Supporting Information

Rhenium Catalyzed Stereoselective Hydrocarboxylation of Alkynes and Olefins: Late-Stage NSAID Drug's Diversification

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1. General information:

Reagent information:

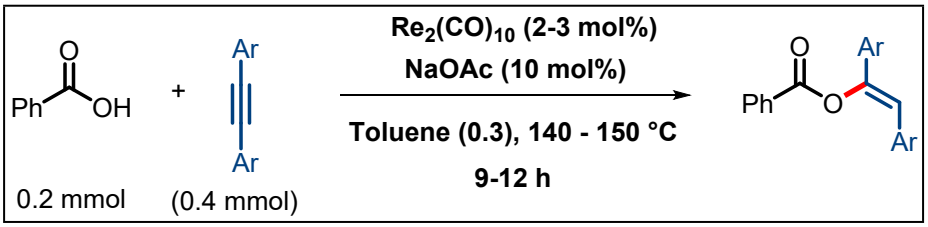
Unless otherwise stated, all reactions were carried out under air atmosphere in screw cap reaction tubes or in screw capped sealed tube. $\mathbf{L_1}$ to $\mathbf{L_9}$ are commercially available and purchased from Sigma Aldrich. All rhenium catalysts were purchased from Sigma Aldrich. All the solvents were bought from Merck, TCI and Spectrochem to ensure sealed bottles and were used as received. Benzyldehydes, heterocycles, boronic acids, silyl alkynes and other reagents were bought from Sigma Aldrich, TCI, and Spectrochem. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using petroleum-ether, diethyl ether, and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel 60F254) and visualized with ultraviolet light (λ = 254 nm).

Analytical information:

^{1}H and ^{13}C were recorded on Bruker 400 MHz and 800 MHz NMR spectrometers. All coupling constants are apparent J values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, bs = broad singlet, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, ttt = triplet of triplet

of triplets). High resolution mass spectra (HRMS) were obtained at the Centre of Biomedical Research Mass Spectrometry Service Center using a Waters GCT Premier instrument run on electron ionization (EI) direct probe or a Waters QTOF Ultima instrument run on electrospray ionization (ESI+).

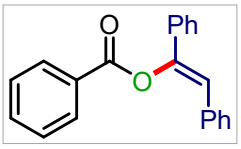
2. General procedure for hydrocarboxylation of Alkynes:



An oven-dried screw-capped sealed tube with a magnetic stir-bar was charged with Re-catalyst (3 mol%, 0.006 mmol), carboxylic acid (0.2 mmol, 1.0 equiv.), internal alkyne (0.4 mmol, 2.0 equiv.), and NaOAc (10 mol%) followed by HPLC-grade toluene ($PhCH_3$, 0.3 mL) was added by micropipette under air. A cap screwed the reaction tube and was vigorously stirred in a preheated oil bath at 140-150 °C for 10-12 h. When the reaction was complete, the reaction mixture was cooled and diluted with ethyl acetate (EtOAc, 5 mL). The mixture was filtered through the short-celite pad and washed with EtOAc (10 mL). The filtrate was concentrated and purified by silica gel (100-200 mesh size) column chromatography using petroleum ether/EtOAc (90/10, v/v) as eluent to give the corresponding pure enol-ester products.

3. Characterization data for hydrocarboxylation of Alkynes:

(Z)-1,2-diphenylvinyl benzoate (1):



TLC: $R_f = 0.5$.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White semi solid.

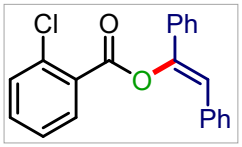
Isolated yield: 88% (52.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 2H), 7.72 – 7.66 (m, 1H), 7.63 (dd, J = 8.2, 1.2 Hz, 2H), 7.60 – 7.54 (m, 4H), 7.38 (tdd, J = 7.0, 4.6, 2.1 Hz, 3H), 7.30 (t, J = 7.5 Hz, 2H), 7.26 – 7.21 (m, 1H), 6.84 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.41, 146.76, 135.79, 134.37, 133.91, 130.40, 129.35, 128.90, 128.89, 128.83, 128.77, 128.70, 127.77, 124.93, 117.27.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}O_2Na^+$ 323.1043, found 323.1026.

(Z)-1,2-diphenylvinyl 2-chlorobenzoate (2):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Colourless semi-solid.

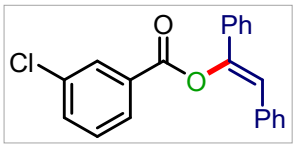
Isolated yield: 91% (60.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.50 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 3H), 7.39 – 7.30 (m, 3H), 7.29 – 7.23 (m, 1H), 6.83 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.87, 146.56, 135.46, 134.77, 134.12, 133.43, 132.19, 131.63, 129.45, 128.77, 128.71, 128.61, 128.54, 127.70, 126.82, 125.01, 117.39,.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}ClO_2Na^+$ 357.0659, found 357.0637.

(Z)-1,2-diphenylvinyl 3-chlorobenzoate (3):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White semi-solid.

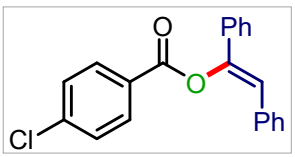
Isolated yield: 94% (62.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.46 – 7.38 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.88 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.29, 146.53, 135.47, 135.12, 134.18, 134.01, 131.05, 130.35, 130.27, 128.92, 128.90, 128.84, 128.77, 128.50, 127.92, 124.91, 117.43.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}ClO_2Na^+$ 357.0659, found 357.0630.

(Z)-1,2-diphenylvinyl 4-chlorobenzoate (4):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid

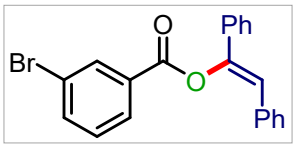
Isolated yield: 90% (60.26 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 4H), 7.45 – 7.37 (m, 3H), 7.36 – 7.27 (m, 3H), 6.85 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.63, 146.60, 140.57, 135.58, 134.25, 131.77, 129.34, 128.89, 128.85, 128.76, 127.89, 127.77, 124.90, 117.38.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}ClO_2Na^+$ 357.0659, found 357.0631.

(Z)-1,2-diphenylvinyl 3-bromobenzoate (5):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

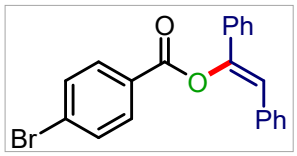
Isolated yield: 86% (65.23 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (t, *J* = 1.7 Hz, 1H), 8.24 – 8.16 (m, 1H), 7.83 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.61 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.31 (m, 6H), 7.28 (dd, *J* = 5.7, 4.5 Hz, 1H), 6.86 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.16, 146.50, 136.92, 135.43, 134.15, 133.25, 131.21, 130.51, 128.94, 128.92, 128.89, 128.83, 128.77, 127.92, 124.89, 123.01, 117.42.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}BrO_2Na^+$ 401.0153, found 401.0167.

(Z)-1,2-diphenylvinyl 4-bromobenzoate (6):[1]



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

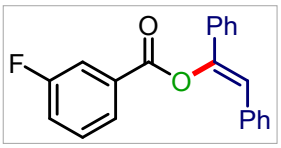
Isolated yield: 89% (67.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.55 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.34 (tdd, *J* = 6.9, 4.6, 2.2 Hz, 3H), 7.28 – 7.19 (m, 3H), 6.79 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.76, 146.55, 135.52, 134.21, 132.32, 131.85, 129.28, 128.87, 128.82, 128.74, 128.18, 127.88, 124.87, 117.36.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}BrO_2Na^+$ 401.0153, found 401.0108.

(Z)-1,2-diphenylvinyl 3-fluorobenzoate (7):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

Isolated yield: 84% (53.48 mg).

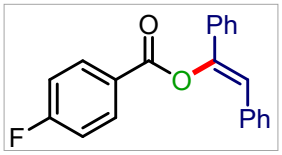
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.88 (dd, *J* = 9.1, 1.8 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.33 (ddd, *J* = 11.7, 7.7, 4.6 Hz, 4H), 7.29 – 7.19 (m, 3H), 6.79 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.09, 163.36, 163.33, 161.63, 146.57, 135.52, 134.21, 131.50, 131.42, 130.67, 130.59, 128.91, 128.90, 128.86, 128.76, 127.91, 126.16, 126.13, 124.92, 121.20, 120.99, 117.42, 117.36, 117.12.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.46, -111.47, -111.48, -111.49, -111.50, -111.52.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}FO_2Na^+$ 341.0954, found 341.0936.

(Z)-1,2-diphenylvinyl 4-fluorobenzoate (8):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Colorless semi-solid.

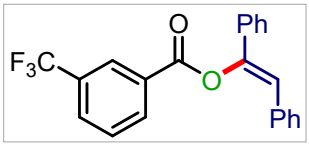
Isolated yield: 82% (52.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.23 (m, 2H), 7.59 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.37 (ddd, *J* = 8.4, 7.8, 3.7 Hz, 3H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.82 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.71, 165.17, 163.48, 146.65, 135.67, 134.30, 133.08, 132.99, 128.85, 128.73, 127.84, 125.61, 125.58, 124.90, 117.35, 116.28, 116.06.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}FO_2Na^+$ 341.0954, found 341.0929.

(Z)-1,2-diphenylvinyl 3-(trifluoromethyl)benzoate (9):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Yellow solid.

Isolated yield: 94% (69.2 mg).

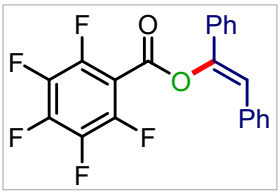
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.37 (m, 3H), 7.36 – 7.27 (m, *J* = 12.7, 4.7 Hz, 3H), 6.88 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.21, 146.54, 135.40, 134.14, 133.51, 131.86, 131.53, 130.48, 130.45, 130.23, 129.69, 128.99, 128.92, 128.83, 128.78, 127.98, 127.25, 127.21, 124.93, 122.34, 117.55.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{15}F_3O_2Na^+$ 391.0922, found 391.0903.

(Z)-1,2-diphenylvinyl 2,3,4,5,6-pentafluorobenzoate (10):



TLC: R_f = 0.6.

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: Light-yellow solid.

Isolated yield: 79% (61.6 mg).

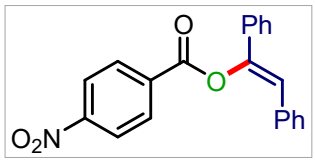
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.33 (m, 5H), 7.30 (dt, *J* = 4.7, 1.8 Hz, 1H), 6.83 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.91, 146.16, 145.18, 136.72, 134.76, 133.70, 131.55, 129.19, 128.98, 128.78, 128.21, 126.71, 125.20, 118.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -136.54, -136.55, -136.57, -136.58, -136.61, -136.62, -136.64, -146.70, -146.71, -146.76, -146.77, -146.78, -146.82, -159.45, -159.47, -159.48, -159.51, -159.52, -159.54, -159.55, -159.58, -159.59, -159.61.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{11}F_5O_2Na^+$ 413.0577, found 413.0564.

(Z)-1,2-diphenylvinyl 4-nitrobenzoate (11):



TLC: R_f = 0.7.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Yellow solid.

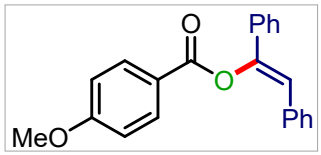
Isolated yield: 51% (35.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.32 (m, 4H), 7.63 – 7.55 (m, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.34 (m, 3H), 7.33 - 7.25 (m, 3H), 6.87 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.49, 151.02, 146.29, 135.00, 134.46, 133.86, 131.33, 128.96, 128.82, 128.67, 128.63, 127.93, 124.75, 123.95, 117.48.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}NO_4Na^+$ 368.0899, found 368.0865.

(Z)-1,2-diphenylvinyl 4-methoxybenzoate (12):



TLC: R_f = 0.3.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

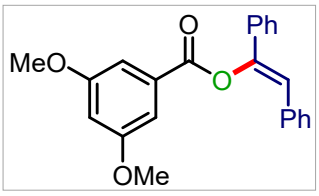
Isolated yield: 90% (59.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H), 7.61 – 7.51 (m, 4H), 7.37 – 7.23 (m, 5H), 7.19 (dd, *J* = 8.4, 6.3 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.78 (s, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.22, 164.15, 146.84, 136.00, 134.50, 132.57, 128.90, 128.80, 128.68, 127.70, 124.92, 121.69, 117.17, 114.19, 55.68.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}O_3Na^+$ 353.1154, found 353.1130.

(Z)-1,2-diphenylvinyl 3,5-dimethoxybenzoate (13):



TLC: R_f = 0.4.

Eluent: petroleum ether/ethyl acetate (85/15, v/v).

Appearance: White solid.

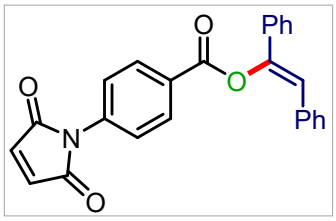
Isolated yield: 89% (64.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 4H), 7.27 – 7.09 (m, 8H), 6.68 (s, 1H), 6.64 (t, *J* = 2.3 Hz, 1H), 3.74 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.25, 161.08, 146.74, 135.73, 134.34, 131.16, 128.92, 128.85, 128.81, 128.76, 127.83, 124.95, 117.26, 107.93, 106.70, 55.82.

HRMS (ESI) m/z: $[M+Na^+]$ calcd for $C_{23}H_{20}O_4Na^+$ 383.1260, found 383.1231.

(Z)-1,2-diphenylvinyl 4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzoate (14):



TLC: R_f = 0.51.

Eluent: petroleum ether/ethyl acetate (80/20, v/v).

Appearance: Brown-yellow solid.

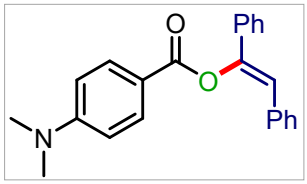
Isolated yield: 93% (73.54 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.7 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.28 (m, 5H), 7.26 – 7.22 (m, 1H), 6.91 (s, 2H), 6.82 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.04, 163.59, 146.57, 136.30, 135.58, 134.61, 134.24, 131.34, 128.88, 128.85, 128.79, 128.27, 127.88, 125.73, 124.88, 117.36.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{17}NO_4Na^+$ 418.1056, found 418.1063.

(Z)-1,2-diphenylvinyl 4-(dimethylamino)benzoate (15):



TLC: R_f = 0.51.

Eluent: petroleum ether/ethyl acetate (80/20, v/v).

Appearance: Colorless semi-solid.

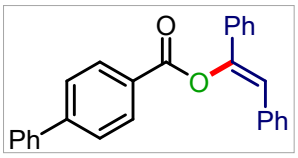
Isolated yield: 81% (55.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.0 Hz, 2H), 7.62 – 7.55 (m, 4H), 7.37 – 7.26 (m, 5H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 3H), 3.10 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.60, 153.49, 147.06, 136.32, 134.69, 132.35, 128.95, 128.89, 128.84, 128.75, 128.65, 128.57, 127.56, 124.95, 117.02, 111.81, 40.67.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}NO_2Na^+$ 366.1470, found 366.1446.

(Z)-1,2-diphenylvinyl [1,1'-biphenyl]-4-carboxylate (16):



TLC: R_f = 0.51.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

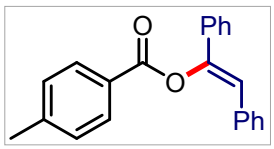
Isolated yield: 73% (55.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.61 – 7.57 (m, 2H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.47 (dd, *J* = 14.8, 7.7 Hz, 3H), 7.40 – 7.28 (m, 5H), 7.21 – 7.16 (m, 1H), 6.80 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.31, 146.77, 146.69, 139.91, 135.79, 134.38, 130.94, 129.14, 128.90, 128.84, 128.78, 128.72, 128.50, 127.99, 127.78, 127.58, 127.46, 124.93, 124.87, 117.27.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{20}O_2Na^+$ 399.1361, found 399.1328.

(Z)-1,2-diphenylvinyl 4-methylbenzoate (17):



TLC: R_f = 0.51.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

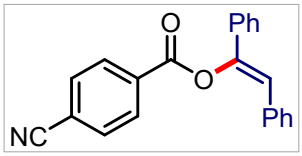
Isolated yield: 82% (51.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.51 (m, 4H), 7.38 – 7.30 (m, 5H), 7.25 (dd, *J* = 12.1, 4.3 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 1H), 6.78 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.50, 146.78, 144.85, 135.88, 134.42, 130.49, 129.64, 128.90, 128.82, 128.74, 128.70, 127.73, 126.59, 124.91, 117.19, 21.94.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}O_2Na^+$ 337.1205, found 337.1186.

(Z)-1,2-diphenylvinyl 4-cyanobenzoate (18):



TLC: R_f = 0.55.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

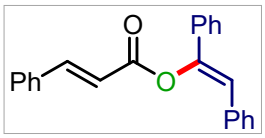
Isolated yield: 71% (*E*:*Z* = 8:1; 46.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.22 - 7.11 (m, 3H), 6.75 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.72, 146.27, 135.03, 133.87, 132.89, 132.58, 130.63, 128.90, 128.78, 128.63, 128.62, 127.87, 124.71, 117.76, 117.41, 117.20.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{15}NO_2Na^+$ 348.1001, found 348.1011.

(Z)-1,2-diphenylvinyl cinnamate (19):



TLC: R_f = 0.45.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

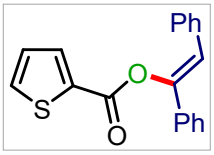
Isolated yield: 79% (51.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.67 – 7.55 (m, 3H), 7.50 – 7.45 (m, 2H), 7.45 – 7.33 (m, 3H), 7.43 - .40 (m, 1H), 7.30 – 7.23 (m, 1H), 6.79 (s, 1H), 6.73 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.60, 147.18, 146.47, 135.62, 134.30, 134.04, 130.88, 129.02, 128.75, 128.67, 128.58, 128.42, 127.64, 124.80, 116.92, 116.79.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}O_2Na^+$ 349.1205, found 349.1180.

(Z)-1,2-diphenylvinyl thiophene-2-carboxylate (20):



TLC: R_f = 0.51.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

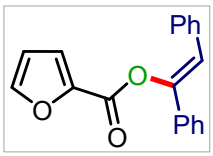
Isolated yield: 68% (41.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.76 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.70 – 7.63 (m, 4H), 7.48 – 7.35 (m, 6H), 7.33 – 7.25 (m, 2H), 6.87 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 146.34, 135.62, 135.09, 134.22, 133.92, 132.60, 129.01, 128.83, 128.81, 128.72, 128.37, 127.83, 124.92, 117.46.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{14}O_2SNa^+$ 329.0613, found 329.0593.

(Z)-1,2-diphenylvinyl furan-2-carboxylate (21):



TLC: R_f = 0.51.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Brown-yellow liquid.

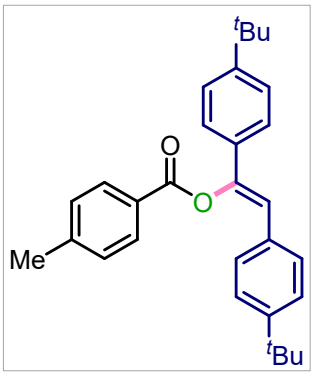
Isolated yield: 74% (43.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 1H), 7.58 (ddd, *J* = 11.7, 6.1, 4.5 Hz, 4H), 7.44 (dd, *J* = 3.5, 0.6 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.32 (ddd, *J* = 15.1, 9.0, 4.5 Hz, 3H), 7.25 – 7.21 (m, 1H), 6.80 (s, 1H), 6.63 (dd, *J* = 3.5, 1.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.22, 147.55, 146.01, 144.07, 135.51, 134.21, 129.16, 128.99, 128.84, 128.73, 127.88, 124.99, 119.82, 117.58, 112.41.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{14}O_3Na^+$ 313.0841, found 313.0823.

(Z)-1,2-bis(4-(tert-butyl)phenyl)vinyl 4-methylbenzoate (22):



TLC: R_f = 0.71

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: colorless liquid.

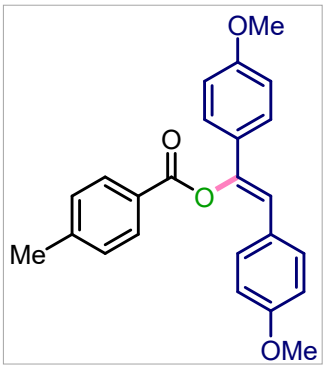
Isolated yield: 82% (70.0 mg); Z:E = 6:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 8.7 Hz, 4H), 7.37 (dd, *J* = 8.2, 6.3 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.76 (s, 1H), 2.49 (s, 3H), 1.32 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.61, 151.64, 150.64, 146.25, 144.72, 133.13, 131.72, 130.53, 129.63, 128.63, 126.80, 125.75, 125.66, 124.53, 116.27, 34.75, 34.70, 31.36, 31.33, 21.94.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{34}O_2Na^+$ 449.2451; found 449.2427.

(Z)-1,2-bis(4-methoxyphenyl)vinyl 4-methylbenzoate (23):



TLC: $R_f = 0.41$

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

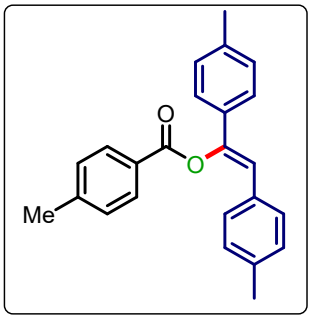
Appearance: colorless liquid.

Isolated yield: 69% (59.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2 Hz, 2H), 7.48 (dd, J = 10.7, 8.9 Hz, 4H), 7.34 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.64 (s, 1H), 3.78 (d, J = 17.0 Hz, 6H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.59, 159.83, 158.86, 145.08, 144.74, 130.47, 130.02, 129.62, 128.69, 127.39, 126.75, 126.08, 114.99, 114.21, 114.12, 55.45, 55.32, 21.93.

(Z)-1,2-di-p-tolylvinyl 4-methylbenzoate (23a):



TLC: $R_f = 0.5$

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

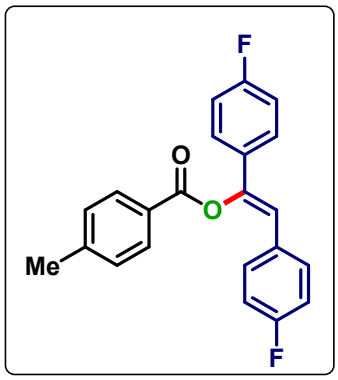
Appearance: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.08 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 – 7.31 (m, 6H), 7.05 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 6.64 (s, 1H), 2.23 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.26, 146.01, 138.38, 137.29, 133.63, 132.90, 131.48, 130.20, 130.00, 129.33, 129.31, 129.22, 129.09, 128.91, 128.80, 128.68, 128.60, 128.55, 128.44, 124.55, 116.11, 21.16.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{22}O_2Na^+$ 365.1512; found 365.1516

(Z)-1,2-bis(4-fluorophenyl)vinyl 4-methylbenzoate (24):



TLC: $R_f = 0.51$

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: colorless liquid.

Isolated yield: 92% (64.5 mg).

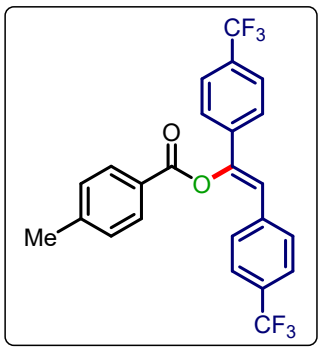
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.48 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 8.7 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.68 (s, 1H), 2.48 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.61, -112.63, -112.64, -112.65, -112.66, -112.67, -112.69, -113.30, -113.32, -113.33, -113.33, -113.34, -113.35, -113.36, -113.36, -113.38.

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.38, 164.30, 163.36, 161.83, 160.89, 145.71, 145.15, 132.06, 132.03, 130.53, 130.45, 129.75, 126.84, 126.76, 126.32, 115.99, 115.84, 115.77, 115.63, 21.95.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{16}F_2O_2Na^+$ 373.1011; found 373.0993

(Z)-1,2-bis(4-(trifluoromethyl)phenyl)vinyl 4-methylbenzoate (24a):



TLC: R_f = 0.5

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

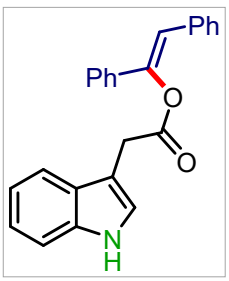
Appearance: colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.3 Hz, 2H), 7.63 - 7.50 (m, 7H), 7.51 – 7.43 (m, 4H), 6.80 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.99, 147.14, 138.72, 137.16, 134.34, 131.04, 130.72, 130.27, 130.12, 129.92, 129.60, 129.25, 129.16, 129.03, 129.01, 128.70, 128.44, 125.88, 125.85, 125.81, 125.77, 125.65, 125.61, 125.58, 125.54, 125.27, 125.22, 122.58, 122.51, 117.77.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{22}F_6O_2Na^+$ 473.9467; found 473.9463

(Z)-1,2-diphenylvinyl 2-(1H-indol-3-yl)acetate (25):



TLC: R_f = 0.6.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Brown semi-solid.

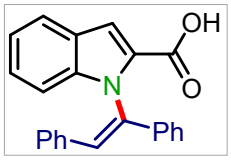
Isolated yield: 89% (62.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.29 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.24 – 7.21 (m, 1H), 7.18 – 7.13 (m, 5H), 6.67 (s, 1H), 4.05 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.54, 146.77, 136.22, 135.71, 134.29, 129.09, 128.93, 128.88, 128.71, 128.66, 128.51, 128.41, 127.63, 127.38, 124.90, 123.68, 122.51, 120.05, 119.05, 117.00, 111.33, 107.47, 31.69.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{19}NO_2Na^+$ 376.1308, found 376.1286.

(Z)-1,2-diphenylvinyl 1H-indole-2-carboxylate (26):



TLC: R_f = 0.62.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Yellow semi-solid.

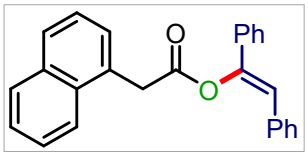
Isolated yield: 85% (57.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.42 (ddd, *J* = 9.6, 5.3, 2.4 Hz, 5H), 7.27 – 7.19 (m, 6H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.38, 149.68, 140.12, 135.12, 133.08, 130.79, 129.25, 129.20, 128.62, 128.56, 128.07, 127.98, 127.17, 123.18, 122.66, 121.19, 121.10, 116.57, 112.82.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{17}O_2Na^+$ 362.1151, found 362.1169.

(Z)-1,2-diphenylvinyl 2-(naphthalen-1-yl)acetate (27):



TLC: R_f = 0.41.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Colorless semi-solid.

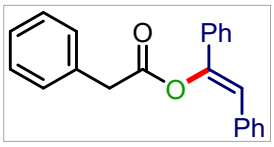
Isolated yield: 90% (65.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 1H), 7.92 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.48 (m, 4H), 7.36 – 7.32 (m, 2H), 7.29 – 7.24 (m, 5H), 7.17 – 7.10 (m, 3H), 6.61 (s, 1H), 4.30 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.90, 146.74, 135.65, 134.16, 134.03, 132.30, 129.62, 128.88, 128.80, 128.76, 128.65, 128.59, 128.46, 127.60, 126.74, 126.11, 125.70, 124.91, 124.08, 117.08, 39.71.

HRMS (ESI) m/z: $[M+Na^+]$ calcd for $C_{26}H_{20}O_2Na^+$ 387.1356, found 387.1348.

(Z)-1,2-diphenylvinyl 2-phenylacetate (28):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

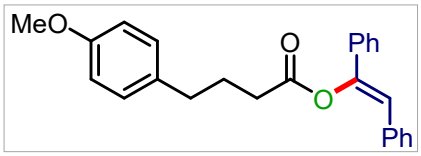
Isolated yield: 86% (54.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 9H), 7.28 – 7.26 (m, 3H), 7.20 – 7.16 (m, 3H), 6.62 (s, 1H), 3.83 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76, 146.51, 135.50, 134.10, 132.90, 129.63, 128.77, 128.70, 128.58, 128.55, 128.43, 127.52, 127.49, 124.71, 116.93, 41.75.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}O_2Na$ 337.1199, found 337.1189.

(Z)-1,2-diphenylvinyl 4-(4-methoxyphenyl)butanoate (29):



TLC: R_f = 0.41.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

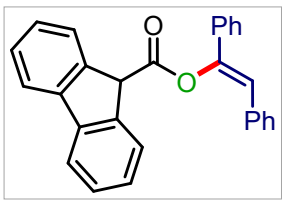
Isolated yield: 87% (64.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 4H), 7.41 – 7.32 (m, 5H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.70 (s, 1H), 3.80 (s, 3H), 2.61 (dt, *J* = 15.0, 7.4 Hz, 4H), 2.05 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.25, 158.11, 146.81, 135.89, 134.54, 133.33, 129.54, 128.84, 128.80, 128.76, 128.66, 127.74, 124.96, 117.00, 114.02, 55.42, 34.20, 33.66, 26.52.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{24}O_3Na$ 395.1618, found 395.1609.

(Z)-1,2-diphenylvinyl 9H-fluorene-9-carboxylate (30):



TLC: R_f = 0.5.

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

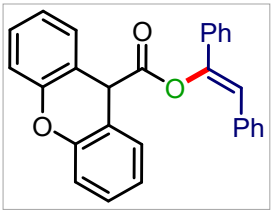
Isolated yield: 86% (66.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 3H), 7.40 (dd, *J* = 7.9, 7.1 Hz, 3H), 7.30 (s, 4H), 7.19 (dd, *J* = 7.2, 4.2 Hz, 4H), 6.58 (s, 1H), 5.04 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.87, 146.71, 141.95, 140.11, 135.76, 133.95, 128.96, 128.79, 128.69, 128.66, 128.62, 128.44, 127.78, 127.59, 127.56, 125.96, 125.06, 124.87, 120.49, 117.40, 116.91, 54.25.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{20}O_2Na$ 411.1356, found 411.1334.

(Z)-1,2-diphenylvinyl 9H-xanthene-9-carboxylate (31):



TLC: R_f = 0.41

Eluent: petroleum ether/ethyl acetate (85/15, v/v).

Appearance: White solid.

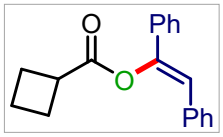
Isolated yield: 92% (74.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.22 – 7.11 (m, 6H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.96 – 6.91 (m, 2H), 6.50 (s, 1H), 5.14 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.38, 151.67, 146.39, 135.62, 133.90, 129.79, 129.45, 128.78, 128.53, 128.49, 128.48, 127.42, 124.63, 123.62, 117.71, 117.50, 117.22, 46.61.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{20}O_3Na$ 427.1305, found 427.1323.

(Z)-1,2-diphenylvinyl cyclobutanecarboxylate (32):



TLC: R_f = 0.7

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: White solid.

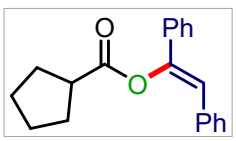
Isolated yield: 64% (35.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 4H), 7.41 – 7.32 (m, 5H), 7.28 – 7.25 (m, 1H), 6.70 (s, 1H), 3.44 (pd, *J* = 8.6, 0.9 Hz, 1H), 2.46 – 2.26 (m, 4H), 2.12 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.94, 146.82, 136.00, 134.56, 133.30, 129.61, 128.92, 128.82, 128.78, 128.71, 128.57, 127.69, 127.03, 124.93, 116.97, 38.27, 25.31, 18.63.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}O_2Na^+$ 301.1199, found 301.1183.

(Z)-1,2-diphenylvinyl cyclopentanecarboxylate (33):



TLC: R_f = 0.65

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: White solid.

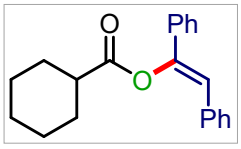
Isolated yield: 70% (40.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dt, *J* = 8.6, 4.5 Hz, 4H), 7.41 – 7.32 (m, 5H), 7.28 – 7.24 (m, 1H), 6.69 (s, 1H), 3.02 (p, *J* = 8.1 Hz, 1H), 2.09 – 1.99 (m, 2H), 1.97 – 1.87 (m, 2H), 1.74 (ddd, *J* = 9.7, 5.6, 2.8 Hz, 2H), 1.69 – 1.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32, 146.93, 136.10, 134.56, 128.91, 128.77, 128.67, 128.55, 127.66, 124.94, 117.00, 44.17, 30.07, 25.85.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{20}O_2Na^+$ 315.1361, found 315.1344.

(Z)-1,2-diphenylvinyl cyclohexanecarboxylate (34):



TLC: R_f = 0.61

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: White solid.

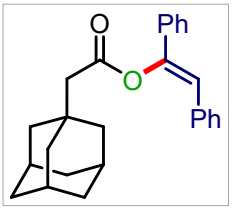
Isolated yield: 77% (47.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 4H), 7.41 – 7.31 (m, 5H), 7.27 – 7.25 (m, 1H), 6.69 (s, 1H), 2.58 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.08 (dd, *J* = 13.1, 2.9 Hz, 2H), 1.88 – 1.78 (m, 2H), 1.75 – 1.64 (m, 1H), 1.63 – 1.50 (m, 4H), 1.41 – 1.25 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.64, 146.85, 136.10, 134.55, 128.90, 128.76, 128.67, 128.55, 127.66, 124.95, 117.05, 43.57, 29.05, 25.81, 25.57.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{22}O_2Na^+$ 329.1512, found 329.1505.

(Z)-1,2-diphenylvinyl 2-((3r,5r,7r)-adamantan-1-yl)acetate (35):



TLC: R_f = 0.55

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: Yellow solid.

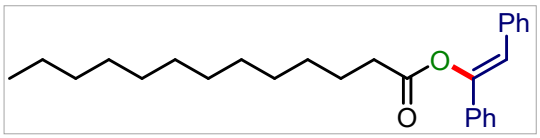
Isolated yield: 72% (53.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 4H), 7.42 – 7.32 (m, 6H), 6.66 (s, 1H), 2.36 (s, 2H), 1.97 (s, 3H), 1.67 (d, *J* = 14.8 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.53, 147.12, 136.26, 134.60, 129.18, 129.11, 128.94, 128.71, 128.66, 128.57, 128.45, 128.29, 127.65, 127.25, 125.22, 120.16, 117.13, 48.70, 48.36, 42.48, 42.33, 36.82, 33.29, 33.11, 29.85, 28.72, 28.67.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{28}O_2Na^+$ 395.1987, found 395.1961.

(Z)-1,2-diphenylvinyl tridecanoate (36):



TLC: $R_f = 0.7$

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: White solid.

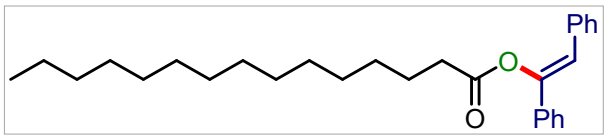
Isolated yield: 84% (65.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 4H), 7.41 – 7.33 (m, 5H), 7.30 – 7.26 (m, 1H), 6.70 (s, 1H), 2.58 (t, J = 7.5 Hz, 2H), 1.72 (dt, J = 14.9, 7.4 Hz, 2H), 1.27 (s, 18H), 0.89 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.53, 146.83, 135.94, 134.56, 128.85, 128.77, 128.72, 128.63, 127.71, 124.95, 116.94, 34.56, 32.07, 29.82, 29.79, 29.74, 29.59, 29.51, 29.41, 29.30, 24.86, 22.84, 14.27.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{36}O_2Na^+$ 415.2608, found 415.2625.

(Z)-1,2-diphenylvinyl palmitate (37):



TLC: $R_f = 0.71$

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: White solid.

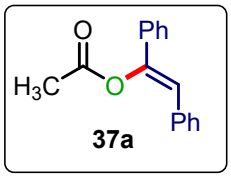
Isolated yield: 81% (68.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dt, J = 14.0, 4.6 Hz, 4H), 7.40 – 7.32 (m, 5H), 7.29 – 7.26 (m, 1H), 6.69 (s, 1H), 2.58 (t, J = 7.5 Hz, 2H), 1.71 (dt, J = 15.0, 7.6 Hz, 2H), 1.26 (s, 22H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.55, 146.83, 135.94, 134.56, 128.86, 128.78, 128.73, 128.64, 127.72, 124.96, 116.95, 34.57, 32.08, 29.84, 29.81, 29.75, 29.60, 29.51, 29.41, 29.31, 24.87, 22.84, 14.28.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{42}O_2Na^+$ 457.3077, found 457.3048.

(Z)-1,2-diphenylvinyl acetate (37a):



TLC: $R_f = 0.8$

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: White solid.

Isolated yield: 85% (35 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.53 (m, 4H), 7.45 – 7.34 (m, 5H), 7.31 - 7.28 (m, 1 Hz, 1H), 6.74 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.58, 146.56, 135.51, 134.33, 128.65, 128.55, 127.64, 124.73, 116.76, 77.32, 77.00, 76.68, 21.08.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{14}O_2Na^+$ 261.0886, found 261.0892.

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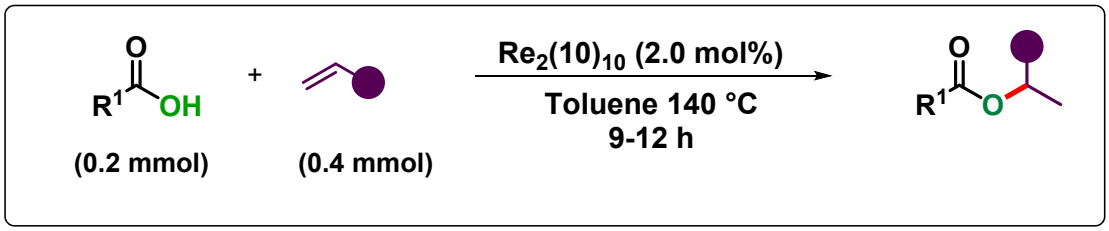
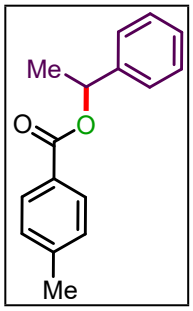
3. General procedure for hydrocarboxylation of Olefines:



An oven-dried screw-capped sealed tube with a magnetic stir-bar was charged with $[Re_2(CO)_{10}$ (2.0 mol%; 0.004 mmol), carboxylic acid (0.2 mmol, 1.0 equiv.), olefin (0.4 mmol, 2.0 equiv.), followed by HPLC-grade toluene ($PhCH_3$, 0.3 mL) was added by micropipette under air. A cap screwed the reaction tube and was vigorously stirred in a preheated oil bath at 140-150 °C for 9-12 h. When the reaction was complete, the reaction mixture was cooled and diluted with ethyl acetate (EtOAc, 5 mL). The mixture was filtered through the short-celite pad and washed with EtOAc (10 mL). The filtrate was concentrated and purified by silica gel (100-200 mesh size) column chromatography using petroleum ether/EtOAc (90/10, v/v) as eluent to give the corresponding pure products.

1-phenylethyl 4-methylbenzoate (38):[2]



TLC: R_f = 0.65

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: colorless liquid.

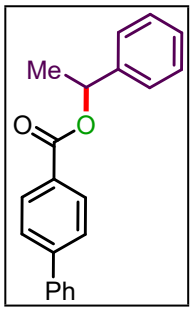
Isolated yield: 69% (36.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.4 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.33 – 7.30 (m, 1H), 7.24 (s, 2H), 6.14 (dd, J = 12.9, 6.4 Hz, 3H), 2.42 (s, 3H), 1.74 – 1.62 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.02, 143.70, 142.07, 129.81, 129.17, 128.65, 128.59, 127.94, 126.15, 72.80, 22.57, 21.78.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}O_2Na^+$ 263.1043, found 263.1040.

1-phenylethyl [1,1'-biphenyl]-4-carboxylate (39)



TLC: R_f = 0.61

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: colorless liquid.

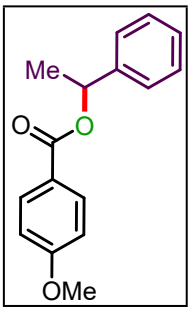
Isolated yield: 63% (37.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.50 (dd, *J* = 7.0, 5.6 Hz, 4H), 7.46 – 7.38 (m, 3H), 7.36 (d, *J* = 7.0 Hz, 1H), 6.20 (q, *J* = 6.5 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 145.70, 141.84, 140.07, 130.22, 129.26, 128.98, 128.61, 128.18, 127.95, 127.33, 127.08, 126.10, 77.39, 77.08, 76.76, 72.98, 22.50.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{18}O_2Na^+$ 325.1199; found 325.1163.

1-phenylethyl 4-methoxybenzoate (40)



TLC: R_f = 0.62

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: colorless liquid.

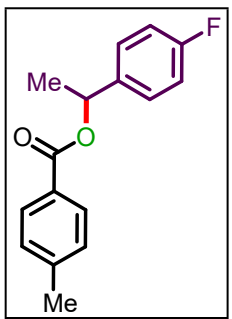
Isolated yield: 65% (33.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.35 (t , *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.18 (q, *J* = 6.6 Hz, 1H), 3.87 (s, 3H), 1.72 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.58, 163.37, 142.05, 131.69, 128.55, 127.83, 126.03, 122.92, 113.60, 77.48, 77.16, 76.84, 72.55, 55.40, 22.52.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{17}O_3Na^+$ 279.0992; found 279.0953.

1-(4-fluorophenyl)ethyl 4-methylbenzoate (41):



TLC: R_f = 0.55

Eluent: petroleum ether/ethyl acetate (97/3, v/v).

Appearance: colorless liquid.

Isolated yield: 62% (35 mg).

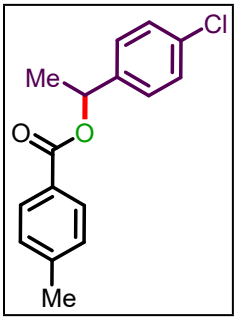
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.41 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.09 (q, *J* = 6.5 Hz, 1H), 2.41 (s, 3H), 1.64 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.99, 163.68, 161.24, 143.85, 137.89, 129.80, 129.22, 128.03, 127.95, 127.79, 115.64, 115.43, 72.16, 22.55, 21.81.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.49, -114.50, -114.51, -114.53, -114.54, -114.55, -114.56.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}FO_2Na^+$ 281.0948; found 281.0952.

1-(4-chlorophenyl)ethyl 4-methylbenzoate (42):



TLC: R_f = 0.61

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: colorless liquid.

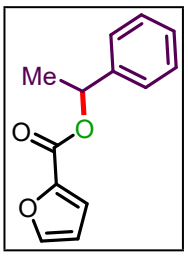
Isolated yield: 62% (34.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.07 (q, *J* = 6.6 Hz, 1H), 2.41 (s, 3H), 1.64 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.94, 143.90, 140.61, 133.72, 129.81, 129.24, 128.86, 127.69, 127.60, 72.11, 22.49, 21.81.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}ClO_2Na^+$ 297.0653; found 281.0652.

1-phenylethyl furan-2-carboxylate (43):



TLC: R_f = 0.60

Eluent: petroleum ether/ethyl acetate (95/5, v/v).

Appearance: colorless liquid.

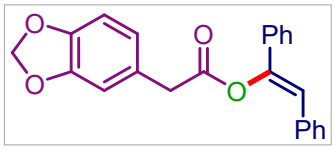
Isolated yield: 51% (27.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 1H), 7.50 – 7.44 (m, 2H), 7.40 (dd, *J* = 11.3, 4.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.26 – 7.22 (m, 1H), 6.51 (dd, *J* = 3.4, 1.7 Hz, 1H), 6.17 (q, *J* = 6.6 Hz, 1H), 1.70 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.01, 146.33, 144.83, 141.28, 128.55, 128.01, 126.11, 117.98, 111.81, 72.88, 22.27.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{12}O_3Na^+$ 239.0679; found 239.0650.

(Z)-1,2-diphenylvinyl 2-(benzo[d][1,3]dioxol-5-yl)acetate (44):



TLC: $R_f = 0.45$

Eluent: petroleum ether/ethyl acetate (80/20, v/v).

Appearance: White solid.

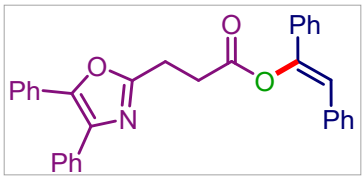
Isolated yield: 79% (56.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 (dt, *J* = 3.3, 1.8 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.29 – 7.23 (m, 4H), 6.82 (t, *J* = 4.8 Hz, 3H), 6.67 (s, 1H), 5.98 (s, 2H), 3.77 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.02, 148.06, 147.17, 146.71, 135.65, 134.29, 128.89, 128.76, 128.58, 127.72, 126.63, 124.90, 123.01, 117.11, 110.23, 108.57, 101.27, 41.44, 29.85.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}O_4Na^+$ 381.1097, found 381.1080.

(Z)-1,2-diphenylvinyl 3-(4,5-dimethyloxazol-2-yl)propanoate (45):



TLC: $R_f = 0.55$

Eluent: petroleum ether/ethyl acetate (80/20, v/v).

Appearance: White solid.

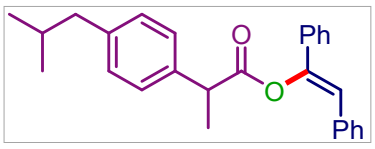
Isolated yield: 71% (49.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.58 – 7.50 (m, 6H), 7.40 – 7.31 (m, 9H), 7.24 (d, *J* = 7.5 Hz, 3H), 6.71 (s, 1H), 3.24 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.91, 146.74, 135.48, 134.42, 132.59, 129.10, 129.04, 128.93, 128.83, 128.79, 128.77, 128.74, 128.71, 128.63, 128.53, 128.34, 128.23, 128.09, 127.81, 126.69, 124.96, 117.00, 31.24, 23.35.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{25}NO_3Na^+$ 494.1727, found 494.1631.

(Z)-1,2-diphenylvinyl 2-(4-isobutylphenyl)propanoate (46):



TLC: $R_f = 0.35$

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

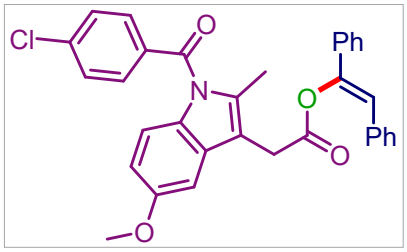
Isolated yield: 90% (69.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 10.0, 6.2 Hz, 4H), 7.29 – 7.24 (m, 5H), 7.23 – 7.17 (m, 5H), 6.63 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 1H), 2.53 (d, *J* = 7.2 Hz, 2H), 1.92 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.05, 146.71, 141.22, 136.56, 135.87, 134.29, 129.65, 128.87, 128.60, 128.57, 128.49, 127.89, 127.55, 124.83, 117.04, 45.53, 45.22, 30.43, 22.54, 18.05.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{28}O_2Na^+$ 407.1982, found 407.1965.

(Z)-1,2-diphenylvinyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (47):



TLC: R_f = 0.31

Eluent: petroleum ether/ethyl acetate (80/20, v/v).

Appearance: White solid.

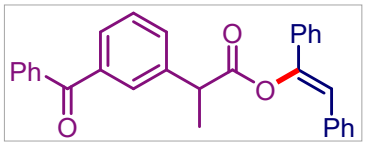
Isolated yield: 87% (93.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.48 – 7.41 (m, 4H), 7.39 – 7.28 (m, 5H), 7.18 – 7.12 (m, 3H), 6.98 (dd, *J* = 5.7, 3.1 Hz, 2H), 6.73 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.67 (s, 1H), 3.91 (s, 2H), 3.77 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.30, 168.21, 156.20, 146.52, 139.35, 136.15, 135.46, 134.04, 133.75, 131.17, 130.81, 130.47, 129.14, 128.91, 128.64, 128.61, 128.36, 128.20, 127.60, 124.73, 117.02, 115.02, 112.17, 111.56, 101.10, 77.32, 77.00, 76.68, 55.67, 30.61, 13.47.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{33}H_{26}ClNO_4Na^+$ 558.1443, found 558.1410.

(Z)-1,2-diphenylvinyl 2-(3-benzoylphenyl)propanoate (48):



TLC: R_f = 0.65

Eluent: petroleum ether/ethyl acetate (85/15, v/v).

Appearance: Colorless semi-solid.

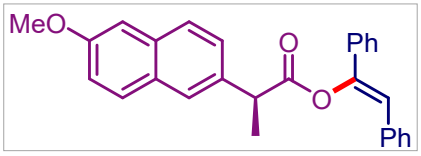
Isolated yield: 89% (77.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.56 (ddd, *J* = 23.8, 14.4, 7.7 Hz, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.27 (m, 7H), 7.20 – 7.15 (m, 3H), 6.64 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.49, 171.48, 146.64, 139.66, 138.31, 137.48, 135.72, 134.13, 132.70, 132.02, 130.19, 129.82, 129.46, 129.00, 128.78, 128.75, 128.73, 128.51, 128.48, 127.69, 124.85, 117.25, 45.74, 18.15.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{24}O_3Na^+$ 455.1618, found 455.1613.

(Z)-1,2-diphenylvinyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (49):



TLC: R_f = 0.51

Eluent: petroleum ether/ethyl acetate (85/15, v/v).

Appearance: White solid.

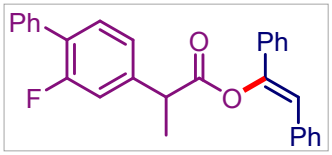
Isolated yield: 88% (71.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 3H), 7.48 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.17 (m, 7H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.60 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 3.96 (s, 3H), 1.67 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.01, 157.96, 146.72, 135.91, 134.44, 134.14, 129.55, 129.14, 128.81, 128.64, 128.58, 128.38, 127.54, 127.51, 126.75, 126.71, 124.88, 119.28, 117.14, 105.73, 55.49, 45.83, 18.20.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}O_3Na^+$ 431.1618, found 431.1589.

(Z)-1,2-diphenylvinyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (50):



TLC: R_f = 0.45

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: White solid.

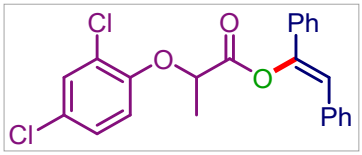
Isolated yield: 91% (76.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.31 (m, 6H), 7.29 – 7.23 (m, 5H), 7.22 – 7.19 (m, 1H), 7.18 – 7.12 (m, 4H), 6.61 (s, 1H), 4.00 (q, *J* = 7.1 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.35, 161.15, 158.68, 146.66, 140.70, 140.62, 135.74, 135.56, 135.55, 134.11, 131.13, 131.09, 129.11, 129.08, 128.83, 128.75, 128.73, 128.70, 128.46, 128.35, 127.95, 127.67, 124.88, 124.23, 124.19, 117.29, 115.98, 115.74, 45.36, 18.04.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{24}FO_2^+$ 423.1755, found 423.1807

(Z)-1,2-diphenylvinyl 2-(2,4-dichlorophenoxy)propanoate (51):



TLC: $R_f = 0.51$

Eluent: petroleum ether/ethyl acetate (90/10, v/v).

Appearance: Colorless semi-solid.

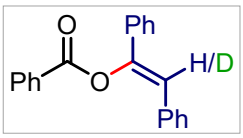
Isolated yield: 80% (66.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 8.3 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.38 – 7.27 (m, 7H), 6.98 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.73 (s, 1H), 6.64 (d, *J* = 8.8 Hz, 1H), 4.92 (q, *J* = 6.8 Hz, 1H), 1.78 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.97, 152.15, 146.45, 135.13, 134.00, 130.46, 129.02, 128.96, 128.80, 128.71, 128.61, 127.94, 127.69, 127.48, 125.06, 117.68, 116.68, 74.57, 18.36.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}Cl_2O_3Na^+$ 435.0525, found 435.0500.

(Z)-1,2-diphenylvinyl-2-d benzoate (52):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 4H), 7.39 (dt, *J* = 11.9, 3.0 Hz, 3H), 7.29 (t, *J* = 7.5 Hz, 3H), 7.24 – 7.20 (m, 1H), 6.83 (s, 0.7H).

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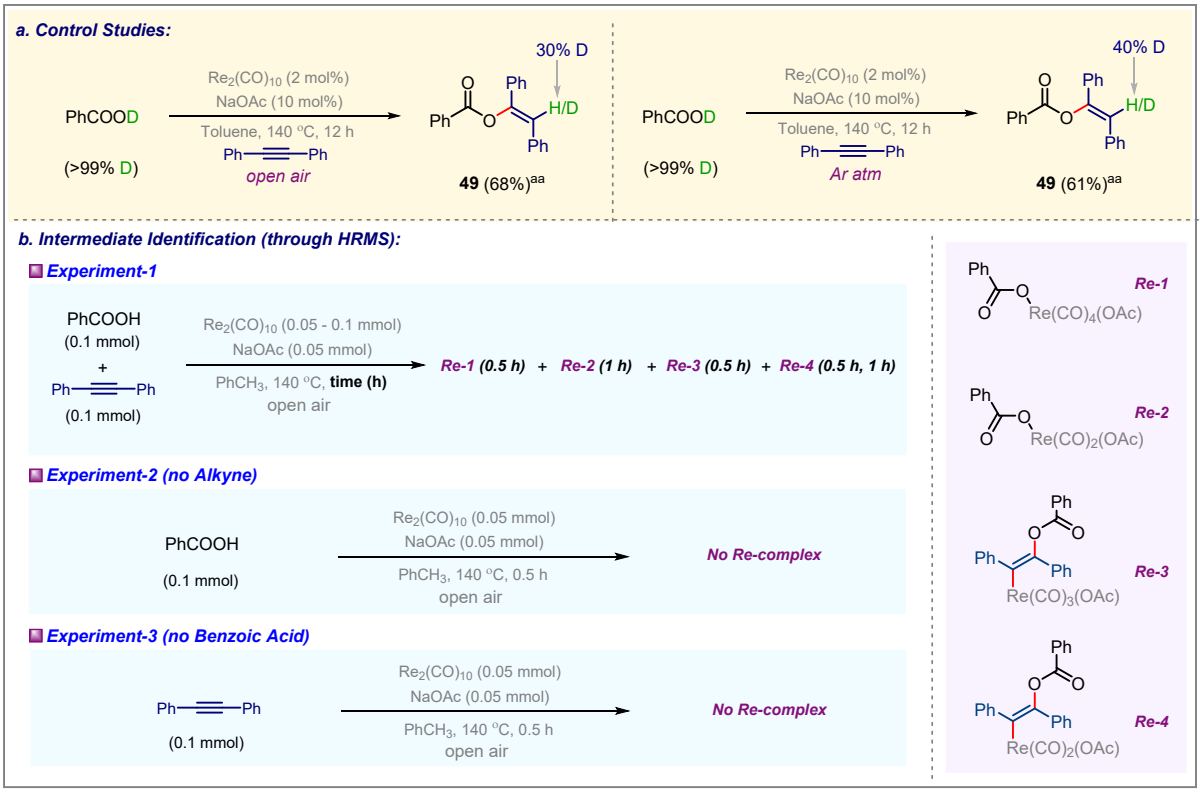
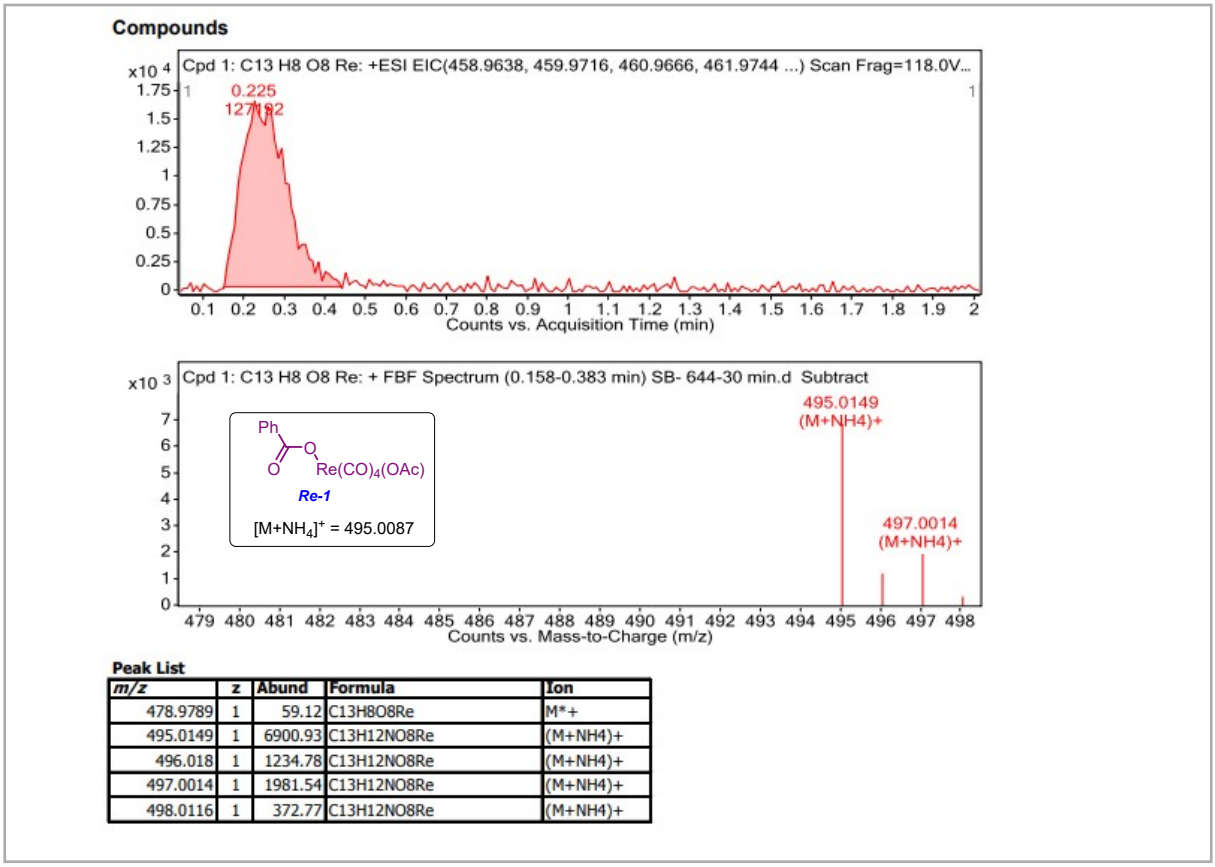
4. Controlled and stoichiometric experiments:



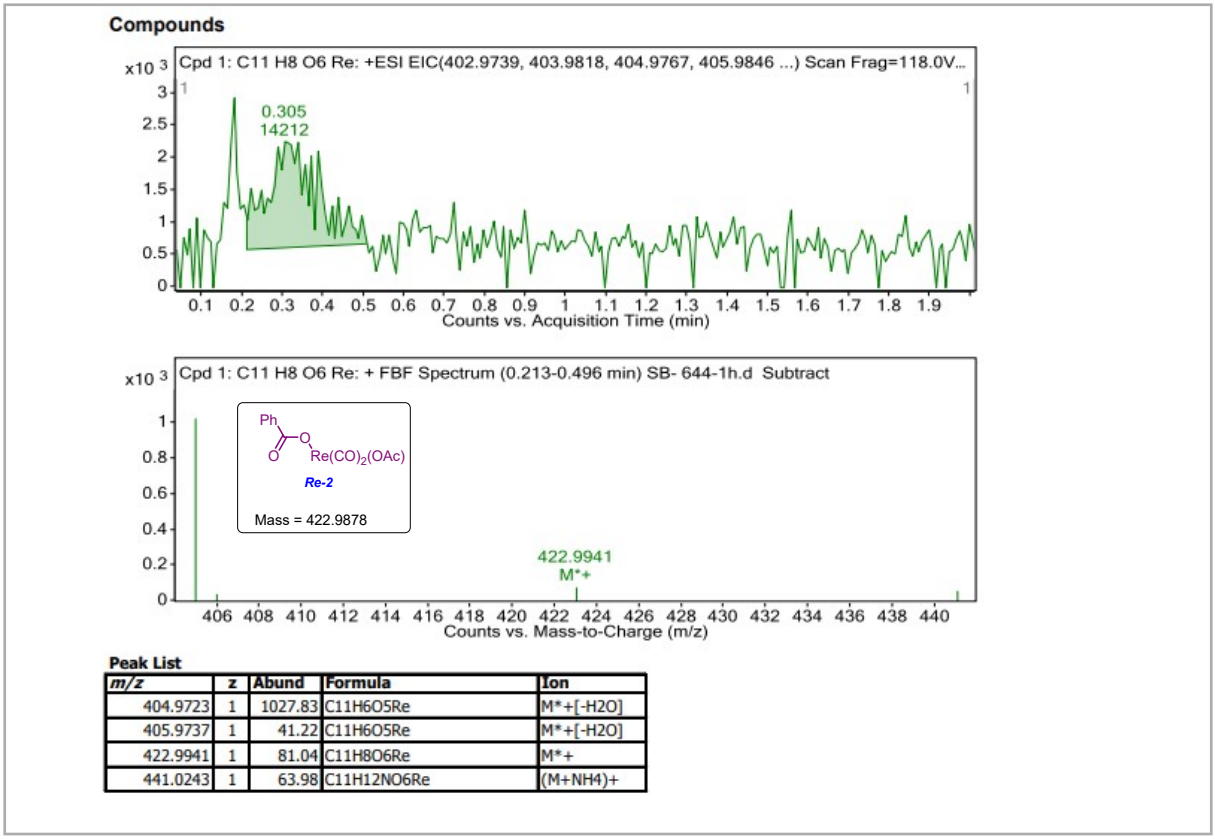
HRMS Data Intermediate Re-1



Peak List

m/z	z	Abund	Formula	Ion
478.9789	1	59.12	C13H8O8Re	M*+
495.0149	1	6900.93	C13H12NO8Re	(M+NH4)+
496.018	1	1234.78	C13H12NO8Re	(M+NH4)+
497.0014	1	1981.54	C13H12NO8Re	(M+NH4)+
498.0116	1	372.77	C13H12NO8Re	(M+NH4)+

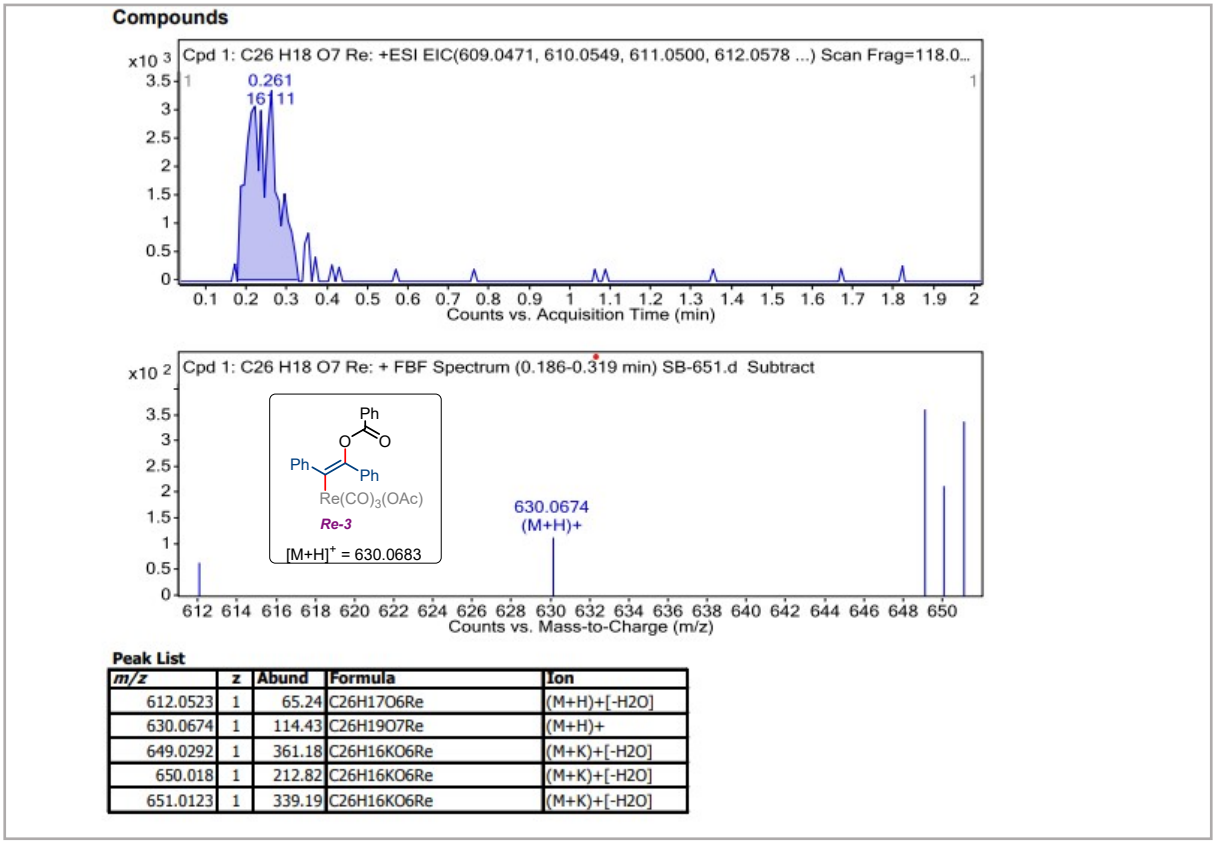
HRMS Data Intermediate Re-2



Peak List

m/z	z	Abund	Formula	Ion
404.9723	1	1027.83	C11H6O5Re	M*+[-H2O]
405.9737	1	41.22	C11H6O5Re	M*+[-H2O]
422.9941	1	81.04	C11H8O6Re	M*+
441.0243	1	63.98	C11H12NO6Re	(M+NH4)+

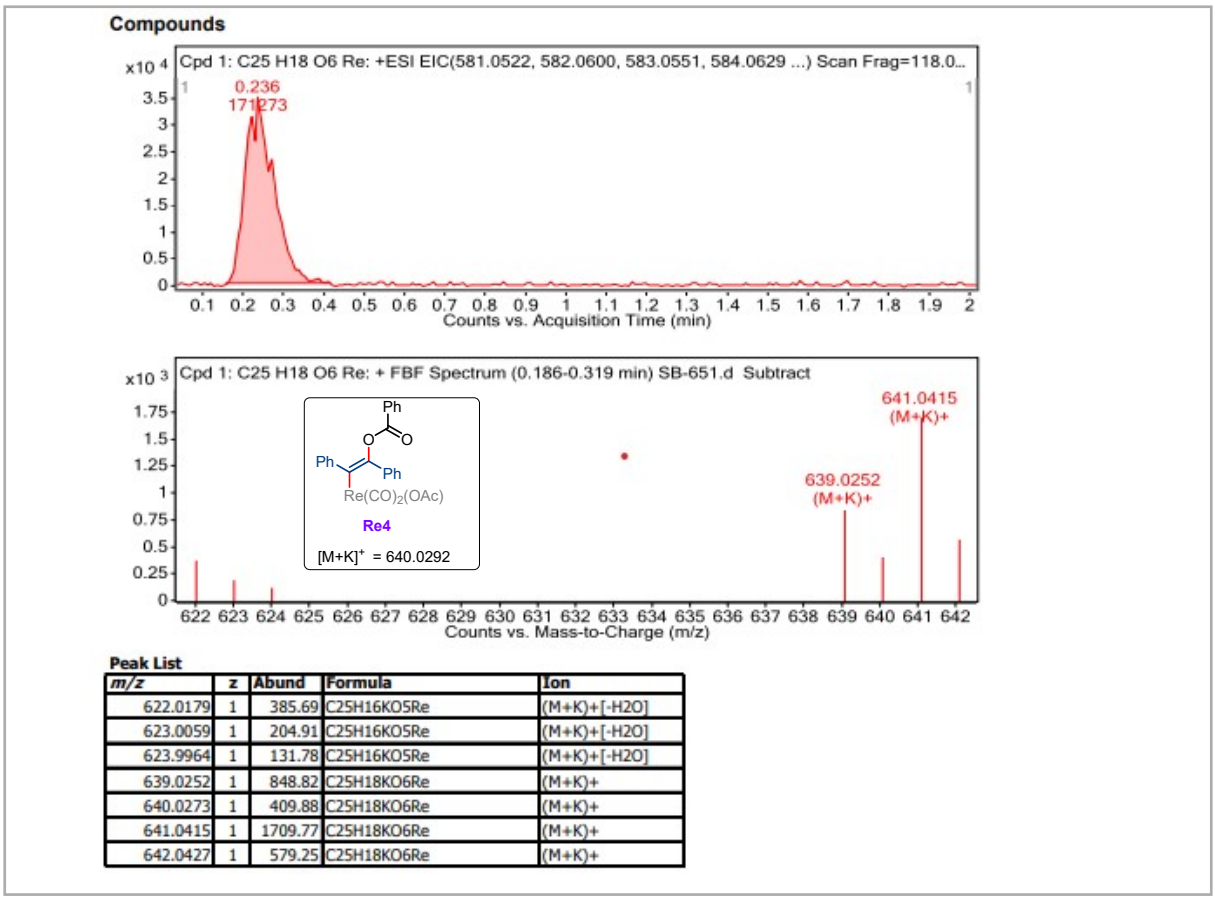
HRMS Data Intermediate Re-3



Peak List

m/z	z	Abund	Formula	Ion
612.0523	1	65.24	C26H17O6Re	(M+H)+[-H2O]
630.0674	1	114.43	C26H19O7Re	(M+H)+
649.0292	1	361.18	C26H16KO6Re	(M+K)+[-H2O]
650.018	1	212.82	C26H16KO6Re	(M+K)+[-H2O]
651.0123	1	339.19	C26H16KO6Re	(M+K)+[-H2O]

HRMS Data Intermediate Re-4



Peak List

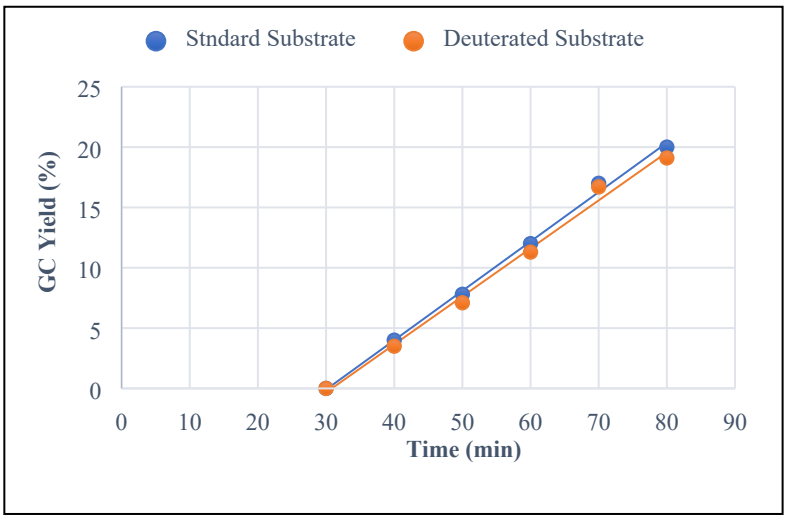
m/z	z	Abund	Formula	Ion
622.0179	1	385.69	C25H16KO5Re	(M+K)+[-H2O]
623.0059	1	204.91	C25H16KO5Re	(M+K)+[-H2O]
623.9964	1	131.78	C25H16KO5Re	(M+K)+[-H2O]
639.0252	1	848.82	C25H18KO6Re	(M+K)+
640.0273	1	409.88	C25H18KO6Re	(M+K)+
641.0415	1	1709.77	C25H18KO6Re	(M+K)+
642.0427	1	579.25	C25H18KO6Re	(M+K)+

KIE experiments in different reaction tubes

To an over-dried 10 mL reaction tube equipped with a magnetic stir bar was added $Re_2(CO)_{10}$ (2.1 mg, 0.002 mmol, 2 mol%), benzoic acid (0.1 mmol, 12.2 mg), diphenyl acetylene (0.2 mmol, 35 mg), dodecane (10 uL) as internal standard. Dry toluene was added to make sure the volume of the reaction solution is 0.3 mL, then the tube was put into preheated oil bath at 140 °C. The reactions were monitored by GC at different reaction times 10 – 80 minutes. We have observed that the reaction initiated at 40 min.

To an over-dried 10 mL reaction tube equipped with a magnetic stir bar was added $Re_2(CO)_{10}$ (2.1 mg, 0.002 mmol, 2 mol%), benzoic acid (0.1 mmol, 12.2 mg), diphenyl acetylene (0.2 mmol, 35 mg), dodecane (10 uL) as internal standard. Dry toluene was added to make sure the volume of the reaction solution is 0.3 mL, then the tube was put into preheated oil bath at 140 °C. The reactions were monitored by GC at different reaction times 10 – 80 minutes. We

have observed that the reaction initiated at 40 min. The reactions were monitored by GC. The initial rate of two reactions showed that the KIE was 1.



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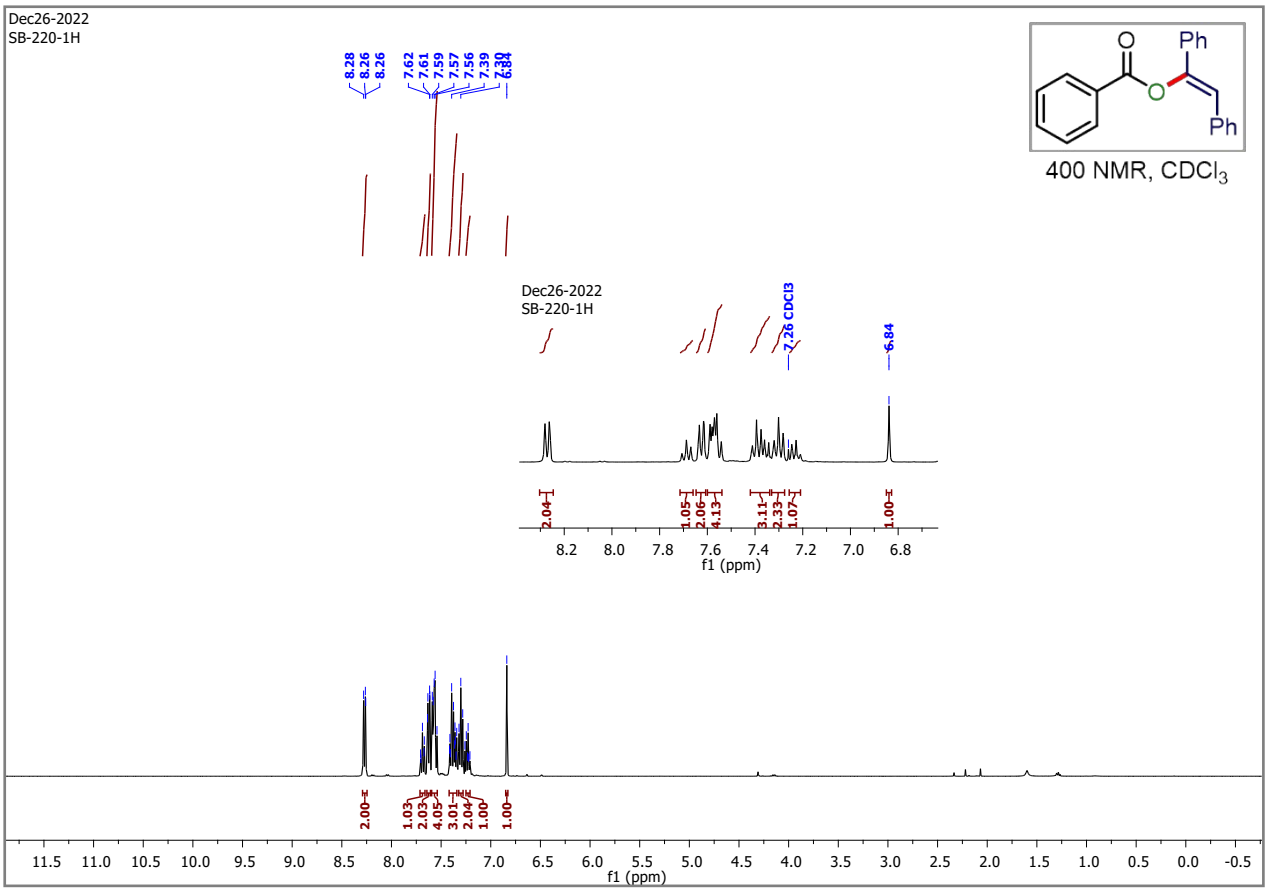
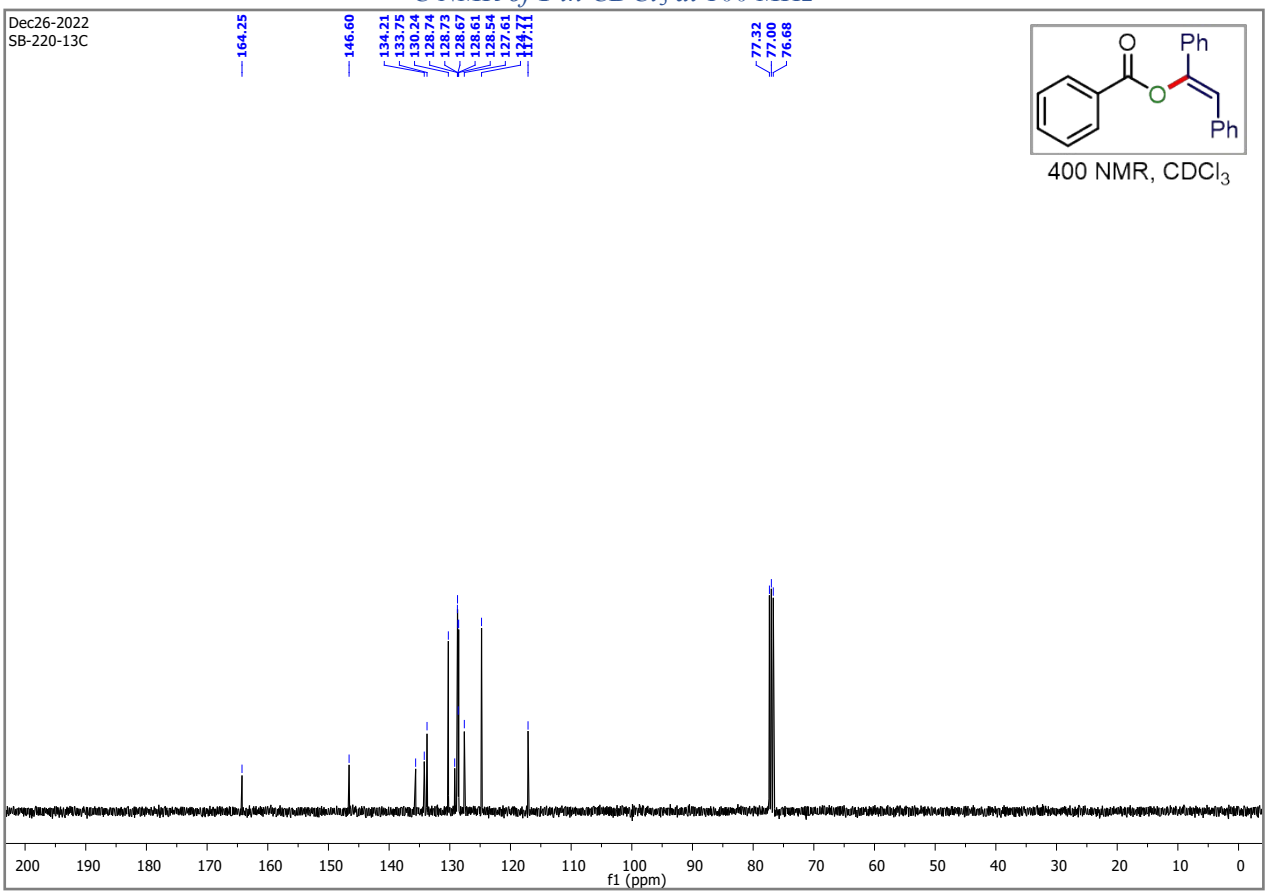
5. NMR Spectra:

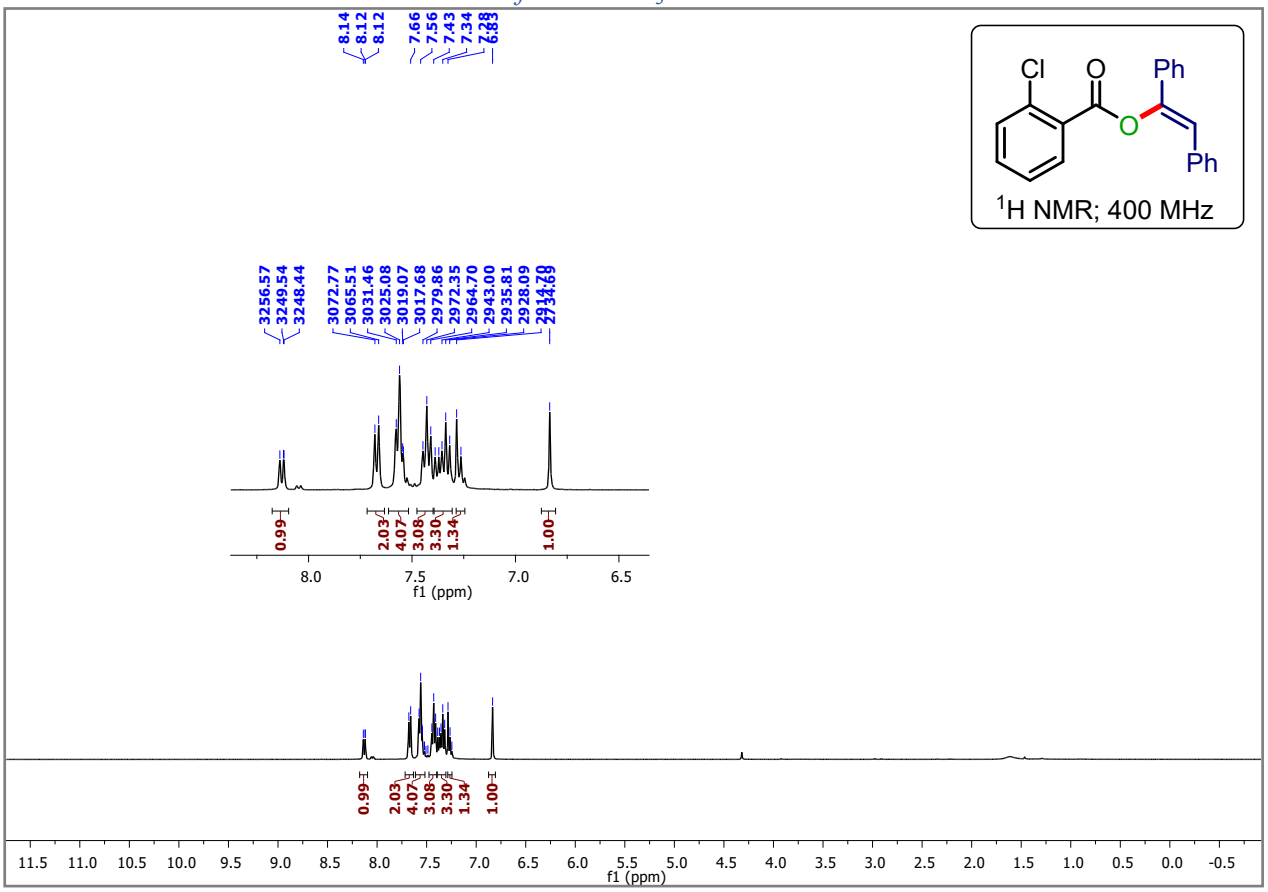
*^{1}H NMR of **1** in $CDCl_3$ at 400 MHz*



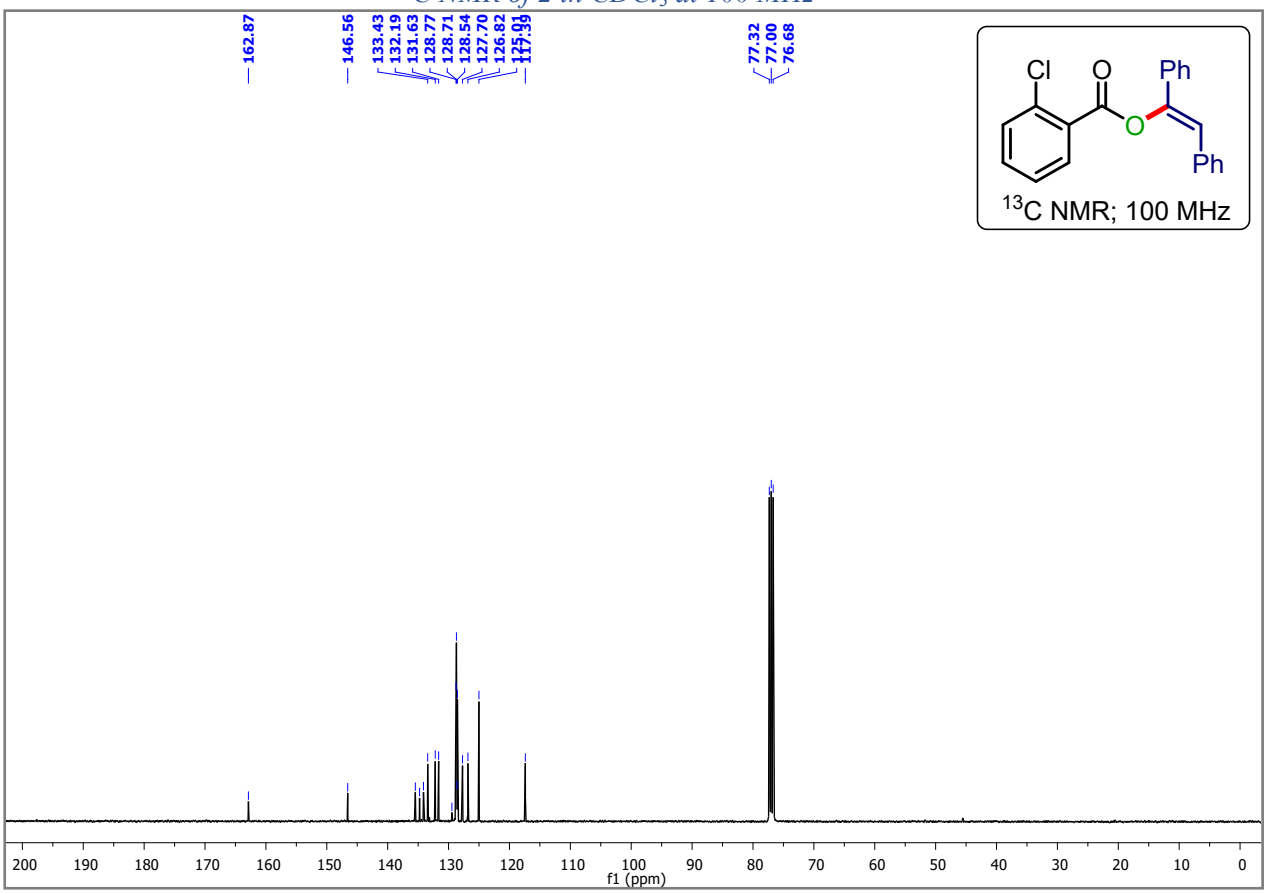
*^{13}C NMR of **1** in $CDCl_3$ at 100 MHz*



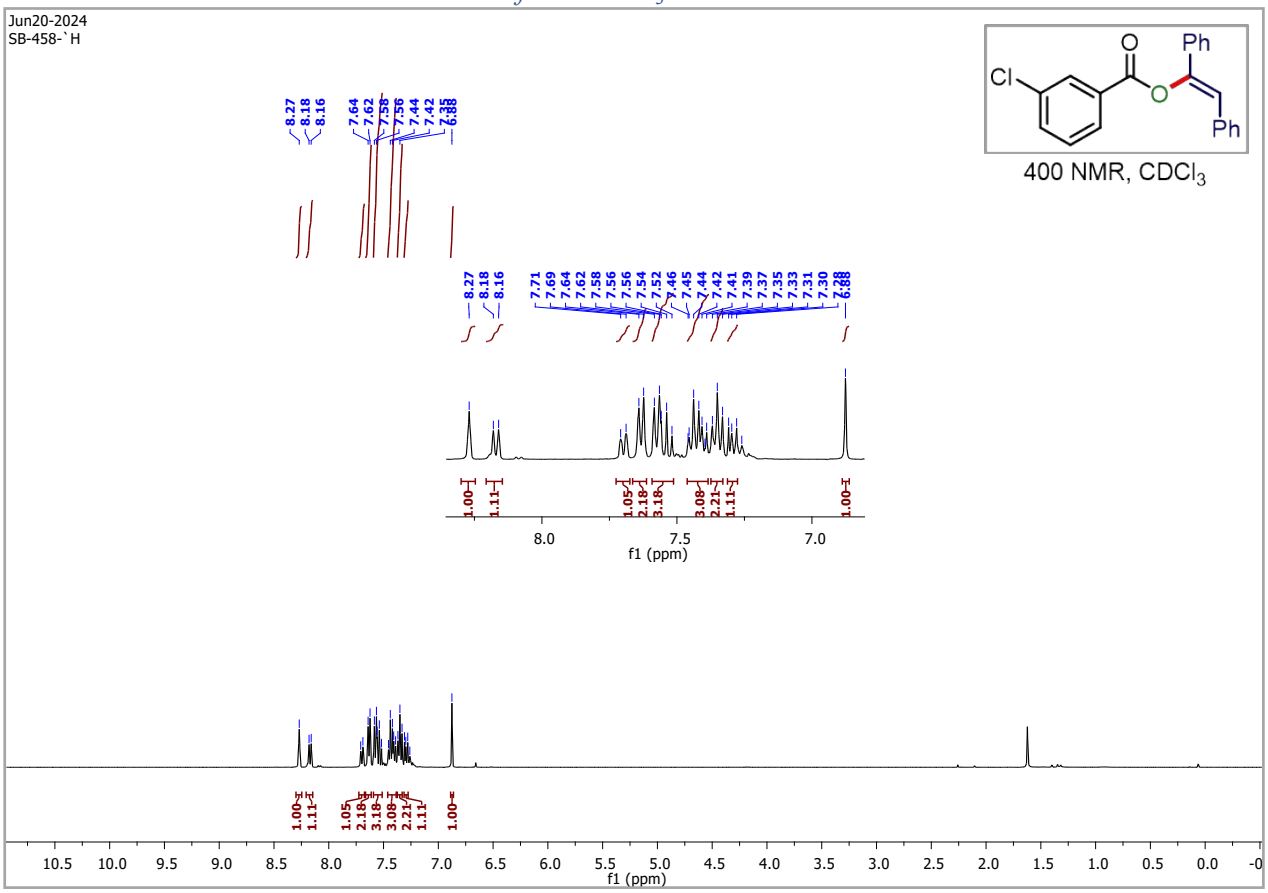
*^{1}H NMR of **2** in $CDCl_3$ at 400 MHz*



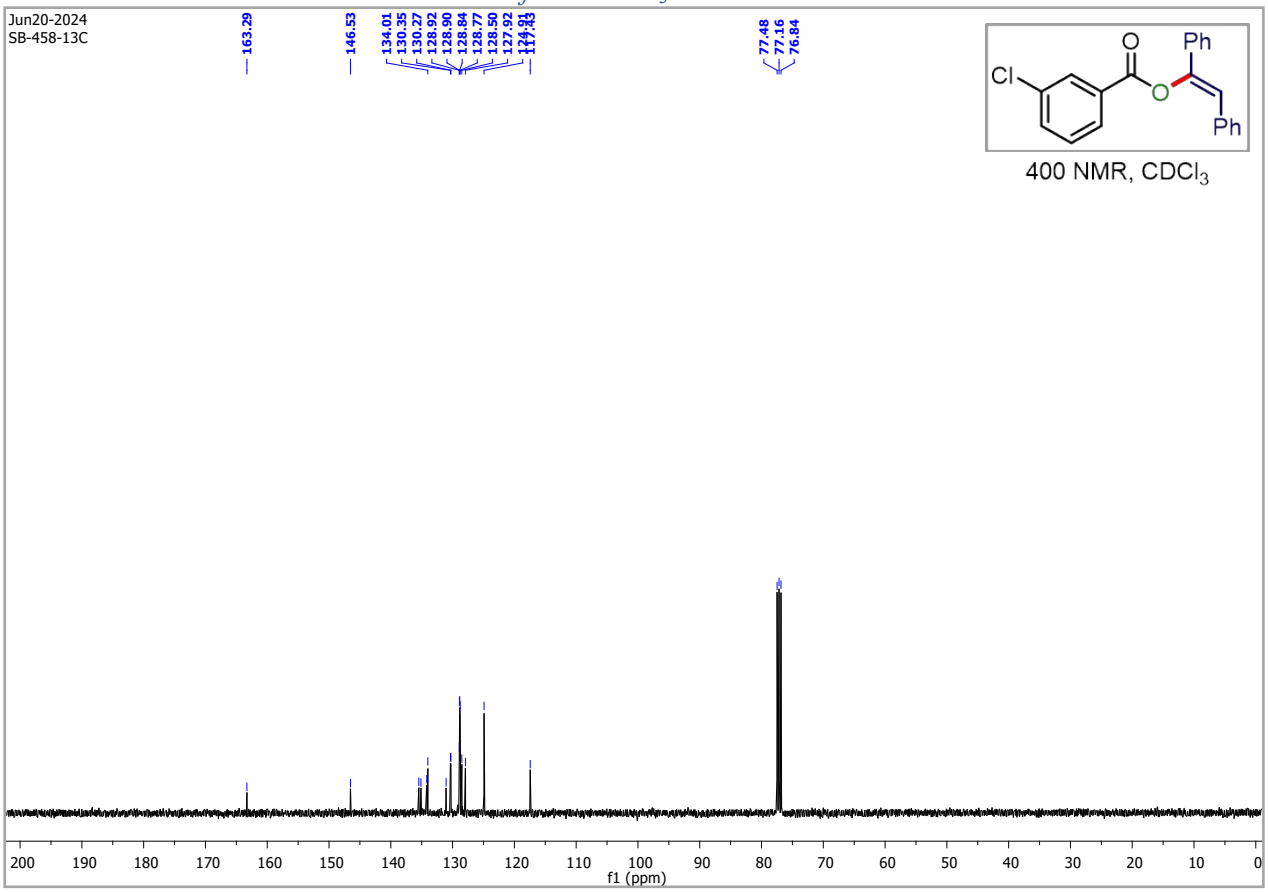
*^{13}C NMR of **2** in $CDCl_3$ at 100 MHz*



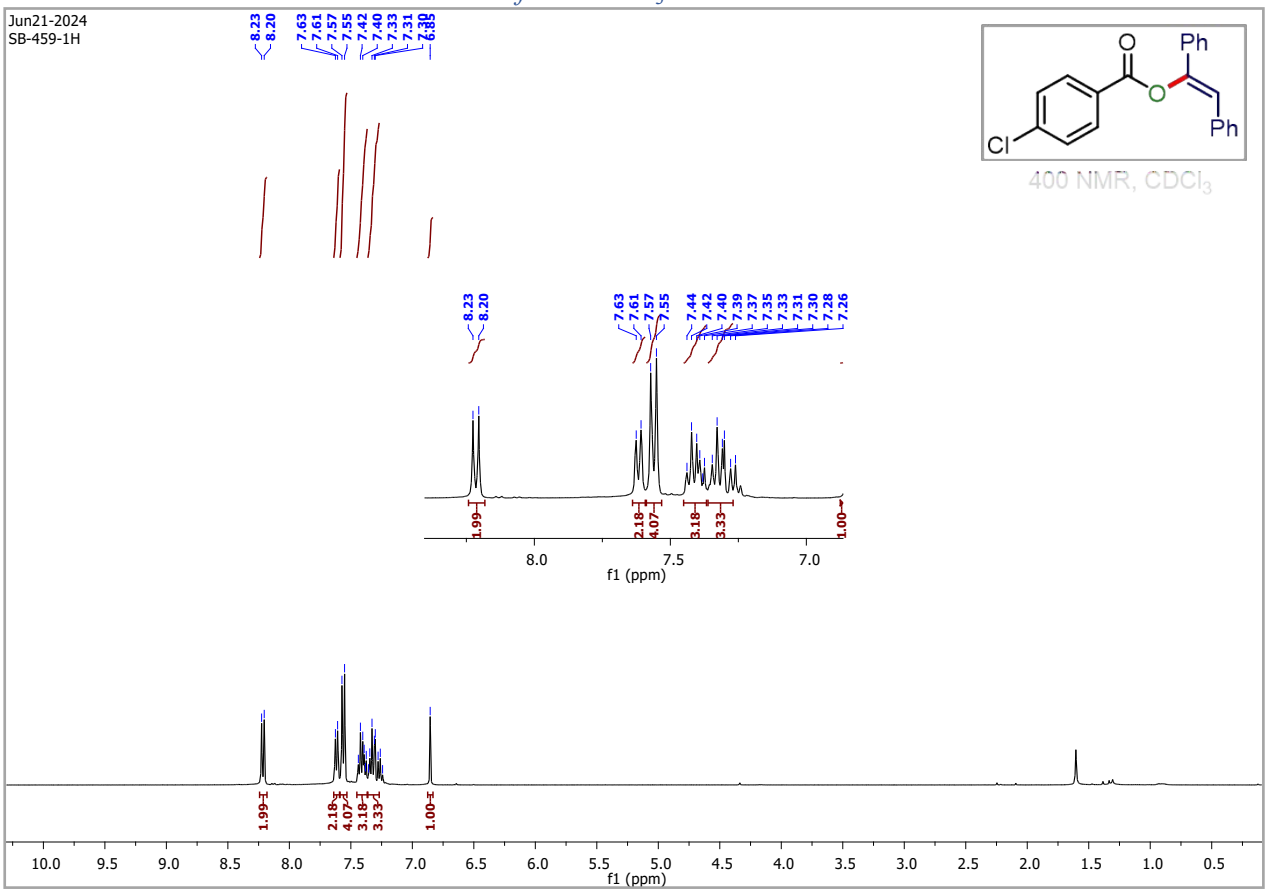
*^{1}H NMR of **3** in $CDCl_3$ at 400 MHz*



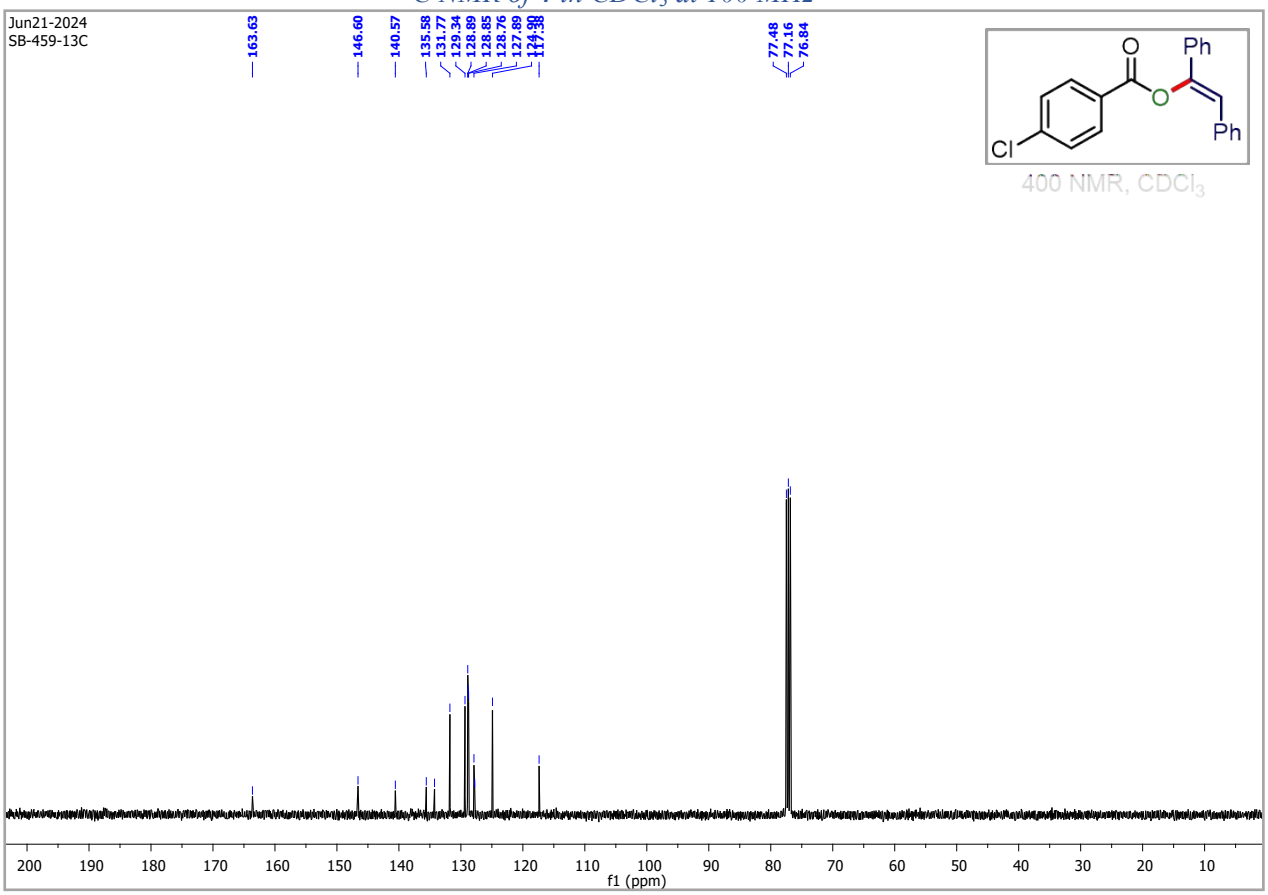
*^{13}C NMR of **3** in $CDCl_3$ at 100 MHz*



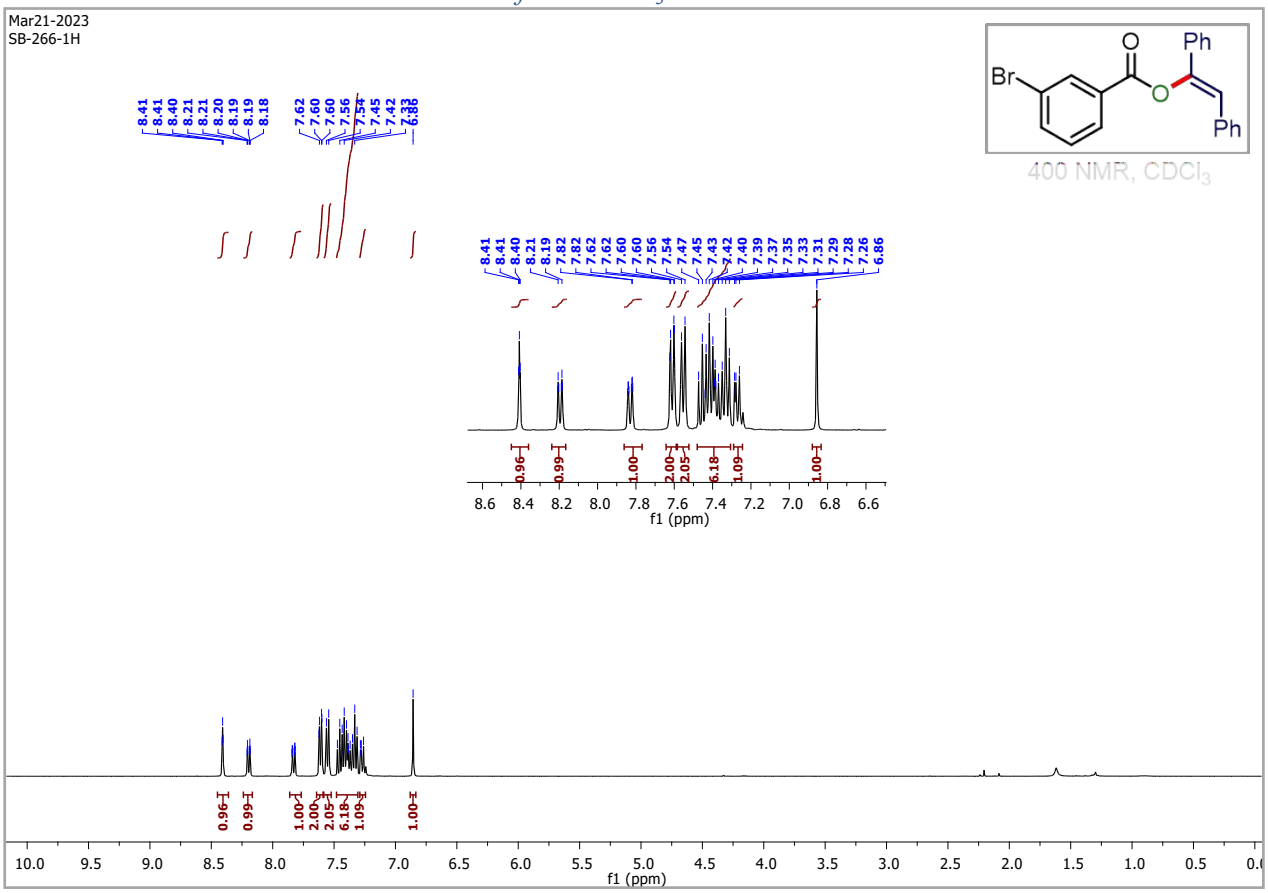
*^{1}H NMR of **4** in $CDCl_3$ at 400 MHz*



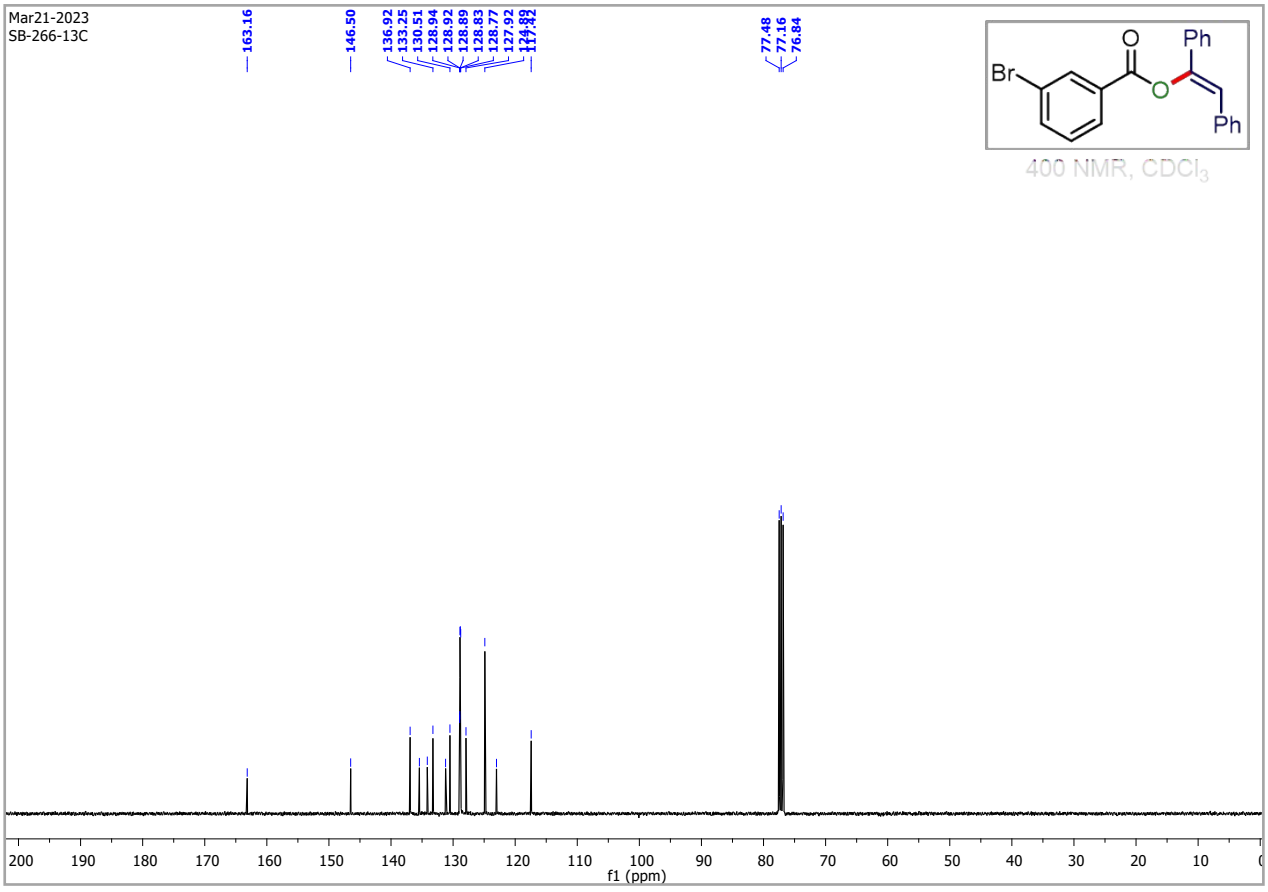
*^{13}C NMR of **4** in $CDCl_3$ at 100 MHz*



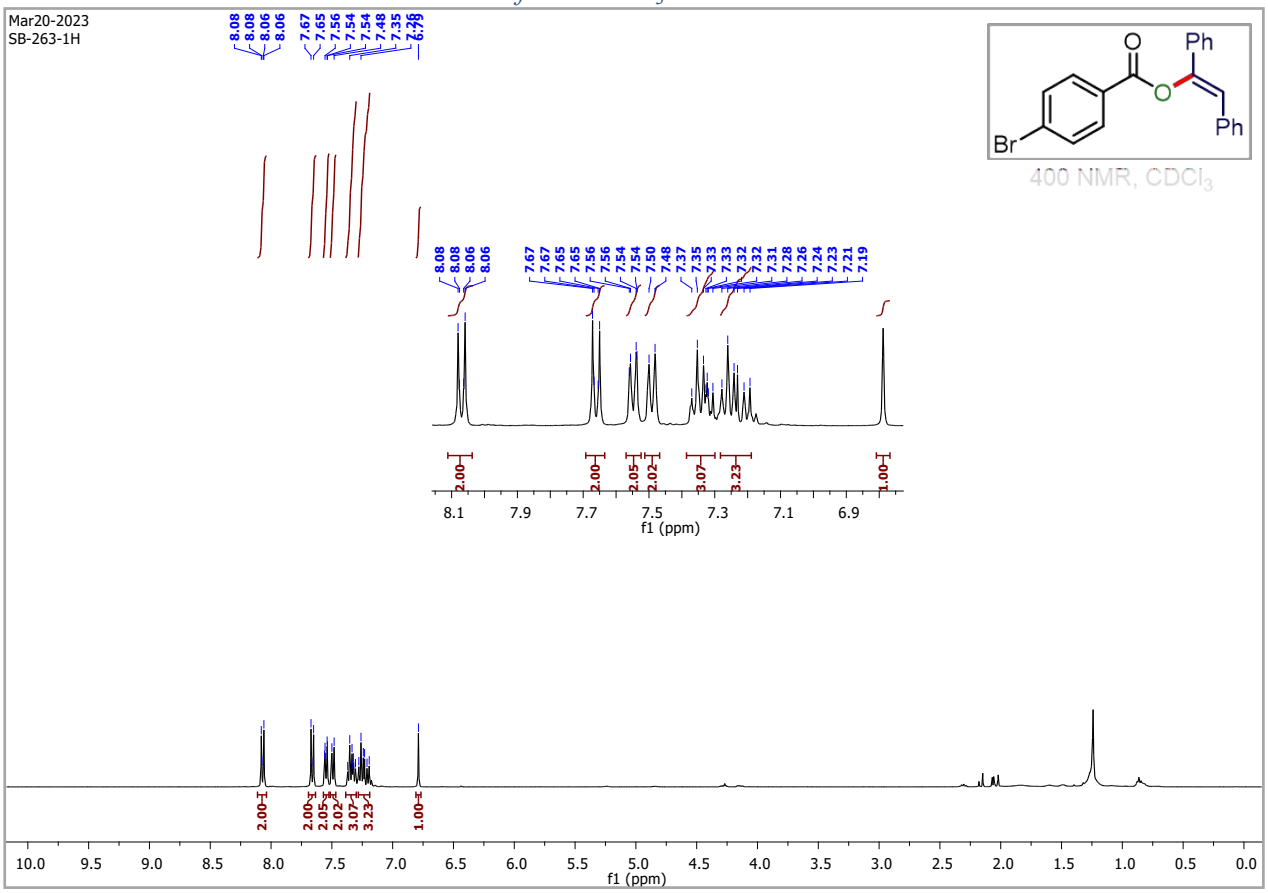
*^{1}H NMR of **5** in $CDCl_3$ at 400 MHz*



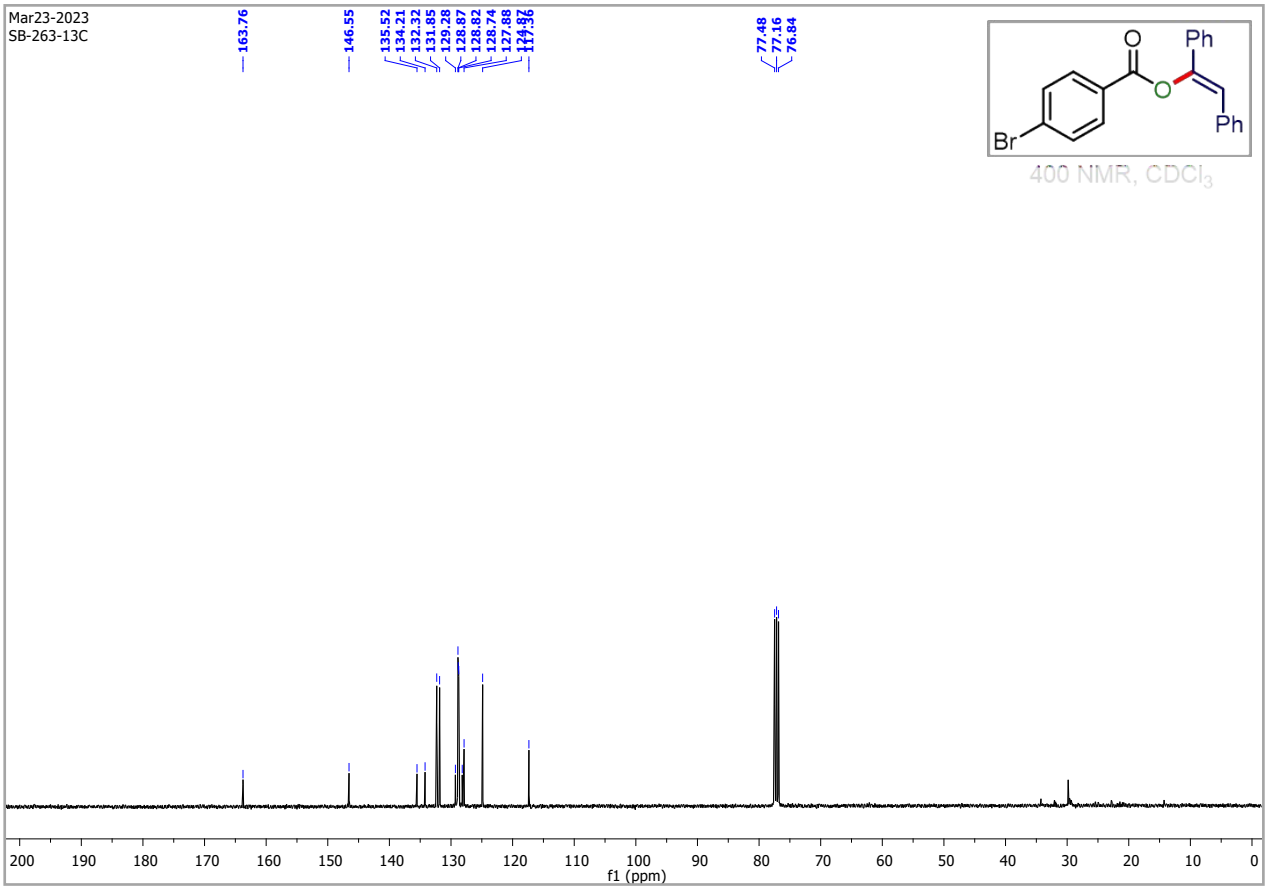
*^{13}C NMR of **5** in $CDCl_3$ at 100 MHz*



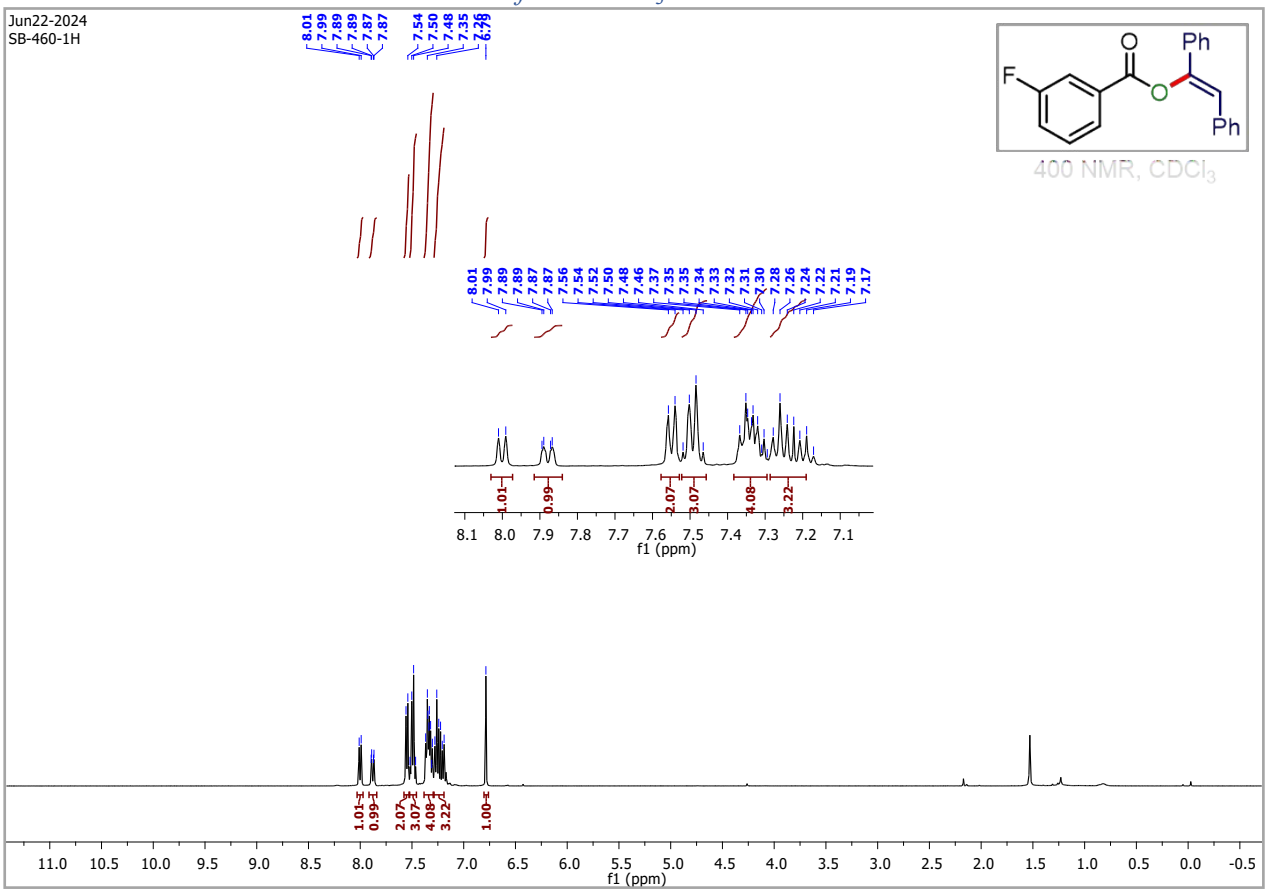
*^{1}H NMR of **6** in $CDCl_3$ at 400 MHz*



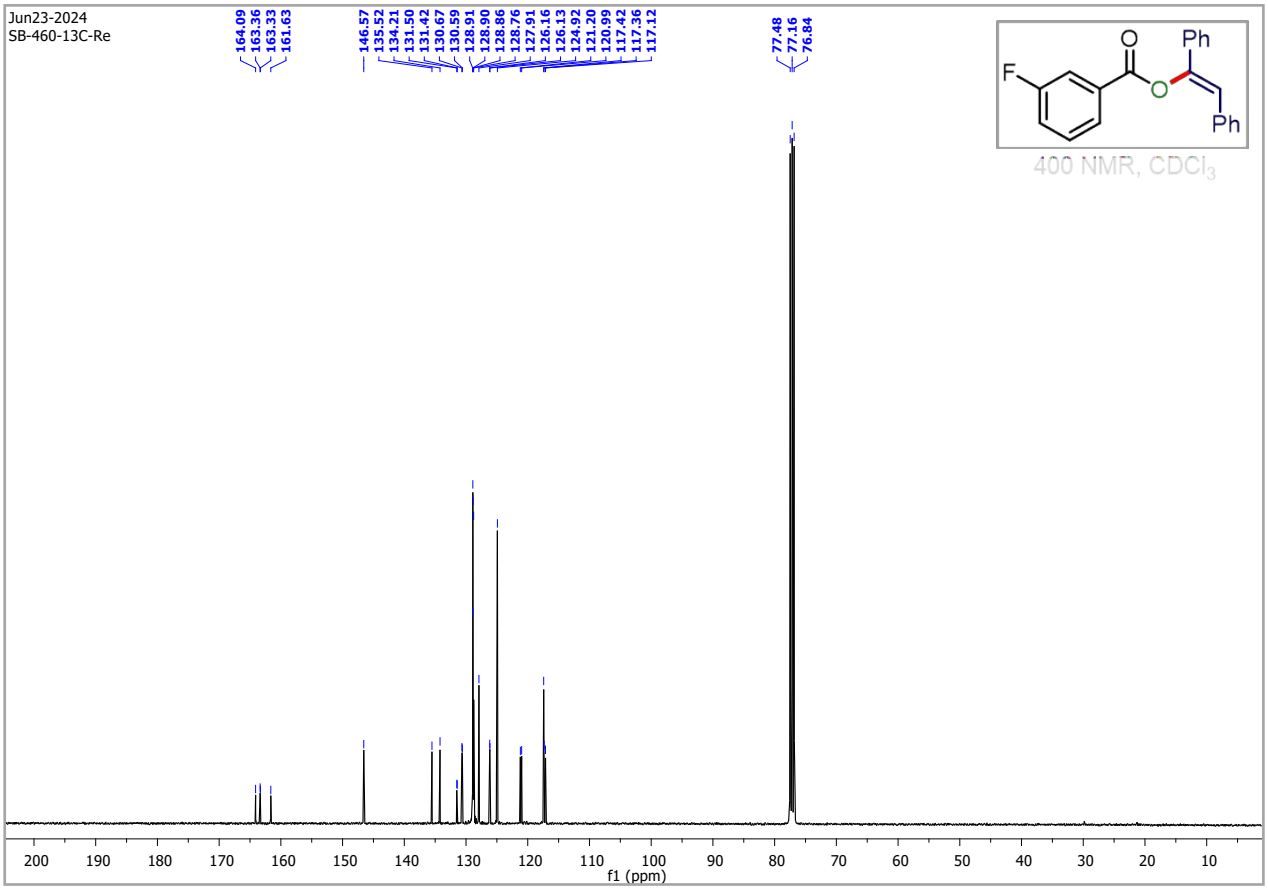
*^{13}C NMR of **6** in $CDCl_3$ at 100 MHz*



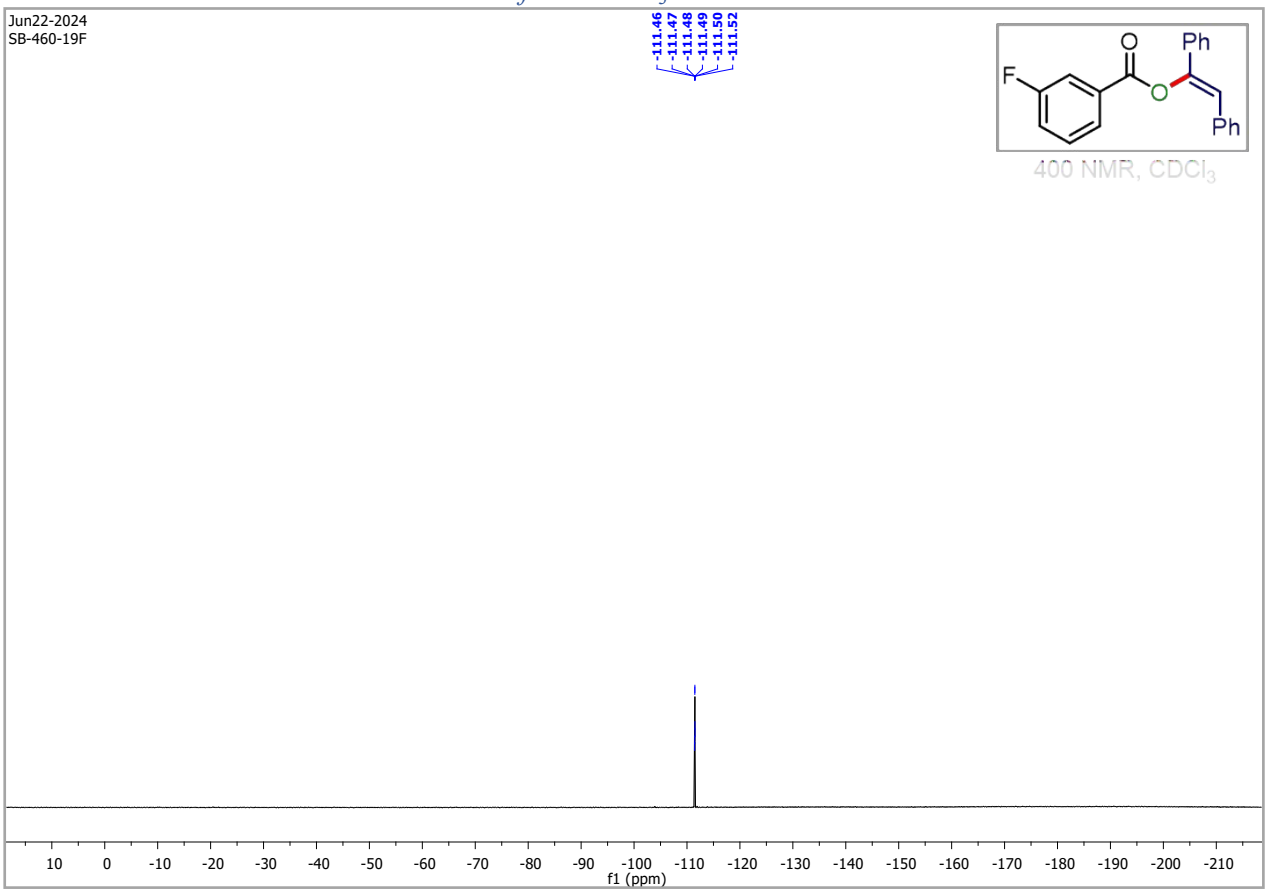
^{1}H NMR of 7 in $CDCl_3$ at 400 MHz



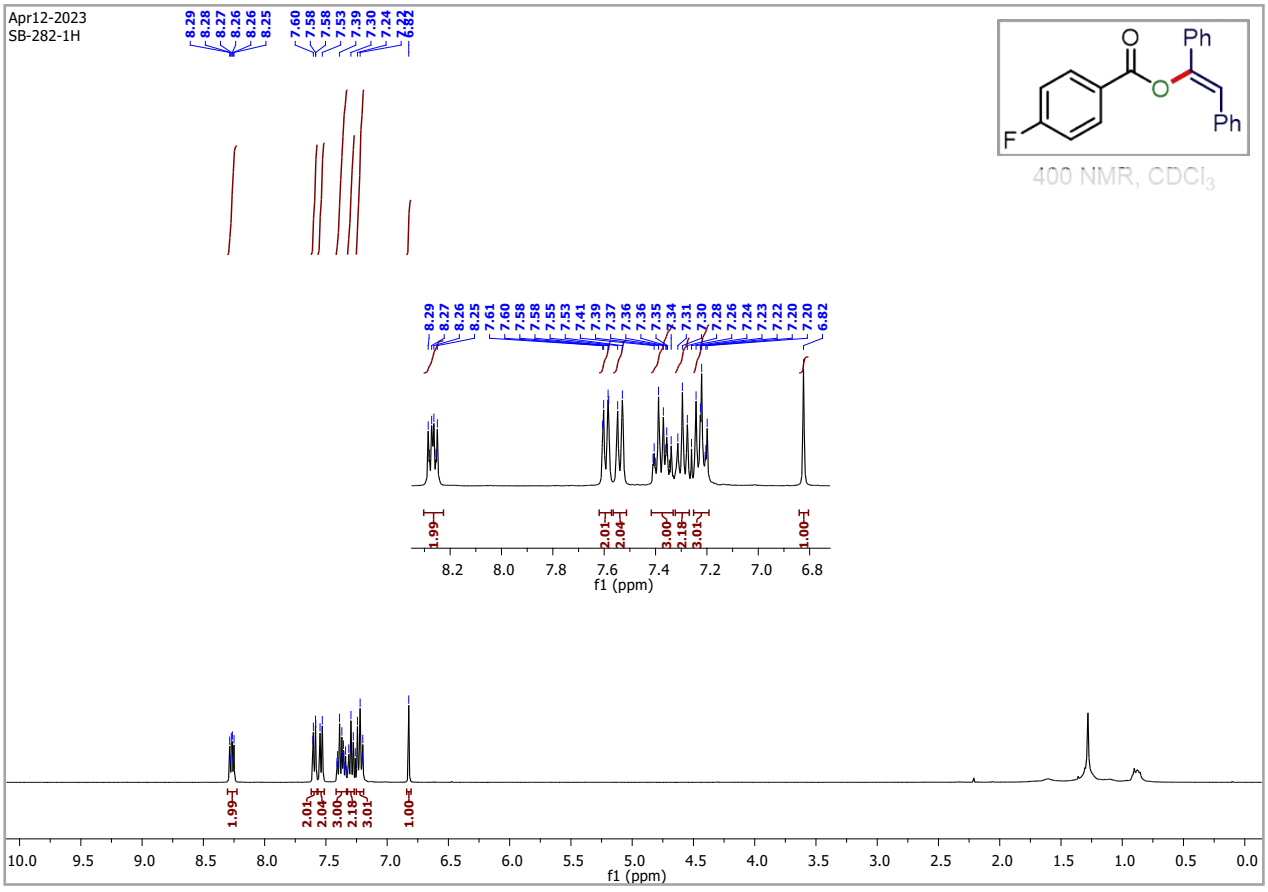
^{13}C NMR of 7 in $CDCl_3$ at 100 MHz



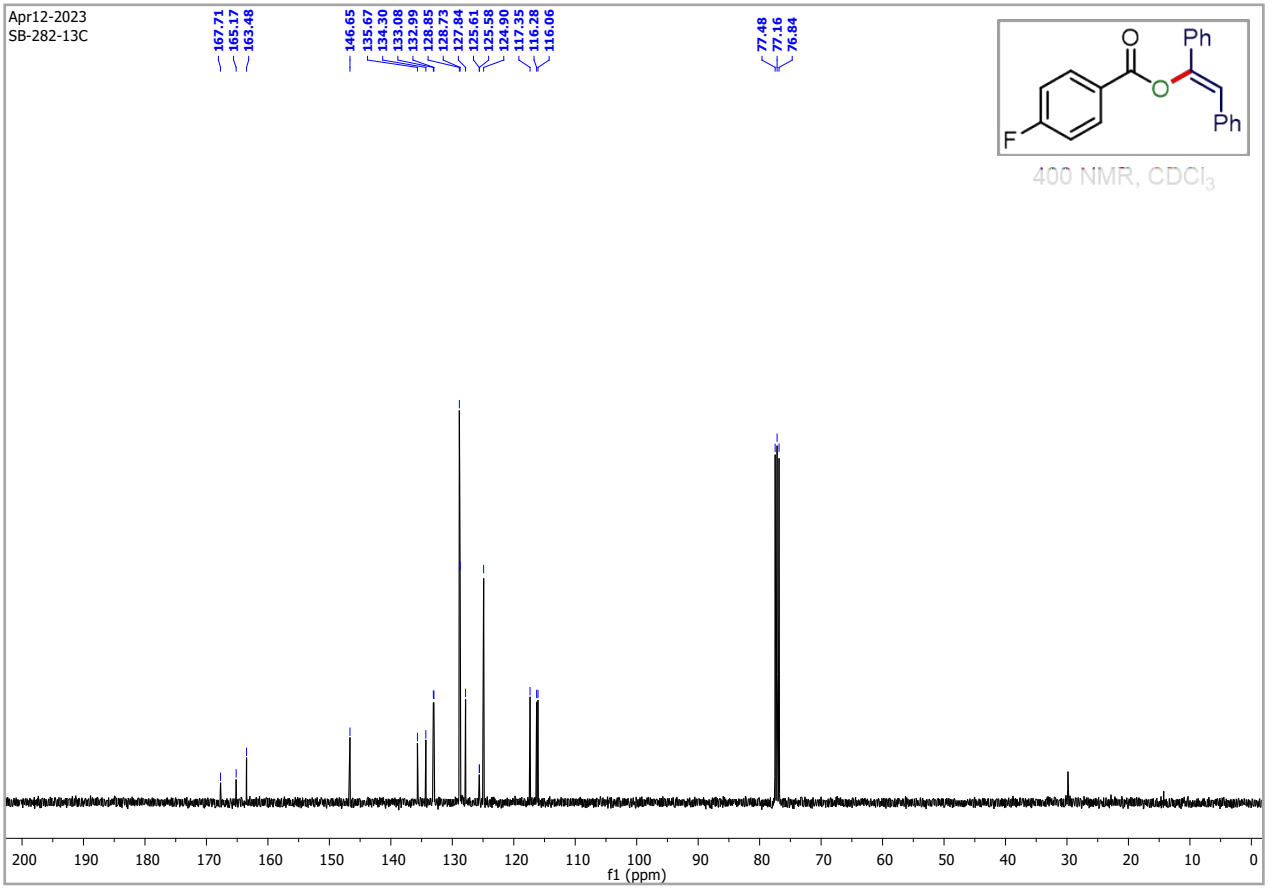
*^{19}F NMR of **7** in $CDCl_3$ at 100 MHz*



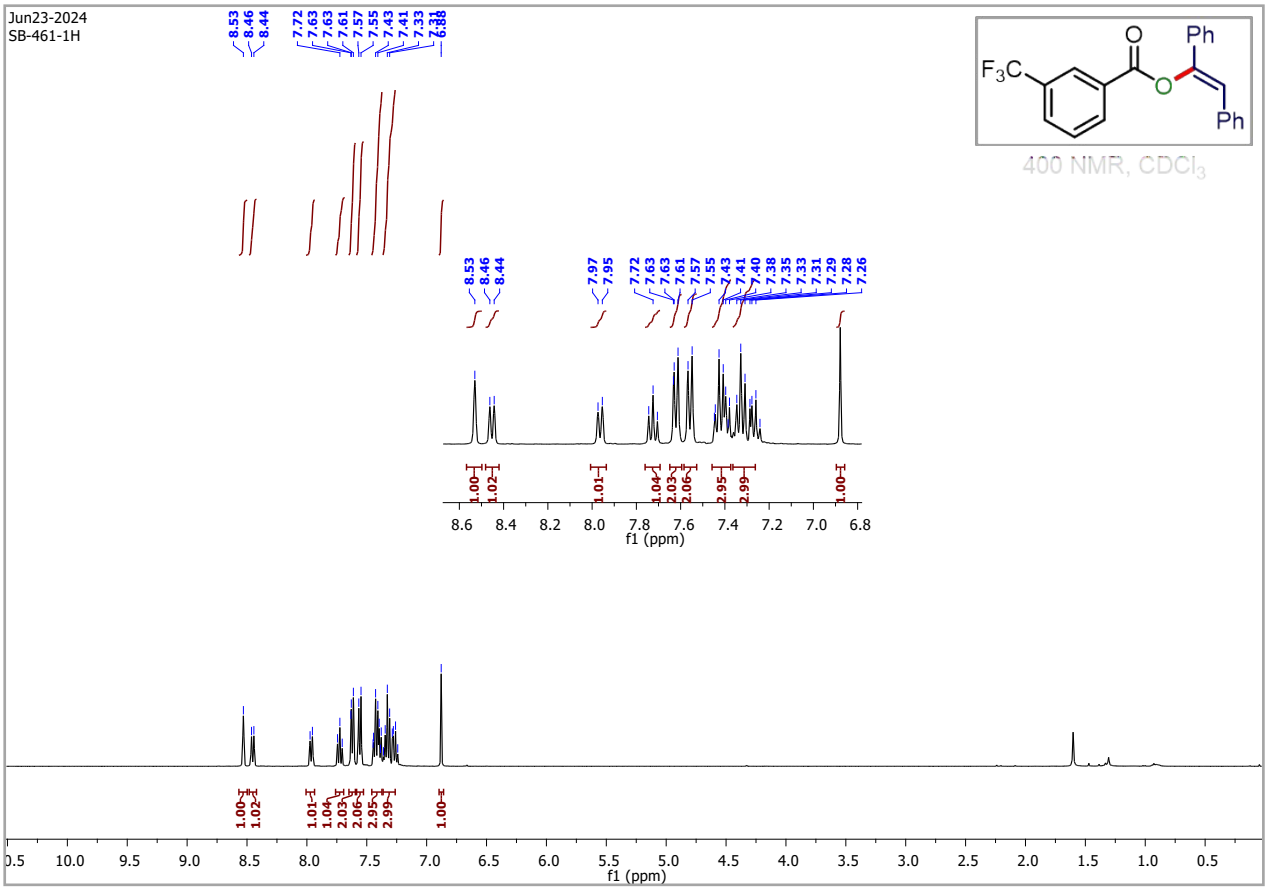
*^{1}H NMR of **8** in $CDCl_3$ at 400 MHz*



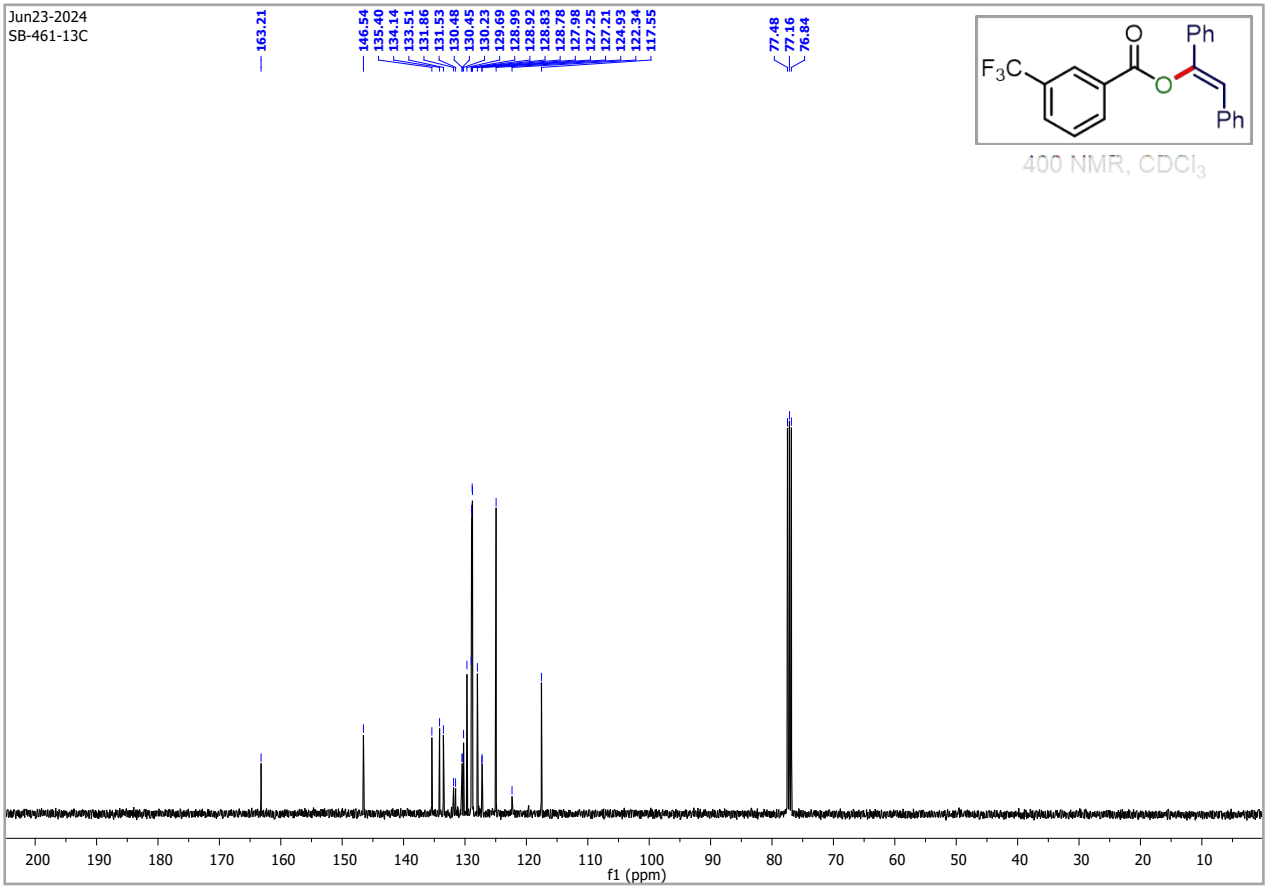
*^{13}C NMR of **8** in $CDCl_3$ at 100 MHz*



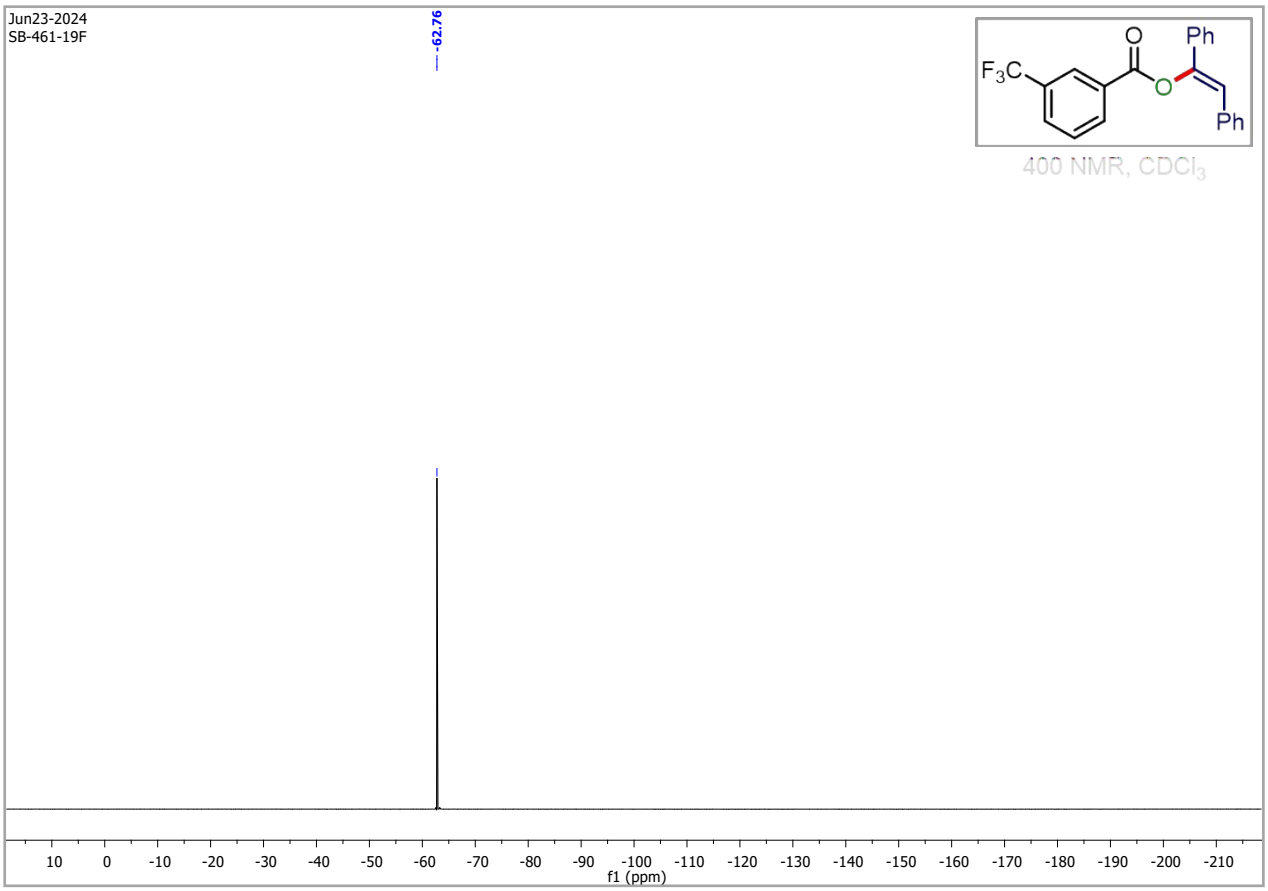
*^{1}H NMR of **9** in $CDCl_3$ at 400 MHz*



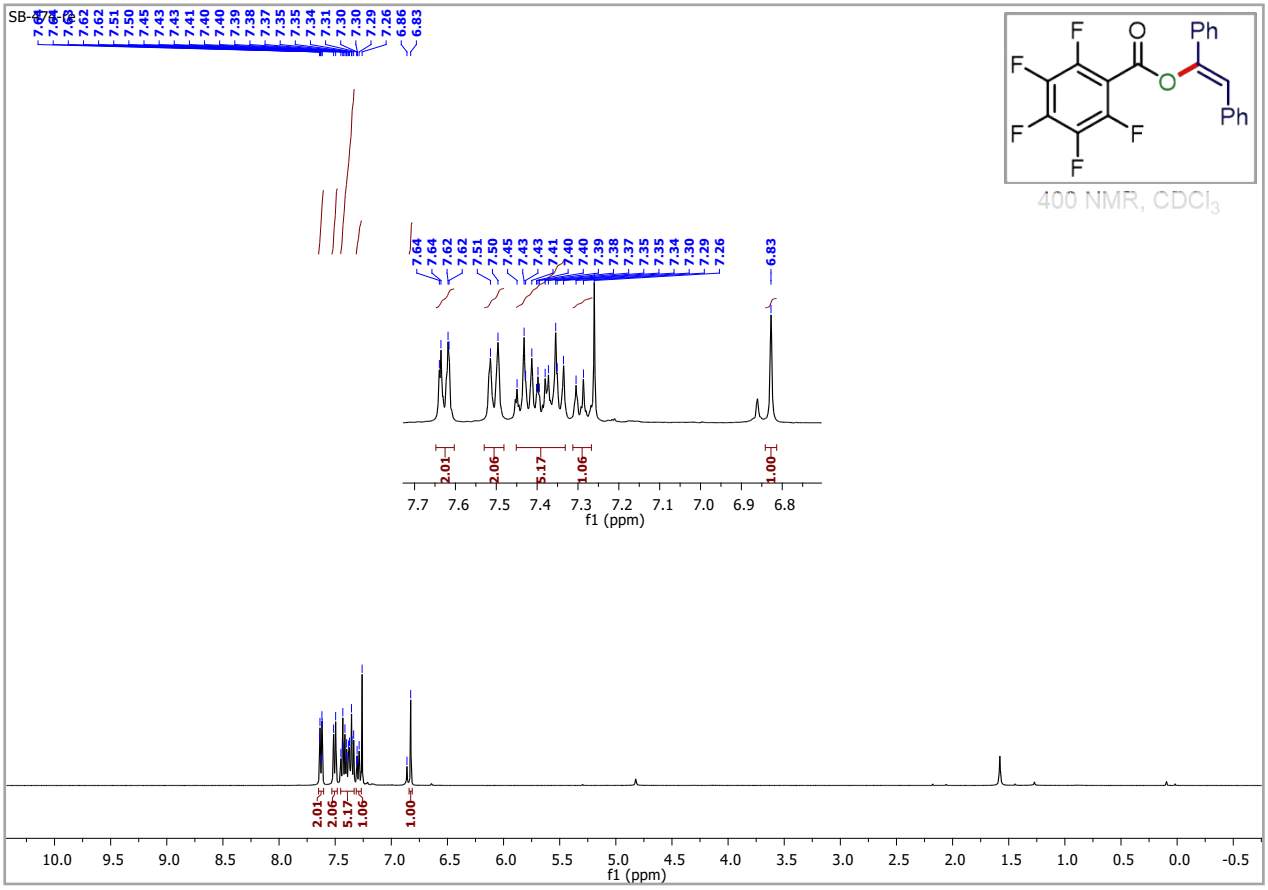
*^{13}C NMR of **9** in $CDCl_3$ at 100 MHz*



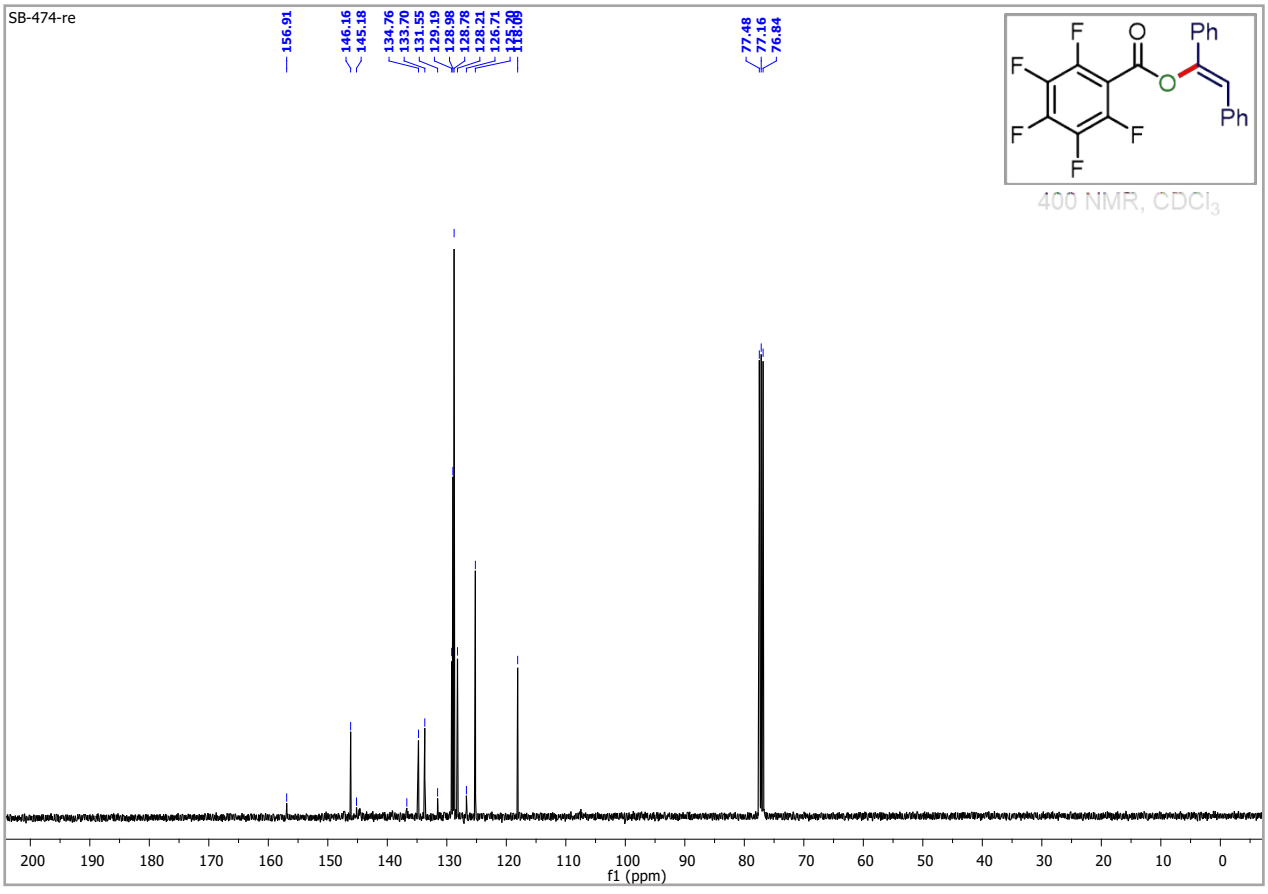
*^{19}F NMR of **9** in $CDCl_3$ at 100 MHz*



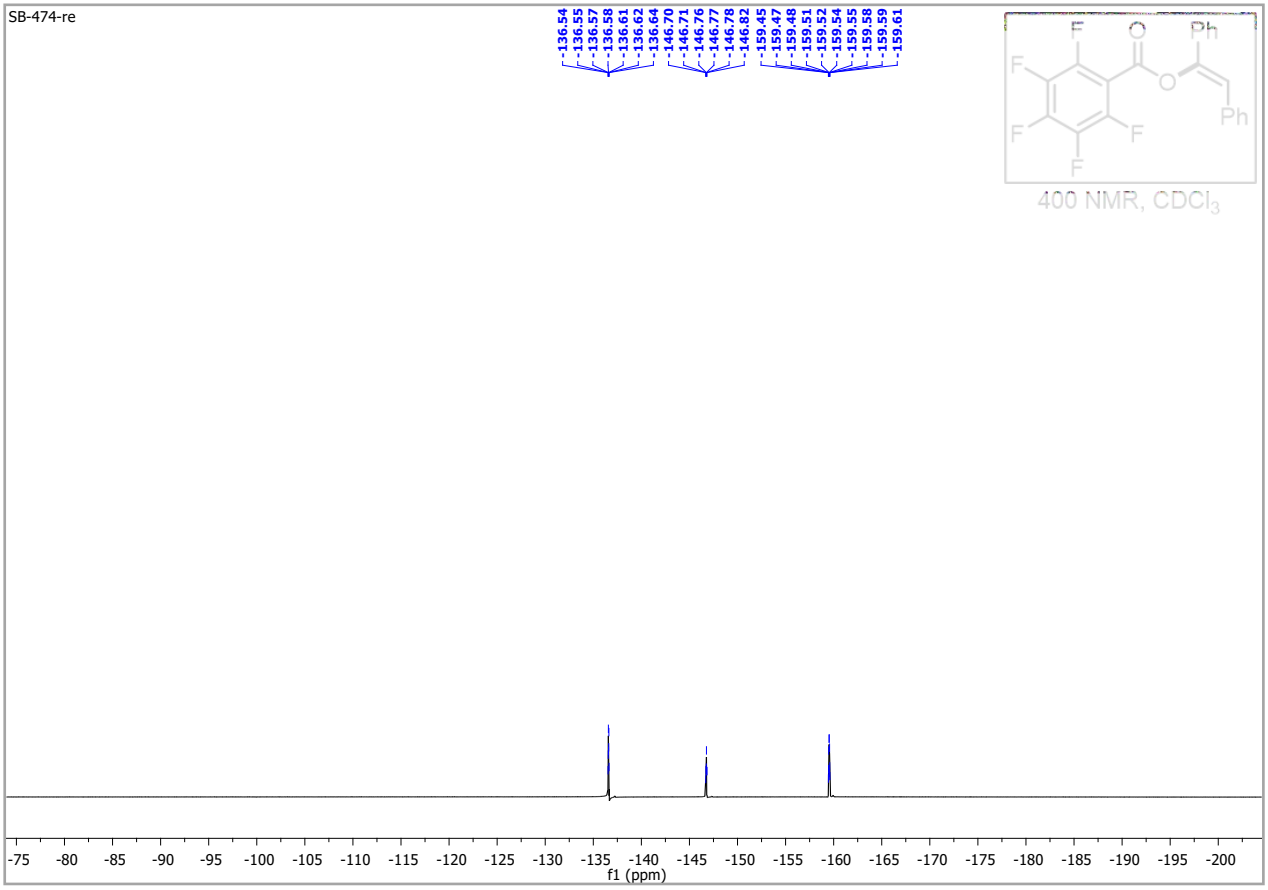
*^{1}H NMR of **10** in $CDCl_3$ at 400 MHz*



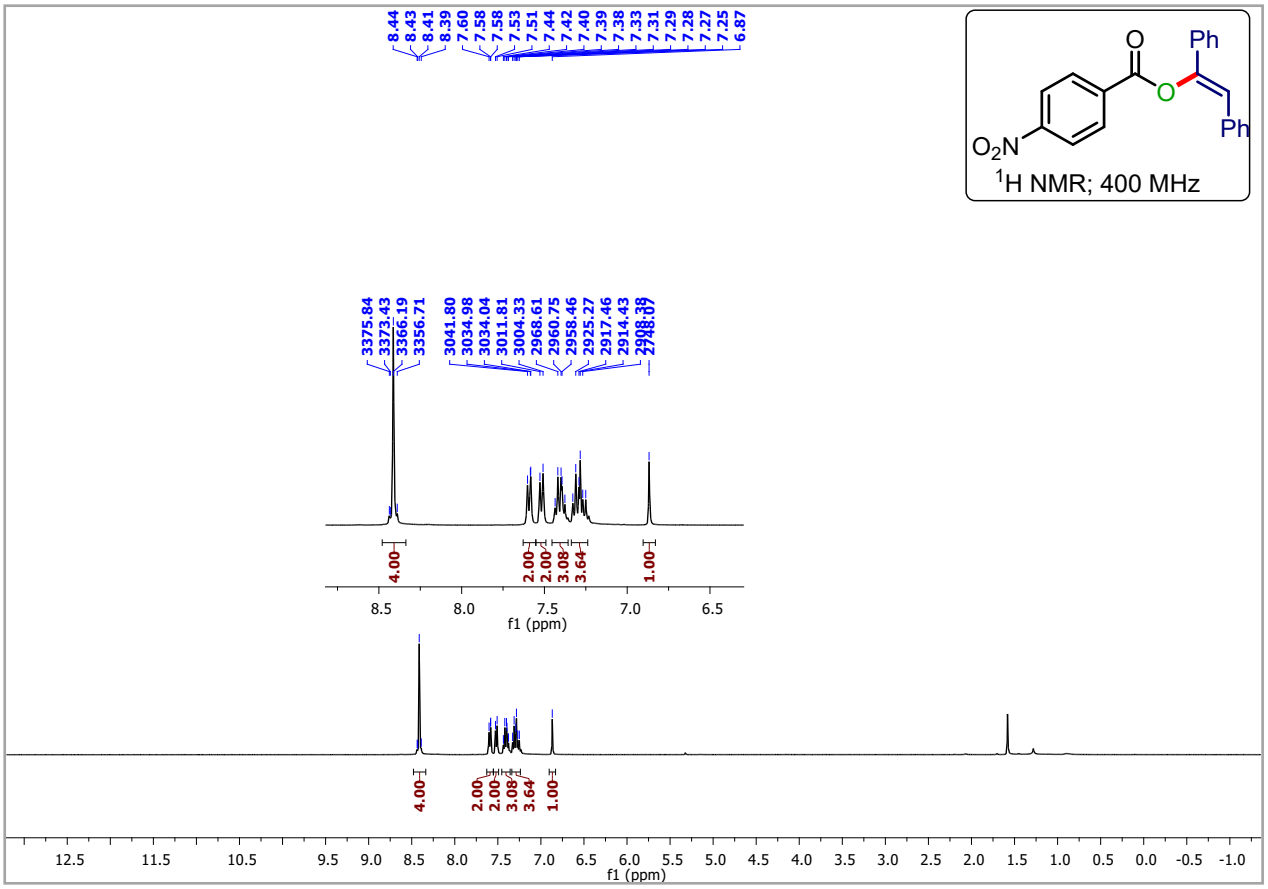
*^{13}H NMR of **10** in $CDCl_3$ at 100 MHz*



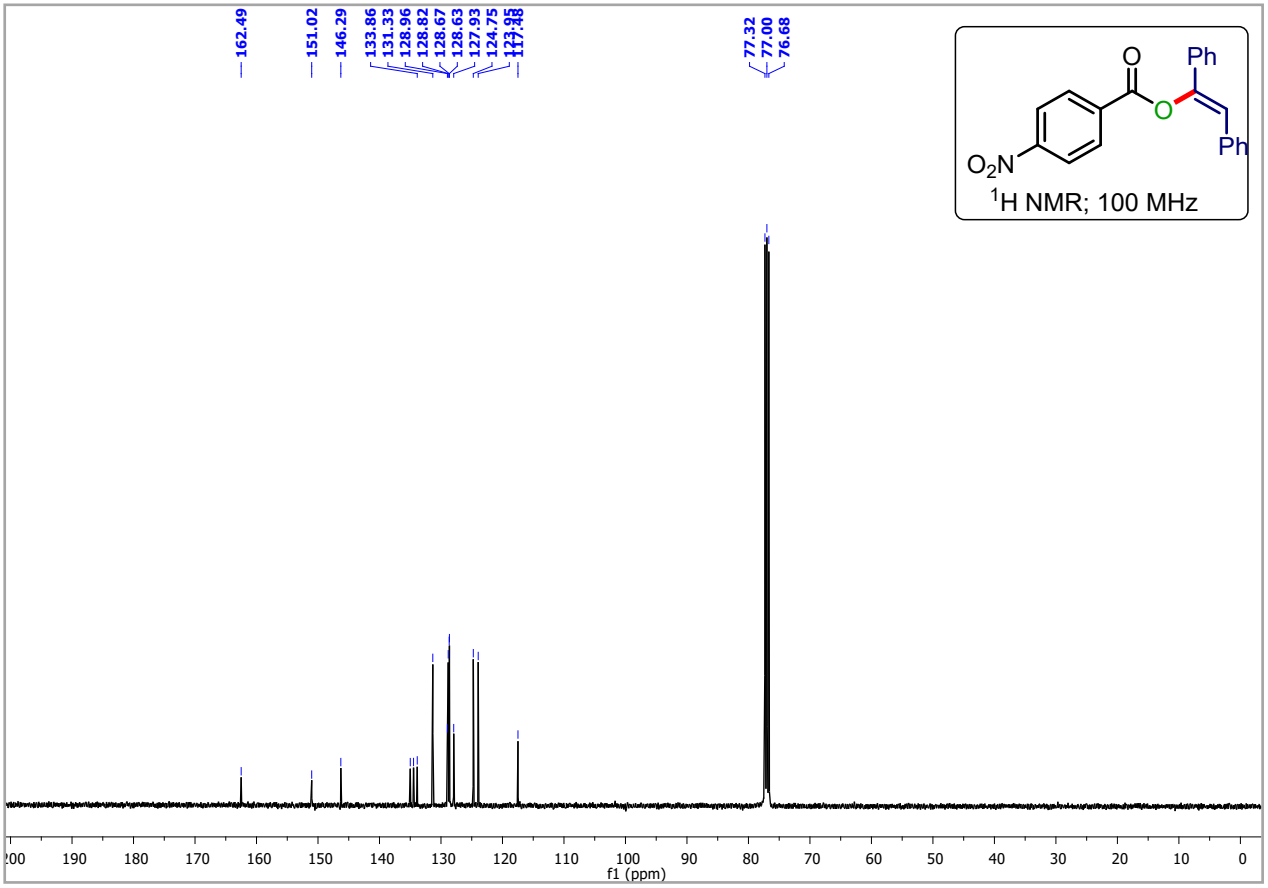
*^{19}F NMR of **10** in $CDCl_3$ at 100 MHz*



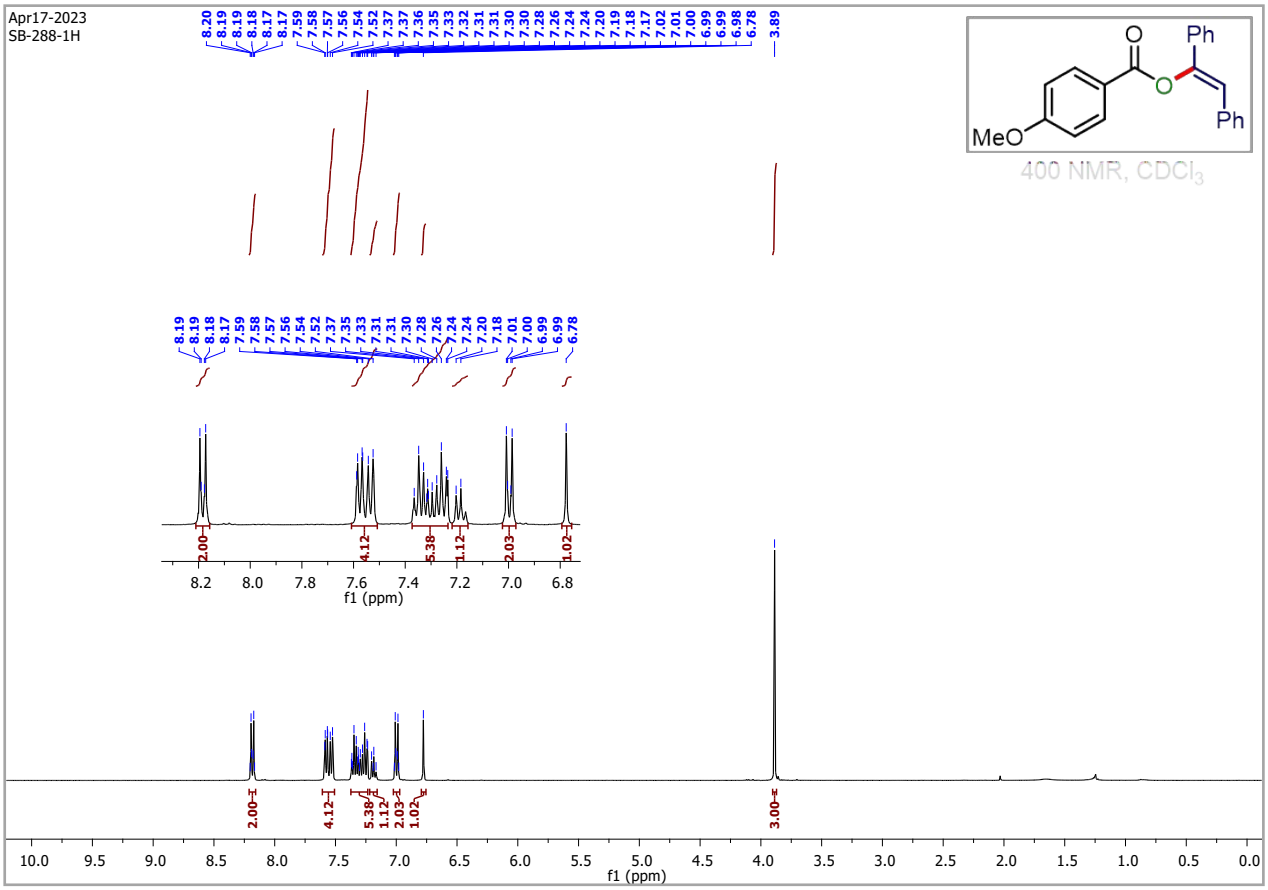
*^{1}H NMR of **11** in $CDCl_3$ at 400 MHz*



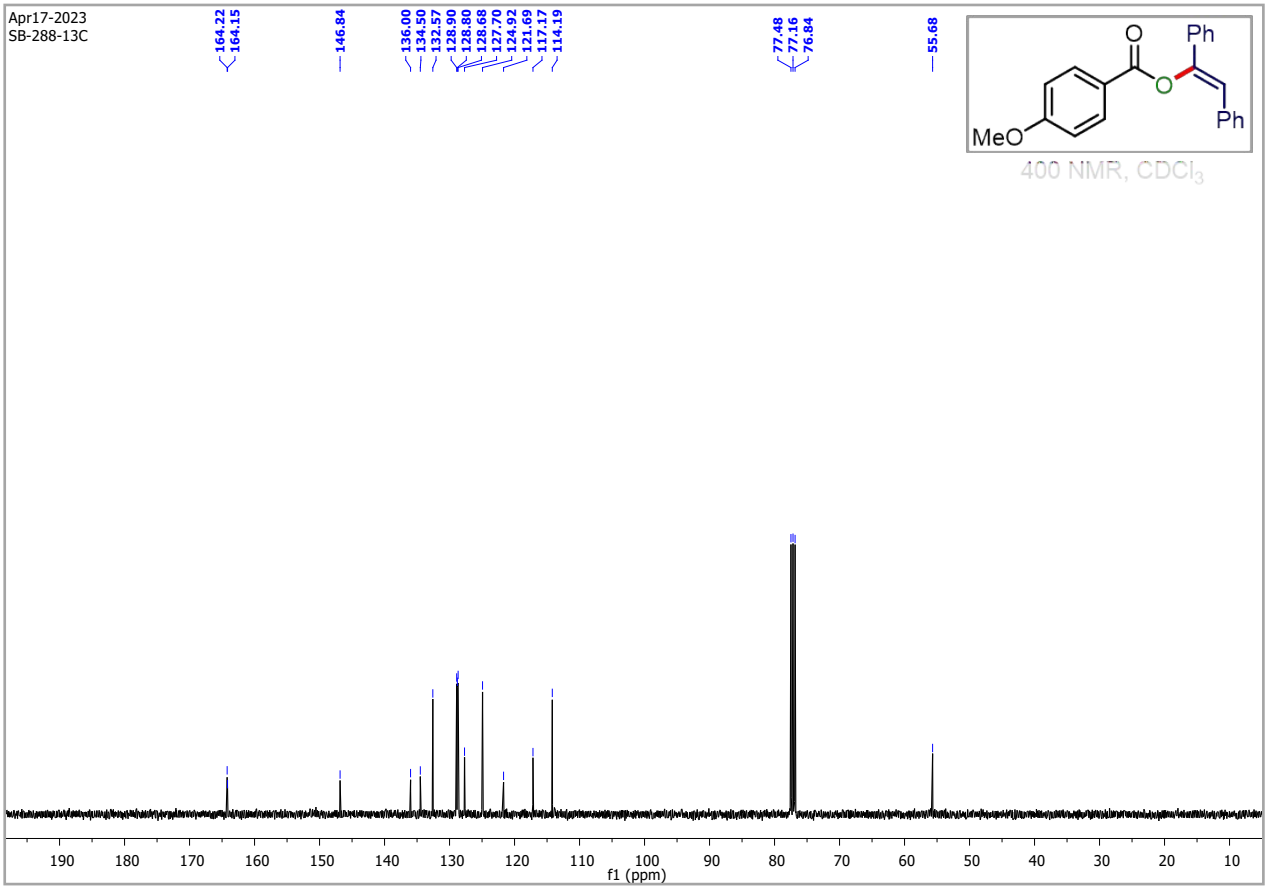
*^{13}C NMR of **11** in $CDCl_3$ at 100 MHz*



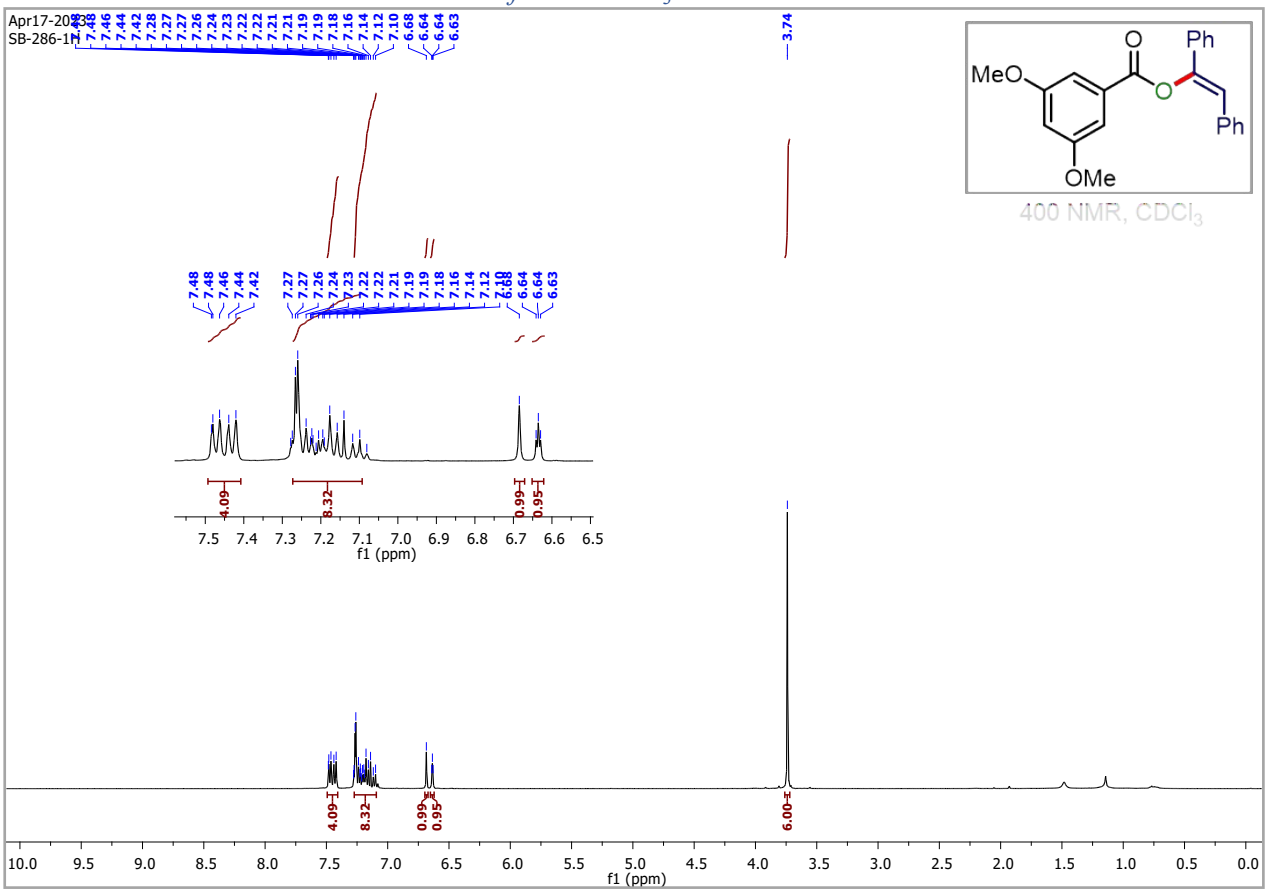
*^{1}H NMR of **12** in $CDCl_3$ at 400 MHz*



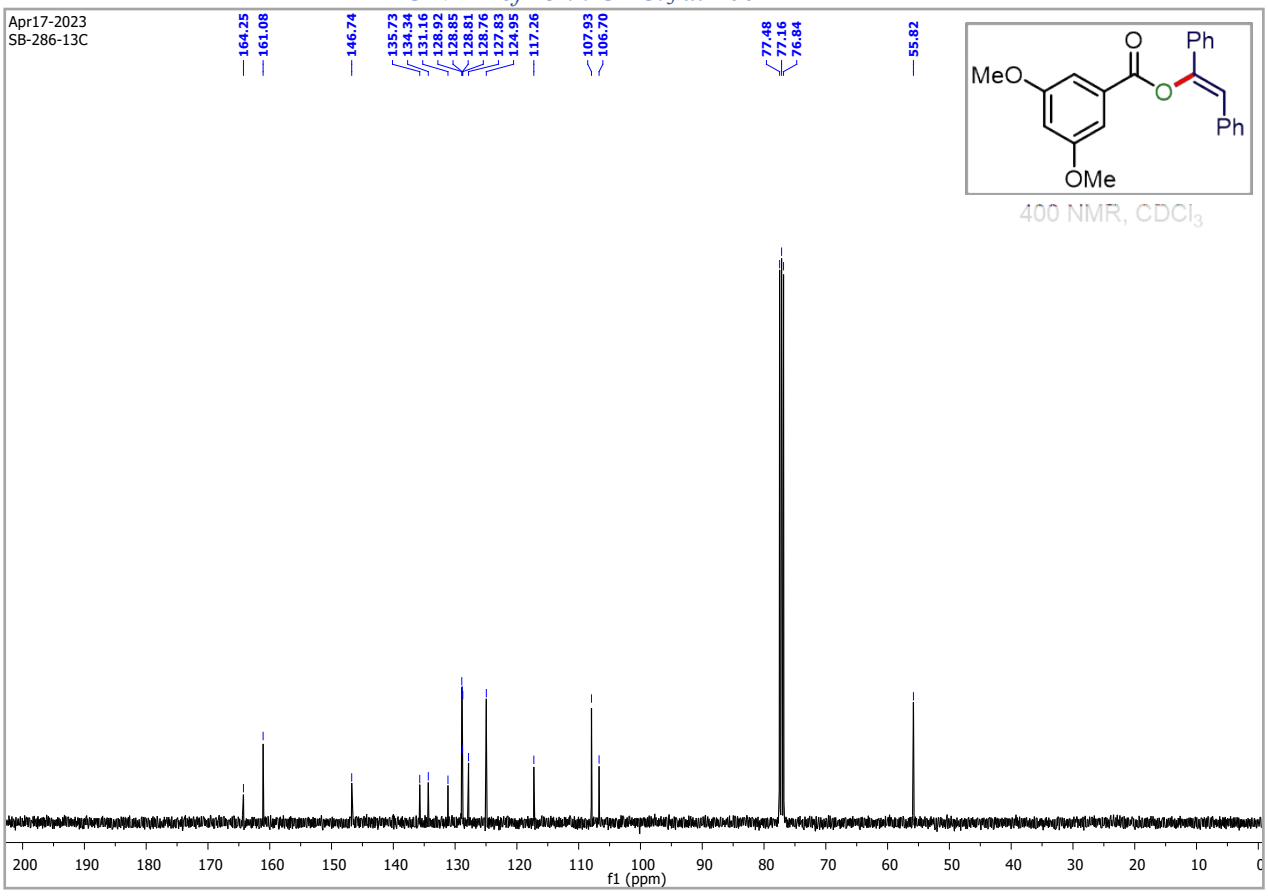
*^{13}C NMR of **12** in $CDCl_3$ at 100 MHz*



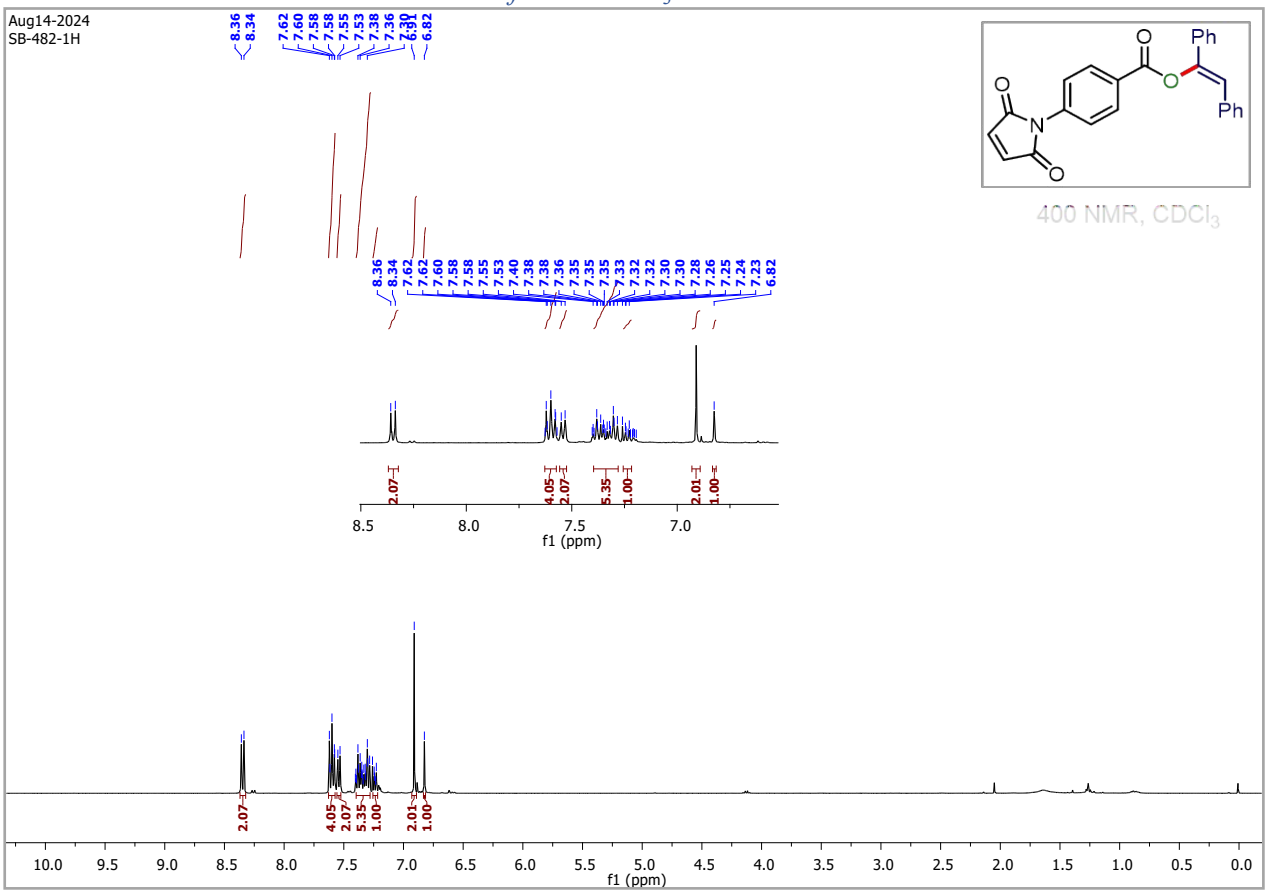
*^{1}H NMR of **13** in $CDCl_3$ at 400 MHz*



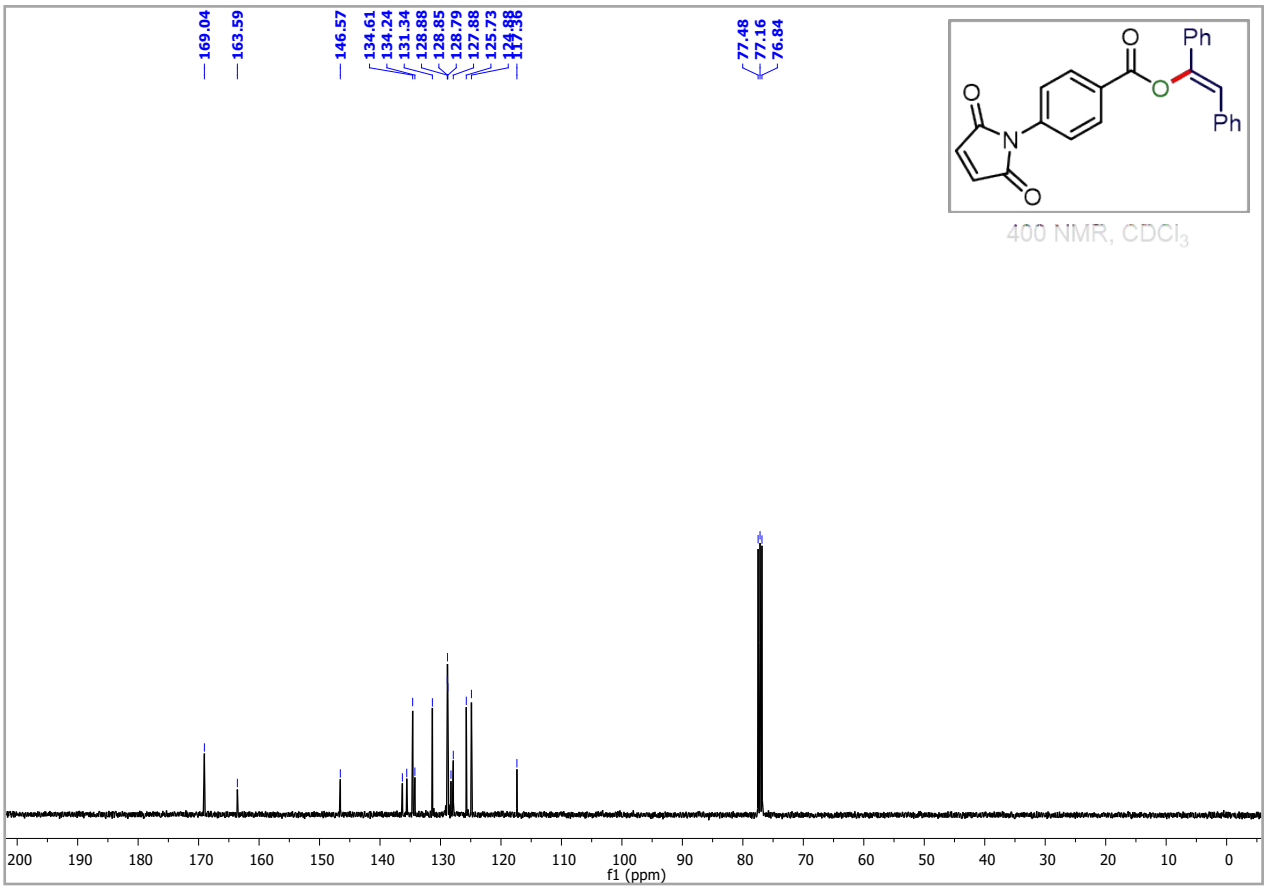
*^{13}C NMR of **13** in $CDCl_3$ at 100 MHz*



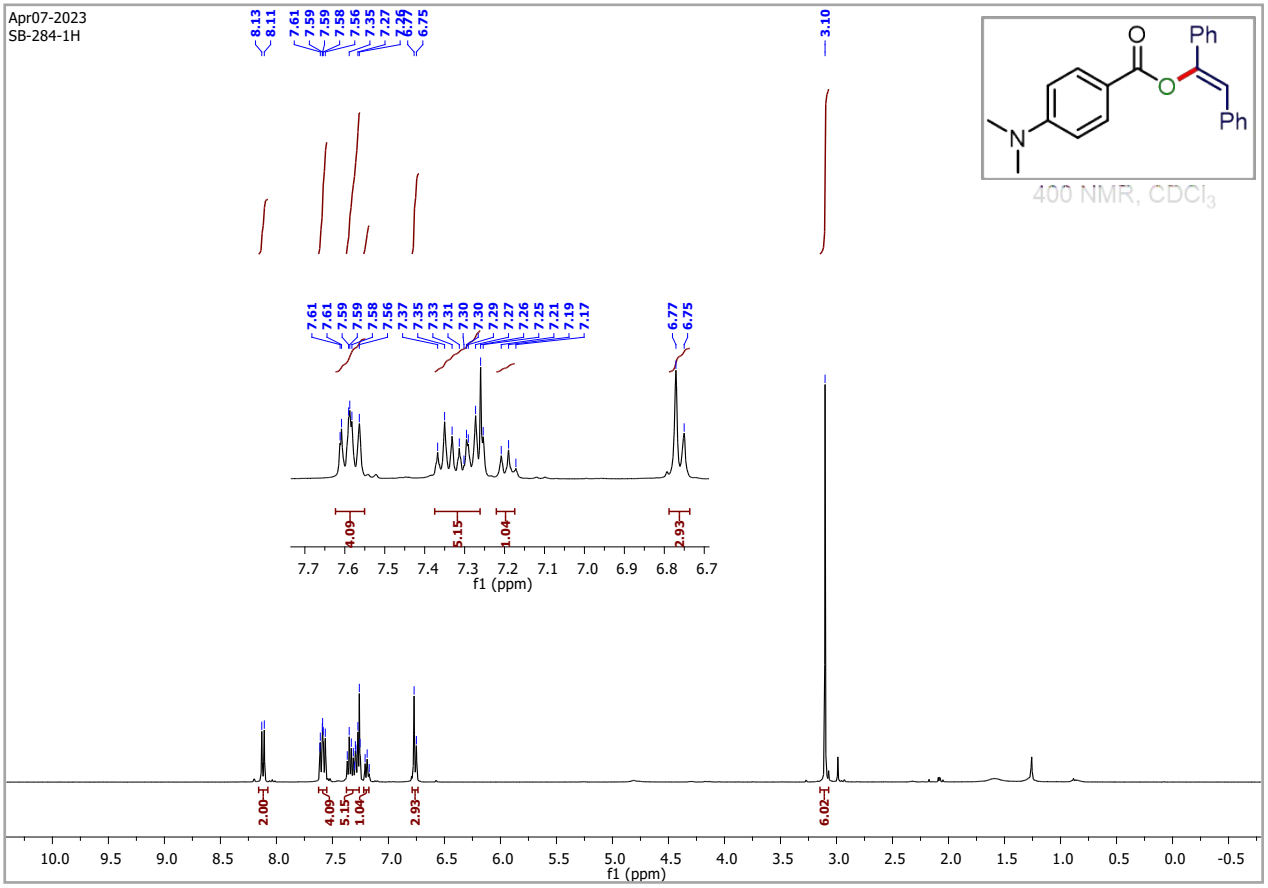
*^{1}H NMR of **14** in $CDCl_3$ at 400 MHz*



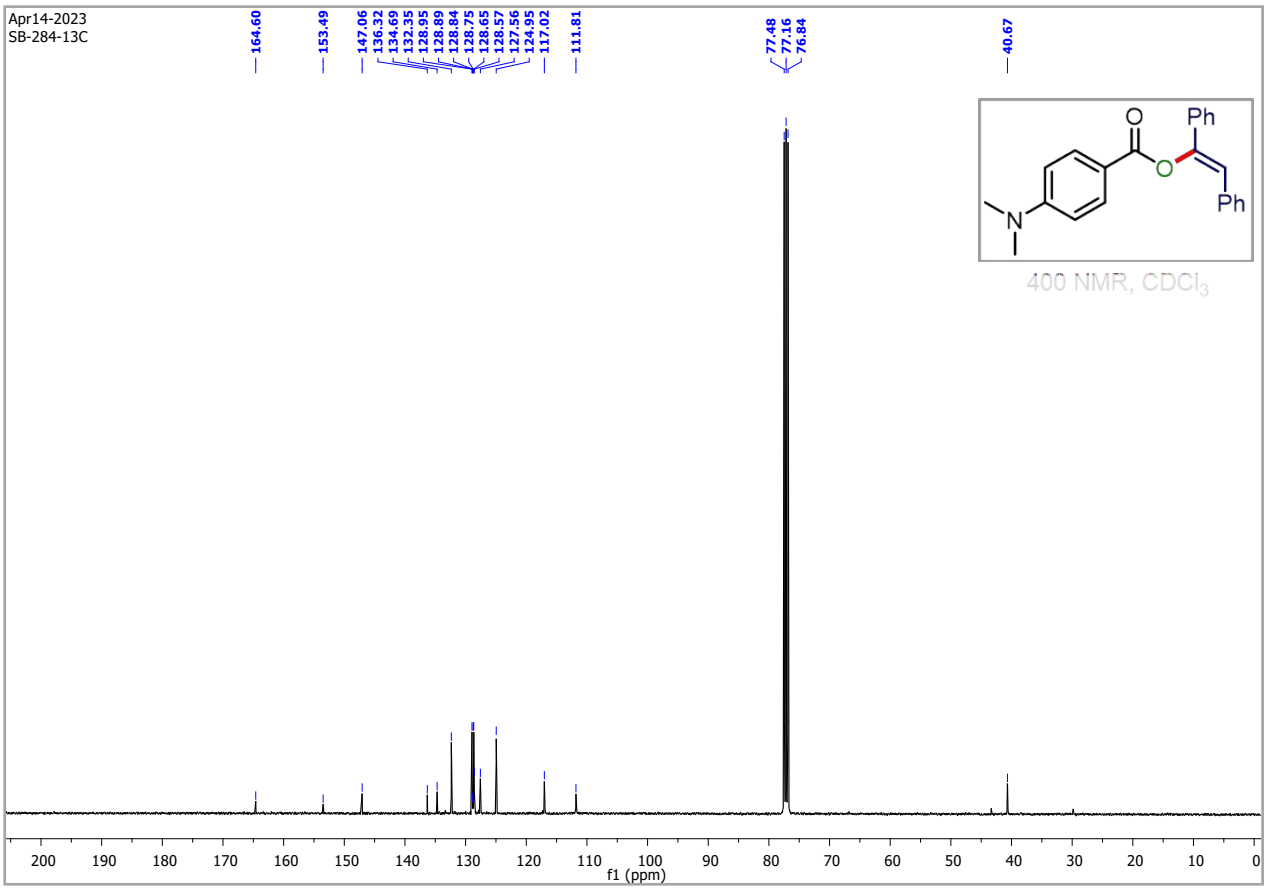
*^{13}C NMR of **14** in $CDCl_3$ at 100 MHz*



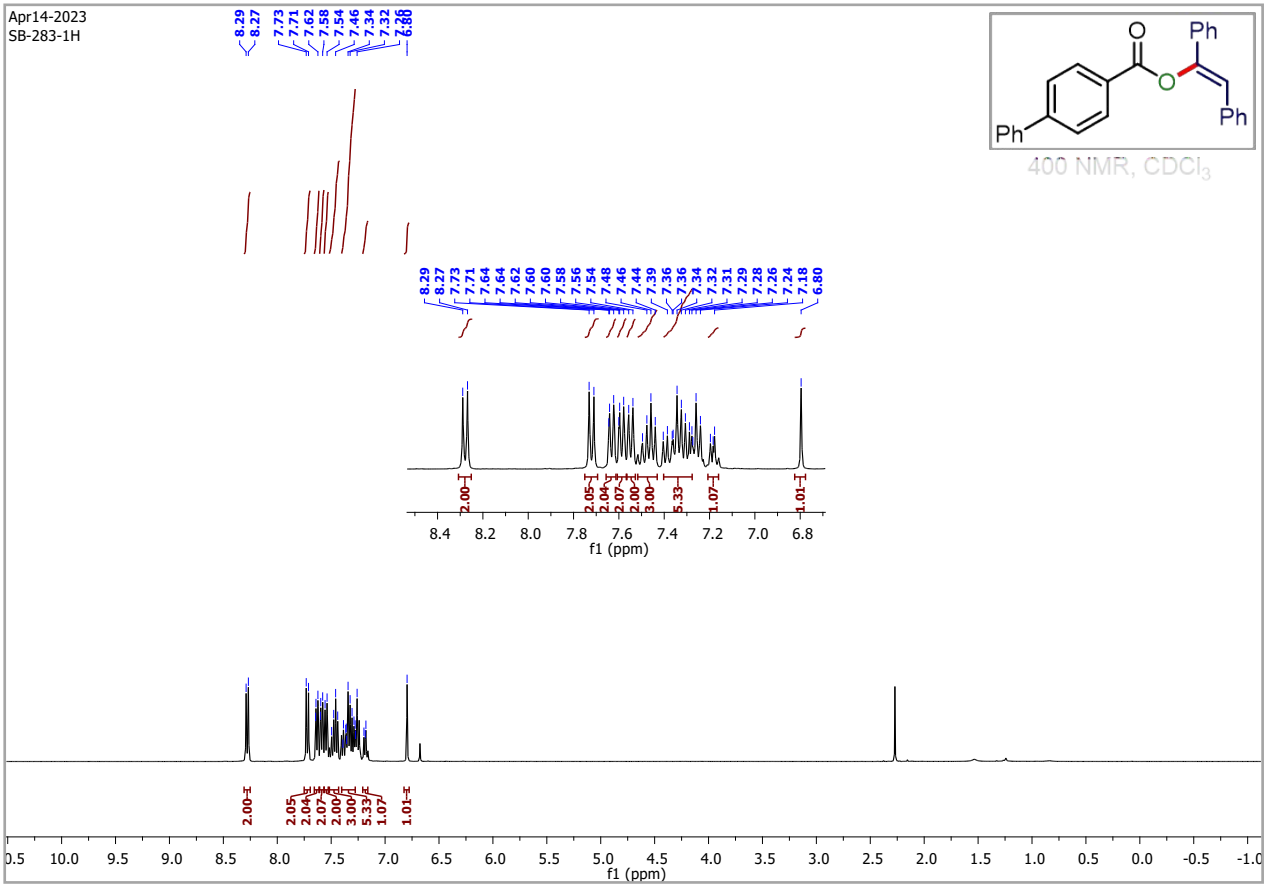
*^{1}H NMR of **15** in $CDCl_3$ at 400 MHz*



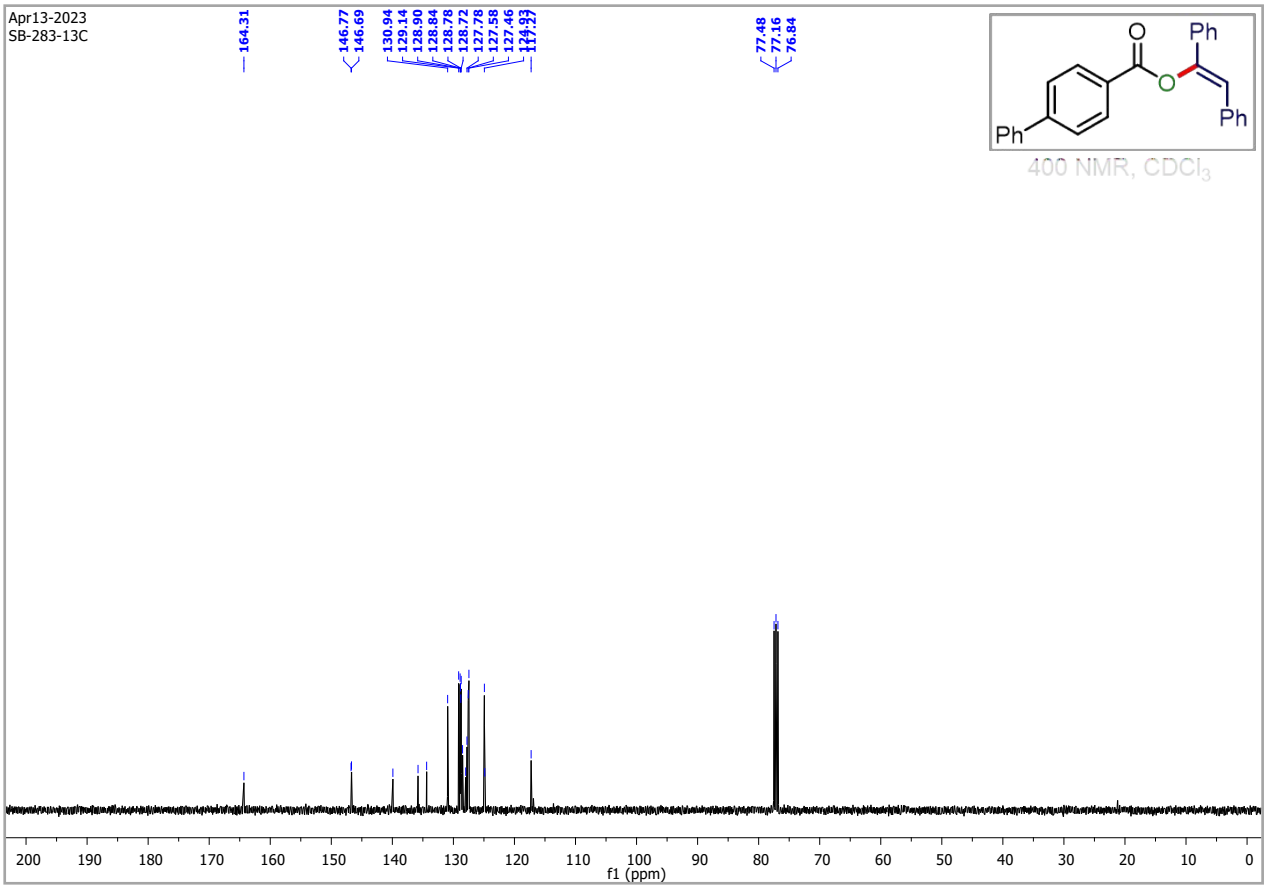
*^{13}C NMR of **15** in $CDCl_3$ at 100 MHz*



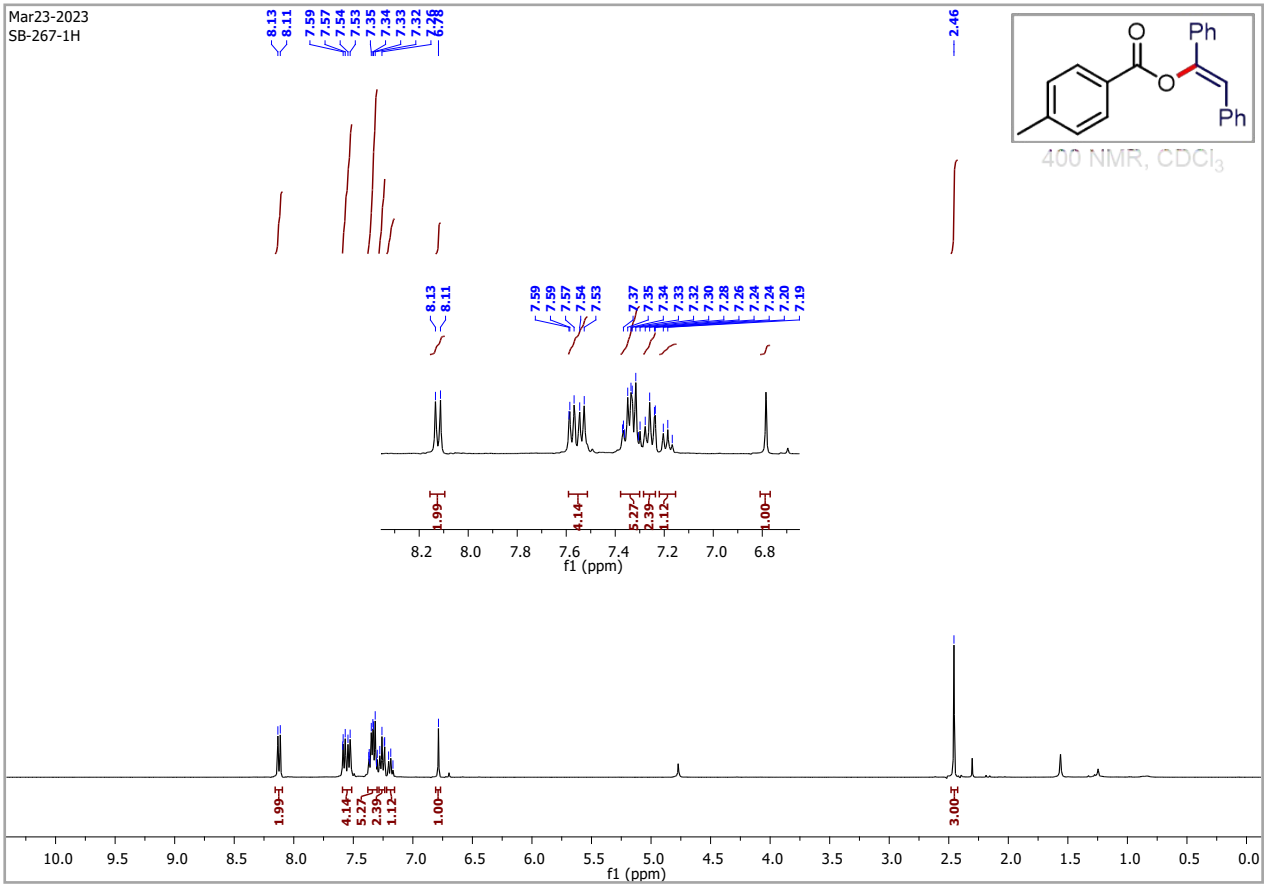
*^{1}H NMR of **16** in $CDCl_3$ at 400 MHz*



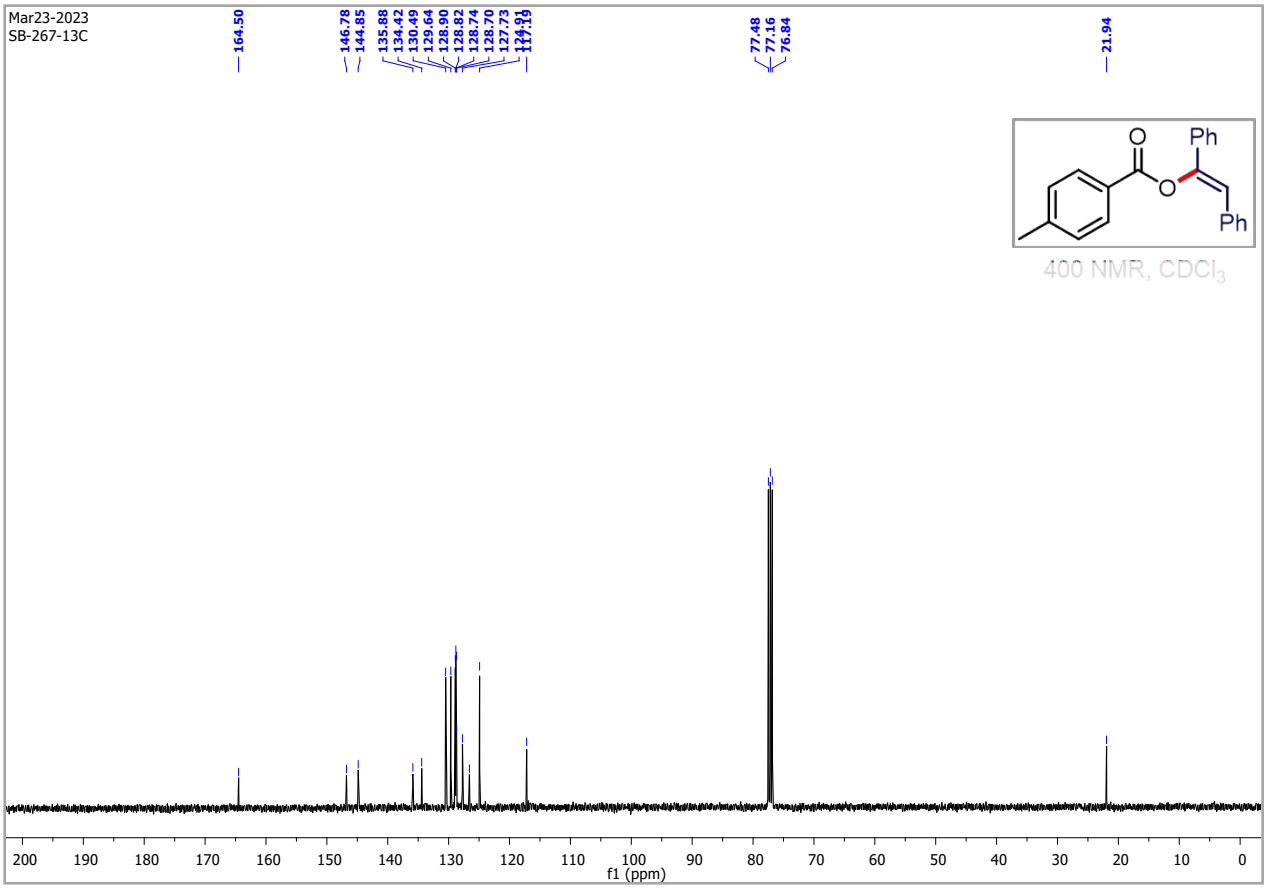
*^{13}C NMR of **16** in $CDCl_3$ at 100 MHz*



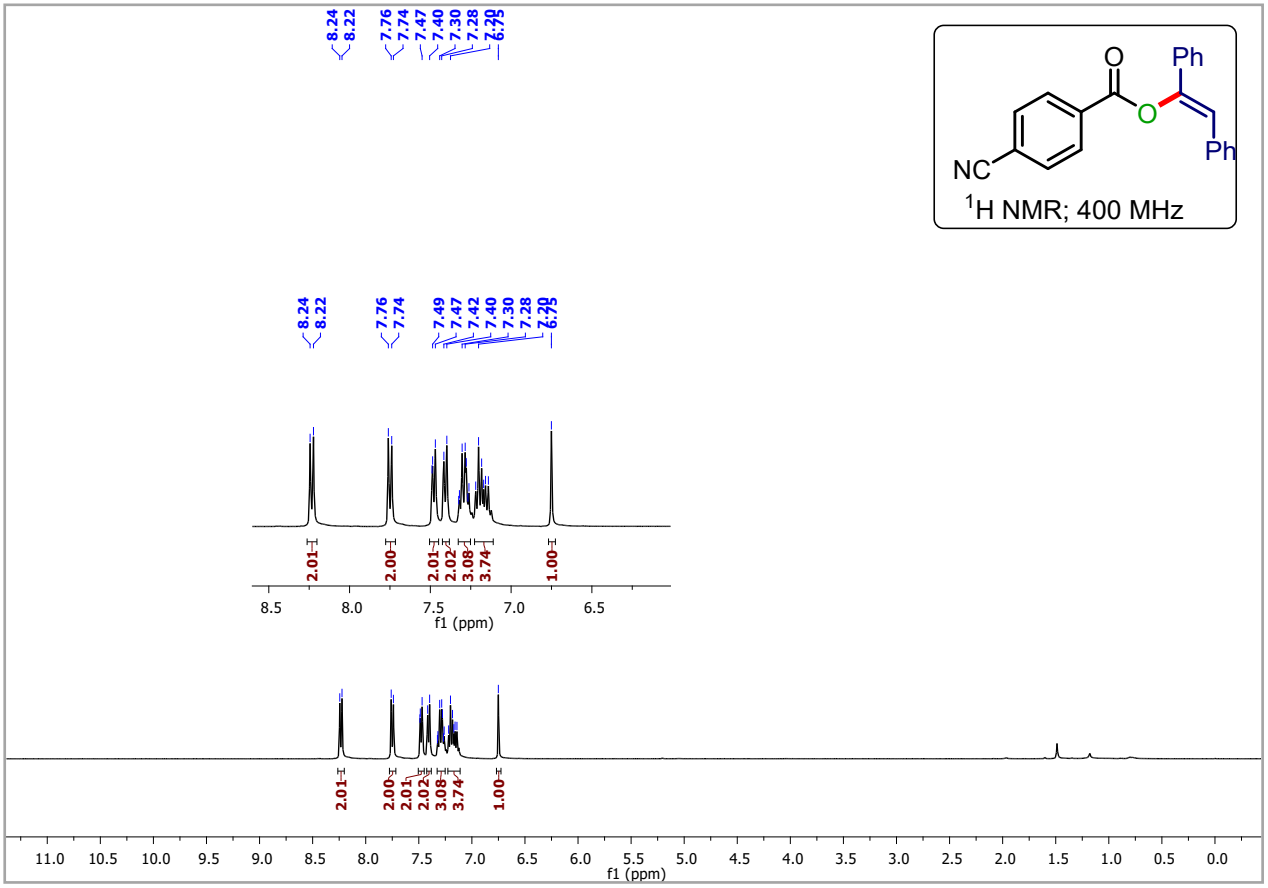
*^{1}H NMR of **17** in $CDCl_3$ at 400 MHz*



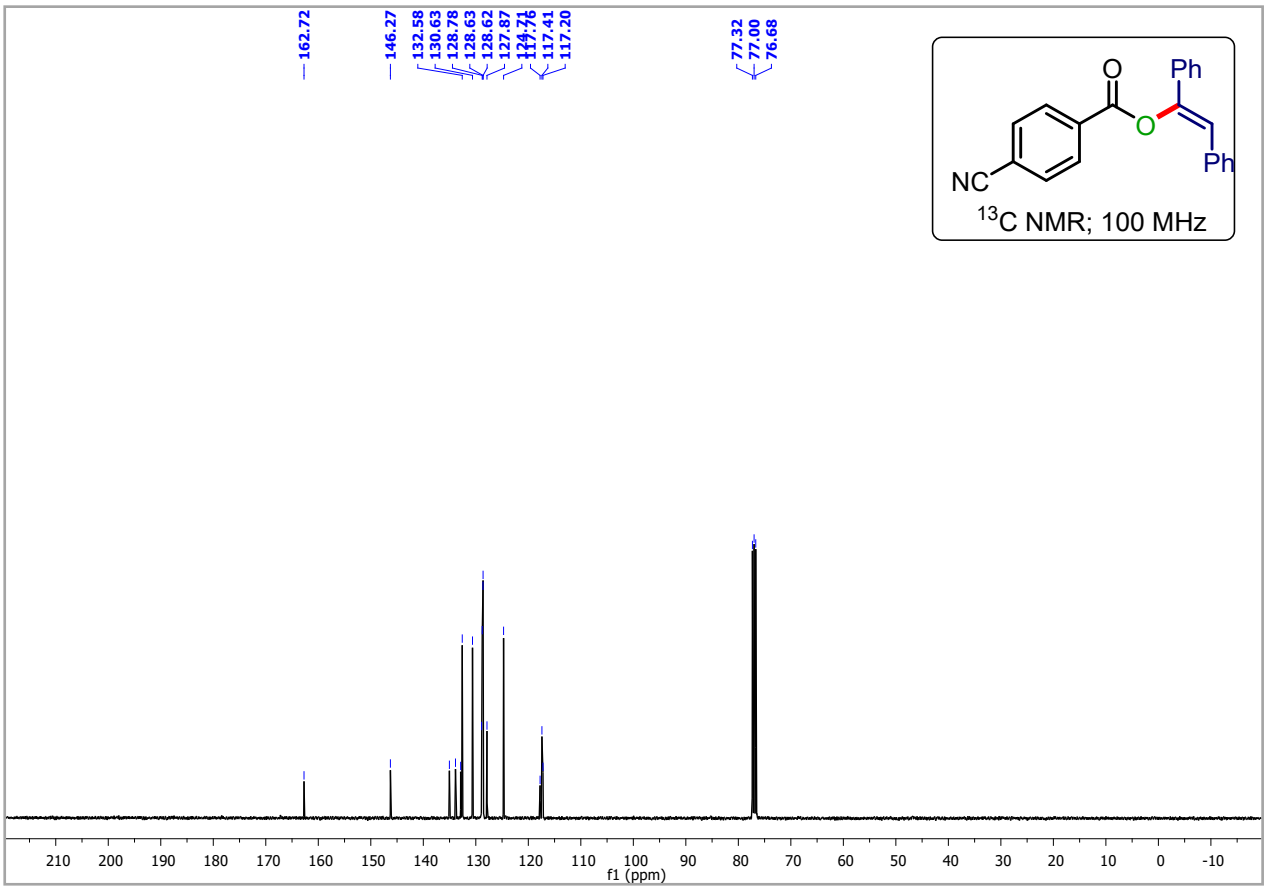
*^{13}C NMR of **17** in $CDCl_3$ at 100 MHz*



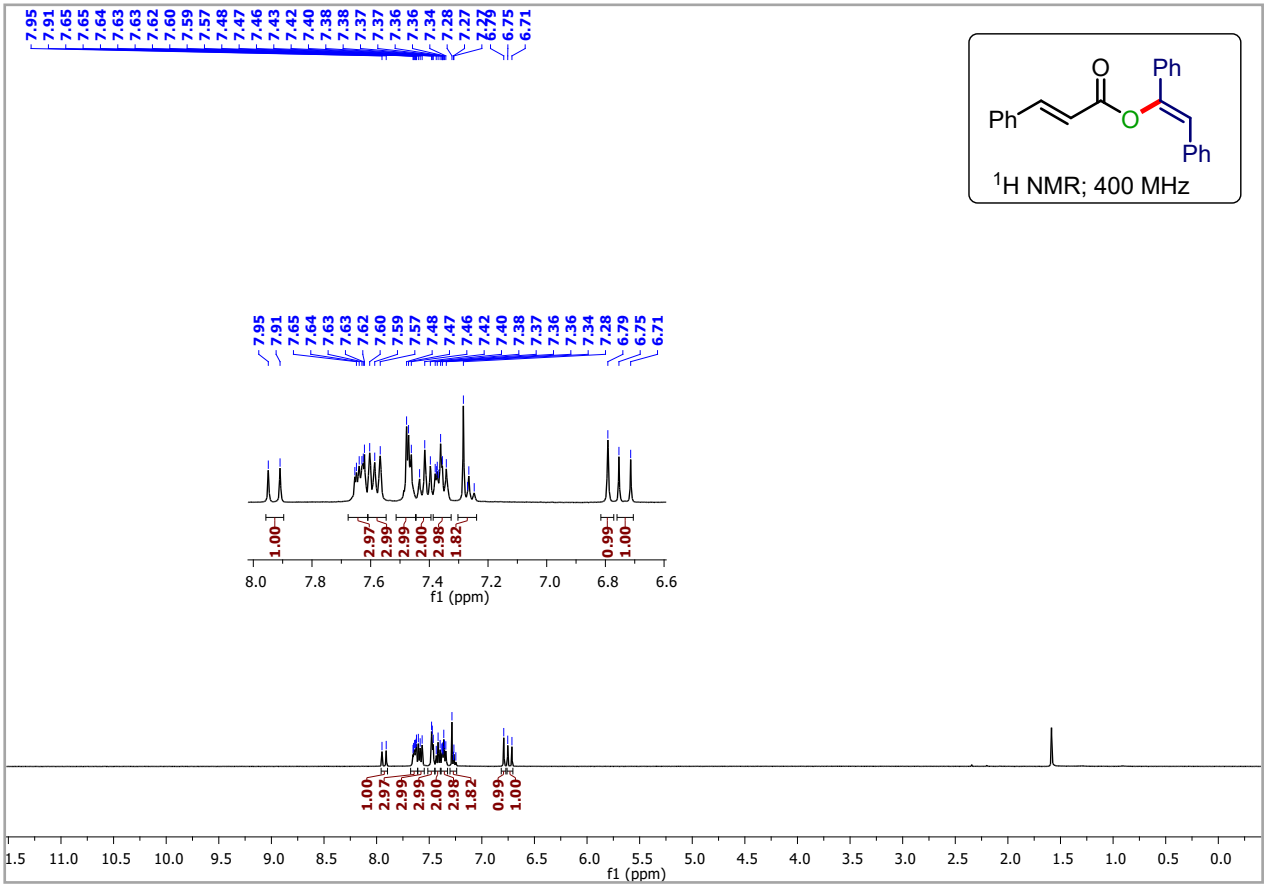
*^{1}H NMR of **18** in $CDCl_3$ at 400 MHz*



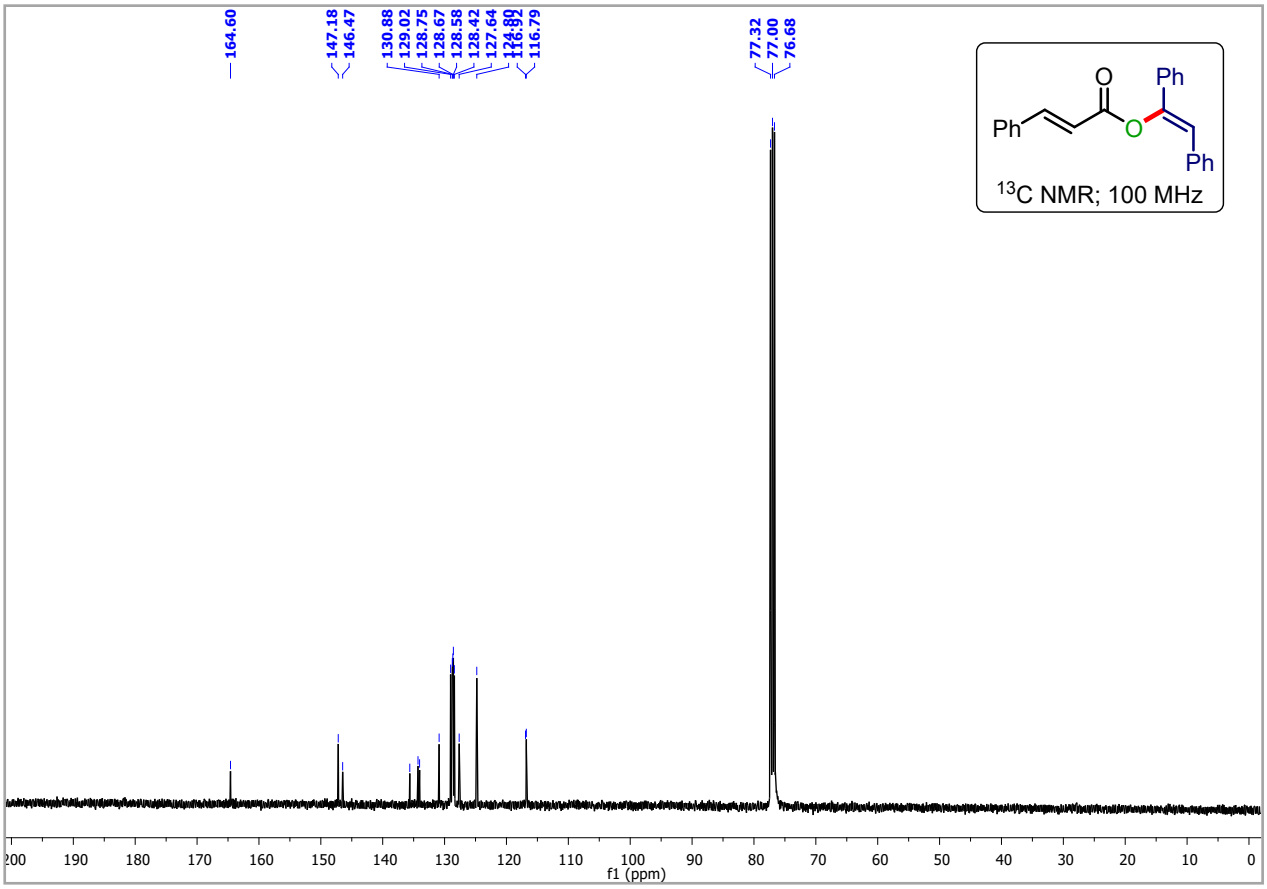
*^{13}C NMR of **18** in $CDCl_3$ at 400 MHz*



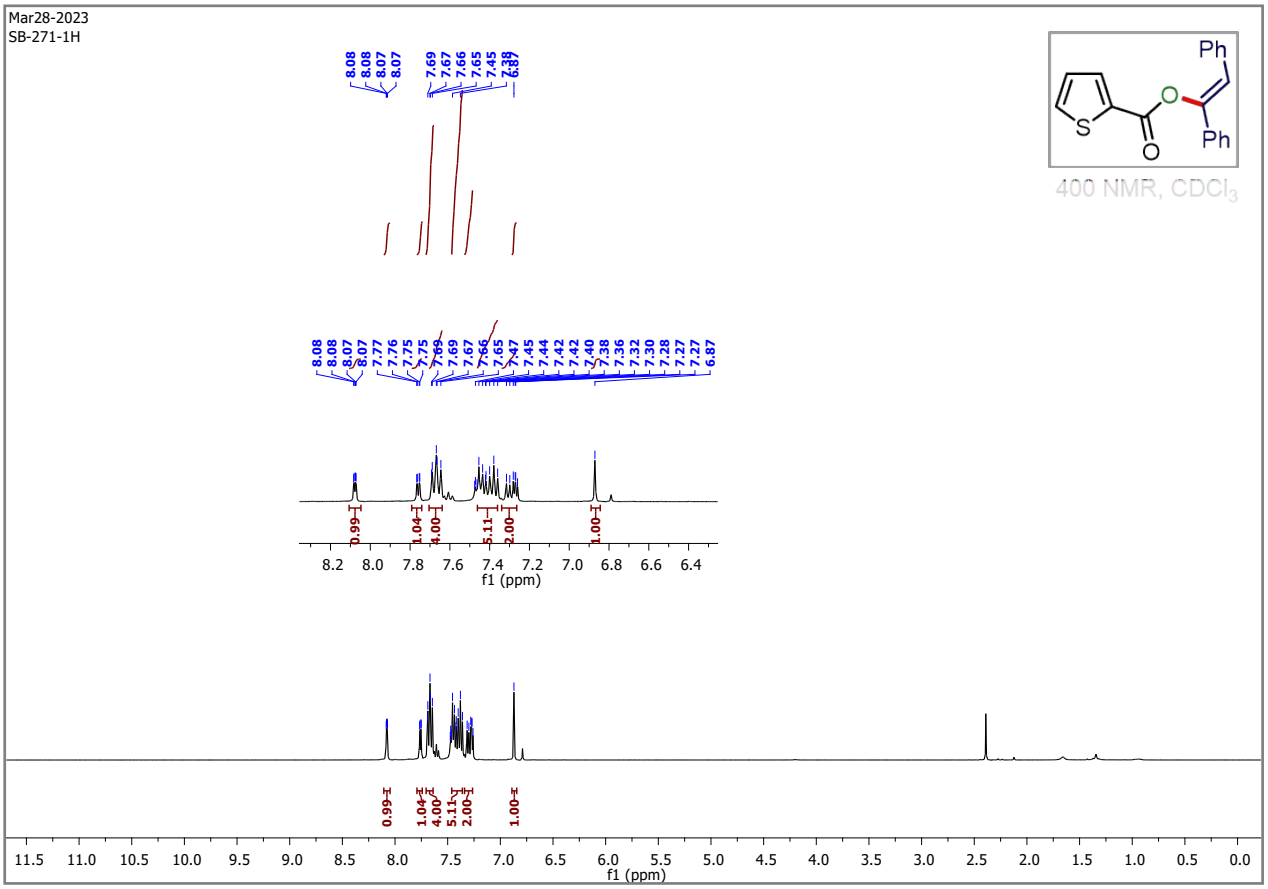
*^{1}H NMR of **19** in $CDCl_3$ at 400 MHz*



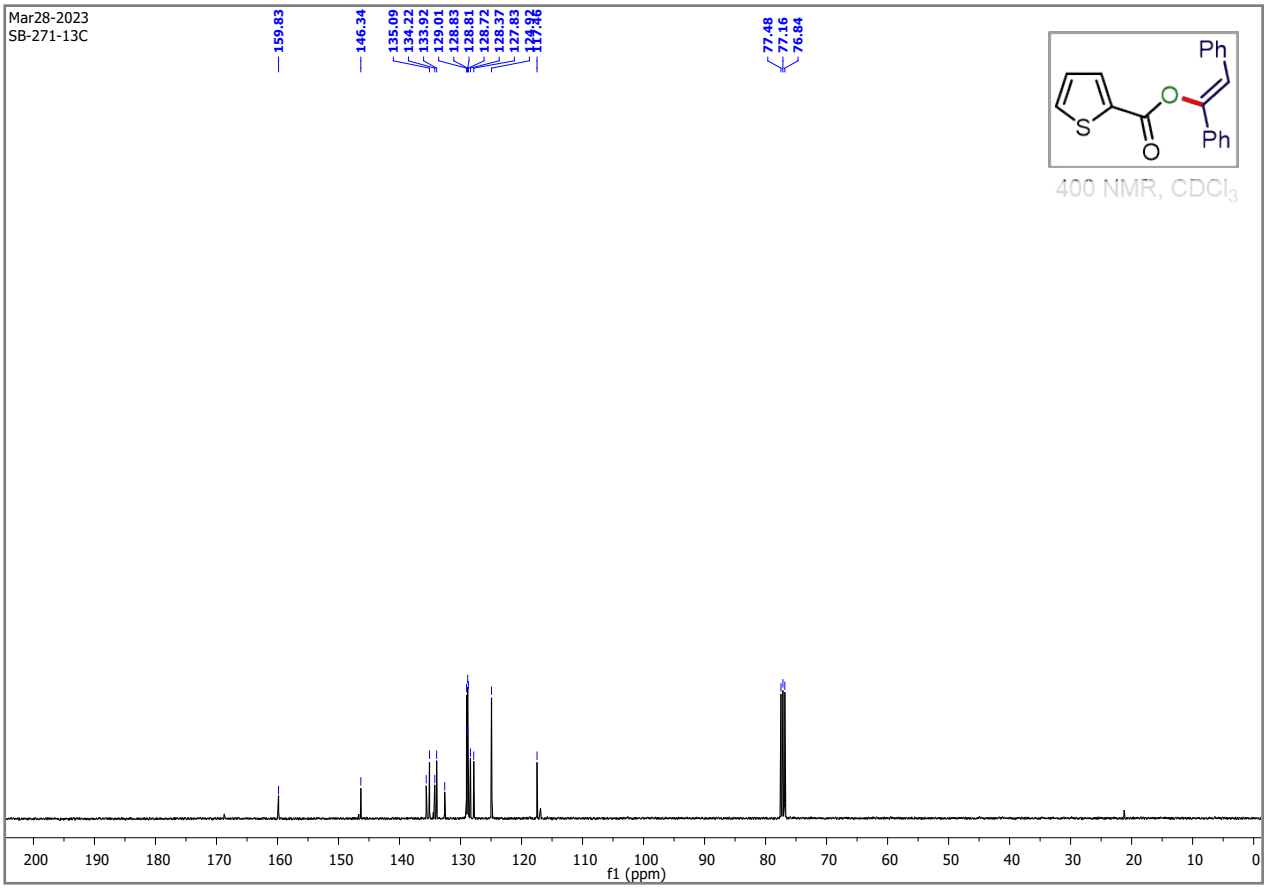
*^{13}C NMR of **19** in $CDCl_3$ at 100 MHz*



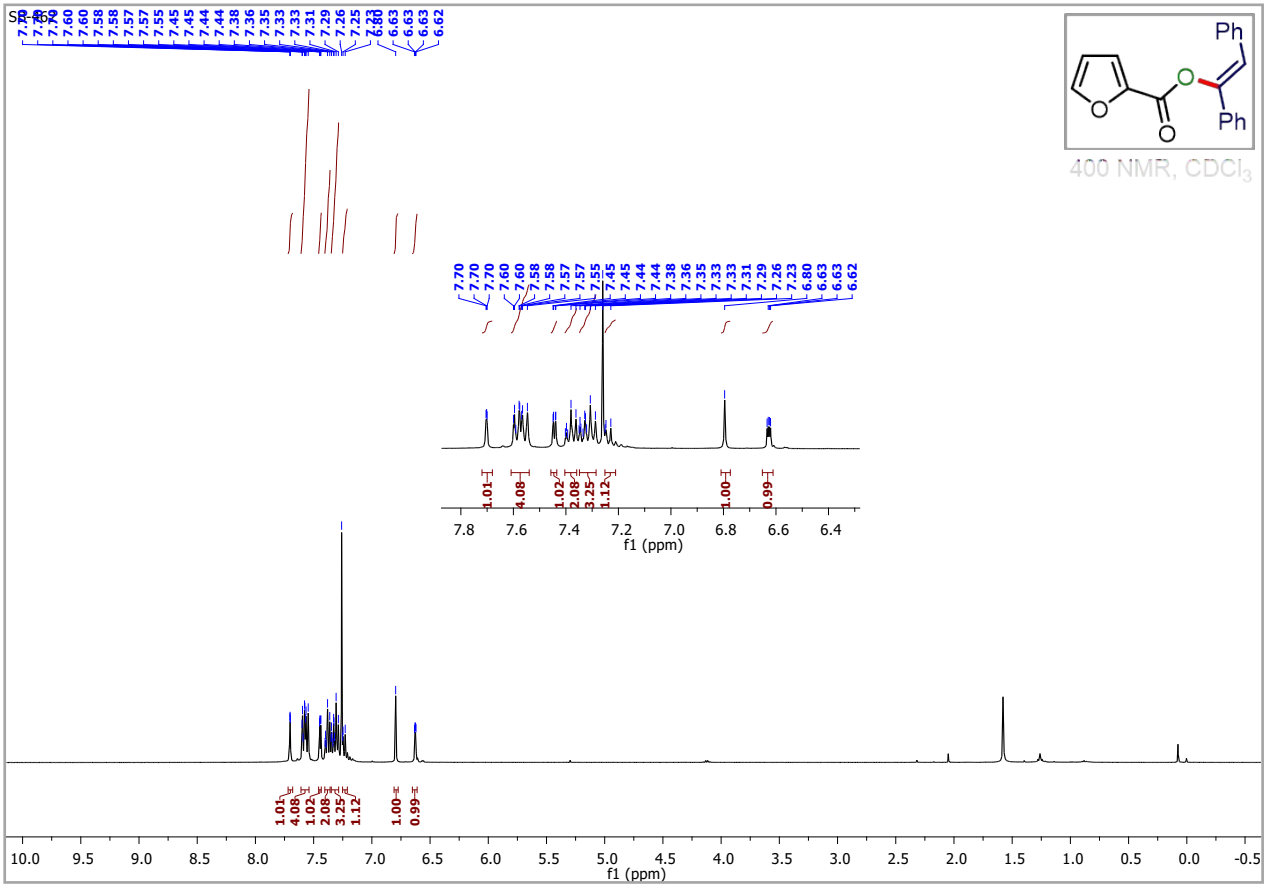
*^{1}H NMR of **20** in $CDCl_3$ at 400 MHz*



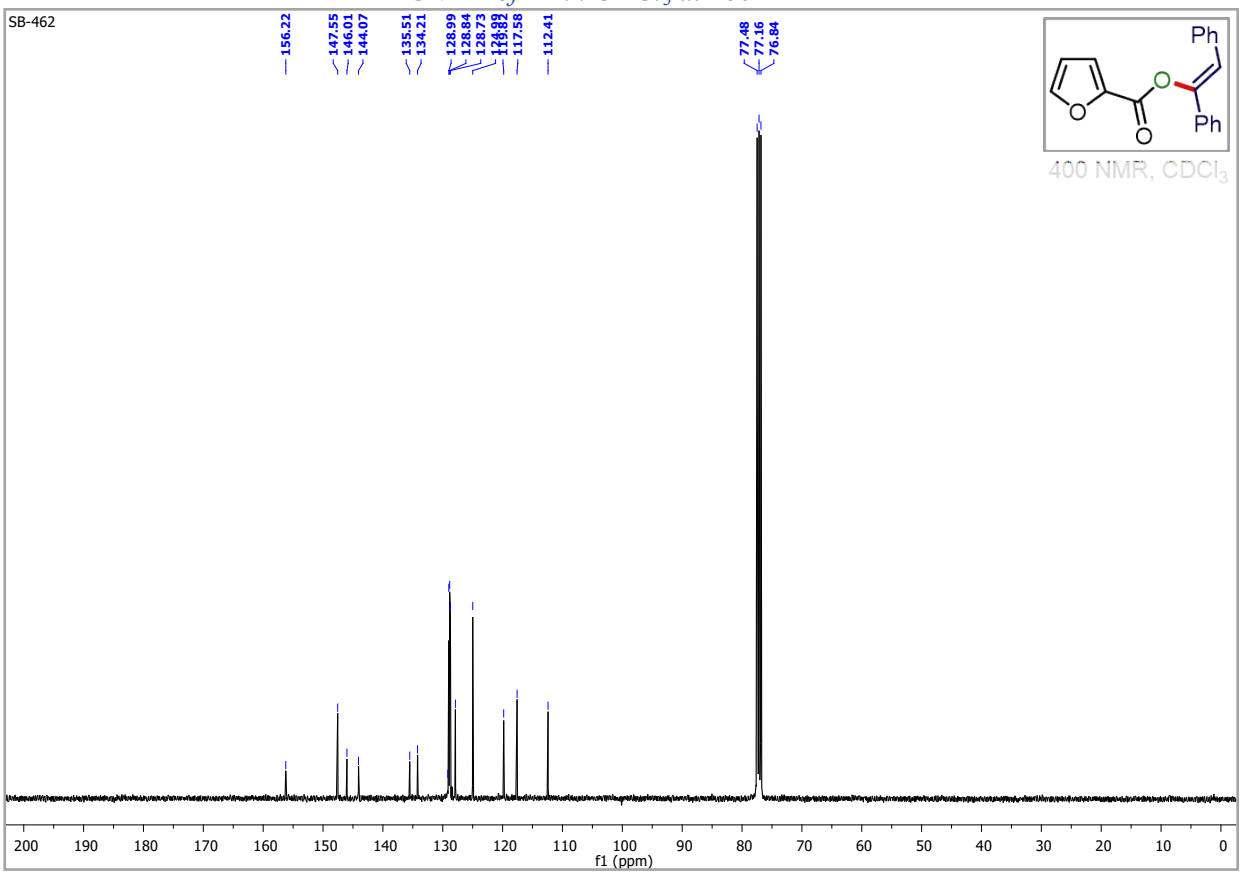
*^{13}C NMR of **20** in $CDCl_3$ at 100 MHz*



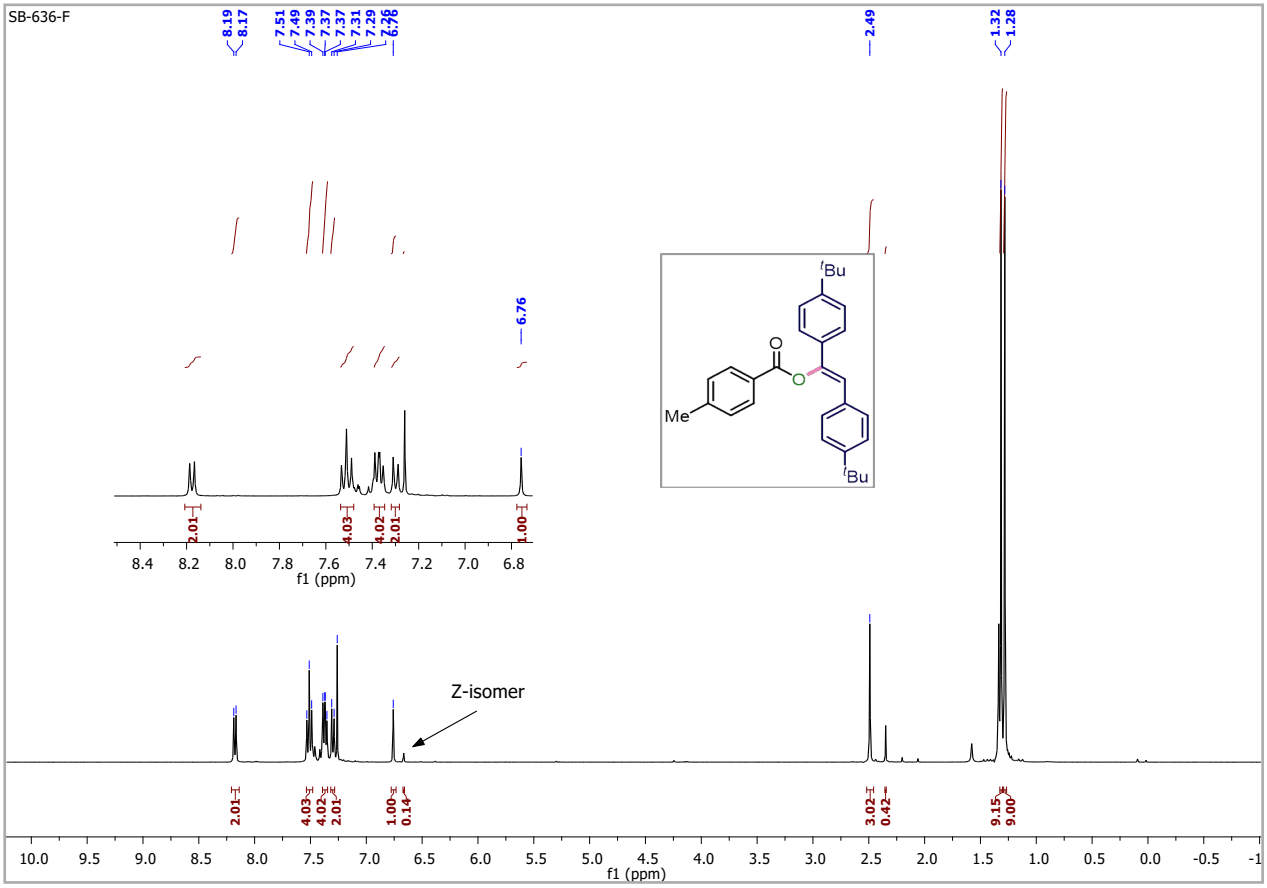
*^{1}H NMR of **21** in $CDCl_3$ at 400 MHz*



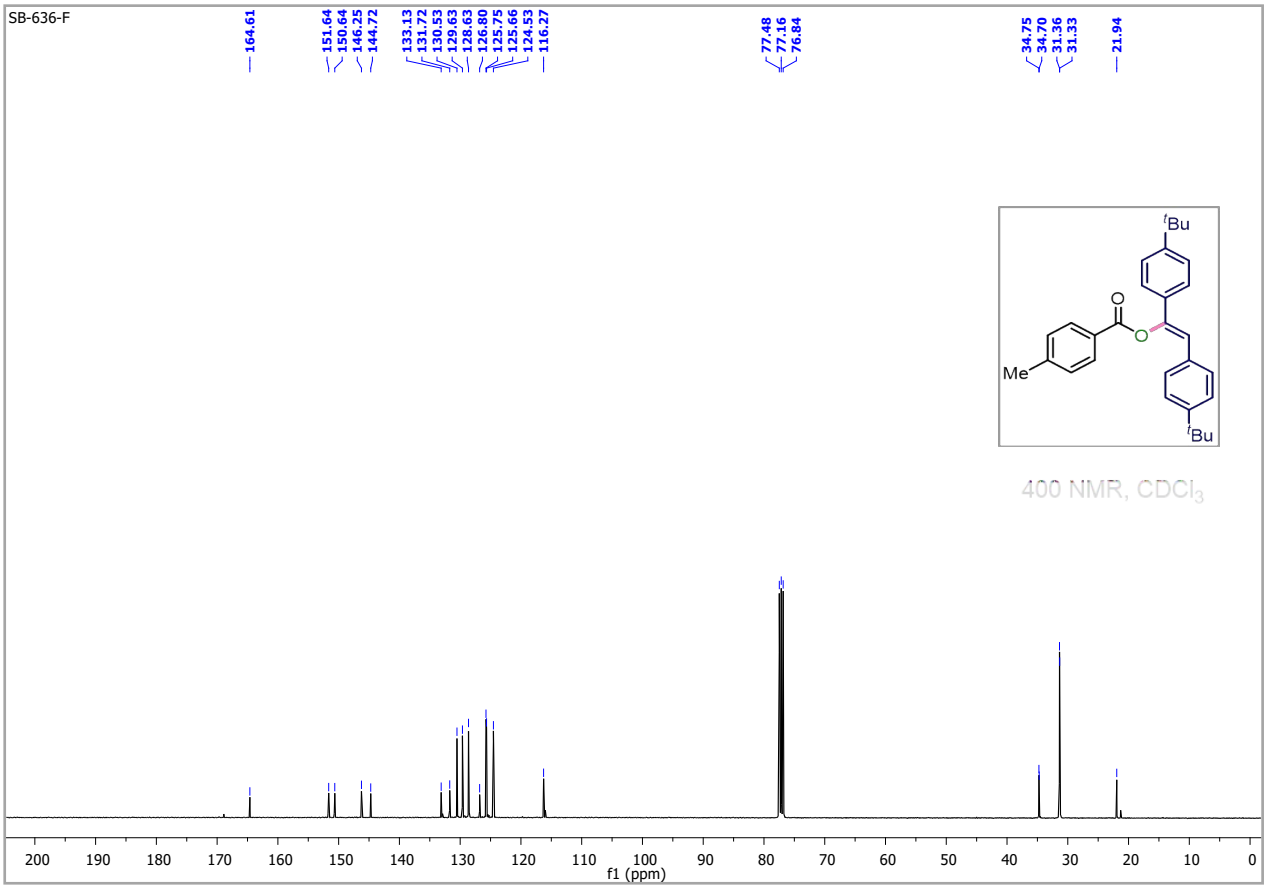
*^{13}CNMR of **21** in $CDCl_3$ at 100 MHz*



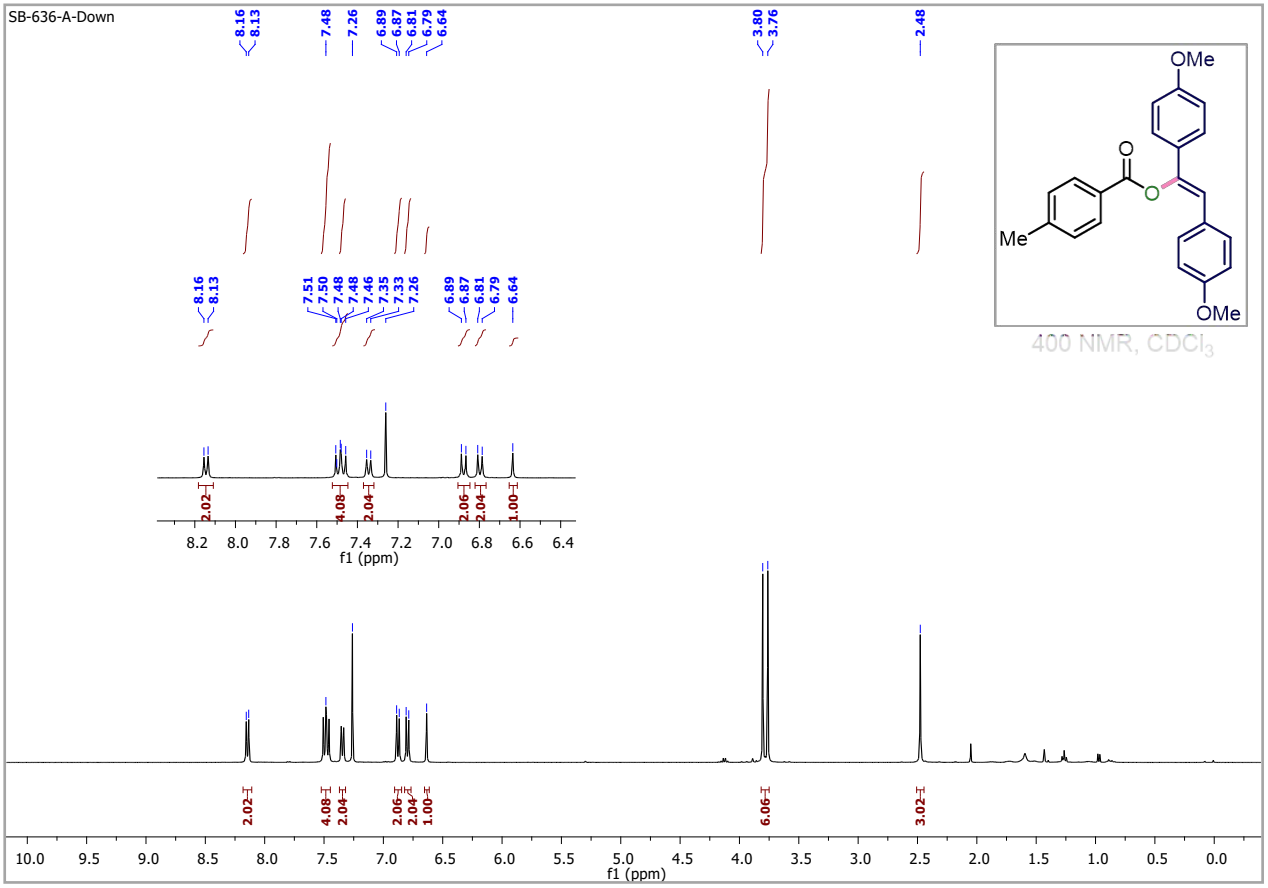
*^{1}H NMR of **22** in $CDCl_3$ at 400 MHz*



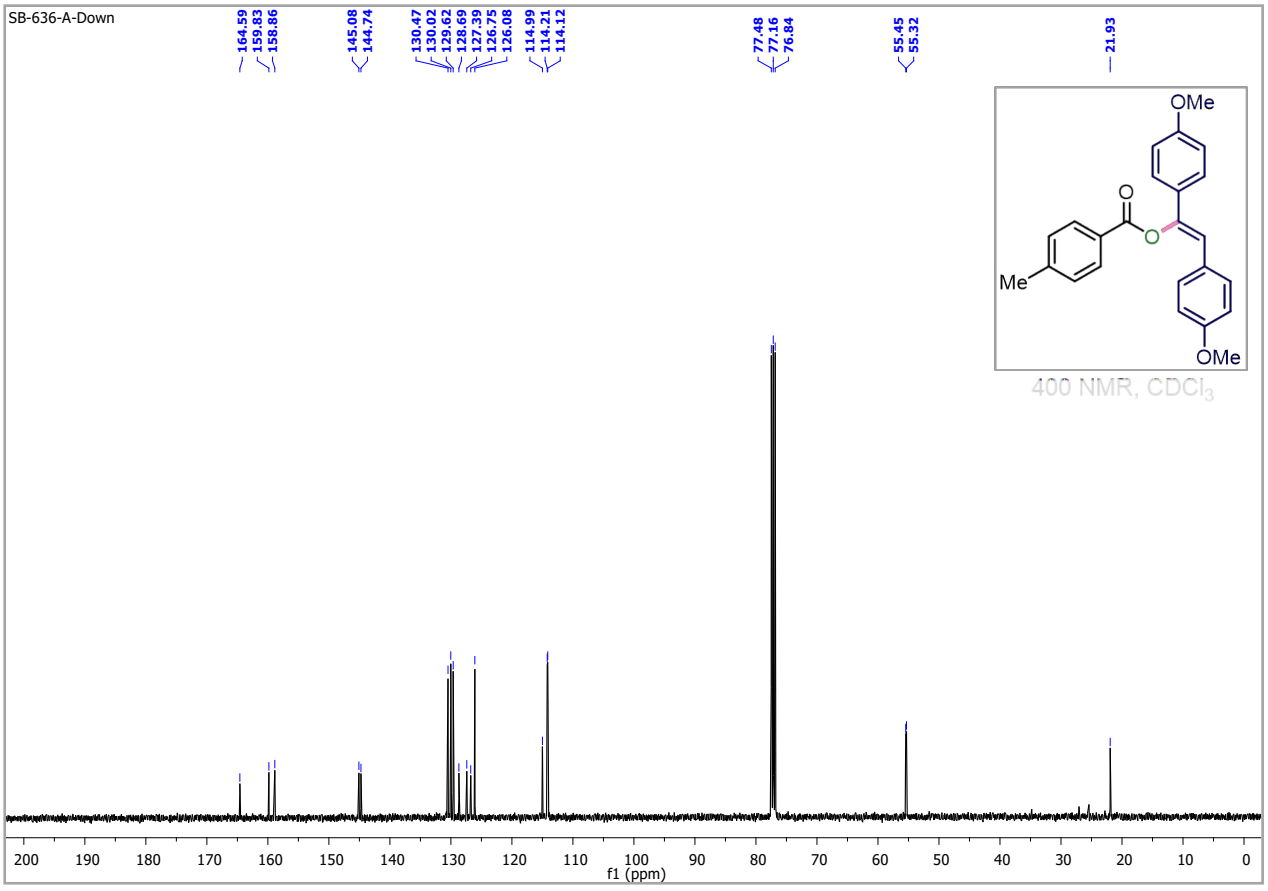
*^{13}C NMR of **22** in $CDCl_3$ at 100 MHz*



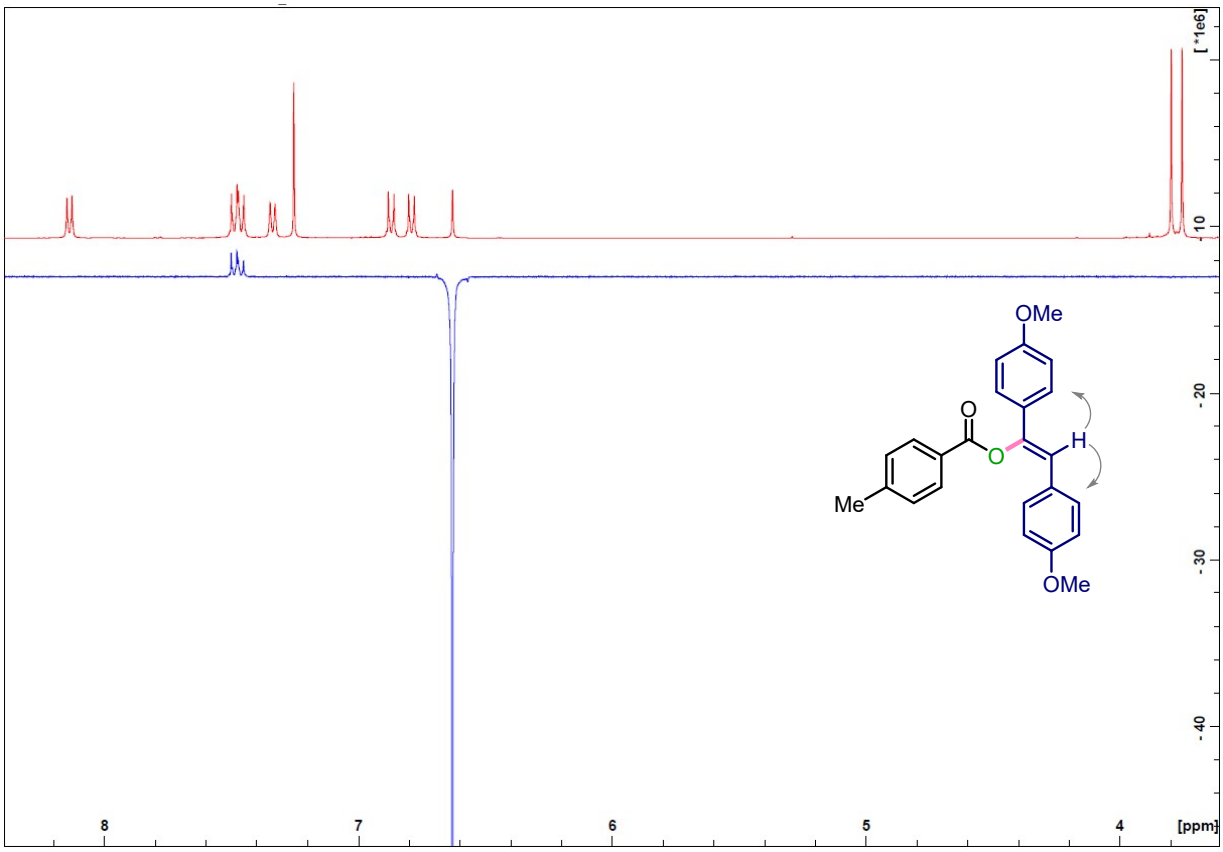
*^{1}H NMR of **23** in $CDCl_3$ at 400 MHz*



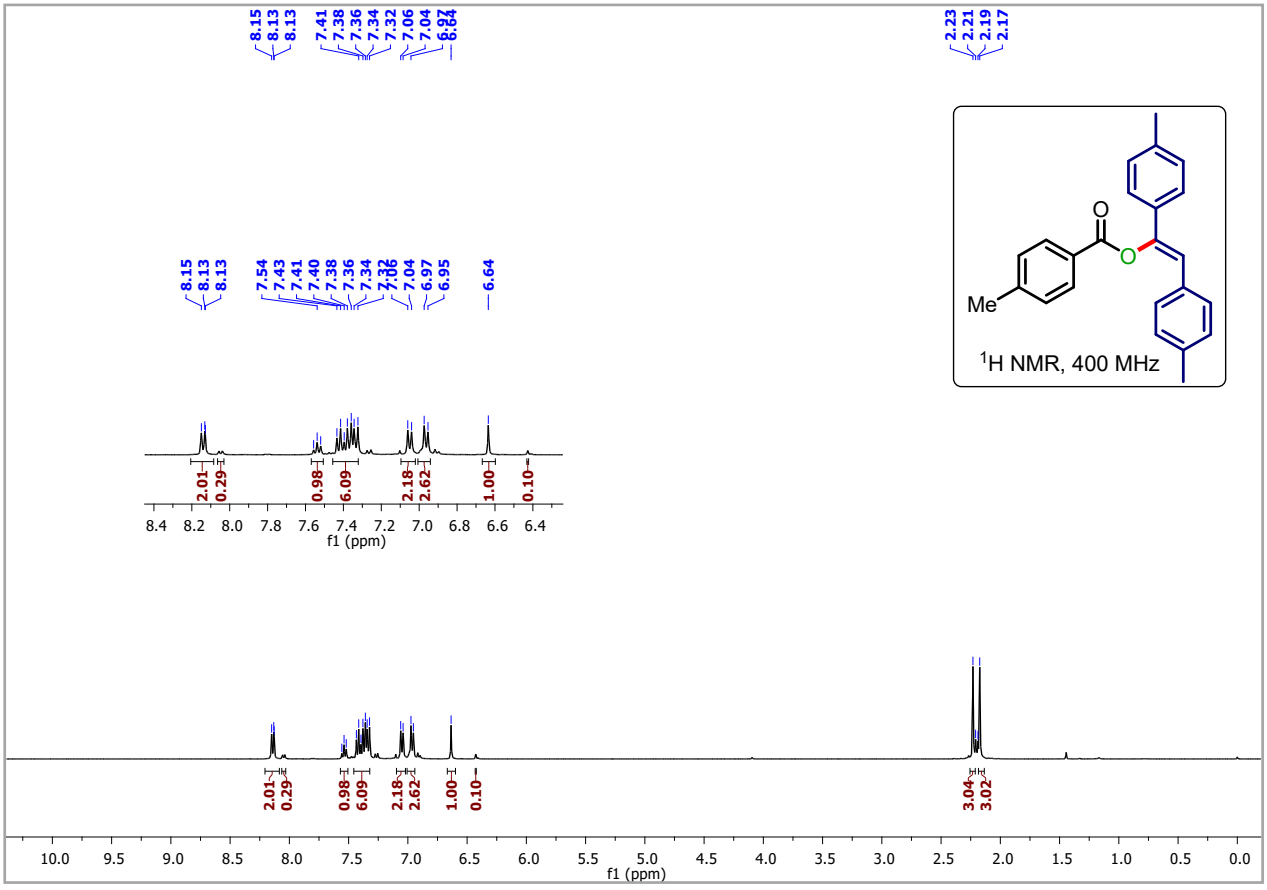
*^{13}C NMR of **23** in $CDCl_3$ at 100 MHz*



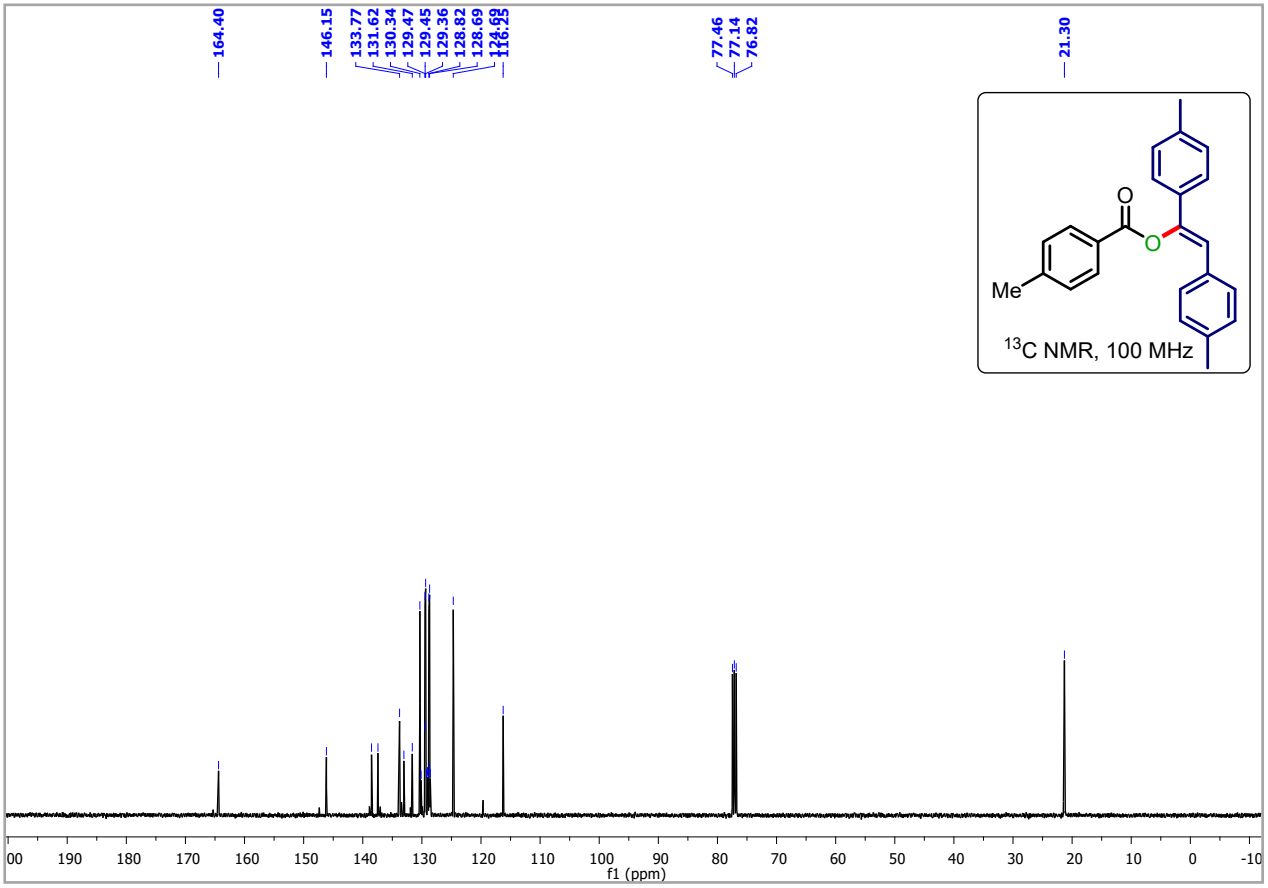
1D NOE of **23**



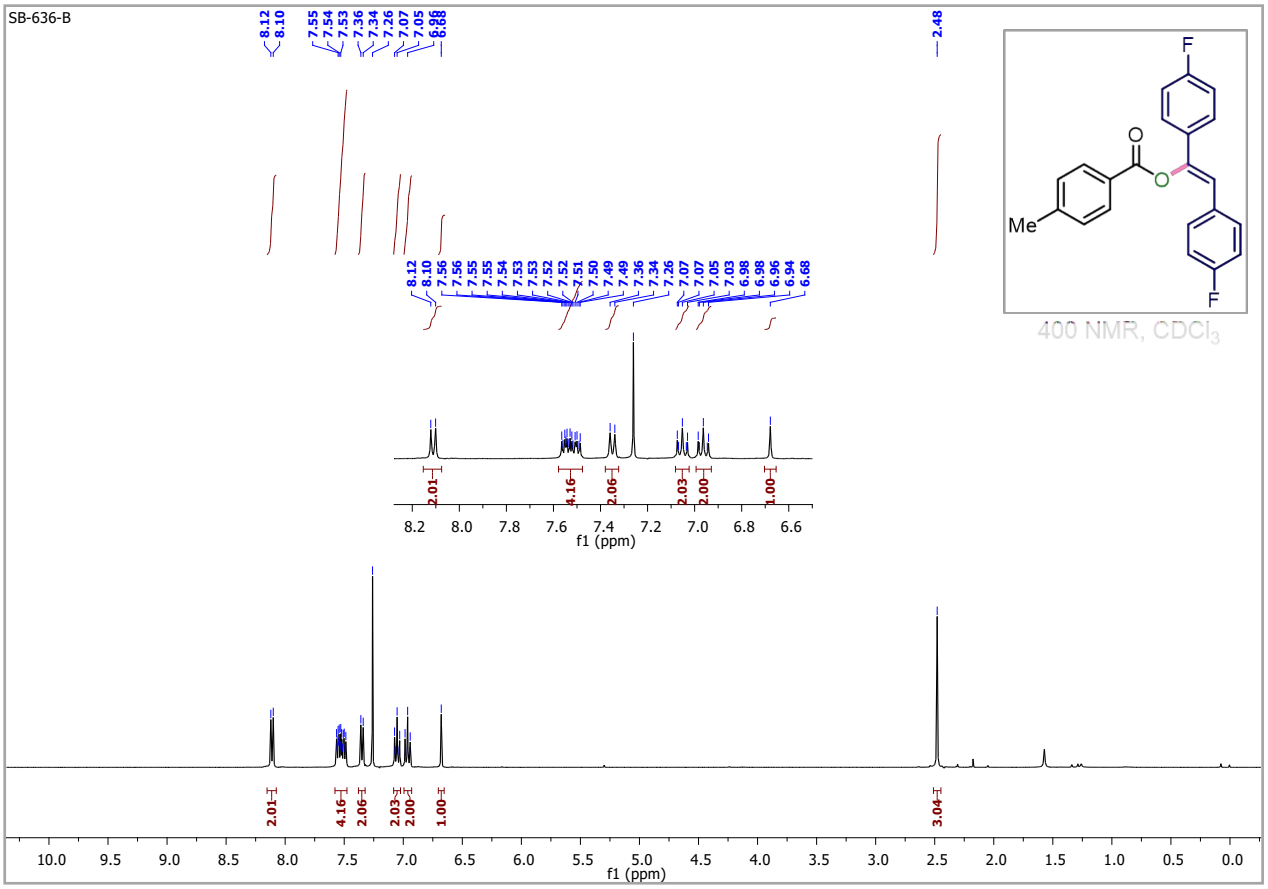
*^{1}H NMR of **23a** in $CDCl_3$ at 400 MHz*



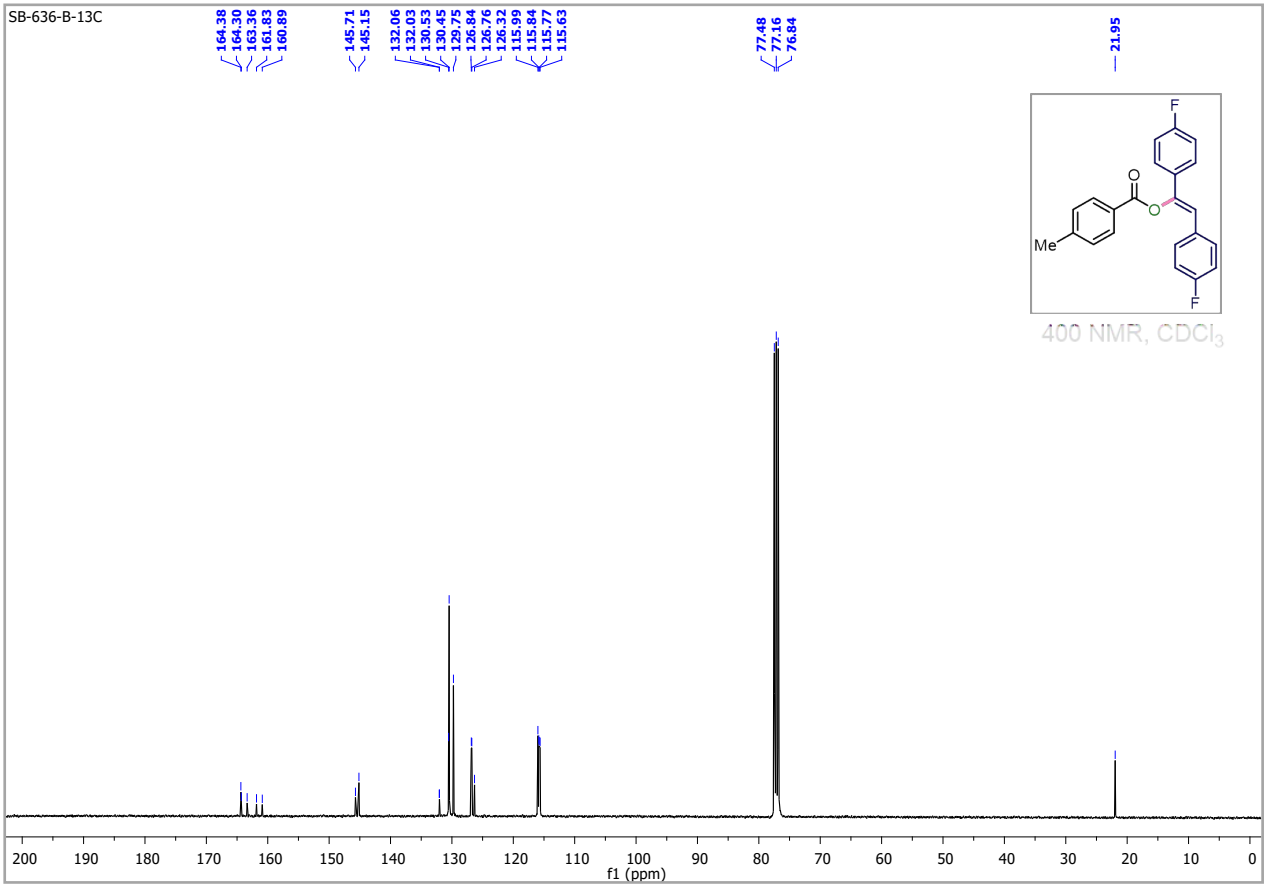
*^{13}C NMR of **23a** in $CDCl_3$ at 100 MHz*



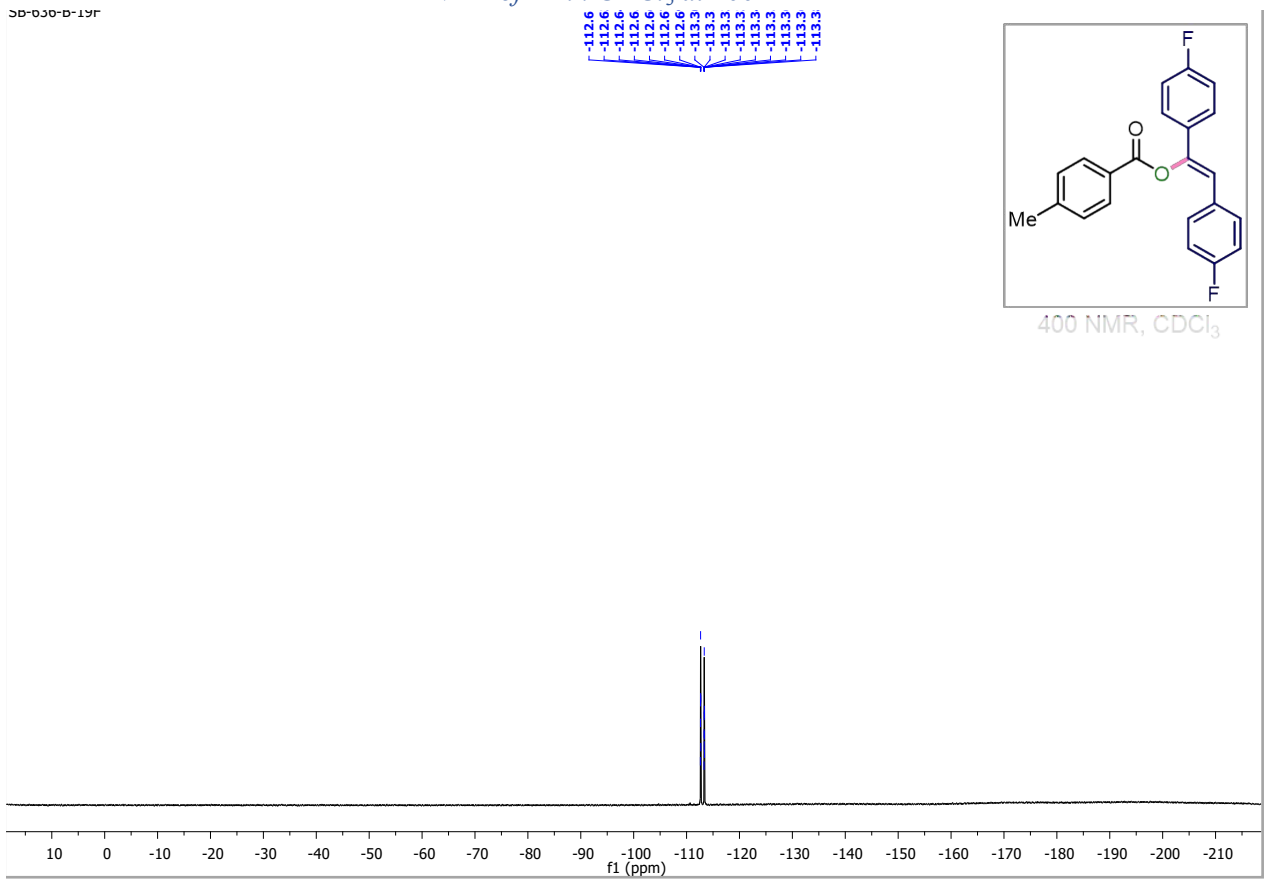
*^{1}H NMR of **24** in $CDCl_3$ at 400 MHz*



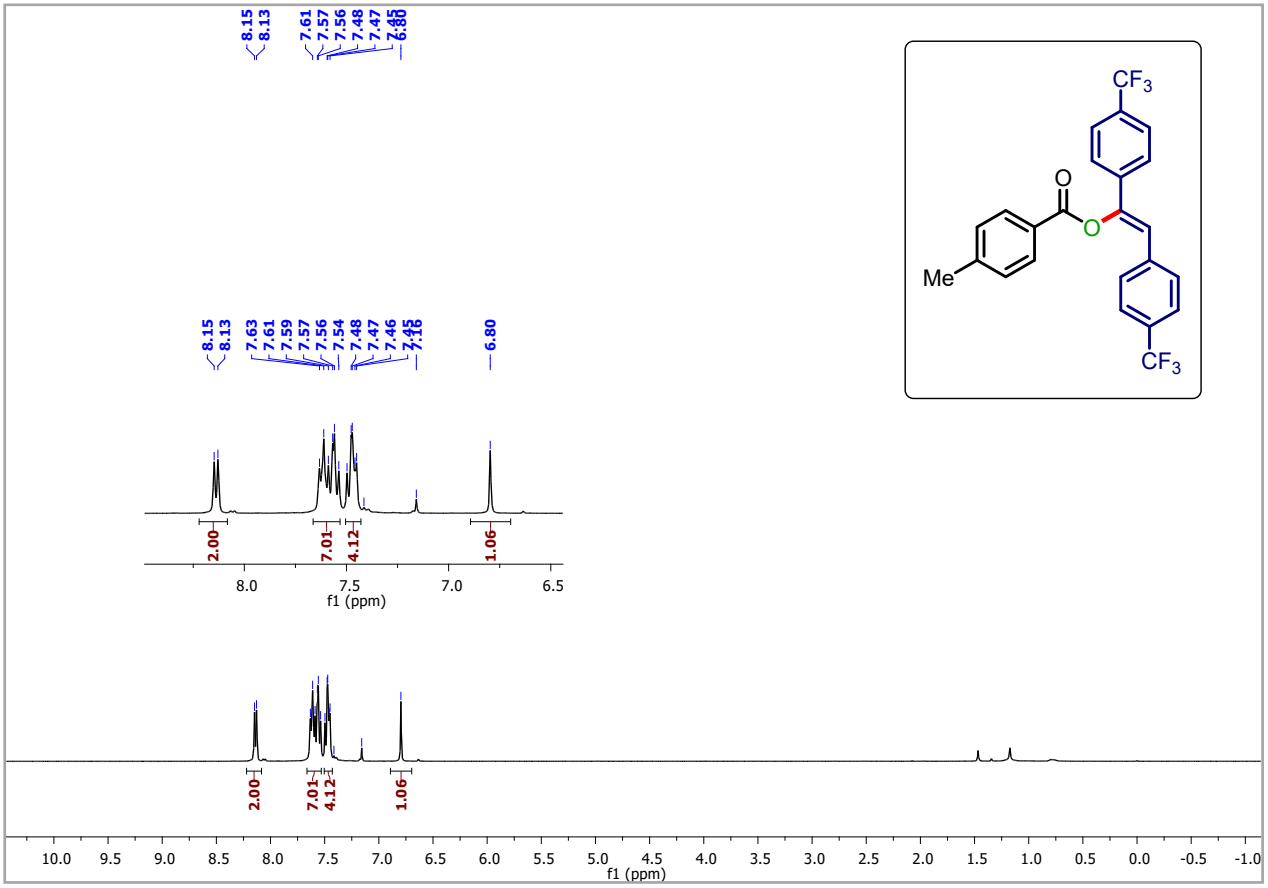
*^{13}CNMR of **24** in $CDCl_3$ at 100 MHz*



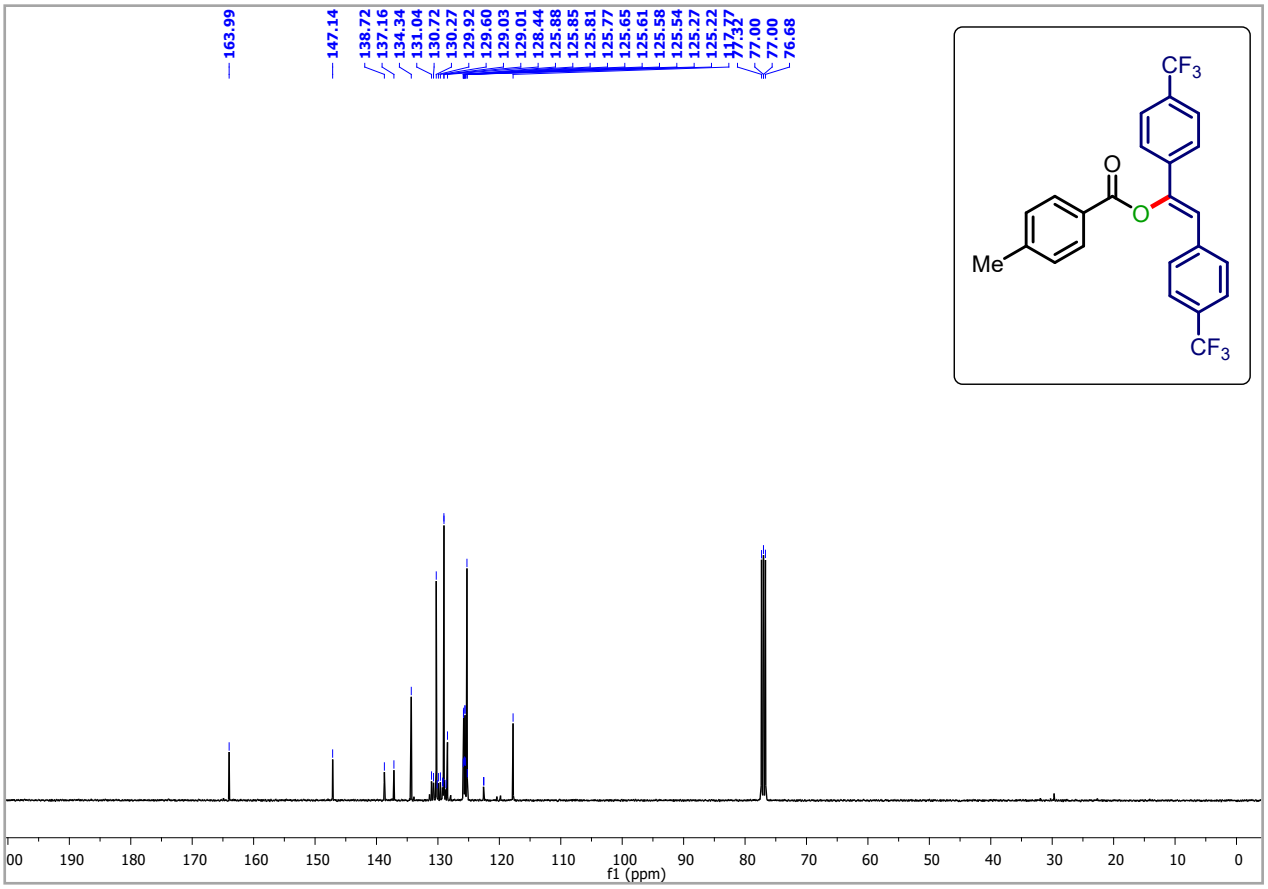
*^{19}F NMR of **24** in $CDCl_3$ at 100 MHz*



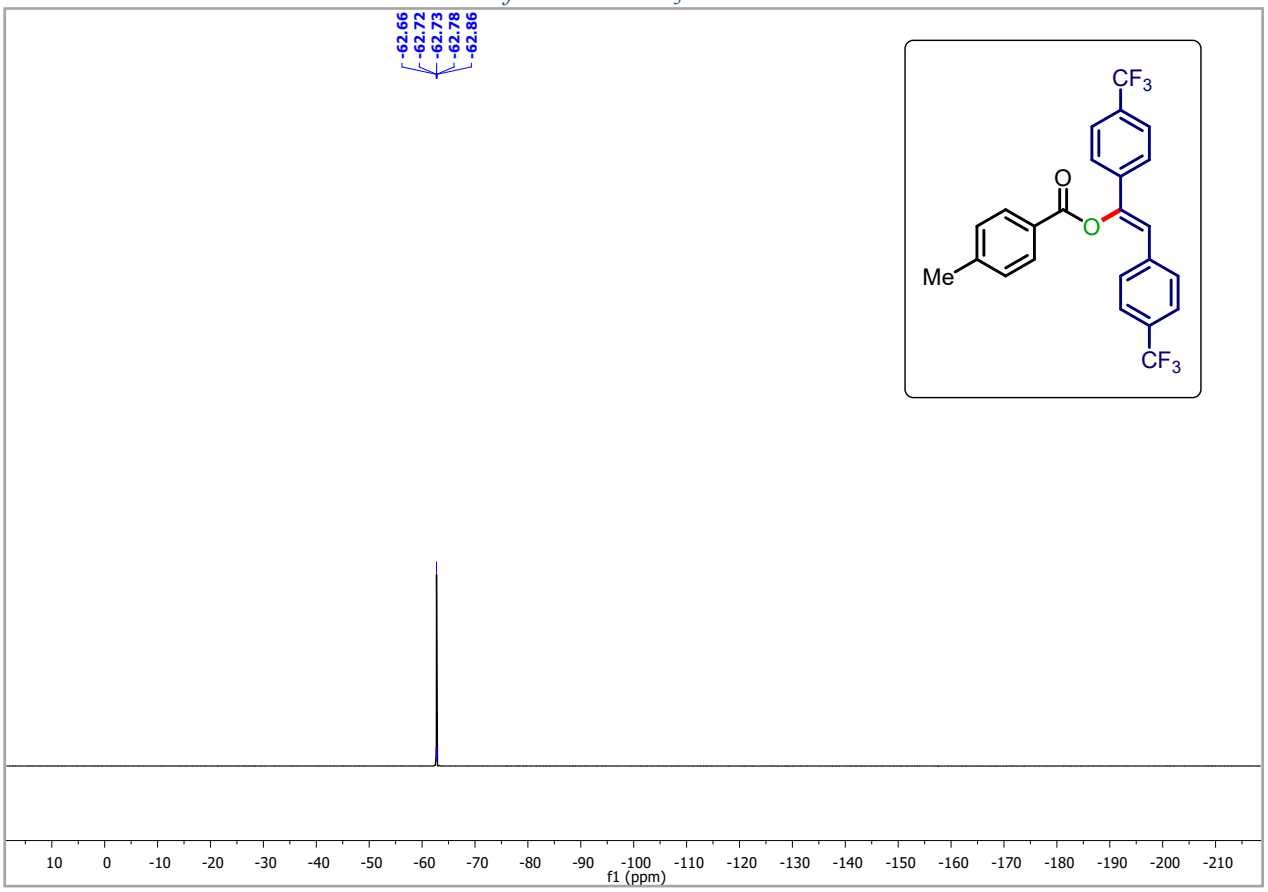
*^{1}H NMR of **24a** in $CDCl_3$ at 400 MHz*



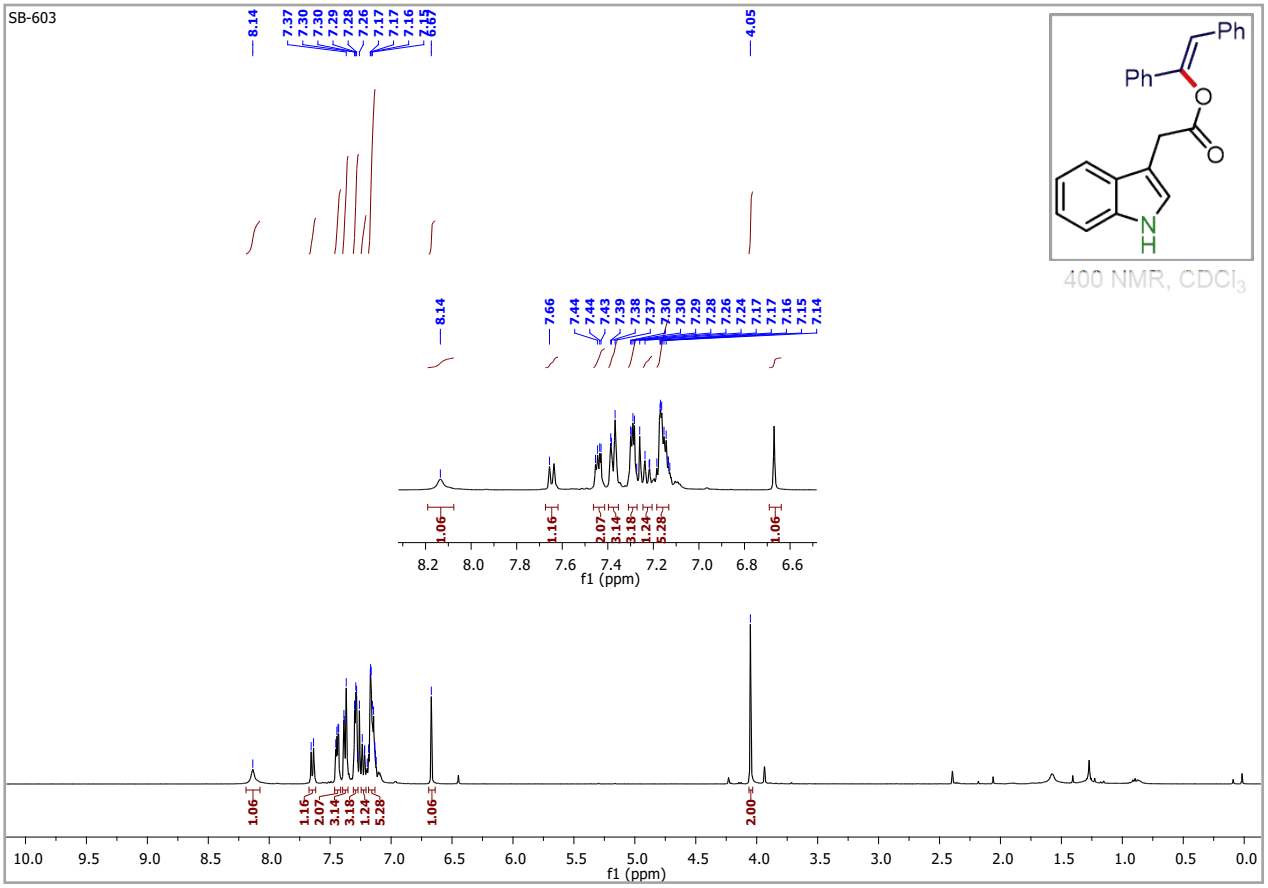
*^{13}CNMR of **24a** in $CDCl_3$ at 100 MHz*



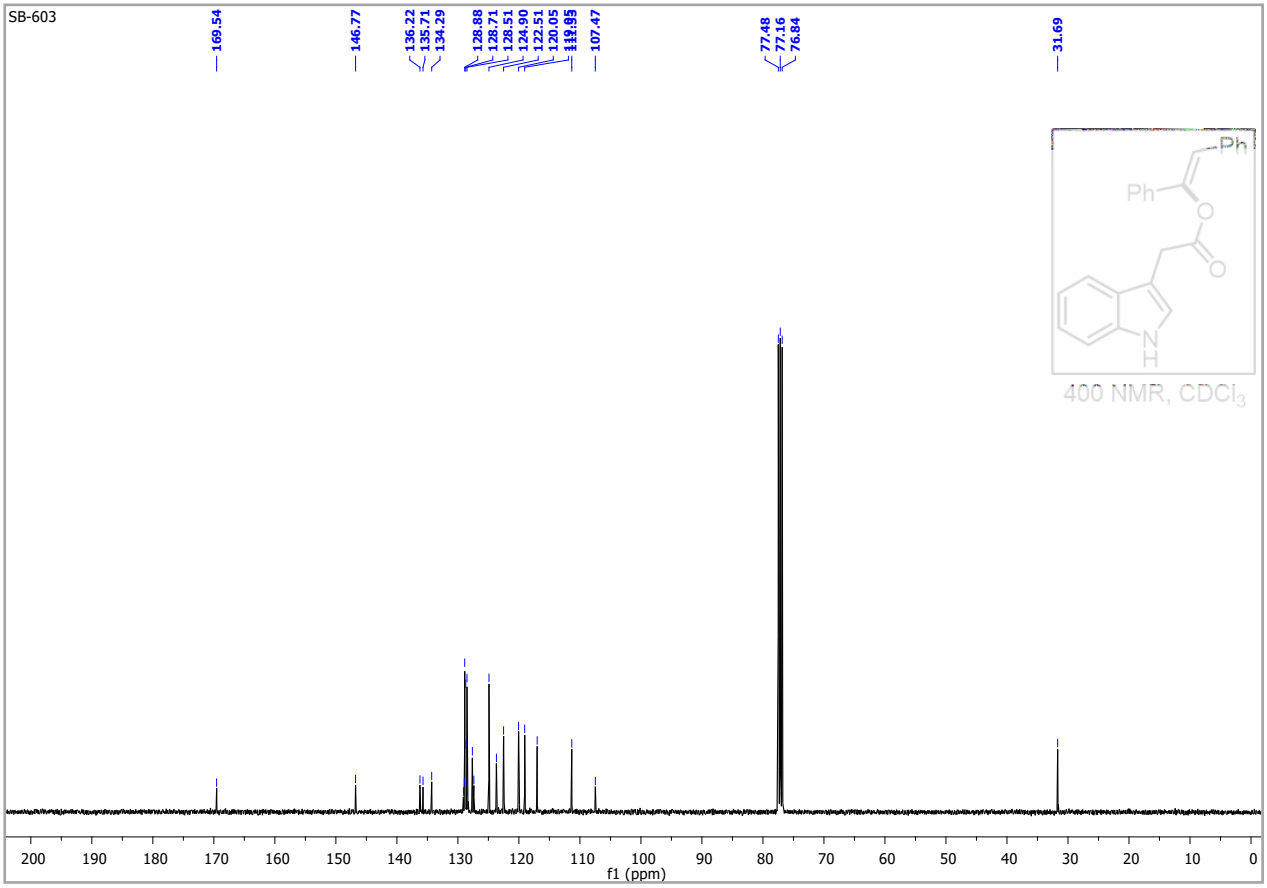
*^{19}F NMR of **24a** in $CDCl_3$ at 100 MHz*



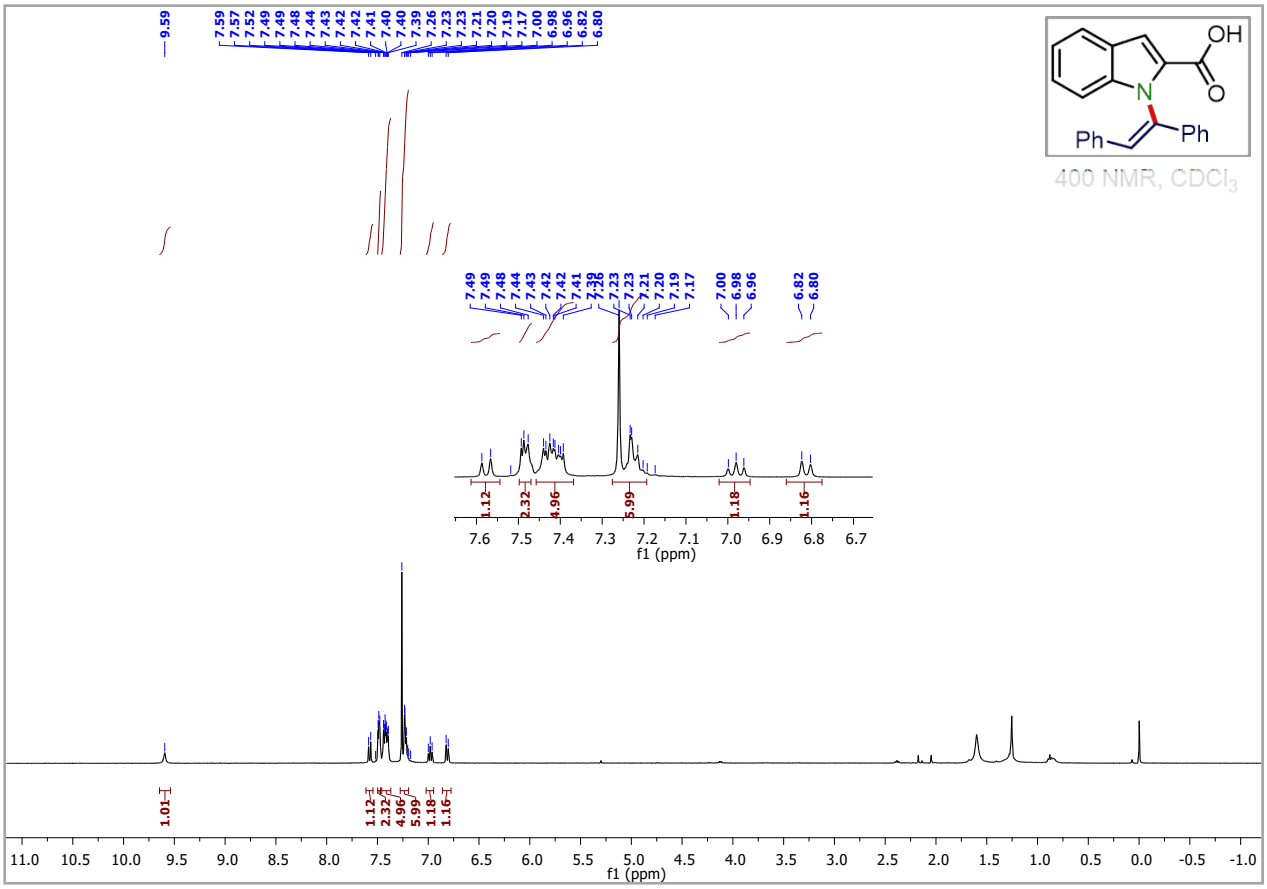
*^{1}H NMR of **25** in $CDCl_3$ at 400 MHz*



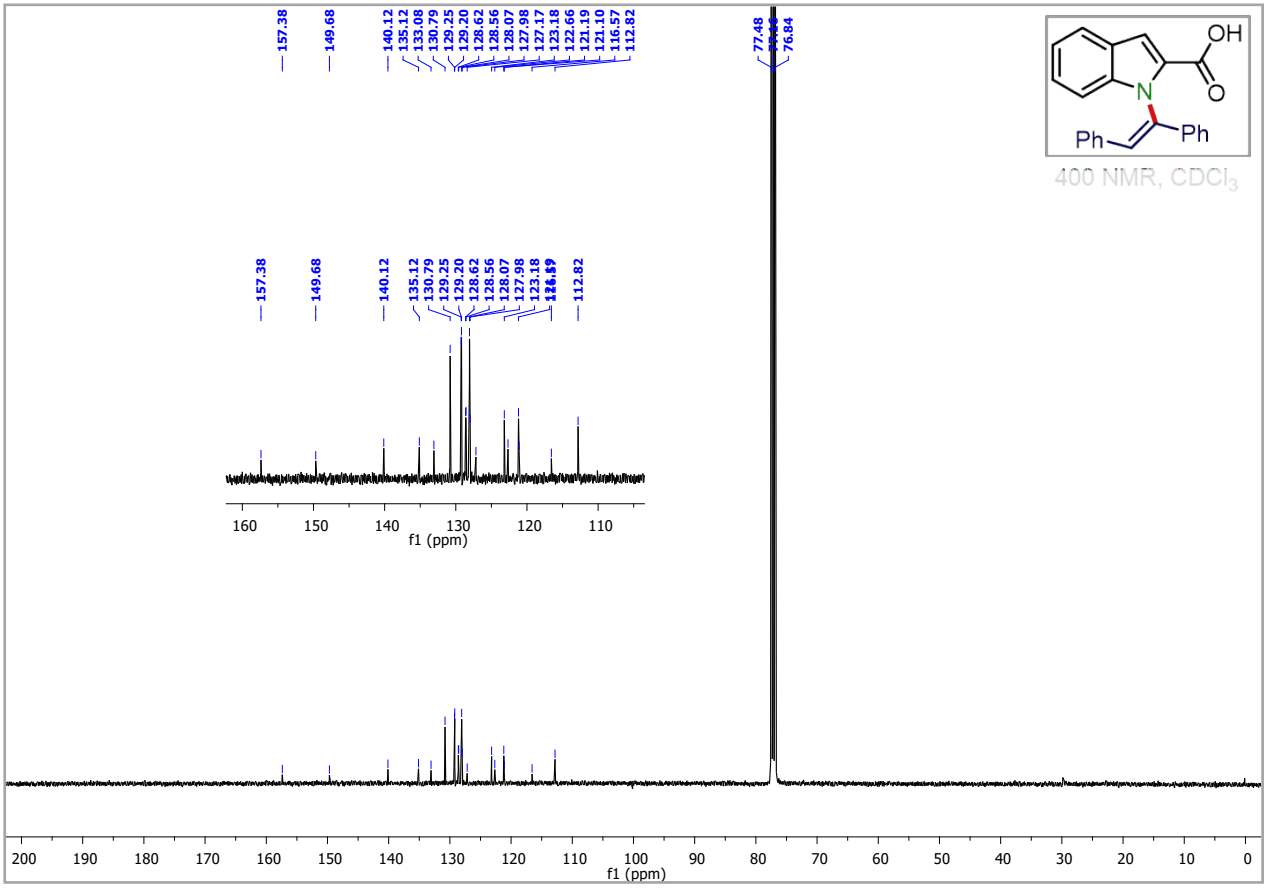
*^{13}C NMR of **25** in $CDCl_3$ at 100 MHz*



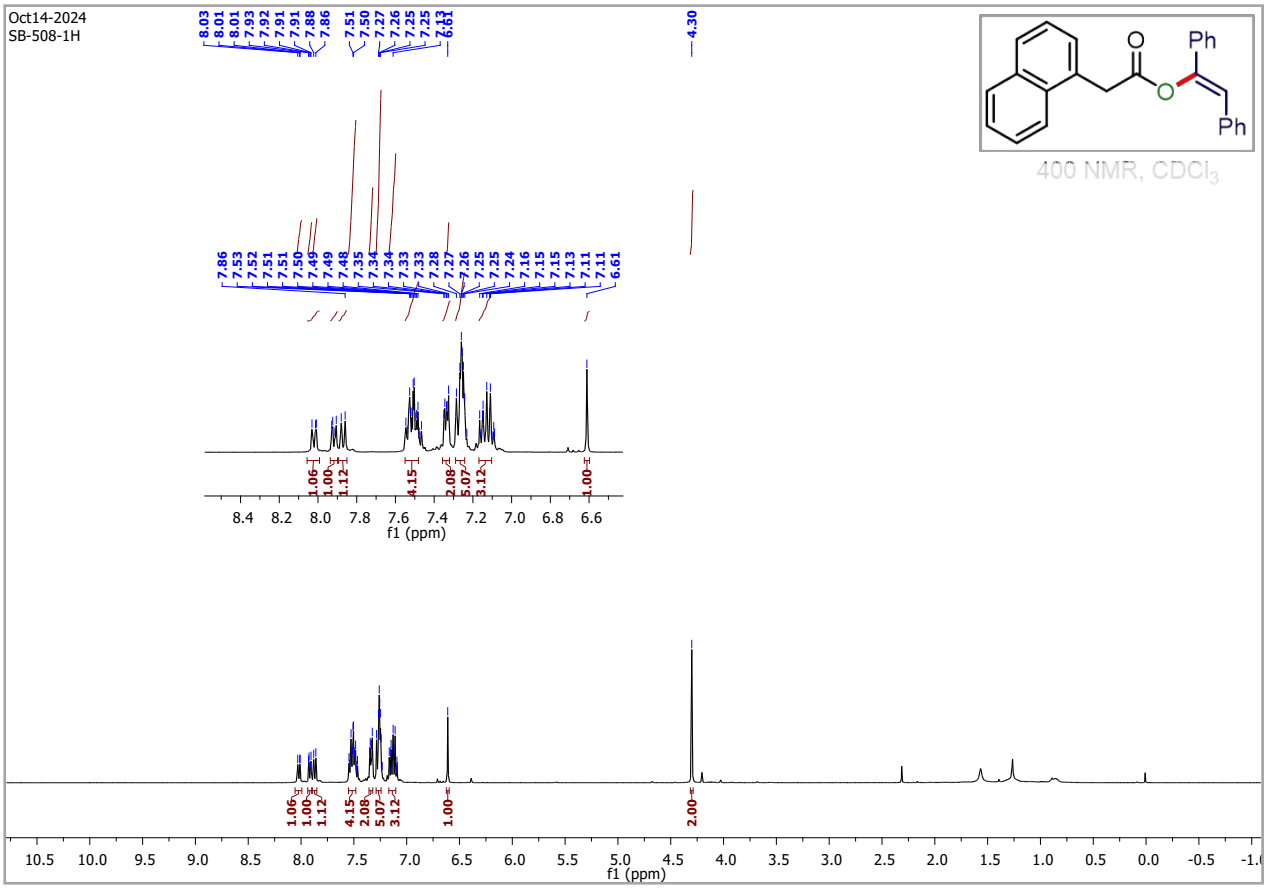
*^{1}H NMR of **26** in $CDCl_3$ at 400 MHz*



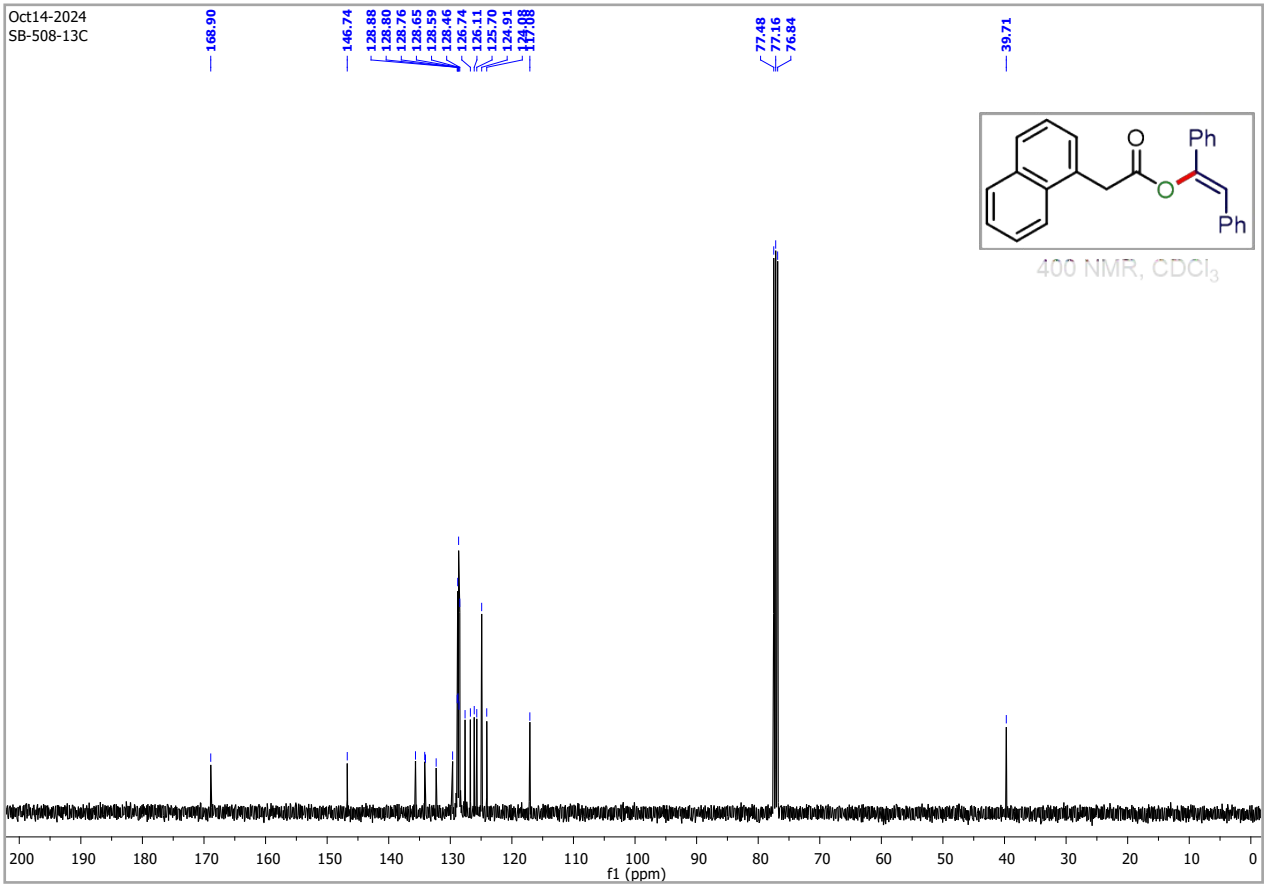
*^{13}C NMR of **26** in $CDCl_3$ at 100 MHz*



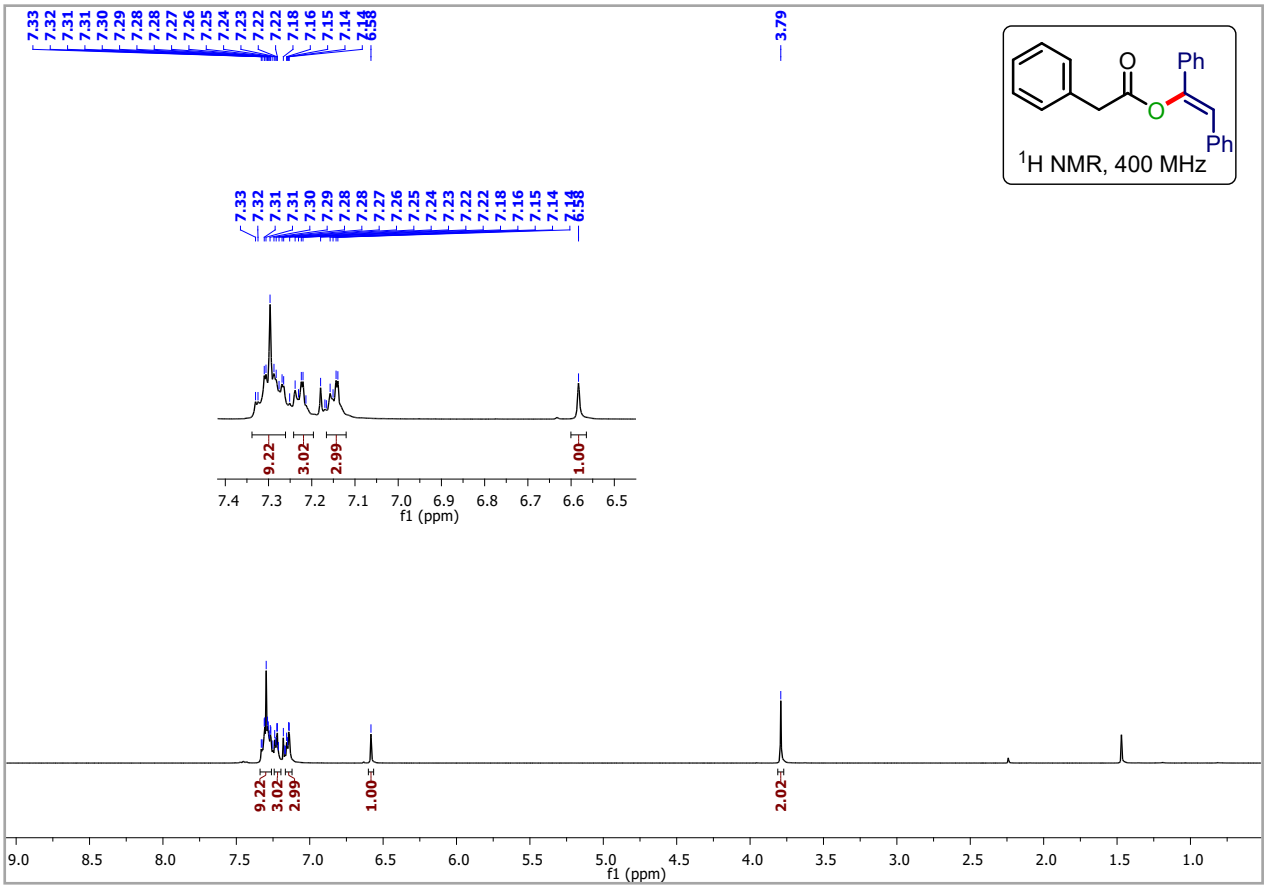
*^{1}H NMR of **27** in $CDCl_3$ at 400 MHz*



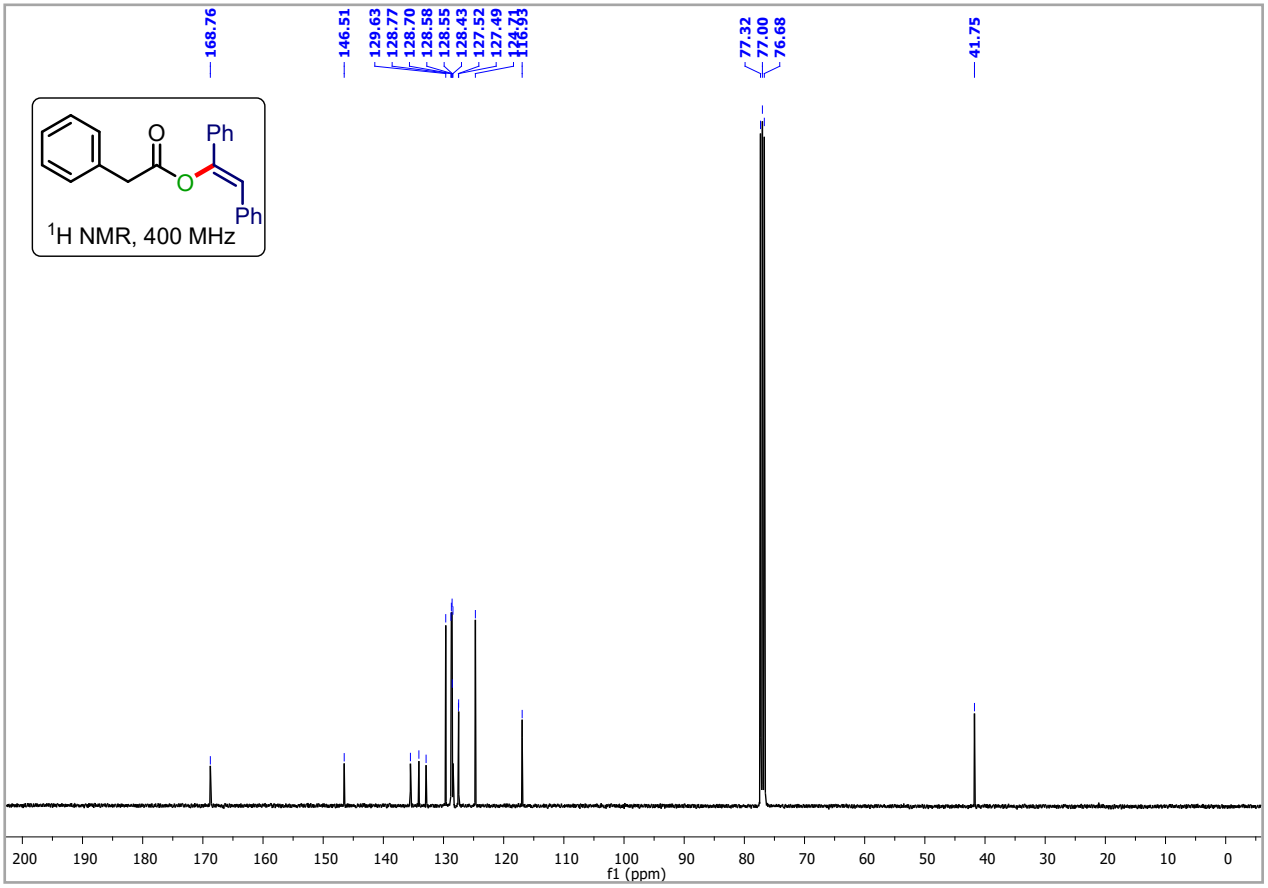
*^{13}C NMR of **27** in $CDCl_3$ at 100 MHz*



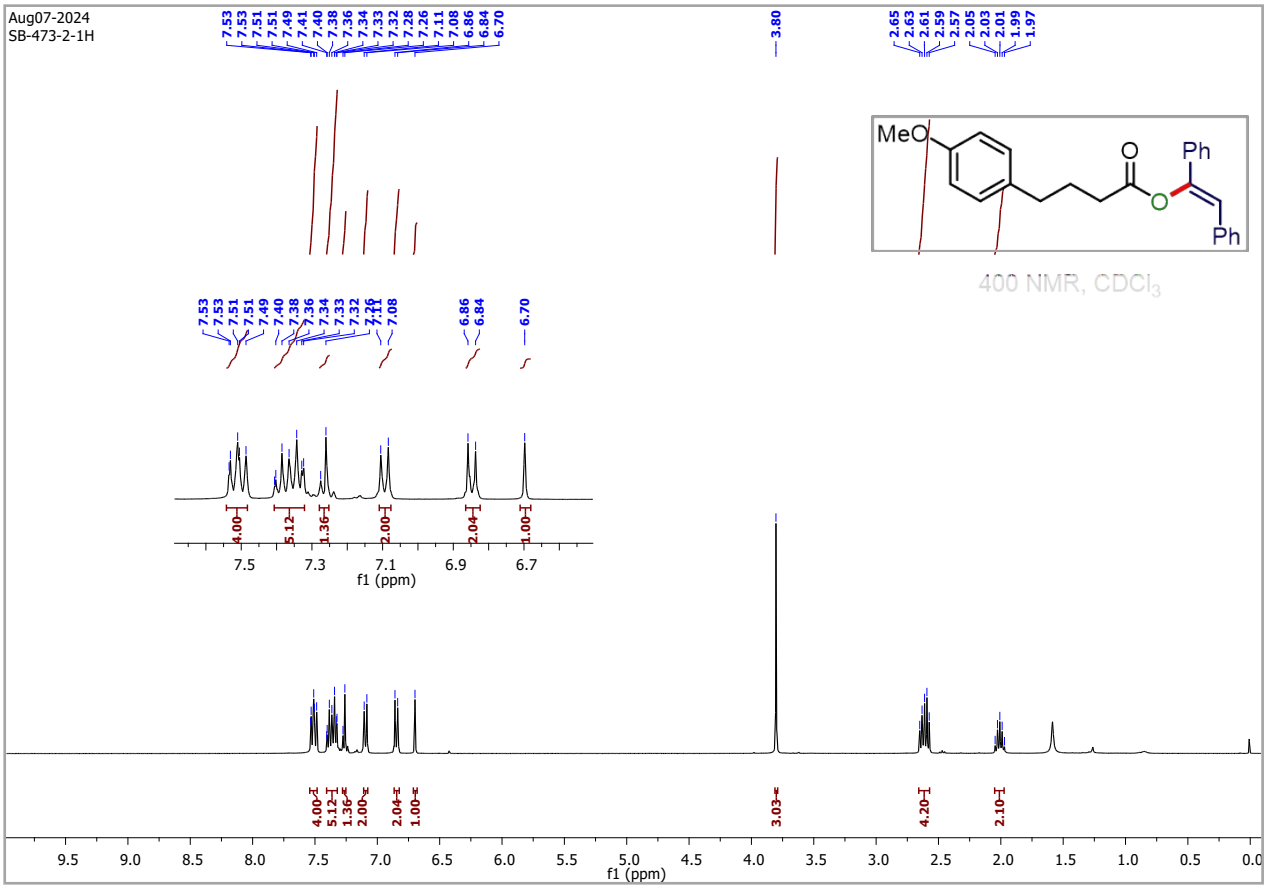
*^{1}H NMR of **28** in $CDCl_3$ at 400 MHz*



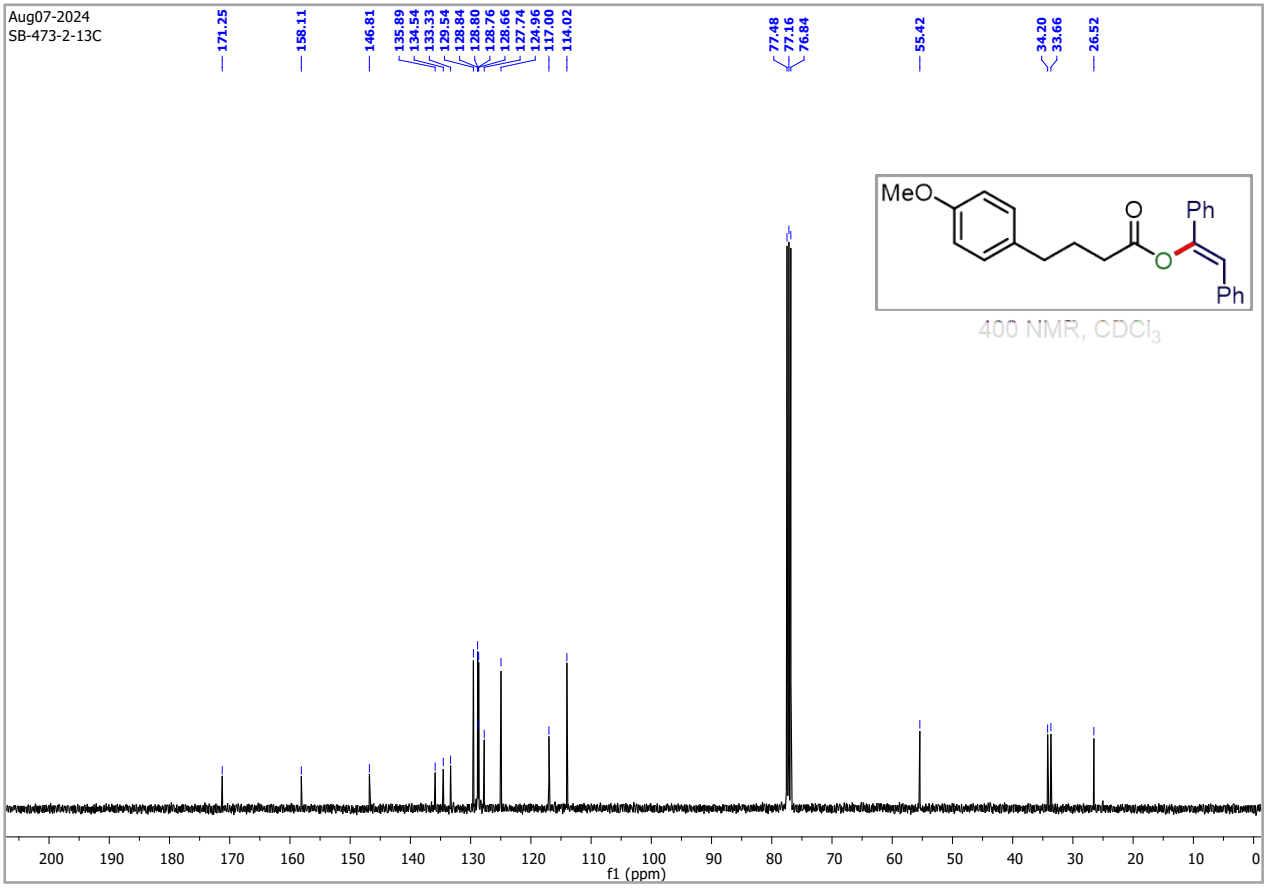
*^{13}C NMR of **28** in $CDCl_3$ at 100 MHz*



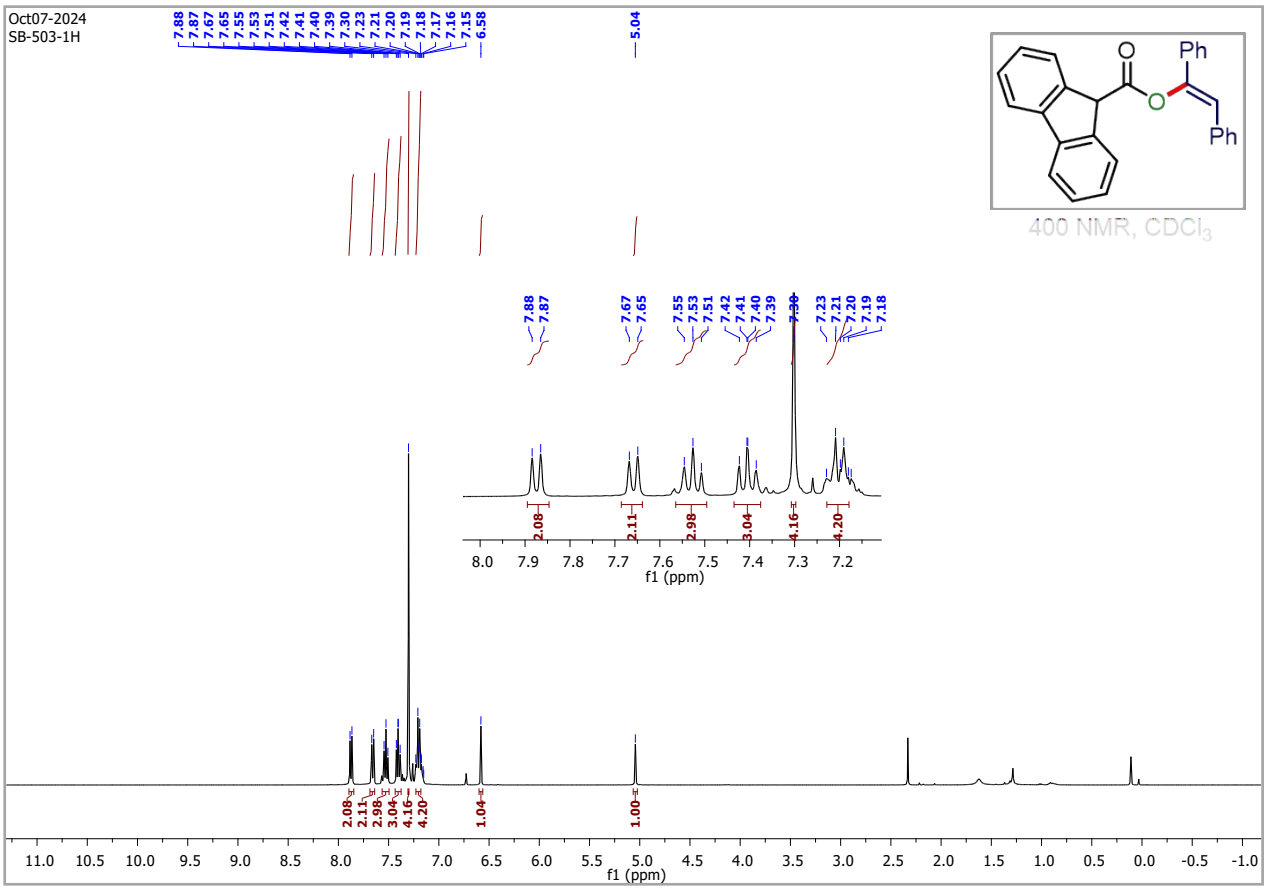
*^1H NMR of **29** in $CDCl_3$ at 400 MHz*



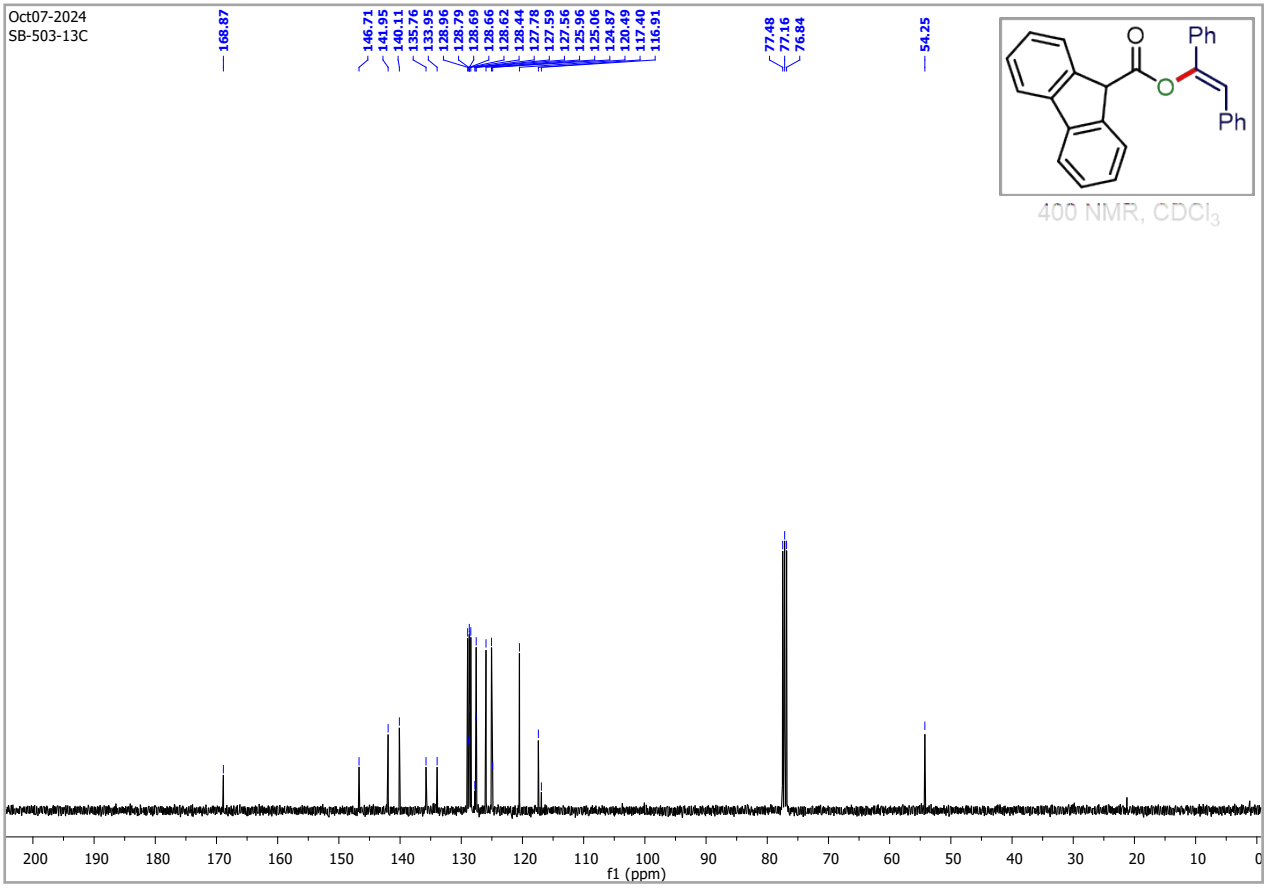
*^{13}C NMR of **29** in $CDCl_3$ at 100 MHz*



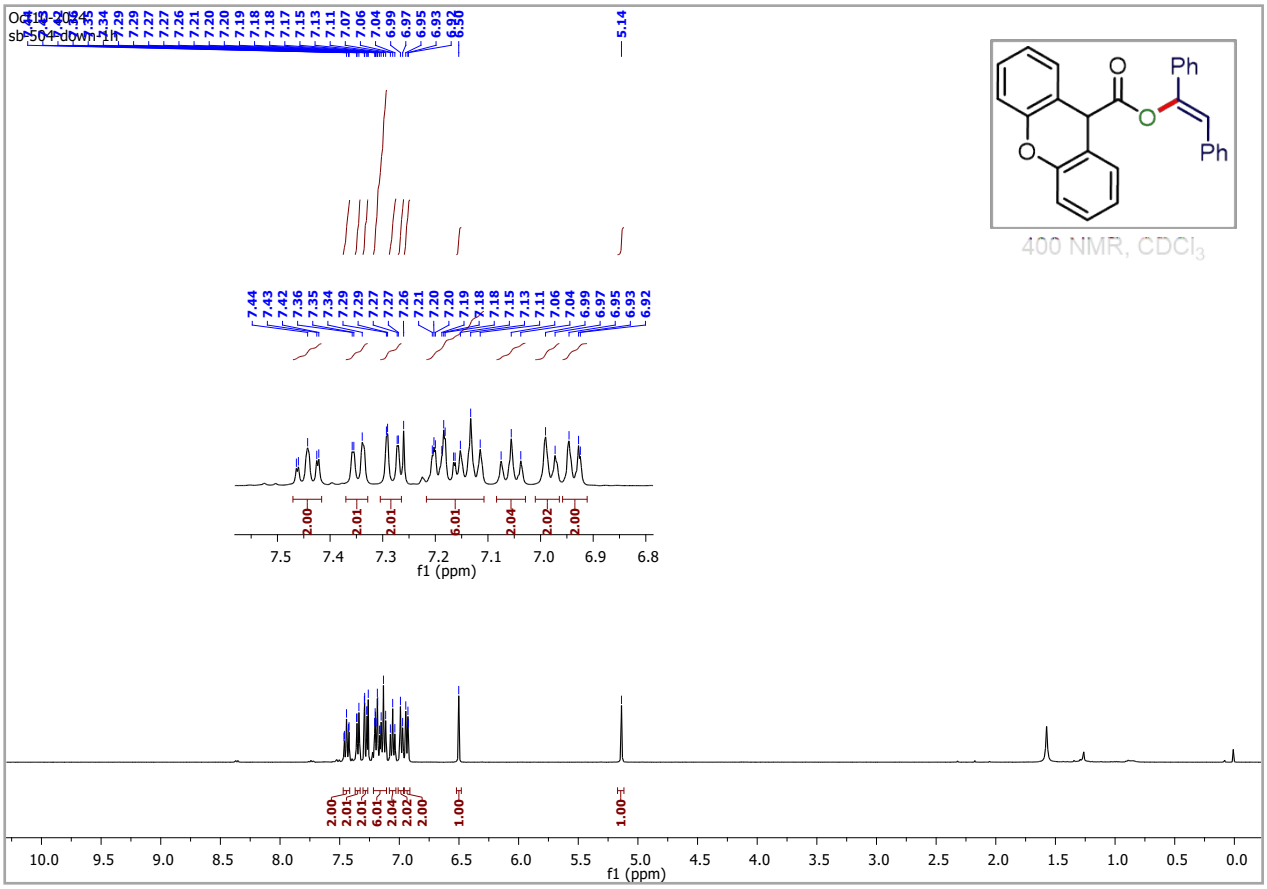
*^{1}H NMR of **30** in $CDCl_3$ at 400 MHz*



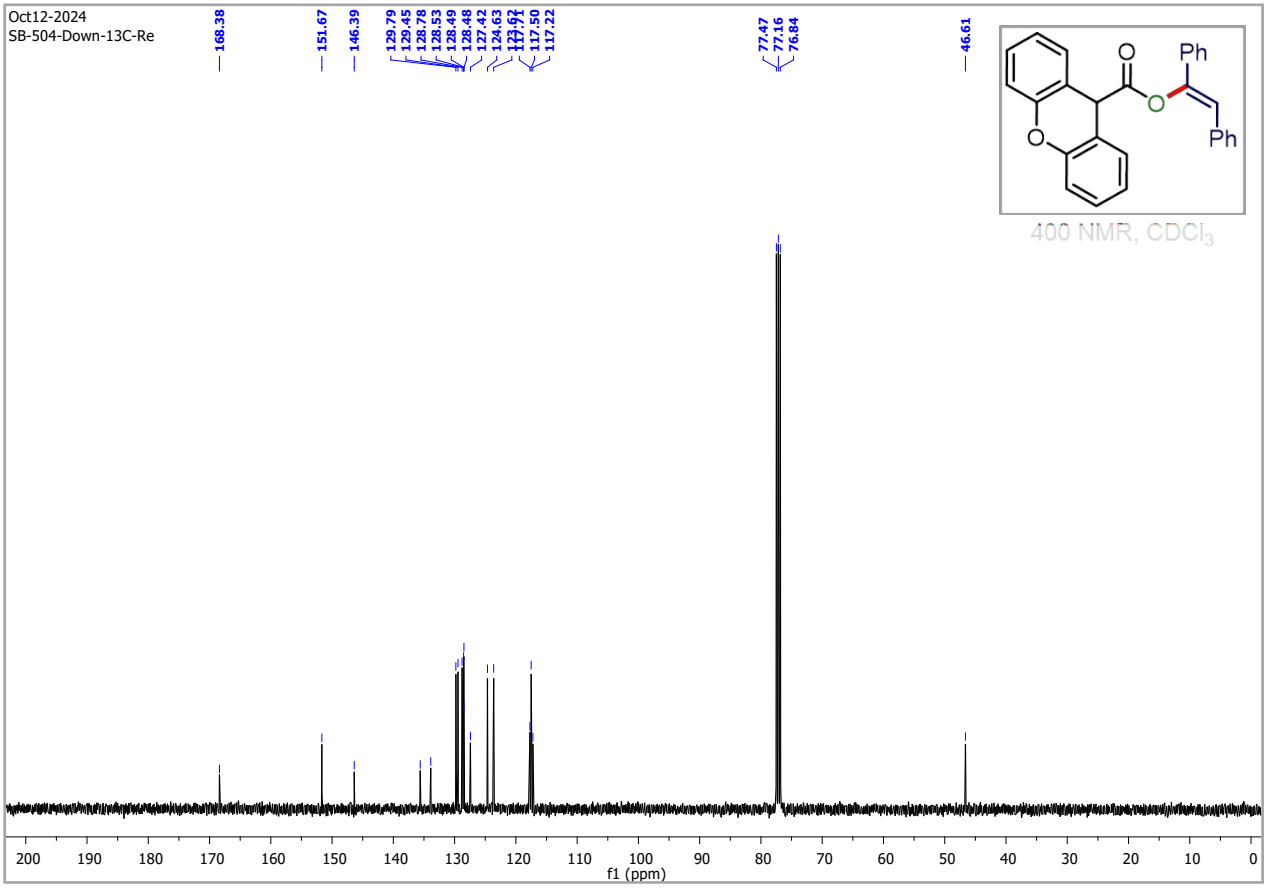
*^{13}C NMR of **30** in $CDCl_3$ at 100 MHz*



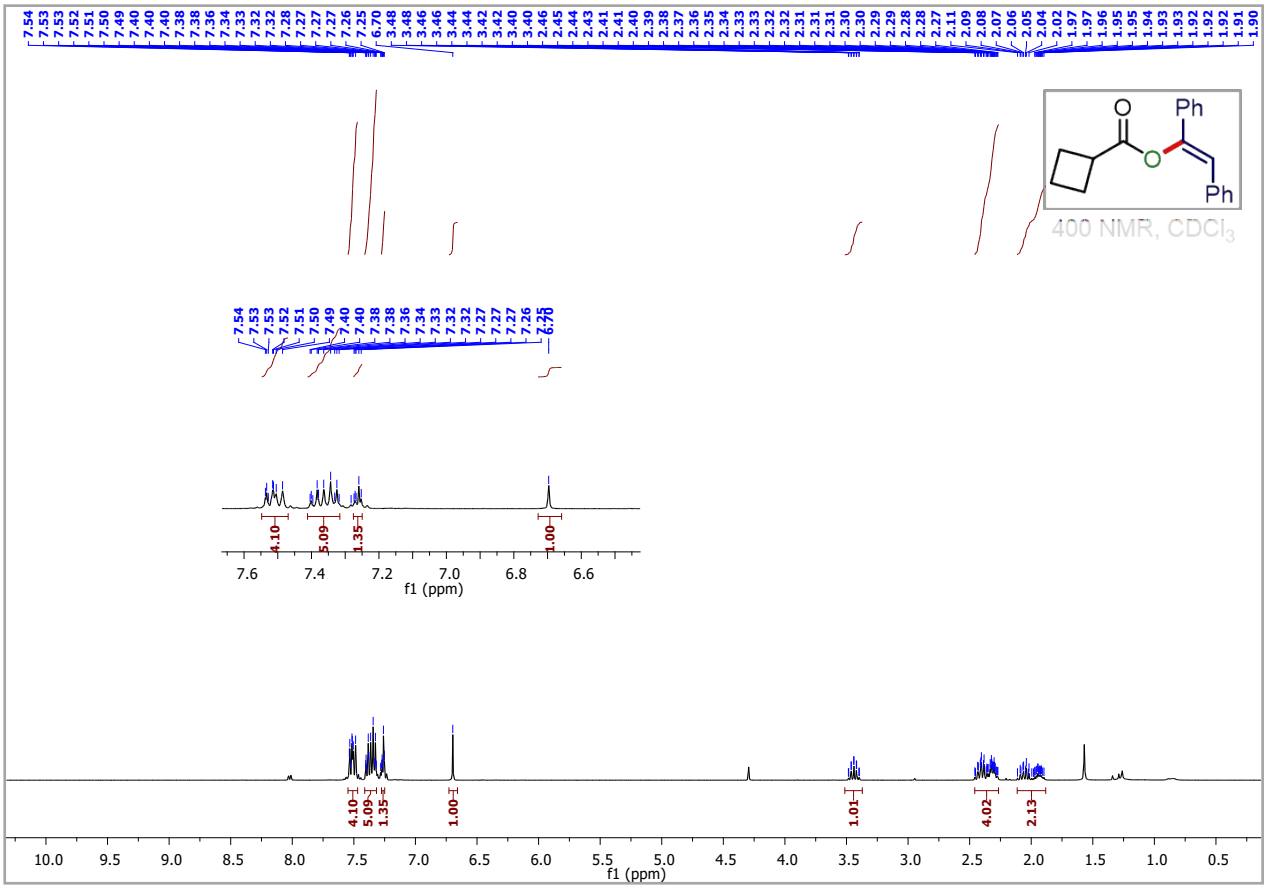
*^{1}H NMR of **31** in $CDCl_3$ at 400 MHz*



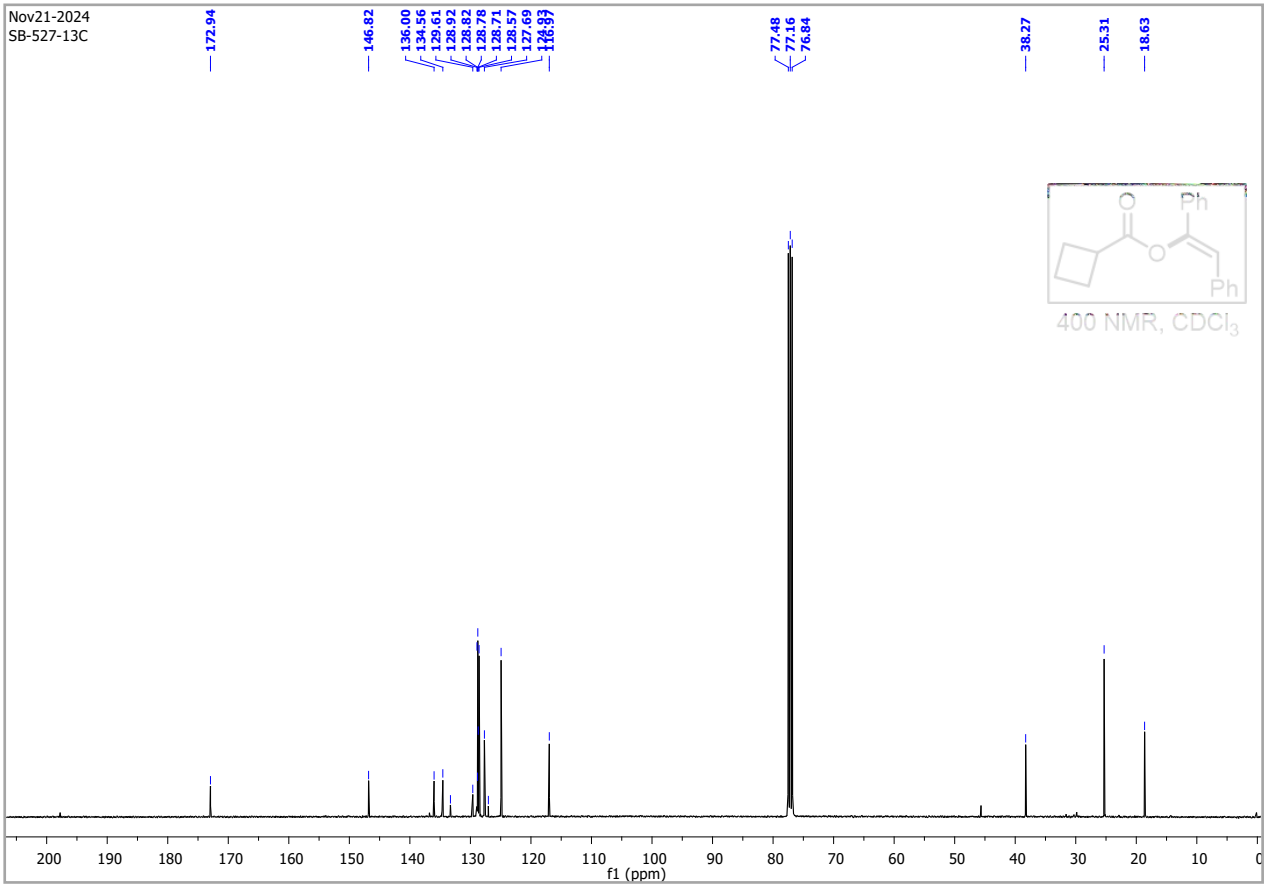
*^{13}C NMR of **31** in $CDCl_3$ at 100 MHz*



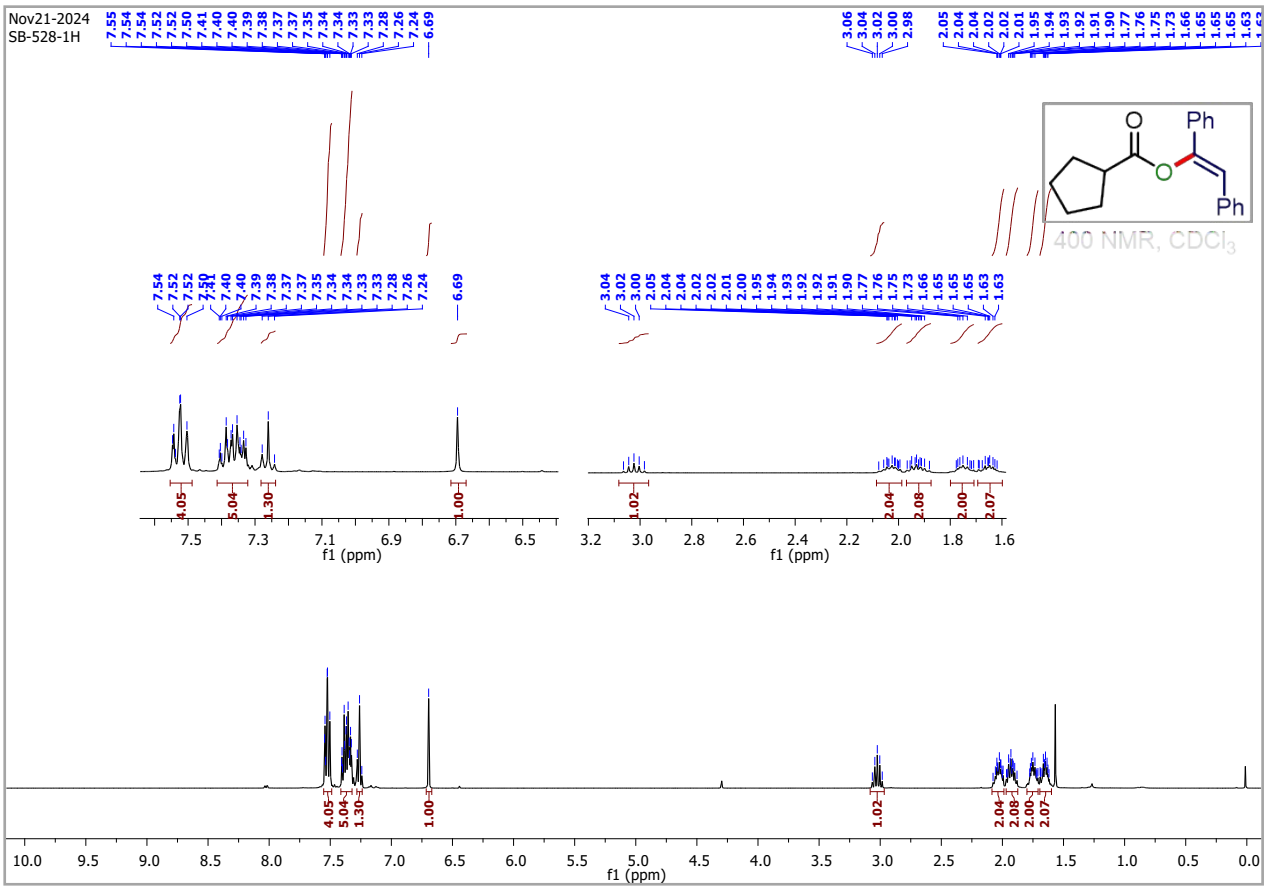
*^{1}H NMR of **32** in $CDCl_3$ at 400 MHz*



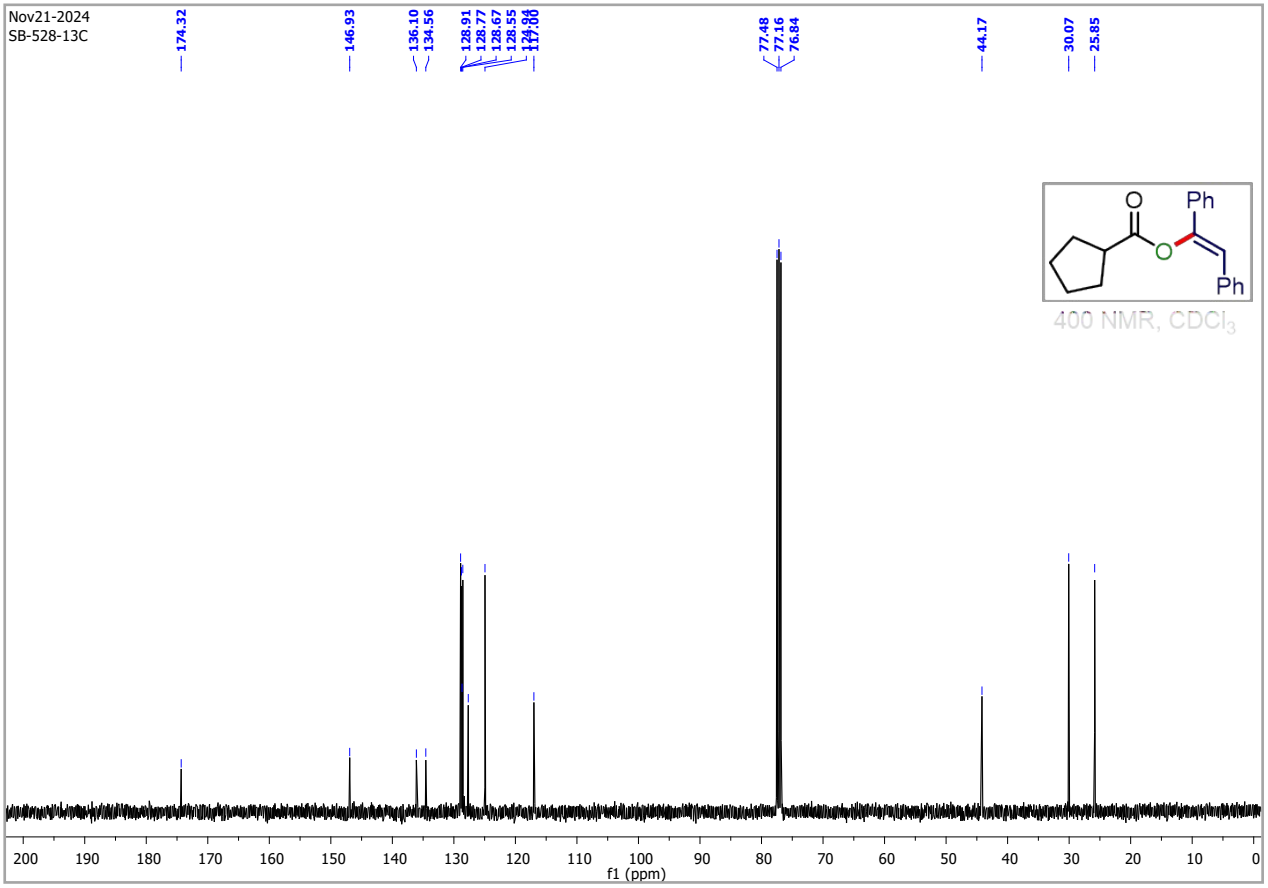
*^{13}C NMR of **32** in $CDCl_3$ at 100 MHz*



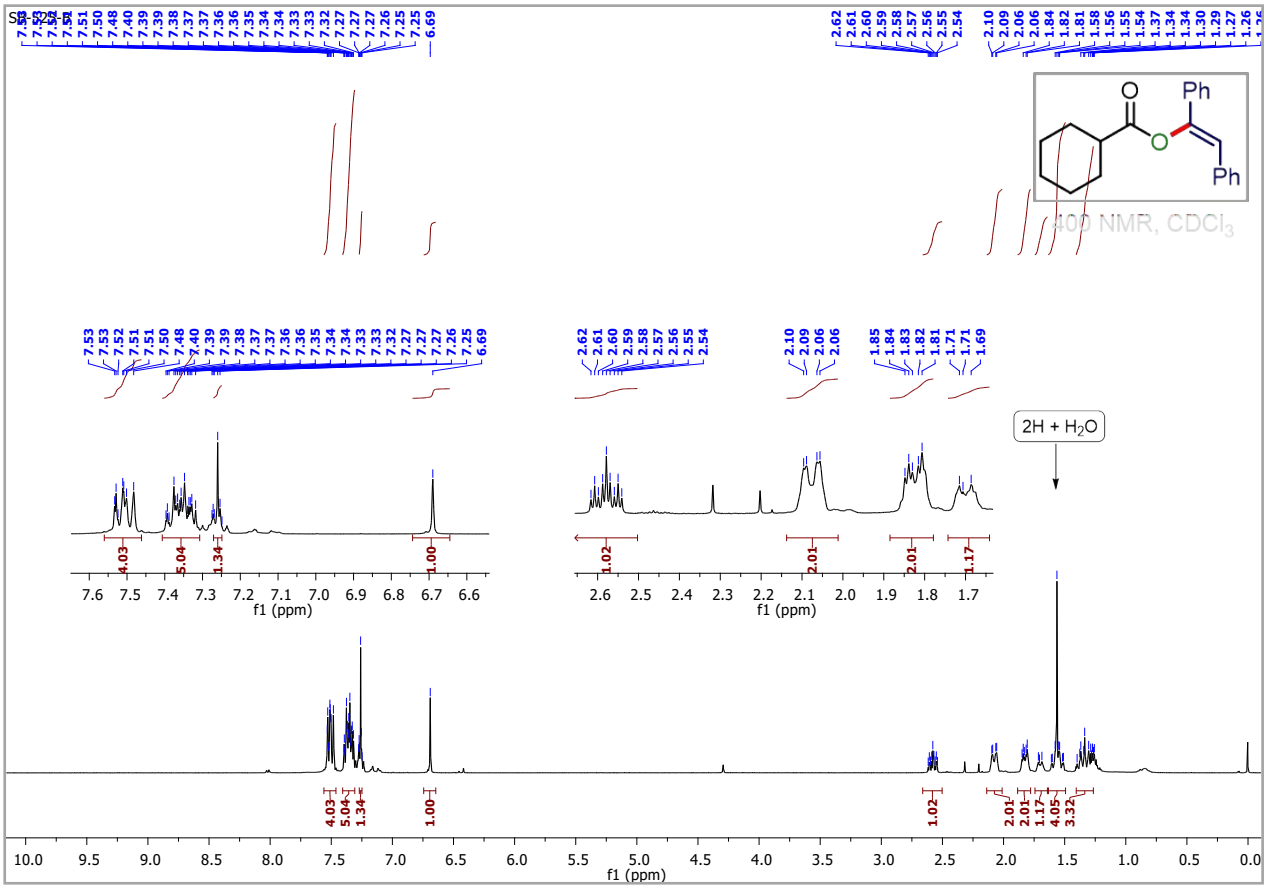
*^{1}H NMR of **33** in $CDCl_3$ at 400 MHz*



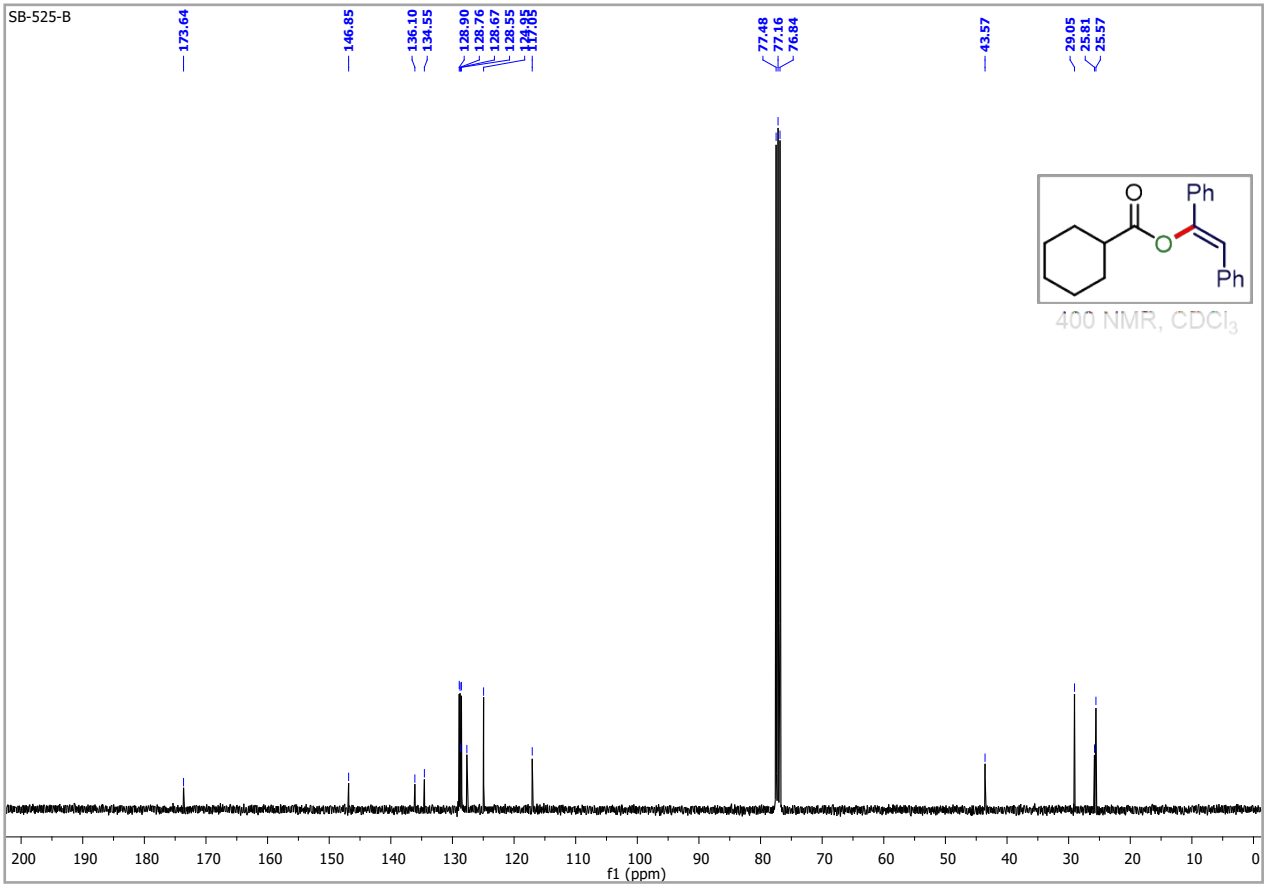
*^{13}C NMR of **33** in $CDCl_3$ at 100 MHz*



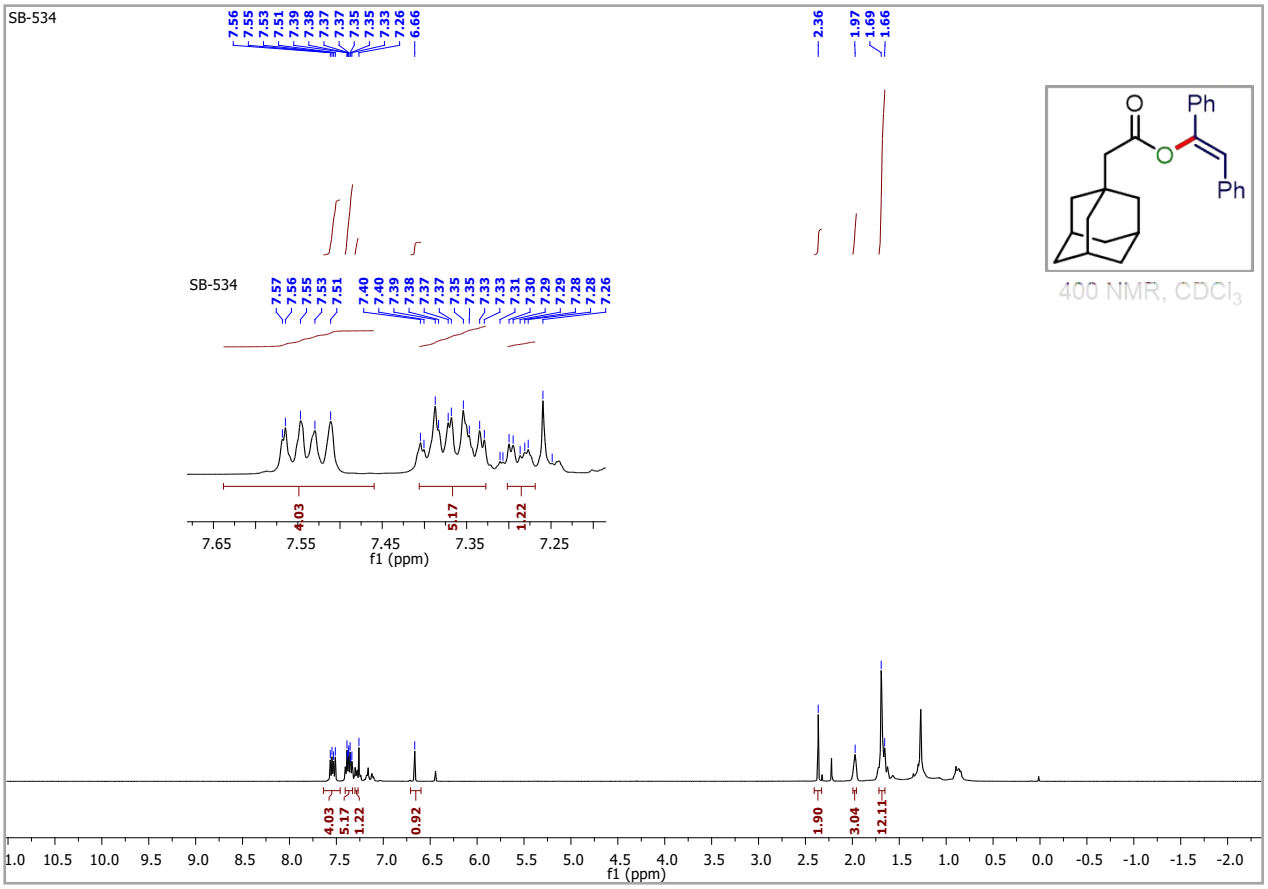
*^{1}H NMR of **34** in $CDCl_3$ at 400 MHz*



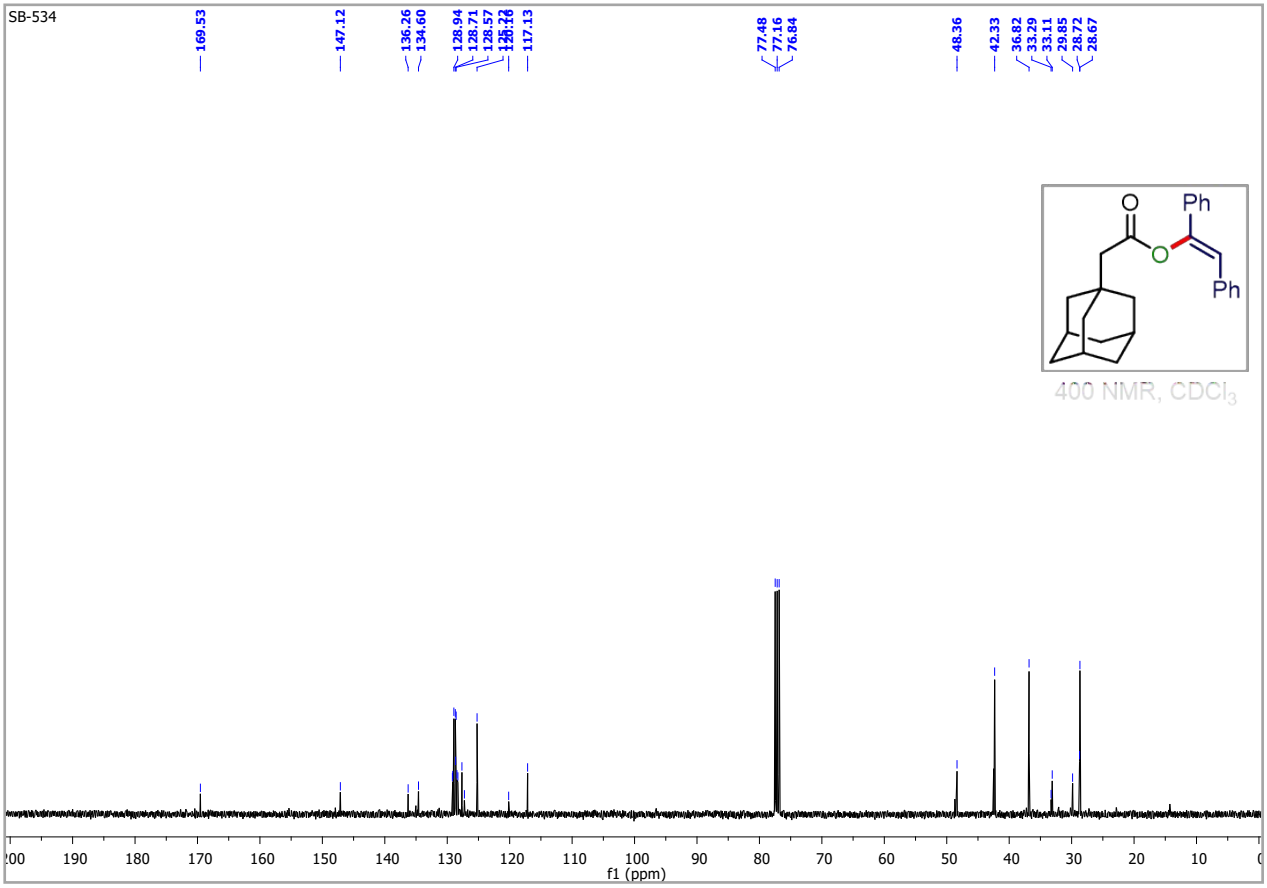
*^{13}C NMR of **34** in $CDCl_3$ at 100 MHz*



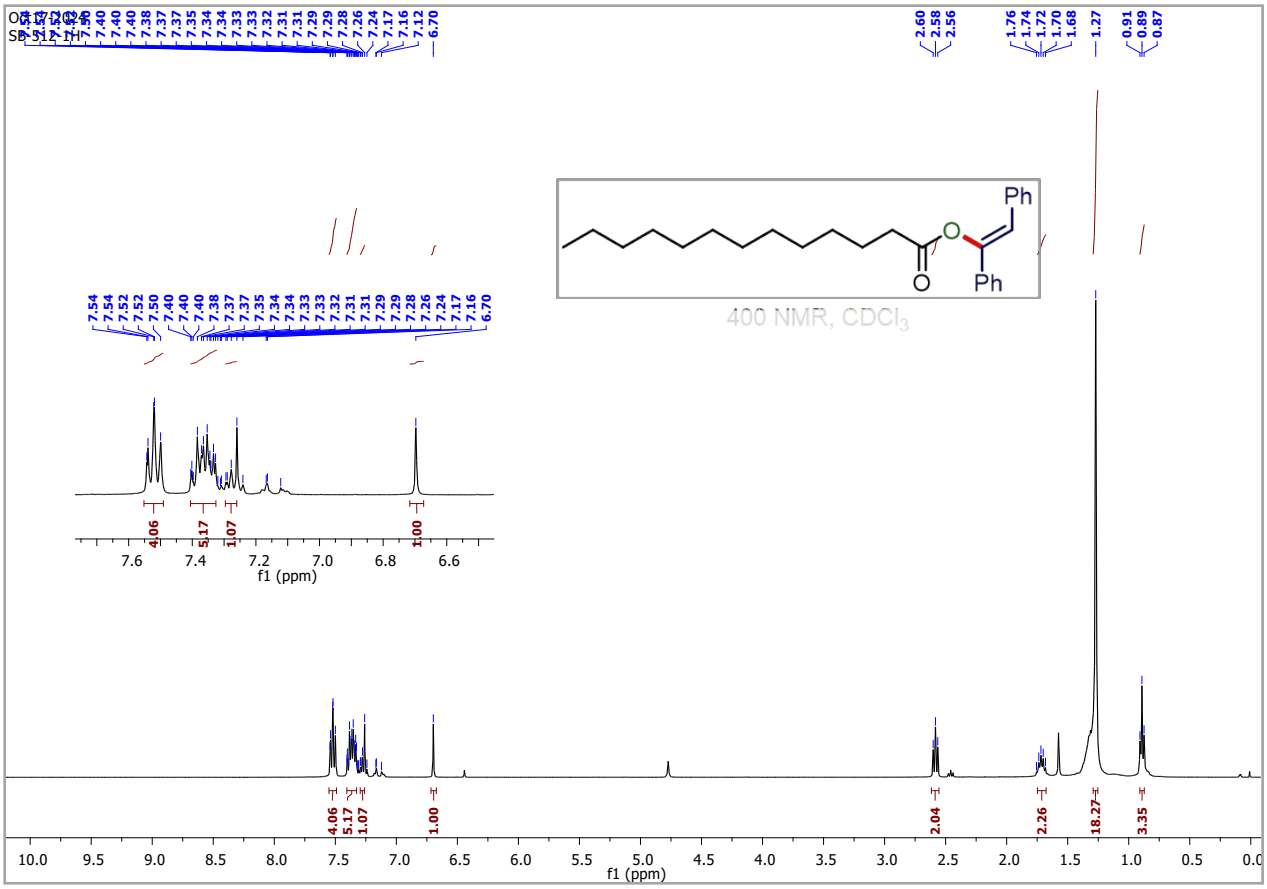
*^{1}H NMR of **35** in $CDCl_3$ at 400 MHz*



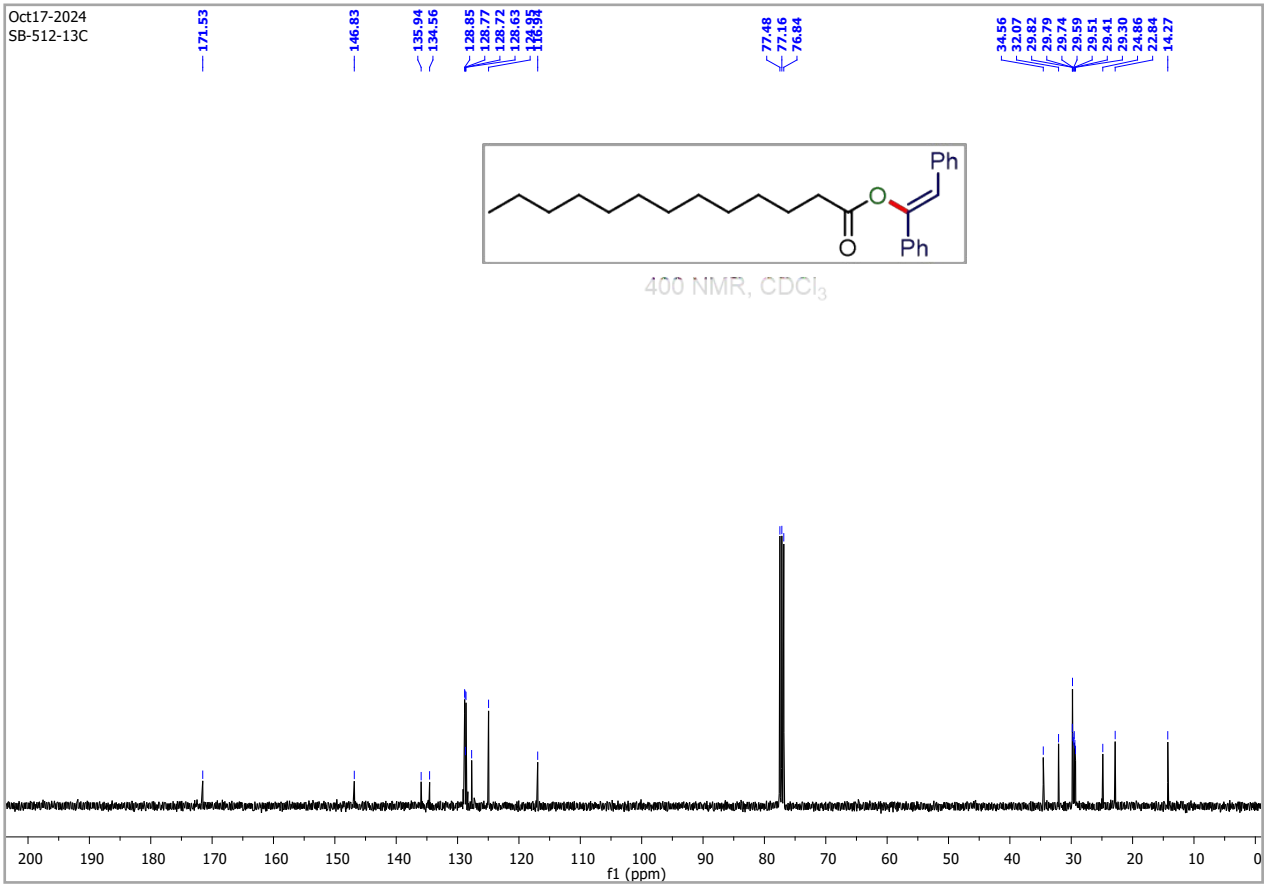
*^{13}C NMR of **35** in $CDCl_3$ at 100 MHz*



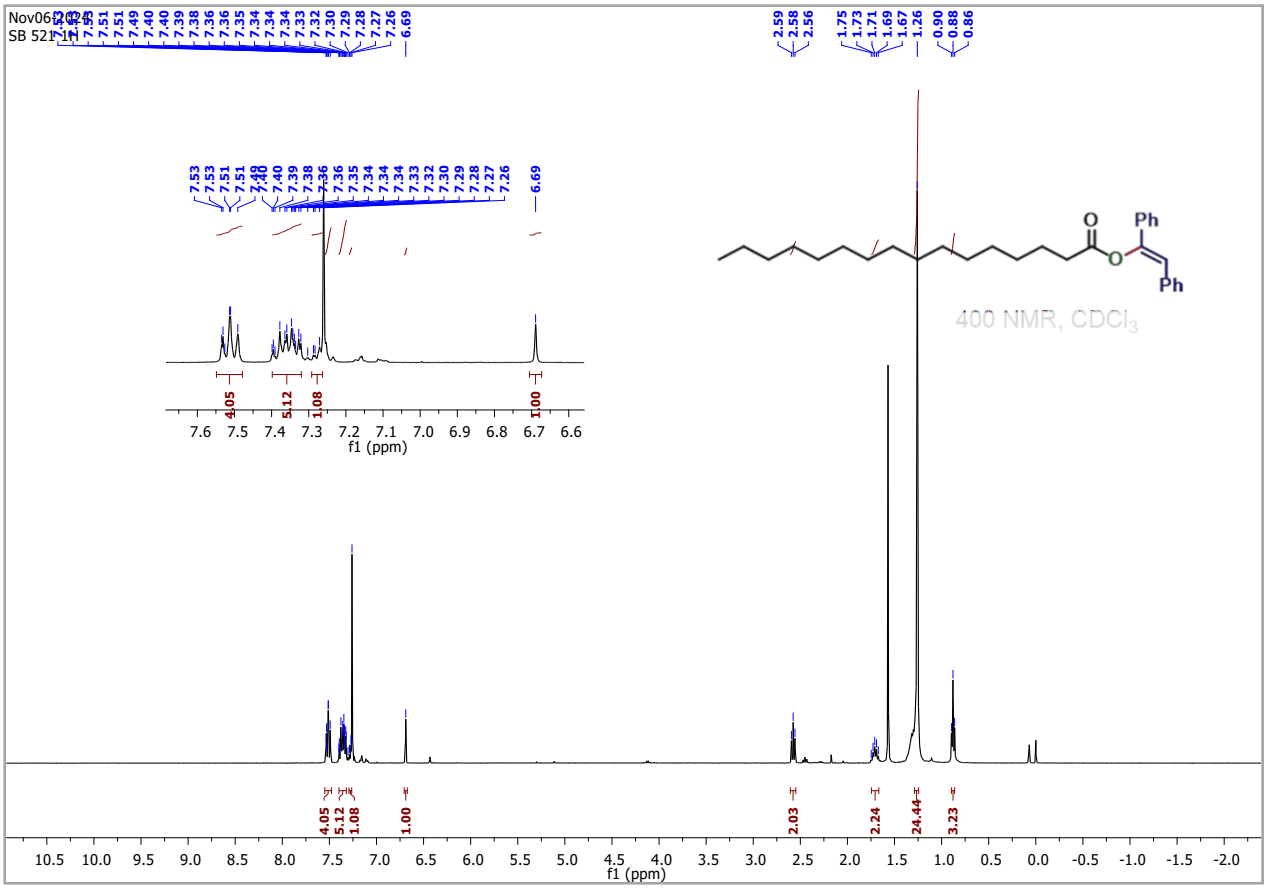
*^{1}H NMR of **36** in $CDCl_3$ at 400 MHz*



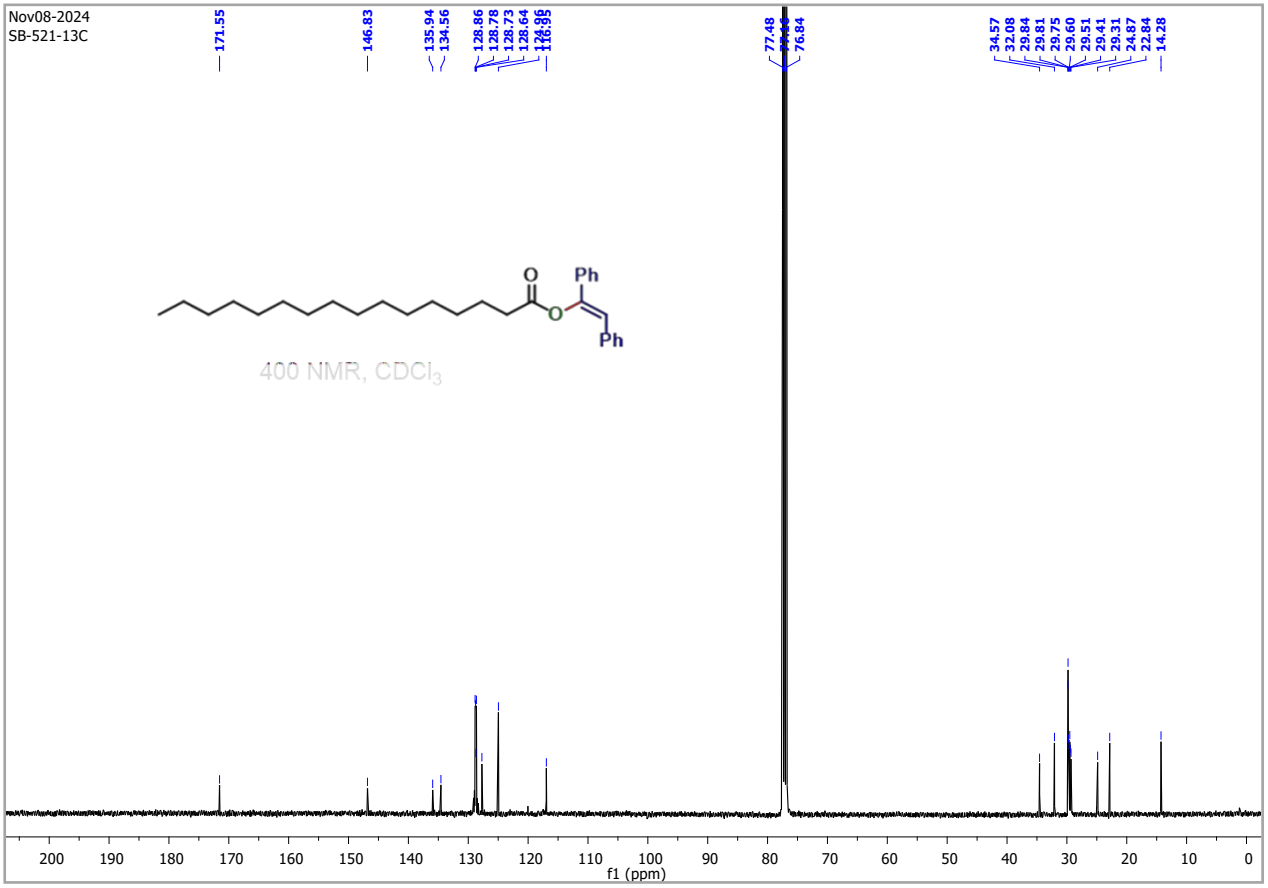
*^{13}C NMR of **36** in $CDCl_3$ at 100 MHz*



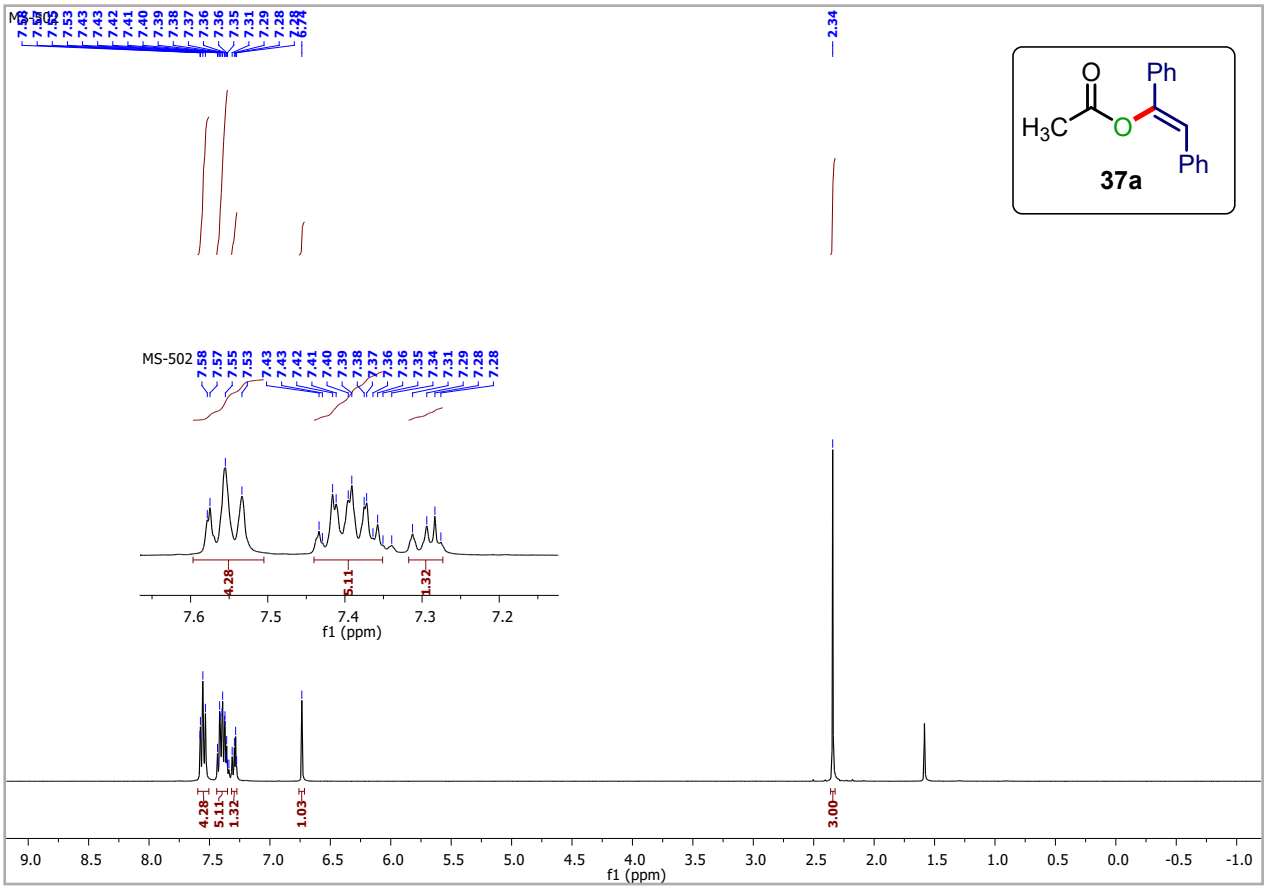
*^{1}H NMR of **37** in $CDCl_3$ at 400 MHz*



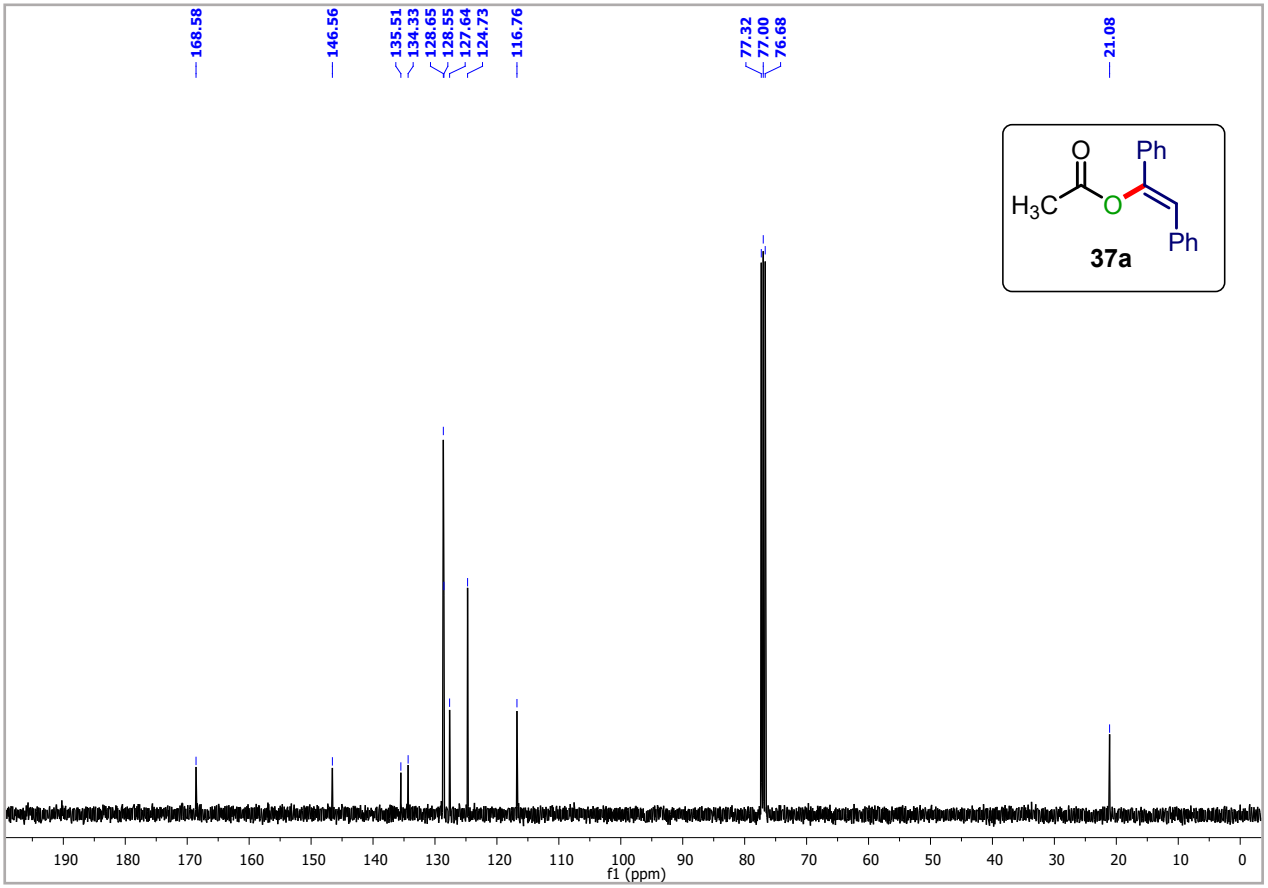
*^{13}C NMR of **37** in $CDCl_3$ at 100 MHz*



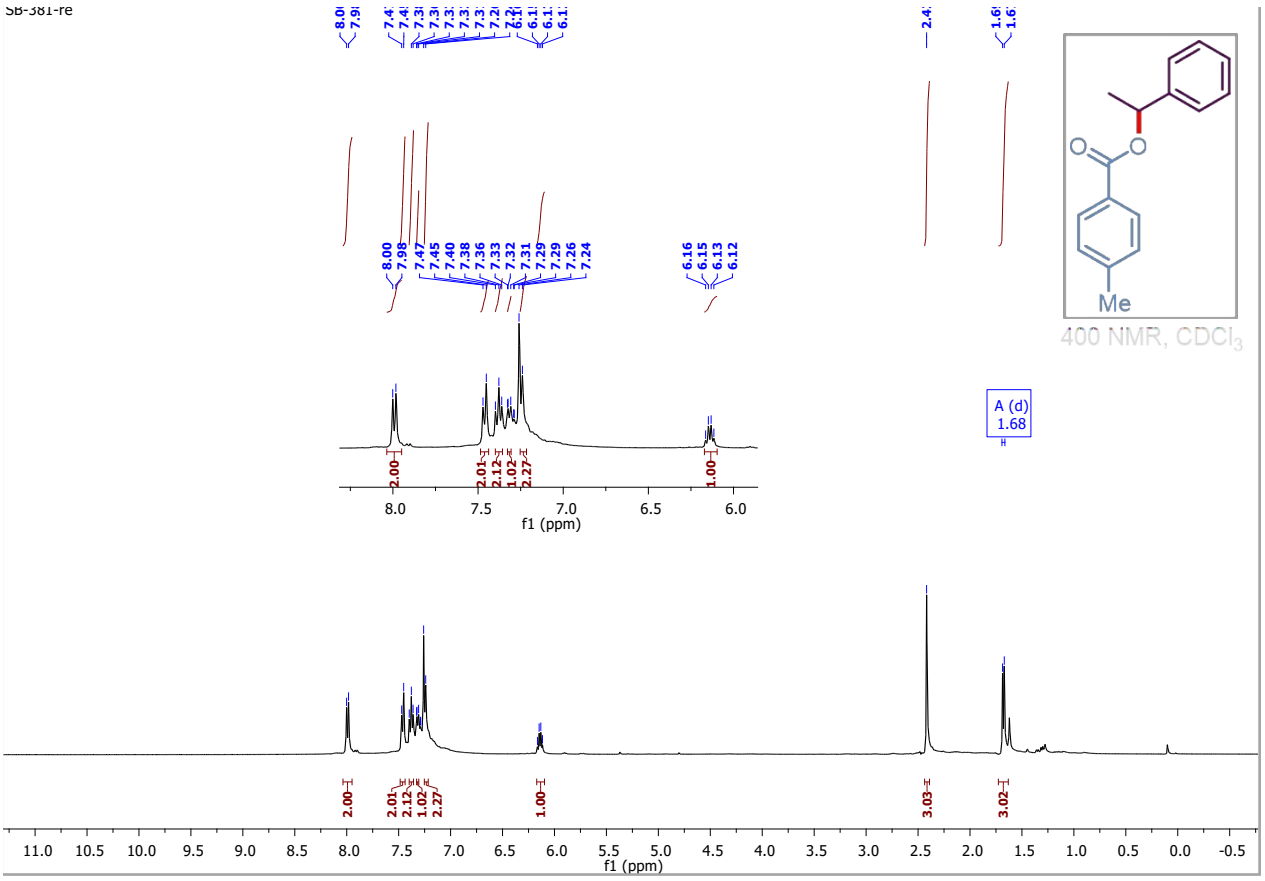
*^{1}H NMR of **37a** in $CDCl_3$ at 400 MHz*



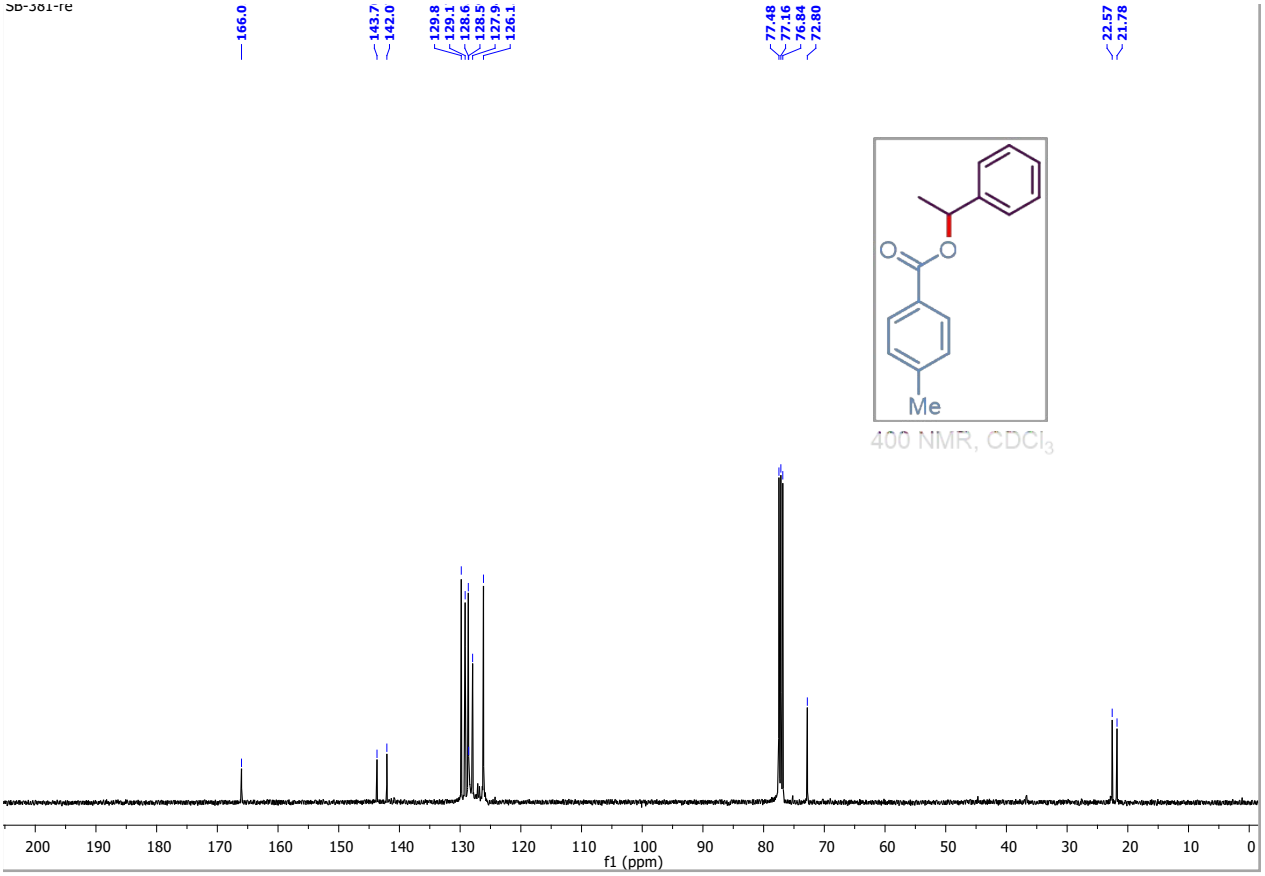
*^{13}C NMR of **37a** in $CDCl_3$ at 100 MHz*



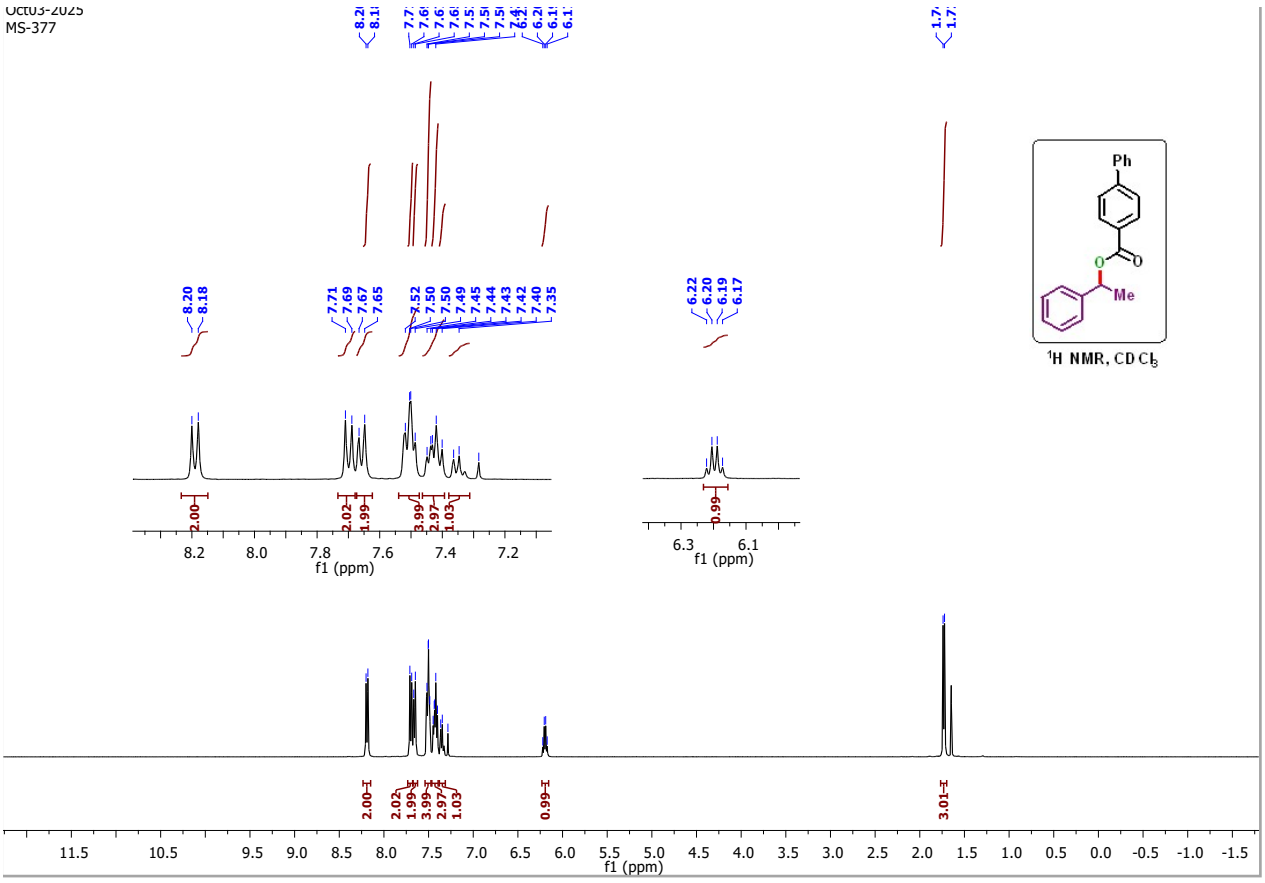
*^{1}H NMR of **38** in $CDCl_3$ at 400 MHz*



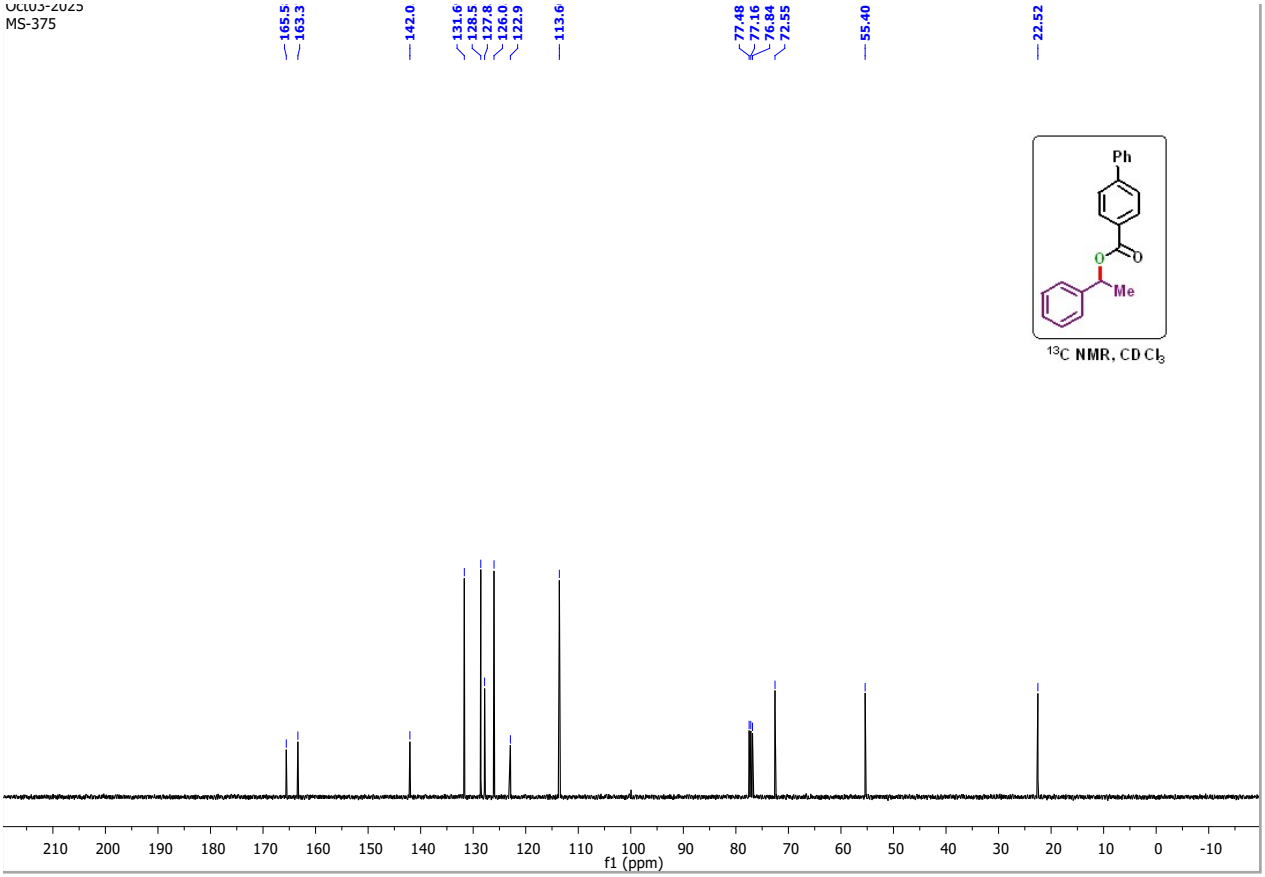
*^{13}C NMR of **38** in $CDCl_3$ at 100 MHz*



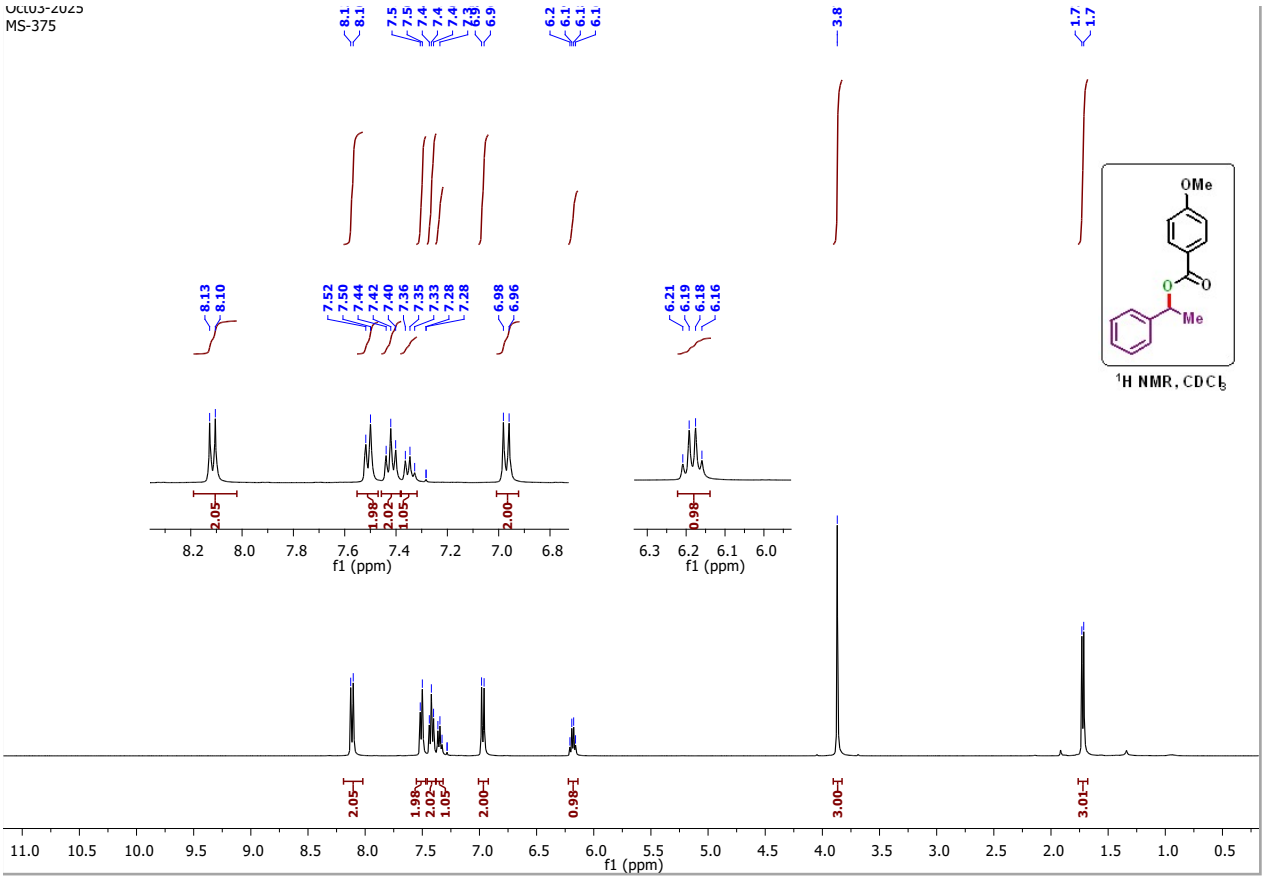
*^{1}H NMR of **39** in $CDCl_3$ at 400 MHz*



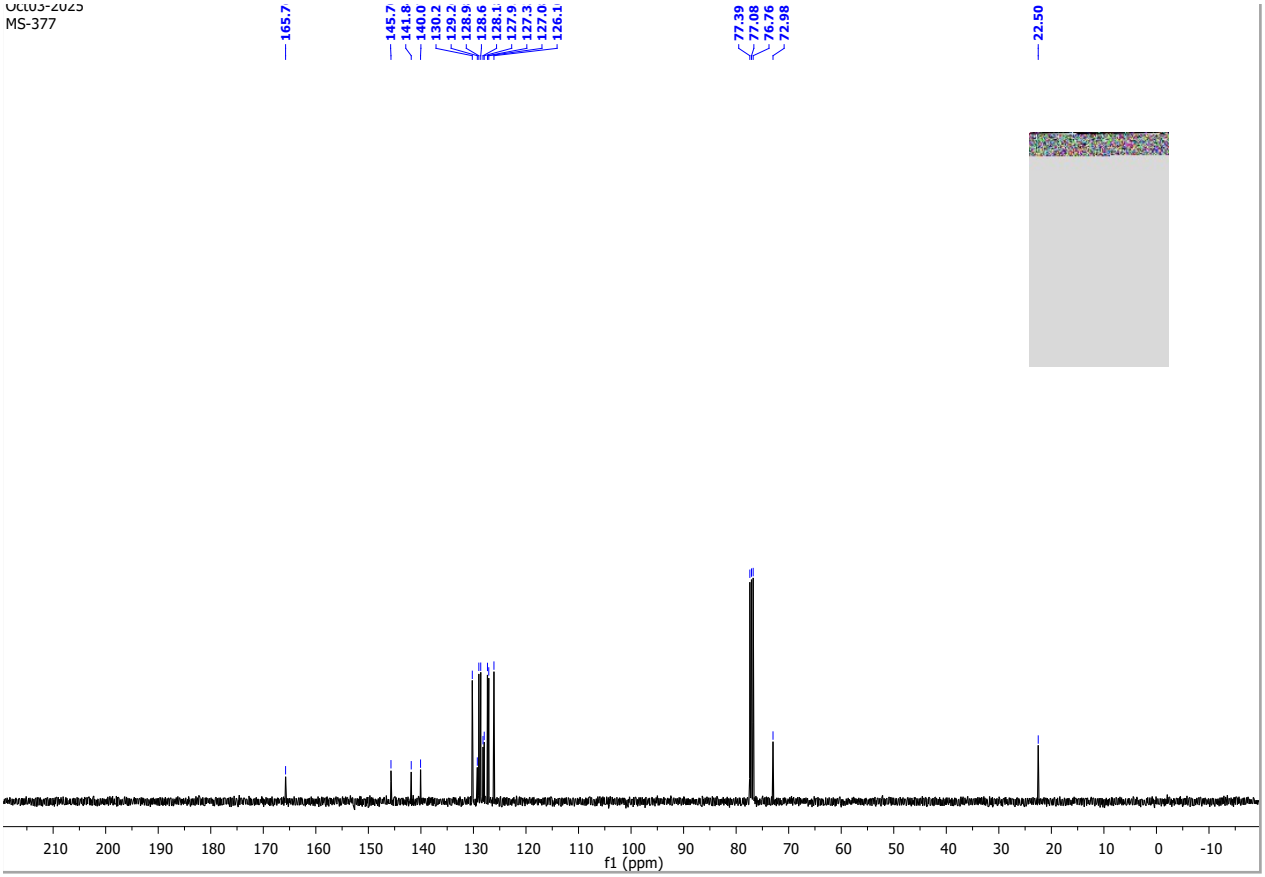
*^{13}C NMR of **39** in $CDCl_3$ at 100 MHz*



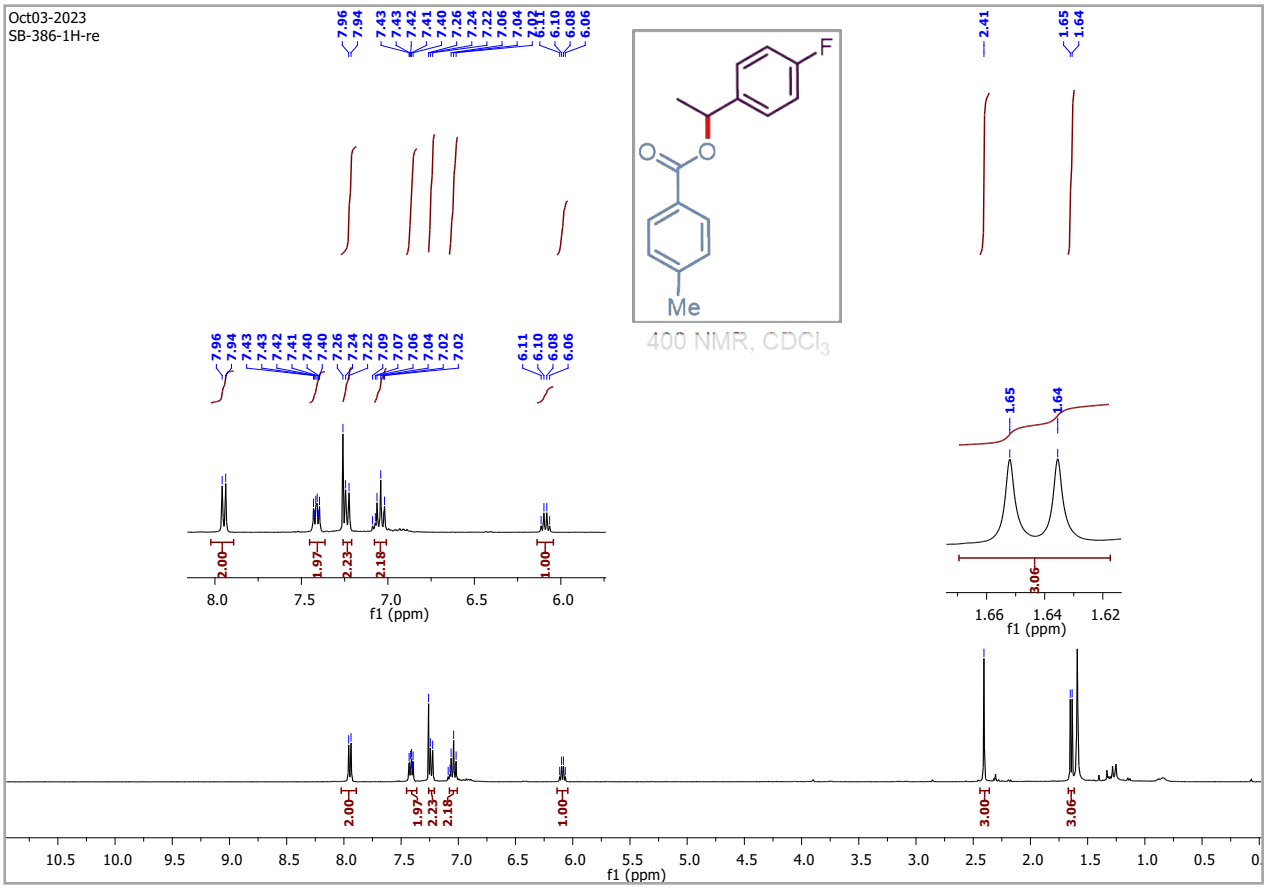
*^{1}H NMR of **40** in $CDCl_3$ at 400 MHz*



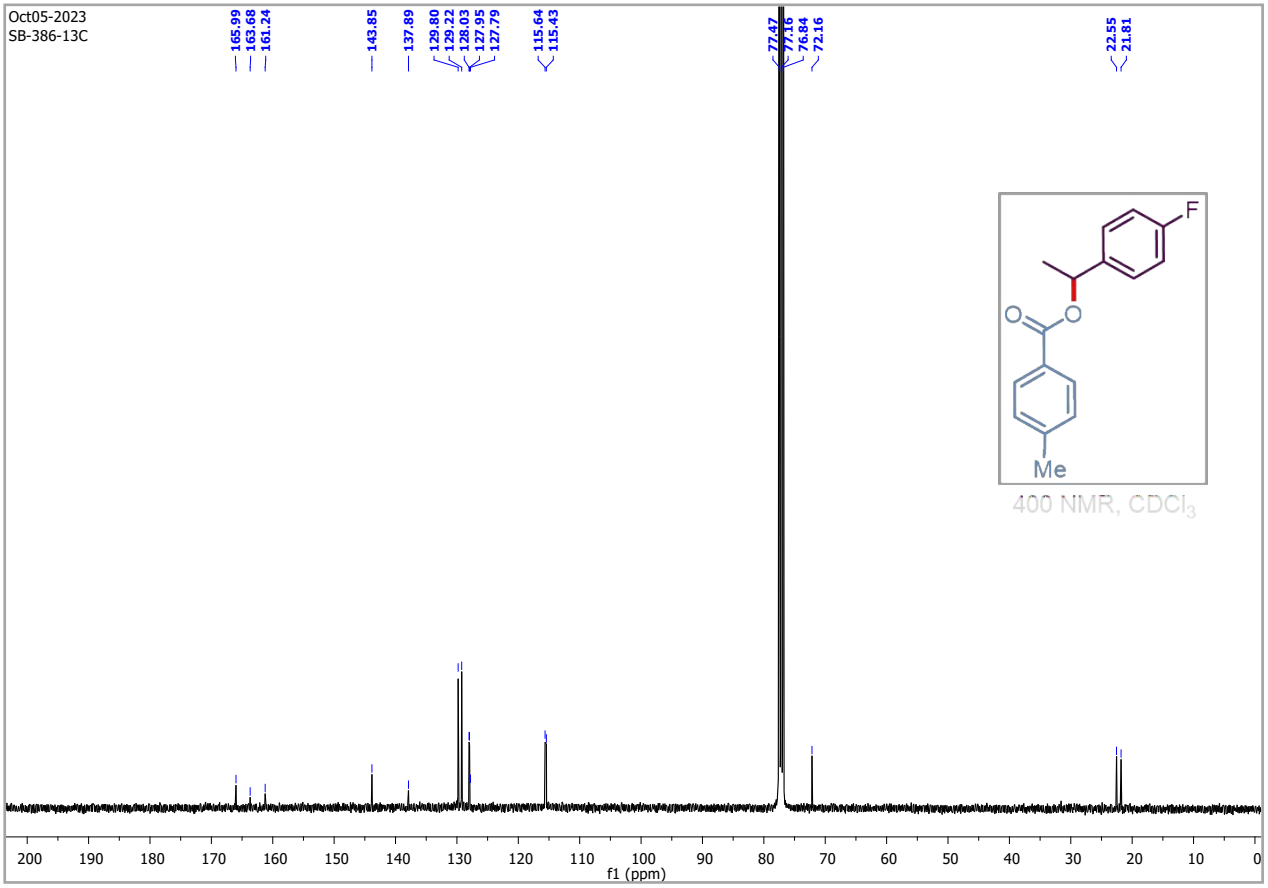
*^{13}C NMR of **40** in $CDCl_3$ at 100 MHz*



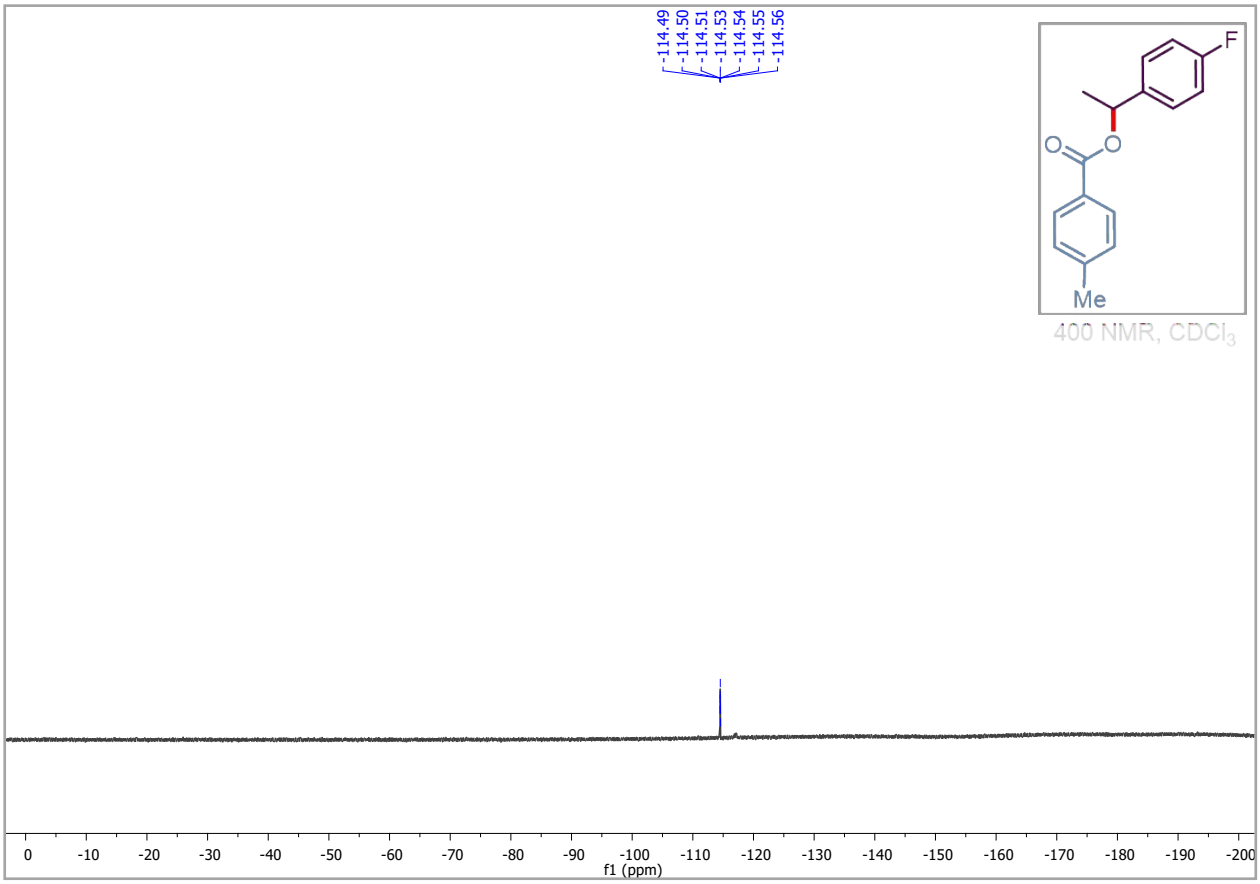
*^{1}H NMR of **41** in $CDCl_3$ at 400 MHz*



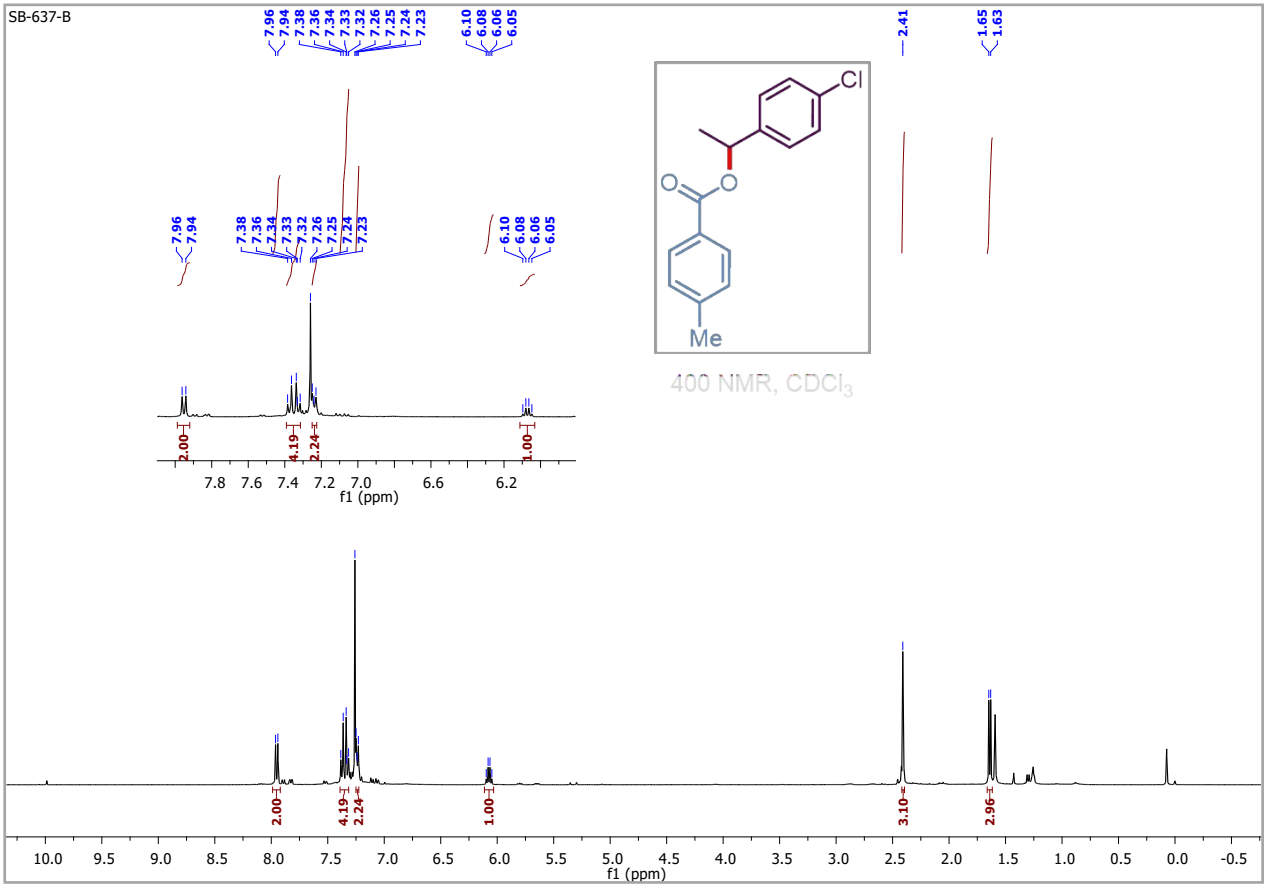
*^{13}C NMR of **41** in $CDCl_3$ at 400 MHz*



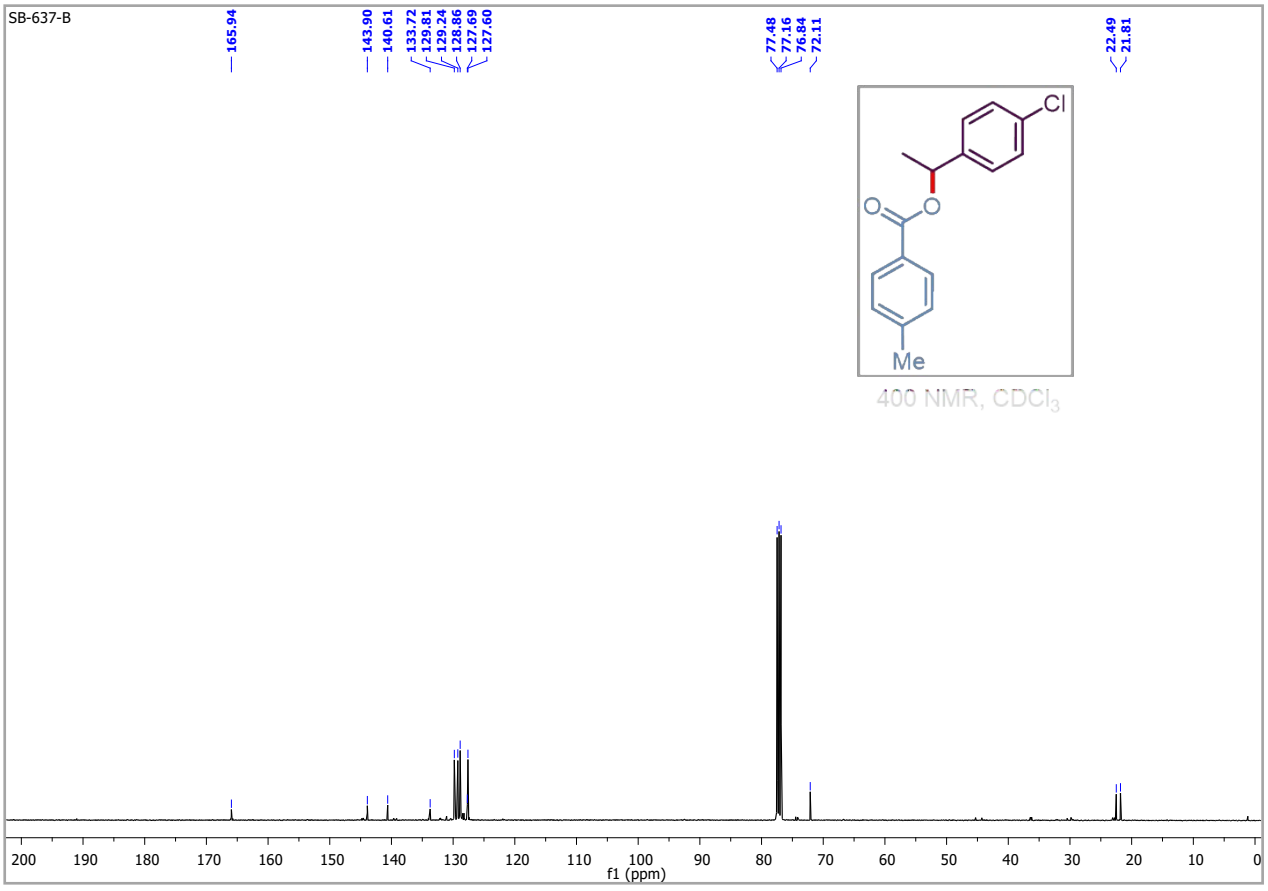
*^{19}F NMR of **41** in $CDCl_3$ at 100 MHz*



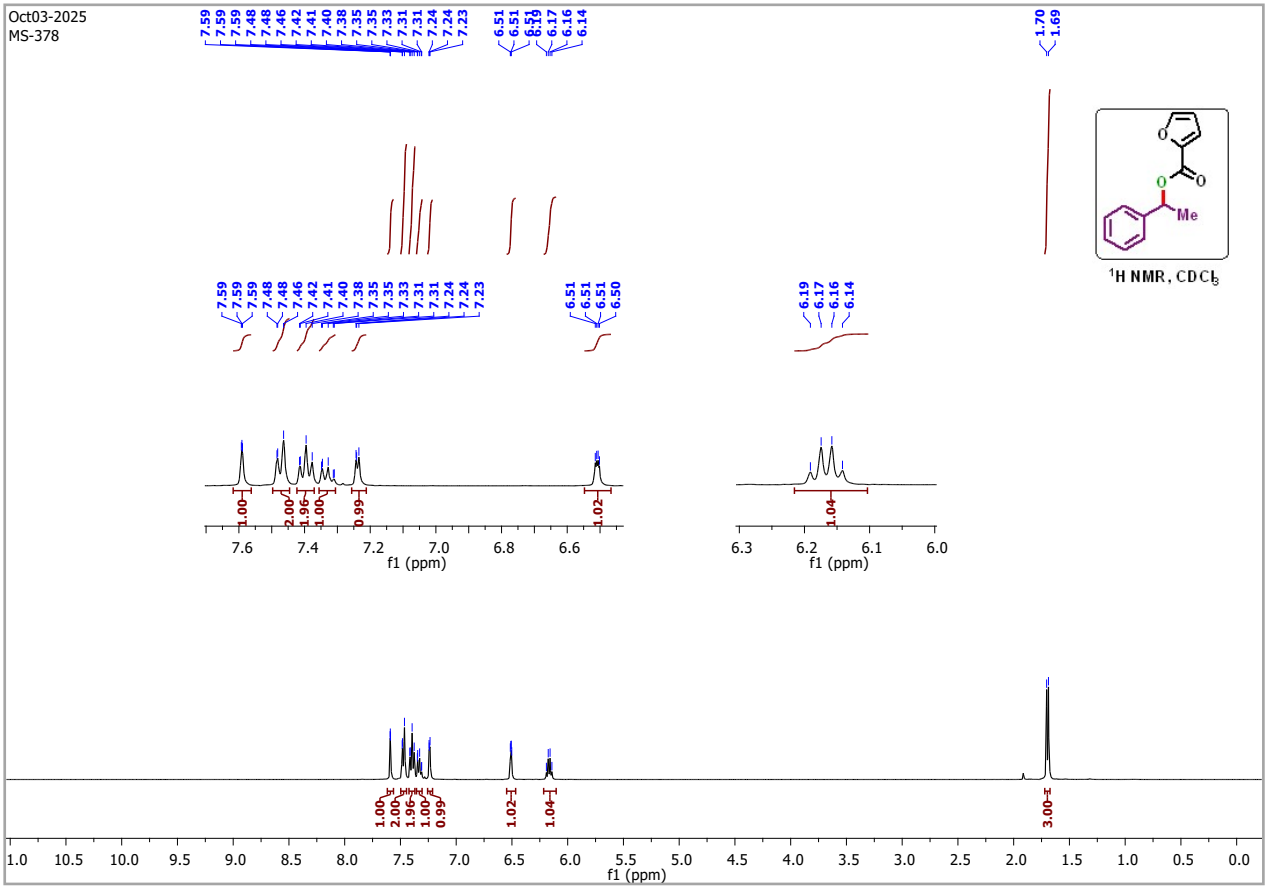
*^{1}H NMR of **42** in $CDCl_3$ at 400 MHz*



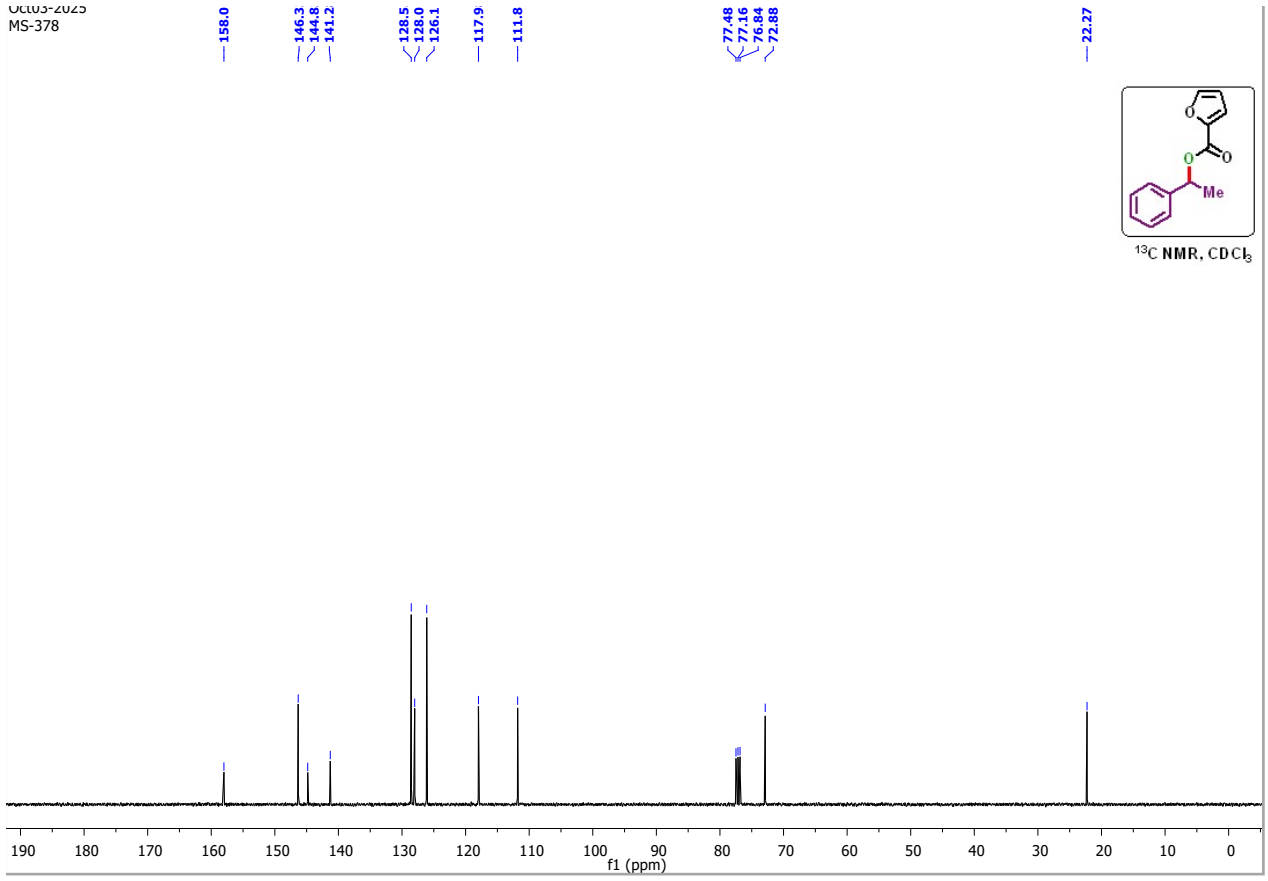
*^{13}C NMR of **42** in $CDCl_3$ at 100 MHz*



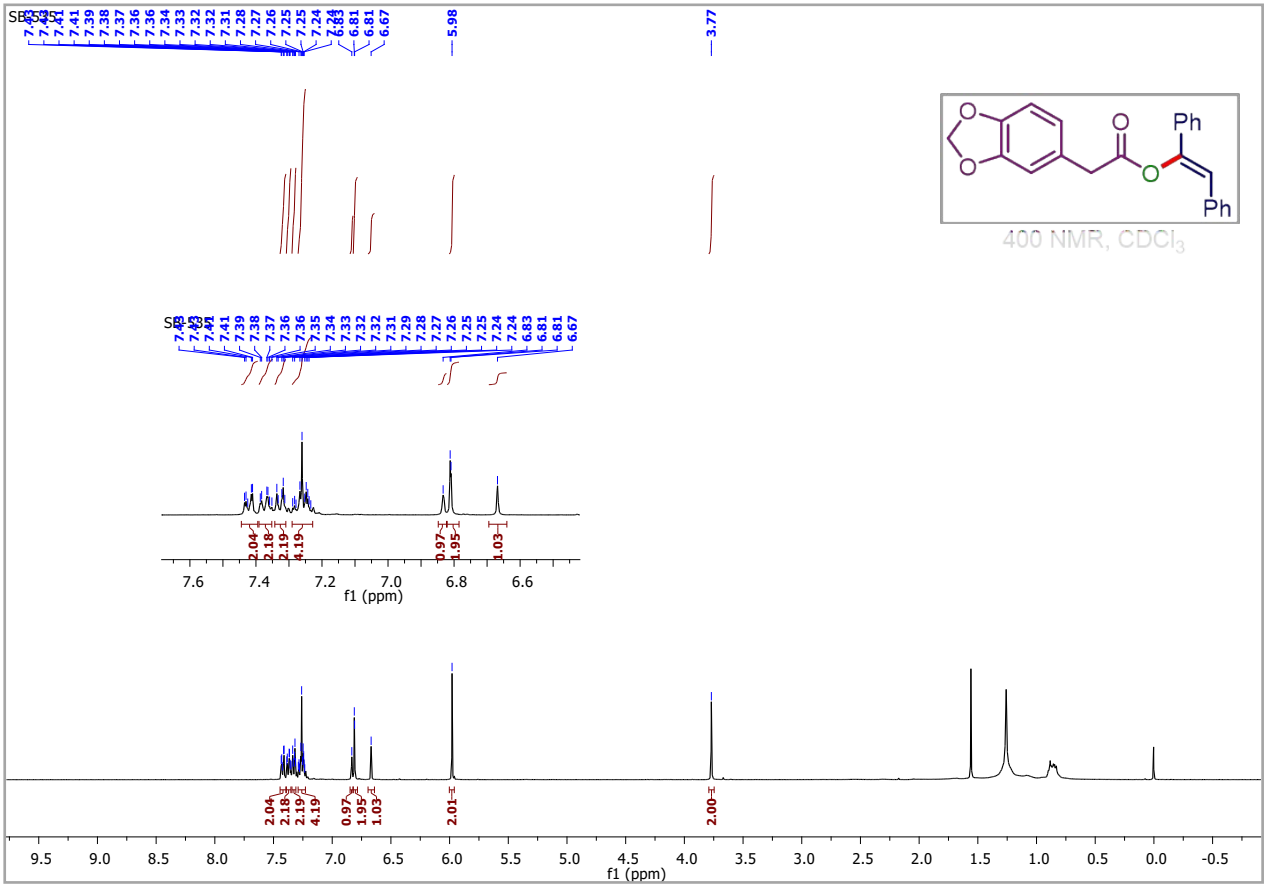
*^{1}H NMR of **43** in $CDCl_3$ at 400 MHz*



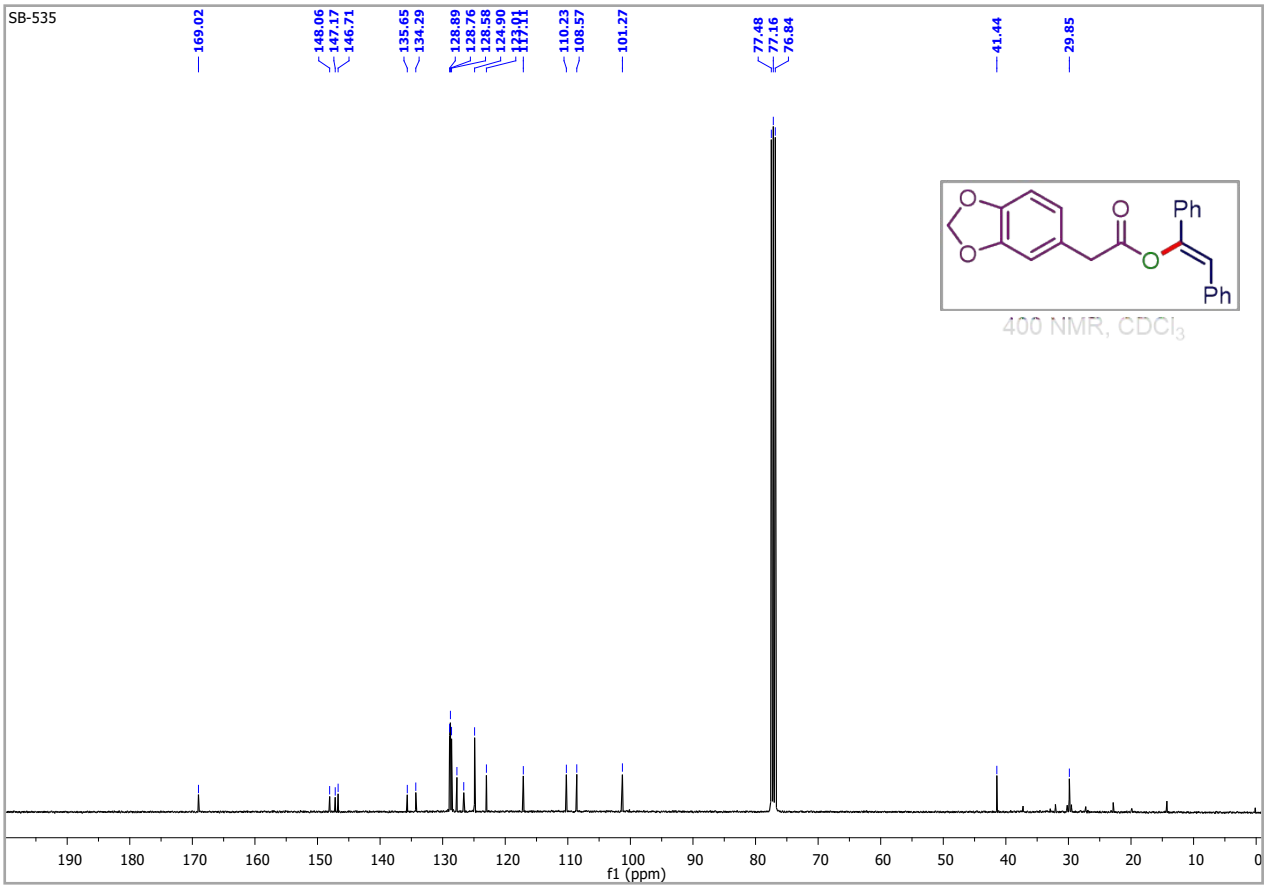
*^{13}C NMR of **43** in $CDCl_3$ at 100 MHz*



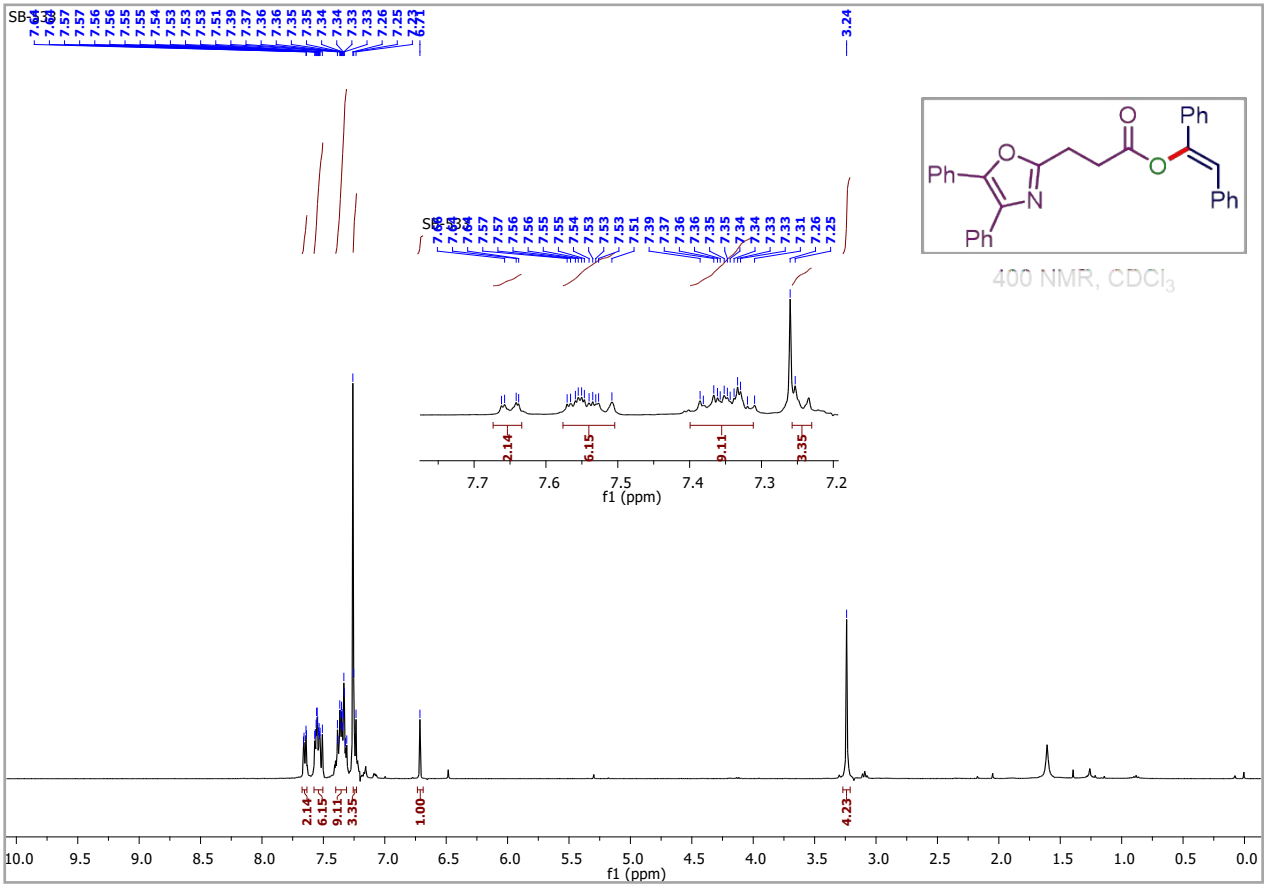
*^{1}H NMR of **44** in $CDCl_3$ at 400 MHz*



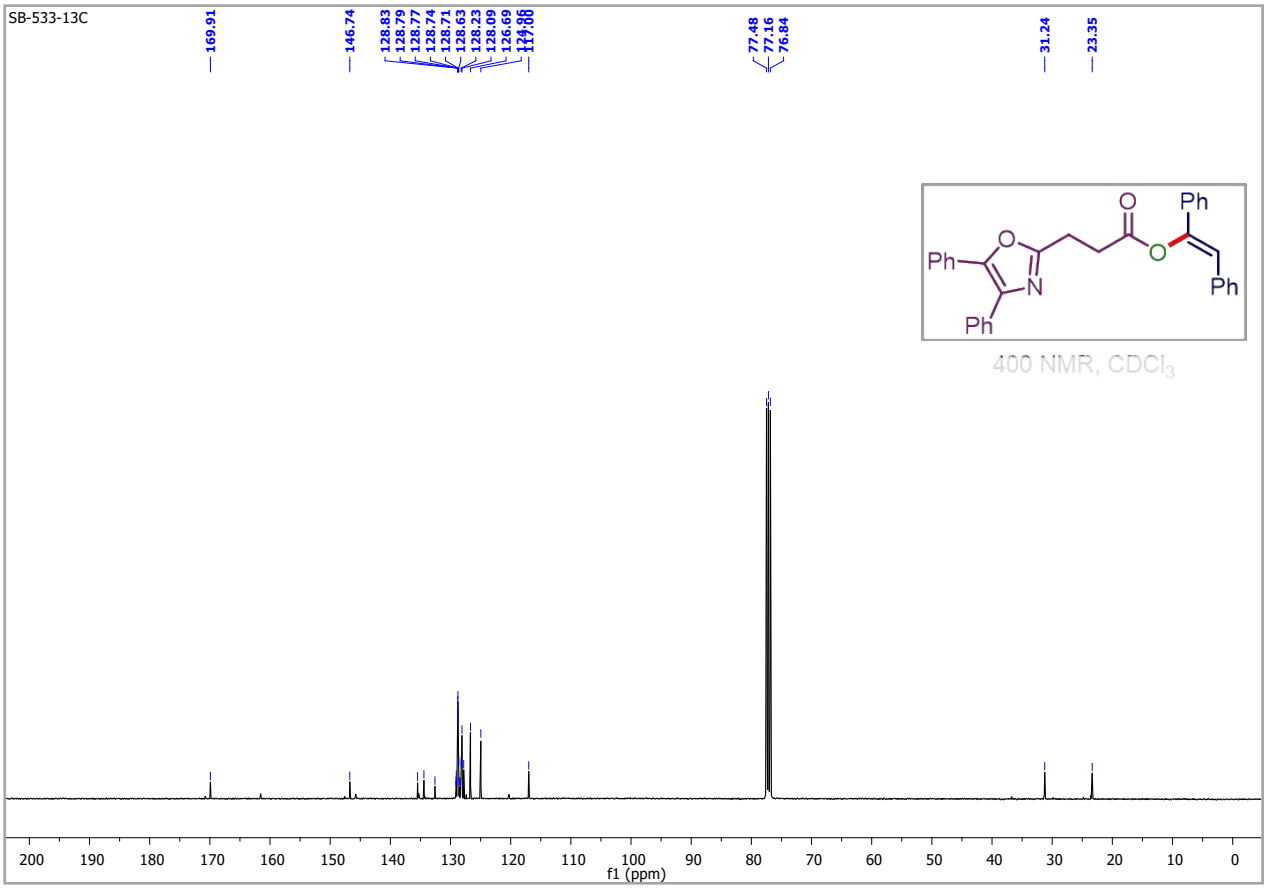
*^{13}C NMR of **44** in $CDCl_3$ at 100 MHz*



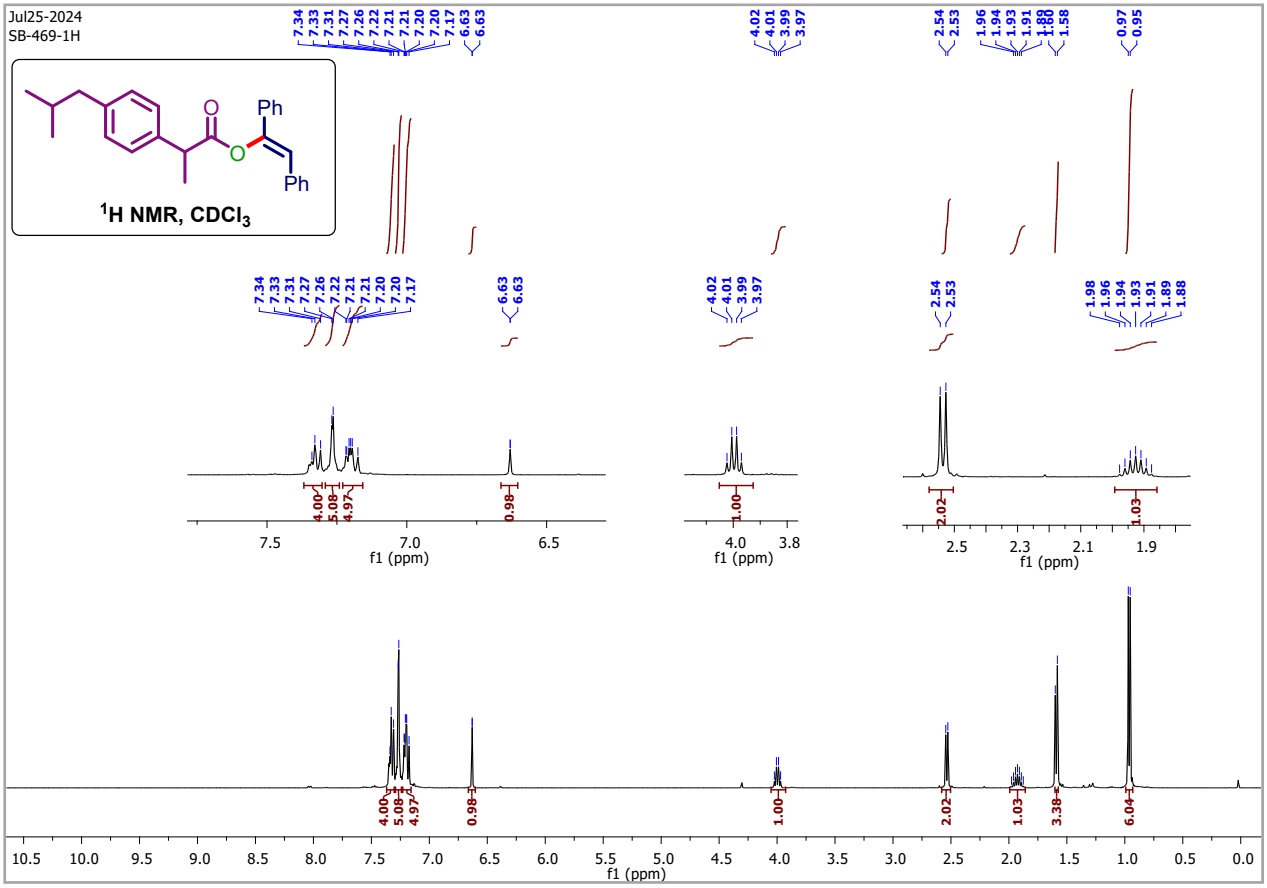
*^{1}H NMR of **45** in $CDCl_3$ at 400 MHz*



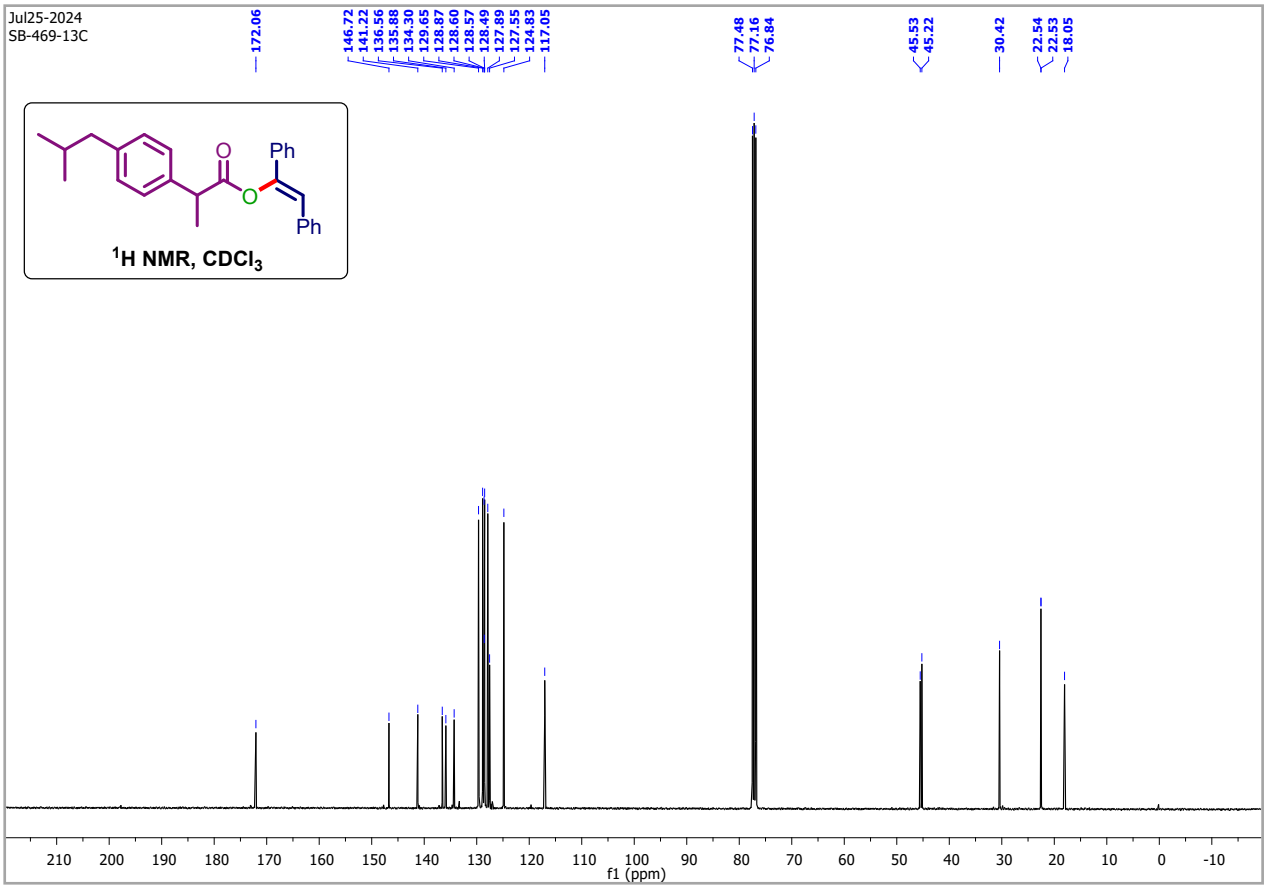
*^{13}CNMR of **45** in $CDCl_3$ at 100 MHz*



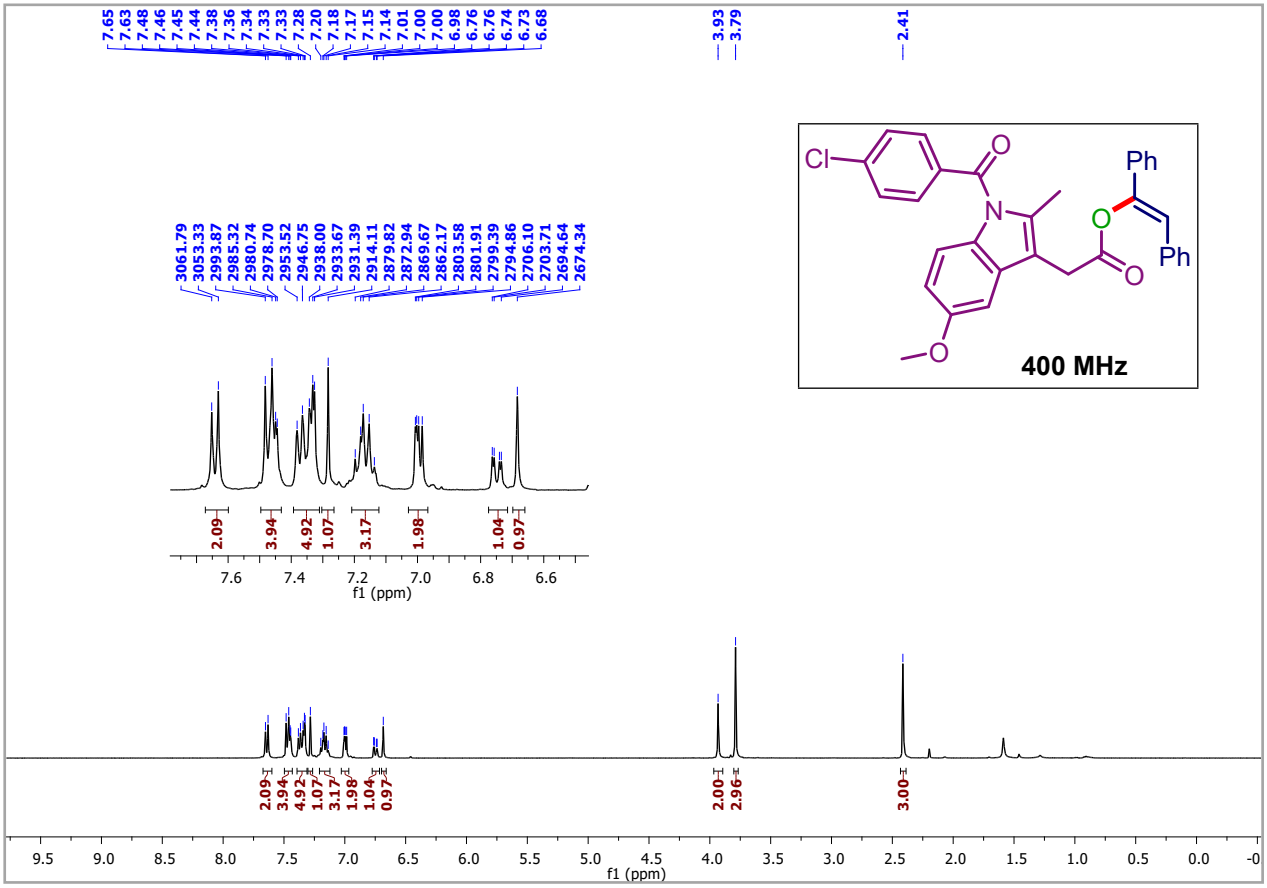
*^{1}H NMR of **46** in $CDCl_3$ at 400 MHz*



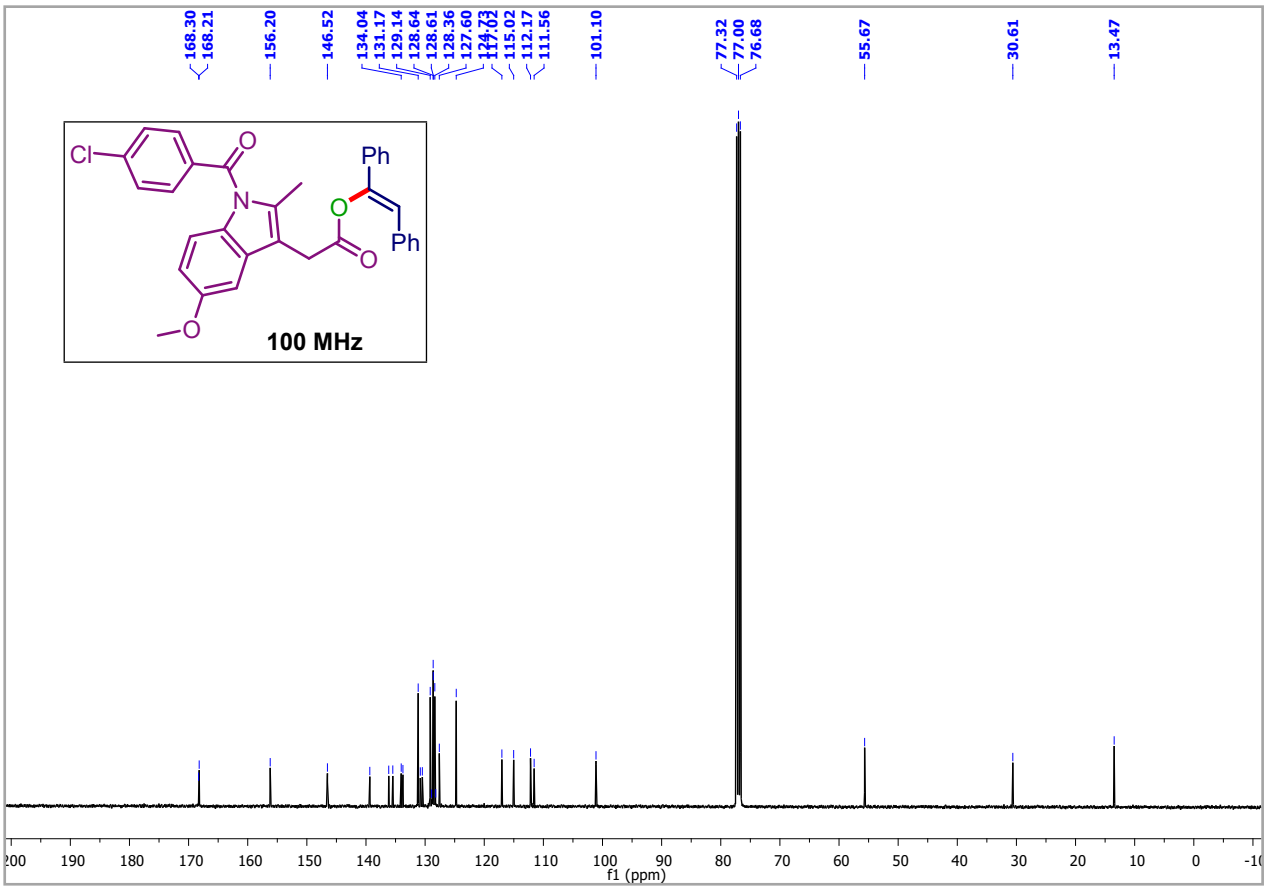
*^{13}C NMR of **46** in $CDCl_3$ at 100 MHz*



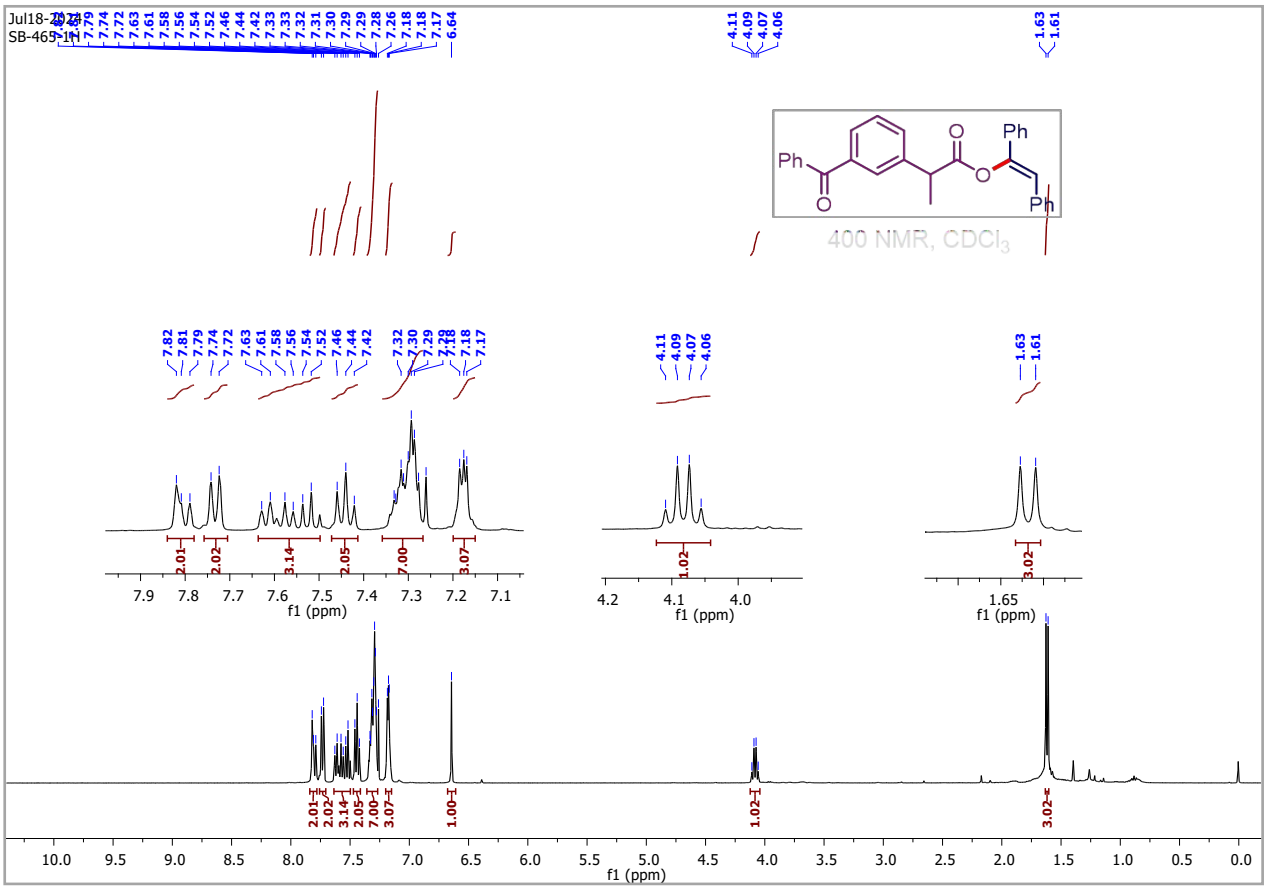
*^{1}H NMR of **47** in $CDCl_3$ at 400 MHz*



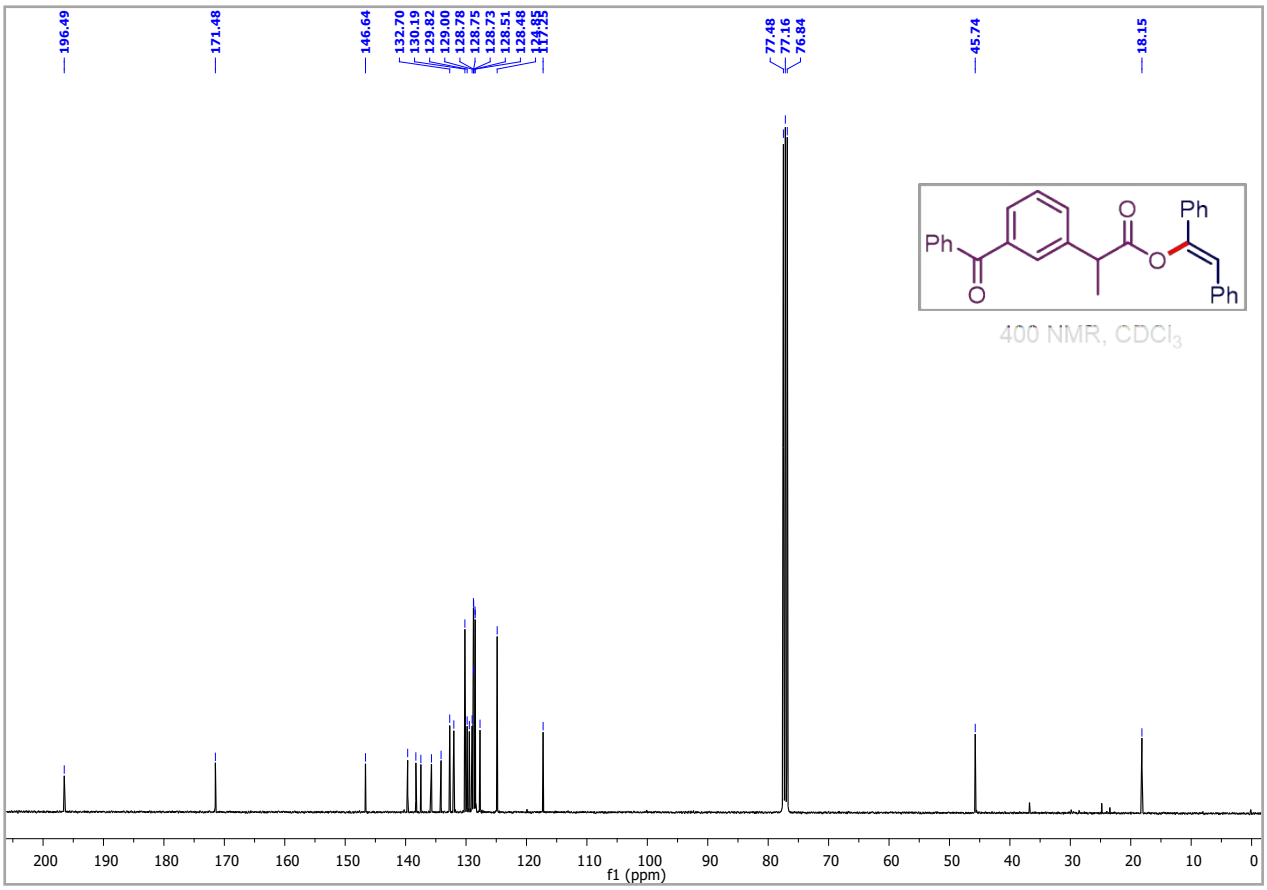
*^{13}C NMR of **47** in $CDCl_3$ at 100 MHz*



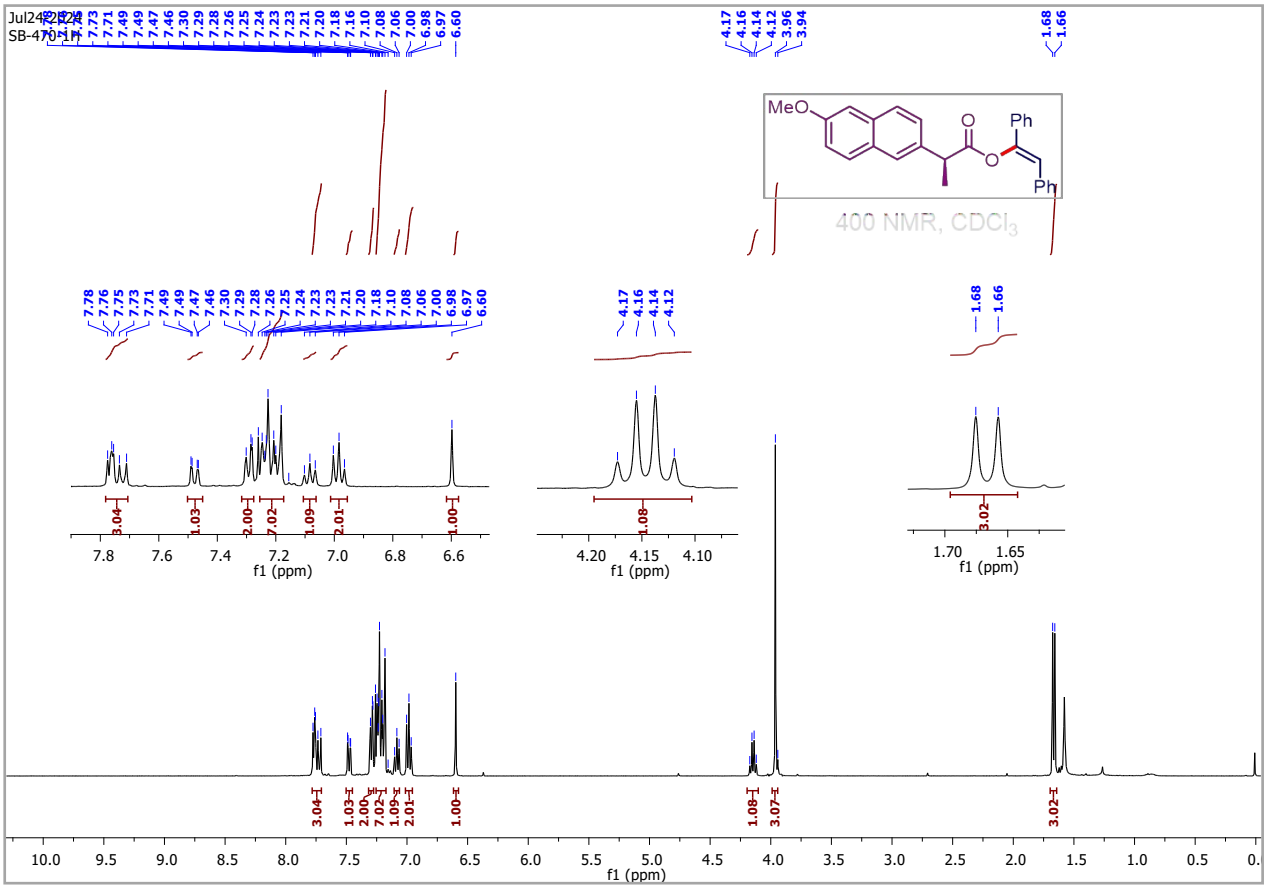
*^{1}H NMR of **48** in $CDCl_3$ at 400 MHz*



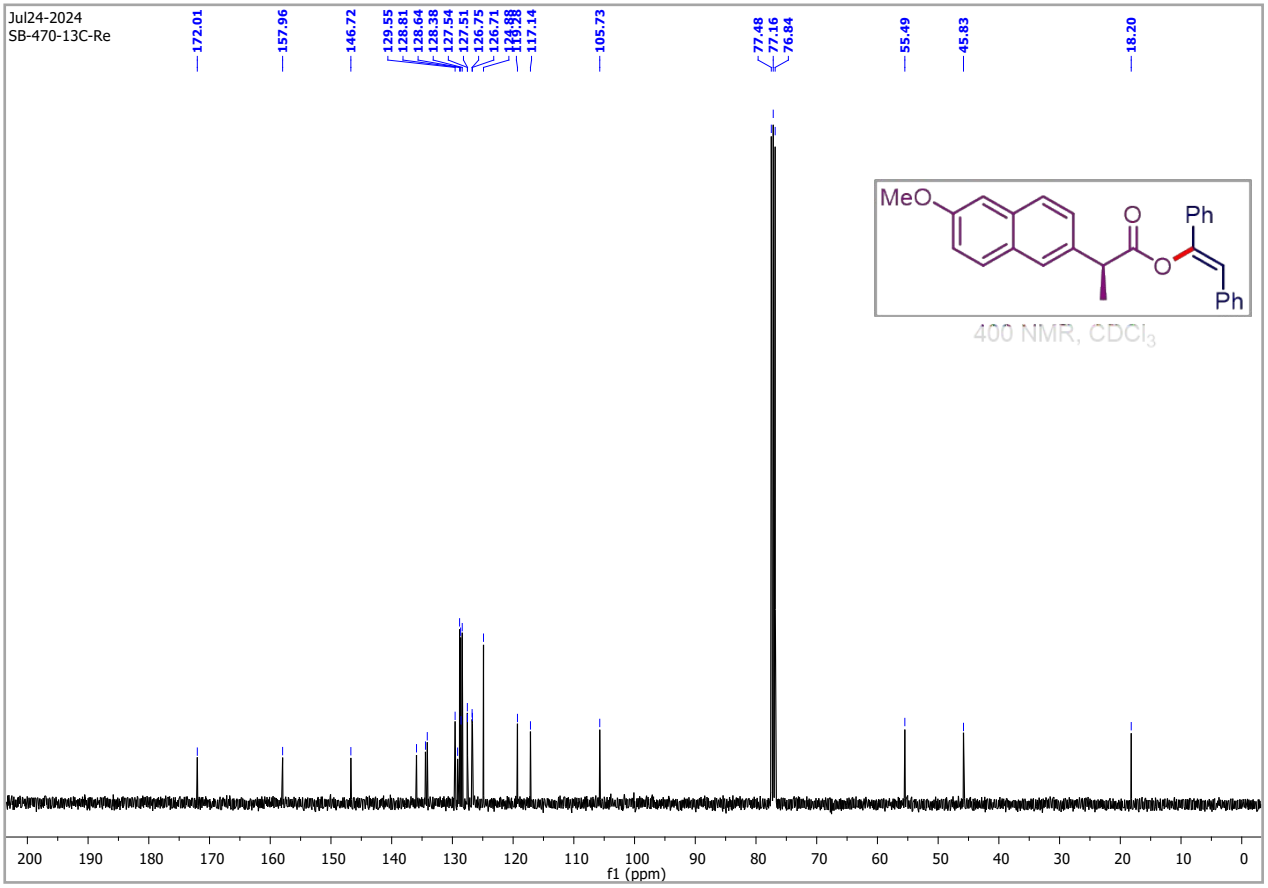
*^{13}C NMR of **48** in $CDCl_3$ at 100 MHz*



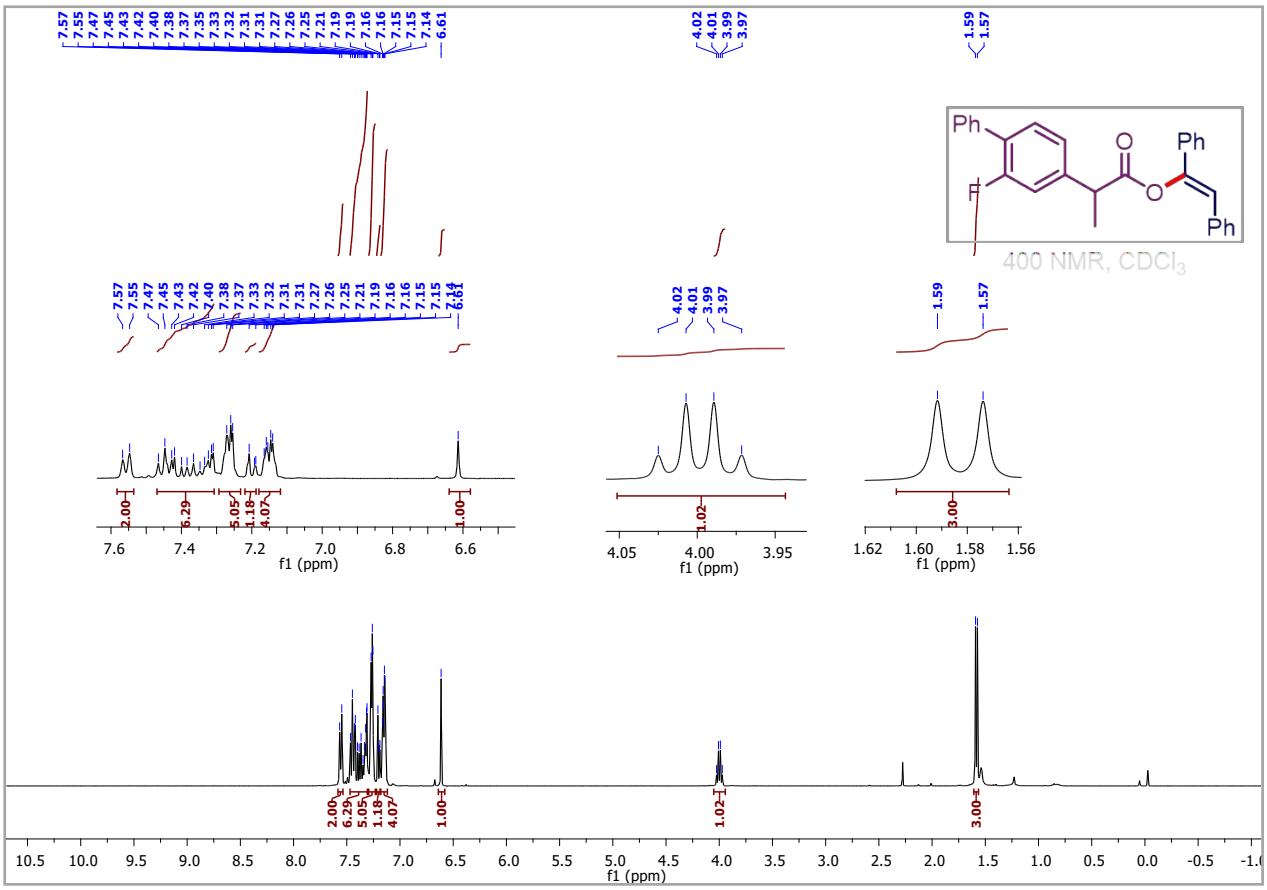
*^{1}H NMR of **49** in $CDCl_3$ at 400 MHz*



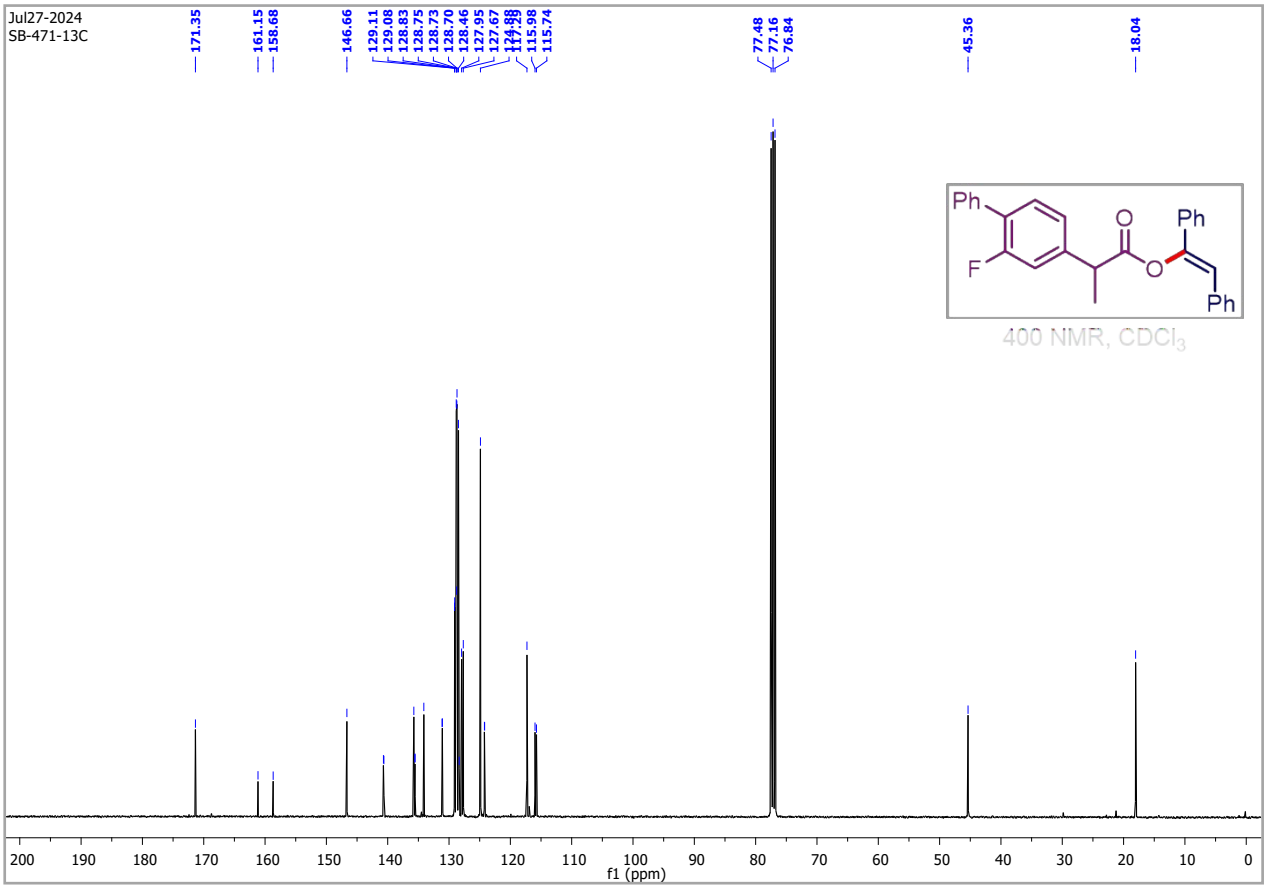
*^{13}C NMR of **49** in $CDCl_3$ at 100 MHz*



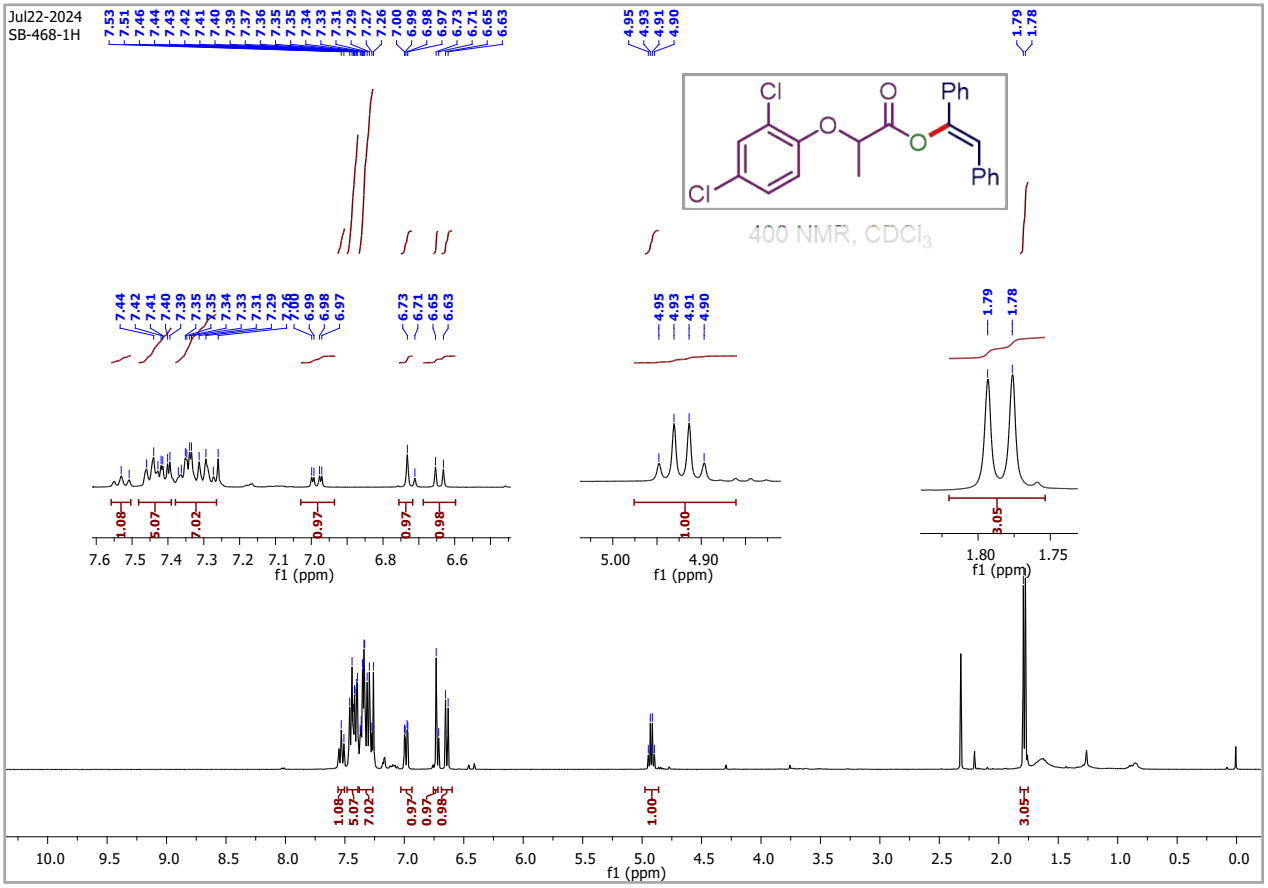
*^{1}H NMR of **50** in $CDCl_3$ at 400 MHz*



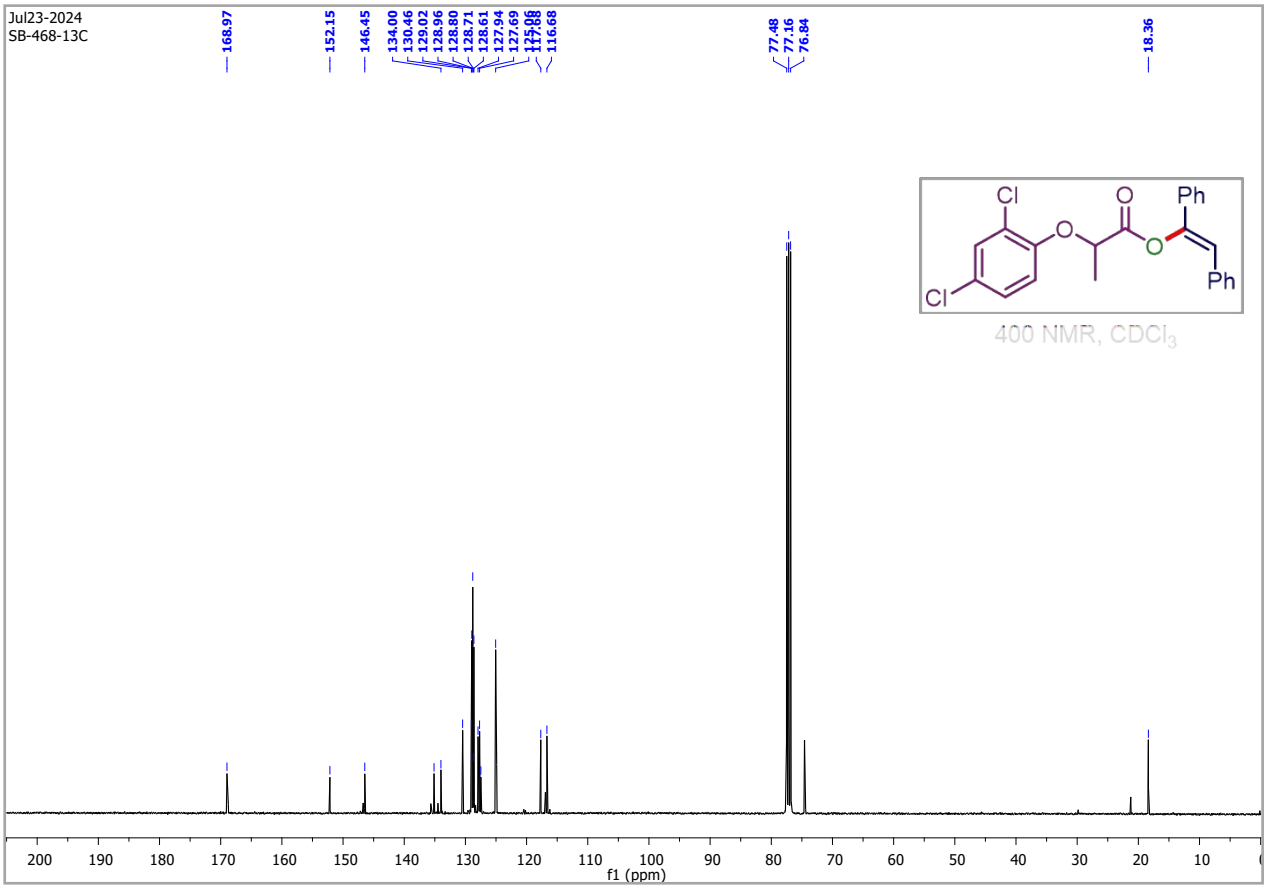
*^{13}C NMR of **50** in $CDCl_3$ at 100 MHz*



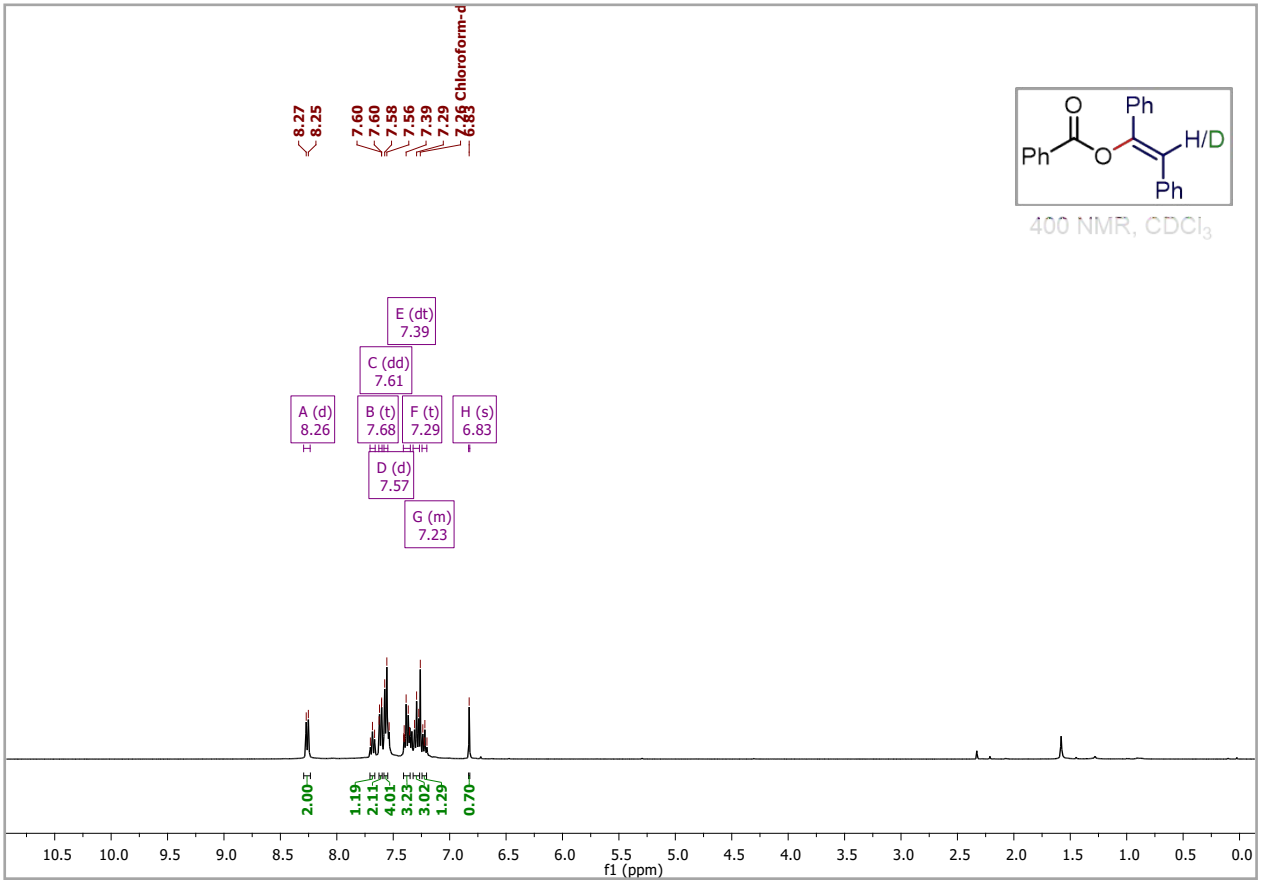
*^{1}H NMR of **51** in $CDCl_3$ at 400 MHz*



*^{13}C NMR of **51** in $CDCl_3$ at 100 MHz*



*^{1}H NMR of **52** in $CDCl_3$ at 400 MHz*



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1. Kikui, N.; Hinoue, T.; Usuki, Y.; Satoh, T. *Synthesis of Enol Esters through Silver-catalyzed or -mediated Hydroacyloxylation of Internal Alkynes*. Chem. Lett. 2018, **47** (2), 141–143.

2. Lu, B.; Zhu, F.; Sun, H.-M.; Shen, Q. Esterification of the Primary Benzylic C–H Bonds with Carboxylic Acids Catalyzed by Ionic Iron(III) Complexes Containing an Imidazolinium Cation. *Org. Lett.* **2017**, 19, 1132 - 1135.