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SUPPORTING INFROMATION

Tuneable Access to Isoquinolines *via* a Transition-Metal-Free C(sp3)-C(sp3) Bond Cleavage Rearrangement Reaction

Jian Wang,* Panyuan Cai, Yimiao He, Yuan Liu, Ling Zhong, Shumin Ding, and Yongjia Shang*

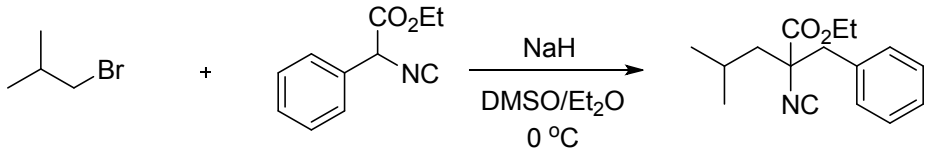
Contents

I. General Information

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were registered on 500 M spectrometers. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm, $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). NMR analysis was carried out at 298 K unless noted otherwise. HRMS was obtained on an ESI-LC-MS/MS or APCI-LC-MS/MS spectrometer.

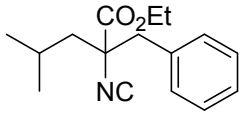
II. Preparation of Starting Materials

ethyl 2-benzyl-2-isocyano-4-methylpentanoate (C1) [1]



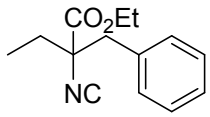
A1 **B1** **C1**

An oven-dried 100 mL schlenk tube charged with **B1** (5 mmol) was refilled with Ar for 3 times. The mixture of 16 mL of Et_2O and 4 mL of DMSO was added by syringe and the reaction mixture was cooled to 0 °C After NaH (60%) (15 mmol, 3.0 equiv) being added slowly, the reaction mixture was stirred for 20 min. Then 3.0 equivalent of **A1** was added by syringe. After the reaction completed, the crude reaction mixture was quenched with saturated NH_4Cl (H_2O), extracted with DCM (20 mL × 3) and washed with brine (50 mL). The organic phase was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford **C1** as a colorless oil in 86% yield.



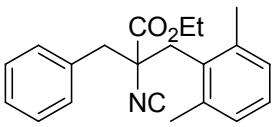
ethyl 2-benzyl-2-isocyano-4-methylpentanoate (C1)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 3H), 7.30-7.26 (m, 2H), 4.18-4.12 (m, 2H), 3.21 (d, *J* = 13.6 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.07-1.92 (m, 2H), 1.85-1.81 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.05 (d, *J* = 6.4 Hz, 2H), 0.90 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 160.4, 133.6, 130.3, 128.4, 127.9, 68.5, 62.5, 46.9, 46.4, 25.1, 23.7, 22.1, 13.9. HRMS (ESI) calcd for $C_{16}H_{21}NO_2$ $[M+H]^+$: 260.1645, Found: 260.1643.



(S)-ethyl 2-benzyl-2-isocyanobutanoate (C2)

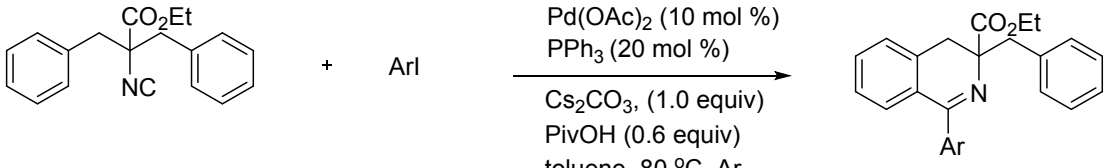
This compound was prepared similarly to **C1**. Colorless oil. 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 5H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.23 (d, *J* = 13.6 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H), 2.15-2.06 (m, 1H), 1.91-1.82 (m, 1H), 1.21 (dd, *J* = 7.8, 6.4 Hz, 3H), 1.06 (dd, *J* = 9.6, 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 160.0, 133.9, 130.2, 128.4, 127.8, 70.1, 62.5, 44.6, 32.5, 14.0, 8.6. HRMS (ESI) calcd for $C_{14}H_{17}NO_2$ $[M+H]^+$: 232.1332, Found: 232.1338.



(S)-ethyl 2-benzyl-3-(2,6-dimethylphenyl)-2-isocyanopropanoate (C3)

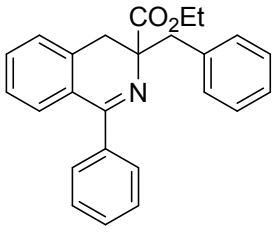
This compound was prepared similarly to **C1**. Colorless oil. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (m, 5H), 7.15-7.07 (m, 3H), 4.17-4.08 (m, 2H), 3.58 (d, *J* = 14.7 Hz, 1H), 3.48-3.40 (m, 2H), 3.12 (d, *J* = 13.4 Hz, 1H), 2.35 (s, 1H), 1.15 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 162.0, 138.2, 133.7, 131.6, 130.6, 128.7, 128.4, 127.9, 127.5, 69.0, 62.9, 45.6, 37.8, 21.2, 13.8. HRMS (ESI) calcd for $C_{21}H_{23}NO_2$ $[M+H]^+$: 322.1802, Found: 322.1800.

ethyl 3-benzyl-1-phenyl-3,4-dihydroisoquinoline-3-carboxylate (1a)[1]



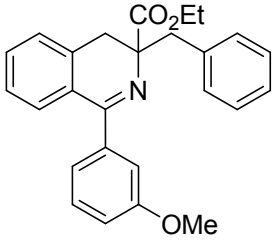
a **b** **1a**

Compound **1a** was prepared according to similar route of literature reported methods: An oven-dried 25 mL schlenk tube charged with $Pd(OAc)_2$ (0.1 mmol, 22.4 mg, 10 mol%) triphenylphosphine (0.2 mmol, 52.4 mg, 20 mol%) and Cs_2CO_3 (1 mmol, 326 mg, 1.0 equiv) was refilled with Ar for 3 times. Then a solution of **b** (1.5 mmol, 1.5 equiv) and PivOH (0.6 mmol, 61 mg, 0.6 equiv) in 0.5 mL of toluene was added by syringe and the tube was placed in an 80 °C oil-bath. A solution of **a** (1 mmol, 1.0 equiv) in 1.0 mL of toluene was added dropwise with a syringe pump to the reaction mixture. The addition was finished within 1 h. The crude reaction mixture was extracted with EtOAc (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the corresponding products.



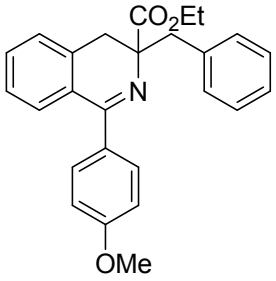
ethyl 3-benzyl-1-phenyl-3,4-dihydroisoquinoline-3-carboxylate (1a)

Colorless oil, 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.47-7.39 (m, 4H), 7.27-7.19 (m, 8H), 4.07-4.03 (m, 2H), 3.35 (d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 3.11 (d, *J* = 11.0 Hz, 1H), 2.95 (d, *J* = 16.0 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 167.8, 137.0, 136.9, 131.8, 130.9, 130.1, 129.7, 128.8, 128.7, 128.6, 128.4, 127.3, 127.1, 67.4, 61.5, 43.1, 33.6, 14.4; HRMS (ESI) calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, Found: 370.1805.



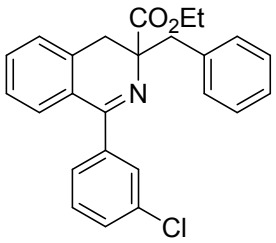
ethyl 3-benzyl-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1b)

This compound was prepared similarly to **1a**. Colorless oil, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.31- 7.24 (m, 5H), 7.23-7.20 (m, 5H), 7.03-7.01 (m, 1H), 4.06 (qd, *J* = 7.0, 1.5 Hz, 2H), 3.85 (s, 3H), 3.34 (d, *J* = 13.5 Hz, 1H), 3.26 (d, *J* = 16.0 Hz, 1H), 3.07 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 16.0 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 167.3, 159.9, 140.4, 137.0, 136.9, 131.7, 130.9, 129.5, 128.8, 128.7, 128.4, 127.3, 127.1, 122.1, 116.0, 114.8, 67.4, 61.5, 55.8, 43.1, 33.3, 14.4; HRMS (APCI) calcd for $C_{26}H_{25}NO_3$ $[M+H]^+$: 400.1907, Found: 400.1910.



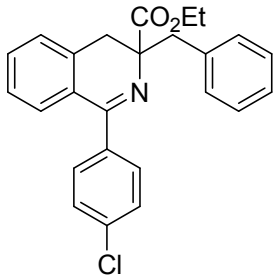
ethyl 3-benzyl-1-(4-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1c)

This compound was prepared similarly to **1a**. Colorless oil, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5, 2H), 7.39 (td, *J* = 7.5, 1.0 Hz, 1H). 7.31-7.31 (m, 1H), 7.25-7.19 (m, 7H), 7.01-6.91 (m, 2H), 4.05-4.01 (m, 2H), 3.85 (s, 3H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.23 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 13.5 Hz, 1H), 2.92 (d, *J* = 16.0 Hz, 1H), 1.07 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 166.3, 160.9, 136.8, 136.7, 131.1, 130.8, 130.4, 128.5, 128.4, 128.3, 128.0, 126.8, 126.6, 113.5, 66.8, 61.0, 55.4, 42.7, 33.0, 14.0; HRMS (APCI) calcd for $C_{26}H_{25}NO_3$ $[M+H]^+$: 400.1907, Found: 400.1909.



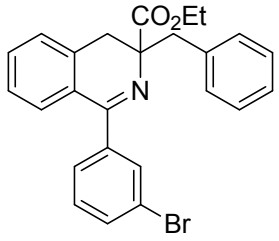
ethyl 3-benzyl-1-(3-chlorophenyl)-3,4-dihydroisoquinoline-3-carboxylate (1d)

This compound was prepared similarly to **1a**. Colorless oil, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.46-7.37 (m, 3H), 7.29-7.20 (m, 8H), 4.10-4.05 (m, 2H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 3.07 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 16.0 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 166.28, 140.8, 136.9, 136.8, 134.7, 132.0, 130.9, 130.1, 129.9, 129.7, 128.9, 128.4, 128.4, 127.8, 127.5, 127.2, 67.5, 61.6, 43.0, 33.2, 14.4; HRMS (APCI) calcd for $C_{25}H_{20}Cl_2NO_2$ $[M+H]^+$: 472.0632, Found: 472.0627.



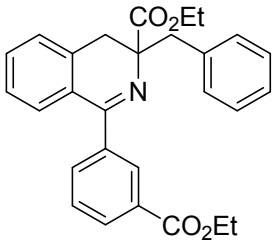
ethyl 3-benzyl-1-(4-chlorophenyl)-3,4-dihydroisoquinoline-3-carboxylate (1e)

This compound was prepared similarly to **1a**. Colorless oil, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.47 (dd, *J* = 56.0, 48.0 Hz, 3H), 7.28-7.20 (m, 8H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 3.11 (d, *J* = 12.0 Hz, 1H), 2.95 (d, *J* = 16.0 Hz, 1H), 1.08 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 166.5, 136.7, 136.4, 131.6, 130.7, 130.5, 130.1, 129.7, 128.5, 128.5, 128.0, 127.0, 126.8, 67.0, 61.2, 42.7, 33.0, 14.0; HRMS (ESI) calcd for $C_{25}H_{22}ClNO_2$ $[M+H]^+$: 404.1412, Found: 404.1418.



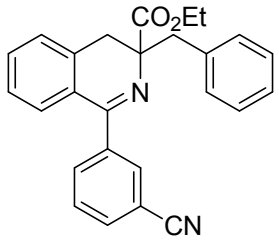
ethyl 3-benzyl-1-(3-bromophenyl)-3,4-dihydroisoquinoline-3-carboxylate (1f)

This compound was prepared similarly to **1a**. Colorless oil, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (t, *J* = 1.5 Hz, 1H), 7.60-7.55 (m, 2H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.27-7.18 (m, 8H), 4.08-4.04 (m, 2H), 3.31 (d, *J* = 13.5 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 13.5 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 165.7, 140.6, 136.5, 136.4, 132.5, 132.1, 131.5, 130.4, 129.7, 128.5, 128.0, 127.9, 127.9, 127.8, 127.0, 126.7, 122.4, 67.0, 61.2, 42.6, 32.8, 14.0; HRMS (APCI) calcd for $C_{25}H_{23}BrNO_2$ $[M+H]^+$: 448.0907, Found: 448.0910.



ethyl 3-benzyl-1-(3-(ethoxycarbonyl)phenyl)-3,4-dihydroisoquinoline-3-carboxylate (1g)

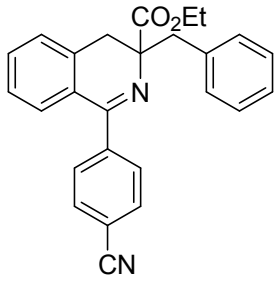
This compound was prepared similarly to **1a**. Colorless oil, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (t, *J* = 1.5 Hz, 1H), 8.17-8.15 (m, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.42 (td, *J* = 7.5, 1.0 Hz, 1H), 7.29 – 7.20 (m, 8H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.09-4.05 (m, 2H), 3.34 (d, *J* = 13.5 Hz, 1H), 3.27 (d, *J* = 16.0 Hz, 1H), 3.08 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 16.0 Hz, 1H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 166.7, 139.4, 136.9, 136.9, 134.0, 131.9, 131.0, 130.9, 130.8, 130.6, 128.9, 128.8, 128.5, 128.4, 128.3, 127.5, 127.1, 67.5, 61.6, 61.5, 43.0, 33.2, 14.8, 14.4; HRMS (APCI) calcd for $C_{28}H_{28}NO_4$ $[M+H]^+$: 442.2013, Found: 442.2016.



ethyl 3-benzyl-1-(3-cyanophenyl)-3,4-dihydroisoquinoline-3-carboxylate (1h)

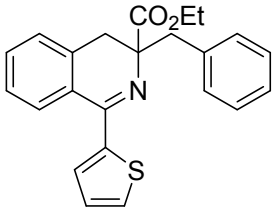
This compound was prepared similarly to **1a**. Colorless oil, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (t, *J* = 1.3 Hz, 1H), 7.91-7.89 (m, 1H), 7.76-7.73 (m, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (td, *J* =

7.5, 1.0 Hz, 1H), 7.31-7.16 (m, 8H), 4.07 (qd, *J* = 7.0, 1.5 Hz, 2H), 3.32-3.25 (m, 2H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.97 (d, *J* = 16.0 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 165.6, 140.2, 137.0, 136.7, 133.9, 133.4, 133.3, 132.3, 130.8, 129.5, 129.1, 128.5, 128.0, 127.6, 127.3, 119.0, 112.9, 67.6, 61.7, 43.0, 33.3, 14.4; HRMS (APCI) calcd for $C_{26}H_{23}N_2O_2$ $[M+H]^+$: 395.1754, Found: 395.1758.



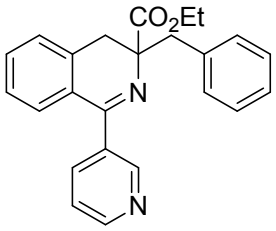
ethyl 3-benzyl-1-(4-cyanophenyl)-3,4-dihydroisoquinoline-3-carboxylate (1i)

This compound was prepared similarly to **1a**. Colorless oil, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.74 (m, 4H), 7.44 (td, *J* = 7.5, 1.0 Hz, 1H), 7.31-7.15 (m, 8H), 4.08-4.03 (m, 2H), 3.30 (d, *J* = 13.5 Hz, 1H), 3.26 (d, *J* = 16.0 Hz, 1H), 3.10 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 16.0 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 166.1, 143.2, 136.9, 136.6, 132.5, 132.3, 130.8, 130.3, 129.1, 128.5, 128.0, 128.0, 127.6, 127.2, 119.0, 113.6, 67.6, 61.7, 43.0, 33.3, 14.4. HRMS (ESI) calcd for $C_{26}H_{22}N_2O_2$ $[M+H]^+$: 395.1754, Found: 395.1758.



ethyl 3-benzyl-1-(thiophen-2-yl)-3,4-dihydroisoquinoline-3-carboxylate (1j)

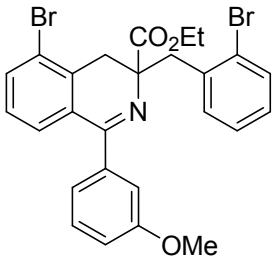
This compound was prepared similarly to **1a**. Colorless oil, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.49-7.48 (m, 1H), 7.44-7.41 (m, 2H), 7.34-7.20 (m, 7H), 7.12 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.05-3.96 (m, 2H), 3.29 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 15.5 Hz, 1H), 3.13 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 15.5 Hz, 1H), 1.02 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 160.4, 143.1, 136.7, 136.6, 131.1, 130.7, 129.4, 128.8, 128.5, 127.9, 127.3, 127.1, 127.0, 126.6, 66.8, 61.0, 43.1, 33.6, 13.9; HRMS (APCI) calcd for $C_{23}H_{21}NO_2S$ $[M+H]^+$: 376.1366, Found: 376.1362.



ethyl 3-benzyl-1-(pyridin-3-yl)-3,4-dihydroisoquinoline-3-carboxylate (1k)

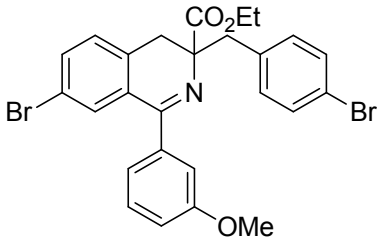
This compound was prepared similarly to **1a**. Colorless oil, 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (d, *J* = 1.5 Hz, 1H), 8.70 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.99 (dt, *J* = 7.5, 2.0 Hz, 1H), 7.44-7.38 (m, 2H), 7.29-7.19 (m, 8H), 4.07-4.02 (m, 2H), 3.31-3.24 (m, 2H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 16.0 Hz, 1H), 1.08 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 164.6, 150.4, 150.1, 136.8, 136.4, 136.4, 134.4, 131.7 130.4, 128.6, 128.0, 127.8, 127.6, 127.2, 126.8, 123.2, 67.1,

61.2, 42.8, 33.0, 14.0; HRMS (APCI) calcd for $C_{24}H_{22}N_2O_2$ [M+H]$^+$: 371.1754, Found: 371.1753.



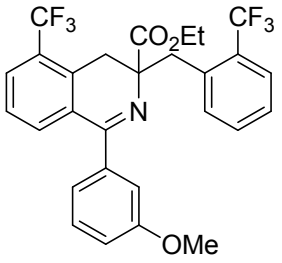
ethyl 5-bromo-3-(2-bromobenzyl)-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1l)

This compound was prepared similarly to **1a**. Colorless oil, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.21-7.14 (m, 4H), 7.09-7.00 (m, 3H), 4.11-4.04 (m, 2H), 3.84 (s, 3H), 3.66-3.55 (m, 3H), 2.99 (d, *J* = 16.5 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 167.1, 159.4, 139.5, 136.4, 136.3, 135.1, 132.7, 132.5, 130.3, 129.1, 128.2, 127.9, 127.4, 127.0, 126.1, 124.3, 121.7, 115.8, 114.4, 66.9, 61.4, 55.4, 42.6, 33.4, 13.9; HRMS (APCI) calcd for $C_{26}H_{23}Br_2NO_3$ [M+H]$^+$: 556.0117, Found: 556,0118.



ethyl 7-bromo-3-(4-bromobenzyl)-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1m)

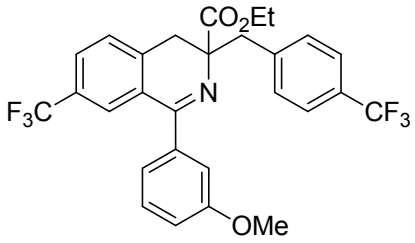
This compound was prepared similarly to **1a**. Colorless oil, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.39-7.36 (m, 3H), 7.18-7.16 (m, 2H), 7.14-7.11 (m, 3H), 7.06-7.03 (m, 1H), 4.02 (q, *J* = 7.0 Hz, 2H), 3.86 (s, 3H), 3.25 (d, *J* = 13.5 Hz, 1H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.11 (d, *J* = 13.5 Hz, 1H), 2.84 (d, *J* = 16.0 Hz, 1H), 1.07 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 166.3, 160.0, 139.5, 135.8, 135.5, 134.5, 132.7, 131.5, 130.3, 130.2, 129.8, 121.9, 121.3, 120.9, 116.4, 114.7, 67.1, 61.7, 55.8, 43.1, 33.4, 14.4; HRMS (APCI) calcd for $C_{26}H_{23}Br_2NO_3$ [M+H]$^+$: 556.0117, Found: 556.0111.



ethyl 1-(3-methoxyphenyl)-5-(trifluoromethyl)-3-(2-(trifluoromethyl)benzyl)-3,4-dihydroisoquinoline-3-carboxylate (1n)

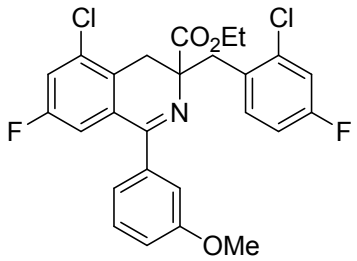
This compound was prepared similarly to **1a**. Colorless oil, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 2.0 Hz, 1H), 7.35-7.28 (m, 2H), 7.20 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.98-3.93 (m, 2H), 3.86 (s, 3H), 3.76 (d, *J* = 15.0 Hz, 1H), 3.66-

3.60 (m, 2H), 2.88 (d, *J* = 16.5 Hz, 1H), 0.98 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 166.2, 158.6, 138.4, 134.9, 134.2, 131.3, 130.6, 130.3, 128.4, 128.3 (q, *J* = 31.1 Hz), 128.2, 127.7, 127.5 (q, *J* = 30.3 Hz), 127.4, 125.8, 125.5, 124.8 (q, *J* = 5.9 Hz), 123.5 (q, *J* = 272.1 Hz), 122.8 (q, *J* = 272.5 Hz), 120.6, 114.9, 113.4, 64.9, 60.4, 54.4, 38.4, 30.5, 12.6; HRMS (APCI) calcd for $C_{28}H_{21}Br_2F_2NO_3$ $[M+H]^+$: 536.1655, Found: 536.1649.



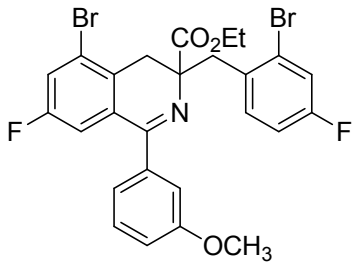
ethyl 1-(3-methoxyphenyl) -7- (trifluoromethyl)-3-(4-(trifluoromethyl)benzyl)-3,4-dihydroisoquinoline-3-carboxylate (1o)

This compound was prepared similarly to **1a**. Colorless oil, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.65 (m, 1H), 7.55 (br s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41-7.38 (m, 4H), 7.20-7.17 (m, 2H), 7.08-7.06 (m, 2H), 4.03-4.00 (m, 2H), 3.86 (s, 3H), 3.39-3.31 (m, 3H), 2.97 (d, *J* = 16.0 Hz, 1H), 1.03 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 166.6, 160.1, 140.8, 140.7, 139.1, 131.3, 130.2, 129.9, 129.5 (q, *J* = 32.3 Hz), 129.2, 129.0, 128.3, 125.2 (q, *J* = 3.5 Hz), 124.6 (q, *J* = 270.3 Hz), 124.0 (q, *J* = 270.9 Hz), 121.9, 116.8, 114.6, 67.0, 61.9, 55.8, 43.7, 34.2, 14.3; HRMS (APCI) calcd for $C_{28}H_{23}F_6NO_3$ $[M+H]^+$: 536.1655, Found: 536.1659.



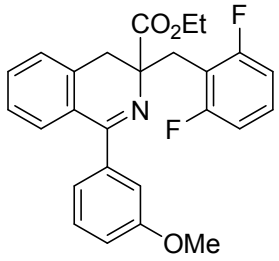
ethyl 5-chloro-3-(2-chloro-4-fluorobenzyl)-7-fluoro-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1p)

This compound was prepared similarly to **1a**. Colorless oil, 96% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.7, 6.5 Hz, 1H), 7.38-7.35 (m, 1H), 7.19 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.15-7.12 (m, 2H), 7.09-7.02 (m, 2H), 6.92-6.85 (m, 2H), 4.11-4.04 (m, 2H), 3.85 (s, 3H), 3.57-3.48 (m, *J* = 14.0, 10.0 Hz, 3H), 2.89 (dd, *J* = 16.5, 1.0 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 166.0, 161.6, 161,3 (d, *J* = 247.4 Hz), 159.6, 138.8, 135.7 (d, *J* = 10.0 Hz), 134.2 (d, *J* = 9.8 Hz), 133.5 (d, *J* = 8.4 Hz), 130.7 (d, *J* = 7.4 Hz), 130.3 (d, *J* = 3.4 Hz), 130.2 (d, *J* = 3.3 Hz), 129.4, 121.5, 119.2 (d, *J* = 24.8 Hz), 116.5 (d, *J* = 24.3 Hz),116.0 114.4, 114.1(d, *J* = 22.5 Hz), 113.7 (d, *J* = 20.5 Hz), 66.8, 61.6, 55.4, 39.4, 30.1, 14.0; HRMS (APCI) calcd for $C_{26}H_{21}Cl_2F_2NO_3$ $[M+H]^+$: 504.0939, Found: 504.0940.



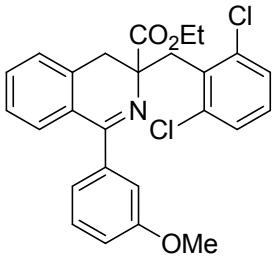
ethyl 5-bromo-3-(2-bromo-4-fluorobenzyl)-7-fluoro-1-(3-methoxyphenyl)-3,4-Dihydroisoquinoline-3-carboxylate (1q)

This compound was prepared similarly to **1a**. Colorless oil, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.5, 6.5 Hz, 1H), 7.38-7.35 (m, 2H), 7.27 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.17-7.12 (m, 2H), 7.05 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.98-6.90 (m, 2H), 4.12-4.04 (m, 2H), 3.86 (s, 3H), 3.61-3.55 (m, 3H), 2.86 (d, *J* = 16.5 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 166.5, 161.1 (d, *J* = 248.6 Hz), 160.7 (d, *J* = 248.9 Hz), 159.6, 138.3, 133.3 (d, *J* = 8.0 Hz), 132.1 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 6.8 Hz), 129.4, 125.9 (d, *J* = 9.3 Hz), 124.1 (d, *J* = 8.9 Hz), 122.4 (d, *J* = 22.6 Hz), 121.6, 119.7 (d, *J* = 23.9 Hz), 116.2, 114.9 (d, *J* = 23.3 Hz), 114.5, 114.3 (d, *J* = 20.6 Hz), 67.1, 61.6, 55.4, 41.8, 32.9, 14.0; HRMS (APCI) calcd for $C_{26}H_{21}Br_2F_2NO_3$ $[M+H]^+$: 591.9929, Found: 591.9931.



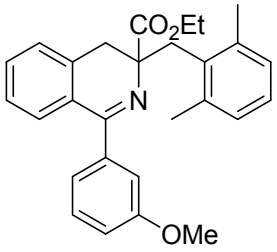
ethyl 3-(2,6-difluorobenzyl)-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1r)

This compound was prepared similarly to **1a**. Colorless oil, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 7.15-7.03 (m, 6H), 6.90 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 2H), 4.01-3.95 (m, 2H), 3.74 (s, 3H), 3.43 (d, *J* = 14.0 Hz, 1H), 3.24 (d, *J* = 14.0 Hz, 1H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.01 (d, *J* = 16.0 Hz, 1H), 1.03 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 167.6, 162.4 (dd, *J* = 246.3, 8.25 Hz), 159.9, 140.4, 136.9, 131.5, 129.5, 128.9 (dd, *J* = 10.3 Hz), 128.7, 128.5, 127.2, 122.1, 116.1, 114.7, 113.3 (dd, *J* = 20.1, 20.1 Hz), 111.3 (dd, *J* = 26.3, 15.0 Hz), 66.4, 61.6, 55.7, 33.9, 31.8, 14.3. HRMS (APCI) calcd for $C_{26}H_{23}F_2NO_3$ $[M+H]^+$: 436.1719, Found: 436.1726.



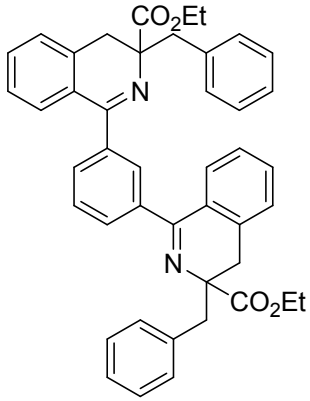
ethyl 3-(2,6-dichlorobenzyl)-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1s)

This compound was prepared similarly to **1a**. Colorless oil, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.26-7.25 (m, 3H), 7.23-7.16 (m, 4H), 7.06-7.05 (m, 1H), 7.01-7.00 (m, 1H), 4.00-3.95 (m, 2H), 3.91 (d, *J* = 14.0 Hz, 1H), 3.84 (s, 3H), 3.80 (d, *J* = 14.0 Hz, 1H), 3.28 (s, 2H), 0.98 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 167.5, 159.9, 140.3, 137.5, 137.1, 134.3, 131.4, 129.4, 129.0, 128.7, 128.6, 128.5, 128.4, 127.2, 122.3, 116.2, 114.7, 67.1, 61.5, 55.8, 40.2, 35.2, 14.2; HRMS (APCI) calcd for $C_{26}H_{23}Cl_2NO_3$ $[M+H]^+$: 468.1128, Found: 468.1123.



ethyl 3-(2,6-dimethylbenzyl)-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1t)

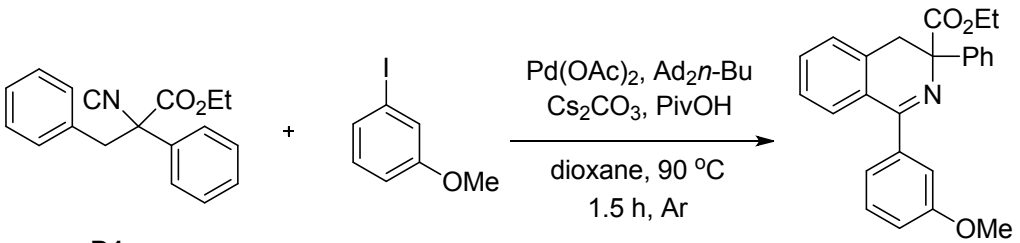
This compound was prepared similarly to **1a**. Colorless oil. 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, *J* = 7.2, 6.4, 3.2 Hz, 1H), 7.28-7.22 (m, 2H), 7.05-7.00 (m, 2H), 3.94-3.88 (m, 1H), 3.88 (s, 1H), 3.71 (d, *J* = 14.2 Hz, 1H), 3.58 (d, *J* = 14.2 Hz, 1H), 3.32 (d, *J* = 15.2 Hz, 1H), 2.95 (d, *J* = 15.2 Hz, 1H), 2.47 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 166.3, 159.4, 140.0, 138.7, 136.9, 134.7, 130.9, 129.0, 128.3, 128.1, 127.8, 126.8, 126.4, 121.7, 115.6, 114.2, 67.9, 60.9, 55.4, 39.4, 34.7, 21.7, 13.8. HRMS (ESI) calcd for $C_{28}H_{29}NO_3$ $[M+H]^+$: 428.2220, Found: 428.2227.



diethyl 1,1'-(1,3-phenylene)bis(3-benzyl-3,4-dihydroisoquinoline-3-carboxylate) (1u)

This compound was prepared similarly to **1a**. Colorless oil, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 12.0, 1.0 Hz, 1H), 7.82-7.78 (m, 2H), 7.56 (dd, *J* = 14.5, 7.5 Hz, 1H), 7.44-7.40 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.30-7.19 (m, 14H), 4.07 (dq, *J* = 14.0, 7.0 Hz, 4H), 3.37-3.26 (m, 4H), 3.11-2.95 (m, 4H), 1.11 (dt, *J* = 10.5, 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.7, 167.2, 167.1, 139.1, 139.0, 137.0, 136.9, 136.9, 131.7, 131.7, 130.9, 130.8, 130.3, 130.2, 128.9, 128.8, 128.7, 128.6, 128.6, 128.4, 128.4, 127.4, 127.1, 67.5, 67.4, 61.6, 61.5, 43.3, 42.6, 33.3, 33.1, 14.4, 14.4; HRMS (APCI) calcd for $C_{44}H_{40}N_2O_4$ $[M+H]^+$: 661,3061, Found: 661.3060.

General procedure for synthesis of six-membered 3,4-dihydroisoquinoline (1v) [2]

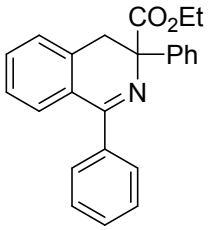


D1 **D2** **1v**, 51%

General procedure for synthesis of six-membered 3,4-dihydroisoquinoline (1v)

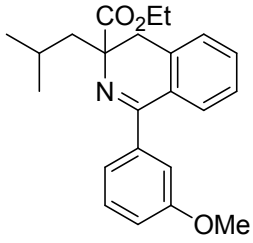
To a mixture of **D2** (0.12 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol %), Ad_2Pn-Bu (7.2. mg, 0.02 mmol, 20 mol %), Cs_2CO_3 (39.0 mg, 0.12 mmol) and PivOH (6.1 mg, 0.06 mmol) in 1,4 -dioxane (1 mL) was added a solution of **D1** (0.1 mmol) in 1,4 -dioxane (1 mL) via a syringe pump

during period of 1.5 h (1 mL) in Ar at 90 °C. The solvent was removed under reduced pressure and the residue was purified by silica gel flash Column chromatography to afford the product **1v** as a colorless oil in 51% yield.



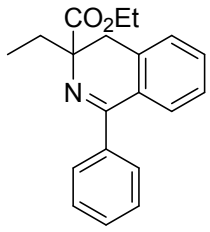
ethyl 1,3-diphenyl-3,4-dihydroisoquinoline-3-carboxylate (1v)

This compound was prepared similarly to **1a**. Colorless oil. 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.41-7.25 (m, 10H), 7.08-7.05 (m, 1H), 4.06 (qd, *J* = 7.2, 2.4 Hz, 2H), 3.90 (s, 3H), 3.79 (d, *J* = 15.6 Hz, 1H), 3.31 (d, *J* = 15.6 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 167.7, 159.5, 141.5, 140.0, 136.7, 131.4, 129.2, 128.7, 128.4, 128.3, 128.2, 127.5, 127.0, 126.7, 122.0, 115.6, 114.7, 67.9, 61.4, 55.5, 35.8, 13.9. HRMS (ESI) calcd for $C_{25}H_{23}NO_3$ $[M+H]^+$:386.1751, Found: 386.1753.



ethyl 3-isobutyl-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1w)

This compound was prepared similarly to **1a**. Colorless oil. 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 2H), 7.30-7.22 (m, 5H), 7.03-7.00 (m, 1H), 4.11 (qd, *J* = 7.2, 1.6 Hz, 2H), 3.86 (s, 3H), 3.27 (d, *J* = 15.6 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.03-1.79 (m, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 166.4, 159.4, 140.3, 136.46, 130.9, 129.1, 128.6, 128.1, 128.0, 126.9, 121.8, 115.4, 114.5, 65.8, 60.9, 55.4, 46.2, 35.3, 24.9, 24.1, 23.7, 14.1. HRMS (ESI) calcd for $C_{23}H_{27}NO_3$ $[M+H]^+$:366.2064, Found: 366.2069.

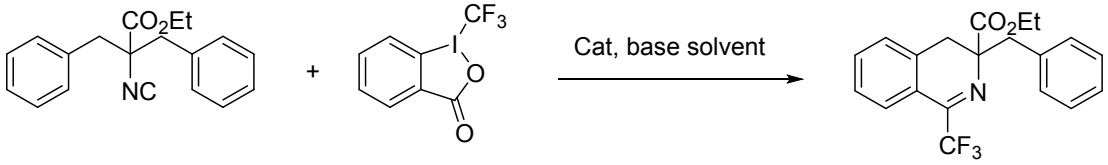


ethyl 3-ethyl-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate (1x)

This compound was prepared similarly to **1a**. Colorless oil. 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.66 (m, 2H), 7.48-7.43 (m, 3H), 7.41-7.37 (m, 1H), 7.29-7.20 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.29 (d, *J* = 15.6 Hz, 1H), 2.98 (d, *J* = 15.6 Hz, 1H), 2.05-1.97 (m, 2H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 167.3, 138.9, 136.5, 131.0, 129.5, 129.2, 128.7, 128.3, 128.2, 128.1, 126.9, 66.3, 60.9, 34.1, 31.3, 14.2, 8.8. HRMS (ESI) calcd for $C_{20}H_{21}NO_2$ $[M+H]^+$:308.1645, Found: 308.1637.

III. Synthesis of 1-CF_3-Dihydroisoquinoline Compounds 4

(1) Optimization of the trifluoromethylarylation of isocyanides



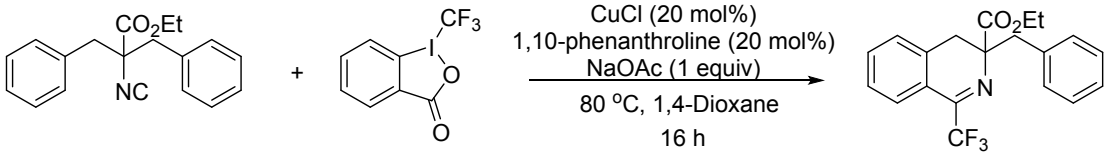
a **c** **4a**

Entry	Catalyst	Ligand	Base (equiv)	solvent	Yield(%)
1	CuCl	Phenanthroline	NaOAc	MeCN	56
2	CuCl	Phenanthroline	NaOAc	DMSO	44
3	CuCl	Phenanthroline	NaOAc	THF	40
4	**CuCl**	**Phenanthroline**	**NaOAc**	**Dioxane**	**60**
5	CuCl	Phenanthroline	NaOAc	DMF	38
6	CuCl	Phenanthroline	NaOAc	MeOH	trace
7	CuCl	Phenanthroline	NaOAc	DCE	35
8	CuCl	Phenanthroline	NaOAc	MTBE	34
9	CuCl	Phenanthroline	CsF	Dioxane	52
10	CuCl	Phenanthroline	K_2CO_3	Dioxane	58
11	CuCl	Phenanthroline	K_2HPO_4	Dioxane	50
12	CuCl	Phenanthroline	K_3PO_4	Dioxane	60
13	CuI	Phenanthroline	NaOAc	Dioxane	48
14	CuTc	Phenanthroline	NaOAc	Dioxane	53
15	CuCl		NaOAc	Dioxane	43

a (0.1 mmol), **c** (0.15 mmol), catalyst (20 mol%), ligand: 20 mol%, base: 1.0 equiv, solvent: 0.5 mL, 80 ^oC, Ar.

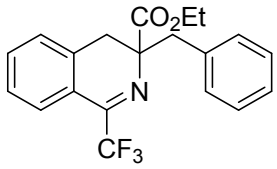
(b) Synthesis and Characterization Data of Compound 4

ethyl 3-benzyl-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate (4a)



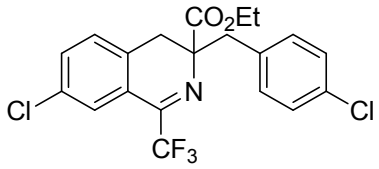
a **c** **4a**

An oven-dried 25 mL Schlenk tube charged with 1-TrifluoroMethyl-1,2-benziodoxol-3(1H)-one (0.15 mmol, 23.7 mg) CuCl (0.02 mmol, 2.0 mg, 20 mol%), 1,10-phenanthroline (0.02 mmol, 20 mol%), NaOAc (0.1 mmol, 8.2 mg, 1 equiv) and **a** (0.1 mmol, 36.9 mg) in 0.5 mL of dioxane was added by syringe and the tube was placed in an 80 °C oil-bath for 16 h. The crude reaction mixture was extracted with EtOAc (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the corresponding products.



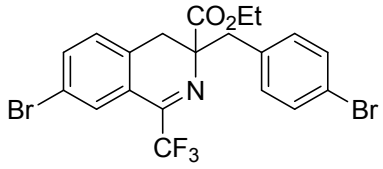
ethyl 3-benzyl-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate (4a)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.45-7.42 (m,1H), 7.34-7.30 (m, 1H), 7.27-7.19 (m, 6H), 4.14-4.03 (m, 2H), 3.25 (d, *J* = 13.5 Hz, 1H), 3.17 (dd, *J* = 19.5, 15.0 Hz, 2H), 2.89 (d, *J* = 16.5 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 155.5 (q, *J* = 33.1 Hz), 136.0, 135.5, 132.5, 130.6, 128.6, 128.2, 127.6, 127.0, 125.7 (q, *J* = 2.5 Hz), 123.3, 120.0 (q, *J* = 277.3 Hz), 66.9, 61.6, 42.5, 32.4, 13.9; HRMS (APCI) calcd for $C_{20}H_{18}F_3NO_2$ $[M+H]^+$: 362.1362, Found: 362.1365.



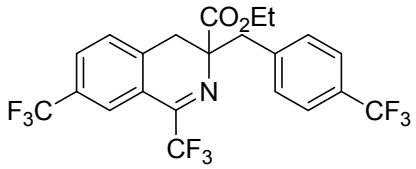
ethyl 7-chloro-3-(4-chlorobenzyl)-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate (4b)

This compound was prepared similarly to **4a**. Colorless oil, 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (br s, 1H), 7.42 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.25-7.23 (m, 2H), 7.18-7.15 (m, 3H), 4.08-4.01 (m, 2H), 3.20-3.16 (m, 3H), 2.81 (d, *J* = 16.5 Hz, 1H), 1.07 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 155.6 (q, *J* = 33.6 Hz), 134.4, 134.1, 133.9, 133.6, 132.9, 132.43, 130.1,128.7, 126.2 (q, *J* = 2.6 Hz), 124.8, 120.1 (q, *J* = 274.1 Hz), 67.2, 62.3 42.8, 32.8, 14.3; HRMS (APCI) calcd for $C_{20}H_{16}Cl_2F_3NO_2$ $[M+H]^+$: 430.0583, Found: 430.0584.



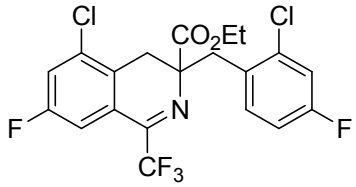
ethyl 7-bromo-3-(4-bromobenzyl)-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate (4c)

This compound was prepared similarly to **4a**. Colorless oil, 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.57 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 0.5 Hz, 1H), 7.10 (dd, *J* = 8.0, 3.5 Hz, 3H), 4.08-4.00 (m, 2H), 3.18-3.14 (m, 3H), 2.78 (d, *J* = 16.5 Hz, 1H), 1.07 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 154.4 (q, *J* = 34.3 Hz), 135.5, 134.5, 134.3, 132.3, 131.3, 130.0, 128.6 (q, *J* = 2.9 Hz), 124.7, 121.3, 121.2, 119.7 (q, *J* = 277.0 Hz), 66.7, 61.9, 42.5, 32.5, 13,9; HRMS (APCI) calcd for $C_{20}H_{16}Br_2F_3NO_2$ $[M+H]^+$: 517.9573, Found: 517.9570.



ethyl 1,7-bis(trifluoromethyl)-3-(4-(trifluoromethyl)benzyl)-3,4-dihydroisoquinoline-3-carboxylate (4d)

This compound was prepared similarly to **4a**. Colorless oil, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 3H), 4.08-4.01 (m, 2H), 3.38-3.29 (m, 3H), 2.92 (d, *J* = 16.5 Hz, 1H), 1.05 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 154.9 (q, *J* = 34.1 Hz), 139.6, 139.3, 131.1,130.5 (q, *J* = 33.3 Hz), 129.6 (q, *J* = 32.1 Hz), 129.2, 129.1, 125.1 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 270.5 Hz), 123.6, 123.4 (q, *J* = 270.9 Hz), 122.5 (q, *J* = 2.6 Hz), 119.7 (q, *J* = 276.9 Hz), 66.5, 62.1, 43.1, 33.2, 13.8; HRMS (APCI) calcd for $C_{22}H_{16}F_9NO_2$ $[M+H]^+$: 498.1110, Found: 498.1109.

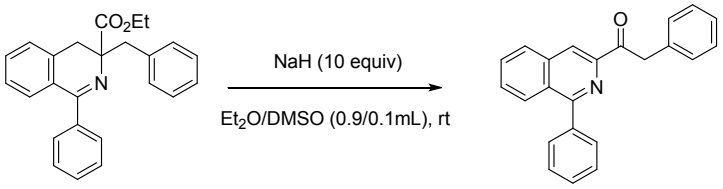


ethyl 5-chloro-3-(2-chloro-4-fluorobenzyl)-7-fluoro-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate (4e)

This compound was prepared similarly to **4a**. Colorless oil, 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.25 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.06 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.92-6.88 (m, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.59 (d, *J* = 14.0 Hz, 1H), 3.51 (d, *J* = 17.0 Hz, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 2.85 (dd, *J* = 17.0, 1.5 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 162.2 (d, *J* = 48.3 Hz),160.2 (d, *J* = 248.9 Hz), 154.6 (d, *J* = 34.0 Hz), 135.9 (d, *J* = 9.9 Hz), 134.7 (d, *J* = 9.6 Hz),133.7 (d, *J* = 8.5 Hz), 129.7 (d, *J* = 3.3 Hz), 129.3 (d, *J* = 3.3 Hz), 125.2 (d, *J* = 8.1 Hz), 120.5 (d, *J* = 24.5 Hz), 119.6 (q, *J* = 275.6 Hz), 116.7 (d, *J* = 24.4 Hz), 114 (d, *J* = 20.8 Hz), 111.6 (d, *J* = 23.8 Hz), 67.0, 62.2, 39.1, 29.4, 13.9; HRMS (APCI) calcd for $C_{20}H_{14}Cl_2F_5NO_2$ $[M+H]^+$: 466.0395, Found: 466.0392.

IV. Detailed Optimization and General Procedures of the C-C Bond Cleavage Reactions

Table 1. Detailed Information of Conditions Optimization



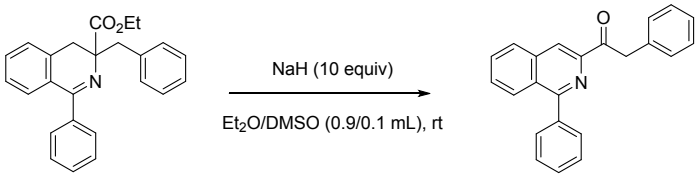
1a **2a**

Entry	solvent	base	yield (%)[b]
1[c]	Et_2O/DMSO (9:1)	NaH	73
2[d]	Et_2O/DMSO (9:1)	NaH	73
3[e]	Et_2O/DMSO (9:1)	NaH	51
4[f]	Et_2O/DMSO (9:1)	NaH	46
5[c]	Et_2O/DMSO (9:1)	LiOtBu	trace
6[c]	Et_2O/DMSO (9:1)	Cs_2CO_3	0
7[c]	Et_2O/DMSO (9:1)	K_2CO_3	0
8[c]	Et_2O/DMSO (9:1)	DBU	0
9[c]	Et_2O/DMSO (9:1)	DIPEA	0
10[c]	Et_2O	NaH	0
11[c]	THF	NaH	0
12[c]	toluene	NaH	0
13[c]	DMSO	NaH	49

[a] Reaction conditions: **1a** (0.1 mmol), 1mL of solvent, rt, Ar. [b] Isolated yields. [c] Base (10 eq). [d] Base (12 eq). [e] Base (8 eq). [f] Base (6 eq).

Procedure A:

2-phenyl-1-(1-phenylisoquinolin-3-yl)ethanone (2a)



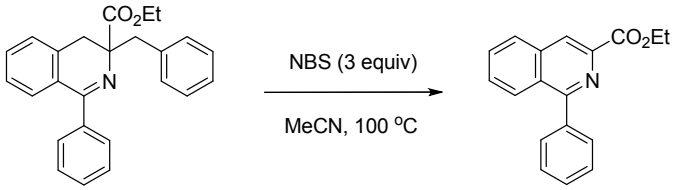
1a **2a**

An oven-dried 25 mL Schlenk tube charged with NaH (1 mmol, 40 mg) and ethyl 3-benzyl-1-phenyl-3,4-dihydroisoquinoline-3-carboxylate **1a** (0.1 mmol, 36.9 mg) was vacuumed and refilled with Ar for 3 times. Then a solution of Et_2O (0.9 mL) and DMSO (0.1 mL) was added in room temperature for 40 min. The crude reaction mixture was quenched with saturated NH_4Cl. The crude reaction mixture was extracted with EtOAc (20 mL × 3) and washed with brine (20 mL). The

organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the corresponding products.

Procedure B:

ethyl 1-phenylisoquinoline-3-carboxylate (3a)

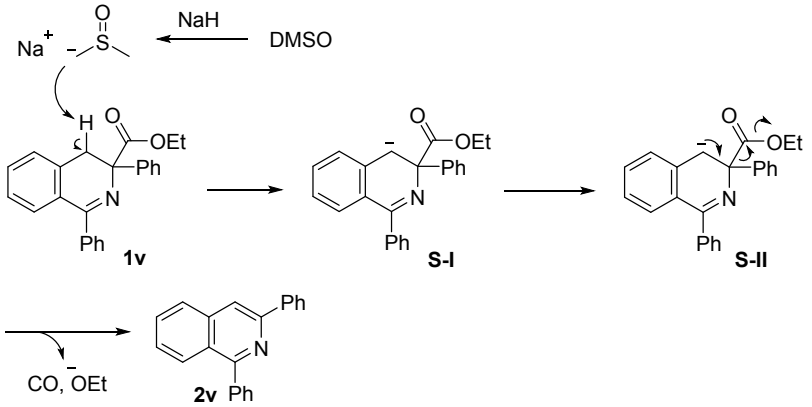


1a **3a**

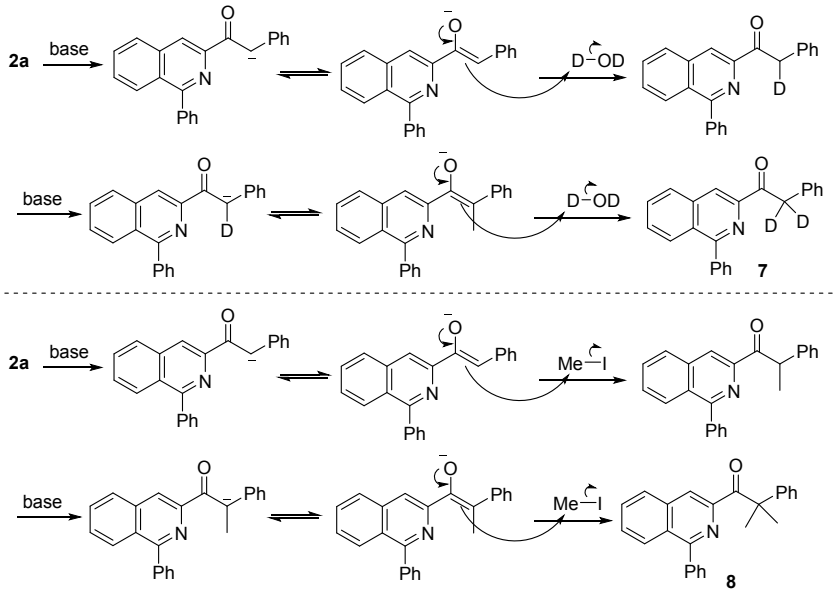
A 25 mL Schlenk tube charged with 3-benzyl-1-phenyl-3,4-dihydroisoquinoline-3-carboxylate **1a** (0.1 mmol, 36.9 mg) and NBS (0.3 mmol, 53.4 mg, 3 equiv) in the solvent of MeCN (1mL) was heated at 100 °C for 12 h. The crude reaction mixture was extracted with EtOAc (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the corresponding products.

V. Mechanism of the Formation of Products 2v, 7 and 8

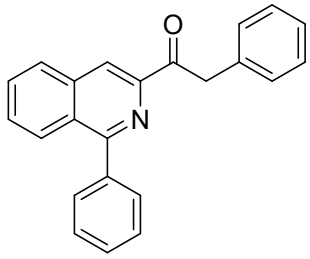
Sodium methylsulfinylmethylide, which was formed by NaH and DMSO, abstracted one of the cyclic benzylic protons of **1v**, generating the anion intermediate **S-I**. The carbanion underwent an intramolecular electron transfer to promote the C-CO_2Et bond cleavage. The title product **2v** was yielded with the release of ethoxy anion and carbon monoxide as the by-products.



The formed product **2a** was deprotonated to generate an anion intermediate, which underwent a deuteration to deliver the mono deuterated intermediate. Product **7** was generated by repeating the above process. (Dimethyl substituted product **8** was generated with a similar mechanism.)

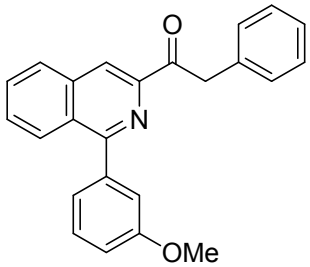


VI. Characterization Data



2-phenyl-1-(1-phenylisoquinolin-3-yl)ethanone (2a)

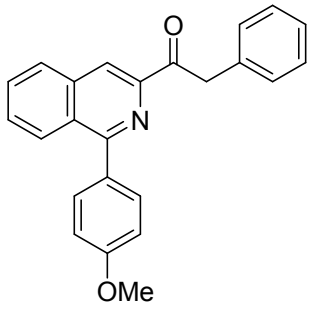
Prepared from ethyl 3-benzyl-1-phenyl-3,4-dihydroisoquinoline-3-carboxylate **1a** (50 mg, 0.14 mmol, 1.0 equiv) and NaH (54 mg, 1.4 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2a** as white solid (23 mg, 0.1 mmol, 73% yield). (new compound). mp: 120-122 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 0.5 Hz, 1H), 8.20-8.18 (m, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.79-7.73 (m, 3H), 7.61-7.56 (m, 4H), 7.40-7.39 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 1H), 4.69 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 159.9, 146.2, 139.2, 136.8, 135.3, 130.5, 130.2, 130.1, 129.4, 129.20, 129.0, 128.4, 127.6, 126.6, 120.2, 44.9; HRMS (APCI) calcd for $C_{23}H_{17}NO$ $[M+H]^+$: 354.1489, Found: 354.1381.



1-(1-(3-methoxyphenyl)isoquinolin-3-yl)-2-phenylethanone (2b)

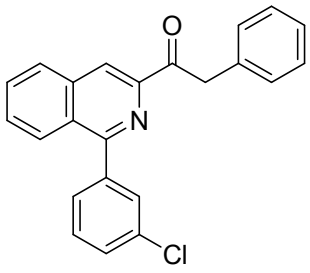
Prepared from 1-(1-(3-methoxyphenyl)isoquinolin-3-yl)-2-phenylethanone **1b** (40 mg, 0.1

mmol, 1.0 equiv) and NaH (40 mg, 0.1 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2b** as white solid (27 mg, 0.077 mmol, 77% yield). (new compound). mp: 58-60 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 0.5 Hz, 1H), 8.12 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.59-7.56 (m, 1H), 7.44-7.41 (m, 1H), 7.32-7.30 (m, 2H), 7.27-7.12 (m, 5H), 7.04-7.02 (m, 1H), 4.60 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 159.8, 159.7, 146.2, 140.6, 136.8, 135.3, 130.5, 130.1, 129.4, 129.4, 129.2, 128.4, 128.3, 127.6, 126.6, 122.6, 120.2, 115.7, 114.6, 55.5, 44.9; HRMS (APCI) calcd for $C_{26}H_{19}NO_2$ $[M+H]^+$: 354.1489, Found: 354.1483.



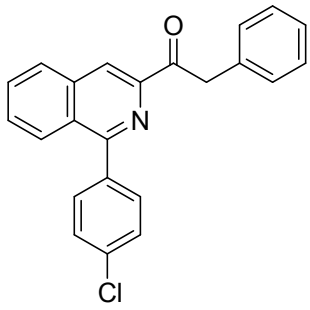
1-(1-(4-methoxyphenyl)isoquinolin-3-yl)-2-phenylethanone (2c)

Prepared from ethyl 3-benzyl-1-(4-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate **1c** (25 mg, 0.06 mmol, 1.0 equiv) and NaH (25 mg, 0.6 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2c** as white solid (13 mg, 0.035 mmol, 58% yield). (new compound). mp: 136-138 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.75-7.71 (m, 3H), 7.67-7.63 (m, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 7.14-7.12 (m, 2H), 4.69 (s, 2H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.3, 160.8, 160.0, 146.6, 137.3, 135.6, 132.1, 132.0, 130.8, 130.4, 129.7, 129.6, 128.8, 128.7, 128.1, 127.0, 120.1, 114.29, 55.9, 45.3; HRMS (APCI) calcd for $C_{26}H_{19}NO_2$ $[M+H]^+$: 354.1489, Found: 354.1491.



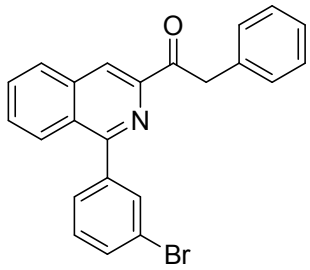
1-(1-(3-chlorophenyl)isoquinolin-3-yl)-2-phenylethanone (2d)

Prepared from ethyl 3-benzyl-1-(3-chlorophenyl)-3,4-dihydroisoquinoline-3-carboxylate **1d** (42 mg, 0.1 mmol, 1.0 equiv) and NaH (40 mg, 1 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2d** as white solid (23.4 mg, 0.065 mmol, 65% yield). (new compound). mp: 95-97 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.70-7.67 (m, 1H), 7.65-7.63 (m, 1H),7.55-7.51 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24-7.21 (m, 1H), 4.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 158.7, 146.6, 141.3, 137.2, 135.6, 134.9, 131.1, 130.7, 130.4, 130.1, 130.0, 129.7, 129.4, 128.8, 128.7, 128.5, 127.5, 127.0, 121.0, 45.5; HRMS (APCI) calcd for $C_{23}H_{16}ClNO$ $[M+H]^+$: 358.0993, Found: 358.0984.



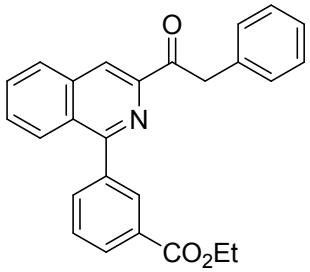
1-(1-(4-chlorophenyl)isoquinolin-3-yl)-2-phenylethanone (2e)

Prepared from ethyl 3-benzyl-1-(4-chlorophenyl)-3,4-dihydroisoquinoline-3-carboxylate **1e** (40 mg, 0.1 mmol, 1.0 equiv) and NaH (40 mg, 1 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2e** as white solid (28 mg, 0.07 mmol, 72% yield). (new compound). mp: 138-140 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.79-7.65 (m, 4H), 7.59-7.56 (m, 2H), 7.38-7.23 (m, 5H), 4.65 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 158.7, 146.2, 137.6, 136.9, 135.2, 131.5, 130.7, 130.0, 129.6, 129.4, 128.7, 128.5, 128.1, 127.2, 126.7, 120.4, 105.0, 45.0; HRMS (APCI) calcd for $C_{23}H_{16}ClNO$ $[M+H]^+$: 358.0993, Found: 358.0987.



1-(1-(3-bromophenyl)isoquinolin-3-yl)-2-phenylethanone (2f)

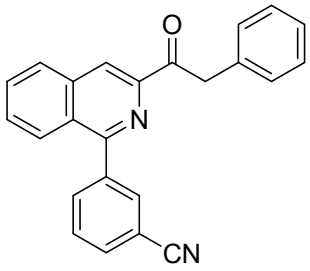
Prepared from ethyl 3-benzyl-1-(3-bromophenyl)-3,4-dihydroisoquinoline-3-carboxylate **1f** (28 mg, 0.06 mmol, 1.0 equiv) and NaH (25 mg, 0.6 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2f** as white solid (18 mg, 0.04 mmol, 65% yield). (new compound). mp: 90-92 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 2.0 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.71-7.66 (m, 3H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.26-7.23 (m, 1H), 4.65 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 158.6, 146.6, 141.6, 137.2, 135.6, 133.5, 132.4, 131.1, 130.4, 130.3, 130.1, 129.7, 129.1, 128.9, 128.5, 127.5, 127.0, 123.0, 121.0, 45.5; HRMS (APCI) calcd for $C_{23}H_{16}BrNO$ $[M+H]^+$: 402.0488, Found: 402.0485.



ethyl 3-(3-(2-phenylacetyl)isoquinolin-1-yl)benzoate (2g)

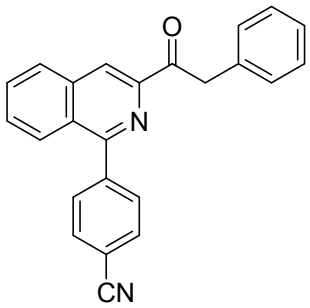
Prepared from ethyl 3-benzyl-1-(3-(ethoxycarbonyl)phenyl)-3,4-dihydroisoquinoline-3-

carboxylate **1g** (19 mg, 0.04 mmol, 1.0 equiv) and NaH (18 mg, 0.4 mmol, 10 equiv) according to the general procedure. Column chromatography purification (EtOAc : petroleum ether 15 : 1) furnished the product **2g** as white solid (7 mg, 0.016 mmol, 40% yield). (new compound). mp: 88-90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.46 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 4.66 (s, 2H), 4.45 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.0, 166.7, 159.3, 146.6, 139.9, 137.2, 135.5, 134.8, 131.6, 131.3, 131.1, 130.5, 130.4, 130.1, 129.7, 129.0, 128.8, 128.6, 127.6 127.0, 120.9, 61.6, 45.4, 14.8; HRMS (APCI) calcd for $C_{26}H_{21}NO_3$ $[M+H]^+$: 396.1594, Found: 396.1593.



3-(3-(2-phenylacetyl)isoquinolin-1-yl)benzonitrile (2h)

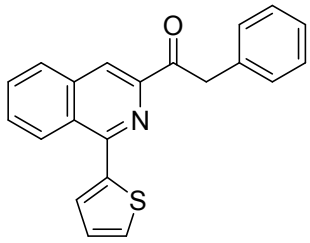
Prepared from ethyl 3-benzyl-1-(3-cyanophenyl)-3,4-dihydroisoquinoline-3-carboxylate **1h** (27 mg, 0.07 mmol, 1.0 equiv) and NaH (27 mg, 0.7 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2h** as white solid (15 mg, 0.046 mmol, 65% yield). (new compound). mp: 130-132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.08-7.99 (m, 4H), 7.86-7.84 (m, 1H), 7.81-7.77 (m, 1H), 7.73-7.69 (m, 2H), 7.37-7.30 (m, 4H), 7.25-7.22 (m, 2H), 4.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 157.6, 146.6, 140.7, 137.2, 135.4, 134.7, 134.1, 132.7, 131.2, 130.4, 130.3, 129.8, 129.6, 128.8, 128.2, 127.0, 126.9, 121.3, 118.9, 113.2, 45.4; HRMS (APCI) calcd for $C_{24}H_{16}N_2O$ $[M+H]^+$: 349.1335, Found: 349.1334.



4-(3-(2-phenylacetyl)isoquinolin-1-yl)benzonitrile (2i)

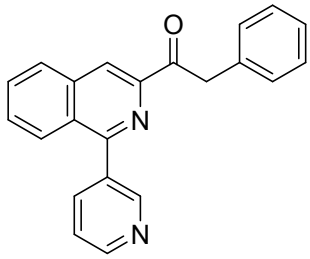
Prepared from ethyl 3-benzyl-1-(4-cyanophenyl)-3,4-dihydroisoquinoline-3-carboxylate **1i** (37 mg, 0.09 mmol, 1.0 equiv) and NaH (38 mg, 0.9 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2i** as white solid (14 mg, 0.039 mmol, 43% yield). (new compound). mp: 153-155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.08-8.06 (m, 2H), 7.89-7.87 (m, 4H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.72-7.69 (m, 1H), 7.35-7.29 (m, 4H), 7.23 (t, *J* = 7.0 Hz, 1H), 4.63 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 158.1, 146.7, 144.0, 137.3, 135.4, 132.7, 131.3, 130.4, 130.3, 129.9, 128.8, 128.3, 127.1, 127.0, 121.5, 121.4, 119.0, 113.2, 45.3; HRMS (APCI) calcd for $C_{24}H_{16}N_2O$ $[M+H]^+$: 349.1335,

Found: 349.1333.



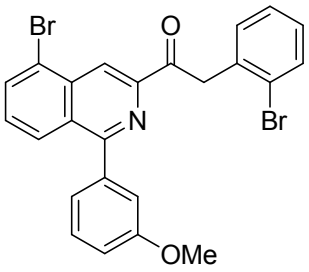
2-phenyl-1-(1-(thiophen-2-yl)isoquinolin-3-yl)ethanone (2j)

Prepared from ethyl 3-benzyl-1-(thiophen-2-yl)-3,4-dihydroisoquinoline-3-carboxylate **1j** (28 mg, 0.07 mmol, 1.0 equiv) and NaH (29 mg, 0.7 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2j** as white solid (18 mg, 0.05 mmol, 73% yield). (new compound). mp: 82-84 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61-8.60 (m, 1H), 8.39 (s, 1H), 8.03-8.01 (m, 1H), 7.77-7.71 (m, 3H), 7.62-7.60 (m, 1H), 7.45-7.43 (m, 2H), 7.32-7.27 (m, 3H), 7.23-7.20 (m, 1H), 4.68 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8, 153.0, 146.3, 143.4, 137.6, 135.5, 131.0, 130.5, 130.5, 129.8, 129.8, 129.0, 128.8, 128.1, 127.9, 127.2, 127.0, 120.3, 45.1; HRMS (APCI) calcd for $C_{21}H_{15}NOS$ $[M+H]^+$: 330.0957, Found: 330.0946.



2-phenyl-1-(1-(pyridin-3-yl)isoquinolin-3-yl)ethanone (2k)

Prepared from ethyl 3-benzyl-1-(pyridin-3-yl)-3,4-dihydroisoquinoline-3-carboxylate **1k** (19 mg, 0.05 mmol, 1.0 equiv) and NaH (20 mg, 0.5 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2k** as white solid (10 mg, 0.04 mmol, 73% yield). (new compound). mp: 90-92 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.83 (d, *J* = 4.9 Hz, 1H), 8.54 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.13-8.08 (m, 2H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.64 55-7.61 (m, 1H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 4.64 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 156.7, 150.5, 149.6, 146.8, 138.6, 137.3, 135.7, 135.4, 131.3, 130.4, 130.3, 129.9, 128.8, 128.6, 127.1, 127.0, 124.0, 121.3, 45.3; HRMS (APCI) calcd for $C_{22}H_{16}N_2O$ $[M+H]^+$: 325.1335, Found: 325.1337.



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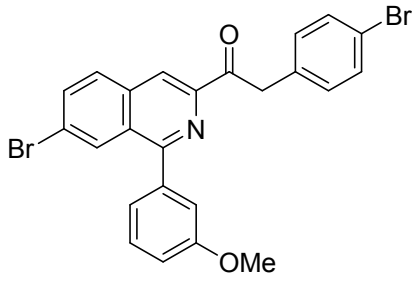
1-(5-bromo-1-(3-methoxyphenyl)isoquinolin-3-yl)-2-(2-bromophenyl)ethanone (2l)

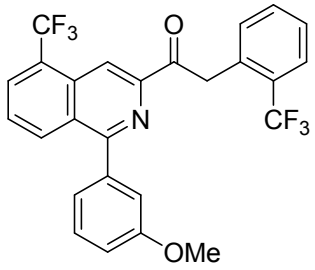
Prepared from ethyl 5-bromo-3-(2-bromobenzyl)-1-(3-methoxyphenyl) -3,4-

Dihydroisoquinoline-3-carboxylate **1l** (18 mg, 0.032 mmol, 1.0 equiv) and NaH (13 mg, 0.32 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2l** as white solid (12 mg, 0.022 mmol, 70% yield). (new compound). mp: 143-145 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.52-7.48 (m, 2H), 7.32-7.26 (m, 4H), 7.17-7.10 (m, 2H), 4.87 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 160.9, 160.1, 147.6, 140.5, 136.6, 136.2, 134.8, 133.1, 132.4, 130.1, 129.9, 129.8, 128.9, 127.8, 127.8, 125.8, 124.7, 123.1, 119.2, 116.4, 115.1, 55.9, 46.3.; HRMS (APCI) calcd for $C_{24}H_{17}Br_2NO_2$ $[M+H]^+$: 509.9699, Found: 509.9691.



1-(7-bromo-1-(3-methoxyphenyl)isoquinolin-3-yl)-2-(4-bromophenyl)ethanone (2m)

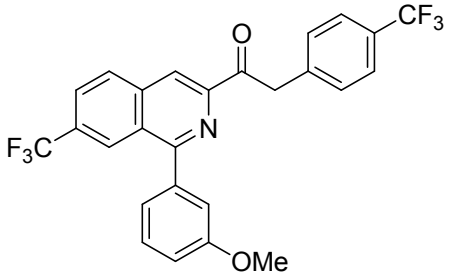
Prepared from ethyl 7-bromo-3-(4-bromobenzyl)-1-(3-methoxyphenyl)-3,4-Dihydroisoquinoline-3-carboxylate **1m** (58 mg, 0.1 mmol, 1.0 equiv) and NaH (40 mg, 1 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2m** as white solid (29 mg, 0.05 mmol, 54% yield). (new compound). mp: 178-180 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.34 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.84-7.82 (m, 1H), 7.54-7.51 (m, 1H), 7.43-7.41 (m, 2H), 7.27-7.25 (m, 4H), 7.14-7.12 (m, 1H), 4.59 (s, 2H), 3.93 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 160.2, 159.4, 146.6, 140.2, 135.7, 134.7, 134.4, 132.2, 131.9, 131.1, 130.3, 130.1, 129.6, 124.3, 122.8, 121.1, 120.3, 116.1, 115.2, 105.4, 55.9, 44.7; HRMS (APCI) calcd for $C_{24}H_{17}Br_2NO_2$ $[M+H]^+$: 509.9699, Found: 509.9698.



1-(1-(3-methoxyphenyl)-5-(trifluoromethyl)isoquinolin-3-yl)-2-(2-(trifluoromethyl)phenyl)ethanone (2n)

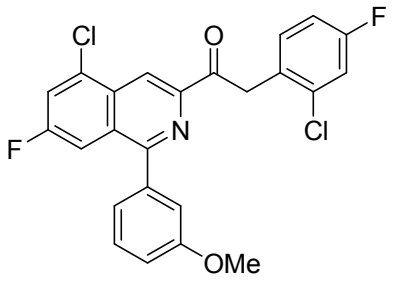
Prepared from ethyl 1-(3-methoxyphenyl)-5-(trifluoromethyl)-3-(2-(trifluoromethyl)benzyl) -3,4-dihydroisoquinoline-3-carboxylate **1n** (20 mg, 0.04 mmol, 1.0 equiv) and NaH (15 mg, 0.4 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2n** as white solid (9.6 mg, 0.02 mmol, 53% yield). (new compound). mp: 170-172 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 7.0 Hz, 1H), 7.73-7.69 (m, 2H), 7.55-7.49 (m, 2H), 7.42-7.37 (m, 2H), 7.32-7.30 (m, 2H), 7.26-7.25 (m, 1H), 7.14-7.12 (m, 1H), 4.93 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 161.0, 159.8, 147.0, 140.0, 133.9, 133.2, 133.1, 132.2, 131.7, 129.6, 129.1 (q, *J* = 5.6 Hz),

128.7, 127.6, 127.0, 126.1 (q, *J* = 5.4 Hz), 126.0 (q, *J* = 272.4 Hz), 123.8 (q, *J* = 272.0 Hz), 122.7, 115.9, 115.5, 115.0, 55.5, 42.5; HRMS (APCI) calcd for $C_{26}H_{17}F_6NO_2$ $[M+H]^+$: 490.1236, Found: 490.1242.



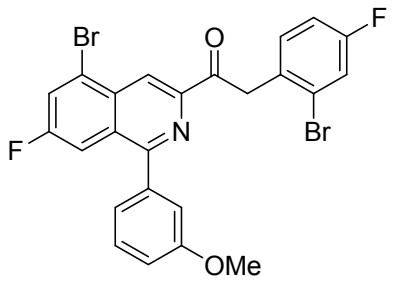
1-(1-(3-methoxyphenyl)-
7-(trifluoromethyl)isoquinolin-3-yl)-2-(4-(trifluoromethyl)phenyl)ethanone (2o)

Prepared from ethyl 1-(3-methoxyphenyl) -7- (trifluoromethyl)-3- (4-(trifluoromethyl)benzyl) -3,4-dihydroisoquinoline-3-carboxylate **1o** (24 mg, 0.045 mmol, 1.0 equiv) and NaH (18 mg, 0.45 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2o** as white solid (15 mg, 0.03 mmol, 67% yield). (new compound). mp: 127-129 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.0 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.94-7.92 (m, 1H), 7.58-7.53 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.28-7.23 (m, 2H), 7.17-7.15 (m, 1H), 4.73 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 161.0, 159.9, 147.4, 139.5, 139.0, 138.3, 130.5, 130.4, 129.8, 127.4, 126.4 (q, *J* = 2.6 Hz), 125.5 (q, *J* = 4.9 Hz), 125.4 (q, *J* = 3.8 Hz), 124.7 (q, *J* = 273.5 Hz), 123.5 (q, *J* = 278.0 Hz), 122.4, 119.6, 115.8, 115.1, 55.5, 44.8; HRMS (APCI) calcd for $C_{26}H_{17}F_6NO_2$ $[M+H]^+$: 490.1236, Found: 490.1244.



2-(2-chloro-4-fluorophenyl)-1-(5-chloro-7-fluoro-1-(3-methoxyphenyl)isoquinolin-3-yl)ethanone (2p)

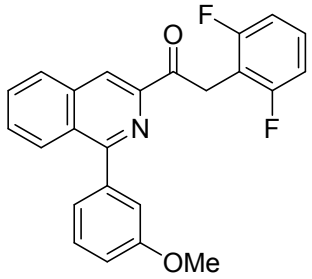
Prepared from ethyl 5-chloro-3-(2-chloro-4-fluorobenzyl)-7-fluoro-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate **1p** (19 mg, 0.04 mmol, 1.0 equiv) and NaH (16 mg, 0.4 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2p** as white solid (11 mg, 0.026 mmol, 65% yield). (new compound). mp: 107-109 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 1.0 Hz, 1H), 7.80-7.77 (m, 1H), 7.68-7.66 (m, 1H), 7.52-7.49 (m, 1H), 7.28-7.26 (m, 3H), 7.18-7.16 (m, 1H), 7.13-7.11 (m, 1H), 6.99-6.95 (m, 1H), 4.79 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 161.7 (d, *J* = 247.0 Hz), 161.1 (d, *J* = 252.5 Hz), 159.9, 159.8, 146.6 (d, *J* = 2.6 Hz), 139.6, 135.7 (d, *J* = 10.6 Hz), 135.4 (d, *J* = 10.5 Hz), 132.8 (d, *J* = 8.6 Hz), 132.3, 129.9 (d, *J* = 9.1 Hz), 129.7, 129.6, 122.3, 121.6 (d, *J* = 28.4 Hz), 116.8 (d, *J* = 24.6 Hz), 116.0, 115.8, 114.8, 114.0 (d, *J* = 20.9Hz), 110.7 (d, *J* = 22.1Hz), 55.5, 42.7; HRMS (APCI) calcd for $C_{24}H_{15}Cl_2F_2NO_2$ $[M+H]^+$: 458.0521, Found: 458.0522.



2-(2-bromo

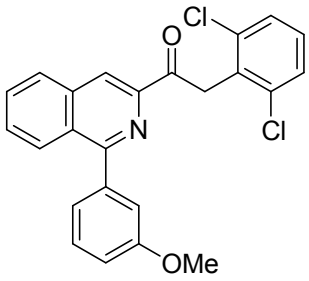
-4-fluorophenyl)-1-(5-bromo-7-fluoro-1-(3-methoxyphenyl)isoquinolin-3-yl)ethanone (2q)

Prepared from ethyl 5-bromo-3-(2-bromo-4-fluorobenzyl)-7-fluoro-1-(3-methoxyphenyl) -3,4-Dihydroisoquinoline-3-carboxylate **1q** (32 mg, 0.054 mmol, 1.0 equiv) and NaH (22 mg, 0.54 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2q** as white solid (14 mg, 0.035 mmol, 65% yield). (new compound). mp: 139-141 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.0 Hz, 1H), 7.86-7.82 (m, 2H), 7.53-7.49 (m, 1H), 7.36-7.34(m, 1H), 7.29-7.26 (m, 3H), 7.13-7.11 (m, 1H), 7.04-7.00 (m, 1H), 4.82 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 161.8 (d, *J* = 247.6 Hz), 161.5 (d, *J* = 253.4 Hz), 160.4, 160.2, 147.2, 140.0, 133.9, 133.1 (d, *J* = 8.3 Hz), 132.0, 130.4 (d, *J* = 8.5 Hz), 130.1, 125.6 (d, *J* = 27.9 Hz), 122.7, 120.3 (d, *J* = 24.3 Hz), 118.9, 116.3, 115.2, 114.9 (d, *J* = 20.6 Hz), 111.7 (d, *J* = 22.0 Hz), 55.9, 44.5; HRMS (APCI) calcd for $C_{24}H_{15}Br_2F_2NO_2$ $[M+H]^+$: 545.9510, Found: 545.9511.



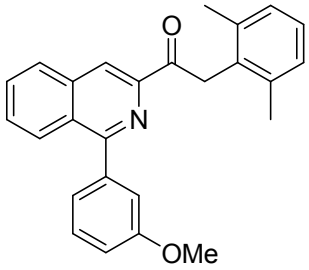
2-(2,4-difluorophenyl)-1-(1-(3-methoxyphenyl)isoquinolin-3-yl)ethanone (2r)

Prepared from 2-(2,4-difluorophenyl)-1-(1-(3-methoxyphenyl)isoquinolin-3-yl)ethanone **1r** (45 mg, 0.1 mmol, 1.0 equiv) and NaH (40 mg, 1 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2r** as white solid (16 mg, 0.041 mmol, 41% yield). (new compound). mp: 70-72 ^{o}C; ^{1}H NMR (500 MHz, CDCl3) δ 8.42 (s, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.29-7.28 (m, 2H), 7.20-7.14 (m, 1H), 7.04-7.02 (m, 1H), 6.87-6.82 (m, 2H), 4.74 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 161.6 (dd, *J* = 245.8, 8.4 Hz), 159.7, 159.5, 145.7, 140.2, 136.5, 130.4, 129.2, 129.1, 129.0, 128.2 (dd, *J* = 20.0, 3.1 Hz), 127.5, 122.4, 119.8, 115,6, 114.3, 111.7 (dd, *J* = 20.9, 20.0 Hz), 110.7 (dd, *J* = 25.6, 14.4 Hz), 55.2, 32.8. HRMS (ESI) calcd for $C_{24}H_{17}F_2NO_2$ $[M+H]^+$: 390.1300, Found: 390.1294.



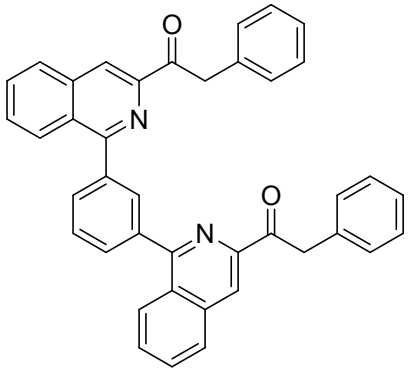
2-(2,6-dichlorophenyl)-1-(1-(3-methoxyphenyl)isoquinolin-3-yl)ethanone (2s)

Prepared from ethyl 3-(2,6-dichlorobenzyl)-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate **1s** (20 mg, 0.041 mmol, 1.0 equiv) and NaH (17 mg, 0.41 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2s** as white solid (6.3 mg, 0.014 mmol, 35% yield). (new compound). mp: 138-140 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 7.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.52-7.49 (m, 1H), 7.40-7.34 (m, 4H), 7.20-7.17 (m, 1H), 7.12-7.10 (m, 1H), 5.13 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 160.3, 160.1, 146.4, 140.9, 137.2, 136.7, 133.6, 130.1, 129.8, 129.7, 128.9, 128.3, 128.1, 123.1, 120.1, 116.4, 114.9, 55.9, 42.2; HRMS (APCI) calcd for $C_{24}H_{17}Cl_2NO_2$ $[M+H]^+$: 422.0709, Found: 422.0710.



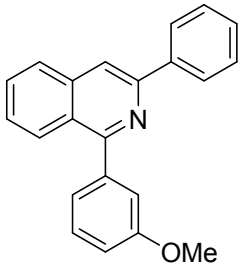
2-(2,6-dimethylphenyl)-1-(1-(3-methoxyphenyl)isoquinolin-3-yl)ethanone (2t)

Prepared from ethyl 3-(2,6-dimethylbenzyl)-1-(3-methoxyphenyl)-3,4-dihydroisoquinoline-3-carboxylate **1t** (43 mg, 0.1 mmol, 1.0 equiv) and NaH (40 mg, 1 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2t** as Colorless oil (13 mg, 0.034 mmol, 34% yield). (new compound). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.27 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.79 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.41-7.38 (m, 2H), 7.14-7.08 (m, 4H), 4.83 (s, 2H), 3.94 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 159.6, 146.6, 140.5, 137.2, 136.8, 133.5, 130.6, 129.5, 129.4, 129.2, 127.9, 127.7, 126.7, 122.7, 119.6, 115.9, 114.5, 55.5, 39.7, 20.6. HRMS (ESI) calcd for $C_{26}H_{23}NO_2$ $[M+H]^+$:382.1802, Found: 382.1796.



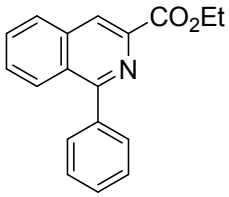
1,1'-(1,1'-(1,3-phenylene)bis(isoquinoline-3,1-diyl))bis(2-phenylethanone) (2u)

Prepared from diethyl 1,1'-(1,3-phenylene)bis(3-benzyl-3,4-dihydroisoquinoline-3-carboxylate) **1u** (23 mg, 0.035 mmol, 1.0 equiv) and NaH (14 mg, 0.35 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2u** as white solid (8 mg, 0.013 mmol, 37% yield). (new compound). mp: 173-175 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 2H), 8.37 (d, *J* = 8.5 Hz, 2H), 8.20 (t, *J* = 1.5 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 8.00-7.99 (m, 2H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.79-7.76 (m, 2H), 7.70-7.74 (m, 2H),7.36-7.35 (m, 4H), 7.21-7.18 (m, 4H), 7.16-7.13(m, 2H), 4.70 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.0, 159.8, 146.7, 139.8, 137.4, 135.6, 132.7, 131.1, 131.0, 130.4, 130.0, 129.7, 129.0, 128.8, 128.7, 127.9, 127.0, 120.8, 45.3; HRMS (APCI) calcd for $C_{40}H_{28}N_2O_2$ $[M+H]^+$: 569.2224, Found: 569.2226.



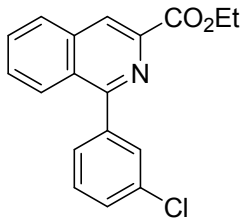
1-(3-methoxyphenyl)-3-phenylisoquinoline (2v)

Prepared from ethyl 1,3-diphenyl-3,4-dihydroisoquinoline-3-carboxylate **1v** (36 mg, 0.1 mmol, 1.0 equiv) and NaH (40 mg, 1 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **2v** as Colorless oil (11 mg, 0.034 mmol, 34% yield). (new compound). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 - 8.25 (m, 2H), 8.18 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.11 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.73-7.69 (m, 1H), 7.54-7.37 (m, 7H), 7.11-7.06 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.6, 150.1, 141.2, 139.6, 137.8, 130.1, 129.3, 128.7, 128.5, 127.6, 127.5, 127.1, 127.0, 125.8, 122.7, 115.9, 115.7, 114.4, 55.5. HRMS (ESI) calcd for $C_{22}H_{17}NO$ $[M+H]^+$:312.1388, Found:312.1379.



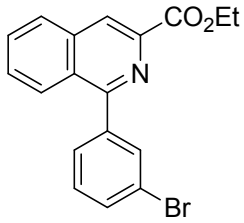
ethyl 1-phenylisoquinoline-3-carboxylate (3a)

Prepared from ethyl 3-benzyl-1-phenyl-3,4-dihydroisoquinoline-3-carboxylate **1a** (37 mg, 0.1 mmol, 1.0 equiv) and NBS (54 mg, 0.3 mmol, 3 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **3a** as white solid (18 mg, 0.066 mmol, 66% yield). (new compound). mp: 90-92 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.80-7.64 (m, 4H), 7.54-7.52 (m, 3H), 4.53 (q, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 161.2, 141.1, 138.9, 136.6, 130.7, 130.3, 129.4, 128.9, 128.4, 128.4, 128.2, 127.9, 123.1, 61.8, 14.4; HRMS (APCI) calcd for $C_{18}H_{15}NO_2$ $[M+H]^+$: 278.1176, Found: 278.1182.



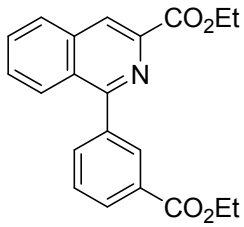
ethyl 1-(3-chlorophenyl)isoquinoline-3-carboxylate (3b)

Prepared from ethyl 3-benzyl-1-(3-chlorophenyl)-3,4-dihydroisoquinoline-3-carboxylate **1d** (35 mg, 0.087 mmol, 1.0 equiv) and NBS (47 mg, 0.26 mmol, 3 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **3b** as white solid (12 mg, 0.055 mmol, 63% yield). (new compound). mp: 110-112 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 2.0 Hz, 1H), 7.71-7.68 (m, 1H), 7.61-7.59 (m, 1H), 7.50-7.46 (m, 2H), 4.53 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 160.0, 141.5, 141.0, 137.0, 134.9, 131.3, 130.7, 130.1, 130.0, 129.5, 129.0, 128.8, 128.4, 127.8, 124.0, 62.3, 14.8.; HRMS (APCI) calcd for $C_{18}H_{14}ClNO_2$ $[M+H]^+$: 312.0786, Found: 312.0793.



ethyl 1-(3-bromophenyl)isoquinoline-3-carboxylate (3c)

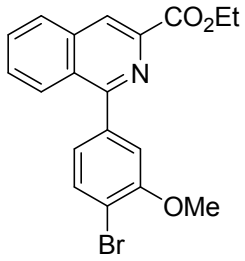
Prepared from ethyl 3-benzyl-1-(3-bromophenyl)-3,4-dihydroisoquinoline-3-carboxylate **1f** (61 mg, 0.14 mmol, 1.0 equiv) and NBS (73 mg, 0.41 mmol, 3 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **3c** as white solid (36 mg, 0.11 mmol, 79% yield). (new compound). mp: 97-99 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 1.5 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 4.53 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 159.8, 141.5, 141.2, 137.0, 133.5, 132.4, 131.3, 130.3, 130.1, 129.3, 129.0, 128.4, 127.8, 124.0, 123.0, 62.3, 14.8; HRMS (APCI) calcd for $C_{18}H_{14}BrNO_2$ $[M+H]^+$: 356.0281, Found: 356.0283.



ethyl 1-(3-(ethoxycarbonyl)phenyl)isoquinoline-3-carboxylate (3d)

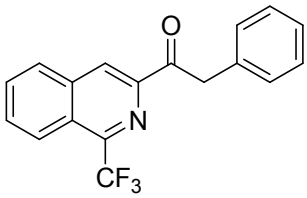
Prepared from ethyl 3-benzyl-1-(3-(ethoxycarbonyl)phenyl)-3,4-dihydroisoquinoline-3-carboxylate **1g** (52 mg, 0.12 mmol, 1.0 equiv) and NBS (64.1 mg, 0.36 mmol, 3 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **3d** as white solid (22 mg, 0.066 mmol, 55% yield). (new compound). mp: 84-86 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.39 (t, *J* = 1.5 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H),

8.05 (t, *J* = 7.5 Hz, 2H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.70-7.67 (m, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 4.53 (q, *J* = 7.0 Hz, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.39 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 166.2, 160.5, 141.6, 139.5, 137.0, 134.9, 131.6, 131.3, 131.1, 130.4, 130.1, 129.0, 128.9, 128.5, 127.9, 123.9, 62.2, 61.5, 14.8, 14.7; HRMS (APCI) calcd for $C_{21}H_{19}NO_4$ $[M+H]^+$: 350.1387, Found: 350.1386.



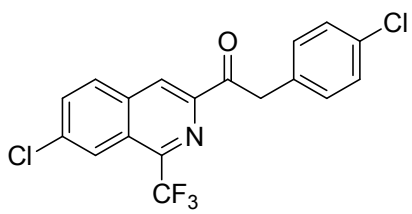
ethyl 1-(4-bromo-3-methoxyphenyl)isoquinoline-3-carboxylate (3e)

Prepared from ethyl 3-benzyl-1-(3-(ethoxycarbonyl)phenyl)-3,4-dihydroisoquinoline-3-carboxylate **1g** (14 mg, 0.03 mmol, 1.0 equiv) and NBS (16 mg, 0.09 mmol, 3 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **3e** as white solid (8 mg, 0.012 mmol, 40% yield). (new compound). mp: 114-116 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.79-7.76 (m, 1H), 7.71- 7.69 (m, 1H), 7.66-7.63 (m, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 6.94-6.91 (m, 1H), 4.57-4.50 (m, 2H), 3.81 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 160.7, 159.4, 141.6, 140.8, 136.4, 133.9, 131.3, 130.0, 129.5, 129.1, 128.8, 128.7, 128.1, 124.4, 117.1, 113.97, 62.2, 56.0, 14.9; HRMS (APCI) calcd for $C_{19}H_{16}BrNO_3$ $[M+H]^+$: 386.0386, Found: 386.0391.



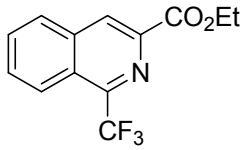
2-phenyl-1-(1-(trifluoromethyl)isoquinolin-3-yl)ethanone (5a)

Prepared from ethyl 3-benzyl-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate **4a** (28 mg, 0.078 mmol, 1.0 equiv) and NaH (32 mg, 0.78 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **4e** as white solid (16 mg, 0.051 mmol, 65% yield). (new compound). mp: 76-78 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.37 (br s, 1H), 8.10-8.08 (m, 1H), 7.86-7.83 (m, 2H), 7.44-7.42 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 4.64 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 145.1, 137.7, 134.9, 131.8, 131.4, 130.5, 130.1, 128.9, 127.2, 126.6, 125.2 (q, *J* = 2.8 Hz), 124.9, 122.3 (q, *J* = 275.5 Hz), 45.3; HRMS (APCI) calcd for $C_{18}H_{12}F_3NO$ $[M+H]^+$: 316.0944, Found: 316.0945.



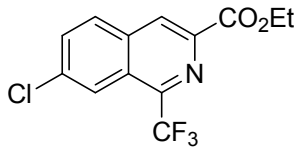
1-(7-chloro-1-(trifluoromethyl)isoquinolin-3-yl)-2-(4-chlorophenyl)ethanone (5b)

Prepared from ethyl 7-chloro-3- (4-chlorobenzyl)-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate **4b** (13 mg, 0.03 mmol, 1.0 equiv) and NaH (36 mg, 0.9 mmol, 10 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **4f** as white solid (8 mg, 0.021 mmol, 70% yield). (new compound). mp: 133-135 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.34 (s, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.81 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.29-7.27 (m, 2H), 4.58 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 145.1, 138.0, 136.8, 136.0, 133.2, 133.1, 131.8, 131.5, 129.1, 127.0, 124.6, 124.4 (q, *J* = 3.0 Hz), 122.9 (q, *J* = 257.4 Hz), 44.6; HRMS (APCI) calcd for $C_{18}H_{10}Cl_2F_3NO$ $[M+H]^+$: 384.0164, Found: 384.0166.



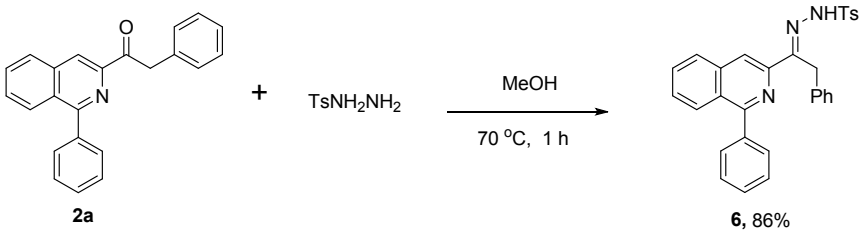
ethyl 1-(trifluoromethyl)isoquinoline-3-carboxylate (5c)

Prepared from ethyl 3-benzyl-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate **4a** (15 mg, 0.042 mmol, 1.0 equiv) and NBS (23 mg, 0.13 mmol, 3 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **4g** as white solid (7 mg, 0.024 mmol, 57% yield). (new compound). mp: 64-66 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.39 (d, *J* = 7.5 Hz, 1H), 8.10 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.91-7.85 (m, 2H), 4.55 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 140.0, 137.1, 131.7, 131.0, 129.0, 127.4, 125.9, 125.0 (q, *J* = 2.8 Hz), 121.8 (q, *J* = 275.1 Hz), 62.2, 14.4; HRMS (APCI) calcd for $C_{13}H_{10}F_3NO_2$ $[M+H]^+$: 270.0736, Found: 270.0737.



ethyl 6-chloro-1-(trifluoromethyl)isoquinoline-3-carboxylate (5d)

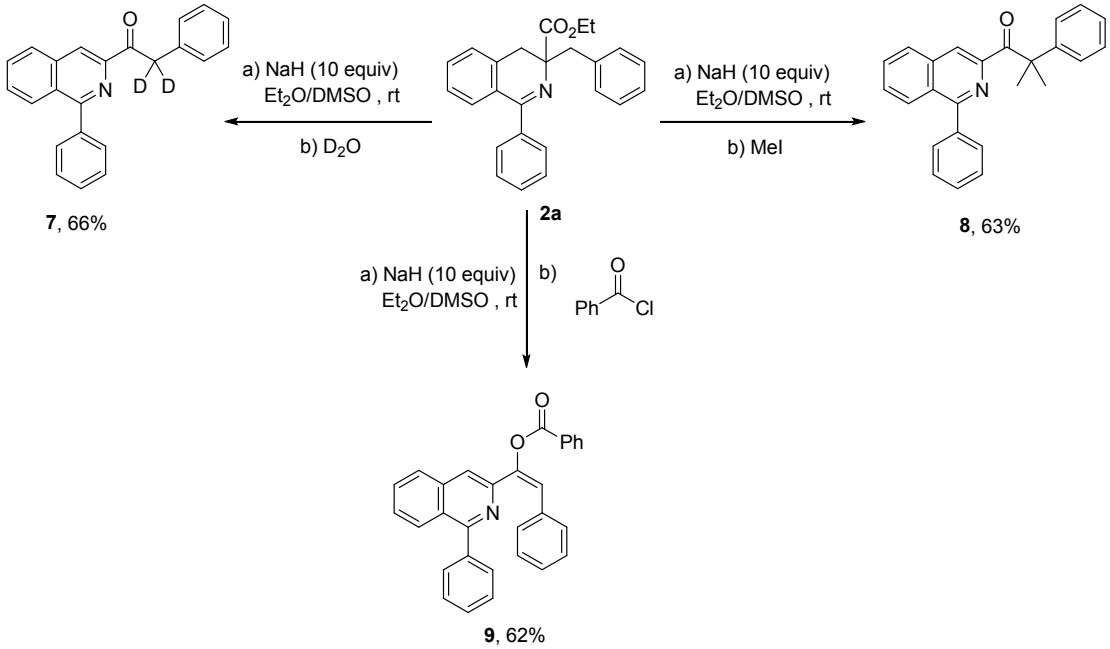
Prepared from ethyl 7-chloro-3- (4-chlorobenzyl)-1-(trifluoromethyl)-3,4-dihydroisoquinoline-3-carboxylate **4b** (19 mg, 0.044 mmol, 1.0 equiv) and NBS (23.7 mg, 0.13 mmol, 3 equiv) according to the general procedure. Column chromatography purification (Petroleum ether : EtOAc 15 : 1) furnished the product **4h** as white solid (9 mg, 0.029 mmol, 65% yield). (new compound). mp: 90-92 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.35 (s, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.83 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.54 (q, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 140.8, 137.7, 135.9, 133.3, 130.8, 127.3, 126.7, 124.6 (q, *J* = 3.0 Hz), 121.9 (q, *J* = 272.5 Hz), 62.7, 14.7; HRMS (APCI) calcd for $C_{13}H_9ClF_3NO_2$ $[M+H]^+$: 304.0347, Found: 304.0348.



4-methyl-N'-(2-phenyl-1-(1-phenylisoquinolin-3-yl)ethylidene)benzenesulfonohydrazide (6)

A mixture of **2a** (0.3 mmol) and tosylhydrazide (0.3 mmol) in MeOH (0.5 mL) were heated at 70 ^{o}C for 1 h to obtain the corresponding *N*-tosylhydrazone as white precipitate. The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the corresponding products.

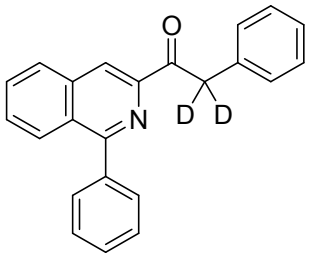
White solid (130 mg, 86% yield). mp: 137-139 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 0.25H), 8.17 (d, *J* = 8.5 Hz, 1.1H), 8.11 (d, *J* = 8.5 Hz, 0.29H), 7.98 (d, *J* = 8.5 Hz, 0.33H), 7.84-7.82 (m, 3.18H), 7.78 (s, 1.15H), 7.74-7.55 (m, 9.02H), 7.52-7.49 (m, 0.74H), 7.31-7.21 (m, 3.34H), 7.21-7.06 (m, 6.36H), 4.48 (s, 0.49H), 4.13 (s, 2.06H), 2.41 (s, 3H), 2.38 (s, 0.7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 159.4, 145.3, 145.1, 144.4, 143.6, 138.3, 137.9, 137.5, 137.2, 135.7, 135.4, 131.5, 131.1, 130.5, 130.2, 130.1, 129.9, 129.9, 129.6, 129.5, 129.3, 128.9, 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.4, 127.0, 126.9, 126.4, 121.5, 118.1, 42.1, 32.4, 22.0; HRMS (APCI) calcd for $C_{30}H_{25}N_3O_2S$ $[M+H]^+$: 492.1740, Found: 492.1746.



Synthesis of Compounds 7-9

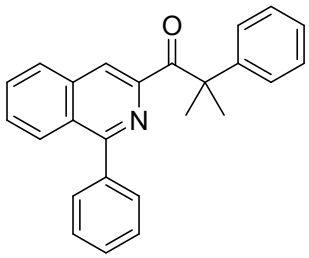
a) An oven-dried 25 mL Schlenk tube charged with NaH (1 mmol, 40 mg) and ethyl 3-benzyl-1-phenyl-3,4-dihydroisoquinoline-3-carboxylate **(1a)** (0.1 mmol, 36.9 mg) was vacuumed and refilled with Ar for 3 times. Then a solution of Et_2O (0.9 mL) and DMSO (0.1 mL) was added in room temperature for 40 min.

b) D_2O (2 equiv)/MeI (2 equiv)/ benzoyl chloride (2 equiv) was added dropwise with a syringe to the reaction mixture when the reaction was completed. The crude reaction mixture was quenched with saturated NH_4Cl. The crude reaction mixture was extracted with EtOAc (20 mL × 3) and washed with brine (20 mL). The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the corresponding products **7**, **8**, and **9**.



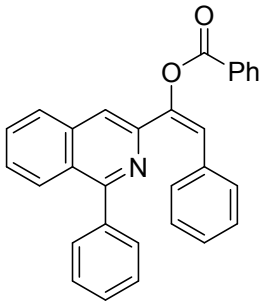
D_2-2-phenyl-1-(1-phenylisoquinolin-3-yl)ethanone (7)

White solid (29 mg, 65% yield). mp: 120-122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.80-7.78 (m, 2H), 7.76-7.73 (m, 1H), 7.67-7.56 (m, 4H), 7.42-7.40 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 1H), 4.65 (s, 0.18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.3, 160.3, 146.6, 139.6, 137.2, 135.6, 130.9, 130.6, 130.4, 129.8, 129.6, 129.4, 128.8, 128.8, 128.7, 128.0, 127.0, 120.6, 44.9 (q, *J* = 19.3 Hz); HRMS (APCI) calcd for $C_{24}H_{17}D_2N_2O_2$ $[M+H]^+$: 342.1430, Found: 342.1439.



2-methyl-2-phenyl-1-(1-phenylisoquinolin-3-yl)propan-1-one (8)

White solid (30 mg, 66% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46-7.41 (m, 3H), 7.29-7.17 (m, 7H), 1.78 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 157.2, 145.6, 144.9, 137.6, 135.8, 129.3, 129.1, 128.1, 128.0, 127.5, 127.1, 126.9, 126.3, 126.2, 125.1, 124.6, 120.7, 50.4, 26.4. HRMS (ESI) calcd for $C_{25}H_{21}NO$ $[M+H]^+$: 352.1696, Found: 352.1698.



2-phenyl-1-(1-phenylisoquinolin-3-yl)vinyl benzoate (9)

White solid (53 mg, 62% yield). mp: 155-157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36-8.35 (m, 2H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.93 (s, 1H), 7.81-7.78 (m, 3H), 7.75-7.72 (m, 1H), 7.69-7.84 (m, 4H), 7.62-7.49 (m, 6H), 7.30-7.21 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 160.9, 145.6, 145.3, 137.9, 134.6, 134.3, 130.9, 130.7, 129.7, 129.3, 128.0, 129.68, 128.3, 128.2, 128.1, 127.8, 126.7, 120.0, 115.0, 105.4; HRMS (APCI) calcd for $C_{30}H_{21}NO_2$ $[M+H]^+$: 428.1645, Found: 428.1647.

VII. References

(1) Wang, J.; Gao, D,; Huang, J.; Tang, S.; Xiong, Z.; Hu, H.; You, S.; Zhu, Q. Palladium-Catalyzed Enantioselective C(sp2)−H Imidoylation byDesymmetrization. *ACS Catal.*, **2017**, *7 (6)*, pp 3832–3836.

(2) Tang, S.; Yang, S.; Sun, H.; Zhou, Y.; Li, J. and Zhu, Q. Pd-Catalyzed Divergent C(sp^2)−H Activation/Cycloimidoylation of 2-Isocyano-2,3-diarylpropanoates. *Org. Lett*. **2018**, *20*, 1832−1836

VIII. Copies of ^{1}H and ^{13}C NMR Spectra

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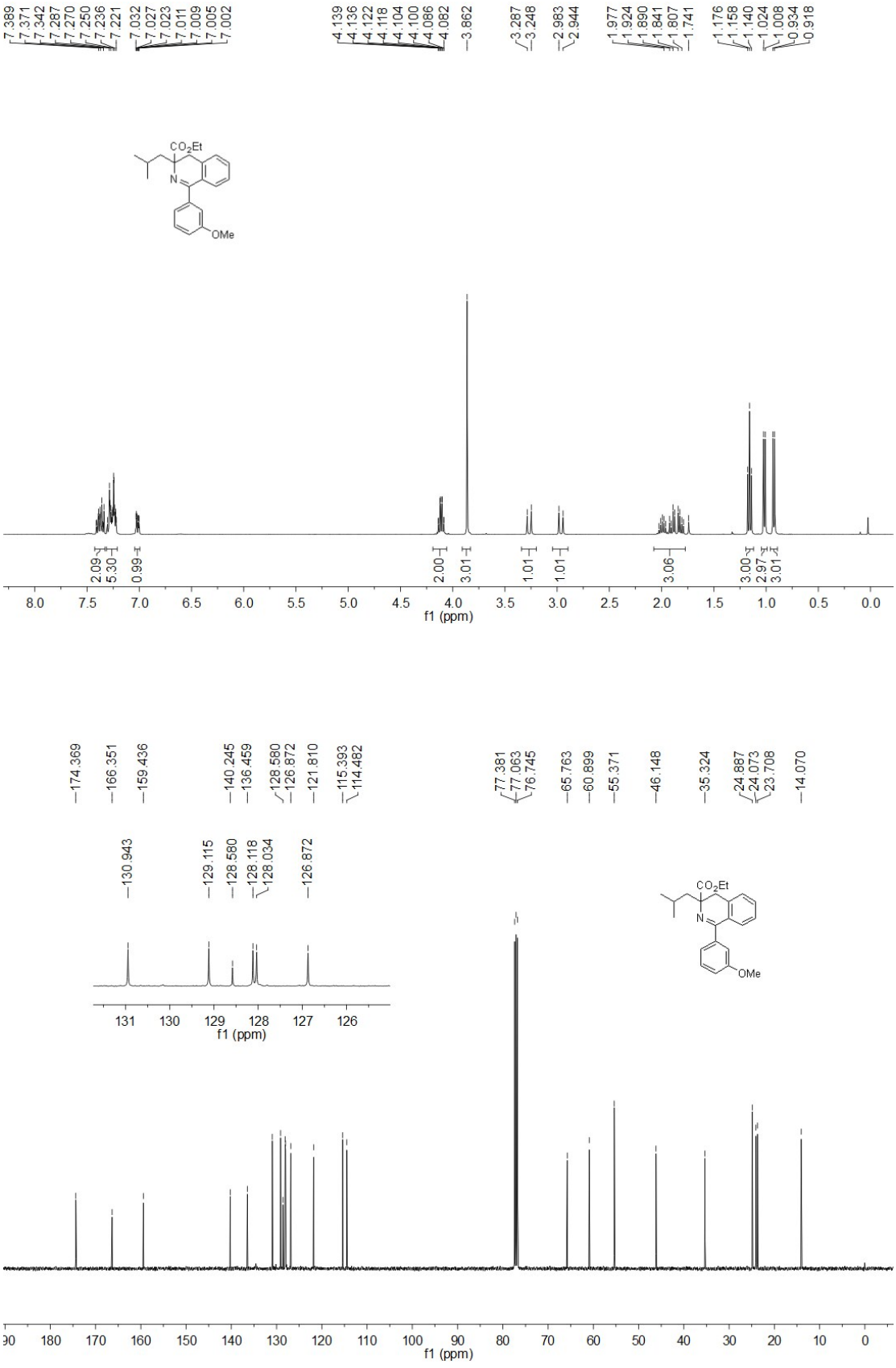

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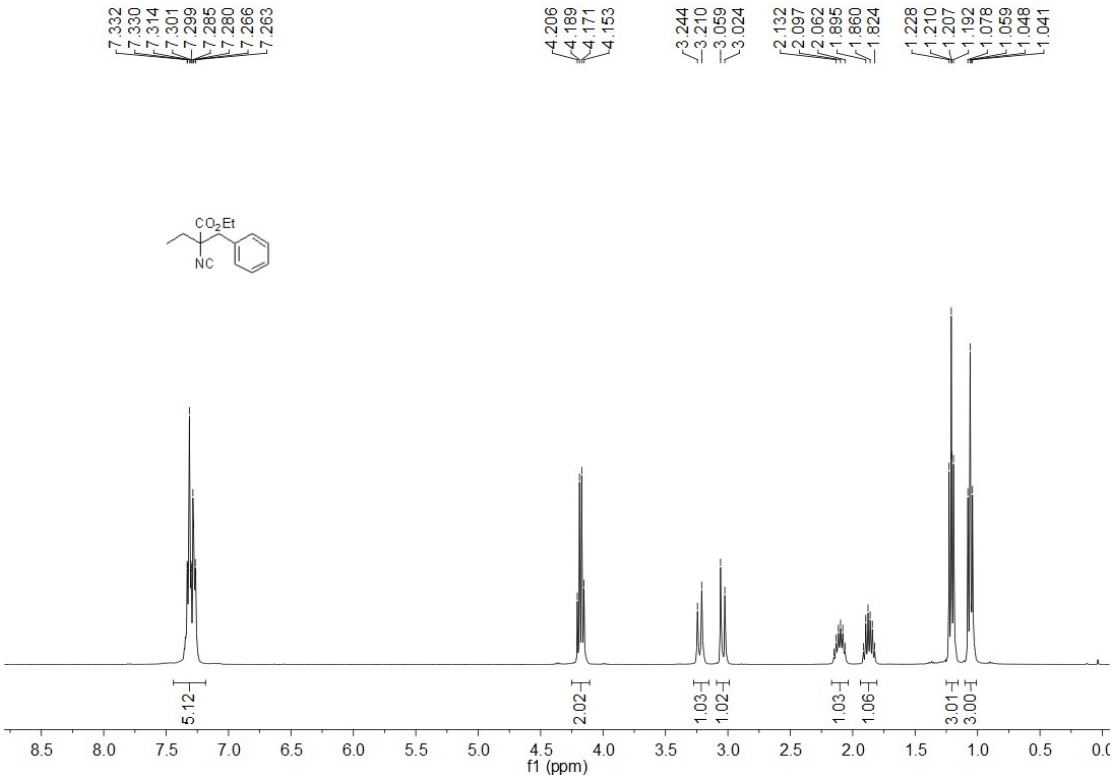
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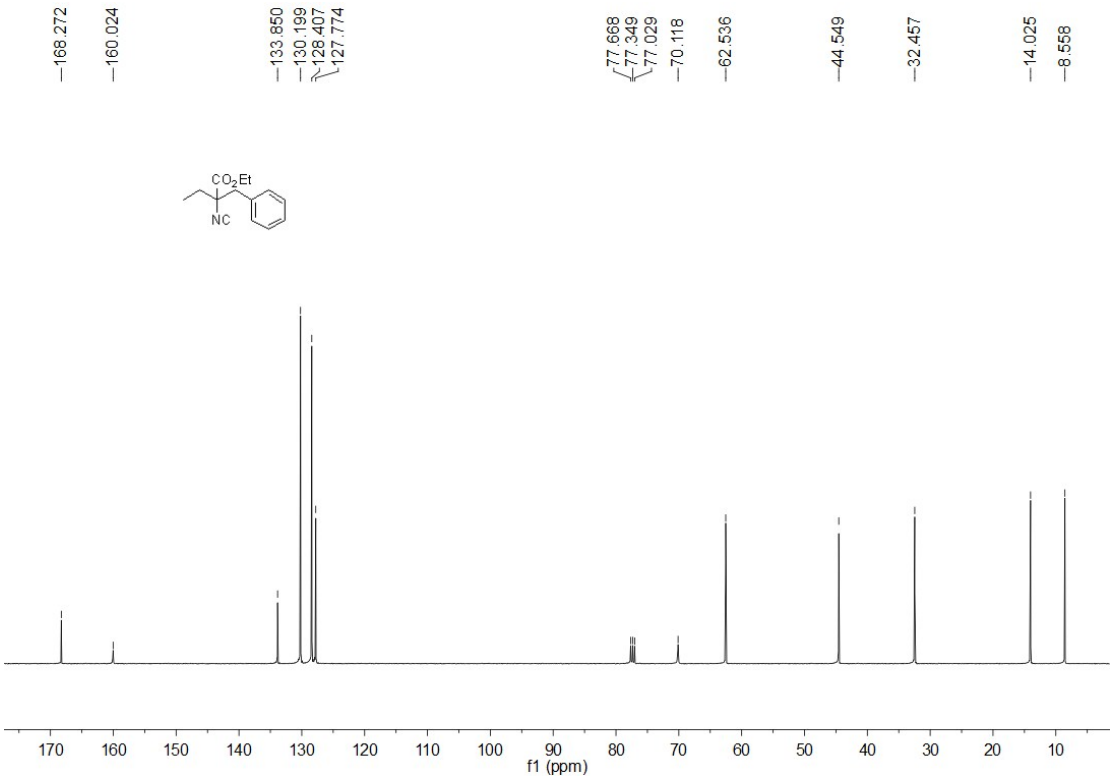
3.00
f1 (ppm)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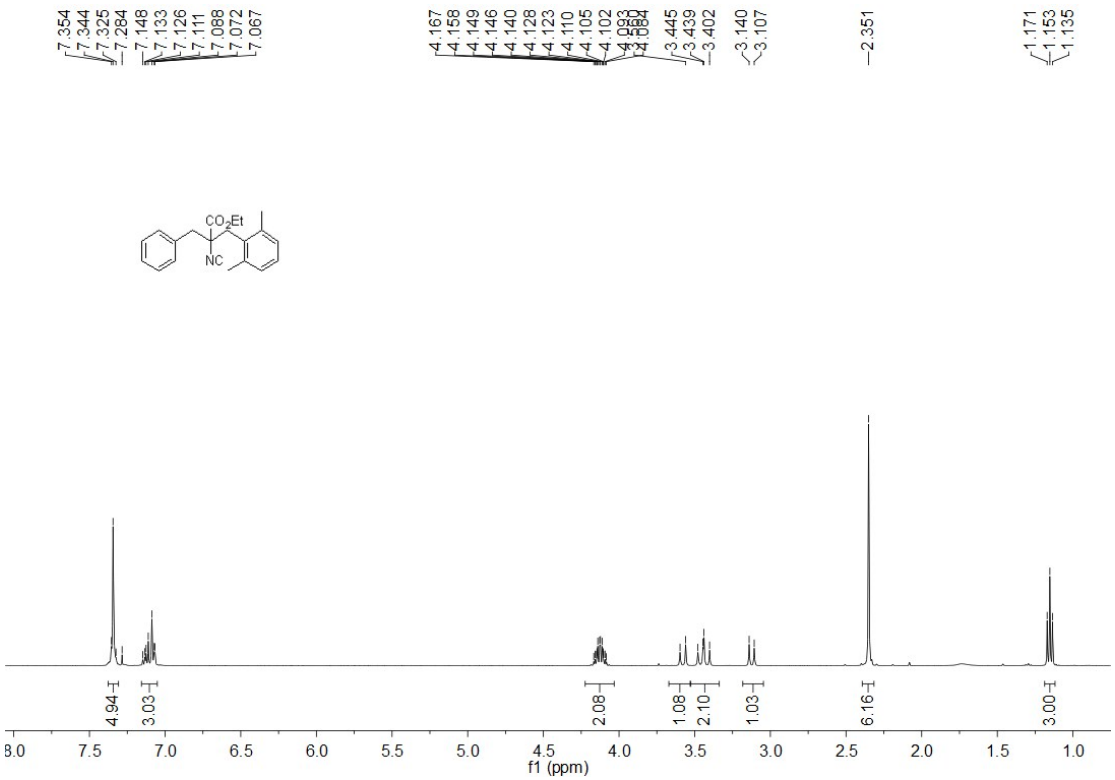
f1 (ppm)

C3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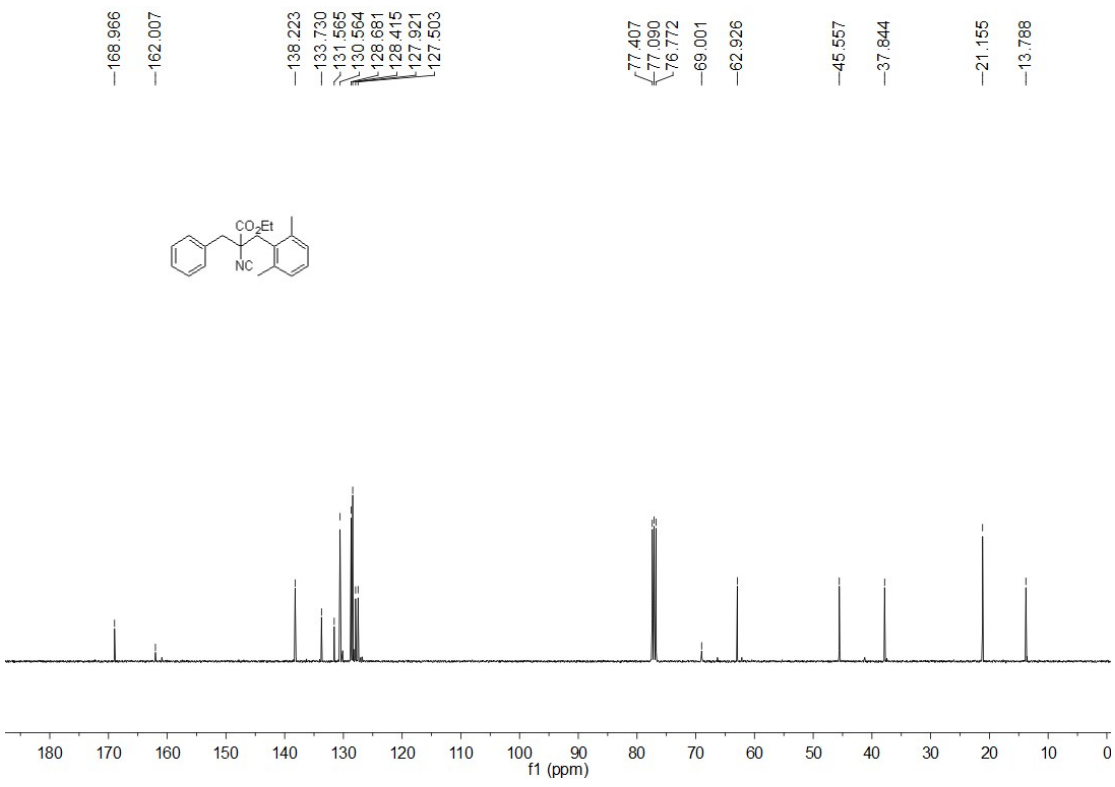
f1 (ppm)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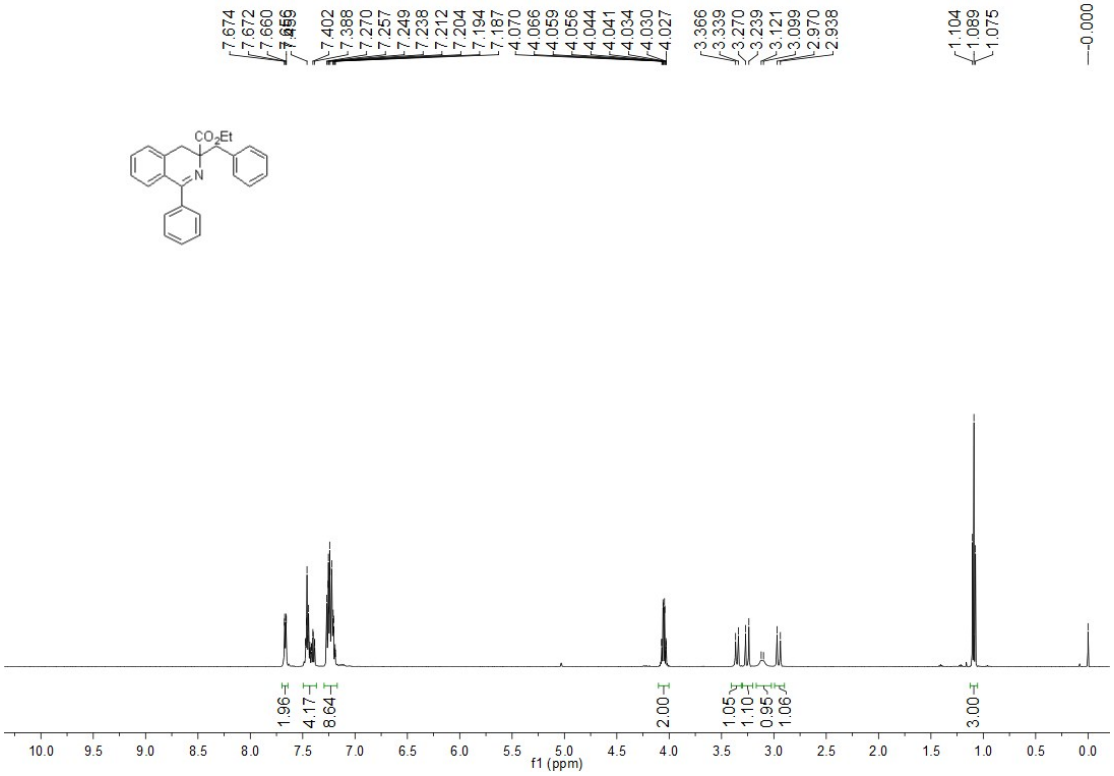
f1 (ppm)

1a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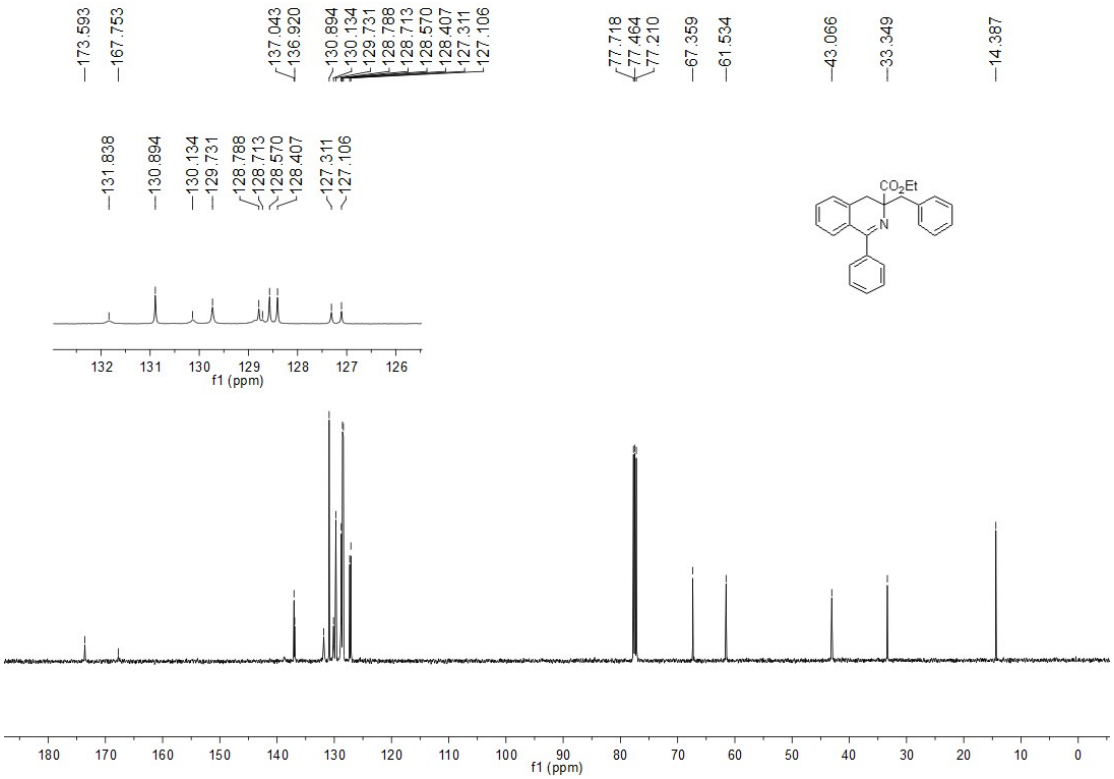
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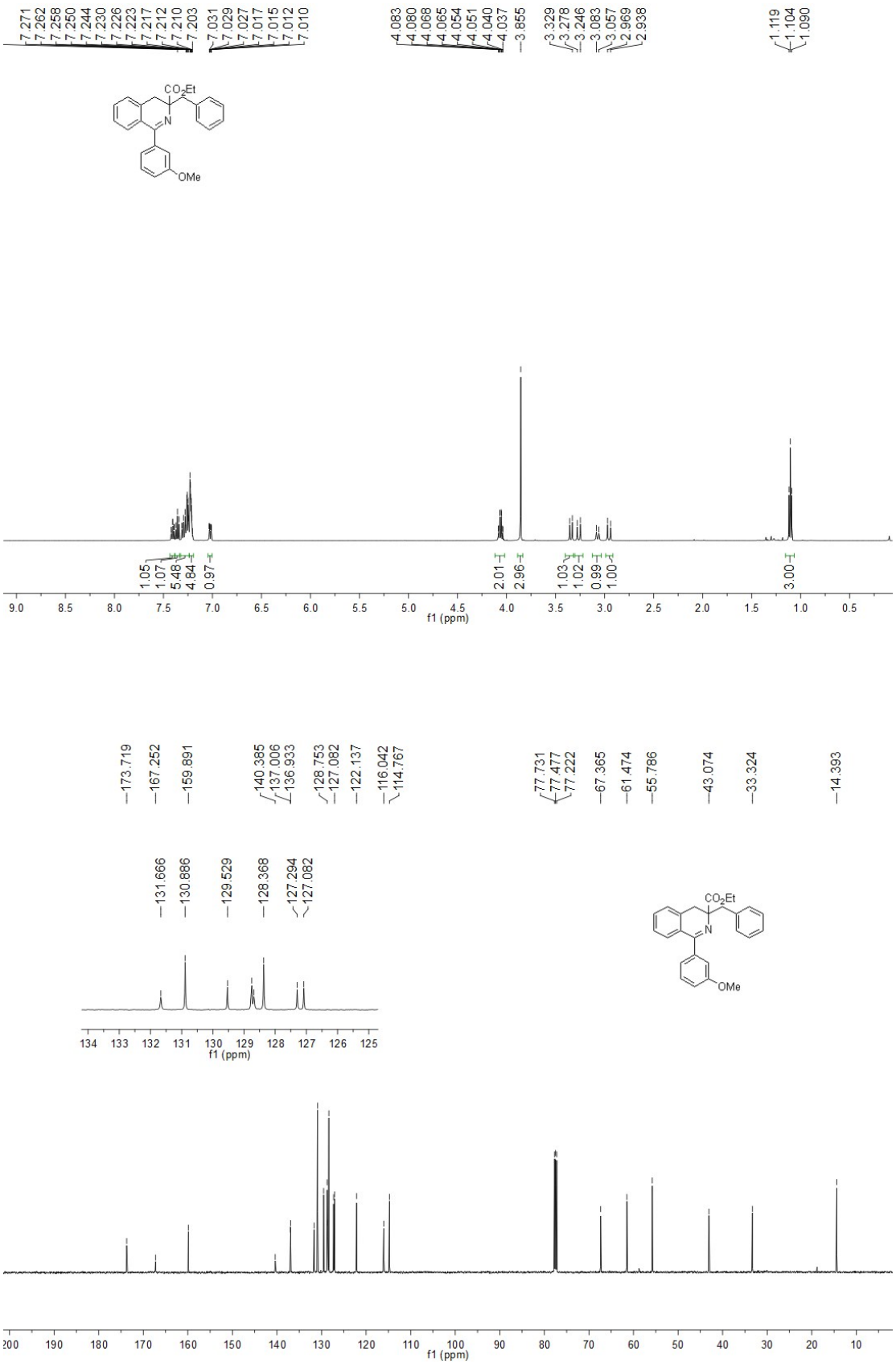
1b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f1 (ppm)

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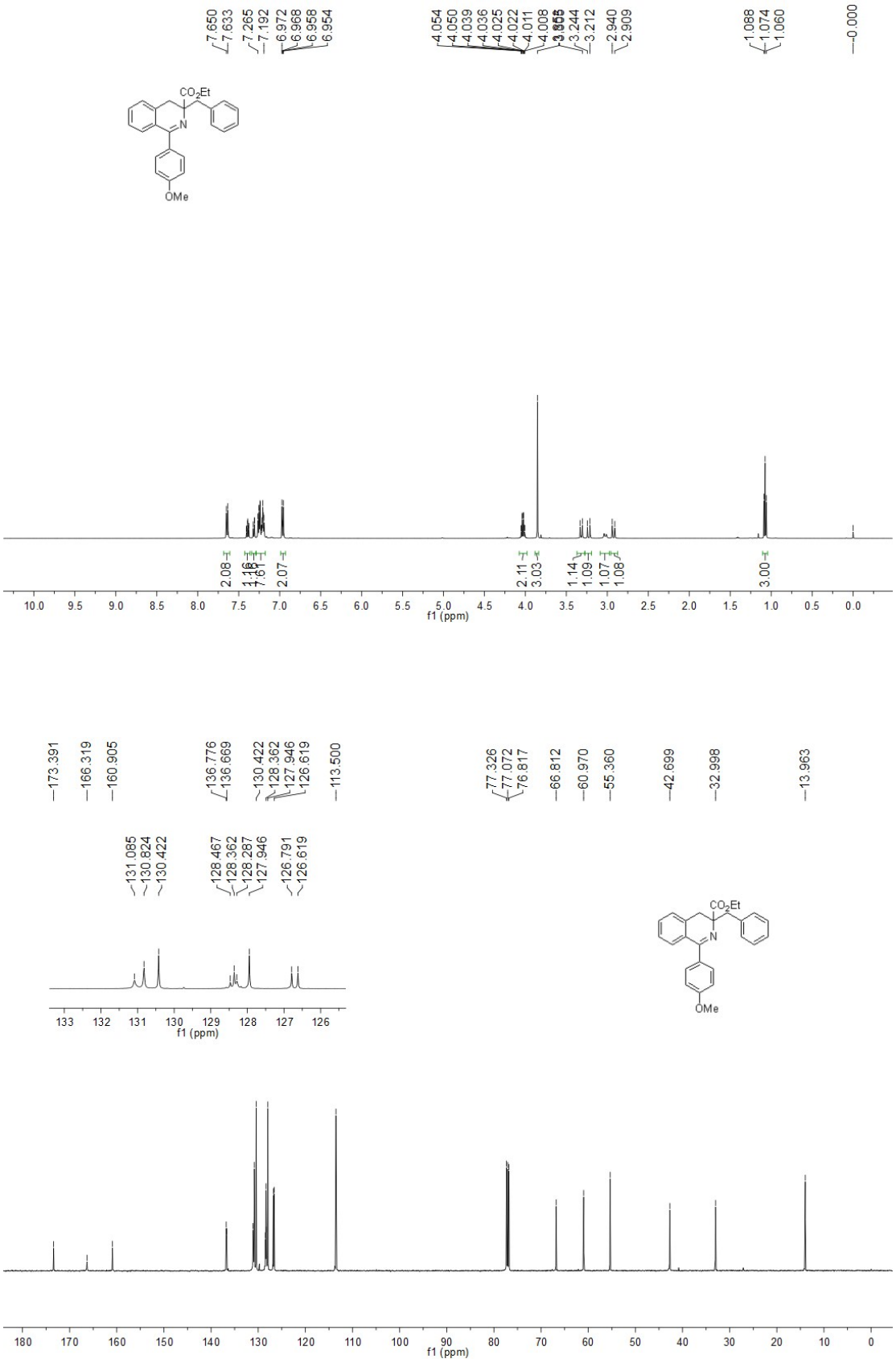
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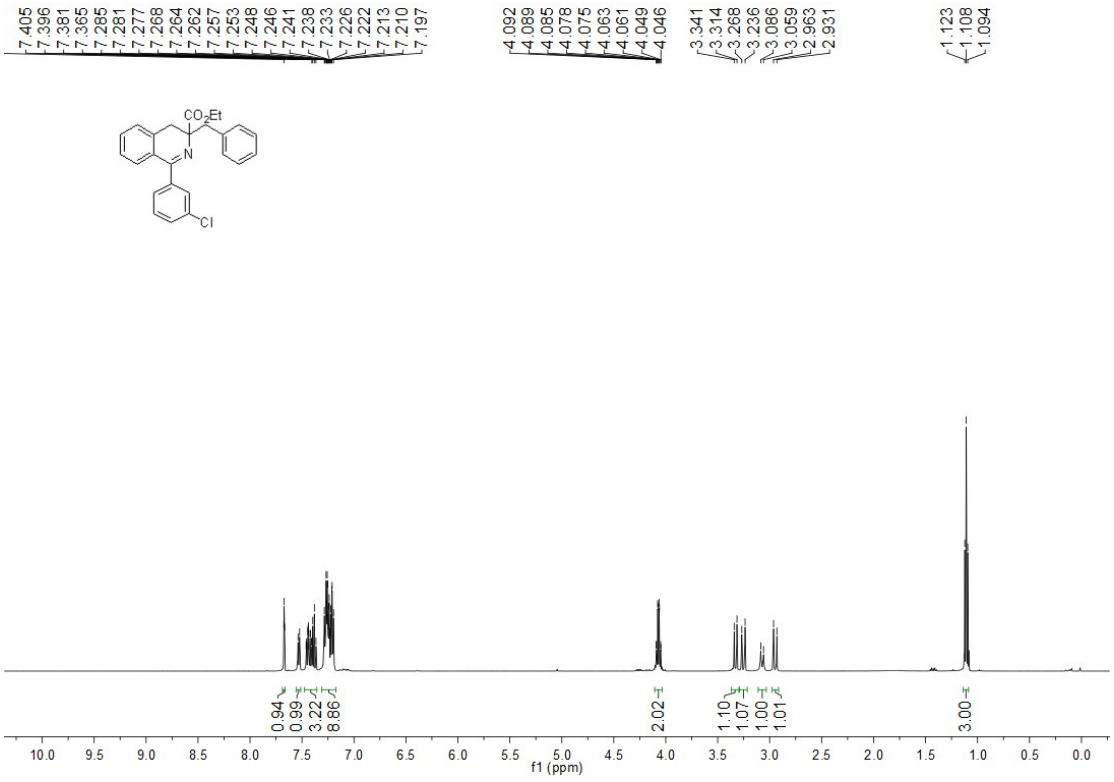
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CO2Et
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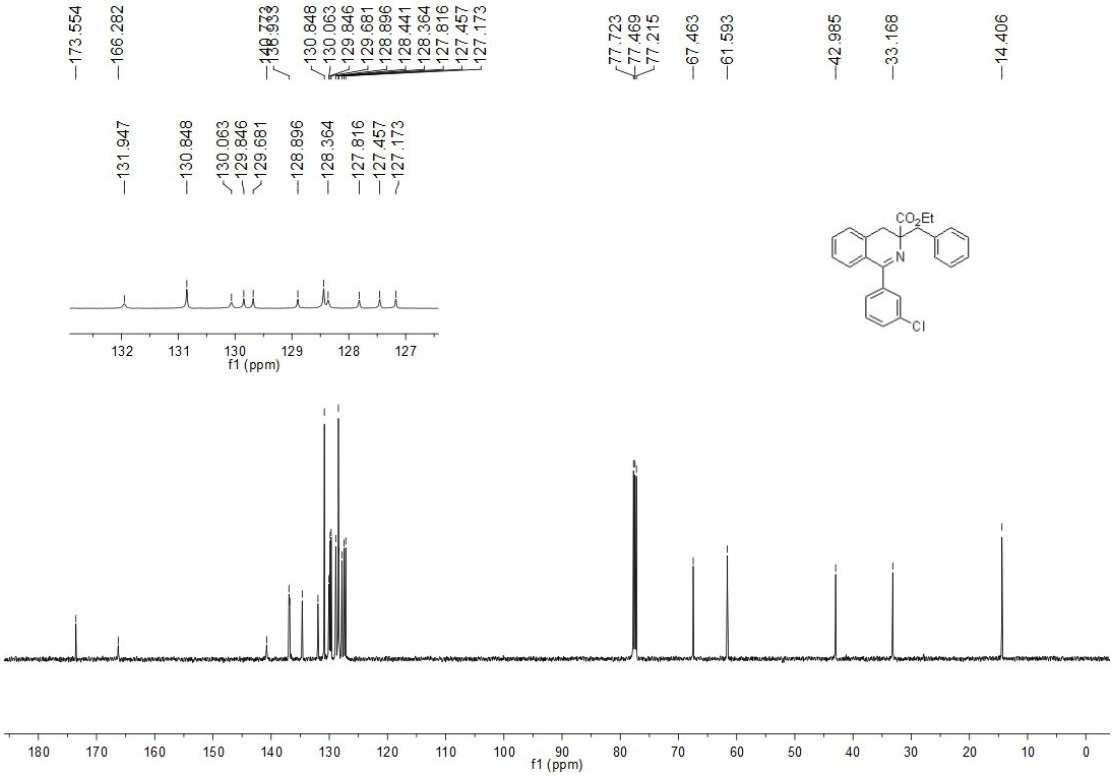
f1 (ppm)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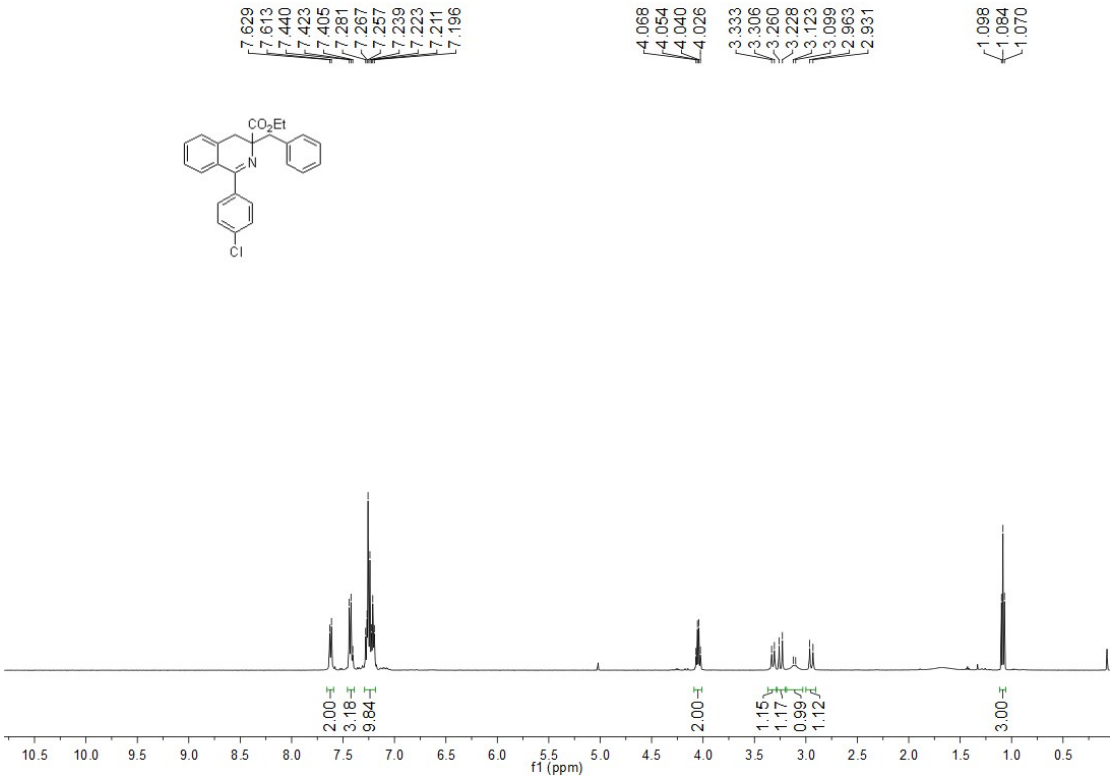
Cl
f1 (ppm)

1e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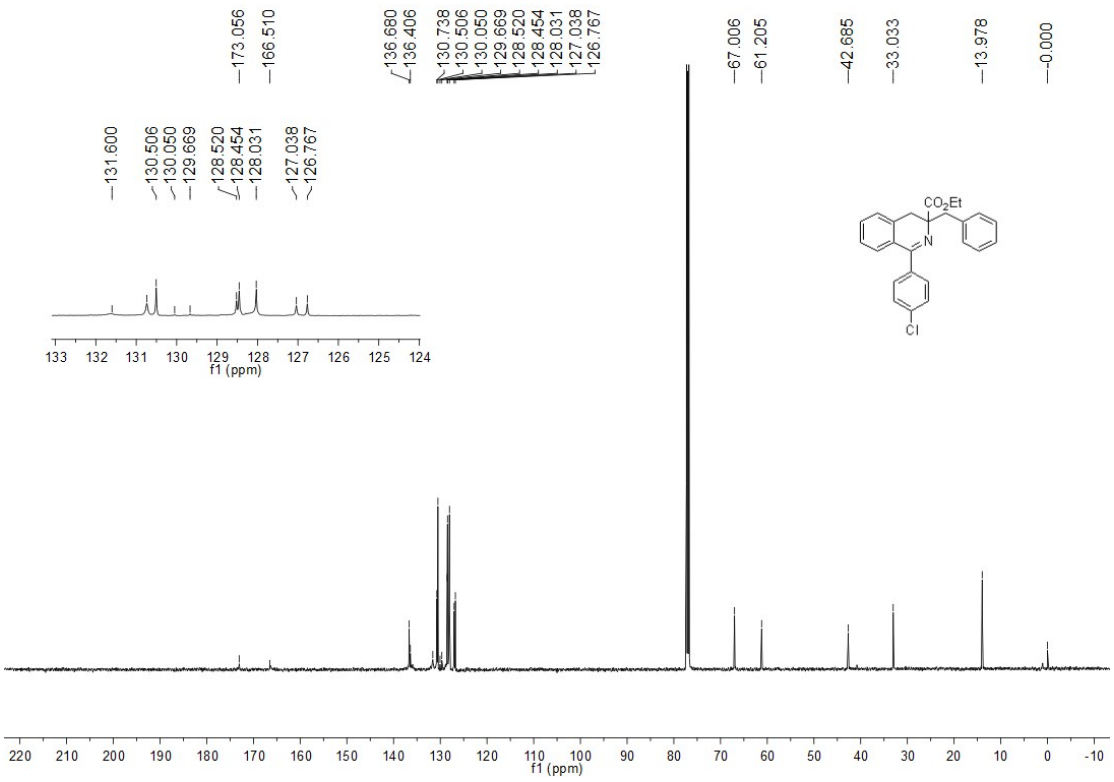
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CO2Et
N
Cl
f1 (ppm)

1f


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1.98
1.00
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0.99
1.04
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f1 (ppm)
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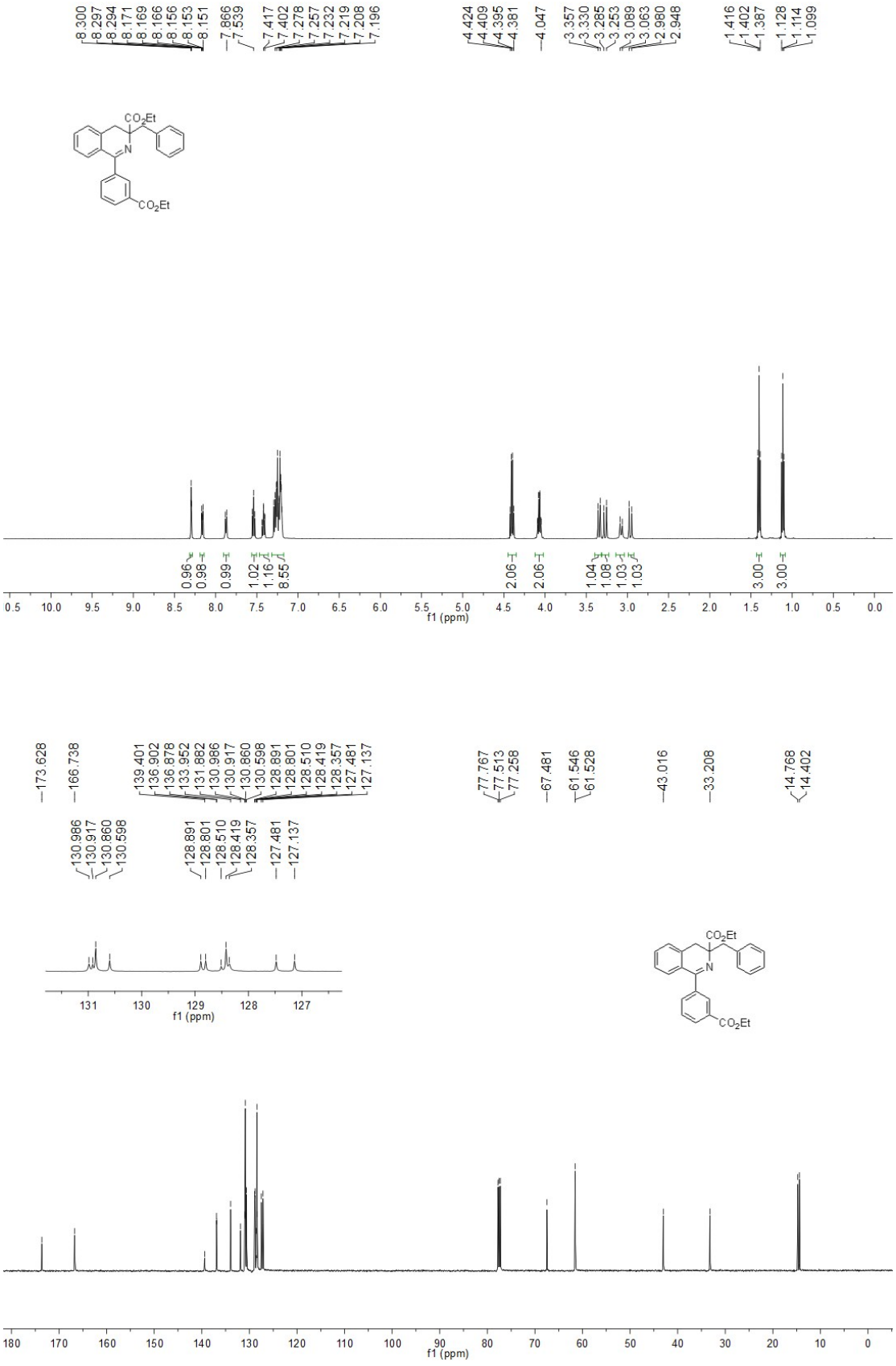
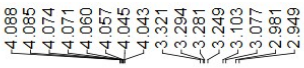
f1 (ppm)
f1 (ppm)

1g

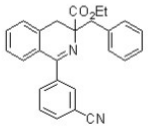

8.300
8.297
8.294
8.171
8.169
8.166
8.156
8.153
8.151
7.866
7.539
7.417
7.402
7.278
7.257
7.232
7.219
7.208
7.196
4.424
4.409
4.395
4.381
4.047
3.357
3.330
3.285
3.253
3.089
3.063
2.980
2.948
1.416
1.402
1.387
1.128
1.114
1.099
CO2Et
N
CO2Et
0.96
0.98
0.99
1.02
1.16
8.55
2.06
2.06
1.04
1.08
1.03
1.03
3.00
3.00
f1 (ppm)
173.628
166.738
139.401
136.902
136.878
133.952
131.882
130.986
130.917
130.860
130.598
128.891
128.801
128.510
128.419
128.357
127.481
127.137
77.767
77.513
77.258
67.481
61.546
61.528
43.016
33.208
14.768
14.402
f1 (ppm)

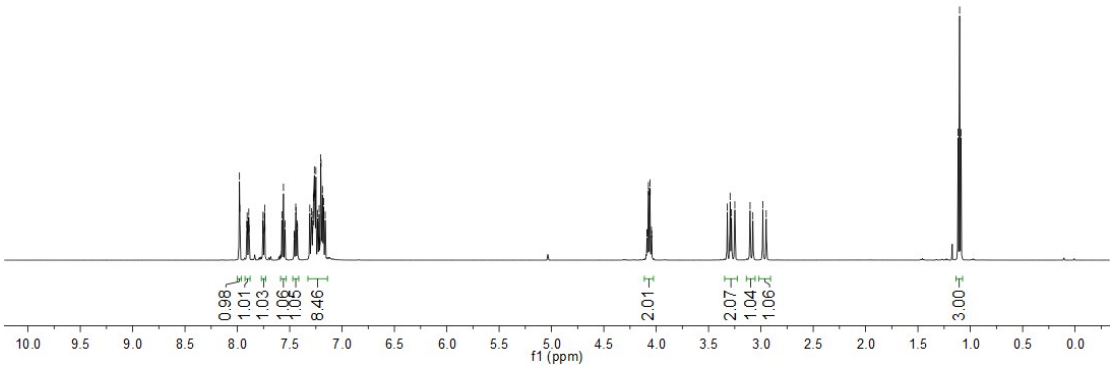
1h

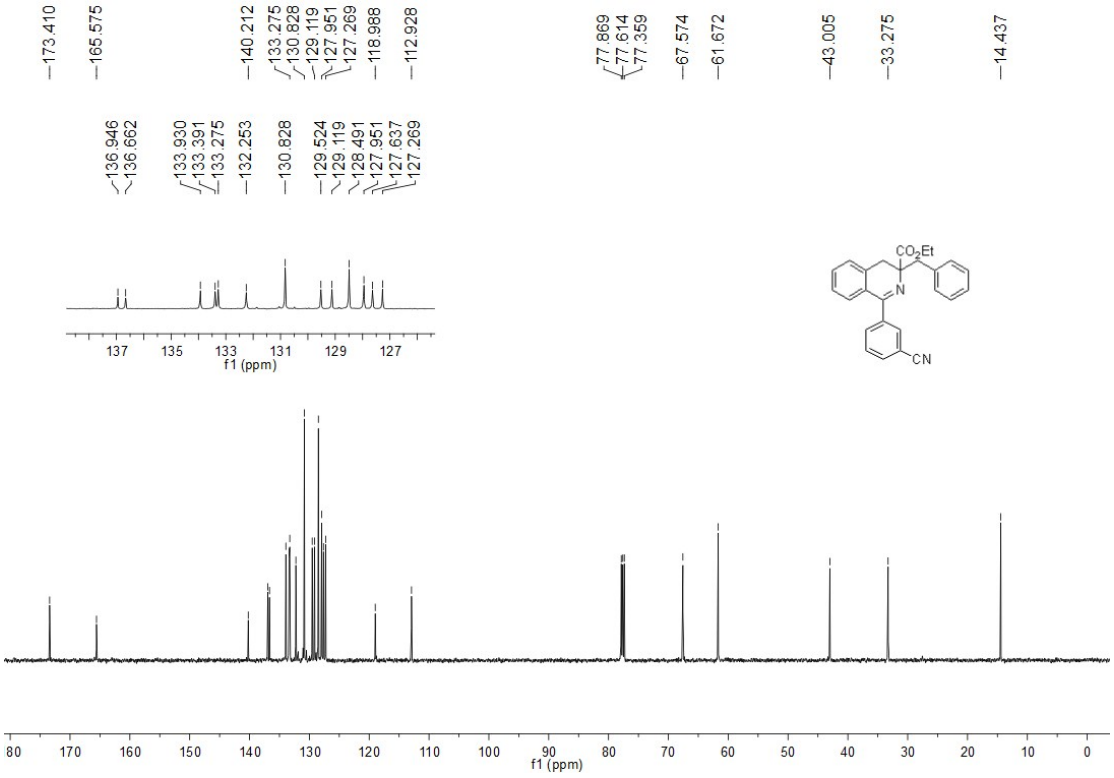

7.440
7.427
7.425
7.308
7.293
7.281
7.278
7.274
7.265
7.261
7.257
7.250
7.233
7.230
7.223
7.219
7.212
7.203
7.200
7.187
7.176
7.161


4.088
4.085
4.074
4.071
4.060
4.057
4.045
4.043
3.321
3.294
3.281
3.249
3.103
3.077
2.981
2.949

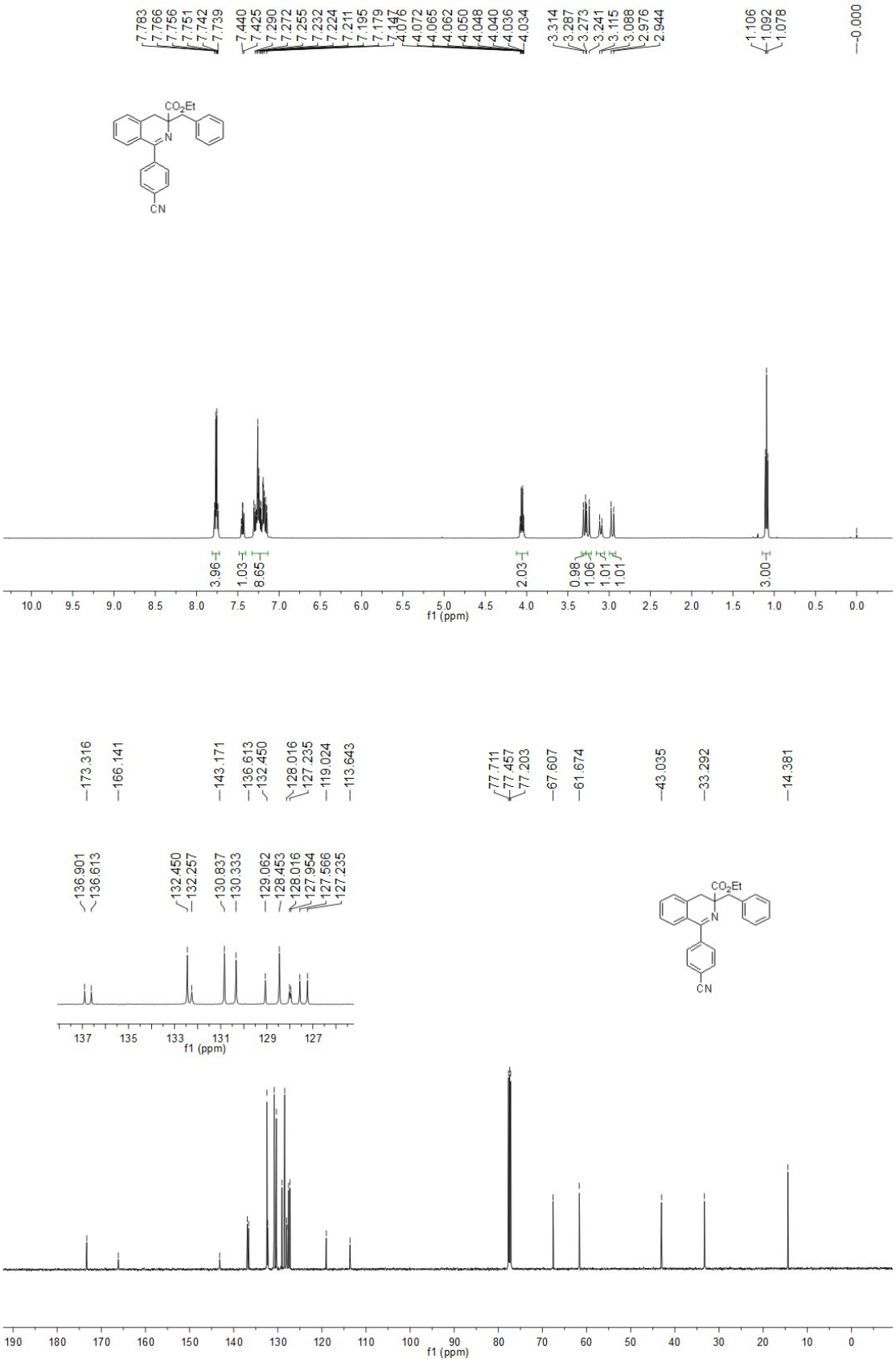

1.117
1.102
1.088


CO2Et
N
CN


0.98
1.01
1.03
1.06
1.05
8.46
2.01
2.07
1.04
1.06
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.410
165.575
140.212
133.275
130.828
129.119
127.951
127.269
118.988
112.928
77.869
77.614
77.359
67.574
61.672
43.005
33.275
14.437
136.946
136.662
133.930
133.391
133.275
132.253
130.828
129.524
129.119
128.491
127.951
127.637
127.269
CO2Et
N
CN
137 135 133 131 129 127
f1 (ppm)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1i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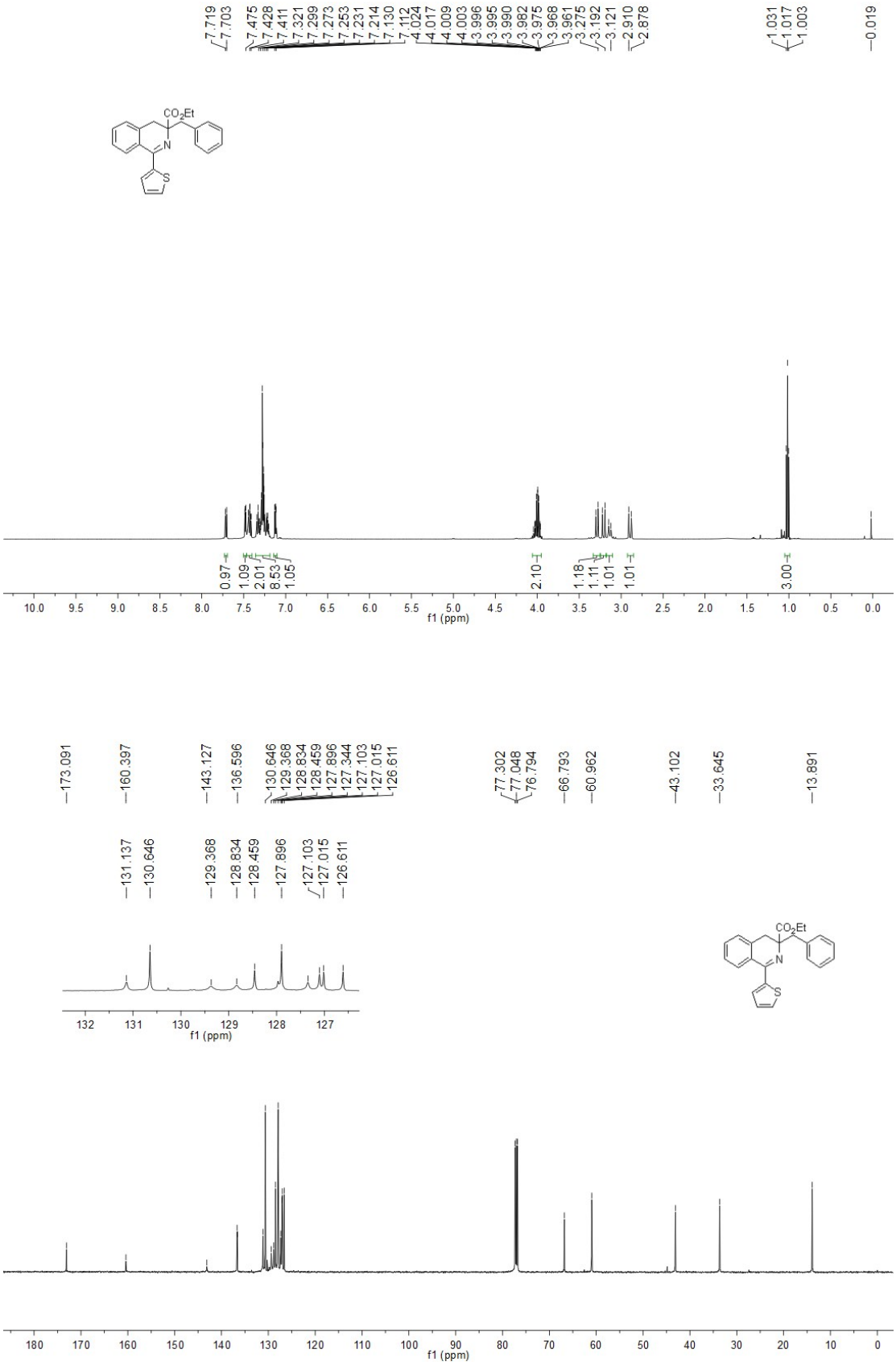
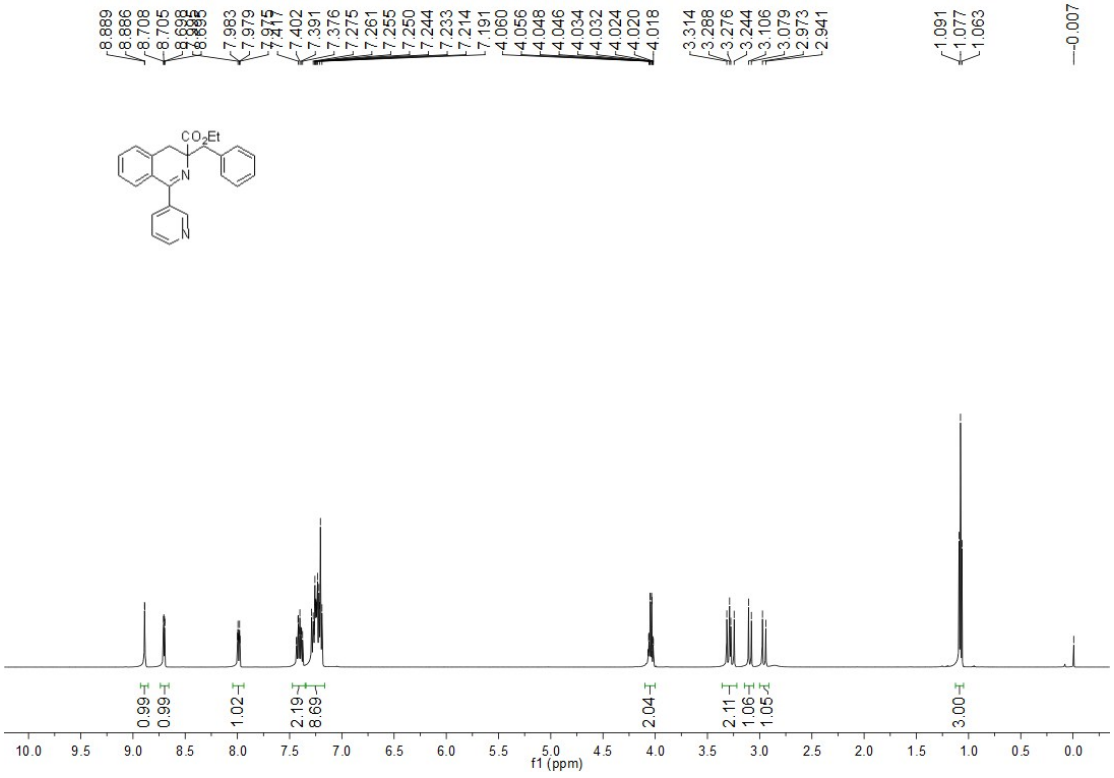
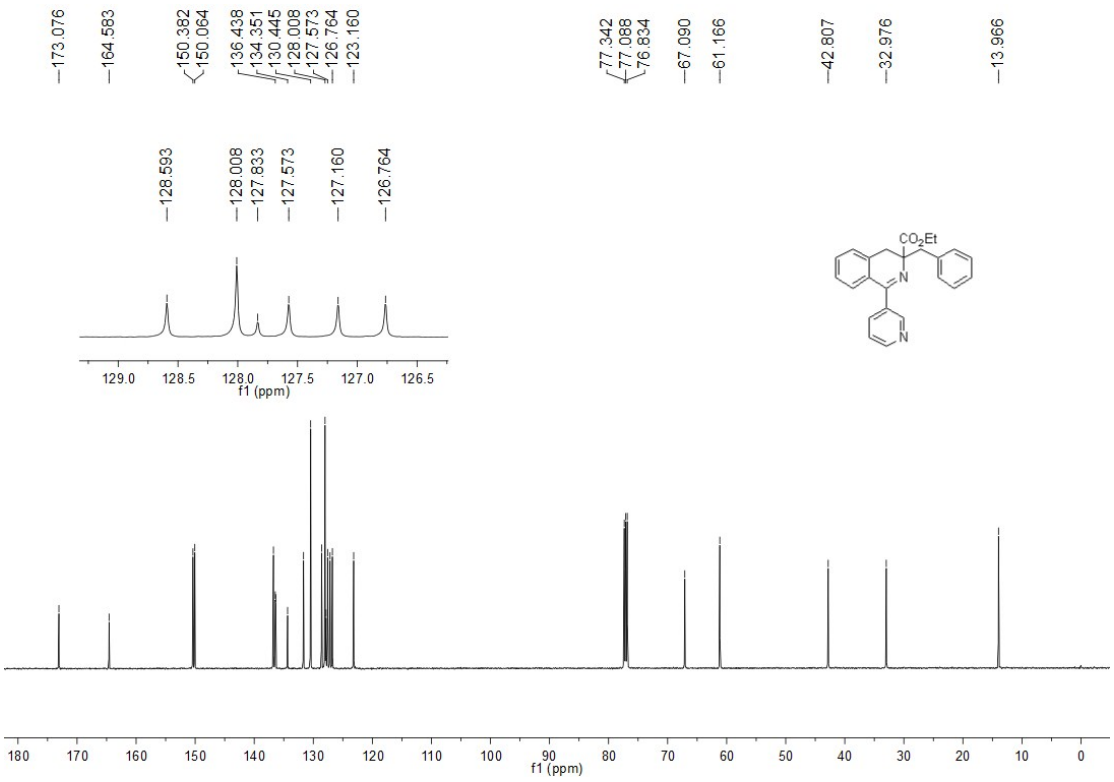
7.766
7.756
7.751
7.742
7.739
7.440
7.425
7.290
7.272
7.255
7.232
7.224
7.211
7.195
7.179
7.147
7.076
4.072
4.065
4.062
4.050
4.048
4.040
4.036
4.034
3.314
3.287
3.273
3.241
3.115
3.088
2.976
2.944
1.106
1.092
1.078
0.000
CO2Et
N
CN
3.96
1.03
8.65
2.03
0.98
1.06
1.01
1.01
3.00
f1 (ppm)
173.316
166.141
143.171
136.613
132.450
128.016
127.235
119.024
113.643
77.711
77.457
77.203
67.607
61.674
43.035
33.292
14.381
136.901
136.613
132.450
132.257
130.837
130.333
129.062
128.453
128.016
127.954
127.566
127.235
f1 (ppm)
f1 (ppm)

1j

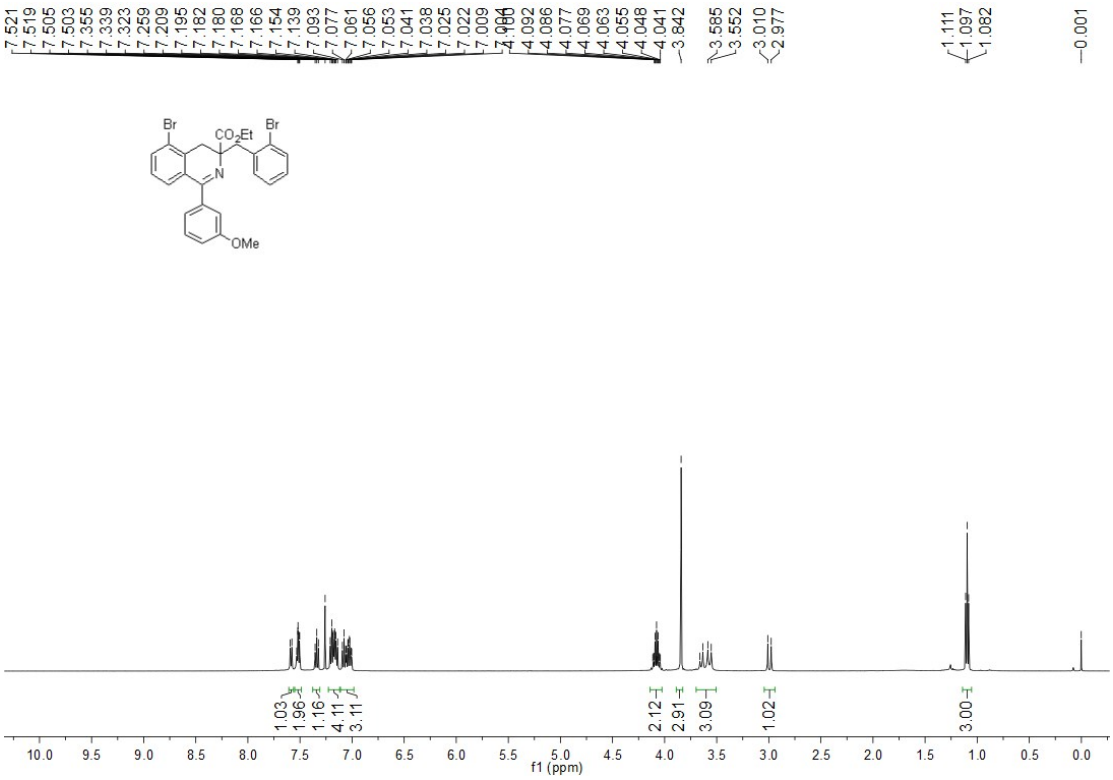

7.719
7.703
7.475
7.428
7.411
7.321
7.299
7.273
7.253
7.231
7.214
7.130
7.112
4.024
4.017
4.009
4.003
3.996
3.995
3.990
3.982
3.975
3.968
3.961
3.275
3.192
3.121
2.910
2.878
1.031
1.017
1.003
0.019
CO2Et
N
S
0.97
1.09
2.01
8.53
1.05
2.10
1.18
1.11
1.01
1.01
3.00
f1 (ppm)
173.091
160.397
143.127
136.596
130.646
129.368
128.834
128.459
127.896
127.344
127.103
127.015
126.611
77.302
77.048
76.794
66.793
60.962
43.102
33.645
13.891
131.137
130.646
129.368
128.834
128.459
127.896
127.103
127.015
126.611
f1 (ppm)
f1 (ppm)

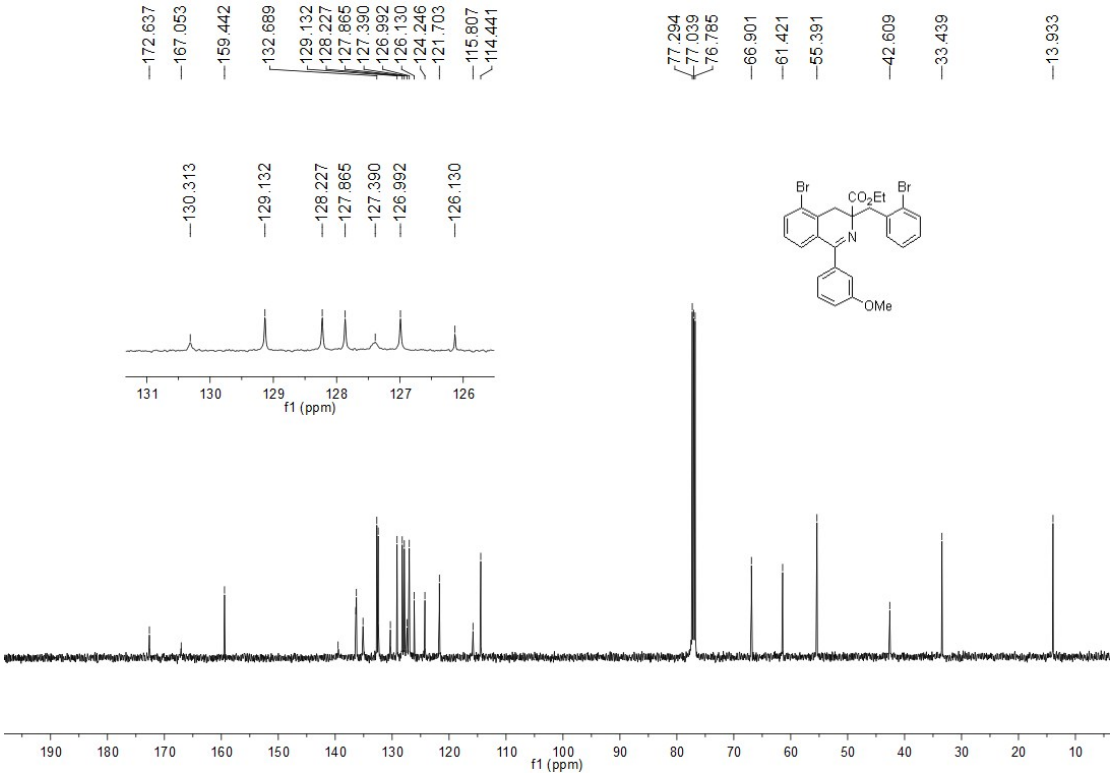
1k


8.889
8.886
8.708
8.705
7.983
7.979
7.402
7.391
7.376
7.275
7.261
7.255
7.250
7.244
7.233
7.214
7.191
4.060
4.056
4.048
4.046
4.034
4.032
4.024
4.020
4.018
3.314
3.288
3.276
3.244
3.106
3.079
2.973
2.941
1.091
1.077
1.063
-0.007
CO2Et
N
N
0.99
0.99
1.02
2.19
8.69
2.04
2.11
1.06
1.05
3.00
f1 (ppm)

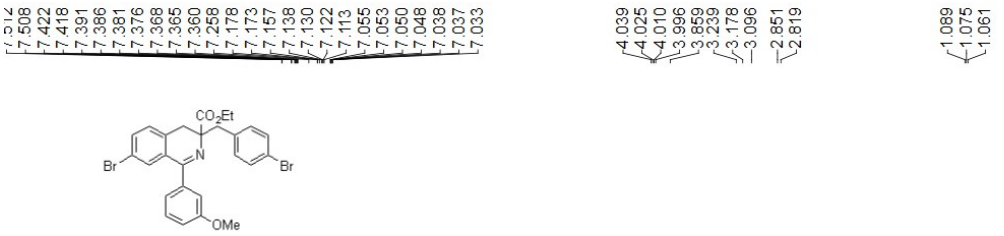

173.076
164.583
150.382
150.064
136.438
134.351
130.445
128.008
127.573
126.764
123.160
77.342
77.088
76.834
67.090
61.166
42.807
32.976
13.966
128.593
128.008
127.833
127.573
127.160
126.764
CO2Et
N
N
f1 (ppm)
f1 (ppm)

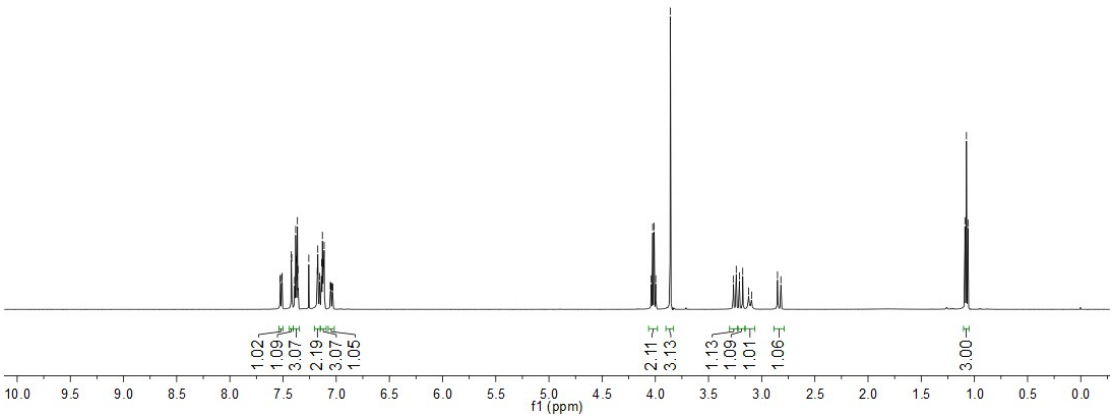
1l

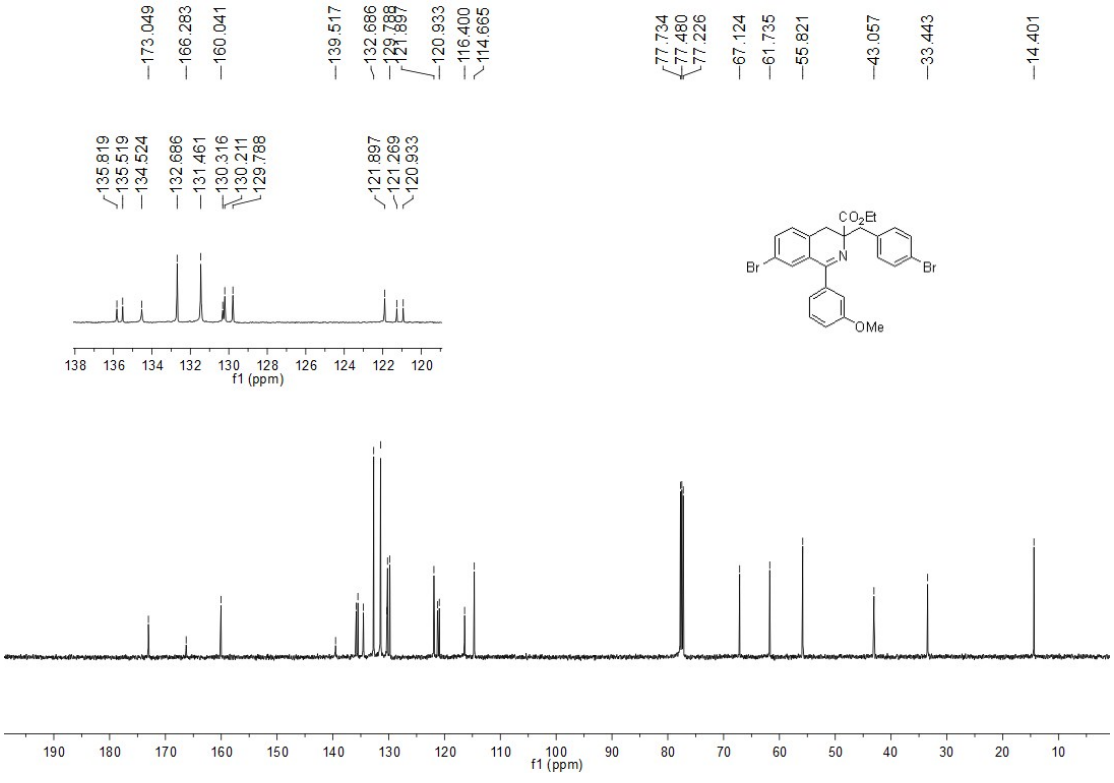

7.521
7.519
7.505
7.503
7.355
7.339
7.323
7.259
7.209
7.195
7.182
7.180
7.168
7.166
7.154
7.139
7.093
7.077
7.061
7.056
7.053
7.041
7.038
7.025
7.022
7.009
4.092
4.086
4.077
4.069
4.063
4.055
4.048
4.041
3.842
3.585
3.552
3.010
2.977
1.111
1.097
1.082
0.001
Br
CO2Et
Br
N
OMe
1.03
1.96
1.16
4.11
3.11
2.12
2.91
3.09
1.02
3.00
f1 (ppm)


172.637
167.053
159.442
132.689
129.132
128.227
127.865
127.390
126.992
126.130
124.246
121.703
115.807
114.441
77.294
77.039
76.785
66.901
61.421
55.391
42.609
33.439
13.933
130.313
129.132
128.227
127.865
127.390
126.992
126.130
Br
CO2Et
Br
N
OMe
f1 (ppm)

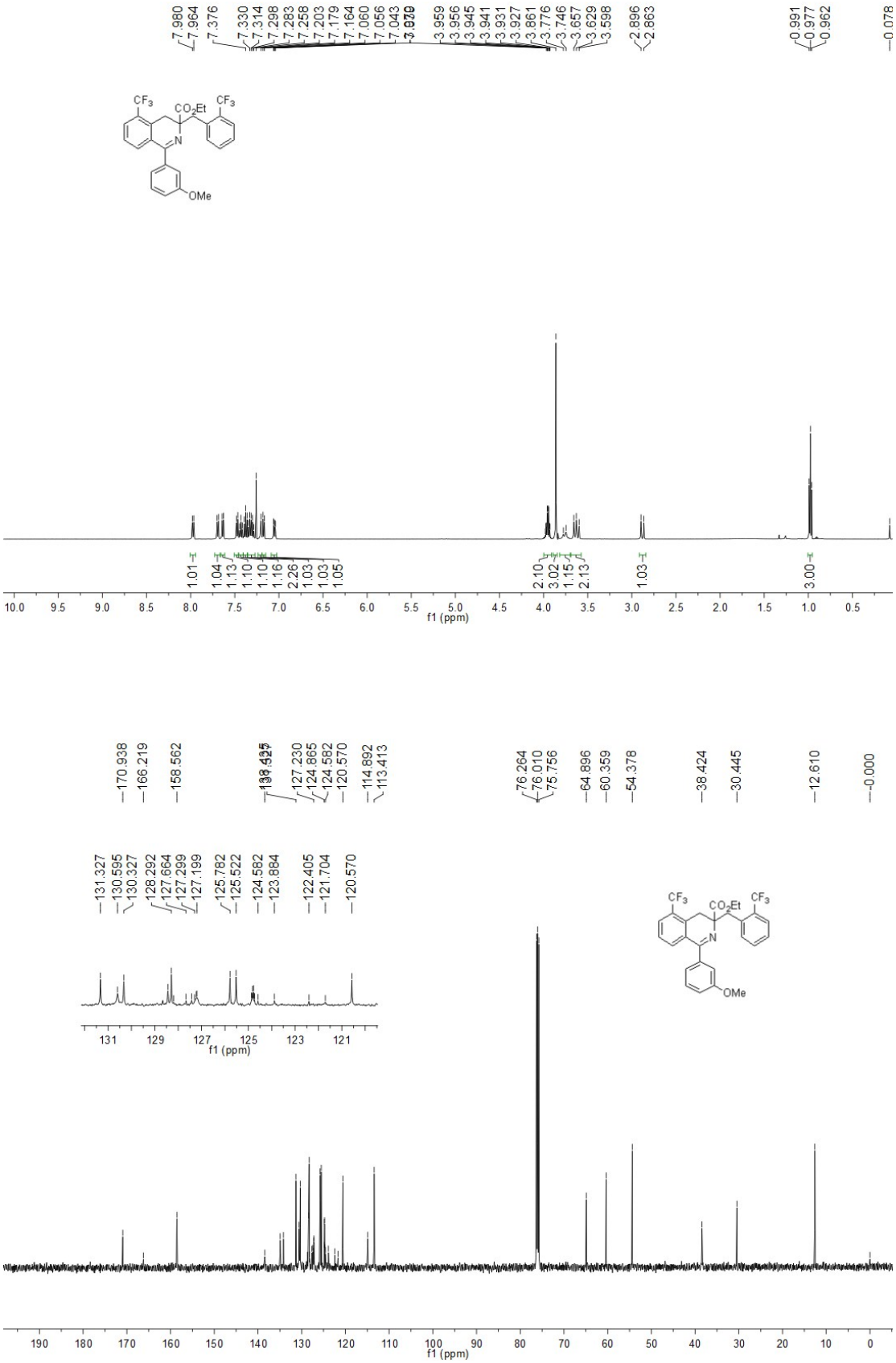
1m


7.514
7.508
7.422
7.418
7.391
7.386
7.381
7.376
7.368
7.365
7.360
7.258
7.178
7.173
7.157
7.138
7.130
7.122
7.113
7.055
7.053
7.050
7.048
7.038
7.037
7.033
4.039
4.025
4.010
3.996
3.859
3.239
3.178
3.096
2.851
2.819
1.089
1.075
1.061
CO2Et
Br
N
Br
OMe

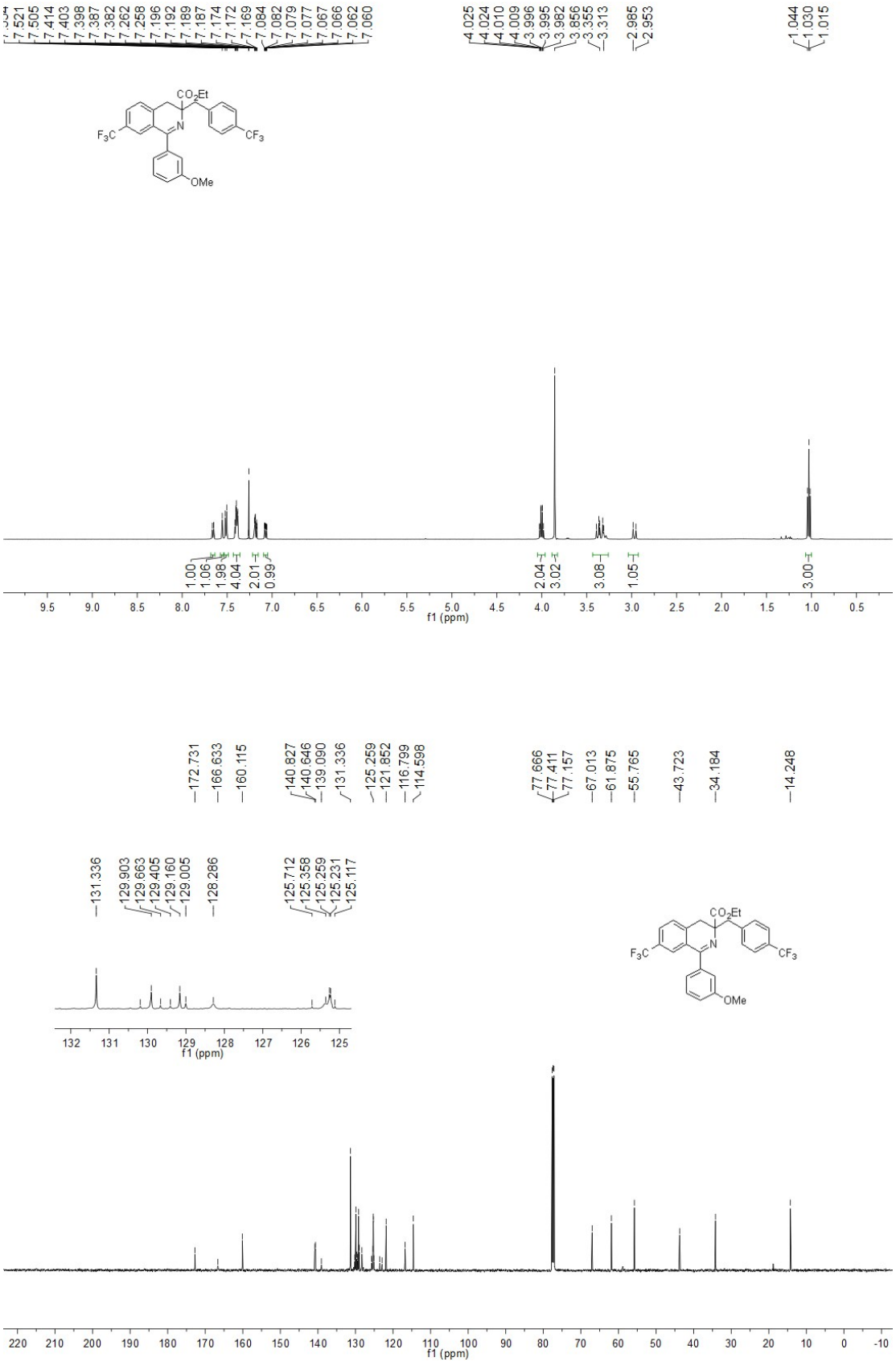

1.02
1.09
3.07
2.19
3.07
1.05
2.11
3.13
1.13
1.09
1.01
1.06
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.049
166.283
160.041
139.517
132.686
129.788
121.897
120.933
116.400
114.665
77.734
77.480
77.226
67.124
61.735
55.821
43.057
33.443
14.401
135.819
135.519
134.524
132.686
131.461
130.316
130.211
129.788
121.897
121.269
120.933
CO2Et
Br
N
Br
OMe
138 136 134 132 130 128 126 124 122 120
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1n


7.980
7.964
7.376
7.330
7.314
7.298
7.283
7.258
7.203
7.179
7.164
7.060
7.056
7.043
3.959
3.956
3.945
3.941
3.931
3.927
3.861
3.776
3.746
3.657
3.629
3.598
2.896
2.863
0.991
0.977
0.962
0.078
CF3
CO2Et
CF3
N
OMe
1.01
1.04
1.13
1.10
1.10
1.16
2.26
1.03
1.03
1.05
2.10
3.02
1.15
2.13
1.03
3.00
f1 (ppm)
170.938
166.219
158.562
127.230
124.865
124.582
120.570
114.892
113.413
76.264
76.010
75.756
64.896
60.359
54.378
38.424
30.445
12.610
0.000
131.327
130.595
130.327
128.292
127.664
127.299
127.199
125.782
125.522
124.582
123.884
122.405
121.704
120.570
f1 (ppm)

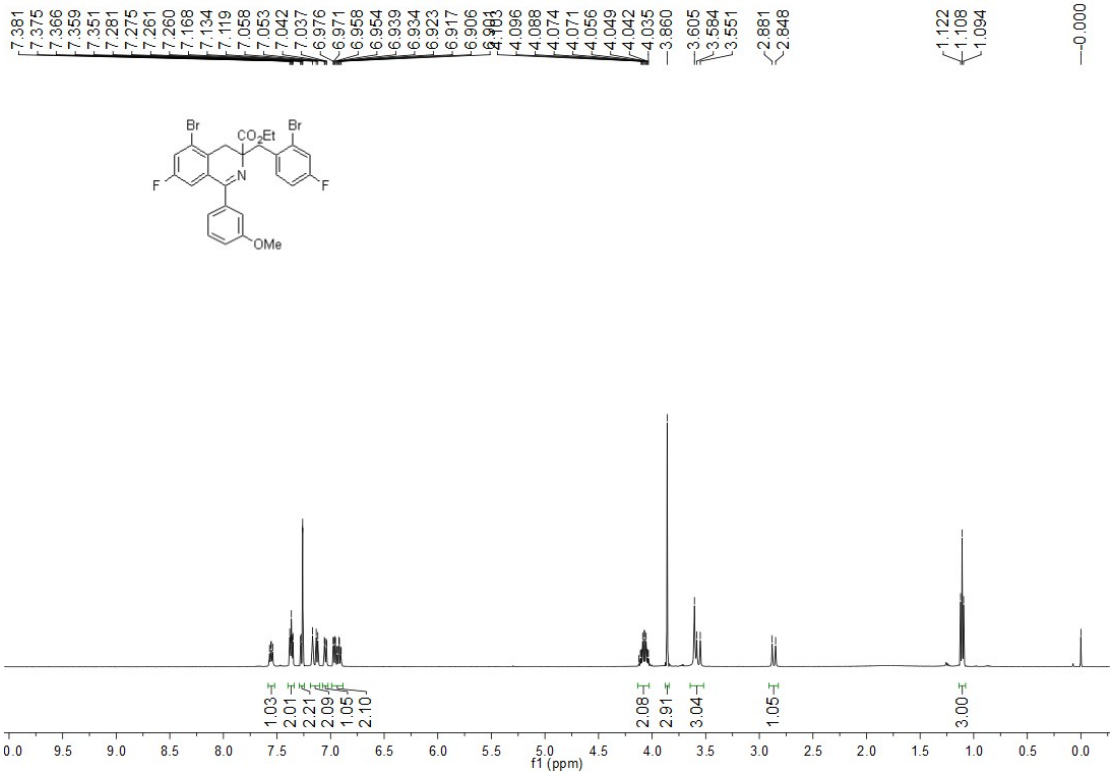
1o

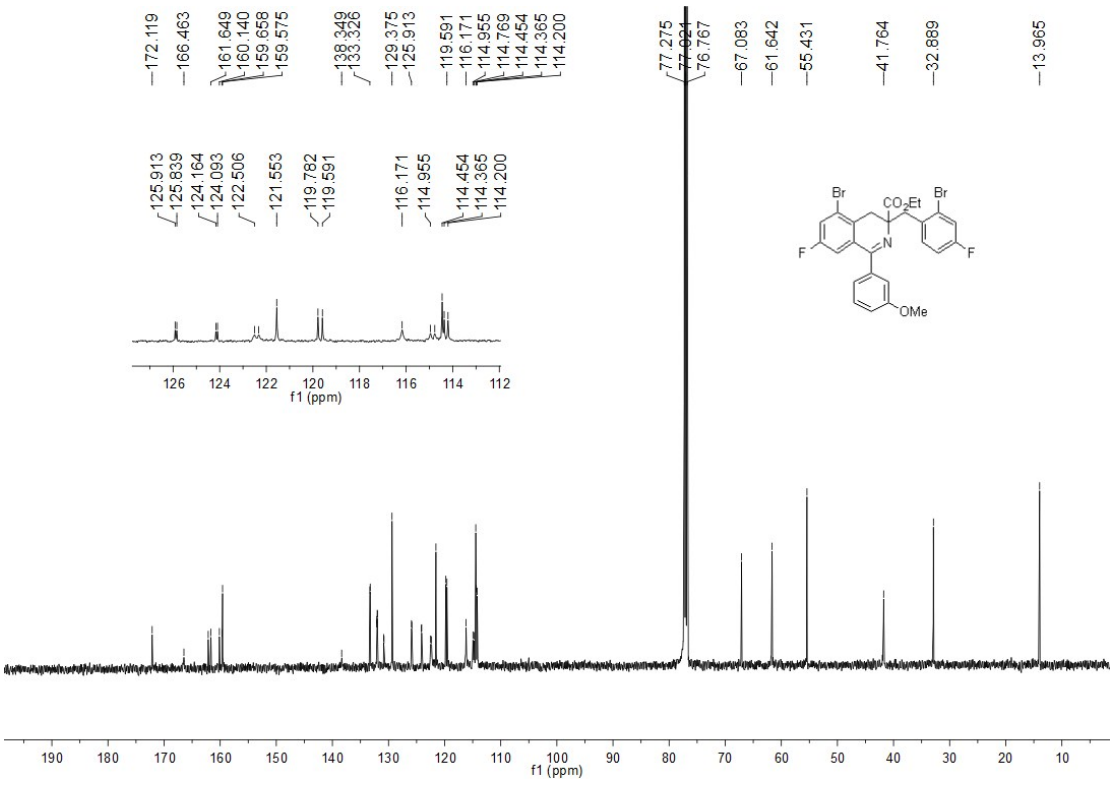

7.521
7.505
7.414
7.403
7.398
7.387
7.382
7.262
7.258
7.196
7.192
7.189
7.187
7.174
7.172
7.169
7.084
7.082
7.079
7.077
7.067
7.066
7.062
7.060
4.025
4.024
4.010
4.009
3.996
3.995
3.982
3.856
3.355
3.313
2.985
2.953
1.044
1.030
1.015
CO2Et
F3C
CF3
N
OMe
1.00
1.06
1.98
4.04
2.01
0.99
2.04
3.02
3.08
1.05
3.00
f1 (ppm)
172.731
166.633
160.115
140.827
140.646
139.090
131.336
125.259
121.852
116.799
114.598
77.666
77.411
77.157
67.013
61.875
55.765
43.723
34.184
14.248
131.336
129.903
129.663
129.405
129.160
129.005
128.286
125.712
125.358
125.259
125.231
125.117
f1 (ppm)
f1 (ppm)

1p

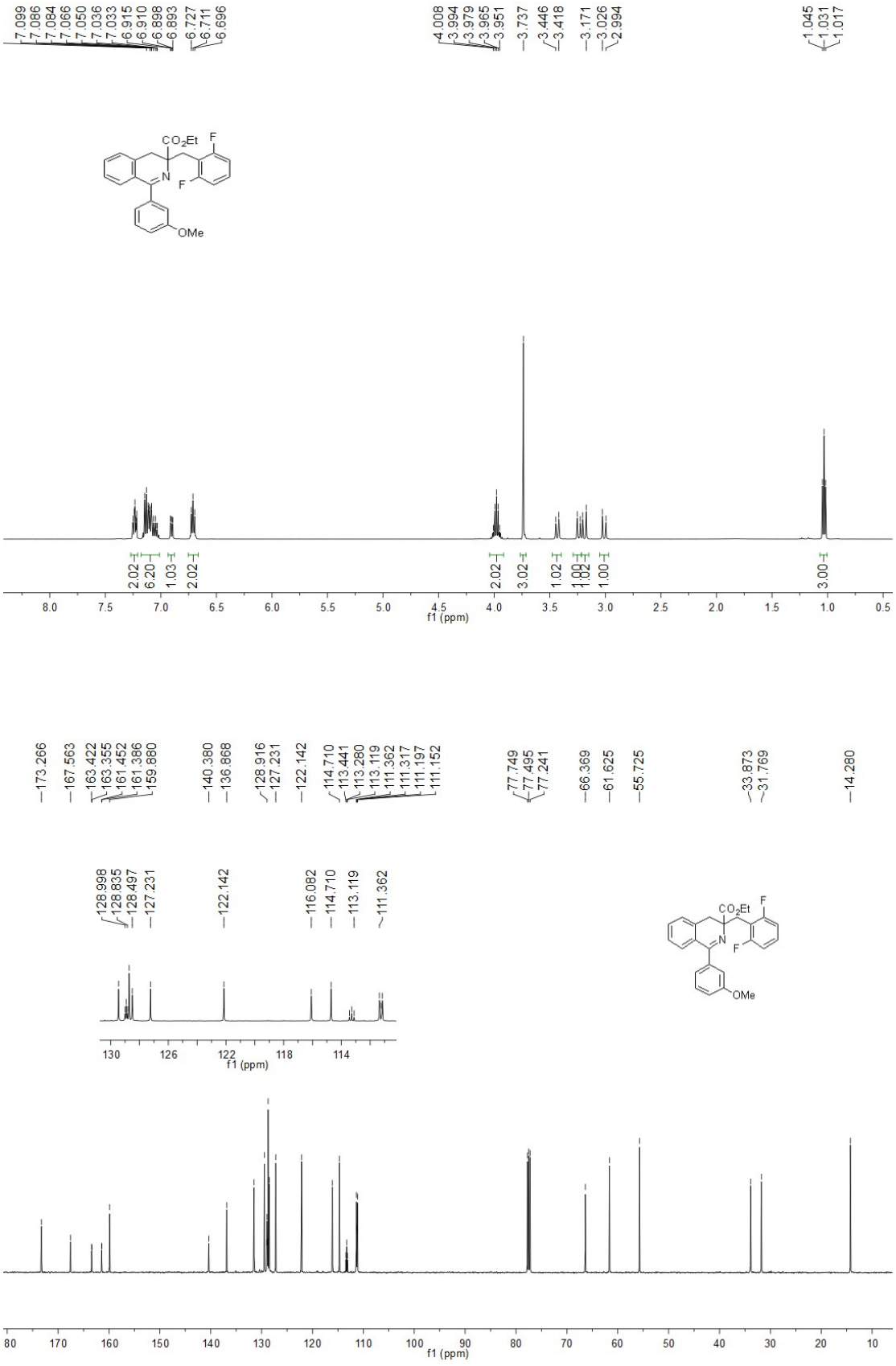

7.130
7.128
7.117
7.115
7.076
7.071
7.059
7.054
7.046
7.045
7.042
7.040
7.030
7.029
7.025
7.023
6.918
6.913
6.900
6.895
6.885
6.879
6.868
6.863
6.846
4.075
4.072
4.065
4.061
4.058
4.050
4.043
4.036
3.851
3.483
2.908
2.906
2.876
2.873
1.125
1.111
1.096
0.002
Cl
CO2Et
Cl
F
N
F
OMe
1.01
1.04
1.09
2.10
2.11
2.11
2.13
3.05
3.12
1.04
3.00
f1 (ppm)
172.346
166.011
162.321
161.599
160.342
159.604
134.248
133.557
130.714
130.357
130.183
129.368
121.486
116.551
116.357
116.007
114.421
114.192
114.012
113.780
113.616
77.294
77.040
76.786
66.769
61.574
55.412
39.416
30.058
13.952
121.486
119.264
119.066
116.551
116.357
116.007
114.421
114.192
114.012
113.780
113.616
f1 (ppm)
f1 (ppm)

1q

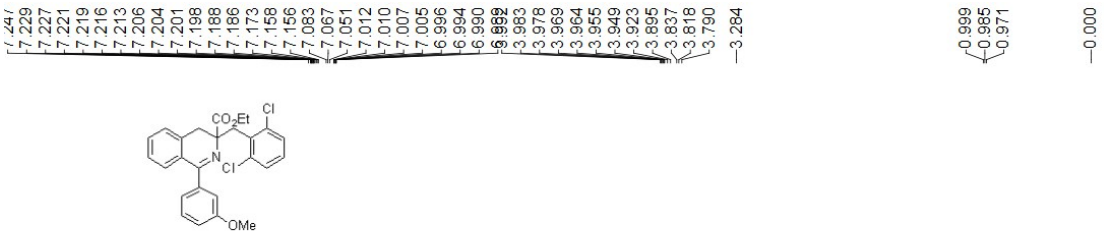

7.381
7.375
7.366
7.359
7.351
7.281
7.275
7.261
7.260
7.168
7.134
7.119
7.058
7.053
7.042
7.037
6.976
6.971
6.958
6.954
6.939
6.934
6.923
6.917
6.906
4.096
4.088
4.074
4.071
4.056
4.049
4.042
4.035
3.860
3.605
3.584
3.551
2.881
2.848
1.122
1.108
1.094
0.000
Br
CO2Et
Br
F
N
F
OMe
1.03
2.01
2.21
2.09
1.05
2.10
2.08
2.91
3.04
1.05
3.00
f1 (ppm)


172.119
166.463
161.649
160.140
159.658
159.575
138.349
133.326
129.375
125.913
119.591
116.171
114.955
114.769
114.454
114.365
114.200
77.275
77.024
76.767
67.083
61.642
55.431
41.764
32.889
13.965
125.913
125.839
124.164
124.093
122.506
121.553
119.782
119.591
116.171
114.955
114.454
114.365
114.200
Br
CO2Et
Br
F
N
F
OMe
f1 (ppm)
f1 (ppm)

1r


7.099
7.086
7.084
7.066
7.050
7.036
7.033
6.915
6.910
6.898
6.893
6.727
6.711
6.696
4.008
3.994
3.979
3.965
3.951
3.737
3.446
3.418
3.171
3.026
2.994
1.045
1.031
1.017
CO2Et
F
N
F
OMe
2.02
6.20
1.03
2.02
2.02
3.02
1.02
1.00
1.00
3.00
f1 (ppm)
173.266
167.563
163.422
163.355
161.452
161.386
159.880
140.380
136.868
128.916
127.231
122.142
114.710
113.441
113.280
113.119
111.362
111.317
111.197
111.152
77.749
77.495
77.241
66.369
61.625
55.725
33.873
31.769
14.280
128.998
128.835
128.497
127.231
122.142
116.082
114.710
113.119
111.362
f1 (ppm)

1s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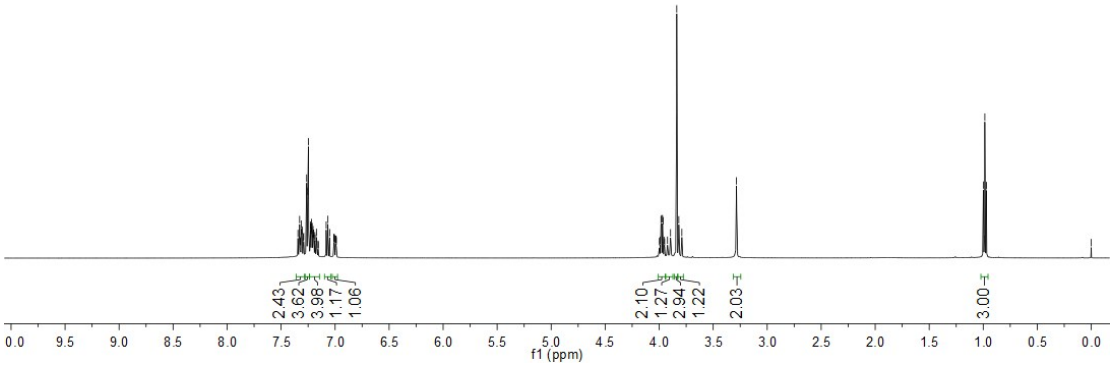
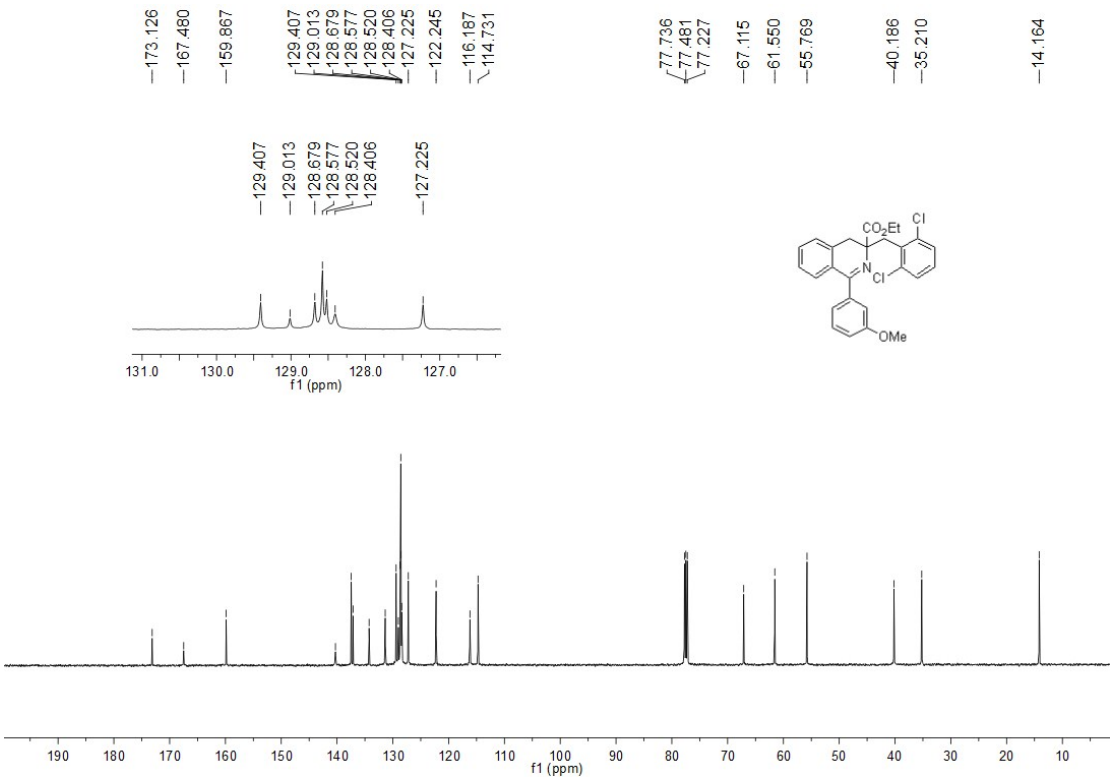
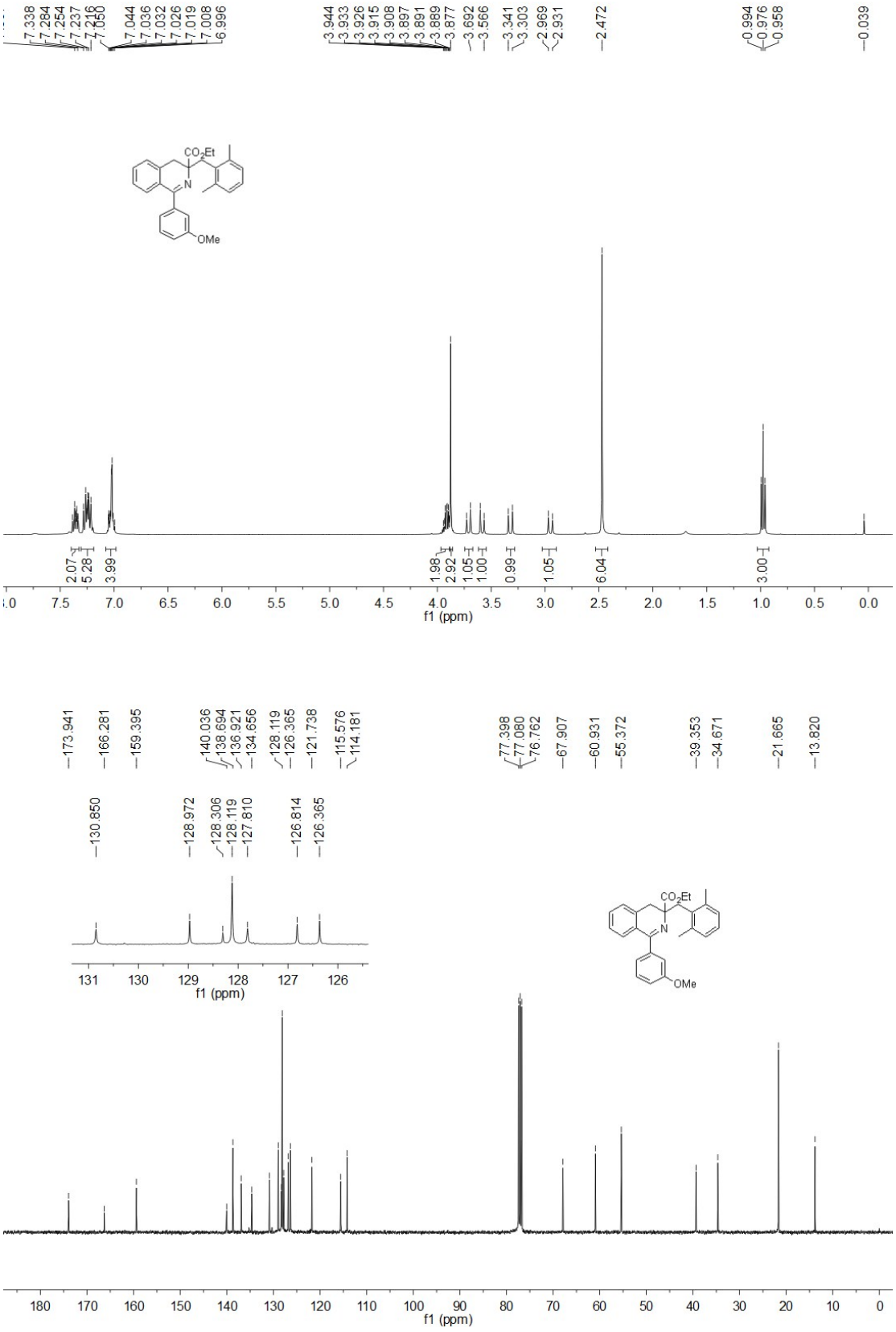
7.229
7.227
7.221
7.219
7.216
7.213
7.206
7.204
7.201
7.198
7.188
7.186
7.173
7.158
7.156
7.083
7.067
7.051
7.012
7.010
7.007
7.005
6.996
6.994
6.990
3.983
3.978
3.969
3.964
3.955
3.949
3.923
3.895
3.837
3.818
3.790
3.284
0.999
0.985
0.971
0.000

CO2Et
Cl
N
Cl
OMe

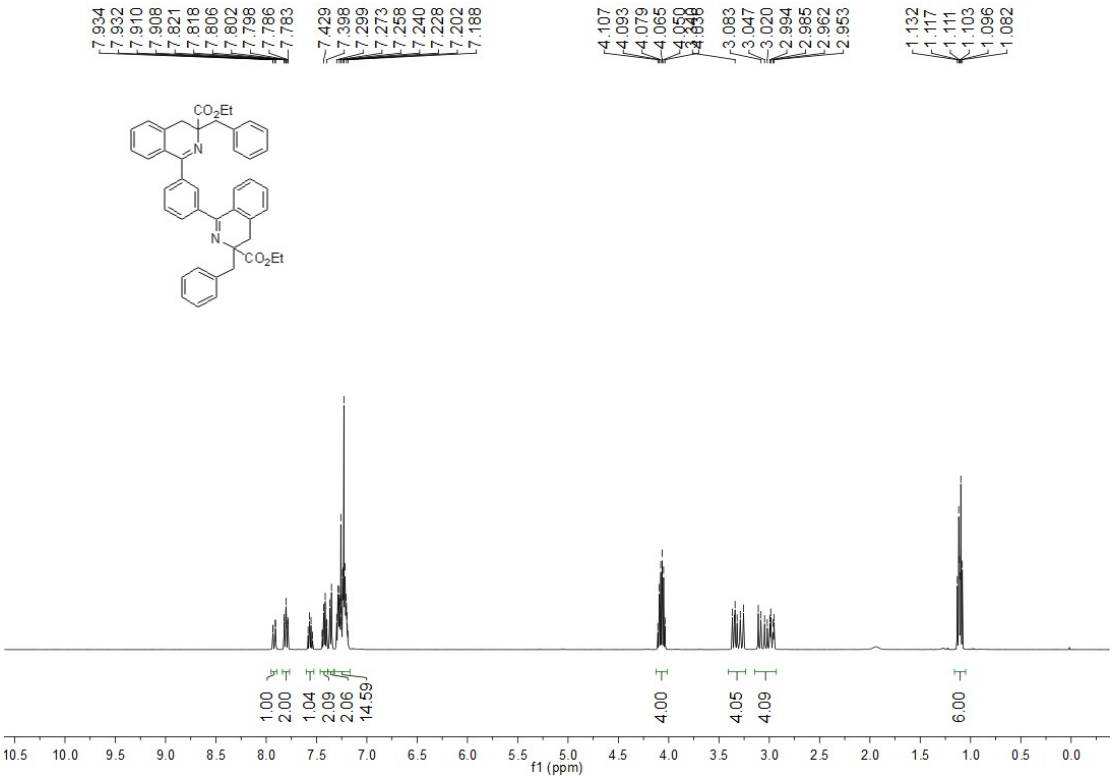

2.43
3.62
3.98
1.17
1.06
2.10
1.27
2.94
1.22
2.03
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

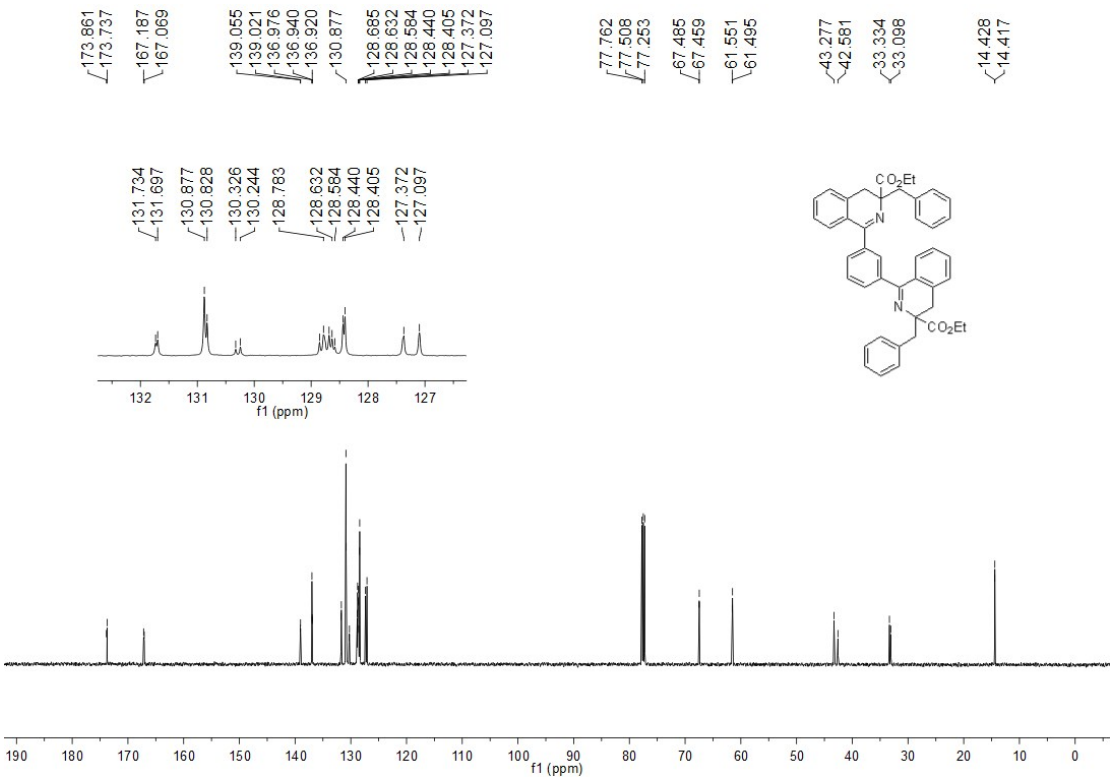

173.126
167.480
159.867
129.407
129.013
128.679
128.577
128.520
128.406
127.225
122.245
116.187
114.731
77.736
77.481
77.227
67.115
61.550
55.769
40.186
35.210
14.164
129.407
129.013
128.679
128.577
128.520
128.406
127.225
131.0
130.0
129.0
128.0
127.0
f1 (ppm)
CO2Et
Cl
N
Cl
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1t

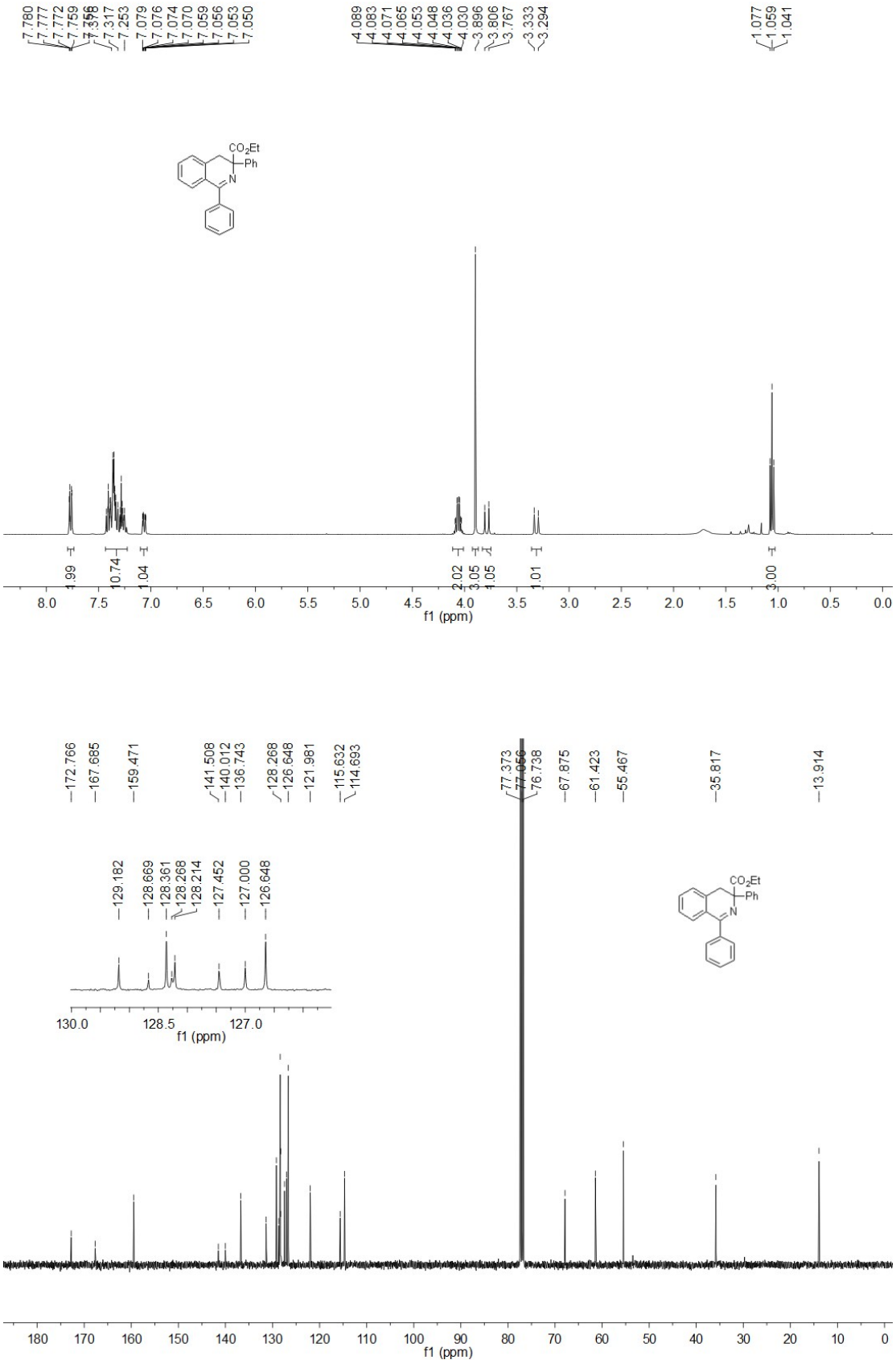

7.338
7.284
7.254
7.237
7.216
7.050
7.044
7.036
7.032
7.026
7.019
7.008
6.996
3.944
3.933
3.926
3.915
3.908
3.897
3.891
3.889
3.877
3.692
3.566
3.341
3.303
2.969
2.931
2.472
0.994
0.976
0.958
0.039
CO2Et
N
OMe
2.07
5.28
3.99
1.98
2.92
1.05
1.00
0.99
1.05
6.04
3.00
f1 (ppm)
173.941
166.281
159.395
140.036
138.694
136.921
134.656
128.119
126.365
121.738
115.576
114.181
77.398
77.080
76.762
67.907
60.931
55.372
39.353
34.671
21.665
13.820
130.850
128.972
128.306
128.119
127.810
126.814
126.365
f1 (ppm)
f1 (ppm)

1u


7.934
7.932
7.910
7.908
7.821
7.818
7.806
7.802
7.798
7.786
7.783
7.429
7.398
7.299
7.273
7.258
7.240
7.228
7.202
7.188
4.107
4.093
4.079
4.065
4.050
4.036
3.083
3.047
3.020
2.994
2.985
2.962
2.953
1.132
1.117
1.111
1.103
1.096
1.082
CO2Et
N
N
CO2Et
1.00
2.00
1.04
2.09
2.06
14.59
4.00
4.05
4.09
6.00
f1 (ppm)

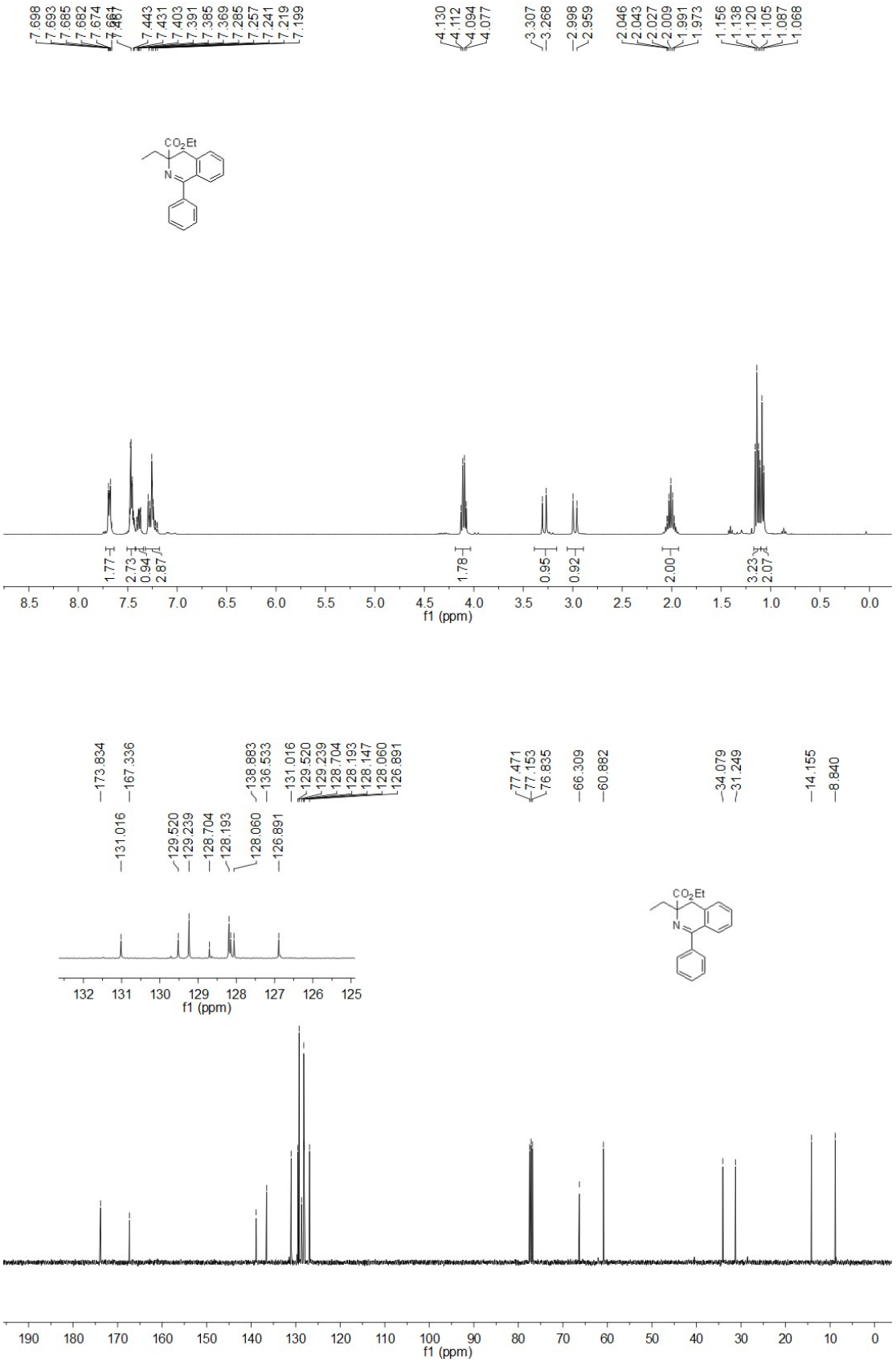

173.861
173.737
167.187
167.069
139.055
139.021
136.976
136.940
136.920
130.877
128.685
128.632
128.584
128.440
128.405
127.372
127.097
77.762
77.508
77.253
67.485
67.459
61.551
61.495
43.277
42.581
33.334
33.098
14.428
14.417
131.734
131.697
130.877
130.828
130.326
130.244
128.783
128.632
128.584
128.440
128.405
127.372
127.097
CO2Et
N
N
CO2Et
f1 (ppm)
f1 (ppm)

1v

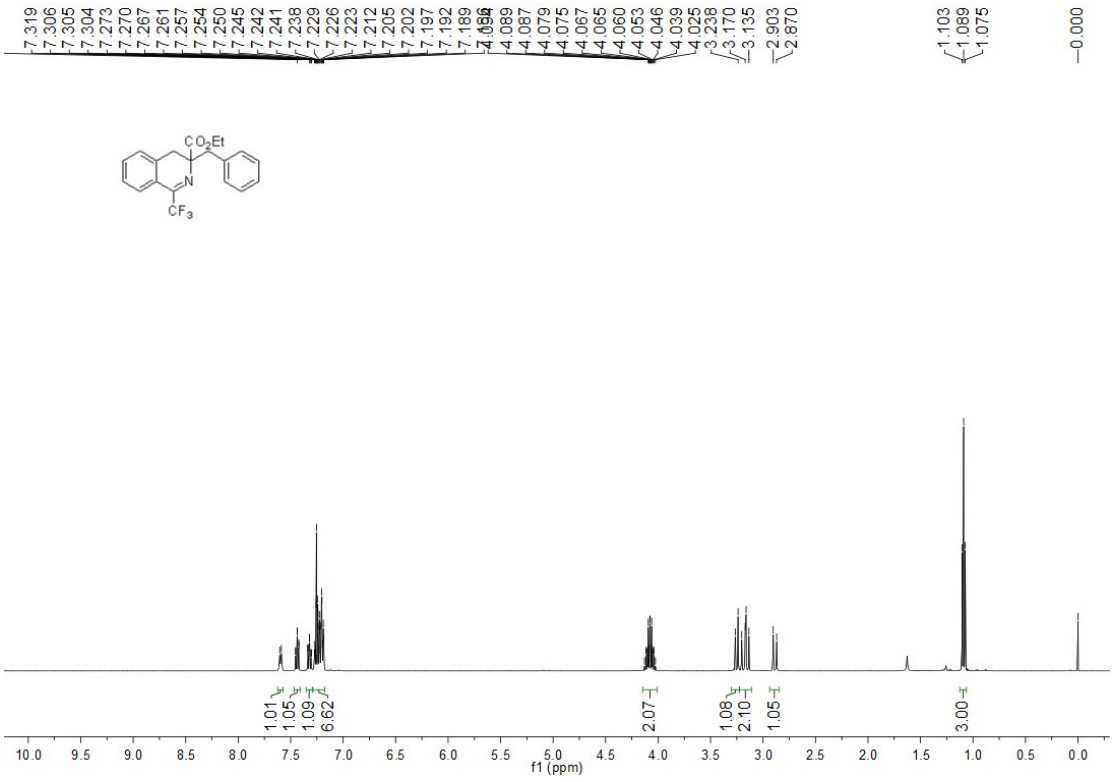

7.780
7.777
7.772
7.759
7.317
7.253
7.079
7.076
7.074
7.070
7.059
7.056
7.053
7.050
4.089
4.083
4.071
4.065
4.053
4.048
4.036
4.030
3.896
3.806
3.767
3.333
3.294
1.077
1.059
1.041
CO2Et
Ph
N
1.99
10.74
1.04
2.02
3.05
1.05
1.01
3.00
f1 (ppm)
172.766
167.685
159.471
141.508
140.012
136.743
128.268
126.648
121.981
115.632
114.693
77.373
77.056
76.738
67.875
61.423
55.467
35.817
13.914
129.182
128.669
128.361
128.268
128.214
127.452
127.000
126.648
130.0
128.5
127.0
f1 (ppm)
CO2Et
Ph
N
f1 (ppm)

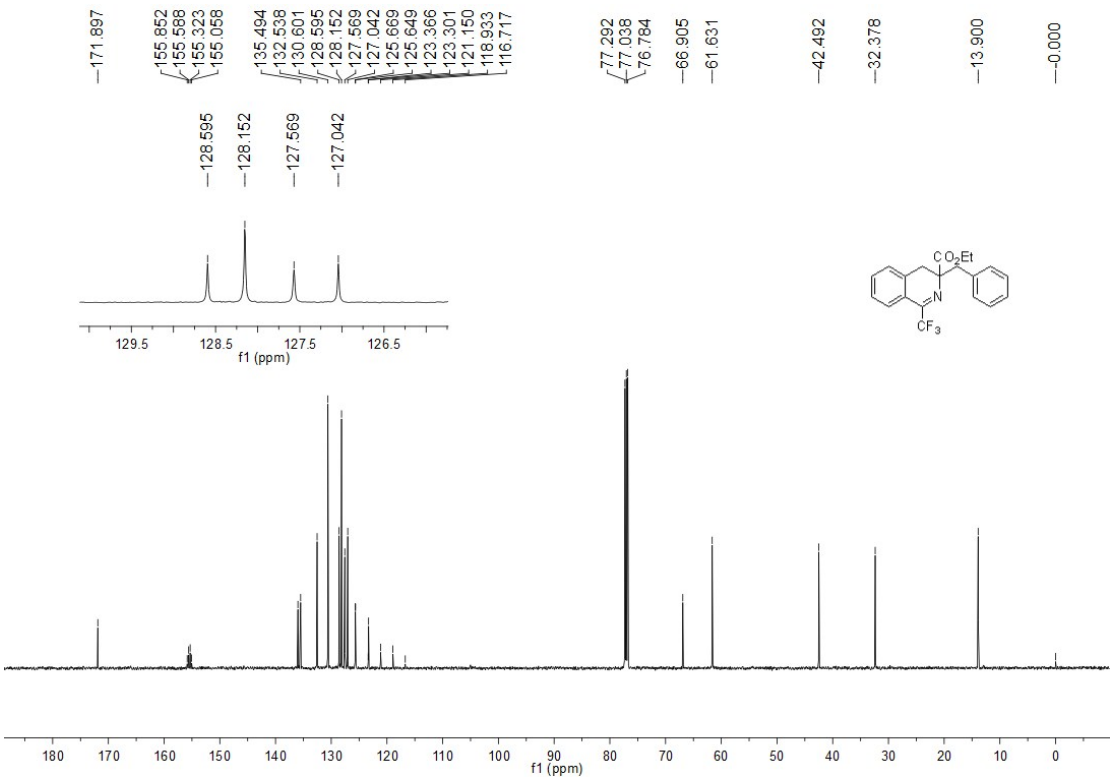
1w

1x

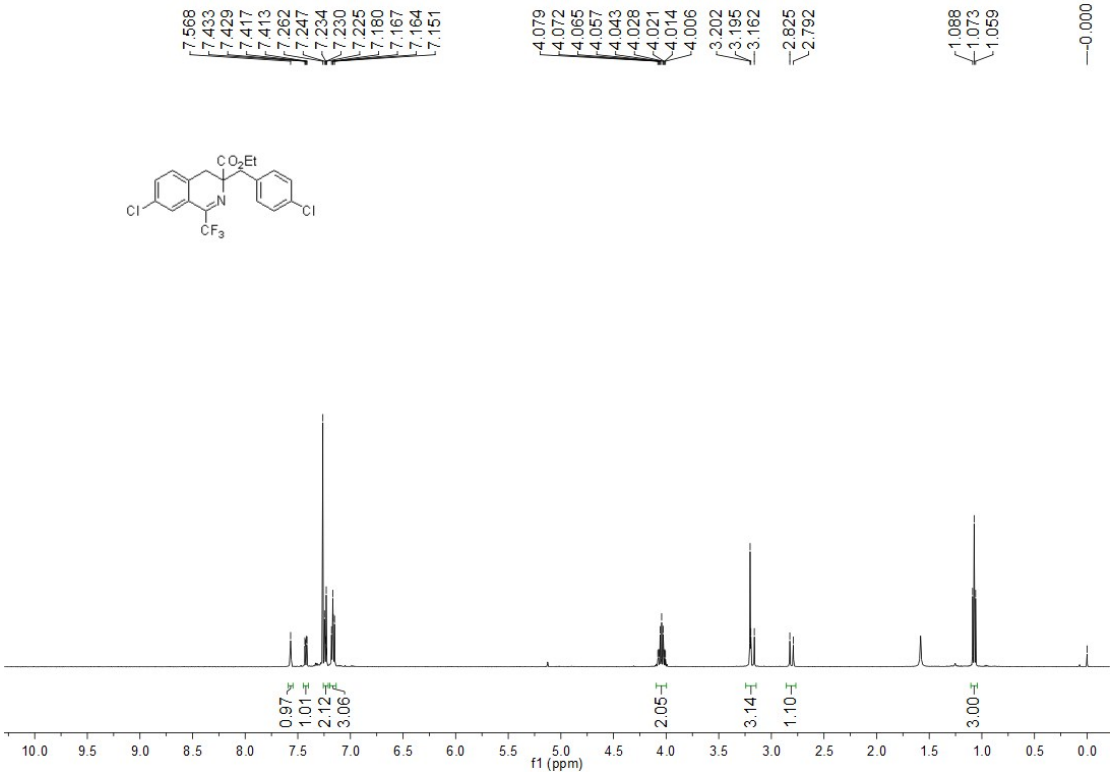

7.698
7.693
7.685
7.682
7.674
7.443
7.431
7.403
7.391
7.385
7.369
7.285
7.257
7.241
7.219
7.199
4.130
4.112
4.094
4.077
3.307
3.268
2.998
2.959
2.046
2.043
2.027
2.009
1.991
1.973
1.156
1.138
1.120
1.105
1.087
1.068
CO2Et
N
1.77
2.73
0.94
2.87
1.78
0.95
0.92
2.00
3.23
2.07
f1 (ppm)
173.834
167.336
138.883
136.533
131.016
129.520
129.239
128.704
128.193
128.147
128.060
126.891
77.471
77.153
76.835
66.309
60.882
34.079
31.249
14.155
8.840
CO2Et
N
f1 (ppm)
f1 (ppm)

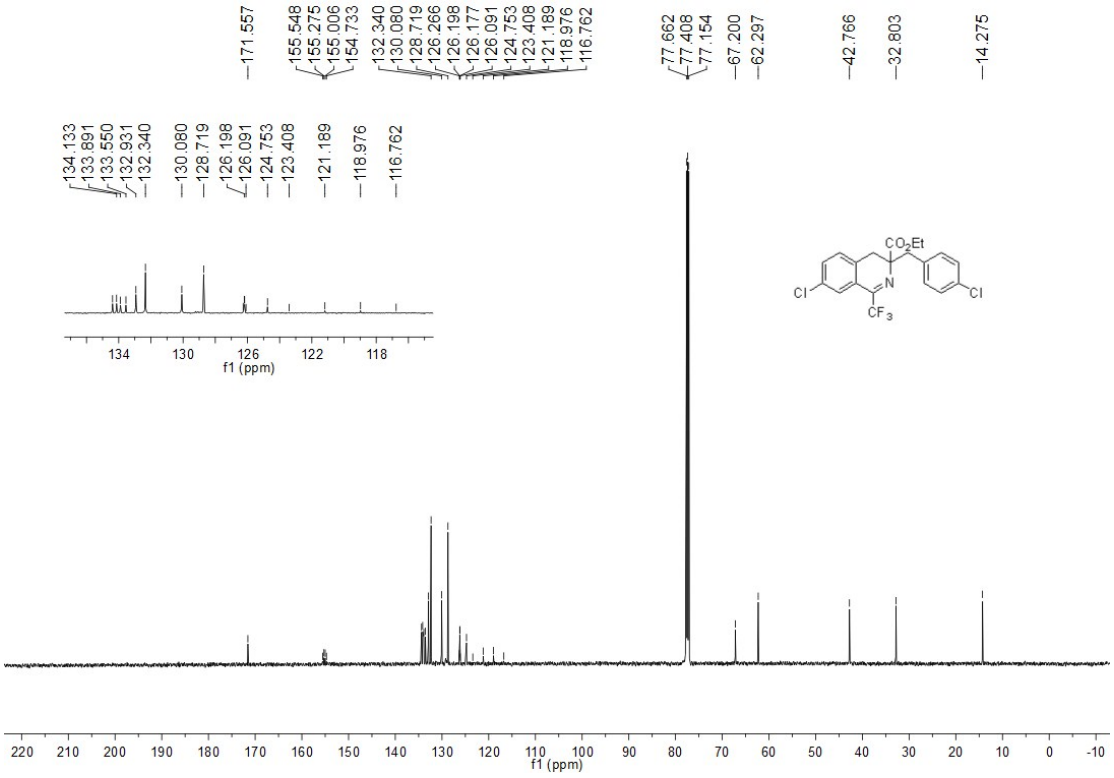
4a


7.319
7.306
7.305
7.304
7.273
7.270
7.267
7.261
7.257
7.254
7.250
7.245
7.242
7.241
7.238
7.229
7.226
7.223
7.212
7.205
7.202
7.197
7.192
7.189
4.089
4.087
4.079
4.075
4.067
4.065
4.060
4.053
4.046
4.039
4.025
3.238
3.170
3.135
2.903
2.870
1.103
1.089
1.075
0.000
CO2Et
N
CF3
1.01
1.05
1.09
6.62
2.07
1.08
2.10
1.05
3.00
f1 (ppm)

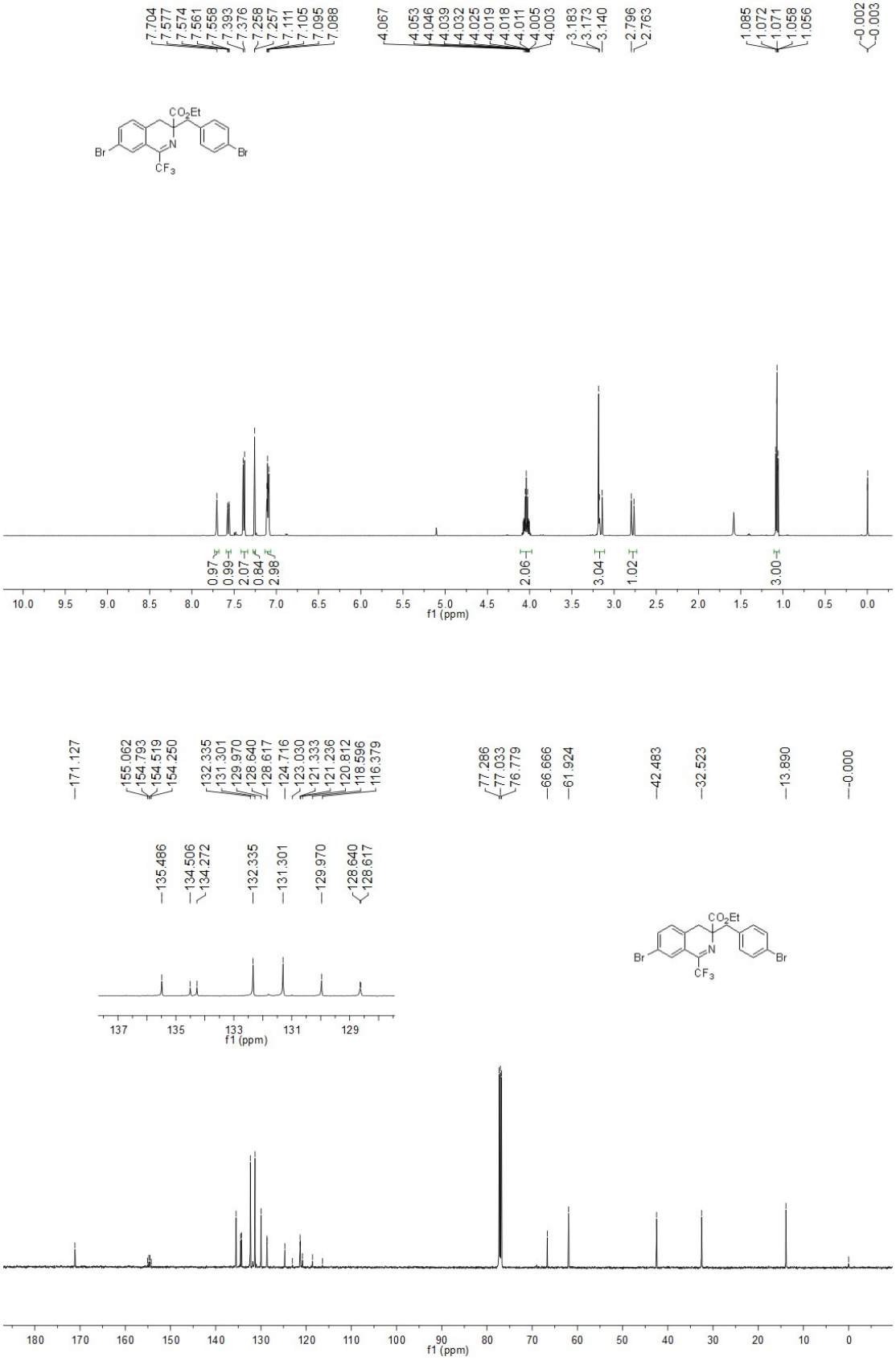

171.897
155.852
155.588
155.323
155.058
135.494
132.538
130.601
128.595
128.152
127.569
127.042
125.669
125.649
123.366
123.301
121.150
118.933
116.717
77.292
77.038
76.784
66.905
61.631
42.492
32.378
13.900
0.000
128.595
128.152
127.569
127.042
CO2Et
N
CF3
f1 (ppm)

4b

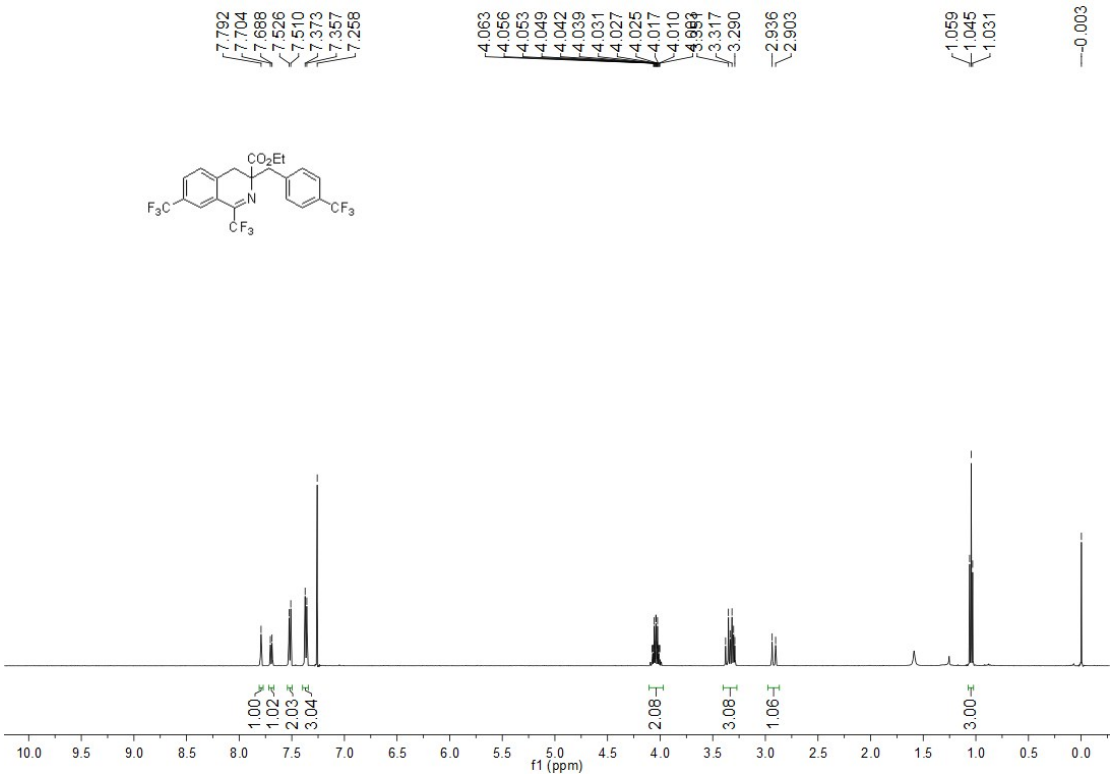

7.568
7.433
7.429
7.417
7.413
7.262
7.247
7.234
7.230
7.225
7.180
7.167
7.164
7.151
4.079
4.072
4.065
4.057
4.043
4.028
4.021
4.014
4.006
3.202
3.195
3.162
2.825
2.792
1.088
1.073
1.059
0.000
CO2Et
Cl
N
CF3
Cl
0.97
1.01
2.12
3.06
2.05
3.14
1.10
3.00
f1 (ppm)

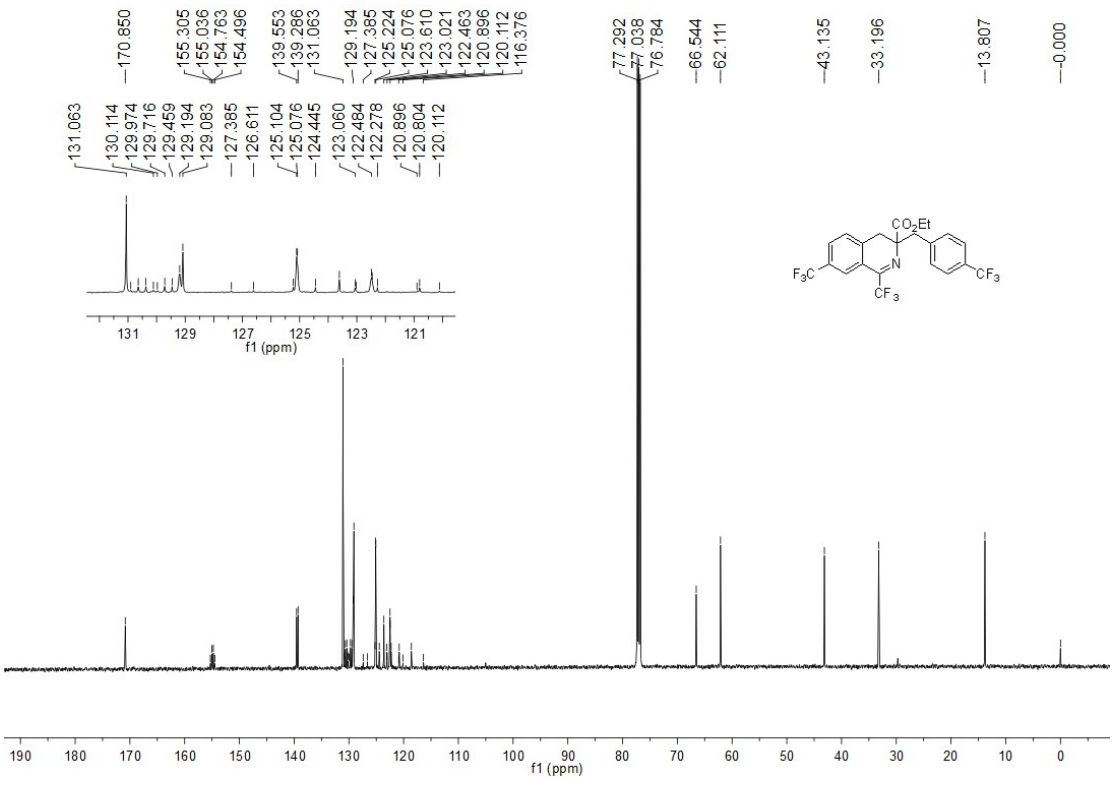

171.557
155.548
155.275
155.006
154.733
132.340
130.080
128.719
126.266
126.198
126.177
126.091
124.753
123.408
121.189
118.976
116.762
77.662
77.408
77.154
67.200
62.297
42.766
32.803
14.275
134.133
133.891
133.550
132.931
132.340
130.080
128.719
126.198
126.091
124.753
123.408
121.189
118.976
116.762
134
130
126
122
118
f1 (ppm)
CO2Et
Cl
N
CF3
Cl
f1 (ppm)

4c

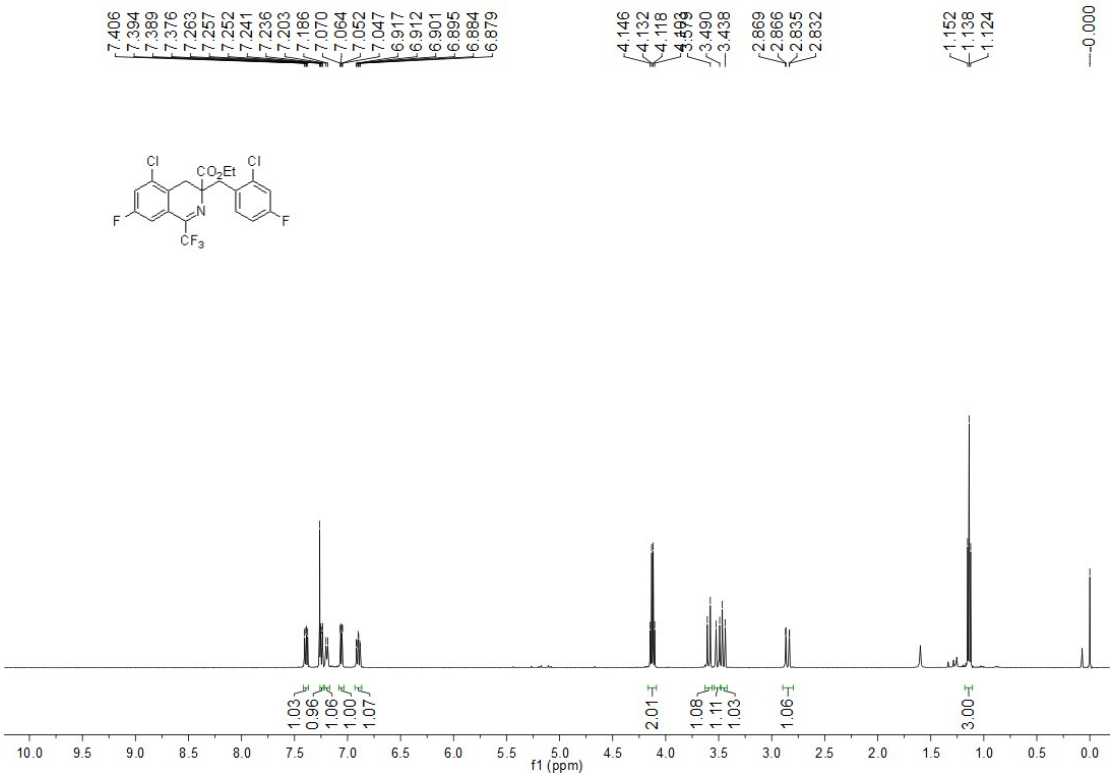

7.704
7.577
7.574
7.561
7.558
7.393
7.376
7.258
7.257
7.111
7.105
7.095
7.088
4.067
4.053
4.046
4.039
4.032
4.025
4.019
4.018
4.011
4.005
4.003
3.183
3.173
3.140
2.796
2.763
1.085
1.072
1.071
1.058
1.056
-0.002
-0.003
CO2Et
Br
N
CF3
Br
0.97
0.99
2.07
0.84
2.98
2.06
3.04
1.02
3.00
f1 (ppm)
171.127
155.062
154.793
154.519
154.250
132.335
131.301
129.970
128.640
128.617
124.716
123.030
121.333
121.236
120.812
118.596
116.379
77.286
77.033
76.779
66.666
61.924
42.483
32.523
13.890
0.000
135.486
134.506
134.272
132.335
131.301
129.970
128.640
128.617
f1 (ppm)
f1 (ppm)

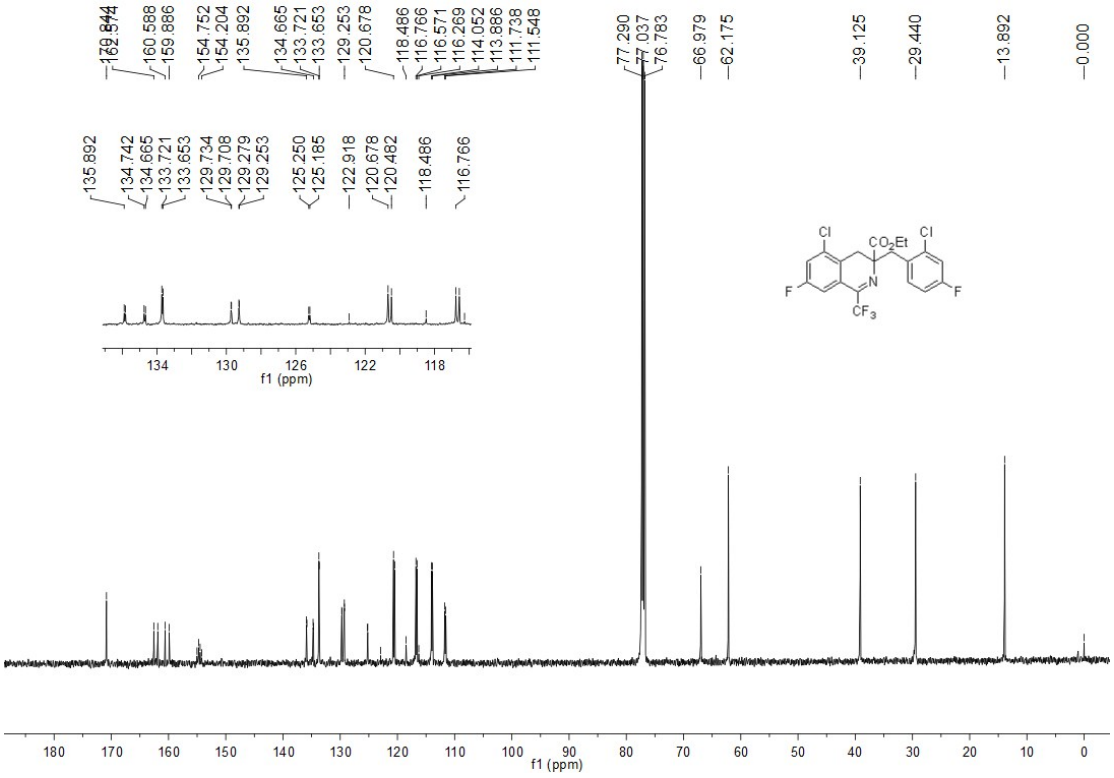
4d


7.792
7.704
7.688
7.526
7.510
7.373
7.357
7.258
4.063
4.056
4.053
4.049
4.042
4.039
4.031
4.027
4.025
4.017
4.010
3.317
3.290
2.936
2.903
1.059
1.045
1.031
0.003
CO2Et
F3C
CF3
CF3
1.00
1.02
2.03
3.04
2.08
3.08
1.06
3.00
f1 (ppm)

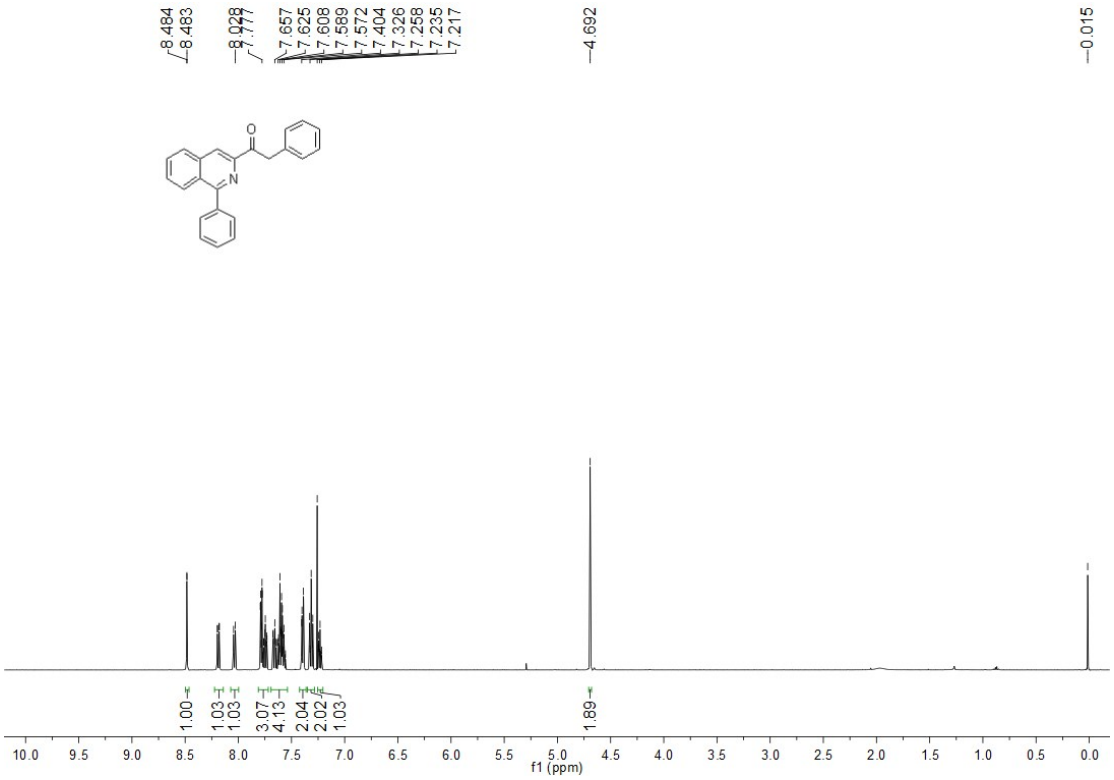

170.850
155.305
155.036
154.763
154.496
139.553
139.286
131.063
129.194
127.385
125.224
125.076
123.610
123.021
122.463
120.896
120.112
116.376
77.292
77.038
76.784
66.544
62.111
43.135
33.196
13.807
0.000
131.063
130.114
129.974
129.716
129.459
129.194
129.083
127.385
126.611
125.104
125.076
124.445
123.060
122.484
122.278
120.896
120.804
120.112
CO2Et
F3C
CF3
CF3
f1 (ppm)

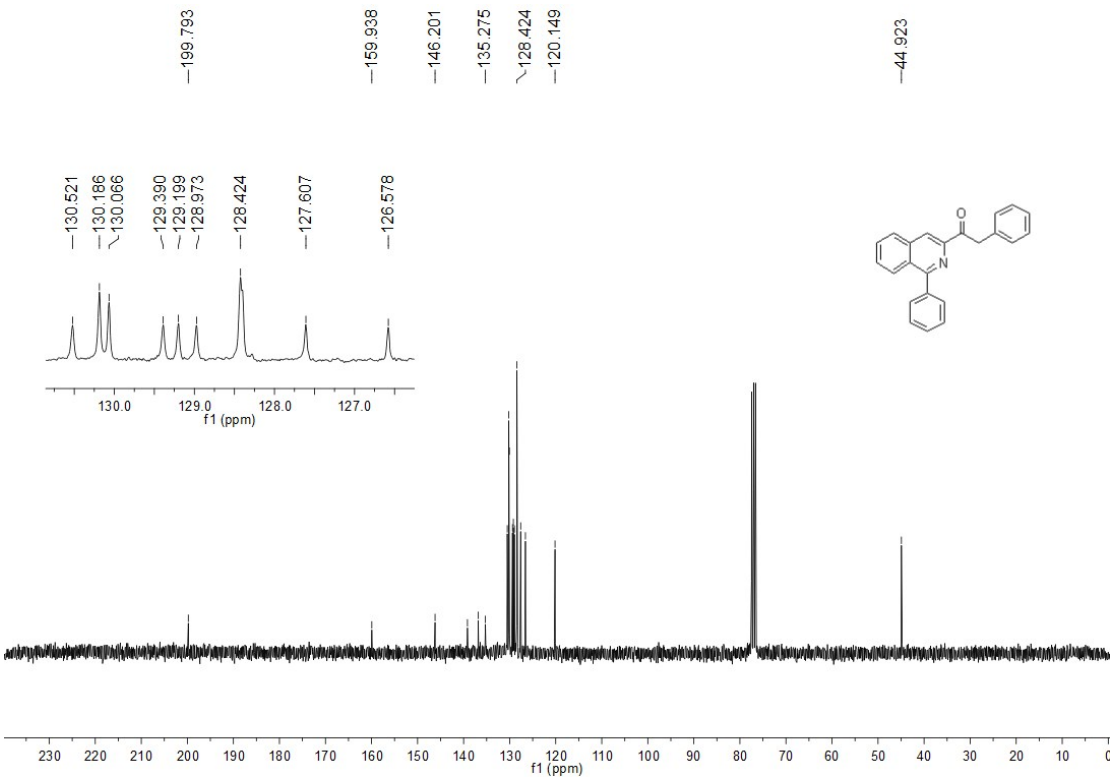
4e


7.406
7.394
7.389
7.376
7.263
7.257
7.252
7.241
7.236
7.203
7.186
7.070
7.064
7.052
7.047
6.917
6.912
6.901
6.895
6.884
6.879
4.146
4.132
4.118
3.490
3.438
2.869
2.866
2.835
2.832
1.152
1.138
1.124
0.000
Cl
CO2Et
Cl
F
N
F
CF3
1.03
0.96
1.06
1.00
1.07
2.01
1.08
1.11
1.03
1.06
3.00
f1 (ppm)

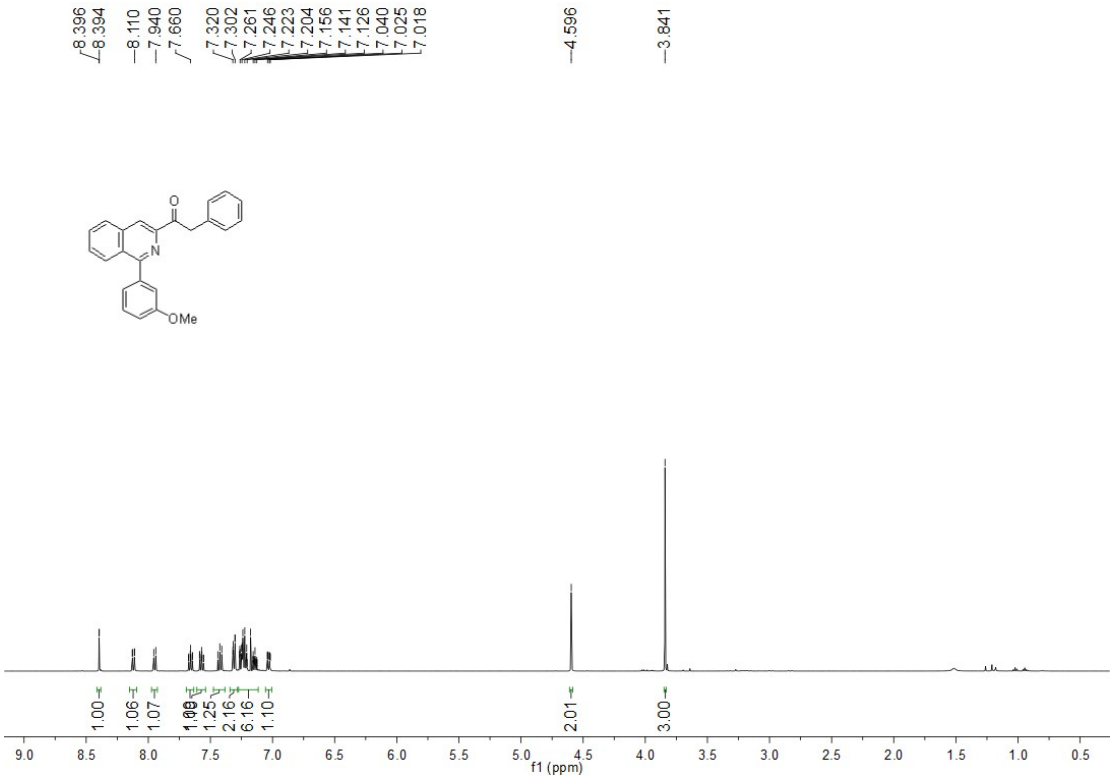

170.844
162.514
160.588
159.886
154.752
154.204
135.892
134.665
133.721
133.653
129.253
120.678
118.486
116.766
116.571
116.269
114.052
113.886
111.738
111.548
77.290
77.037
76.783
66.979
62.175
39.125
29.440
13.892
0.000
135.892
134.742
134.665
133.721
133.653
129.734
129.708
129.279
129.253
125.250
125.185
122.918
120.678
120.482
118.486
116.766
134
130
126
122
118
f1 (ppm)
Cl
CO2Et
Cl
F
N
F
CF3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

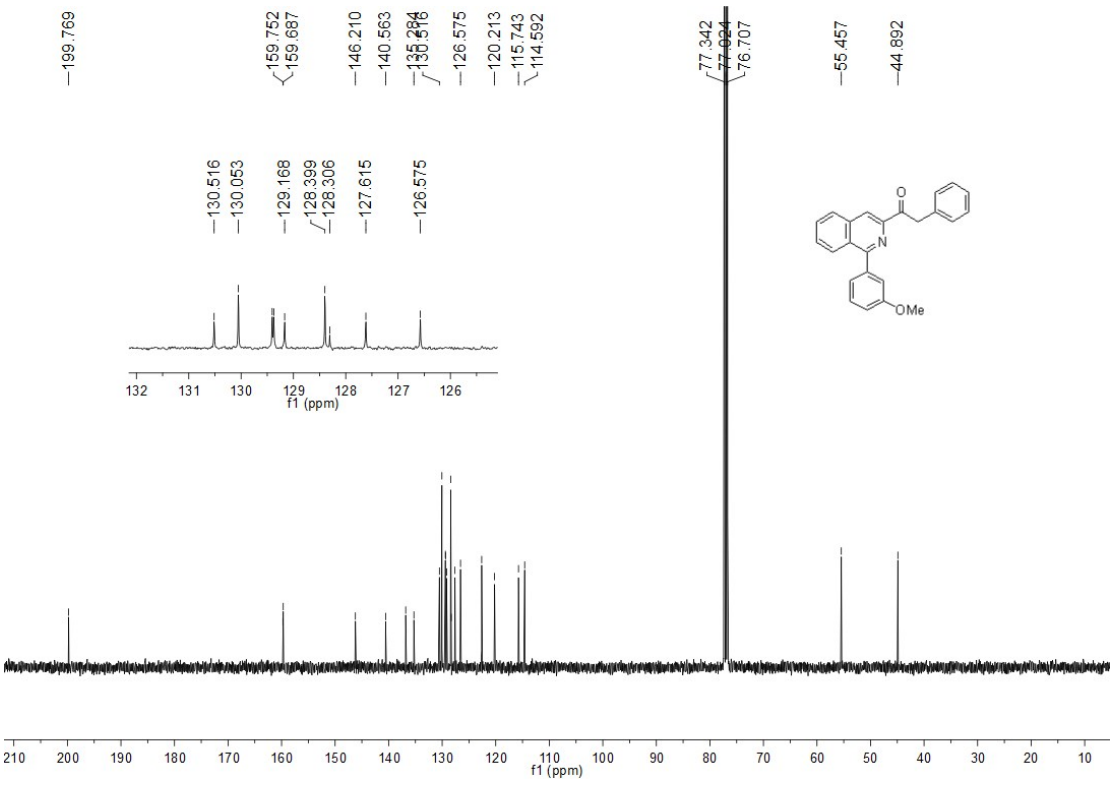
2a


8.484
8.483
8.028
7.777
7.657
7.625
7.608
7.589
7.572
7.404
7.326
7.258
7.235
7.217
4.692
0.015
1.00
1.03
1.03
3.07
4.13
2.04
2.02
1.03
1.89
f1 (ppm)

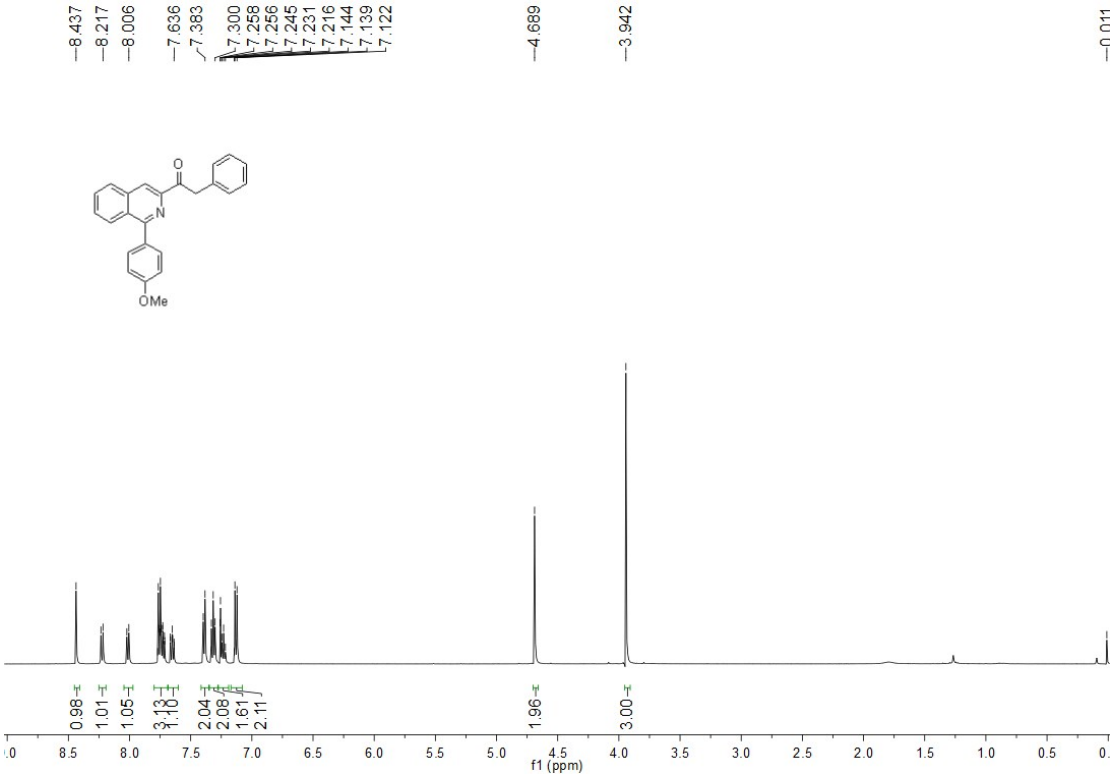

199.793
159.938
146.201
135.275
128.424
120.149
44.923
130.521
130.186
130.066
129.390
129.199
128.973
128.424
127.607
126.578
f1 (ppm)

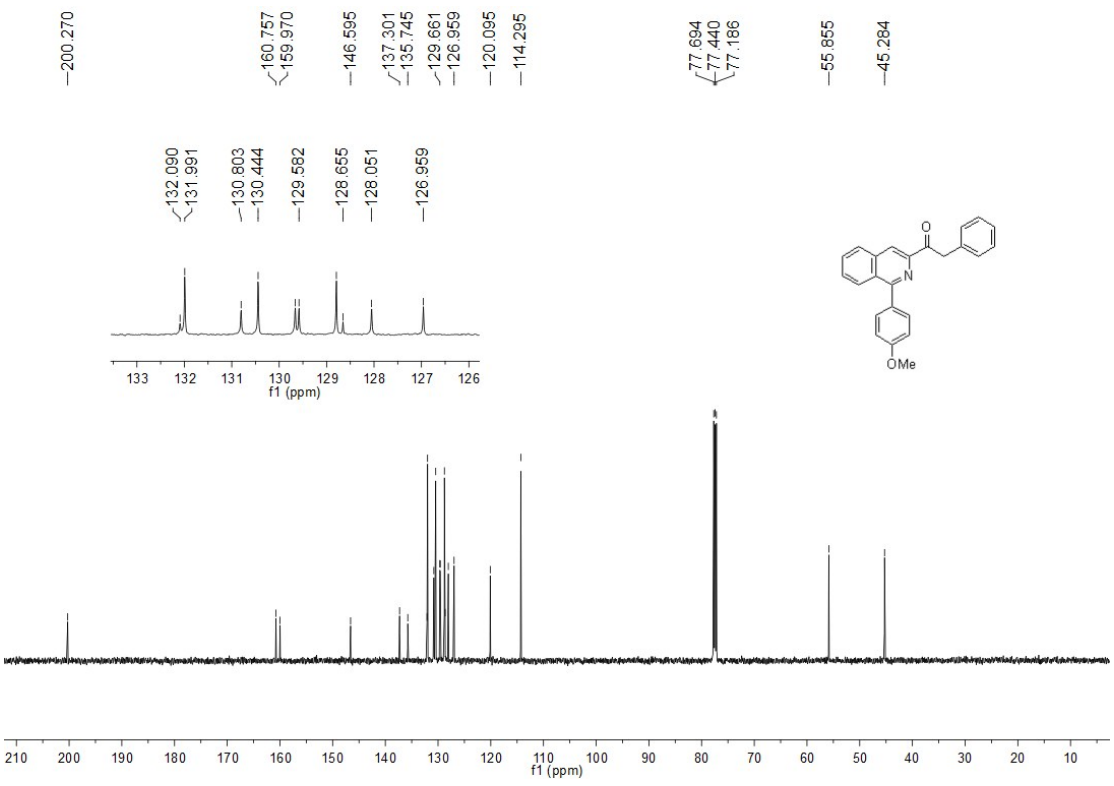
2b


8.396
8.394
8.110
7.940
7.660
7.320
7.302
7.261
7.246
7.223
7.204
7.156
7.141
7.126
7.040
7.025
7.018
4.596
3.841
O
N
OMe
1.00
1.06
1.07
1.25
2.16
6.16
1.10
2.01
3.00
f1 (ppm)

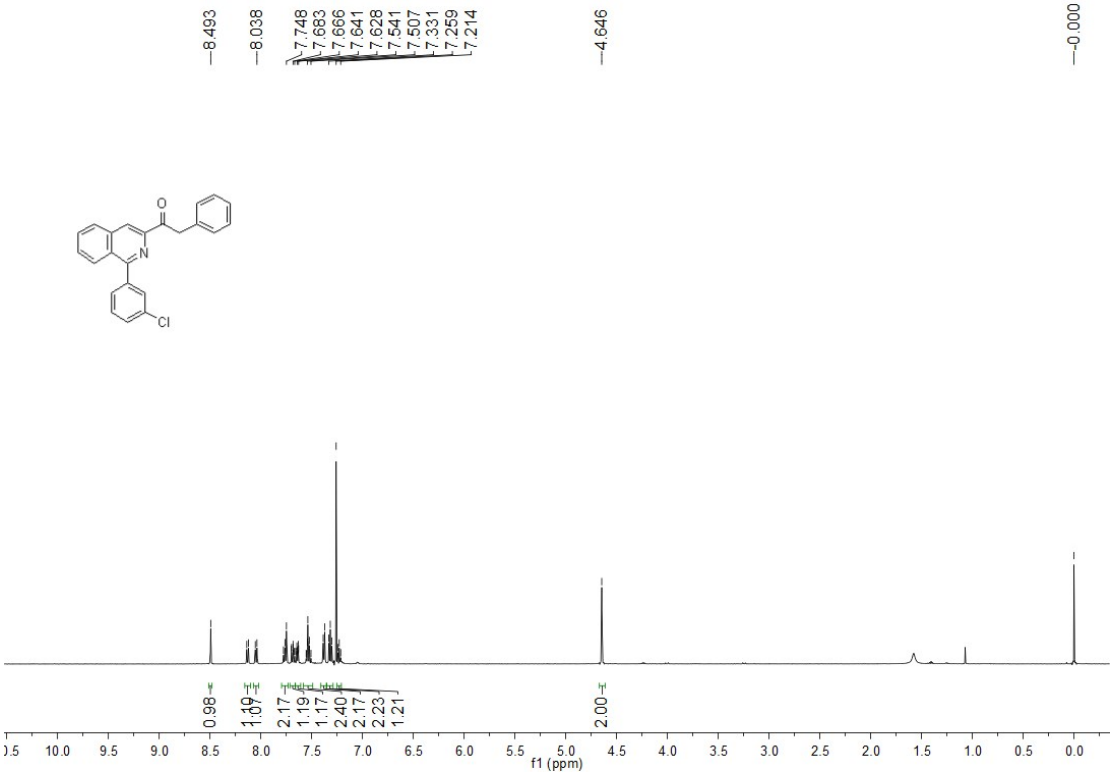

199.769
159.752
159.687
146.210
140.563
135.284
130.516
126.575
120.213
115.743
114.592
77.342
77.024
76.707
55.457
44.892
130.516
130.053
129.168
128.399
128.306
127.615
126.575
O
N
OMe
f1 (ppm)

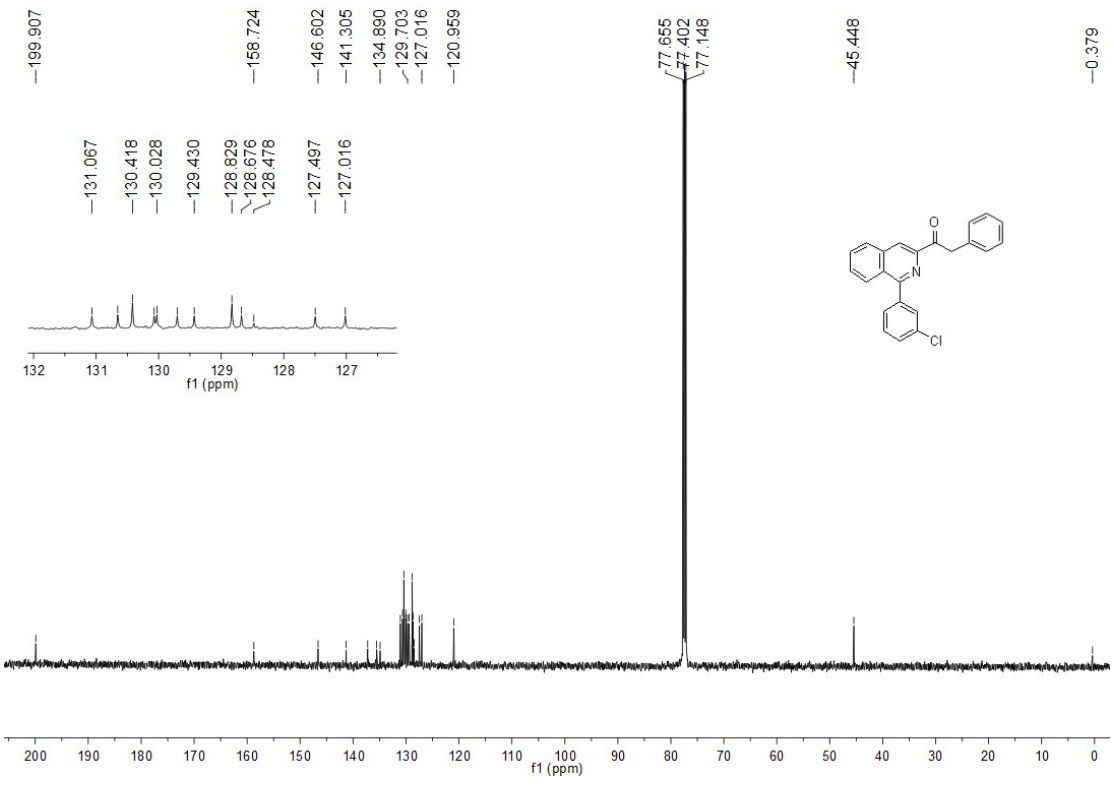
2c


8.437
8.217
8.006
7.636
7.383
7.300
7.258
7.256
7.245
7.231
7.216
7.144
7.139
7.122
4.689
3.942
0.98
1.01
1.05
3.13
1.10
2.04
2.08
1.61
2.11
1.96
3.00
f1 (ppm)

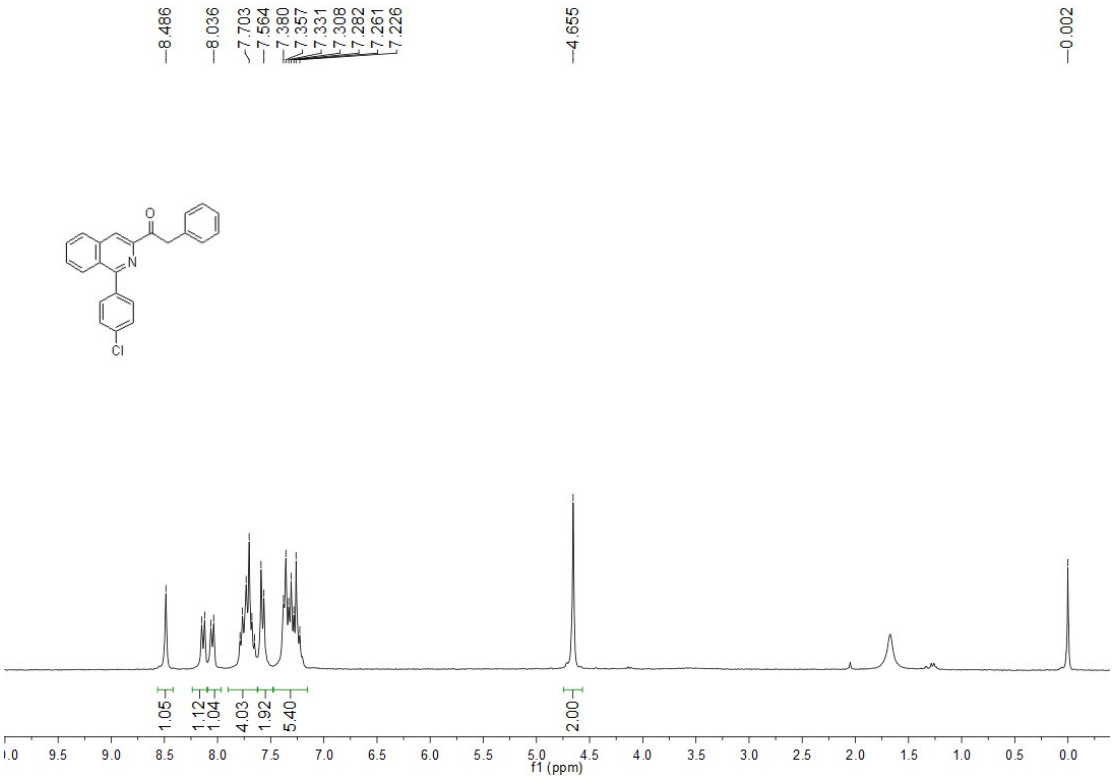

200.270
160.757
159.970
146.595
137.301
135.745
129.661
126.959
120.095
114.295
77.694
77.440
77.186
55.855
45.284
132.090
131.991
130.803
130.444
129.582
128.655
128.051
126.959
OMe
f1 (ppm)

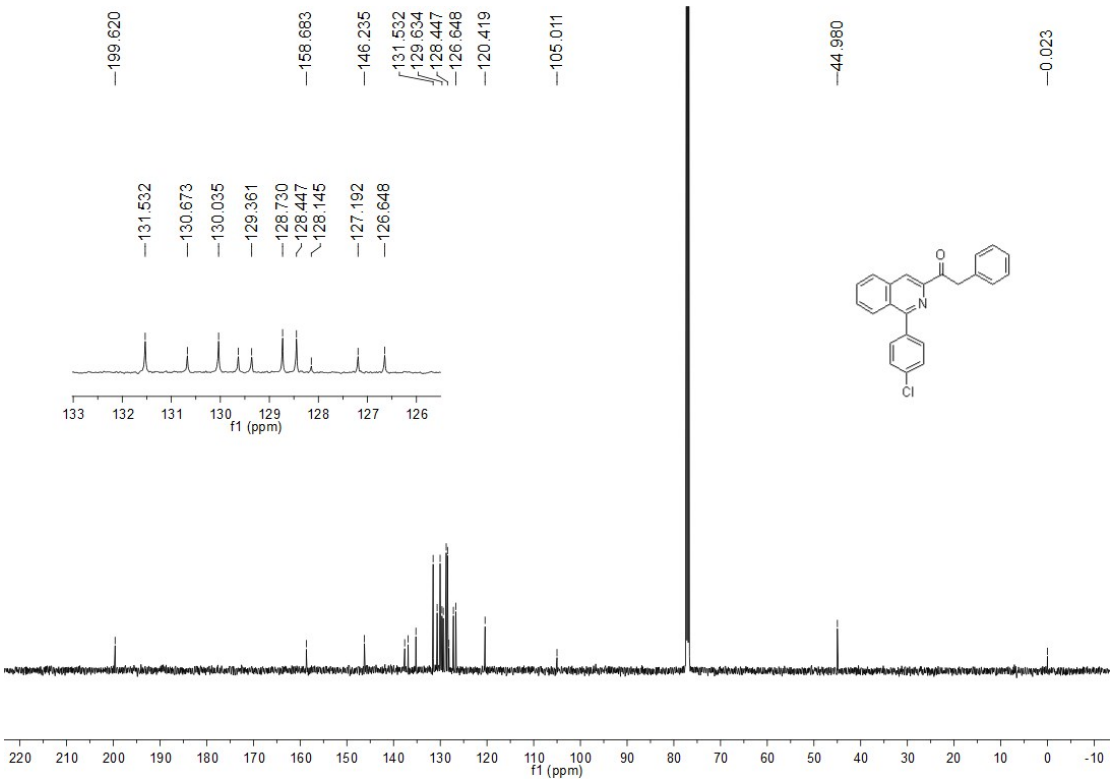
2d


8.493
8.038
7.748
7.683
7.666
7.641
7.628
7.541
7.507
7.331
7.259
7.214
4.646
0.000
0.98
1.07
2.17
1.19
1.17
2.40
2.17
2.23
1.21
2.00
f1 (ppm)

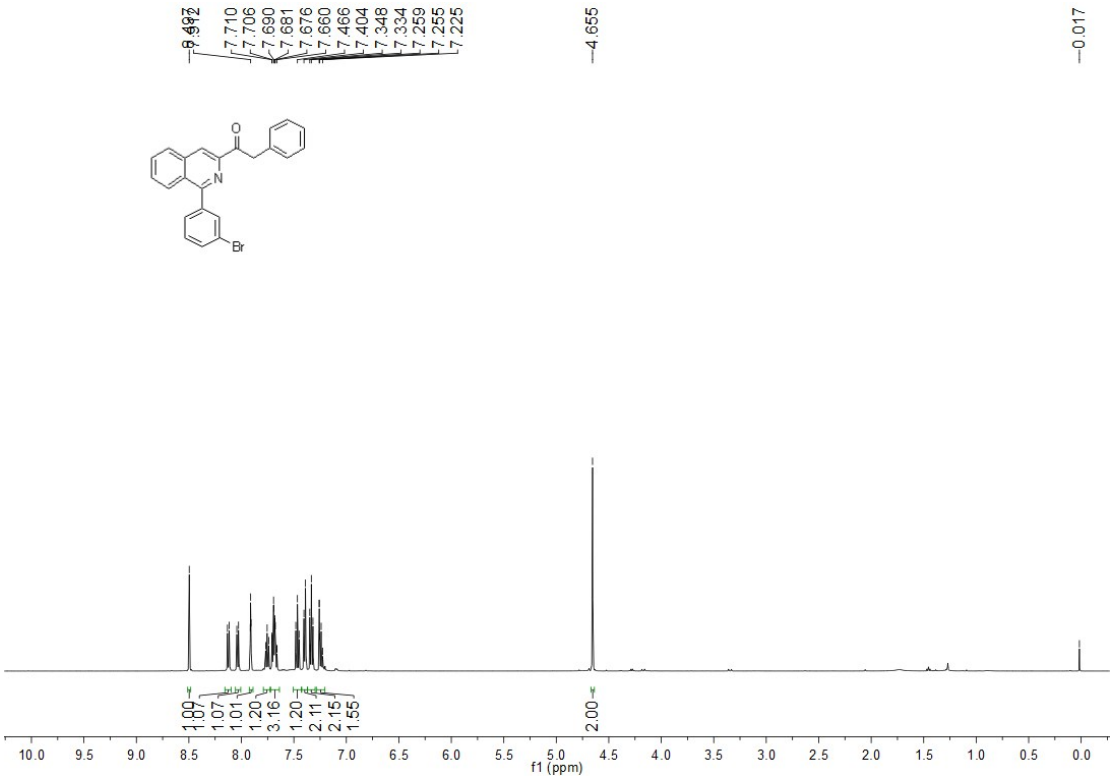

199.907
158.724
146.602
141.305
134.890
129.703
127.016
120.959
77.655
77.402
77.148
45.448
0.379
131.067
130.418
130.028
129.430
128.829
128.676
128.478
127.497
127.016
f1 (ppm)

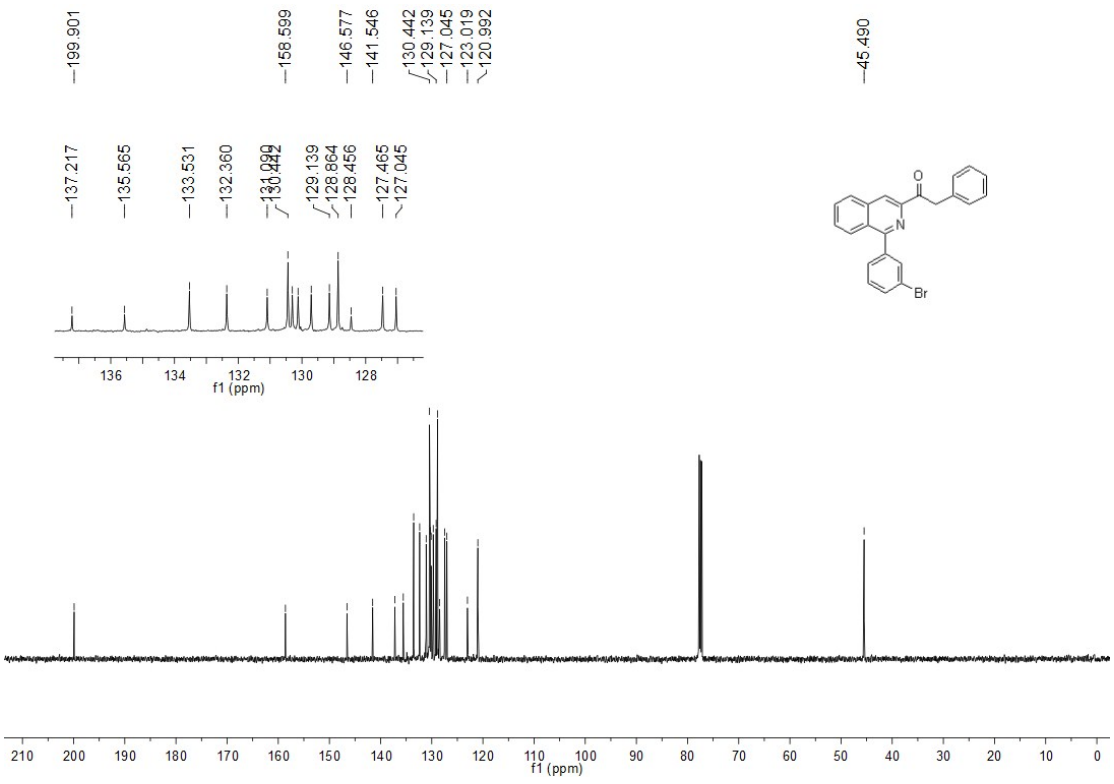
2e


8.486
8.036
7.703
7.564
7.380
7.357
7.331
7.308
7.282
7.261
7.226
4.655
0.002
O
N
Cl
1.05
1.12
1.04
4.03
1.92
5.40
2.00
f1 (ppm)

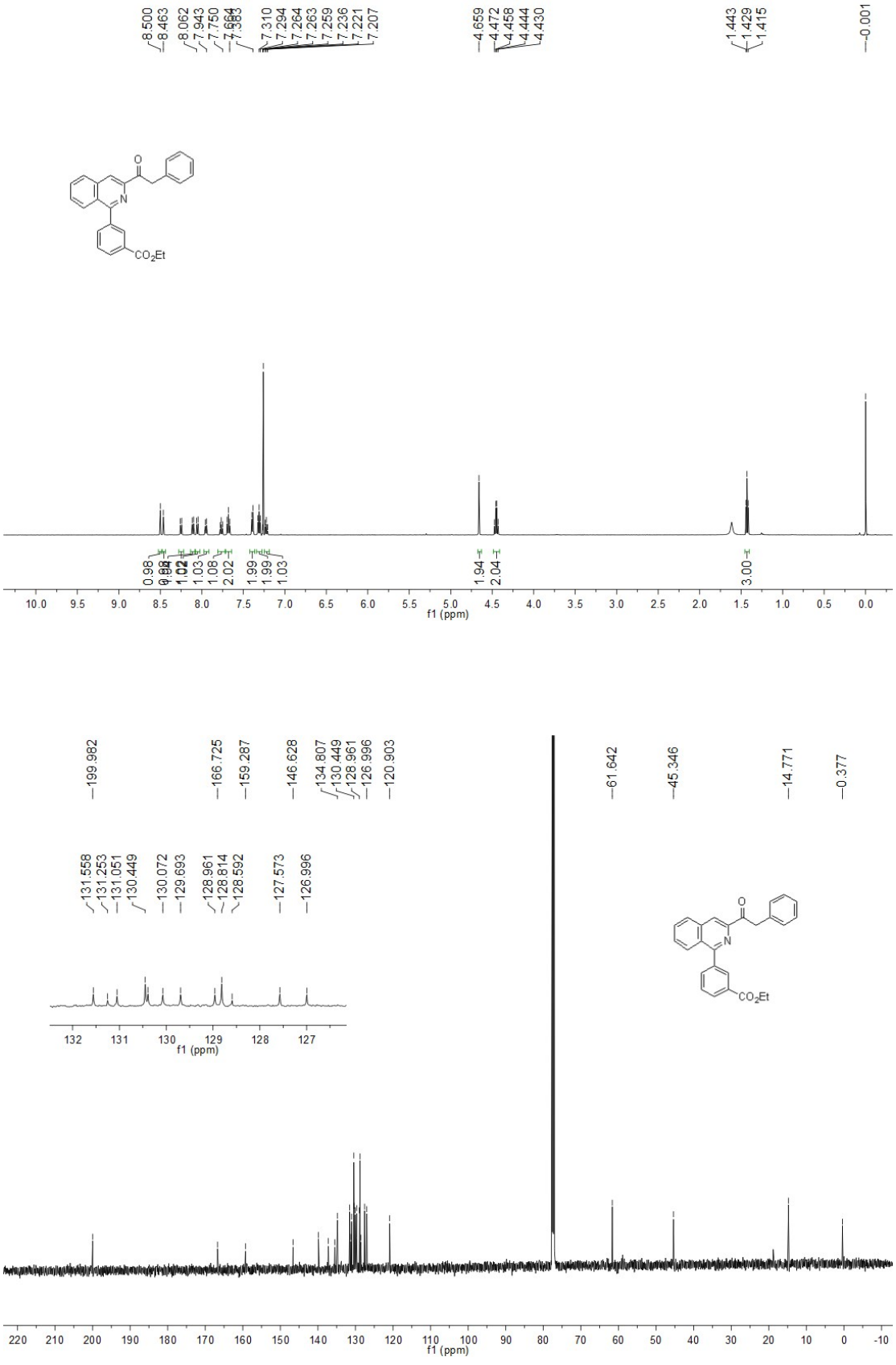

199.620
158.683
146.235
131.532
129.634
128.447
126.648
120.419
105.011
44.980
0.023
131.532
130.673
130.035
129.361
128.730
128.447
128.145
127.192
126.648
O
N
Cl
f1 (ppm)

2f

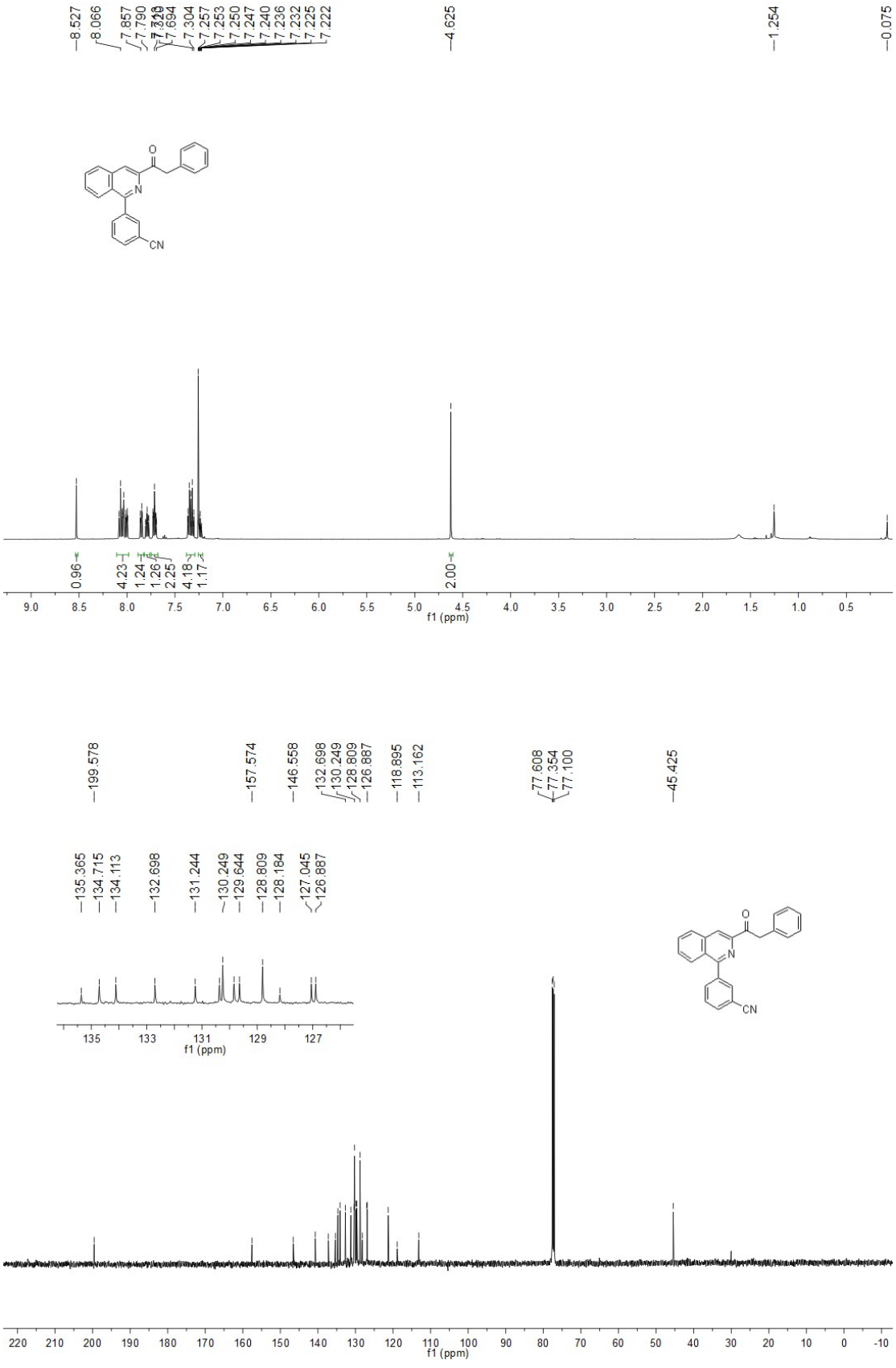

9.497
7.710
7.706
7.690
7.681
7.676
7.660
7.466
7.404
7.348
7.334
7.259
7.255
7.225
4.655
0.017
O
N
Br
1.00
1.07
1.01
1.20
3.16
1.20
2.11
2.15
1.55
2.00
f1 (ppm)


199.901
158.599
146.577
141.546
130.442
129.139
127.045
123.019
120.992
45.490
137.217
135.565
133.531
132.360
131.090
130.442
129.139
128.864
128.456
127.465
127.045
O
N
Br
136
134
132
130
128
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

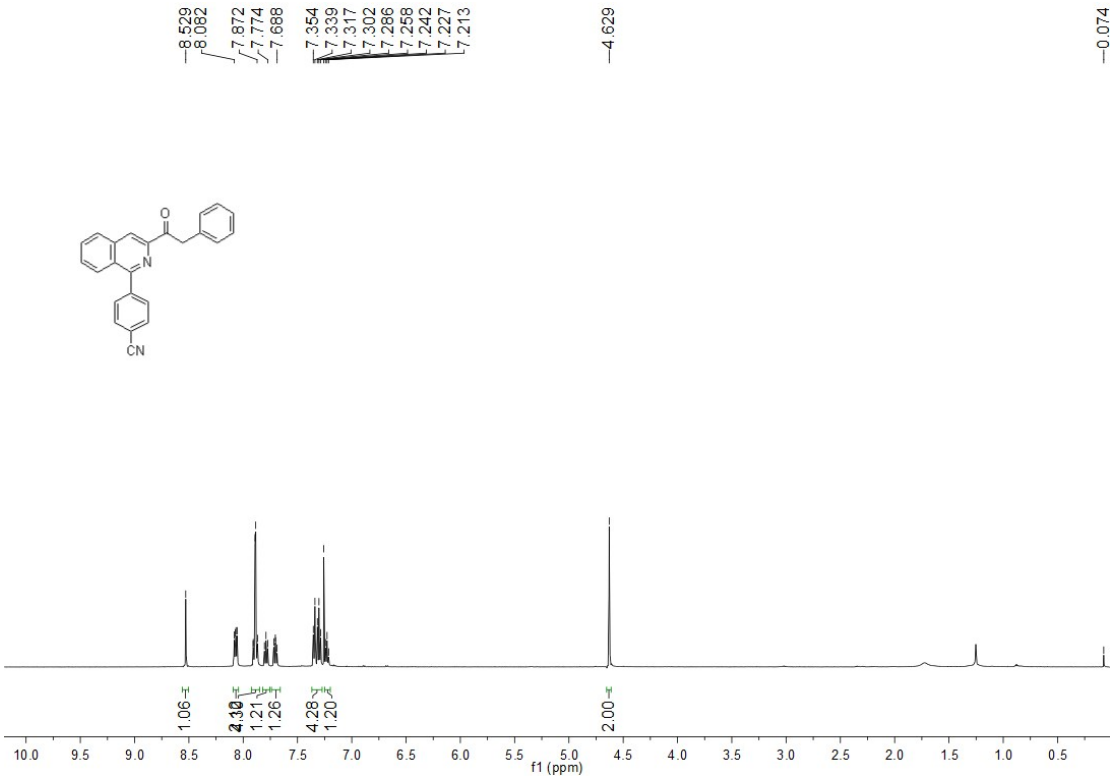
2g

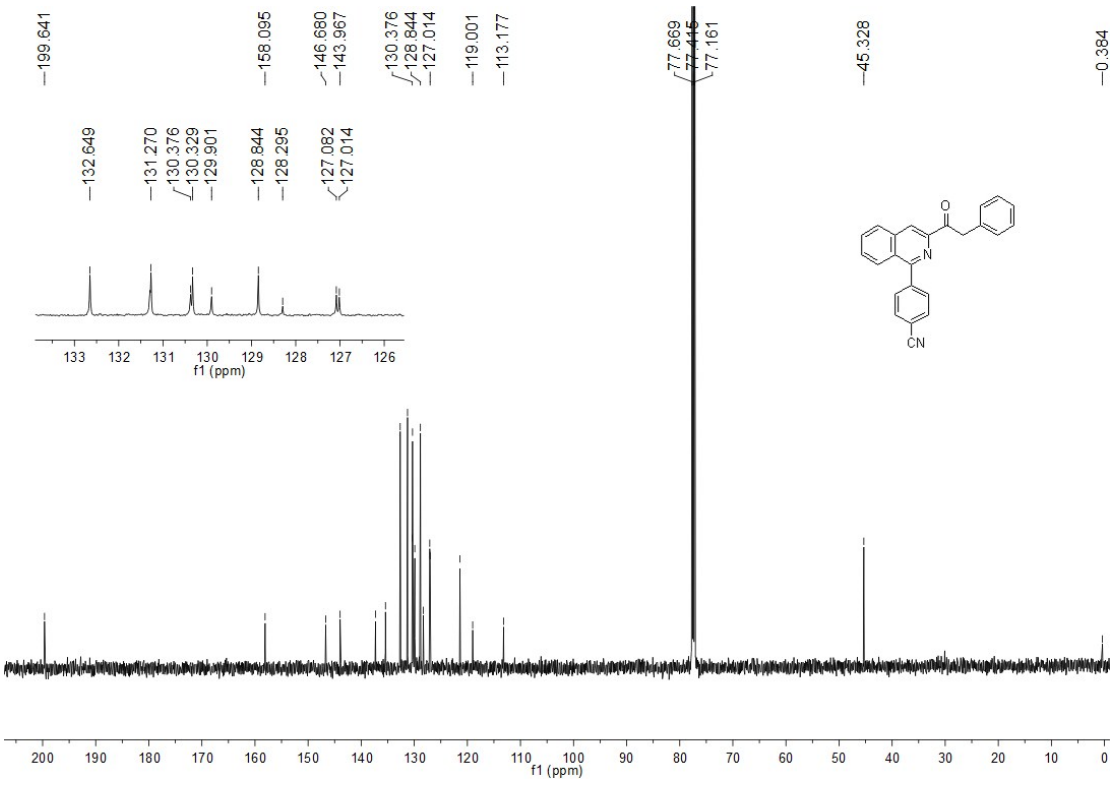

8.500
8.463
8.062
7.943
7.750
7.310
7.294
7.264
7.263
7.259
7.236
7.221
7.207
4.659
4.472
4.458
4.444
4.430
1.443
1.429
1.415
-0.001
O
N
CO2Et
0.98
1.03
1.08
2.02
1.99
1.99
1.03
1.94
2.04
3.00
f1 (ppm)
199.982
166.725
159.287
146.628
134.807
130.449
128.961
126.996
120.903
61.642
45.346
14.771
0.377
131.558
131.253
131.051
130.449
130.072
129.693
128.961
128.814
128.592
127.573
126.996
f1 (ppm)

2h

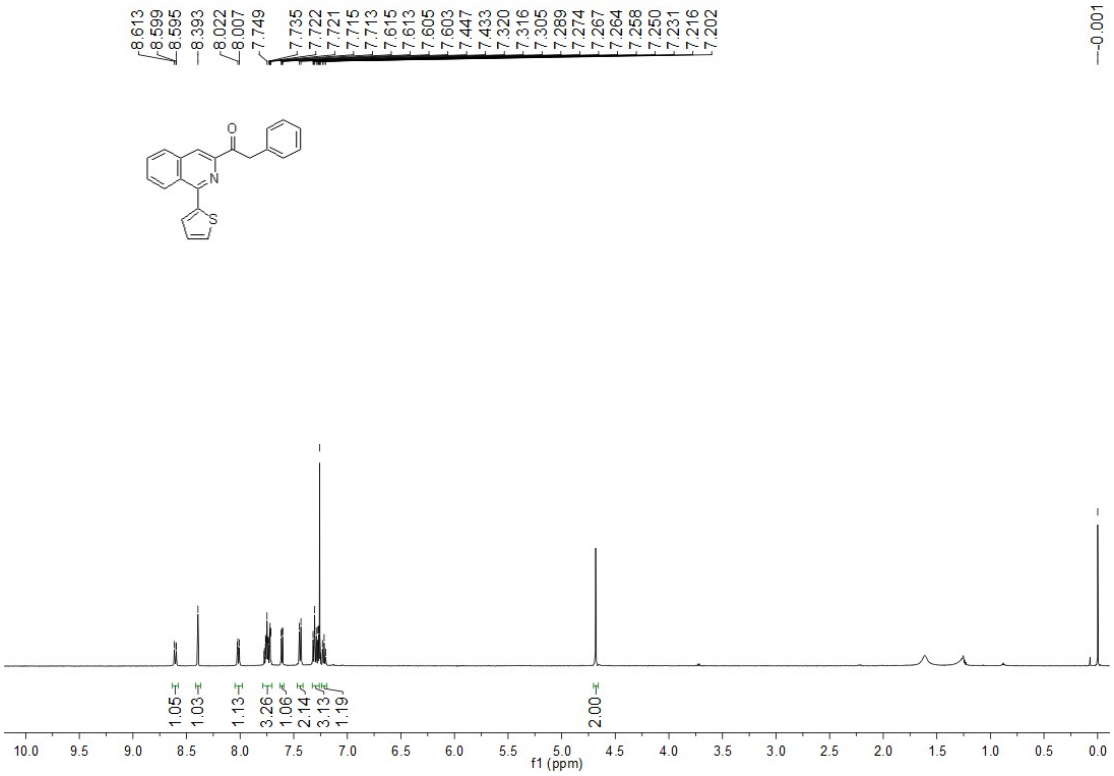

8.527
8.066
7.857
7.790
7.694
7.304
7.257
7.253
7.250
7.247
7.240
7.236
7.232
7.225
7.222
4.625
1.254
0.075
O
N
CN
0.96
4.23
1.24
1.26
2.25
4.18
1.17
2.00
f1 (ppm)
199.578
157.574
146.558
132.698
130.249
128.809
126.887
118.895
113.162
77.608
77.354
77.100
45.425
135.365
134.715
134.113
132.698
131.244
130.249
129.644
128.809
128.184
127.045
126.887
f1 (ppm)

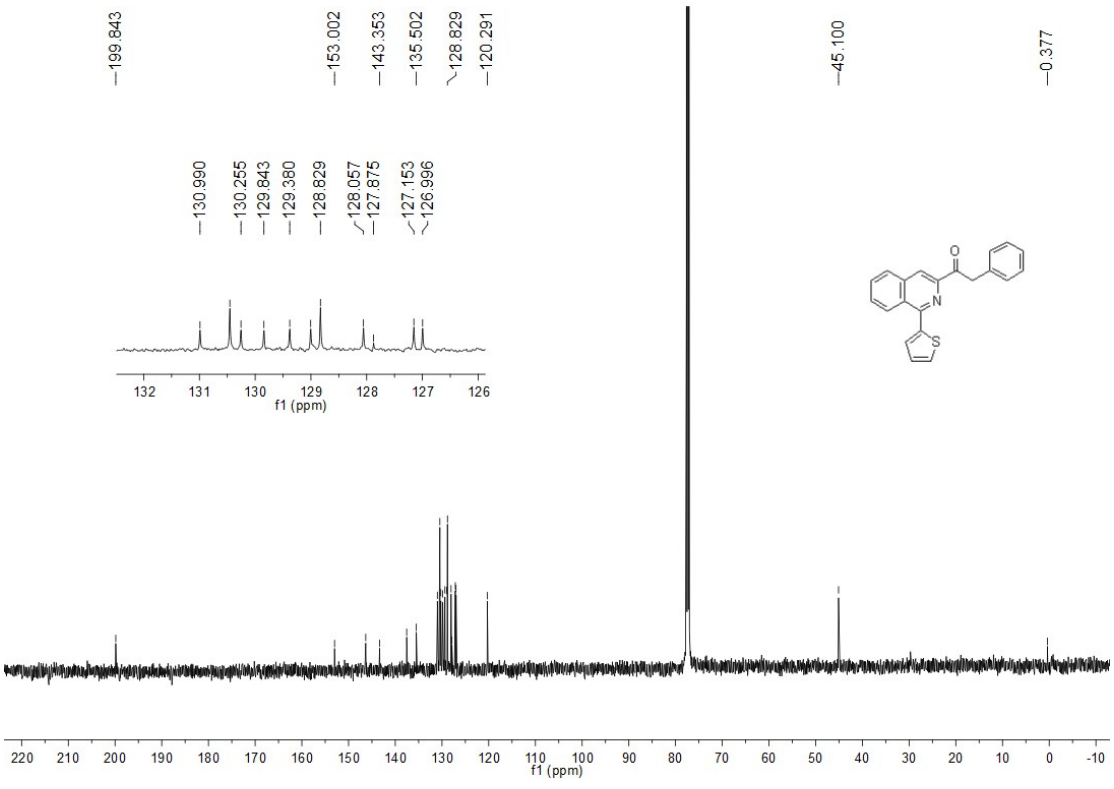
2i


8.529
8.082
7.872
7.774
7.688
7.354
7.339
7.317
7.302
7.286
7.258
7.242
7.227
7.213
4.629
0.074
O
N
CN
1.06
1.21
1.26
4.28
1.20
2.00
f1 (ppm)

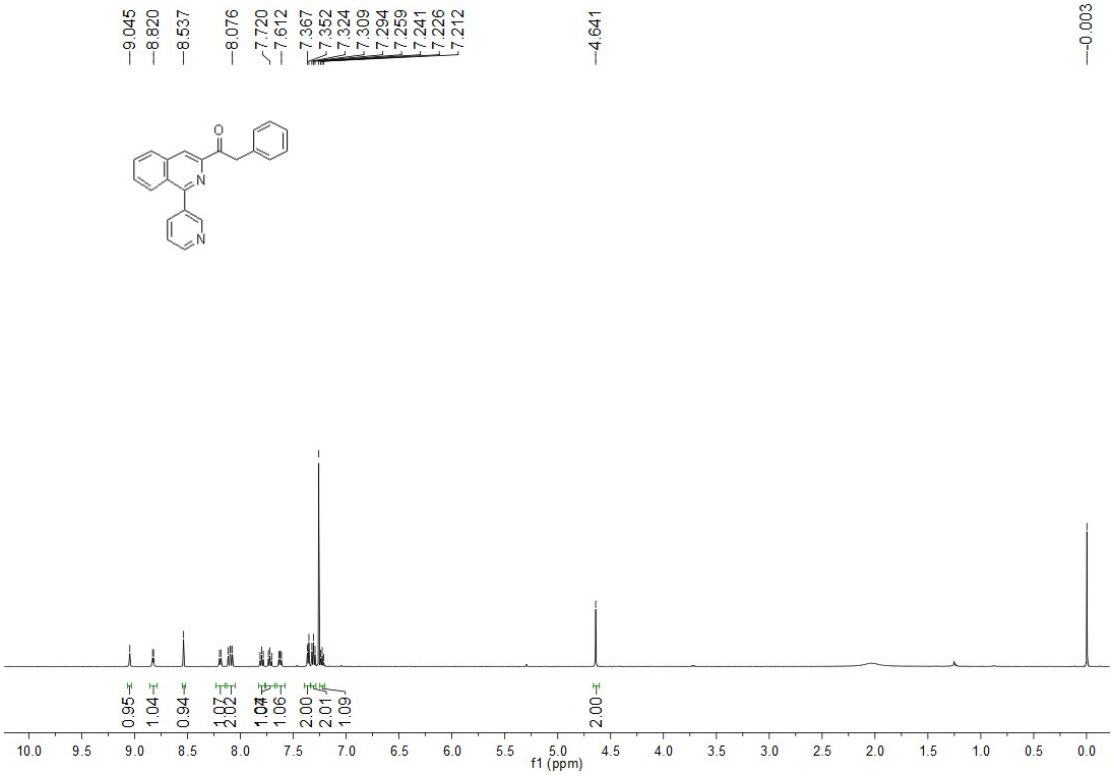

199.641
158.095
146.680
143.967
130.376
128.844
127.014
119.001
113.177
77.669
77.416
77.161
45.328
0.384
132.649
131.270
130.376
130.329
129.901
128.844
128.295
127.082
127.014
O
N
CN
f1 (ppm)

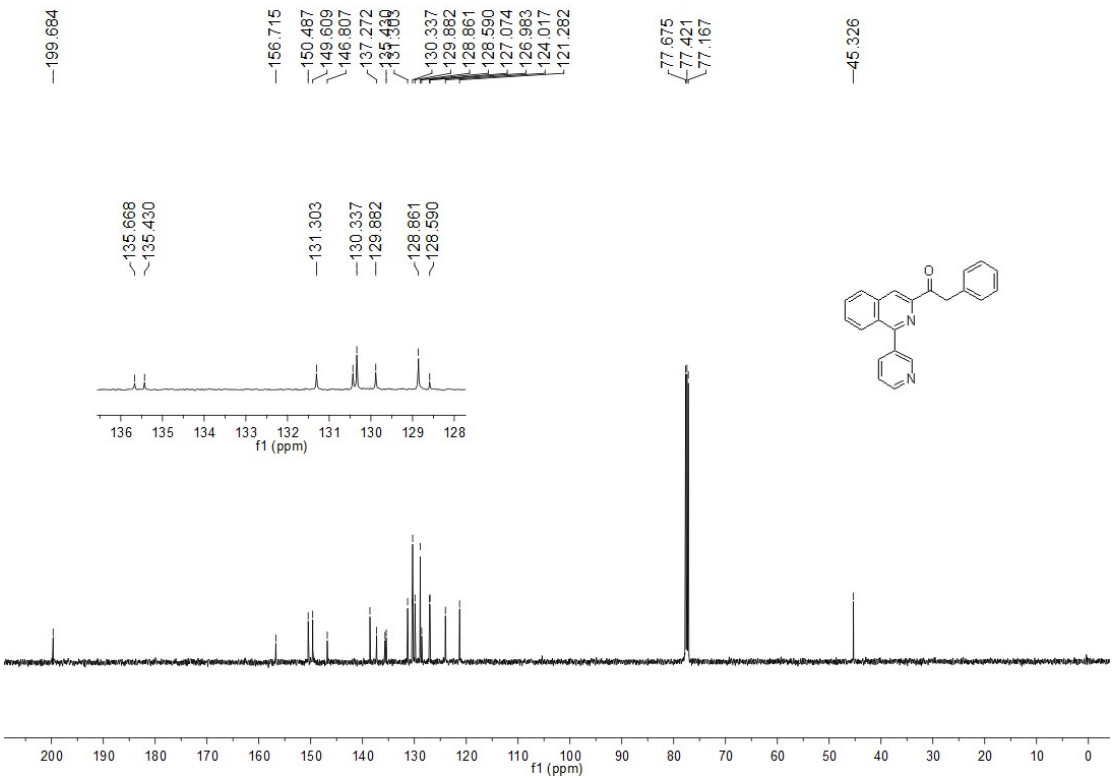
2j


8.613
8.599
8.595
8.393
8.022
8.007
7.749
7.735
7.722
7.721
7.715
7.713
7.615
7.613
7.605
7.603
7.447
7.433
7.320
7.316
7.305
7.289
7.274
7.267
7.264
7.258
7.250
7.231
7.216
7.202
0.001
1.05
1.03
1.13
3.26
1.06
2.14
3.13
1.19
2.00
f1 (ppm)

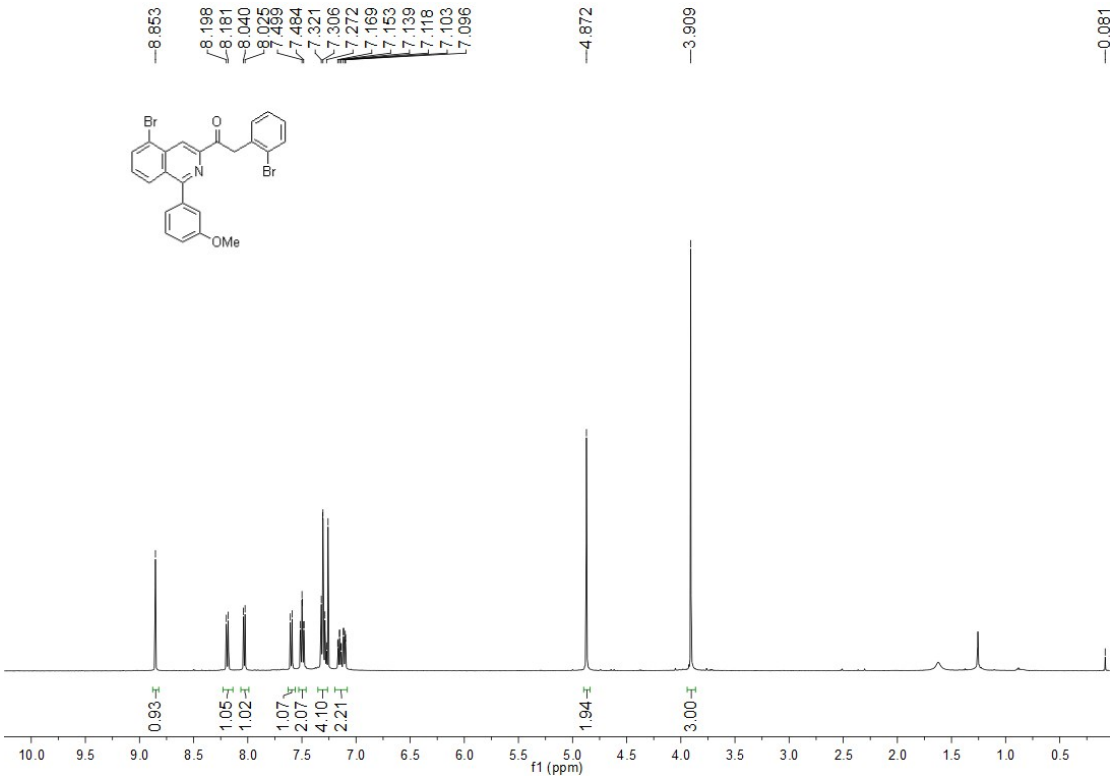

199.843
153.002
143.353
135.502
128.829
120.291
45.100
0.377
130.990
130.255
129.843
129.380
128.829
128.057
127.875
127.153
126.996
f1 (ppm)

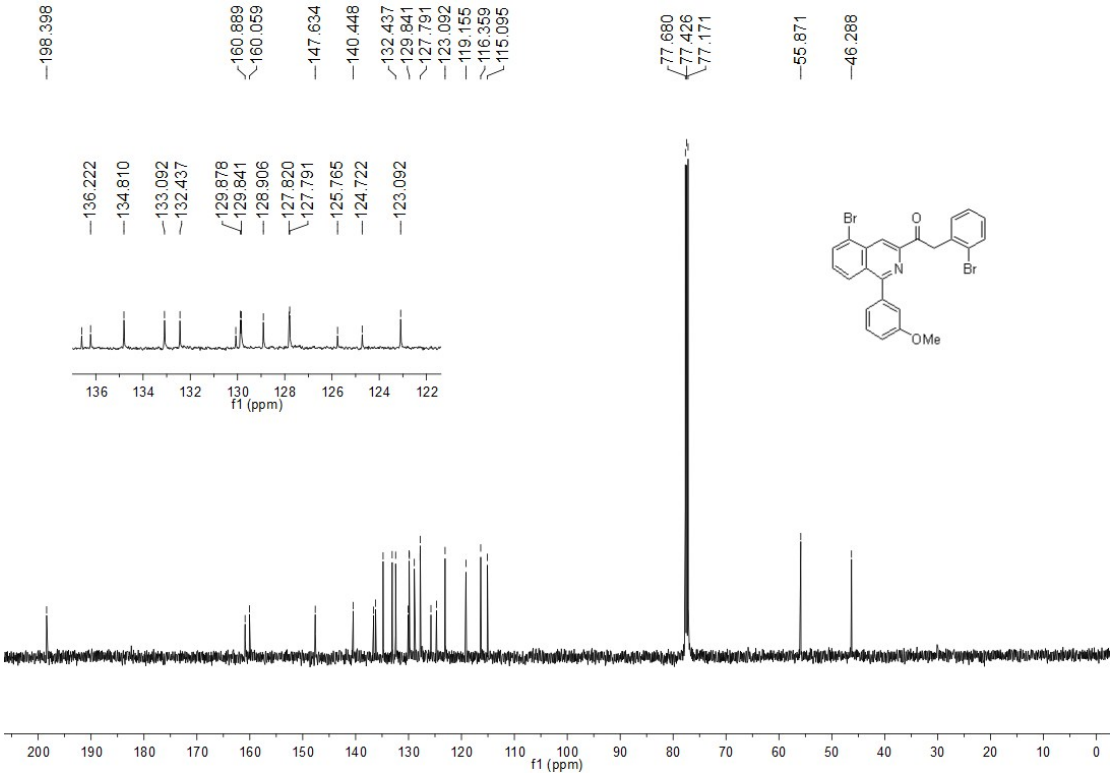
2k


9.045
8.820
8.537
8.076
7.720
7.612
7.367
7.352
7.324
7.309
7.294
7.259
7.241
7.226
7.212
4.641
0.003
0.95
1.04
0.94
1.07
2.02
1.04
1.06
2.00
2.01
1.09
2.00
f1 (ppm)

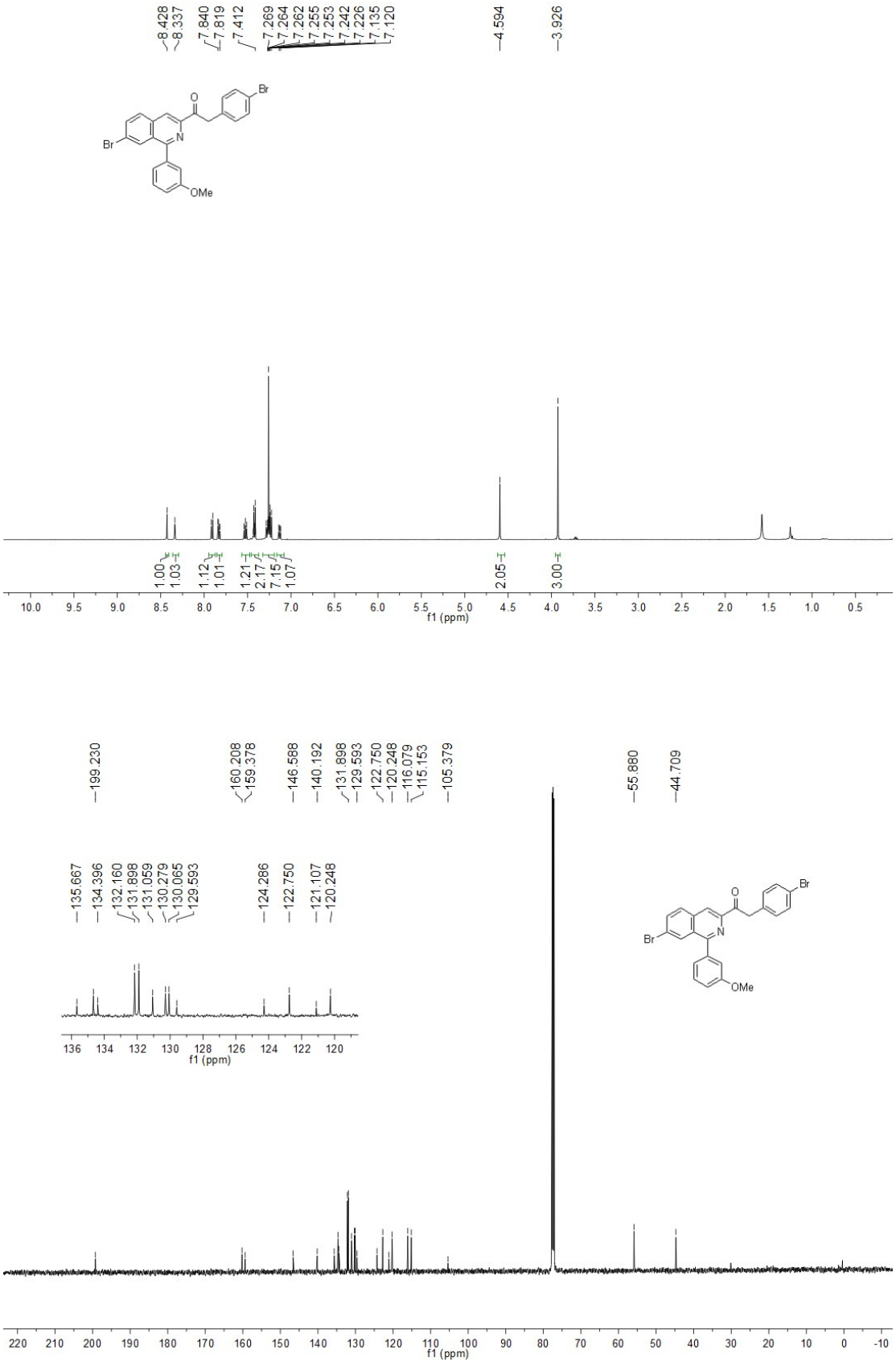

199.684
156.715
150.487
149.609
146.807
137.272
135.668
135.430
131.303
130.337
129.882
128.861
128.590
127.074
126.983
124.017
121.282
77.675
77.421
77.167
45.326
f1 (ppm)

2l

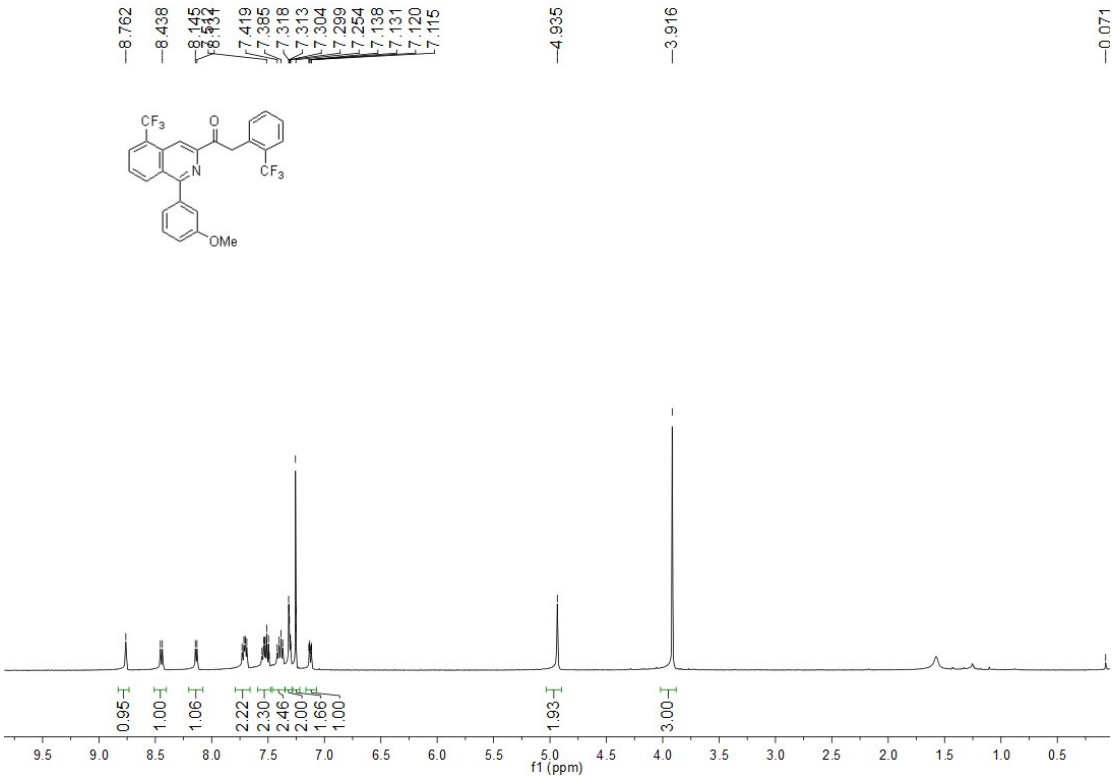

8.853
8.198
8.181
8.040
8.025
7.499
7.484
7.321
7.306
7.272
7.169
7.153
7.139
7.118
7.103
7.096
4.872
3.909
0.081
Br
O
N
Br
OMe
0.93
1.05
1.02
1.07
2.07
4.10
2.21
1.94
3.00
f1 (ppm)

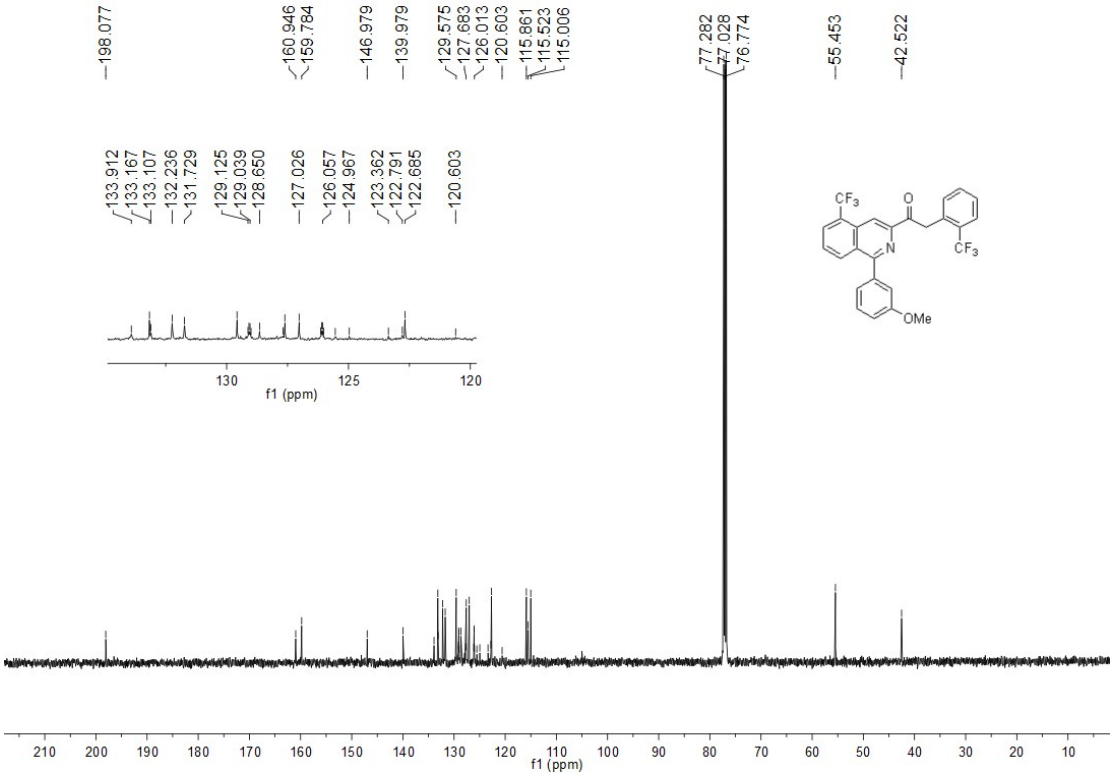

198.398
160.889
160.059
147.634
140.448
132.437
129.841
127.791
123.092
119.155
116.359
115.095
77.680
77.426
77.171
55.871
46.288
136.222
134.810
133.092
132.437
129.878
129.841
128.906
127.820
127.791
125.765
124.722
123.092
f1 (ppm)
Br
O
N
Br
OMe
f1 (ppm)

2m

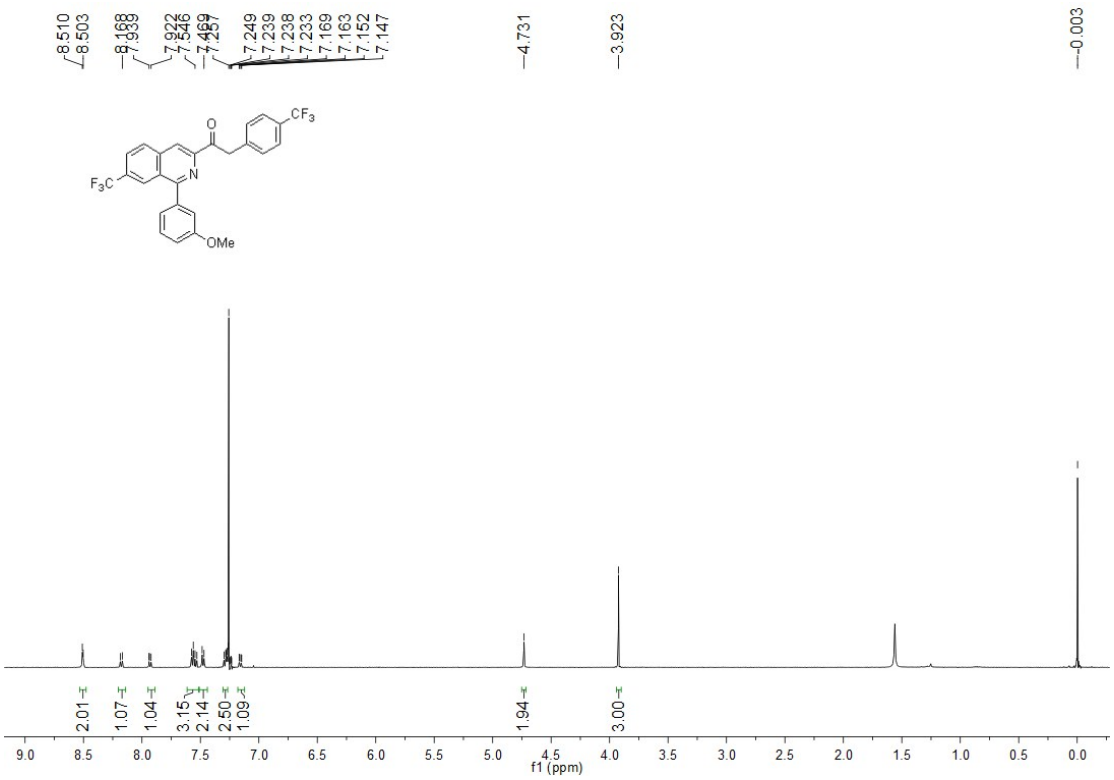

8.428
8.337
7.840
7.819
7.412
7.269
7.264
7.262
7.255
7.253
7.242
7.226
7.135
7.120
4.594
3.926
Br
O
N
Br
OMe
1.00
1.03
1.12
1.01
1.21
2.17
7.15
1.07
2.05
3.00
f1 (ppm)
199.230
160.208
159.378
146.588
140.192
131.898
129.593
122.750
120.248
116.079
115.153
105.379
55.880
44.709
135.667
134.396
132.160
131.898
131.059
130.279
130.065
129.593
124.286
122.750
121.107
120.248
f1 (ppm)

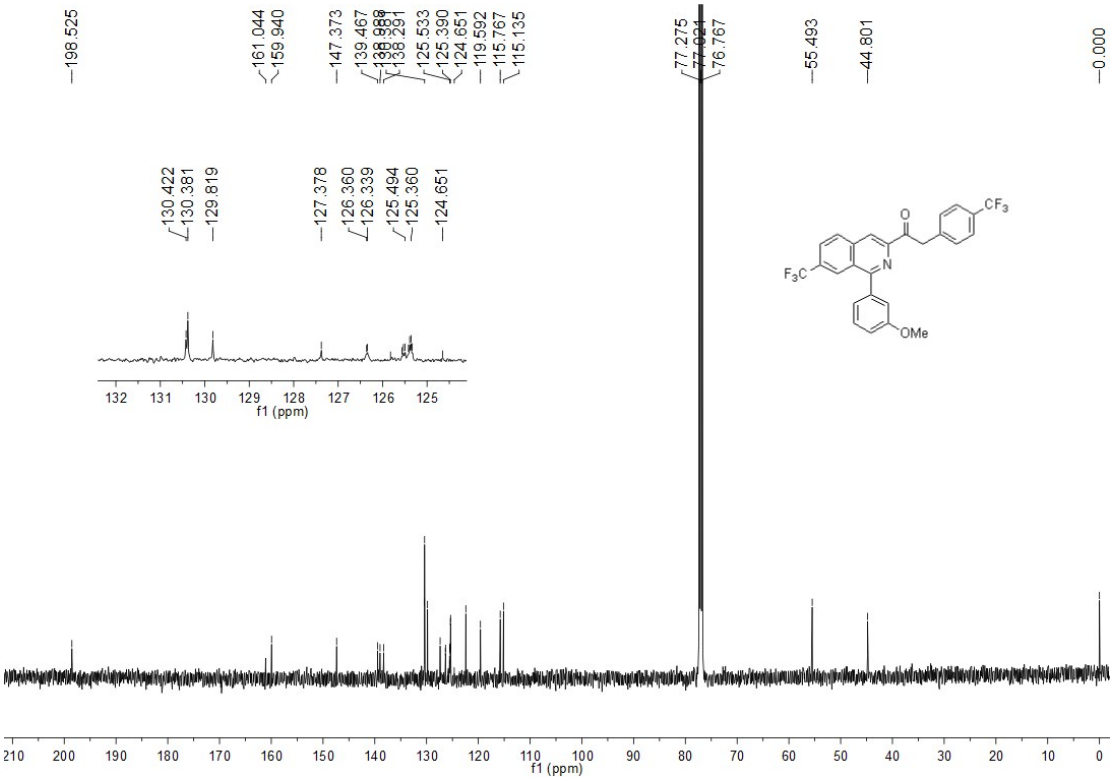
2n


8.762
8.438
8.145
8.134
7.419
7.385
7.318
7.313
7.304
7.299
7.254
7.138
7.131
7.120
7.115
4.935
3.916
0.071
CF3
O
N
CF3
OMe
0.95
1.00
1.06
2.22
2.30
2.46
2.00
1.66
1.00
1.93
3.00
f1 (ppm)

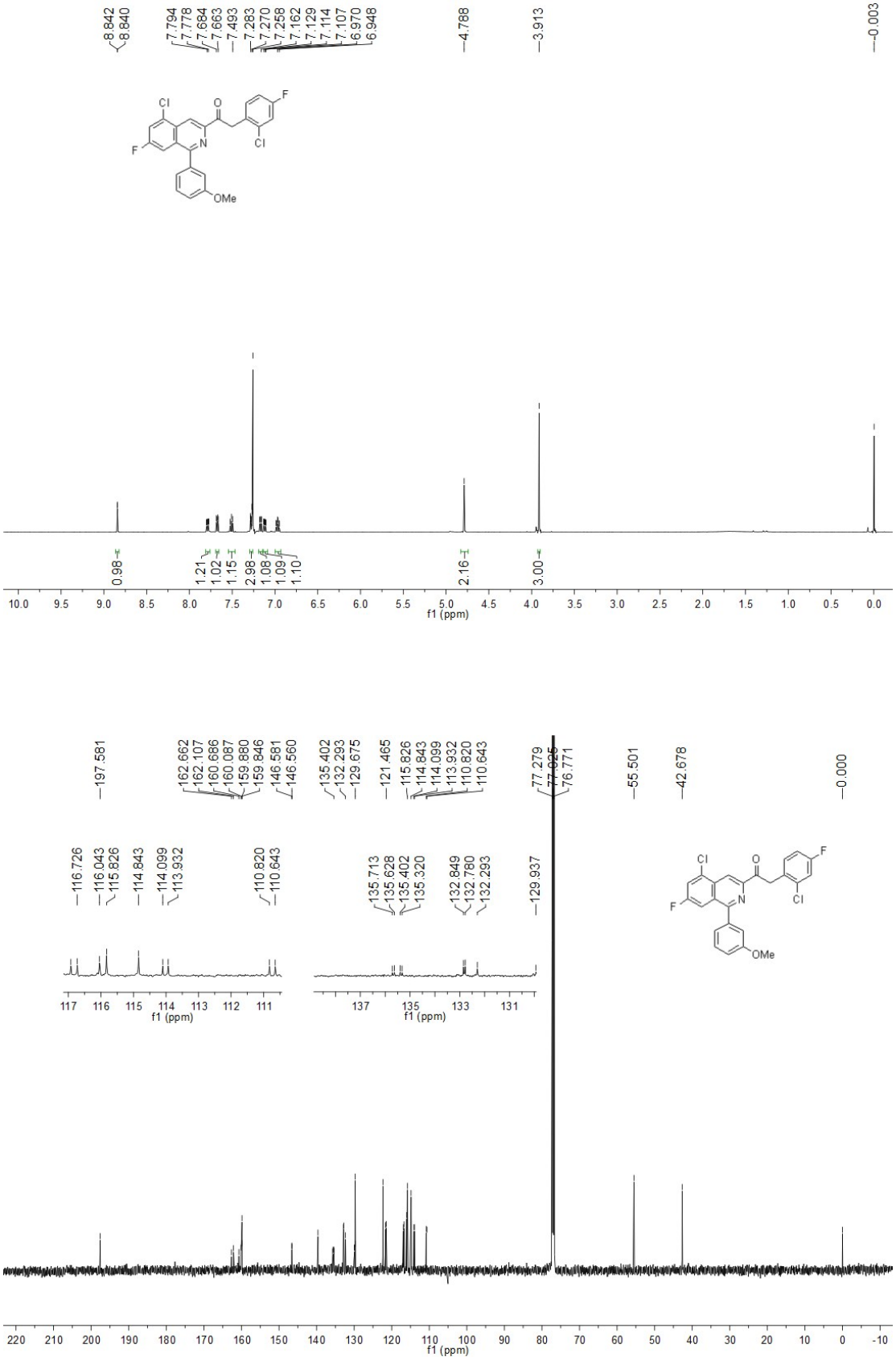

198.077
160.946
159.784
146.979
139.979
129.575
127.683
126.013
120.603
115.861
115.523
115.006
77.282
77.028
76.774
55.453
42.522
133.912
133.167
133.107
132.236
131.729
129.125
129.039
128.650
127.026
126.057
124.967
123.362
122.791
122.685
120.603
CF3
O
N
CF3
OMe
130
125
120
f1 (ppm)
f1 (ppm)

2o

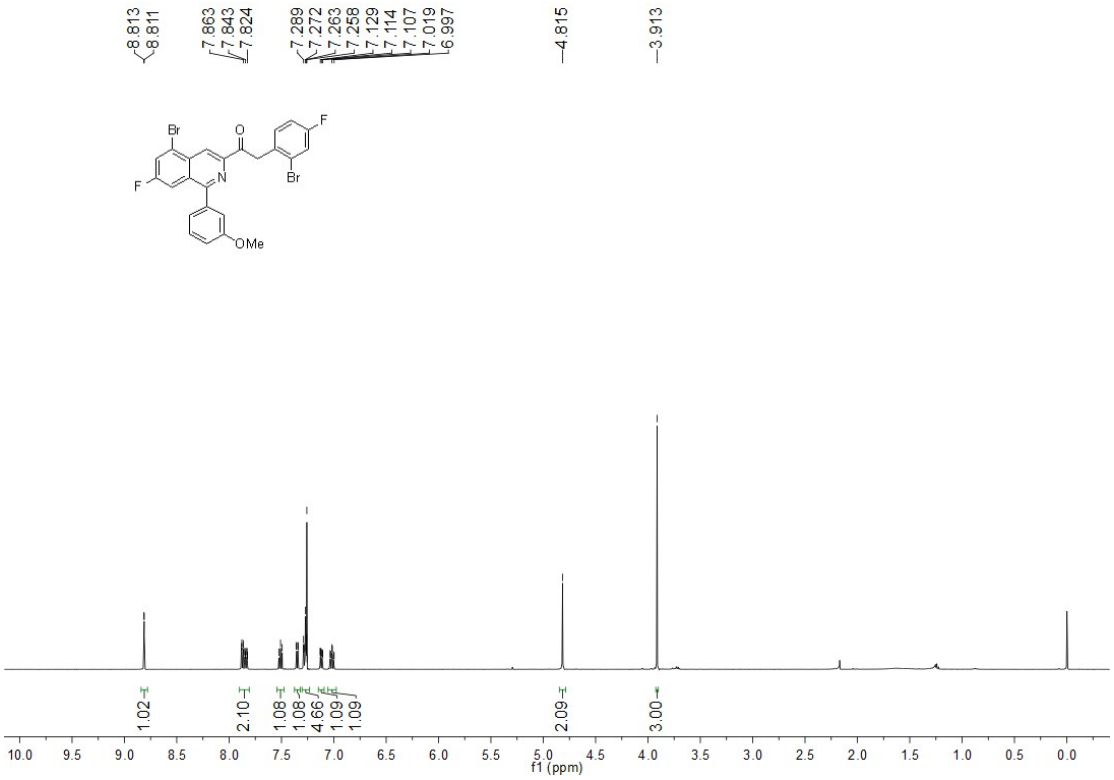

8.510
8.503
8.168
7.939
7.922
7.546
7.469
7.257
7.249
7.239
7.238
7.233
7.169
7.163
7.152
7.147
4.731
3.923
0.003
CF3
O
N
F3C
OMe
2.01
1.07
1.04
3.15
2.14
2.50
1.09
1.94
3.00
f1 (ppm)

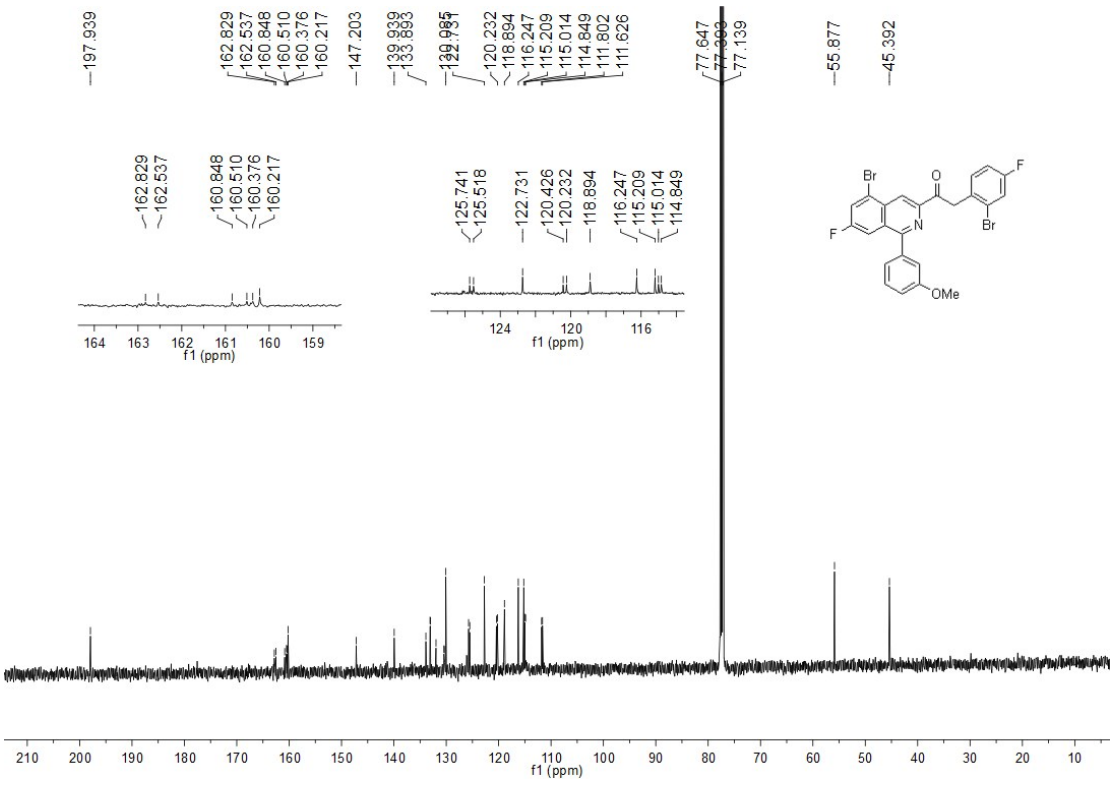

198.525
161.044
159.940
147.373
139.467
125.533
125.390
124.651
119.592
115.767
115.135
77.275
77.024
76.767
55.493
44.801
0.000
130.422
130.381
129.819
127.378
126.360
126.339
125.494
125.360
124.651
CF3
O
N
F3C
OMe
f1 (ppm)
f1 (ppm)

2p

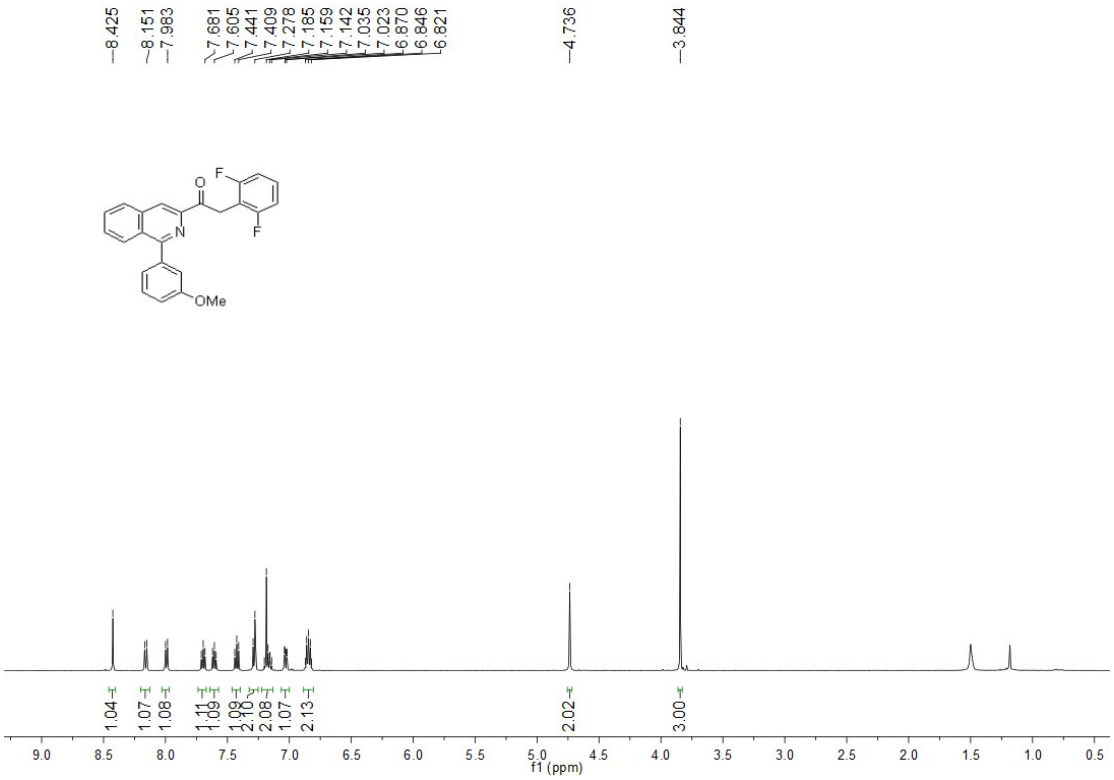

8.842
8.840
7.794
7.778
7.684
7.663
7.493
7.283
7.270
7.258
7.162
7.129
7.114
7.107
6.970
6.948
4.788
3.913
0.003
Cl
O
F
F
Cl
N
OMe
0.98
1.21
1.02
1.15
2.98
1.08
1.09
1.10
2.16
3.00
f1 (ppm)
197.581
162.662
162.107
160.686
160.087
159.880
159.846
146.581
146.560
135.402
132.293
129.675
121.465
115.826
114.843
114.099
113.932
110.820
110.643
77.279
77.025
76.771
55.501
42.678
0.000
116.726
116.043
115.826
114.843
114.099
113.932
110.820
110.643
135.713
135.628
135.402
135.320
132.849
132.780
132.293
129.937
f1 (ppm)
f1 (ppm)

2q


8.813
8.811
7.863
7.843
7.824
7.289
7.272
7.263
7.258
7.129
7.114
7.107
7.019
6.997
4.815
3.913
Br
O
F
F
Br
N
OMe
1.02
2.10
1.08
1.08
4.66
1.09
1.09
2.09
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.939
162.829
162.537
160.848
160.510
160.376
160.217
147.203
139.939
133.993
120.232
118.894
116.247
115.209
115.014
114.849
111.802
111.626
77.647
77.383
77.139
55.877
45.392
Br
O
F
F
Br
N
OMe
164 163 162 161 160 159
f1 (ppm)
124 120 116
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2r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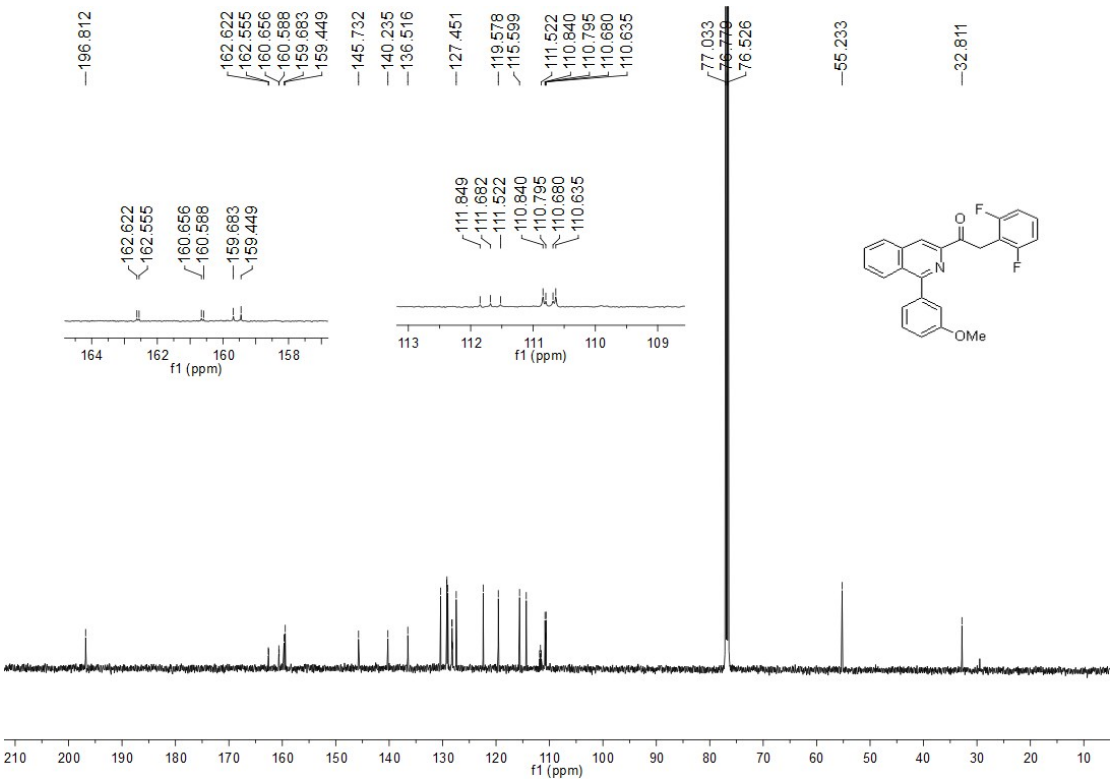
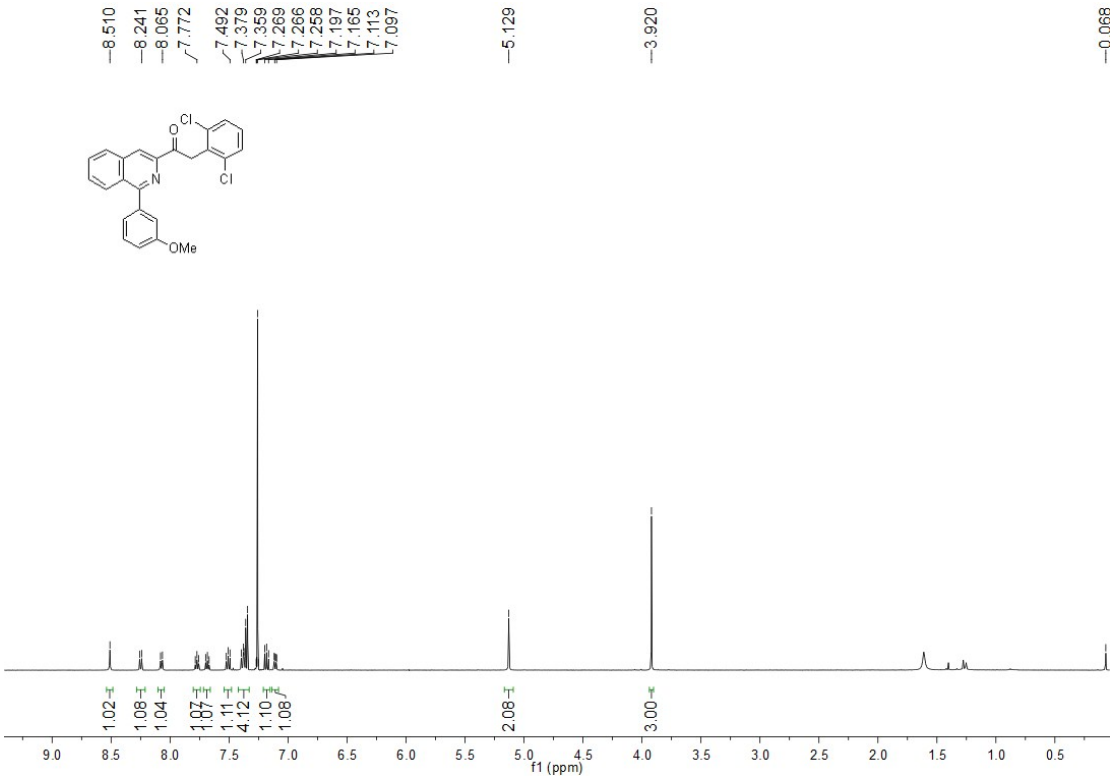
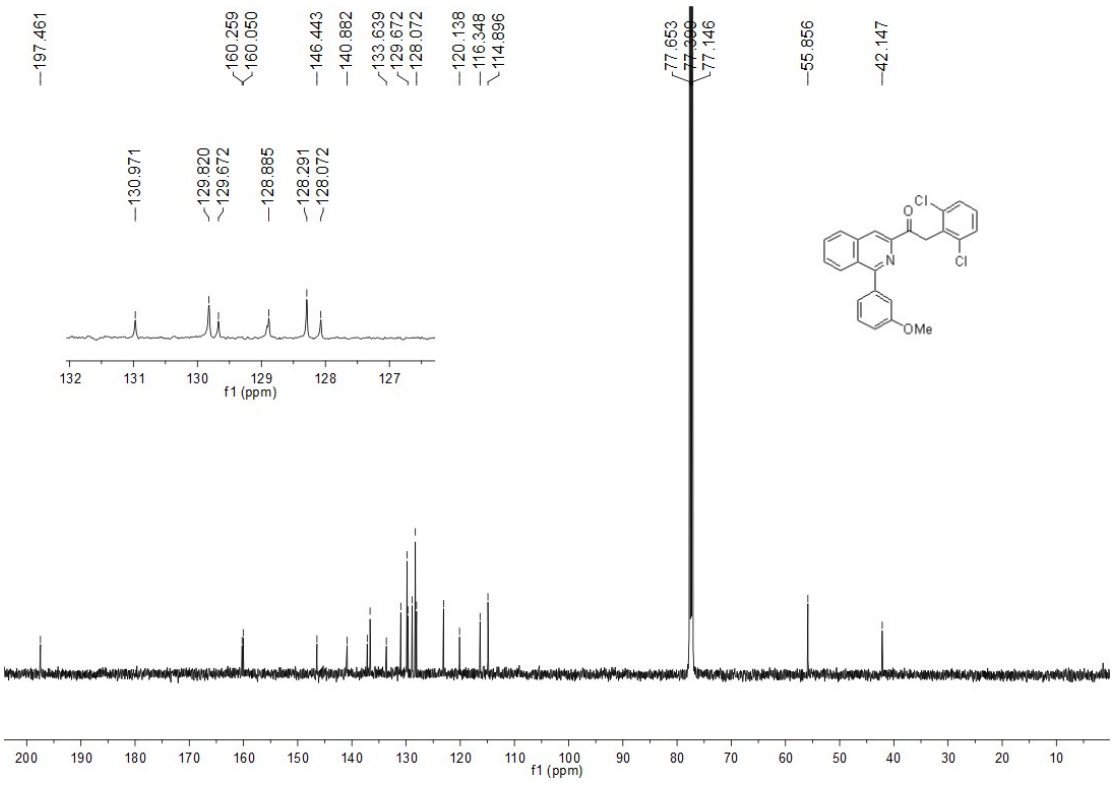
8.151
7.983
7.681
7.605
7.441
7.409
7.278
7.185
7.159
7.142
7.035
7.023
6.870
6.846
6.821
4.736
3.844
F
O
N
F
OMe
1.04
1.07
1.08
1.11
1.09
1.09
2.10
2.08
1.07
2.13
2.02
3.00
f1 (ppm)

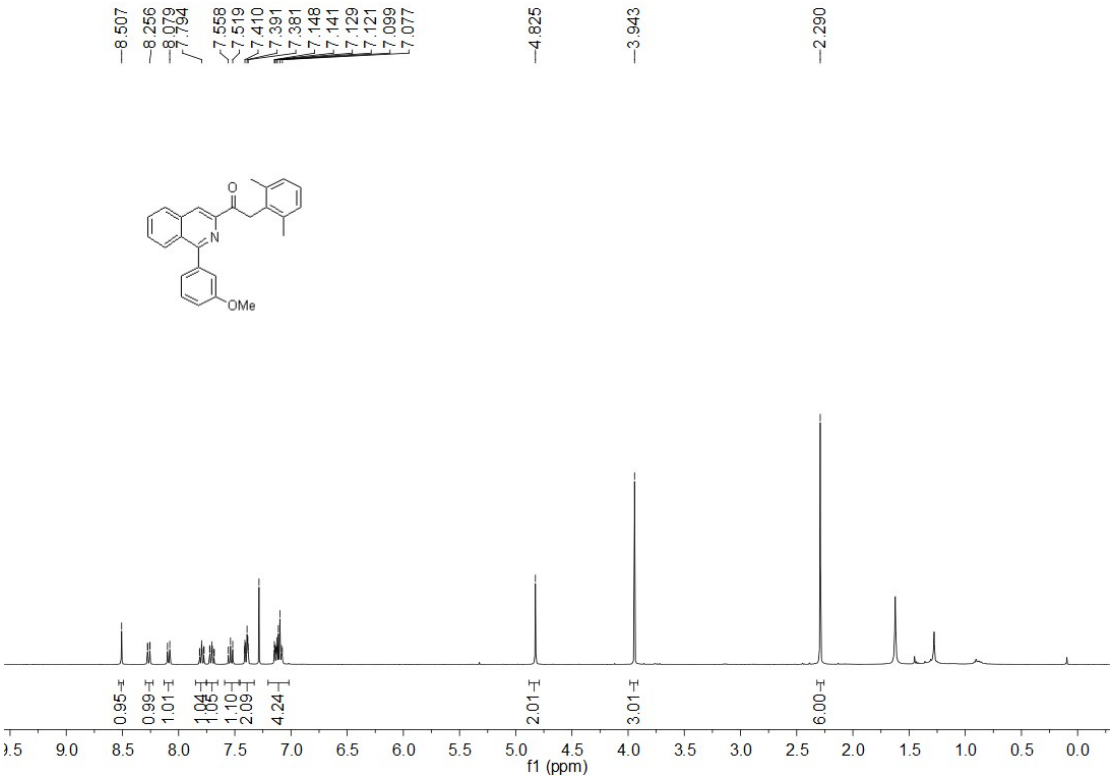

196.812
162.622
162.555
160.656
160.588
159.683
159.449
145.732
140.235
136.516
127.451
119.578
115.599
111.522
110.840
110.795
110.680
110.635
77.033
76.770
76.526
55.233
32.811
111.849
111.682
111.522
110.840
110.795
110.680
110.635
F
O
N
F
OMe
f1 (ppm)

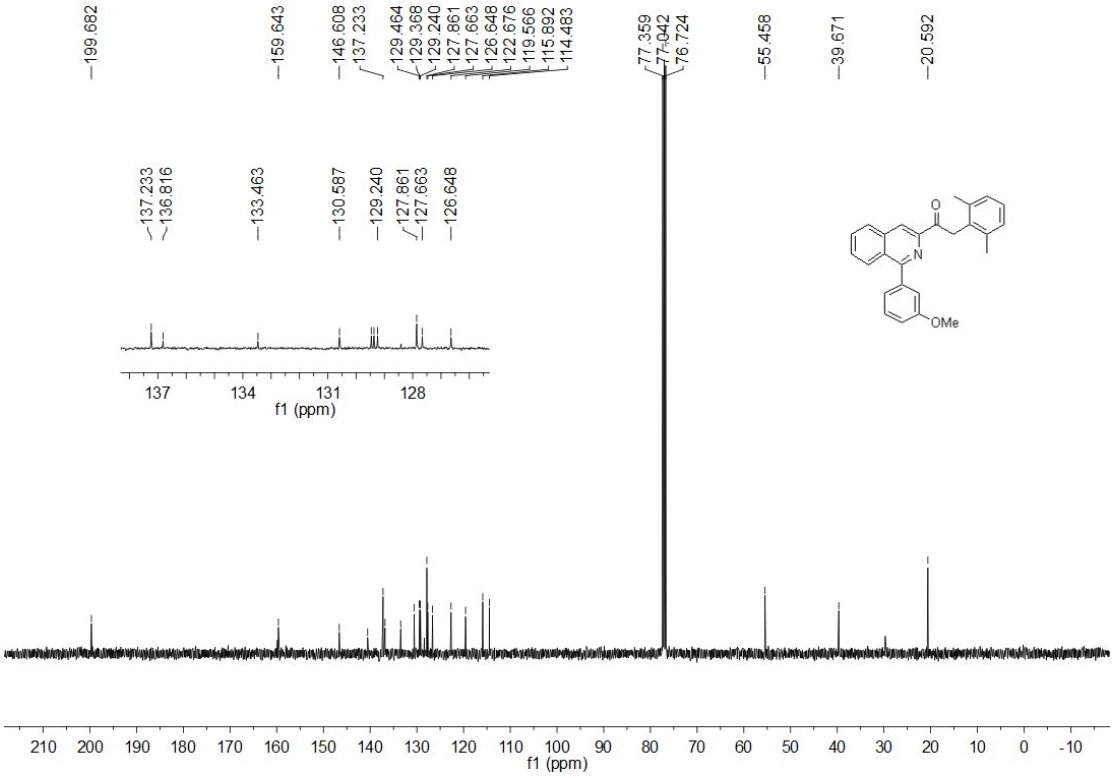
2s


8.510
8.241
8.065
7.772
7.492
7.379
7.359
7.269
7.266
7.258
7.197
7.165
7.113
7.097
5.129
3.920
0.068
Cl
O
N
Cl
OMe
1.02
1.08
1.04
1.07
1.07
1.11
4.12
1.10
1.08
2.08
3.00
f1 (ppm)

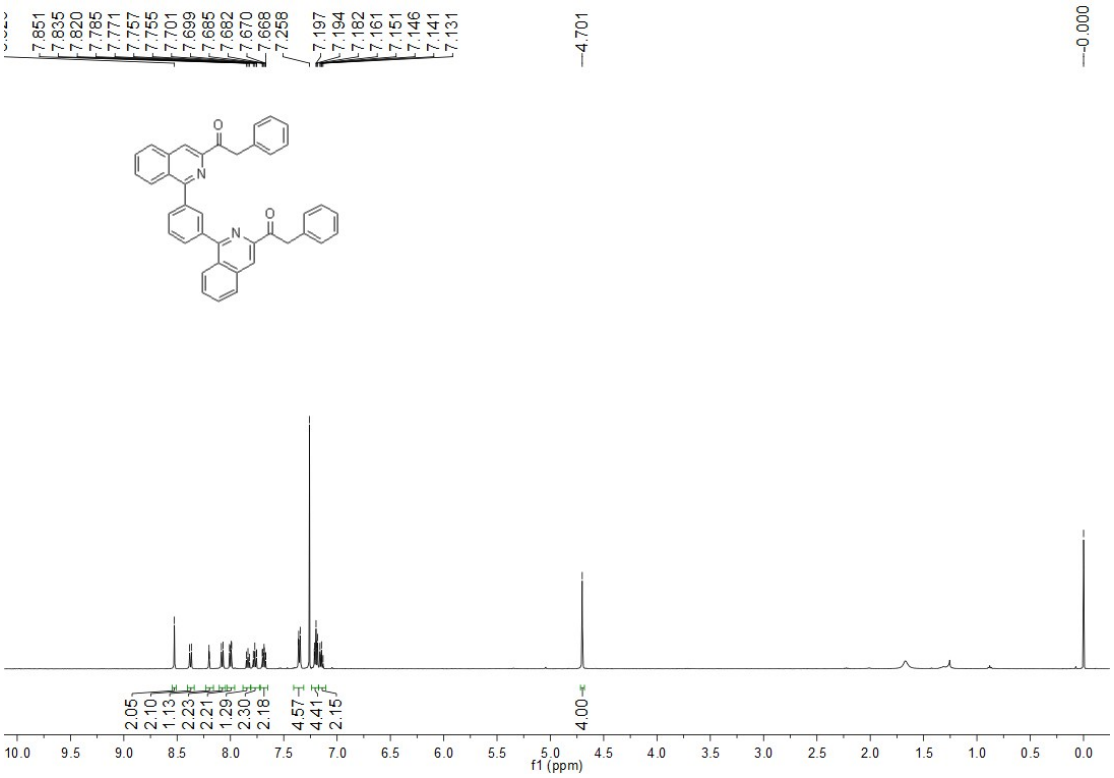

197.461
160.259
160.050
146.443
140.882
133.639
129.672
128.072
120.138
116.348
114.896
77.653
77.399
77.146
55.856
42.147
130.971
129.820
129.672
128.885
128.291
128.072
Cl
O
N
Cl
OMe
f1 (ppm)
f1 (ppm)

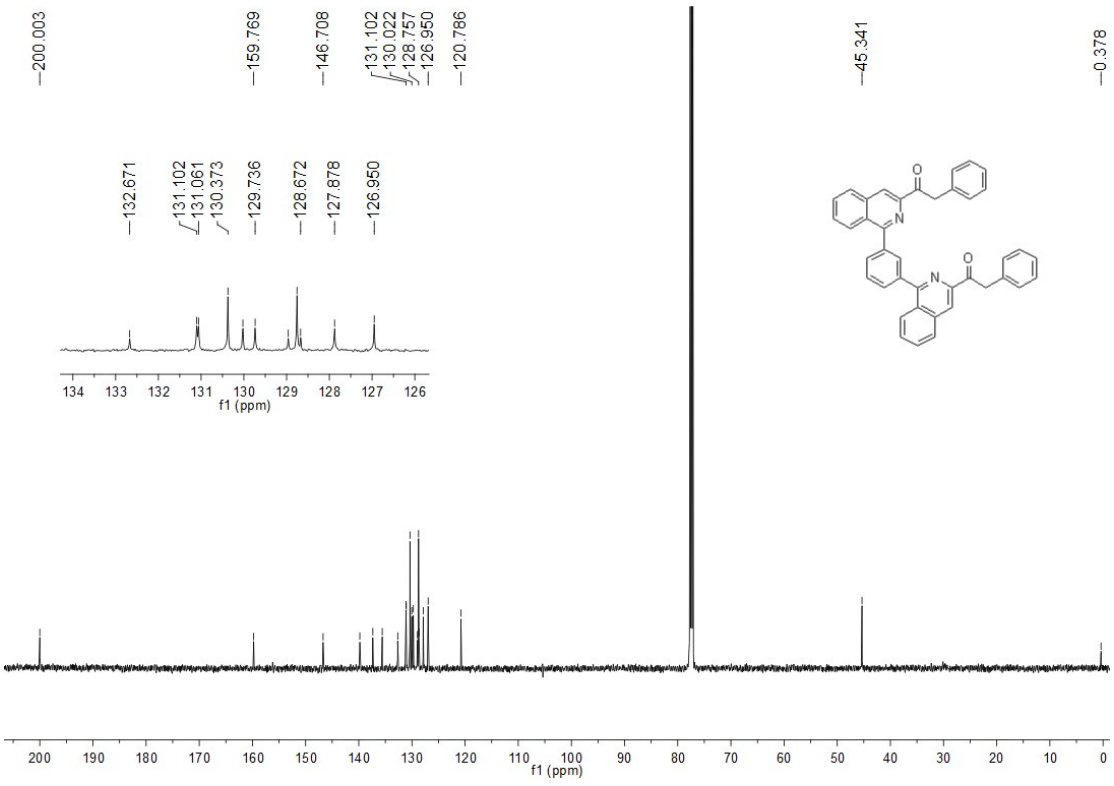
2t


8.507
8.256
8.079
7.794
7.558
7.519
7.410
7.391
7.381
7.148
7.141
7.129
7.121
7.099
7.077
4.825
3.943
2.290
O
N
OMe
0.95
0.99
1.01
1.04
1.05
1.10
2.09
4.24
2.01
3.01
6.00
f1 (ppm)

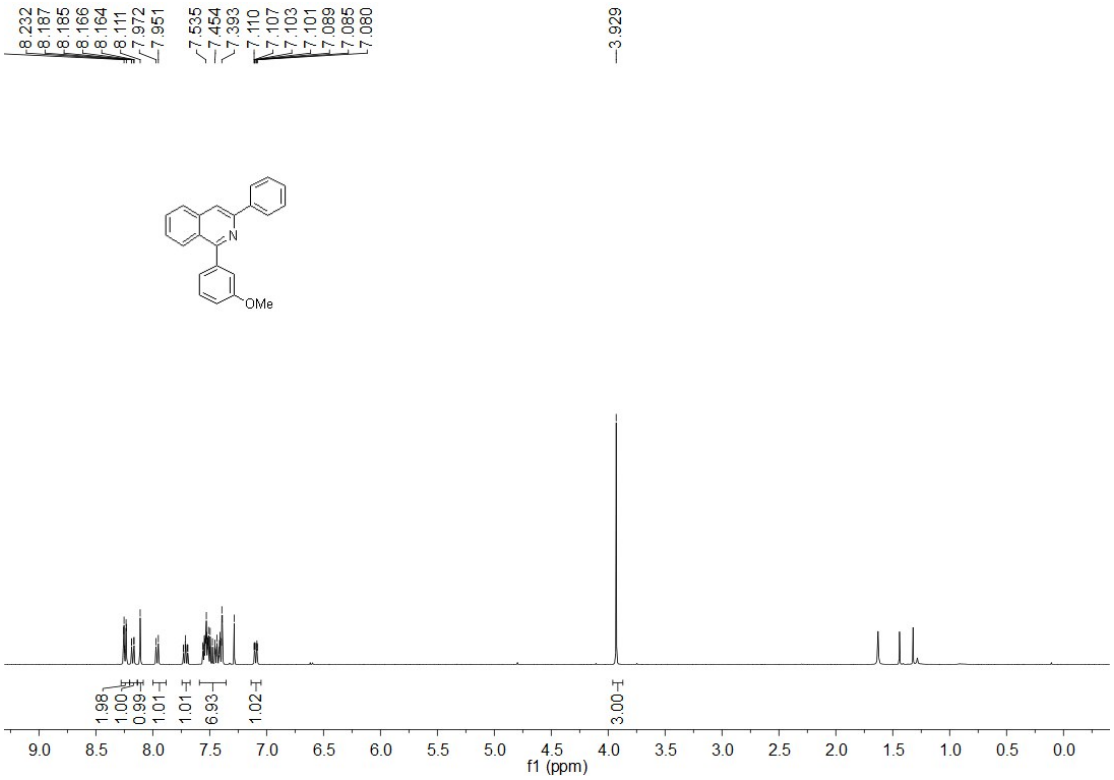

199.682
159.643
146.608
137.233
129.464
129.368
129.240
127.861
127.663
126.648
122.676
119.566
115.892
114.483
77.359
77.042
76.724
55.458
39.671
20.592
137.233
136.816
133.463
130.587
129.240
127.861
127.663
126.648
O
N
OMe
137
134
131
128
f1 (ppm)
f1 (ppm)

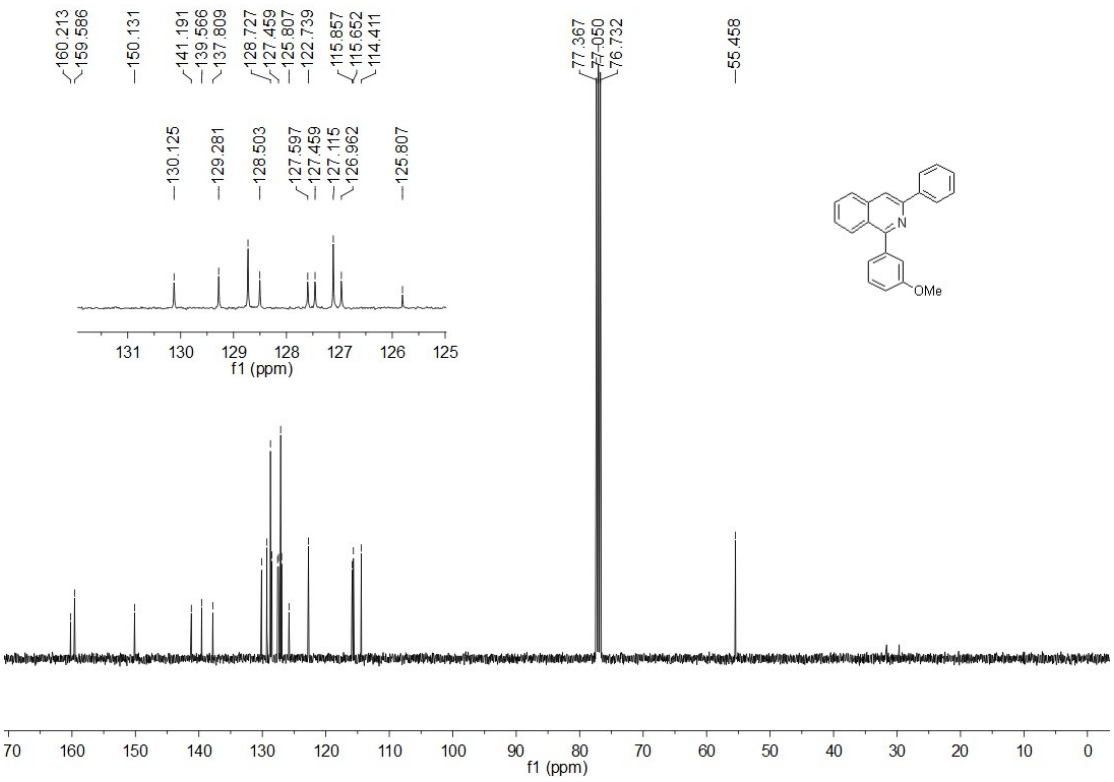
2u


7.851
7.835
7.820
7.785
7.771
7.757
7.755
7.701
7.699
7.685
7.682
7.670
7.668
7.258
7.197
7.194
7.182
7.161
7.151
7.146
7.141
7.131
4.701
0.000
2.05
2.10
1.13
2.23
2.21
1.29
2.30
2.18
4.57
4.41
2.15
4.00
f1 (ppm)

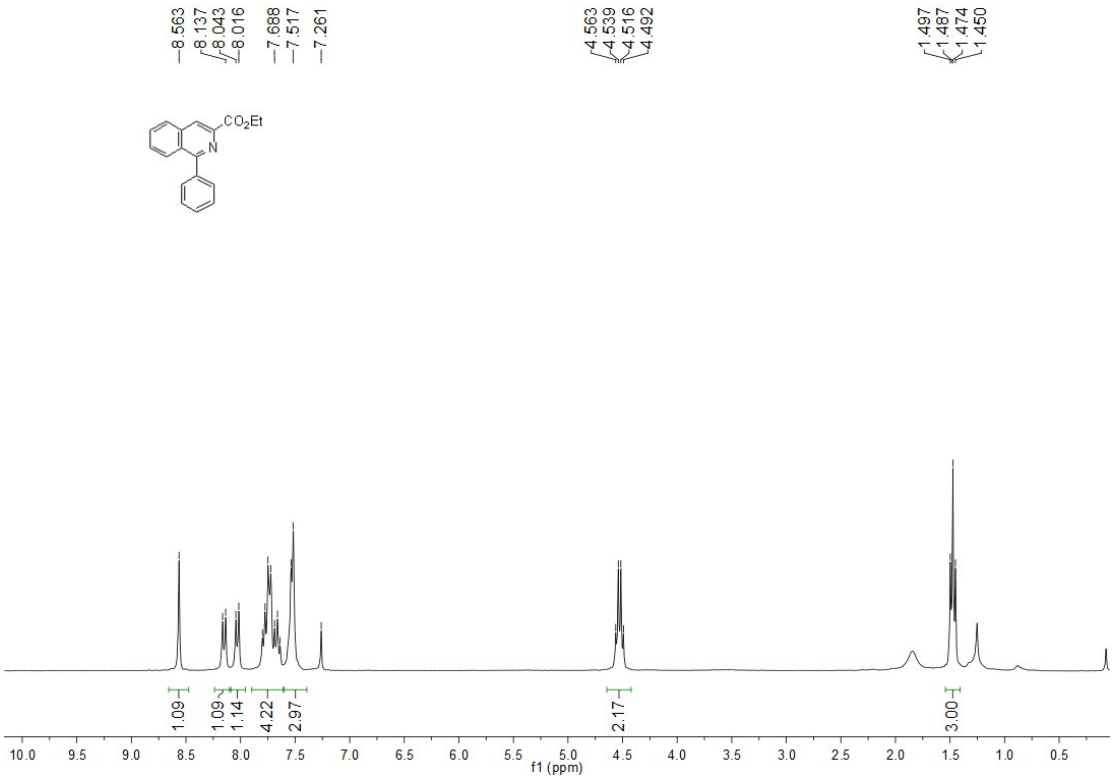

200.003
159.769
146.708
131.102
130.022
128.757
126.950
120.786
45.341
0.378
132.671
131.102
131.061
130.373
129.736
128.672
127.878
126.950
f1 (ppm)

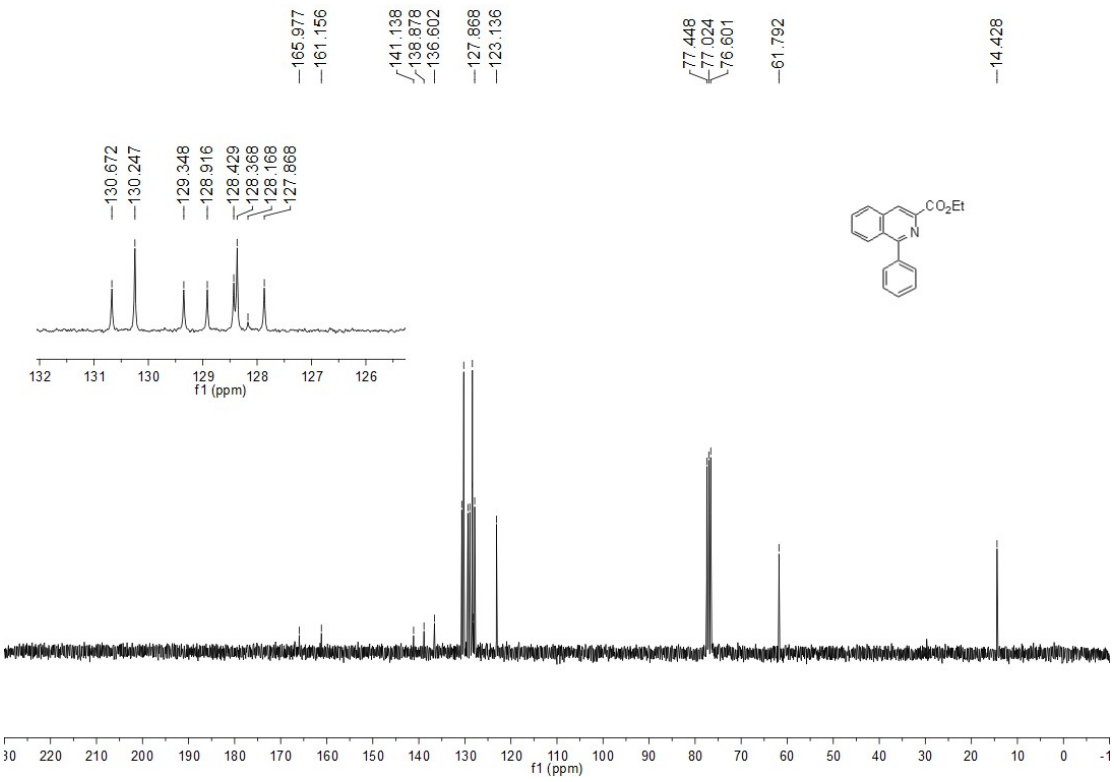
2v


8.232
8.187
8.185
8.166
8.164
8.111
7.972
7.951
7.535
7.454
7.393
7.110
7.107
7.103
7.101
7.089
7.085
7.080
3.929
N
OMe
1.98
1.00
0.99
1.01
1.01
6.93
1.02
3.00
f1 (ppm)

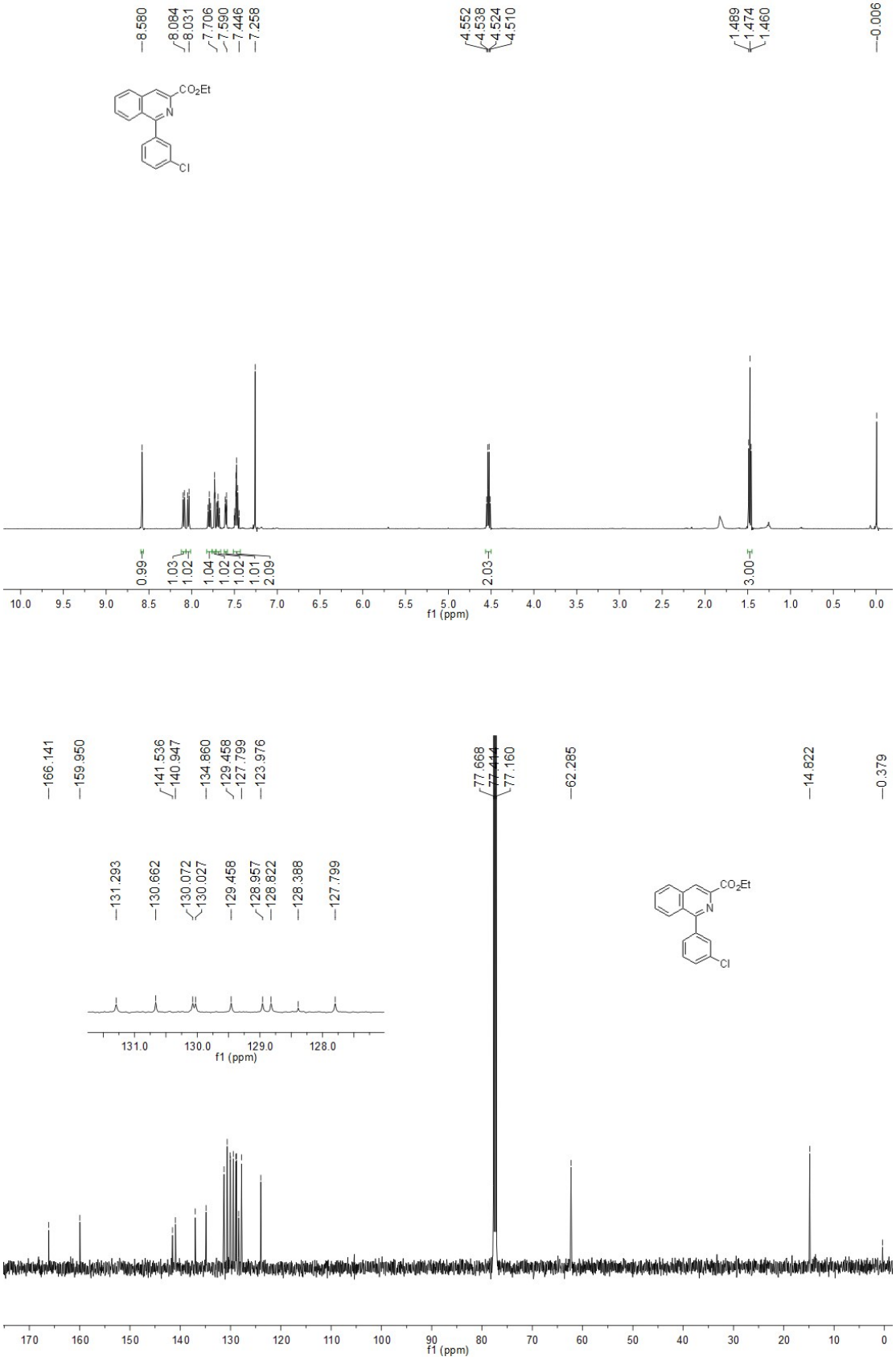

160.213
159.586
150.131
141.191
139.566
137.809
128.727
127.459
125.807
122.739
115.857
115.652
114.411
77.367
77.050
76.732
55.458
130.125
129.281
128.503
127.597
127.459
127.115
126.962
125.807
N
OMe
f1 (ppm)
f1 (ppm)

3a

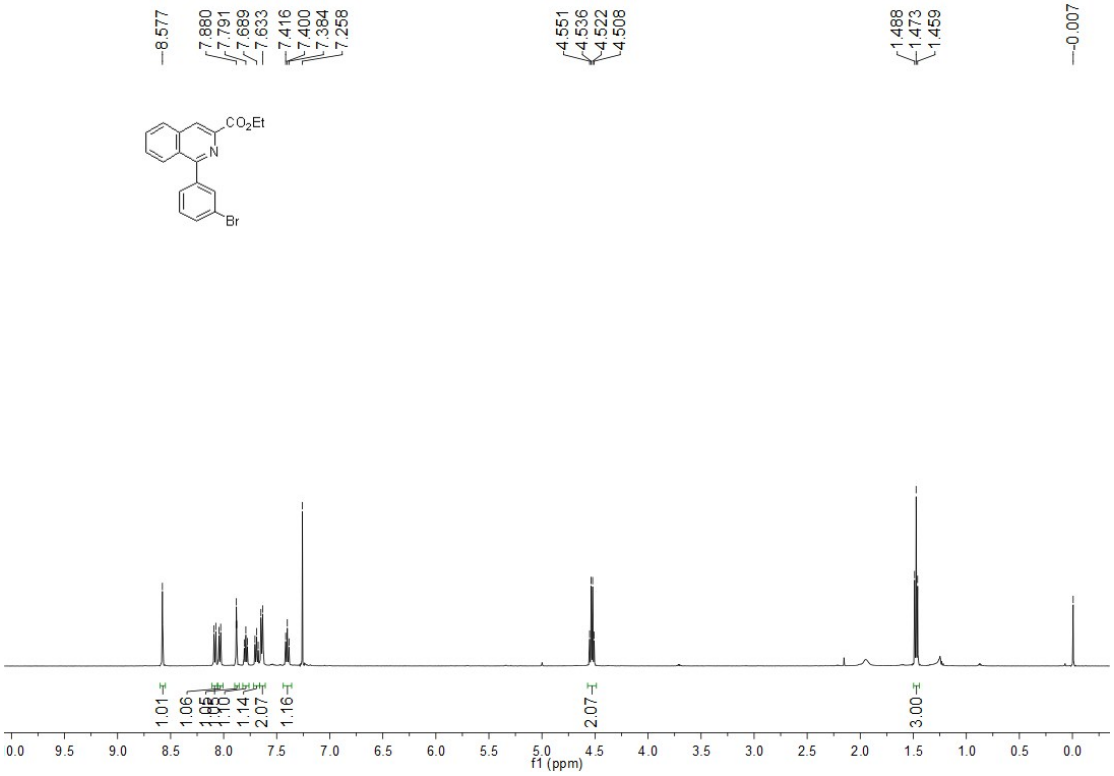

8.563
8.137
8.043
8.016
7.688
7.517
7.261
4.563
4.539
4.516
4.492
1.497
1.487
1.474
1.450
CO2Et
N
1.09
1.09
1.14
4.22
2.97
2.17
3.00
f1 (ppm)

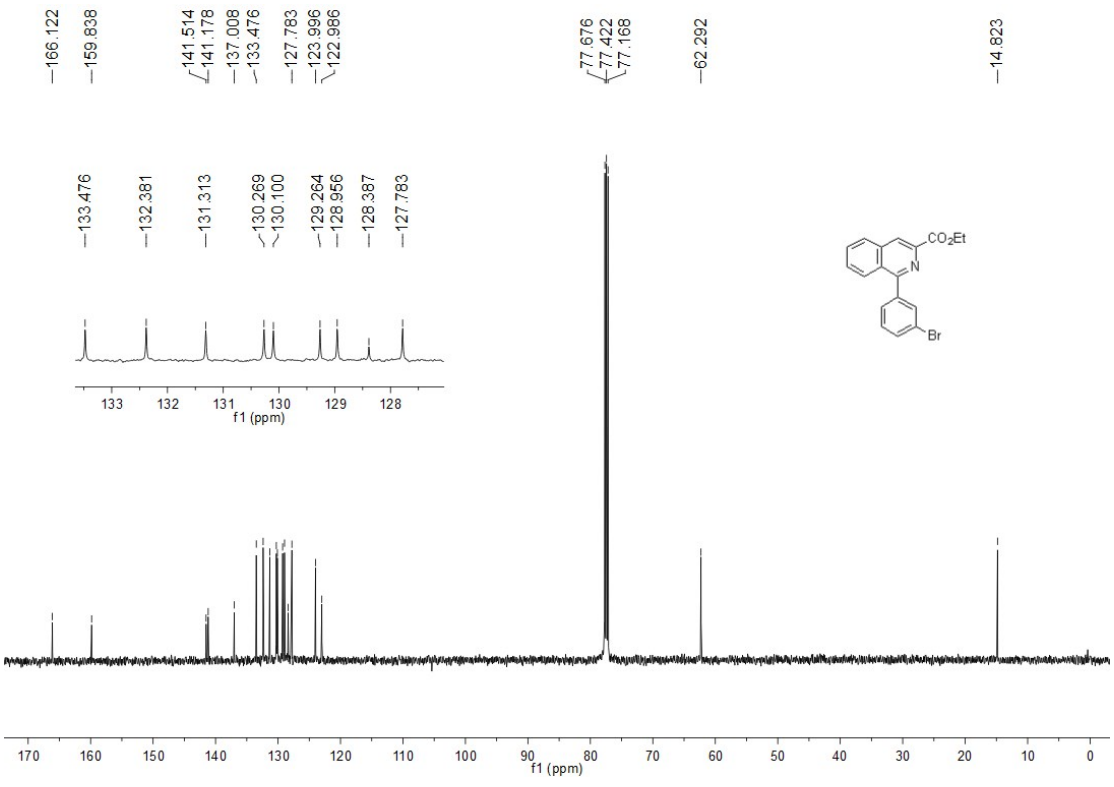

165.977
161.156
141.138
138.878
136.602
127.868
123.136
77.448
77.024
76.601
61.792
14.428
130.672
130.247
129.348
128.916
128.429
128.368
128.168
127.868
CO2Et
N
f1 (ppm)

3b


8.580
8.084
8.031
7.706
7.590
7.446
7.258
4.552
4.538
4.524
4.510
1.489
1.474
1.460
0.006
CO2Et
N
Cl
0.99
1.03
1.02
1.04
1.02
1.02
1.01
2.09
2.03
3.00
f1 (ppm)
166.141
159.950
141.536
140.947
134.860
129.458
127.799
123.976
77.668
77.444
77.160
62.285
14.822
0.379
131.293
130.662
130.072
130.027
129.458
128.957
128.822
128.388
127.799
CO2Et
N
Cl
131.0
130.0
129.0
128.0
f1 (ppm)
f1 (ppm)

3c

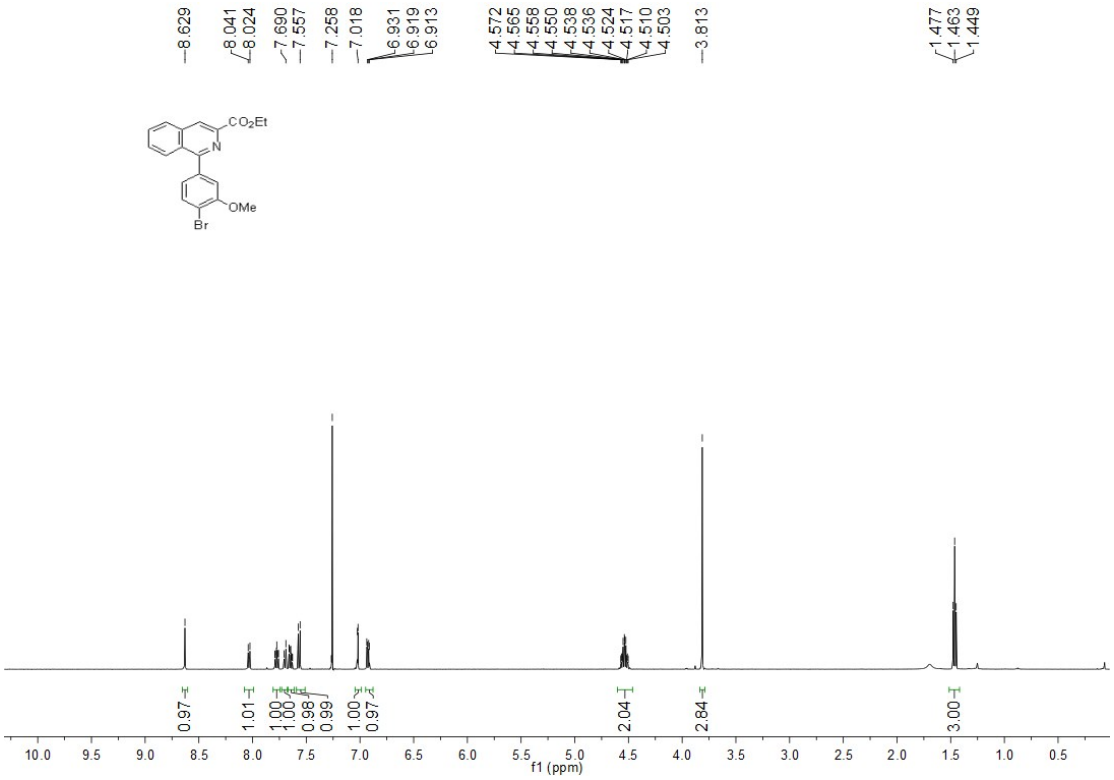

8.577
7.880
7.791
7.689
7.633
7.416
7.400
7.384
7.258
4.551
4.536
4.522
4.508
1.488
1.473
1.459
0.007
CO2Et
N
Br
1.01
1.06
2.07
1.16
2.07
3.00
f1 (ppm)

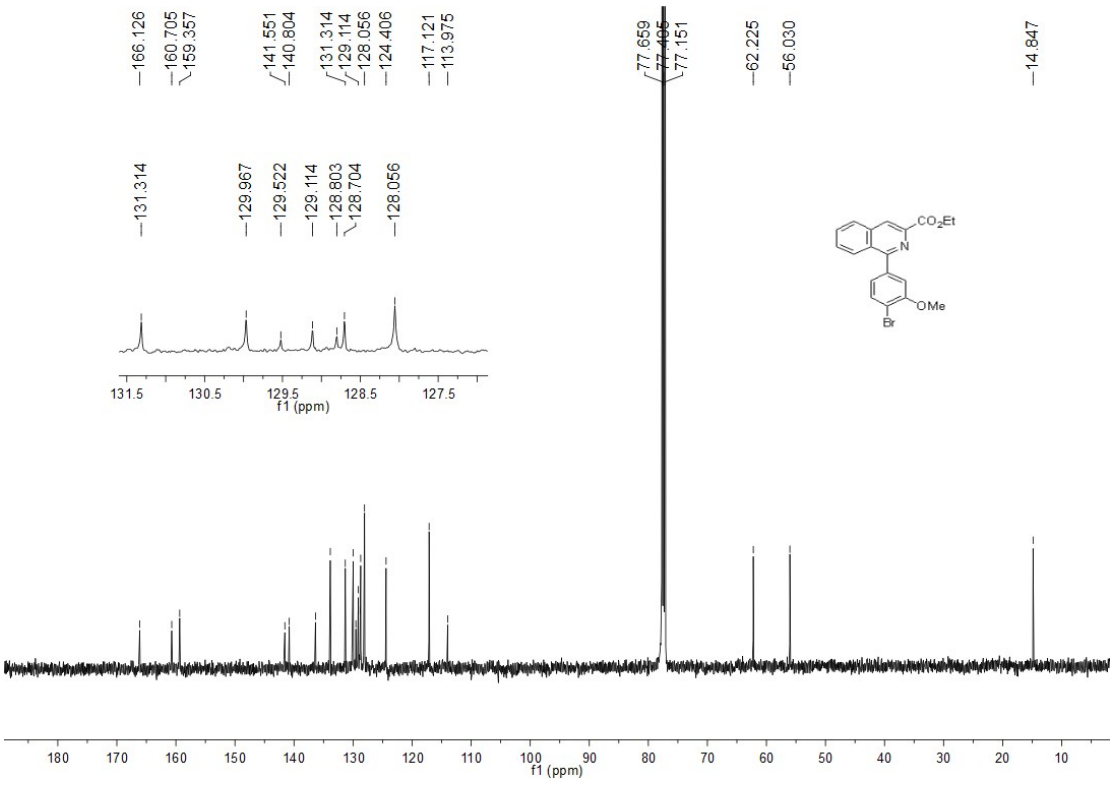

166.122
159.838
141.514
141.178
137.008
133.476
127.783
123.996
122.986
77.676
77.422
77.168
62.292
14.823
133.476
132.381
131.313
130.269
130.100
129.264
128.956
128.387
127.783
CO2Et
N
Br
f1 (ppm)
f1 (ppm)

3d

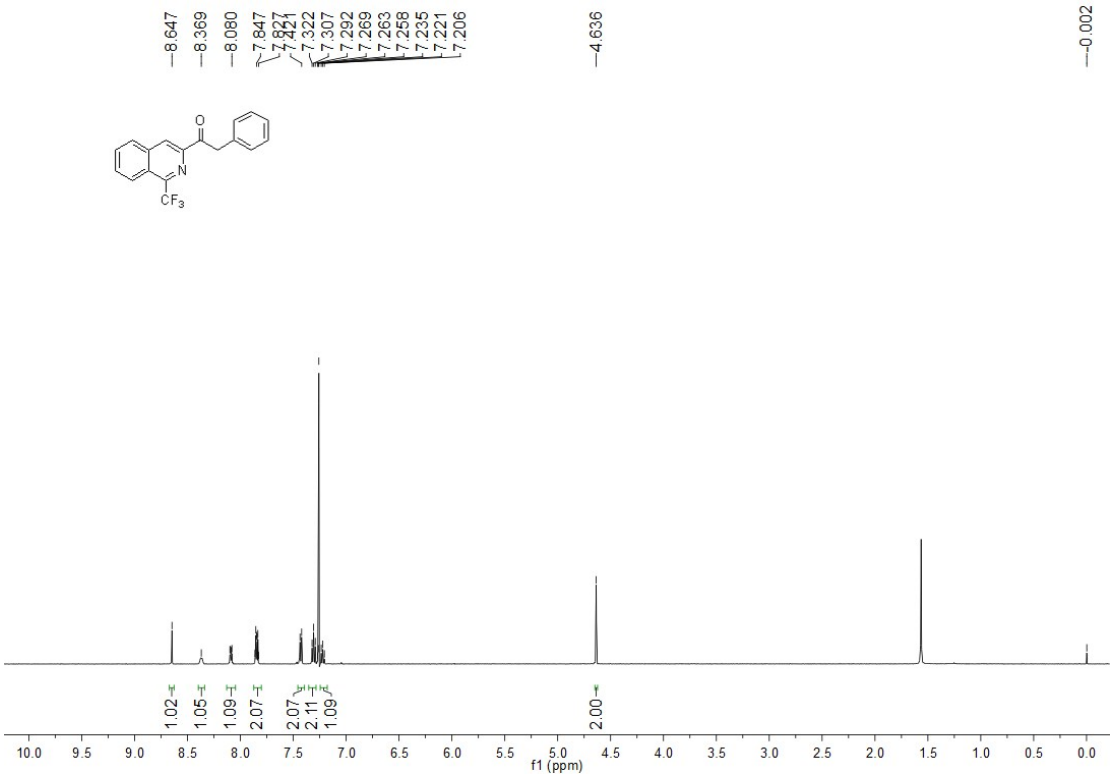

8.589
8.385
8.053
7.807
7.680
7.605
7.258
4.551
4.536
4.522
4.508
4.423
4.408
4.394
4.380
1.487
1.472
1.458
1.405
1.391
1.377
0.009
CO2Et
CO2Et
N
0.97
0.95
1.03
1.98
1.03
1.02
1.06
1.00
2.08
2.07
3.00
2.98
f1 (ppm)
166.723
166.189
160.508
137.003
134.927
131.616
131.253
131.105
130.410
130.056
128.978
128.932
128.496
127.850
123.895
77.667
77.413
77.159
62.239
61.542
14.803
14.720
0.370
f1 (ppm)

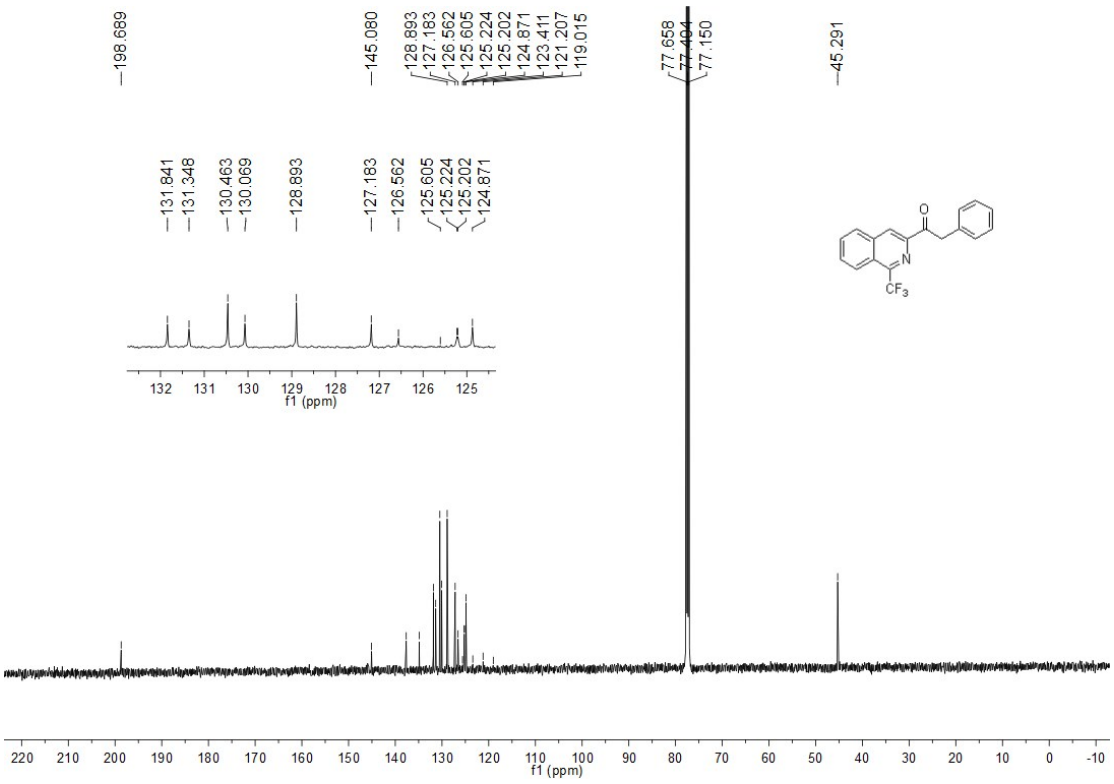
3e


8.629
8.041
8.024
7.690
7.557
7.258
7.018
6.931
6.919
6.913
4.572
4.565
4.558
4.550
4.538
4.536
4.524
4.517
4.510
4.503
3.813
1.477
1.463
1.449
CO2Et
N
OMe
Br
0.97
1.01
1.00
1.00
0.98
0.99
1.00
0.97
2.04
2.84
3.00
f1 (ppm)

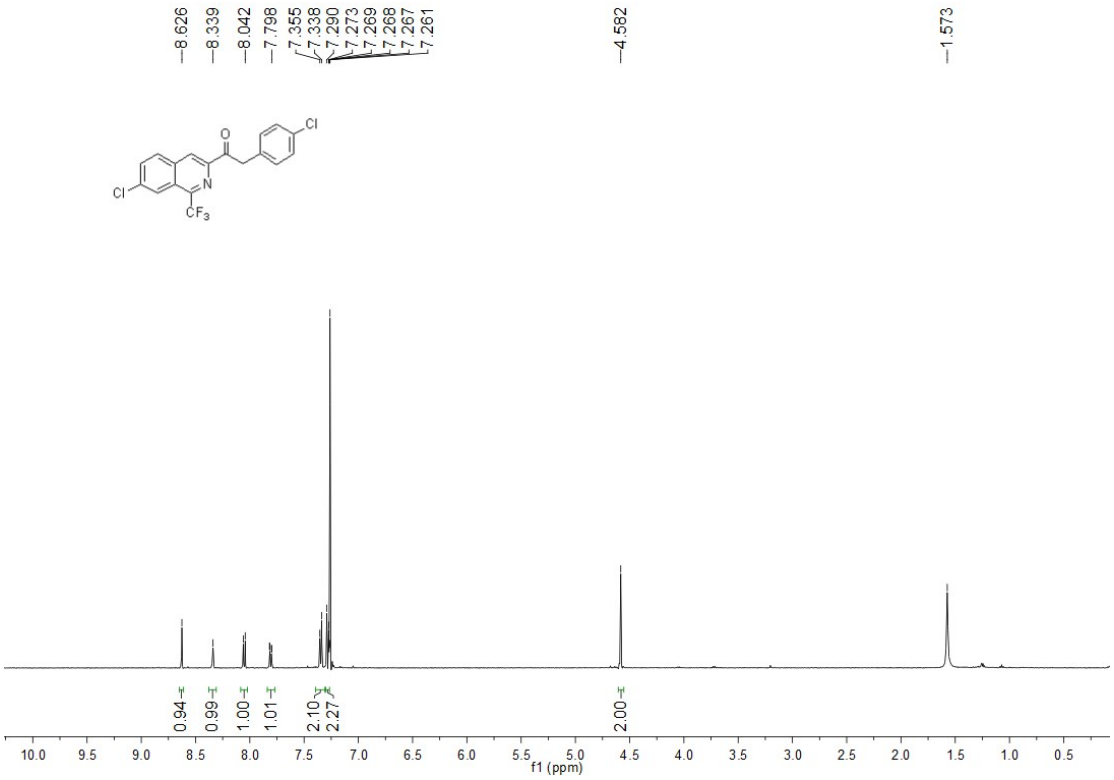

166.126
160.705
159.357
141.551
140.804
131.314
129.114
128.056
124.406
117.121
113.975
77.659
77.486
77.151
62.225
56.030
14.847
131.314
129.967
129.522
129.114
128.803
128.704
128.056
131.5
130.5
129.5
128.5
127.5
f1 (ppm)
CO2Et
N
OMe
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

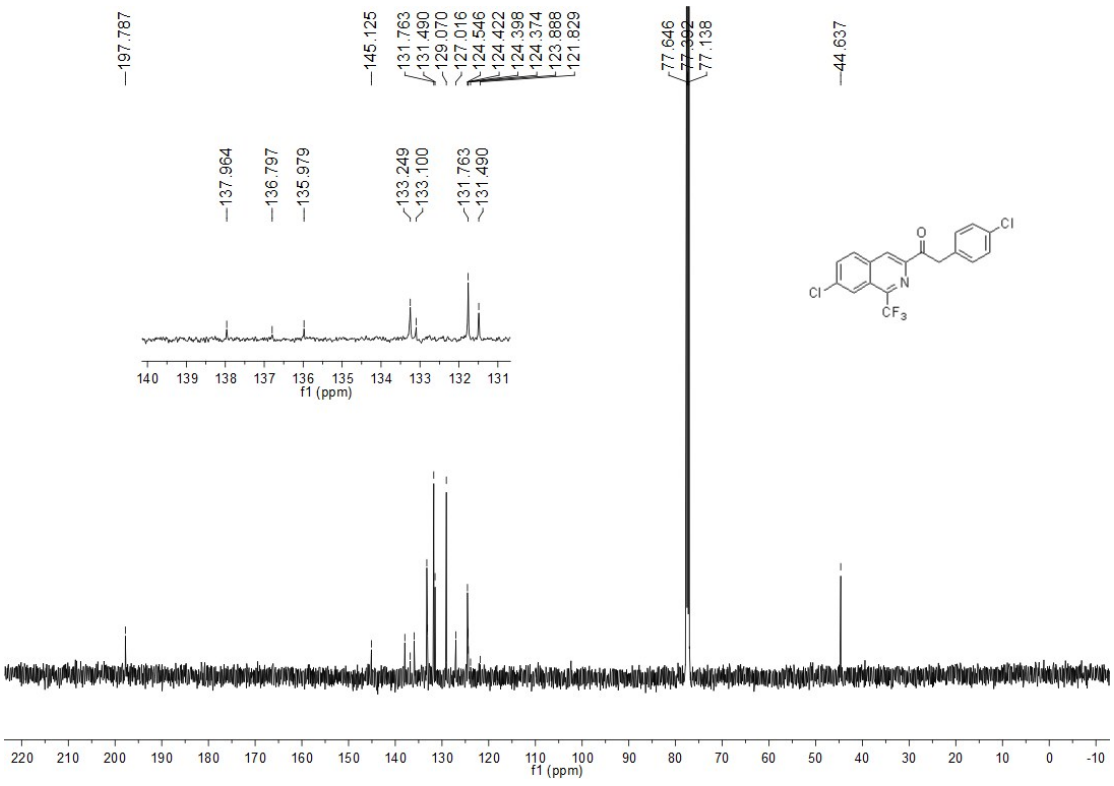
5a


8.647
8.369
8.080
7.847
7.827
7.421
7.322
7.307
7.292
7.269
7.263
7.258
7.235
7.221
7.206
4.636
0.002
1.02
1.05
1.09
2.07
2.07
2.11
1.09
2.00
f1 (ppm)

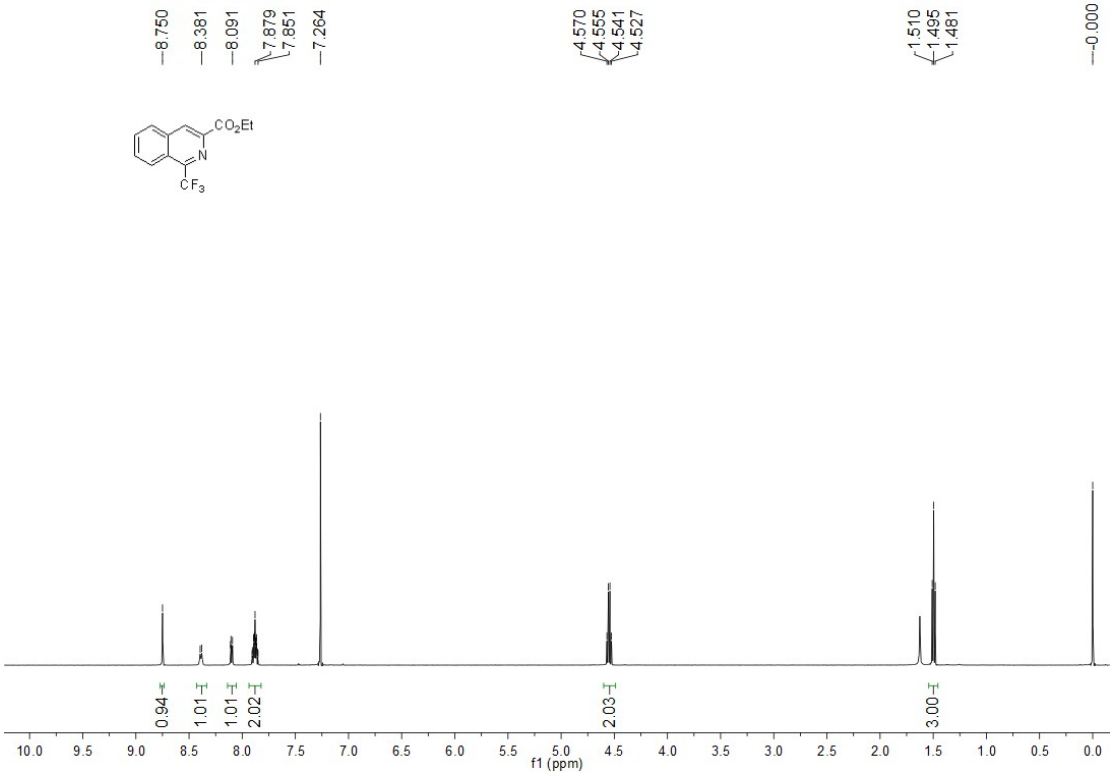

198.689
145.080
128.893
127.183
126.562
125.605
125.224
125.202
124.871
123.411
121.207
119.015
77.658
77.404
77.150
45.291
131.841
131.348
130.463
130.069
128.893
127.183
126.562
125.605
125.224
125.202
124.871
f1 (ppm)

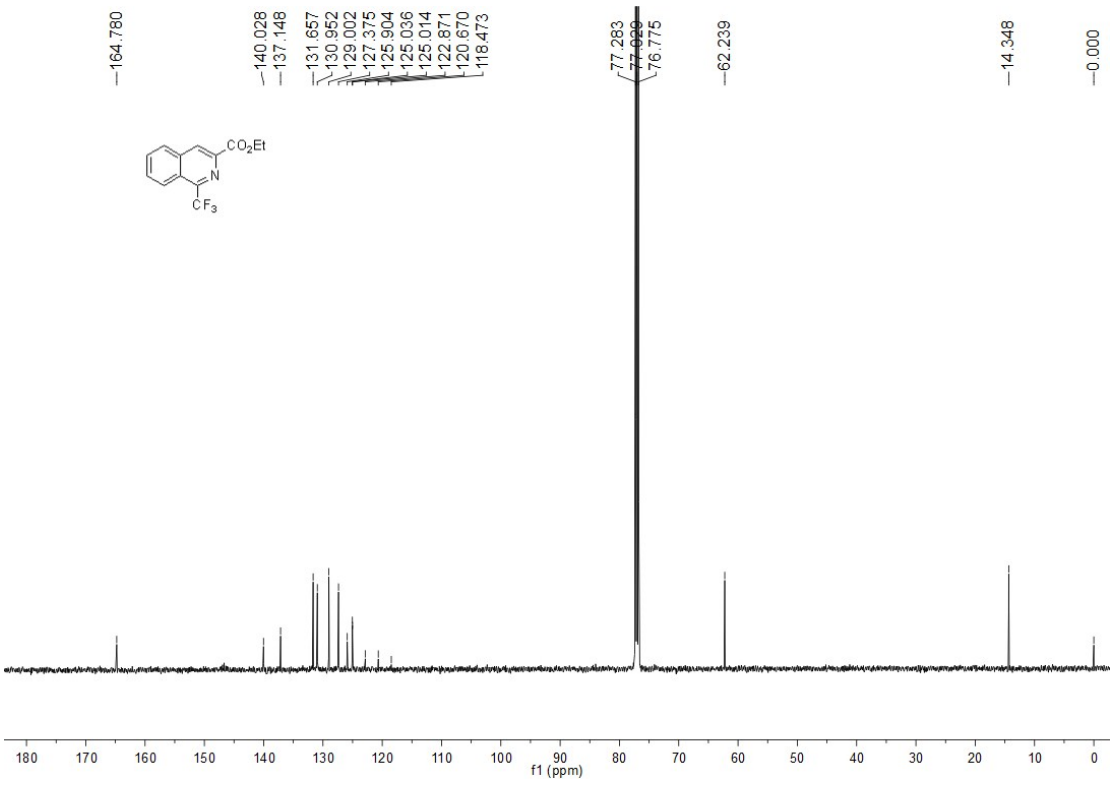
5b


8.626
8.339
8.042
7.798
7.355
7.338
7.290
7.273
7.269
7.268
7.267
7.261
4.582
1.573
Cl
O
N
Cl
CF3
0.94
0.99
1.00
1.01
2.10
2.27
2.00
f1 (ppm)

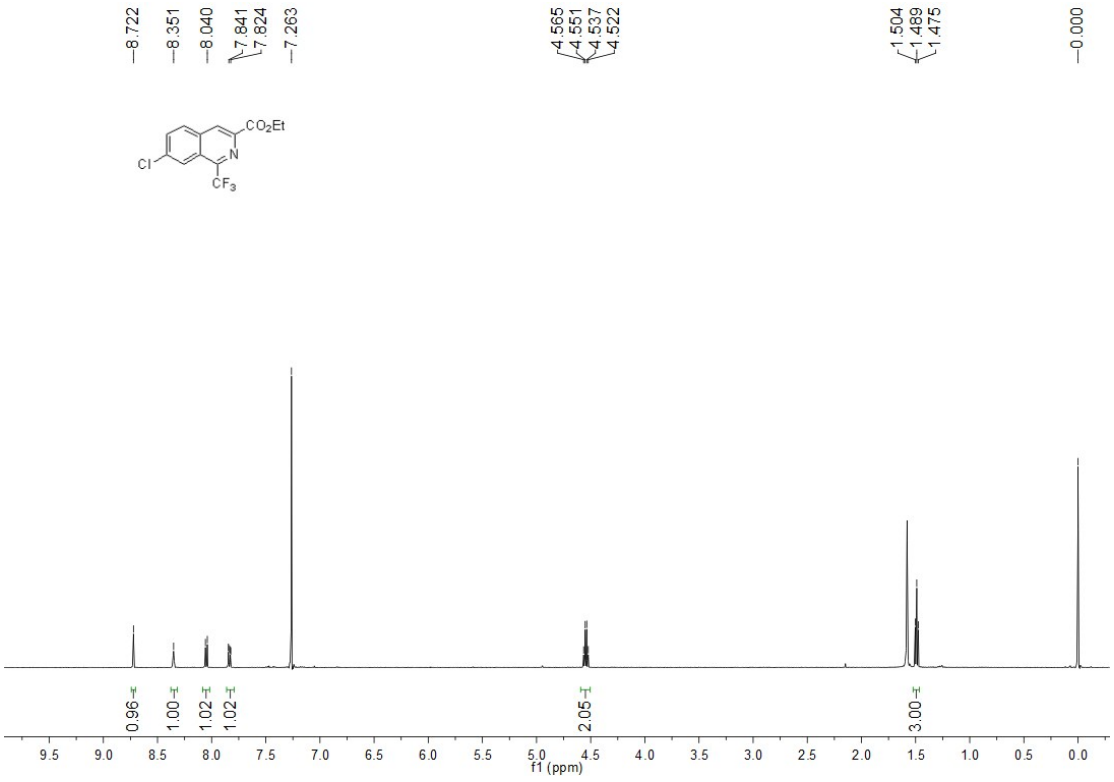

197.787
145.125
131.763
131.490
129.070
127.016
124.546
124.422
124.398
124.374
123.888
121.829
77.646
77.392
77.138
44.637
137.964
136.797
135.979
133.249
133.100
131.763
131.490
Cl
O
N
Cl
CF3
f1 (ppm)

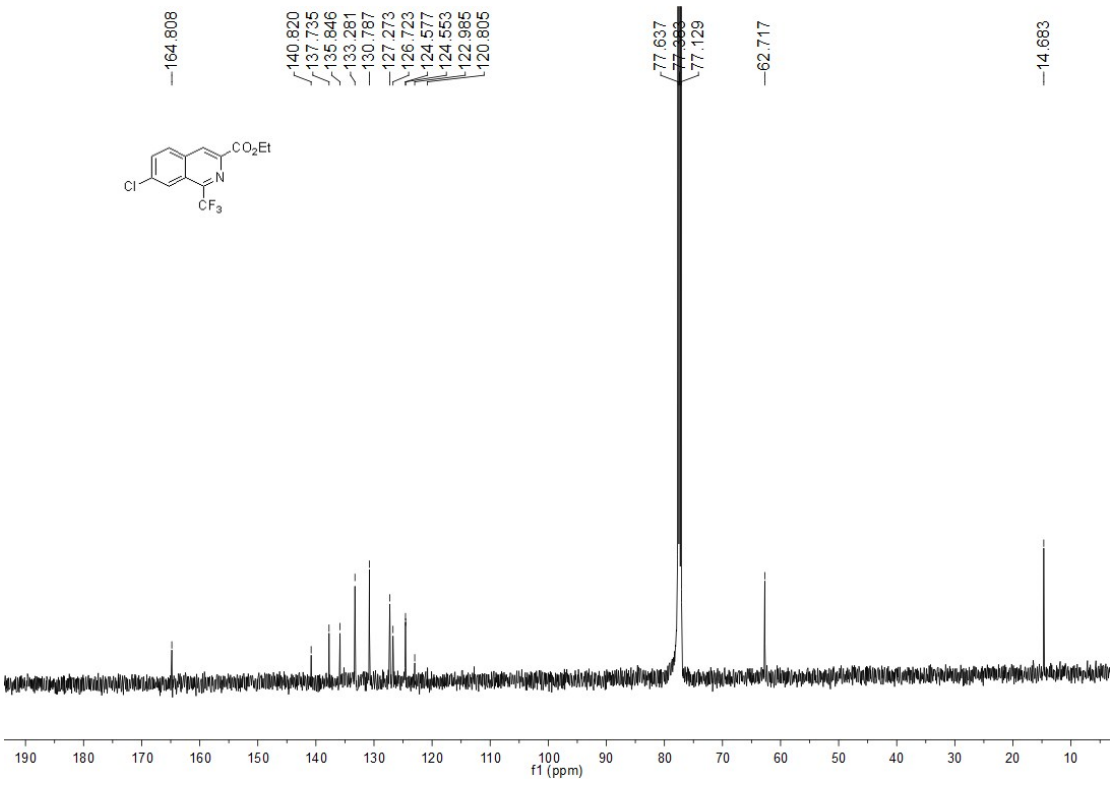
5c


8.750
8.381
8.091
7.879
7.851
7.264
4.570
4.555
4.541
4.527
1.510
1.495
1.481
0.000
CO2Et
N
CF3
0.94
1.01
1.01
2.02
2.03
3.00
f1 (ppm)

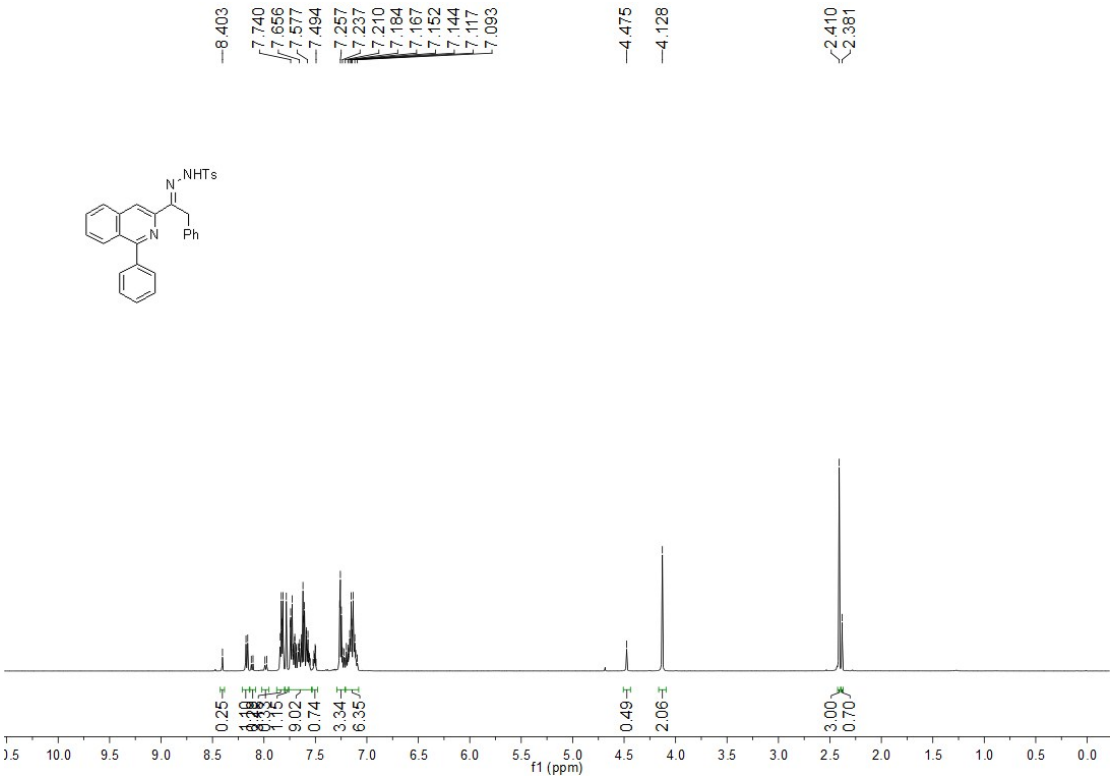

164.780
140.028
137.148
131.657
130.952
129.002
127.375
125.904
125.036
125.014
122.871
120.670
118.473
77.283
77.020
76.775
62.239
14.348
0.000
CO2Et
N
CF3
f1 (ppm)

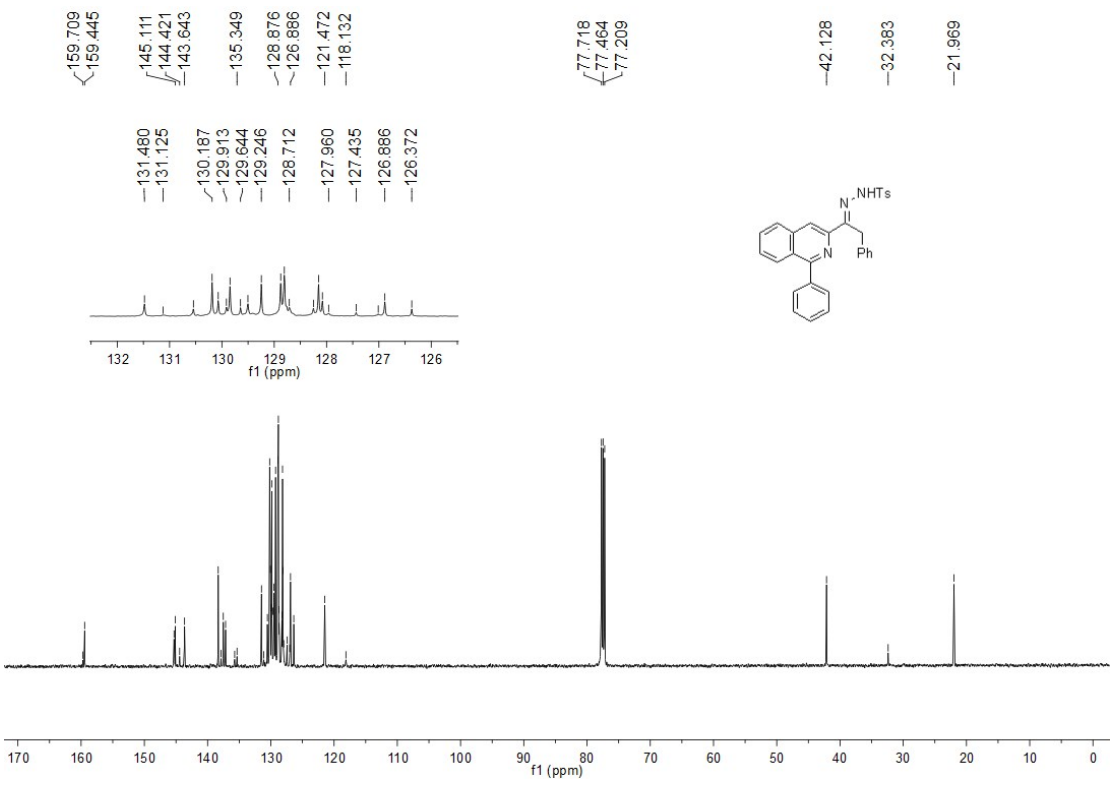
5d


8.722
8.351
8.040
7.841
7.824
7.263
4.565
4.551
4.537
4.522
1.504
1.489
1.475
0.000
CO2Et
Cl
N
CF3
0.96
1.00
1.02
1.02
2.05
3.00
f1 (ppm)

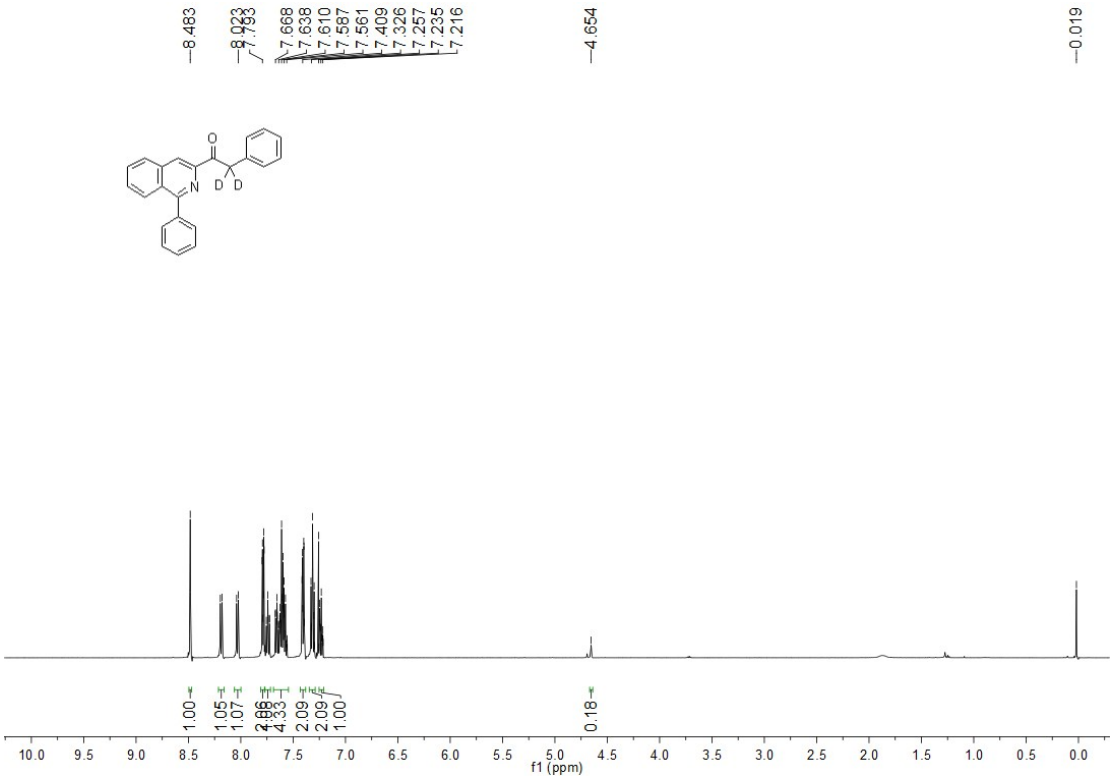

164.808
140.820
137.735
135.846
133.281
130.787
127.273
126.723
124.577
124.553
122.985
120.805
77.637
77.383
77.129
62.717
14.683
CO2Et
Cl
N
CF3
f1 (ppm)

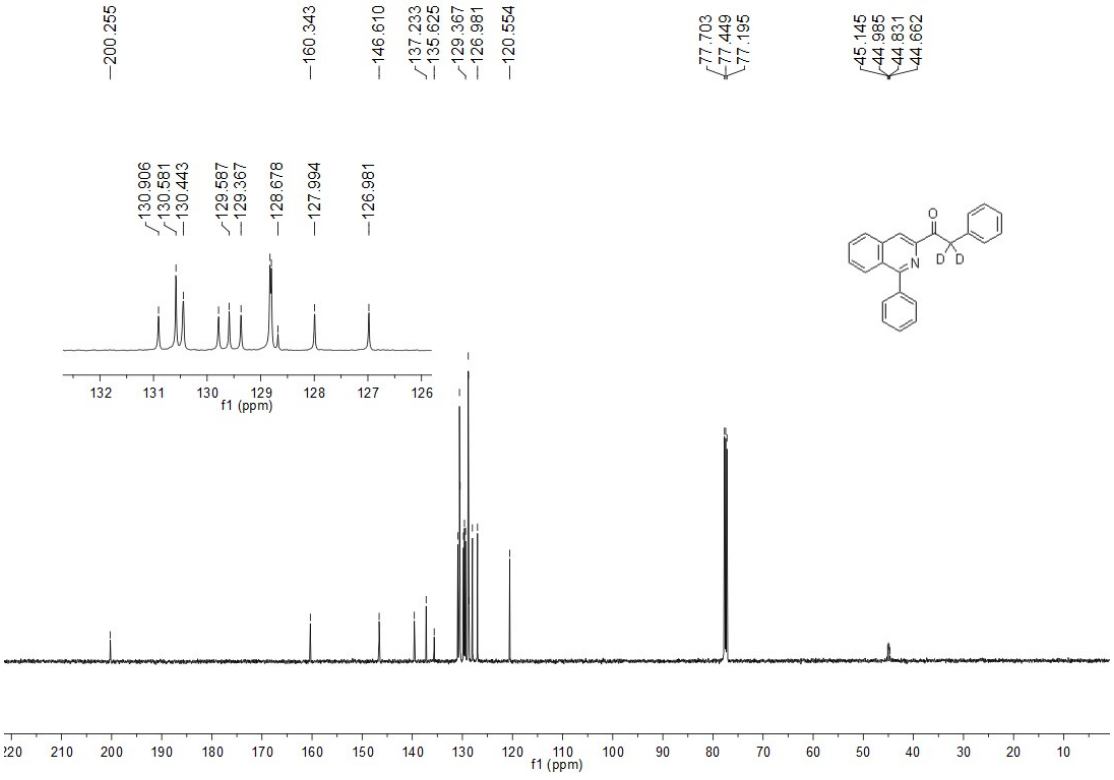
6


8.403
7.740
7.656
7.577
7.494
7.257
7.237
7.210
7.184
7.167
7.152
7.144
7.117
7.093
4.475
4.128
2.410
2.381
NHTs
Ph
f1 (ppm)

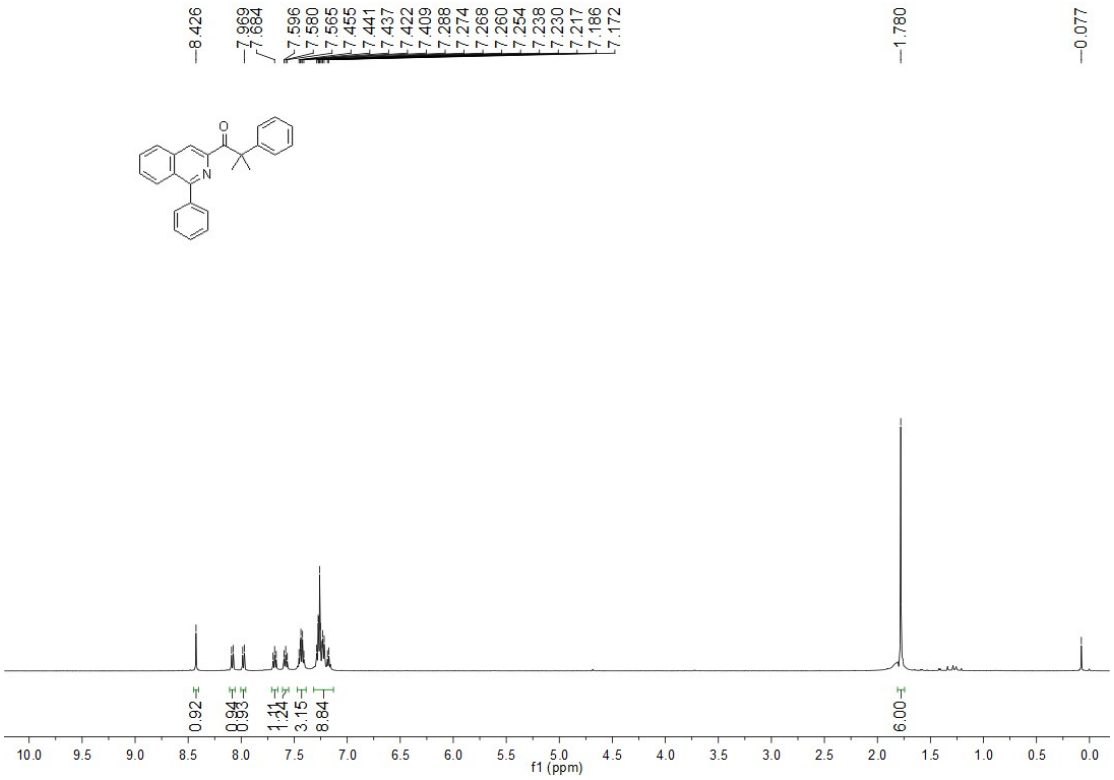

159.709
159.445
145.111
144.421
143.643
135.349
128.876
126.886
121.472
118.132
77.718
77.464
77.209
42.128
32.383
21.969
131.480
131.125
130.187
129.913
129.644
129.246
128.712
127.960
127.435
126.886
126.372
NHTs
Ph
f1 (ppm)

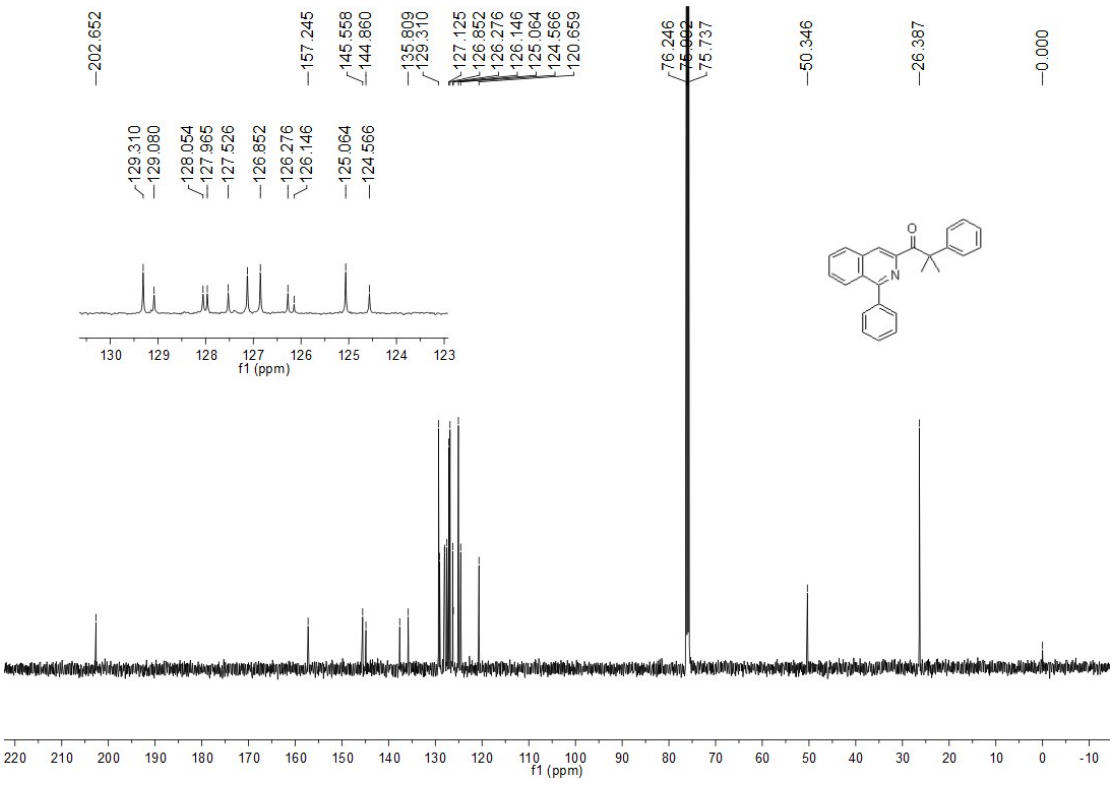
7


8.483
8.023
7.993
7.668
7.638
7.610
7.587
7.561
7.409
7.326
7.257
7.235
7.216
4.654
0.019
O
N
D D
1.00
1.05
1.07
2.09
2.09
1.00
0.18
f1 (ppm)

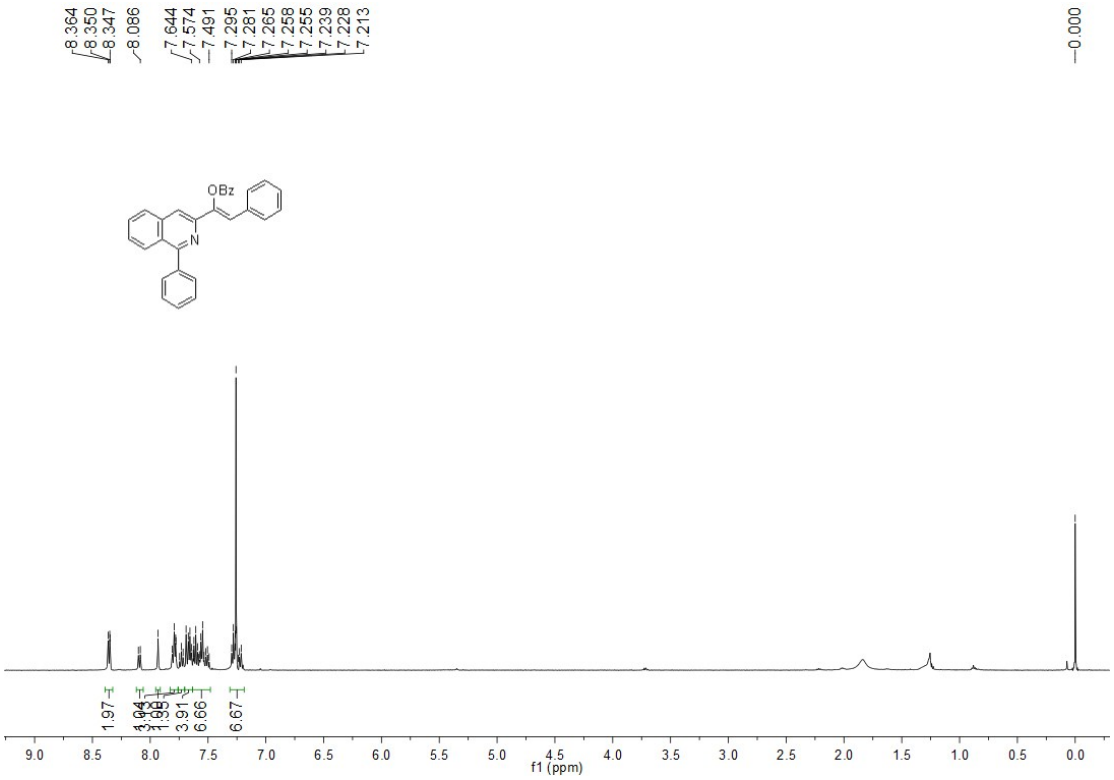

200.255
160.343
146.610
137.233
135.625
129.367
126.981
120.554
77.703
77.449
77.195
45.145
44.985
44.831
44.662
130.906
130.581
130.443
129.587
129.367
128.678
127.994
126.981
O
N
D D
f1 (ppm)

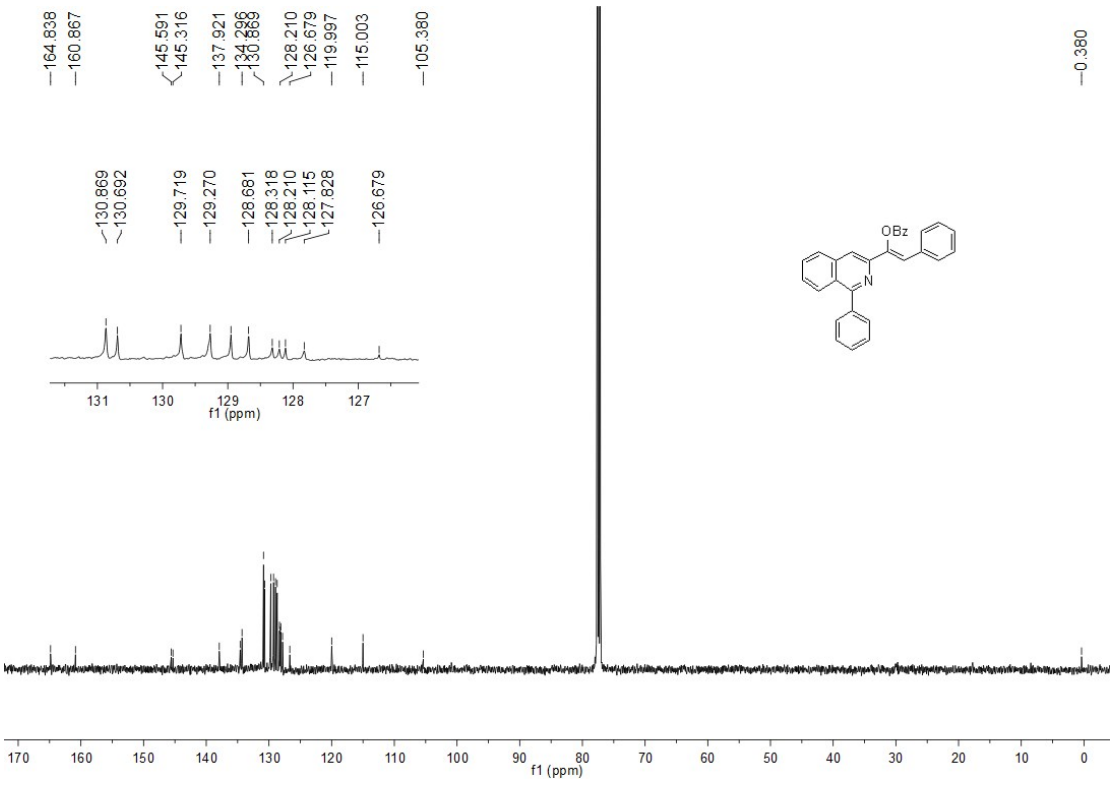
8


8.426
7.969
7.684
7.596
7.580
7.565
7.455
7.441
7.437
7.422
7.409
7.288
7.274
7.268
7.260
7.254
7.238
7.230
7.217
7.186
7.172
1.780
0.077
0.92
0.94
0.93
1.11
1.24
3.15
8.84
6.00
f1 (ppm)


202.652
157.245
145.558
144.860
135.809
129.310
127.125
126.852
126.276
126.146
125.064
124.566
120.659
76.246
75.737
50.346
26.387
0.000
129.310
129.080
128.054
127.965
127.526
126.852
126.276
126.146
125.064
124.566
f1 (ppm)

9


8.364
8.350
8.347
8.086
7.644
7.574
7.491
7.295
7.281
7.265
7.258
7.255
7.239
7.228
7.213
0.000
OBz
N
1.97
1.04
1.03
1.00
3.91
6.66
6.67
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.838
160.867
145.591
145.316
137.921
134.296
130.869
128.210
126.679
119.997
115.003
105.380
130.869
130.692
129.719
129.270
128.681
128.318
128.210
128.115
127.828
126.679
0.380
OBz
N
131
130
129
128
127
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

IX. X-Ray Crystal of Compound 9

CCDC number: CCDC 1902347