supplementary information for:

Palladium-Catalyzed Oxidative Carbonylation of *N*-Aryl Enamino Esters with CO and Alcohols: synthesis of *N*-Aryl Aminomethylenemalonates

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CONTENTS

1. General Information.

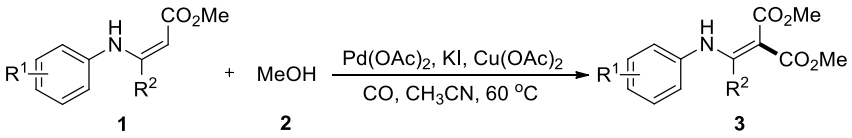
^{1}H and ^{13}C NMR spectra were recorded on Varian instrument (400 MHz) and (100 MHz). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Coupling constants, J were reported in Hertz unit (Hz). Analytical thin layer chromatography was performed on 10-25um silica gel GF254, visualization was carried out with UV light. Flash column chromatography was performed with SiO_2 (Silicycle Silica Gel 60 (200-300 mesh)). Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. The enamino esters **1** were prepared according to the following literatures:

(1) S. Würtz, S. Rakshit, J. J. Neumann, T. Dröge and F. Glorius, *Angew. Chem. Int. Ed.*, 2008, **47**, 7230-7233.

(2) Z.-J. Zhang, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Org. Lett.*, 2013, **15**, 4822-4825.

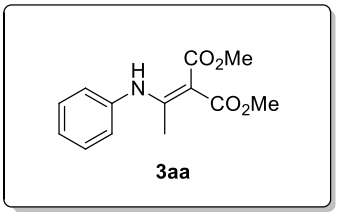
(3) M.-N. Zhao, X.-L. Lian, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *RSC Adv.*, 2014, **4**, 62042-62045.

2. Typical Procedure for Carbonylation of *N*-Aryl Enamino Esters.



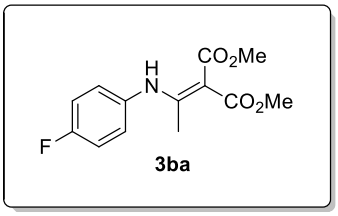
Enamino esters **1** (0.2 mmol), $Pd(OAc)_2$ (5 mol %, 2.2 mg), $Cu(OAc)_2$ (0.24 mmol, 43.6 mg), KI (0.04 mmol, 6.6 mg), MeOH (1.0 mmol, 32 mg) and CH_3CN (2 mL) was charged in a 10 mL round bottom flask. Then, the flask was evacuated and back-filled with CO (3-times, balloon) and stirred at 60 °C. When the reaction was completed (detected by TLC), the mixture was cooled down to room temperature and vented to discharge the excess CO. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding *N*-aryl aminomethylenemalonates **3** with hexanes/ethyl acetate (10/1) as the eluent.

3. Characterization Data of *N*-Aryl Aminomethylenemalonates.



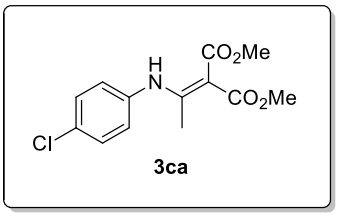
3aa

3aa: colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.31 (s, 1 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.29-7.23 (m, 1 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 2.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 162.1, 137.8, 129.1, 126.4, 125.8, 93.8, 51.8, 51.1, 18.0. HRMS calcd (ESI) m/z for $C_{13}H_{15}NNaO_4$: $[M+Na]^+$ 272.0893, found 272.0895.



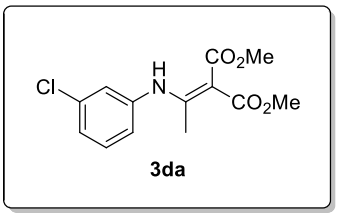
3ba

3ba: yellow solid, mp 52-54 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.18 (s, 1 H), 7.07 (d, *J* = 5.6 Hz, 4 H), 3.78 (s, 3 H), 3.74 (s, 3 H), 2.02 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.0, 168.9, 162.3 161.1 (d, J_{CF} = 241.5 Hz), 133.9 (d, J_{CF} = 3.1 Hz), 127.9 (d, J_{CF} = 8.5 Hz), 116.1 (d, J_{CF} = 22.6 Hz), 93.9, 52.0, 51.2, 17.9. HRMS calcd (ESI) m/z for $C_{13}H_{14}FNNaO_4$: $[M+Na]^+$ 290.0799, found 290.0797.



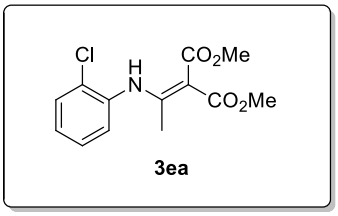
3ca

3ca: yellow solid, mp 75-77 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.24 (s, 1 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 2.06 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 168.8, 161.6, 136.5, 132.1, 129.4, 127.0, 94.5, 52.0, 51.3, 18.0. HRMS calcd (ESI) m/z for $C_{13}H_{14}ClNNaO_4$: $[M+Na]^+$ 306.0504, found 306.0507.



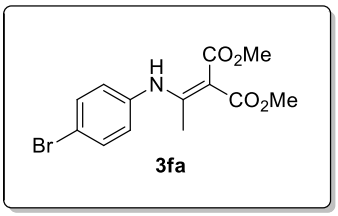
3da

3da: yellow solid, mp 64-66 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.27 (s, 1 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 7.13 (s, 1 H), 7.00 (d, *J* = 7.2 Hz, 1 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 2.09 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 168.7, 161.2, 139.2, 134.8, 130.2, 126.5, 125.8, 123.8, 95.0, 52.1, 51.3, 18.1. HRMS calcd (ESI) m/z for $C_{13}H_{14}ClNNaO_4$: $[M+Na]^+$ 306.0504, found 306.0508.



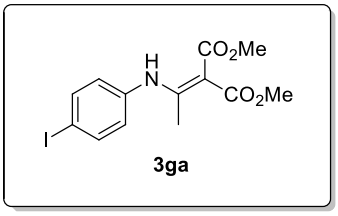
3ea

3ea: yellow solid, mp 52-54 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.23 (s, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.30-7.26 (m, 1 H), 7.23-7.17 (m, 2 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 168.7, 161.5, 135.4, 130.7, 130.1 127.7, 127.6, 127.2, 95.0, 51.9, 51.3, 17.8. HRMS calcd (ESI) m/z for $C_{13}H_{14}ClNNaO_4$: $[M+Na]^+$ 306.0504, found 306.0508.



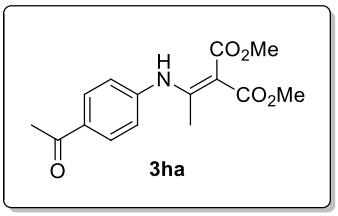
3fa

3fa: yellow solid, mp 84-86 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.20 (s, 1 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 168.7, 161.3, 136.9, 132.3, 127.2, 119.8, 94.6, 51.9, 51.2, 17.9. HRMS calcd (ESI) m/z for $C_{13}H_{14}BrNNaO_4$: $[M+Na]^+$ 349.9998, found 350.0012.

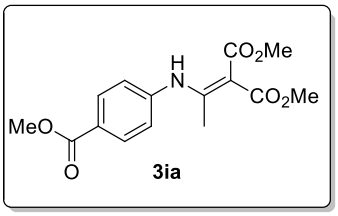


3ga

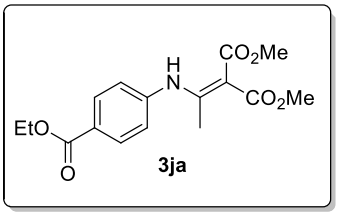
3ga: yellow solid, mp 80-82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.22 (s, 1 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.0 Hz, 2 H), 3.77 (s, 3 H), 3.72 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 168.7, 161.2, 138.2, 137.6, 127.4, 94.7, 90.7, 52.0, 51.2, 17.9. HRMS calcd (ESI) m/z for $C_{13}H_{14}INNaO_4$: $[M+Na]^+$ 397.9860, found 397.9865.



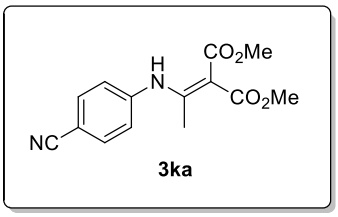
3ha: white solid, mp 111-113 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.43 (s, 1 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 3.81 (s, 3 H), 3.76 (s, 3 H), 2.60 (s, 3 H), 2.18 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.6, 168.6, 168.4, 160.0, 142.3, 134.0, 129.7, 129.5, 124.1, 96.2, 52.0, 51.3, 26.4, 18.1. HRMS calcd (ESI) m/z for $C_{15}H_{17}NNaO_5$: $[M+Na]^+$ 314.0999, found 314.0993.



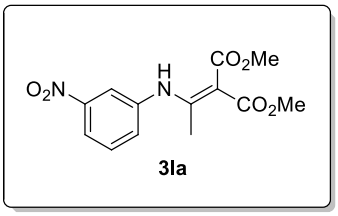
3ia: white solid, mp 109-112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.44 (s, 1 H), 8.05 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 3.94 (s, 3 H), 3.82 (s, 3 H), 3.78 (s, 3 H), 2.19 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6, 168.4, 166.1, 160.2, 142.2, 130.7, 127.1, 124.1, 96.0, 52.0, 51.9, 51.3, 18.1. HRMS calcd (ESI) m/z for $C_{15}H_{17}NNaO_6$: $[M+Na]^+$ 330.0948, found 330.0934.



3ja: white solid, mp 108-110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.40 (s, 1 H), 8.03 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 4.39-4.33 (m, 2 H), 3.79 (s, 3 H), 3.74 (s, 3 H),,2.14 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 168.6, 165.8, 160.4, 142.1, 130.7, 127.6, 124.2, 95.9, 61.1, 52.1, 51.4, 18.2, 14.3. HRMS calcd (ESI) m/z for $C_{16}H_{19}NNaO_6$: $[M+Na]^+$ 344.1105, found 344.1094.

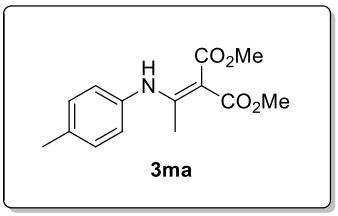


3ka: yellow solid, mp 133-135 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.40 (s, 1 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 3.78 (s, 3 H), 3.73 (s, 3 H), 2.14 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.5, 168.2, 159.2, 142.2, 133.3, 124.4, 118.3, 108.6, 97.3, 52.2, 51.5, 18.1. HRMS calcd (ESI) m/z for $C_{14}H_{14}N_2NaO_4$: $[M+Na]^+$ 297.0846, found 297.0843.



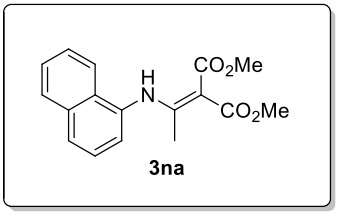
3la

3la: yellow solid, mp 109-111 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.40 (s, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 7.80 (s, 1 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 1 H), 3.80 (s, 3 H), 3.76 (s, 3 H), 2.14 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 168.4, 160.1, 148.7, 139.4, 131.0, 130.1, 120.7, 119.9, 96.5, 52.2, 51.5, 18.0. HRMS calcd (ESI) m/z for $C_{13}H_{14}N_2NaO_6$: $[M+Na]^+$ 317.0744, found 314.0741.



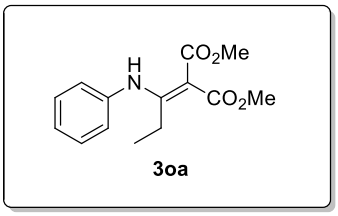
3ma

3ma: yellow solid, mp 80-82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.24 (s, 1 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 6.98 (d, *J* = 7.6 Hz, 2 H), 3.78 (s, 3 H), 3.74 (s, 3 H), 2.35 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 169.1, 162.6, 136.5, 135.2, 129.8, 125.8, 93.3, 51.9, 51.2, 21.0, 18.1. HRMS calcd (ESI) m/z for $C_{14}H_{17}NNaO_4$: $[M+Na]^+$ 286.1050, found 286.1060.



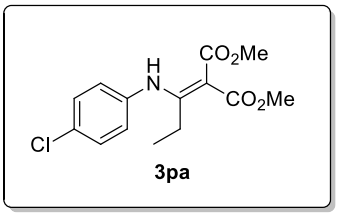
3na

3na: yellow solid, mp 101-103 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.53 (s, 1 H), 7.96 (d, *J* = 6.8 Hz, 1 H), 7.89 (d, *J* = 6.8 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.55 (s, 2 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 1 H), 3.81 (s, 6 H), 1.98 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.3, 169.0, 163.6, 134.2, 134.0, 130.3, 128.2, 127.6, 127.1, 126.6, 125.2, 124.4, 122.5, 93.8, 51.9, 51.2, 17.9. HRMS calcd (ESI) m/z for $C_{17}H_{17}NNaO_4$: $[M+Na]^+$ 322.1050, found 322.1062.



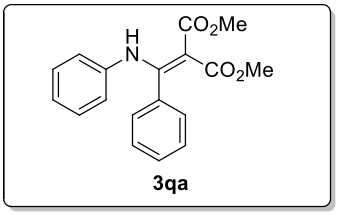
3oa

3oa: yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.12 (s, 1 H), 7.38 (t, *J* = 6.0 Hz, 2 H), 7.29 (d, *J* = 7.2 Hz, 1 H), 7.15 (d, *J* = 7.2 Hz, 2 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 2.47-2.44 (m, 2 H), 1.02 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 169.1, 167.4, 137.9, 129.2, 126.8, 126.5, 92.9, 52.0, 51.1, 23.0, 13.0. HRMS calcd (ESI) m/z for $C_{14}H_{17}NNaO_4$: $[M+Na]^+$ 286.1050, found 286.1063.



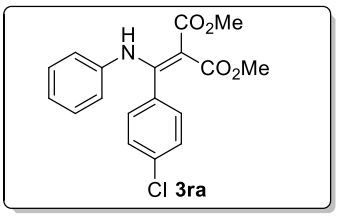
3pa

3pa: brown liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.00 (s, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 3.76 (s, 3 H), 3.71 (s, 3 H), 2.43-2.38 (m, 2 H), 0.98 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 168.7, 166.8, 136.5, 132.4, 129.4, 127.7, 93.6, 52.0, 51.2, 22.9, 12.9. HRMS calcd (ESI) m/z for $C_{14}H_{16}ClNNaO_4$: $[M+Na]^+$ 320.0660, found 320.0674.



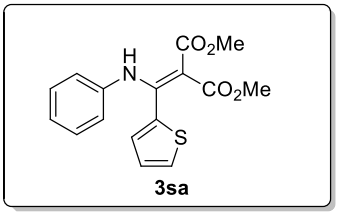
3qa

3qa: yellow solid, mp 105-107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.18 (s, 1 H), 7.29-7.26 (m, 5 H), 7.07 (t, *J* = 7.6 Hz, 2 H), 6.97 (d, *J* = 7.2 Hz, 1 H), 6.67 (d, *J* = 7.6 Hz, 2 H), 3.80 (s, 3 H), 3.31 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.3, 168.0, 161.3, 138.7, 133.7, 129.5, 128.6, 128.4, 128.3, 124.5, 123.6, 96.8, 51.7, 51.5. HRMS calcd (ESI) m/z for $C_{18}H_{17}NNaO_4$: $[M+Na]^+$ 334.1050, found 344.1065.



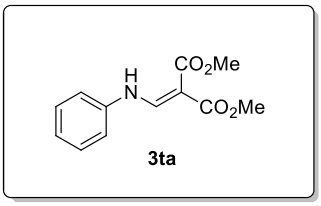
3ra

3ra: yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.12 (s, 1 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.10 (t, *J* = 7.6 Hz, 2 H), 7.00 (d, *J* = 7.2 Hz, 1 H), 6.68 (d, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H), 3.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 167.8, 160.0, 138.4, 135.6, 132.2, 129.9, 128.8, 128.7, 124.8, 123.9, 97.1, 51.8, 51.6. HRMS calcd (ESI) m/z for $C_{18}H_{16}ClNNaO_4$: $[M+Na]^+$ 368.0660, found 368.0671.



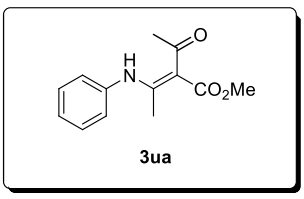
3sa

3sa: yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.90 (s, 1 H), 7.36 (d, *J* = 4.8 Hz, 1 H), 7.15-7.14 (m, 3 H), 7.02 (t, *J* = 7.6 Hz, 1 H), 6.94 (t, *J* = 4.0 Hz, 1 H), 6.78 (d, *J* = 7.6 Hz, 2 H), 3.80 (s, 3 H), 3.48 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 167.9, 153.8, 139.0, 134.1, 130.3, 129.3, 128.7, 126.9, 124.8, 123.6, 98.2, 52.1, 51.6. HRMS calcd (ESI) m/z for $C_{16}H_{15}NNaO_4S$: $[M+Na]^+$ 340.0614, found 340.0620.



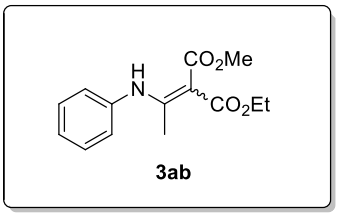
3ta

3ta: colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.04 (d, *J* = 13.6 Hz, 1 H), 8.54 (d, *J* = 14.0 Hz, 1 H), 7.36-7.34 (m, 2 H), 7.17-7.12 (m, 3 H), 3.85 (s, 3 H), 3.78 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 165.7, 152.0, 138.9, 129.6, 124.9, 117.0, 92.6, 51.4, 51.2 HRMS calcd (ESI) m/z for $C_{12}H_{13}NNaO_4$: $[M+Na]^+$ 258.0737, found 258.0733.



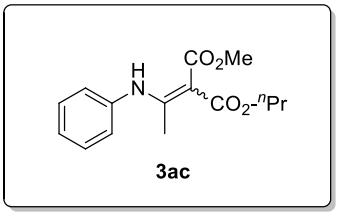
3ua

3ua: yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 13.98 (s, 1 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.30-7.27 (m, 1 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 3.80 (s, 3 H), 2.31 (s, 3 H), 2.14 (s, 3 H).



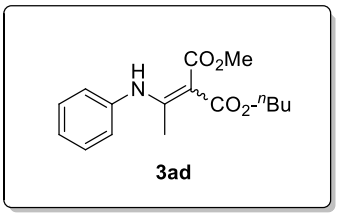
3ab

3ab: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.29, 11.26 (s, s, sum = 1 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.25 (t, *J* = 6.8 Hz, 1 H), 7.10 (d, *J* = 7.2 Hz, 2 H), 4.27-4.20 (m, 2 H), 3.78, 3.75 (s, s, sum = 3 H), 2.09 (s, 3 H), 1.34-1.26 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.14, 168.93, 168.64, 168.51, 161.77, 161.65, 137.92, 129.17, 128.93, 126.37, 126.33, 125.78, 125.74, 94.23, 94.16, 60.68, 59.76, 51.79, 51.06, 17.92, 14.32, 14.13. HRMS calcd (ESI) m/z for $C_{14}H_{17}NNaO_4$: $[M+Na]^+$ 286.1050, found 286.1057.



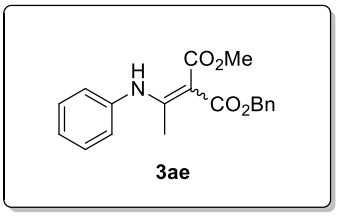
3ac

3ac: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.28 (s, 1 H), 7.36 (t, *J* = 7.2 Hz, 2 H), 7.29-7.23 (m, 1 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 4.17-4.10 (m, 2 H), 3.78, 3.74 (s, s, sum = 3 H), 2.09 (s, 3 H), 1.73-1.68 (m, 2 H), 1.01-0.96 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.13, 168.96, 168.63, 161.77, 137.90, 129.12, 126.32, 125.72, 94.20, 94.08, 66.42, 65.28, 51.72, 50.97, 22.03, 21.90, 17.91, 10.49, 10.36. HRMS calcd (ESI) m/z for $C_{15}H_{19}NNaO_4$: $[M+Na]^+$ 300.1206, found 300.1219.



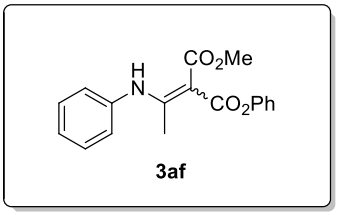
3ad

3ad: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.28 (s, 1 H), 7.36 (t, *J* = 6.8 Hz, 2 H), 7.26-7.25 (m, 1 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 4.21-4.14 (m, 2 H), 3.78, 3.74 (s, s, sum = 3 H), 2.09 (s, 3 H), 1.70-1.63 (m, 2 H), 1.47-1.40 (m, 2 H), 0.95 (d, *J* = 5.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.14, 168.95, 168.65, 161.75, 161.68, 137.90, 129.14, 126.33, 126.29, 125.74, 125.70, 94.22, 94.16, 64.62, 63.53, 51.73, 50.98, 30.69, 30.57, 19.15, 19.06, 17.92, 17.88, 13.64. HRMS calcd (ESI) m/z for $C_{16}H_{21}NNaO_4$: $[M+Na]^+$ 314.1363, found 314.1375.



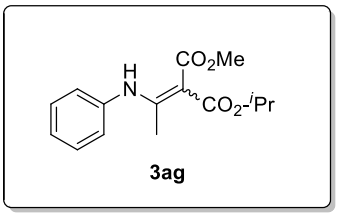
3ae

3ae: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.33, 11.29 (s, s, sum = 1 H), 7.42-7.24 (m, 8 H), 7.10-7.07 (m, 2 H), 5.24, 5.23 (s, s, sum = 2 H), 3.77, 3.72 (s, s, sum = 3 H), 2.10, 2.05 (s, s, sum = 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.98, 168.94, 168.30, 168.26, 162.48, 162.31, 137.79, 136.71, 136.12, 129.14, 128.35, 128.30, 128.19, 127.95, 127.58, 127.08, 126.44, 126.41, 125.78, 125.75, 93.79, 93.75, 66.60, 65.18, 51.76, 50.98, 18.00. HRMS calcd (ESI) m/z for $C_{19}H_{19}NNaO_4$: $[M+Na]^+$ 348.1206, found 348.1221.



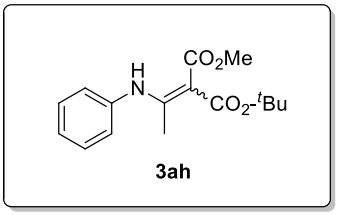
3af

3af: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.53, 11.32 (s, s, sum = 1 H), 7.40-7.29 (m, 4 H), 7.27-7.08 (m, 6 H), 3.83, 3.82 (s, s, sum = 3 H), 2.23, 2.17 (s, s, sum = 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.29, 168.77, 167.41, 167.09, 163.96, 163.89, 151.26, 150.64, 137.58, 137.46, 129.23, 129.17, 126.71, 125.84, 125.66, 125.40, 121.95, 121.54, 93.12, 93.02, 52.03, 51.26, 18.21, 18.17. HRMS calcd (ESI) m/z for $C_{18}H_{17}NNaO_4$: $[M+Na]^+$ 334.1050, found 334.1064.



3ag

3ag: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.25, 11.20 (s, s, sum = 1 H), 7.36 (t, *J* = 7.2 Hz, 2 H), 7.24 (d, *J* = 7.2 Hz, 1 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 5.17-5.04 (m, 1 H), 3.78, 3.74 (s, s, sum = 3 H), 2.08 (s, 3 H), 1.31, 1.27 (d, d, *J* = 6.4 Hz, 6.4 Hz, sum = 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.17, 168.79, 168.20, 167.91, 161.30, 161.06, 137.96, 137.91, 129.08, 126.22, 126.14, 125.66, 125.60, 94.66, 94.59, 67.90, 66.93, 51.60, 50.88, 21.85, 21.63, 17.76, 17.70. HRMS calcd (ESI) m/z for $C_{15}H_{19}NNaO_4$: $[M+Na]^+$ 300.1206, found 300.1211.



3ah

3ah: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.13, 11.08 (s, s, sum = 1 H), 7.34 (d, *J* = 7.2 Hz, 2 H), 7.24-7.22 (m, 1 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 3.76, 3.74 (s, s, sum = 3 H), 2.08, 2.05 (s, s, sum = 3 H), 1.53, 1.50 (s, s, sum = 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.52, 168.95, 168.29, 167.71, 160.57, 160.42, 138.17, 138.13, 129.11, 129.06, 126.11, 126.03, 125.65, 96.27, 95.86, 80.48, 79.97, 51.65, 50.88, 28.37, 28.03, 17.70, 17.56. HRMS calcd (ESI) m/z for $C_{16}H_{21}NNaO_4$: $[M+Na]^+$ 314.1363, found 314.1373.

4. General Computational Calculation Details

All the calculations were performed with Gaussian 09 program[1]. The geometry optimizations of minima and transition states were carried out in the gas phase with the B3LYP functional[2] and the 6-31G(d) basis set[3-5] for C, H, O and N atoms and the SDD basis set[4] was used for Pd. Frequency analyses were carried out at the same level to verify all of the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to evaluate the zero-point vibrational energy and thermal corrections at 298 K. Single point energies were calculated at the M06/SDD/6-311++G(d, p) level[6-8] for all the optimized geometries. Solvent effects (Solvent=Acetonitrile) were considered by self-consistent reaction field (SCRF) calculations based on the SMD[9] solvation model.

Reference

(1) Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts,

R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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4.1 Mechanism for the current reaction and the Cartesian coordinates for all intermediates

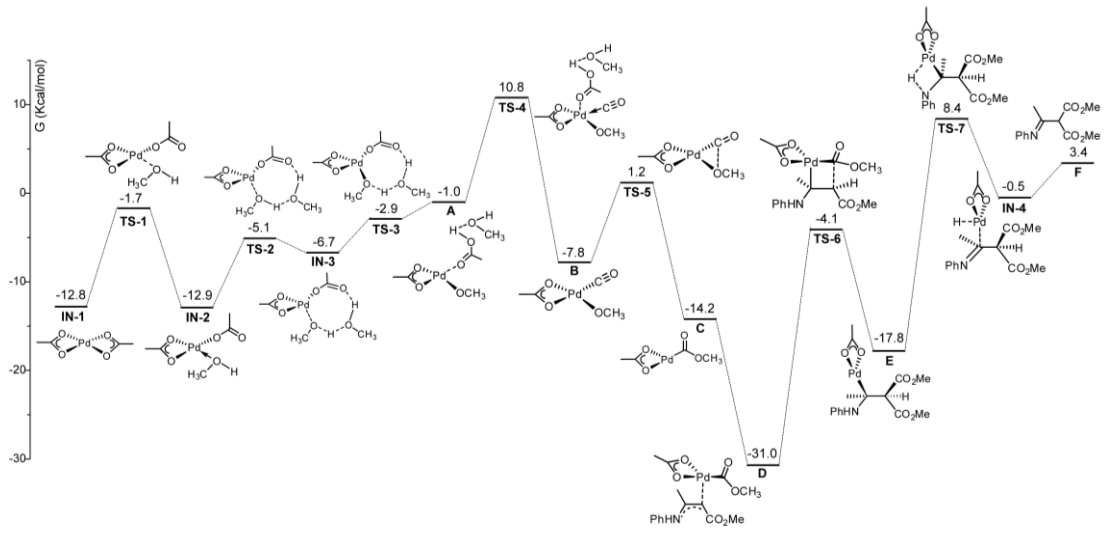


Figure S1 | Energy profiles of this carbonylation reaction pathway.

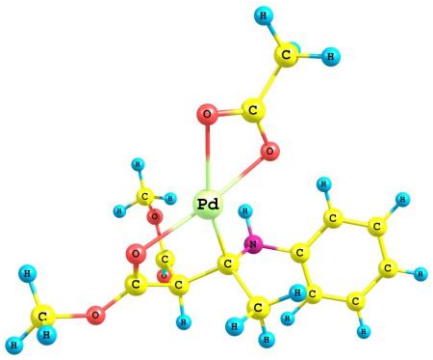


Figure S2 | Optimized Geometries of the Intermediate E.

Cartesian coordinates of all optimized structures

IN-1

Pd	-0.507290000	2.915481000	-1.025526000
C	0.761773000	0.895308000	-1.516692000
O	0.389139000	1.185551000	-0.327388000
C	1.516938000	-0.359677000	-1.822885000
H	2.299223000	-0.153553000	-2.558520000
H	1.947942000	-0.774220000	-0.909345000
H	0.830231000	-1.094740000	-2.258773000
O	0.436797000	1.725859000	-2.434865000
C	-2.558418000	6.171002000	-0.213167000
C	-1.777937000	4.932038000	-0.522281000
O	-1.408014000	4.650266000	-1.714792000
O	-1.446471000	4.097568000	0.389472000
H	-2.020410000	7.046874000	-0.589688000
H	-2.716082000	6.261002000	0.863109000
H	-3.524996000	6.129854000	-0.726880000

TS-1

O	-1.521930000	0.751822000	-1.312582000
H	-1.974093000	0.957519000	-0.474015000
Pd	0.655753000	1.349578000	-0.098867000
C	2.632986000	0.055405000	-0.735468000
O	1.476255000	-0.480525000	-0.599322000
C	3.821783000	-0.745756000	-1.168036000
H	4.732056000	-0.339023000	-0.720625000
H	3.691413000	-1.794234000	-0.890035000
H	3.918603000	-0.683296000	-2.258461000
O	2.716888000	1.309503000	-0.510746000
C	-1.631589000	4.145468000	1.749646000
C	-0.929774000	2.990425000	1.089410000
O	0.163476000	3.224155000	0.444262000

O	-1.354801000	1.807319000	1.169455000
H	-1.361750000	5.088607000	1.269327000
H	-1.327796000	4.190467000	2.802228000
H	-2.713367000	3.992851000	1.716686000
C	-1.764279000	-0.610838000	-1.663015000
H	-1.453959000	-1.302024000	-0.869247000
H	-2.825171000	-0.773827000	-1.894936000
H	-1.172636000	-0.818201000	-2.556777000

IN-2

O	-1.418468000	0.738332000	-1.073923000
H	-1.853400000	1.452635000	-0.451442000
Pd	0.569253000	1.061618000	-0.641469000
C	2.677537000	0.005491000	-1.258260000
O	1.553641000	-0.469223000	-1.651600000
C	3.976590000	-0.611241000	-1.675656000
H	4.737943000	-0.439520000	-0.911130000
H	3.845348000	-1.680704000	-1.856674000
H	4.311881000	-0.141439000	-2.607965000
O	2.640079000	1.046321000	-0.515856000
C	-1.014636000	4.301257000	1.745272000
C	-1.012470000	3.078962000	0.848628000
O	0.165516000	2.675717000	0.504516000
O	-2.094023000	2.554431000	0.500505000
H	-0.386038000	4.121505000	2.622713000
H	-2.033986000	4.538947000	2.053276000
H	-0.584522000	5.150650000	1.204045000
C	-1.938044000	-0.573214000	-0.806121000
H	-1.885087000	-0.816243000	0.261053000
H	-2.979383000	-0.606732000	-1.143326000
H	-1.347228000	-1.290357000	-1.378716000

TS-2

O	-2.115756000	0.378337000	-1.156714000
H	-2.407239000	0.902426000	-0.346115000
Pd	-0.278021000	1.240062000	-1.664159000
C	2.074382000	0.633823000	-1.433203000
O	1.146424000	-0.136324000	-0.999631000
C	3.519537000	0.251904000	-1.333341000
H	4.140239000	1.146832000	-1.246420000
H	3.676262000	-0.410825000	-0.479073000
H	3.812323000	-0.282333000	-2.245084000
O	1.713493000	1.731035000	-1.981568000
C	-1.926633000	4.995085000	-2.815536000

C	-1.537154000	3.834198000	-1.913778000
O	-1.227000000	2.756830000	-2.572788000
O	-1.513300000	3.971093000	-0.680559000
H	-1.013858000	5.469622000	-3.194450000
H	-2.497653000	5.732446000	-2.247870000
H	-2.500509000	4.643594000	-3.676754000
C	-2.073937000	-1.020986000	-0.826344000
H	-1.321986000	-1.228915000	-0.058211000
H	-3.066221000	-1.327300000	-0.479435000
H	-1.824309000	-1.563833000	-1.738844000
O	-2.525016000	2.006117000	0.796080000
H	-2.102643000	2.796587000	0.364519000
C	-2.891873000	2.266645000	2.140496000
H	-3.343936000	1.357089000	2.545935000
H	-2.018978000	2.526711000	2.754057000
H	-3.627082000	3.079854000	2.204604000

IN-3

O	-2.189258000	0.504518000	-1.268751000
H	-2.568290000	1.011592000	-0.467741000
Pd	-0.310337000	1.343432000	-1.587693000
C	2.000328000	0.738475000	-1.082585000
O	1.025732000	-0.018651000	-0.735089000
C	3.423483000	0.352322000	-0.818235000
H	4.039747000	1.246029000	-0.695197000
H	3.483516000	-0.283114000	0.068487000
H	3.805649000	-0.213720000	-1.676099000
O	1.707803000	1.824414000	-1.690043000
C	-1.975038000	5.024555000	-2.955329000
C	-1.663683000	3.867786000	-2.018489000
O	-1.135954000	2.847328000	-2.625494000
O	-1.888616000	3.961243000	-0.801401000
H	-1.048951000	5.574843000	-3.158631000
H	-2.692441000	5.700557000	-2.486152000
H	-2.359726000	4.658203000	-3.910579000
C	-2.225973000	-0.909967000	-1.017368000
H	-1.942477000	-1.416200000	-1.941370000
H	-1.534314000	-1.194773000	-0.217270000
H	-3.250186000	-1.188622000	-0.748897000
O	-2.983330000	2.019559000	0.659041000
H	-2.614634000	2.818649000	0.190474000
C	-2.328367000	1.900586000	1.921998000
H	-2.705761000	0.996364000	2.407115000
H	-1.238146000	1.822039000	1.812628000

H	-2.561220000	2.762328000	2.558487000

TS-3

O	-2.297025000	0.318953000	-1.182251000
H	-2.798179000	1.036660000	-0.148356000
Pd	-0.536258000	1.228248000	-1.508825000
C	1.823326000	0.697269000	-1.128278000
O	0.879912000	-0.111041000	-0.799450000
C	3.261450000	0.317445000	-0.940651000
H	3.876821000	1.213209000	-0.830417000
H	3.370179000	-0.335068000	-0.070844000
H	3.604181000	-0.231753000	-1.825691000
O	1.485718000	1.812621000	-1.643448000
C	-2.474728000	4.897986000	-2.892700000
C	-2.210266000	3.731805000	-1.963387000
O	-1.467791000	2.808698000	-2.415971000
O	-2.770072000	3.783127000	-0.822691000
H	-2.378744000	5.836059000	-2.338707000
H	-3.507255000	4.833588000	-3.254502000
H	-1.792264000	4.884259000	-3.743249000
C	-2.240575000	-1.089340000	-1.024894000
H	-1.983791000	-1.571828000	-1.975735000
H	-1.508955000	-1.399914000	-0.265741000
H	-3.236788000	-1.437851000	-0.719231000
O	-3.125304000	1.823791000	0.539485000
H	-2.904291000	2.784523000	-0.121776000
C	-2.352067000	1.827287000	1.746637000
H	-2.587816000	0.928230000	2.323038000
H	-1.276016000	1.854154000	1.533243000
H	-2.631584000	2.708711000	2.329025000

A

O	-2.280060000	0.116809000	-1.225671000
H	-2.768494000	0.928146000	0.056312000
Pd	-0.532583000	1.016513000	-1.504343000
C	1.822697000	0.488056000	-1.064388000
O	0.866417000	-0.319979000	-0.770683000
C	3.251364000	0.093650000	-0.834230000
H	3.878160000	0.983135000	-0.740281000
H	3.332192000	-0.531176000	0.058857000
H	3.603047000	-0.492046000	-1.691906000
O	1.508228000	1.608739000	-1.578880000
C	-2.504159000	4.682745000	-3.006123000
C	-2.219869000	3.546814000	-2.056323000

O	-1.484383000	2.612060000	-2.433352000
O	-2.800307000	3.664603000	-0.901184000
H	-2.340768000	5.637730000	-2.497954000
H	-3.558246000	4.644751000	-3.302470000
H	-1.870980000	4.607646000	-3.890198000
C	-2.221312000	-1.293686000	-1.202905000
H	-1.967134000	-1.703296000	-2.190866000
H	-1.495951000	-1.676765000	-0.469585000
H	-3.219205000	-1.665723000	-0.927664000
O	-2.984988000	1.694174000	0.681732000
H	-2.768490000	2.838873000	-0.263368000
C	-2.163016000	1.626252000	1.845295000
H	-2.429765000	0.753151000	2.452935000
H	-1.095869000	1.571593000	1.590162000
H	-2.343773000	2.529281000	2.434555000

TS-4

O	0.085771000	1.199084000	-1.528321000
H	1.274139000	1.912943000	-0.617724000
Pd	-0.488934000	-0.173321000	-0.225681000
C	-2.016405000	-0.293632000	1.727508000
O	-1.936222000	0.784203000	1.044914000
C	-2.975823000	-0.416039000	2.874692000
H	-3.954511000	-0.727887000	2.490733000
H	-2.625576000	-1.171329000	3.582043000
H	-3.097192000	0.549796000	3.371411000
O	-1.274342000	-1.276092000	1.381413000
C	3.523280000	-2.376825000	0.461245000
C	2.638125000	-1.173158000	0.243439000
O	1.545469000	-1.275719000	-0.326668000
O	3.159217000	-0.058803000	0.700448000
H	3.001101000	-3.286719000	0.164978000
H	3.818270000	-2.433835000	1.513743000
H	4.439545000	-2.265265000	-0.128719000
C	-0.955493000	2.049509000	-1.957733000
H	-1.652265000	1.533048000	-2.634253000
H	-1.527702000	2.472286000	-1.117703000
H	-0.496781000	2.880218000	-2.513781000
O	1.995733000	2.158811000	0.031321000
H	2.624636000	0.776426000	0.447074000
C	1.444710000	2.962108000	1.072956000
H	1.143880000	3.944924000	0.688566000
H	0.576306000	2.483775000	1.546098000
H	2.224435000	3.108622000	1.825236000

C	-1.100794000	-1.471118000	-2.000188000
O	-1.804686000	-1.448877000	-2.898626000

B

O	3.039395000	-0.138903000	-2.096293000
Pd	3.281460000	0.245108000	-0.177159000
C	3.206786000	-1.086419000	1.906566000
O	3.096843000	-1.639797000	0.756403000
C	3.117851000	-1.898672000	3.163507000
H	3.718311000	-2.807243000	3.061804000
H	3.453180000	-1.313336000	4.021730000
H	2.076811000	-2.203885000	3.320061000
O	3.375419000	0.179929000	1.944001000
C	3.633796000	-1.361969000	-2.466454000
H	4.733977000	-1.311746000	-2.498479000
H	3.332645000	-2.198855000	-1.818798000
H	3.276999000	-1.580123000	-3.484427000
C	3.538836000	2.047954000	-0.719813000
O	3.697238000	3.124023000	-1.060514000

TS-5

O	2.442034000	-0.015472000	-1.897988000
Pd	2.835524000	0.358767000	0.112989000
C	3.050023000	-0.177666000	2.516513000
O	2.817244000	-1.118799000	1.696213000
C	3.148113000	-0.410452000	3.995327000
H	3.400504000	-1.453685000	4.196365000
H	3.891454000	0.258662000	4.436004000
H	2.178075000	-0.189052000	4.455945000
O	3.176696000	1.012512000	2.042053000
C	3.439945000	-0.691977000	-2.681212000
H	4.417840000	-0.201419000	-2.617353000
H	3.531372000	-1.725880000	-2.335195000
H	3.098927000	-0.679516000	-3.721816000
C	2.879991000	1.555207000	-1.347544000
O	3.001501000	2.458804000	-2.068527000

C

O	3.607628000	0.058340000	-1.863038000
Pd	3.811240000	0.757640000	0.547108000
C	3.839013000	1.848901000	2.792823000
O	4.264966000	0.661495000	2.733354000
C	3.802795000	2.618837000	4.085560000
H	3.184304000	2.078079000	4.809326000

H	4.815610000	2.679019000	4.497106000
H	3.403751000	3.623156000	3.933634000
O	3.421015000	2.423434000	1.714153000
C	3.360967000	-0.013568000	-3.290541000
H	3.949719000	0.751024000	-3.802667000
H	3.671184000	-1.012931000	-3.592786000
H	2.297624000	0.142585000	-3.486548000
C	3.292285000	1.233555000	-1.248993000
O	2.832666000	2.209798000	-1.771930000

D

C	-0.430587000	-0.918475000	0.232383000
O	0.444184000	-0.116460000	0.001661000
Pd	-0.355589000	-2.769423000	-0.407178000
O	0.391163000	-4.846050000	-0.836366000
C	1.448187000	-4.542754000	-0.194392000
O	1.562720000	-3.389927000	0.341125000
C	-2.827243000	-3.654282000	-0.655303000
C	-2.292188000	-2.518957000	-1.349398000
O	-1.520565000	-0.617337000	0.999119000
C	-1.530600000	0.717359000	1.551805000
H	-2.444883000	0.781526000	2.143247000
H	-0.652717000	0.874819000	2.183188000
H	-1.536169000	1.462834000	0.752138000
C	2.594069000	-5.519822000	-0.087582000
H	3.333898000	-5.285925000	-0.862349000
H	3.086163000	-5.425229000	0.883865000
H	2.244069000	-6.543234000	-0.241272000
H	-2.671717000	-1.558509000	-1.019558000
C	-3.497735000	-3.457259000	0.677402000
H	-3.192188000	-2.502947000	1.107214000
H	-4.587515000	-3.453270000	0.548269000
H	-3.249606000	-4.265601000	1.370497000
C	-1.987234000	-2.604086000	-2.794055000
O	-1.844742000	-3.642546000	-3.435528000
O	-1.875617000	-1.384731000	-3.352323000
C	-1.488455000	-1.364222000	-4.736680000
H	-0.506338000	-1.827197000	-4.863417000
H	-2.220057000	-1.897362000	-5.349310000
H	-1.452365000	-0.309726000	-5.009863000
N	-2.774897000	-4.868227000	-1.203773000
H	-2.294243000	-4.891663000	-2.110795000
C	-3.112336000	-6.119439000	-0.594735000
C	-4.435766000	-6.422985000	-0.261371000

C	-2.093609000	-7.058745000	-0.396571000
C	-4.737933000	-7.666497000	0.295598000
H	-5.221761000	-5.699101000	-0.453685000
C	-2.409522000	-8.302427000	0.151001000
H	-1.073203000	-6.788999000	-0.653180000
C	-3.727197000	-8.607515000	0.501329000
H	-5.765909000	-7.902273000	0.555917000
H	-1.620868000	-9.032472000	0.310183000
H	-3.966251000	-9.576806000	0.929708000

TS-6

O	1.658472000	5.454791000	-1.875237000
Pd	1.582091000	8.016473000	-0.632101000
C	3.698303000	9.421966000	-0.239336000
O	2.597493000	9.711469000	0.348216000
C	4.905925000	10.298197000	0.014215000
H	5.081362000	10.388026000	1.091104000
H	5.791420000	9.888133000	-0.474820000
H	4.711366000	11.305681000	-0.370100000
O	3.774471000	8.432092000	-1.022044000
C	2.381069000	4.983758000	-3.032402000
H	3.152321000	5.706356000	-3.309227000
H	2.832024000	4.040618000	-2.724508000
H	1.695864000	4.834170000	-3.870506000
C	0.963910000	6.604888000	-2.065736000
O	0.797250000	7.141994000	-3.144833000
C	-0.338655000	6.692215000	-0.862851000
H	-1.111565000	6.835211000	-1.615635000
C	-0.360767000	7.895696000	0.064518000
C	-1.159627000	9.088905000	-0.437189000
H	-0.825104000	10.019387000	0.023793000
H	-1.055450000	9.184190000	-1.520632000
H	-2.223731000	8.955243000	-0.195723000
C	-0.506285000	5.297160000	-0.305278000
O	0.287436000	5.039786000	0.759903000
O	-1.277760000	4.492566000	-0.775108000
C	0.234580000	3.687626000	1.257774000
H	0.931536000	3.660635000	2.094842000
H	-0.778463000	3.438656000	1.582583000
H	0.545024000	2.993441000	0.473903000
N	-0.389938000	7.665792000	1.426833000
H	-0.049068000	6.758629000	1.725551000
C	-0.599800000	8.632699000	2.456074000
C	0.123643000	9.832272000	2.509129000

C	-1.528660000	8.329889000	3.460785000
C	-0.114284000	10.729377000	3.551930000
H	0.889649000	10.038207000	1.768054000
C	-1.742489000	9.224727000	4.508859000
H	-2.086735000	7.398744000	3.407176000
C	-1.042704000	10.432479000	4.551931000
H	0.448707000	11.657955000	3.590293000
H	-2.464585000	8.982028000	5.283657000
H	-1.214198000	11.133550000	5.363973000

E

O	-0.873994000	-2.440733000	-3.276301000
Pd	1.327141000	0.352531000	-1.205680000
C	3.320719000	1.587187000	-0.234995000
O	2.178110000	1.474516000	0.354954000
C	4.406913000	2.377078000	0.455515000
H	4.511247000	2.046536000	1.493778000
H	5.355732000	2.262738000	-0.072003000
H	4.129273000	3.437115000	0.474777000
O	3.500555000	1.058577000	-1.362766000
C	-0.241718000	-2.641303000	-4.563351000
H	0.795455000	-2.953830000	-4.425137000
H	-0.825039000	-3.423800000	-5.046185000
H	-0.272912000	-1.716231000	-5.142964000
C	-0.330802000	-1.538230000	-2.479250000
O	0.657790000	-0.871268000	-2.811619000
C	-0.989646000	-1.374030000	-1.131405000
H	-2.077732000	-1.436793000	-1.251852000
C	-0.575145000	0.024304000	-0.533940000
C	-1.460101000	1.112479000	-1.140336000
H	-1.162237000	2.102579000	-0.785966000
H	-1.373804000	1.101823000	-2.232147000
H	-2.520636000	0.969432000	-0.889005000
C	-0.642065000	-2.556924000	-0.217967000
O	0.690899000	-2.684001000	-0.061235000
O	-1.459886000	-3.289119000	0.284259000
C	1.114433000	-3.752630000	0.807256000
H	2.202925000	-3.704945000	0.813403000
H	0.712602000	-3.602809000	1.812446000
H	0.768383000	-4.714989000	0.422058000
N	-0.597475000	-0.024485000	0.916416000
H	0.313192000	-0.296265000	1.272059000
C	-1.185537000	0.993257000	1.723212000
C	-0.386206000	1.890288000	2.447475000

C	-2.580667000	1.056409000	1.861577000
C	-0.976748000	2.833438000	3.289861000
H	0.691686000	1.858024000	2.317755000
C	-3.164920000	2.018295000	2.684862000
H	-3.198049000	0.328636000	1.343140000
C	-2.366250000	2.908986000	3.406382000
H	-0.345628000	3.522316000	3.845680000
H	-4.247084000	2.055711000	2.780538000
H	-2.822773000	3.650129000	4.056705000

TS-7

O	-0.090801000	-3.145669000	-3.692783000
Pd	0.181497000	-0.772452000	0.194463000
C	2.631634000	-0.600923000	0.771941000
O	1.773110000	-1.018318000	1.624588000
C	4.075178000	-0.444966000	1.182933000
H	4.343144000	-1.196562000	1.929627000
H	4.729180000	-0.519459000	0.311247000
H	4.212883000	0.545219000	1.633659000
O	2.254687000	-0.295108000	-0.400115000
C	1.042098000	-3.476288000	-4.517905000
H	1.959667000	-3.459521000	-3.924859000
H	0.842532000	-4.479467000	-4.894168000
H	1.133151000	-2.764601000	-5.342381000
C	-0.054781000	-1.928695000	-3.119057000
O	0.835629000	-1.128060000	-3.285266000
C	-1.335890000	-1.693360000	-2.309070000
H	-2.107525000	-1.450156000	-3.055535000
C	-1.283262000	-0.483273000	-1.354709000
C	-1.142751000	0.868738000	-2.024522000
H	-1.064948000	1.670987000	-1.288047000
H	-0.252035000	0.866248000	-2.655089000
H	-2.017951000	1.071060000	-2.658973000
C	-1.857509000	-2.973670000	-1.648238000
O	-0.931807000	-3.530578000	-0.847464000
O	-2.963904000	-3.424910000	-1.831788000
C	-1.338254000	-4.731665000	-0.166514000
H	-0.482452000	-5.022219000	0.441975000
H	-2.211226000	-4.534212000	0.460574000
H	-1.583574000	-5.511310000	-0.892012000
N	-1.965521000	-0.641436000	-0.186575000
H	-1.105948000	-1.367674000	0.878797000
C	-2.645939000	0.447490000	0.448918000
C	-2.176545000	1.089025000	1.598912000

C	-3.896208000	0.796653000	-0.084435000
C	-2.950222000	2.082044000	2.204286000
H	-1.206505000	0.817206000	2.006175000
C	-4.652892000	1.798224000	0.520353000
H	-4.272333000	0.269117000	-0.956145000
C	-4.185512000	2.444908000	1.667574000
H	-2.575414000	2.575736000	3.096592000
H	-5.617900000	2.064267000	0.097682000
H	-4.781415000	3.220606000	2.139534000

IN-4

O	-0.784878000	-2.389747000	-3.946399000
Pd	0.585746000	0.181858000	-0.260766000
C	2.991281000	0.630681000	0.346600000
O	2.347051000	-0.452086000	0.636582000
C	4.437490000	0.727426000	0.760694000
H	4.535485000	0.502609000	1.827493000
H	5.022351000	-0.019979000	0.213165000
H	4.828418000	1.724305000	0.548946000
O	2.410715000	1.562595000	-0.273992000
C	0.080864000	-3.437987000	-4.421383000
H	0.548213000	-3.953555000	-3.578868000
H	-0.564948000	-4.115963000	-4.979111000
H	0.859171000	-3.025333000	-5.068182000
C	-0.189587000	-1.430066000	-3.216799000
O	1.000027000	-1.382366000	-2.997797000
C	-1.232726000	-0.404186000	-2.766259000
H	-1.674341000	-0.005114000	-3.690811000
C	-0.660162000	0.824860000	-2.041196000
C	0.179077000	1.733064000	-2.916706000
H	0.641634000	2.533401000	-2.337090000
H	0.964243000	1.140218000	-3.393454000
H	-0.435975000	2.178481000	-3.710501000
C	-2.436354000	-1.027828000	-2.043480000
O	-2.081426000	-2.046388000	-1.244017000
O	-3.571156000	-0.643792000	-2.202010000
C	-3.155599000	-2.651599000	-0.500251000
H	-2.691294000	-3.445619000	0.083894000
H	-3.622670000	-1.911415000	0.153714000
H	-3.906171000	-3.057810000	-1.182786000
N	-1.216201000	1.160626000	-0.880341000
H	-0.270654000	-1.045287000	-0.004527000
C	-1.276349000	2.491804000	-0.392218000
C	-1.032902000	2.738300000	0.969047000

C	-1.725972000	3.543738000	-1.207443000
C	-1.183218000	4.021938000	1.487587000
H	-0.720464000	1.916669000	1.606742000
C	-1.891732000	4.821522000	-0.674020000
H	-1.975975000	3.354763000	-2.246333000
C	-1.610930000	5.071366000	0.670088000
H	-0.975231000	4.199379000	2.539148000
H	-2.245409000	5.623669000	-1.316260000
H	-1.735992000	6.069588000	1.079511000

F

O	-0.458840000	-2.466874000	-3.710572000
C	0.529531000	-3.509847000	-3.636263000
H	0.632125000	-3.863085000	-2.607097000
H	0.160514000	-4.306505000	-4.282269000
H	1.497878000	-3.144710000	-3.987928000
C	-0.200013000	-1.370684000	-2.971835000
O	0.808628000	-1.213850000	-2.321162000
C	-1.353632000	-0.371971000	-3.096005000
H	-1.531156000	-0.203071000	-4.164604000
C	-1.018315000	0.961936000	-2.426764000
C	0.095353000	1.756307000	-3.068827000
H	0.147575000	2.769168000	-2.665956000
H	1.055481000	1.256968000	-2.901751000
H	-0.061188000	1.810365000	-4.153452000
C	-2.659369000	-0.954630000	-2.543469000
O	-2.434061000	-1.699369000	-1.447249000
O	-3.745731000	-0.765048000	-3.036437000
C	-3.610451000	-2.215899000	-0.802696000
H	-3.246833000	-2.797417000	0.044623000
H	-4.242260000	-1.392127000	-0.461455000
H	-4.179330000	-2.846649000	-1.490657000
N	-1.732681000	1.296514000	-1.425081000
C	-1.514155000	2.474206000	-0.682494000
C	-0.331071000	2.681073000	0.044637000
C	-2.553939000	3.411981000	-0.582728000
C	-0.188132000	3.818265000	0.840336000
H	0.457893000	1.935804000	-0.003077000
C	-2.393624000	4.554493000	0.197831000
H	-3.476396000	3.231537000	-1.126774000
C	-1.212311000	4.763428000	0.915012000
H	0.730845000	3.964336000	1.402308000
H	-3.200585000	5.280491000	0.255056000
H	-1.096179000	5.649481000	1.532817000

4.2 The ruled out mechanism and the Cartesian coordinates for all intermediates

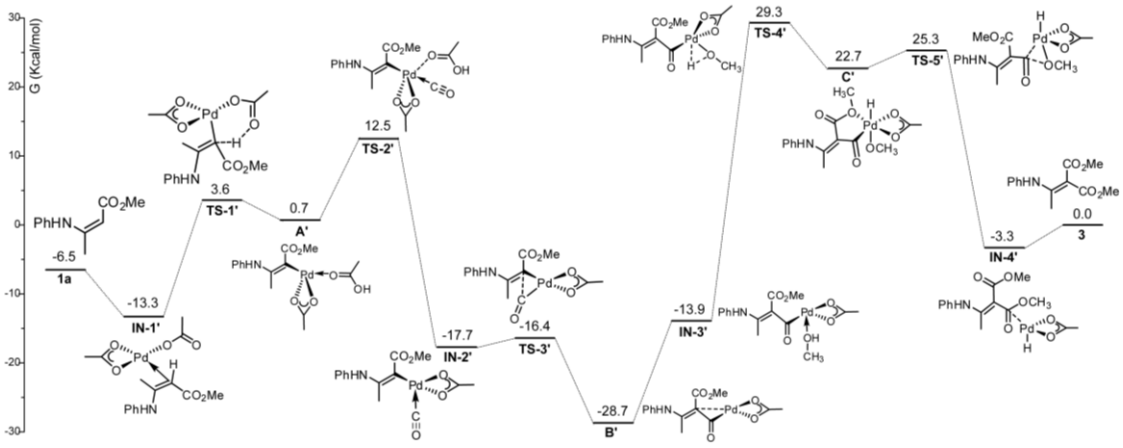


Figure S3 | Energy profiles of the alkenyl C-H activation and carbonylation.

Within this mechanism, the first step is that the insertion of $Pd(OAc)_2$ into the alkenyl C-H bond forms **IN-1'**. Then the alkenyl hydrogen atom migrates to the acetate group via **TS-1'** to form alkenylpalladium intermediate **A'**, with a free energy barrier of 3.6 Kcal/mol. The CO molecule would replace the acetic acid group coordinate to the palladium atom by overcoming a barrier of 11.8 Kcal/mol (**TS-2'**). Subsequently, the migratory insertion of CO into C–Pd bond occur via a three-membered ring form transition state **TS-3'** (ΔG = 1.3 Kcal/mol) and yield the acylpalladium complex **B'**. A methanol molecule would coordinate to the palladium atom and transfer the H atom to the remained acetate group on palladium by overcoming the **TS-4'** (ΔG = 43.2 Kcal/mol). A sextuple-coordinate Pd(IV) intermediate (**C'**) was found, and the forthcoming -OMe transmission is proceeded via **TS-5'** (ΔG = 2.6 Kcal/mol). Finally, the carbonylation product **3** was obtained by dissociation of a palladium hydride species. No stereoisomer was obtained when different alcohols were employed in this reaction, because the configuration of C=C double bond always remains intact in this course.

This mechanism was ruled out, because the high activation energy from **IN-3'** to **C'** (which should overcome the **TS-4'** (ΔG = 43.2 Kcal/mol))

Cartesian coordinates of all optimized structures

1a

C	-3.116182000	-3.542225000	-0.778646000
C	-2.719374000	-2.466564000	-1.538583000
H	-2.909048000	-1.465780000	-1.173452000

C	-3.792714000	-3.301174000	0.546848000
H	-4.879852000	-3.420942000	0.474933000
H	-3.434040000	-3.995950000	1.312488000
H	-3.594595000	-2.279480000	0.877871000
C	-2.036493000	-2.598709000	-2.804065000
O	-1.701555000	-3.656432000	-3.348881000
O	-1.771061000	-1.393529000	-3.372663000
C	-1.086022000	-1.443549000	-4.628836000
H	-0.112333000	-1.931067000	-4.523969000
H	-1.673042000	-1.990328000	-5.372562000
H	-0.959518000	-0.403700000	-4.934038000
N	-2.876784000	-4.819092000	-1.200642000
H	-2.327078000	-4.841279000	-2.064686000
C	-3.151561000	-6.061773000	-0.597885000
C	-4.326532000	-6.341161000	0.117823000
C	-2.215398000	-7.093129000	-0.791045000
C	-4.532958000	-7.611254000	0.656987000
H	-5.092774000	-5.583668000	0.227433000
C	-2.439852000	-8.361984000	-0.265422000
H	-1.306672000	-6.883269000	-1.349330000
C	-3.596005000	-8.627919000	0.472250000
H	-5.447827000	-7.807908000	1.209840000
H	-1.702212000	-9.143677000	-0.426113000
H	-3.767774000	-9.616190000	0.888673000

IN-1’

C	0.367392000	-4.836928000	-1.268474000
C	0.518787000	-3.940019000	-2.329055000
C	-0.008322000	-2.652239000	-2.242202000
C	-0.692341000	-2.264020000	-1.084383000
C	-0.861573000	-3.161365000	-0.025490000
C	-0.321410000	-4.444602000	-0.119272000
H	0.781523000	-5.838599000	-1.338704000
H	1.054226000	-4.240262000	-3.225204000
H	0.119168000	-1.931884000	-3.044362000
H	-1.426124000	-2.865265000	0.852401000
H	-0.451729000	-5.140939000	0.704104000
N	-1.267340000	-0.956393000	-1.054960000
H	-1.839158000	-0.672473000	-1.861908000
C	-1.083634000	0.012535000	-0.167923000
C	-1.682261000	1.308106000	-0.393530000
H	-1.756410000	1.925860000	0.494674000
C	-0.265229000	-0.205660000	1.069313000
H	-0.907063000	-0.610036000	1.863601000

H	0.544859000	-0.918883000	0.897104000
H	0.130405000	0.755553000	1.408136000
C	-2.816353000	1.431125000	-1.340440000
O	-3.077814000	0.641762000	-2.247286000
O	-3.551477000	2.529519000	-1.103074000
C	-4.618942000	2.783114000	-2.031913000
H	-5.093886000	3.698952000	-1.680785000
H	-4.220340000	2.919575000	-3.040696000
H	-5.331859000	1.954598000	-2.034905000
Pd	-0.065875000	2.200312000	-1.470659000
C	1.253261000	1.559675000	-3.482868000
O	0.350120000	0.796994000	-2.968675000
C	1.975303000	1.128159000	-4.729577000
H	2.849431000	1.759627000	-4.899558000
H	2.276049000	0.079418000	-4.647556000
H	1.298267000	1.215261000	-5.587288000
O	1.491907000	2.671856000	-2.927840000
C	0.137034000	5.273776000	1.495127000
C	0.093374000	3.862434000	0.920486000
O	-0.184123000	3.857312000	-0.358473000
O	0.307768000	2.871547000	1.620545000
H	1.000087000	5.808278000	1.082902000
H	0.223331000	5.229609000	2.582547000
H	-0.759515000	5.832332000	1.209068000

TS-1’

C	0.665997000	-5.403572000	-0.215923000
C	-0.055494000	-5.098360000	-1.372747000
C	-0.508417000	-3.800200000	-1.597139000
C	-0.245587000	-2.790365000	-0.659514000
C	0.454793000	-3.101753000	0.513723000
C	0.916241000	-4.401742000	0.723145000
H	1.022495000	-6.415063000	-0.044397000
H	-0.261932000	-5.871256000	-2.107758000
H	-1.057335000	-3.554910000	-2.502199000
H	0.614415000	-2.340651000	1.269270000
H	1.459590000	-4.632587000	1.635248000
N	-0.773870000	-1.499674000	-0.917641000
H	-1.726619000	-1.450322000	-1.303717000
C	-0.222164000	-0.283645000	-0.750483000
C	-0.981533000	0.898783000	-0.927438000
H	-0.977666000	1.549170000	0.329777000
C	1.220061000	-0.186856000	-0.318581000
H	1.288878000	-0.114191000	0.774120000

H	1.800230000	-1.055556000	-0.638697000
H	1.663116000	0.719731000	-0.735260000
C	-2.381200000	0.780152000	-1.371355000
O	-2.988987000	-0.258570000	-1.650135000
O	-3.007782000	1.978544000	-1.426873000
C	-4.379070000	1.949711000	-1.847102000
H	-4.707104000	2.989440000	-1.832863000
H	-4.464617000	1.535070000	-2.855195000
H	-4.981933000	1.347155000	-1.162016000
Pd	-0.027833000	2.538429000	-1.759326000
C	0.872355000	2.817624000	-4.055476000
O	0.333193000	1.727597000	-3.628043000
C	1.339381000	2.897453000	-5.483828000
H	1.818730000	1.959812000	-5.778792000
H	0.472864000	3.050432000	-6.137843000
H	2.028455000	3.735164000	-5.609597000
O	0.972222000	3.801081000	-3.264700000
C	-0.612842000	4.408356000	2.154295000
C	-0.570867000	3.376335000	1.051991000
O	-0.153960000	3.730948000	-0.083932000
O	-0.982739000	2.197956000	1.339782000
H	-1.651453000	4.728560000	2.296516000
H	-0.005215000	5.275217000	1.891257000
H	-0.270163000	3.967117000	3.093900000

A’

C	0.650102000	-5.420844000	-0.021373000
C	-0.332008000	-5.249296000	-1.000245000
C	-0.785706000	-3.973864000	-1.327579000
C	-0.267993000	-2.844797000	-0.671383000
C	0.697798000	-3.021802000	0.331299000
C	1.158852000	-4.301888000	0.639785000
H	1.008446000	-6.415303000	0.228237000
H	-0.742080000	-6.111248000	-1.519506000
H	-1.536615000	-3.837877000	-2.101327000
H	1.067885000	-2.166469000	0.885332000
H	1.909112000	-4.422562000	1.416702000
N	-0.805889000	-1.584474000	-1.010472000
H	-1.811055000	-1.544988000	-1.206533000
C	-0.202747000	-0.366776000	-1.114891000
C	-0.952139000	0.800833000	-1.282043000
H	-0.868280000	1.451208000	0.412605000
C	1.306603000	-0.306691000	-1.066645000
H	1.666097000	-0.064012000	-0.059026000

H	1.754647000	-1.257877000	-1.363535000
H	1.656608000	0.478761000	-1.738996000
C	-2.404202000	0.719896000	-1.436420000
O	-3.093046000	-0.306834000	-1.447861000
O	-2.992280000	1.940519000	-1.556138000
C	-4.415075000	1.930618000	-1.732122000
H	-4.702102000	2.978629000	-1.825759000
H	-4.689320000	1.377401000	-2.634484000
H	-4.911312000	1.471933000	-0.871923000
Pd	-0.085337000	2.523018000	-1.918743000
C	1.072745000	2.980905000	-4.074702000
O	0.600147000	1.828682000	-3.737108000
C	1.740819000	3.141379000	-5.414834000
H	1.662682000	2.224502000	-6.002309000
H	1.278140000	3.972982000	-5.955679000
H	2.796496000	3.393515000	-5.266143000
O	0.969096000	3.948249000	-3.267641000
C	-0.965377000	4.247439000	2.062899000
C	-0.788343000	3.271144000	0.934213000
O	-0.527459000	3.658452000	-0.215962000
O	-0.932820000	2.010788000	1.264832000
H	-1.996739000	4.195293000	2.428052000
H	-0.743251000	5.258656000	1.722107000
H	-0.308782000	3.973538000	2.894612000

TS-2’

C	-0.262813000	-5.523830000	1.121665000
C	-1.219243000	-5.338393000	0.120153000
C	-1.587749000	-4.054176000	-0.273738000
C	-1.009365000	-2.930552000	0.338946000
C	-0.069896000	-3.118932000	1.364292000
C	0.306772000	-4.408944000	1.738823000
H	0.028912000	-6.525748000	1.422770000
H	-1.675488000	-6.197016000	-0.364927000
H	-2.318300000	-3.908334000	-1.064933000
H	0.342702000	-2.261496000	1.884986000
H	1.037232000	-4.539304000	2.532771000
N	-1.463954000	-1.654488000	-0.059243000
H	-2.465110000	-1.555364000	-0.252910000
C	-0.774975000	-0.487358000	-0.218585000
C	-1.445056000	0.714278000	-0.441258000
H	-1.620088000	1.461426000	1.384505000
C	0.734138000	-0.547658000	-0.206989000
H	1.146956000	-0.204121000	0.749009000

H	1.092578000	-1.563306000	-0.384970000
H	1.126540000	0.105300000	-0.989073000
C	-2.881394000	0.712958000	-0.713810000
O	-3.641904000	-0.259390000	-0.651933000
O	-3.352432000	1.937601000	-1.059353000
C	-4.748389000	2.006577000	-1.383476000
H	-4.933900000	3.051328000	-1.634002000
H	-4.978498000	1.361186000	-2.235468000
H	-5.359735000	1.700662000	-0.529970000
Pd	-0.538664000	2.447855000	-0.961723000
C	0.187202000	3.260982000	-3.222422000
O	-0.254721000	2.069669000	-3.034799000
C	0.635693000	3.676143000	-4.598504000
H	0.013110000	3.202333000	-5.361827000
H	0.599087000	4.763641000	-4.694364000
H	1.670462000	3.347558000	-4.752755000
O	0.264247000	4.056227000	-2.236401000
C	-2.305515000	4.156975000	3.030919000
C	-1.872723000	3.272189000	1.891293000
O	-1.545826000	3.706575000	0.789931000
O	-1.871696000	1.979992000	2.201207000
H	-3.306223000	3.867102000	3.367226000
H	-2.302854000	5.199479000	2.712450000
H	-1.624068000	4.023306000	3.878002000
C	1.243357000	2.568530000	0.354642000
O	2.348738000	2.819196000	0.180614000

IN-2’

C	0.173373000	-6.163224000	-0.118486000
C	-1.016837000	-5.812936000	-0.761119000
C	-1.467226000	-4.495359000	-0.741526000
C	-0.737295000	-3.502646000	-0.065786000
C	0.442618000	-3.863561000	0.604053000
C	0.896284000	-5.182160000	0.561826000
H	0.527992000	-7.189568000	-0.140800000
H	-1.594397000	-6.566562000	-1.289604000
H	-2.383029000	-4.219010000	-1.257312000
H	0.987825000	-3.124014000	1.179412000
H	1.812962000	-5.444309000	1.083432000
N	-1.276685000	-2.199721000	-0.034924000
H	-2.293401000	-2.121437000	0.045970000
C	-0.655043000	-0.982265000	-0.098915000
C	-1.378215000	0.186483000	0.061615000
C	0.825064000	-0.949893000	-0.404369000

H	1.424588000	-0.918291000	0.513275000
H	1.130384000	-1.830605000	-0.974809000
H	1.063268000	-0.058556000	-0.988401000
C	-2.796222000	0.178866000	0.360334000
O	-3.524412000	-0.819931000	0.383812000
O	-3.308510000	1.414745000	0.621438000
C	-4.714330000	1.454116000	0.903733000
H	-4.945603000	2.505888000	1.076089000
H	-5.288447000	1.069513000	0.056519000
H	-4.949536000	0.859352000	1.790722000
Pd	-0.494734000	1.991944000	-0.268782000
C	0.301049000	3.075230000	-2.381136000
O	-0.178801000	1.884505000	-2.360291000
C	0.717195000	3.689640000	-3.689330000
H	1.316923000	2.976611000	-4.262718000
H	-0.177545000	3.917867000	-4.279762000
H	1.279697000	4.609384000	-3.518568000
O	0.396867000	3.718010000	-1.288461000
C	-0.624078000	2.228253000	1.583117000
O	-0.685395000	2.374241000	2.715853000

TS-3’

C	0.163814000	-5.820618000	-0.492414000
C	-0.826632000	-5.280465000	-1.316454000
C	-1.204581000	-3.946485000	-1.179652000
C	-0.596040000	-3.137742000	-0.208413000
C	0.378215000	-3.686445000	0.636293000
C	0.761266000	-5.019206000	0.481705000
H	0.461301000	-6.859210000	-0.603455000
H	-1.302912000	-5.896139000	-2.074221000
H	-1.963615000	-3.518301000	-1.828650000
H	0.813292000	-3.084541000	1.426326000
H	1.518945000	-5.434495000	1.140308000
N	-1.058463000	-1.802459000	-0.078422000
H	-2.072084000	-1.650748000	-0.139724000
C	-0.362315000	-0.654319000	0.069183000
C	-1.036292000	0.565824000	0.227539000
C	1.145648000	-0.714644000	0.057487000
H	1.537541000	-0.860205000	1.071774000
H	1.503798000	-1.540580000	-0.561707000
H	1.554832000	0.221151000	-0.326076000
C	-2.496582000	0.620905000	0.281756000
O	-3.258804000	-0.330426000	0.088874000
O	-2.971609000	1.850507000	0.579380000

C	-4.401080000	1.970578000	0.654158000
H	-4.588094000	3.014632000	0.905029000
H	-4.856824000	1.717871000	-0.306632000
H	-4.803294000	1.310415000	1.427090000
Pd	-0.083996000	2.373273000	-0.210253000
C	0.612581000	4.018409000	-1.981000000
O	0.022254000	2.939964000	-2.315607000
C	0.982348000	5.043141000	-3.022771000
H	1.262935000	4.548702000	-3.956205000
H	0.109437000	5.675219000	-3.225159000
H	1.794737000	5.679423000	-2.665125000
O	0.863303000	4.237900000	-0.747899000
C	-0.223673000	1.736491000	1.524481000
O	-0.169447000	1.573243000	2.675286000

B’

C	0.734704000	-5.441424000	0.775230000
C	1.197719000	-4.357159000	0.027055000
C	0.705854000	-3.073788000	0.266067000
C	-0.241779000	-2.874234000	1.276340000
C	-0.717324000	-3.959835000	2.021202000
C	-0.228059000	-5.240518000	1.767116000
H	1.116217000	-6.439502000	0.580794000
H	1.933032000	-4.509164000	-0.757714000
H	1.033065000	-2.237457000	-0.343172000
H	-1.458763000	-3.793136000	2.797510000
H	-0.597156000	-6.080282000	2.348693000
N	-0.802276000	-1.584968000	1.524872000
H	-1.827312000	-1.493690000	1.516663000
C	-0.163674000	-0.438785000	1.772793000
C	-0.905862000	0.766867000	1.927655000
C	1.333928000	-0.463050000	1.959603000
H	1.634958000	-1.395166000	2.446884000
H	1.860963000	-0.398078000	1.003607000
H	1.653579000	0.382017000	2.571365000
C	-2.381551000	0.750319000	1.957816000
O	-3.081193000	-0.245739000	1.775240000
O	-2.903994000	1.954329000	2.235147000
C	-4.339969000	2.031173000	2.272853000
H	-4.562792000	3.069733000	2.514856000
H	-4.760217000	1.762320000	1.300505000
H	-4.738435000	1.361015000	3.038506000
Pd	-0.094239000	2.159412000	0.464988000
C	0.632412000	3.315202000	-1.691813000

O	0.057881000	2.192624000	-1.806210000
C	1.053903000	4.100738000	-2.913424000
H	1.029308000	3.469588000	-3.803978000
H	0.365618000	4.942388000	-3.053305000
H	2.055203000	4.516511000	-2.768492000
O	0.848694000	3.820928000	-0.534828000
C	-0.189654000	2.048352000	2.342297000
O	0.109325000	2.582397000	3.363815000

IN-3’

C	-1.746858000	-5.845548000	4.325505000
C	-1.162045000	-5.617339000	3.078728000
C	-0.829427000	-4.323365000	2.677053000
C	-1.058374000	-3.241988000	3.539897000
C	-1.656109000	-3.471522000	4.788253000
C	-2.000290000	-4.765364000	5.174226000
H	-2.009712000	-6.854417000	4.629923000
H	-0.976757000	-6.447855000	2.403119000
H	-0.416527000	-4.150295000	1.689339000
H	-1.837639000	-2.630943000	5.452457000
H	-2.460597000	-4.929158000	6.144578000
N	-0.789548000	-1.899060000	3.174197000
H	-1.513351000	-1.205181000	3.395291000
C	0.287809000	-1.363299000	2.554961000
C	0.290132000	-0.002959000	2.203294000
C	1.474276000	-2.252584000	2.278263000
H	1.470689000	-3.123494000	2.935442000
H	1.465315000	-2.607087000	1.240042000
H	2.394409000	-1.687404000	2.414646000
C	-0.819336000	0.863190000	2.591574000
O	-1.873817000	0.497789000	3.127093000
O	-0.583982000	2.173940000	2.362071000
C	-1.617751000	3.085794000	2.760601000
H	-1.243587000	4.073912000	2.493749000
H	-2.550840000	2.871542000	2.232093000
H	-1.794193000	3.016806000	3.837113000
Pd	0.886235000	1.694336000	-0.105496000
C	1.721876000	3.934271000	-0.973365000
O	0.830488000	3.365649000	-1.671429000
C	2.328484000	5.249627000	-1.407570000
H	3.344805000	5.072074000	-1.777950000
H	1.733442000	5.703106000	-2.202950000
H	2.404714000	5.930418000	-0.554616000
O	2.149541000	3.398661000	0.109640000

C	1.407226000	0.565266000	1.396978000
O	2.584140000	0.298102000	1.513001000
O	-0.521989000	0.164294000	-0.935374000
H	-0.226068000	0.143381000	-1.860493000
C	-1.927415000	0.498713000	-0.913717000
H	-2.095876000	1.509656000	-1.297804000
H	-2.490385000	-0.233283000	-1.502826000
H	-2.240203000	0.438443000	0.128628000

TS-4’

C	0.020153000	-4.607908000	6.763781000
C	-0.799019000	-4.780323000	5.646210000
C	-0.729111000	-3.889790000	4.574895000
C	0.185865000	-2.829673000	4.610136000
C	1.000515000	-2.648767000	5.735236000
C	0.913979000	-3.535603000	6.807462000
H	-0.042975000	-5.300249000	7.598183000
H	-1.508664000	-5.602024000	5.611119000
H	-1.393093000	-4.002359000	3.723945000
H	1.703004000	-1.820305000	5.757436000
H	1.551259000	-3.390257000	7.675024000
N	0.258981000	-1.862013000	3.568463000
H	0.225230000	-0.873350000	3.848241000
C	0.360308000	-2.040793000	2.240230000
C	0.320076000	-0.916669000	1.374018000
C	0.574515000	-3.440014000	1.727310000
H	0.840978000	-4.114362000	2.541367000
H	-0.322029000	-3.817553000	1.225923000
H	1.363337000	-3.444256000	0.973883000
C	0.195942000	0.424003000	1.940619000
O	0.159705000	0.709965000	3.138358000
O	0.101529000	1.413206000	1.011464000
C	0.076825000	2.767771000	1.505464000
H	0.073690000	3.392273000	0.612861000
H	-0.822468000	2.930499000	2.102915000
H	0.962774000	2.962640000	2.113143000
Pd	0.801974000	0.543503000	-1.123321000
C	2.930497000	1.992462000	-1.133053000
O	2.004916000	2.420150000	-1.872825000
C	4.269380000	2.690887000	-1.066699000
H	4.976936000	2.165217000	-1.718871000
H	4.178323000	3.722934000	-1.411719000
H	4.669787000	2.660140000	-0.049696000
O	2.769821000	0.925369000	-0.428162000

C	0.406184000	-1.123827000	-0.080125000
O	0.319297000	-2.176513000	-0.662830000
O	-0.861764000	0.120999000	-2.246243000
H	0.664154000	-0.209250000	-2.480091000
C	-1.284929000	1.242991000	-3.009333000
H	-1.710071000	2.030718000	-2.369719000
H	-0.476439000	1.685441000	-3.606478000
H	-2.067250000	0.891363000	-3.695945000

C’

C	-1.441932000	-5.440681000	5.806694000
C	-2.112547000	-5.361255000	4.584526000
C	-1.813301000	-4.342177000	3.680232000
C	-0.817850000	-3.407821000	3.991906000
C	-0.151355000	-3.478970000	5.221258000
C	-0.466345000	-4.493206000	6.124699000
H	-1.683578000	-6.231927000	6.510274000
H	-2.884021000	-6.084713000	4.336962000
H	-2.361439000	-4.257432000	2.747369000
H	0.614621000	-2.745530000	5.456922000
H	0.056138000	-4.544625000	7.075541000
N	-0.515535000	-2.315817000	3.126030000
H	-0.544127000	-1.374277000	3.537715000
C	-0.220249000	-2.324244000	1.817677000
C	-0.032354000	-1.093127000	1.133242000
C	-0.052059000	-3.651892000	1.129784000
H	0.013150000	-4.460631000	1.857685000
H	-0.887295000	-3.847977000	0.449609000
H	0.844876000	-3.640527000	0.509252000
C	-0.085683000	0.160533000	1.878401000
O	-0.363005000	0.299549000	3.067422000
O	0.248742000	1.252625000	1.132126000
C	0.076623000	2.563223000	1.724421000
H	0.467354000	3.253383000	0.978696000
H	-0.984342000	2.741165000	1.908488000
H	0.639471000	2.616292000	2.656986000
Pd	0.370522000	0.772777000	-1.046841000
C	2.573953000	2.154831000	-1.313802000
O	1.563913000	2.870538000	-1.500924000
C	3.978405000	2.701053000	-1.449315000
H	4.400566000	2.367694000	-2.404538000
H	3.964547000	3.792575000	-1.431277000
H	4.619549000	2.313330000	-0.652458000
O	2.459950000	0.899834000	-1.014682000

C	0.141595000	-1.095746000	-0.320723000
O	0.146922000	-2.043085000	-1.062988000
O	-1.603988000	0.911023000	-1.049242000
H	0.437058000	0.288431000	-2.479459000
C	-2.369841000	0.347203000	-2.087269000
H	-2.184273000	0.824279000	-3.062205000
H	-2.208181000	-0.736861000	-2.198717000
H	-3.428993000	0.502533000	-1.831728000

TS-5’

C	-4.841080000	-4.318227000	5.076636000
C	-5.283210000	-4.127343000	3.765966000
C	-4.578201000	-3.293899000	2.897500000
C	-3.406262000	-2.664169000	3.335711000
C	-2.967015000	-2.846591000	4.652957000
C	-3.685805000	-3.669859000	5.518806000
H	-5.397338000	-4.962516000	5.751177000
H	-6.189604000	-4.615256000	3.419010000
H	-4.943077000	-3.115081000	1.891093000
H	-2.060685000	-2.349187000	4.986664000
H	-3.337572000	-3.808446000	6.538309000
N	-2.682380000	-1.759363000	2.506027000
H	-2.501625000	-0.824014000	2.889159000
C	-2.219589000	-1.931929000	1.254848000
C	-1.591413000	-0.854290000	0.585261000
C	-2.354846000	-3.296059000	0.629777000
H	-2.647409000	-4.036746000	1.373577000
H	-3.098422000	-3.286315000	-0.173935000
H	-1.412043000	-3.592411000	0.169177000
C	-1.382987000	0.407930000	1.284208000
O	-1.801556000	0.705678000	2.400940000
O	-0.600663000	1.295457000	0.603423000
C	-0.392867000	2.605128000	1.190396000
H	0.304987000	3.096834000	0.515198000
H	-1.346489000	3.134378000	1.239411000
H	0.024601000	2.491547000	2.191778000
Pd	0.059677000	0.568816000	-1.406435000
C	2.487350000	1.660346000	-1.051193000
O	1.750436000	2.600203000	-1.397206000
C	3.967898000	1.852817000	-0.781012000
H	4.541251000	1.445577000	-1.621822000
H	4.197434000	2.915008000	-0.676657000
H	4.270813000	1.306919000	0.117297000
O	2.050454000	0.442810000	-0.911535000

C	-1.203420000	-1.024020000	-0.820756000
O	-1.255580000	-1.999673000	-1.515626000
O	-1.952329000	0.558223000	-1.737460000
H	0.429718000	-0.058992000	-2.738859000
C	-2.436522000	0.214630000	-3.022983000
H	-2.071942000	0.916439000	-3.782662000
H	-2.137096000	-0.805020000	-3.304246000
H	-3.533440000	0.261175000	-2.989729000

IN-4’

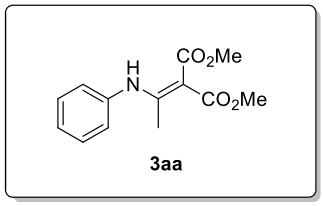
C	-2.868755000	-3.579494000	4.398034000
C	-3.674769000	-3.224694000	3.314554000
C	-3.195846000	-2.358233000	2.331900000
C	-1.890293000	-1.859038000	2.420981000
C	-1.084001000	-2.205184000	3.513176000
C	-1.575259000	-3.061916000	4.497119000
H	-3.248626000	-4.249281000	5.163946000
H	-4.687520000	-3.610029000	3.238201000
H	-3.836642000	-2.052947000	1.511418000
H	-0.074838000	-1.808197000	3.578553000
H	-0.942935000	-3.328256000	5.339156000
N	-1.373043000	-0.924454000	1.478919000
H	-0.940200000	-0.071667000	1.856326000
C	-1.345654000	-0.987478000	0.138576000
C	-0.769679000	0.068849000	-0.617852000
C	-1.866707000	-2.248526000	-0.506772000
H	-1.817168000	-3.078543000	0.200275000
H	-2.903096000	-2.125095000	-0.833214000
H	-1.288053000	-2.496475000	-1.396051000
C	-0.149667000	1.193720000	0.087960000
O	-0.188883000	1.365137000	1.306845000
O	0.495643000	2.113247000	-0.690512000
C	0.953208000	3.315308000	-0.005070000
H	1.533799000	3.851217000	-0.752793000
H	0.082896000	3.880140000	0.336008000
H	1.575107000	3.041030000	0.847590000
Pd	1.978888000	1.059857000	-2.199792000
C	4.146683000	2.740773000	-1.623937000
O	3.404858000	3.637671000	-2.031091000
C	5.579654000	3.018195000	-1.185711000
H	6.271486000	2.620124000	-1.936891000
H	5.738789000	4.093835000	-1.086782000
H	5.800190000	2.513659000	-0.240029000
O	3.822983000	1.474672000	-1.522154000

C	-0.982907000	0.018465000	-2.073083000
O	-1.913739000	-0.524410000	-2.632695000
O	-0.025239000	0.655884000	-2.856534000
H	2.703164000	0.236337000	-3.258213000
C	-0.317290000	0.709732000	-4.279867000
H	0.397142000	1.422386000	-4.686390000
H	-0.178916000	-0.279827000	-4.719178000
H	-1.344764000	1.043508000	-4.424925000

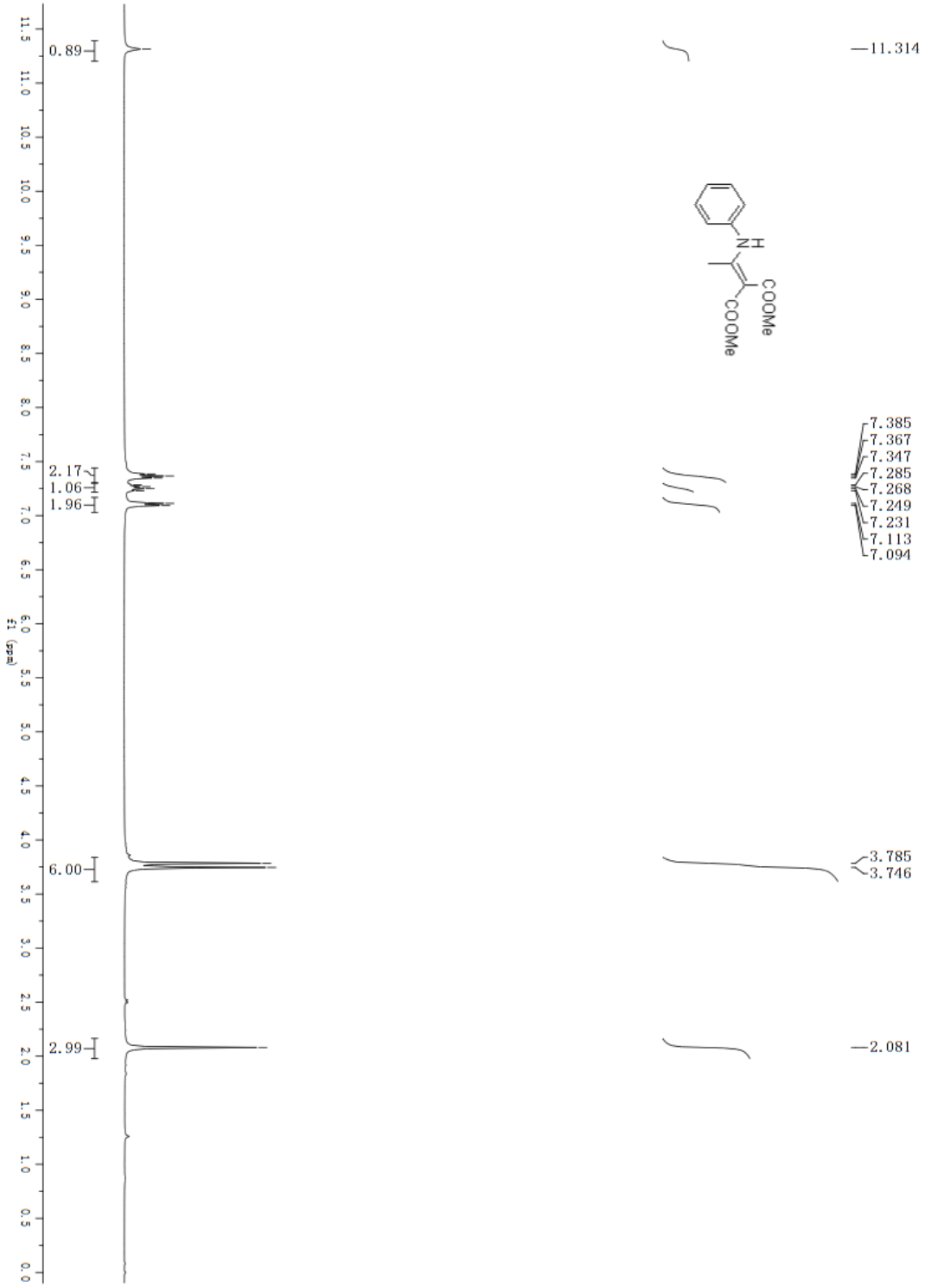
3

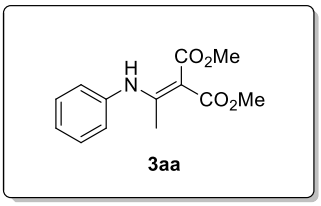
O	-0.695491000	-2.017188000	-3.533945000
C	0.198847000	-2.893950000	-4.229380000
H	0.766184000	-3.509478000	-3.525438000
H	-0.436921000	-3.519603000	-4.857474000
H	0.902572000	-2.325053000	-4.843839000
C	-0.105451000	-1.173568000	-2.653102000
O	1.108122000	-1.105480000	-2.541473000
C	-1.084912000	-0.336790000	-1.918993000
C	-0.753810000	0.992066000	-1.626178000
C	0.556369000	1.606215000	-2.056030000
H	0.468275000	2.692073000	-2.122112000
H	1.358004000	1.357938000	-1.353731000
H	0.867906000	1.206035000	-3.020266000
C	-2.360227000	-0.896072000	-1.464415000
O	-2.423095000	-2.242396000	-1.515406000
O	-3.304416000	-0.240544000	-1.008693000
C	-3.654168000	-2.822091000	-1.065623000
H	-3.529723000	-3.897716000	-1.196630000
H	-3.836152000	-2.582331000	-0.014291000
H	-4.495933000	-2.458771000	-1.661493000
C	-1.499881000	3.103956000	-0.489291000
C	-0.366017000	3.523049000	0.221547000
C	-2.577913000	3.988351000	-0.646019000
C	-0.303276000	4.819319000	0.732137000
H	0.450261000	2.830289000	0.394263000
C	-2.513583000	5.275403000	-0.117339000
H	-3.458275000	3.659311000	-1.191553000
C	-1.372635000	5.700895000	0.566443000
H	0.582041000	5.132813000	1.278640000
H	-3.355704000	5.949542000	-0.247552000
H	-1.320930000	6.706667000	0.973247000
N	-1.647762000	1.789561000	-0.991830000
H	-2.561578000	1.340841000	-0.859427000

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

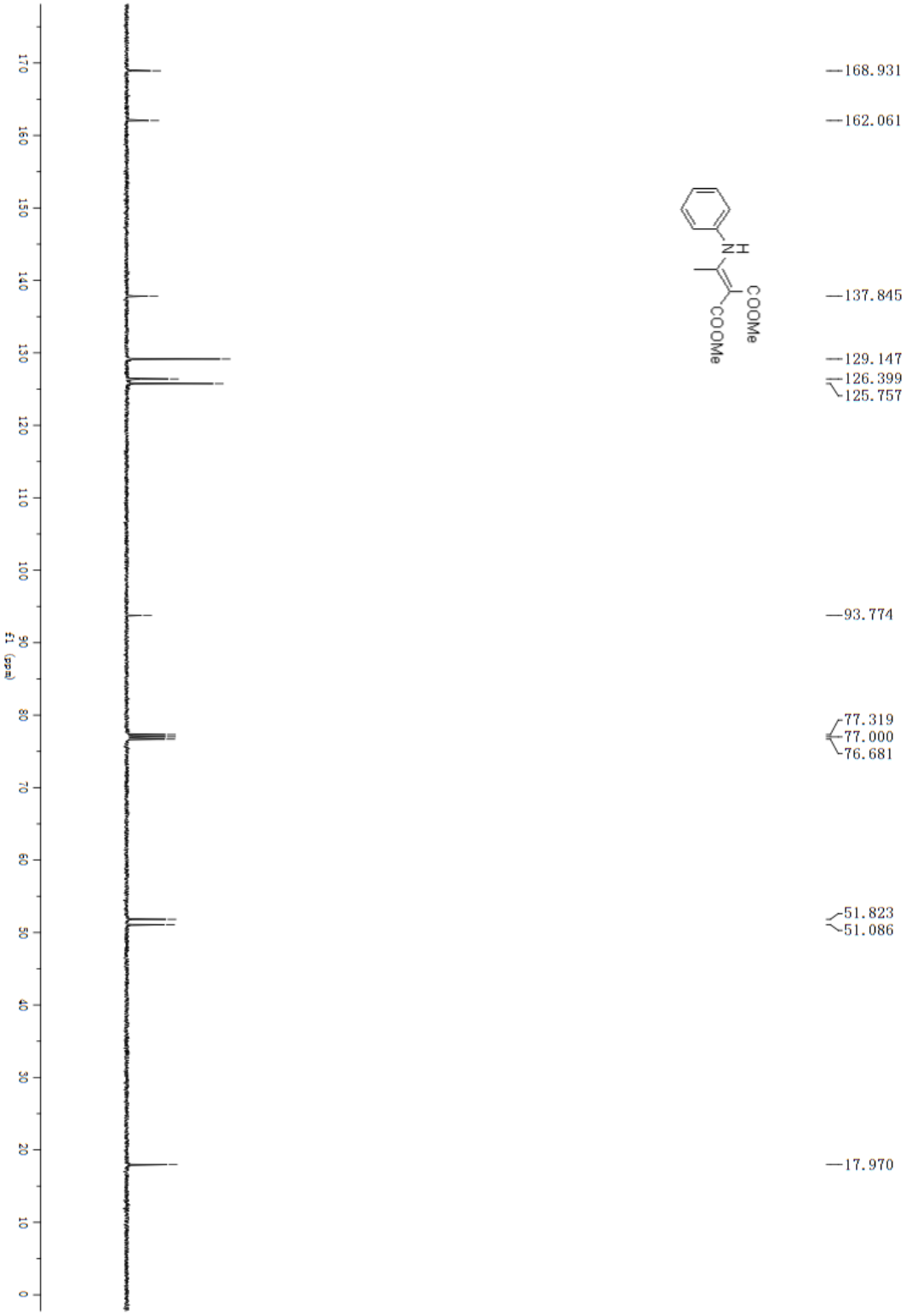


3aa




CO2Me
H
N
CO2Me

3aa


168.931
162.061
137.845
129.147
126.399
125.757
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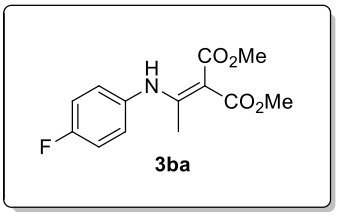
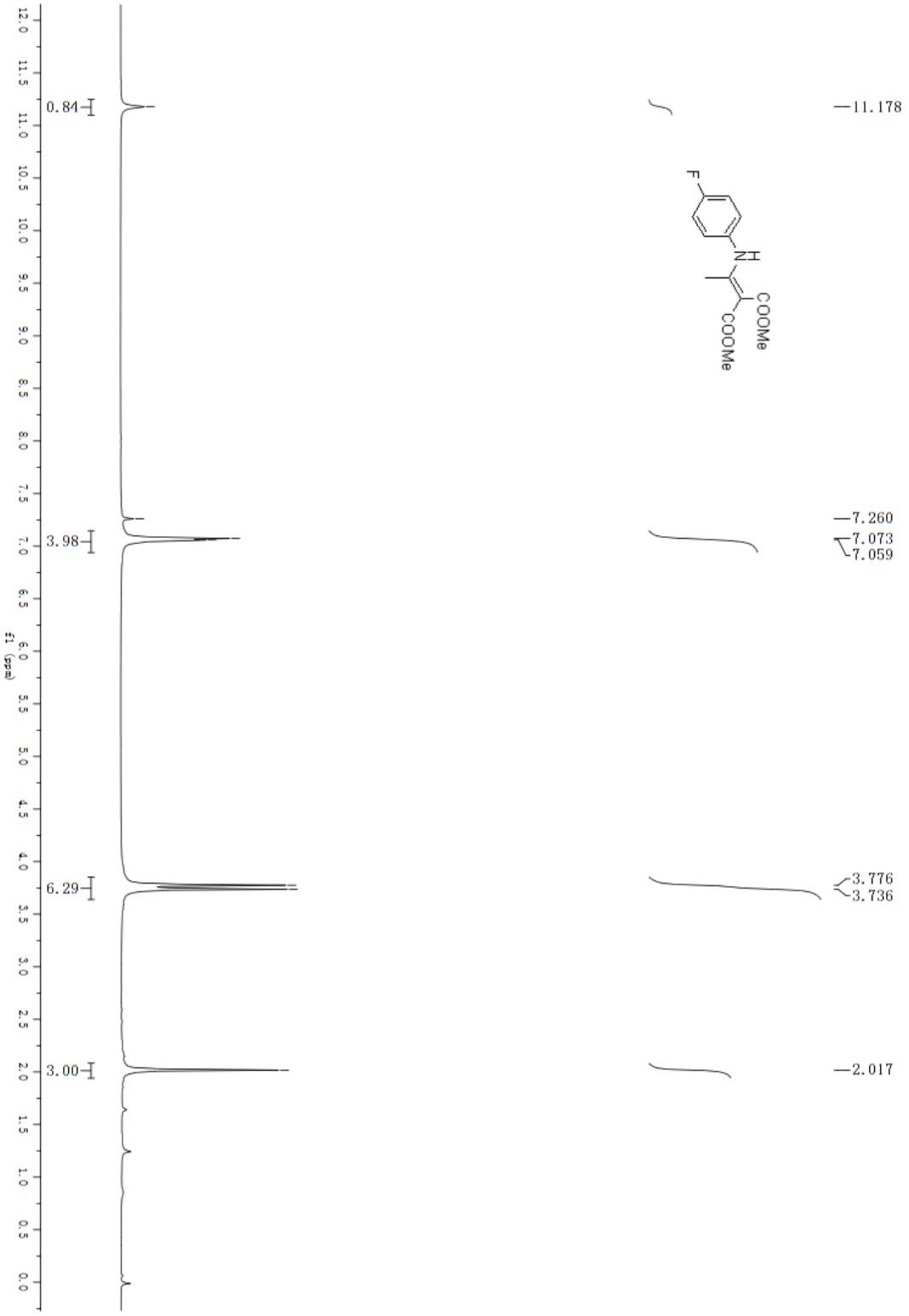
77.000
76.681
51.823
51.086
17.970
COOMe
COOMe
H
N
f1 (ppm)


CO2Me
H
N
CO2Me
F

3ba


0.84
3.98
6.29
3.00
f1 (ppm)
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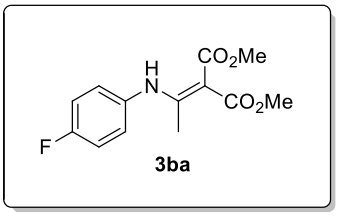
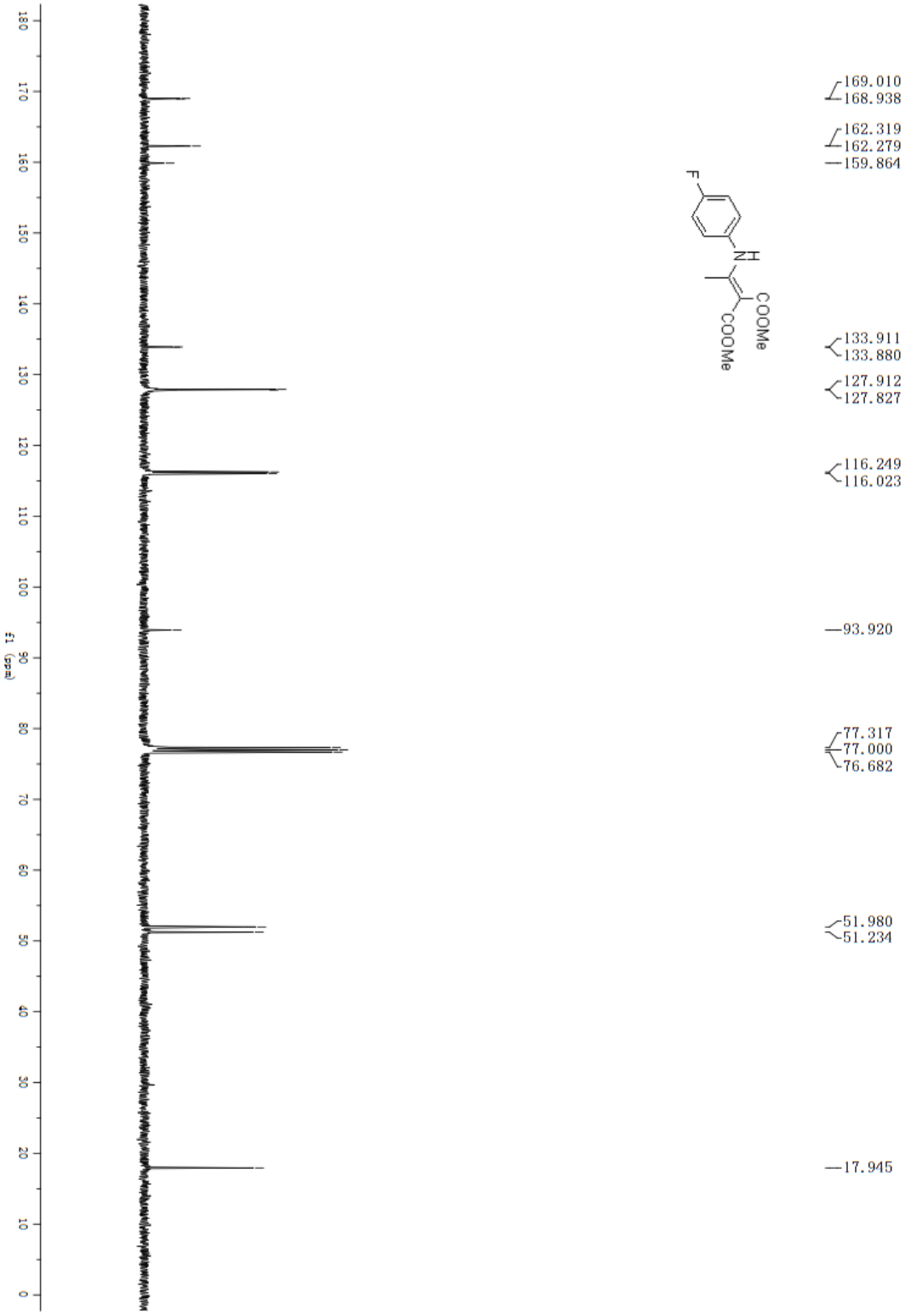
7.073
7.059
3.776
3.736
2.017
F
NH
COOMe
COOMe


CO2Me
H
N
CO2Me
F

3ba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162.319
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159.864
133.911
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127.912
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116.249
116.023
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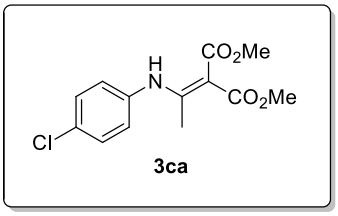
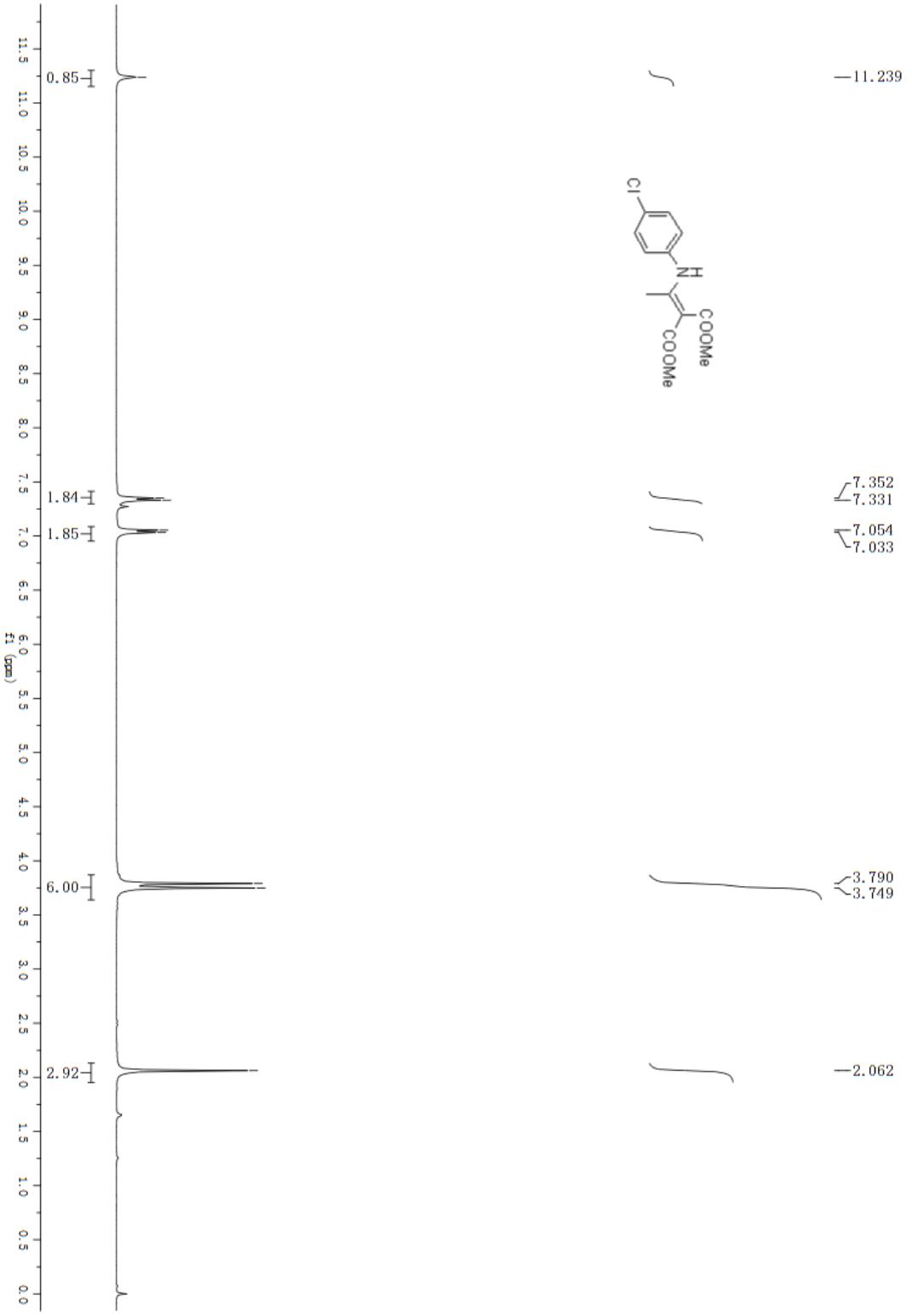
77.317
77.000
76.682
51.980
51.234
17.945
F
NH
COOMe
COOMe
f1 (ppm)


H
N
CO2Me
CO2Me
Cl

3ca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1.85
6.00
2.92
f1 (ppm)
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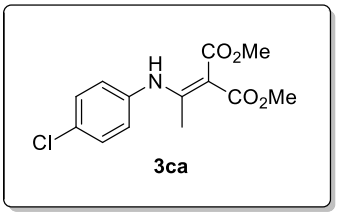
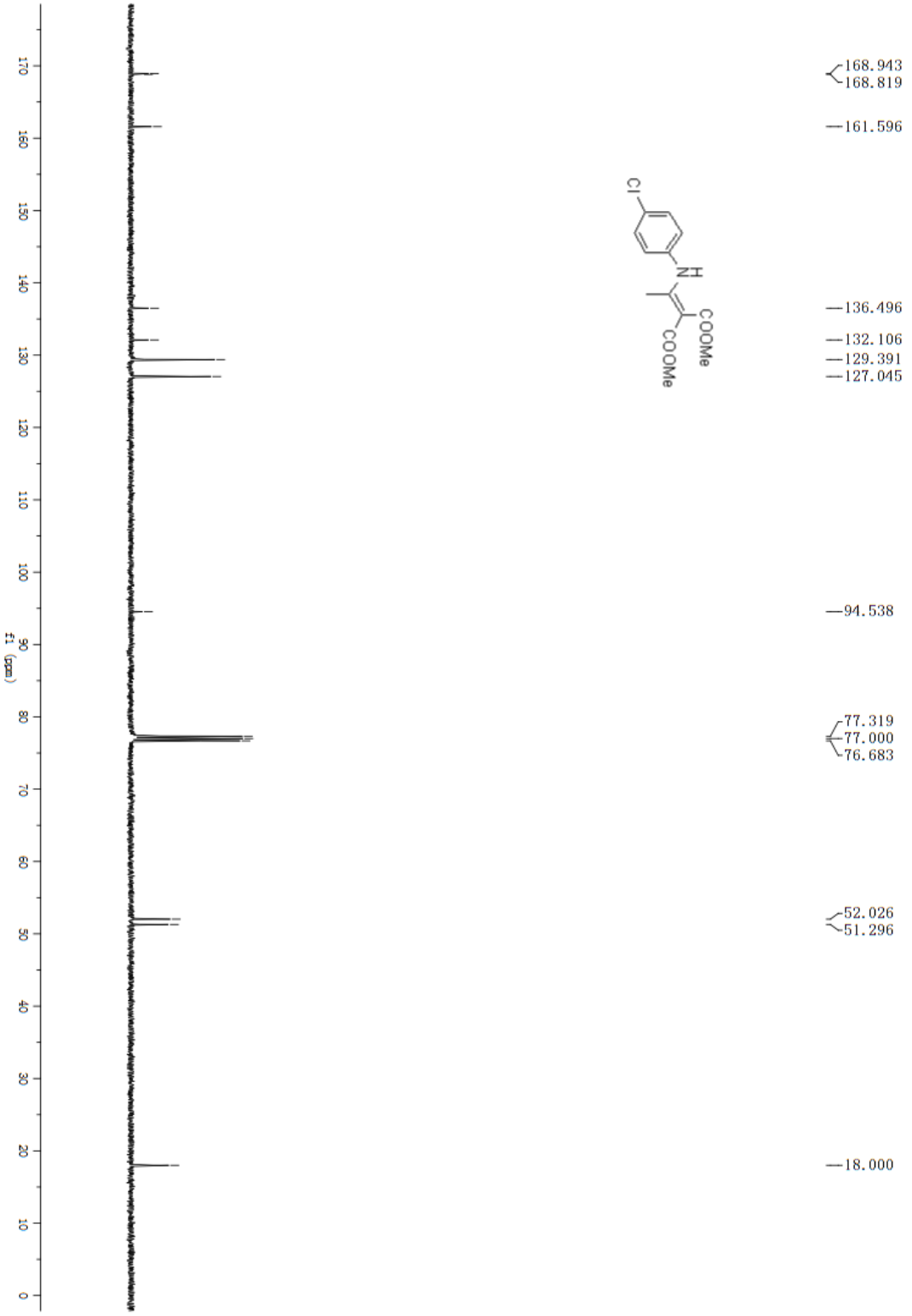
3.749
2.062
Cl
H
N
COOMe
COOMe


CO2Me
H
N
CO2Me
Cl

3ca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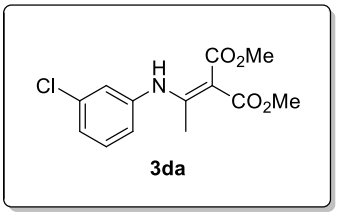
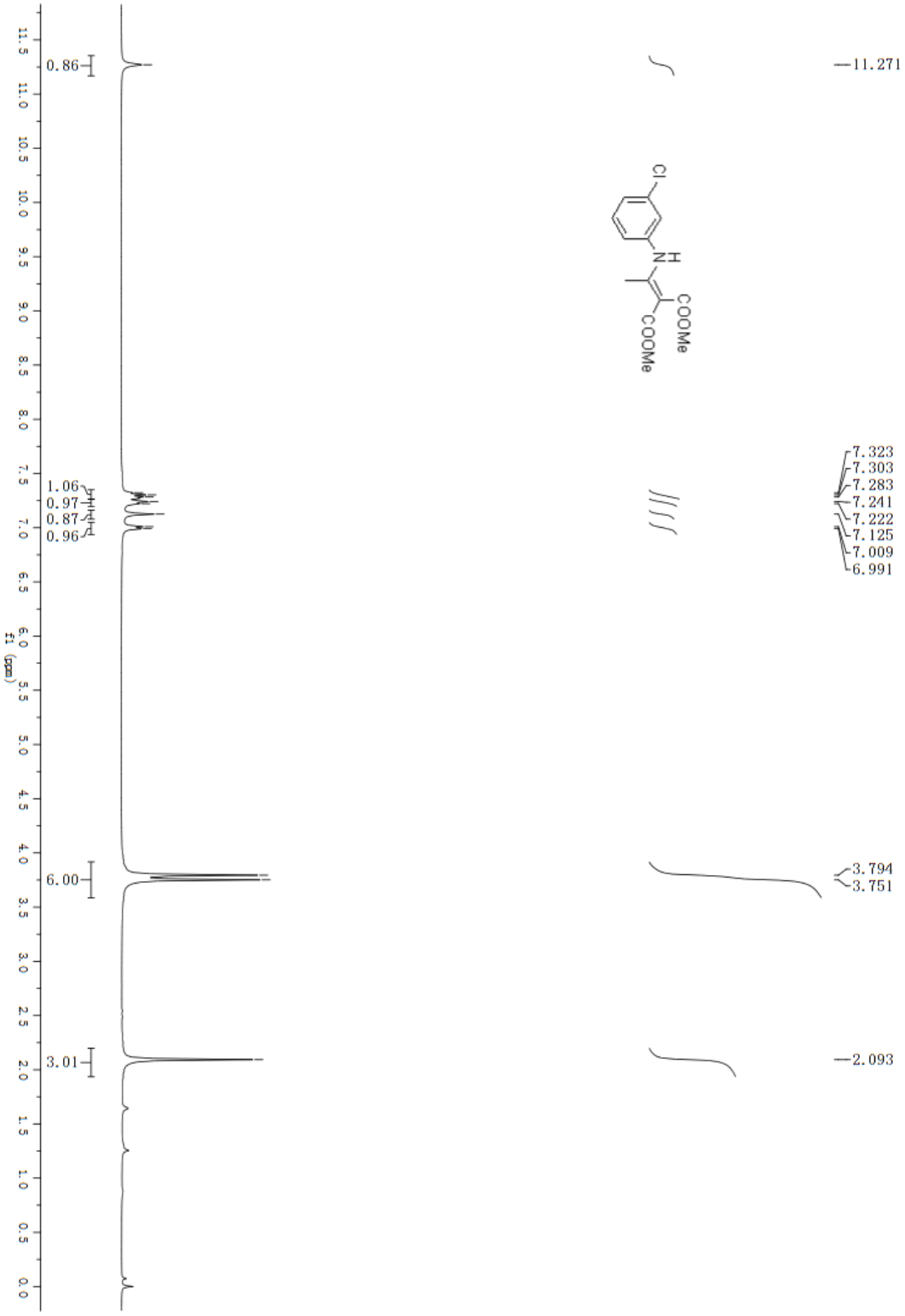
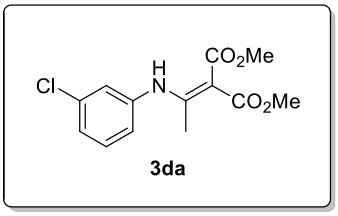
77.000
76.683
52.026
51.296
18.000
Cl
COOMe
COOMe
f1 (ppm)

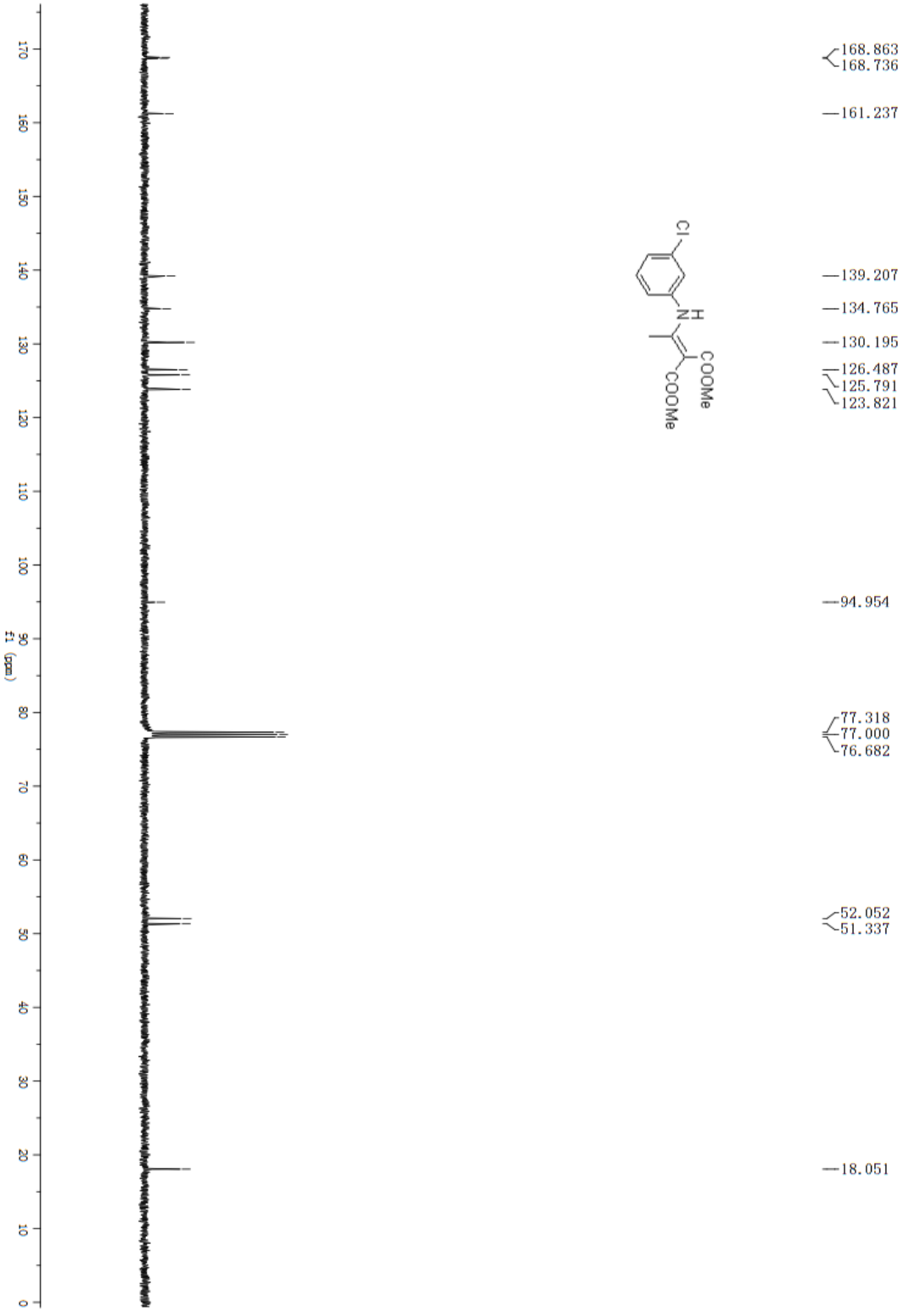

Cl
H
N
CO2Me
CO2Me

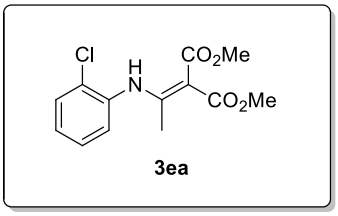
3da


0.86
1.06
0.97
0.87
0.96
6.00
3.01
f1 (ppm)
11.271
7.323
7.303
7.283
7.241
7.222
7.125
7.009
6.991
3.794
3.751
2.093
Cl
H
N
COOMe
COOMe

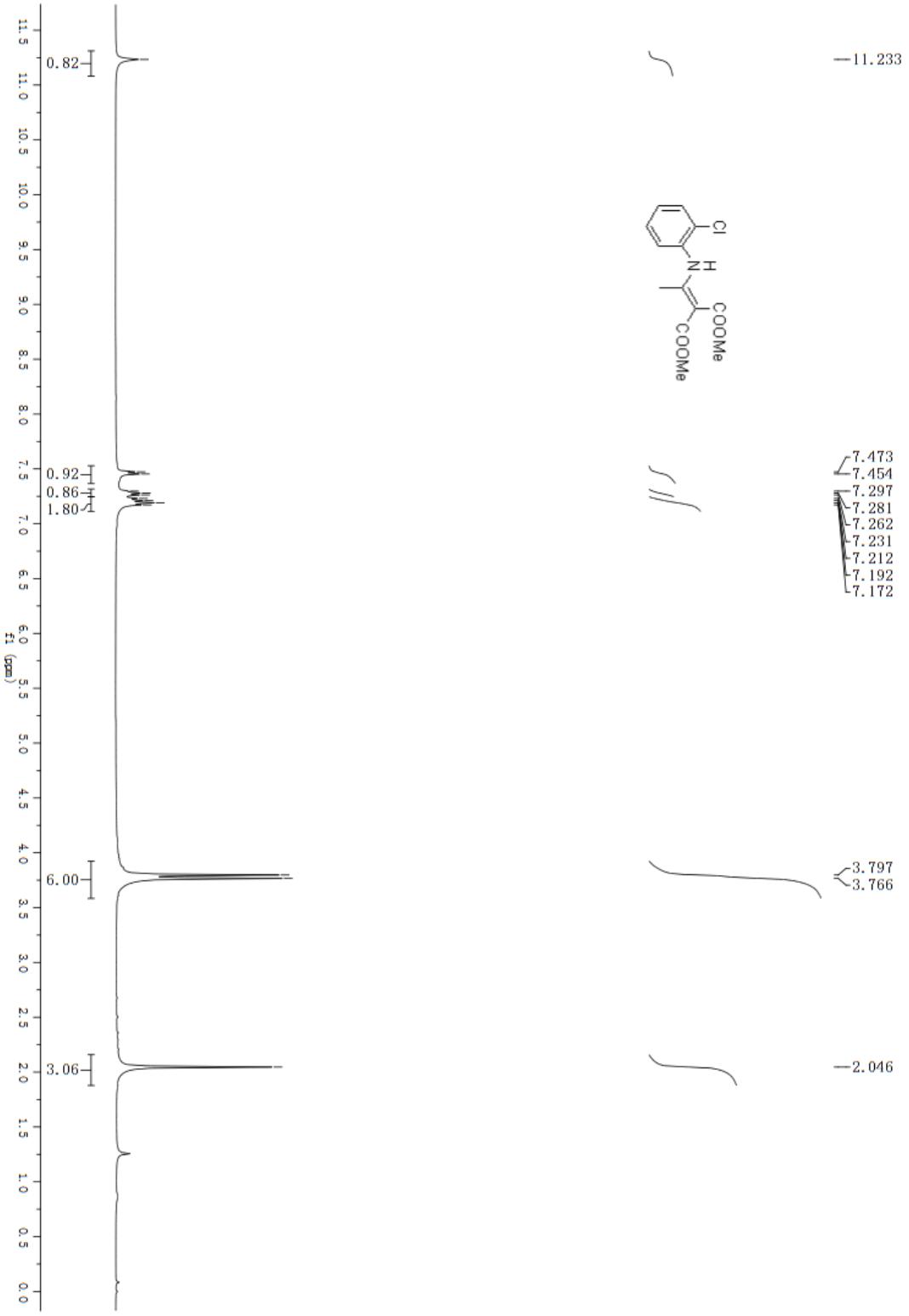

Cl
H
N
CO2Me
CO2Me

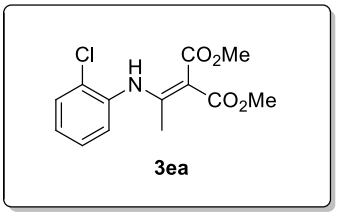
3da


f1 (ppm)
168.863
168.736
161.237
139.207
134.765
130.195
126.487
125.791
123.821
94.954
77.318
77.000
76.682
52.052
51.337
18.051
Cl
H
N
COOMe
COOMe

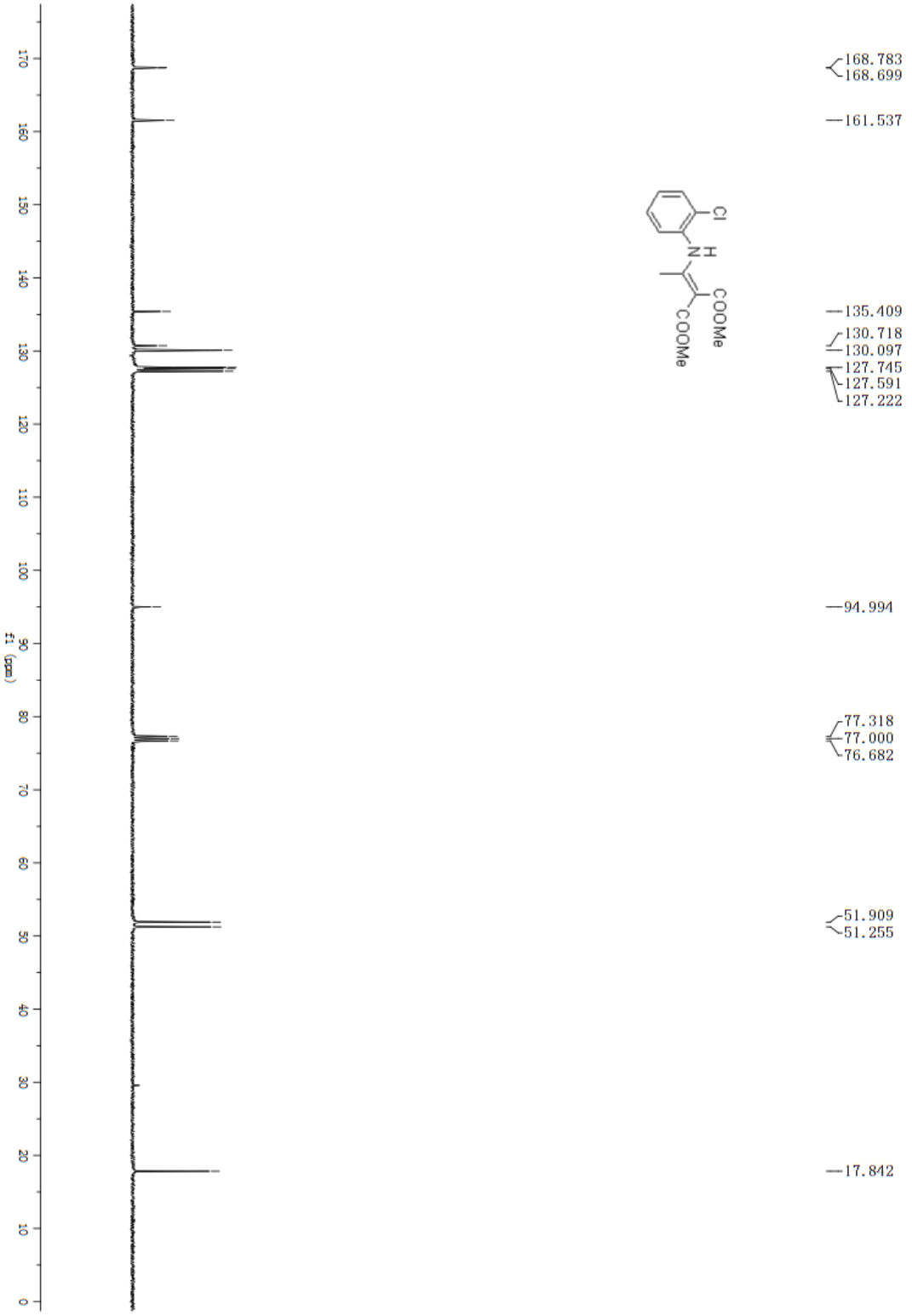

Cl
H
N
CO2Me
CO2Me

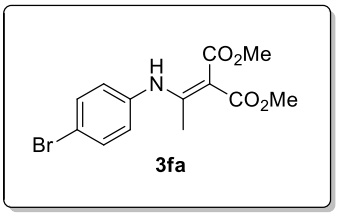
3ea


0.82
0.92
0.86
1.80
6.00
3.06
f1 (ppm)
11.233
7.473
7.454
7.297
7.281
7.262
7.231
7.212
7.192
7.172
3.797
3.766
2.046
Cl
H
N
COOMe
COOMe

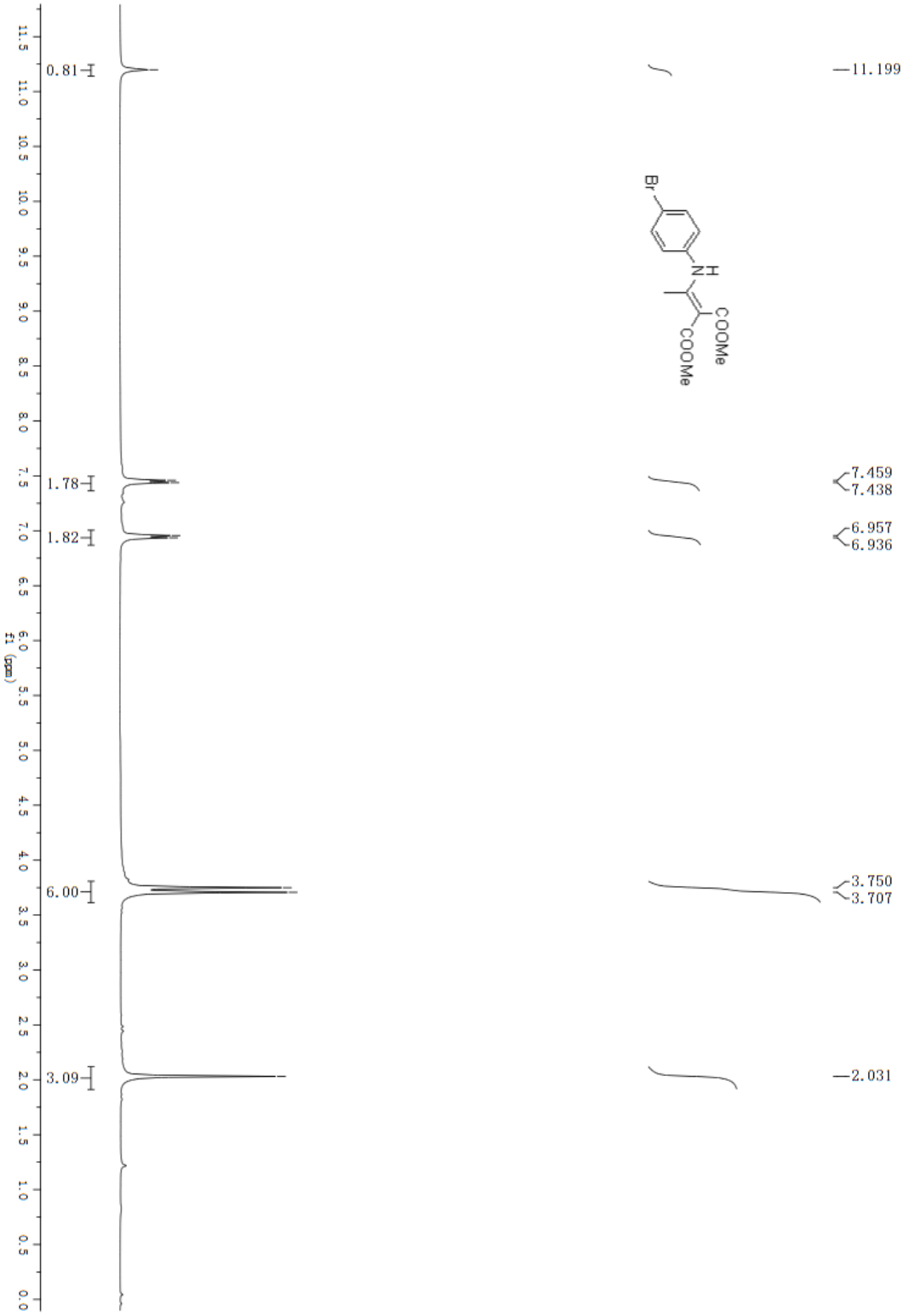

Cl
H
N
CO2Me
CO2Me

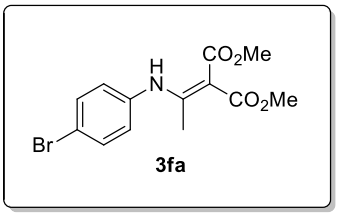
3ea


168.783
168.699
161.537
135.409
130.718
130.097
127.745
127.591
127.222
94.994
77.318
77.000
76.682
51.909
51.255
17.842
f1 (ppm)
Cl
H
N
COOMe
COOMe

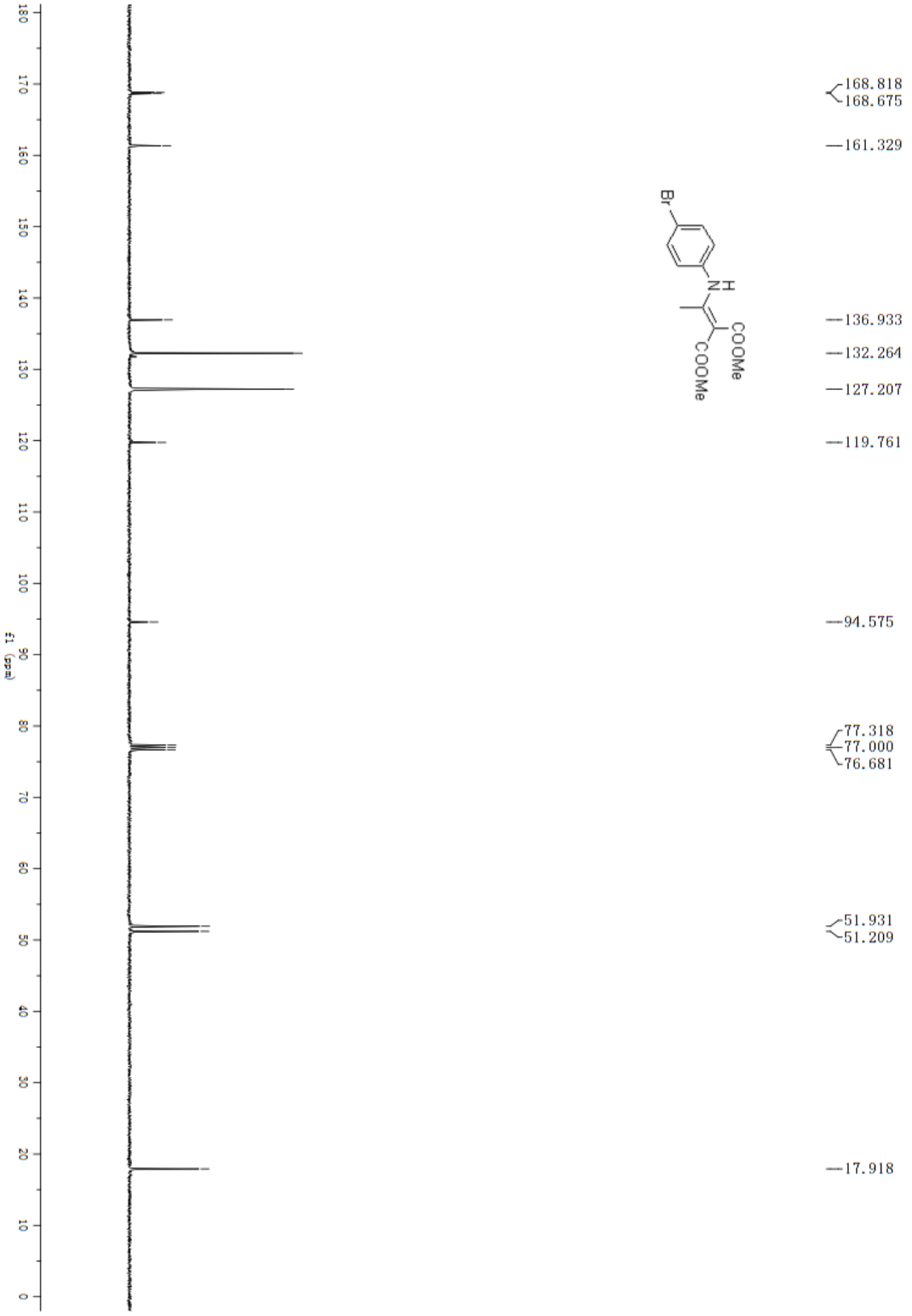

CO2Me
H
N
CO2Me
Br

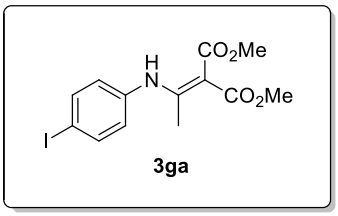
3fa


11.199
Br
N
H
COOMe
COOMe
7.459
7.438
6.957
6.936
3.750
3.707
2.031
0.81
1.78
1.82
6.00
3.09
f1 (ppm)

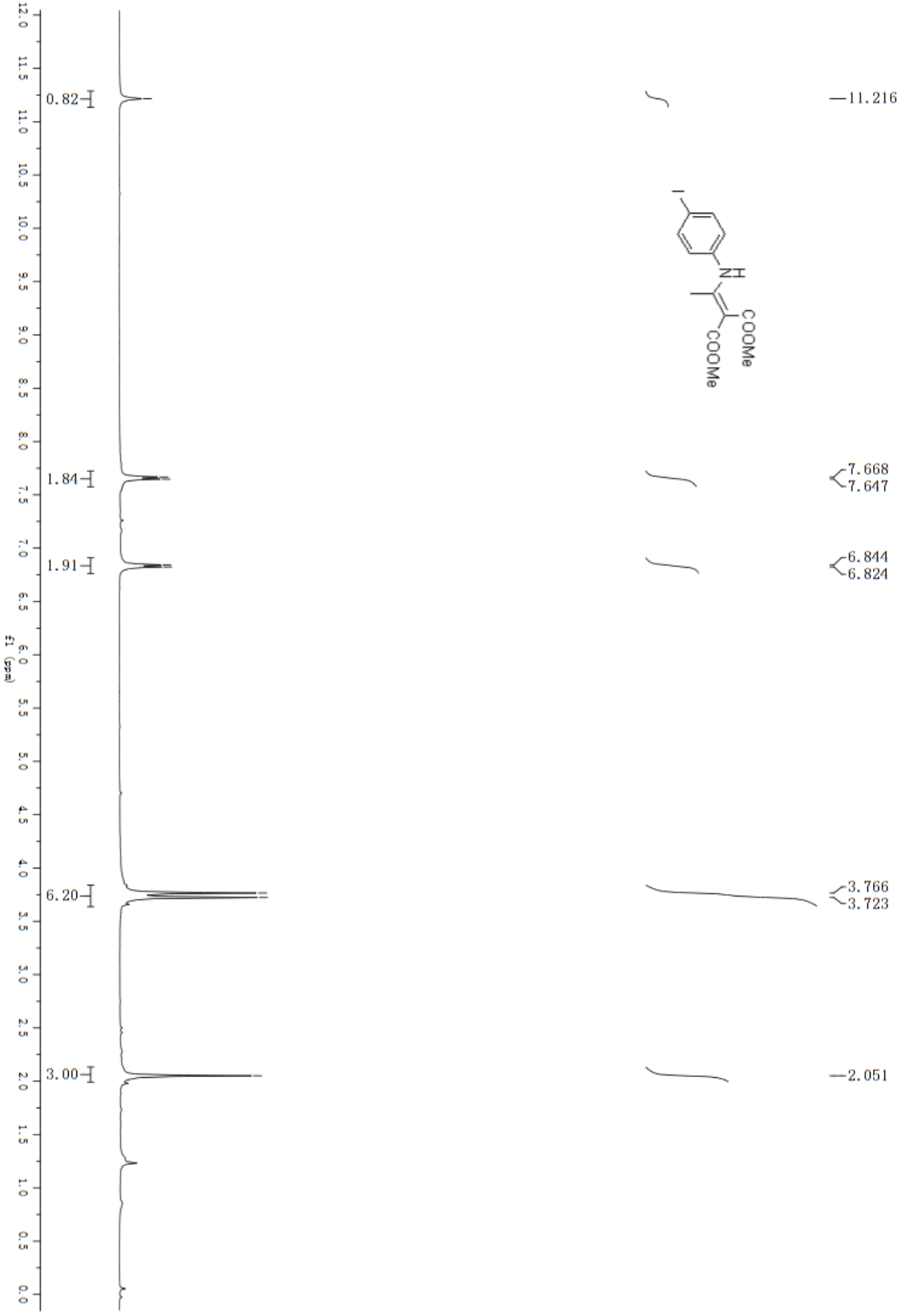

CO2Me
H
N
CO2Me
Br

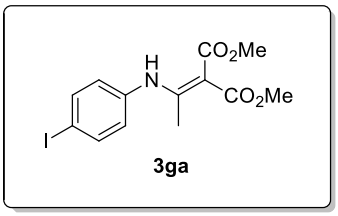
3fa


168.818
168.675
161.329
136.933
132.264
127.207
119.761
94.575
77.318
77.000
76.681
51.931
51.209
17.918
Br
NH
COOMe
COOMe
f1 (ppm)

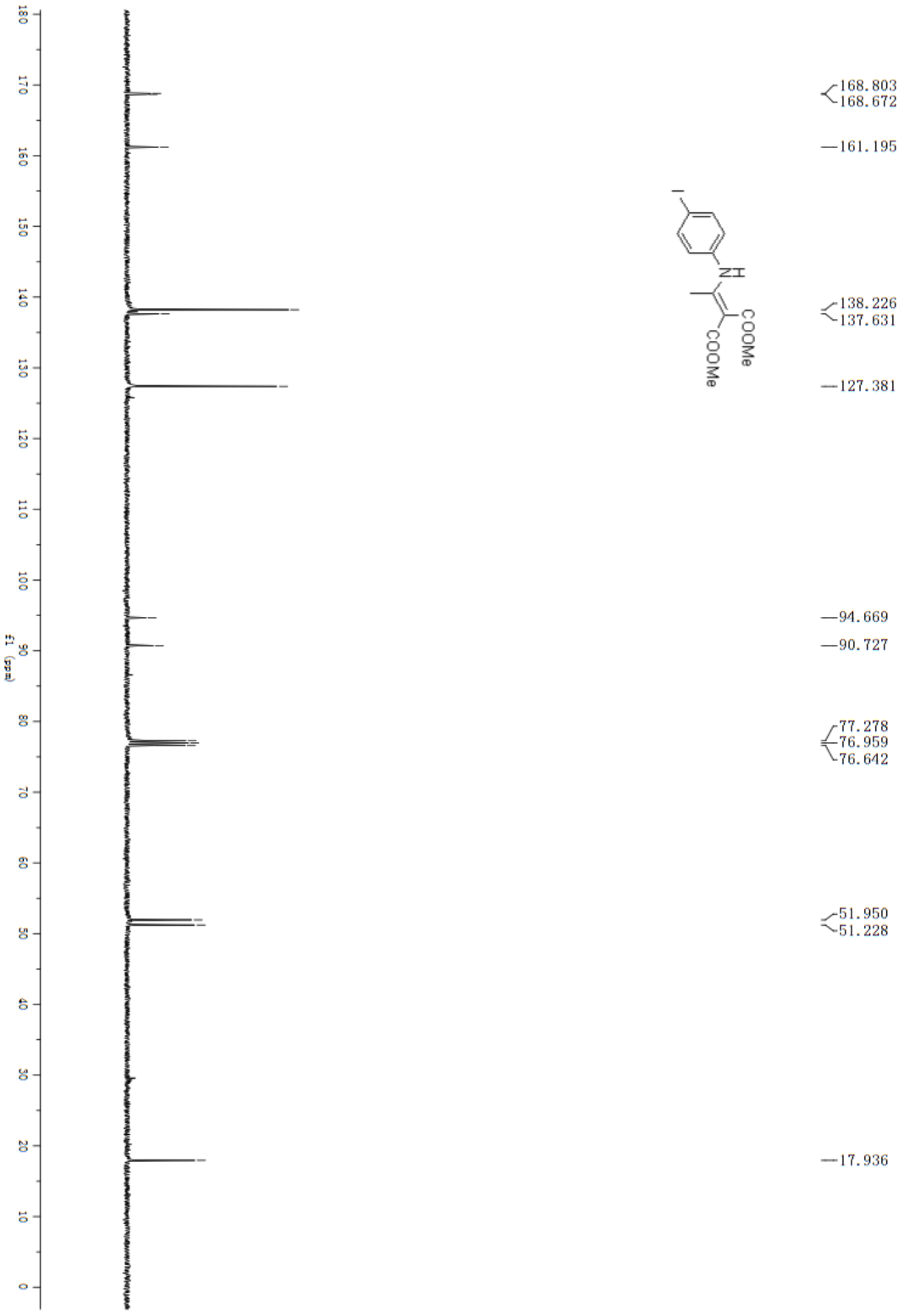

CO2Me
H
N
CO2Me
I

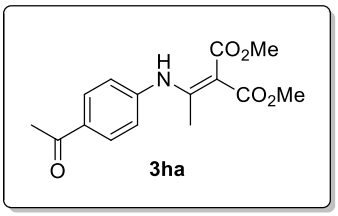
3ga


0.82
1.84
1.91
6.20
3.00
f1 (ppm)
11.216
7.668
7.647
6.844
6.824
3.766
3.723
2.051
I
H
N
COOMe
COOMe

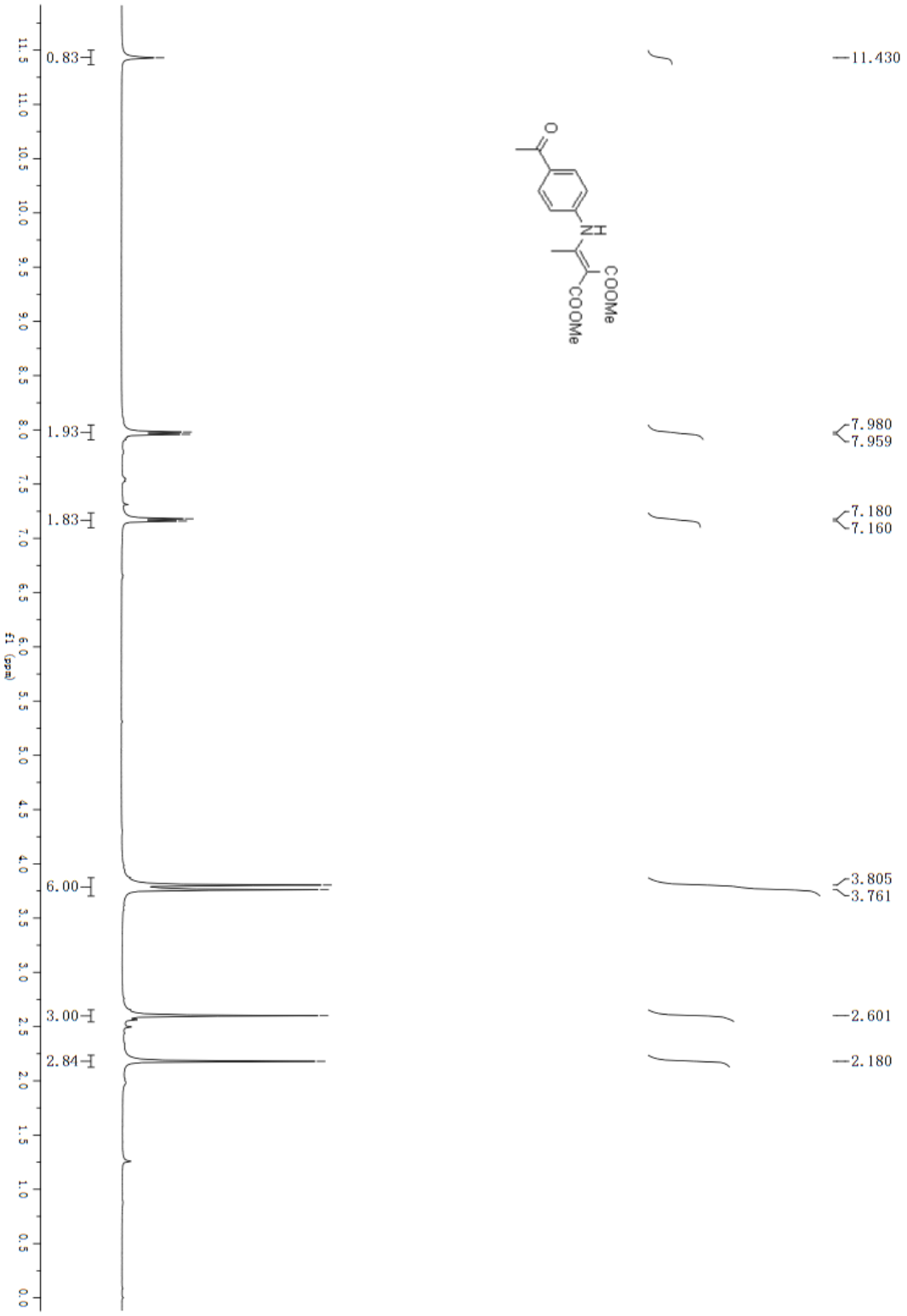

H
N
CO2Me
CO2Me
I

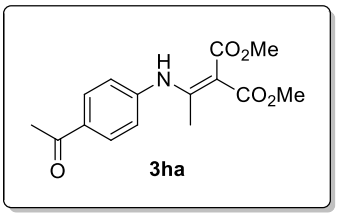
3ga

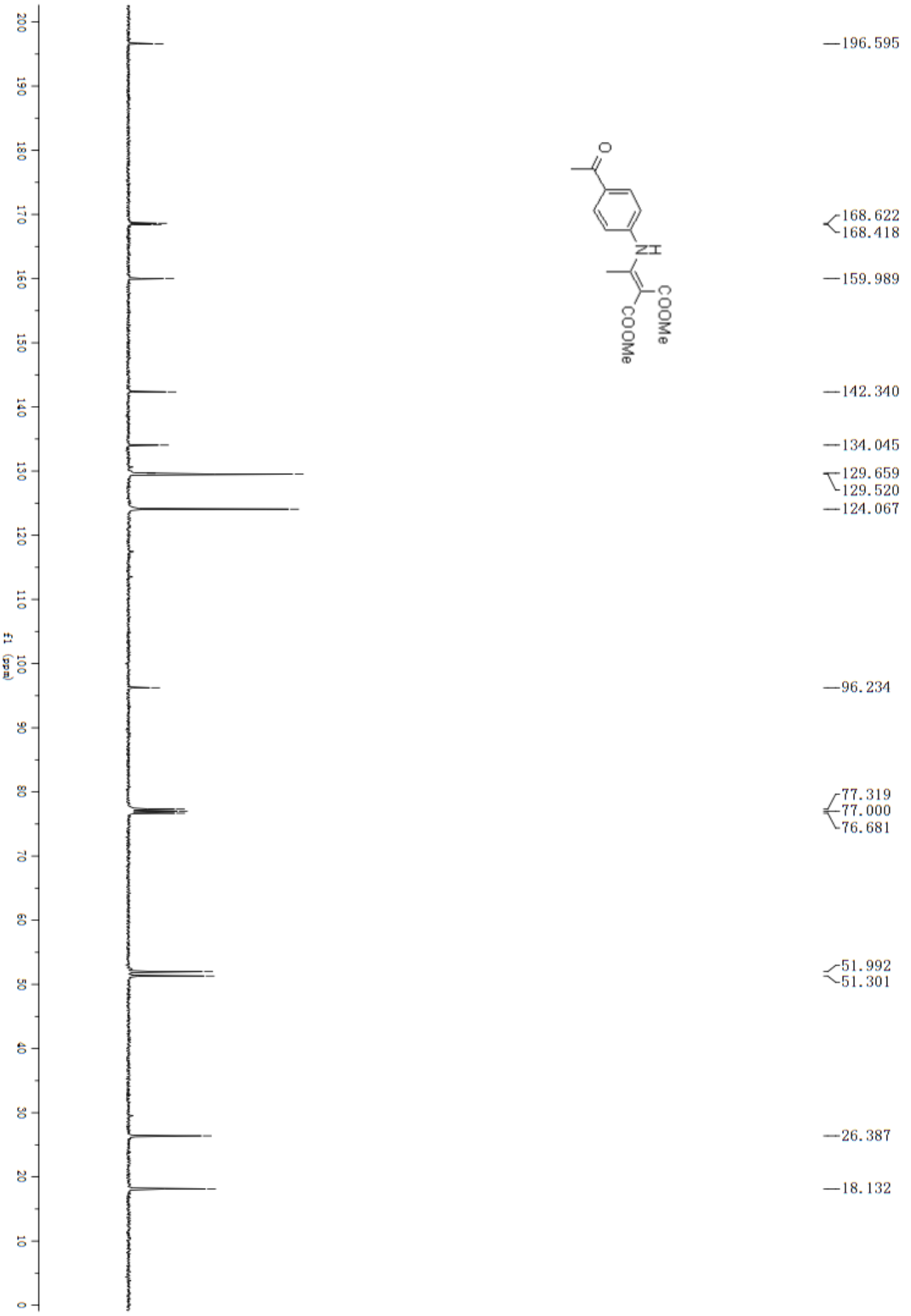

168.803
168.672
161.195
138.226
137.631
127.381
94.669
90.727
77.278
76.959
76.642
51.950
51.228
17.936
COOMe
COOMe
f1 (ppm)

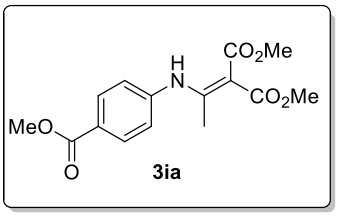

CO2Me
H
N
CO2Me
O

3ha

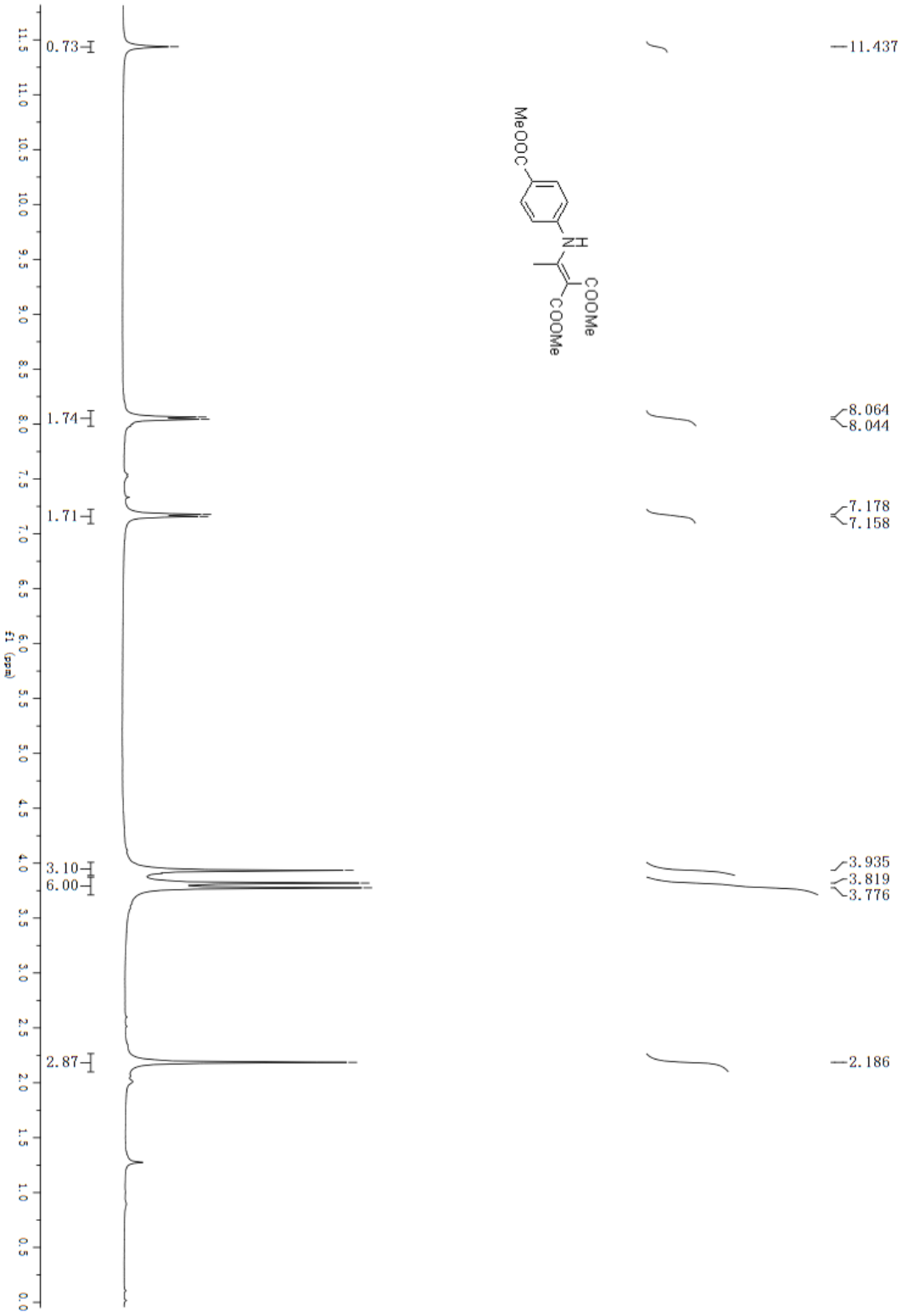

0.83
1.93
1.83
6.00
3.00
2.84
f1 (ppm)
11.430
7.980
7.959
7.180
7.160
3.805
3.761
2.601
2.180
COOMe
COOMe

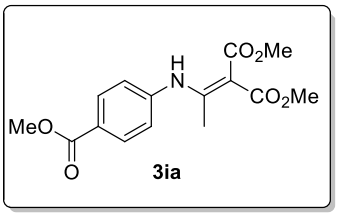

H
N
CO2Me
CO2Me
O
3ha

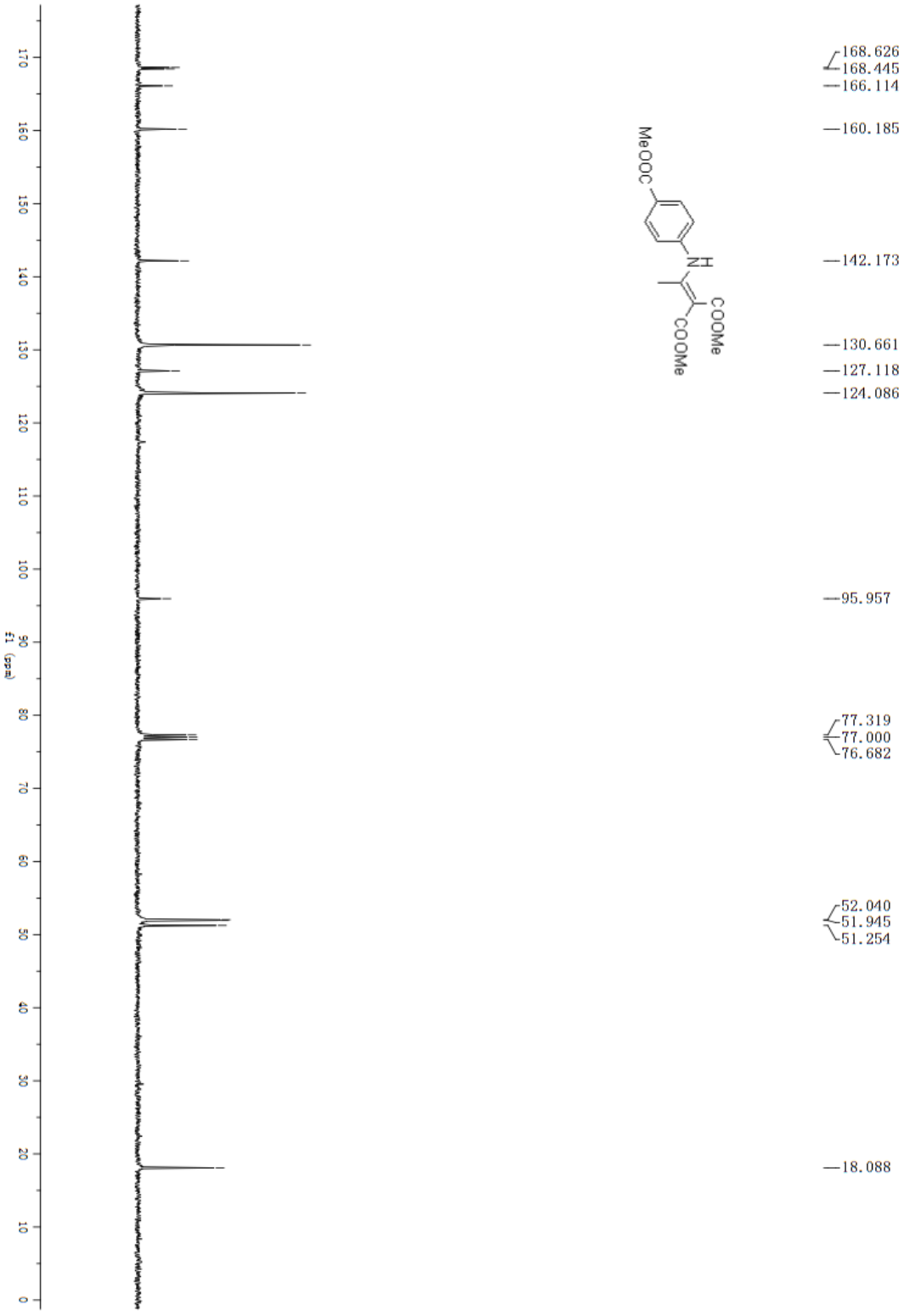

196.595
168.622
168.418
159.989
142.340
134.045
129.659
129.520
124.067
96.234
77.319
77.000
76.681
51.992
51.301
26.387
18.132
O
H
N
COOMe
COOMe
f1 (ppm)

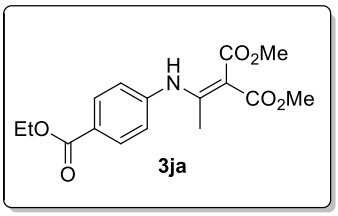

CO2Me
H
N
CO2Me
MeO
O

3ia

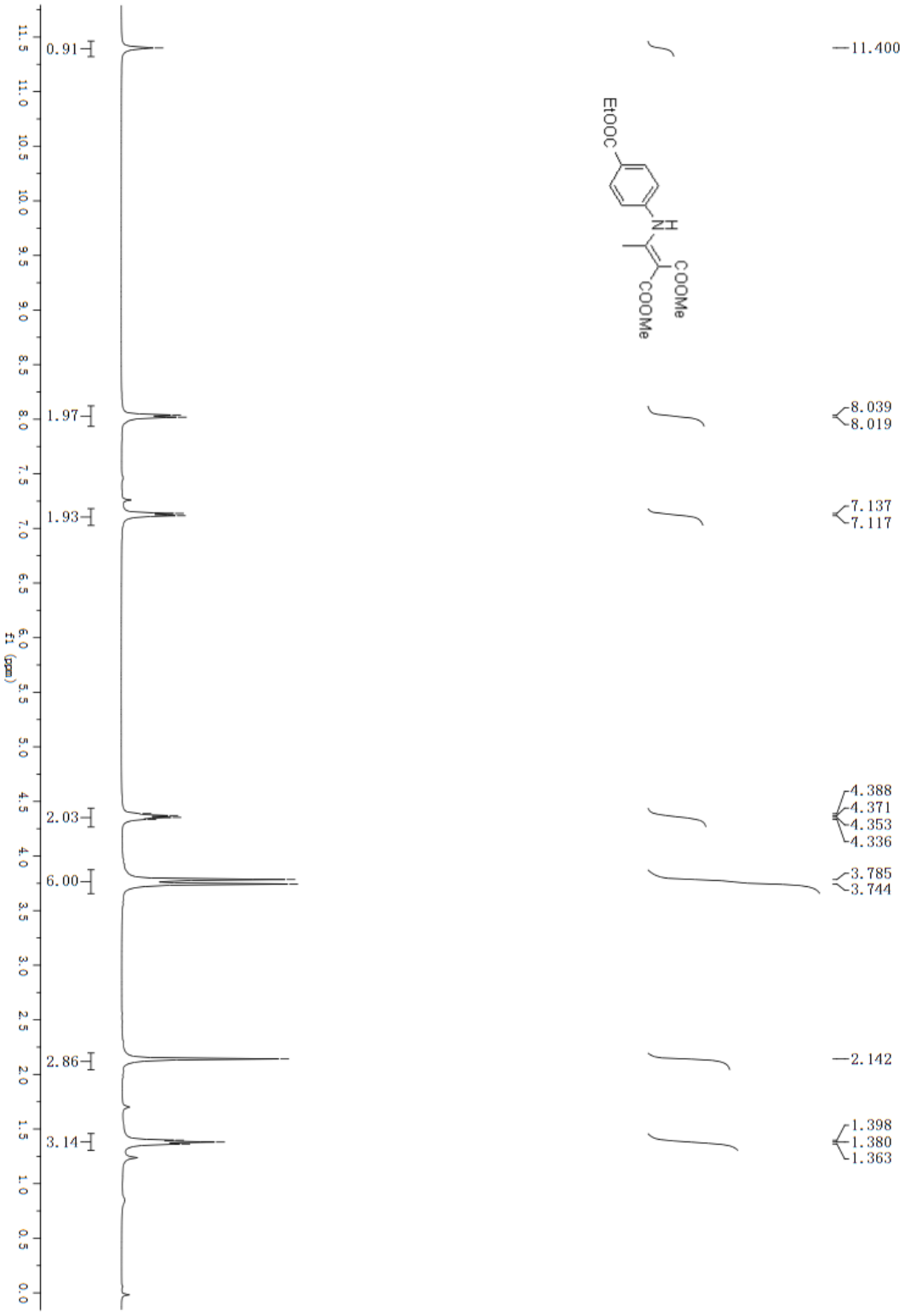

0.73
1.74
1.71
3.10
6.00
2.87
f1 (ppm)
MeOOC
COOMe
COOMe
11.437
8.064
8.044
7.178
7.158
3.935
3.819
3.776
2.186

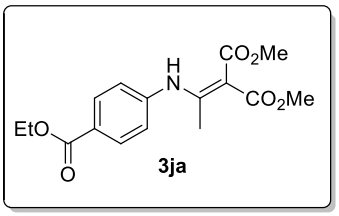

H
N
CO2Me
CO2Me
MeO
O
3ia


168.626
168.445
166.114
160.185
142.173
130.661
127.118
124.086
95.957
77.319
77.000
76.682
52.040
51.945
51.254
18.088
MeOOC
COOMe
COOMe
f1 (ppm)

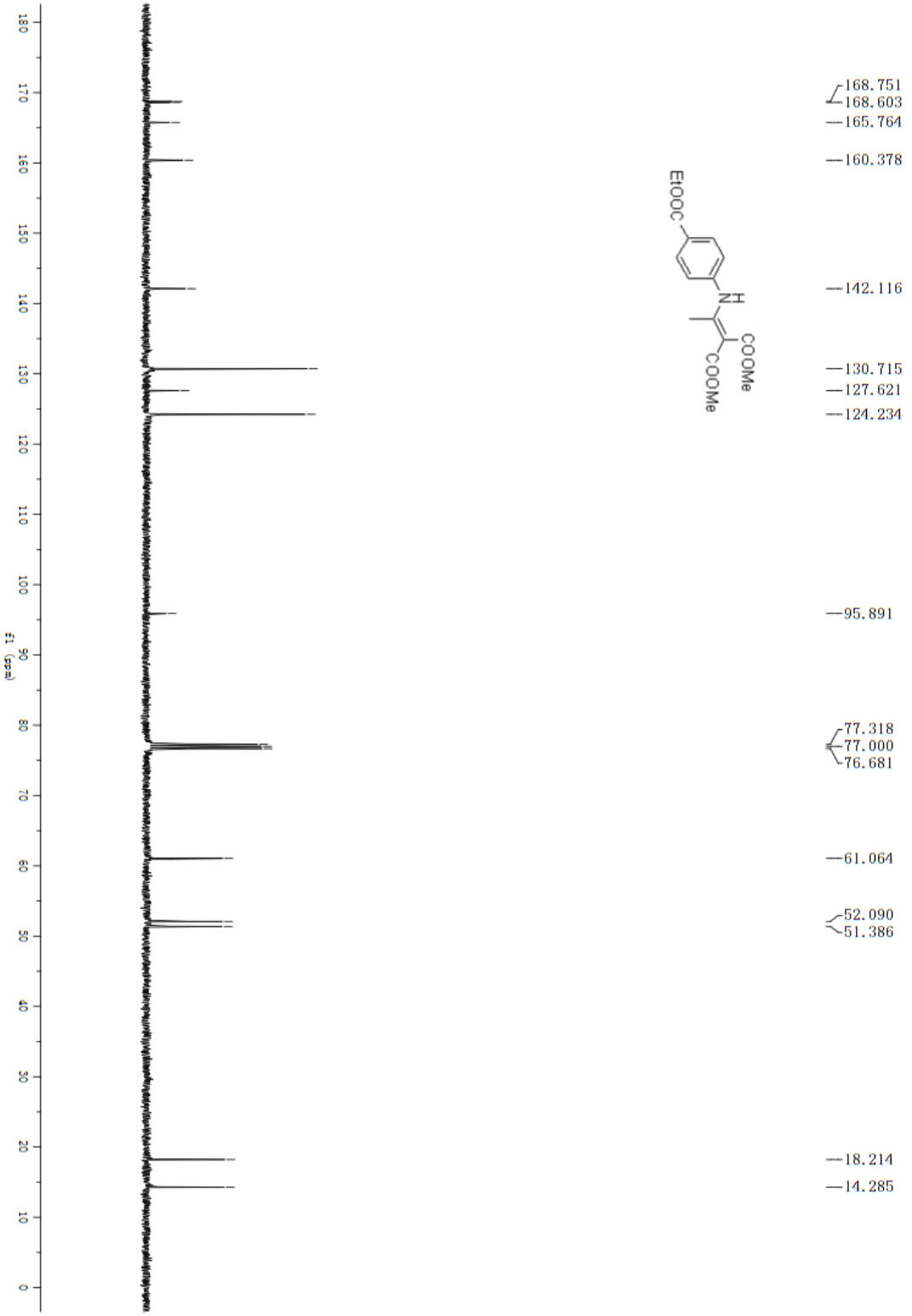

CO2Me
H
N
CO2Me
EtO
O

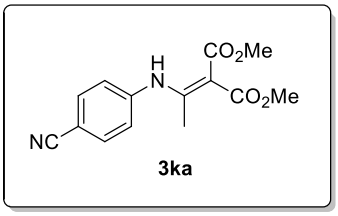
3ja


0.91
1.97
1.93
2.03
6.00
2.86
3.14
f1 (ppm)
EtOOC
COOMe
COOMe
11.400
8.039
8.019
7.137
7.117
4.388
4.371
4.353
4.336
3.785
3.744
2.142
1.398
1.380
1.363

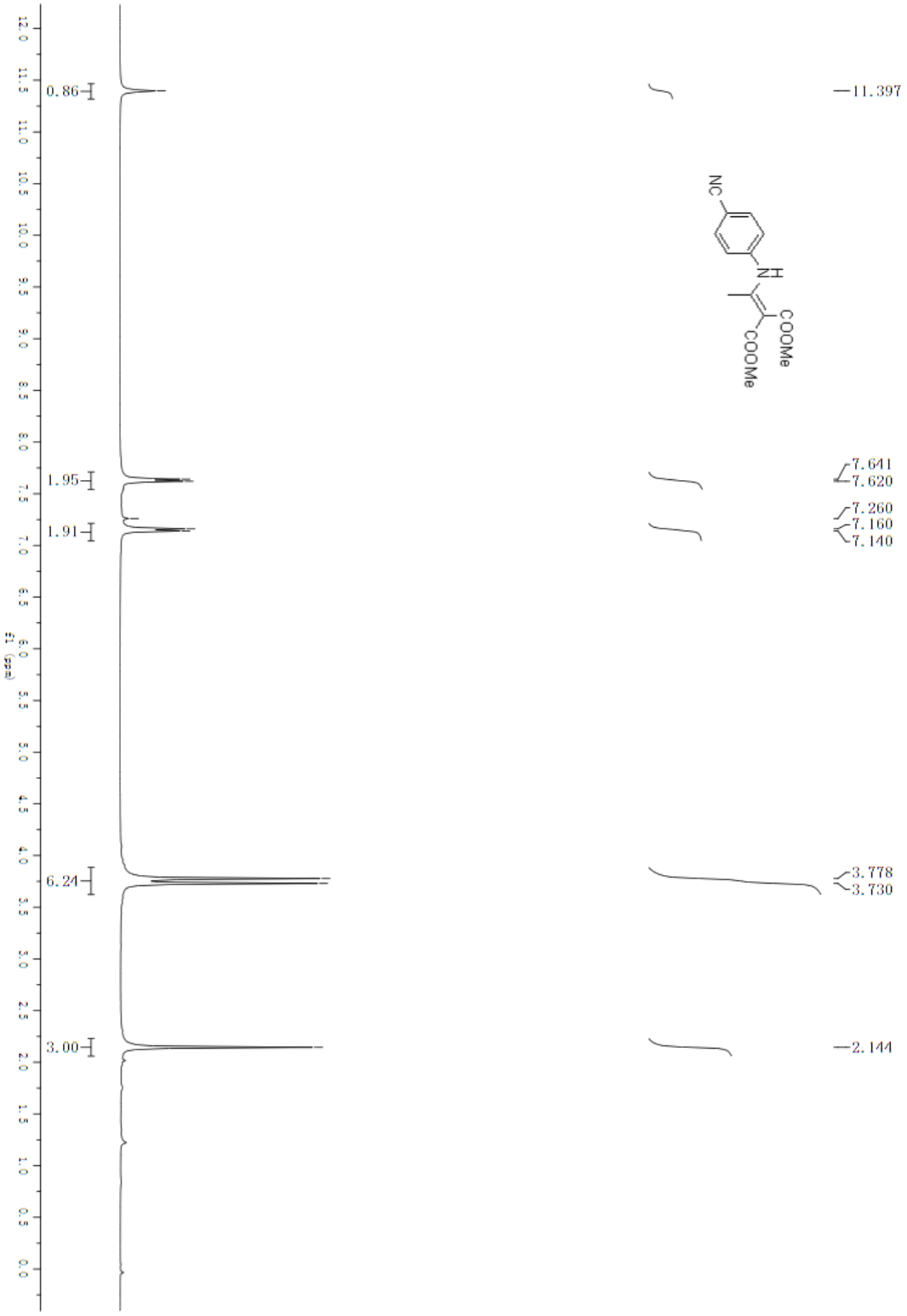

CO2Me
H
N
CO2Me
EtO
O

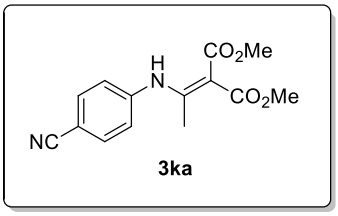
3ja


168.751
168.603
165.764
160.378
142.116
130.715
127.621
124.234
95.891
77.318
77.000
76.681
61.064
52.090
51.386
18.214
14.285
EtOOC
COOMe
COOMe
f1 (ppm)

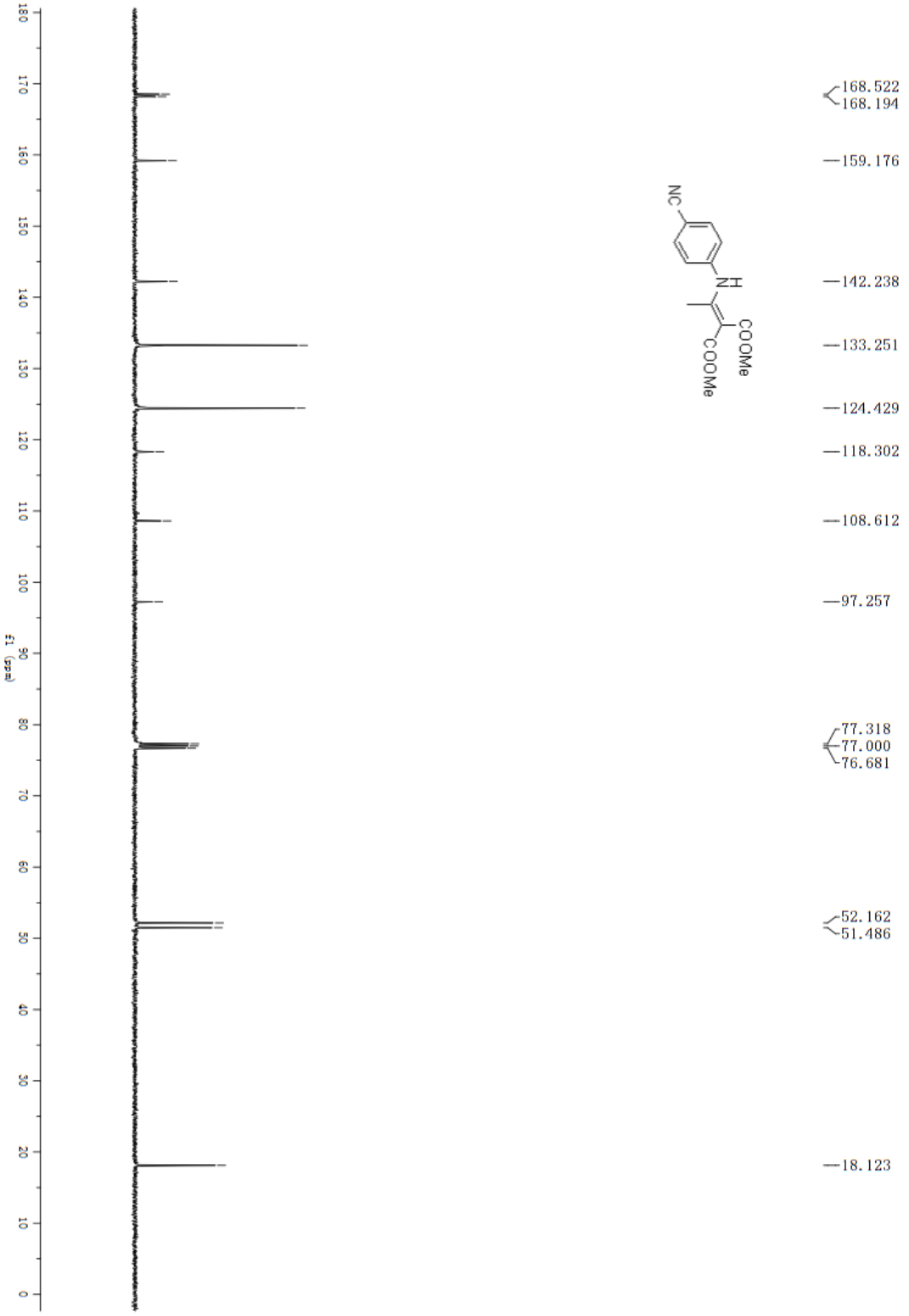

H
N
CO2Me
CO2Me
NC

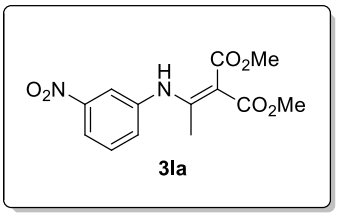
3ka


0.86
1.95
1.91
6.24
3.00
f1 (ppm)
11.397
7.641
7.620
7.260
7.160
7.140
3.778
3.730
2.144
NC
NH
COOMe
COOMe

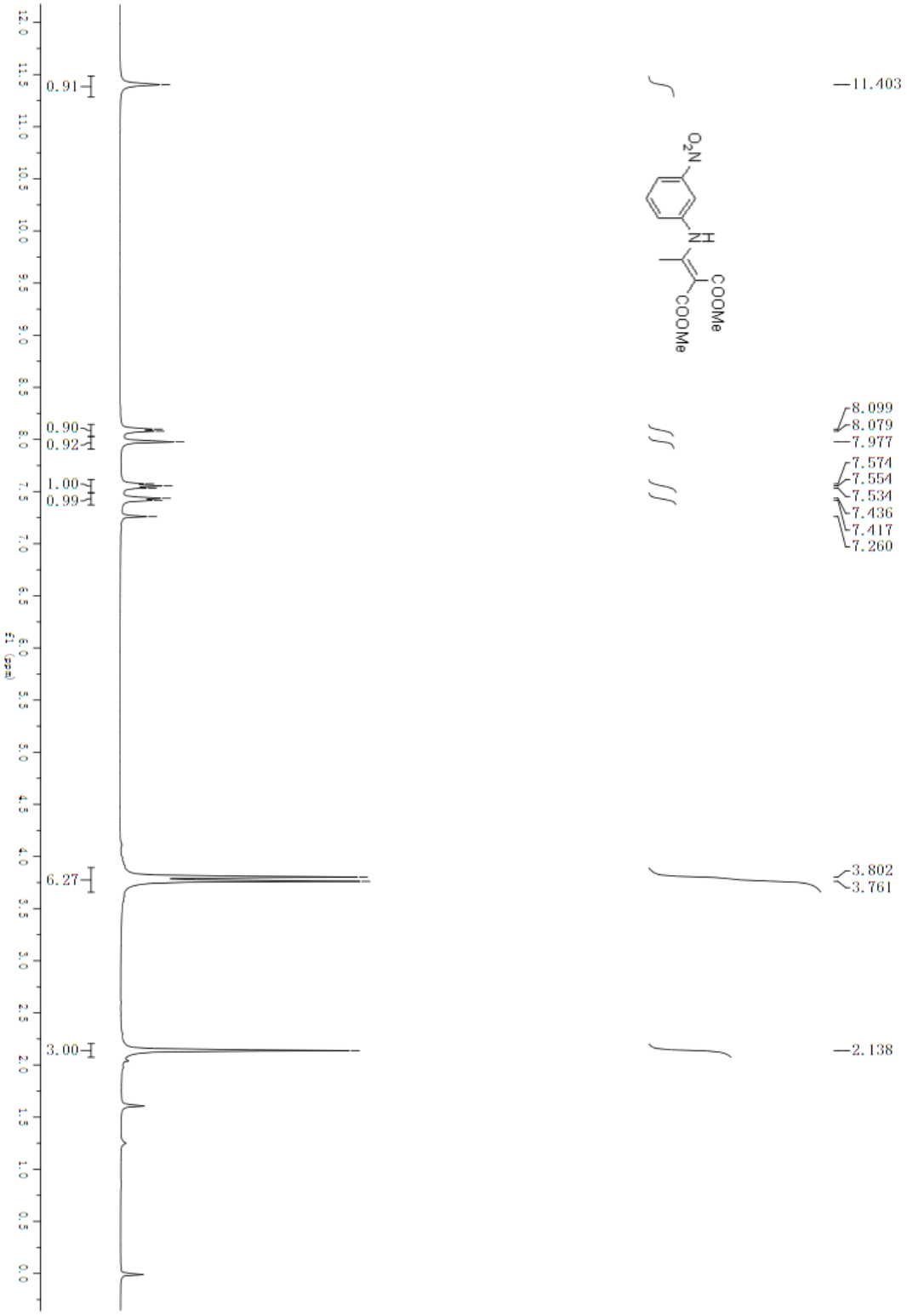

CO2Me
H
N
CO2Me
NC

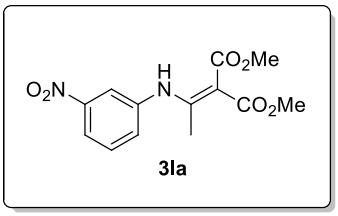
3ka


168.522
168.194
159.176
142.238
133.251
124.429
118.302
108.612
97.257
77.318
77.000
76.681
52.162
51.486
18.123
NC
N
H
COOMe
COOMe

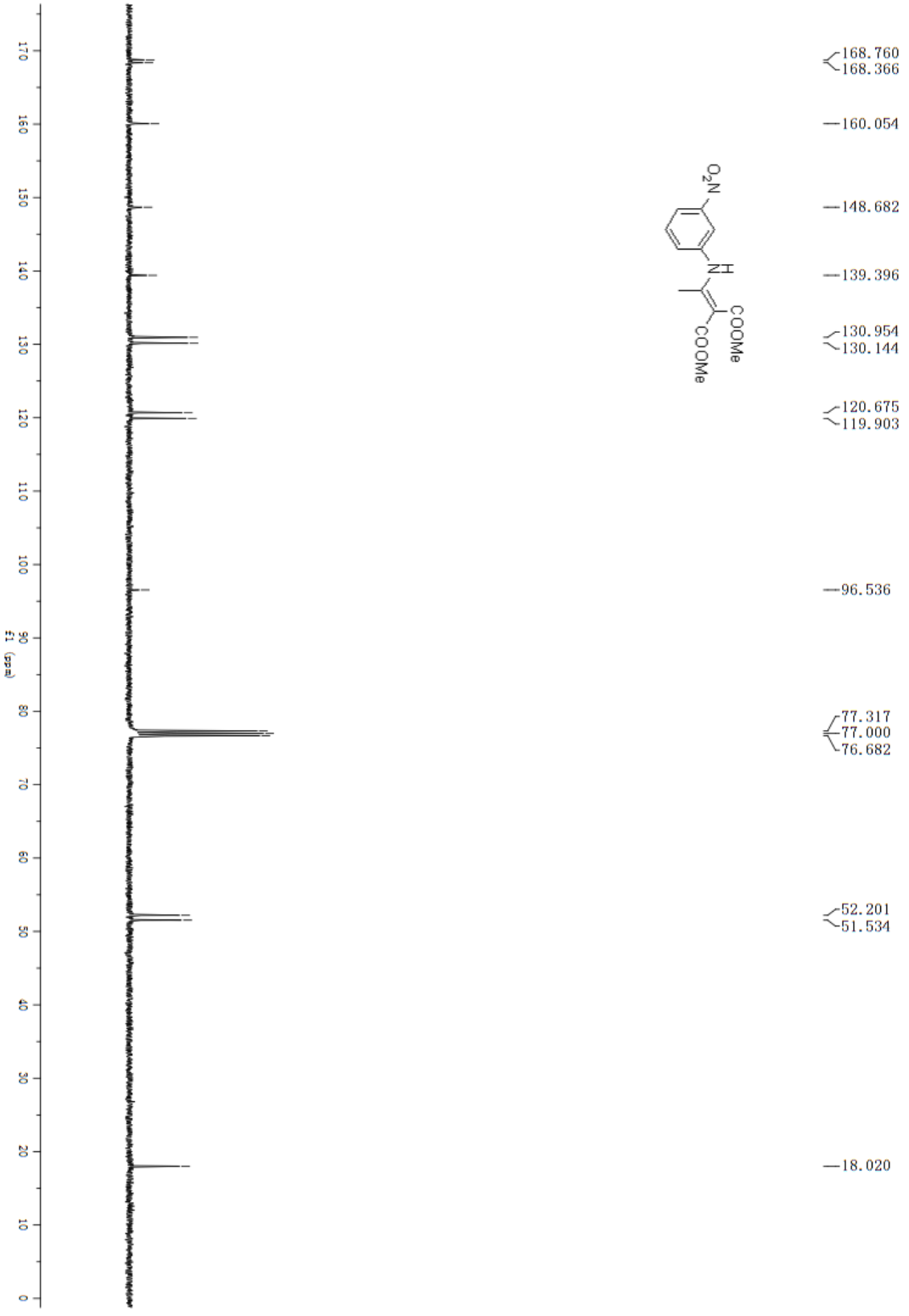

O2N
H
N
CO2Me
CO2Me

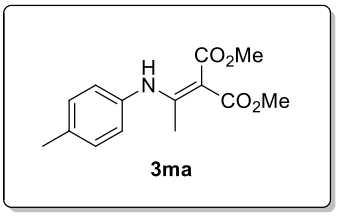
3la


0.91
0.90
0.92
1.00
0.99
6.27
3.00
O2N
H
N
COOMe
COOMe
11.403
8.099
8.079
7.977
7.574
7.554
7.534
7.436
7.417
7.260
3.802
3.761
2.138
f1 (ppm)

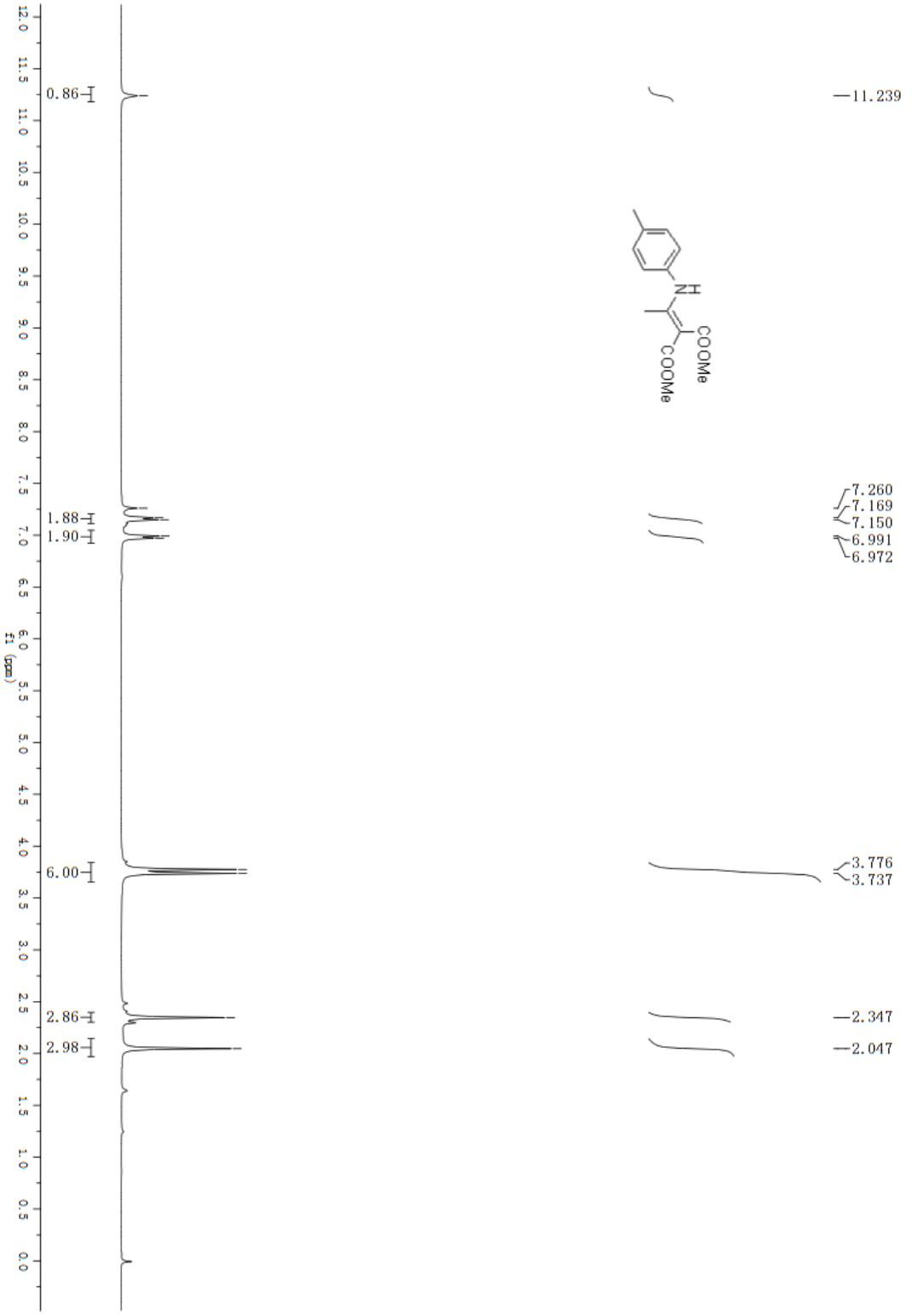

O2N
H
N
CO2Me
CO2Me

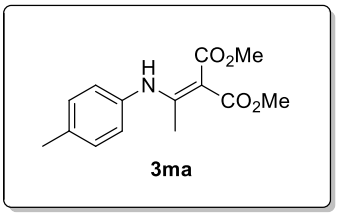
3la


f1 (ppm)
O2N
H
N
COOMe
COOMe
168.760
168.366
160.054
148.682
139.396
130.954
130.144
120.675
119.903
96.536
77.317
77.000
76.682
52.201
51.534
18.020

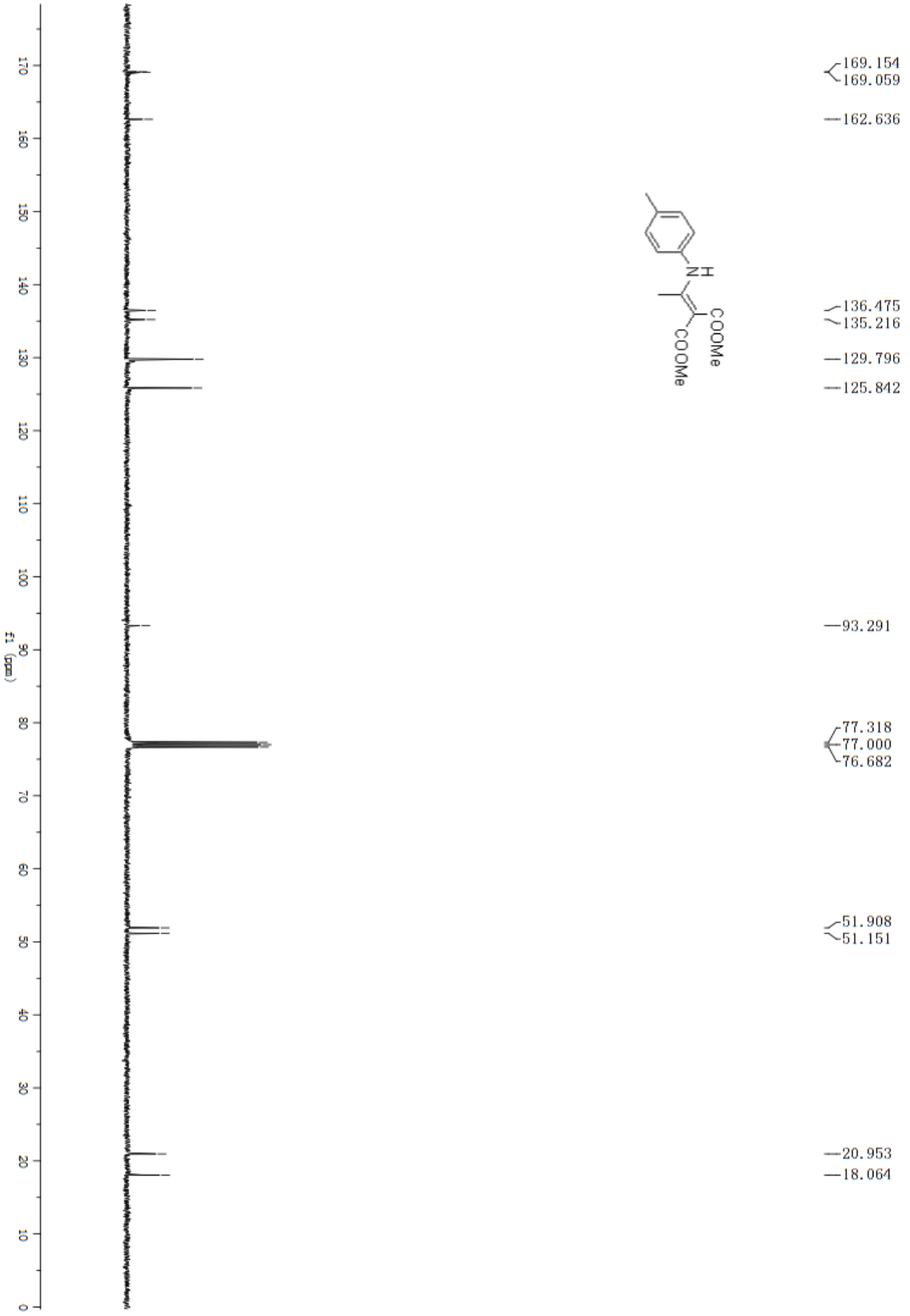

H
N
CO2Me
CO2Me

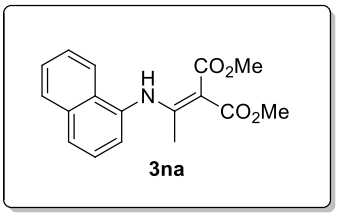
3ma


0.86
1.88
1.90
6.00
2.86
2.98
f1 (ppm)
11.239
7.260
7.169
7.150
6.991
6.972
3.776
3.737
2.347
2.047
COOMe
COOMe

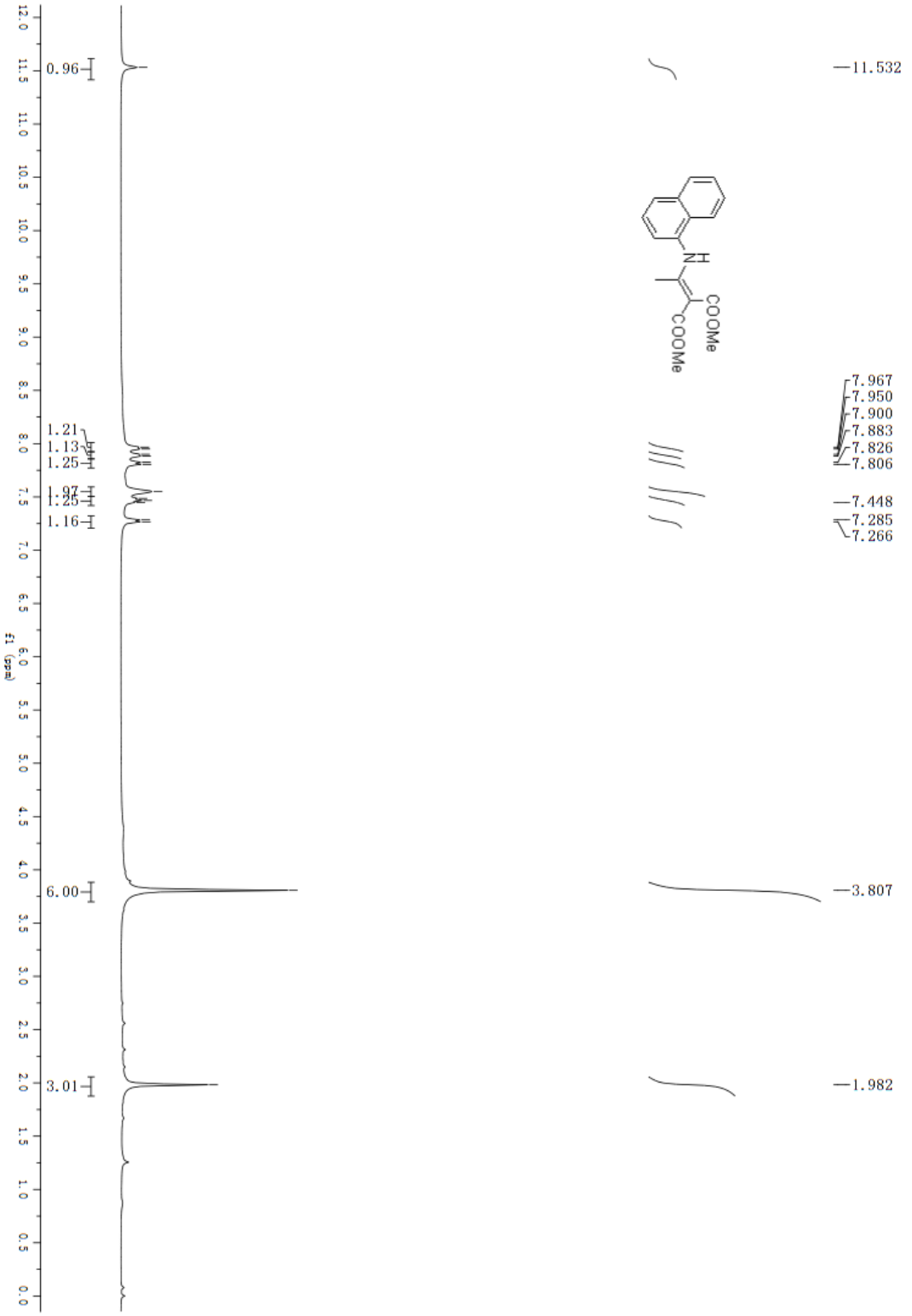

H
N
CO2Me
CO2Me

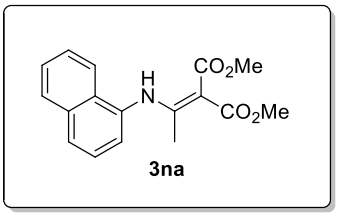
3ma


169.154
169.059
162.636
136.475
135.216
129.796
125.842
93.291
77.318
77.000
76.682
51.908
51.151
20.953
18.064
COOMe
COOMe
f1 (ppm)

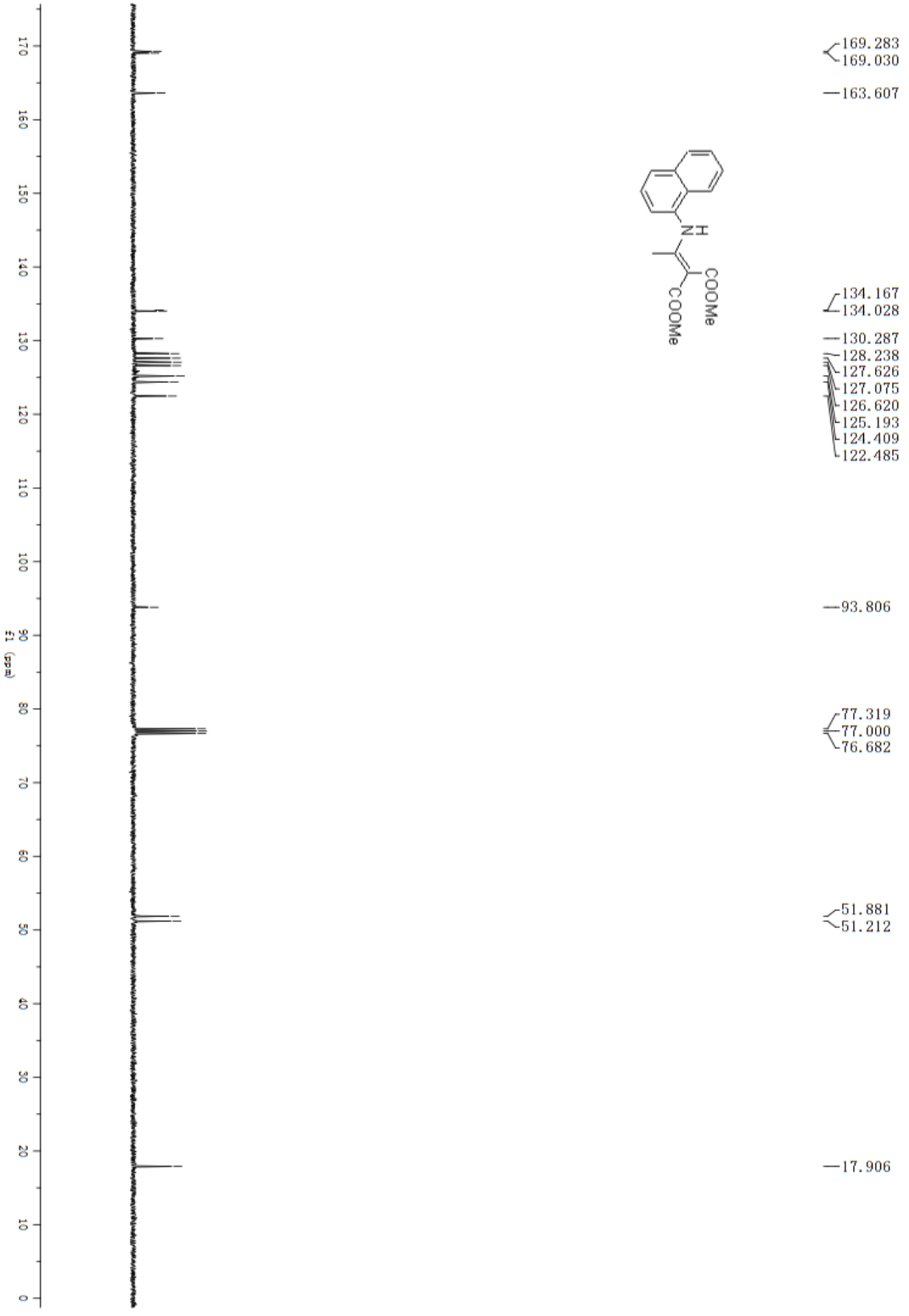

H
N
CO2Me
CO2Me

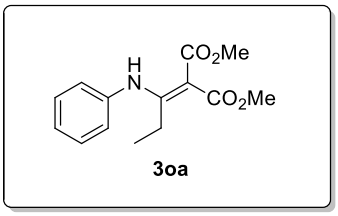
3na


0.96
1.21
1.13
1.25
1.97
1.25
1.16
6.00
3.01
f1 (ppm)
11.532
7.967
7.950
7.900
7.883
7.826
7.806
7.448
7.285
7.266
3.807
1.982
COOMe
COOMe

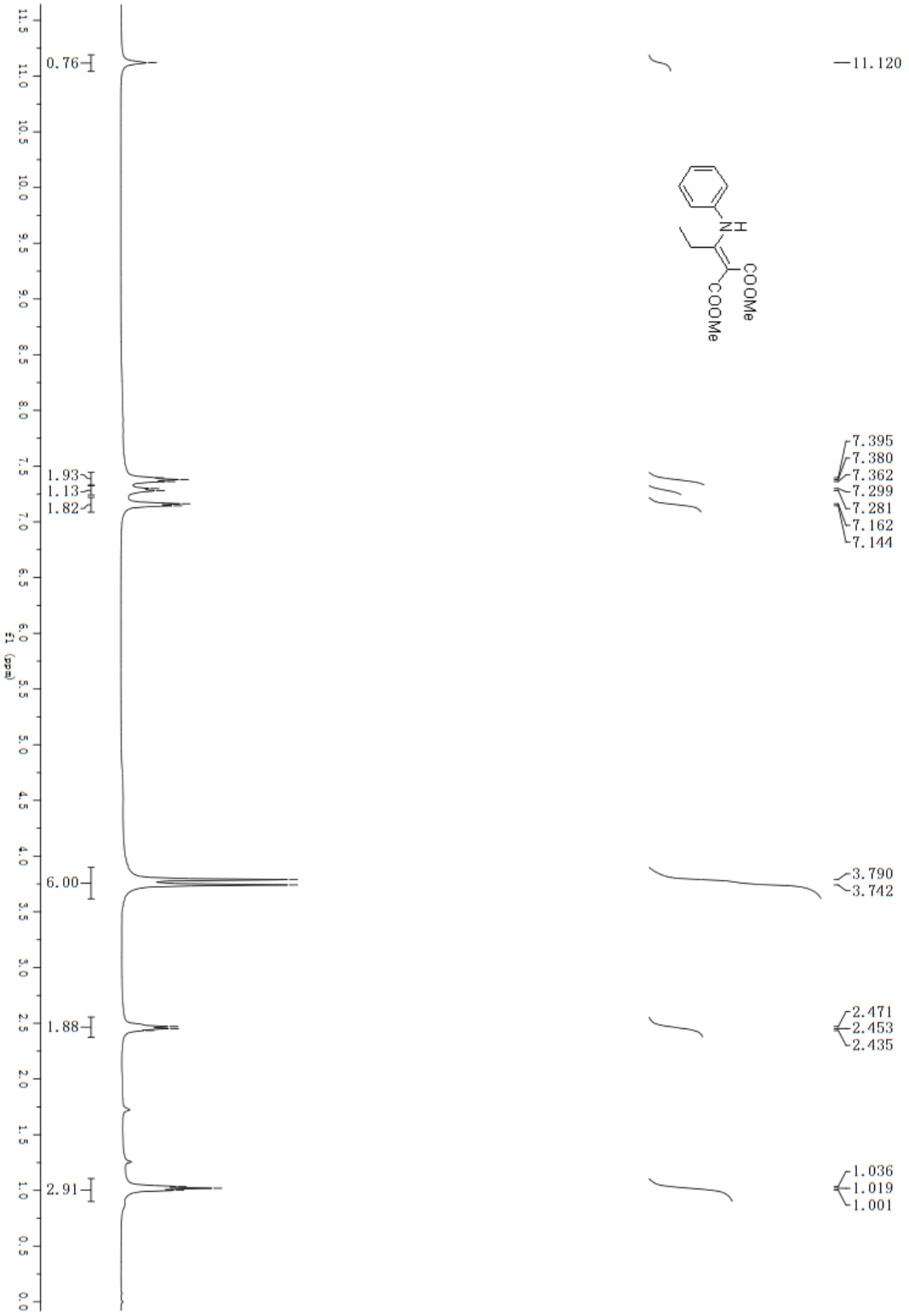

H
N
CO2Me
CO2Me

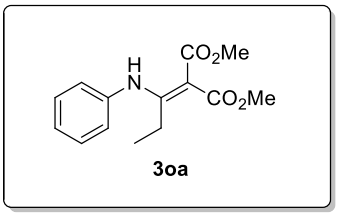
3na


169.283
169.030
163.607
134.167
134.028
130.287
128.238
127.626
127.075
126.620
125.193
124.409
122.485
93.806
77.319
77.000
76.682
51.881
51.212
17.906
H
N
COOMe
COOMe
f1 (ppm)

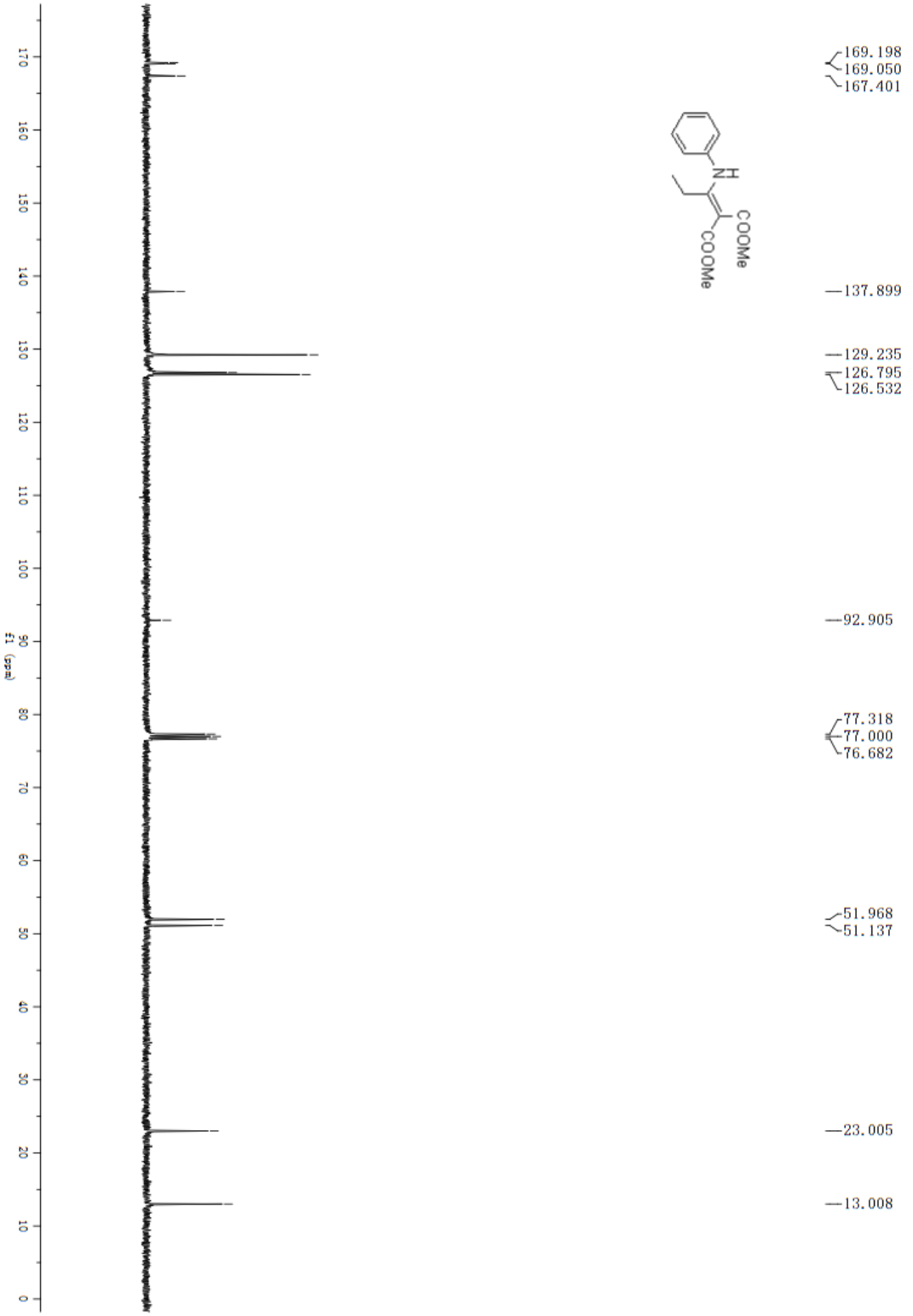

CO2Me
H
N
CO2Me

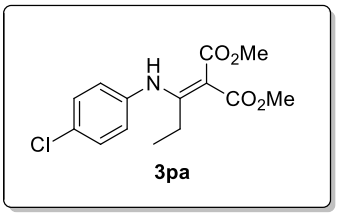
3oa


0.76
1.93
1.13
1.82
6.00
1.88
2.91
f1 (ppm)
11.120
7.395
7.380
7.362
7.299
7.281
7.162
7.144
3.790
3.742
2.471
2.453
2.435
1.036
1.019
1.001
COOMe
COOMe

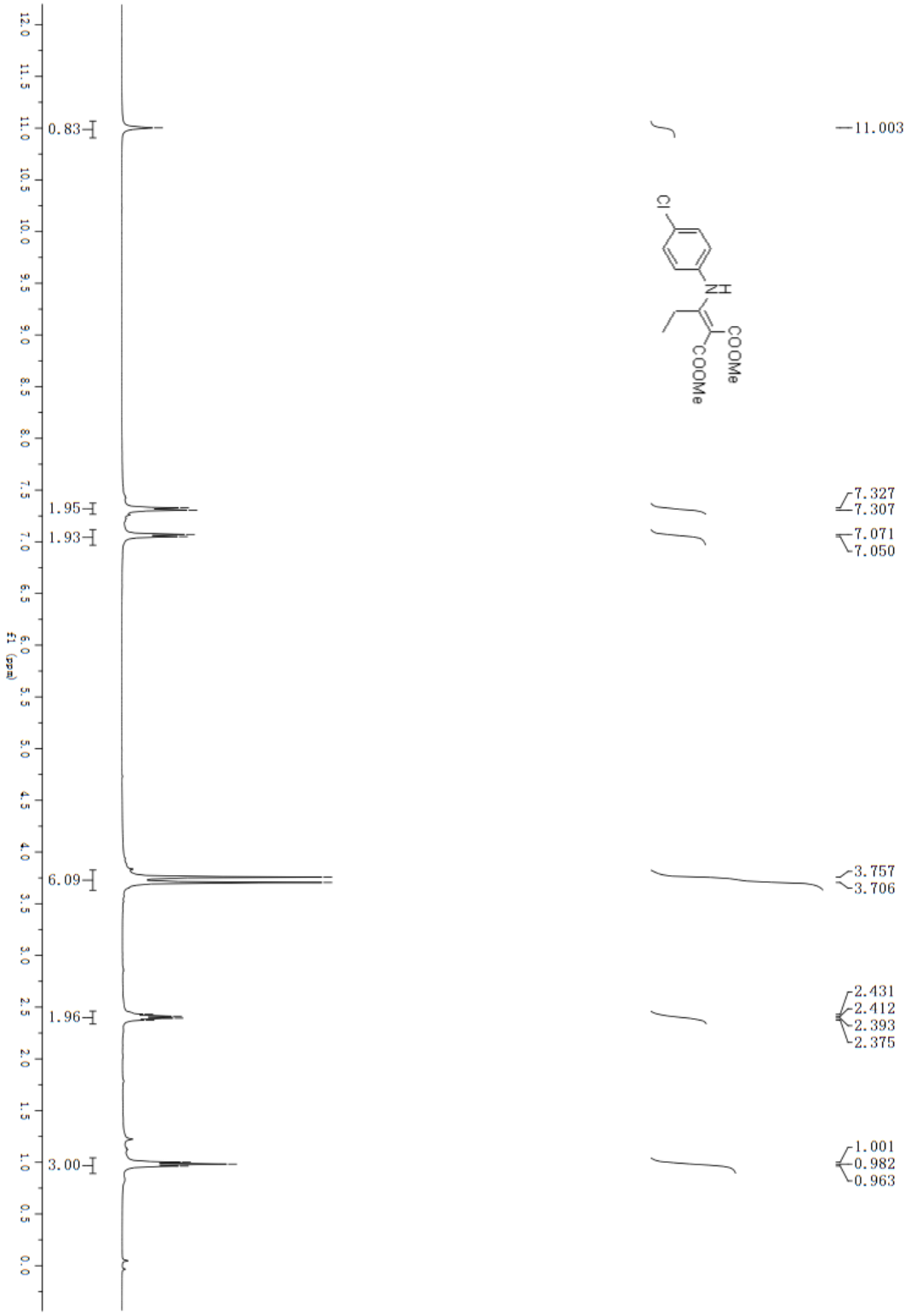

H
N
CO2Me
CO2Me

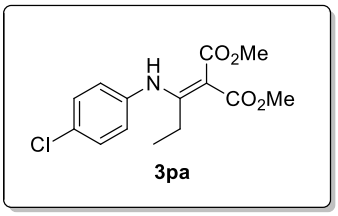
3oa


169.198
169.050
167.401
137.899
129.235
126.795
126.532
92.905
77.318
77.000
76.682
51.968
51.137
23.005
13.008
COOMe
COOMe
f1 (ppm)

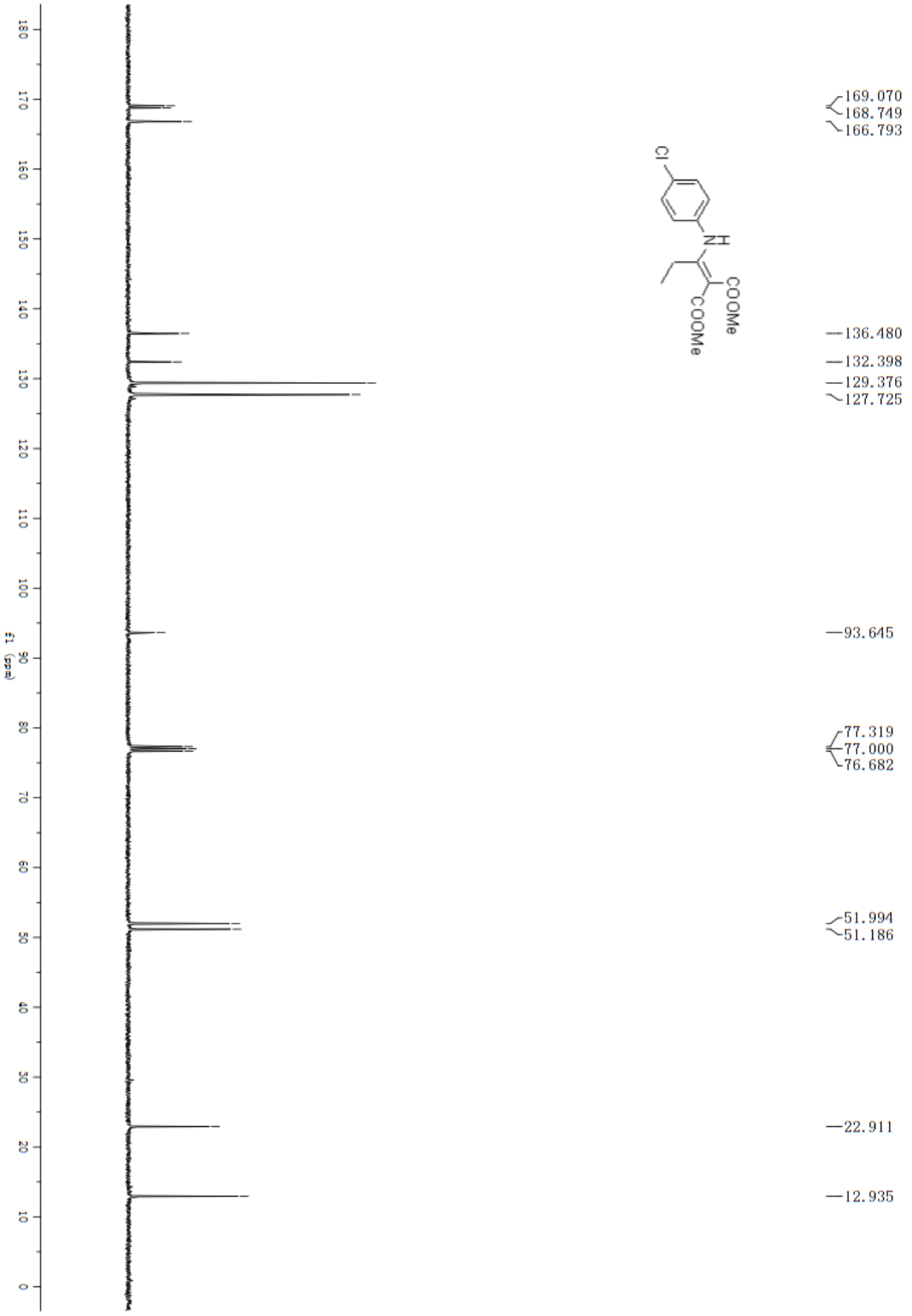

CO2Me
H
N
CO2Me
Cl

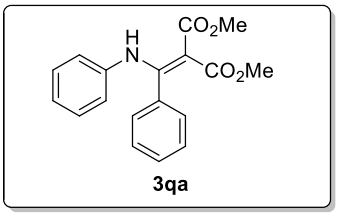
3pa


0.83
1.95
1.93
6.09
1.96
3.00
f1 (ppm)
11.003
7.327
7.307
7.071
7.050
3.757
3.706
2.431
2.412
2.393
2.375
1.001
0.982
0.963
Cl
H
N
COOMe
COOMe

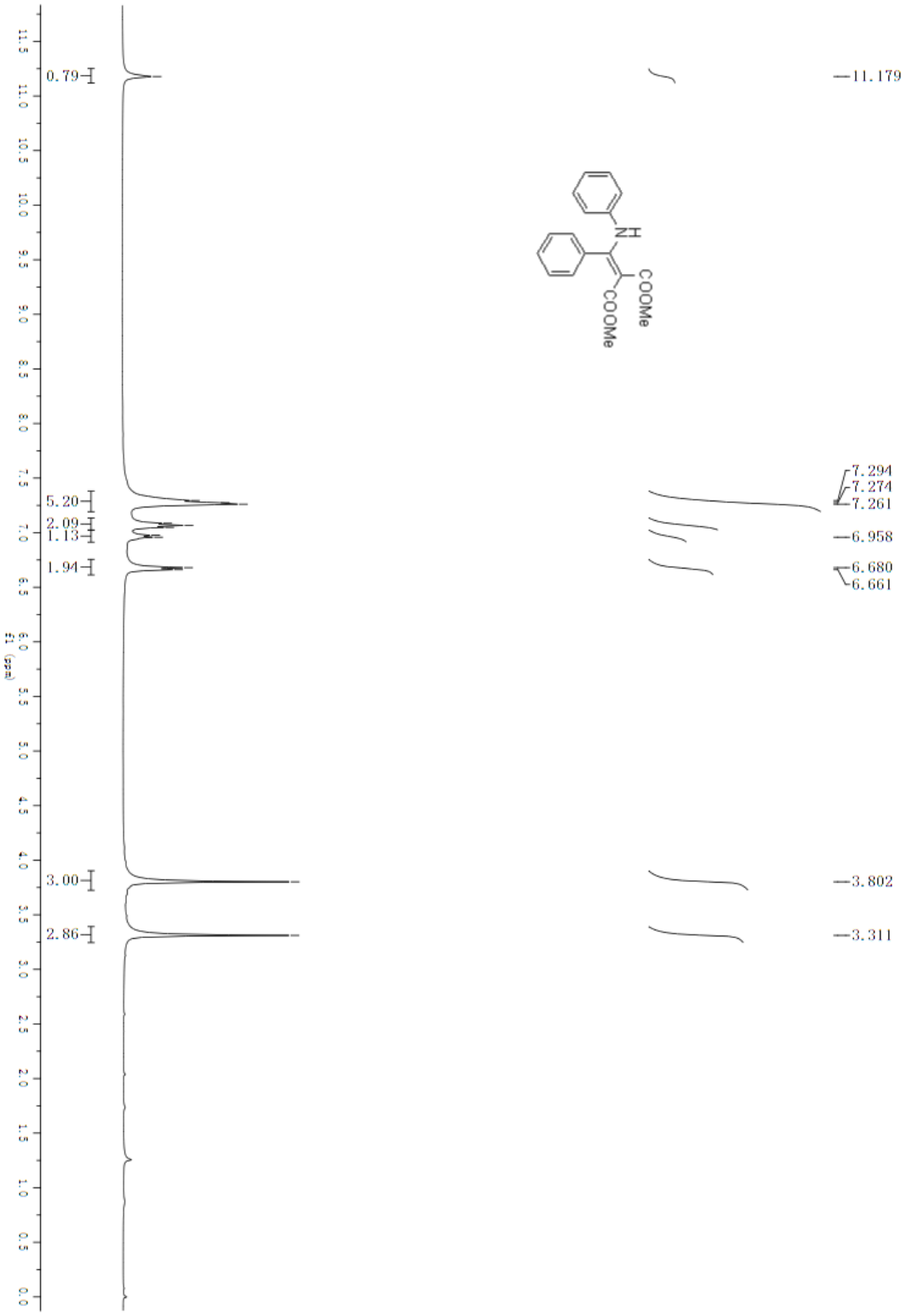

CO2Me
H
N
CO2Me
Cl

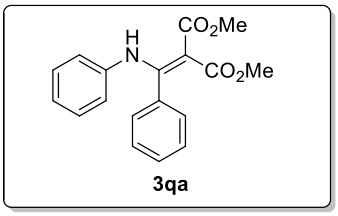
3pa


169.070
168.749
166.793
136.480
132.398
129.376
127.725
93.645
77.319
77.000
76.682
51.994
51.186
22.911
12.935
COOMe
COOMe
Cl
H
N
f1 (ppm)

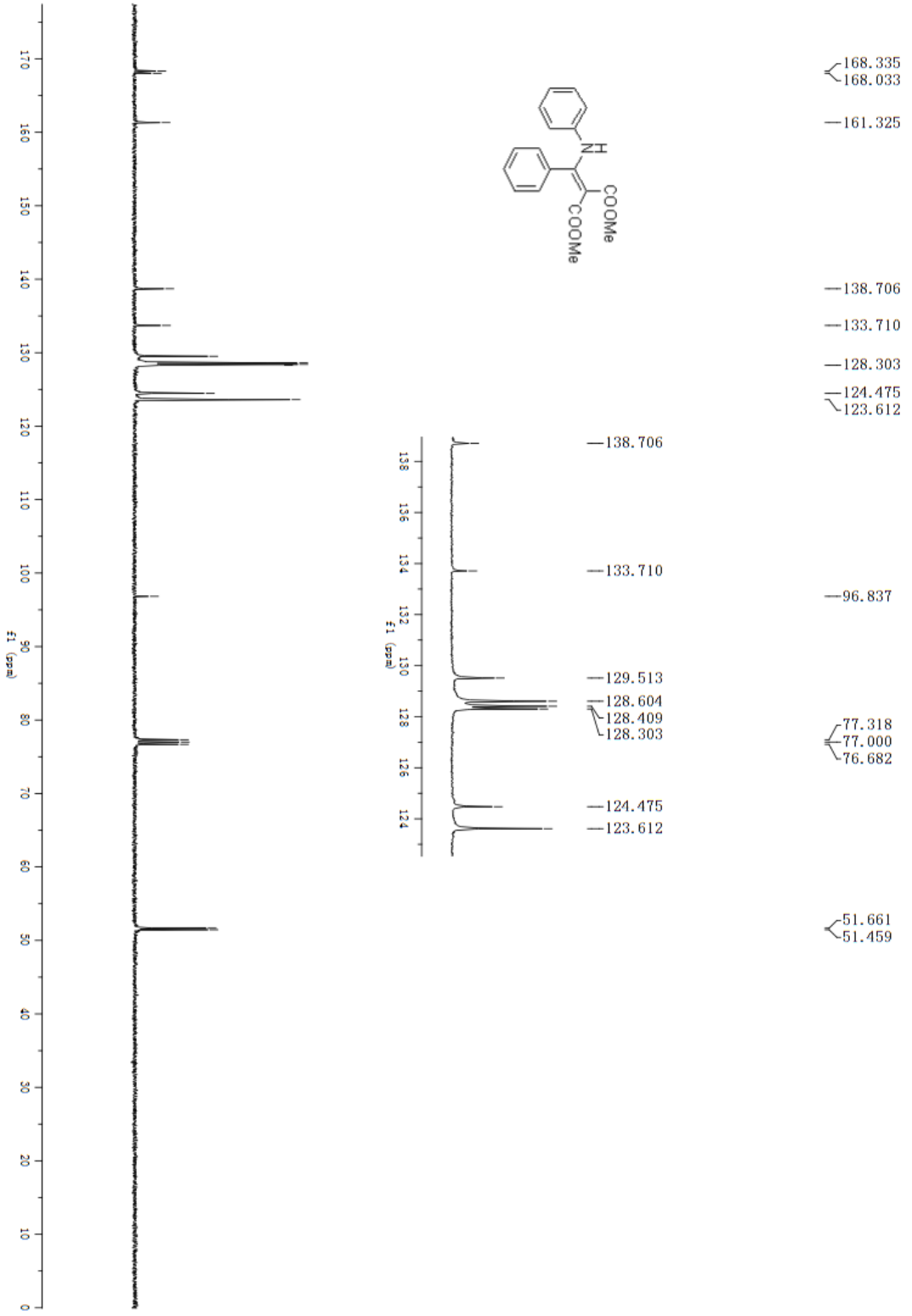

CO2Me
H
N
CO2Me

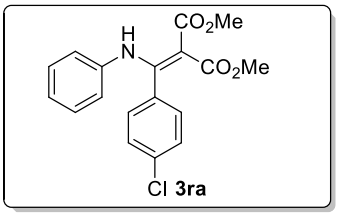
3qa

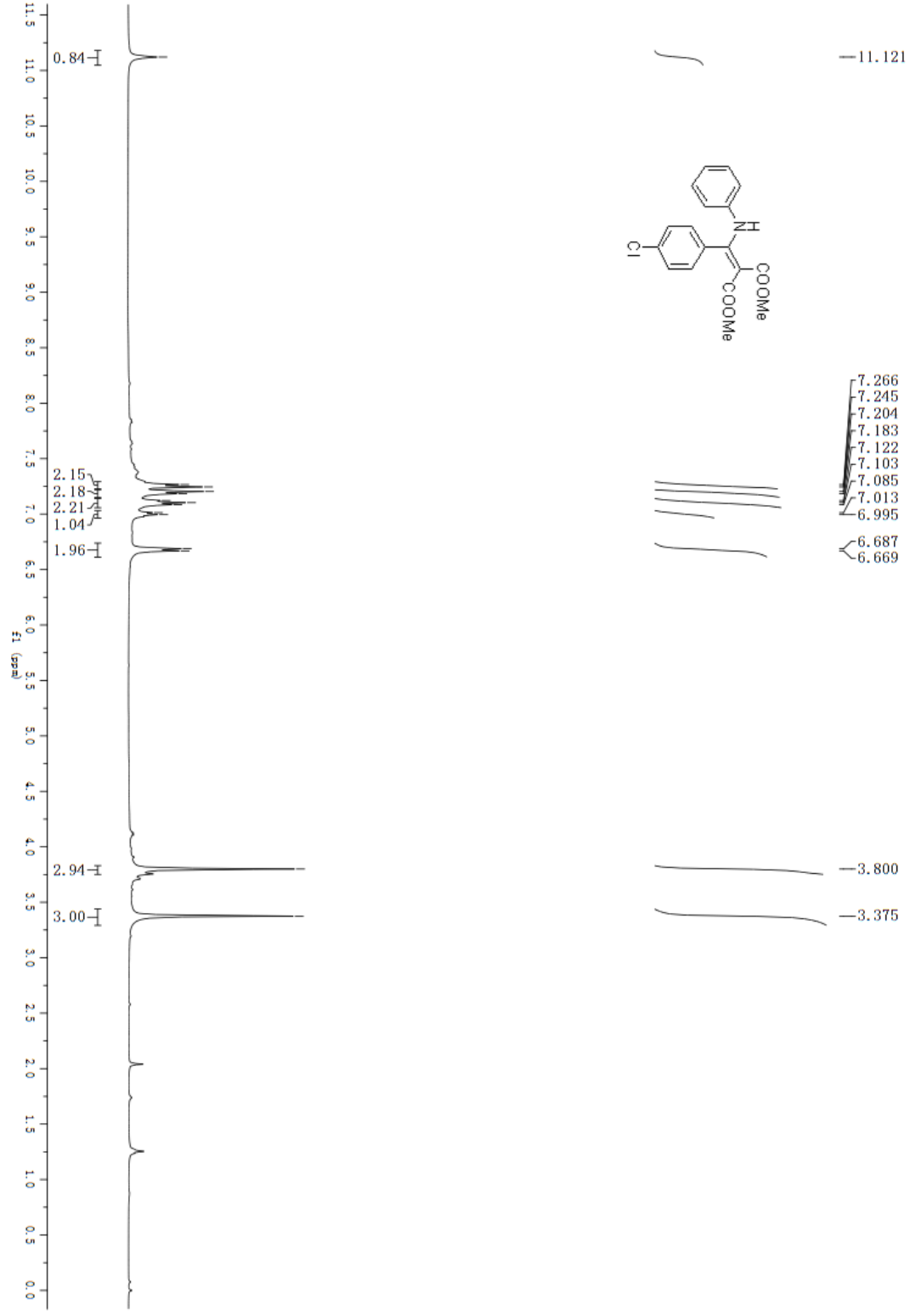

0.79
5.20
2.09
1.13
1.94
3.00
2.86
f1 (ppm)
11.179
7.294
7.274
7.261
6.958
6.680
6.661
3.802
3.311
COOMe
COOMe

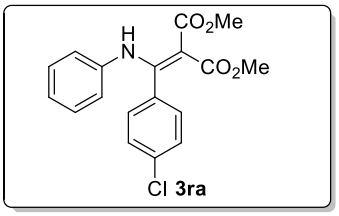

CO2Me
H
N
CO2Me

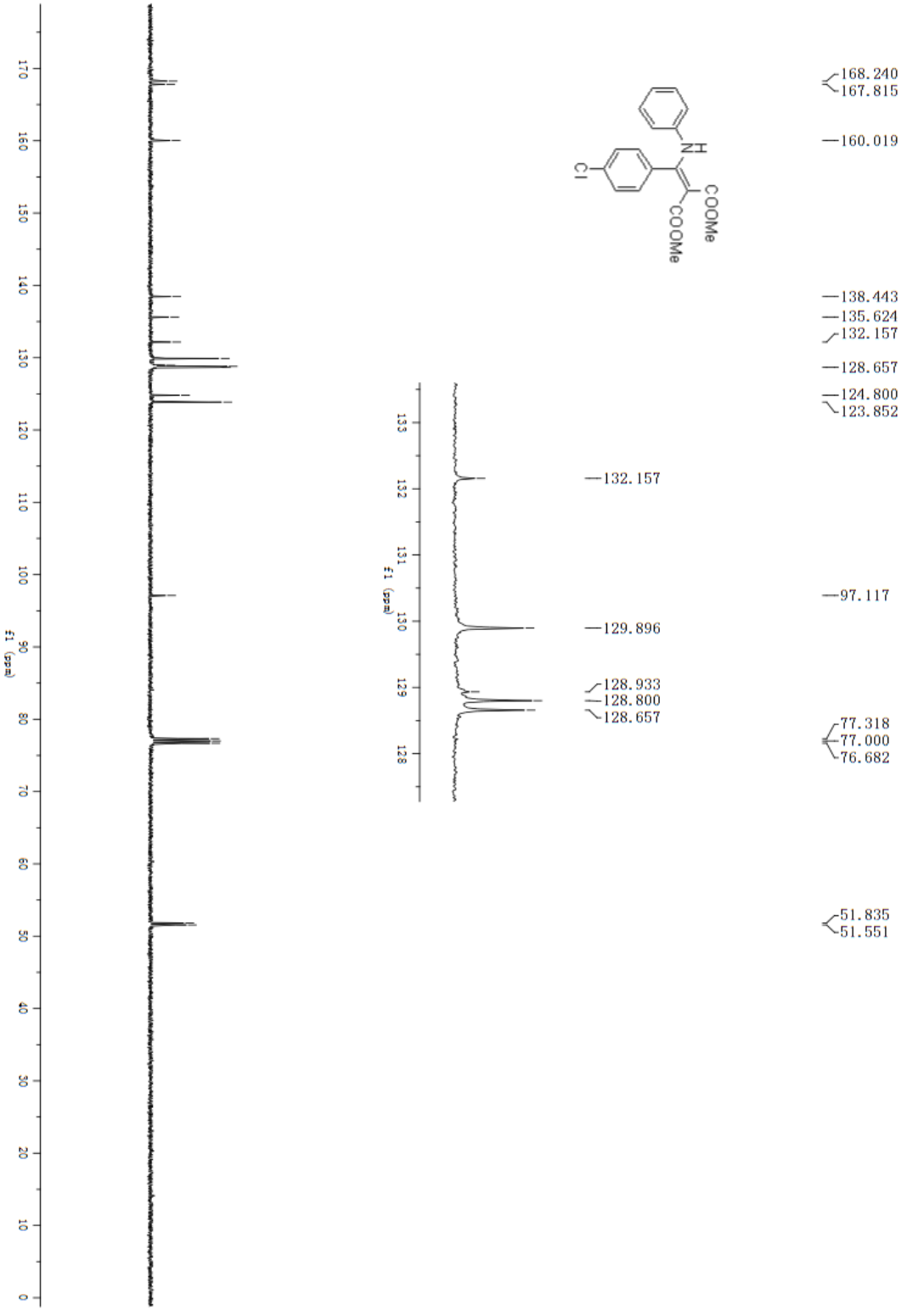
3qa

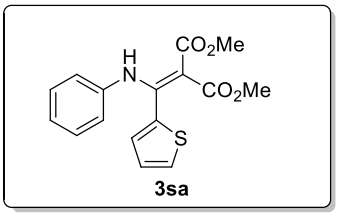

168.335
168.033
161.325
138.706
133.710
128.303
124.475
123.612
96.837
129.513
128.604
128.409
128.303
77.318
77.000
76.682
51.661
51.459
COOMe
COOMe
f1 (ppm)


CO2Me
H
N
CO2Me
Cl 3ra


0.84
2.15
2.18
2.21
1.04
1.96
2.94
3.00
11.121
7.266
7.245
7.204
7.183
7.122
7.103
7.085
7.013
6.995
6.687
6.669
3.800
3.375
COOMe
COOMe
Cl
f1 (ppm)

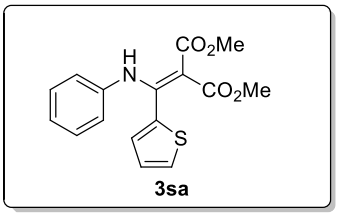

CO2Me
H
N
CO2Me
Cl 3ra


168.240
167.815
160.019
138.443
135.624
132.157
128.657
124.800
123.852
132.157
97.117
129.896
128.933
128.800
128.657
77.318
77.000
76.682
51.835
51.551
COOMe
COOMe
Cl
f1 (ppm)

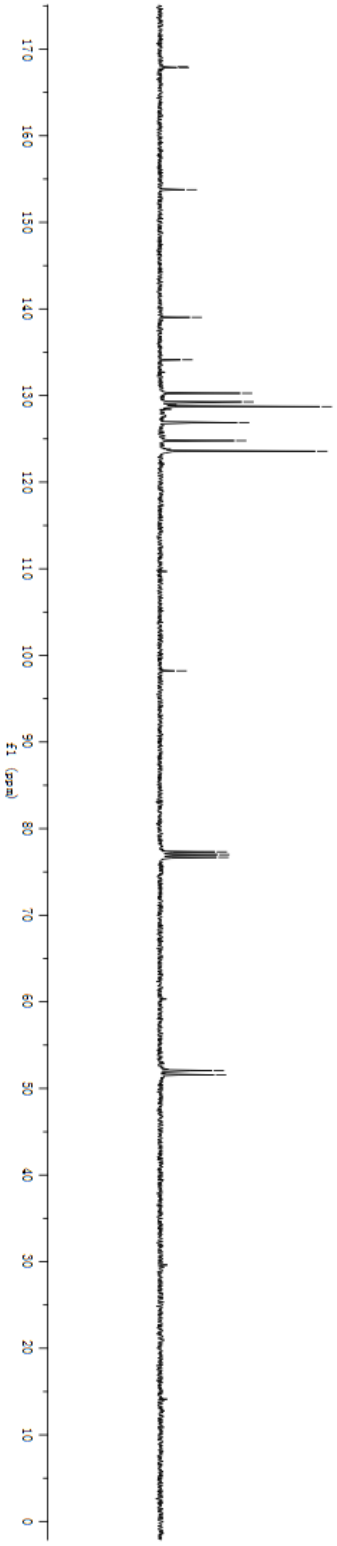

CO2Me
H
N
CO2Me
S

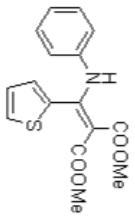
3sa


0.76
1.11
2.83
1.25
1.10
1.94
3.00
2.87
f1 (ppm)
10.897
7.365
7.353
7.154
7.135
7.041
7.022
7.005
6.946
6.936
6.926
6.793
6.774
3.791
3.478
COOMe
COOMe

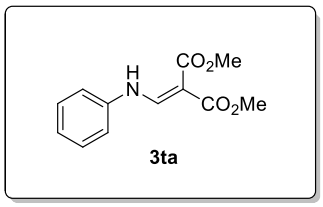


3sa

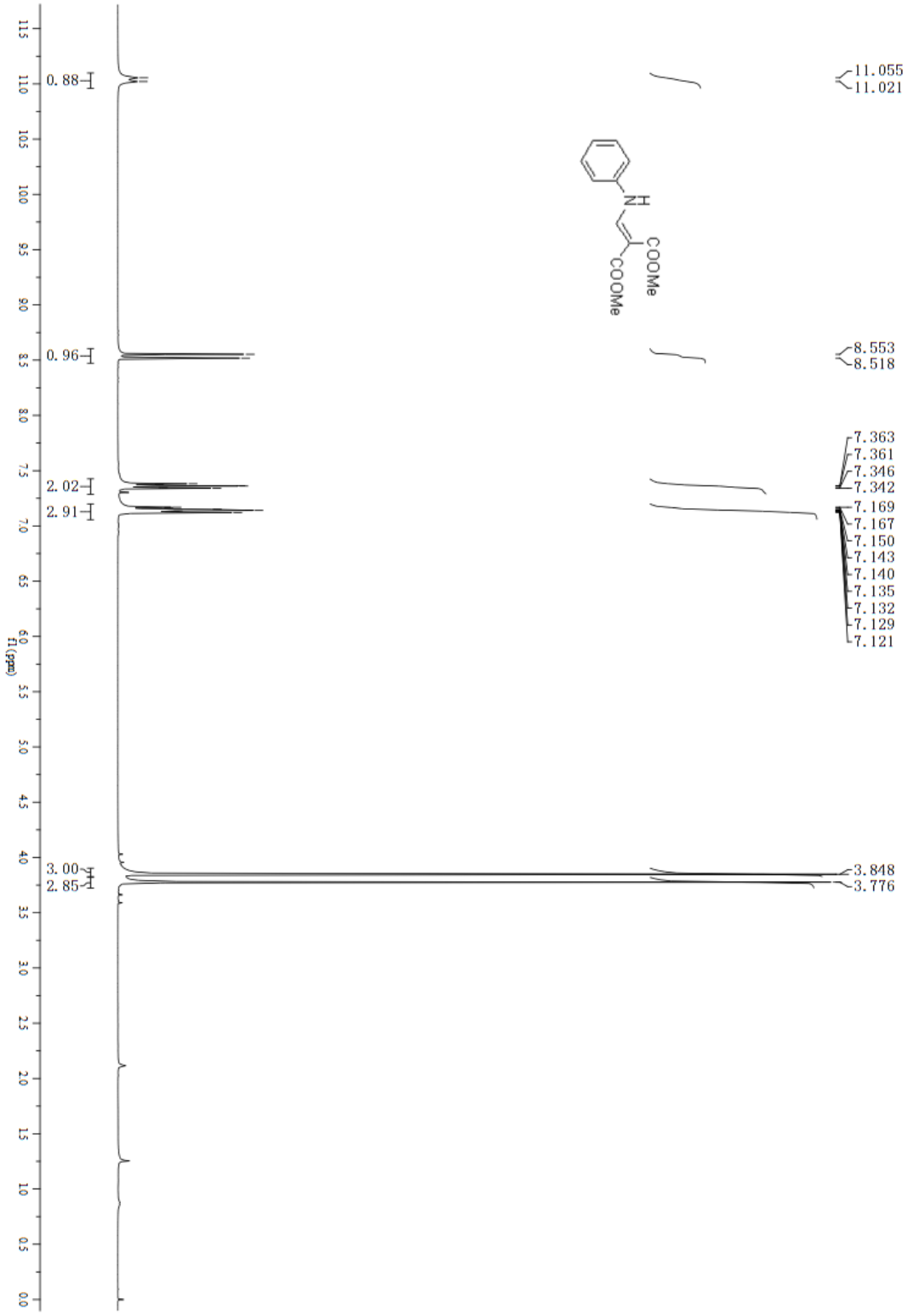


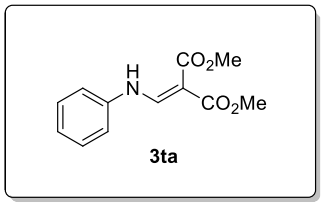


167.948
167.881
153.771
139.035
134.124
130.264
129.269
128.721
126.859
124.795
123.577
98.217
77.318
77.000
76.682
52.052
51.566

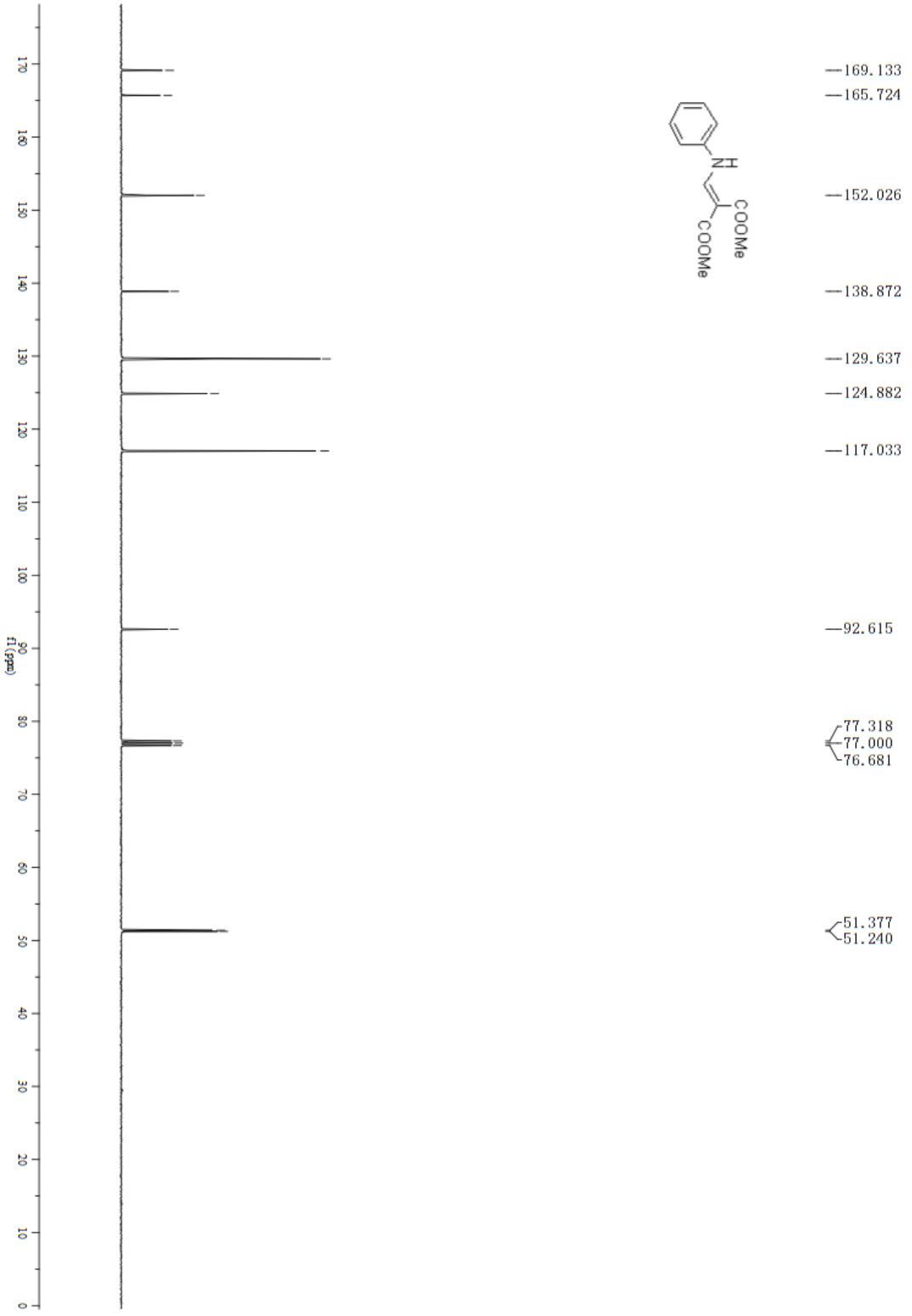

CO2Me
H
N
CO2Me

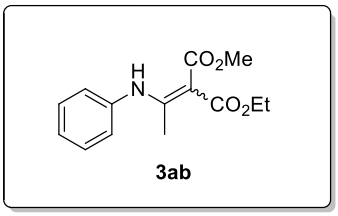
3ta


11.055
11.021
8.553
8.518
7.363
7.361
7.346
7.342
7.169
7.167
7.150
7.143
7.140
7.135
7.132
7.129
7.121
3.848
3.776
0.88
0.96
2.02
2.91
3.00
2.85
f1(ppm)
COOMe
COOMe

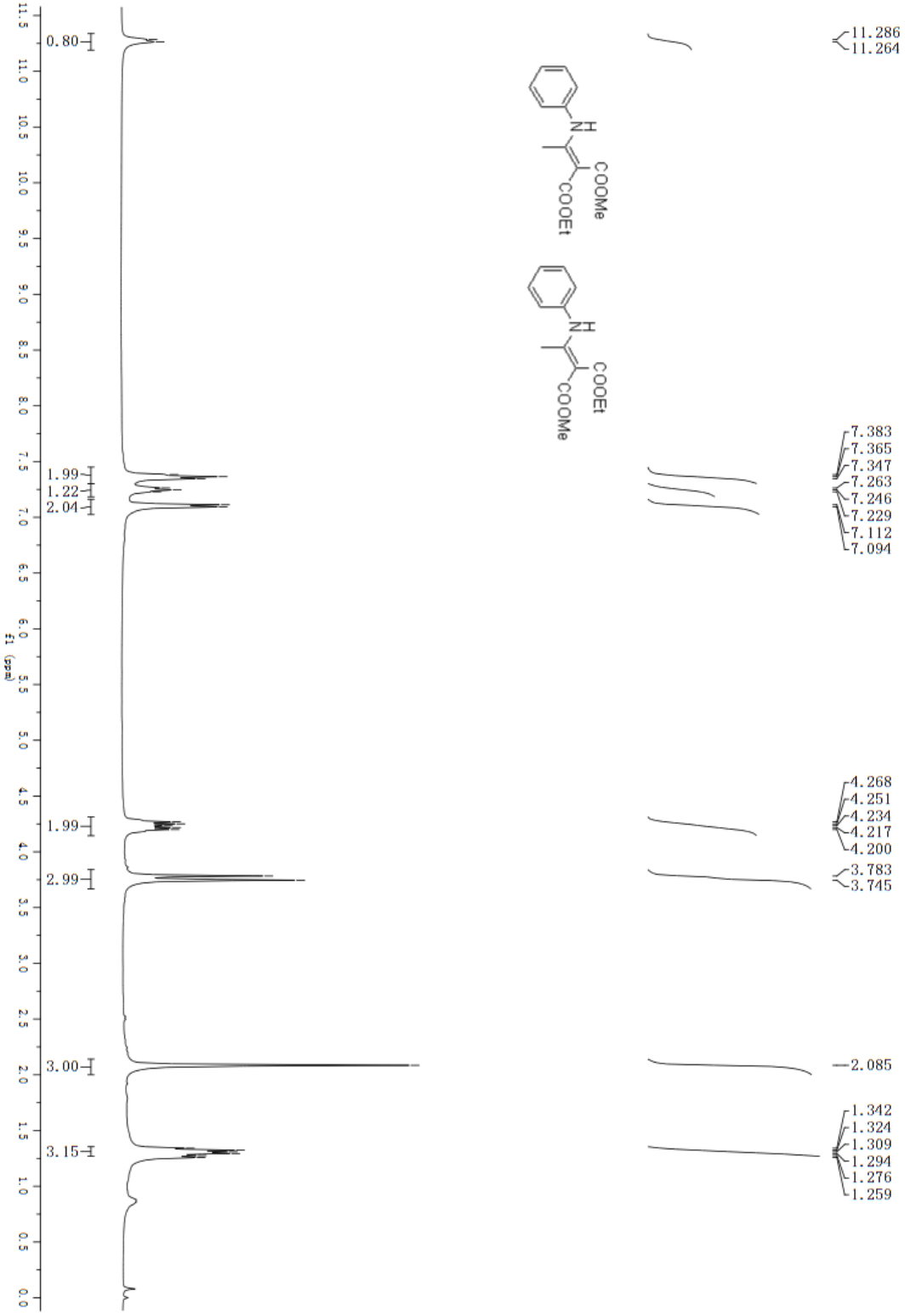

CO2Me
H
N
CO2Me

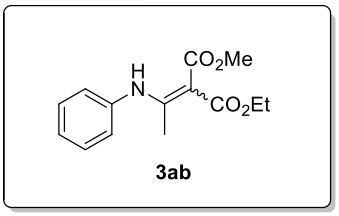
3ta


169.133
165.724
152.026
138.872
129.637
124.882
117.033
92.615
77.318
77.000
76.681
51.377
51.240
COOMe
COOMe
f1 (ppm)

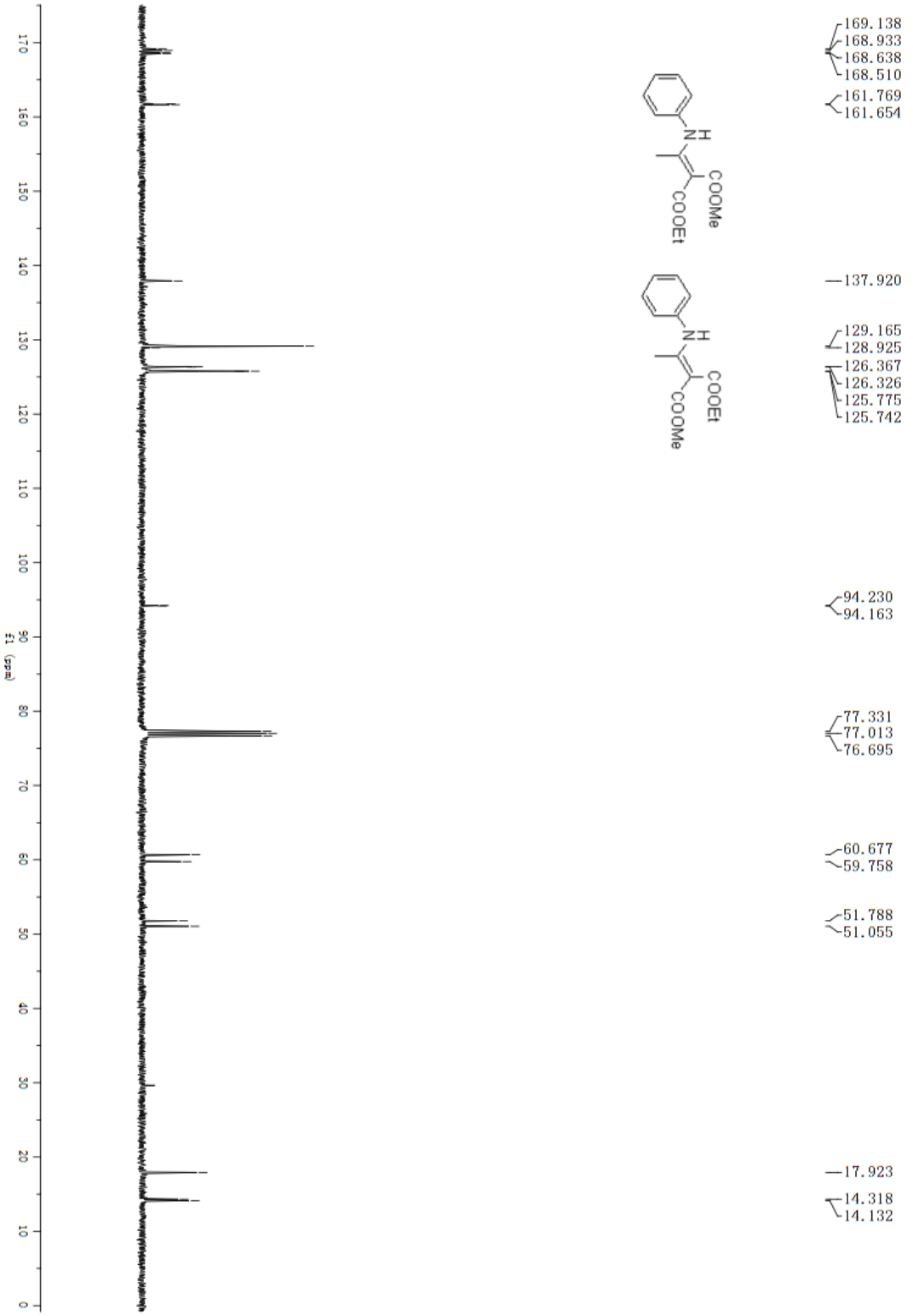

CO2Me
H
N
CO2Et

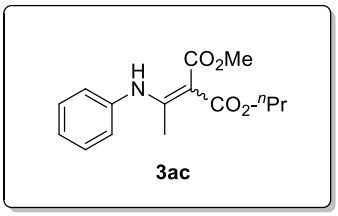
3ab


0.80
1.99
1.22
2.04
1.99
2.99
3.00
3.15
f1 (ppm)
COOMe
COOEt
COOEt
COOMe
11.286
11.264
7.383
7.365
7.347
7.263
7.246
7.229
7.112
7.094
4.268
4.251
4.234
4.217
4.200
3.783
3.745
2.085
1.342
1.324
1.309
1.294
1.276
1.259

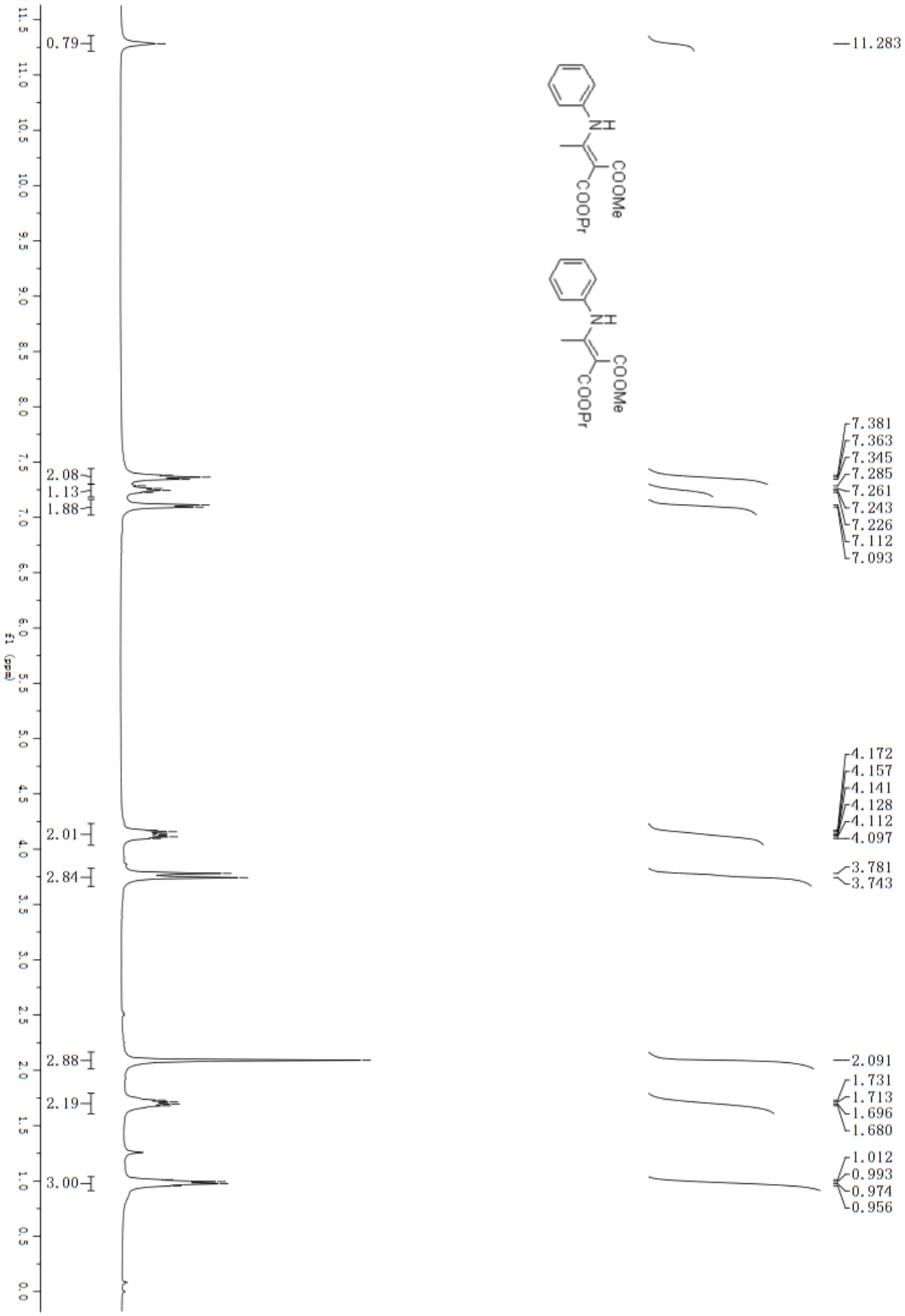

CO2Me
H
N
CO2Et

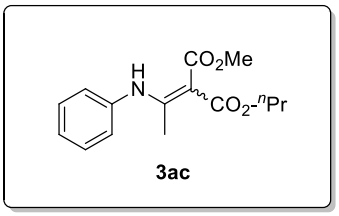
3ab


169.138
168.933
168.638
168.510
161.769
161.654
137.920
129.165
128.925
126.367
126.326
125.775
125.742
94.230
94.163
77.331
77.013
76.695
60.677
59.758
51.788
51.055
17.923
14.318
14.132
COOMe
COOEt
COOEt
COOMe
f1 (ppm)

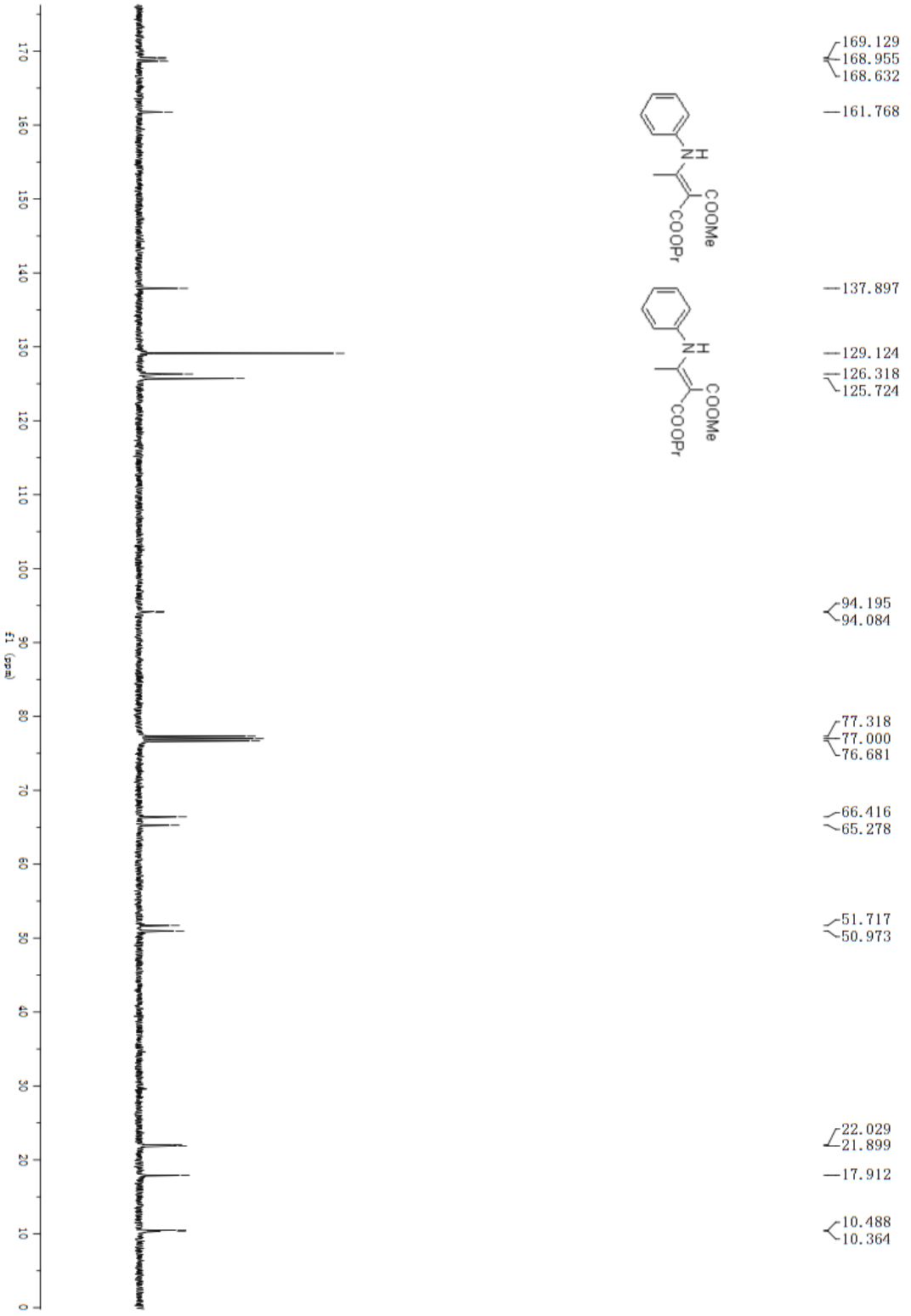

CO2Me
H
N
CO2-nPr

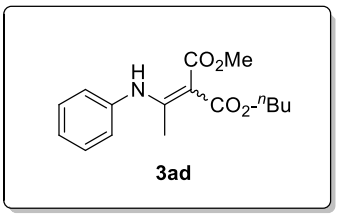
3ac


0.79
2.08
1.13
1.88
2.01
2.84
2.88
2.19
3.00
f1 (ppm)
COOMe
COOPr
11.283
7.381
7.363
7.345
7.285
7.261
7.243
7.226
7.112
7.093
4.172
4.157
4.141
4.128
4.112
4.097
3.781
3.743
2.091
1.731
1.713
1.696
1.680
1.012
0.993
0.974
0.956

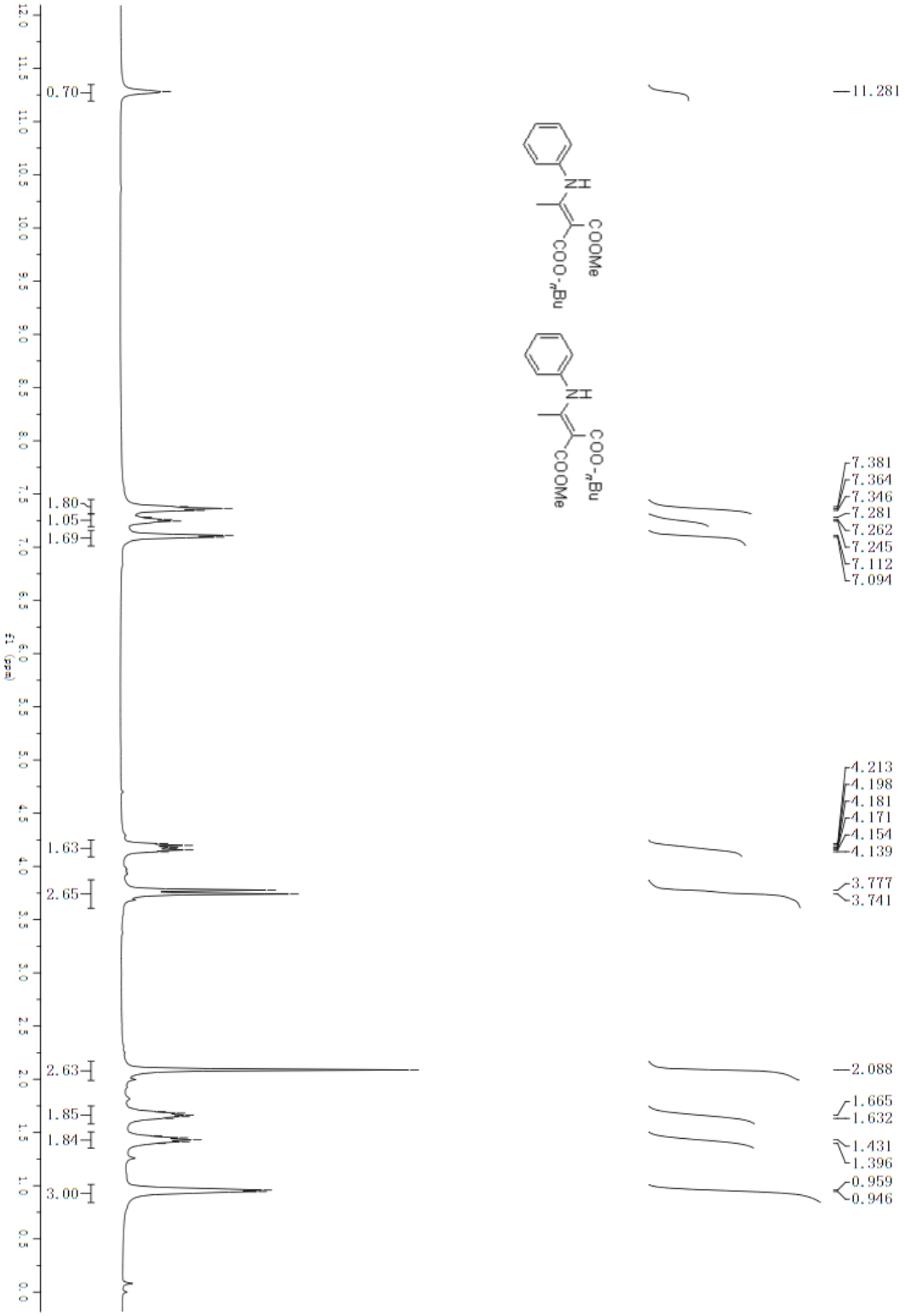

CO2Me
H
N
CO2-nPr

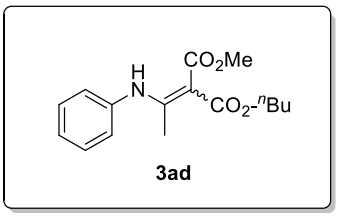
3ac


169.129
168.955
168.632
161.768
137.897
129.124
126.318
125.724
94.195
94.084
77.318
77.000
76.681
66.416
65.278
51.717
50.973
22.029
21.899
17.912
10.488
10.364
COOMe
COOPr
f1 (ppm)

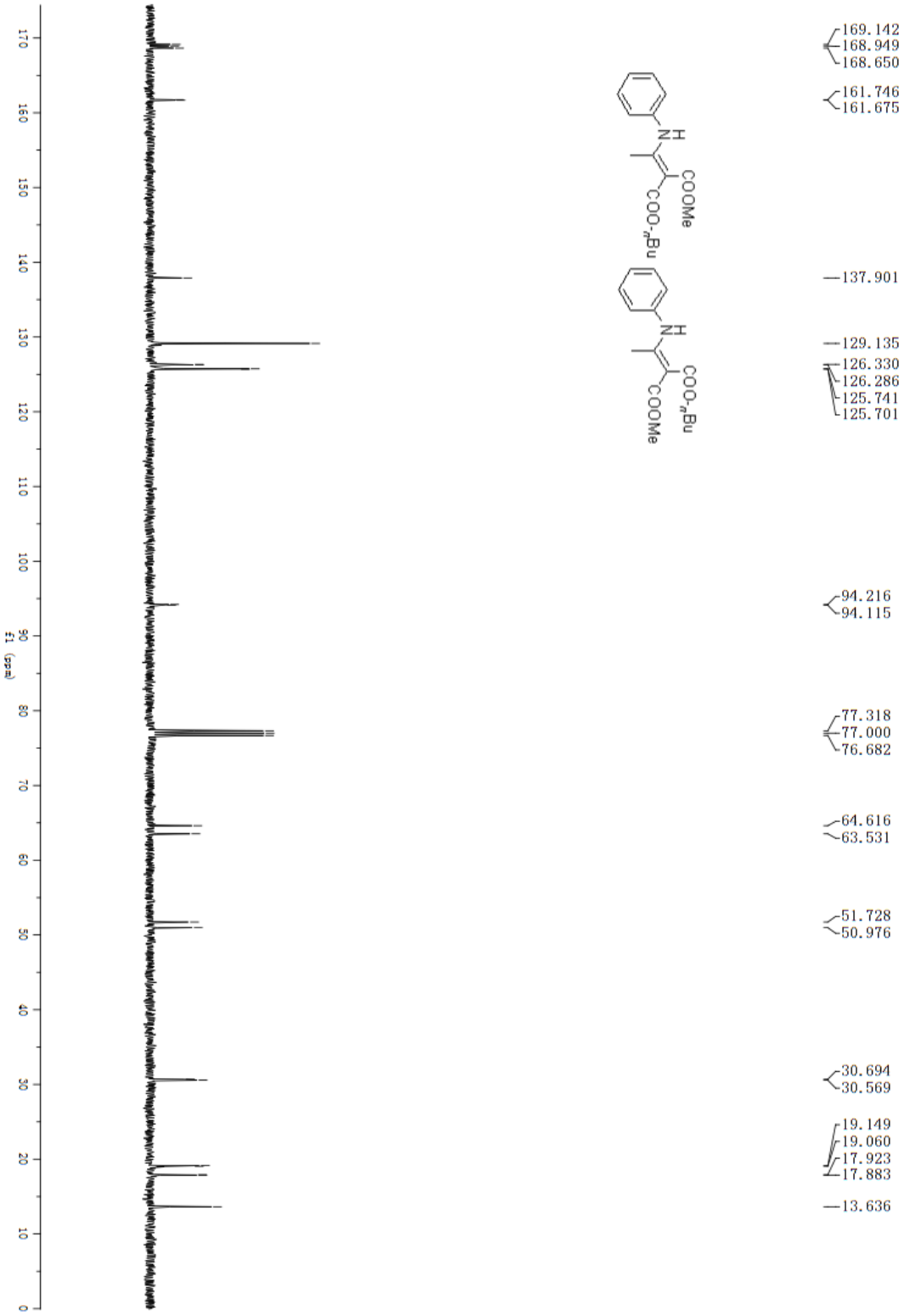

CO2Me
H
N
CO2-nBu

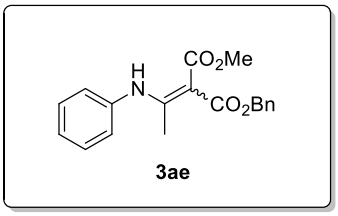
3ad


0.70
1.80
1.05
1.69
1.63
2.65
2.63
1.85
1.84
3.00
11.281
7.381
7.364
7.346
7.281
7.262
7.245
7.112
7.094
4.213
4.198
4.181
4.171
4.154
4.139
3.777
3.741
2.088
1.665
1.632
1.431
1.396
0.959
0.946
COOMe
COO-nBu
COO-nBu
COOMe
f1 (ppm)

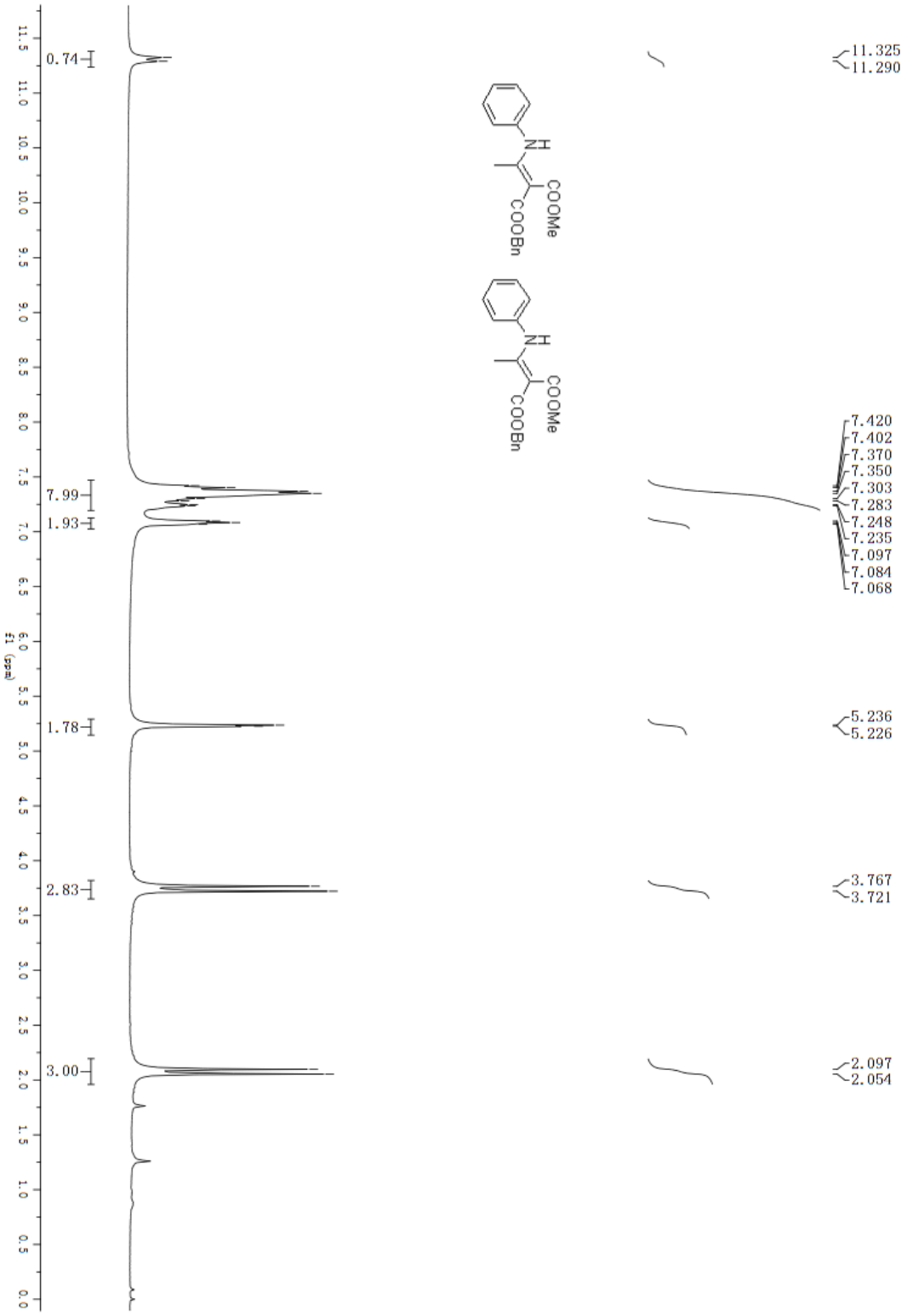

CO2Me
H
N
CO2-nBu

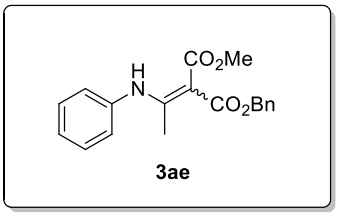
3ad


169.142
168.949
168.650
161.746
161.675
137.901
129.135
126.330
126.286
125.741
125.701
94.216
94.115
77.318
77.000
76.682
64.616
63.531
51.728
50.976
30.694
30.569
19.149
19.060
17.923
17.883
13.636
f1 (ppm)

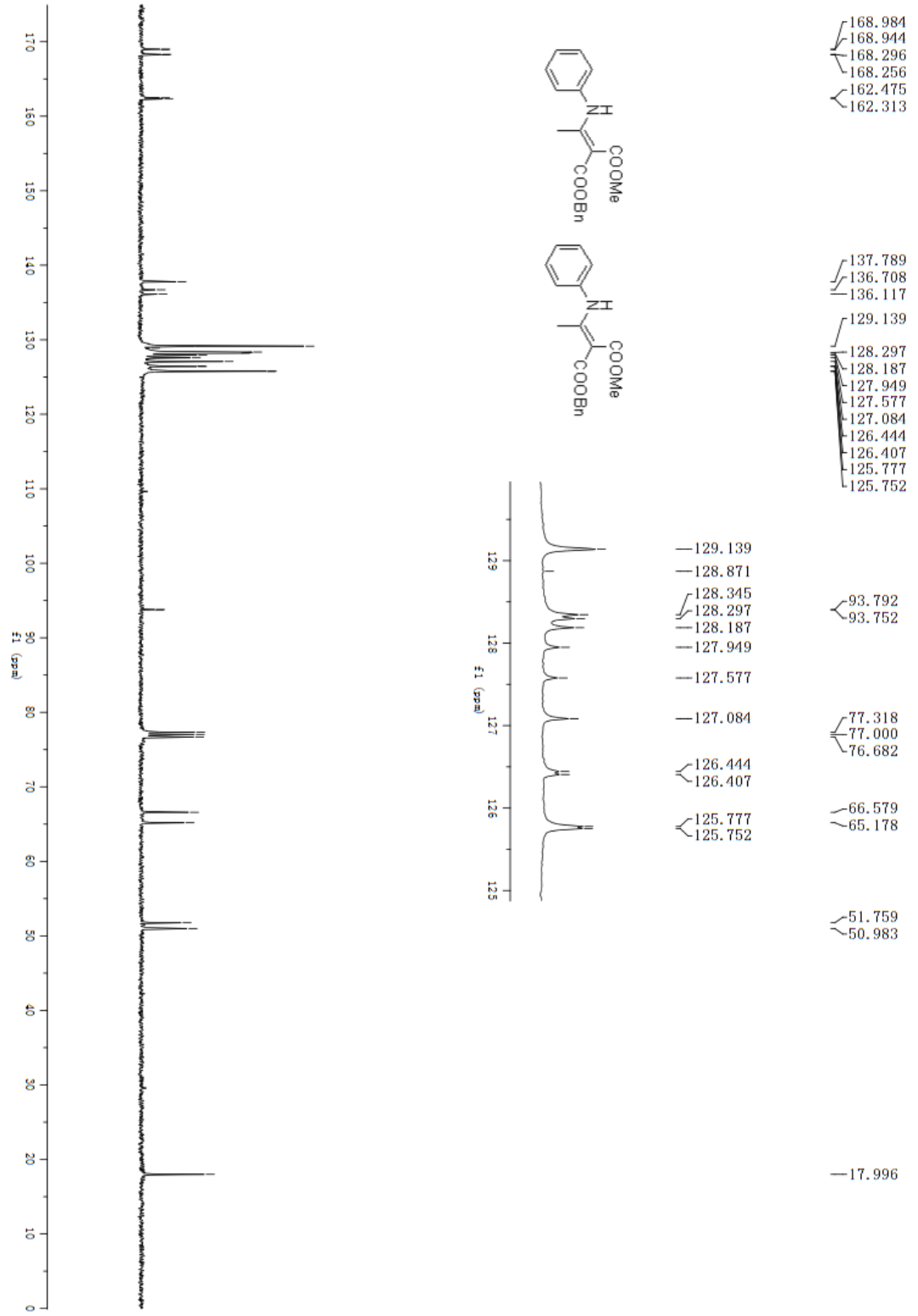

CO2Me
H
N
CO2Bn

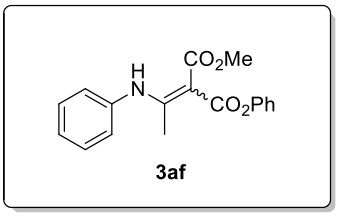
3ae


0.74
7.99
1.93
1.78
2.83
3.00
f1 (ppm)
COOMe
COOBn
11.325
11.290
7.420
7.402
7.370
7.350
7.303
7.283
7.248
7.235
7.097
7.084
7.068
5.236
5.226
3.767
3.721
2.097
2.054

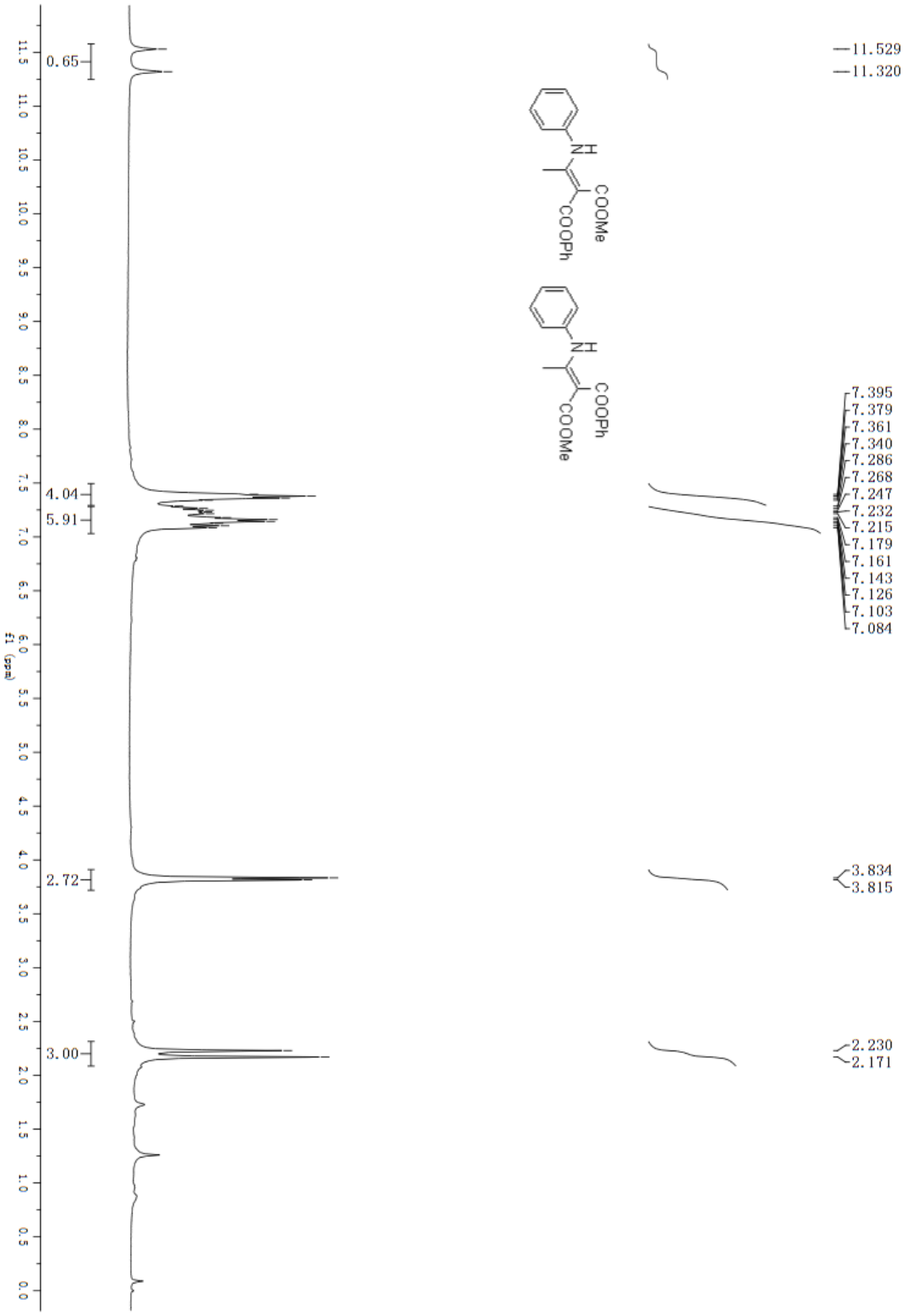

CO2Me
H
N
CO2Bn

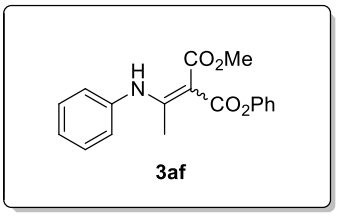
3ae


168.984
168.944
168.296
168.256
162.475
162.313
COOMe
COOBn
137.789
136.708
136.117
129.139
128.297
128.187
127.949
127.577
127.084
126.444
126.407
125.777
125.752
COOMe
COOBn
129.139
128.871
128.345
128.297
128.187
127.949
127.577
127.084
126.444
126.407
125.777
125.752
93.792
93.752
77.318
77.000
76.682
66.579
65.178
51.759
50.983
17.996

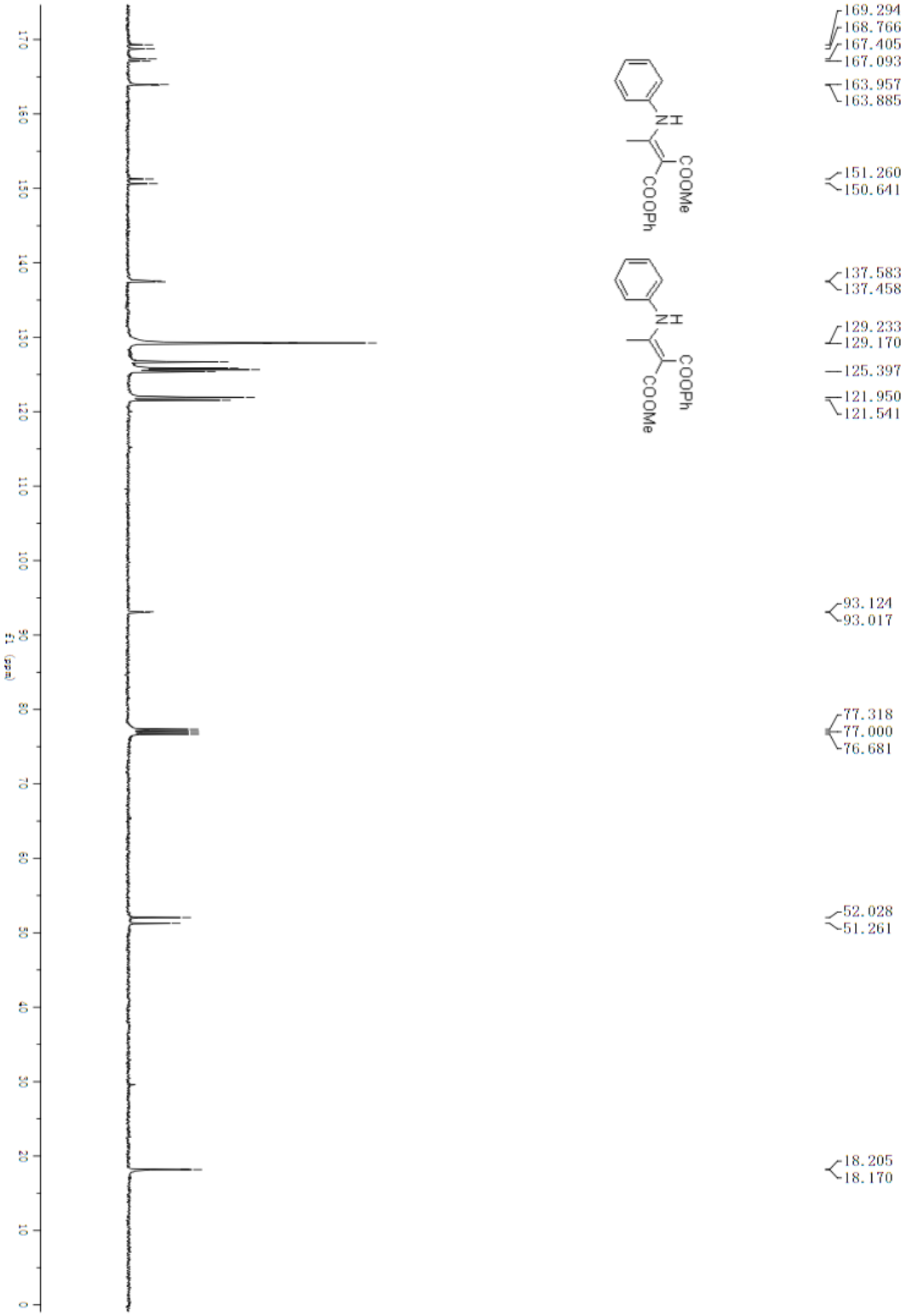

CO2Me
H
N
CO2Ph

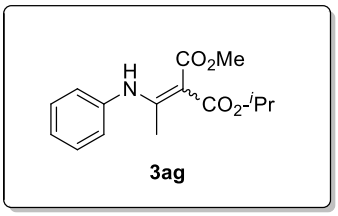
3af


0.65
4.04
5.91
2.72
3.00
f1 (ppm)
11.529
11.320
7.395
7.379
7.361
7.340
7.286
7.268
7.247
7.232
7.215
7.179
7.161
7.143
7.126
7.103
7.084
3.834
3.815
2.230
2.171
COOMe
COOPh
COOPh
COOMe

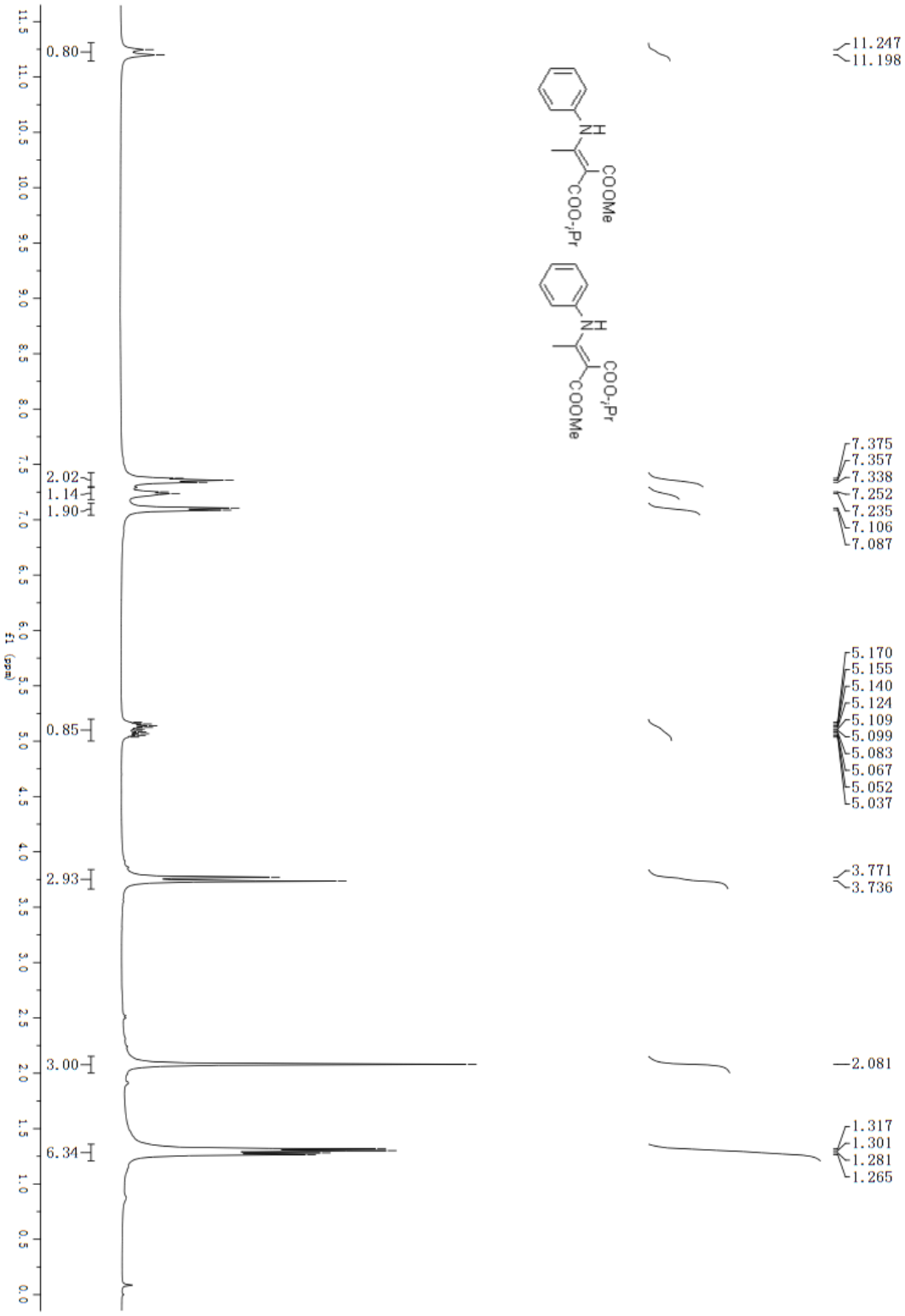

H
N
CO2Me
CO2Ph

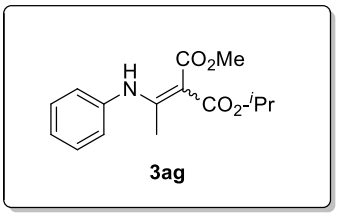
3af


169.294
168.766
167.405
167.093
163.957
163.885
151.260
150.641
137.583
137.458
129.233
129.170
125.397
121.950
121.541
93.124
93.017
77.318
77.000
76.681
52.028
51.261
18.205
18.170
COOMe
COOPh
COOPh
COOMe
f1 (ppm)

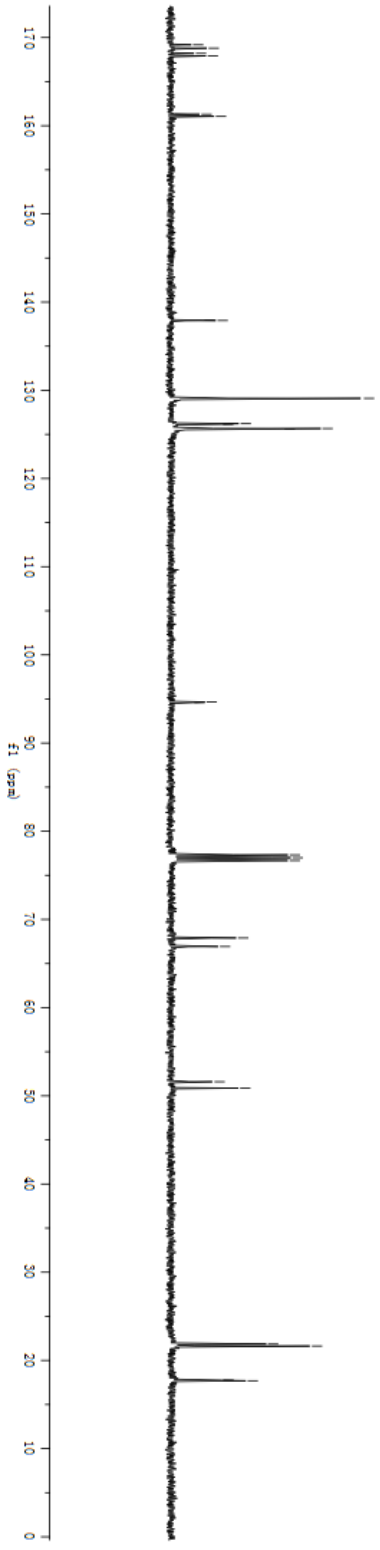

CO2Me
H
N
CO2-iPr

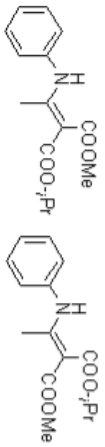
3ag


11.247
11.198
7.375
7.357
7.338
7.252
7.235
7.106
7.087
5.170
5.155
5.140
5.124
5.109
5.099
5.083
5.067
5.052
5.037
3.771
3.736
2.081
1.317
1.301
1.281
1.265
0.80
2.02
1.14
1.90
0.85
2.93
3.00
6.34
COOMe
COO-iPr
COO-iPr
COOMe
f1 (ppm)

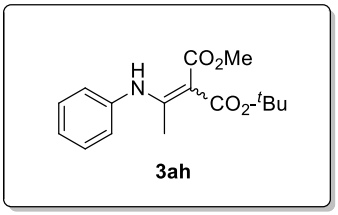


3ag

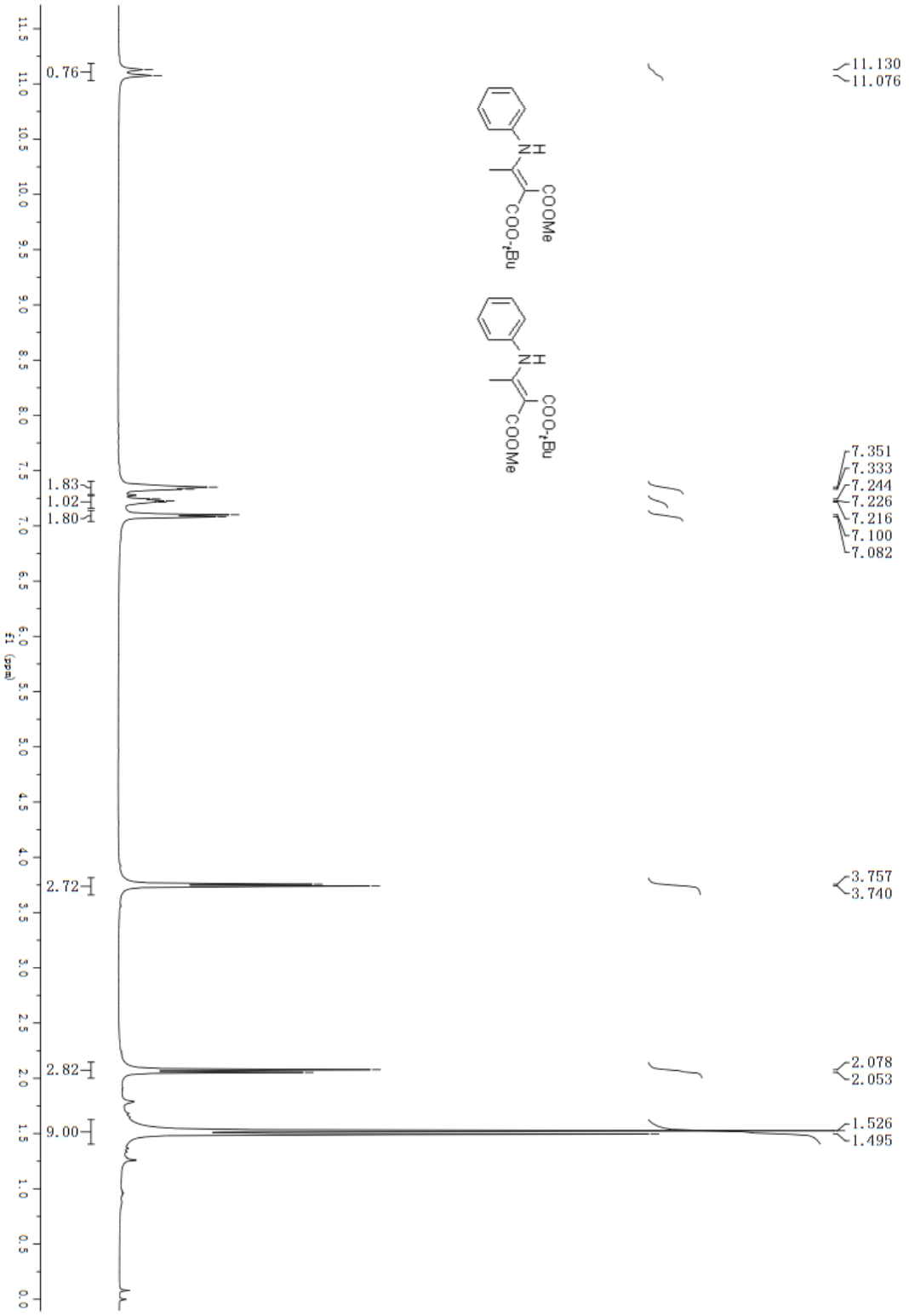


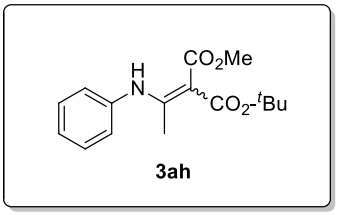


169.171
168.794
168.199
167.910
161.299
161.056
137.958
137.911
129.084
126.216
126.143
125.663
125.596
94.664
94.588
77.318
77.000
76.681
67.900
66.930
51.601
50.876
21.854
21.632
17.759
17.695

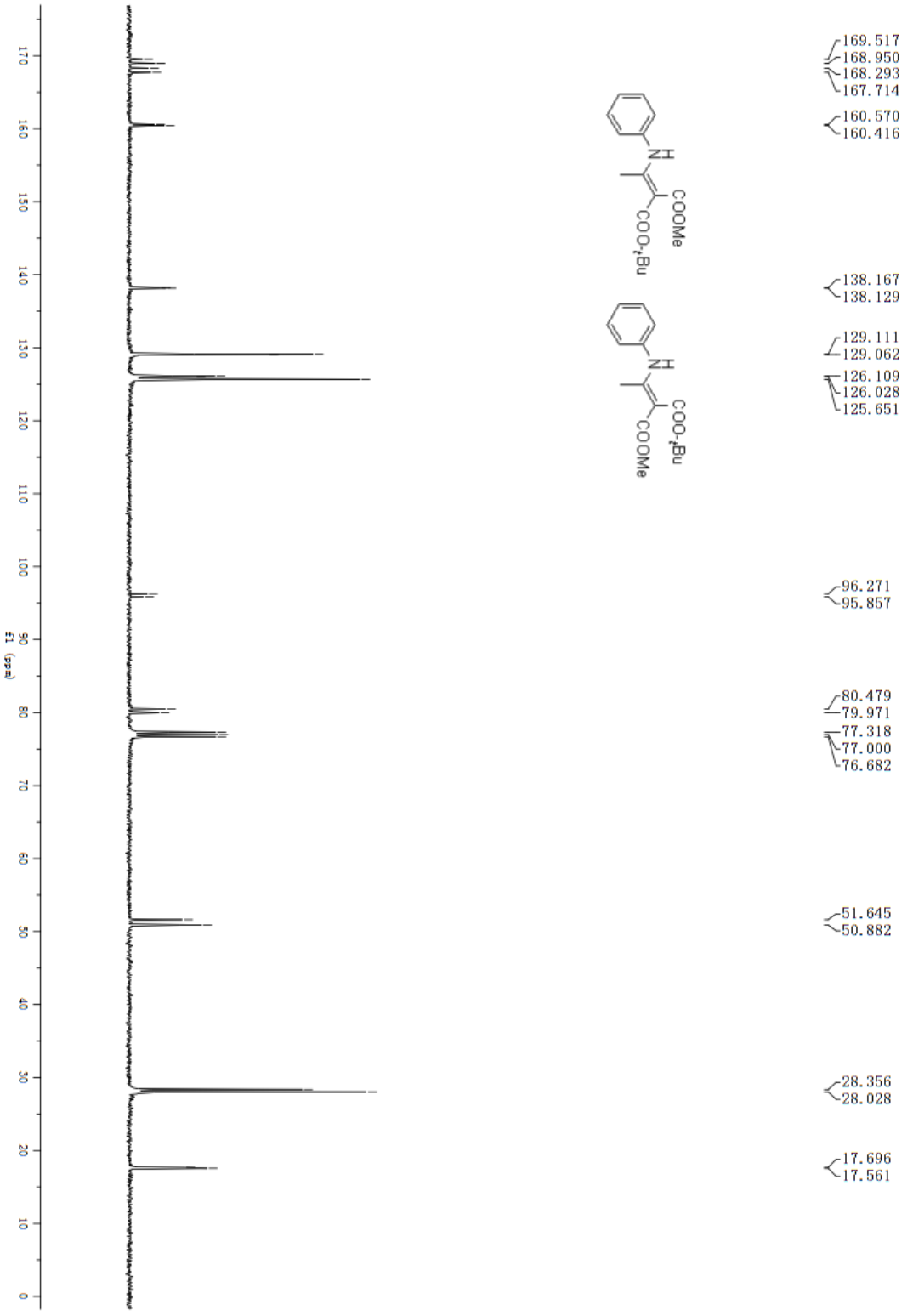

CO2Me
H
N
CO2-tBu

3ah


11.130
11.076
7.351
7.333
7.244
7.226
7.216
7.100
7.082
3.757
3.740
2.078
2.053
1.526
1.495
0.76
1.83
1.02
1.80
2.72
2.82
9.00
COOMe
COO-tBu
COO-tBu
COOMe
f1 (ppm)


CO2Me
H
N
CO2-tBu

3ah


169.517
168.950
168.293
167.714
160.570
160.416
138.167
138.129
129.111
129.062
126.109
126.028
125.651
96.271
95.857
80.479
79.971
77.318
77.000
76.682
51.645
50.882
28.356
28.028
17.696
17.561
COOMe
COO-tBu
COO-tBu
COOMe
f1 (ppm)

6. X-Ray Structure of 3ha.