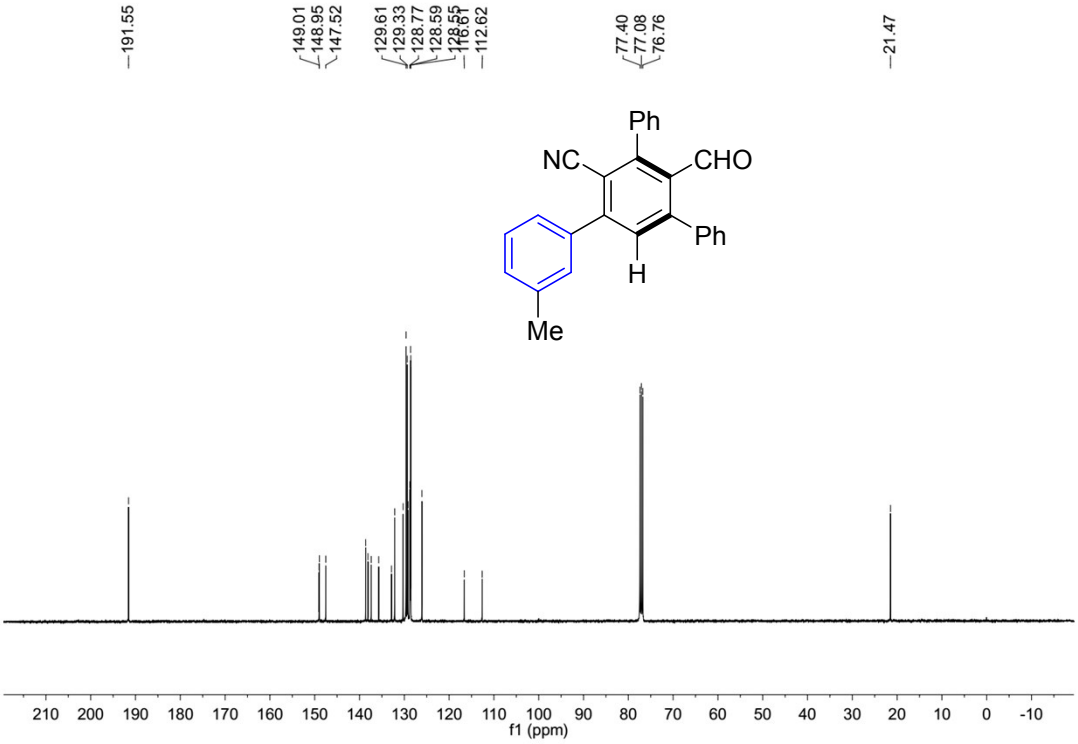


4'-Formyl-2-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3h)

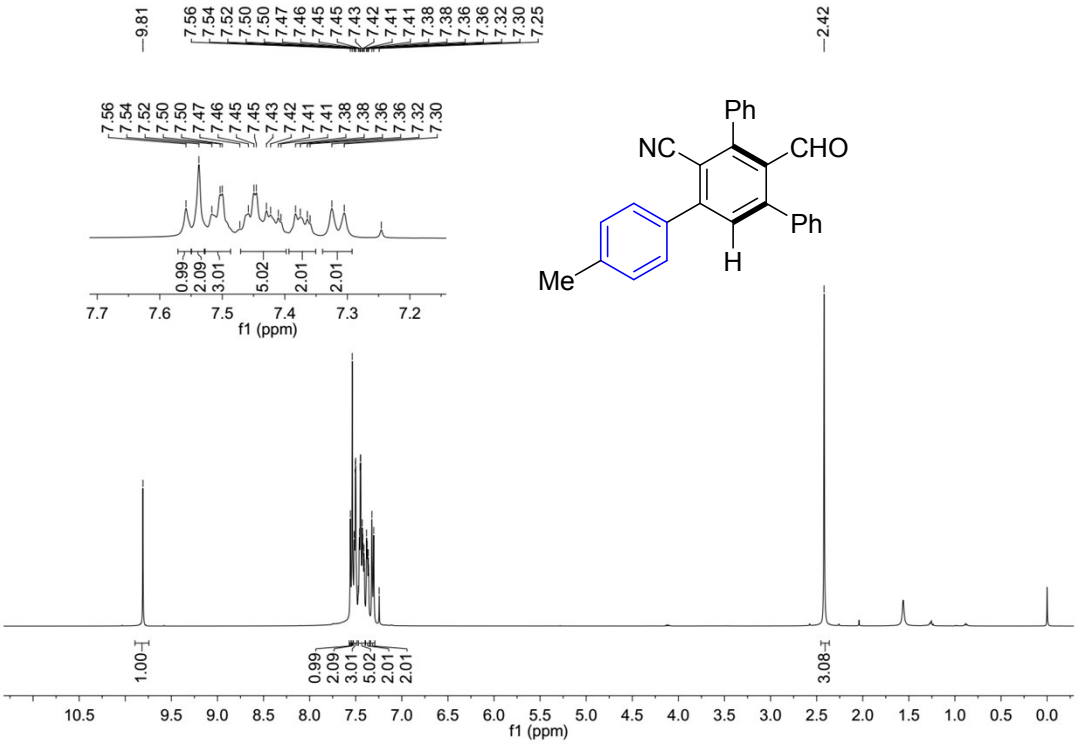


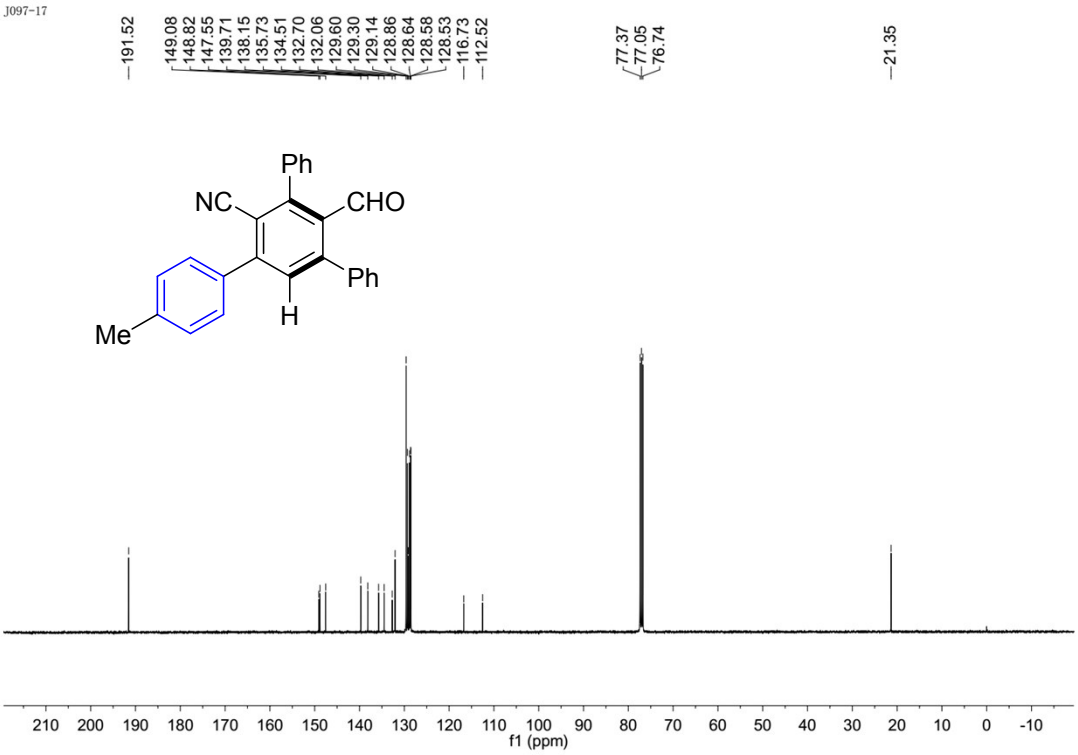
4'-Formyl-3-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3i)



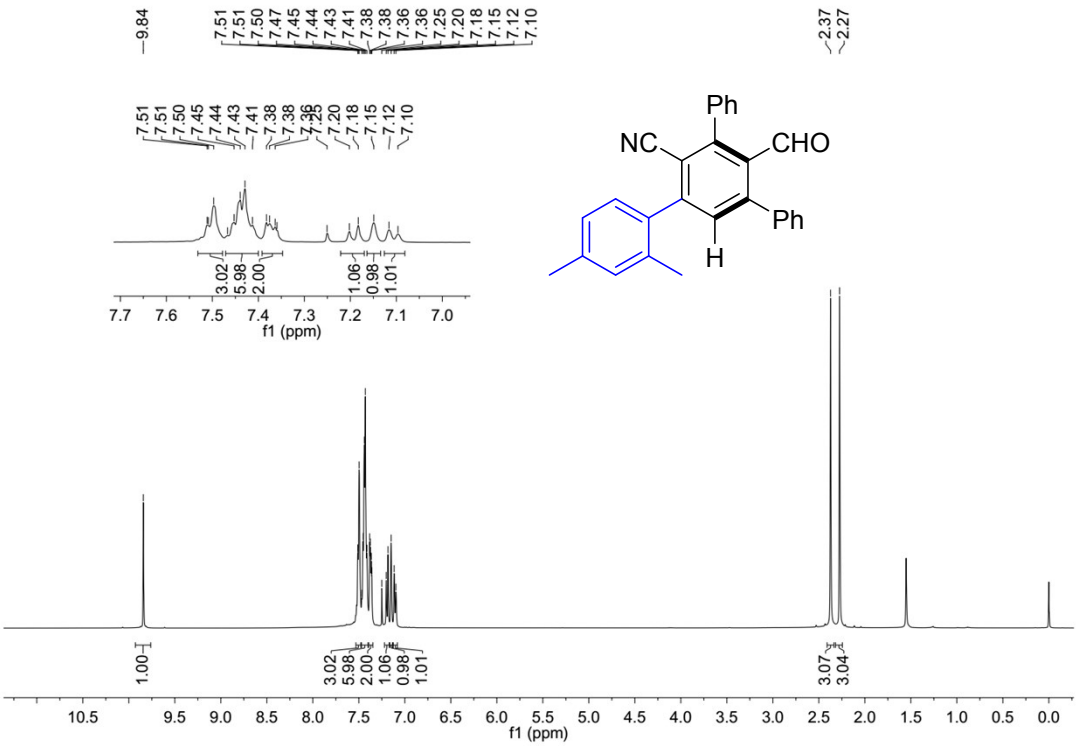


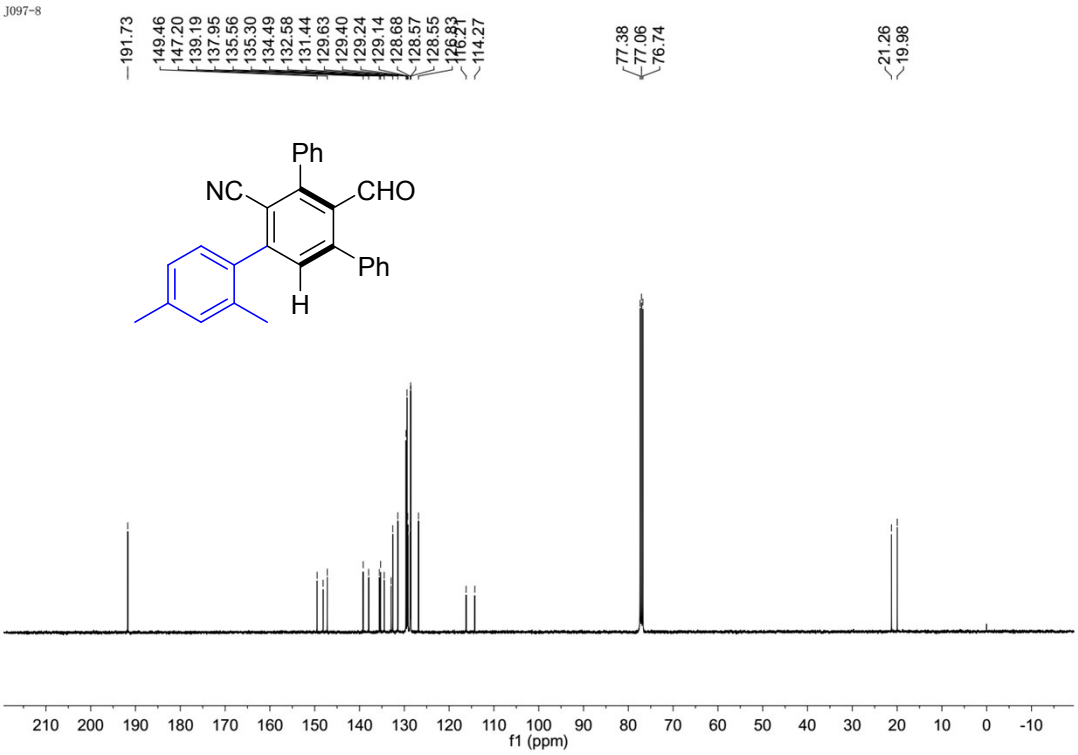
4'-Formyl-4-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3j)



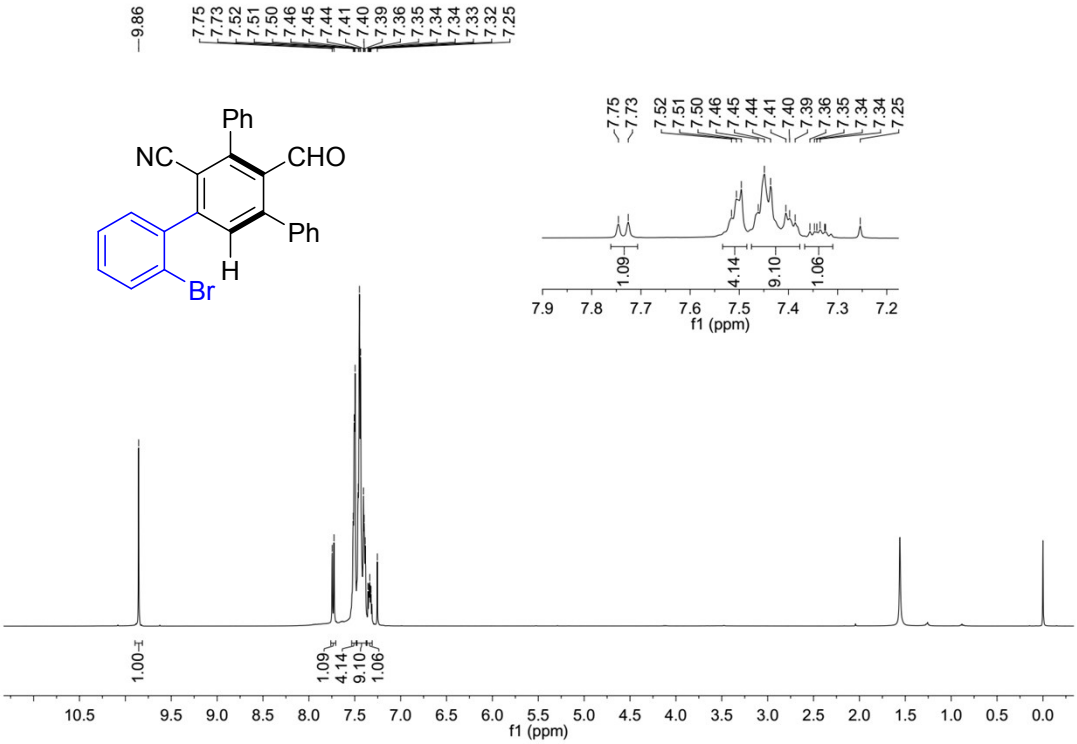


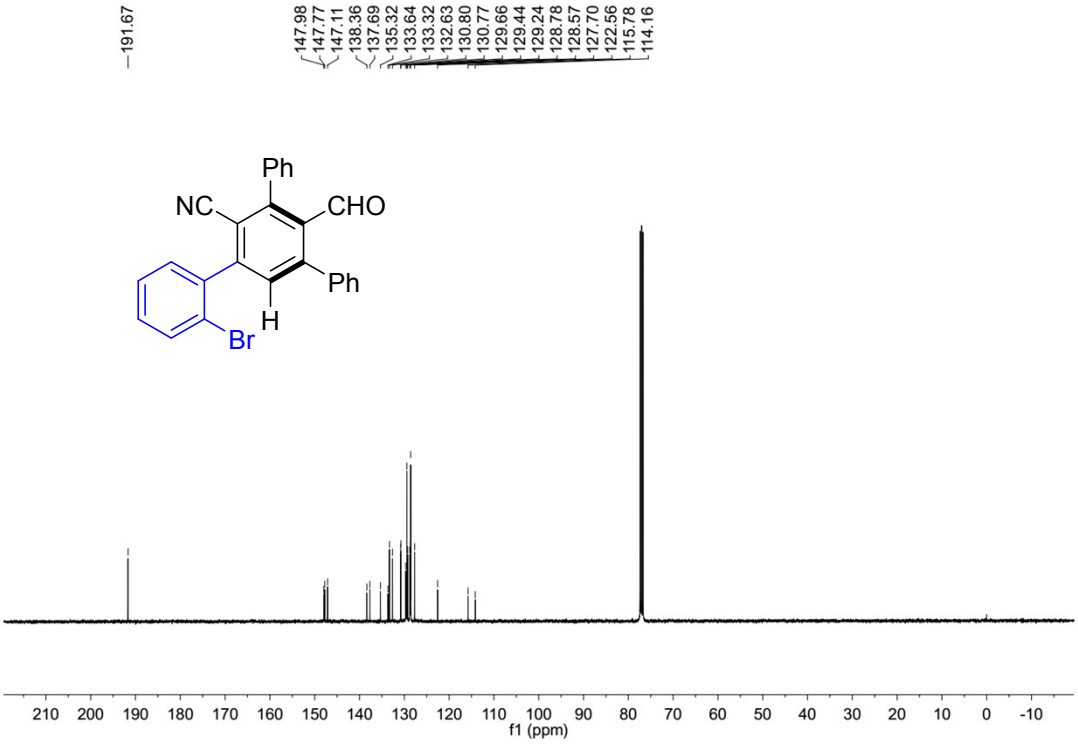
4'-Formyl-2,4-dimethyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3k)



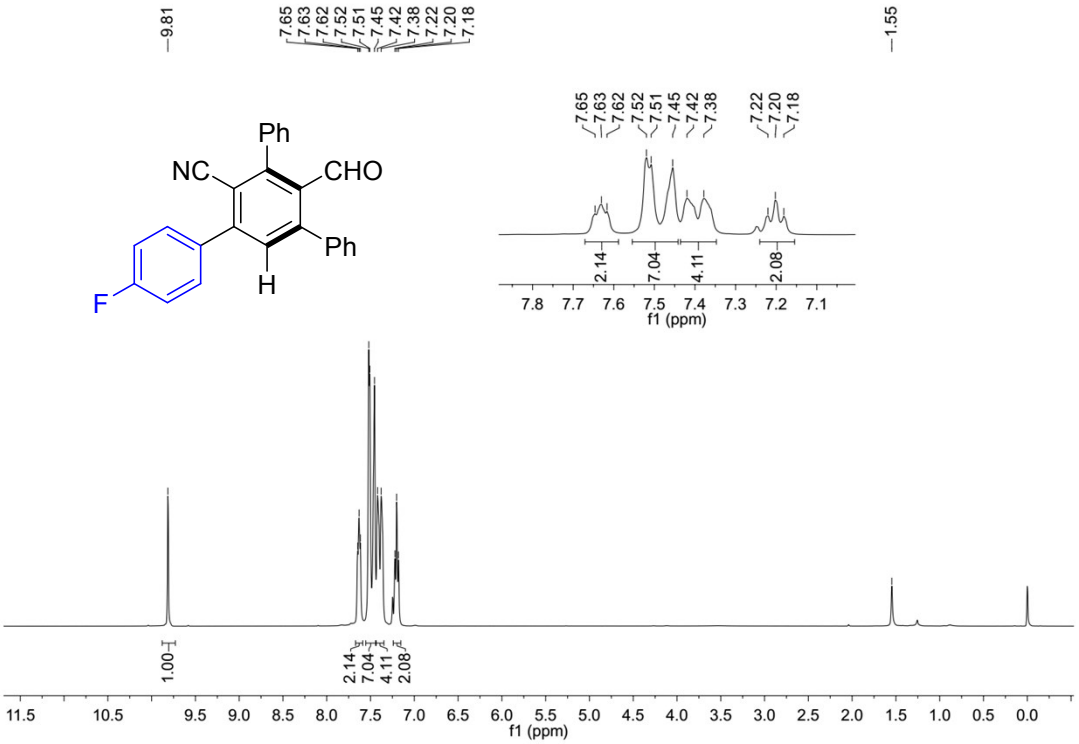


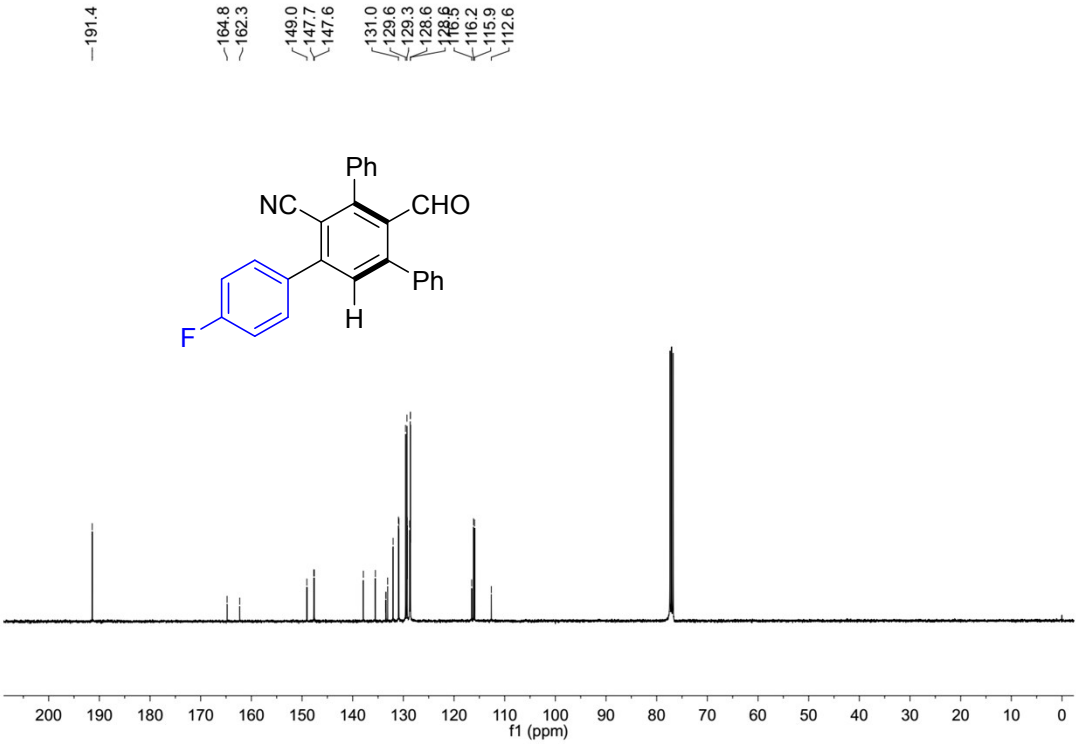
2-Bromo-4'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3l)

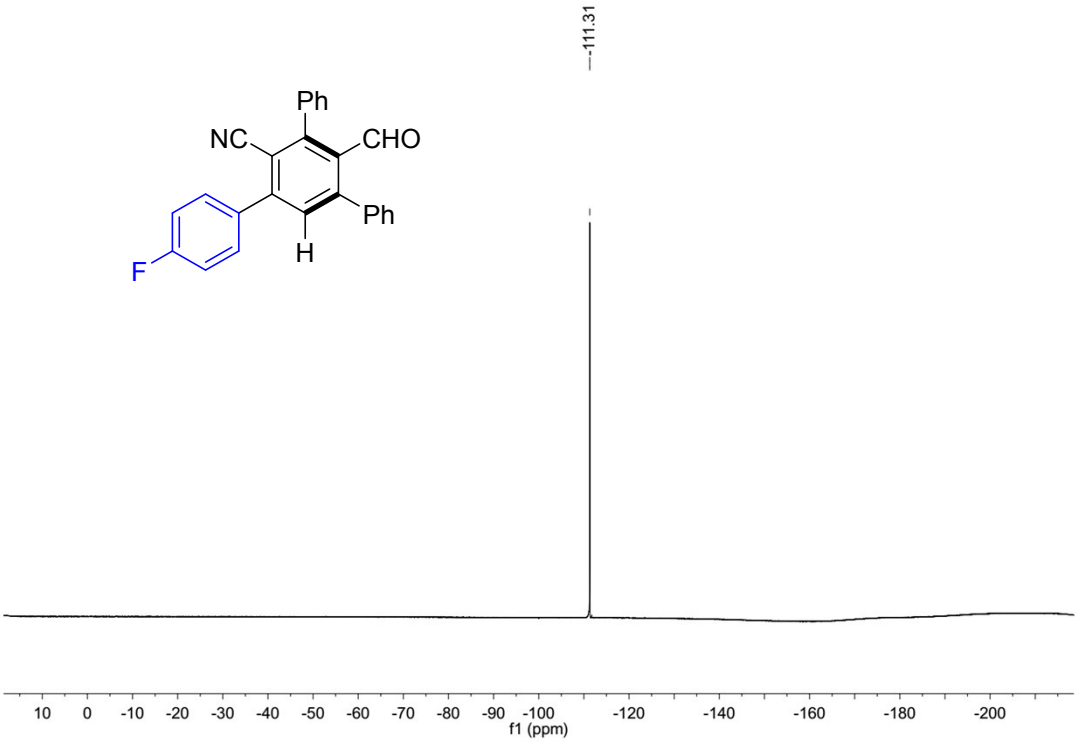




4-Fluoro-4'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3m)



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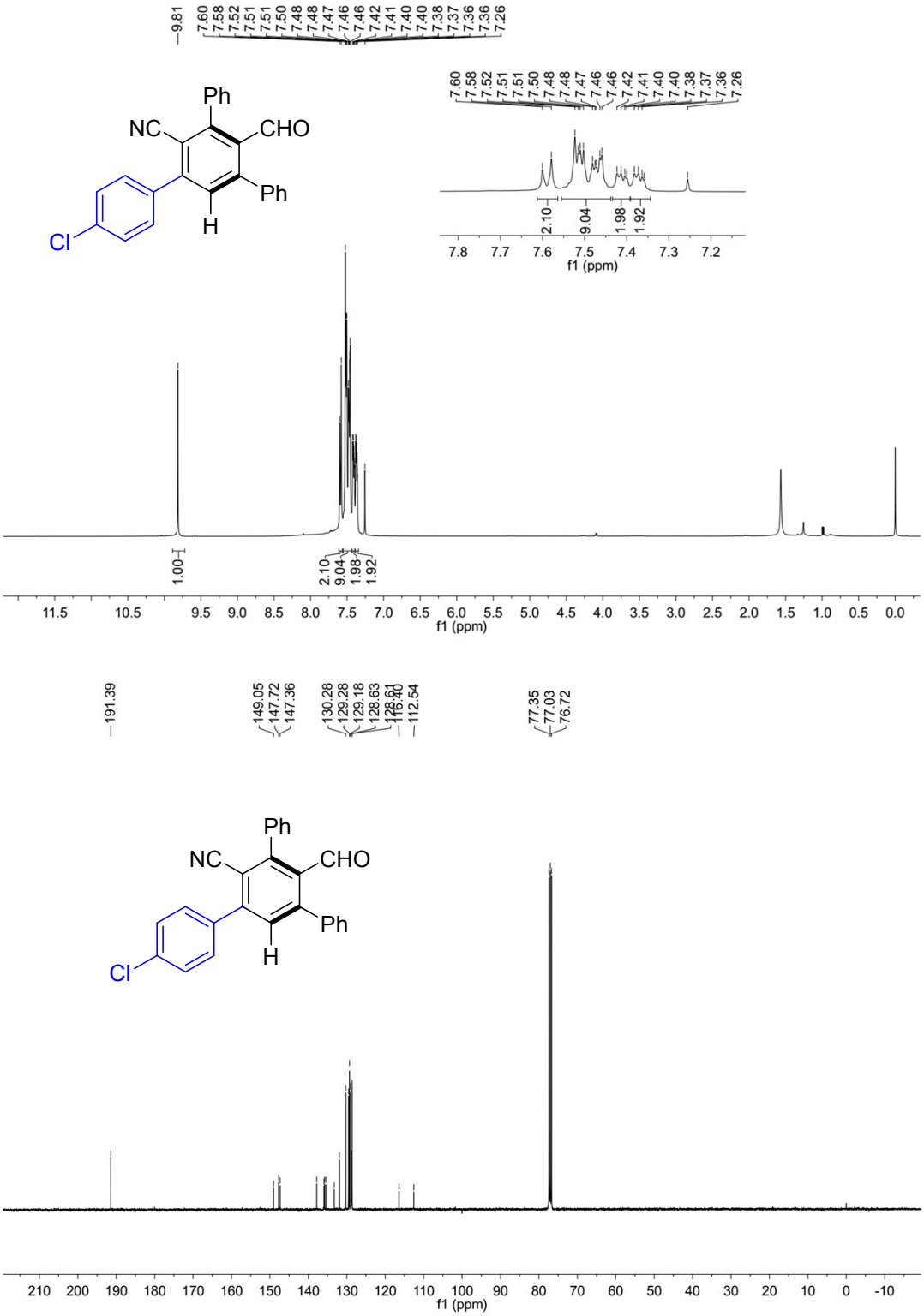
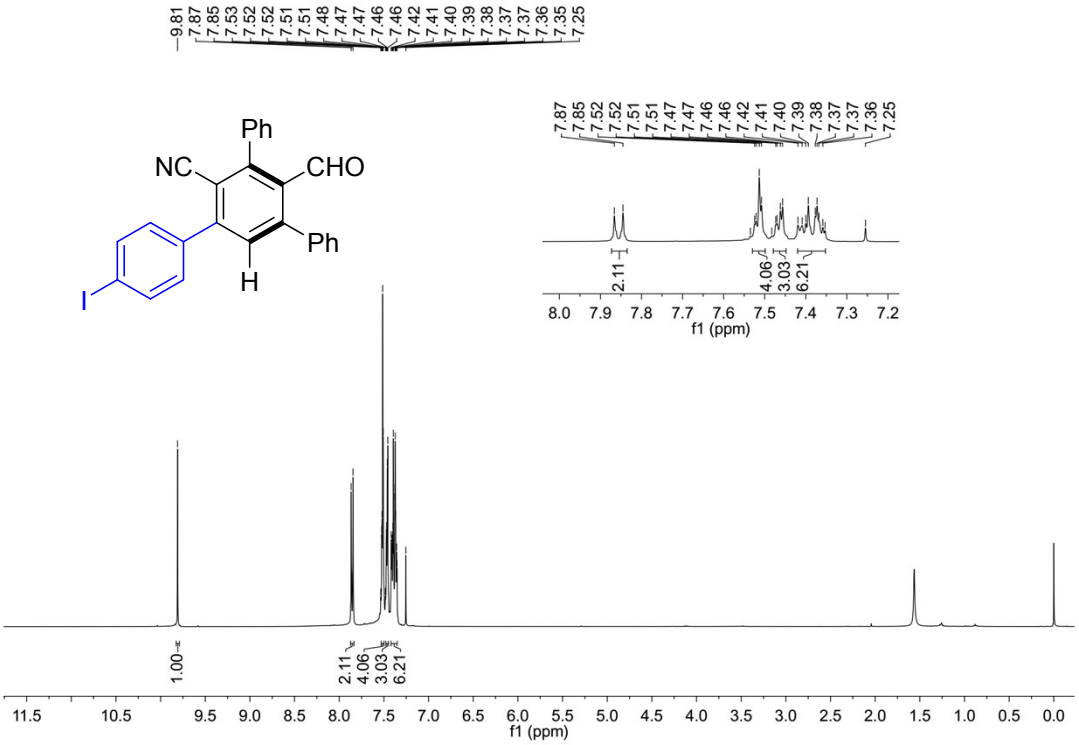
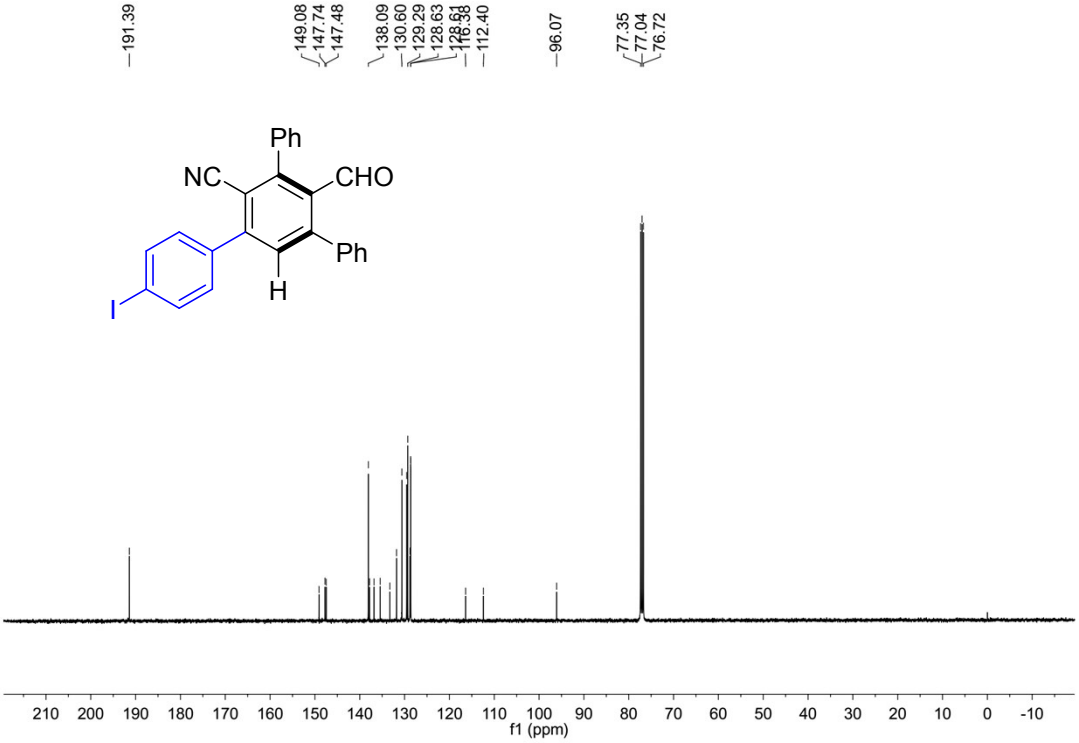
Ph
NC
CHO
Ph
H
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

4-Chloro-4'-formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3n)

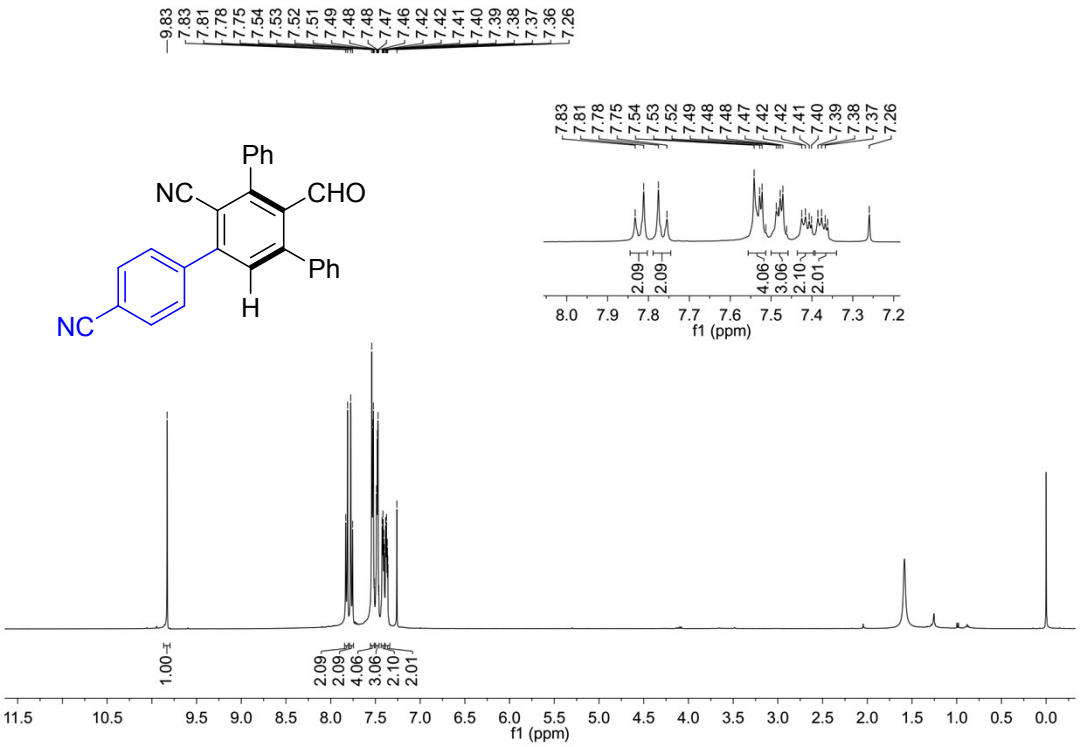


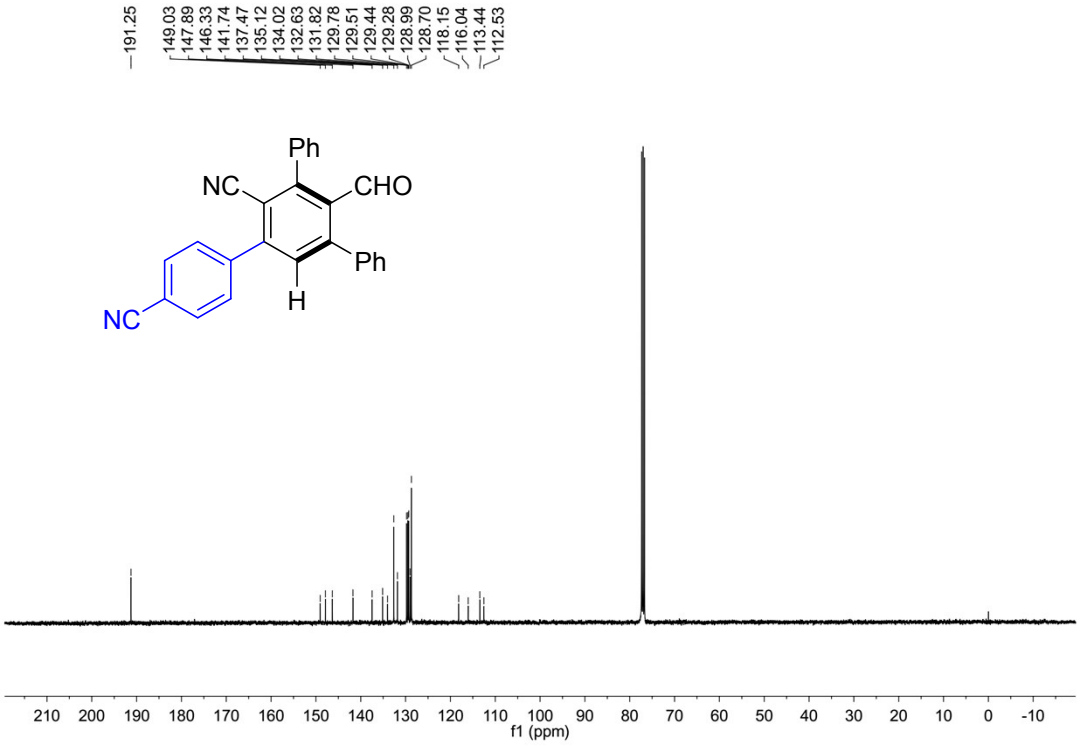
4'-Formyl-4-iodo-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3o)



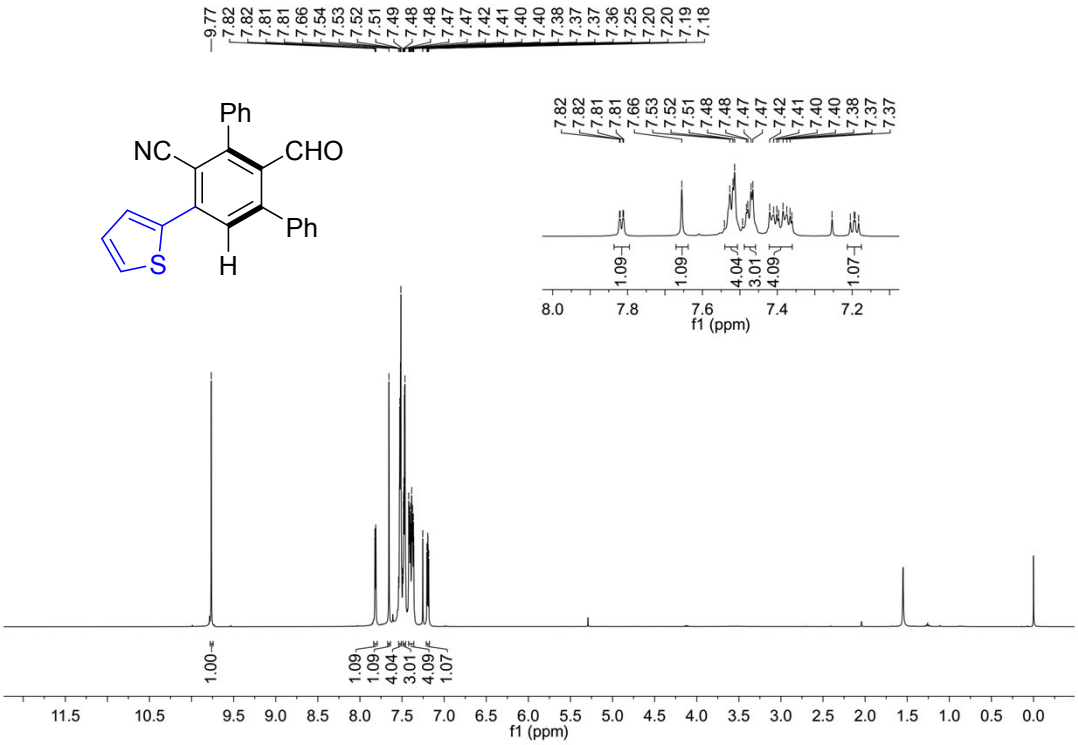


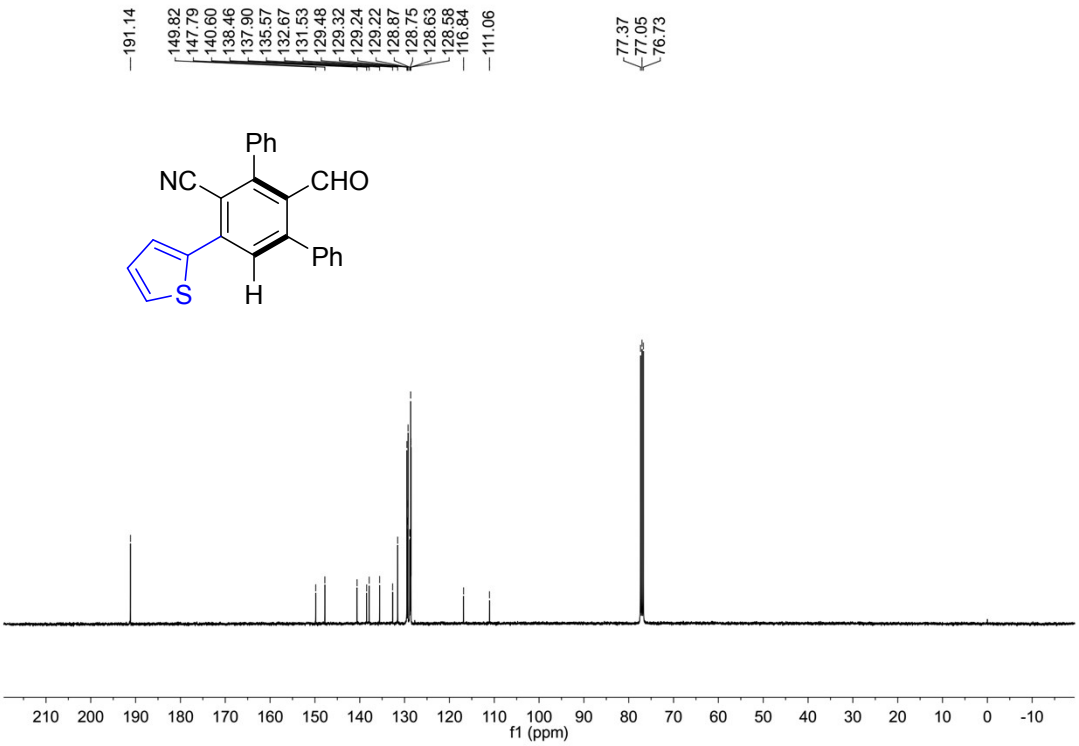
4'-Formyl-5'-phenyl-[1,1':3',1''-terphenyl]-2',4-dicarbonitrile (3p)



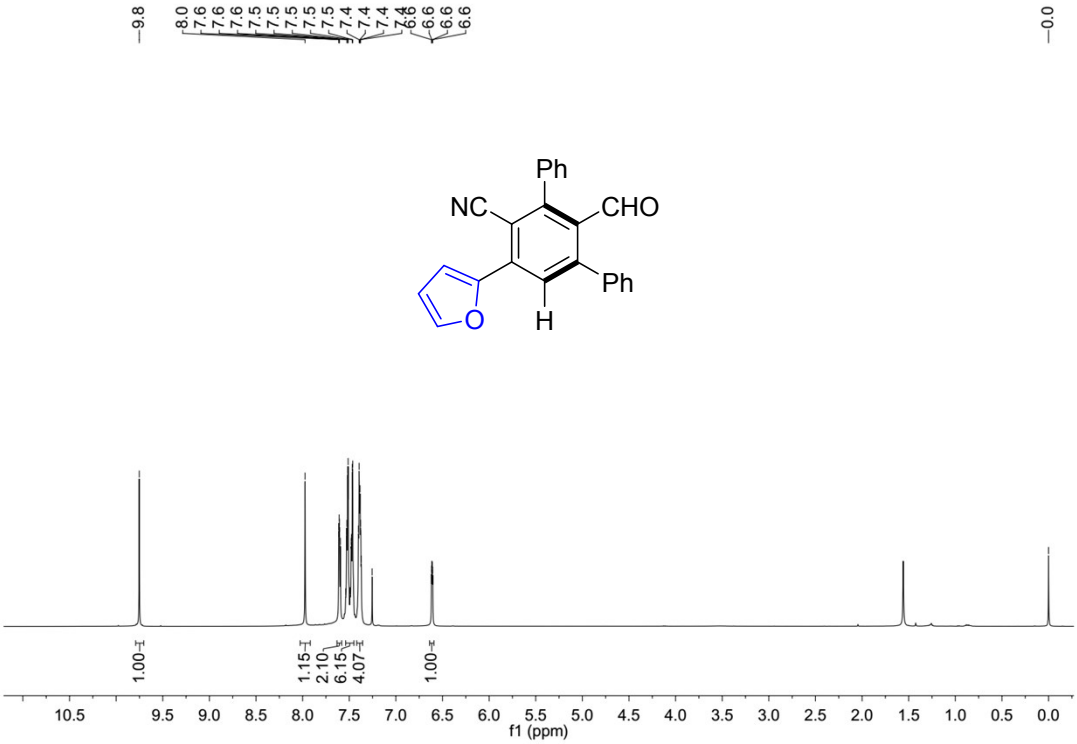


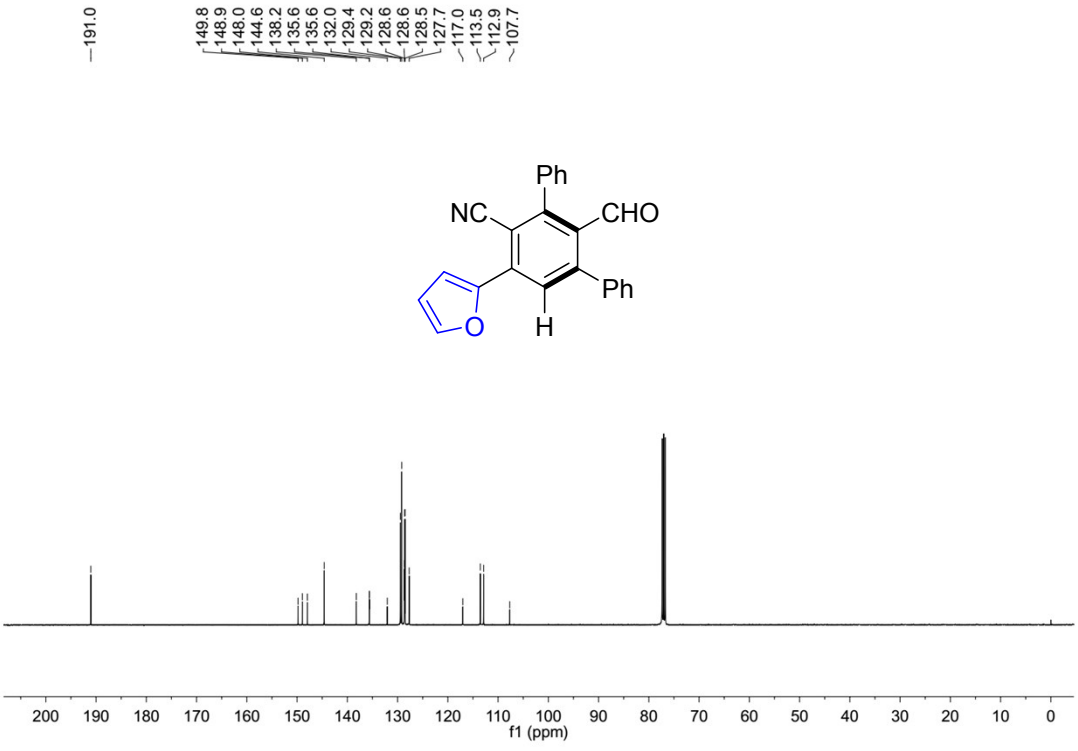
2'-Formyl-5'-(thiophen-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3q)



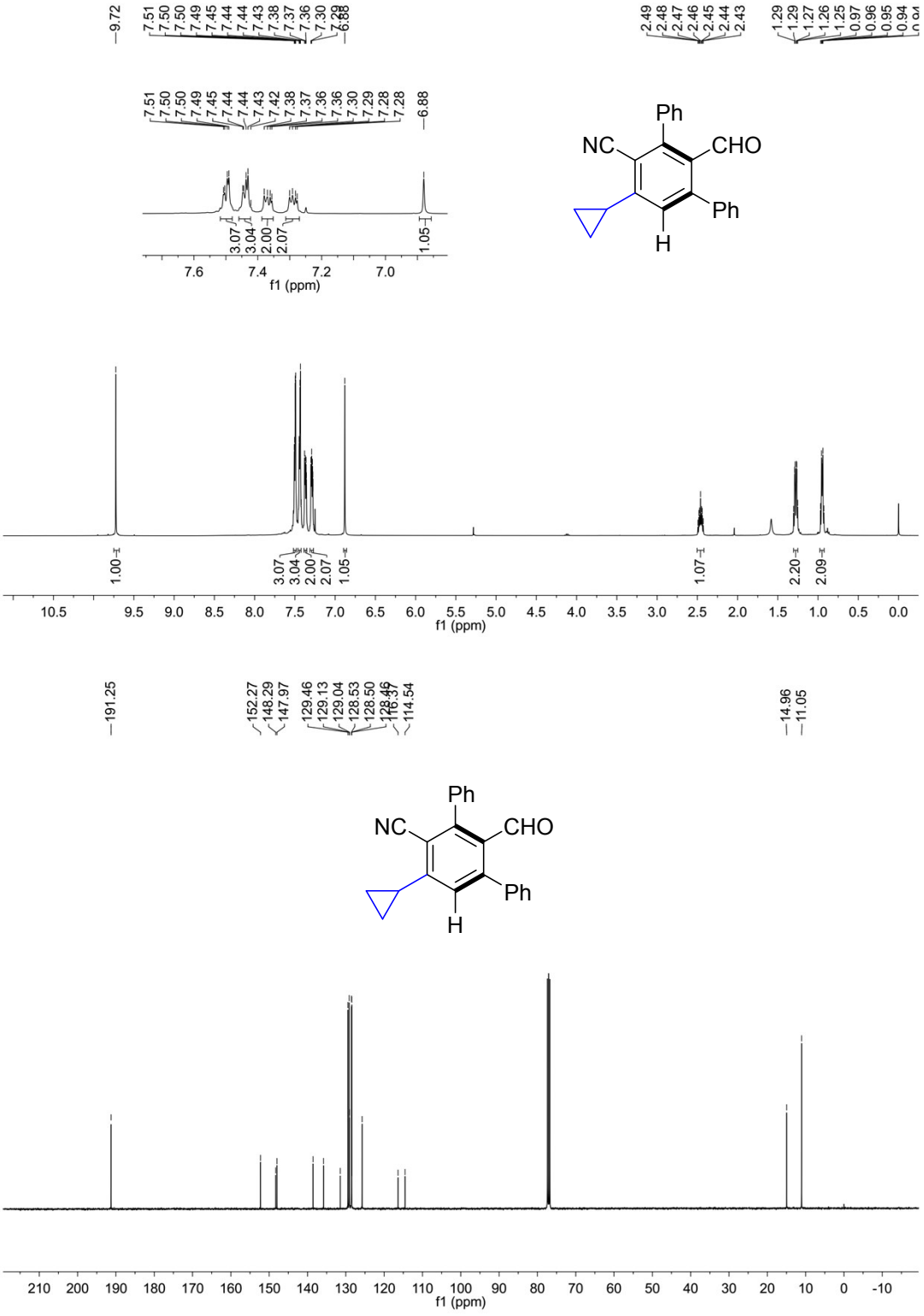


2'-Formyl-5'-(furan-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3r)

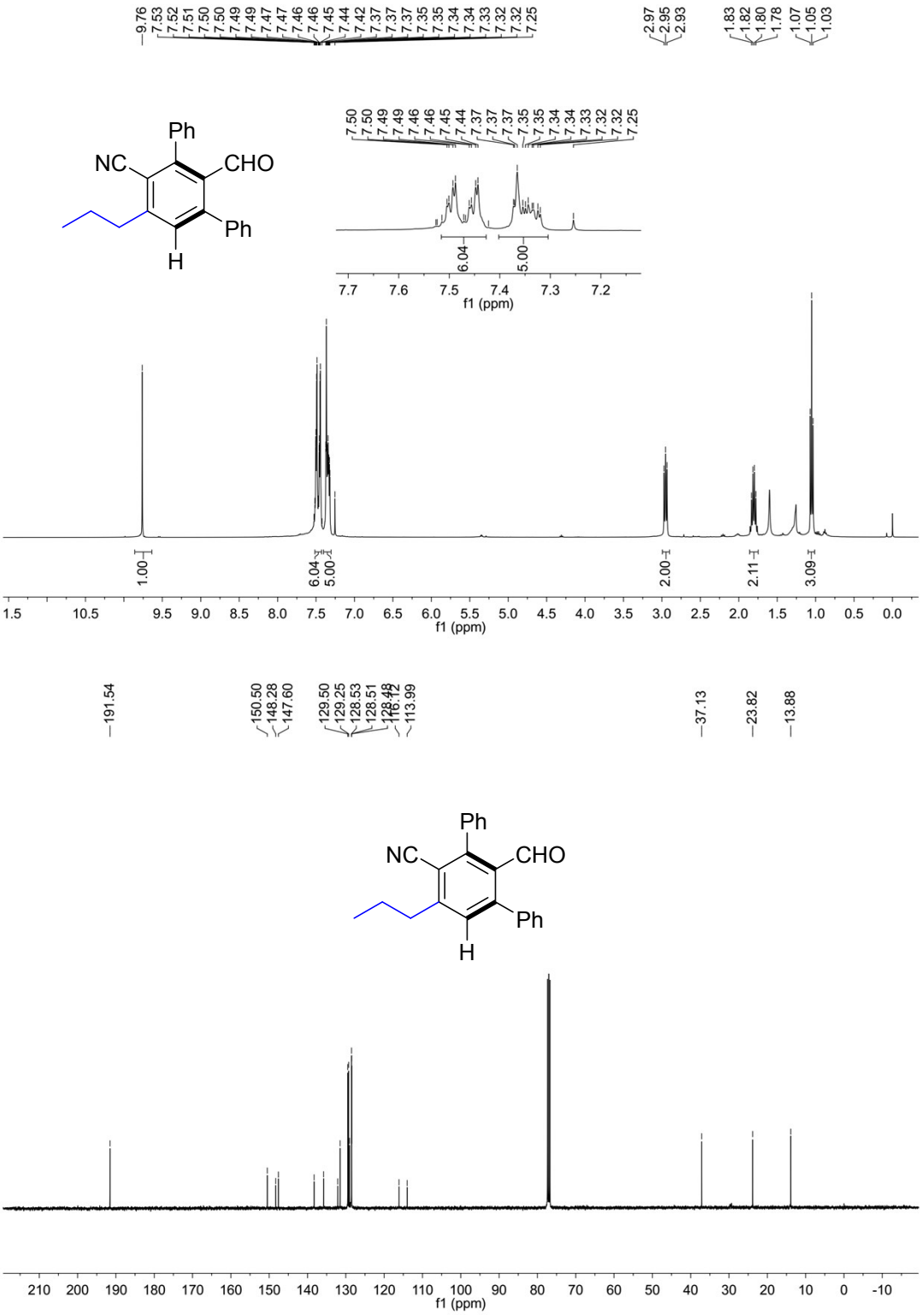




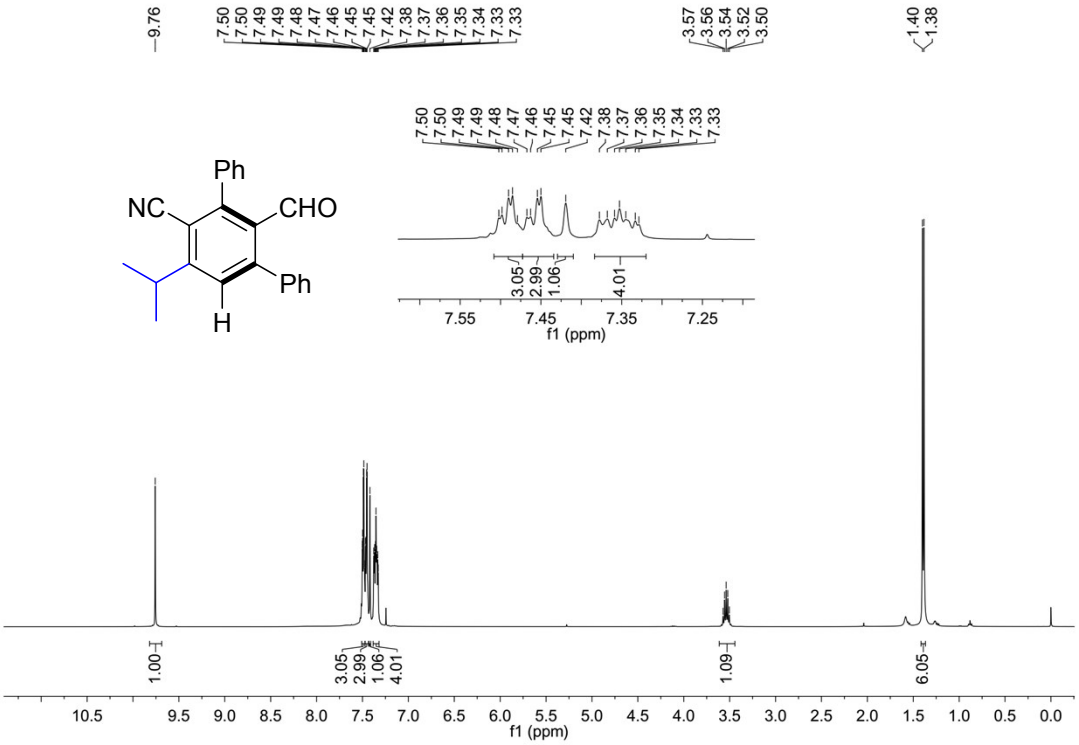
5'-Cyclopropyl-2'-formyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3s)

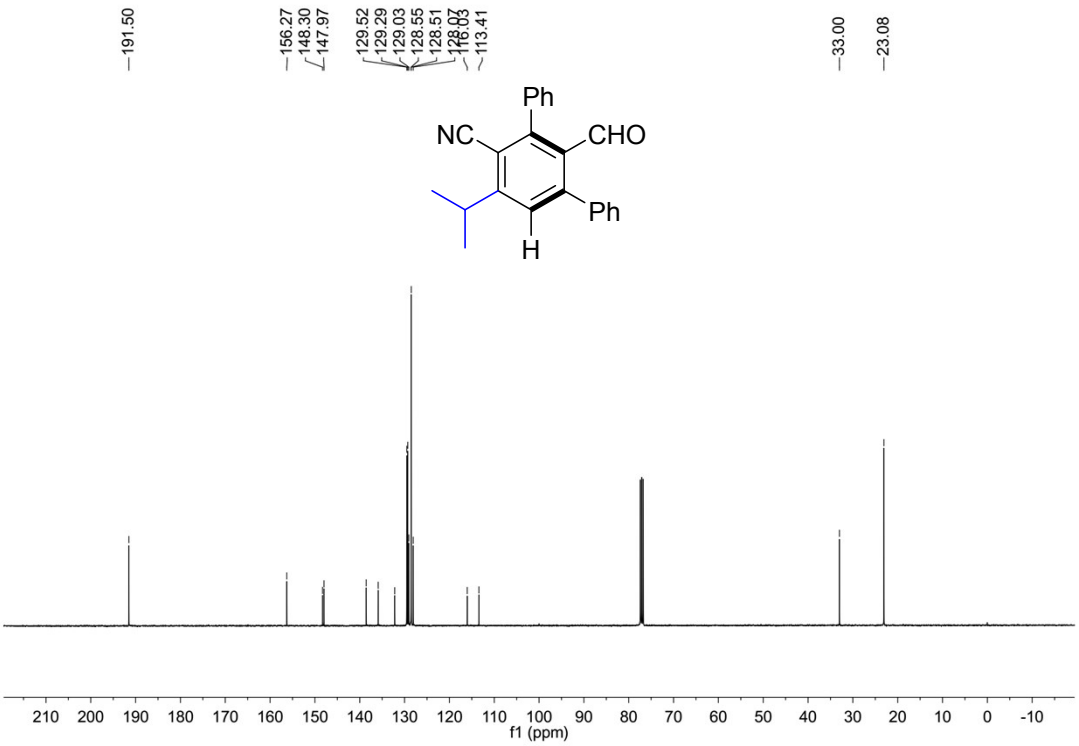


2'-Formyl-5'-propyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3t)

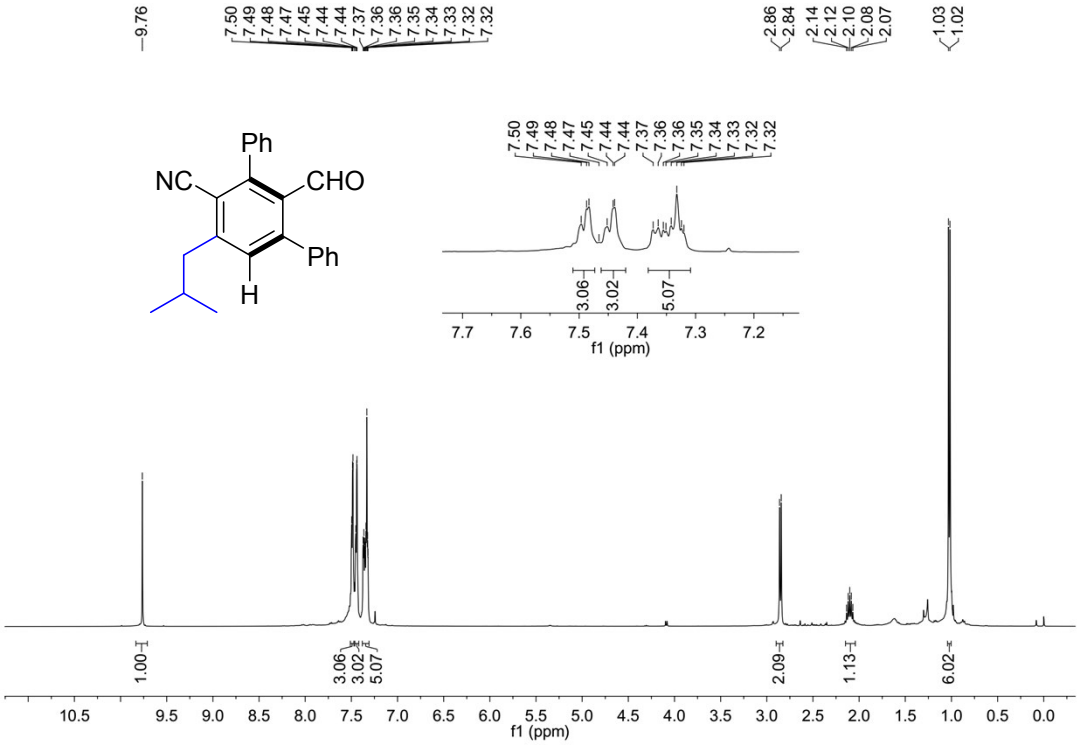


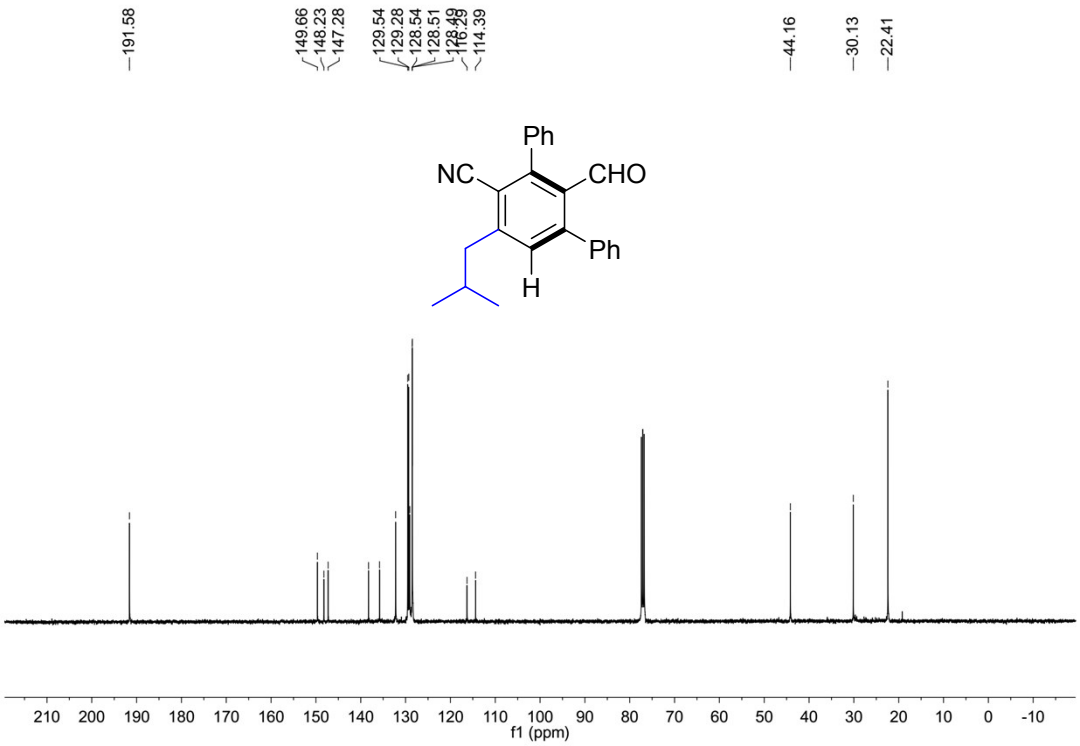
2'-Formyl-5'-isopropyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3u)



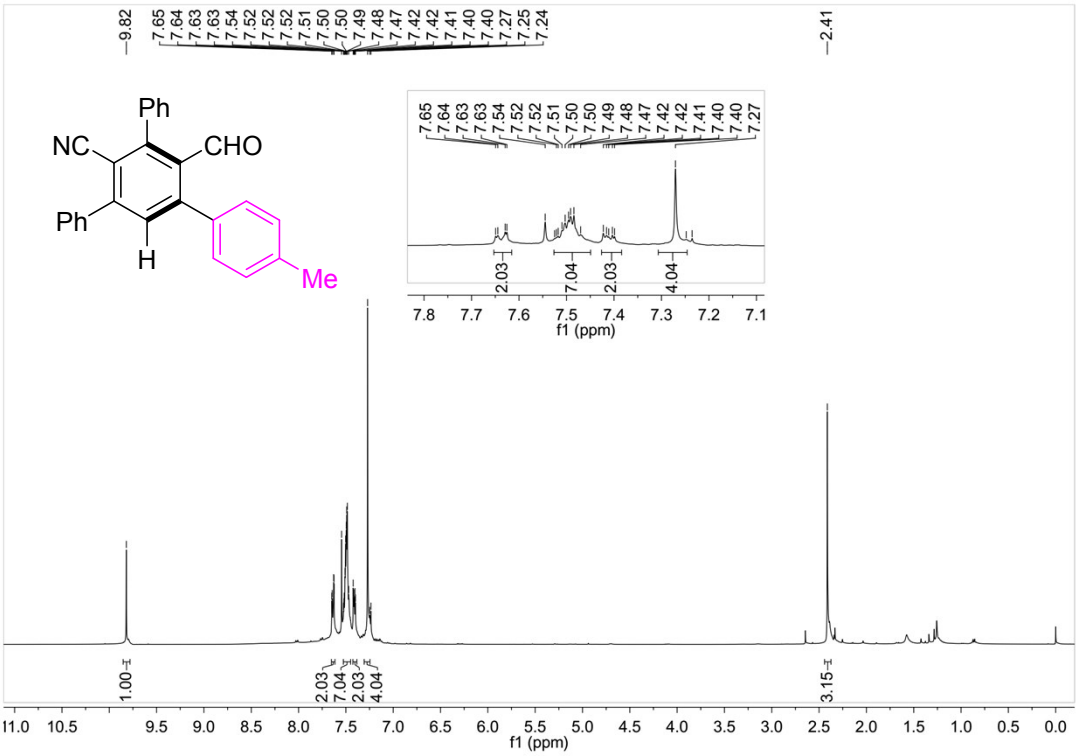


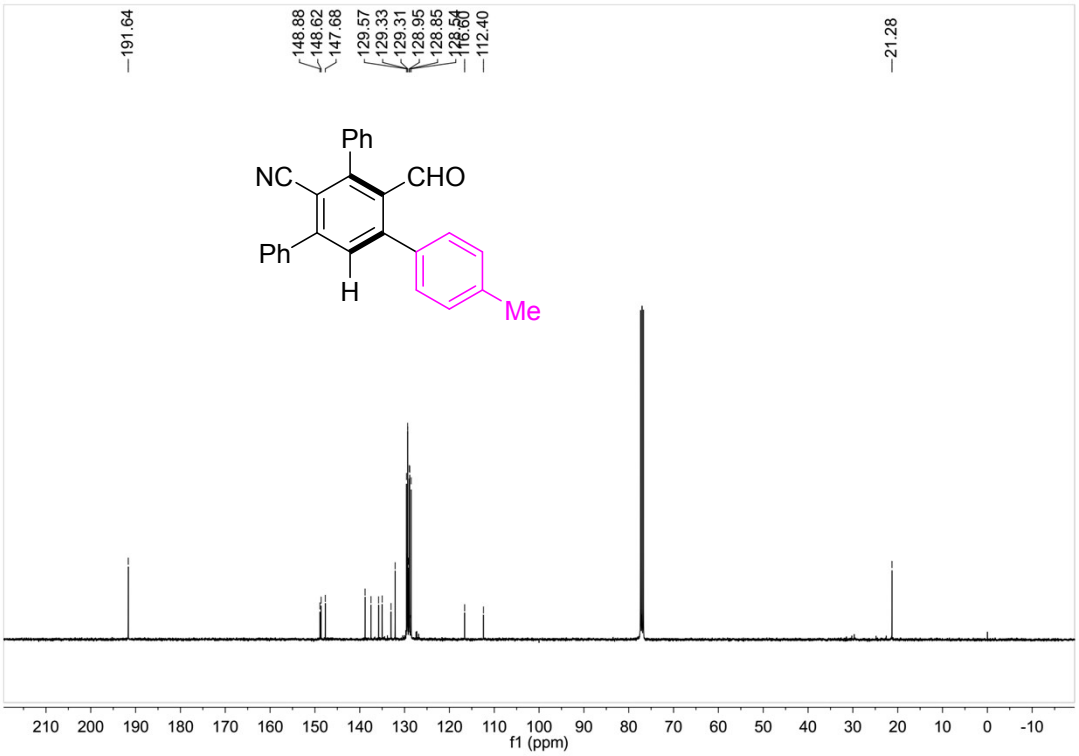
2'-Formyl-5'-isobutyl-[1,1':3',1''-terphenyl]-4'-carbonitrile (3v)



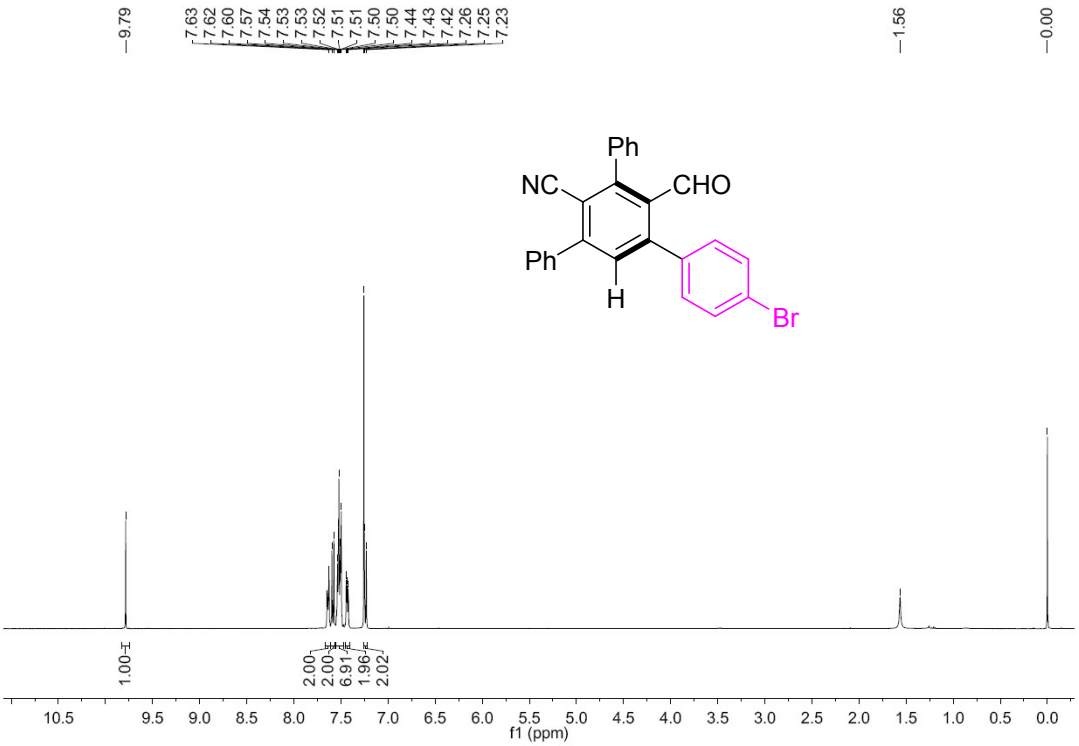


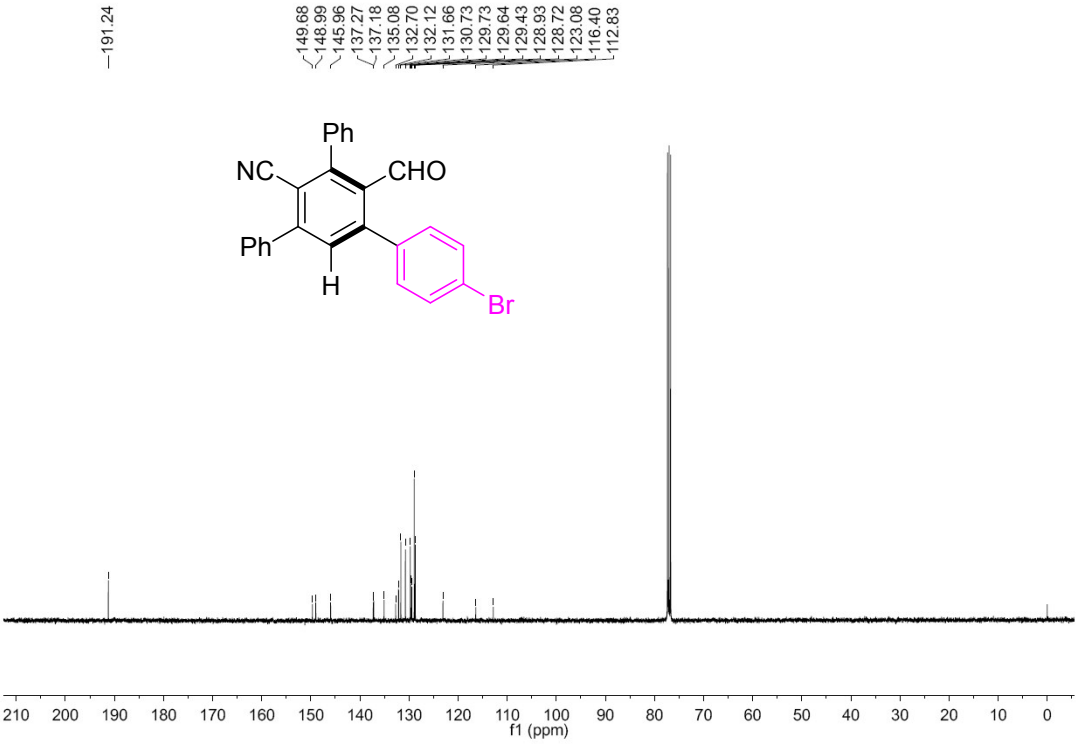
4'-Formyl-5'-(p-tolyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4a)



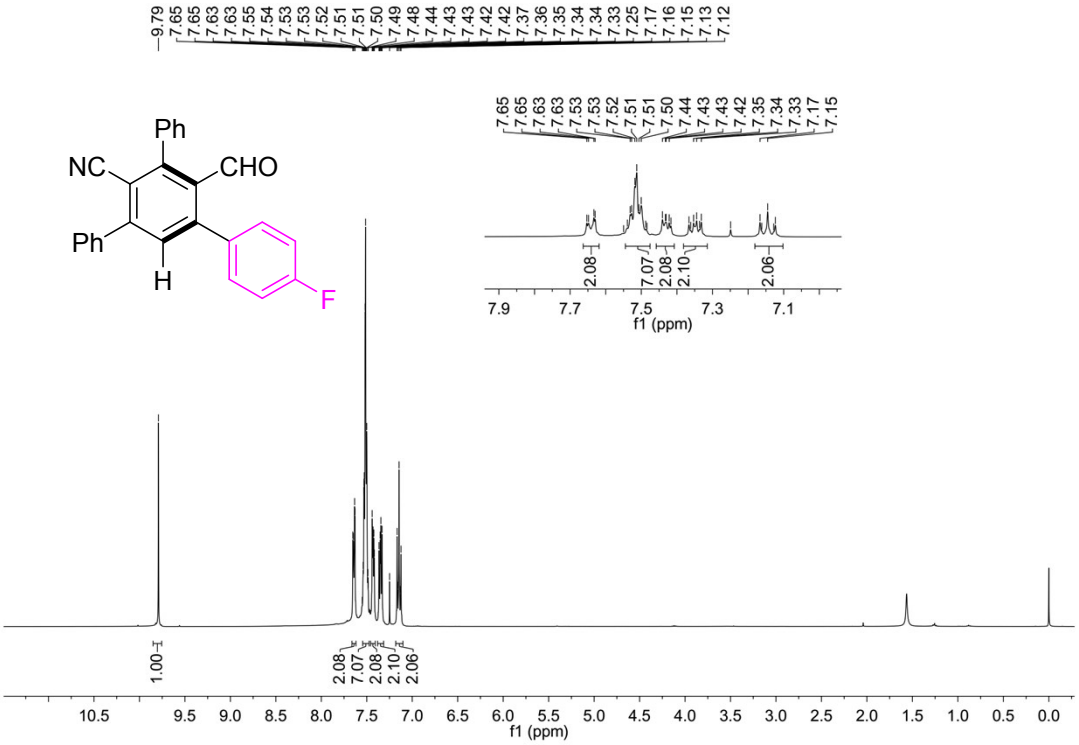


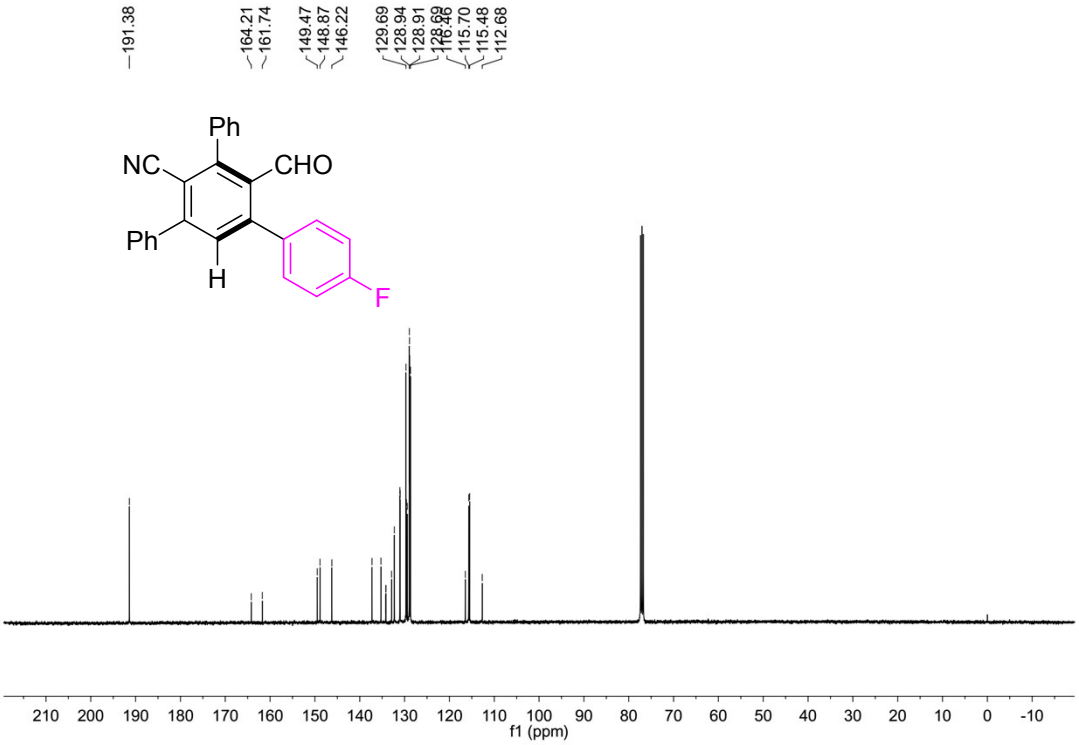
5'-(4-Bromophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4b)

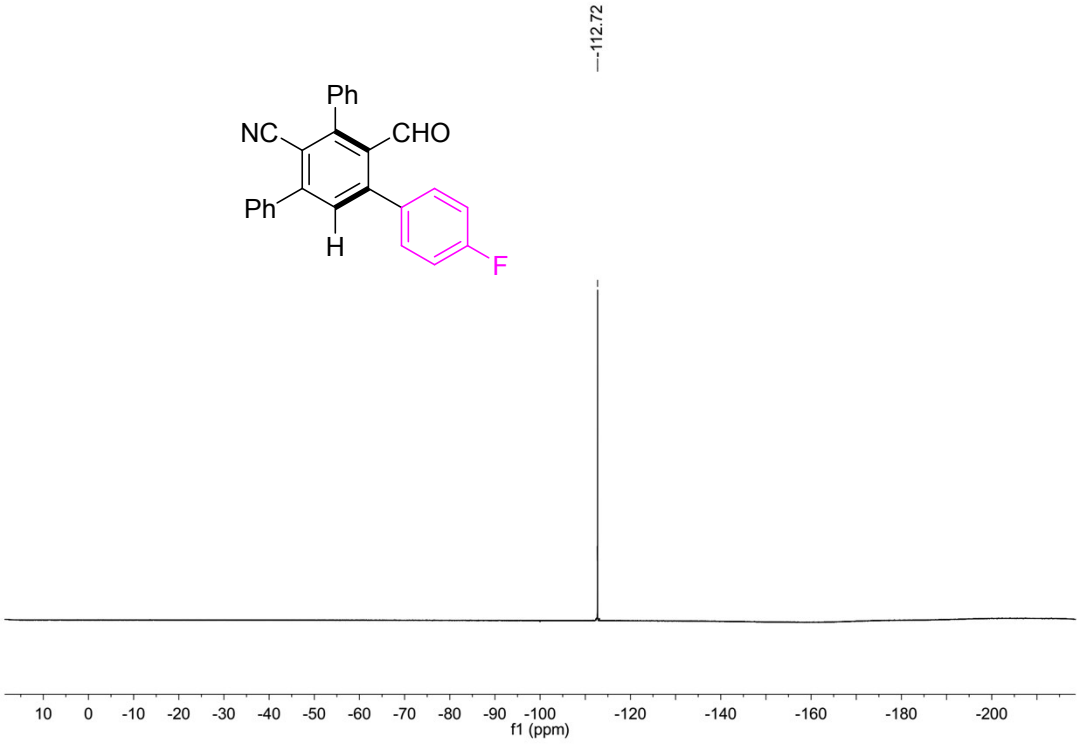




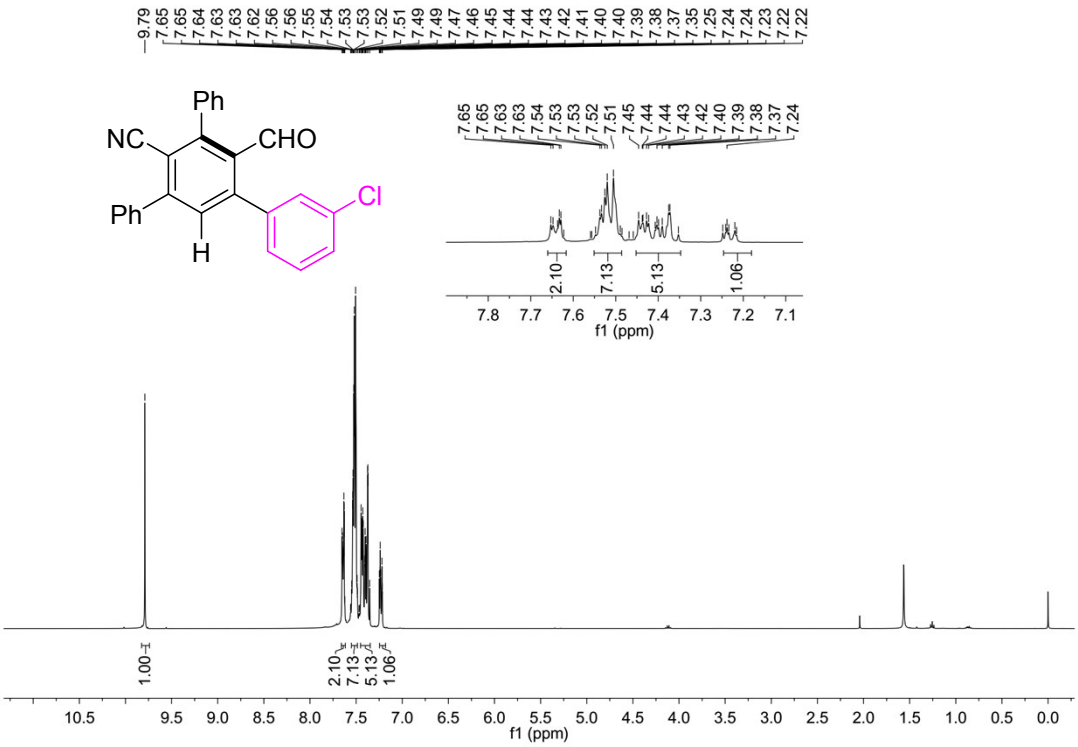
5'-(4-Fluorophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4c)

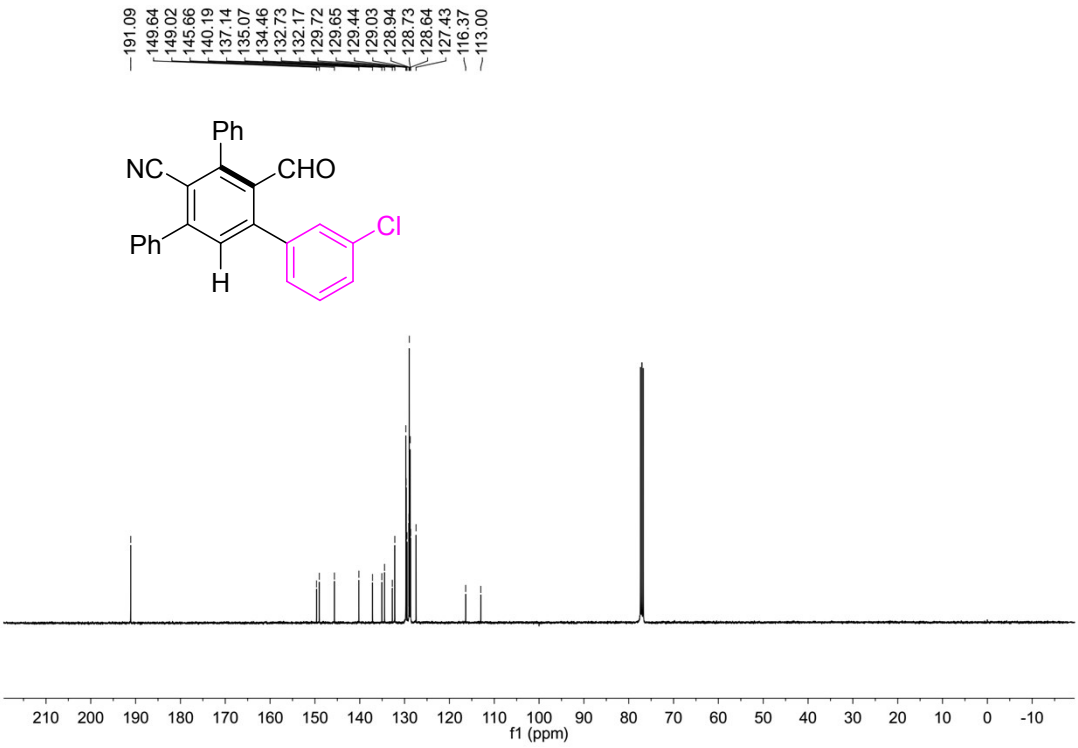




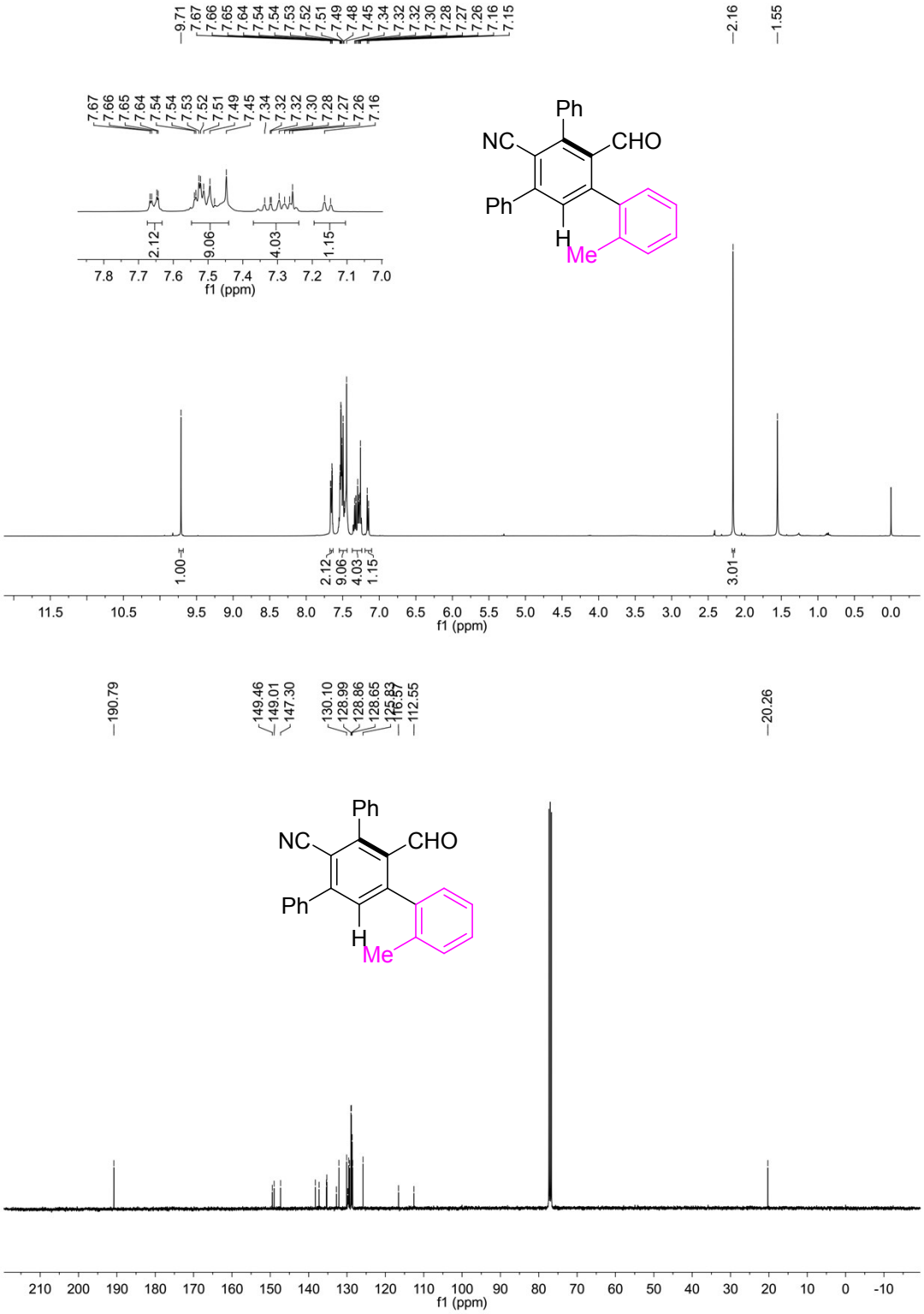

-112.72
Ph
NC
CHO
Ph
H
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

5'-(3-Chlorophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4d)

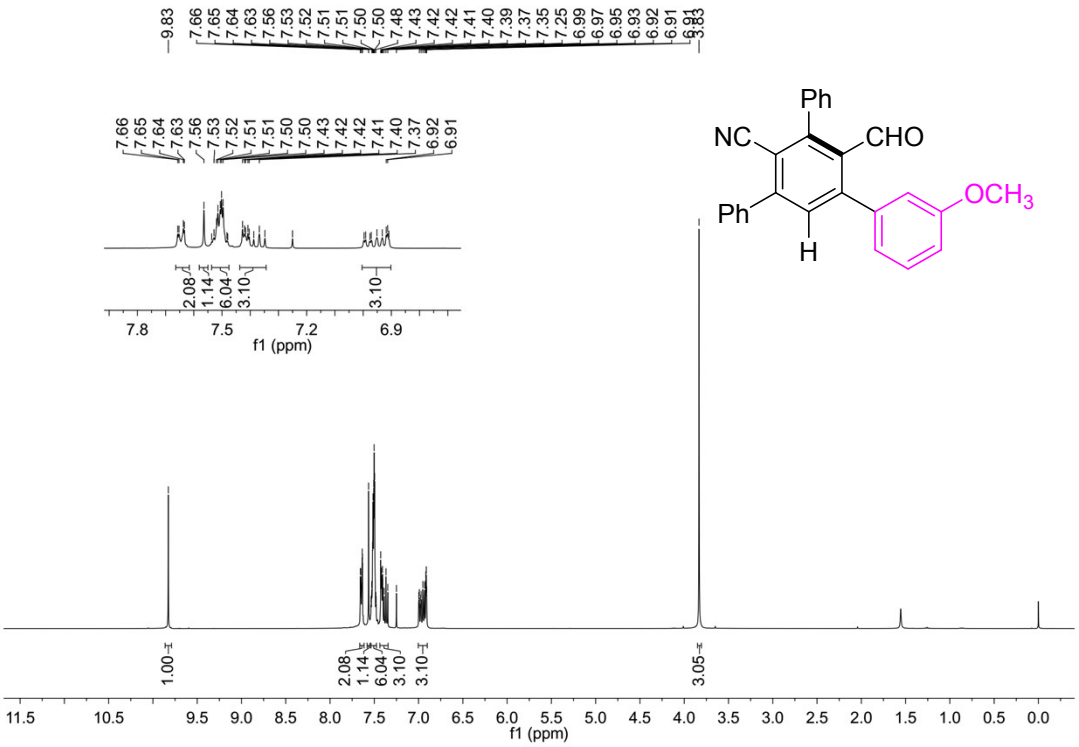


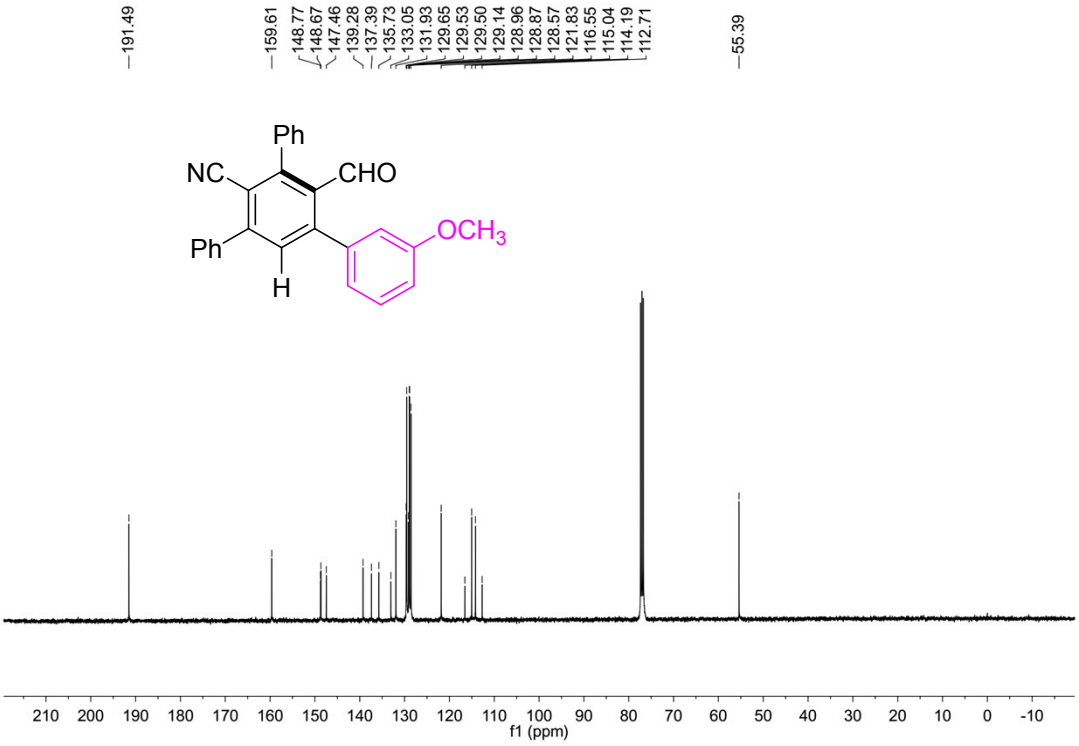


4'-Formyl-5'-(o-tolyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4e)

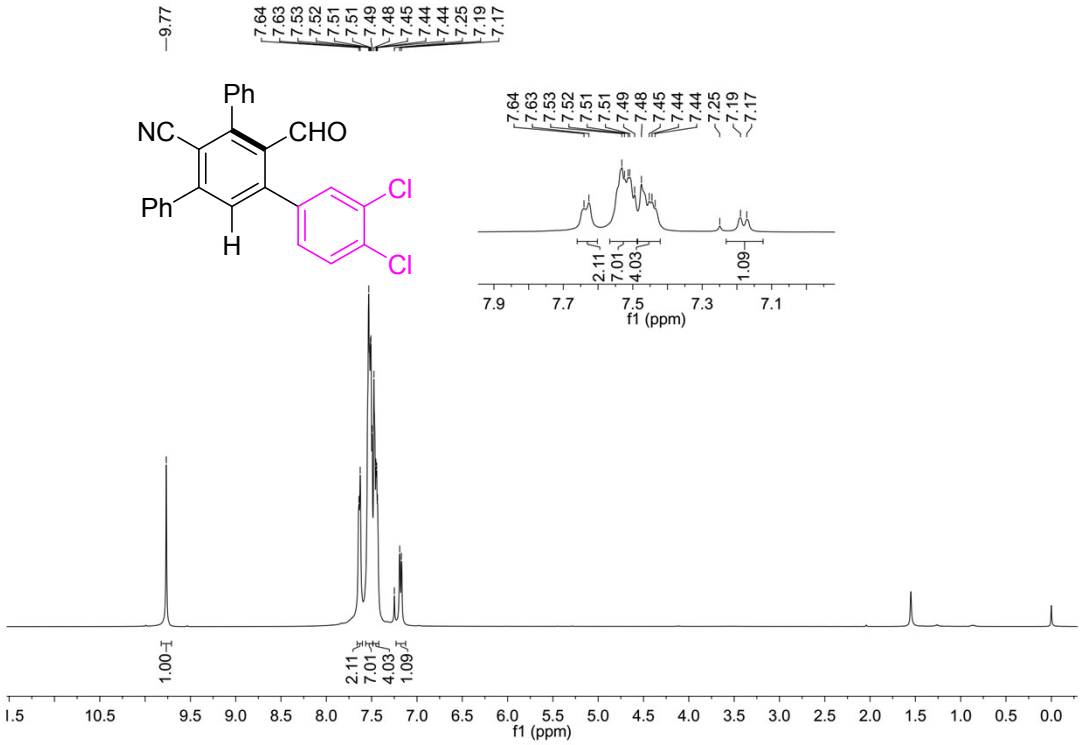


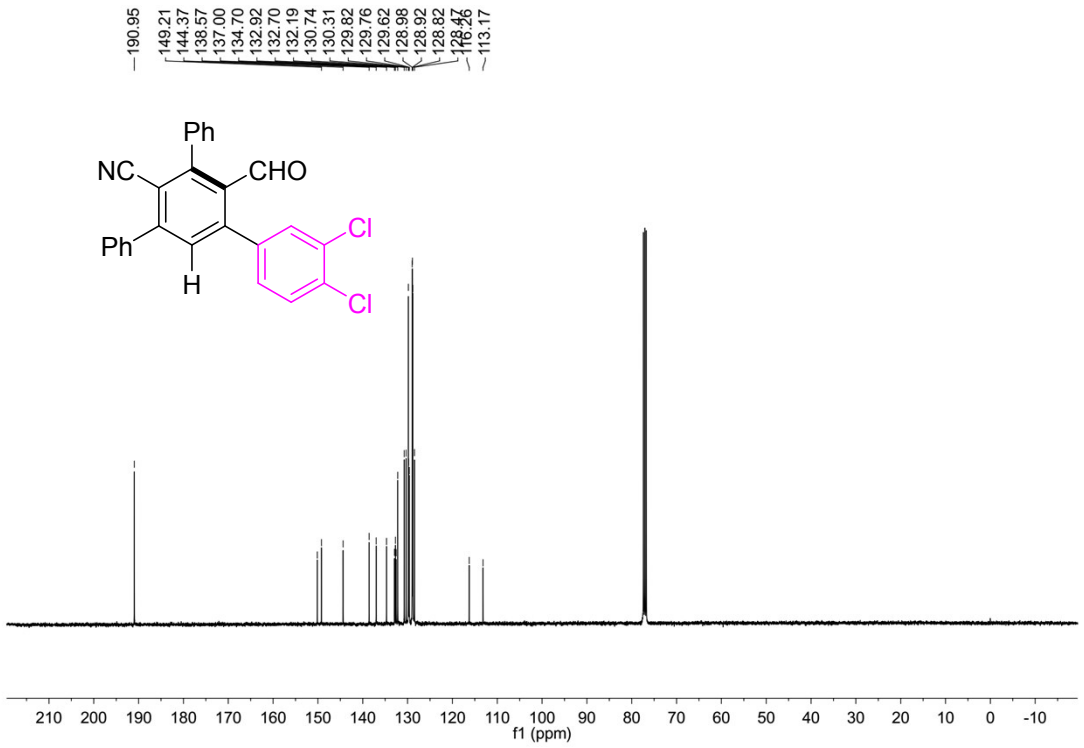
4'-Formyl-5'-(3-methoxyphenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4f)



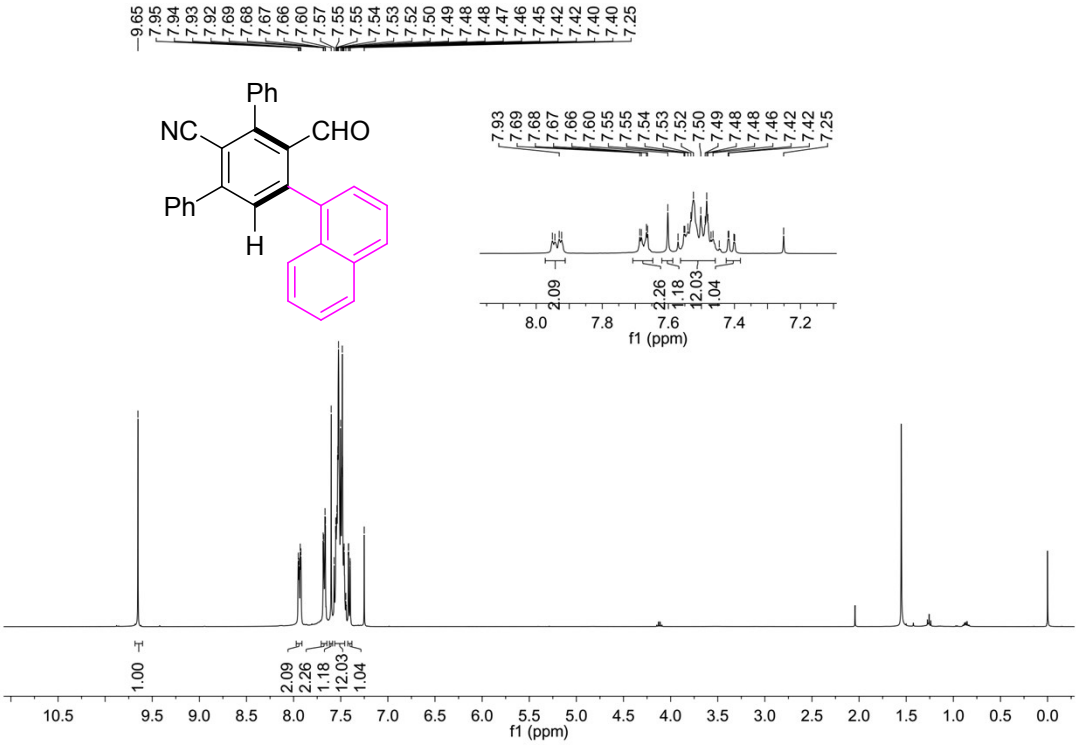


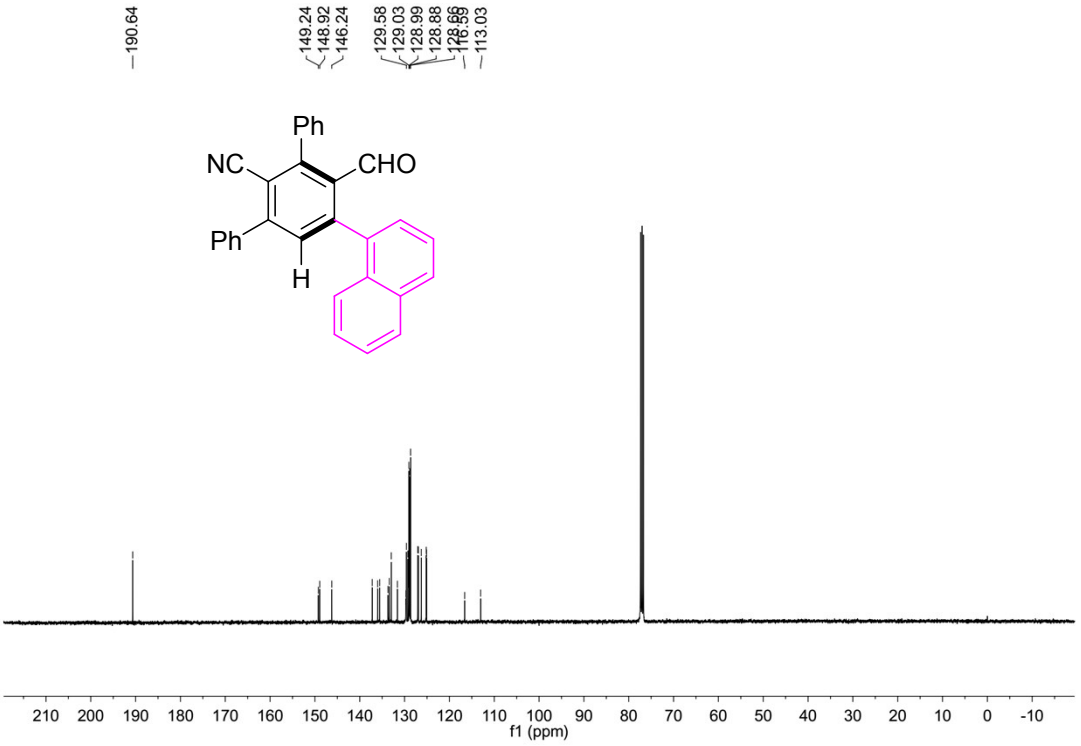
5'-(3,4-Dichlorophenyl)-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4g)



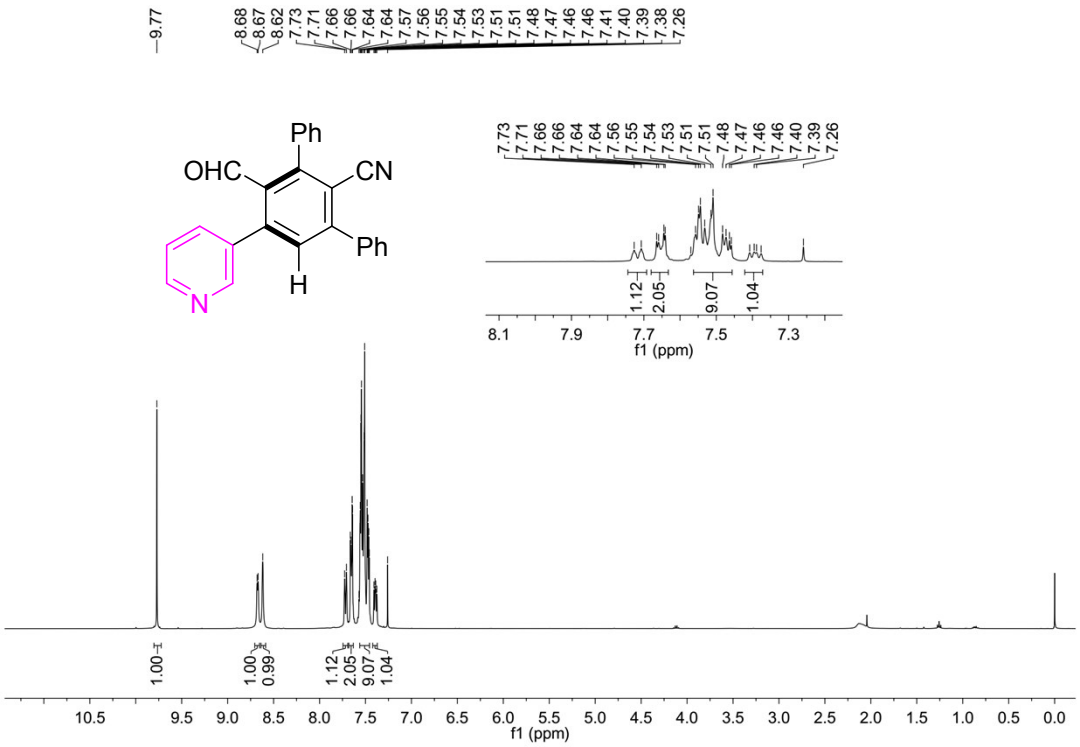


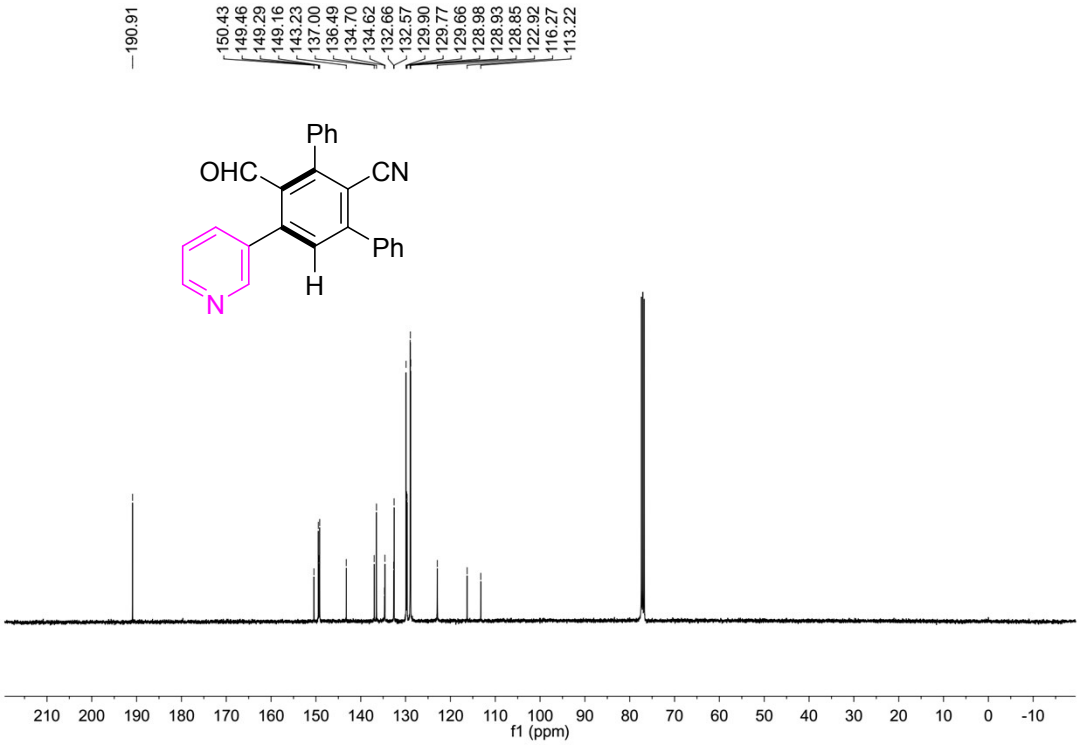
4'-Formyl-5'-(naphthalen-1-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4h)



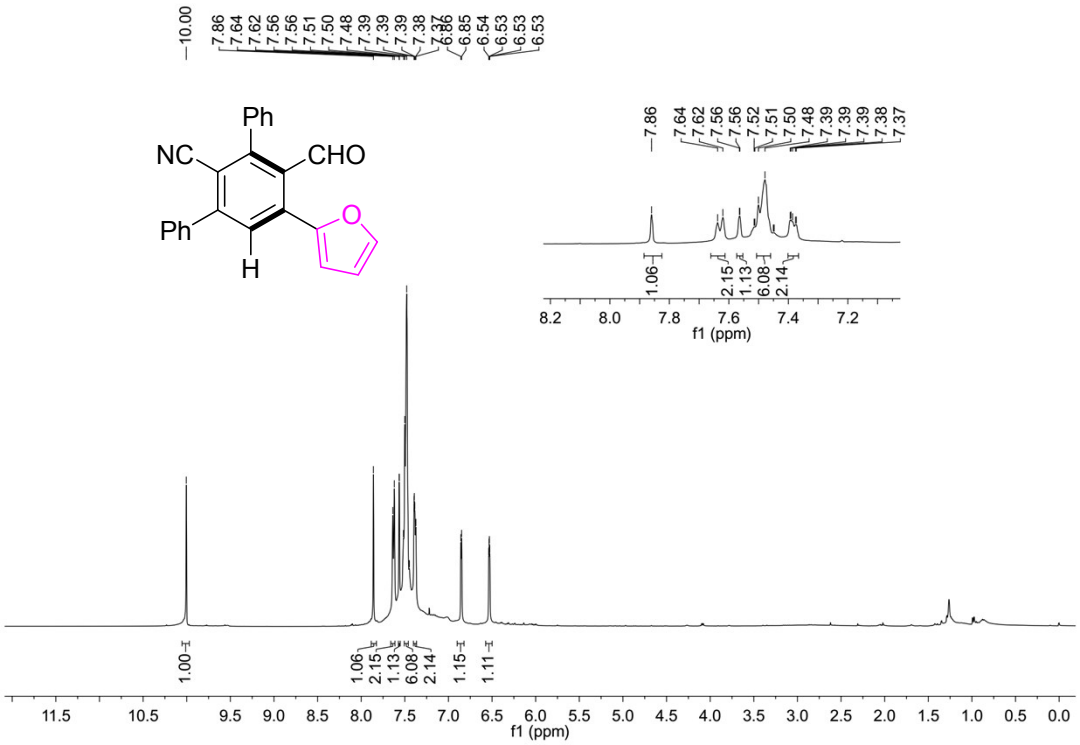


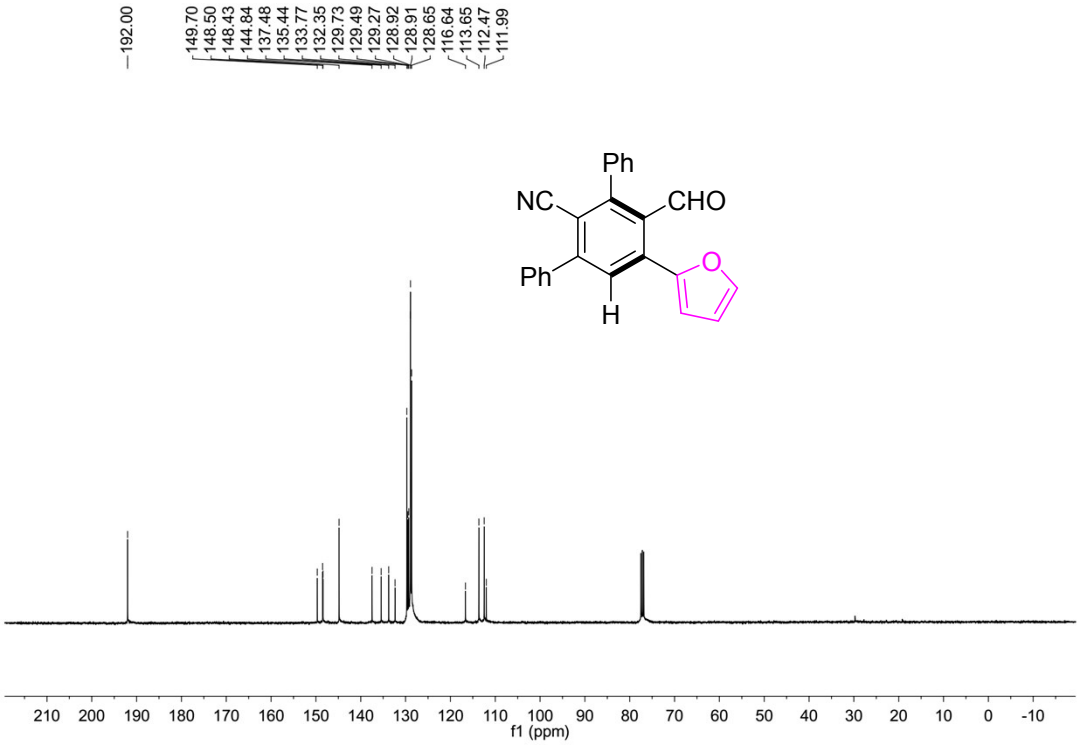
4'-Formyl-5'-(pyridin-3-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4i)



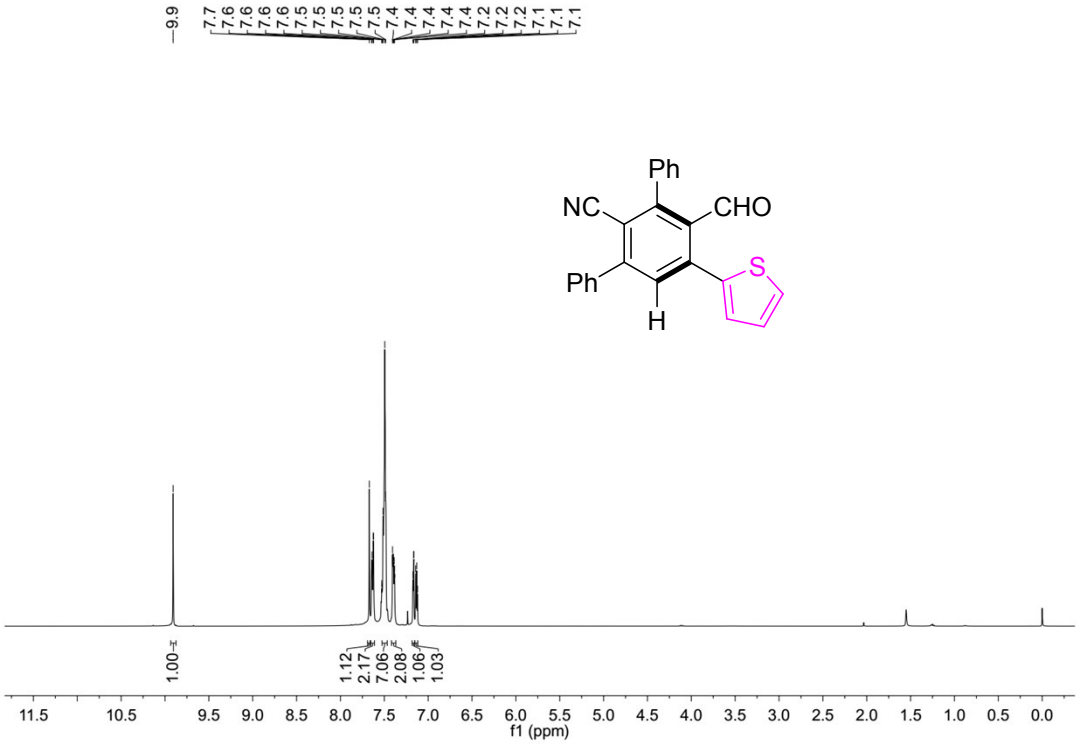


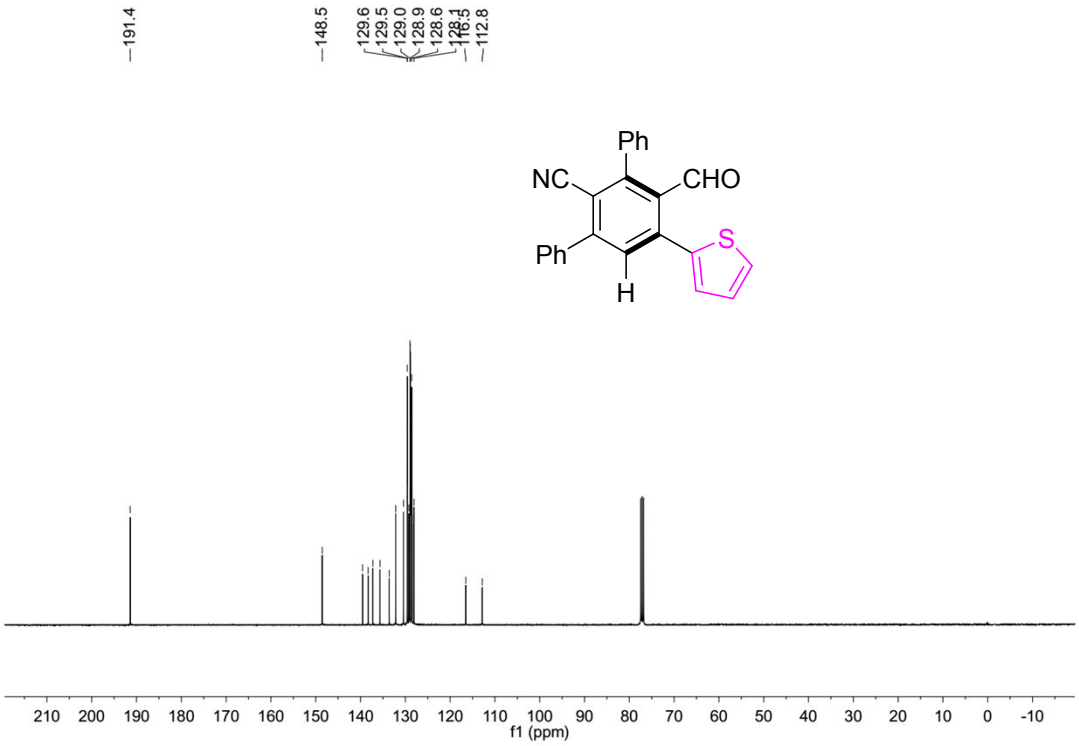
4'-Formyl-5'-(furan-2-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4j)



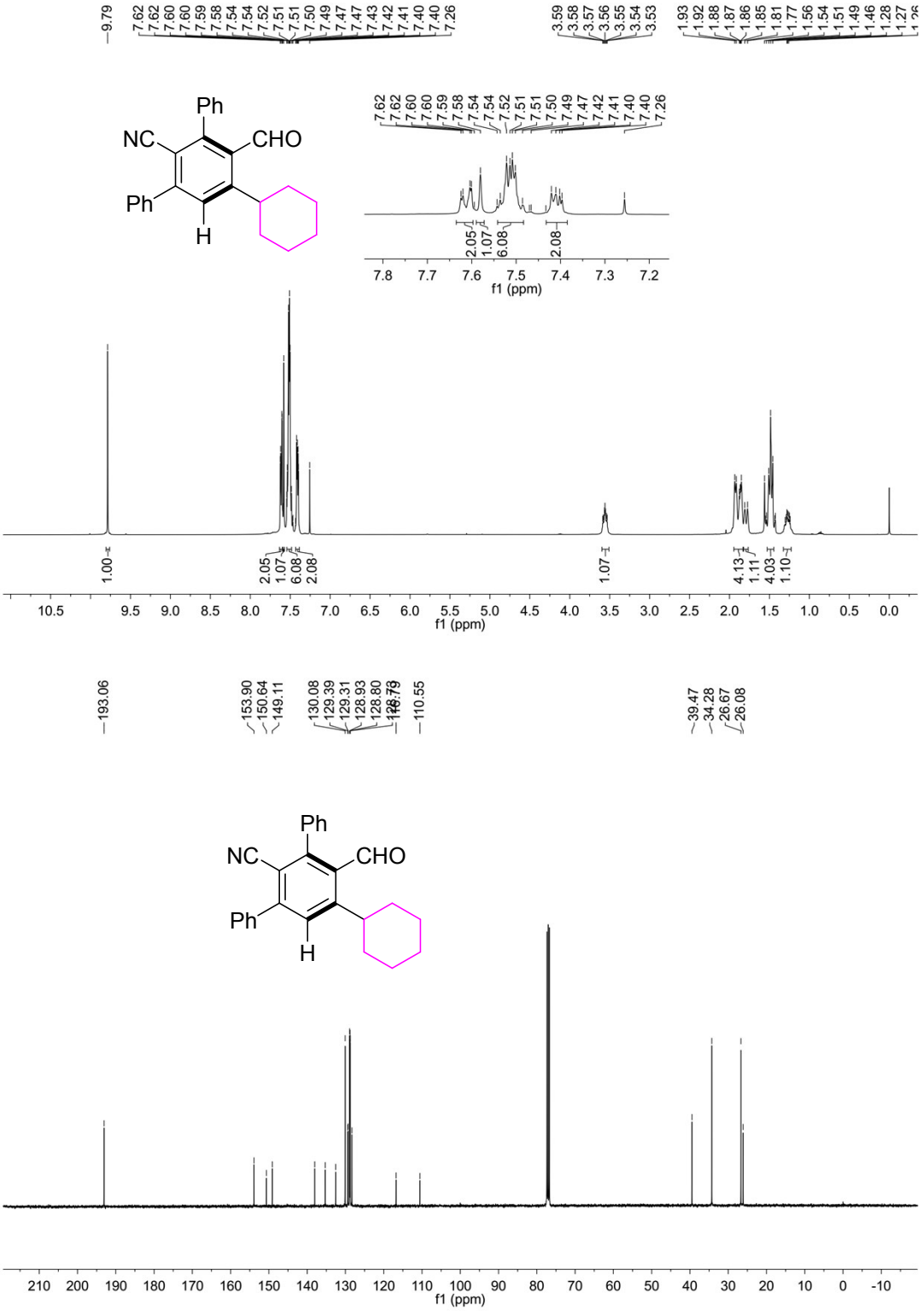


4'-Formyl-5'-(thiophen-2-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (4k)

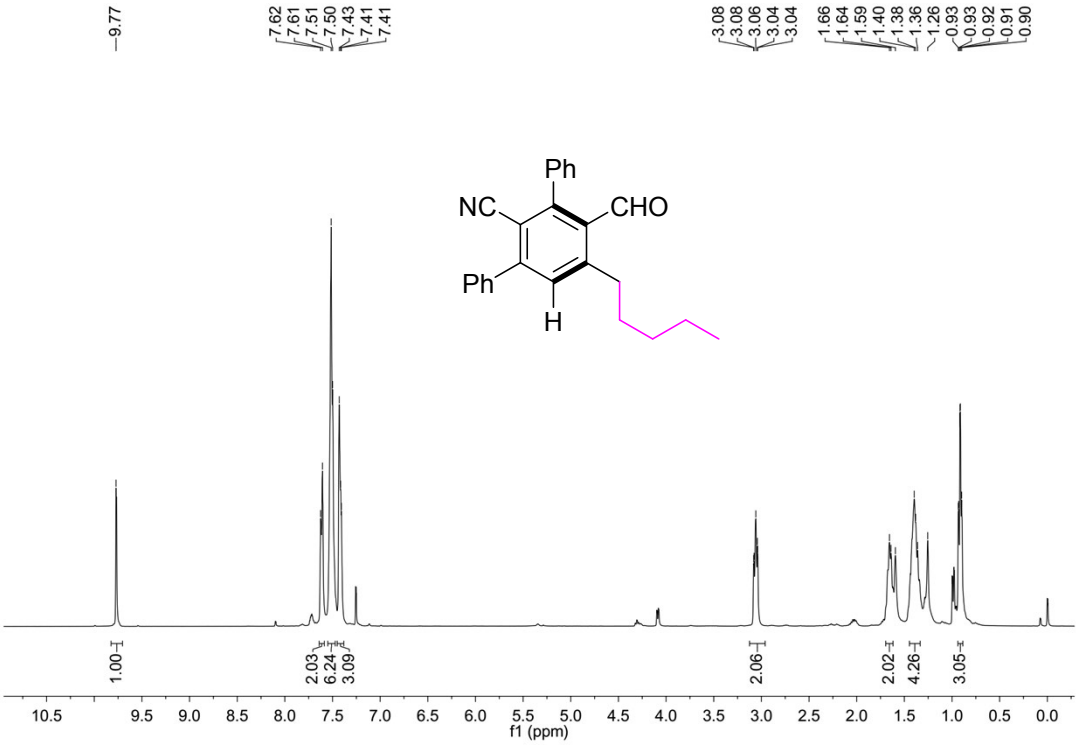


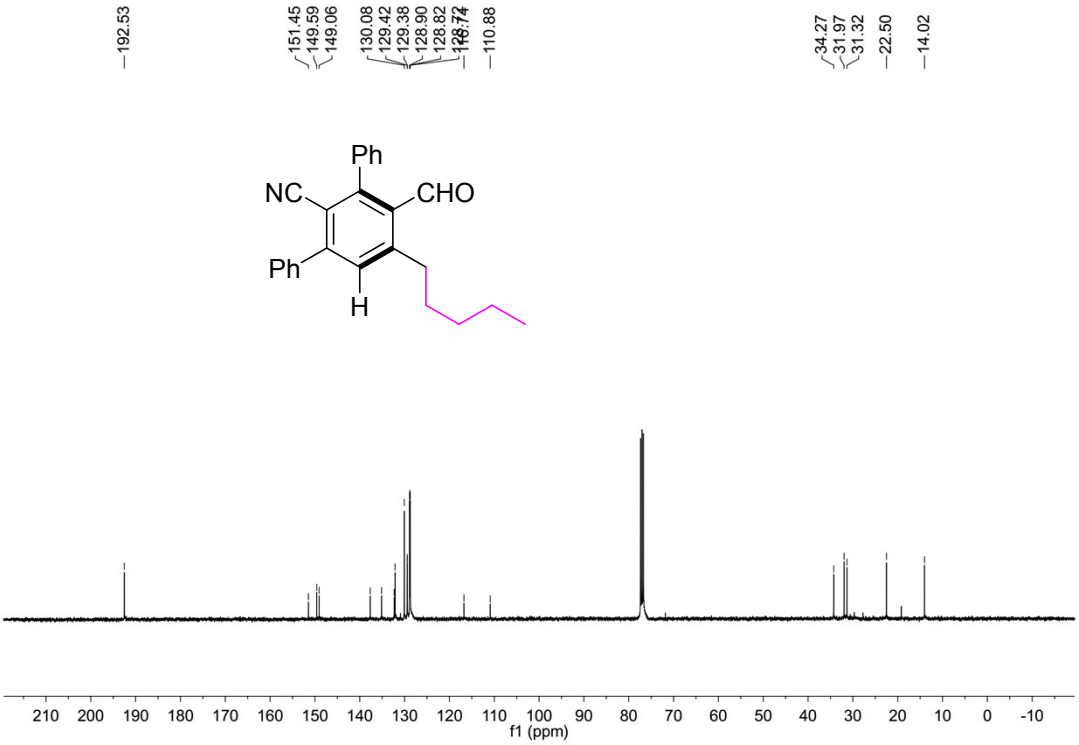


5'-Cyclohexyl-4'-formyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4l)

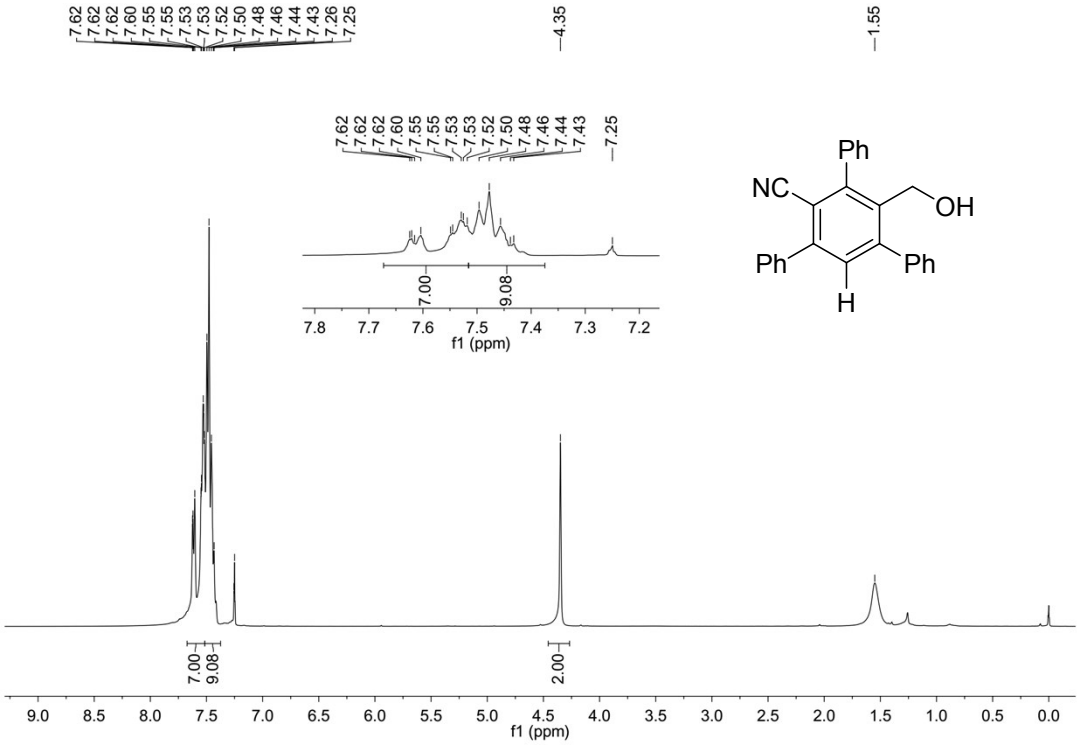


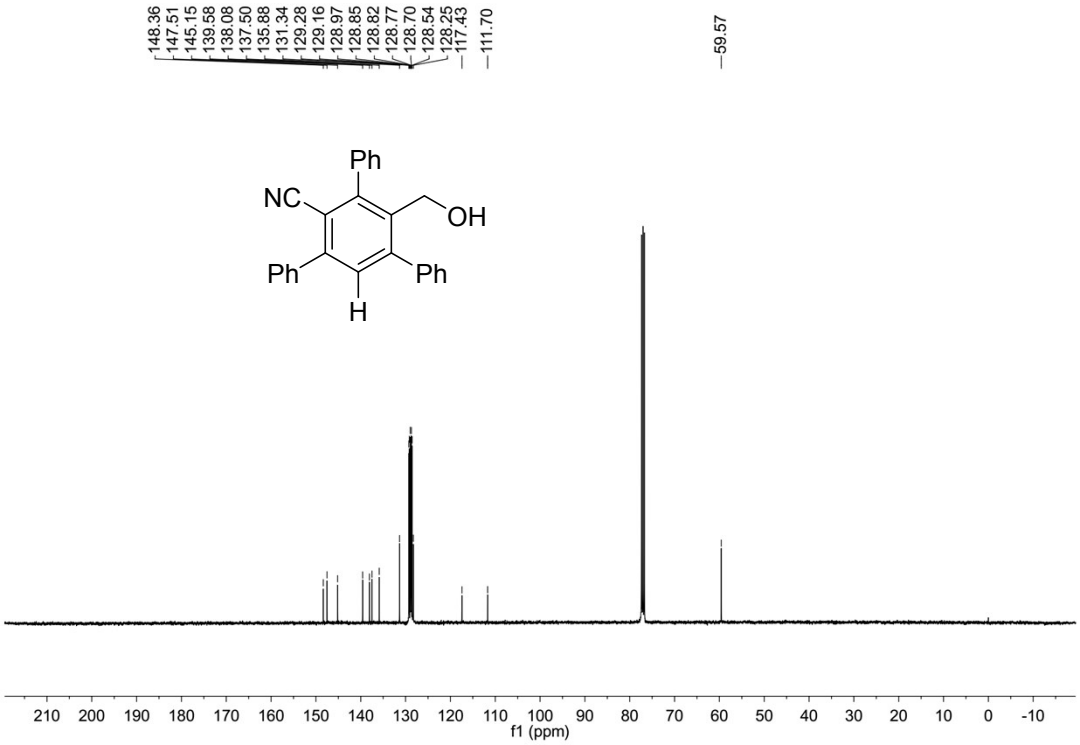
4'-Formyl-5'-pentyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (4m)



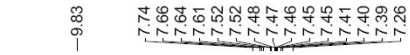


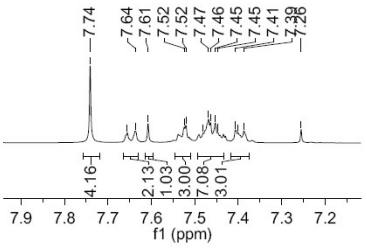
4'-(Hydroxymethyl)-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (5)

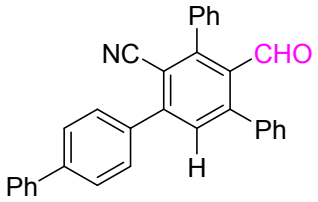


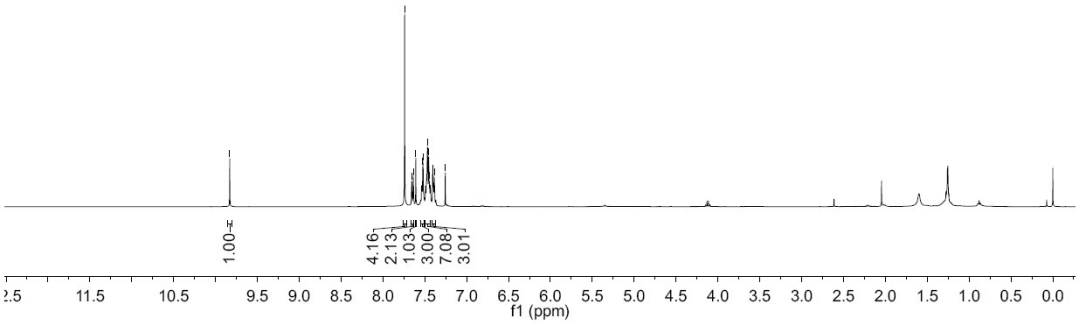


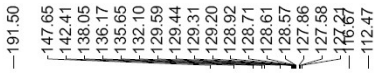
6'-Formyl-5'-phenyl-[1,1':3',1'':4'',1'''-quaterphenyl]-2'-carbonitrile (6)

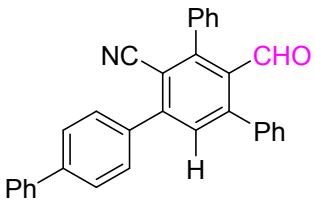


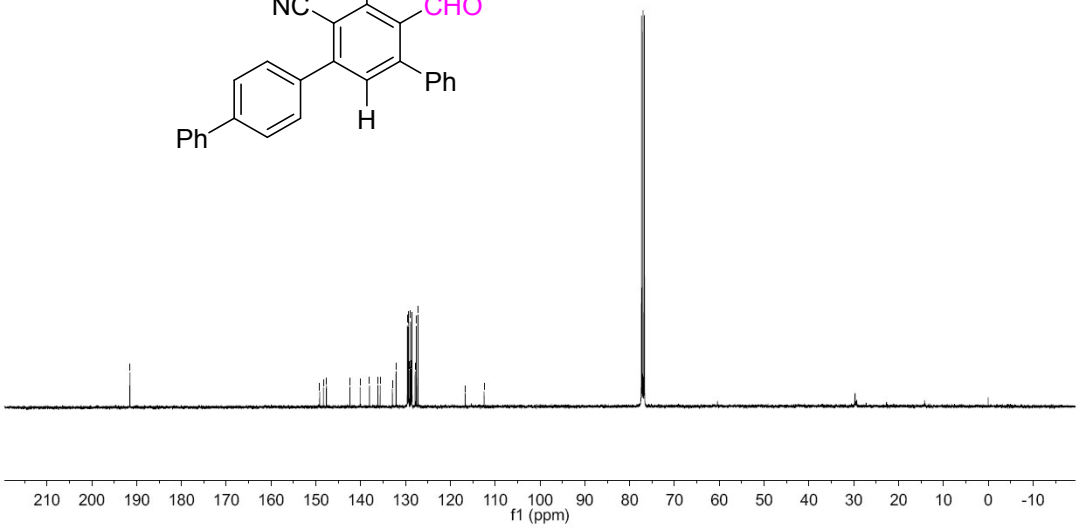




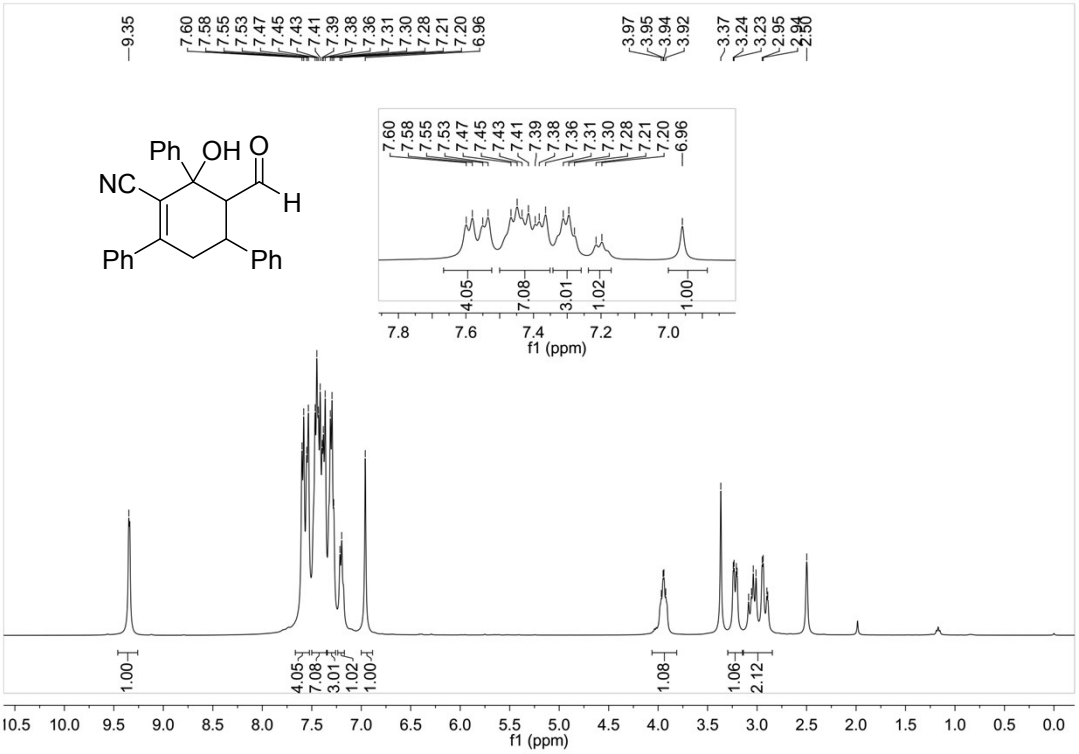


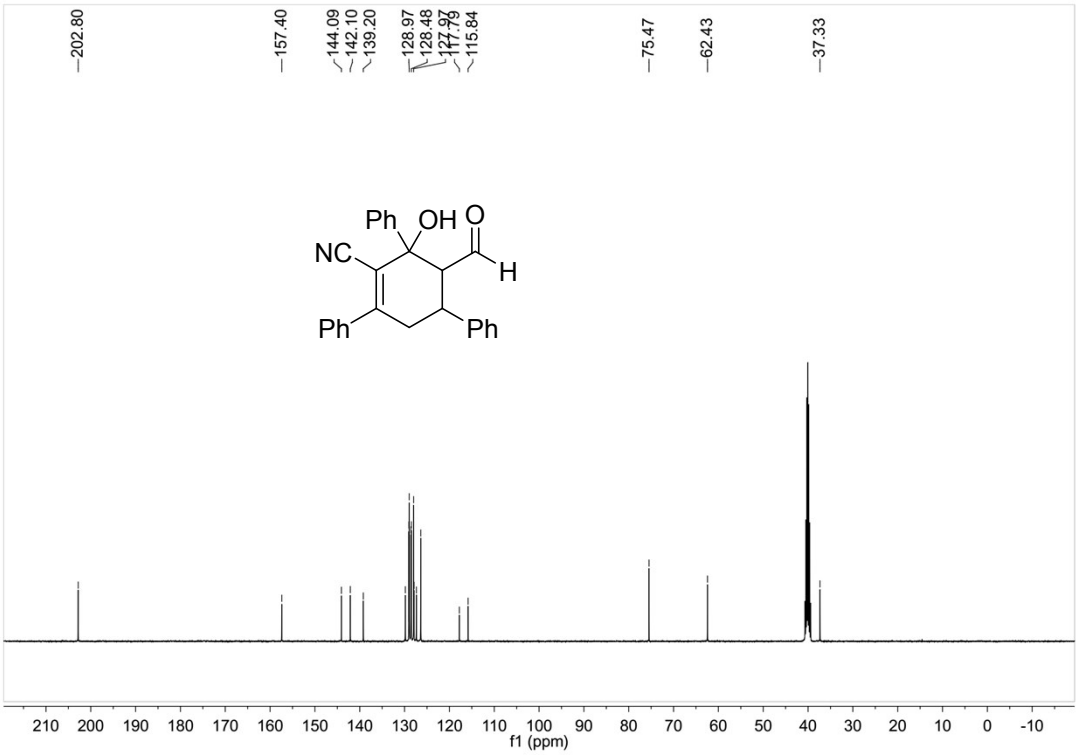






6'-Formyl-1'-hydroxy-5'-phenyl-1',4',5',6'-tetrahydro-[1,1':3',1''-terphenyl]-2'-carbonitrile (7)





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