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Electronic Supplementary Information

Synthesis of β-enamino malonates through caesium carbonate-promoted reaction of nitro-substituted donor-acceptor cyclopropanes

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A. Experimental Procedures and Characterization Data

General Remarks. Melting points were determined by the open capillary tube method and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. High-resolution mass spectra (ESI) were recorded on a Q-TOF mass spectrometer. X-ray crystallographic data were collected on a CCD diffractometer using graphite-monochromated Mo Kα radiation. Thin layer chromatography (TLC) was performed on precoated alumina sheets and detected under UV light. Silica gel (200−400 mesh) was used for column chromatography. Cyclopropanes **1a−j** were prepared as per our reported procedure[1] and all are known compounds.[1-3]

General procedure for the synthesis of β-enamino malonates 5a-af and 10a-b: To a suspension of nitrocyclopropane dicarboxylates **1** (1.0 mmol) in water (2 mL) were added aromatic primary amine **4** (1.0 mmol), sodium dodecyl sulfate (58 mg, 0.2 mmol), and caesium carbonate (358 mg, 1.1 mmol) and stirred at room temperature for 12 h. Next, the reaction mixture was mixed with silica gel to make slurry, charged on a silica gel column and eluted using ethyl acetate/hexane (1:9 v/v) to obtain the pure product.

Diethyl 2-(2-phenyl-1-(phenylamino)ethylidene)malonate (5a): Colourless liquid (0.299 mg, 87%). R_f = 0.51 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.12 (s, 1H), 7.19–7.06 (m, 6H), 6.90 (dd, J_1 =19.2 Hz, J_2 = 7.2 Hz, 4H), 4.15 (q, J = 7.0 Hz, 2H), 4.00 (q, J = 7.0 Hz, 2H), 3.80 (s, 2H), 1.23 (t, J = 7.0 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.5, 162.9, 138.0, 136.6, 129.1, 128.4, 128.3, 126.7, 126.6, 126.4, 95.8, 60.7, 60.0, 35.2, 14.4, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{23}NO_4Na$, 376.1519; found: 376.1522.

Diethyl (2-(2-phenyl-1-(*p*-tolylamino)ethylidene)malonate (5b): Colourless liquid (0.243 mg, 68%). R_f = 0.62 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.21 (s, 1H), 7.24–7.16 (m, 3H), 7.06 (t, J = 6.2 Hz, 4H) 6.87 (d, J = 8.0 Hz, 2H), 4.25 (q, J = 3.6 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 3.91 (s, 2H), 2.34 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 168.6, 166.7, 163.3, 136.7, 136.6, 135.2, 129.6, 128.4, 128.3, 126.5, 126.4, 95.3, 61.5, 60.6, 59.9, 41.7, 35.1, 21.0, 14.4,

14.0 ppm. HRMS (ESI–TOF) *m/z*: [M + H]$^+$ calcd for $C_{22}H_{26}NO_4$, 368.1856; found: 368.1858.

Diethyl 2-(1-((2-iodophenyl)amino)-2-phenylethylidene)malonate (5e): Colourless liquid (0.343 mg, 73%). R_f = 0.68 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.89 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H) 7.12–7.19 (m, 1H), 7.06 (t, *J* = 4.0 Hz, 3H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.86–6.81 (m, 3H), 4.17 (q, *J* = 7.2 Hz, 2H) 4.05 (q, *J* = 7.2 Hz, 2H), 3 .70 (s, 2H), 1.24 (t, *J* = 7.2 Hz ,3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 168.4, 161.9, 140.2, 139.4, 135.8, 128.7, 128.6, 128.3, 126.6, 99.1, 97.0, 60.9, 60.2, 35.6, 14.3, 14.1 ppm. HRMS (ESI–TOF) *m/z*: [M + H]$^+$ calcd for $C_{21}H_{23}INO_4$, 480.0666; found: 480.0678.

Diethyl 2-(1-(naphthalen-1-ylamino)-2-phenylethylidene)malonate (5f): Yellow liquid: (0.300 mg, 76%). R_f = 0.63 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.43 (s, 1H), 7.88 (t, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.54–7.47 (m, 2H), 7.38–7.31 (m, 3H), 7.11–7.06 (m, 2H), 6.90–6.88 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.80 (s, 2H), 1.38 (t, *J* = 7.6 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 168.6, 164.2, 136.5, 134.1, 134.0, 130.8, 128.7, 128.5, 128.1, 127.8, 126.9, 126.3, 125.1, 122.5, 96.1, 63.0, 62.6, 60.8, 60.1, 46.3, 37.5, 35.8, 14.4, 14.0 ppm. HRMS (ESI–TOF) *m/z*: [M + Na]$^+$ calcd for $C_{25}H_{25}NO_4Na$, 426.1676; found: 426.1683.

Diethyl 2-(2-(*p*-tolyl)-1-(*m*-tolylamino)ethylidene)malonate (5h): Colourless liquid (0.291 mg, 82%). R_f = 0.61 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.01 (s, 1H), 7.05 (dd, J_1 = 14.4 Hz, J_2 = 6.6 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 3H) 6.81 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.64 (s, 1H), 4.13 (q, *J* = 7.0 Hz, 2H) 4.00 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 2H), 2.20 (s, 3H), 2.15 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 168.6, 163.3, 139.0, 137.9, 135.9, 133.7, 129.4, 128.9, 128.8, 128.3, 127.3, 123.4, 95.5, 60.7, 59.9, 34.9, 21.2, 21.0, 14.4, 14.0 ppm. HRMS (ESI–TOF) *m/z*: [M + Na]$^+$ calcd for $C_{23}H_{27}NO_4Na$, 404.1832; found: 404.1856.

Diethyl 2-(2-(*p*-tolyl)-1-(*p*-tolylamino)ethylidene)malonate (5i): Colourless liquid (0.269 mg, 75%). R_f = 0.55 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.19 (s, 1H),

7.06 (dd, J_1 = 7.8 Hz, J_2 = 18.6 Hz, 4H), 6.91 (dd, J_1 = 8.2 Hz, J_2 = 19.0 Hz, 4H), 4.25 (q, J = 7.2 Hz, 2H) 4.10 (q, J = 7.2 Hz, 2H), 3.86 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 1.34 (t, J = 7.2 Hz 3H), 1.18 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 163.5, 136.5, 135.9, 135.3, 133.7, 129.6, 129.0, 128.2, 126.4, 95.2, 60.6, 59.8, 34.7, 21.02, 20.98, 14.4, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{28}NO_4$, 382.2013; found: 382.2013.

Diethyl 2-(1-(2-bromo)-4-(methylphenyl)amino)-2-(*p*-tolyl)ethylidene)malonate (5j): Colourless liquid (0.304 mg, 71%). R_f = 0.69 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.90 (s, 1H), 7.28 (s, 1H), 6.88 (t, J = 6.6 Hz, 3H), 6.78 (d, J = 7.2 Hz, 3H), 4.15 (q, J = 7.0 Hz, 2H), 4.01 (q, J = 7.0 Hz, 2H), 3.67 (s, 2H), 2.22 (s, 3H), 2.19 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 168.4, 162.9, 138.5, 136.0, 134.4, 133.4, 133.1, 129.4, 128.9, 128.5, 128.44, 128.38, 121.9, 60.8, 60.0, 35.0, 21.0, 20.7, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{27}BrNO_4$, 460.1118; found: 460.1103.

Diethyl 2-(1-(naphthalen-1-ylamino)-2-(*p*-tolyl)ethylidene)malonate (5k): Yellow liquid (0.335 mg, 86%). R_f = 0.63 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.46 (s, 1H), 7.87 (q, J = 7.8 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.52–7.46 (m, 2H), 7.34 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 6.88 (d, J = 7.6 Hz, 2H), 6.79 (d, J = 7.6 Hz, 2H), 4.34 (q, J = 7.0 Hz, 2H), 4.19 (q, J = 7.0 Hz, 2H), 3.78 (s, 2H), 2.23 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 168.6, 164.5, 135.8, 134.1, 133.4, 130.8, 129.4, 128.8, 128.3, 128.2, 128.1, 127.7, 126.9, 126.4, 125.09, 125.08, 122.7, 95.9, 60.8, 60.0, 41.7, 35.4, 20.9, 14.4, 14.1 ppm. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{27}NO_4Na$, 440.1832; found: 440.1859.

Diethyl 2-2-(4-isopropylphenyl)-1-(phenylamino)ethylidene)malonate (5l): Colourless liquid (0.301 mg, 89%). R_f = 0.66 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.14 (s, 1H), 7.18–7.09 (m, 3H), 6.96 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 7.6 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 4.16 (q, J = 7.0 Hz, 2H), 3.97 (q, J = 7.2 Hz, 2H), 3.77 (s, 2H), 2.80–2.70 (m, 1H), 1.22 (t, J = 7.0 Hz, 3H), 1.12 (d, J = 6.8 Hz, 6H), 1.04 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.5, 163.3, 147.0, 138.0, 133.9,

129.3, 129.0, 128.4, 126.6, 126.5, 126.3, 95.7, 60.6, 59.9, 34.7, 33.7, 24.0, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{30}NO_4$, 396.2169; found: 396.2174.

Diethyl 2-(2-(4-isopropylphenyl)-1-(*p*-tolylamino)ethylidene)malonate (5m): Colourless liquid (0.305 mg, 86%). R_f = 0.73 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 11.11 (s, 1H), 7.19 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 3H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.76 (s, 2H), 2.80–2.72 (m, 1H), 2.24 (s, 3H), 1.22 (t, *J* = 6.8 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 6H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 168.6, 163.7, 147.0, 136.5, 135.3, 134.0, 129.6, 128.4, 126.4, 126.3, 95.2, 60.6, 59.8, 34.6, 33.7, 24.0, 21.0, 14.4, 13.9 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{32}NO_4$, 410.2326; found: 410.2337.

Diethyl 2-(2-(4-isopropylphenyl)-1-(naphthalen-1-ylamino)ethylidene)malonate (5n): Yellow liquid (0.291 mg, 76%). R_f = 0.69 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 11.26 (s, 1H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.30–7.22 (m, 2H), 7.18–7.13 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 4.16 (q, *J* = 6.8 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.63 (s, 2H), 2.61–2.54 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 168.8, 164.6, 146.8, 134.2, 134.1, 133.6, 130.9, 128.5, 128.0, 127.7, 126.8, 126.4, 126.1, 125.1, 122.7, 121.0, 109.6, 95.9, 60.8, 60.0, 35.4, 33.7, 24.0, 14.5, 14.1 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{32}NO_4$, 446.2326; found: 446.2322.

Diethyl 2-(2-(4-chlorophenyl)-1-(phenylamino)ethylidene)malonate (5q): Colourless liquid (0.340 mg, 88%). R_f = 0.59 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 11.06 (s, 1H), 7.18–7.12 (m, 3H), 7.04–6.98 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 3H), 6.78 (d, *J* = 7.2 Hz, 1H), 4.15(q, *J* = 7.0, 2H) 4.04 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 2H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.4, 162.0, 138.6, 137.8, 134.1, 129.5, 129.1, 128.7, 126.9, 126.8, 126.7, 126.6, 96.1, 60.8, 60.0, 34.9, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}ClNO_4$, 388.1310; found: 388.1313.

Diethyl 2-(2-(4-chlorophenyl)-1-(*p*-tolylamino)ethylidene)malonate (5r): Colourless liquid (0.316 mg, 90%). R_f = 0.61 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ

11.15 (s, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.85 (m, 2H), 4.32–4.23 (m, 2H), 4.19–4.09 (m, 2H), 3.85 (s, 2H), 2.35 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 168.5, 162.8, 136.8, 135.3, 135.1, 132.2, 129.8, 129.7, 128.4, 126.6, 115.3, 95.4, 60.8, 60.0, 34.6, 21.0, 14.4, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{25}ClNO_4$, 402.1467; found: 402.1470.

Diethyl 2-(1-((2-bromo-4-methylphenyl)amoino)-2-4-chlorophenyl)ethylidene) malonate (5s): Colourless liquid (Yield: 0.345 mg, 82%). R_f = 0.66 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.80 (s, 1H), 7.23 (s, 1H), 7.20 (d, J = 4.0 Hz, 1H), 7.05–6.98 (m, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.80 (q, J = 7.6 Hz, 2H), 6.73 (s, 1H), 4.20–142 (m, 2H), 4.11–4.06 (m, 2H), 3.66 (s, 2H), 2.24 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H) 1.15 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 168.4, 161.7, 139.0, 137.9, 134.2, 133.9, 133.5, 129.4, 128.9, 128.8, 128.5, 126.8, 126.7, 122.4, 96.8, 60.9, 60.2, 35.2, 20.7, 14.3, 14.1 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{24}BrClNO_4$, 480.0572; found: 480.0570.

Diethyl 2-(2-((4-bromophenyl)-1-(*p*-tolylamino)ethylidene)malonate (5t): Colourless liquid (0.301 mg, 87%). R_f = 0.64 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.02 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 7.6 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H) 4.14 (q, J = 7.0 Hz, 2H), 4.01 (q, J = 7.2 Hz, 2H), 3.71 (s, 2H), 2.24 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 168.5, 162.7, 136.9, 135.8, 135.1, 132.0, 131.3, 130.2, 129.7, 126.6, 120.3, 95.4, 60.8, 60.0, 34.7, 21.0, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{24}BrNO_4Na$, 468.0781; found: 468.0776.

Diethyl 2-(1-((2-bromo-4-methylphenyl)amino)-2-(4-bromophenyl)ethylidene) malonate (5u): Colourless liquid (0.385 mg, 94%). R_f = 0.57 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.83 (s, 1H), 7.27 (s, 1H), 7.19 (t, J = 4.2 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.77 (t, J = 4.2 Hz, 3H), 4.16 (q, J = 7.0Hz, 2H), 4.04 (q, J = 7.0 Hz, 2H), 3.64 (s, 2H), 2.22 (s, 3H), 1.23 (t, J = 7.0 Hz, 3H) 1.12 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 168.3, 162.0, 138.8, 135.1, 134.2, 133.5, 131.3,

130.3, 128.7, 128.5, 122.2, 120.4, 96.8, 60.9, 60.2, 35.0, 20.7, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{24}Br_2NO_4$, 524.0067; found: 524.0097.

Diethyl 2-(2-(4-fluorophenyl)-1-(phenylamino)ethylidene)malonate (5v): Colourless liquid (0.299 mg, 81%). R_f = 0.68 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 11.06 (s, 1H), 7.19–7.11 (m, 3H), 6.84 (d, *J* = 6.0 Hz, 4H), 6.77 (t, *J* = 8.6 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.5, 166.7, 162.74, 162.67, 160.3, 137.8, 132.23, 132.20, 130.0, 129.9, 129.1, 128.8, 126.8, 126.7, 115.2, 115.0, 95.8, 61.5, 60.8, 60.0, 41.7, 34.5, 29.7, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}FNO_4$, 372.1606; found: 372.1618.

Diethyl 2-(2-(4-fluorophenyl)-1-(*m*-tolylamino)ethylidene)malonate (5w): Colourless liquid (0.315 mg, 88%). R_f = 0.63 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 11.02 (s, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.92–6.84 (m, 3H), 6.77 (t, *J* = 8.6 Hz, 2H), 6.66–6.60 (m, 2H), 4.13 (q, *J* = 7.0 Hz, 2H) 4.00 (q, *J* = 7.0 Hz, 2H), 3.72 (s, 2H), 2.13 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.5, 162.9, 162.7, 160.3, 139.1, 137.7, 132.5, 132.4, 130.1, 130.0, 128.9, 127.6, 127.5, 123.6, 115.1, 114.9, 95.6, 60.7, 60.0, 34.6, 21.2, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{25}FNO_4$, 386.1762; found: 386.1754.

Diethyl 2-(2-(4-fluorophenyl)-1-(*p*-tolylamino)ethylidene)malonate (5x): Colourless liquid (0.299 mg, 84%). R_f = 0.55 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 11.01 (s, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.89– 6.85 (m, 2H), 6.80–6.72 (m, 4H), 4.14 (q, *J* = 7.0, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 2H), 2.23 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 168.5, 163.1, 162.7, 160.3, 136.8, 135.2, 132.38, 132.35, 131.2, 130.0, 129.9, 129.7, 129.2, 126.6, 115.9, 115.8, 115.6, 115.1, 114.9, 95.4, 95.3, 61.7, 61.5, 60.7, 59.9, 34.4, 21.0, 14.3, 14.0 ppm. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{24}FNO_4Na$, 408.1582; found: 408.1609.

Diethyl 2-(2-(4-fluorophenyl)-1-(naphthalen-1-ylamino)ethylidene)malonate (5y): Colourless liquid (0.295 mg, 76%). R_f = 0.61 (hexane/EtOAc 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 11.34 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.53–7.45 (m, 2H), 7.38–7.29 (m,2H), 7.10–7.05 (m, 1H), 6.81–6.77 (m, 2H), 6.74–6.69 (m, 2H), 4.37–

4.30 (m, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 2H), 1.39 (t. *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 168.6, 164.0, 162.6, 134.0, 132.09, 132.05, 130.8, 130.2, 130.1, 130.0, 129.9, 128.1, 127.9, 127.0, 126.5, 125.2, 125.0, 122.5, 116.0, 114.9, 114.7, 95.9, 66.3, 63.1, 62.8, 60.9, 60.1, 36.7, 35.1, 14.4, 14.1. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{24}FNO_4Na$, 444.1582; found: 444.1603.

Diethyl 2-(2-naphthalen-1-yl)-1-(*p*-tolylamino)ethylidene)malonate (5ab): Colourless liquid (0.274 mg, 78%). R_f = 0.62 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.5 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.78–7.75 (m, 2H), 7.55 – 7.45 (m, 4H), 6.94 (d, *J* = 8.4Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 4.36–4.28 (m, 4H), 3.90 (q, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 168.3, 163.2, 136.3, 135.2, 133.6, 132.8, 131.4, 129.7, 128.7, 127.2, 126.1, 125.6, 125.53, 125.45, 125.4, 122.8, 115.3, 95.7, 60.5, 60.1, 32.3, 20.8, 14.4, 13.7 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{28}NO_4$, 418.2013; found: 418.2053.

Diethyl (1-((2-bromo-4-methylphenyl)amino)-2-(naphthalene-yl)ethylidene) malonate (5ac): Colourless liquid (0.339 mg, 81%); R_f = 0.59 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.15 (s, 1H), 7.72 (t, *J* = 4.6 Hz, 1H), 3.80 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.36–7.29 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.20–4.16 (m, 4H), 3.83 (q, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) 0.86 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.1, 162.7, 138.3, 134.1, 133.5, 133.4, 132.7, 132.3, 131.4, 128.7, 128.6, 128.5, 127.5, 127.2, 126.0, 125.9, 125.5, 123.8, 122.8, 121.1, 97.1, 63.0, 60.7, 60.1, 32.3, 20.5, 14.3, 13.8 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{27}BrNO_4$, 496.1118; found: 496.1129.

Diethyl-(2-((naphthalene-l-yl-1(naphthalene-1-yl)amino)ethylidene)malonate (5ad): Yellow liquid (0.353 mg, 93%); R_f = 0.56 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.29 (s, 1H), 7.75–7.69 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.37–7.31 (m, 3H), 7.19–7.14 (m,1H), 6.93 (q, *J* = 7.0 Hz, 5H), 6.75 (t, *J* = 6.8 Hz, 2H), 4.18 (t, *J* = 7.2 Hz, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.66 (s, 2H), 1.24 (t, *J* = 7.2Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 168.6, 164.3, 136.5, 134.08, 134.06, 130.8,

128.4, 128.12, 128.10, 127.8, 126.9, 126.5, 126.3, 125.14, 125.10, 122.6, 96.0, 60.8, 60.1, 35.8, 14.4, 14.1 ppm. HRMS (ESI–TOF) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{28}NO_4$, 454.2013; found: 454.2028.

Diethyl (*Z*)-2-(1-(1*H*-benzo[d][1,2,3]triazol-1-yl)-2-(*p*-tolyl)vinyl)malonate (10a): Colourless liquid (0.289 mg, 79%). R_f = 0.62 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.90 (q, *J* = 3.2 Hz, 2H), 7.43–7.39 (m, 4H), 7.28 (d, *J* = 7.6 Hz, 2H), 5.35 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 4H), 2.43 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ166.4, 166.3, 144.5, 144.3, 138.8, 133.0, 130.8, 129.6, 129.06, 128.97, 128.91, 127.7, 127.2, 127.1, 118.6, 118.3, 62.3, 62.0, 58.0, 52.1, 21.4, 14.0, 13.9 ppm. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{23}N_3O_4Na$, 416.1581; found: 416.1586.

Diethyl (Z)-2-(1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-(4-isopropylphenyl)vinyl)malonate (10b) Colourless liquid (0.307 mg,85%); R_f = 0.66 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.92–7.89 (m, 2H), 7.45–7.41 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.36 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 4H), 3.03 (s, 1H), 1.32 (d, *J* = 6.8 Hz, 6H), 1.20 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 147.9, 144.3, 133.0, 131.2, 130.0, 129.0, 127.7, 127.2, 127.1, 126.9, 118.3, 62.0, 52.2, 34.0, 23.9, 23.7, 13.9 ppm. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{27}N_3O_4Na$, 444.1894 found: 444.1920.

Diethyl 2-(2-oxo-2-phenyl-1-(phenylamino)ethylidene)malonate (11): To a solution of **5a** (353 mg, 1.0 mmol) in 1,4-dioxane (3 mL) was added selenium dioxide (111 mg, 1.0 mmol) and the reaction mixture was heated under reflux for 5 h. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was diluted with water and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using EtOAc/hexane (1:9) as eluent to obtain product **11**. Colourless liquid (0.298 mg, 81%); R_f = 0.55 (hexane/EtOAc 9:1); ^{1}H NMR (100 MHz, $CDCl_3$): δ 11.67 (s, 1H), 7.87–7.85 (m, 2H), 7.54–7.50 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.18–7.07 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 2H), 4.38 (dd, J_1 =14.0 Hz, J_2 = 7.0 Hz, 2H), 3.98–3.93 (m, 2H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 169.3, 165.7, 163.4, 137.1, 135.5, 133.8, 129.0, 128.68,

128.66, 126.7, 125.0, 93.6, 60.8, 60.6, 14.3, 13.5 ppm. HRMS (ESI–TOF) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{22}NO_5$, 368.1493; found: 368.1493.

References:

1. T. Selvi and K. Srinivasan, *J. Org. Chem.,* 2014, **79**, 3653−3658.
2. G. Yang, W. Liu, Z. He and Zh. He, *Org. Lett.*, 2016, **18**, 4936−4939;
3. S. Thangamalar and K. Srinivasan, *Eur. J. Org. Chem.*, 2023, **26**, No. e202201084.

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

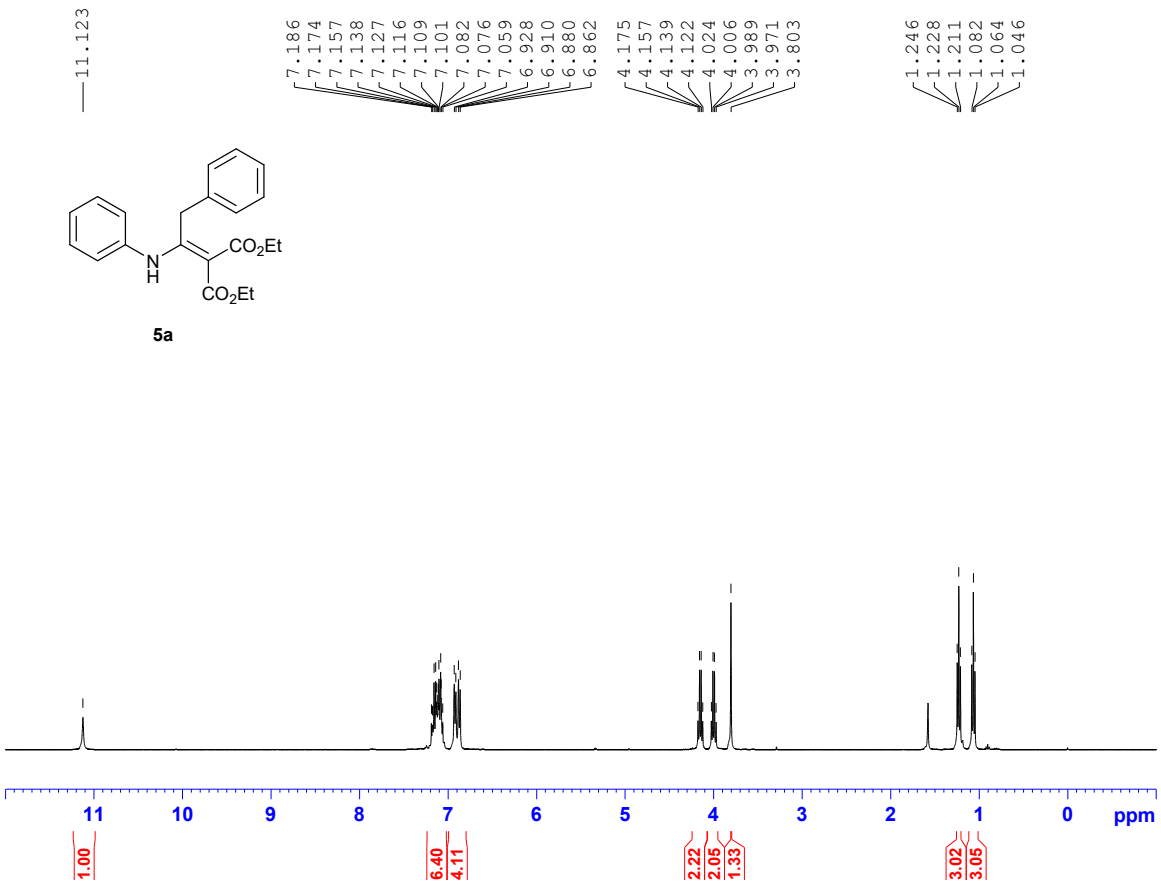

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**

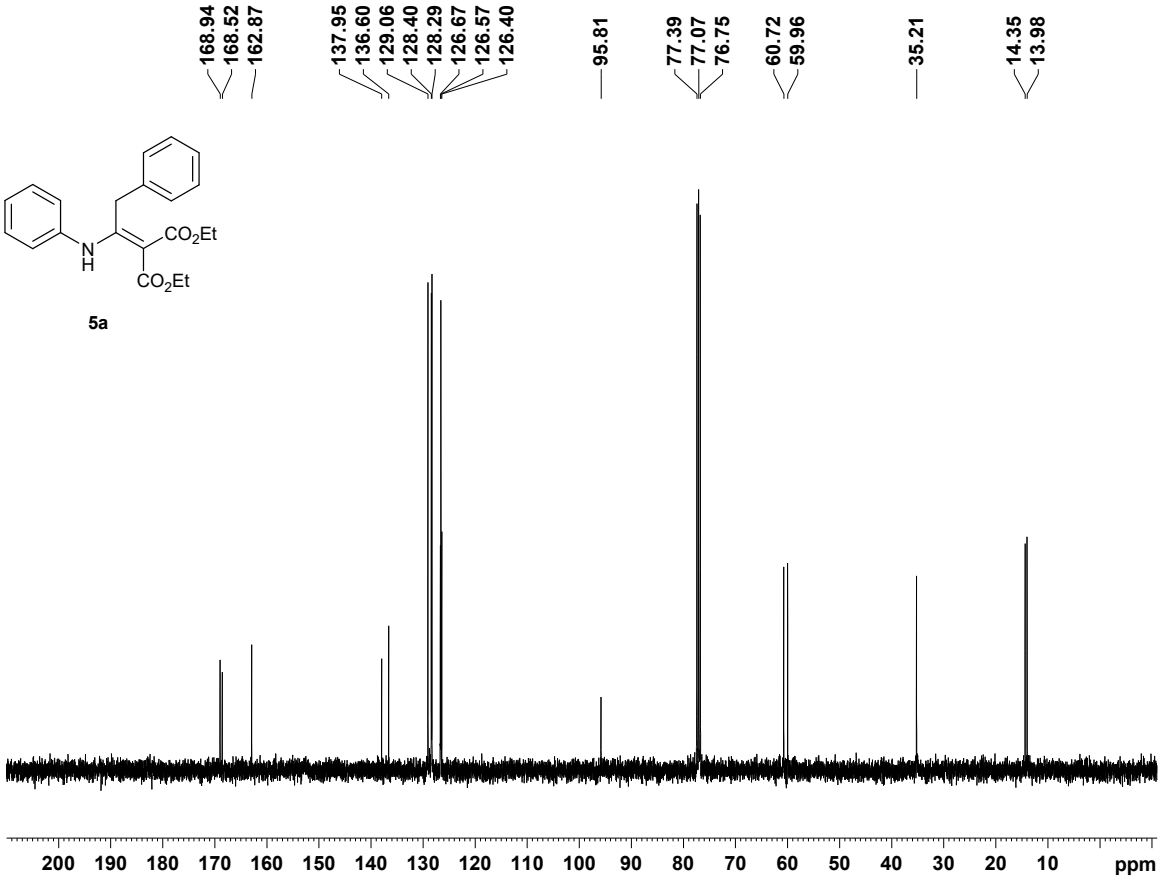

Figure S2. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5a**

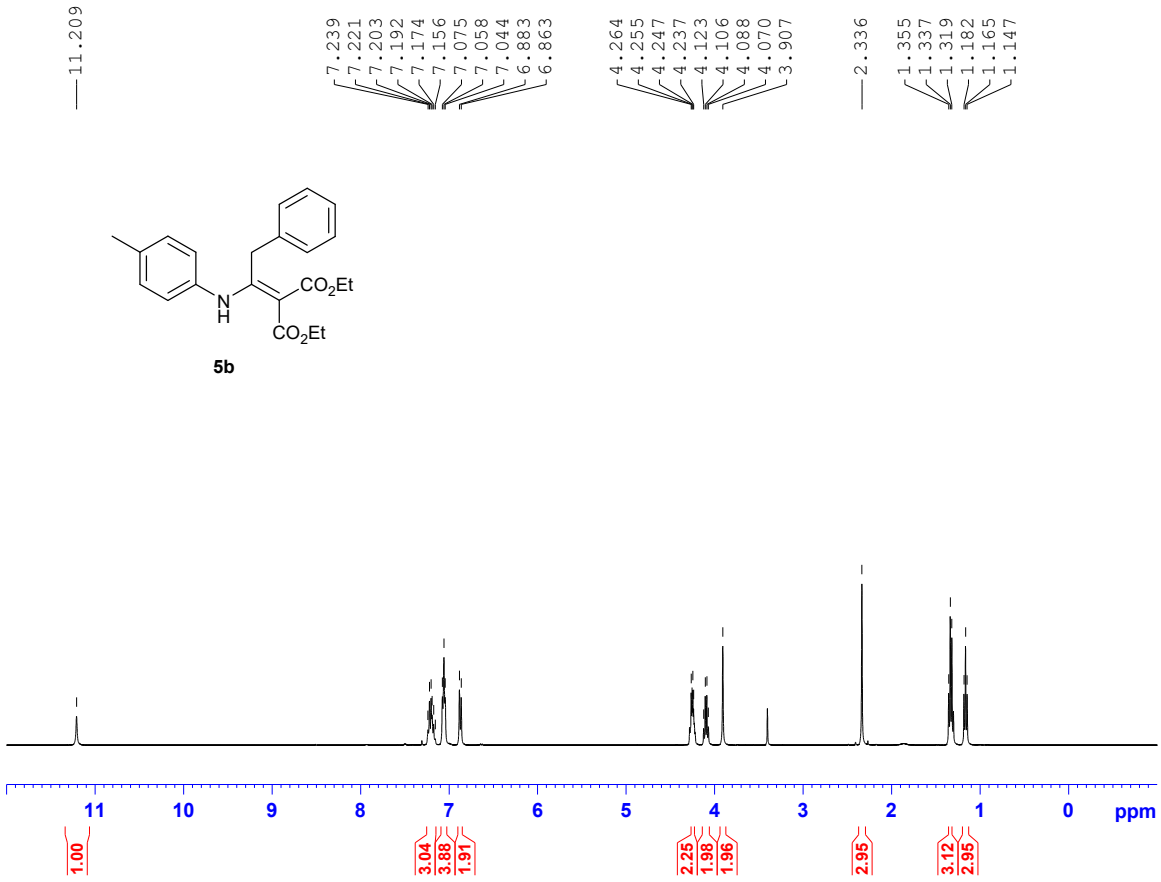

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5b**

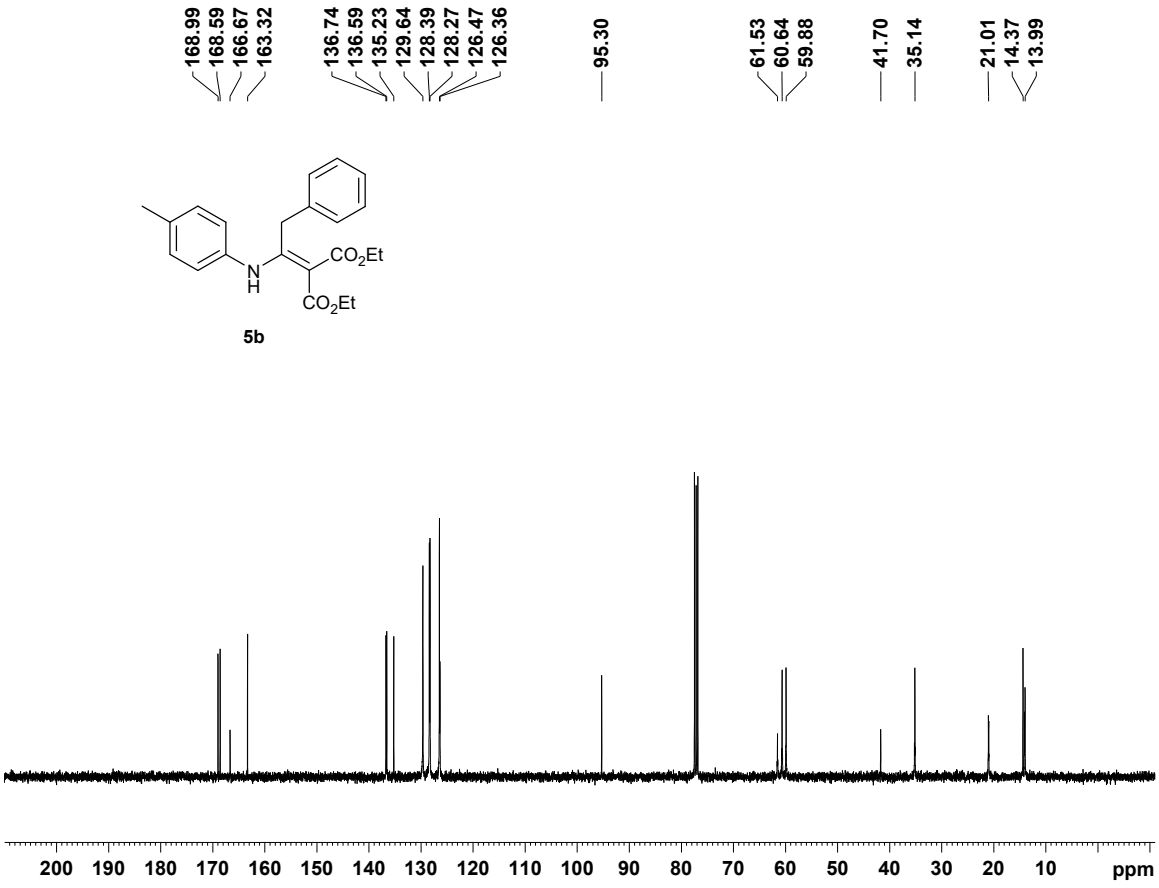

Figure S4. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5b**

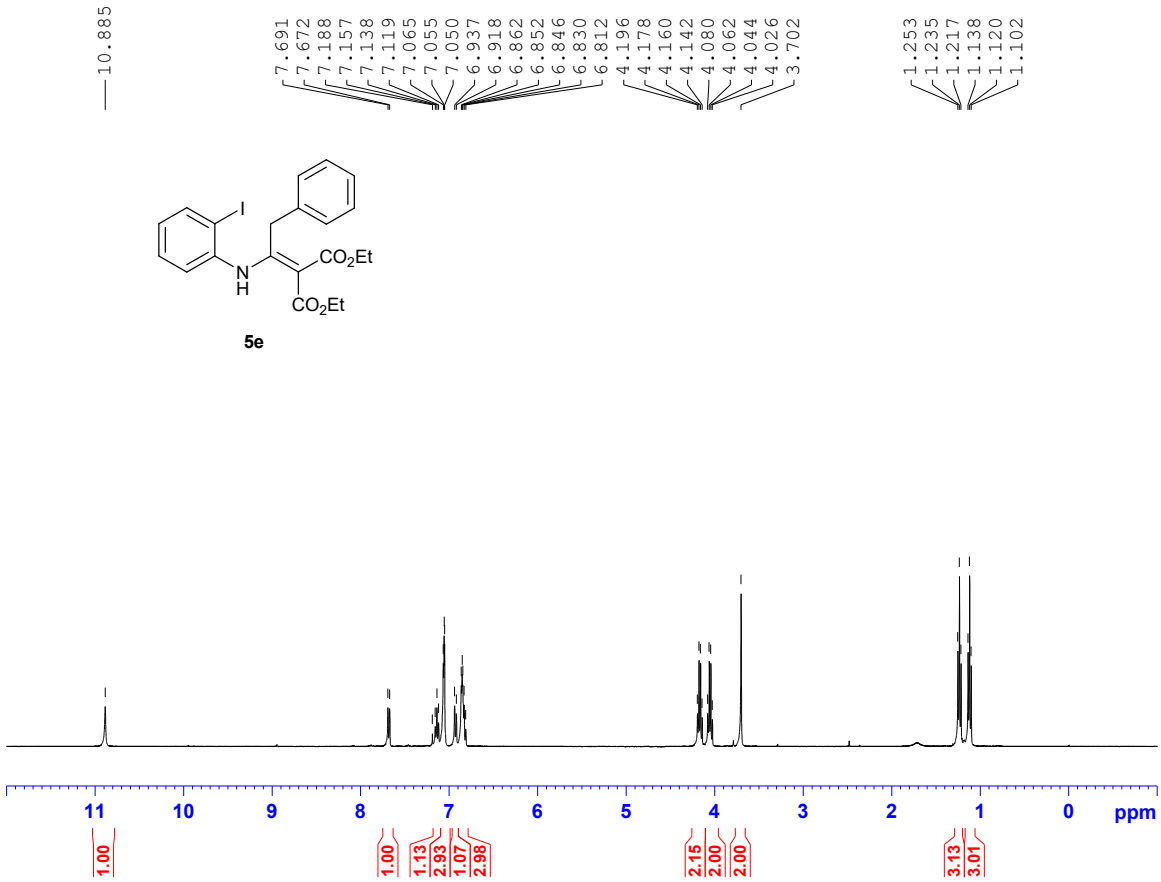

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5e**

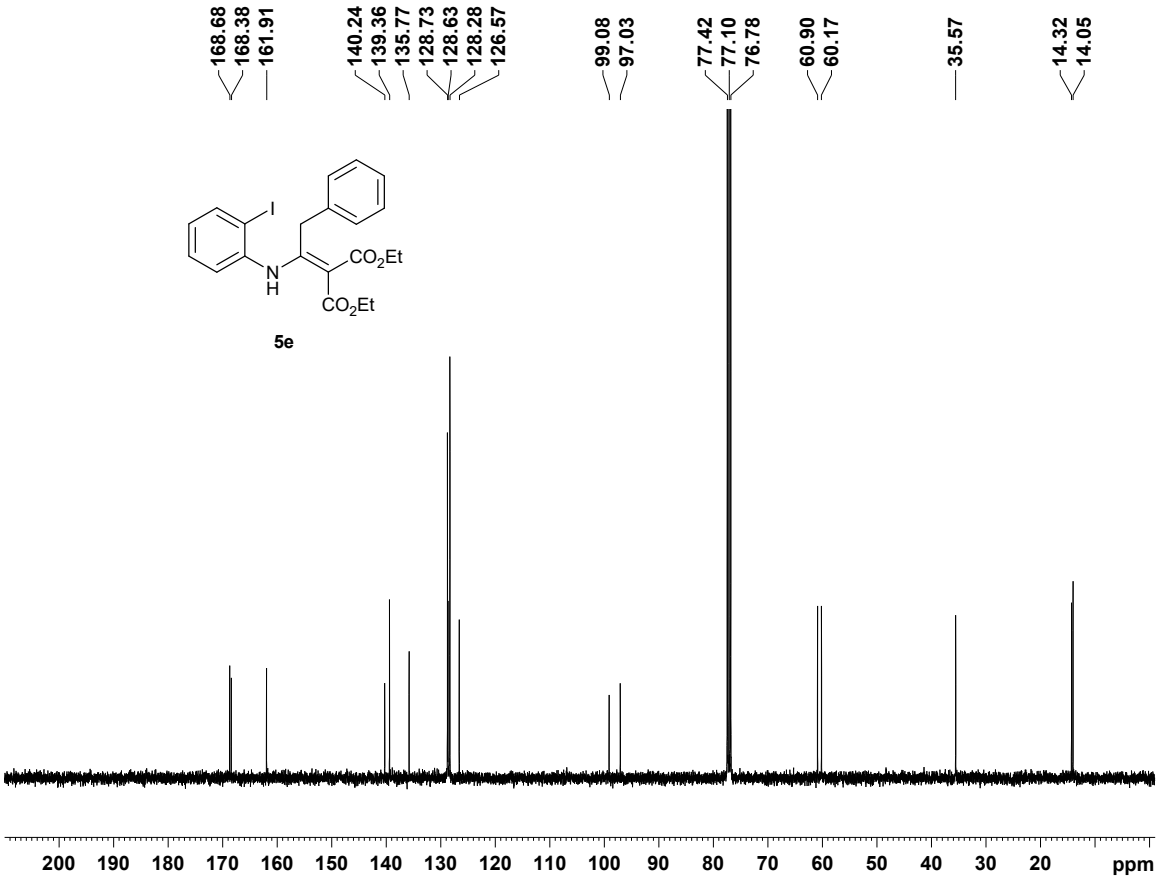

Figure S6. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5e**

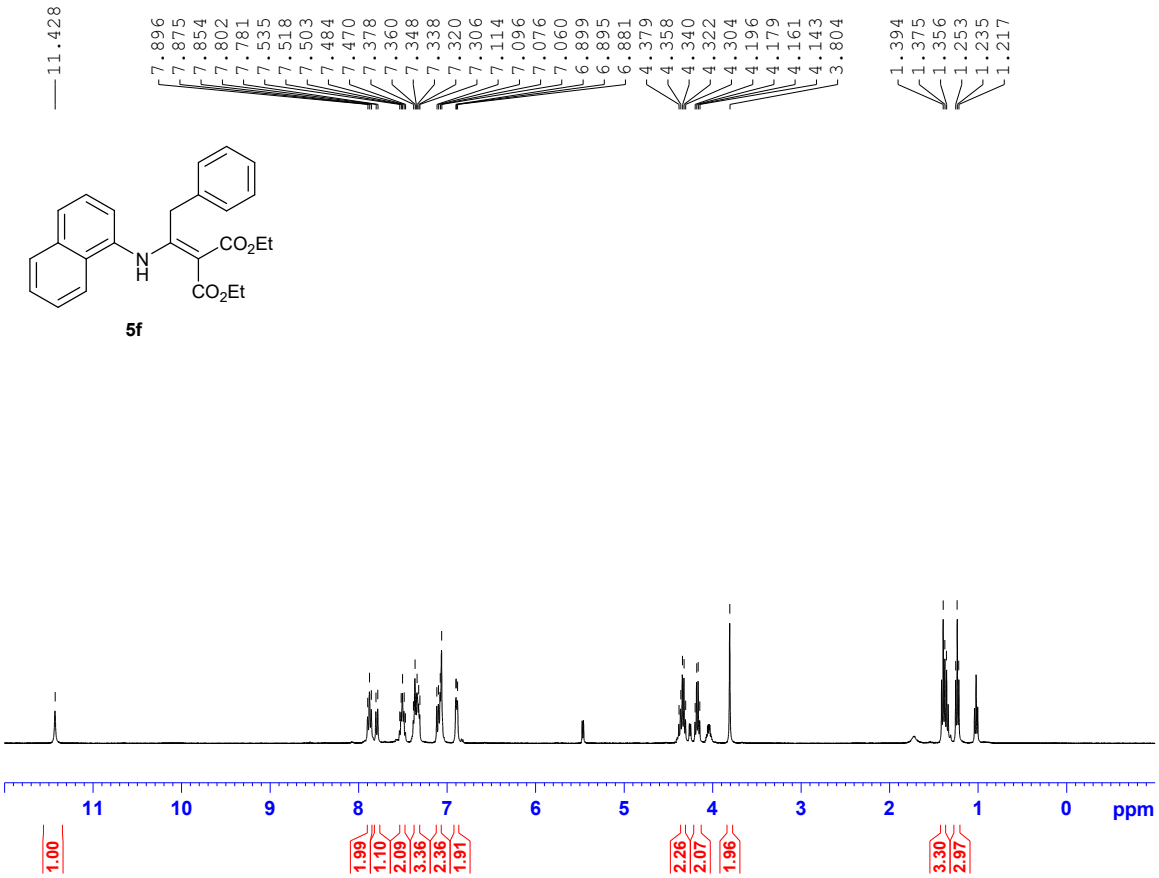

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5f**

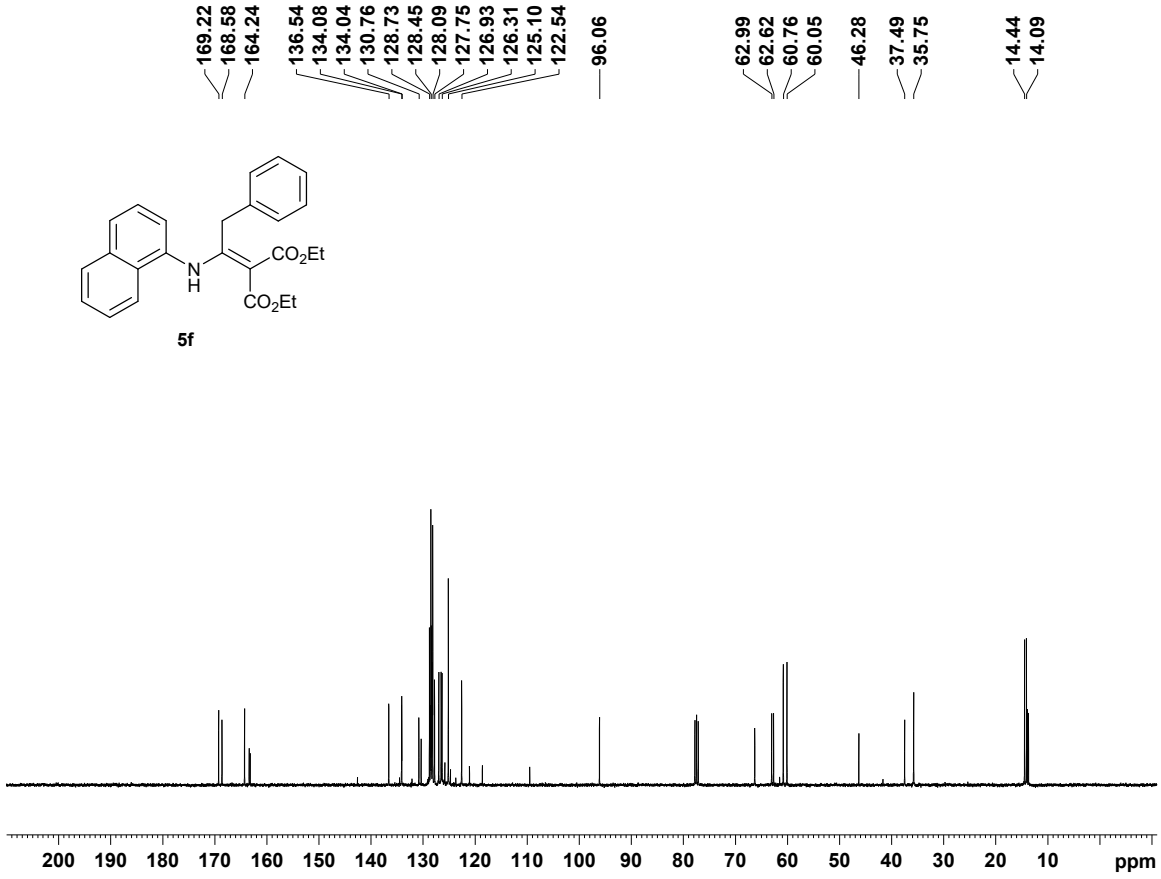

Figure S8. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5f**

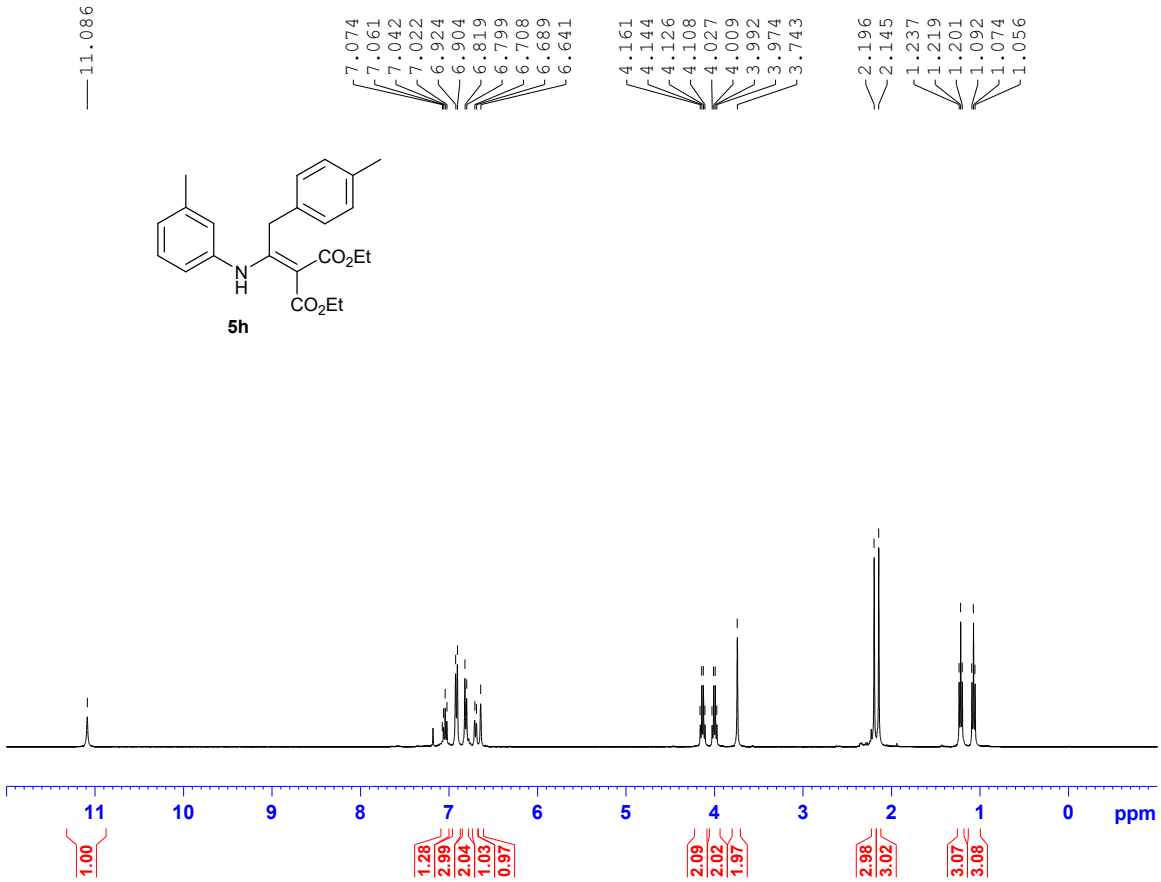

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5h**

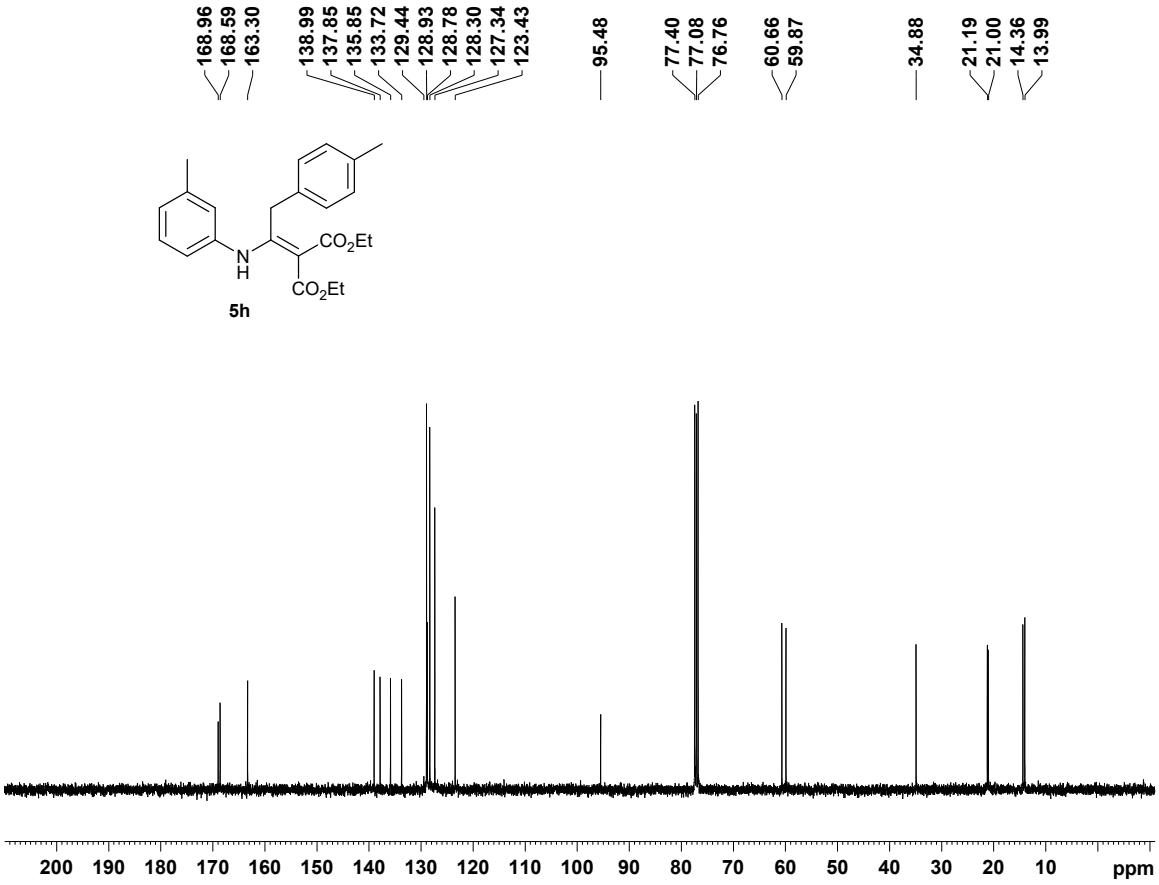

Figure S10. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5h**

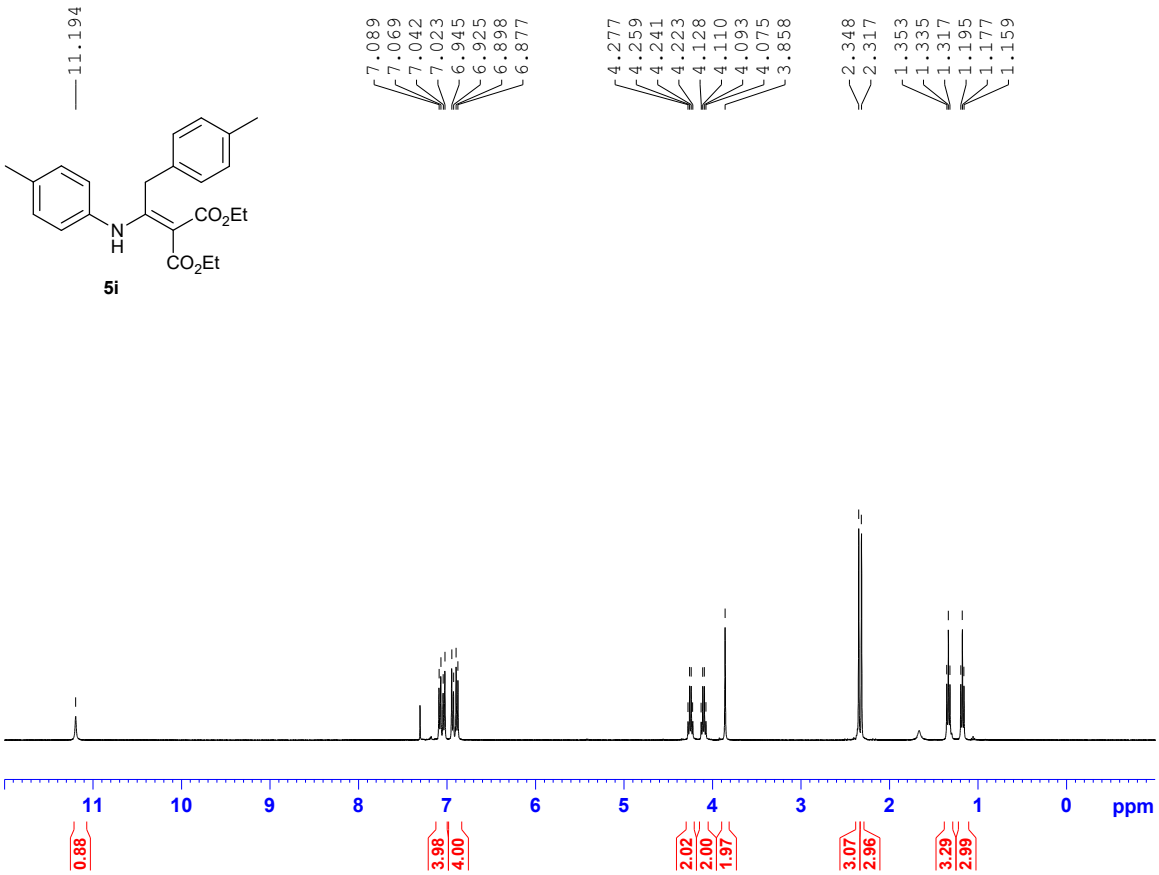

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5i**

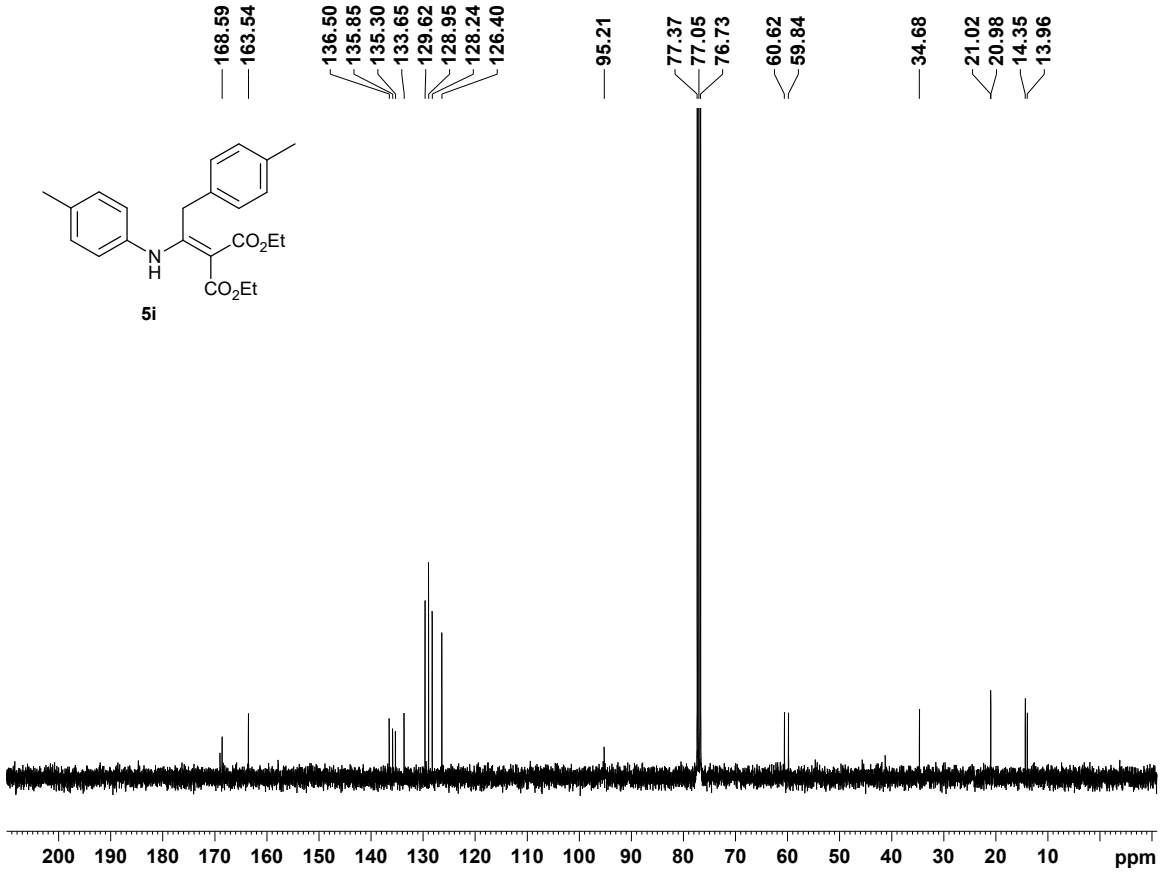

Figure S12. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5i**

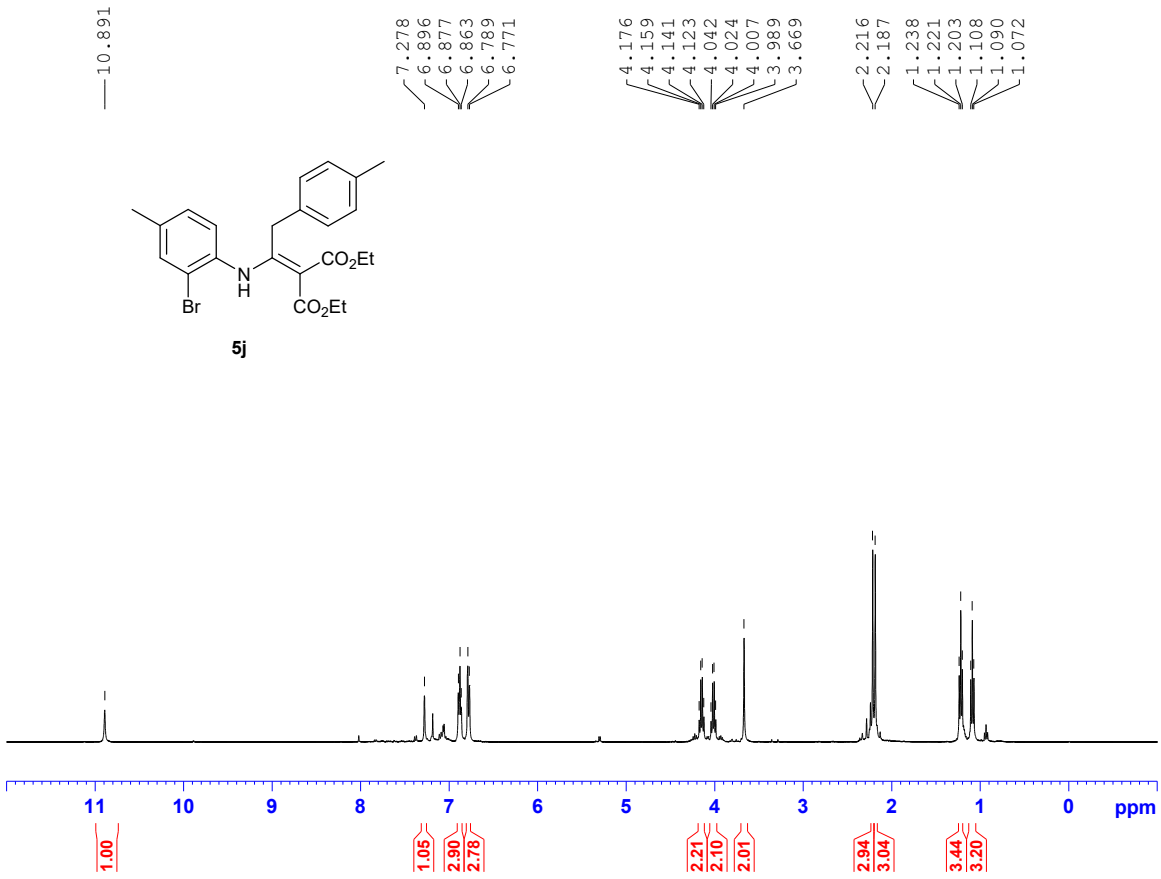

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5j**

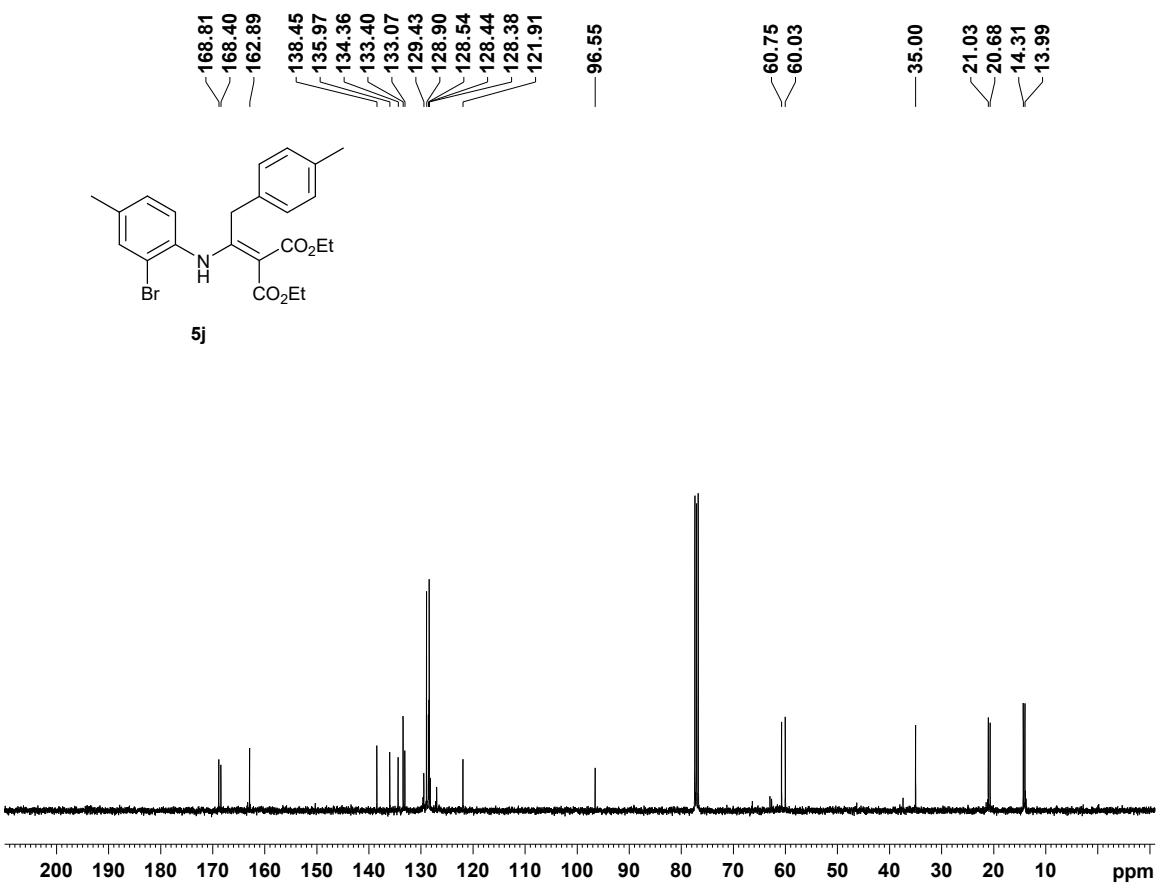

Figure S14. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5j**

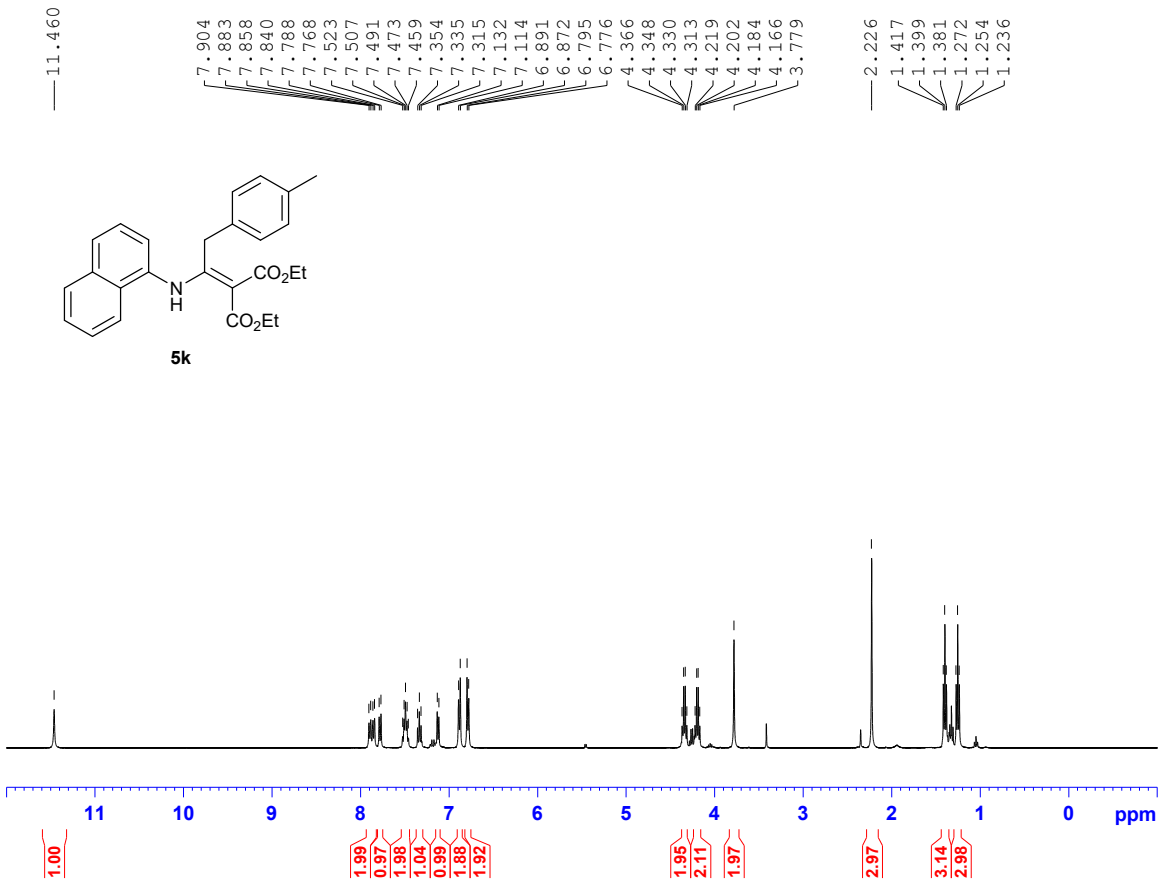

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5k**

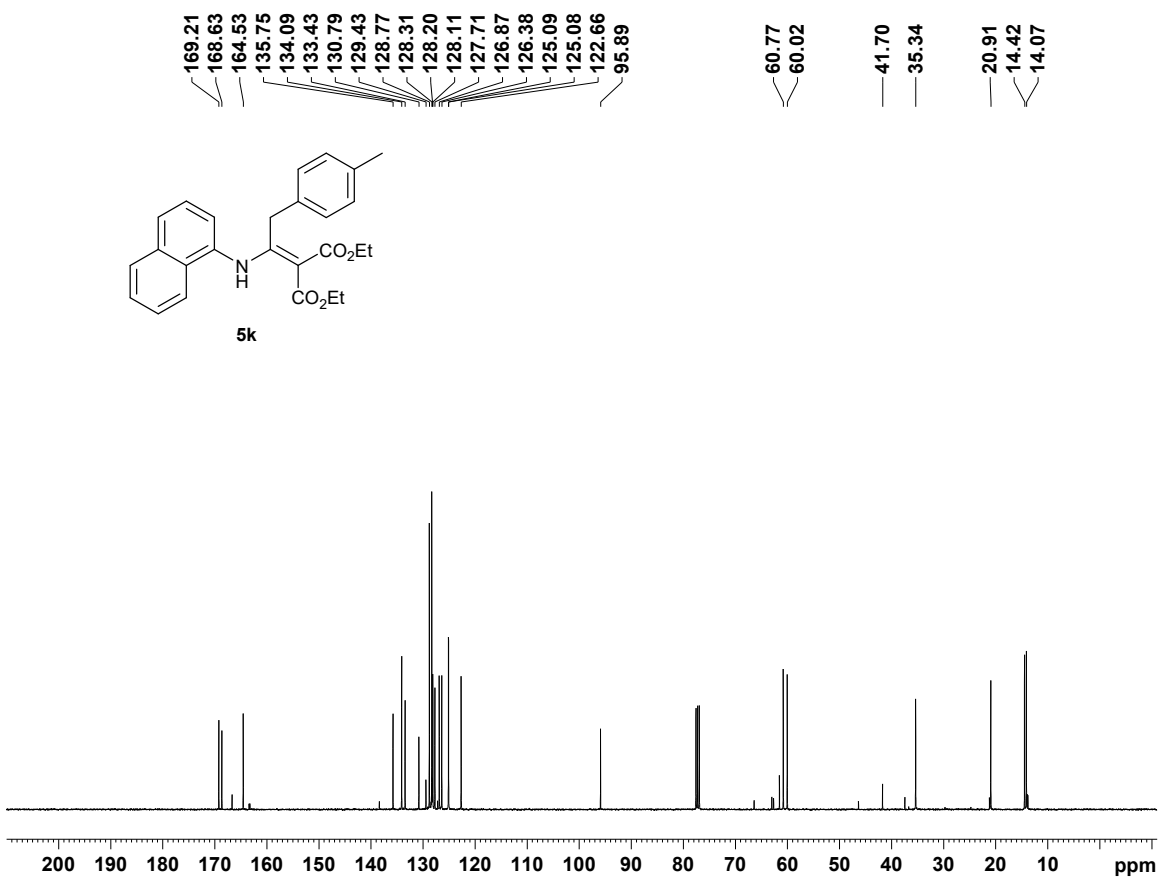

Figure S16. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5k**

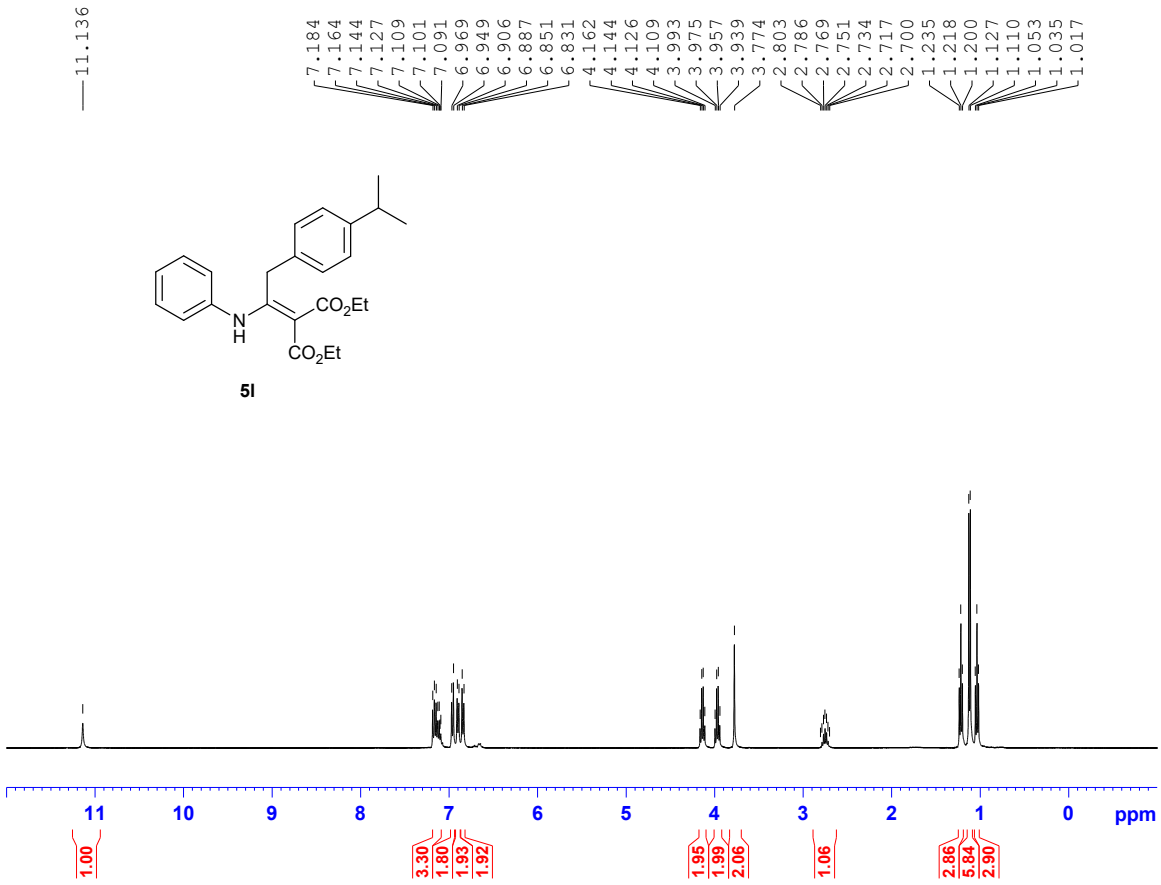

Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5l**

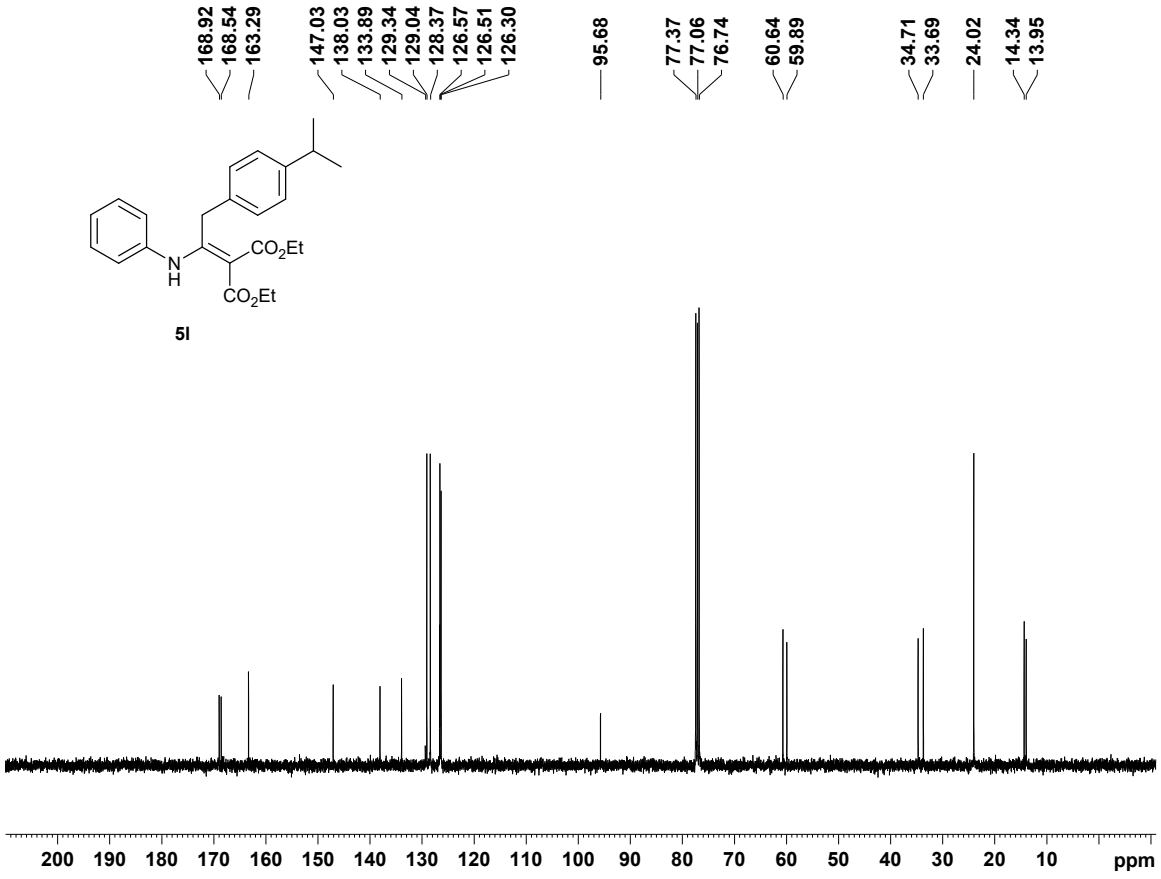

Figure S18. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5l**

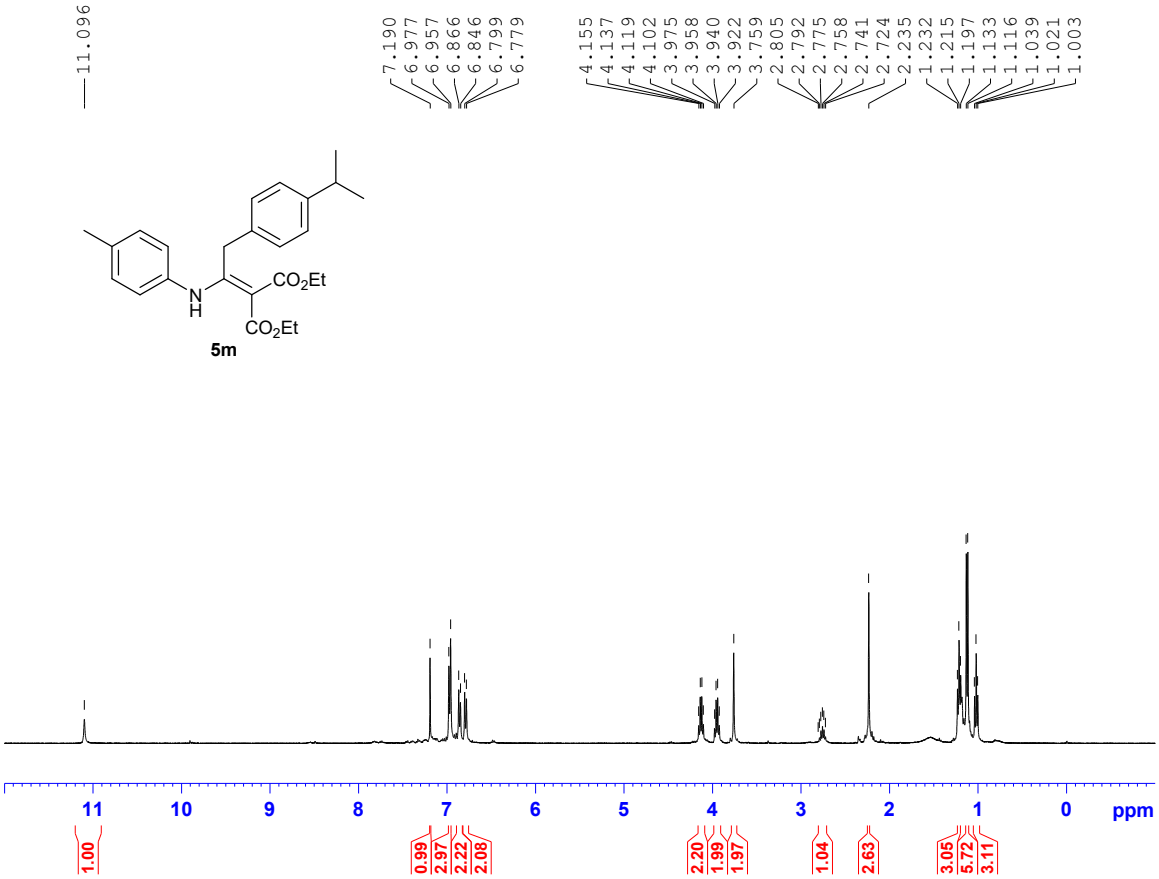

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5m**

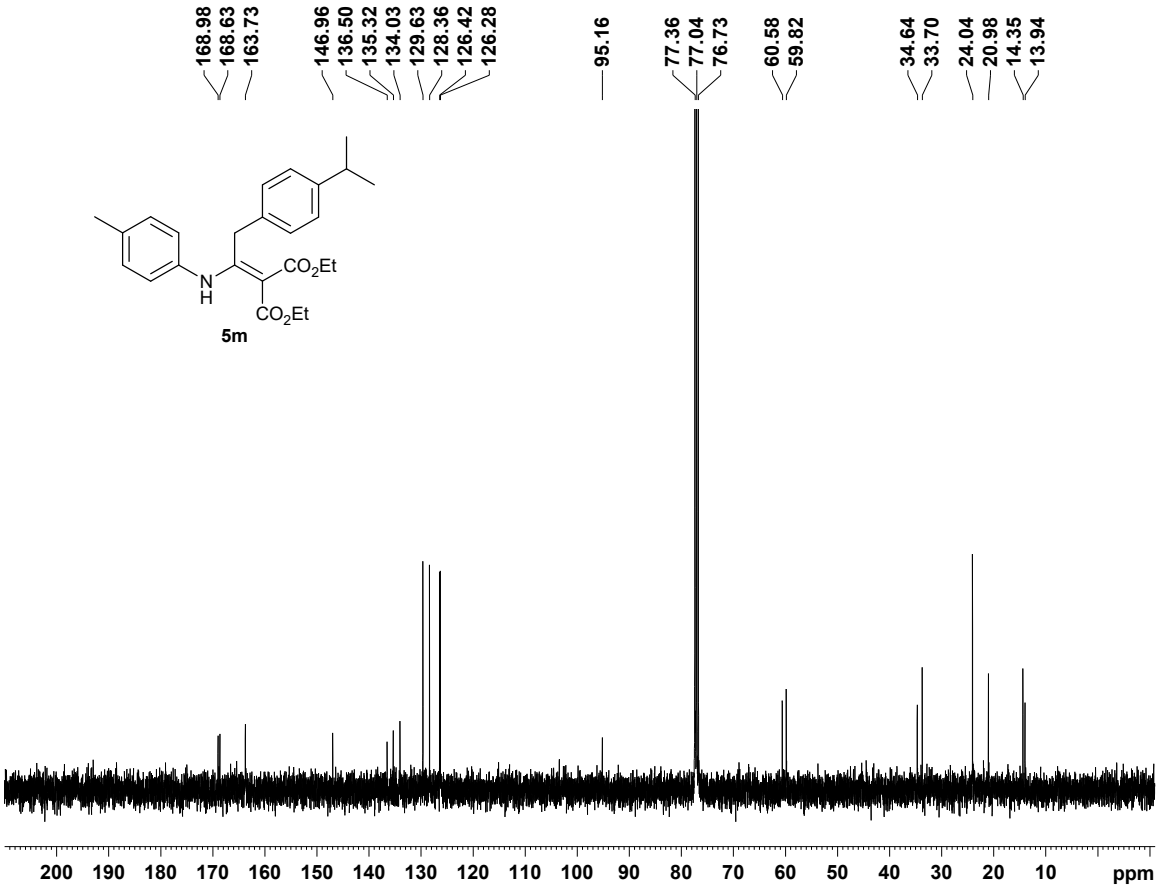

Figure S20. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5m**

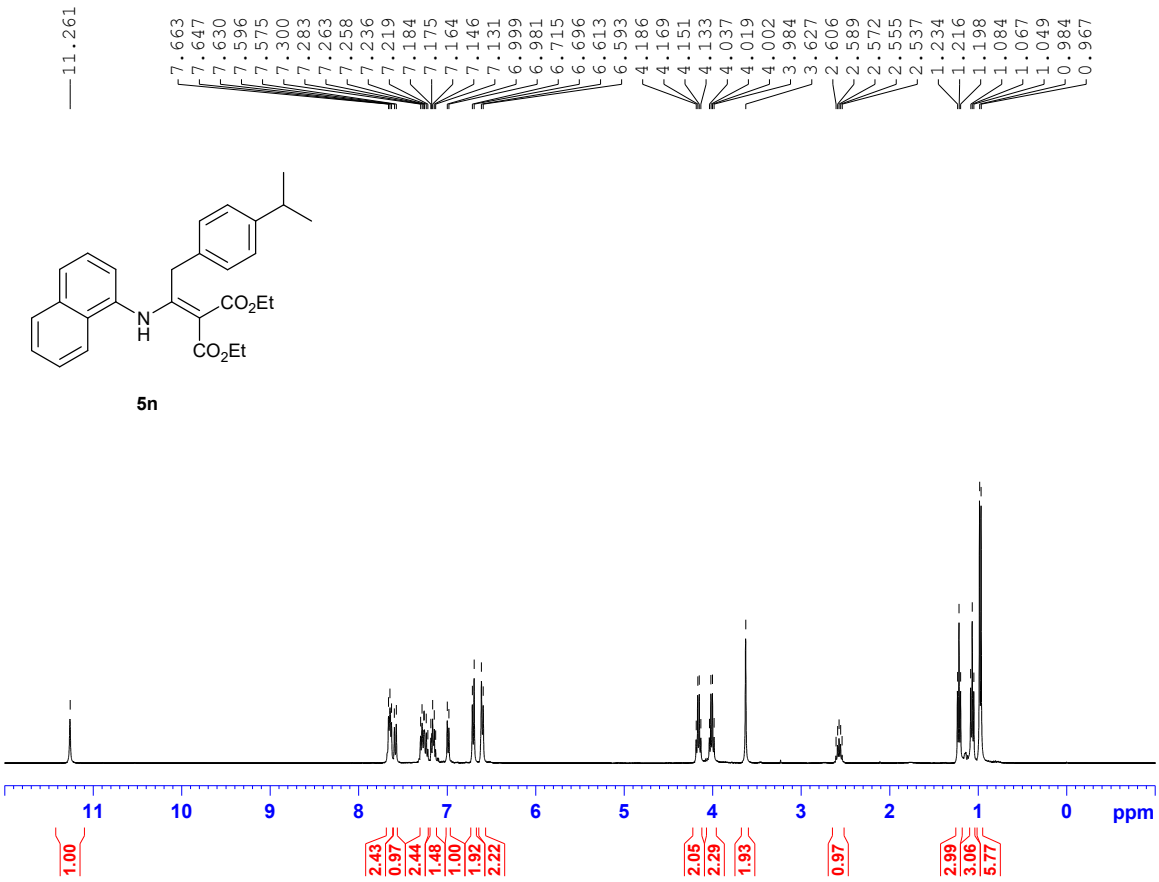

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5n**

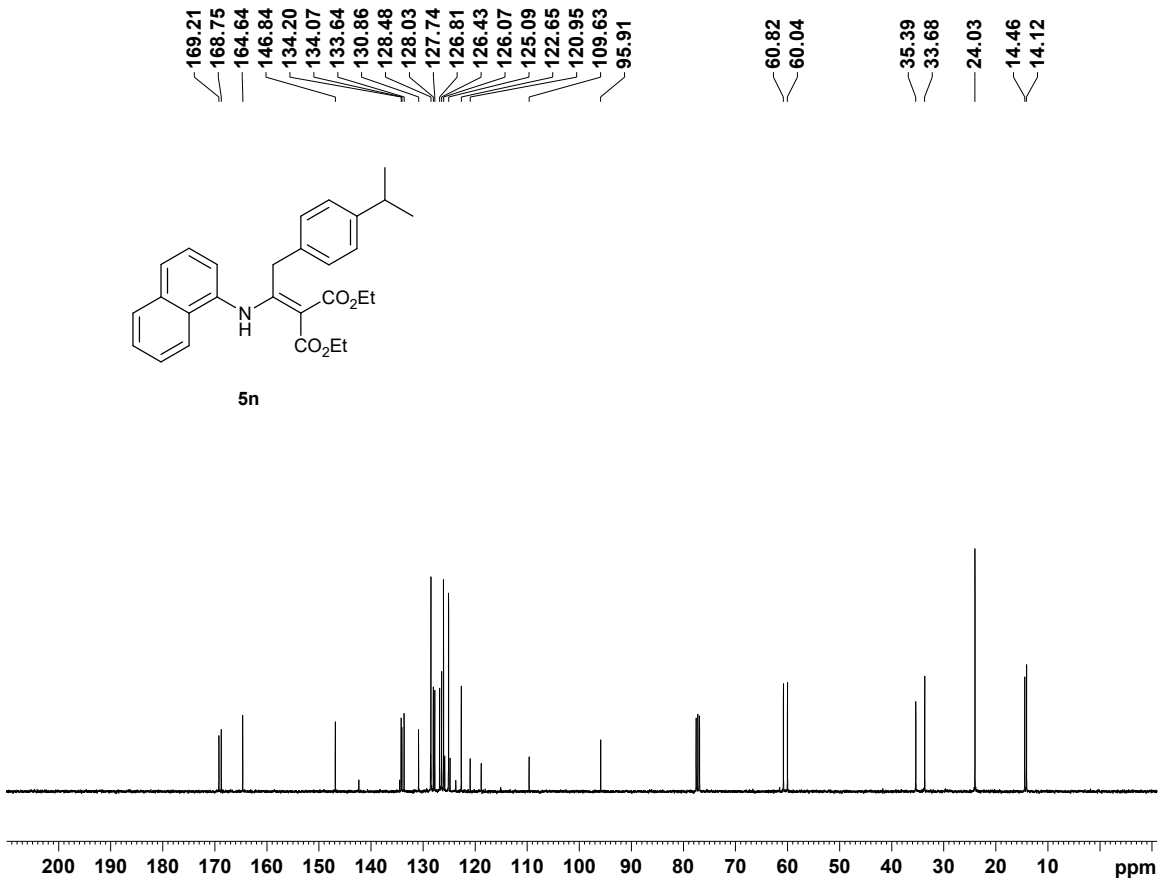

Figure S22. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5n**

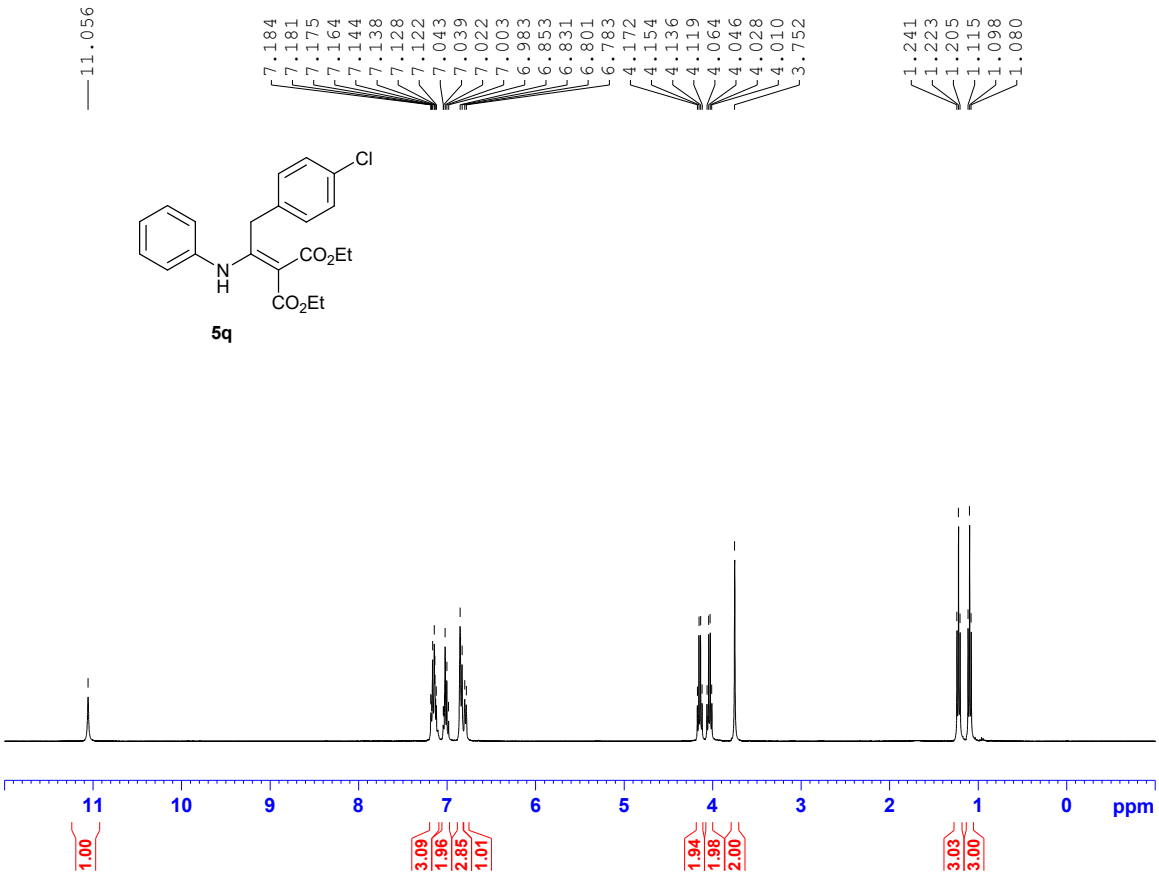

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5q**

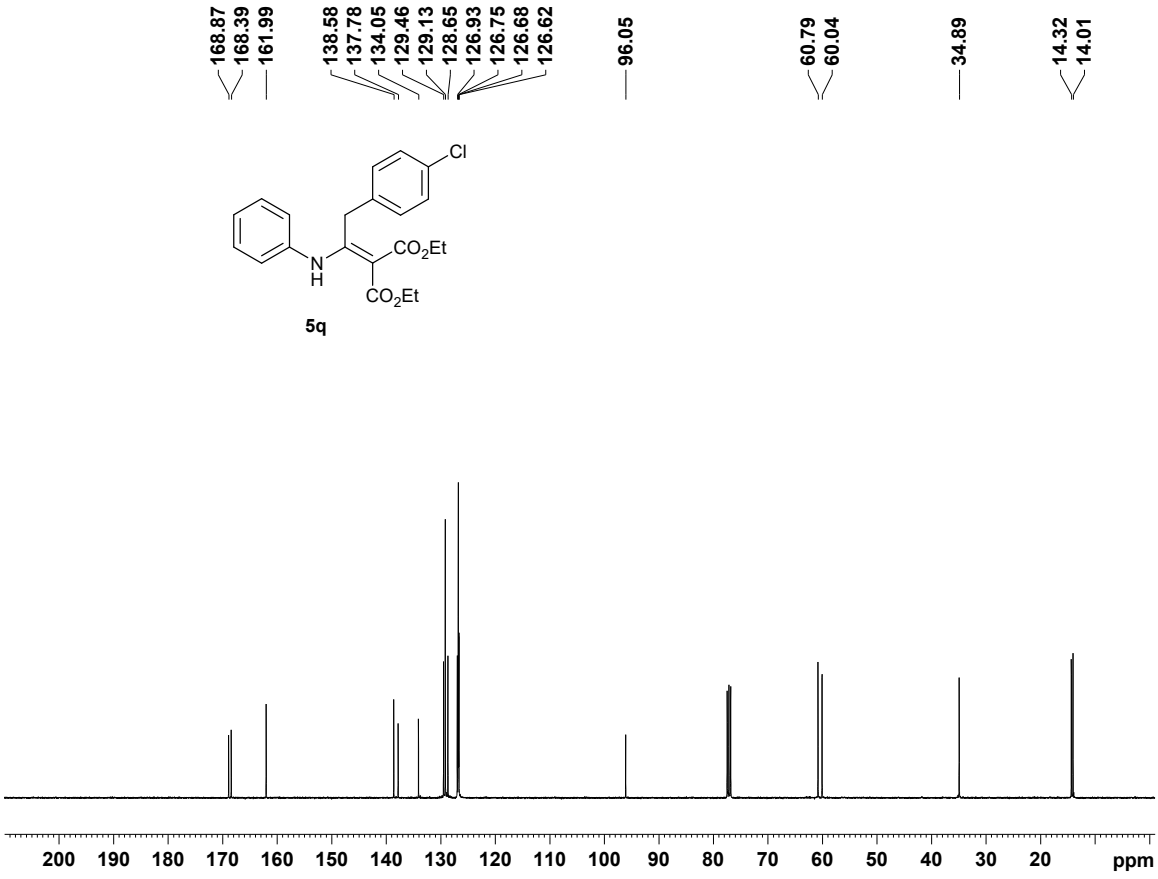

Figure S24. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5q**

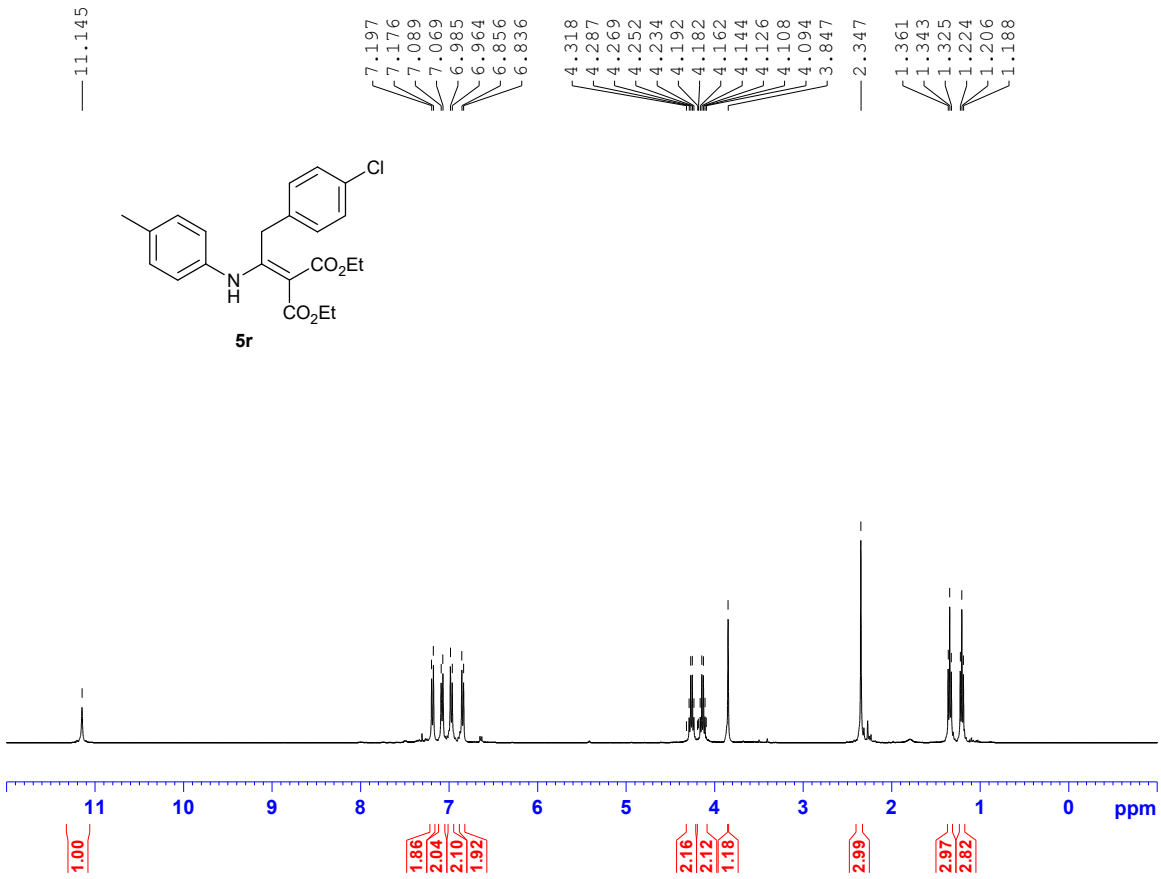

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5r**

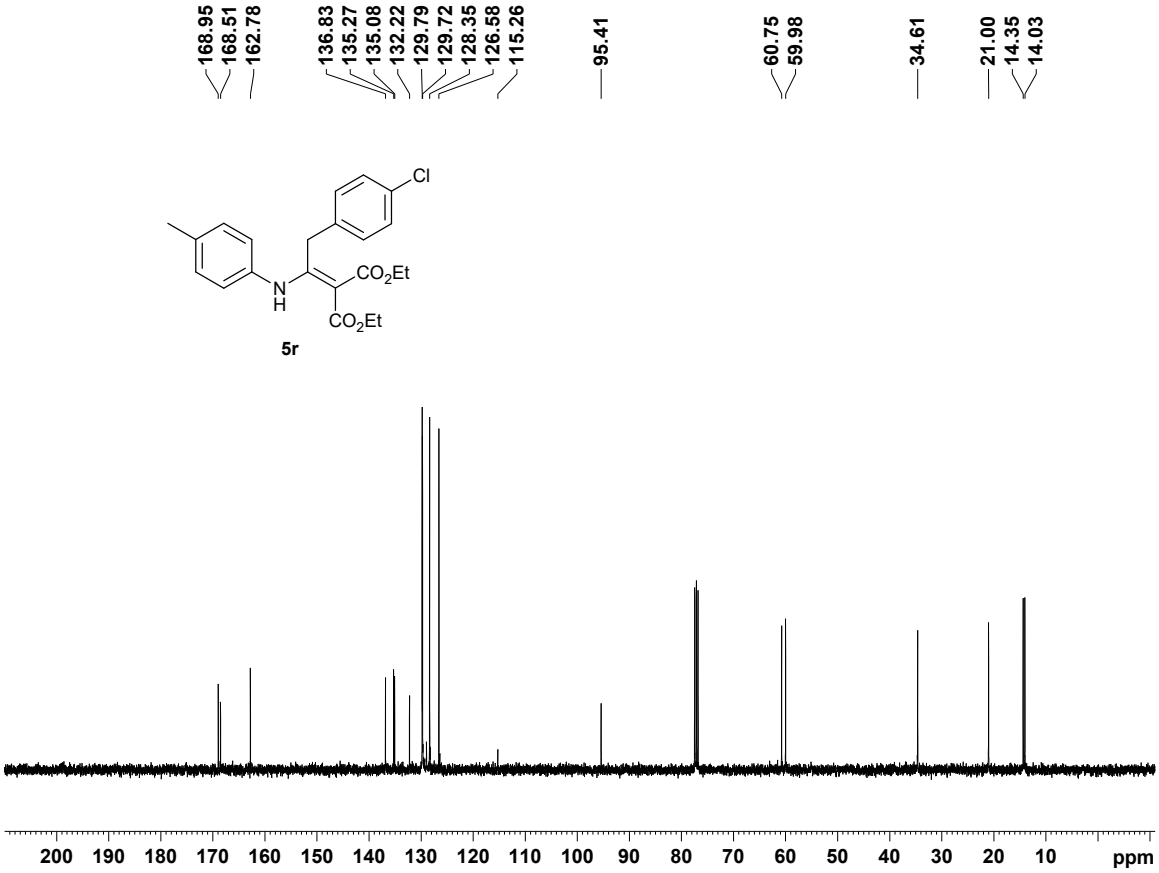

Figure S26. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5r**

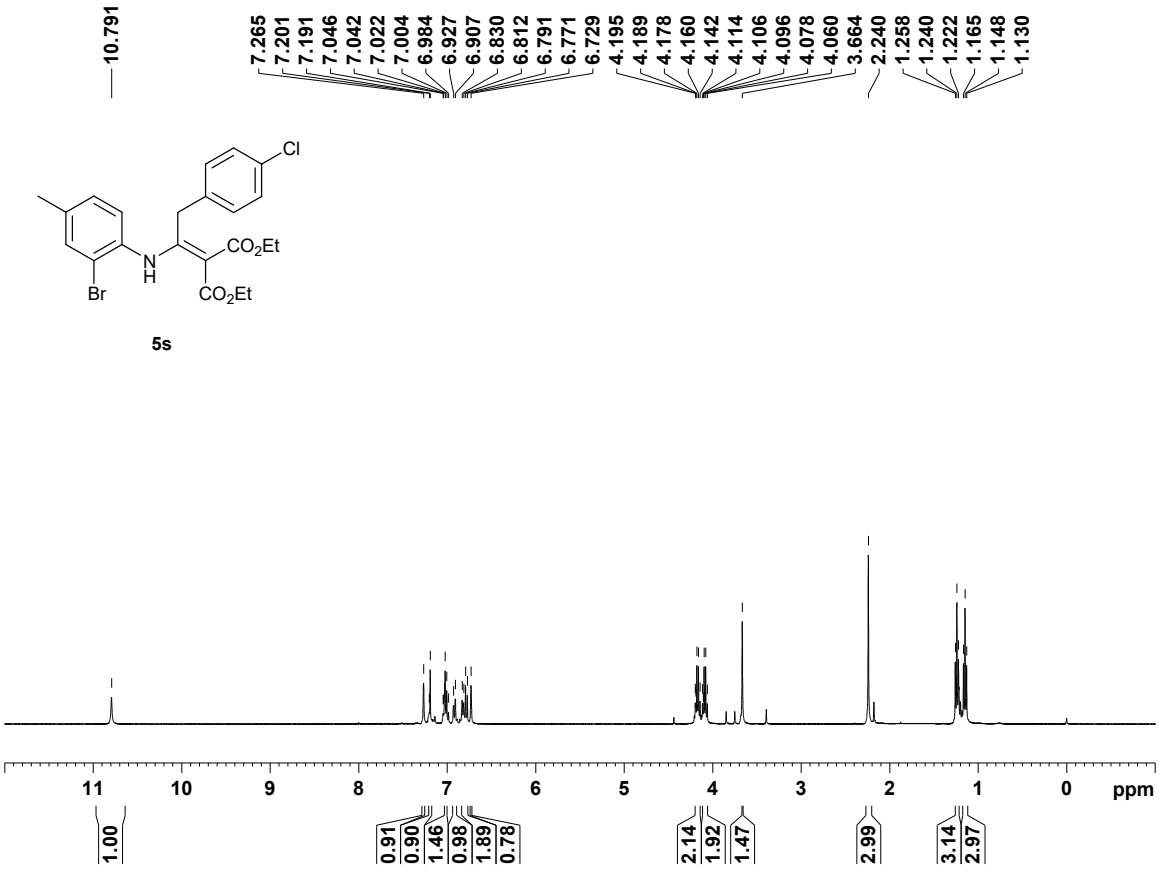

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5s**

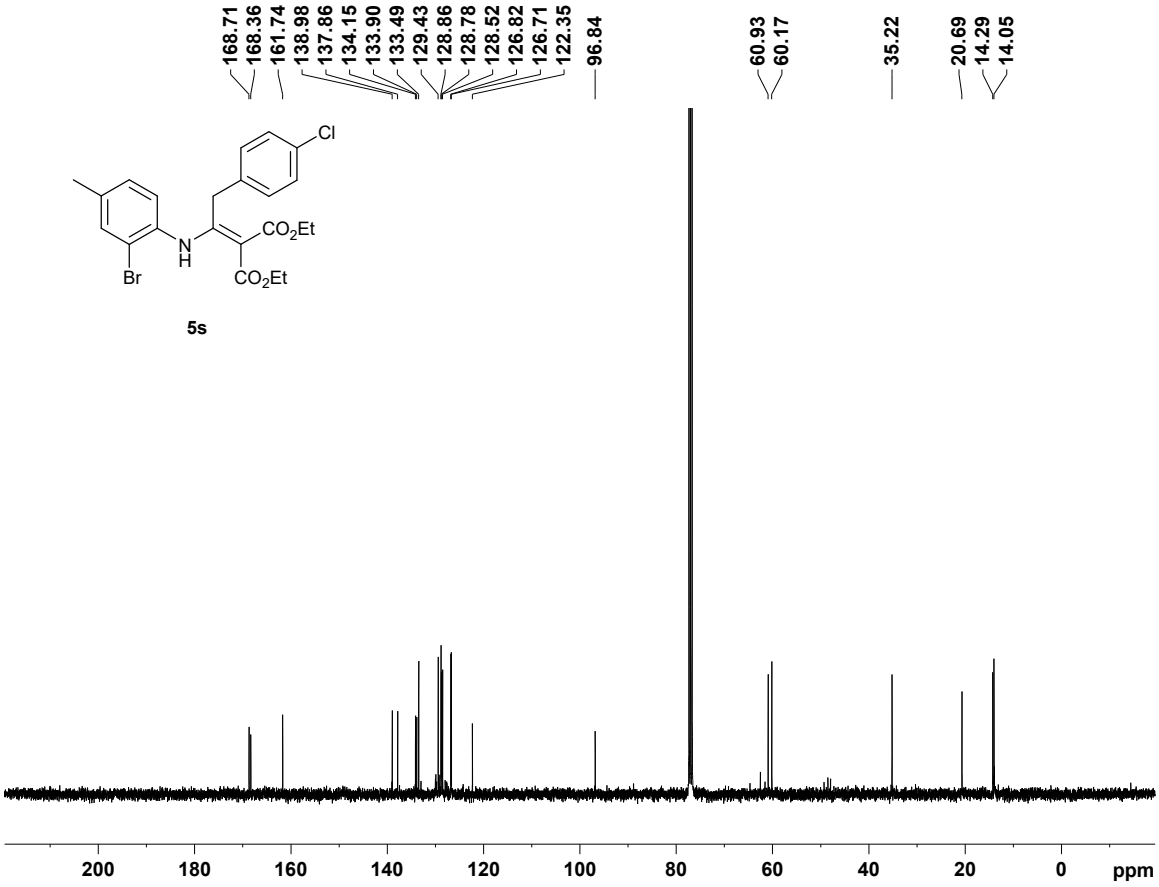

Figure S28. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5s**

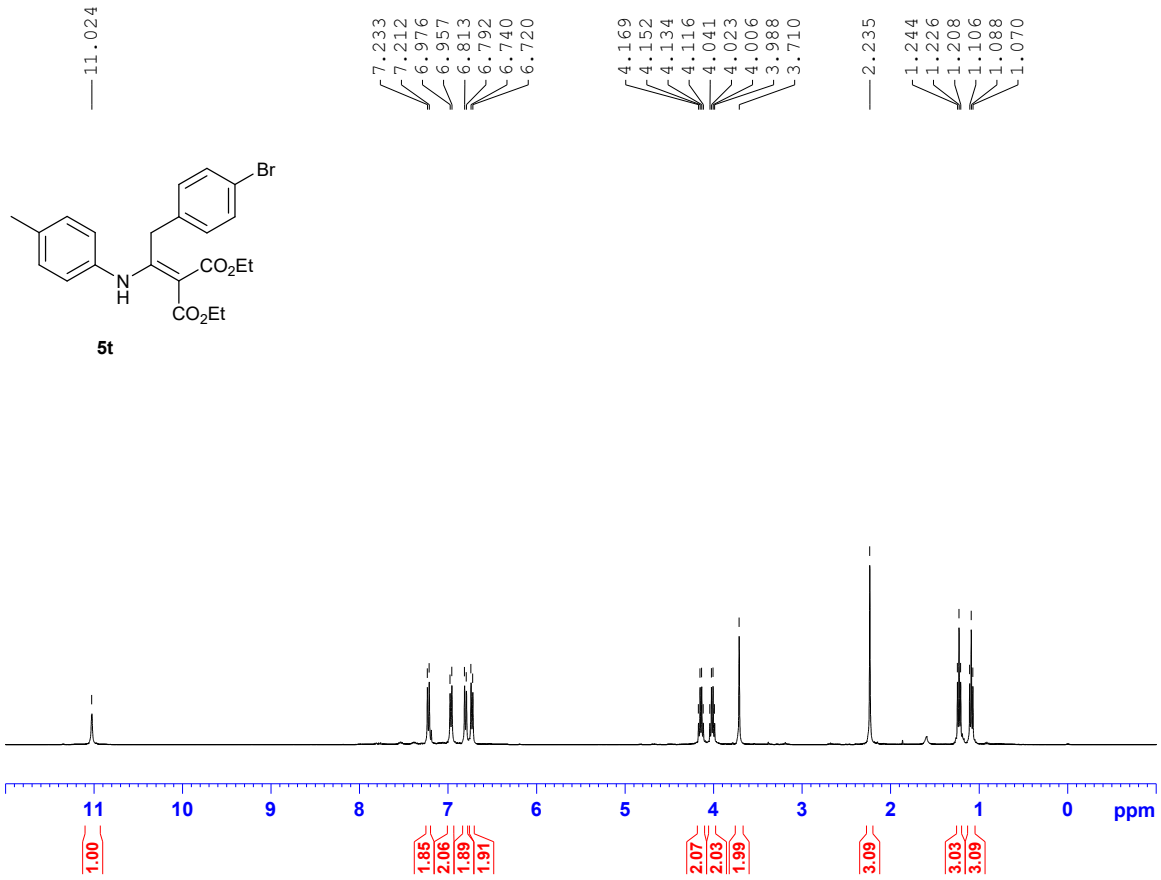

Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5t**

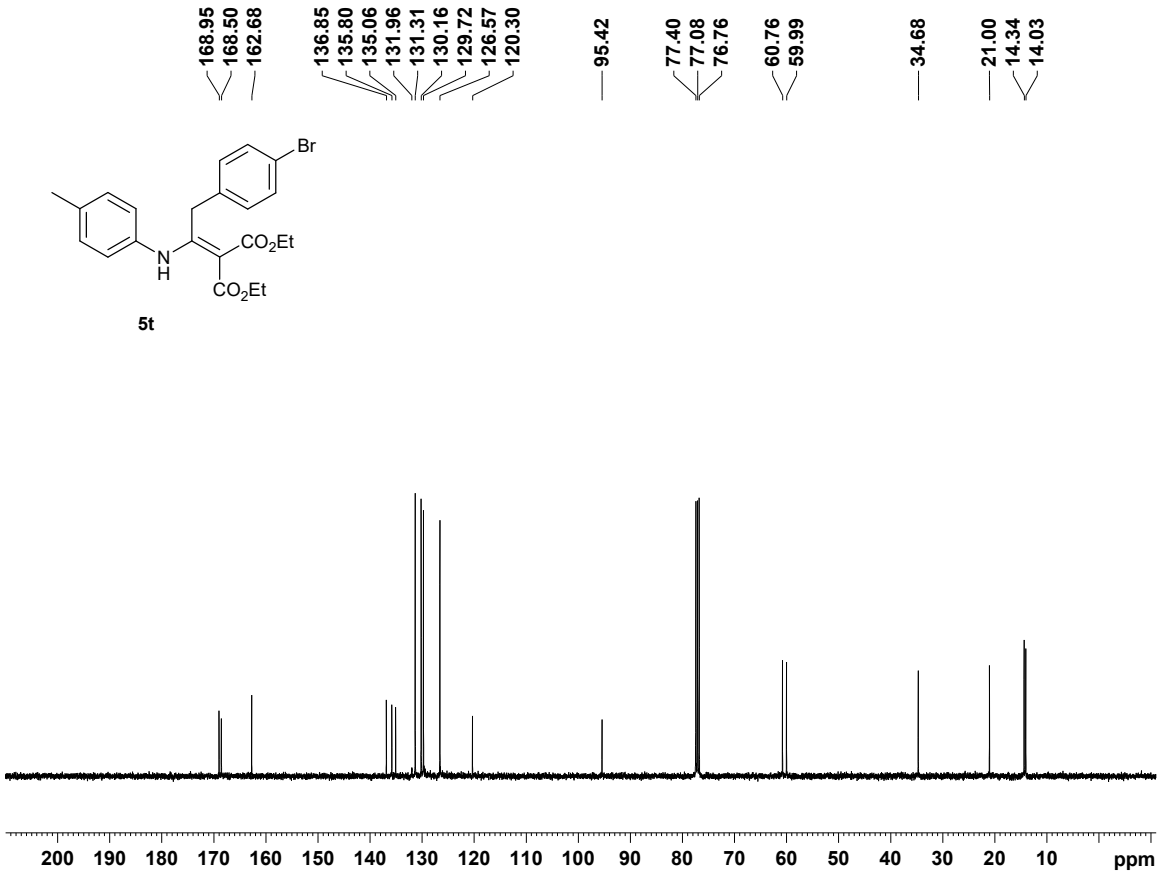

Figure S30. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5t**

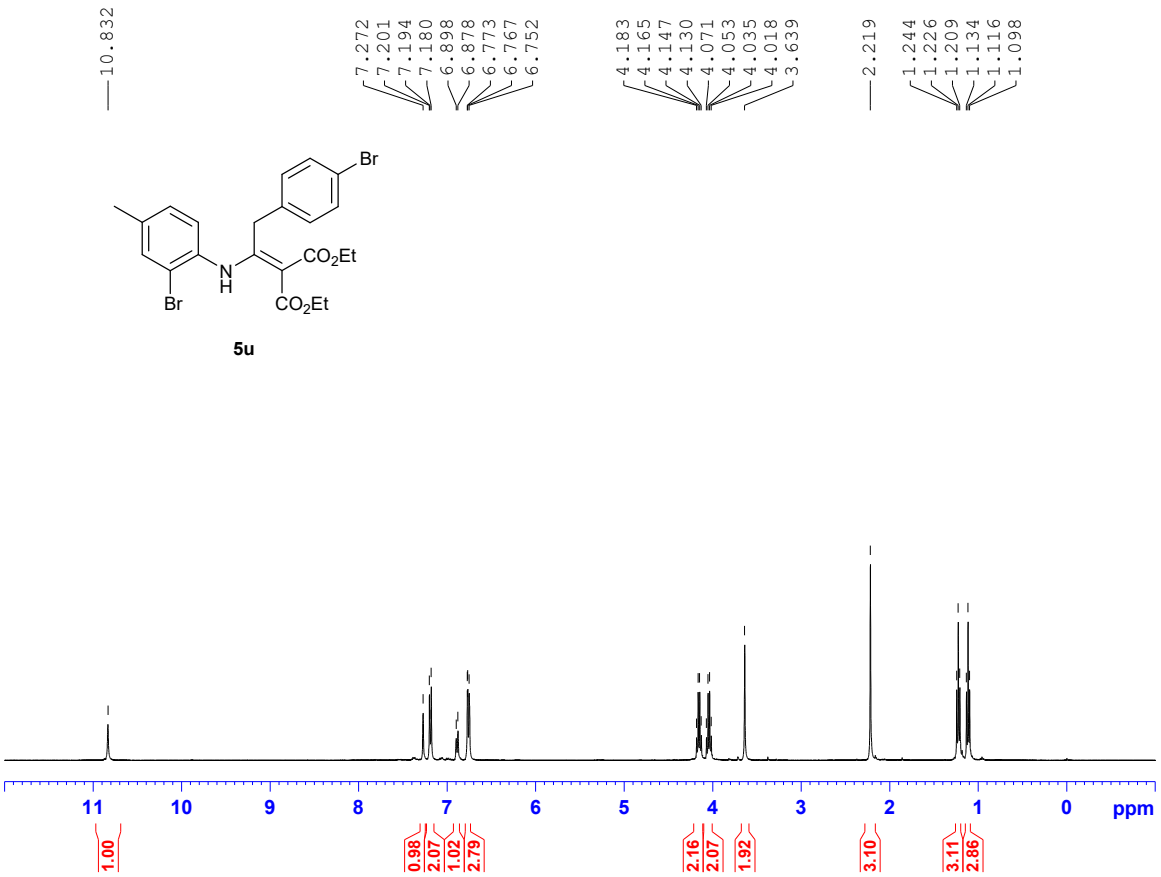

Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5u**

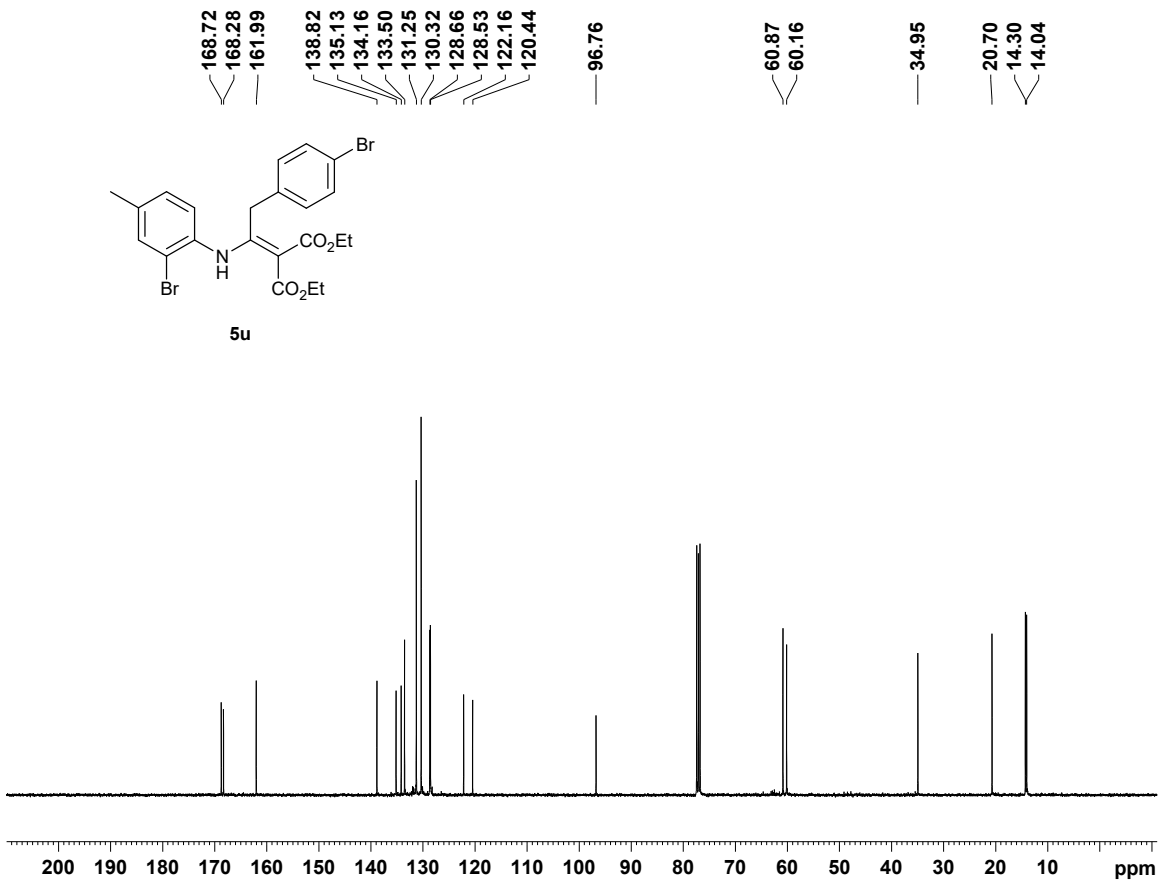

Figure S32. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5u**

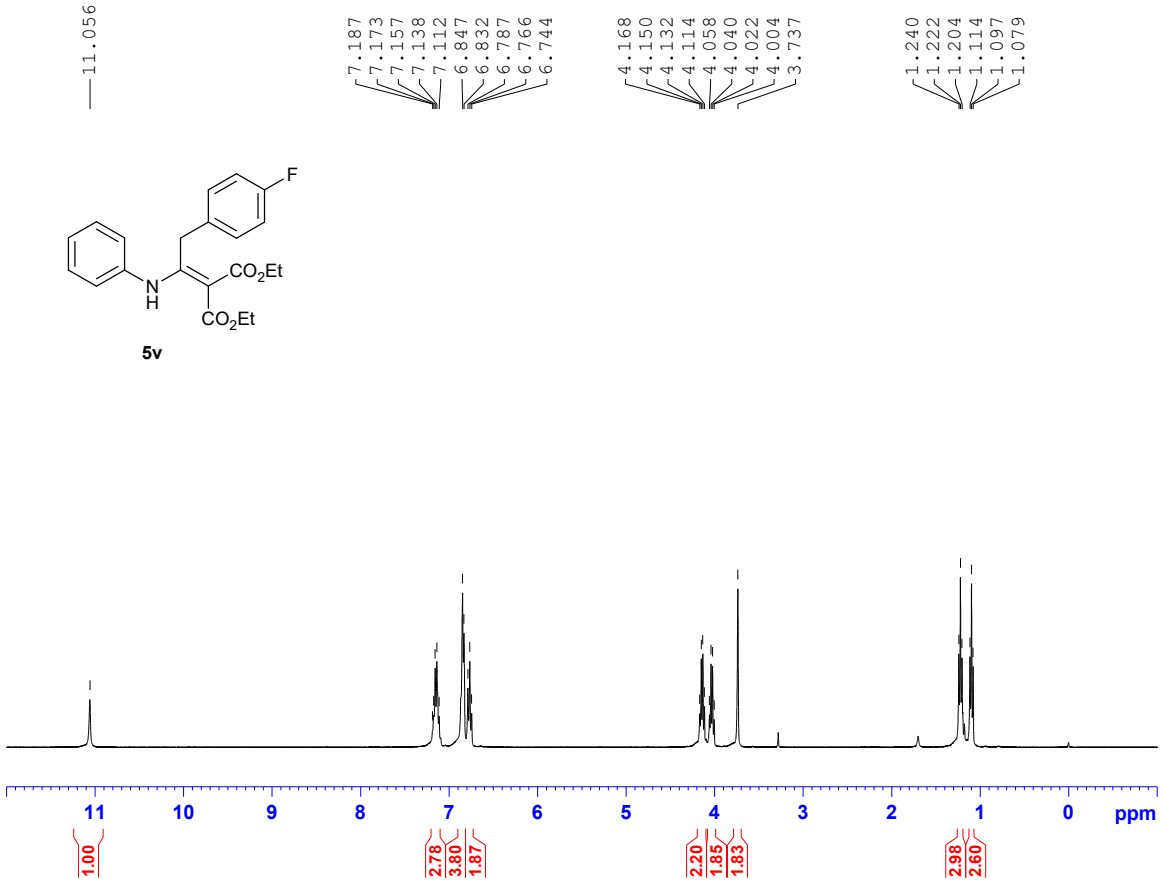

Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5v**

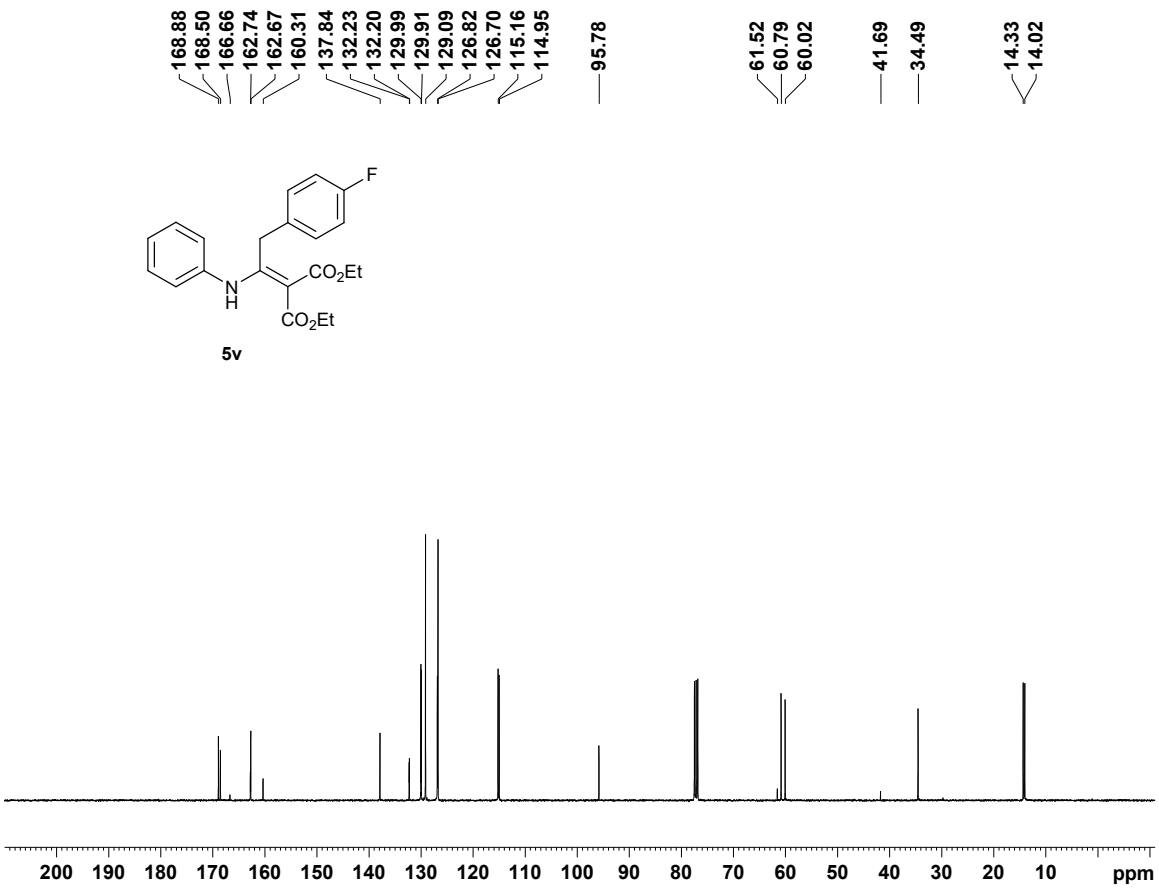

Figure S34. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5v**

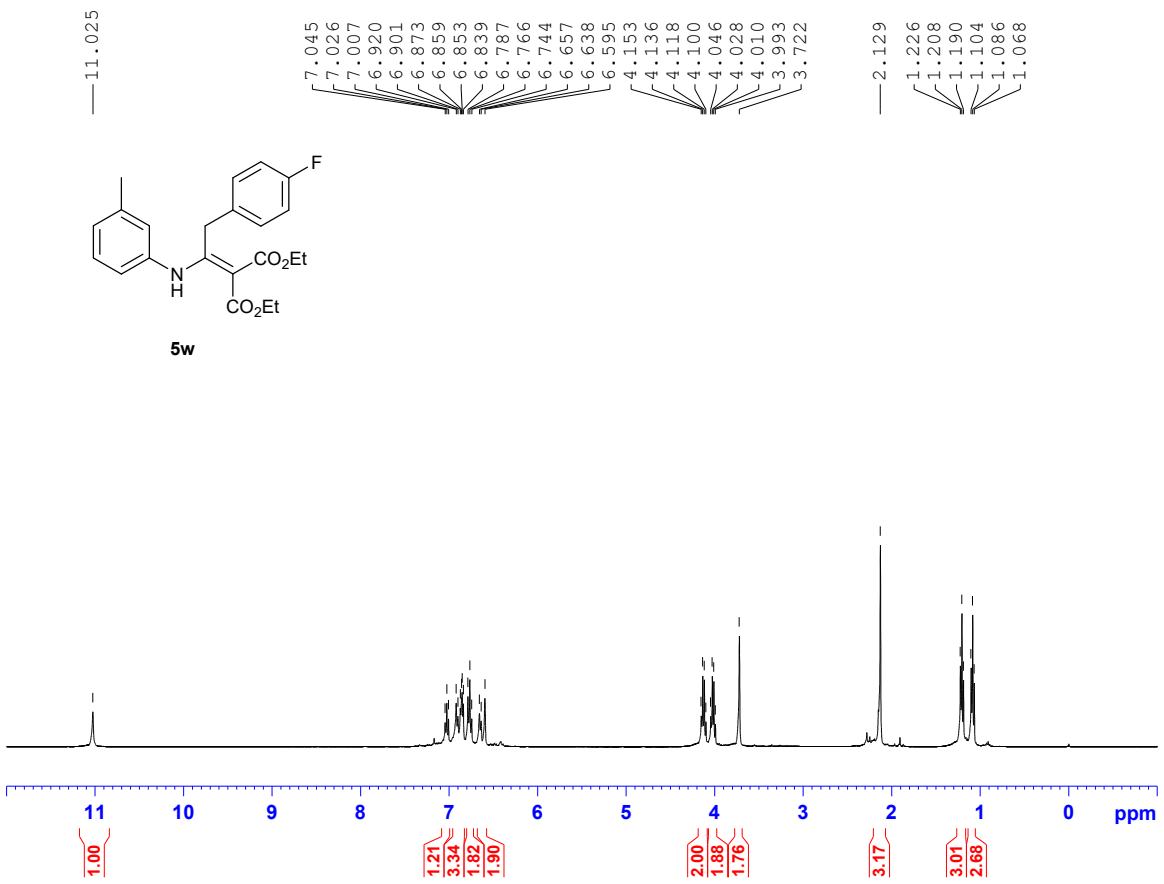

Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5w**

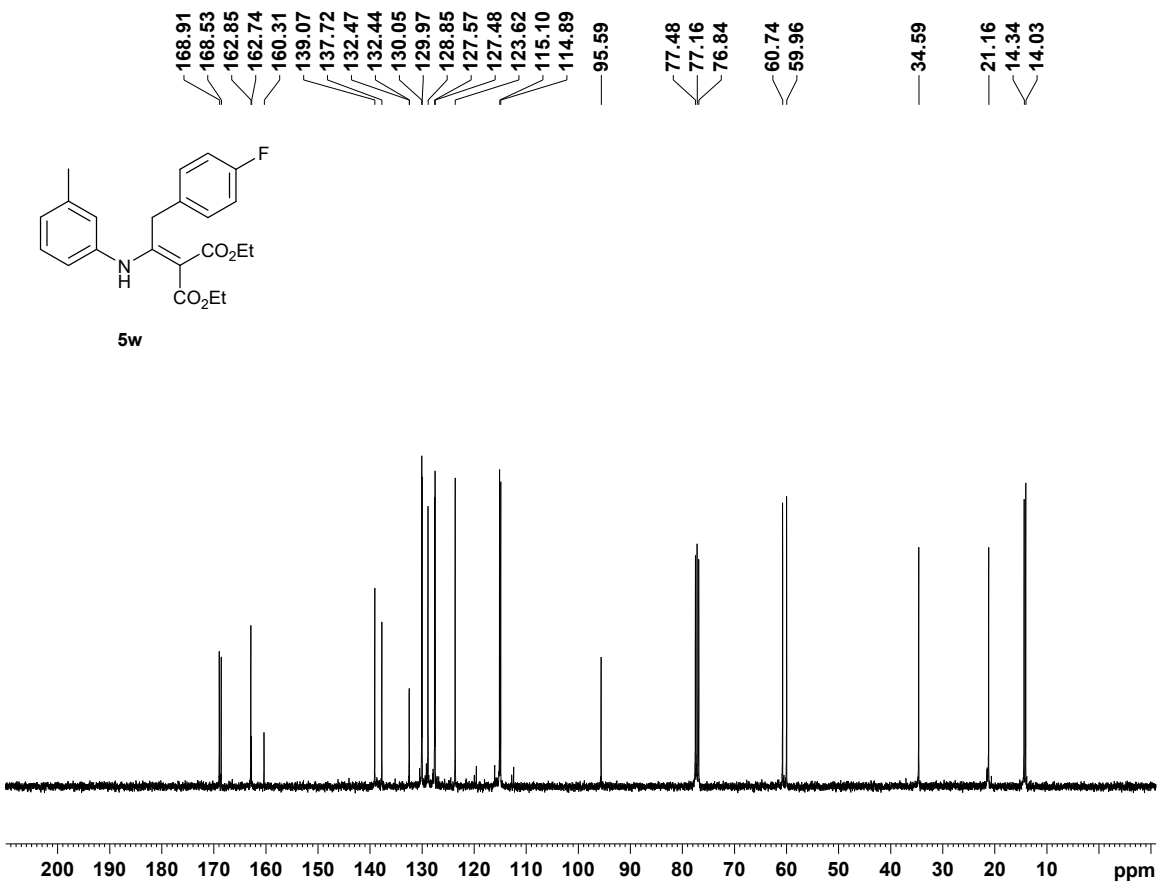

Figure S36. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5w**

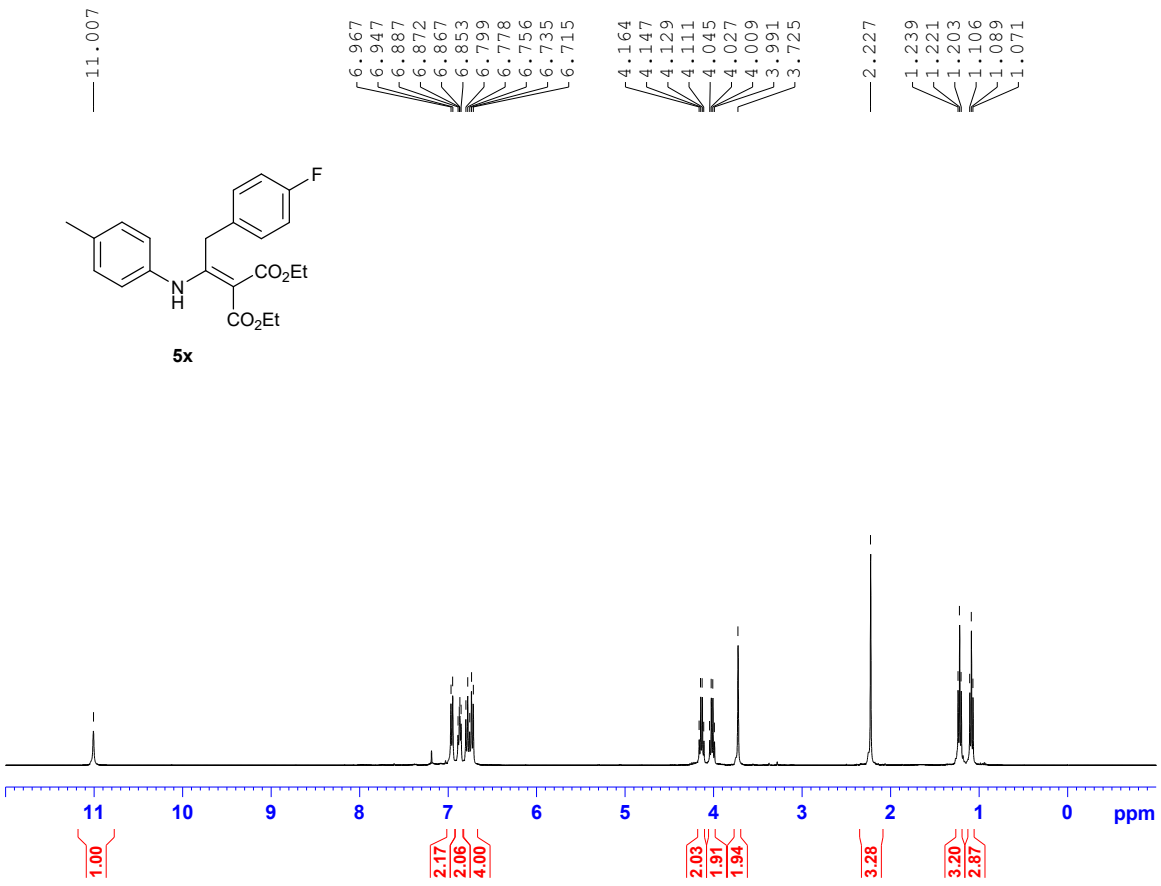

Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5x**

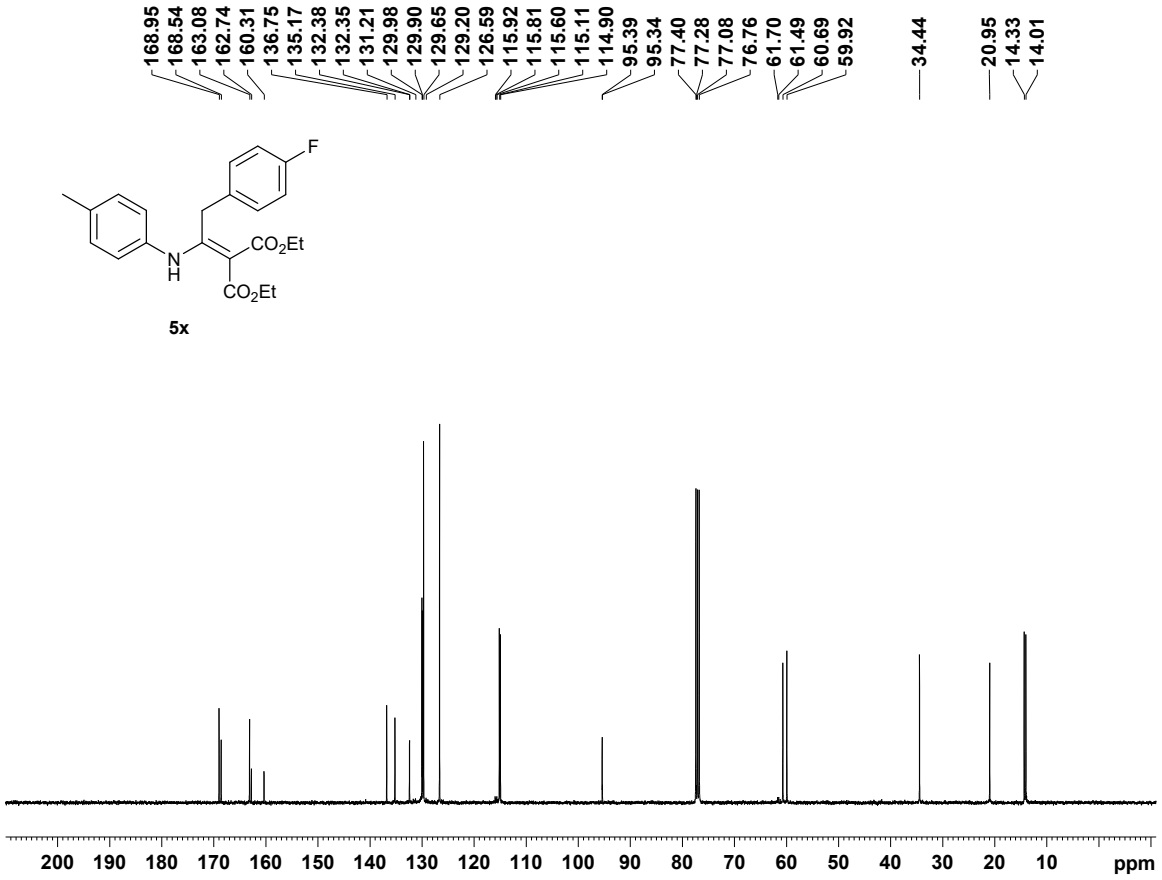

Figure S38. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5x**

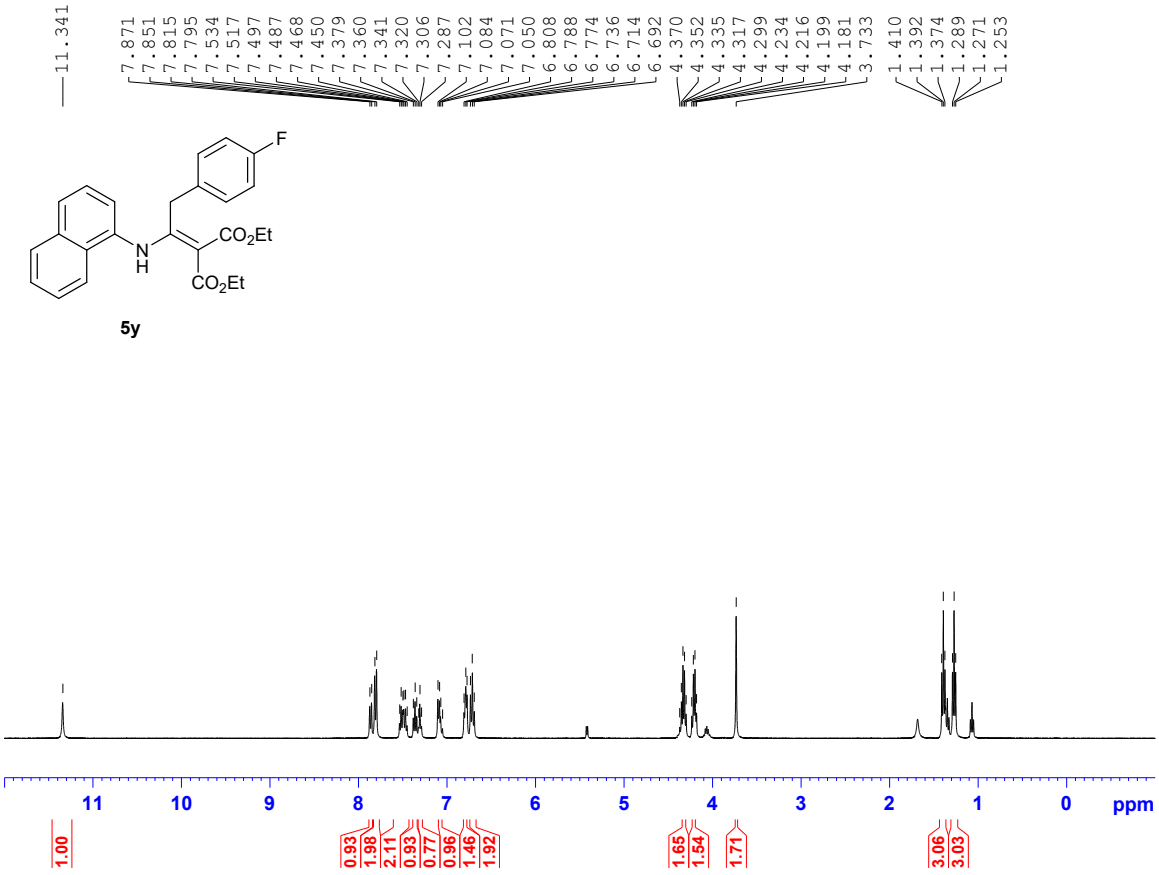

Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5y**

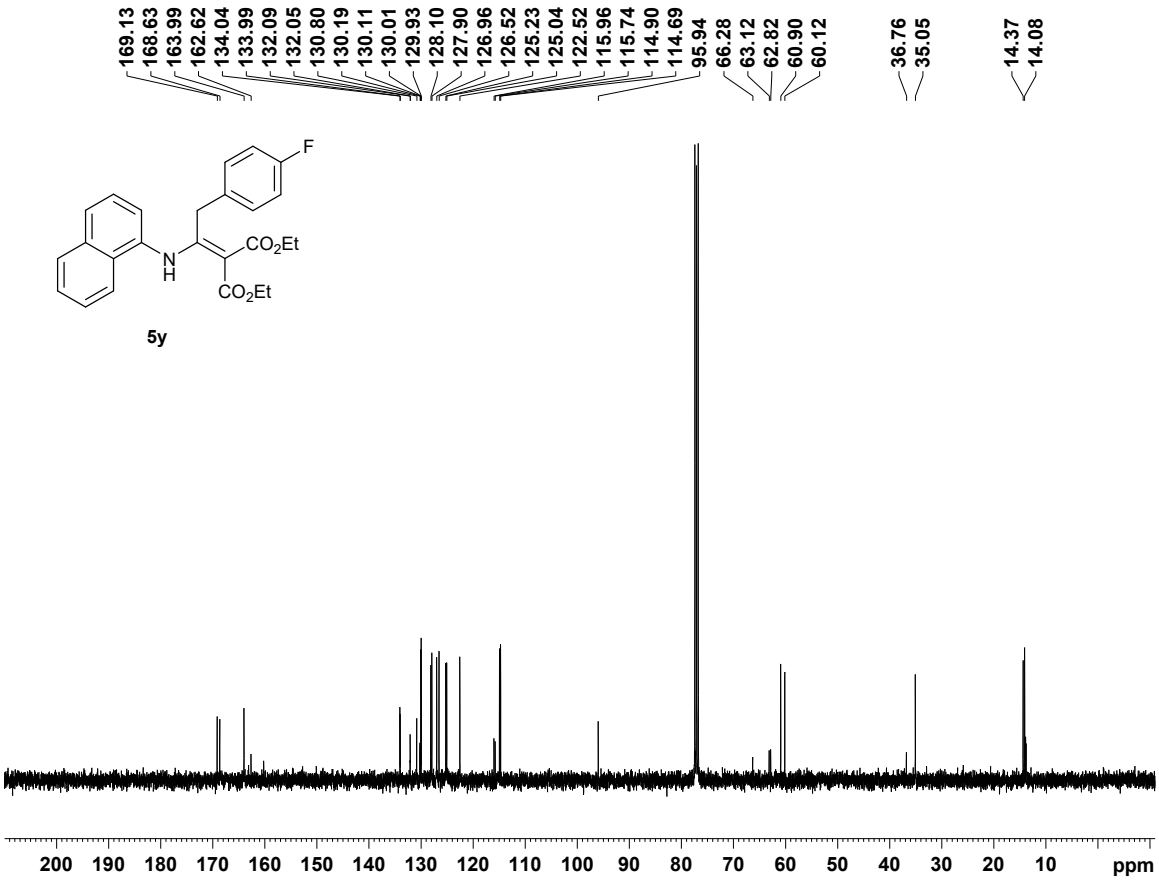

Figure S40. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5y**

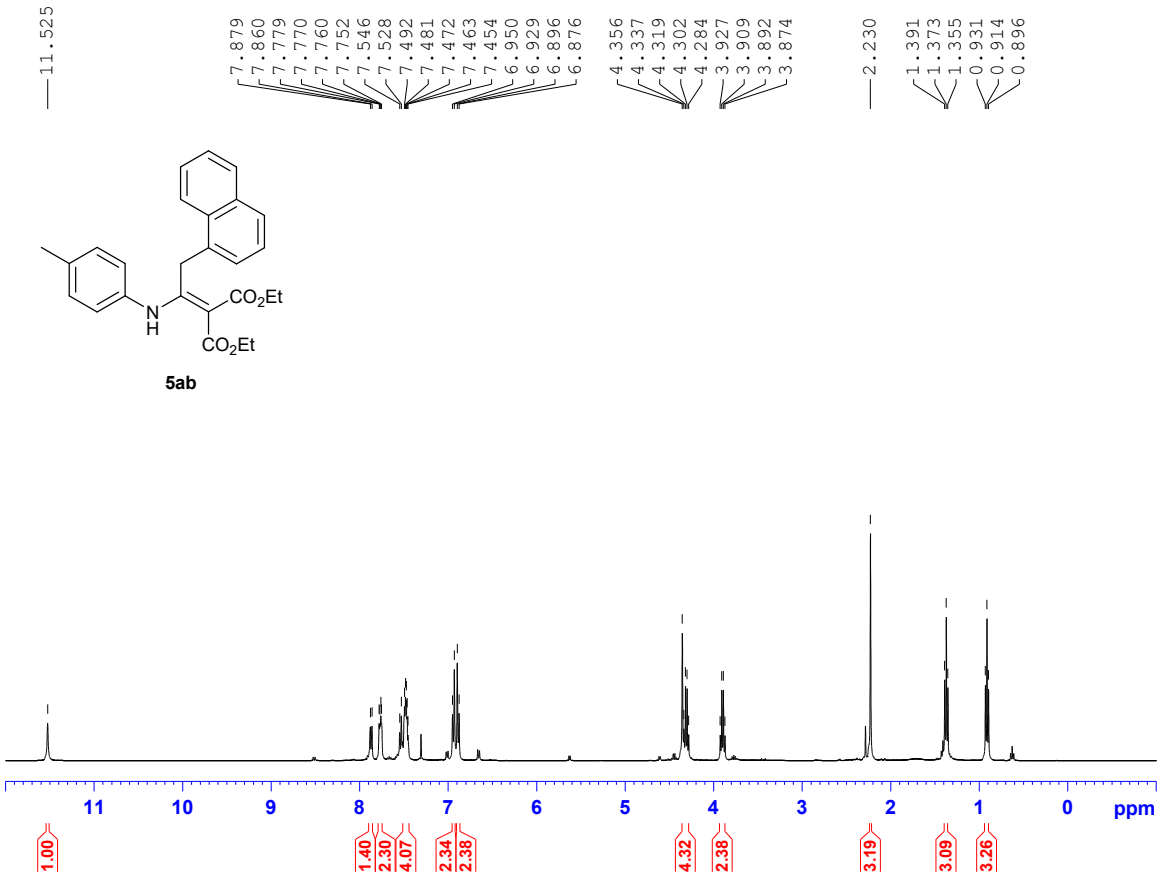

Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ab**

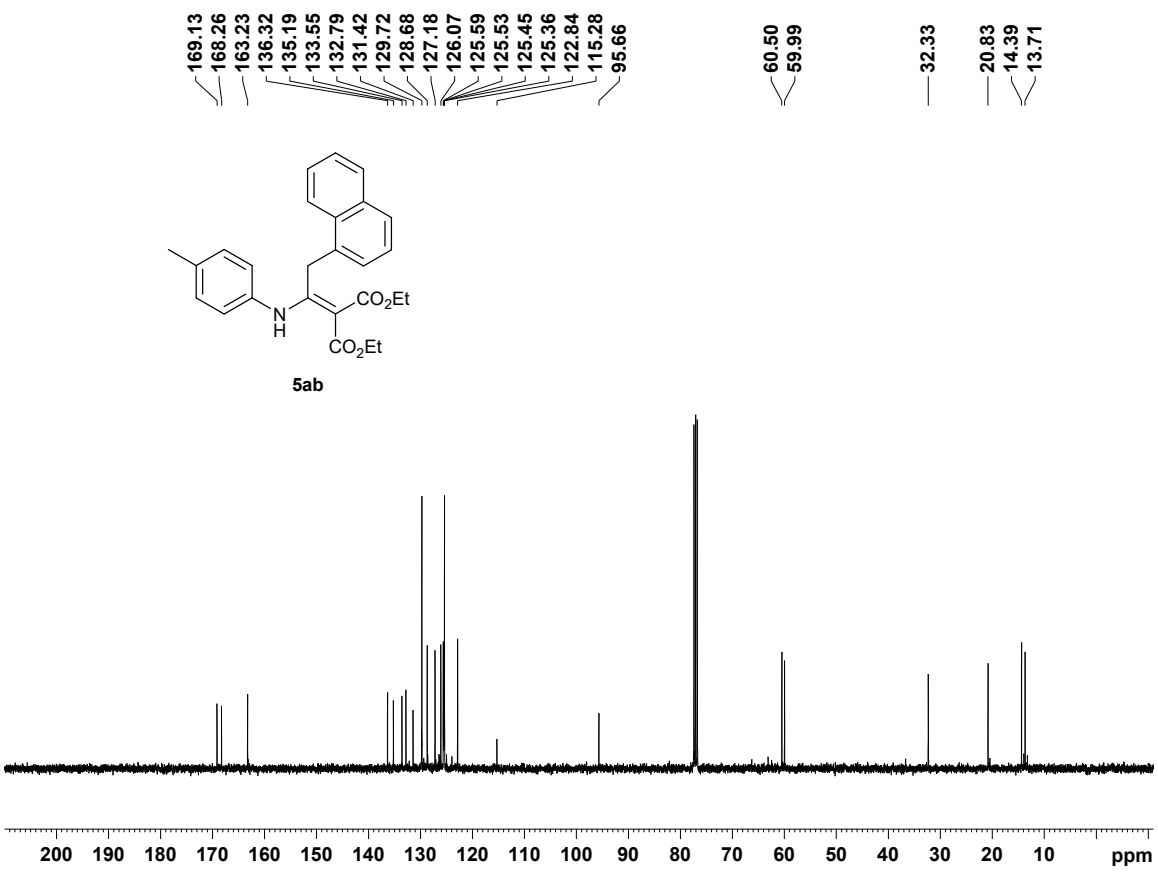

Figure S42. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5ab**

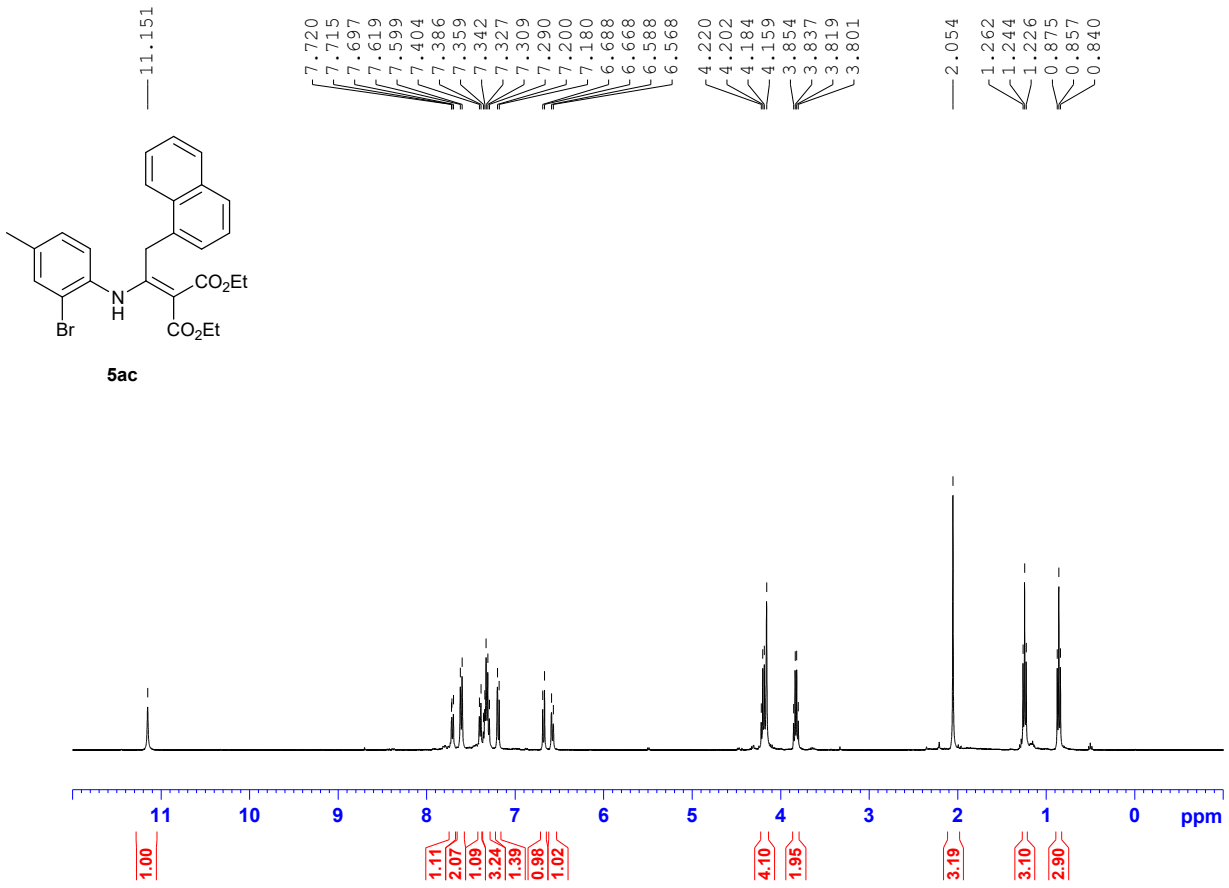

Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ac**

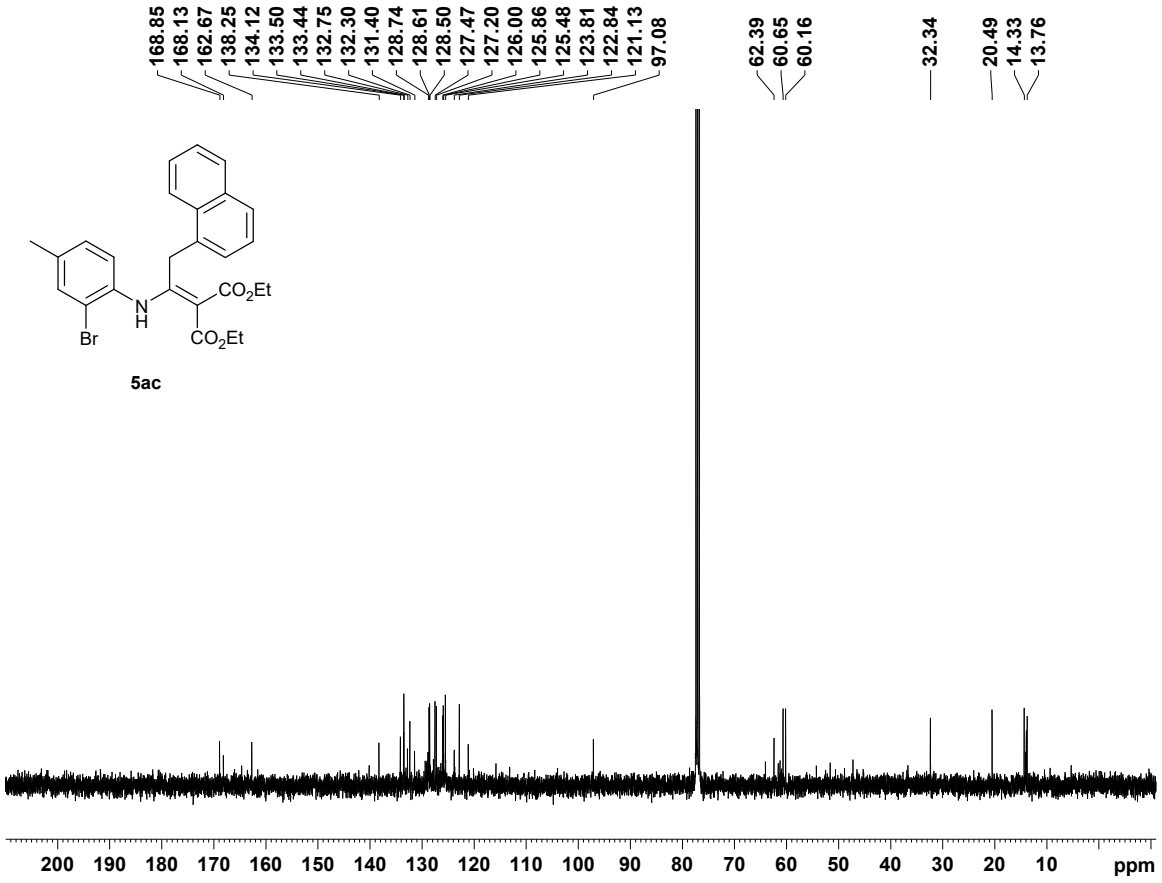

Figure S44. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5ac**

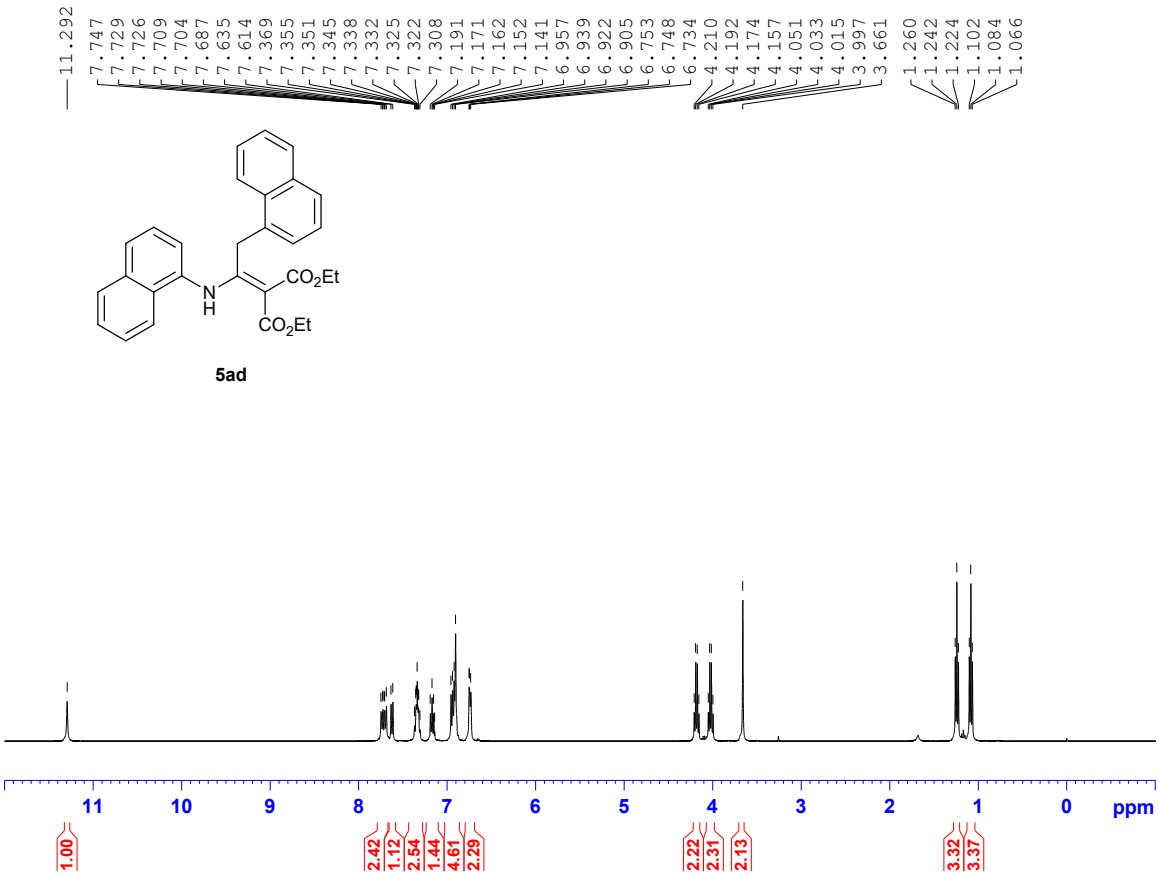

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5ad**

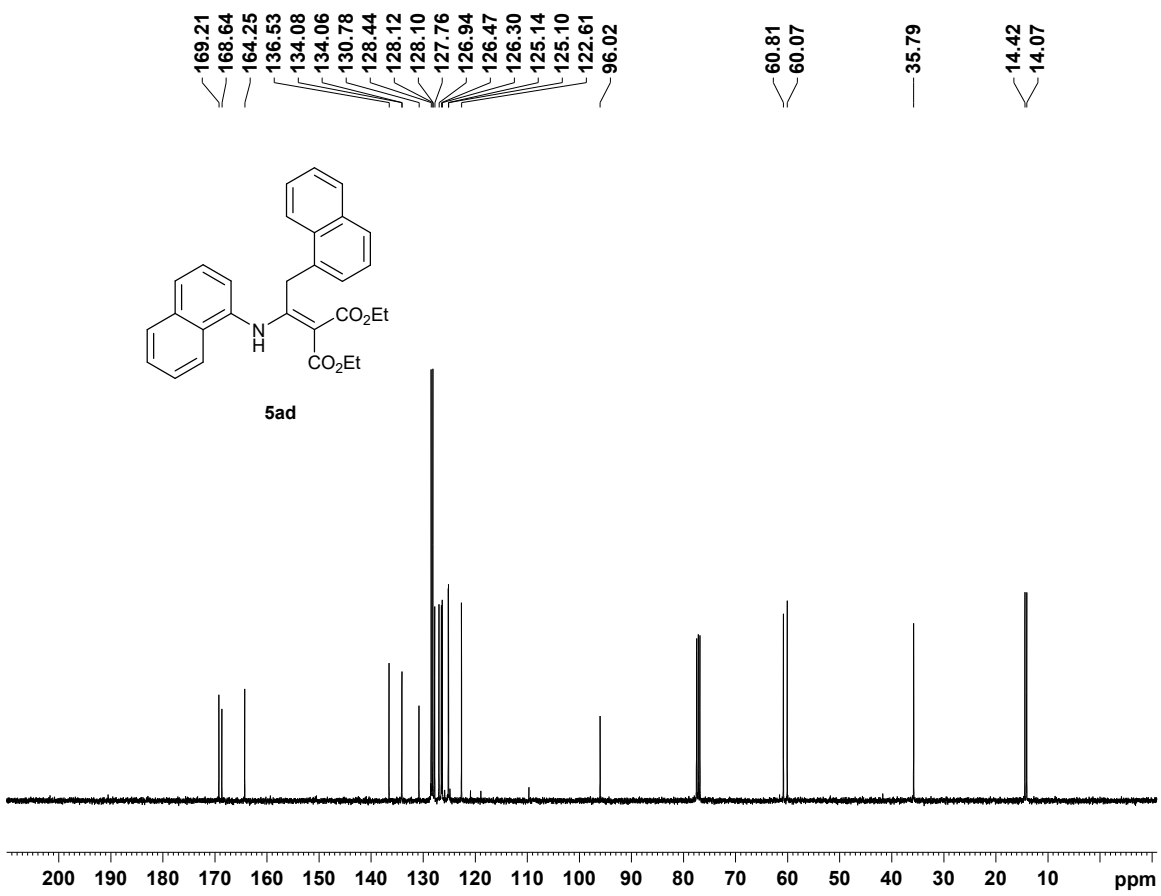

Figure S46. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5ad**

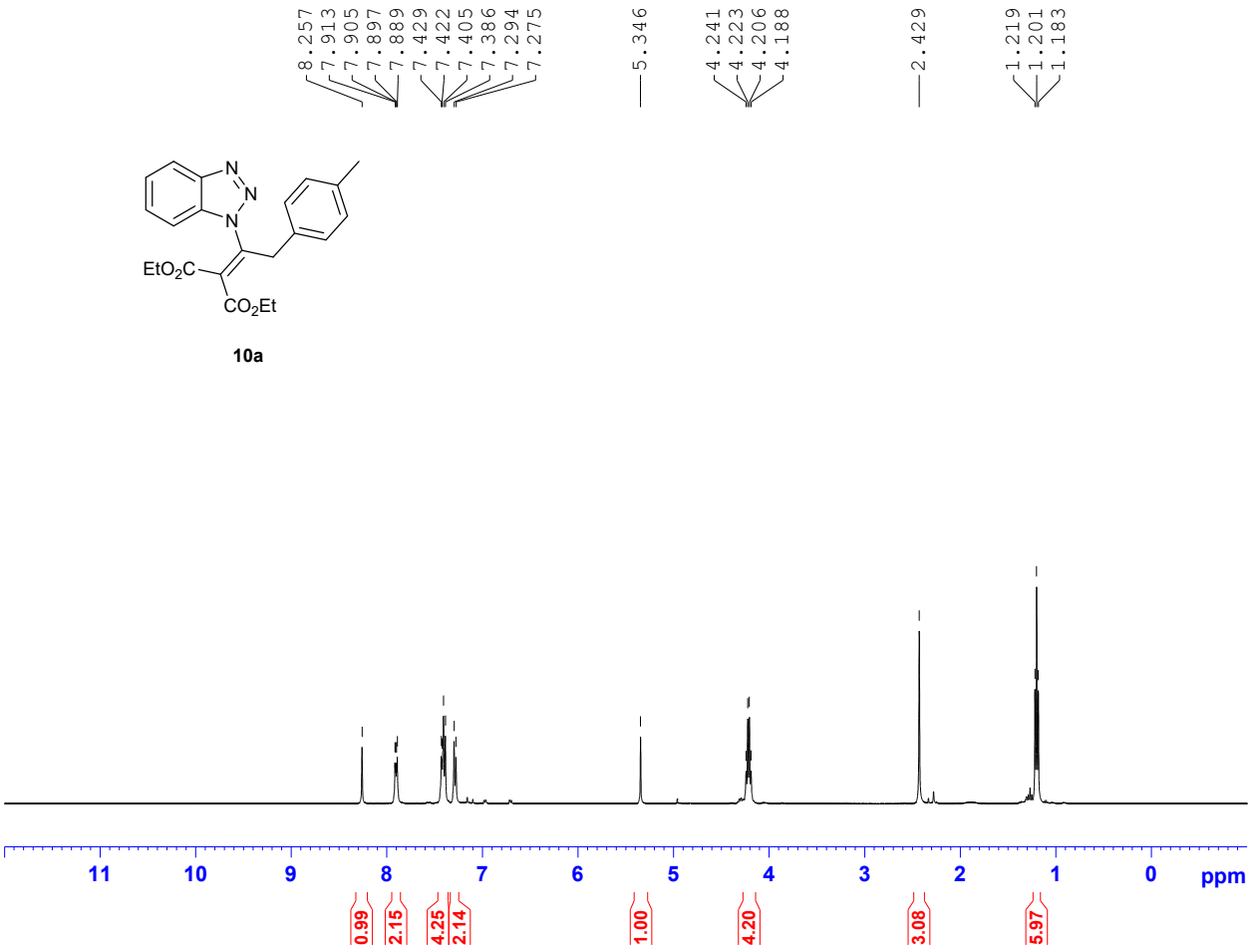

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10a**

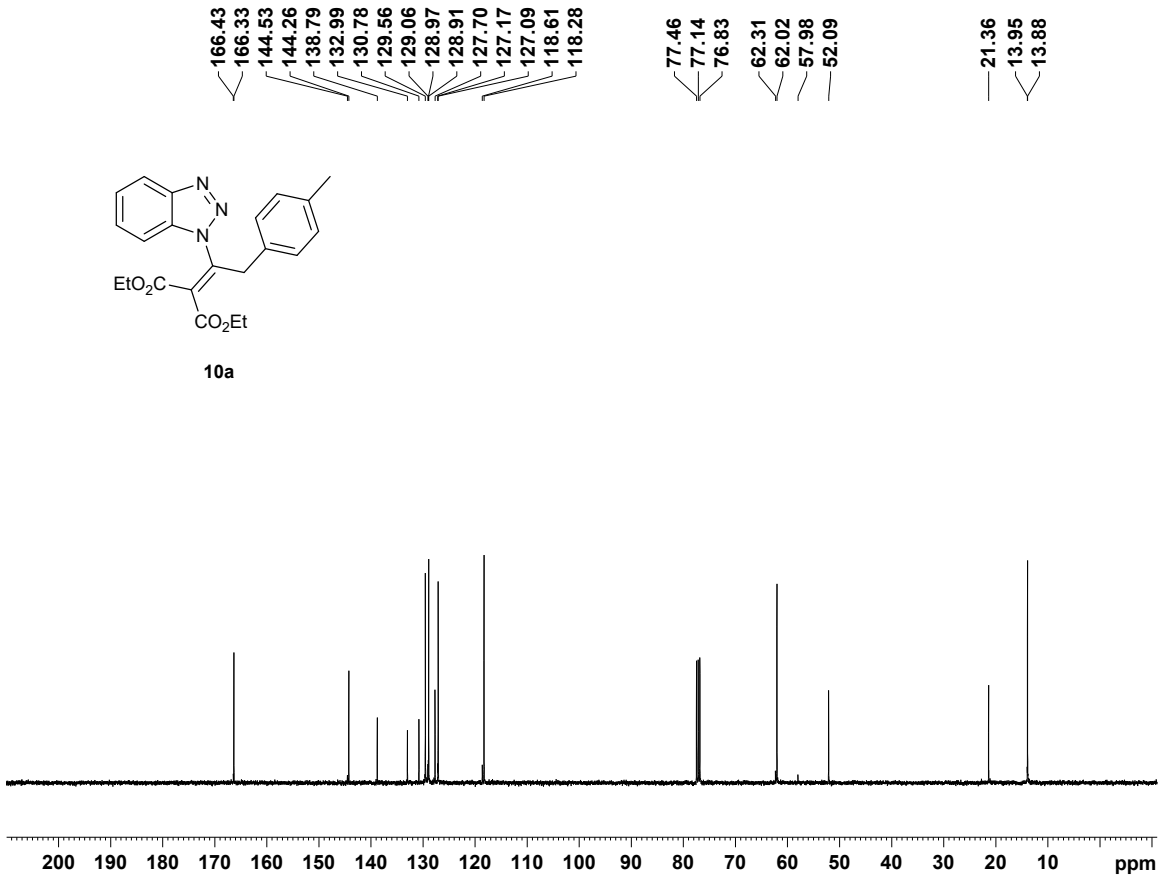

Figure S48. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **10a**

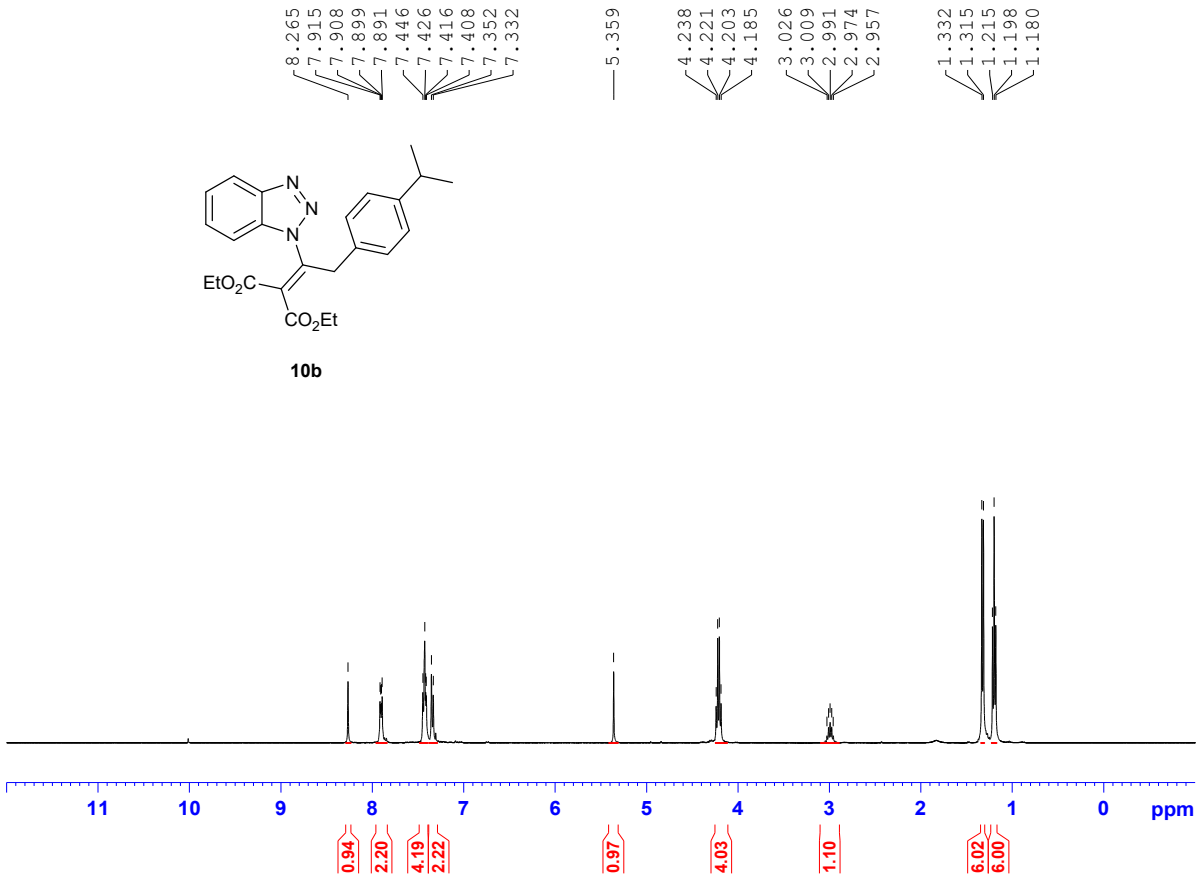

Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10b**

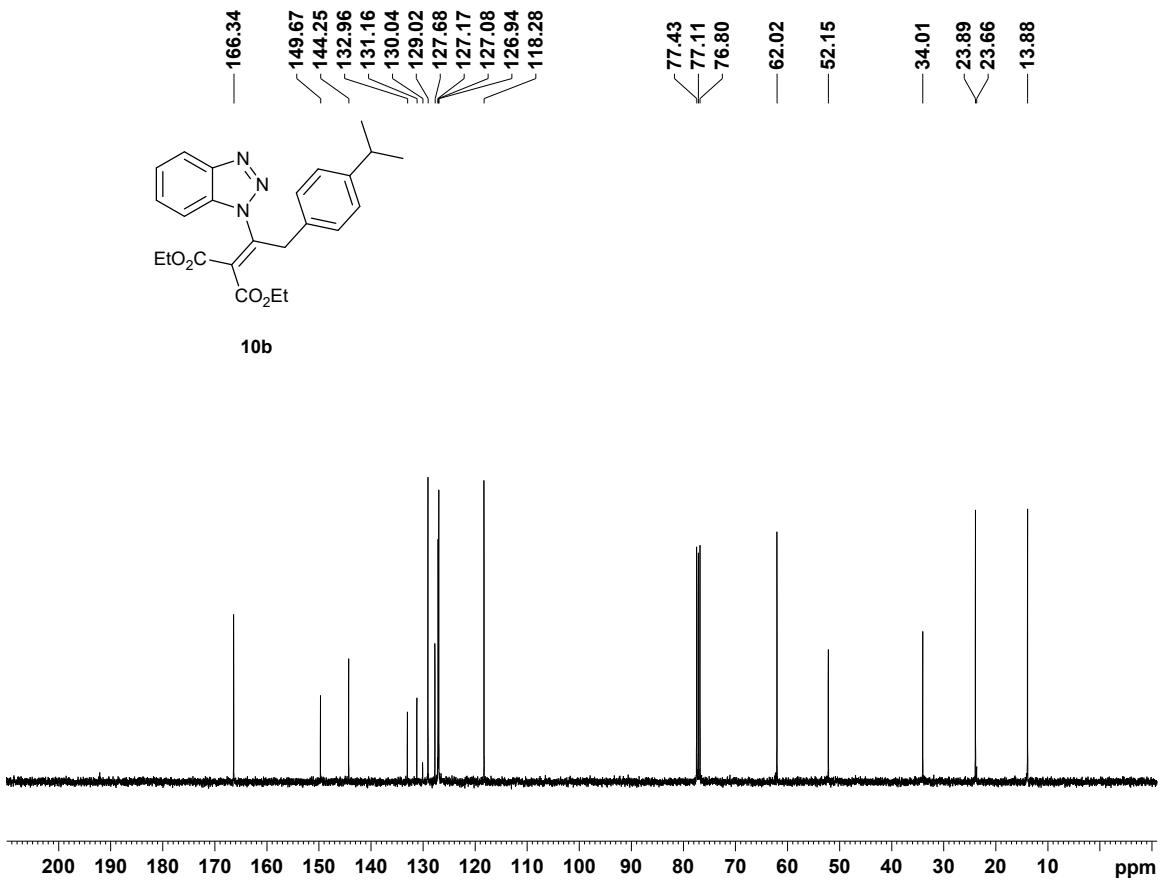

Figure S50. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **10b**

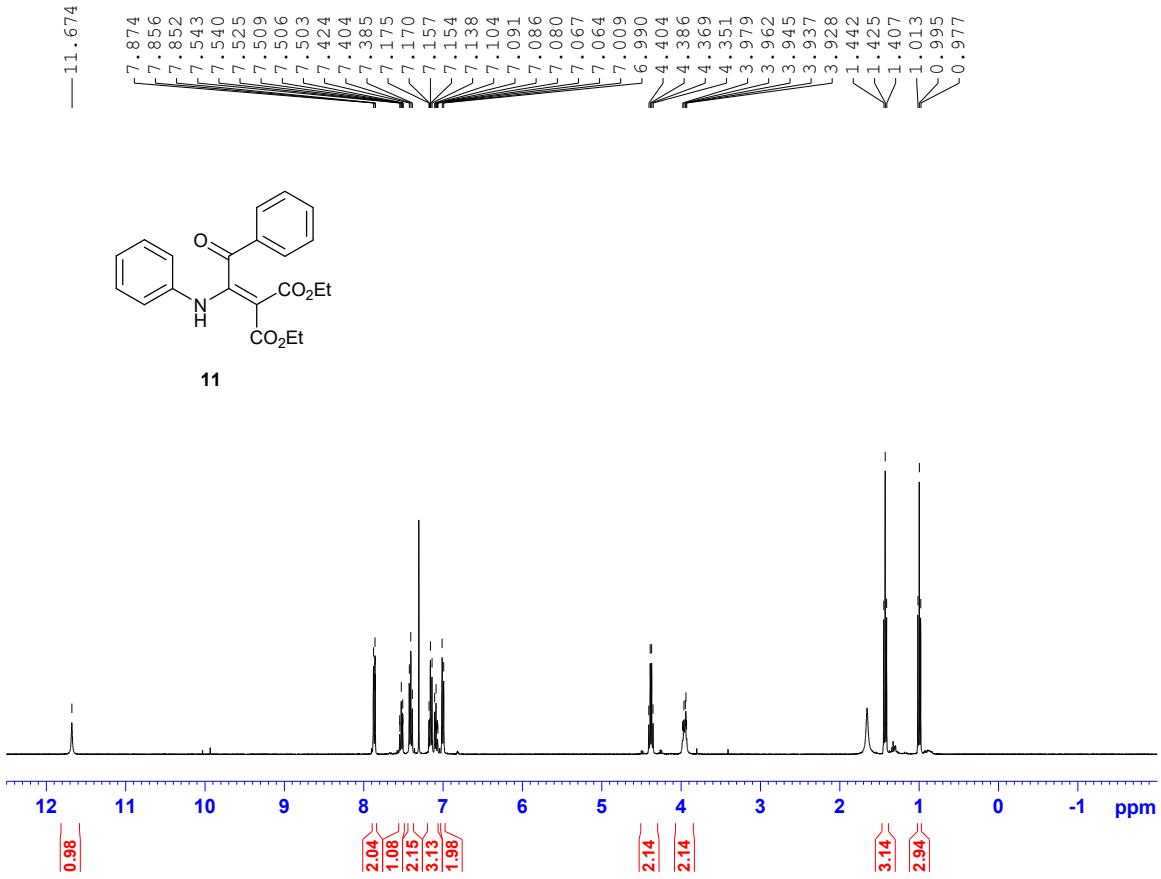

Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

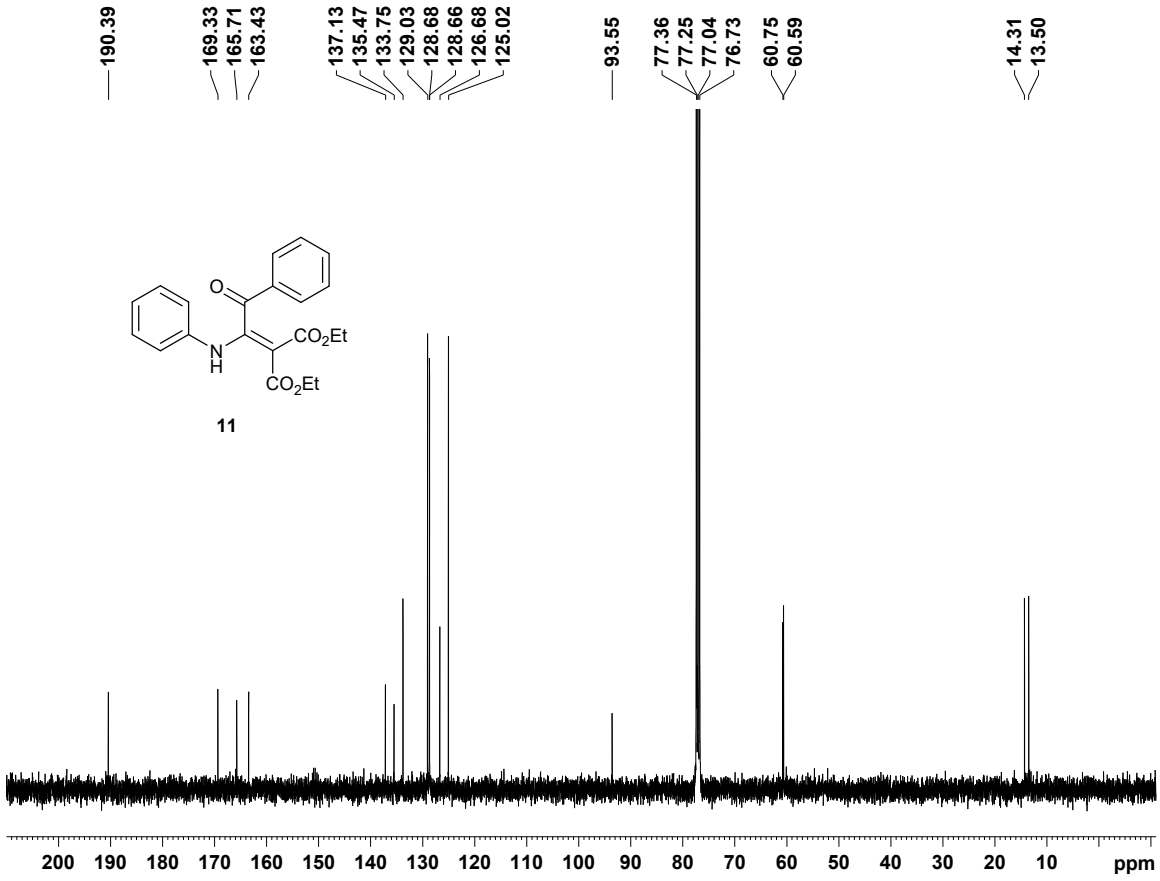

Figure S52. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **11**