Supplementary Information

for

Palladium(II)-Catalyzed Synthesis of Functionalized Indenones via Oxidation and Cyclization of 2-(2-Arylethynylphenyl)acetonitriles

Xuxing Chen, Qian He, Yuyuan Xie, and Chunhao Yang*

State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zuchongzhi Road, Shanghai 201203, PR China

chyang@simm.ac.cn

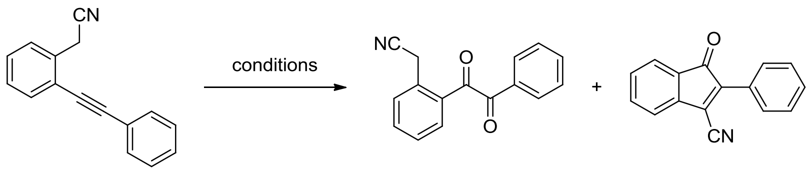
Table of Contents

General information

Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness, Yantai Huiyou Company, China). Column chromatography was carried out on silica gel (200-300 mesh). Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded at Varian Mercury-300 and Varian Mercury-500 spectrometers. Tetramethylsilane (TMS) was used as internal standard. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multipet (m) and broad (br). Low- and high-resolution mass spectra (LRMS and HRMS) were recorded on a Finnigan/MAT-95 (EI), Finnigan LCQ/DECA and Micromass Ultra Q-TOF (ESI) spectrometer. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and were uncorrected.

Optimization of reaction conditions

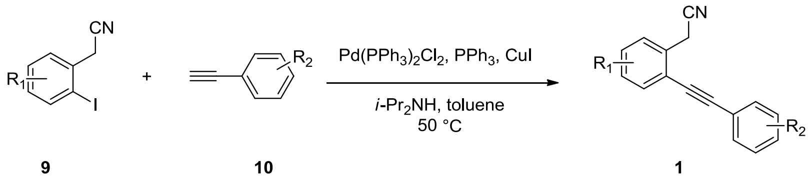
Table S1 Optimization of reaction conditions for synthesis of indenones in a cascade process. [a]



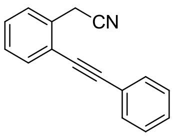
Entry	Catalysts (mol%)	Sulfoxide (3.0 equiv)	Additive (1.2 equiv)	Solvent (1 mL)	Temp (°C)	Time (h)	Yield(%)[b]	
							3a	**2a**
1	$PdCl_2$(10)	DMSO	none	DMSO	140	15	0	65
2	$PdCl_2$(10)/$AgSbF_6$(20)	DMSO	none	DMSO	100	12	44	0
3	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	none	DCE	100	1	98	0
4	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	MsOH	DCE	100	5	45	0
5	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	TsOH	DCE	100	5	51	0
6	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	KOAc	DCE	100	5	0	0
7	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	$K_3PO_4 \cdot 3H_2O$	DCE	100	5	0	18
8	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	K_3PO_4	DCE	100	5	35	18
9	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	K_2CO_3	DCE	100	5	8	29
10	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	Cs_2CO_3	DCE	100	5	0	36
11	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	CsF	DCE	100	5	0	0
12	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	TEA	DCE	100	5	0	0
13	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	DIPEA	DCE	100	5	0	0
14	$PdCl_2$(10)/$AgSbF_6$(20)	Ph_2SO	DBU	DCE	100	5	0	0

[a] **1a** (0.23 mmol, 1.0 equiv), all of reagents were mixed and heated. [b] Determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard.

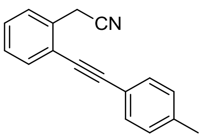
General procedure for the synthesis of substrates



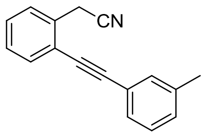
The aryl iodides **9** (2.06 mmol), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (2 mol%), PPh_3 (4 mol%) were placed in a nitrogen-filled Schlenk tube. After addition of ***i***-Pr_2NH (4.12 mmol) and toluene (10 mL), the mixture was stirred at room temperature for 5 minutes and terminal alkynes **10** (2.5 mmol) was added. The reaction mixture was allowed to stir at 50 °C for 12 h and the resulting solution was filtered and washed with saturated brine and extracted with ethyl acetate (2 × 20 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel using petroleum ether/ethyl acetate (30:1) as the eluent.



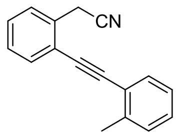
2-(2-(phenylethynyl)phenyl)acetonitrile (1a)[1]**:** As a brown solid; yield: 95%; m.p. 58–60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.45 (m, 4 H), 7.43–7.31 (m, 5 H), 3.98 (s, 2 H); MS (EI): m/z 217 $[M]^+$.



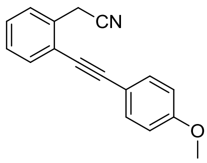
2-(2-(p-tolylethynyl)phenyl)acetonitrile (1b)[2]**:** As a white crystalline solid; yield: 93%; m.p. 78–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–7.54 (m, 1 H), 7.53–7.48 (m, 1 H), 7.48–7.41 (m, 2 H), 7.41–7.29 (m, 2 H), 7.23–7.15 (m, 2 H), 3.98 (s, 2 H), 2.38 (s, 3 H); MS (EI): m/z 231 $[M]^+$.



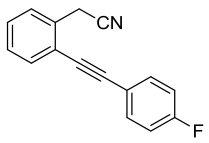
2-(2-(m-tolylethynyl)phenyl)acetonitrile (1c): As a brown solid; yield: 96%; m.p. 34–36 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.2, 1.8 Hz, 1 H), 7.51 (d, *J* = 7.0 Hz, 1 H), 7.42–7.30 (m, 4 H), 7.27 (t, *J* = 7.5 Hz, 1 H), 7.19 (d, *J* = 7.5 Hz, 2 H), 3.98 (s, 1H), 2.37 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.25, 132.36, 132.15, 131.67, 129.80, 128.97, 128.71, 128.42, 128.17, 128.13, 122.91, 122.29, 117.50, 95.92, 85.65, 22.80, 21.27; HRMS (EI): *m/z* Calcd. For $C_{17}H_{13}N$ $[M]^+$: 231.1048; Found: 231.1041.



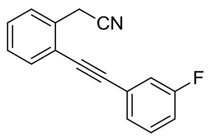
2-(2-(o-tolylethynyl)phenyl)acetonitrile (1d): As a pale yellow solid; yield: 96%; m.p. 34–36 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 6.5 Hz, 1 H), 7.53(d, *J* = 7.3 Hz, 2 H), 7.44–7.31 (m, 2 H), 7.32–7.13 (m, 3 H), 3.99 (s, 2 H), 2.53 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.07, 132.47, 132.08, 131.44, 129.66, 128.99, 128.94, 128.20, 128.16, 125.79, 123.08, 122.33, 117.50, 94.62, 89.87, 22.88, 20.98; HRMS (EI): *m/z* Calcd. For $C_{17}H_{13}N$ $[M]^+$: 231.1048; Found: 231.1040.



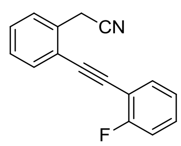
2-(2-((4-methoxyphenyl)ethynyl)phenyl)acetonitrile (1e): As a white crystalline solid; yield: 91%; m.p. 66–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58–7.52 (m, 1 H), 7.53–7.44 (m, 3 H), 7.40–7.28 (m, 2 H), 6.90 (d, *J* = 8.9 Hz, 2 H), 3.97 (s, 2 H), 3.84 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.45, 161.95, 142.30, 141.38, 135.42, 131.05, 129.59, 128.33, 124.17, 121.27, 120.76, 119.02, 114.71, 114.57, 55.47; HRMS (EI): m/z Calcd. For $C_{17}H_{13}NO$ $[M]^+$: 247.0997; Found: 247.1002.



2-(2-((4-fluorophenyl)ethynyl)phenyl)acetonitrile (1f): As a white crystalline solid; yield: 83%; m.p. 75–77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.46 (m, 4 H), 7.43–7.30 (m, 2 H), 7.14–7.02 (m, 2 H), 3.96 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.84 (d, *J* = 251.4 Hz, C-F), 133.57 (d, *J* = 8.5 Hz, CH-CH-CF), 132.39, 131.65, 129.13, 128.29, 128.25, 122.69, 118.62 (d, *J* = 3.5 Hz, C-CH-CH-CF), 117.40, 115.87 (d, *J* = 22.1 Hz, CH-CF), 94.61, 85.71, 22.85; HRMS (EI): m/z Calcd. For $C_{16}H_{10}FN$ $[M]^+$: 235.0797; Found: 235.0790.

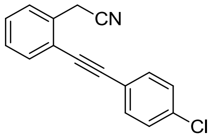


2-(2-((3-fluorophenyl)ethynyl)phenyl)acetonitrile (1g): As a brown powder; yield: 97%; m.p. 79–81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.55 (m, 1 H), 7.54–7.48 (m, 1 H), 7.44–7.31 (m, 4 H), 7.28–7.21 (m, 1 H), 7.15–7.01 (m, 1 H), 3.96 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.40 (d, *J* = 247.1 Hz, C-F), 132.54, 131.81, 130.15 (d, *J* = 8.6 Hz, CH-CH-CF), 129.42, 128.32, 128.28, 127.54 (d, *J* = 3.1 Hz, CH-CH-CH-CF), 124.30 (d, *J* = 9.4 Hz, C-CH-CF), 122.35, 118.38 (d, *J* = 23.0 Hz, CH-CF), 117.35, 116.25 (d, *J* = 21.1 Hz, CH-CF), 94.29 (d, *J* = 3.5 Hz, C-C-CH-CF), 86.80, 22.84; HRMS (EI): m/z Calcd. For $C_{16}H_{10}FN$ $[M]^+$: 235.0797; Found: 235.0796.

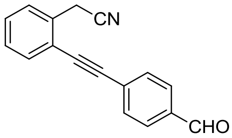


2-(2-((2-fluorophenyl)ethynyl)phenyl)acetonitrile (1h): As a brown powder; yield: 99%; m.p. 76–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.57 (m, 1 H), 7.57–7.50 (m, 2 H), 7.45–7.29 (m, 3 H), 7.20–7.07 (m, 2 H), 4.02 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.69 (d, *J* = 251.8 Hz, C-F), 133.20, 132.31, 131.97, 130.63 (d, *J* = 8.1 Hz, CH-CH-CF), 129.40, 128.18, 128.16 (d, *J* = 6 Hz, CH-CH-CF), 124.17 (d, *J* = 3.7 Hz, CH-CH-CH-CF), 122.39, 117.49, 115.65 (d, *J* = 20.7 Hz, CH-CF), 111.22 (d, *J* = 15.5 Hz, C-CF), 91.12 (d, *J* = 3.4 Hz, C-C-CF), 88.98, 22.69; HRMS (EI):

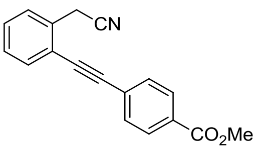
m/z Calcd. For $C_{16}H_{10}FN$ $[M]^+$: 235.0797; Found: 235.0793.



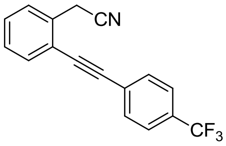
2-(2-((4-chlorophenyl)ethynyl)phenyl)acetonitrile (1i)[2]: As a wihte powder; yield: 84%; m.p. 94–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–7.53 (m, 1 H), 7.53–7.45 (m, 3 H), 7.44–7.30 (m, 4 H), 3.96 (s, 2 H); MS (EI): m/z 251 $[M]^+$. .



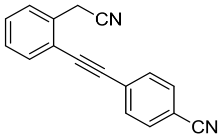
2-(2-((4-formylphenyl)ethynyl)phenyl)acetonitrile (1j): As a pale yellow powder; yield: 97%; m.p. 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (s, 1 H), 7.90 (dt, *J* = 8.2, 1.9 Hz, 2 H), 7.71 (dd, *J* = 8.2, 1.8 Hz, 2 H), 7.61 (dd, *J* = 7.3, 1.5 Hz, 1 H), 7.56–7.49 (m, 1 H), 7.44 (td, *J* = 7.5, 1.6 Hz, 1 H), 7.38 (td, *J* = 7.5, 1.6 Hz, 1 H), 3.98(s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.36, 135.84, 132.70, 132.15, 131.93, 129.78, 129.69, 128.67, 128.47, 128.38, 122.11, 117.23, 94.57, 89.73, 22.89; HRMS (EI): m/z Calcd. For $C_{17}H_{11}NO$ $[M]^+$: 245.0841; Found: 245.0835.



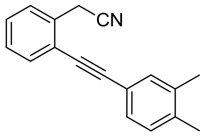
methyl 4-((2-(cyanomethyl)phenyl)ethynyl)benzoate (1k): As a white powder; yield: 89%; m.p. 132–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 8.3, 1.6 Hz, 2 H), 7.65–7.57 (m, 3 H), 7.55–7.49 (m, 1 H), 7.42 (td, *J* = 7.8, 1.6 Hz, 1 H), 7.37 (td, *J* = 7.6, 1.6 Hz, 1 H), 3.98 (s, 2 H), 3.94 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.43, 132.61, 131.86, 131.53, 130.06, 129.65, 129.57, 128.36, 128.31, 127.11, 122.28, 117.29, 94.75, 88.74, 52.34, 22.86; HRMS (EI): m/z Calcd. For $C_{18}H_{13}NO_2$ $[M]^+$: 275.0946; Found: 275.0949.



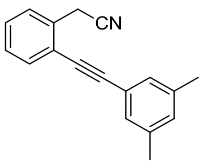
2-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)acetonitrile (1l)[2]: As a pale yellow solid; yield: 98%; m.p. 64–66 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.56 (m, 5 H), 7.51 (d, *J* = 7.5 Hz, 1 H), 7.46–7.32 (m, 2 H), 3.97 (s, 2 H); MS (EI): m/z 285 $[M]^+$.



4-((2-(cyanomethyl)phenyl)ethynyl)benzonitrile (1m): As a white powder; yield: 93%; m.p. 108–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.62 (m, 4 H), 7.62–7.56 (m, 1 H), 7.55–7.48 (m, 1 H), 7.43 (td, *J* = 7.2, 1.6 Hz 1 H), 7.39 (td, *J* = 7.5, 1.6 Hz 1 H), 3.95 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.74, 132.20, 132.11, 131.96, 129.95, 128.57, 128.43, 127.36, 121.86, 118.36, 117.15, 112.15, 93.75, 90.11, 22.91; HRMS (EI): m/z Calcd. For $C_{17}H_{10}N_2$ $[M]^+$: 242.0844; Found: 242.0843.

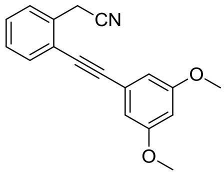


2-(2((3,4-dimethylphenyl)ethynyl)phenyl)acetonitrile (1n): As a brown solid; yield: 84%; m.p. 31–33 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.48 (m, 2 H), 7.42–7.32 (m, 3 H), 7.29 (dd, *J* = 7.3, 1.7 Hz, 1 H), 7.13 (d, *J* = 7.7 Hz, 1 H), 3.98 (s, 2 H), 2.29 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.98, 136.91, 132.59, 132.26, 131.58, 129.82, 129.08, 128.79, 128.14, 128.07, 123.10, 119.70, 117.57, 96.13, 85.18, 22.80, 19.88, 19.64. HRMS (EI): *m*/*z* Calcd. For $C_{18}H_{15}N$ $[M]^+$: 245.1204; Found: 245.1201.

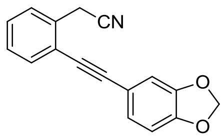


2-(2-((3,5-dimethylphenyl)ethynyl)phenyl)acetonitrile (1o): As a pale brown solid; yield:

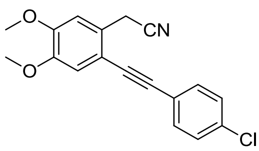
81%; m.p. 32–33 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58–7.46 (m, 2 H), 7.42–7.29 (m, 2 H), 7.18 (t, *J* = 0.7 Hz, 2 H), 7.01 (t, *J* = 0.7 Hz, 1 H), 3.98 (s, 2 H), 2.33 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.13, 132.32, 131.65, 130.84, 129.28, 128.90, 128.16, 128.09, 122.99, 122.09, 117.55, 96.13, 85.32, 22.79, 21.16; HRMS (EI): *m/z* Calcd. For $C_{18}H_{15}N$ $[M]^+$: 245.1204; Found: 245.1197.



2-(2-((3,5-dimethoxyphenyl)ethynyl)phenyl)acetonitrile (1p): As a pale yellow solid; yield: 63%; m.p. 93–95 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.0, 1.9 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.42–7.29 (m, 2 H), 6.71 (d, *J* = 2.2 Hz, 2 H), 6.50 (t, *J* = 2.3 Hz, 1 H), 3.97 (s, 2 H), 3.81 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.65, 132.44, 131.79, 129.15, 128.19, 123.76, 122.65, 117.51, 110.18, 109.39, 102.20, 95.66, 85.56, 55.50, 22.82; HRMS (EI): m/z Calcd. For $C_{18}H_{15}NO_2$ $[M]^+$: 277.1103; Found: 277.1104.

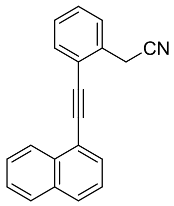


2-(2-(benzo[d][1,3]dioxol-5-ylethynyl)phenyl)acetonitrile (1q): As a pale yellow solid; yield: 84%; m.p. 114–115 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.44 (m, 2 H), 7.40–7.29 (m, 2 H), 7.09 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.99 (d, *J* = 1.6 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 6.00 (s, 2 H), 3.95 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.42, 147.60, 132.25, 131.54, 128.84, 128.18, 126.45, 122.95, 117.50, 115.69, 111.46, 108.65, 101.49, 95.72, 84.51, 22.83; HRMS (EI): m/z Calcd. For $C_{17}H_{11}NO_2$ $[M]^+$: 261.0790; Found: 261.0782.



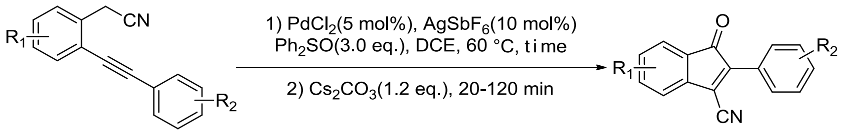
2-(2-((4-chlorophenyl)ethynyl)-4,5-dimethoxyphenyl)acetonitrile (1r): As a white powder;

yield: 83%; m.p. 118–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 7.03 (s, 1 H), 6.95 (s, 1 H), 3.95 (s, 3 H), 3.92 (s, 2 H), 3.91 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.01, 148.57, 134.66, 132.66, 128.85, 124.84, 121.22, 117.69, 114.53, 114.43, 111.13, 92.91, 87.17, 56.16, 56.14, 22.41; HRMS (EI): m/z Calcd. For $C_{18}H_{14}ClNO_2$ $[M]^+$: 311.0713; Found: 311.0713.



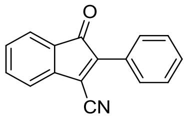
2-(2-(naphthalen-1-ylethynyl)phenyl)acetonitrile (1s): As a yellow powder; yield: 88%; m.p. 72–74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.2 Hz, 2 H), 7.80 (dd, *J* = 7.1, 1.1 Hz, 1 H), 7.74–7.68 (m, 1 H), 7.66–7.54 (m, 3 H), 7.53–7.44 (m, 1 H), 7.44–7.36 (m, 2 H), 4.09 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.21, 133.03, 132.64, 131.62, 130.87, 129.44, 129.20, 128.49, 128.29, 128.26, 127.13, 126.63, 125.92, 125.32, 122.95, 120.13, 117.54, 93.79, 90.75, 23.00; HRMS (EI): m/z Calcd. For $C_{20}H_{13}N$ $[M]^+$: 267.1048; Found: 267.1048.

General procedure for the synthesis of indenones

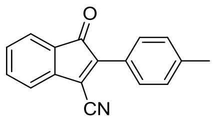


1 2

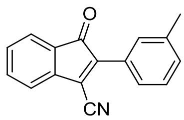
After stirring for 5 min at room temperature, the mixture of **1** (0.23 mmol), $PdCl_2$ (5 mol%), $AgSbF_6$ (10 mol%) and Ph_2SO (0.69 mmol) in dry DCE (1 mL) was heated at 60 °C under air for the specified time, then Cs_2CO_3 (0.28 mmol, 1.2 equiv) was added, stirred for additional 20~120 min. After cooling, the reaction solution was washed with saturated brine and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel, with petroleum ether/ethyl acetate (80:1) as the eluent to give the pure product.



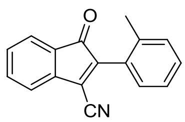
1-oxo-2-phenyl-1*H*-indene-3-carbonitrile (2a): As a red powder: yield: 97%; m.p. 149–151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02–7.88 (m, 2 H), 7.65–7.54 (m, 2 H), 7.55–7.46 (m, 3 H), 7.42–7.32 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.79, 143.04, 140.86, 135.42, 131.07, 130.18, 129.19, 128.98, 128.44, 128.34, 124.32, 122.33, 121.18, 114.11; HRMS (EI): *m*/*z* Calcd. For $C_{16}H_9NO$ $[M]^+$: 231.0684; Found: 231.0684.



1-oxo-2-(p-tolyl)-1*H*-indene-3-carbonitrile (2b): As a red powder; yield: 81%; m.p. 156–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2 H), 7.60–7.55 (m, 1 H), 7.55–7.49 (m, 1 H), 7.41–7.28 (m, 4 H), 2.43 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.09, 143.01, 141.82, 141.10, 135.38, 129.91, 129.75, 129.13, 128.38, 125.73, 124.23, 121.06, 120.99, 114.35, 21.68; HRMS (EI): *m*/*z* Calcd. For $C_{17}H_{11}NO$ $[M]^+$: 245.0841; Found: 245.0838.

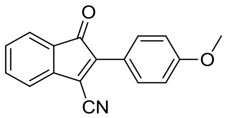


1-oxo-2-(m-tolyl)-1*H*-indene-3-carbonitrile (2c): As a dark red powder; yield: 85%; m.p. 128–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (brs, 2 H), 7.56 (dd, *J* = 16.2, 7.6 Hz, 2 H), 7.45–7.28 (m, 4 H), 2.44 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.86, 143.22, 140.94, 138.72, 135.39, 131.96, 130.09, 129.66, 128.89, 128.39, 128.36, 126.38, 124.26, 122.10, 121.11, 114.17, 21.51; HRMS (EI): *m*/*z* Calcd. For $C_{17}H_{11}NO$ $[M]^+$: 245.0841; Found: 245.0846.

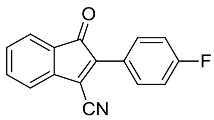


1-oxo-2-(o-tolyl)-1*H*-indene-3-carbonitrile (2d): As a red crystalline solid; yield: 87%; m.p.

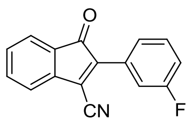
98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.48 (m, 2 H), 7.45–7.27 (m, 6 H), 2.35 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.24, 147.57, 140.62, 137.34, 135.28, 131.02, 130.43, 130.34, 129.82, 128.18, 127.93, 126.55, 126.01, 124.49, 121.28, 113.29, 20.79; HRMS (EI): *m*/*z* Calcd. For $C_{17}H_{11}NO$ $[M]^+$: 245.0841; Found: 245.0841.



2-(4-methoxyphenyl)-1-oxo-1*H*-indene-3-carbonitrile (2e): As a reddish brown powder; yield: 95%; m.p. 142–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dt, *J* = 8.9, 2.0 Hz, 2 H), 7.61–7.45 (m, 2 H), 7.38–7.27 (m, 2 H), 7.02 (dt, *J* = 8.9, 2.0 Hz, 2 H), 3.88 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.45, 161.95, 142.30, 141.38, 135.42, 131.05, 129.59, 128.33, 124.17, 121.27, 120.76, 119.02, 114.71, 114.57, 55.47; HRMS (EI): *m*/*z* Calcd. For $C_{17}H_{11}NO_2$ $[M]^+$: 261.0790; Found: 261.0787.

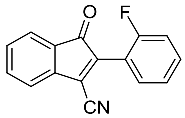


2-(4-fluorophenyl)-1-oxo-1H-indene-3-carbonitrile (2f): As a red powder; yield: 80%; m.p. 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05–7.96 (m, 2 H), 7.61–7.51 (m, 2 H), 7.41–7.30 (m, 2 H), 7.25–7.15 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.73, 164.25 (d, *J* = 254.2 Hz, C-F), 141.77, 140.77, 135.53, 131.46 (d, *J* = 8.6 Hz, CH-CH-CF), 130.23, 128.19, 124.71 (d, *J* = 3.4 Hz, C-CH-CH-CF), 124.41, 121.84 (d, *J* = 2.4 Hz, C-C-CH-CH-CF), 121.21, 116.34 (d, *J* = 21.9 Hz, CH-CF), 114.08; HRMS (EI): *m*/*z* Calcd. For $C_{16}H_8FNO$ $[M]^+$: 249.0590; Found: 249.0598.

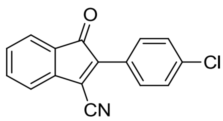


2-(3-fluorophenyl)-1-oxo-1*H*-indene-3-carbonitrile (2g): As a red powder; yield: 75%; m.p.

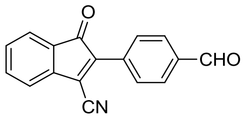
155–157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1 H), 7.69 (dt, *J* = 10.0, 2.0 Hz, 1 H), 7.63–7.44 (m, 3 H), 7.43–7.36 (m, 2 H), 7.27–7.13 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.26 (s), 162.70 (d, *J* = 247.2 Hz, C-F), 141.47 (d, *J* = 2.8 Hz, C-C-CH-CF), 140.50 (s), 135.55 (s), 130.63 (d, *J* = 8.5 Hz, CH-CH-CF), 130.57 (s), 130.24 (d, *J* = 8.4 Hz, C-CH-CF), 128.24 (s), 124.86 (d, *J* = 3.2 Hz, CH-CH-CH-CF), 124.50 (s), 123.44 (s), 121.47 (s), 118.08 (d, *J* = 21.3 Hz, CH-CF), 116.14 (d, *J* = 23.6 Hz, CH-CF), 113.76 (s); HRMS (EI): *m*/*z* Calcd. For $C_{16}H_8FNO$ $[M]^+$: 249.0590; Found:249.0590.



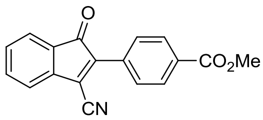
2-(2-fluorophenyl)-1-oxo-1*H*-indene-3-carbonitrile (2h): As a red powder; yield: 68%; m.p. 154–156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.45 (m, 4 H), 7.44–7.35 (m, 2 H), 7.33–7.26 (m, 1 H), 7.25–7.19 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.63, 160.53 (d, *J* = 253.8 Hz, C-F), 140.72, 139.38 (d, *J* = 2.3 Hz, C-C-C-CF), 135.39, 132.54 (d, *J* = 8.5 Hz, CH-CH-CF), 131.40 (d, *J* = 2.3 Hz, CH-C-CF), 130.54, 128.03, 126.80 (d, *J* = 2 Hz, C-C-CF), 124.50, 124.46 (d, *J* = 3.5 Hz, CH-CH-CH-CF), 121.51, 116.52 (d, *J* = 21.6 Hz, CH-CF), 116.42 (d, *J* = 14.8 Hz, C-CF), 112.98; HRMS (EI): *m*/*z* Calcd. For $C_{16}H_8FNO$ $[M]^+$: 249.0590; Found: 249.0589.



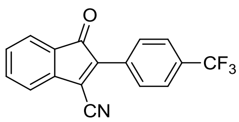
2-(4-chlorophenyl)-1-oxo-1*H*-indene-3-carbonitrile (2i): As an orange red powder; yield: 82%; m.p. 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 8.9, 2.1 Hz, 2 H), 7.57 (ddd, *J* = 15.2, 7.5, 1.2 Hz, 2 H), 7.38 (dt, *J* = 8.9, 2.1 Hz, 2 H), 7.43–7.33 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.63, 141.76, 140.79, 137.55, 135.67, 130.54, 130.51, 129.48, 128.36, 126.99, 124.57, 122.60, 121.45, 114.06; HRMS (EI): *m*/*z* Calcd. For $C_{16}H_8ClNO$ $[M]^+$: 265.0294; Found: 265.0289.



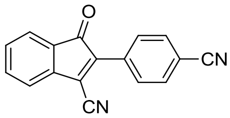
2-(4-formylphenyl)-1-oxo-1*H*-indene-3-carbonitrile (2j): As a scarlet powder; yield: 67%; m.p. 168–170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.09 (s, 1 H), 8.12 (d, *J* = 8.4 Hz 2 H), 8.01 (d, *J* = 8.4 Hz 2 H), 7.66–7.56 (m, 2 H), 7.43 (t, *J* = 6.4 Hz, 2 H);^{13}C NMR (126 MHz, $CDCl_3$) δ 193.01, 191.45, 141.51, 140.38, 137.24, 135.63, 133.86, 130.92, 129.96, 129.74, 128.24, 124.79, 124.62, 121.72, 113.60; HRMS (EI): *m/z* Calcd. For $C_{17}H_9NO_2$ $[M]^+$: 259.0633; Found: 259.0633.



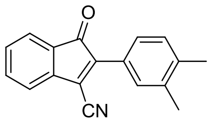
methyl 4-(3-cyano-1-oxo-1*H*-inden-2-yl)benzoate (2k): As an orange red powder; yield: 75%; m.p. 156–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (dt, *J* = 8.6, 2.0 Hz, 2 H), 8.02 (dt, *J* = 8.5, 1.9 Hz, 2 H), 7.59 (ddd, *J* = 16.4, 7.7, 1.2 Hz, 2 H), 7.46–7.36 (m, 2 H), 3.96 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.21, 166.27, 141.81, 140.50, 135.55, 132.48, 131.89, 130.71, 130.01, 129.11, 128.28, 124.52, 124.17, 121.57, 113.71, 52.45; HRMS (EI): *m/z* Calcd. For $C_{18}H_{11}NO_3$ $[M]^+$: 289.0739; Found: 289.0747.



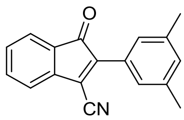
1-oxo-2-(4-(trifluoromethyl)phenyl)-1*H*-indene-3-carbonitrile (2l): As an orange yellow crystalline solid; yield: 54%; m.p. 145–148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H), 7.65–7.54 (m, 2 H), 7.42 (t, *J* = 7.0 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.06, 141.44, 140.35, 135.61, 132.37 (q, *J* = 32.8 Hz, C-CF_3), 131.68, 130.83, 129.47, 128.20, 125.88 (q, *J* = 3.8 Hz, CH-C-CF_3), 124.60, 124.51, 123.66 (q, *J* = 272.7 Hz, C-F_3), 121.67, 113.57; HRMS (EI): *m/z* Calcd. For $C_{17}H_8F_3NO$ $[M]^+$: 299.0558; Found: 299.0569.



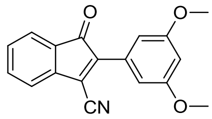
2-(4-cyanophenyl)-1-oxo-1*H*-indene-3-carbonitrile (2m): As an orange red powder; yield: 49%; m.p. 175–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dt, *J* = 8.4, 1.9 Hz, 2 H), 7.80 (dt, *J* = 8.4, 1.9 Hz, 2 H), 7.68–7.53 (m, 2 H), 7.49–7.37 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.75, 140.70, 140.16, 135.71, 132.57, 132.55, 131.12, 129.60, 128.15, 125.16, 124.73, 121.87, 118.13, 114.19, 113.40; HRMS (EI): *m/z* Calcd. For $C_{17}H_8N_2O$ $[M]^+$: 256.0637; Found: 256.0639.



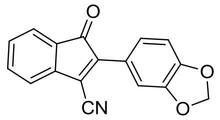
2-(3,4-dimethylphenyl)-1-oxo-1*H*-indene-3-carbonitrile (2n): As a red powder; yield: 87%; m.p. 143–145 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77–7.68 (m, 2 H), 7.61–7.49 (m, 2 H), 7.39–7.27 (m, 3 H), 2.34 (s, 3 H), 2.33 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.19, 194.19, 143.15, 141.17, 140.67, 137.41, 135.37, 130.30, 130.10, 129.84, 129.20, 128.41, 126.83, 126.13, 124.19, 120.94, 114.41, 20.03, 19.91; HRMS (EI): *m/z* Calcd. For $C_{18}H_{13}NO$ $[M]^+$: 259.0997; Found: 259.1002.



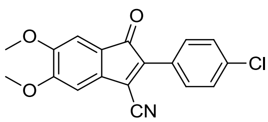
2-(3,5-dimethylphenyl)-1-oxo-1*H*-indene-3-carbonitrile (2o): As a red powder; yield: 92%; m.p. 159–160 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.47 (m, 4 H), 7.40–7.32 (m, 2 H), 7.14 (s, 1 H), 2.39 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.97, 143.48, 141.02, 138.61, 135.37, 132.97, 130.00, 128.39, 128.32, 126.88, 124.23, 121.92, 121.05, 114.21, 21.38; HRMS (EI): *m/z* Calcd. For $C_{18}H_{13}NO$ $[M]^+$: 259.0997; Found: 259.0995.



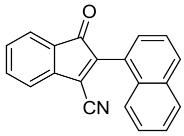
2-(3,5-dimethoxyphenyl)-1-oxo-1*H*-indene-3-carbonitrile (2p): As a dark red powder; yield: 60%; m.p. 178–181 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.49 (m, 2 H), 7.41–7.33 (m, 2 H), 7.14 (d, *J* = 2.3 Hz, 2 H), 6.59 (t, *J* = 2.3 Hz, 1 H), 3.85 (s, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.98, 162.32, 144.20, 142.14, 136.82, 131.65, 131.34, 129.82, 125.71, 124.05, 122.64, 115.55, 108.31, 105.43, 56.97; HRMS (EI): *m*/*z* Calcd. For $C_{18}H_{13}NO_3$ $[M]^+$: 291.0895; Found: 291.0892.



2-(benzo[*d*][1,3]dioxol-5-yl)-1-oxo-1*H*-indene-3-carbonitrile (2q): As a reddish brown powder; yield: 54%; m.p. 201–203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.3, 1.8 Hz, 1 H), 7.58–7.53 (m, 1 H), 7.53–7.48 (m, 2 H), 7.37–7.28 (m, 2 H), 6.94 (d, *J* = 8.3 Hz, 1 H), 6.06 (s, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.45, 151.68, 149.66, 143.64, 142.57, 136.90, 131.19, 129.68, 126.37, 125.69, 124.01, 122.32, 121.11, 115.93, 110.42, 110.30, 103.21; HRMS (EI): *m*/*z* Calcd. For $C_{17}H_9NO_3$ $[M]^+$: 275.0582; Found: 275.0589.

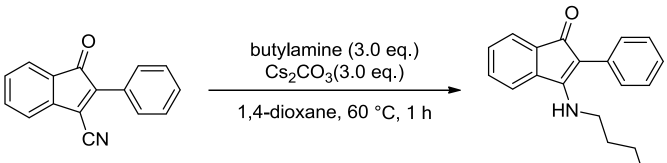


2-(4-chlorophenyl)-5,6-dimethoxy-1-oxo-1*H*-indene-3-carbonitrile (2r): As a celadon powder; yield: 53%; m.p. 208–211 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 6.8, 2.0 Hz, 2 H), 7.47 (dt, *J* = 6.8, 2.0 Hz, 2 H), 7.14 (s, 1 H), 6.87 (s, 1 H), 4.02 (s, 3 H), 3.93 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.82, 154.77, 150.18, 141.22, 137.06, 135.43, 130.19, 129.28, 127.16, 120.87, 120.32, 114.25, 108.22, 105.04, 56.73, 56.52; HRMS (EI): *m*/*z* Calcd. For $C_{18}H_{12}ClNO_3$ $[M]^+$: 325.0506; Found: 325.0509.



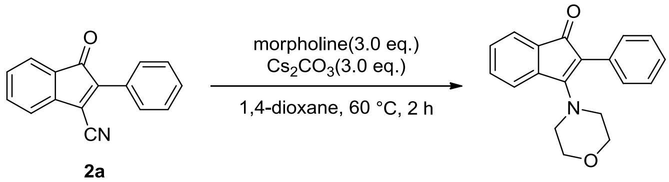
2-(naphthalen-1-yl)-1-oxo-1*H*-indene-3-carbonitrile (2s): As a red powder; yield: 57%; m.p. 141–143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06–7.88 (m, 2 H), 7.78-7.72 (m, 1 H), 7.70–7.49 (m, 6 H), 7.44 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.92, 147.58, 142.17, 136.85, 135.20, 132.65, 132.48, 131.89, 130.18, 130.10, 129.69, 128.60, 128.18, 128.01, 127.47, 127.08, 126.60, 126.07, 122.82, 114.61; HRMS (EI): *m*/*z* Calcd. For $C_{20}H_{11}NO$ $[M]^+$: 281.0841; Found: 281.0831.

Transformations of 3-cynoindenones

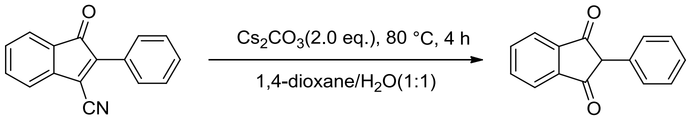


2a **4**

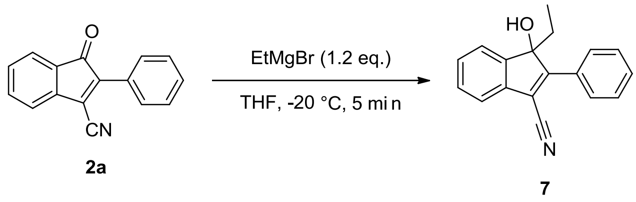
3-(butylamino)-2-phenyl-1*H*-inden-1-one (4)[3]: The mixture of **2a** (0.13 mmol), butylamine (0.39 mmol) and Cs_2CO_3 (0.39 mmol) in dry dioxane (2 mL) was heated at 60 °C for 1 h. After cooling, the reaction solution was washed with saturated brine and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel, with petroleum ether/ethyl acetate (4:1) as the eluent to give **4** as an orange red powder in 84% yield; m.p. 101–102 °C; ^{1}H NMR (300 MHz, DMSO-*d6*) δ 8.07 (t, *J* = 6.0 Hz, 1 H), 7.70 (d, *J* = 7.0 Hz, 1 H), 7.48–7.27 (m, 5 H), 7.23 (m, 3 H), 3.10 (brs, 2 H), 1.29 (t, *J* = 7.2 Hz, 2 H), 0.94 (q, *J* = 7.6 Hz, 2 H), 0.62 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, DMSO-*d6*) δ 191.10, 159.60, 139.74, 135.18, 134.97, 131.79, 131.62, 130.62, 128.13, 126.75, 120.15, 119.02, 105.19, 44.69, 31.95, 19.88, 14.04; HRMS (ESI): *m*/*z* Calcd. For $C_{19}H_{20}NO$ $[M+H]^+$: 278.1545; Found: 278.1548.



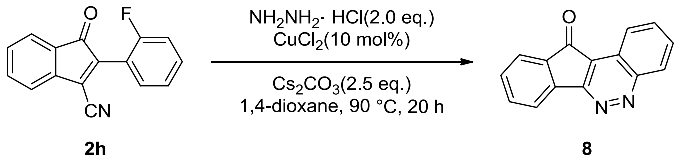
3-morpholino-2-phenyl-1*H*-inden-1-one (5): The mixture of **2a** (0.13 mmol), morpholine (0.39 mmol) and Cs_2CO_3 (0.39 mmol) in dry dioxane (2 mL) was heated at 60 °C for 1 h. After cooling, the reaction solution was washed with saturated brine and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel, with petroleum ether/ethyl acetate (4:1) as the eluent to give **5** as red oil in 44% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.49 (m, 1 H), 7.44–7.28 (m, 8 H), 3.77 (t, *J* = 4.6 Hz, 4 H), 3.47 (t, *J* = 4.7 Hz, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.73, 162.80, 139.82, 134.72, 133.05, 131.62, 130.32, 129.70, 128.02, 126.90, 121.38, 120.97, 112.98, 66.74, 50.76; HRMS (EI): *m*/*z* Calcd. For $C_{19}H_{17}NO_2$ $[M]^+$: 291.1259; Found: 291.1258.



2-phenyl-1*H*-indene-1,3(2*H*)-dione (6)[4]: The mixture of **2a** (0.13 mmol) and Cs_2CO_3 (0.26 mmol) in 2 mL of dioxane/H_2O (1:1) was heated at 80 °C for 4 h. After cooling, the reaction solution was acidified by HCl aq. (1 N) to pH 4.0, then washed with saturated brine and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel, with petroleum ether/ethyl acetate (4:1) as the eluent to give **6** as white shiny flakes in 38% yield; m.p. 135–137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 5.7, 3.1 Hz, 2 H), 7.91 (dd, *J* = 5.6, 3.1 Hz, 2 H), 7.39–7.28 (m, 3 H), 7.23–7.11 (m, 2 H), 4.27 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.33, 142.67, 136.04, 133.15, 129.03, 128.78, 127.89, 123.80, 59.84; HRMS (EI): *m*/*z* Calcd. For $C_{15}H_{10}O_2$ $[M]^+$: 222.0681; Found: 222.0682.

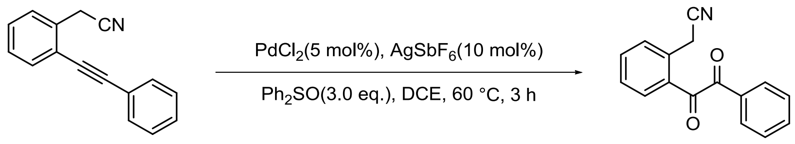


1-ethyl-1-hydroxy-2-phenyl-1*H*-indene-3-carbonitrile (7): To a solution of **2a** (0.13 mmol) in THF (2 mL), EtMgBr (0.16 mmol) was added at –20 °C, and was stirred for 5 min. Then saturated aq. NH_4Cl (2 mL) was added dropwise, the resulting solution washed with saturated brine and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions was dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel, with petroleum ether/ethyl acetate (8:1) as the eluent to give **7** as colorless oil in 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19–8.02 (m, 2 H), 7.55–7.40 (m, 5 H), 7.42–7.31 (m, 2 H), 2.30 (s, 1 H), 2.26–2.09 (m, 1 H), 2.08–1.89 (m, 1 H), 0.44 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.80, 146.13, 138.21, 132.15, 130.80, 129.87, 129.14, 128.36, 128.28, 122.70, 120.81, 115.55, 110.50, 87.77, 31.12, 7.83; HRMS (ESI): *m*/*z* Calcd. For $C_{18}H_{15}NONa$ $[M+Na]^+$: 284.1051; Found: 284.1046.



11*H*-indeno[1,2-c]cinnolin-11-one (8): The mixture of **2h** (0.13 mmol), hydrazine monohydrochloride (0.26 mmol), $CuCl_2$ (10 mol%) and Cs_2CO_3 (0.33 mmol) in dry dioxane (2 mL) was heated at 90 °C under air for 20 h. After cooling, the reaction solution was washed with saturated brine and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel, with petroleum ether/ethyl acetate (4:1) as the eluent to give **8** as an orange red powder in 93% yield; m.p. > 300 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72–8.59 (m, 1 H), 8.57–8.43 (m, 1 H), 8.18 (d, *J* = 7.4 Hz, 1 H), 7.87–7.73 (m, 3 H), 7.67 (t, *J* = 7.4 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.37, 157.84, 152.98, 142.77, 135.88, 134.29, 133.79, 131.22, 130.84, 130.56, 124.91, 123.30, 121.92, 121.35, 119.90; HRMS (EI): *m*/*z* Calcd. For $C_{15}H_8N_2O$ $[M]^+$: 232.0637; Found: 232.0638.

Isolation of 1,2-dicarbonyl compound 3a



2-(2-(2-oxo-2-phenylacetyl)phenyl)acetonitrile (3a): After stirring for 5 min at room temperature, the mixture of **1a** (0.23 mmol), $PdCl_2$ (5 mol%), $AgSbF_6$ (10 mol%) and Ph_2SO (0.69 mmol) in dry DCE (1 mL) was heated at 60 °C under air for 3 h. After cooling, the reaction solution was washed with saturated brine and extracted with ethyl acetate (2 × 15 mL). The combined organic fractions was dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was chromatographed on silica gel, with petroleum ether/ethyl acetate (10:1 to 6:1) as the eluent to give the 1,2-dicarbonyl compound **3a** as a brown oil in 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.3 Hz, 2 H), 7.77-7.64 (m, 3 H), 7.54 (t, J = 7.7 Hz, 2 H), 7.46 (t, J = 7.4 Hz, 2 H), 4.36 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.22, 193.83, 135.20, 134.90, 134.27, 132.75, 132.62, 131.04, 130.27, 130.00, 129.20, 128.63, 117.39, 23.25; HRMS (EI): m/z Calcd. For $C_{16}H_{11}NO_2$ $[M]^+$: 249.0790; Found: 249.0792.

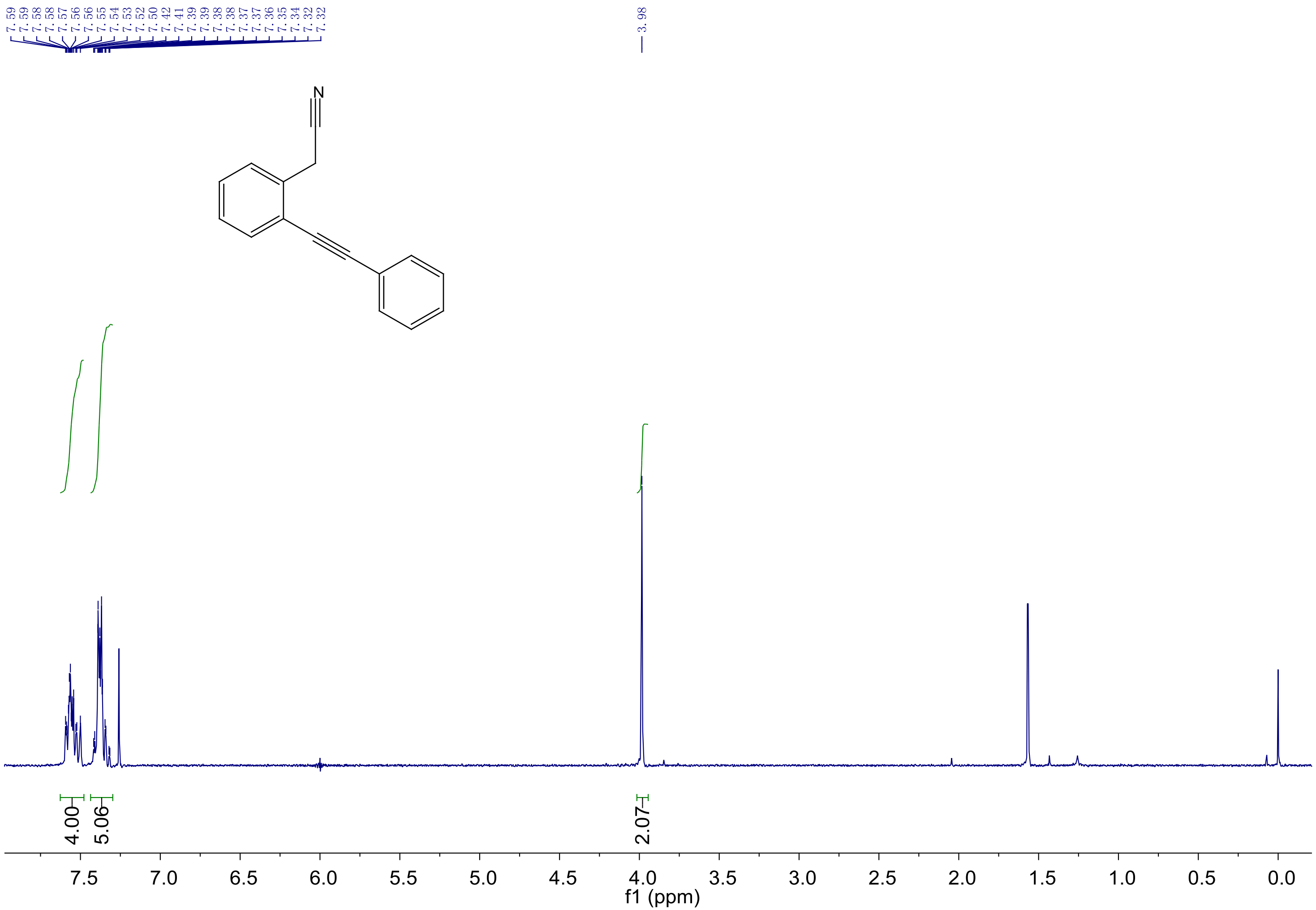
Reference

(1) Shen, H.; Xie, Z. *J. Am. Chem. Soc.* **2010**, *132*, 11473.
(2) Severin, R.; Reimer, J.; Doye, S. *J. Org. Chem.* **2010**, *75*, 3518.
(3) Ismail, I. M.; El-Sharief, A. M. S.; Ammar, Y. A.; Amer, R. M. *Egypt. J. Chem.* **1985**, *27*, 229.
(4) Lu, C.-D.; Chen, Z.-Y.; Liu, H.; Hu, W.-H.; Mi, A.-Q.; Doyle, M. P. *J. Org. Chem.* **2004**, *69*, 4856.

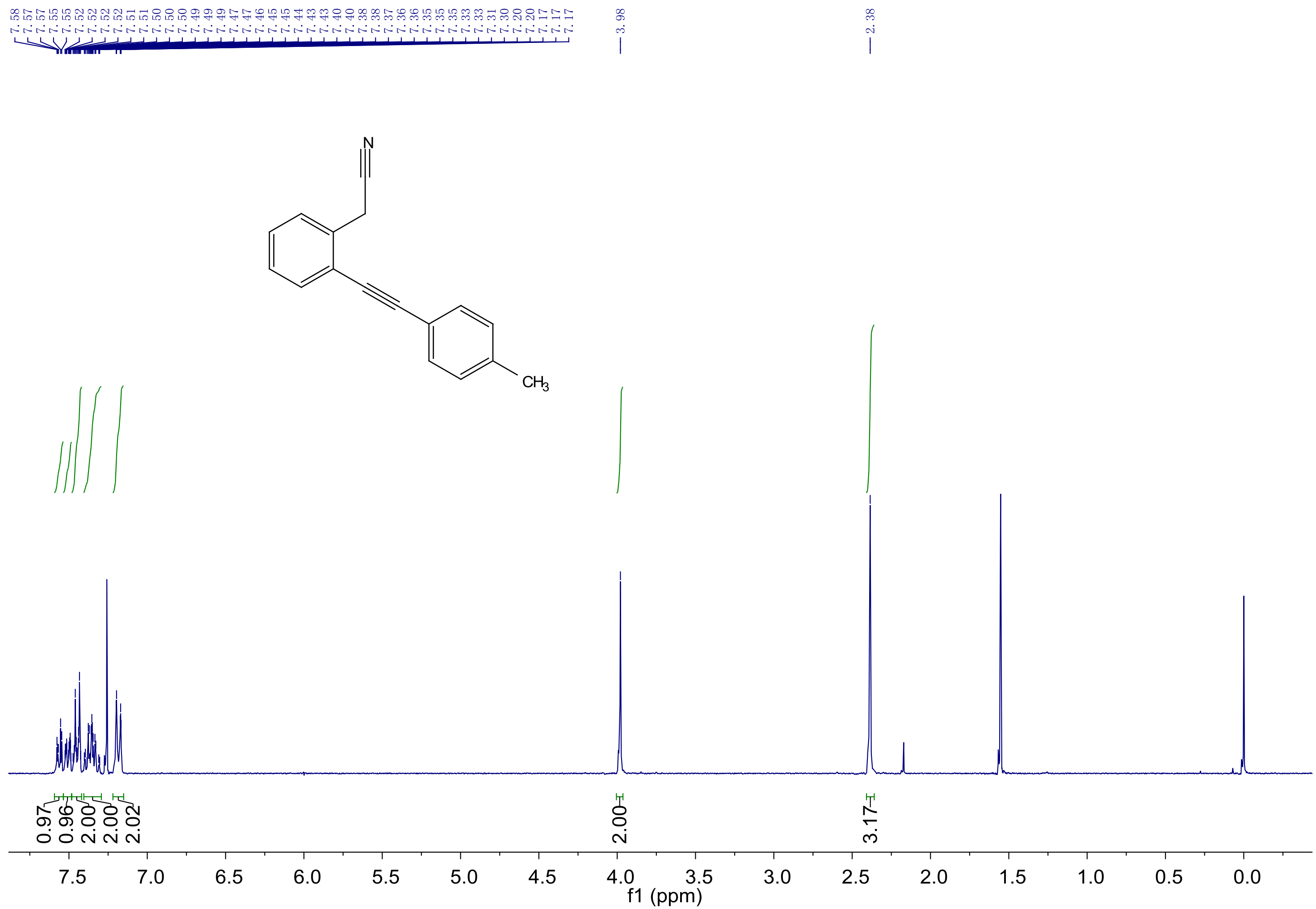
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2013

^{1}H NMR and ^{13}C NMR spectra

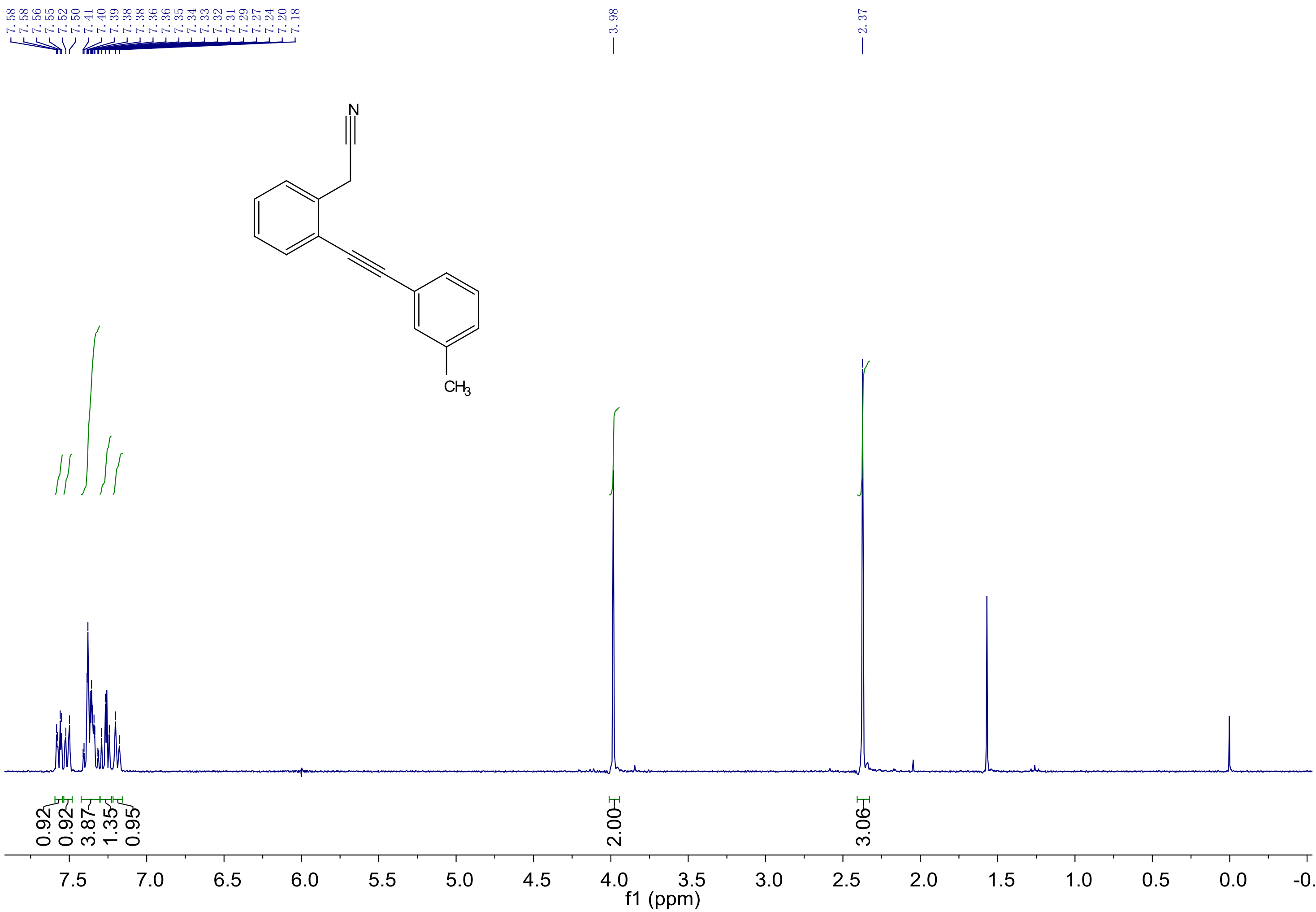
1a

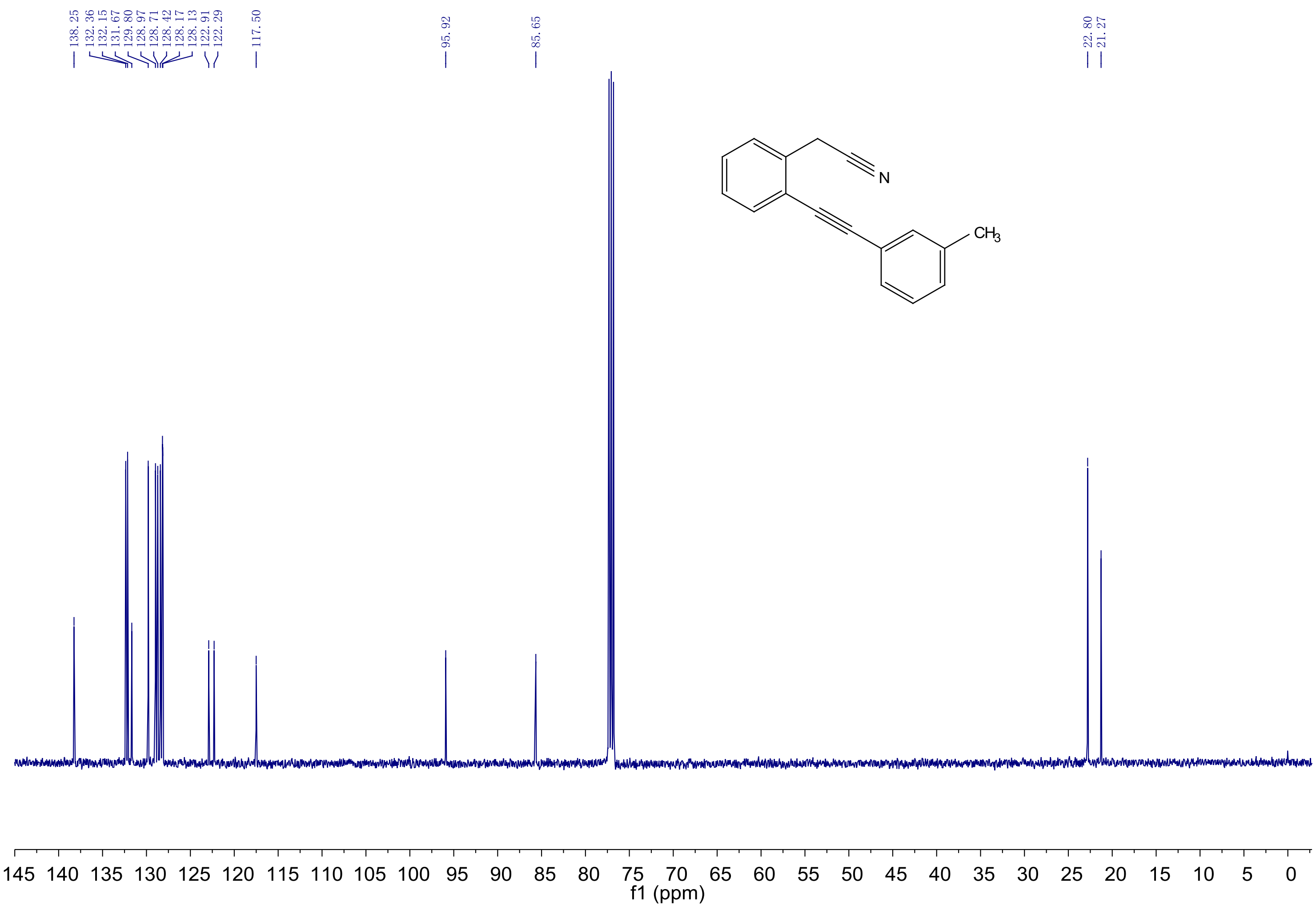


1b

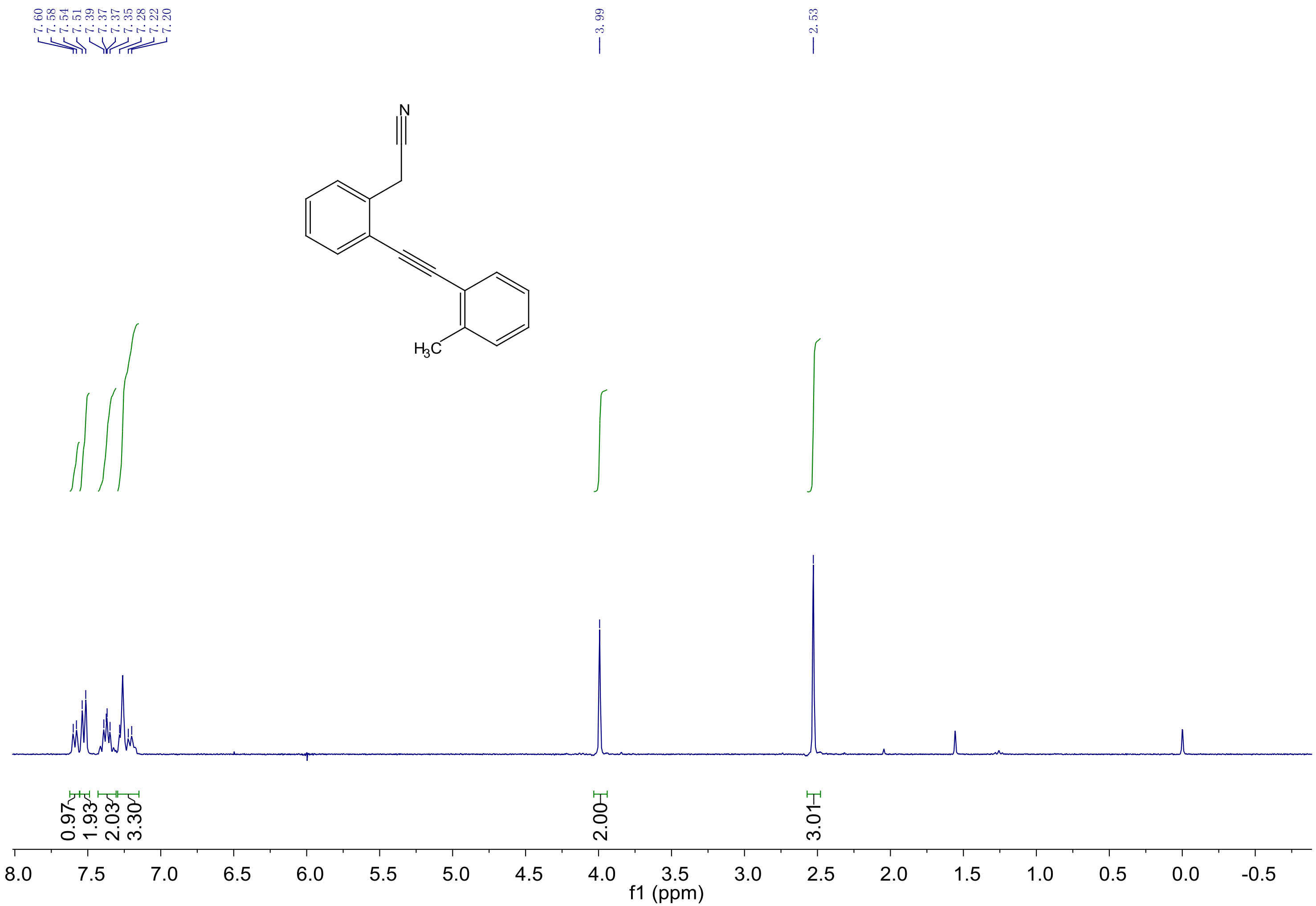

7.58
7.57
7.57
7.55
7.55
7.52
7.52
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.49
7.49
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.40
7.40
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.35
7.33
7.33
7.33
7.31
7.30
7.20
7.20
7.17
7.17
7.17
3.98
2.38
N
CH3
0.97
0.96
2.00
2.00
2.02
2.00
3.17
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

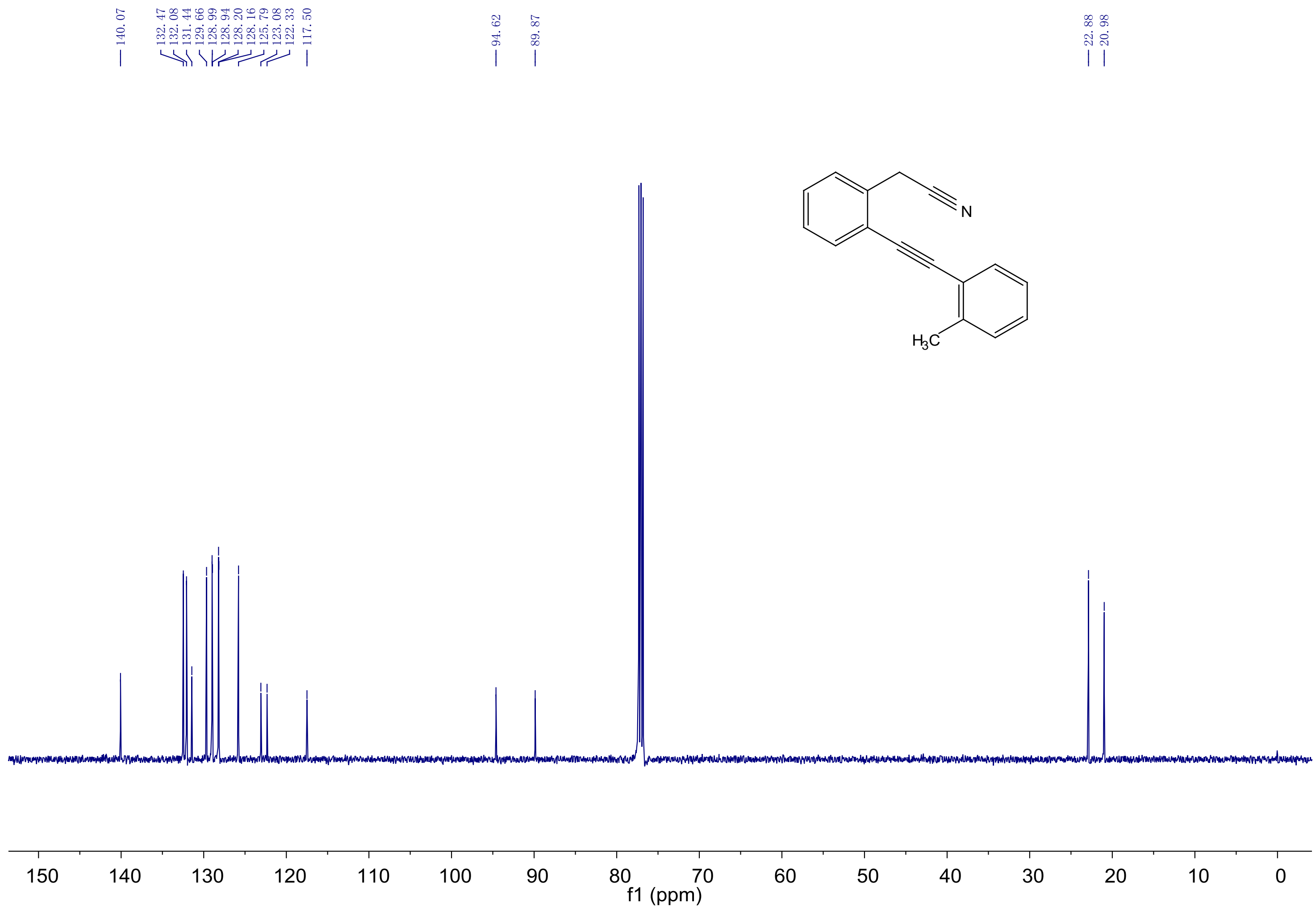
1c


7.58
7.58
7.56
7.55
7.52
7.50
7.41
7.40
7.39
7.38
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.29
7.27
7.24
7.20
7.18
3.98
2.37
N
CH3
0.92
0.92
3.87
1.35
0.95
2.00
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


138.25
132.36
132.15
131.67
129.80
128.97
128.71
128.42
128.17
128.13
122.91
122.29
117.50
95.92
85.65
22.80
21.27
N
CH3
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

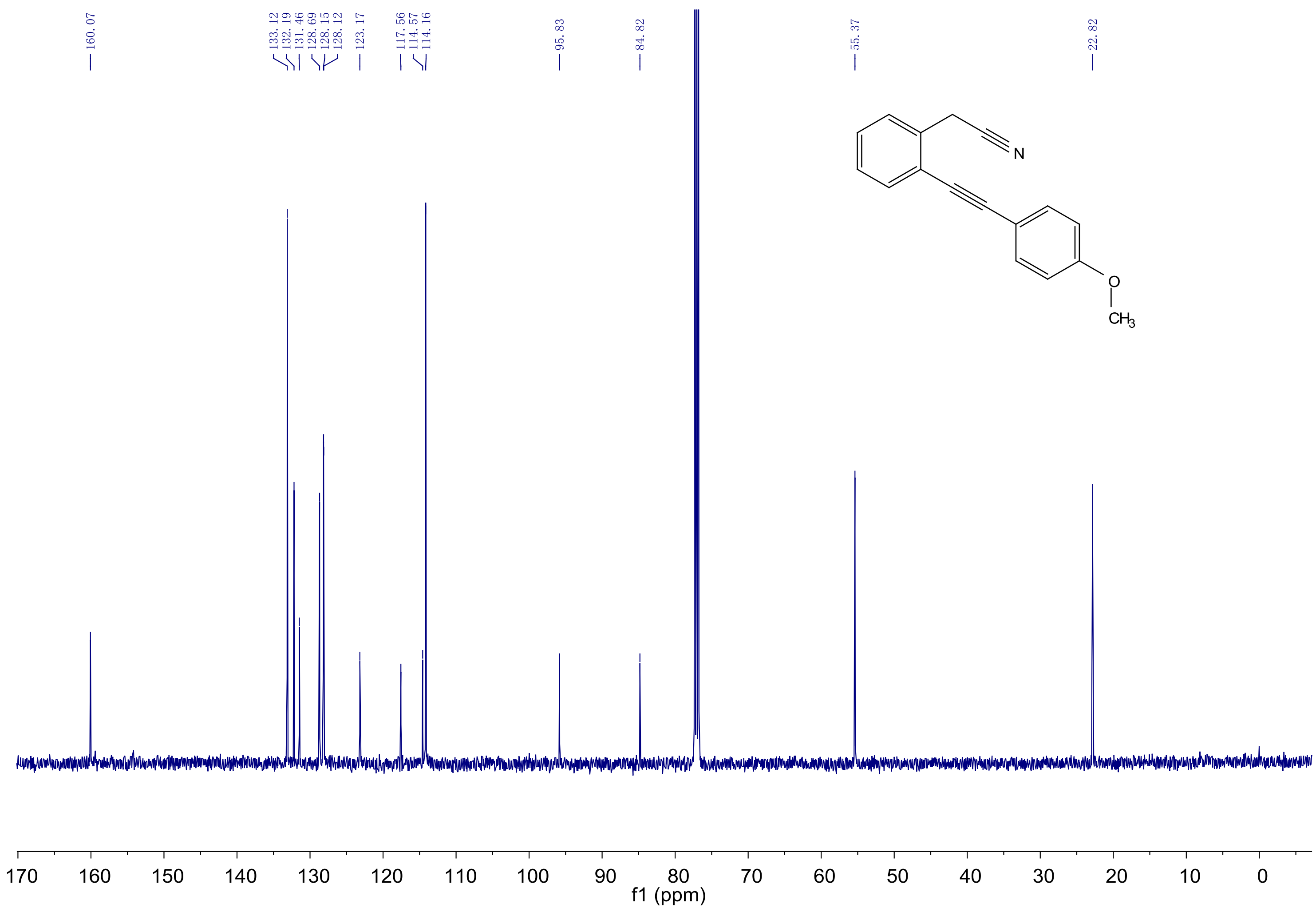
1d


7.60
7.58
7.54
7.51
7.39
7.37
7.37
7.35
7.28
7.22
7.20
3.99
2.53
N
H3C
0.97
1.93
2.03
3.30
2.00
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

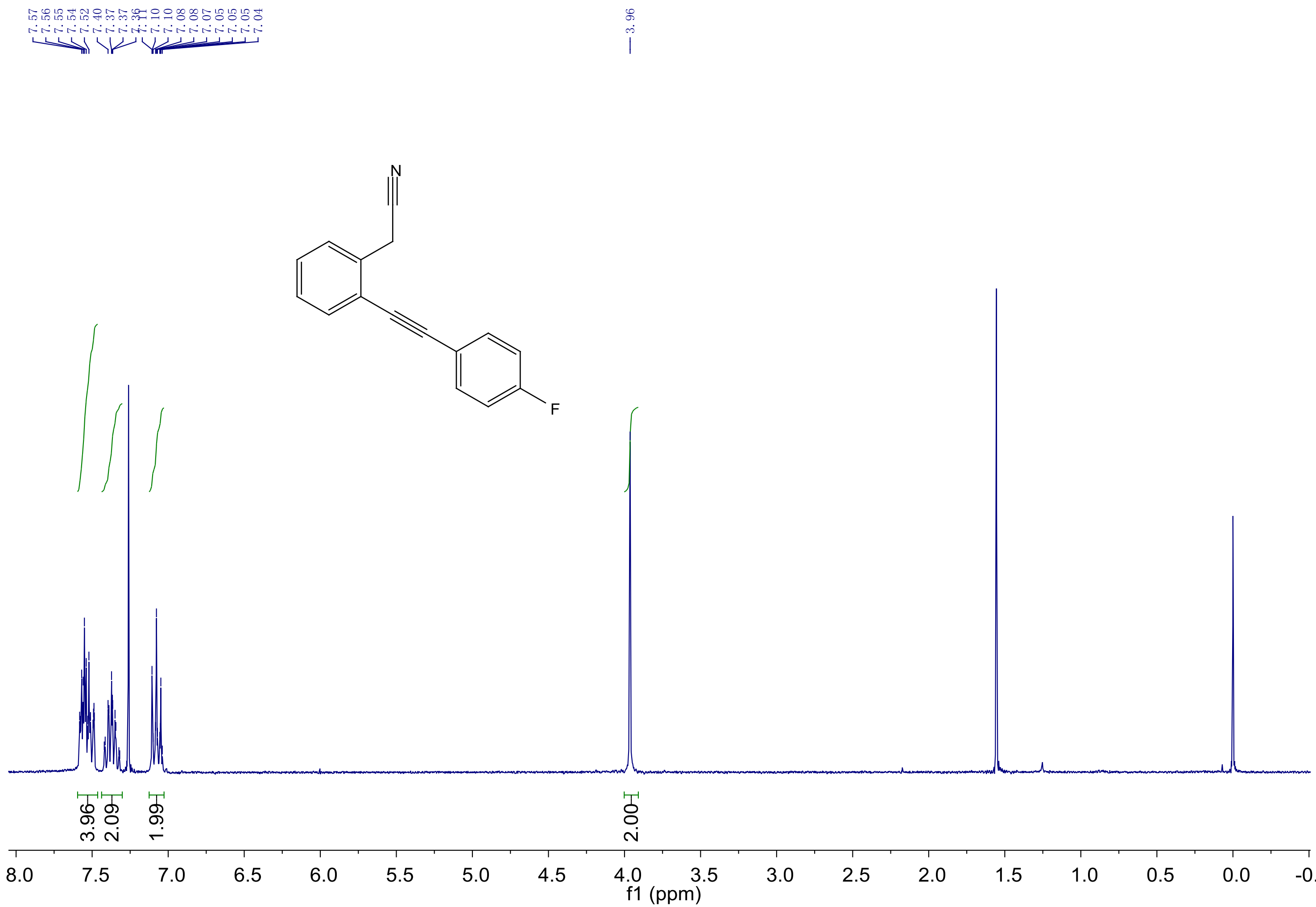

140.07
132.47
132.08
131.44
129.66
128.99
128.94
128.20
128.16
125.79
123.08
122.33
117.50
94.62
89.87
22.88
20.98
N
H3C
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

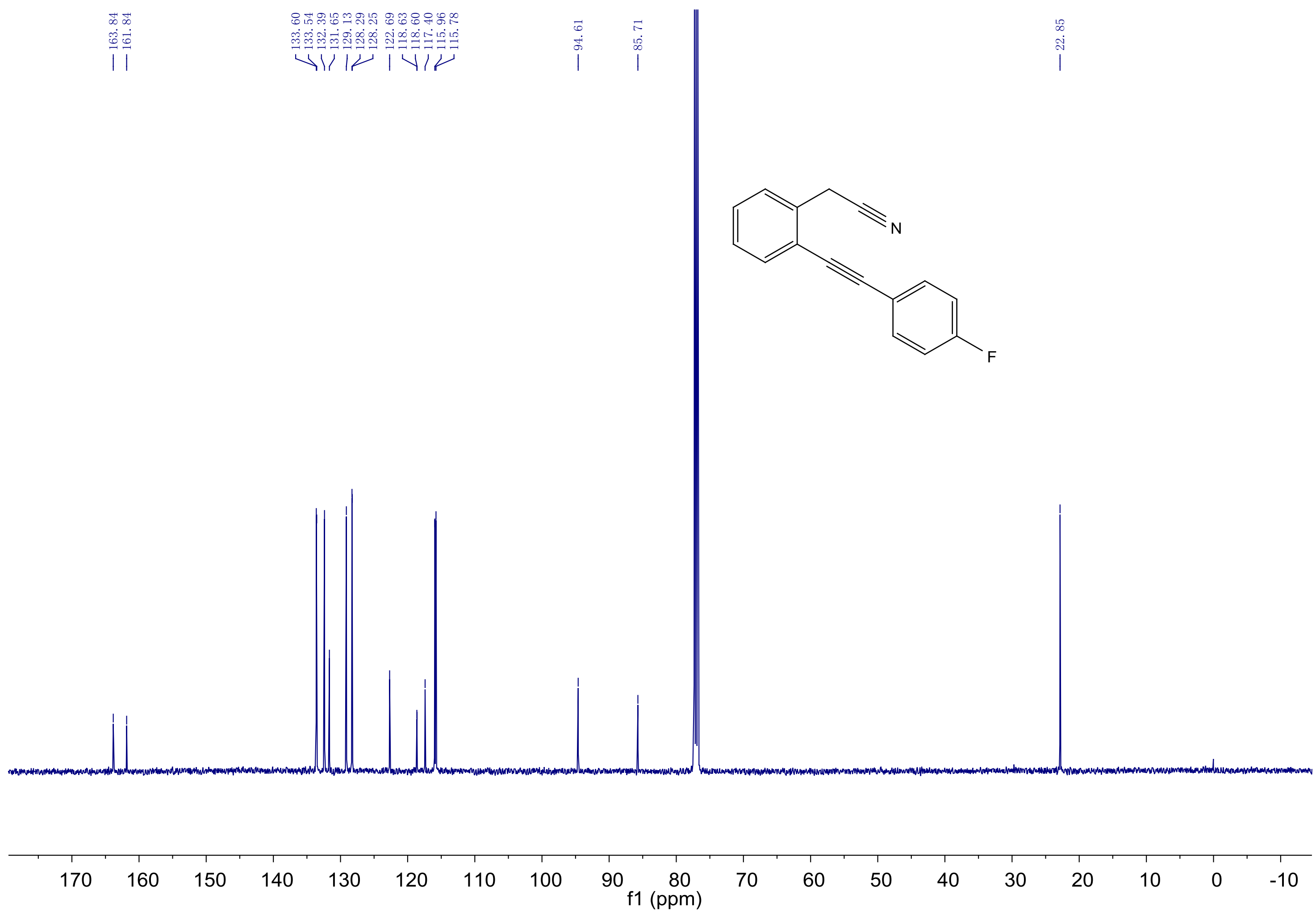
1e


7.54
7.51
7.50
7.50
7.49
7.48
7.48
7.48
7.37
7.36
7.35
7.34
6.92
6.91
6.89
6.89
3.97
3.84
N
O
CH3
0.95
2.97
2.16
2.17
2.00
3.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

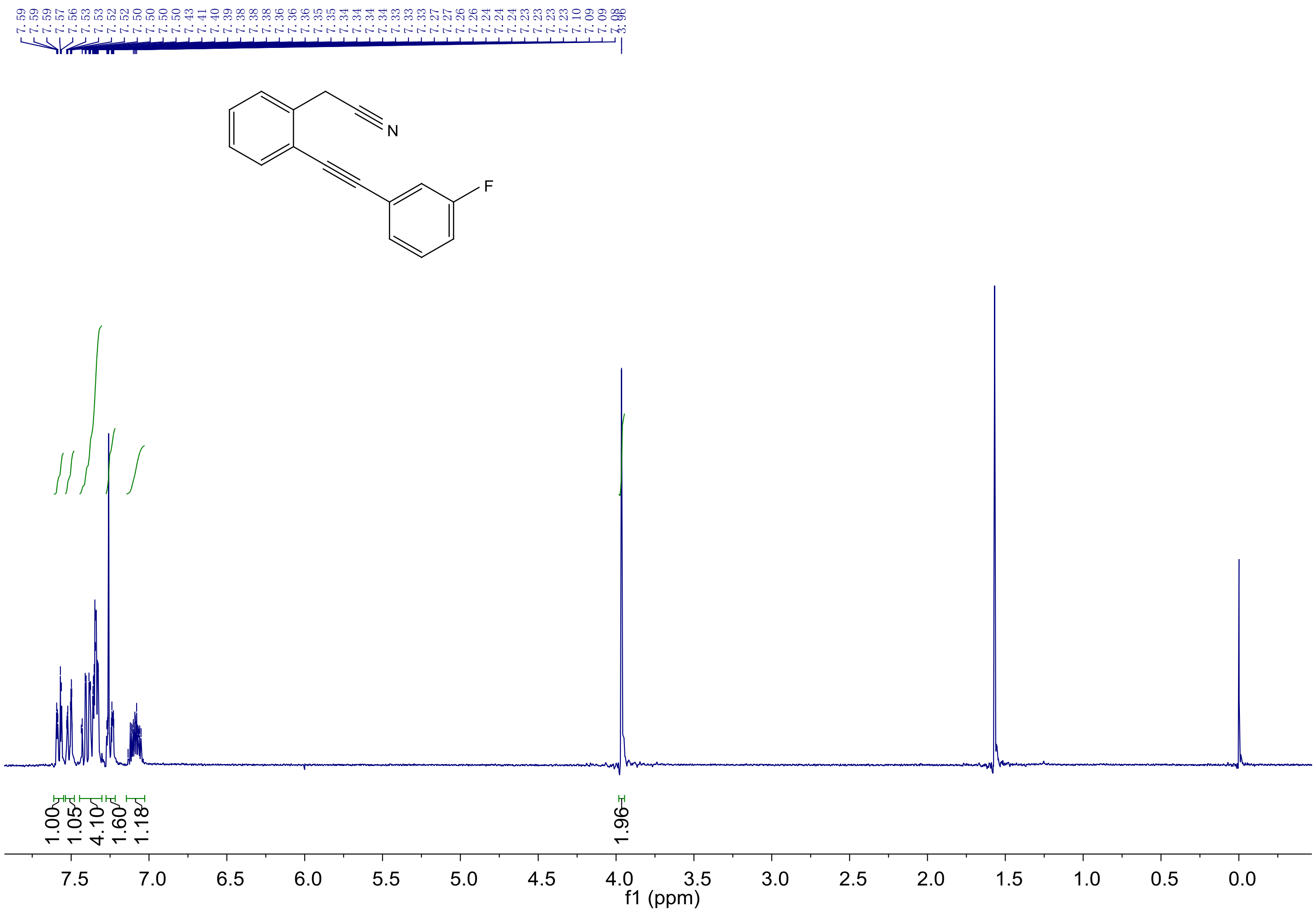

160.07
133.12
132.19
131.46
128.69
128.15
128.12
123.17
117.56
114.57
114.16
95.83
84.82
55.37
22.82
N
O
CH3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

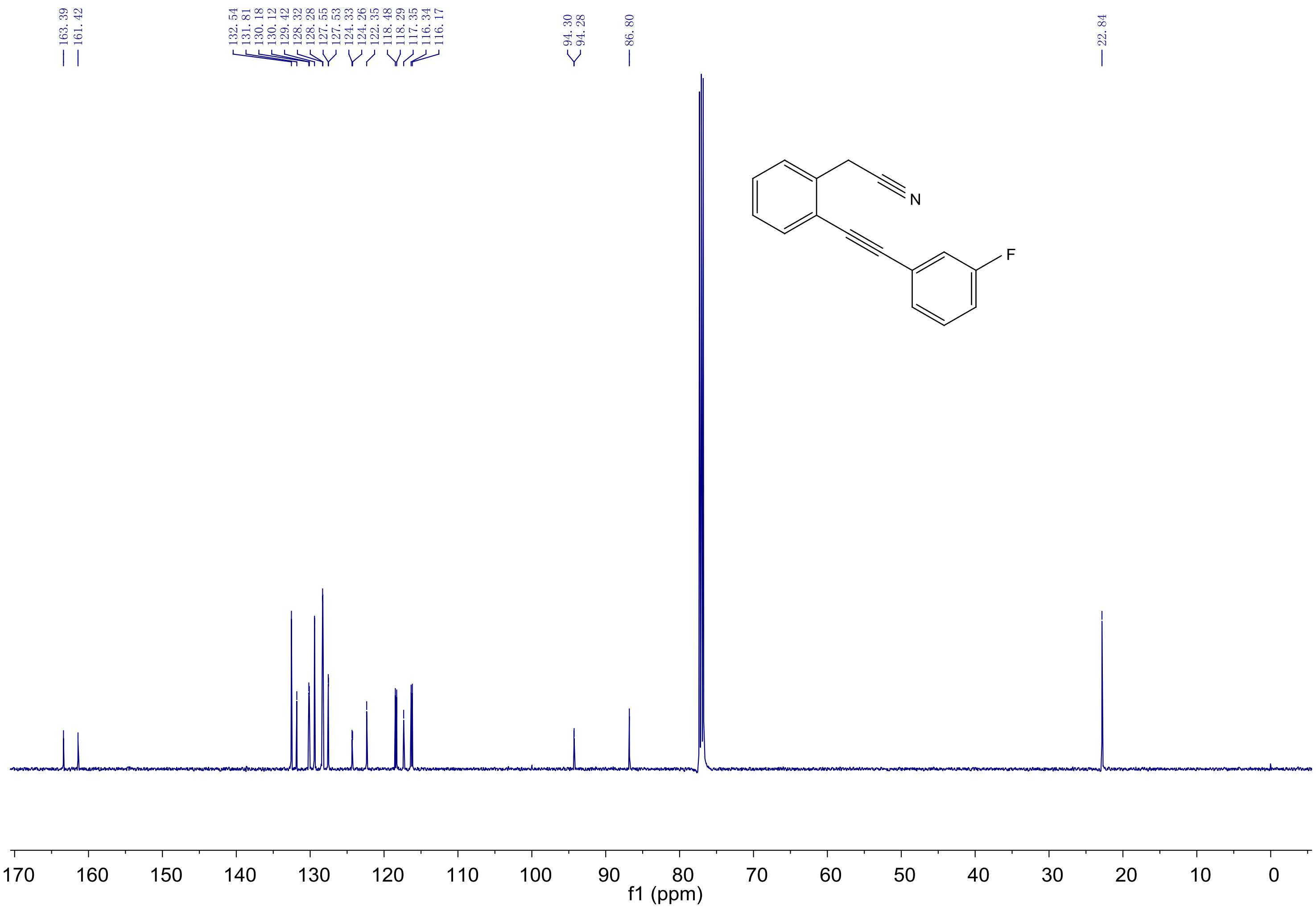
1f


7.57
7.56
7.55
7.54
7.52
7.40
7.37
7.37
7.36
7.11
7.10
7.10
7.08
7.08
7.07
7.05
7.05
7.05
7.04
3.96
N
F
3.96
2.09
1.99
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

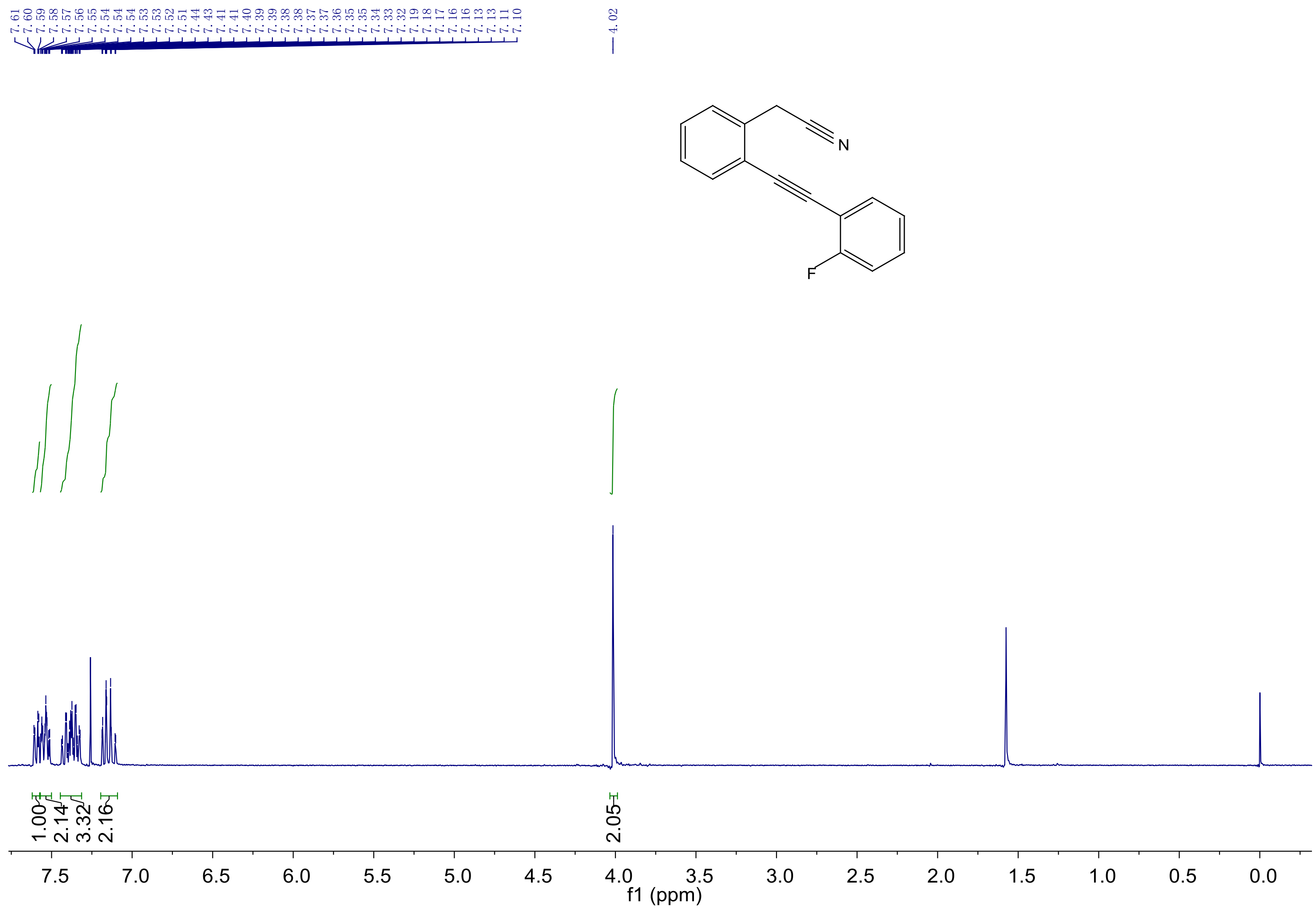

163.84
161.84
133.60
133.54
132.39
131.65
129.13
128.29
128.25
122.69
118.63
118.60
117.40
115.96
115.78
94.61
85.71
22.85
N
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

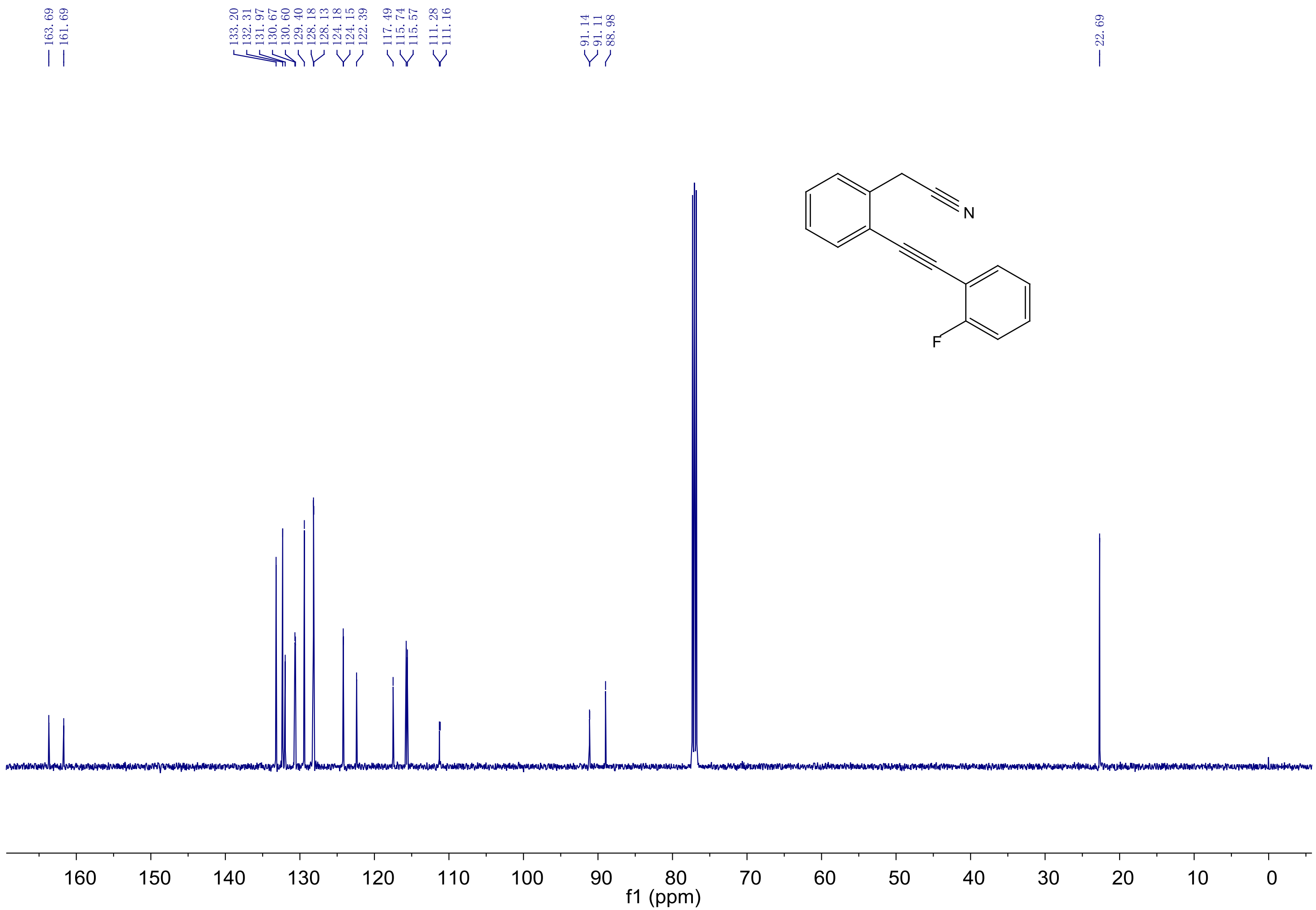
1g


N
F
1.00
1.05
4.10
1.60
1.18
1.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

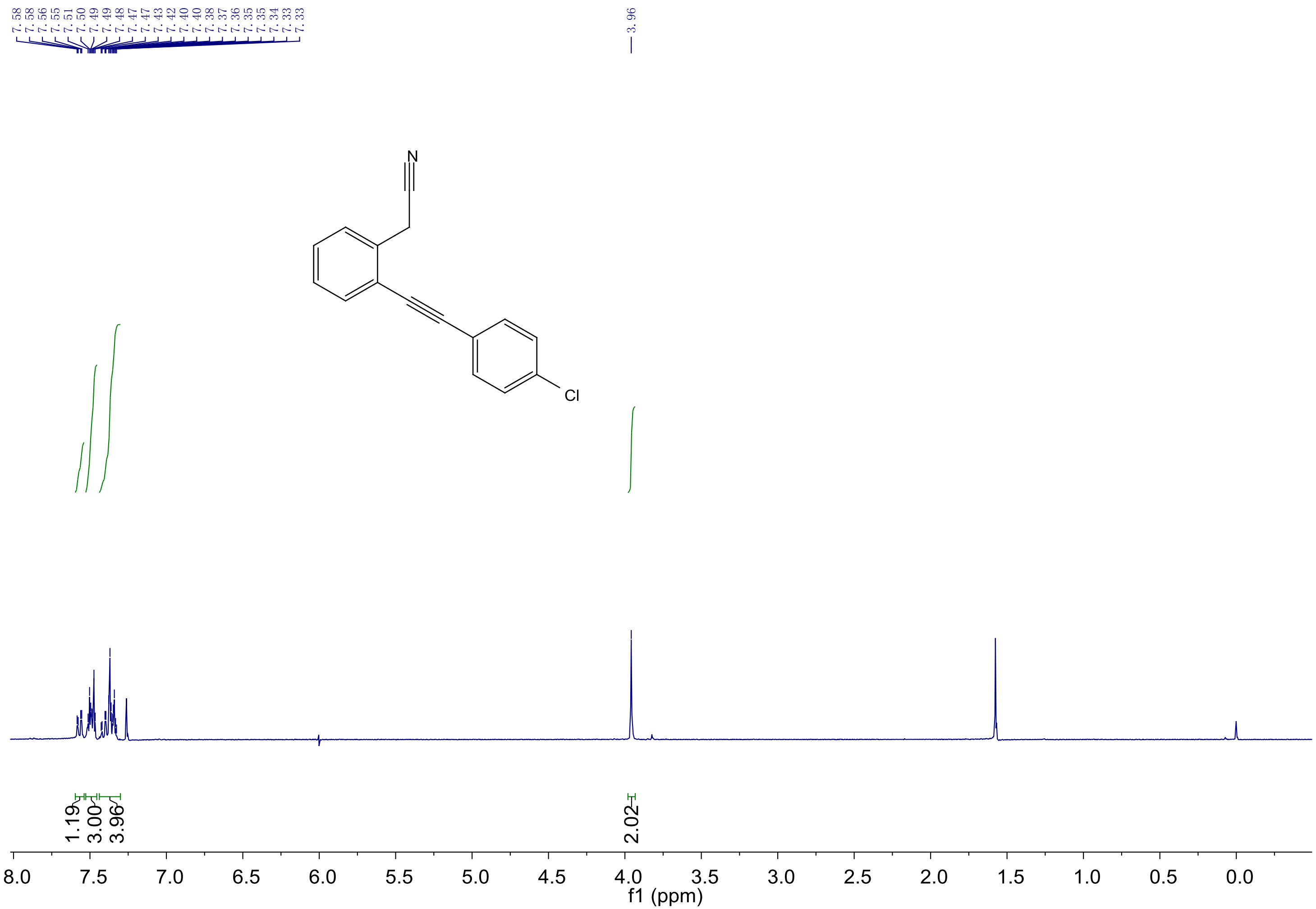

163.39
161.42
132.54
131.81
130.18
130.12
129.42
128.32
128.28
127.55
127.53
124.33
124.26
122.35
118.48
118.29
117.35
116.34
116.17
94.30
94.28
86.80
22.84
N
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1h


7.61
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.54
7.54
7.53
7.53
7.52
7.51
7.44
7.43
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.19
7.18
7.17
7.16
7.16
7.13
7.13
7.11
7.10
4.02
1.00
2.14
3.32
2.16
2.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

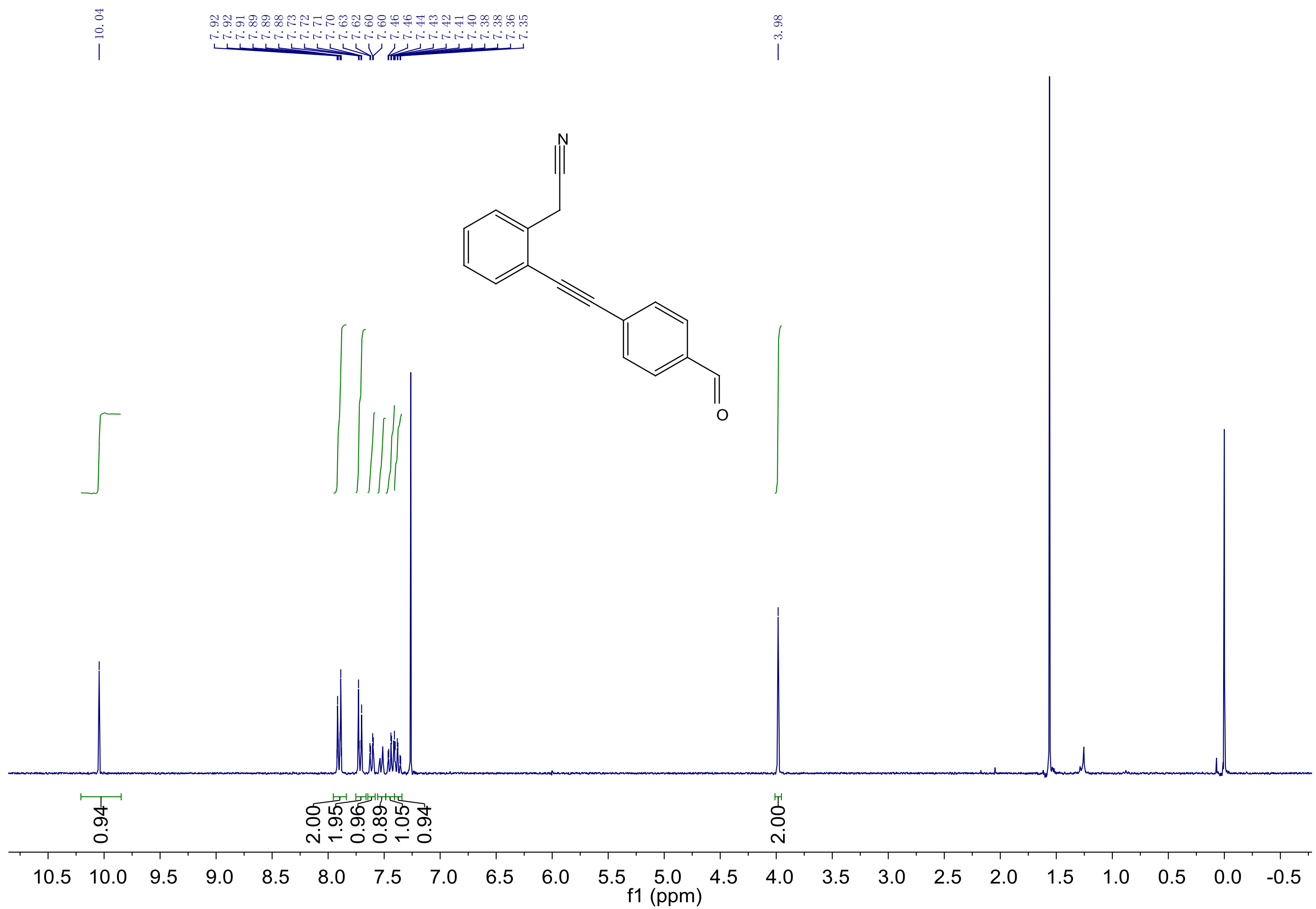

163.69
161.69
133.20
132.31
131.97
130.67
130.60
129.40
128.18
128.13
124.18
124.15
122.39
117.49
115.74
115.57
111.28
111.16
91.14
91.11
88.98
22.69
N
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

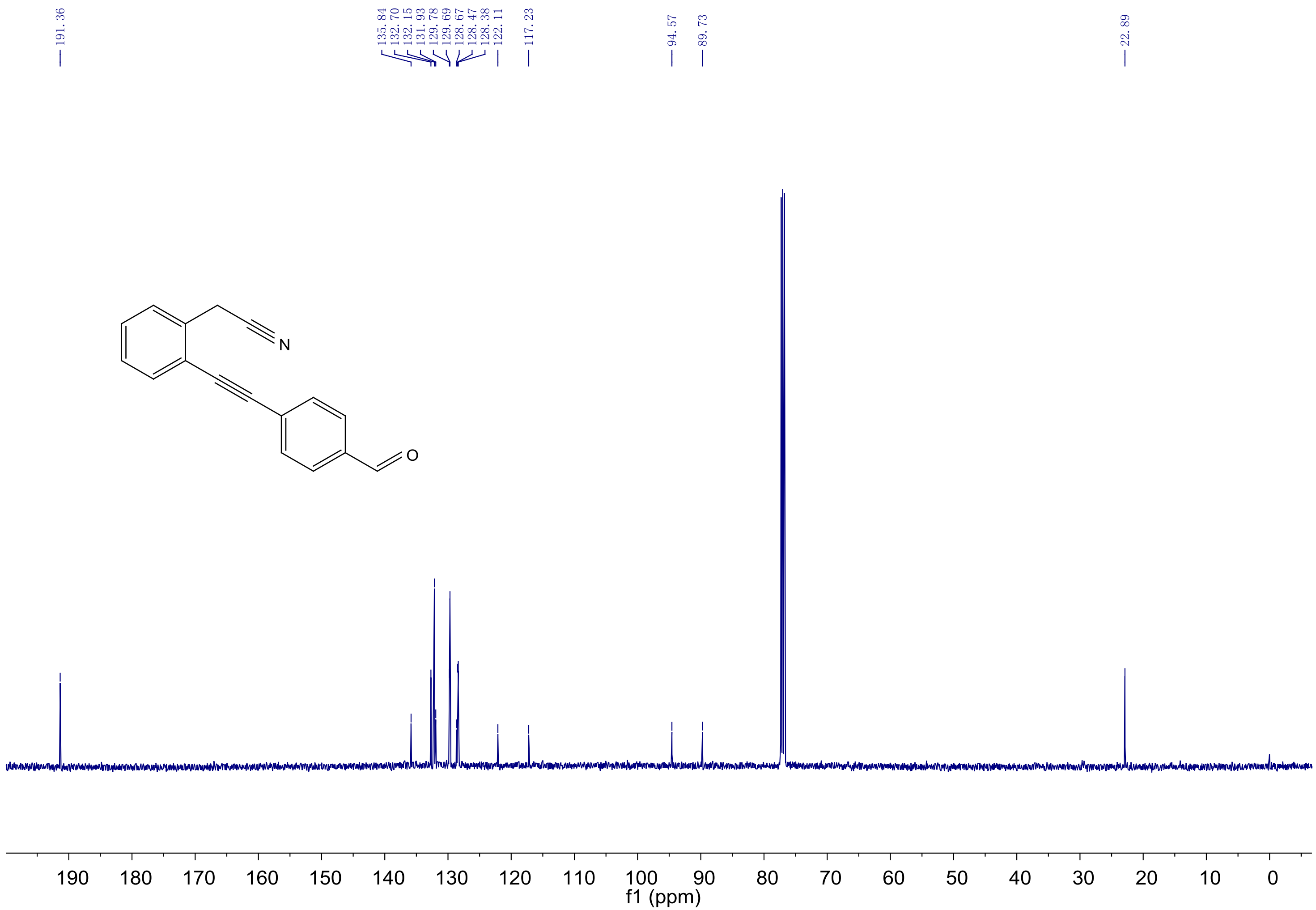
1i


7.58 7.58 7.56 7.55 7.51 7.50 7.49 7.49 7.48 7.47 7.47 7.43 7.42 7.40 7.40 7.38 7.37 7.36 7.35 7.35 7.34 7.33 7.33
3.96
N
Cl
1.19
3.00
3.96
2.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

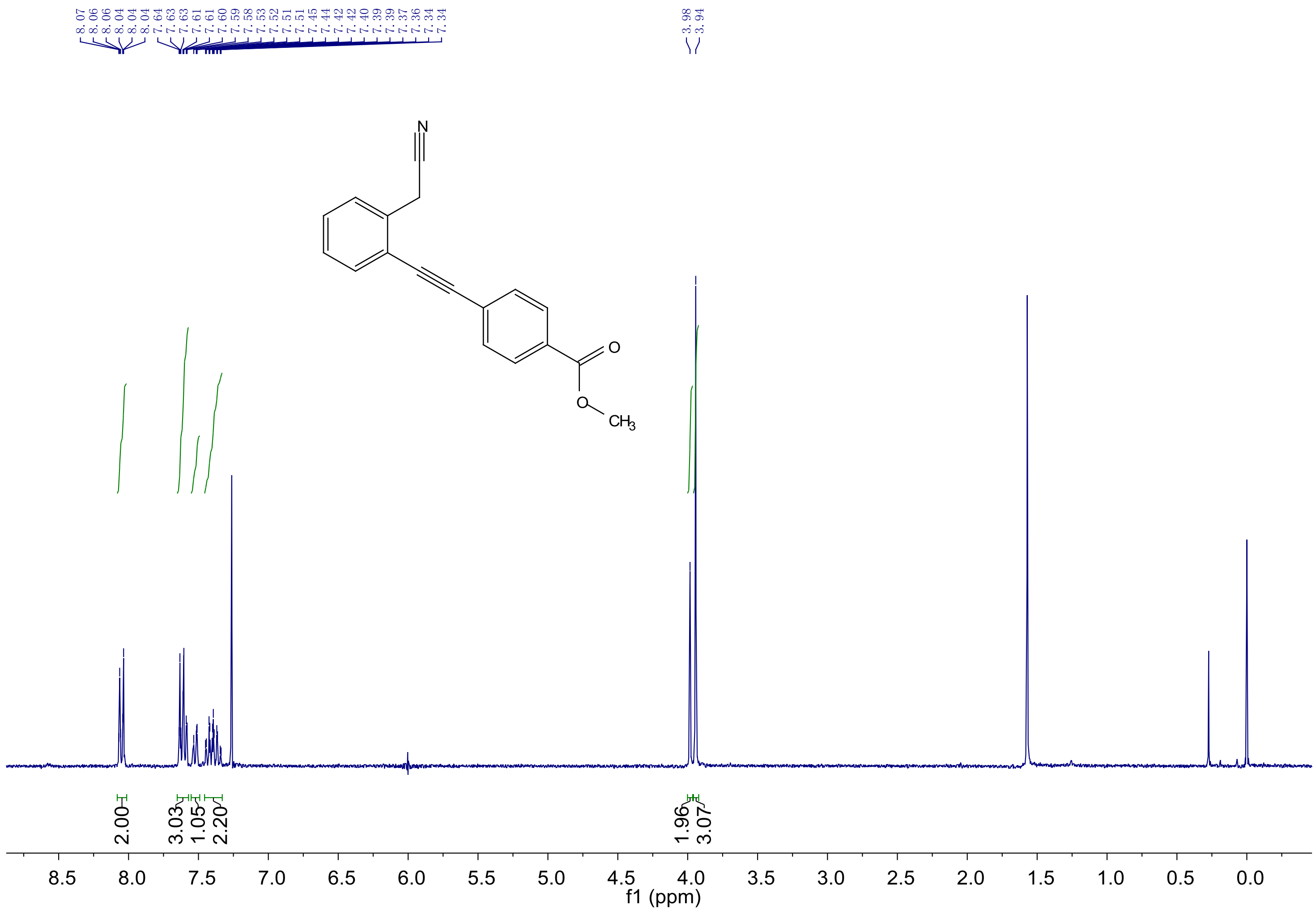
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

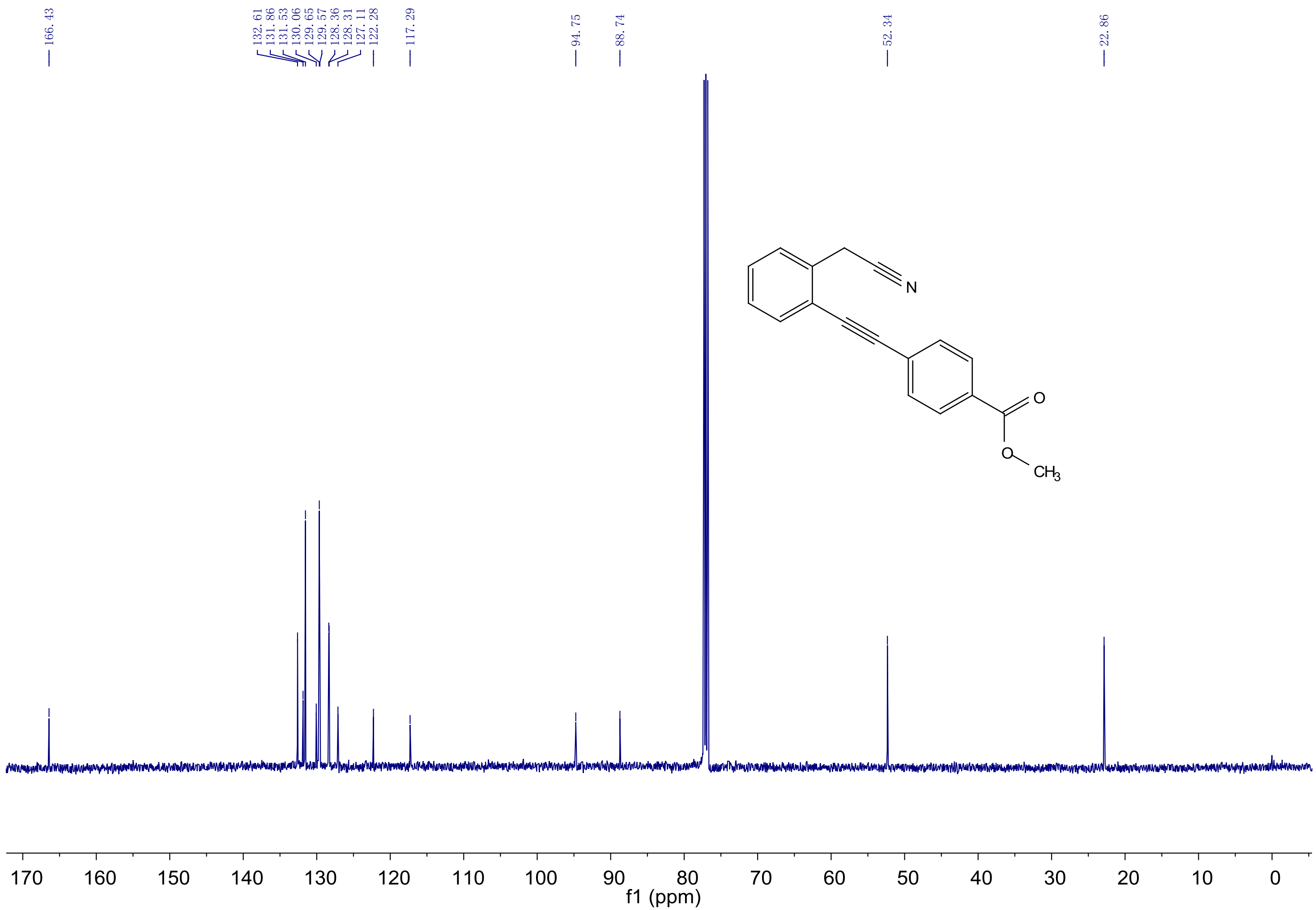
1j



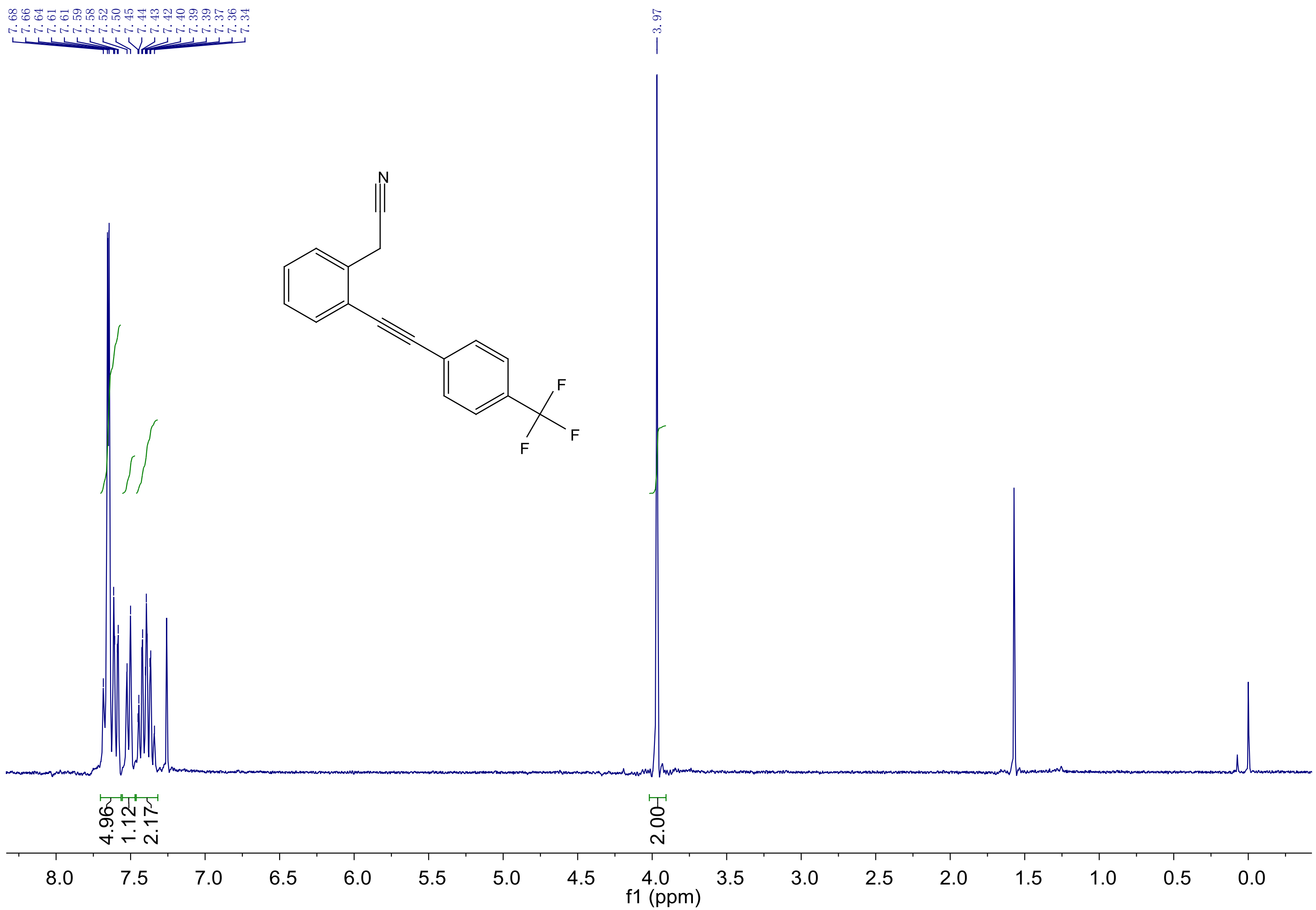

191.36
135.84
132.70
132.15
131.93
129.78
129.69
128.67
128.47
128.38
122.11
117.23
94.57
89.73
22.89
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1k

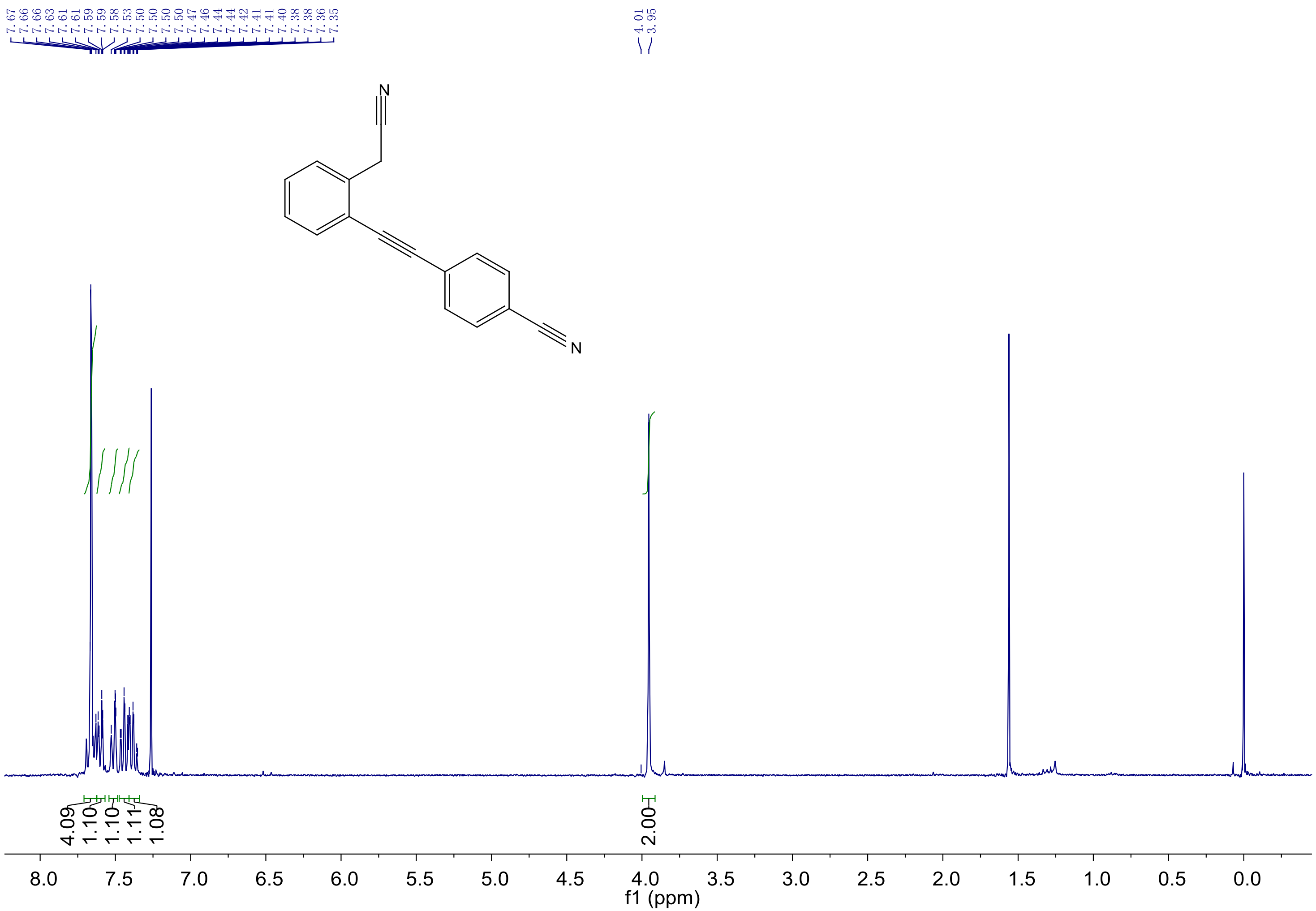

8.07
8.06
8.06
8.04
8.04
8.04
7.64
7.63
7.63
7.61
7.61
7.60
7.59
7.58
7.53
7.52
7.51
7.51
7.45
7.44
7.42
7.42
7.40
7.39
7.39
7.37
7.36
7.34
7.34
3.98
3.94
N
O
O
CH3
2.00
3.03
1.05
2.20
1.96
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

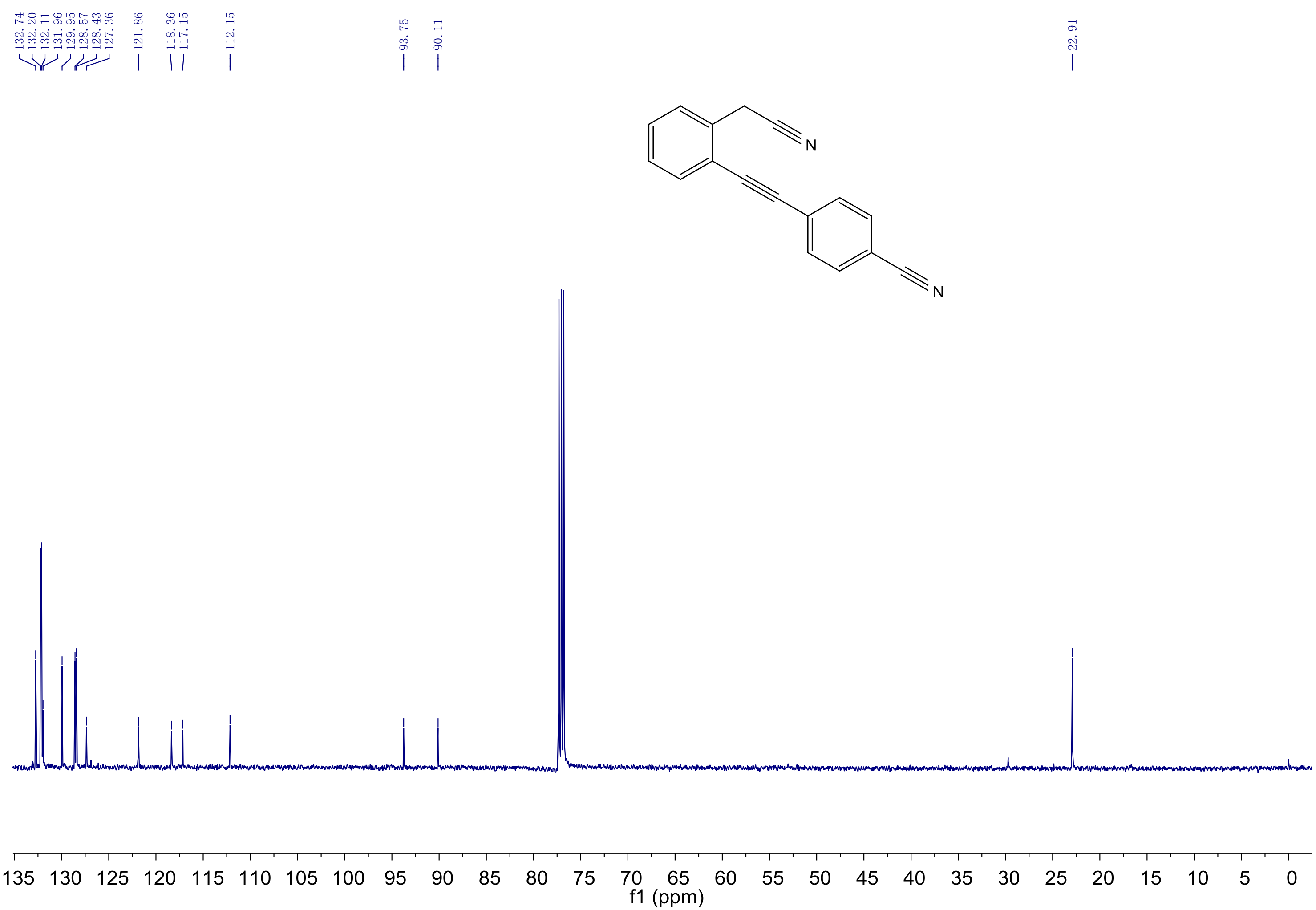

166.43
132.61
131.86
131.53
130.06
129.65
129.57
128.36
128.31
127.11
122.28
117.29
94.75
88.74
52.34
22.86
N
O
O
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1l

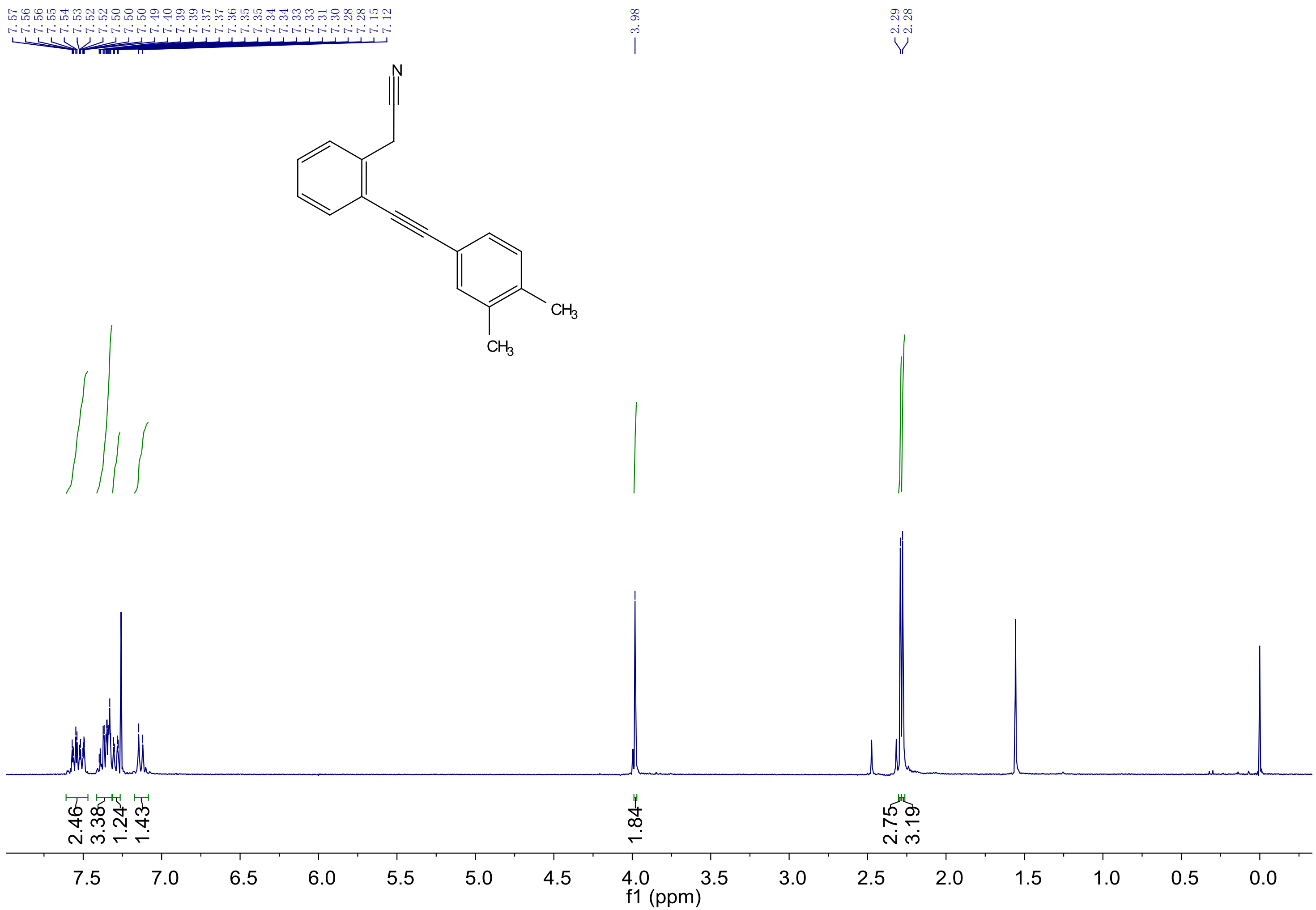

7.68
7.66
7.64
7.61
7.61
7.59
7.58
7.52
7.50
7.45
7.44
7.43
7.42
7.40
7.39
7.39
7.37
7.36
7.34
3.97
N
F
F
F
4.96
1.12
2.17
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

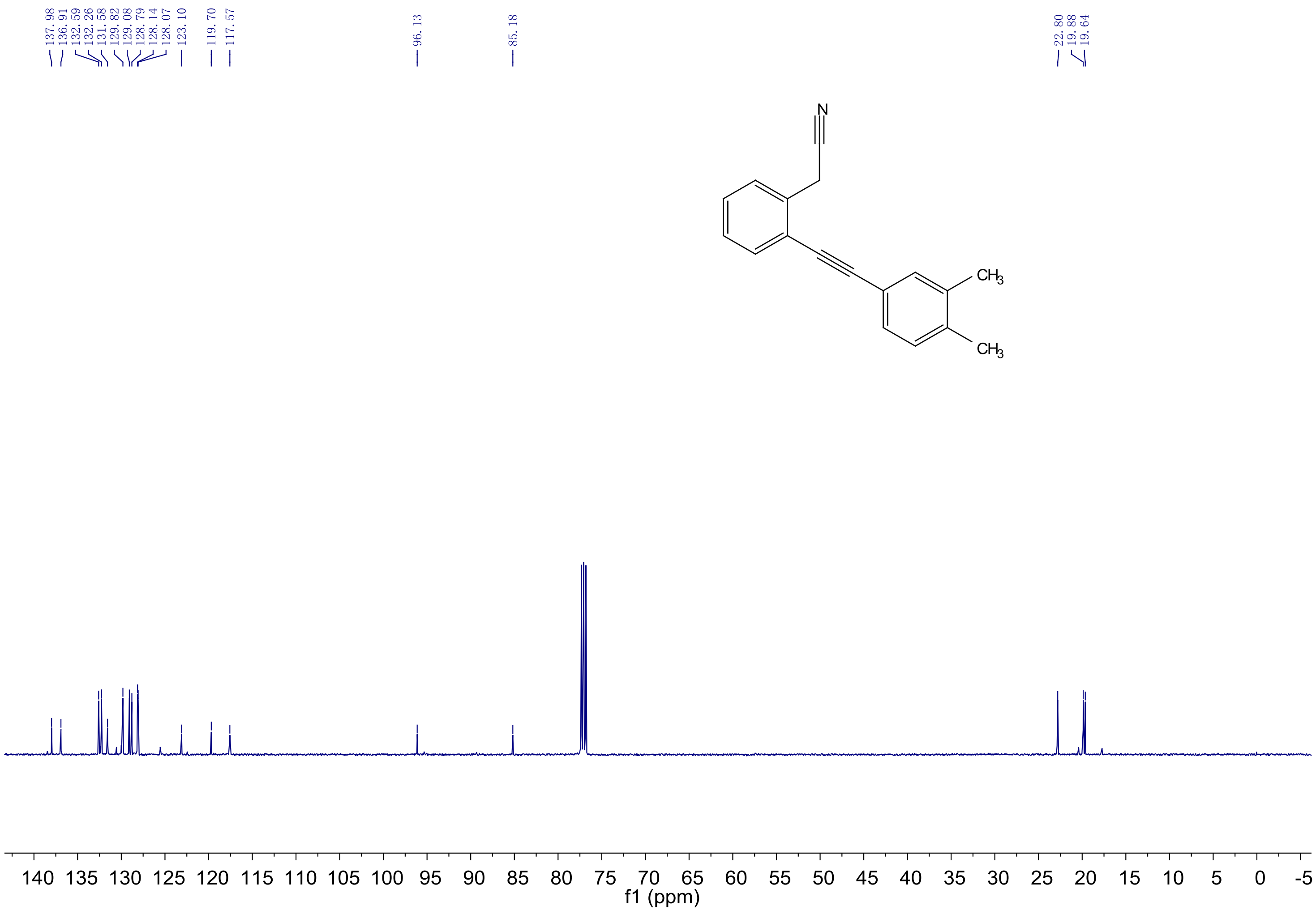
1m


7.67 7.66 7.66 7.63 7.61 7.61 7.59 7.59 7.58 7.53 7.50 7.50 7.50 7.47 7.46 7.44 7.44 7.42 7.41 7.41 7.40 7.38 7.38 7.36 7.35
4.01 3.95
N
N
4.09 1.10 1.10 1.11 1.08
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

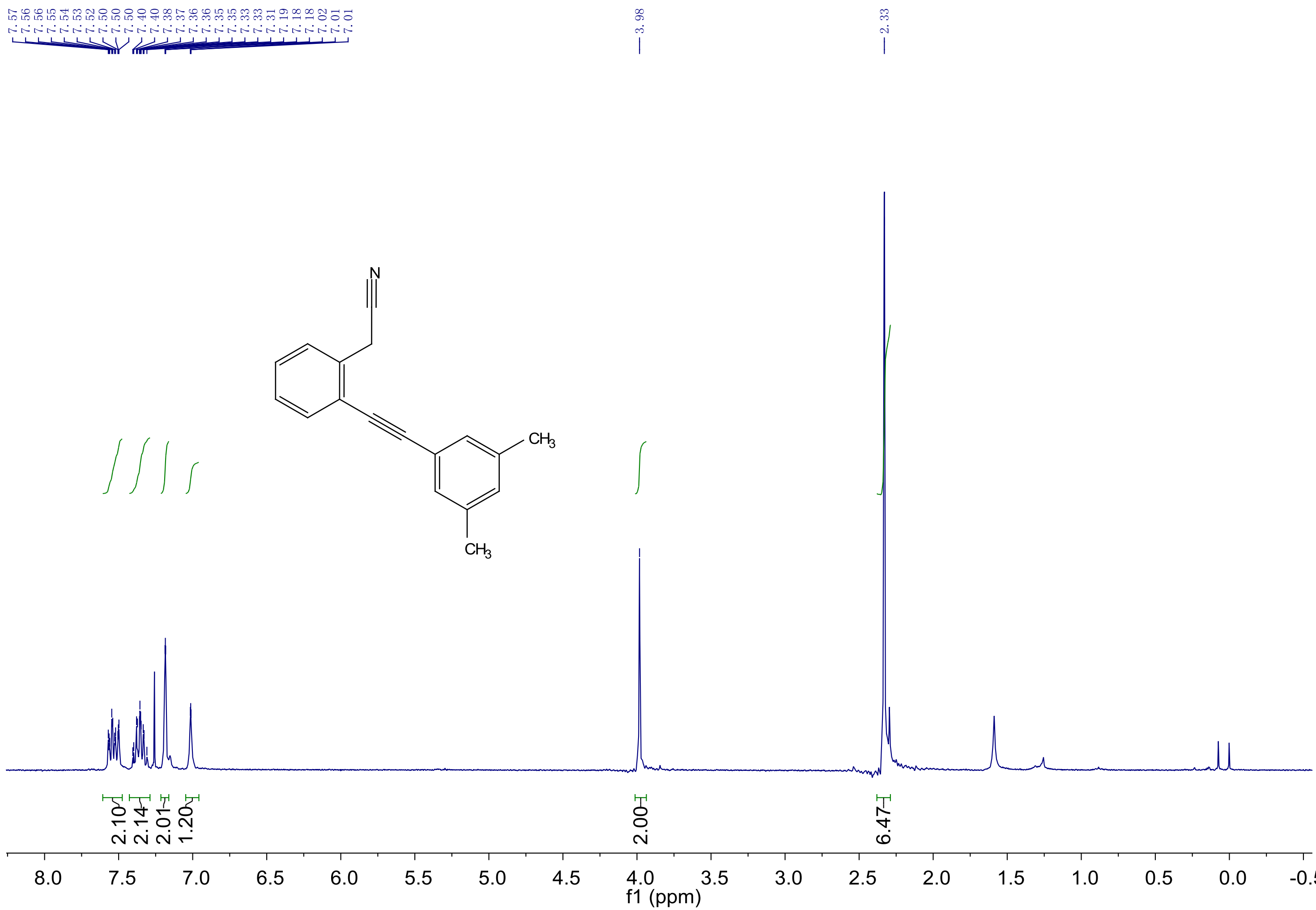

132.74
132.20
132.11
131.96
129.95
128.57
128.43
127.36
121.86
118.36
117.15
112.15
93.75
90.11
22.91
N
N
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

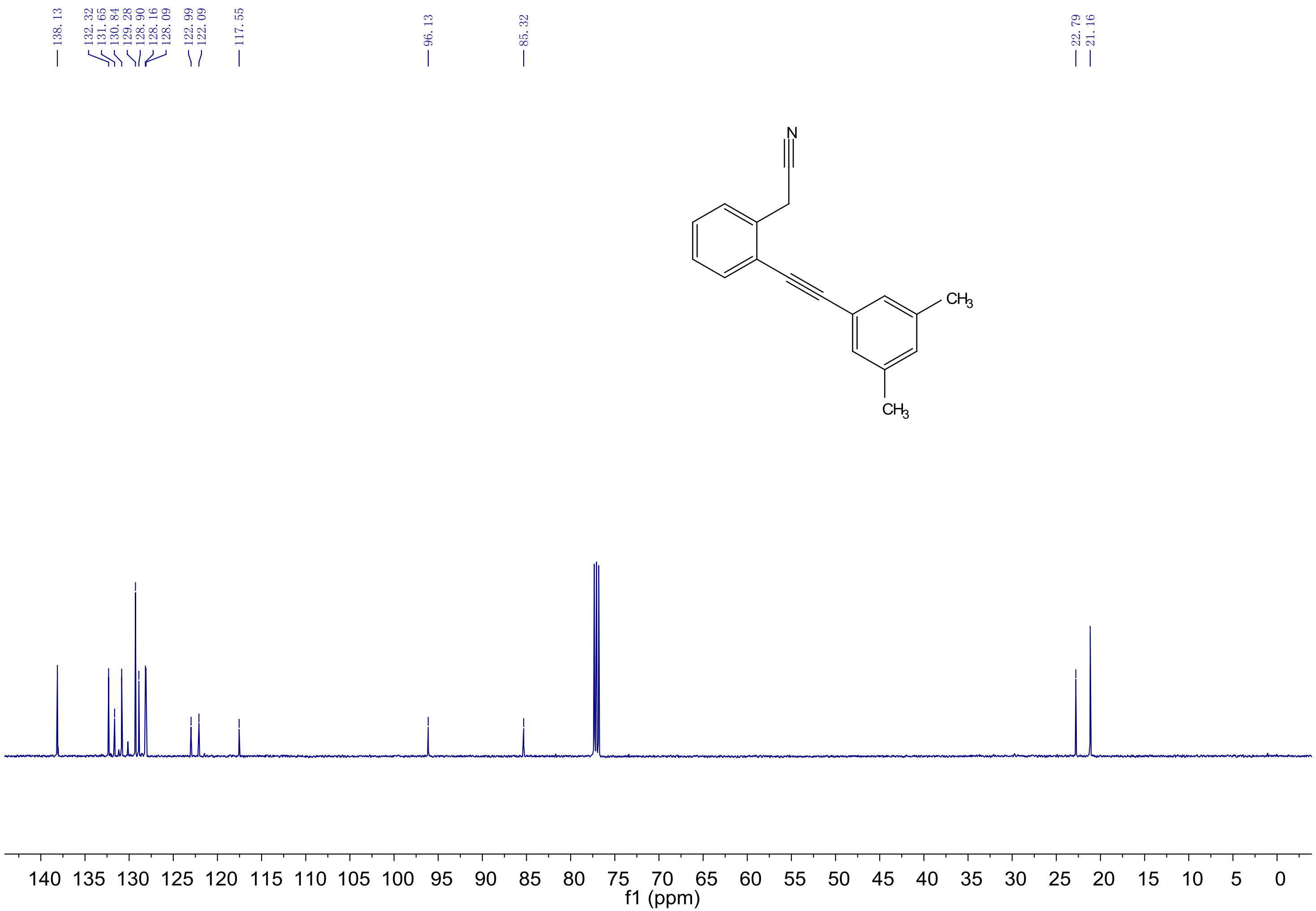
1n


7.57
7.56
7.56
7.55
7.54
7.53
7.52
7.52
7.50
7.50
7.50
7.49
7.40
7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.31
7.30
7.28
7.28
7.15
7.12
3.98
2.29
2.28
N
CH3
CH3
2.46
3.38
1.24
1.43
1.84
2.75
3.19
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

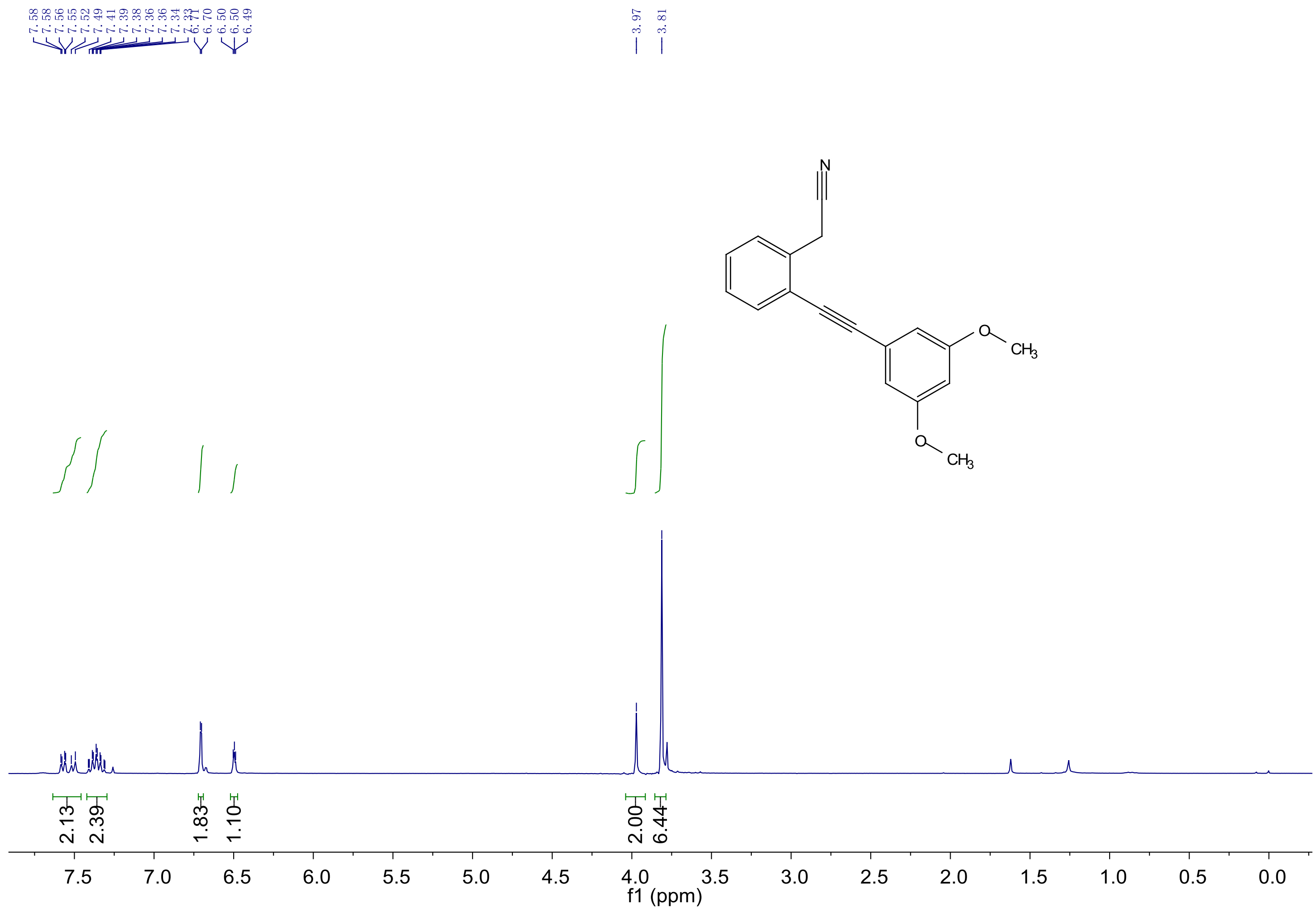

137.98
136.91
132.59
132.26
131.58
129.82
129.08
128.79
128.14
128.07
123.10
119.70
117.57
96.13
85.18
22.80
19.88
19.64
N
CH3
CH3
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

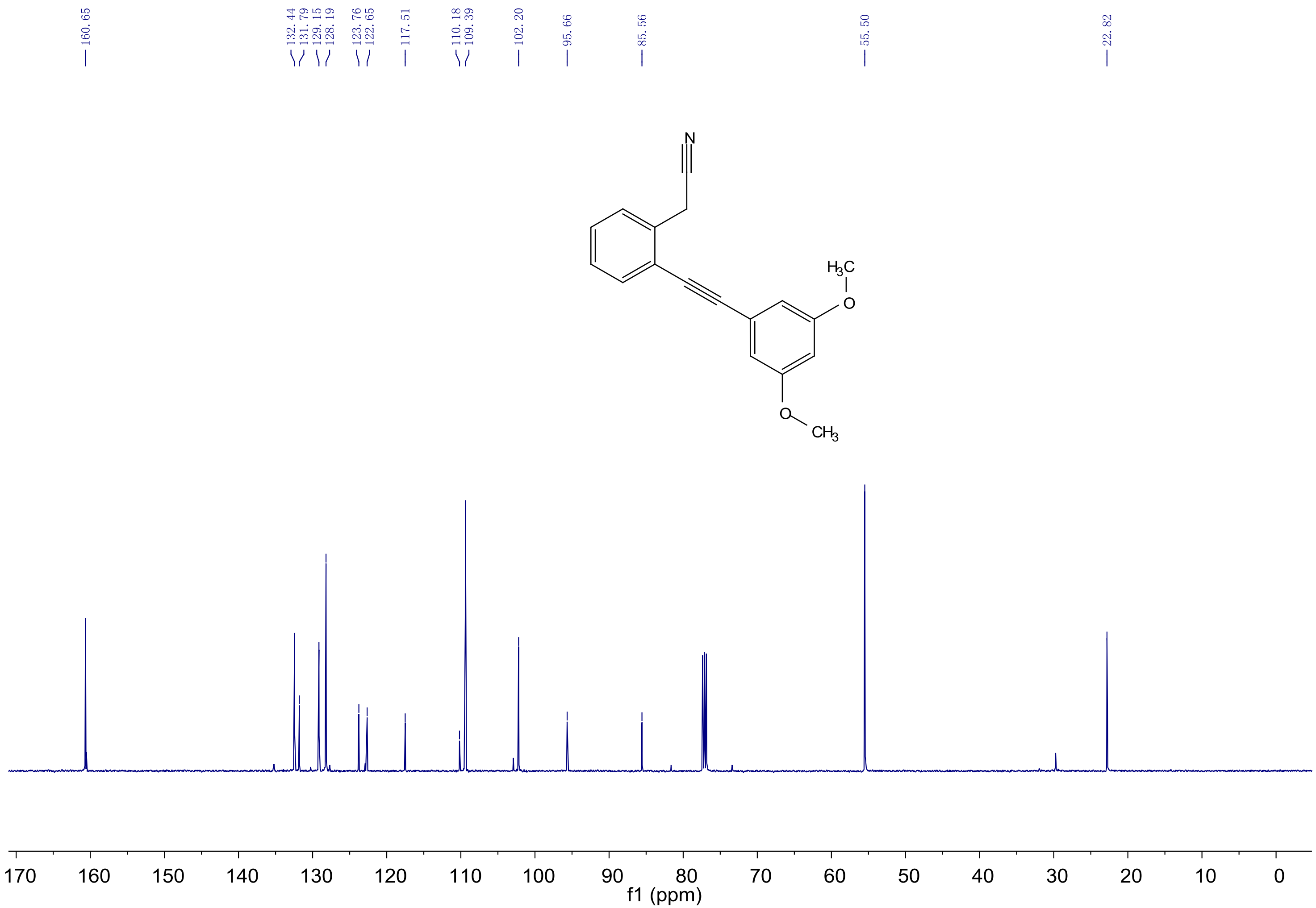
1o


7.57
7.56
7.56
7.55
7.54
7.53
7.52
7.50
7.50
7.50
7.40
7.38
7.37
7.36
7.36
7.35
7.35
7.33
7.33
7.31
7.19
7.18
7.18
7.02
7.01
7.01
3.98
2.33
N
CH3
CH3
2.10
2.14
2.01
1.20
2.00
6.47
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

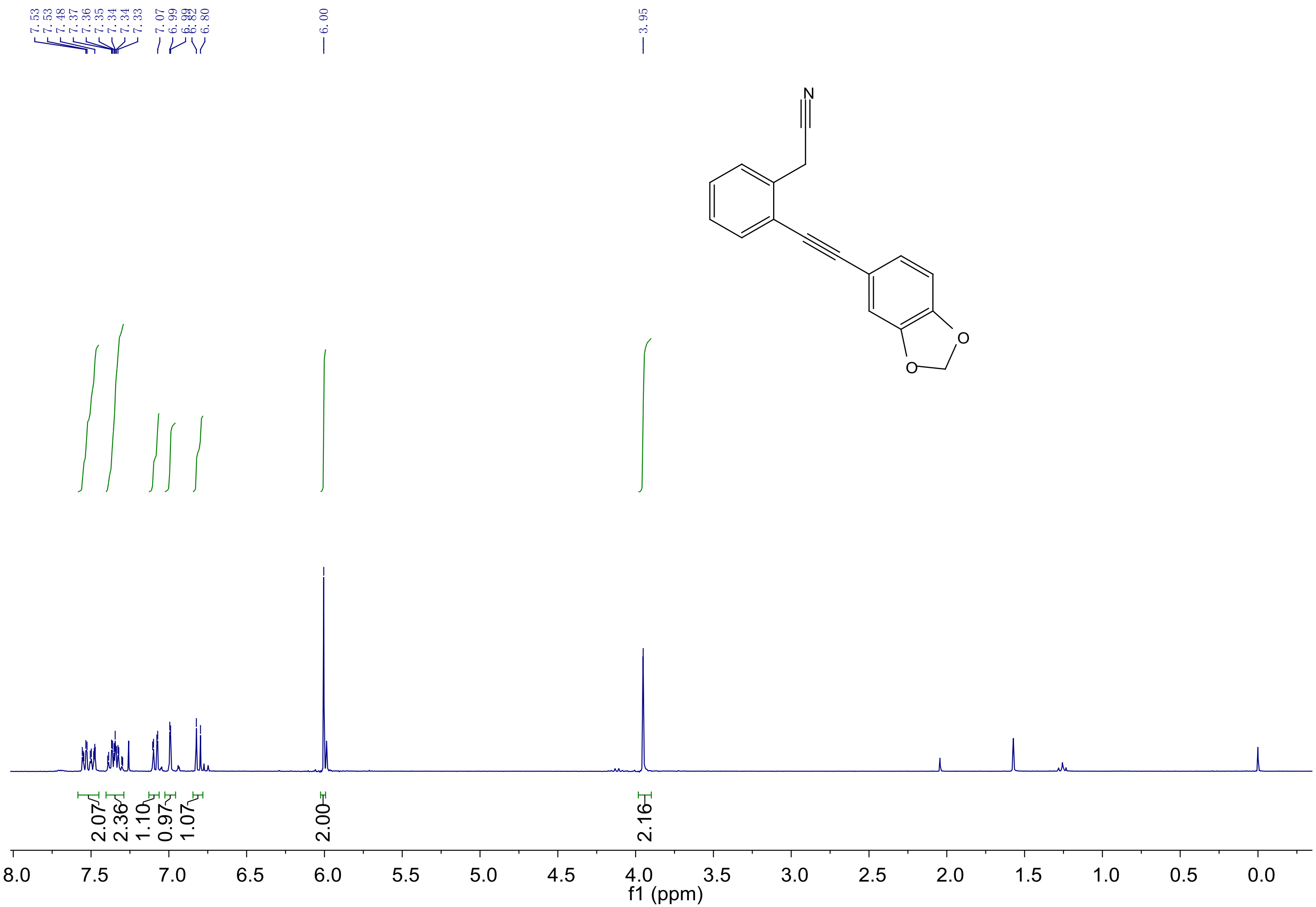

138.13
132.32
131.65
130.84
129.28
128.90
128.16
128.09
122.99
122.09
117.55
96.13
85.32
22.79
21.16
N
CH3
CH3
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

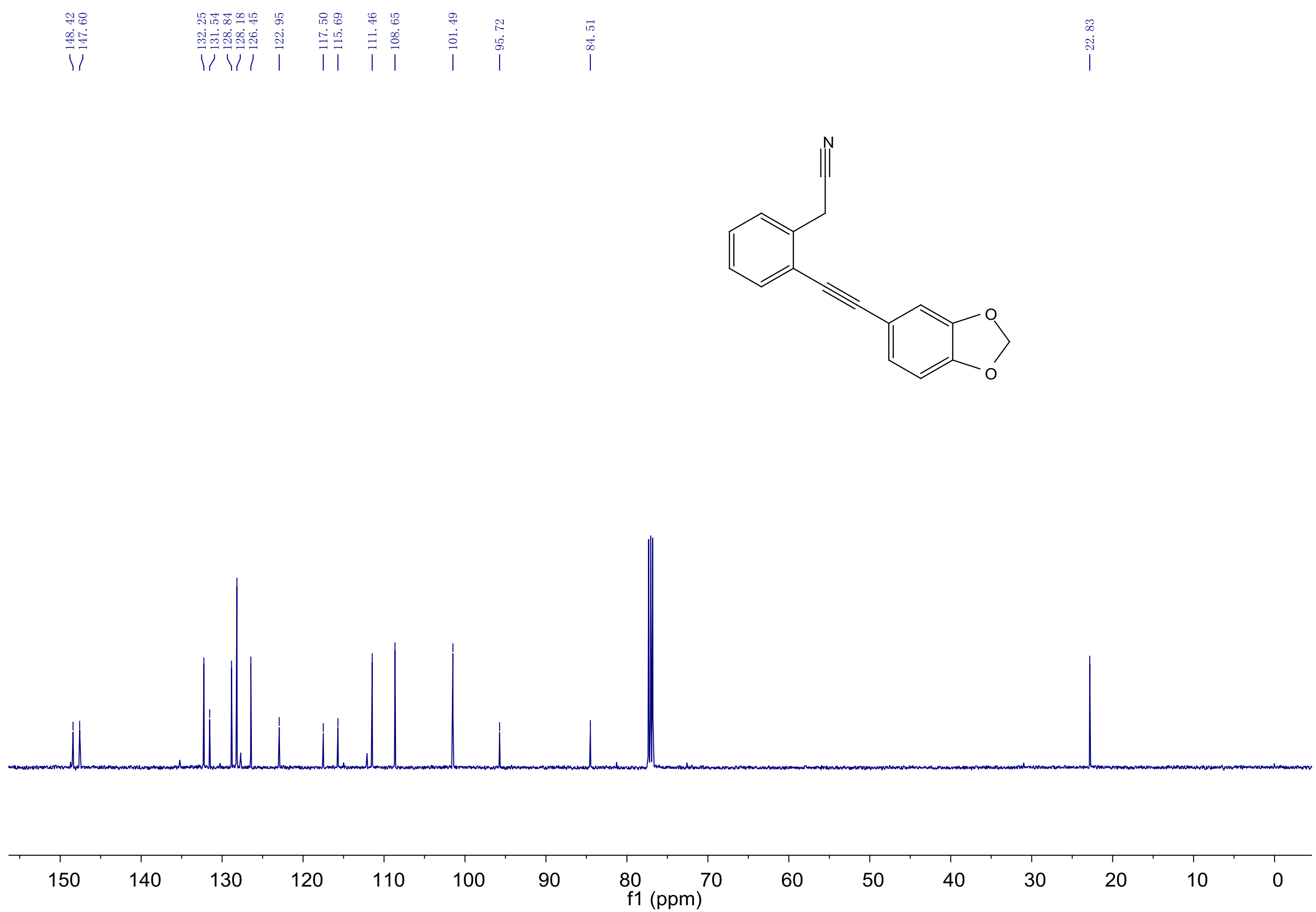
1p


7.58
7.58
7.56
7.55
7.52
7.49
7.41
7.39
7.38
7.36
7.36
7.34
7.33
6.71
6.70
6.50
6.50
6.49
3.97
3.81
N
O
CH3
O
CH3
2.13
2.39
1.83
1.10
2.00
6.44
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

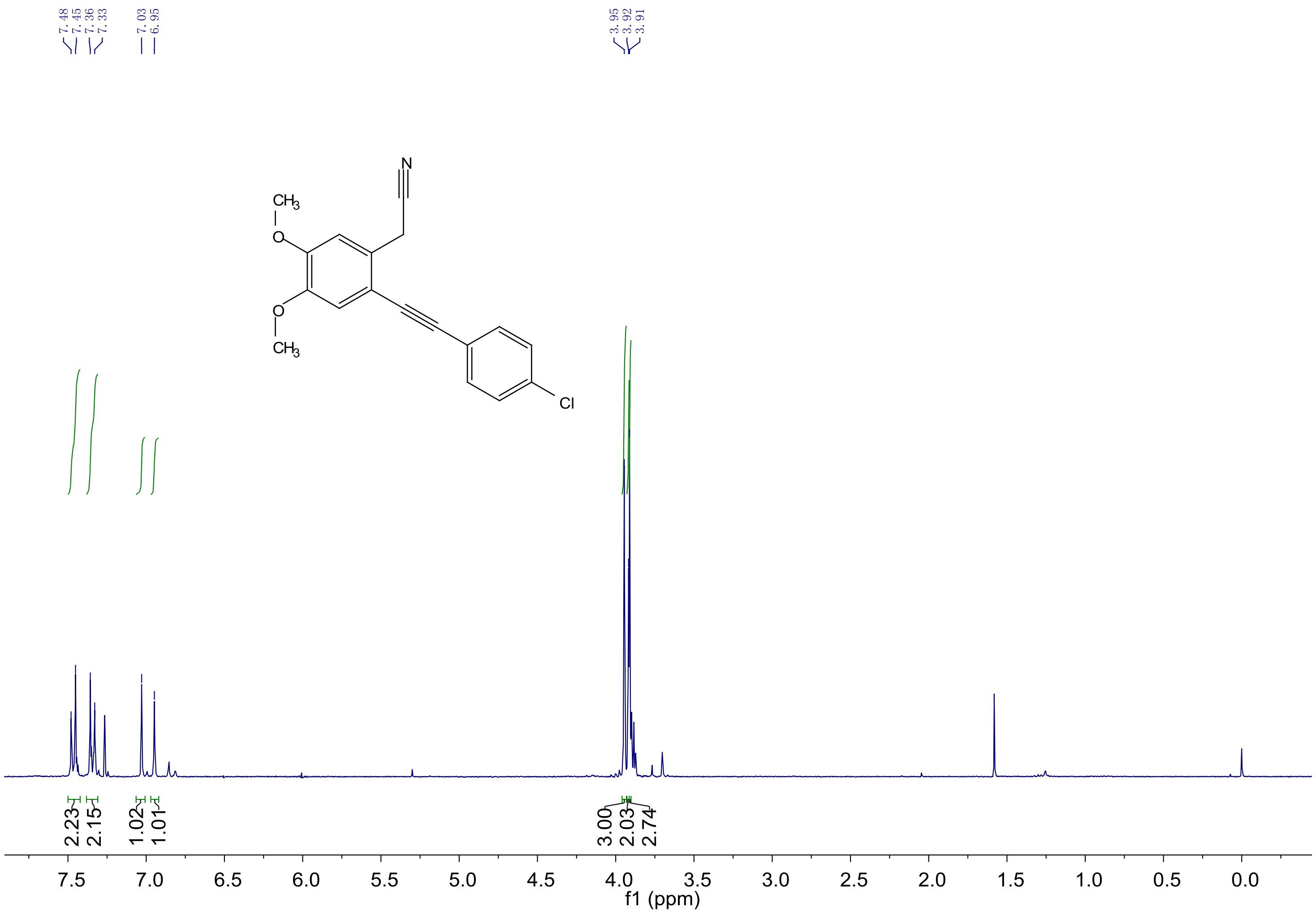

160.65
132.44
131.79
129.15
128.19
123.76
122.65
117.51
110.18
109.39
102.20
95.66
85.56
55.50
22.82
N
H3C
O
O
CH3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

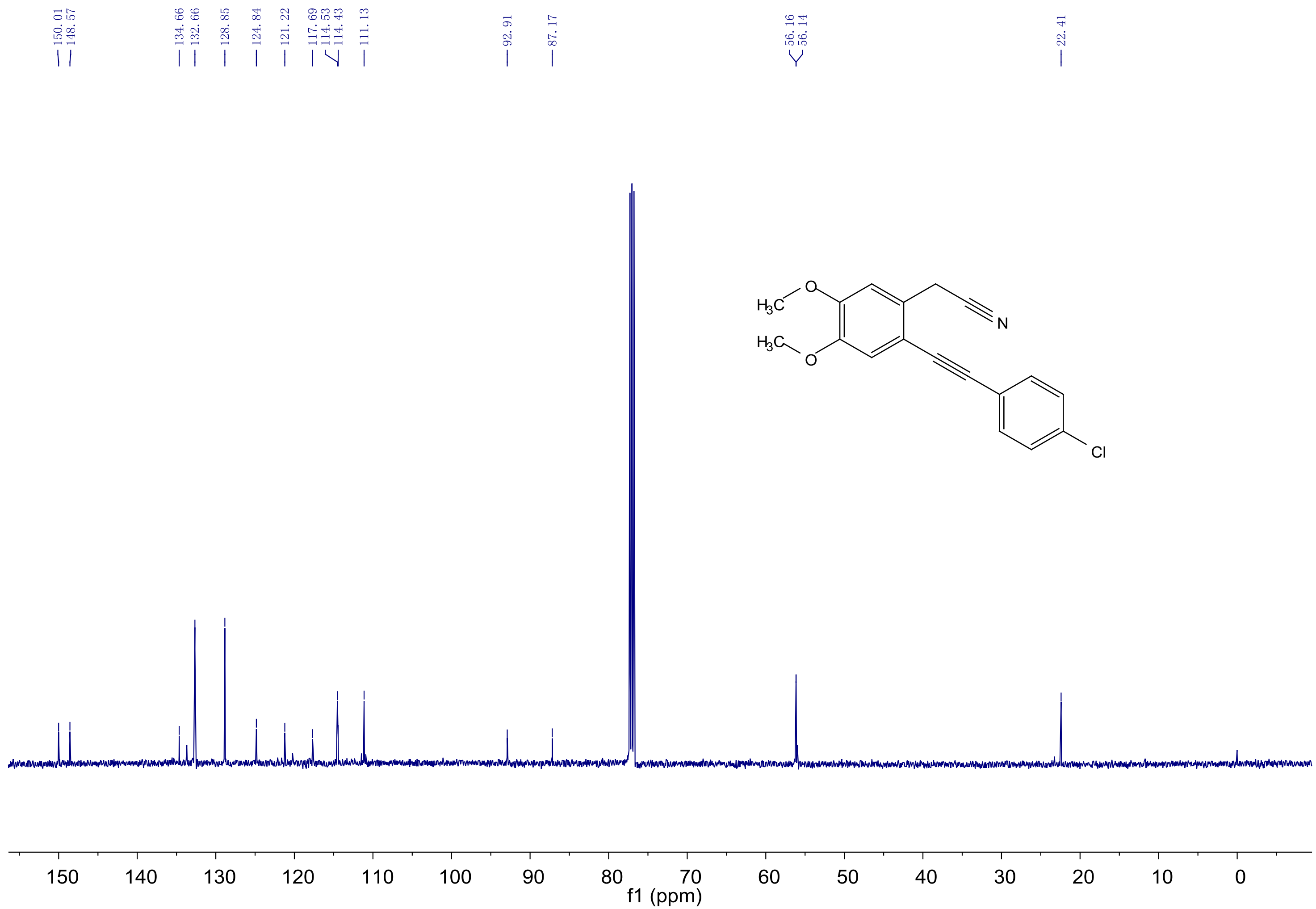
1q


7.53
7.53
7.48
7.37
7.36
7.35
7.34
7.34
7.33
7.07
6.99
6.99
6.82
6.80
6.00
3.95
N
O
O
2.07
2.36
1.10
0.97
1.07
2.00
2.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

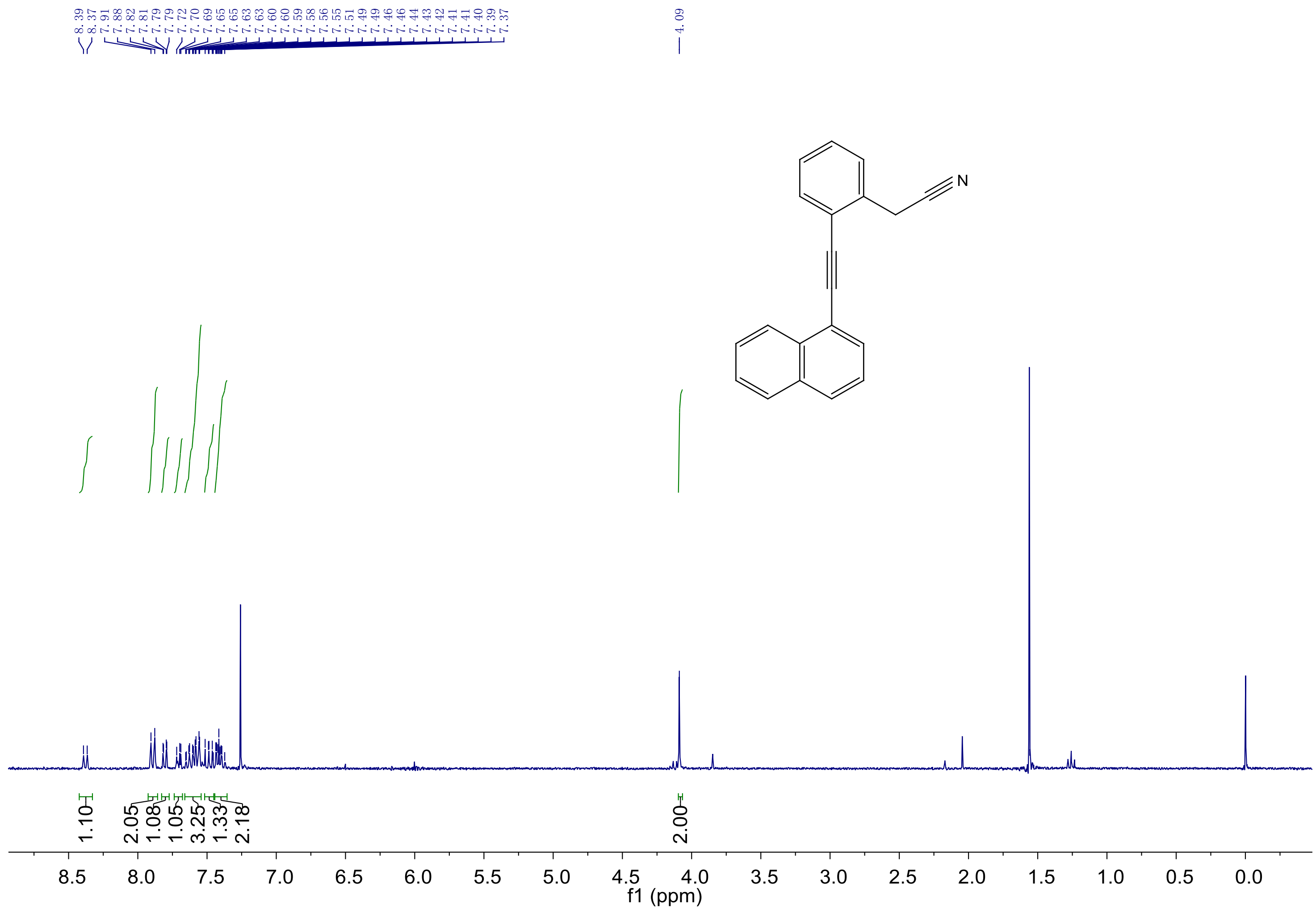

148.42
147.60
132.25
131.54
128.84
128.18
126.45
122.95
117.50
115.69
111.46
108.65
101.49
95.72
84.51
22.83
N
O
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

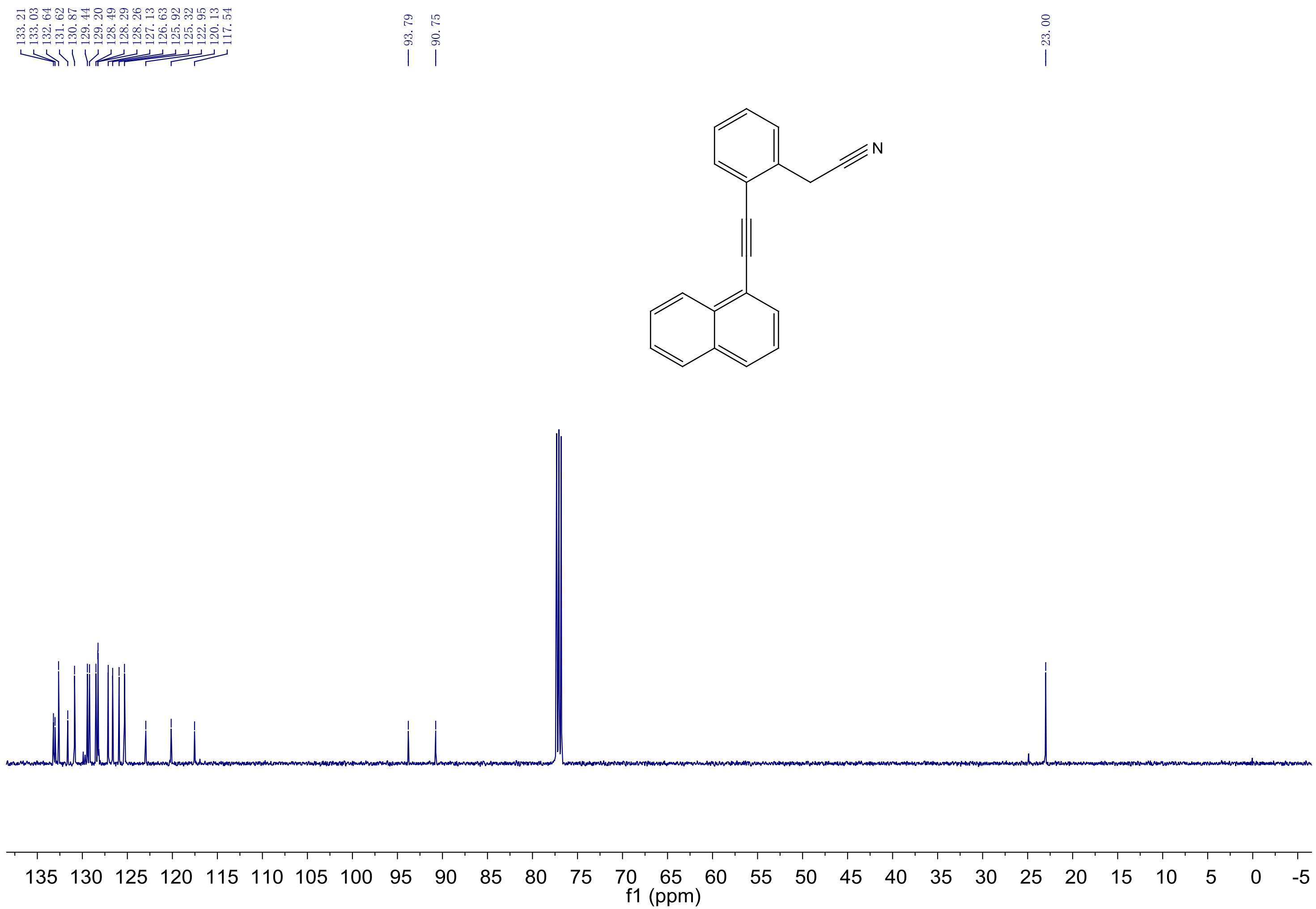
1r


7.48
7.45
7.36
7.33
7.03
6.95
3.95
3.92
3.91
N
CH3
O
O
CH3
Cl
2.23
2.15
1.02
1.01
3.00
2.03
2.74
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

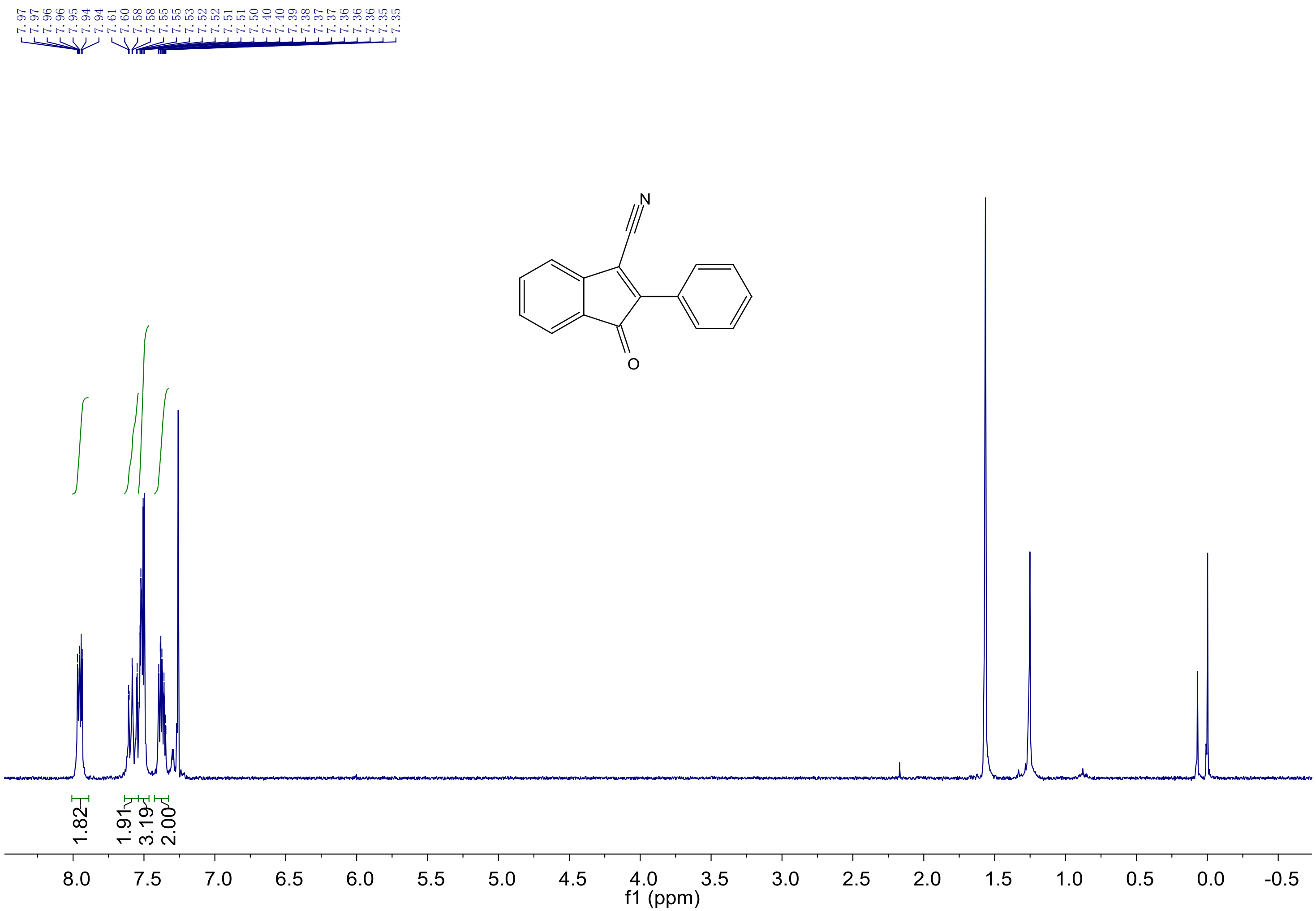

150.01
148.57
134.66
132.66
128.85
124.84
121.22
117.69
114.53
114.43
111.13
92.91
87.17
56.16
56.14
22.41
H_3C
O
H_3C
O
N
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

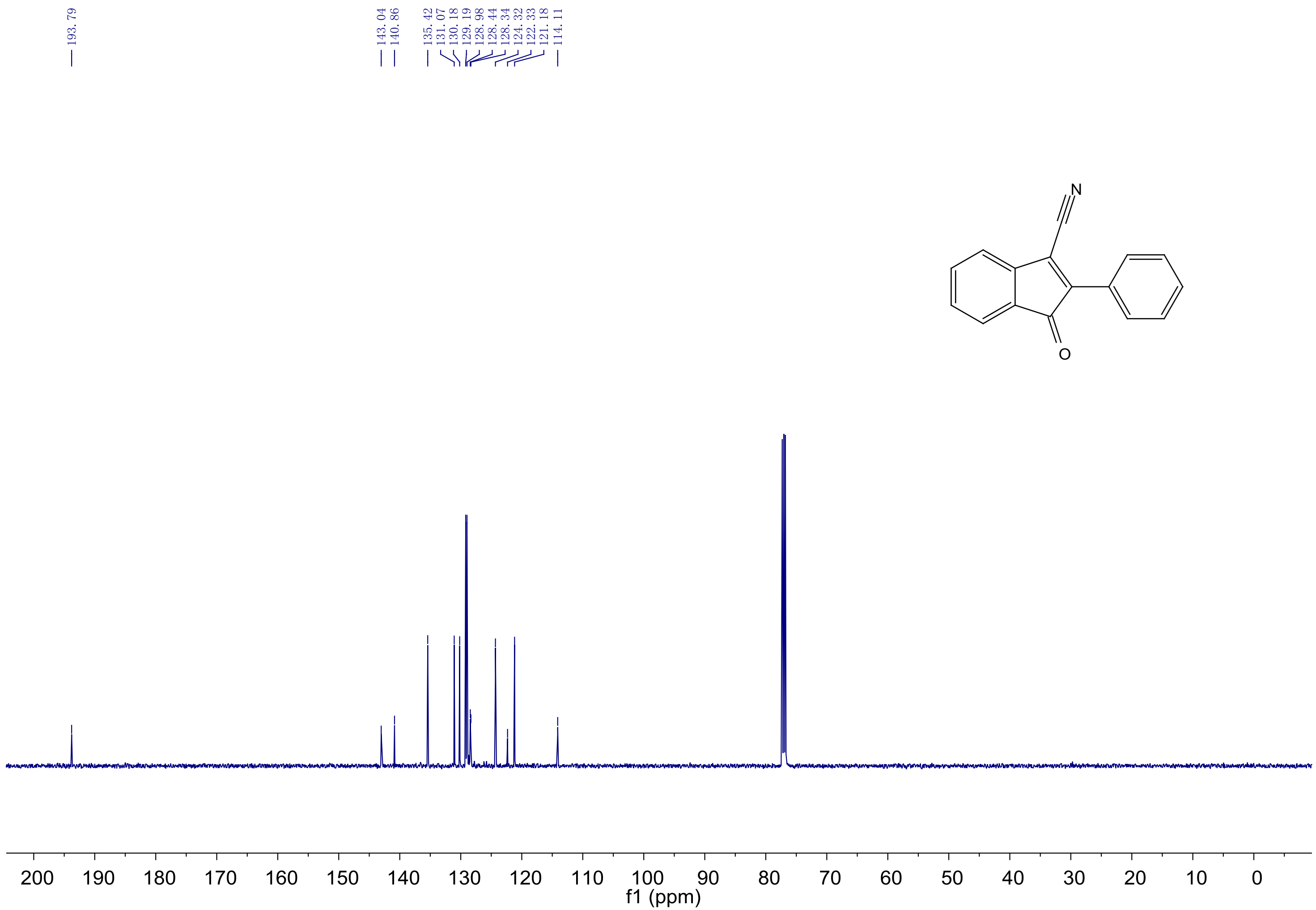
1s


8.39
8.37
7.91
7.88
7.82
7.81
7.79
7.79
7.72
7.70
7.69
7.65
7.65
7.63
7.63
7.60
7.59
7.58
7.56
7.55
7.51
7.49
7.49
7.46
7.46
7.44
7.43
7.42
7.41
7.40
7.39
7.37
4.09
N
1.10
2.05
1.08
1.05
3.25
1.33
2.18
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

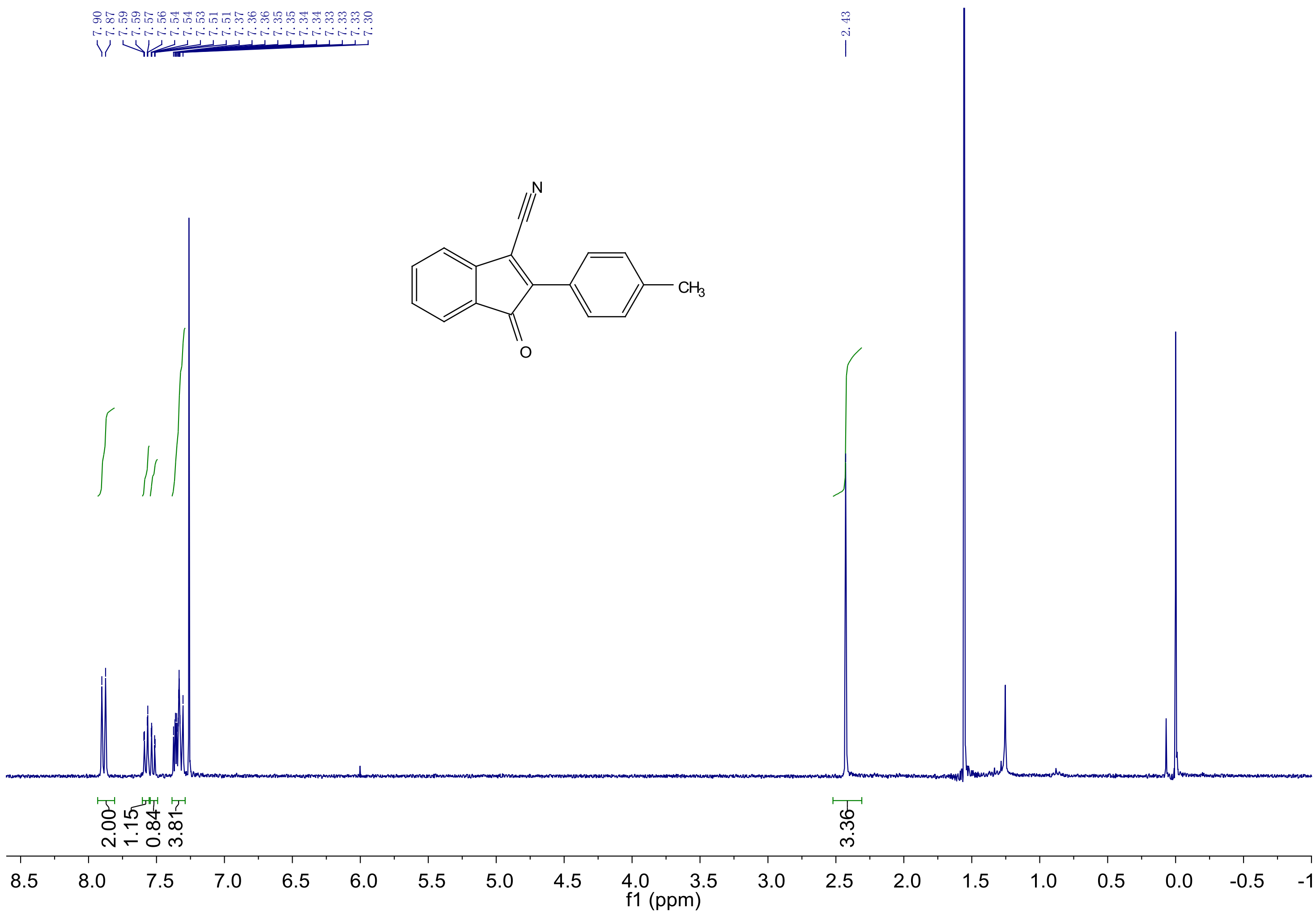

133.21
133.03
132.64
131.62
130.87
129.44
129.20
128.49
128.29
128.26
127.13
126.63
125.92
125.32
122.95
120.13
117.54
93.79
90.75
23.00
N
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

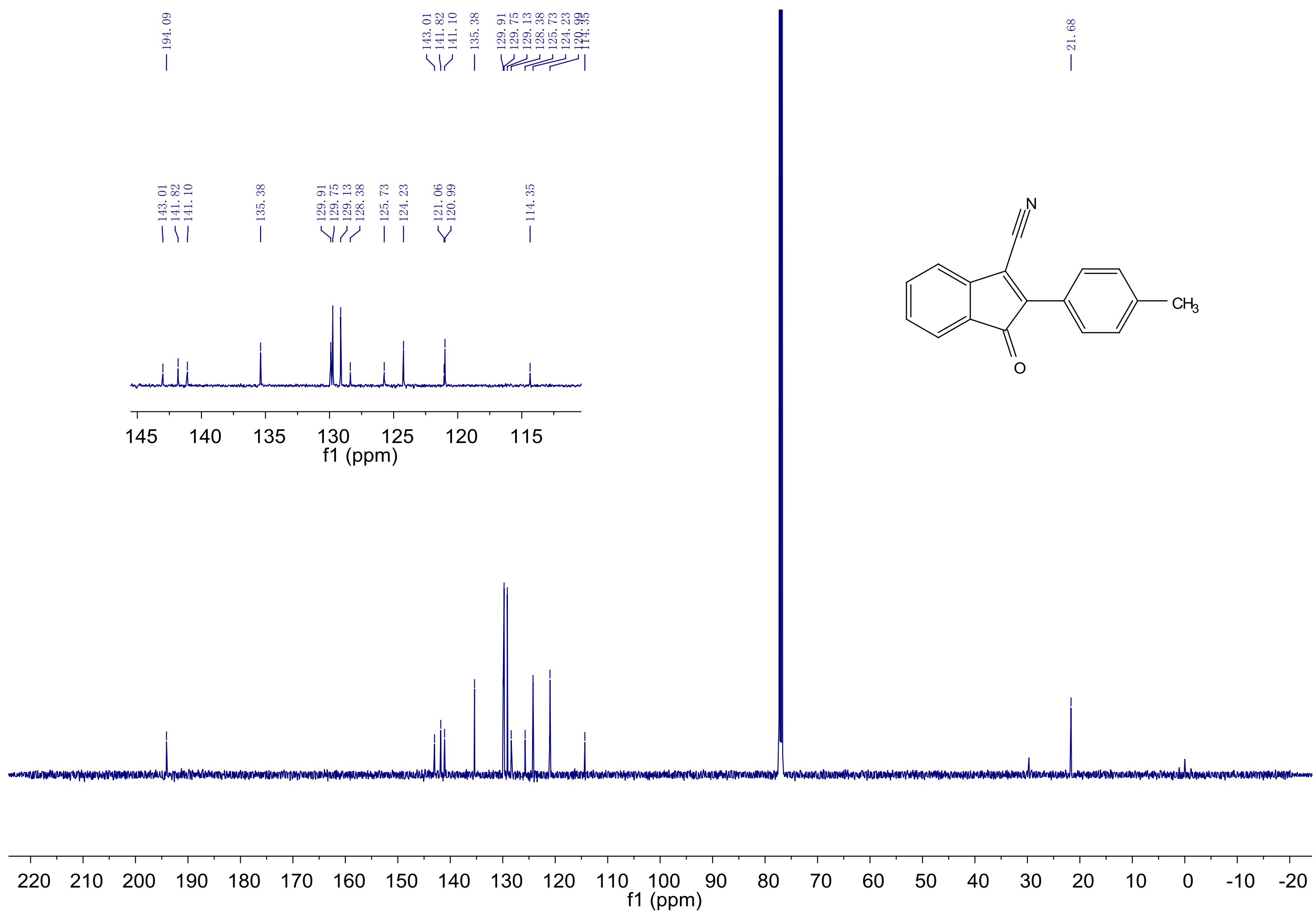
2a


7.97 7.97 7.96 7.96 7.95 7.94 7.94 7.61 7.60 7.58 7.58 7.55 7.55 7.53 7.52 7.52 7.51 7.51 7.50 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35
N
O
1.82
1.91
3.19
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

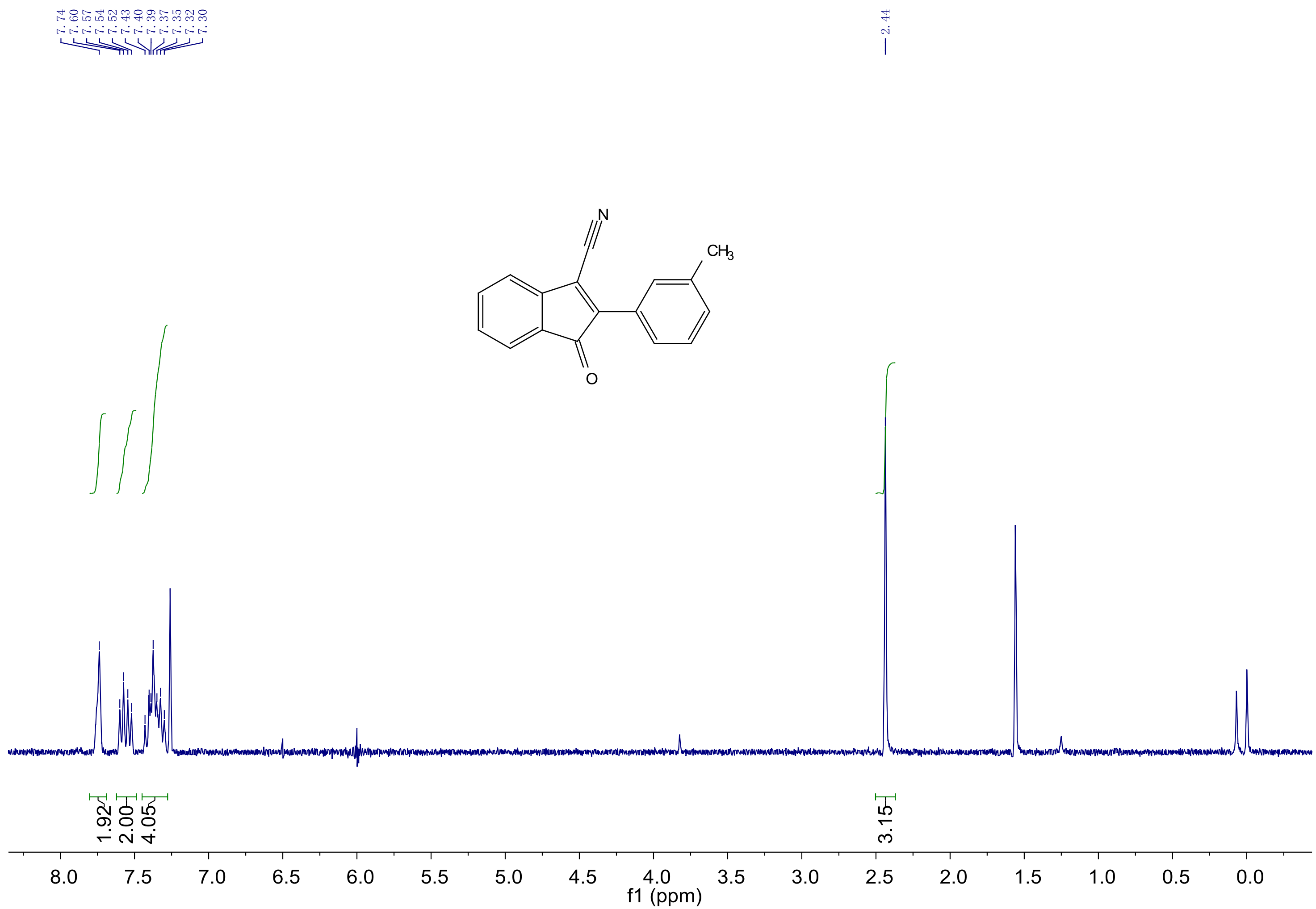

193.79
143.04
140.86
135.42
131.07
130.18
129.19
128.98
128.44
128.34
124.32
122.33
121.18
114.11
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2b

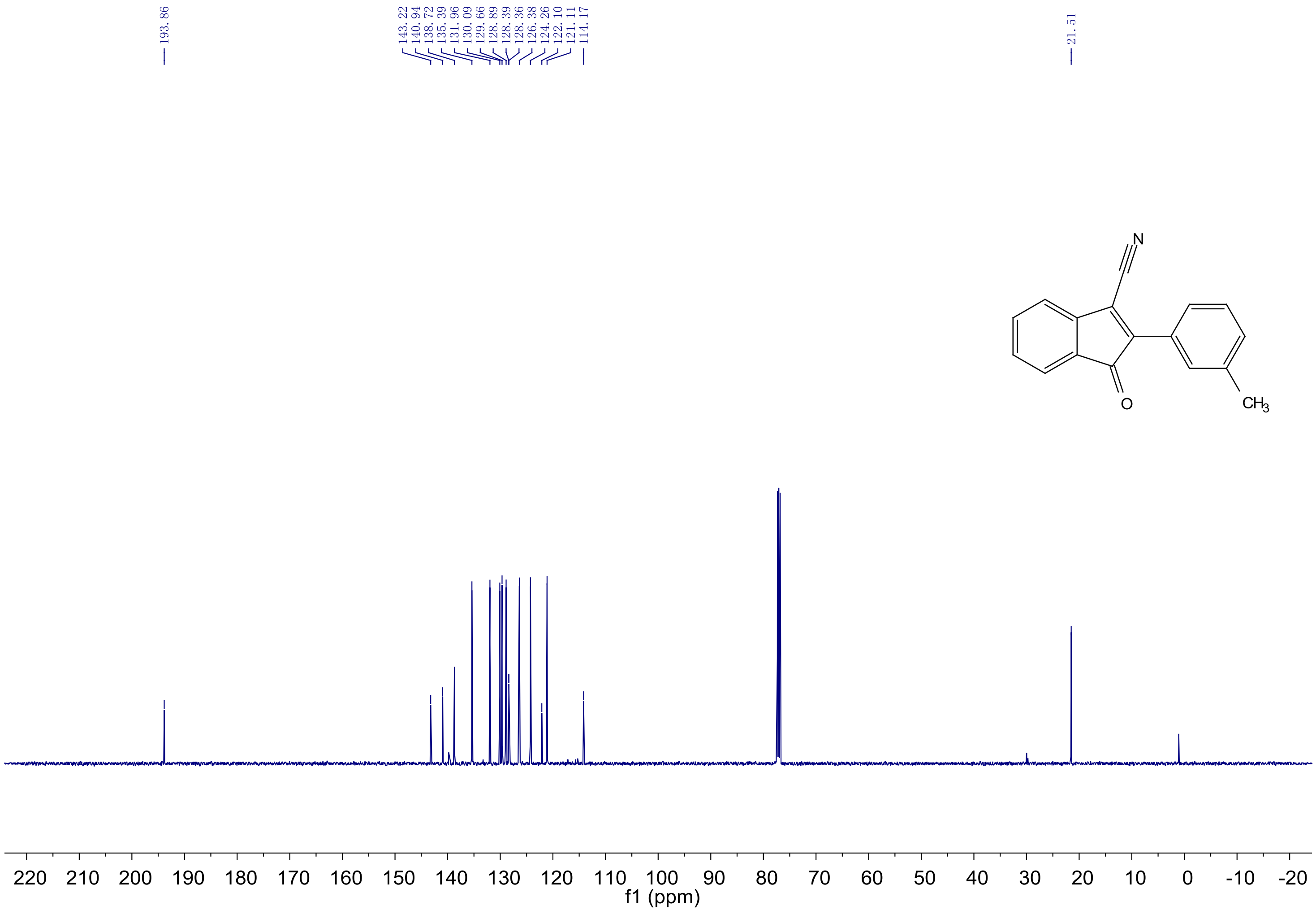

7.90
7.87
7.59
7.59
7.57
7.56
7.54
7.54
7.53
7.51
7.51
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.30
2.43
N
CH3
O
2.00
1.15
0.84
3.81
3.36
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


194.09
143.01
141.82
141.10
135.38
129.91
129.75
129.13
128.38
125.73
124.23
120.99
114.35
21.68
121.06
f1 (ppm)
N
CH3
O

2c

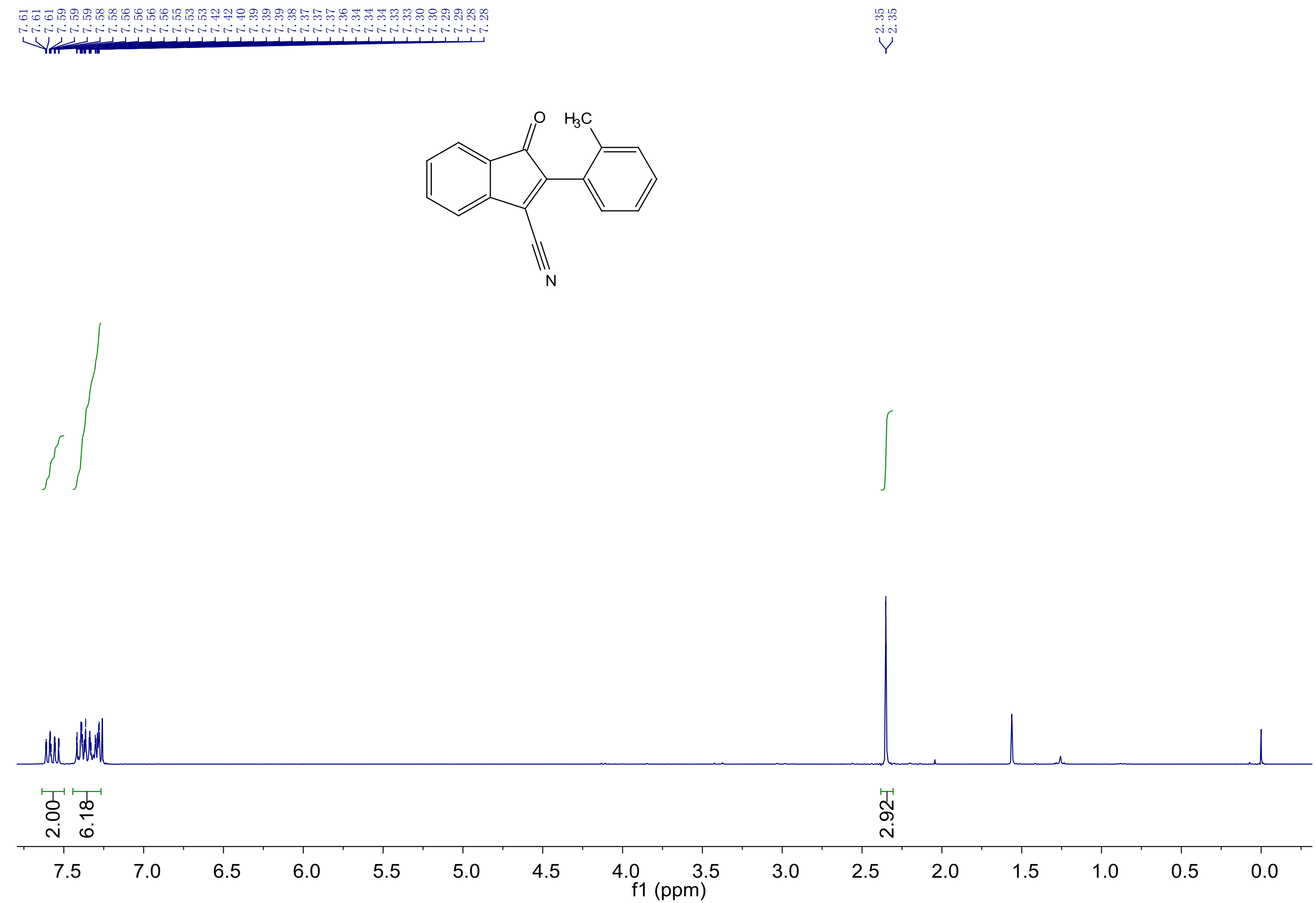

7.74
7.60
7.57
7.54
7.52
7.43
7.40
7.39
7.37
7.35
7.32
7.30
2.44
N
CH3
O
1.92
2.00
4.05
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

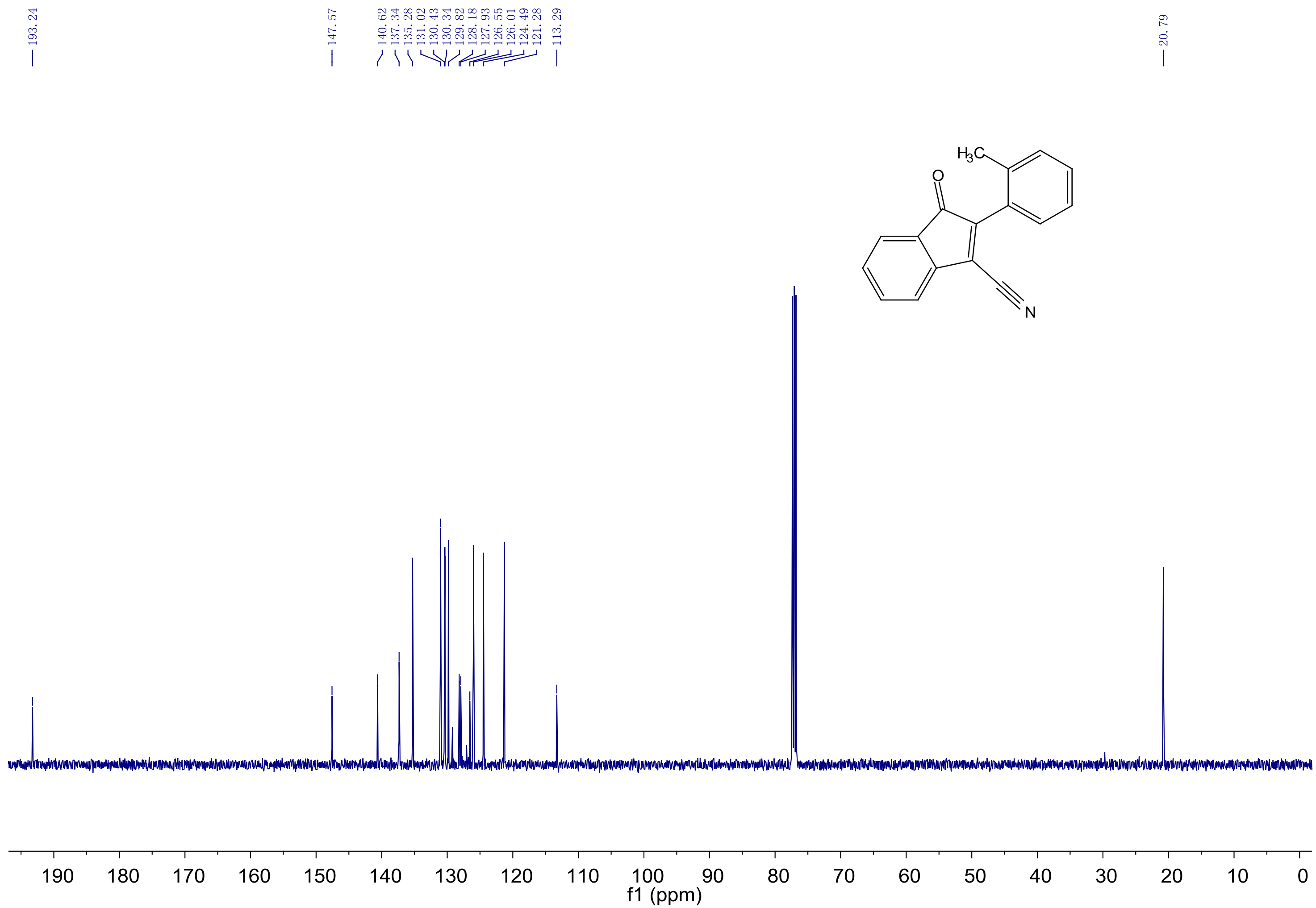
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



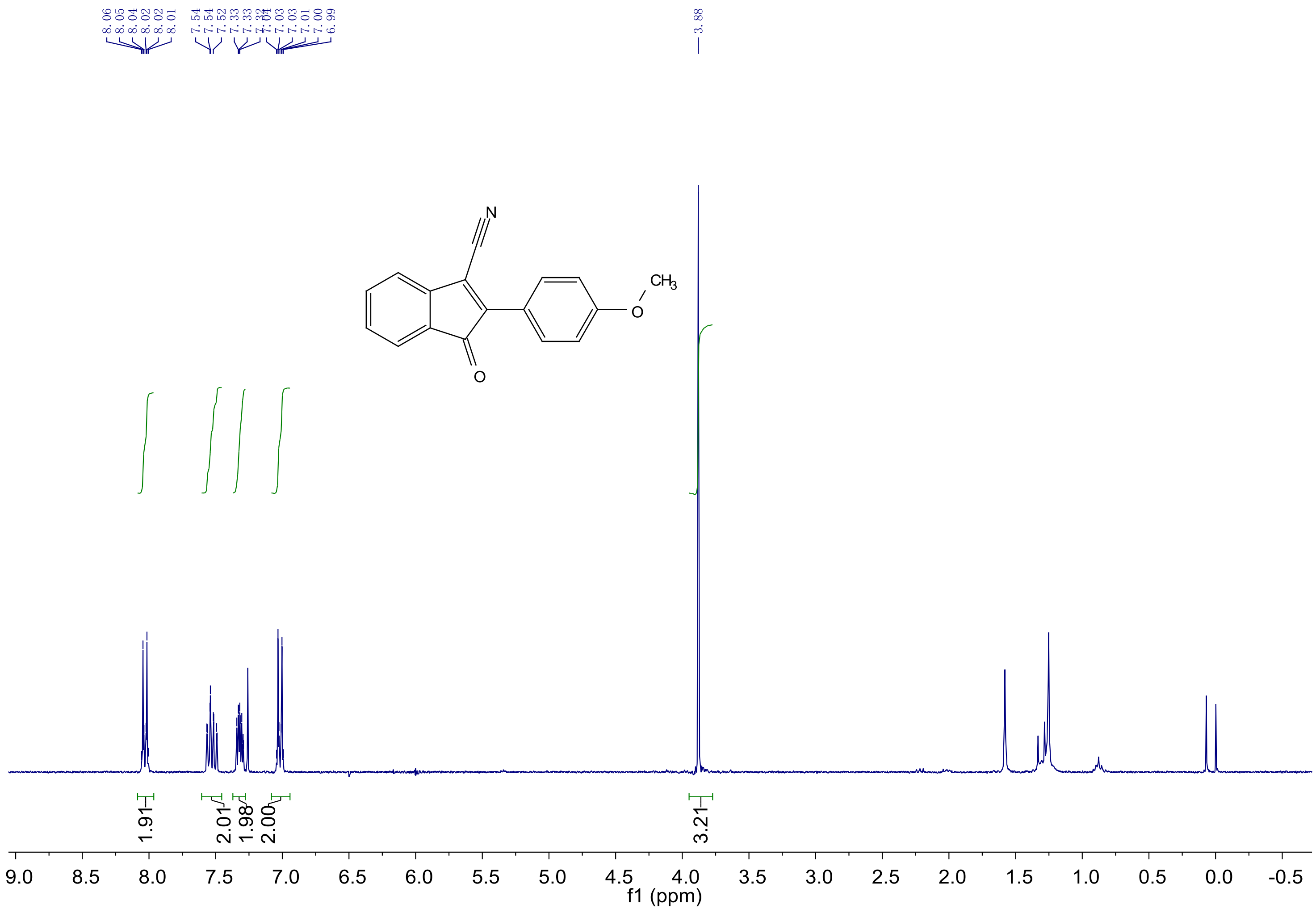
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2013

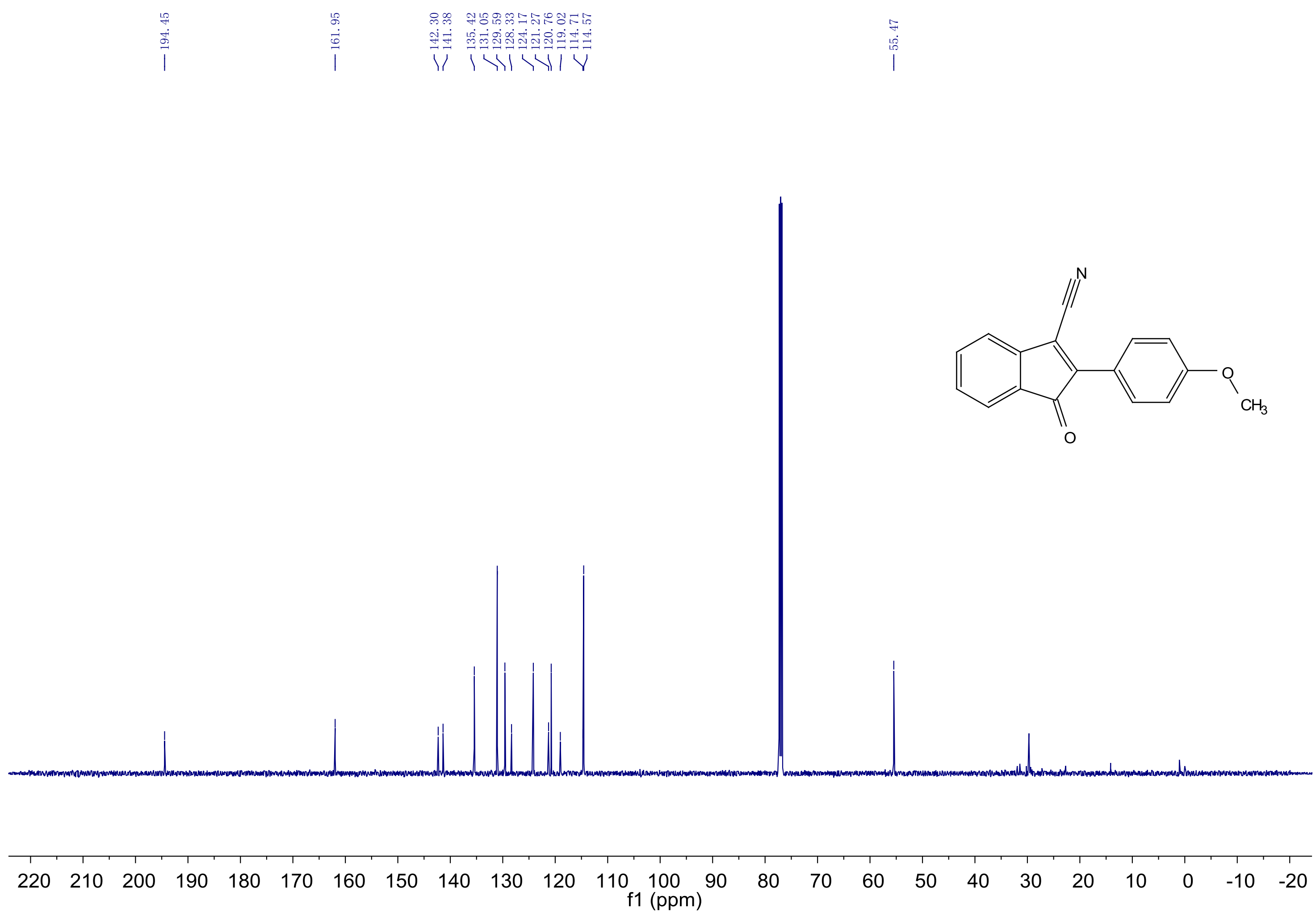
2d



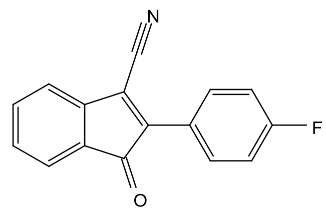

193.24
147.57
140.62
137.34
135.28
131.02
130.43
130.34
129.82
128.18
127.93
126.55
126.01
124.49
121.28
113.29
20.79
H_3C
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

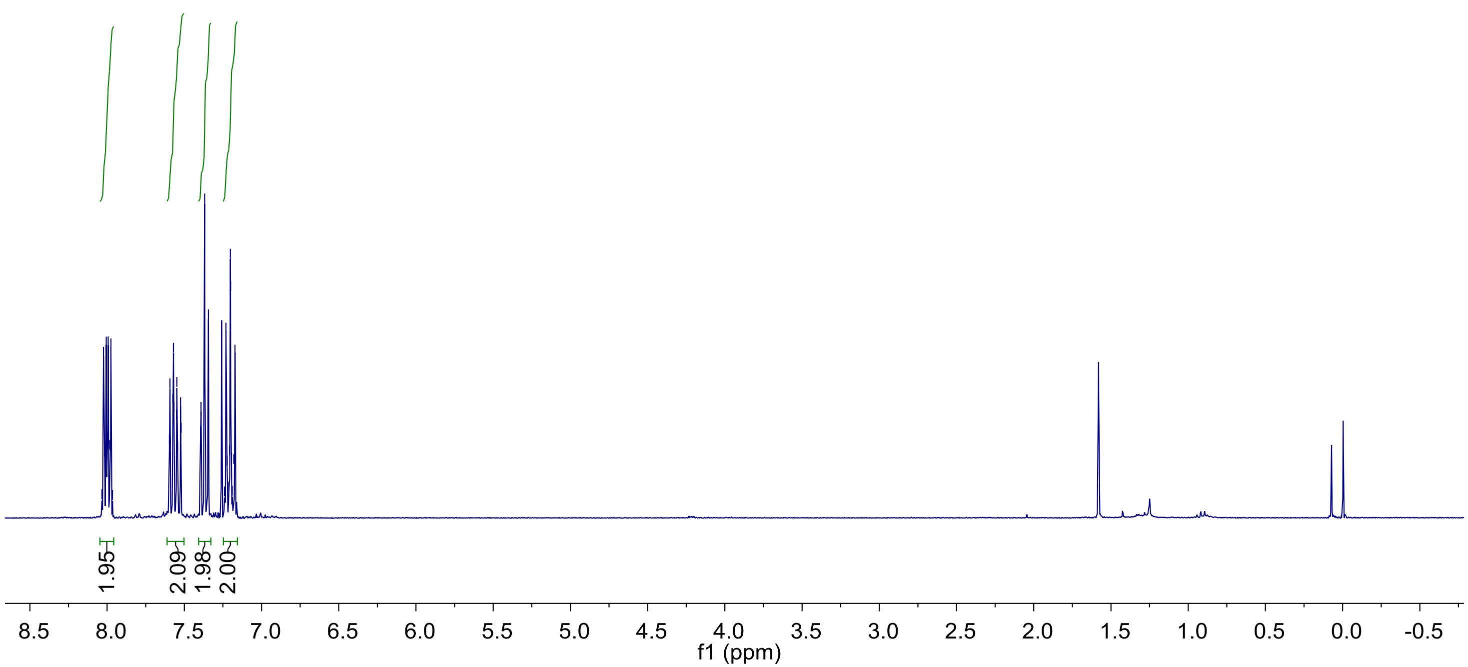
2e

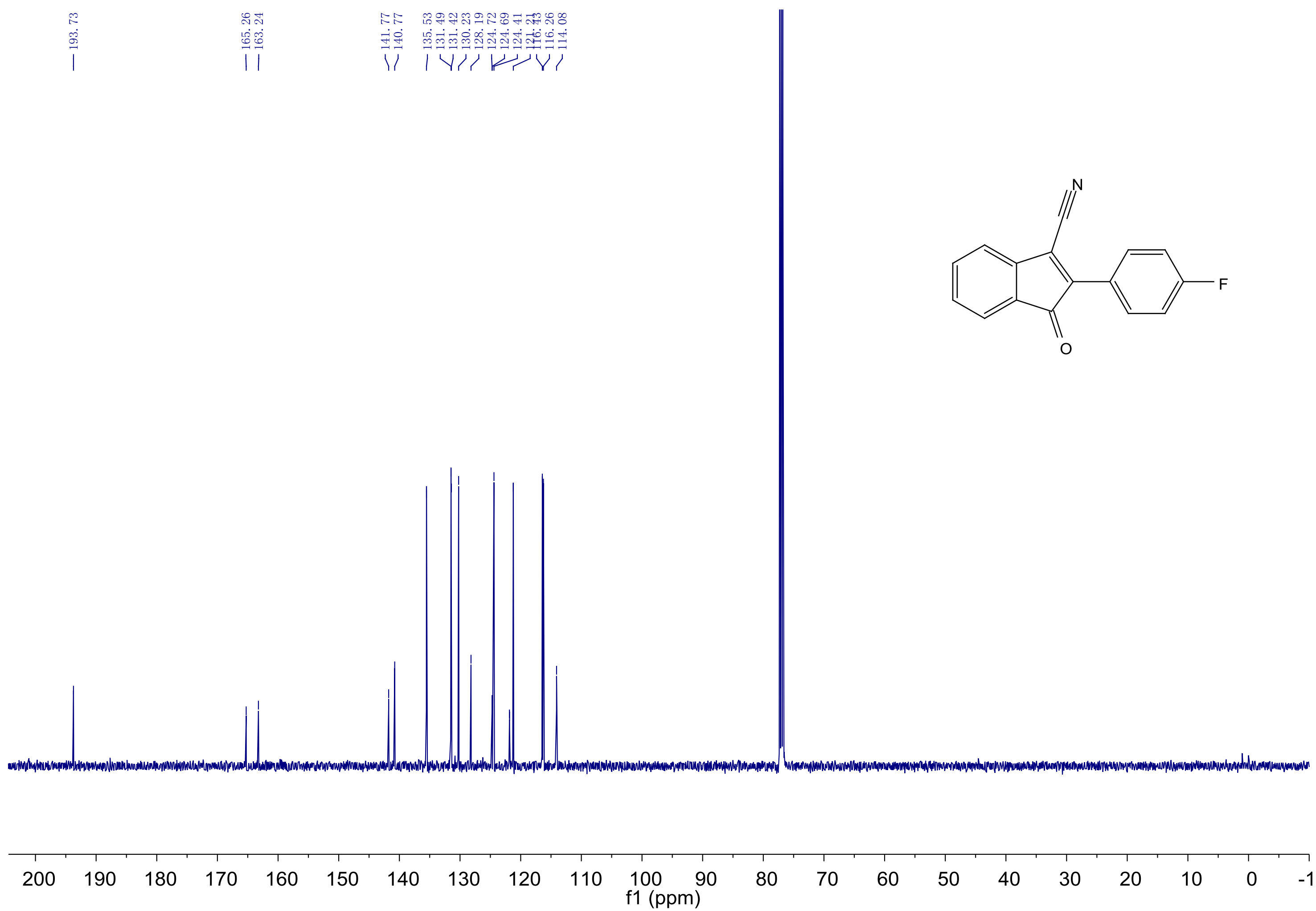

8.06
8.05
8.04
8.02
8.02
8.01
7.54
7.54
7.52
7.33
7.33
7.32
7.04
7.03
7.03
7.01
7.00
6.99
3.88
N
CH3
O
O
1.91
2.01
1.98
2.00
3.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


194.45
161.95
142.30
141.38
135.42
131.05
129.59
128.33
124.17
121.27
120.76
119.02
114.71
114.57
55.47
N
O
O
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

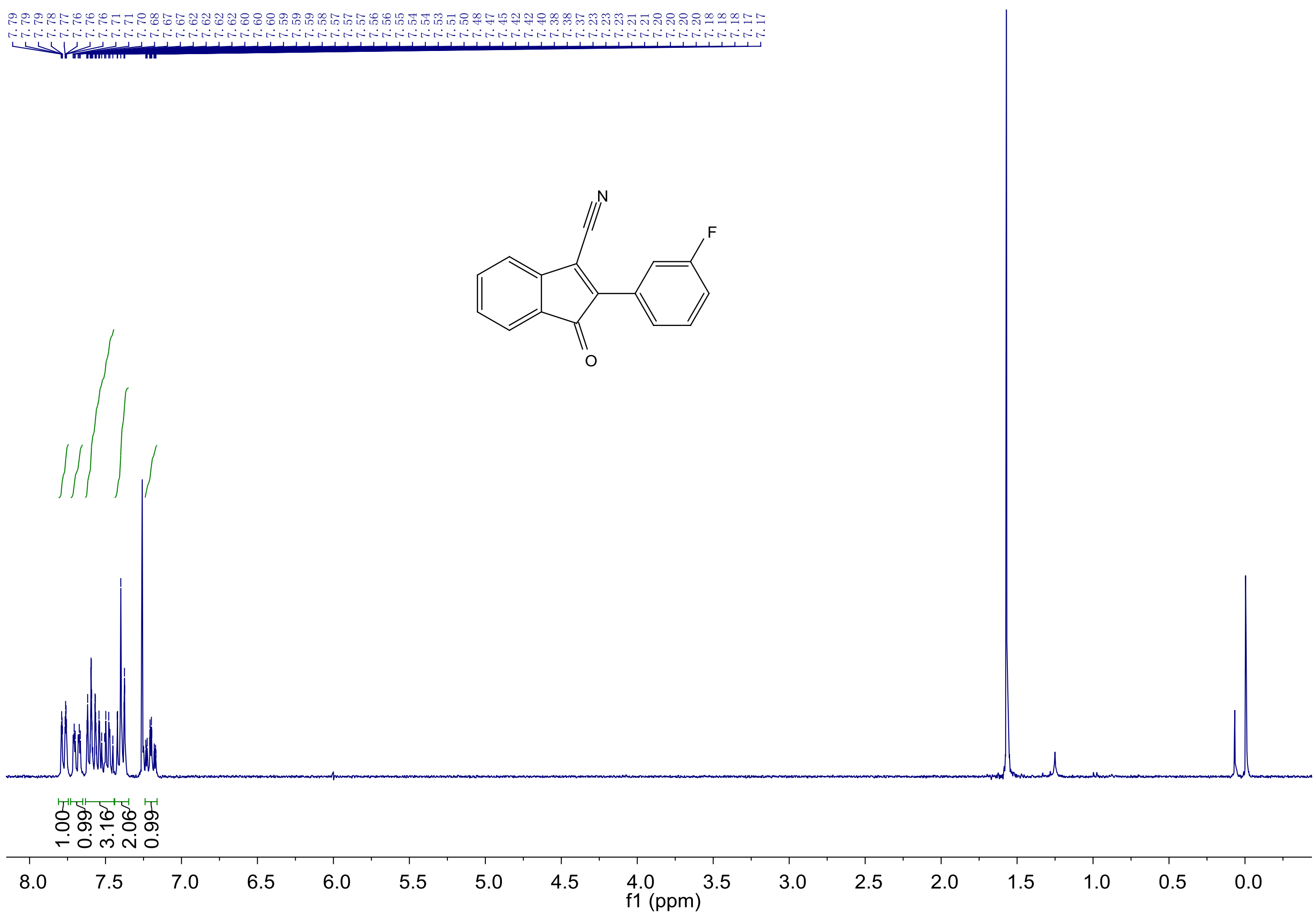
2f

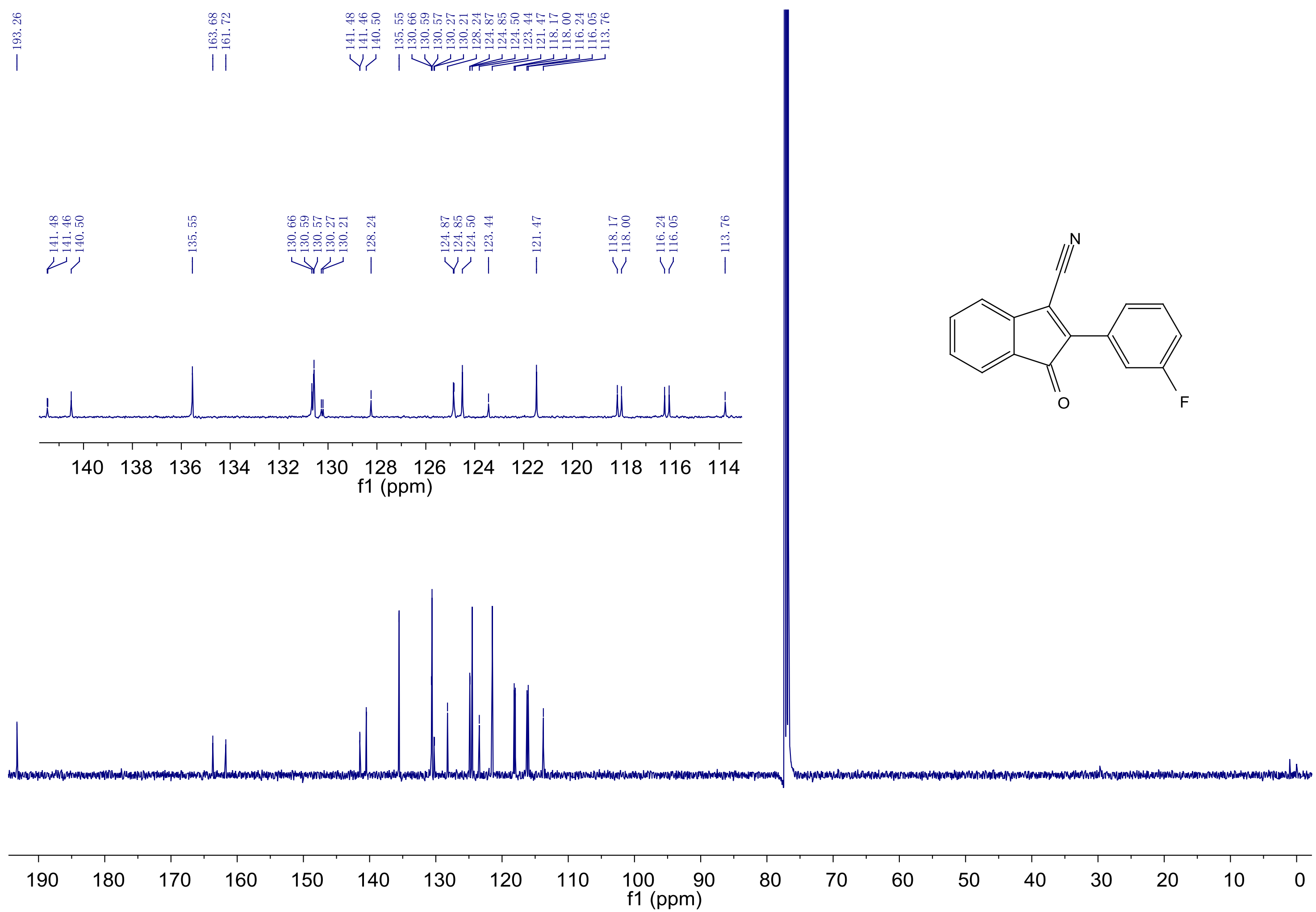

N
F
O


8.03 8.02 8.02 8.01 8.00 8.00 7.99 7.98 7.98 7.60 7.59 7.59 7.57 7.57 7.57 7.55 7.55 7.54 7.52 7.52 7.39 7.39 7.37 7.34 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.17
1.95
2.09
1.98
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

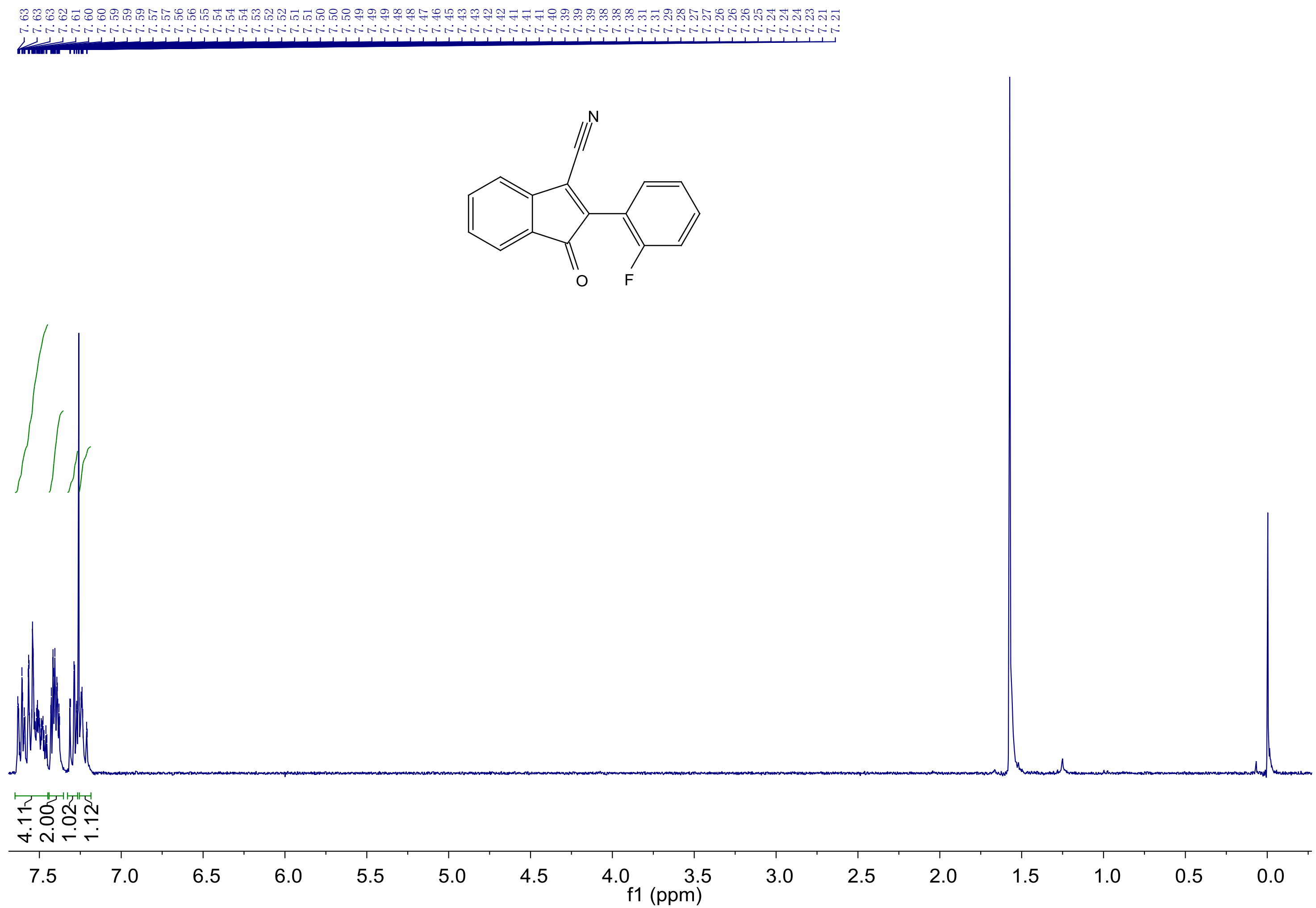

193.73
165.26
163.24
141.77
140.77
135.53
131.49
131.42
130.23
128.19
124.72
124.69
124.41
121.21
116.43
116.26
114.08
N
F
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

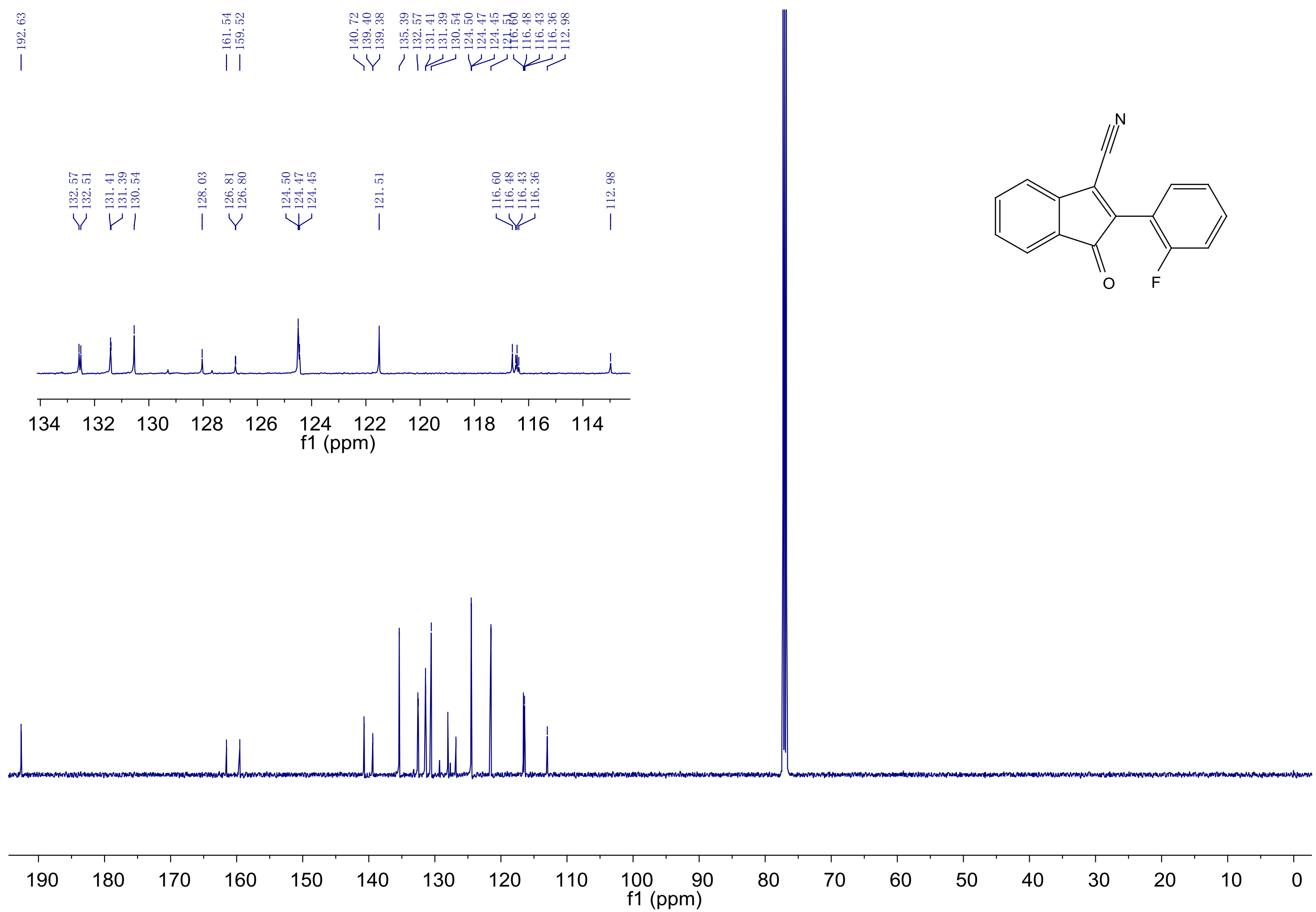
2g


N
F
O
1.00
0.99
3.16
2.06
0.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

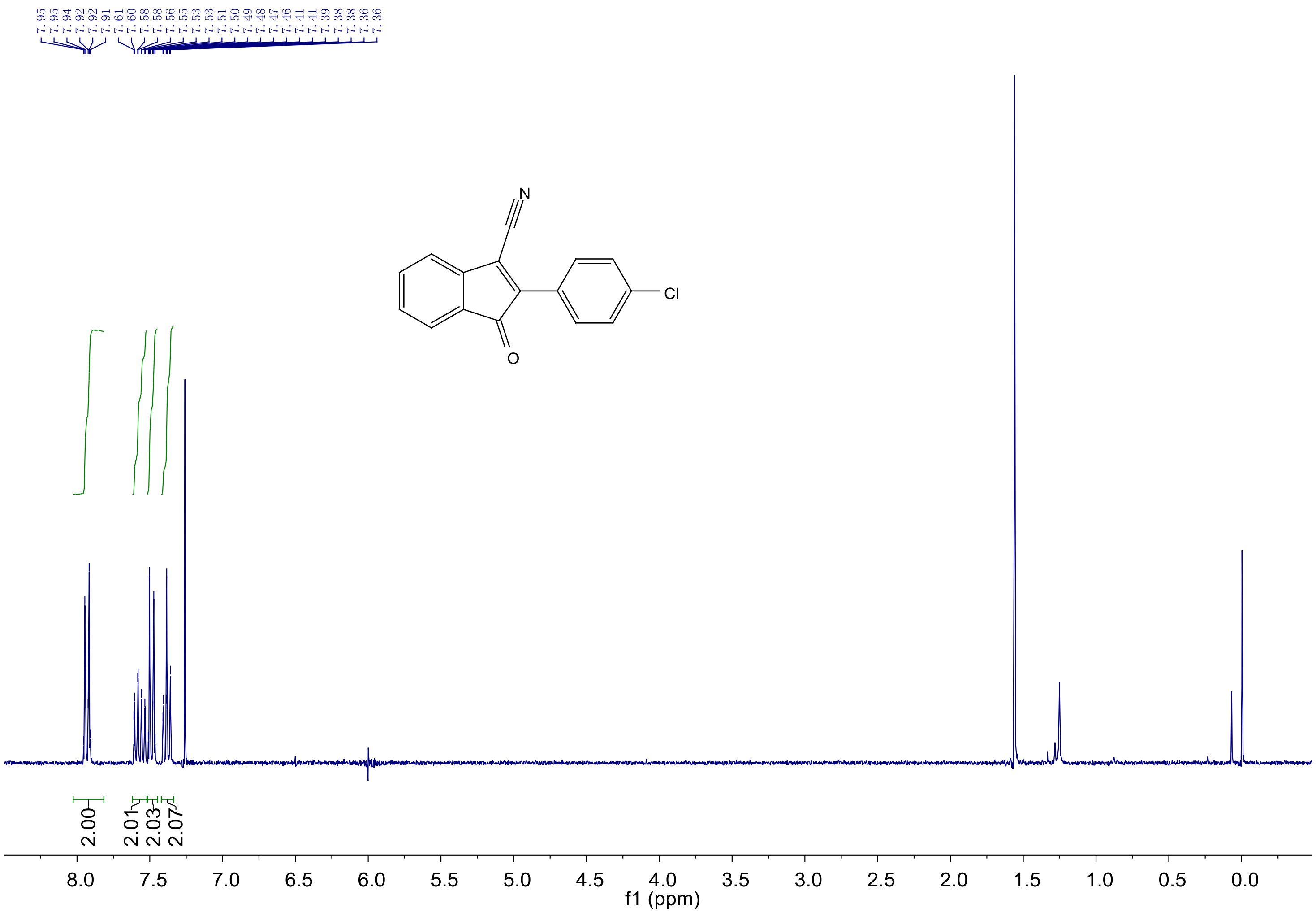

193.26
163.68
161.72
141.48
141.46
140.50
135.55
130.66
130.59
130.57
130.27
130.21
128.24
124.87
124.85
124.50
123.44
121.47
118.17
118.00
116.24
116.05
113.76
140 138 136 134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
N
O
F

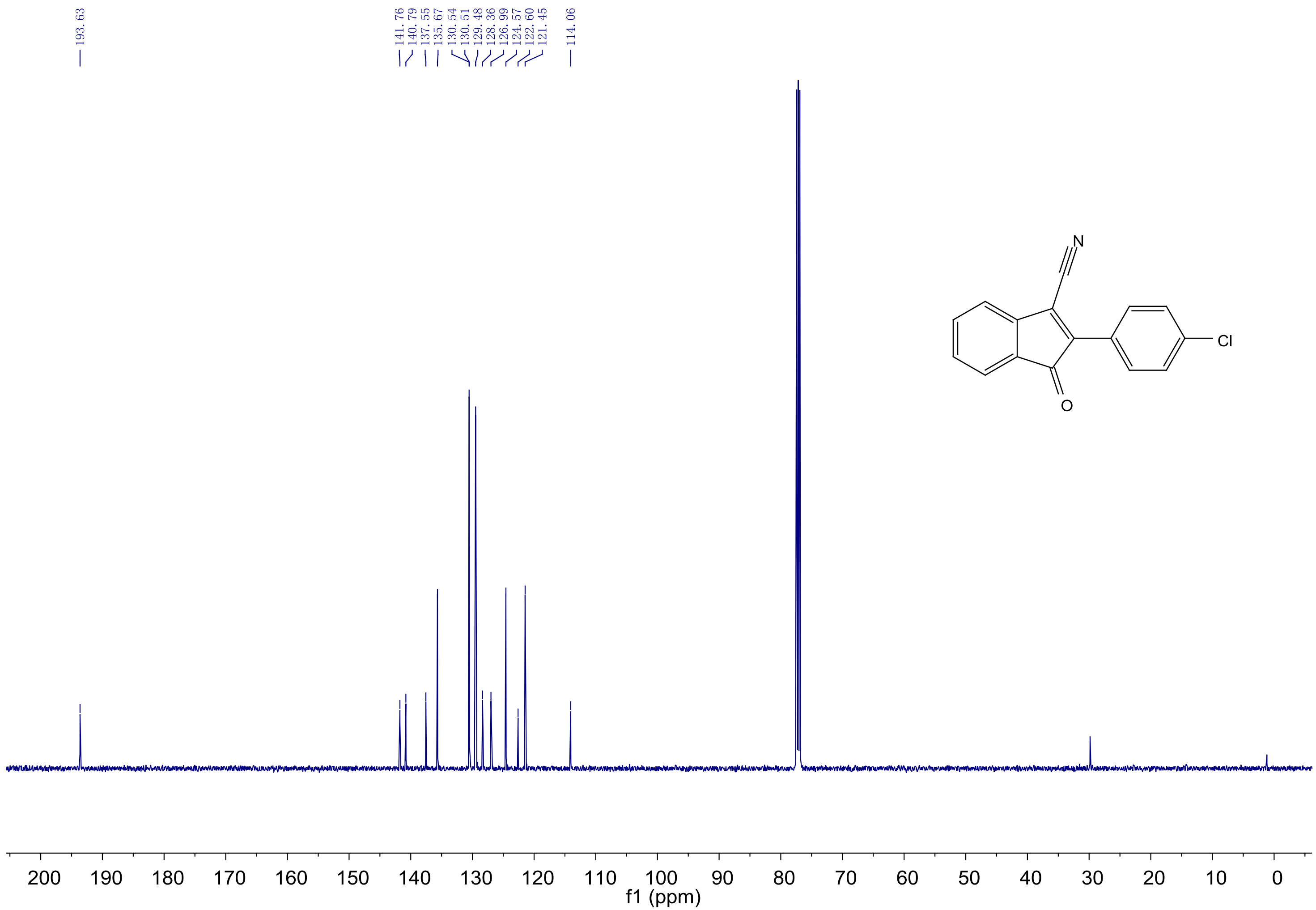
2h


7.63 7.63 7.63 7.62 7.61 7.60 7.60 7.59 7.59 7.59 7.57 7.57 7.56 7.56 7.55 7.54 7.54 7.54 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.50 7.49 7.49 7.49 7.48 7.48 7.47 7.46 7.45 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.31 7.31 7.29 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.21 7.21
N
O
F
4.11
2.00
1.02
1.12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

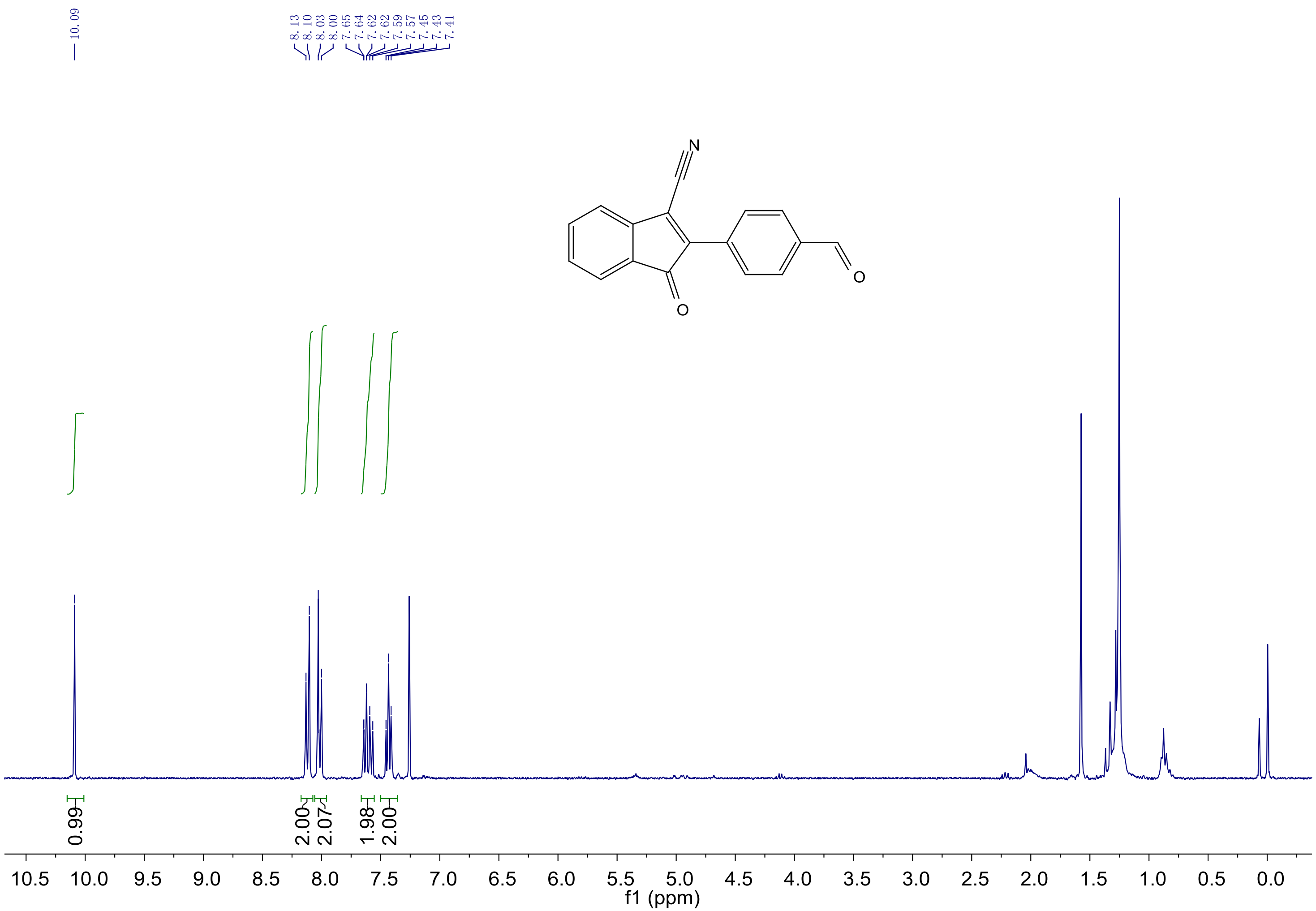

192.63
161.54
159.52
140.72
139.40
139.38
135.39
132.57
131.41
131.39
130.54
124.50
124.47
124.45
121.51
116.60
116.48
116.43
116.36
112.98
132.57
132.51
131.41
131.39
130.54
128.03
126.81
126.80
124.50
124.47
124.45
121.51
116.60
116.48
116.43
116.36
112.98
134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
N
O
F

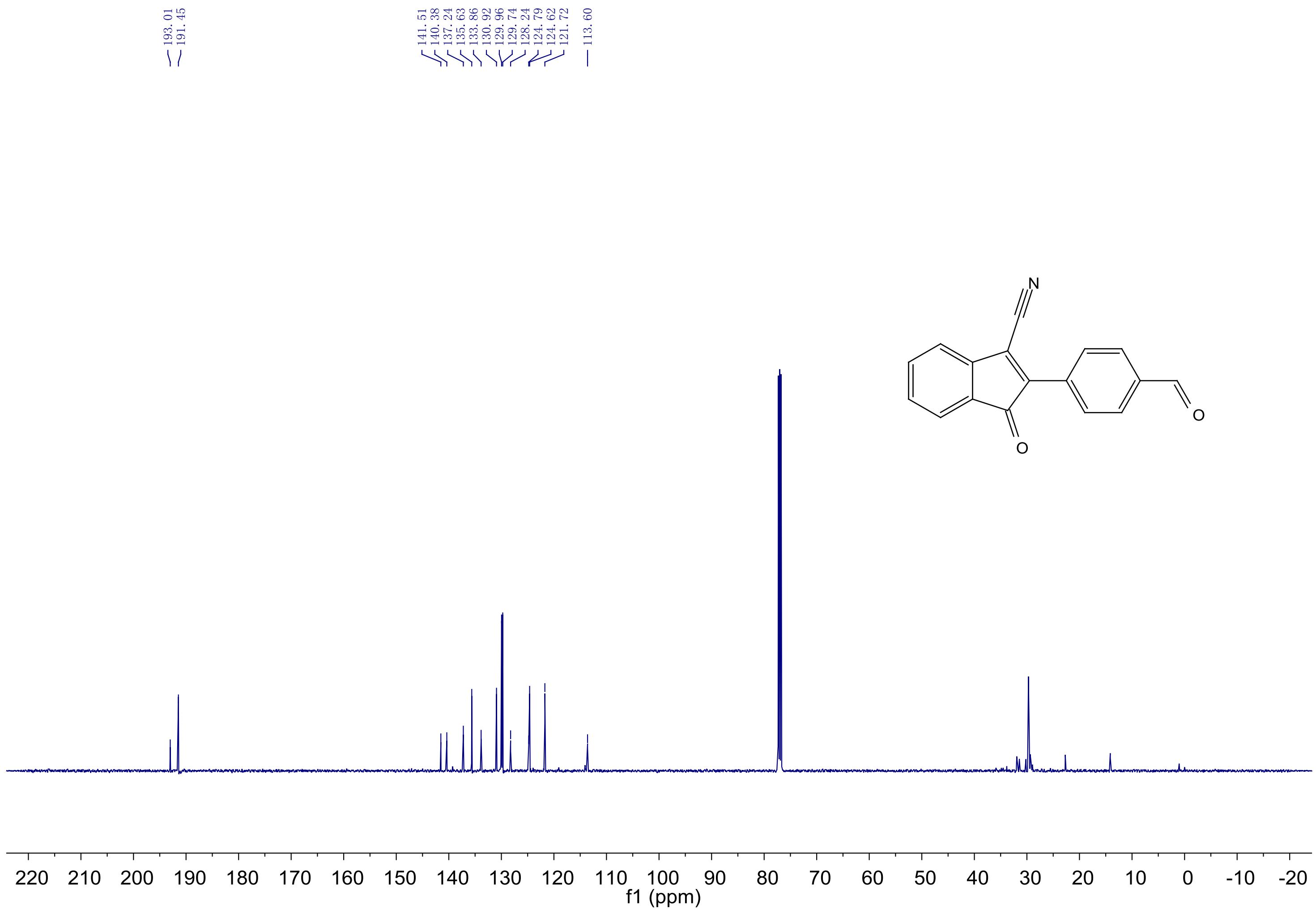
2i


7.95
7.95
7.94
7.92
7.92
7.91
7.61
7.60
7.58
7.58
7.56
7.55
7.53
7.53
7.51
7.50
7.49
7.48
7.47
7.46
7.41
7.41
7.39
7.38
7.38
7.36
7.36
N
Cl
O
2.00
2.01
2.03
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

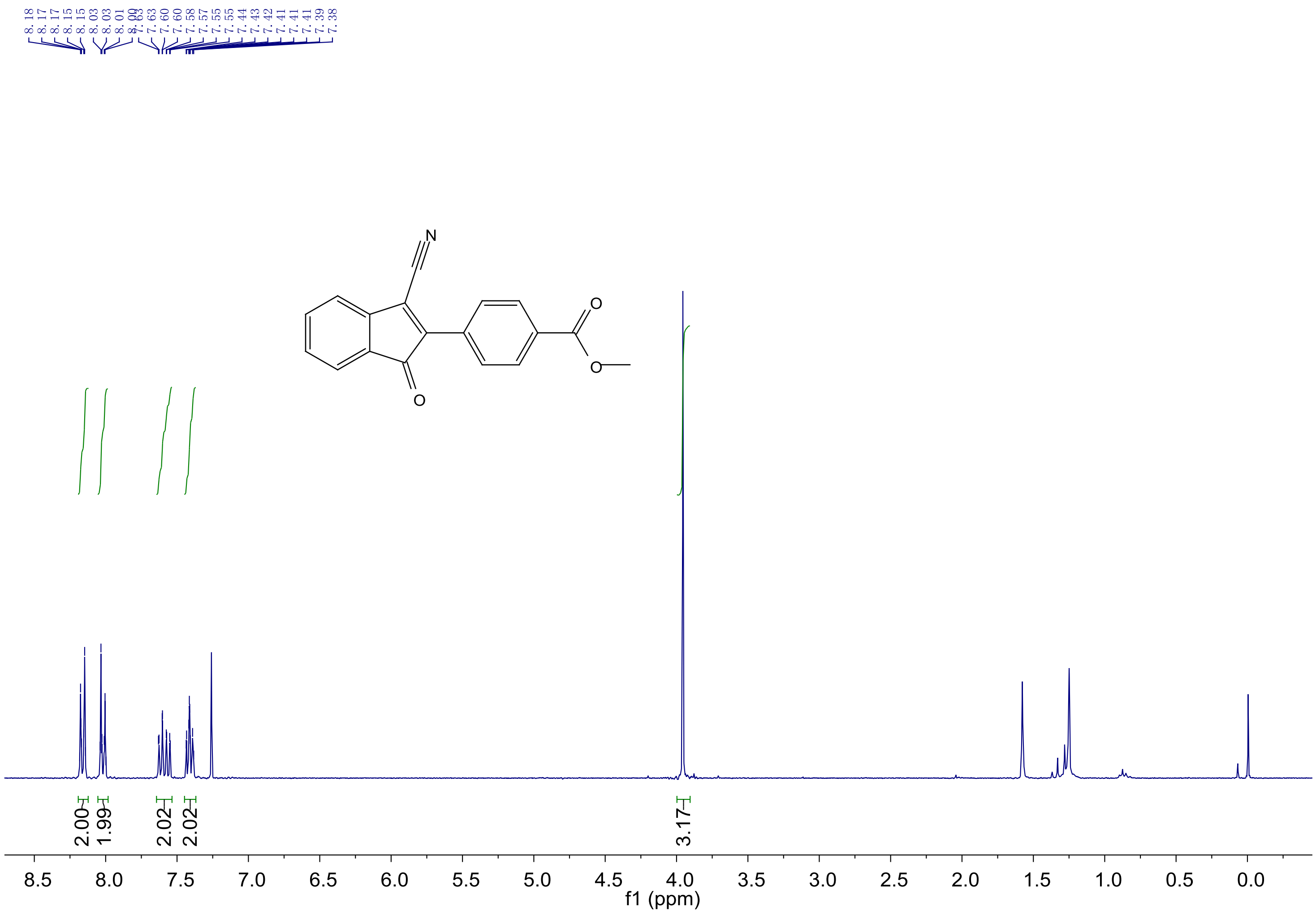

193.63
141.76
140.79
137.55
135.67
130.54
130.51
129.48
128.36
126.99
124.57
122.60
121.45
114.06
N
Cl
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

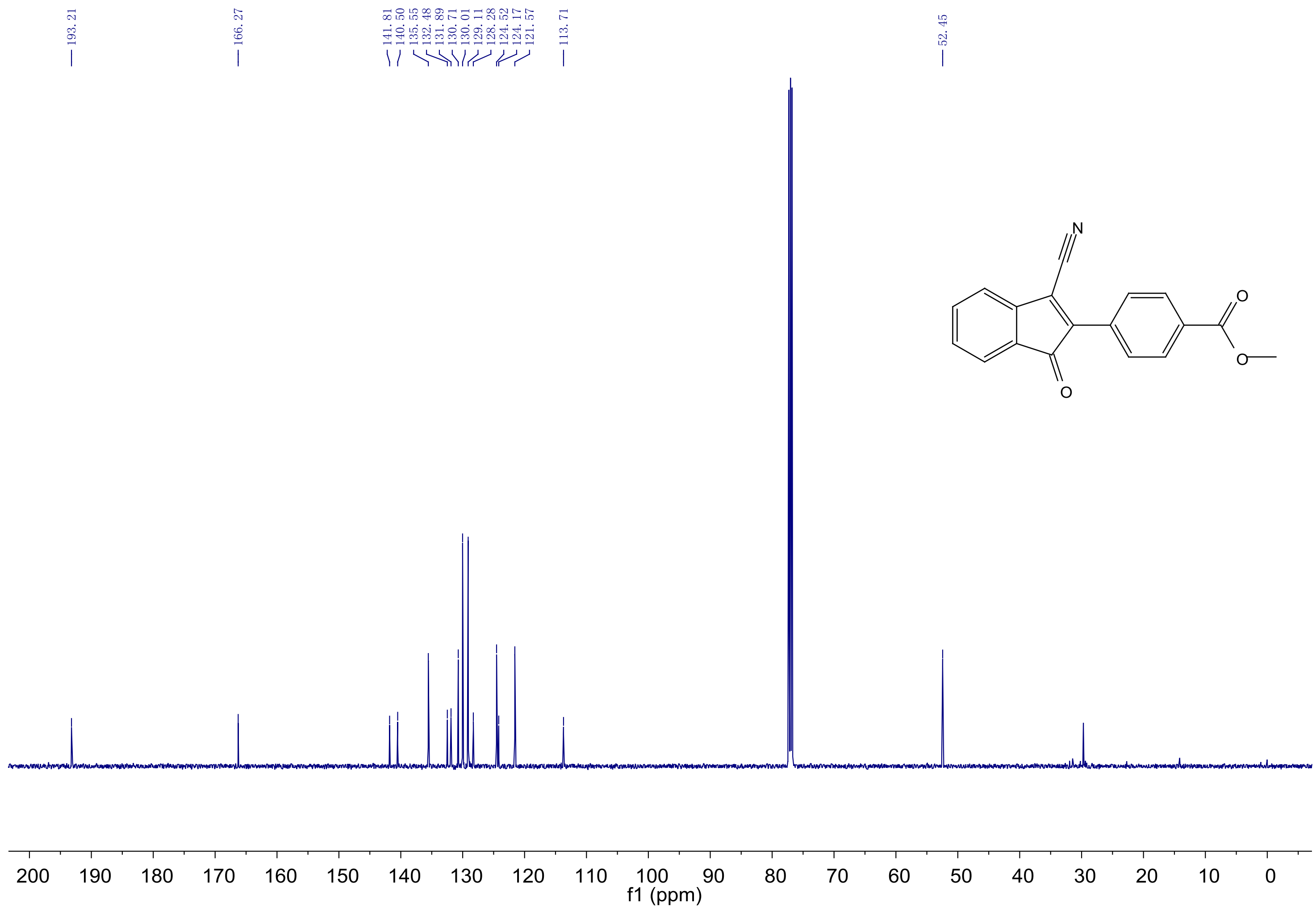
2j


10.09
8.13
8.10
8.03
8.00
7.65
7.64
7.62
7.62
7.59
7.57
7.45
7.43
7.41
N
O
O
0.99
2.00
2.07
1.98
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

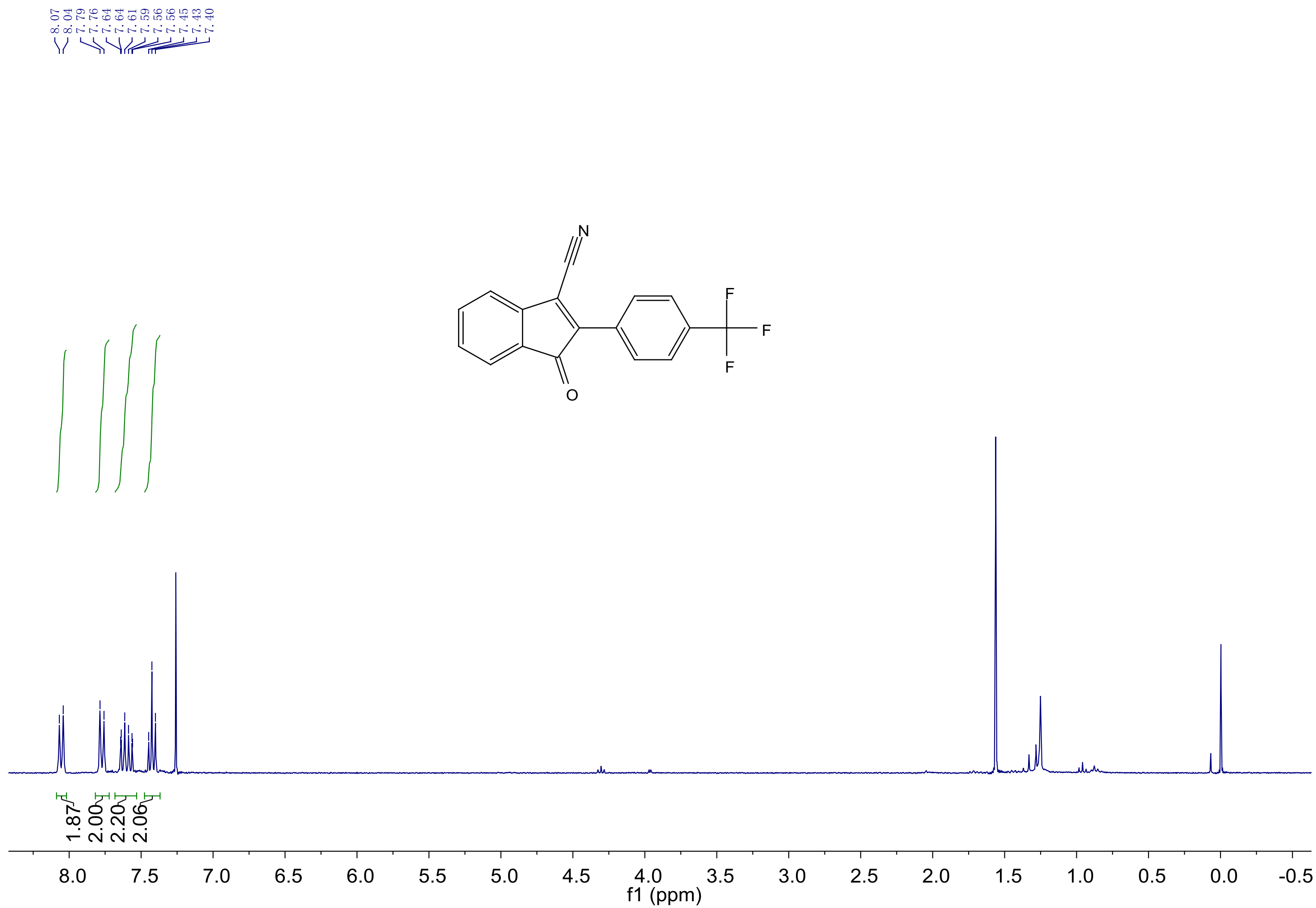

193.01
191.45
141.51
140.38
137.24
135.63
133.86
130.92
129.96
129.74
128.24
124.79
124.62
121.72
113.60
N
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

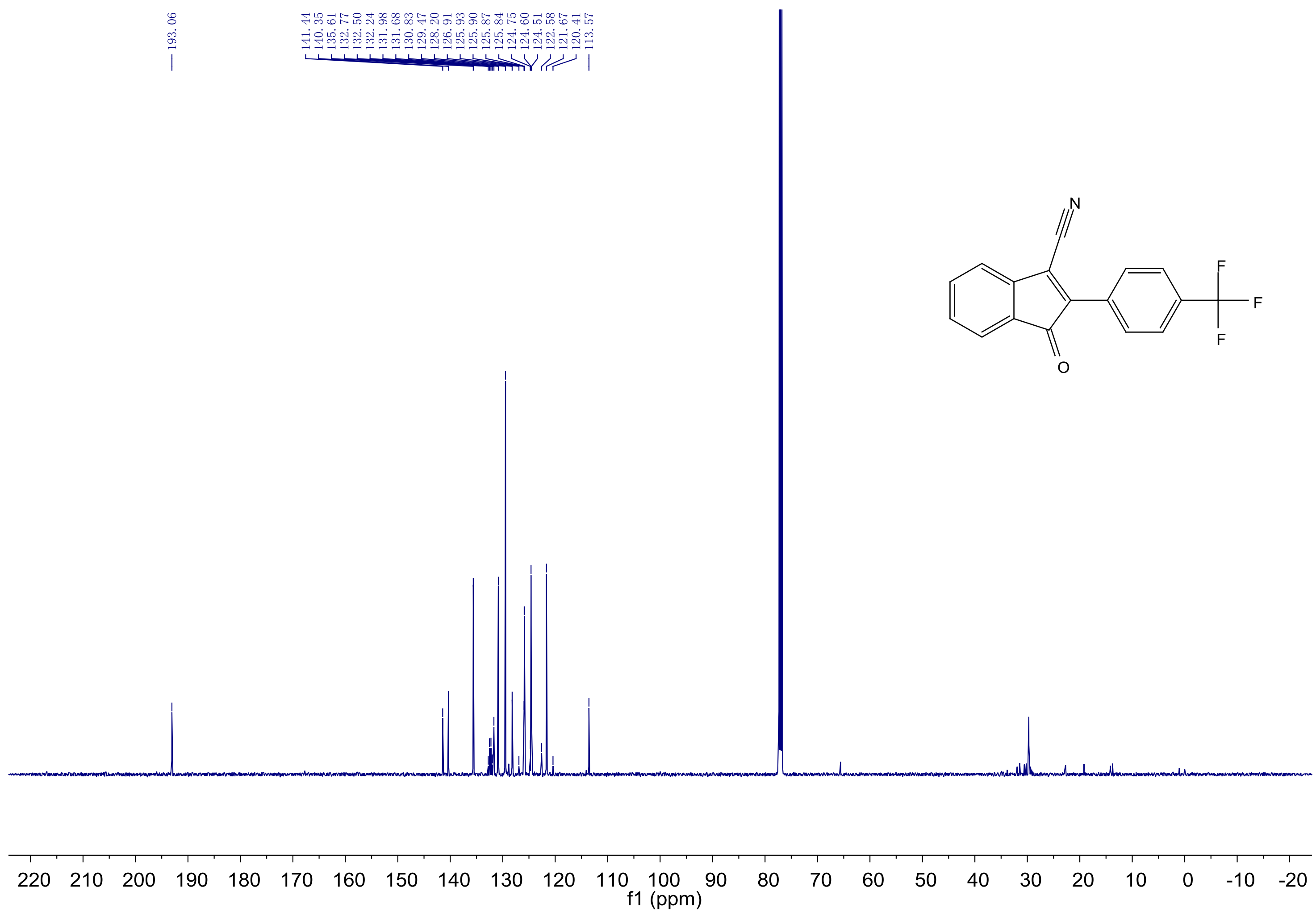
2k


8.18
8.17
8.17
8.15
8.15
8.03
8.03
8.01
8.00
7.63
7.60
7.60
7.58
7.57
7.55
7.44
7.43
7.42
7.41
7.41
7.41
7.39
7.38
N
O
O
O
2.00
1.99
2.02
2.02
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

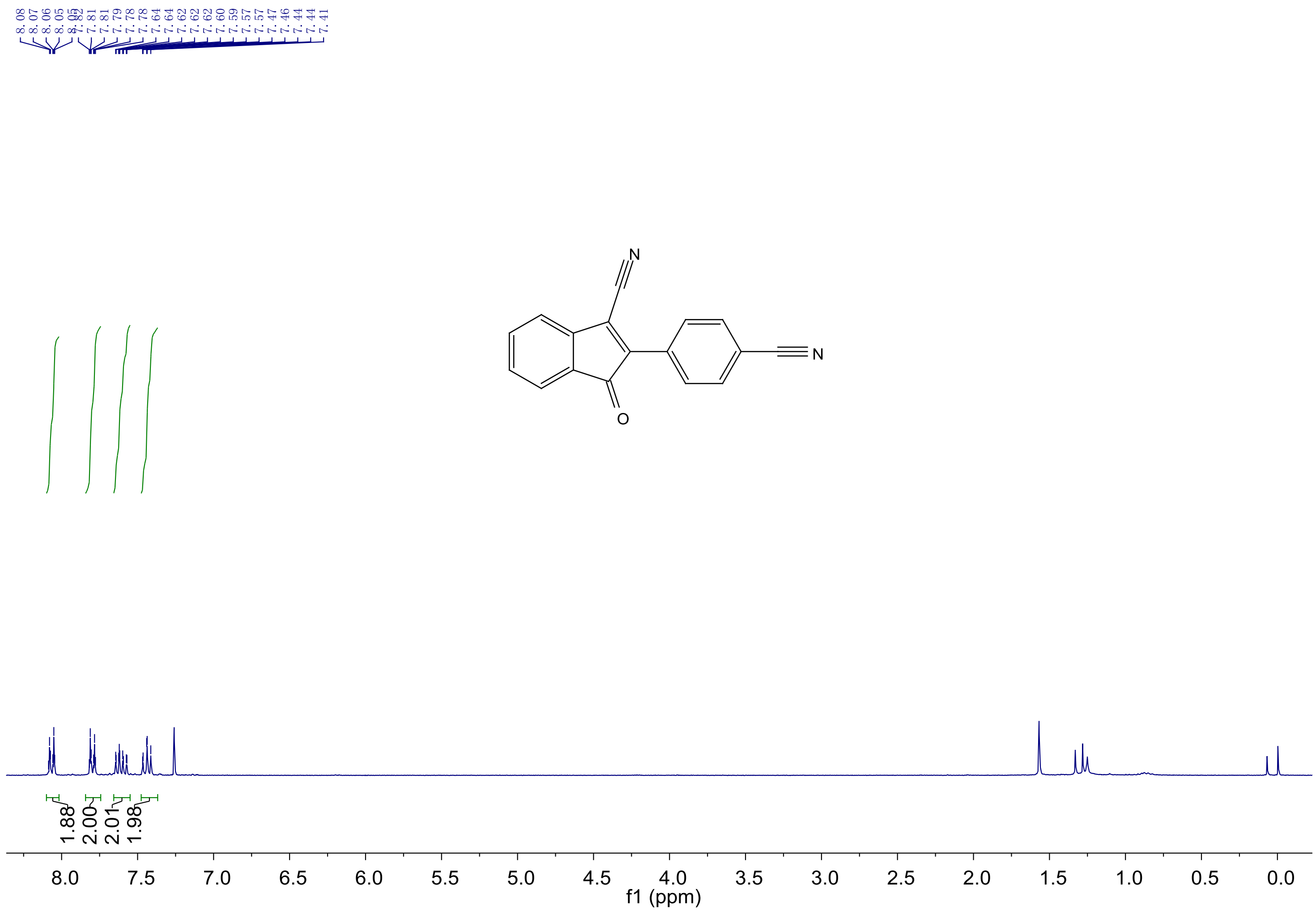

193.21
166.27
141.81
140.50
135.55
132.48
131.89
130.71
130.01
129.11
128.28
124.52
124.17
121.57
113.71
52.45
N
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

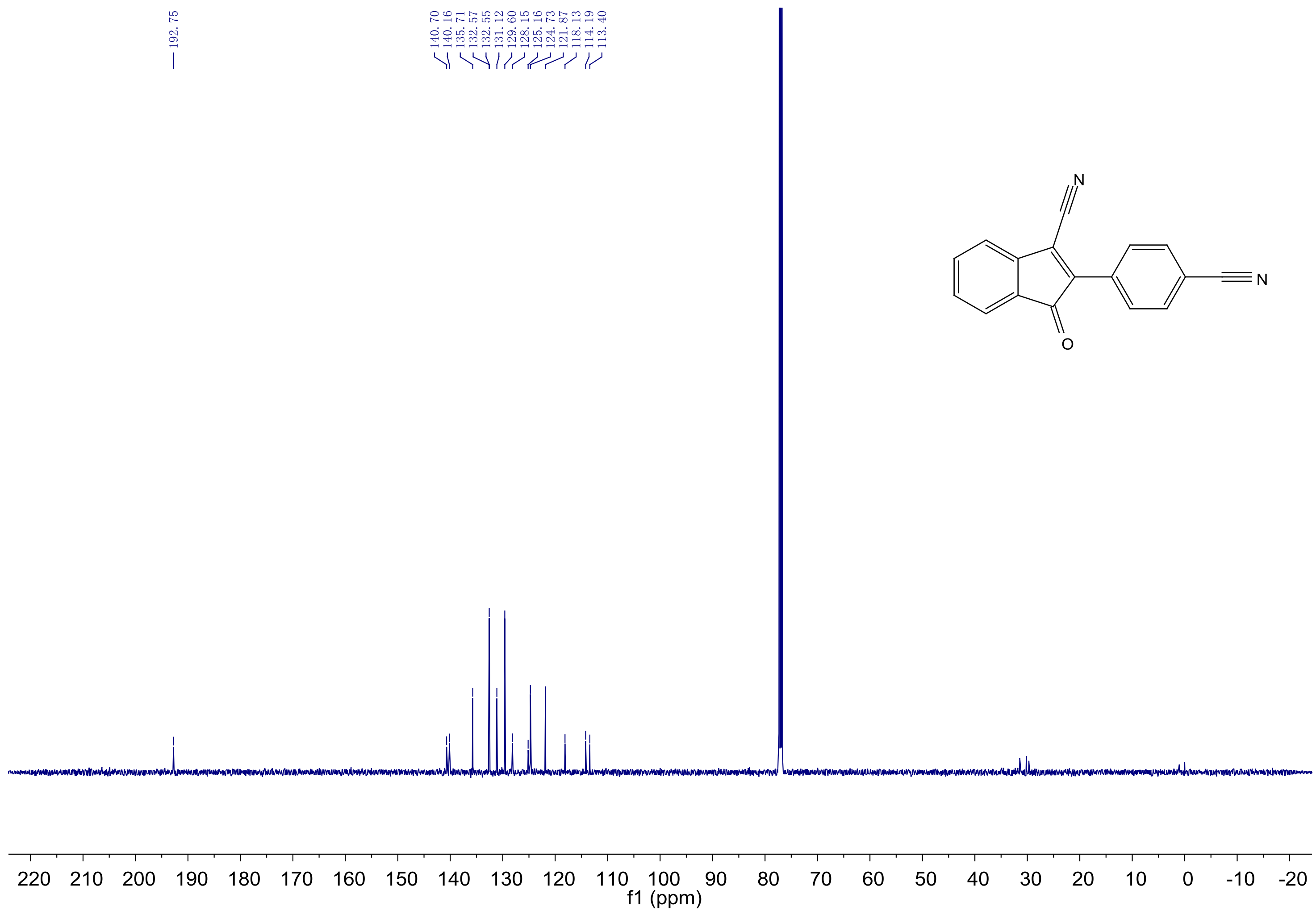
2l


8.07
8.04
7.79
7.76
7.64
7.64
7.61
7.59
7.56
7.56
7.45
7.43
7.40
N
F
F
F
O
1.87
2.00
2.20
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

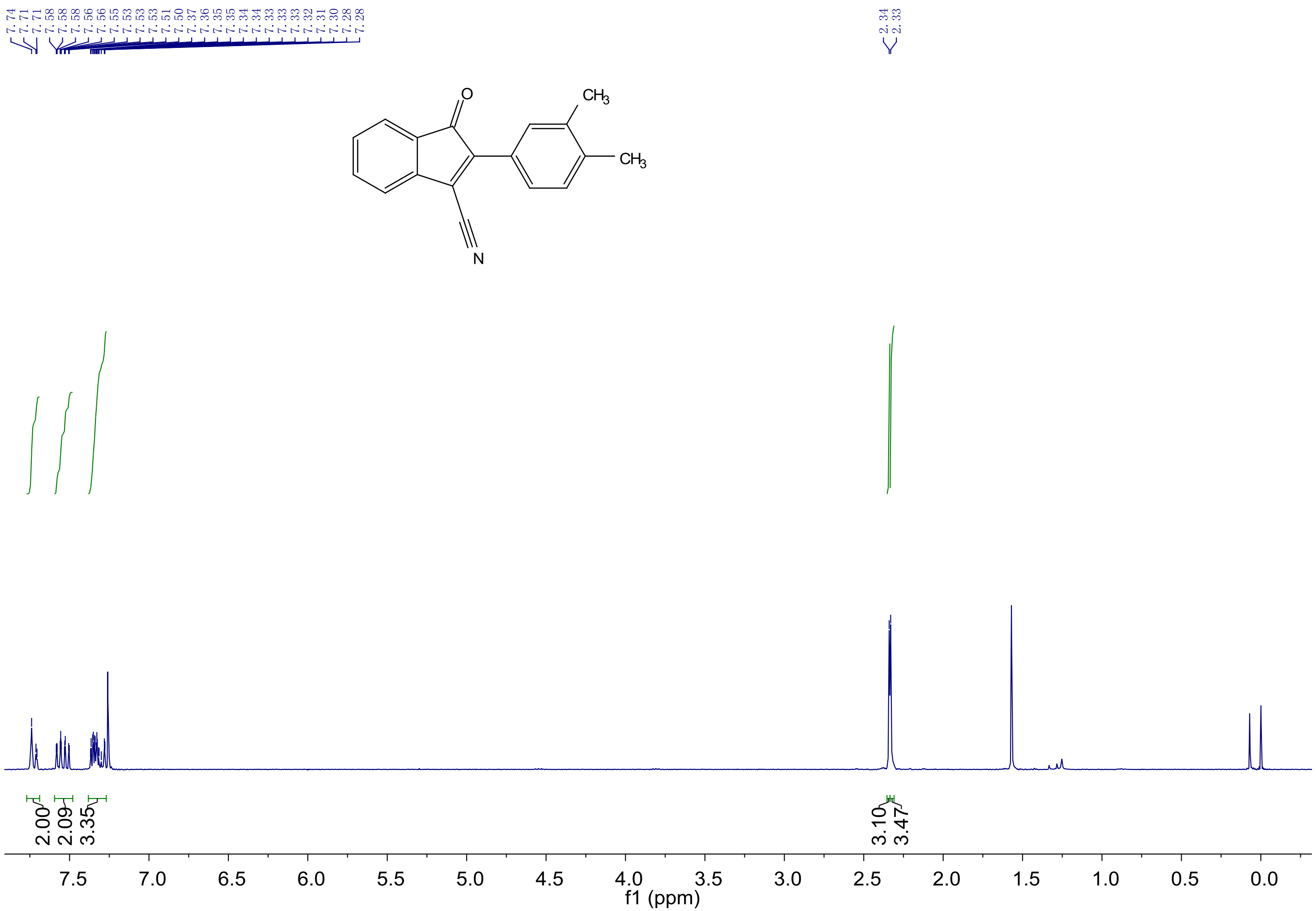

193.06
141.44
140.35
135.61
132.77
132.50
132.24
131.98
131.68
130.83
129.47
128.20
126.91
125.93
125.90
125.87
125.84
124.75
124.60
124.51
122.58
121.67
120.41
113.57
N
F
F
F
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

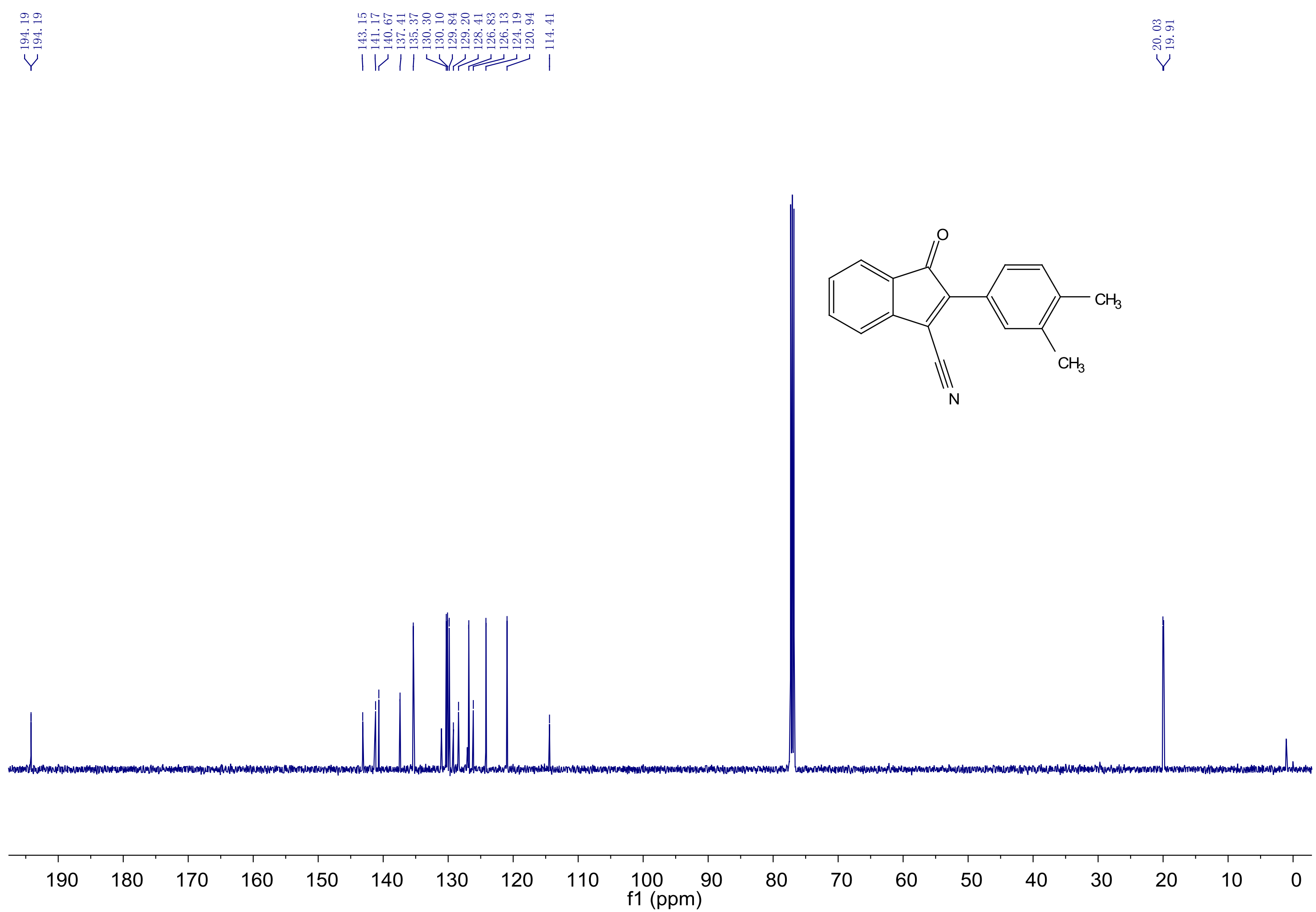
2m


8.08
8.07
8.06
8.05
8.05
7.82
7.81
7.81
7.79
7.78
7.78
7.64
7.64
7.62
7.62
7.62
7.60
7.59
7.57
7.57
7.47
7.46
7.44
7.44
7.41
N
N
O
1.88
2.00
2.01
1.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

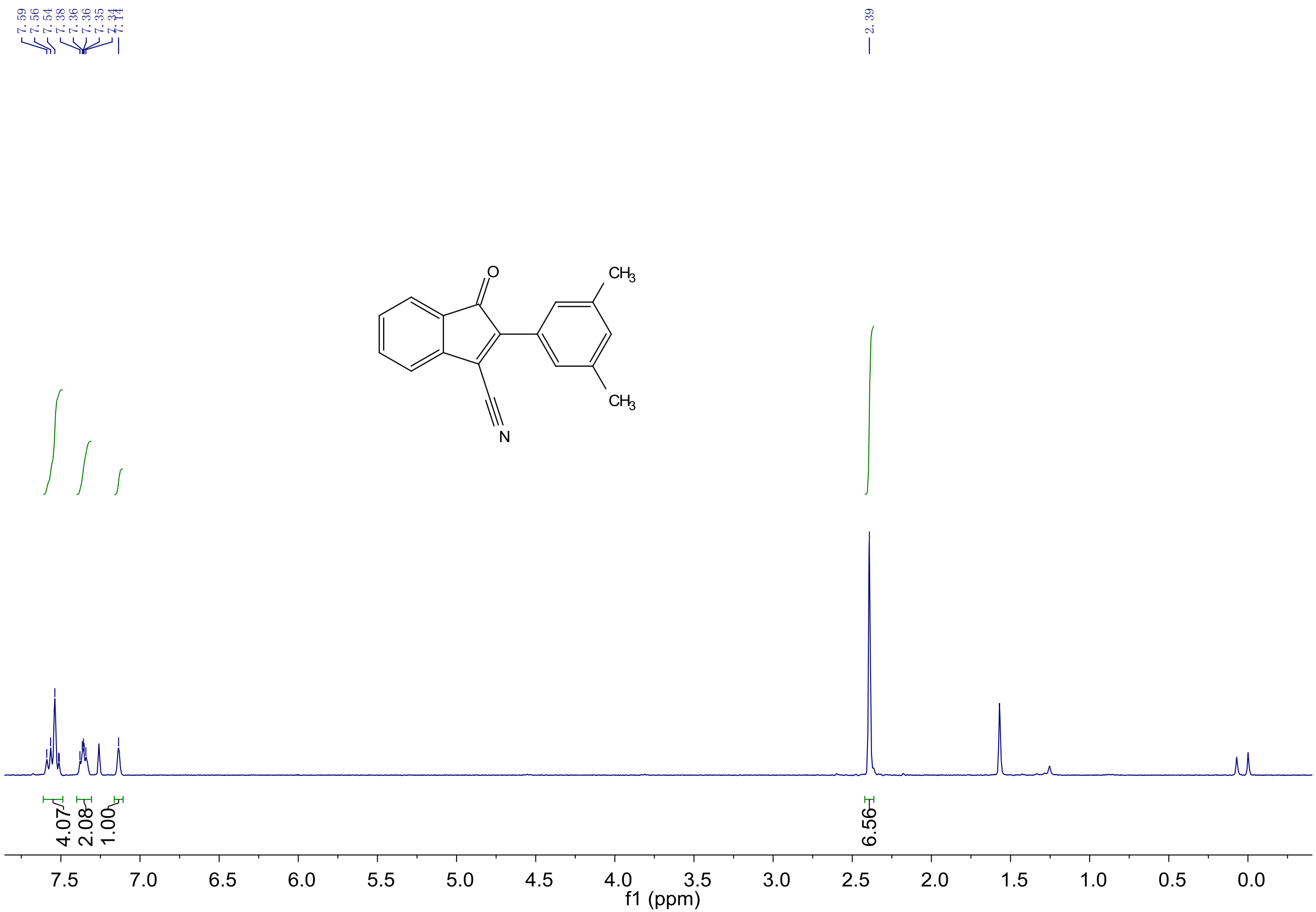

192.75
140.70
140.16
135.71
132.57
132.55
131.12
129.60
128.15
125.16
124.73
121.87
118.13
114.19
113.40
N
N
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

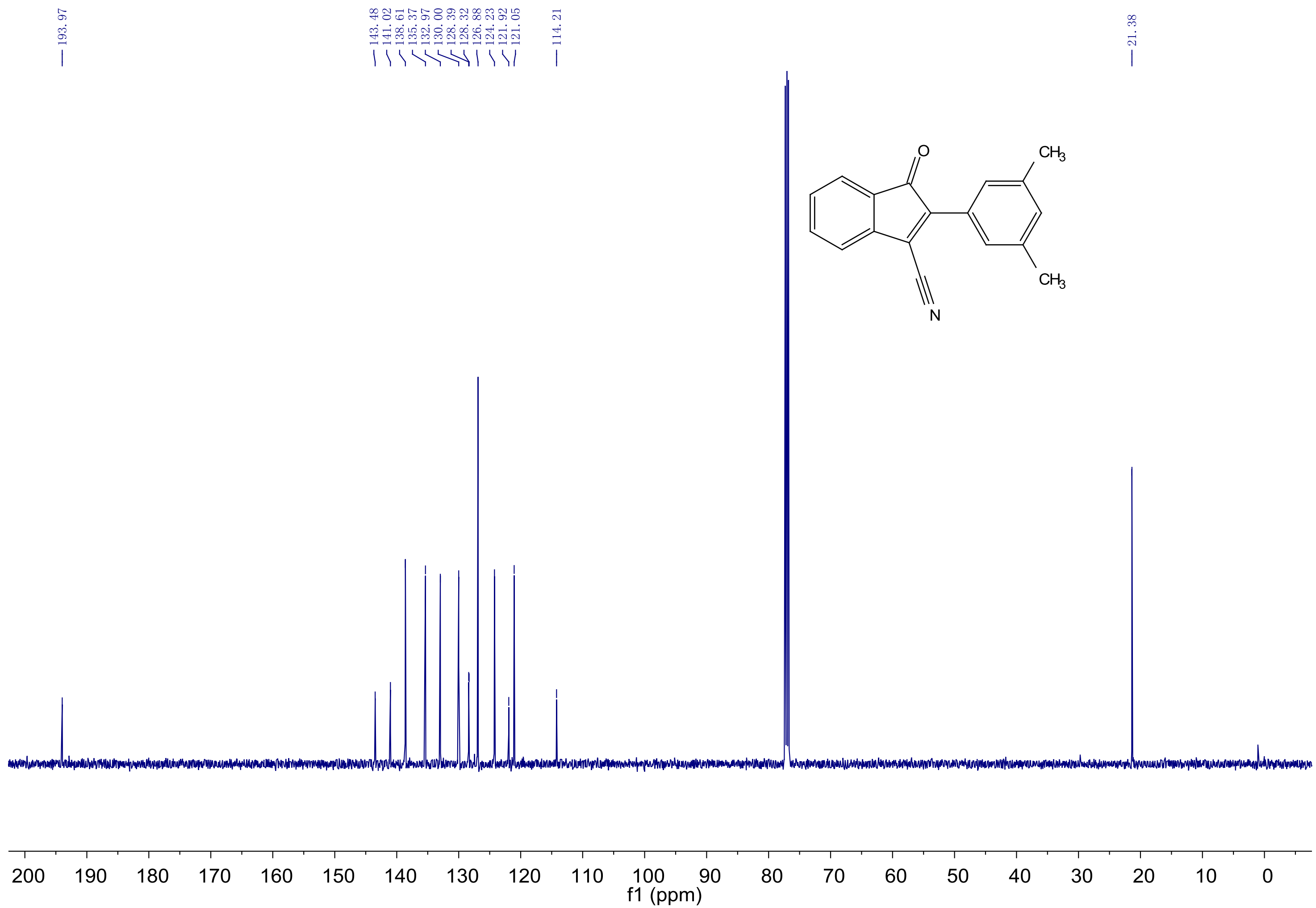
2n


7.74
7.71
7.71
7.58
7.58
7.58
7.56
7.56
7.55
7.53
7.53
7.53
7.51
7.50
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.32
7.31
7.30
7.28
7.28
2.34
2.33
O
CH3
CH3
N
2.00
2.09
3.35
3.10
3.47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

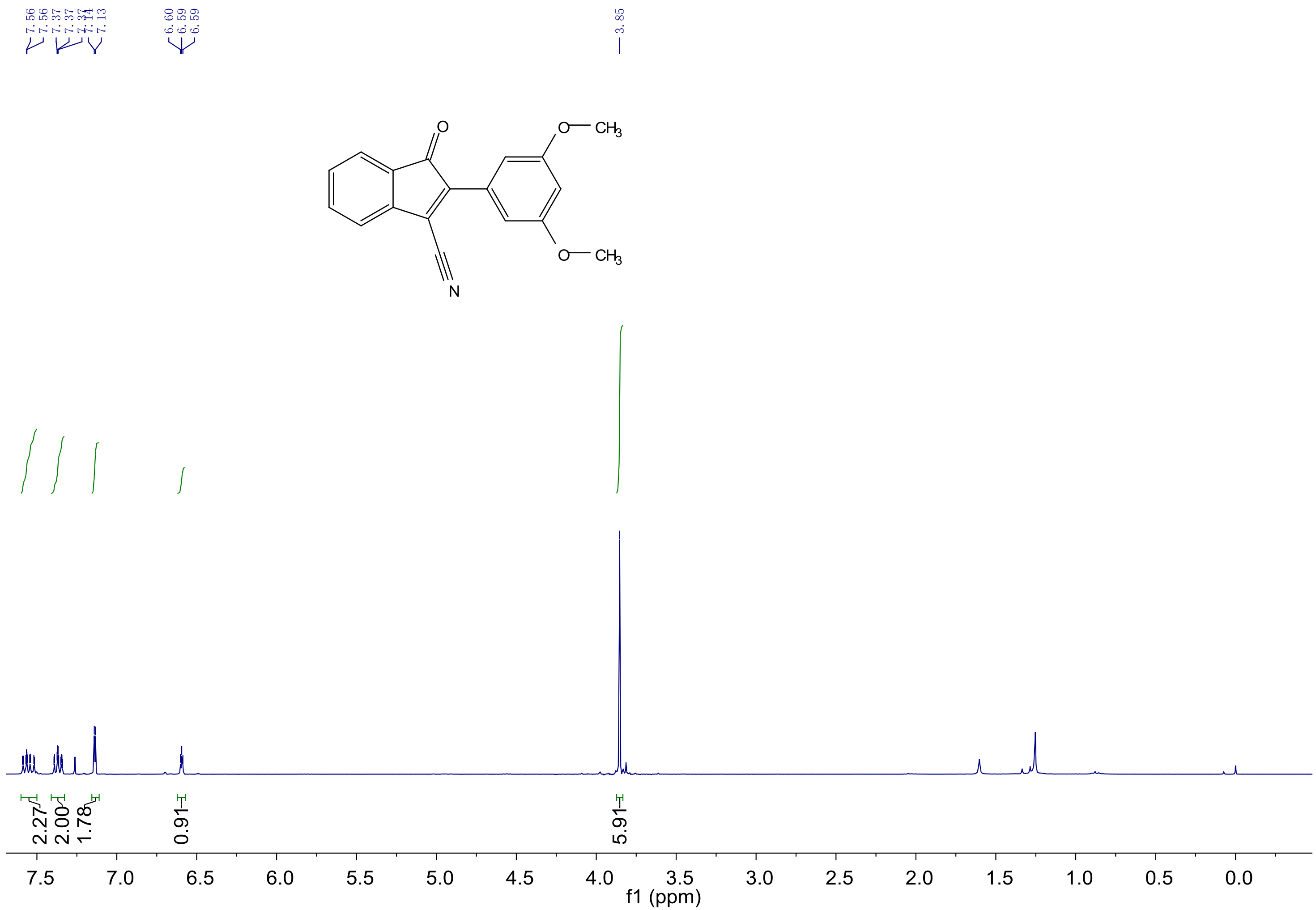

194.19
194.19
143.15
141.17
140.67
137.41
135.37
130.30
130.10
129.84
129.20
128.41
126.83
126.13
124.19
120.94
114.41
20.03
19.91
O
CH3
CH3
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

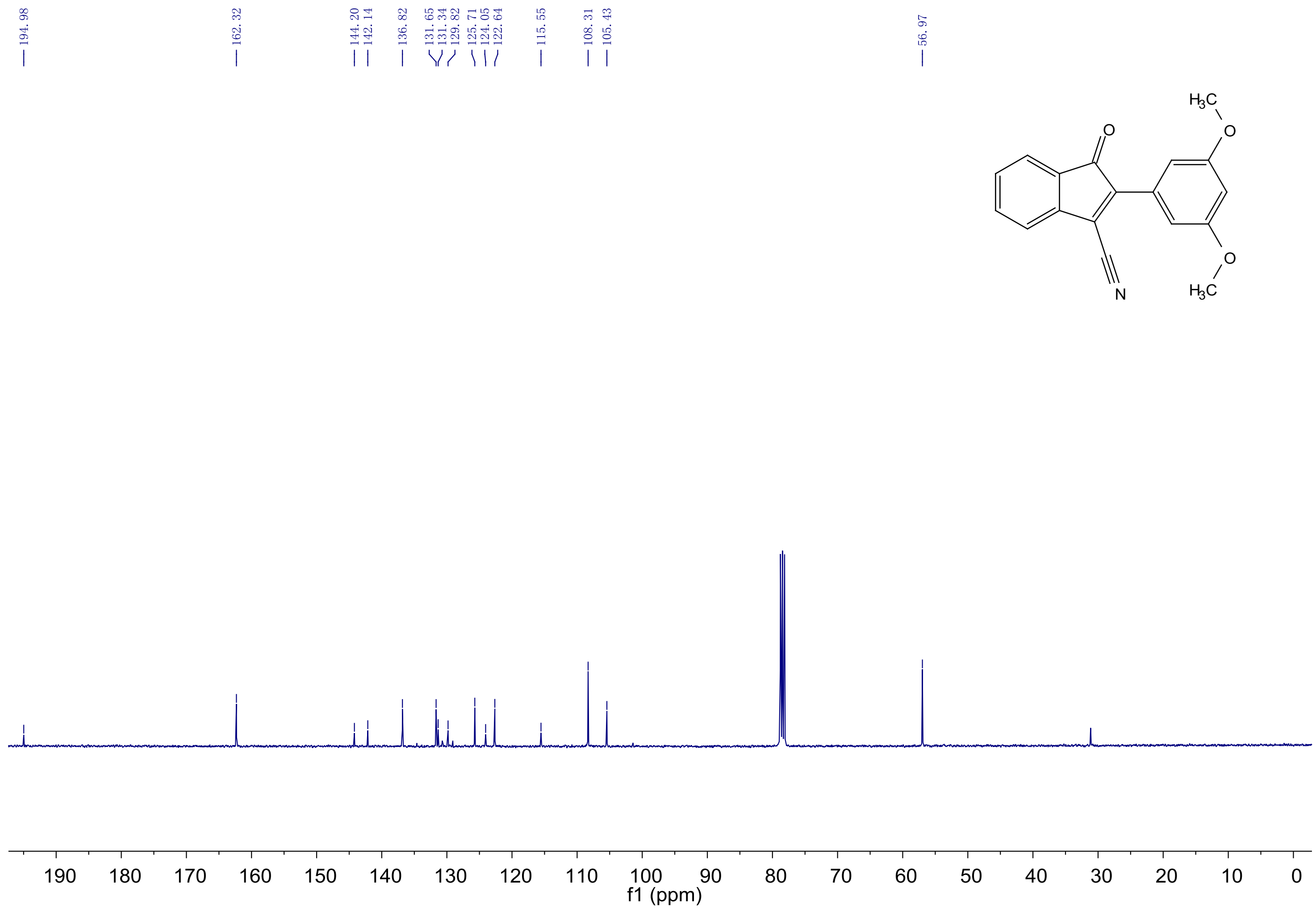
2o


7.59
7.56
7.54
7.38
7.36
7.36
7.35
7.34
7.14
2.39
O
CH3
CH3
N
4.07
2.08
1.00
6.56
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

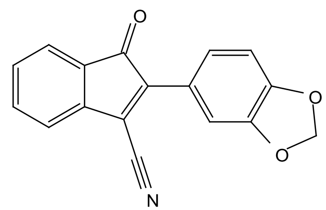

193.97
143.48
141.02
138.61
135.37
132.97
130.00
128.39
128.32
126.88
124.23
121.92
121.05
114.21
21.38
O
CH3
CH3
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

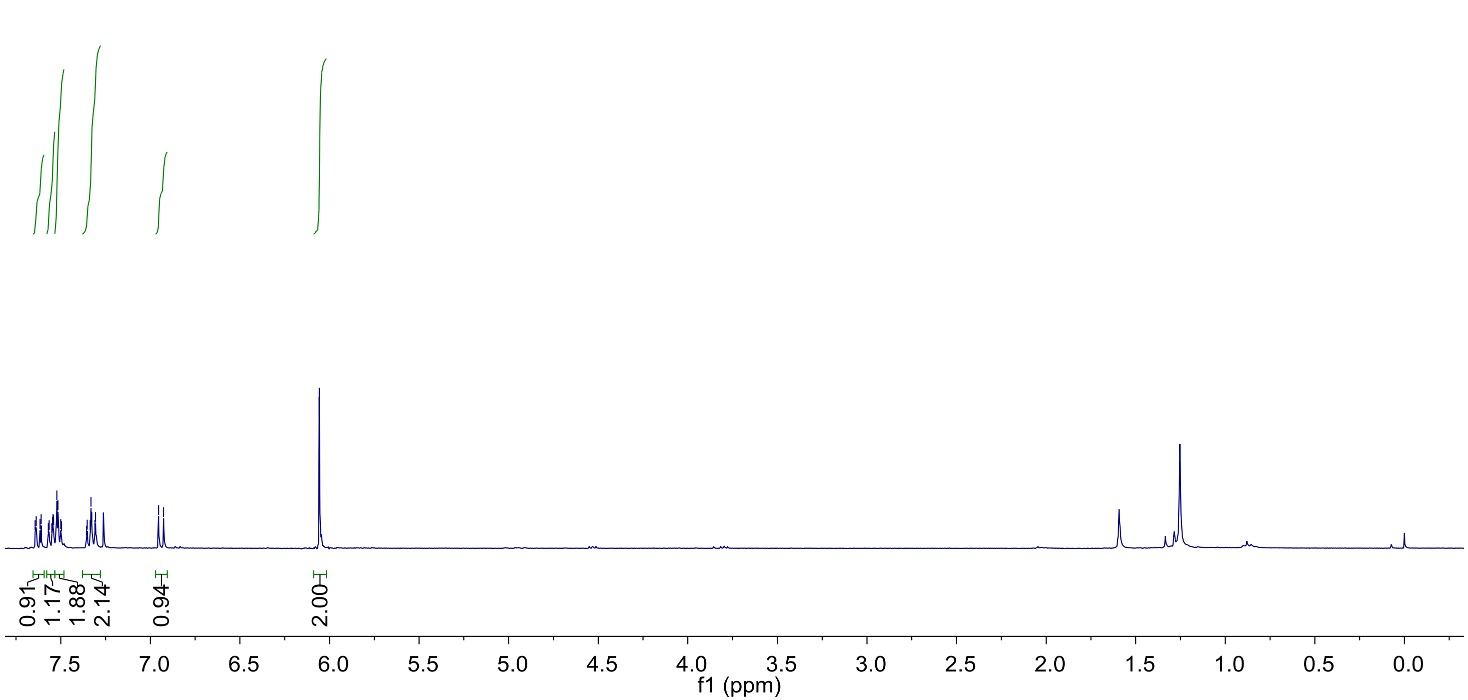
2p

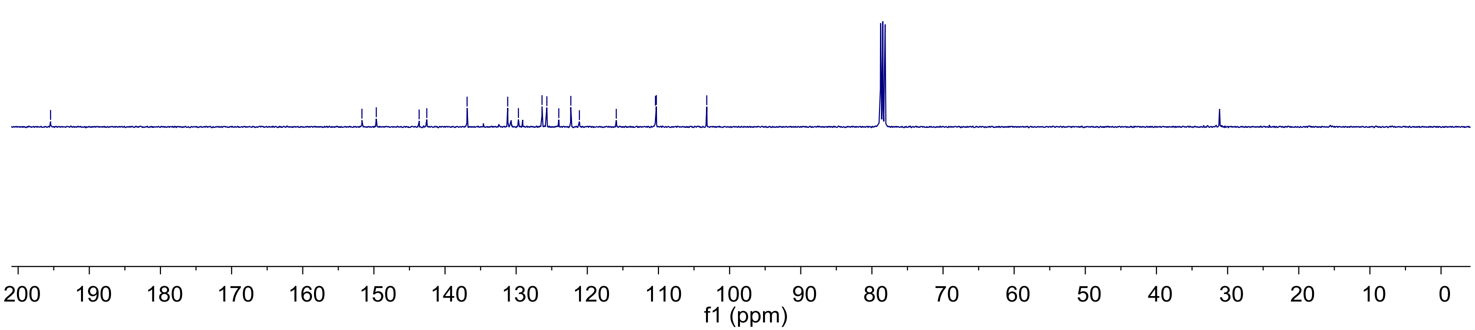

7.56
7.56
7.37
7.37
7.37
7.14
7.13
6.60
6.59
6.59
3.85
2.27
2.00
1.78
0.91
5.91
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

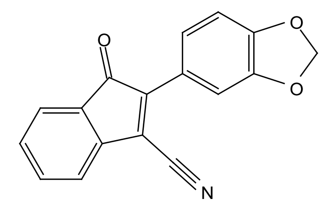

194.98
162.32
144.20
142.14
136.82
131.65
131.34
129.82
125.71
124.05
122.64
115.55
108.31
105.43
56.97
O
H3C
O
O
H3C
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2q

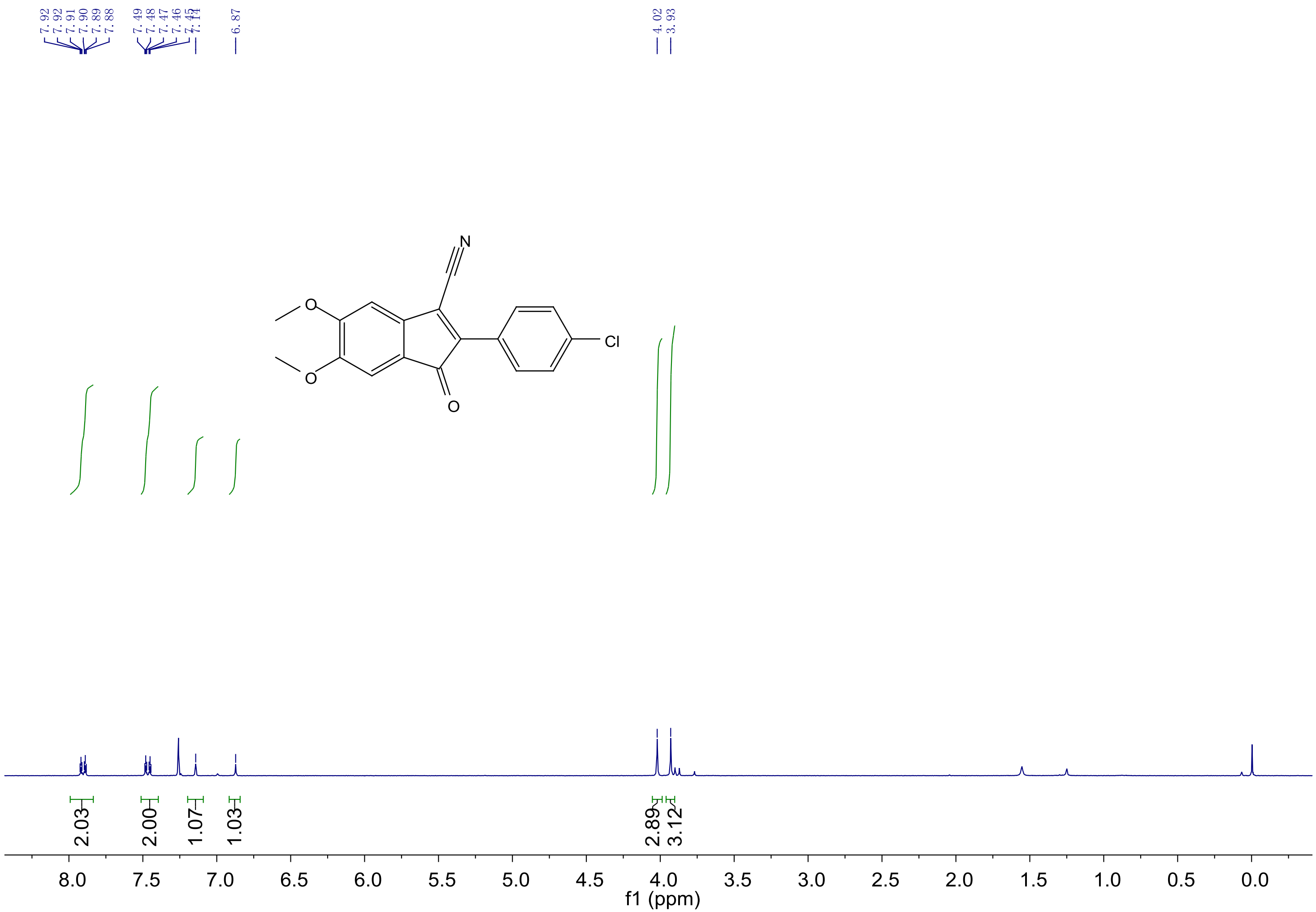


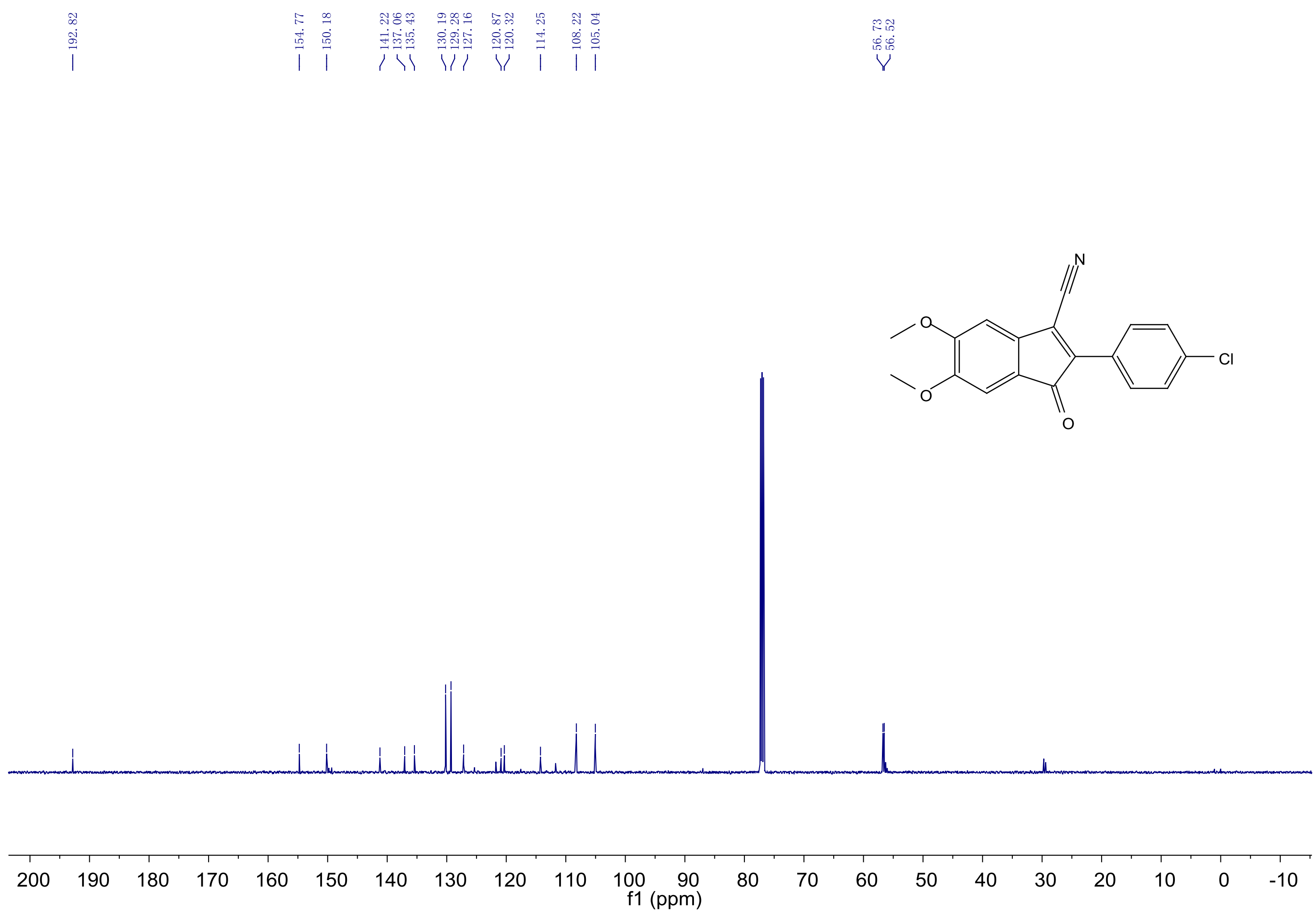

7.64
7.61
7.54
7.54
7.52
7.52
7.33
7.33
7.31
6.95
6.93
6.06
0.91
1.17
1.88
2.14
0.94
2.00
f1 (ppm)


195.45
151.68
149.66
143.64
142.57
136.90
131.19
129.68
126.37
125.69
124.01
122.32
121.11
115.93
110.42
110.30
103.21
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

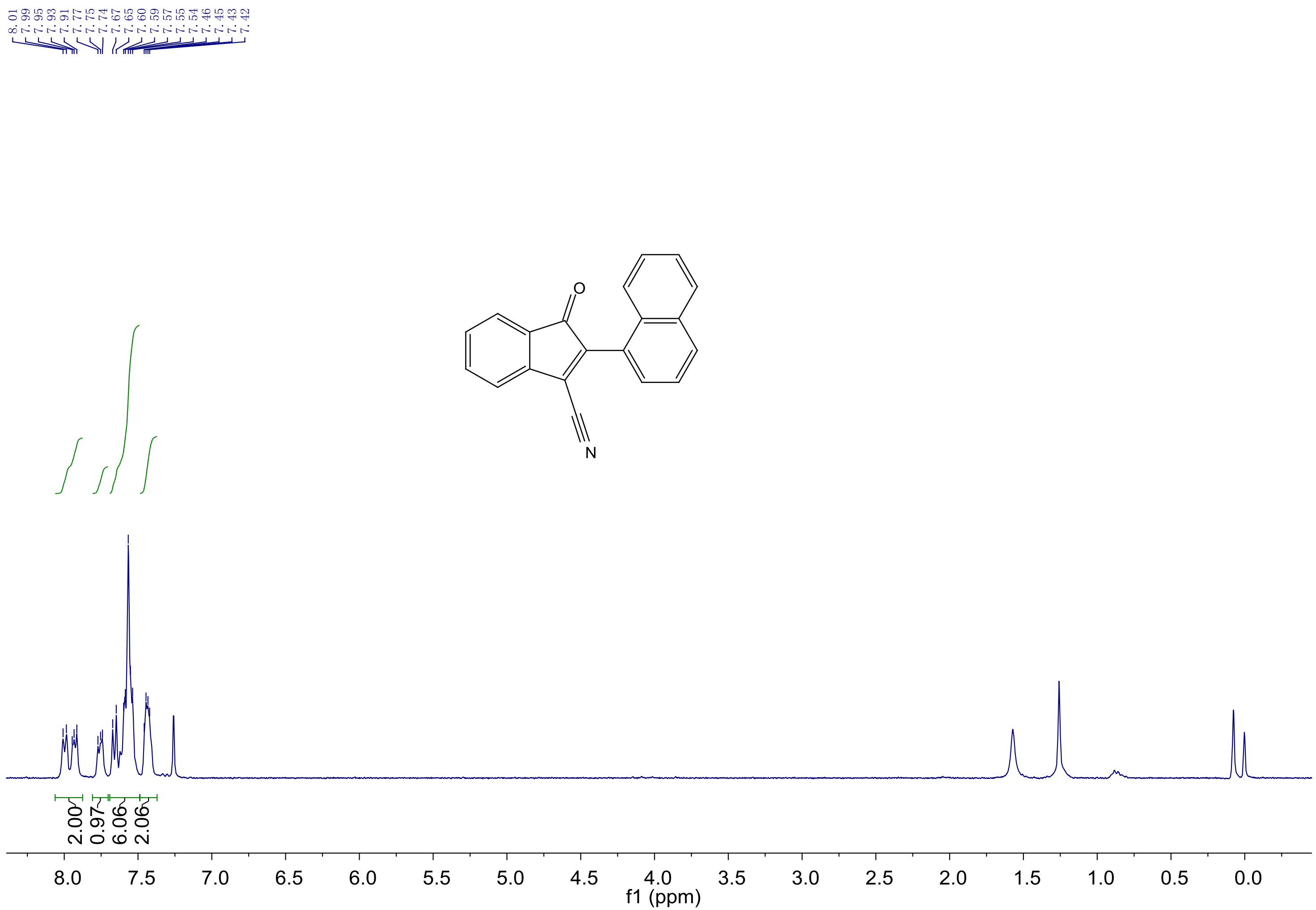

O
O
O
N

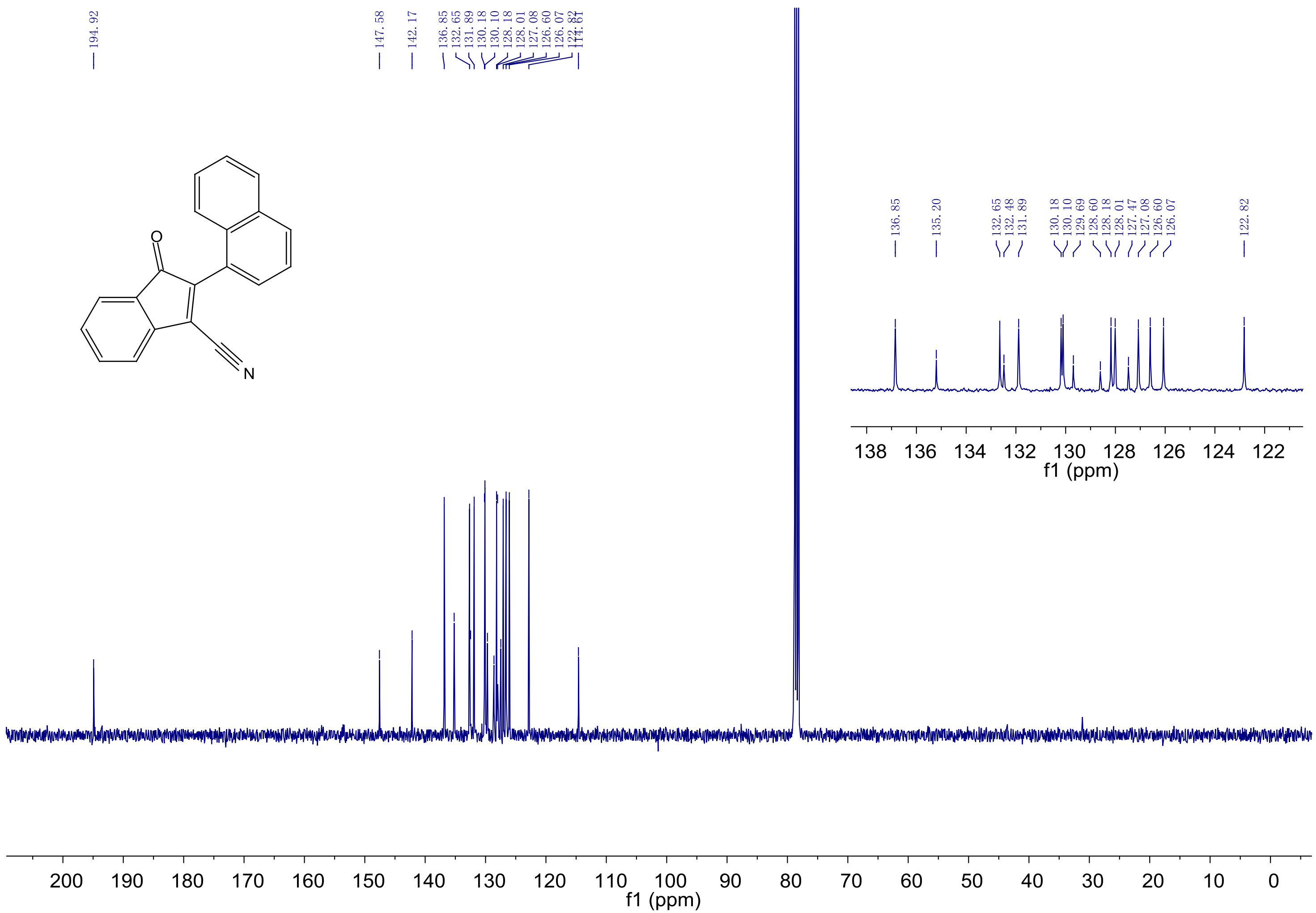
2r


7.92
7.92
7.91
7.90
7.89
7.88
7.49
7.48
7.47
7.46
7.45
7.14
6.87
4.02
3.93
N
O
O
O
Cl
2.03
2.00
1.07
1.03
2.89
3.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

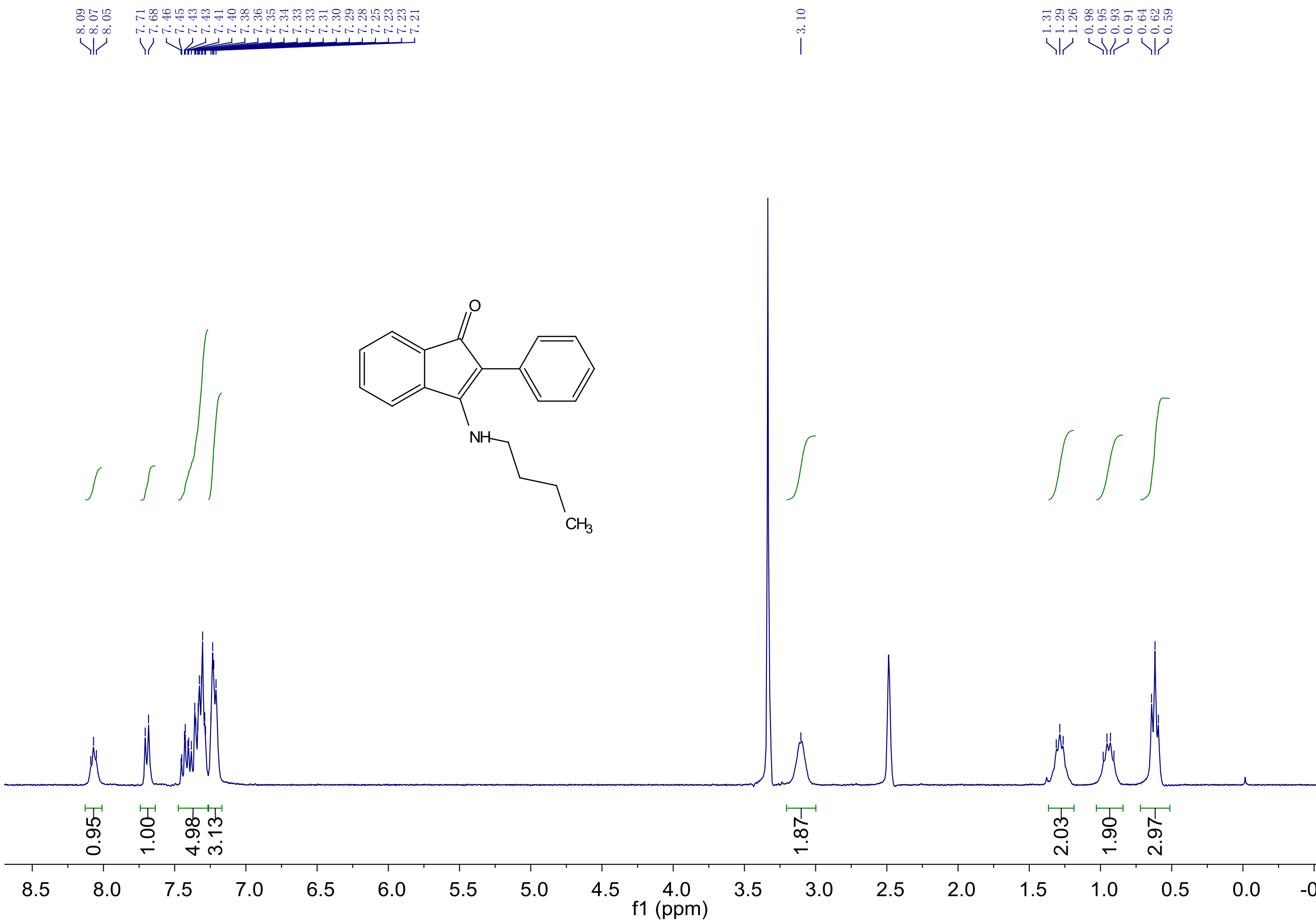

192.82
154.77
150.18
141.22
137.06
135.43
130.19
129.28
127.16
120.87
120.32
114.25
108.22
105.04
56.73
56.52
N
O
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

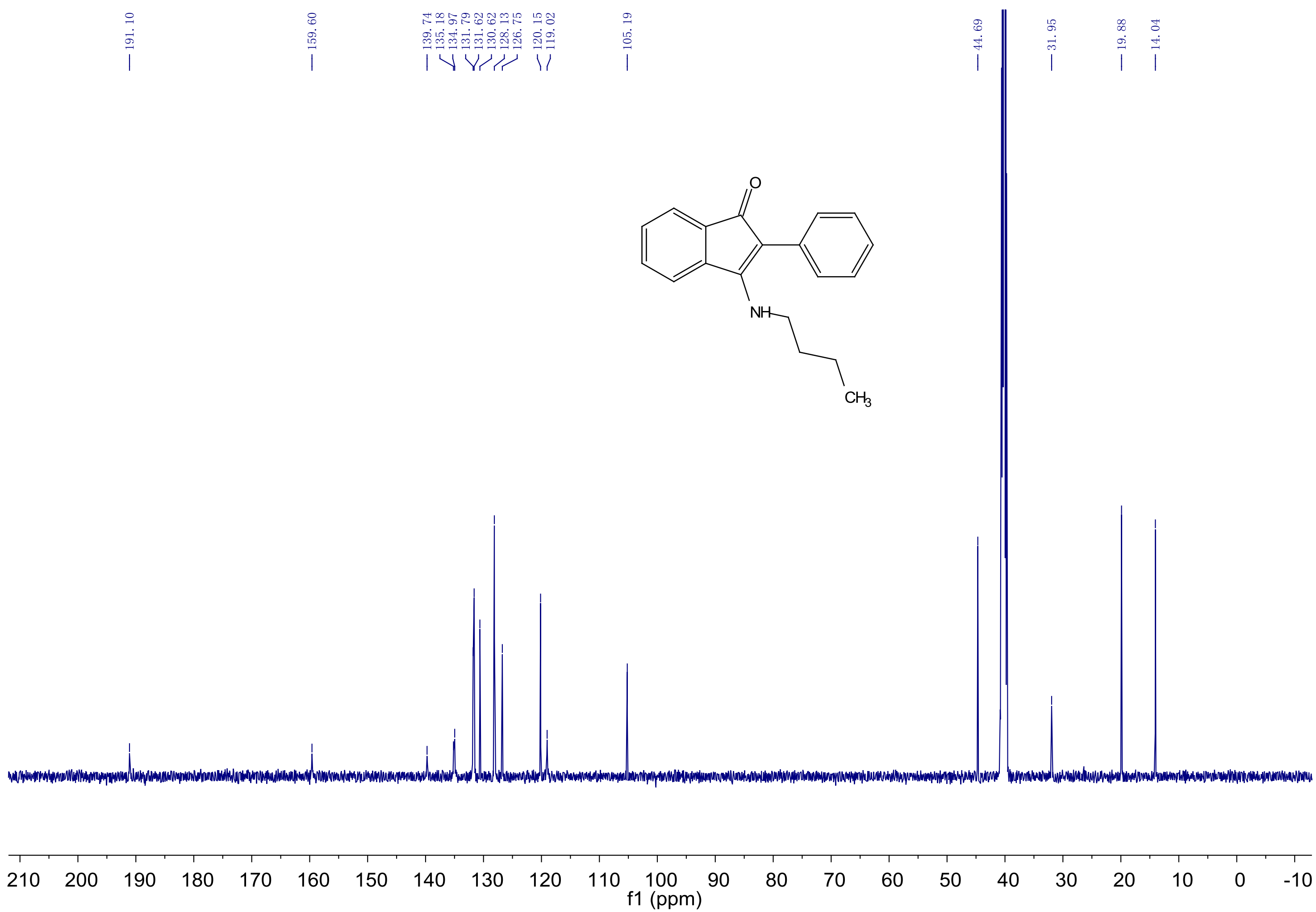
2s


O
N
8.01
7.99
7.95
7.93
7.91
7.77
7.75
7.74
7.67
7.65
7.60
7.59
7.57
7.55
7.54
7.46
7.45
7.43
7.42
2.00
0.97
6.06
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

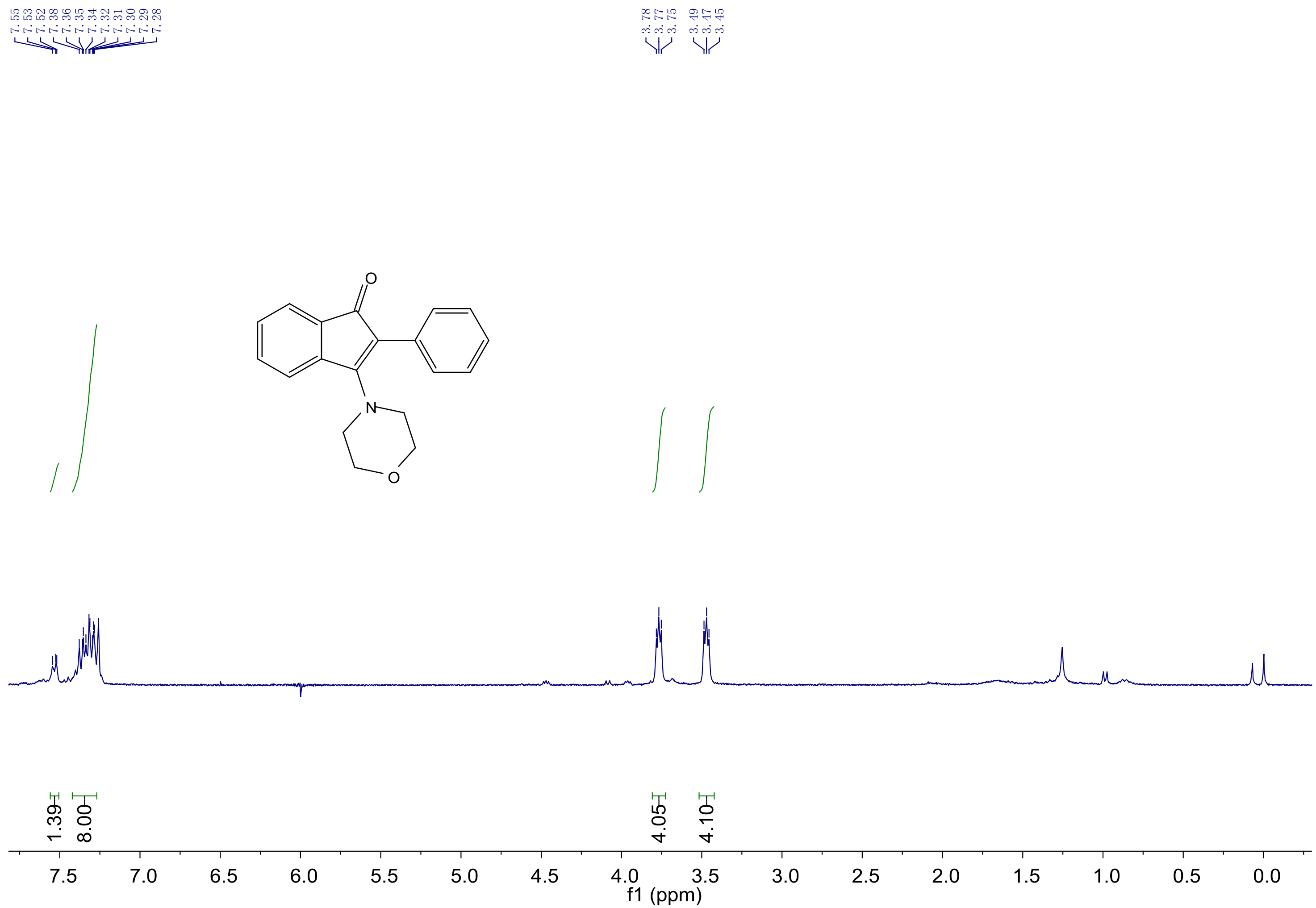

194.92
147.58
142.17
136.85
132.65
131.89
130.18
130.10
128.18
128.01
127.08
126.60
126.07
122.82
114.61
O
N
136.85
135.20
132.65
132.48
131.89
130.18
130.10
129.69
128.60
128.18
128.01
127.47
127.08
126.60
126.07
122.82
138 136 134 132 130 128 126 124 122
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

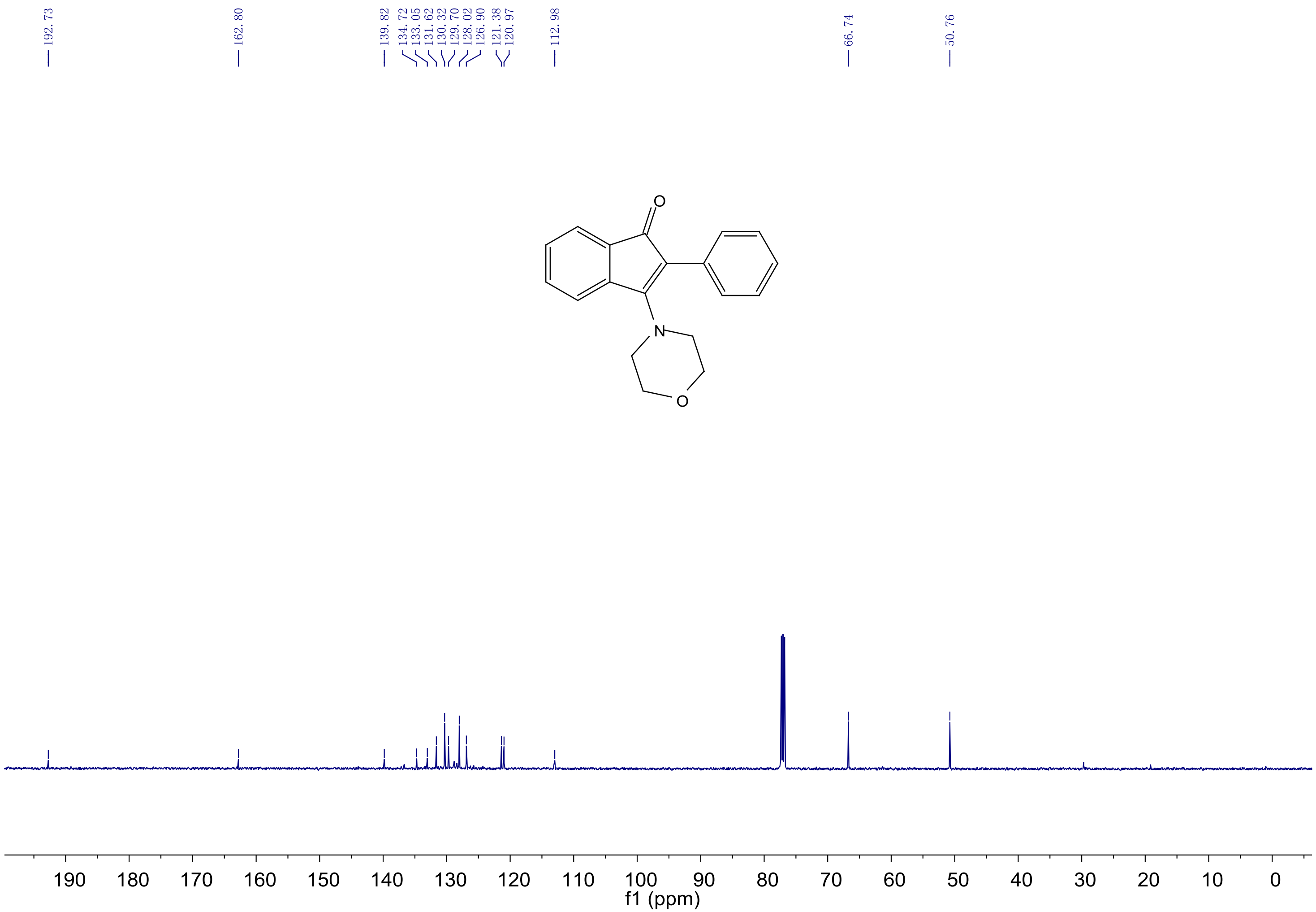
4


8.09
8.07
8.05
7.71
7.68
7.46
7.45
7.43
7.43
7.43
7.41
7.40
7.38
7.36
7.35
7.34
7.33
7.33
7.31
7.30
7.29
7.28
7.25
7.23
7.23
7.21
3.10
1.31
1.29
1.26
0.98
0.95
0.93
0.91
0.64
0.62
0.59
O
NH
CH3
0.95
1.00
4.98
3.13
1.87
2.03
1.90
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

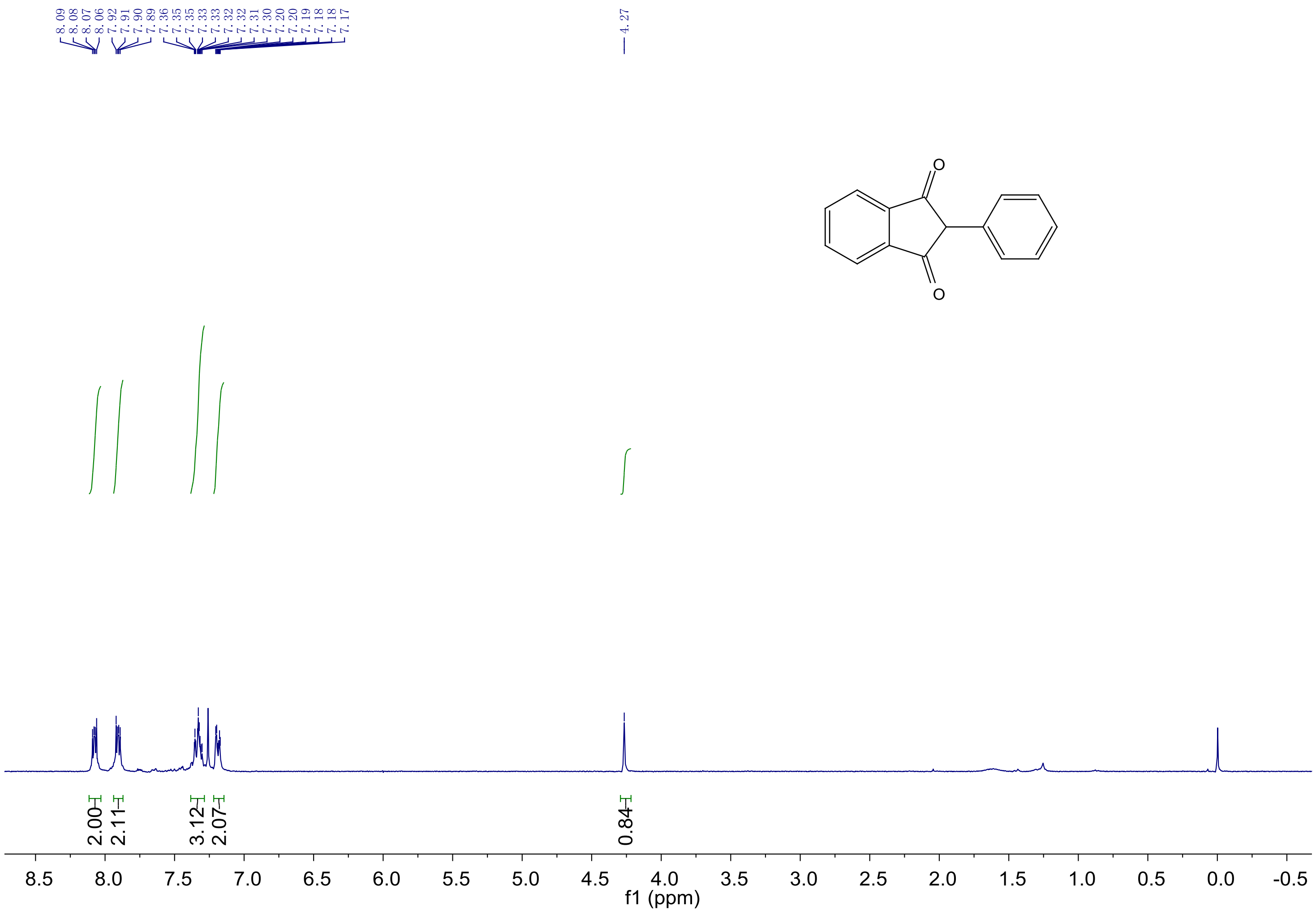

191.10
159.60
139.74
135.18
134.97
131.79
131.62
130.62
128.13
126.75
120.15
119.02
105.19
44.69
31.95
19.88
14.04
O
NH
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

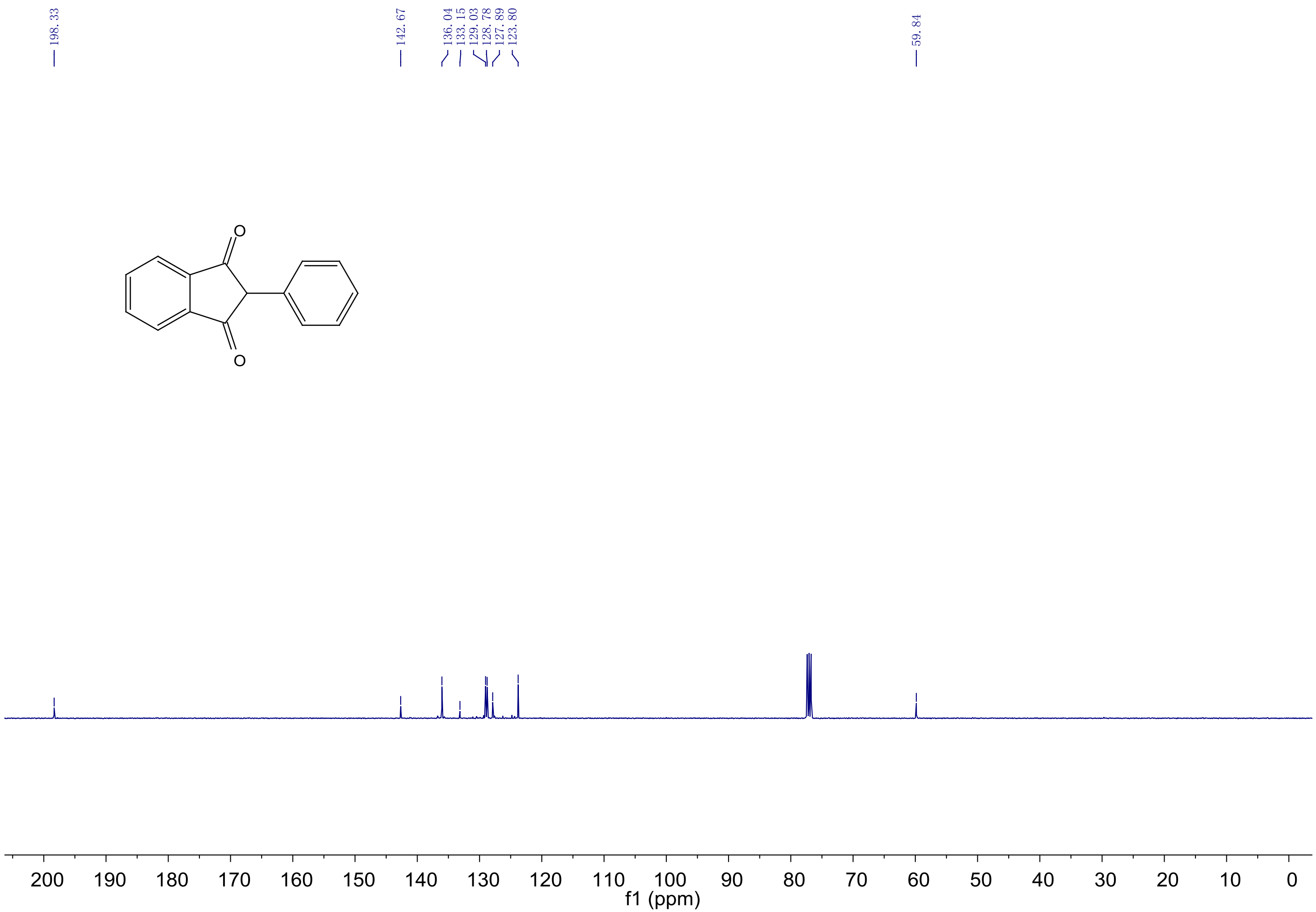
5


7.55
7.53
7.52
7.38
7.36
7.35
7.34
7.32
7.31
7.30
7.29
7.28
3.78
3.77
3.75
3.49
3.47
3.45
O
N
O
1.39
8.00
4.05
4.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

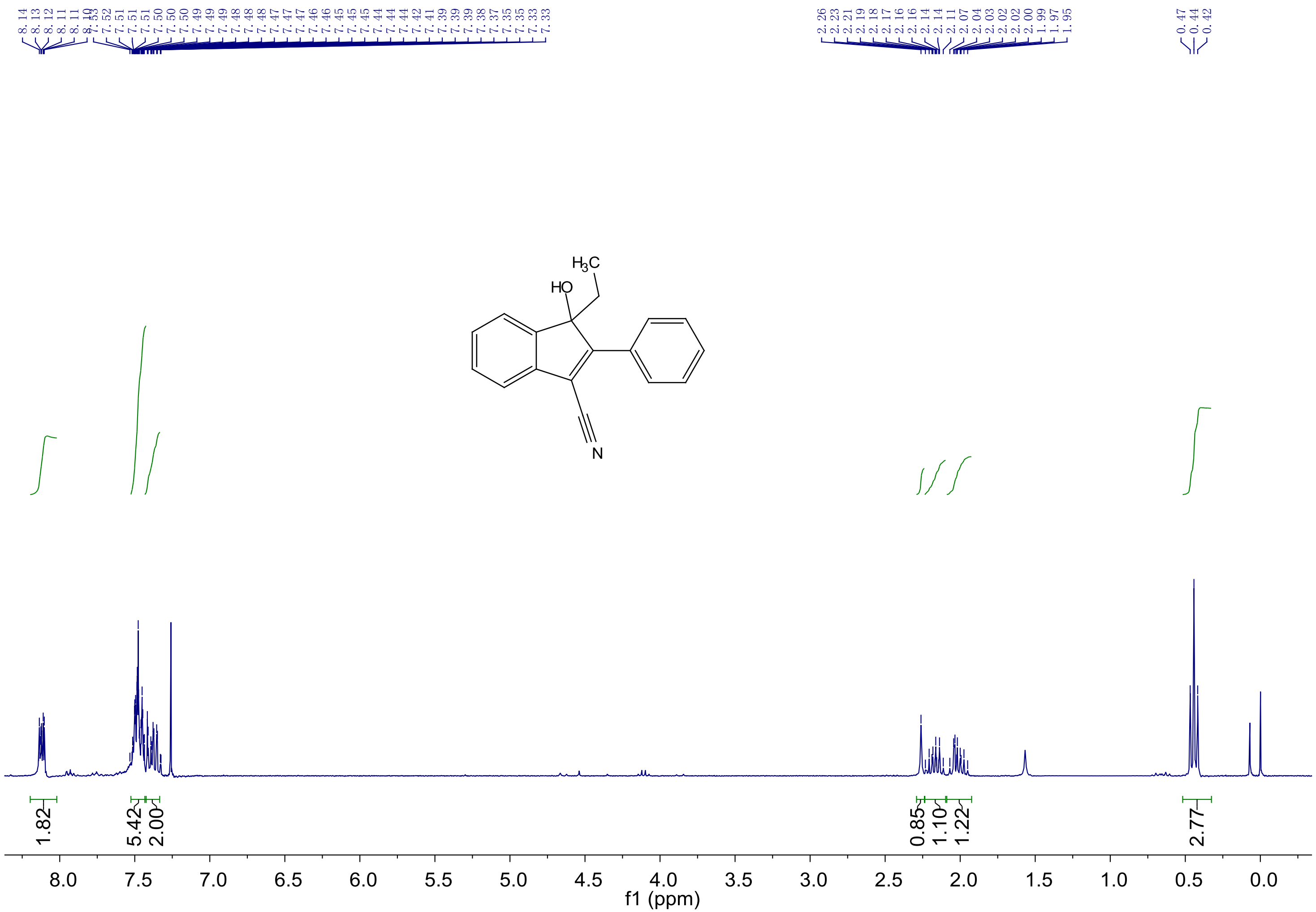

192.73
162.80
139.82
134.72
133.05
131.62
130.32
129.70
128.02
126.90
121.38
120.97
112.98
66.74
50.76
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

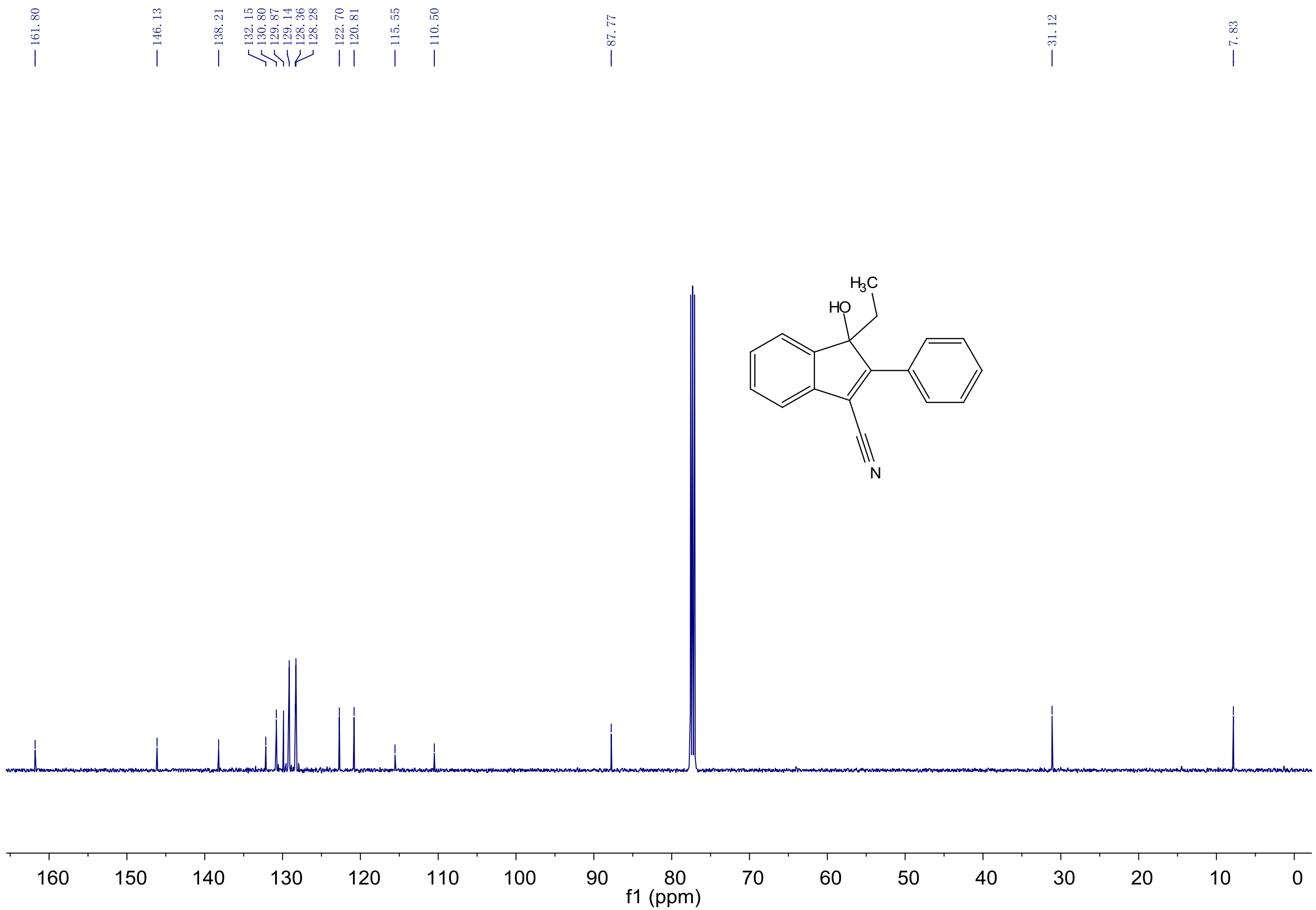
6


O
O
8.09
8.08
8.07
8.06
7.92
7.91
7.90
7.89
7.36
7.35
7.35
7.33
7.33
7.32
7.32
7.31
7.30
7.20
7.20
7.19
7.18
7.18
7.17
4.27
2.00
2.11
3.12
2.07
0.84
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

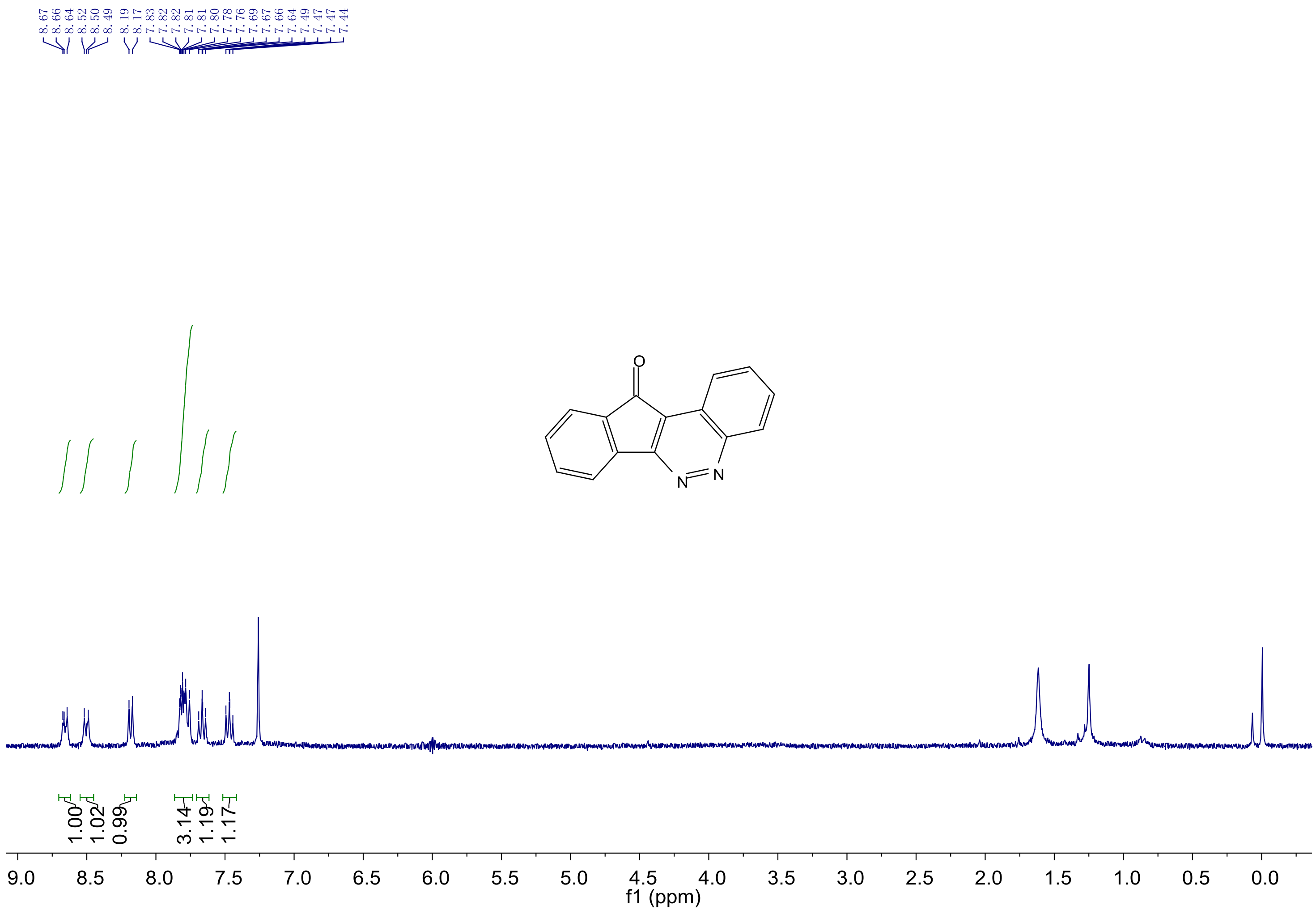

198.33
142.67
136.04
133.15
129.03
128.78
127.89
123.80
59.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

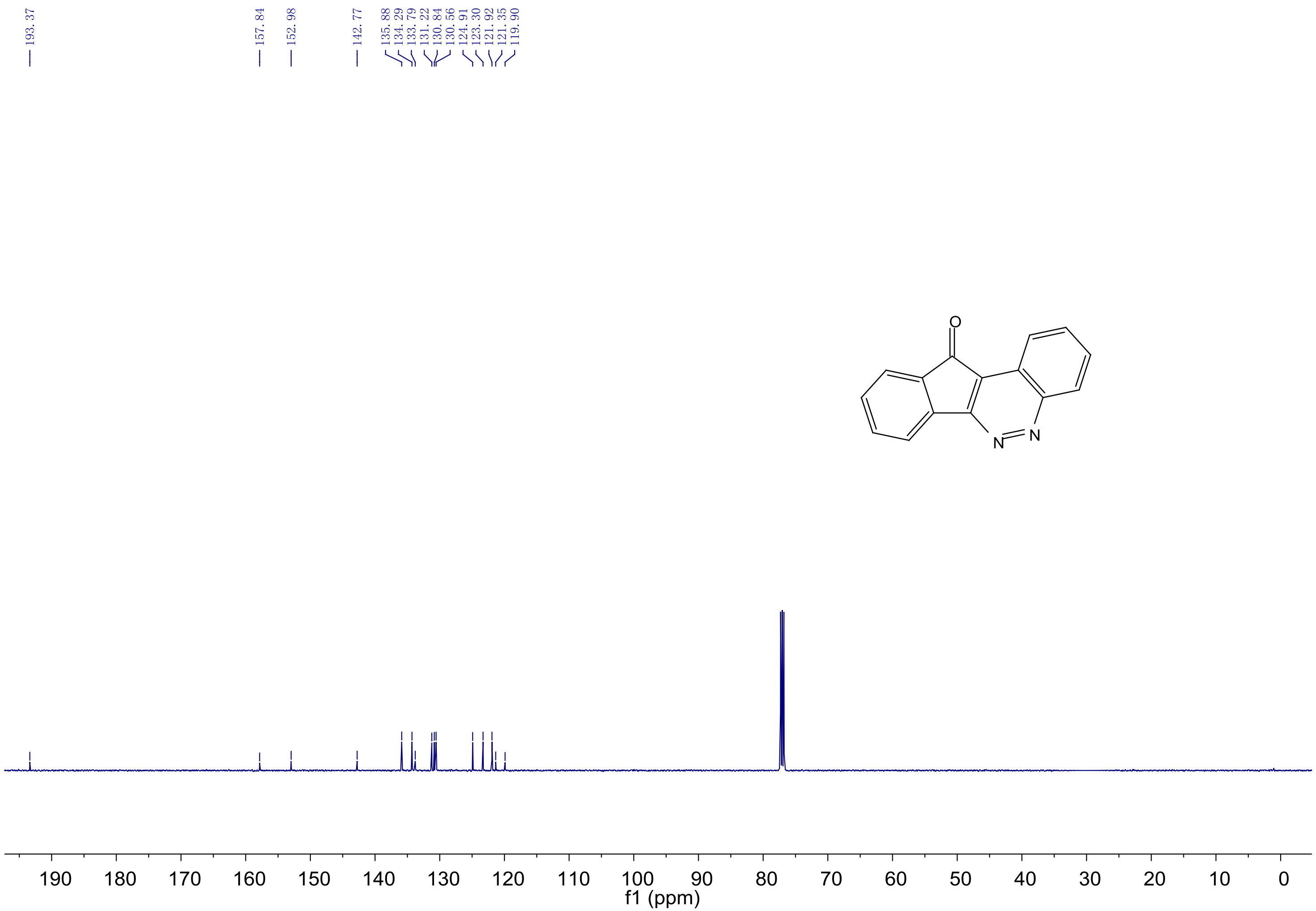
7


H3C
HO
N
8.14 8.13 8.12 8.11 8.11 8.10 7.53 7.52 7.51 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.42 7.41 7.39 7.39 7.39 7.38 7.37 7.35 7.35 7.33 7.33
2.26 2.23 2.21 2.19 2.18 2.17 2.16 2.16 2.14 2.14 2.11 2.07 2.04 2.03 2.02 2.02 2.00 1.99 1.97 1.95
0.47 0.44 0.42
1.82
5.42
2.00
0.85
1.10
1.22
2.77
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

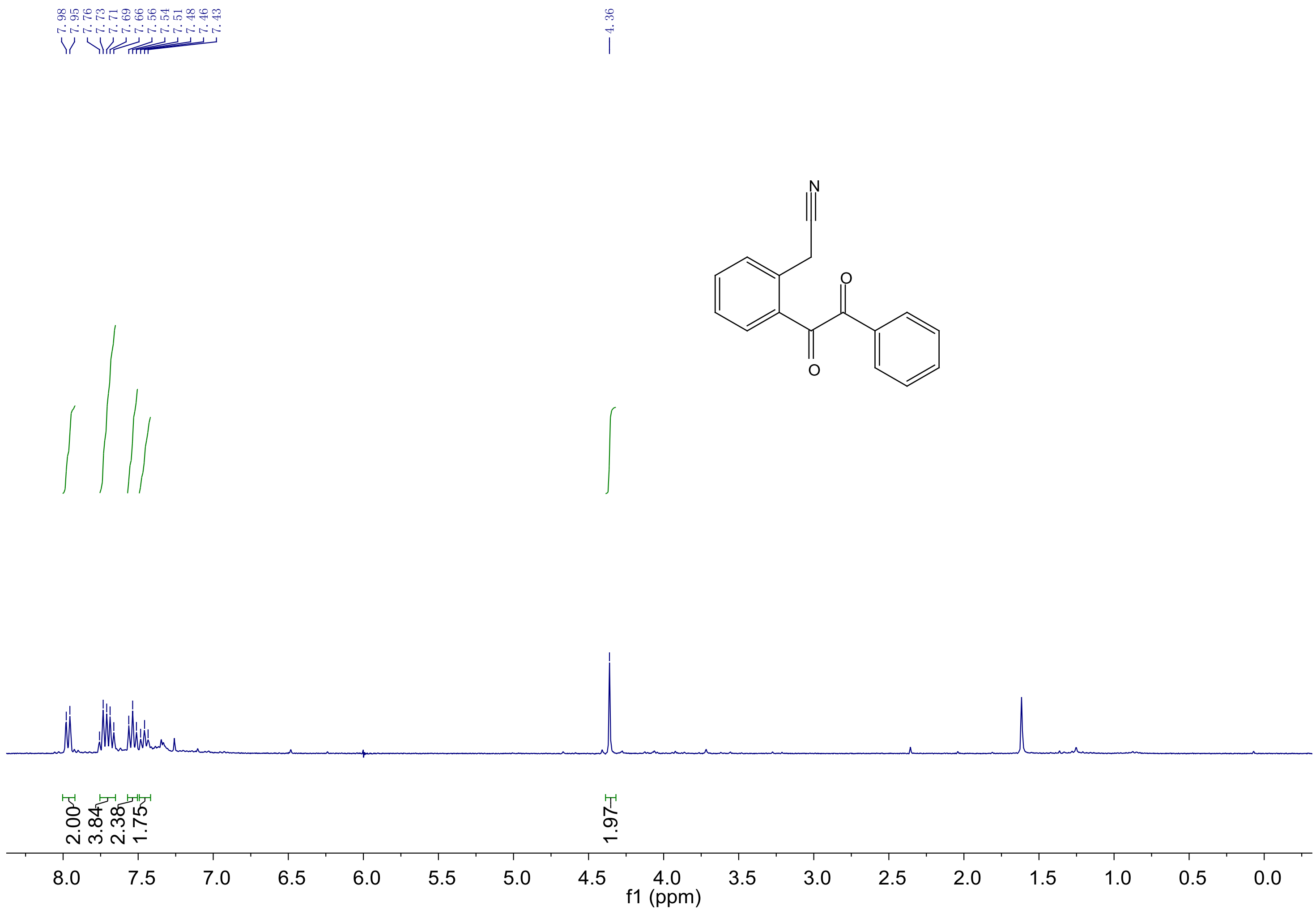

161.80
146.13
138.21
132.15
130.80
129.87
129.14
128.36
128.28
122.70
120.81
115.55
110.50
87.77
31.12
7.83
HO
H3C
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

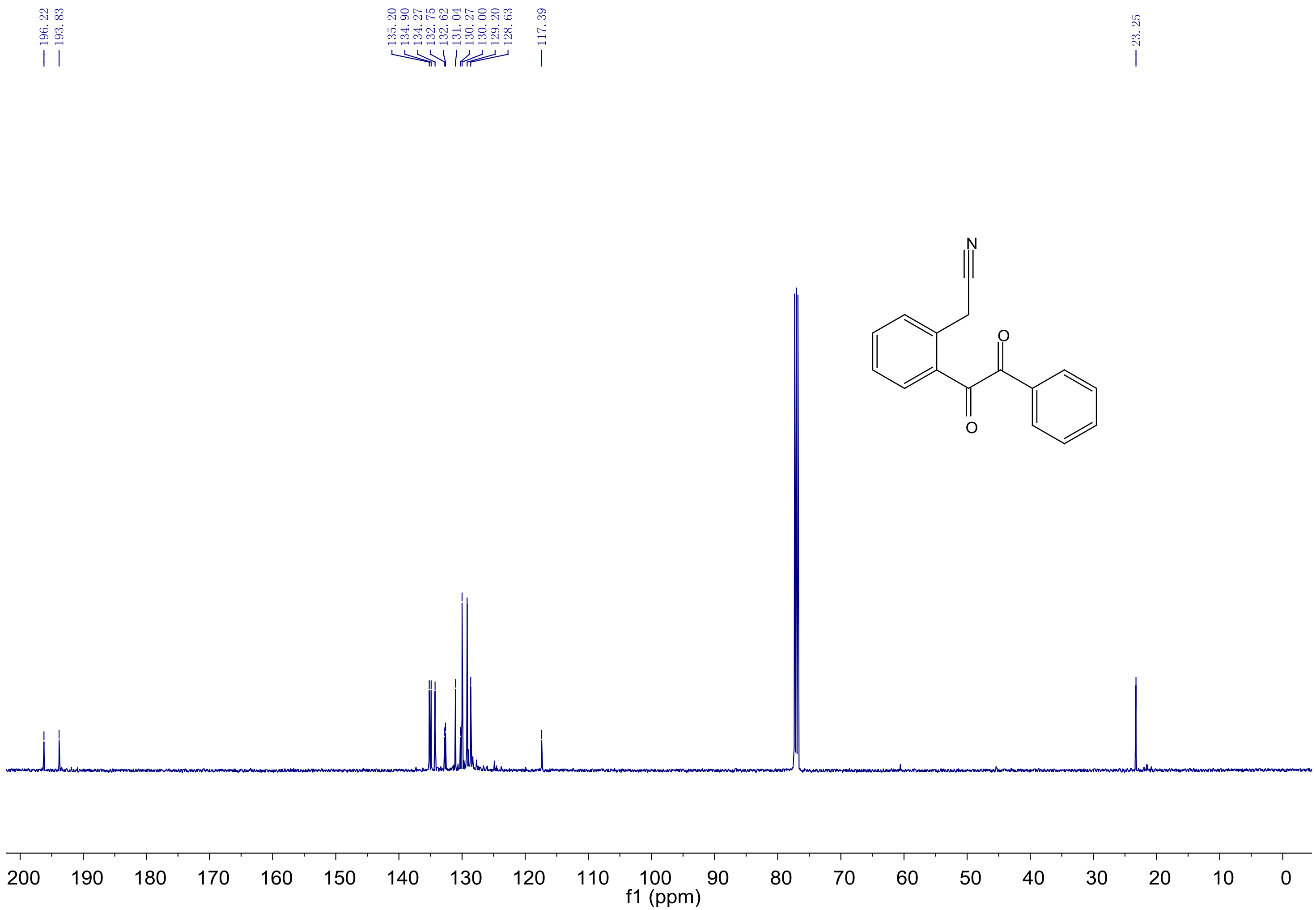
8


8.67
8.66
8.64
8.52
8.50
8.49
8.19
8.17
7.83
7.82
7.82
7.81
7.81
7.80
7.78
7.76
7.69
7.67
7.66
7.64
7.49
7.47
7.47
7.44
1.00
1.02
0.99
3.14
1.19
1.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


193.37
157.84
152.98
142.77
135.88
134.29
133.79
131.22
130.84
130.56
124.91
123.30
121.92
121.35
119.90
O
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3a


7.98
7.95
7.76
7.73
7.71
7.69
7.66
7.56
7.54
7.51
7.48
7.46
7.43
4.36
N
O
O
2.00
3.84
2.38
1.75
1.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


196.22
193.83
135.20
134.90
134.27
132.75
132.62
131.04
130.27
130.00
129.20
128.63
117.39
23.25
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

X-ray structure of 2d