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Supporting Information

Brønsted Acid-Promoted [3 + 3] Cycloaddition of Azomethine Ylides with Quinone Monoimine: A Practical Method towards Dihydrobenzoxazine Derivatives

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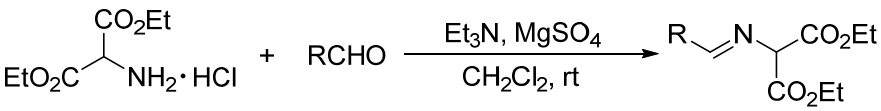
General Information

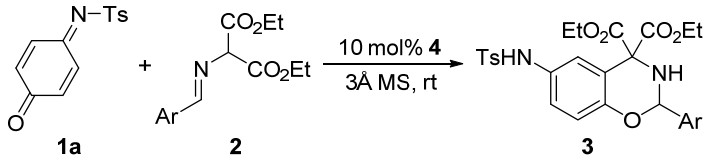
All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Dichloromethane and dichloroethane employed in the reactions was freshly distilled from CaH_2. Quinone monoimines were pepared by the literature.[1] Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 300MHz NMR instrument (referenced internally to Me_4Si). Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS) with the resonance of the non-deuterated solvent or TMS as the internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on an Autopol V Plus polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique.

Preparation of α-Iminoesters 2[2]



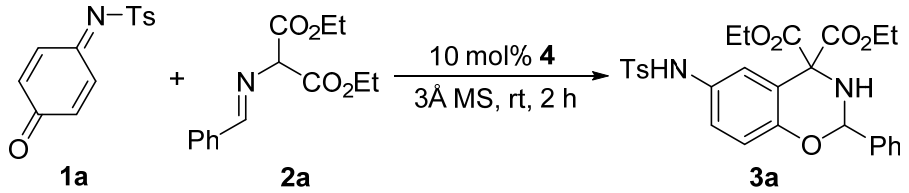
All α-iminoesters were prepared using the reported procedure. A suspension of diethyl-2-aminomalonate hydrochloride (14.8 mmol), $MgSO_4$ (14.8 mmol) and Et_3N (14.8 mmol) in dry CH_2Cl_2 (36 mL) was stirred at room temperature for 1 h, and aldehyde (16.2 mmol) was added. The resulting mixture was stirred at room temperature for 12 h, and then was filtered. To the filtrate was added water (5 mL). The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure to afford α-iminoesters **2**, which was used in the next step without further purification.

General Procedure for the [3 + 3] Cycloaddition of Azomethine Ylides with Quinone Monoimine by Phosphoric Acid



Under nitrogen atmosphere, phosphoric acid (10.4 mg, 0.03 mmol), quinone monoimine **1** (78.3 mg, 0.3 mmol) and 3Å MS (50 mg) were dissolved in 2 mL of DCE. The resulting mixture was stirred at rt for about 1 hour, followed by addition of α-iminoesters **2** (0.45 mmol) and DCE or DCM (1 mL). Upon the completion of the reaction as monitored by TLC, the mixture was concentrated in vacuo. The residue was purified through flash column chromatography (EtOAc /petroleum ether) to afford the corresponding cycloaddition product.

Phosphoric Acid-Catalyzed [3 + 3] Cycloaddition of Azomethine Ylide with Quinone Monoimine on the Gram Scale

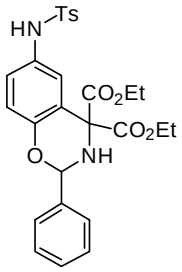


Under nitrogen atmosphere, phosphoric acid (0.13 g, 0.4 mmol), quinone monoimine **1** (1.04 g, 4 mmol) and 3Å MS (2.0 g) were dissolved in 20 mL of DCE. The resulting mixture was stirred at rt for about 1 hour, followed by addition of α-iminoesters **2** (1.18 g, 4.5 mmol) and DCE (20 mL). Upon the completion of the reaction as monitored by TLC (about 2 hours), the mixture was concentrated in vacuo. The residue was purified through flash column chromatography (EtOAc/PE = 1:5) to afford the corresponding product as white solid, 1.78 g, 85%yield.

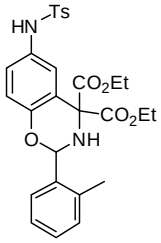
References:

1. L. Liao, C. Shu, M. Zhang, Y. Liao, X. Hu, Y. Zhang, Z. Wu, W. Yuan, X. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 10471.
2. a) S. Cabrera, R. G. Arrayas, J. C. Carretero, *J. Am. Chem. Soc.* **2005**, *127*, 16394; b) J. L. Vicario, S. Reboredo, D. Badia, L. Carrillo, *Angew. Chem. Int. Ed.* **2007**, *46*, 5168.

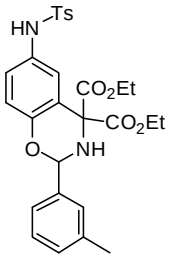
Characterization Data for the Cycloaddition Products 3



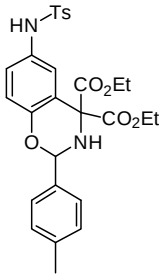
Diethyl 6-(4-methylphenylsulfonamido)-2-phenyl-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (**3a**): Prepared according to the general procedure as described above using phosphoric acid in 98% yield. Reaction time = 2 h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p. 122–124°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 2.8 Hz, 4H), 7.41 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.03 (s, 1H), 6.92 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 5.63 (d, *J* = 11.5 Hz, 1H), 4.43 – 4.10 (m, 4H), 3.54 (d, *J* = 11.5 Hz, 1H), 2.37 (s, 3H), 1.30 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.8, 152.8, 143.4, 137.5, 136.0, 129.4, 129.1, 128.8, 128.4, 127.1, 126.2, 125.1, 124.3, 118.4, 117.9, 83.9, 66.7, 63.1, 62.4, 21.3, 13.8, 13.7; IR (film) ν_{max} 3264, 2983, 1732, 1598, 1496, 1463, 1390, 1328, 1240, 1161, 1092, 1030, 955, 862, 814, 736, 700, 666, 602, 557, 539; HRMS (ESI) calcd for $C_{27}H_{28}N_2O_7S^+$ $(M+H)^+$ 525.1695, found 525.1691.



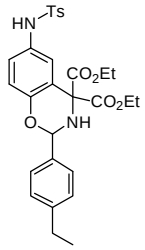
Diethyl 6-(4-methylphenylsulfonamido)-2-(o-tolyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (**3b**): Prepared according to the general procedure as described above using phosphoric acid in 96% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p. 150 – 151 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.24 (m, 5H), 7.02 (s, 1H), 6.91 (dd, J = 8.8, 2.6 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 5.73 (d, *J* = 12.1 Hz, 1H), 4.26 (m, 4H), 3.42 (d, *J* = 12.1 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H), 1.30 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.8, 153.3, 143.4, 136.0, 135.8, 135.7, 130.4, 129.4, 129.0, 128.7, 127.1, 126.0, 125.3, 125.2, 124.3, 118.4, 117.7, 81.7, 66.7, 63.1, 62.3, 21.3, 18.5, 13.9, 13.7; IR (film) ν_{max} 3261, 2982,1732, 1599, 1496, 1464, 1390, 1329, 1261, 1161, 1092, 1031, 963, 815, 732, 665, 610, 560, 542; HRMS (ESI) calcd for $C_{28}H_{30}N_2O_7S^+$ $(M+H)^+$ 539.1852, found 539.1848.



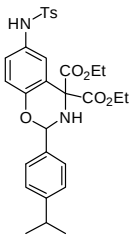
Diethyl 6-(4-methylphenylsulfonamido)-2-(m-tolyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (**3c**): Prepared according to the general procedure as described above using phosphoric acid in 95% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, 148 – 149 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.5, 5.6 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 3H), 6.89 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.60 (s, 1H), 5.57 (d, *J* = 11.4 Hz, 1H), 4.35 – 4.17 (m, 4H), 3.52 (d, *J* = 11.4 Hz, 1H), 2.38 (d, *J* = 1.4 Hz, 6H), 1.29 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.8, 152.9, 143.4, 138.1, 137.4, 136.0, 129.6, 129.4, 129.0, 128.3, 127.1, 126.7, 125.1, 124.3, 123.2, 118.4, 117.8, 84.0, 66.8, 63.0, 62.4, 21.3, 21.2, 13.8, 13.7; IR (film) ν_{max} 3268, 2981, 2917, 1732, 1597, 1495, 1390, 1328, 1261, 1161, 1092, 1028, 814, 747, 667, 556, 539. HRMS (ESI) calcd for $C_{28}H_{30}N_2O_7S^+$ $(M+H)^+$ 539.1852, found 539.1845.



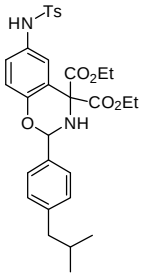
Diethyl 6-(4-methylphenylsulfonamido)-2-(p-tolyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3d): Prepared according to the general procedure as described above using phosphoric acid in 93% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p. 130 – 131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 10.0, 5.3 Hz, 3H), 7.20 (dd, *J* = 8.0, 3.9 Hz, 4H), 7.10 (d, *J* = 12.9 Hz, 1H), 6.91 (dd, J = 8.8, 2.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.59 (d, *J* = 11.4 Hz, 1H), 4.34 – 4.18 (m, 4H), 3.53 (d, *J* = 11.4 Hz, 1H), 2.36 (s, 6H), 1.32 – 1.25 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.9, 152.9, 143.3, 138.6, 136.0, 134.7, 129.4, 129.1, 129.0, 127.1, 126.1, 125.1, 124.3, 118.3, 117.8, 83.9, 66.7, 63.0, 62.4, 21.3, 21.0, 13.8, 13.7; IR (film) ν_{max} 3408, 3215, 2984, 1722, 1681, 1600, 1495, 1471, 1393, 1334, 1232, 1162, 1092, 1019, 814, 696, 552, 528; HRMS (ESI) calcd for $C_{28}H_{30}N_2O_7S^+$ $(M+H)^+$ 539.1852, found 539.1844.



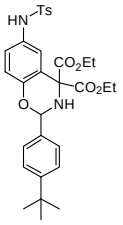
Diethyl 2-(4-ethylphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3] oxazine-4,4(3H)-dicarboxylate (3e): Prepared according to the general procedure as described above using phosphoric acid in 93% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p. 126 – 128 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.24 – 7.18 (m, 3H), 6.98 (s, 1H), 6.90 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.59 (d, *J* = 11.3 Hz, 1H), 4.34 – 4.17 (m, 4H), 3.53 (d, *J* = 11.3 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.32 – 1.21 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.8, 153.0, 145.1, 143.4, 136.0, 134.9, 129.4, 129.0, 127.9, 127.1, 126.2, 125.2, 124.4, 118.4, 117.8, 84.0, 66.7, 63.0, 62.35, 28.5, 21.3, 15.4, 13.8, 13.7; IR (film) ν_{max} 3268, 2968, 2934, 2874, 1731, 1599, 1495, 1392, 1240, 1162, 1092, 1031, 964, 815, 735, 666, 545; HRMS (ESI) calcd for $C_{29}H_{32}N_2O_7S^+$ $(M+H)^+$ 553.2008, found 553.2002.



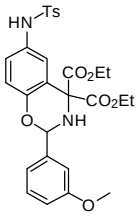
Diethyl 2-(4-isopropylphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3] oxazine-4,4(3H)-dicarboxylate (3f): Prepared according to the general procedure as described above (solvent DCM instead of DCE) using phosphoric acid in 92% yield. Reaction time = 2 h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford pale yellow solid, m.p. 94 – 96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.28 (dd, *J* = 10.8, 2.6 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.11 (s, 1H), 6.92 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 5.60 (d, *J* = 11.3 Hz, 1H), 4.32 – 4.19 (m, 4H), 3.55 (d, *J* = 11.3 Hz, 1H), 2.99 – 2.87 (m, 1H), 2.37 (s, 3H), 1.32 – 1.25 (m, 12H).^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.8, 153.0, 149.7, 143.3, 135.0, 129.4, 129.0, 127.1, 126.4, 126.2, 125.1, 124.3, 118.4, 117.8, 84.0, 66.8, 63.0, 62.4, 33.8, 23.8, 23.8, 21.3, 13.8, 13.7; IR (film) ν_{max} 3270, 2963, 2256, 1731, 1599, 1576, 1492, 1157, 912, 815, 666, 552; HRMS (ESI) calcd for $C_{30}H_{34}N_2O_7S^+$ $(M+H)^+$ 567.2165, found 567.2160.



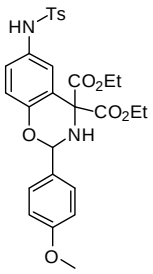
Diethyl 2-(4-isobutylphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3] oxazine-4,4(3H)-dicarboxylate (3g): Prepared according to the general procedure as described above (solvent DCM instead of DCE) using phosphoric acid in 66% yield. Reaction time = 4 h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford yellow semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 6.8 Hz, 2H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.20 (dd, *J* = 8.0, 5.6 Hz, 4H), 6.99 (s, 1H), 6.91 (dd, J = 8.8, 2.6 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 5.60 (d, *J* = 11.4 Hz, 1H), 4.33 – 4.17 (m, 4H), 3.54 (d, *J* = 11.4 Hz, 1H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.86 (m, 1H), 1.30 (dt, *J* = 13.5, 4.3 Hz, 6H), 0.90 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.8, 153.0, 143.3, 142.5, 136.0, 134.9, 129.6, 129.4, 129.1, 129.0, 127.1, 125.9, 125.2, 124.4, 118.4, 117.8, 84.0, 66.7, 63.0, 62.4, 45.0, 30.0, 22.1, 21.3, 13.8, 13.7; IR (film) ν_{max} 3267, 2958, 2869, 1732, 1600, 1495, 1465, 1386, 1240, 1162, 1092, 1031, 911, 814, 732, 665, 600, 556; HRMS (ESI) calcd for $C_{31}H_{36}N_2O_7S^+$ $(M+H)^+$ 581.2321, found 538.2316.



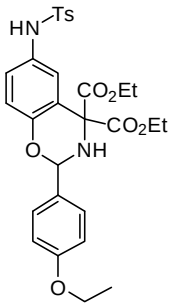
Diethyl 2-(4-(tert-butyl)phenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3] oxazine-4,4(3H)-dicarboxylate (3h): Prepared according to the general procedure as described above using phosphoric acid in 60% yield. Reaction time = 4h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford yellow semi -solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.49 (m, 4H), 7.47 – 7.42 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.90 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.85 (s, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 5.60 (d, *J* = 11.3 Hz, 1H), 4.34 – 4.22 (m, 4H), 3.55 (d, *J* = 11.3 Hz, 1H), 2.38 (s, 3H), 1.33 – 1.28 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.8, 153.1, 152.0, 143.3, 136.0, 134.6, 129.4, 128.9, 127.1, 125.9, 125.3, 125.2, 124.5, 118.4, 117.8, 84.0, 34.5, 31.2, 31.1, 21.3, 13.8, 13.7. IR (film) ν_{max} 3270, 3060, 2964, 2871, 1732, 1599, 1494, 1368, 1219, 1161, 1028, 911, 815, 666, 610, 546; HRMS (ESI) calcd for $C_{31}H_{36}N_2O_7S^+$ $(M+H)^+$ 581.2321, found 581.2314.



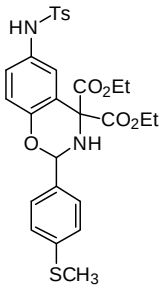
Diethyl 2-(3-methoxyphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3] oxazine-4,4(3H)-dicarboxylate (3i): Prepared according to the general procedure as described above (solvent DCM instead of DCE) using phosphoric acid in 82% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p. 125 – 127 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.13 (m, 4H), 6.97 – 6.89 (m, 2H), 6.84 (t, *J* = 7.9 Hz, 2H), 5.60 (d, *J* = 11.3 Hz, 1H), 4.37 – 4.15 (m, 4H), 3.84 (s, 3H), 3.56 (d, *J* = 11.4 Hz, 1H), 2.39 (s, 3H), 1.31 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.8, 159.6, 152.9, 143.4, 139.0, 136.0, 129.5, 129.4, 129.0, 127.1, 125.2, 124.5, 118.5, 118.4, 117.9, 114.5, 111.7, 83.8, 66.7, 63.0, 62.4, 55.2, 21.3, 13.8, 13.7; IR (film) ν_{max} 3262, 2982, 1732, 1598,1495, 1466, 1391, 1329, 1262, 1161, 1092, 1036, 815, 737, 673, 604, 554; HRMS (ESI) calcd for $C_{28}H_{30}N_2O_8S^+$ $(M+H)^+$ 555.1801, found 555.1797.



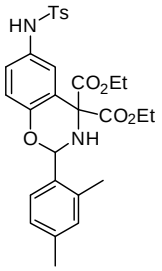
Diethyl 2-(4-methoxyphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3] oxazine-4,4(3H)-dicarboxylate (3j): Prepared according to the general procedure as described above using phosphoric acid in 90% yield. Reaction time = 2 h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford yellow semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.51 (dd, *J* = 9.2, 2.4 Hz, 2H), 7.41 (d, *J* = 2.6 Hz, 1H), 7.24 – 7.16 (m, 2H), 6.91 (m, 3H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.57 (d, *J* = 11.1 Hz, 1H), 4.22 (m, 4H), 3.81 (s, 3H), 3.49 (d, *J* = 11.1 Hz, 1H), 2.37 (s, 3H), 1.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.8, 160.0, 153.0, 143.4, 136.0, 129.8, 129.4, 128.9, 127.5, 127.2, 127.1, 125.2, 124.5, 118.3, 117.8, 113.7, 83.8, 66.7, 63.0, 62.4, 55.2, 21.3, 13.8, 13.7; IR (film) ν_{max} 3259, 2981, 1732, 1599, 1577, 1513, 1393, 1261, 1161, 1092, 1025, 814, 672, 552; HRMS (ESI) calcd for $C_{28}H_{30}N_2O_8S$ + $(M+H)^+$ 555.1801, found 555.1796.



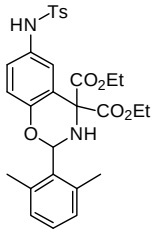
Diethyl 2-(4-ethoxyphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3] oxazine-4,4(3H)-dicarboxylate (3k): Prepared according to the general procedure as described above using phosphoric acid in 93% yield. Reaction time = 2 h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford yellow semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 2H), 7.53 – 7.46 (m, 2H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.96 – 6.86 (m, 3H), 6.78 (d, *J* = 8.8 Hz, 1H), 5.57 (d, *J* = 11.1 Hz, 1H), 4.33 – 4.16 (m, 4H), 4.04 (q, *J* = 7.0 Hz, 2H), 3.50 (d, *J* = 11.2 Hz, 1H), 2.36 (s, 3H), 1.44 – 1.37 (m, 3H), 1.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.9, 159.3, 152.9, 143.3, 136.0, 130.2, 129.7, 129.4,, 129.0, 127.5, 127.1, 125.1, 124.3, 118.3, 117.7, 114.3, 83.8, 66.8, 63.4, 63.0, 62.4, 21.3, 14.6, 13.8, 13.7; IR (film) ν_{max} 3410, 3217, 2984, 1731, 1681, 1601, 1576, 1512, 1393, 1238, 1161, 1116, 1092, 1043, 921, 814, 735, 697, 553, 528; HRMS (ESI) calcd for $C_{29}H_{32}N_2O_8S$ + $(M+H)^+$ 569.1958, found 569.1953.



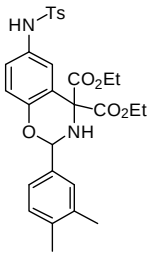
Diethyl 6-(4-methylphenylsulfonamido)-2-(4-(methylthio)phenyl)-2H-benzo[e] [1,3] oxazine-4,4(3H)-dicarboxylate (3l): Prepared according to the general procedure as described above using phosphoric acid in 77% yield. Reaction time = 2 h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, yellow semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.24 – 7.16 (m, 2H), 6.94 – 6.87 (m, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.57 (d, *J* = 11.4 Hz, 1H), 4.35 – 4.13 (m, 4H), 3.50 (d, *J* = 11.4 Hz, 1H), 2.48 (d, *J* = 4.6 Hz, 3H), 2.36 (s, 3H), 1.28 (q, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.8, 152.8, 143.4, 139.5, 136.0, 134.3, 129.4, 129.0, 127.1, 126.7, 126.3, 125.2, 124.4, 118.4, 117.8, 83.6, 66.6, 63.1, 62.4, 21.3, 15.6, 13.8, 13.7. IR (film) ν_{max} 3261, 2982, 1732, 1694, 1592, 1495, 1392, 1327, 1228, 1161, 1092, 1020, 959, 814, 734, 671, 607, 561, 542; HRMS (ESI) calcd for $C_{28}H_{30}N_2O_7S_2$ + $(M+H)^+$ 571.1573, found 571.1567.



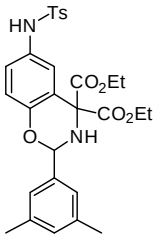
Diethyl 2-(2,4-dimethylphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3m): Prepared according to the general procedure as described above using phosphoric acid in 95% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p 125 – 127 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.3 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 2.6 Hz, 1H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 – 6.99 (m, 2H), 6.93 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.72 (d, *J* = 12.0 Hz, 1H), 4.35 – 4.16 (m, 4H), 3.42 (d, *J* = 12.0 Hz, 1H), 2.34 (dd, *J* = 14.9, 5.2 Hz, 9H), 1.35 – 1.27 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 167.9, 153.3, 143.3, 138.4, 136.1, 135.6, 132.9, 131.2, 129.4, 129.1, 127.1, 126.6, 125.3, 125.1, 124.2, 118.4, 117.7, 81.7, 66.8, 63.1, 62.3, 21.3, 20.9, 18.4, 13.9, 13.7; IR (film) ν_{max} 3264, 2983, 1732, 1598, 1495, 1392, 1331, 1245, 1162, 1092, 1033, 967, 927, 815, 735, 666, 613, 570, 549; HRMS (ESI) calcd for $C_{29}H_{32}N_2O_7S^+$ $(M+H)^+$ 553.2008, found 563.2004.



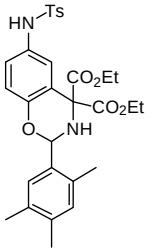
Diethyl 2-(2,6-dimethylphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3n): Prepared according to the general procedure as described above (solvent DCM instead of DCE) using phosphoric acid in 58% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford pale yellow solid, m.p. 120 – 122 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.45 (d, *J* = 2.6 Hz, 1H), 7.25 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.16 (dd, *J* = 8.4, 6.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.92 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.83 (s, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 5.98 (d, *J* = 10.5 Hz, 1H), 4.33 – 4.19 (m, 4H), 3.79 (d, *J* = 10.5 Hz, 1H), 2.48 (s, 6H), 2.39 (s, 3H), 1.33 – 1.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 167.9, 153.0, 143.4, 136.6, 136.2, 133.0, 129.4, 129.3, 128.7, 128.6, 127.1, 125.3, 124.8, 118.3, 117.4, 82.6,66.6, 63.0, 62.4, 21.3, 20.2, 13.8, 13.7; IR (film) ν_{max} 3263, 2982, 1732, 1596, 1496, 1469, 1392, 1330, 1239, 1162, 1092, 1030, 911, 814, 777, 732, 666, 617, 67, 545; HRMS (ESI) calcd for $C_{29}H_{32}N_2O_7S^+$ $(M+H)^+$ 553.2008, found 553.2004.



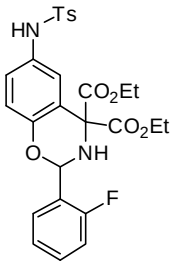
Diethyl 2-(3,4-dimethylphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3o): Prepared according to the general procedure as described above using phosphoric acid in 74% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p. 118 – 120 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.18 (dd, *J* = 11.6, 8.0 Hz, 3H), 6.95 (s, 1H), 6.90 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 5.56 (d, *J* = 11.2 Hz, 1H), 4.26 (m, *J* = 20.8, 14.8, 7.1 Hz, 4H), 3.52 (d, *J* = 11.2 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 6H), 1.29 (dd, *J* = 13.2, 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.8, 143.3, 137.3, 136.6, 136.0, 135.0, 129.6, 129.4, 128.9, 127.2, 127.1, 125.1, 124.4, 123.5, 118.3, 117.8, 84.0, 66.8, 63.0, 62.3, 21.3, 19.6, 19.4, 13.8, 13.7; IR (film) ν_{max} 3267, 2981, 1733, 1598, 1496, 1454, 1390, 1329, 1238, 1162, 1092, 1021, 924, 815, 735, 705, 672, 556, 542; HRMS (ESI) calcd for $C_{29}H_{32}N_2O_7S^+$ $(M+H)^+$ 553.2008, found 553.2002.



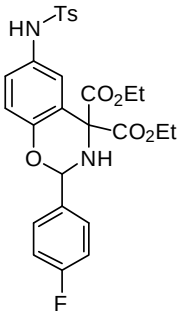
Diethyl 2-(3,5-dimethylphenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3p): Prepared according to the general procedure as described above using phosphoric acid in 68% yield. Reaction time = 2h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford pale yellow solid, m.p. 123 – 125 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 12.3, 5.8 Hz, 2H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 4H), 7.02 (s, 1H), 6.96 – 6.86 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 5.55 (d, *J* = 11.3 Hz, 1H), 4.27 (m, 4H), 3.53 (d, *J* = 11.4 Hz, 1H), 2.37 (d, *J* = 5.4 Hz, 3H), 2.35 (s, 6H), 1.34 – 1.27 (m, 6H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 169.3, 167.8, 153.0, 143.4, 138.0, 137.4, 136.0, 130.5, 129.4, 129.0, 127.1, 125.2, 124.4, 123.8, 118.4, 117.8, 84.1, 66.8, 63.0, 62.4, 21.30, 21.11, 13.8, 13.7; IR (film) ν_{max} 3264, 2982, 1732, 1599, 1495, 1390, 1329, 1238, 1161, 1092, 1025, 915, 855, 814, 731, 666, 614, 560, 544; HRMS (ESI) calcd for $C_{29}H_{32}N_2O_7S^+$ $(M+H)^+$ 553.2008, found 553.2004.



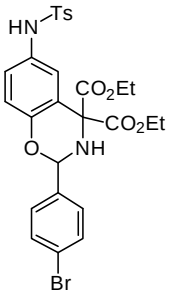
Diethyl 6-(4-methylphenylsulfonamido)-2-(2,4,5-trimethylphenyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3q): Prepared according to the general procedure as described above using phosphoric acid in 76% yield. Reaction time = 4h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, m.p. 76 – 78 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 2H), 7.42 (d, *J* = 2.3 Hz, 2H), 7.26 – 7.20 (m, 2H), 6.97 (s, 1H), 6.89 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 6.52 (s, 1H), 5.68 (d, *J* = 11.7 Hz, 1H), 4.33 – 4.18 (m, 4H), 3.41 (d, *J* = 11.7 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H), 1.33 – 1.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.9, 153.4, 143.3, 137.0, 136.1, 134.0, 133.0, 132.8, 131.8, 129.4, 128.9, 127.1, 126.4, 125.2, 124.4, 118.4, 117.7, 81.8, 66.8, 63.0, 62.3, 21.3, 19.2, 19.1, 17.9, 13.9, 13.7; IR (film) ν_{max} 3273, 2980, 1734, 1617, 1496, 1448, 1368, 1215, 1161, 1092, 1032, 957, 861, 814, 735, 672,551; HRMS (ESI) calcd for $C_{30}H_{34}N_2O_7S^+$ $(M+H)^+$ 567.2165, found 567.2158.



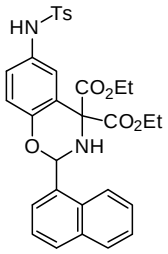
Diethyl 2-(2-fluorophenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3r): Prepared according to the general procedure as described above (solvent DCM instead of DCE) using phosphoric acid in 81% yield. Reaction time = 6h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford yellow solid, m.p. 149 – 151 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.55 (m, 3H), 7.43 (d, J = 2.6 Hz, 1H), 7.40 – 7.30 (m, 1H), 7.24 – 7.03 (m, 5H), 6.93 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 5.84 (d, J = 12.0 Hz, 1H), 4.35 – 4.13 (m, 4H), 3.67 (d, J = 12.0 Hz, 1H), 2.36 (s, 3H), 1.29 (q, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 167.7, 159.99 (d, *J* = 249.5 Hz),152.8, 143.4, 135.9, 130.6 (d, *J* = 8.3 Hz),129.38, 129.30, 127.45 (d, *J* = 3.3 Hz), 127.11, 125.1, 124.80 (d, *J* = 12.4 Hz), 124.22 (d, *J* = 3.5 Hz), 124.1, 118.4, 117.7, 115.6 (d, *J* = 21.1 Hz), 79.3 (d, *J* = 3.8 Hz), 66.8, 63.2, 62.5, 21.3, 13.7, 13.6; IR (film) ν_{max} 3263, 2983, 1732, 1621, 1596, 1496, 1460, 1388, 1328, 1238, 1162, 1092, 1030, 939, 815, 763, 673, 609, 561, 543; HRMS (ESI) calcd for $C_{27}H_{27}FN_2O_7S^+$ $(M+H)^+$ 543.1601, found 543.1596.



Diethyl 2-(4-fluorophenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3s): Prepared according to the general procedure as described above using phosphoric acid in 75% yield. Reaction time = 6h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford yellow semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 4H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.19 (t, *J* = 8.2 Hz, 2H), 7.12 – 7.02 (m, 2H), 6.95 – 6.83 (m, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.59 (d, *J* = 11.5 Hz, 1H), 4.32 – 4.17 (m, 4H), 3.48 (d, *J* = 11.5 Hz, 1H), 2.36 (s, 3H), 1.32 – 1.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.7, 162.88 (d, *J* = 247.5 Hz), 152.6, 143.4, 136.0, 133.5(d, *J* = 3.2 Hz), 129.4, 129.2, 128.1(d, *J* = 8.4 Hz), 127.1, 126.9, 125.1, 124.3, 118.3, 117.8, 115.2 (d, *J* = 21.7 Hz), 83.3, 66.6, 63.1, 62.4, 21.3, 13.8, 13.6; IR (film) ν_{max} 3265, 2983, 1732, 1600, 1496, 1390, 1329, 1228, 1160, 1092, 1030,815,737,672,545; HRMS (ESI) calcd for $C_{27}H_{27}FN_2O_7S^+$ $(M+H)^+$ 543.1601, found 543.1598.

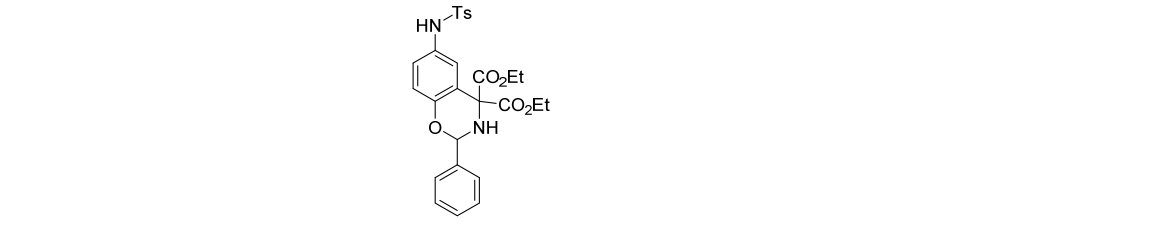


Diethyl 2-(4-bromophenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3t): Prepared according to the general procedure as described above using phosphoric acid in 35% yield. Reaction time = 10h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford white solid, yellow semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.45 (m, 6H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.53 (s, 1H), 5.55 (d, *J* = 11.6 Hz, 1H), 4.33 – 4.18 (m, 4H), 3.48 (d, *J* = 11.6 Hz, 1H), 2.37 (s, 3H), 1.29 (dd, *J* = 13.6, 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 167.7, 152.6, 143.4, 136.5, 136.0, 131.5, 129.4, 129.1, 128.0, 127.1, 125.2, 124.5, 122.9, 118.4, 117.9, 115.8, 83.22, 66.53, 63.12, 62.44, 21.30, 13.81, 13.65; IR (film) ν_{max} 3267, 2982, 1732, 1597, 1494, 1393, 1369,1329, 1261, 1161, 1092, 1013, 861, 813, 735, 666, 605, 560, 541; HRMS (ESI) calcd for $C_{27}H_{27}BrN_2O_7S^+$ $(M+H)^+$ 603.0801, found 603.0793.



Diethyl 6-(4-methylphenylsulfonamido)-2-(naphthalen-1-yl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (3u): Prepared according to the general procedure as described above using phosphoric acid in 60% yield. Reaction time = 4 h. It was purified by flash chromatography (EtOAc/PE = 1/5) to afford, brown semi-solid. ^{1}HNMR (300 MHz, $CDCl_3$) δ 8.35 – 8.17 (m, 1H), 7.98 – 7.85 (m, 3H), 7.64 (t, *J* = 7.2 Hz, 2H), 7.59 – 7.48 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.09 – 6.84 (m, 3H), 6.31 (d, *J* = 11.7 Hz, 1H), 4.50 – 4.33 (m, 2H), 4.31 – 4.13 (m, 2H), 3.66 (d, *J* = 11.7 Hz, 1H), 2.41 (d, *J* = 6.4 Hz, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 169.3, 167.7, 153.1, 143.4, 136.1, 133.6, 133.0, 130.4, 129.5, 129.4, 129.1, 128.5, 127.1, 126.3, 125.6, 125.2, 125.0, 124.4, 123.8, 123.4, 118.5, 118.0, 81.9, 66.8, 63.1, 62.5, 21.3, 13.9, 13.7; IR (film) ν_{max} 3261, 2982, 2927, 1732, 1598, 1495, 1392, 1331, 1261, 1161, 1092, 1030, 955, 804, 779, 736, 705, 673, 608, 558, 542; HRMS (ESI) calcd for $C_{31}H_{30}N_2O_7S^+$ $(M+H)^+$ 575.1852, found 575.1847.

NMR Spectra of products 3



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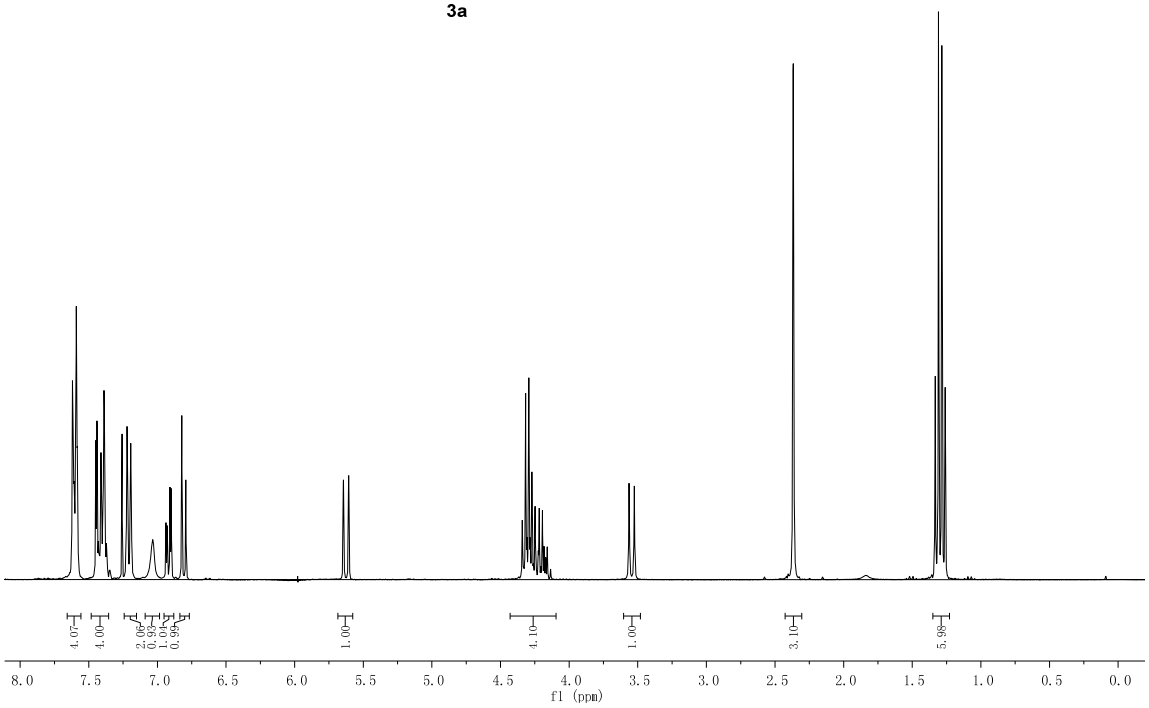

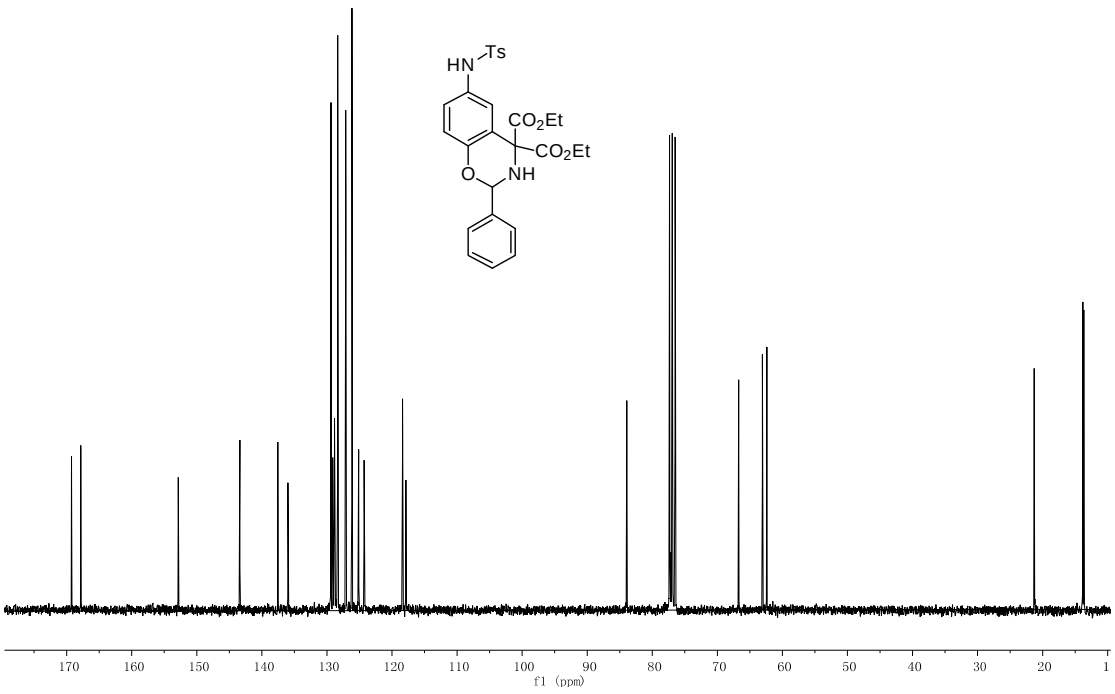

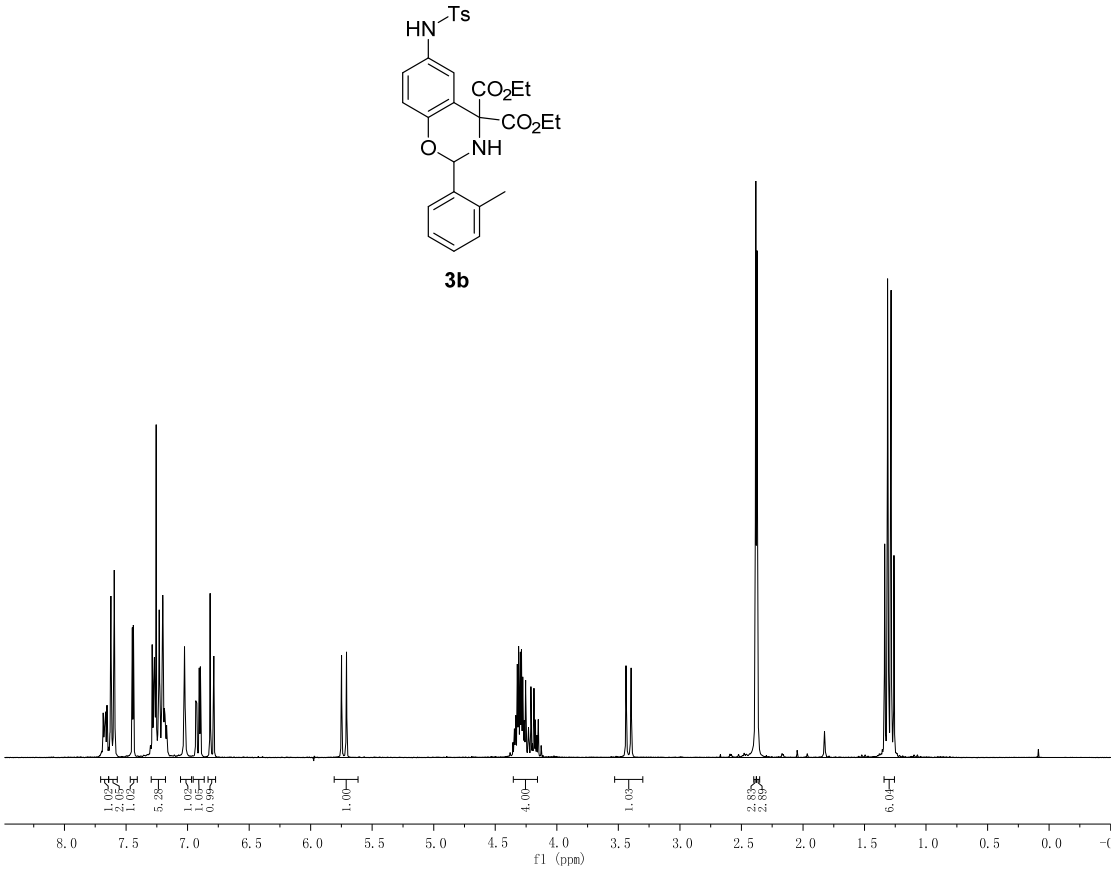
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4.00
1.03
2.83
2.89
6.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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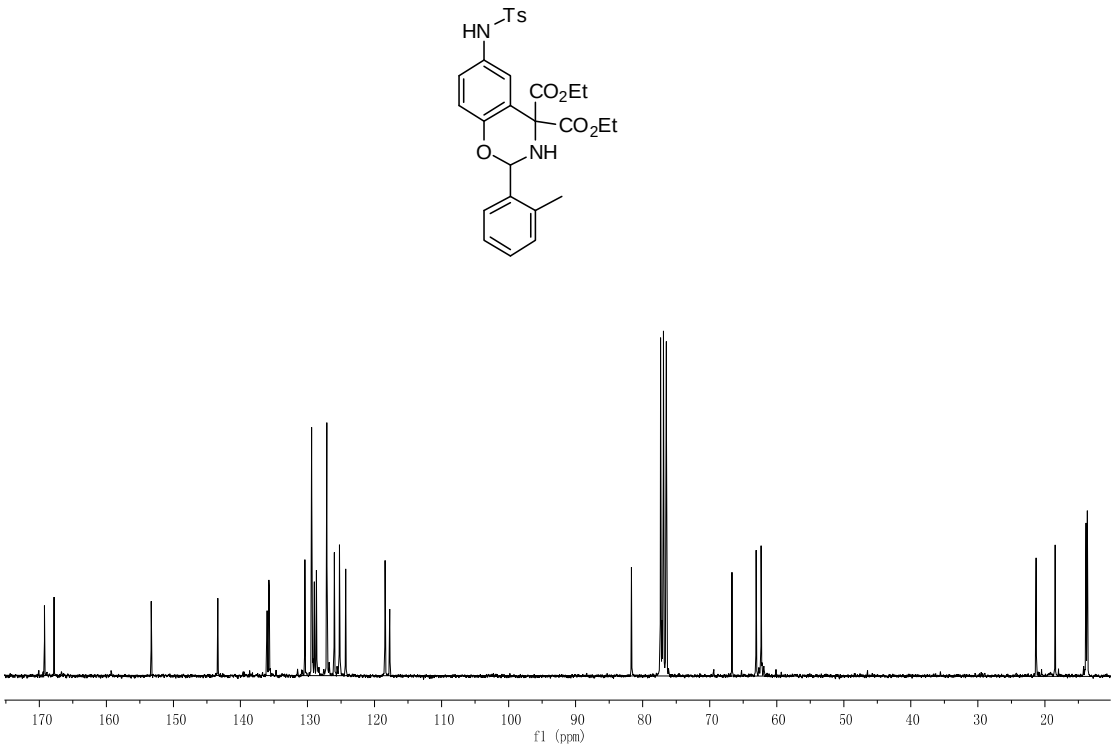
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3b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Ts
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CO2Et
O
NH
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150
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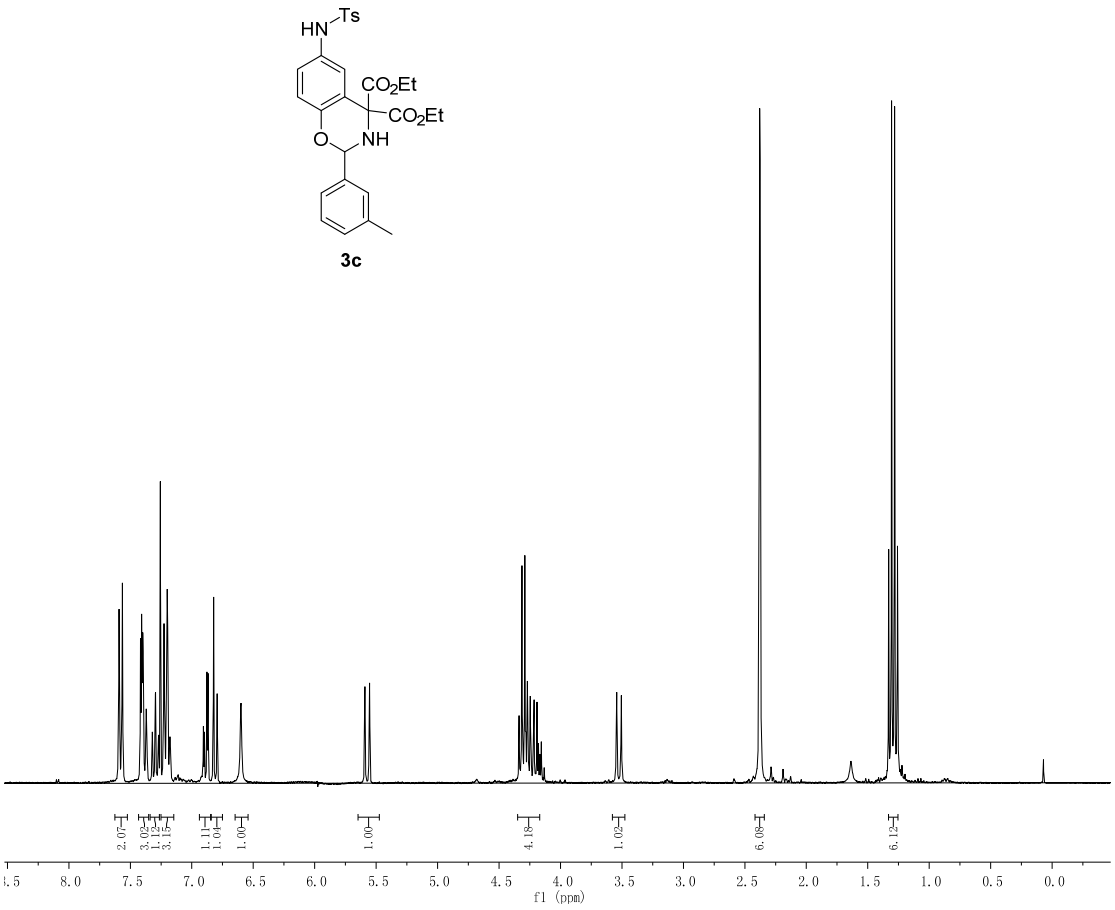
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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Ts
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CO2Et
O
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3.17
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1.01
1.00
1.00
4.18
1.02
6.08
6.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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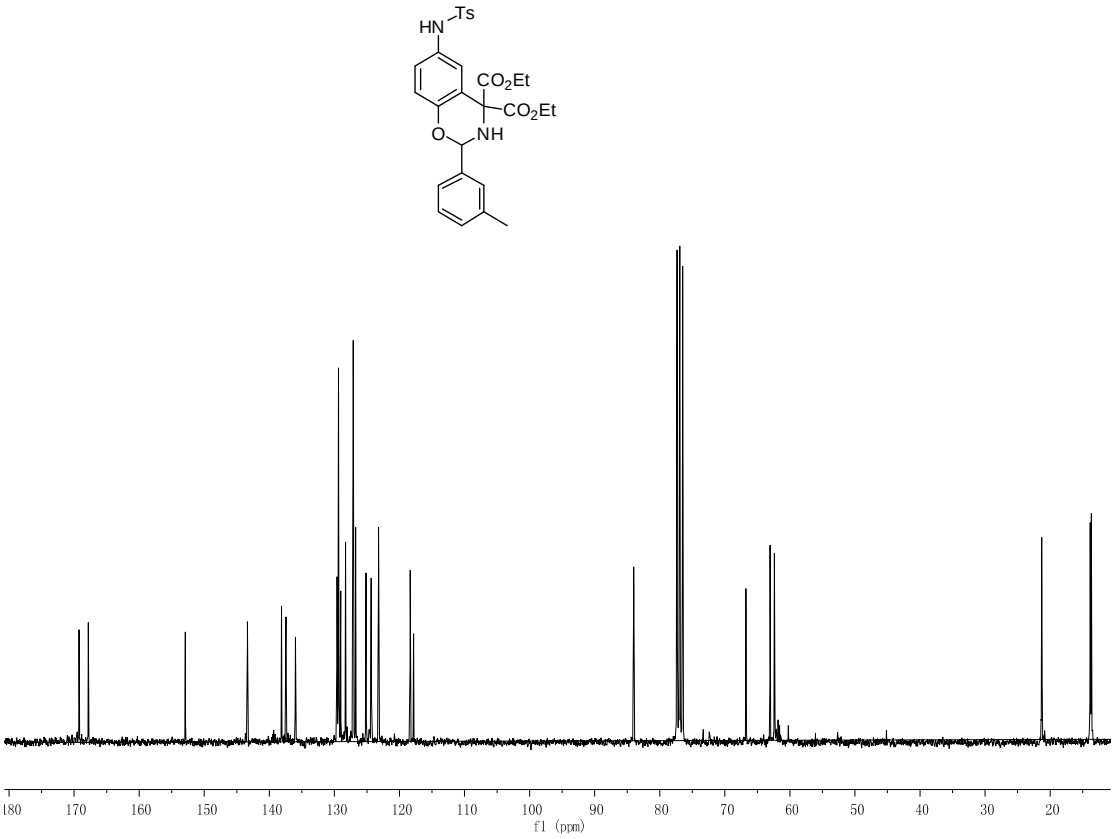
f1 (ppm)

3c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Ts
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CO2Et
O
NH
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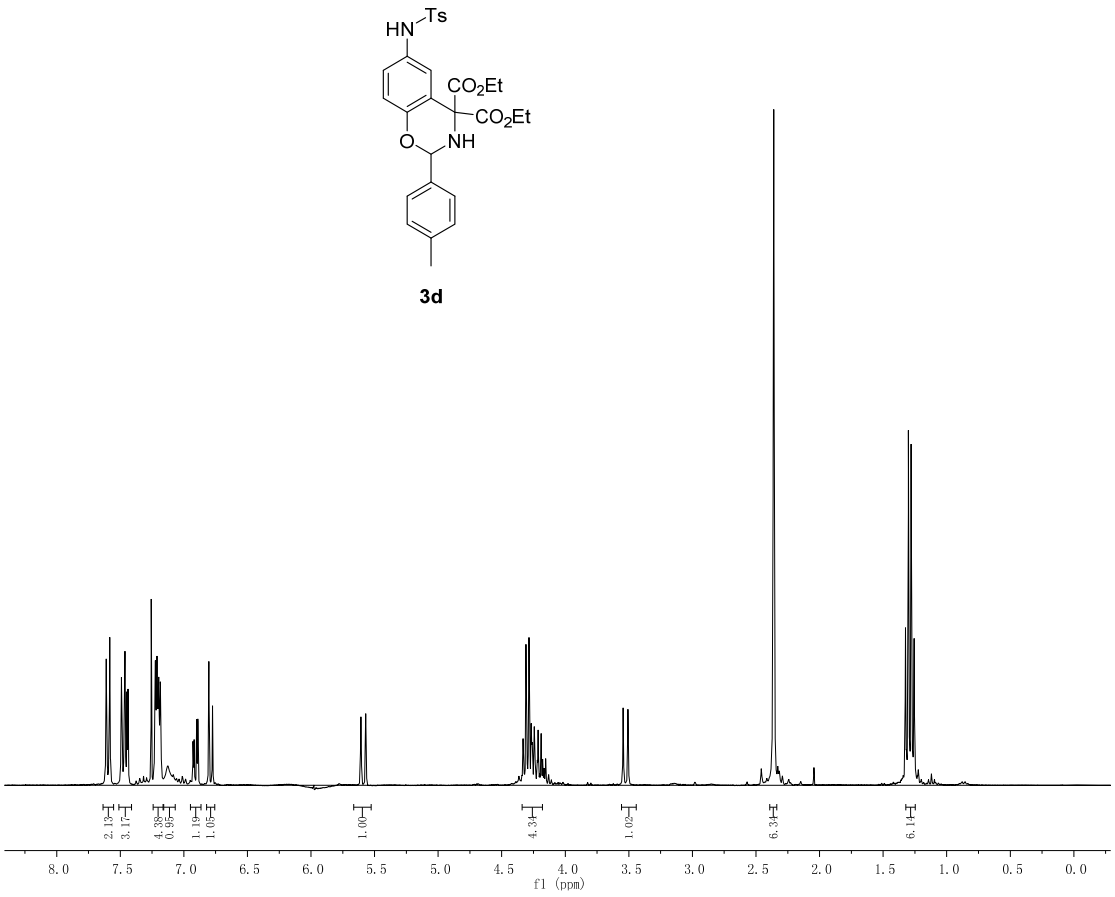
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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CO2Et
O
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6.14
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7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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1.0
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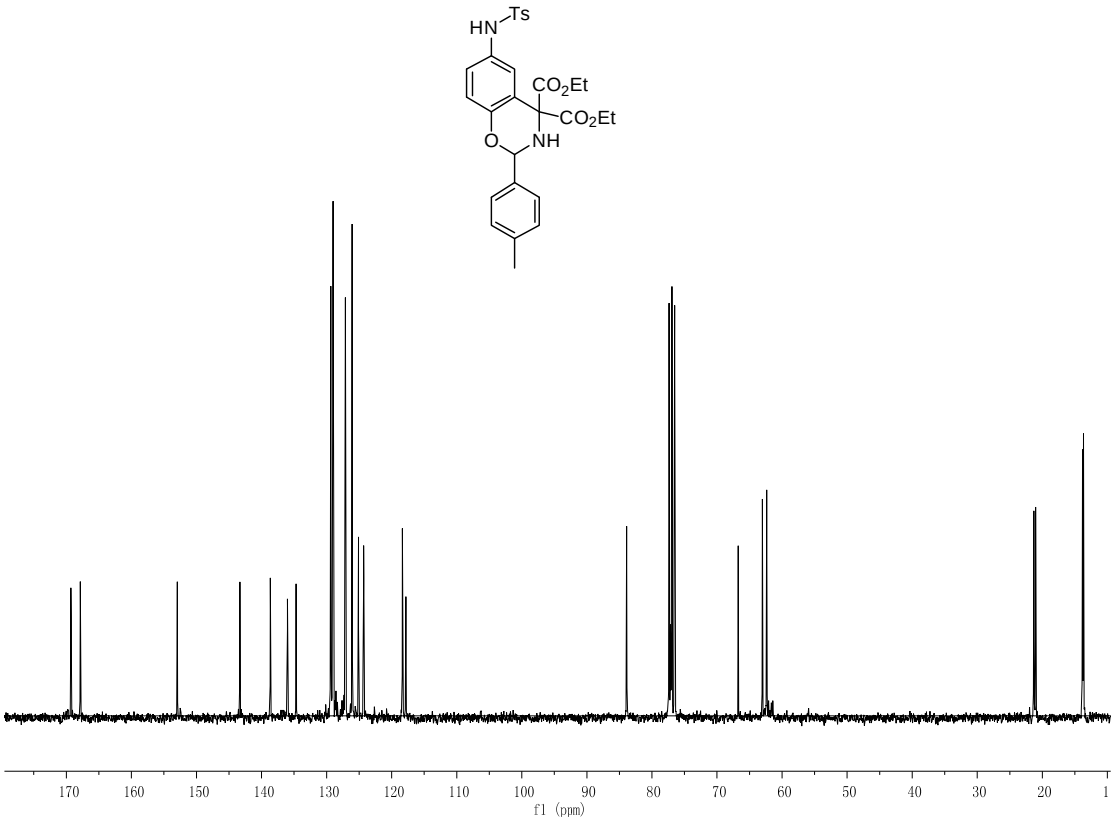
0.0
f1 (ppm)

3d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Ts
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CO2Et
O
NH
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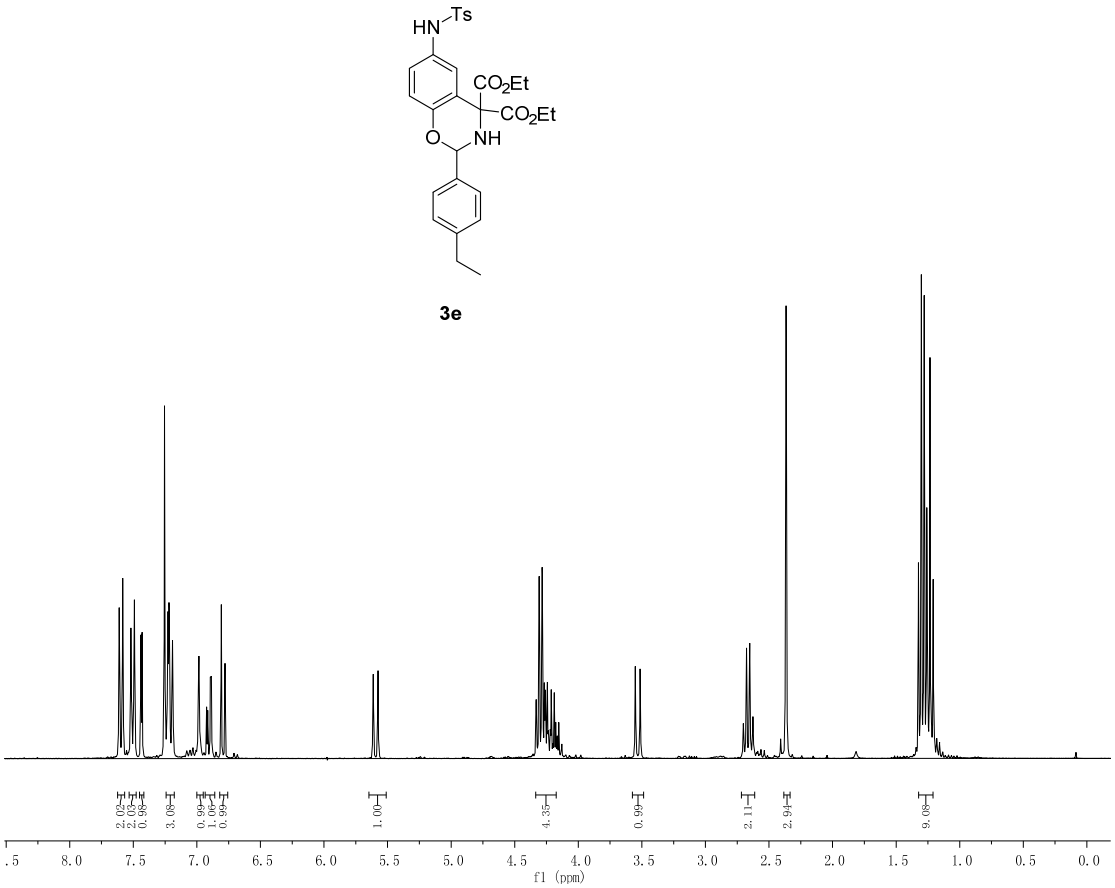
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)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Ts
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CO2Et
O
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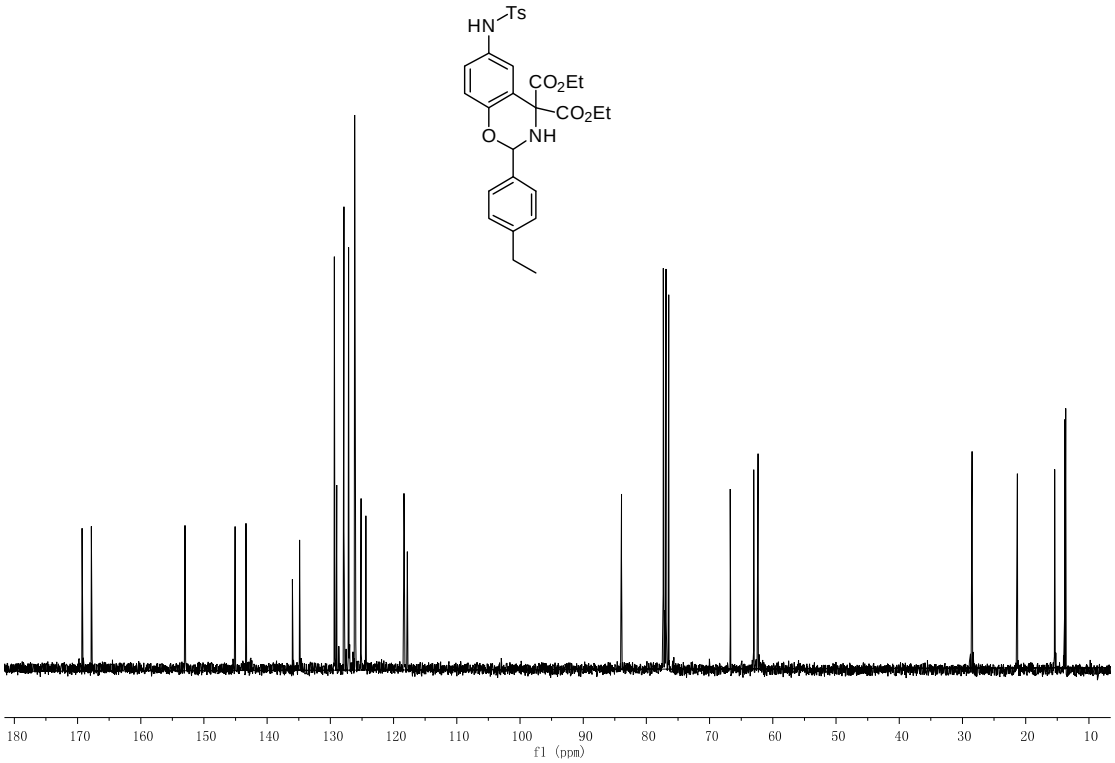
0.99
2.11
2.94
9.08
f1 (ppm)

3e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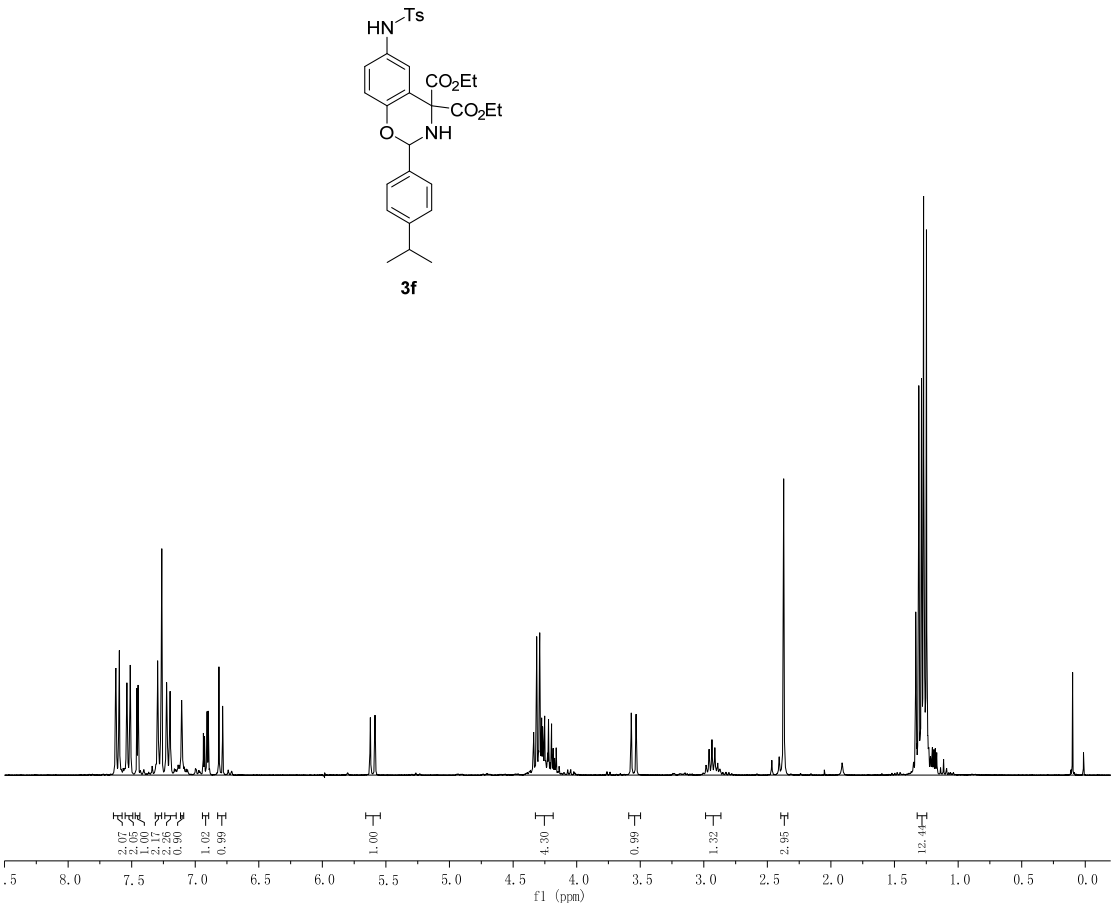
Ts
CO2Et
CO2Et
O
NH
f1 (ppm)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CO2Et
CO2Et
O
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1.00
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1.02
0.99
1.00
4.30
0.99
1.32
2.95
12.44
8.0
7.5
7.0
6.5
6.0
5.5
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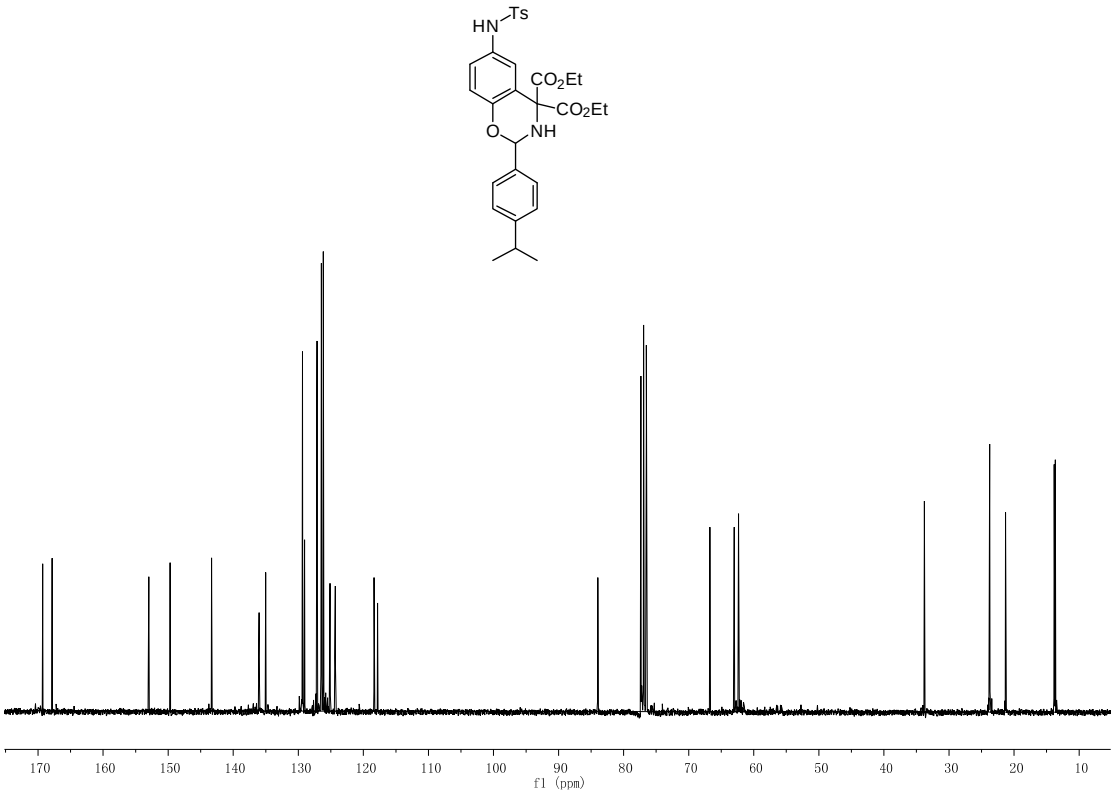
0.0
f1 (ppm)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Ts
CO2Et
CO2Et
O
NH
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110
100
90
80
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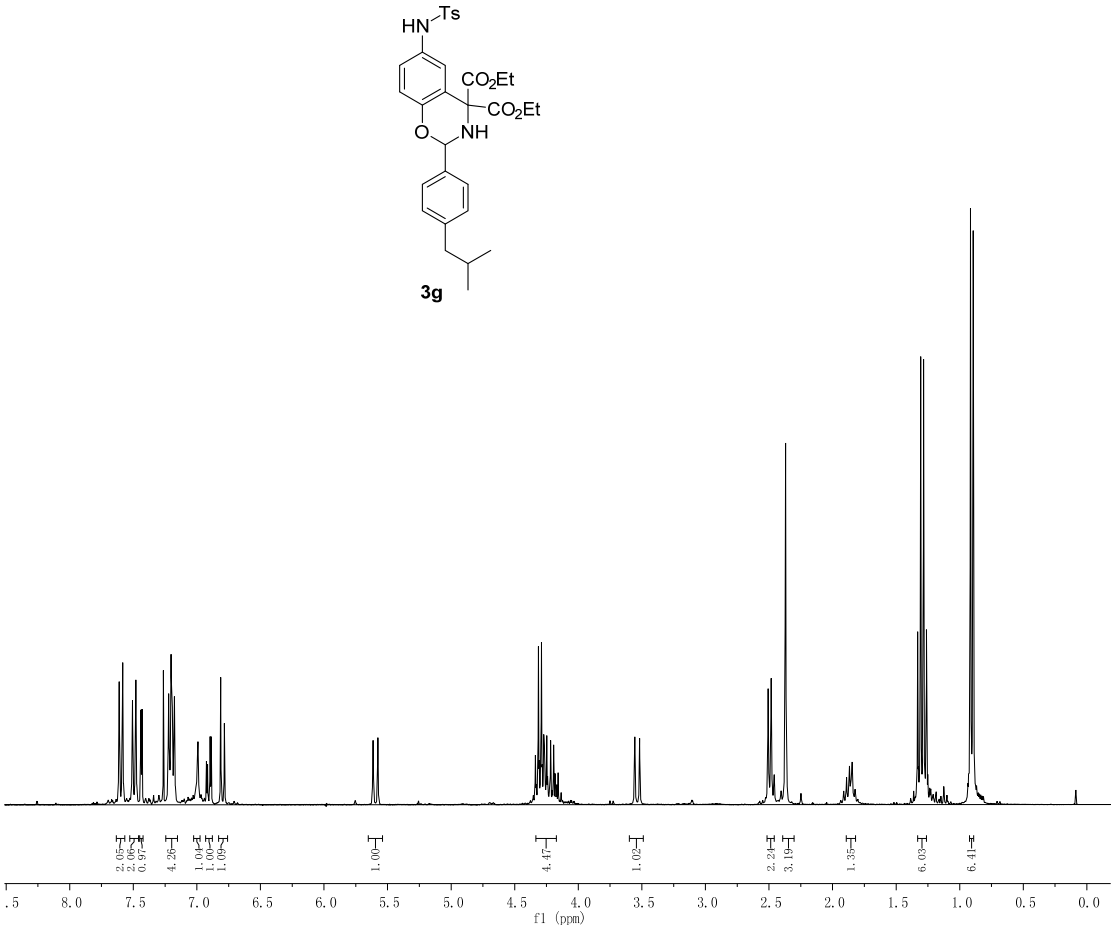
60
50
40
30
20
10
f1 (ppm)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Ts
CO2Et
CO2Et
O
NH
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0.97
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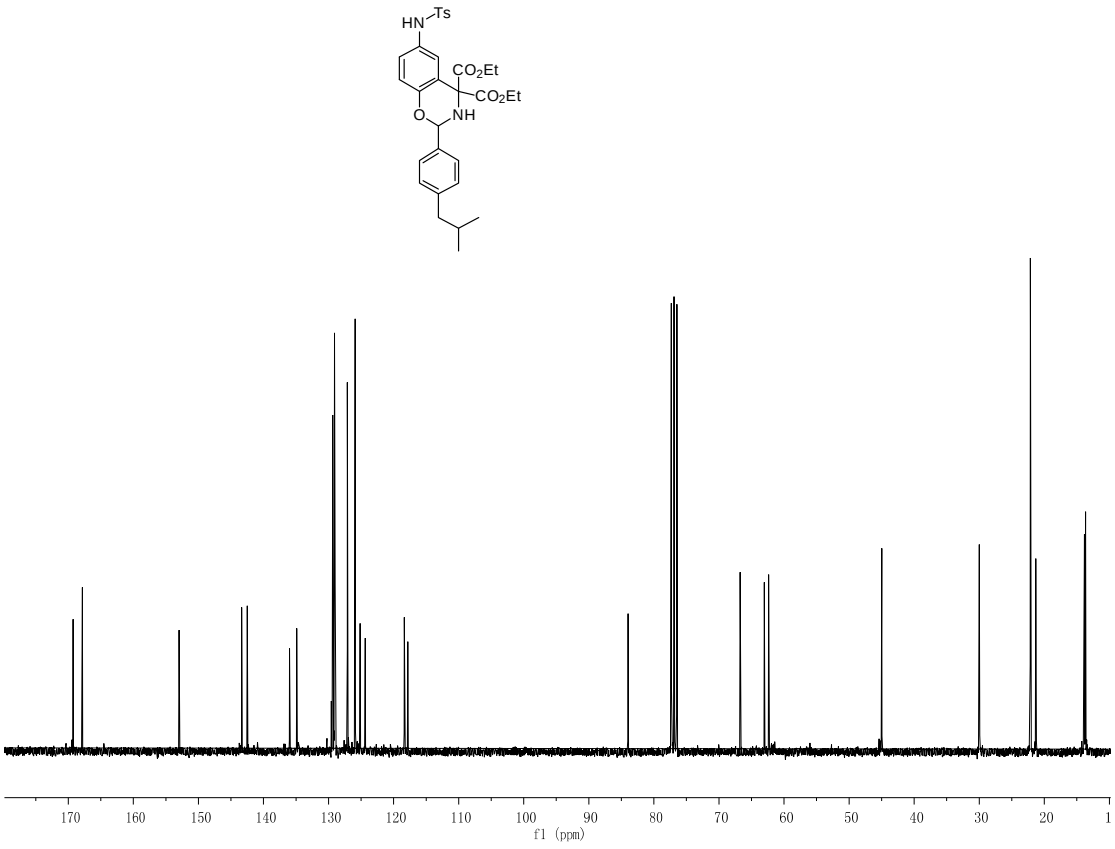
1.35
6.03
6.41
f1 (ppm)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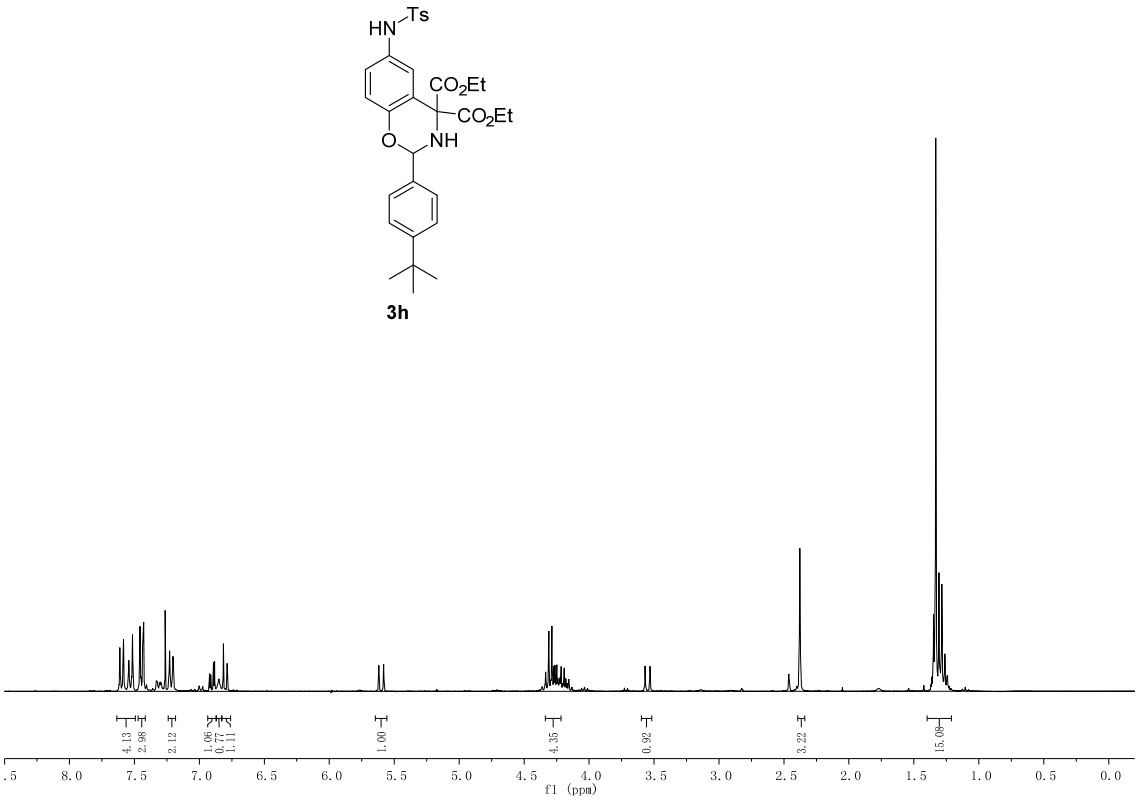
Ts
CO2Et
CO2Et
O
NH
f1 (ppm)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CO2Et
O
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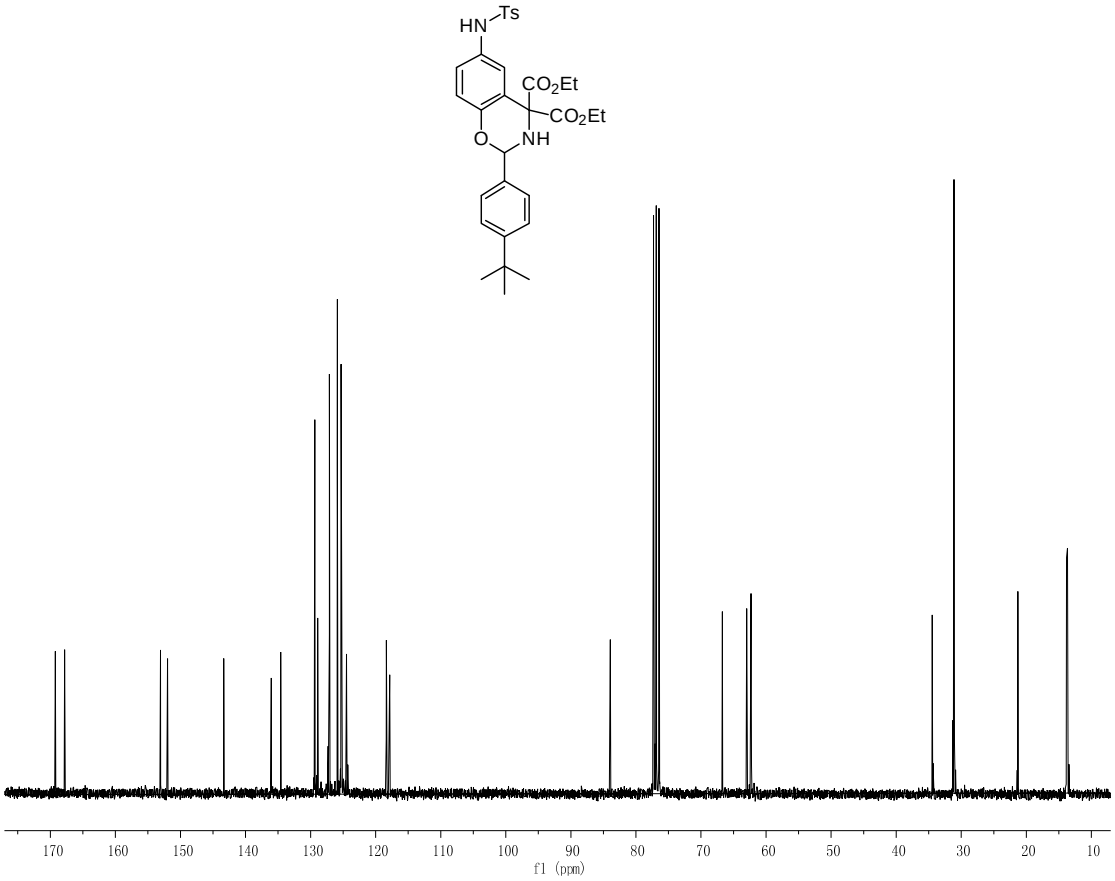
15.09
f1 (ppm)

3h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Ts
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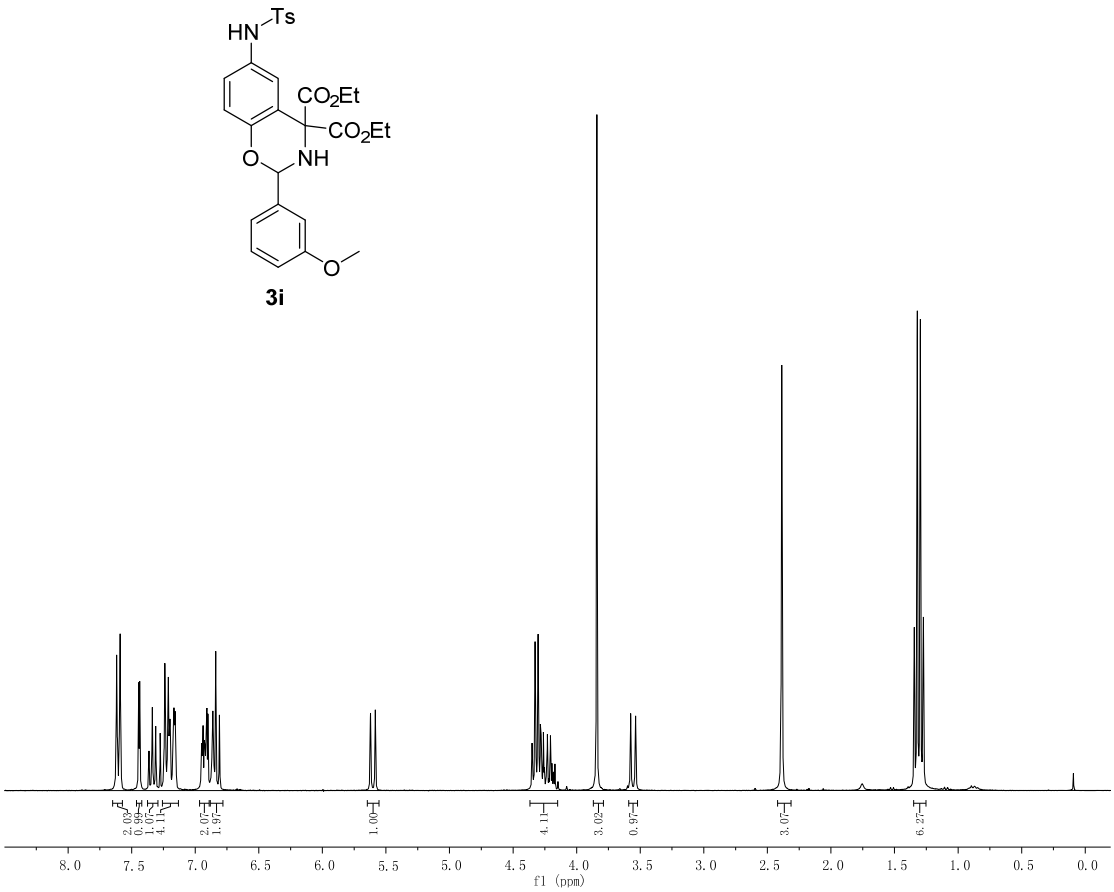
CO2Et
O
NH
f1 (ppm)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CO2Et
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NH
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3.02
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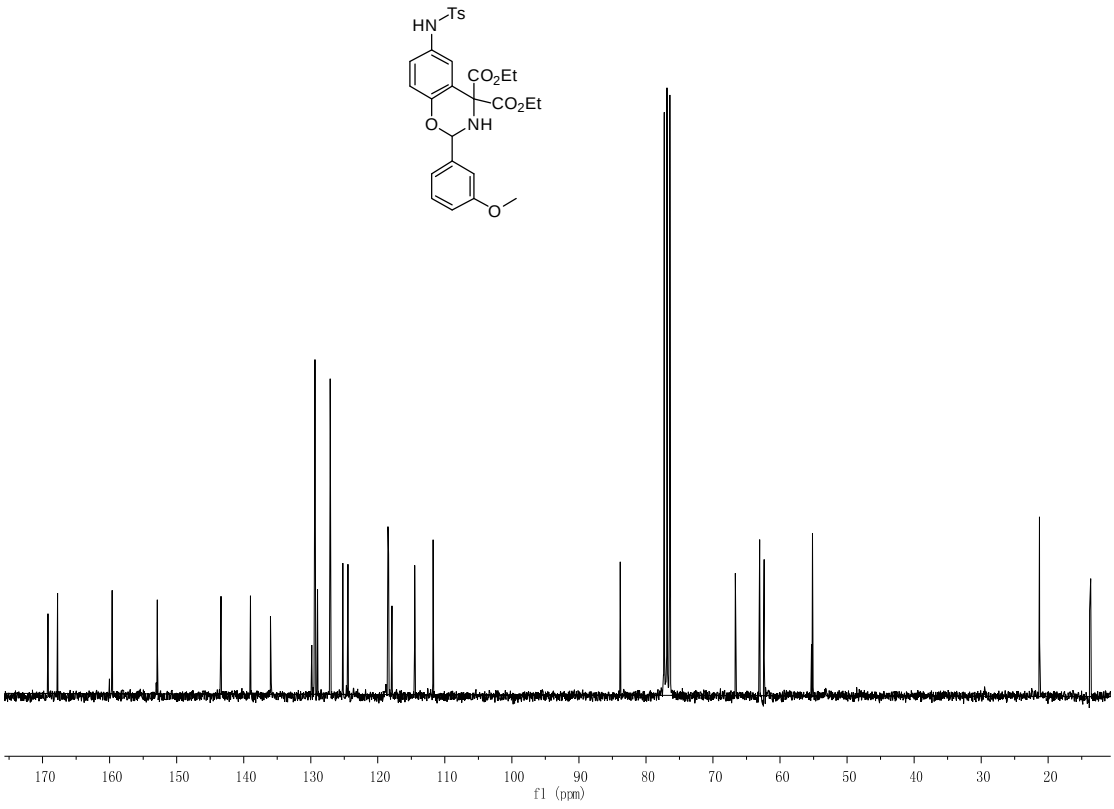
0.0
f1 (ppm)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Ts
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CO2Et
O
NH
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130
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110
100
90
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70
60
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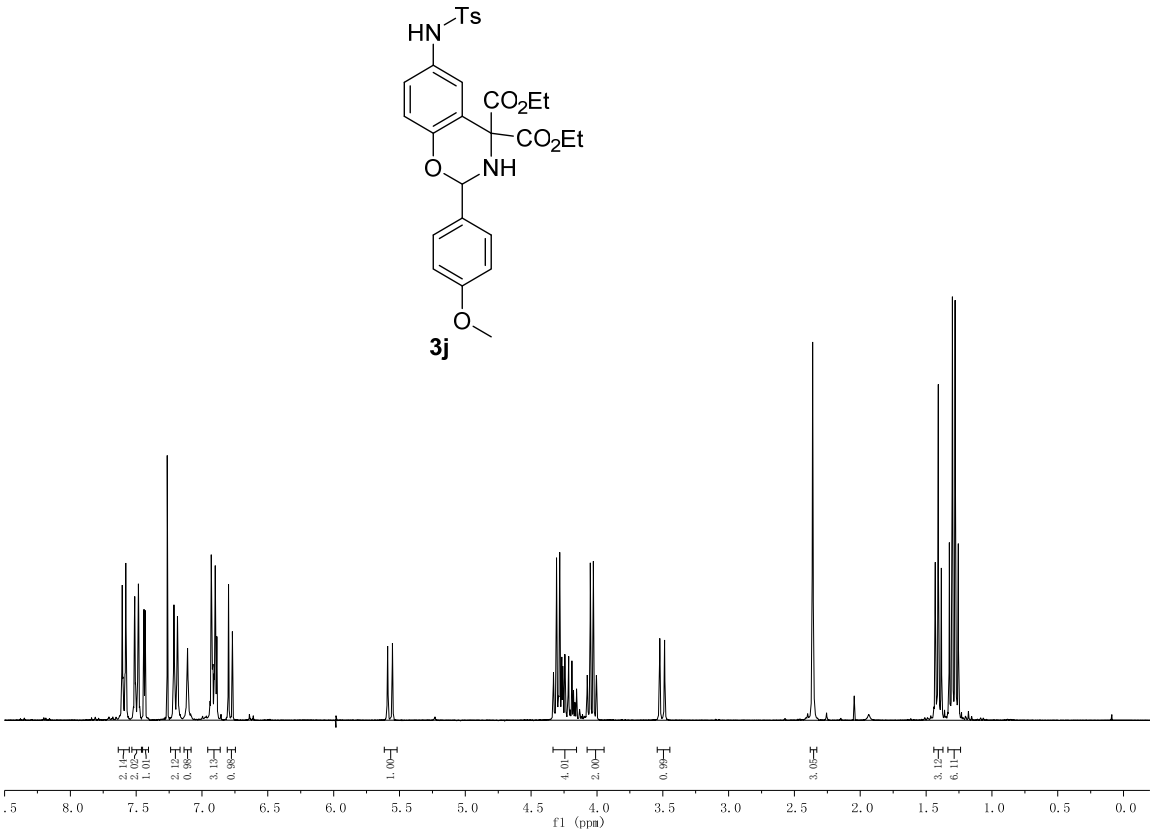
30
20
f1 (ppm)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Ts
CO2Et
CO2Et
O
NH
O
3j
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2.12
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1.00
4.01
2.00
0.99
3.05
3.12
6.11
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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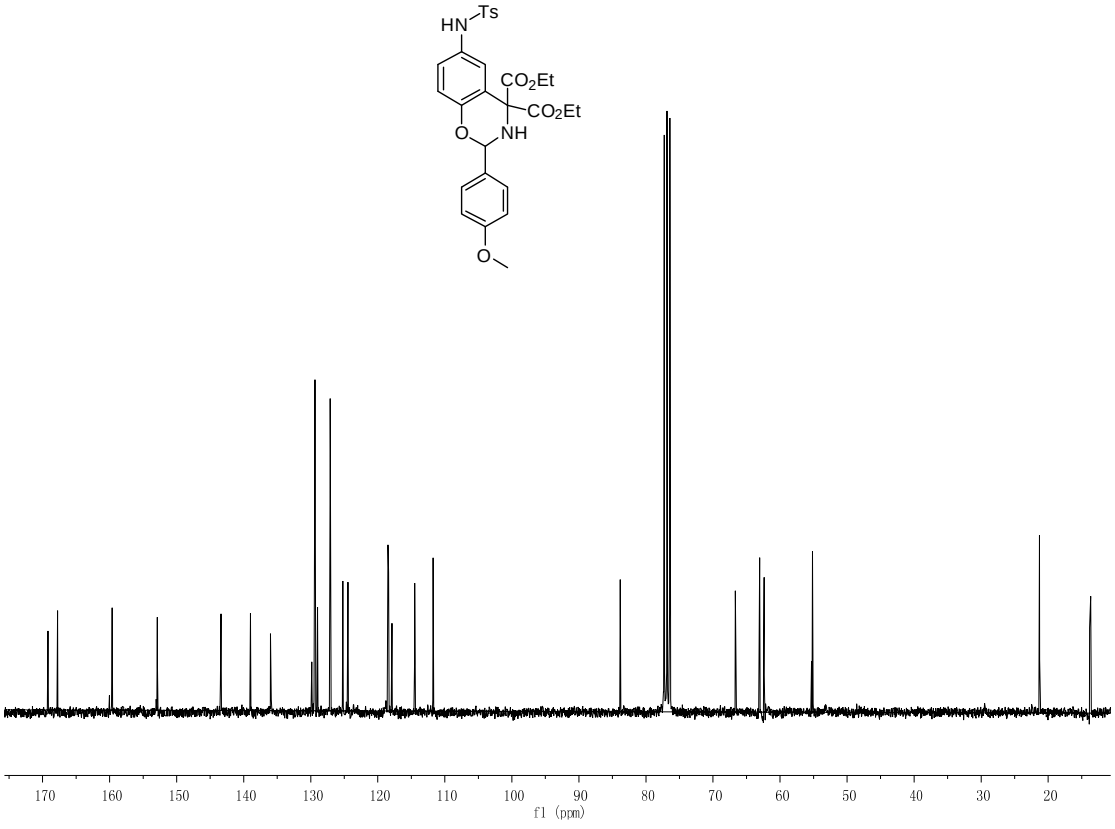
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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Ts
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CO2Et
O
NH
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110
100
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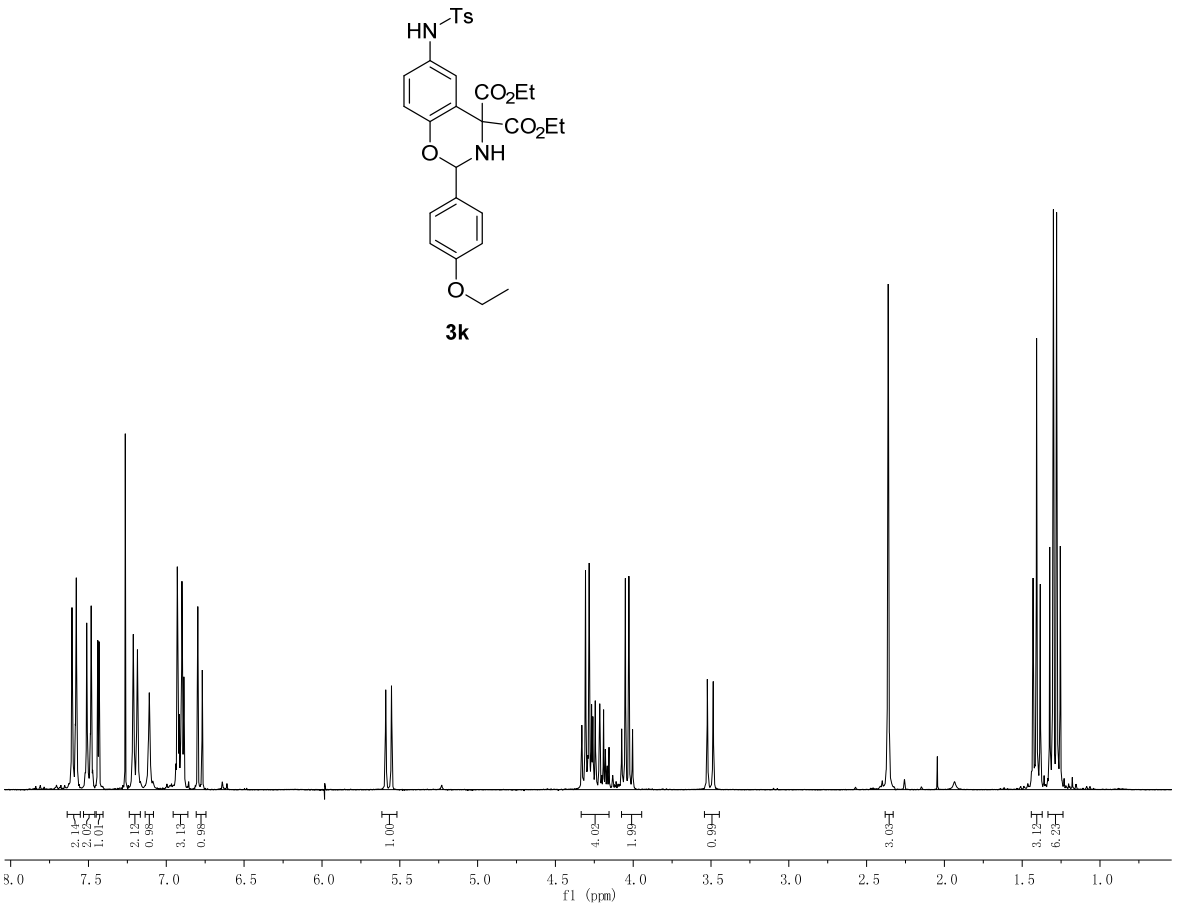
30
20
f1 (ppm)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Ts
CO2Et
CO2Et
O
NH
O
3k
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2.12
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0.98
1.00
4.02
1.99
0.99
3.03
3.12
6.23
8.0
7.5
7.0
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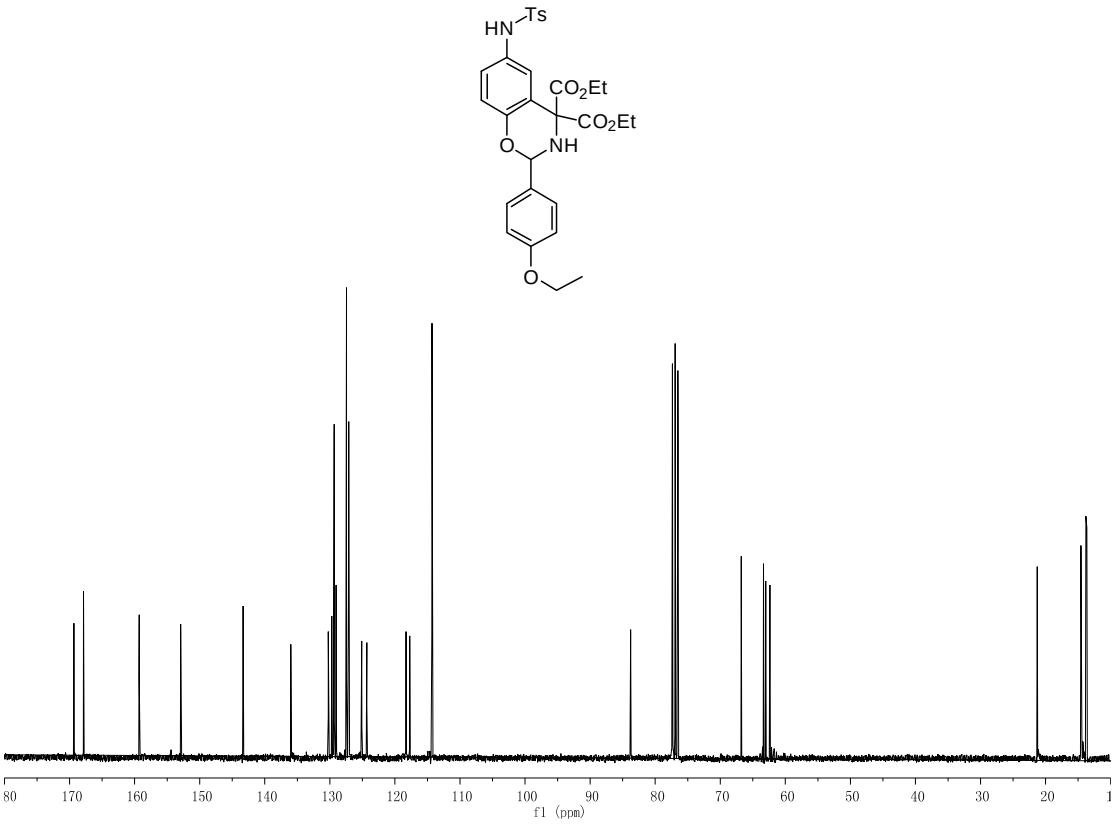
f1 (ppm)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CO2Et
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NH
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60
50
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30
20
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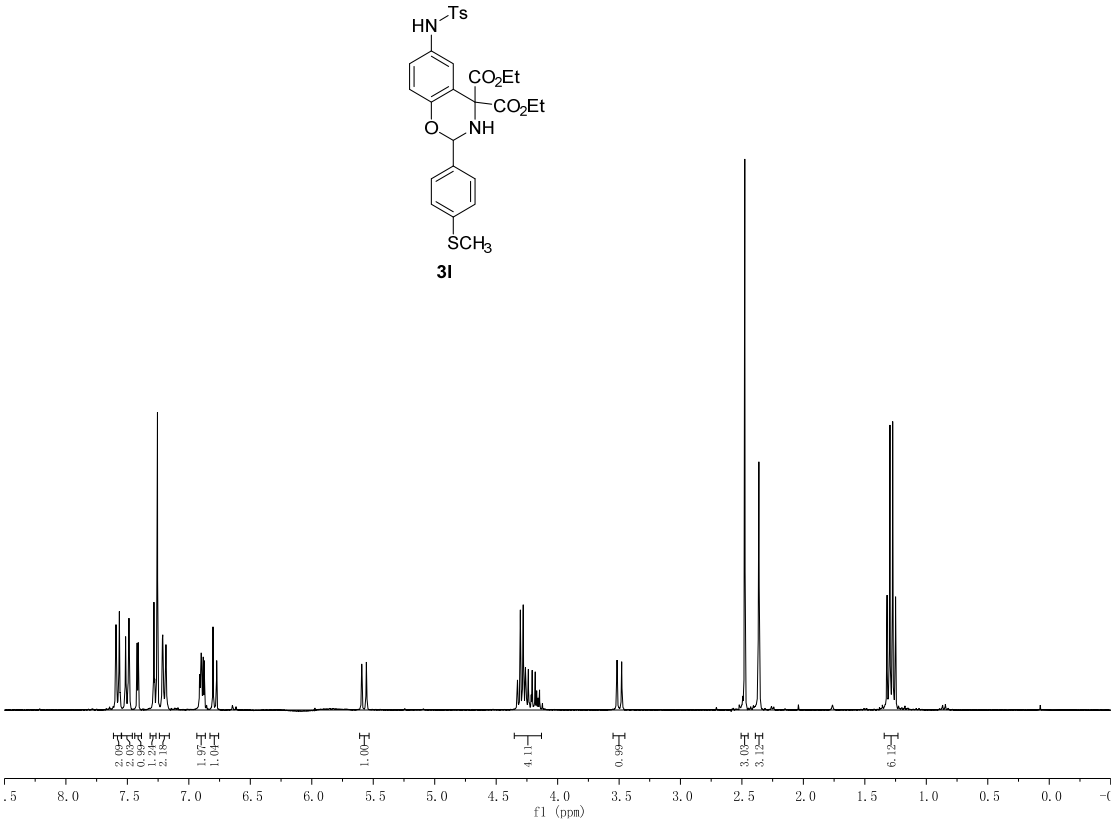
f1 (ppm)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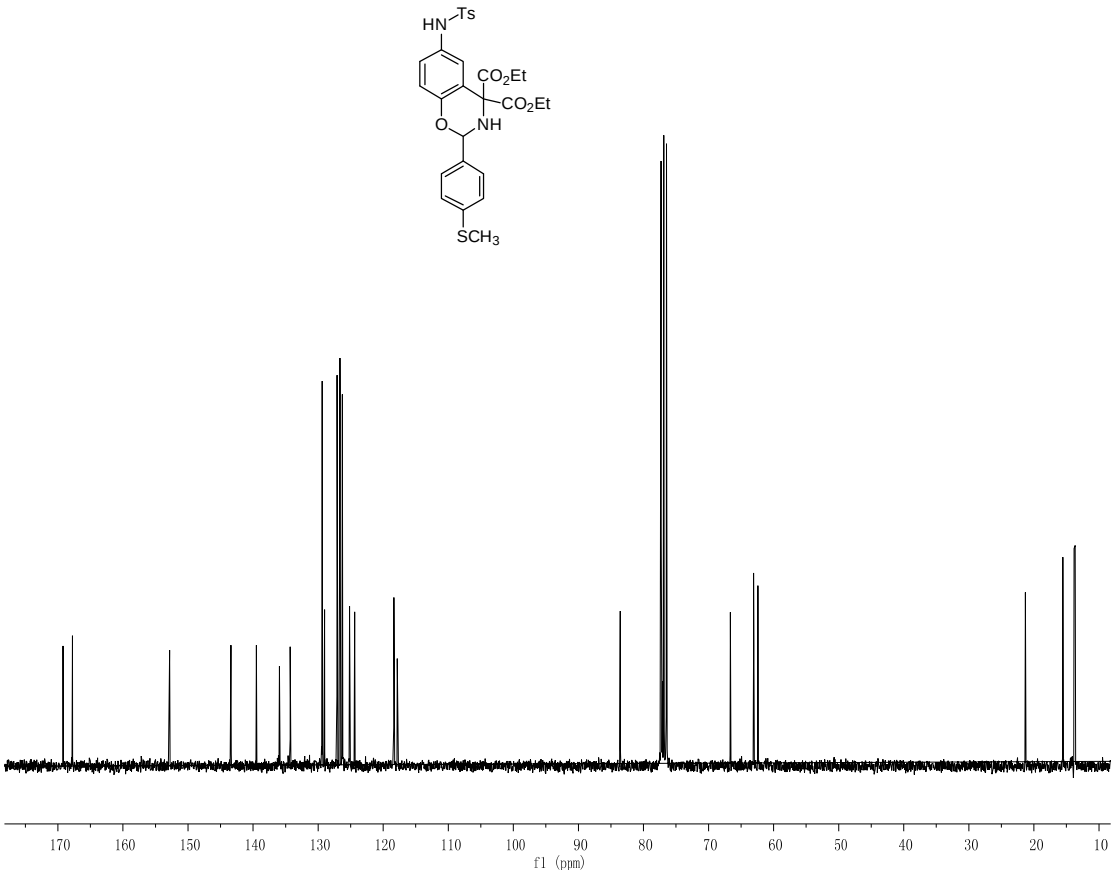
f1 (ppm)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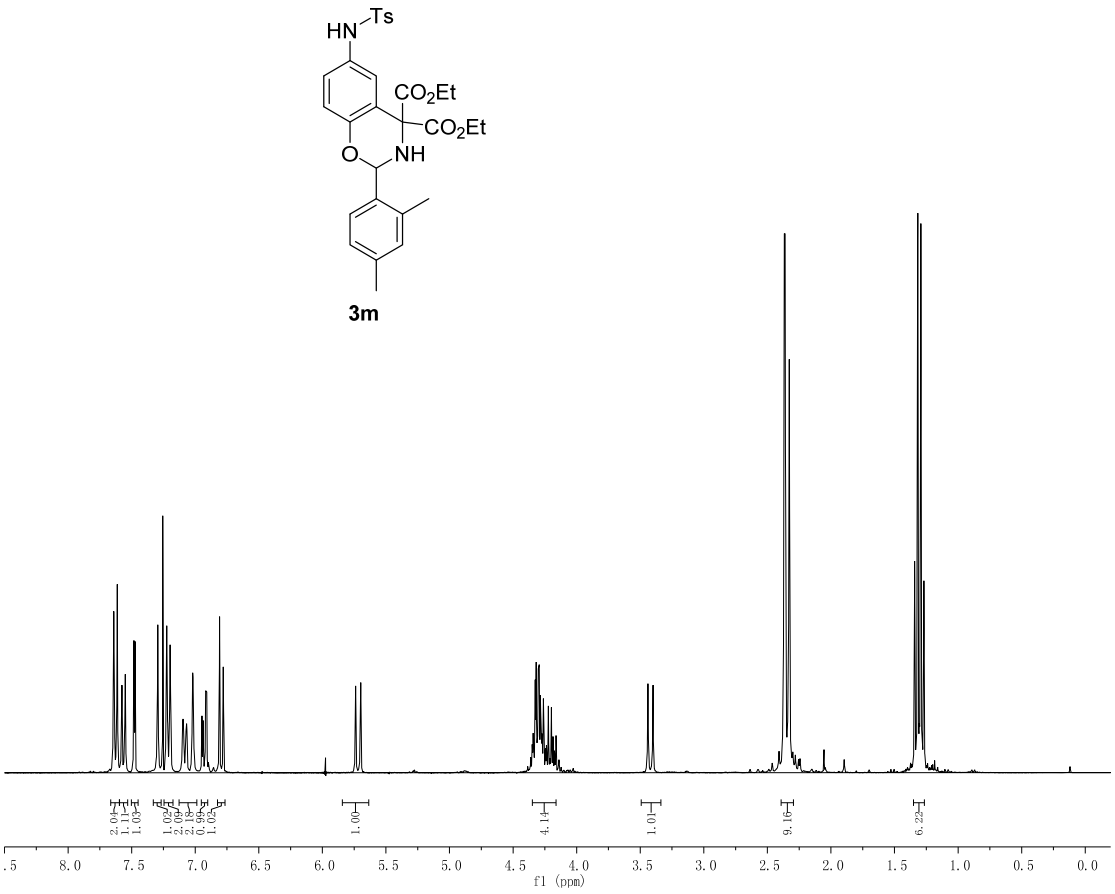
Ts
CO2Et
CO2Et
O
NH
SCH3
f1 (ppm)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CO2Et
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NH
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3.01
1.00
4.14
1.01
9.16
6.22
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8.0
7.5
7.0
6.5
6.0
5.5
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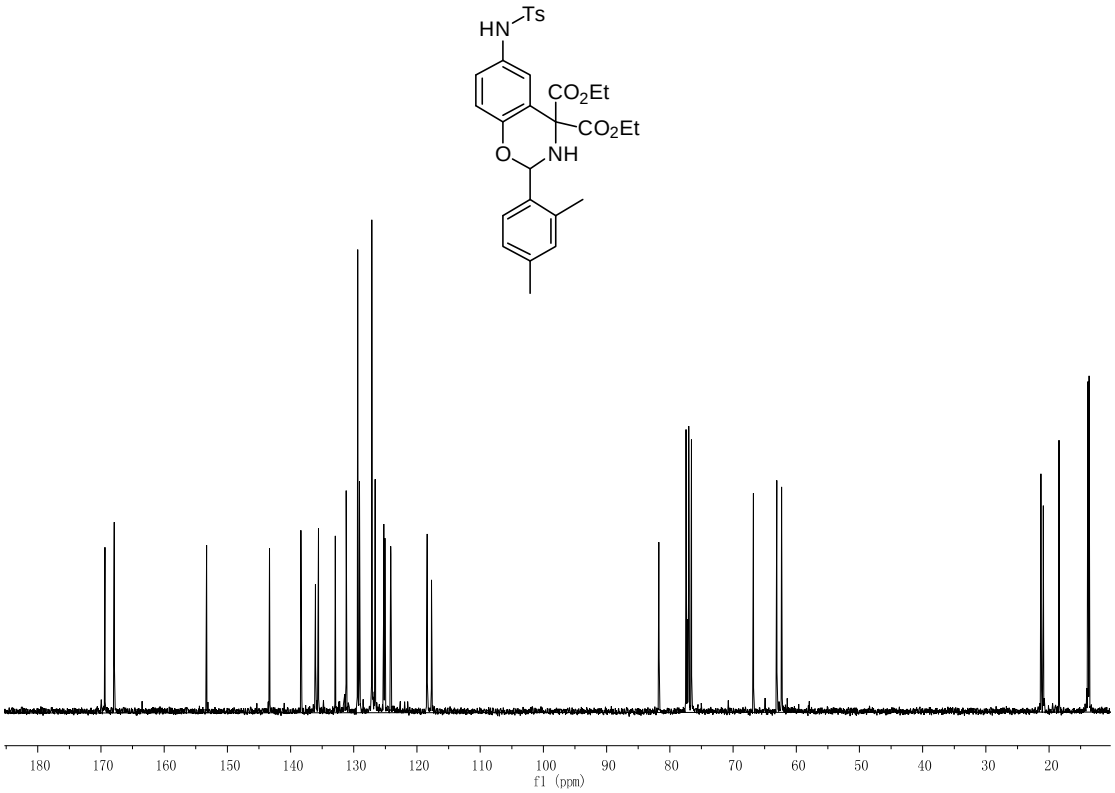
f1 (ppm)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CO2Et
CO2Et
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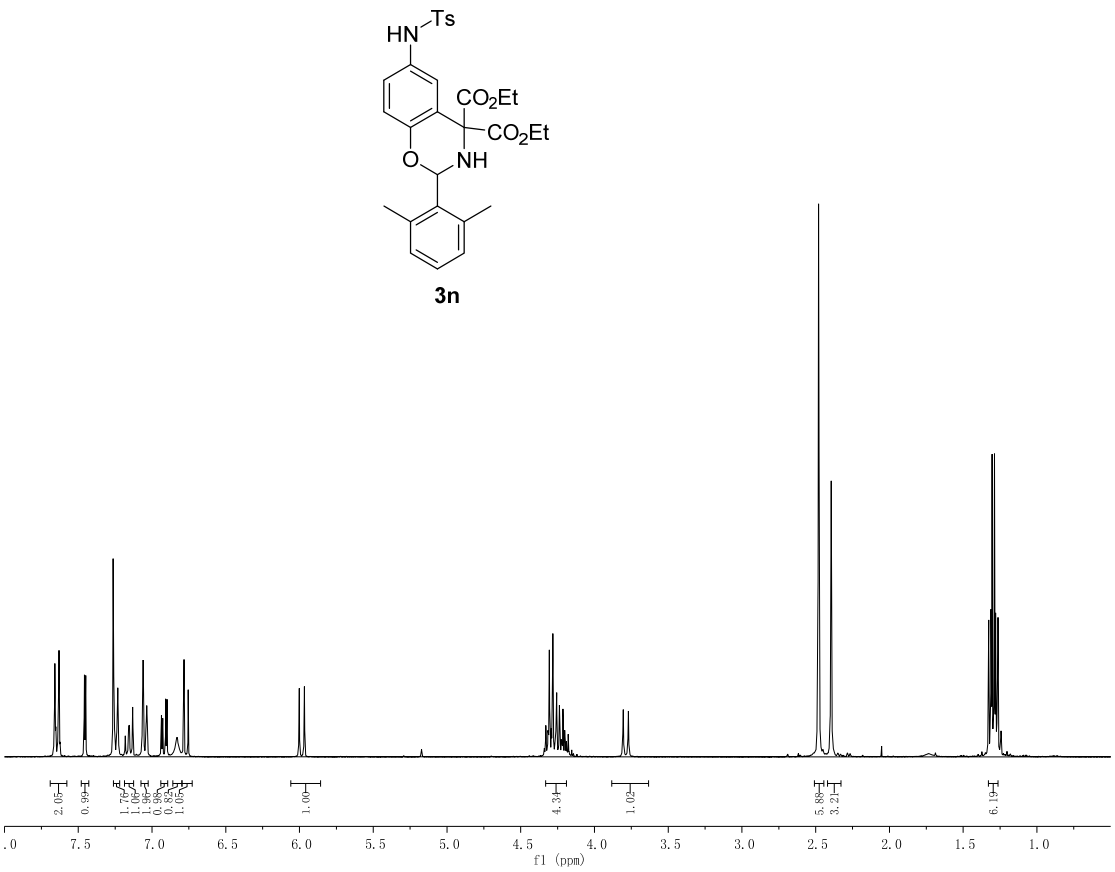
20
f1 (ppm)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Ts
CO2Et
CO2Et
O
NH
3n
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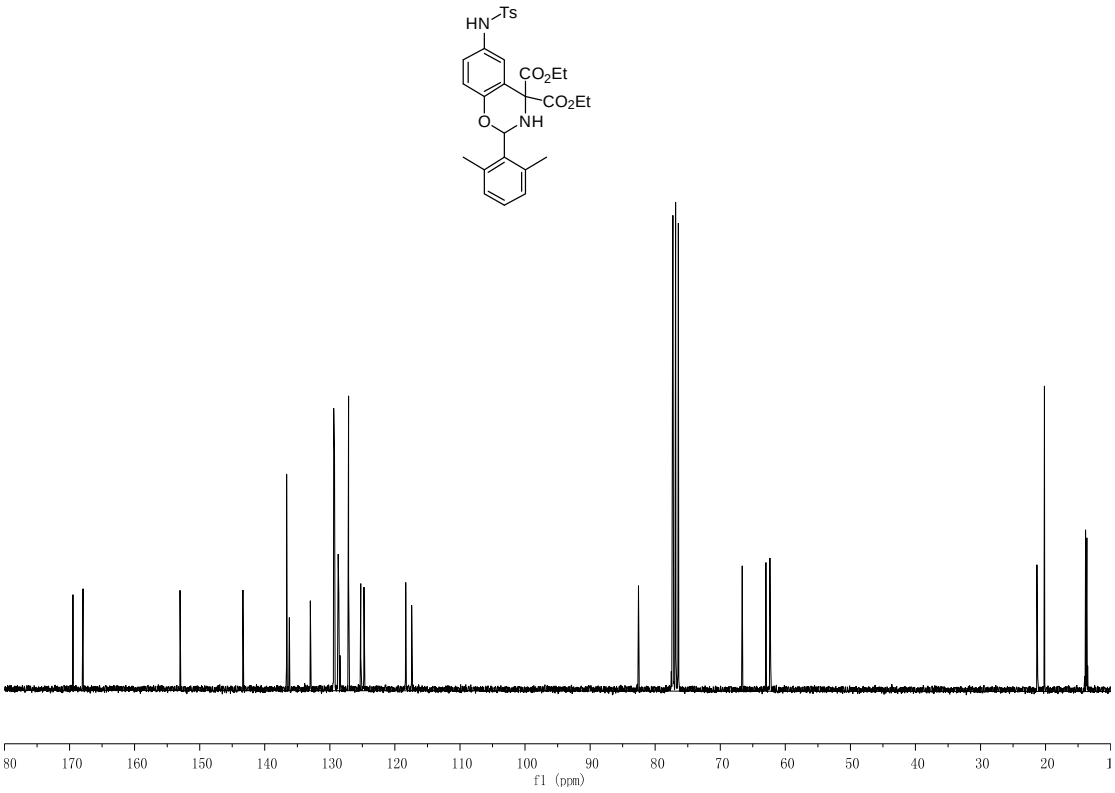
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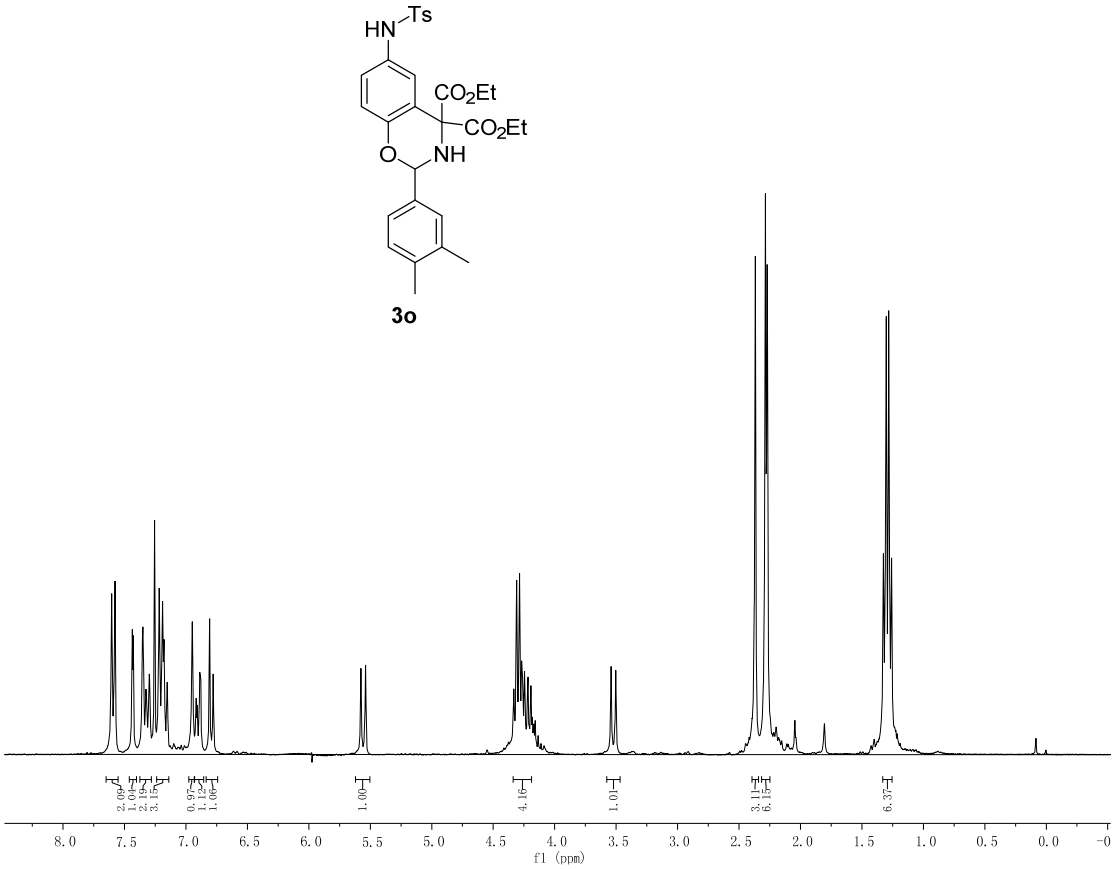
Ts
CO2Et
CO2Et
O
NH
f1 (ppm)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CO2Et
O
NH
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1.00
4.16
1.01
3.11
6.15
6.37
8.0
7.5
7.0
6.5
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5.0
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4.0
3.5
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2.5
2.0
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1.0
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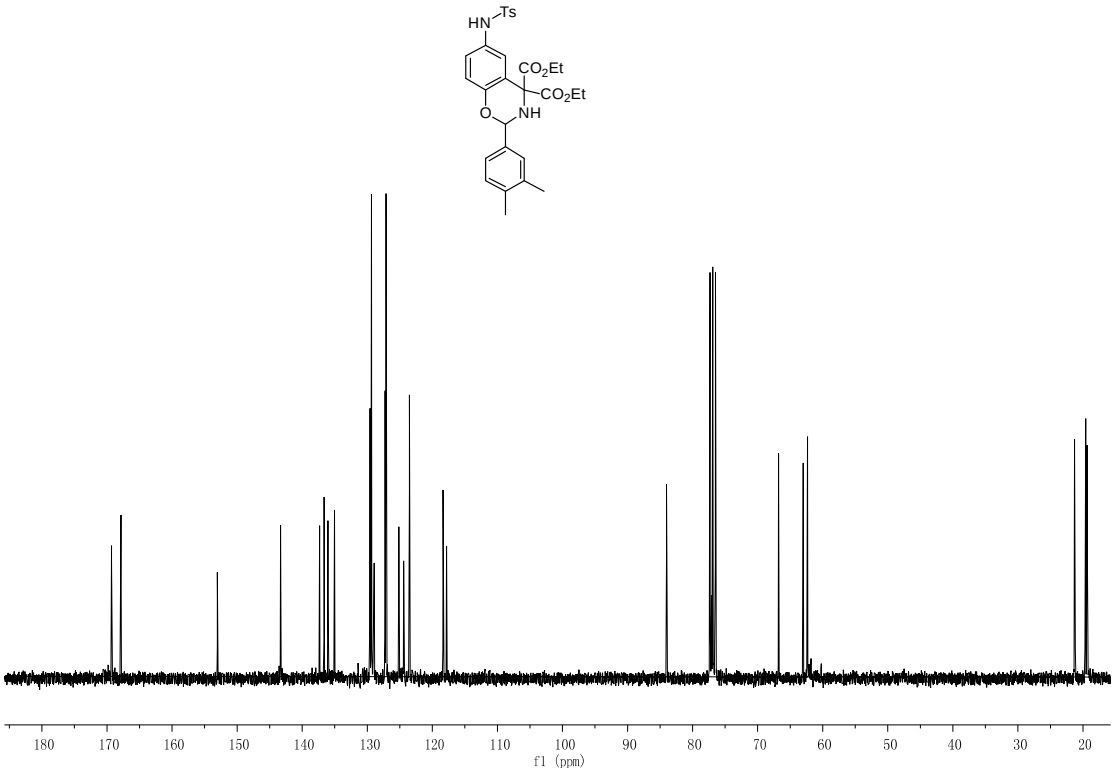
0.0
f1 (ppm)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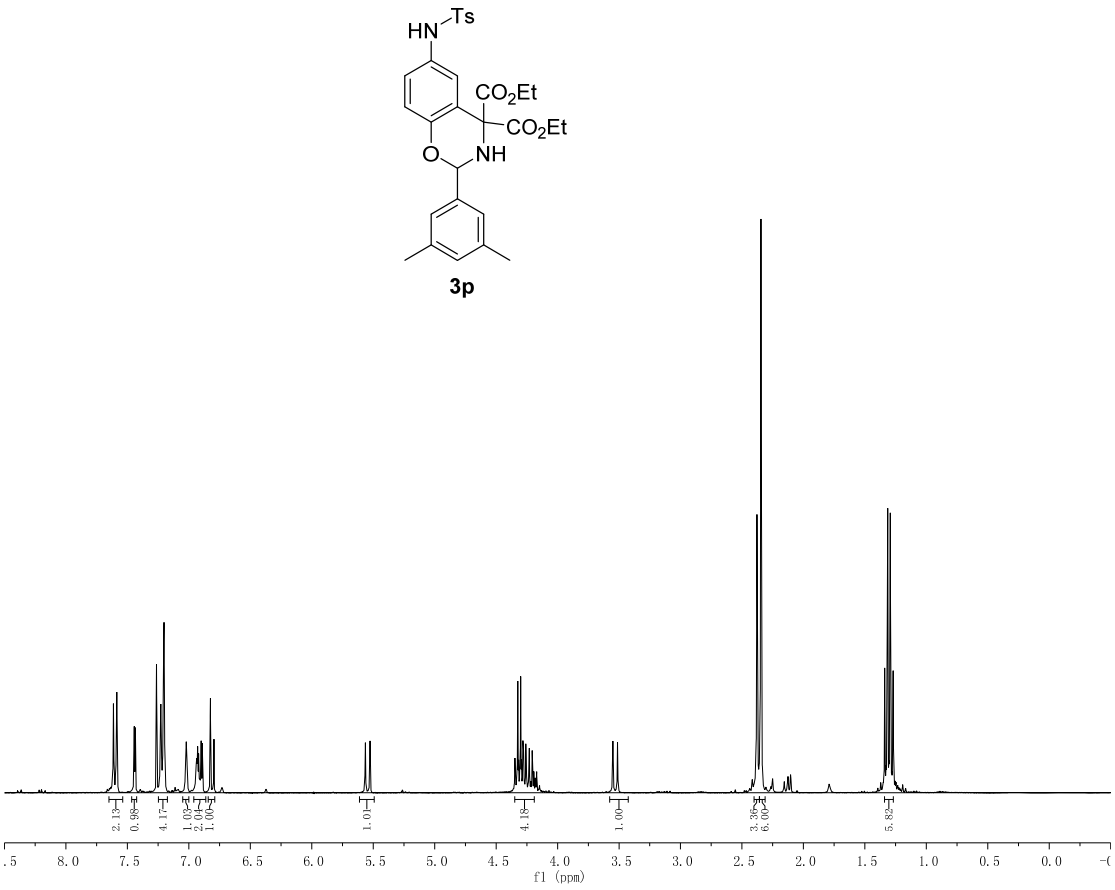
Ts
CO2Et
CO2Et
O
NH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


HN
Ts
CO2Et
CO2Et
O
NH
3p
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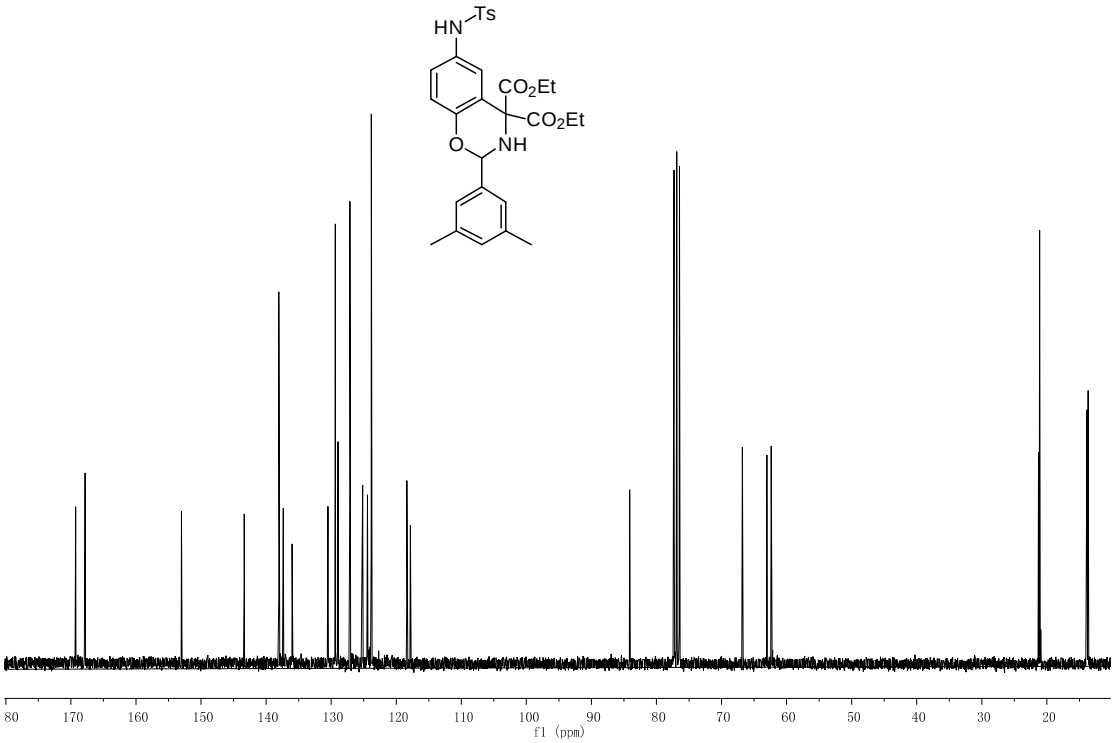
0.98
4.17
1.03
2.04
1.00
1.01
4.18
1.00
3.36
6.00
5.82
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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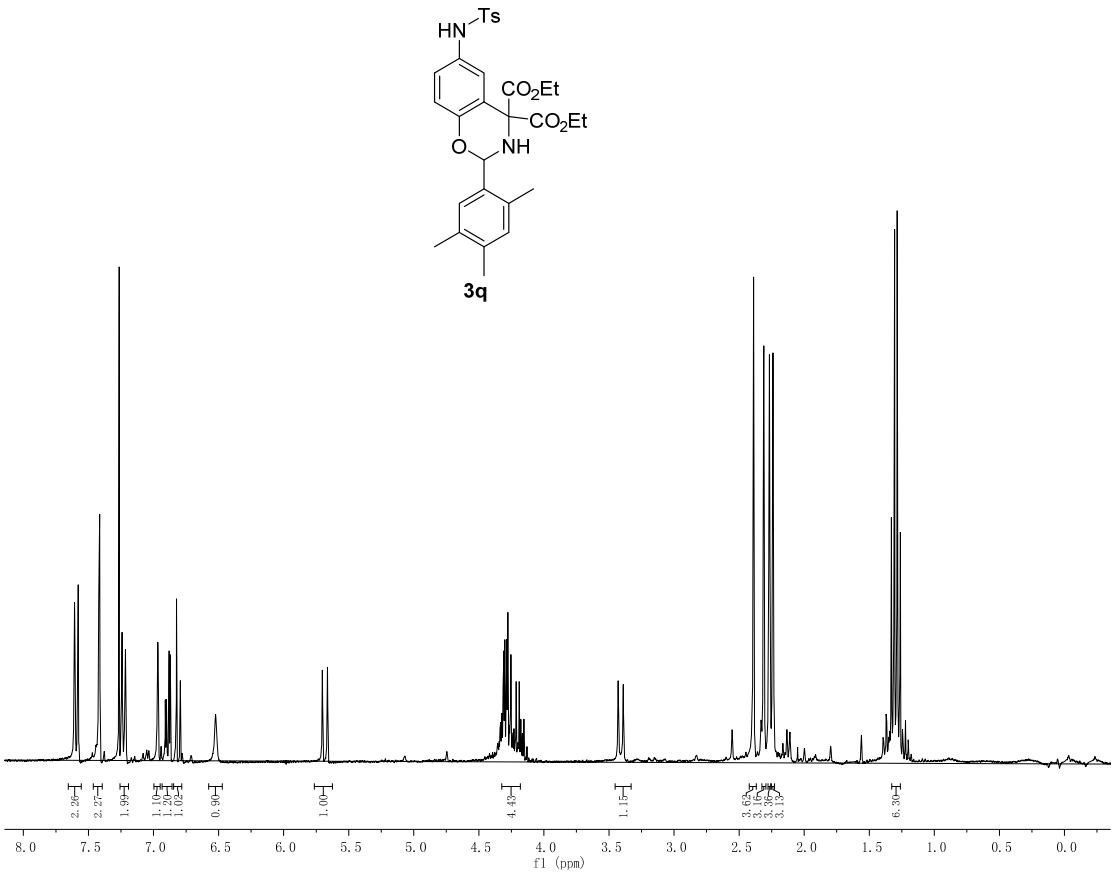
Ts
CO2Et
CO2Et
O
NH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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Ts
CO2Et
CO2Et
O
NH
3q
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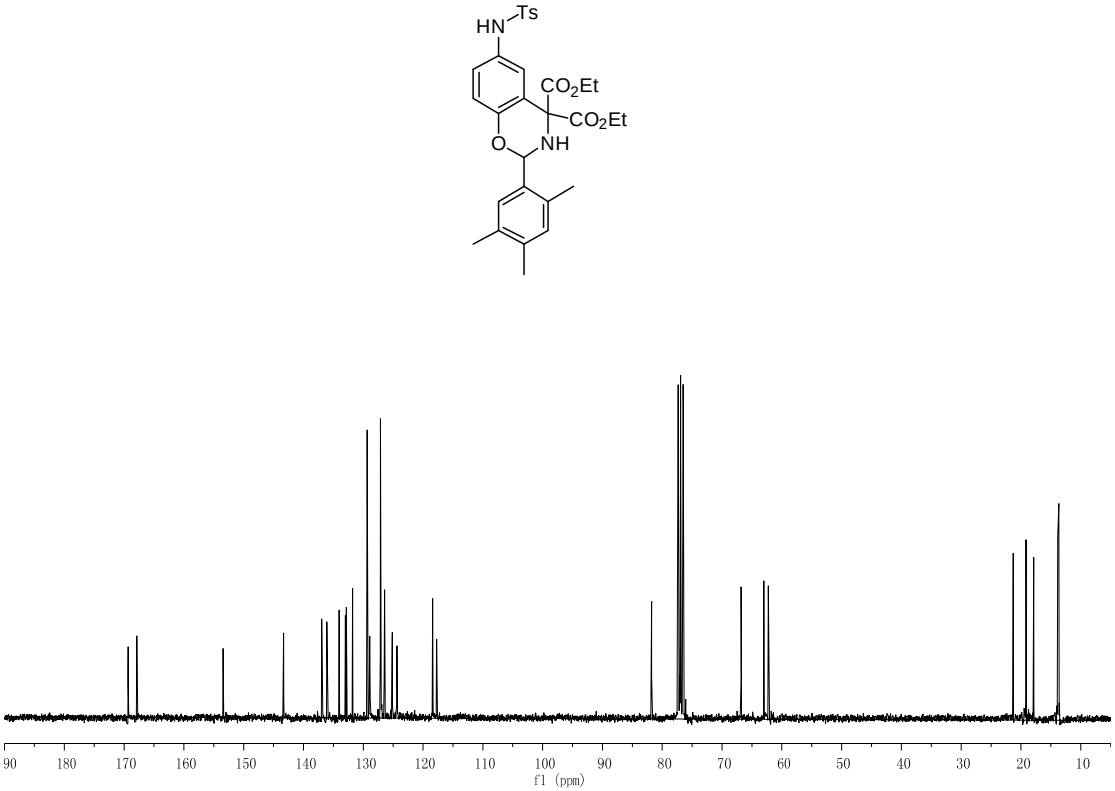
1.99
1.10
1.22
1.02
0.90
1.00
4.43
1.15
3.60
3.15
3.39
3.13
6.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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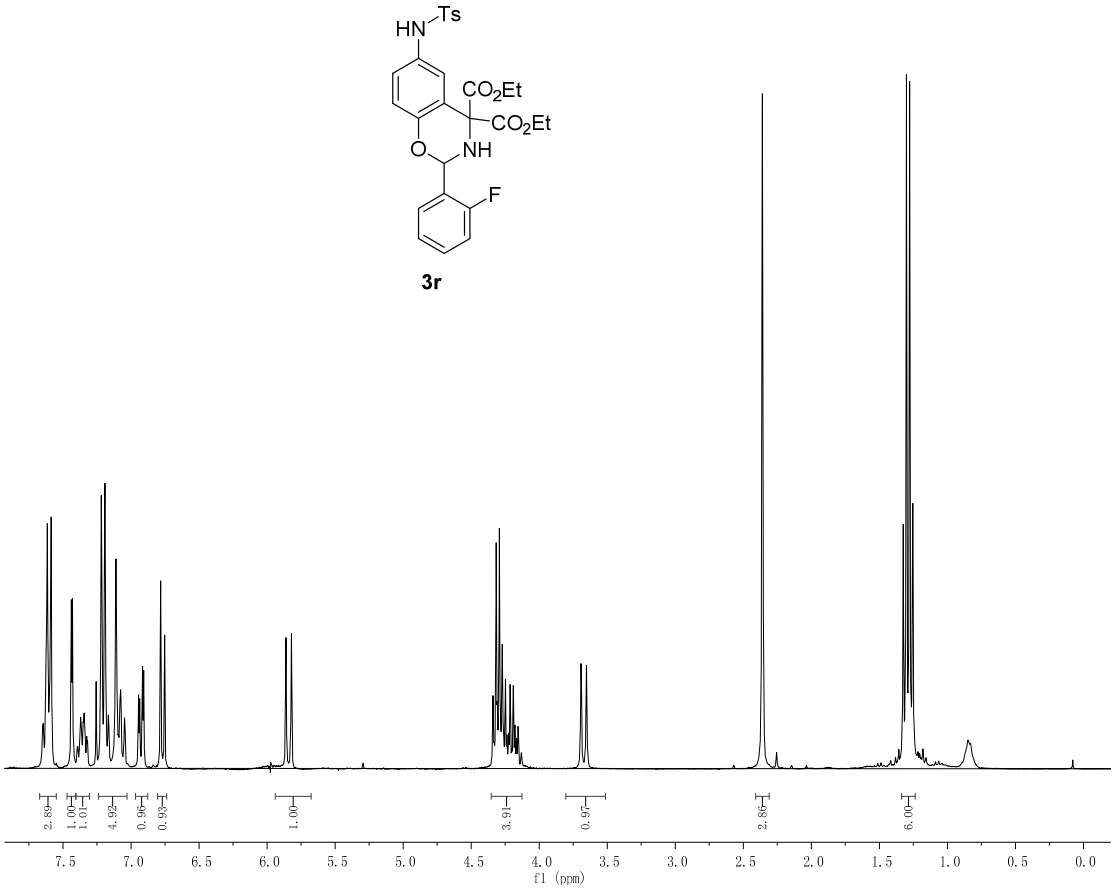
Ts
CO2Et
CO2Et
O
NH
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


HN
Ts
CO2Et
CO2Et
O
NH
F
3r
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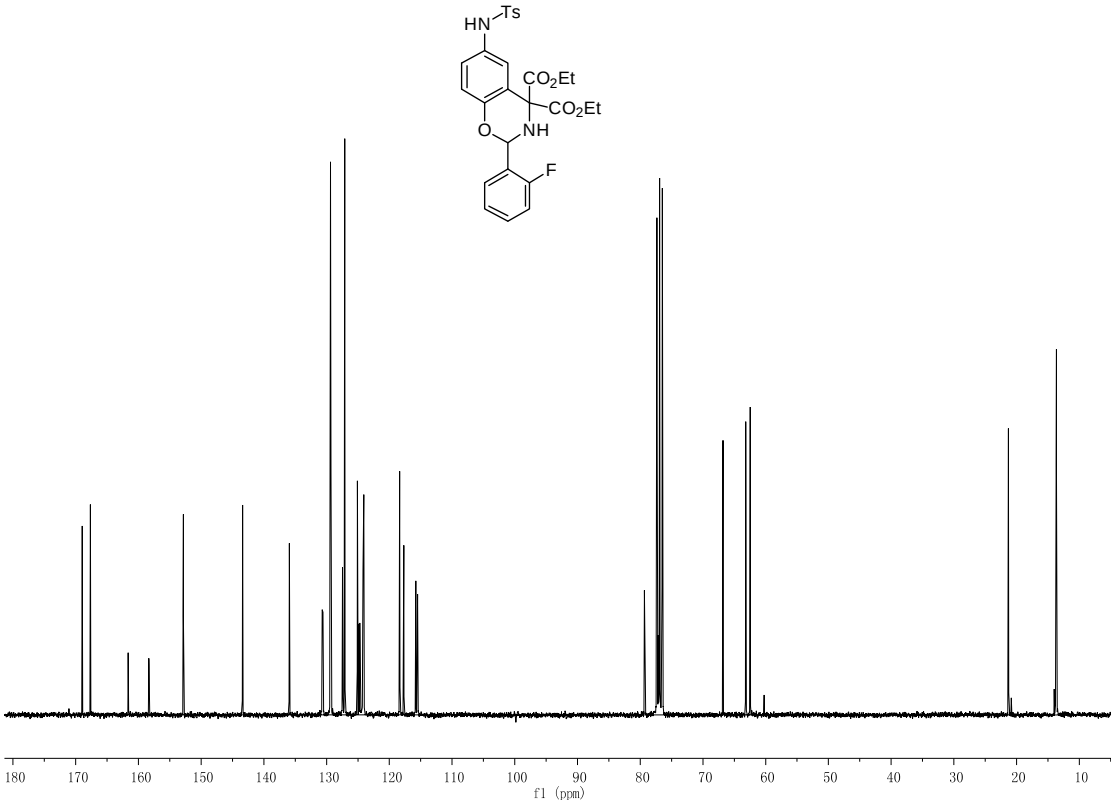
1.00
1.01
4.92
0.96
0.93
1.00
3.91
0.97
2.88
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HN
Ts
CO2Et
CO2Et
O
NH
F
180
170
160
150
140
130
120
110
100
90
80
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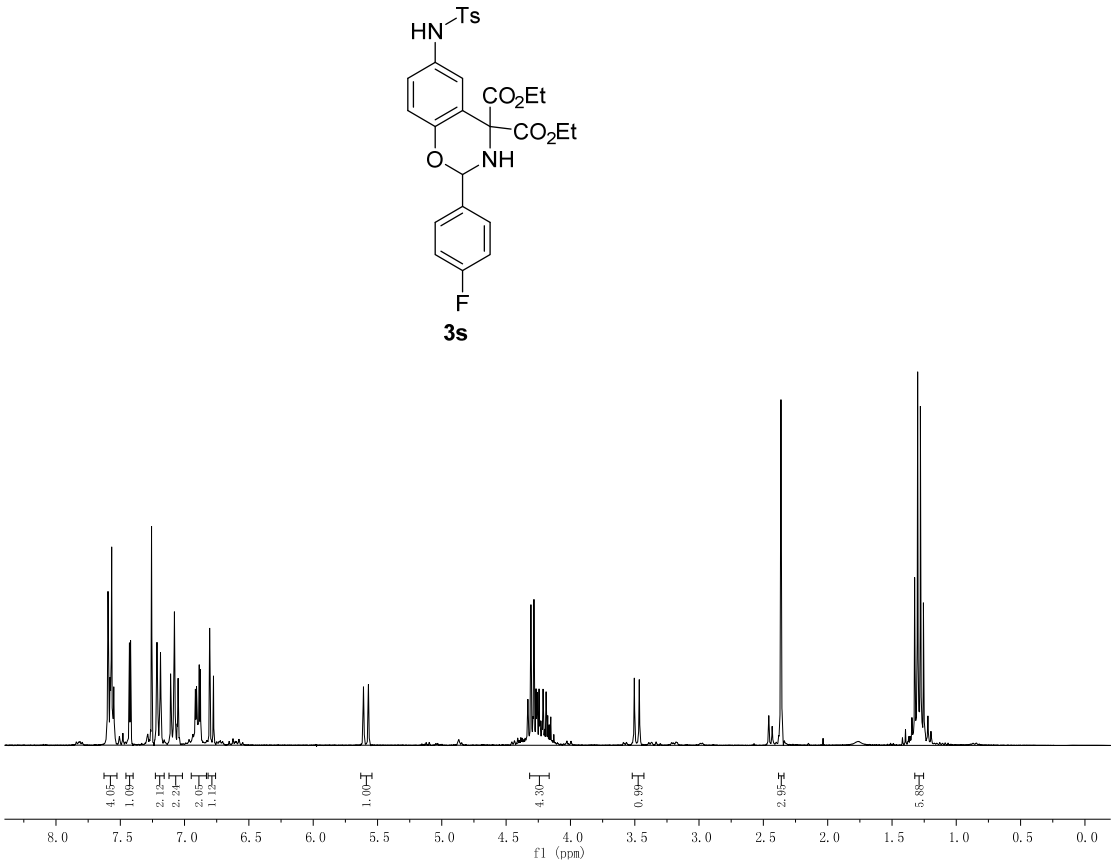
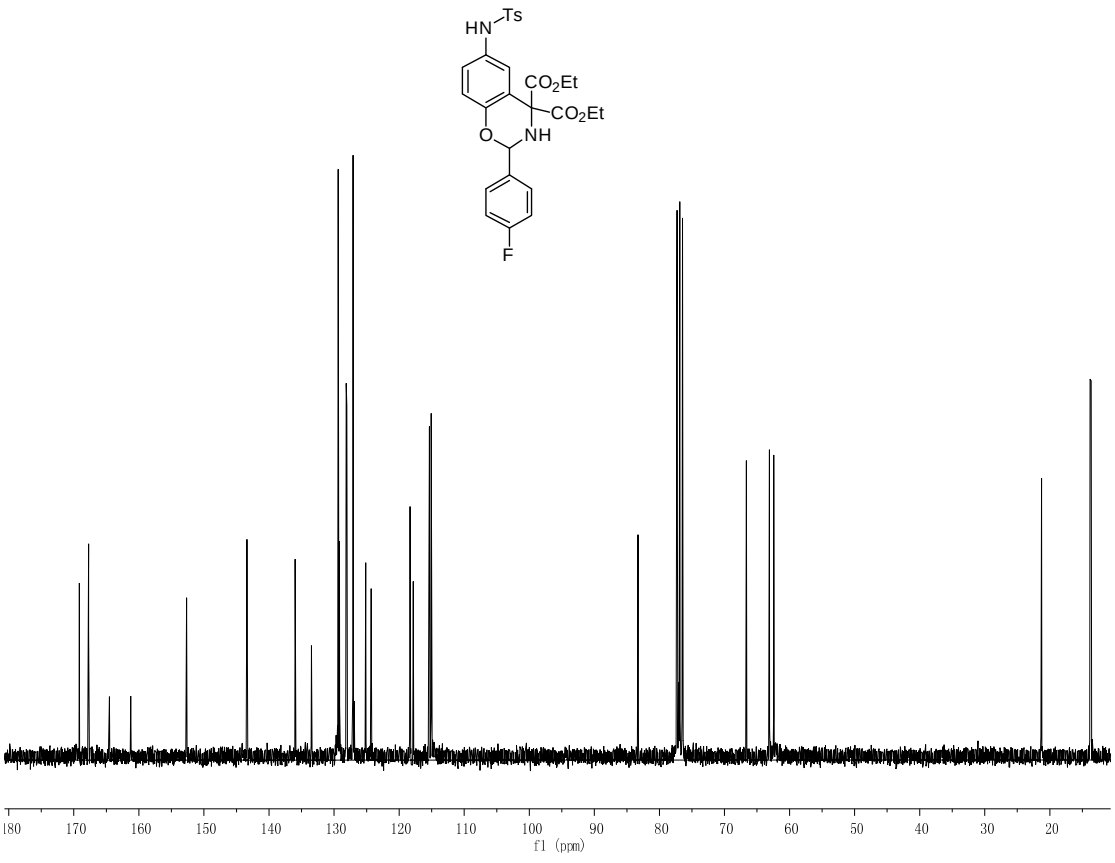
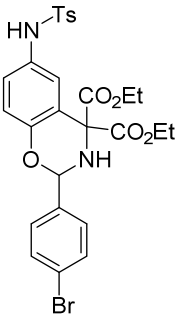
60
50
40
30
20
10
f1 (ppm)

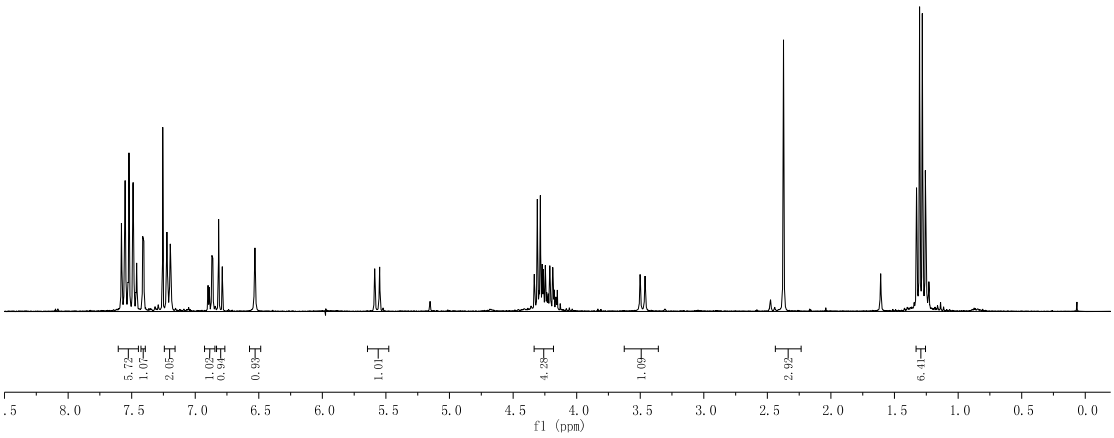

HN
Ts
CO2Et
CO2Et
O
NH
F
4.05
1.09
2.12
2.24
2.05
1.12
1.00
4.30
0.99
2.95
5.88
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3s


HN
Ts
CO2Et
CO2Et
O
NH
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


HN
Ts
CO2Et
CO2Et
O
NH
Br

3t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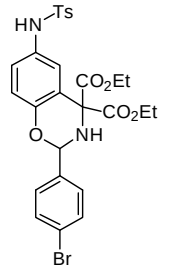
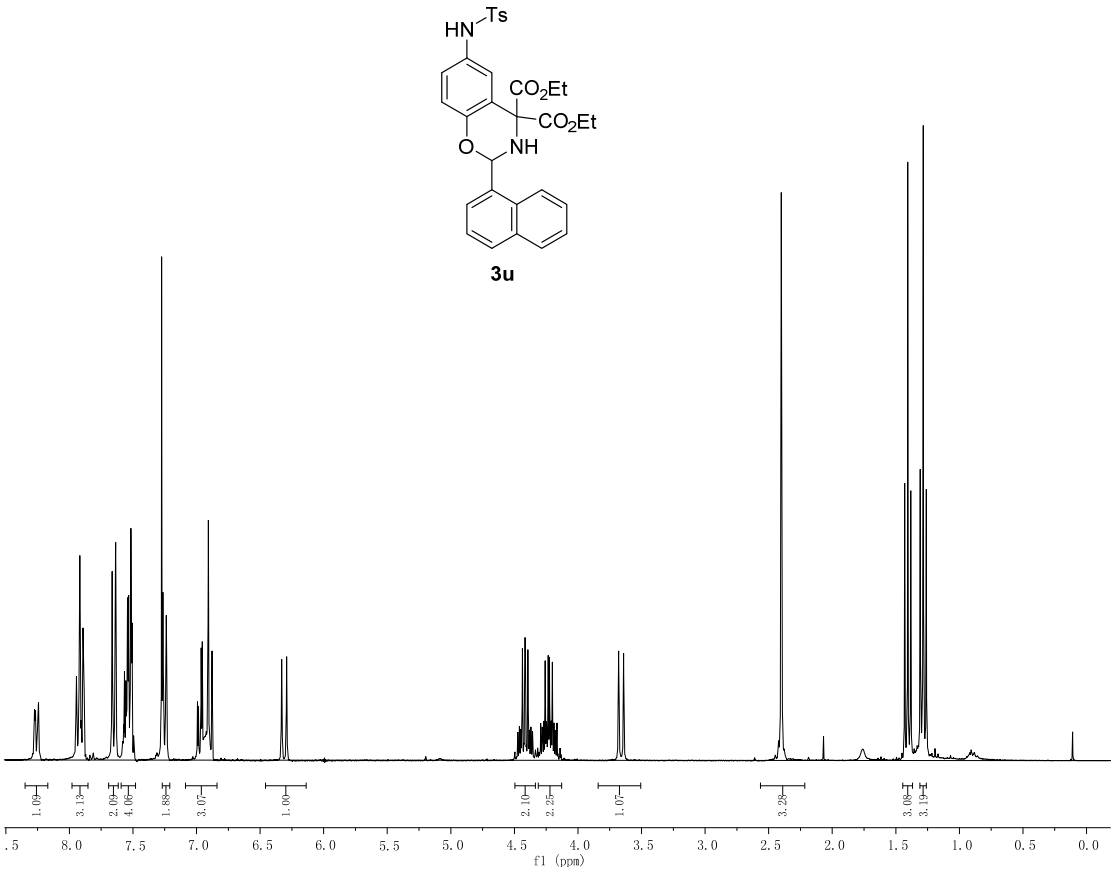
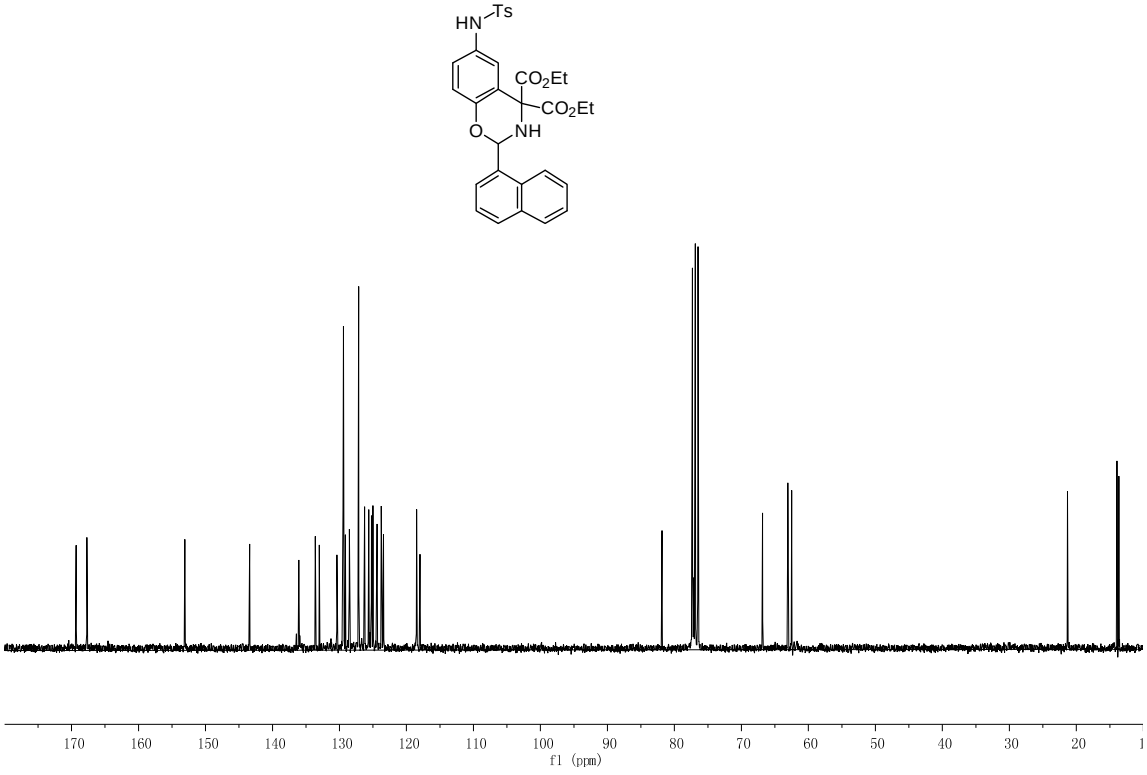
0.93
1.01
4.28
1.09
2.92
6.41
f1 (ppm)


HN
Ts
CO2Et
CO2Et
O
NH
Br

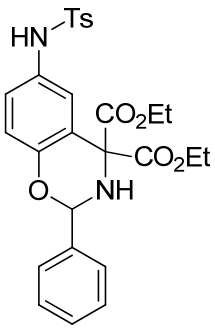
f1 (ppm)


HN
Ts
CO2Et
CO2Et
O
NH
1.09
3.13
2.09
4.06
1.88
3.07
1.00
2.10
2.25
1.07
3.28
3.08
3.19
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)

3u


HN
Ts
CO2Et
CO2Et
O
NH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

X-Ray Crystallographic Data



3a

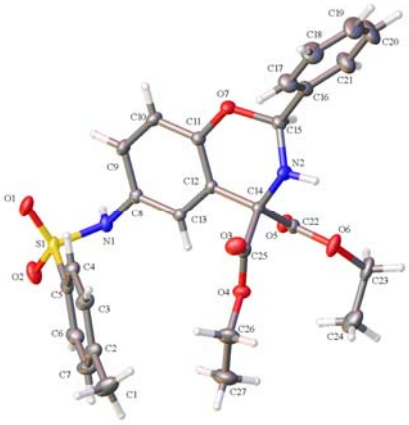


Table 1. Crystal data and structure refinement for **3a**

Identification code	**3a**	
Empirical formula	$C_{27}H_{28}N_2O_7S$	
Formula weight	524.57	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 18.485(4) Å	α= 90°.
	b = 14.715(3) Å	β= 105.79(3)°.
	c = 20.774(4) Å	γ = 90°.
Volume	5437(2) $Å^3$	
Z	8	
Density (calculated)	1.282 Mg/m^3	
Absorption coefficient	0.166 mm^{-1}	
F(000)	2208	
Crystal size	0.42 x 0.39 x 0.36 mm^3	
Theta range for data collection	2.038 to 27.495°.	
Index ranges	-24<=h<=23, -19<=k<=19, -26<=l<=26	
Reflections collected	33938	
Independent reflections	6213 [R(int) = 0.0430]	
Completeness to theta = 26.000°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8808	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6213 / 0 / 337	
Goodness-of-fit on F^2	1.243	
Final R indices [I>2sigma(I)]	R1 = 0.0691, wR2 = 0.1787	
R indices (all data)	R1 = 0.0713, wR2 = 0.1842	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.667 and -0.807 $e.Å^{-3}$	