

Supporting Information

An efficient method for the preparation of *tert*-butyl esters from benzyl cyanide and *tert*-butyl hydroperoxide under the metal free condition

Xiuling Chen, Yan Li, Minghu Wu,* haibing Guo, longqiang Jiang, jian Wang, Shaofa Sun*

Non-power Nuclear Technology Collaborative Innovation Center, School of Nuclear Technology and Chemistry & Life Science, Hubei University of Science and Technology, Xianning 437100 (China)

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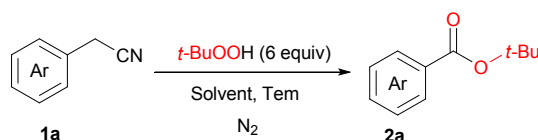
1. General remarks

All non-aqueous reactions and manipulations were performed in air atmosphere using standard Schlenk techniques. All solvents before use were dried, degassed by standard methods, and stored under nitrogen. The reactions were monitored by GC and GC-MS. The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer at 400 MHz and 100 MHz respectively (Hunan university), and chemical shifts were reported in parts per million (ppm) downfield from TMS using the solvent resonance as internal standard. Flash column chromatography was performed using silica gel 30-60 μm . GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 7820A (Hunan university). The electron ionization (EI) method was used as the ionization method for the HRMS measurement (Thermo Finnigan MAT 95 XP, Hunan University). Melting point was recorded on X-4 (digital display micro melting point measuring instrument, Gonyiyuhua). Benzonitriles were purchased from Energy Chemical, Alfa Aesar, Aladdin or Maya Reagent; 2-phenylacetonitrile was dried and degassed by standard methods and stored under nitrogen before use. The TBHP was purchased from Energy Chemical, dried by MgSO_4 before use.

2. General procedure

5 mol% catalyst, 0.2 mmol benzonitriles, 1.2 mmol TBHP, 110 mg 4Å MS were dissolved in 2 mL CH_3CN under N_2 atmosphere and stirred at 60 $^\circ\text{C}$ in sealed tube. After completion of the reaction, the resulting solution was cooled to room temperature, washed with saturated NaCO_3 aqueous solution, and extracted with CHCl_3 three times. The organic layer was dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with petroleum ether to afford the desired product.

3. Optimization of reaction conditions^a



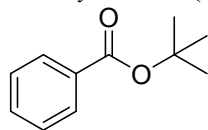
Entry	Metal cat. (5 mol %)	Ms 4 Å ^b	Solvent	Yield (2a) ^c
1	CuCl	-	acetone	34
2	CuCl	-	DCE	35
3	CuCl	-	1,4-dioxane	40
4	CuCl	-	THF	36
5	CuCl	-	toluene	37
6	CuCl	-	<i>n</i> -hexane	39
7	CuCl	-	DMSO	27
8	CuCl	-	DMF	35
9	CuCl	-	CH_3CN	45
10	MnCl_2	-	CH_3CN	41
11	MnCO_3	-	CH_3CN	20
12	FeCl_3	-	CH_3CN	18
13	AgNO_3	-	CH_3CN	41
14	--	-	CH_3CN	46
15	--	+	CH_3CN	89
16 ^d	--	+	CH_3CN	86
17 ^e	--	+	CH_3CN	60
18 ^f	--	+	CH_3CN	29
19 ^g	--	+	CH_3CN	--

^aReaction conditions: 2-phenylacetonitrile **1a** (0.2 mmol), TBHP (1.2 mmol), cat (5 mol%), additive (110 mg), solvent (2 ml), in 25 mL schlenk tube, 60 $^\circ\text{C}$, N_2 , 16 h. ^bAbbreviation: + or - shows the presence or absence of 4A

molecular sieves. ^cGC yields based on **1a** using *n*-hexadecane as internal standard. ^d80 °C. ^e100 °C. ^f40 °C. ^gdi-*tert*-butyl peroxide (DTBP) was employed as oxidant under N₂ atmosphere.

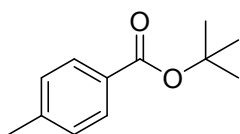
¹H NMR and ¹³C NMR data of products

tert-butyl benzoate (**2a**)¹



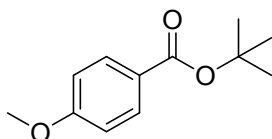
Following the general procedure (petroleum ether), **2a** was obtained as a white liquid, isolated yield: 82%. ¹H NMR (CDCl₃, 400 MHz): δ 7.98 (d, 2H, *J* = 4.0 Hz), 7.51 (t, 1H, *J* = 7.4 Hz), 7.41 (t, 2H, *J* = 7.6 Hz), 1.60 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 165.8, 132.4, 132.0, 129.4, 128.2, 81.0, 28.2; GC-MS: *m/z* = 178.

tert-butyl 4-methylbenzoate (**2b**)¹



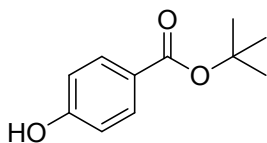
Following the general procedure (petroleum ether), **2b** was obtained as a white liquid, isolated yield: 81%. ¹H NMR (CDCl₃, 400 MHz): δ 7.76 (d, 2H, *J* = 8.4 Hz), 7.17 (d, 2H, *J* = 8.0 Hz), 2.33 (s, 3H), 1.33 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 164.5, 144.2, 129.3, 129.1, 124.9, 83.9, 26.3, 21.7; GC-MS: *m/z* = 192.

tert-butyl 4-methoxybenzoate (**2c**)¹



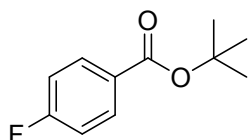
Following the general procedure (petroleum ether), **2c** was obtained as a white liquid, isolated yield: 82%. ¹H NMR (CDCl₃, 400 MHz): δ 7.93 (d, 2H, *J* = 8.8 Hz), 6.88 (d, 2H, *J* = 8.8 Hz), 3.84 (s, 3H), 1.58 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 165.6, 163.0, 131.4, 124.5, 113.4, 80.5, 55.4, 28.3; GC-MS: *m/z* = 208.

tert-butyl 4-hydroxybenzoate (**2d**)²



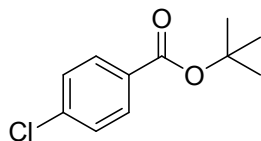
Following the general procedure (petroleum ether), **2d** was obtained as a white solid, mp = 128-130 °C isolated yield: 72%. ¹H NMR (CDCl₃, 400 MHz): δ 7.88 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.8 Hz), 1.59 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 165.6, 166.3, 160.1, 131.7, 124.0, 115.1, 81.0, 28.3; GC-MS: *m/z* = 194.

tert-butyl 4-fluorobenzoate (**2e**)³



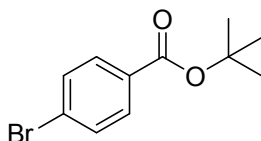
Following the general procedure (petroleum ether), **2e** was obtained as a pale yellow liquid, isolated yield: 81%. ¹H NMR (CDCl₃, 400 MHz): δ 7.98 (d, 2H, *J* = 4.4 Hz), 7.07 (d, 2H, *J* = 8.6 Hz), 1.59 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 164.5 (d, *J*_{F-C} = 251.3 Hz), 163.8, 130.8 (d, *J*_{F-C} = 9.2 Hz), 127.2 (d, *J*_{F-C} = 2.9 Hz), 114.1 (d, *J*_{F-C} = 21.7 Hz), 80.2, 27.2; ¹⁹F NMR (376 MHz, CDCl₃): δ -106.9 (s, 1F); GC-MS: *m/z* = 196.

tert-butyl 4-chlorobenzoate (**2f**)¹



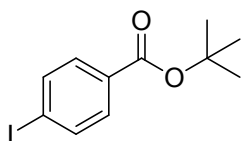
Following the general procedure (petroleum ether), **2f** was obtained as white liquid, isolated yield: 78%. ¹H NMR (CDCl₃, 400 MHz): δ 7.91 (d, 2H, *J* = 8.4 Hz), 7.36 (d, 2H, *J* = 8.4 Hz), 1.59 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 164.8, 138.8, 130.8, 130.4, 128.4, 81.4, 28.1; GC-MS: *m/z* = 212.

tert-butyl 4-bromobenzoate (**2g**)¹



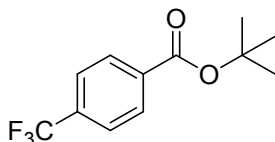
Following the general procedure (petroleum ether), **2g** was obtained as a pale yellow liquid, isolated yield: 83%. ¹H NMR (CDCl₃, 400 MHz): δ 7.83 (d, 2H, *J* = 8.4 Hz), 7.53 (d, 2H, *J* = 8.4 Hz), 1.58 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 165.0, 131.5, 131.0, 130.9, 127.4, 81.5, 28.2; GC-MS: *m/z* = 256.

tert-butyl 4-iodobenzoate (**2h**)⁴



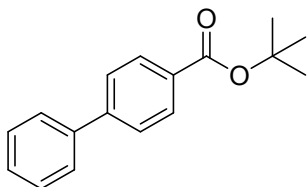
Following the general procedure (petroleum ether), **2h** was obtained as a yellow liquid, isolated yield: 69%. ¹H NMR (CDCl₃, 400 MHz): δ 7.74 (d, 2H, *J* = 8.4 Hz), 7.67 (d, 2H, *J* = 8.8 Hz), 1.57 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 165.2, 137.5, 131.5, 131.0, 100.1, 81.4, 28.2; GC-MS: *m/z* = 303.

tert-butyl 4-(trifluoromethyl)benzoate (**2i**)⁵



Following the general procedure (petroleum ether), **3a** was obtained as a pale yellow liquid, isolated yield: 78%. ¹H NMR (CDCl₃, 400 MHz): δ 8.09 (d, 2H, *J* = 8.4 Hz), 7.66 (d, 2H, *J* = 8.4 Hz), 1.60 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 164.5, 135.2, 134.0 (q, *J*_{F-C} = 32,3 Hz), 129.8, 125.2 (q, *J*_{F-C} = 3.8 Hz), 123.7 (q, *J*_{F-C} = 270.9 Hz), 81.9, 28.1; ¹⁹F NMR (376 MHz, CDCl₃): δ -63.0 (s, 3F); GC-MS: *m/z* = 246.

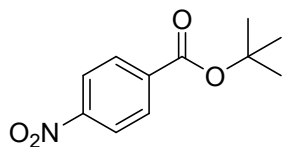
tert-butyl [1,1'-biphenyl]-4-carboxylate (**2j**)⁶



Following the general procedure (petroleum ether), **2j** was obtained as a pale yellow liquid, isolated yield: 73%. ¹H NMR (CDCl₃, 400 MHz): δ 8.09 (d, 2H, *J* = 8.0 Hz), 7.65 (t, 4H, *J* = 8.4 Hz), 7.47 (t, 2H, *J* = 7.6 Hz), 7.40 (t,

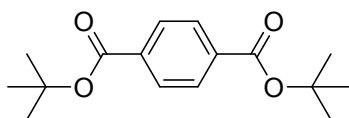
1H, $J = 7.4$ Hz), 1.65 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.7, 145.2, 140.2, 130.8, 130.0, 128.9, 128.0, 127.3, 126.9, 81.0, 28.3; GC-MS: $m/z = 254$.

tert-butyl 4-nitrobenzoate (**2k**)³



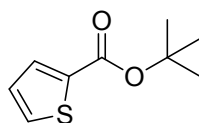
Following the general procedure (petroleum ether), **2k** was obtained as a white solid, mp = 112-114 °C isolated yield: 90%. ^1H NMR (CDCl_3 , 400 MHz): δ 8.23 (d, 2H, $J = 8.8$ Hz), 8.12 (d, 2H, $J = 8.8$ Hz), 1.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.7, 150.2, 137.4, 130.5, 123.3, 82.6, 28.1; HRMS (EI): calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_4$: 223.0845; found: 223.0882.

di-*tert*-butyl terephthalate (**2l**)⁶



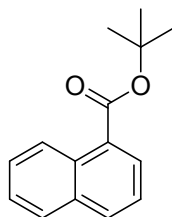
Following the general procedure (petroleum ether), **2l** was obtained as white solid, mp = 117-119 °C, isolated yield: 72%. ^1H NMR (CDCl_3 , 400 MHz): δ 8.00 (s, 4H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.1, 135.4, 129.2, 81.6, 28.1; GC-MS: $m/z = 278$.

tert-butyl thiophene-2-carboxylate (**2m**)¹



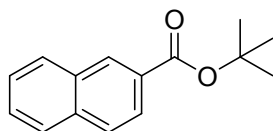
Following the general procedure (petroleum ether), **2m** was obtained as a pale yellow liquid, isolated yield: 72%. ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, 1H, $J = 3.6$ Hz), 7.48 (d, 1H, $J = 5.2$ Hz), 7.05 (t, 1H, $J = 4.2$ Hz), 1.57 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.6, 135.9, 132.7, 131.6, 127.5, 81.7, 28.2; GC-MS: $m/z = 184$.

tert-butyl-1-naphthoate (**2n**)¹



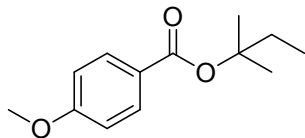
Following the general procedure (petroleum ether), **2n** was obtained as a pale yellow liquid, isolated yield: 80%. ^1H NMR (CDCl_3 , 400 MHz): δ 8.87 (d, 1H, $J = 8.4$ Hz), 8.09 (d, 1H, $J = 7.2$ Hz), 7.98 (d, 1H, $J = 8.0$ Hz), 7.87 (d, 1H, $J = 8.0$ Hz), 7.60 (t, 1H, $J = 7.6$ Hz), 7.47-7.54 (m, 2H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 133.9, 132.7, 131.2, 129.6, 129.3, 128.5, 127.4, 126.0, 125.8, 124.5, 81.5, 28.4; GC-MS: $m/z = 228$.

tert-butyl-2-naphthoate (**2o**)¹



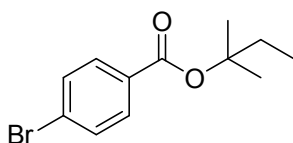
Following the general procedure (petroleum ether), **2o** was obtained as a white solid, mp = 81-83 °C, isolated yield: 84%. ¹H NMR (CDCl₃, 400 MHz): δ 8.55 (s, 1H), 8.03 (d, 1H, *J* = 8.4 Hz), 7.94 (d, 1H, *J* = 8.0 Hz), 7.86 (d, 2H, *J* = 5.2 Hz), 7.51-7.59 (m, 1H), 1.66 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 135.3, 132.5, 130.7, 129.3, 128.0, 127.9, 127.7, 126.5, 125.4, 81.2, 28.3; GC-MS: *m/z* = 228.

tert-pentyl 4-methoxybenzoate (**2p**)



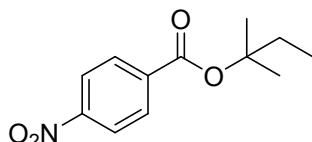
Following the general procedure (petroleum ether), **3a** was obtained as a pale yellow liquid, isolated yield: 82%. ¹H NMR (CDCl₃, 400 MHz): δ 7.86 (d, 2H, *J* = 8.8 Hz), 7.80 (d, 2H, *J* = 8.2 Hz), 3.75 (s, 3H), 1.82 (q, 2H, *J* = 7.6 Hz), 1.58 (s, 9H), 0.87 (t, 3H, *J* = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 165.5, 163.0, 131.3, 124.5, 113.4, 82.9, 55.4, 33.8, 25.7, 8.3; HRMS (EI): calcd for C₁₃H₁₈O₃: 222.1256; found: 222.1241.

tert-pentyl 4-bromobenzoate (**2q**)



Following the general procedure (petroleum ether), **2q** was obtained as a pale yellow liquid, isolated yield: 88%. isolated yield: 93%. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 7.83 (d, 2H, *J* = 8.4 Hz), 7.53 (d, 2H, *J* = 8.4 Hz), 1.91 (q, 2H, *J* = 7.4 Hz), 1.55 (s, 9H), 0.95 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 164.9, 131.5, 131.0, 130.9, 127.4, 83.9, 33.7, 26.0, 8.3; HRMS (EI): calcd for C₁₂H₁₅BrO₂: 270.0255; found: 270.0269.

tert-pentyl 4-nitrobenzoate (**2r**)



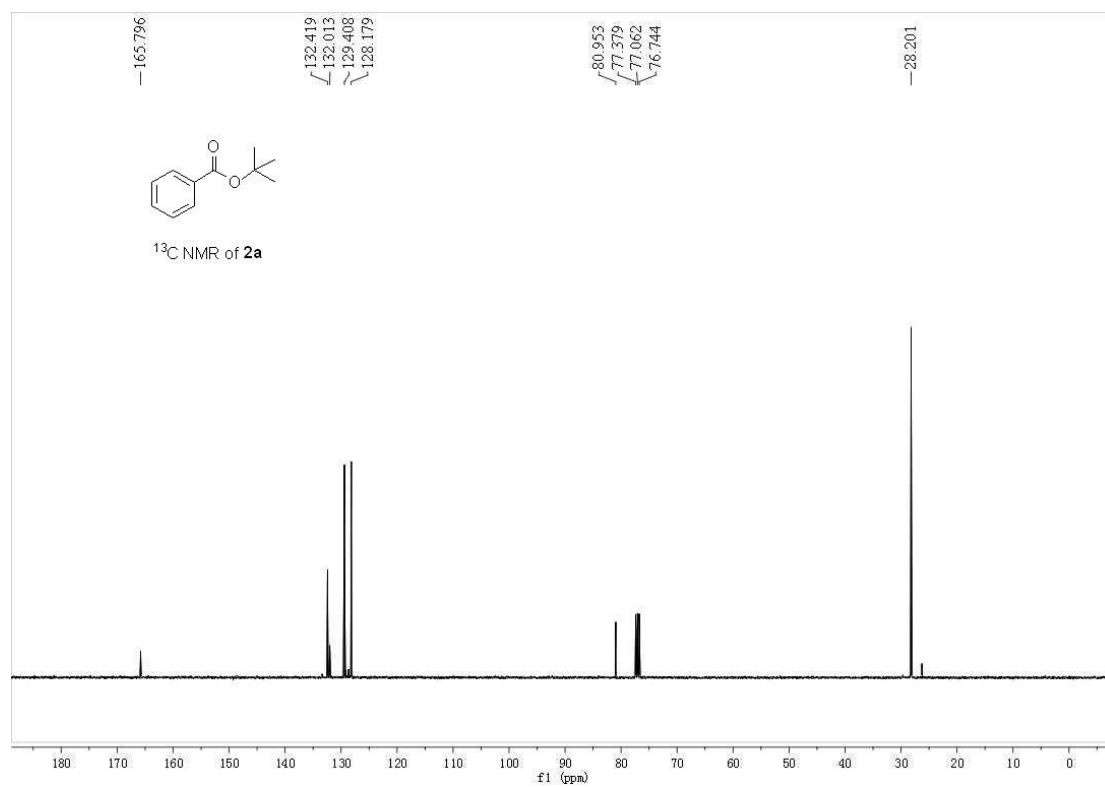
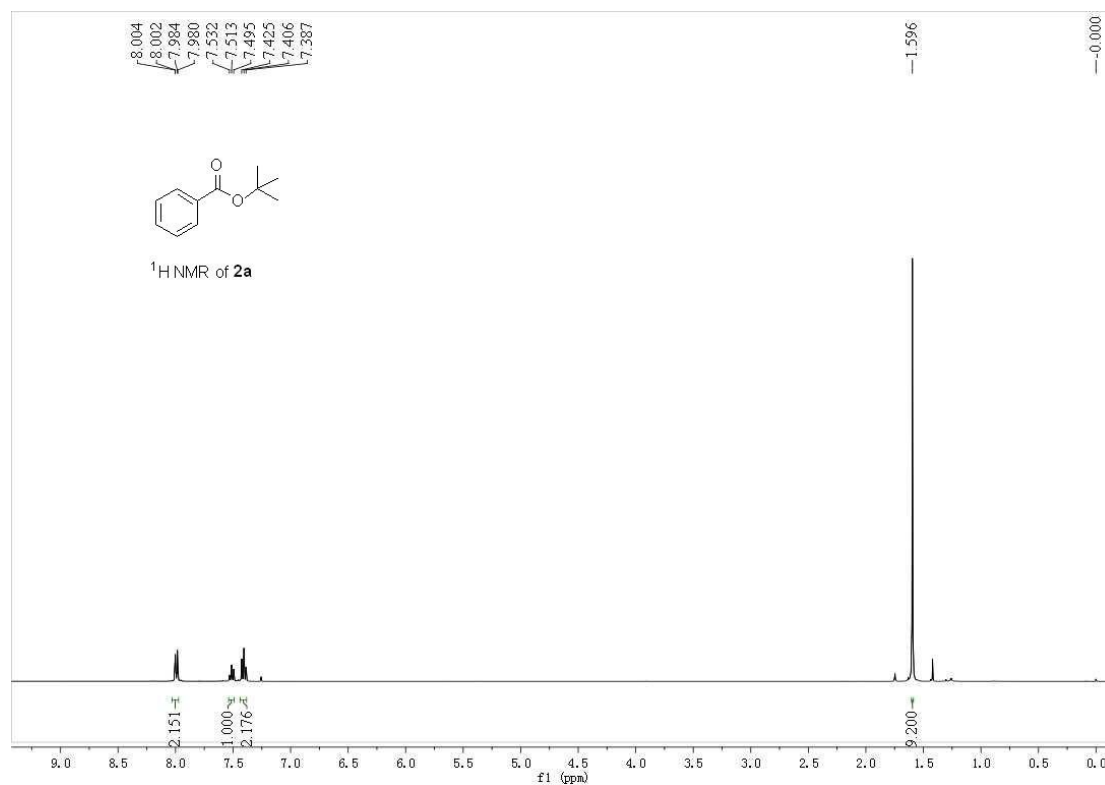
Following the general procedure (petroleum ether), **2r** was obtained as a pale yellow liquid, isolated yield: 83%. ¹H NMR (CDCl₃, 400 MHz): δ 8.23 (d, 2H, *J* = 8.8 Hz), 8.12 (d, 2H, *J* = 8.8 Hz), 1.93 (q, 2H, *J* = 7.6 Hz), 1.57 (s, 9H), 0.95 (t, 3H, *J* = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 163.6, 150.2, 137.4, 130.5, 123.4, 85.1, 33.6, 25.5, 8.3; HRMS (EI): calcd for C₁₂H₁₅NO₄: 237.1001; found: 237.1018.

4. References

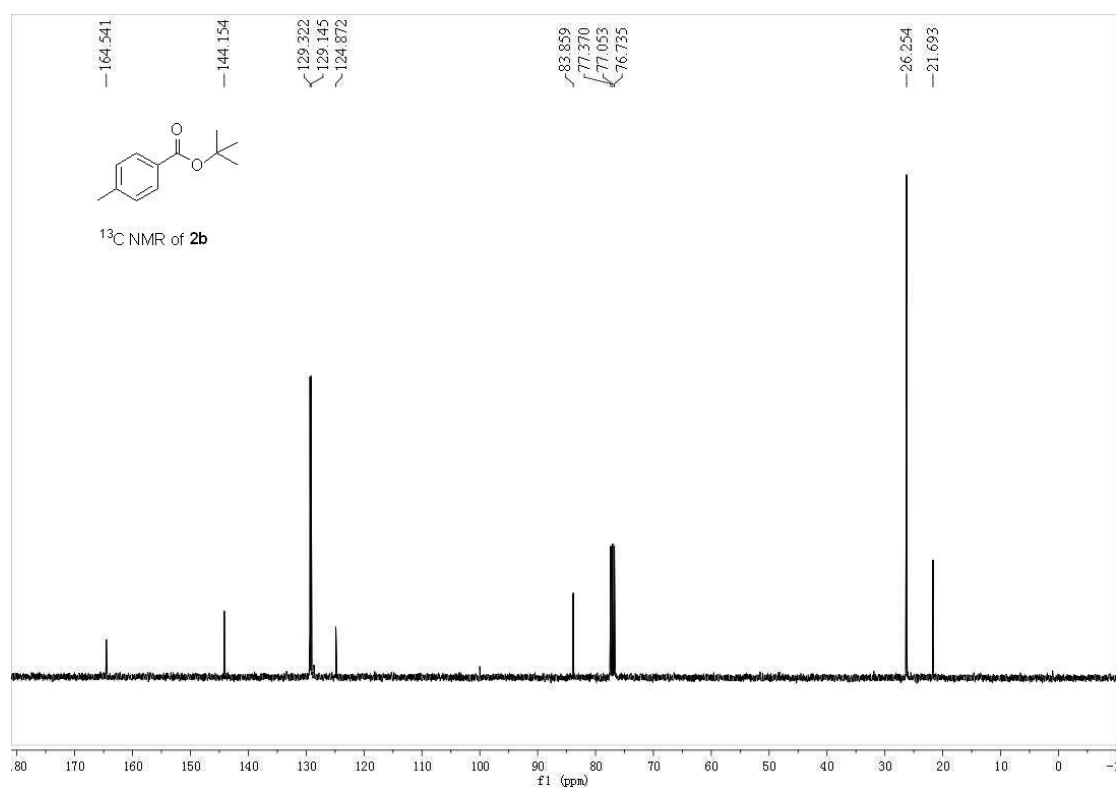
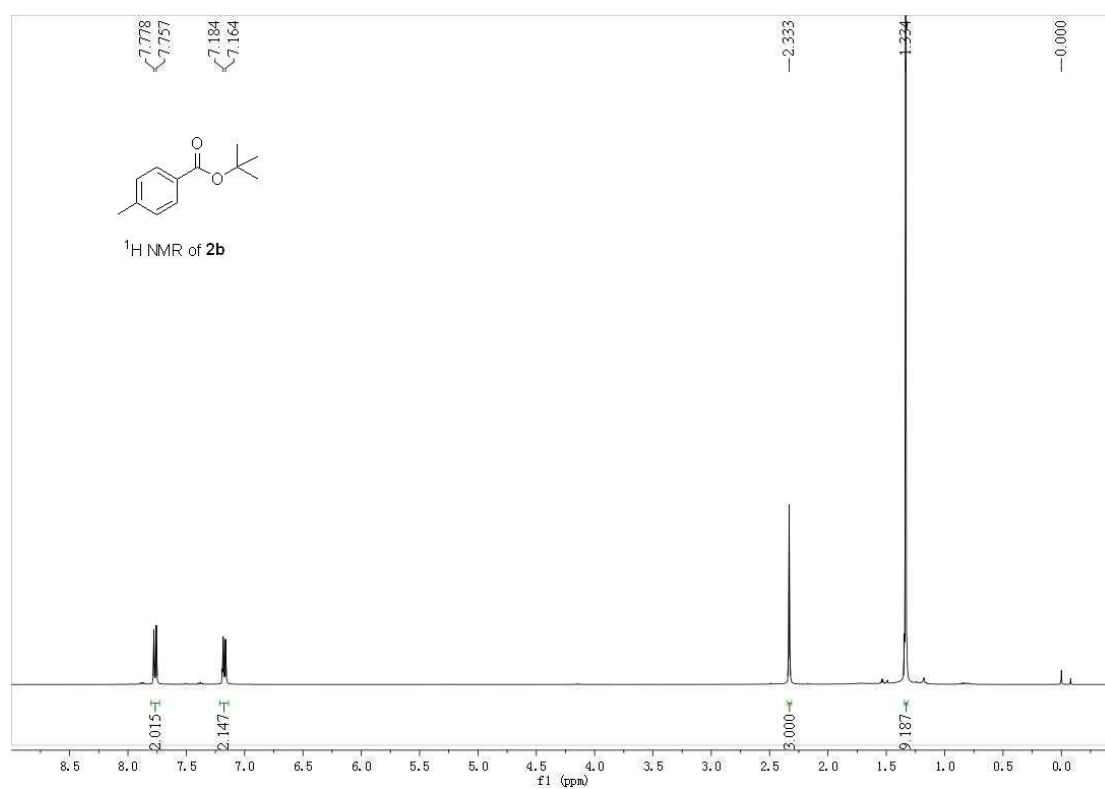
1. S. Pramanik, R. R. Reddy and P. Ghorai, *Org. Lett.*, 2015, **17**, 1393-1396.
2. C. Marculescu, H. Kossen, R. E. Morgan, P. Mayer, S.A. Fletcher, B. Tolner, K. A. Chester, L. H. Jones and J. R. Baker, *Chem. Commun.*, 2014, **50**, 7139-7142.
3. N. Zhang, R. Yang, D. Zhang-Negrerie, Y. Du and K. Zhao, *J. Org. Chem.*, 2013, **78**, 8705-8711.
4. T. C. Wang, W. Bury, D. A. Gómez-Gualdrón, N. A. Vermeulen, J. E. Mondloch, P. Deria, K. Zhang, P. Z. Moghadam, A. A. Sarjeant, R. Q. Snurr, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 3585-3591.
5. Z. Xin, T. M. Gøgsig, A. T. Lindhardt and T. Skrydstrup, *Org. Lett.*, 2012, **14**, 84-287.
6. H. Zhang, R. Shi, A. Ding, L. Lu, B. Chen and A. Lei, *Angew. Chem. Int. Ed.*, 2012, **51**, 12542-12545.

5. Copies of ^1H , ^{13}C NMR and ^{19}F NMR spectra

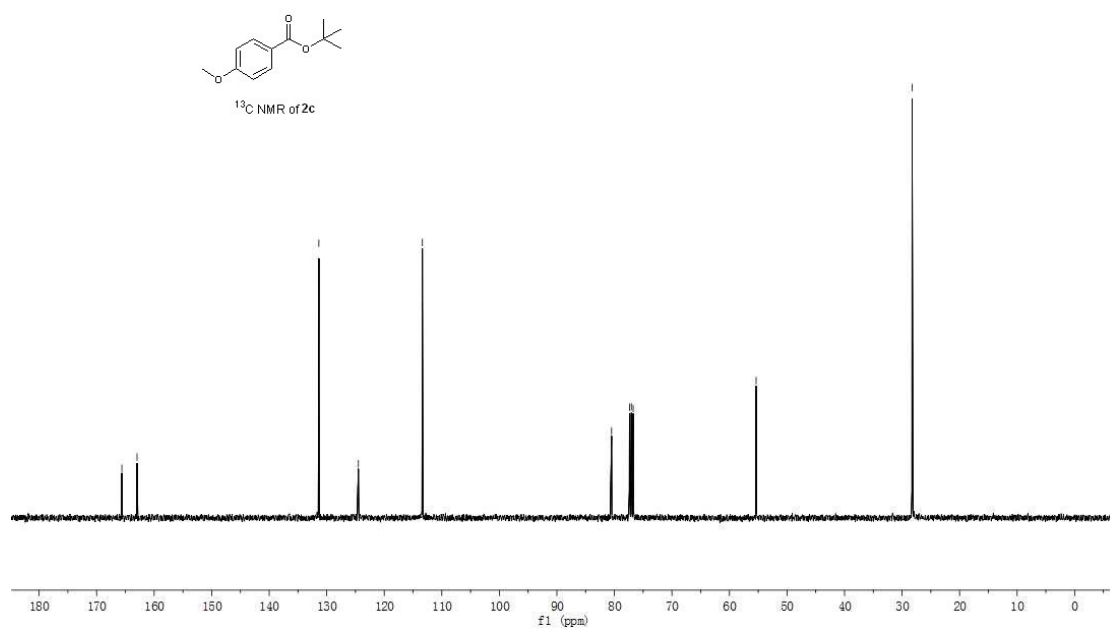
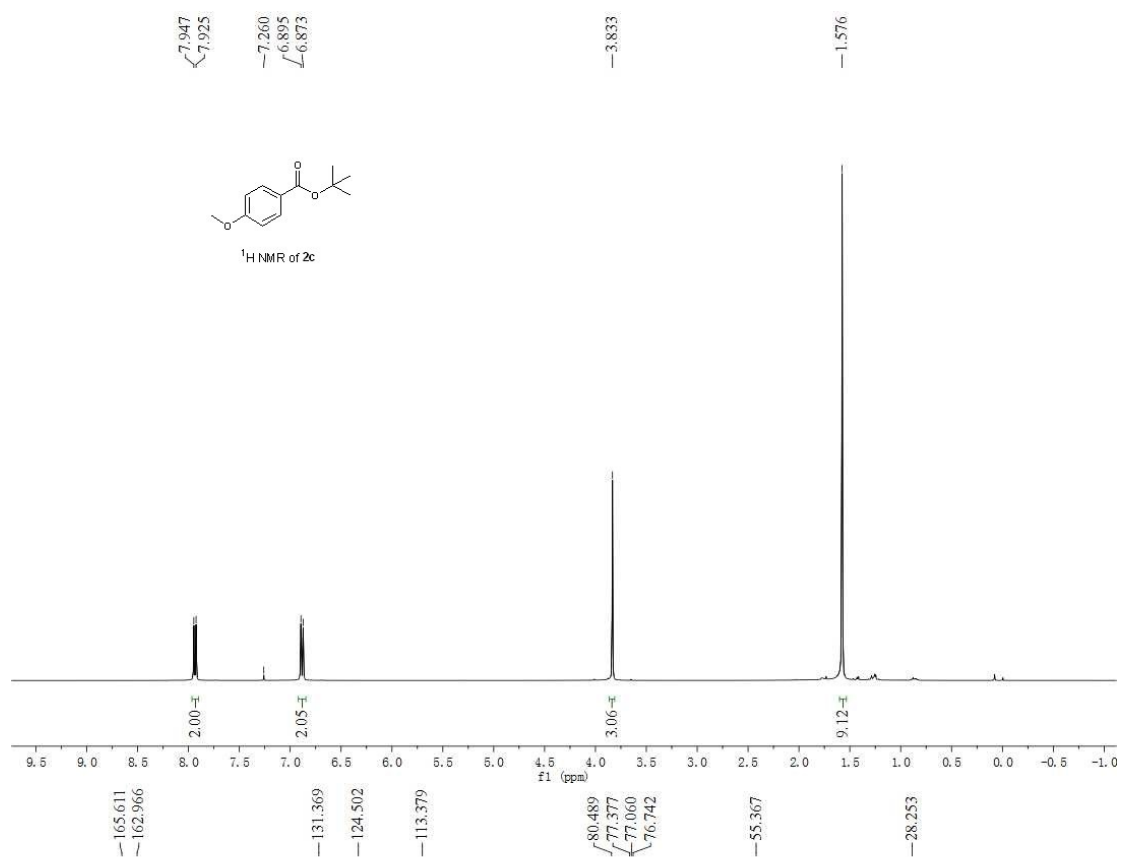
^1H NMR and ^{13}C NMR of **2a**



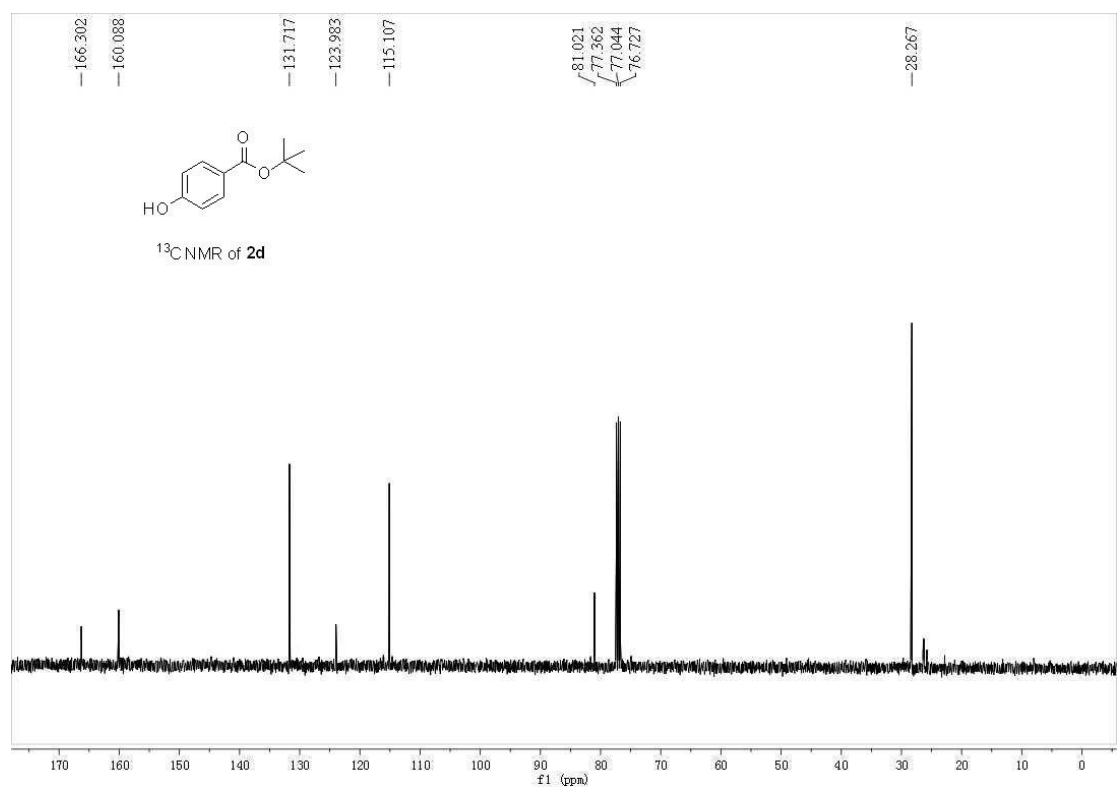
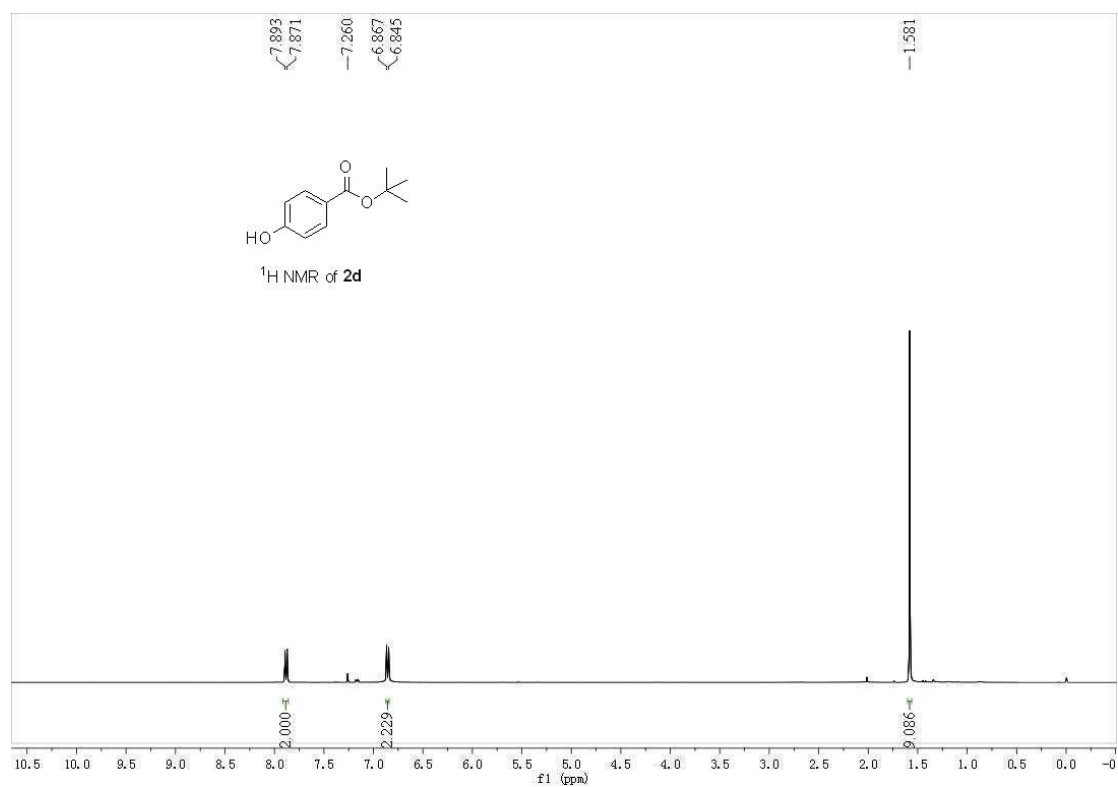
^1H NMR and ^{13}C NMR of **2b**



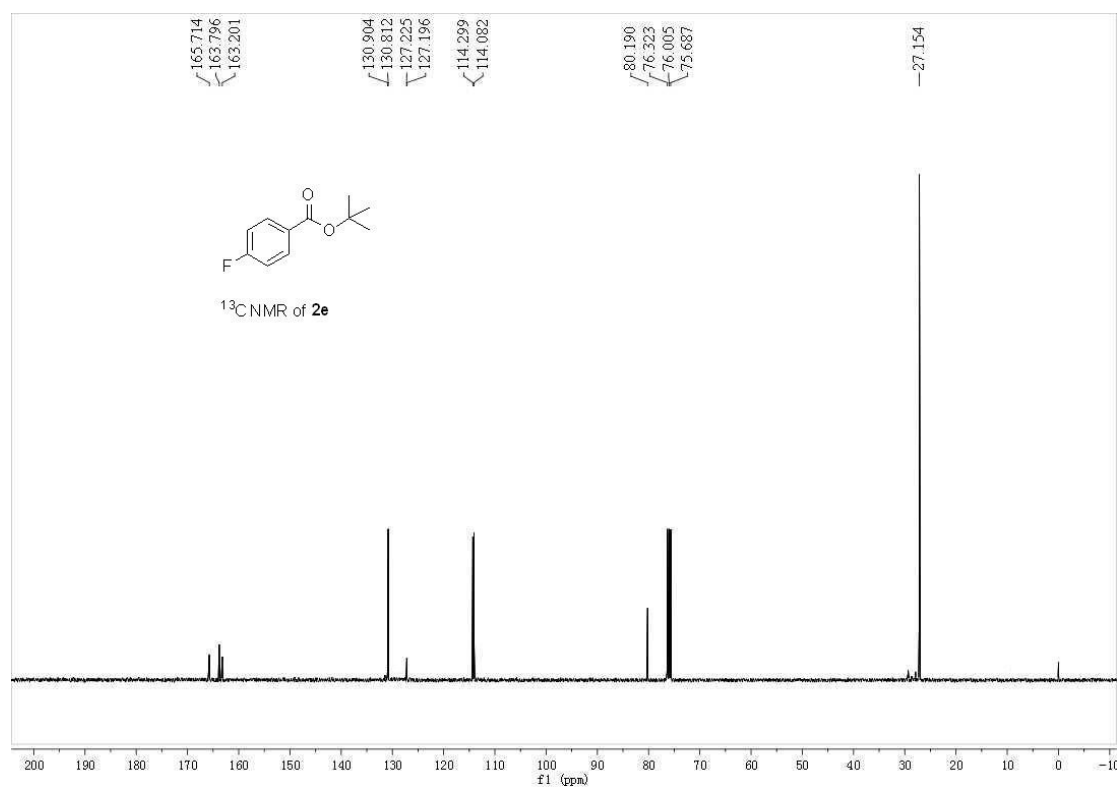
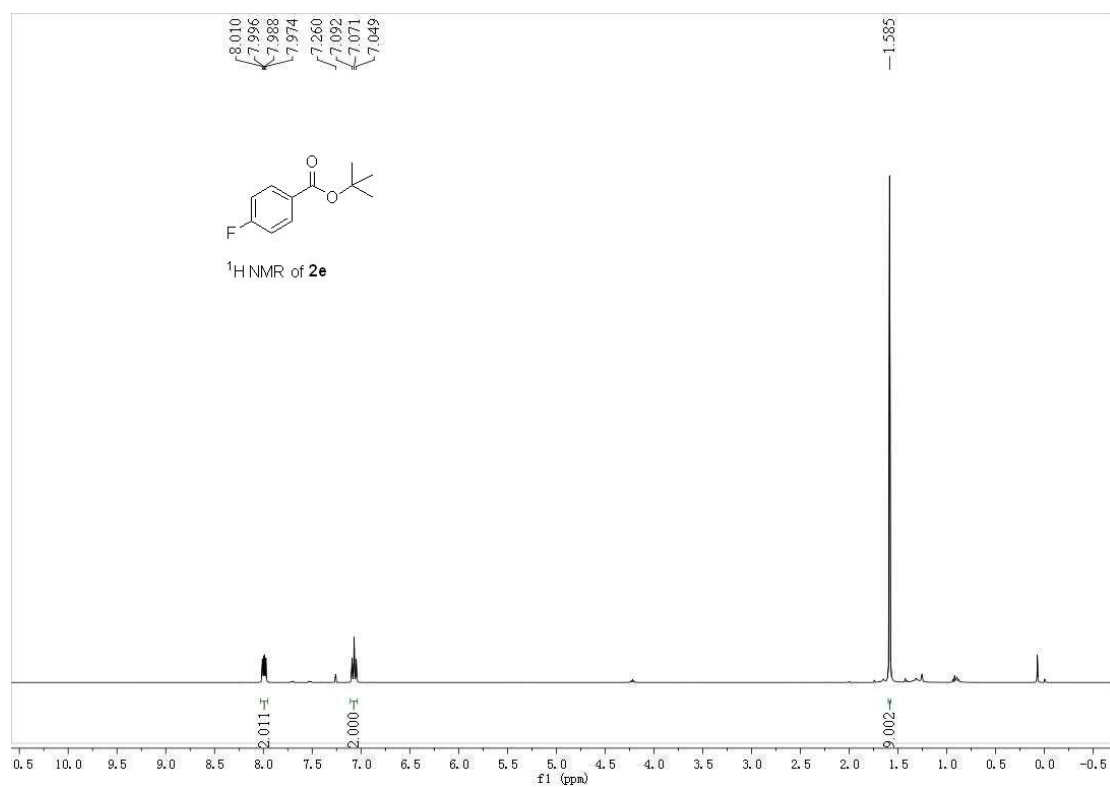
¹H NMR and ¹³C NMR of 2c

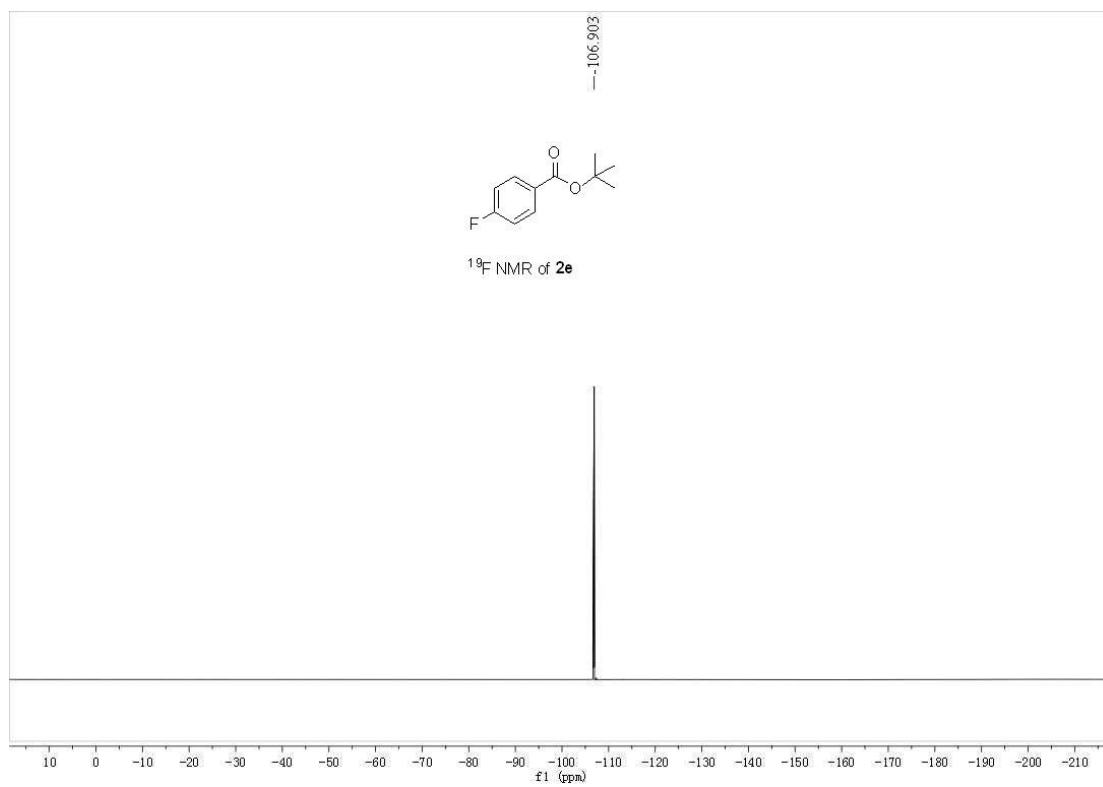


¹H NMR and ¹³C NMR of 2d

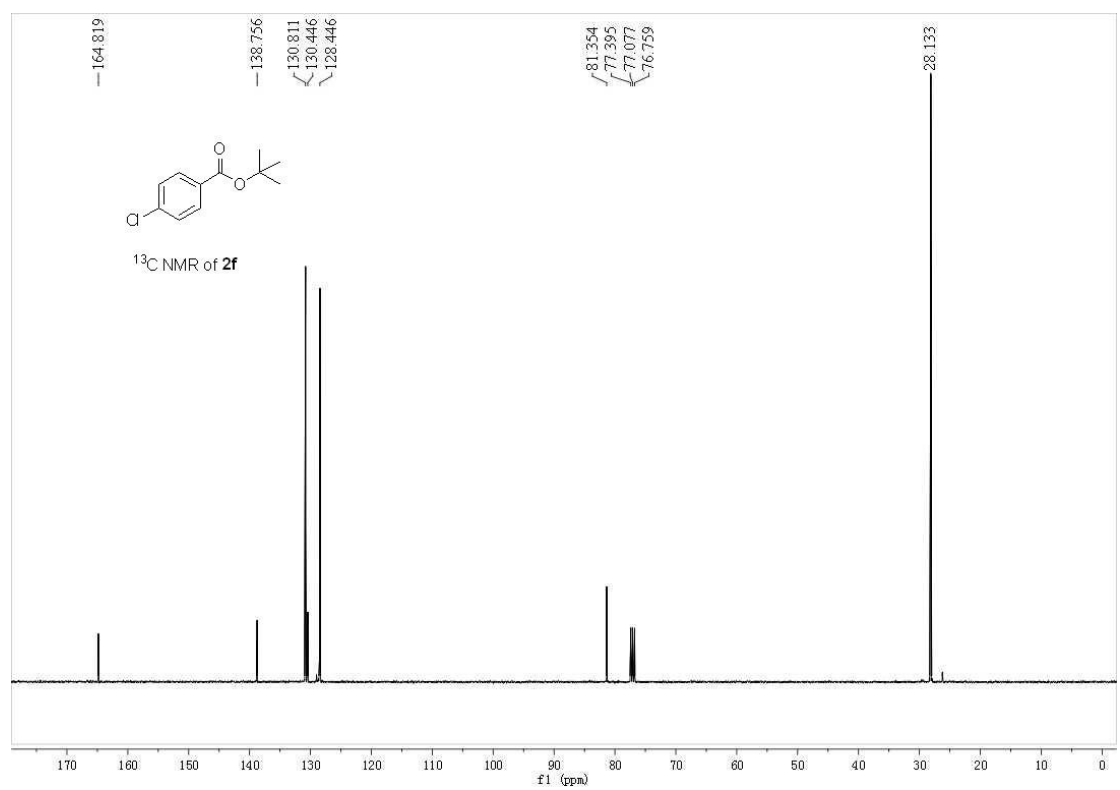
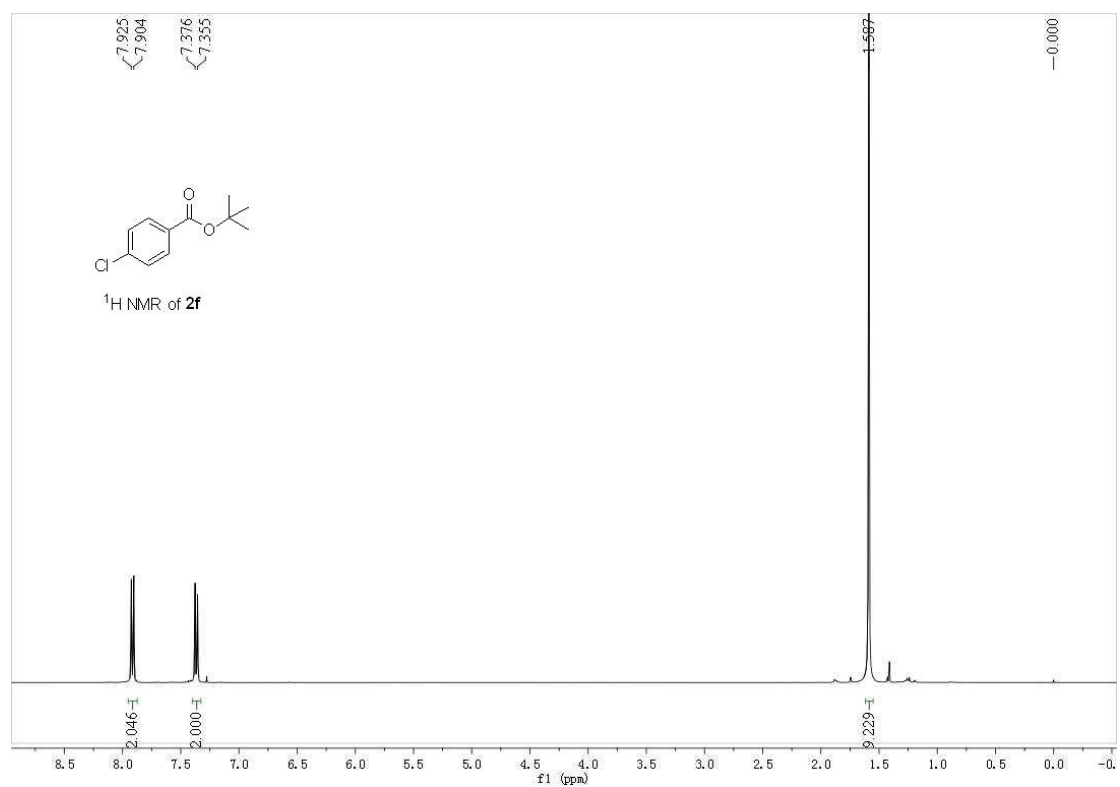


^1H NMR, ^{13}C NMR and ^{19}F NMR of **2e**

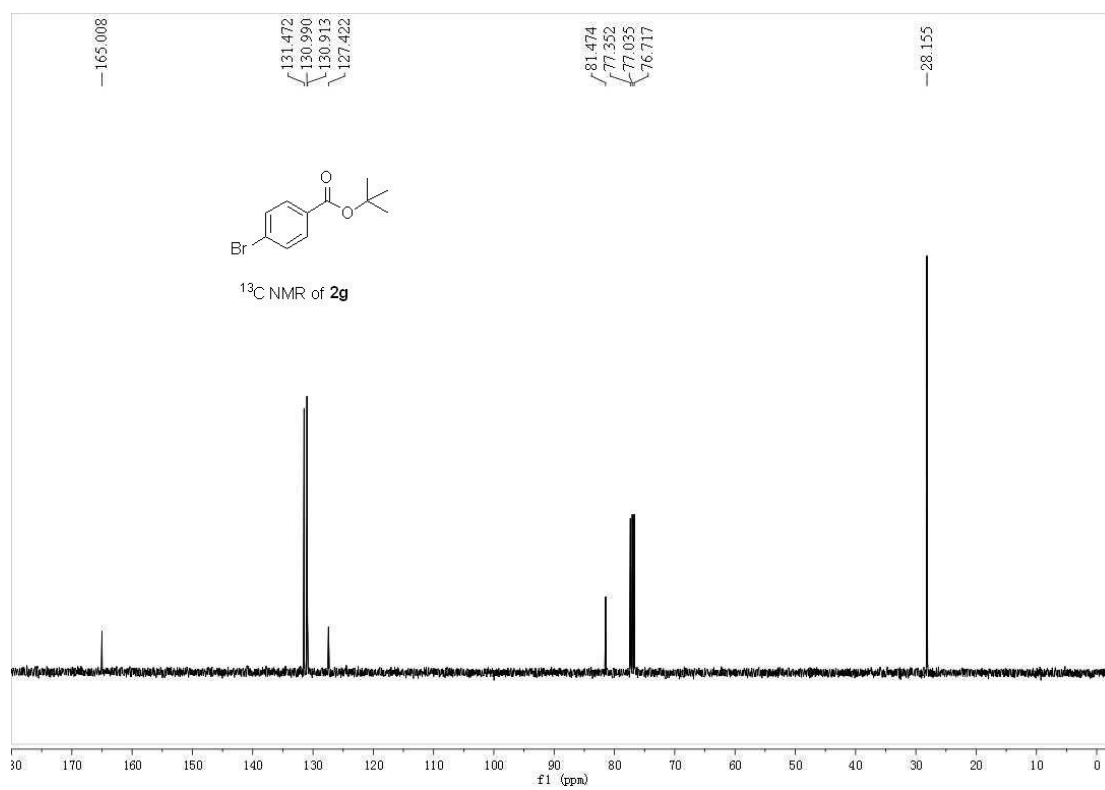
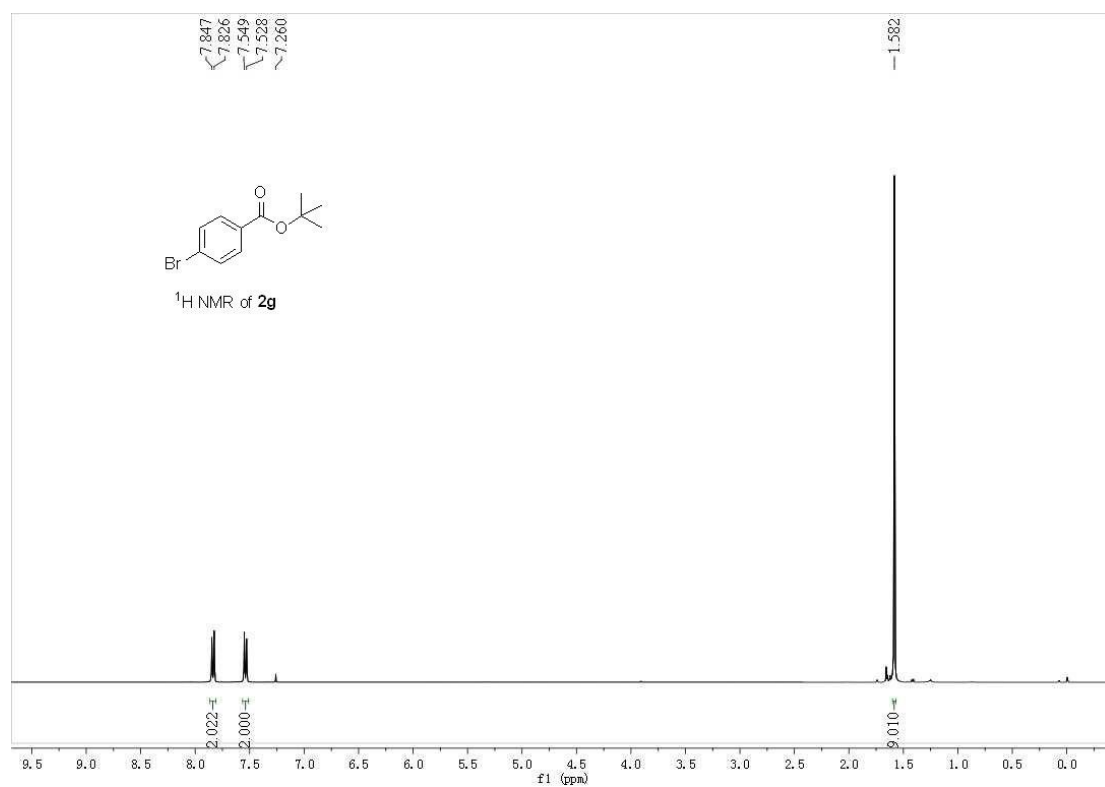




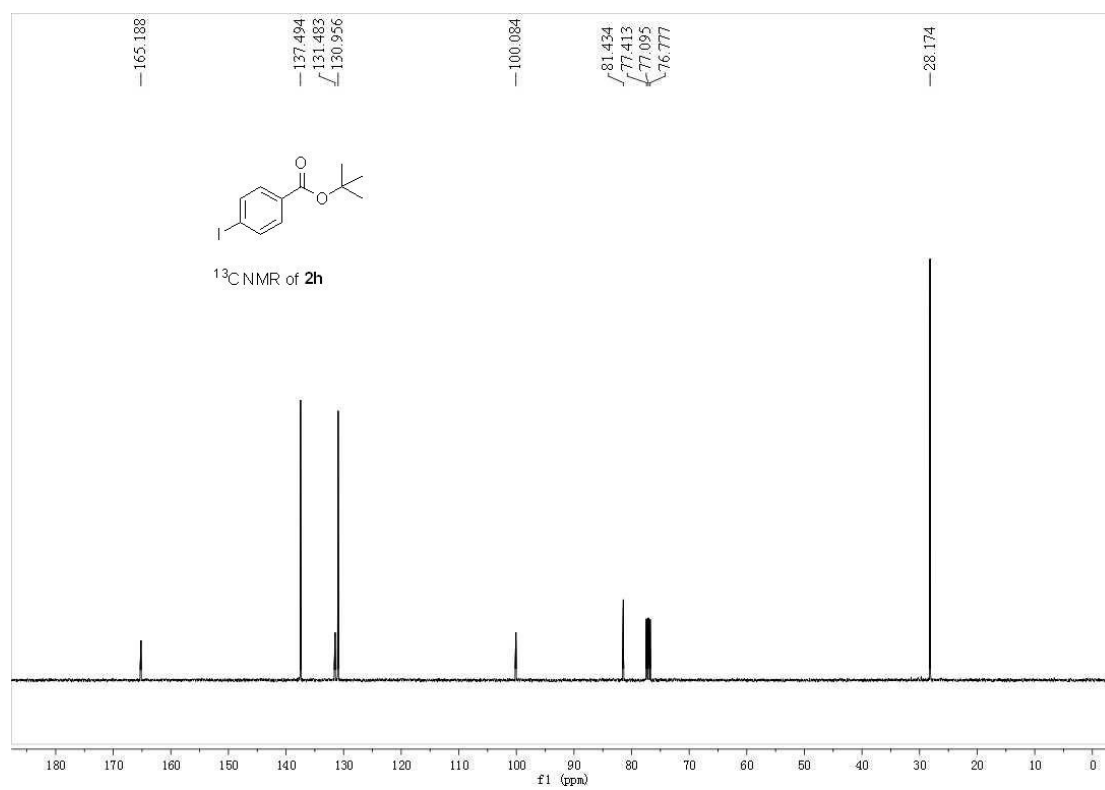
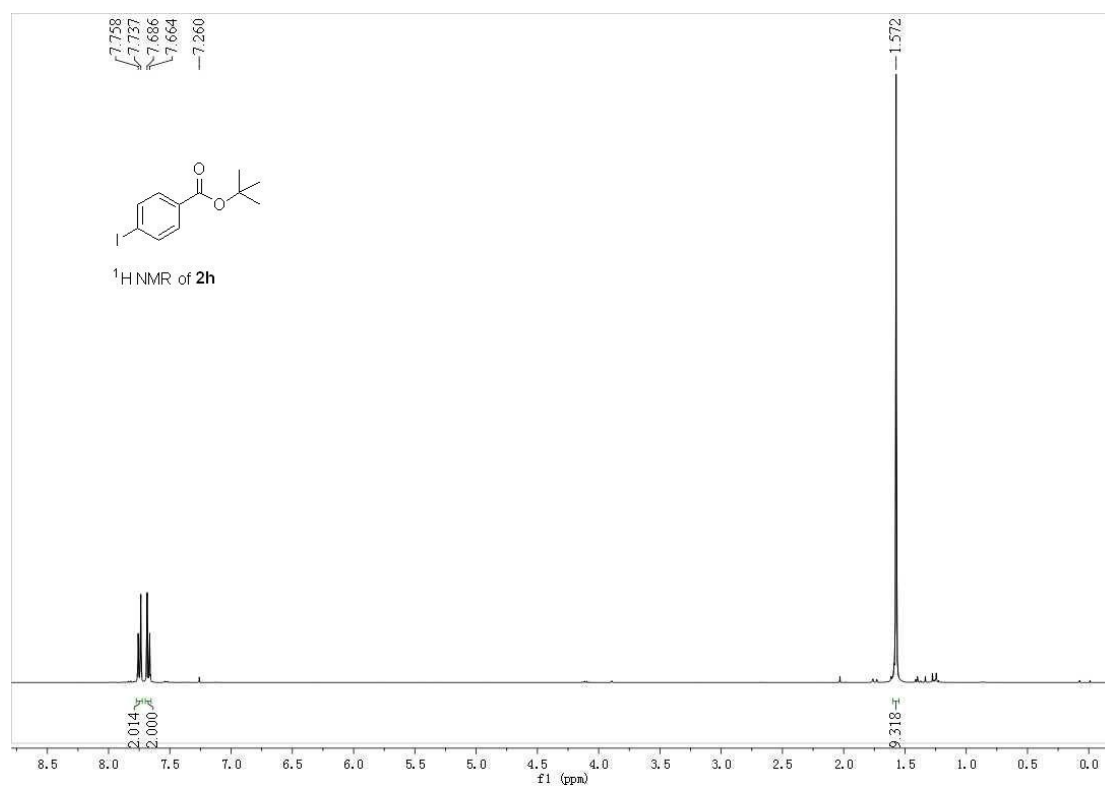
^1H NMR and ^{13}C NMR of **2f**



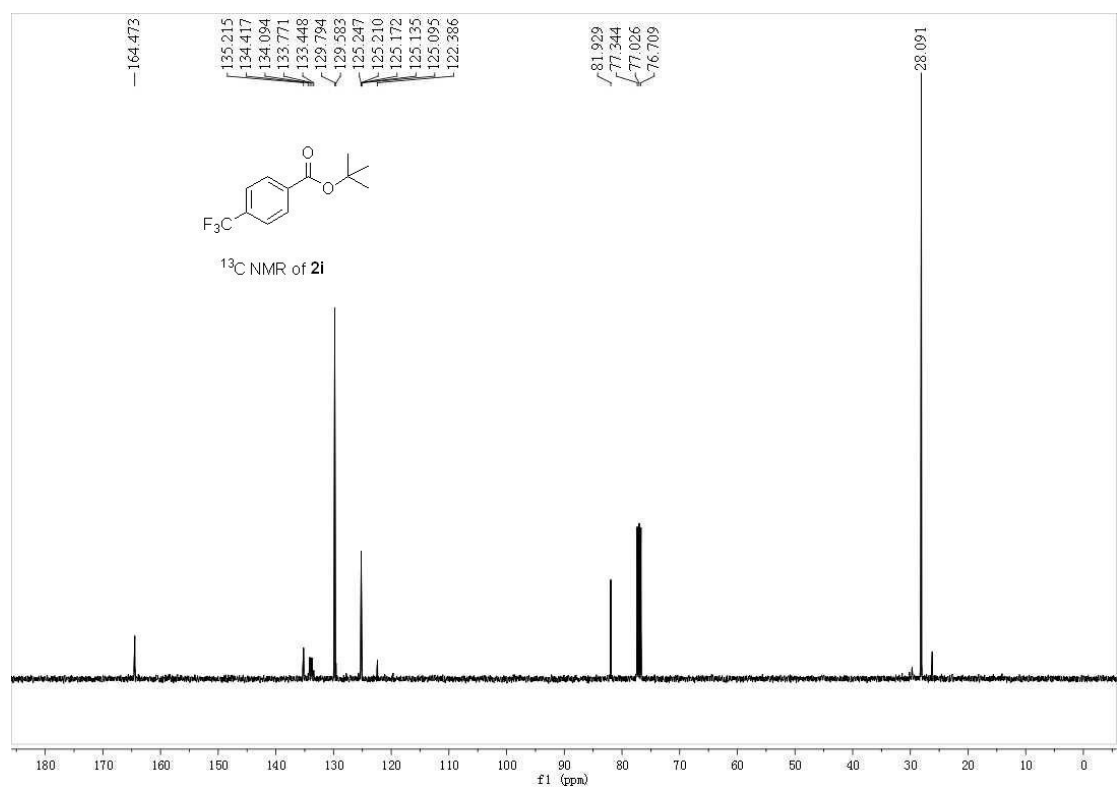
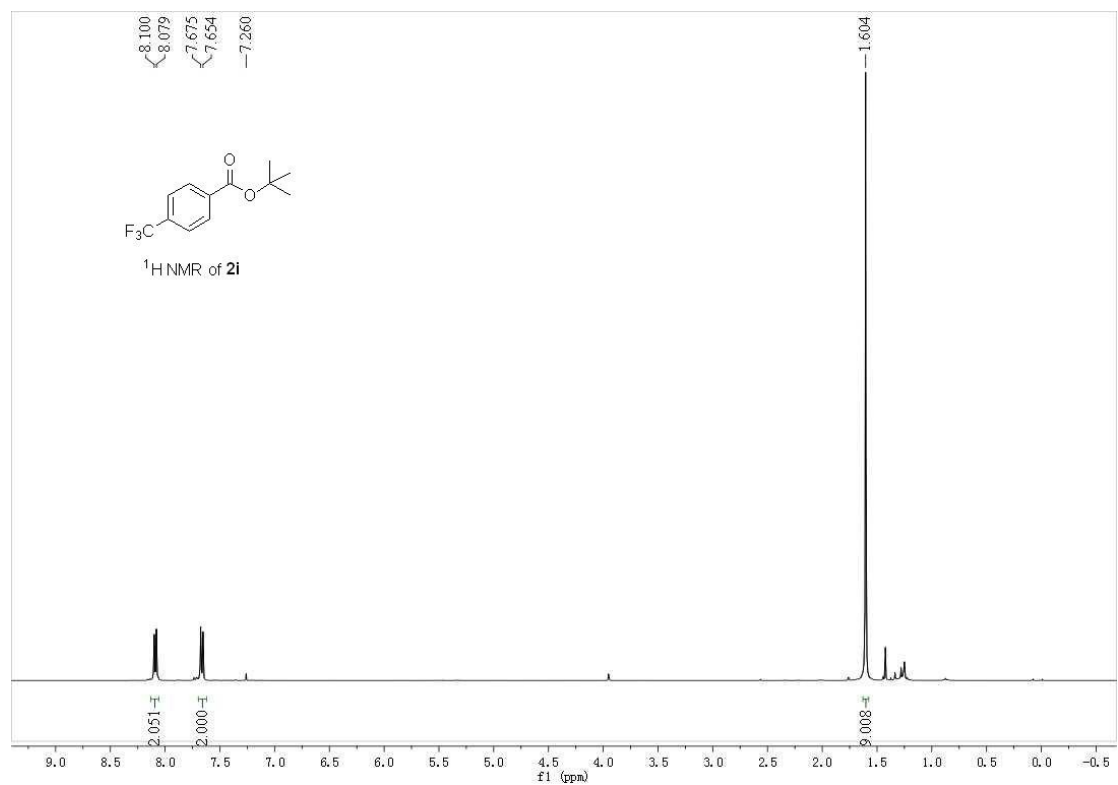
^1H NMR and ^{13}C NMR of **2g**

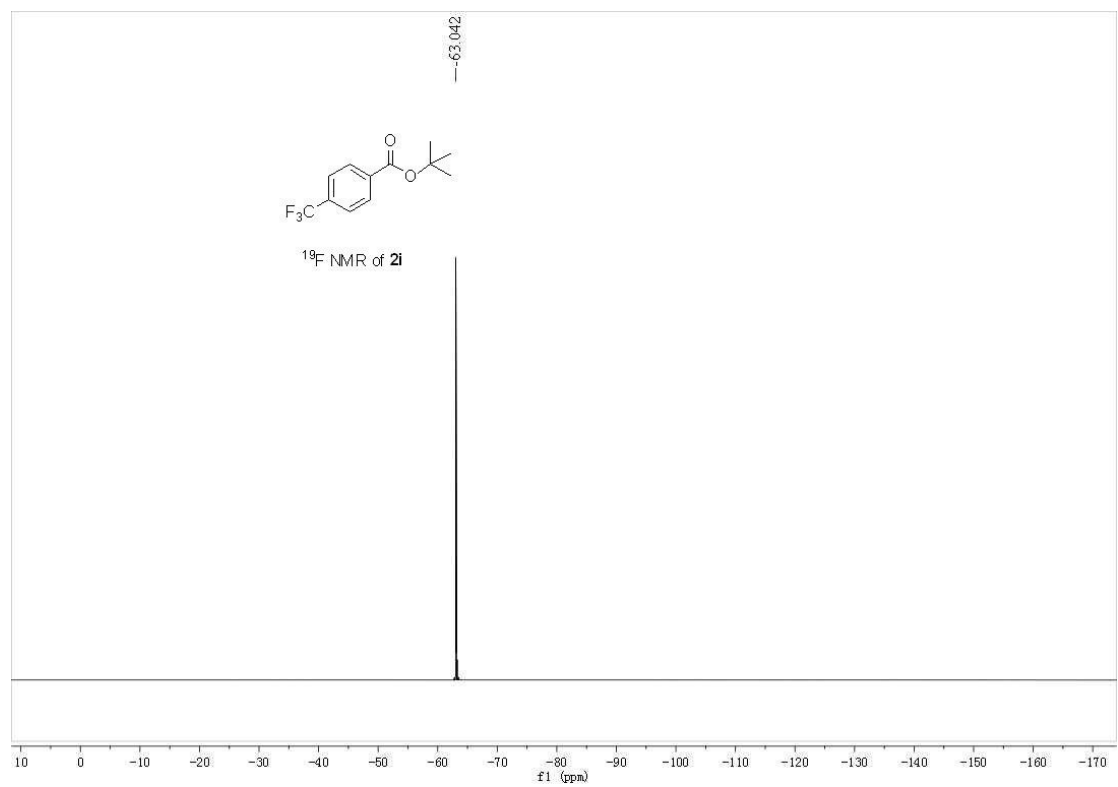


¹H NMR and ¹³C NMR of **2h**

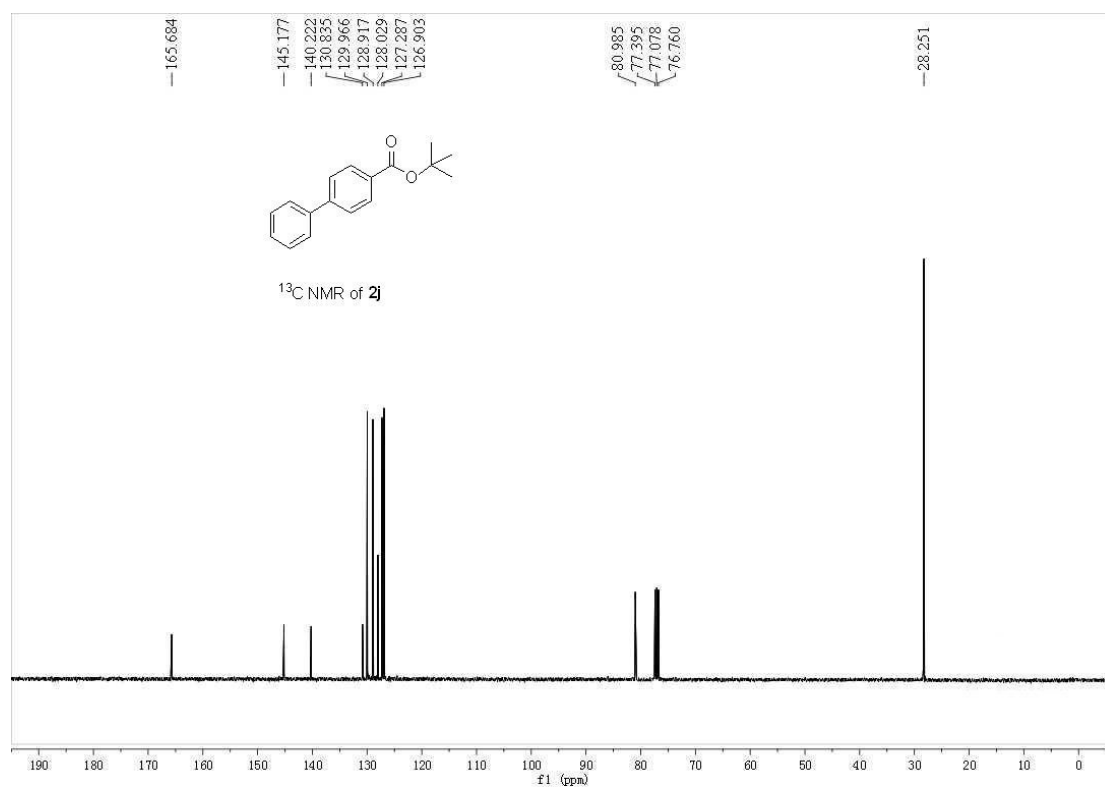
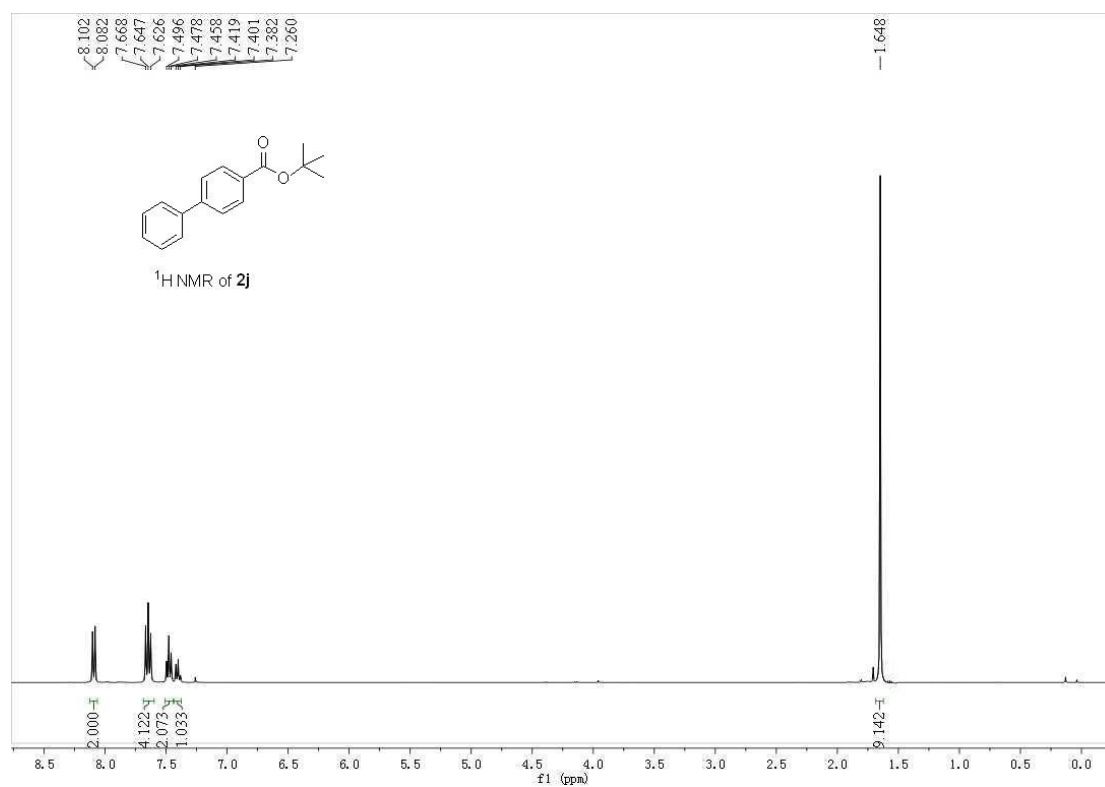


^1H NMR, ^{13}C NMR and ^{19}F NMR of **2i**

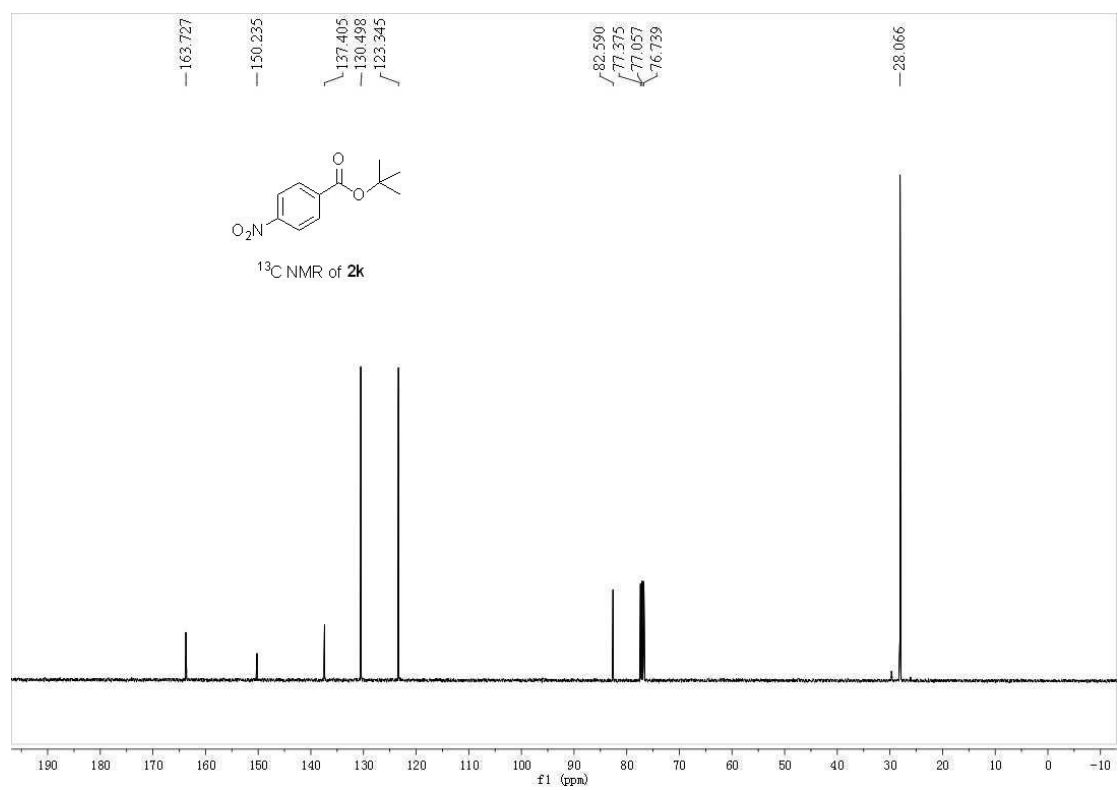
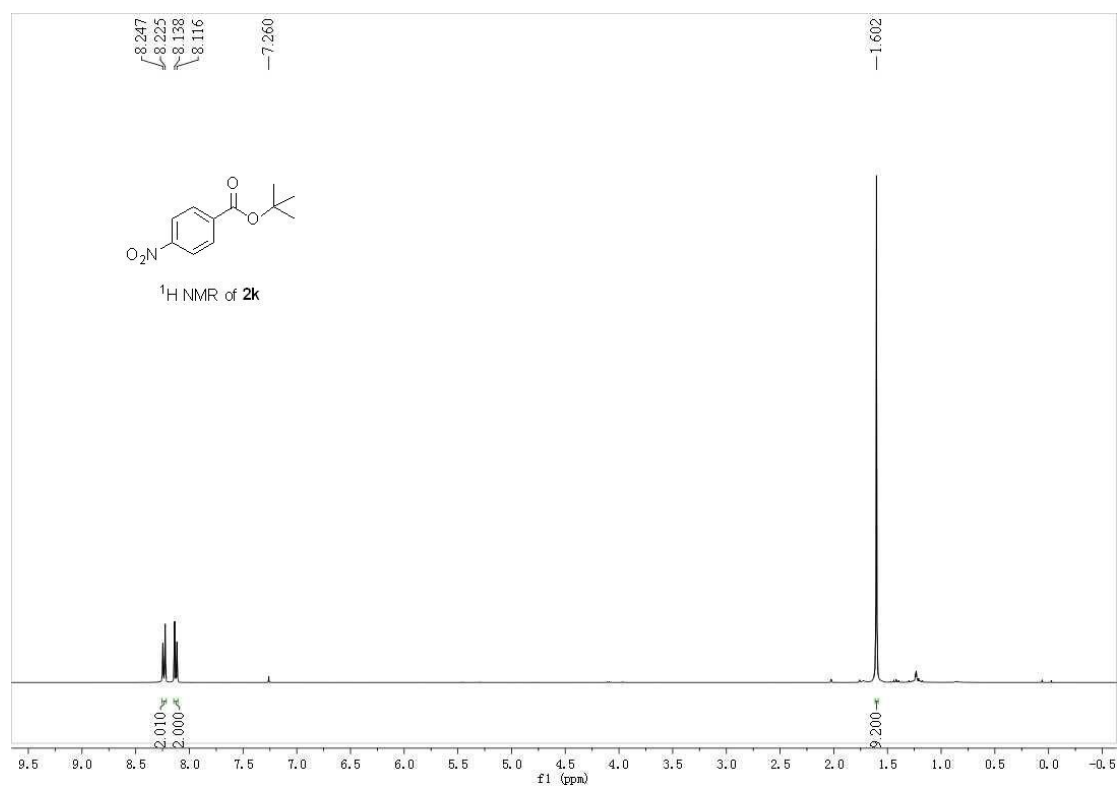




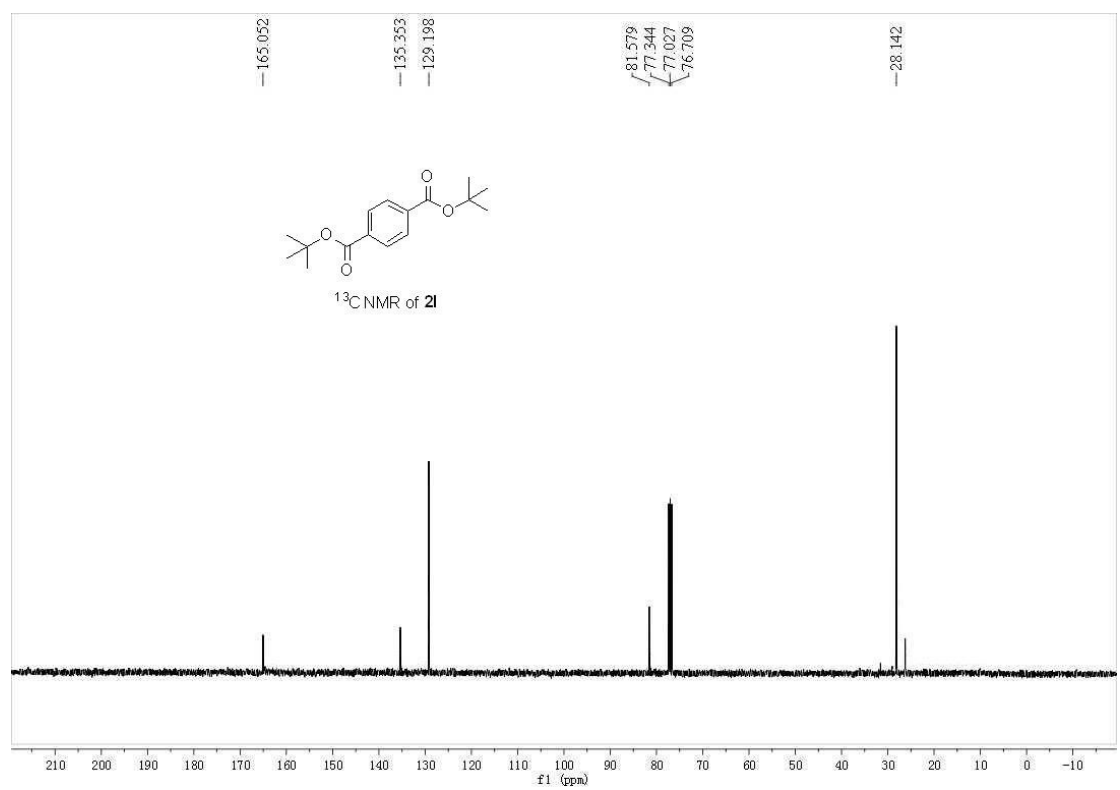
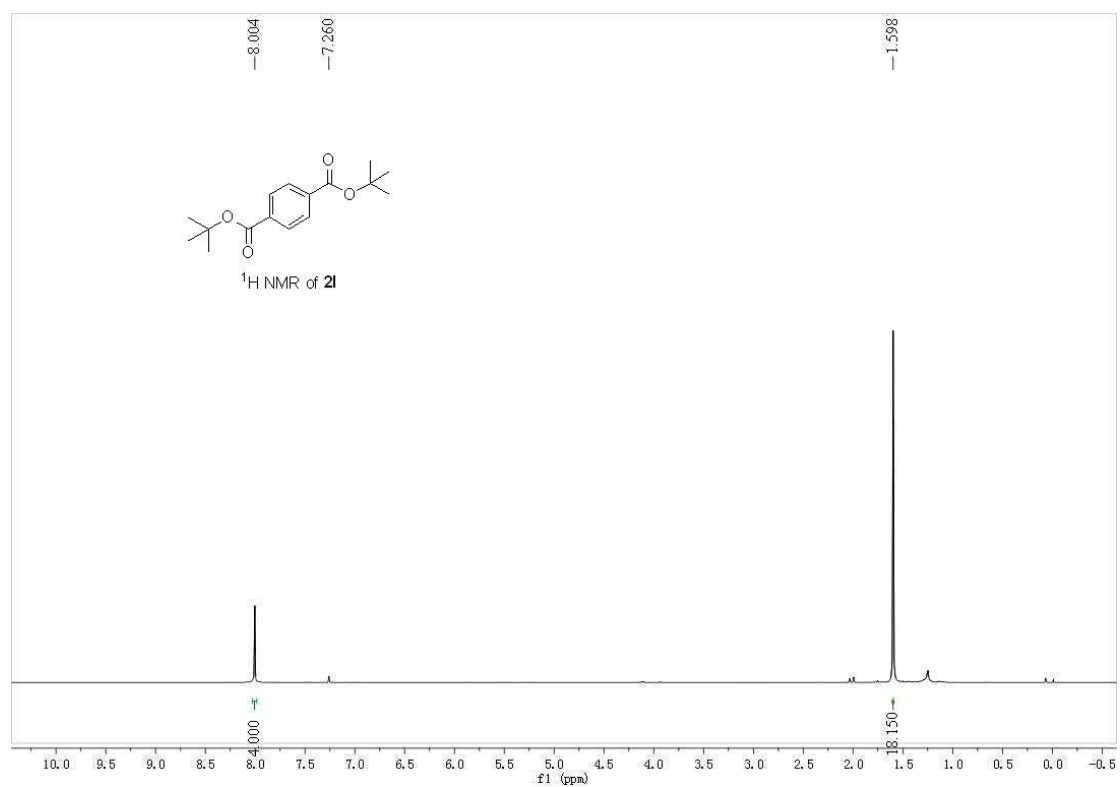
¹H NMR and ¹³C NMR of 2j



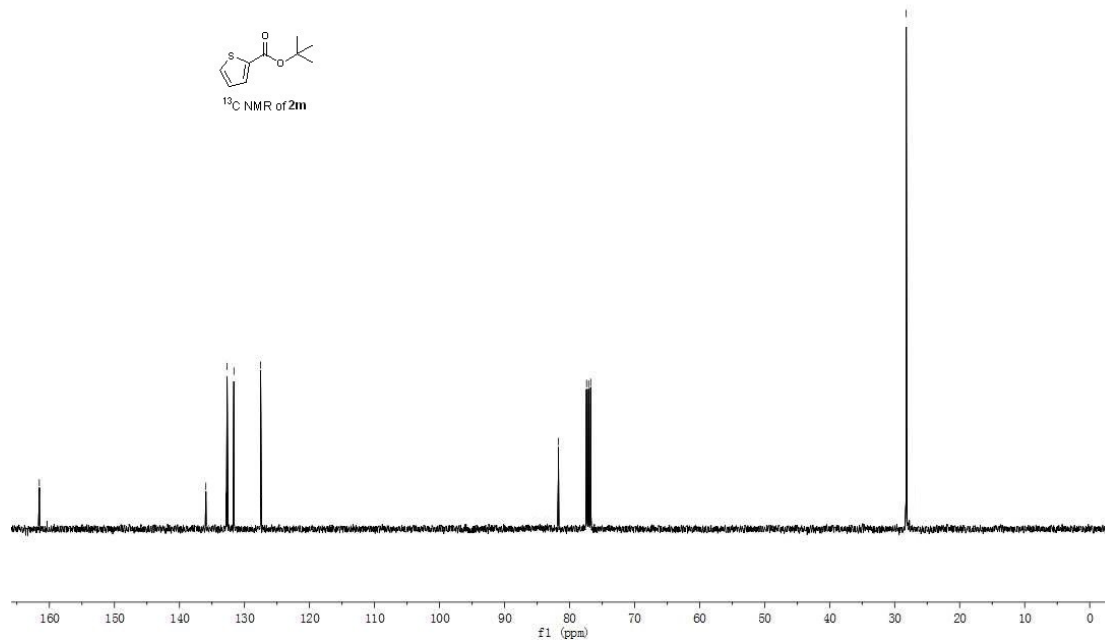
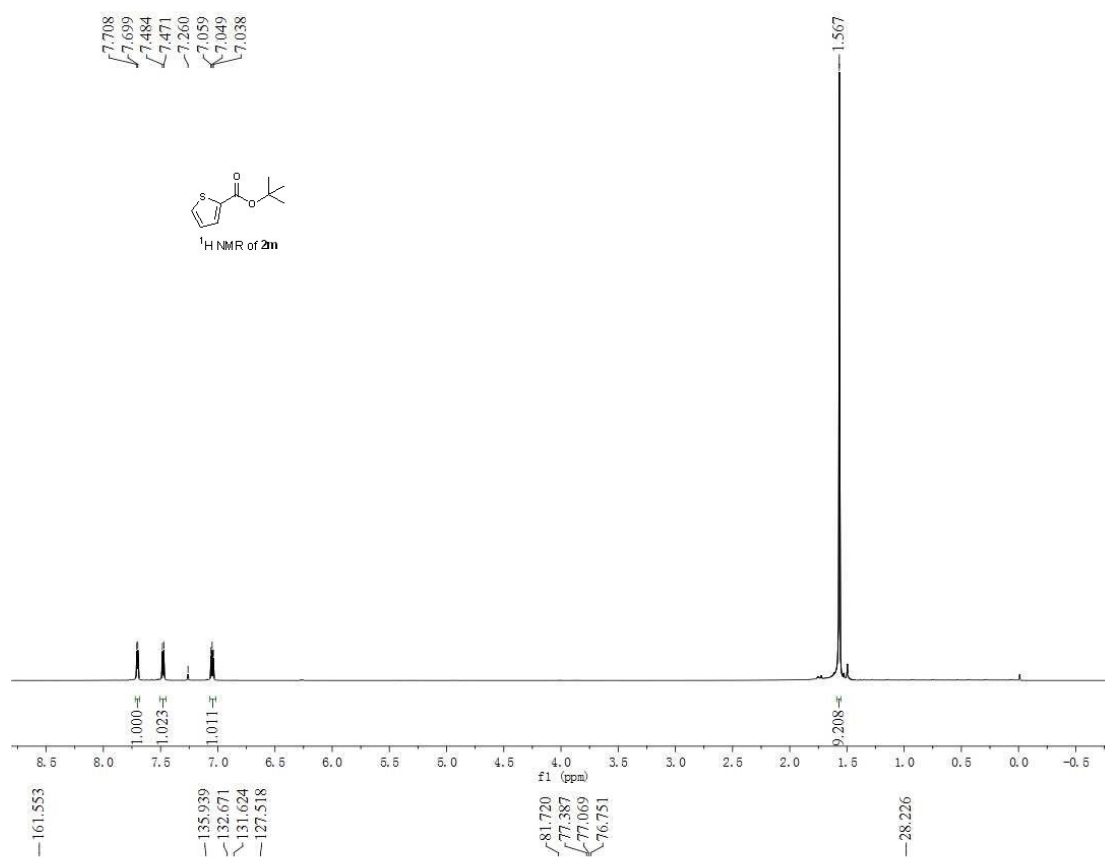
¹H NMR and ¹³C NMR of **2k**



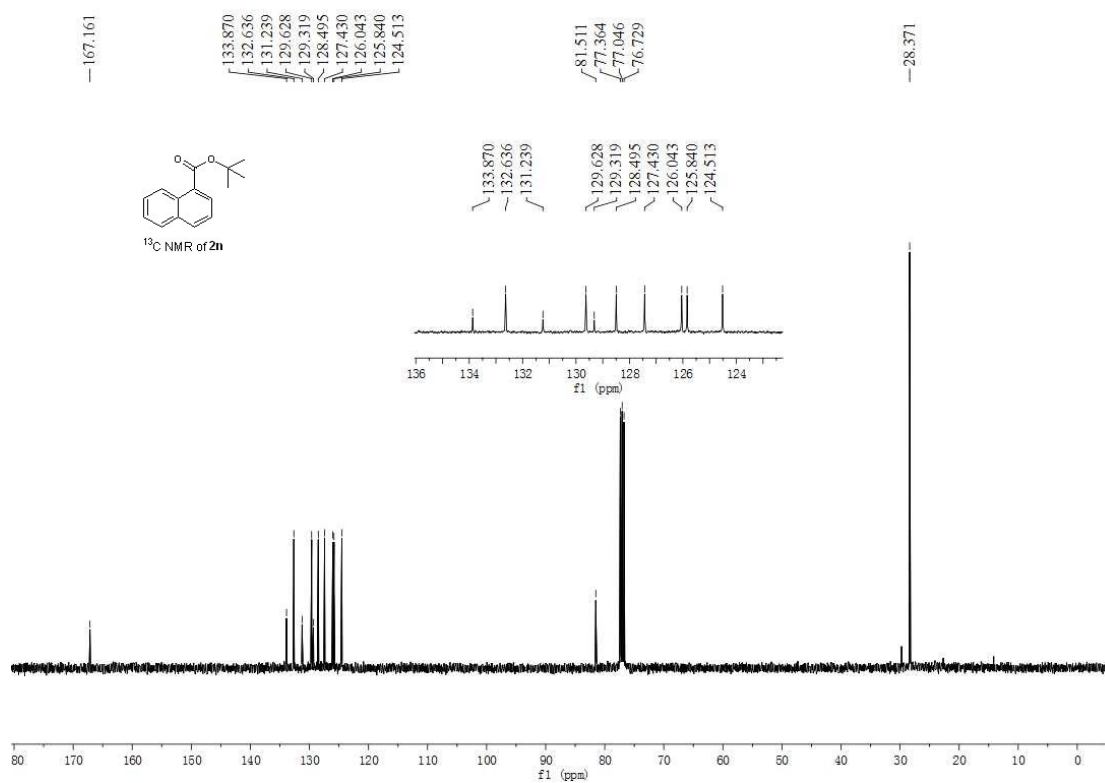
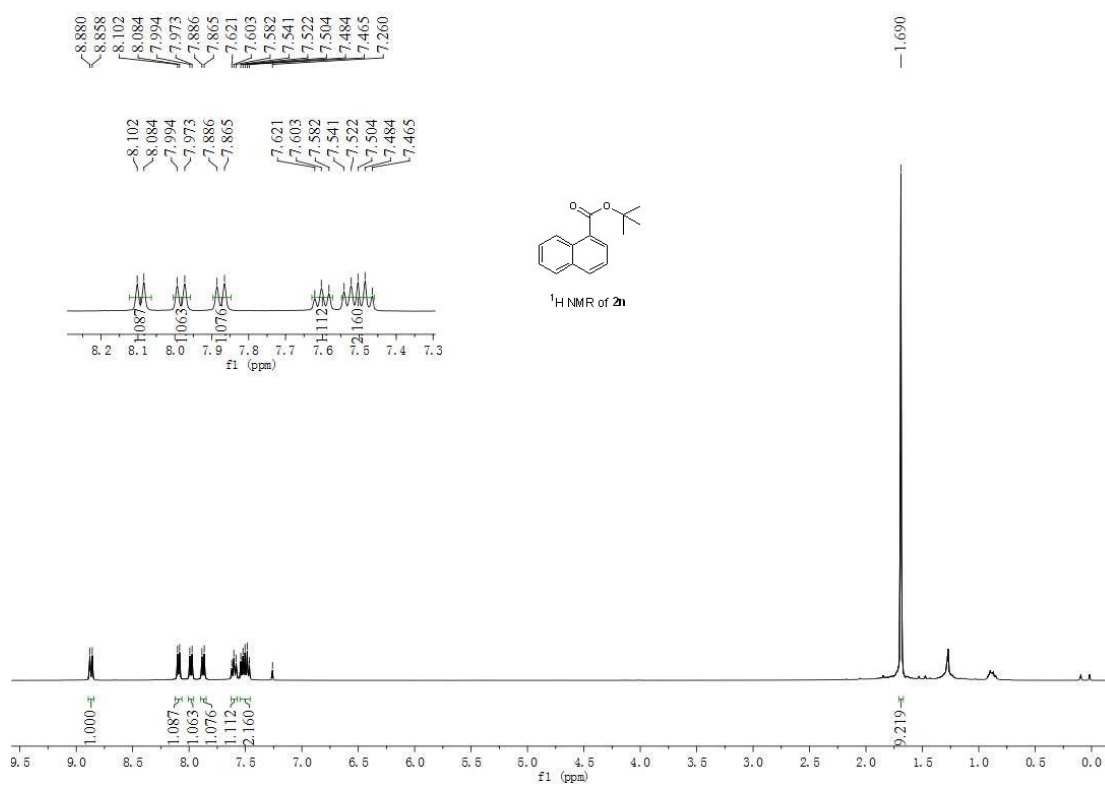
^1H NMR and ^{13}C NMR of **21**



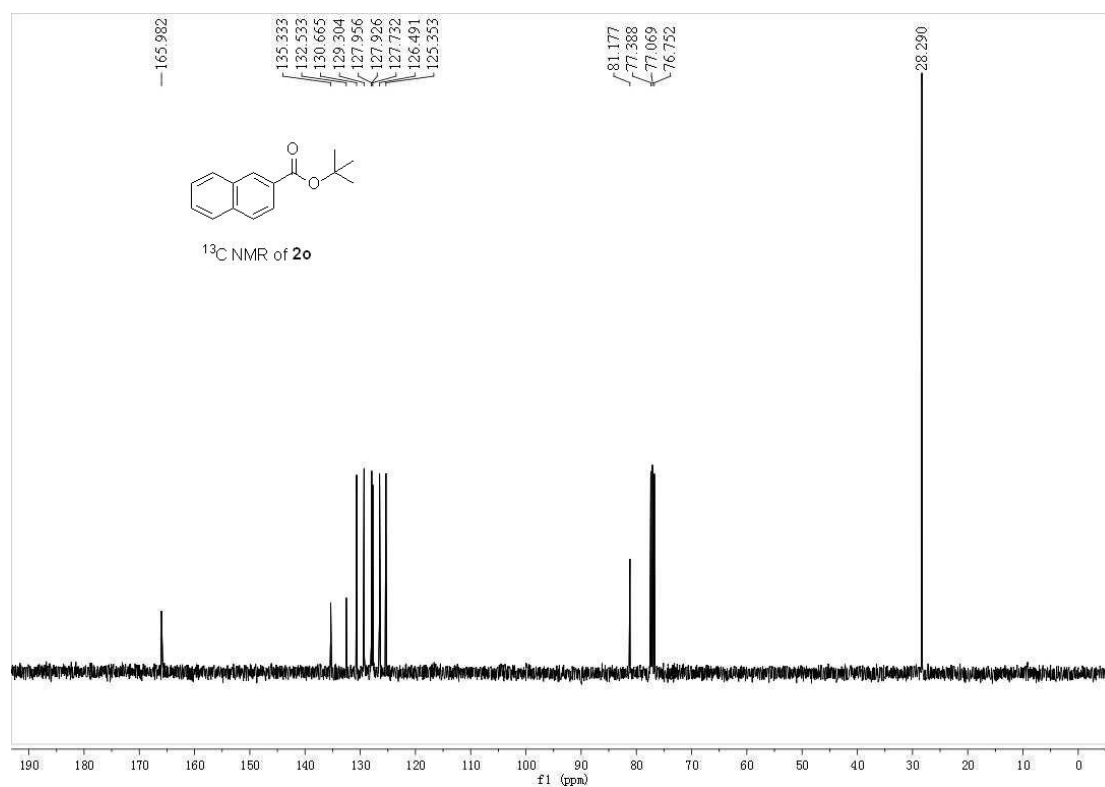
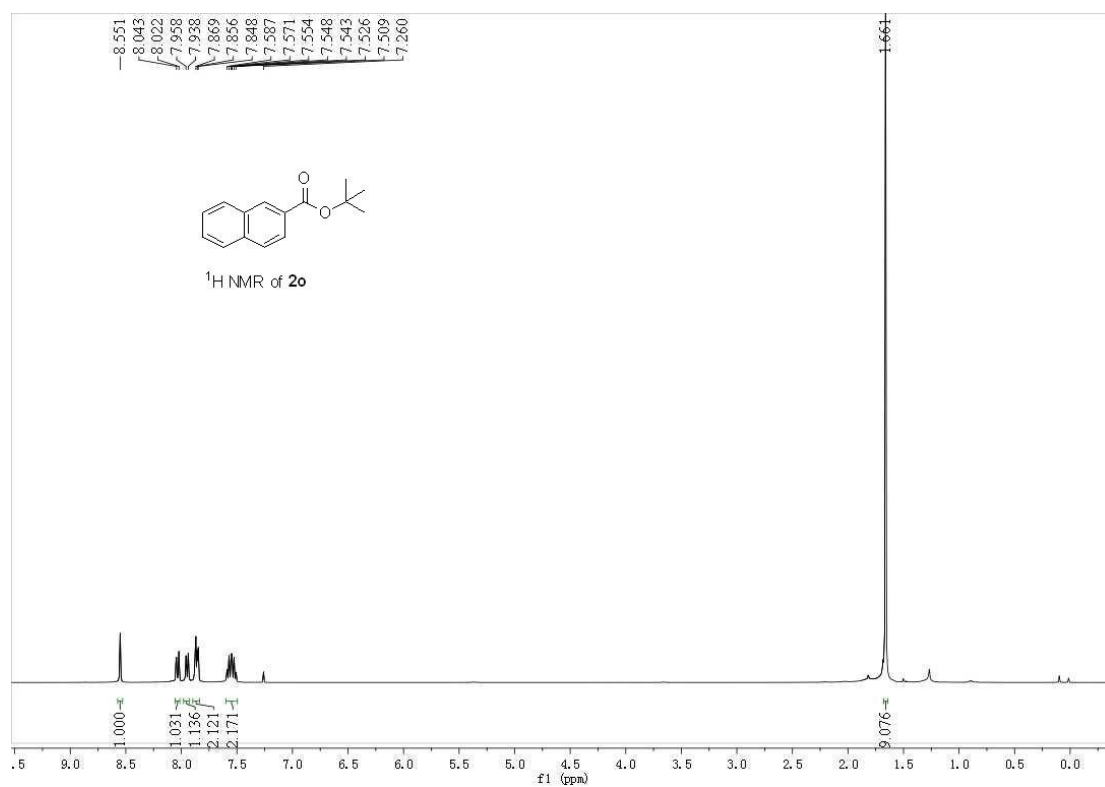
^1H NMR and ^{13}C NMR of **2m**



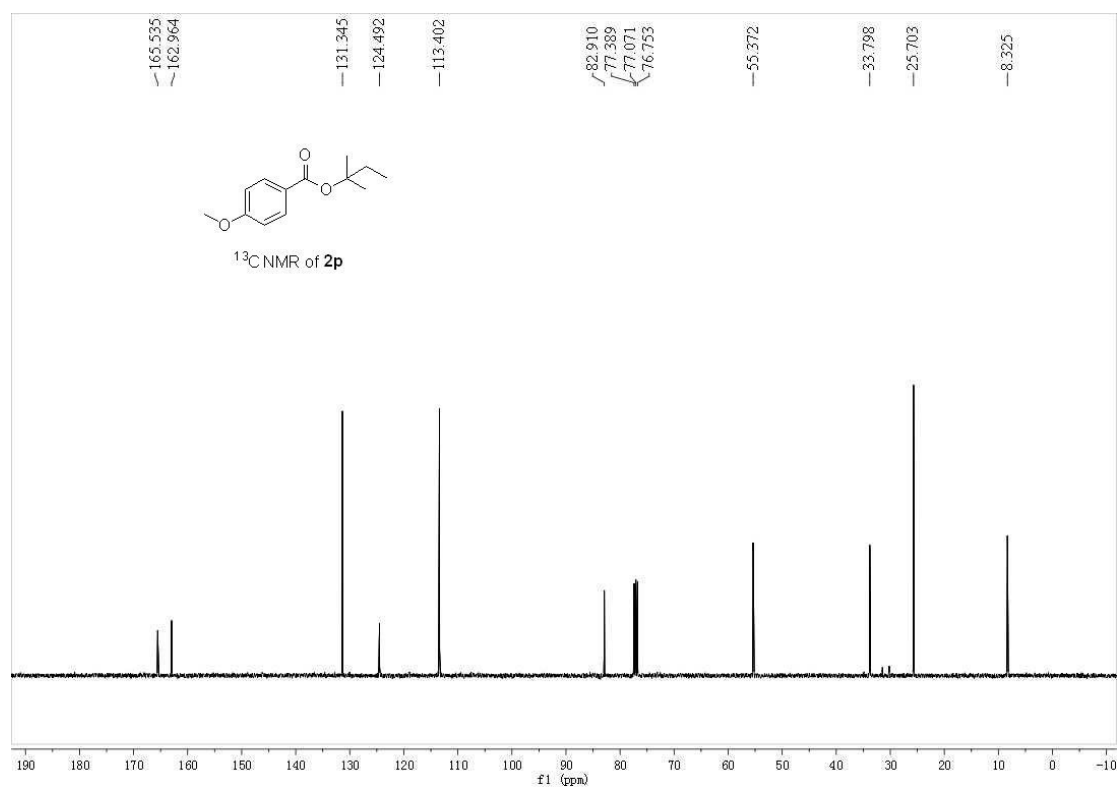
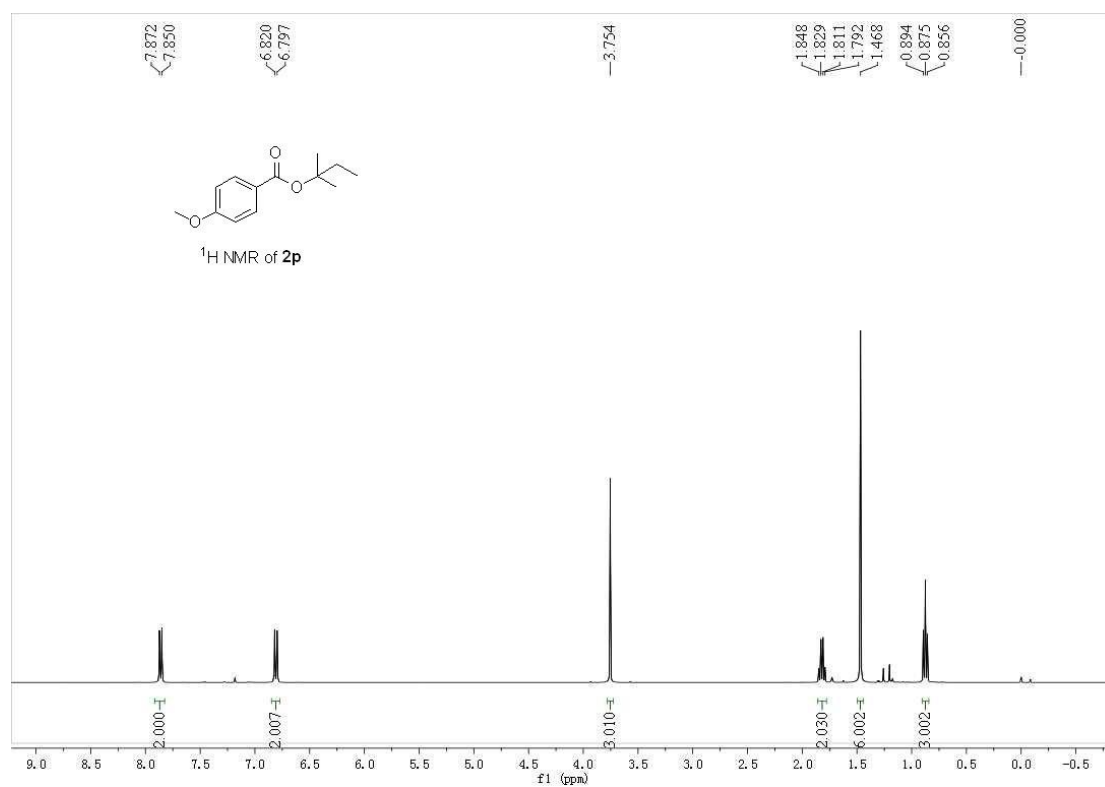
¹H NMR and ¹³C NMR of **2n**



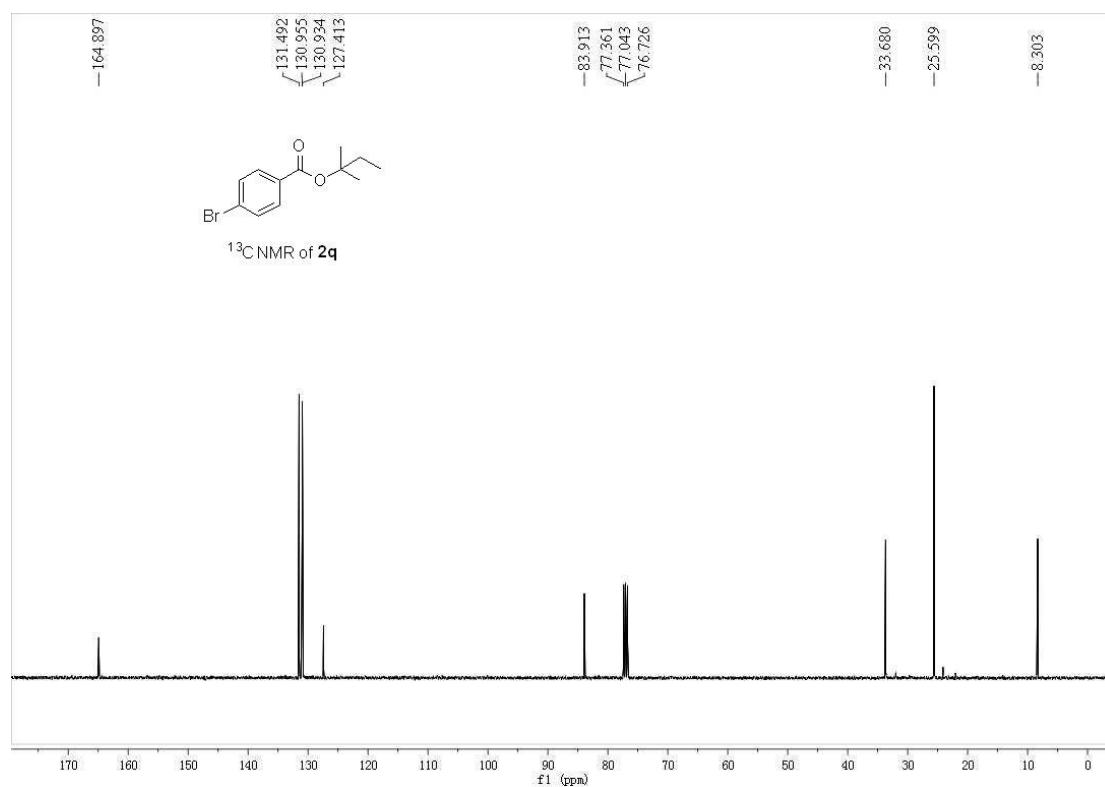
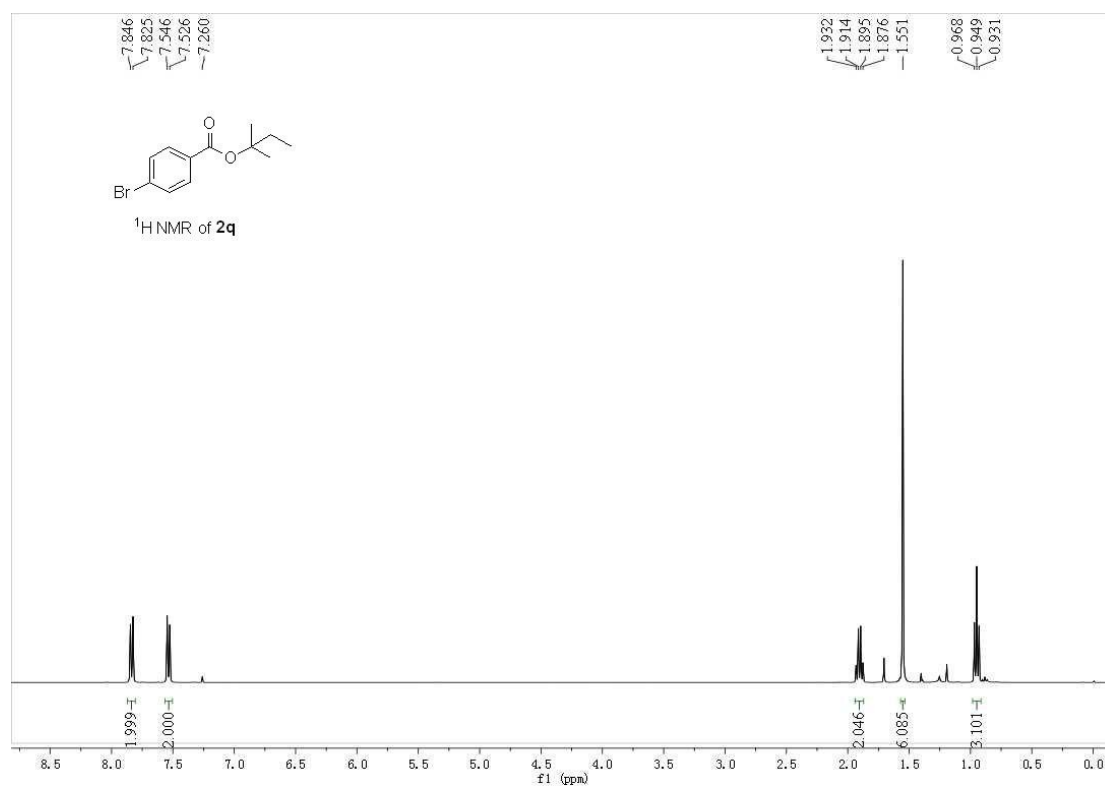
^1H NMR and ^{13}C NMR of **2o**



¹H NMR and ¹³C NMR of 2p



^1H NMR and ^{13}C NMR of **2q**



^1H NMR and ^{13}C NMR of **2r**

