Supporting Information

$BF_3 \cdot OEt_2$-Promoted Tandem Meinwald Rearrangement and Nucleophilic Substitution of Oxiranecarbonitriles

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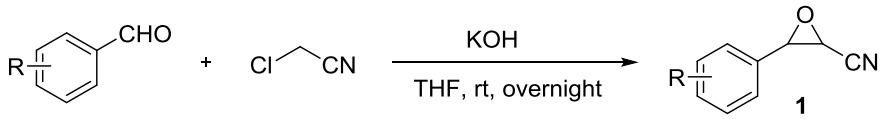
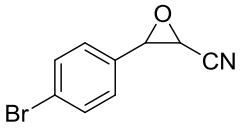
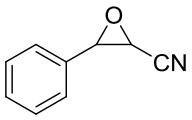
1. Synthesis of 3-aryloxirane-2-carbonitriles 1.

Scope of 3-aryloxirane-2-carbonitriles[a]

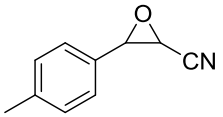




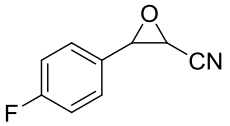
1a
trans: 48%
cis: 23%



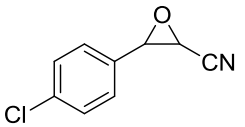
1b
trans: 67%
cis: 26%



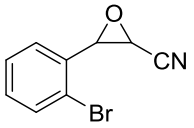
1c
trans: 55%
cis: 19%



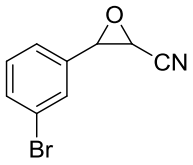
1d
trans: 55%
cis: 31%



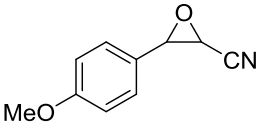
1e
trans: 38%
cis: 23%



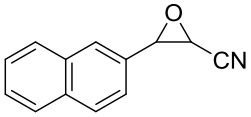
1f 80%[b]
trans:cis = 56:44



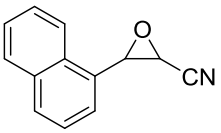
1g
trans: 55%
cis: 19%



1h[c]
cis: 15%



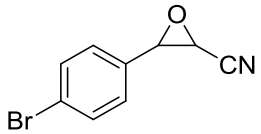
1i
trans: 55%
cis: 19%



1j
trans: 40%
cis: 14%

[a]Reaction conditions: Aldehyde (10 mmol), chloroacetonitrile (905 mg, 12 mmol), and KOH (675 mg, 12 mmol) in 50 mL of THF reacted for 10 h at room temperature. [b]Having almost the same R_f values and could not be separated. [c]Sensitive to acidic conditions, so only *cis*-isomer of **1h** was isolated the without treatment with $NaHSO_3$ because *trans*-isomer of **1h** and 4-methoxybenzaldehyde have the same R_f values.

3-(4-Bromophenyl)oxirane-2-carbonitrile (1a).[1]



trans-isomer (*trans*-**1a**): colorless crystals, 1.074 g, 48%. M.p. 97−98 °C. R_f = 0.76, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 4.26 (d, J = 1.6 Hz, 1H), 3.38 (d, J = 1.6Hz, 1H).

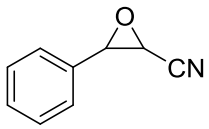
^{13}C NMR (101 MHz, $CDCl_3$): δ 132.2, 131.8, 127.3, 124.0, 115.6, 57.9, 44.5.

cis-isomer (*cis*-**1a**): colorless crystals, 525 mg, 23%. M.p. 105−106 °C. R_f = 0.45, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.22 (d, J = 3.6 Hz, 1H), 3.79 (d, J = 3.6 Hz, 1H).

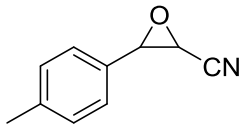
^{13}C NMR (101 MHz, $CDCl_3$): δ 131.9, 130.4, 127.9, 124.0, 114.7, 57.2, 45.0.

3-Phenyloxirane-2-carbonitrile (1b).[1]



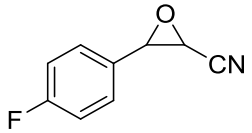
trans-isomer (*trans*-**1b**): colorless oil, 974 mg, 67%. R_f = 0.76, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.38 (m, 3H), 7.29 – 7.24 (m, 2H), 4.28 (d, J = 1.8 Hz, 1H), 3.40 (d, J = 1.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 132.7, 129.8, 128.9, 125.6, 116.0, 58.4, 44.6.
cis-isomer (*cis*-**1b**): colorless crystals, 381 mg, 26%. M.p. 60−61 °C. R_f = 0.55, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 5H), 4.25 (d, J = 3.6 Hz, 1H), 3.78 (d, J = 3.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 131.3, 129.7, 128.6, 126.3, 115.0, 57.7, 45.1.

3-(4-Methylphenyl)oxirane-2-carbonitrile (1c).[1]



trans-isomer (*trans*-**1c**): colorless oil, 871 mg, 55%. R_f = 0.76, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.25 (s, 1H), 3.40 (s, 1H), 2.36 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 130.0, 129.7, 129.6, 125.6, 116.1, 58.5, 44.6, 21.3.
cis-isomer (*cis*-**1c**): colorless crystals, 296 mg, 19%. M.p. 56−58 °C. R_f = 0.59, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.22 (d, J = 3.6 Hz, 1H), 3.76 (d, J = 3.6 Hz, 1H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 139.7, 129.4, 128.3, 126.2, 115.1, 57.7, 45.1, 21.3.

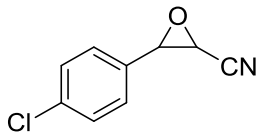
3-(4-Fluorophenyl)oxirane-2-carbonitrile (1d).[1]



trans-isomer (*trans*-**1d**): colorless crystals, 893 mg, 55%. M.p. 62−63 °C. R_f = 0.76, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 2H), 7.12 – 7.06 (m, 2H), 4.28 (d, J = 1.6 Hz, 1H), 3.39 (d, J = 1.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 164.8, 162.3, 128.5, 128.5, 127.6, 127.5, 116.2, 116.0, 115.8, 57.9, 44.6.
^{19}F NMR (377 MHz, $CDCl_3$): δ -110.73.
cis-isomer (*cis*-**1d**): colorless crystals, 506 mg, 31%. M.p. 54−55 °C. R_f = 0.53, 33% ethyl acetate

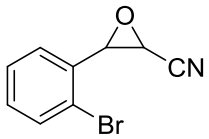
in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.38 (m, 2H), 7.16 – 7.10 (m, 2H), 4.24 (d, J = 3.6 Hz, 1H), 3.77 (d, J = 3.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.5 (d, J = 249.5 Hz), 128.2 (d, J = 9.1 Hz), 127.2 (d, J = 3.0 Hz), 115.8 (d, J = 22.2 Hz), 114.9, 57.1, 45.0.
^{19}F NMR (376 MHz, $CDCl_3$): δ -111.12.

3-(4-Chlorophenyl)oxirane-2-carbonitrile (1e).[1]



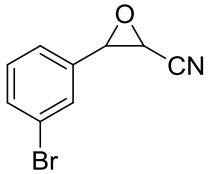
trans-isomer (*trans*-**1e**): colorless crystals, 683 mg, 38%. M.p. 74−75 °C. R_f = 0.75, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 4.27 (d, J = 1.6 Hz, 1H), 3.39 (d, J = 1.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 135.8, 131.2, 129.2, 127.0, 115.7, 57.8, 44.6.
cis-isomer (*cis*-**1e**): colorless crystals, 422 mg, 23%. Mp: 105−106 °C. R_f = 0.59, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.39 (m, 2H), 7.36 – 7.33 (m, 2H), 4.22 (d, J = 3.7 Hz, 1H), 3.77 (d, J = 3.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 135.7, 129.9, 128.9, 127.6, 114.7, 57.1, 45.0.

***cis/trans*-3-(2-Bromophenyl)oxirane-2-carbonitrile (1f).**[1]



Colorless oil, 1.79 g, 80%. R_f = 0.73, 33% ethyl acetate in petroleum ether. *cis:trans* = 44:56;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.58 (m, 1H), 7.42–7.24 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 4.56 (d, J = 1.4 Hz, 1H) (*trans*-isomer), 4.46 (d, J = 3.6 Hz, 1H) (*cis*-isomer), 3.86 (d, J = 3.6 Hz, 1H) (*cis*-isomer), 3.31 (d, J = 1.4 Hz, 1H) (*trans*-isomer).
^{13}C NMR (101 MHz, $CDCl_3$): δ 132.8, 132.7, 132.6, 131.5, 130.9, 130.8, 127.9, 127.7, 127.4, 126.1, 122.7, 122.5, 115.7, 114.6, 58.3, 57.7, 44.5, 44.0.

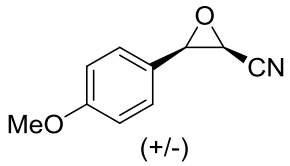
3-(3-Bromophenyl)oxirane-2-carbonitrile (1g).[1]



trans-isomer (*trans*-**1d**): colorless crystals, 1.19 g, 53%. M.p. 84−86 °C. R_f = 0.76, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dt, J = 7.6, 1.2 Hz, 1H), 7.41 (s, 1H), 7.29 – 7.22 (m, 2H), 4.26

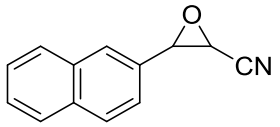
(d, J = 1.6 Hz, 1H), 3.40 (d, J = 2.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 132.9, 130.5, 128.5, 124.4, 123.1, 115.6, 57.5, 44.5.
cis-isomer (*cis*-**1d**): colorless crystals, 445 mg, 20%. M.p. 61−62 °C. R_f = 0.57, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.35 – 7.29 (m, 2H), 4.21 (d, J = 3.2 Hz, 1H), 3.78 (d, J = 3.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 132.8, 130.3, 129.5, 124.7, 122.7, 114.6, 56.8, 44.9.

cis-3-(4-Methoxyphenyl)oxirane-2-carbonitrile (_cis_-1h)[2]



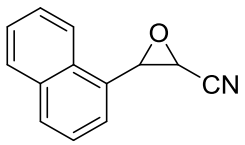
It is sensitive to acidic condition, so just the *cis*-isomer of **1h** was isolated without treatment with $NaHSO_3$ because *trans*-isomer of **1h** and 4-methoxybenzaldehyde have the same R_f values.
Colorless oil, 263 mg, 15%. R_f = 0.65, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 4.19 (d, J = 3.6 Hz, 1H), 3.82 (s, 3H), 3.74 (d, J = 3.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6, 127.6, 123.2, 115.2, 114.1, 57.6, 55.3, 45.1.

3-(Naphthalen-2-yl)oxirane-2-carbonitrile (1i).[1]



trans-isomer (*trans*-**1g**): colorless crystals, 877 mg, 55%. M.p. 109−111 °C. R_f = 0.78, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.81 (m, 4H), 7.56 – 7.52 (m, 2H), 7.27 (dd, J = 8.4, 1.2 Hz, 1H), 4.45 (d, J = 1.4 Hz, 1H), 3.55 (d, J = 1.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 133.9, 132.9, 130.0, 129.1, 128.0, 127.9, 127.0, 126.9, 126.1, 121.8, 116.0, 58.8, 44.7.
cis-isomer (*cis*-**1g**): colorless crystals, 294 mg, 19%. M.p. 137−139 °C. R_f = 0.53, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.86 (m, 4H), 7.56 – 7.52 (m, 2H), 7.49 (dd, J = 8.4, 1.6 Hz, 1H), 4.42 (d, J = 3.8 Hz, 1H), 3.86 (d, J = 3.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 133.9, 132.9, 128.8, 128.7, 128.1, 127.9, 126.9, 126.7, 126.3, 123.0, 115.0, 57.9, 45.2.

3-(Naphthalen-1-yl)oxirane-2-carbonitrile (1j).[1]



trans-isomer (*trans*-**1h**): colorless crystals, 775 mg, 40%. M.p. 64−66 °C. R_f = 0.76, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 8.0, 6.8 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (dd, J = 8.0, 7.2 Hz, 1H), 7.42 (d, J = 6.8 Hz, 1H), 4.90 (s, 1H), 3.43 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 133.2, 130.9, 129.8, 128.9, 127.2, 126.5, 125.2, 122.6, 122.2, 116.2, 57.1, 43.7.

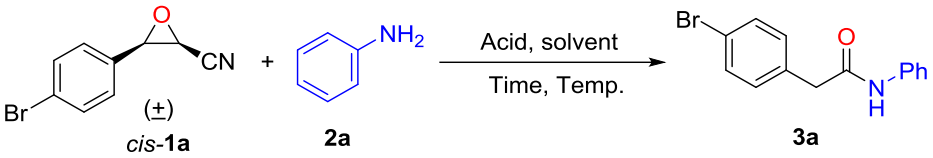
cis-isomer (*cis*-**1h**): colorless crystals, 269 mg, 14%. M.p. 76−77 °C. R_f = 0.61, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.98 (m, 1H), 7.96 – 7.91 (m, 2H), 7.63 – 7.52 (m, 4H), 4.84 (d, J = 3.6 Hz, 1H), 3.99 (d, J = 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 133.3, 130.9, 129.8, 129.1, 127.4, 127.0, 126.3, 125.3, 123.7, 121.9, 114.9, 56.1, 44.8.

2. Optimization on the Tandem Reaction Conditions

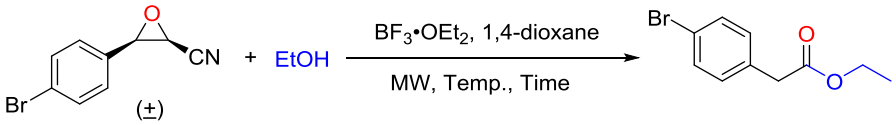
Table S1. Optimization on the reaction of *cis*-3-(4-bromophenyl)oxirane-2-carbonitrile (*cis*-1a) and aniline under refluxed conditions [a]



Entry	**2**/equiv.	Acid/equiv.	Temp.	Solvent	Time/h	Yield/%
1	1	BF_3•OEt_2/1.3	refluxed	THF	9	trace
2	1	BF_3•OEt_2/1.3	refluxed	MeCN	9	trace
3	1	BF_3•OEt_2/1.3	refluxed	DCE	9	mess
4	1	BF_3•OEt_2/1.3	refluxed	toluene	9	mess
5	1	BF_3•OEt_2/1.3	refluxed	DMF	9	--
6	1	BF_3•OEt_2/1.3	refluxed	*i*-PrOH	9	--
7	1	BF_3•OEt_2/1.3	refluxed	EtOH	9	--
8	1	BF_3•OEt_2/1.3	refluxed	1,4-dioxane	9	42

[a]Reactions were conducted on a 0.5 mmol scale of *cis*-**1a** in 5 mL of commercial solvent. All yields are isolated yields.

Table S2. Optimization on the reaction of *cis*-3-(4-bromophenyl)oxirane-2-carbonitrile (*cis*-1a) and ethanol under microwave irradiation conditions[a]

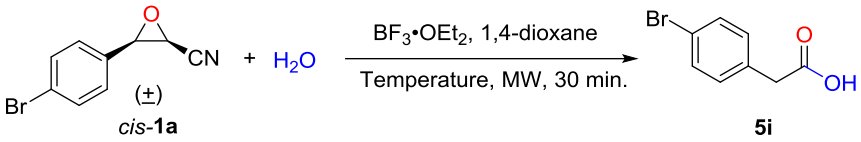


Entry	**4**/equiv.	BF_3•OEt_2/ equiv.	Temp./ °C	Time/min	Yield/%
1	1.1	1.3	190	30	41
2	1.5	1.3	190	30	46
3	1.8	1.3	190	30	49
4	2.0	1.3	190	30	48
5	2.2	1.3	190	30	49
6	2.5	1.3	190	30	46
7	3.0	1.3	190	30	43
8	**1.8**	**1.0**	**190**	**30**	**51**
9	1.8	1.5	190	30	50
10	1.8	0.8	190	30	49
11	1.8	0.5	190	30	43
12	1.8	1.0	180	30	51
13	**1.8**	**1.0**	**175**	**30**	**53**
14	1.8	1.0	130	30	28
15	1.8	1.0	110	30	21
16	1.8	1.0	175	20	49
17	1.8	1.0	175	40	53

[a]Reactions were conducted on a 0.5 mmol scale of *cis*-**1a** in 5 mL of anhydrous 1,4-dioxane and

anhydrous EtOH purified with standard process was used. All yields are isolated yields.

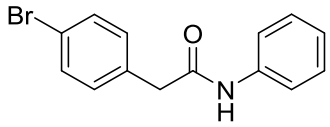
Table S3. Optimization on the reaction of *cis*-3-(4-bromophenyl)oxirane-2-carbonitrile (*cis*-1a) and water under microwave irradiation conditions[a]



Entry	H_2O/equiv.	BF_3•OEt_2/ equiv.	Temp./ ºC	Yield/%
1	1.8	1	190	50
2	1.8	1	175	52
3	1.8	1	160	50
4	2.0	1	175	29
5	1.4	1	175	59
6	1.2	1	175	64
7	**1**	**1**	**175**	**70**
8	1	1.2	175	61
9	**1.2**	**1.2**	**175**	**78**
10	1.5	1.5	175	54

[a]Reactions were conducted on a 0.5 mmol scale of *cis*-**1a** in 5 mL of 1,4-dioxane with water. All yields are isolated yields.

3. Characterization Data for Products 3, 5, and 6a.

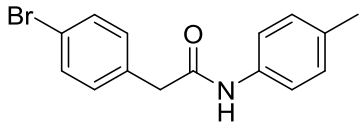


2-(4-Bromophenyl)-*N*-phenylacetamide (3a)[3]

Colorless solid 111 mg, 77%. M.p. 190–192 °C. R_f = 0.48, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H), 3.68 (s, 2H), 1.66 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 137.4, 133.3, 132.3, 131.2, 129.0, 124.7, 121.7, 119.9, 44.1.



2-(4-Bromophenyl)-*N*-(*p*-tolyl)acetamide (3b)

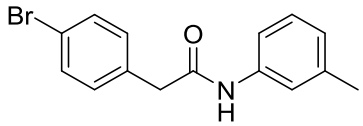
Colorless solid 119 mg, 78%. M.p. 213–214 °C. R_f = 0.47, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.07 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 3.60 (s, 2H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 168.3, 136.6, 135.5, 132.1, 131.4, 131.1, 129.0, 119.7, 119.1, 42.4, 20.4.

IR (KBr): v 1012, 1073, 1113, 1404, 1488, 1602, 1650, 3280 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO^+$ 304.0332, found 304.0333.



2-(4-Bromophenyl)-*N*-(*m*-tolyl)acetamide (3c)

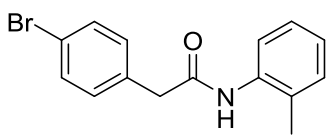
Colorless solid 87 mg, 57%. M.p. 161–162 °C. R_f = 0.38, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.08 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.42 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.61 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 168.5, 139.0, 137.9, 135.4, 131.4, 131.1, 128.5, 123.9, 119.7, 119.6, 116.3, 42.5, 21.2.

IR (KBr): v 1012, 1070, 1198, 1411, 1487, 1536, 1591, 1663, 3272 cm^{-1}.

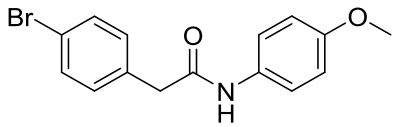
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO^+$ 304.0332, found 304.0331.



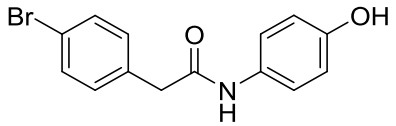
2-(4-Bromophenyl)-*N*-(*o*-tolyl)acetamide (3d)

Colorless solid 97 mg, 64%. M.p. 210–211 °C. R_f = 0.34, 33% ethyl acetate in petroleum ether.

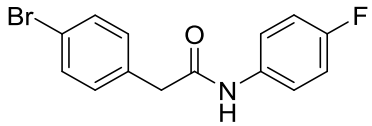
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.51 (s, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 3.66 (s, 2H), 2.15 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 168.6, 136.1, 135.7, 131.7, 131.3, 131.1, 130.2, 125.9, 125.2, 125.1, 119.6, 41.9, 17.7.
IR (KBr): v 1012, 1071, 1142, 1180, 1384, 1413, 1489, 1532, 1588, 1657, 3258 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO^+$ 304.0332, found 304.0339.



2-(4-Bromophenyl)-*N*-(4-methoxyphenyl)acetamide (3e)
The residue was subjected to silica gel column chromatography (PE/EA 5:1, *v/v*) to give the desired product as colorless solid 130 mg, 81%. M.p. 205–206 °C. R_f = 0.32, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.02 (s, 1H), 7.52 – 7.48 (m, 4H), 7.28 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 3.71 (s, 3H), 3.59 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 168.1, 155.2, 135.5, 132.2, 131.4, 131.1, 120.6, 119.7, 113.8, 55.1, 42.4.
IR (KBr): v 1031, 1074, 1142, 1180, 1384, 1409, 1451, 1489, 1512, 1604, 1649, 3282 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO_2^+$ 320.0281, found 320.0276.

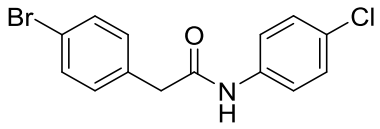


2-(4-Bromophenyl)-*N*-(4-hydroxyphenyl)acetamide (3f)
Colorless solid 93 mg, 61%. M.p. 245–247 °C. R_f = 0.44, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.90 (s, 1H), 9.16 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 3.56 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 167.8, 153.3, 135.7, 131.3, 131.1, 130.7, 120.9, 119.7, 115.0, 42.4.
IR (KBr): v 1013, 1070, 1240, 1298, 1346, 1412, 1453, 1487, 1511, 1541, 1661, 3216, 3285 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}BrNO_2^+$ 306.0124, found 306.0123.

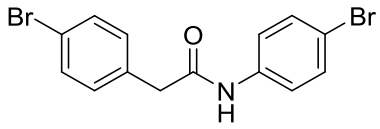


2-(4-Bromophenyl)-*N*-(4-fluorophenyl)acetamide (3g)
Colorless solid 101 mg, 66%. M.p. 182–183 °C. R_f = 0.42, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.22 (s, 1H), 7.61 – 7.58 (m, 2H), 7.52 (d, J = 8.0, Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 8.8 Hz, 2H), 3.62 (s, 2H).

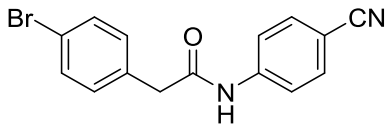
^{13}C NMR (101 MHz, DMSO-d_6): δ 168.5, 157.9 (d, $J_{C\text{-}F}$ = 240.4 Hz), 135.5 (d, $J_{C\text{-}F}$ = 2.0 Hz), 135.3, 131.4, 131.1, 120.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 119.7, 115.2 (d, $J_{C\text{-}F}$ = 23.2 Hz), 42.3.
^{19}F NMR (376 MHz, DMSO-d_6): δ -119.29.
IR (KBr): v 1013, 1071, 1222, 1405, 1487, 1511, 1532, 1663, 3279 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}BrFNO^+$ 308.0081, found 308.0083.



2-(4-Bromophenyl)-*N*-(4-chlorophenyl)acetamide (3h)
Colorless solid 105 mg, 65%. M.p. 195–197 °C. R_f = 0.48, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.30 (s, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.63 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 168.8, 138.0, 135.1, 131.4, 131.1, 128.6, 126.8, 120.6, 119.8, 42.4.
IR (KBr): v 1012, 1072, 1181, 1408, 1486, 1524, 1592, 1657, 3257 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}BrClNO^+$ 323.9785, found 323.9787.

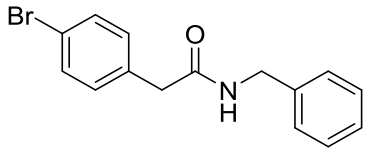


***N*,2-Bis(4-bromophenyl)acetamide (3i)**
Colorless solid 140 mg, 76%. M.p. 211–213 °C. R_f = 0.43, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.30 (s, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 3.63 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 168.8, 138.4, 135.1, 131.5, 131.4, 131.1, 121.0, 119.8, 114.8, 42.4.
IR (KBr): v 1012, 1070, 1407, 1487, 1524, 1589, 1659, 3261 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}Br_2NO^+$ 367.9280, found 367.9279.



2-(4-Bromophenyl)-*N*-(4-cyanophenyl)acetamide (3j)
The residue was subjected to silica gel column chromatography (PE/EA 5:1, *v/v*) to give the desired product as colorless solid 71 mg, 45%. M.p. 172–173 °C. R_f = 0.17, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.61 (s, 1H), 7.77 (s, 4H), 7.52 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.69 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 169.5, 143.3, 134.8, 133.3, 131.5, 131.2, 119.9, 119.1, 119.0, 105.0, 42.5.

IR (KBr): *v* 1013, 1072, 1142, 1175, 1257, 1311, 1408, 1488, 1528, 1596, 1672, 2224, 3315 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{12}BrN_2O^+$ 315.0128, found 315.0120.



_N_-Benzyl-2-(4-bromophenyl)acetamide (3k)

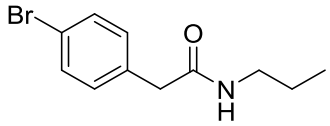
The residue was subjected to silica gel column chromatography (PE/EA 5:1, *v/v*) to give the desired product as colorless solid 81 mg, 53%. M.p. 174–175 °C. R_f = 0.22, 33% ethyl acetate in petroleum ether.

^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 5.69 (s, 1H), 4.41 (d, J = 5.8 Hz, 2H), 3.55 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 137.9, 133.7, 132.1, 131.1, 128.7, 127.6, 127.6, 121.4, 43.7, 43.1.

IR (KBr): *v* 1044, 1073, 1286, 1384, 1416, 1450, 1606, 1643, 1666, 2967, 3282 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO^+$ 304.0332, found 304.0333.



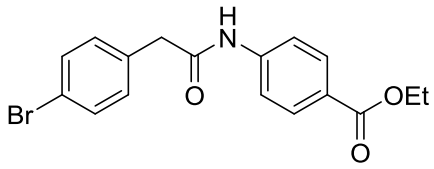
2-(4-Bromophenyl)-_N_-propylacetamide (3l)

The residue was subjected to silica gel column chromatography (PE/EA 5:1, *v/v*) to give the desired product as colorless solid 55 mg, 43%. M.p. 113–115 °C. R_f = 0.15, 33% ethyl acetate in petroleum ether.

^1H NMR (400 MHz, DMSO-d_6): δ 8.02 (s, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 3.37 (s, 2H), 2.99 (q, J = 7.2 Hz, 2H), 1.39 (sext, J = 7.2 Hz, 2H), 0.82 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 169.4, 136.0, 131.2, 131.0, 119.4, 41.6, 40.4, 22.3, 11.3.

IR (KBr): *v* 1012, 1071, 1086, 1179, 1402, 1441, 1484, 1548, 1591, 1650, 2951, 3299 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{15}BrNO^+$ 256.0332, found 256.0335.

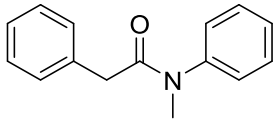


Ethyl 4-(2-(4-bromophenyl)acetamido)benzoate (3m)

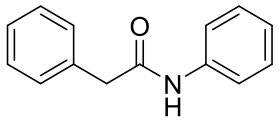
The residue was subjected to silica gel column chromatography (PE/EA 6:1, *v/v*) to give the desired product as colorless solid 83 mg, 46%. Mp: 163–165 °C. R_f = 0.22, 33% ethyl acetate in petroleum ether.

^1H NMR (400 MHz, DMSO-d_6): δ 10.51 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.27 (q, J = 7.0 Hz, 2H), 3.68 (s, 2H), 1.30 (t, J = 7.0 Hz, 3H).

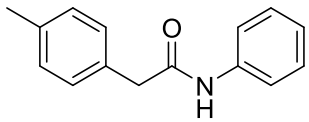
^{13}C NMR (101 MHz, DMSO-d_6): δ 169.2, 165.2, 143.4, 135.0, 131.5, 131.1, 130.2, 124.2, 119.8, 118.4, 60.4, 42.5, 14.2.
IR (KBr): v 1050, 1177, 1276, 1332, 1364, 1488, 1518, 1535, 1596, 1614, 1693, 2977, 3344 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}BrNO_3^+$ 362.0386, found 362.0388.



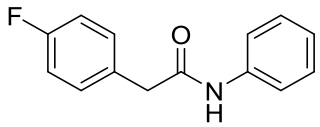
2-(4-Bromophenyl)-N-methyl-N-phenylacetamide (3n)
The residue was subjected to silica gel column chromatography (PE/EA 10:1, *v/v*) to give the desired product as pale yellow oil 95 mg, 63%. R_f = 0.38, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 5H), 7.12 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.8 Hz, 2H), 3.40 (s, 2H), 3.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 143.7, 134.3, 131.3, 130.8, 129.8, 128.0, 127.5, 120.5, 40.3, 37.6.
IR (KBr): v 1012, 1072, 1121, 1377, 1495, 1595, 1658, 3290 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO^+$ 304.0332, found 304.0336.



***N*,2-Diphenylacetamide (3o)**[4]
Colorless solid 70 mg, 66%. M.p. 123–124 °C (lit.[2] mp 118−120 °C). R_f = 0.38, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.15 (s, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.34 – 7.23 (m, 7H), 7.03 (t, J = 7.6 Hz, 1H), 3.64 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 169.0, 139.2, 136.0, 129.1, 128.7, 128.3, 126.5, 123.2, 119.1, 43.3.



***N*-Phenyl-2-(*p*-tolyl)acetamide (3p)**[4]
Colorless solid 62 mg, 55%. M.p. 154–156 °C (lit.[4] mp 156−18 °C). R_f = 0.43, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.10 (s, 1H), 7.58 (d, J = 7.7 Hz, 2H), 7.28 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.02 (t, J = 7.7 Hz, 1H), 3.57 (s, 2H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 169.2, 139.2, 135.5, 132.9, 128.9, 128.8, 128.7, 123.1, 119.0, 42.9, 20.6.



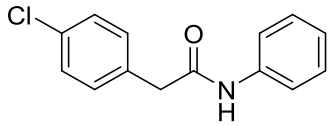
2-(4-Fluorophenyl)-*N*-phenylacetamide (3q)[4]

Colorless solid 62 mg, 54%. M.p. 133–134 °C (lit.[4] mp 124−126 °C). R_f = 0.35, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.15 (s, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.17 – 7.12 (m, 2H), 7.03 (t, J = 7.8 Hz, 1H), 3.63 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 168.9, 161.1 (d, $J_{C\text{-}F}$ = 243.4 Hz), 139.1, 132.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.9 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.7, 123.2, 119.1, 115.0 (d, $J_{C\text{-}F}$ = 21.2 Hz), 42.2.

^{19}F NMR (376 MHz, DMSO-d_6): δ -116.59.

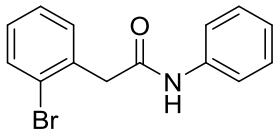


2-(4-Chlorophenyl)-*N*-phenylacetamide (3r)[4]

Colorless solid 81 mg, 66%. M.p. 175–176 °C (lit.[4] mp 170−172 °C). R_f = 0.32, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.16 (s, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.39 (d, J=8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.03 (t, J = 7.8 Hz, 1H), 3.64 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 168.7, 139.1, 135.0, 131.2, 131.0, 128.7, 128.2, 123.2, 119.1, 42.4.



2-(2-Bromophenyl)-*N*-phenylacetamide (3s)

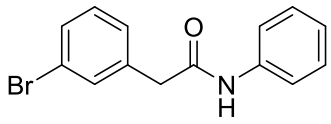
The residue was subjected to silica gel column chromatography (PE/EA 10:1, *v/v*) to give the desired product as colorless solid 70 mg, 48%. M.p. 160–161 °C. R_f = 0.51, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.20 (s, 1H), 7.62 – 7.58 (m, 3H), 7.42 (d, J = 6.8 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.8 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 3.84 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 167.8, 139.2, 135.7, 132.2, 128.7, 128.7, 127.6, 124.6, 123.1, 119.0, 43.2.

IR (KBr): ν 1027, 1255, 1347, 1411, 1444, 1535, 1599, 1658, 3266 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}BrNO^+$ 290.0175, found 290.0180.

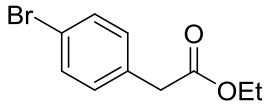


2-(3-Bromophenyl)-*N*-phenylacetamide (3t)

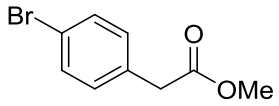
Colorless solid 67 mg, 46%. M.p. 154–155 °C. R_f = 0.44, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (s, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.55 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.04 (t, J = 7.4 Hz, 1H), 3.66 (s, 2H).

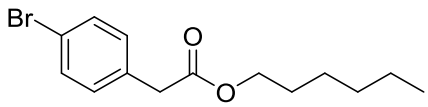
^{13}C NMR (101 MHz, DMSO-d_6): δ 168.5, 139.1, 138.6, 131.9, 130.4, 129.4, 128.7, 128.3, 123.3, 121.4, 119.1, 42.6.
IR (KBr): v 1094, 1384, 1443, 1498, 1546, 1599, 1659, 3288 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}BrNO^+$ 290.0175, found 290.0174.



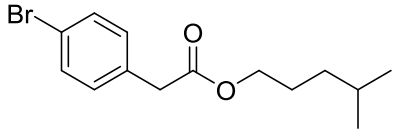
Ethyl 2-(4-bromophenyl)acetate (5a)[5]
Colorless oil 65 mg, 53%. R_f = 0.71, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.15 (q, J = 7.0 Hz, 2H), 3.56 (s, 2H), 1.25 (t, J = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 133.1, 131.6, 131.0, 121.0, 61.0, 40.7, 14.1.



Methyl 2-(4-bromophenyl)acetate (5b)[5]
Colorless oil 49 mg, 43%. R_f = 0.68, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.69 (s, 3H), 3.58 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 132.9, 131.6, 131.0, 121.1, 52.1, 40.5.

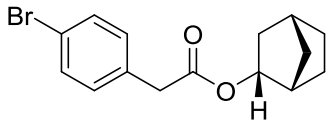


Hexyl 2-(4-bromophenyl)acetate (5c).
The residue was subjected to silica gel column chromatography (PE/EA 50:1, *v/v*) to give the desired product as colorless oil 85 mg, 55%. R_f = 0.85, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 4.08 (t, J = 6.6 Hz, 2H), 3.56 (s, 2H), 1.60 (quintet, J = 6.6 Hz, 2H), 1.28 (m, 6H), 0.88 (t, J = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 133.1, 131.6, 131.0, 121.0, 65.2, 40.8, 31.3, 28.4, 25.4, 22.5, 13.9.
IR (KBr): v 1014, 1073, 1165, 1255, 1344, 1471, 1496, 1508, 1749, 2933, 2961 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{20}BrO_2^+$ 299.0641, found 299.0643.



4-Methylpentyl 2-(4-bromophenyl)acetate (5d).
The residue was subjected to silica gel column chromatography (PE/EA 50:1, *v/v*) to give the desired product as colorless oil 83 mg, 54%. R_f = 0.87, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 4.07 (t, J = 6.8 Hz,

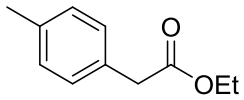
2H), 3.56 (s, 2H), 1.64 – 1.47 (m, 3H), 1.20 – 1.14 (m, 2H), 0.87 (d, J = 6.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 133.1, 131.6, 131.0, 121.0, 65.4, 40.8, 34.8, 27.6, 26.4, 22.4.
IR (KBr): v 1014, 1073, 1166, 1259, 1339, 1385, 1408, 1468, 1489, 1590, 1736, 2929, 2957 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{20}BrO_2^+$ 299.0641, found 299.0644.



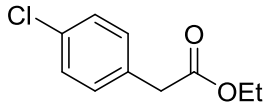
(1*S*,2*R*,4*R*)-Bicyclo[2.2.1]heptan-2-yl 2-(4-bromophenyl)acetate (5e)
Colorless oil 74 mg, 48%. R_f = 0.89, 33% ethyl acetate in petroleum ether.

$[\alpha]_D^{25}$ = +12.0 (c 0.50, chloroform).

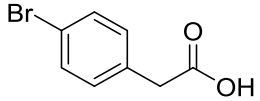
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.96 – 4.93 (m, 1H), 3.56 (s, 2H), 2.45 (s, 1H), 2.20 (s, 1H), 2.01 – 1.93 (m, 1H), 1.67 – 1.61 (m, 1H), 1.59 – 1.53 (m, 1H), 1.38 – 1.36 (m, 1H), 1.33 – 1.31 (m, 1H), 1.29 – 1.21 (m, 2H), 0.96 – 0.91 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 133.2, 131.6, 131.0, 121.0, 76.3, 41.0, 40.2, 37.3, 36.9, 36.4, 29.2, 20.9.
IR (KBr): v 1013, 1072, 1146, 1162, 1255, 1336, 1489, 1732, 2873, 2960 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}BrO_2^+$ 309.0485, found 309.0486.



Ethyl 2-(4-methylphenyl)acetate (5f)[6]
Colorless oil 37 mg, 42%. R_f = 0.78, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 4.13 (q, J = 6.8 Hz, 2H), 3.56 (s, 2H), 2.32 (s, 3H), 1.24 (t, J = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.8, 136.6, 131.1, 129.2, 129.0, 60.7, 41.0, 21.0, 14.1.



Ethyl 2-(4-chlorophenyl)acetate (5g)[6]
Colorless oil 44 mg, 44%. R_f = 0.78, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.57 (s, 2H), 1.25 (t, J = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1, 133.0, 132.6, 130.6, 128.6, 61.0, 40.7, 14.1.

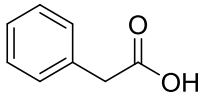


2-(4-Bromophenyl)acetic acid (5h)[7]
The residue was subjected to silica gel column chromatography (PE/EA 8:1, v/v) to give the desired

product as colorless solid 84 mg, 78%. M.p. 121–123 °C. R_f = 0.11, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.73 (s, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 3.61 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.9, 132.1, 131.8, 131.1, 121.5, 40.3.

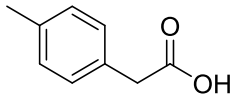


2-Phenylacetic acid (5i)[7]

Colorless solid 52 mg, 76%. M.p. 75–78 °C (lit.[6] mp 76−78 °C). R_f = 0.11, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.44 (s, 1H), 7.35 – 7.25 (m, 5H), 3.65 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.7, 133.2, 129.4, 128.6, 127.4, 41.0.

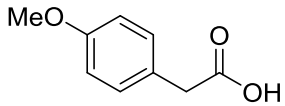


2-(4-Methylphenyl)acetic acid (5j)[8]

Colorless solid 56 mg, 75%. M.p. 91–94 °C (lit.[8] mp 91−92 °C). R_f = 0.23, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.10 (s, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.61 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.6, 137.0, 130.2, 129.3, 129.2, 40.5, 21.1.

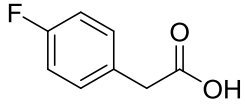


2-(4-Methoxyphenyl)acetic acid (5k)[8]

The residue was subjected to silica gel column chromatography (PE/EA 8:1, *v/v*) to give the desired product as colorless solid 45 mg, 54%. M.p. 75–78 °C (lit.[6] mp 85−87 °C). R_f = 0.12, 33% ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 3.59 (s, 2H), 3.49 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.0, 158.9, 130.4, 125.4, 114.1, 55.3, 40.0.



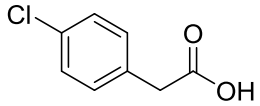
2-(4-Fluorophenyl)acetic acid (5l)[7]

Colorless solid 53 mg, 69%. M.p. 75–78 °C (lit.[8] mp 82−85 °C). R_f = 0.12, 33% ethyl acetate in petroleum ether.

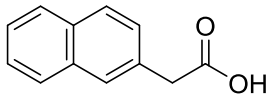
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.30 (s, 1H), 7.26 – 7.23 (m, 2H), 7.04 – 7.00 (m, 2H), 3.62 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.7, 162.15 (d, $J_{C\text{-}F}$ = 247.5 Hz), 131.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.9

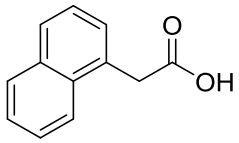
(d, $J_{C\text{-}F}$ = 3.0 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.2 Hz), 40.1.
^{19}F NMR (377 MHz, $CDCl_3$): δ -115.23.



2-(4-Chlorophenyl)acetic acid (5m)[7]
Colorless solid 44 mg, 52%. M.p. 106–109 °C (lit.[6] mp 104−106 °C). R_f = 0.11, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.08 (s, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 3.62 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 177.1, 133.4, 131.6, 130.7, 128.8, 40.2.

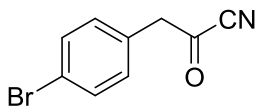


2-(Naphthalen-2-yl)acetic acid (5n)[7]
Colorless solid 46 mg, 49%. M.p. 148–151 °C. R_f = 0.12, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.33 (s, 1H), 7.82 – 7.78 (m, 3H), 7.73 (s, 1H), 7.48 – 7.43 (m, 2H), 7.40 (d, J = 8.4 Hz, 1H), 3.81 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 177.6, 133.4, 132.5, 130.7, 128.3, 128.2, 127.7, 127.3, 126.2, 126.0, 41.1.



2-(Naphthalen-1-yl)acetic acid (5o)[7]
Colorless solid 36 mg, 39%. M.p. 129–132 °C. R_f = 0.12, 33% ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.53 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.2 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.43 – 7.37 (m, 2H), 4.06 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 177.9, 133.8, 132.0, 129.7, 128.8, 128.3, 128.2, 126.5, 125.8, 125.4, 123.7, 38.8.

2-(4-Bromophenyl)acetyl cyanide (6a).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 4.16 (s, 2H) (obtained from ^{1}H NMR spectrum of mixed **5h** and **6a**).
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_9H_7BrO^+$ 223.9706, found 223.9708.

References

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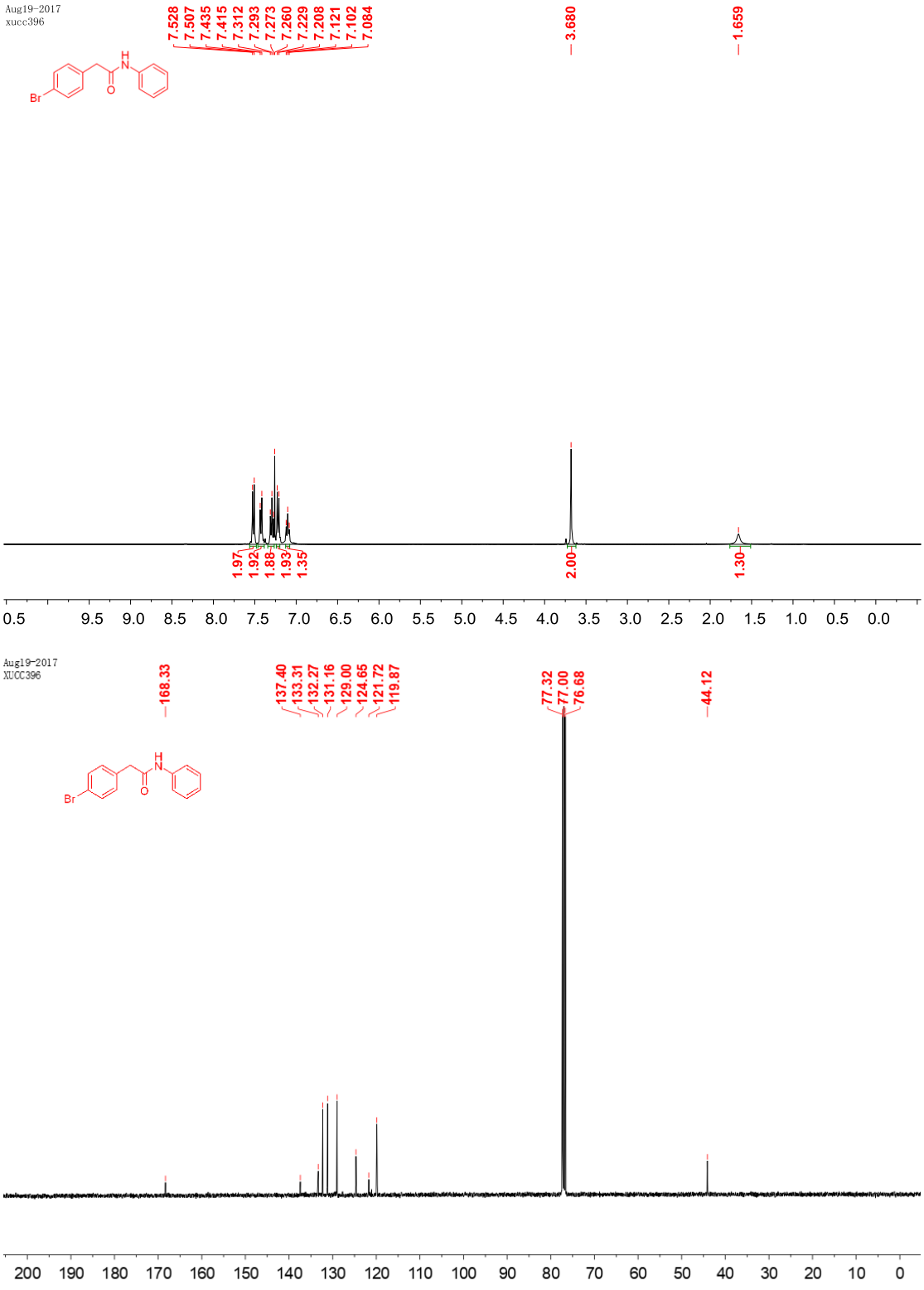
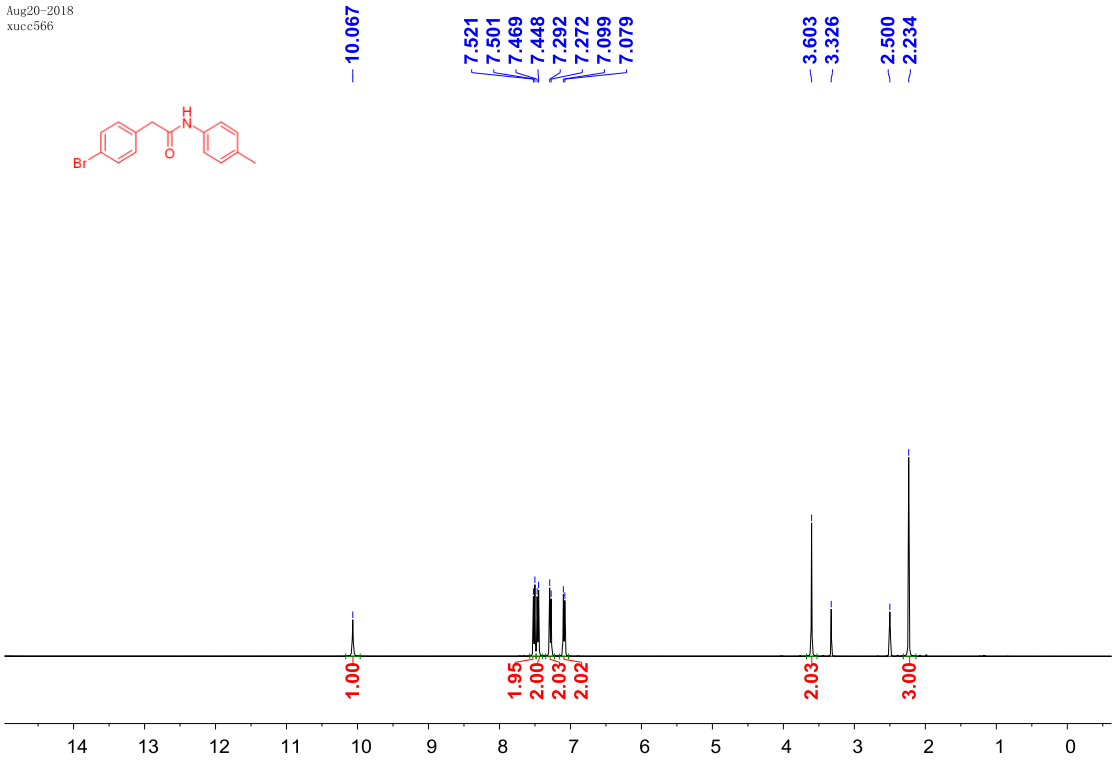
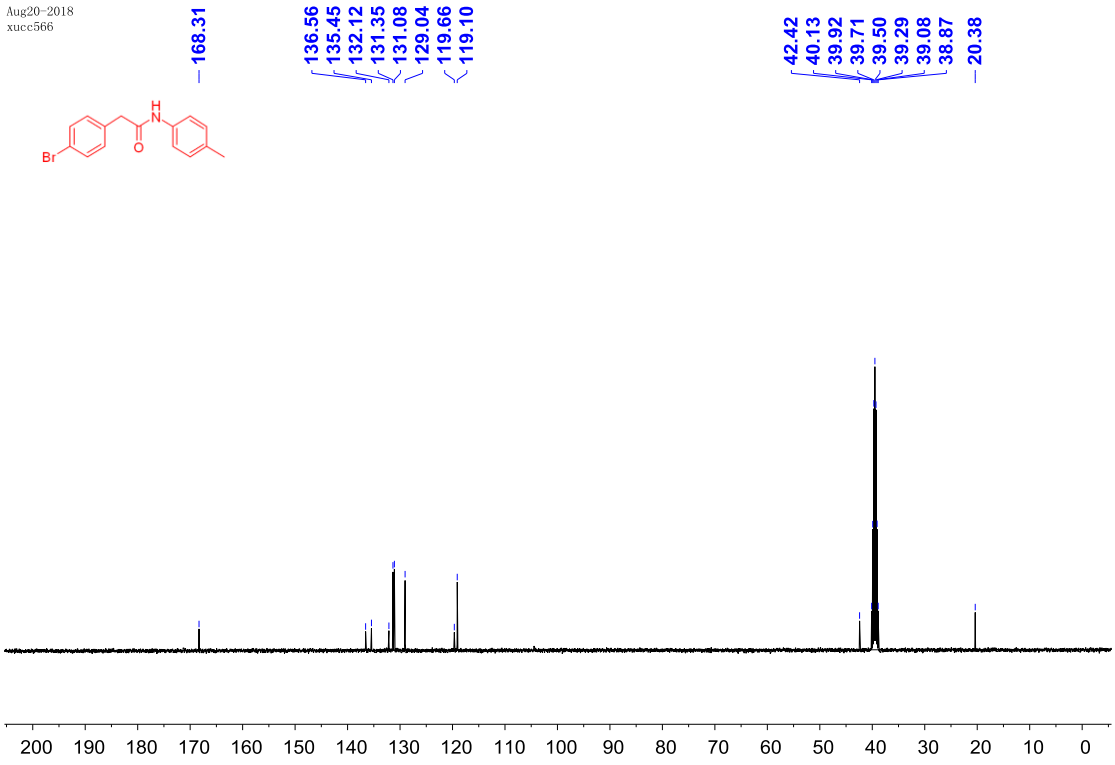
4. Copies of NMR Spectra of All Products 3, 5, 1 and HRMS and GC-MS of 6.

^{1}H and ^{13}C spectra of **3a**.

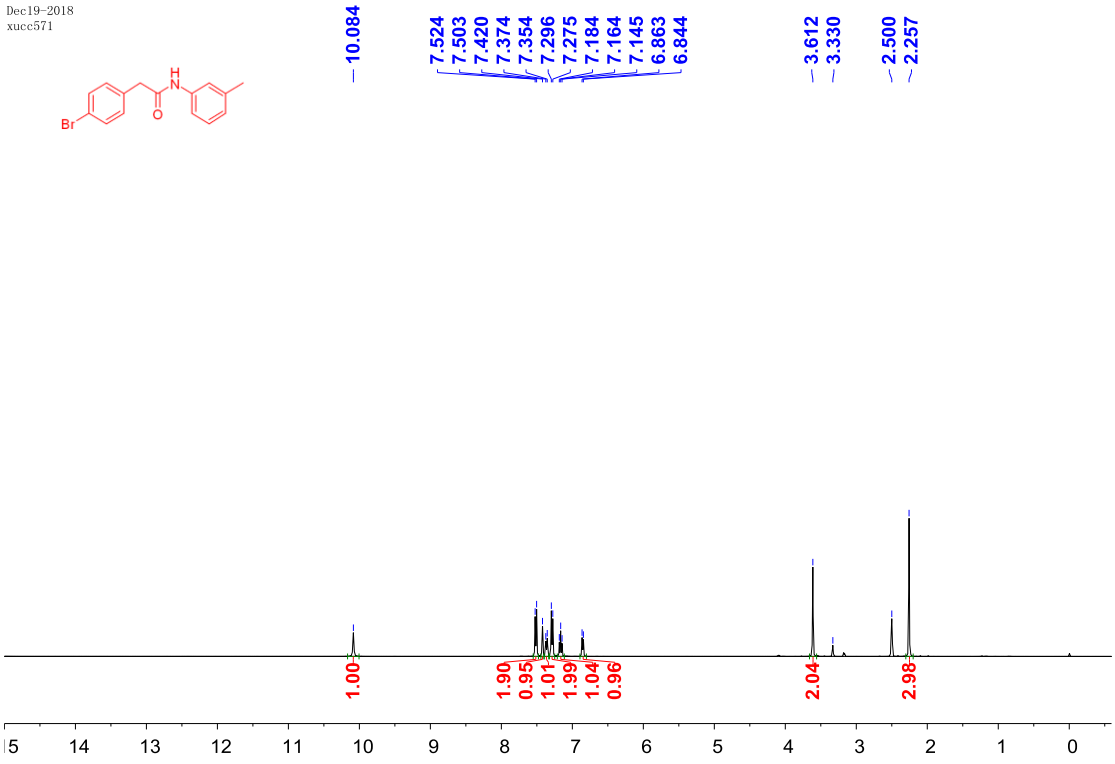


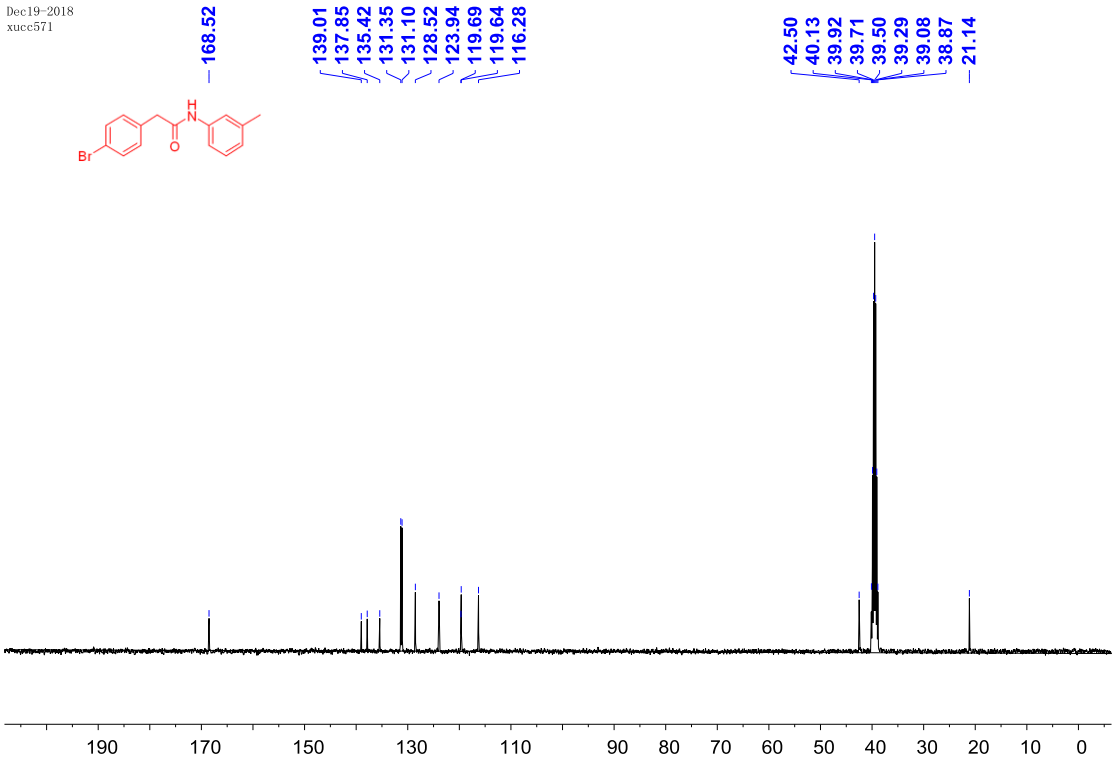
^{1}H and ^{13}C spectra of **3b**.



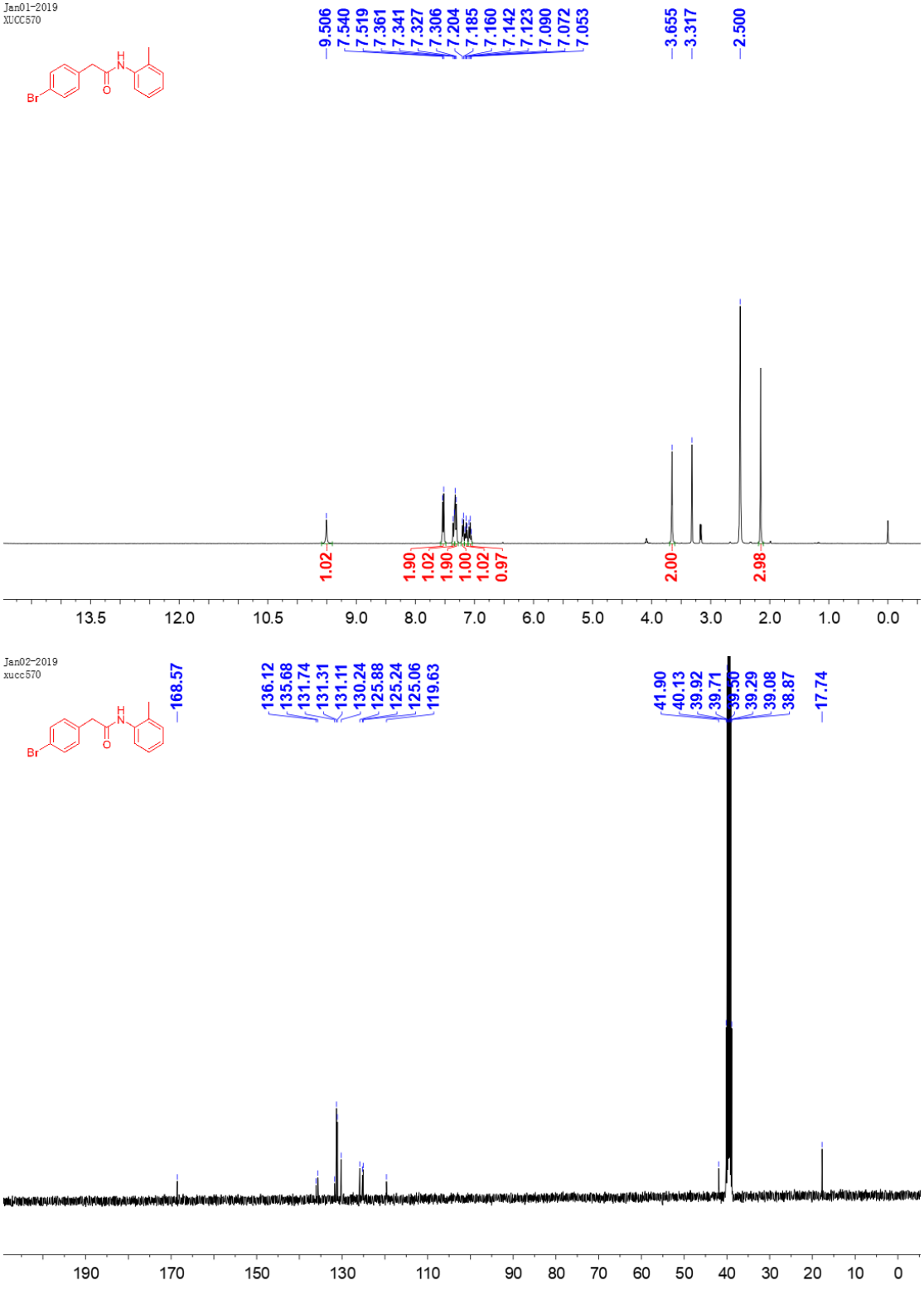


^{1}H and ^{13}C spectra of **3c**.

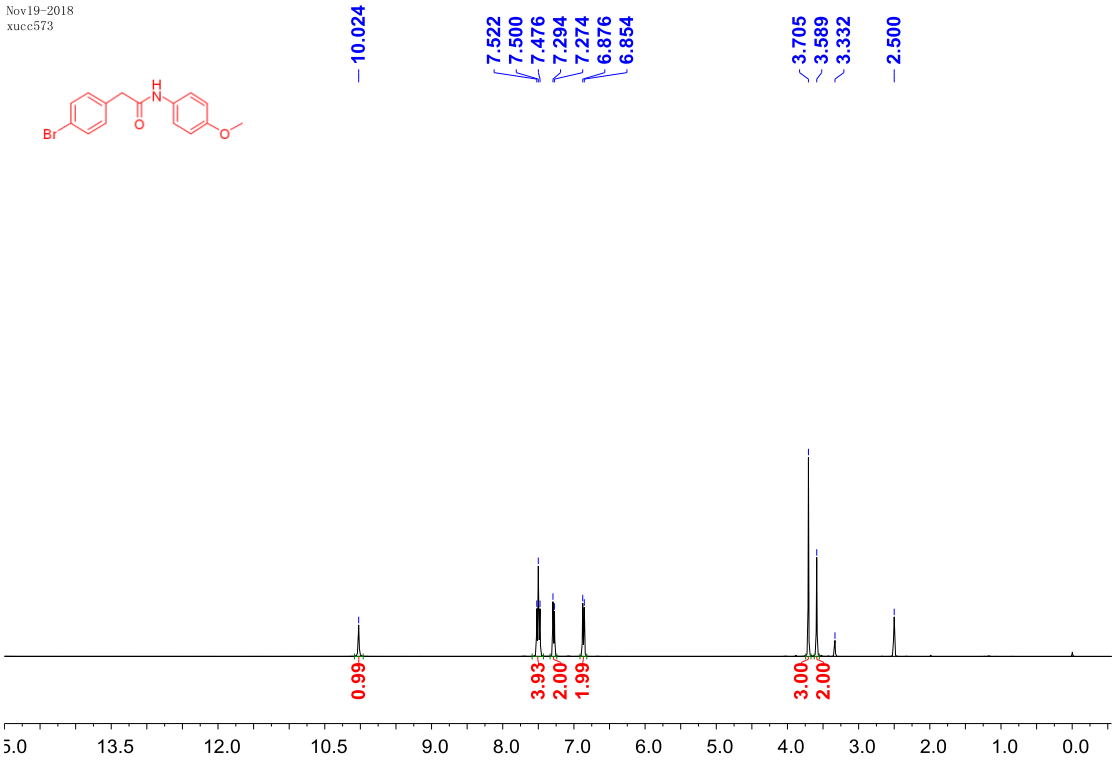


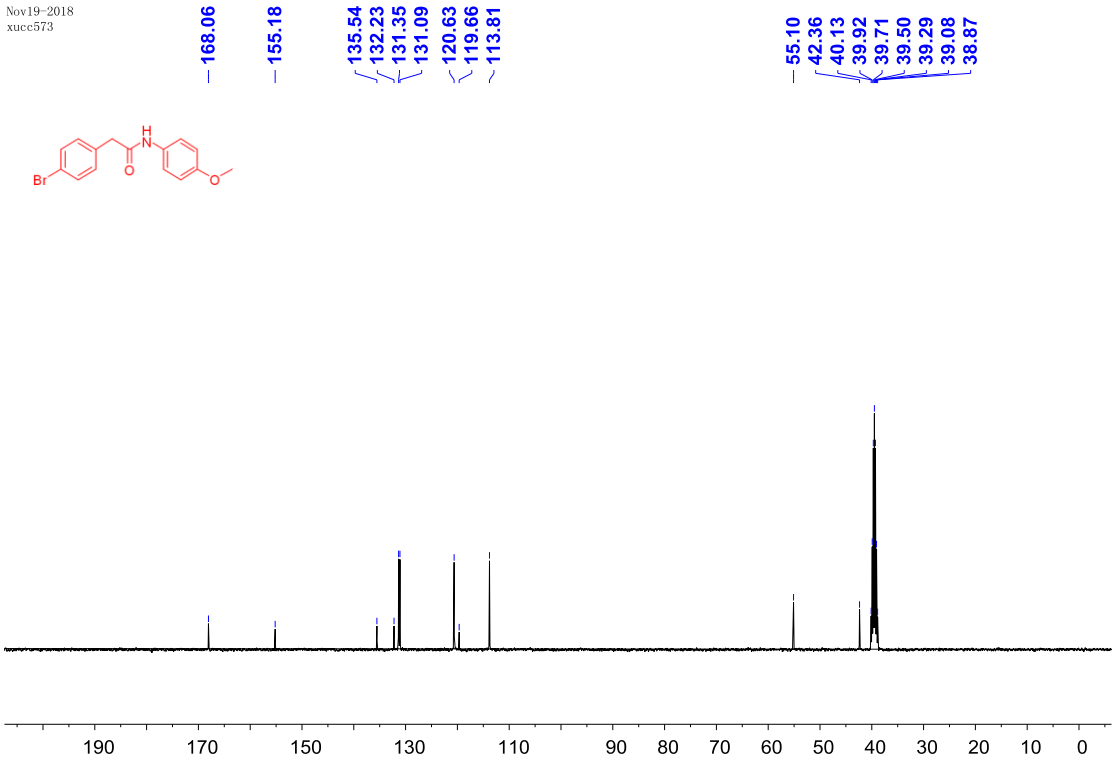


^{1}H and ^{13}C spectra of **3d**.

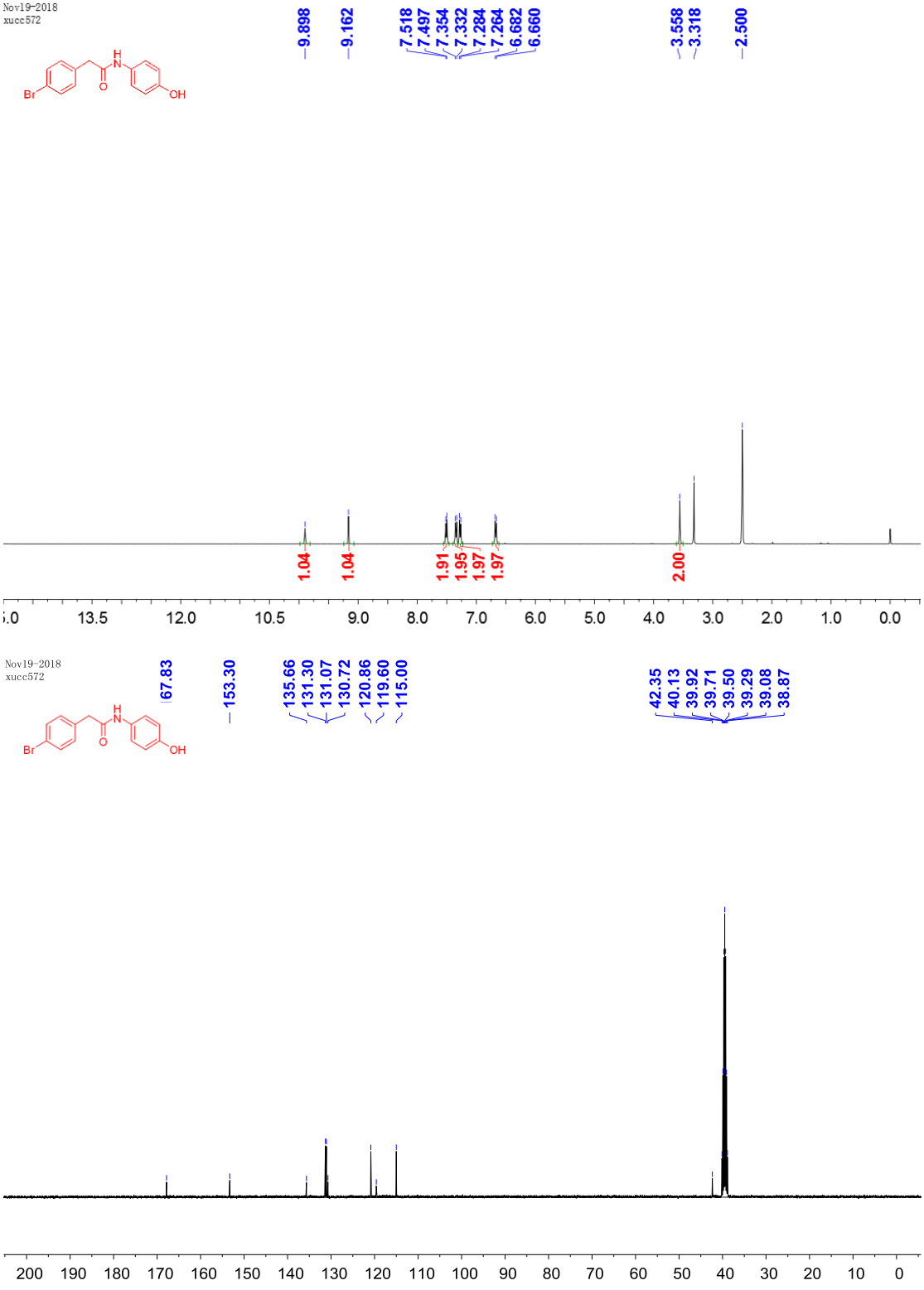


^{1}H and ^{13}C spectra of **3e**.

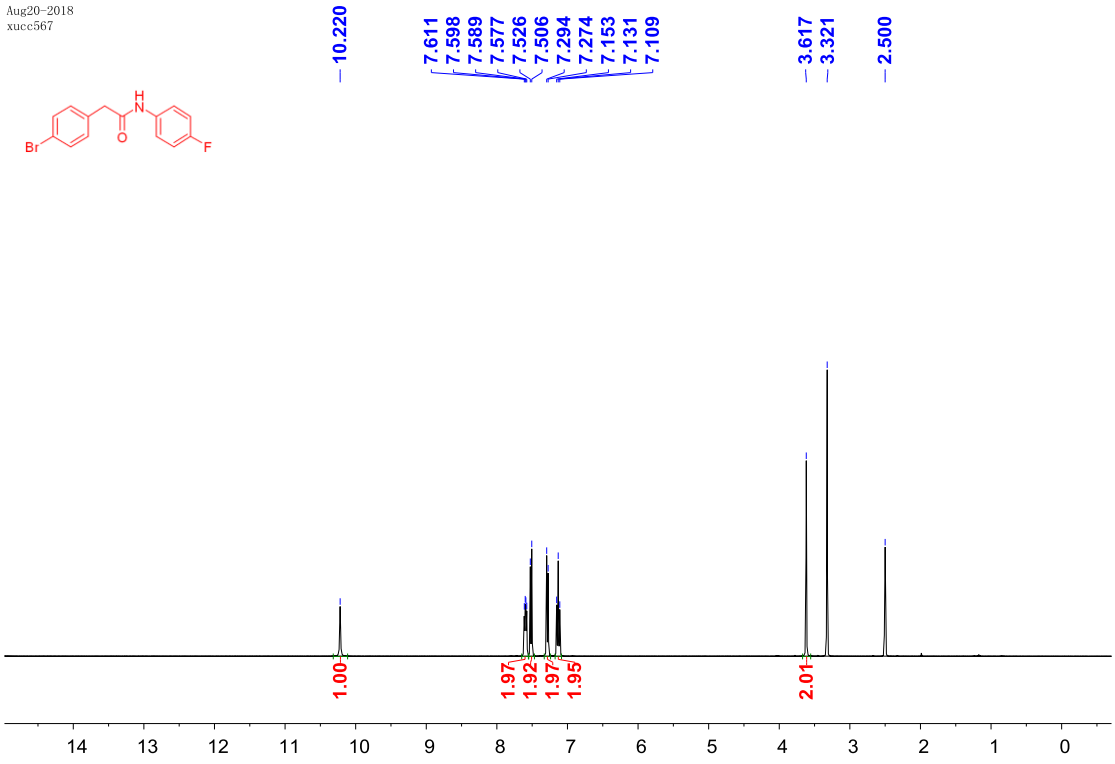


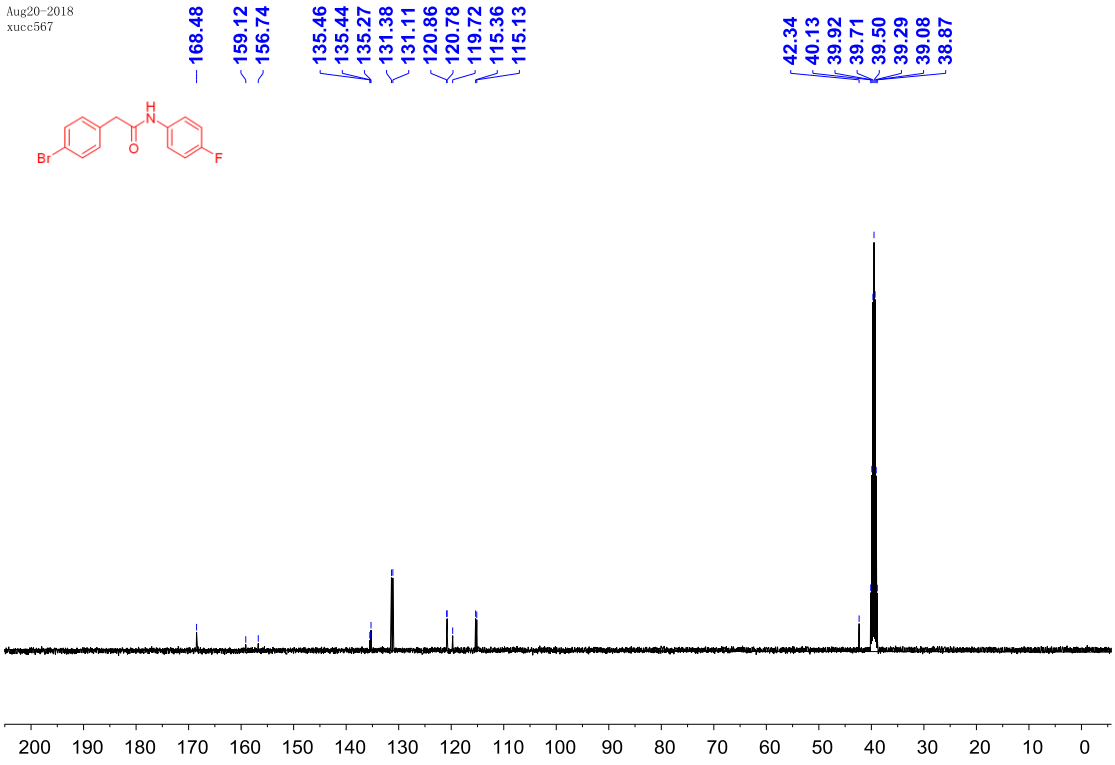


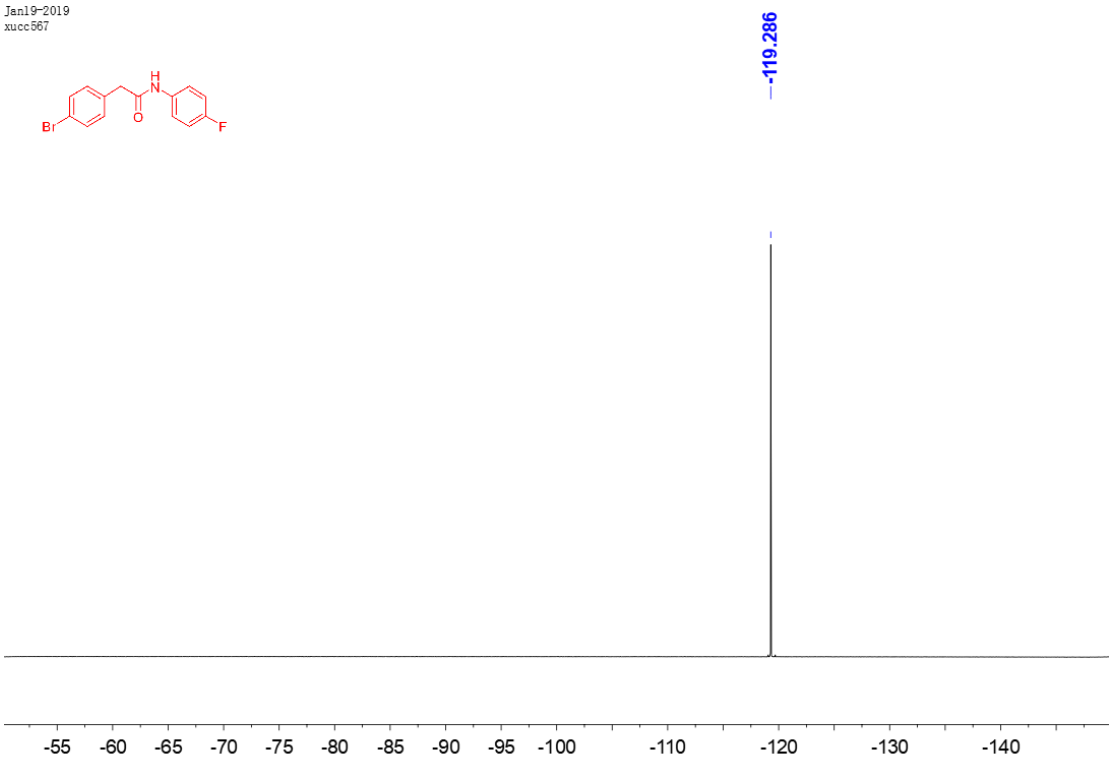
^{1}H and ^{13}C spectra of **3f**.



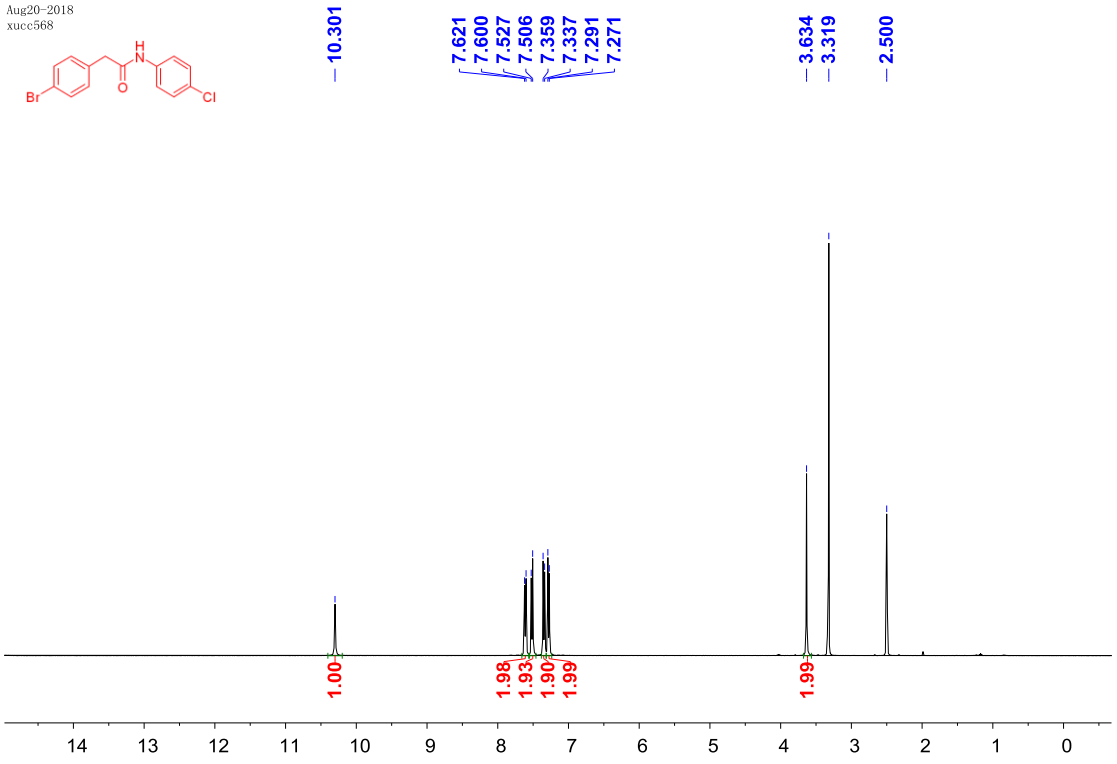
^{1}H, ^{13}C and ^{19}F spectra of **3g**.

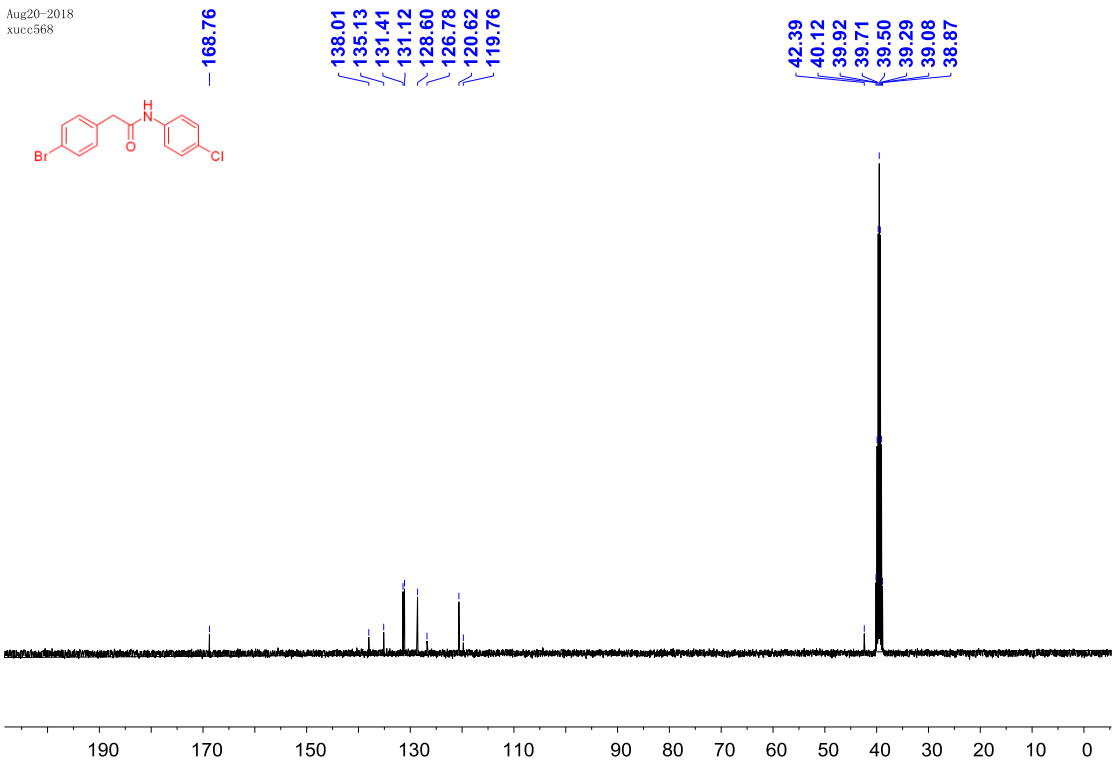




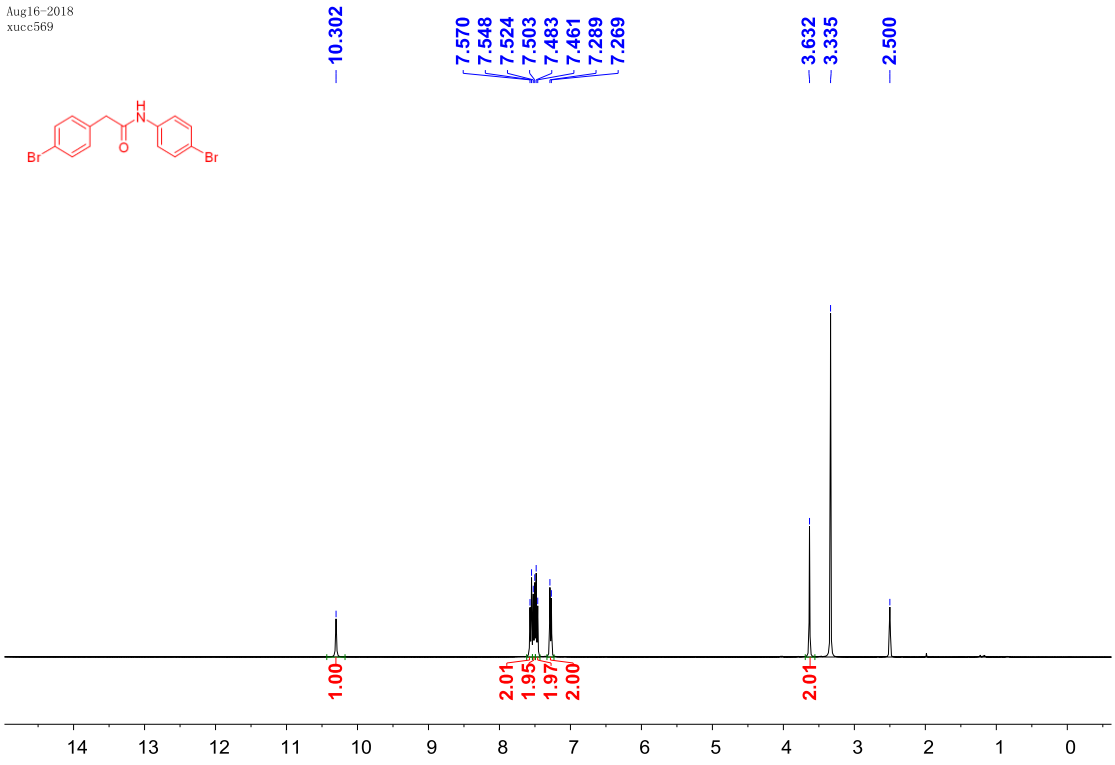


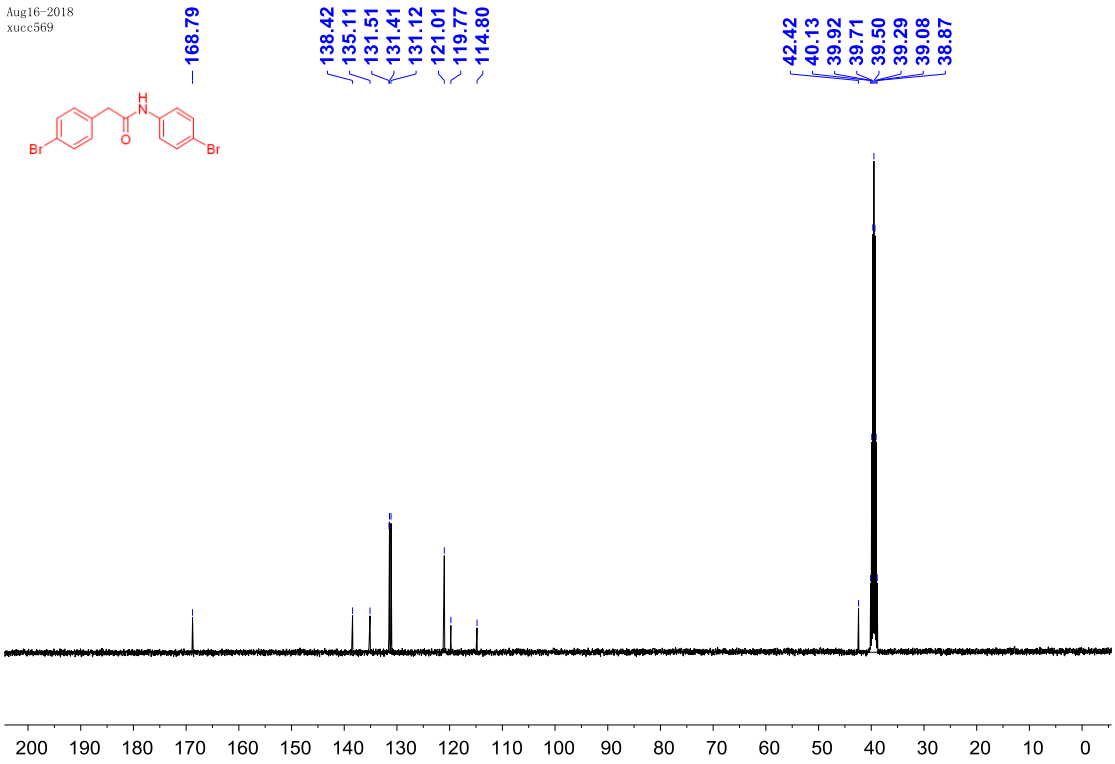
^{1}H and ^{13}C spectra of **3h**.



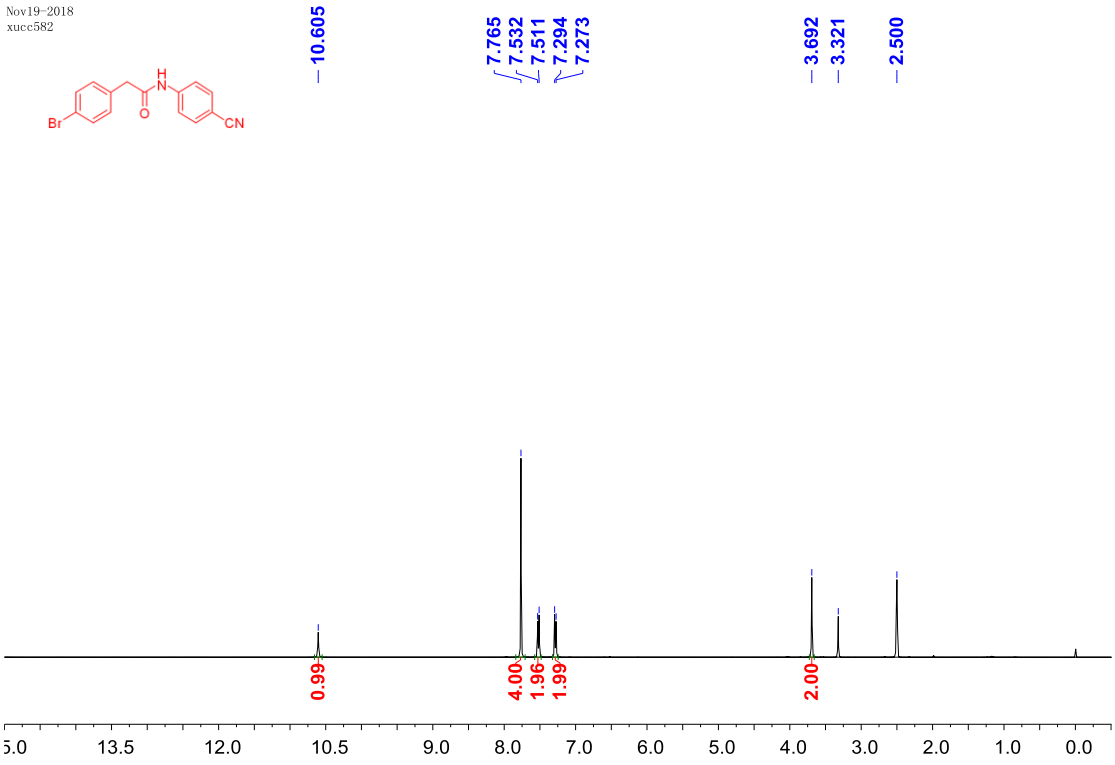


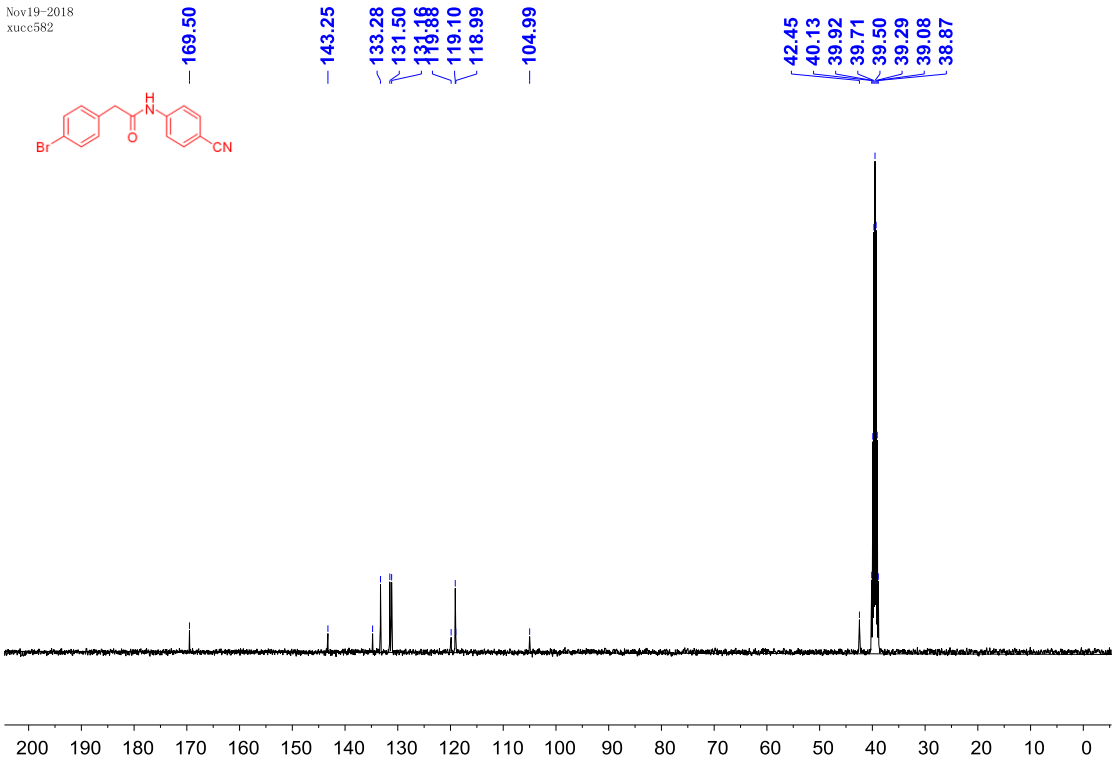
^{1}H and ^{13}C spectra of **3i**.



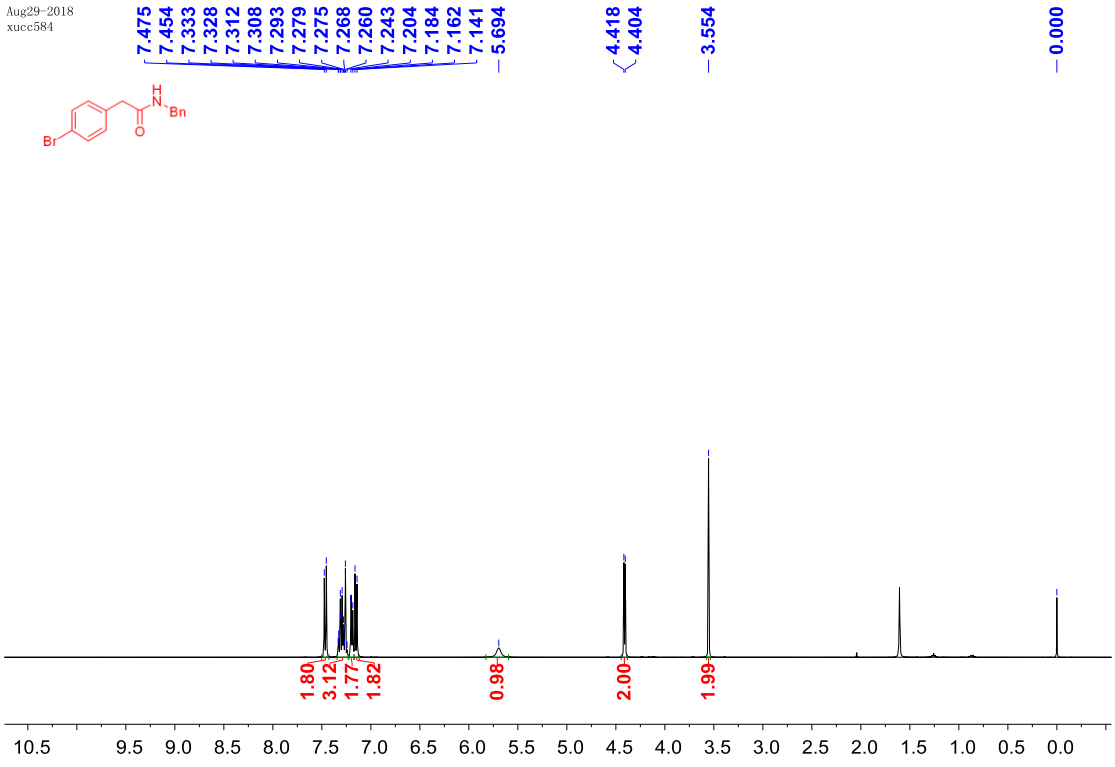


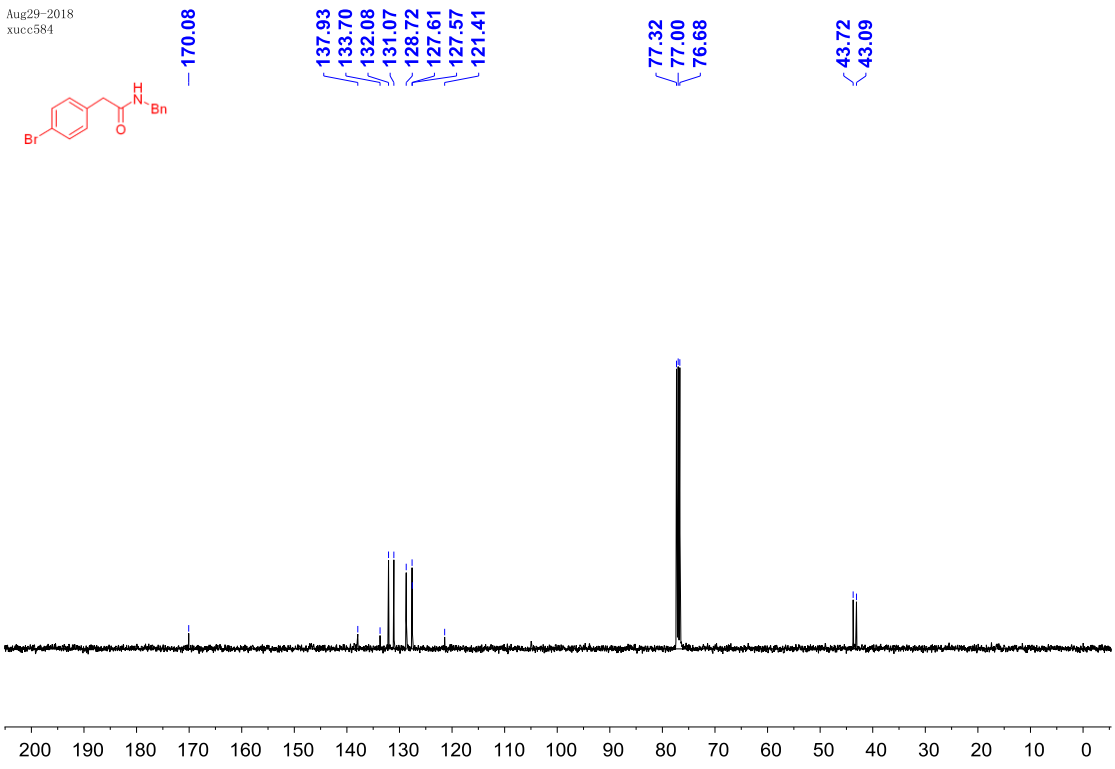
^{1}H and ^{13}C spectra of **3j**.



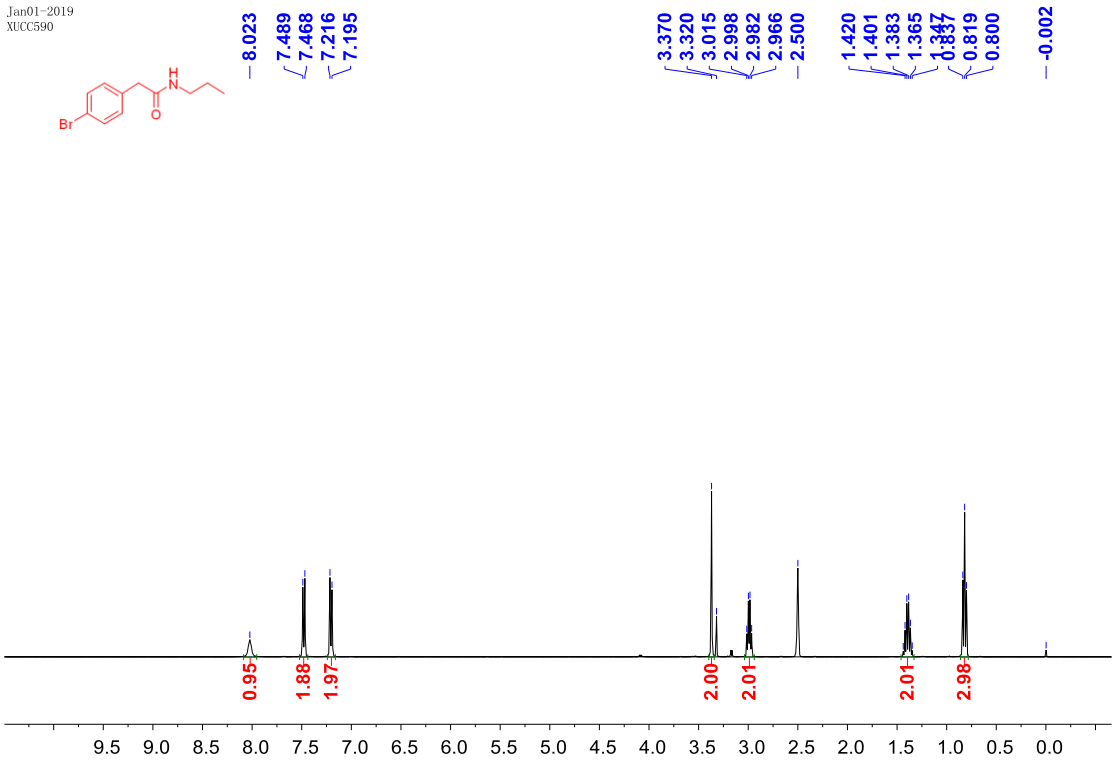


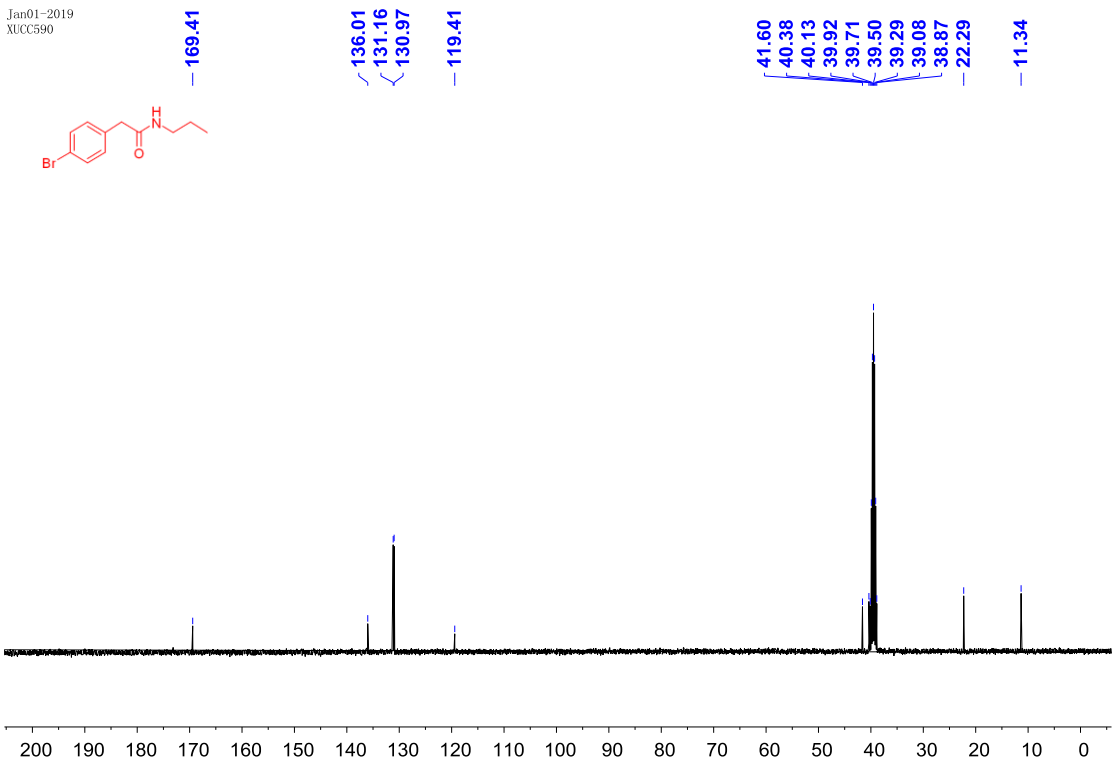
^{1}H and ^{13}C spectra of **3k**.



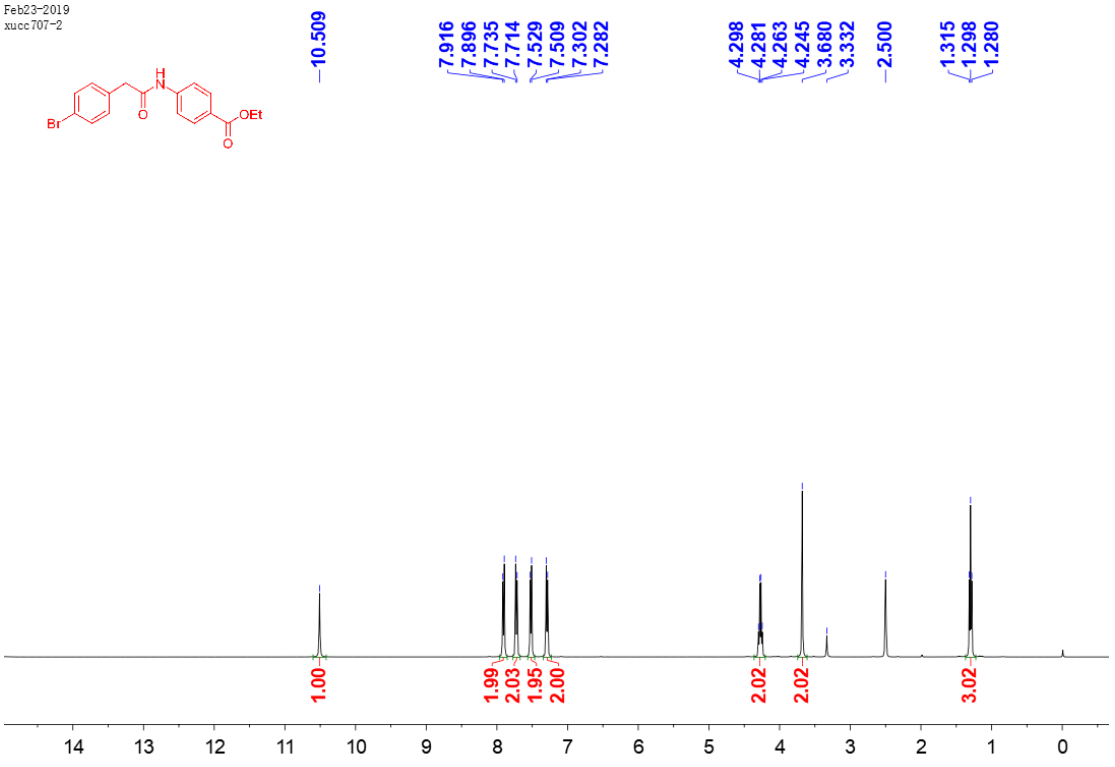


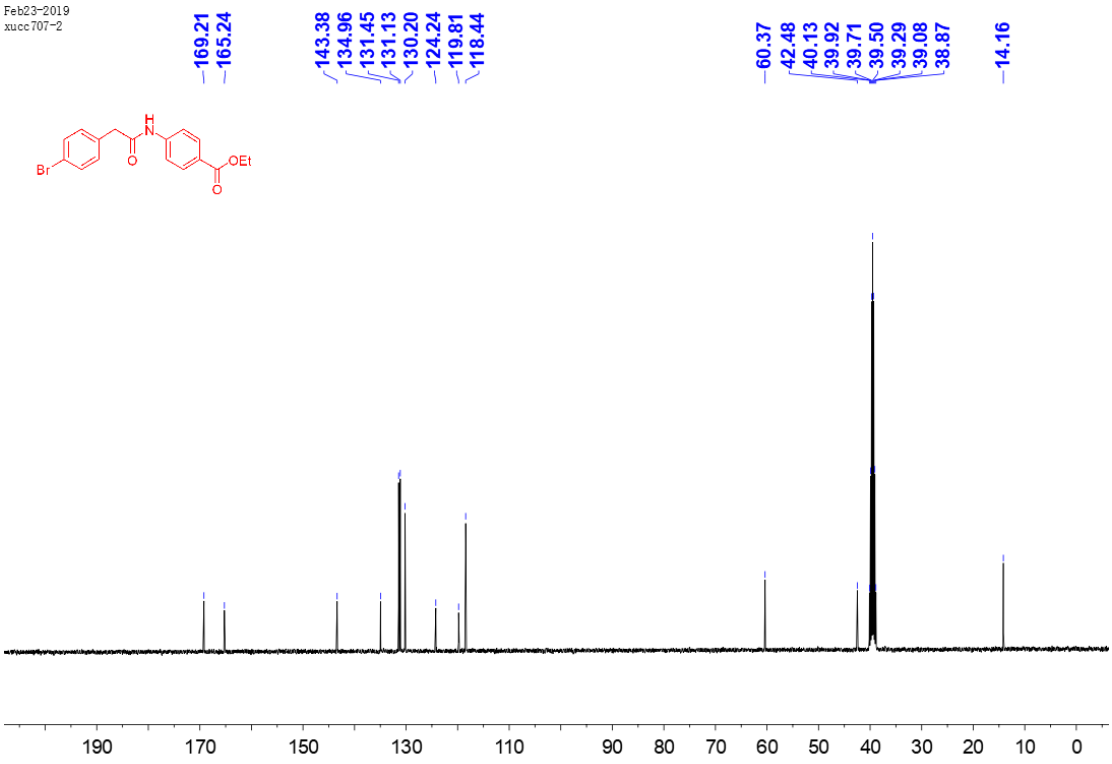
^{1}H and ^{13}C spectra of **3l**.



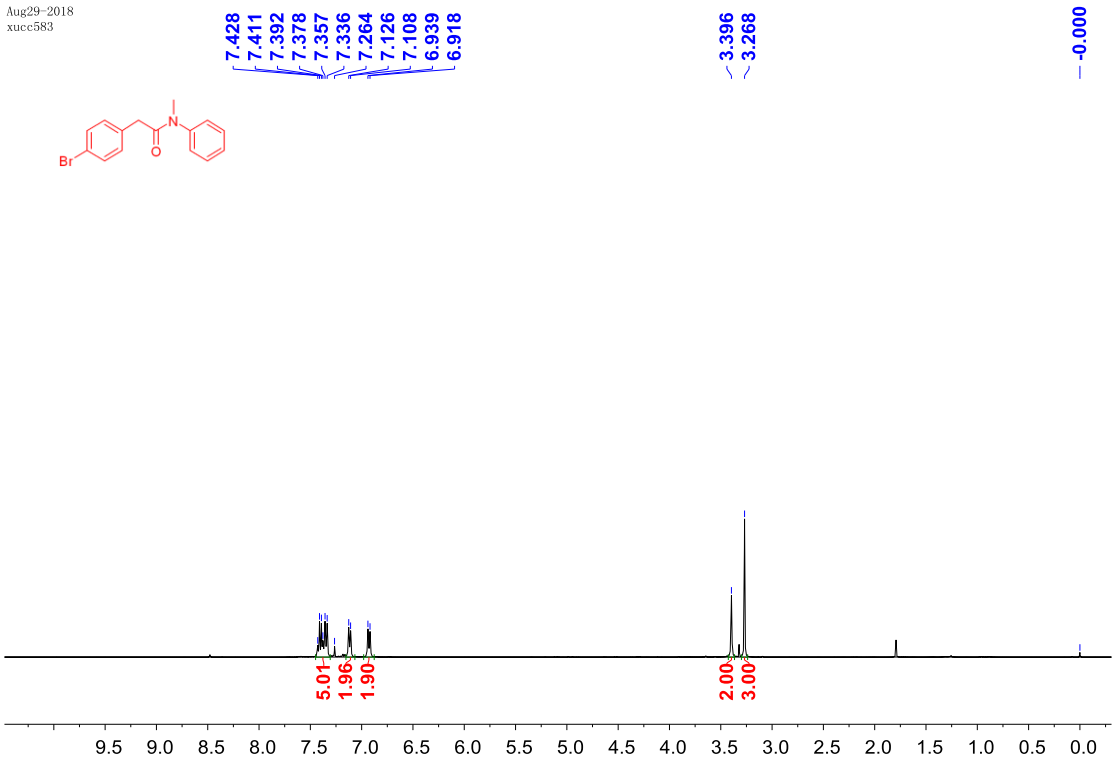


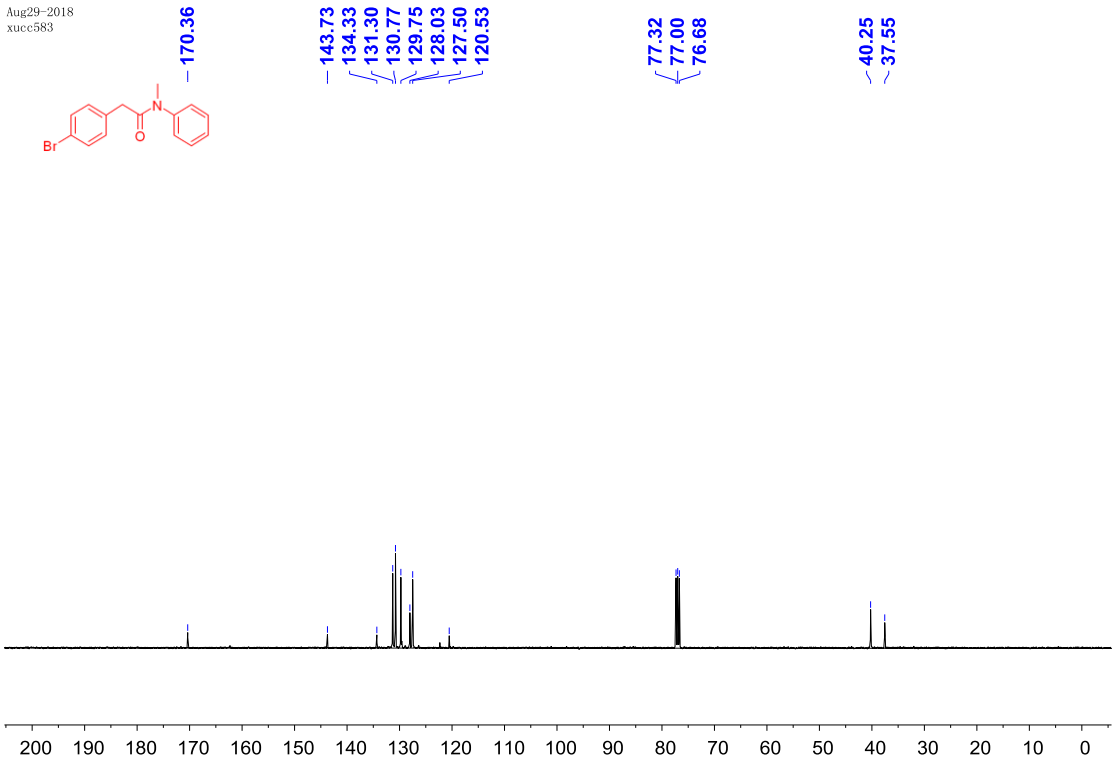
^{1}H and ^{13}C spectra of **3m**.



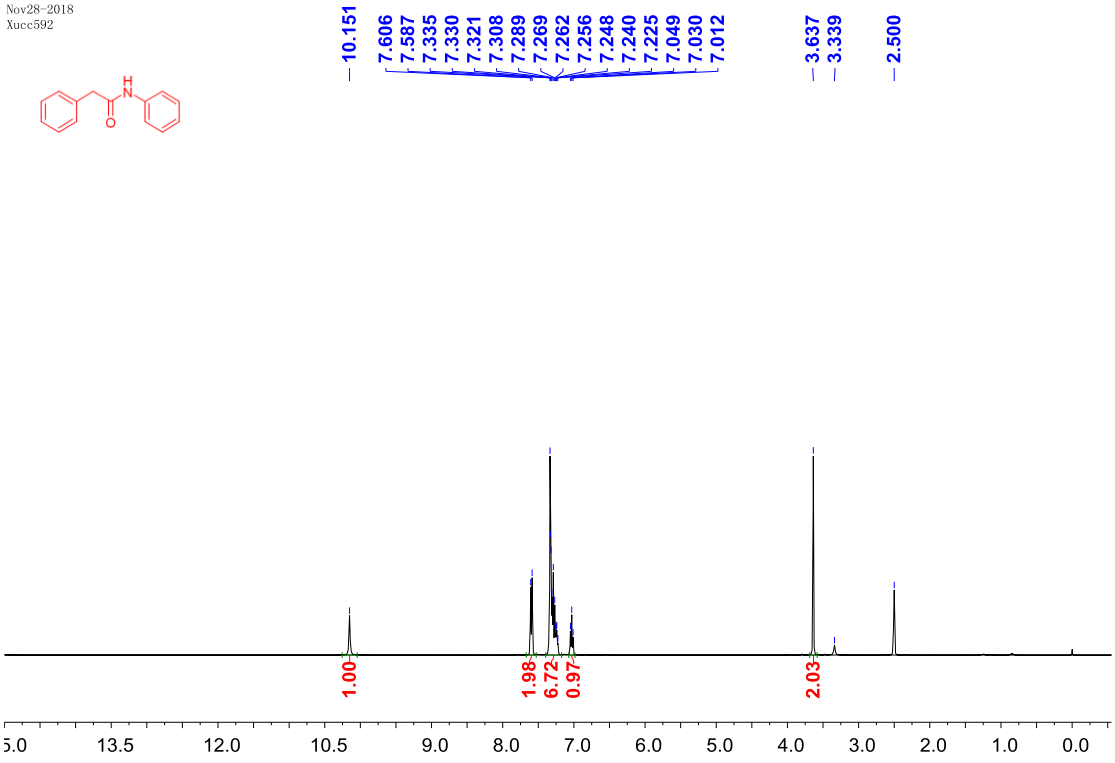


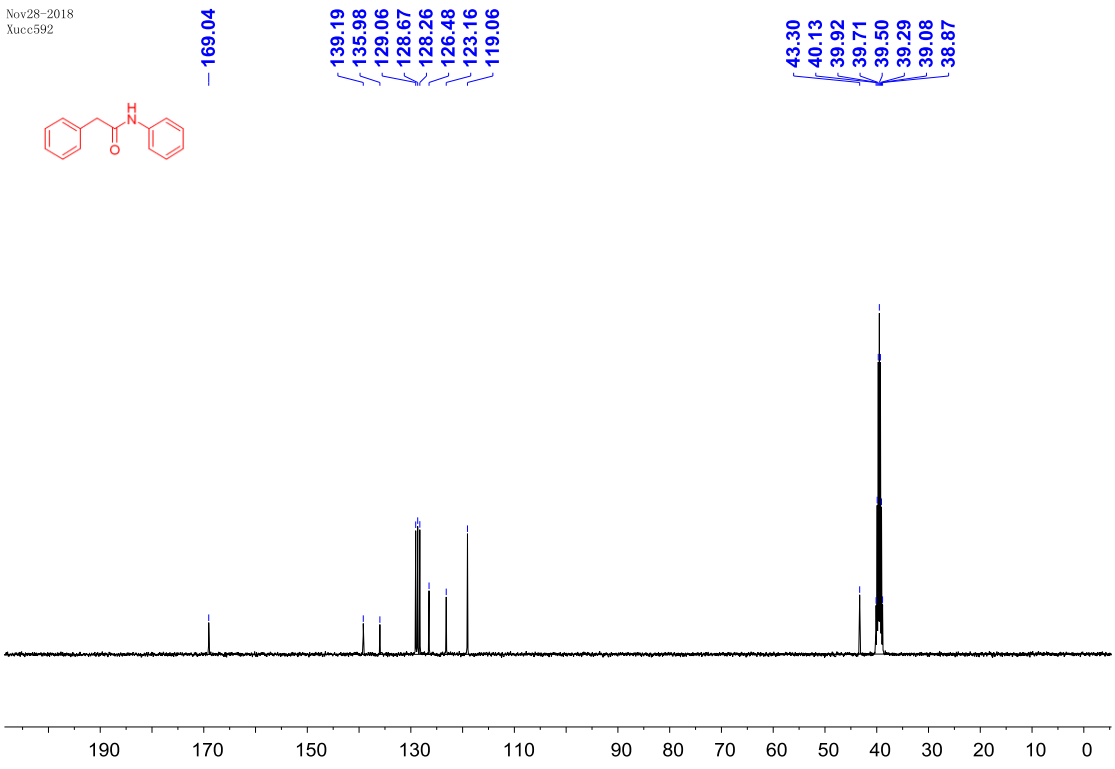
^{1}H and ^{13}C spectra of **3n**.



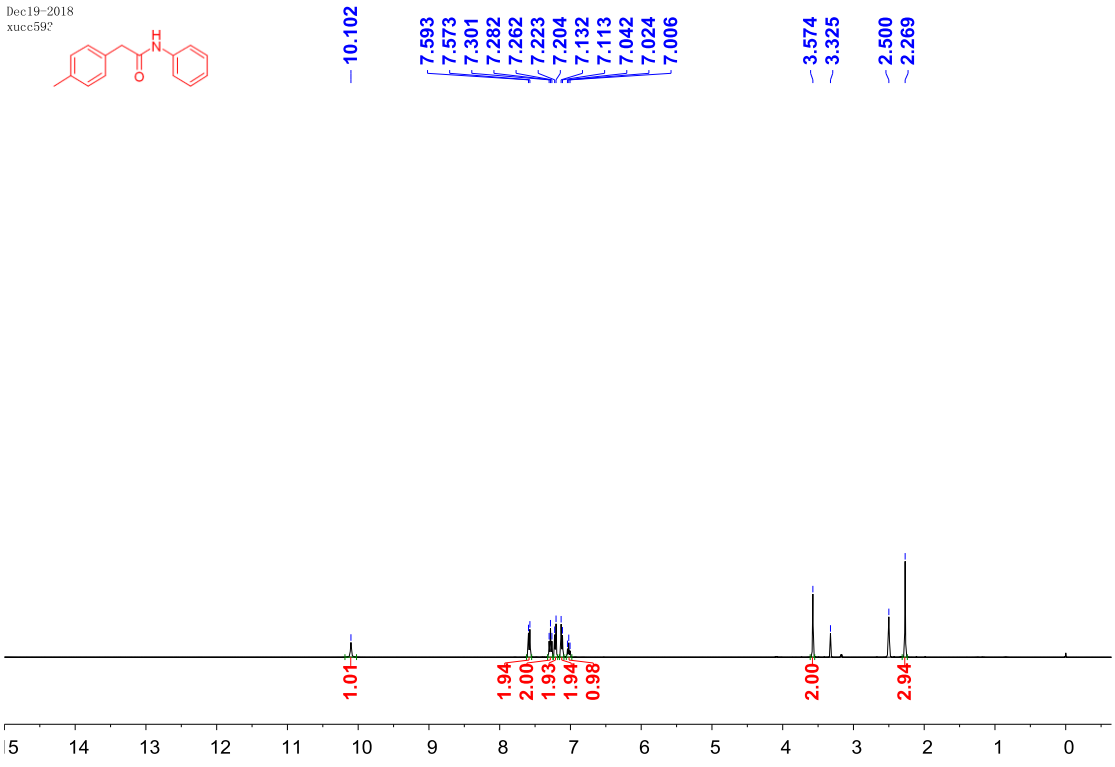


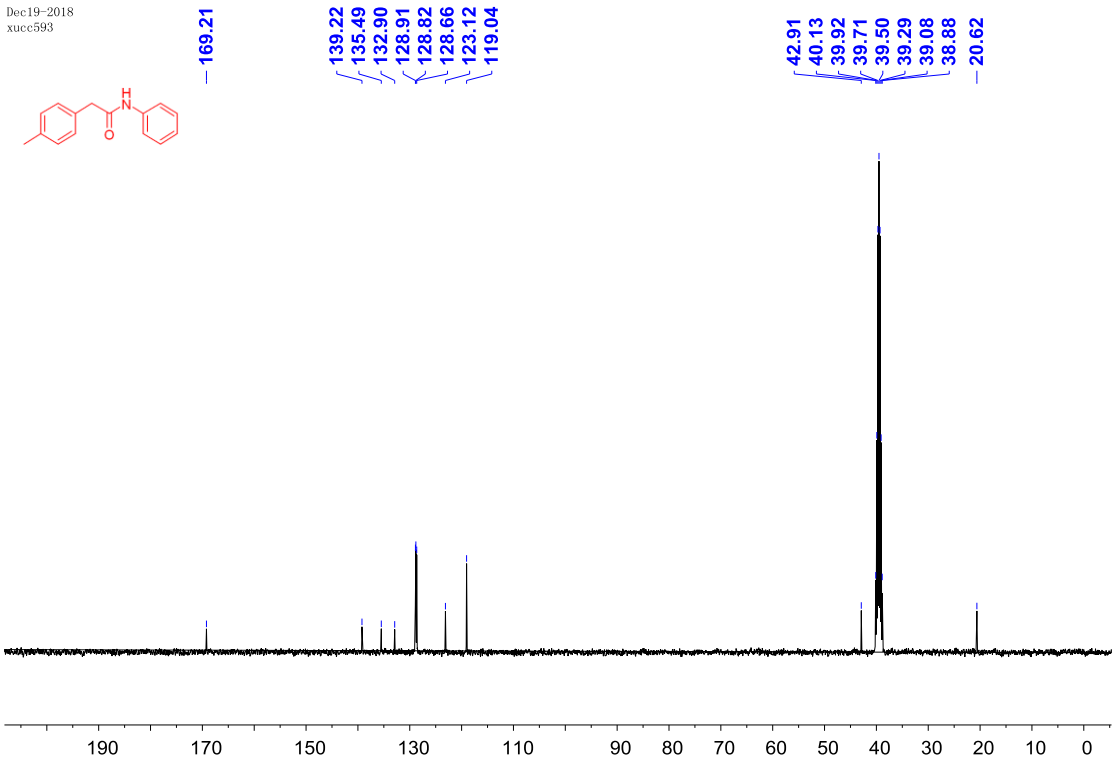
^{1}H and ^{13}C spectra of **3o**.



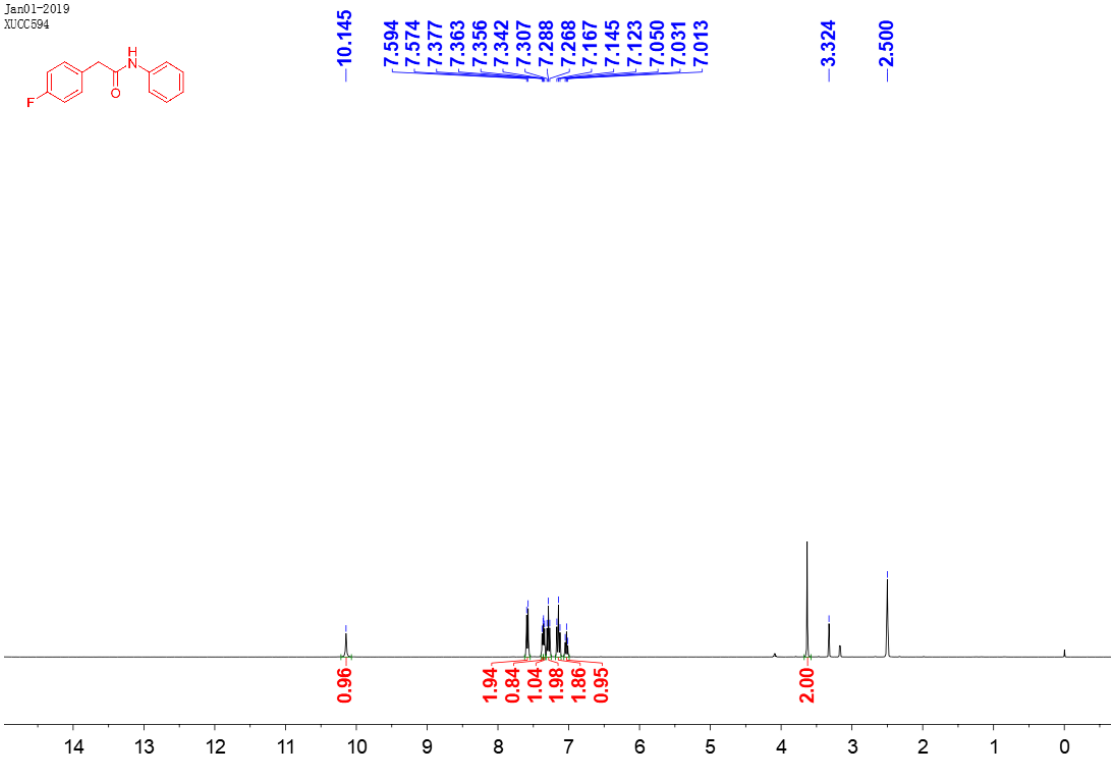


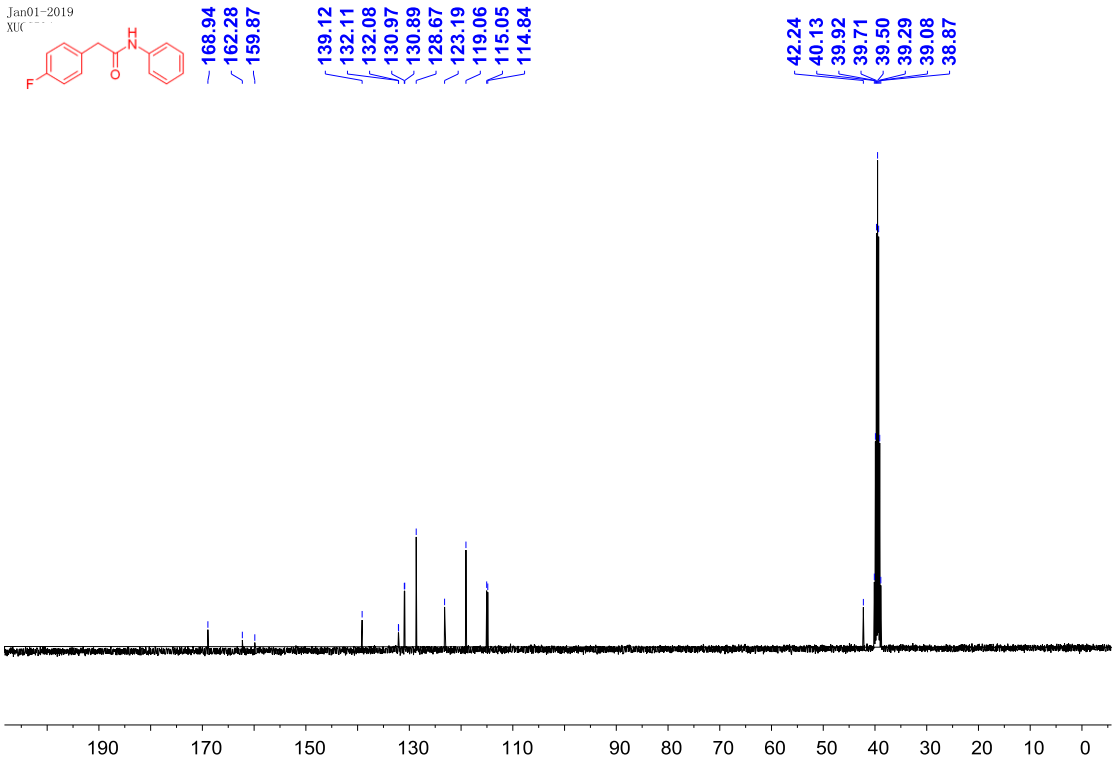
^{1}H and ^{13}C spectra of **3p**.





^{1}H, ^{13}C and ^{19}F spectra of **3q**.

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114.84
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39.92
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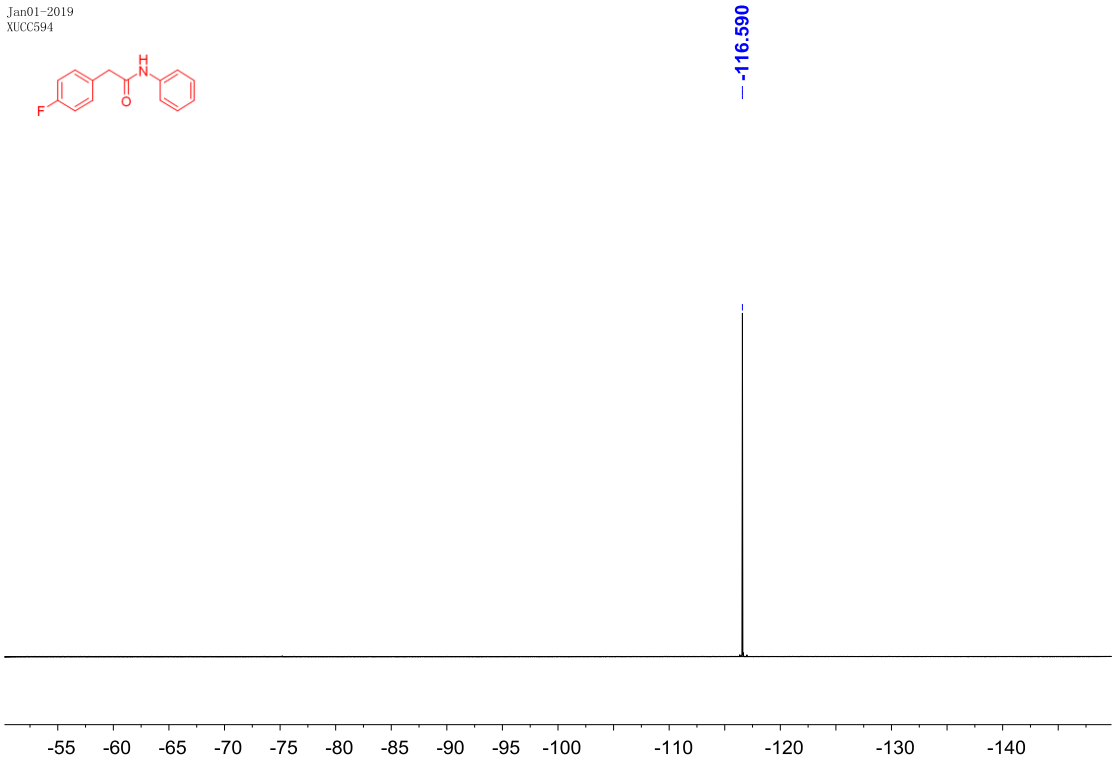
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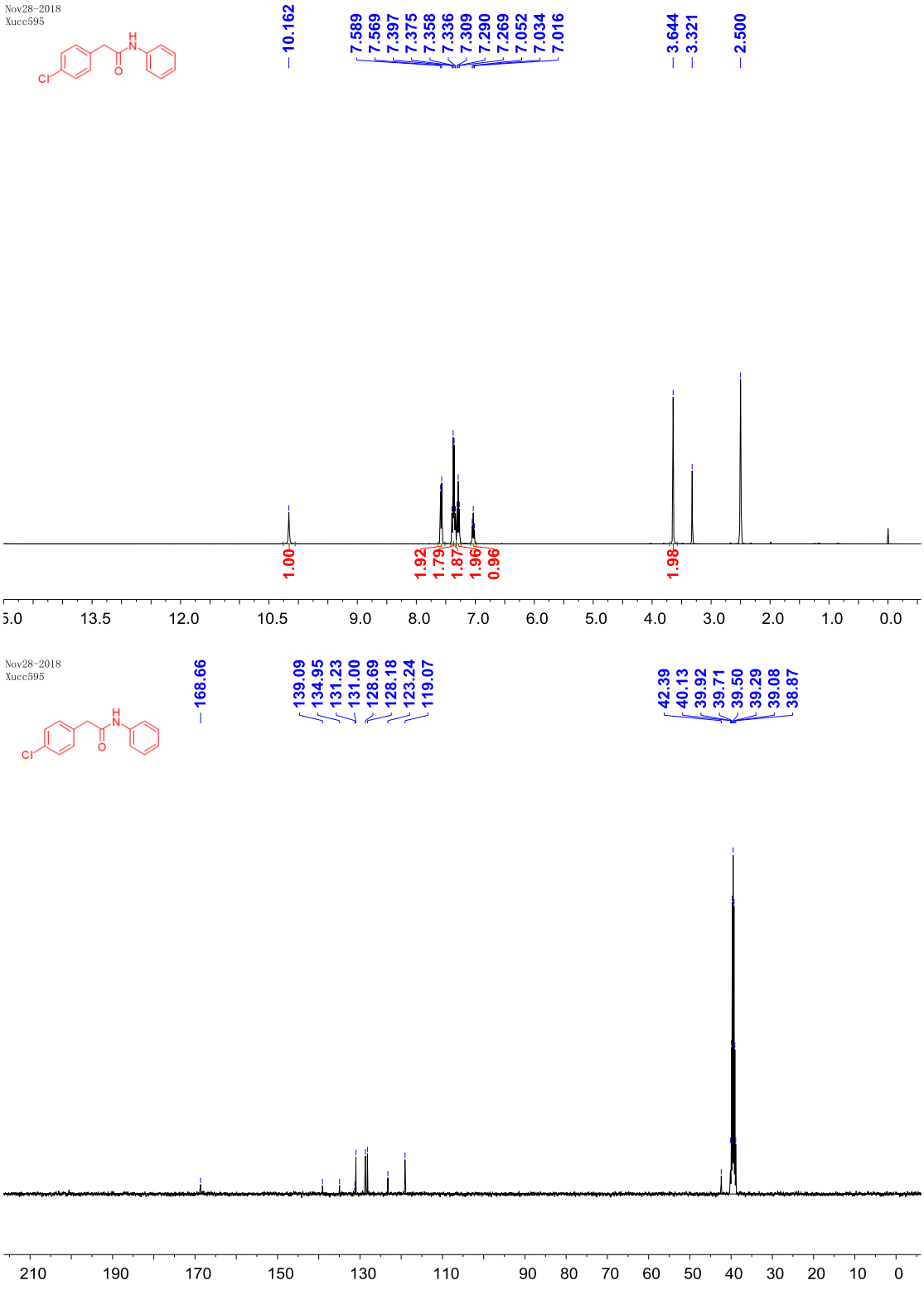
^{1}H and ^{13}C spectra of **3r**.



^{1}H and ^{13}C spectra of **3s**.

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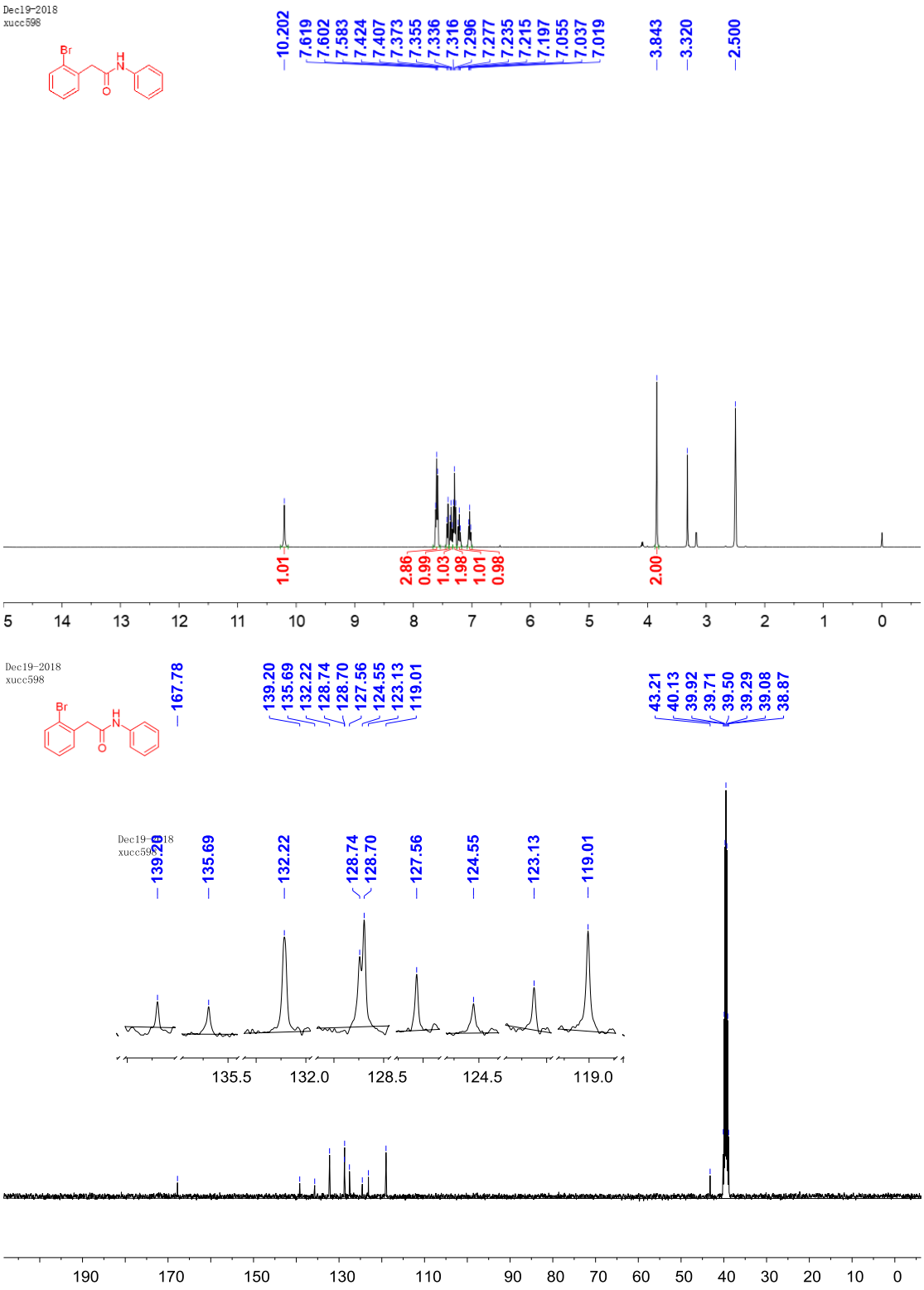
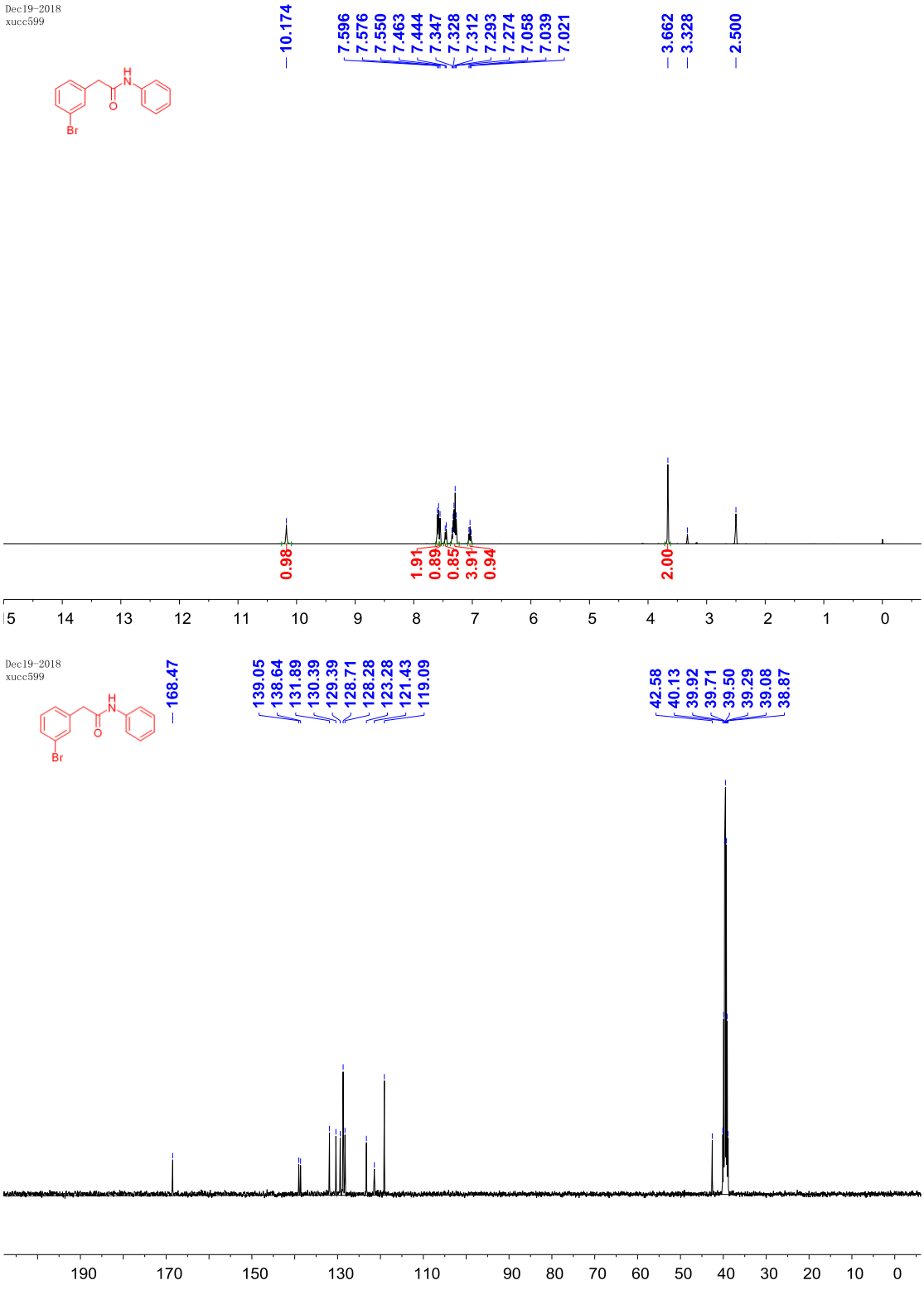
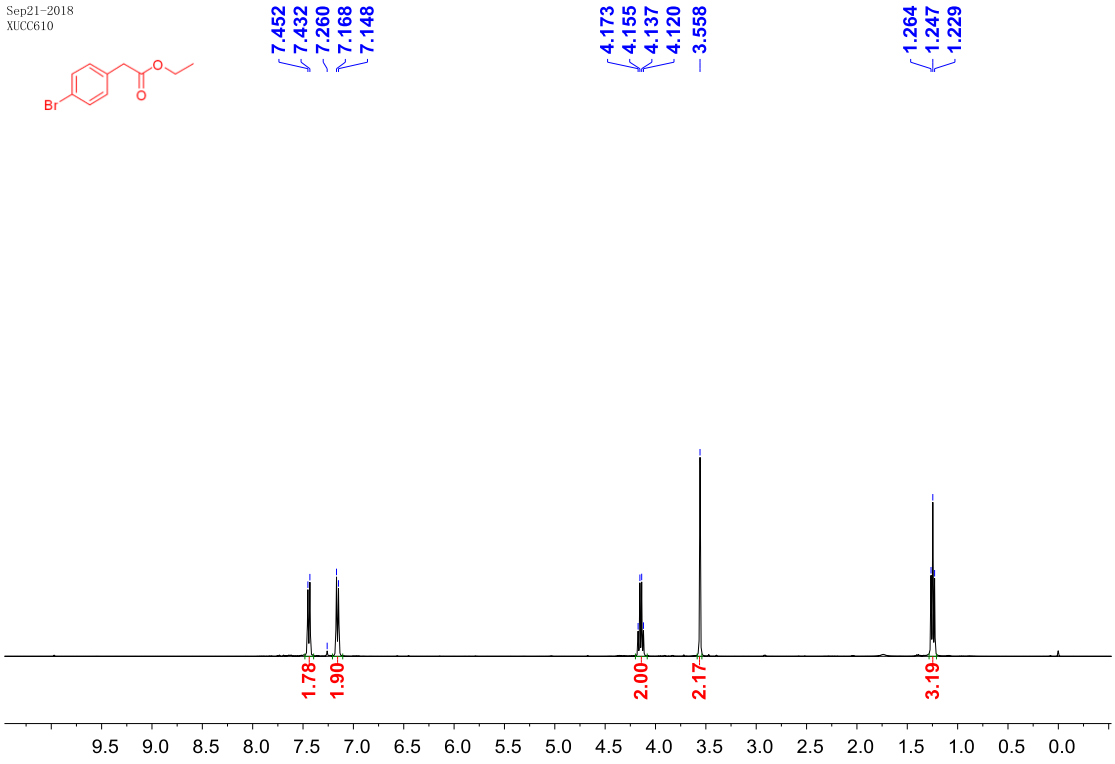
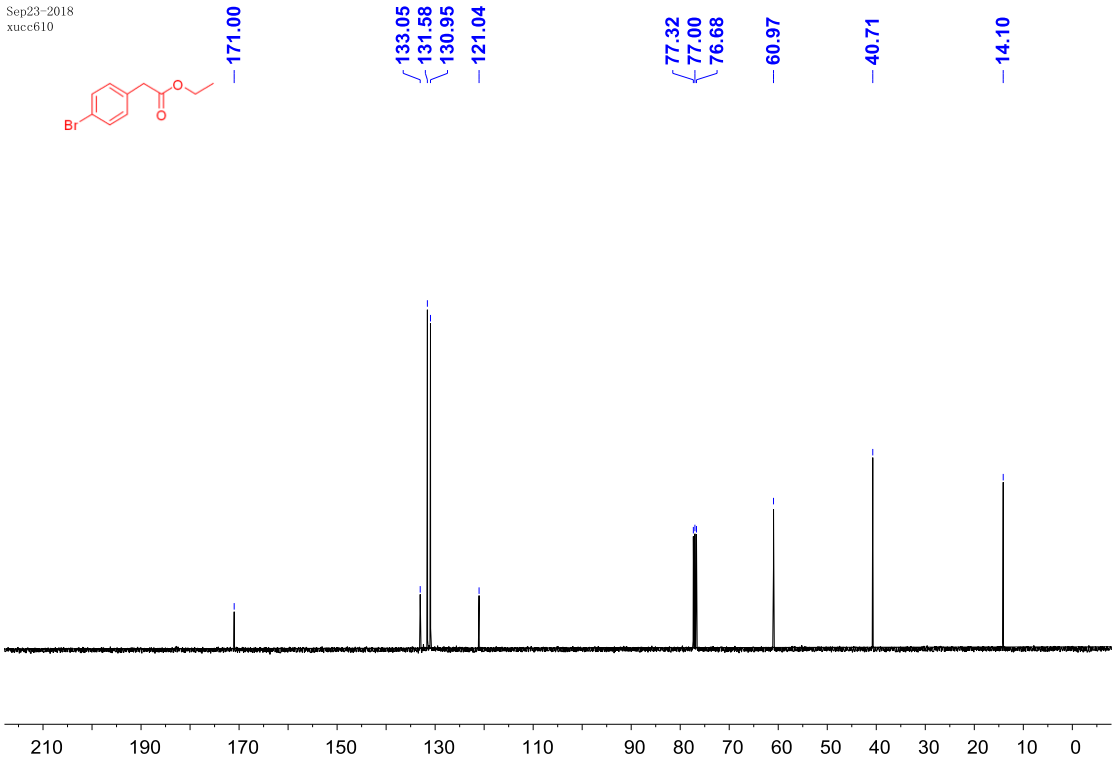


^{1}H and ^{13}C spectra of **3t**.

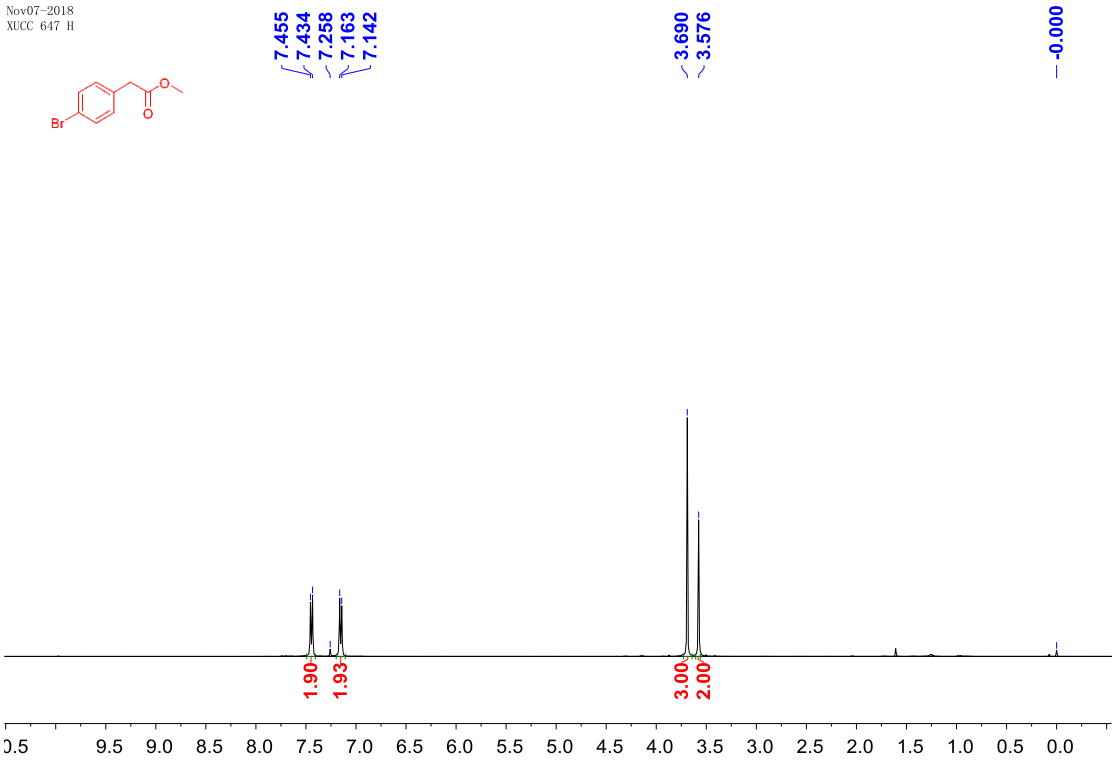


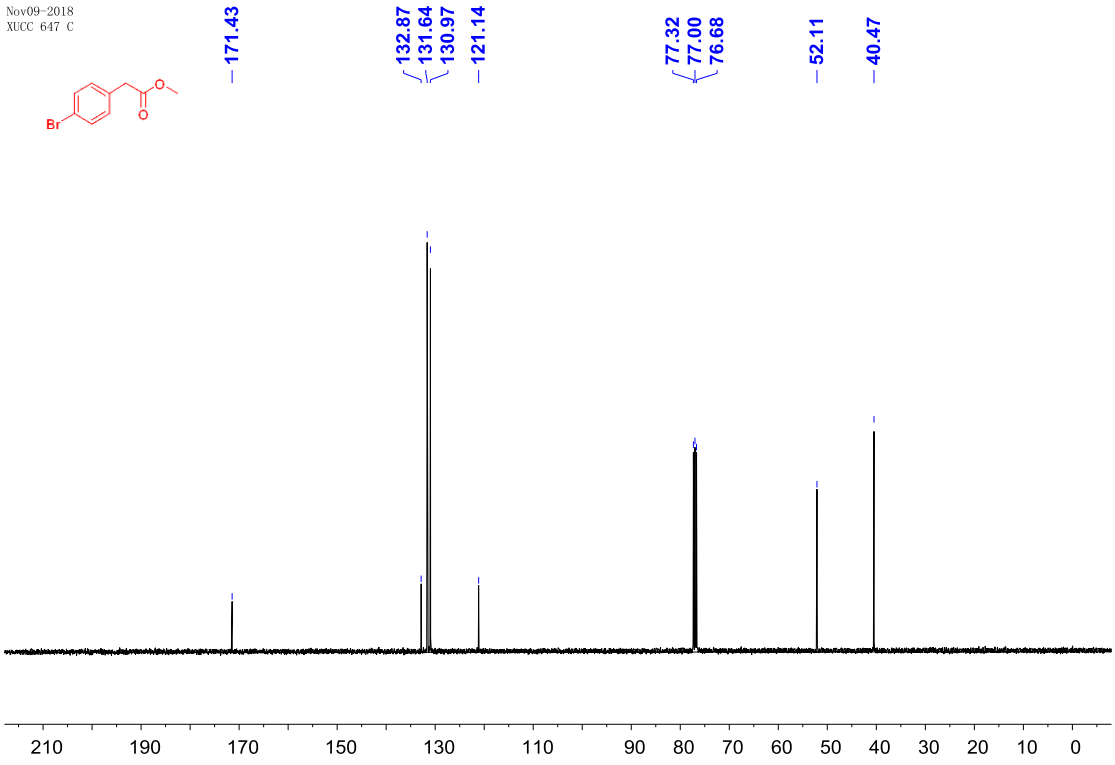
^{1}H and ^{13}C spectra of **5a**.



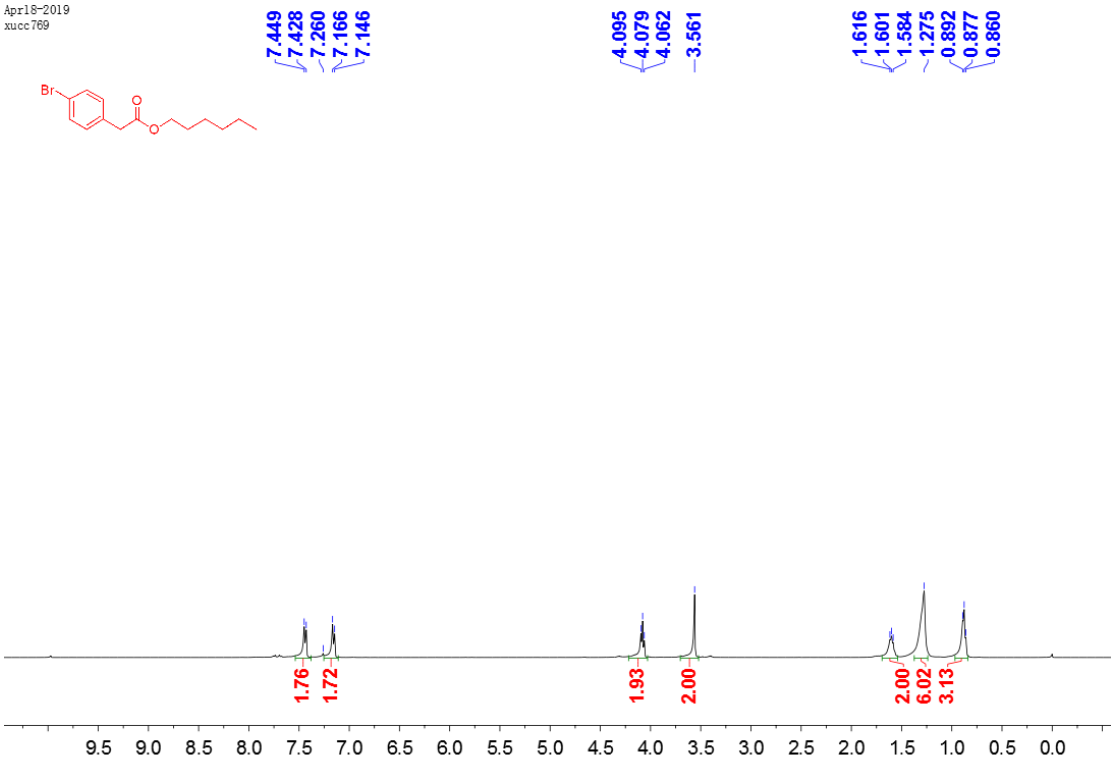


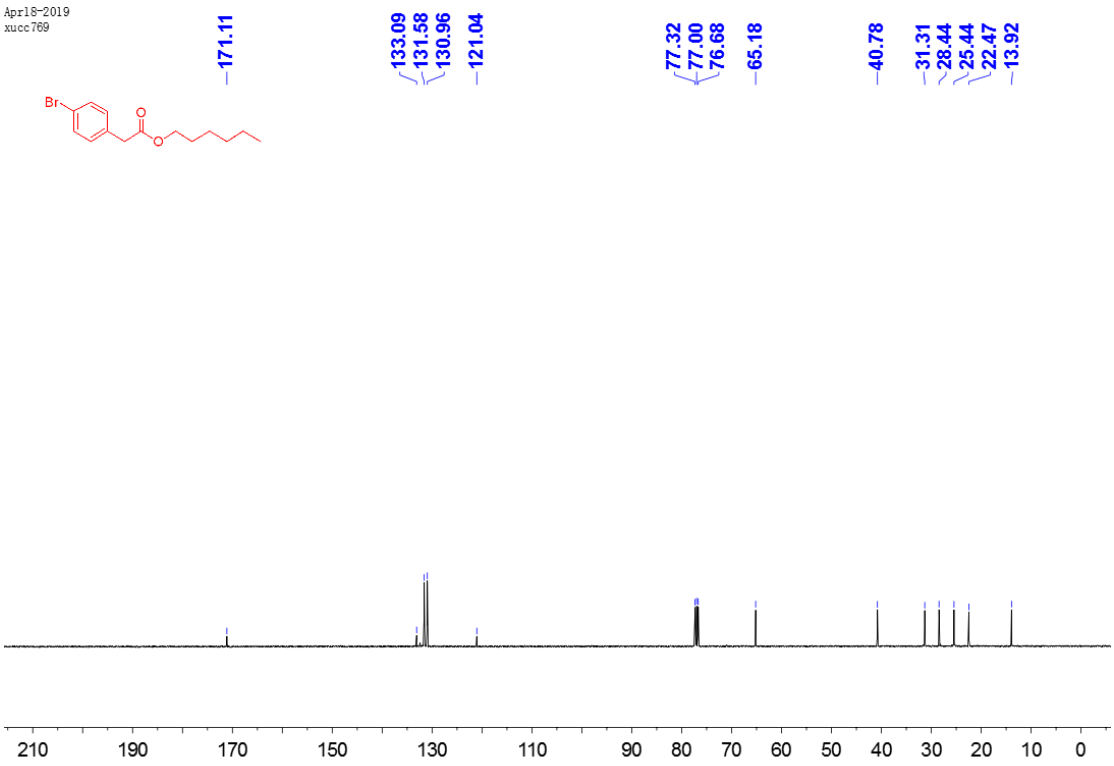
^{1}H and ^{13}C spectra of **5b**.



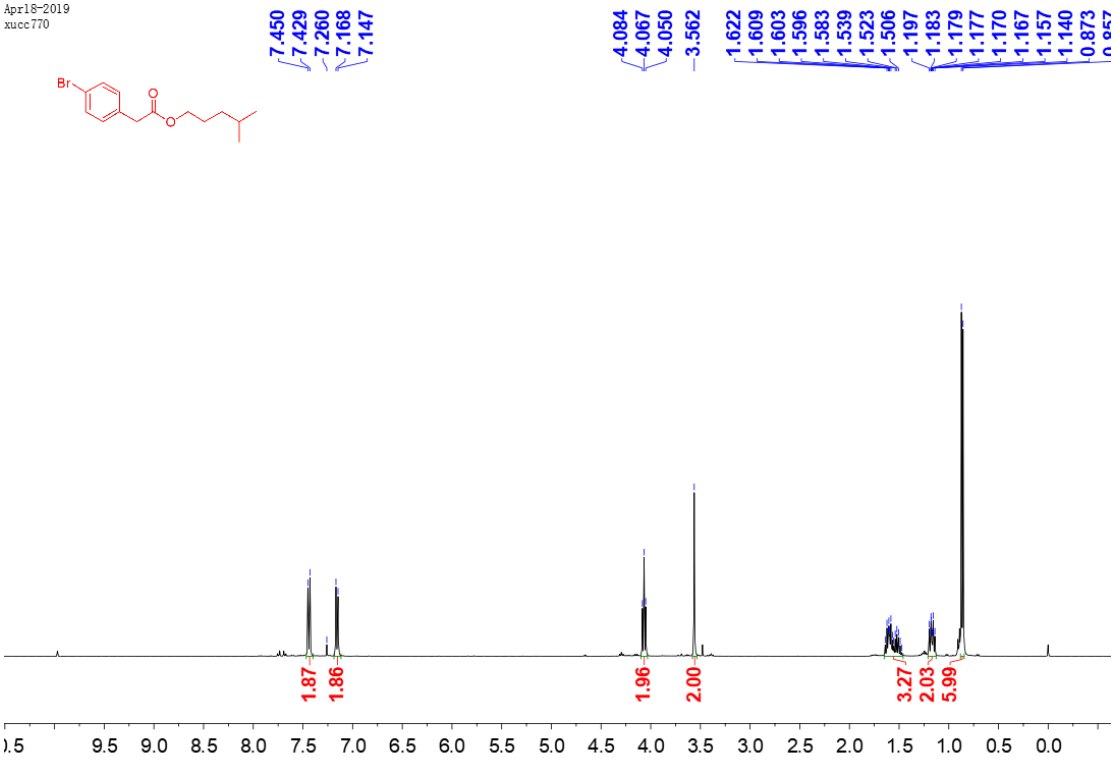


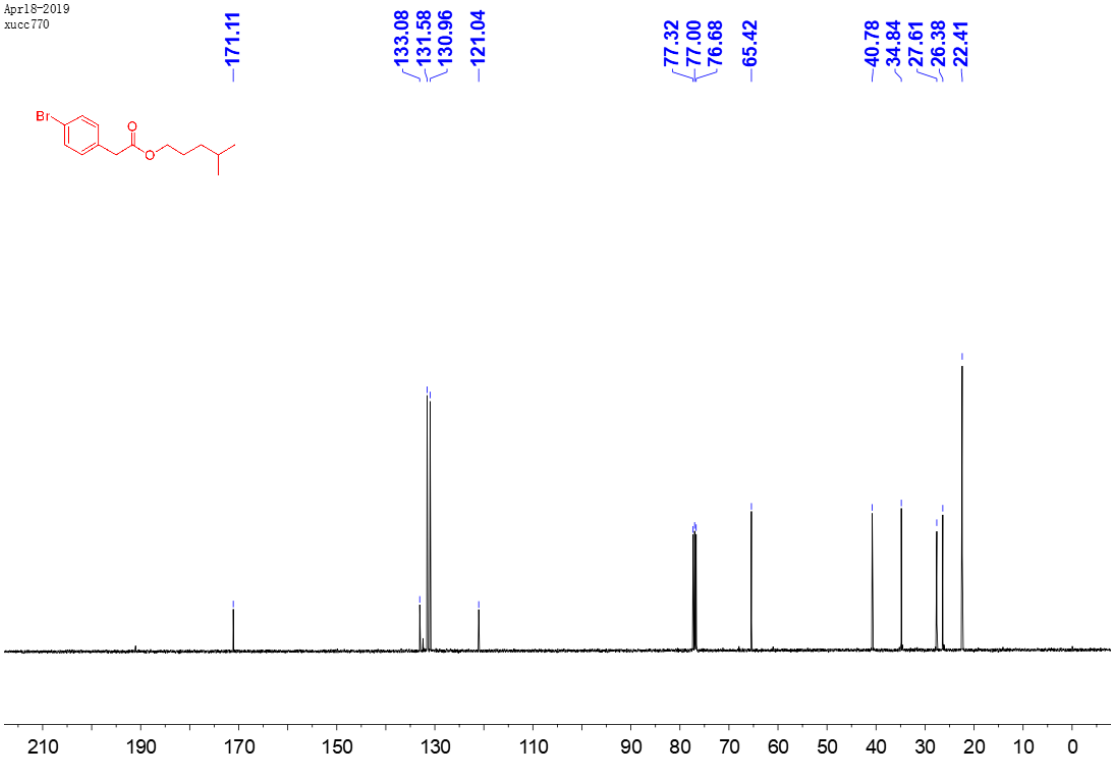
^{1}H and ^{13}C spectra of **5c**.



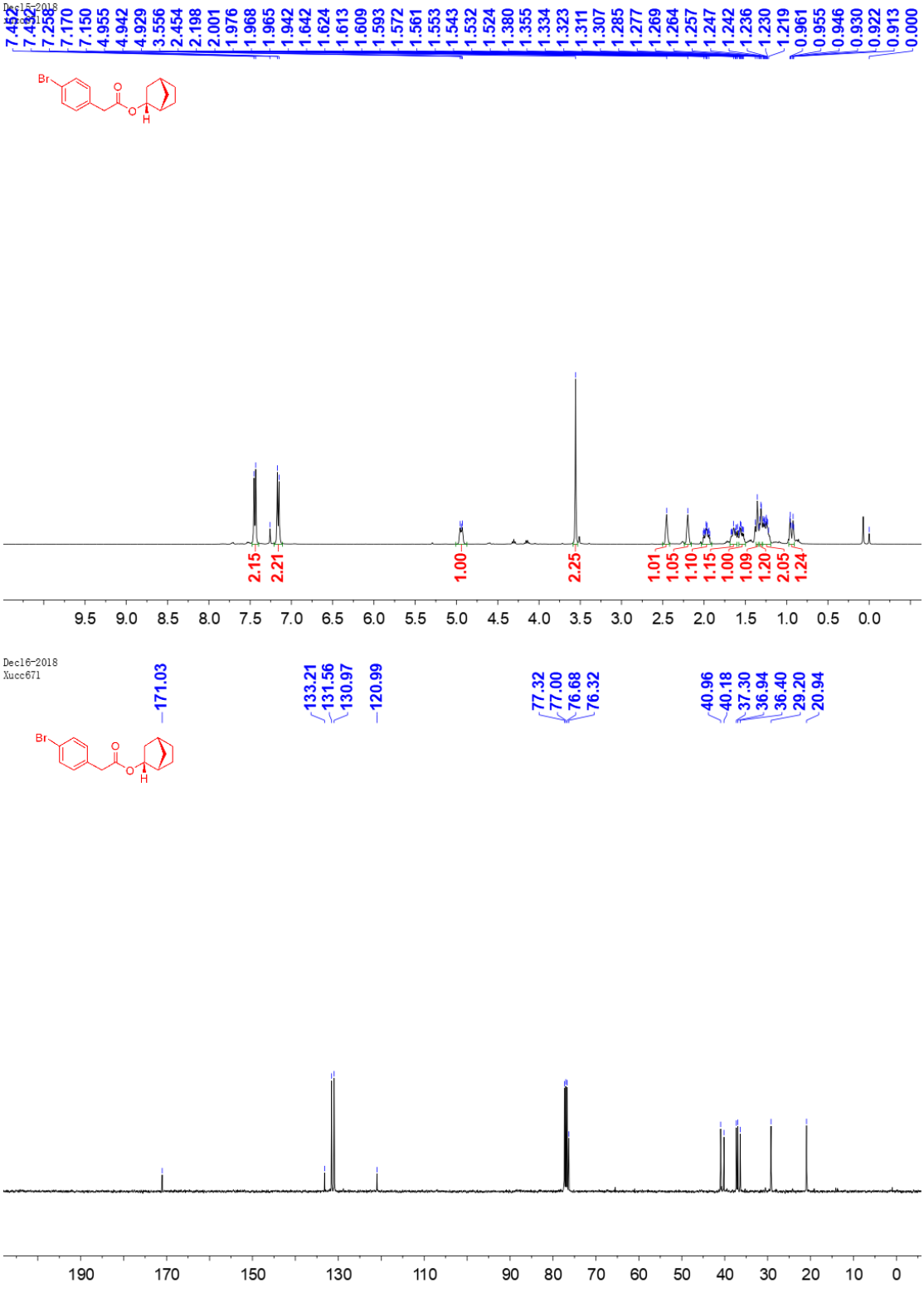


^{1}H and ^{13}C spectra of **5d**.

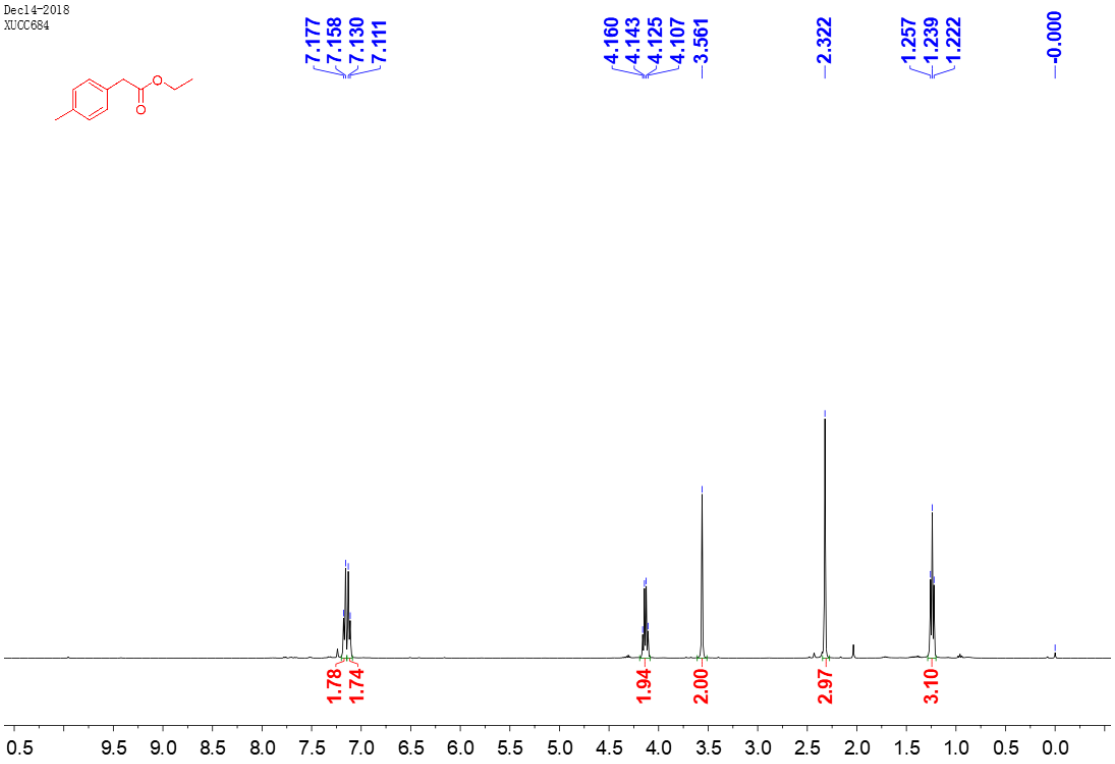


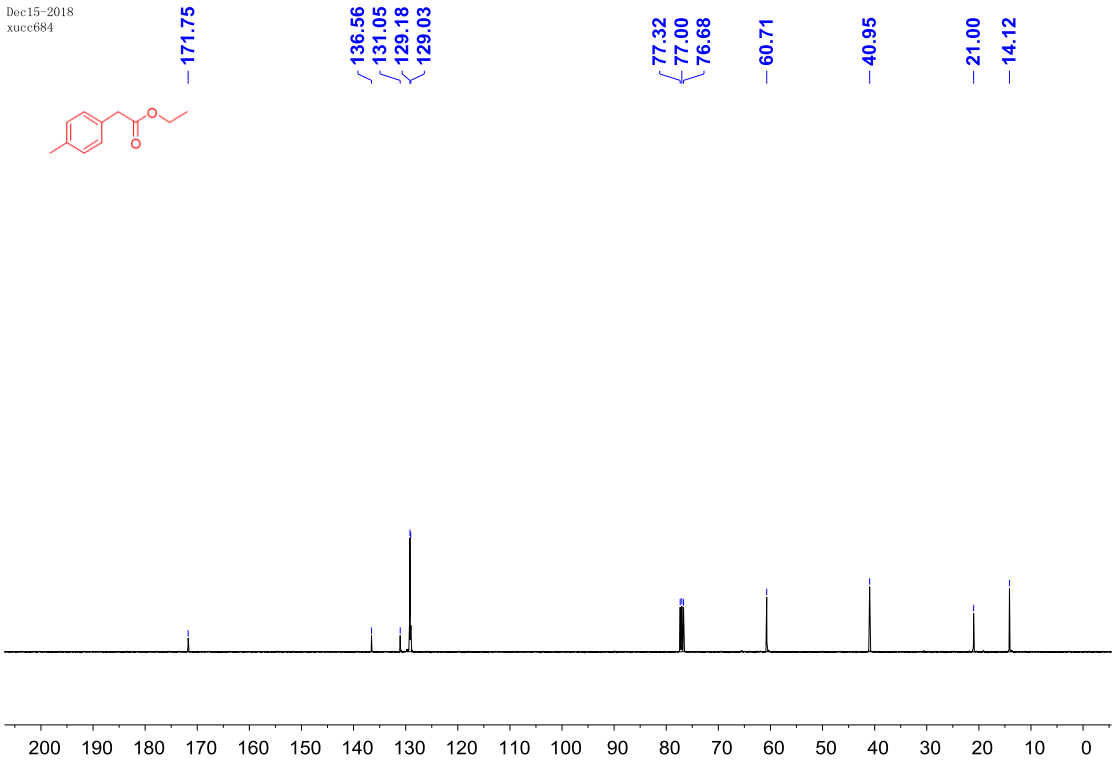


^{1}H and ^{13}C spectra of **5e**.

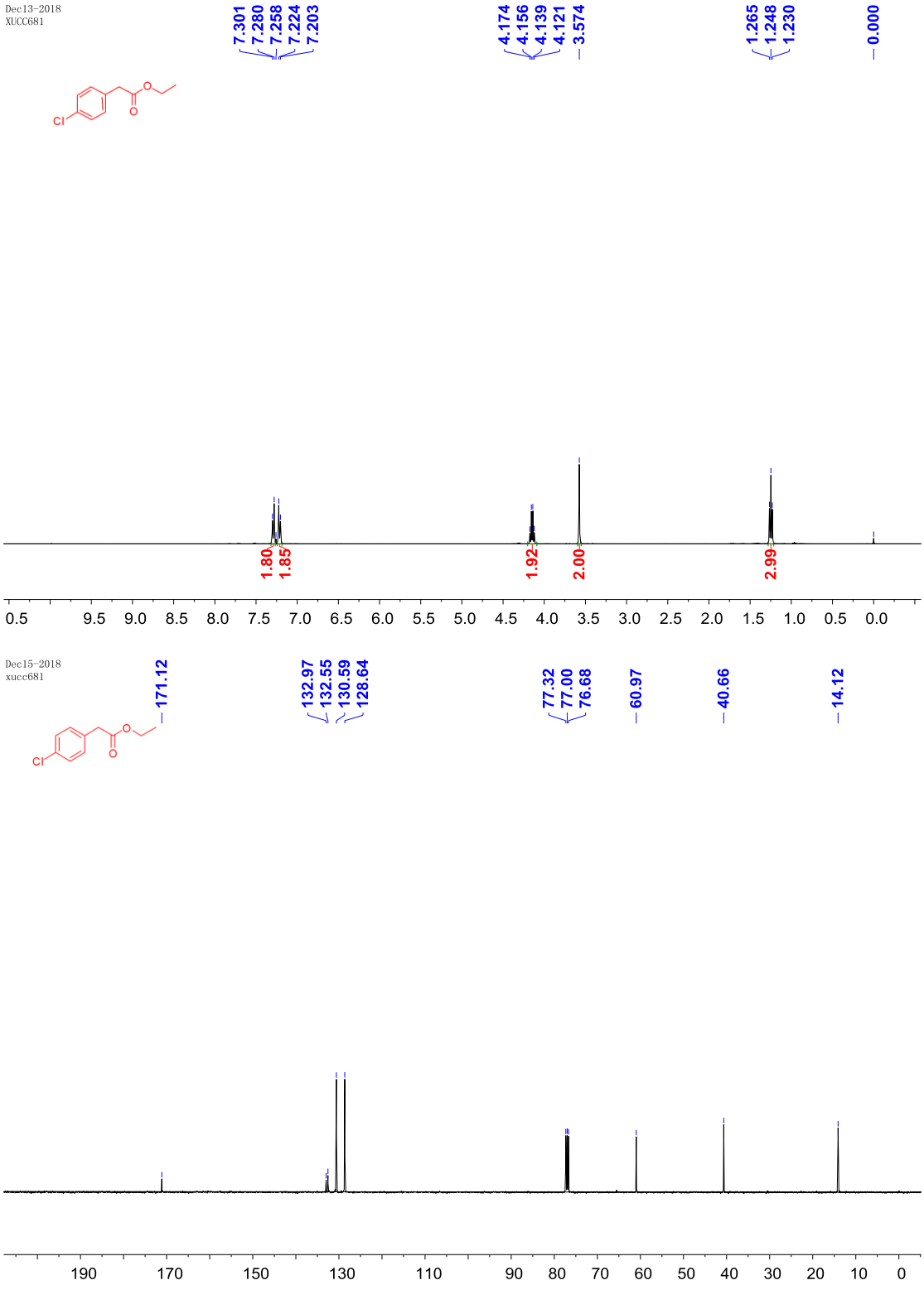


^{1}H and ^{13}C spectra of **5f**.

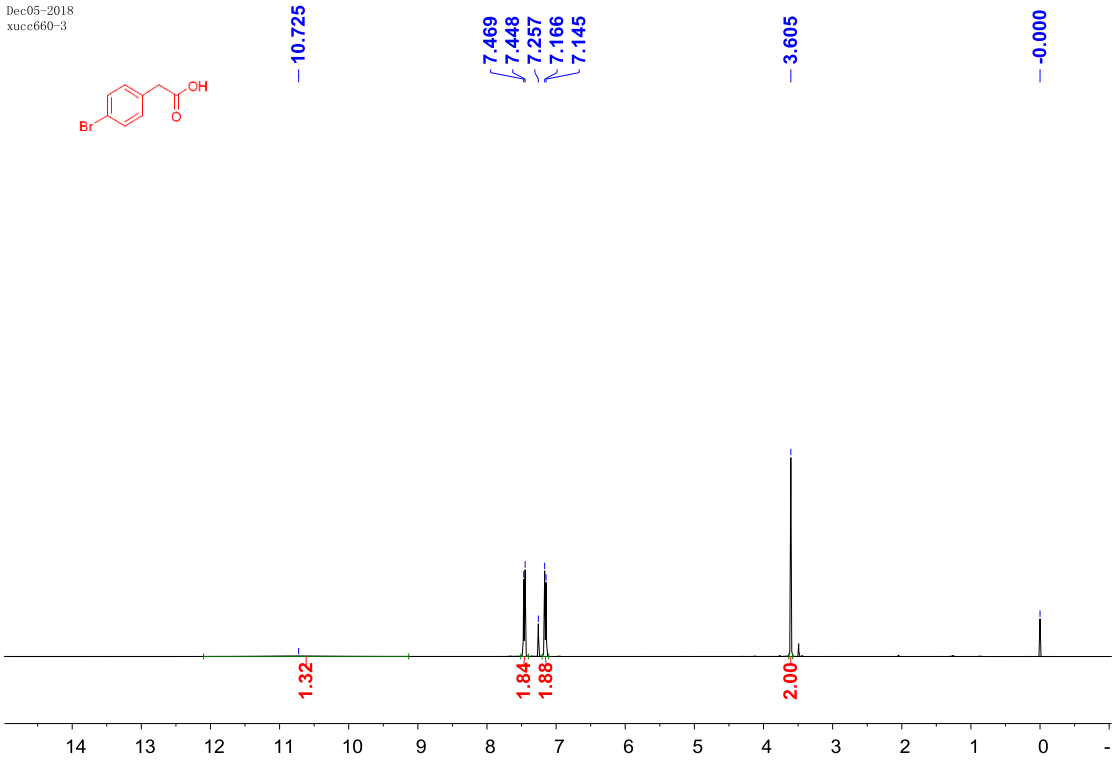


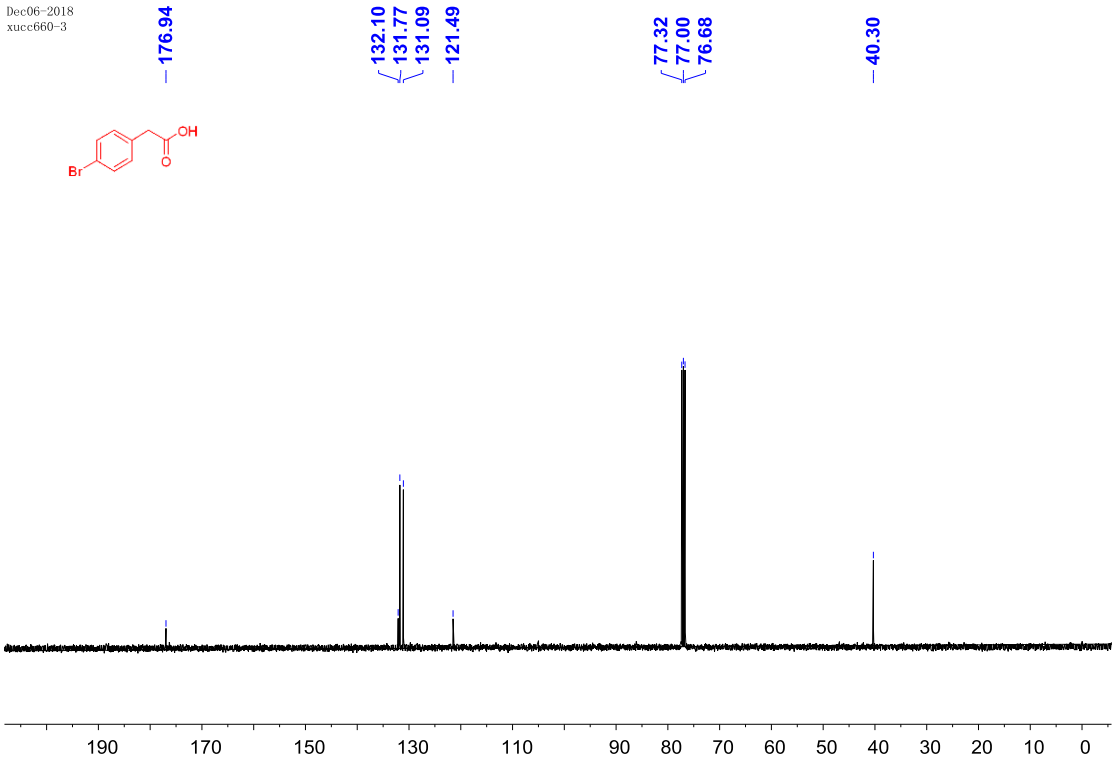


^{1}H and ^{13}C spectra of **5g**.

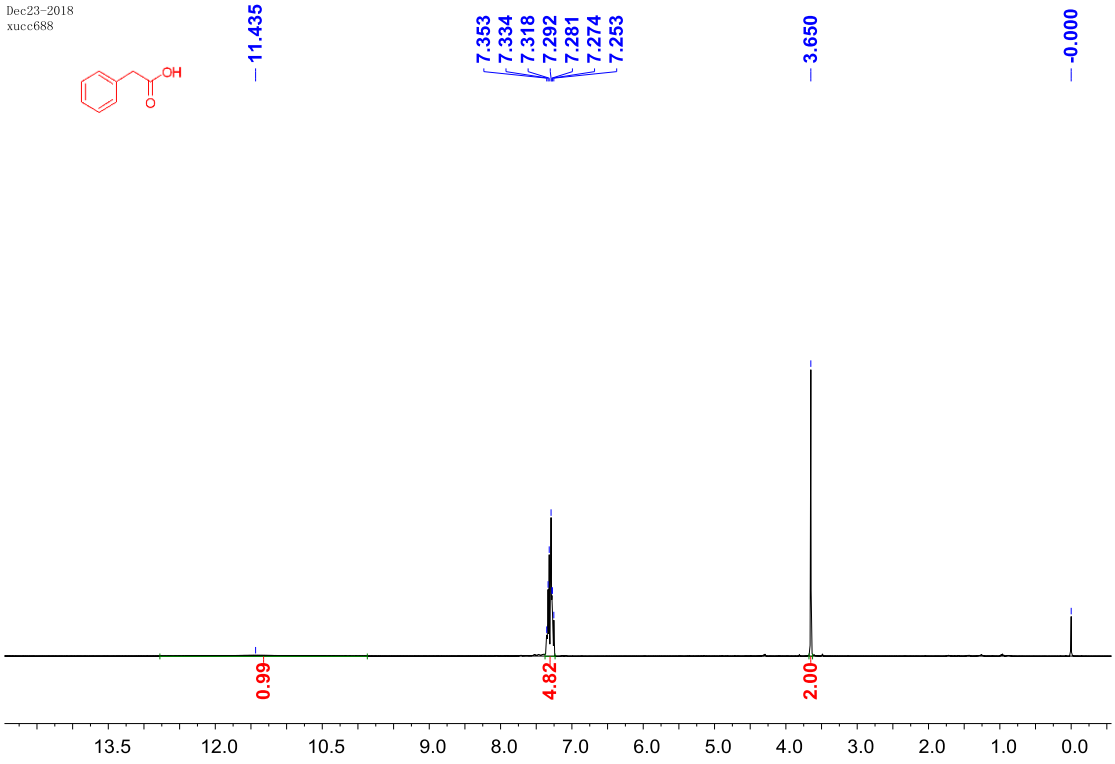


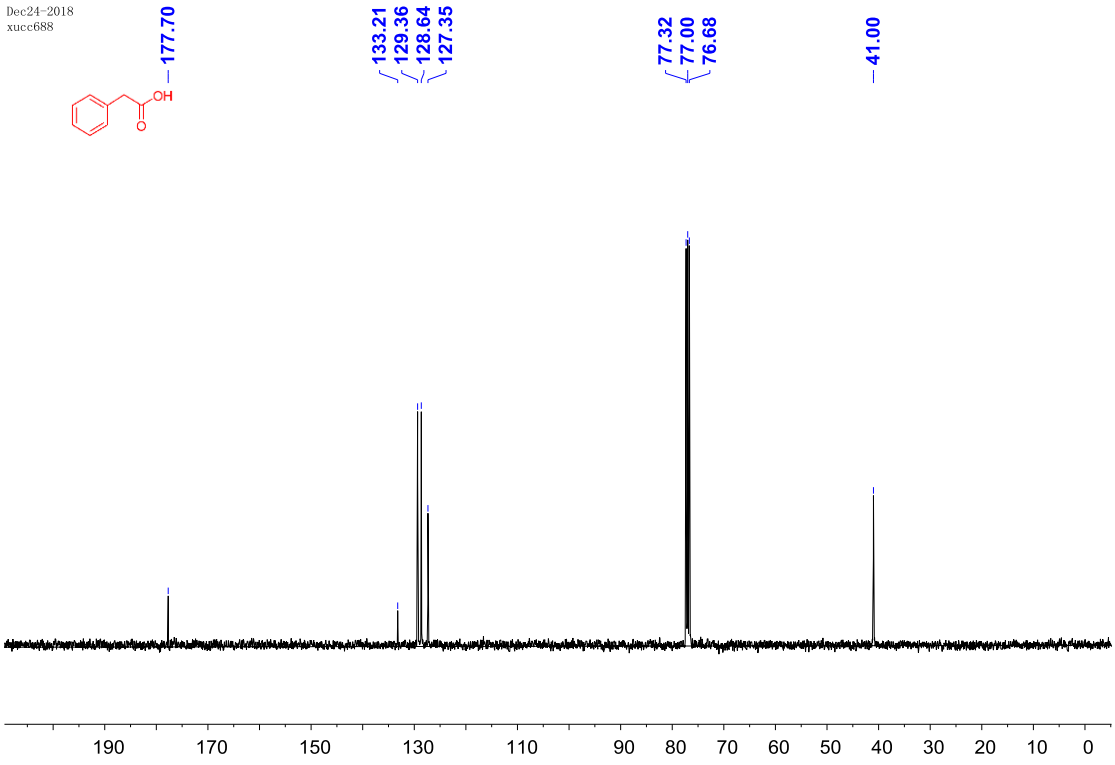
^{1}H and ^{13}C spectra of **5h**.



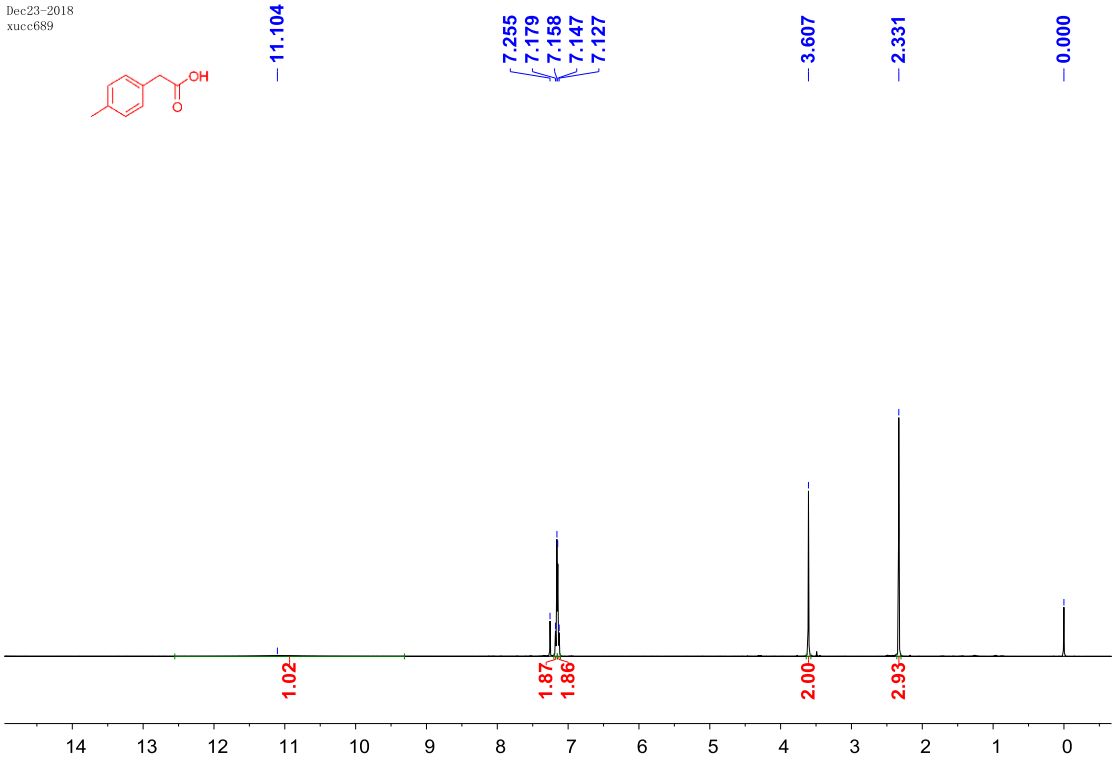


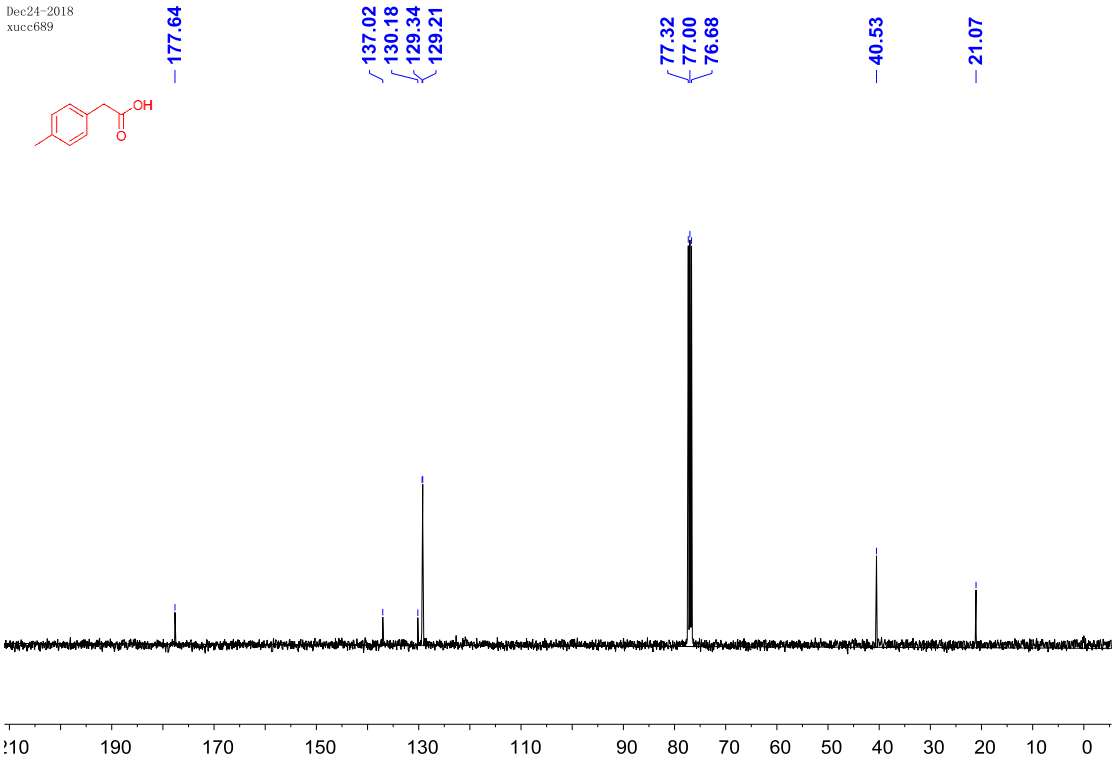
^{1}H and ^{13}C spectra of **5i**.



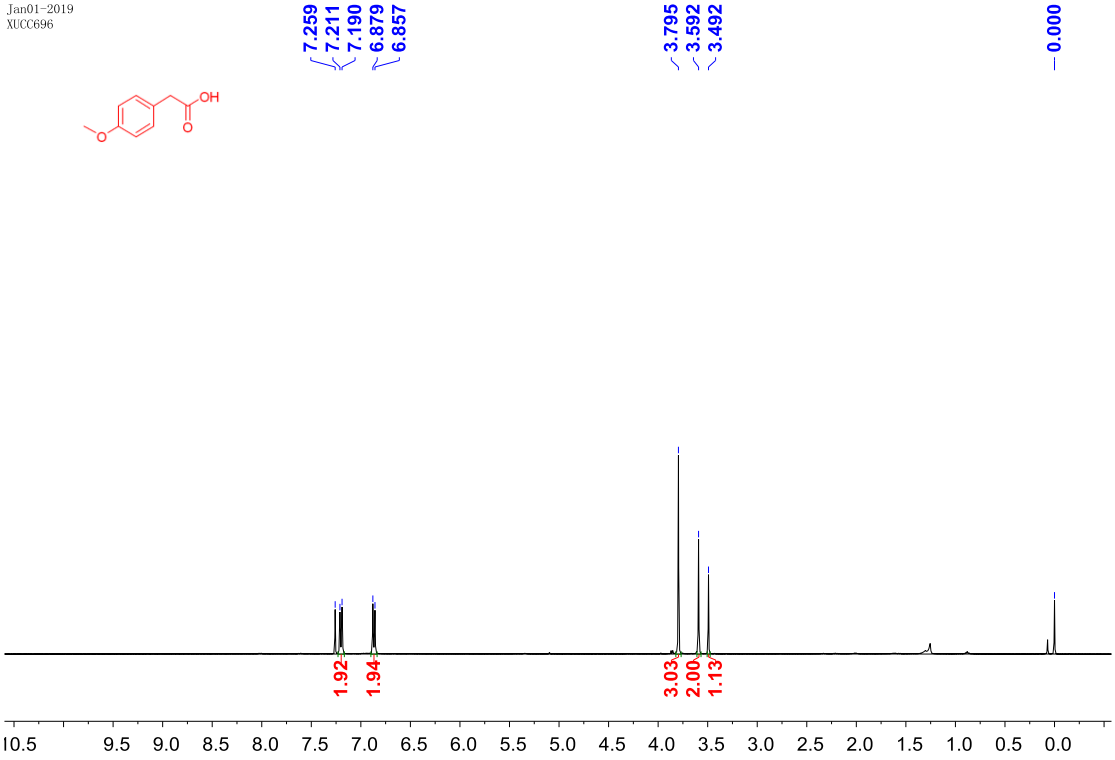


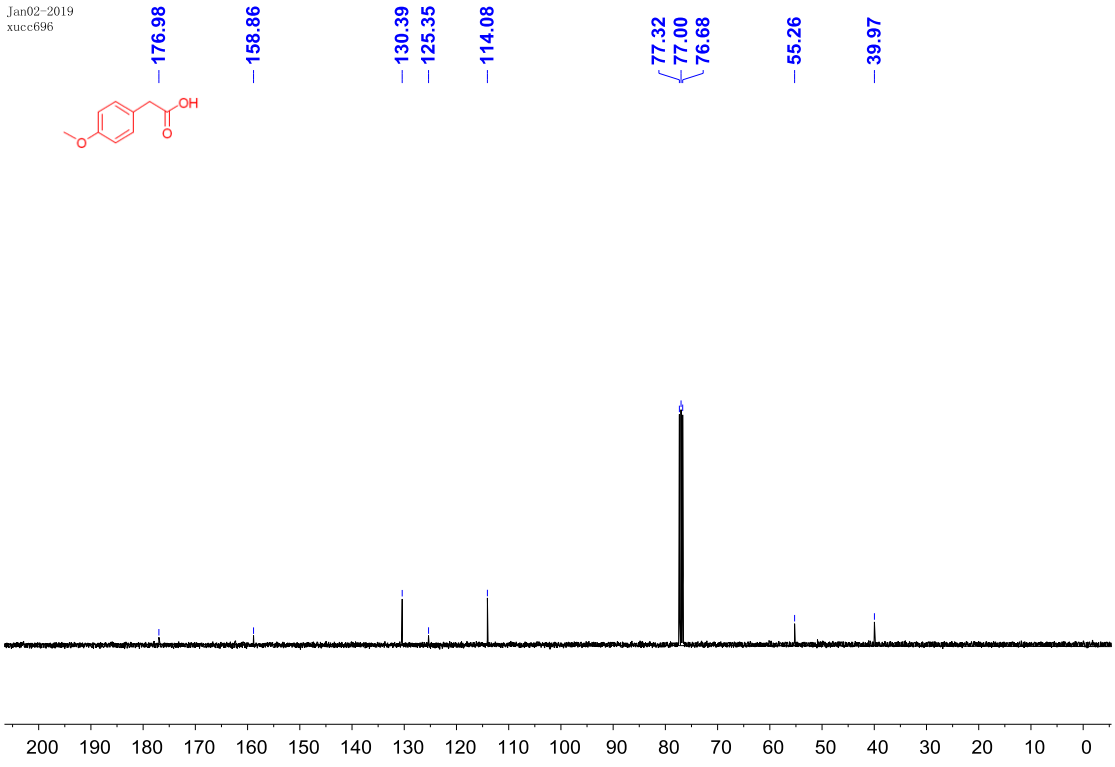
^{1}H and ^{13}C spectra of **5j**.



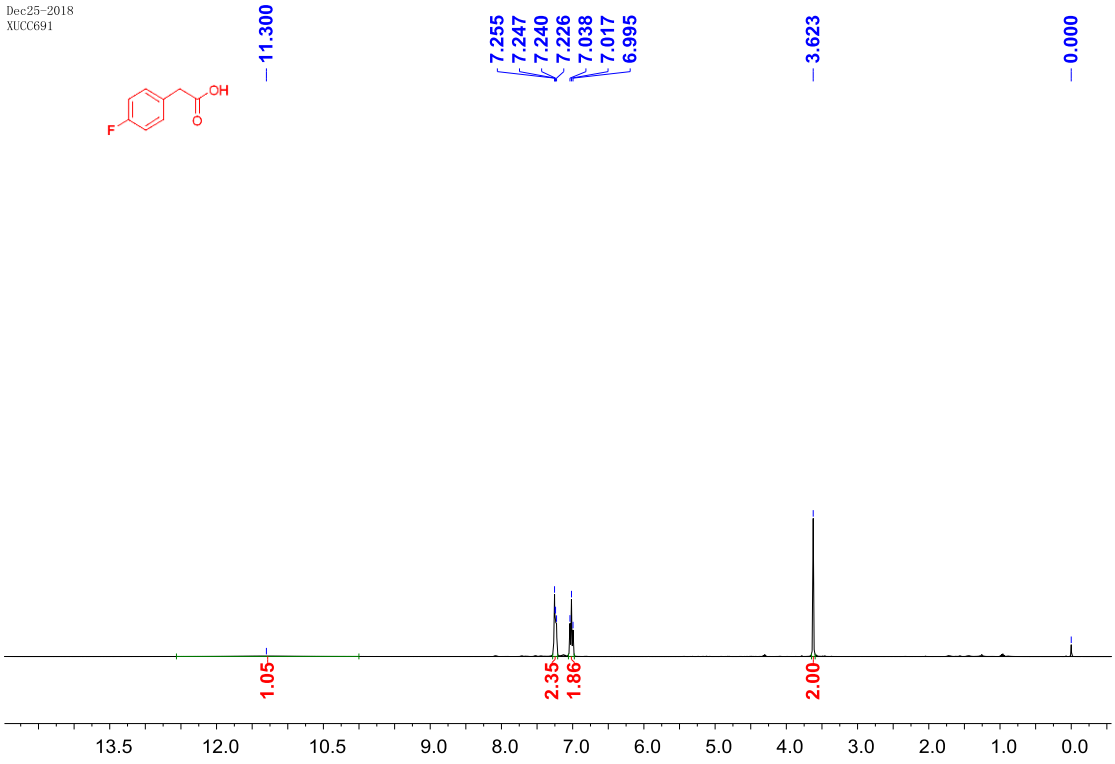


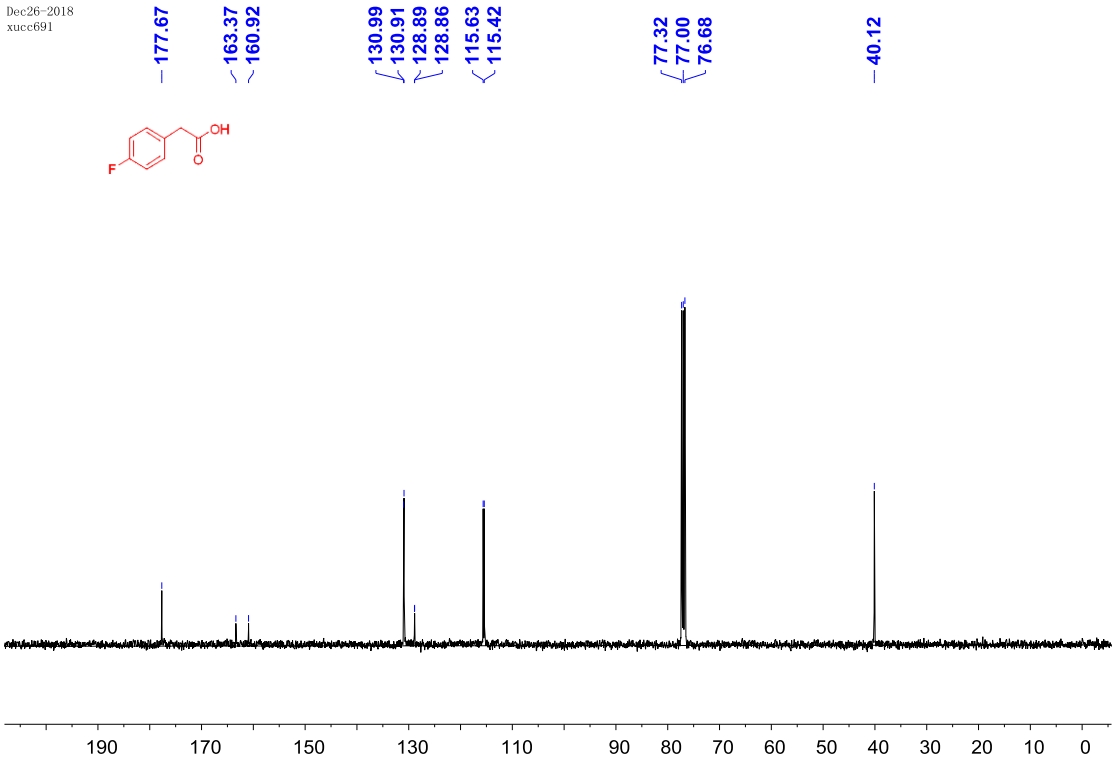
^{1}H and ^{13}C spectra of **5k**.

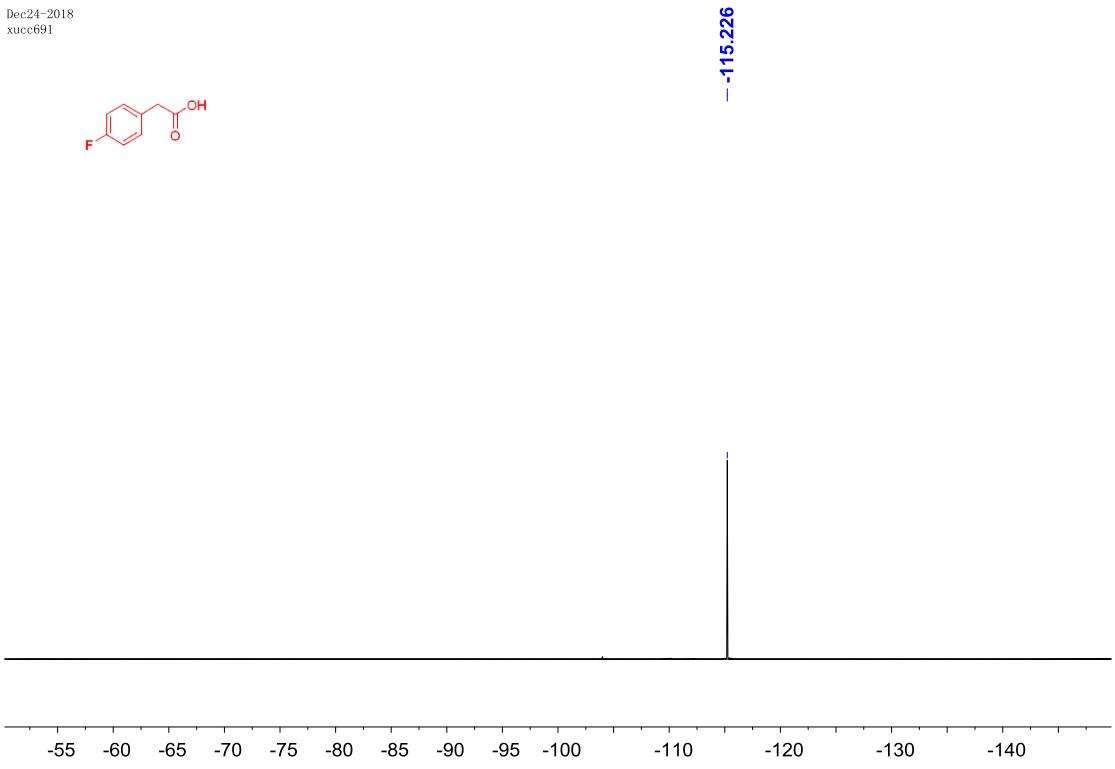




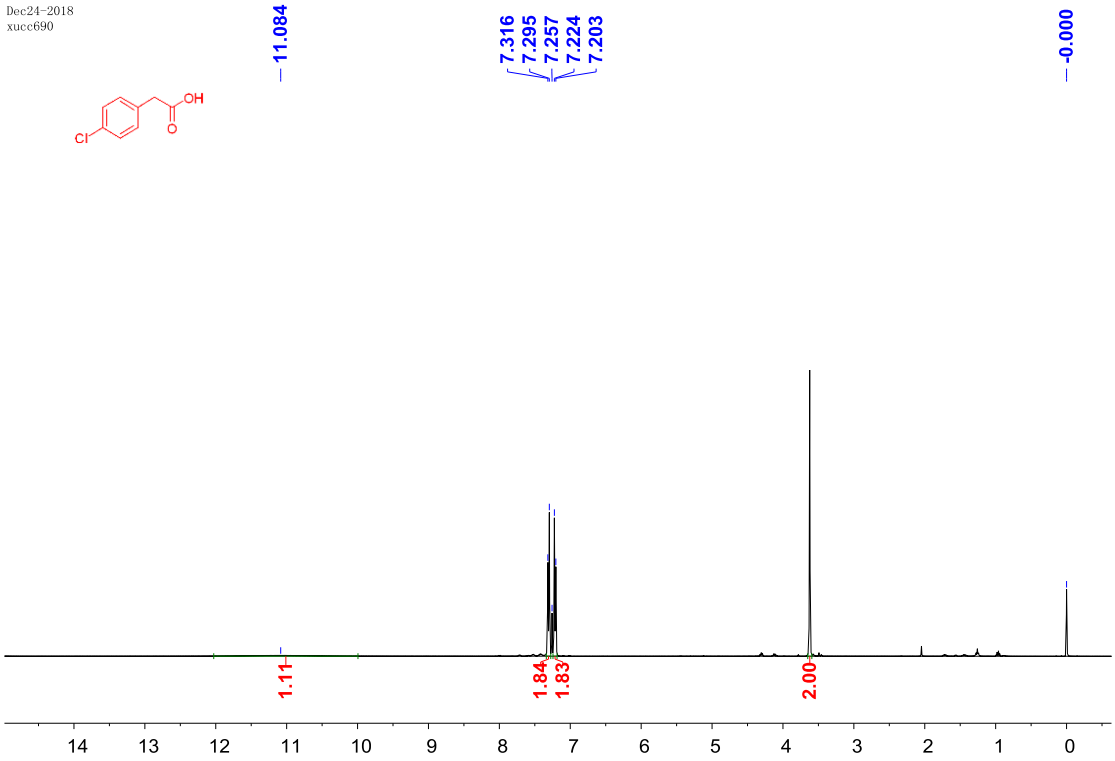
^{1}H, ^{13}C and ^{19}F spectra of **5l**.

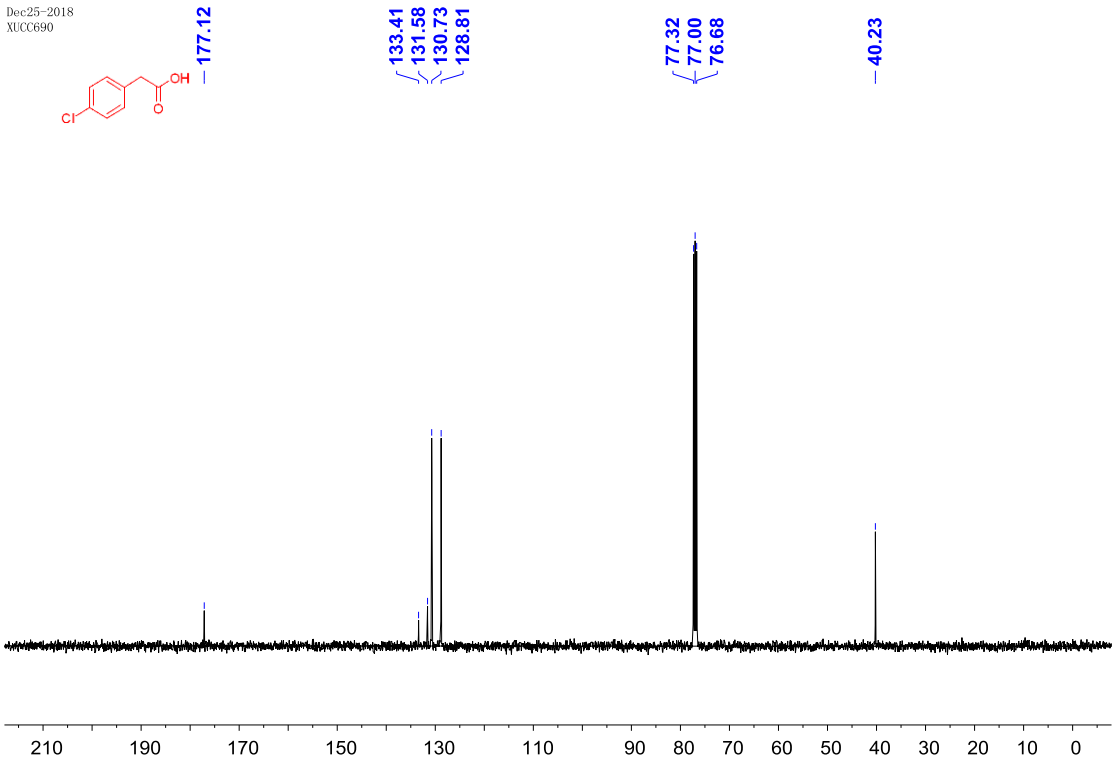




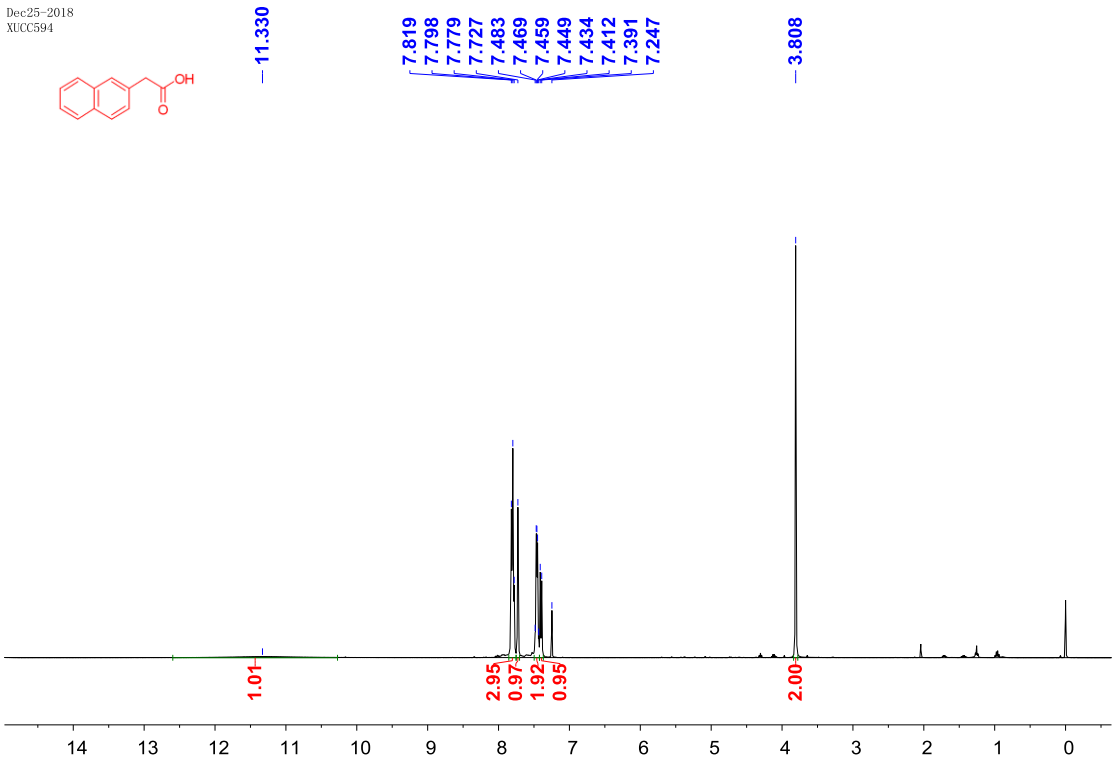


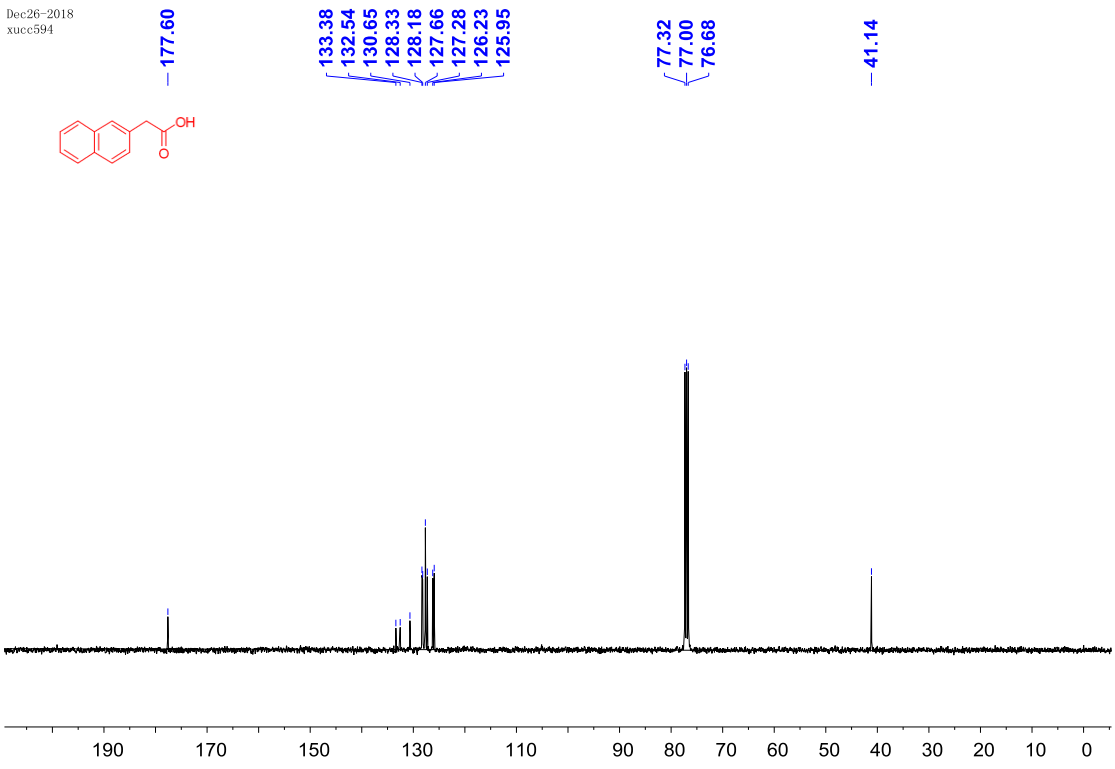
^{1}H and ^{13}C spectra of **5m**.



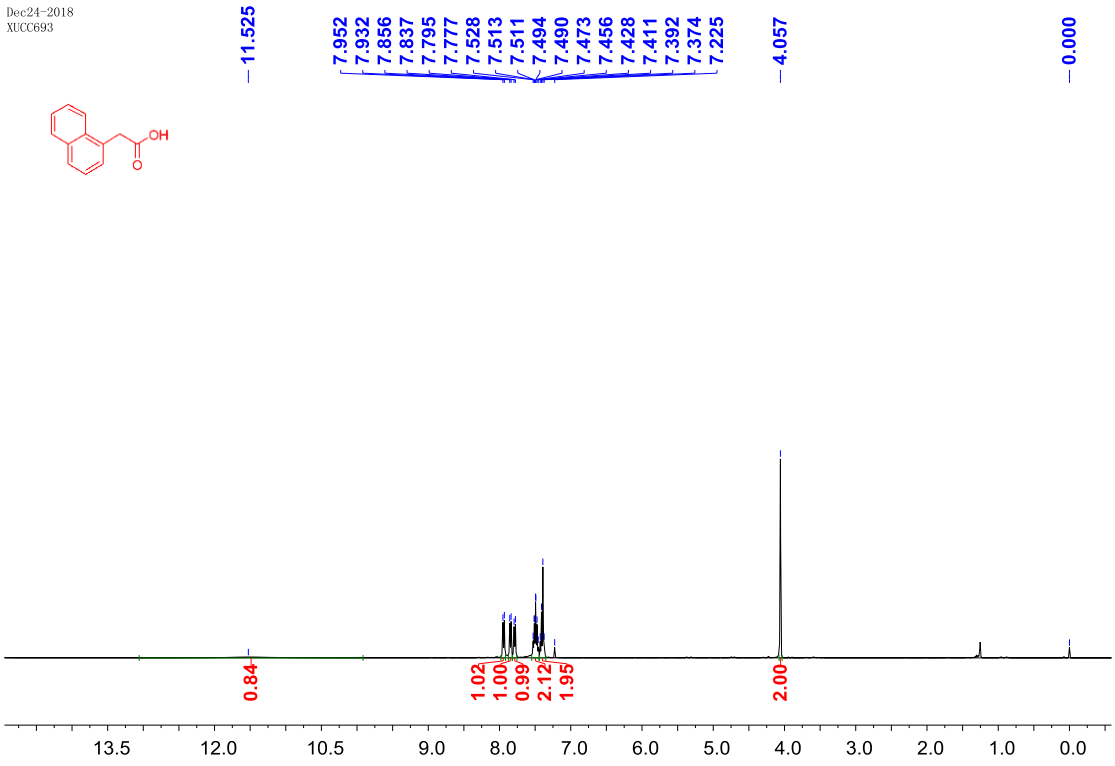


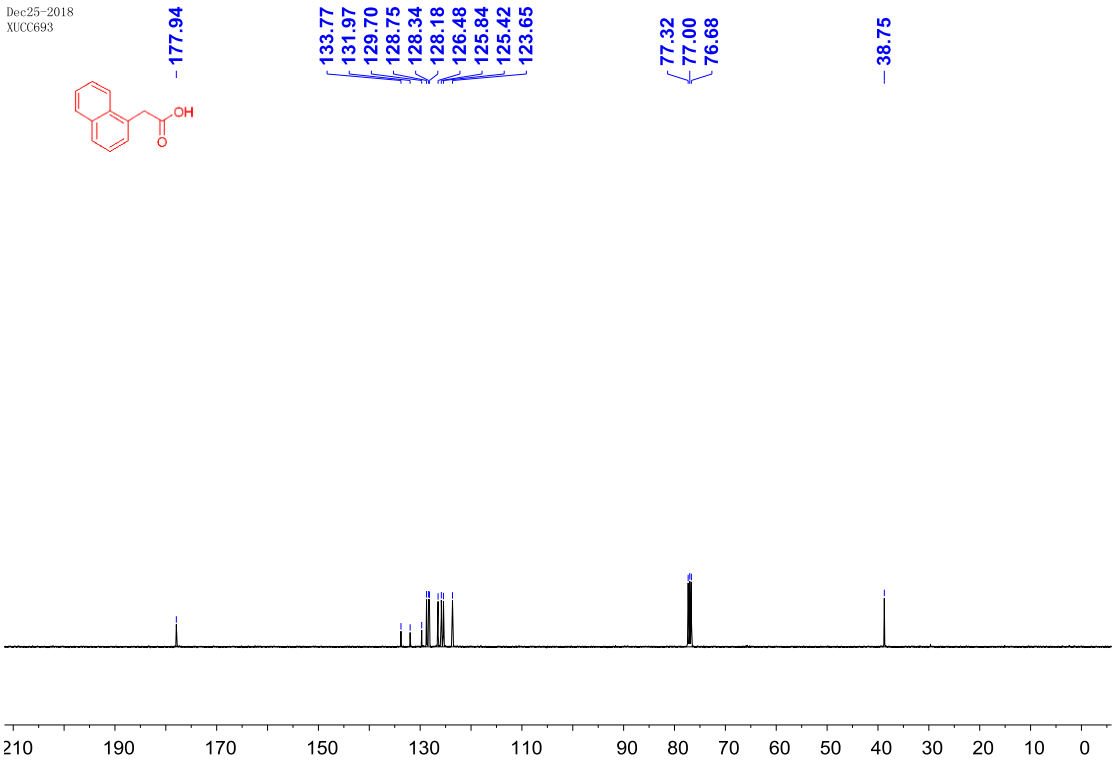
^{1}H and ^{13}C spectra of **5n**.



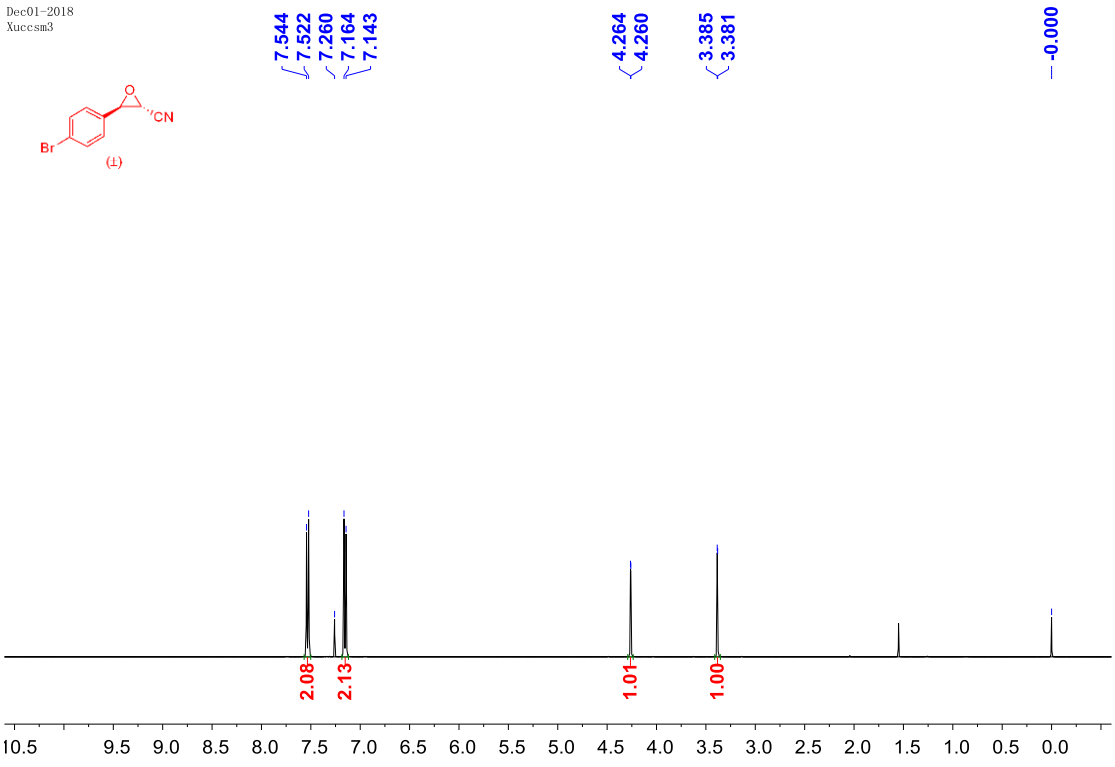


^{1}H and ^{13}C spectra of **5o**.

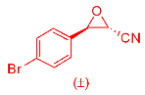




^{1}H and ^{13}C spectra of **1a**.

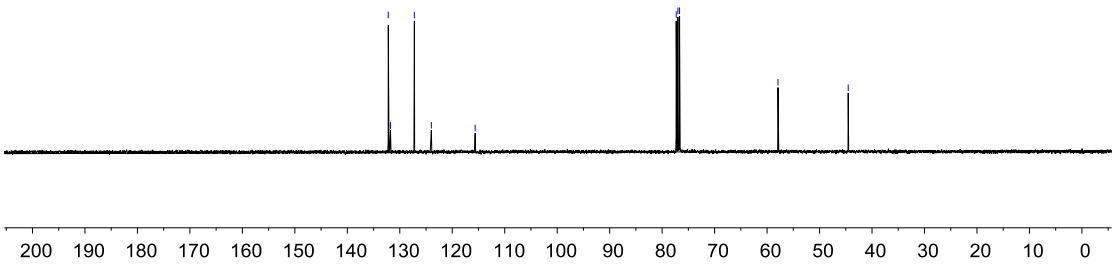


Dec02-2018
xuccsm3



(±)

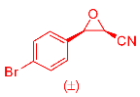
132.19
131.77
127.22
123.98
115.63
77.32
77.00
76.68
57.92
44.54



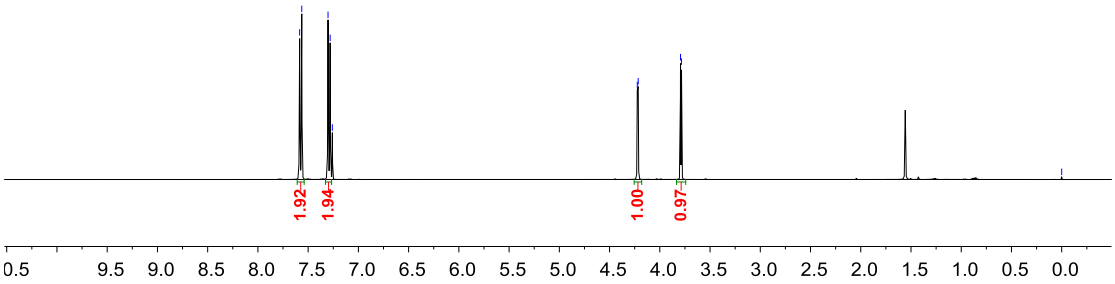
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Oct07-2017
Xucc 404 H

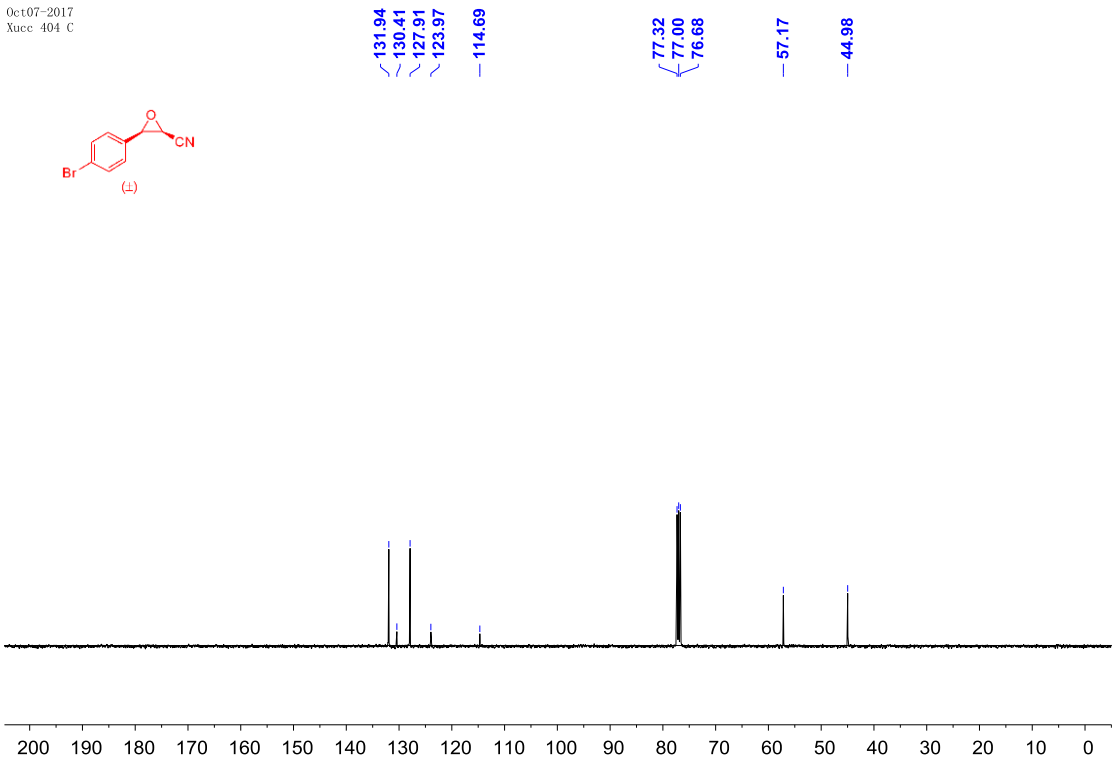
7.585
7.564
7.302
7.281
7.259
4.224
4.215
3.794
3.785
0.000



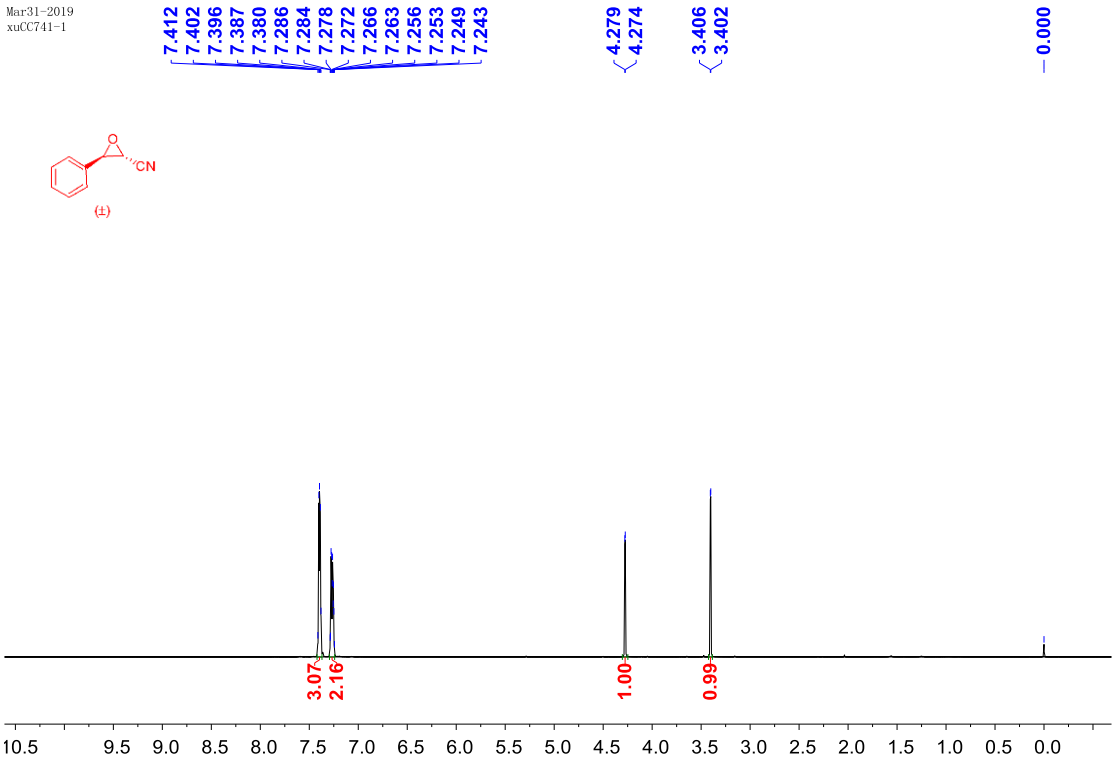
(±)

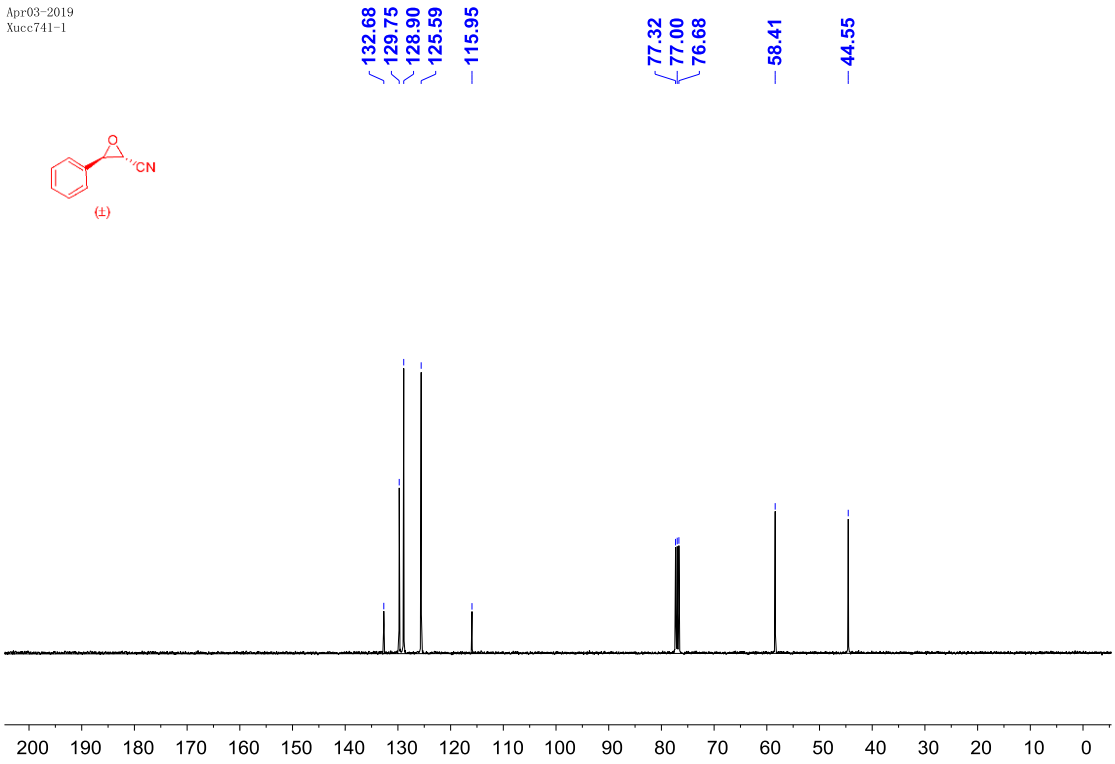


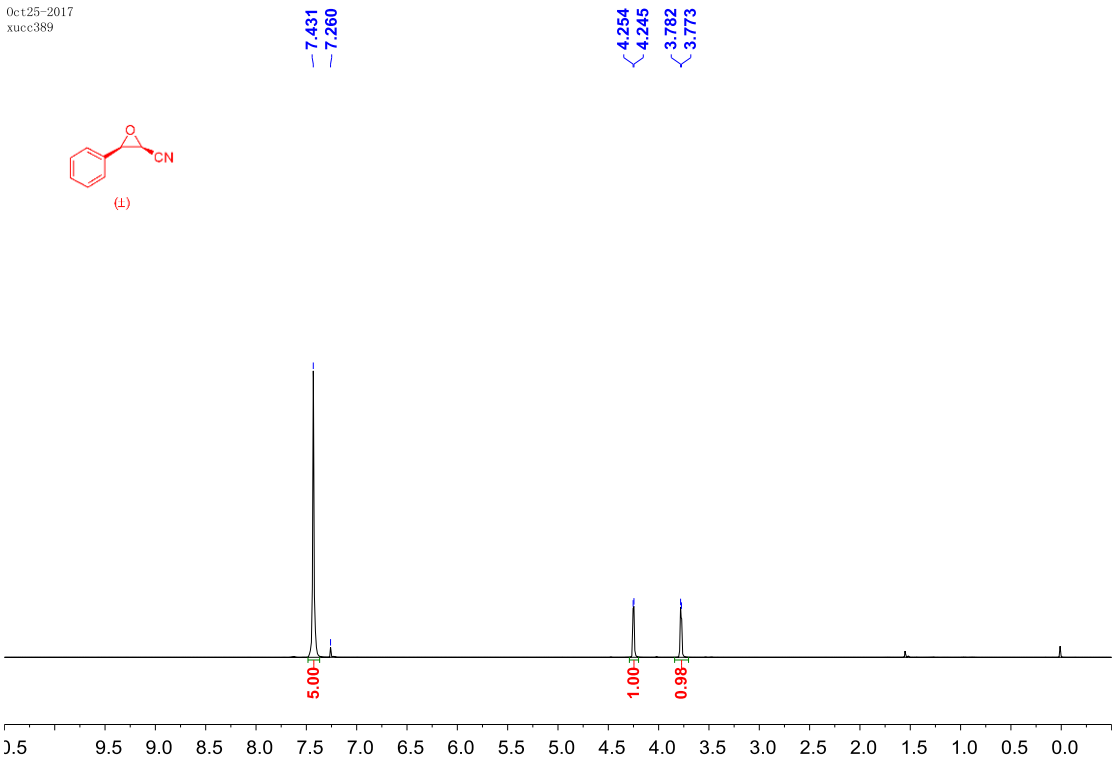
0.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

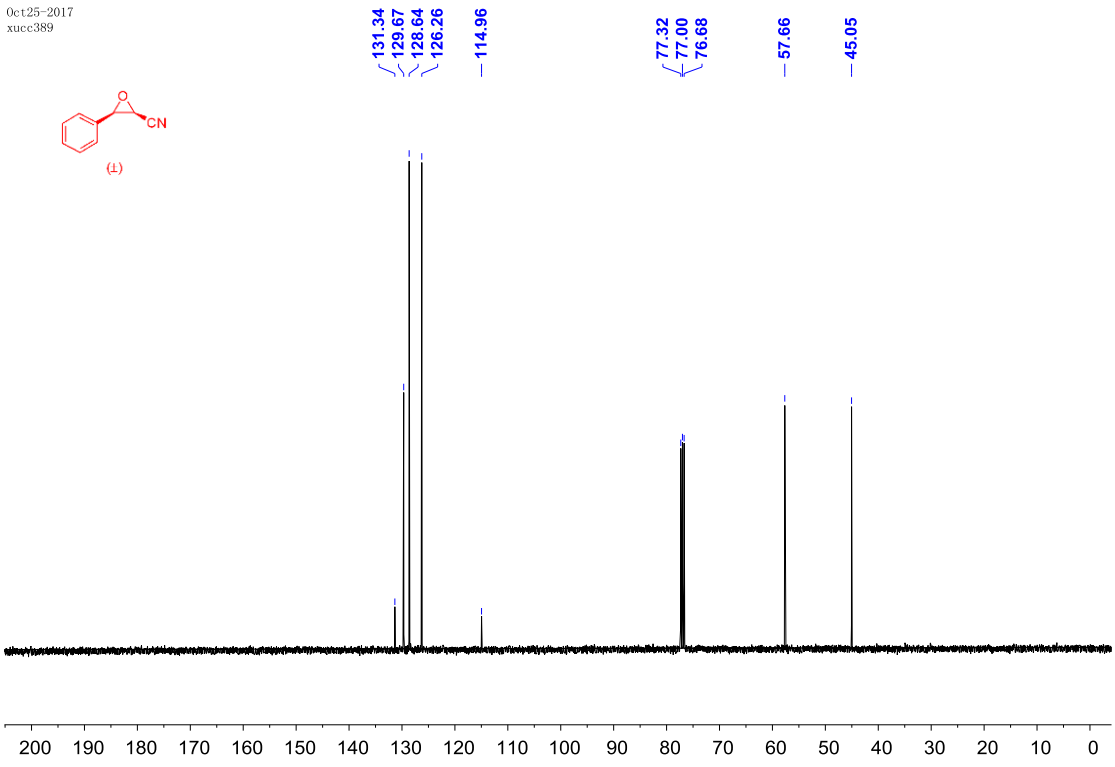


^{1}H and ^{13}C spectra of **1b**.

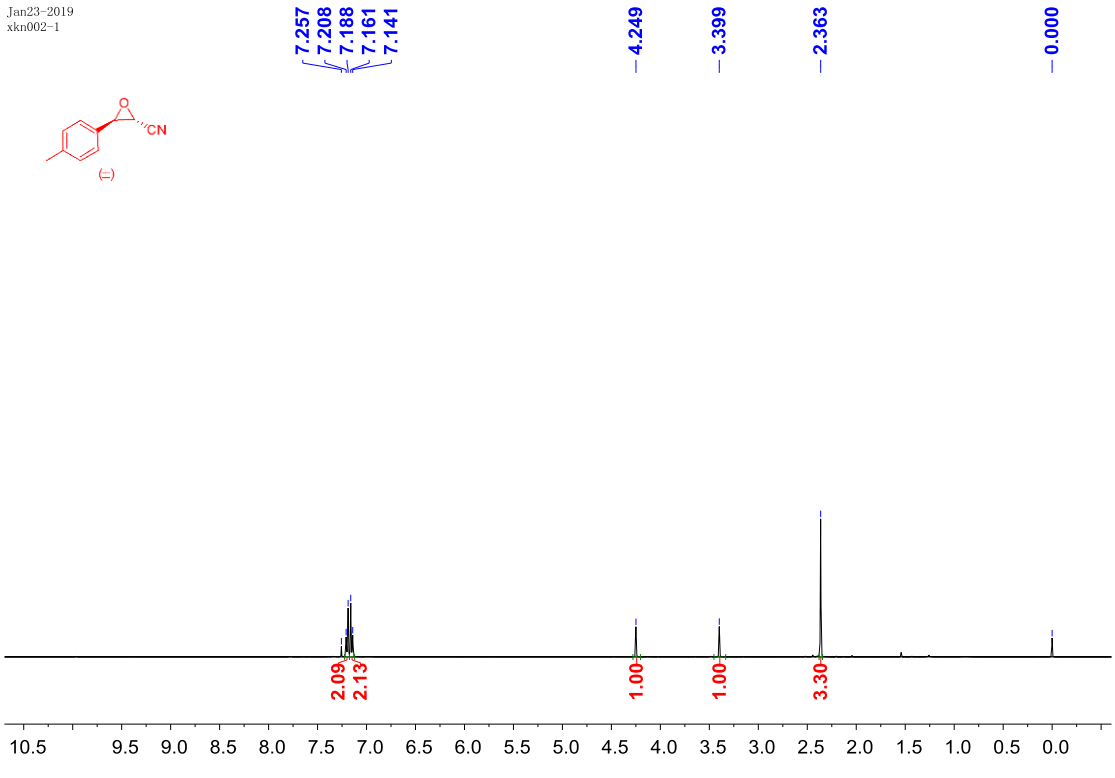


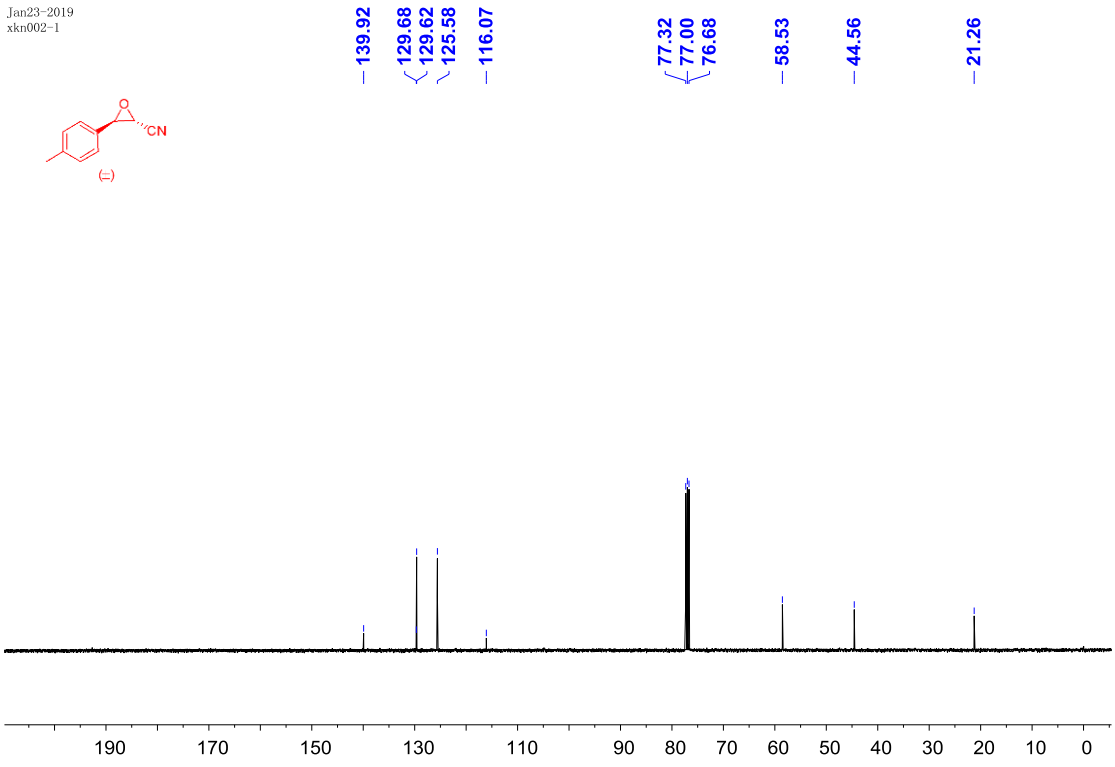

Apr03-2019
Xucc741-1
132.68
129.75
128.90
125.59
115.95
77.32
77.00
76.68
58.41
44.55
CN
(±)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

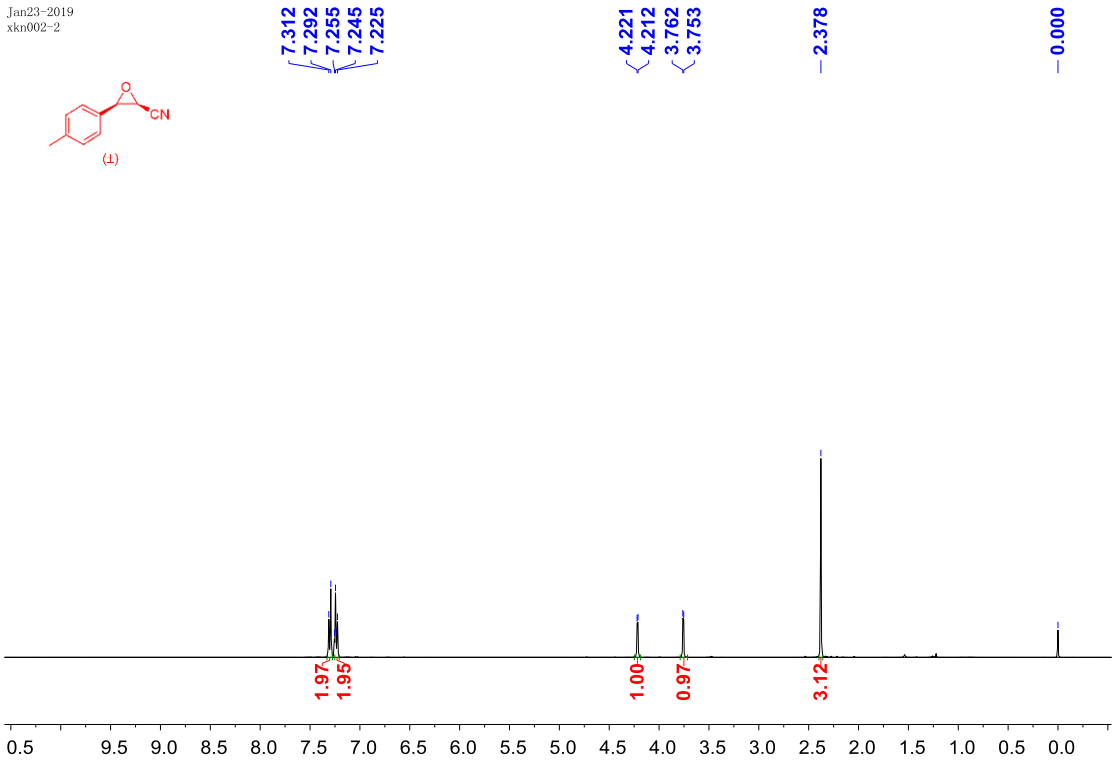

Oct25-2017
xucc389
7.431
7.260
4.254
4.245
3.782
3.773
CN
(±)
5.00
1.00
0.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

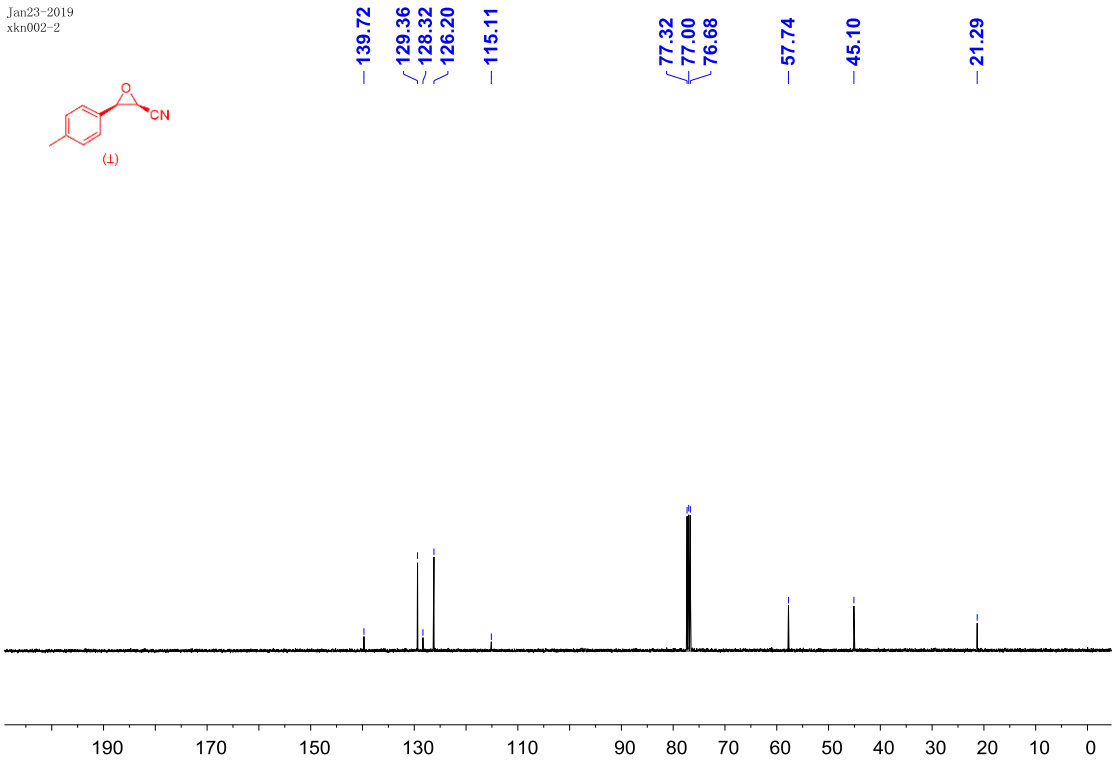


^{1}H and ^{13}C spectra of **1c**.

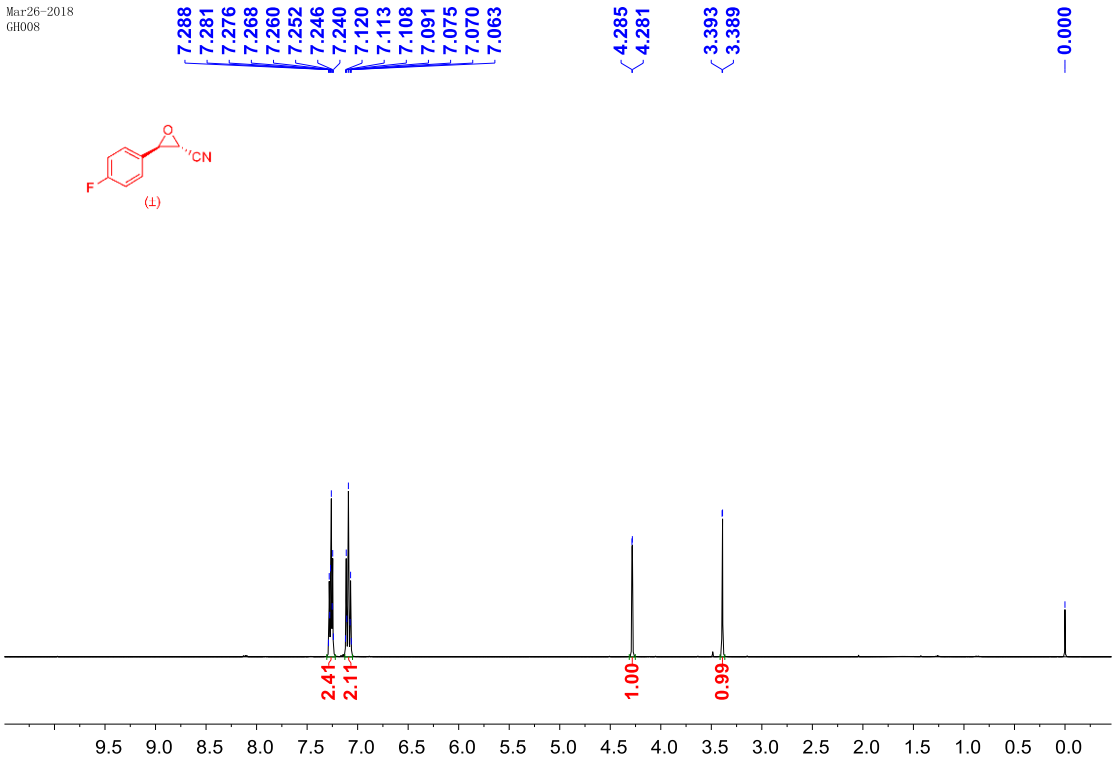


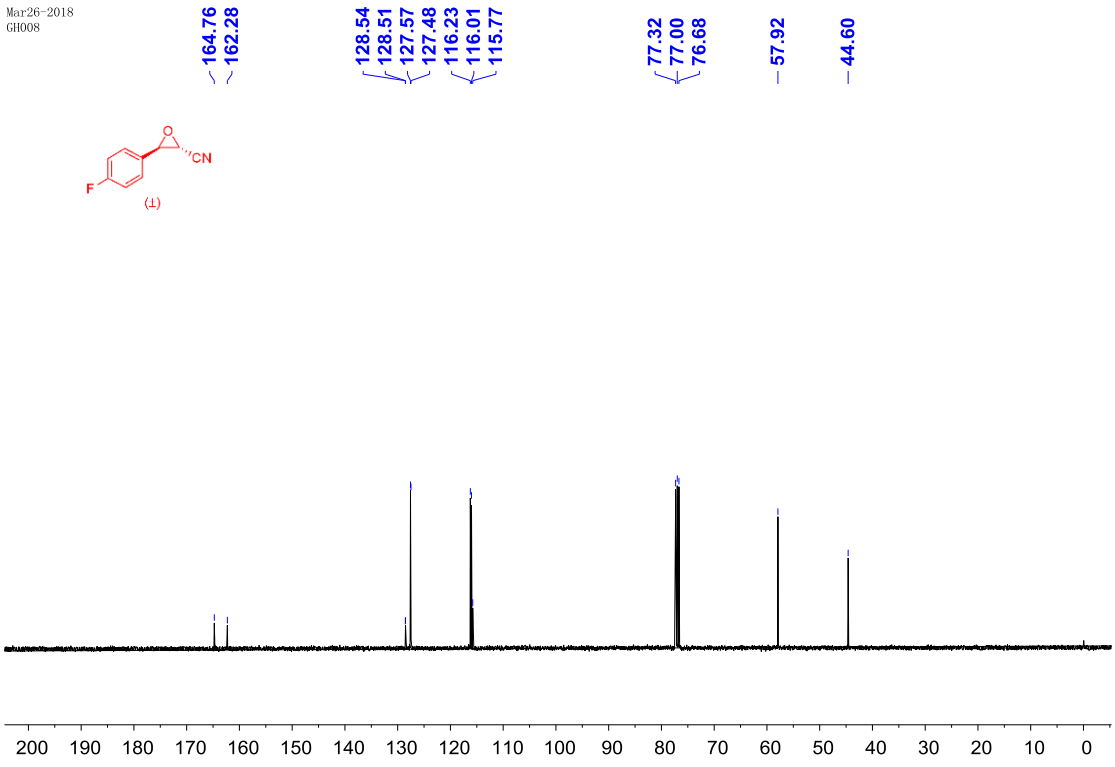

Jan23-2019
xkn002-1
139.92
129.68
129.62
125.58
116.07
77.32
77.00
76.68
58.53
44.56
21.26
CN
(±)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

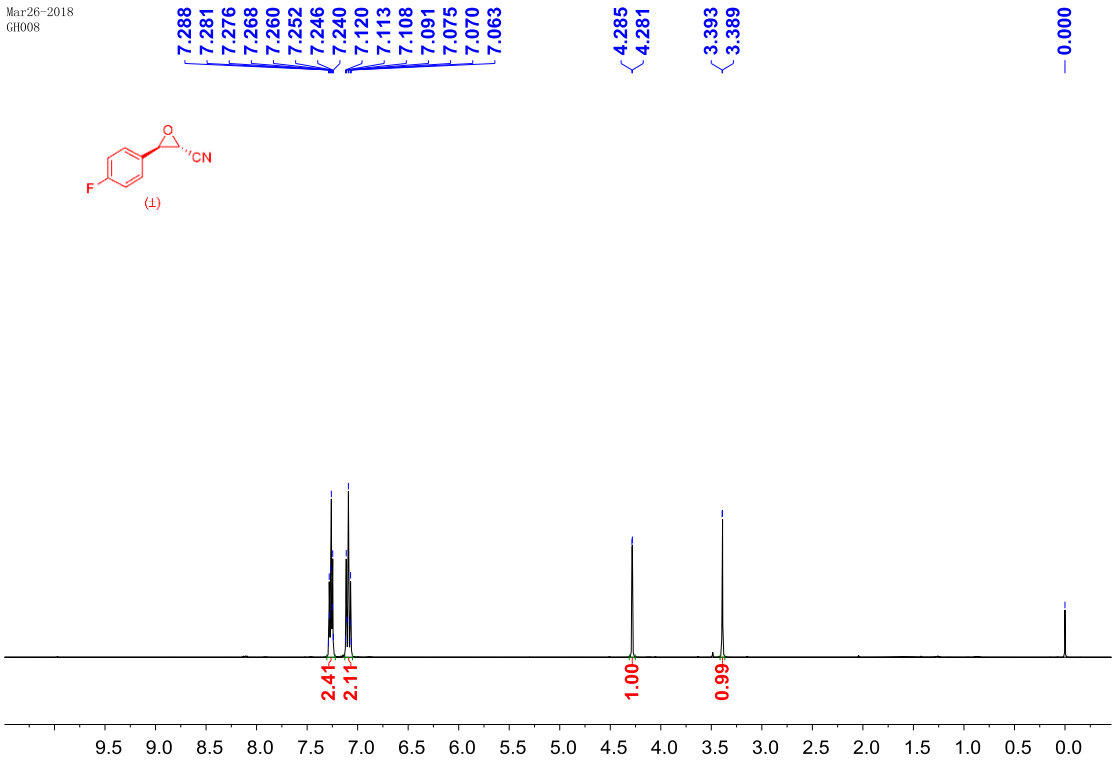

Jan23-2019
xkn002-2
7.312
7.292
7.255
7.245
7.225
4.221
4.212
3.762
3.753
2.378
0.000
CN
(±)
1.97
1.95
1.00
0.97
3.12
0.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

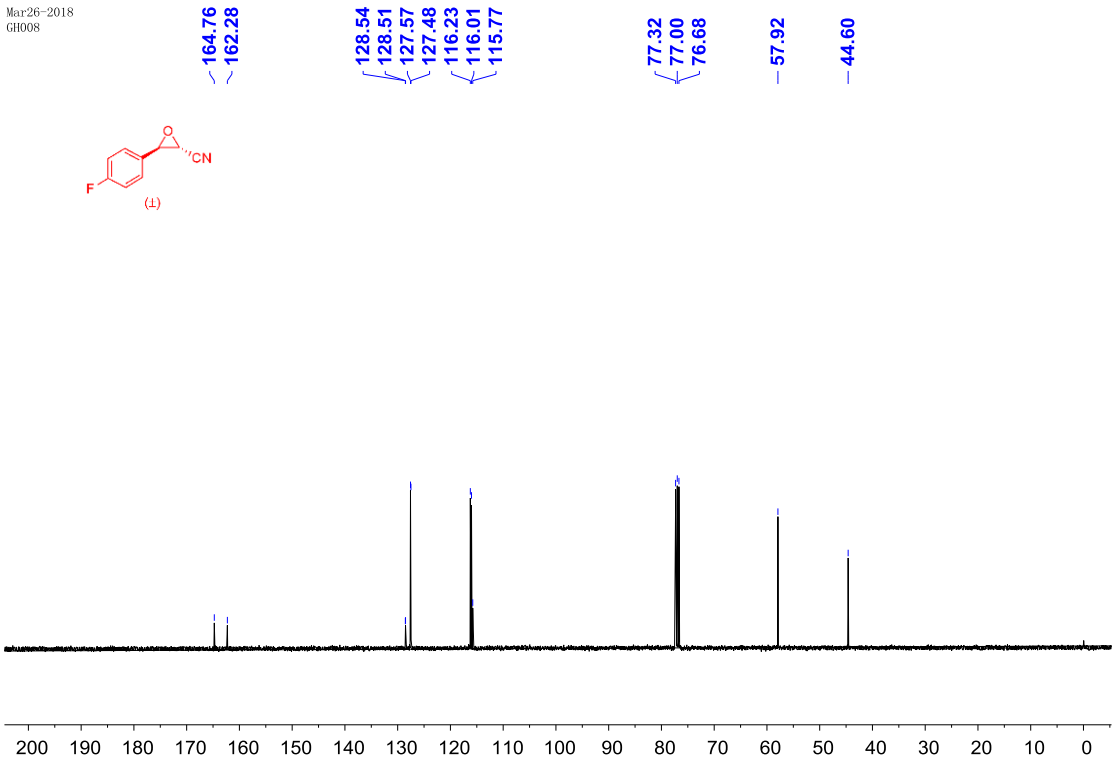


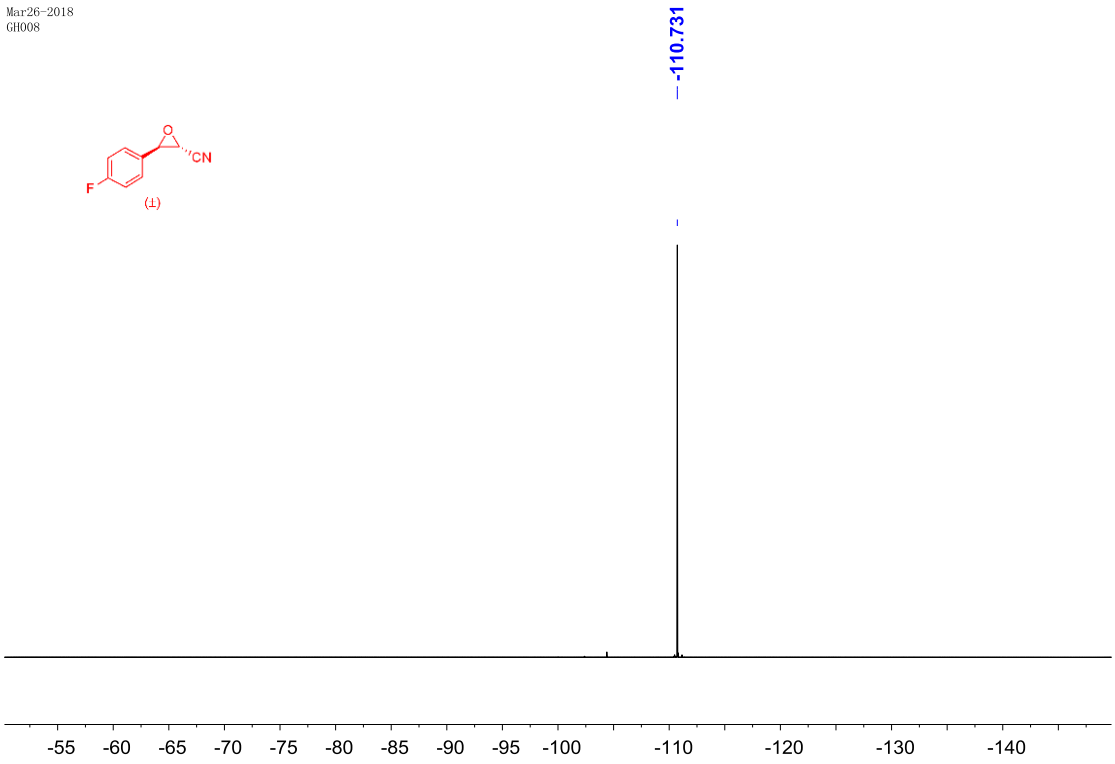
^{1}H, ^{13}C and ^{19}F spectra of **1d**.



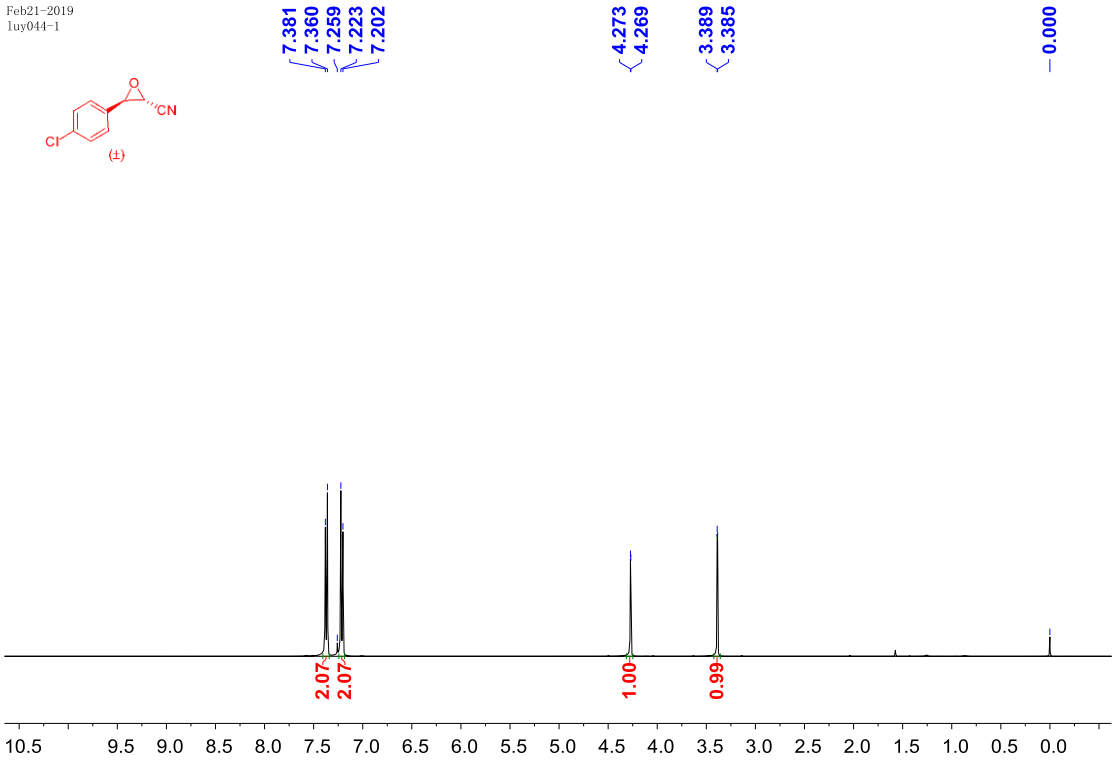

Mar26-2018
GH008
164.76
162.28
128.54
128.51
127.57
127.48
116.23
116.01
115.77
77.32
77.00
76.68
57.92
44.60
CN
F
(±)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

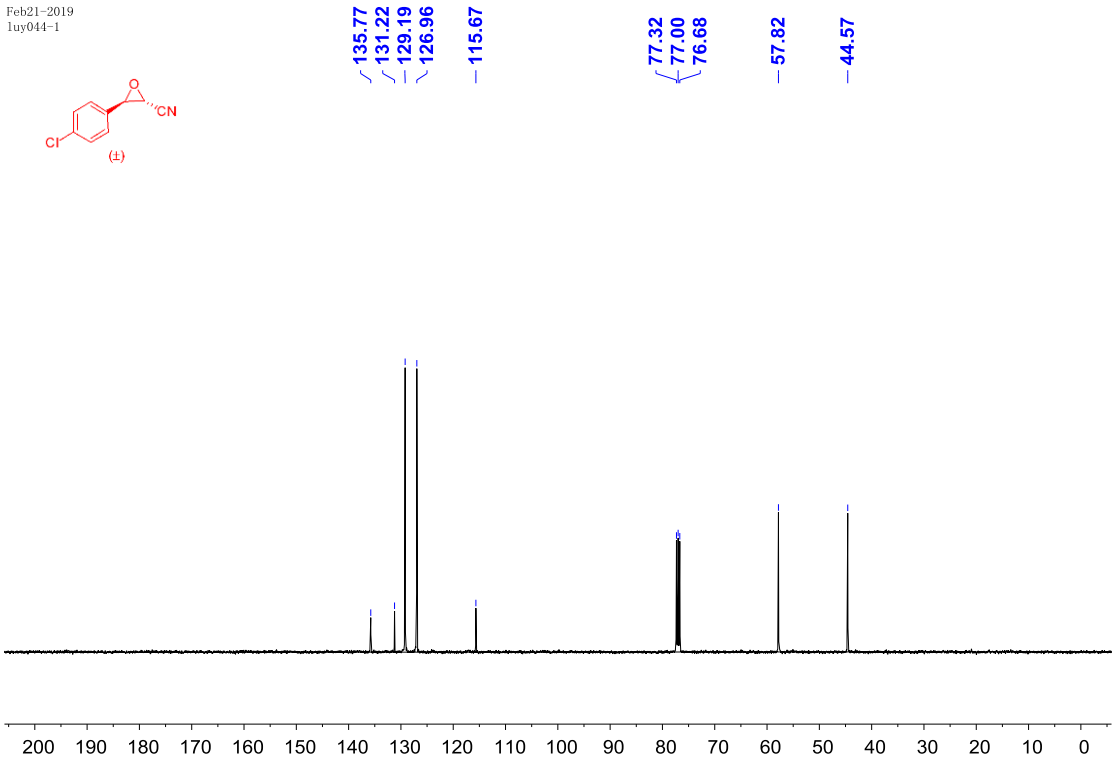

Mar26-2018
GH008
7.288
7.281
7.276
7.268
7.260
7.252
7.246
7.240
7.120
7.113
7.108
7.091
7.075
7.070
7.063
4.285
4.281
3.393
3.389
0.000
CN
F
(±)
2.41
2.11
1.00
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

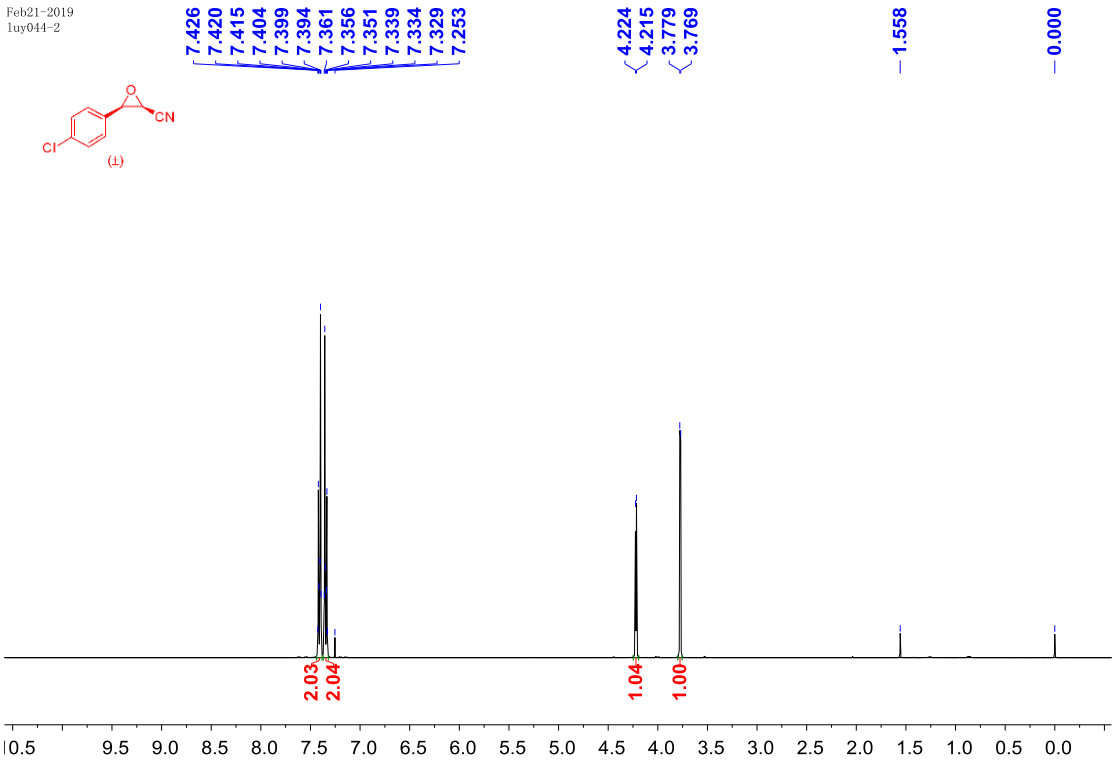

Mar26-2018
GH008
164.76
162.28
128.54
128.51
127.57
127.48
116.23
116.01
115.77
77.32
77.00
76.68
57.92
44.60
CN
F
(±)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

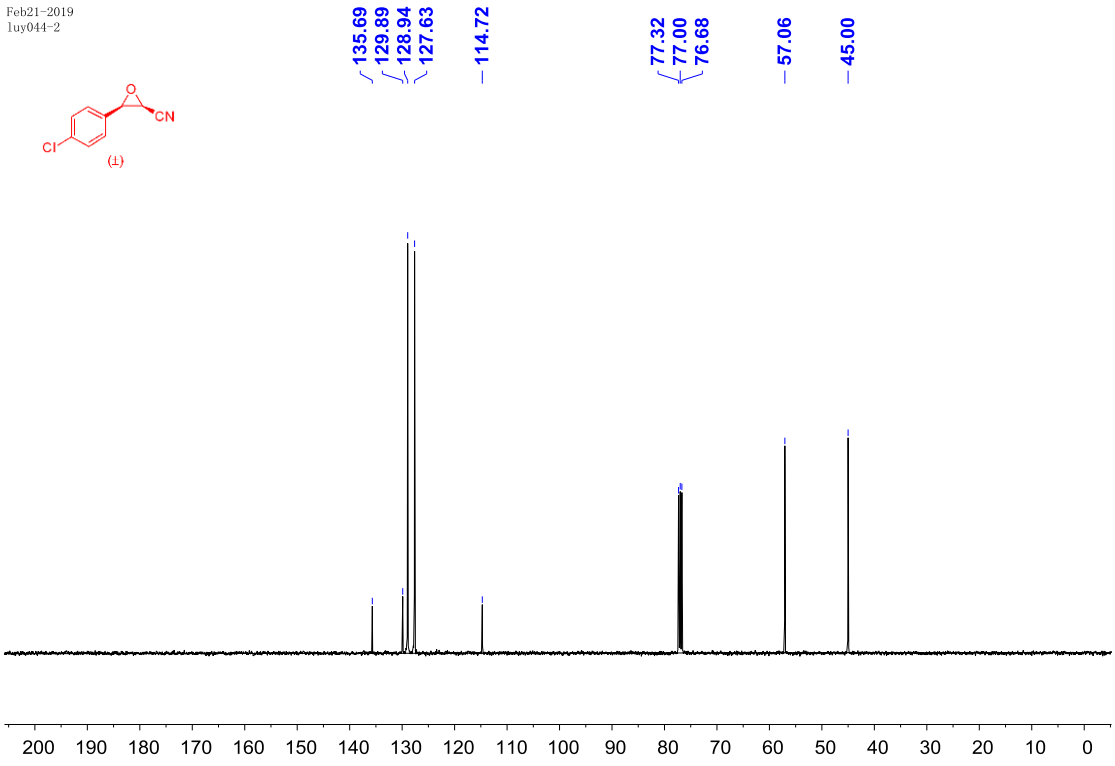

Mar26-2018
GH008
-110.731
CN
F
(±)
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140

^{1}H and ^{13}C spectra of **1e**.

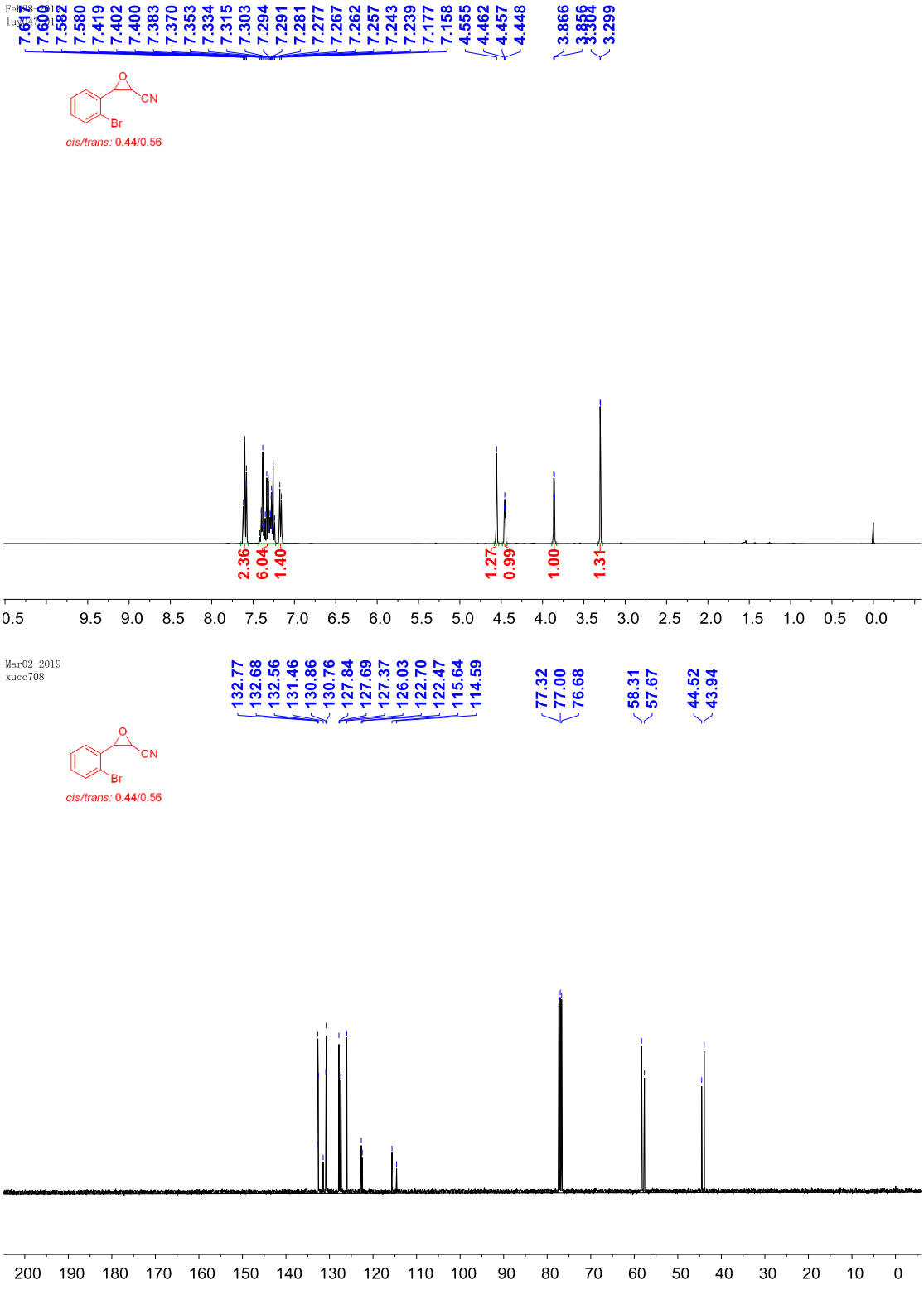




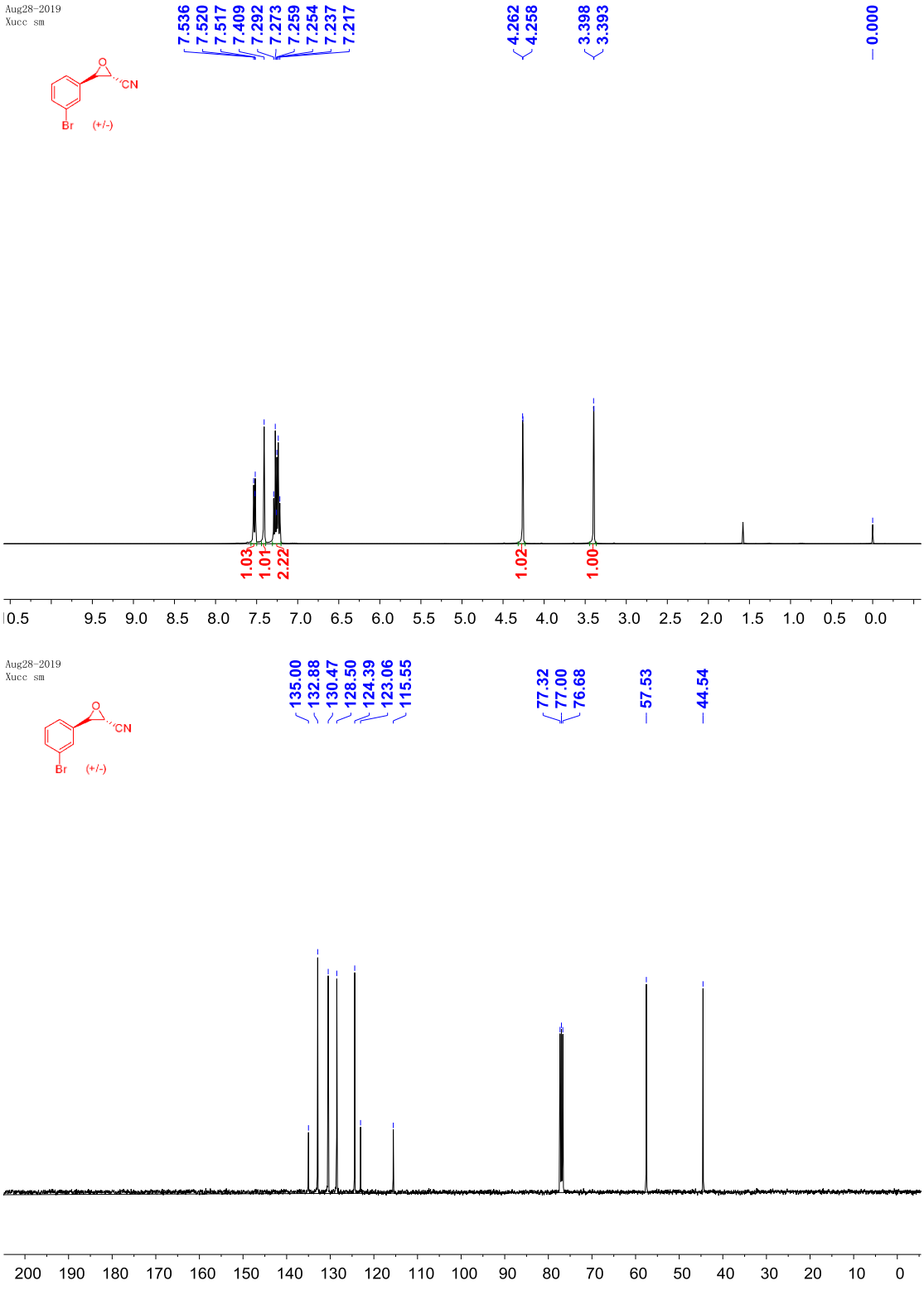

Feb21-2019
luy044-2
7.426
7.420
7.415
7.404
7.399
7.394
7.361
7.356
7.351
7.339
7.334
7.329
7.253
4.224
4.215
3.779
3.769
1.558
0.000
CN
Cl
(±)
2.03
2.04
1.04
1.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

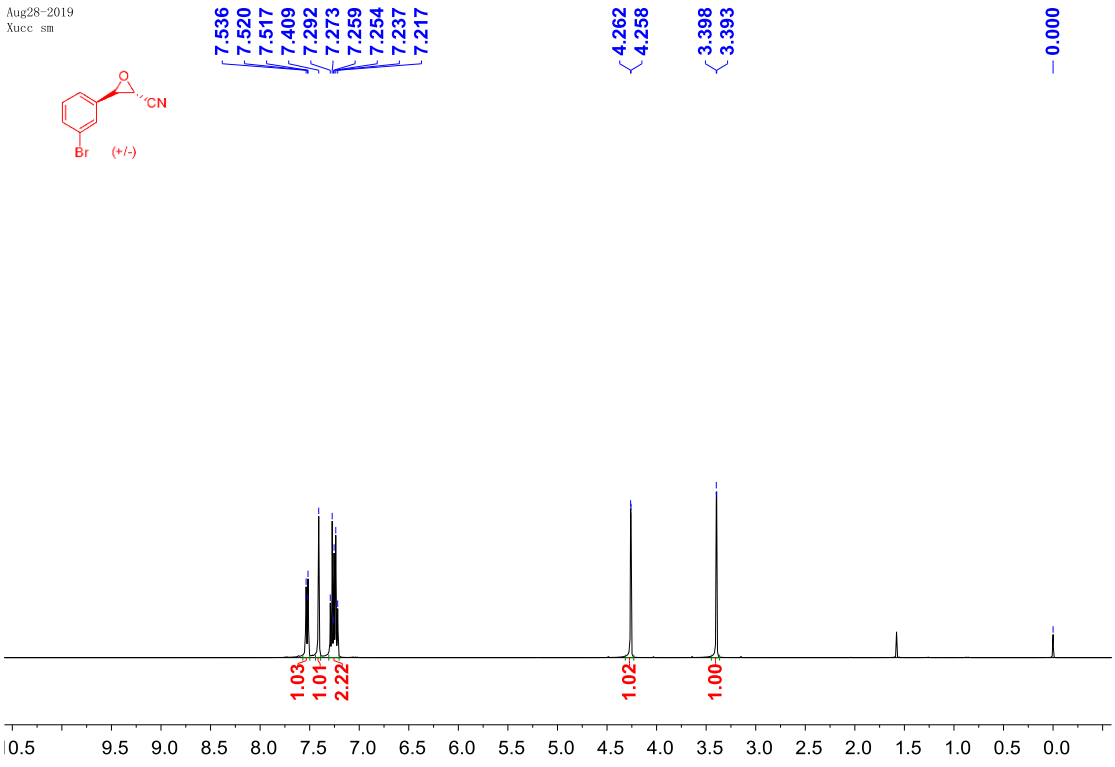

Feb21-2019
luy044-2
135.69
129.89
128.94
127.63
114.72
77.32
77.00
76.68
57.06
45.00
CN
Cl
(±)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

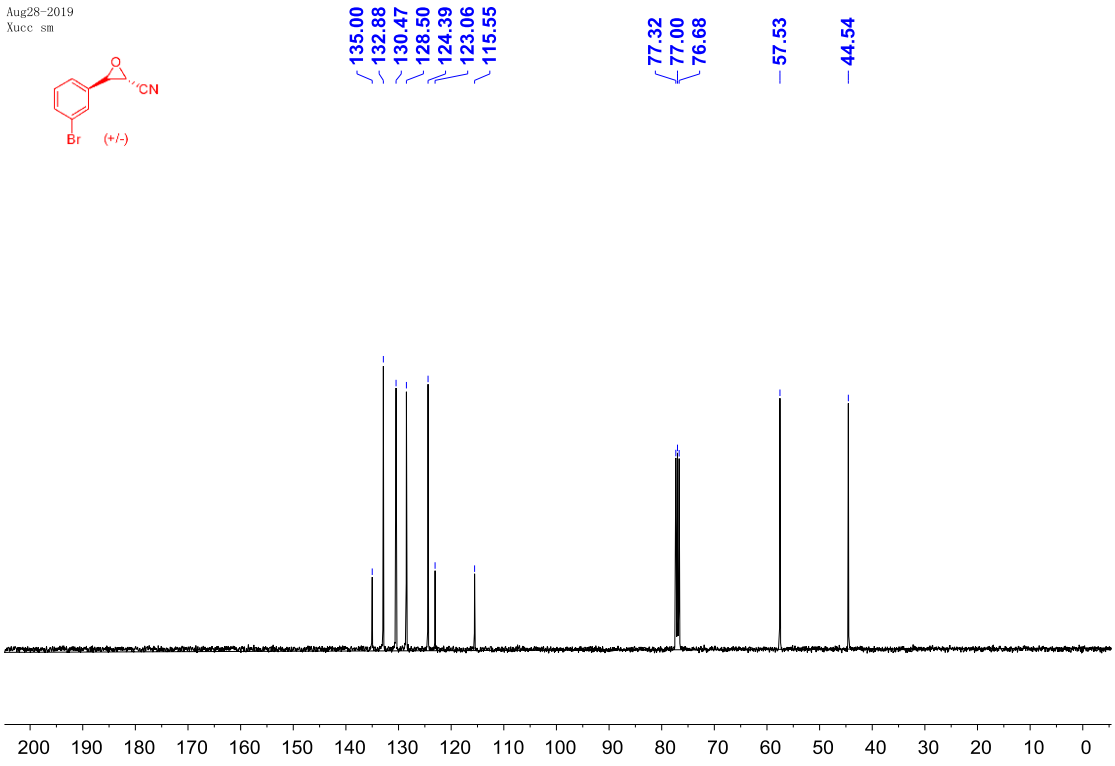
^{1}H and ^{13}C spectra of **1f**.



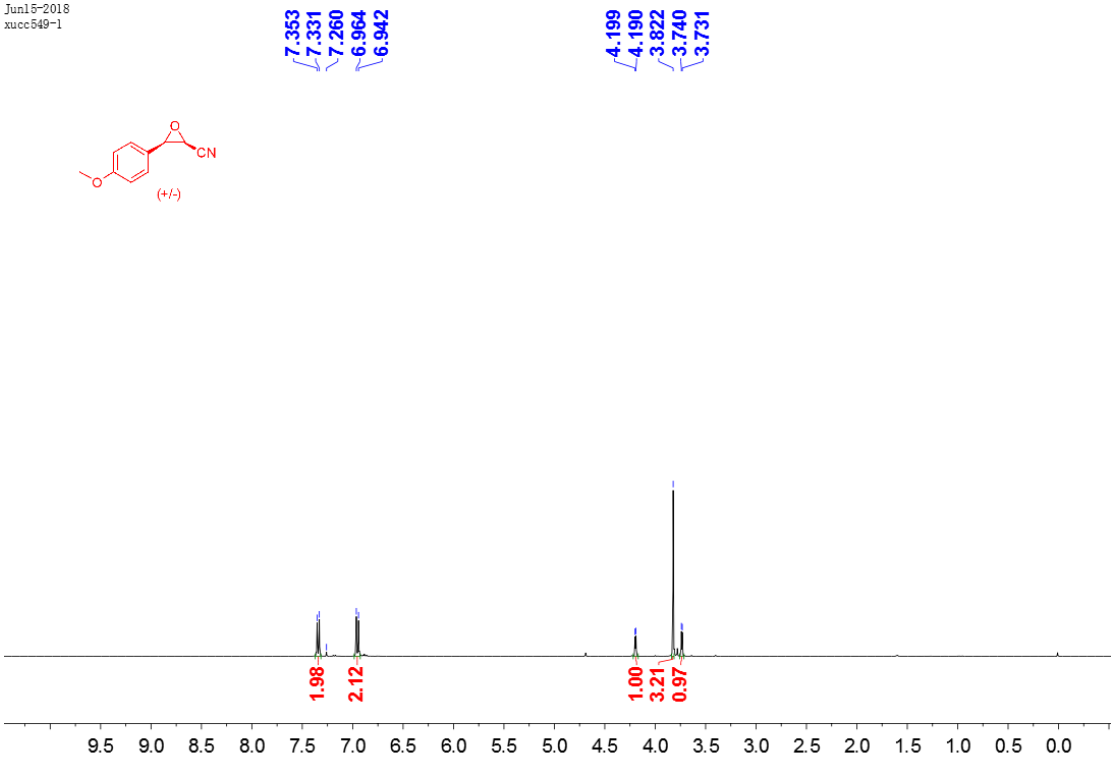
^{1}H and ^{13}C spectra of **1g**.

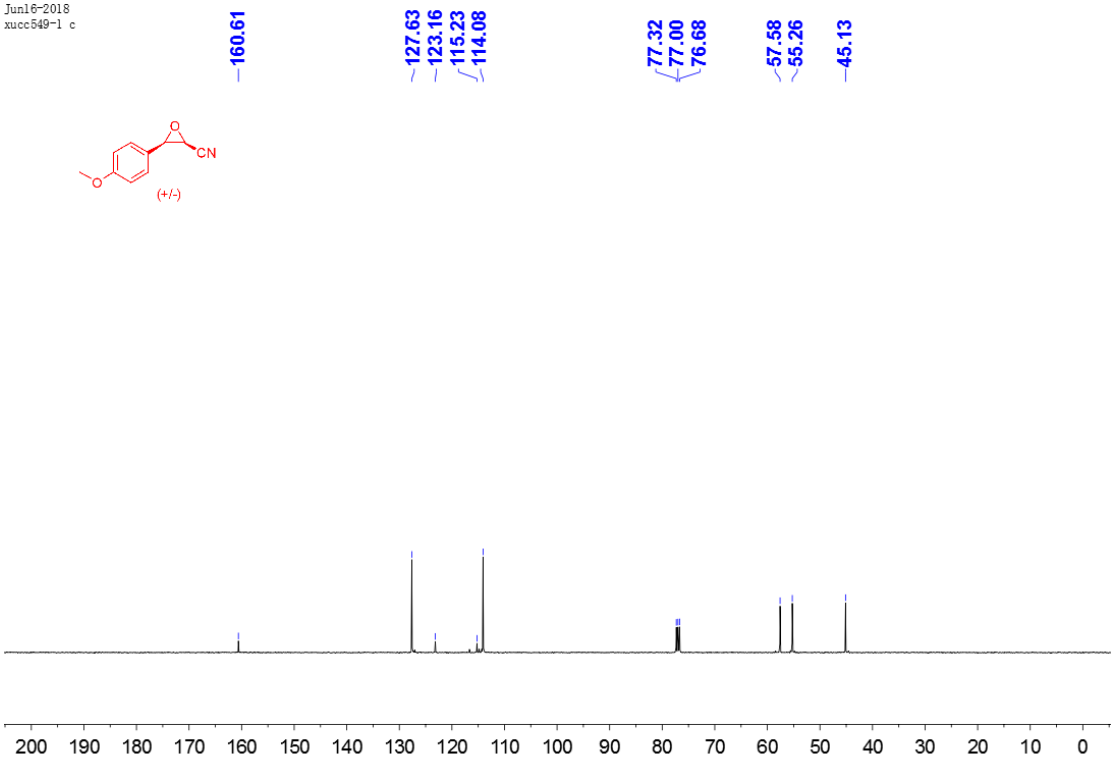



Aug28-2019
Xucc sm
7.536
7.520
7.517
7.409
7.292
7.273
7.259
7.254
7.237
7.217
4.262
4.258
3.398
3.393
0.000
CN
Br
(+/-)
1.03
1.01
2.22
1.02
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

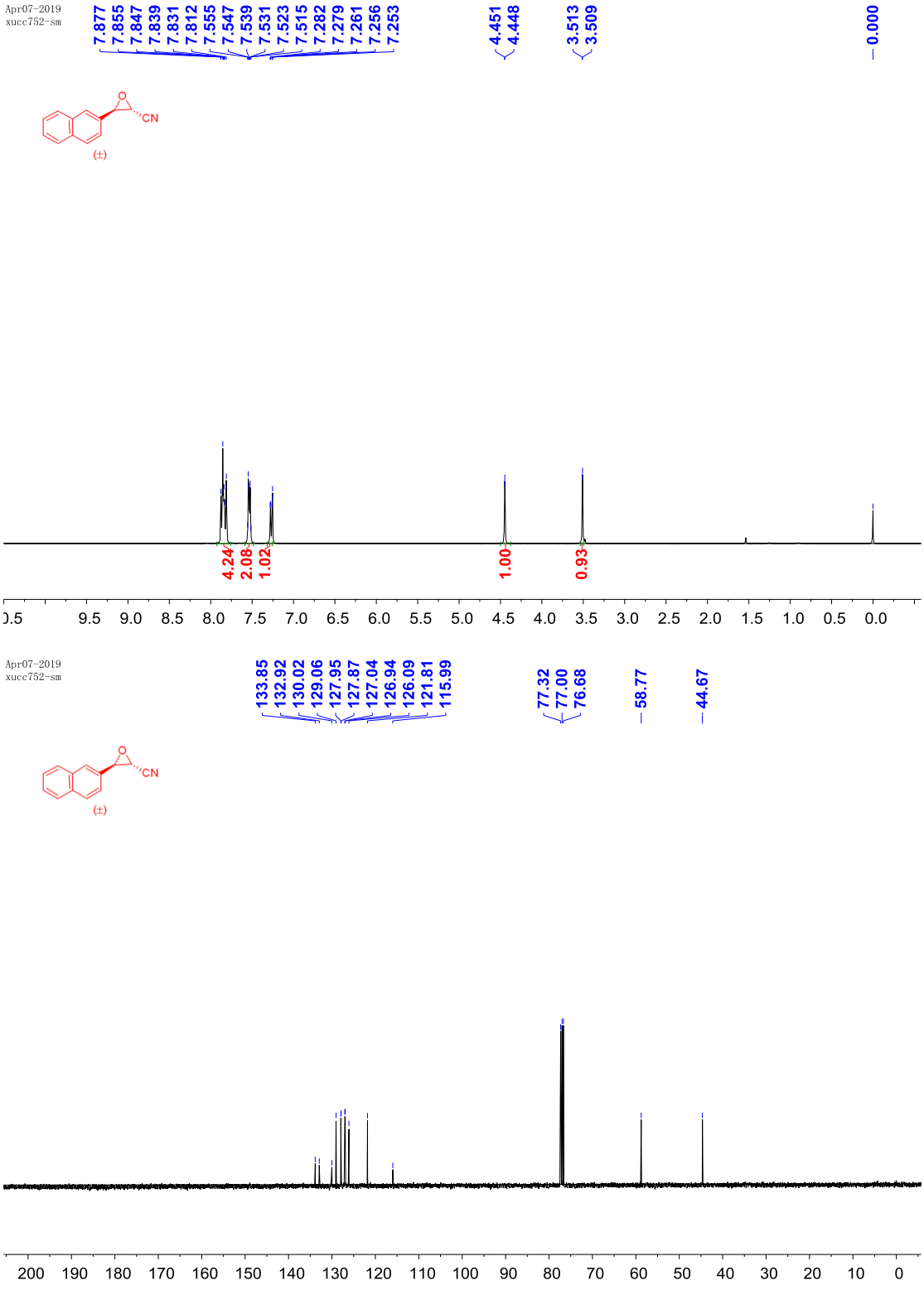

Aug28-2019
Xucc sm
135.00
132.88
130.47
128.50
124.39
123.06
115.55
77.32
77.00
76.68
57.53
44.54
CN
Br
(+/-)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

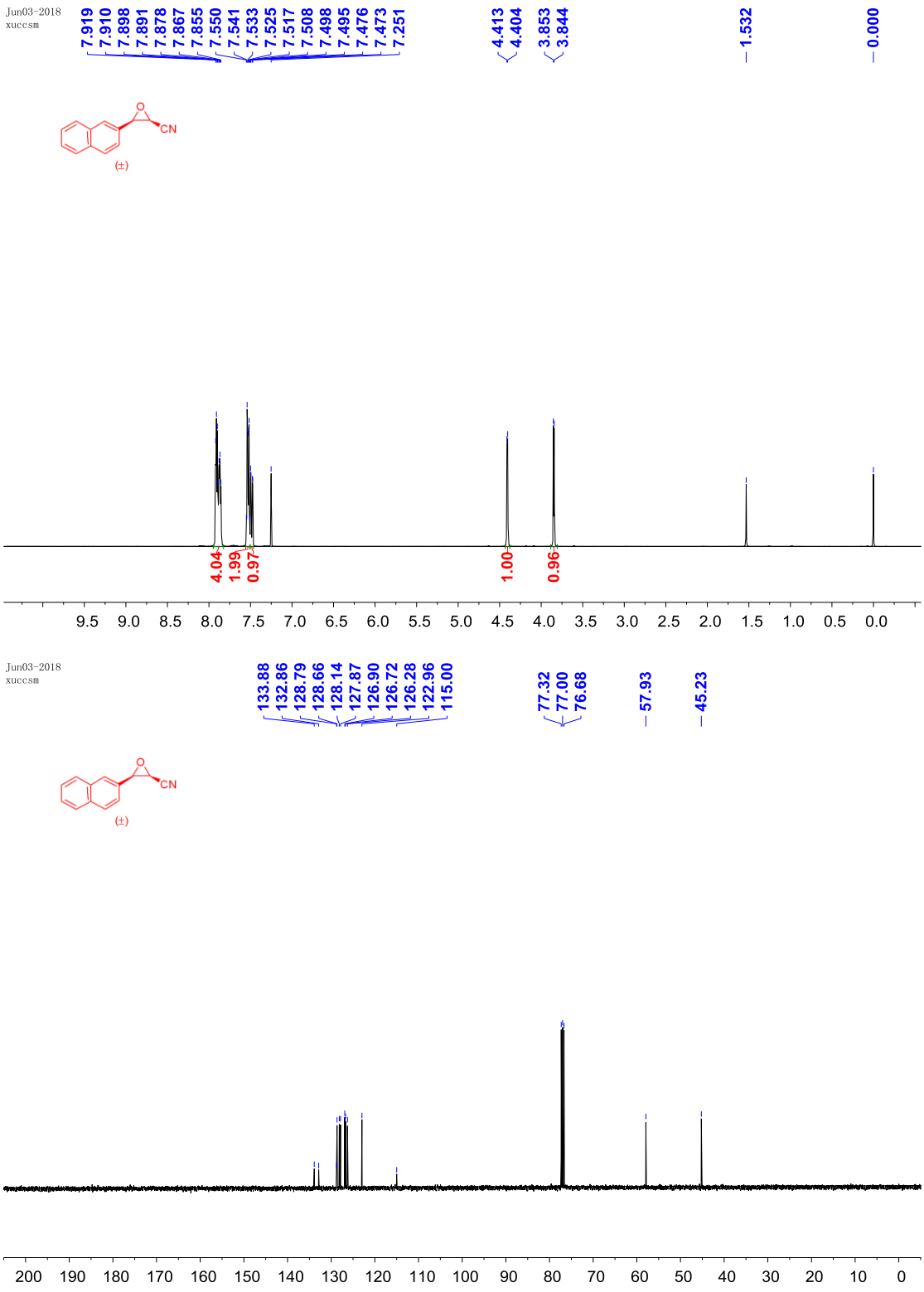
^{1}H and ^{13}C spectra of **1h**.



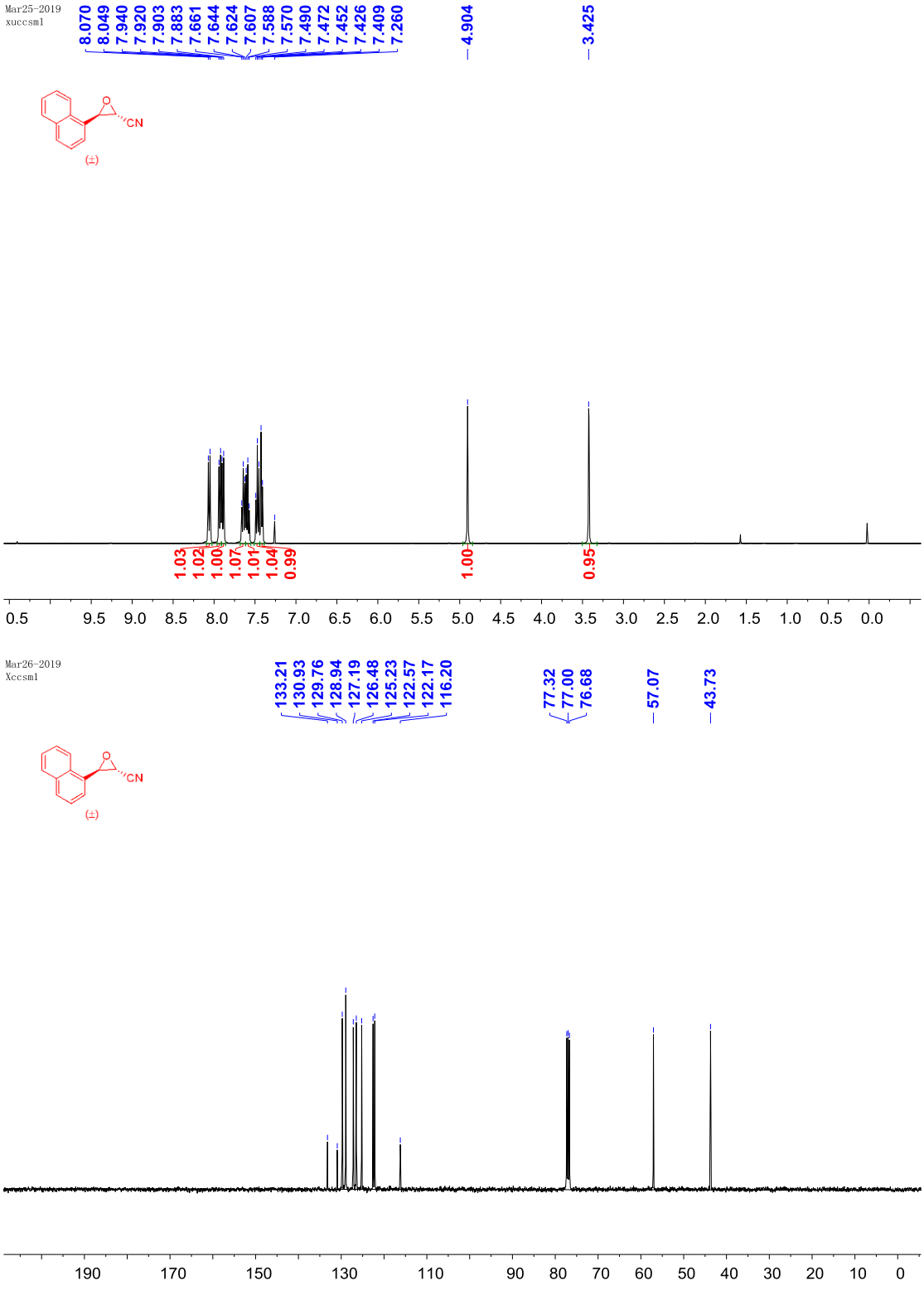


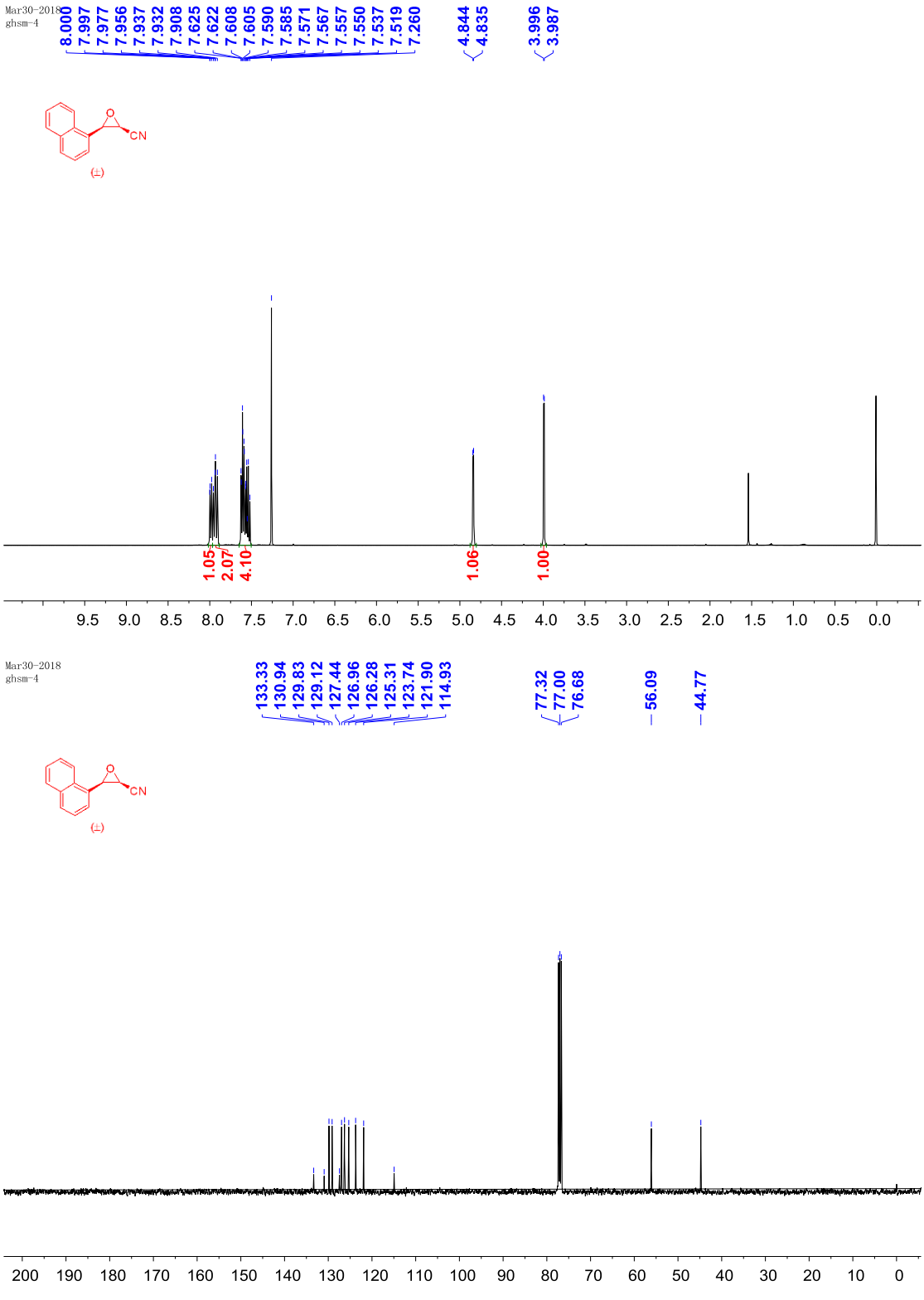
^{1}H and ^{13}C spectra of **1i**.



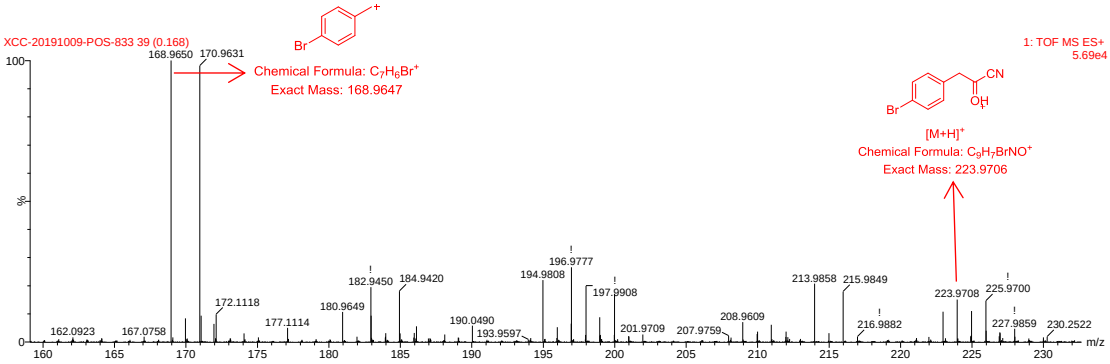

Jun03-2018
xuccsm
7.919
7.910
7.898
7.891
7.878
7.867
7.855
7.550
7.541
7.533
7.525
7.517
7.508
7.498
7.495
7.476
7.473
7.251
4.413
4.404
3.853
3.844
1.532
0.000
CN
(±)
4.04
1.99
0.97
1.00
0.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Jun03-2018
xuccsm
133.88
132.86
128.79
128.66
128.14
127.87
126.90
126.72
126.28
122.96
115.00
77.32
77.00
76.68
57.93
45.23
CN
(±)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

^{1}H and ^{13}C spectra of **1j**.



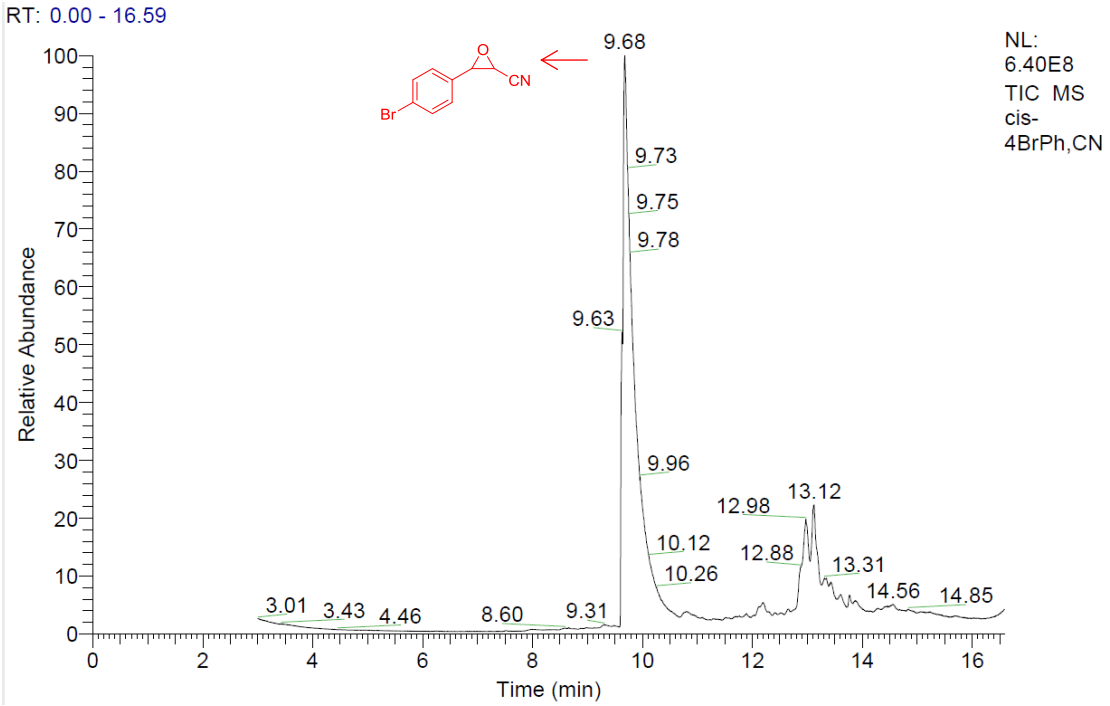

Mar30-2018
ghsm-4
8.000
7.997
7.977
7.956
7.937
7.932
7.908
7.625
7.622
7.608
7.605
7.590
7.585
7.571
7.567
7.557
7.550
7.537
7.519
7.260
4.844
4.835
3.996
3.987
CN
(±)
1.05
2.07
4.10
1.06
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Mar30-2018
ghsm-4
133.33
130.94
129.83
129.12
127.44
126.96
126.28
125.31
123.74
121.90
114.93
77.32
77.00
76.68
56.09
44.77
CN
(±)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

HRMS of **6a**.

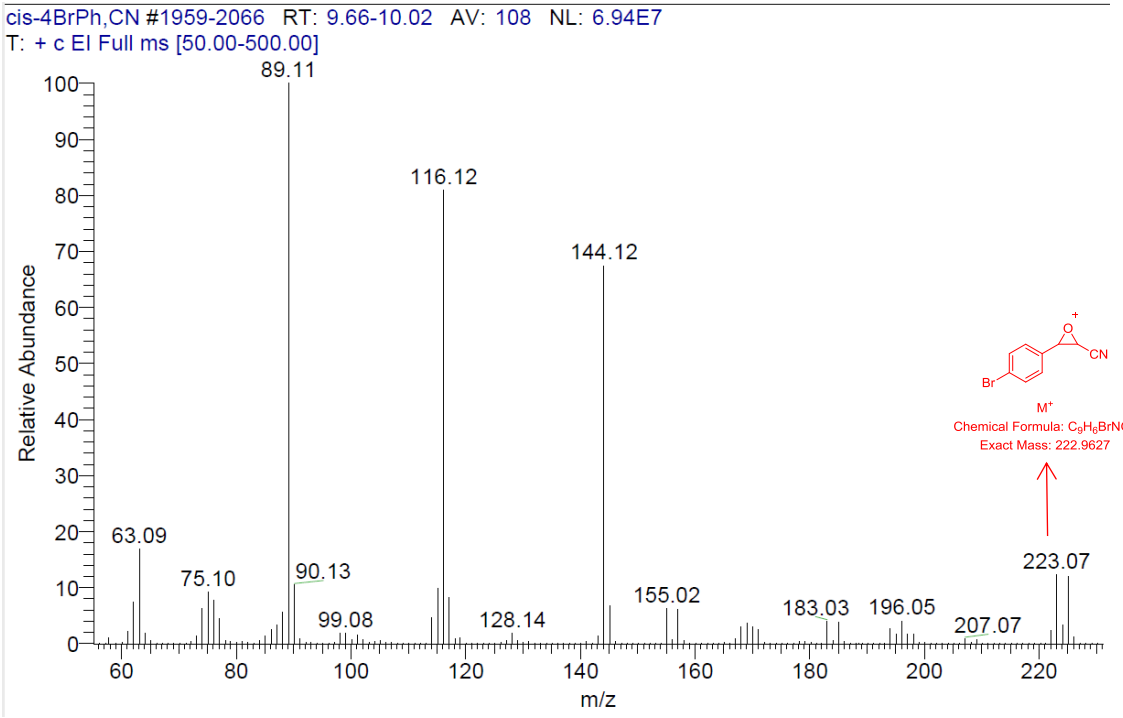


GC-MS of **1a**.

GC profile of **1a**

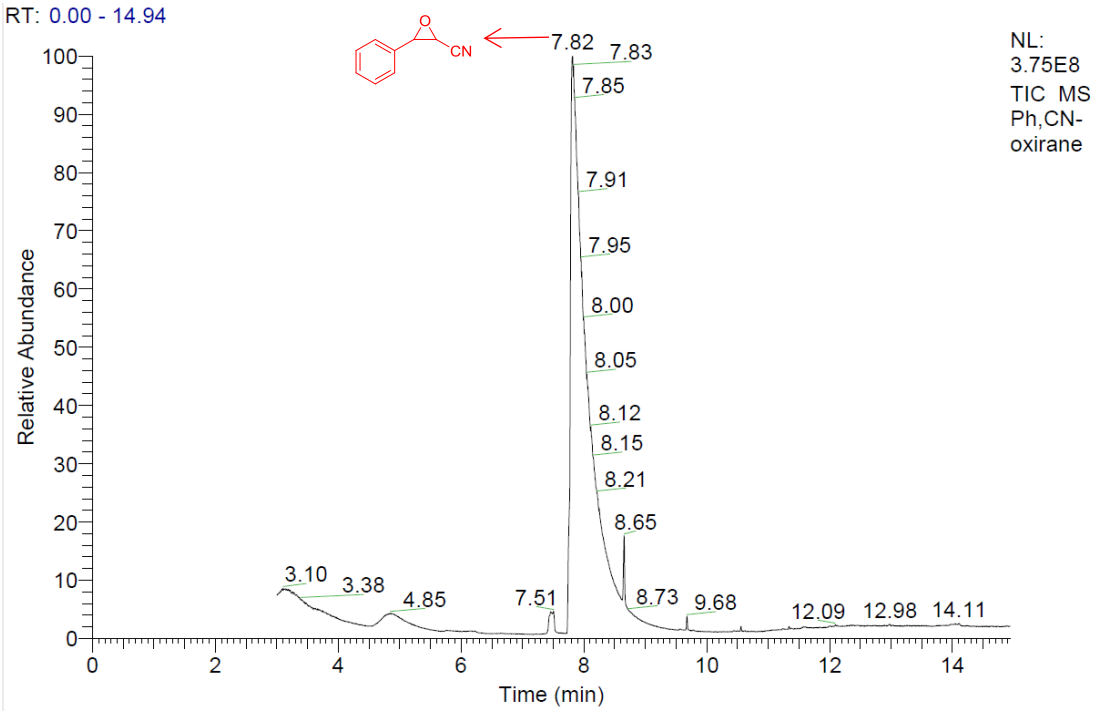


EI MS of **1a**

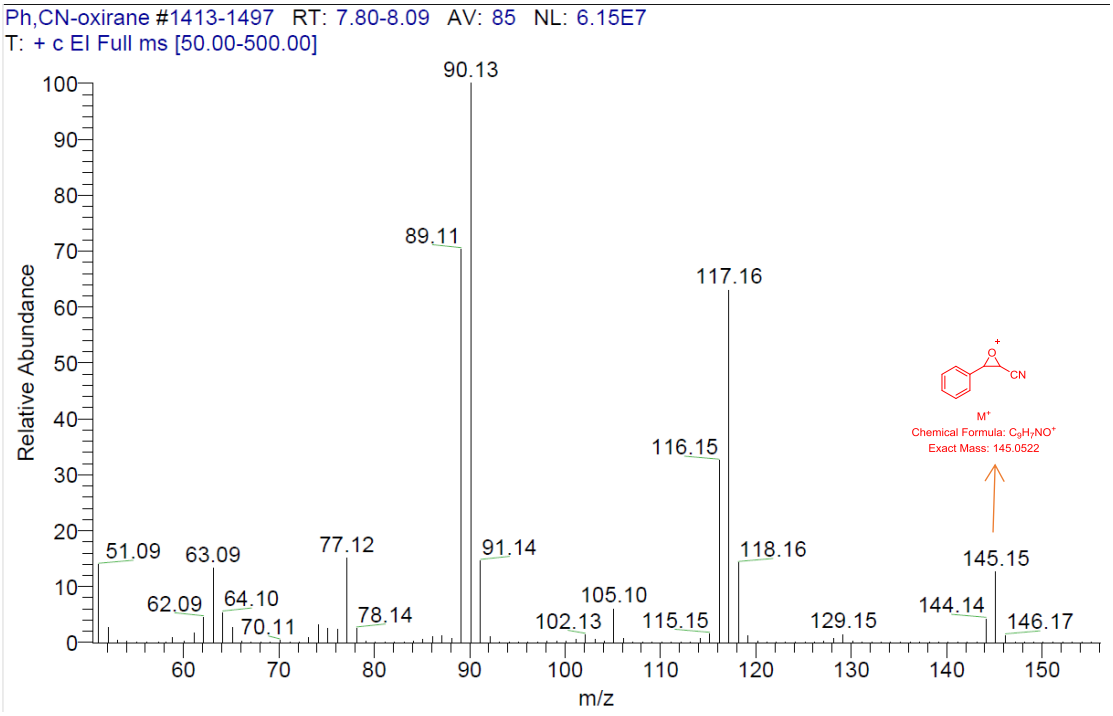


GC-MS of **1b**.

GC profile of **1b**

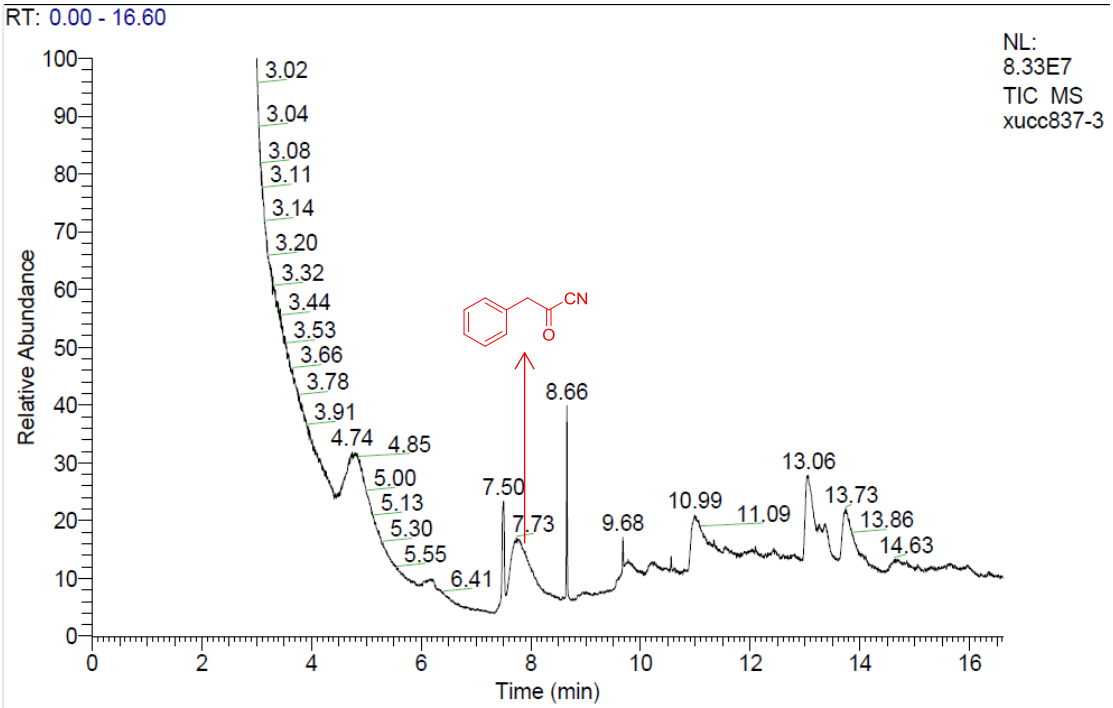


EI MS of **1b**

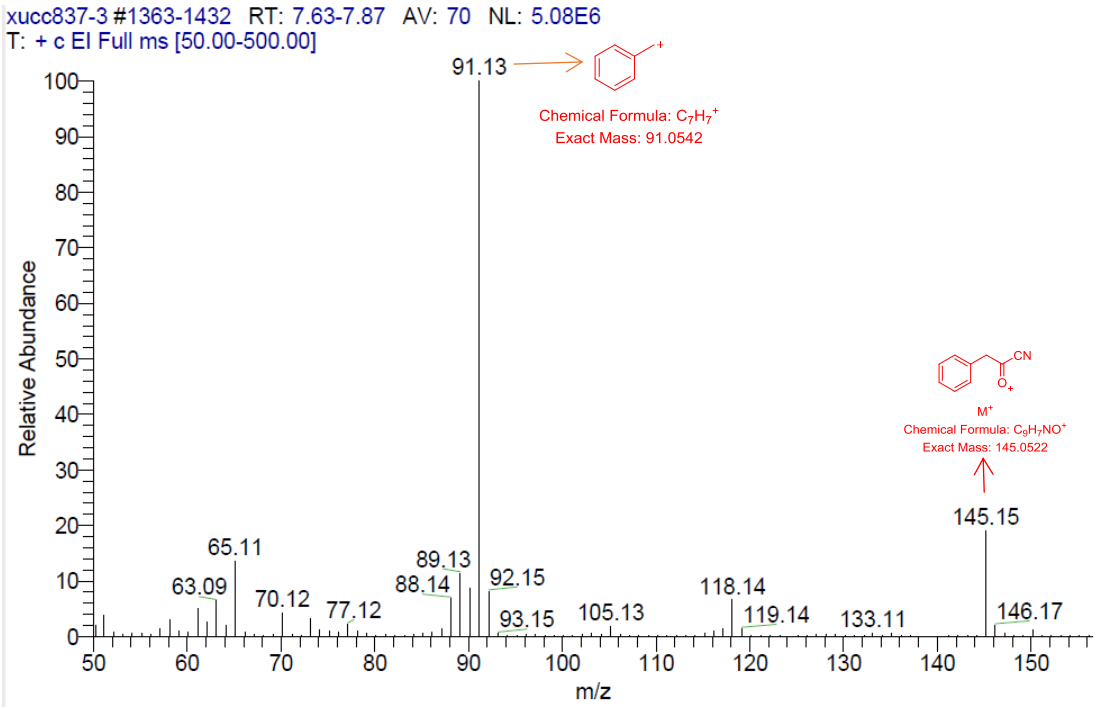


GC-MS of **6b**.

GC profile of **6b**



EI MS of **6b**


xucc837-3 #1363-1432 RT: 7.63-7.87 AV: 70 NL: 5.08E6
T: + c EI Full ms [50.00-500.00]
91.13
Chemical Formula: C7H7+
Exact Mass: 91.0542
M+
Chemical Formula: C9H7NO+
Exact Mass: 145.0522
145.15
65.11
63.09
70.12
77.12
89.13
88.14
92.15
93.15
105.13
118.14
119.14
133.11
146.17
Relative Abundance
m/z