DABCO - Catalyzed Esterification Of *N*-Pivaloyl-Activated Amides

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1. Materials and methods

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Spectrochem®, SRL®, Acros Organics®, RANKEM®, Fisher Scientific®, and used as received without further purification. Unless stated otherwise, reactions were conducted in oven-dried glassware and under normal atmospheric conditions. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer operating with the ^{13}C resonance frequency of 100 MHz and proton resonance frequency of 400 MHz. Data from the ^{1}H NMR spectroscopy are reported as chemical shift (δ) in units of parts per million (ppm) and referenced to residual solvent peaks ($CHCl_3$: 7.26 ppm and DMSO-d5: 2.50 ppm for ^{1}H NMR). Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet) and m (multiplet). Data from ^{13}C NMR spectra are reported in terms of chemical shift (δ) in units of parts per million (ppm) and referenced to residual solvent peaks ($CHCl_3$: 77.16 ppm, DMSO-d_5: 39.52 ppm for ^{13}C NMR). High-resolution mass spectra were recorded on Electrospray Ionization mode on WATERS- XEVO G2-XS-QToS mass spectrometer in positive (ESI+) ion mode. Mass spectra were recorded on Perkin Elmer Clarus 600/Shimadzu QP2020 GC-MS spectrometer in EI mode. Melting points were recorded with REMI DDMS 2545. The instrument is calibrated with benzoic acid before the measurement.

Abbreviation used in this supporting information

DCM – Dichloromethane

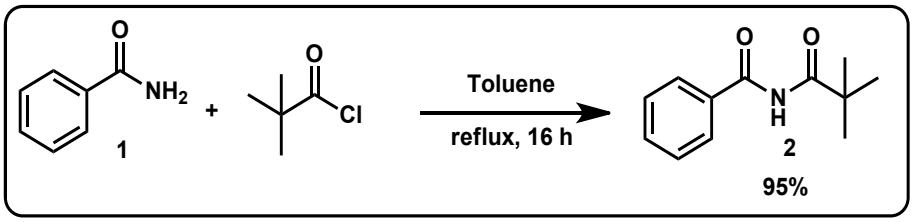
DMF – Dimethyl formamide

TEA – Triethyl amine

EtOAc – Ethyl acetate

RT – Room temperature

Synthesis of N-pivaloyl benzamide



To a stirred solution of benzamide (1g, 8.23 mmol), in 20 mL of toluene at room temperature, pivaloyl chloride (991 mg, 8.23 mmol) was added dropwise. After addition, the reaction mixture was refluxed for 16 h. Progress of the reaction was monitored by TLC [hexane-EtOAc (7:3)]. After completion, the reaction mixture was washed with 5% $NaHCO_3$ solution (2 x 50 mL) and water (1 x 50 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The obtained crude mixture was washed with hexane (10 mL) to get pure product as an off-white solid in 1.60 g (95 % yield).

Physical Characteristics:

Colour and appearance: Off-white solid

M.pt: 127 °C – 129 °C (Lit. m.pt = 126 °C – 127 °C[1]

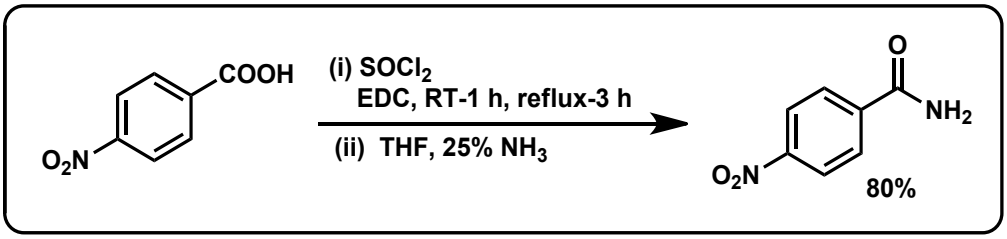
Spectral data:

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 1.24 (9H, s), 7.51 (2H, t, *J* = 8 Hz), 7.61 (1H, t, *J* = 8 Hz), 7.71 (2H, t, *J* = 8 Hz), 10.41 (1H, s). **^{13}C NMR** (100 MHz, DMSO-d_6) δ (ppm): 26.8, 128.7, 128.8, 132.7, 135.1, 168.52, 177.6. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 205.05

General Procedure: Synthesis of benzamides and cinnamamides

To a solution of substituted benzoic acid or cinnamic acid in ethylene dichloride at RT under N_2 atmosphere, thionyl chloride was added slowly and the reaction mixture was stirred for 1 hour at room temperature and then refluxed for 3 hours. Excess thionyl chloride was distilled off. Without further purification the crude product was taken to next step. To a cold (5 ºC) ammonia THF solution, the prepared acid chloride in THF was added dropwise and stirred vigorously at RT for 3 h. The obtained solid is filtered, washed with water and dried.

Synthesis of 4-nitrobenzamide



The general procedure stated above was followed. 4-Nitro benzoic acid (500 mg, 2.99 mmol), thionyl chloride (0.65 mL, 8.97 mmol), 25% of ammonia solution (4 mL, 59.8 mmol). Pure product was obtained as white solid in 397 mg (80% yield).

Physical Characteristics:

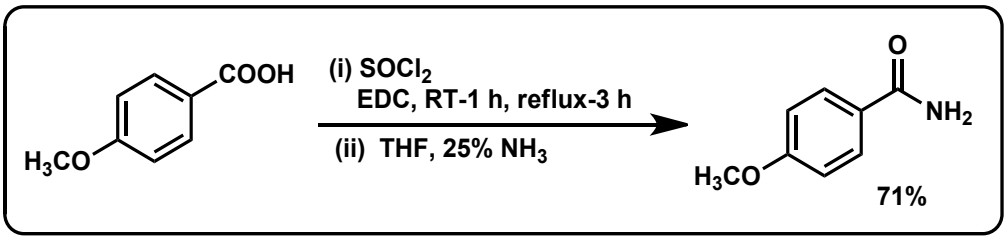
Colour and appearance: White solid

M.pt: 200 °C – 201 °C (Lit. m.pt = 196 °C – 198 °C)[2]

Spectral data:

^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 7.74 (1H, br, s), 8.09 (2H, d, *J* = 12 Hz), 8.30 (3H, d, *J* = 12 Hz). **^{13}C NMR**: (100 MHz, DMSO-d_6) δ (ppm): 123.9, 129.3, 140.4, 149.5, 166.7. **GC-MS (EI^{+}) *m/z***: $[M]^{+}$ 166.05

Synthesis of 4-methoxybenzamide



The general procedure stated above was followed. 4-Methoxy benzoic acid (500 mg, 3.28 mmol), thionyl chloride (0.70 mL, 9.86 mmol), 25% of ammonia solution (4.5 mL 65.6 mmol). Pure product was obtained as white solid in 351 mg (71% yield).

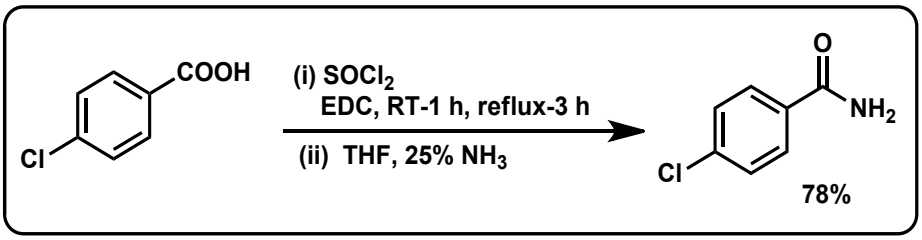
Physical Characteristics:

Colour and appearance: White solid

M.pt: 165 °C – 166 °C (Lit. m.pt = 165 °C – 167 °C)[3]

Spectral data: **^{1}H NMR**: (400 MHz, DMSO-d_6) δ (ppm): 3.80 (3H, s), 6.97 (2H, d, *J* = 12 Hz), 7.19 (1H, s), 7.85 (3H, d, *J* = 8 Hz). **^{13}C NMR**: (100 MHz, DMSO-d_6) δ (ppm): 55.7, 113.8, 126.9, 129.8, 162.0, 167.9. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 151.10.

Synthesis of 4- chlorobenzamide



The general procedure stated above was followed. 4-Chloro benzoic acid (500 mg, 3.20 mmol), thionyl chloride (0.69 mL, 9.61 mmol), 25% of ammonia solution (4.3 mL 64.0 mmol). Pure product was obtained as white solid in 387 mg (78% yield).

Physical Characteristics:

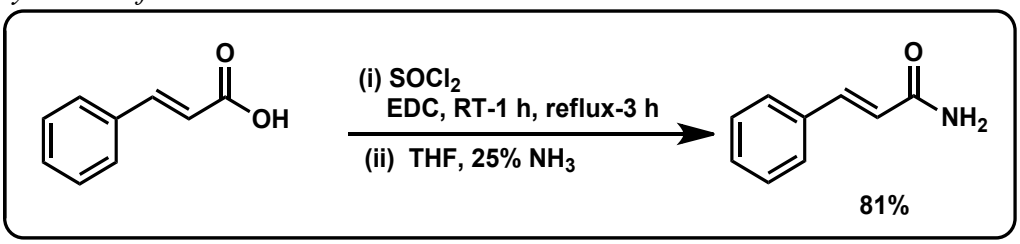
Colour and appearance: White solid

M.pt: 175 °C – 176 °C (Lit. m.pt = 178 °C – 180 °C)[2]

Spectral data:

^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 7.47 (1H, br, s), 7.52 (2H, d, *J* = 12 Hz), 7.89 (2H, d, *J* = 8 Hz), 8.06 (1H, s). **^{13}C NMR**: (100 MHz, DMSO-d_6) δ (ppm): 128.7, 129.8, 133.4, 136.5, 167.3. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 155.05.

Synthesis of cinnamic amide



The general procedure stated above was followed. Cinnamicacid (500 mg, 3.37 mmol), thionyl chloride (0.73 mL, 10.1 mmol), 25% of ammonia solution (4.6 mL, 67.4 mmol). Pure product was obtained as white solid in 401 mg (81% yield).

Physical Characteristics:

Colour and appearance: White solid

M.pt: 148 °C – 150 °C (Lit. m.pt = 145 °C – 146 °C)[4]

Spectral data:

^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 6.64 (1H, d, *J* = 16 Hz), 7.14 (1H, br, s), 7.35- 7.46 (4H, m), 7.56 (3H, d, *J* = 8 Hz). **^{13}C NMR**: (100 MHz, DMSO-d_6) δ (ppm): 127.5, 132.7, 134.1, 134.6, 140.0, 144.4, 172.0. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 147.00.

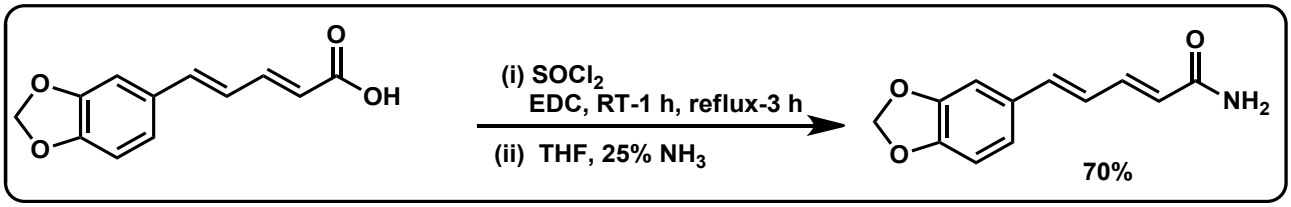
Synthesis of piperic amide

Synthesis of piperic acid from piperine

A literature reported procedure was followed for synthesis of piperic acid from piperine.[6]

To a cold solution of piperic acid in EDC at 0 °C under N_2 atmosphere, thionyl chloride was added slowly, the reaction mixture was stirred for 1h at room temperature and then refluxed for 3 hours. Excess thionyl chloride was distilled off. Without further purification the crude product was taken to next step.

To a cold solution (5 ºC) of ammonia, the prepared acid chloride in THF was added dropwise and stirred vigorously at RT for 3 h. The obtained solid was filtered, washed with water, and dried.



The general procedure stated above was followed. Piperic acid (500 mg, 2.29 mmol), thionyl chloride (0.49 mL, 6.88 mmol), 25% of ammonia solution (3 mL 45.8 mmol). The pure product was obtained as brown solid in 348 mg (70% yield).

Physical Characteristics:

Colour and appearance: Brown Solid

M.pt: 189 °C – 191 °C

Spectral data:

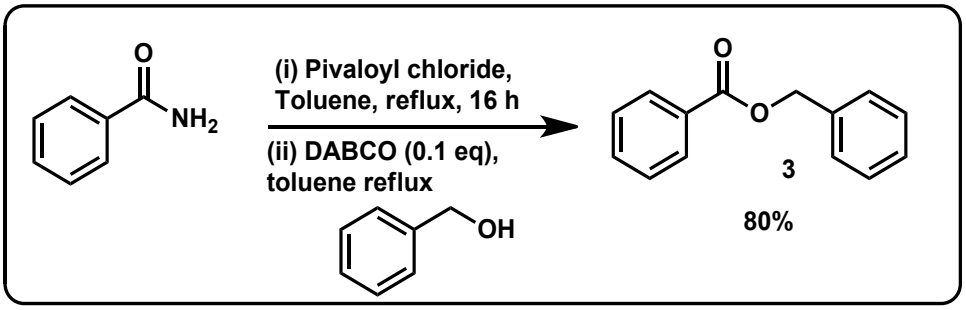
^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 6.04 -6.09 (3H, m), 6.86- 6.91 (3H, m), 6.95- 7.01 (2H, m), 7.14 (1H, dd, *J* = 12 Hz, *J* = 4 Hz), 7.25 (1H, s), 7.48 (1H, s). **^{13}C NMR**: (100 MHz, DMSO-d_6) δ (ppm): 101.7, 106.1, 108.9, 123.0, 125.0, 125.7, 131.2, 138.3, 140.3, 148.1, 148.3, 167.5. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 217.10.

General procedure-A: **Esterification of benzamide with alkyl alcohols**

To a stirred solution of benzamide (1 eq.), in toluene (10 mL) at room temperature, pivaloyl chloride (1 eq.), was added dropwise. After addition, the reaction mixture was refluxed for 16 h.

The reaction mixture was cooled down to room temperature and then alkyl alcohol (2 eq.) and DABCO (0.1 eq.) were added at room temperature and heated to toluene reflux temperature. Progress of the reaction was monitored by TLC. Starting material consumed within 6-24 h with all the tested alcohols. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The pure product was obtained after column chromatography.

Esterification of benzamide with benzyl alcohol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), benzyl alcohol (178 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as pale-yellow liquid in 139 mg (80% yield).

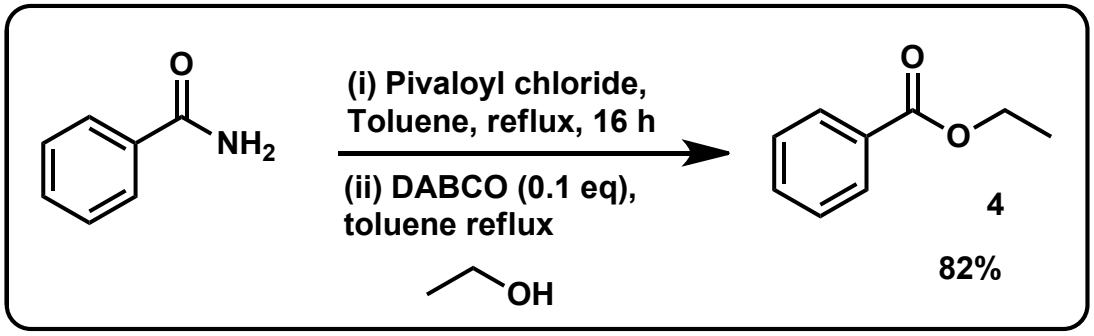
Physical Characteristics:

Colour and appearance: Pale yellow liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.41 (2H, s), 7.38-7.59 (7H, m), 7.51 (1H, t, J = 4 Hz), 8.12 (2H,d, J = 8 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 66.7, 128.1, 128.4, 128.6, 129.7, 130.1, 133.6, 136.1, 140.9,166.4. **GC-MS (EI$^+$) *m/z***: (M^+): 212.05

Esterification of benzamide with ethanol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), ethanol (76 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a colourless liquid in 101 mg (82% yield).

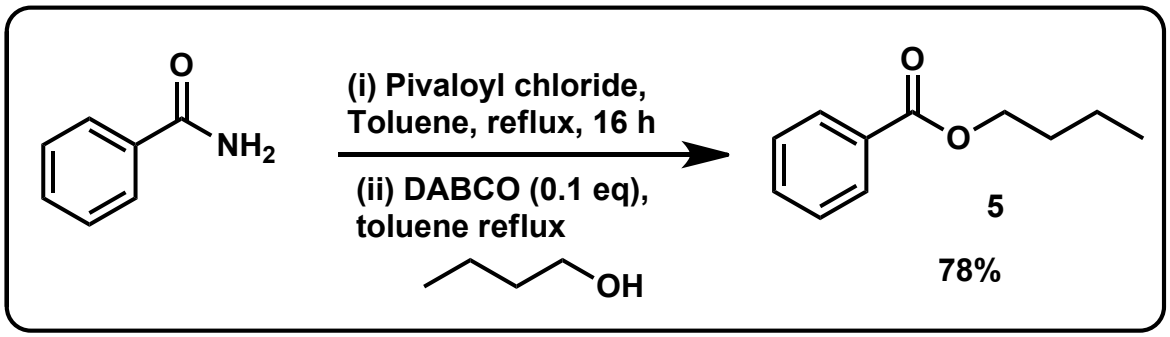
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.32 (3H, t, J = 8 Hz), 4.28 - 4.33 (2H, m), 7.36 (2H, t, J = 8 Hz), 7.47 (1H, t, J = 8 Hz), 7.97 (2H, d, J = 8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 14.3, 60.9, 128.3, 129.5, 130.5, 132.8, 166.6. **GC-MS (EI$^+$) *m/z***: (M^+): 150.00.

Esterification of benzamide with *N*-Butanol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), n-Butanol (122 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a colourless liquid in 114 mg (95% yield).

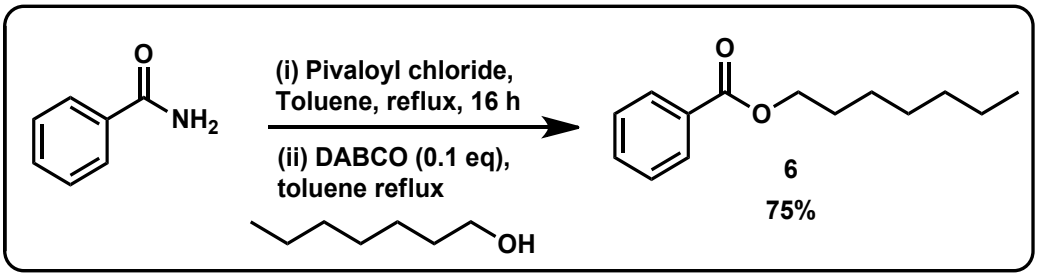
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.90 (3H, t, *J* = 8 Hz), 1.35 – 1.45 (2H, m), 1.64 – 1.171 (2H, m), 4.25 (2H, t, *J* = 8 Hz), 7.35 (2H, t, *J* = 8 Hz), 7.44 – 7.48 (1H, m), 7.96 (2H, d, *J* = 4 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 13.7, 19.2, 30.7, 64.8, 128.3, 129.5, 130.5, 132.7, 166.7. **GC-MS (EI$^+$) *m/z***: (M^+): 178.10.

Esterification of benzamide with n-heptanol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), n-heptanol (191 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a colourless liquid in 136 mg (75% yield).

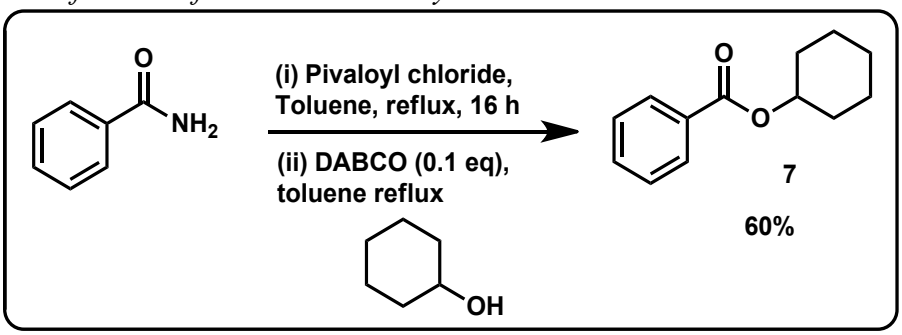
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.80 (3H, t, *J* = 8 Hz), 1.22 – 1.38 (8H, m), 1.65 – 1.72 (2H, m), 4.23 (2H, t, *J* = 8 Hz), 7.35 (2H, t, *J* = 8 Hz), 7.46 (1H, t, *J* = 8 Hz), 7.96 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 14.0, 22.6, 26.0, 28.7, 28.9, 31.7, 65.1, 128.3, 129.5, 130.5, 132.7, 166.6. **GC-MS (EI$^+$) *m/z***: (M^+): 220.10.

Esterification of benzamide with cyclo-hexanol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), cyclohexanol (43 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a colourless liquid in 100 mg (60% yield).

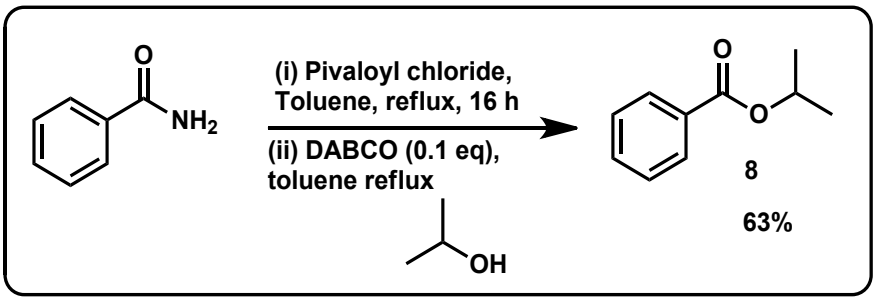
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.33 – 1.40 (3H, m), 1.48 – 1.54 (3H, m), 1.69 – 1.73 (2H, m), 1.85 – 1.89 (2H, m), 4.93 – 4.99 (1H, m), 7.35 (2H, t, *J* = 8 Hz), 7.44 – 7.48 (1H, m), 7.97 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 23.6, 25.5, 31.6, 73.0, 128.2, 129.5, 131.0, 132.6, 166.0. **GC-MS (EI$^+$) *m/z***: (M^+): 204.00.

Esterification of benzamide with iso-propylalcohol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), iso-propylalcohol (99 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a colourless liquid in 85 mg (63% yield).

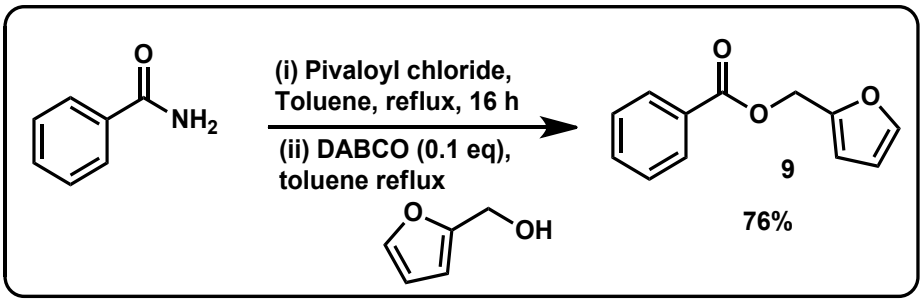
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.31 (6H, d, *J* = 8 Hz), 5.17 – 5.23 (1H, m), 7.36 (2H, t, *J* = 8 Hz), 7.47 (1H, t, *J* = 8 Hz), 7.98 (2H, d, *J* = 8 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 17.1, 63.5, 123.5, 124.7, 126.1, 127.9, 161.3. **GC-MS (EI$^+$) *m/z***: (M^+): 164.05.

Esterification of benzamide with furfuryl alcohol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), Furfuryl alcohol (161 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as yellow liquid in 176 mg (76% yield).

Physical Characteristics:

Colour and appearance: Yellow liquid

Spectral data:

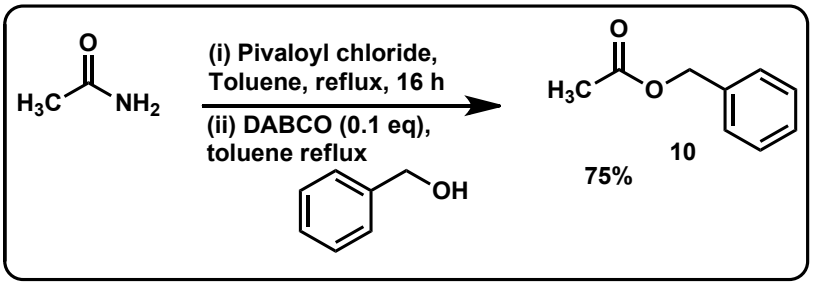
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.22 (2H, s), 6.29 (1H, d, J = 4 Hz), 6.40 (1H, d, J = 4 Hz), 7.30 – 7.35 (3H, m), 7.45 (1H, t, J = 8 Hz), 7.96 (2H, d, J = 8 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 58.5, 110.6, 110.7, 128.3, 129.7, 129.9, 133.0, 143.3, 149.5, 166.2. **GC-MS (EI$^+$) *m/z***: (M^+): 202.05.

General procedure-B one-pot condition: Esterification of various amides with benzyl alcohol

To a stirred solution of various amides (1 eq.), in toluene (10 mL) at room temperature, pivaloyl chloride (1 eq.), was added dropwise. After addition the reaction mixture was refluxed for 16 h. The reaction mixture was cooled down to room temperature. Without further purification the crude product was taken to next step.

To the above synthesized imide in toluene, benzyl alcohol (2 eq.) and DABCO (0.1 eq.) was added at room temperature and heated to toluene reflux temperature. Progress of the reaction was monitored by TLC. Starting material consumed within 6-8 h with all the tested amides. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The pure product was obtained after column chromatography.

Esterification of Acetamide with benzyl alcohol



The general procedure-B stated above was followed. Acetamide (100 mg, 1.69 mmol), pivaloyl chloride (203 mg, 1.69mmol), benzyl alcohol (365 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as colourless liquid in 190 mg (75% yield).

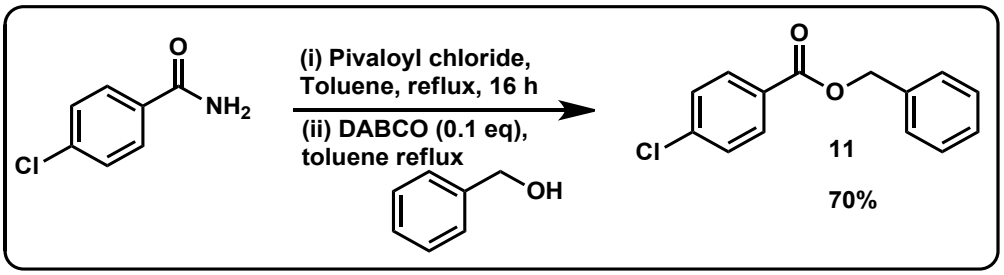
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.01 (3H, s), 5.02 (2H, s), 7.22 – 7.25 (1H, m), 7.27 (4H, d, *J* = 4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 21.0, 66.3, 128.28, 128.29, 128.5, 135.9, 170.9. **GC-MS (EI^{+})** ***m/z***: (M^{+}): 150.10.

Esterification of 4-chloro benzamide with benzyl alcohol



The general procedure-B stated above was followed. 4-Chlorobenzamide (100 mg, 0.64 mmol), pivaloyl chloride (77 mg, 0.64mmol), benzyl alcohol (137 mg, 1.28 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as yellow liquid in 110 mg (70% yield).

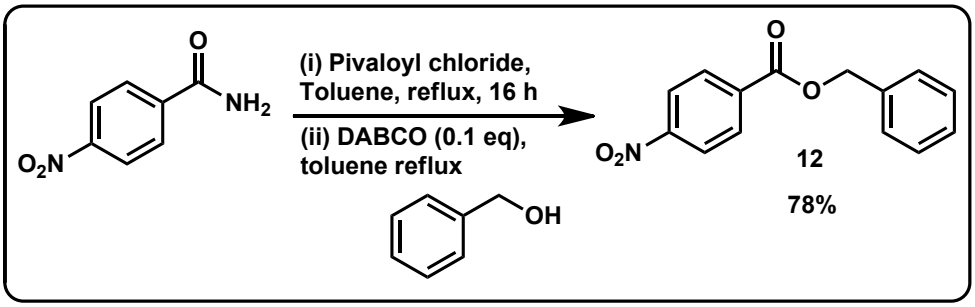
Physical Characteristics:

Colour and appearance: Yellow liquid

Spectral data:

^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 5.26 (2H, s), 7.25 – 7.32 (5H, m), 7.34 (2H, d, J = 8 Hz) , 7.91 (2H, d, J = 8 Hz).**^{13}C NMR:** (100 MHz, DMSO-d_6) δ (ppm): 66.9, 128.2, 128.4, 128.61, 128.68, 128.7, 131.1, 135.8, 139.5, 165.6. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 246.05

Esterification of 4-nitro benzamide with benzyl alcohol



The general procedure-B stated above was followed. 4-Nitrobenzamide (100 mg, 0.60 mmol), pivaloyl chloride (72 mg, 0.60mmol), benzyl alcohol (129 mg, 1.20 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as pale yellow solid in 120 mg (78% yield).

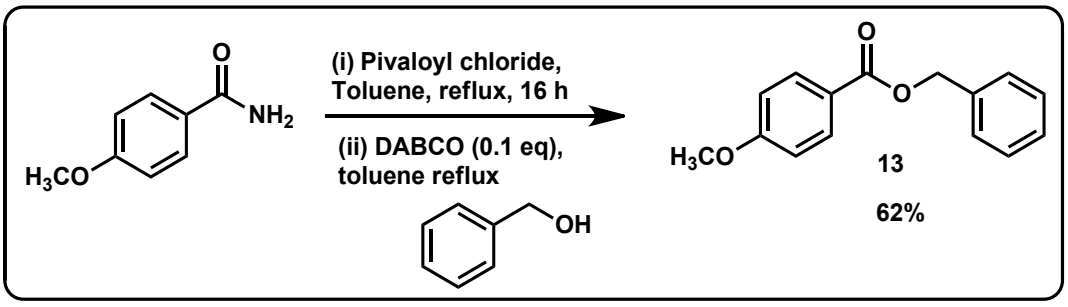
Physical Characteristics:

Colour and appearance: Pale yellow solid

Spectral data:

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 5.35 (2H, s), 7.30 – 7.35 (3H, m), 7.37 – 7.41 (2H, m), 8.16 – 8.23 (2H, m).**^{13}C NMR:** (100 MHz, $CDCl_3$) δ (ppm): 62.9, 118.8, 123.7, 123.9, 124.0, 126.0, 130.5, 130.7, 145.8, 159.8. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 257.05

Esterification of 4-methoxybenzamide with benzyl alcohol



The general procedure-B stated above was followed. 4-Methoxybenzamide (100 mg, 0.66 mmol), pivaloyl chloride (79.5 mg, 0.66mmol), benzyl alcohol (143 mg, 1.32 mmol). Pure product was

obtained after column chromatography (Hexane: EtOAc (90:10)) as colourless liquid in 99 mg (62% yield).

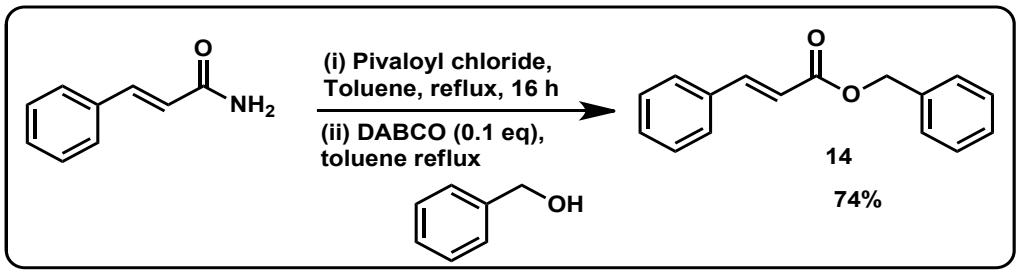
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR: (400 MHz, $CDCl_3$) δ: 3.74 (3H, s), 5.25 (2H, s), 6.82 (2H, d, *J* = 8 Hz), 7.24 – 7.31 (3H, m), 7.35 (2H, d, *J* = 8 Hz), 7.95 (2H, d, *J* = 8 Hz). **^{13}C NMR:** (100 MHz, $CDCl_3$)) δ: 55.4, 6 6.4, 113.6, 122.5, 128.12, 128.16, 128.5, 131.7, 136.3, 163.4, 166.2. **GC-MS (EI$^+$)** ***m/z***: $[M]^+$ 242.10.

Esterification of cinnamic-amide with benzyl alcohol



The general procedure-B stated above was followed. Cinnamic amide (100 mg, 0.67 mmol), pivaloyl chloride (80 mg, 0.67mmol), benzylalcohol (144 mg, 1.34 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as pale yellow liquid in 118 mg (74% yield).

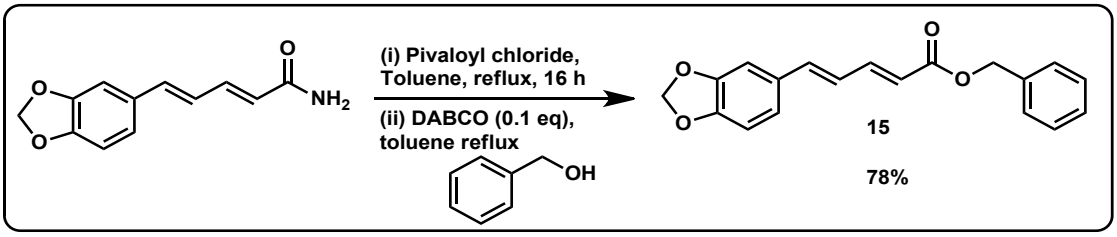
Physical Characteristics:

Colour and appearance: Pale yellow liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.17 (2H, s), 6.40 (1H, d, *J* = 16 Hz), 7.27 – 7.30 (5H, m), 7.31- 7.35 (3H, m), 7.42 – 7.44 (2H, m), 7.65 (1H, d, *J* = 16 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 66.4, 117.9, 128.1, 128.30, 128.32, 128.6, 128.9, 130.3, 134.3, 145.2, 166.8 **GC-MS (EI$^+$)** ***m/z***: (M^+): 238.10.

Esterification of piperic-amide with benzyl alcohol



The general procedure-B stated above was followed. Piperic amide (100 mg, 0.46 mmol), pivaloyl chloride (55 mg, 0.46mmol), benzyl alcohol (99 mg, 0.92 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as yellow viscous oil in 96 mg (78 % yield).

Physical Characteristics:

Colour and appearance: Yellow viscous oil

Spectral data:

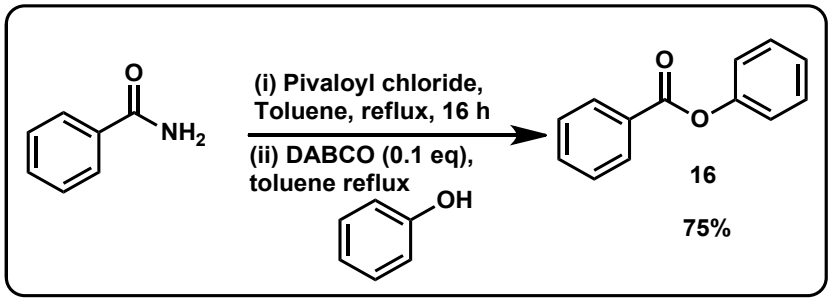
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.13 (2H, s), 5.89 (2H, s), 6.57-6.74 (3H, m), 6.82 (1H, d, *J* = 4Hz), 6.90 (1H, s), 7.23-7.40 (6H, m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 66.1, 101.4, 105.9, 108.5, 120.0, 123.0, 124.4, 127.0, 128.1, 128.2, 128.4, 130.5, 136.2, 140.4, 145.3, 148.3, 148.6, 166.9. **GC-MS (EI$^+$) *m/z***: (M^+): 308.10.

General procedure-C one-pot condition: Esterification of benzamide with phenols.

To a stirred solution of benzamide (1 eq.), in toluene (10 mL) at room temperature, pivaloyl chloride (1 eq.), was added dropwise. After addition, the reaction mixture was refluxed for 16 h. The reaction mixture was cooled down to room temperature. Without further purification the crude prodSuct was taken to next step.

To the above synthesized imide in toluene, phenol (2 eq.) and DABCO (0.1 eq.) were added at room temperature and heated to toluene reflux temperature. Progress of the reaction was monitored by TLC. Starting material consumed within 6-24 h with all the tested phenols. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. Pure product was obtained after column chromatography.

Esterification of benzamide with phenol



The general procedure-C stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825 mmol), Phenol (317 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as white solid in 122 mg (75% yield).

Physical Characteristics:

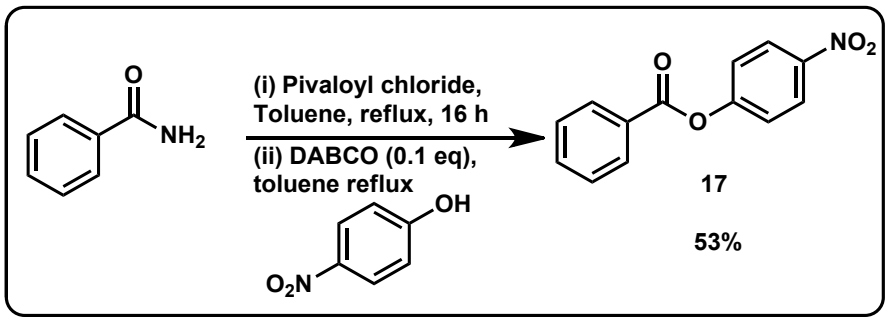
Colour and appearance: White solid

M.pt: 72 °C – 75 °C (Lit. m.pt = 71 °C – 72 °C)[5]

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 7.12 – 7.20 (3H, m), 7.34 (2H, t, J = 8 Hz), 7.42 (2H, t, J = 8 Hz), 7.52 – 7.56 (1H, m), 8.12 (2H, d, J = 8 Hz).**^{13}C NMR** (100 MHz, DMSO- d_6) δ (ppm): 121.7, 125.9, 128.6, 129.5, 129.6, 130.2, 133.6, 151.0, 165.2. **GC-MS (EI^{+}) *m/z***: (M^{+}): 198.10

Esterification of Benzamide with nitrophenol



The general procedure-C stated above was followed benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.826 mmol), 4-nitrophenol (470 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as off-white solid in 106 mg (53% yield).

Physical Characteristics:

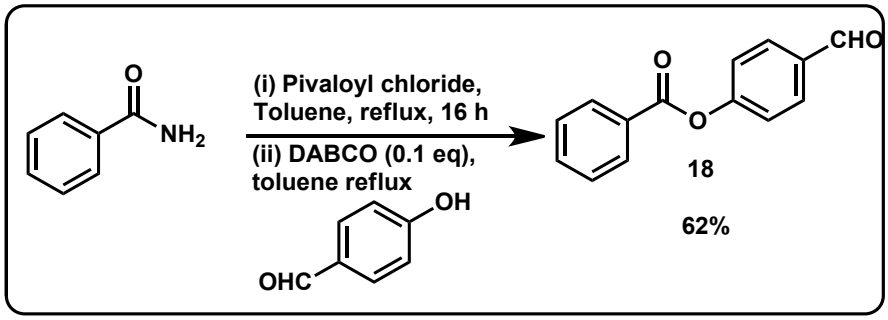
Colour and appearance: Off-white solid

M.pt: 142 °C – 145 °C (Lit. m.pt = 145 °C – 146 °C)[5]

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 7.61 – 7.65 (4H, m), 7.76 – 7.80 (1H, m), 8.16 (2H, d, *J* = 8 Hz), 8.35 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, DMSO- d_6) δ (ppm): 123.8, 125.7, 128.7, 129.5, 130.4, 134.9, 145.6, 155.9, 164.4. **GC-MS (EI$^+$) *m/z***: (M^+): 243.00

Esterification of Benzamide with 4-hydroxybenzaldehyde



The general procedure-C stated above was followed. benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.825 mmol), 4-hydroxybenzaldehyde (412 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as white solid in 115 mg (62% yield).

Physical Characteristics:

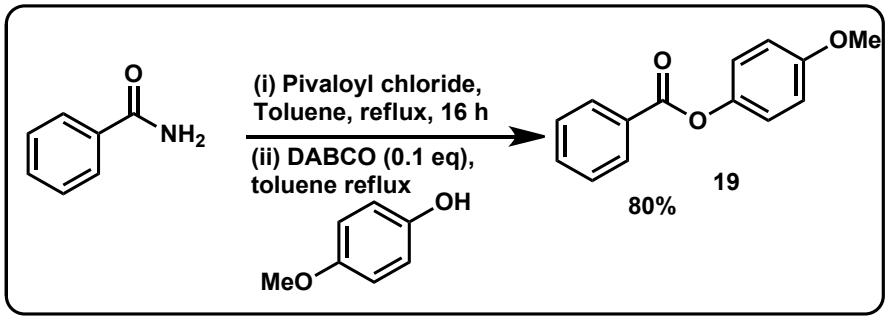
Colour and appearance: White solid

M.pt: 82 °C – 85 °C (Lit. m.pt = 83 °C – 85 °C)[8]

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 7.55(2H, d, *J* = 8 Hz), 7.63(2H, t, *J* = 8 Hz), 7.75 – 7.79(1H, m), 8.04 (2H, d, *J* = 8 Hz), 8.14 – 8.17(2H, m). **^{13}C NMR** (100 MHz, DMSO- d_6) δ (ppm): 123.3, 128.9, 129.5, 130.3, 131.6, 134.5, 134.7, 155.6, 164.6, 192.5. **GC-MS (EI$^+$) *m/z***: (M^+): 226.05.

Esterification of Benzamide with methoxyphenol



The general procedure-C stated above was followed. benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.825 mmol), methoxyphenol *(*419 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as white solid in 150 mg (80% yield).

Physical Characteristics:

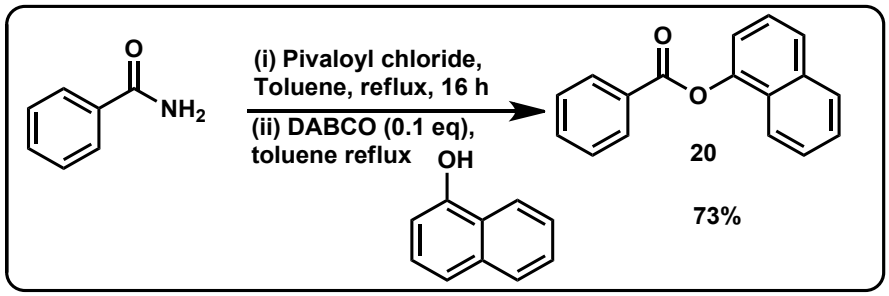
Colour and appearance: White solid

M.pt: 85 °C – 88 °C (Lit. m.pt = 83.1 °C – 84.7 °C)[7]

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 3.78 (3H, s), 7.01 (2H, s, *J* = 8 Hz), 7.20 (2H, d, *J* = 8 Hz), 7.60 (2H, t, *J* = 8 Hz), 7.74 (1H, t, *J* = 8 Hz), 8.12 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, DMSO- d_6) δ (ppm): 55.9, 114.9, 123.1, 129.4, 129.5, 130.1, 134.4, 144.4, 157.4, 165.3. **GC-MS (EI^{+}) *m/z***: (M^{+}): 228.10.

Esterification of benzamide with 4-hydroxy naphthalene



The general procedure-C stated above was followed. Benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.825 mmol), 4-hydroxynaphthalene (486 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as colourless liquid in 149 mg (73% yield).

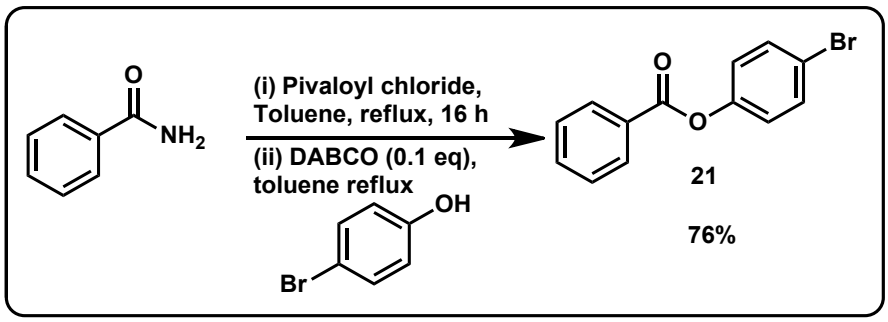
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 7.45 (1H, d, *J* = 4 Hz), 7.55 – 7.58 (3H, m), 7.62 (2H, t, *J* = 8 Hz), 7.74 (1H, t, *J* = 8 Hz), 7.85 (1H, d, *J* = 8 Hz), 7.96 (1H, d, *J* = 8 Hz), 8.00 – 8.03 (1H, m), 8.41 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, DMSO- d_6) δ (ppm): 118.3, 121.3, 125.5, 126.1, 126.56, 126.59, 127.0, 128.1, 128.8, 129.4, 130.3, 133.8, 134.7, 146.9, 165.2. **GC-MS (EI$^+$) *m/z***: (M^+): 248.10.

Esterification of benzamide with bromophenol



The general procedure-C stated above was followed. benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.825 mmol), 4-bromophenol (584 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as off-white solid in 173 mg (76% yield).

Physical Characteristics:

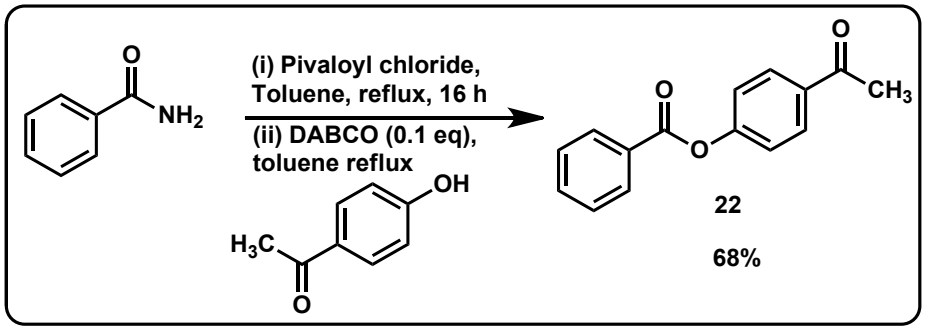
Colour and appearance: Off-white solid

M.pt: 101 °C – 102 °C (Lit. m.pt = 99 °C – 100 °C)[6]

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 7.29 (2H, d, *J* = 8 Hz), 7.61 (2H, t, *J* = 8 Hz), 7.66 (2H, d, *J* = 8 Hz), 7.74 – 7.78 (1H, m), 8.13 (2H, d, *J* = 8 Hz).**^{13}C NMR** (100 MHz, DMSO- d_6) δ (ppm): 118.8, 124.7, 129.1, 129.4, 130.3, 132.9, 134.6, 150.3, 164.8. **GC-MS (EI$^+$) *m/z***: (M^+): 277.10

Esterification of benzamide with 4-hydroxy acetophenone



The general procedure-C stated above was followed. Benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.825 mmol), 4-hydroxyacetophenone (459 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as white solid in 134 mg (68% yield).

Physical Characteristics:

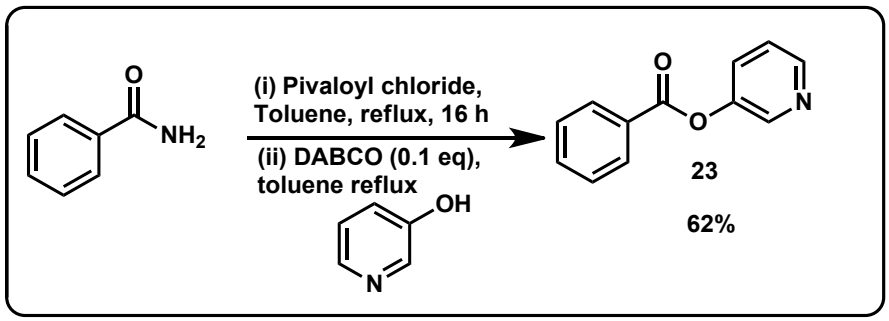
Colour and appearance: White solid

M.pt: 131 °C – 132 °C (Lit. m.pt = 132 °C – 134 °C)[9]

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 2.61 (3H, s), 7.46 (2H, d, *J* = 8 Hz), 7.62 (2H, t, *J* = 8 Hz), 7.77(1H, t, *J* = 8 Hz), 8.07 (2H, d, *J* = 8 Hz), 8.15 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, DMSO- d_6) δ (ppm): 27.2, 122.7, 129.0, 129.4, 130.3, 130.4, 134.7, 135.1, 154.7, 164.7, 197.4. **GC-MS (EI^{+}) *m/z***: (M^{+}): 240.10.

Esterification of Benzamide with 3-hydroxypyridine



The general procedure-C stated above was followed. Benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.825 mmol), 3-hydroxypyridine (321 mg, 3.38 mmol). Pure product was

obtained after column chromatography (Hexane: EtOAc (90:10)) as off-white solid in 101 mg 62% yield).

Physical Characteristics:

Colour and appearance: Off-white solid

M.pt: 51 °C – 52 °C (Lit. m.pt = 50 °C – 50.5 °C)[10]

Spectral data:

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 7.53 – 7.56 (1H, m), 7.63 (2H, t, *J* = 8 Hz), 7.75 – 7.84 (2H, m), 8.17 (2H, d, *J* = 8 Hz), 8.54 (1H, d, *J* = 4 Hz)), 8.61 (1H, d, *J* = 4 Hz).

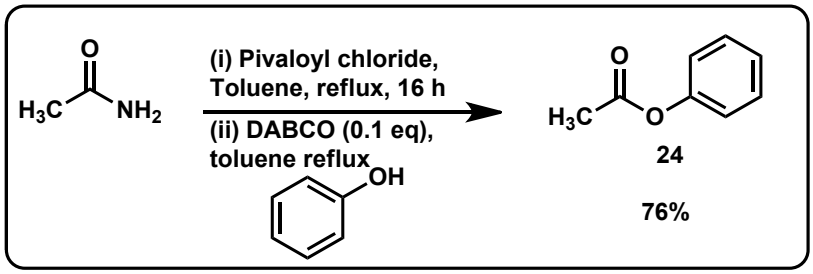
^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm): 124.8, 128.8, 129.4, 130.3, 130.4, 134.7, 143.9, 147.5, 147.8, 164.8. **GC-MS (EI$^+$) *m/z***: (M^+): 199.05.

General procedure-D: Esterification of various amides with phenols.

To a stirred solution of various amides (1 eq.), in toluene (10 mL) at room temperature, pivaloyl chloride (1 eq.), was added dropwise. After addition the reaction mixture was refluxed for 16 h. The reaction mixture was cooled down to room temperature. Without further purification the crude product was taken to next step.

To the above synthesized imide in toluene, benzyl alcohol (2 eq.) and DABCO (0.1 eq.) was added at room temperature and heated upto toluene reflux 110 C. Progress of the reaction was monitored by TLC. Starting material consumed within 8 h- 24 h with all tested amides. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. Pure product was obtained after column chromatography.

Esterification of acetamide with phenol



The general procedure-D stated above was followed. Acetamide (100 mg, 1.69 mmol), pivaloyl chloride (203 mg, 1.69 mmol), Phenol (317 mg, 3.38 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as colourless liquid in 174 mg (76% yield).

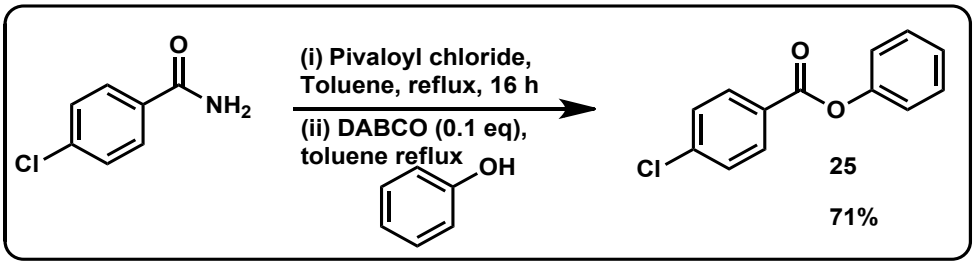
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.21 (3H, s), 7.00 (2H, d, *J* =8 Hz), 7.12 – 7.17 (1H, m), 7.29 (2H, t, *J* = 8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 21.1, 121.5, 125.8, 129.4, 150.7, 169.4. **GC-MS (EI$^+$) *m/z***: (M^+): 136.10

Esterification of 4-chloro benzamide with phenol



The general procedure-D stated above was followed. 4-chlorobenzamide (100 mg, 0.64 mmol), pivaloyl chloride (77 mg, 0.64mmol), phenol (120 mg, 1.28 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as pale brown solid in 105 mg (71% yield).

Physical Characteristics:

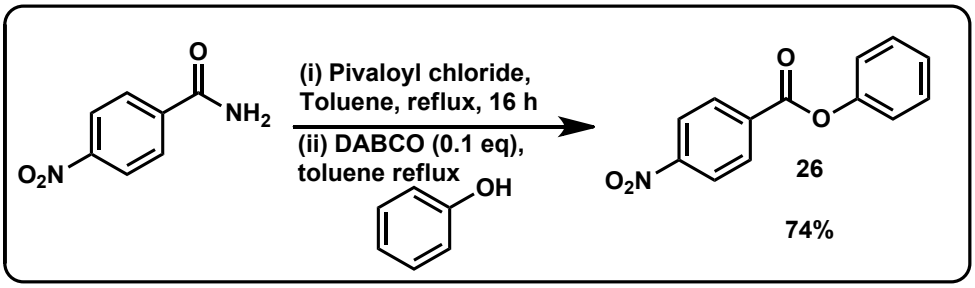
Colour and appearance: Pale brown solid

M.pt: 103 °C – 105 °C (Lit. m.pt = 104 °C – 106 °C)[11]

Spectral data:

^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 7.12 (2H, d, *J* = 8 Hz), 7.16 – 7.21 (1H, m), 7.32 – 7.41(4H, m), 8.05 (2H, d, *J* = 8 Hz). **^{13}C NMR:** (100 MHz, DMSO-d_6) δ (ppm): 121.6, 126.0, 128.0, 128.9, 129.5, 131.5, 140.1, 150.8, 163.3. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 232.10

Esterification of 4-nitro benzamide with Phenol



The general procedure-D stated above was followed. 4-Nitrobenzamide (100 mg, 0.60 mmol), pivaloyl chloride (72 mg, 0.60mmol), phenol (112 mg, 1.20 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as off-white solid in 107 mg (74% yield).

Physical Characteristics:

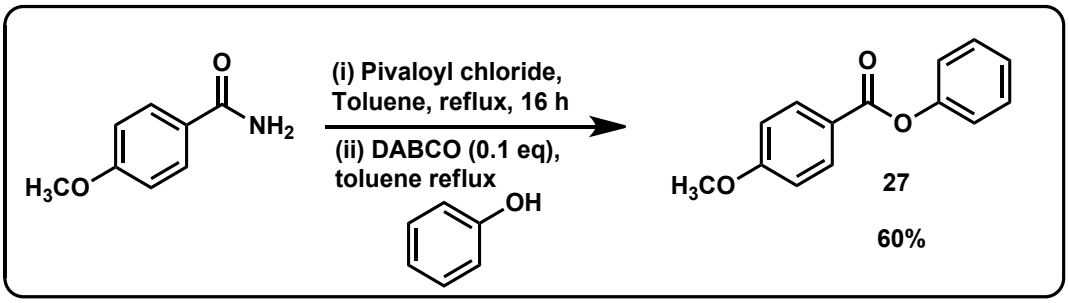
Colour and appearance: Off-white solid

M.pt: 125 °C – 128 °C (Lit. m.pt = 127 °C – 129 °C)[12]

Spectral data:

^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 7.15 – 7.18 (2H, m), 7.24 (1H, t, *J* = 8 Hz), 7.38 (2H, t, *J* = 8 Hz), 8.27 – 8.32 (4H, m). **^{13}C NMR:** (100 MHz, DMSO-d_6) δ (ppm): 121.4, 123.7,126.4, 129.7, 131.3, 135.0, 150.5, 150.9, 163.3. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 243.10

Esterification of 4-methoxybenzamide with phenol



The general procedure-D stated above was followed. 4-Methoxybenzamide (100 mg, 0.66 mmol), pivaloyl chloride (79.5 mg, 0.66mmol), phenol (124 mg, 1.32 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as pale yellow solid in 90 mg (60% yield).

Physical Characteristics:

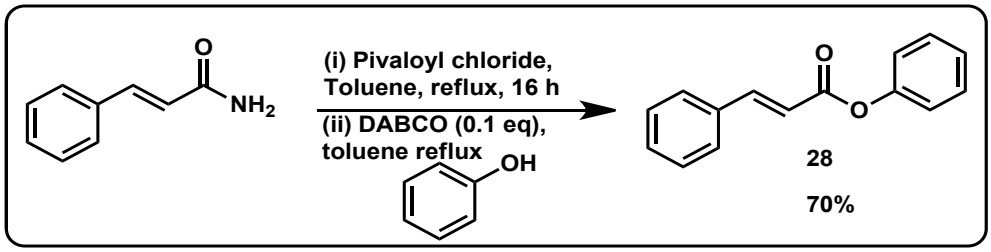
Colour and appearance: Pale yellow solid

M.pt: 71 °C – 72 °C (Lit. m.pt = 74 °C – 76 °C)[11]

Spectral data:

^{1}H NMR: (400 MHz, DMSO-d_6) δ (ppm): 3.87 (3H, s), 7.13(2H, d, *J* = 8 Hz), 7.24 – 7.32 (3H, m), 7.47 (2H, d, *J* = 8 Hz), 8.09 (2H, d *J* = 8 Hz).**^{13}C NMR:** (100 MHz, DMSO-d_6) δ (ppm): 56.1, 114.7, 121.4, 122.4, 126.3, 129.9, 132.4, 151.1, 164.2, 164.7. **GC-MS (EI$^+$) *m/z***: $[M]^+$ 228.10.

Esterification of cinnamic-amide with Phenol



The general procedure-D stated above was followed. Cinnamic amide (100 mg, 0.67 mmol), pivaloyl chloride (80 mg, 0.67mmol), phenol (126 mg, 1.34 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as pale brown solid in 105 mg (70% yield).

Physical Characteristics:

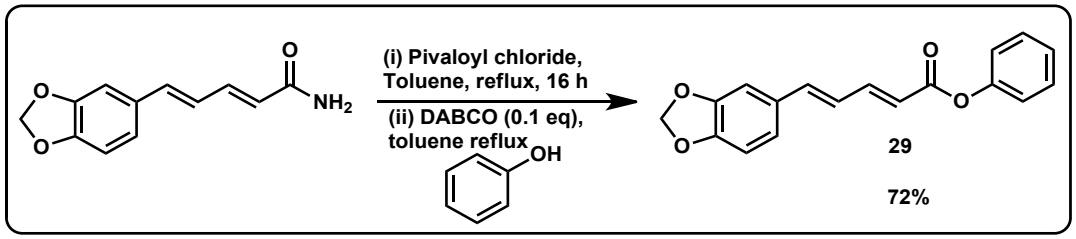
Colour and appearance: Pale brown solid

M.pt: 72 °C – 75°C (Lit. m.pt = 74°C - 76°C)[13]

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.53 (1H, d, *J* = 16 Hz), 7.08 (2H, d, *J* = 8 Hz), 7.14 (1H, t, *J* = 8 Hz), 7.28 – 7.32 (5H, m), 7.46 – 7.48 (2H, m), 7.78 (1H, d, *J* = 16 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 117.3, 121.7, 125.8, 128.3, 129.0, 129.5, 130.7, 134.2, 146.6, 150.8, 165.4. **GC-MS (EI$^+$) *m/z***: (M^+): 224.00.

Esterification of piperic-amide with phenol



The general procedure-D stated above was followed. piperic amide (100 mg, 0.46 mmol), pivaloyl chloride (55 mg, 0.46mmol), phenol (87 mg, 0.92 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as yellow solid in 97 mg (72% yield).

Physical Characteristics:

Colour and appearance: Yellow solid

M.pt: 130 °C – 132 °C

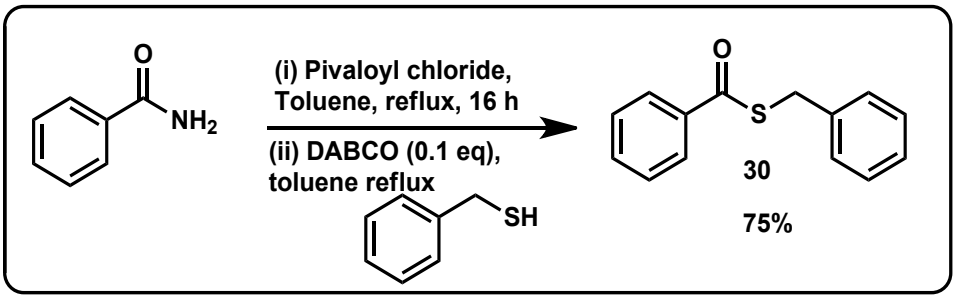
Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.07 (2H, s), 6.22 (1H, d, *J* = 16 Hz), 6.94 (1H, d, *J* = 8 Hz), 7.05 (3H, m), 7.17 (2H, d, *J* = 8 Hz), 7.27 (2H, t, *J* = 8 Hz)), 7.43 (2H, t, *J* = 8 Hz), 7.55 – 7.61 (1H, m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 101.9, 106.3, 109.0, 119.1, 122.2, 124.0, 125.0, 126.1, 129.9, 130.7, 142.1, 147.6, 148.5, 148.9, 151.0, 165.4. **GC-MS (EI$^+$) *m/z***: (M^+): 294.10.

General procedure-E: Esterification of benzamide with thiols.

To a stirred solution of benzamide (1 eq.), in toluene (10 mL) at room temperature, pivaloyl chloride (1 eq.), was added dropwise. After addition, the reaction mixture was refluxed for 16 h. The reaction mixture was cooled down to room temperature. Without further purification the crude product was taken to next step. To the above synthesized imide in toluene, thiol (2 eq.) and DABCO (0.1 eq.) were added at room temperature and refluxed. Progress of the reaction was monitored by TLC. Starting material consumed within 6-8 h with all the tested alcohols. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. Pure product was obtained after column chromatography.

Esterification of benzamide with benzylmercapton



The general procedure-E stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825mmol), benzylmercapton (204 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as colourless liquid in 141 mg (75% yield).

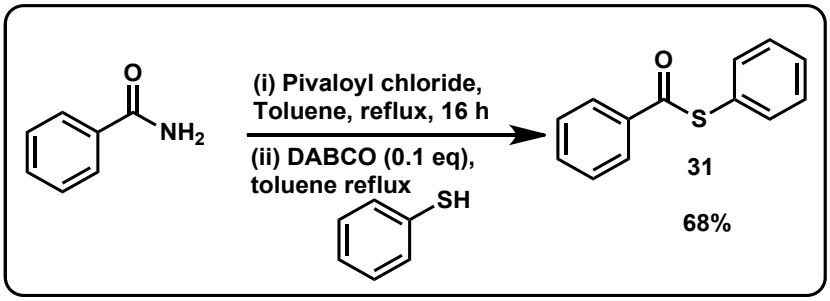
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.21 (2H, s), 7.10 – 7.15 (1H, m), 7.20 (2H, d, *J* = 8 Hz), 7.26 – 7.32 (2H, m), 7.43 (1H, d, *J* = 8 Hz), 7.86 (2H, d, *J* = 8 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 33.4, 127.3, 127.4, 128.70, 128.73, 129.0, 133.5, 136.8, 137.5, 191.2. **GC-MS (EI$^+$) *m/z***: (M^+): 228.10.

Esterification of Benzamide with benzylmercapton



The general procedure-E stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825 mmol), thio-phenol (181 mg, 1.65 mmol). Pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as white solid in 120 mg (68% yield).

Physical Characteristics:

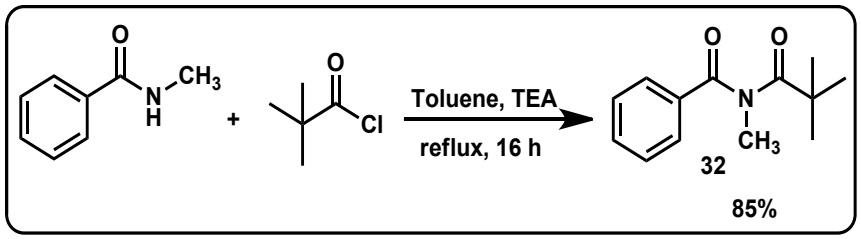
Colour and appearance: White solid

M.pt: 50°C – 51°C (Lit. m.pt = 52° - 53°)[14]

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.41 (4H, m), 7.43- 7.46 (2H, m), 7.50 – 7.54 (1H, m), 7.95 (2H, d, *J* = 8 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 127.3, 127.5, 128.7, 129.2, 129.5, 133.6, 135.1, 136.6, 190.2. **GC-MS (EI$^+$) *m/z***: (M^+): 214.00.

Synthesis of N-methyl N-pivaloyl benzamide



To a stirred solution of *N*-methyl benzamide (250 g, 1.84 mmol), triethylamine (371mg, 3.68 mmol) in 10 mL of toluene at room temperature, pivaloyl chloride (222 mg, 1.84 mmol) was added dropwise. After addition, the reaction mixture was heated to 80 C for 24 h. Progress of the reaction was monitored by TLC [hexane-EtOAc (8:2)]. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. Pure product was obtained after column chromatography as white solid 342 mg (85% yield).

Colour and appearance: White solid

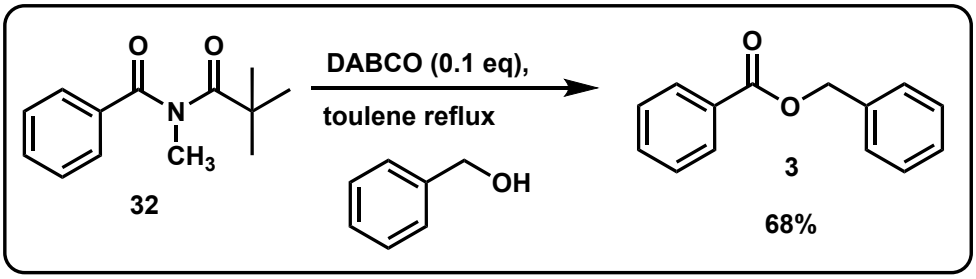
Spectral data:

H NMR: (400 MHz, DMSO-d_6) δ (ppm): 1.26 (9H, s), 3.08 (3H, s), 7.51 (2H, t, *J* = 8 Hz), 7.58 – 7.62 (1H, m), 7.67 (2H, t, *J* = 4 Hz).**^{13}C NMR:** (100 MHz, DMSO-d_6) δ (ppm): 28.4, 35.0, 42.5, 129.0, 129.2, 132.7, 134.8, 174.9, 186.1. **GC-MS (EI$^+$) *m/z***: (M^+): 219.10.

General procedure F: Transamidation of *N*-methyl-*N*-pivaloylbenzamide with alcohols

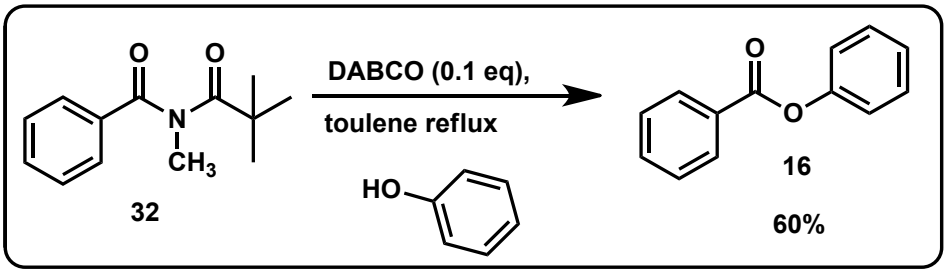
To the *N*-methyl-*N*-pivaloyl benzamide in toluene, alcohol (2 eq.) and DABCO (0.1 eq.) was added at room temperature and refluxed. Progress of the reaction was monitored by TLC. Starting material consumed within 8-12 h with the tested alcohols. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. Pure product was obtained after column chromatography.

Transamidation of N-methyl N-pivaloyl benzamide with benzylalcohol



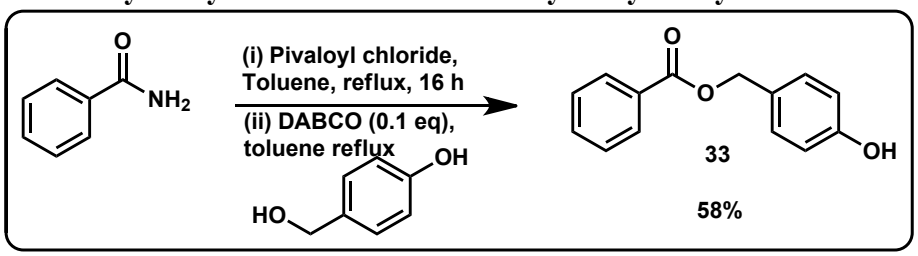
The general procedure-F stated above was followed. *N*-methyl-*N*-pivaloylbenzamide (100 mg, 0.45 mmol), benzylalcohol (98.6 mg, 0.90 mmol). Pure product was obtained after column chromatography pale-yellow liquid in 64 mg (68% yield).

Transamidation of N-methyl N-pivaloyl benzamide with phenol



The general procedure-F stated above was followed. *N*-methyl-*N*-pivaloylbenzamide (100 mg, 0.45 mmol), phenol (84.6 mg, 0.90 mmol). Pure product was obtained after column chromatography pale yellow liquid in 53 mg (60% yield).

Selectivity study-A: Esterification of 4-hydroxy benzyl alcohol



The general procedure-A stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825 mmol), 4-Hydroxy benzyl alcohol (204 mg, 1.65 mmol). The pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a white solid in 109 mg (58% yield).

Physical Characteristics:

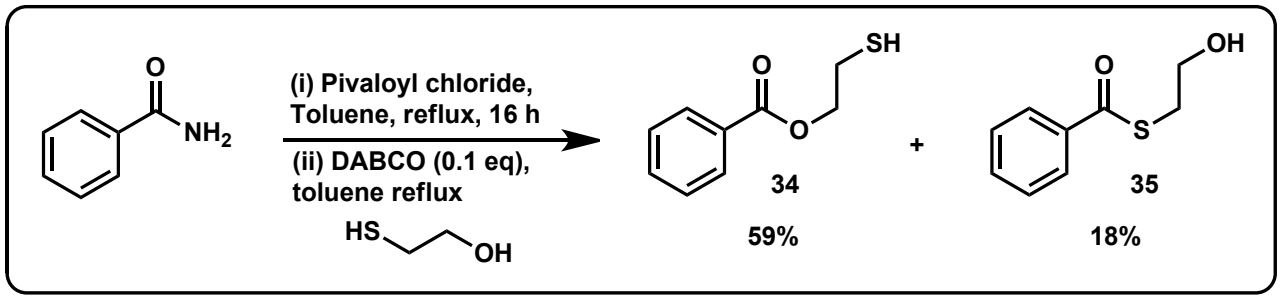
Colour and appearance: White solid

M.pt: 70 °C – 72 °C

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.54 (2H, d, *J* = 4 Hz), 5.29 (1H, t, *J* = 8 Hz), 7.24 (2H, d, *J* = 8 Hz), 7.43 (2H, d, *J* = 8 Hz), 7.61 (2H, t, *J* = 8 Hz), 7.73 – 7.77 (1H, m), 8.14 (2H, d).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 62.8, 121.9, 128.0, 129.43, 129.46, 130.2, 134.4, 140.8, 149.7, 165.1.**GC-MS (EI$^+$) *m/z***: (M^+): 228.05.

Selectivity study-B: Esterification of ethyl mercaptan



The general procedure-B stated above was followed. Benzamide (100 mg, 0.825 mmol), pivaloyl chloride (99 mg, 0.825 mmol), and ethylmercaptan (128 mg, 1.65 mmol). The pure product was obtained after column chromatography (Hexane: EtOAc (90:10)).

Compound-1: Physical Characteristics:

Colour and appearance: Colourless liquid - 88 mg (59% yield).

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.49 (1H, t, *J* = 8 Hz), 2.79 – 2.84 (2H, m), 4.37 (2H, t, *J* = 8 Hz), 7.37 (2H, t, *J* = 8 Hz), 7.47 – 7.51 (1H, m), 7.98 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 23.4, 66.1, 128.4, 129.6, 129.9, 133.1, 166.2. **GC-MS (EI$^+$) *m/z***: (M^+): 182.00.

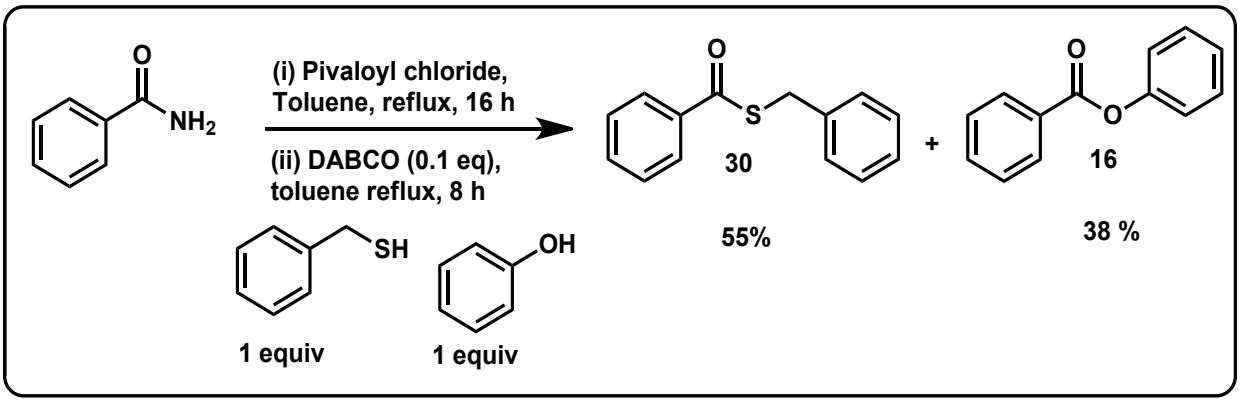
Compound-2: Physical Characteristics:

Colour and appearance: Pale green liquid - 27 mg (18% yield).

Spectral data:

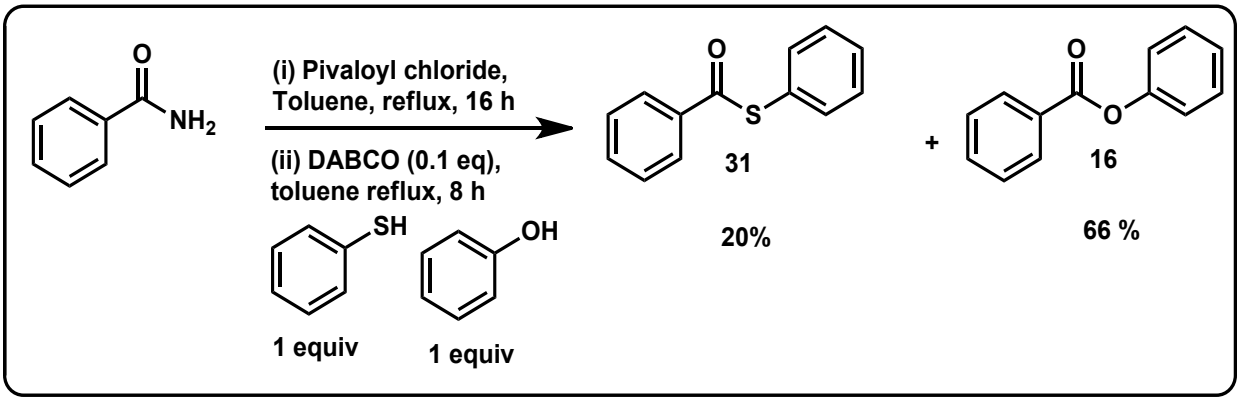
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.16 (2H, t, *J* = 8 Hz), 3.58 – 3.62 (2H, m), 5.09 (1H, t, *J* = 8 Hz), 7.54 (2H, t, *J* = 8 Hz), 7.65 – 7.69 (1H, m), 7.93 (2H, d, *J* = 8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 31.8, 60.2, 127.2, 129.5, 134.2, 136.9, 191.5. **GC-MS (EI$^+$) *m/z***: (M^+): 182.05.

Competitive study C: Benzyl mercaptan vs phenol



To a stirred solution of benzamide (100 mg, 0.825 mmol, 1 eq.), in toluene at room temperature, pivaloyl chloride (99 mg, 0.825 mmol, 1 eq.), was added dropwise. After addition, the reaction mixture was refluxed for 16 h. The reaction mixture was cooled down to room temperature. Without further purification, an equimolar mixture of benzyl mercaptan (102 mg, 0.825 mmol, 1 eq.) and phenol (81 mg, 0.825 mmol, 1 eq.) with DABCO (0.1 eq.) was added at room temperature and heated to toluene reflux temperature. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude mass was column purified to get pure products (**30**) in 102 mg (55%) and (**16**) in 61 mg (38%).

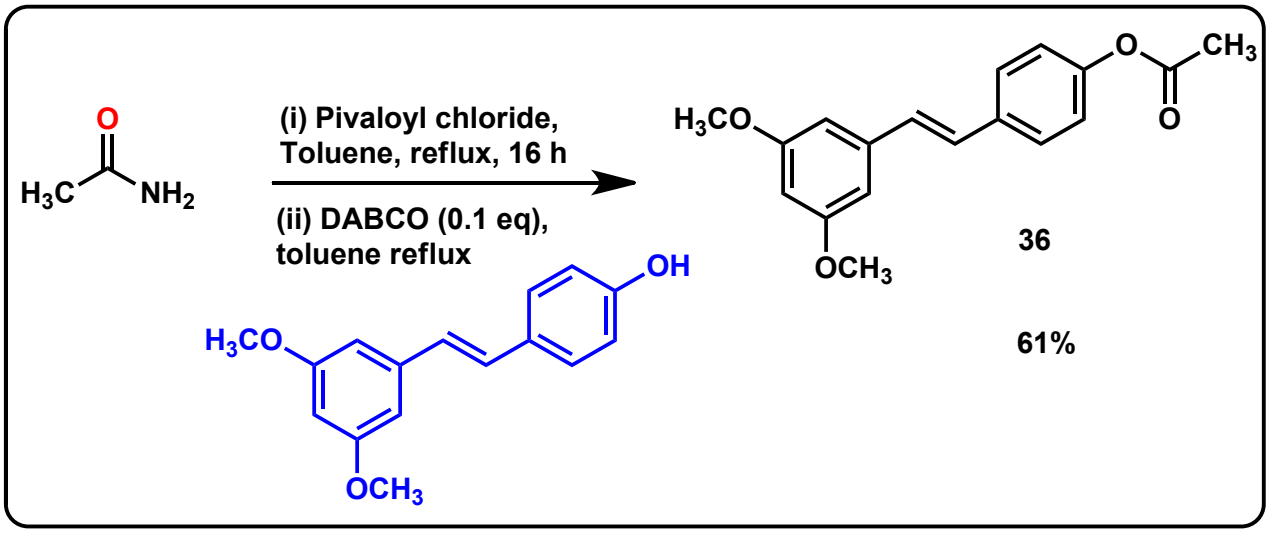
Competitive study D: Thiophenol vs phenol



To a stirred solution of benzamide (100 mg, 0.825 mmol, 1 eq.), in toluene at room temperature, pivaloyl chloride (99 mg, 0.825 mmol, 1 eq.), was added dropwise. After addition, the reaction mixture was refluxed for 16 h. The reaction mixture was cooled down to room temperature. Without further purification, an equimolar mixture of thiophenol (90 mg, 0.825 mmol, 1 equiv.), phenol (81 mg, 0.825 mmol, 1 equiv) and DABCO (0.1 eq.) were added at room temperature and

heated up to toluene reflux 110 C. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was washed with 5% HCl solution, 5% $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude mass was column purified to get pure **31** in 35 mg (20%) and **16** in 107 mg (66%).

Synthesis of acetylated pterostilbene



The general procedure-D stated above was followed. Acetamide (25 mg, 0.423 mmol), pivaloyl chloride (51 mg, 0.423 mmol), and Pterostilbene (216 mg, 0.84 mmol). The pure product was obtained after column chromatography (Hexane: EtOAc (80:20)) as a brown solid in 76 mg (61% yield).

Physical Characteristics:

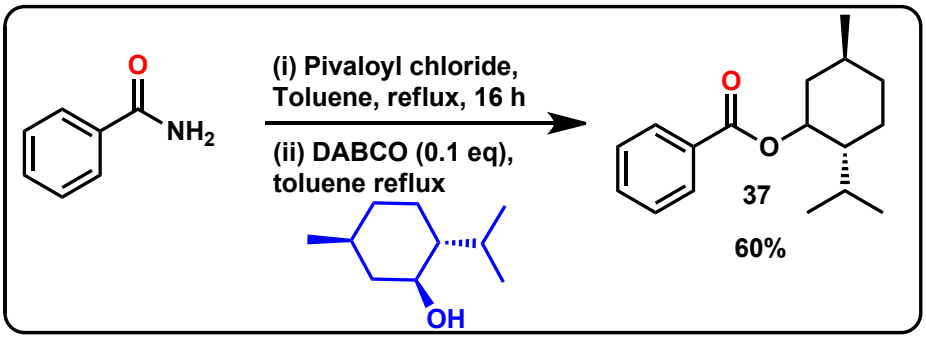
Colour and appearance: Brown solid

M.pt: 125 °C – 126°C (Lit. m.pt = 122°C - 123°C)[15]

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.31(3H, s), 3.83 (6H, s), 6.40 (1H, s), 6.66 (2H, s), 6.96 – 7.10 (4H, m), 7.51 (2H, d, J = 8 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 21.1, 55.4, 100.0, 104.6, 121.8, 127.5, 128.1, 128.9, 134.9, 139.1, 150.1, 161.0, 169.5. **GC-MS (EI$^+$) *m/z***: (M^+): 298.10

Esterification of benzamide with menthol



The general procedure-B stated above was followed. Benzamide (100 mg, 0.826 mmol), pivaloyl chloride (99 mg, 0.825 mmol) and menthol (257 mg, 1.65 mmol). The pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a colourless liquid in 128 mg (60% yield).

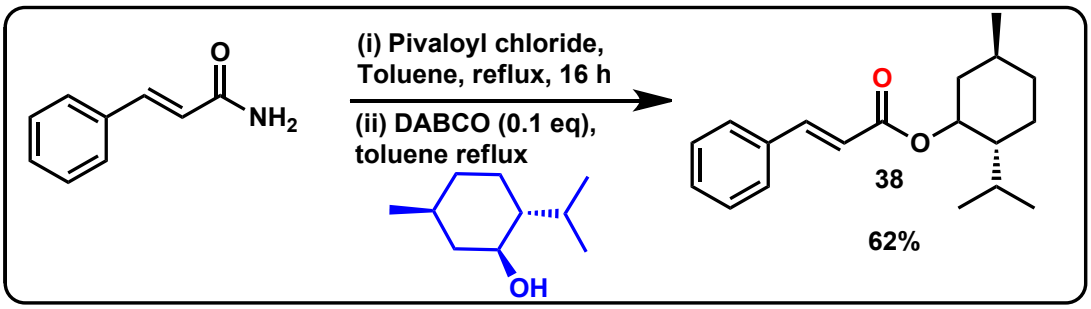
Physical Characteristics:

Colour and appearance: Colourless liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.72 (3H, d, J = 8 Hz), 0.85 (6H, dd, J = 4 Hz, J = 4 Hz), 0.98 – 1.12 (2H, m), 1.18 (1H, s), 1.45 – 1.52 (2H, m), 1.64 – 1.68 (2H, m), 1.86 – 1.92 (1H, m), 2.03 – 2.07 (1H, m), 4.83 – 4.90 (1H, m), 7.36 (2H, t, J = 8 Hz), 7.45 – 7.49 (1H, m), 7.97 (2H, d, J = 8 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 16.5, 20.7, 22.0, 23.6, 26.5, 31.4, 34.3, 41.0, 47.3, 74.8, 128.3, 129.5, 130.9, 132.6, 166.1. **GC-MS (EI$^+$) *m/z***: (M^+): 260.10

Esterification of cinnamamide with menthol



The general procedure-C stated above was followed. Cinnamamide (100 mg, 0.67 mmol), pivaloyl chloride (80 mg, 0.67mmol) and menthol (212 mg, 1.35 mmol). The pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a pale-yellow liquid in 106 mg (62% yield).

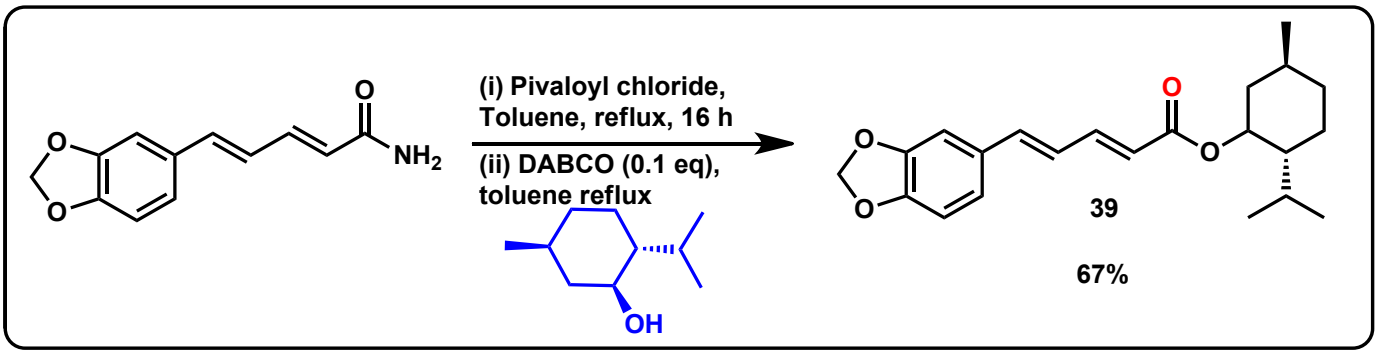
Physical Characteristics:

Colour and appearance: Pale yellow liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.72 (3H, d, *J* = 8 Hz), 0.85 (6H, dd, *J* = 4 Hz, *J* = 4 Hz), 0.96 – 1.04 (2H, m), 1.18 (1H, s,), 1.35 – 1.42 (2H, m), 1.63 (2H, d, *J* = 8 Hz), 1.83 – 1.87 (1H, m), 2.00 (1H, d, *J* = 8 Hz), 4.72 – 4.78 (1H, m), 6.36 (1H, d, *J* = 16 Hz), 7.29 (3H, d, *J* = 4Hz), 7.44 – 7.46 (2H, m), 7.60 (1H, d, *J* = 16 Hz).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 16.4, 20.7, 22.0, 23.5, 26.3, 31.4, 34.3, 41.0, 47.2, 74.2, 118.7, 128.0, 128.8, 130.1, 134.5, 144.3, 166.6.**GC-MS (EI^{+})** ***m/z***: (M^{+}): 286.10.

Esterification of pipericamide with menthol



The general procedure-C stated above was followed. Piperic amide (100 mg, 0.46 mmol), pivaloyl chloride (55 mg, 0.46mmol) and menthol (143 mg, 0.92 mmol). The pure product was obtained after column chromatography (Hexane: EtOAc (90:10)) as a pale-yellow liquid in 109 mg (67% yield).

Physical Characteristics:

Colour and appearance: Pale yellow liquid

Spectral data:

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.71 (3H, d, *J* = 8 Hz), 0.82 – 0.85 (6H, m), 1.21 (2H, s), 1.26 (2H, s), 1.32 – 1.39 (1H, m), 1.60 – 1.64 (1H, m),1.79 – 1.87 (1H, m), 1.96 (1H, d, *J* = 12 Hz), 4.67 - 4.74 (1H, m), 5.86 (1H, d, *J* = 12 Hz), 5.92 (2H, s), 6.59 – 6.66 (1H, m), 6.71 – 6.76 (2H, m), 6.84 (1H, dd, *J* = 8 Hz), 6.92 (1H, s), 7.29 – 7.36 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 16.4, 20.7, 22.0, 23.5, 26.3, 30.2, 31.4, 41.9, 47.2, 74.0, 101.3, 105.8, 108.5, 121.0, 122.8, 124.6, 130.6, 139.9, 144.4, 148.2, 148.5, 166.7.

HRMS (ESI-MS) ***m/z*:** Calculated for $C_{22}H_{29}NO_4$ $[M+H]^{+}$ 357.2065, found: 357.2083.

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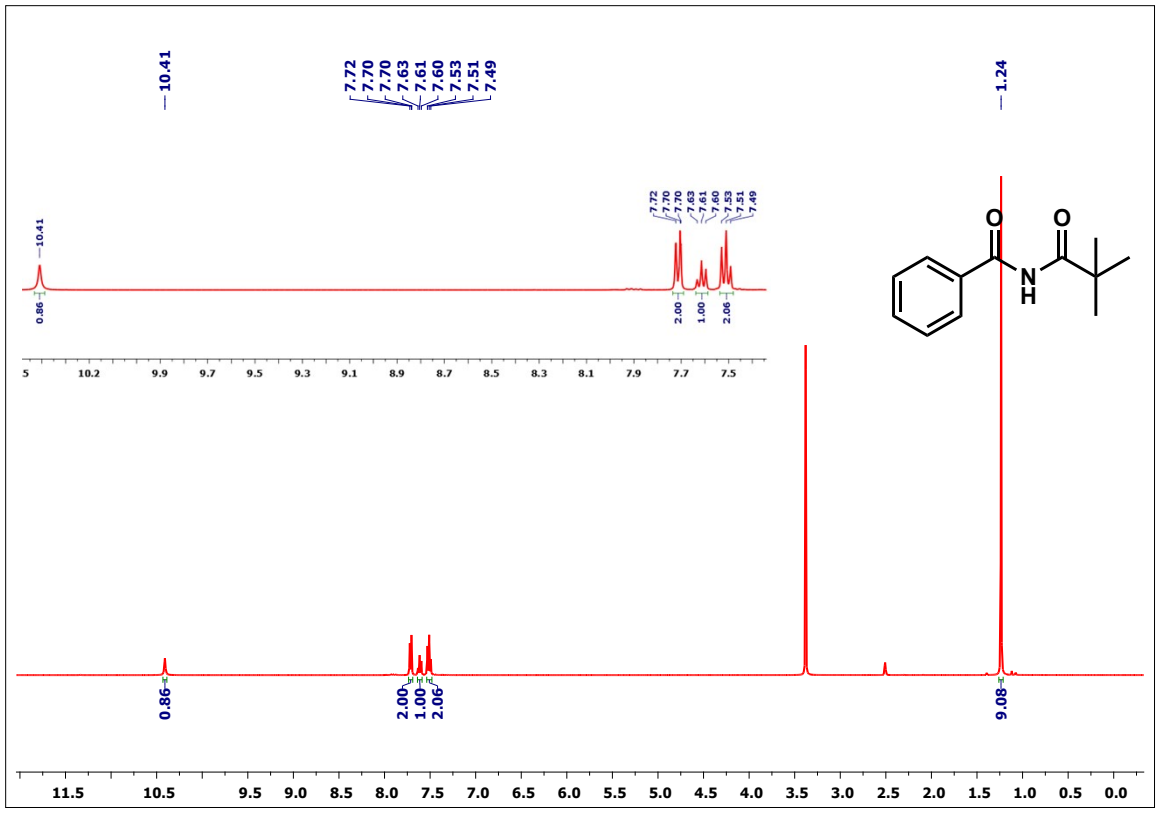

Figure S1: 400 MHz ^{1}H NMR spectrum of *N*-pivaloyl benzamide **1** in DMSO-d$_6$

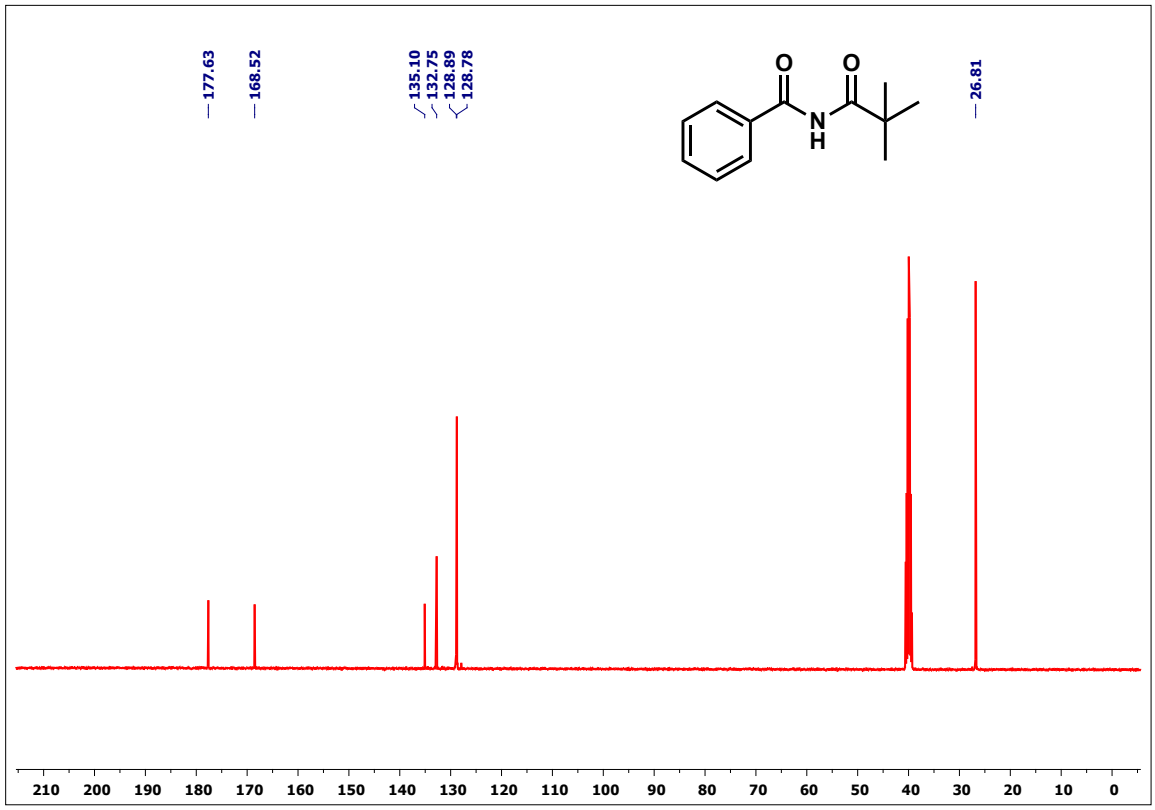

Figure S2: 100 MHz ^{13}C NMR spectrum of *N*-pivaloyl benzamide **1** in DMSO-d$_6$

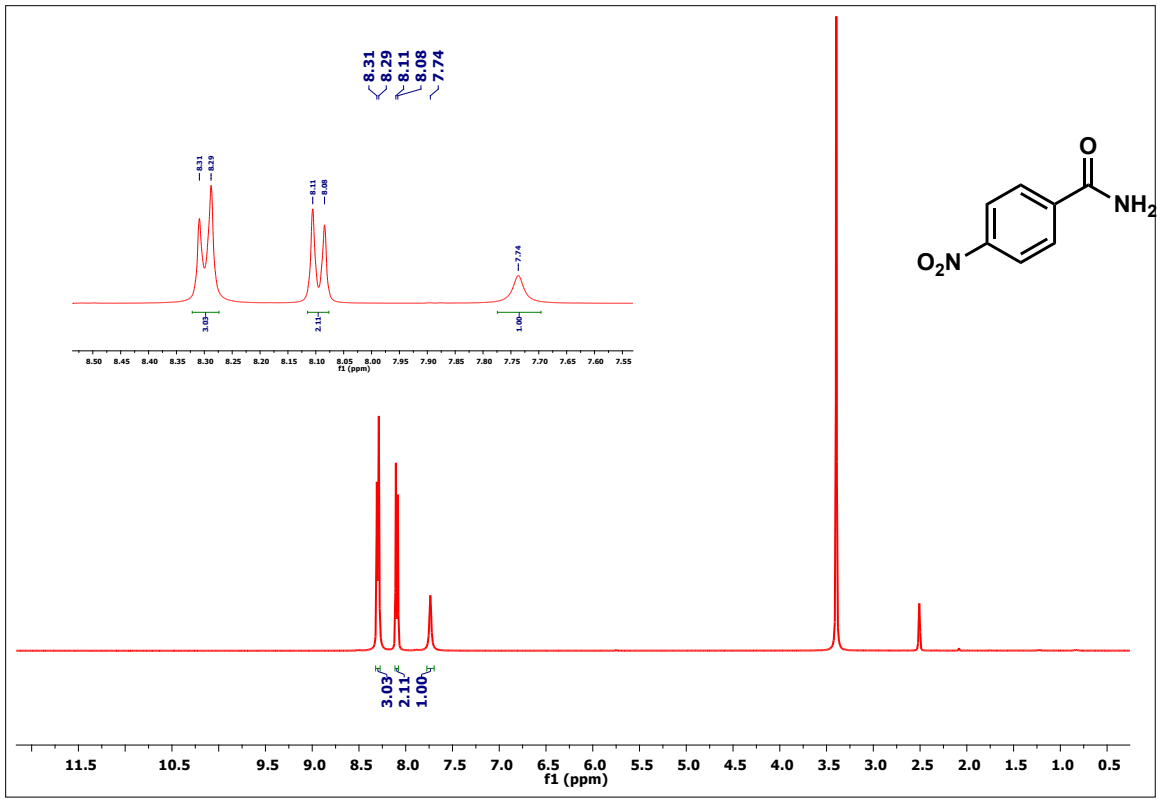

Figure S3: 400 MHz ^{1}H NMR spectrum of 4-nitro benzamide in DMSO-d_6

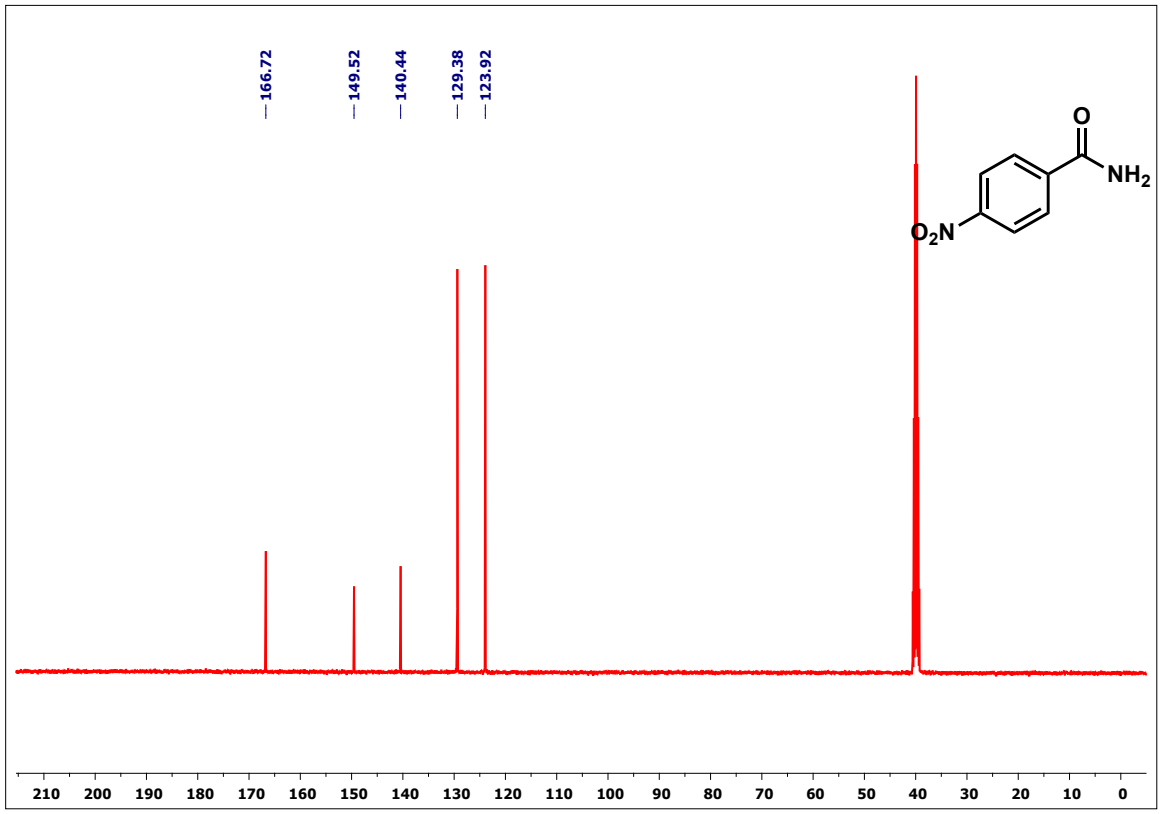

Figure S4: 100 MHz ^{13}C NMR spectrum of 4- nitro benzamide in DMSO-d_6

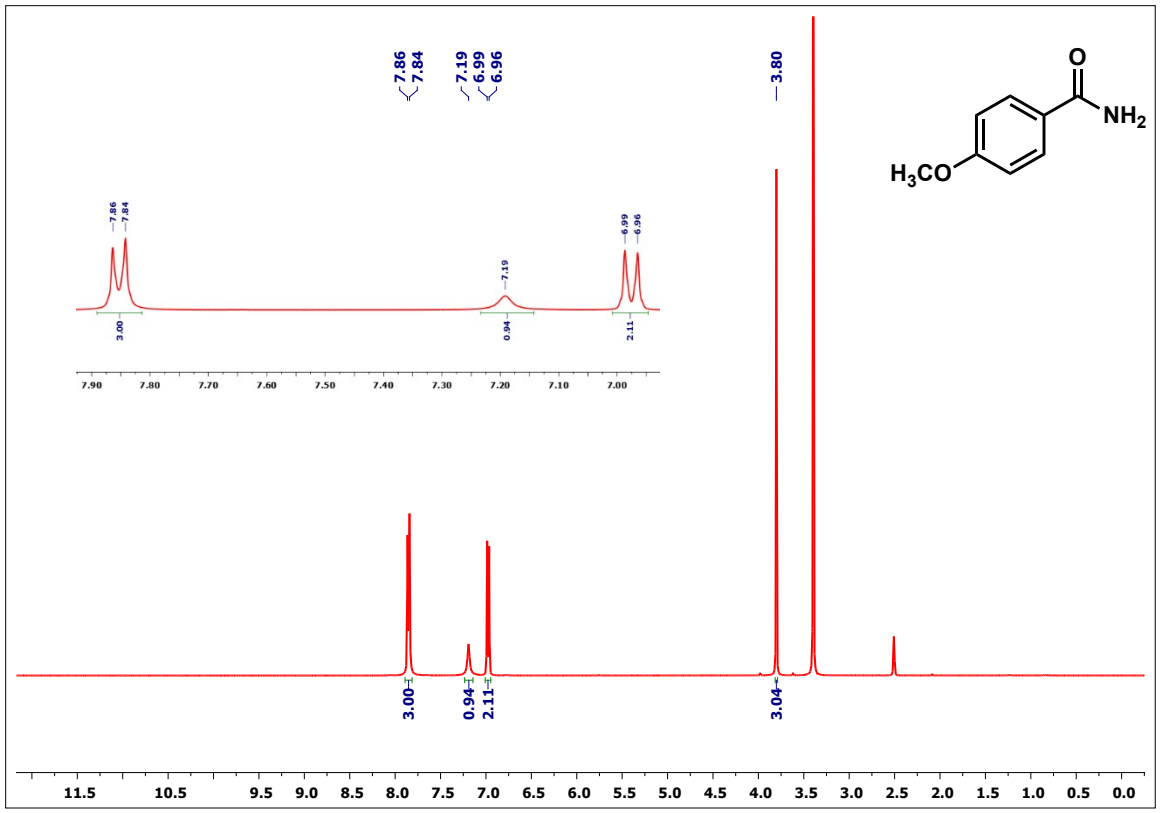

Figure S5: 400 MHz ^{1}H NMR spectrum of 4-methoxy benzamide in DMSO-d_6

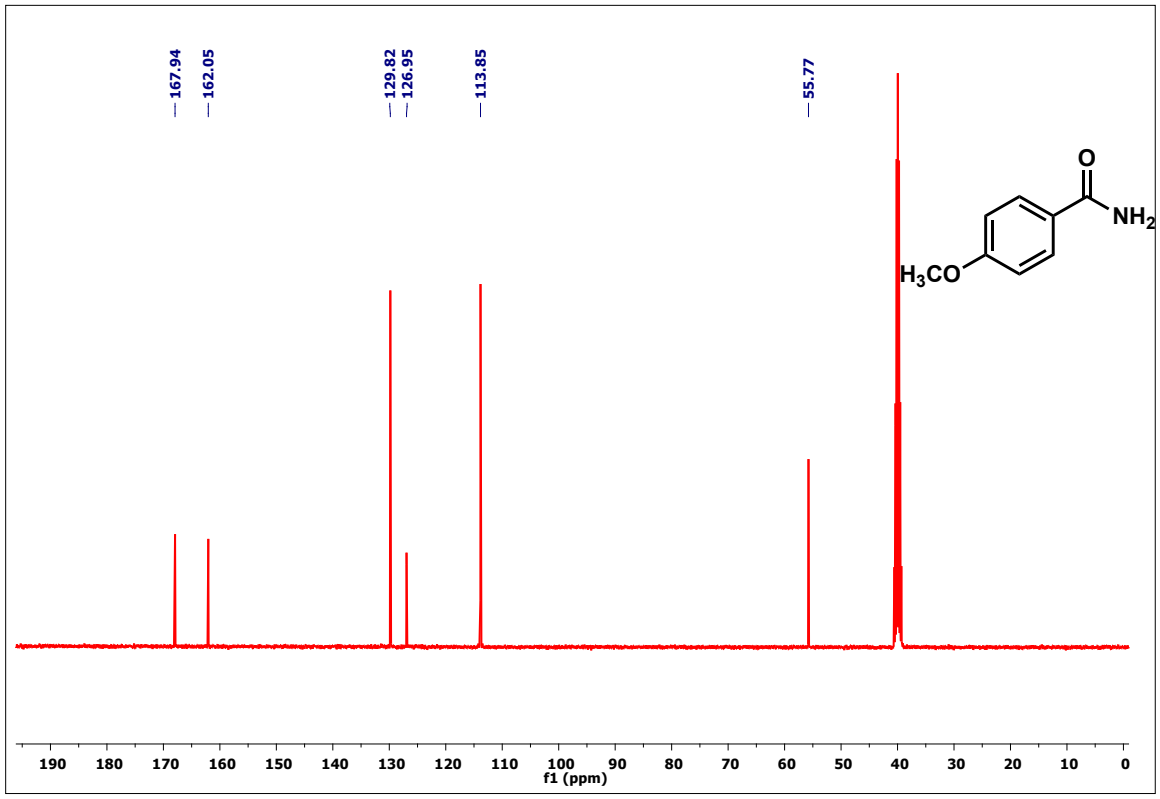

Figure S6: 100 MHz ^{13}C NMR spectrum of 4-methoxy benzamide in DMSO-d_6

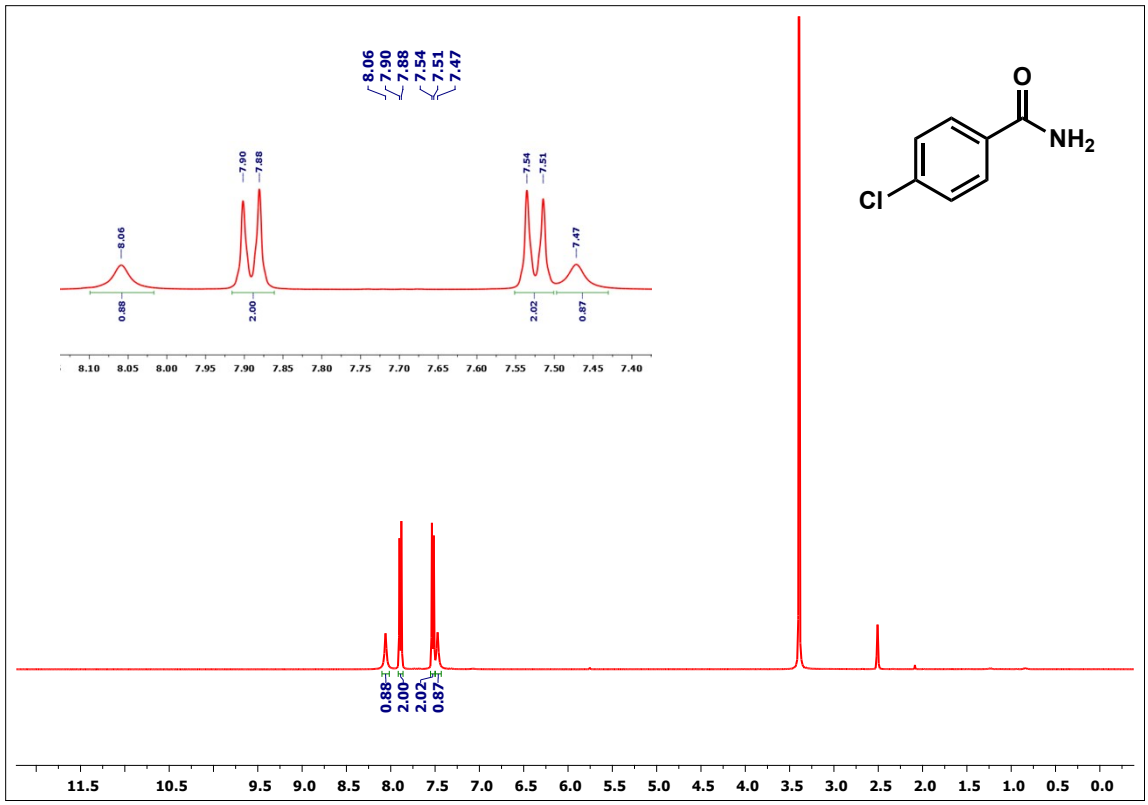

Figure S7: 400 MHz ^{1}H NMR spectrum of 4-chloro benzamide in DMSO-d_6

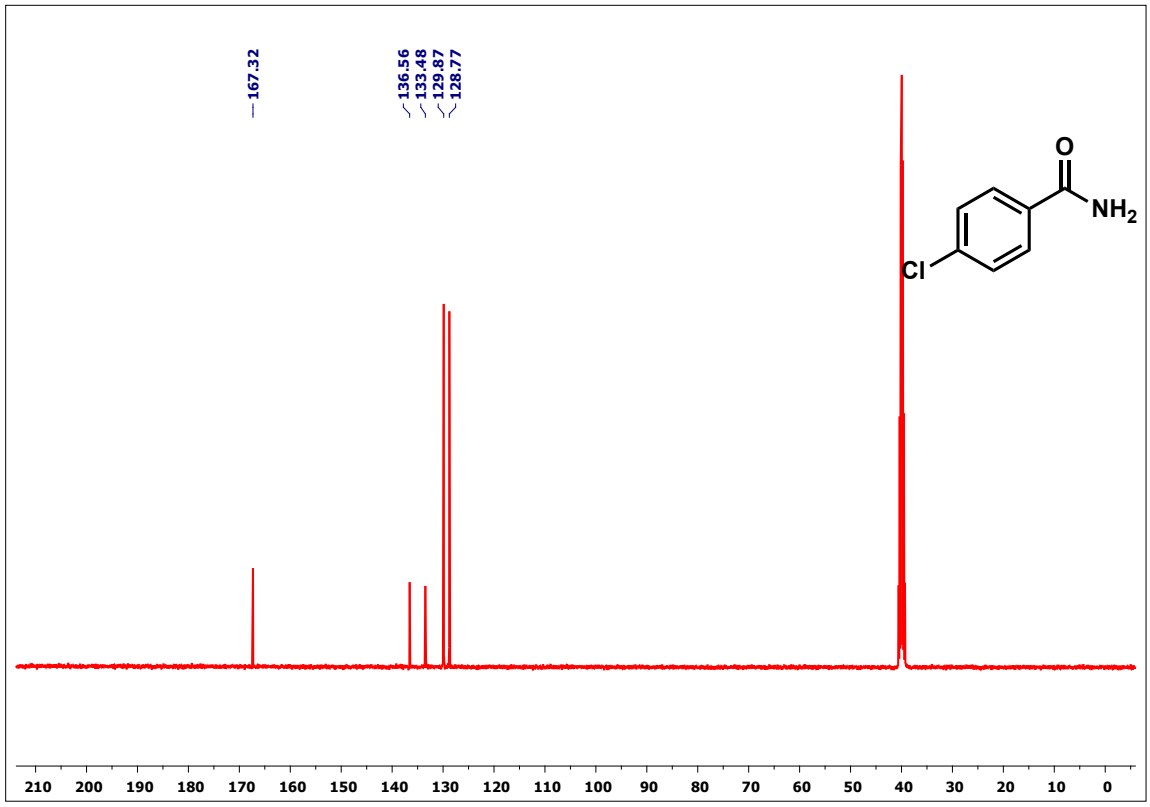

Figure S8: 100 MHz ^{13}C NMR spectrum of 4-chloro benzamide in DMSO-d_6

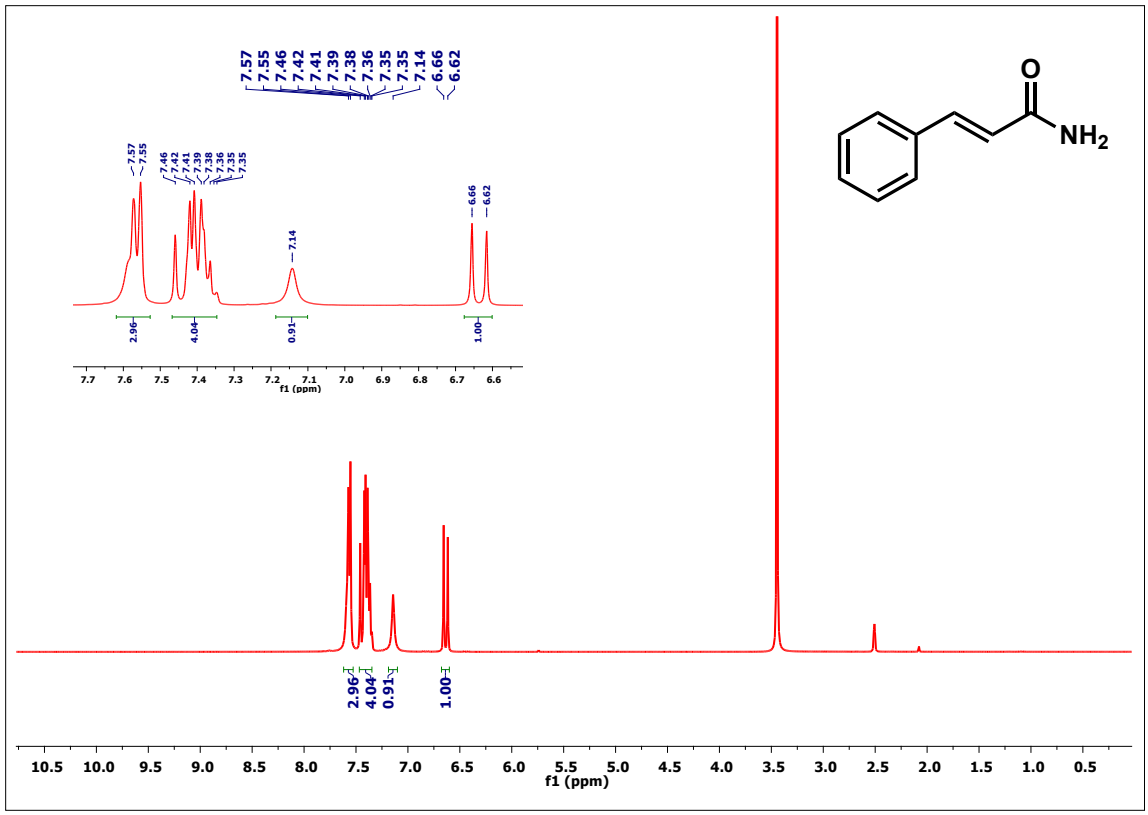

Figure S9: 400 MHz ^{1}H NMR spectrum of cinnamamide in DMSO-d_6

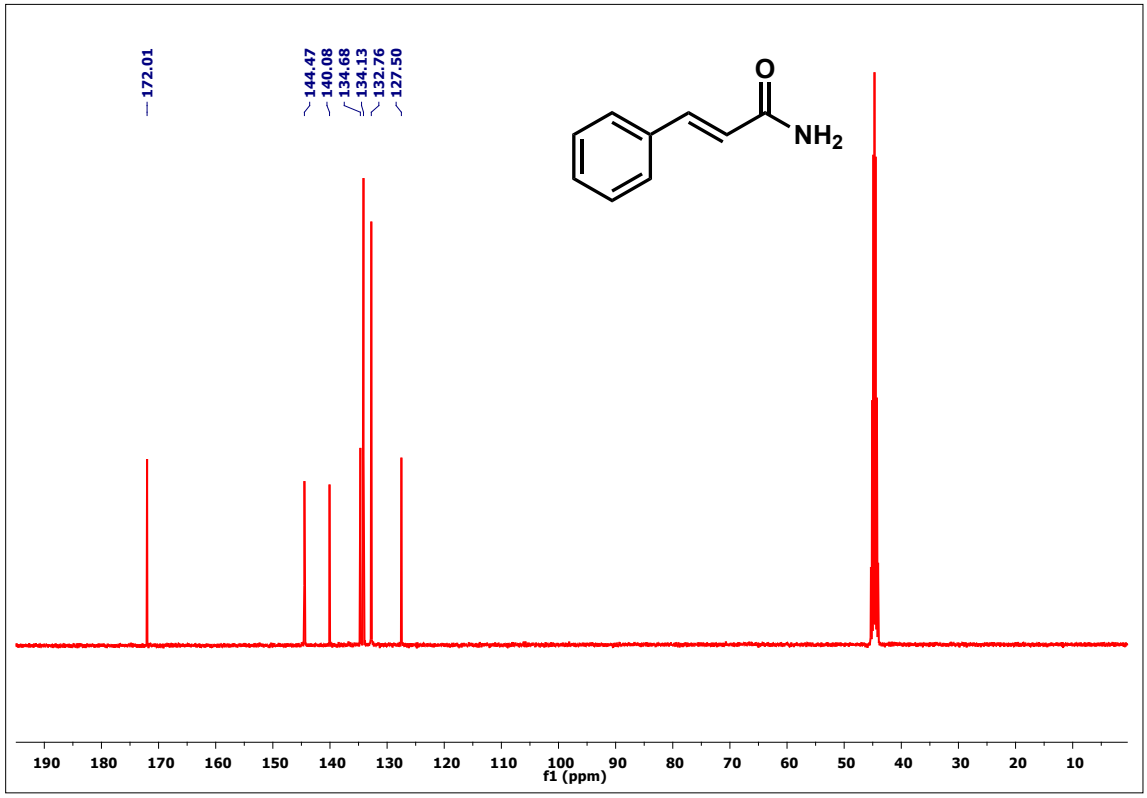

Figure S10: 100 MHz ^{13}C NMR spectrum of cinnamamide in DMSO-d_6

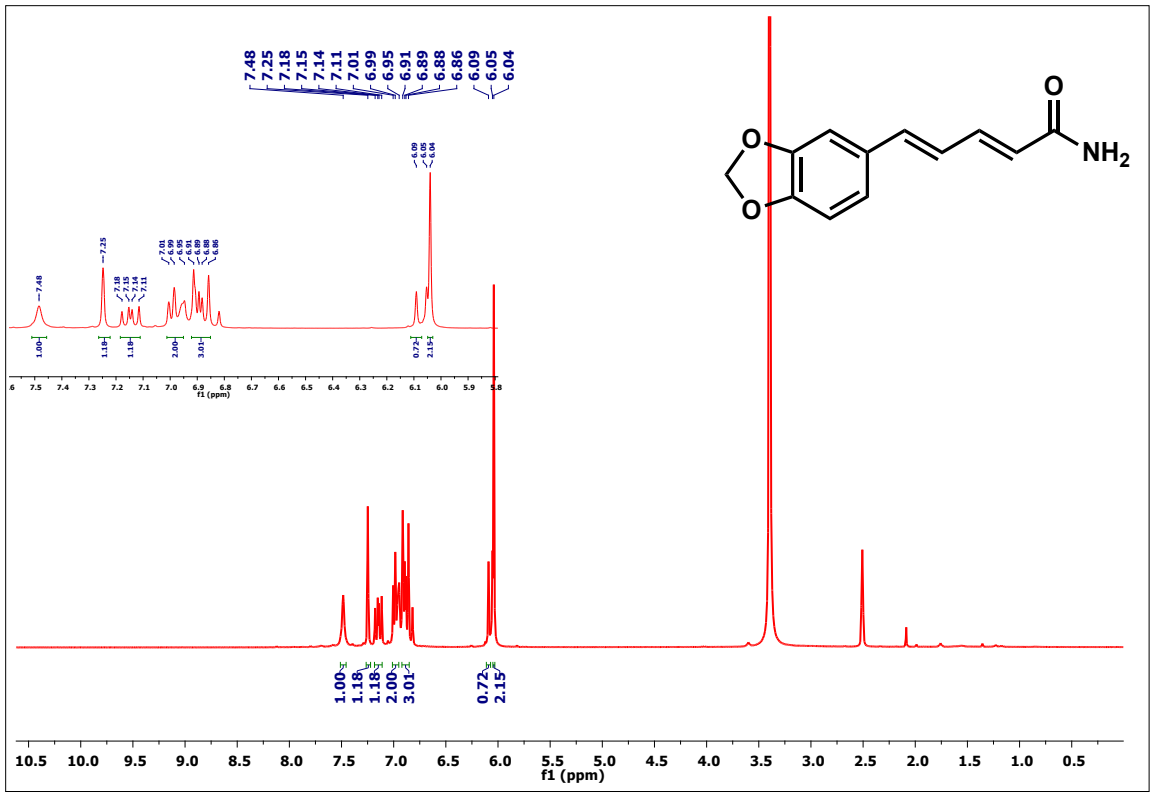

Figure S11: 400 MHz ^{1}H NMR spectrum of pipericamide in DMSO-d_6

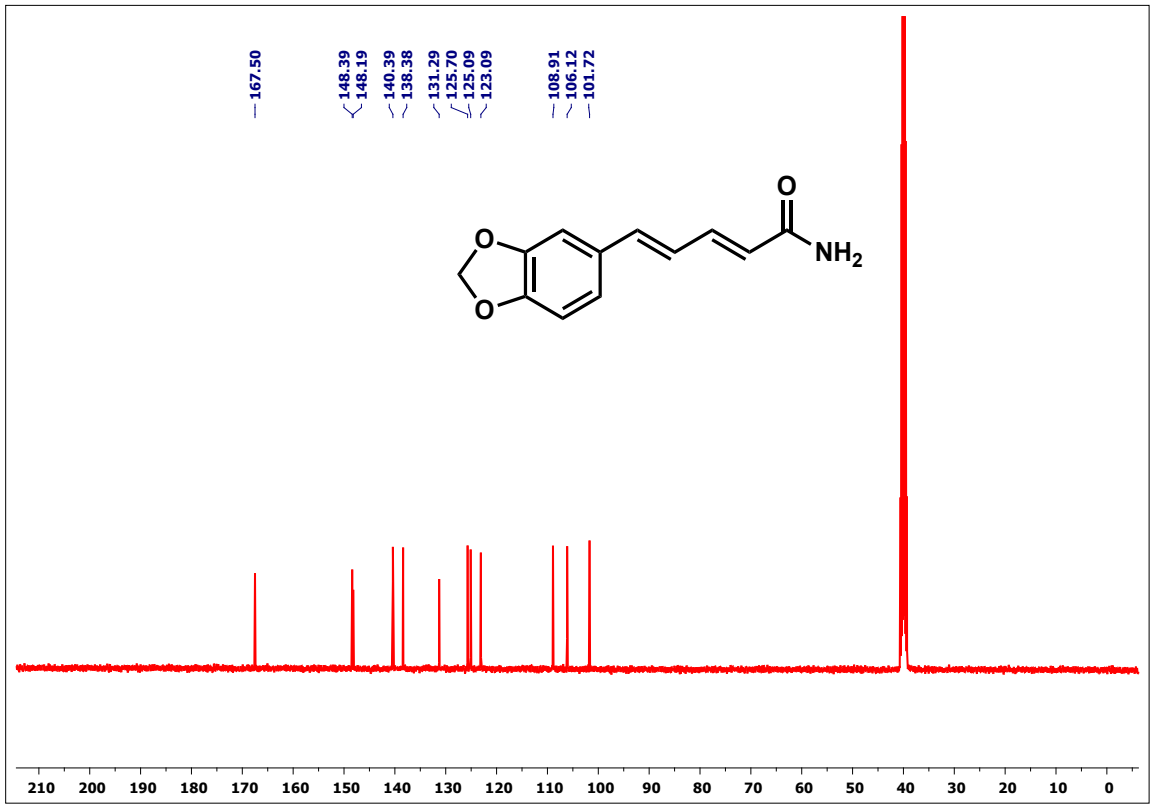

Figure S12: 100 MHz ^{13}C NMR spectrum of piperic amide in DMSO-d_6

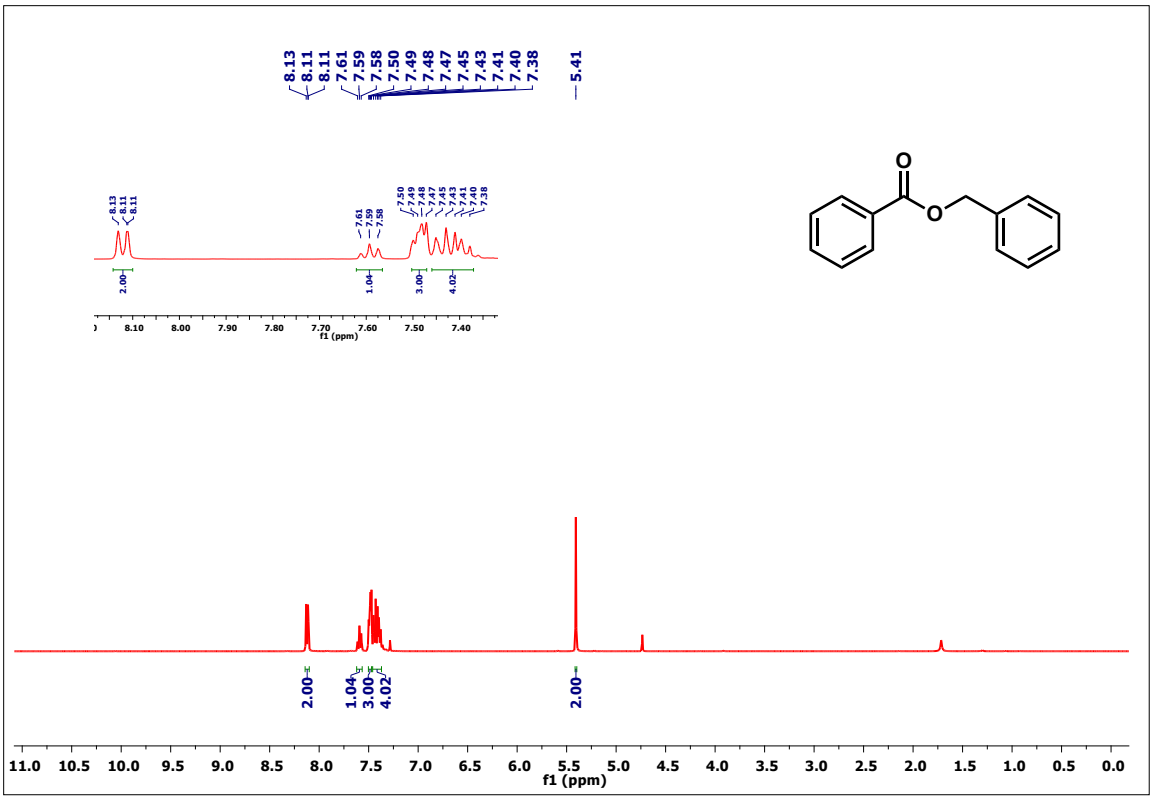

Figure S13: 400 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$

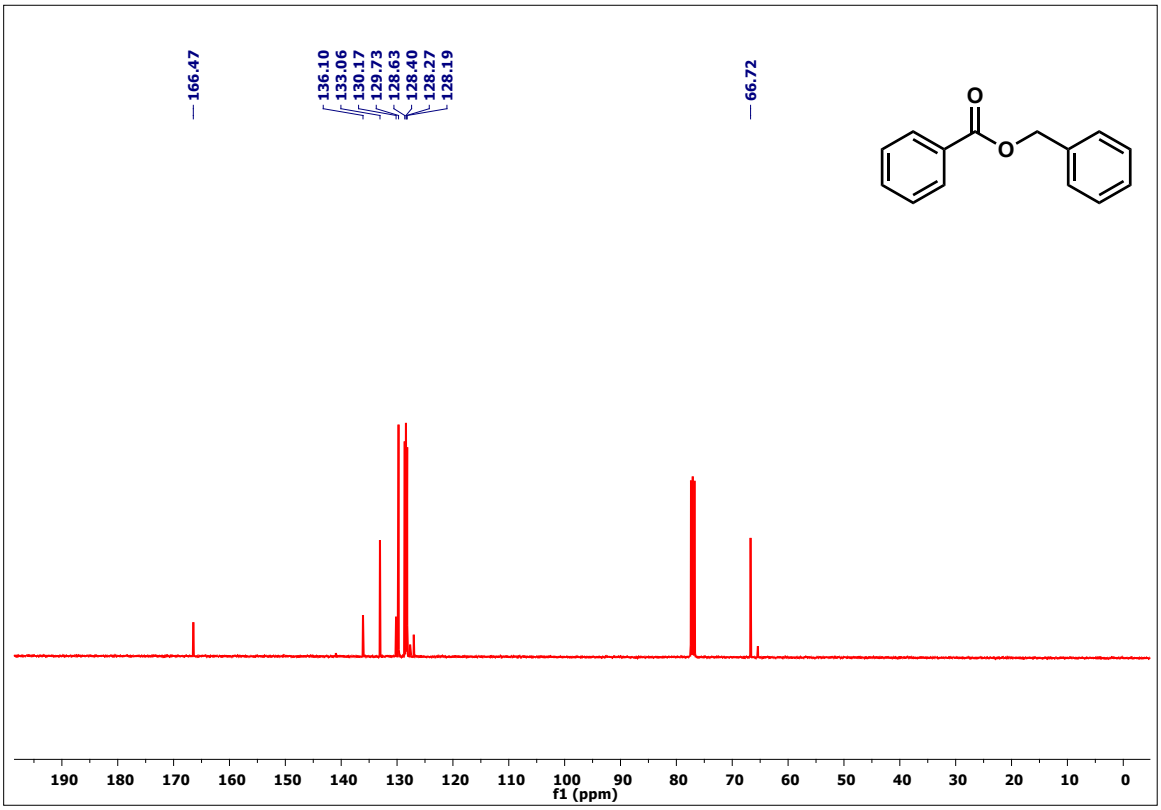

Figure S14: 100 MHz ^{13}C NMR spectrum of **3** in $CDCl_3$

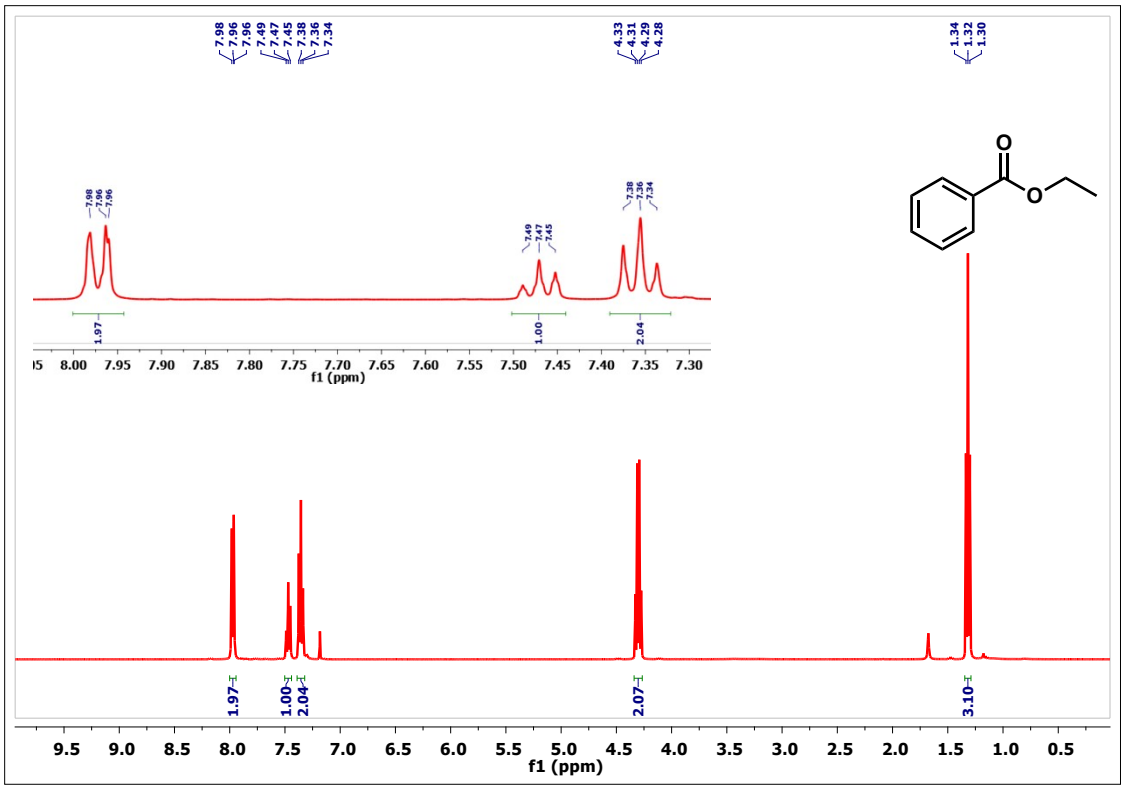

Figure S15: 400 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$

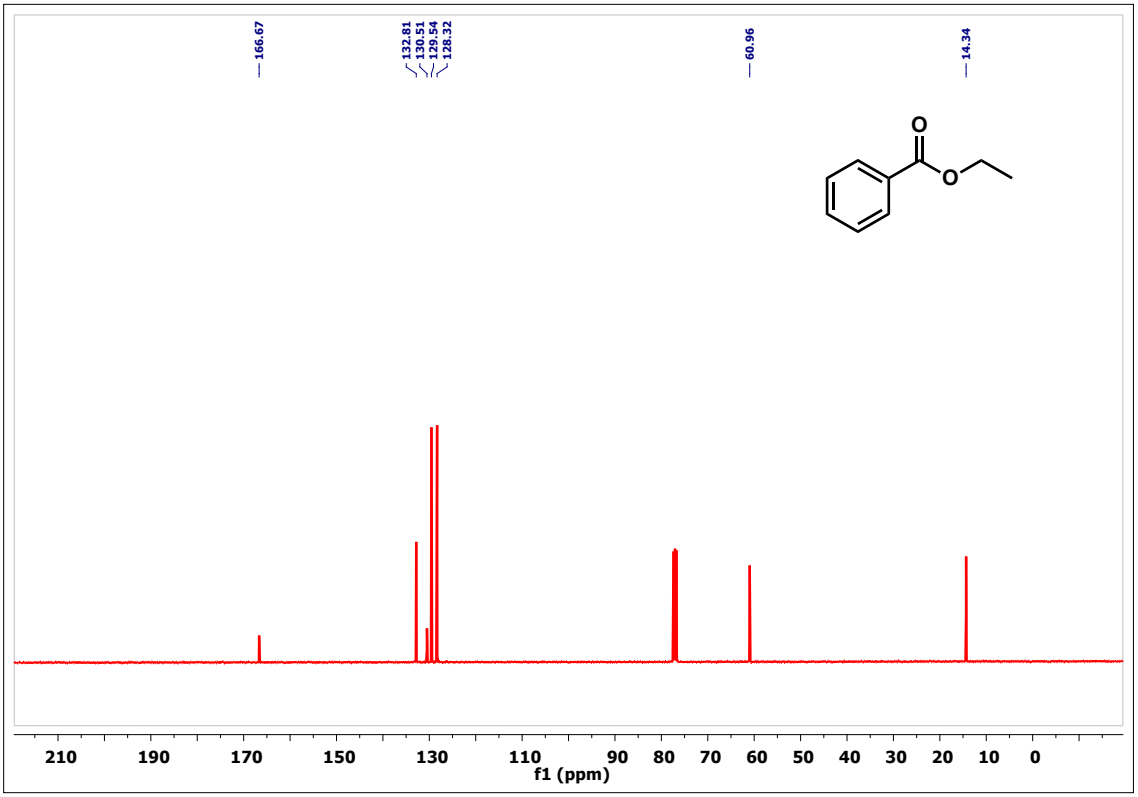

Figure S16: 100 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$

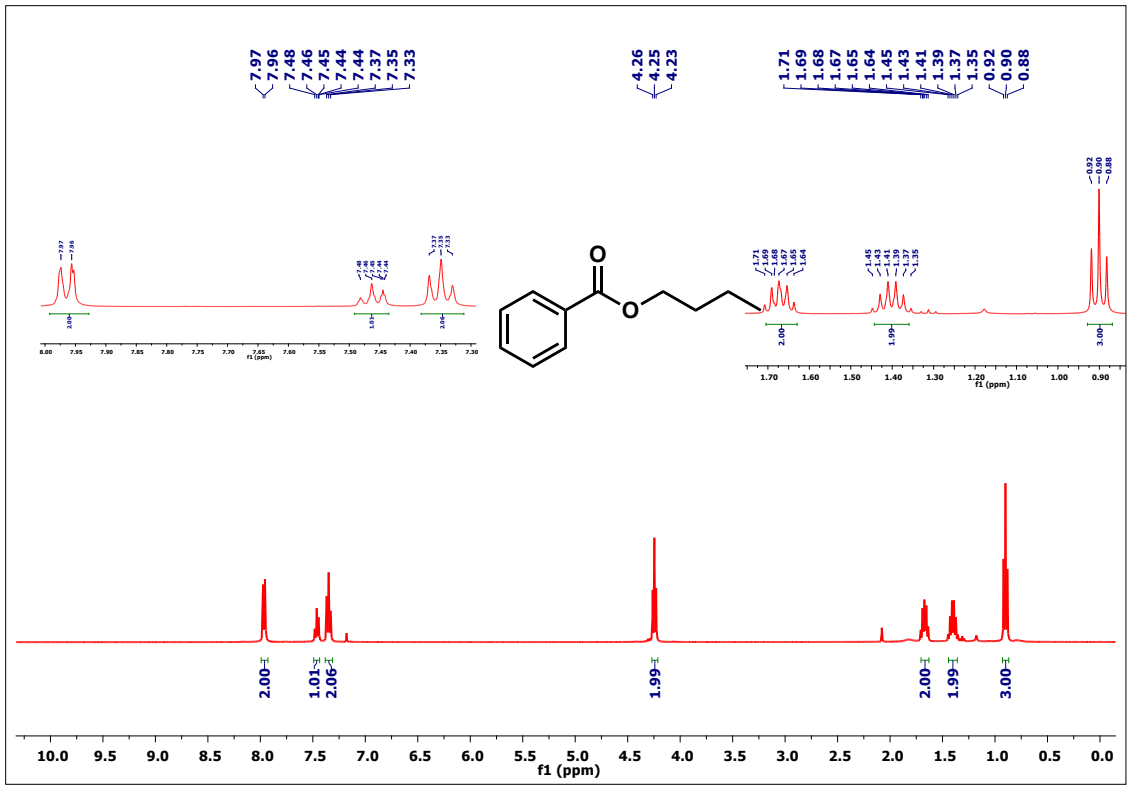

Figure S17: 400 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$

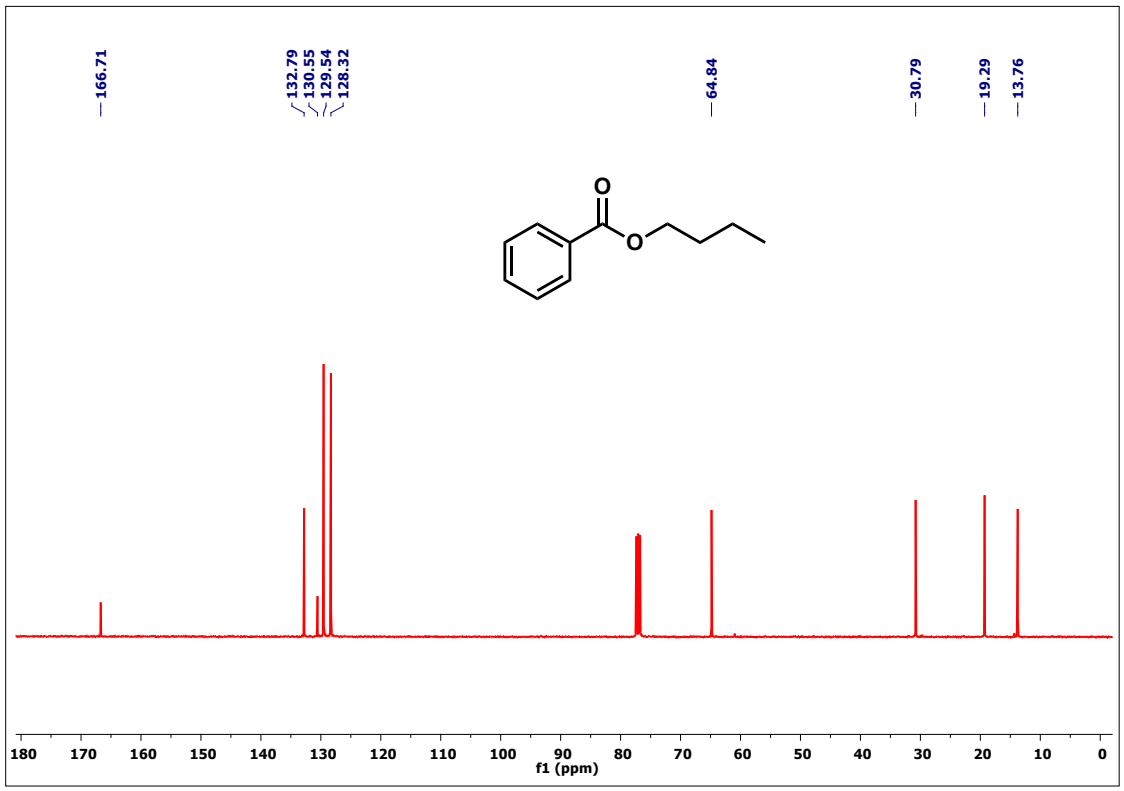

Figure S18: 100 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$

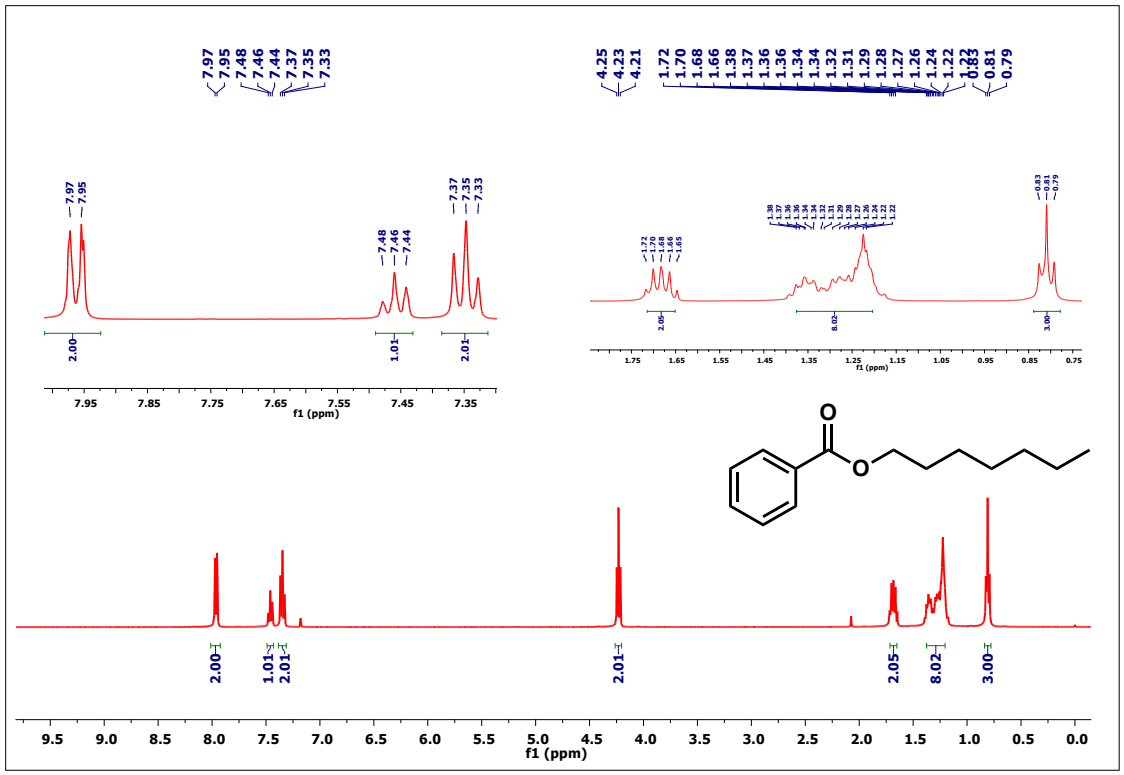

Figure S19: 400 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$

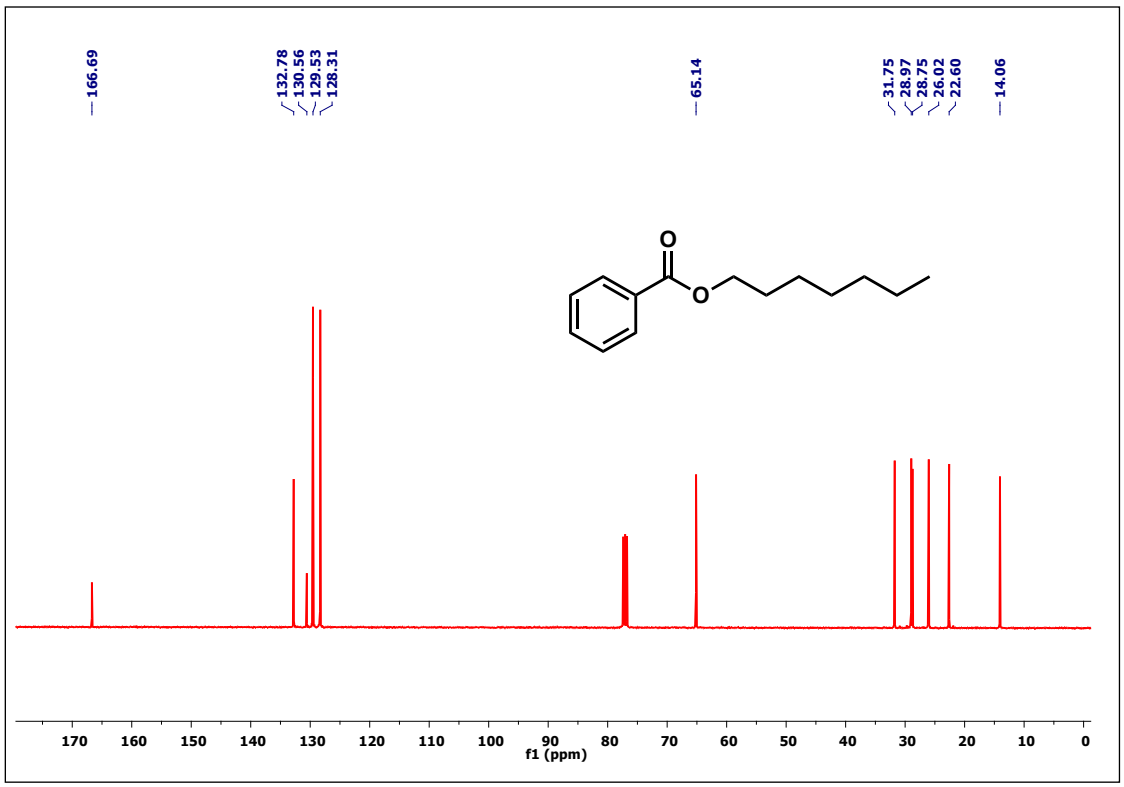

Figure S20: 100 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$

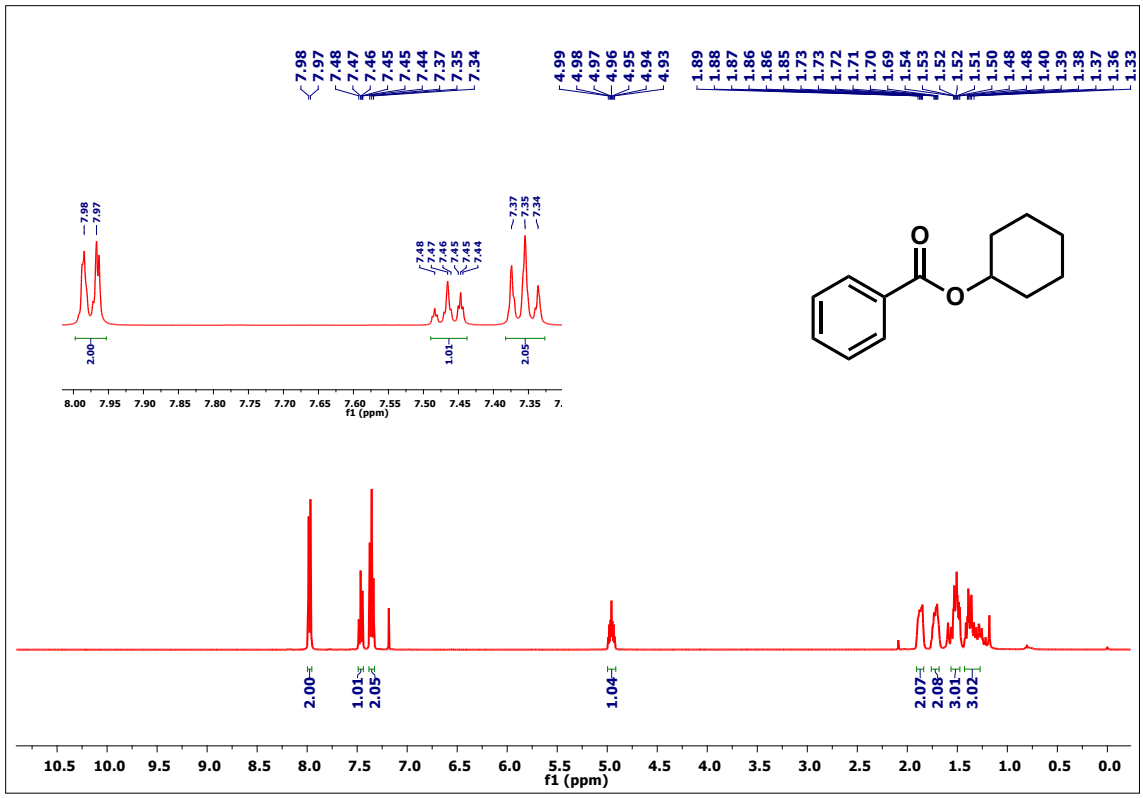

Figure S21: 400 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$

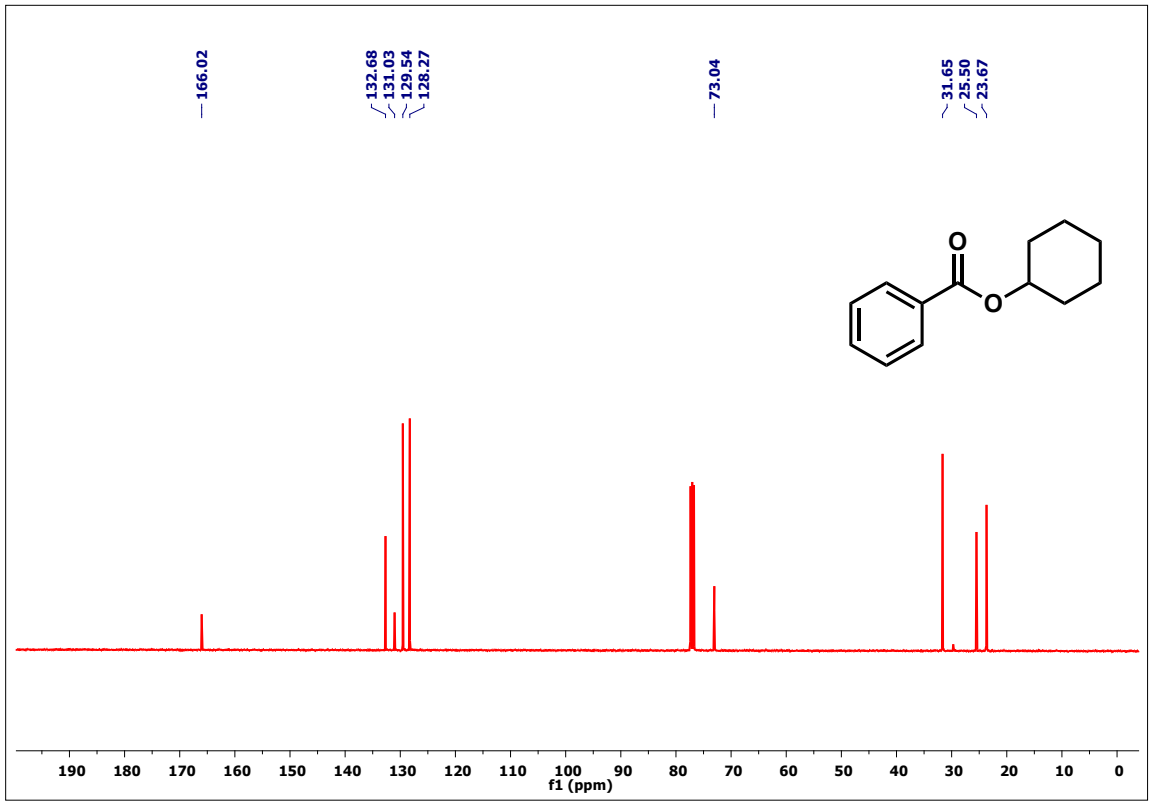

Figure S22: 100 MHz ^{13}C NMR spectrum of **7** in $CDCl_3$

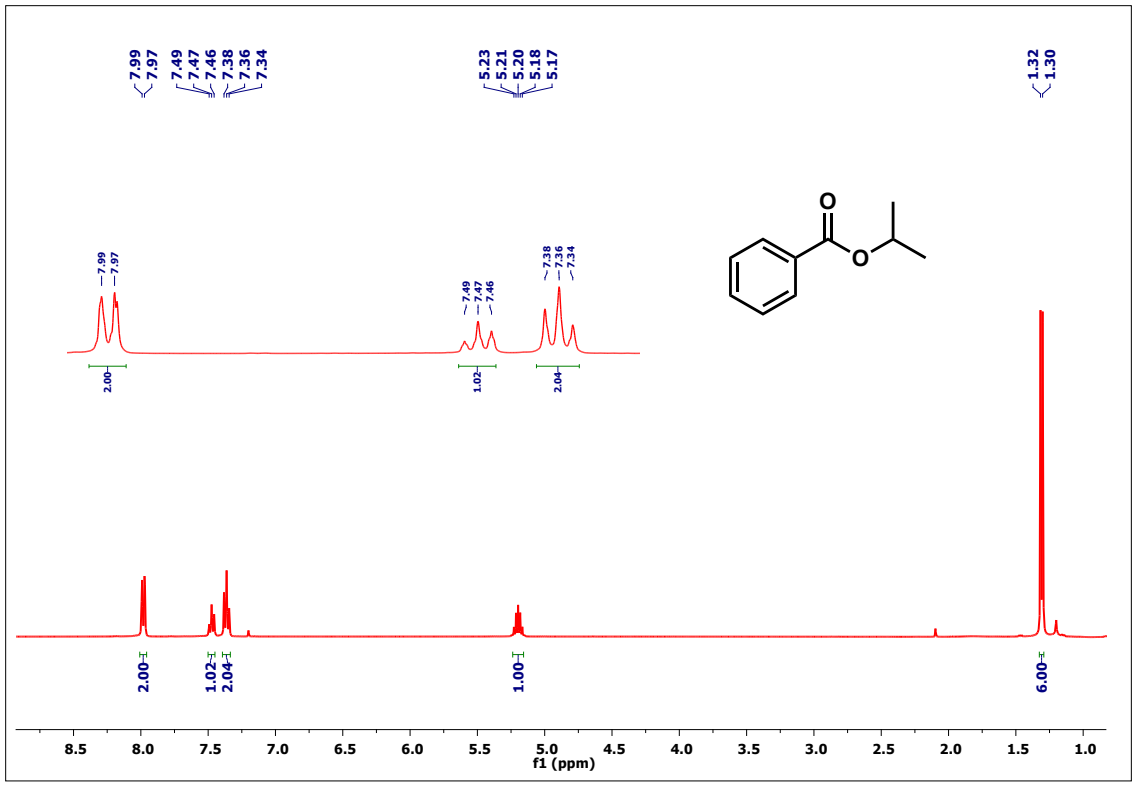

Figure S23: 400 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$

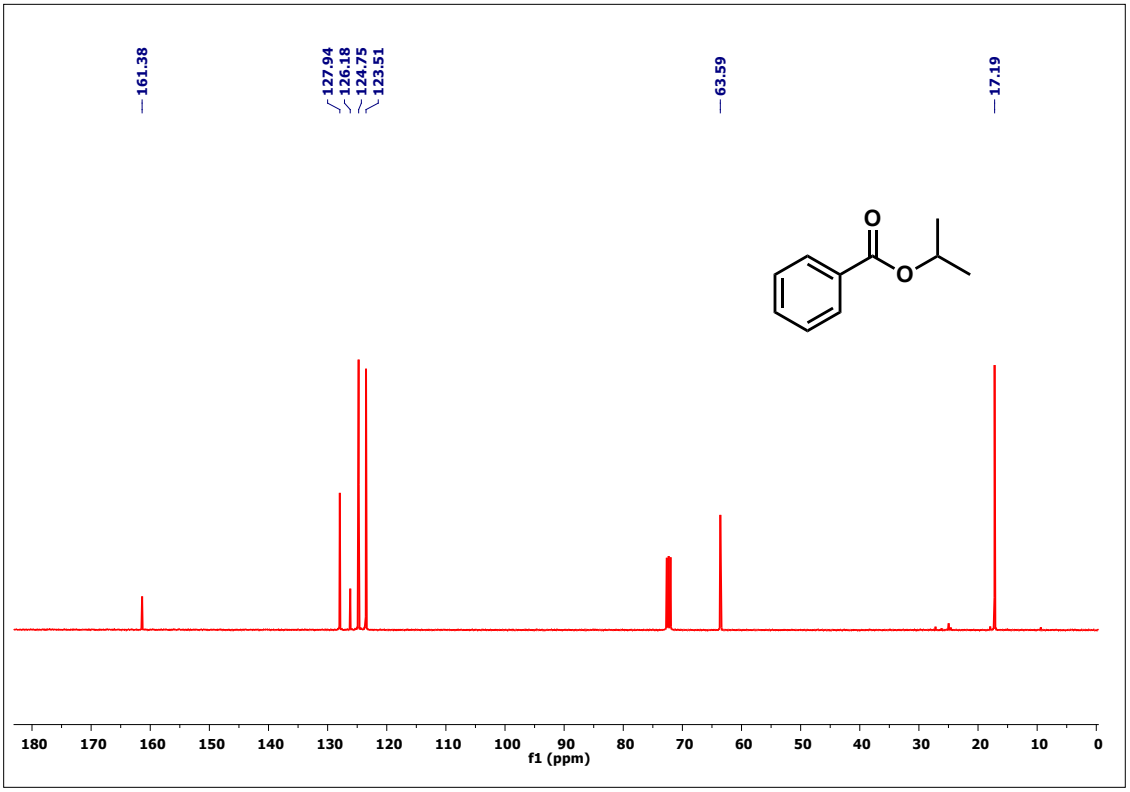

Figure S24: 100 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$

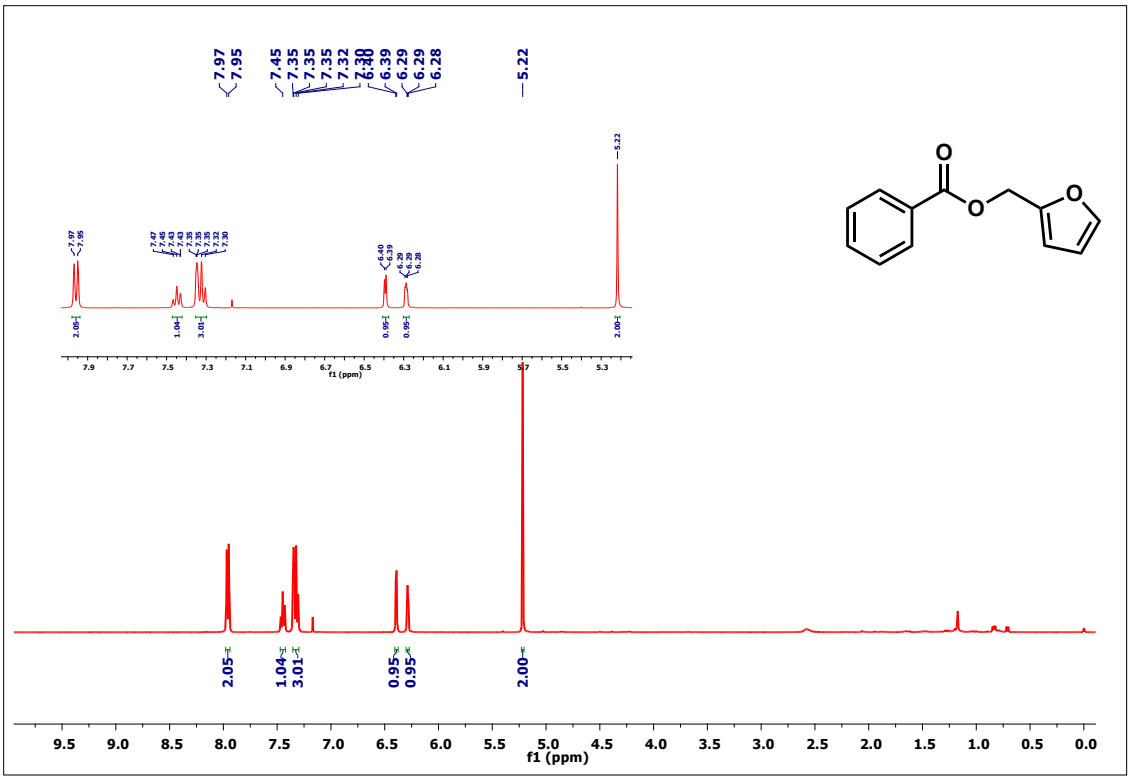

Figure S25: 400 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$

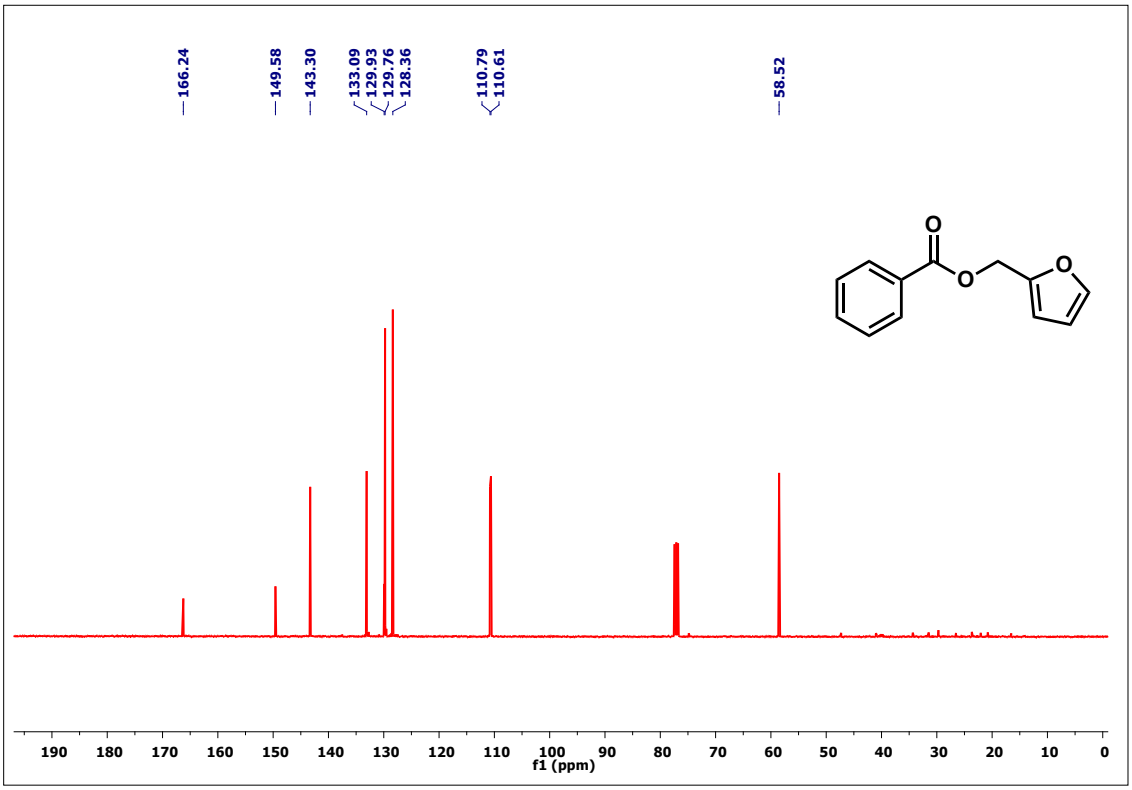

Figure S26: 100 MHz ^{13}C NMR spectrum of **9** in $CDCl_3$

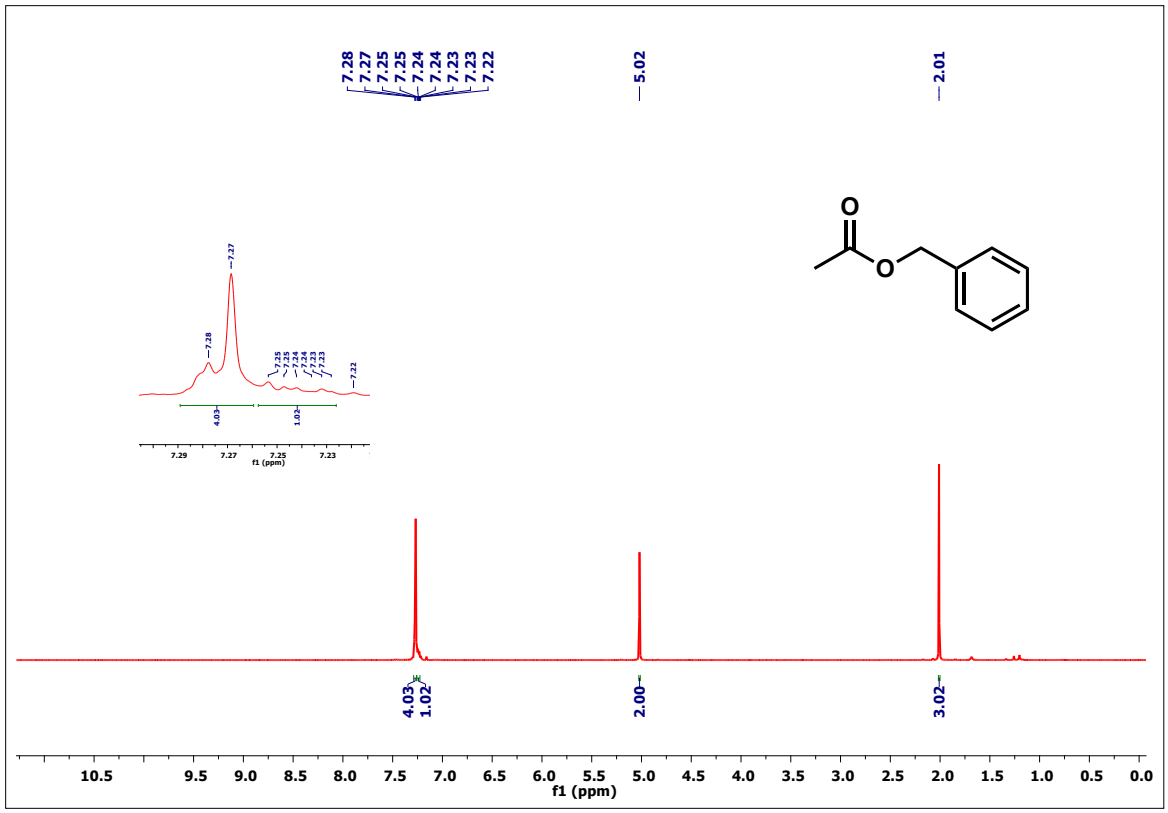

Figure S27: 400 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$

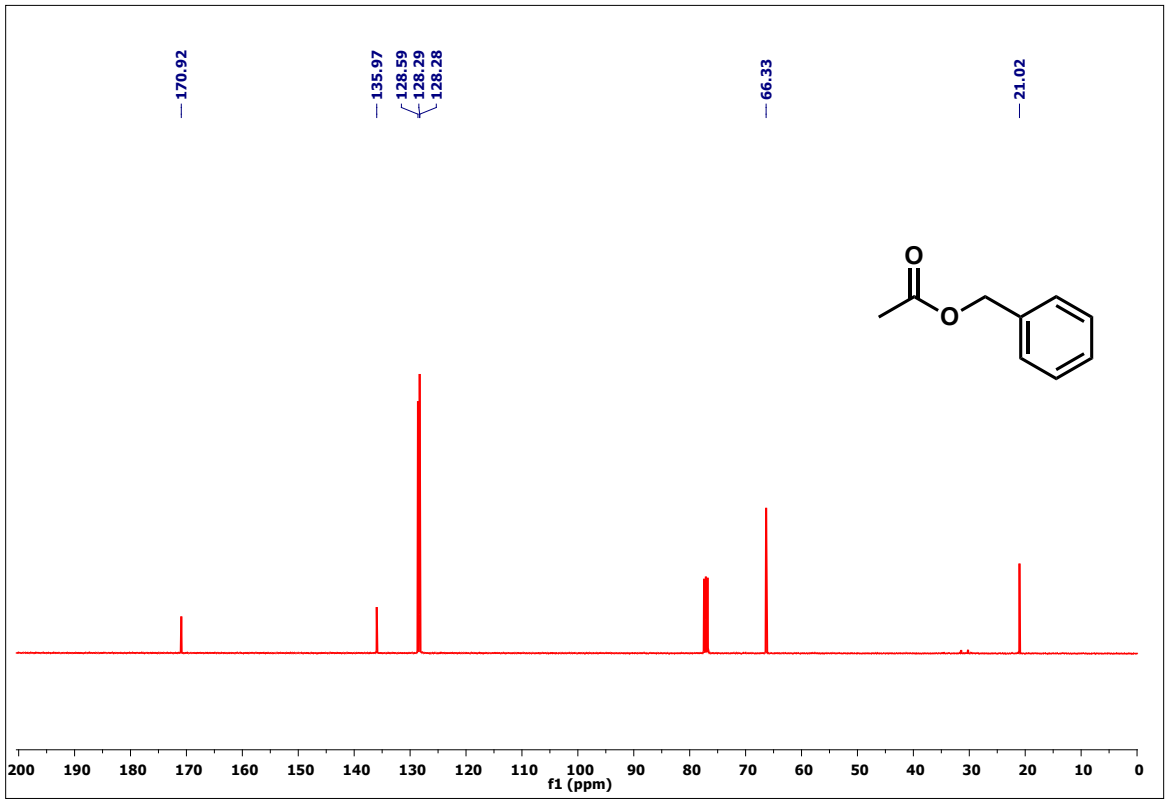

Figure S28: 100 MHz ^{13}C NMR spectrum of **10** in $CDCl_3$

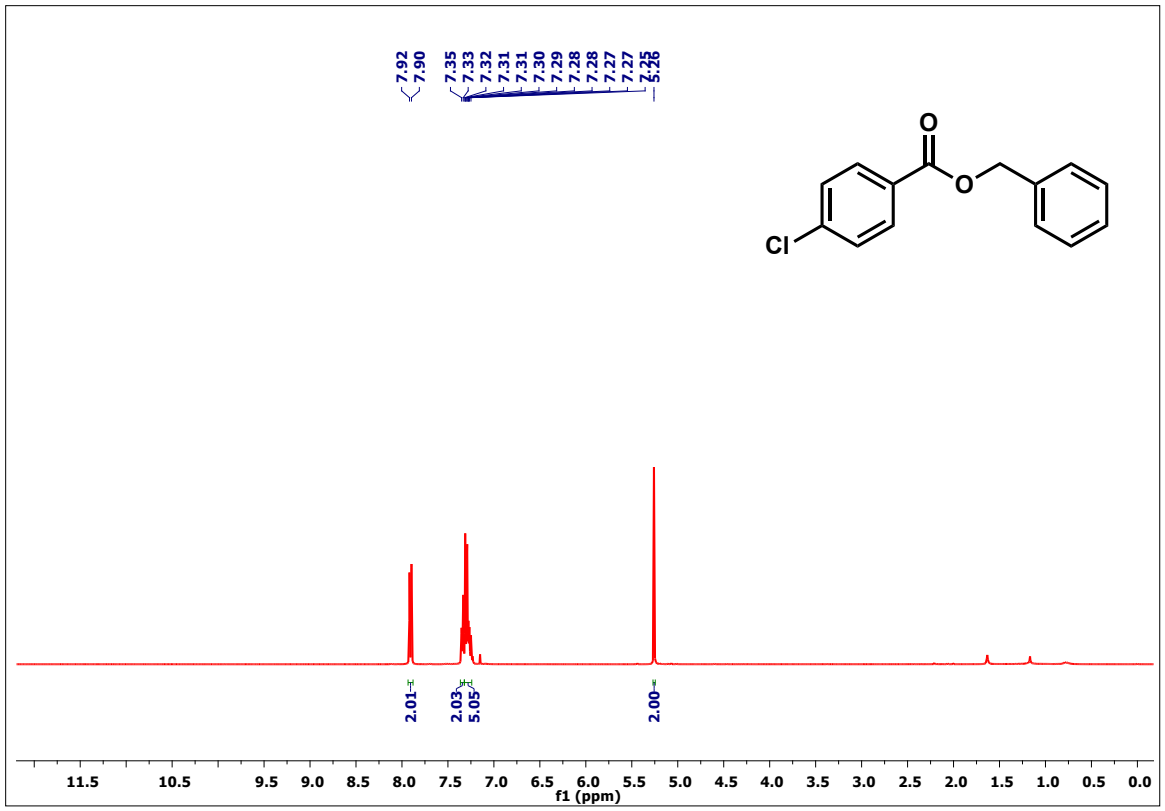

Figure S29: 400 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$

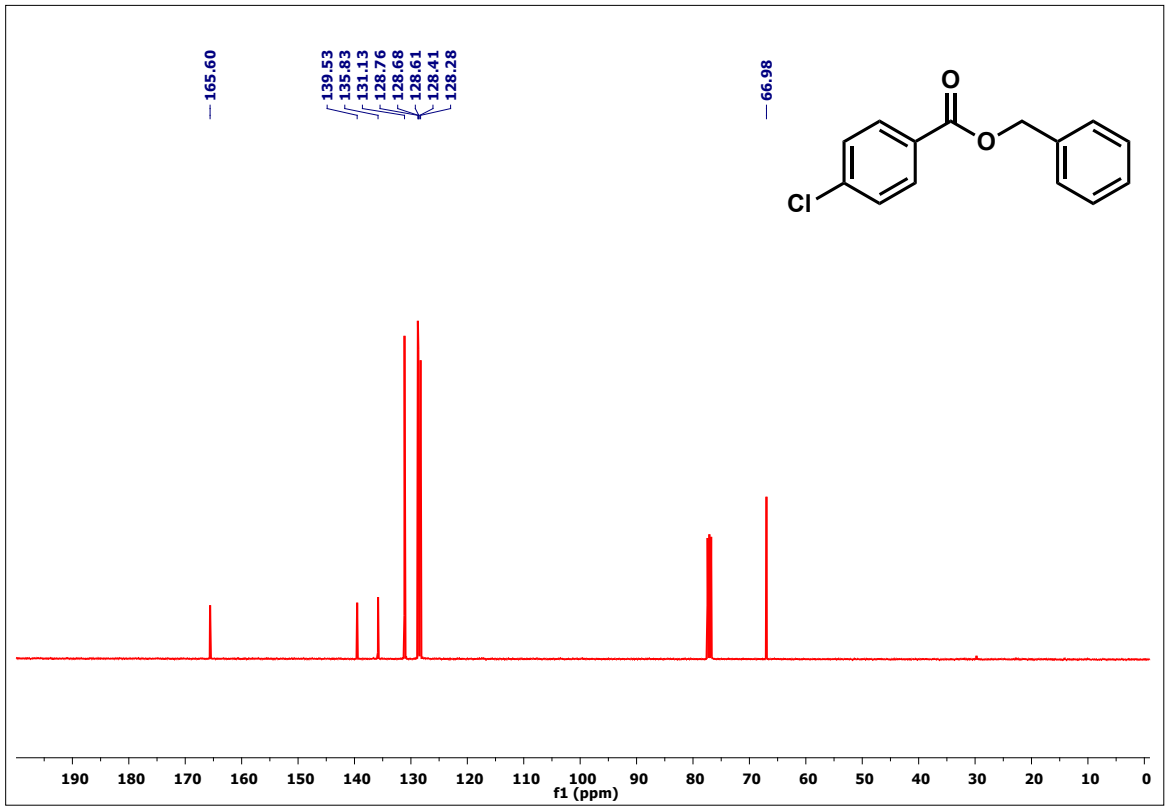

Figure S30: 100 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$

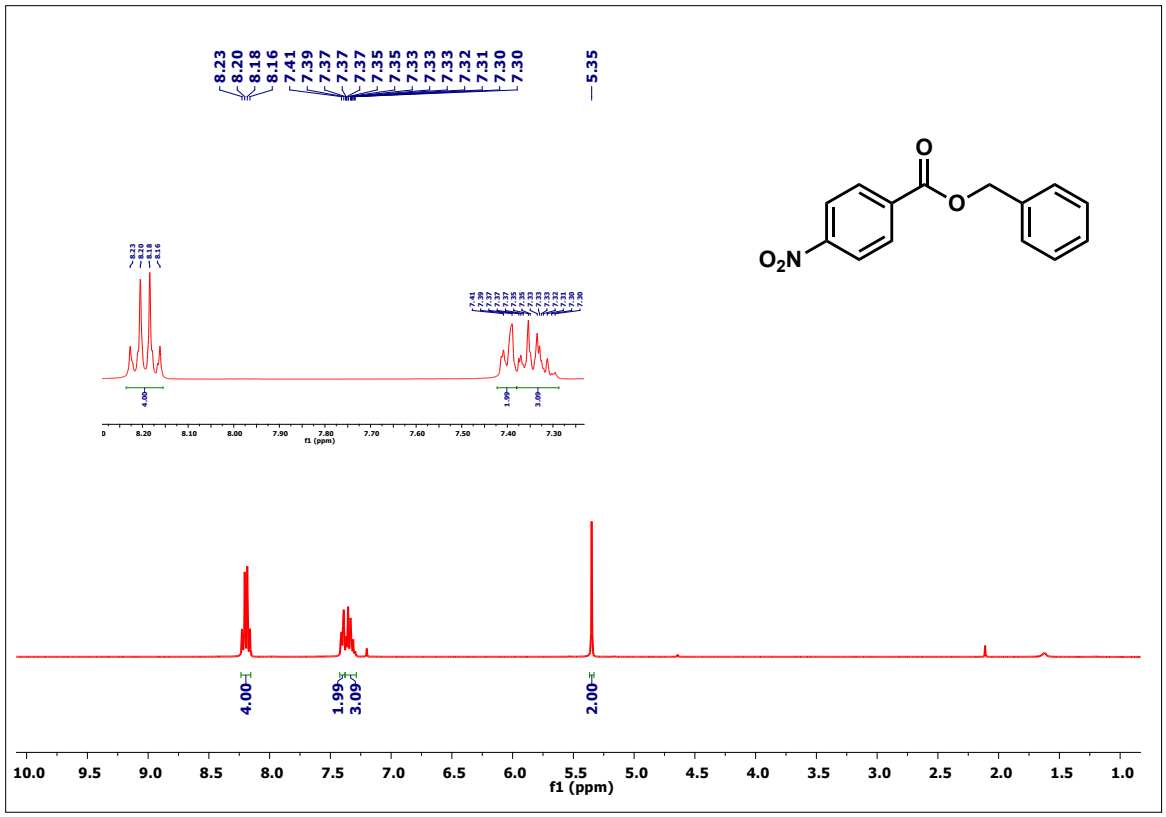

Figure S31: 400 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$

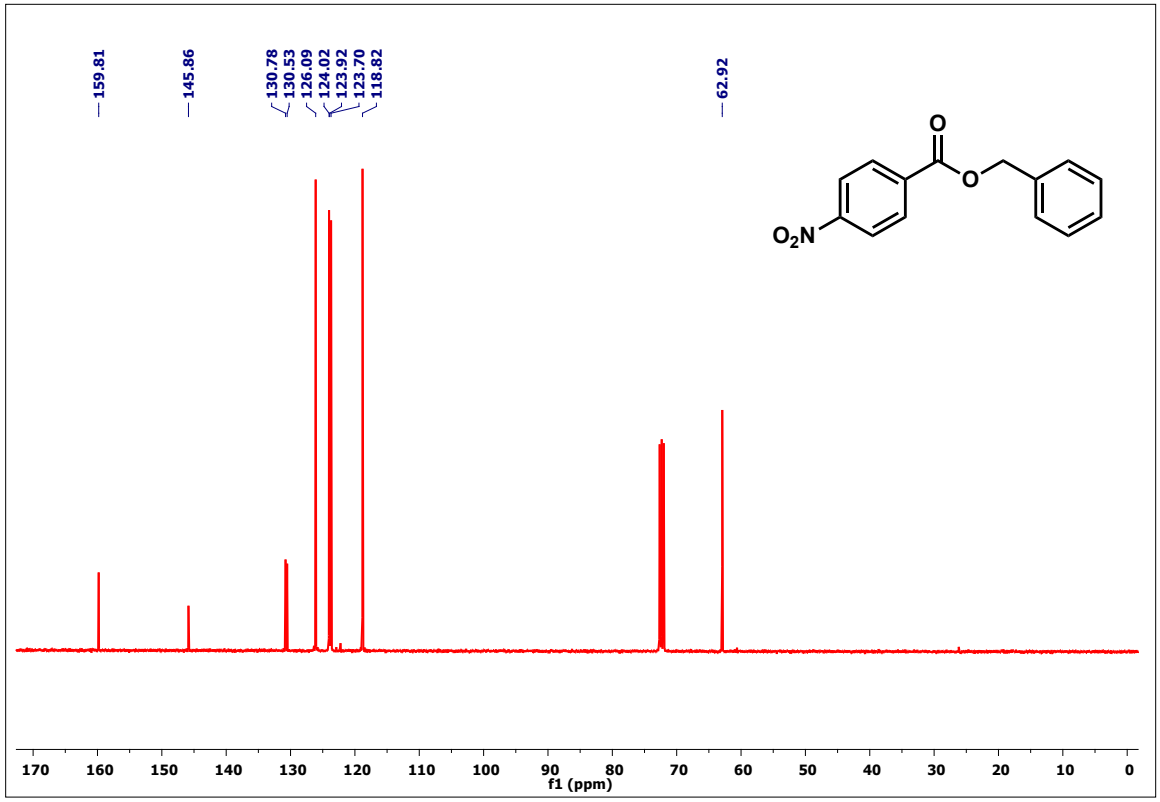

Figure S32: 100 MHz ^{13}C NMR spectrum of **12** in $CDCl_3$

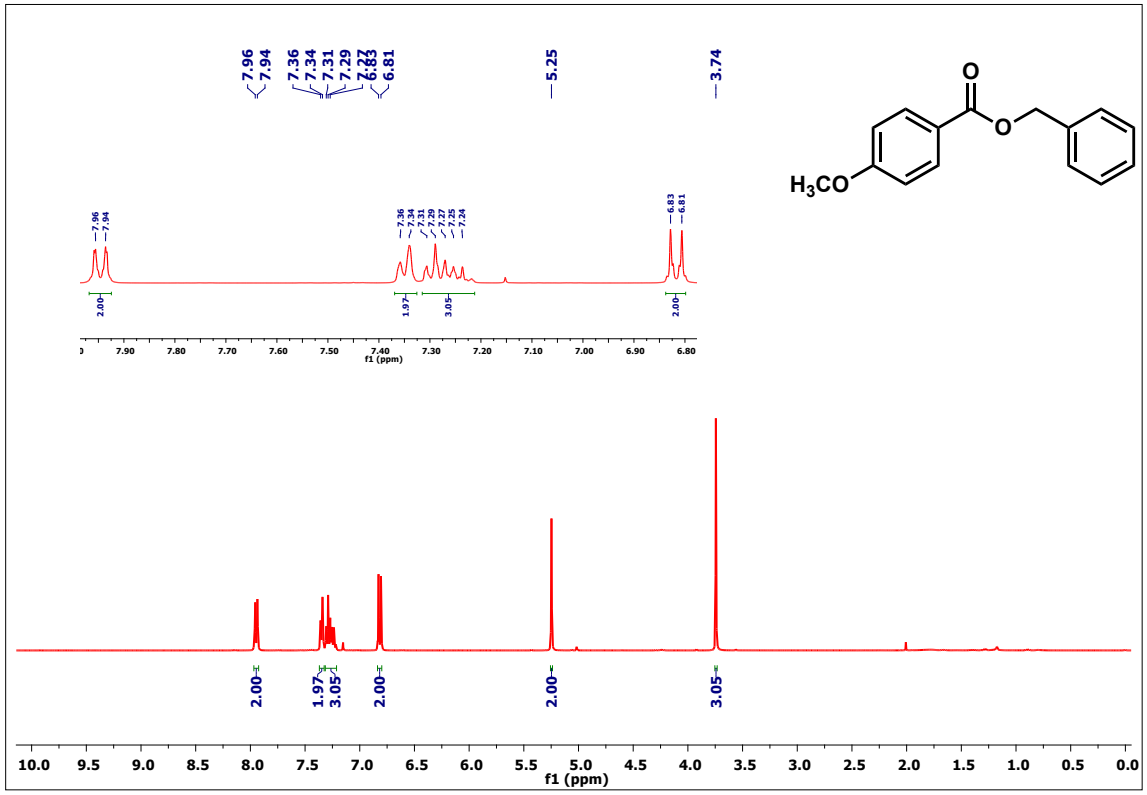

Figure S33: 400 MHz ^{1}H NMR spectrum of **13** in $CDCl_3$

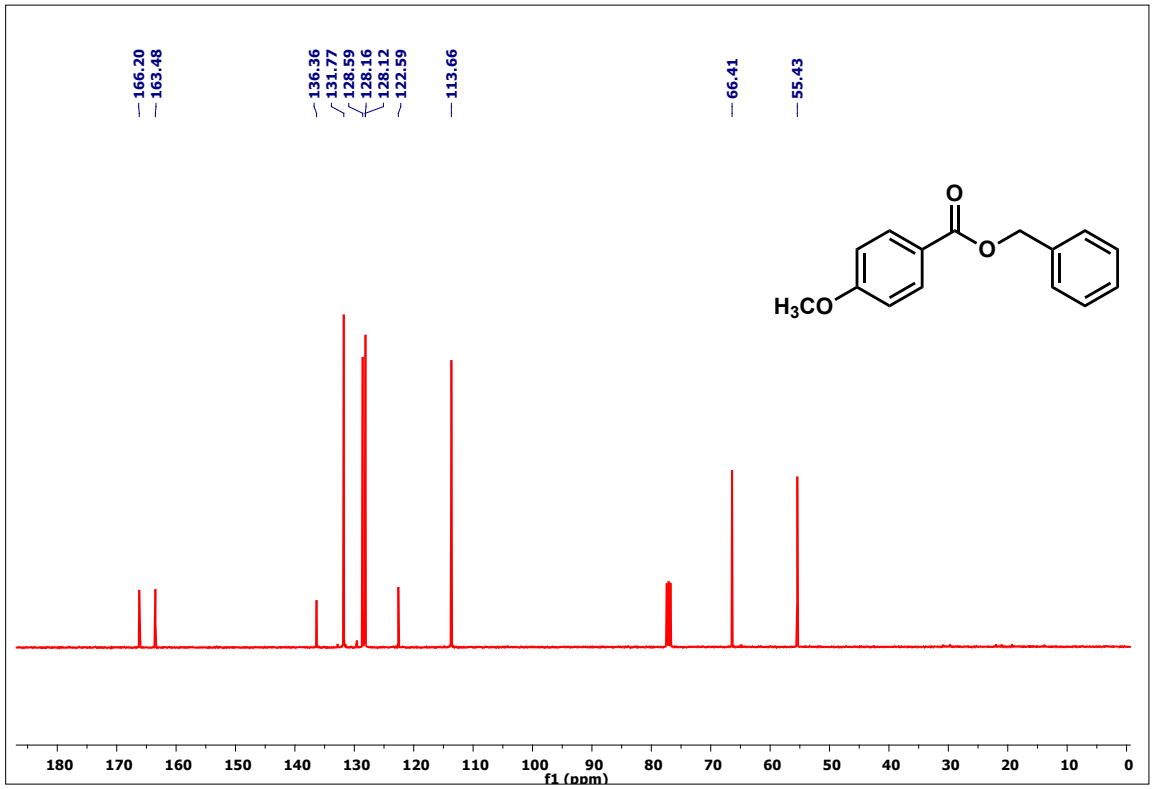

Figure S34: 100 MHz ^{13}C NMR spectrum of **13** in $CDCl_3$

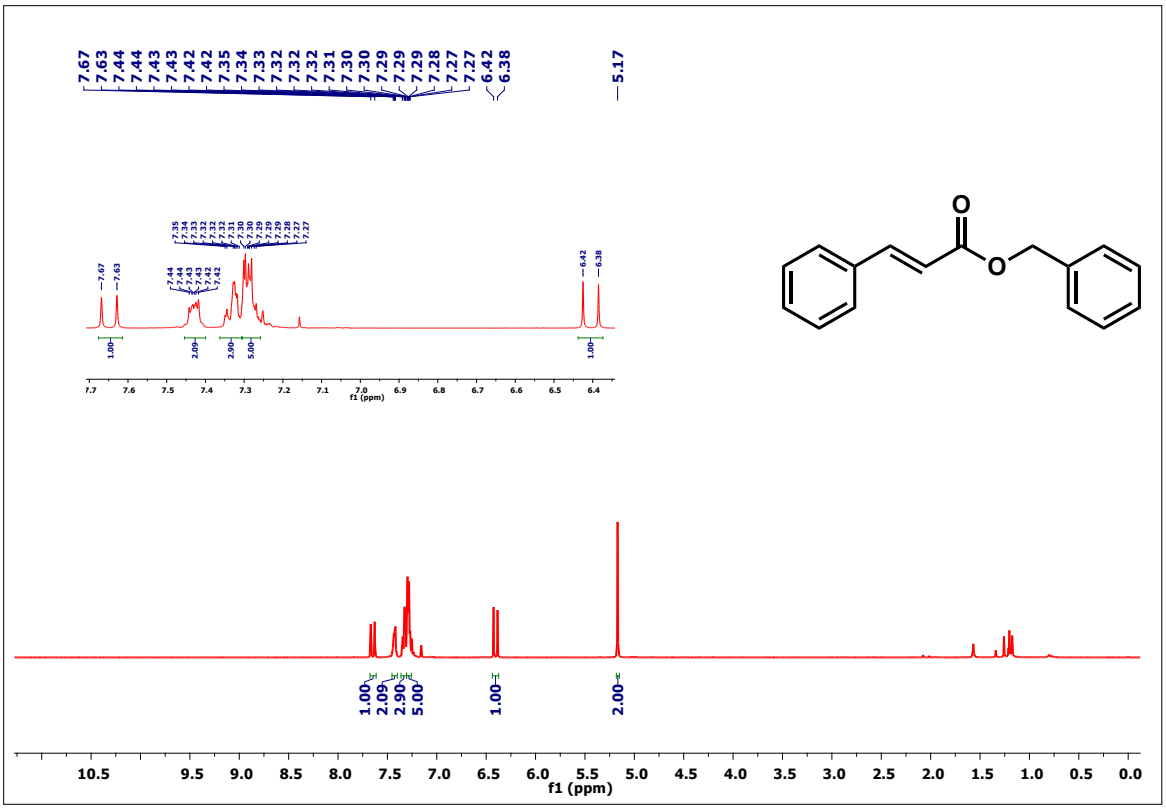

Figure S35: 400 MHz ^{1}H NMR spectrum of **14** in $CDCl_3$

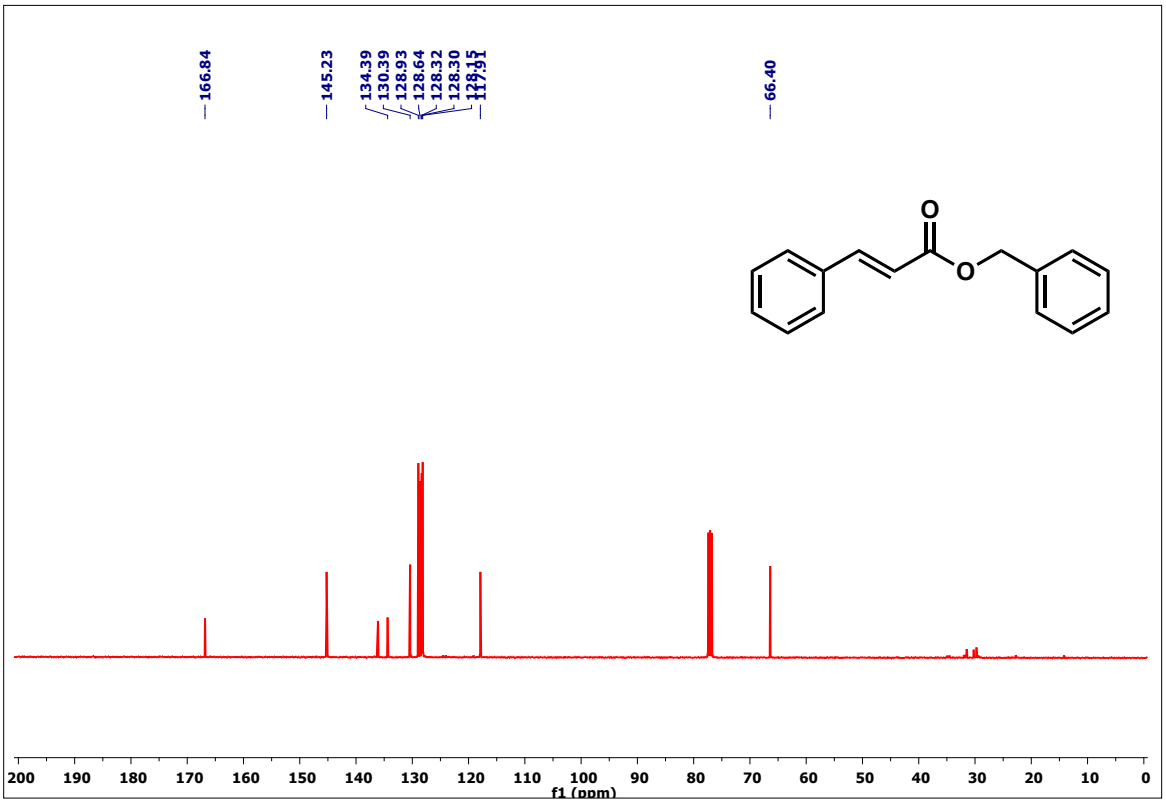

Figure S36: 100 MHz ^{13}C NMR spectrum of **14** in $CDCl_3$

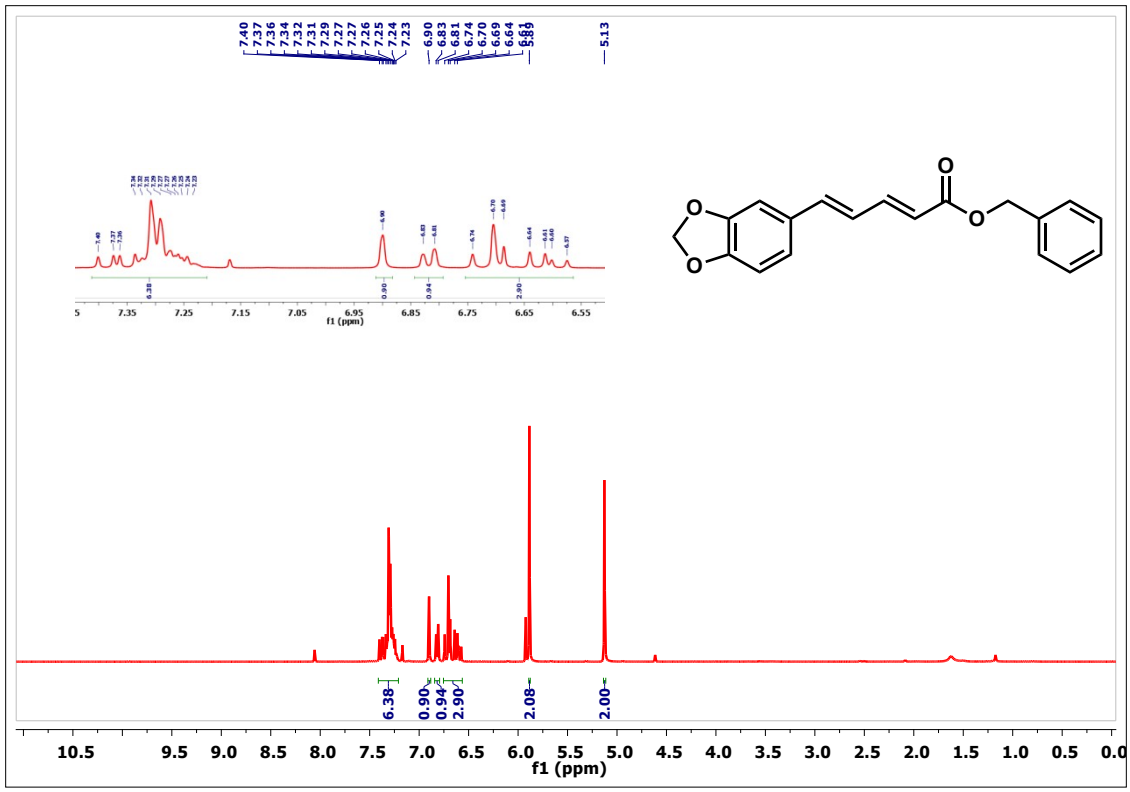

Figure S37: 400 MHz ^{1}H NMR spectrum of **15** in $CDCl_3$

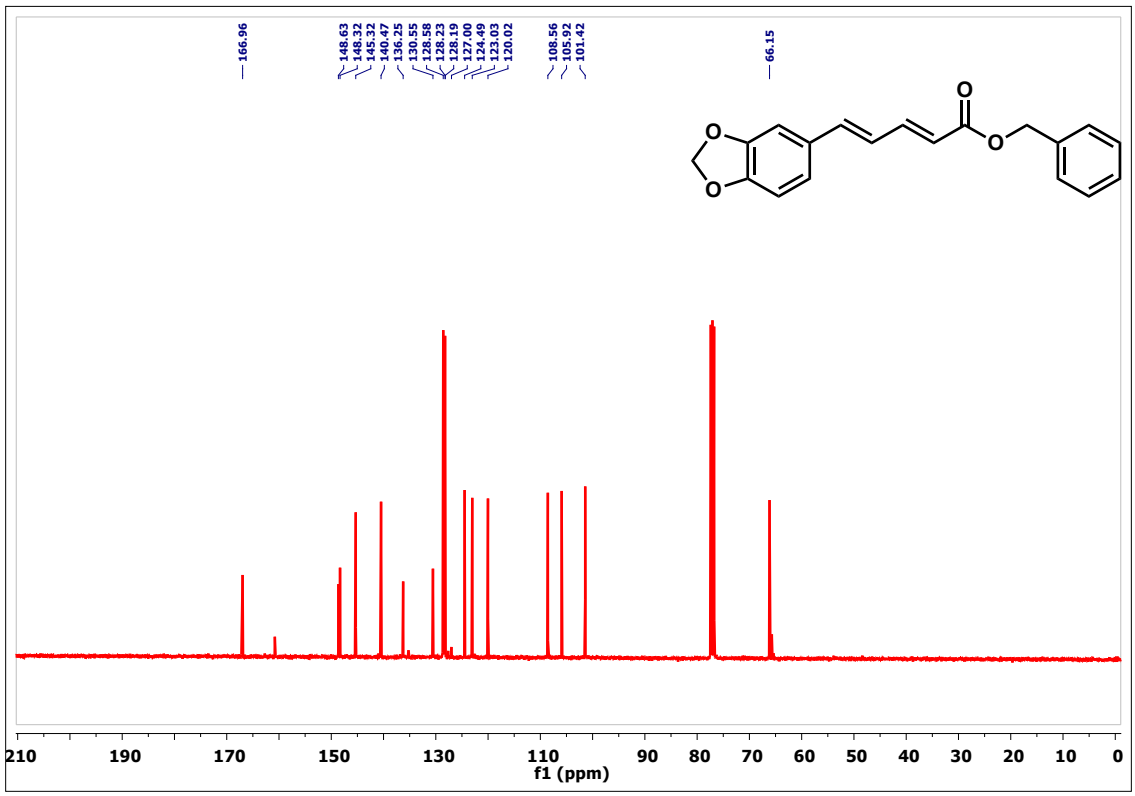

Figure S38: 100 MHz ^{13}C NMR spectrum of **15** in $CDCl_3$

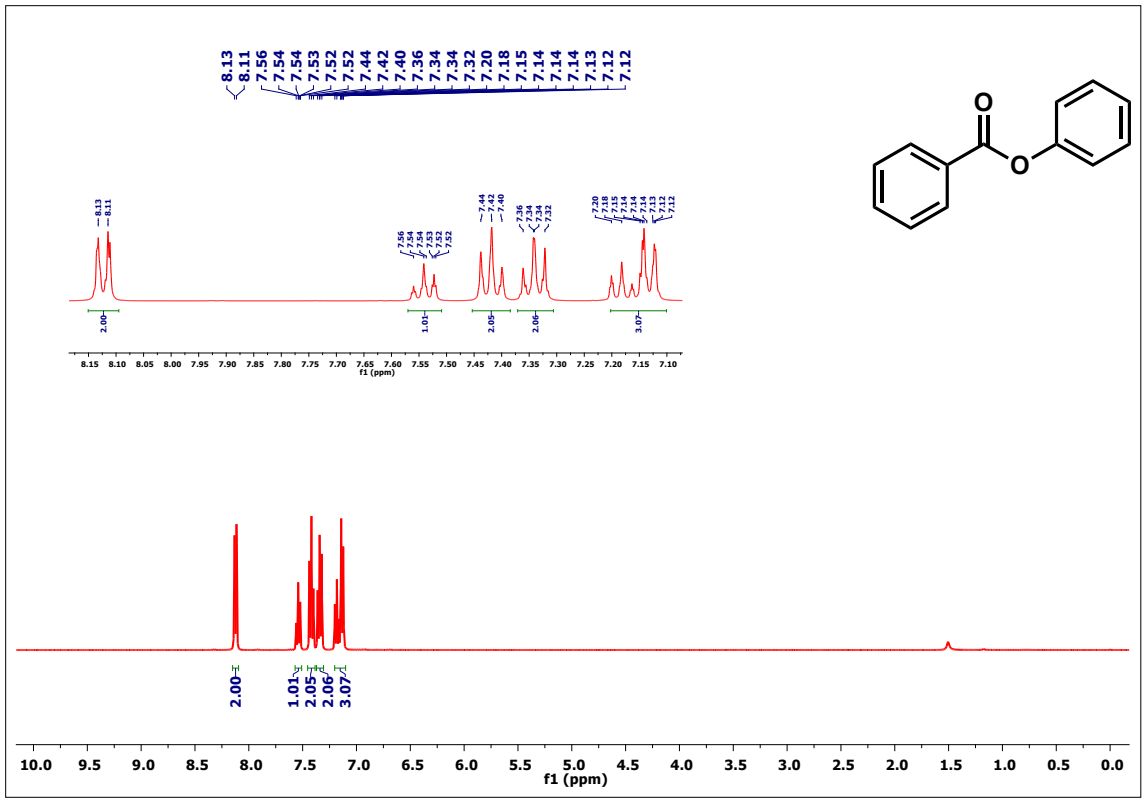

Figure S39: 400 MHz ^{1}H NMR spectrum of **16** in $CDCl_3$

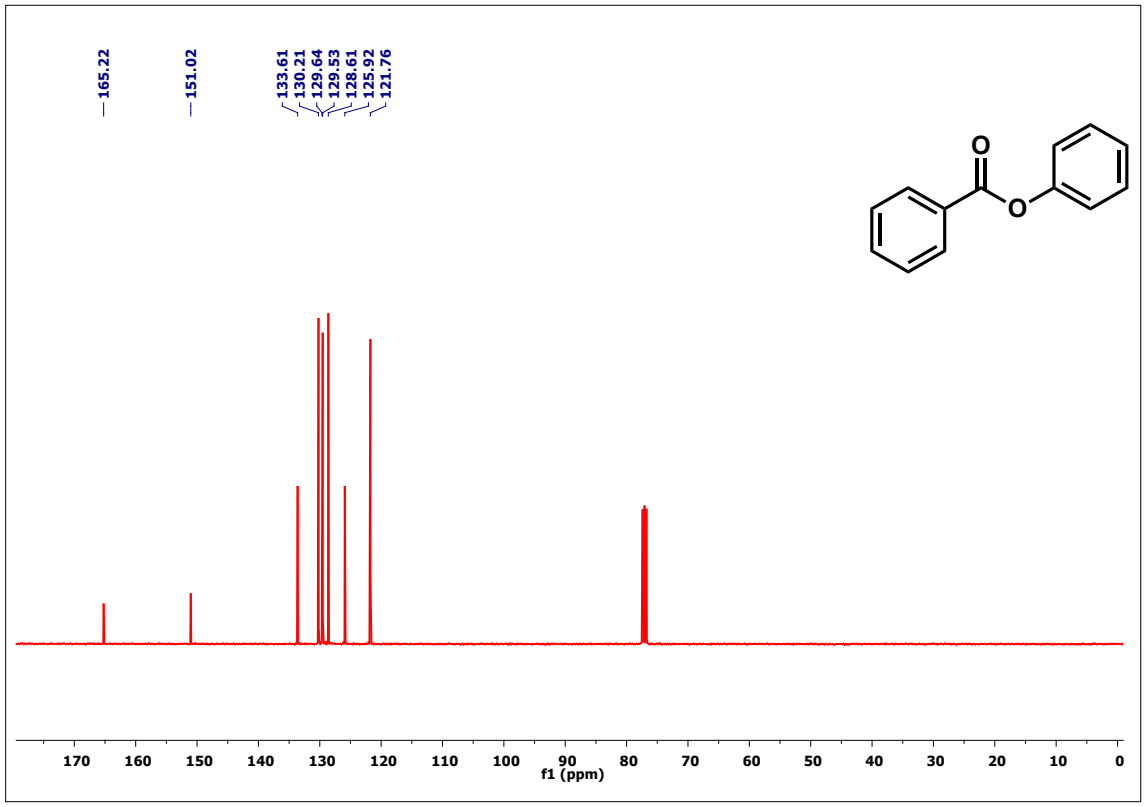

Figure S40: 100 MHz ^{13}C NMR spectrum of **16** in $CDCl_3$

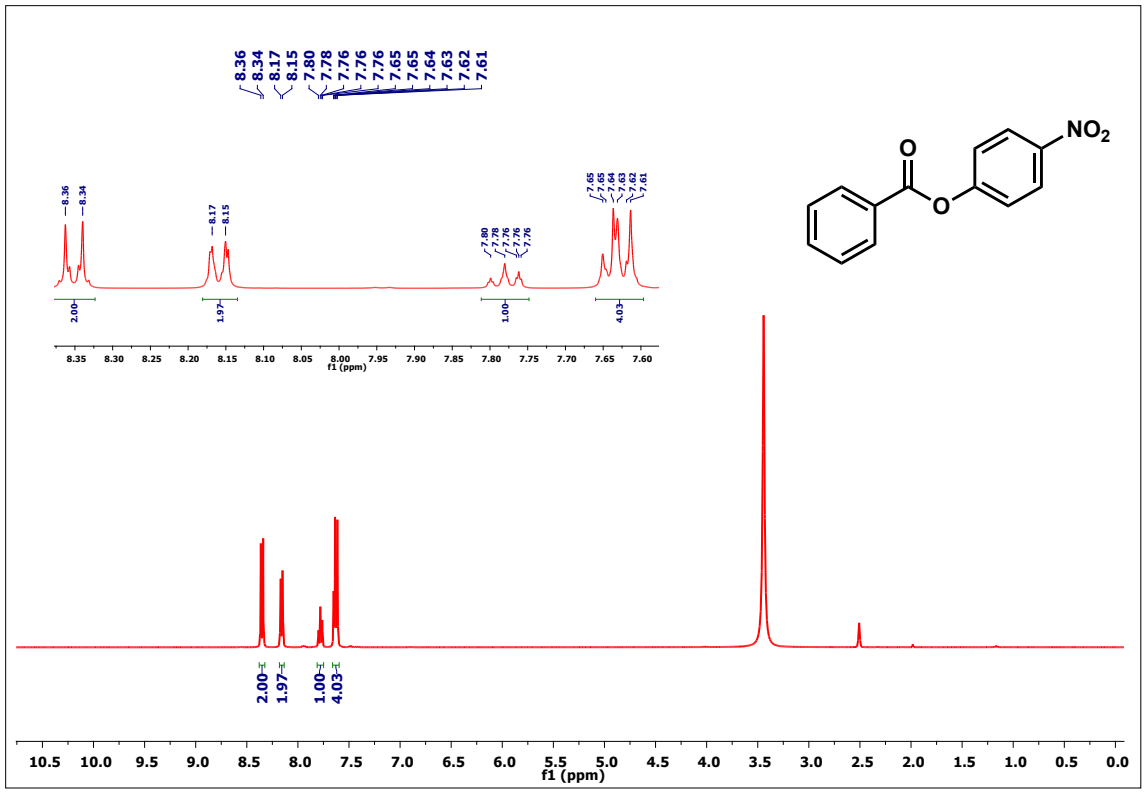

Figure S41: 400 MHz ^{1}H NMR spectrum of **17** in DMSO-d_6

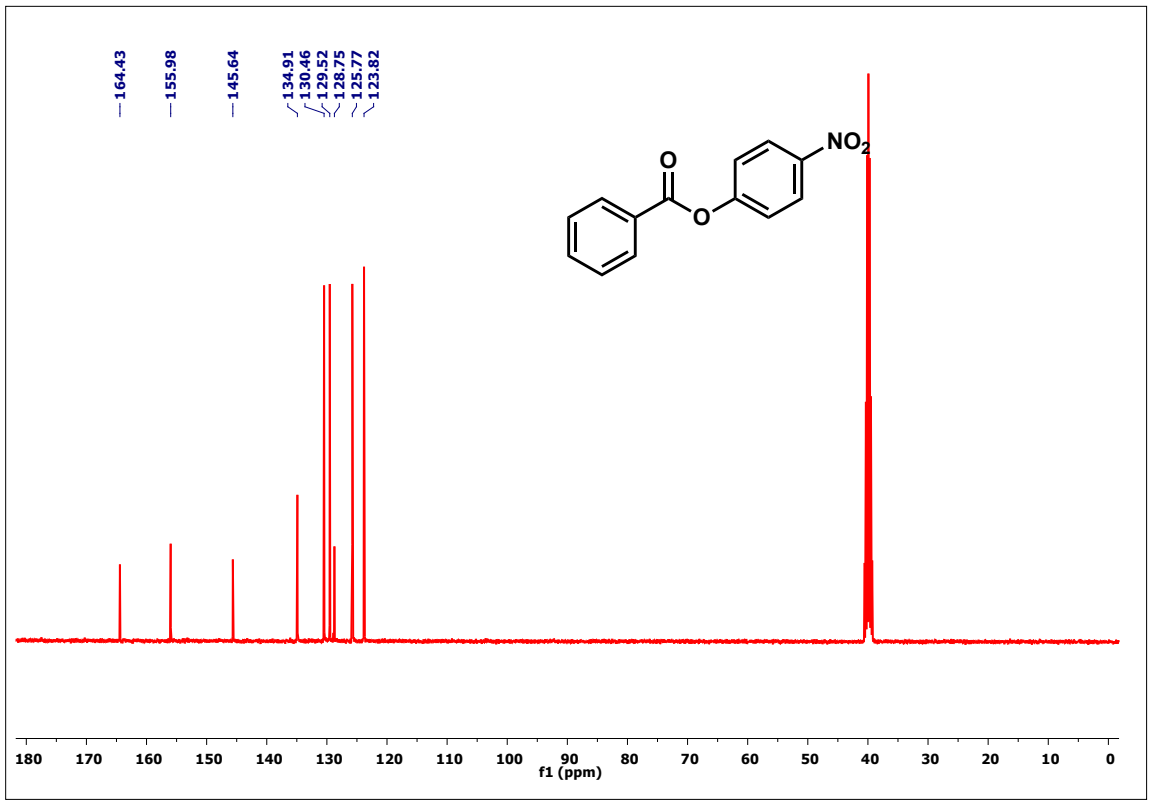

Figure S42: 100 MHz ^{13}C NMR spectrum of **17** in DMSO-d_6

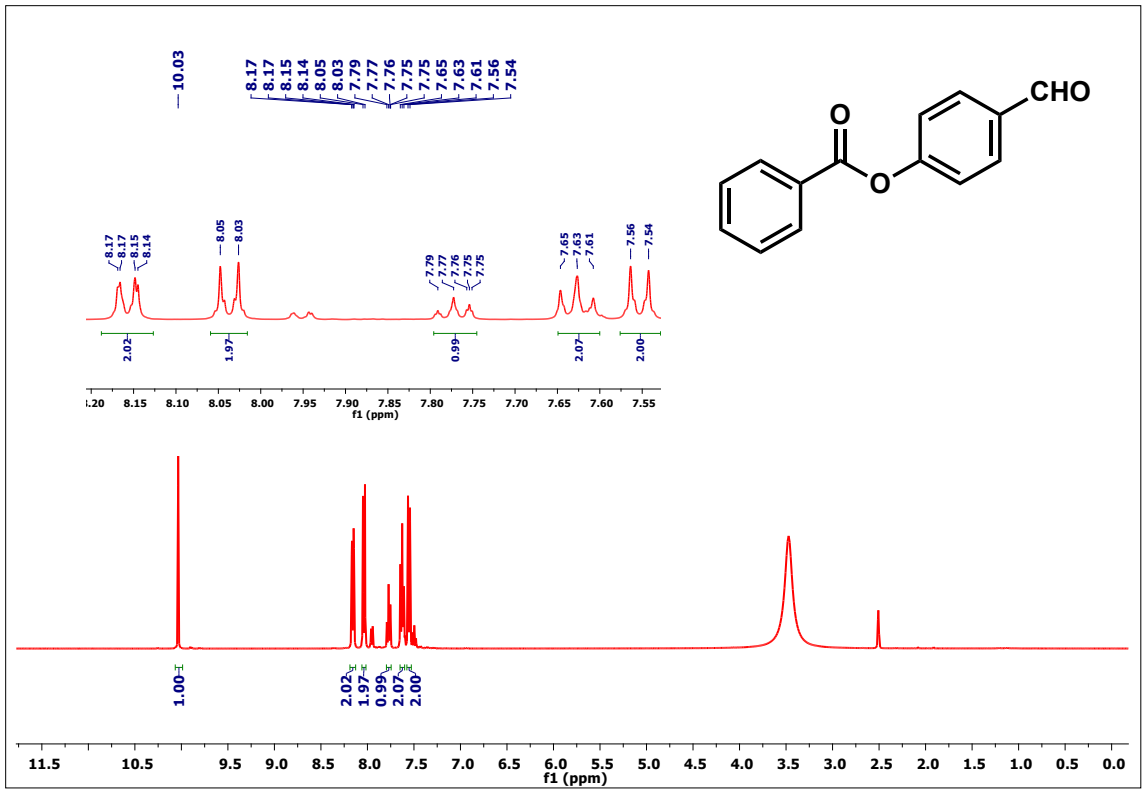

Figure S43: 400 MHz ^{1}H NMR spectrum of **18** in DMSO-d_6

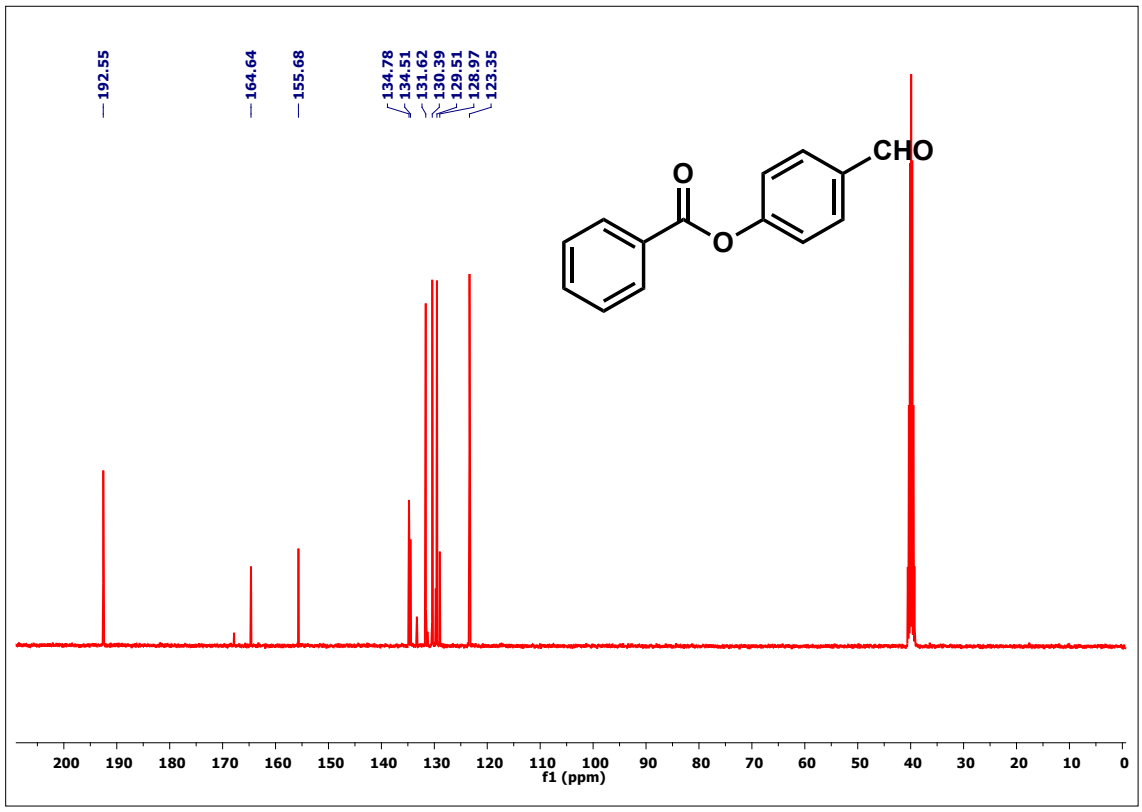

Figure S44: 100 MHz ^{13}C NMR spectrum of **18** in DMSO-d_6

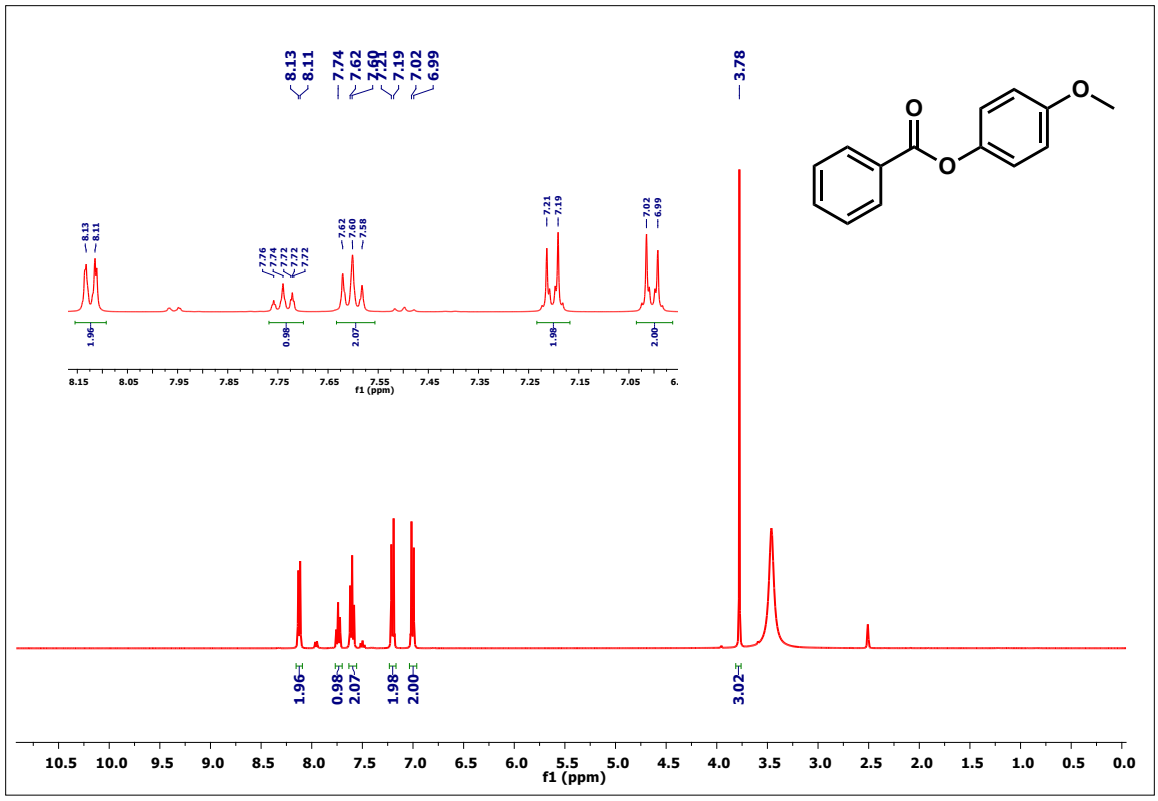

Figure S45: 400 MHz ^{1}H NMR spectrum of **19** in DMSO-d_6

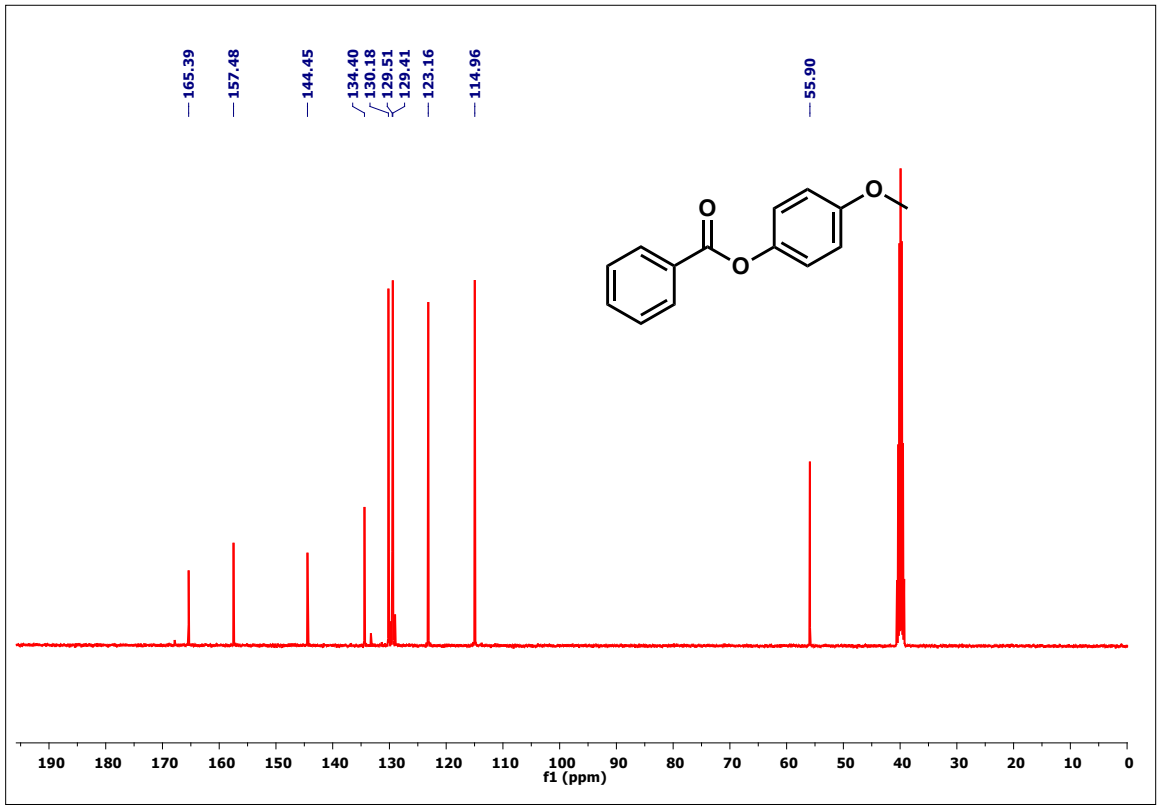

Figure S46: 100 MHz ^{13}C NMR spectrum of **19** in DMSO-d_6

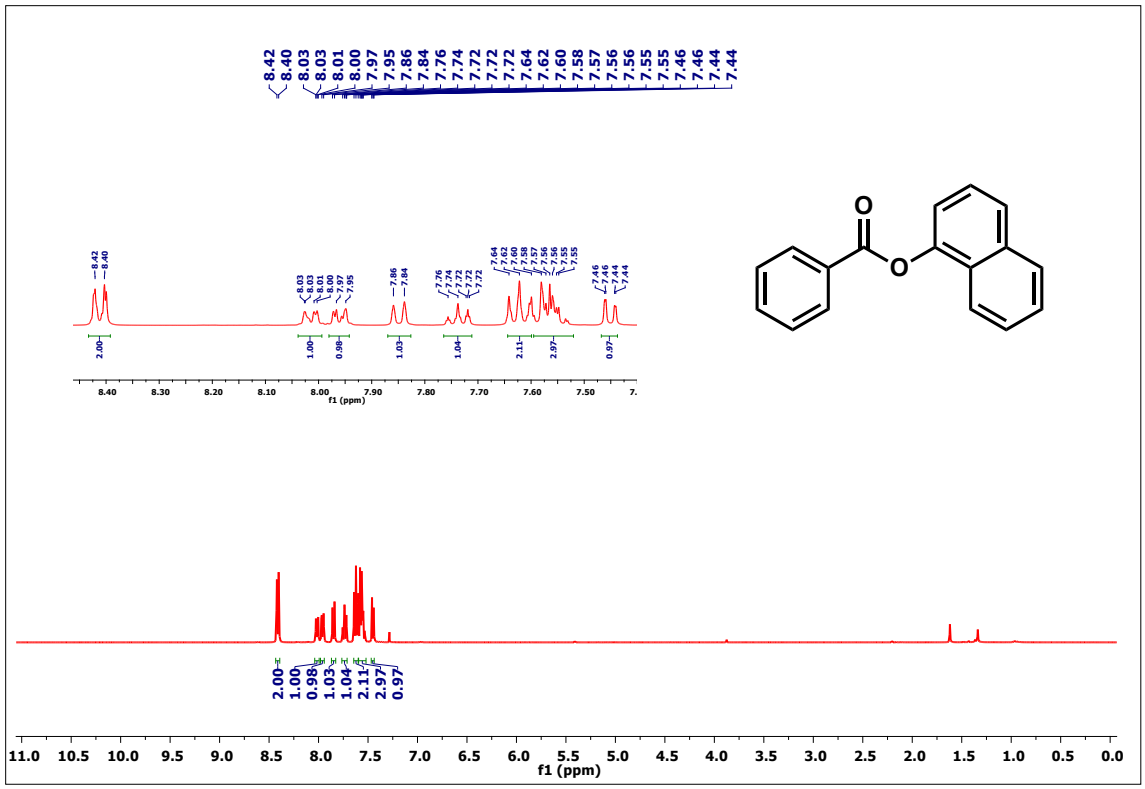

Figure S47: 400 MHz ^{1}H NMR spectrum of **20** in $CDCl_3$

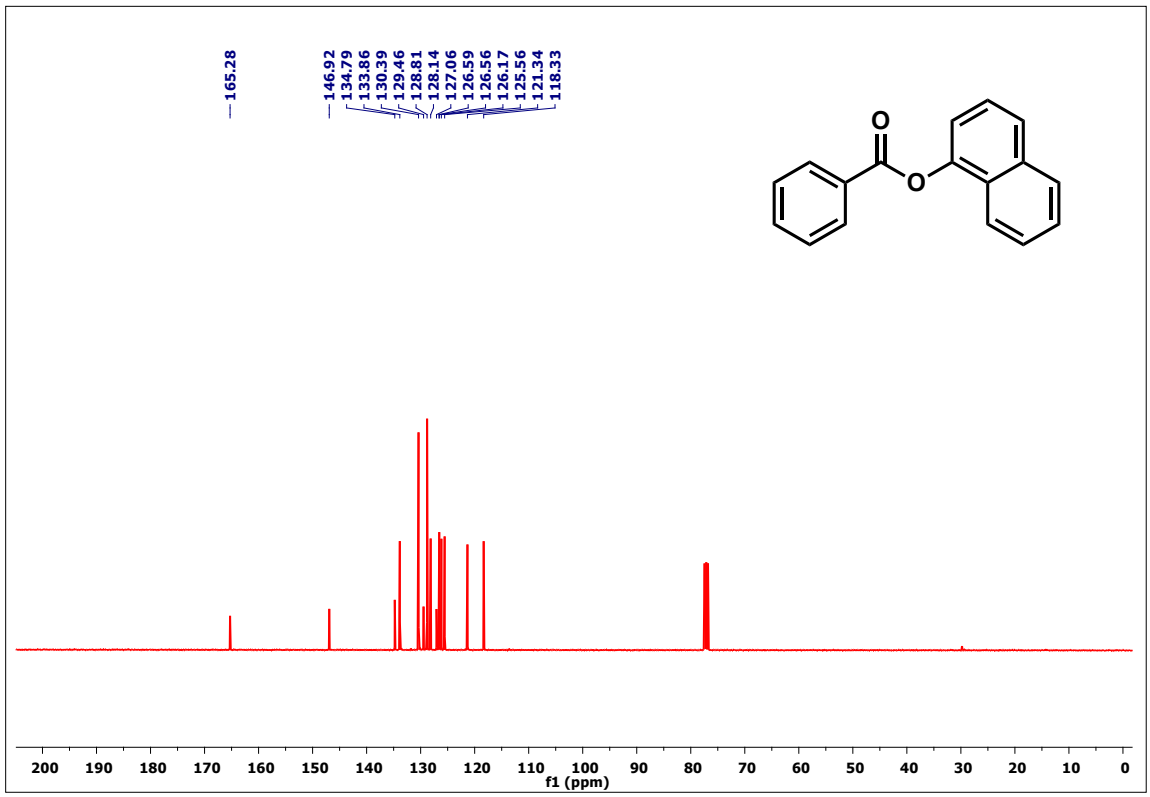

Figure S48: 100 MHz ^{13}C NMR spectrum of **20** in $CDCl_3$

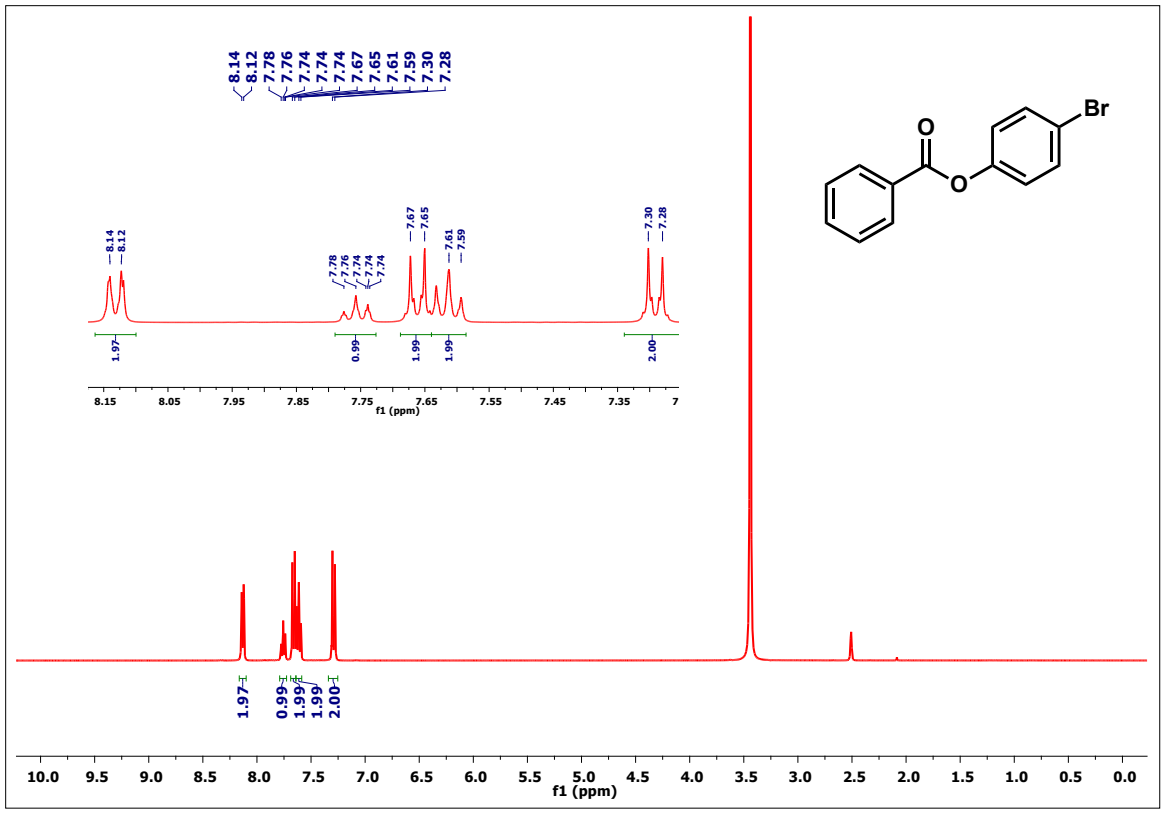

Figure S49: 400 MHz ^{1}H NMR spectrum of **21** in DMSO-d_6

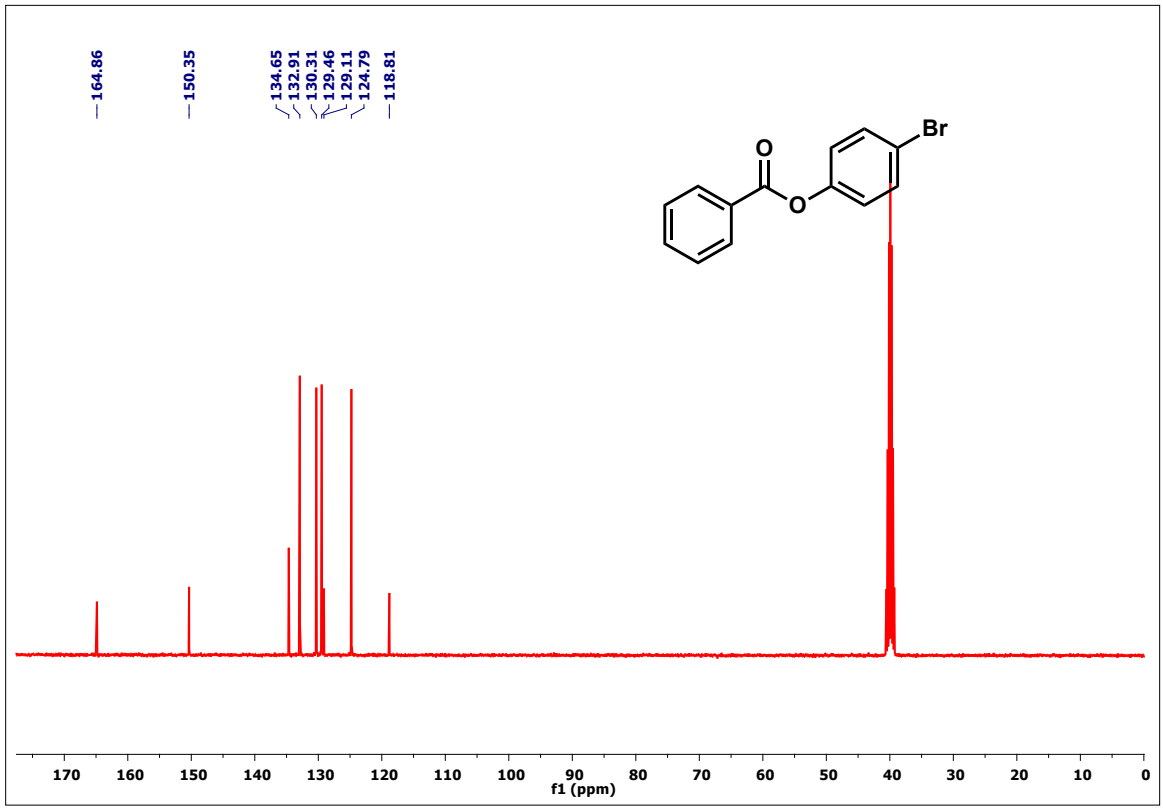

Figure S50: 100 MHz ^{13}C NMR spectrum of **21** in DMSO-d_6

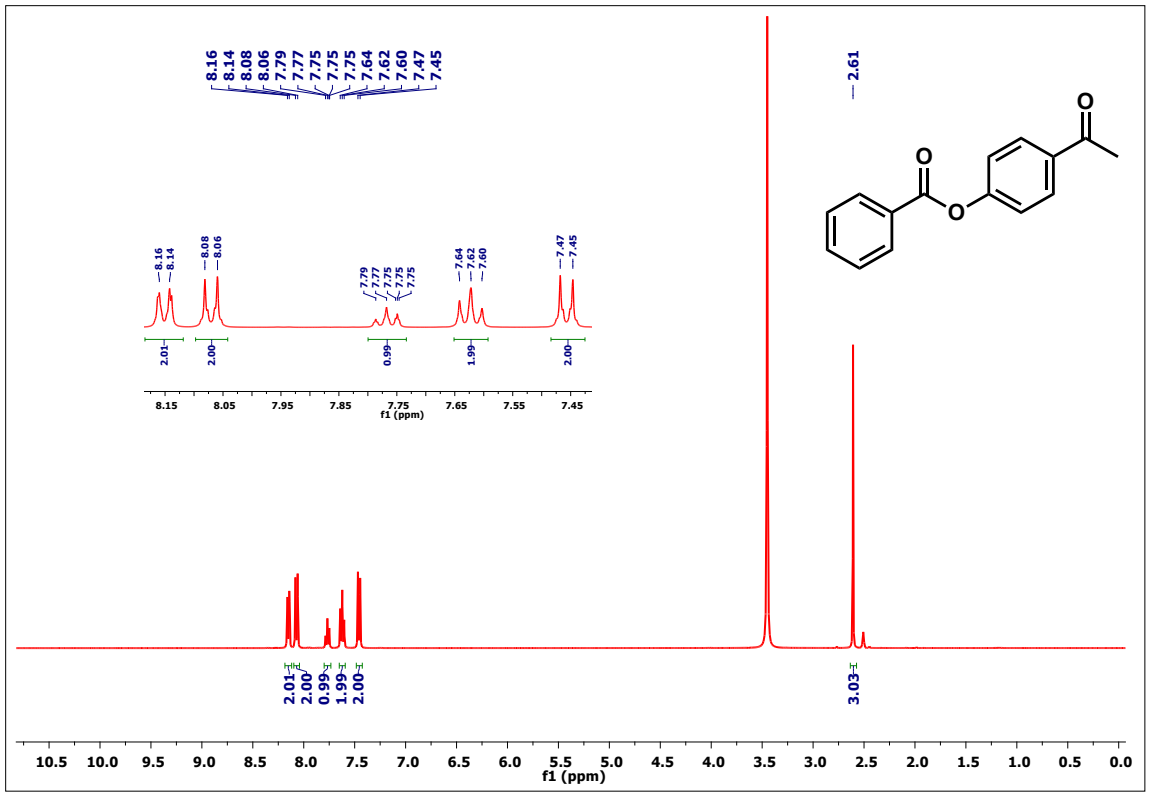

Figure S51: 400 MHz ^{1}H NMR spectrum of **22** in DMSO-d_6

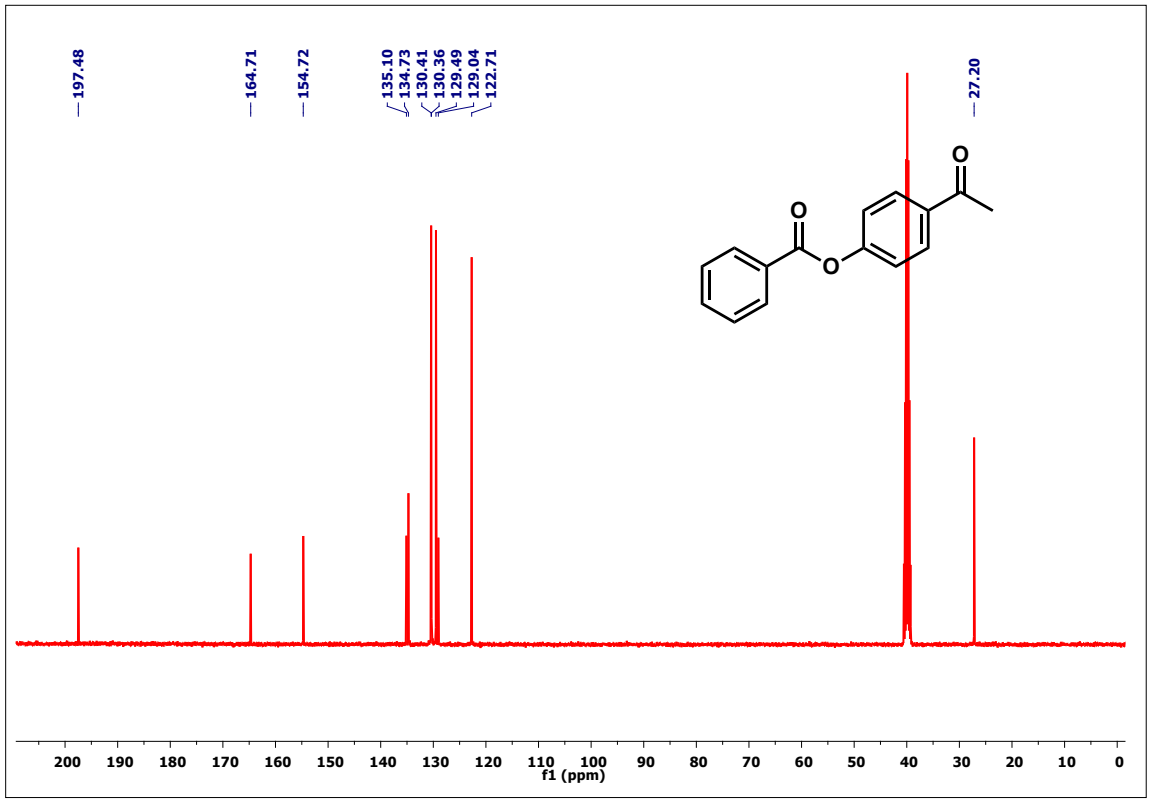

Figure S52: 100 MHz ^{13}C NMR spectrum of **22** in DMSO-d_6

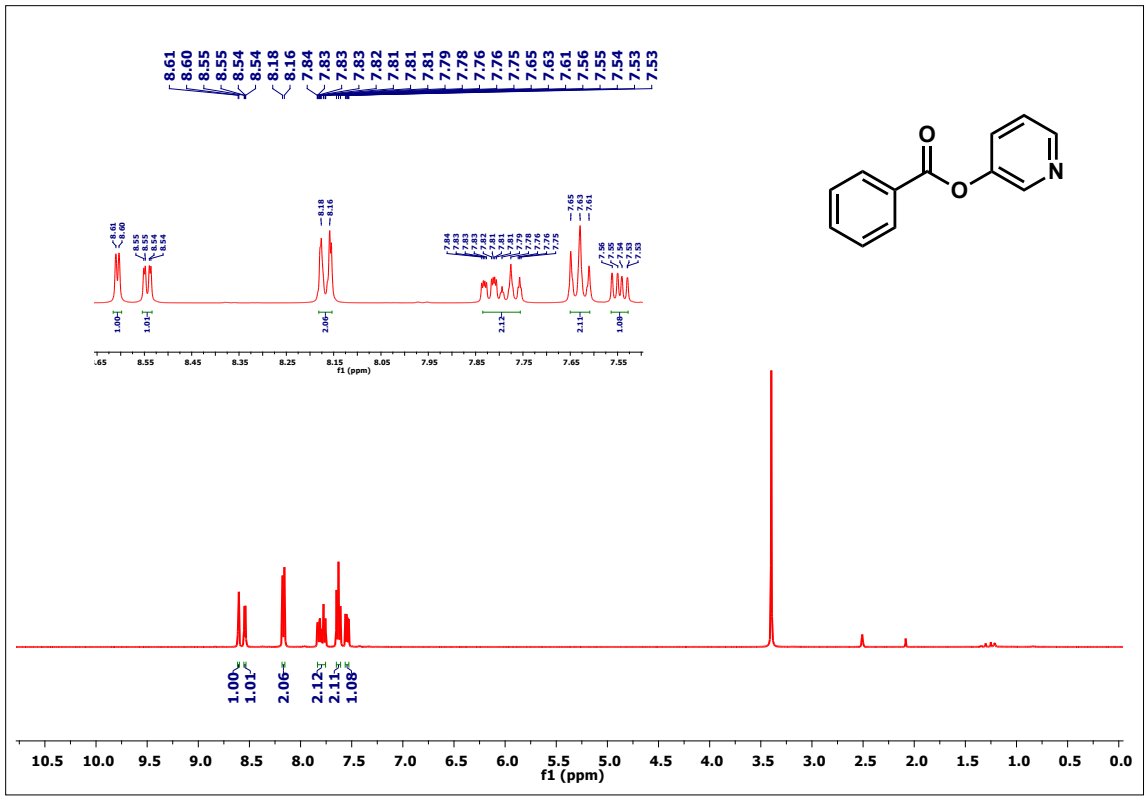

Figure S53: 400 MHz ^{1}H NMR spectrum of **23** in DMSO-d_6

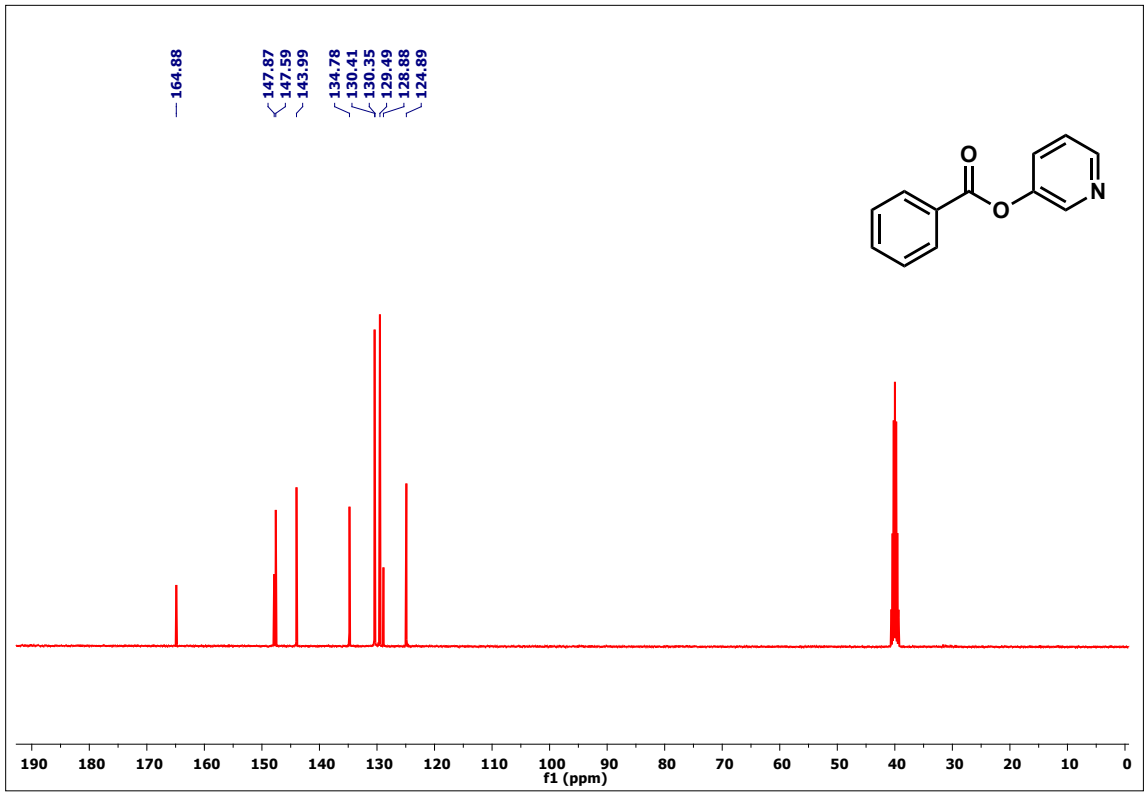

Figure S54: 100 MHz ^{13}C NMR spectrum of **23** in DMSO-d_6

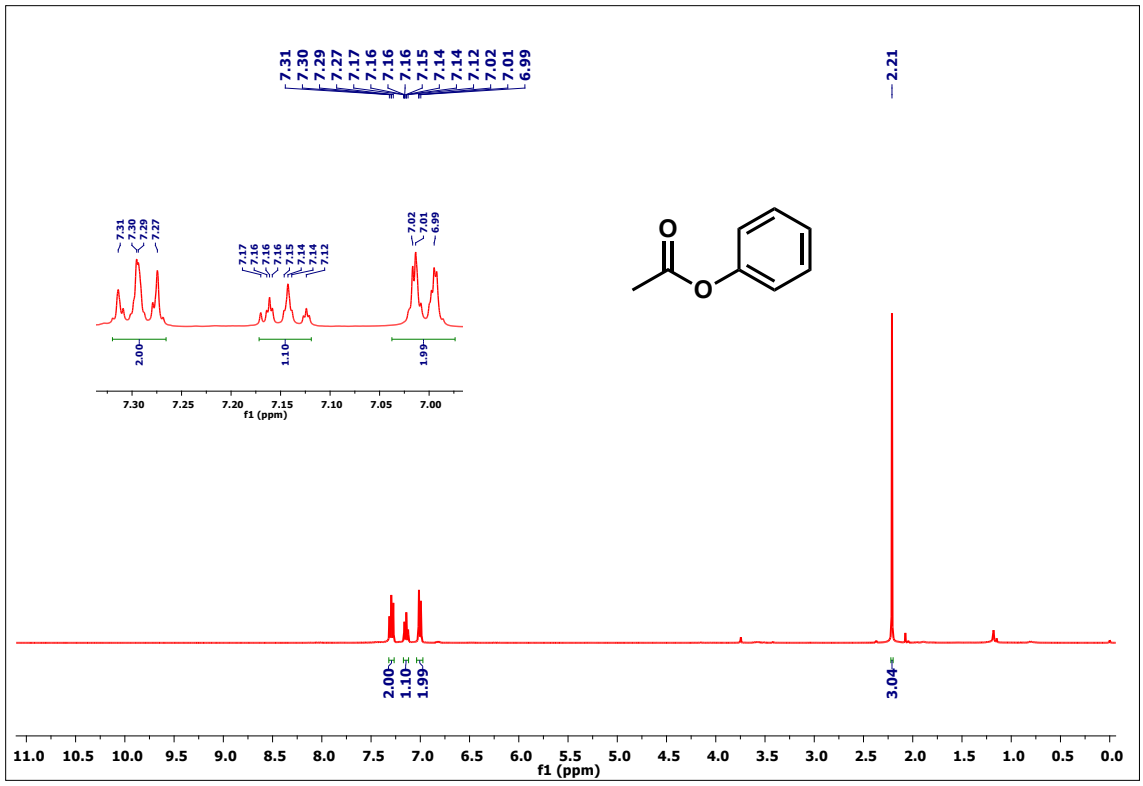

Figure S55: 400 MHz ^{1}H NMR spectrum of **24** in $CDCl_3$

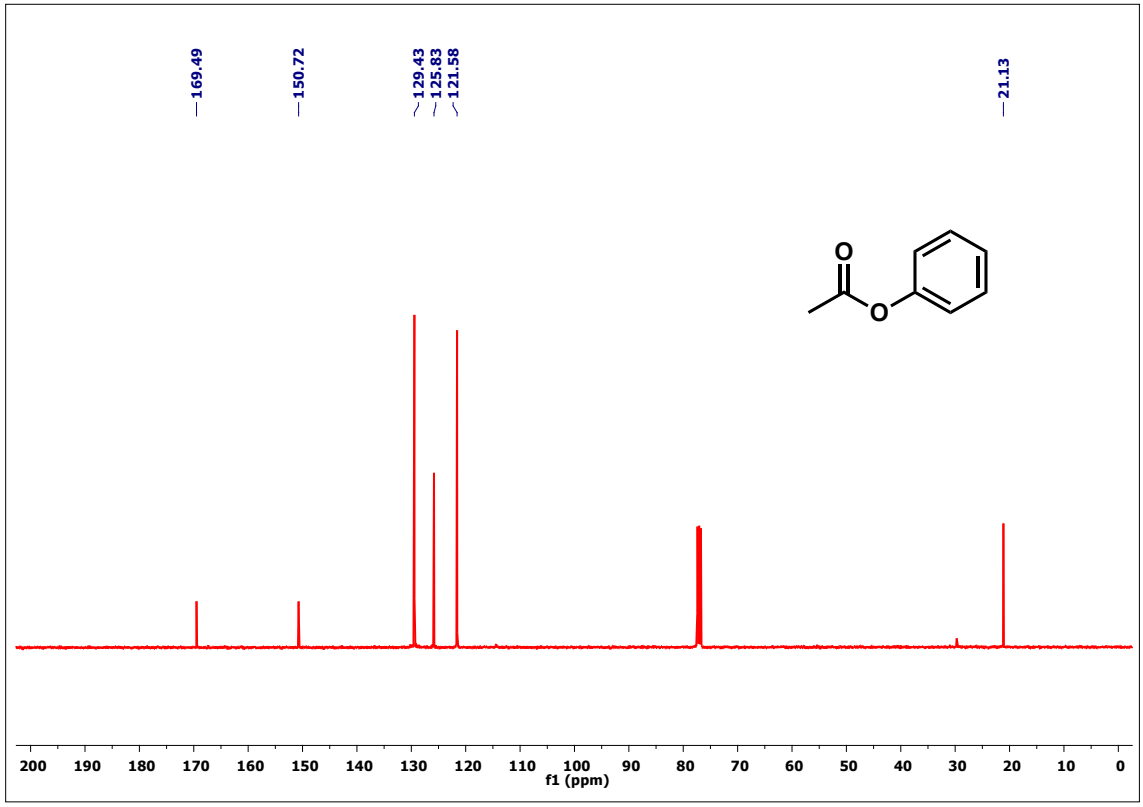

Figure S56: 100 MHz ^{13}C NMR spectrum of **24** in $CDCl_3$

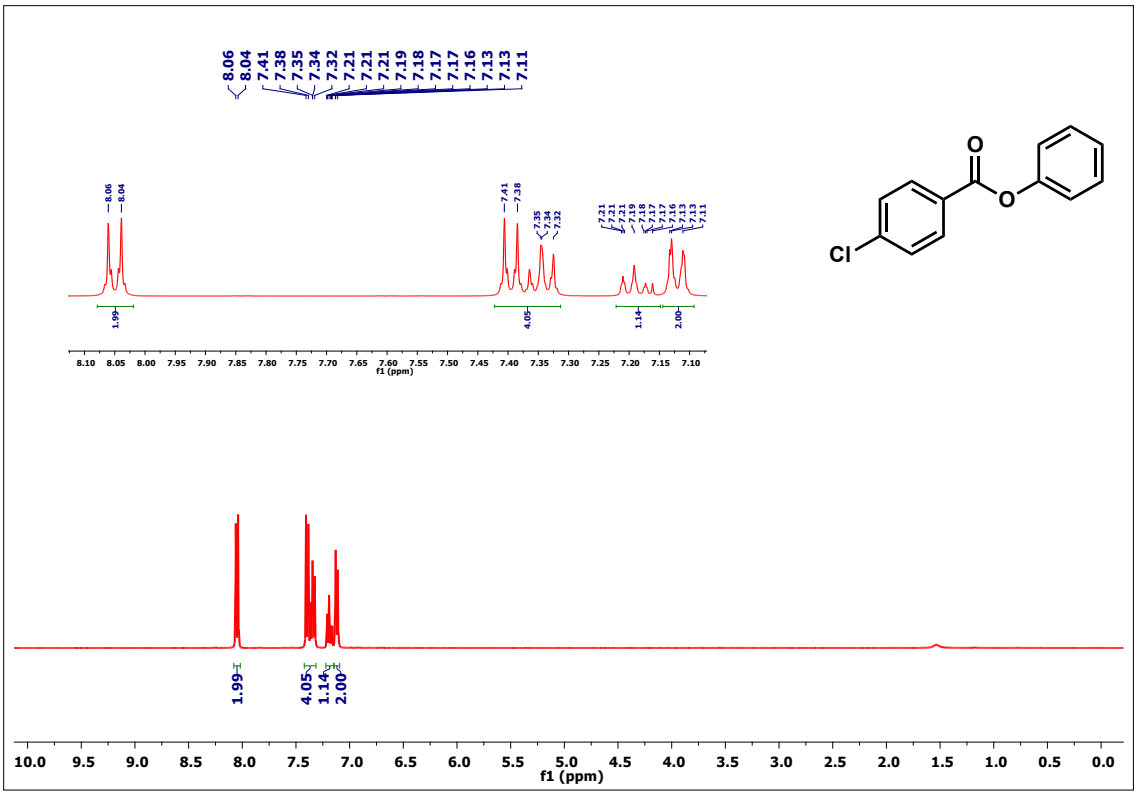

Figure S59: 400 MHz ^{1}H NMR spectrum of **25** in $CDCl_3$

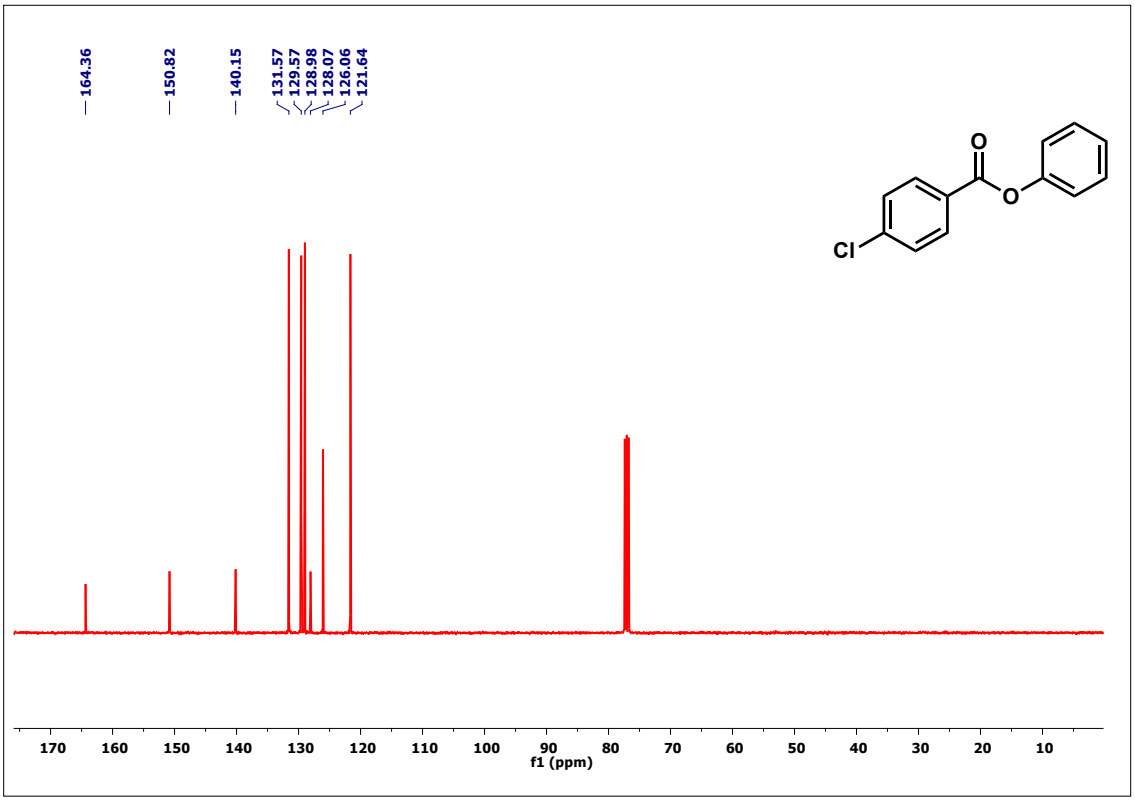

Figure S60: 100 MHz ^{13}C NMR spectrum of **25** in $CDCl_3$

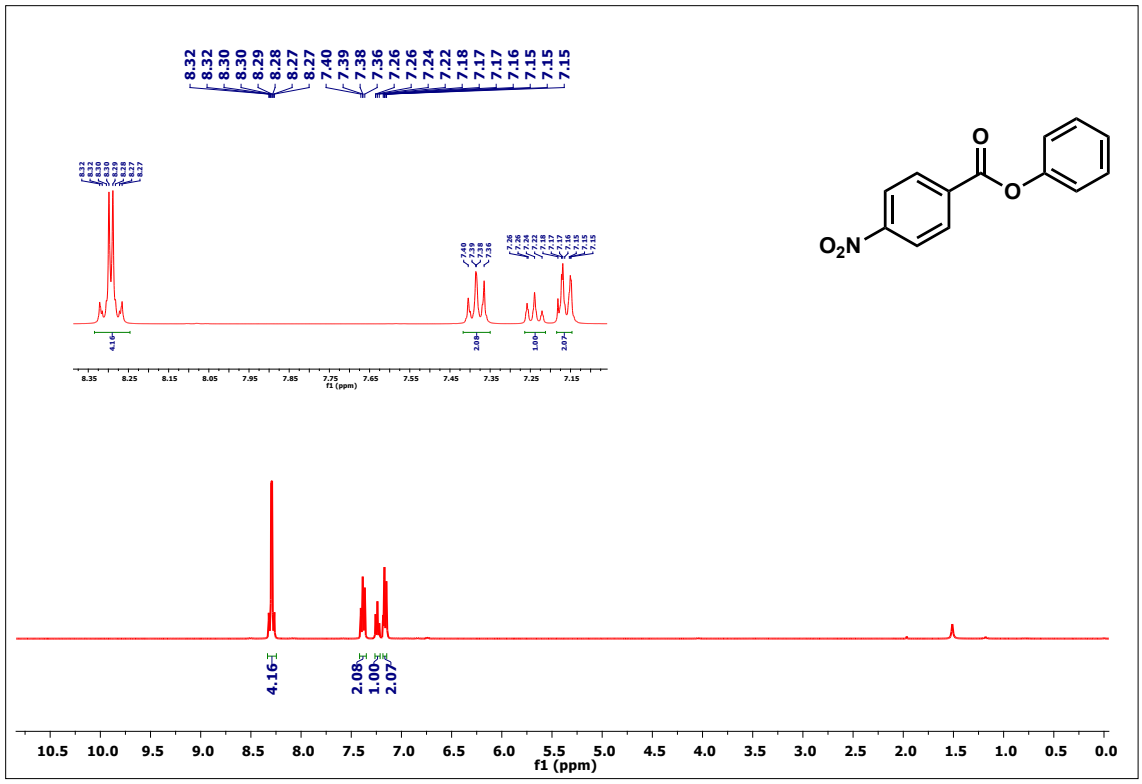

Figure S57: 400 MHz ^{1}H NMR spectrum of **26** in $CDCl_3$

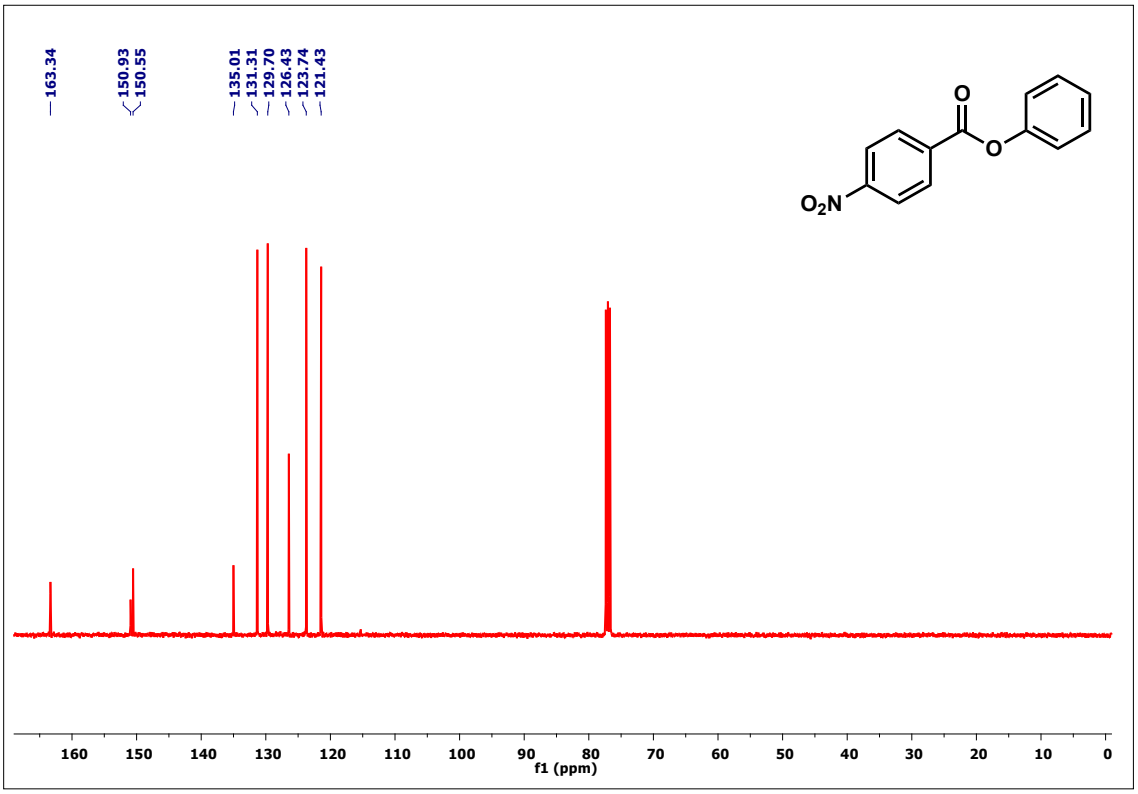

Figure S58: 100 MHz ^{13}C NMR spectrum of **26** in $CDCl_3$

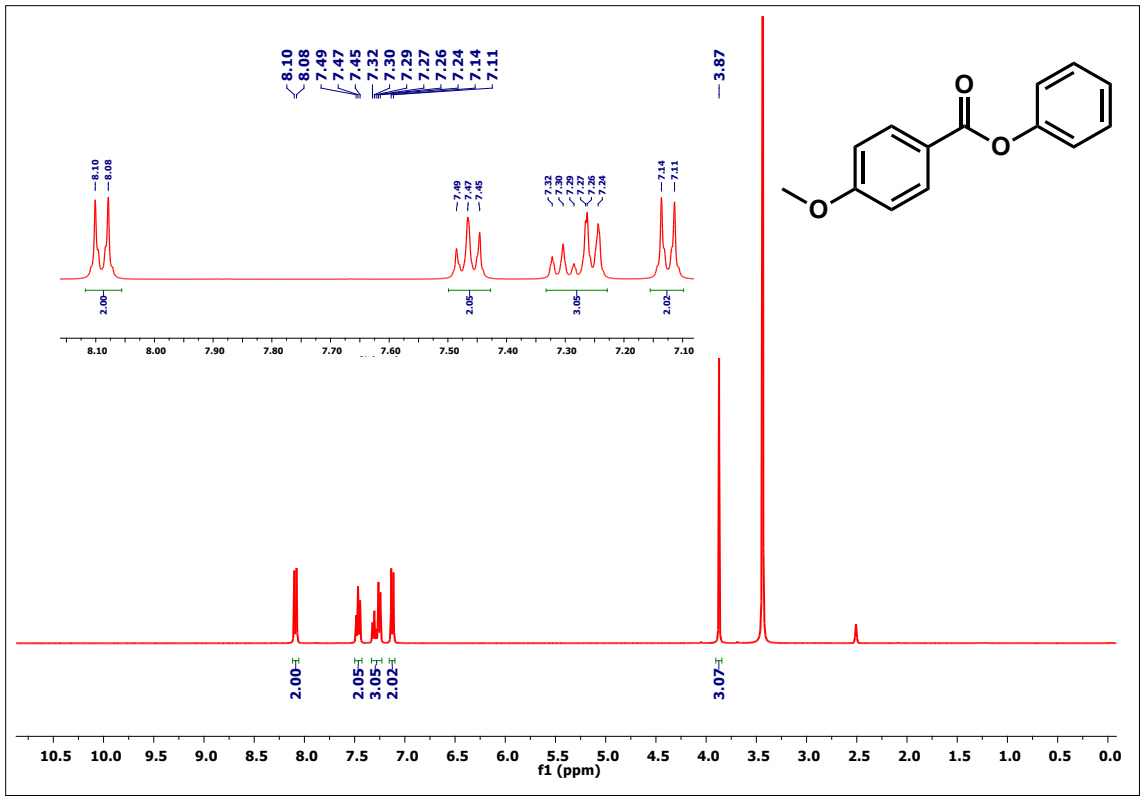

Figure S61: 400 MHz ^{1}H NMR spectrum of **27** in DMSO-d_6

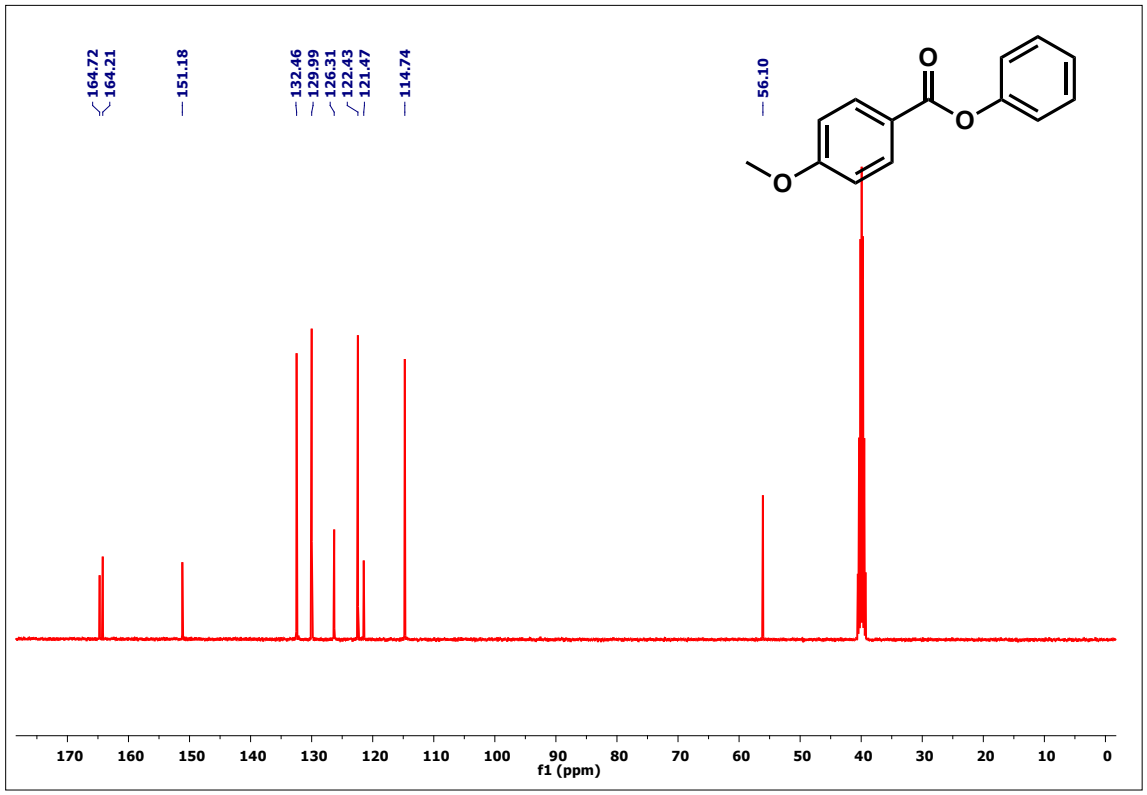

Figure S62: 100 MHz ^{13}C NMR spectrum of **27** in DMSO-d_6

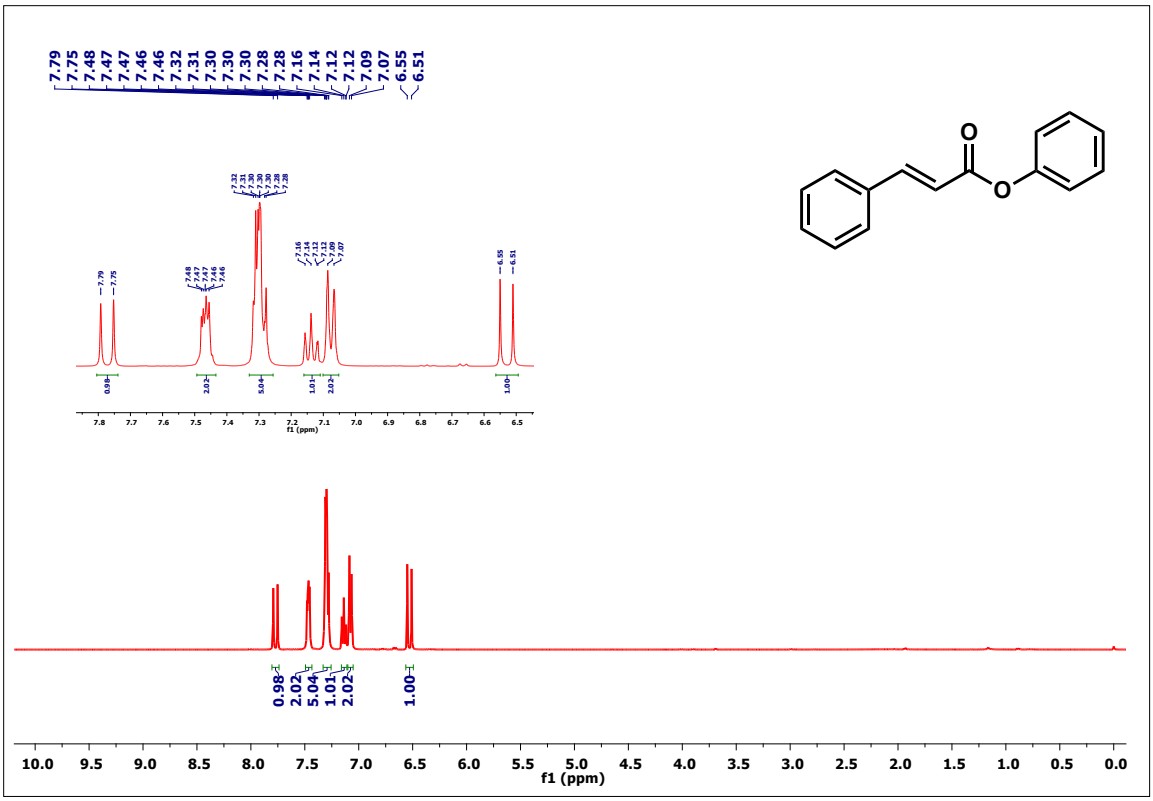

Figure S63: 400 MHz ^{1}H NMR spectrum of **28** in $CDCl_3$

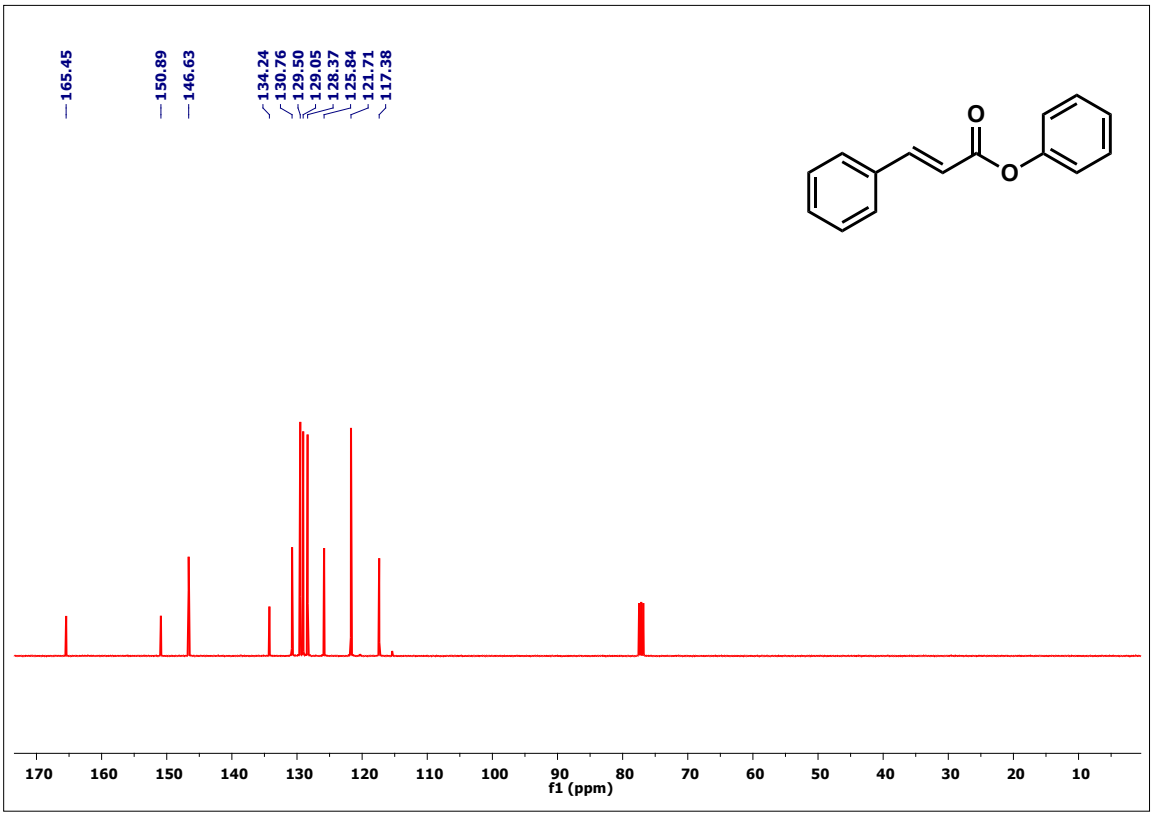

Figure S64: 100 MHz ^{13}C NMR spectrum of **28** in $CDCl_3$

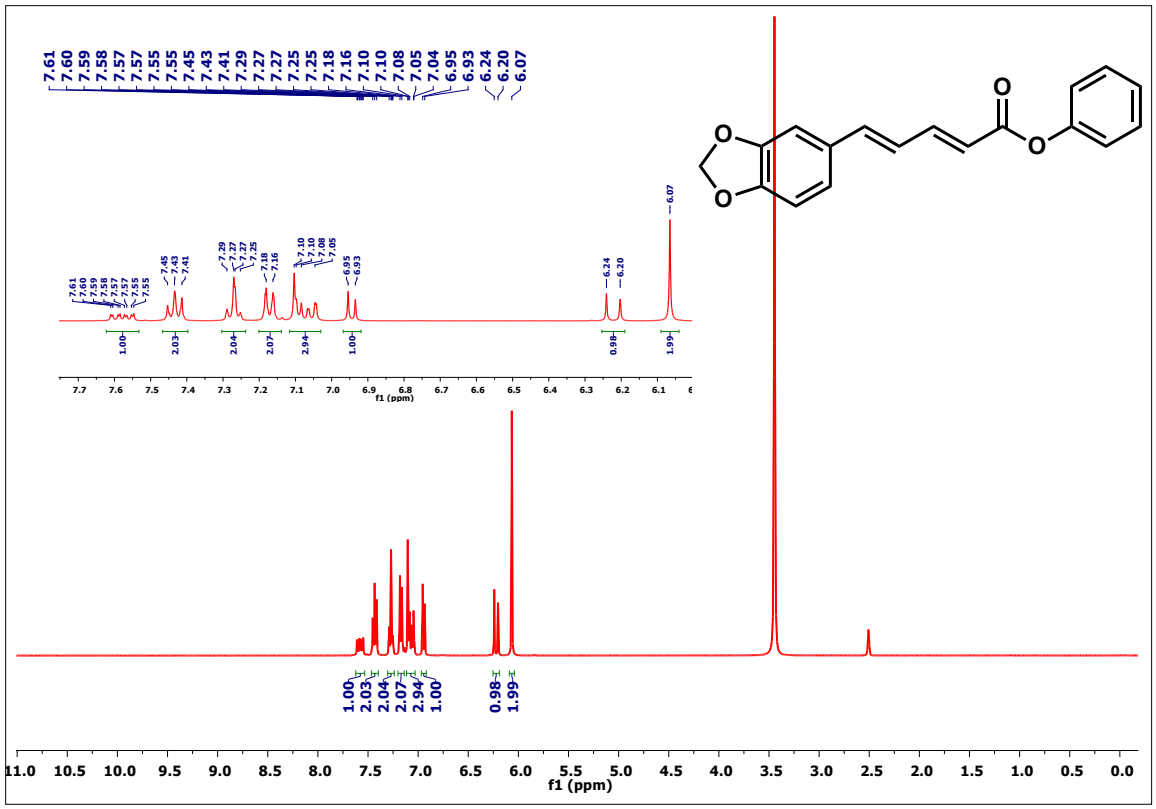

Figure S65: 400 MHz ^{1}H NMR spectrum of **29** in DMSO-d_6

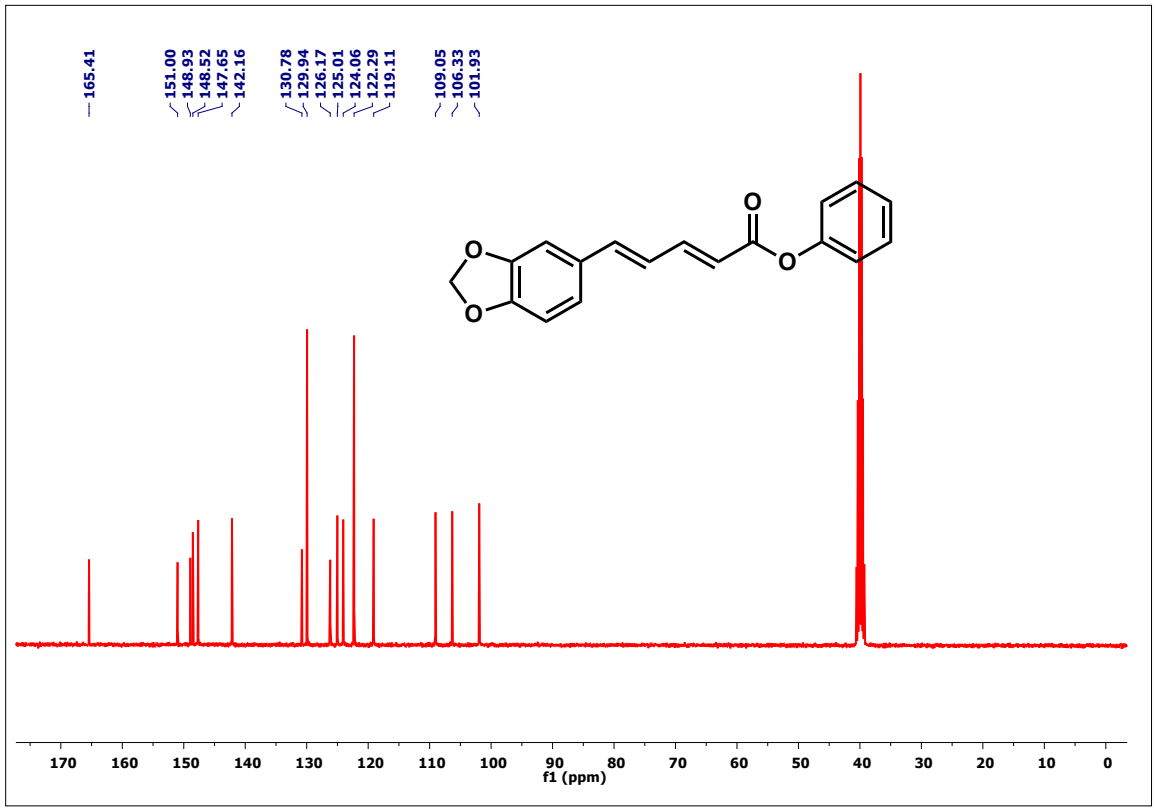

Figure S66: 100 MHz ^{13}C NMR spectrum of **29** in DMSO-d_6

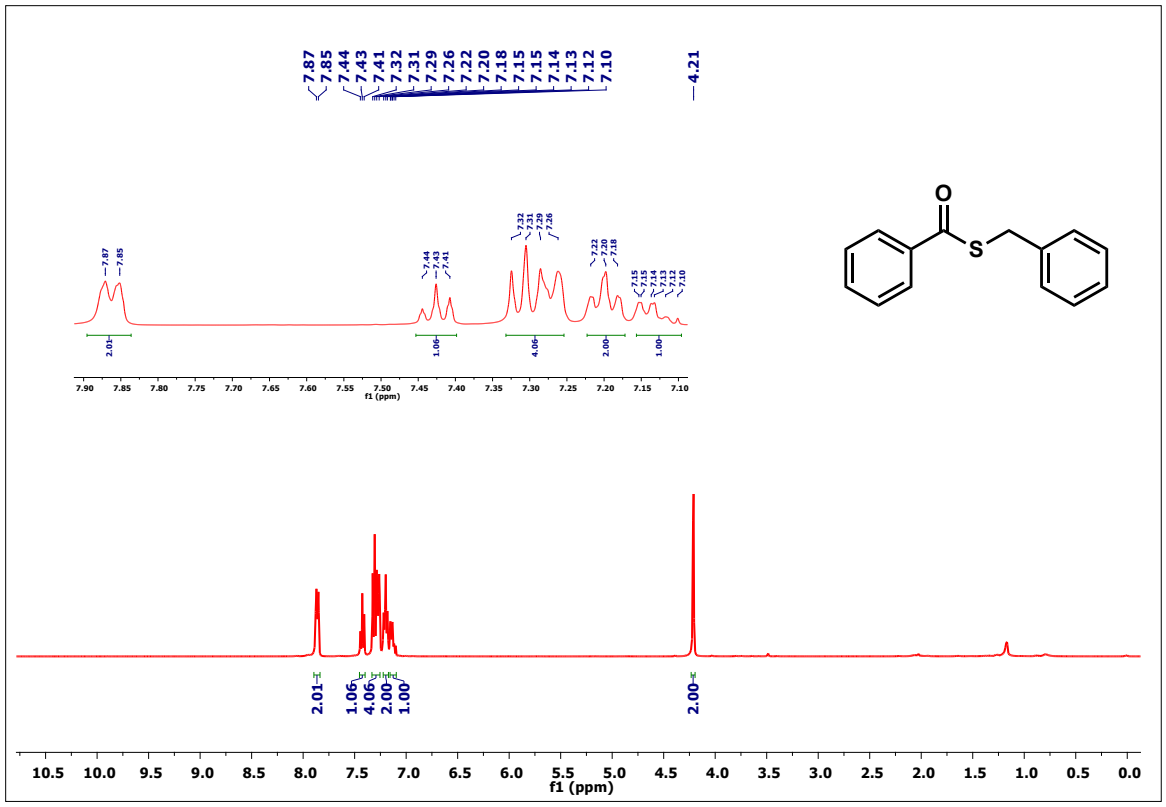

Figure S67: 400 MHz ^{1}H NMR spectrum of **30** in $CDCl_3$

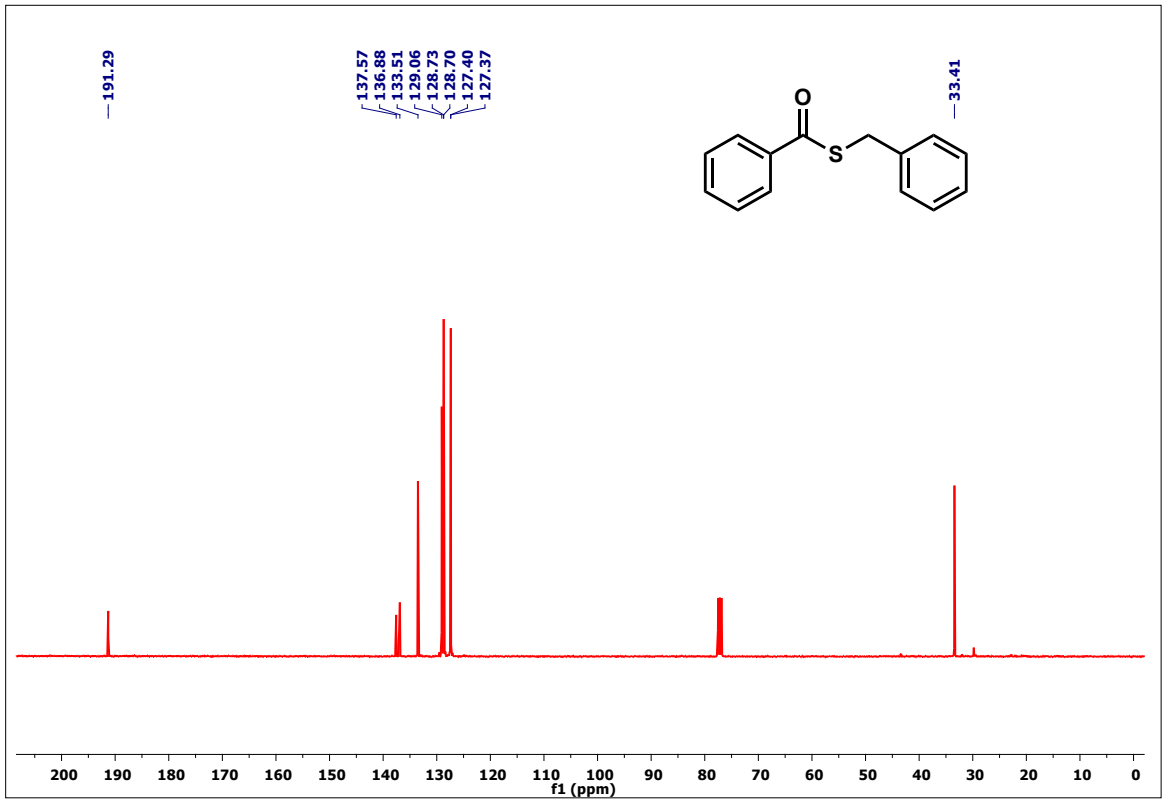

Figure S68: 100 MHz ^{13}C NMR spectrum of **30** in $CDCl_3$

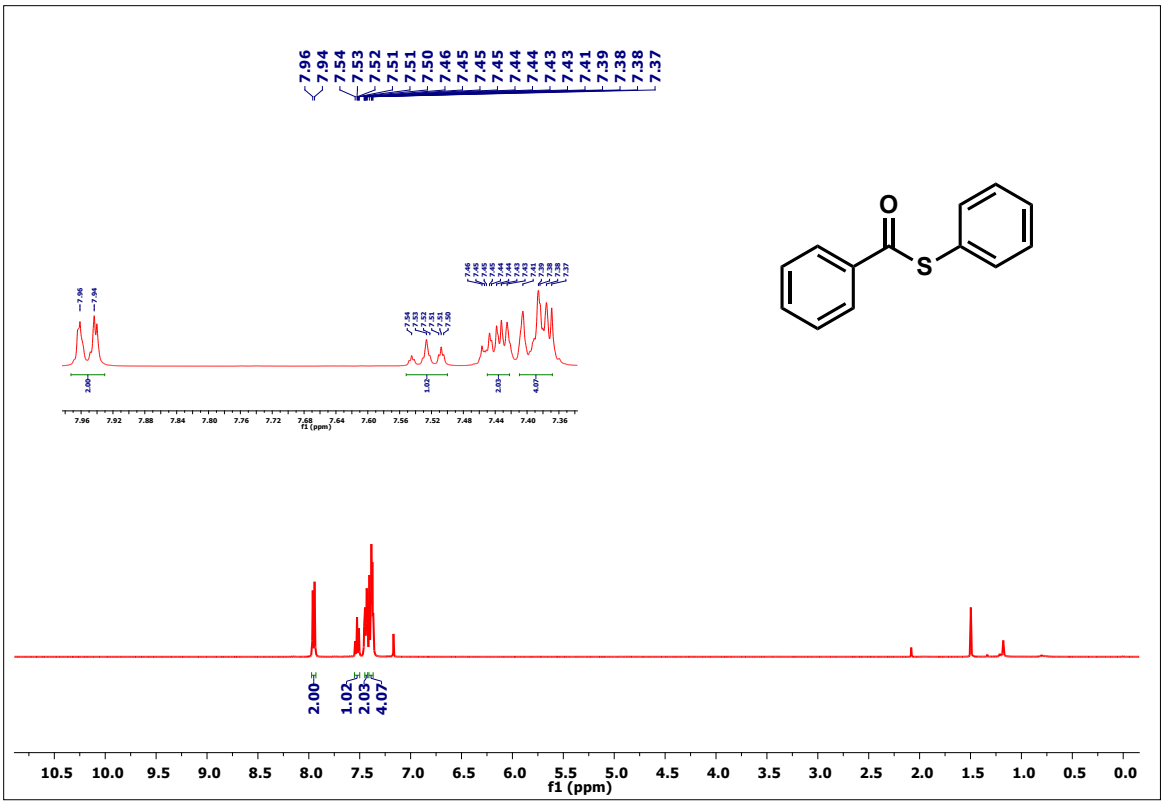

Figure S69: 400 MHz ^{1}H NMR spectrum of **31** in $CDCl_3$

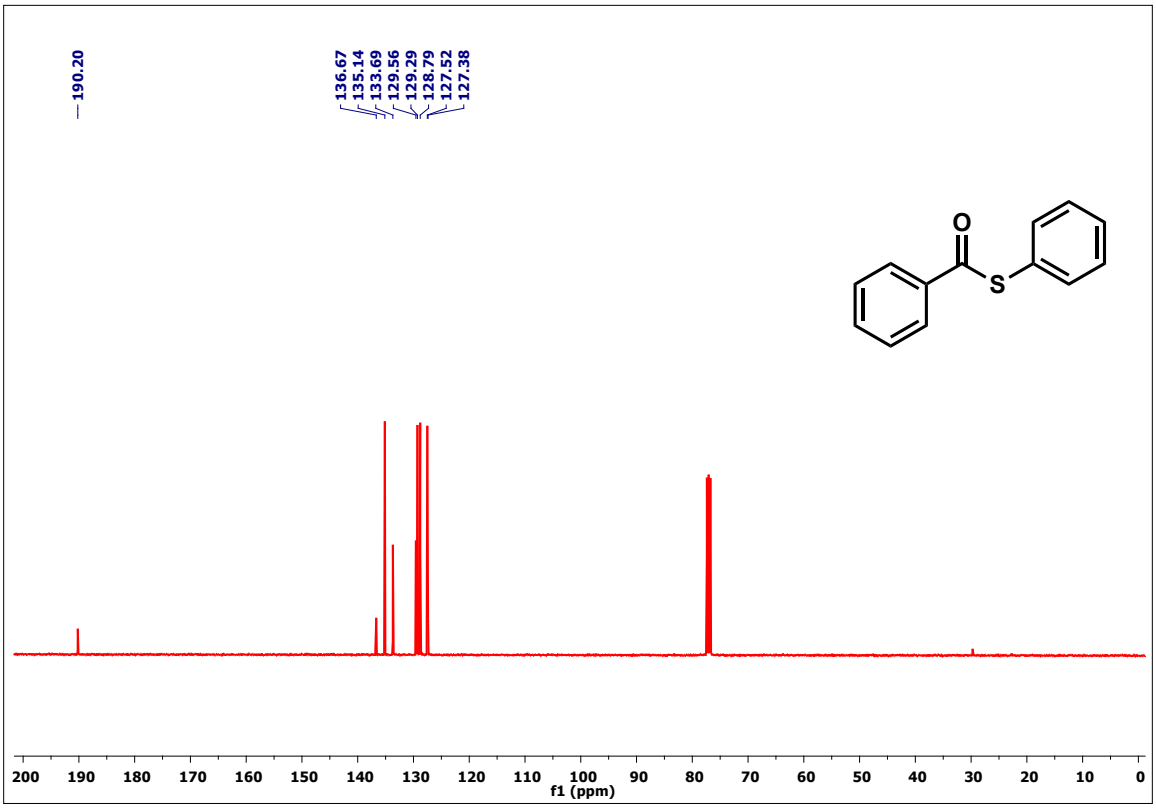

Figure S70: 100 MHz ^{13}C NMR spectrum of **31** in $CDCl_3$

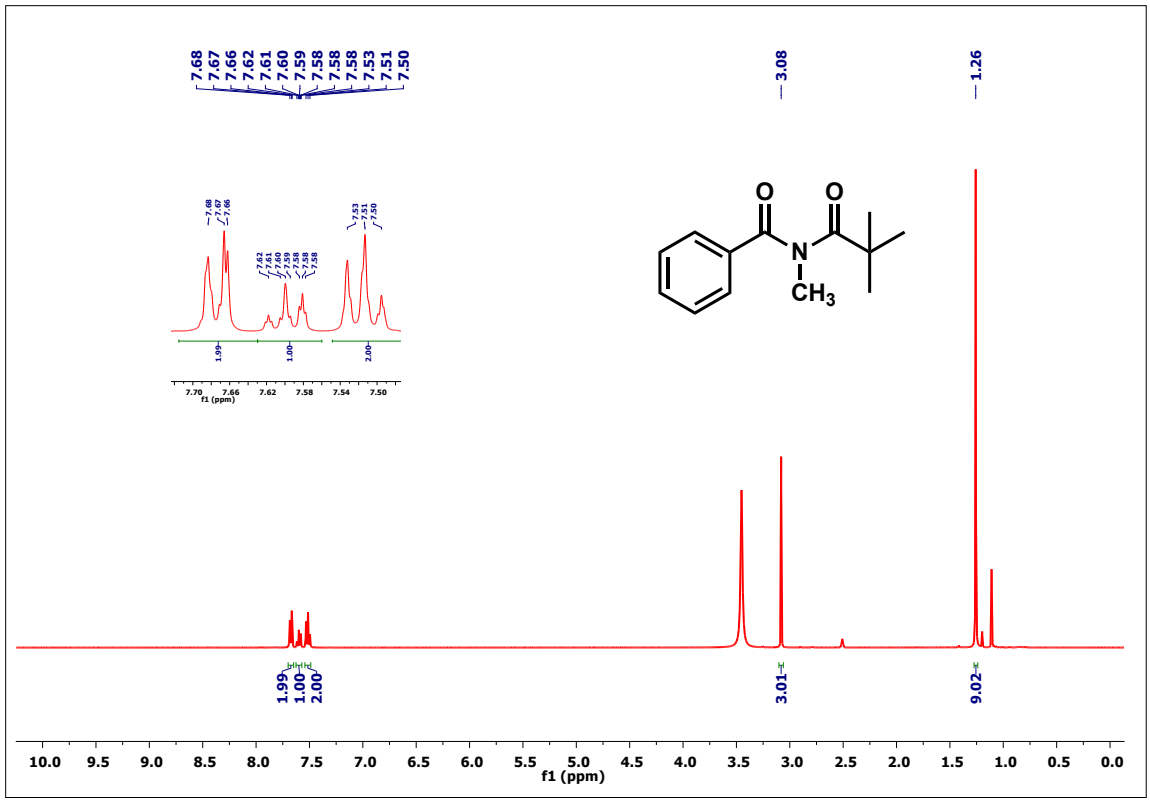

Figure S71: 400 MHz ^{1}H NMR spectrum of **32** in DMSO-d_6

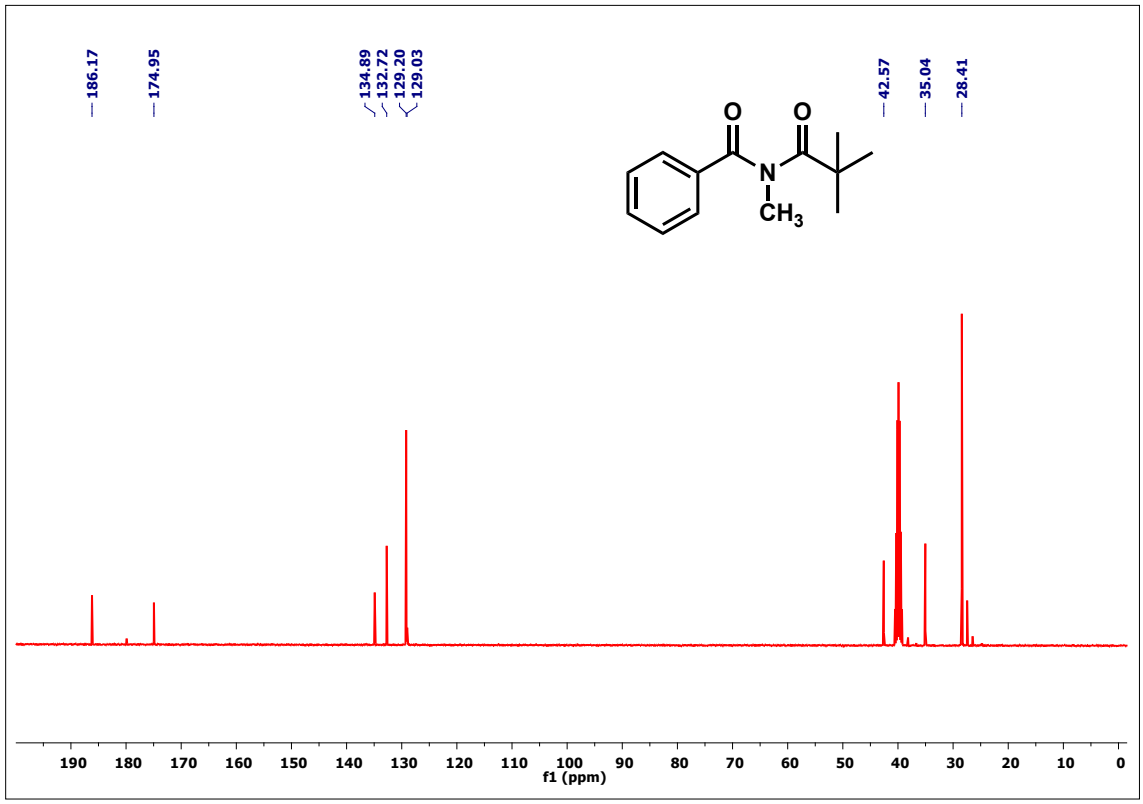

Figure S72: 100 MHz ^{13}C NMR spectrum of **32** in DMSO-d_6

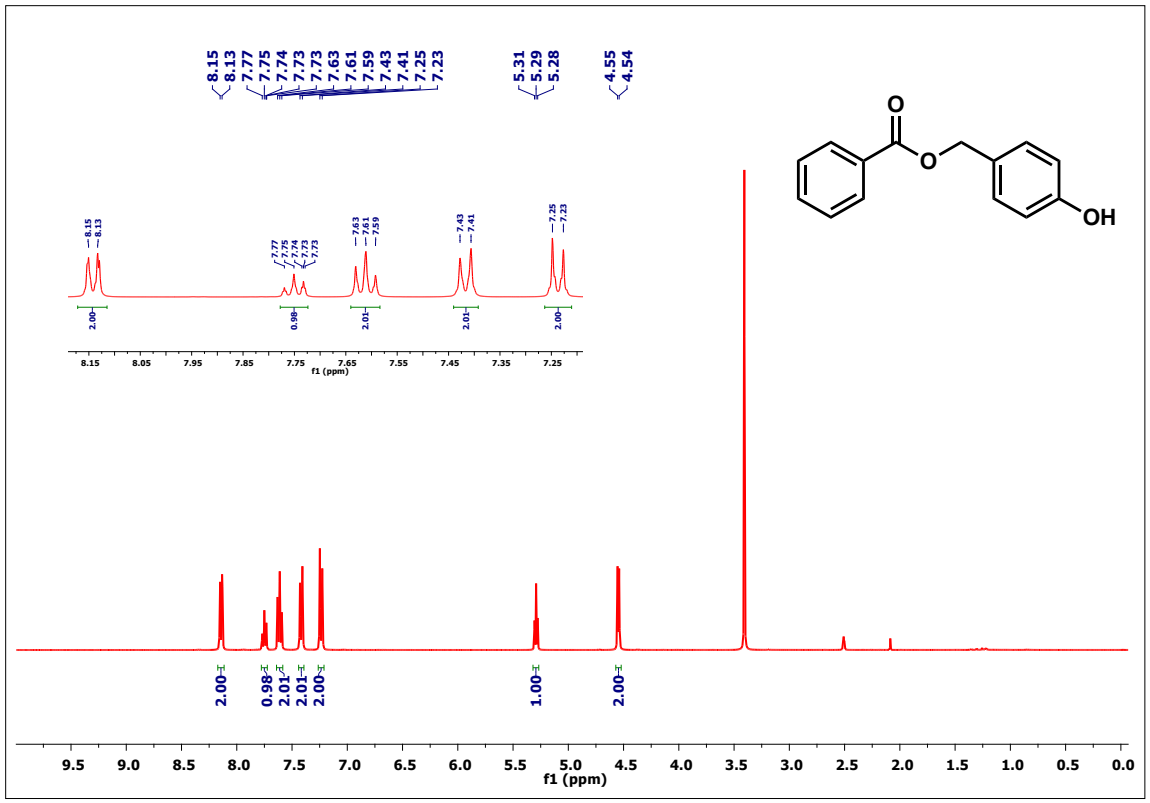

Figure S73: 400 MHz ^{1}H NMR spectrum of **33** in DMSO-d_6

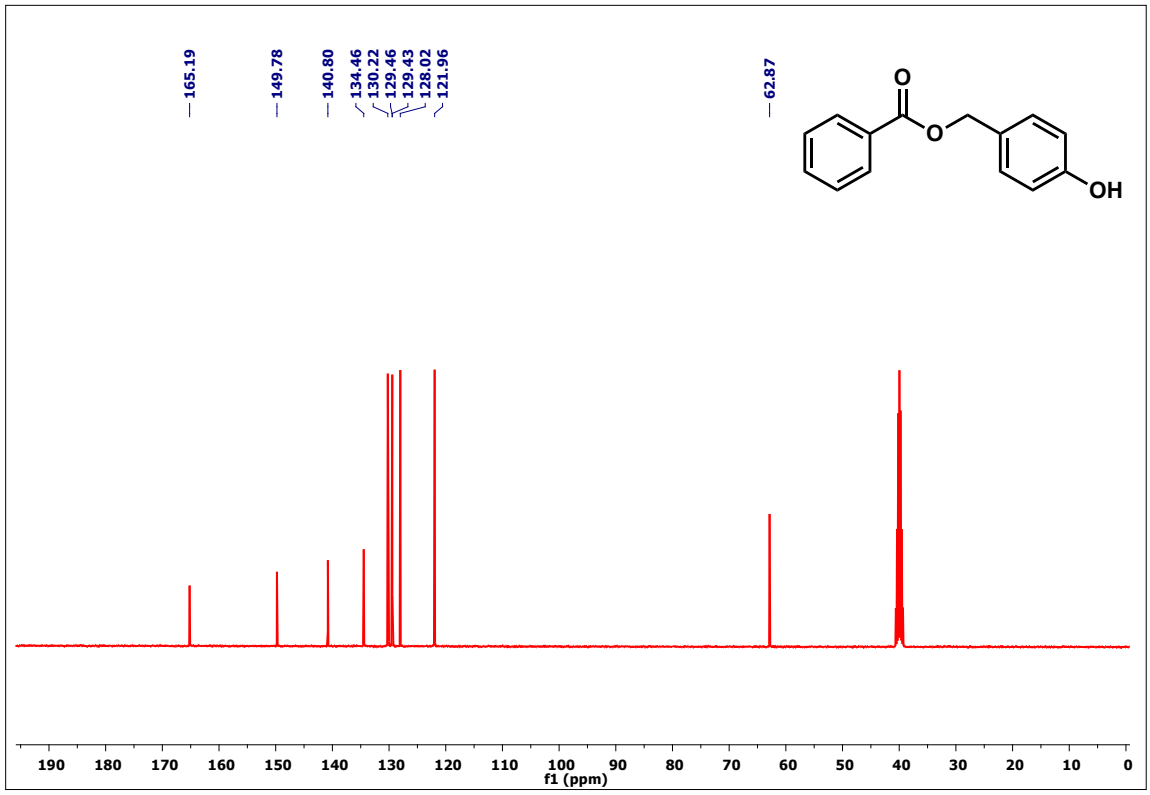

Figure S74: 100 MHz ^{13}C NMR spectrum of **33** in DMSO-d_6

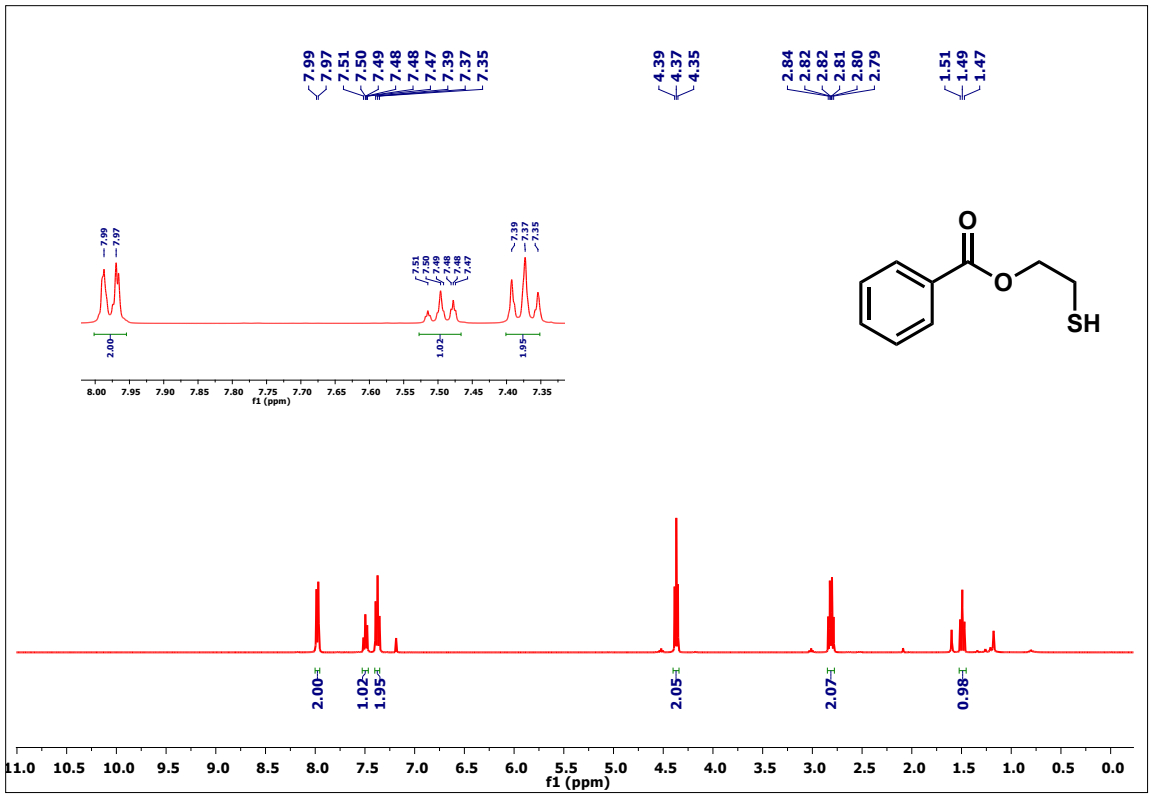

Figure S75: 400 MHz ^{1}H NMR spectrum of **34** in $CDCl_3$

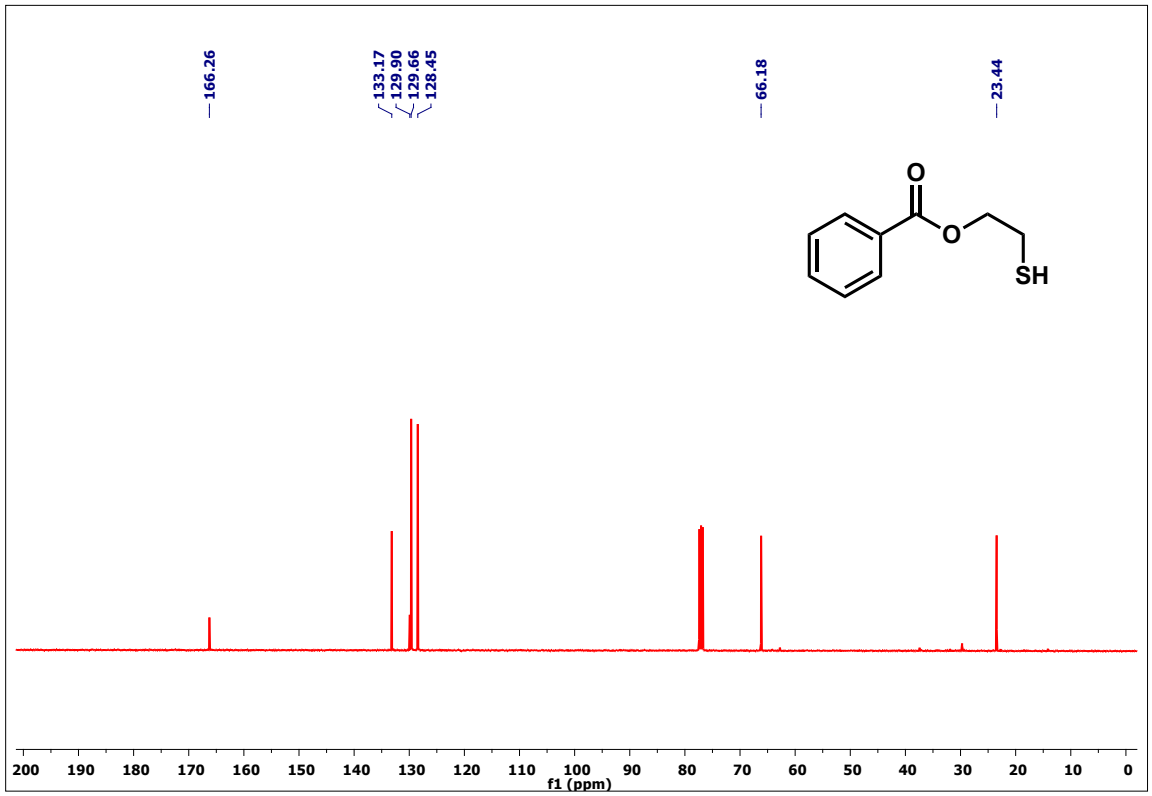

Figure S76: 100 MHz ^{13}C NMR spectrum of **34** in $CDCl_3$

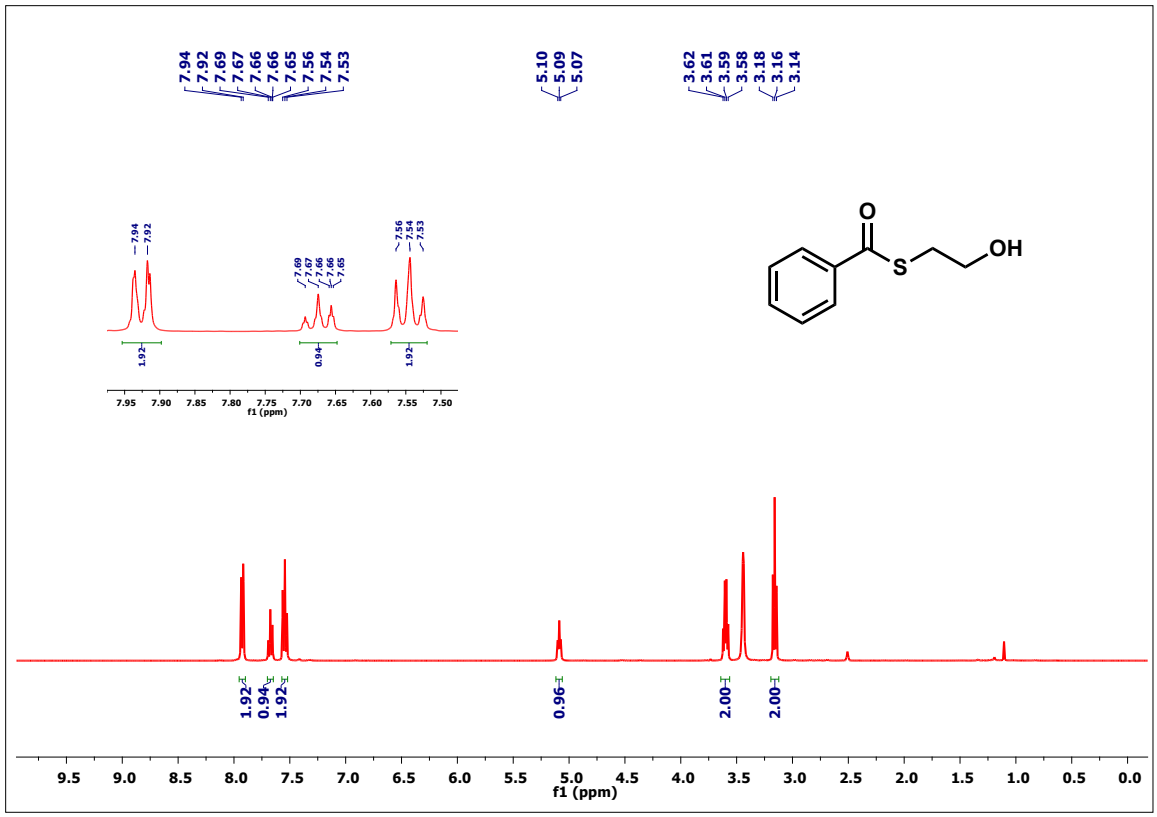

Figure S77: 400 MHz ^{1}H NMR spectrum of **35** in $CDCl_3$

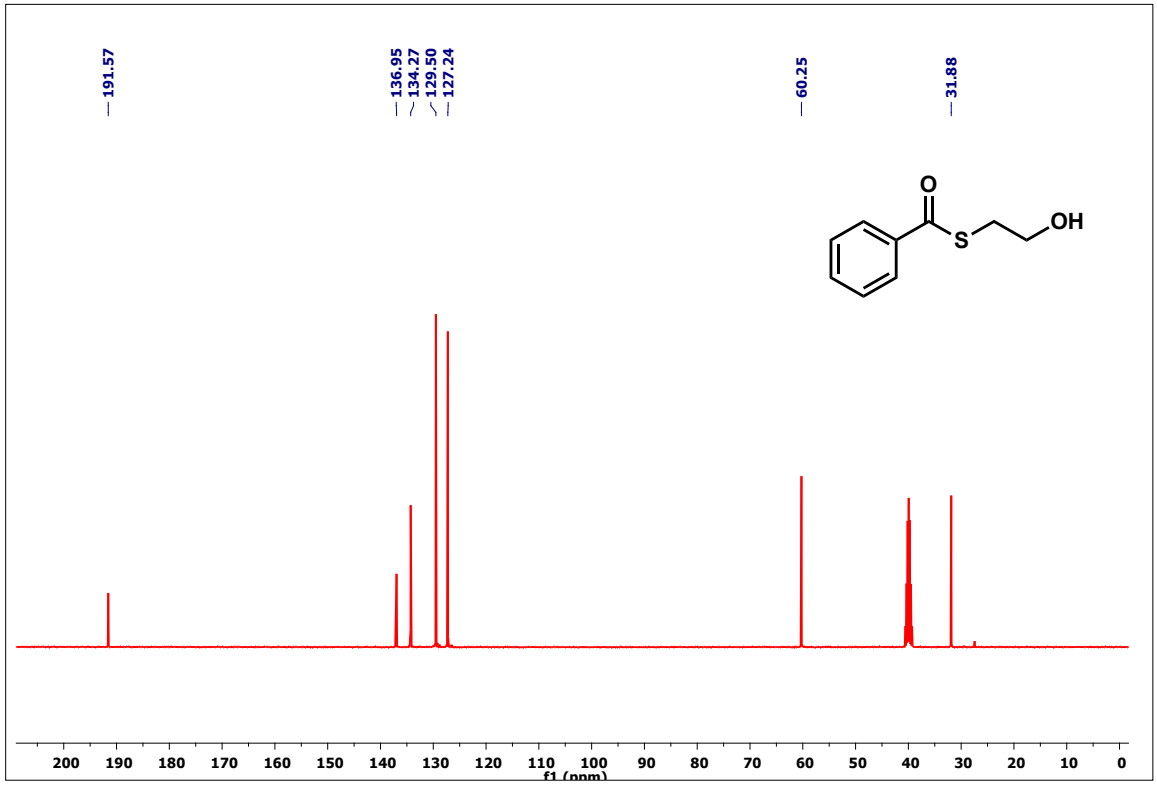

Figure S78: 100 MHz ^{13}C NMR spectrum of **35** in $CDCl_3$

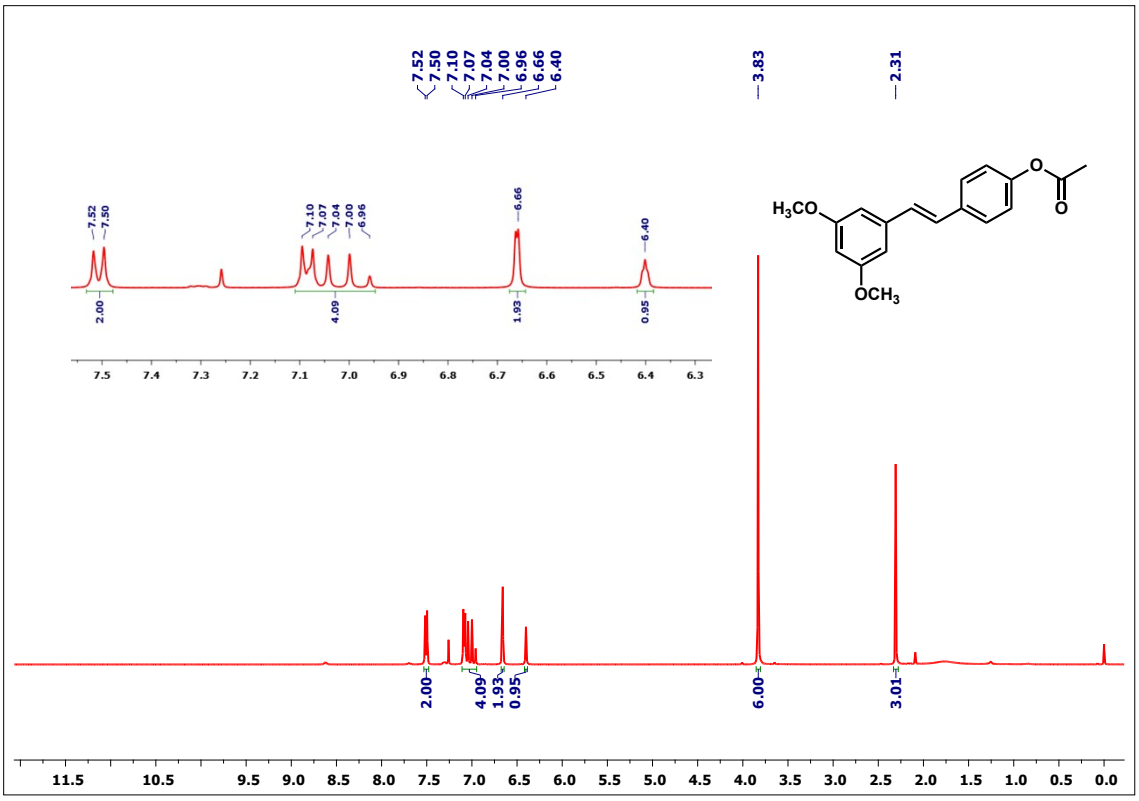

Figure S79: 400 MHz ^{1}H NMR spectrum of **36** in $CDCl_3$

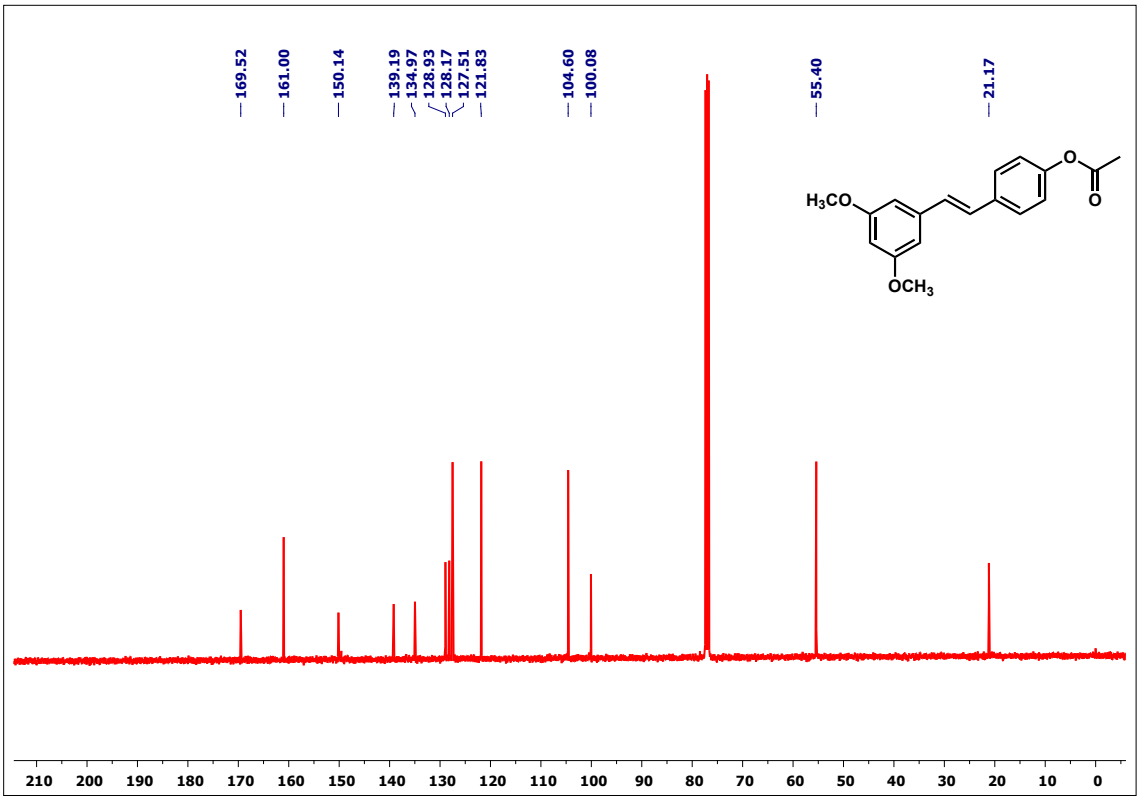

Figure S80: 100 MHz ^{13}C NMR spectrum of **36** in $CDCl_3$

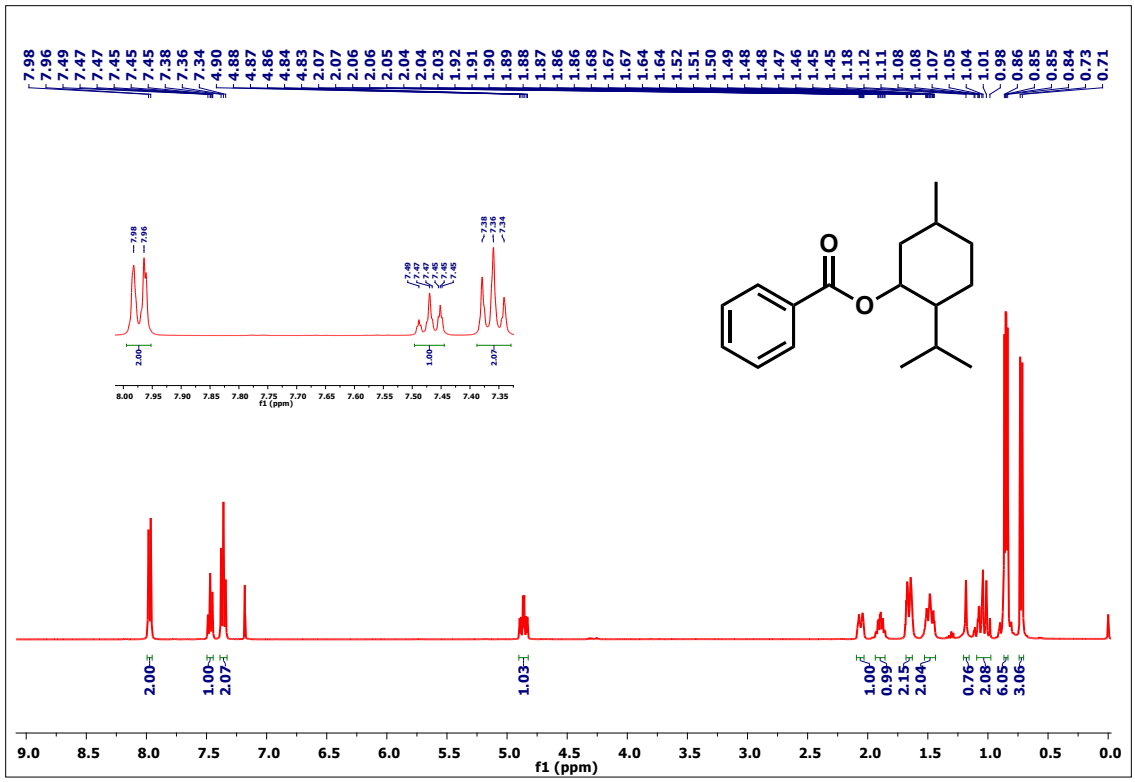

Figure S81: 400 MHz ^{1}H NMR spectrum of **37** in $CDCl_3$

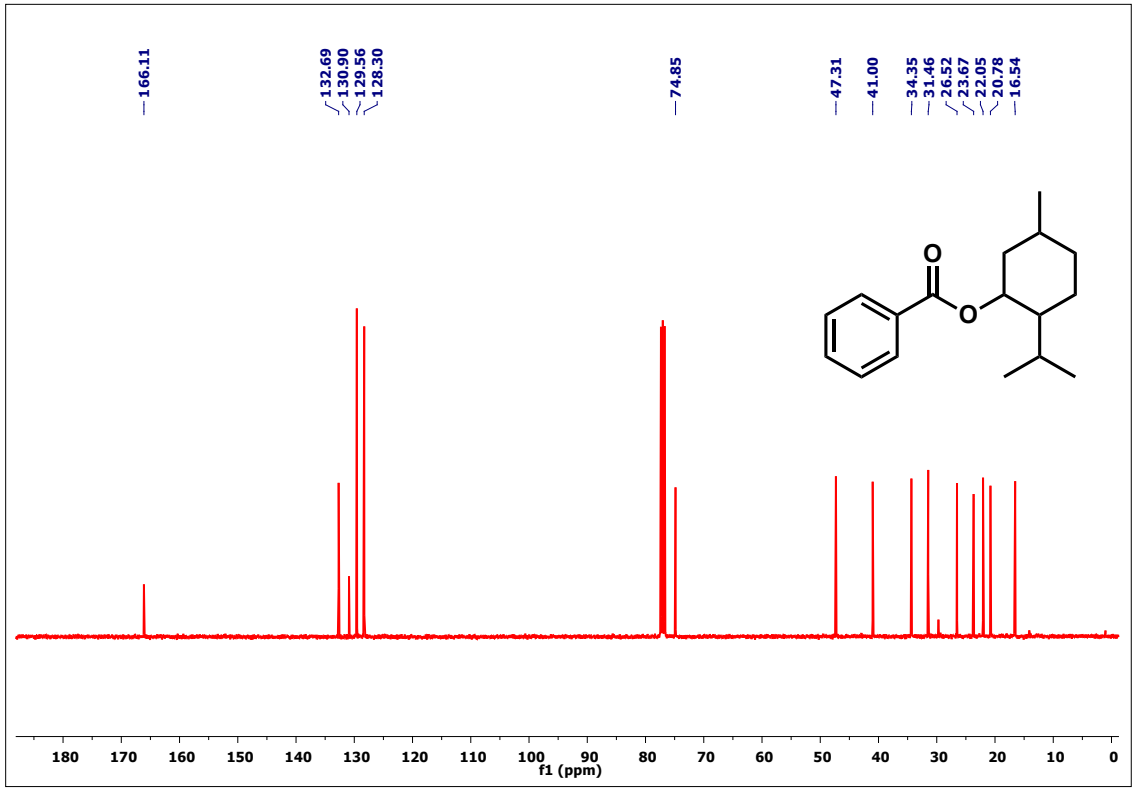

Figure S82: 100 MHz ^{13}C NMR spectrum of **37** in $CDCl_3$

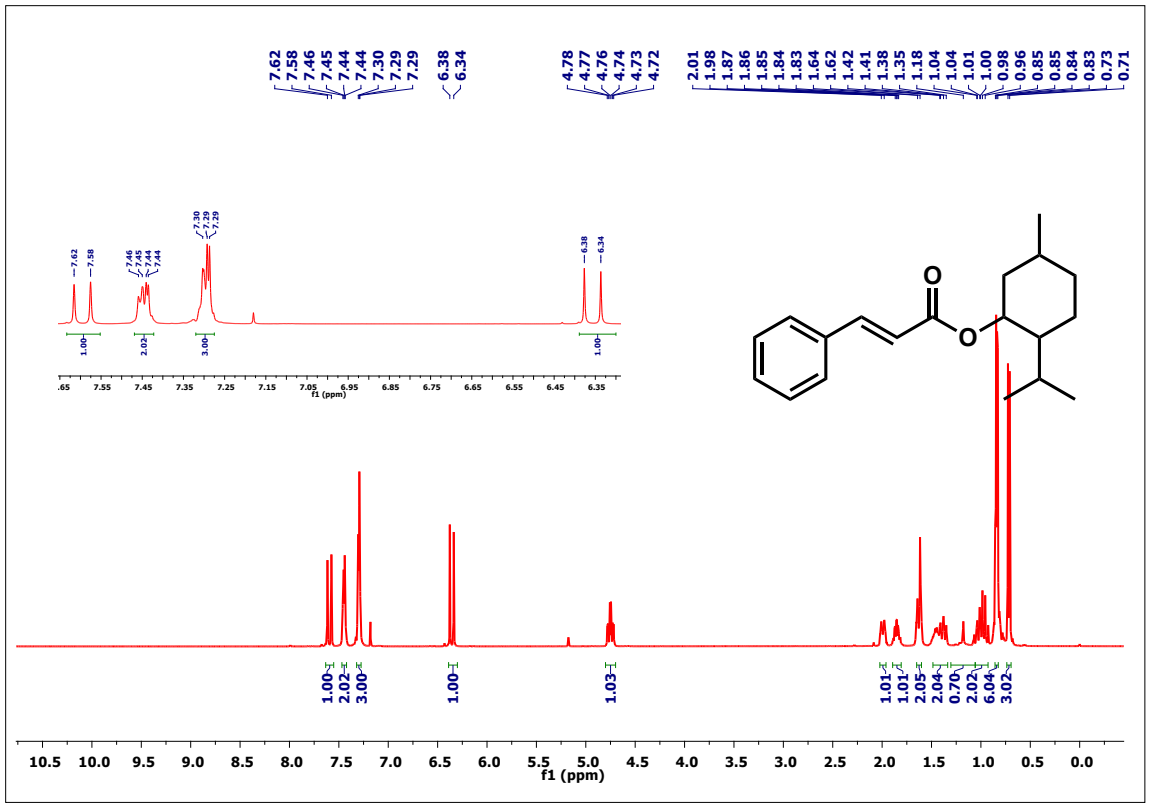

Figure S83: 400 MHz ^{1}H NMR spectrum of **38** in $CDCl_3$

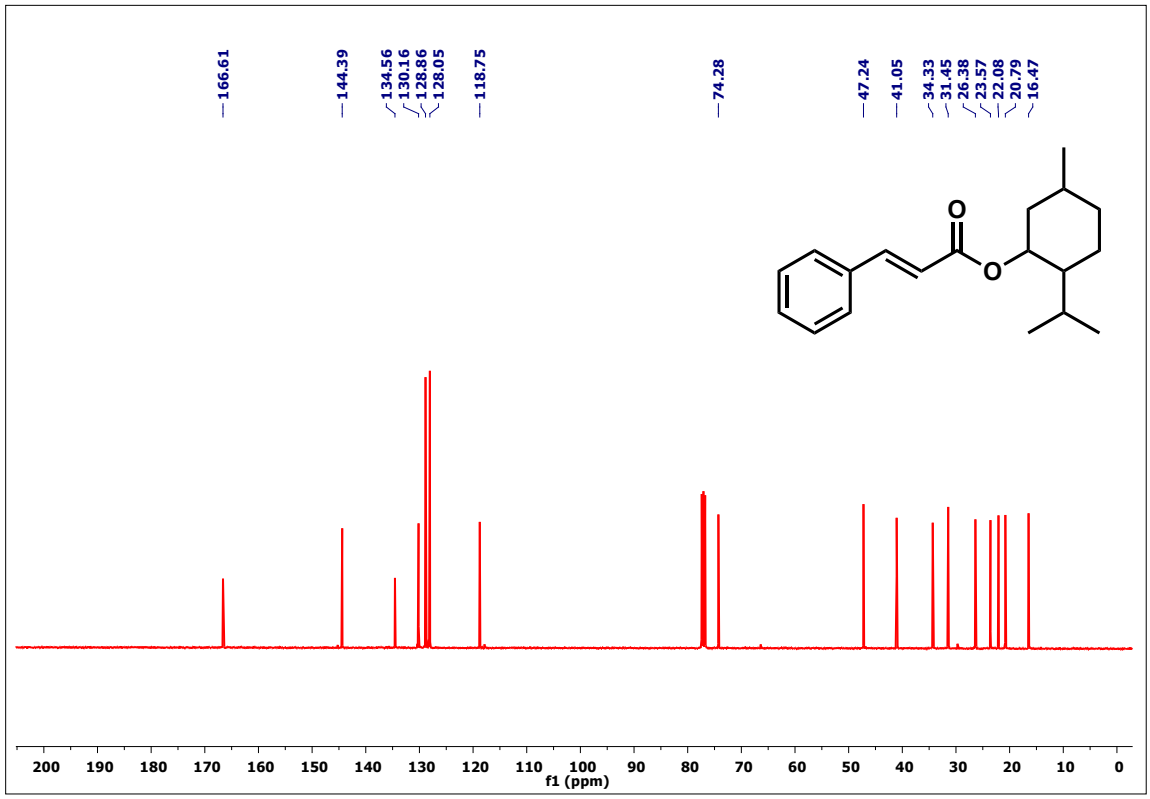

Figure S84: 100 MHz ^{13}C NMR spectrum of **38** in $CDCl_3$

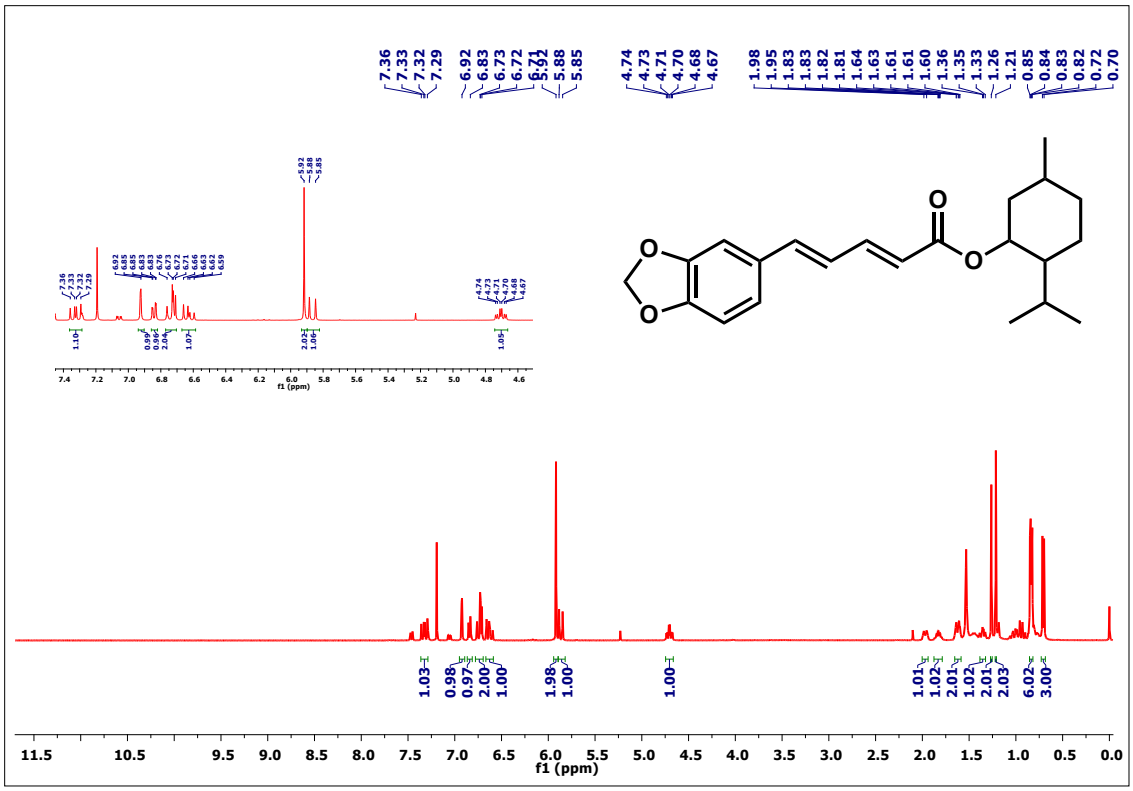

Figure S85: 400 MHz ^{1}H NMR spectrum of **39** in $CDCl_3$

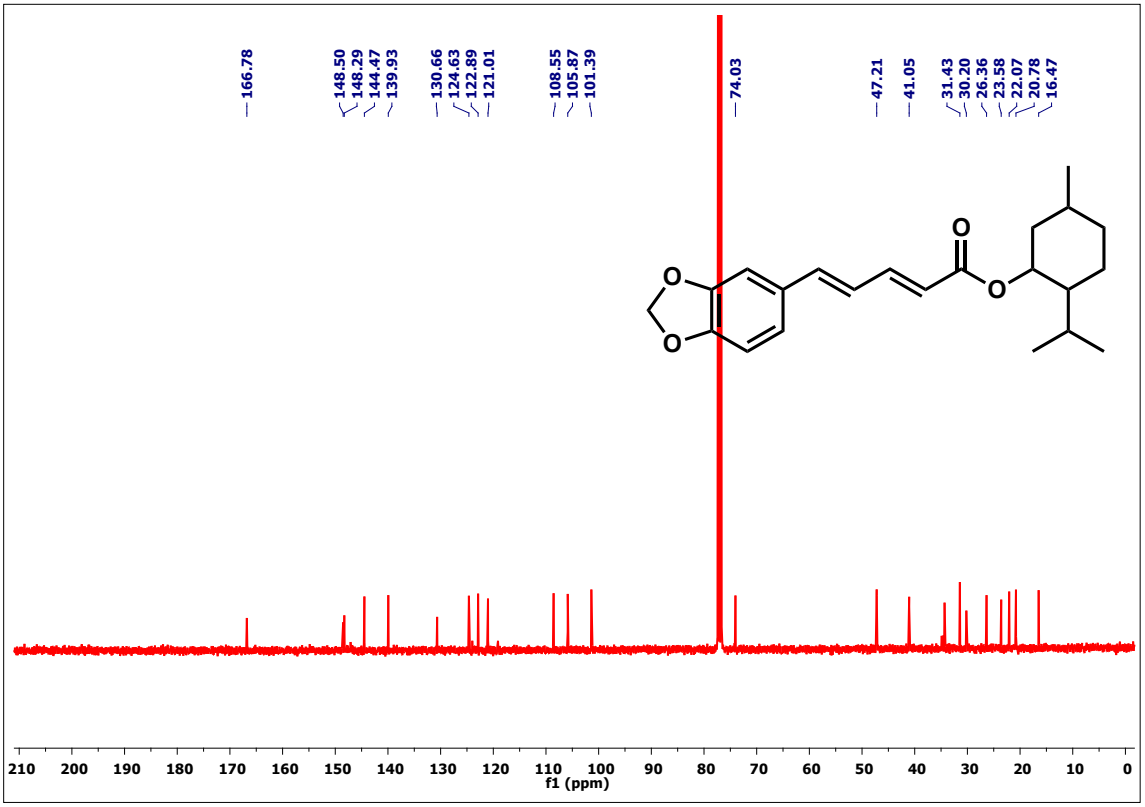

Figure S86: 100 MHz ^{13}C NMR spectrum of **39** in $CDCl_3$