Supporting Information

A KI-Mediated Radical Anti-Markovnikov Addition of Simple Ketones/Esters to Unactivated Alkenes

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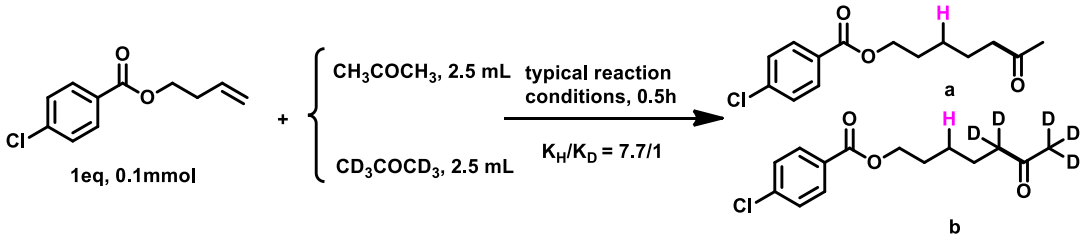
General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. Electron paramagnetic resonance (EPR) data were measured on a Bruker A300 EPR spectrometer (X-band). All products were identified by ^{1}H and ^{13}C NMR, MS, HRMS, and Element Analysis. The starting materials were purchased from Energy Chemicals, Alfa Aesar, Acros Organics, J&K Chemicals, Adamas, or Aldrich and used without further purification.

Typical procedure

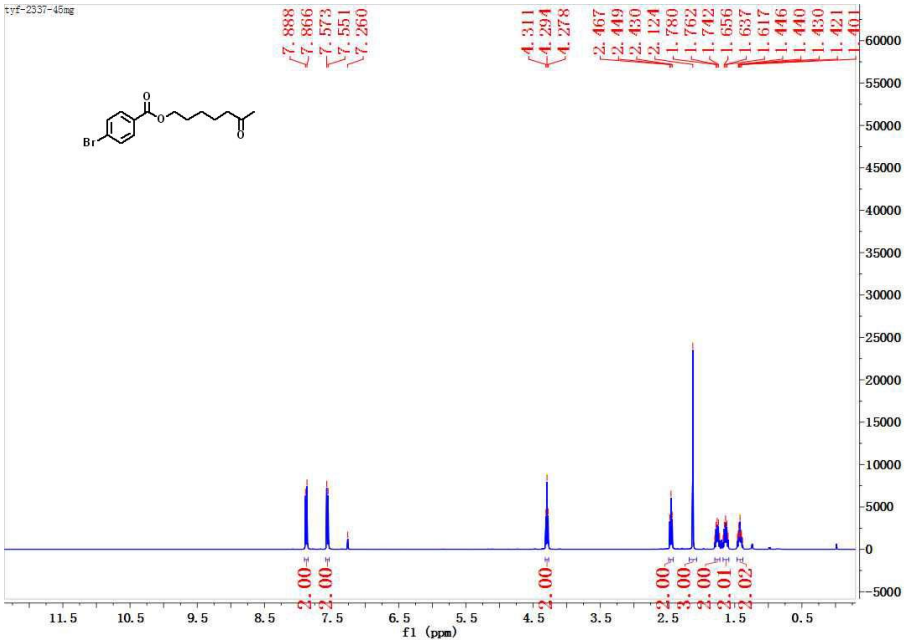
Reaction of ester with alkenes: A mixture of alkenes (1 equiv., 0.10 mmol), *tert*-butyl acetate (5 mL), KI (5 mol%, 0.005 mmol), and DTBP (3 equiv., 0.30 mmol) was heated at 130 ^{o}C (the measured temperature of the oil bath) for 8 hrs in a sealed tube (35 mL). After the reaction finished, the solvent was recycled and the residue was purified by column chromatography to afford the desired product.

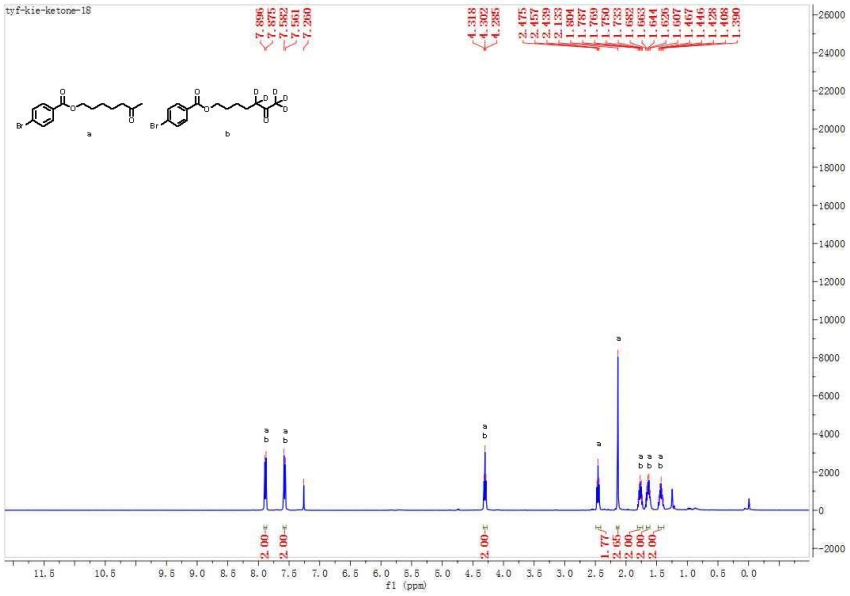
Competing Kinetic Isotope Effect (KIE) Experiment:



Conversion 27%, a(yield, 23.9%), b(yield, 3.1%)

^{1}H NMR





Note: The value of k_H/k_D was calculated from the ^{1}H NMR spectra above which should be the mixture of compound **a** and **b** (the KIE scheme). The sum of the integral of **a** and **b** at chemical shift 4.29 – 4.32 was integrated as 2.00 (both **a** and **b** keep the same double bond hydrogen). Compound **a** has 2 hydrogen atoms at chemical shift 2.44 – 2.48, while **b** has no H atoms. The amount of **a** could be defined as 1.77, on the other hand, the sum of **a** and **b** is 2.00, so the amount of **b** is 0.23 (2.00 – 1.77 = 0.23). As a result, k_H / k_D=1.77 / 0.23 = 7.7.

Physical data and references for the following products:

All known compounds are determined by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

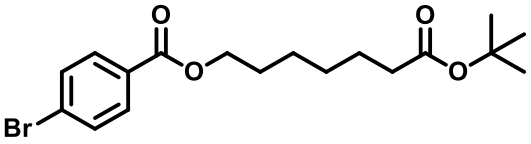
References:

1. J. Xie, Z-Z. Huang, *Chem. Commun.* 2010, **46**, 1947.
2. D. Tsukamoto, Y. Shiraishi, T. Hirai, *J. Org. Chem.* 2010, **75**, 1450.
3. B. Schweitzer-Chaput, J. Demaerel, H. Engler, M. Klussmann, *Angew. Chem. Int. Ed.* 2014, **53**, 8737.
4. X.-L. Lan, N.-X. Wang, W. Zhang, J.-L. Wen, C.-B. Bai, Y. Xing, Y.-H. Li, *Org. Lett.*, 2015, **17**, 4460.
5. X.-Q. Chu, H. Meng, Y. Zi, X.-P. Xu, S.-J. Ji, *Chemistry - A European Journal,* 2014, **20**, 17198.
6. Z.-J. Li, Y.-X. Xiao, Z.-Q. Liu, *Chem. Commun.* 2015, **51**, 9969.

Physical data for the following products:

1a. 7-(tert-butoxy)-7-oxoheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1).

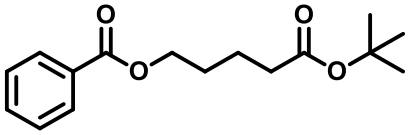


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 6.8 Hz, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.64 – 1.57 (m, 2H), 1.43 (s, 9H), 1.47 – 1.35 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 165.9, 131.6, 131.1, 129.3, 127.9, 80.0, 65.2, 35.4, 28.7, 28.5, 28.1, 25.7, 24.9.

HRMS (ESI, m/z): Calculated for $C_{18}H_{25}Br_1O_4$ $(M+Na)^+$ 407.0828, found 407.0825.

2a. 5-(tert-butoxy)-5-oxopentyl benzoate



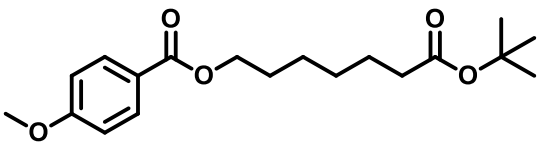
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 8.02 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 6.0 Hz, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.71 (m, 4H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $cdcl_3$): δ 172.6, 166.5, 132.8, 130.4, 129.5, 128.3, 80.2, 64.5, 35.0, 28.1, 28.1, 21.7.

HRMS (ESI, m/z): Calculated for $C_{16}H_{22}O_4$ $(M+ Na)^+$ 301.1410, found 301.1411.

3a. 7-(tert-butoxy)-7-oxoheptyl 4-methoxybenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



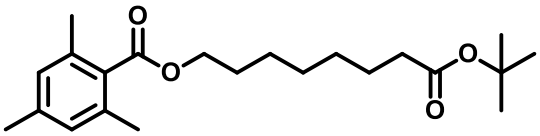
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.65 – 1.57 (m, 2H), 1.44 (s, 9H), 1.47 – 1.36 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 166.4, 163.2, 131.5, 122.9, 113.5, 80.0, 64.6, 55.4, 35.5, 29.7, 28.7, 28.6, 28.1, 25.8, 25.0.

HRMS (ESI, m/z): Calculated for $C_{19}H_{28}O_5$ $(M+Na)^+$ 359.1829, found 359.1832.

4a. 8-(tert-butoxy)-8-oxooctyl 2,4,6-trimethylbenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



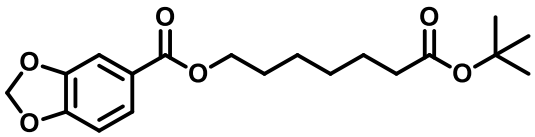
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 2.28 (s, 6H), 2.27 (s, 3H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.69 (m, 2H), 1.61 – 1.54 (m, 2H), 1.44 (s, 9H), 1.40 – 1.32 (m, 6H).

^{13}C NMR (100 MHz, $cdcl_3$): δ 173.2, 170.3, 139.1, 135.0, 131.2, 128.3, 79.9, 64.9, 35.5, 28.9, 28.9, 28.6, 28.1, 25.9, 25.0, 21.1, 19.7.

HRMS (ESI, m/z): Calculated for $C_{22}H_{34}O_4$ $(M+Na)^+$ 385.2349, found 385.2353.

5a. 7-(tert-butoxy)-7-oxoheptyl benzo[d][1,3]dioxole-5-carboxylate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



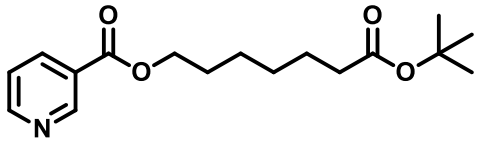
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 4.27 (t, *J* = 6.8 Hz, 2H), 2.22 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.65 – 1.57 (m, 2H), 1.44 (s, 9H), 1.48 – 1.37 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 166.0, 151.5, 147.7, 125.2, 124.5, 109.5, 107.9, 101.7, 80.0, 64.9, 35.5, 28.7, 28.6, 28.1, 25.8, 25.0.

HRMS (ESI, m/z): Calculated for $C_{19}H_{26}O_6$ $(M+Na)^+$ 373.1622, found 373.1630.

6a. 7-(tert-butoxy)-7-oxoheptyl nicotinate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



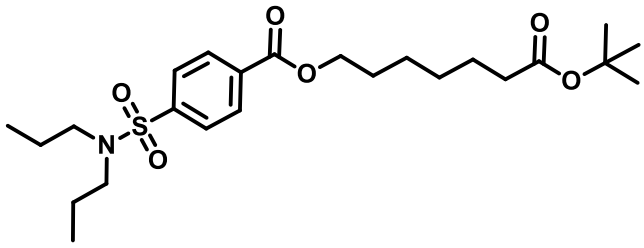
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.75 (d, *J* = 3.6 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.32 (t, *J* = 6.8 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.63 – 1.55 (m, 2H), 1.48 – 1.37 (m, 4H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 165.2, 153.3, 150.8, 136.9, 123.2, 80.0, 65.4, 35.4, 29.6, 28.6, 28.4, 28.1, 25.7, 24.9.

HRMS (ESI, m/z): Calculated for $C_{17}H_{25}N_1O_4$ $(M+Na)^+$ 330.1678, found 330.1680.

7a. 7-(tert-butoxy)-7-oxoheptyl 4-(N,N-dipropylsulfamoyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1).



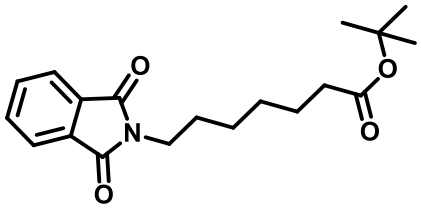
^{1}H NMR (400 MHz, $CDCl_3$):δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 4.34 (t, *J* = 6.8 Hz, 2H), 3.11 – 3.07 (m, 4H), 2.22 (t, *J* = 7.6 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.65 – 1.49 (m, 6H), 1.48 – 1.38 (m, 4H), 1.43 (s, 9H), 0.86 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 165.3, 144.1, 133.7, 130.1, 126.9, 80.0, 65.6, 49.9, 35.4, 28.7, 28.5, 28.1, 25.7, 24.9, 21.9, 11.1.

HRMS (ESI, m/z): Calculated for $C_{24}H_{39}NO_6S(M+Na)^+$ 492..2390, found 492.2397.

8a. tert-butyl 7-(1,3-dioxoisoindolin-2-yl)heptanoate

A colorless solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



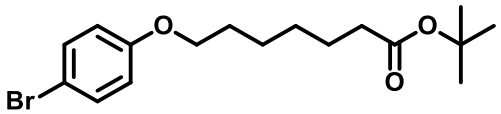
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.70 (dd, *J* = 5.6, 3.2 Hz, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.19 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.65 (m, 2H), 1.58 – 1.55 (m, 2H), 1.42 (s, 9H), 1.36 – 1.33 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 168.4, 133.8, 132.2, 123.1, 80.0, 37.9, 35.5, 28.6, 28.5, 28.1, 26.6, 24.9.

HRMS (ESI, m/z): Calculated for $C_{19}H_{25}N_1O_4N(M+Na)^+$ 354.1676, found 354.1673.

9a. tert-butyl 7-(4-bromophenoxy)heptanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



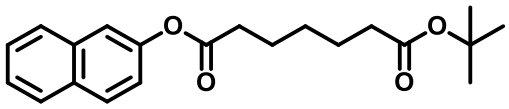
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 9.2 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.65 – 1.57 (m, 2H), 1.44 (s, 9H), 1.50 – 1.33 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 157.7, 129.2, 125.2, 115.7, 79.9, 68.1, 35.4, 29.0, 28.7, 28.1, 25.7, 24.9.

HRMS (ESI, m/z): Calculated for $C_{17}H_{25}BrO_3(M+H)^+$ 357.1060, found 357.1063.

10a. 1-tert-butyl 7-naphthalen-2-yl heptanedioate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



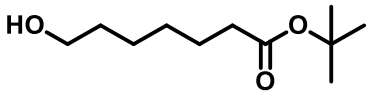
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.84 (m, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.51 – 7.44(m, 2H), 7.22 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.68 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.52 – 1.46 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$):δ 173.0, 172.2, 148.4, 133.8, 131.4, 129.3, 127.7, 127.6, 126.5, 125.6, 121.2, 118.5, 80.1, 35.4, 34.3, 28.6, 28.1, 24.7, 24.6.

HRMS (ESI, m/z): Calculated for $C_{21}H_{26}O_4$ $(M+Na)^+$ 365.1723, found 365.1711.

11a. tert-butyl 7-hydroxyheptanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



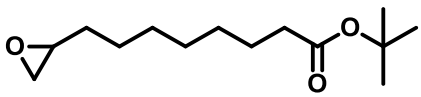
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (t, *J* = 6.8 Hz, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.56 (m, 4H), 1.44 (s, 9H), 1.37 – 1.35 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 80.0, 62.9, 35.5, 32.6, 28.8, 28.1, 25.4, 25.0.

HRMS (ESI, m/z): Calculated for $C_{11}H_{22}O_3(M+Na_1)^+$ 225.1461, found 225.1458.

12a. tert-butyl 8-(oxiran-2-yl)octanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1).



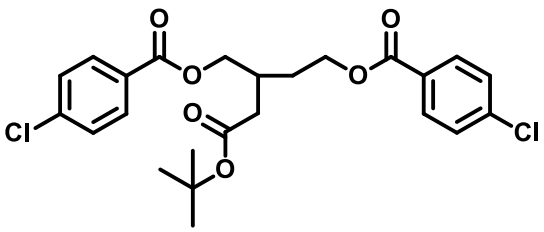
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 – 2.84 (m, 1H), 2.70 (t, *J* = 4.4 Hz, 1H), 2.42 (dd, *J* = 4.8, 2.4 Hz, 1H), 2.17 (t, *J* = 7.6 Hz, 2H), 1.57 – 1.44 (m, 6H), 1.41 (s, 9H), 1.33 – 1.25 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 79.8, 52.4, 47.0, 35.5, 32.4, 29.2, 29.1, 29.0, 28.1, 25.8, 25.0.

HRMS (ESI, m/z): Calculated for $C_{14}H_{26}O_3(M+Na)^+$ 265.1774, found 265.1771.

13a. 2-(2-(tert-butoxy)-2-oxoethyl)butane-1,4-diyl bis(4-chlorobenzoate)

A colorless solid after purification by flash column chromatography (petroleum ether/ethyl acetate =20/1).



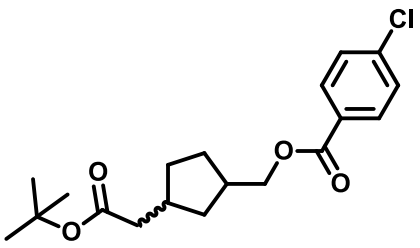
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 4 H), 7.40 (dd, *J* = 8.0, 4.4 Hz, 4H), 4.44 (dd, *J* = 12.0, 6.0 Hz, 2H), 4.36 (d, *J* = 5.2 Hz, 2H), 2.56 – 2.53 (m, 1H), 2.49 – 2.37 (m, 2H), 1.96 (dt, *J* = 14.0, 6.8 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 165.6, 165.5, 139.6, 139.5, 130.9, 128.8, 128.7, 128.5, 128.4, 81.0, 66.9, 62.9, 37.6, 32.4, 30.3, 28.1.

HRMS (ESI, m/z): Calculated for $C_{24}H_{26}Cl_2O_6$ $(M+Na)^+$ 503.0999, found 503.1007.

14a. (3-(2-(tert-butoxy)-2-oxoethyl)cyclopentyl)methyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1)

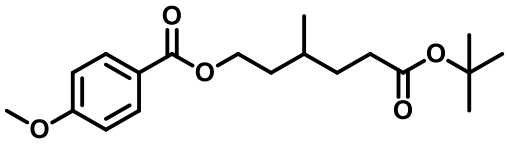


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 4.20 (d, *J* = 6.8 Hz, 2H), 2.51 – 2.40 (m, 1H), 2.39 – 2.31 (m, 1H), 2.25 (t, *J* = 7.6 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.74 – 1.69 (m, 1H), 1.44 (s, 9H), 1.52 – 1.22 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 165.8, 139.3, 130.9, 128.9, 128.7, 80.1, 69.0, 41.7, 37.5, 35.7, 35.1, 32.4, 29.2, 28.1.

HRMS (ESI, m/z): Calculated for $C_{19}H_{25}Cl_1O_4N(M+Na)^+$ 375.1334, found 375.1331.

15a. 6-(tert-butoxy)-3-methyl-6-oxohexyl 4-methoxybenzoate

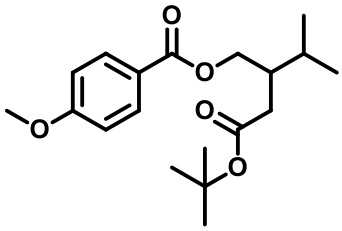


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.31 (td, *J* = 6.8, 2.0 Hz, 2H), 3.84 (s, 3H), 2.31 – 2.17 (m, 2H), 1.83 – 1.75 (m, 1H), 1.73 – 1.63 (m, 2H), 1.61 – 1.45 (m, 2H), 1.42 (s, 9H), 0.96 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, cdcl$_3$): δ 173.1, 166.3, 163.2, 131.5, 122.8, 113.5, 80.0, 62.9, 55.3, 35.4, 33.2, 31.9, 29.6, 28.0, 19.1.

HRMS (ESI, m/z): Calculated for $C_{19}H_{28}O_5$ (M+ K)$^+$ 375.1568, found 375.1567.

16a. 4-(tert-butoxy)-2-isopropyl-4-oxobutyl 4-methoxybenzoate



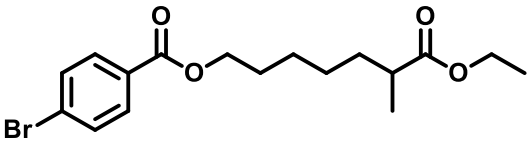
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.32 (dd, *J* = 11.2, 5.6 Hz, 1H), 4.24 (dd, *J* = 11.2, 6.0 Hz, 1H), 3.86 (s, 3H), 2.39 – 2.27 (m, 2H), 2.25 – 2.17 (m, 1H), 1.87 (td, *J* = 13.6, 6.8 Hz, 1H), 1.43 (s, 9H), 0.98 (d, *J* = 4.0 Hz, 3H), 0.96 (d, *J* = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, cdcl$_3$): δ 172.3, 166.3, 163.3, 131.6, 122.7, 113.6, 80.4, 65.3, 55.4, 40.4, 35.2, 28.8, 28.1, 19.6, 19.5.

HRMS (ESI, m/z): Calculated for $C_{19}H_{28}O_5$ (M+ Na)$^+$ 359.1829, found 359.1828.

17a. 7-ethoxy-6-methyl-7-oxoheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)

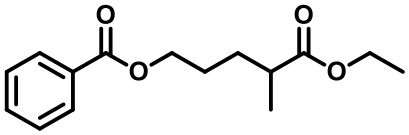


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.41 (dq, *J* = 14.0, 6.8 Hz, 1H), 1.79 – 1.70 (m, 2H), 1.69 – 1.63 (m, 1H), 1.47 – 1.40 (m, 5H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 165.9, 131.6, 131.0, 129.3, 127.9, 65.2, 60.1, 39.5, 33.6, 28.5, 26.9, 25.9, 17.1, 14.2.

HRMS (ESI, m/z): Calculated for $C_{17}H_{23}Br_1O_4$ $(M+Na)^+$ 393.0672, found 393.0677.

18a. 5-ethoxy-4-methyl-5-oxopentyl benzoate



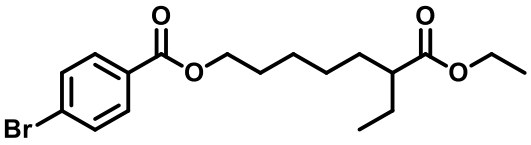
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 8.00 (m, 2H), 7.54 – 7.50 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 4.29 (t, *J* = 6.4, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.52 – 2.43 (m, 1H), 1.84 – 1.72 (m, 3H), 1.60 – 1.53 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $cdcl_3$): δ 176.2, 166.4, 132.7, 130.1, 129.4, 128.2, 64.6, 60.1, 39.1, 30.1, 26.4, 17.0, 14.1.

HRMS (ESI, m/z): Calculated for $C_{15}H_{20}O_4$ $(M+ Na)^+$ 287.1254, found 287.1257.

19a. 6-(ethoxycarbonyl)octyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



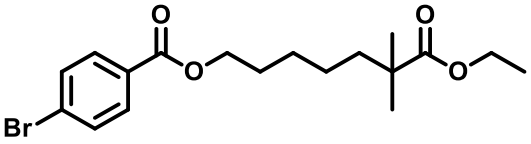
^{1}H NMR (400 MHz, $CDCl_3$):δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.25 (dq, *J* = 9.6, 5.6 Hz, 1H), 1.75 (dt, *J* = 14.0, 7.2 Hz, 2H), 1.68 – 1.56 (m, 2H), 1.55 – 1.38 (m, 4H), 1.37 – 1.31 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 165.7, 131.5, 131.0, 129.3, 127.8, 65.1, 59.9, 47.1, 31.8, 28.4, 27.0, 25.9, 25.4, 14.3, 11.7.

HRMS (ESI, m/z): Calculated for $C_{18}H_{25}Br_1O_4$ $(M+Na)^+$ 407.0828, found 407.0825.

20a. 7-ethoxy-6,6-dimethyl-7-oxoheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



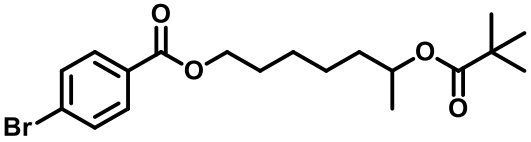
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.4 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.55 – 1.51 (m, 2H), 1.44 – 1.37 (m, 2H), 1.30 – 1.21 (m, 5H), 1.15 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 165.9, 131.6, 131.1, 129.3, 127.9, 65.2, 60.2, 42.1, 40.5, 28.5, 26.5, 25.1, 24.6, 14.2.

HRMS (ESI, m/z): Calculated for $C_{18}H_{25}Br_1O_4Na_1(M+Na)^+$ 407.0828, found 407.0822.

21a. 6-(pivaloyloxy)heptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).

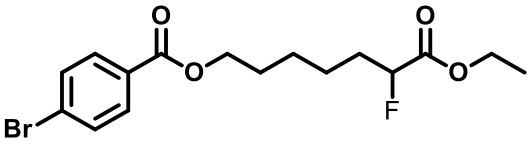


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 4.90 (dq, *J* = 12.8, 6.4 Hz, 1H), 4.32 (t, *J* = 6.4 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.68 – 1.36 (m, 6H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.20 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 165.9, 131.7, 131.1, 129.3, 127.9, 70.2, 65.2, 38.7, 35.7 28.6, 27.1, 25.9, 25.1, 19.9.

HRMS (ESI, m/z): Calculated for $C_{19}H_{27}Br_1O_4$ $(M+Na)^+$ 421.0985, found 421.0990.

22a. 7-ethoxy-6-fluoro-7-oxoheptyl 4-bromobenzoate



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.89 (dt, *J* = 50.0, 6.0 Hz, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.95 – 1.85 (m, 2H), 1.81 – 1.74 (m, 2H), 1.59 – 1.45 (m, 4H), 1.29 (t, *J* = 7.2 Hz, 3H).

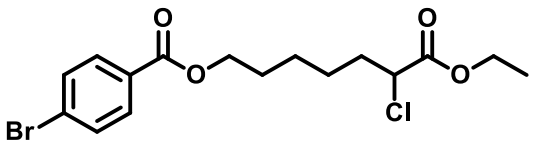
^{13}C NMR (100 MHz, $cdcl_3$): δ 169.8 (d, *J* = 23.7 Hz), 165.8, 131.6, 131.0, 129.2, 127.9, 89.0 (d, *J* = 184.9 Hz), 65.0 (s), 61.4, 32.21 (d, *J* = 21.1 Hz), 28.4, 25.6, 24.1 (d, *J* = 3.0 Hz), 14.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -191.86 – -192.25 (m, 1F).

HRMS (ESI,m/z): Calculated for $C_{16}H_{20}BrFO_4(M+NH_4)^+$ 392.0867, found 392.0868.

23a. 6-chloro-7-ethoxy-7-oxoheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)

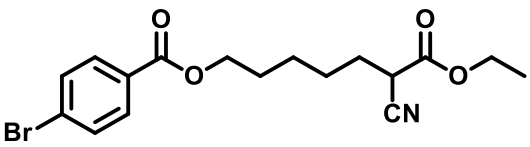


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 4.28 – 4.20 (m, 3H), 2.07 – 1.90 (m, 2H), 1.81 – 1.75 (m, 2H), 1.59 – 1.47 (m, 4H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 165.8, 131.7, 131.0, 129.2, 128.0, 65.0, 62.0, 57.2, 34.7, 28.4, 25.6, 25.4, 14.0.

HRMS (ESI, m/z): Calculated for $C_{16}H_{20}BrClO_4(M+Na)^+$ 413.0126, found 413.0131.

24a. **6-cyano-7-ethoxy-7-oxoheptyl 4-bromobenzoate**



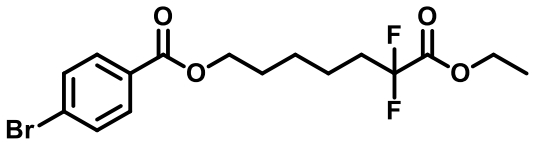
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 4.25 (q, *J* = 6.8 Hz, 2H), 3.50 (t, *J* = 6.8 Hz, 1H), 1.97 (dd, *J* = 14.8, 7.2 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.63 – 1.45 (m, 4H), 1.31 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 165.8, 131.7, 131.0, 129.2, 128.0, 116.4, 64.8, 62.8, 37.5, 29.6, 28.3, 26.5, 25.4, 14.0.

HRMS(ESI, m/z): Calculated for $C_{17}H_{20}BrNO_4$ $(M+Na)^+$ 404.0468, found 404.0460.

25a. 7-ethoxy-6,6-difluoro-7-oxoheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.34 – 4.28 (m, 4H), 2.15 – 2.03 (m, 2H), 1.82 – 1.73 (m, 2H), 1.61 – 1.43 (m, 4H), 1.34 (t, *J* = 7.2 Hz, 3H).

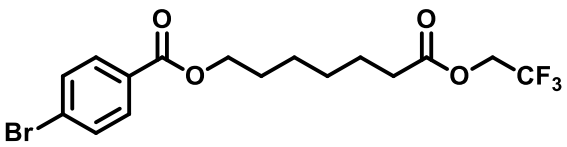
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 164.1 (t, *J* = 33.0 Hz), 131.7, 131.0, 129.1, 128.0, 116.1 (t, *J* = 251.0 Hz), 64.9, 62.8, 34.3 (t, *J* = 23.4 Hz), 28.4, 25.6, 21.2 (t, *J* = 4.3 Hz), 14.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -105.98 (t, *J* = 16.5 Hz, 2F).

HRMS(ESI, m/z): Calculated for $C_{16}H_{19}BrF_2O_4(M+NH_4)^+$ 410.0773, found 410.0772.

26a. 7-oxo-7-(2,2,2-trifluoroethoxy)heptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.46 (q, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.65 (m, 4H), 1.50 – 1.38 (m, 4H).

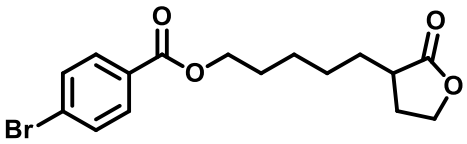
^{13}C NMR (100 MHz, $cdcl_3$): δ 172.0, 165.9, 131.7, 131.1, 129.3, 128.0, 122.98 (q, *J* = 278.5 Hz), 65.1, 60.2 (q, *J* = 36.7 Hz), 33.5, 28.6, 28.5, 25.7, 24.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.86 (t, *J* = 8.3 Hz, 3F).

HRMS (ESI, m/z): Calculated for $C_{16}H_{18}BrF_3O_4$ $(M+Na)^+$ 433.0233, found 433.0229.

27a. 5-(2-oxotetrahydrofuran-3-yl)pentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1).



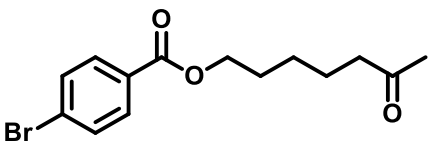
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.36 – 4.28 (m, 3H), 4.22 – 4.15 (m, 1H), 2.56 – 2.48 (m, 1H), 2.42 – 2.34 (m, 1H), 1.98 – 1.88 (m, 2H), 1.82 – 1.74 (m, 2H), 1.54 – 1.38 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 165.7, 131.5, 130.9, 129.1, 127.8, 66.4, 64.9, 39.0, 30.0, 28.5, 28.3, 26.8, 25.7.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}Br_1O_4$ $(M+Na)^+$ 377.0359 found 377.0355.

1b. 6-oxoheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



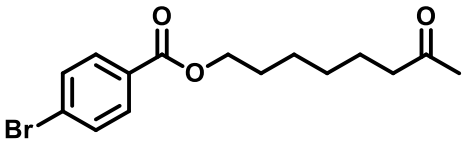
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.80 – 1.73 (m, 2H), 1.67 – 1.68 (m, 2H), 1.46 – 1.38 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.5, 165.8, 131.6, 131.0, 129.3, 127.9, 65.0, 43.4, 29.8, 28.5, 25.6, 23.3.

HRMS (ESI, m/z): Calculated for $C_{14}H_{17}BrO_3$ $(M+Na)^+$ 335.0253, found 335.0258.

2b. 7-oxooctyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



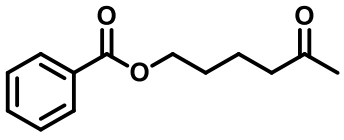
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 2.13 (s, 3H), 1.79 – 1.72 (m, 2H), 1.59 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.38 – 1.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 165.9, 131.6, 131.0, 129.3, 127.9, 65.2, 43.6, 29.9, 28.8, 28.5, 25.8, 23.6.

HRMS (ESI, m/z): Calculated for $C_{15}H_{19}Br_1O_3$ $(M+ Na)^+$ 349.0410, found 349.0414.

3b. 5-oxohexyl benzoate

A colorless after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



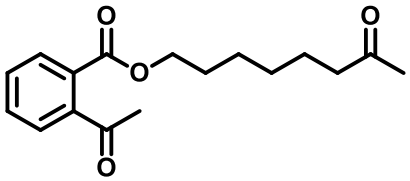
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 6.8 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 6.8 Hz, 2H), 2.13 (s, 3H), 1.80 – 1.71 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.2, 166.5, 132.8, 130.3, 129.5, 128.3, 64.4, 42.9, 29.8, 28.1, 20.2.8

HRMS (ESI, m/z): Calculated for $C_{13}H_{16}O_3$ $(M+NH_4)^+$ 238.1438, found 238.1437.

4b. 7-oxooctyl 2-acetylbenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



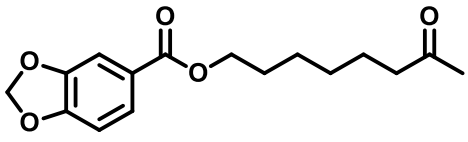
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.55 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 2.52 (s, 3H), 2.42 (t, *J* = 7.6 Hz, 2H), 2.12 (s, 3H), 1.76 – 1.68 (m, 2H), 1.61 – 1.54 (m, 2H), 1.44 – 1.28 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 202.9, 166.9, 142.7, 131.9, 129.9, 129.6, 129.0, 126.3, 65.6, 43.5, 30.1, 29.8, 28.7, 28.2, 25.7, 23.5.

HRMS (ESI, m/z): Calculated for $C_{17}H_{22}O_4$ $(M+H)^+$ 291.1591, found 291.1592.

5b. 7-oxooctyl benzo[d][1,3]dioxole-5-carboxylate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



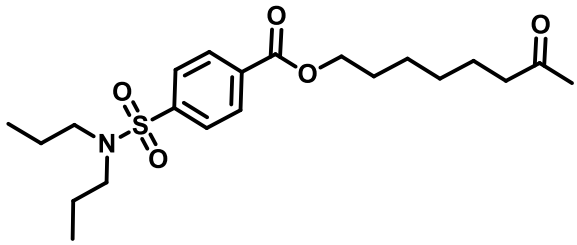
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.02 (s, 2H), 4.25 (t, *J* = 6.8 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.77 – 1.69 (m, 2H), 1.62 – 1.55 (m, 2H), 1.46 – 1.30 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 165.9, 151.4, 147.6, 125.2, 124.4, 109.4, 107.9, 101.7, 64.8, 43.6, 29.9, 28.7, 28.5, 25.8, 23.6.

HRMS (ESI, m/z): Calculated for $C_{16}H_{20}O_5$ $(M+Na)^+$ 315.1203, found 315.1207.

6b. 7-oxooctyl 4-(N,N-dipropylsulfamoyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



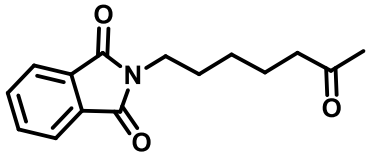
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 3.09 – 3.05 (m, 4H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.10 (s, 3H), 1.79 – 1.72 (m, 2H), 1.61 – 1.47 (m, 6H), 1.45 – 1.30 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.8, 165.2, 144.1, 133.7, 130.1, 126.9, 65.5, 49.9, 43.5, 29.8, 28.7, 28.4, 25.8, 23.5, 21.9, 11.1.

HRMS (ESI, m/z): Calculated for $C_{21}H_{33}NO_5S_1$ $(M+Na)^+$ 434.1972, found 434.1979.

7b. 2-(6-oxoheptyl)isoindoline-1,3-dione

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



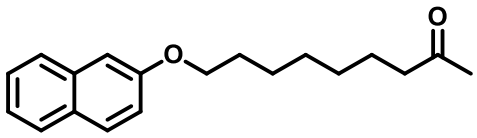
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.69 (dd, *J* = 5.6, 3.2 Hz, 2H), 3.65 (t, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.10 (s, 3H), 1.69 – 1.55 (m, 4H), 1.35 – 1.27 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 168.3, 133.8, 132.1, 123.1, 43.4, 37.7, 29.8, 28.3, 26.3, 23.2.

HRMS (ESI, m/z): Calculated for $C_{15}H_{17}N_1O_3$ $(M+Na)^+$ 282.1101, found 282.1096.

8b. 9-(naphthalen-2-yloxy)nonan-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



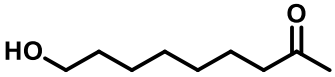
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.72 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 11.2, 2.4 Hz, 2H), 4.07 (t, *J* = 6.4 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.88 – 1.81 (m, 2H), 1.64 – 1.57 (m, 2H), 1.55 – 1.48 (m, 2H), 1.44 – 1.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 157.0, 157.0, 134.6, 129.2, 128.8, 127.6, 126.6, 126.2, 123.4, 118.9, 106.5, 67.9, 43.7, 29.8, 29.1, 29.1, 29.0, 25.9, 23.7.

HRMS(ESI,m/z): Calculated for $C_{19}H_{24}O_2$ $(M+H)^+$ 285.1849, found 285.1848.

9b. 9-hydroxynonan-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



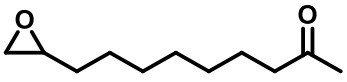
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (t, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 7.6 Hz, 2H), 2.09 (s, 3H), 2.02 (s, 1H), 1.56 – 1.47 (m, 4H), 1.35 – 1.21 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.5, 62.7, 43.6, 32.5, 29.8, 29.1, 29.0, 25.4, 23.6.

HRMS (ESI, m/z): Calculated for $C_9H_{18}O_2$ $(M+ Na)^+$ 181.1199, found 181.1202.

10b. 9-(oxiran-2-yl)nonan-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



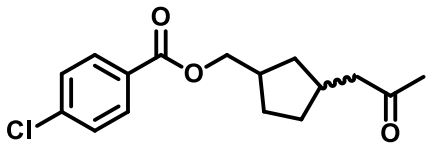
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.87 – 2.83 (m, 1H), 2.71 – 2.68 (m, 1H), 2.41 (dd, *J* = 5.2, 2.8 Hz, 1H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.08(s, 3H),1.55 – 1.20 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.2, 52.2, 47.0, 43.6, 32.3, 29.8, 29.2, 29.1, 28.9, 25.8, 23.6.

HRMS (ESI, m/z): Calculated for $C_{11}H_{20}O_2$ $(M+ Na)^+$ 207.1366, found 207.1369.

11b. (3-(2-oxopropyl)cyclopentyl)methyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)

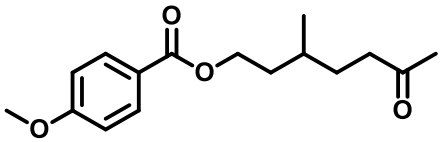


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 4.21 – 4.17 (m, 2H), 2.50 – 2.36 (m, 4H), 2.13 (s, 3H), 1.96 – 1.87 (m, 2H), 1.76 – 1.69 (m, 1H), 1.43 – 1.30 (m, 2H), 1.22 – 1.12 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 165.8, 139.2, 130.9, 128.8, 128.6, 68.9, 49.8, 37.4, 35.2, 34.4, 32.6, 30.1, 29.1.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}Cl_1O_3$ $(M+Na)^+$ 317.0915, found 317.0912.

12b. 3-methyl-6-oxoheptyl 4-methoxybenzoate

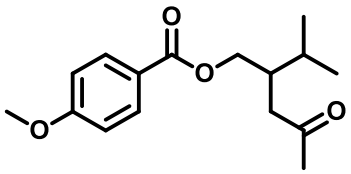


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 4.35 – 4.25 (m, 2H), 3.83 (s, 3H), 2.51 – 2.37 (m, 2H), 2.11 (s, 3H), 1.81 – 1.73 (m, 1H), 1.70 – 1.41 (m, 4H), 0.94 (d, *J* = 5.6 Hz, 3H).

^{13}C NMR (100 MHz, cdcl$_3$): δ 208.8, 166.3, 163.2, 131.4, 122.7, 113.5, 62.8, 55.3, 41.2, 35.3, 30.5, 29.8, 29.6, 19.2.

HRMS (ESI, m/z): Calculated for $C_{16}H_{22}O_4$ $(M+ K)^+$ 317.1150, found 317.1149.

13b. 2-isopropyl-4-oxopentyl 4-methoxybenzoate



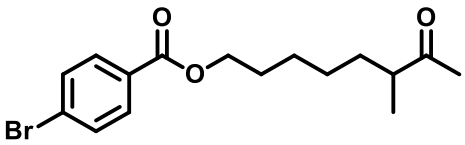
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.31 (dd, *J* = 11.2, 5.6 Hz, 1H), 4.17 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.86 (s, 3H), 2.50 (d, *J* = 6.4 Hz, 2H), 2.41 – 2.33 (m, 1H), 2.15 (s, 3H), 1.88 – 1.80 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, cdcl$_3$): δ 208.0, 166.3, 163.4, 131.5, 122.6, 113.6, 65.8, 55.4, 43.2, 39.1, 30.5, 28.9, 19.7, 19.5.

HRMS (ESI, m/z): Calculated for $C_{16}H_{22}O_4$ $(M+K)^+$ 317.1150, found 317.1149.

14b[1]. 6-methyl-7-oxooctyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



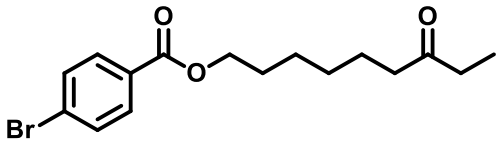
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 2.53 – 2.46 (m, 1H), 2.13 (s, 3H), 1.78 – 1.63 (m, 3H), 1.46 – 1.29 (m, 5H), 1.08 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6, 165.9, 131.7, 131.1, 129.3, 127.9, 65.2, 47.1, 32.7, 28.5, 28.0, 26.9, 26.1, 16.3.

HRMS (ESI, m/z): Calculated for $C_{16}H_{21}Br_1O_3$ $(M+Na)^+$ 363.0566, found 363.0573.

14b[2]. 7-oxononyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



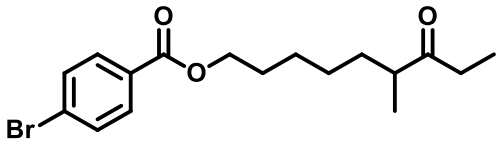
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 2.44 – 2.39 (m, 4H), 1.79 – 1.72 (m, 2H), 1.64 – 1.57 (m, 2H), 1.48 – 1.31 (m, 4H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6, 165.9, 131.7, 131.1, 129.4, 127.9, 65.2, 42.2, 35.9, 28.9, 28.5, 25.9, 23.7, 7.8.

HRMS (ESI, m/z): Calculated for $C_{16}H_{21}BrO_3$ $(M+NH_4)^+$ 358.1012, found 358.1014.

15b. 6-methyl-7-oxononyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



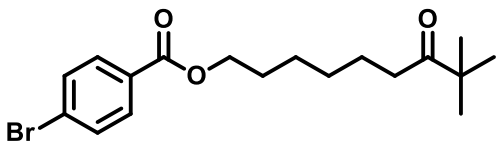
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 2.55 – 2.38 (m, 3H), 1.77 – 1.62 (m, 3H), 1.44 – 1.25 (m, 5H), 1.07 – 1.01 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.4, 165.9, 131.6, 131.0, 129.2, 127.9, 65.2, 46.0, 34.3, 32.9, 28.5, 27.0, 26.1, 16.6, 7.8.

HRMS (ESI, m/z): Calculated for $C_{17}H_{23}Br_1O_3$ $(M+Na)^+$ 377.0723, found 377.0724.

16b. 8,8-dimethyl-7-oxononyl 4-bromobenzoate

A colorless after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



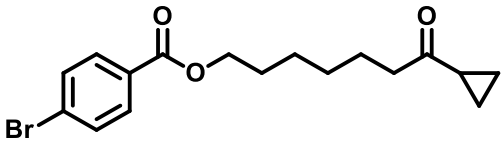
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.56 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.43 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.31 (dt, *J* = 14.8, 8.0 Hz, 2H), 1.11 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 216.0, 165.9, 131.6, 131.0, 129.2, 127.9, 65.2, 44.0, 36.2, 28.9, 28.5, 26.3, 25.9, 23.7.

HRMS (ESI, m/z): Calculated for $C_{18}H_{25}Br_1O_3$ $(M+Na)^+$ 391.0879, found 391.0884.

17b. 7-cyclopropyl-7-oxoheptyl 4-bromobenzoate

A colorless after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



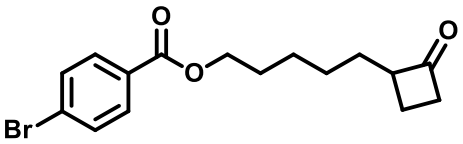
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.93 – 1.87 (m, 1H), 1.78 – 1.70 (m, 2H), 1.62 (dt, *J* = 14.4, 7.2 Hz, 2H), 1.47 – 1.29 (m, 4H), 0.98 – 0.93 (m, 2H), 0.85– 0.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.0, 165.8, 131.6, 131.0, 129.2, 127.9, 65.2, 43.3, 28.8, 28.4, 25.8, 23.7, 20.3, 10.6.

HRMS (ESI, m/z): Calculated for $C_{17}H_{21}Br_1O_3$ $(M+Na)^+$ 375.0566, found 375.0572.

18b. 5-(2-oxocyclobutyl)pentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.31 – 3.21 (m, 1H), 3.05 – 2.95 (m, 1H), 2.93 – 2.84 (m, 1H), 2.15 (ddd, *J* = 21.2, 10.4, 5.2 Hz, 1H), 1.75 – 1.57 (m, 4H), 1.53 – 1.36 (m, 4H), 1.23 – 1.89 (m, 1H).

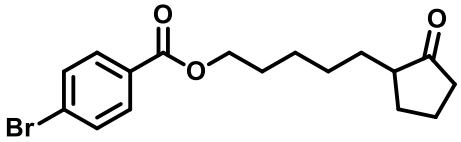
^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 165.8, 131.6, 131.0, 129.2, 127.8, 65.1, 60.2, 44.4,

29.3, 28.4, 26.6, 25.8, 16.8.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}Br_1O_3$ $(M+Na)^+$ 361.0410, found 361.0417.

19b. 5-(2-oxocyclopentyl)pentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



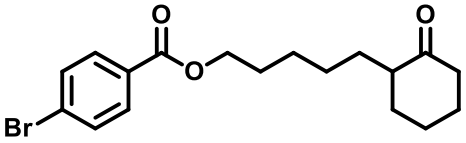
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 2.32 – 1.94 (m, 5H), 1.80 – 1.70 (m, 4H), 1.54 – 1.34 (m, 5H), 1.30 – 1.23 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 131.6, 131.0, 129.2, 127.8, 65.1, 49.0, 38.1 29.5, 29.4, 28.4, 27.1, 26.0, 20.7.

HRMS (ESI, m/z): Calculated for $C_{17}H_{21}Br_1O_3$ $(M+Na)^+$ 375.0566 found 375.0573.

20b. 8-(oxiran-2-yl)octanenitrile

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).

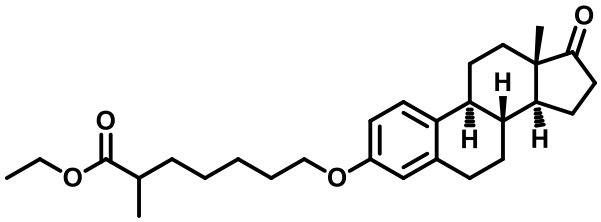


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 2.41 – 2.36 (m, 1H), 2.32 – 2.22 (m, 2H), 2.13 – 1.99 (m, 2H), 1.88 – 1.72 (m, 4H), 1.70 – 1.62 (m, 2H), 1.47 – 1.30 (m, 5H), 1.24 – 1.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.3, 165.9, 131.7, 131.1, 129.4, 127.9, 65.3, 50.7, 42.0, 33.9, 29.3, 28.6, 28.0, 26.9, 26.2, 24.9.

HRMS (ESI, m/z): Calculated for $C_{18}H_{23}Br_1O_3(M+H)^+$ 367.0903, found 367.0902.

28a. ethyl 2-methyl-7-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)heptanoate



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.4 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.91 (t, *J* = 6.4 Hz, 2H), 2.91 – 2.87 (m, 2H), 2.53 – 2.38 (m, 3H), 2.30 – 2.22 (m, 1H), 2.18 – 1.93 (m, 4H), 1.79 – 1.34 (m, 14H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 3H).

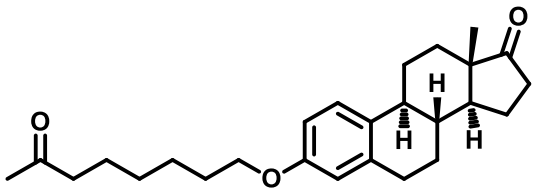
^{13}C NMR (100 MHz, $cdcl_3$): δ 220.7, 176.8, 157.1, 137.6, 131.8, 126.2, 114.5, 112.1, 67.7, 60.1, 50.4, 48.0, 44.0, 39.5, 38.4, 35.8, 33.7, 31.6, 29.6, 29.2, 27.0, 26.5, 26.0, 25.9, 21.6, 17.1, 14.2, 13.8.

HRMS (ESI, m/z): Calculated for $C_{28}H_{40}O_4$ $(M+H)^+$ 441.2999, found 441.3006.

21b.

(8R,9S,13S,14S)-13-methyl-3-((7-oxooctyl)oxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one

A colorless solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



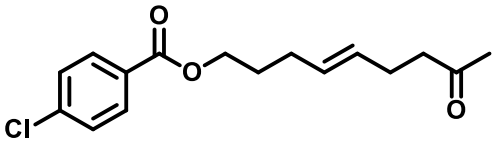
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.4 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 2.91 – 2.86 (m, 2H), 2.53 – 2.35 (m, 5H), 2.29 – 2.16 (m, 3H), 2.13 (s, 3H), 2.11 – 1.93 (m, 3H), 1.79 – 1.72 (m, 2H), 1.67 – 1.50 (m, 5H), 1.50 – 1.43 (m, 3H), 1.41 – 1.31 (m, 2H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 220.8, 209.0, 157.1, 137.7, 131.9, 126.3, 114.5, 112.1, 67.7, 50.4, 48.0, 44.0, 43.6, 38.4, 35.9, 31.6, 29.8, 29.6, 29.1, 28.9, 26.6, 25.9, 25.9, 23.7, 21.6, 13.8.

HRMS (ESI, m/z): Calculated for $C_{26}H_{36}O_3$ $(M+NH_4)^+$ 414.3003, found 414.3002.

22b. (E)-8-oxonon-4-en-1-yl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



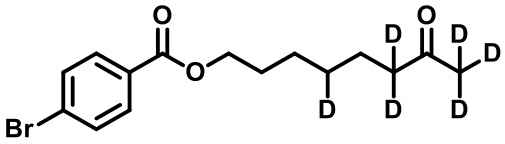
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 5.47 – 5.44 (m, 2H), 4.30 (t, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.29 – 2.24 (m, 2H), 2.16 – 2.11 (m, 5H), 1.85 – 1.78 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.3, 165.7, 139.3, 130.9, 129.8, 129.6, 128.9, 128.7, 64.6, 43.4, 29.7, 28.9, 28.4, 26.7.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}Cl_1O_3$ $(M+H)^+$ 295.1095, found 295.1096.

23b.

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



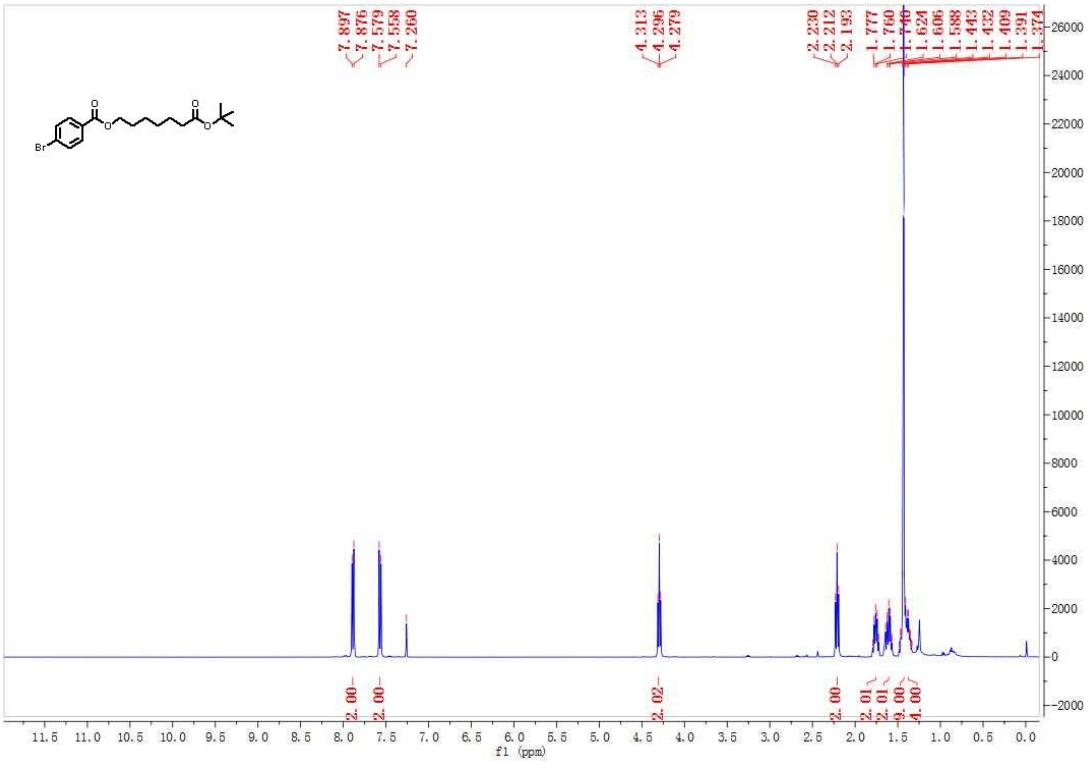
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.4 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.57 (d, *J* = 7.6 Hz, 2H), 1.43 (dd, *J* = 15.2, 7.2 Hz, 2H), 1.36 – 1.29 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.2, 165.9, 131.6, 131.0, 129.3, 127.9, 65.2, 43.0 – 42.5(m), 29.7, 28.7 – 28.1 (m), 28.4, 25.7, 23.4.

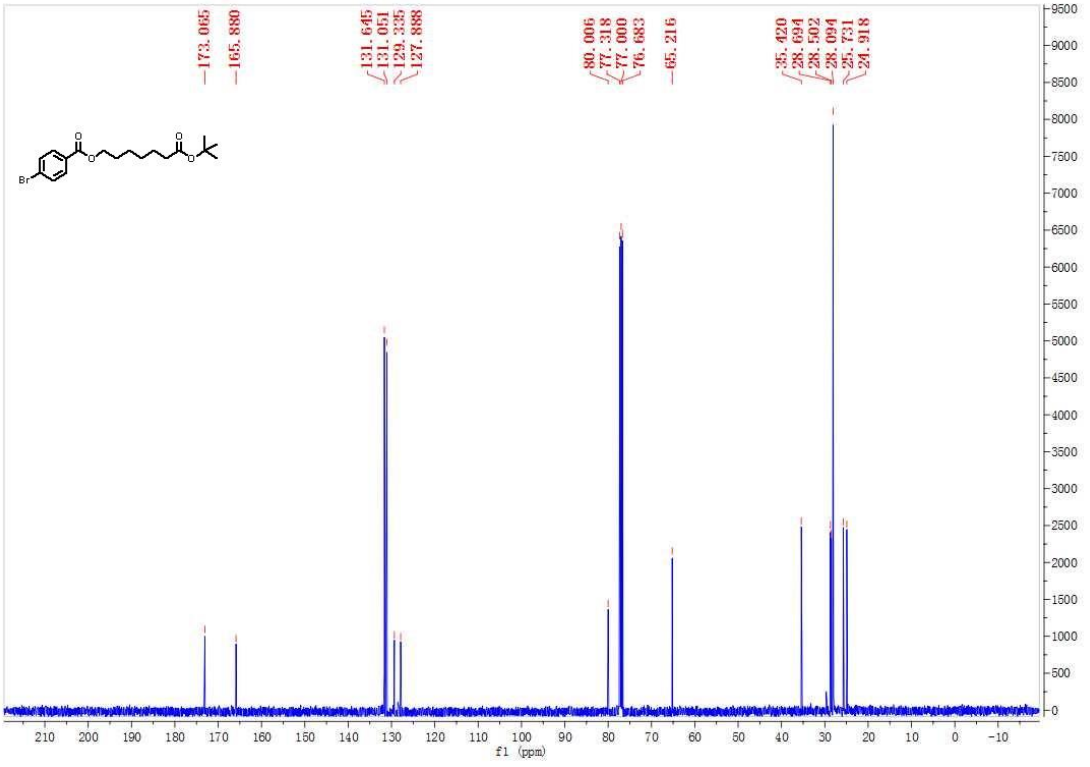
HRMS (ESI, m/z): Calculated for $C_{15}H_{13}D_6BrO_3(M+Na)^+$ 355.0786, found 355.0791.

Copies of the ^{1}H NMR, ^{13}C NMR, ^{135}DEPT

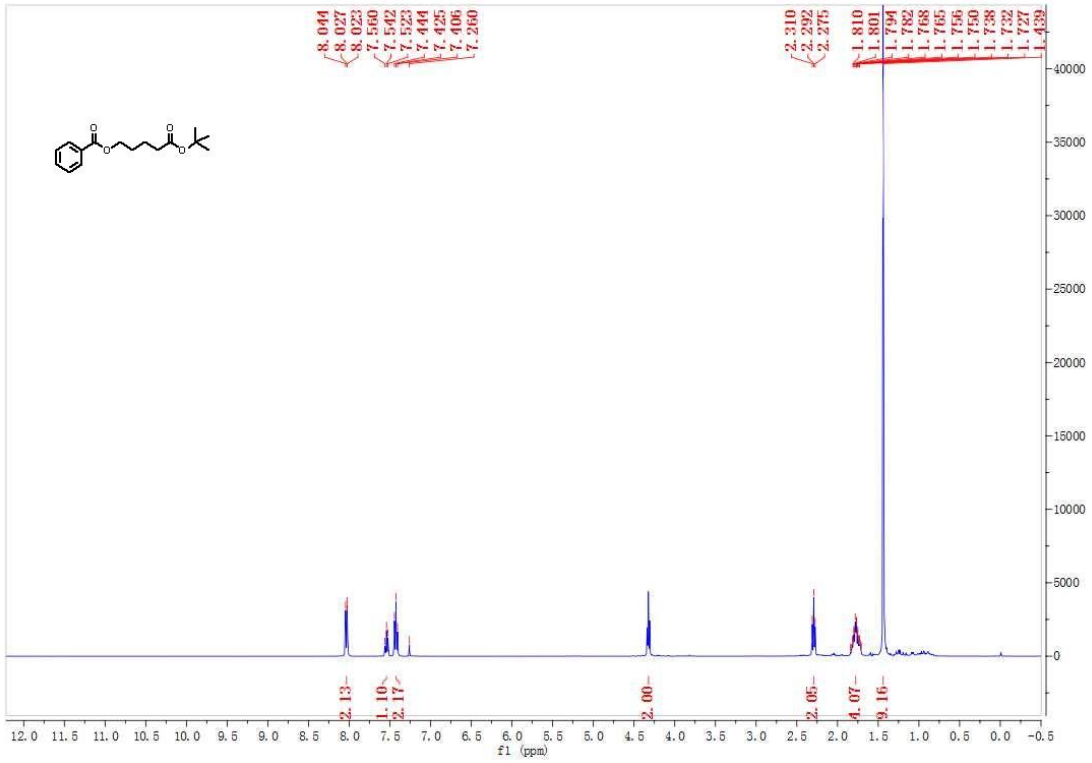
1a-^{1}H NMR



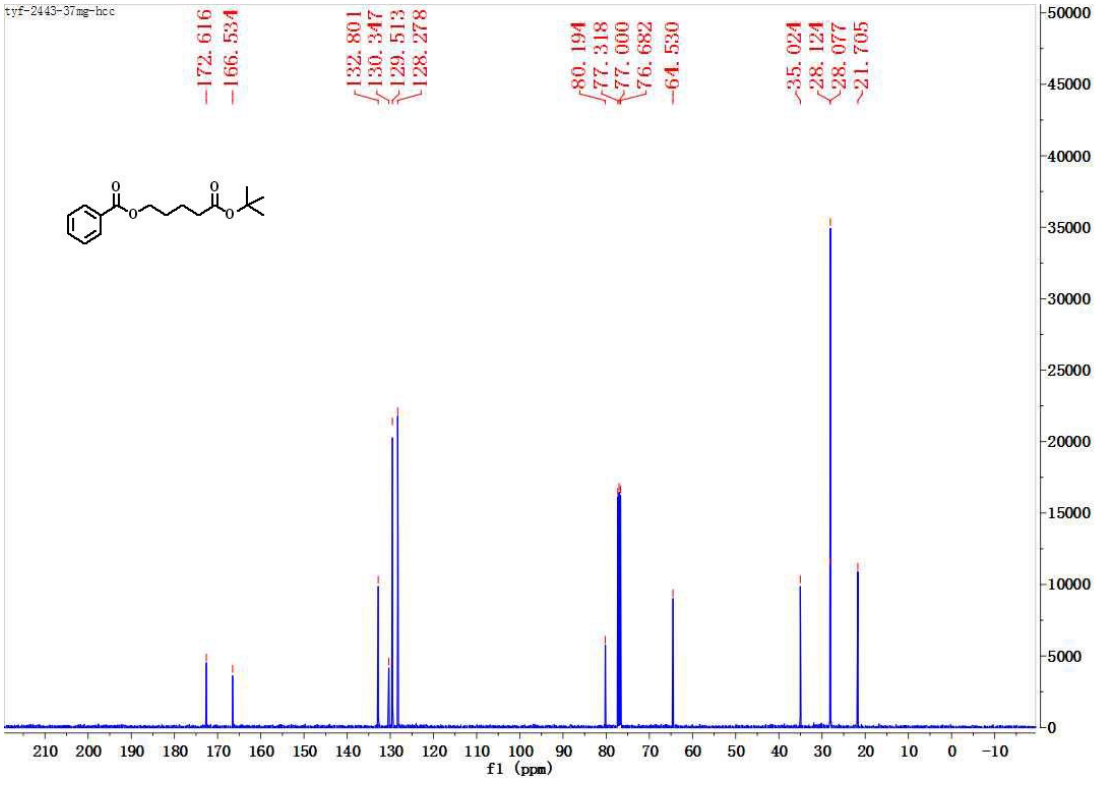
1a-^{13}C NMR



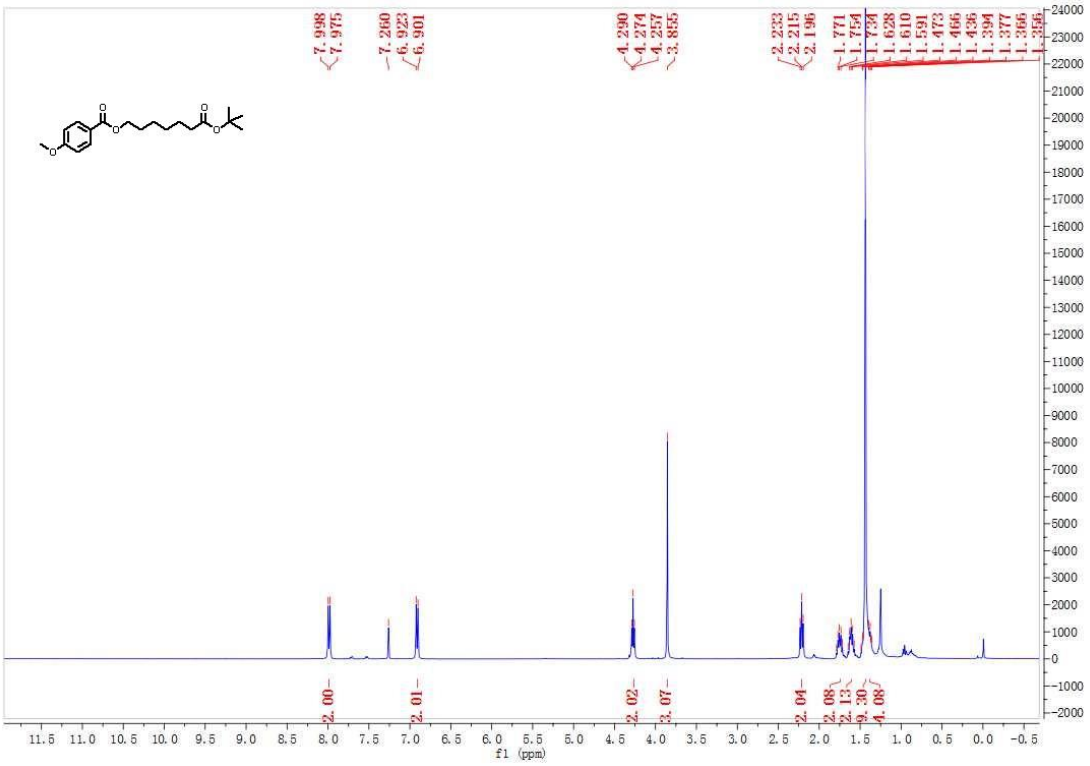
2a-^{1}H NMR



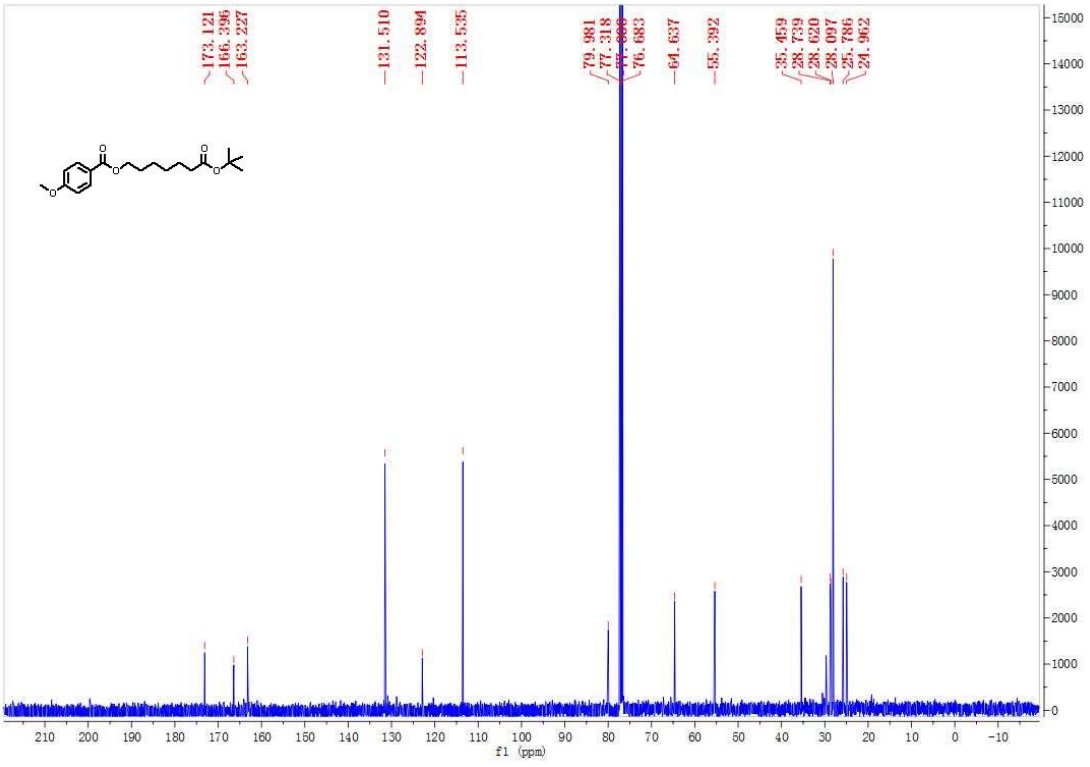
2a-^{13}C NMR



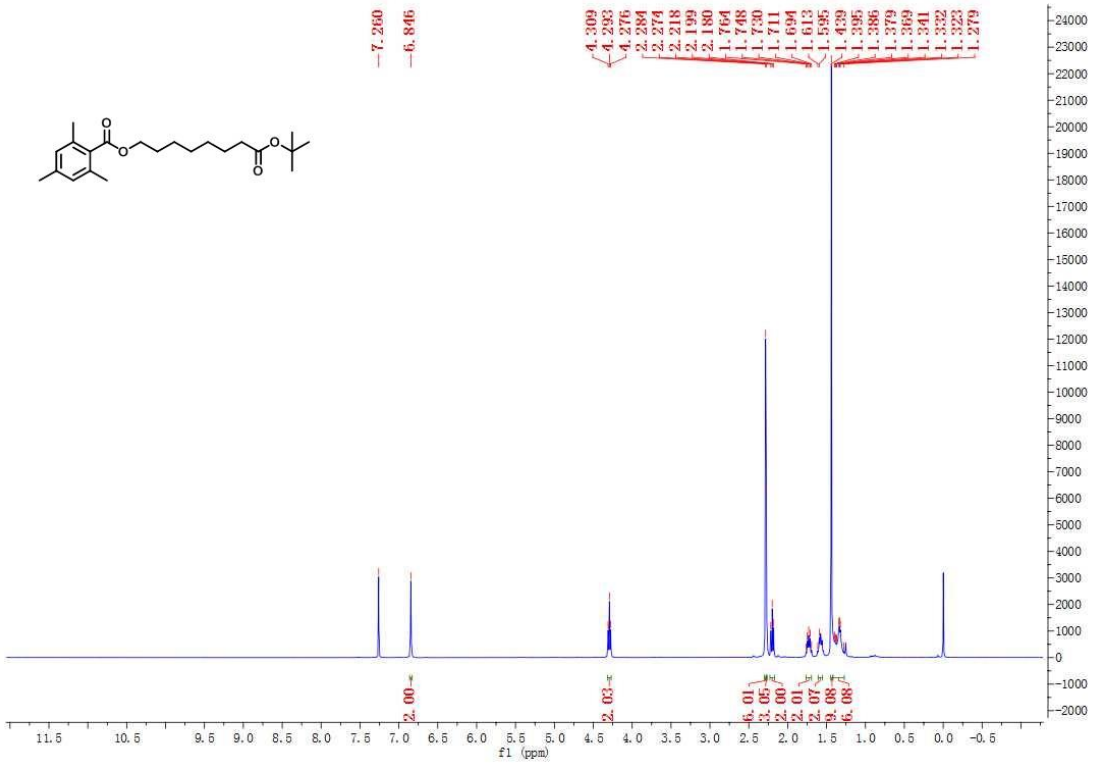
3a-^{1}H NMR



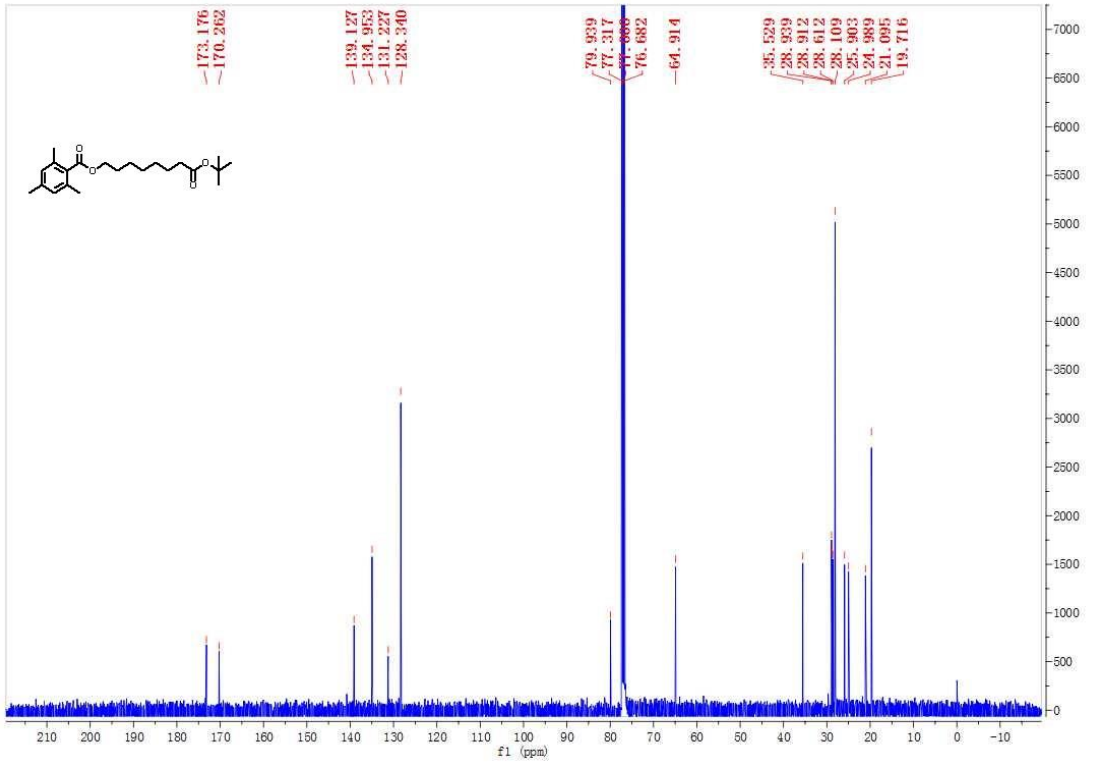
3a-^{13}C NMR



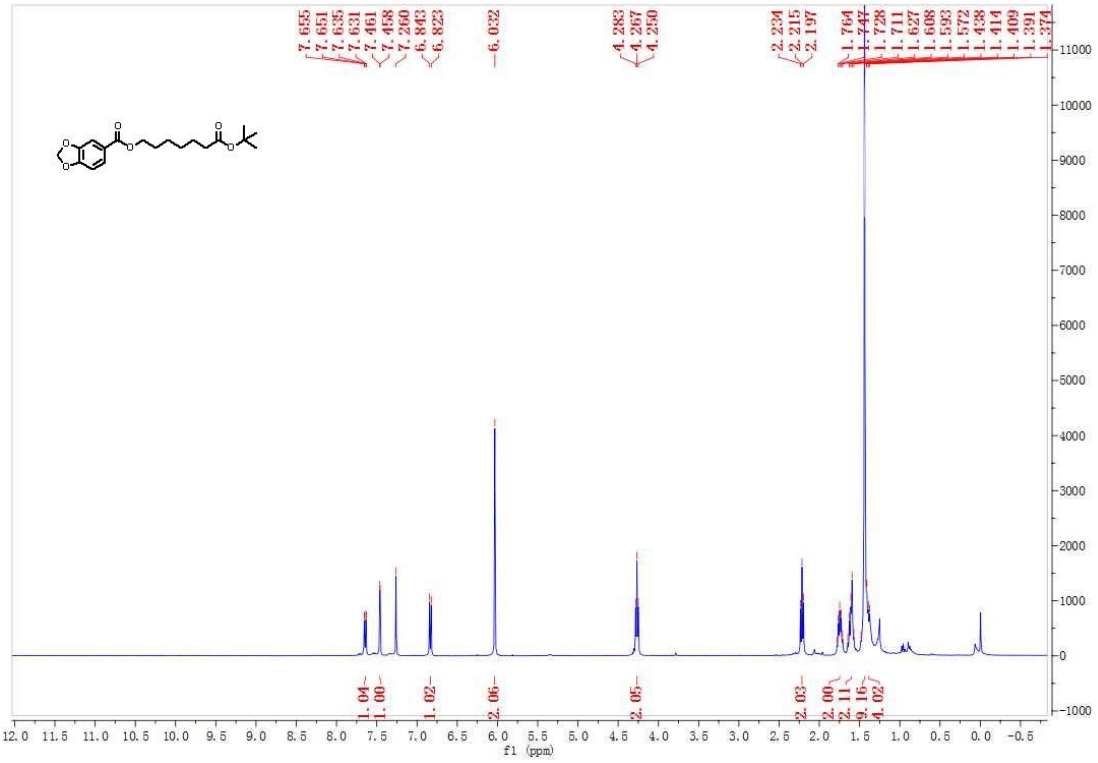
4a-^{1}H NMR



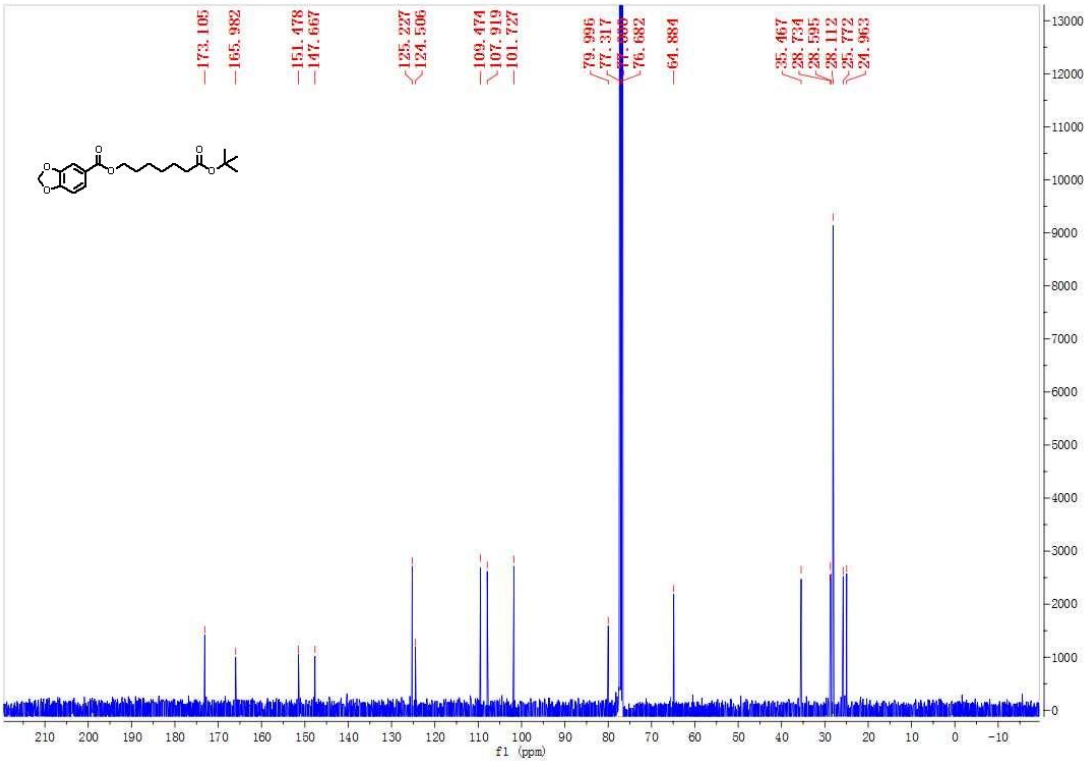
4a-^{13}C NMR



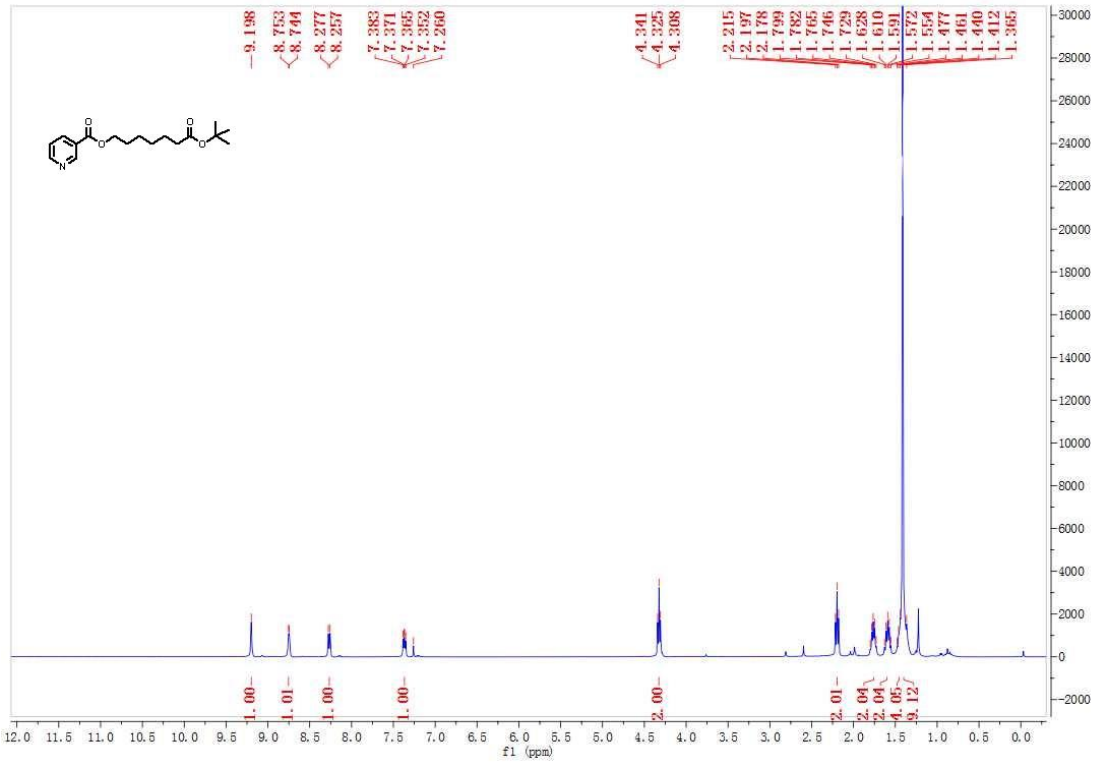
5a-^{1}H NMR



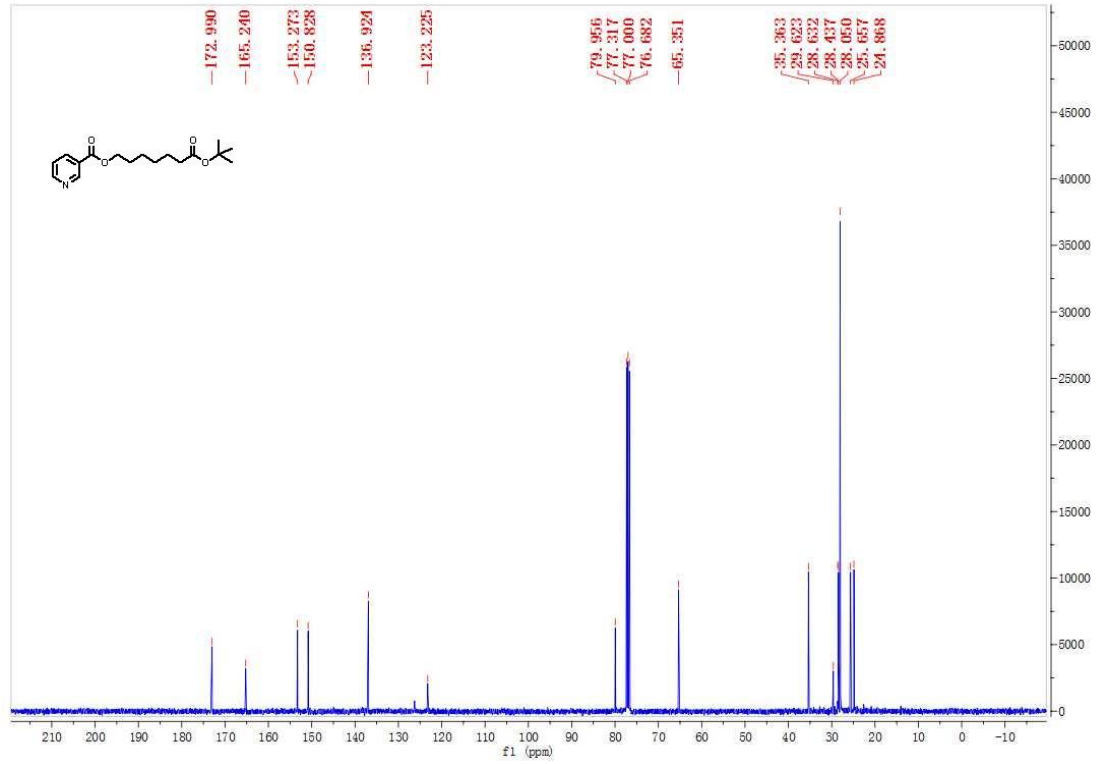
5a-^{13}C NMR



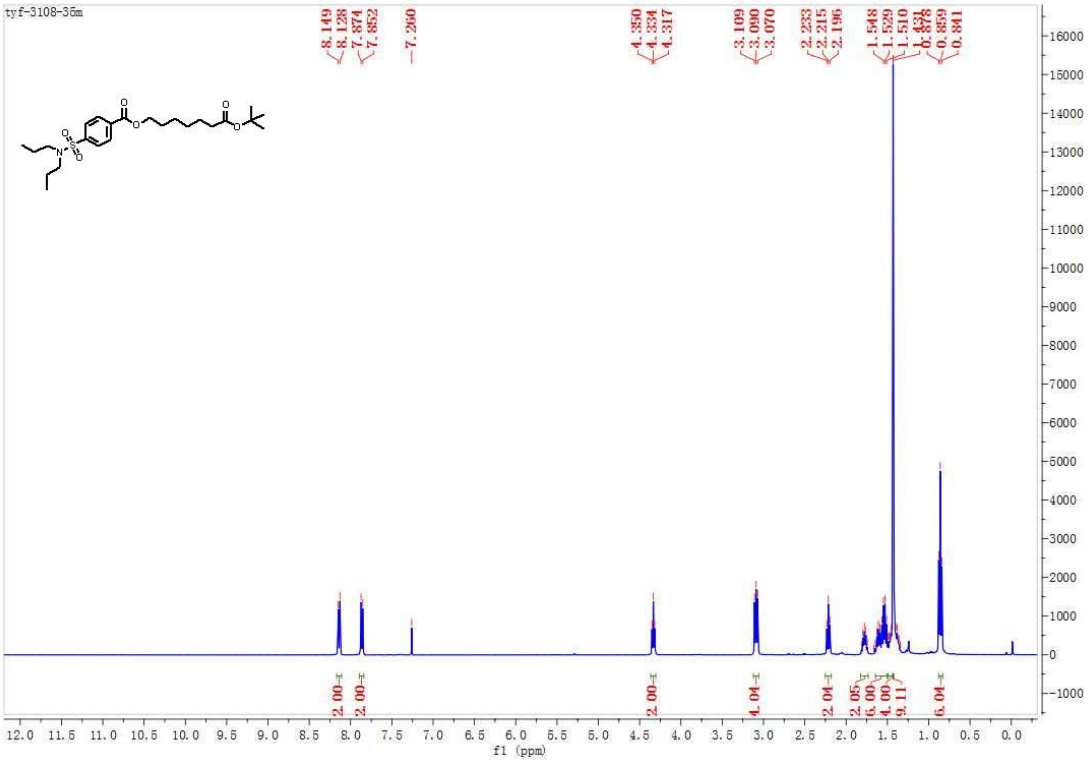
6a-^{1}H NMR



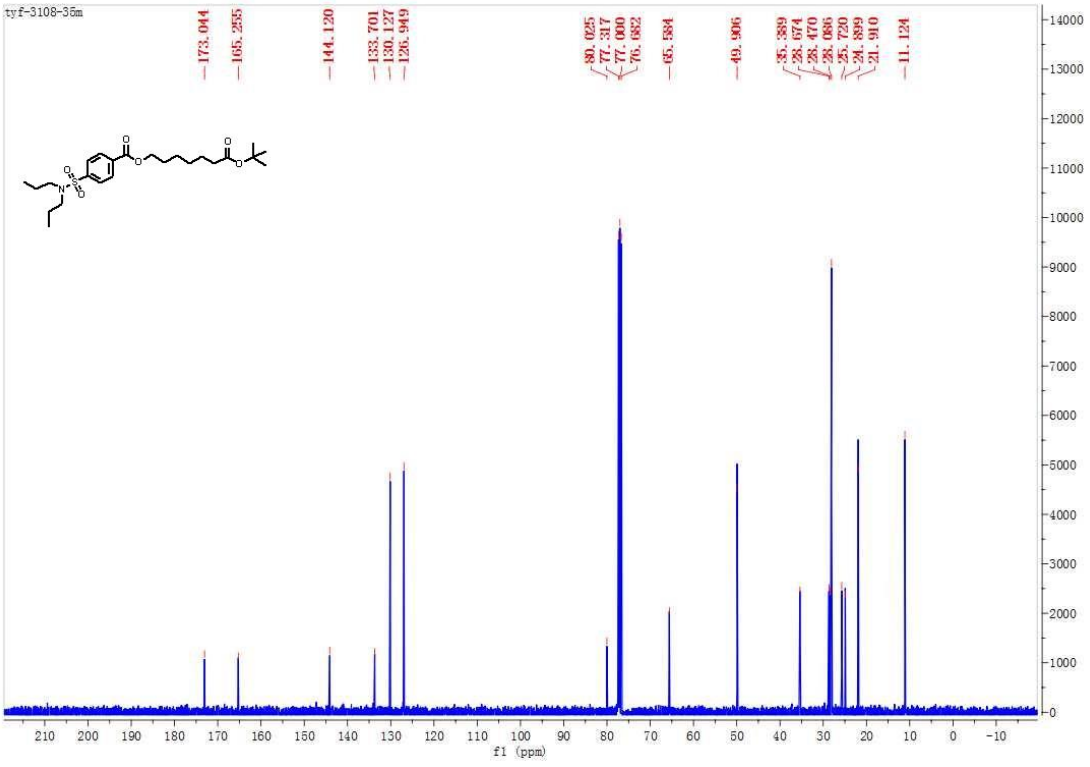
6a-^{13}C NMR



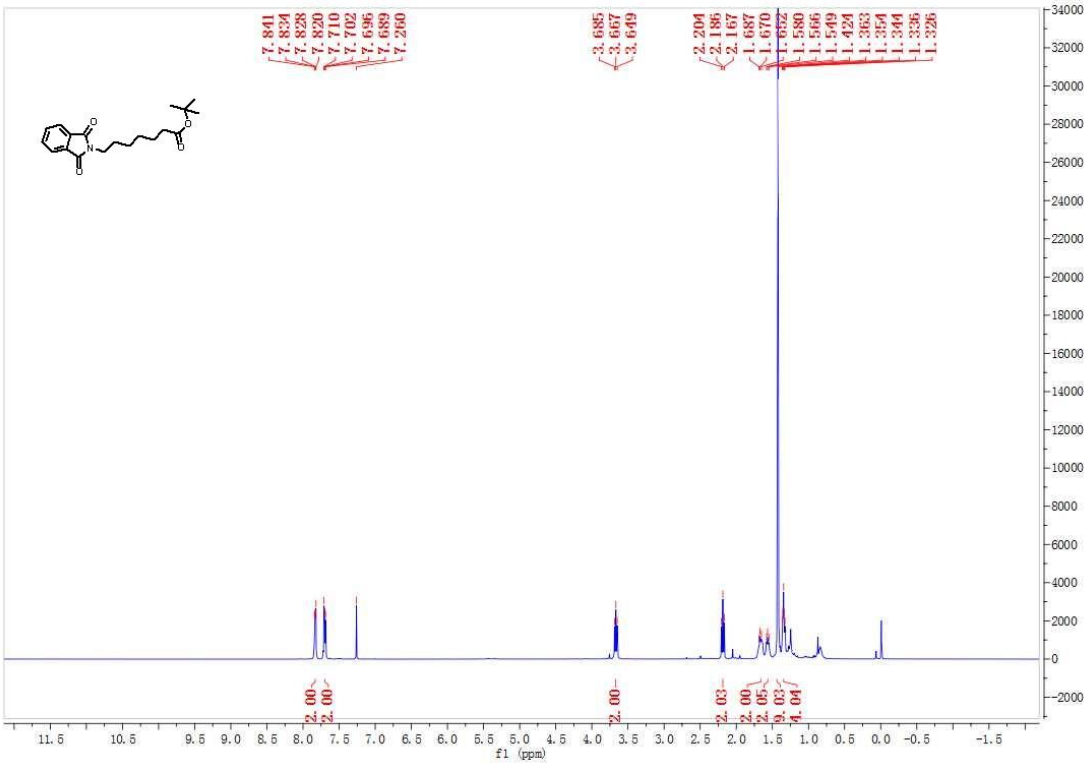
7a-^{1}H NMR



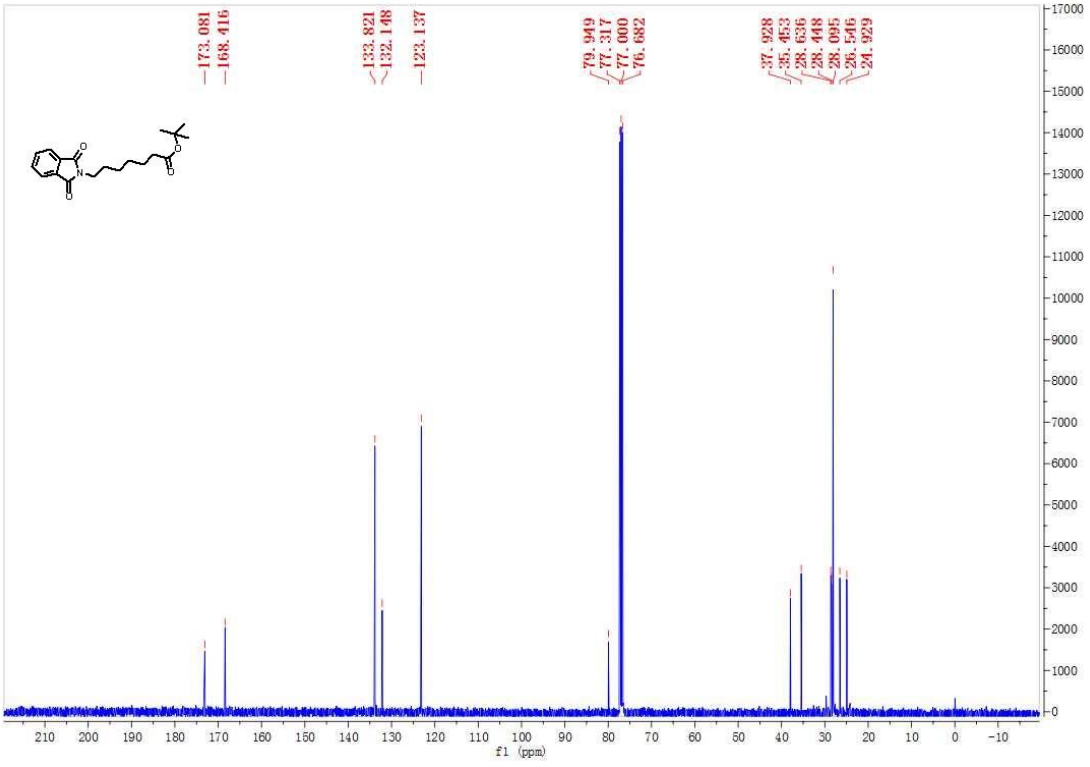
7a-^{13}C NMR



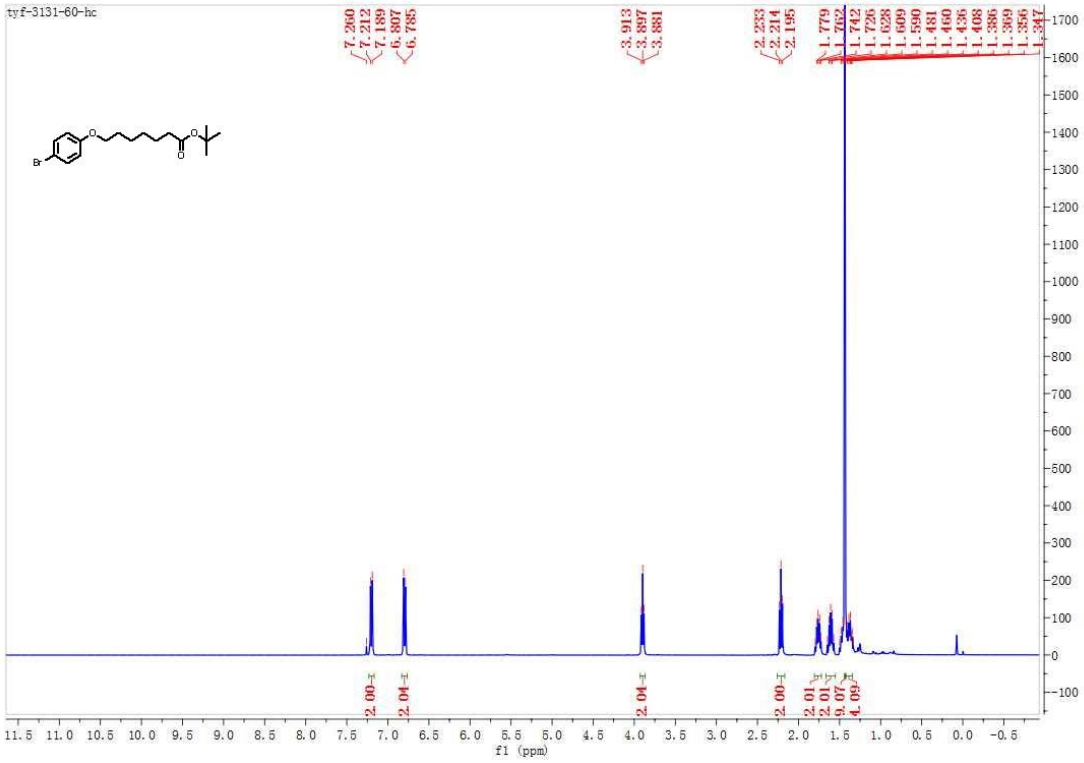
8a-^{1}H NMR



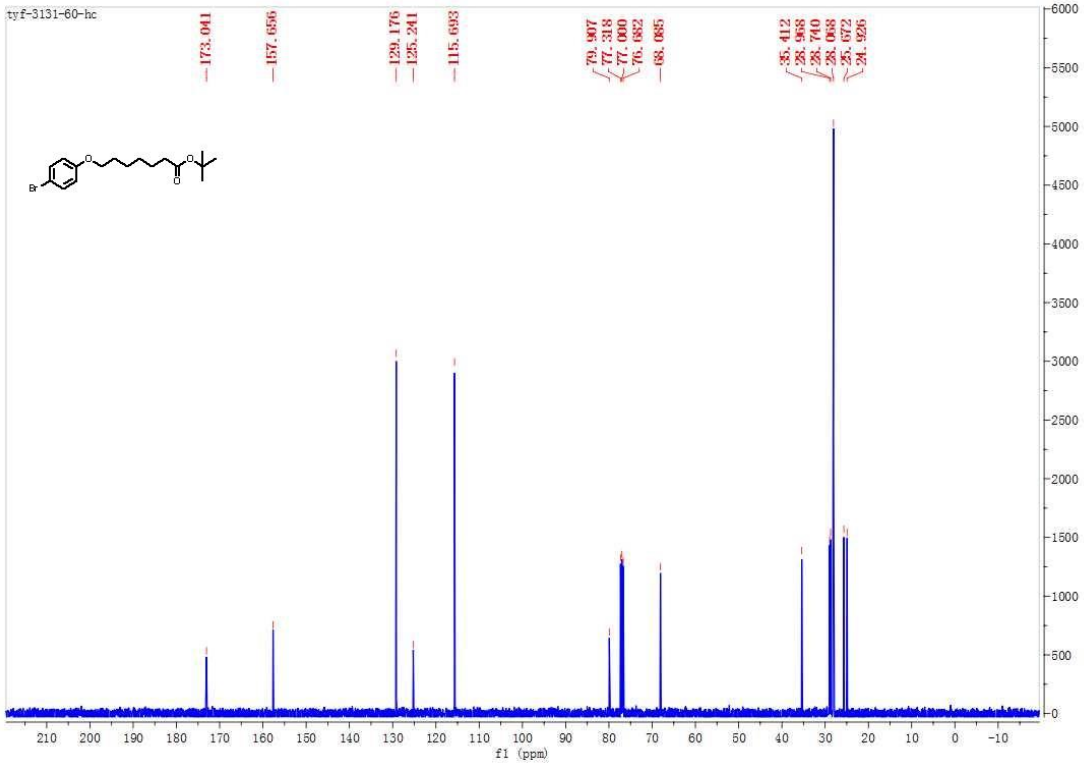
8a-^{13}C NMR



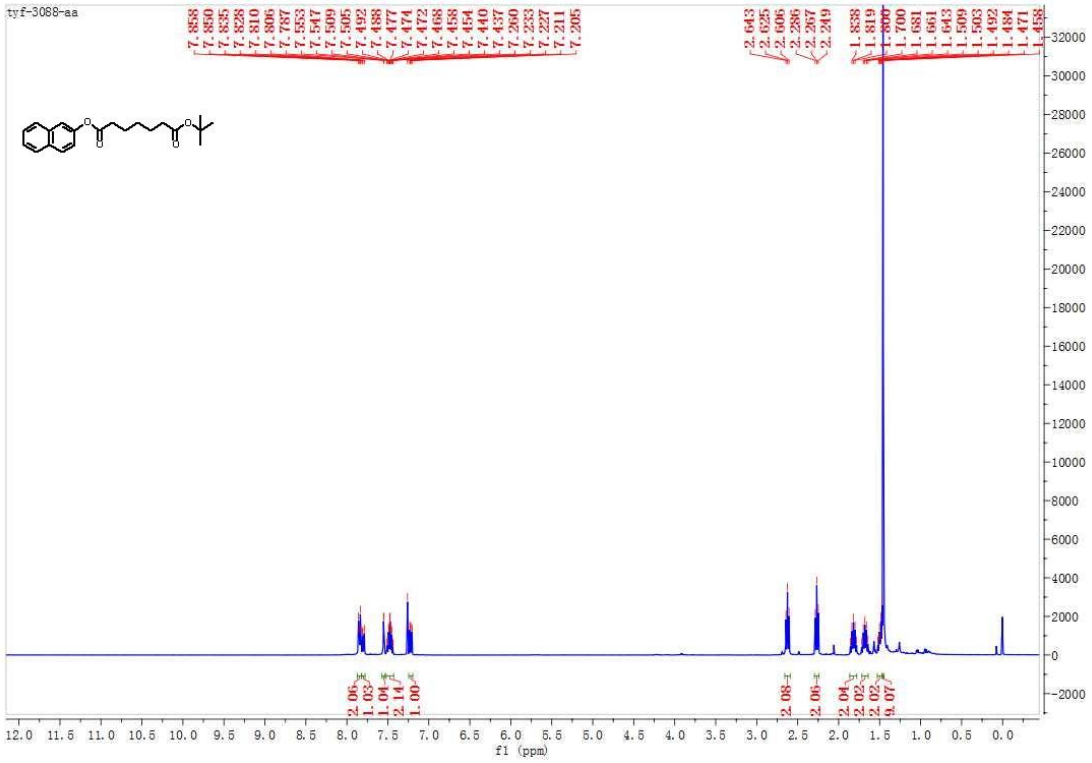
9a-^{1}H NMR



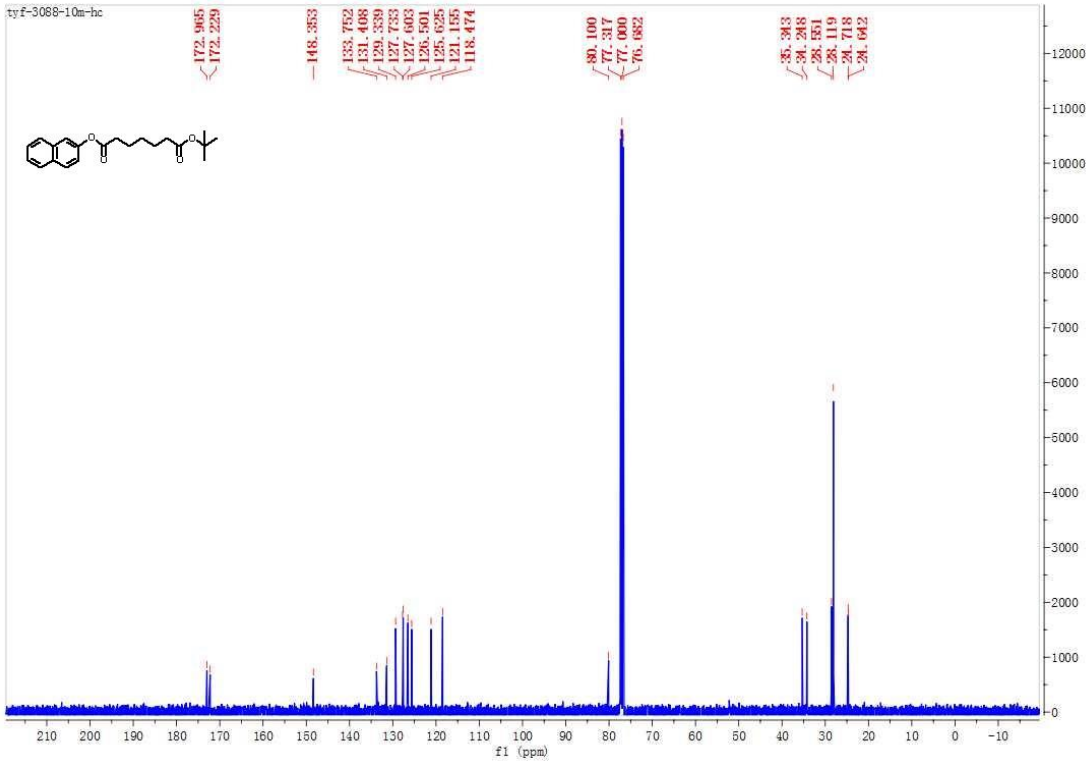
9a-^{13}C NMR



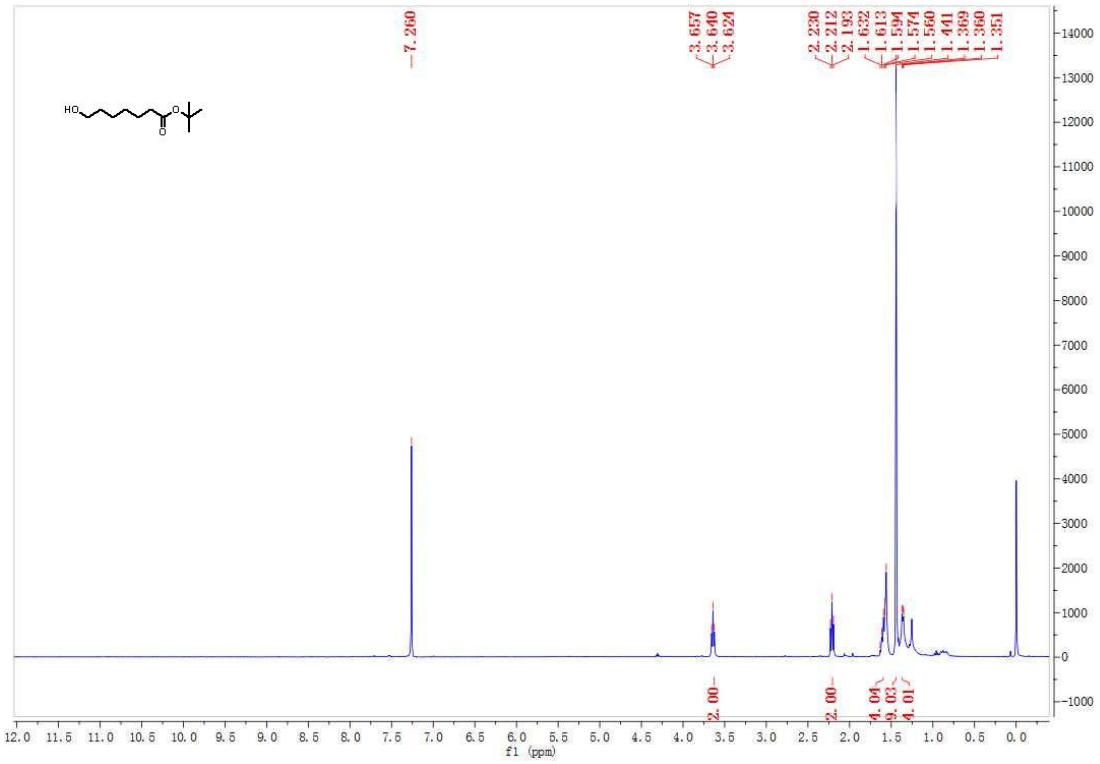
10a-^{1}H NMR



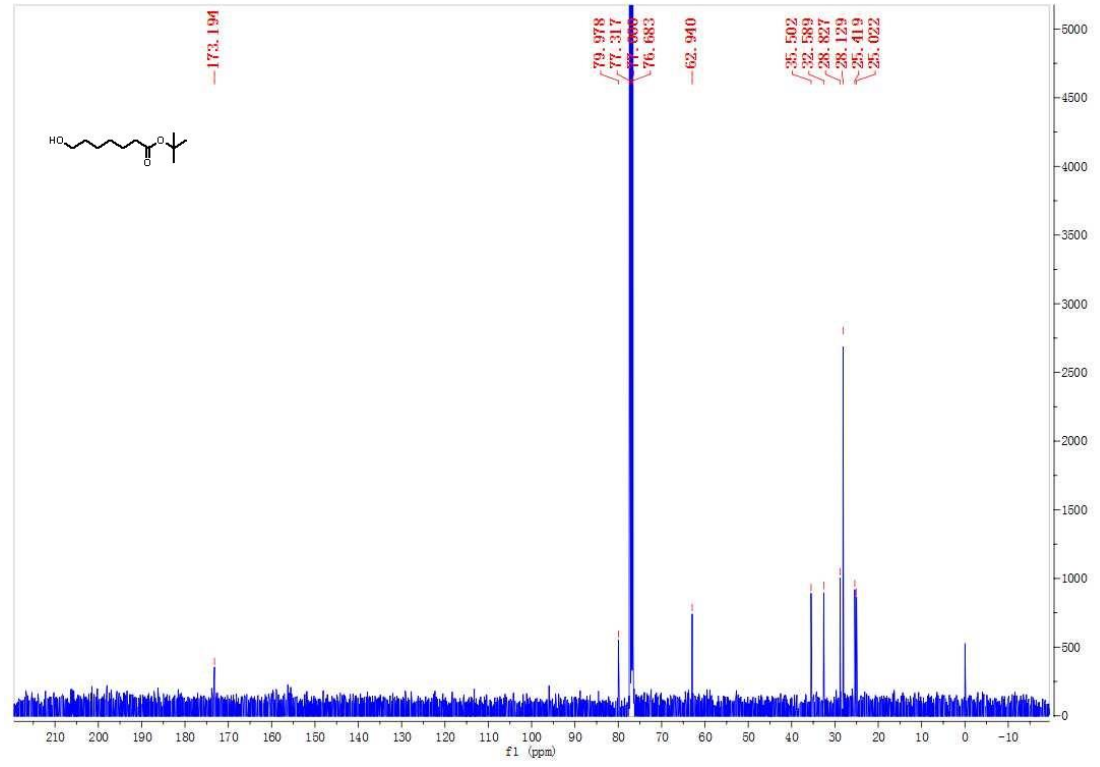
10a-^{13}C NMR



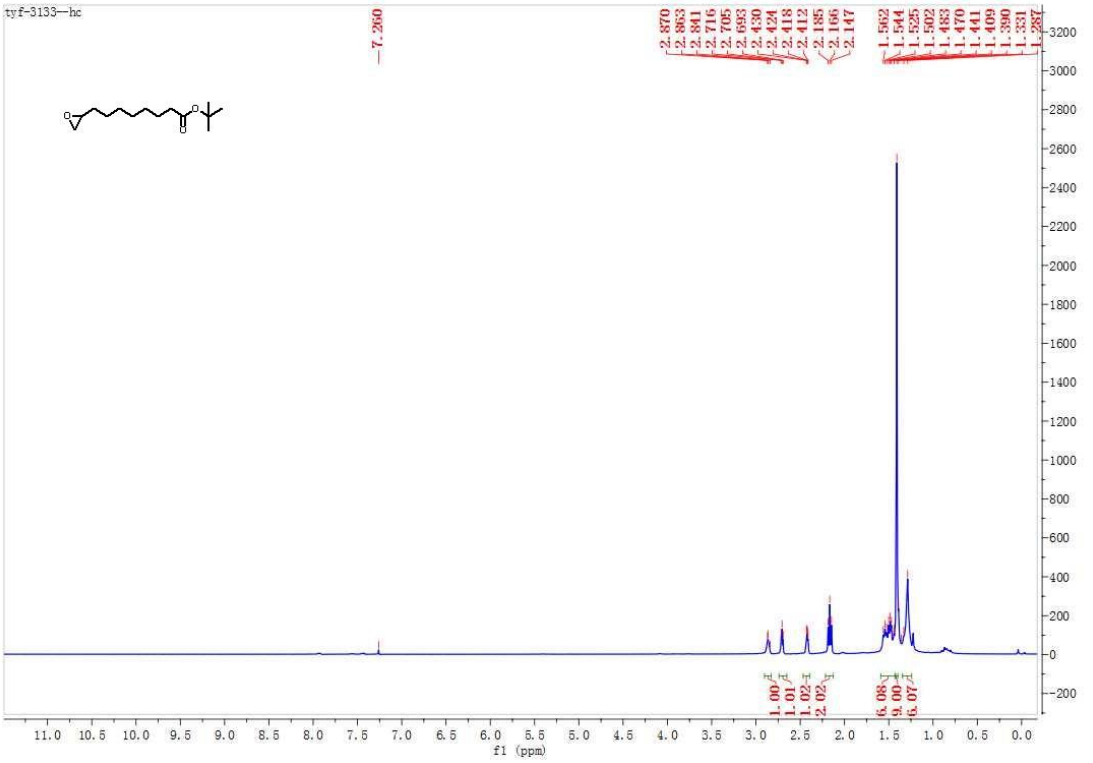
11a-^{1}H NMR



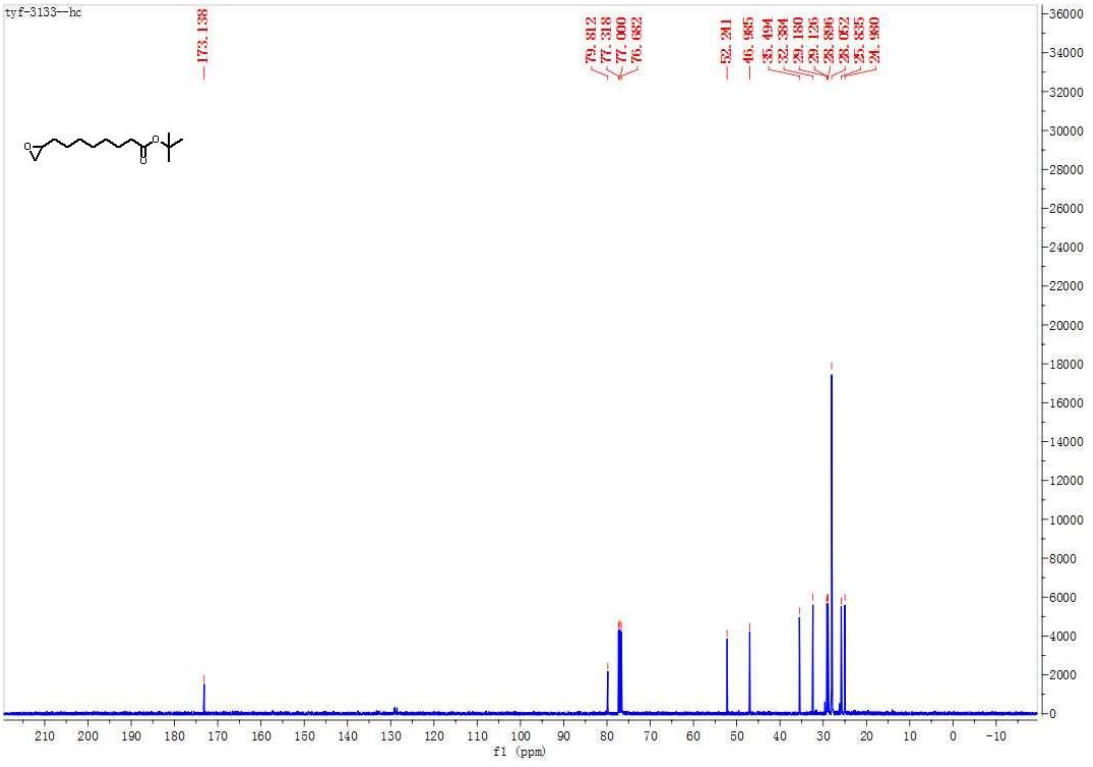
11a-^{13}C NMR



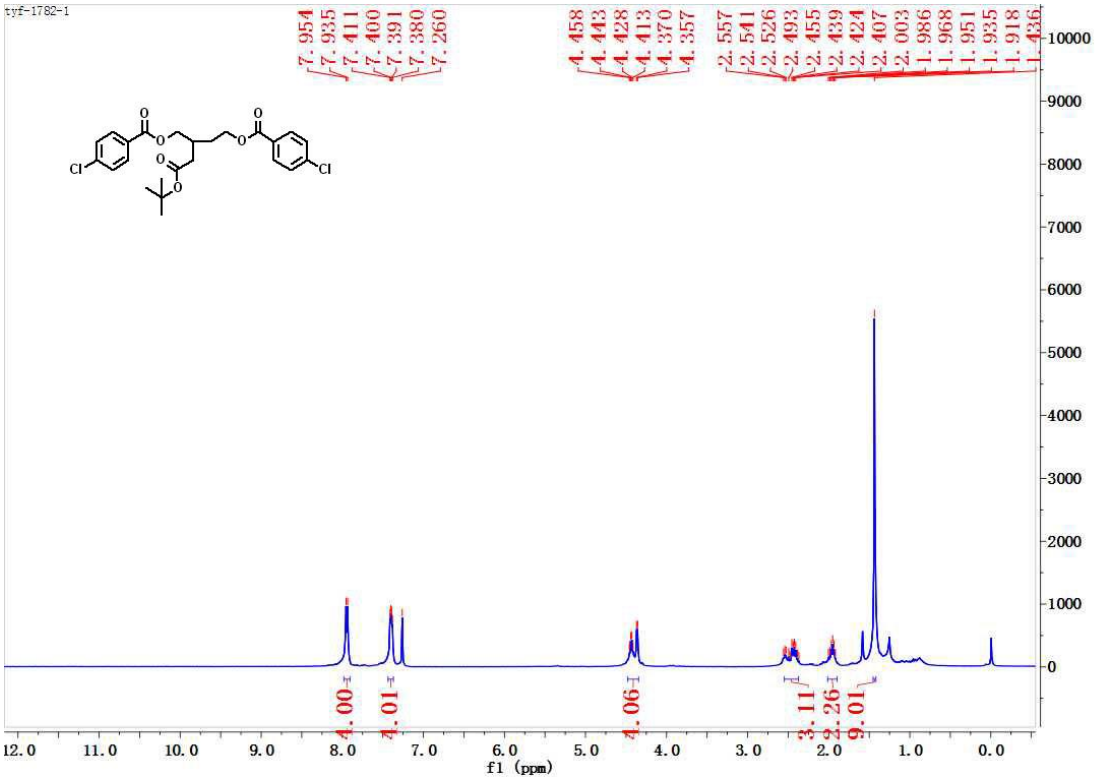
12a-^{1}H NMR



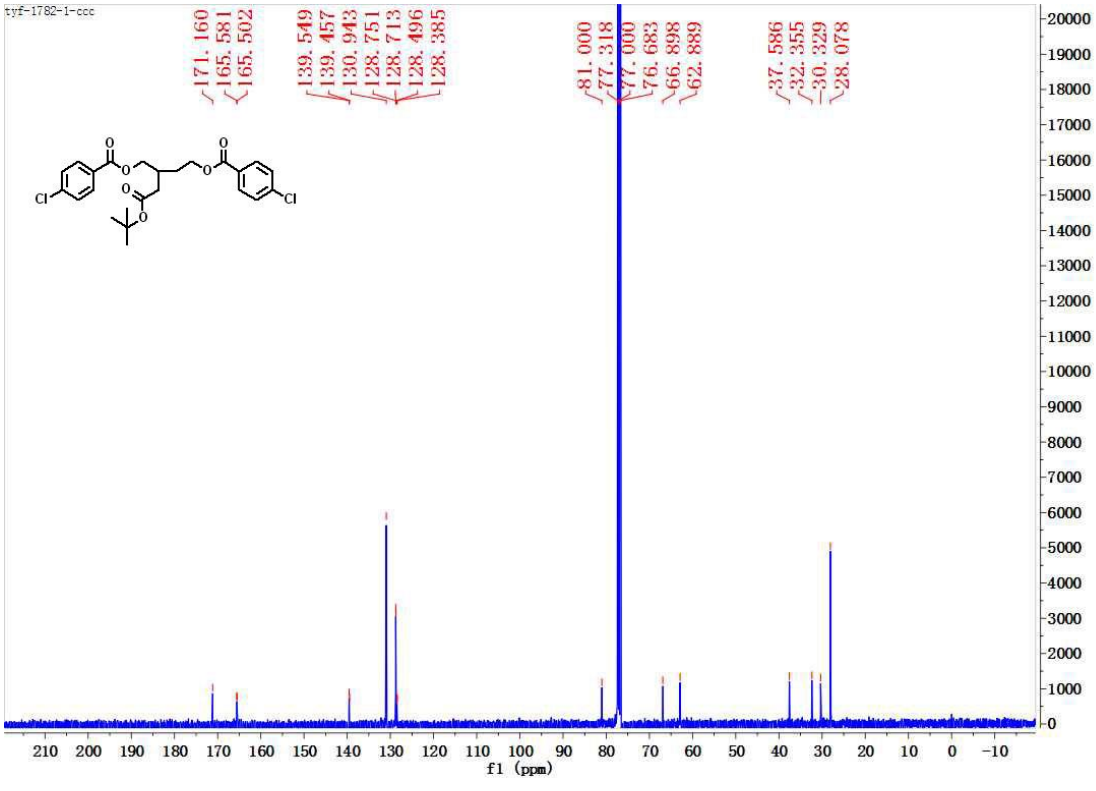
12a-^{13}C NMR



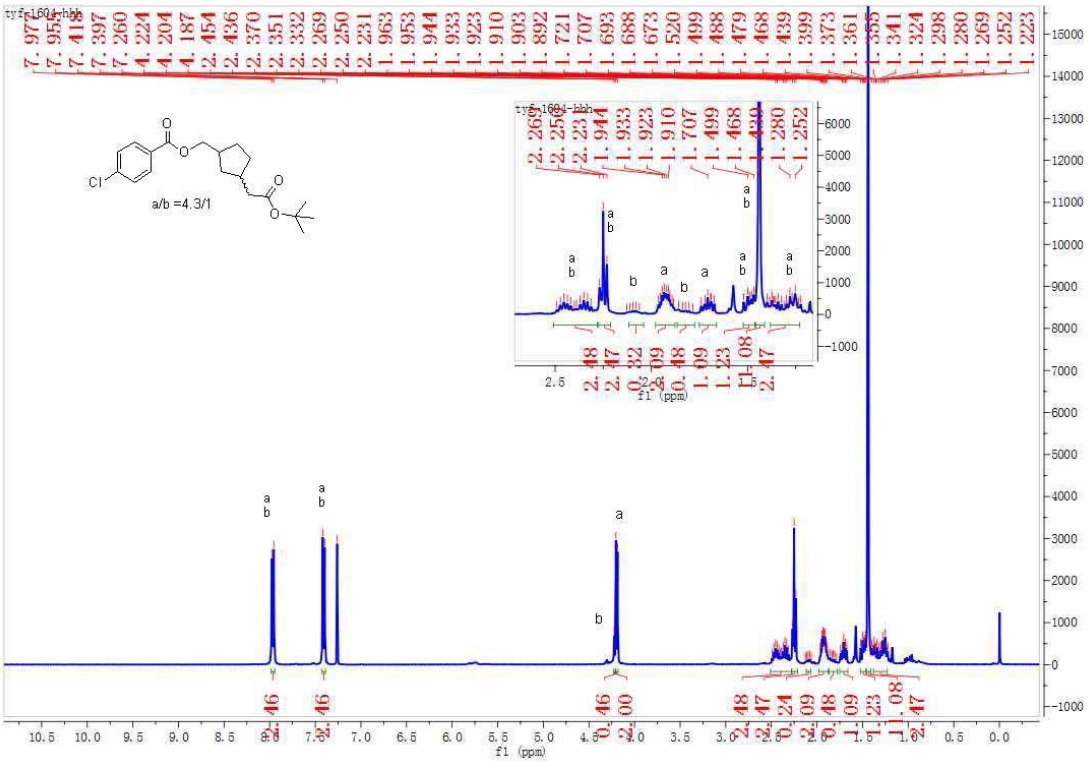
13a-^{1}H NMR



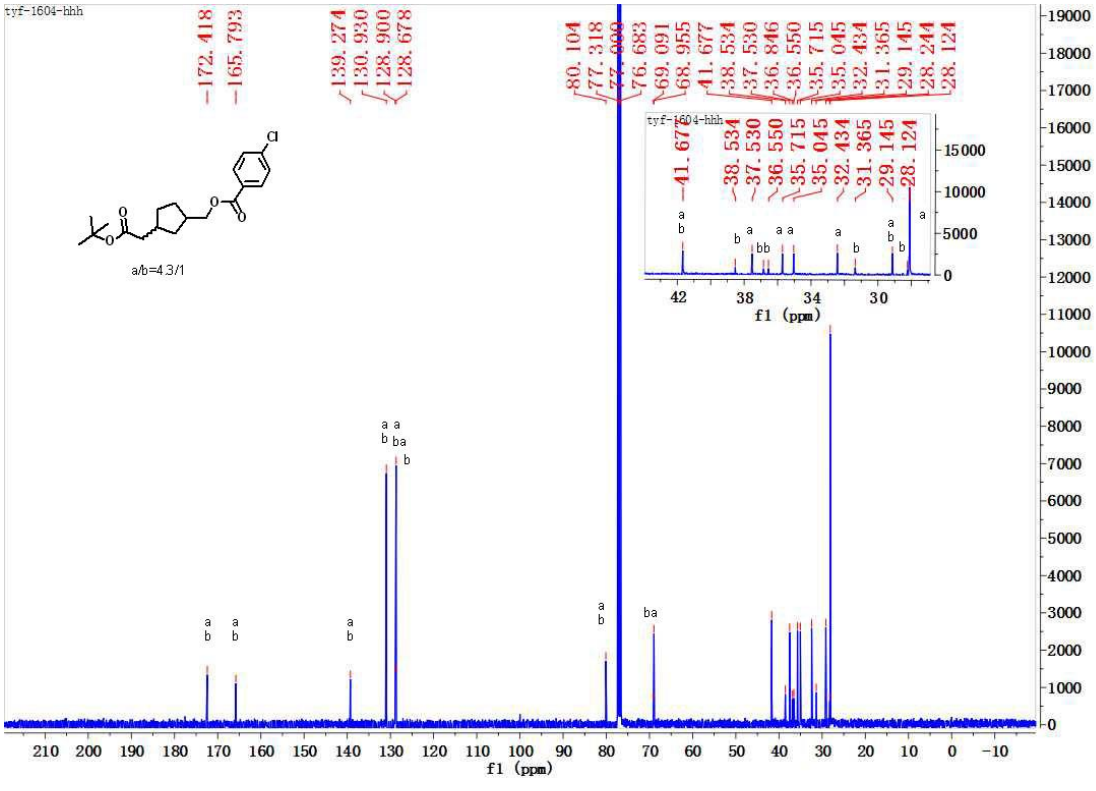
13a-^{13}C NMR



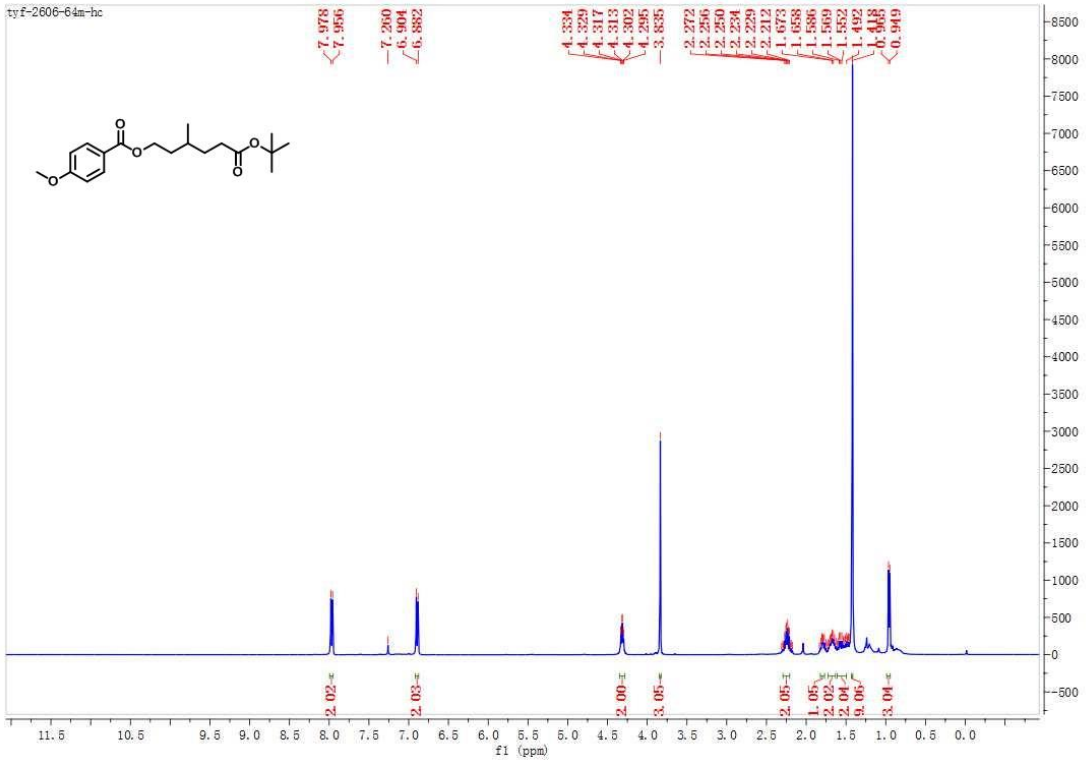
14a-^{1}H NMR



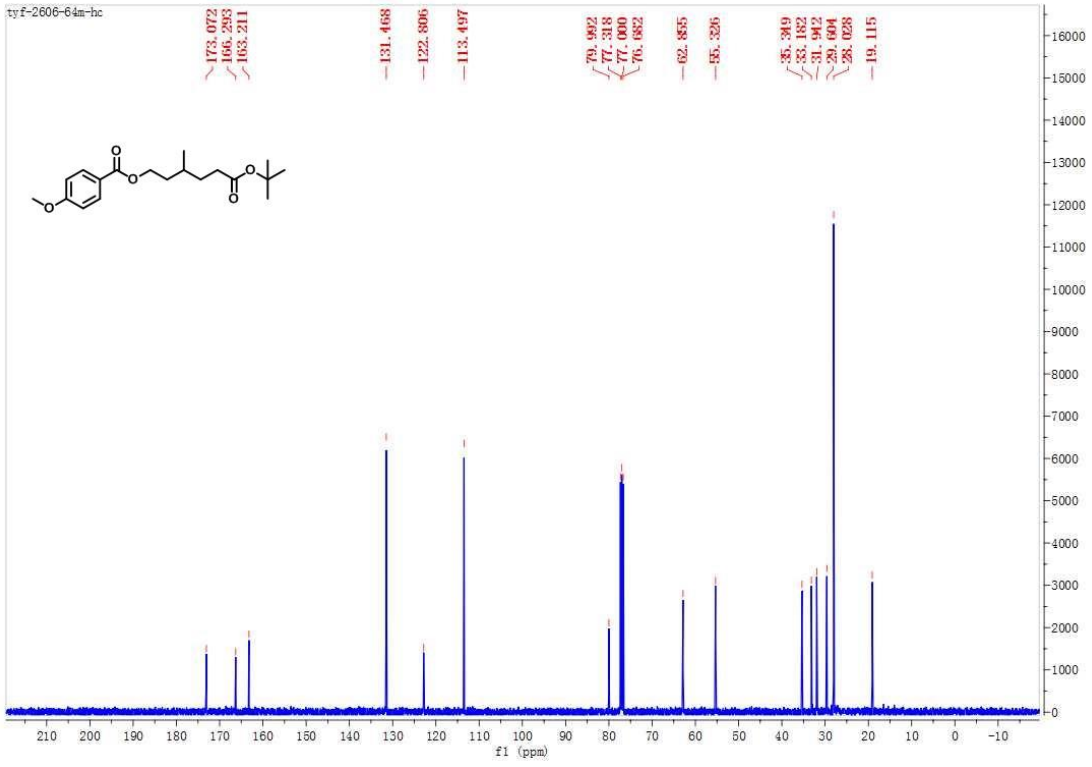
14a-^{13}C NMR



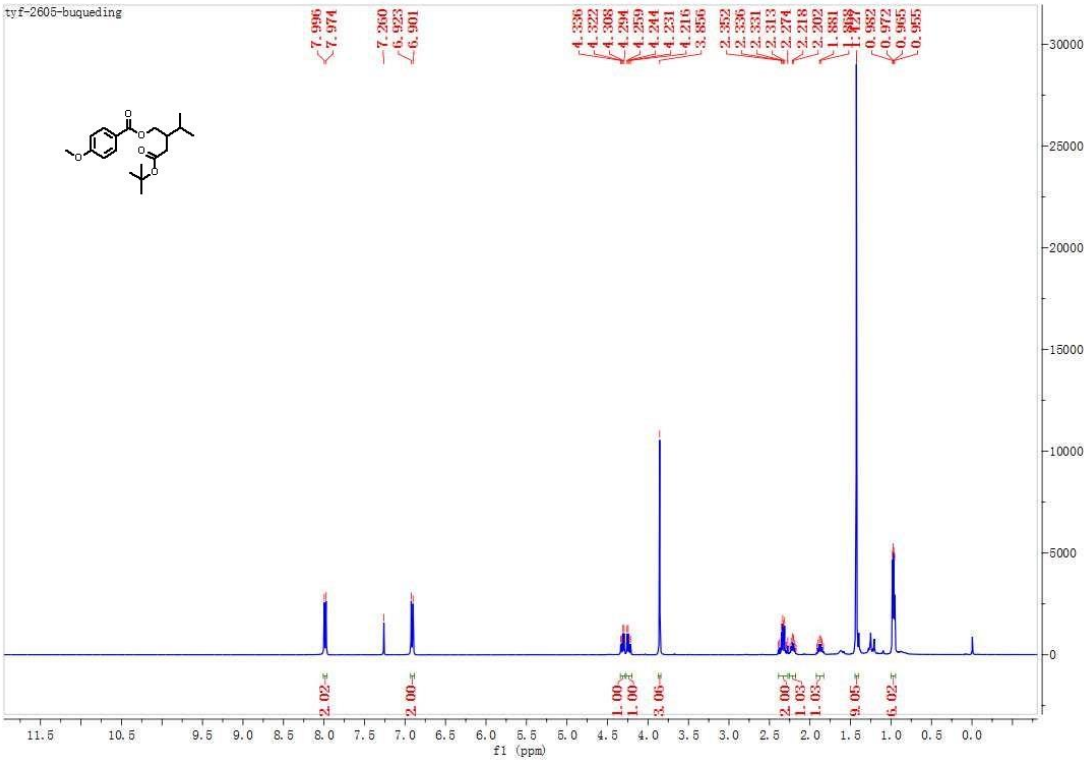
15a-^{1}H NMR



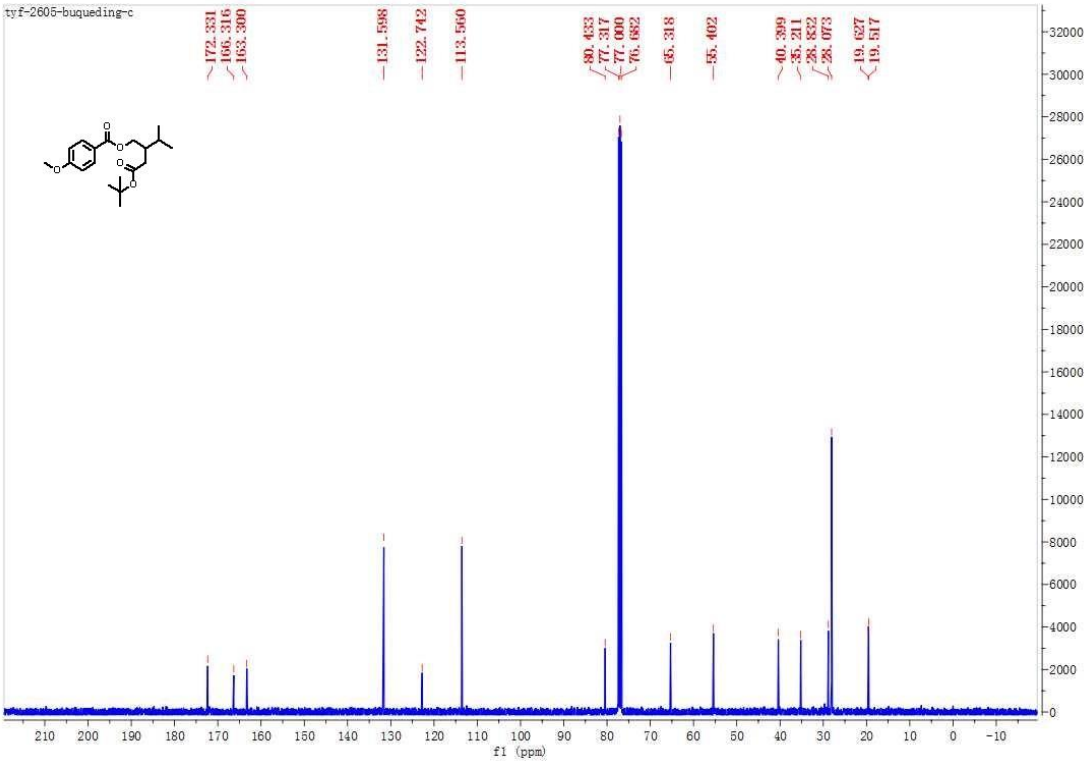
15a-^{13}C NMR



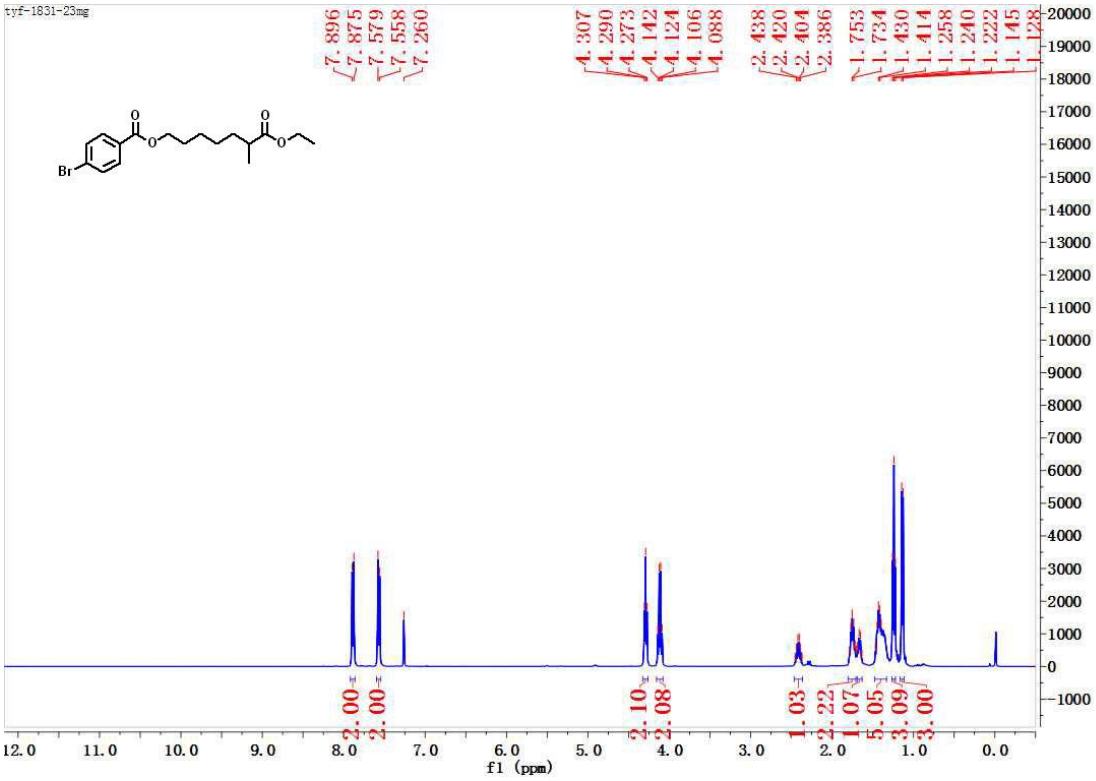
16a-^{1}H NMR



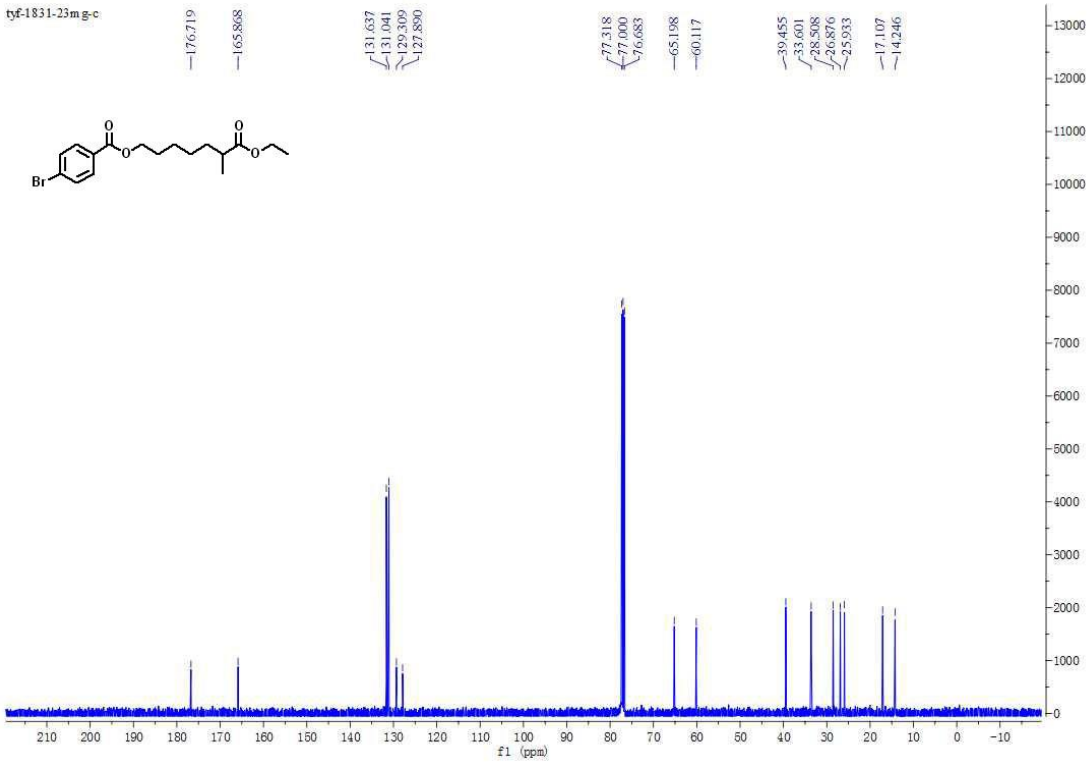
16a-^{13}C NMR



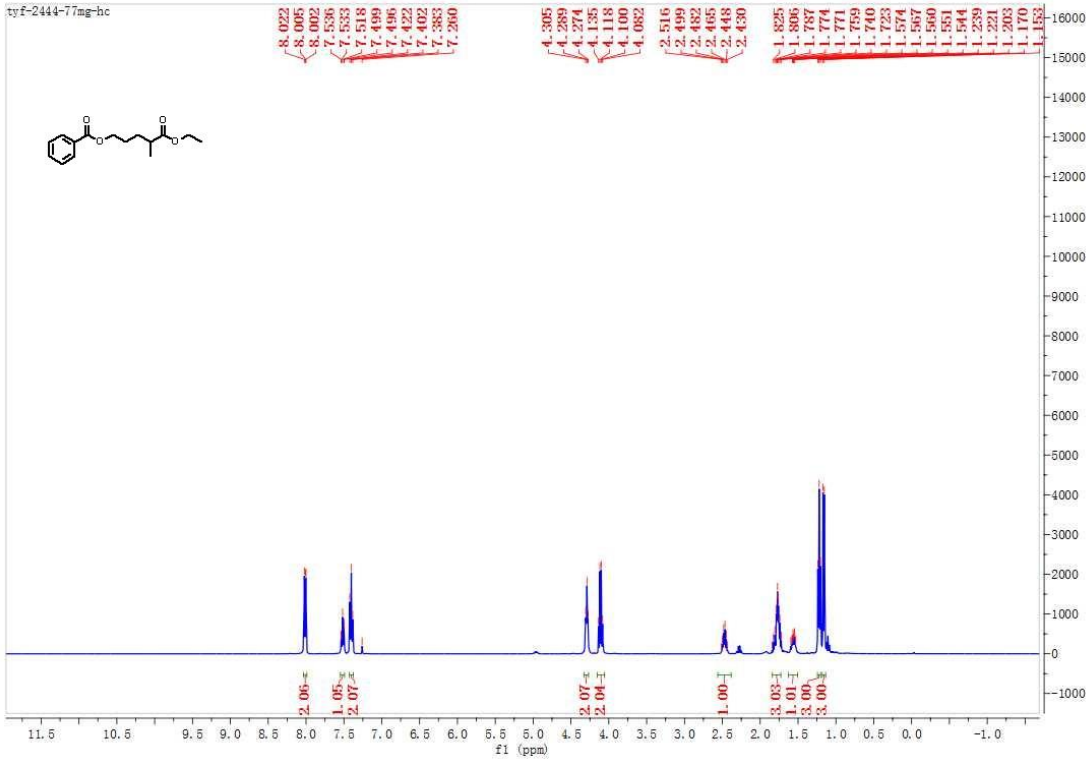
17a-^{1}H NMR



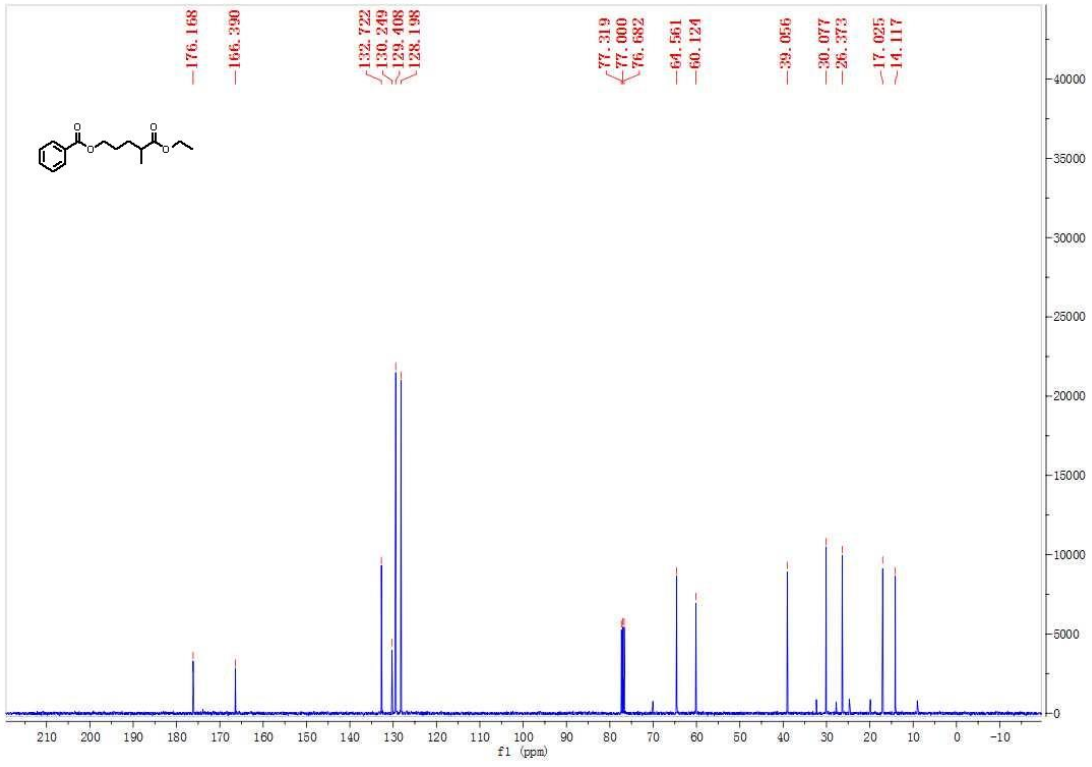
17a-^{13}C NMR



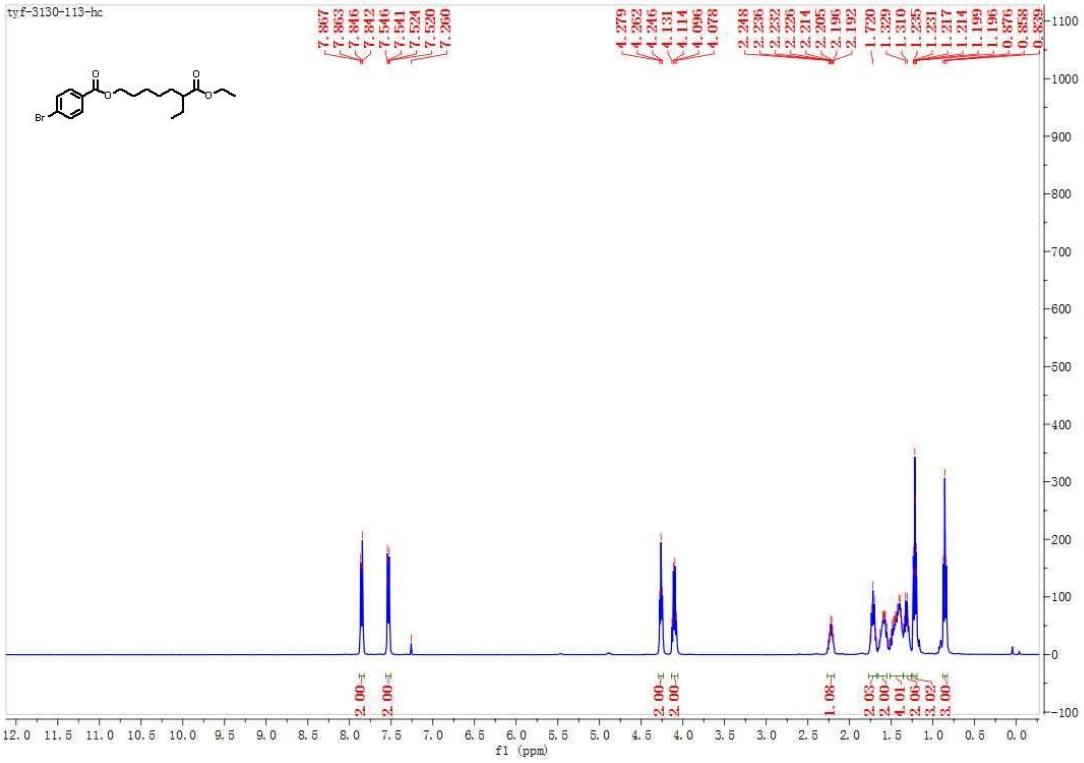
18a-^{1}H NMR



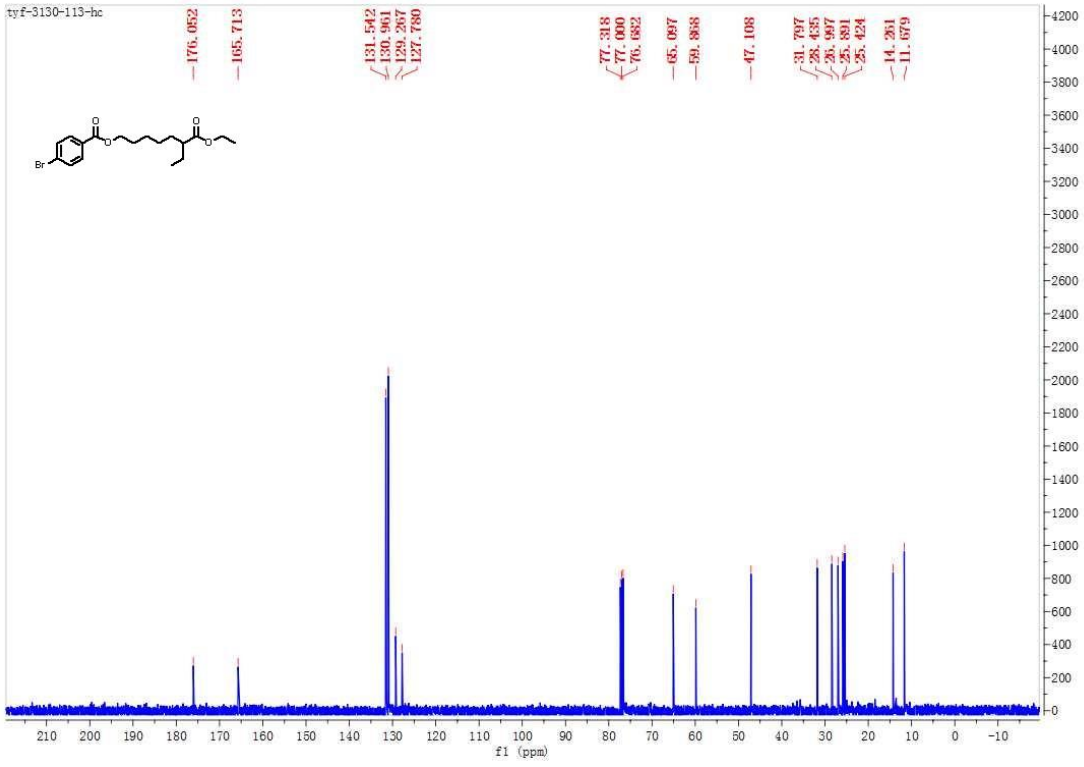
18a-^{13}C NMR



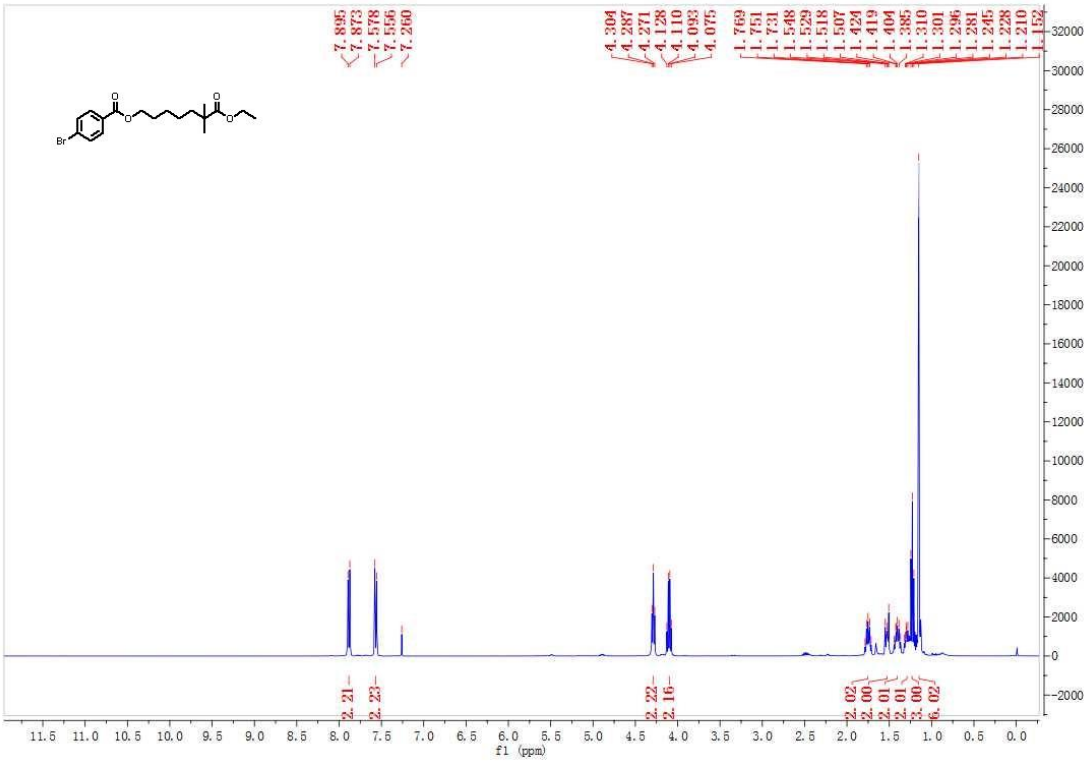
19a-^{1}H NMR



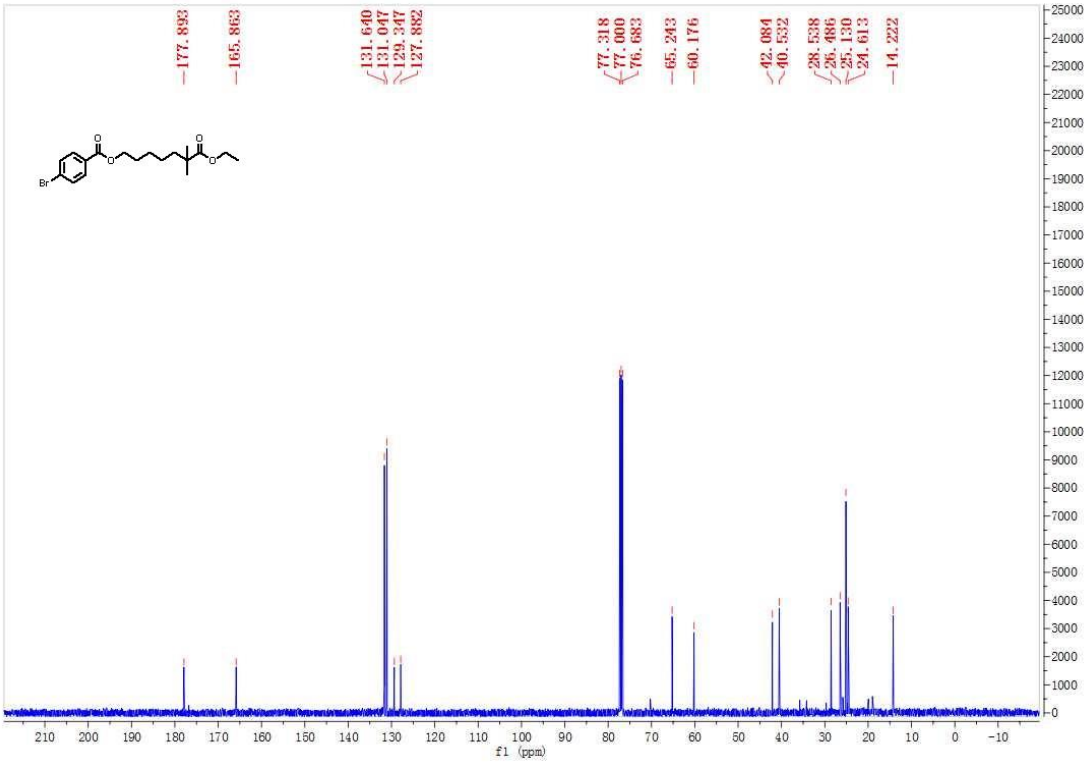
19a-^{13}C NMR



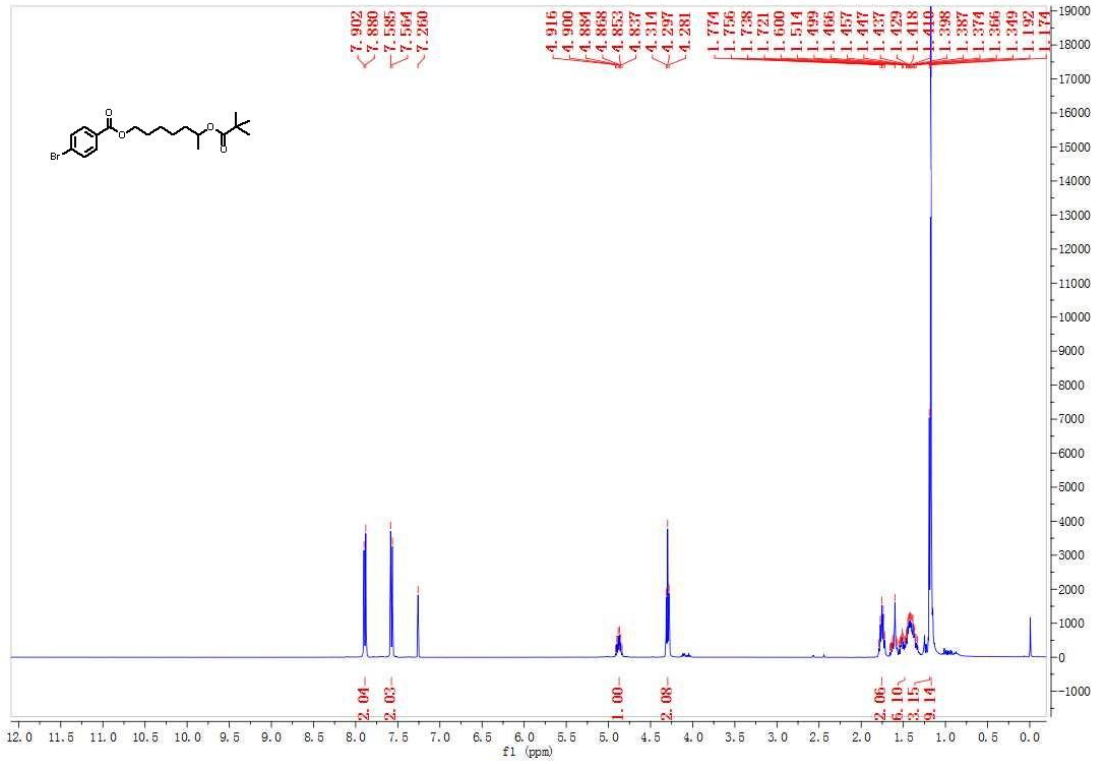
20a-^{1}H NMR



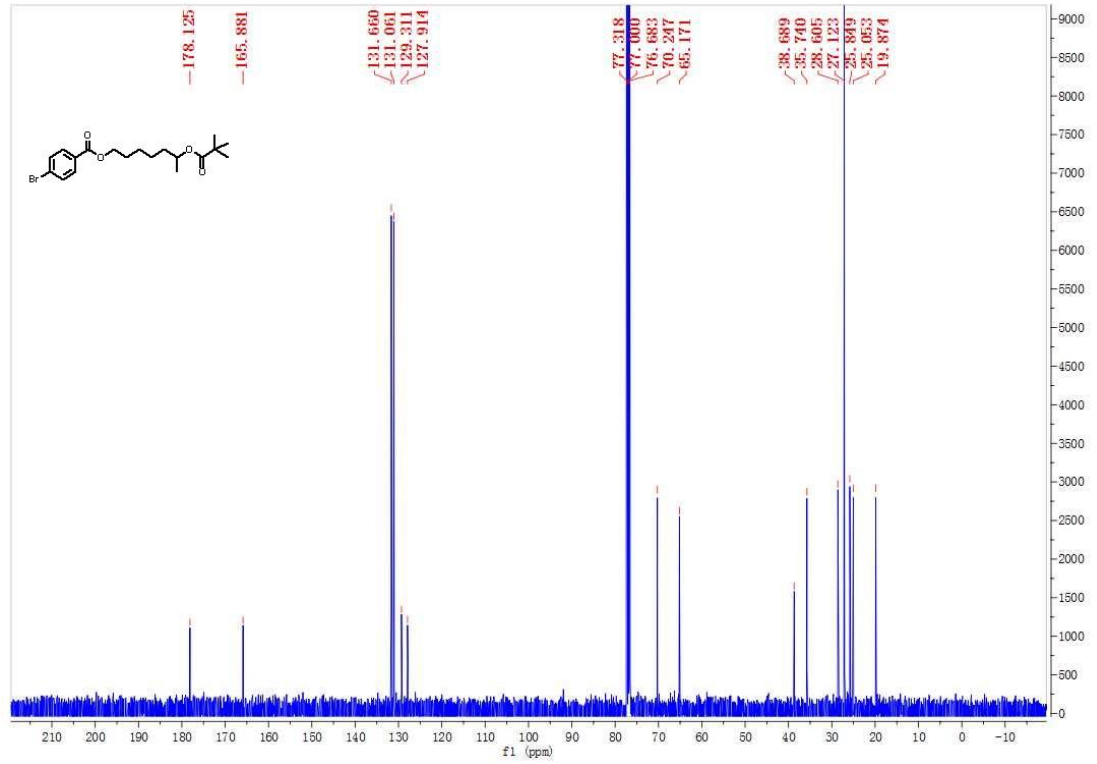
20a-^{13}C NMR



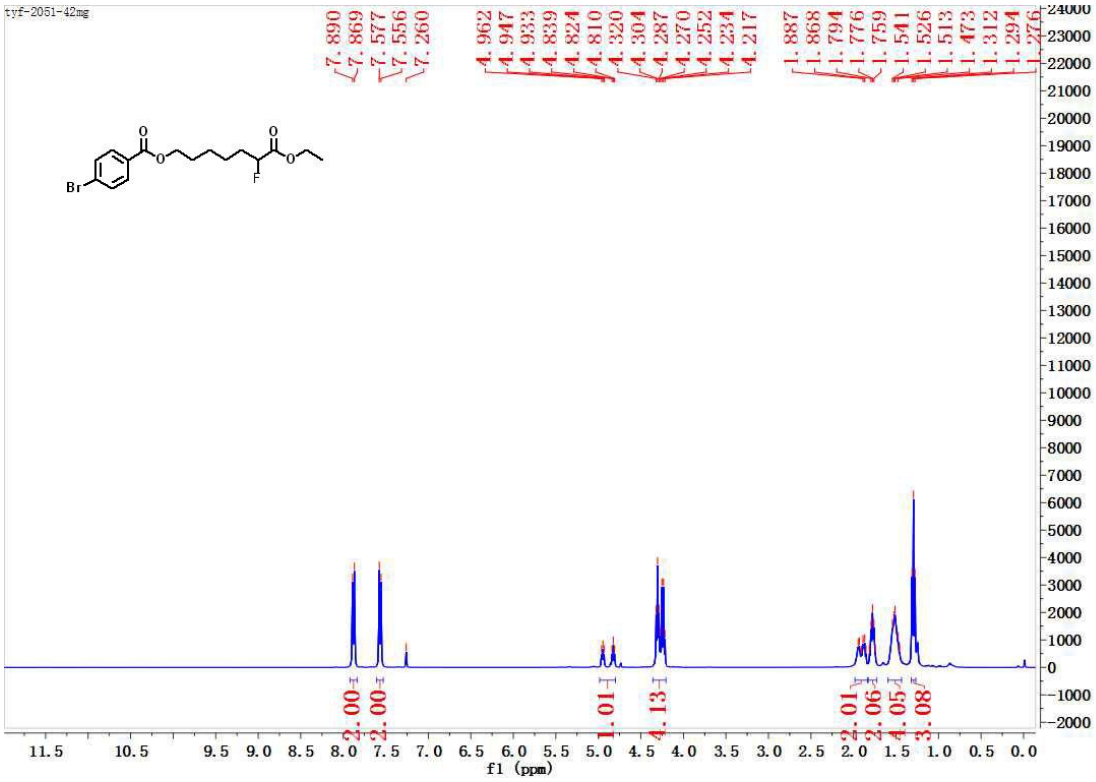
21a-^{1}H NMR



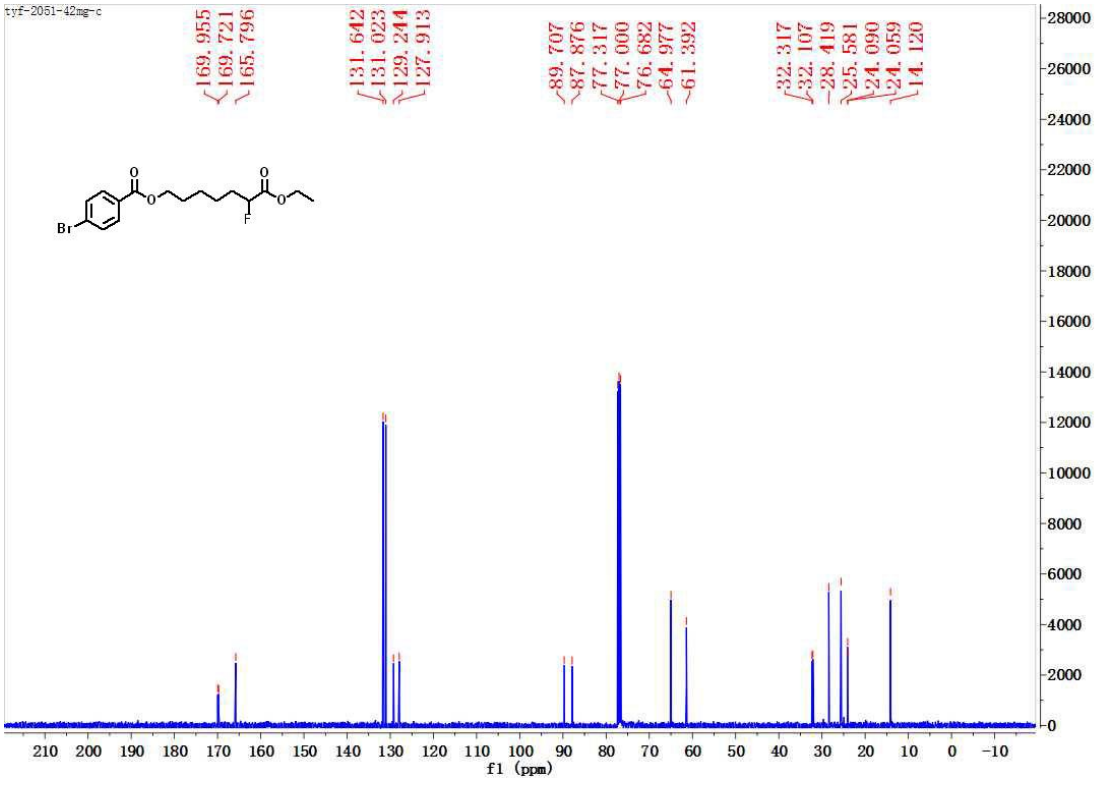
21a-^{13}C NMR



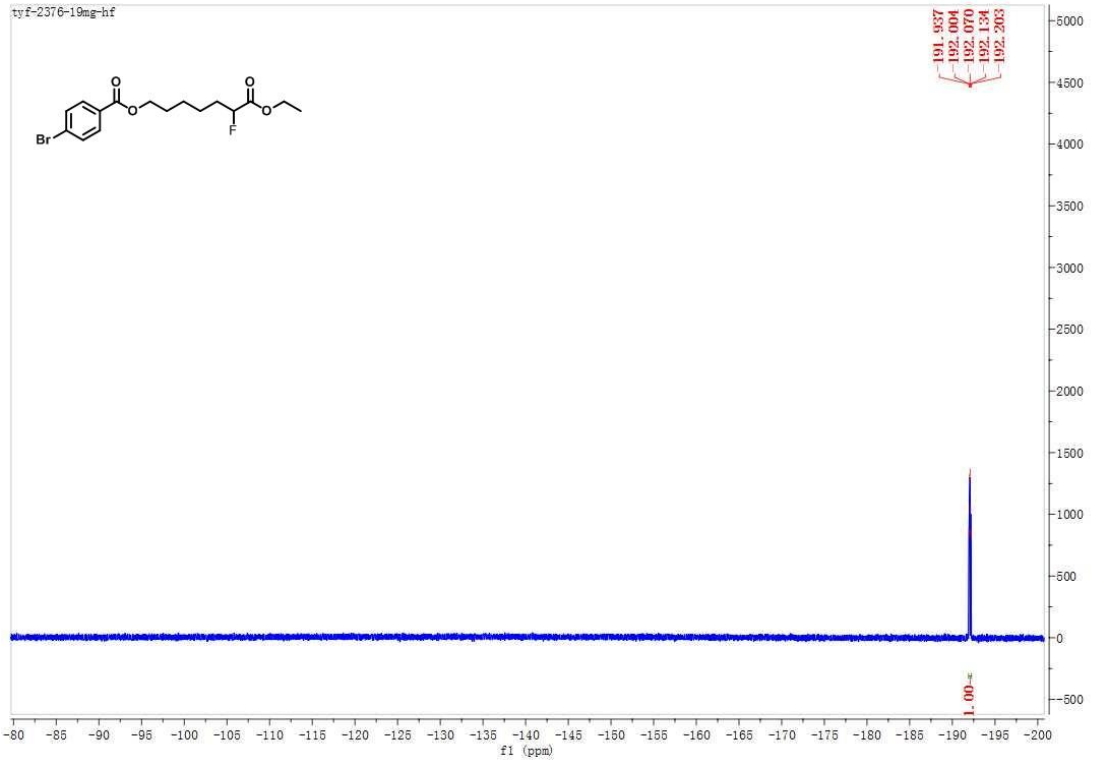
22a-^{1}H NMR



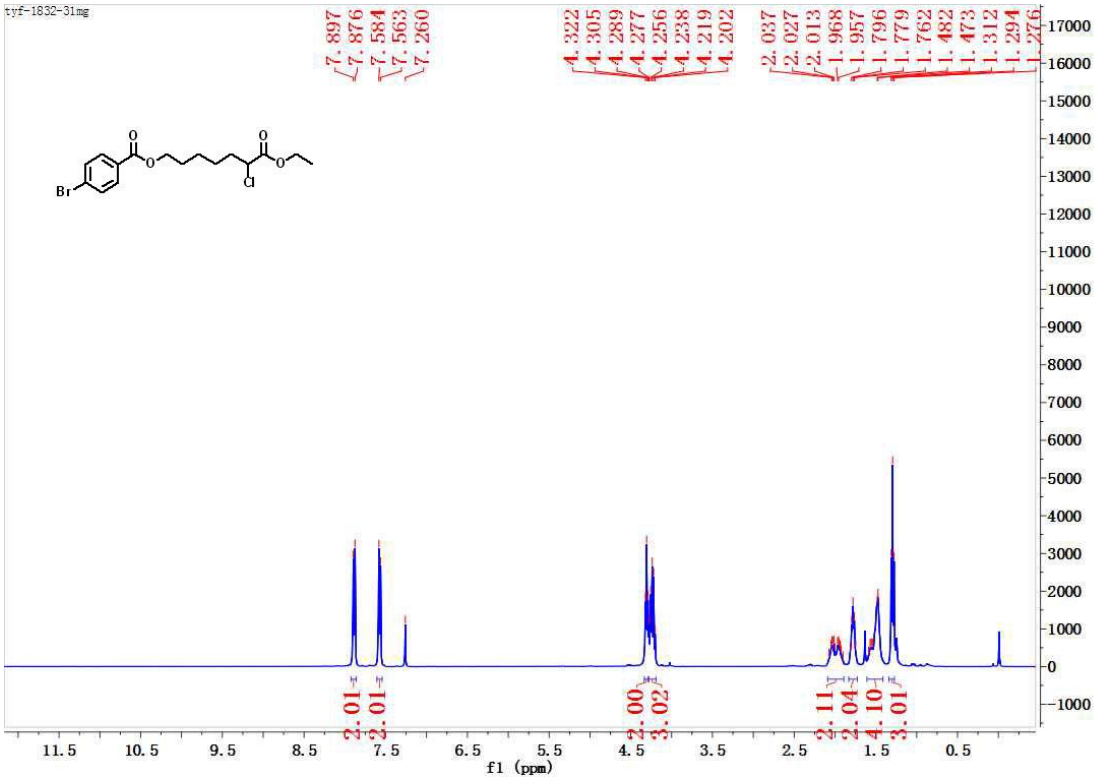
22a-^{13}C NMR



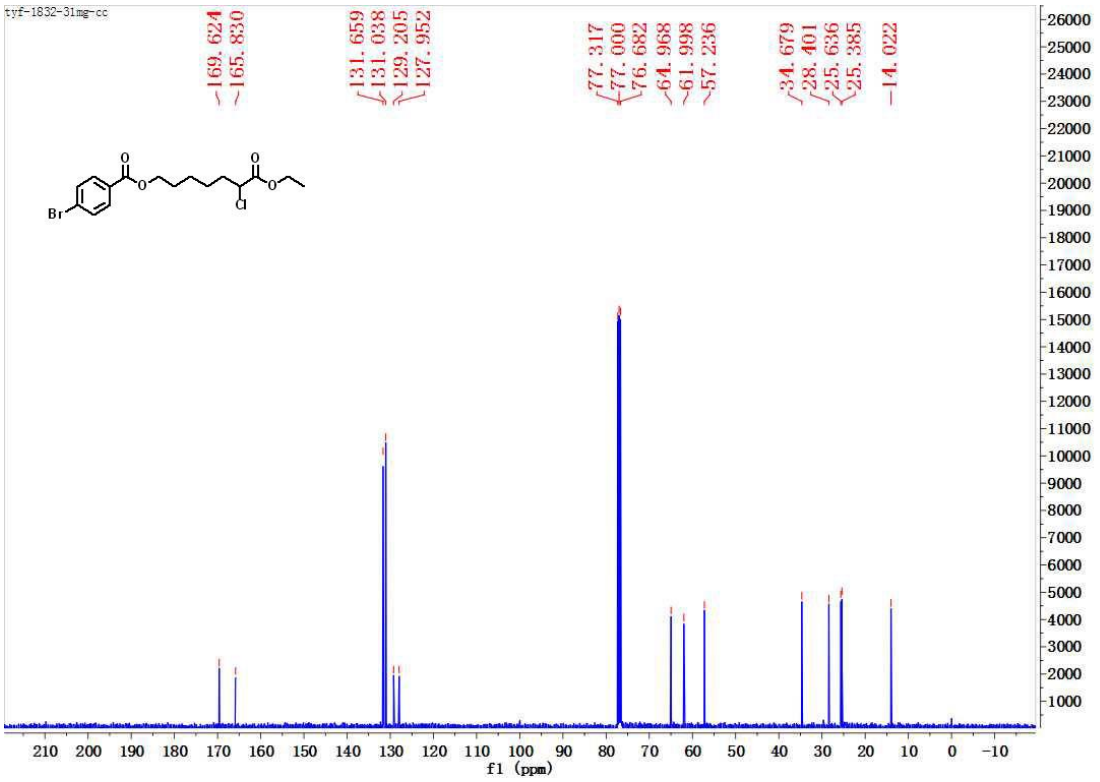
22a-^{19}F NMR



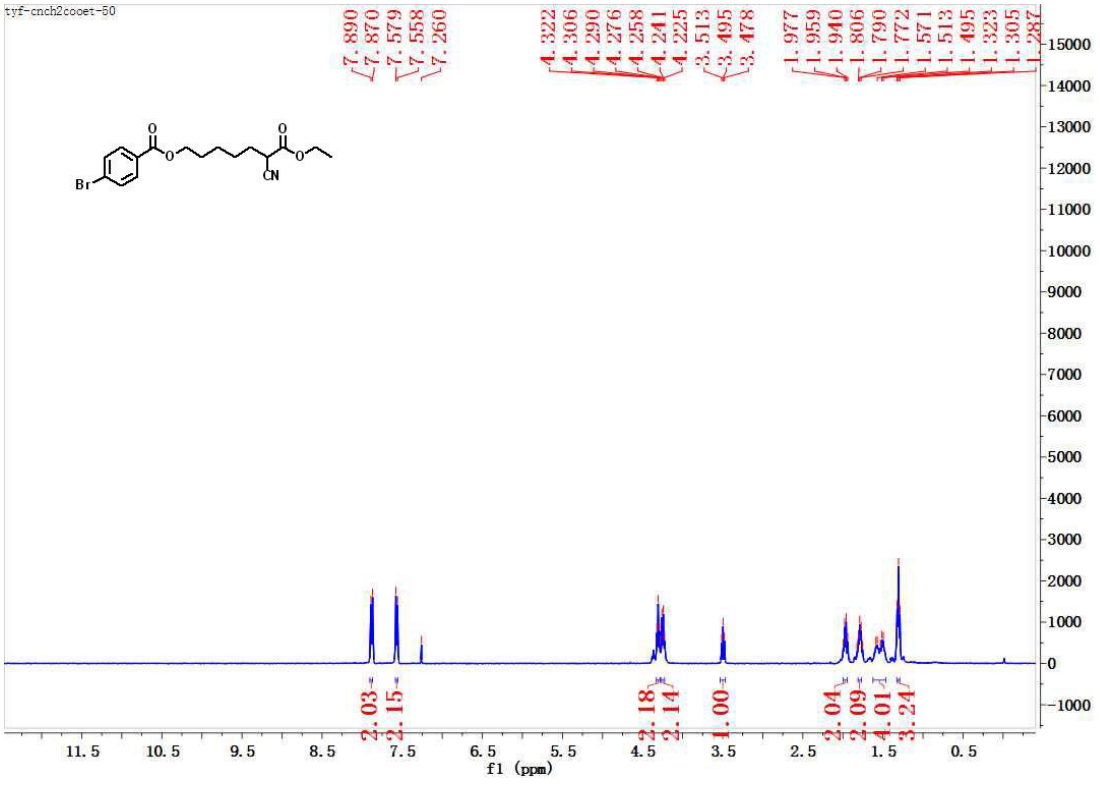
23a-^{1}H NMR



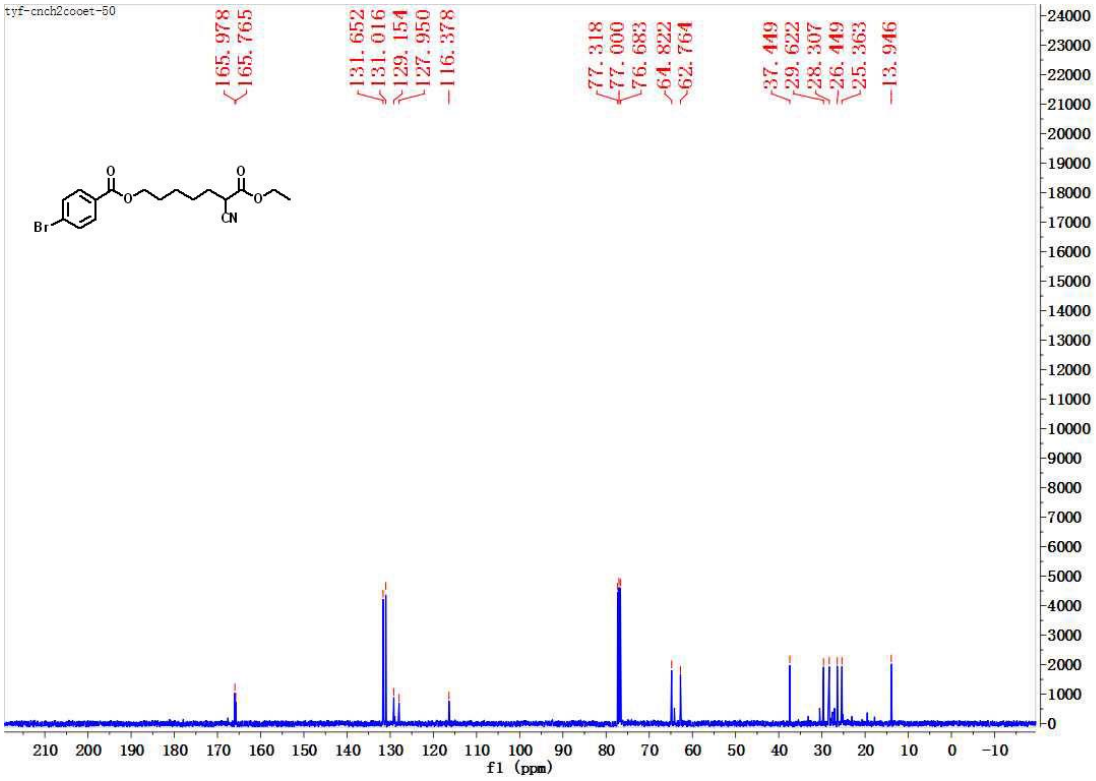
23a-^{13}C NMR



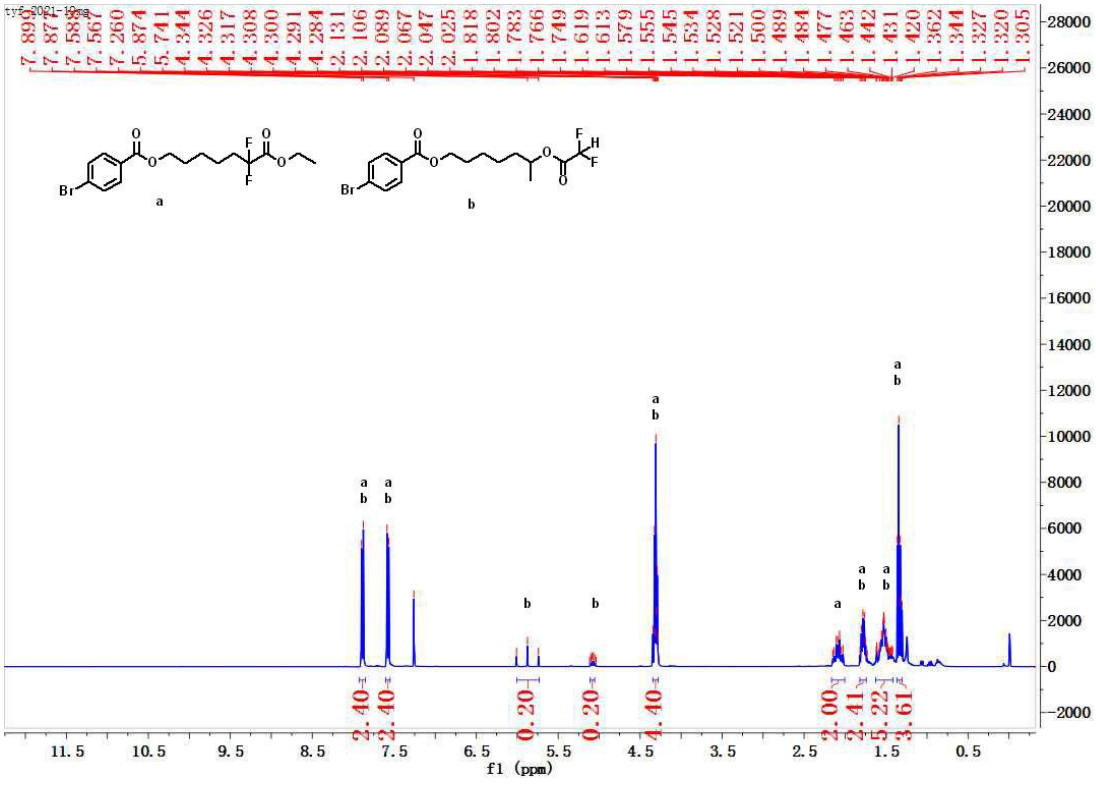
24a-^{1}H NMR



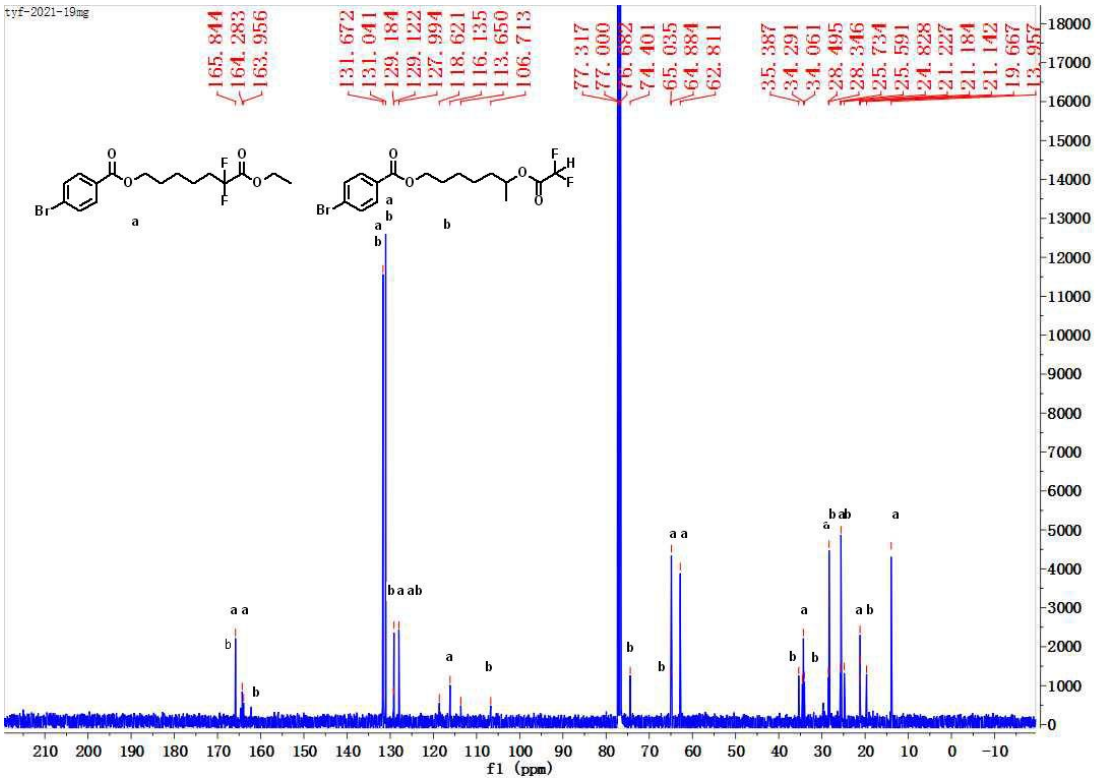
24a-^{13}C NMR



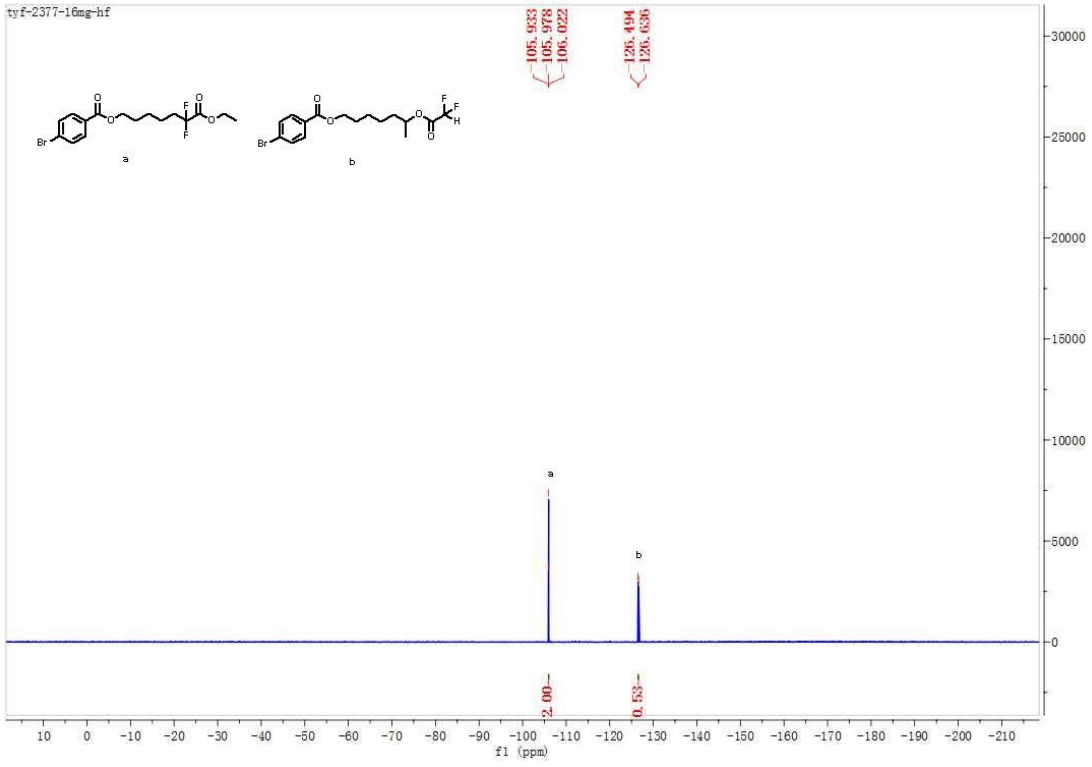
25a-^{1}H NMR



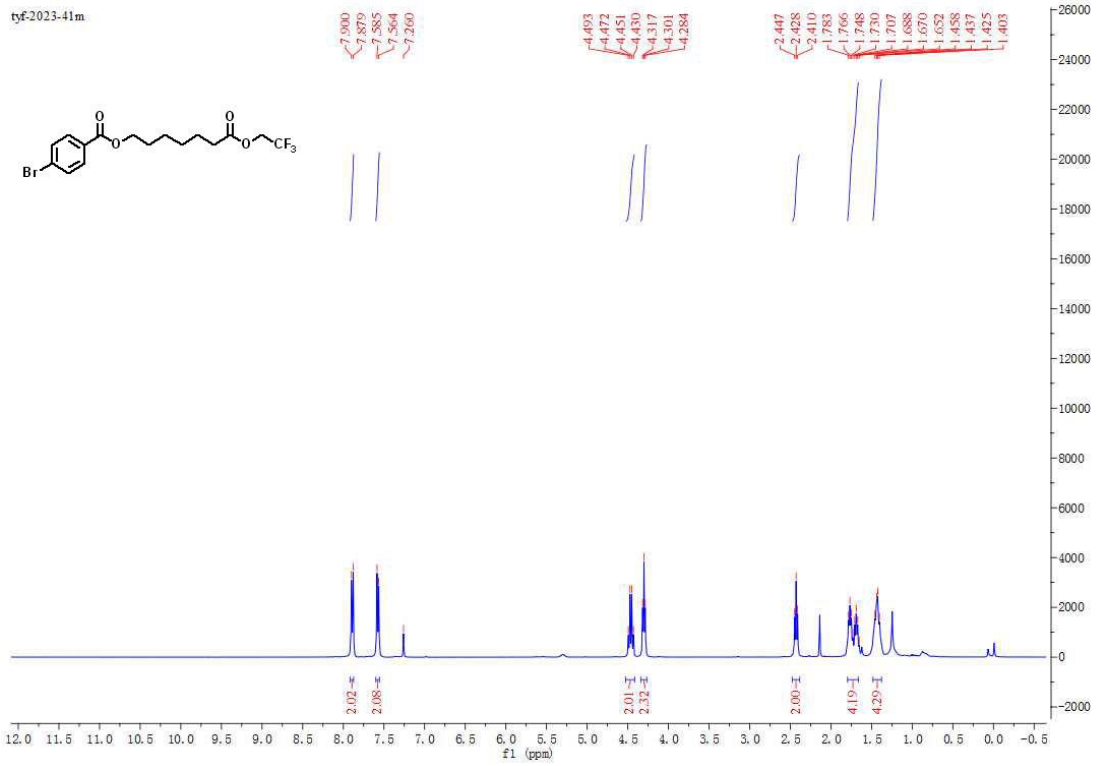
25a-^{13}C NMR



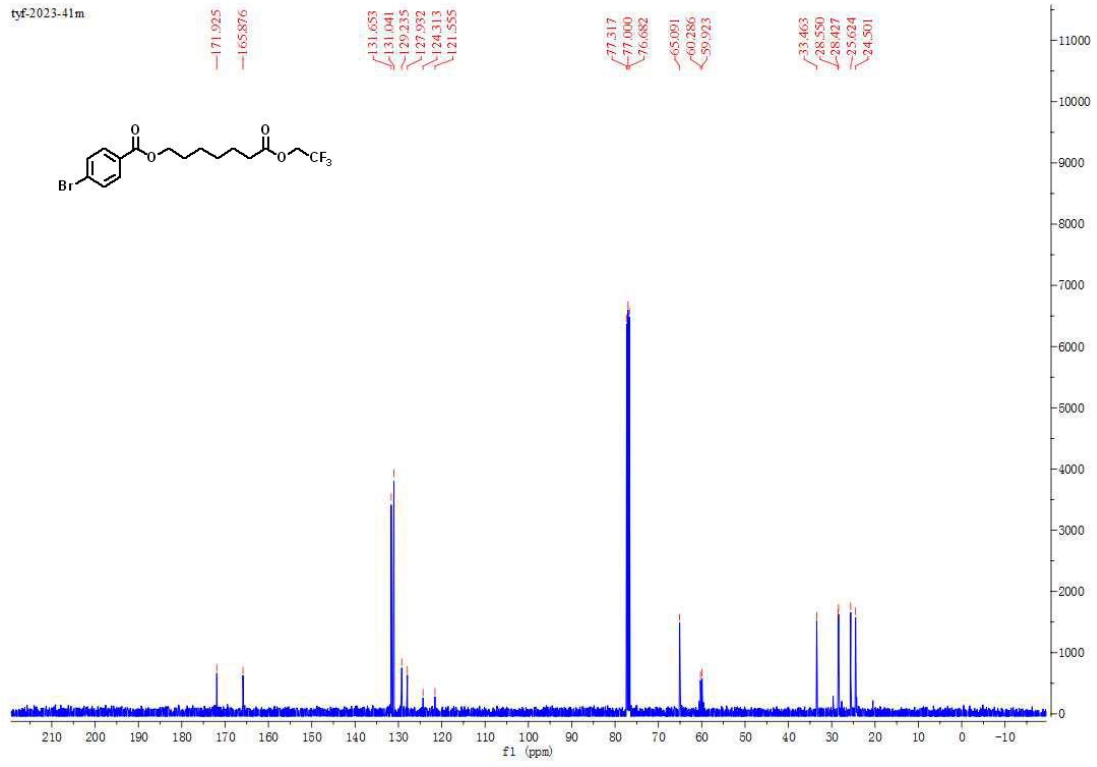
25a-^{19}F



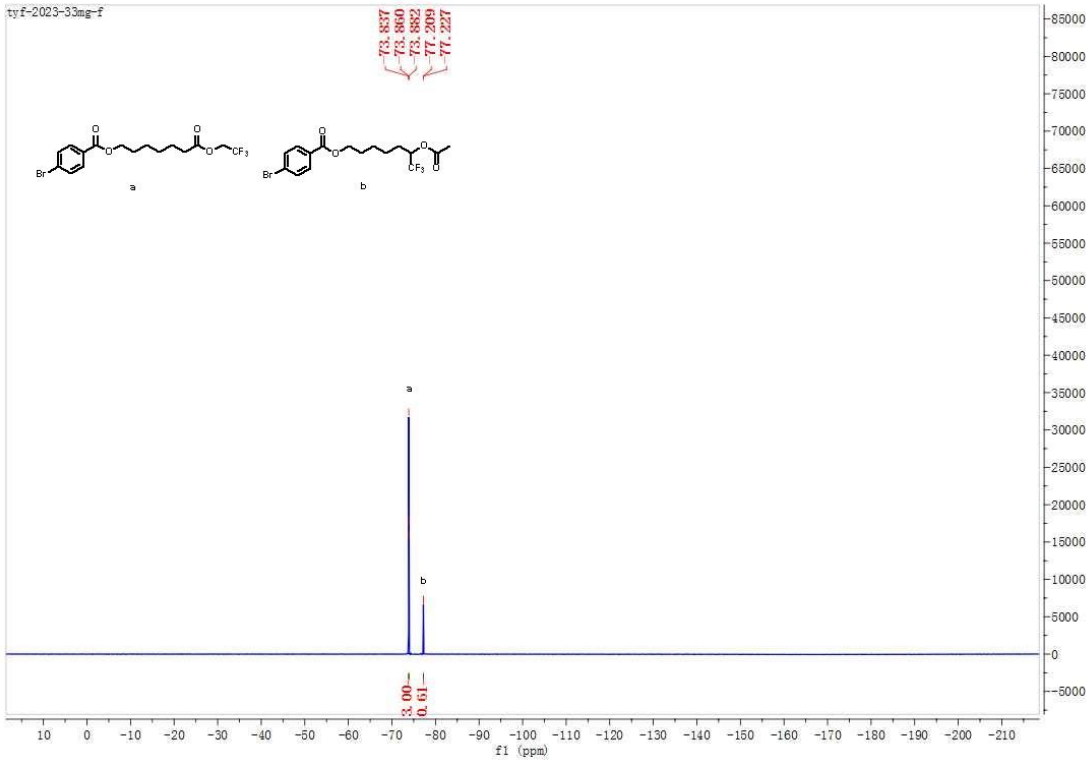
26a-^{1}H NMR



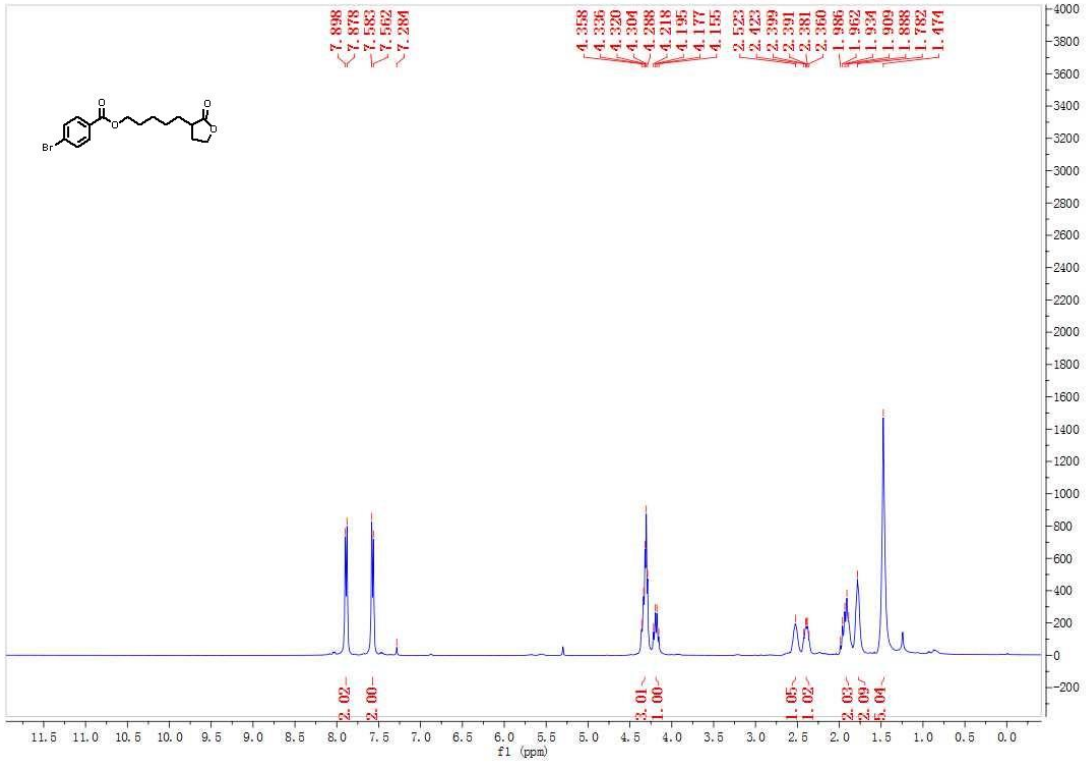
26a-^{13}C NMR



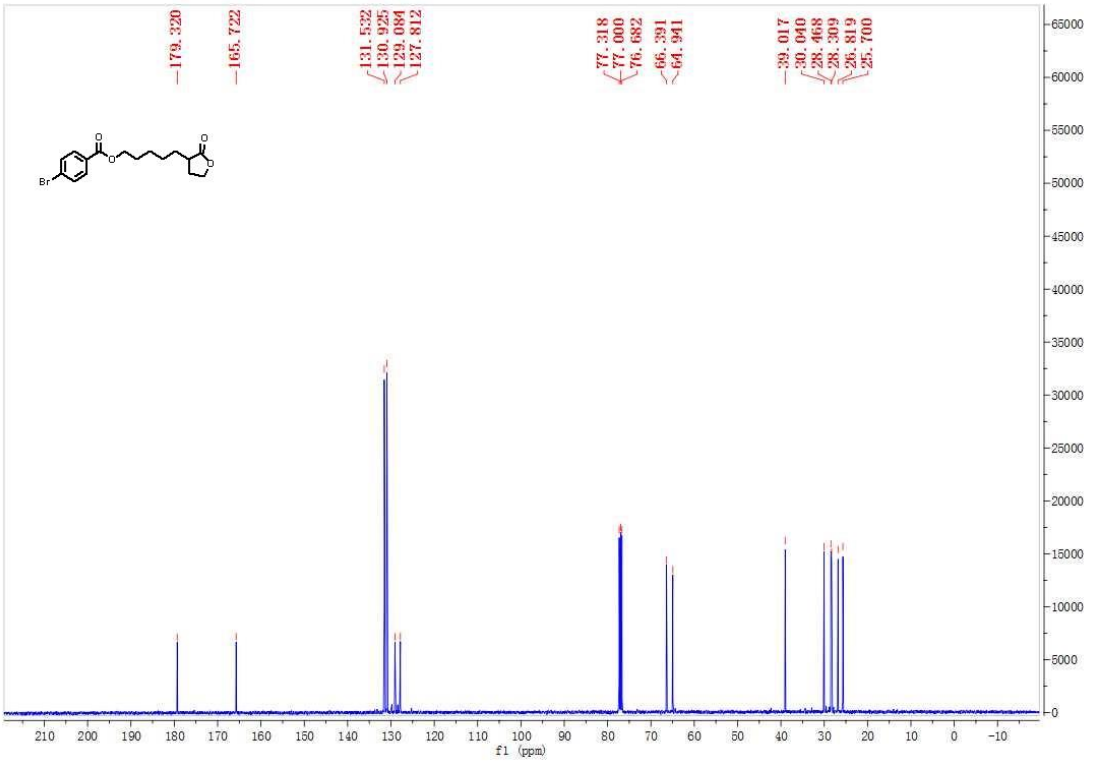
26a-^{19}F



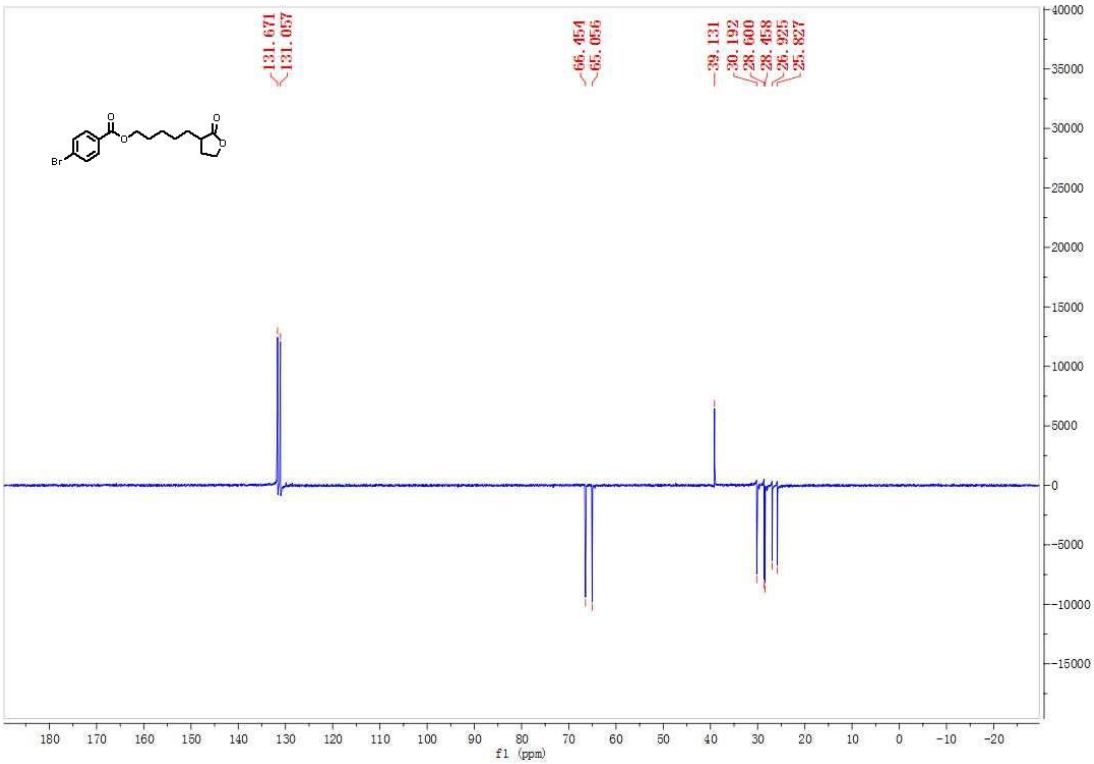
27a-^{1}H NMR



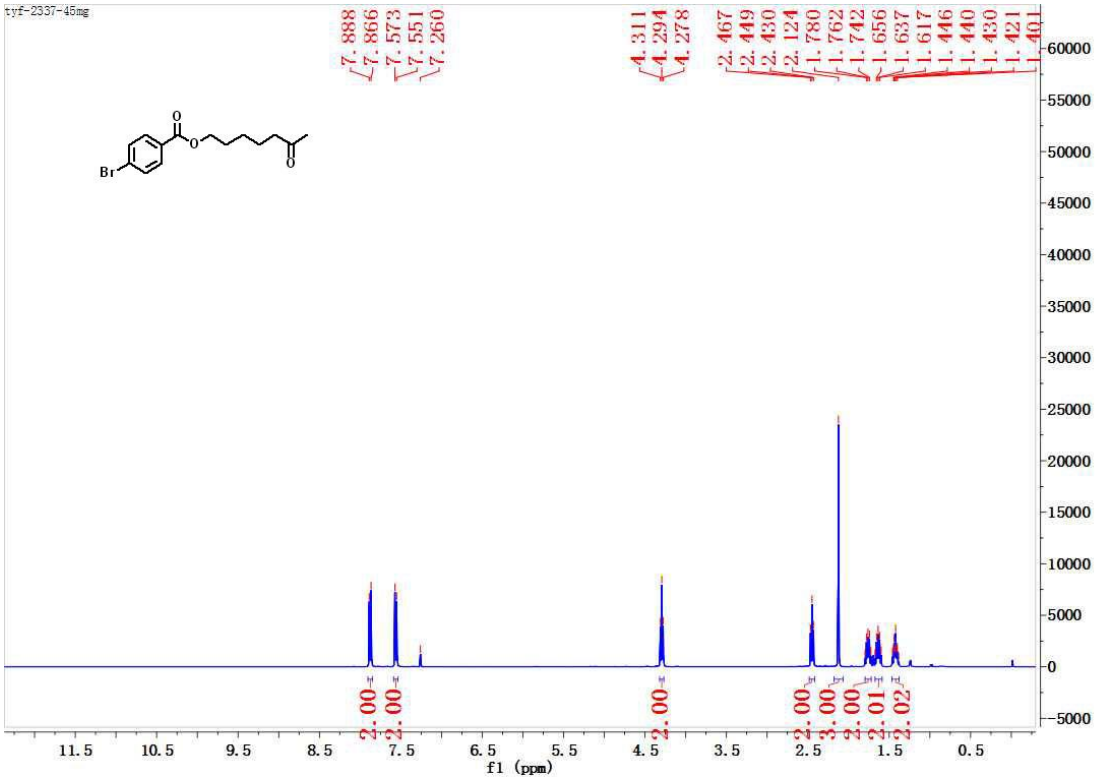
27a-^{13}C NMR



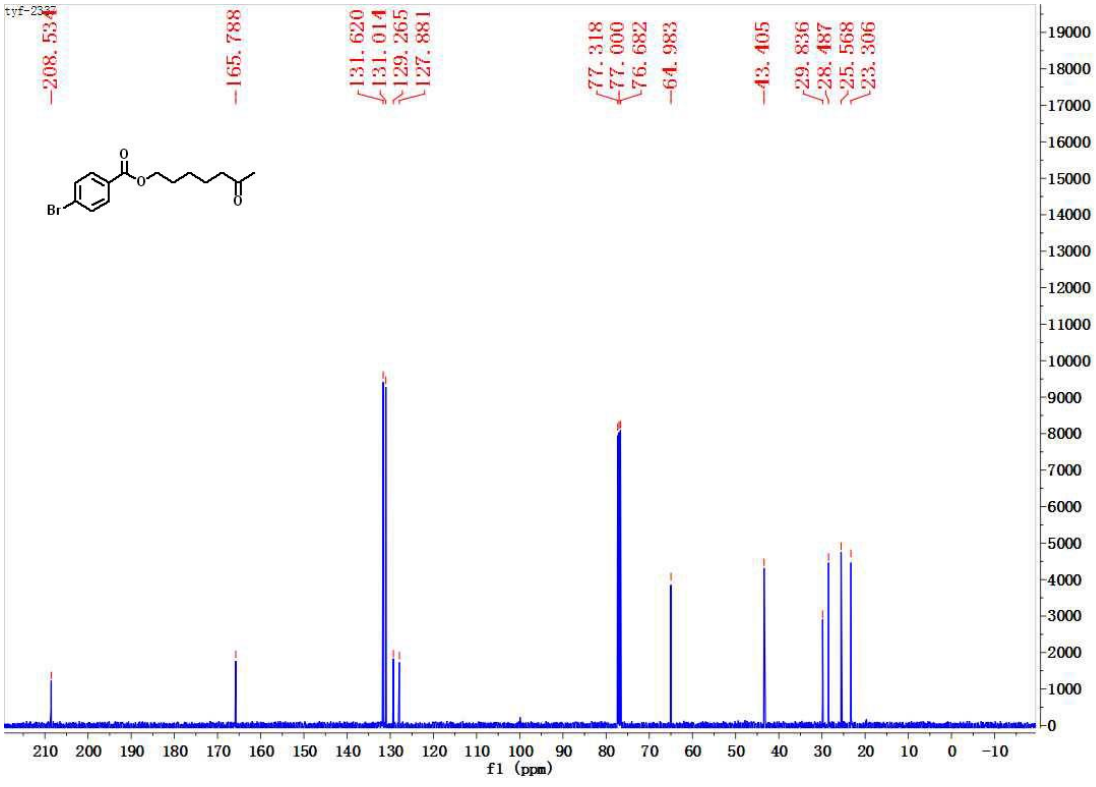
27a-^{13}DEPT



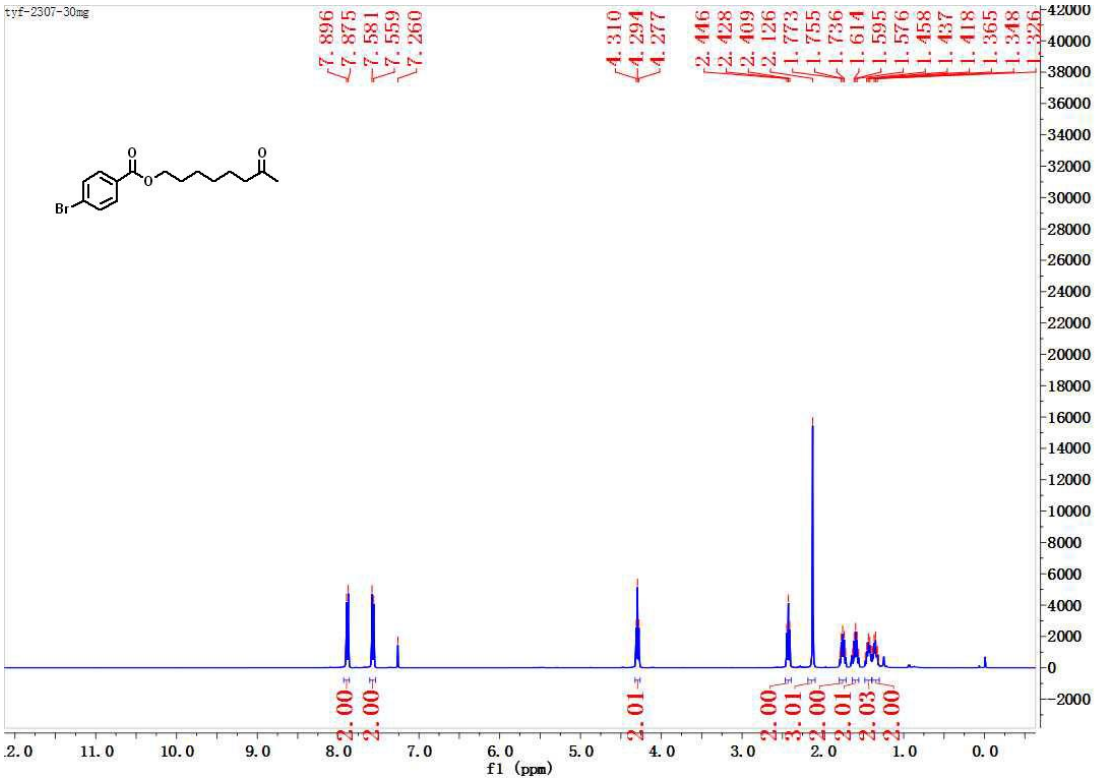
1b-^{1}H NMR



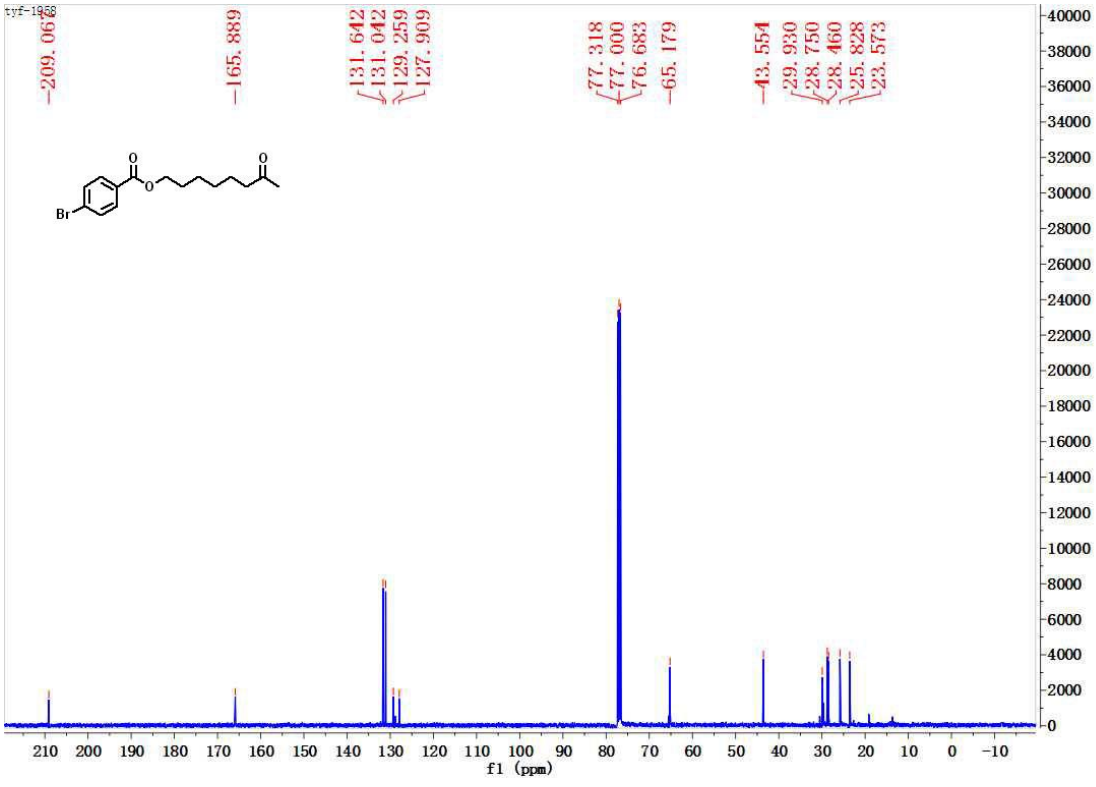
1b-^{13}C NMR



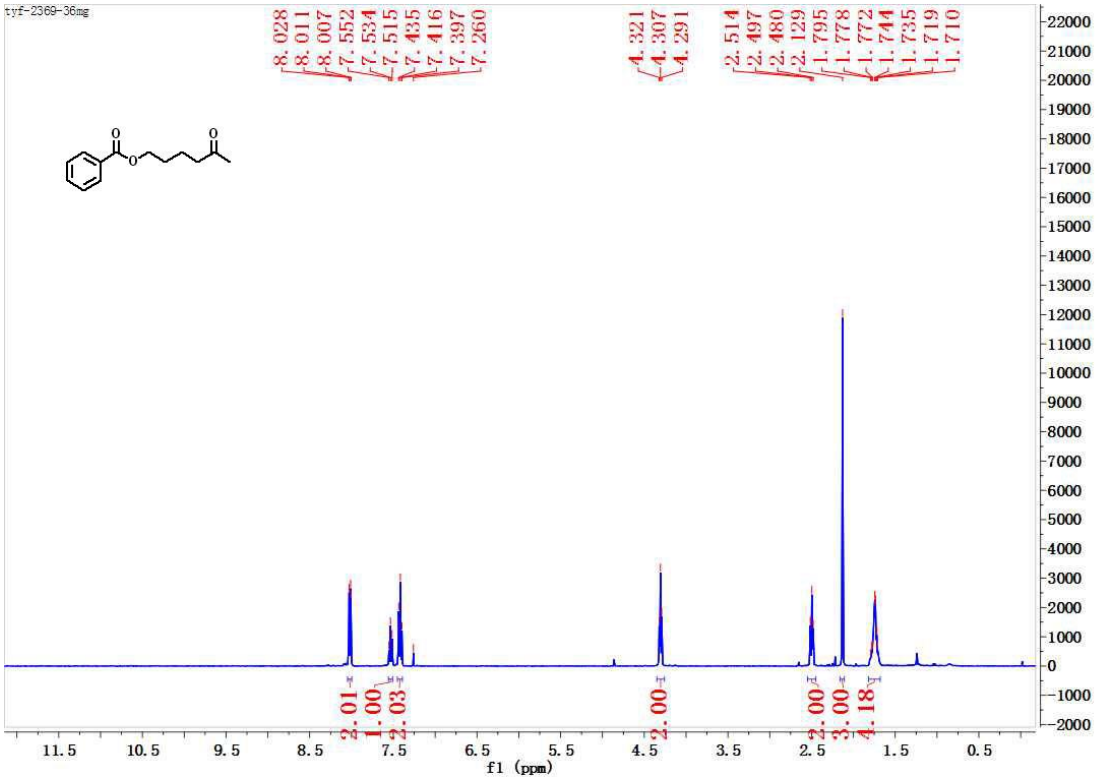
2b-^{1}HNMR



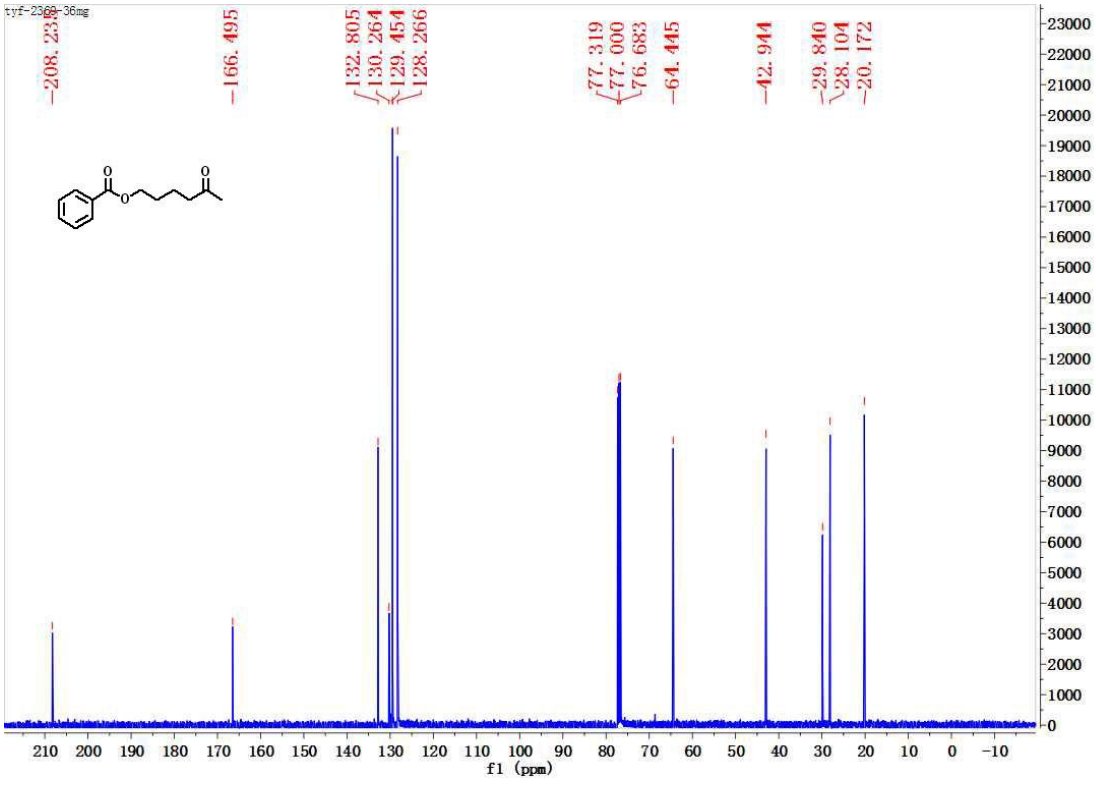
2b-^{13}C NMR



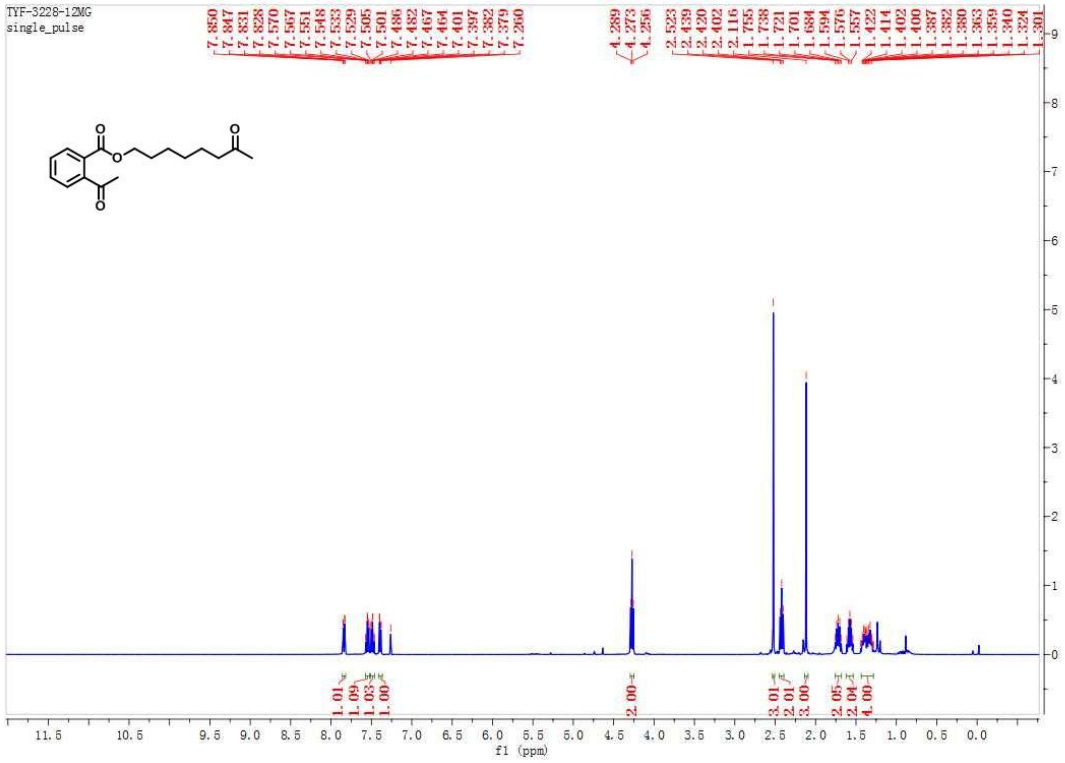
3b-^{1}H NMR



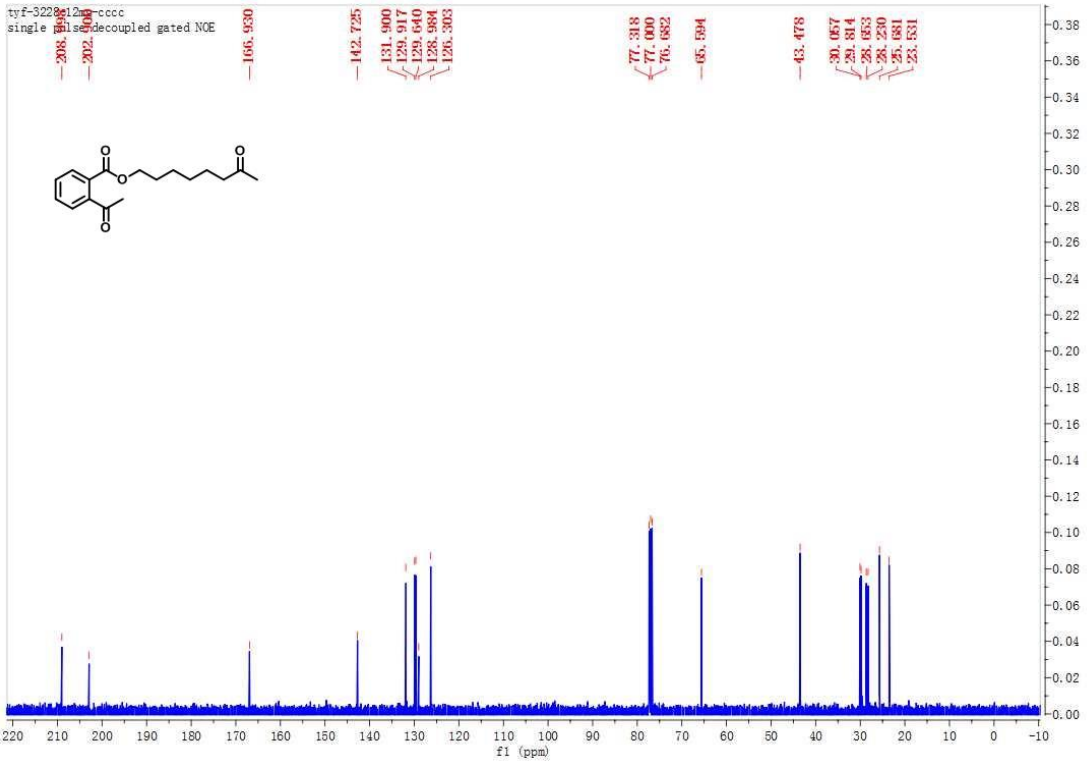
3b-^{13}C NMR



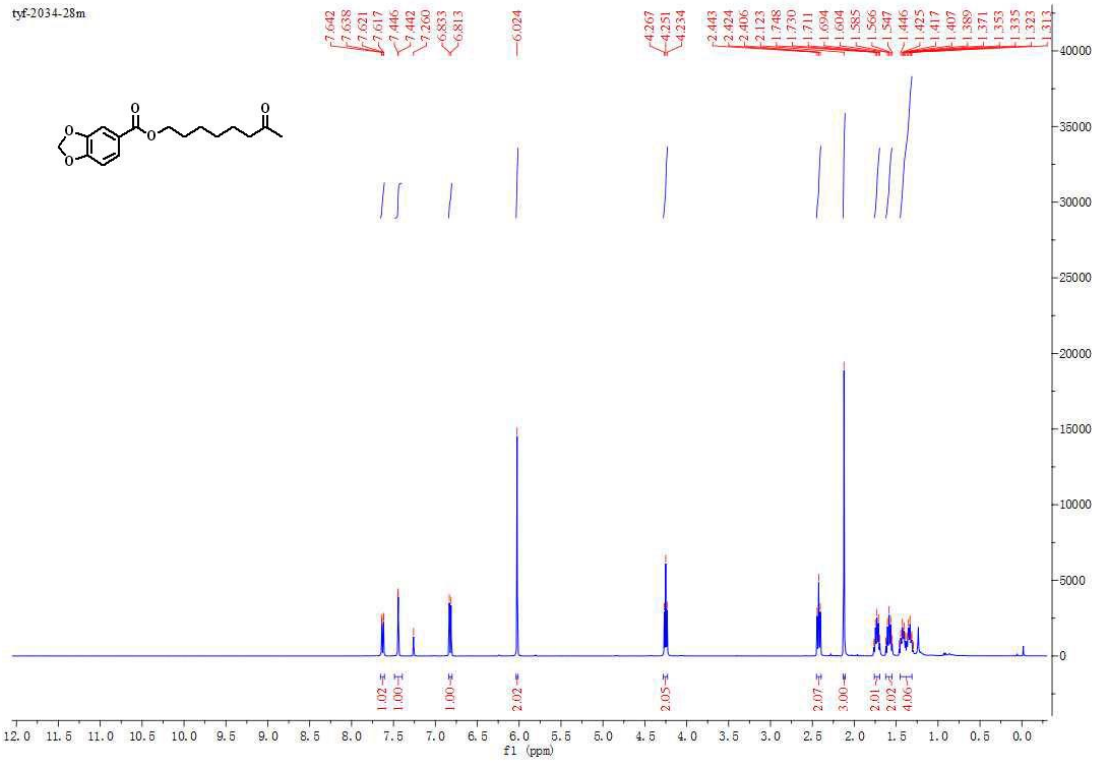
4b-^{1}H NMR



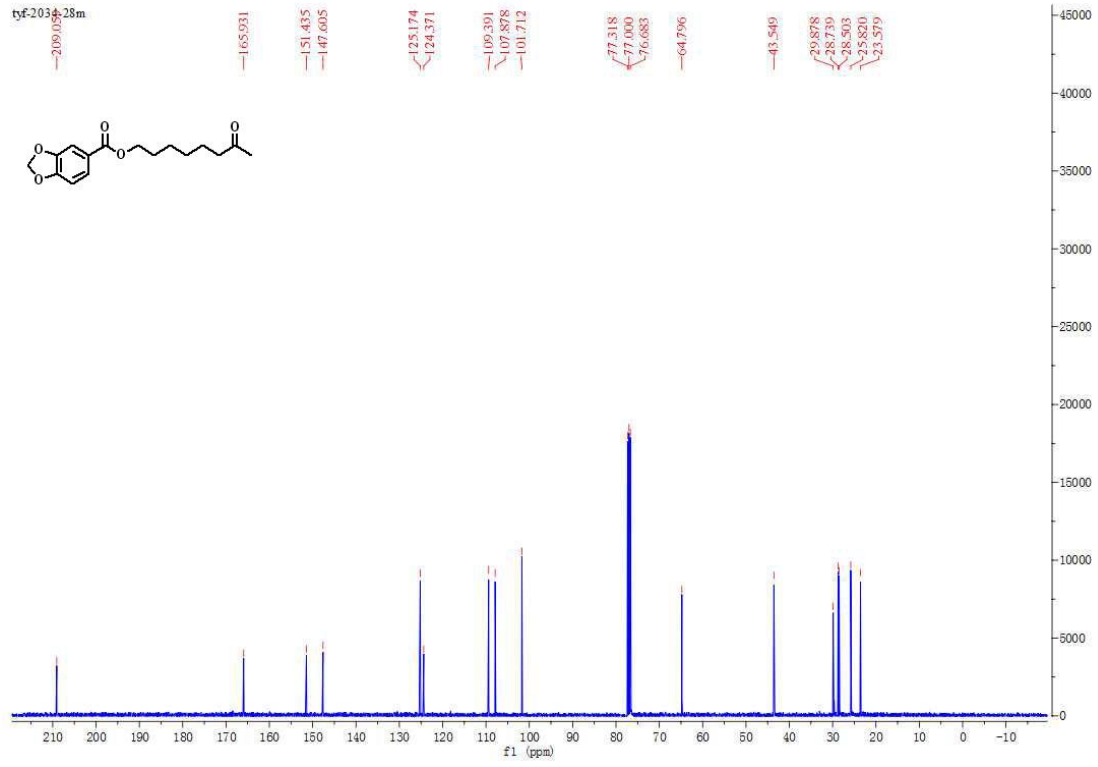
4b-^{13}C NMR



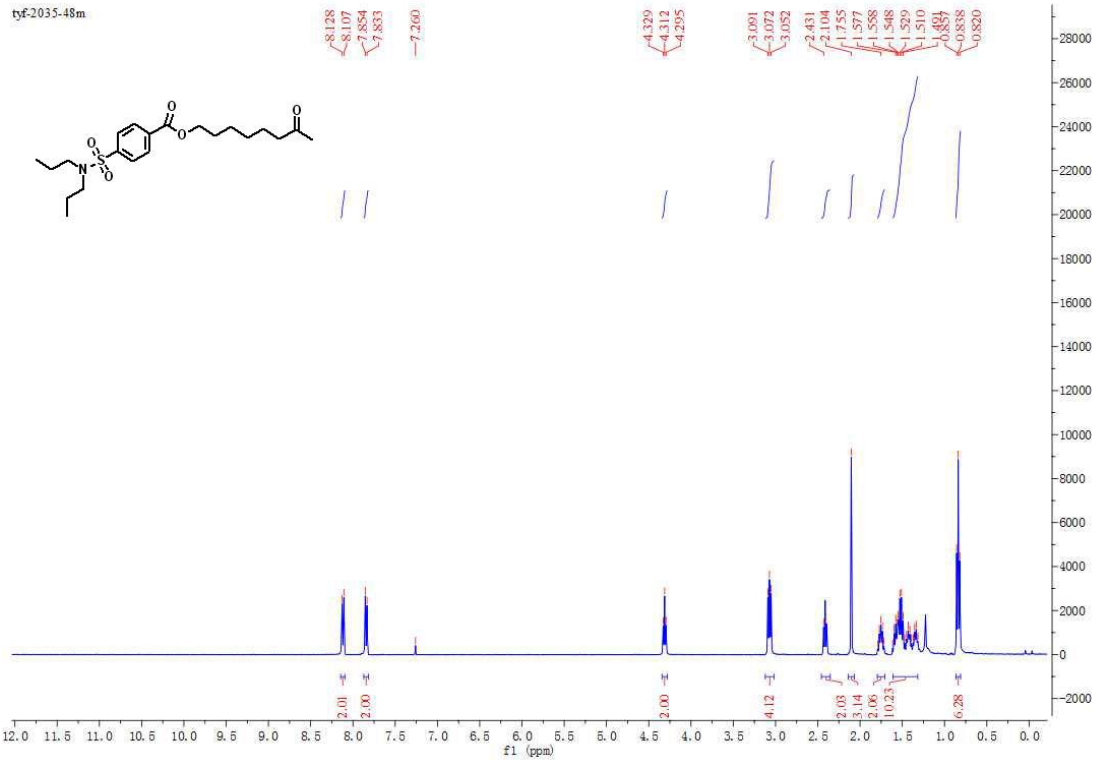
5b-^{1}H NMR



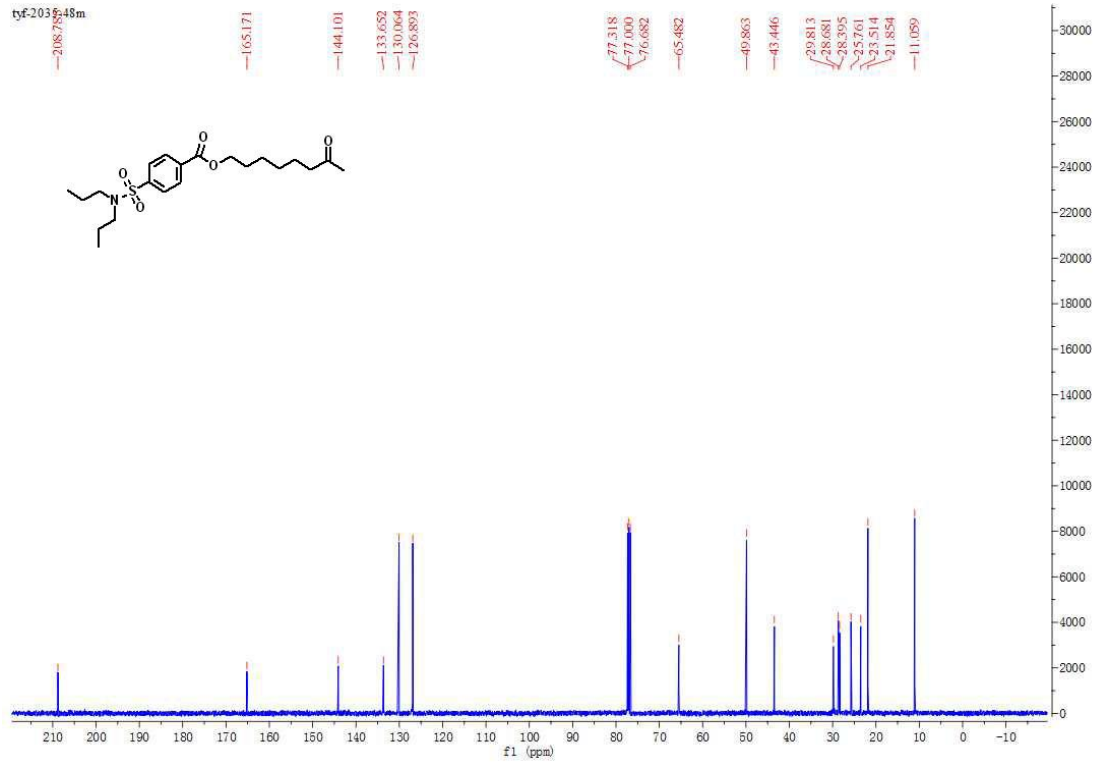
5b-^{13}C NMR



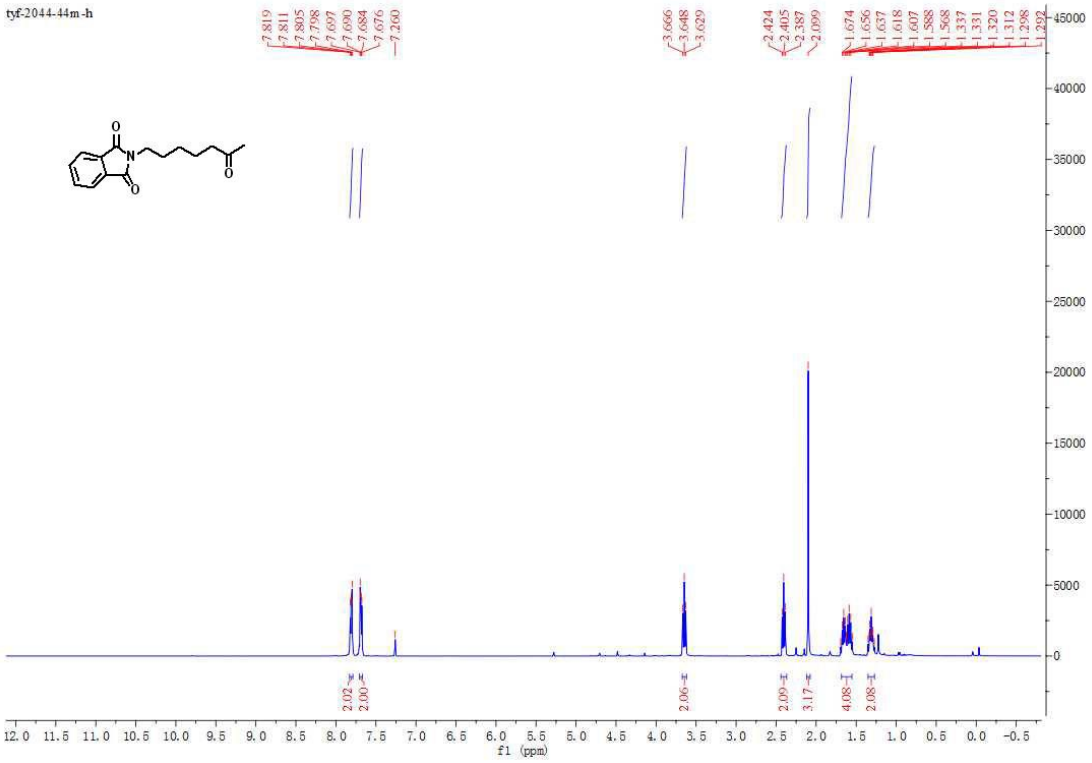
6b-^{1}H NMR



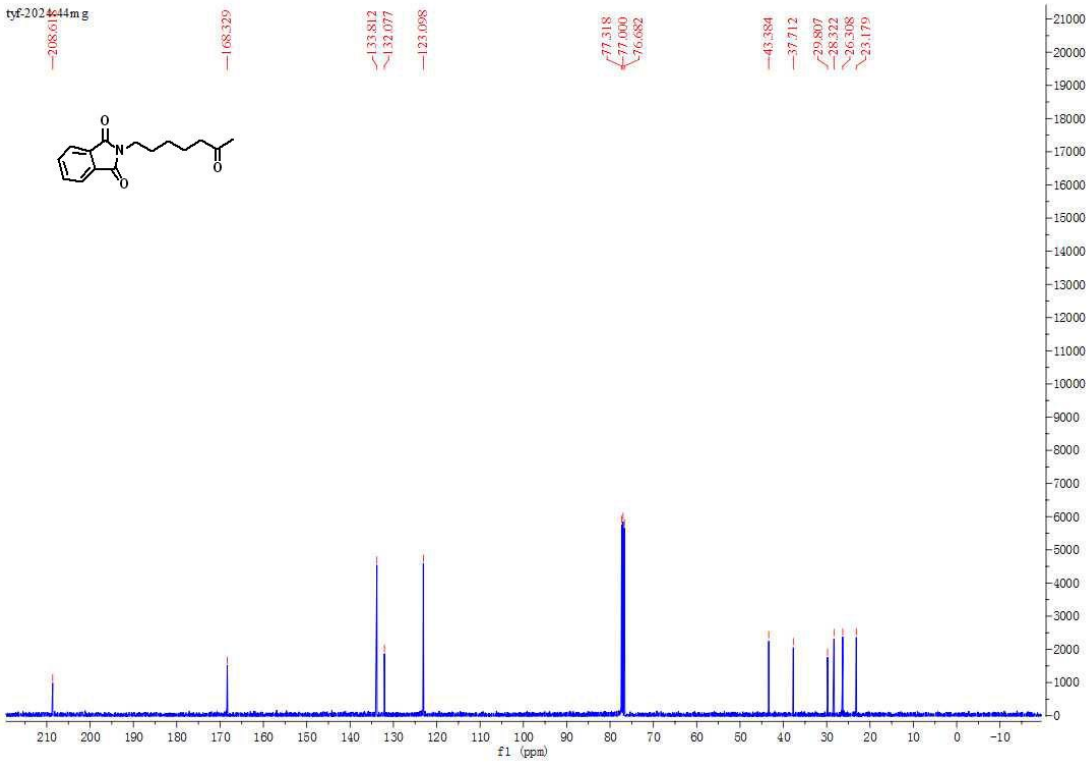
6b-^{13}C NMR



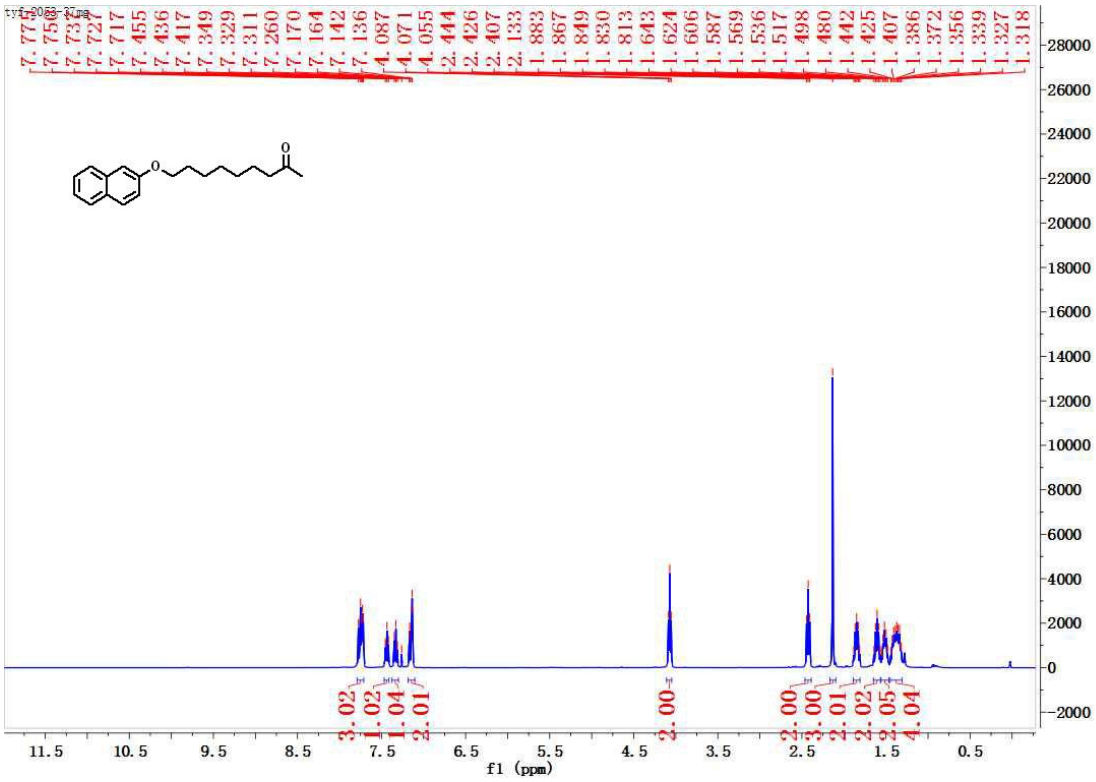
7b-^{1}H NMR



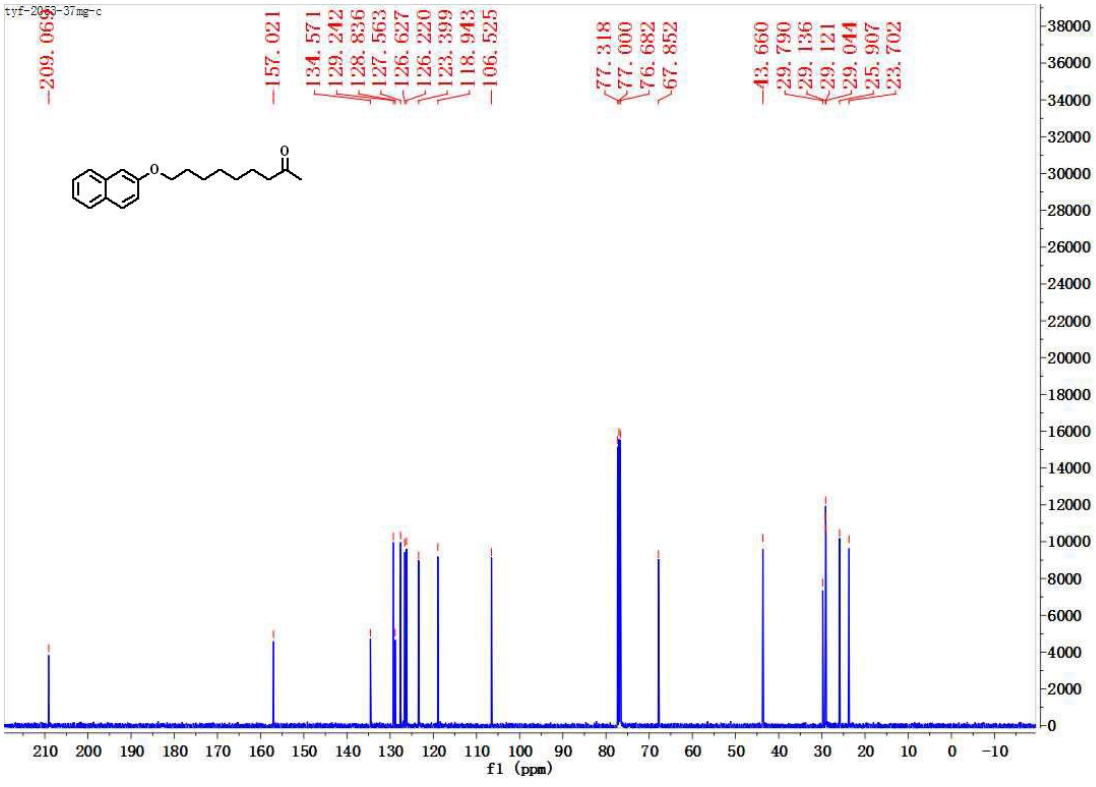
7b-^{13}C NMR



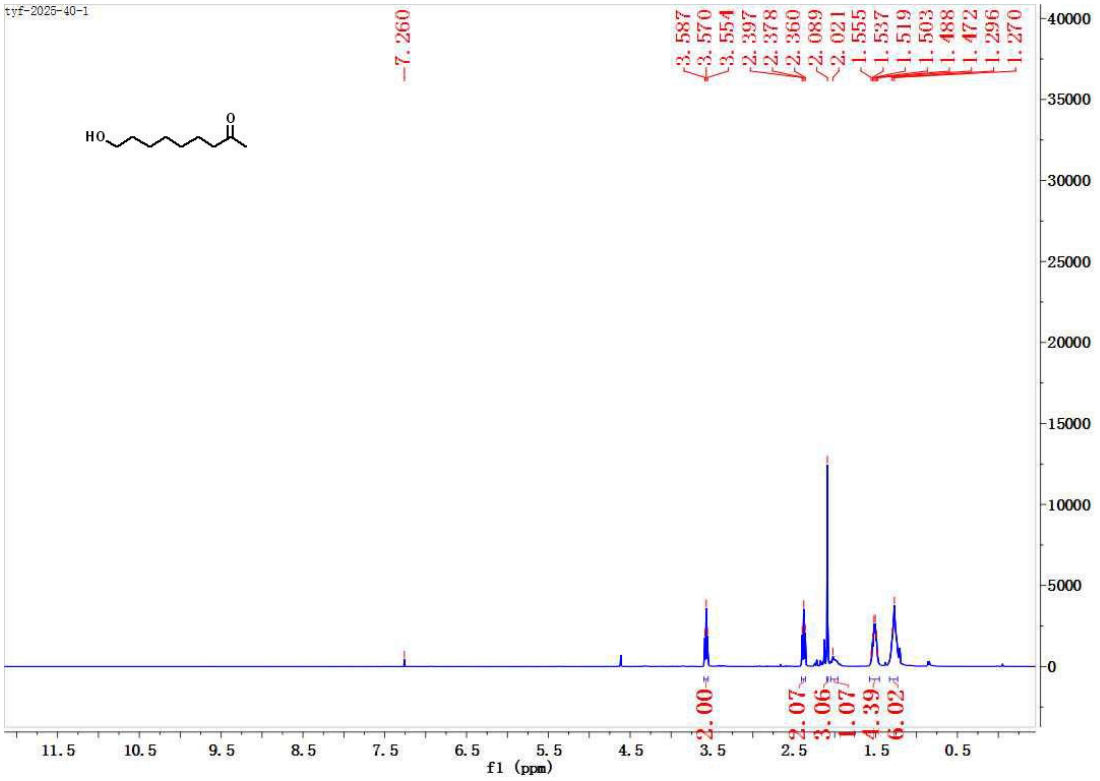
8b-^{1}H NMR



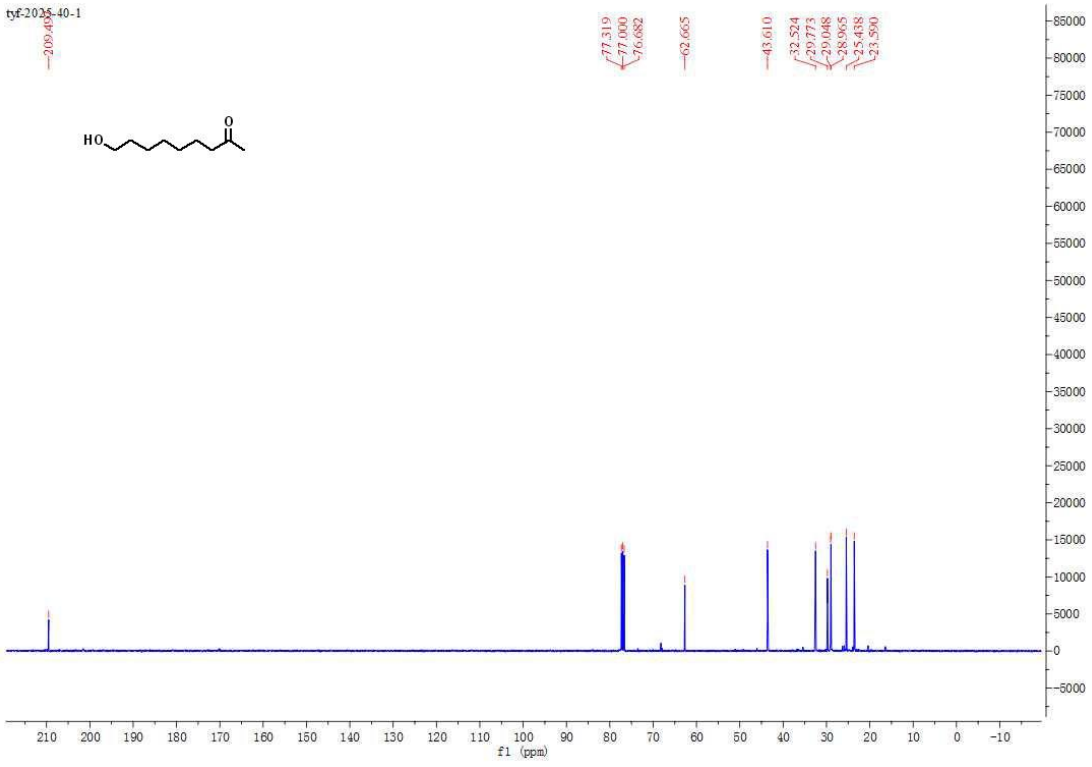
8b-^{13}C NMR



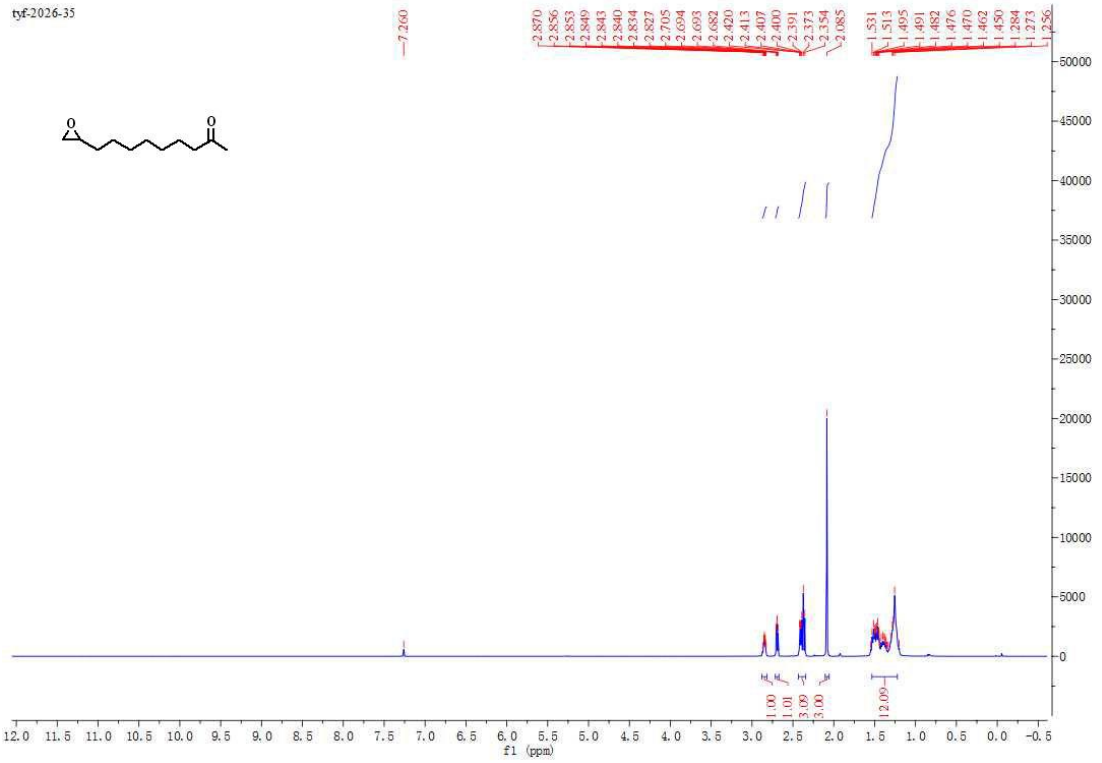
9b-^{1}H NMR



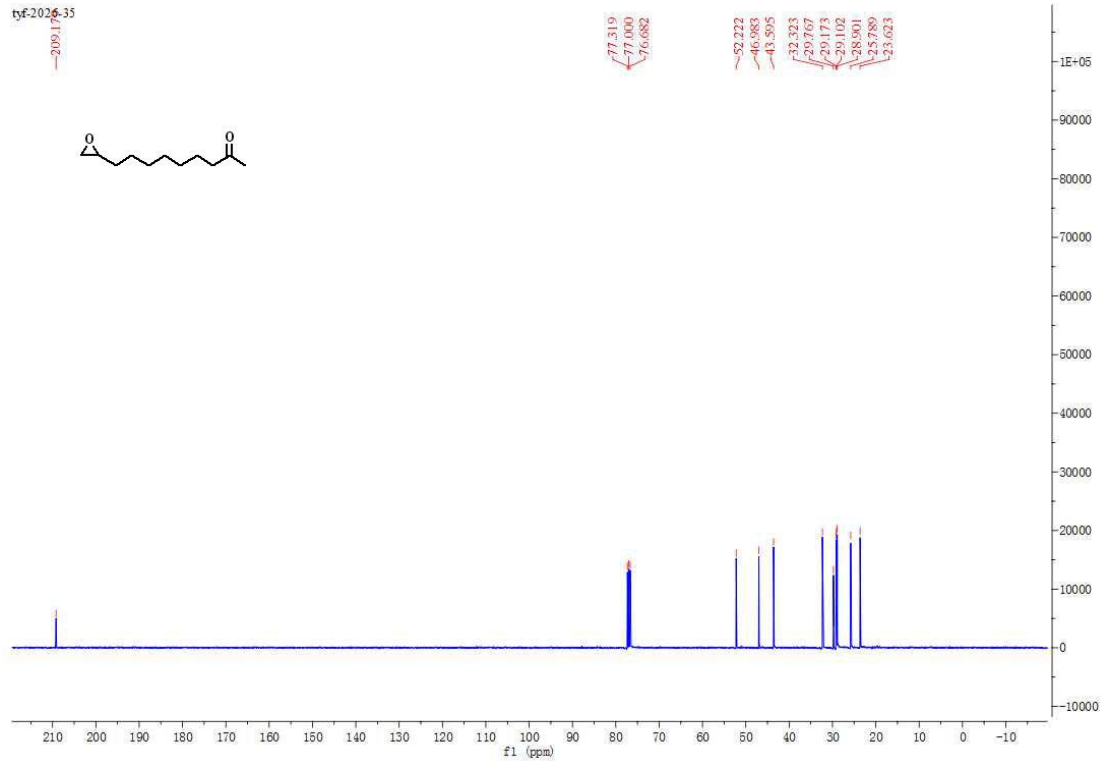
9b-^{13}C NMR



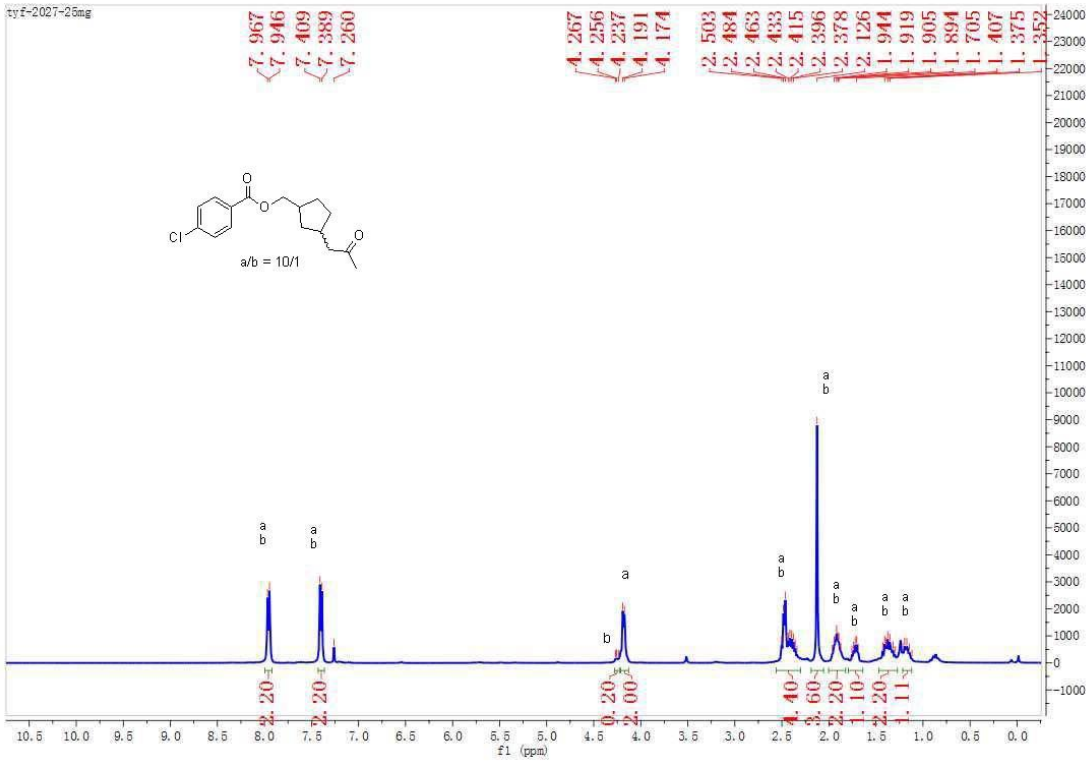
10b-^{1}H NMR



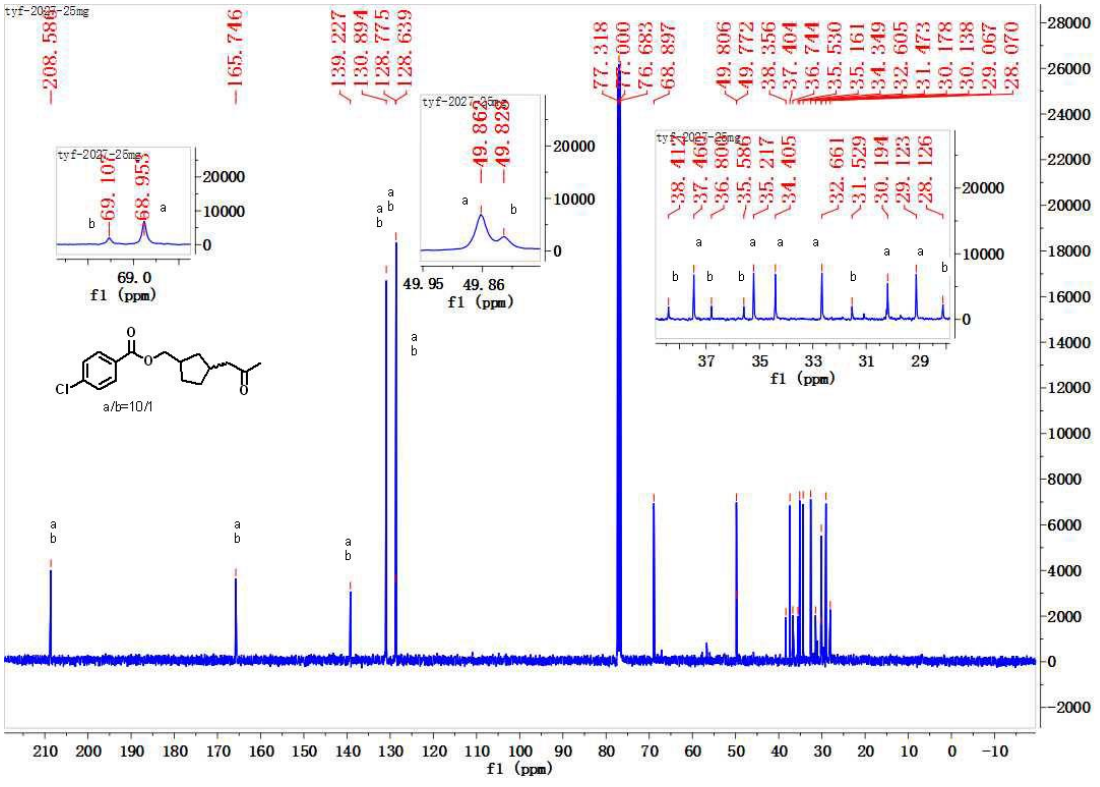
10b-^{13}C NMR



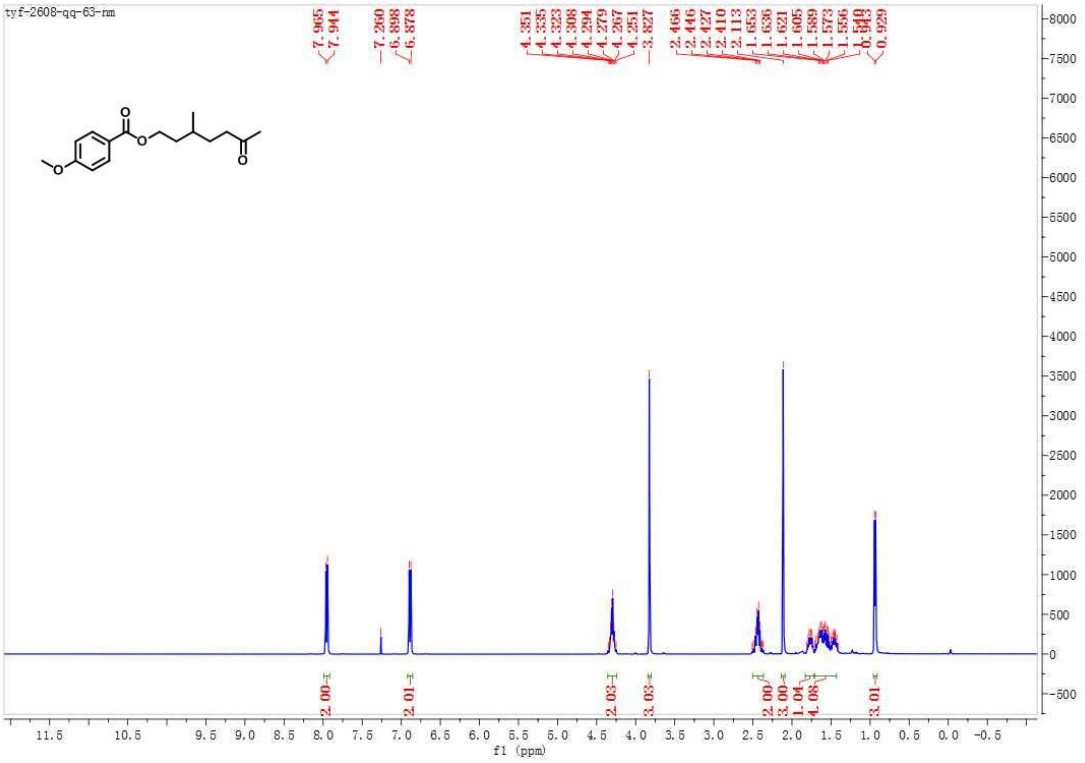
11b-^{1}H NMR



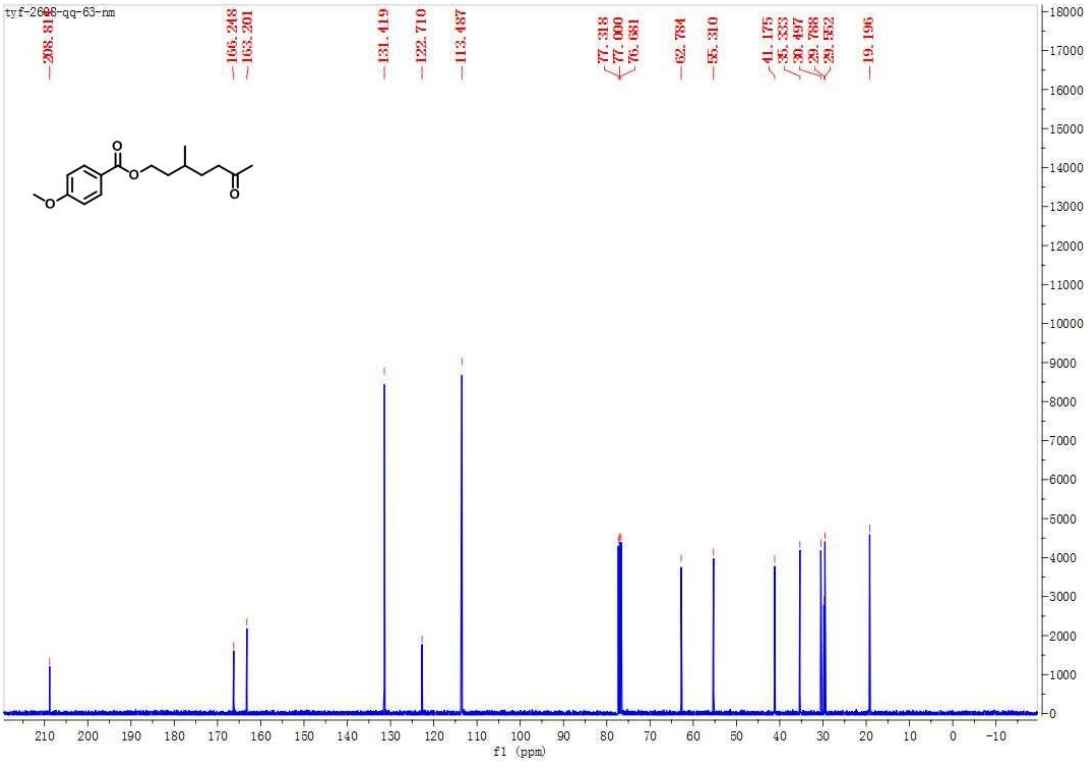
11b-^{13}C NMR



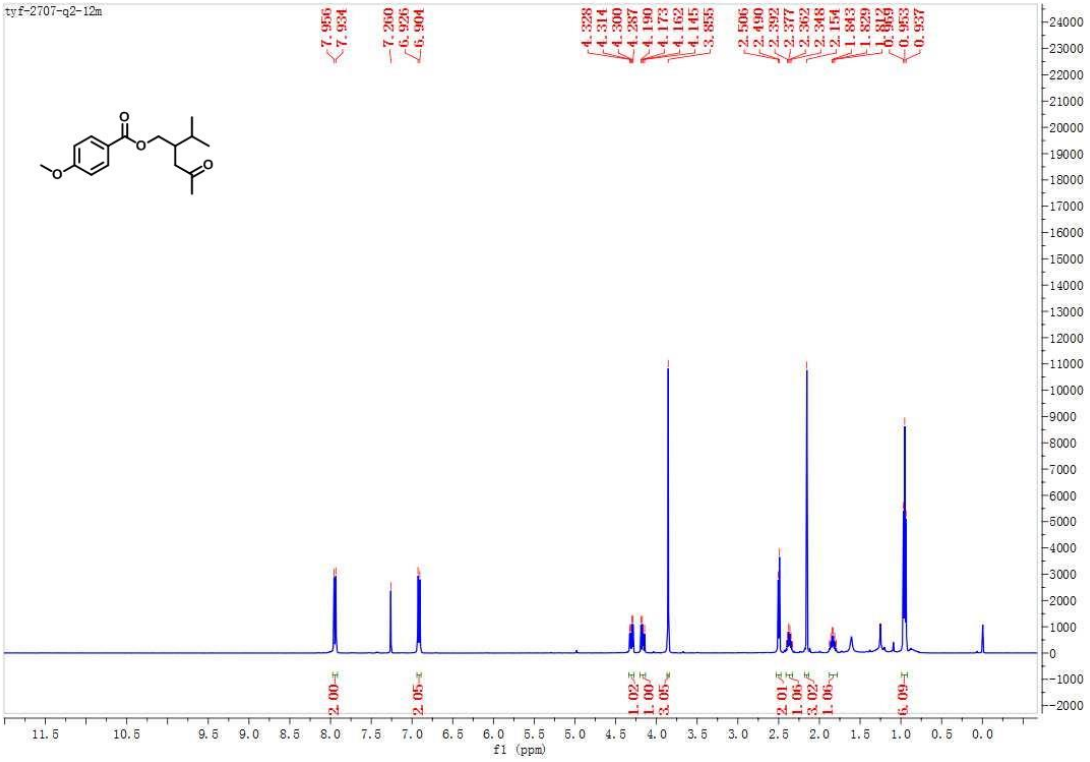
12b-^{1}H NMR



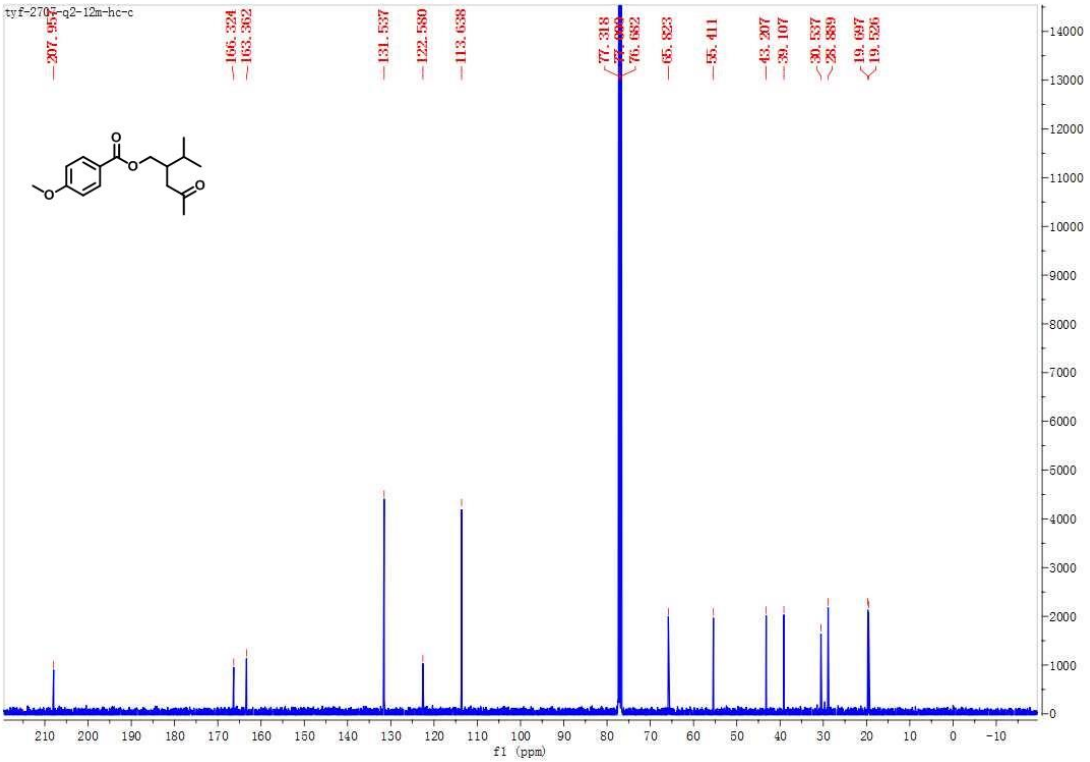
12b-^{13}C NMR



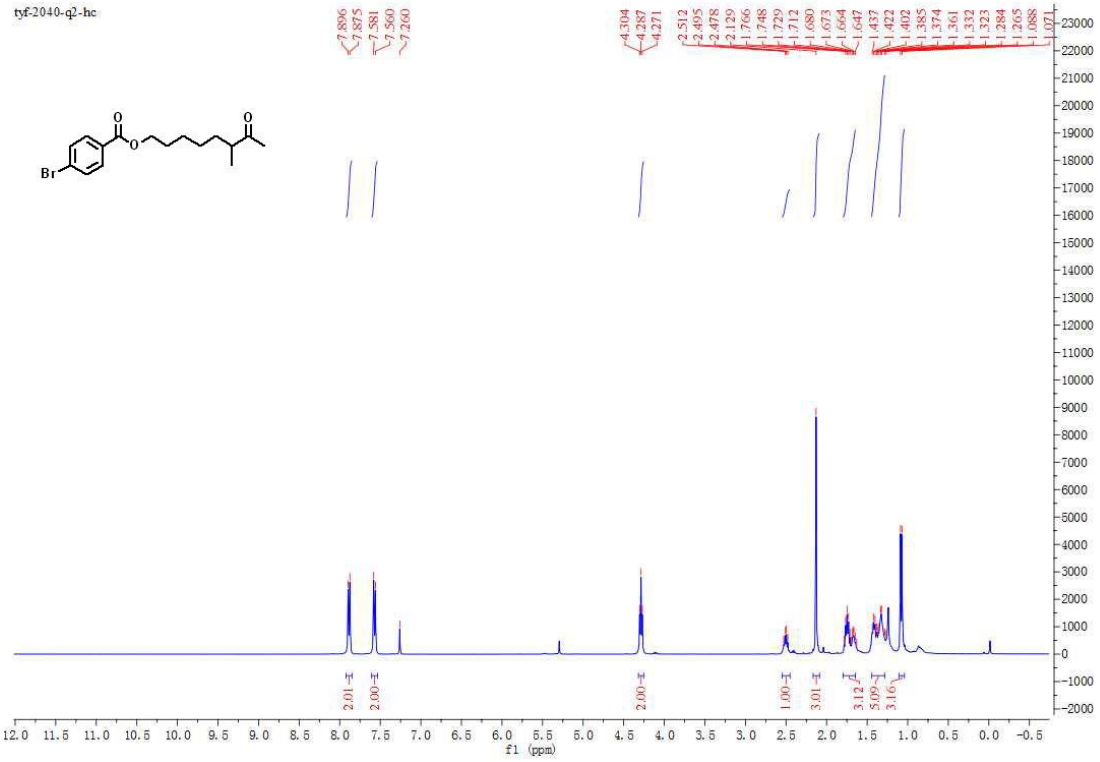
13b-^{1}H NMR



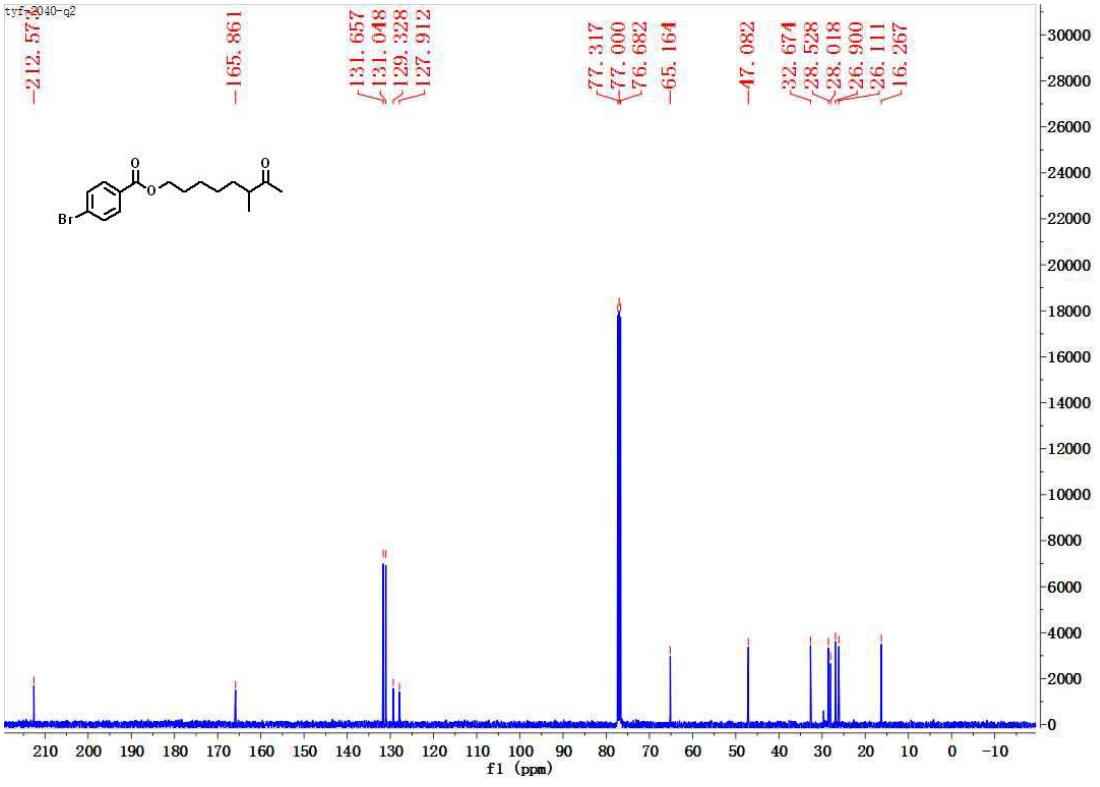
13b-^{13}C NMR



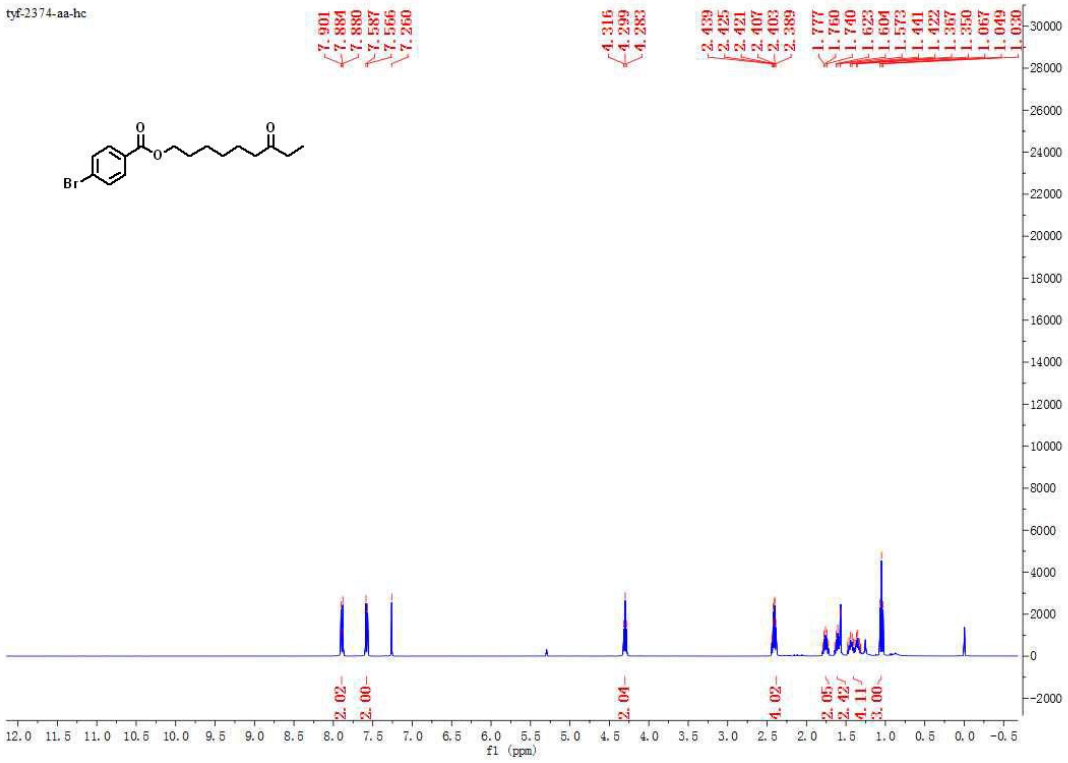
14b[1]-^{1}H NMR



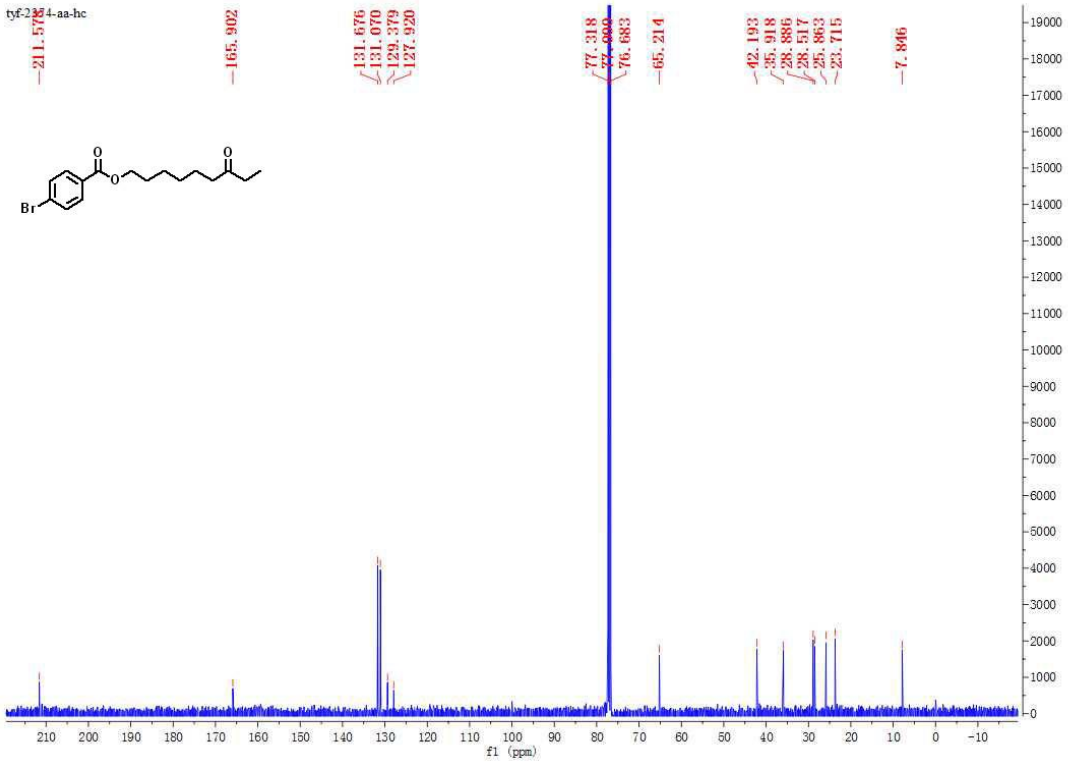
14b[1]-^{13}C NMR



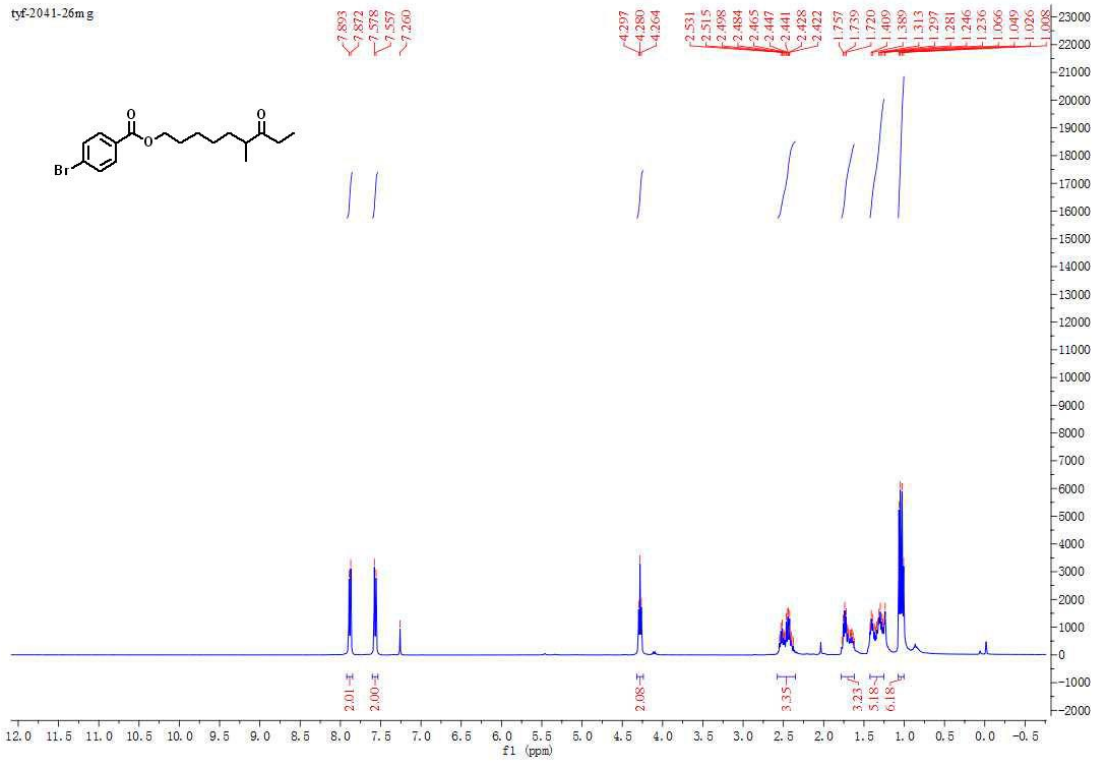
14b²-^{1}H NMR



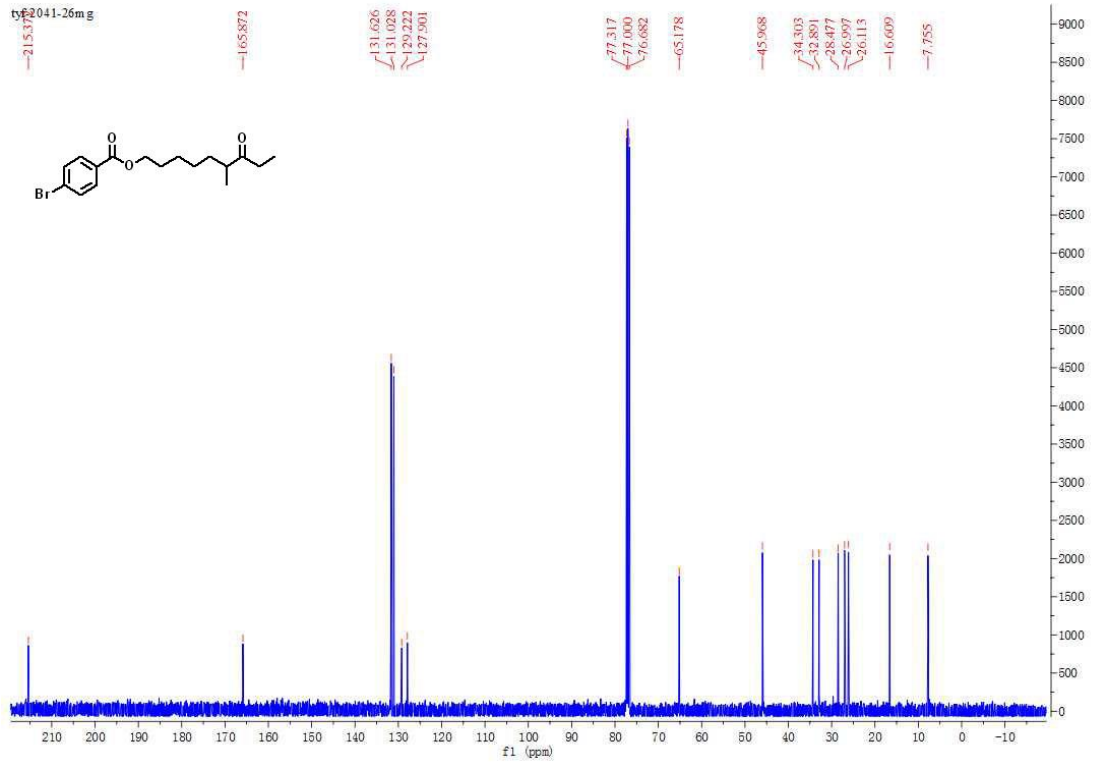
14b²-^{13}C NMR



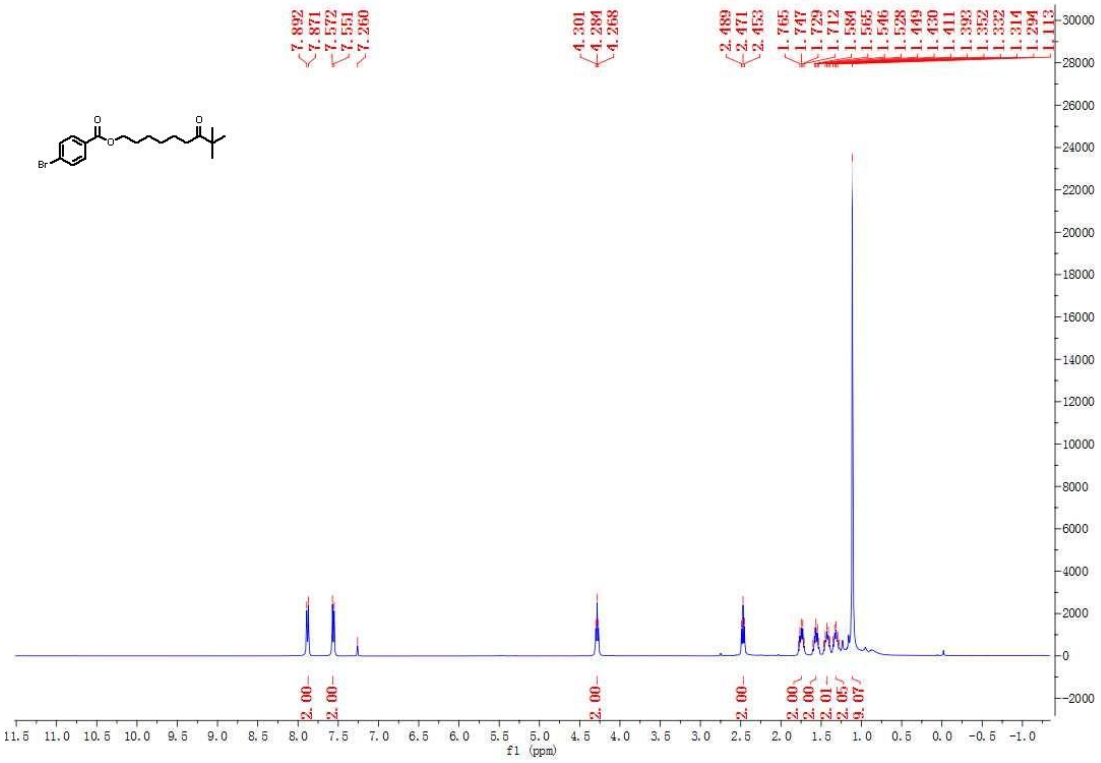
15b-^{1}H NMR



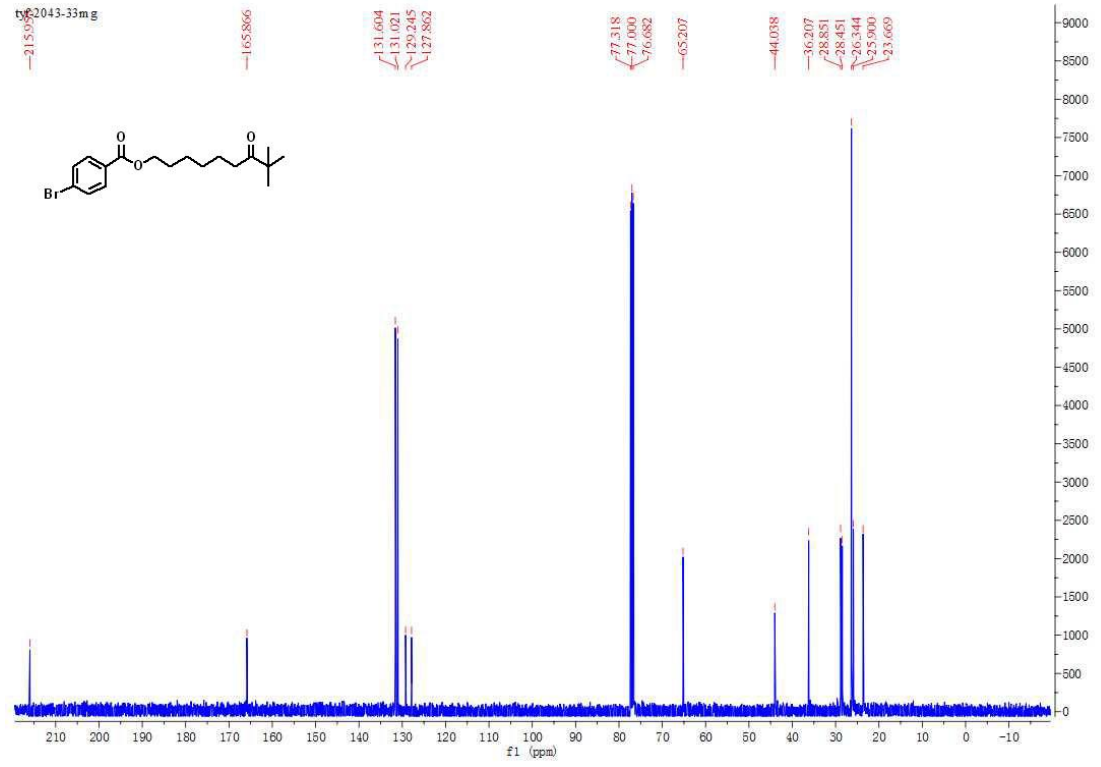
15b-^{13}C NMR



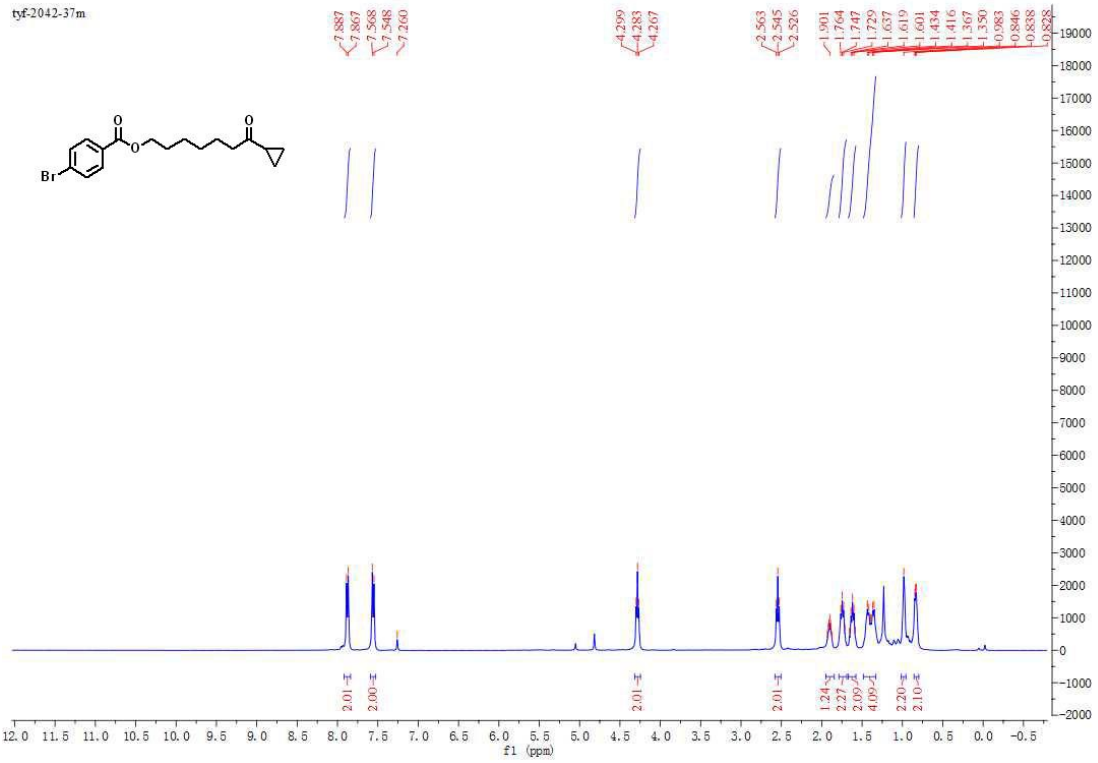
16b-^{1}H NMR



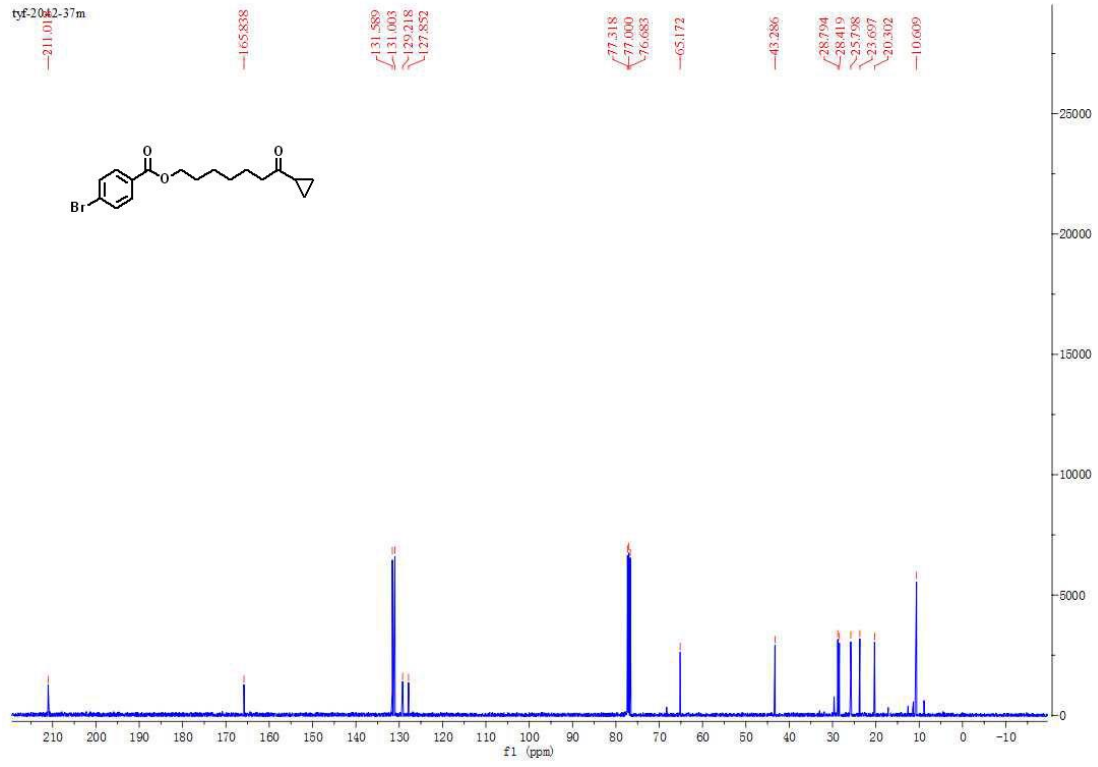
16b-^{13}C NMR



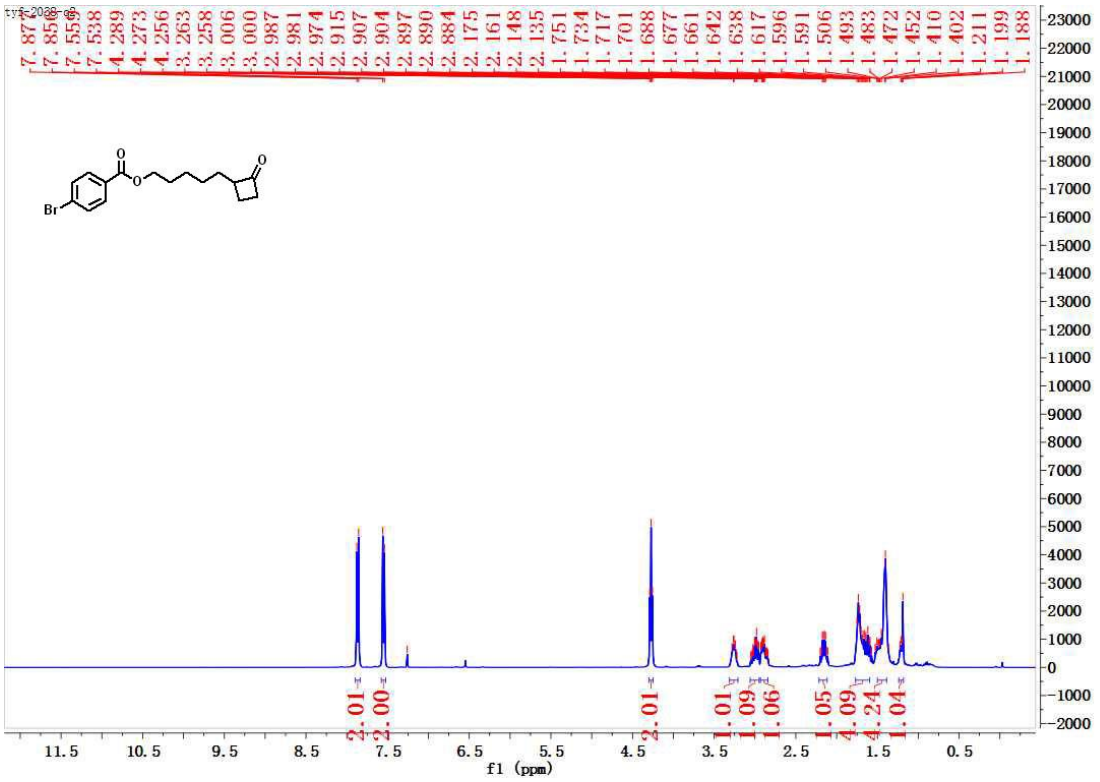
17b-^{1}H NMR



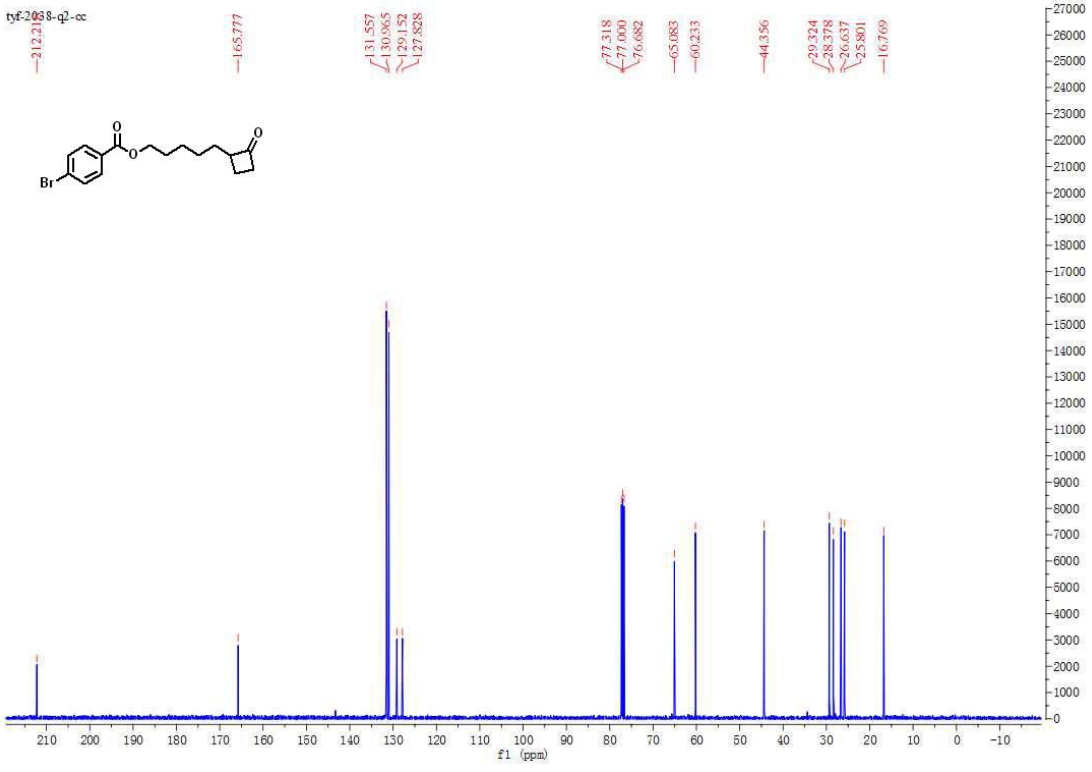
17b-^{13}C NMR



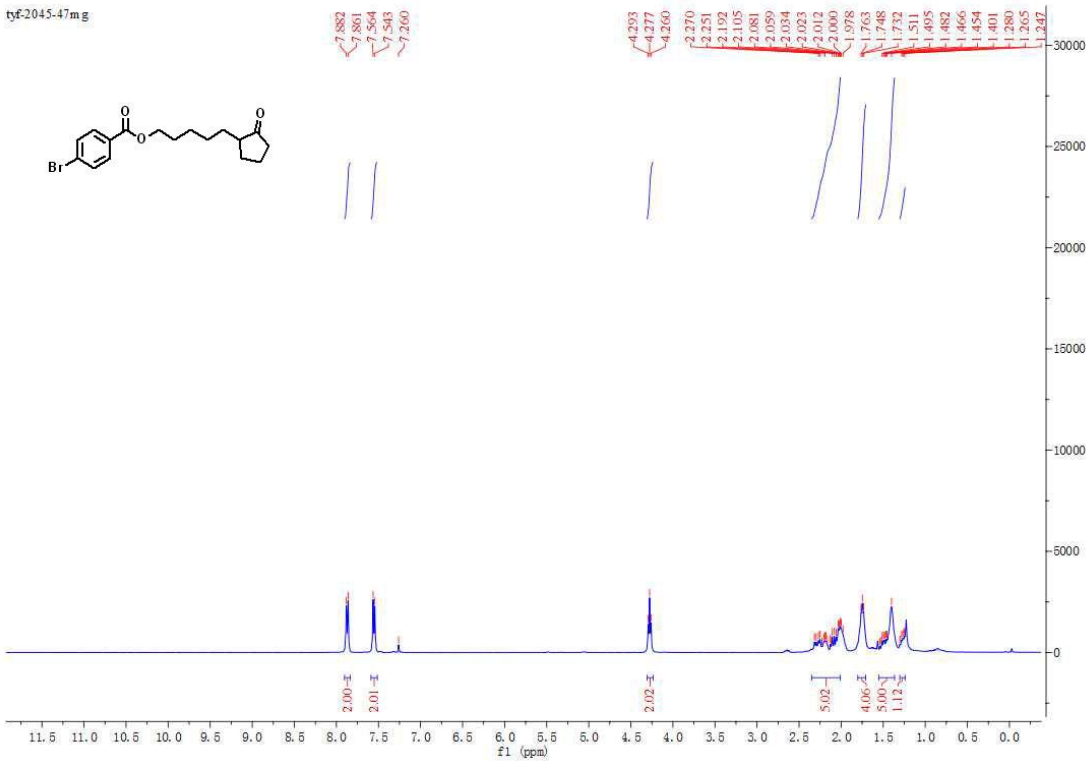
18b-^{1}H NMR



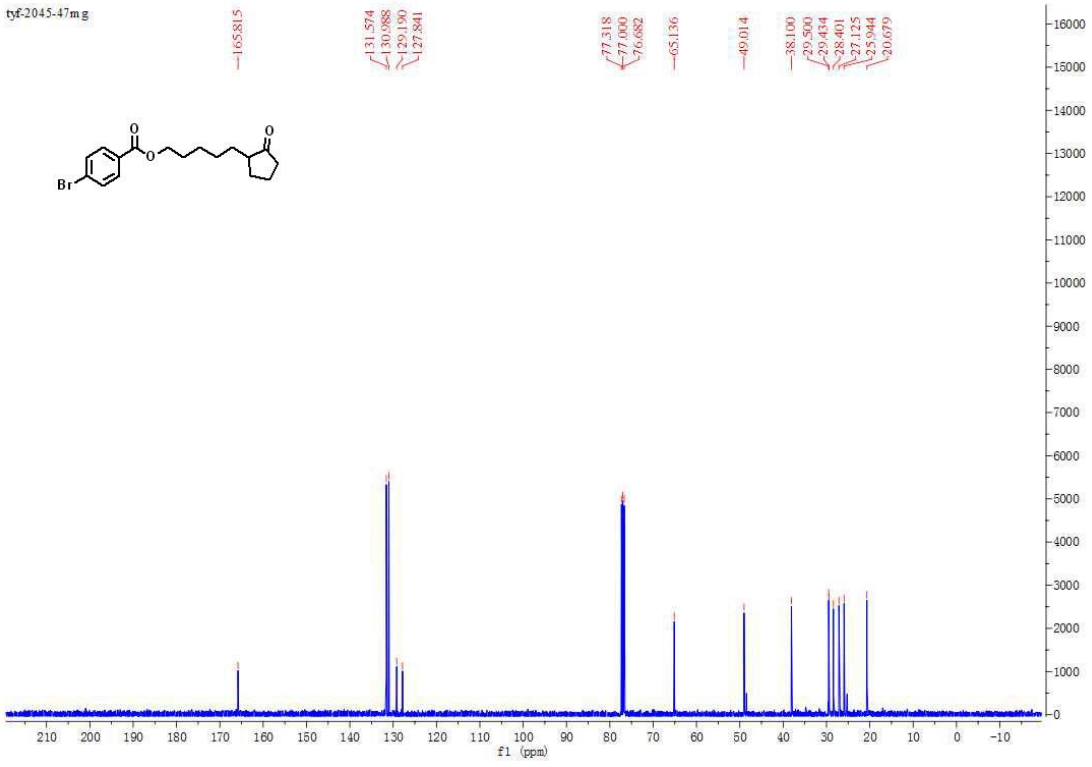
18b-^{13}C NMR



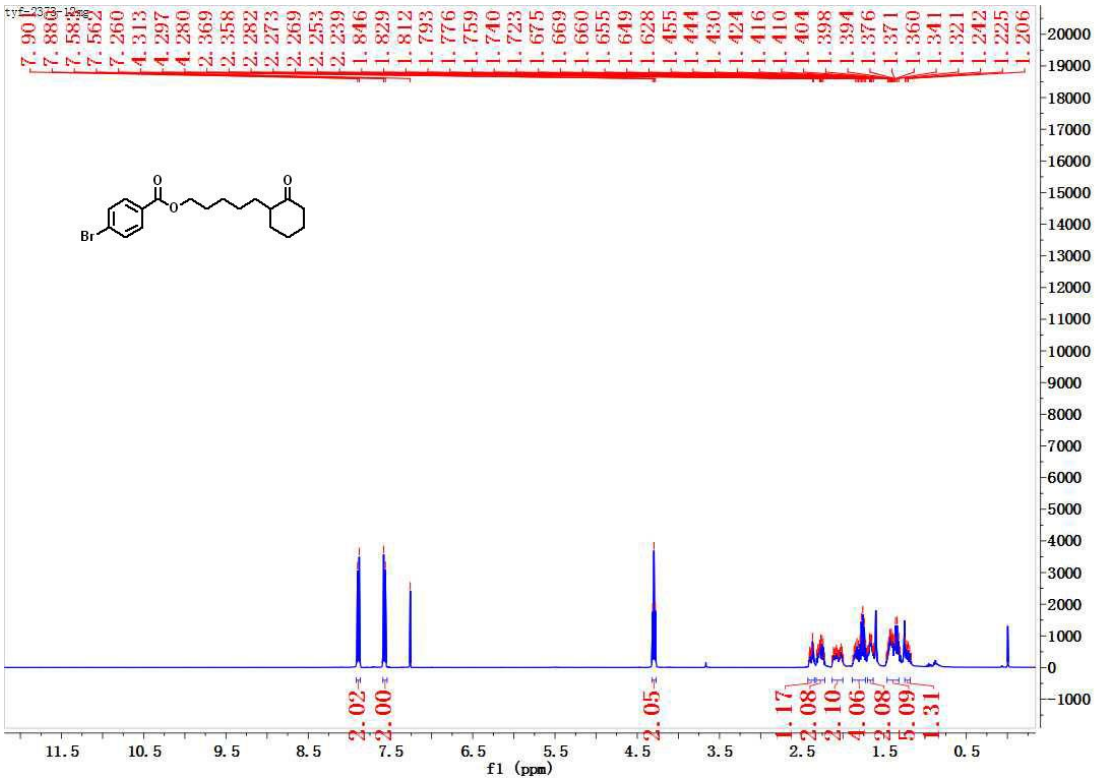
19b-^{1}H NMR



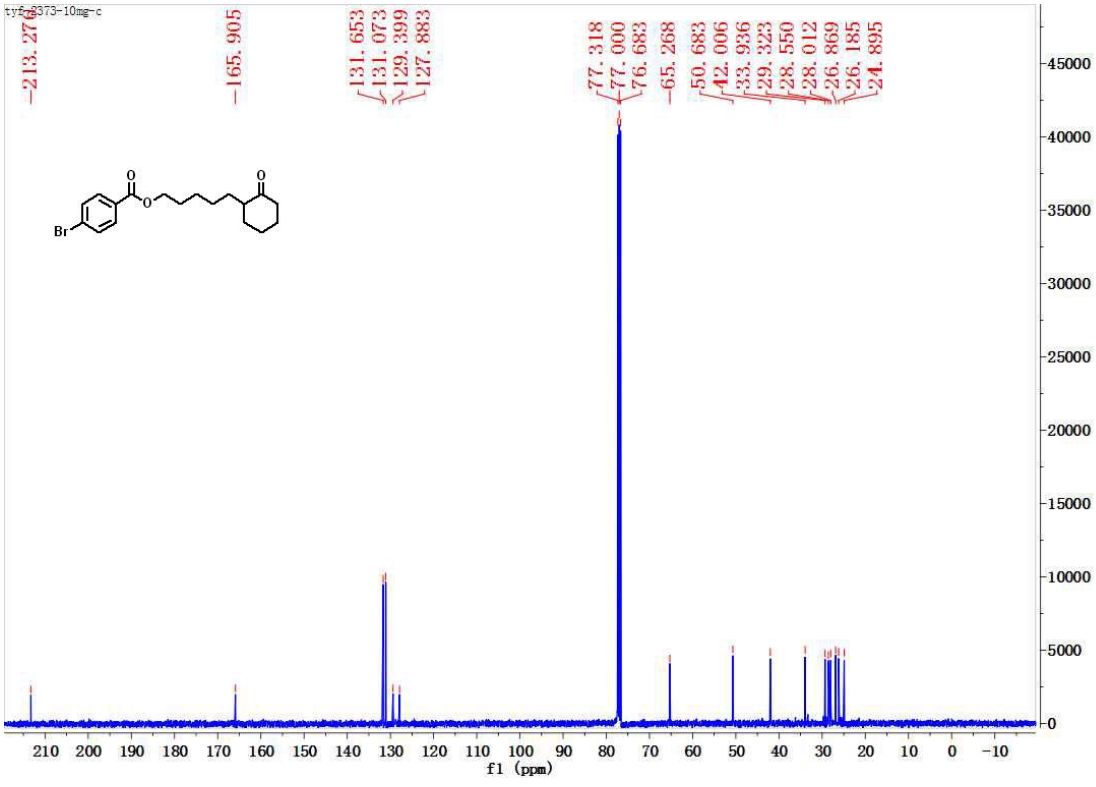
19b-^{13}C NMR



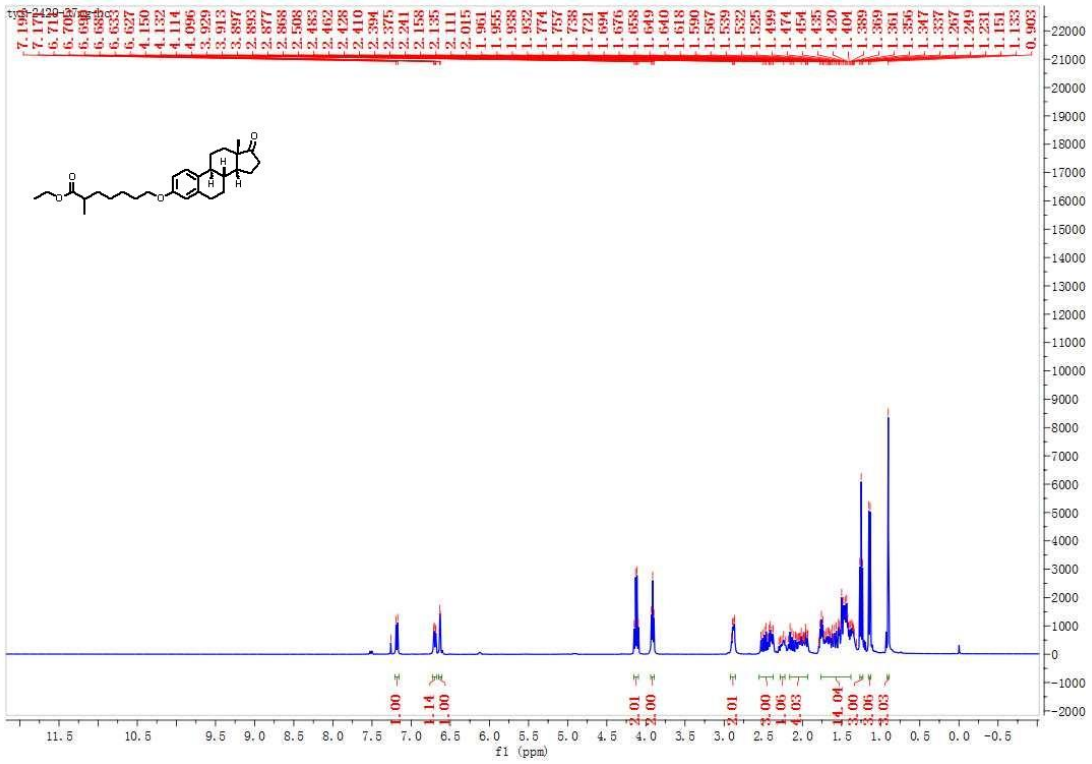
20b-^{1}H NMR



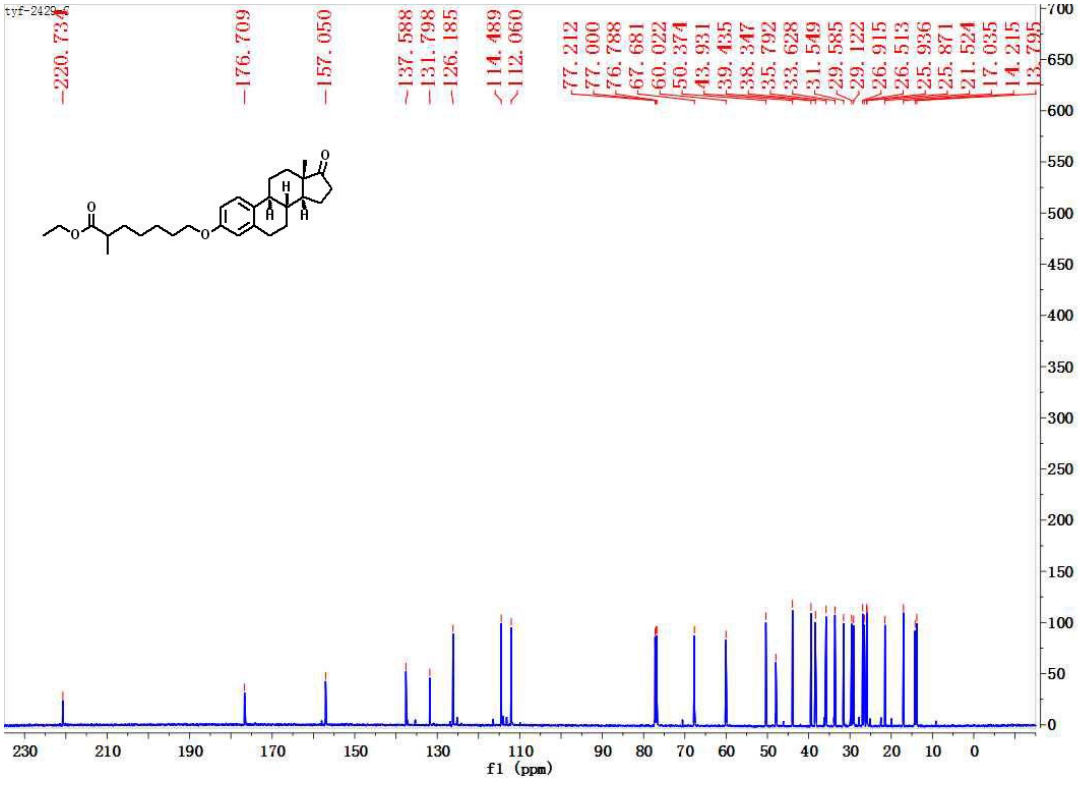
20b-^{13}C NMR



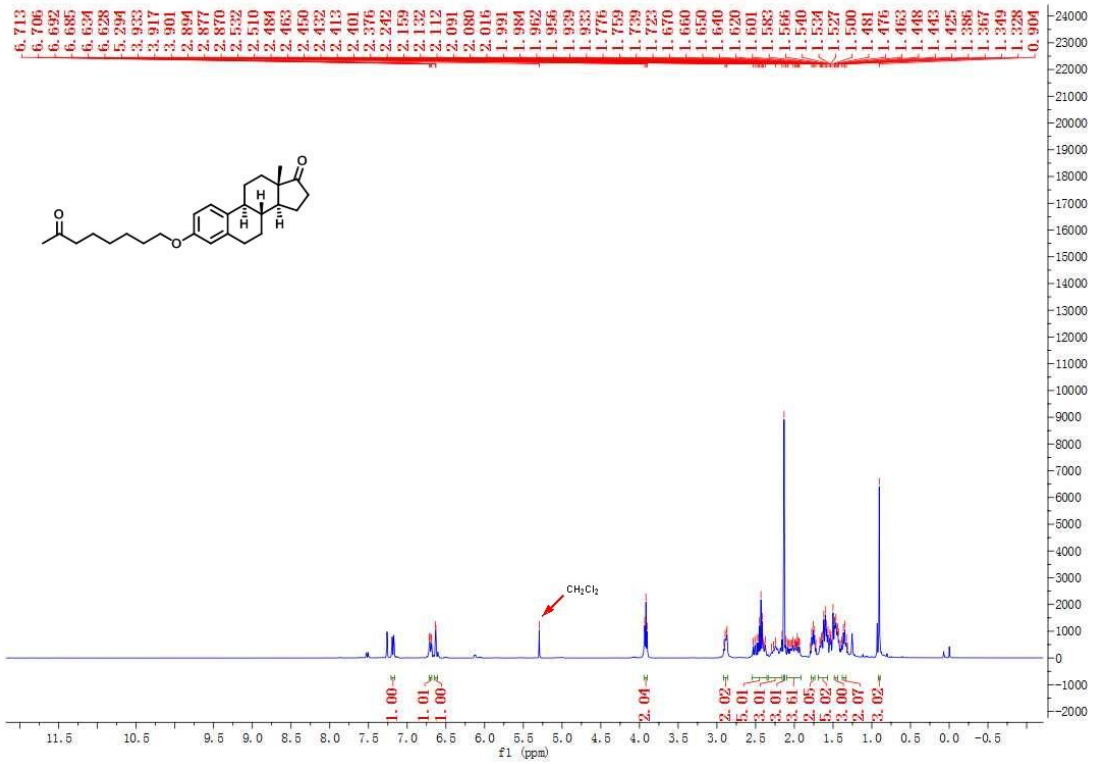
28a-^{1}H NMR



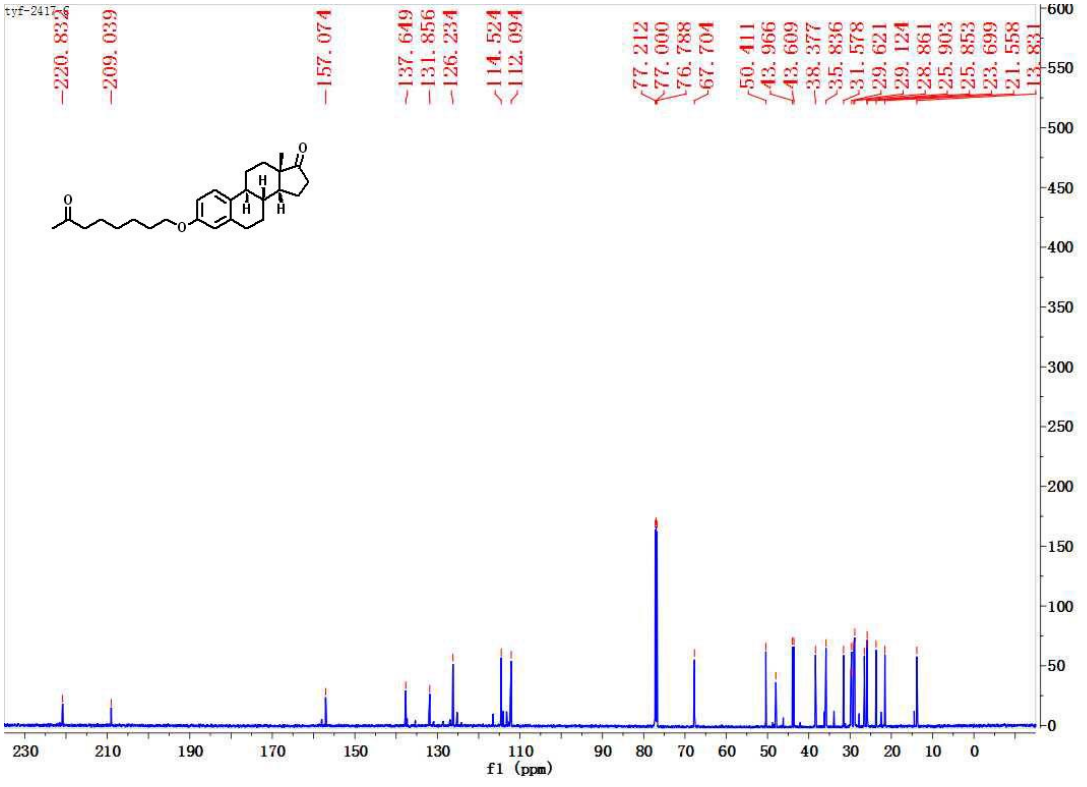
28a-^{13}C NMR



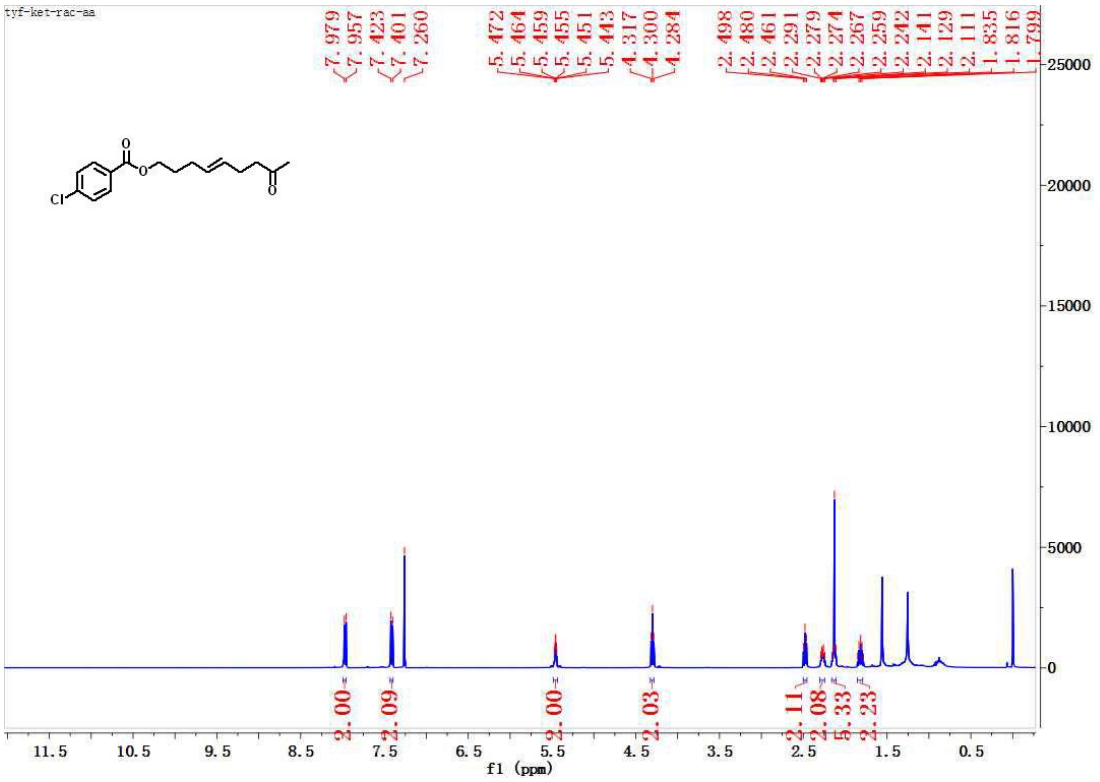
21b-^{1}H NMR



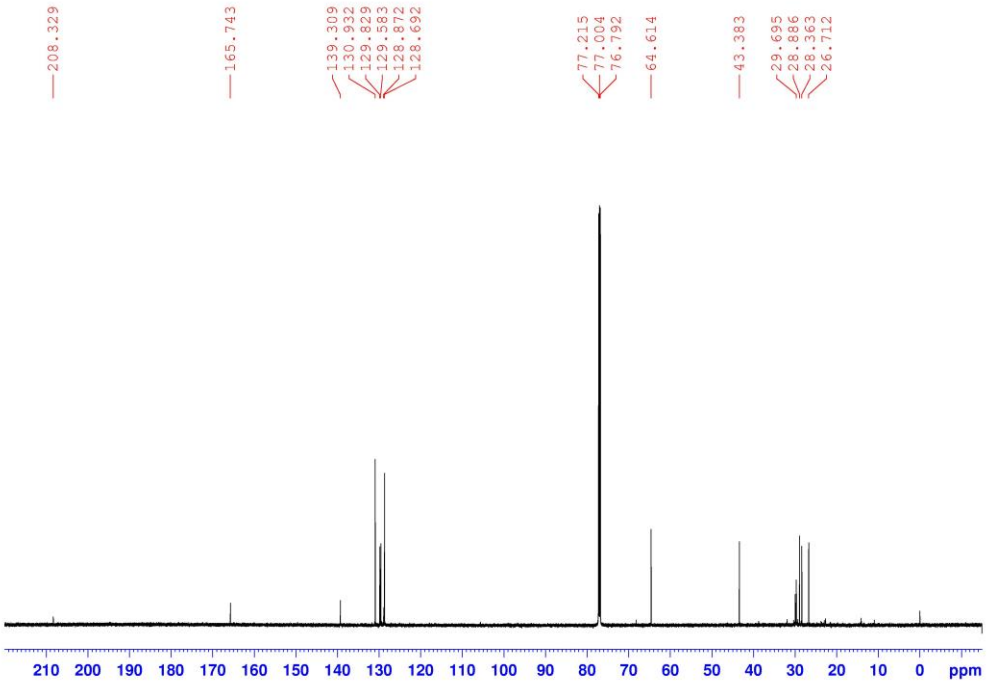
21b-^{13}C NMR



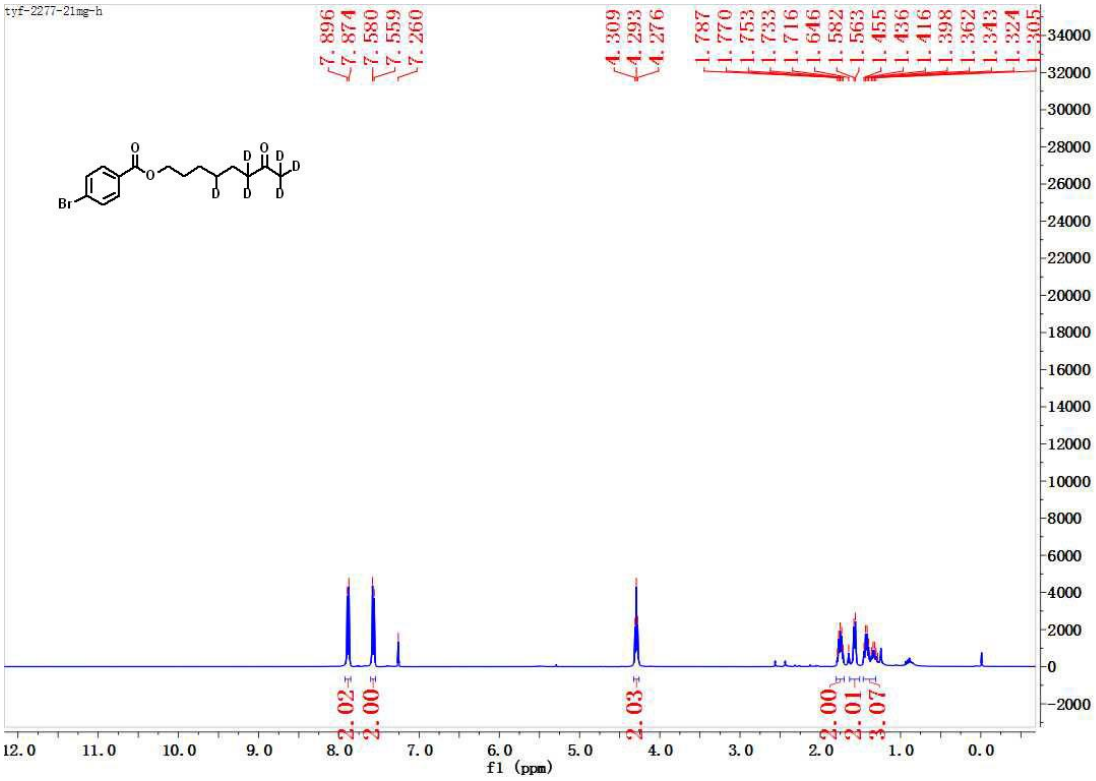
22b-^{1}H NMR



22b-^{13}C NMR



23b-^{1}H NMR



23b-^{13}C NMR