Electronic Supplementary Material (ESI) for Chemical Communications.

Functionalization of Arylacetic Acids *via* Directing Group Assisted Remote *meta*-C–H Activation

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Supporting Information

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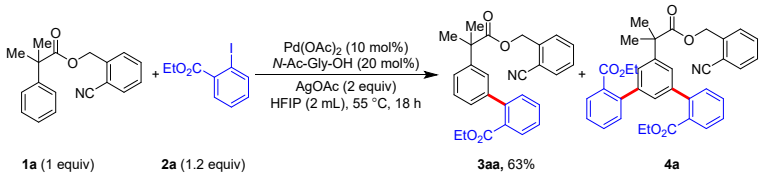
Experimental:

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CDCl_3$ (δ_H = 7.25 ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker Advance 400 (100 MHz) spectrometer at RT in $CDCl_3$. Chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ_C = 77.00 ppm (central line of the triplet)]. In ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. In $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra. The assignment of signals was confirmed by ^{1}H, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. Melting points are recorded using Tempo and Mettler FP1 melting point apparatus in capillary tubes and are uncorrected. A single crystal of **7** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using direct methods, and refined with the olex2. refinement package using Gauss−Newton minimization. All small-scale reactions were carried out by using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether the boiling range of 60−80 °C was used. $Pd(OAc)_2$, Ac-Gly-OH, AgOAc and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from Sigma-Aldrich and used as received. Olefin coupling partners, DCC, DMF, DCM, K_2CO_3, LiOH and HCl were purchased from Sigma-Aldrich/TCI/local sources and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

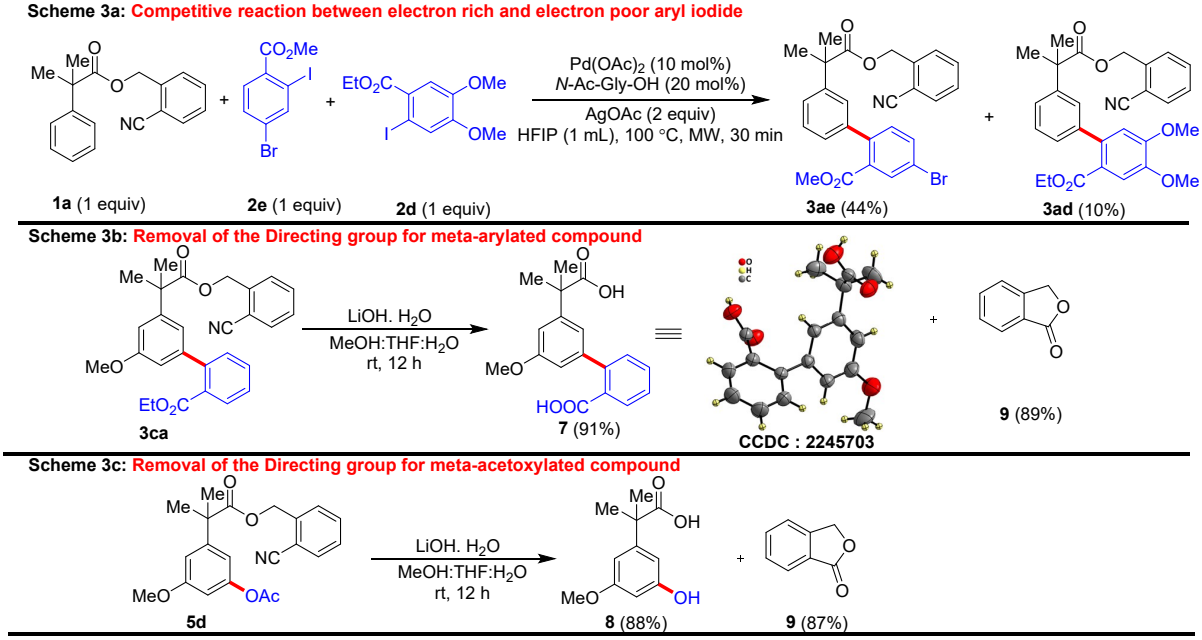
Table S1: Screening conditions for the *m*-selective arylation.



S. No	Deviation from the conditions	Observations
1	Room temperature instead of 55 °C	No product
2	16 h instead of 18 h	60% **3aa**
3	2.4 equiv of iodoarene	80% **3aa**
4	24 h instead of 18 h	25% **3aa** and 41% **4a**
5	3.6 equiv of iodoarene to entry 4	10% **3aa** and 65% **4a**
6	MW at 80 °C for 15 min	55% **3aa**
7	MW at 100 °C for 25 min	73% **3aa**
8	MW at 100 °C, 30 min, *N*-Ac-gly-OH (40 mol%)	89% **3aa** with trace amount of **4a**

Unfortunately, no product was observed when the reaction was carried out at room temperature for 18 h (entry 1, Table S1). While 60% of the product **3aa** was obtained when the reaction time is changed to 16 h (entry 2, Table S1). Notably, the yield of **3aa** was increased to 80% by doubling the amount of **2a** (entry 3, Table S1). On the other hand, prolonged reaction times (to 24 h instead of 18 h) led to the bis-arylated product **4a** along with the mono-arylated one **3aa** (entry 4, Table S1). Further increasing the concentration of **2a** (to 3.6 equiv), under the condition of entry 4 of Table S1, the yield of the bis-arylated product **4a** was raised to 65% along with isolation of minor amount of mono-arylated product **3aa** (10%) in trace amount (entry 5, Table S1). Further, to make this present protocol greener, the reaction is planned under microwave acceleration conditions instead of a conventional process. Thus, the reaction was carried out at 80 °C for 15 min under microwave assisting conditions. Gratifyingly, the mono-arylated product **3aa** was isolated in 55% without any significant loss in the site selectivity (entry 6, Table S1). Encouraged by this outcome, the temperature (100 °C) and time were increased (25 min), which witnessed gear up 73% yield of **3aa** (entry 7, Table S1). Next, the quantity of the ligand *N*-Ac-Gly-OH was increased to 40 mol% and prolonged the reaction time for 30 min at 100 °C. Gratifyingly, the product **3aa** was isolated in 89% of yield with a trace amount of bis-arylated product **4a** (entry 8, Table S1). Finally, it was determined that "entry 8 of Table S1" was best for the further substrate scope.

Scheme S1. Further explorations.



All the precursors (**1a-1h)** were prepared according to the reported procedure.[1]

General Procedure-1 (GP-1) for microwave assisted *meta*-selective C–H arylation (3):

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with cyano-ester **1** (56-65 mg, 0.2 mmol), iodoarene **2** (93-192 mg, 0.3 mmol), $Pd(OAc)_2$ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (67 mg, 0.4 mmol), and hexafluoroisopropanol (HFIP) (2 mL). The resulting reaction mixture was subjected to microwave irradiation 100 °C for 30 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired *meta*-arylated product **3** in 14% to 90% yields, as viscous colourless/pale-yellow/brown liquid or solid.

General Procedure-2 (GP-2) for microwave assisted one-pot homo-bis-*meta*-selective C–H arylation (4):

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with cyano-ester **1** (56-62 mg, 0.2 mmol), iodoarene **2** (198-245 mg, 0.72 mmol), $Pd(OAc)_2$ (5 mg, 10 mol%), *N*-Ac-Gly-OH (10 mg, 40 mol%), AgOAc (134 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (2 mL). The resulting reaction mixture was was subjected to microwave irradiation at 100 °C for 40 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired homo-bis-*meta*-arylated product **4** in 61% to 69% yields, as viscous colourless/pale-yellow/brown liquid or solid.

General Procedure-3 (GP-3) for microwave assisted *meta*-selective C–H acetoxylation (5):

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with cyano-ester **1** (56-71 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL). The resulting reaction mixture was subjected to microwave irradiation at 100 °C for 45 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired *meta*-acetoxylated product **6** in 60% to 71% yields, as viscous colourless/pale-yellow/brown liquid or solid.

General Procedure-4 (GP-4) for microwave assisted *meta*-selective C–H cyanation (6):

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with cyano-ester **1** (56-71 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2

mL). The resulting reaction mixture was subjected to microwave irradiation at 100 °C for 45 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture was diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired *meta*-cyanated product **8** in 53% to 65% yields, as viscous colourless/pale-yellow/brown liquid or solid.

General Procedure-5 (GP-5) for cleavage of the directing group: To the solution of **3ca** or **6d** (0.2 mmol) in MeOH (1.6 mL), THF (0.8 mL), H_2O (0.4 mL) in 25 mL round bottom flask, was added $LiOH{\cdot}H_2O$ (67mg, 1.6 mmol) at room temperature. The resulting reaction mixture was stirred at room temperature for 12 h. The organic solvents were removed under the reduced pressure, diluted with H_2O (15 mL), and to the aqueous phase, was added 2M HCl. The resulted solution was extracted with EtOAc (3 × 15 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered through column chromatography. The diacid product **7** was isolated (52 mg, 91%), as a white crystalline solid. The hydroxylarylacetic acid was isolated **8** (37 mg, 88%), as brown liquid. In both of these above reaction, isobenzofuran-1(3*H*)-one **9** was isolated in 89% and 87%, respectively, as pale-yellow amorphous solid, which was derived from *ortho*-cyano-benzyl moiety of the precursors **3aa** and **5d**.

General Procedure-6 (GP-6) for microwave assisted *meta*-dual-hetero-functionalisation (10&11):

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with substrate **3aa** or **5g** (0.2 mmol), ethyl acrylate (0.24 mmol), $Pd(OAc)_2$ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (67 mg, 0.4 mmol), and hexafluoroisopropanol (HFIP) (2 mL). The resulting reaction mixture was subjected to microwave irradiation 100 °C for 30 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column

chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired *meta*-dual-hetero functionalised products (**10** & **11**) as viscous colourless /brown liquid.

Plausible Mechanistic Pathways:

Control experiment to detect the intermediate:

To identify any possible intermediate formation using mass spectral analysis and gain insight into the reaction mechanism, several reactions have been conducted using the substrate **1a** with and without all the coupling partners (i.e., *ortho*-iodobenzoate ester, PIDA, and CuCN) and the crude reaction mixtures were subjected for HRMS measurements in order to find out the mass peaks of any anticipated intermediate(s) formation. To our delight, in a reaction where the catalyst and ligand were taken in stoichiometric ratio with respect to the starting substrate **1a** and without any coupling partner, the M^+ ion of the macrocyclic palladacycle intermediate **II** was detected in HRMS, albeit in a low intensity (Figure S1).

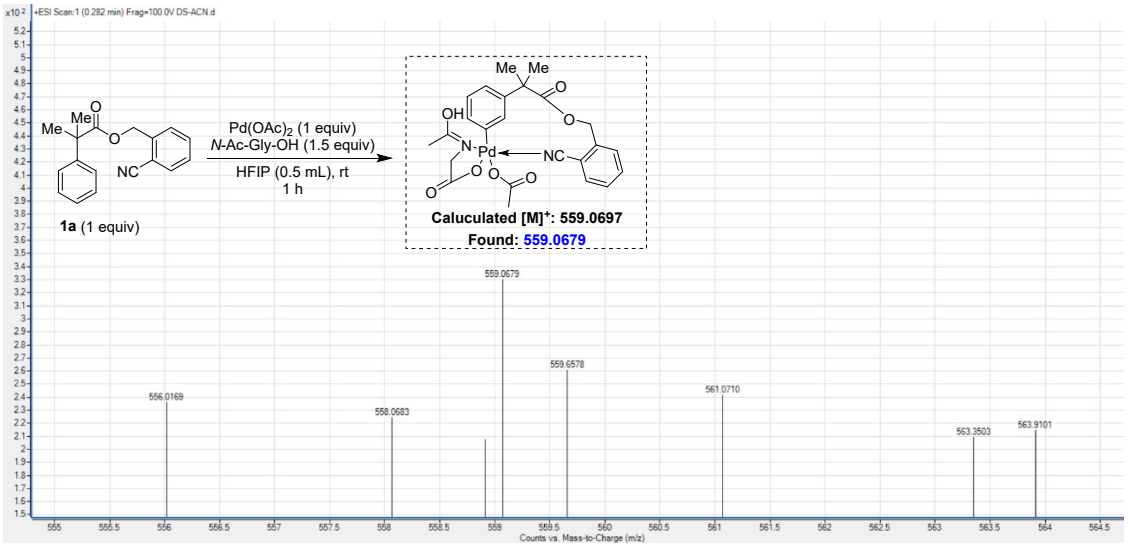
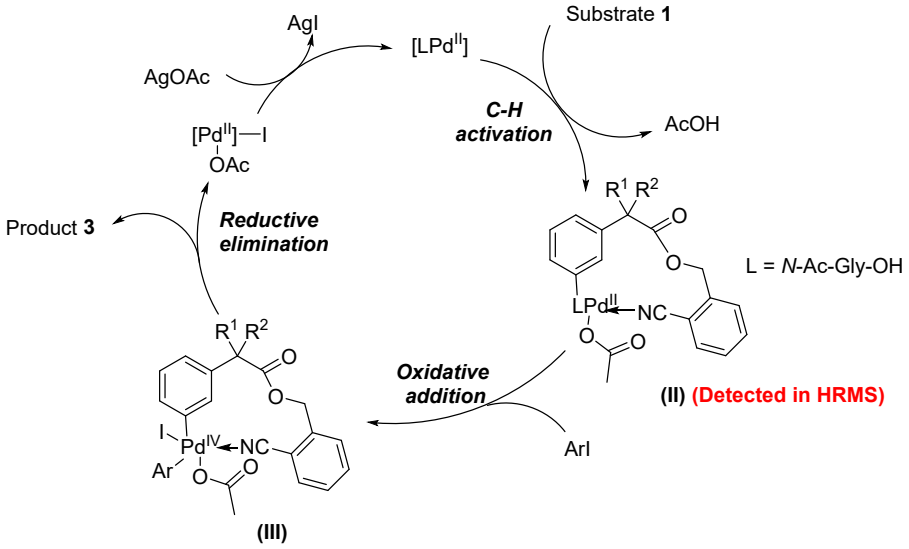


Figure S1. HRMS detection of macrocyclic palladacycle intermediate **II**.

Plausible catalytic path for *meta*-C–H arylation:

The plausible catalytic cycle for the *meta*-arylation has been proposed based on the previous reports,[2–4] and identification of mass spectral analysis macrocyclic palladacycle intermediate **II**, as described in Scheme S2. Essentially, the weak coordination of nitrile group with Pd^{II} leads the metal-center to the close vicinity of the *meta*-C–H bond and facilitate to form 12 membered palladacycle **II** by cleaving the *meta*-C–H bond. Then iodoarene undergo oxidative addition with Pd-centre of **II** resulted in forming Pd^{IV} intermediate **III**. Subsequently,

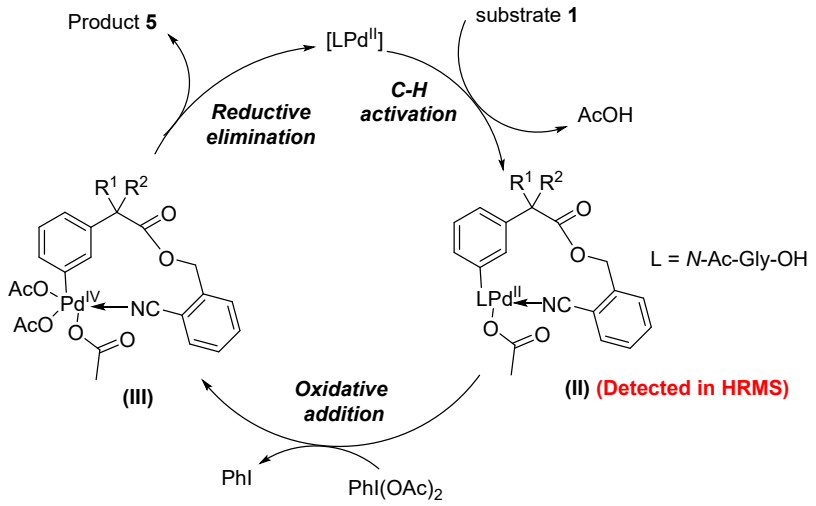
reductive elimination occasioned the *meta*-arylated product **3** by leaving the I-Pd-OAc. Sequentially, the active pre catalyst will be regenerated with the use of AgOAc to restart the catalytic cycle.



Scheme S2: Catalytic cycle for *meta*-arylation to furnish **3**.

Plausible catalytic path for *meta*-C–H acetoxylation:

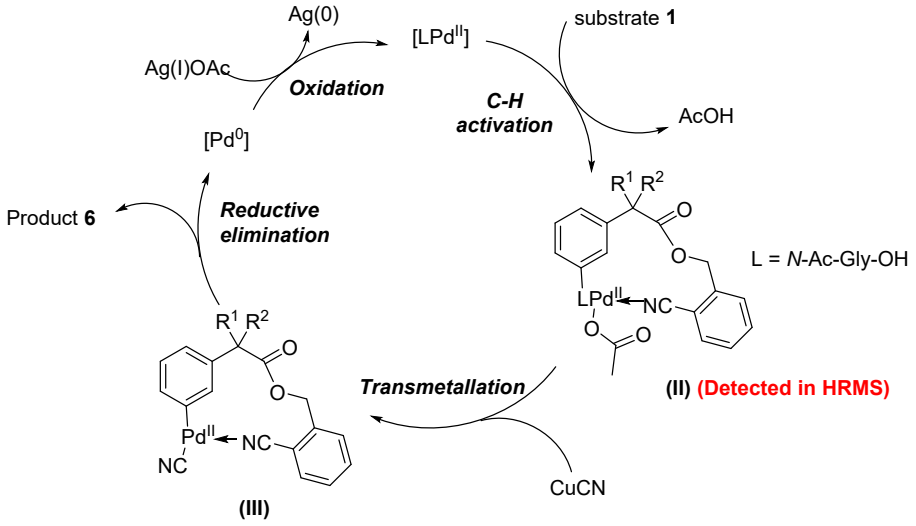
The plausible catalytic cycle for the *meta*-acetoxylation has been proposed based on the previous reports,[4,5] and identification of mass spectral analysis macrocyclic palladacycle intermediate **II**, as described in Scheme S3. Essentially, the weak coordination of nitrile group with Pd^{II} leads the metal-center to the close vicinity of the *meta*-C–H bond and to facilitate to form 12 membered palladacycle **II** by cleaving the *meta*-C–H bond. Then (diacetoxyiodo)benzene undergo oxidative addition with Pd-centre of **II** resulted in forming Pd^{IV} intermediate **III**. Subsequently, reductive elimination occasioned the *meta*-acetoxylated product **5** by regenerating the active Pd^{II} catalyst to restart the catalytic cycle.



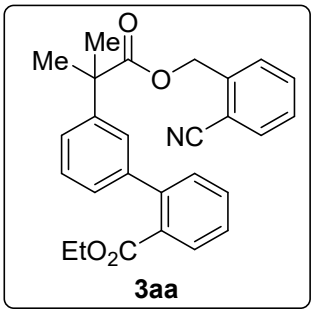
Scheme S3: Catalytic cycle for *meta*-acetoxylation to furnish **5**.

Plausible catalytic path for *meta*-C–H cyanation:

The plausible catalytic cycle for the *meta*-cyanation has been proposed based on the previous reports,[4,6] and identification of mass spectral analysis macrocyclic palladacycle intermediate **II**, as described in Scheme S4. Essentially, the weak coordination of nitrile group with Pd^{II} leads the metal-center to the close vicinity of the *meta*-C–H bond and facilitate to form 12 membered palladacycle **II** by cleaving the *meta*-C–H bond. Then the transmetallation between Pd-intermediate **II** and CuCN resulted in forming Pd^{II} intermediate **III**. Subsequently, reductive elimination occasioned the *meta*-cyanated product **6** by leaving the Pd^{0}. The reoxidation of the Pd^{0} to Pd^{II} can be done by the silver(I) salt.

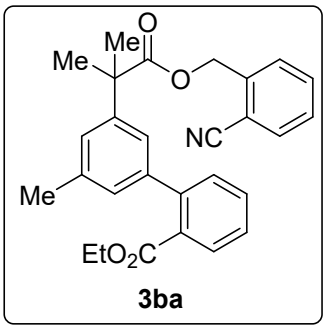


Scheme S4: Catalytic cycle for *meta*-cyanation to furnish **6**.



3aa

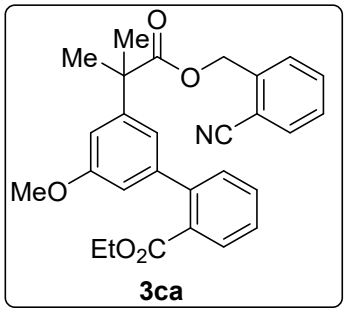
Ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-2-carboxylate (3aa): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2a** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3aa** (76 mg, 89%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**3aa**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2979, 2226, 1725, 1464, 1283, 1248, 1136, 763 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 (dtd, *J* = 15.2, 7.6, 1.3 Hz, 2H), 7.38 – 7.28 (m, 5H), 7.24 (dt, *J* = 2.4, 1.1 Hz, 1H), 7.20 (ddd, *J* = 6.4, 2.3, 1.8 Hz, 1H), 5.29 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 1.64 (s, 7H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 168.7, 143.9, 142.1, 141.5, 139.4, 132.8, 132.8, 131.4, 131.0, 130.5, 129.6, 128.9, 128.5, 128.1, 127.2, 126.8, 125.7, 124.5, 116.9, 111.7, 63.9, 60.9, 46.6, 26.4 (2C), 13.5 ppm. HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{27}H_{25}NO_4$ 427.1778; Found 427.1780.



3ba

Ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-5'-methyl-[1,1'-biphenyl]-2-carboxylate (3ba): GP-1 was carried out by using cyano-ester **1b** (56 mg, 0.2 mmol), iodo arene **2a** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%),

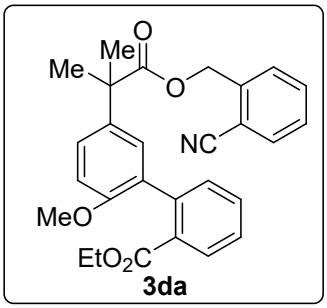
AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ba** (79 mg, 90%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1b**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**3ba**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2978, 2227, 1720, 1596, 1456, 1245, 1125, 862, 760, 711 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45 (dt, *J* = 7.7, 3.9 Hz, 1H), 7.41 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.32 (dd, *J* = 7.7, 0.9 Hz, 2H), 7.09 (s, 1H), 7.05 – 7.01 (m, 2H), 5.30 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.62 (s, 6H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 168.9, 143.9, 142.2, 141.4, 139.5, 137.6, 132.8, 132.8, 131.5, 130.9, 130.5, 129.5, 128.9, 128.4, 127.6, 127.1, 125.3, 122.8, 116.9, 111.8, 63.9, 60.8, 46.5, 26.4 (2C), 21.5, 13.6 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{28}H_{28}NO_4$ 442.2013; Found 442.2017.



3ca

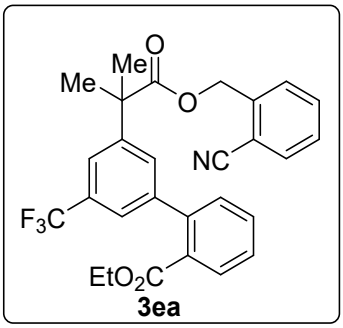
Ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-5'-methoxy-[1,1'-biphenyl]-2-carboxylate (3ca): GP-1 was carried out by using cyano-ester **1c** (62 mg, 0.2 mmol), iodo arene **2a** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ca** (75 mg, 82%) as a pale yellow colour liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1c**) = 0.50, *Rf*(**2a**) = 0.70, *Rf*(**3ca**) = 0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2977, 2226, 1722, 1593, 1454, 1252, 1130, 1047, 863, 765, 709 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 (dtd, *J* = 16.4, 7.6, 1.3 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.88 – 6.84 (m, 1H), 6.82 (t, *J* = 1.6 Hz, 1H), 6.75 (dd, *J* = 2.3, 1.4 Hz, 1H), 5.29 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.78

(s, 3H), 1.62 (s, 6H), 0.95 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 168.8, 159.3, 145.4, 142.7, 142.0, 139.4, 132.8, 132.8, 131.5, 131.0, 130.3, 129.5, 128.9, 128.4, 127.3, 118.5, 116.9, 111.9, 111.7, 111.0, 64.0, 60.9, 55.3, 46.6, 26.4 (2C), 13.6 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{28}H_{28}NO_5$ 458.1962; Found 458.1974.



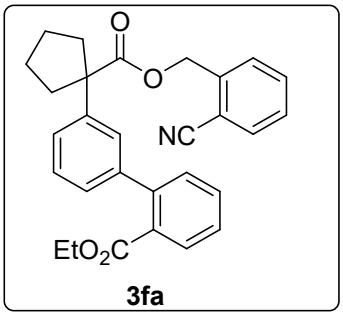
3da

Ethyl 5'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-2'-methoxy-[1,1'-biphenyl]-2-carboxylate (**3da**): GP-1 was carried out by using cyano-ester **1d** (62 mg, 0.2 mmol), iodo arene **2a** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3da** (78.5 mg, 86%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1d**) = 0.50, *Rf*(**2a**) = 0.70, *Rf*(**3da**) = 0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 2227, 1723, 1601, 1498, 1457, 1372, 1251, 1134, 1030, 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.7, 1.2 Hz, 1H), 7.61 (dd, J = 7.6, 1.1 Hz, 1H), 7.52 (td, J = 7.5, 1.5 Hz, 1H), 7.42 (dtd, J = 15.2, 7.6, 1.3 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.24 (dd, J = 7.7, 1.0 Hz, 1H), 7.17 (d, J = 2.5 Hz, 1H), 6.83 (d, J = 8.6 Hz, 1H), 5.28 (s, 2H), 4.04 (q, J = 7.1 Hz, 2H), 3.70 (s, 3H), 1.63 (s, 6H), 0.96 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 168.2, 154.9, 139.6, 138.5, 136.2, 132.8, 131.9, 131.4, 131.2, 130.5, 129.3, 128.8, 128.4, 127.5, 127.2, 125.8, 116.9, 111.7, 109.8, 63.9, 60.5, 55.3, 45.9, 26.5 (2C), 13.6 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{28}H_{28}NO_5$ 458.1962; Found 458.1975.



3ea

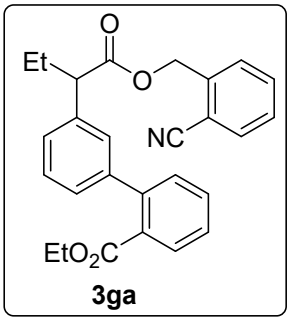
Ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate (3ea): GP-1 was carried out by using cyano-ester **1e** (69 mg, 0.2 mmol), iodo arene **2a** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ea** (78 mg, 79%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1e**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**3ea**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2981, 2227, 1722, 1452, 1246, 1119, 762, 711 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.47 (dtd, *J* = 7.4, 2.7, 1.3 Hz, 3H), 7.42 (s, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.34 – 7.28 (m, 2H), 5.30 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 1.67 (s, 6H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 167.9, 144.9, 142.5, 140.8, 139.0, 132.9, 132.8, 131.4, 131.0, 130.5, 130.2, 130.1, 129.4, 129.0, 128.7, 127.9, 124.0 ($J_{C\text{-}F}$ = 271 Hz), 123.9 ($J_{C\text{-}F}$ = 4 Hz) , 121.2 ($J_{C\text{-}F}$ = 4 Hz), 116.8, 111.9, 64.3, 60.9, 46.7, 31.5, 26.3 (2C), 22.6, 14.0, 13.5 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{28}H_{25}F_3NO_4$ 496.1730; Found 496.1744.



3fa

Ethyl 3'-(1-(((2-cyanobenzyl)oxy)carbonyl)cyclopentyl)-[1,1'-biphenyl]-2-carboxylate (3fa): GP-1 was carried out by using cyano-ester **1f** (62 mg, 0.2 mmol), iodo arene **2a** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6

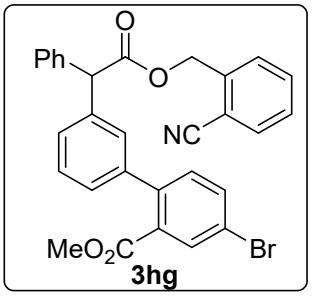
mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3fa** (80 mg, 88%) as a pale yellow colour liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1f**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**3fa**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2961, 2226, 1720, 1454, 1282, 1242, 1145, 762, 710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 (dd, *J* = 6.0, 4.4 Hz, 3H), 7.23 – 7.17 (m, 2H), 5.25 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.77 – 2.63 (m, 2H), 2.03 – 1.89 (m, 2H), 1.80 – 1.68 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 168.7, 142.6, 142.2, 141.4, 139.5, 132.8, 132.8, 131.4, 131.0, 130.5, 129.6, 128.6, 128.4, 127.9, 127.2, 126.9, 126.9, 125.7, 116.8, 111.6, 63.9, 60.8, 59.1, 36.1 (2C), 23.5(2C), 13.6 ppm. HRMS (ESI) m/z: $[(M)]^+$ Calcd for $C_{29}H_{27}NO_4$ 453.1935; Found 453.1939.



3ga

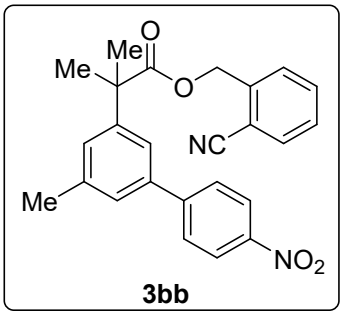
Ethyl 3'-(1-((2-cyanobenzyl)oxy)-1-oxobutan-2-yl)-[1,1'-biphenyl]-2-carboxylate (3ga): GP-1 was carried out by using cyano-ester **1g** (56 mg, 0.2 mmol), iodo arene **2a** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ga** (74 mg, 87%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1g**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**3ga**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3614, 3001, 2621, 2253, 1632, 1435, 1385, 1271, 1039, 918, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.50 (tdd, *J* = 7.7, 3.3, 1.4 Hz, 2H), 7.43 – 7.27 (m, 6H), 7.25 – 7.16 (m, 2H), 5.30 (dd, *J* = 13.3 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.59 (t, *J* = 7.7 Hz, 1H), 2.20 – 2.09 (m, 1H), 1.91 – 1.80 (m, 1H), 0.94 (t, *J* = 5.9 Hz, 3H), 0.91 (t, *J* = 6.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 168.7, 141.9, 141.8, 139.3, 138.3, 132.9, 132.8, 131.3, 131.0, 130.5, 129.6, 128.9, 128.5, 128.2, 128.0, 127.4, 127.2, 126.7, 116.8, 111.8, 63.7, 60.8, 53.2, 26.6, 13.6, 12.1 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{27}H_{26}NO_4$ 428.1856; Found 428.1869.



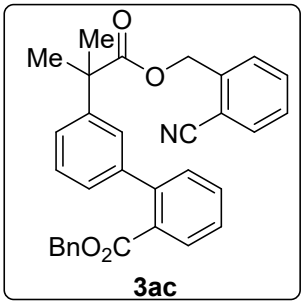
3hg

Methyl 4-bromo-3'-(2-((2-cyanobenzyl)oxy)-2-oxo-1-phenylethyl)-[1,1'-biphenyl]-2-carboxylate (3hg): GP-1 was carried out by using cyano-ester **1h** (65 mg, 0.2 mmol), iodo arene **2g** (136 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3hg** (94 mg, 87%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1h**) = 0.60, *Rf*(**2g**) = 0.70, *Rf*(**3hg**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3617, 3003, 2625, 2352, 2253, 1633, 1435, 1385, 1271, 1038, 918, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.1 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.52 – 7.48 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 3H), 7.35 – 7.27 (m, 7H), 7.22 – 7.17 (m, 3H), 5.37 (s, 2H), 5.14 (s, 1H), 3.52 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 167.5, 140.8, 140.4, 138.9, 138.1, 137.9, 134.1, 132.9, 132.8, 132.5, 132.5, 132.2, 129.2, 128.7 (2C), 128.6 (2C), 128.5, 128.5, 127.8, 127.4, 127.1, 121.2, 116.8, 112.0, 64.3, 56.6, 52.1 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{30}H_{23}{}^{81}BrNO_4$ 540.0805; Found 540.0815; Calcd for $C_{30}H_{23}{}^{81}BrNO_4$ 542.0785; Found 542.0808.



3bb

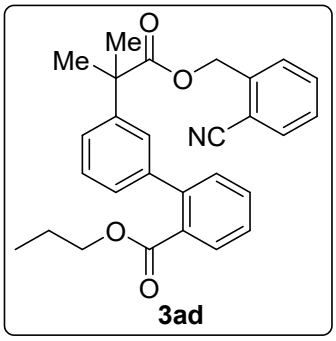
2-cyanobenzyl 2-methyl-2-(5-methyl-4'-nitro-[1,1'-biphenyl]-3-yl)propanoate (3bb): GP-1 was carried out by using cyano-ester **1b** (58 mg, 0.2 mmol), iodo arene **2b** (99 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3bb** (37 mg, 45%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1b**) = 0.60, *Rf*(**2b**) = 0.50, *Rf*(**3bb**) = 0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 1732, 1595, 1517, 1345, 1243, 1132, 848, 766, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.24 (m, 2H), 7.68 – 7.64 (m, 2H), 7.62 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.38 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.20 (s, 1H), 5.29 (s, 2H), 2.41 (s, 3H), 1.66 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 147.7, 147.0, 145.0, 139.3, 139.0, 138.9, 132.9, 132.7, 129.2, 128.6, 127.9(2C), 127.0, 126.7, 124.0(2C), 122.0, 116.8, 112.1, 64.2, 46.6, 26.4 (2C), 21.6. ppm. HRMS (ESI) m/z: $[(M+NH_4]^+$ Calcd for $C_{25}H_{26}N_3O_4$ 432.1918; Found 432.1927.



3ac

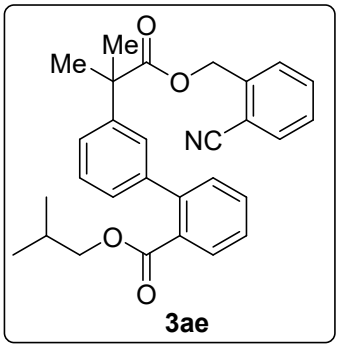
Benzyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-2-carboxylate (3ac): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2c** (135 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column

chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ac** (83 mg, 85%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2c**) = 0.70, *Rf*(**3ac**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 2226, 1722, 1457, 1244, 1130, 758, 704 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.34 – 7.27 (m, 5H), 7.21 (dd, *J* = 5.0, 2.1 Hz, 4H), 6.94 – 6.85 (m, 2H), 5.22 (s, 2H), 5.02 (s, 2H), 1.62 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 168.7, 144.1, 142.1, 141.4, 139.3, 135.2, 132.8, 132.7, 131.2, 131.0, 130.7, 129.8, 128.8, 128.4, 128.3, 127.9, 127.9, 127.2, 126.9, 125.9, 124.6, 116.9, 111.7, 66.9, 63.9, 46.6, 26.4 (2C) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{32}H_{28}NO_4$ 490.2013; Found 490.2024.

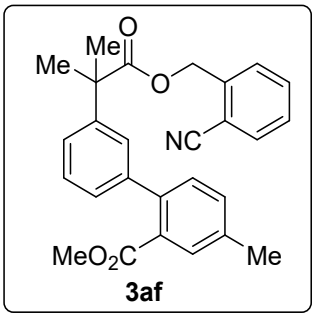


Propyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-2-carboxylate (3ad): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2d** (116 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ad** (77 mg, 88%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2d**) = 0.70, *Rf*(**3ad**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2969, 2226, 1723, 1462, 1244, 1134, 763,709 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.62 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.50 (ddd, *J* = 7.2, 6.7, 1.3 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.38 – 7.29 (m, 4H), 7.27 – 7.25 (m, 1H), 7.21 (dt, *J* = 6.6, 1.9 Hz, 1H), 5.30 (s, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 1.64 (s, 6H), 1.33 (dd, *J* = 14.1, 6.8 Hz, 2H), 0.63 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 169.0, 144.0, 142.0, 141.5, 139.4, 132.8, 132.8, 131.5, 131.0, 130.6, 129.6, 128.8, 128.5, 128.1, 127.2, 126.8, 125.7, 124.6, 116.9, 111.7, 66.6, 63.9, 46.6,

26.4 (2C), 21.5, 10.2 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{28}H_{28}NO_4$ 442.2013; Found 442.2030.

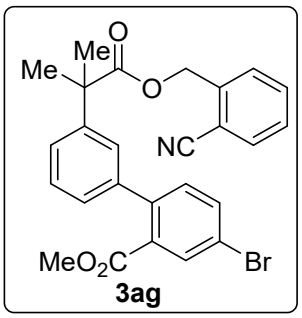


Isobutyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-2-carboxylate (3ae): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2e** (121 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ae** (72 mg, 79%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2e**) = 0.70, *Rf*(**3ae**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2963, 2226, 1720, 1462, 1242, 1129, 974, 761, 708 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.46 (td, *J* = 7.7, 1.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.36 (dt, *J* = 3.4, 1.7 Hz, 1H), 7.34 – 7.29 (m, 4H), 7.28 – 7.26 (m, 1H), 7.21 (dt, *J* = 6.7, 1.9 Hz, 1H), 5.30 (s, 2H), 3.78 (d, *J* = 6.6 Hz, 2H), 1.64 (s, 6H),1.61(m, 1H) 0.64 (d, *J* = 6.7 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 169.0, 144.1, 142.0, 141.5, 139.4, 132.8, 132.8, 131.5, 131.0, 130.6, 129.6, 128.8, 128.4, 128.2, 127.2, 126.8, 125.7, 124.6, 116.8, 111.7, 71.2, 63.9, 46.6, 27.3, 26.4 (2C), 18.8(2C) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{29}H_{30}NO_4$ 456.2169; Found 456.2180.



3af

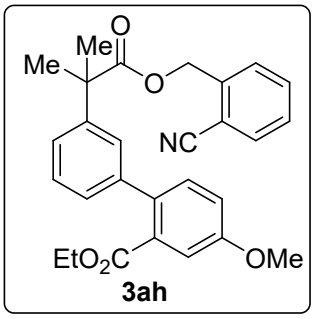
Methyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-4-methyl-[1,1'-biphenyl]-2-carboxylate (3af): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2f** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3af** (69 mg, 81%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2f**) = 0.70, *Rf*(**3ae**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2973, 2226, 1722, 1600, 1445, 1290, 1242, 1207, 1134, 1097, 974, 760, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.45 (td, *J* = 7.7, 1.4 Hz, 1H), 7.38 – 7.26 (m, 5H), 7.25 – 7.18 (m, 3H), 5.29 (s, 2H), 3.58 (s, 3H), 2.42 (s, 3H), 1.64 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 169.3, 143.8, 141.2, 139.4, 139.2, 137.1, 132.8, 131.9, 130.8, 130.5, 130.1, 128.8, 128.4, 128.1, 126.7, 125.8, 124.4, 116.8, 111.7, 63.9, 51.8, 46.5, 26.3 (2C), 20.9 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{27}H_{26}NO_4$ 428.1856; Found 428.1865.



3ag

methyl 4-bromo-3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-2-carboxylate (3ag): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2g** (136 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column

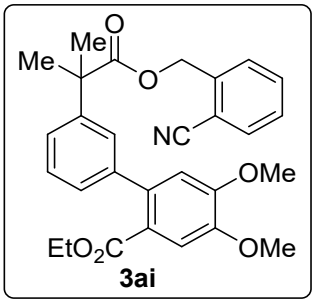
chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ag** (83 mg, 84%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2g**) = 0.70, *Rf*(**3ag**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2973, 2226, 1724, 1457, 1238, 1135, 1094, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.1 Hz, 1H), 7.62 (td, *J* = 8.0, 1.6 Hz, 2H), 7.47 (td, *J* = 7.7, 1.4 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.29 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.22 – 7.16 (m, 3H), 5.29 (s, 2H), 3.60 (s, 3H), 1.64 (s, 7H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 167.6, 144.0, 141.0, 140.0, 139.3, 134.1, 132.8, 132.8, 132.5, 132.5, 132.2, 128.9, 128.5, 128.3, 126.6, 125.7, 124.9, 121.1, 116.8, 111.8, 64.0, 52.2, 46.6, 26.3 (2C) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{26}H_{23}{}^{79}BrNO_4$ 492.0805; Found 492.0814: Calcd for $C_{26}H_{23}{}^{81}BrNO_4$ 494.0785; Found 494.0800.



3ah

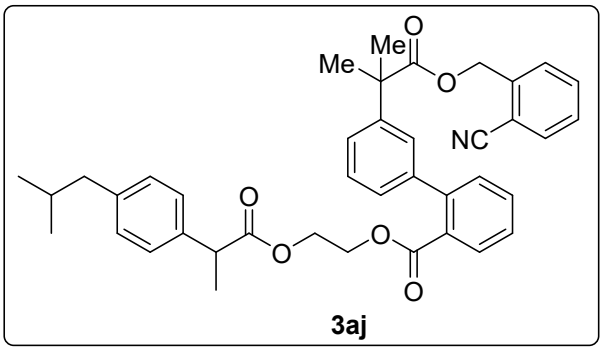
Ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-4-methoxy-[1,1'-biphenyl]-2-carboxylate (3ah): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2h** (122 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **3ah** (80 mg, 88%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2h**) = 0.40, *Rf*(**3ah**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3608, 2998, 2622, 2347, 2253, 2127, 1725, 1630, 1437, 1268, 1039, 919, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.47 (td, *J* = 7.7, 1.4 Hz, 1H), 7.38 – 7.28 (m, 5H), 7.25 – 7.20 (m, 2H), 7.17 (dt, *J* = 6.8, 1.8 Hz, 1H), 7.05 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.29 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.64 (s, 7H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 168.6, 158.6, 143.9, 141.3, 139.4, 134.6, 132.8, 132.8, 132.3, 131.7, 128.8, 128.5, 128.4, 128.0, 126.9, 125.8, 125.3, 124.2, 117.2, 116.9, 114.2, 111.7, 63.9,

60.9, 55.5, 46.6, 26.4(2C), 13.5 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{28}H_{28}NO_5$ 458.1962; Found 458.1973.



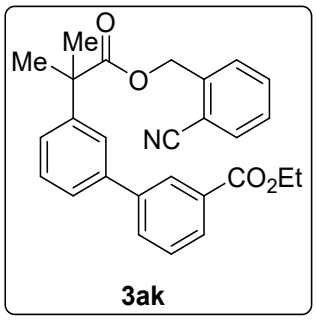
3ai

Ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-4,5-dimethoxy-[1,1'-biphenyl]-2-carboxylate (3ai): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2i** (134 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ah** (85 mg, 87%) as a colourless solid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2i**) = 0.30, *Rf*(**3ai**) = 0.10, UV detection]. MP: 102-104 °C. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2956, 2227, 1741, 1500, 1252, 1173, 1108, 769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 1H), 7.47 (td, *J* = 7.7, 1.4 Hz, 1H), 7.41 (s, 1H), 7.35 (ddd, *J* = 8.3, 5.3, 0.9 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.20 (dd, *J* = 2.1, 1.4 Hz, 1H), 7.19 – 7.14 (m, 1H), 6.77 (s, 1H), 5.28 (s, 2H), 3.96 (s, 5H), 3.90 (s, 3H), 1.63 (s, 6H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 168.0, 150.9, 147.7, 143.7, 142.0, 139.4, 136.9, 132.8, 132.8, 128.9, 128.5, 127.9, 126.9, 125.7, 124.3, 122.6, 116.8, 113.3, 112.6, 111.8, 64.0, 60.6, 56.1, 56.1, 46.6, 26.5 (2C), 13.5 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{29}H_{30}NO_6$ 488.2068; Found 488.2058.



3aj

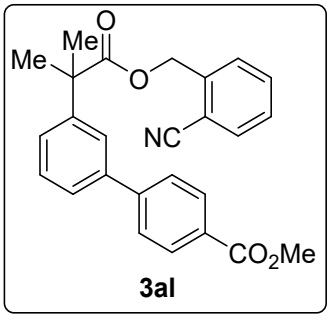
2-((2-(4-isobutylphenyl)propanoyl)oxy)ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-2-carboxylate (3aj): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2j** (192 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **3aj** (109 mg, 87%) as a colourless solid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2j**) = 0.30, *Rf*(**3aj**) = 0.10, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3624, 3000, 2252, 1734, 1435, 1381, 1264, 1039, 918, 744 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 7.75 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.53 (td, *J* = 7.6, 1.4 Hz, 1H), 7.42 (ddd, *J* = 7.6, 5.2, 1.3 Hz, 2H), 7.35 (s, 2H), 7.30 – 7.29 (m, 2H), 7.27 (s, 1H), 7.20 (t, *J* = 1.5 Hz, 1H), 7.17 – 7.13 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.27 (s, 2H), 4.22 – 4.14 (m, 2H), 4.02 (ddd, *J* = 12.1, 6.0, 3.6 Hz, 1H), 3.93 (ddd, *J* = 12.2, 6.3, 3.6 Hz, 1H), 3.68 – 3.62 (m, 1H), 2.40 (d, *J* = 7.2 Hz, 2H), 1.83 – 1.77 (m, 1H), 1.62 (s, 6H), 0.87 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 175.9, 174.3, 168.0, 143.9, 142.5, 141.3, 140.5, 139.4, 137.3, 132.8, 132.8, 131.3, 130.7, 130.5, 129.8, 129.3(2C), 128.9, 128.4, 128.1, 127.2, 127.1 (2C), 126.8, 125.8, 125.3, 124.6, 116.8, 111.8, 64.0, 62.4, 62.0, 46.6, 45.0, 44.8, 30.1, 26.4 (2C), 22.3 (2C), 18.4 ppm. HRMS (ESI) m/z: $[(M+K)]^+$ Calcd for $C_{40}H_{41}KNO_6$ 670.2565; Found 670.2573.



3ak

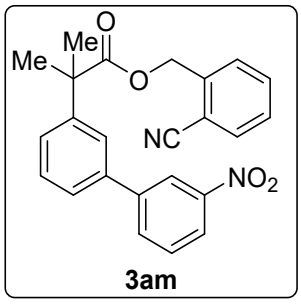
Ethyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-3-carboxylate (3ak): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2k** (110 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3ak** (33 mg,

38%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2k**) = 0.70, *Rf*(**3ak**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3614, 3164, 3003, 2253, 1632, 1435, 1383, 1270, 1038, 918, 752 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 8.21 (t, *J* = 1.6 Hz, 1H), 8.08 – 7.99 (m, 1H), 7.74 – 7.67 (m, 1H), 7.59 (dd, *J* = 13.1, 5.4 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.42 (ddd, *J* = 11.5, 5.7, 3.3 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.29 – 7.25 (m, 2H), 5.29 (s, 2H), 4.42 (dt, *J* = 7.1, 6.0 Hz, 2H), 1.68 (d, *J* = 5.4 Hz, 6H), 1.42 (t, *J* = 7.1 Hz, 3H). HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{27}H_{26}NO_4$ 428.1856; Found 428.1865.



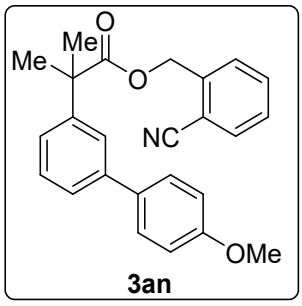
3al

Methyl 3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1'-biphenyl]-4-carboxylate (3al): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2l** (105 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3al** (16 mg, 20%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2l**) = 0.70, *Rf*(**3al**) = 0.40, UV detection]. ^1H NMR (400 MHz, CDCl3) δ 8.11 – 8.07 (m, 2H), 7.61 – 7.55 (m, 3H), 7.52 – 7.48 (m, 2H), 7.46 – 7.38 (m, 3H), 7.34 (d, *J* = 1.2 Hz, 1H), 7.29 – 7.27 (m, 1H), 5.29 (s, 2H), 3.95 (s, 2H), 1.68 (s, 6H). HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{26}H_{24}NO_4$ 414.1700; Found 414.1720.



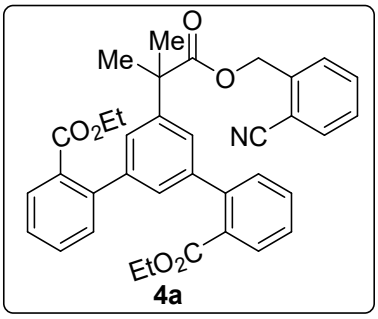
3am

2-cyanobenzyl 2-methyl-2-(3'-nitro-[1,1'-biphenyl]-3-yl)propanoate (3am): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2m** (99 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3am** (33 mg, 41%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2m**) = 0.50, *Rf*(**3am**) = 0.030, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3616, 3003, 2622, 2253, 2119, 1632, 1435, 1383, 1270, 1039, 918, 751 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 8.37 (t, *J* = 1.9 Hz, 1H), 8.21 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.53 – 7.28 (m, 6H), 5.29 (s, 2H), 1.69 (s, 6H). HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{24}H_{24}N_3O_4$ 418.1761; Found 418.1767.



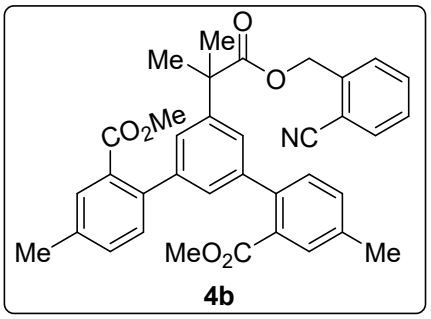
3an

2-cyanobenzyl 2-(4'-methoxy-[1,1'-biphenyl]-3-yl)-2-methylpropanoate ((3an): GP-1 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2n** (93 mg, 0.4 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **3an** (11 mg, 14%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2n**) = 0.70, *Rf*(**3an**) = 0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3615, 3002, 2621, 2349, 2253, 1632, 1435, 1383, 1039, 918, 752 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 7.63 – 7.55 (m, 1H), 7.48 – 7.40 (m, 4H), 7.40 – 7.32 (m, 3H), 7.02 – 6.92 (m, 2H), 6.65 (dd, *J* = 8.7, 3.0 Hz, 1H), 5.29 (s, 2H), 3.86 (s, 3H), 1.67 (s, 6H). HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{25}H_{27}N_2O_3$ 403.2016; Found 403.2028.



4a

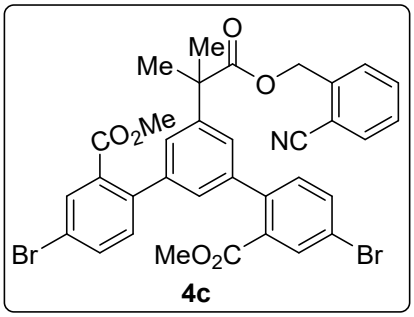
Diethyl 5'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate (4a):): GP-2 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2a** (198 mg, 0.72 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 75/25), furnished the product **4a** (78 mg, 68%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**4a**) = 0.15, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3612, 3003, 2253, 1634, 1435, 1385, 1039, 919, 753 cm^{-1}. 1H NMR (400 MHz, CDCl3) δ 7.80 (dt, *J* = 8.1, 4.0 Hz, 2H), 7.59 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.37 – 7.29 (m, 5H), 7.23 (d, *J* = 1.6 Hz, 2H), 7.19 (t, *J* = 1.6 Hz, 1H), 5.31 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 4H), 1.65 (s, 6H), 0.99 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (151 MHz, CDCl3) δ 175.8, 168.6 (2C), 143.8, 141.9 (2C), 141.4 (2C), 139.4, 132.8, 132.8, 131.5 (2C), 131.0 (2C), 130.6 (2C), 129.6 (2C), 129.0, 128.4, 127.3 (2C), 126.9, 124.7 (2C), 116.9, 111.8, 64.0, 60.9(2C), 46.7, 26.6 (2C), 13.7 (2C) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{36}H_{34}NO_6$ 576.2381; Found 576.2372.



4b

Dimethyl 5'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-4,4''-dimethyl-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate (4b): GP-2 was carried out by using cyano-ester

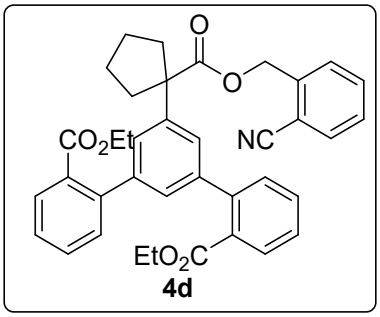
1a (56 mg, 0.2 mmol), iodo arene **2f** (198 mg, 0.72 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 75/25), furnished the product **4b** (76 mg, 66%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2f**) = 0.70, *Rf*(**4b**) = 0.15, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2945, 2226, 1723, 1437, 1294, 1249, 1205, 1136, 765 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 0.8 Hz, 2H), 7.58 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.41 (td, *J* = 7.7, 1.4 Hz, 1H), 7.34 – 7.29 (m, 4H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.17 (dd, *J* = 3.7, 1.4 Hz, 3H), 5.31 (s, 2H), 3.59 (s, 6H), 2.42 (s, 6H), 1.64 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 169.4 (2C), 143.6, 141.1, 139.4, 139.0, 137.2, 132.8, 132.8, 131.9, 130.9, 130.5, 130.2, 128.9, 128.4, 126.7, 124.6, 116.9, 111.7, 63.9, 51.9 (2C), 46.6, 26.5 (2C), 20.9 (2C) ppm. HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{36}H_{37}N_2O_6$ 593.2646; Found 593.2654.



4c

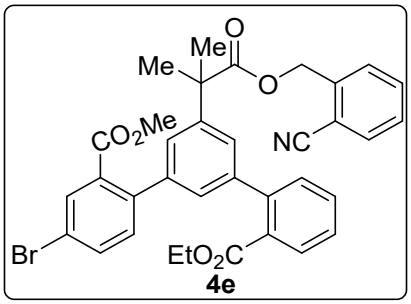
Dimethyl 4,4''-dibromo-5'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate (4c): GP-2 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), iodo arene **2g** (245 mg, 0.72 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 75/25), furnished the product **4c** (97 mg, 69%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1a**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**4c**) = 0.15, UV detection].IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2941, 2352, 1728, 1439, 1277, 1247, 1138, 771 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.1 Hz, 2H), 7.64 (dd, *J* = 8.2, 2.1 Hz, 2H), 7.58 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.45 (td, *J* = 7.7, 1.3 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 1.6 Hz, 2H), 7.11 (t, *J* = 1.6 Hz, 1H), 5.30 (s, 2H), 3.62 (s, 6H), 1.64 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 167.5,

144.1, 140.6, 140.2, 139.2, 134.2, 132.8, 132.6, 132.2, 129.2, 128.5, 126.4, 125.0, 121.4, 116.8, 111.9, 64.1, 52.2 (2C), 46.6, 26.5 (2C) ppm. HRMS (ESI) m/z: $[(M+K)]^+$ Calcd for $C_{34}H_{27}{}^{79}Br{}^{79}BrKNO_6$ 741.9837; Found 741.9794: Calcd for $C_{34}H_{27}{}^{79}Br{}^{81}BrKNO_6$ 743.9816; Found 743.9802: Calcd for $C_{34}H_{27}{}^{81}Br{}^{81}BrKNO_6$ 745.9796; Found 745.9744.



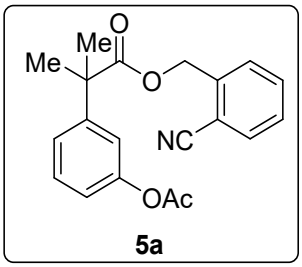
4d

Diethyl 5'-(1-(((2-cyanobenzyl)oxy)carbonyl)cyclopentyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate (4d): GP-2 was carried out by using cyano-ester **1f** (62 mg, 0.2 mmol), iodo arene **2a** (198 mg, 0.72 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 40 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 75/25), furnished the product **4a** (73 mg, 61%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**1f**) = 0.60, *Rf*(**2a**) = 0.70, *Rf*(**4d**) = 0.15, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3623, 3002, 2622, 2252, 1631, 1434, 1383, 1038, 918, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.7, 1.2 Hz, 2H), 7.60 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.50 (td, *J* = 7.5, 1.4 Hz, 2H), 7.41 (ddd, *J* = 7.5, 4.4, 1.3 Hz, 3H), 7.33 (ddd, *J* = 7.6, 3.6, 1.1 Hz, 3H), 7.29 (d, *J* = 1.6 Hz, 2H), 7.19 (t, *J* = 1.6 Hz, 1H), 5.27 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 4H), 2.70 (dt, *J* = 9.4, 5.0 Hz, 2H), 1.98 (dd, *J* = 7.5, 5.4 Hz, 2H), 1.74 (td, *J* = 6.7, 3.5 Hz, 4H), 1.01 (t, *J* = 7.1 Hz, 6H) ppm. 13C NMR (150 MHz, CDCl3) δ 175.1, 168.6 (2C), 142.4, 141.9, 141.2, 139.6, 132.9, 132.7, 131.4, 131.0, 130.6, 129.6, 128.7, 128.4, 127.2, 127.0, 125.9, 116.8, 111.6, 64.0, 60.9 (2C), 59.1, 36.3 (2C), 23.6 (2C), 13.7 (2C) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{38}H_{36}NO_6$ 602.2537; Found 602.2546.



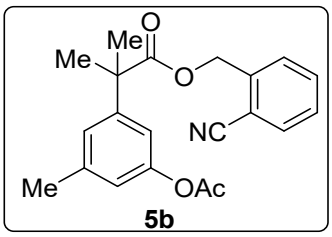
4e

2''-ethyl 2-methyl 4-bromo-5'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate (4e): An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with mono arylated precursor **3aa** (85 mg, 0.2 mmol), Iodo arene **2** (245 mg, 0.48 mmol), $Pd(OAc)_2$ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.3 mmol), and hexafluoroisopropanol (HFIP) (2 mL). The resulting reaction mixture was subjected to microwave irradiation at 100 °C for 40 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 75/25), furnished the product **4e** (84 mg, 66%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf*(**3aa**) = 0.40, *Rf*(**2g**) = 0.70, *Rf*(**4e**) = 0.15, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3621, 3002, 2620, 2253, 2121, 1631, 1435, 1385, 1039, 918, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.1 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.63 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.59 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.22 (dd, *J* = 4.9, 3.2 Hz, 2H), 7.17 (dt, *J* = 7.2, 1.6 Hz, 2H), 5.31 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 1.64 (s, 6H), 0.99 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 168.6, 167.6, 143.9, 141.7, 141.6, 139.8, 139.3, 134.1, 132.8, 132.6, 132.6, 132.2, 131.4, 131.1, 130.6, 129.7, 129.1, 128.5, 127.4, 126.7, 125.1, 124.7, 121.2, 116.8, 111.8, 64.1, 61.0, 52.3, 46.7, 26.5 (2C), 13.7 ppm. HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{35}H_{34}{}^{79}BrN_2O_6$ 657.1595; Found 657.1625: Calcd for $C_{35}H_{34}{}^{81}BrN_2O_6$ 659.1574; Found 659.1612.



5a

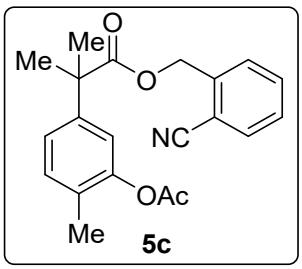
2-cyanobenzyl 2-(3-acetoxyphenyl)-2-methylpropanoate (5a): GP-3 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 45 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **5a** (42 mg, 63%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1a**) = 0.60, *Rf*(**5a**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3613, 3002, 2619, 2252, 1632, 1435, 1382, 1270, 1039, 918, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.51 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 (td, *J* = 7.6, 0.9 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.05 (t, *J* = 2.0 Hz, 1H), 6.99 (ddd, *J* = 8.0, 2.2, 0.9 Hz, 1H), 5.27 (s, 2H), 2.29 (s, 3H), 1.62 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 169.4, 150.7, 145.7, 139.3, 132.9, 132.9, 129.3, 128.8, 128.5, 123.3, 120.2, 119.2, 116.9, 111.7, 64.1, 46.5, 26.2 (2C), 21.2 ppm. HRMS (ESI) m/z: $[(M+NH)_4]^+$ Calcd for $C_{20}H_{23}N_2O_4$ 355.1652; Found 355.1665.



5b

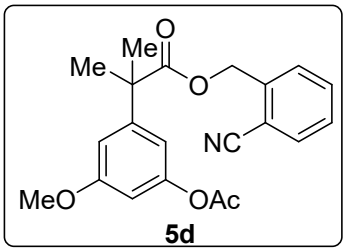
2-cyanobenzyl 2-(3-acetoxy-5-methylphenyl)-2-methylpropanoate (5b): GP-3 was carried out by using cyano-ester **1b** (56 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), Pd(OAc)2 (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 45 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **5b** (46 mg, 66%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, R*f*(**1b**) = 0.60, R*f*(**5b**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2975, 2226, 1737, 1600, 1453, 1372, 1206, 1136, 1023, 768 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.51 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 (td, *J* = 7.7, 1.1 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.97 (s, 1H), 6.87 – 6.78 (m, 2H), 5.27 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H), 1.60 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 169.5, 150.6, 145.4, 139.4, 139.3, 132.8, 132.8, 128.8, 128.5, 124.1, 120.8, 116.9, 116.1, 111.7, 64.0, 46.4, 26.2 (2C), 21.4, 21.1 ppm. HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{21}H_{25}N_2O_4$ 369.1809; Found 369.1823.



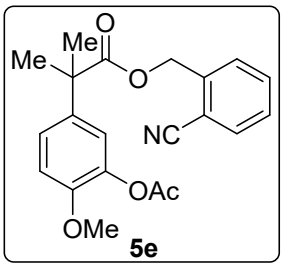
5c

2-cyanobenzyl 2-(3-acetoxy-4-methylphenyl)-2-methylpropanoate (5c): GP-3 was carried out by using cyano-ester **1i** (56 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 45 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **5c** (42 mg, 60%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, R*f*(**1i**) = 0.60, R*f*(**5c**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2979, 2226, 1735, 1452, 1971, 1200, 1128, 1011, 948, 900, 828, 762cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.38 (td, *J* = 7.7, 0.7 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.20 – 7.11 (m, 2H), 6.99 (d, *J* = 1.9 Hz, 1H), 5.26 (s, 2H), 2.31 (s, 3H), 2.15 (s, 3H), 1.60 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 169.1, 149.2, 143.1, 139.3, 132.9, 132.8, 130.9, 128.7, 128.4, 123.4, 119.5, 116.9, 111.6, 64.0, 46.1, 26.2 (2C), 20.7, 15.7 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{21}H_{22}NO_4$ 352.1543; Found 352.1558.



5d

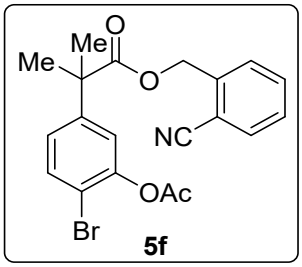
2-cyanobenzyl 2-(3-acetoxy-5-methoxyphenyl)-2-methylpropanoate (5d): GP-3 was carried out by using cyano-ester **1c** (62 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 45 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **5d** (45 mg, 64%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, R*f*(**1c**) = 0.50, R*f*(**5d**) = 0.10, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2977, 2227, 1734, 1600, 1455, 1370, 1204, 1137, 1054, 895, 767, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.52 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 (td, *J* = 7.6, 1.1 Hz, 1H), 7.27 – 7.24 (m, 1H), 6.75 – 6.71 (m, 1H), 6.65 (t, *J* = 1.8 Hz, 1H), 6.54 (t, *J* = 2.1 Hz, 1H), 5.27 (s, 2H), 3.75 (s, 3H), 2.28 (s, 3H), 1.59 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 169.3, 160.2, 151.5, 146.4, 139.3, 132.9, 132.8, 128.8, 128.5, 116.9, 111.6, 111.5, 109.8, 105.8, 64.0, 55.4, 46.5, 26.1 (2C), 21.1 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{21}H_{22}NO_5$ 368.1492; Found 368.1505.



5e

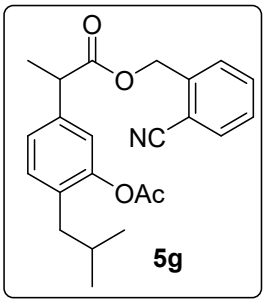
2-cyanobenzyl 2-(3-acetoxy-4-methoxyphenyl)-2-methylpropanoate (5e): GP-3 was carried out by using cyano-ester **1d** (62 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 45 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **5e** (45 mg, 61%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, R*f*(**1d**) = 0.50, R*f*(**5e**) = 0.10, UV

detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3613, 3003, 2625, 2351, 2252, 2077, 1632, 1435, 1383, 1271, 1038, 918, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.52 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 (td, *J* = 7.7, 1.1 Hz, 1H), 7.23 (dd, *J* = 7.8, 0.4 Hz, 1H), 7.19 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 5.26 (s, 2H), 3.82 (s, 3H), 2.31 (s, 3H), 1.60 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 168.8, 149.8, 139.4, 136.6, 132.9, 132.8, 128.7, 128.4, 124.1, 120.6, 116.9, 112.0, 111.6, 64.0, 55.9, 45.7, 26.2 (2C), 20.6 ppm. HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{21}H_{25}N_2O_5$ 385.1758; Found 385.1760.

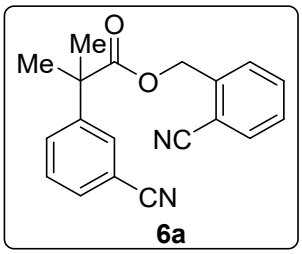


5f

2-cyanobenzyl 2-(3-acetoxy-4-bromophenyl)-2-methylpropanoate (5f): GP-3 was carried out by using cyano-ester **1j** (71 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 45 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **5f** (59 mg, 71%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, R*f*(**1j**) = 0.60, R*f*(**5f**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3619, 3002, 2623, 2253, 2092, 1632, 1435, 1385, 1271, 1038, 918, 836, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.40 (td, *J* = 7.6, 1.0 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.10 (q, *J* = 2.0 Hz, 2H), 5.26 (s, 2H), 2.35 (s, 3H), 1.60 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 175.1, 168.4, 148.2, 145.1, 139.1, 133.0, 133.0, 129.0, 128.7, 125.0, 121.5, 116.9, 114.6, 111.9, 64.3, 46.3, 26.1 (2C), 20.8 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{20}H_{19}{}^{79}BrNO_4$ 416.0492; Found 416.0498; Calcd for $C_{20}H_{19}{}^{81}BrNO_4$ 418.0472; Found 418.0478.

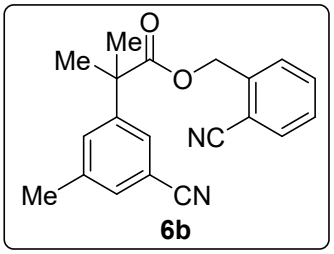


2-cyanobenzyl 2-(3-acetoxy-4-isobutylphenyl)propanoate (5g): GP-3 was carried out by using cyano-ester **1k** (64 mg, 0.2 mmol), (diacetoxyiodo)benzene (154 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 45 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **5g** (47 mg, 62%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, R*f*(**1k**) = 0.60, R*f*(**5g**) = 0.20, UV detection].IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2954, 2226, 1744, 1451, 1372, 1197, 1110, 766 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.49 (td, *J* = 7.7, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.00 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.85 (d, *J* = 1.7 Hz, 1H), 5.26 (q, *J* = 13.3 Hz, 1H), 4.99 (dd, *J* = 11.3, 5.7 Hz, 2H), 3.90 (q, *J* = 7.2 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.84 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 169.3, 147.9, 142.2, 139.3, 132.8, 132.8, 129.1, 129.0, 128.5, 128.0, 127.1, 123.2, 116.9, 111.7, 63.9, 44.7, 39.3, 30.0, 22.3 (2C), 20.8, 17.1 ppm. HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{23}H_{29}N_2O_4$ 397.2122; Found 397.2125.



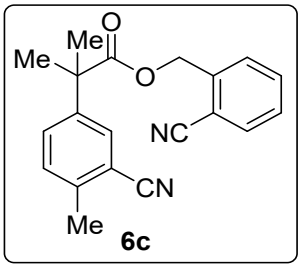
2-cyanobenzyl 2-(3-cyanophenyl)-2-methylpropanoate (6a): GP-4 was carried out by using cyano-ester **1a** (56 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20),

furnished the product **6a** (39 mg, 63%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1a**) = 0.60, *Rf*(**6a**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3612, 3002, 2252, 1969, 1632, 1435, 1383, 1270, 1039, 918, 744 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.61 – 7.51 (m, 4H), 7.46 – 7.39 (m, 2H), 7.32 (dd, *J* = 7.8, 0.5 Hz, 1H), 5.26 (s, 2H), 1.63 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 145.4, 138.7, 133.1, 132.9, 130.5, 129.5, 129.3, 129.3, 128.9, 118.7, 116.8, 112.5, 112.2, 64.5, 46.6, 26.0 (2C) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{19}H_{17}N_2O_2$ 305.1285; Found 305.1299.



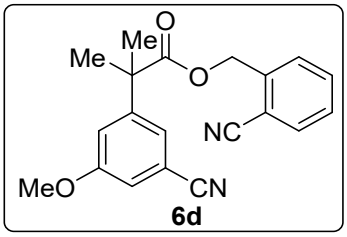
6b

2-cyanobenzyl 2-(3-cyano-5-methylphenyl)-2-methylpropanoate (6b): GP-4 was carried out by using cyano-ester **1b** (56 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **6b** (39 mg, 62%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1b**) = 0.60, *Rf*(**6b**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3610, 3002, 2620, 2351, 2253, 1632, 1435, 1382, 1270, 1038, 918, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.56 (td, *J* = 7.7, 1.3 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38 – 7.31 (m, 4H), 5.27 (s, 2H), 2.38 – 2.33 (m, 3H), 1.60 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 145.3, 139.4, 138.8, 133.1, 132.8, 131.4, 130.9, 129.4, 128.9, 126.6, 118.9, 116.8, 112.3, 112.2, 64.5, 46.4, 26.1 (2C), 21.2 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{20}H_{19}N_2O_2$ 319.1441; Found 319.1447.



6c

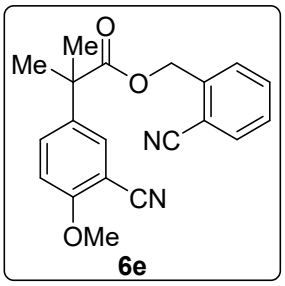
2-cyanobenzyl 2-(3-cyano-4-methylphenyl)-2-methylpropanoate (6c): GP-4 was carried out by using cyano-ester **1i** (56 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **6c** (37 mg, 62%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1i**) = 0.60, *Rf*(**6c**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3617, 3002, 2620, 2253, 1632, 1435, 1383, 1038, 918, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.56 (td, *J* = 7.7, 1.4 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.34 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.28 – 7.23 (m, 1H), 5.26 (s, 2H), 2.51 (s, 3H), 1.60 (s, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 142.5, 140.4, 138.9, 133.1, 132.9, 130.4, 130.3, 129.7, 129.3, 128.9, 118.0, 116.8, 112.7, 112.2, 64.4, 46.1, 26.1 (2C), 19.9 ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{20}H_{19}N_2O_2$ 319.1441; Found 319.1447.



6d

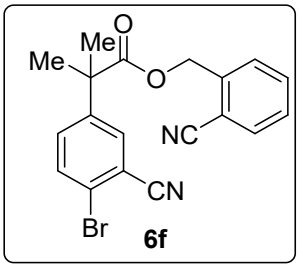
2-cyanobenzyl 2-(3-cyano-5-methoxyphenyl)-2-methylpropanoate (6d): GP-4 was carried out by using cyano-ester **1c** (62 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **6d** (39 mg, 59%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1c**) = 0.60, *Rf*(**6d**) = 0.15, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3619, 3002, 2626, 2353, 2252, 1631, 1435, 1382, 1039, 918, 750

cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.56 (td, *J* = 7.7, 1.2 Hz, 1H), 7.45 (ddd, *J* = 10.5, 8.8, 4.6 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.11 – 7.04 (m, 1H), 7.01 (dd, *J* = 2.4, 1.2 Hz, 1H), 5.26 (s, 2H), 3.80 (s, 3H), 1.61 (d, *J* = 8.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 174.9, 159.7, 147.1, 138.8, 133.1, 132.9, 129.3, 128.9, 122.2, 118.7, 117.6, 116.8, 114.8, 113.1, 112.2, 64.5, 55.6, 46.6, 26.0 (2C) ppm. HRMS (ESI) m/z: $[(M+H)]^+$ Calcd for $C_{29}H_{19}N_2O_3$ 335.1390; Found 335.1394.

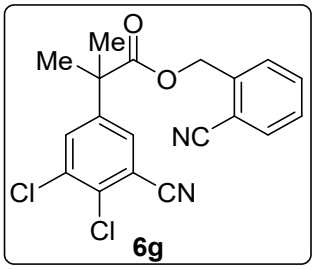


6e

2-cyanobenzyl 2-(3-cyano-4-methoxyphenyl)-2-methylpropanoate (6e): GP-4 was carried out by using cyano-ester **1d** (62 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **6e** (41 mg, 61%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1d**) = 0.60, *Rf*(**6e**) = 0.15, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3622, 3003, 2351, 2253, 1630, 1435, 1385, 1272, 1039, 918, 749 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.55 (ddd, *J* = 11.4, 8.3, 1.9 Hz, 2H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.43 (td, *J* = 7.6, 1.1 Hz, 1H), 7.34 (dd, *J* = 7.7, 0.5 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 1H), 5.25 (s, 2H), 3.91 (s, 3H), 1.59 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 160.0, 138.8, 136.7, 133.1, 132.9, 132.2, 131.0, 129.3, 128.9, 116.8, 116.4, 112.1, 111.3, 101.5, 64.4, 56.1, 45.7, 26.1 (2C) ppm. HRMS (ESI) m/z: $[(M+Na]^+$ Calcd for $C_{20}H_{18}NaN_2O_3$ 357.1210; Found 357.1207.

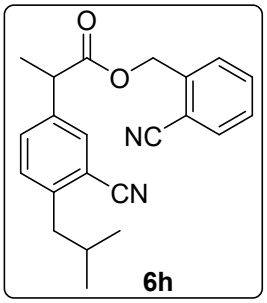


2-cyanobenzyl 2-(4-bromo-3-cyanophenyl)-2-methylpropanoate (6f): GP-4 was carried out by using cyano-ester **1j** (71 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **6f** (49 mg, 64%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1j**) = 0.60, *Rf*(**6f**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3622, 3003, 2351, 2252, 1631, 1435, 1382, 1270, 1039, 918, 751, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.58 (ddd, *J* = 7.5, 6.5, 4.8 Hz, 3H), 7.49 – 7.40 (m, 2H), 7.35 (dd, *J* = 7.7, 0.5 Hz, 1H), 5.25 (s, 2H), 1.61 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 144.3, 138.6, 133.2, 133.1, 132.9, 131.9, 131.8, 129.5, 129.1, 123.6, 117.1, 116.8, 115.8, 112.3, 64.8, 46.3, 26.0 (2C) ppm. HRMS (ESI) m/z: $[(M+NH_4)]^+$ Calcd for $C_{19}H_{19}{}^{79}BrN_3O_2$ 400.0655; Found 400.0664: Calcd for $C_{19}H_{19}{}^{81}BrN_3O_2$ 402.0635; Found 402.0652.



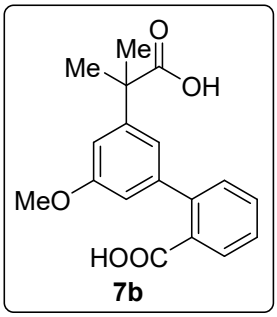
2-cyanobenzyl 2-(3,4-dichloro-5-cyanophenyl)-2-methylpropanoate (6g): GP-4 was carried out by using cyano-ester **1l** (69 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **6g** (39 mg, 53%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1l**) = 0.50, *Rf*(**6g**) = 0.15, UV detection]. IR (MIR-

ATR, 4000–600 cm^{-1}): ν_{max} = 3617, 3002, 2622, 2349, 2252, 2118, 1634, 1435, 1383, 1270, 1038, 918, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.62 (t, *J* = 1.9 Hz, 1H), 7.59 (dt, *J* = 7.7, 3.8 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.46 (td, *J* = 7.7, 1.2 Hz, 1H), 7.38 (dd, *J* = 7.7, 0.6 Hz, 1H), 5.27 (s, 2H), 1.61 (s, 6H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.2, 144.9, 138.4, 134.4, 133.7, 133.2, 133.0, 132.6, 129.9, 129.7, 129.2, 116.8, 115.4, 115.1, 112.4, 65.0, 46.3, 26.0 (2C) ppm. HRMS (ESI) m/z: $[(M+2K]^{2+}$ Calcd for $C_{19}H_{14}Cl_2K_2N_2O_2$ 224.9848; Found 224.9854.



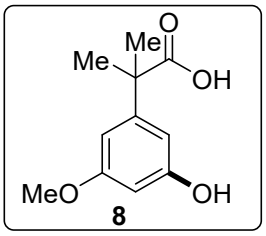
6h

2-cyanobenzyl 2-(3-cyano-4-isobutylphenyl)propanoate (6h): GP-4 was carried out by using cyano-ester **1k** (64 mg, 0.2 mmol), CuCN (43 mg, 0.48 mmol), $Pd(OAc)_2$ (7 mg, 15 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) at 100 °C for 45 minutes under microwave irradiation. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **6h** (39 mg, 56%) as a thick brown coloured liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**1k**) = 0.60, *Rf*(**6h**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3608, 3001, 2351, 2253, 1632, 1436, 1383, 1039, 919, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.55 (td, *J* = 7.7, 1.3 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.34 (s, 2H), 5.33 (t, *J* = 10.8 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.85 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 141.6, 140.9, 138.9, 134.1, 133.3, 132.9, 129.0, 128.7, 127.4, 117.8, 116.8, 112.2, 111.8, 64.3, 44.3, 43.0, 29.9, 22.1, 18.1 (2C) ppm. HRMS (ESI) m/z: $[(M+NH_4]^+$ Calcd for $C_{22}H_{26}N_3O_2$ 364.2020; Found 364.2036.



7b

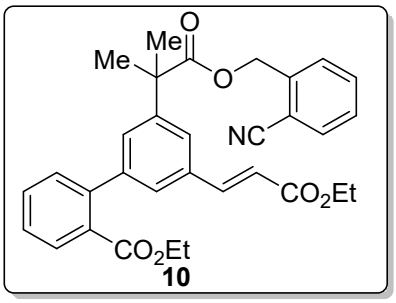
3'-(2-carboxypropan-2-yl)-5'-methoxy-[1,1'-biphenyl]-2-carboxylic acid (7b): Gp-5 is followed as to the solution of **3ca** (91 mg, 0.2 mmol) in MeOH (1.6 mL), THF (0.8 mL), H_2O (0.4 mL) was added LiOH·H_2O (67mg, 1.6 mmol) at room temperature. The resulting mixture was stirred at room temperature for 12 h. the organic solvent removed under the reduced pressure, resulted mixture was diluted with H_2O (15 mL) the aquous phase was diluted with 2M HCl and extracted with EtOAc (3 × 15 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. The diacid product **7** was obtained in 91% (57 mg) yield as a white crystalline solid. Melting point: 135-137 ℃. Melting point: 124-126 ℃. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3617, 3003, 2252, 1631, 1435, 1382, 1039, 918, 750 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 6.92 (s, 2H), 6.79 (s, 1H), 3.83 (s, 3H), 1.57 (s, 6H) ppm. ^{13}C NMR (101 MHz, CDCl3) δ 183.2, 173.2, 159.4, 144.4, 143.6, 142.3, 132.0, 130.9, 130.8, 129.3, 127.3, 120.4, 111.4, 110.8, 55.3, 46.0, 25.9 (2C) ppm. HRMS (ESI) m/z: $[(M+Na]^+$ Calcd for $C_{18}H_{18}NaO_5$ 337.1046; Found 337.1048.



8

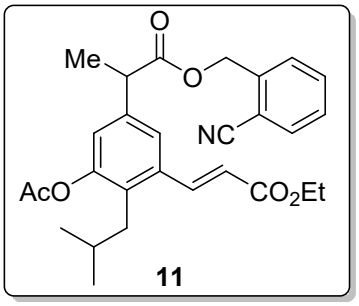
2-(3-hydroxy-5-methoxyphenyl)-2-methylpropanoic acid (8): Gp-5 is followed as to the solution of **5d** (73 mg, 0.2 mmol) in MeOH (1.6 mL), THF (0.8 mL), H_2O (0.4 mL) was added LiOH.H_2O (67mg, 1.6 mmol) at room temperature. The resulting mixture was stirred at room temperature for 12 h. the organic solvent removed under the reduced pressure, resulted mixture was diluted with H_2O (15 mL) the aqueous phase was diluted with 2M HCl and extracted with EtOAc (3 × 15 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. The product **8** was obtained in 88% (37 mg) yield as a light brown

coloured liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3622, 3003, 2253, 1630, 1435, 1271, 1039, 918, 749 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 6.53 – 6.50 (m, 1H), 6.48 – 6.43 (m, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 3H), 1.54 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 160.8, 156.7, 146.5, 105.7, 105.5, 104.8, 104.6, 99.7, 55.3, 46.3, 26.0 (2C) ppm. HRMS (ESI) m/z: $[(M+Na]^+$ Calcd for $C_{11}H_{14}NaO_4$ 233.0784; Found 233.0796.

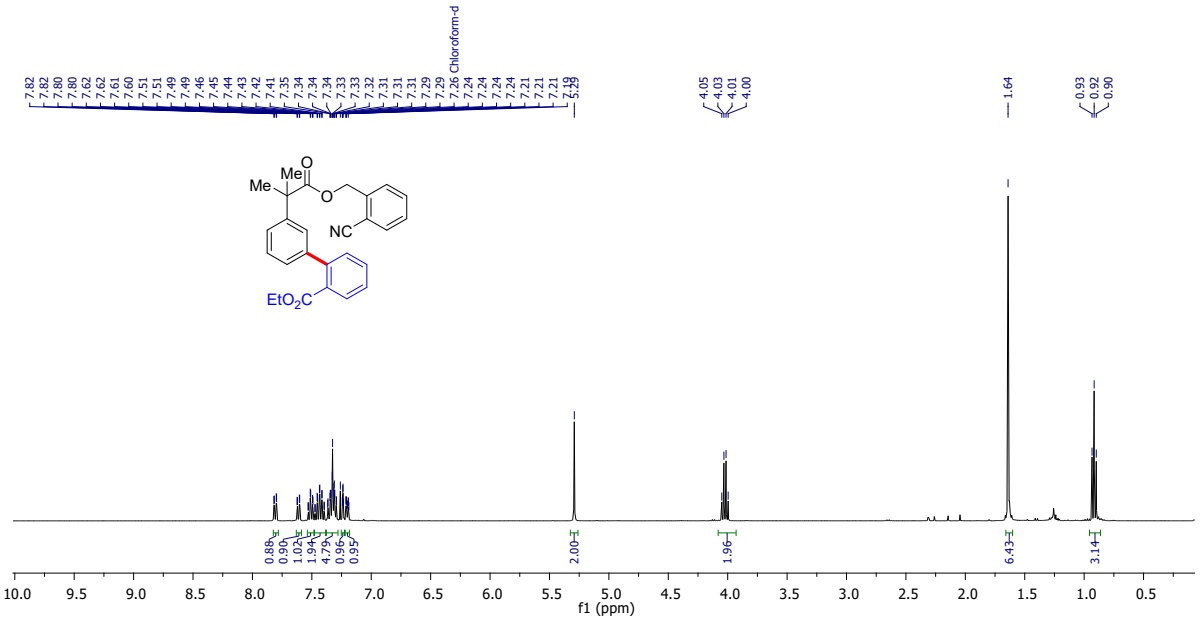


10

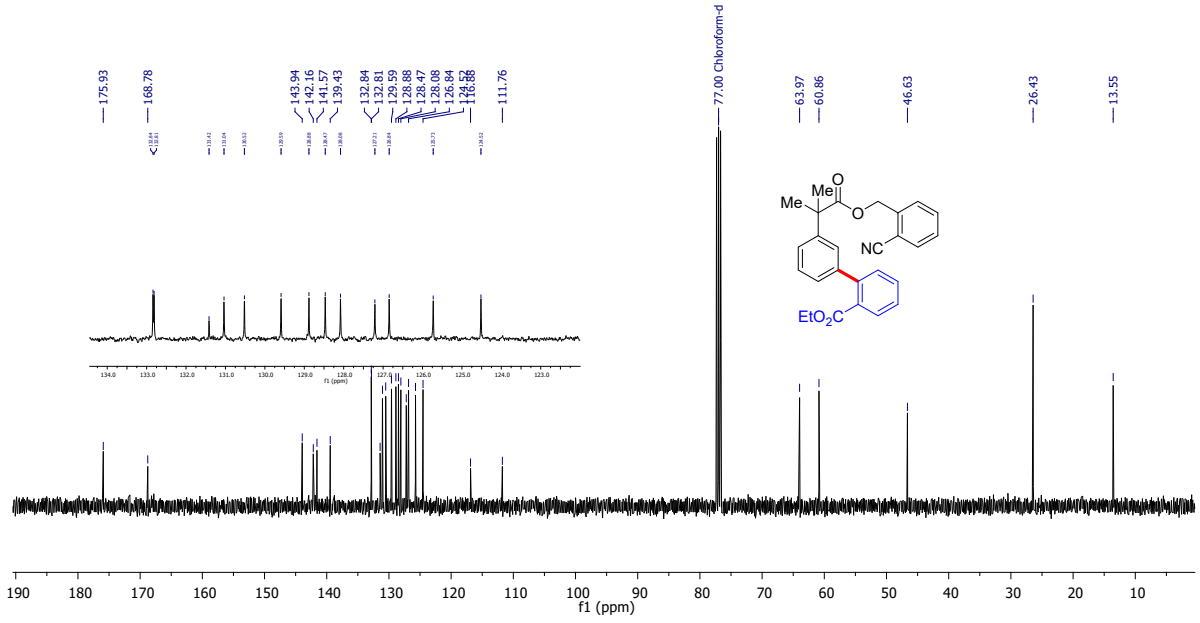
Ethyl (E)-3'-(1-((2-cyanobenzyl)oxy)-2-methyl-1-oxopropan-2-yl)-5'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylate (10): GP-6 was carried out by using substrate **3aa** (85 mg, 0.2 mmol), ethyl acrylate (48 mg, 0.48 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 °C for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **10** (83 mg, 79%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 80:20, *Rf*(**3aa**) = 0.60, *Rf*(**10**) = 0.35, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2978, 2226, 1711, 1456, 1251, 1130, 762 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 7.85 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 (dtd, *J* = 8.8, 7.6, 1.2 Hz, 2H), 7.40 (d, *J* = 1.6 Hz, 1H), 7.36 (ddd, *J* = 4.0, 2.9, 1.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.25 (t, J = 1.7 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.29 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.64 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 175.5, 168.3, 166.8, 144.7, 144.2, 142.4, 141.5, 139.2, 134.3, 132.9, 132.8, 131.2, 131.2, 130.5, 129.9, 129.1, 128.6, 127.8, 127.6, 126.3, 124.4, 118.8, 116.8, 112.0, 64.2, 60.9, 60.5, 46.6, 26.4 (2C), 14.3, 13.6 ppm. HRMS (ESI) m/z: $[(M+H]^+$ Calcd for $C_{32}H_{32}NO_6$ 526.2224; Found 526.2208.



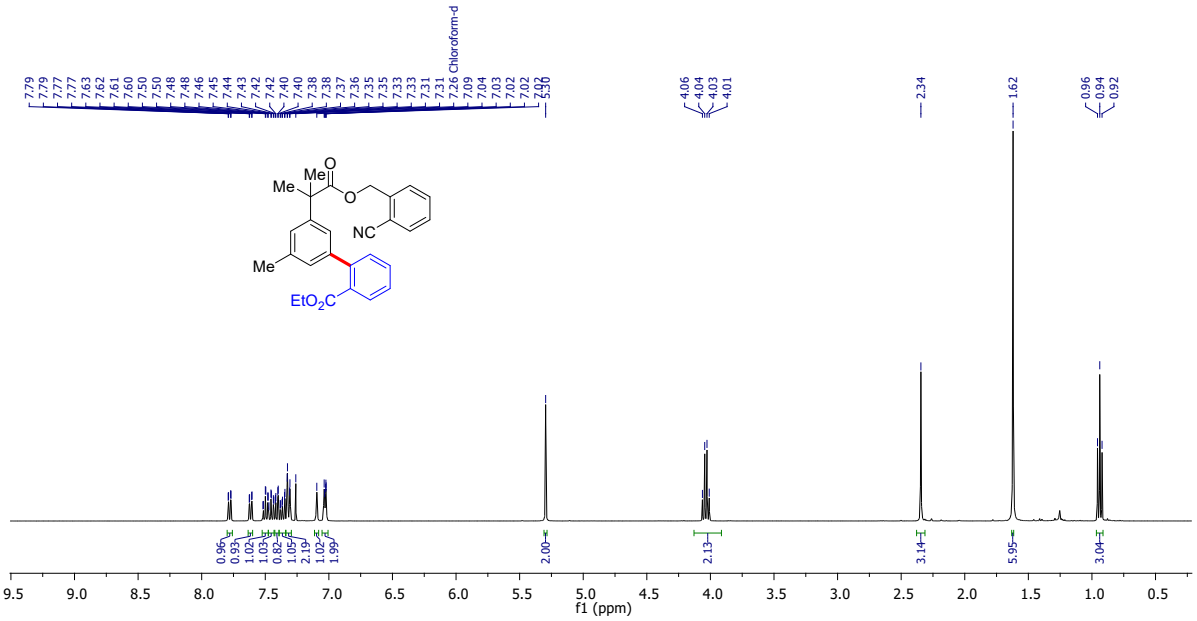
Ethyl (E)-3-(3-acetoxy-5-(1-((2-cyanobenzyl)oxy)-1-oxopropan-2-yl)-2-isobutylphenyl)acrylate (11): GP-6 was carried out by using substrate **5g** (78 mg, 0.2 mmol), ethyl acrylate (48 mg, 0.48 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (2 mL) under microwave irradiation at 100 ℃ for 30 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **11** (55 mg, 56%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 80:20, R*f*(**5g**) = 0.60, R*f*(**11**) = 0.35, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2951, 2226, 1719, 1371, 1176, 761 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 7.92 (d, *J* = 15.6 Hz, 1H), 7.63 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.40 – 7.36 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 1.5 Hz, 1H), 6.91 (d, *J* = 1.6 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 5.32 (d, *J* = 13.3 Hz, 1H), 5.23 (d, *J* = 13.3 Hz, 1H), 4.26 (dt, *J* = 7.1, 4.5 Hz, 3H), 4.08 (t, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.18 (s, 3H), 1.41 (d, *J* = 7.2 Hz, 3H), 1.33 (d, *J* = 7.1 Hz, 4H), 0.92 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 173.1, 169.1, 166.4, 148.3, 146.4, 141.8, 141.3, 139.3, 139.2, 134.7, 132.7, 129.6, 129.0, 128.5, 125.6, 125.2, 122.1, 111.8, 64.0, 60.7, 44.7, 38.0, 29.9, 22.2 (2C), 20.7, 16.4, 14.3 ppm. HRMS (ESI) m/z: $[(M+K]^+$ Calcd for $C_{28}H_{31}KNO_6$ 516.1783; Found 516.1771.



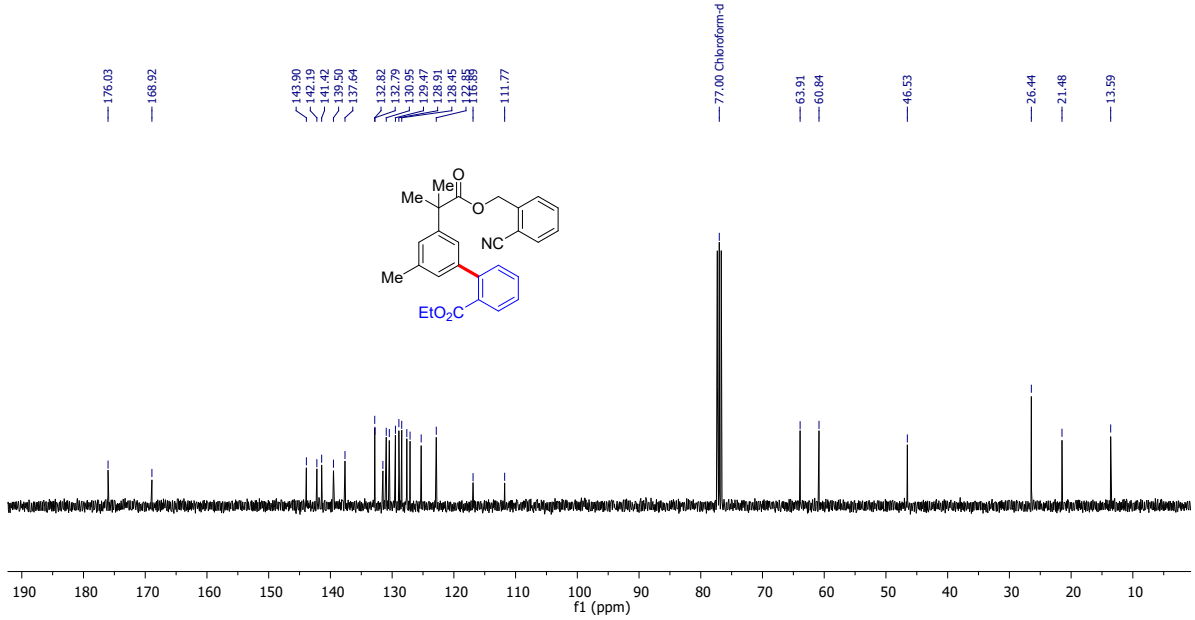
^{1}H NMR (400 MHz) spectrum of **3aa** in $CDCl_3$



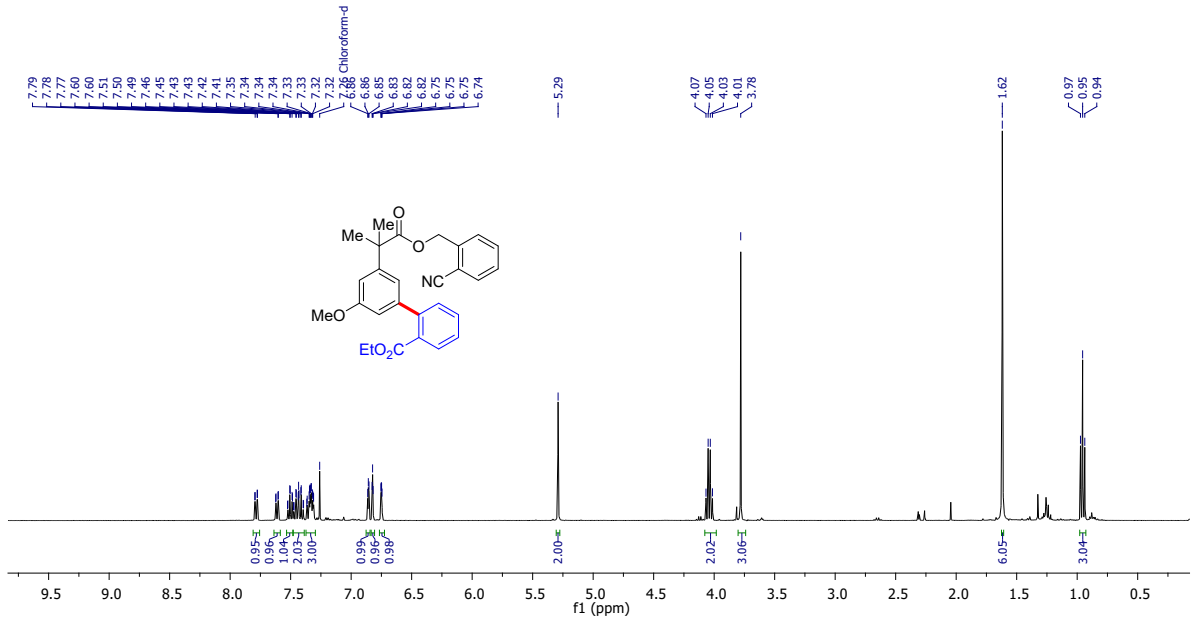
^{13}C NMR (100 MHz) spectrum of **3aa** in $CDCl_3$



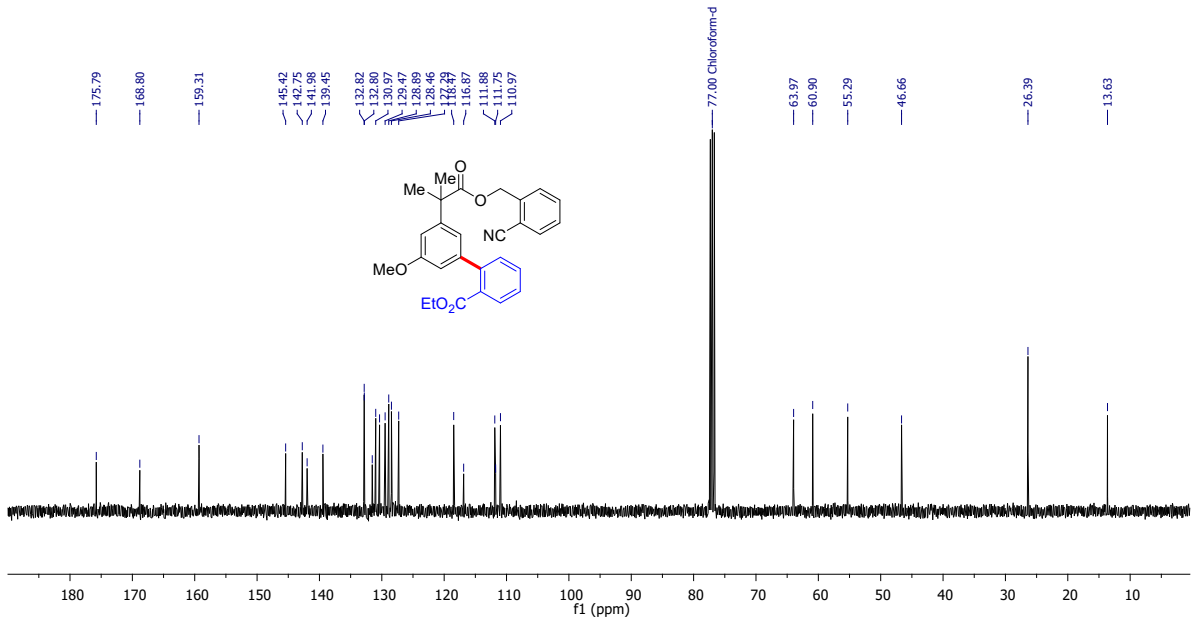
^{1}H NMR (400 MHz) spectrum of **3ba** in $CDCl_3$



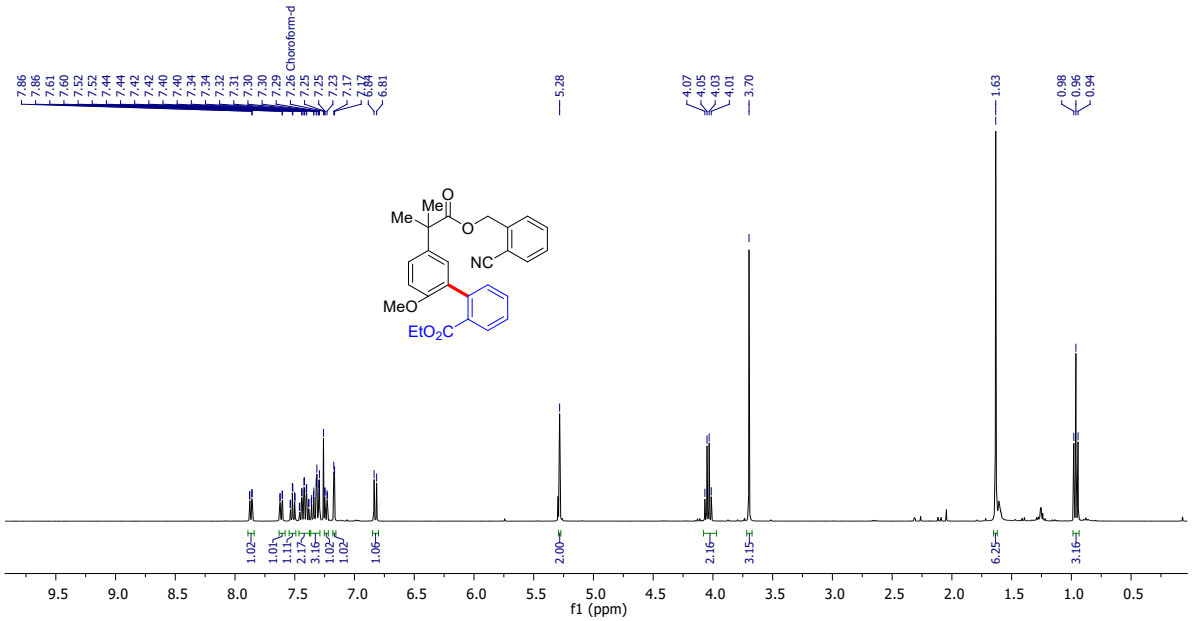
^{13}C NMR (100 MHz) spectrum of **3ba** in $CDCl_3$



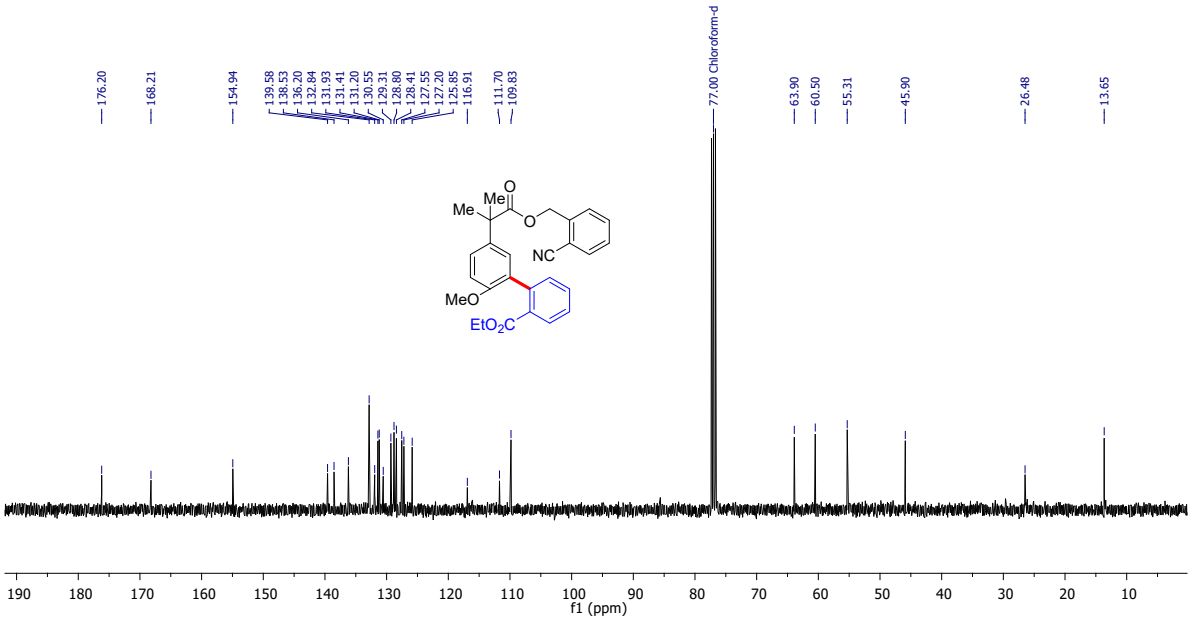
^{1}H NMR (400 MHz) spectrum of **3ca** in $CDCl_3$



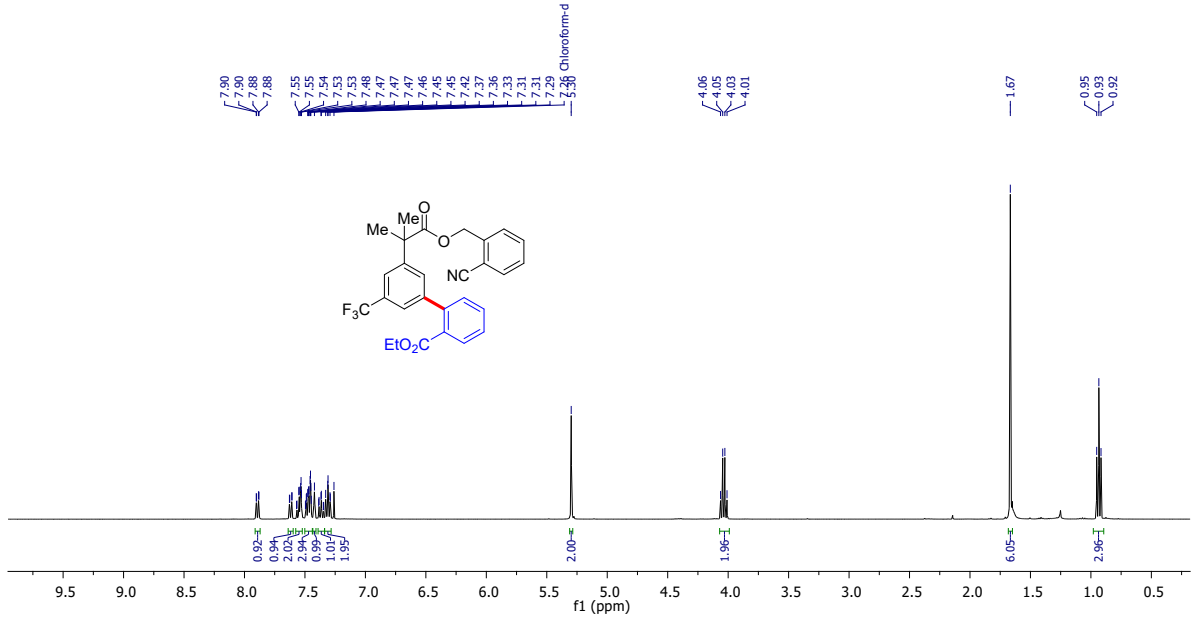
^{13}C NMR (100 MHz) spectrum of **3ca** in $CDCl_3$



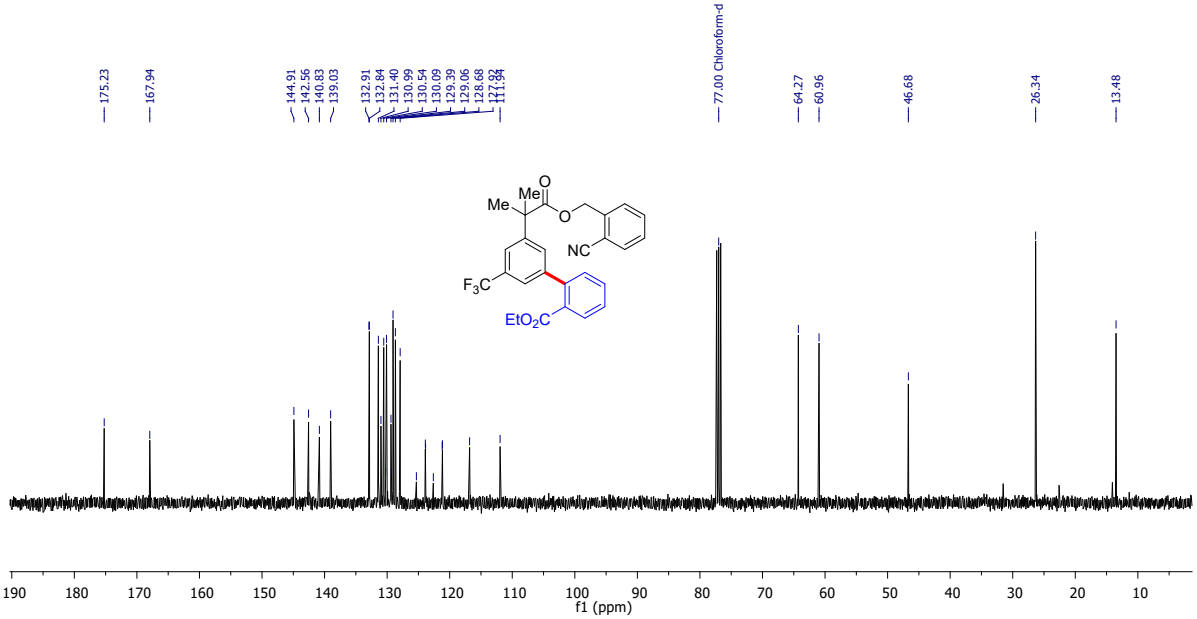
^{1}H NMR (400 MHz) spectrum of **3da** in $CDCl_3$



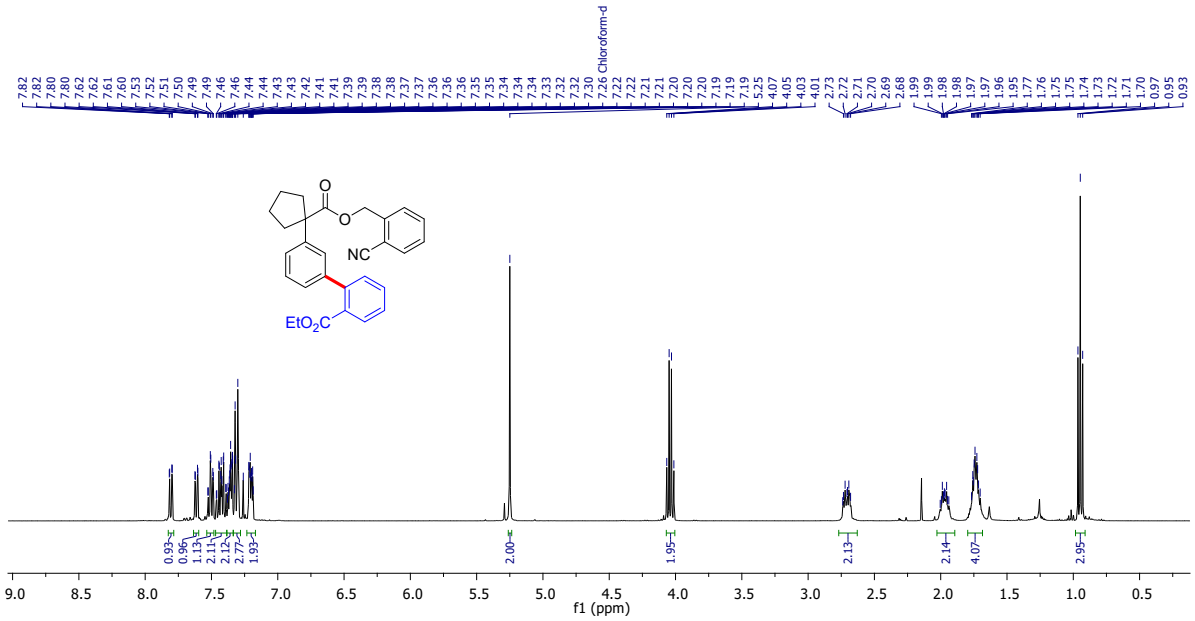
^{13}C NMR (100 MHz) spectrum of **3da** in $CDCl_3$



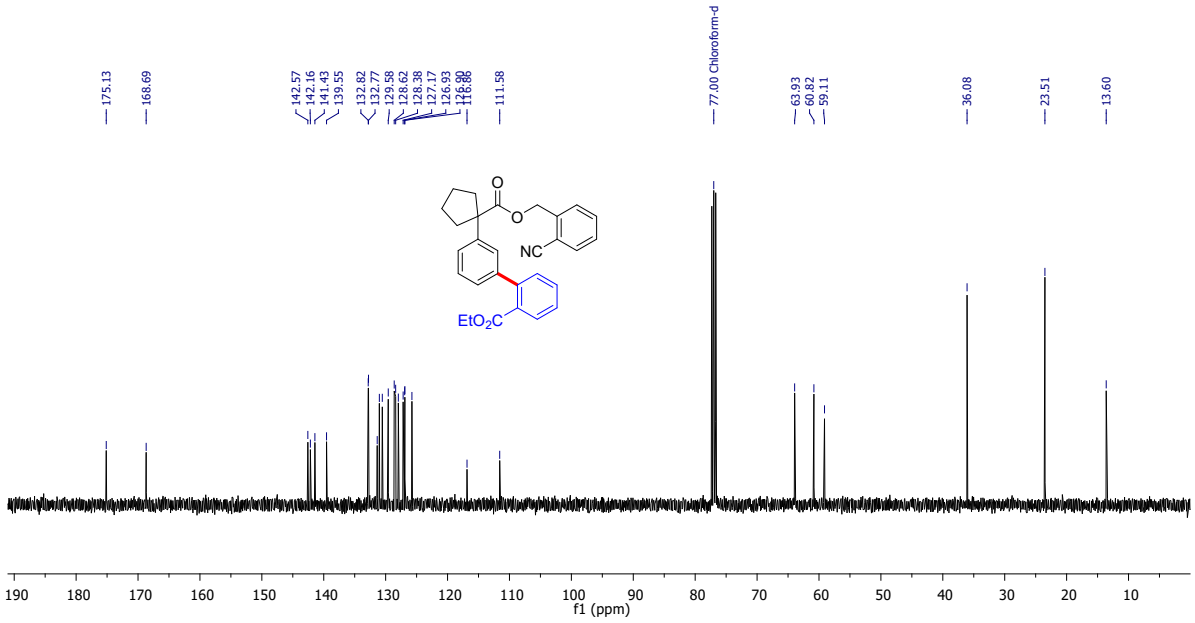
^{1}H NMR (400 MHz) spectrum of **3ea** in $CDCl_3$



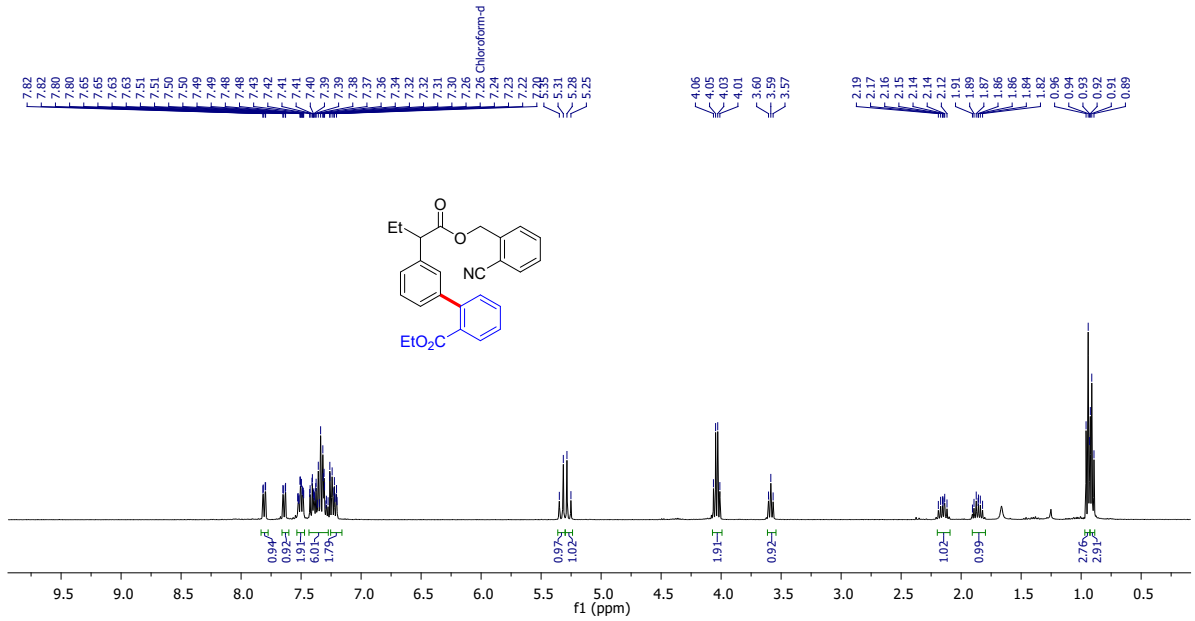
^{13}C NMR (100 MHz) spectrum of **3ea** in $CDCl_3$



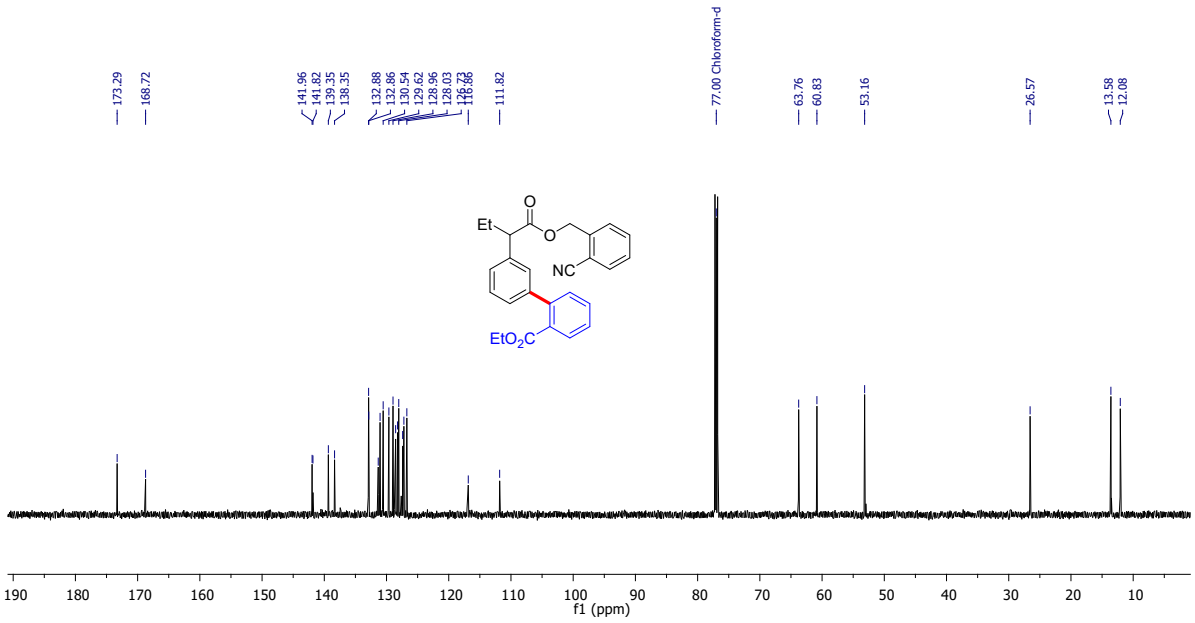
^{1}H NMR (400 MHz) spectrum of **3fa** in $CDCl_3$



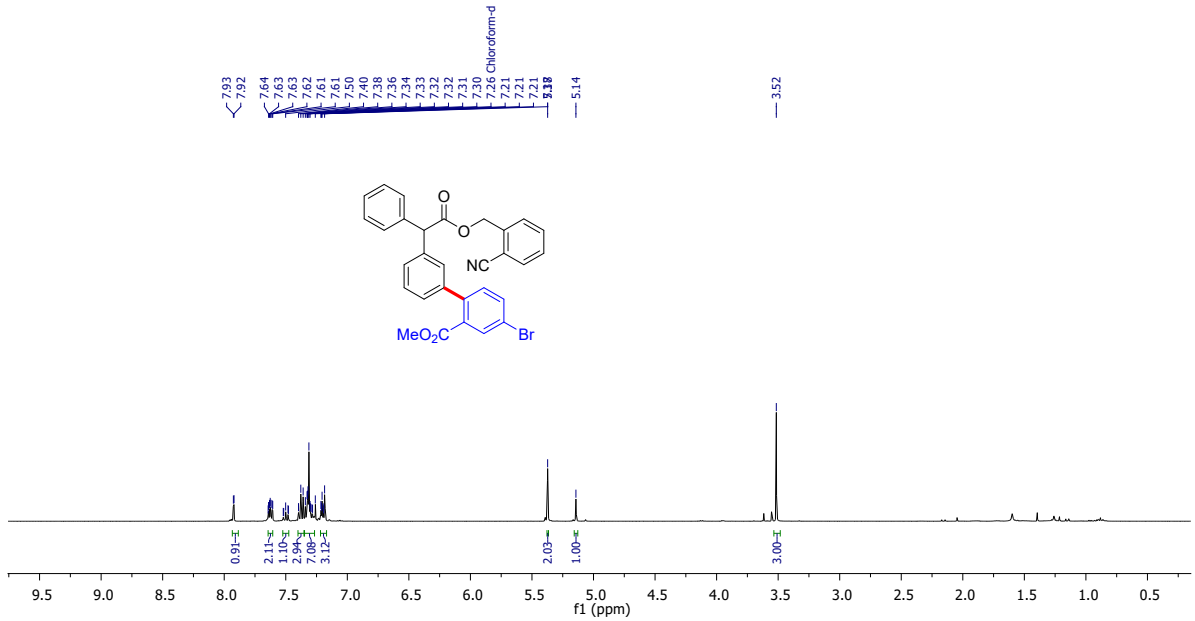
^{13}C NMR (100 MHz) spectrum of **3fa** in $CDCl_3$



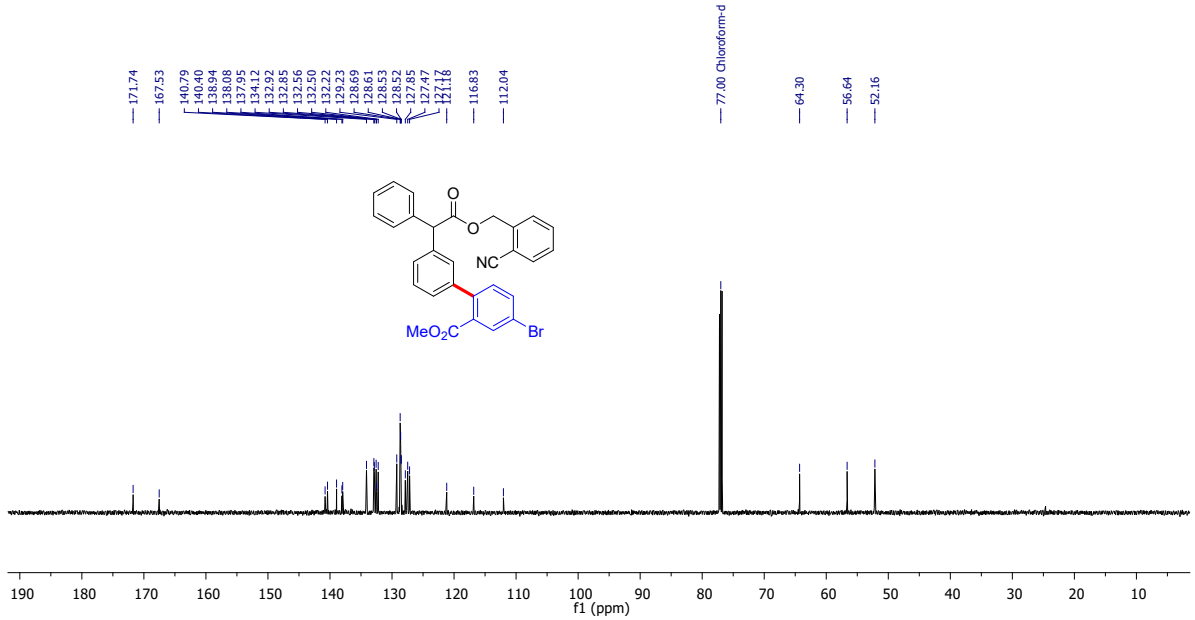
^{1}H NMR (400 MHz) spectrum of **3ga** in $CDCl_3$



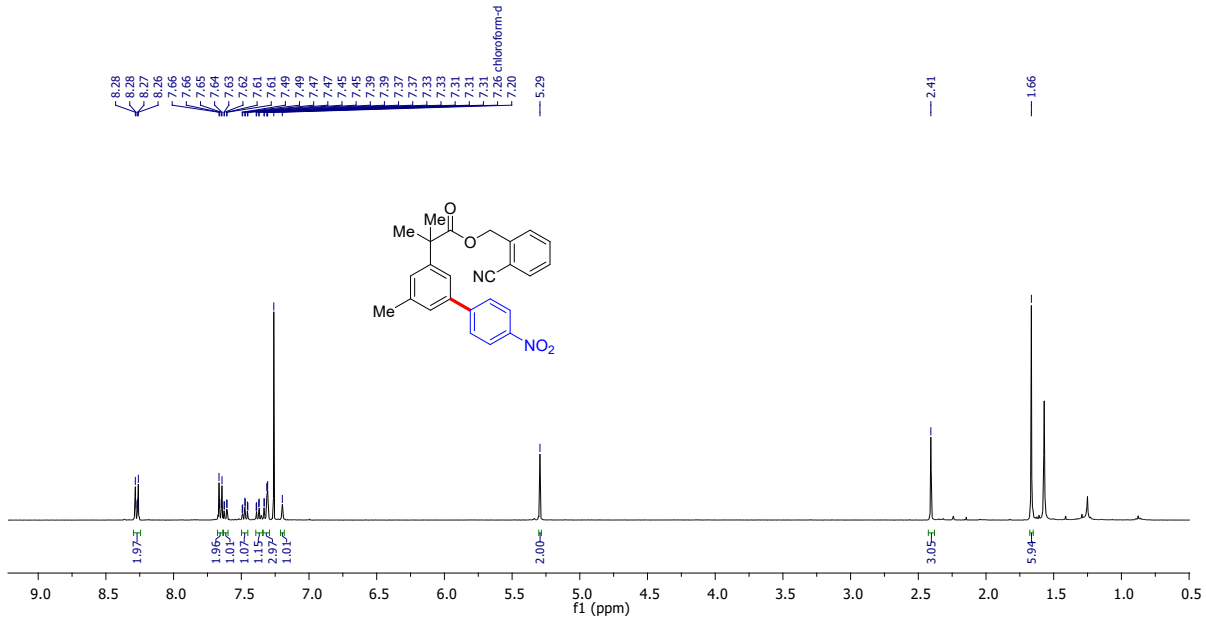
^{13}C NMR (151 MHz) spectrum of **3ga** in $CDCl_3$



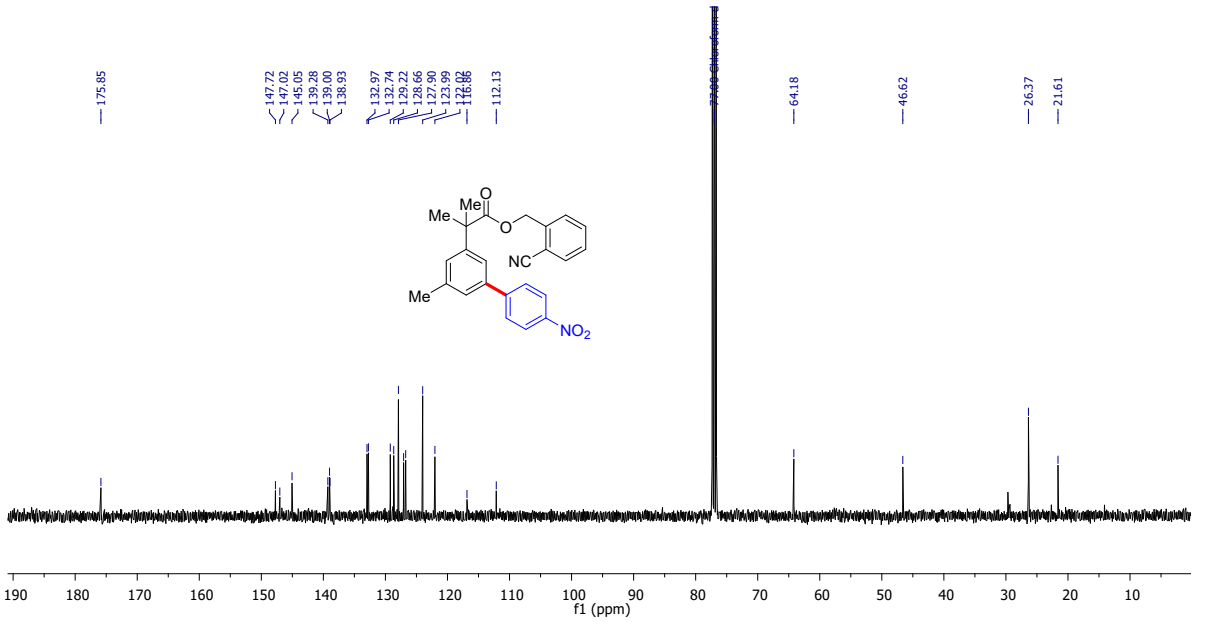
^{1}H NMR (400 MHz) spectrum of **3hg** in $CDCl_3$



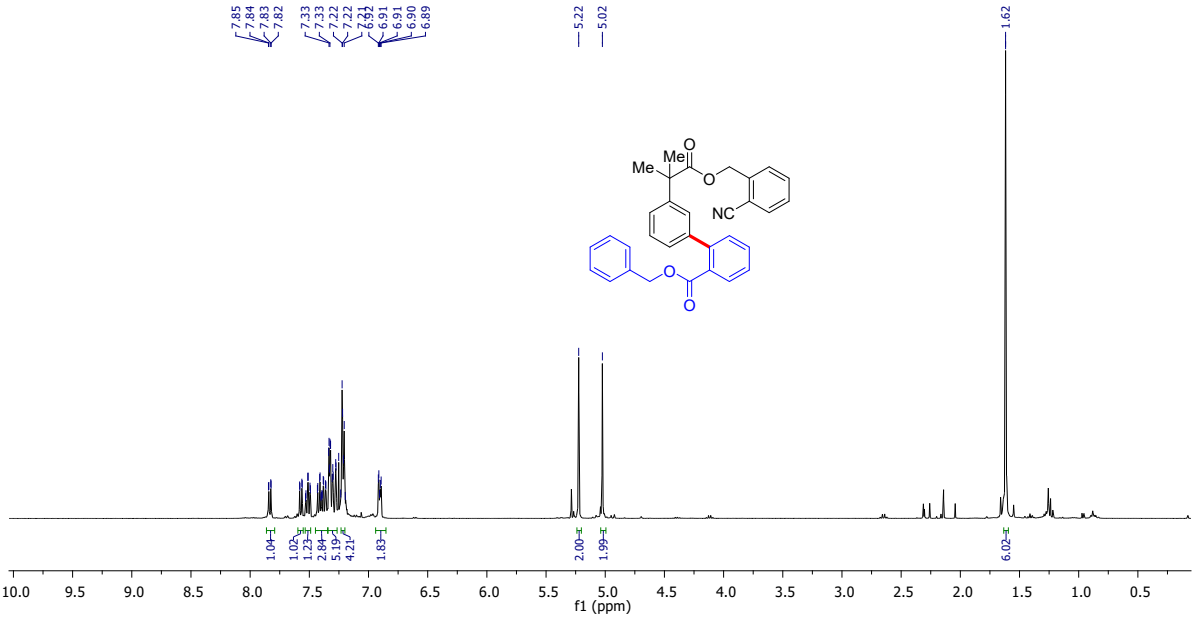
^{13}C NMR (151 MHz) spectrum of **3hg** in $CDCl_3$



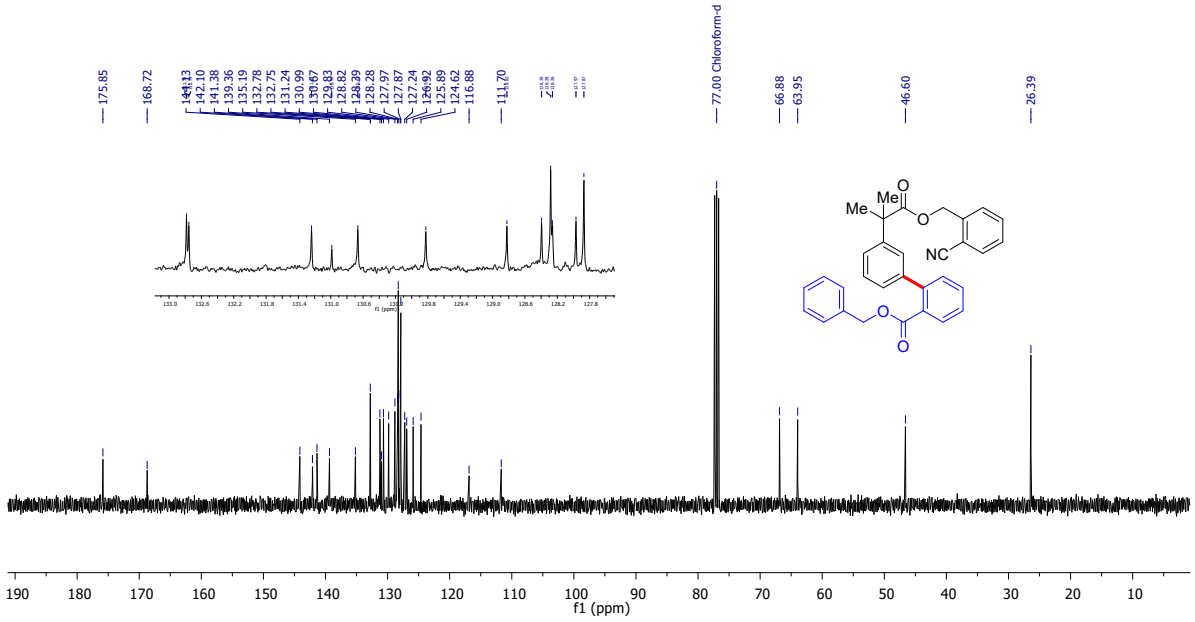
^{1}H NMR (400 MHz) spectrum of **3bb** in $CDCl_3$



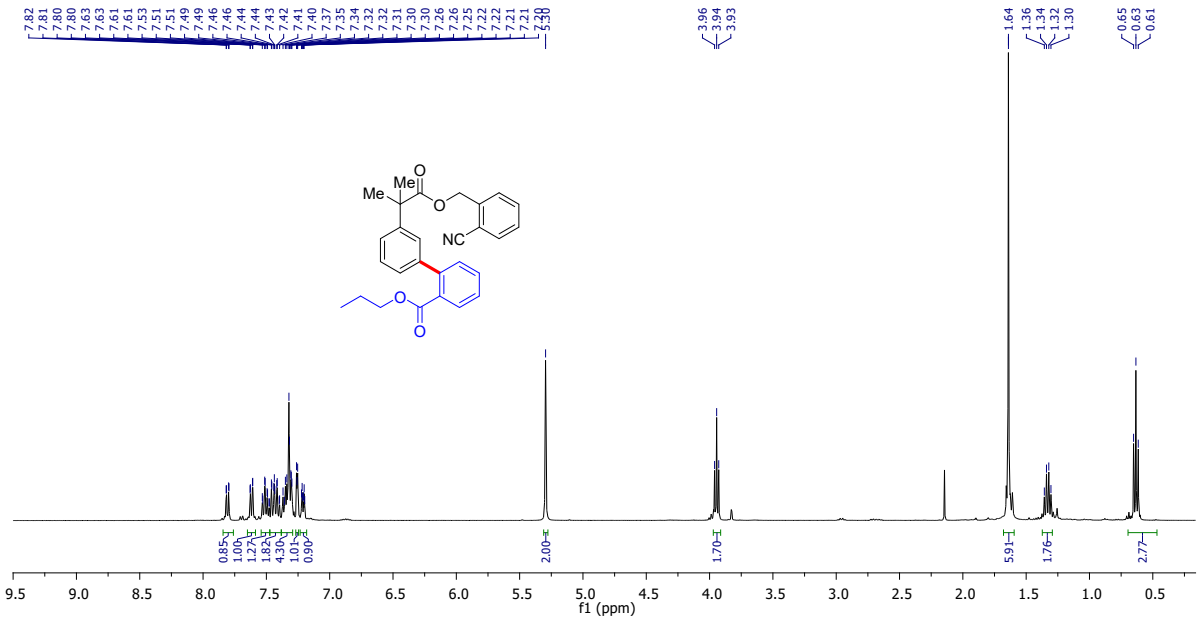
^{13}C NMR (100 MHz) spectrum of **3bb** in $CDCl_3$



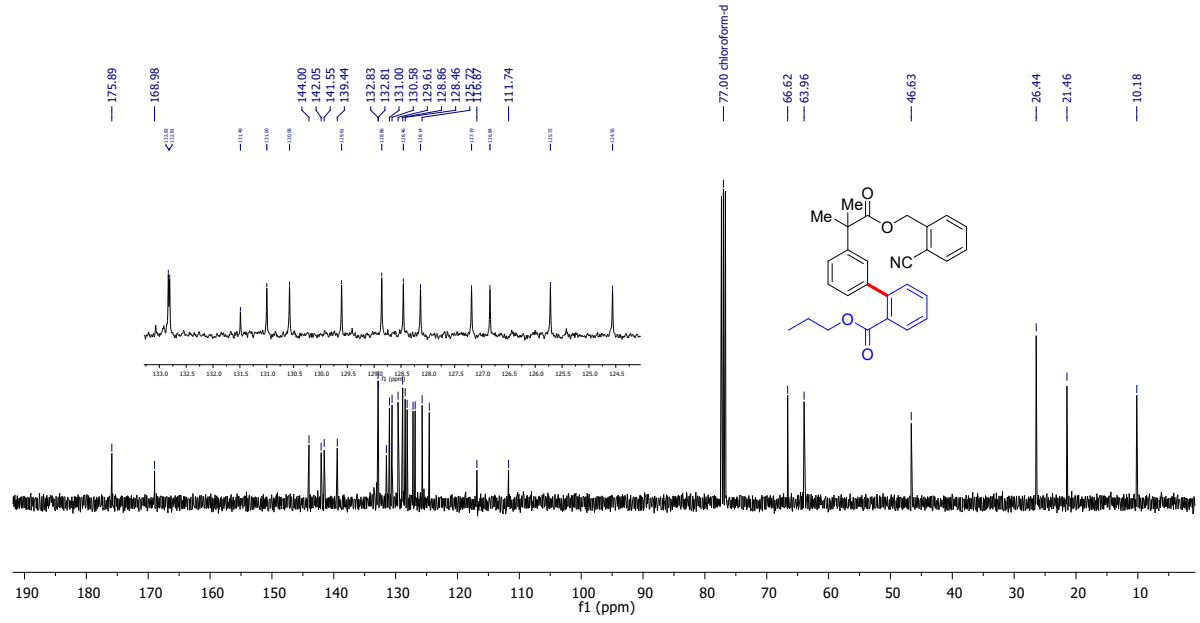
^{1}H NMR (400 MHz) spectrum of **3ac** in $CDCl_3$



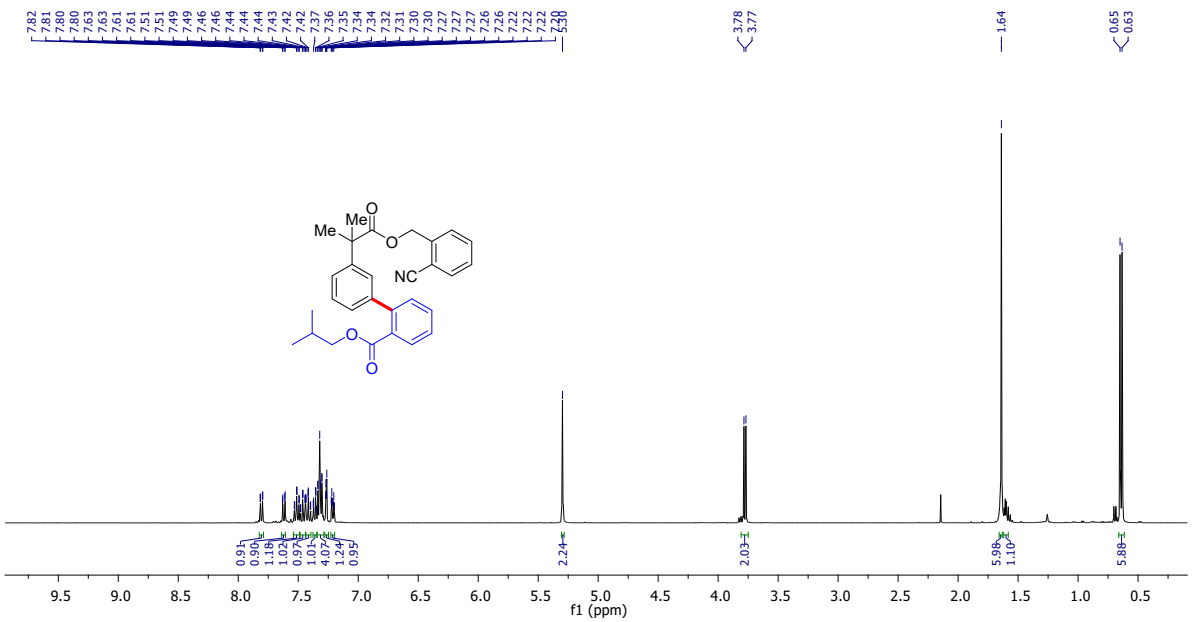
^{13}C NMR (100 MHz) spectrum of **3ac** in $CDCl_3$



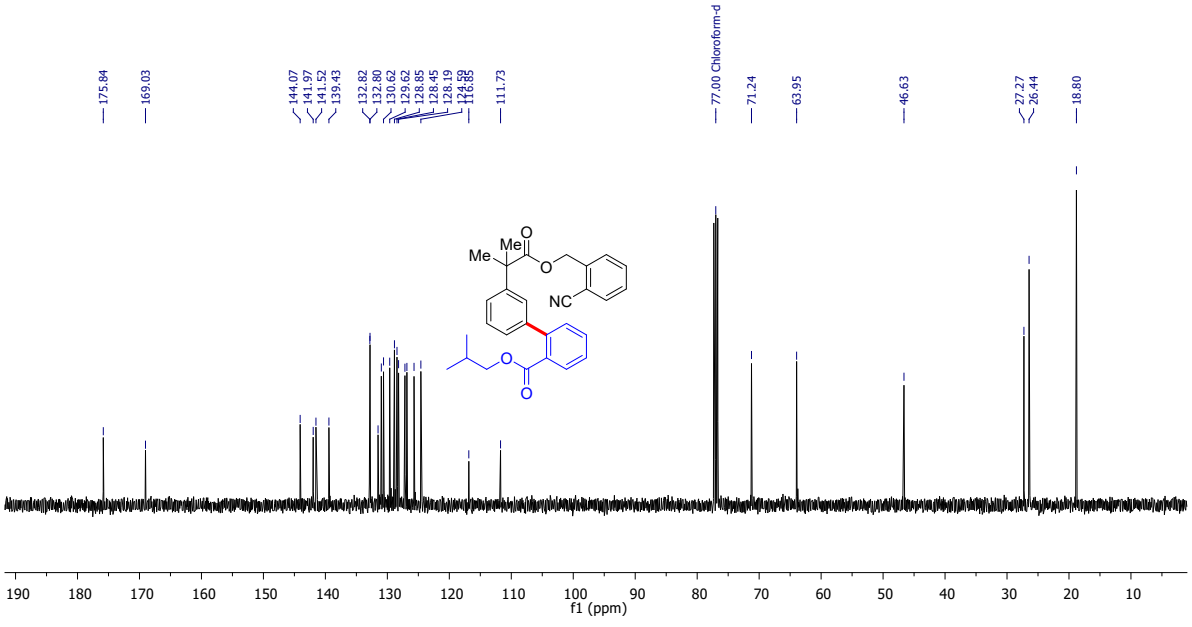
^{1}H NMR (400 MHz) spectrum of **3ad** in $CDCl_3$



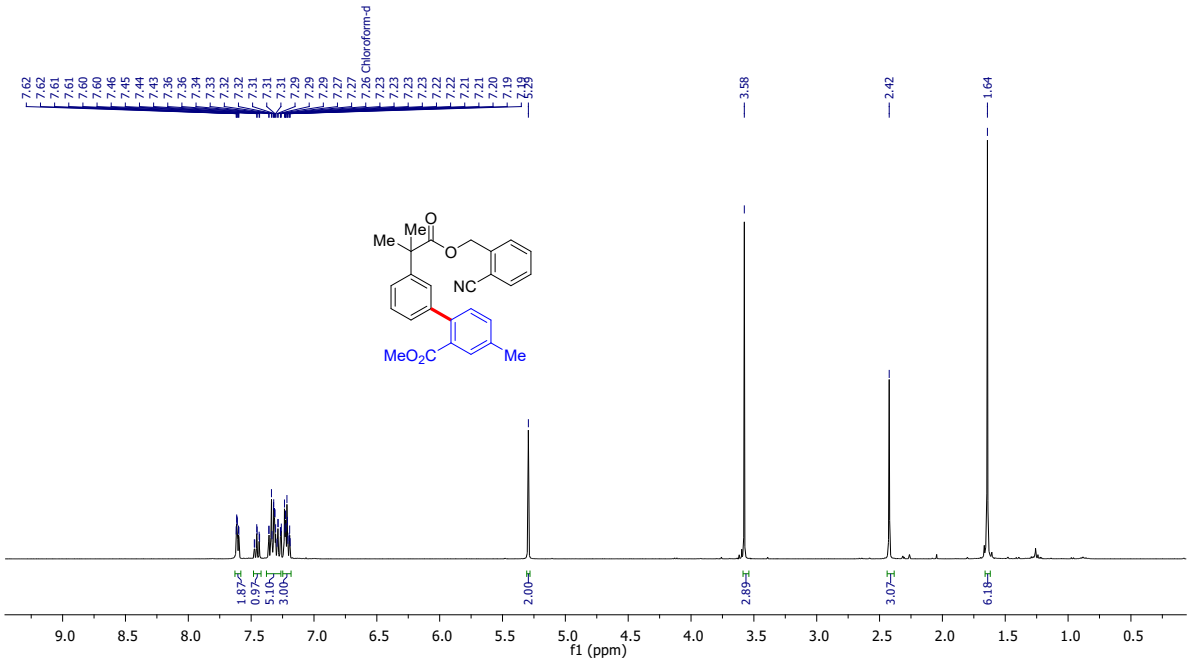
^{13}C NMR (100 MHz) spectrum of **3ad** in $CDCl_3$



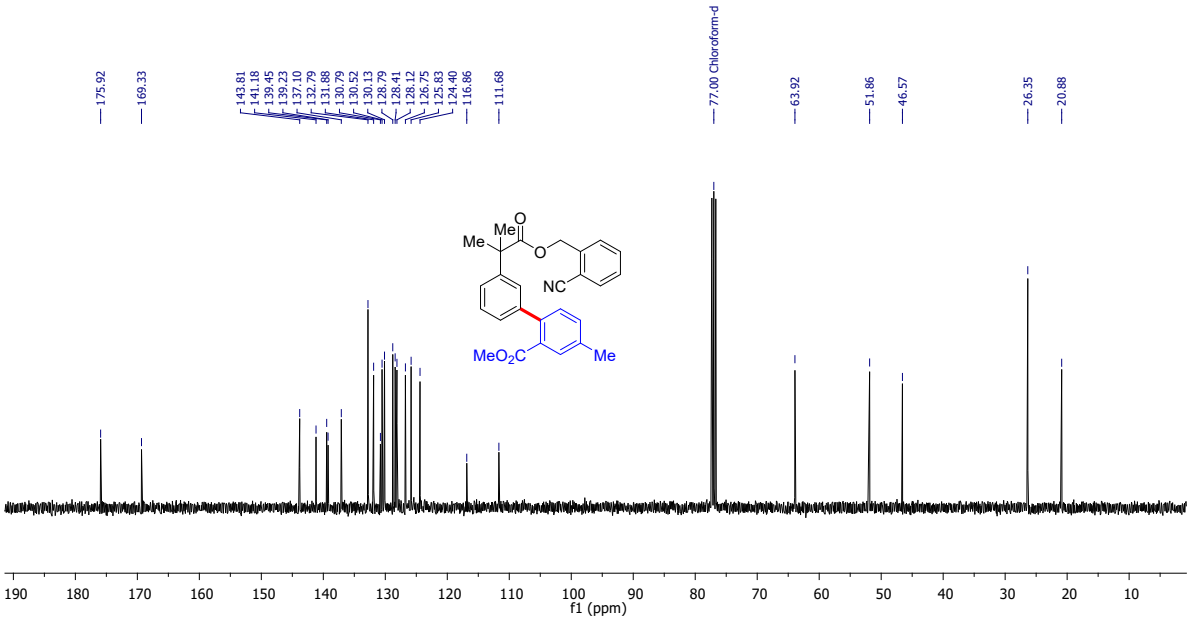
^{1}H NMR (400 MHz) spectrum of **3ae** in $CDCl_3$



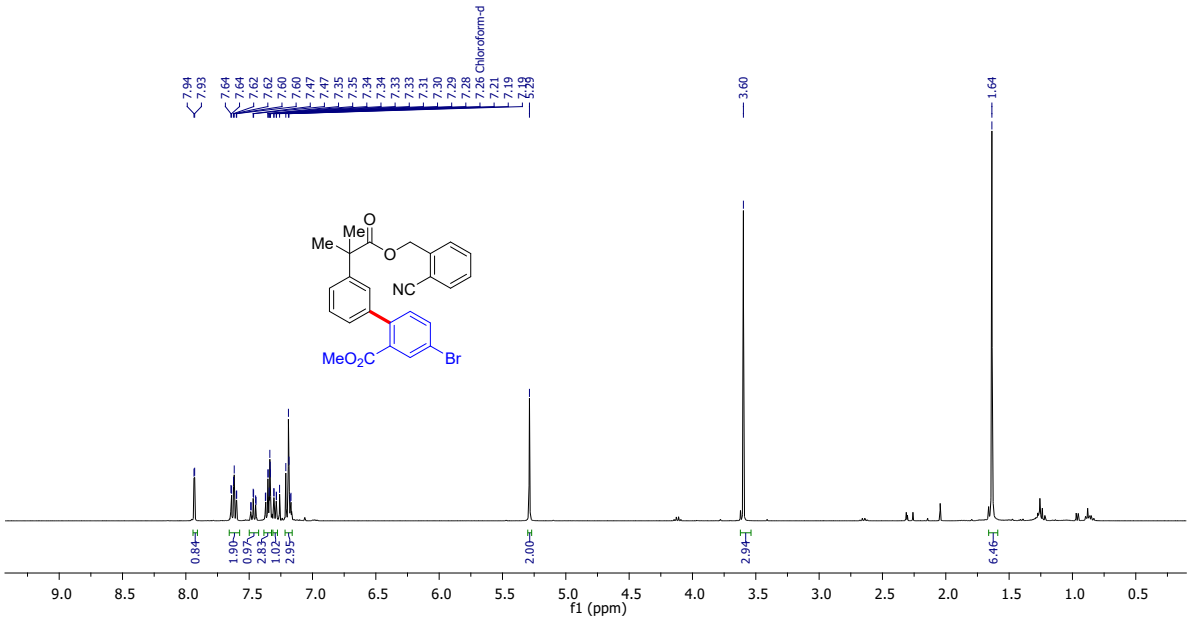
^{13}C NMR (100 MHz) spectrum of **3ae** in $CDCl_3$



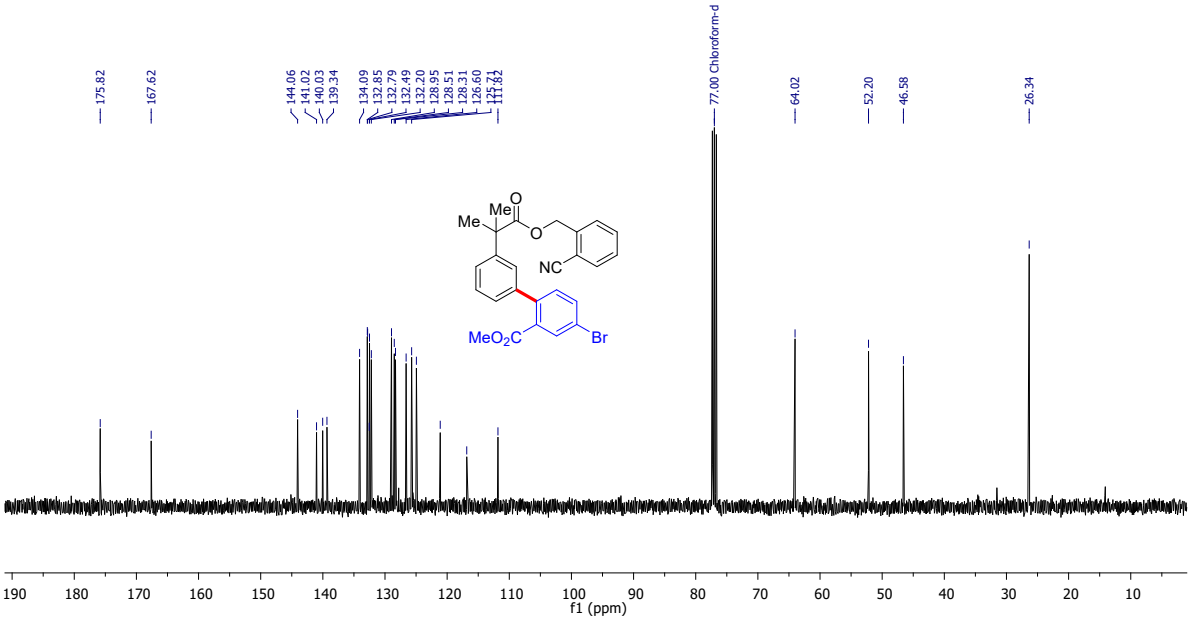
^{1}H NMR (400 MHz) spectrum of **3af** in $CDCl_3$



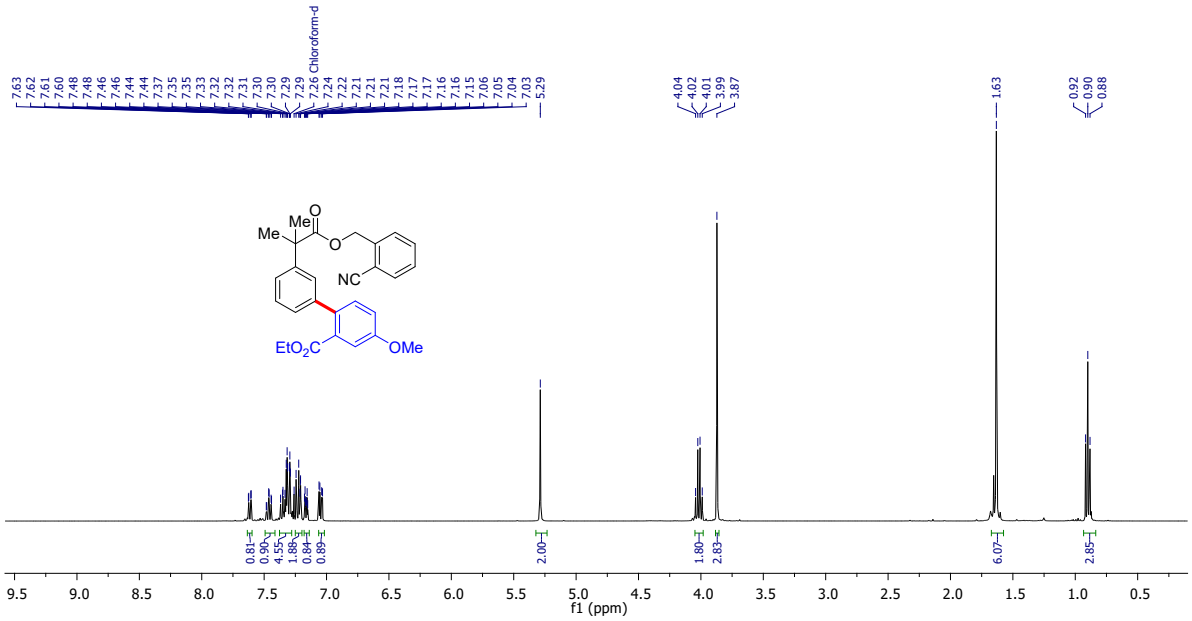
^{13}C NMR (100 MHz) spectrum of **3af** in $CDCl_3$



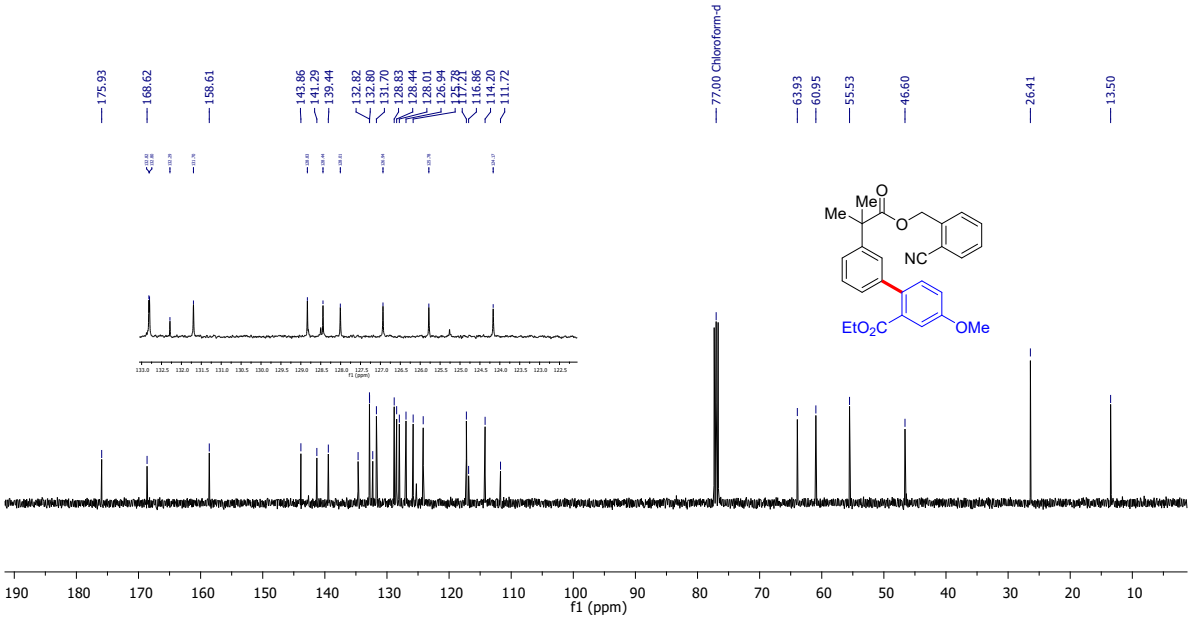
^{1}H NMR (400 MHz) spectrum of **3ag** in $CDCl_3$



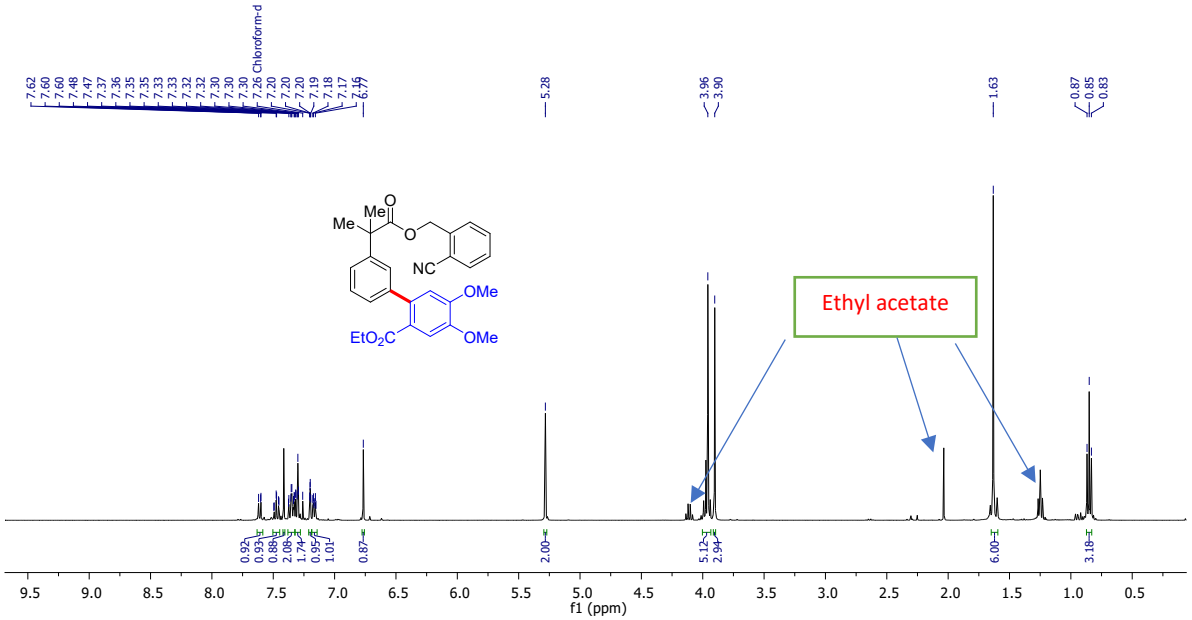
^{13}C NMR (100 MHz) spectrum of **3ag** in $CDCl_3$



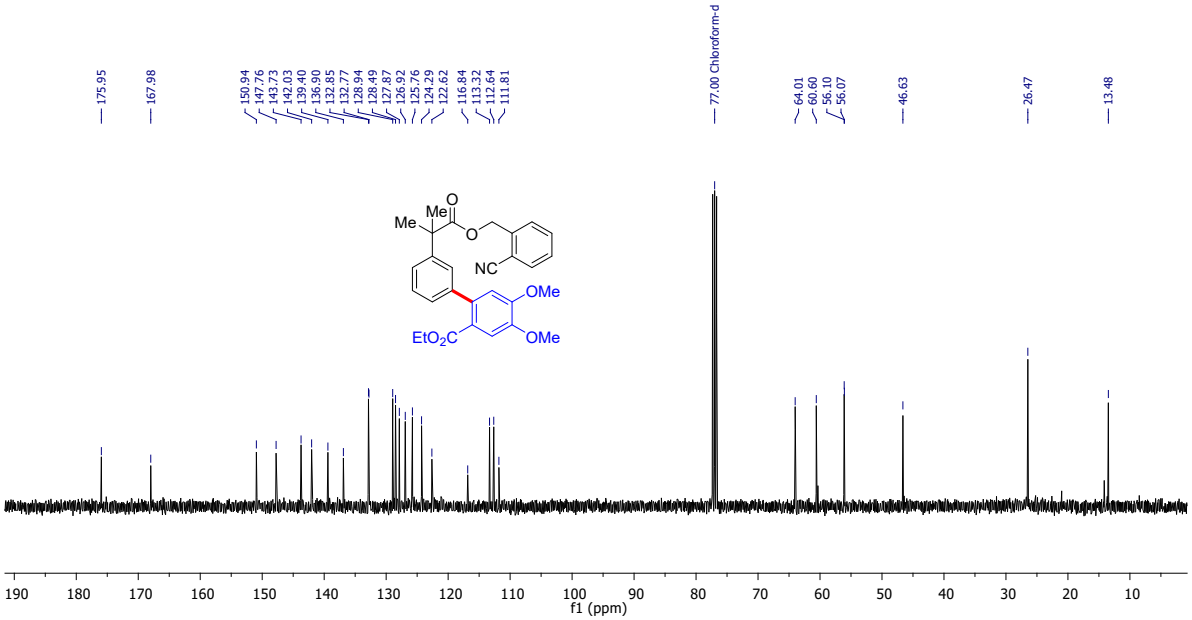
^{1}H NMR (400 MHz) spectrum of **3ah** in $CDCl_3$



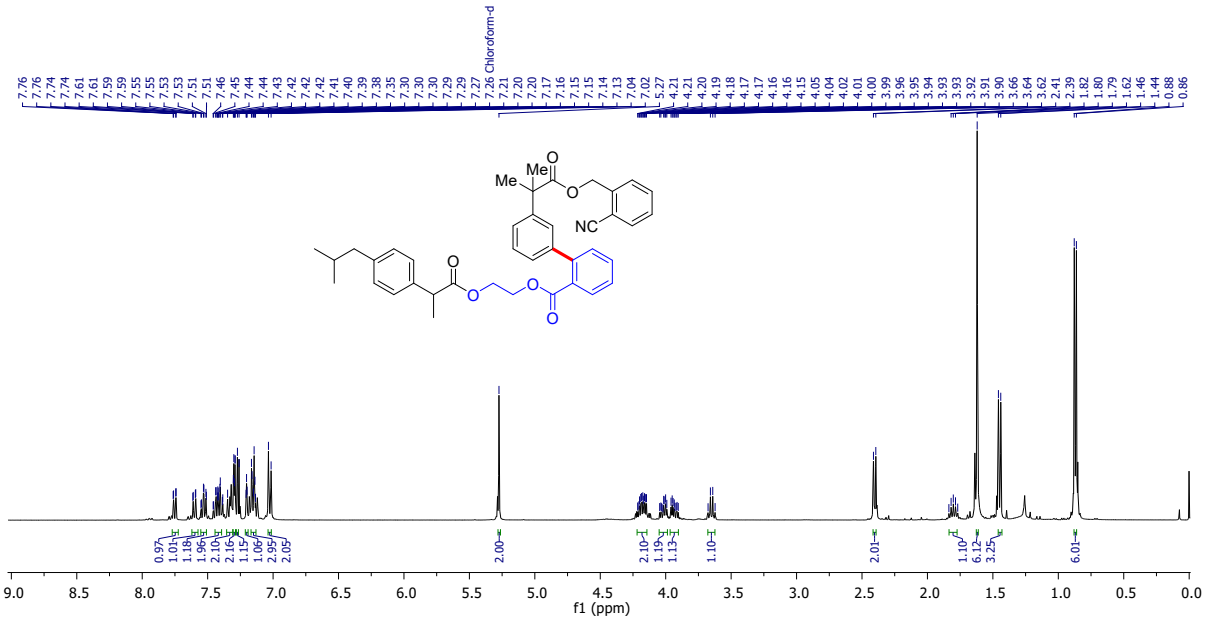
^{13}C NMR (100 MHz) spectrum of **3ah** in $CDCl_3$



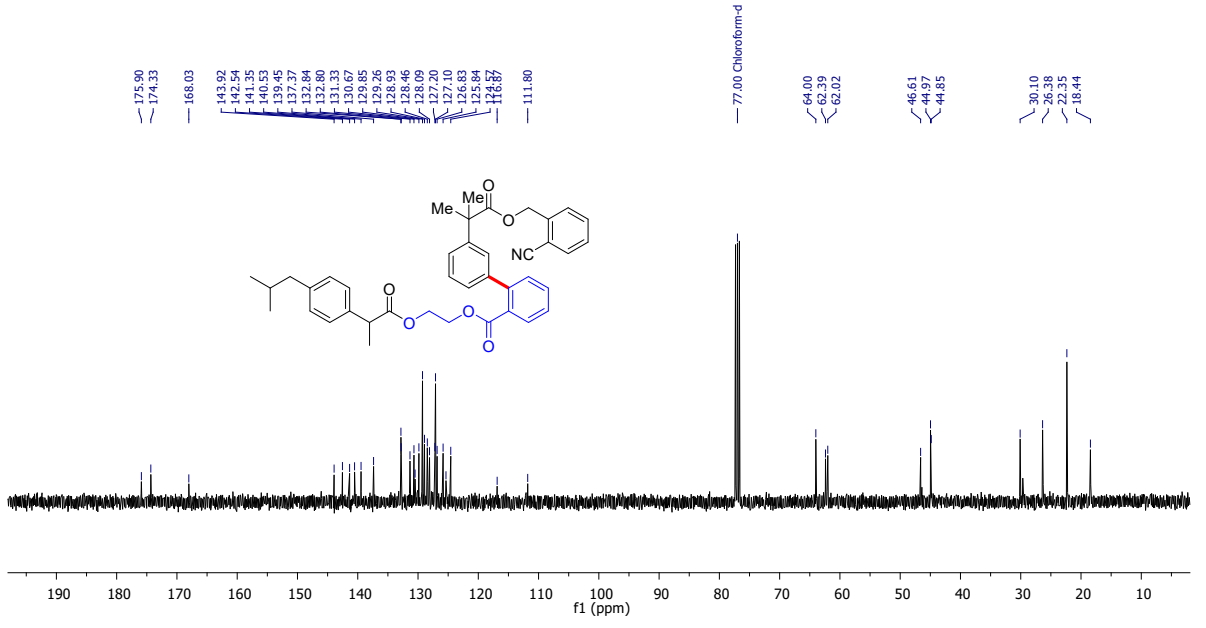
^{1}H NMR (400 MHz) spectrum of **3ai** in $CDCl_3$



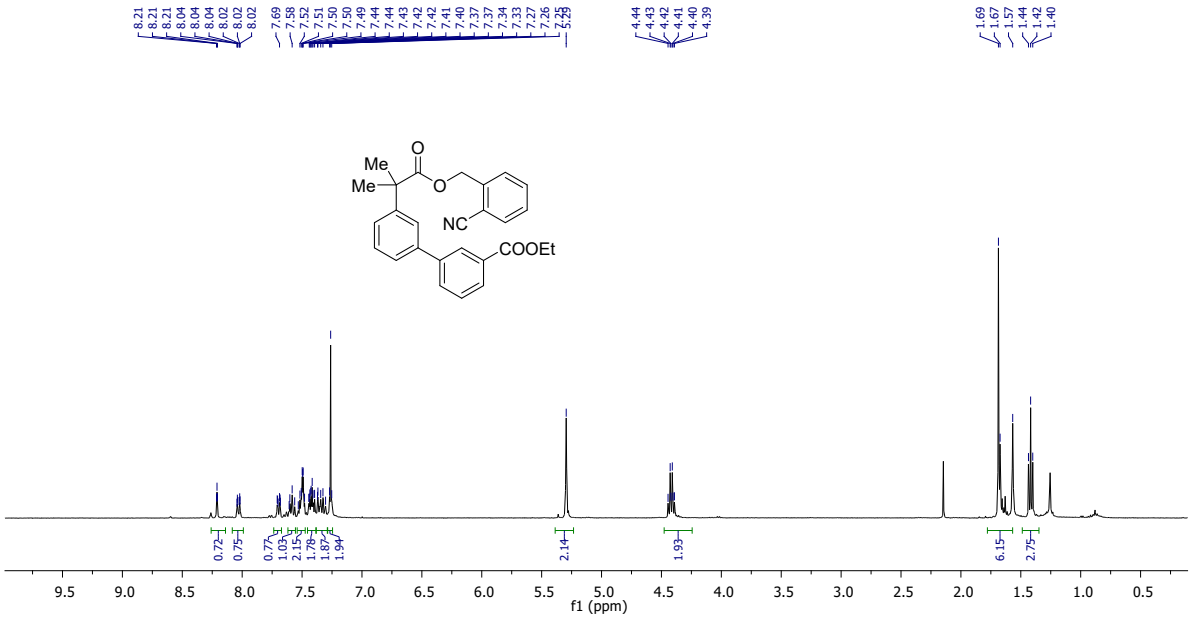
^{13}C NMR (100 MHz) spectrum of **3ai** in $CDCl_3$



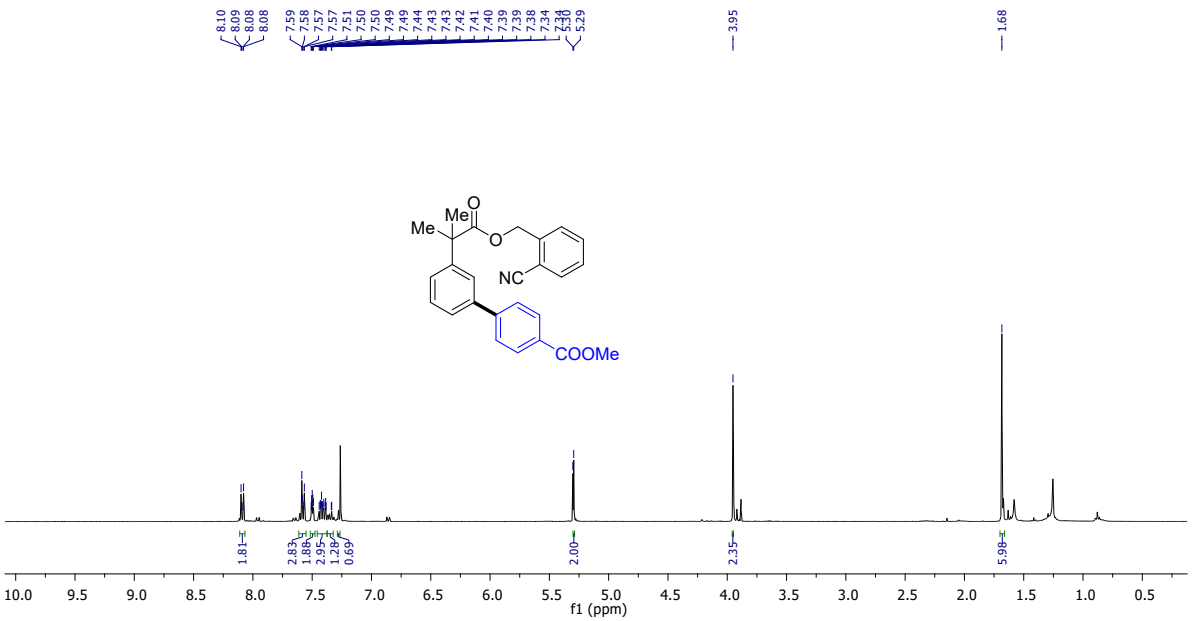
^{1}H NMR (400 MHz) spectrum of **3aj** in $CDCl_3$



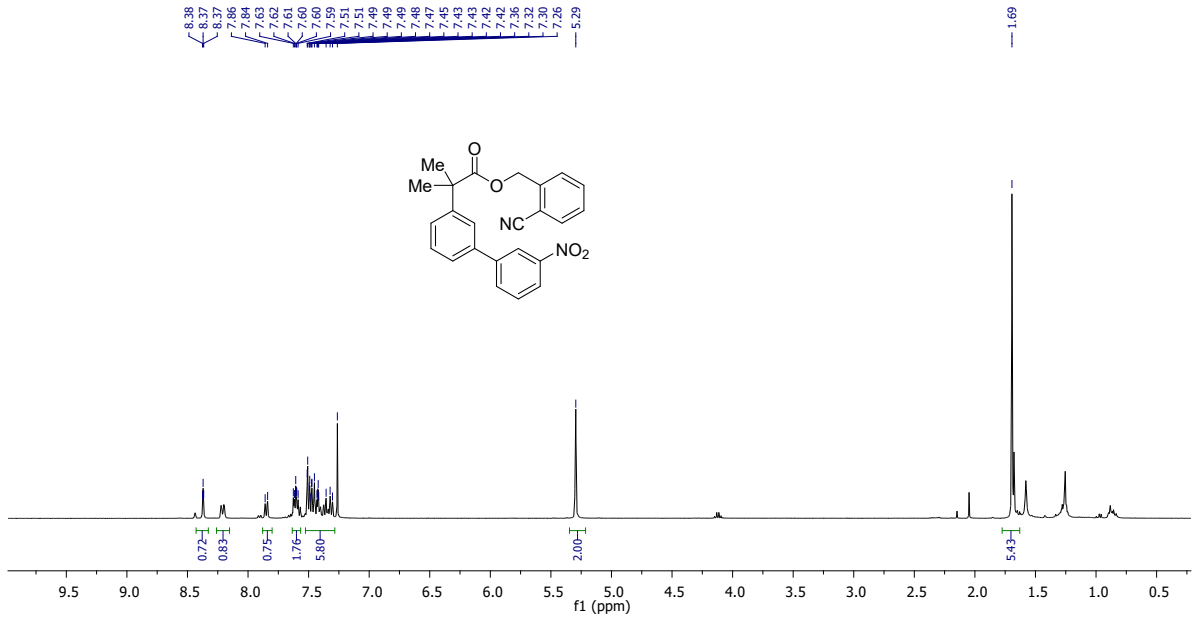
^{13}C NMR (100 MHz) spectrum of **3aj** in $CDCl_3$



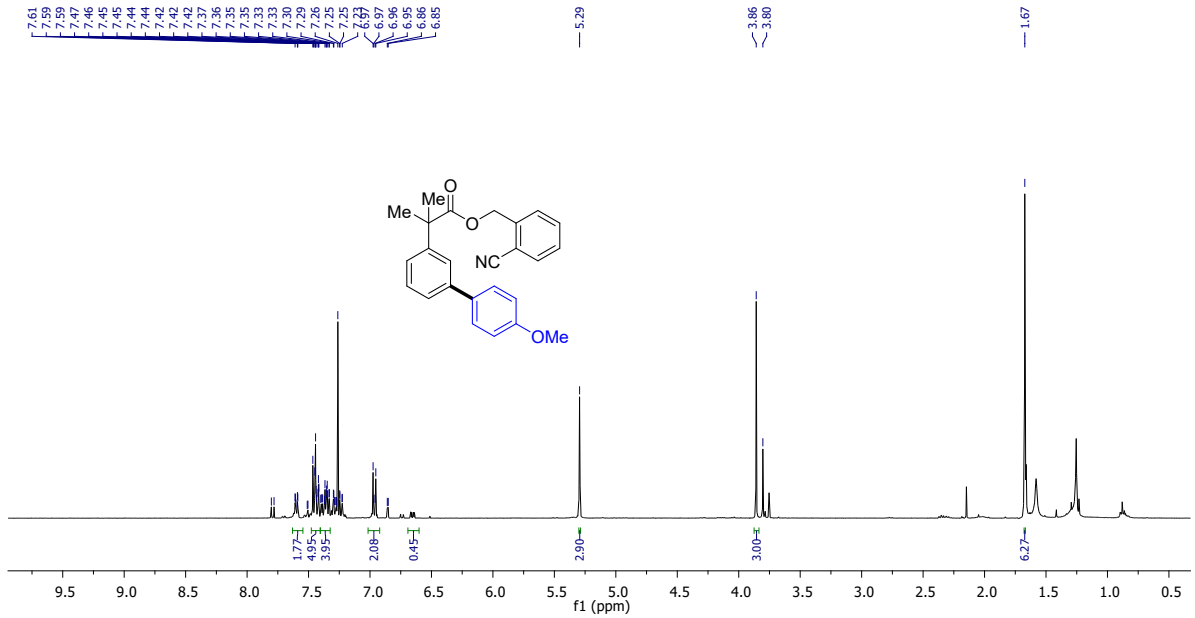
^{1}H NMR (400 MHz) spectrum of **3ak** in $CDCl_3$



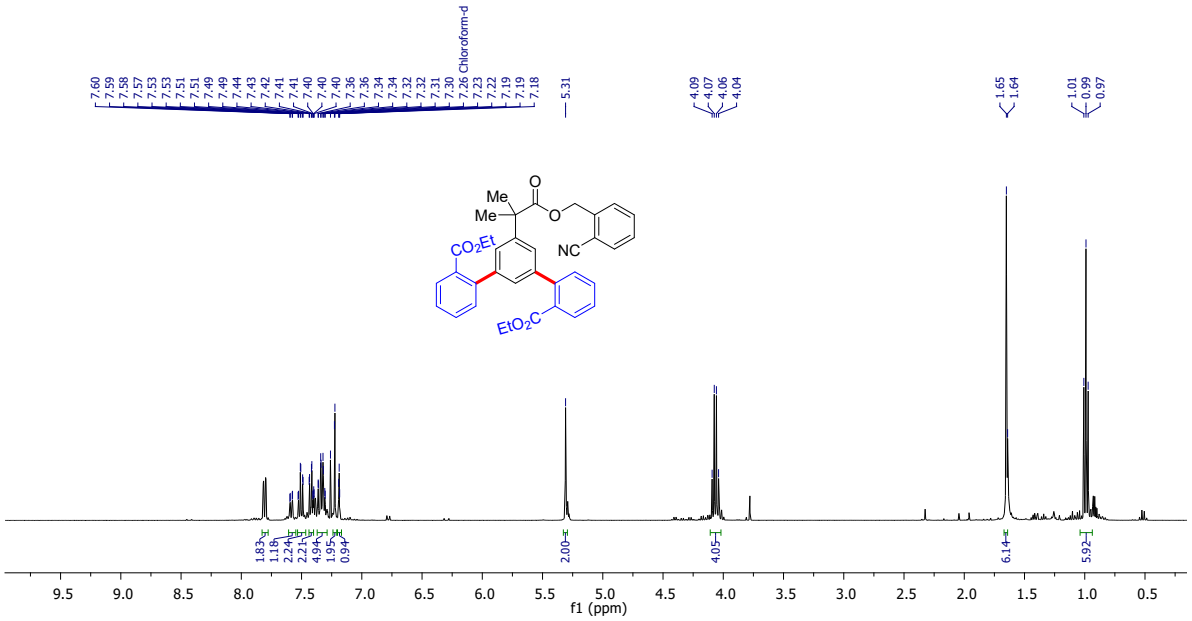
^{1}H NMR (400 MHz) spectrum of **3al** in $CDCl_3$



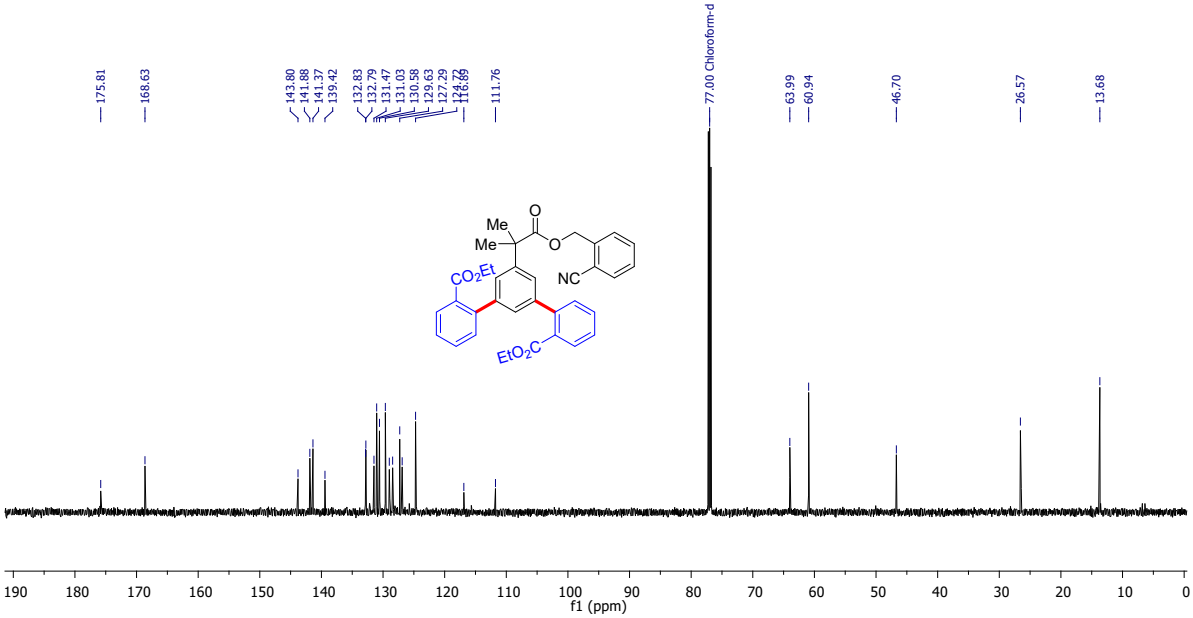
^{1}H NMR (400 MHz) spectrum of **3am** in $CDCl_3$



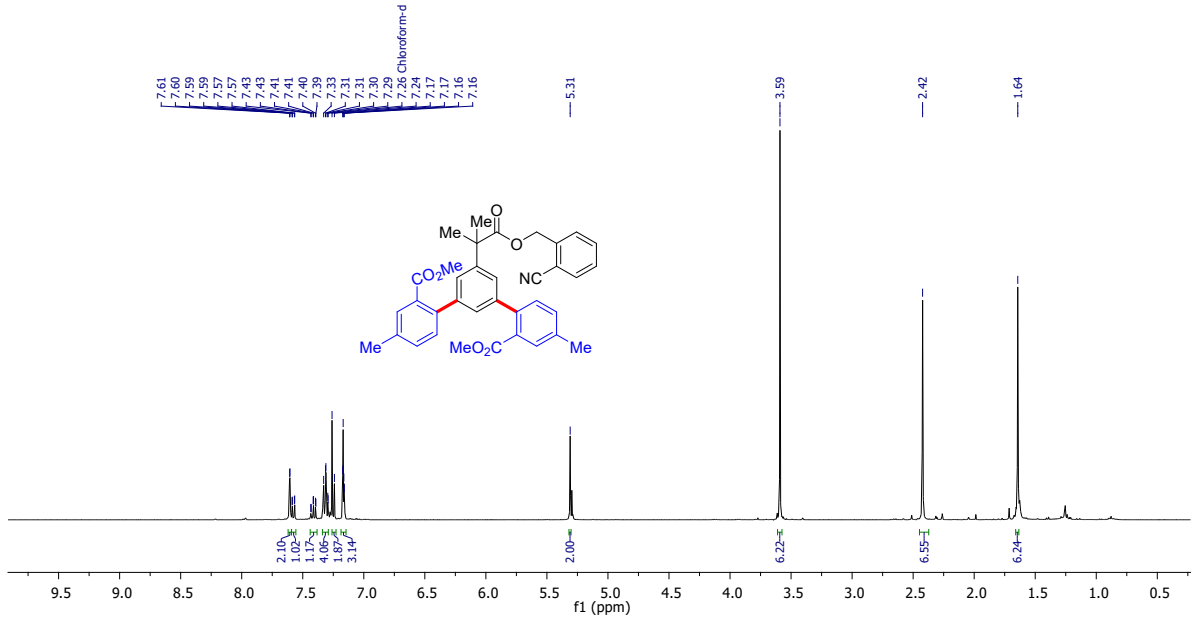
^{1}H NMR (400 MHz) spectrum of **3an** in $CDCl_3$



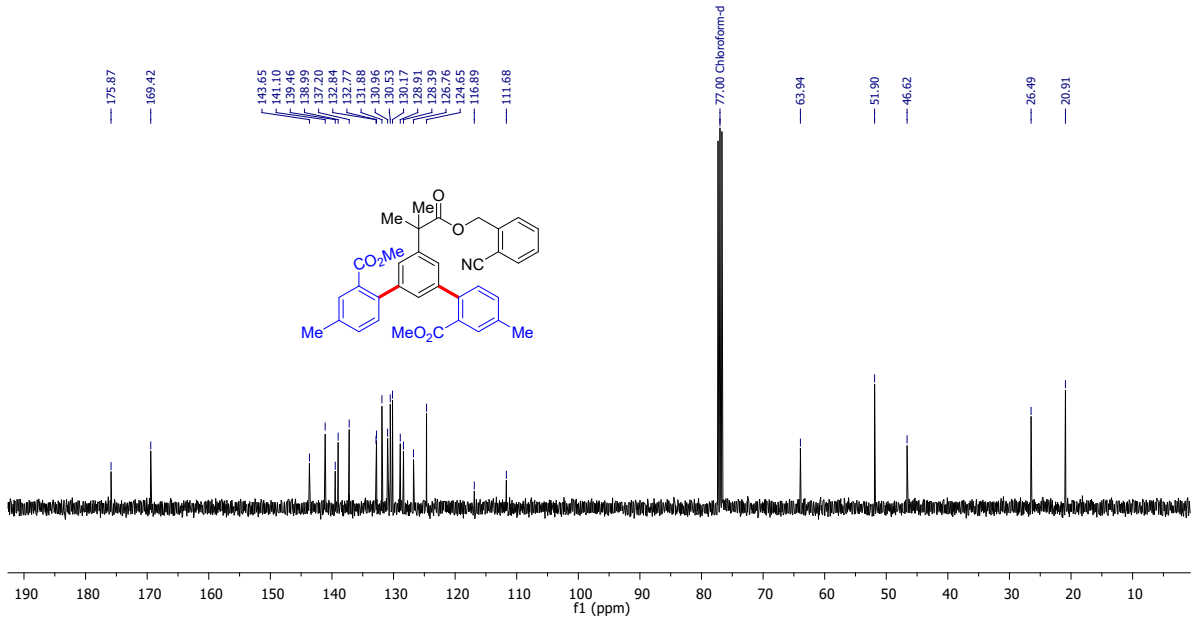
^{1}H NMR (400 MHz) spectrum of **4a** in $CDCl_3$



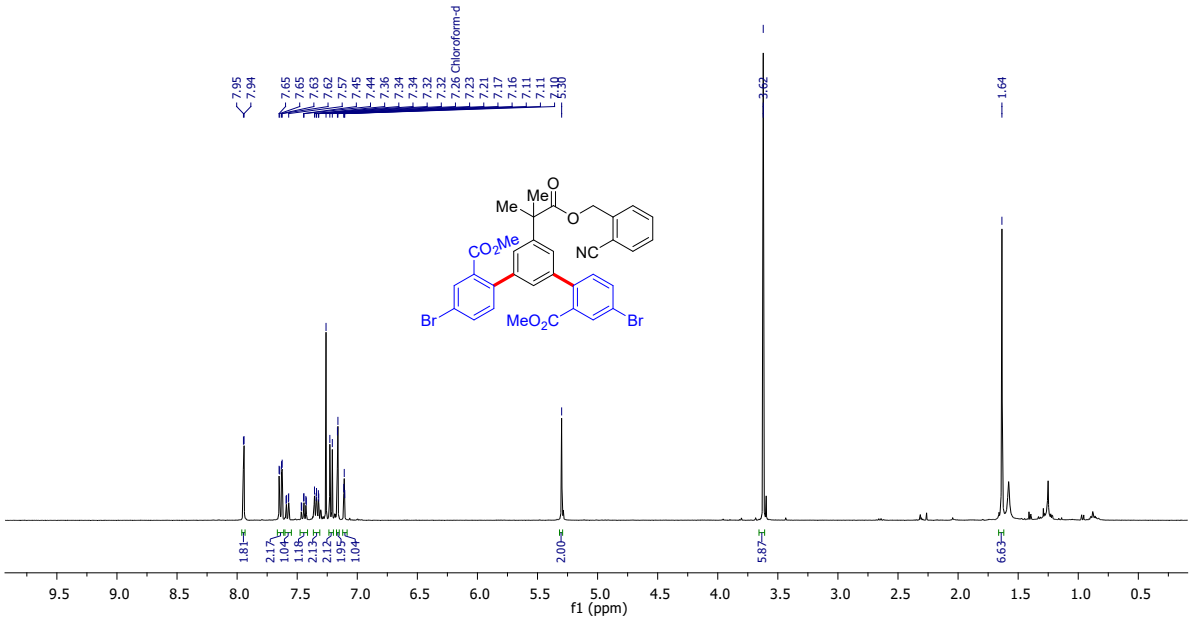
^{13}C NMR (151 MHz) spectrum of **4a** in $CDCl_3$



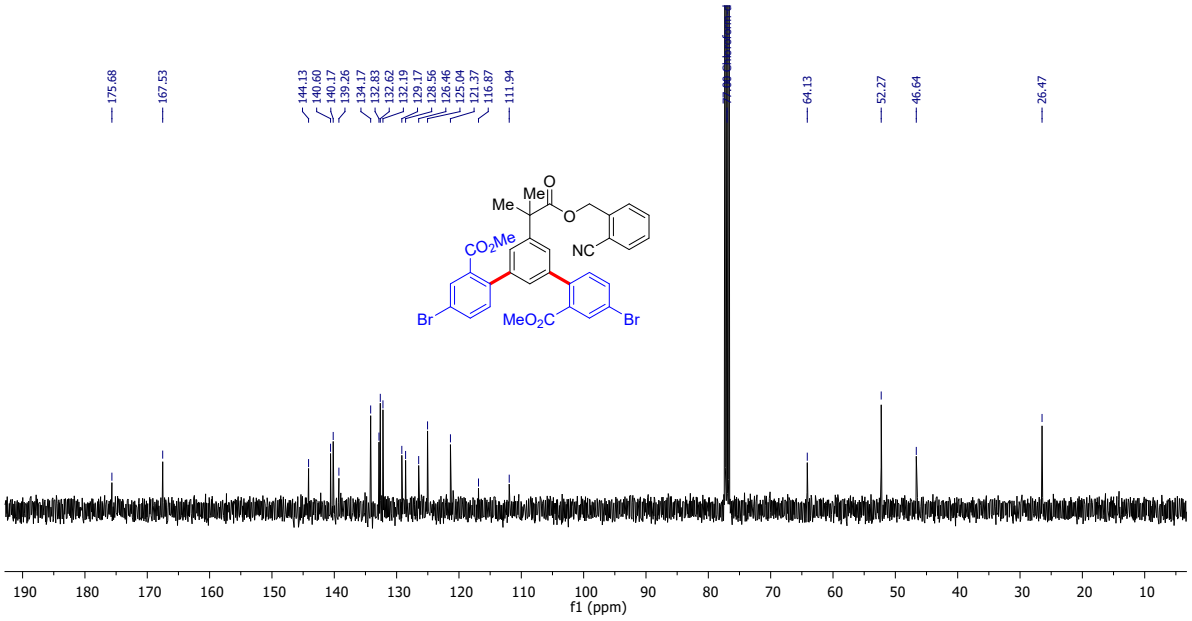
^{1}H NMR (400 MHz) spectrum of **4b** in $CDCl_3$



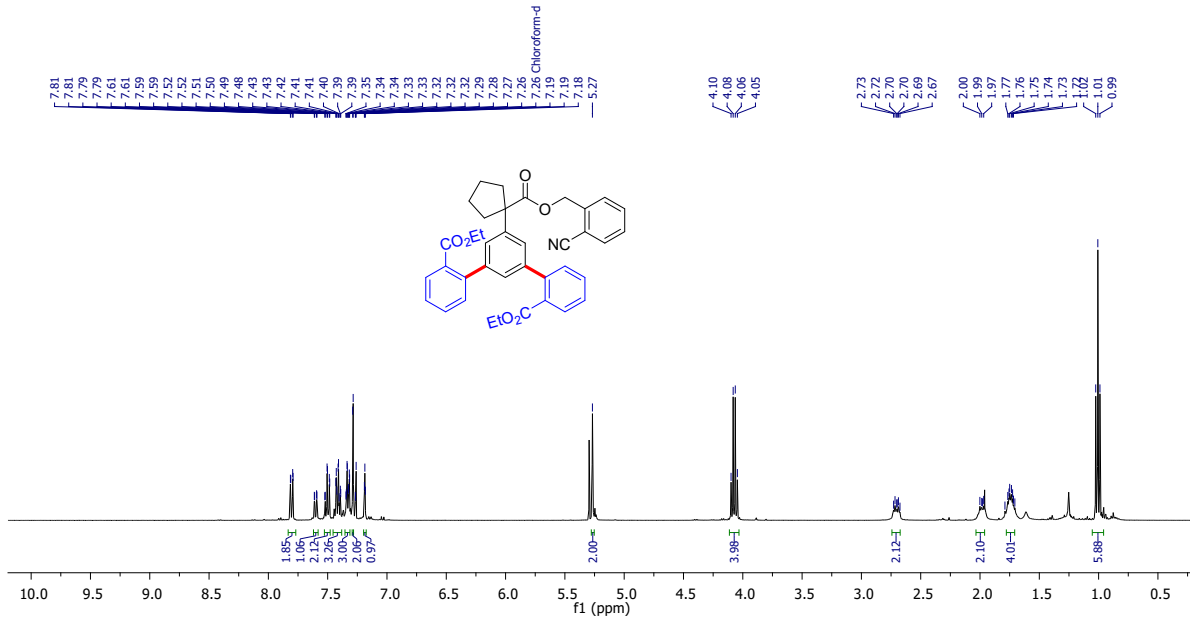
^{13}C NMR (100 MHz) spectrum of **4b** in $CDCl_3$



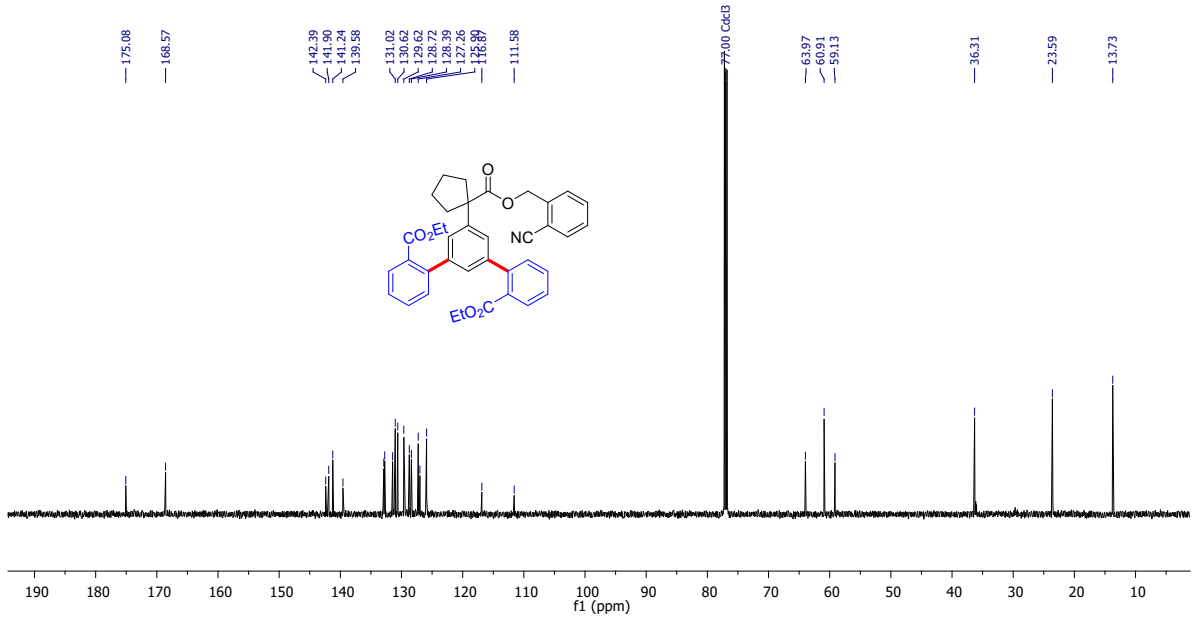
^{1}H NMR (400 MHz) spectrum of **4c** in $CDCl_3$



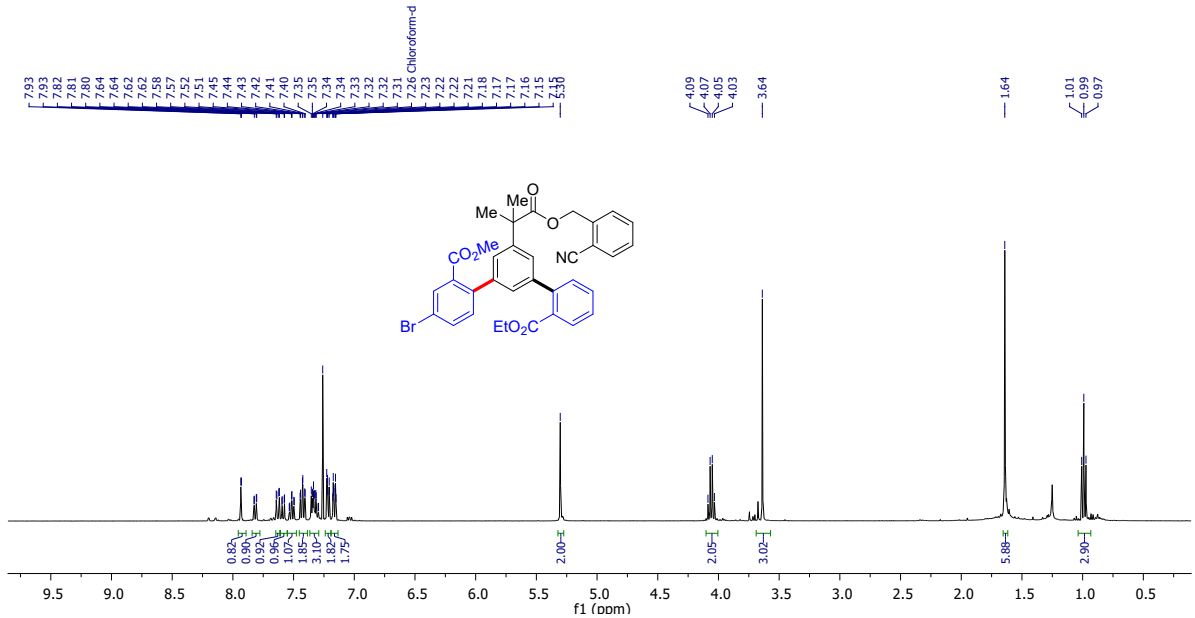
^{13}C NMR (100 MHz) spectrum of **4c** in $CDCl_3$



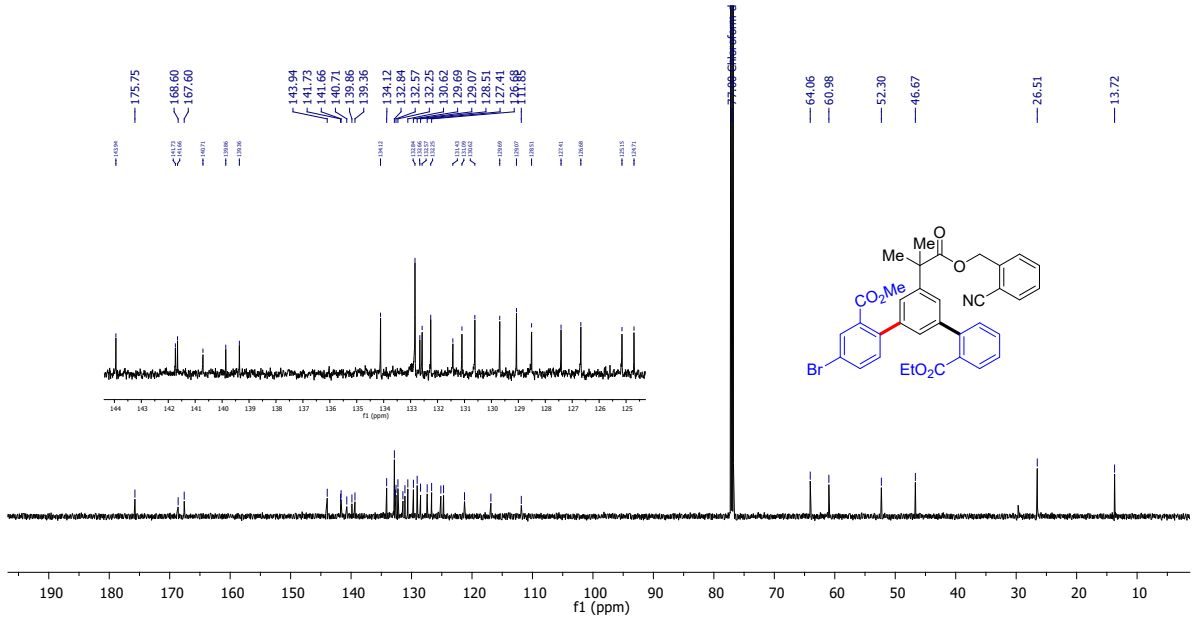
^{1}H NMR (400 MHz) spectrum of **4d** in $CDCl_3$



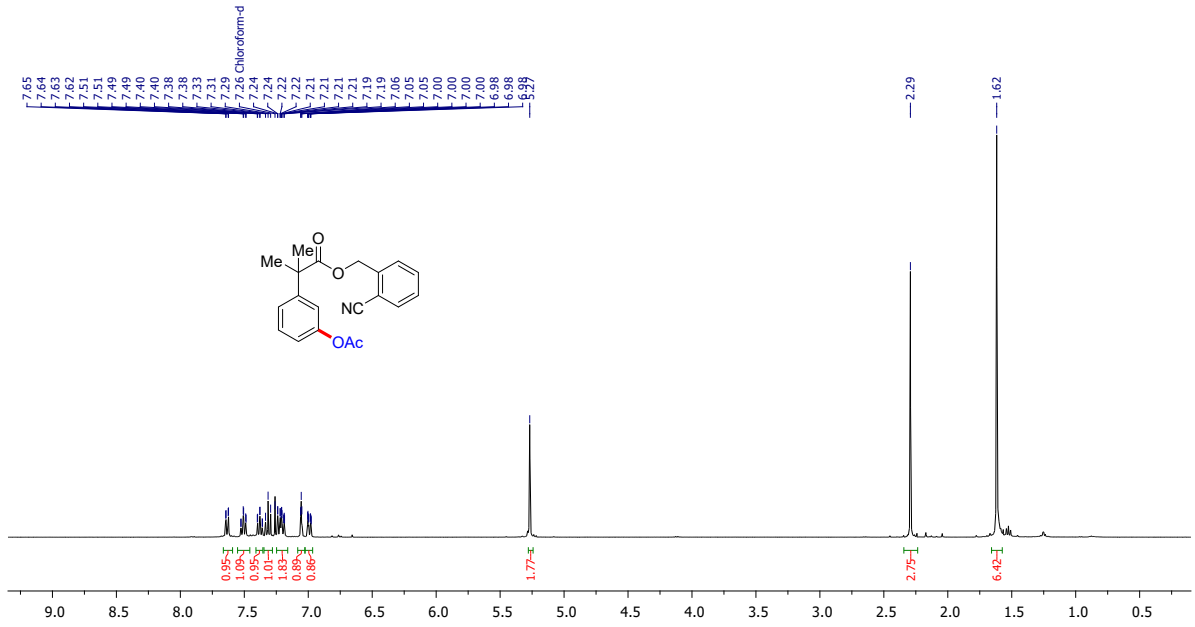
^{13}C NMR (151 MHz) spectrum of **4d** in $CDCl_3$



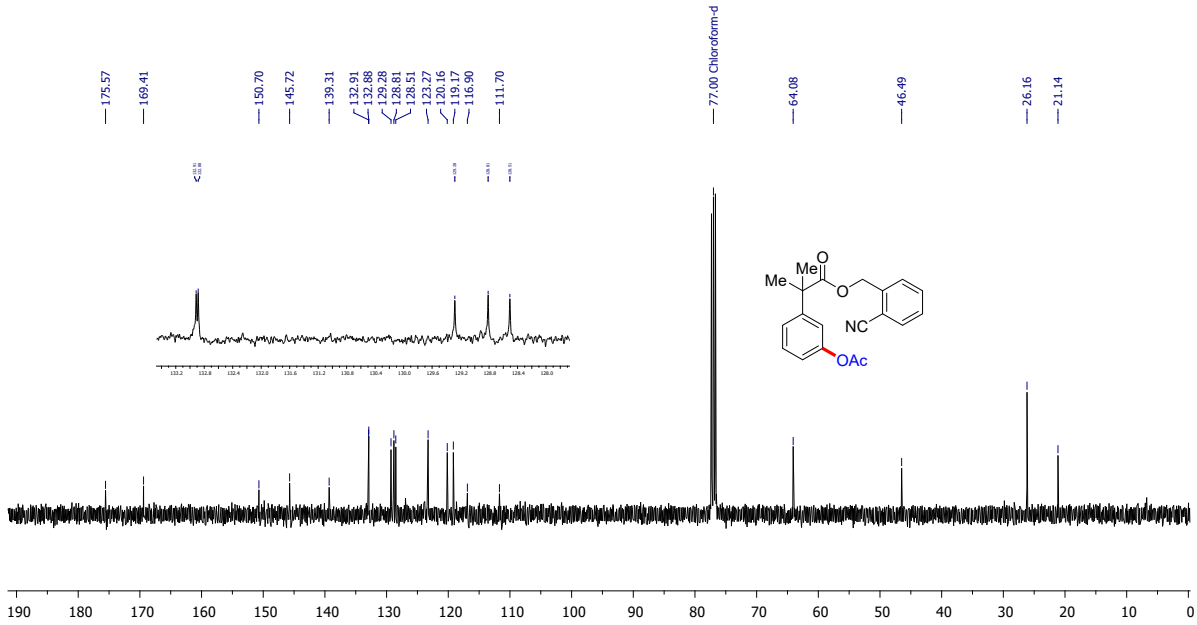
^{1}H NMR (400 MHz) spectrum of **4e** in $CDCl_3$



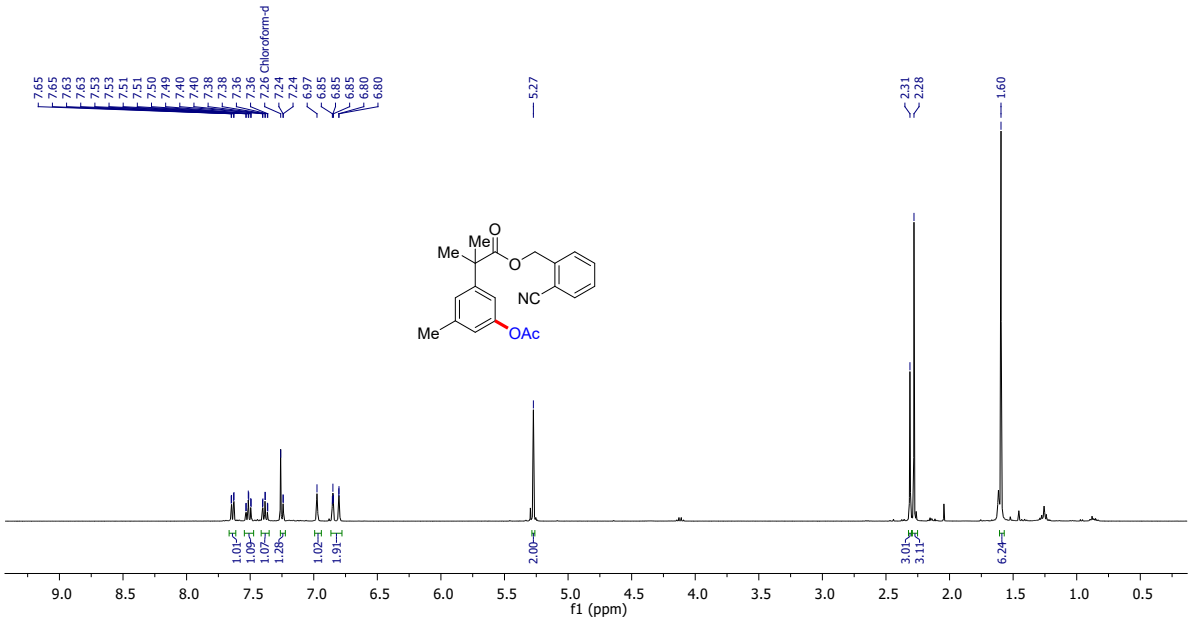
^{13}C NMR (151 MHz) spectrum of **4e** in $CDCl_3$



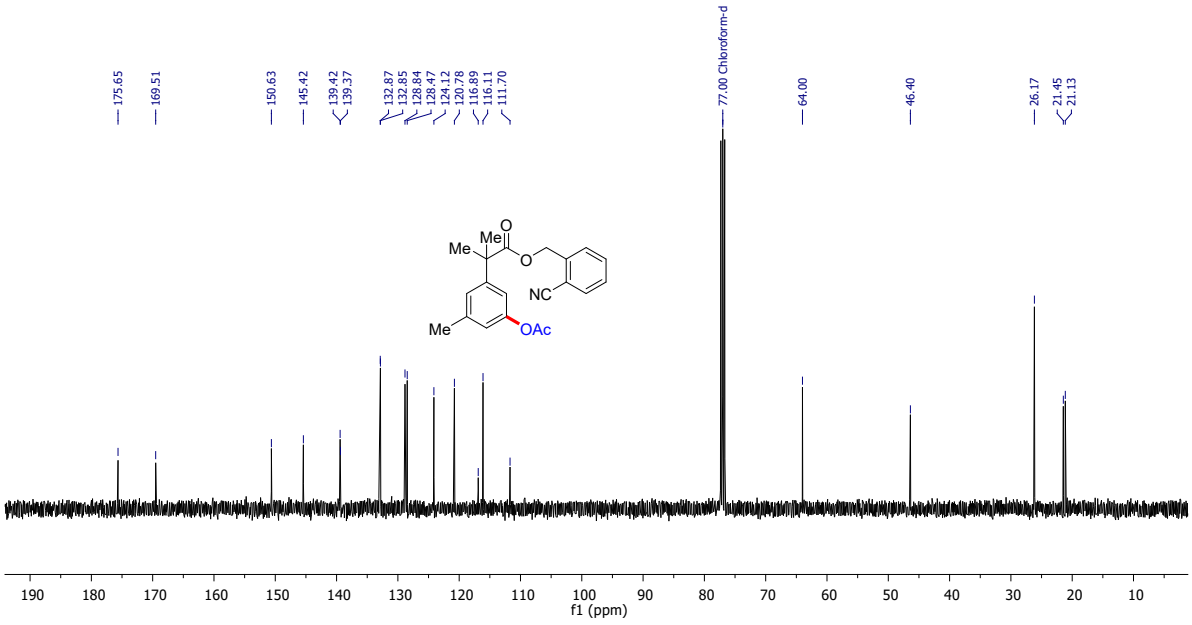
^{1}H NMR (400 MHz) spectrum of **5a** in $CDCl_3$



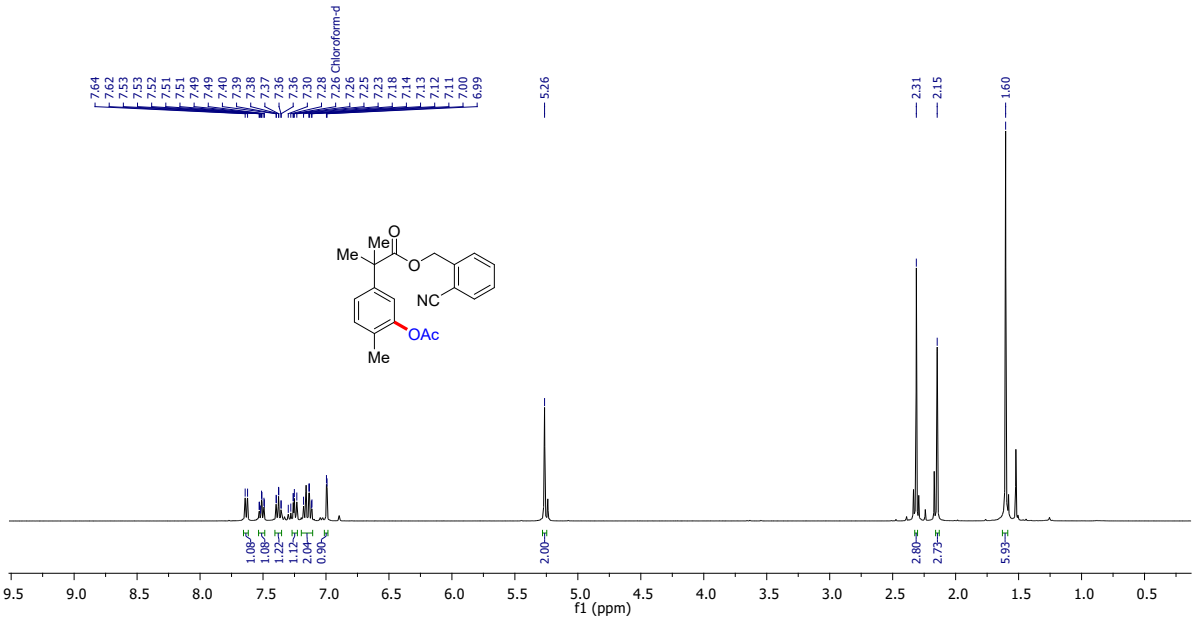
^{13}C NMR (100 MHz) spectrum of **5a** in $CDCl_3$



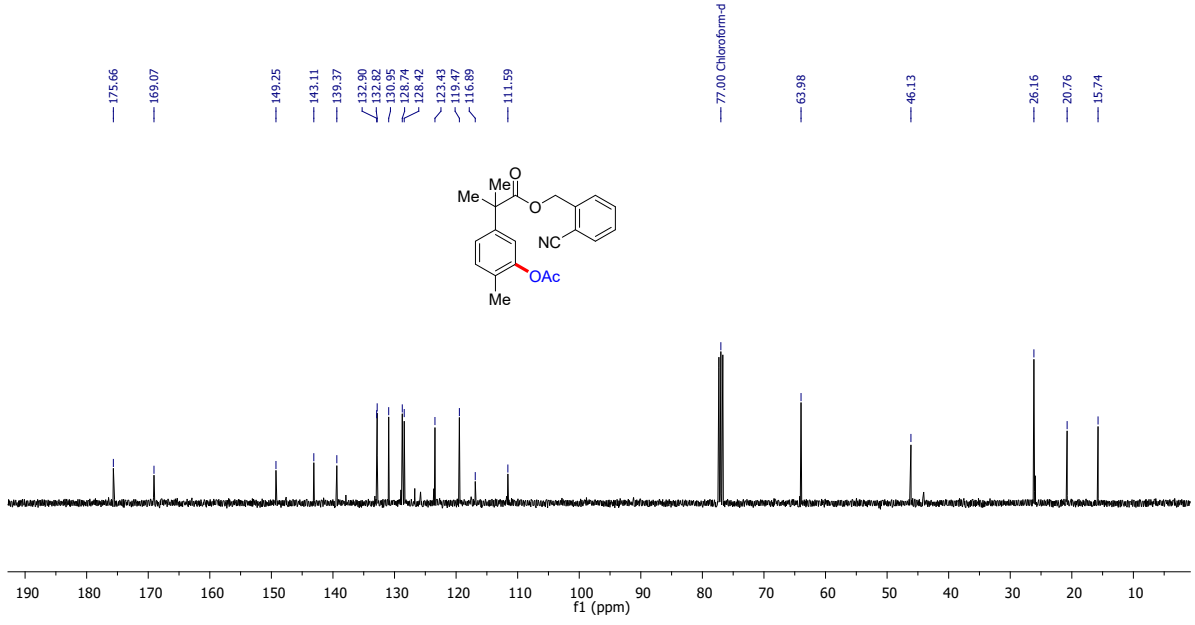
^{1}H NMR (400 MHz) spectrum of **5b** in $CDCl_3$



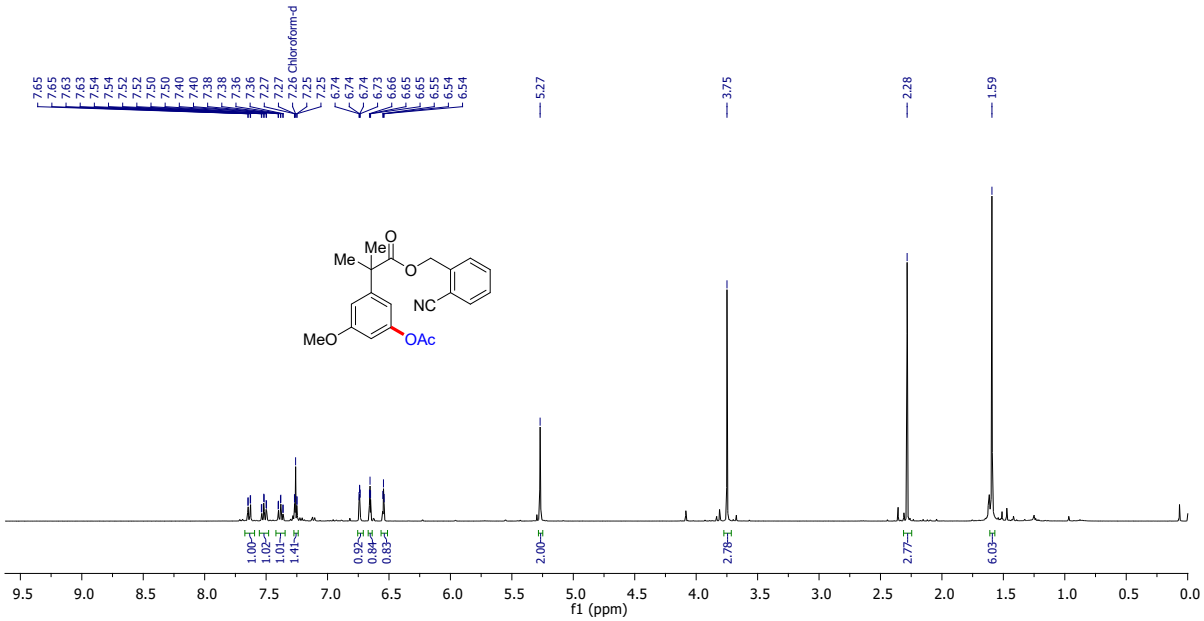
^{13}C NMR (100 MHz) spectrum of **5b** in $CDCl_3$



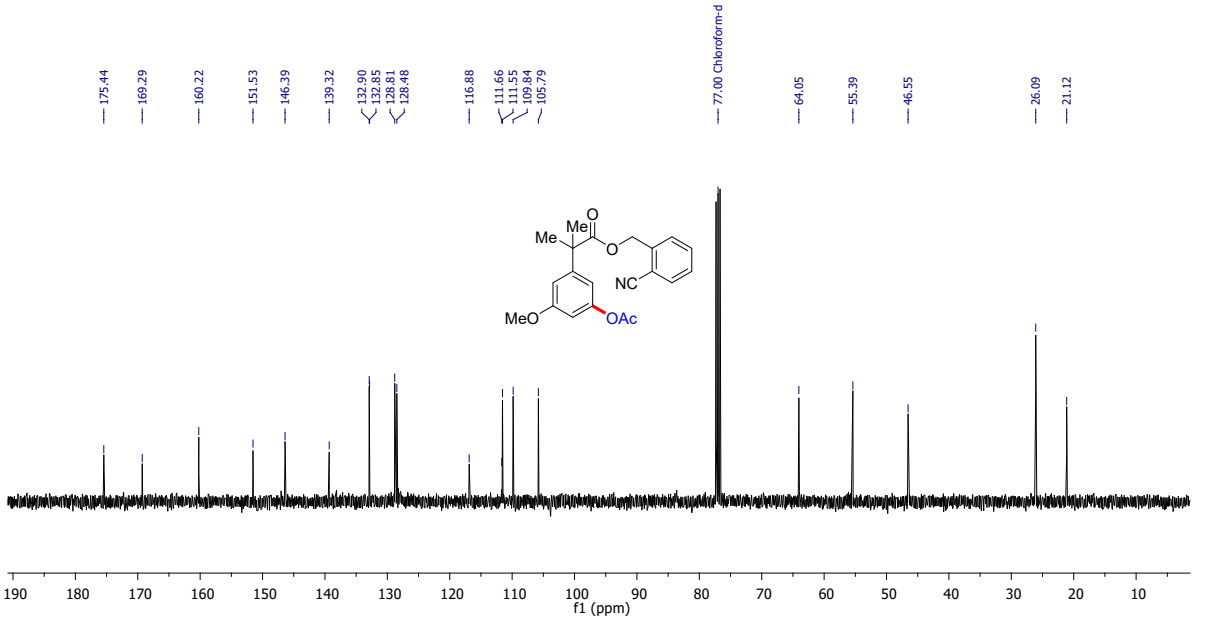
^{1}H NMR (400 MHz) spectrum of **5c** in $CDCl_3$



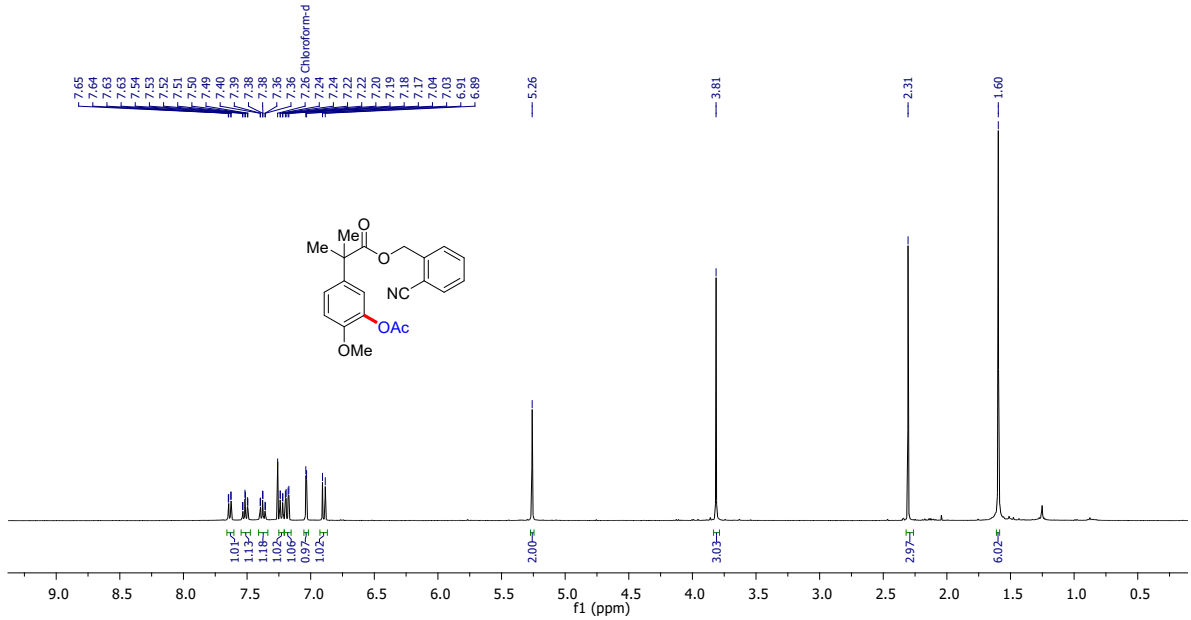
^{13}C NMR (100 MHz) spectrum of **5c** in $CDCl_3$



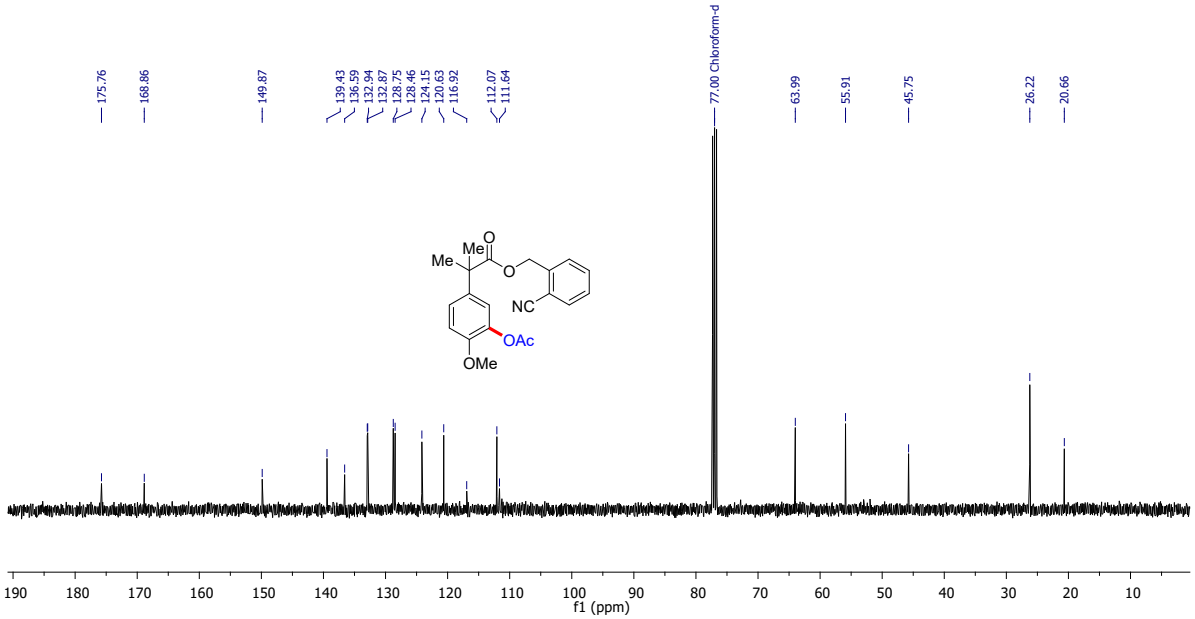
^{1}H NMR (400 MHz) spectrum of **5d** in $CDCl_3$



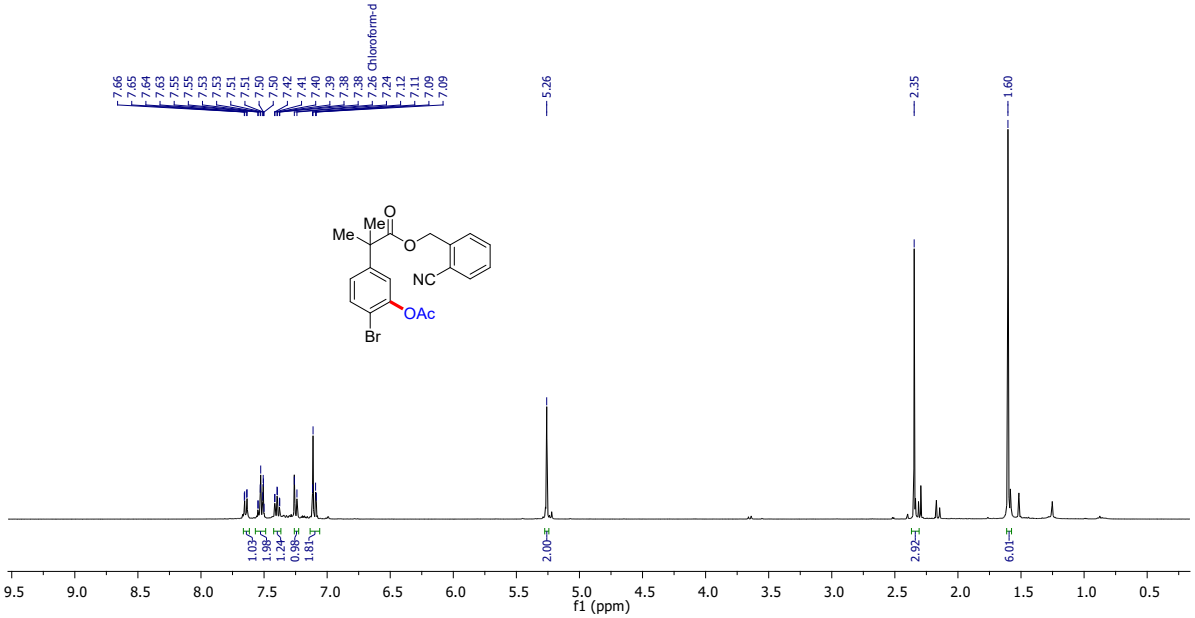
^{13}C NMR (100 MHz) spectrum of **5d** in $CDCl_3$



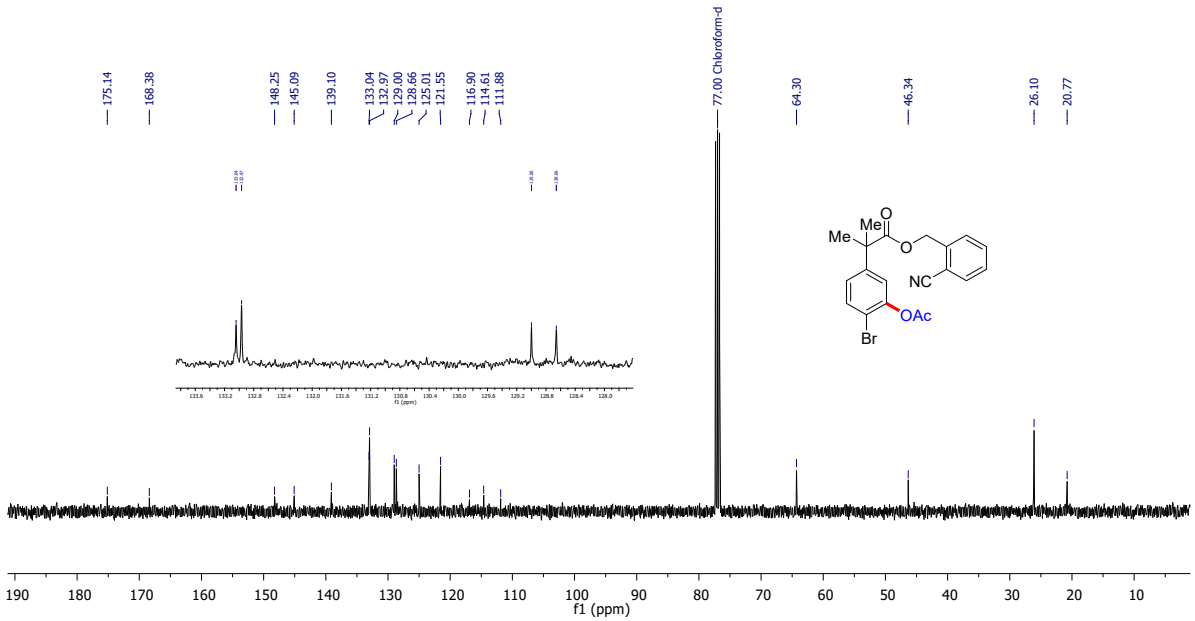
^{1}H NMR (400 MHz) spectrum of **5e** in $CDCl_3$



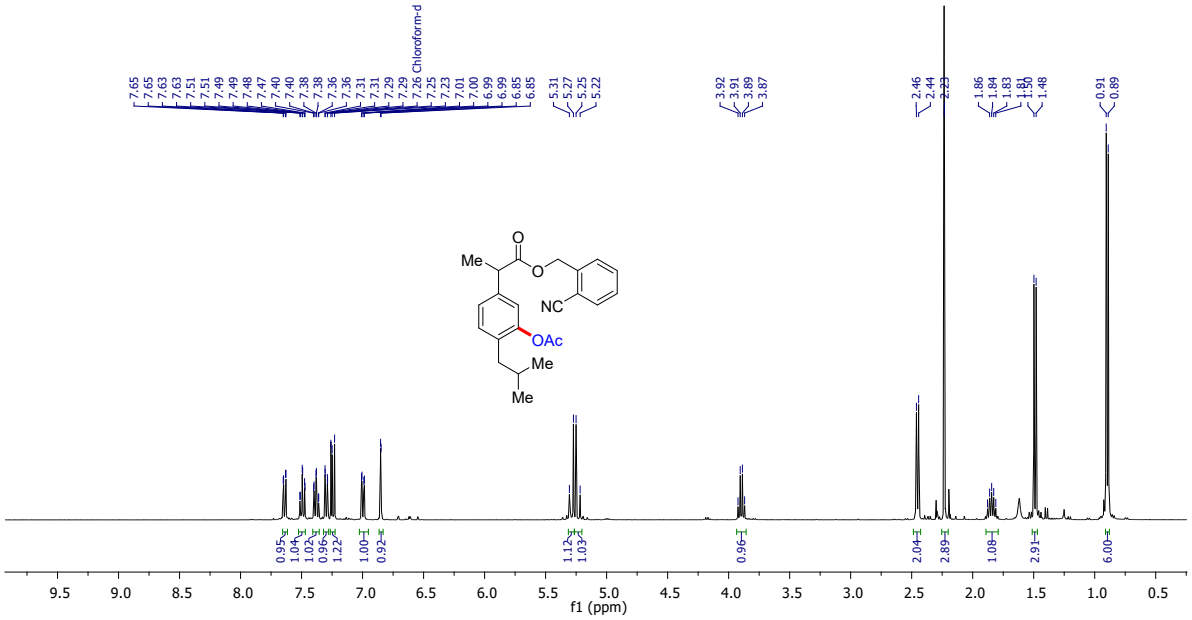
^{13}C NMR (100 MHz) spectrum of **5e** in $CDCl_3$



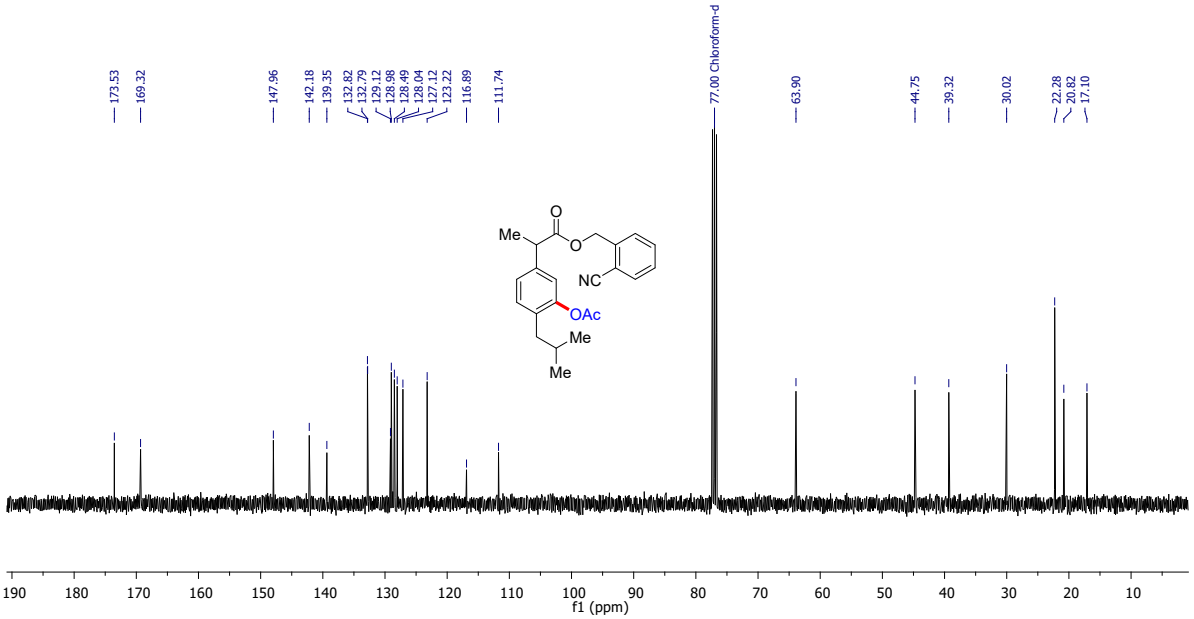
^{1}H NMR (400 MHz) spectrum of **5f** in $CDCl_3$



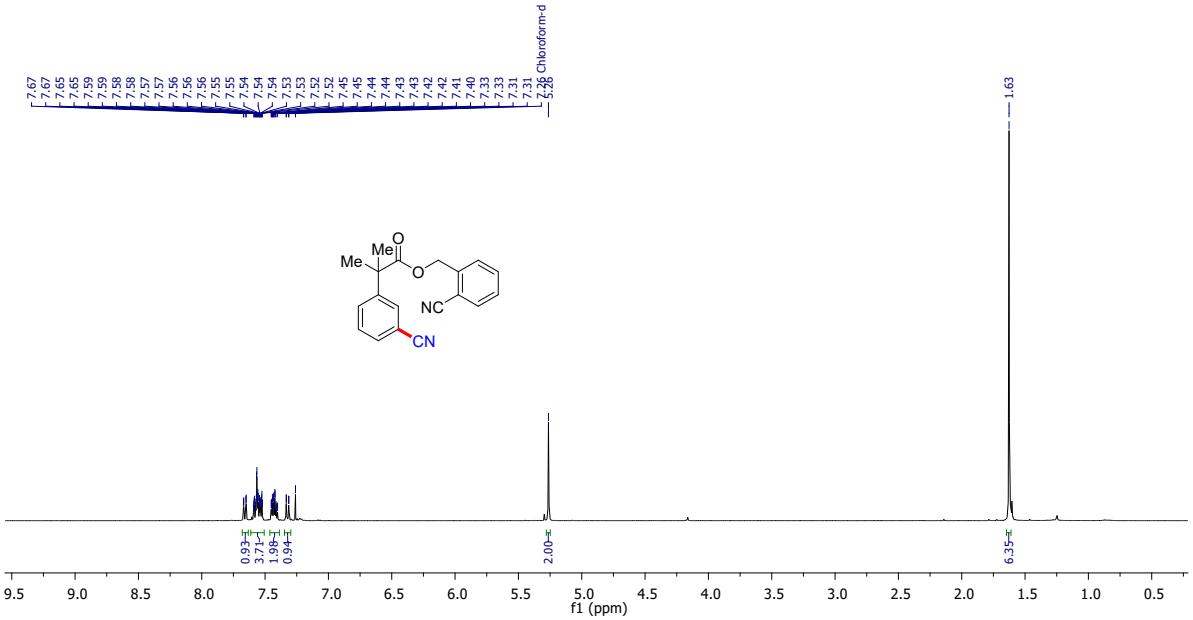
^{13}C NMR (100 MHz) spectrum of **5f** in $CDCl_3$



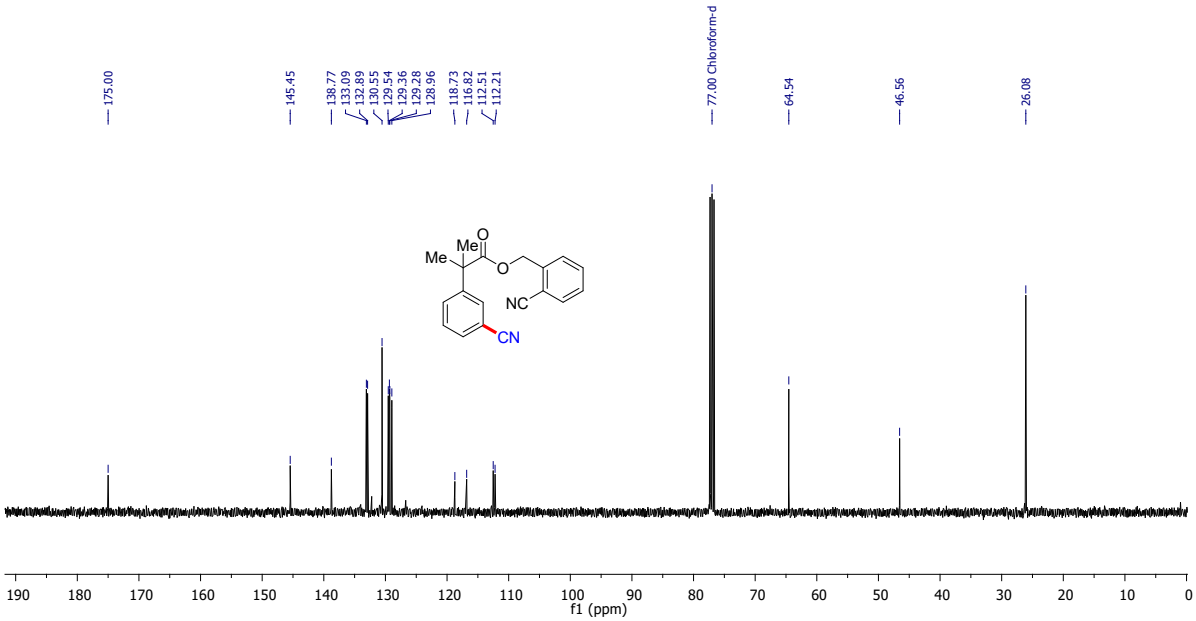
^{1}H NMR (400 MHz) spectrum of **5g** in $CDCl_3$



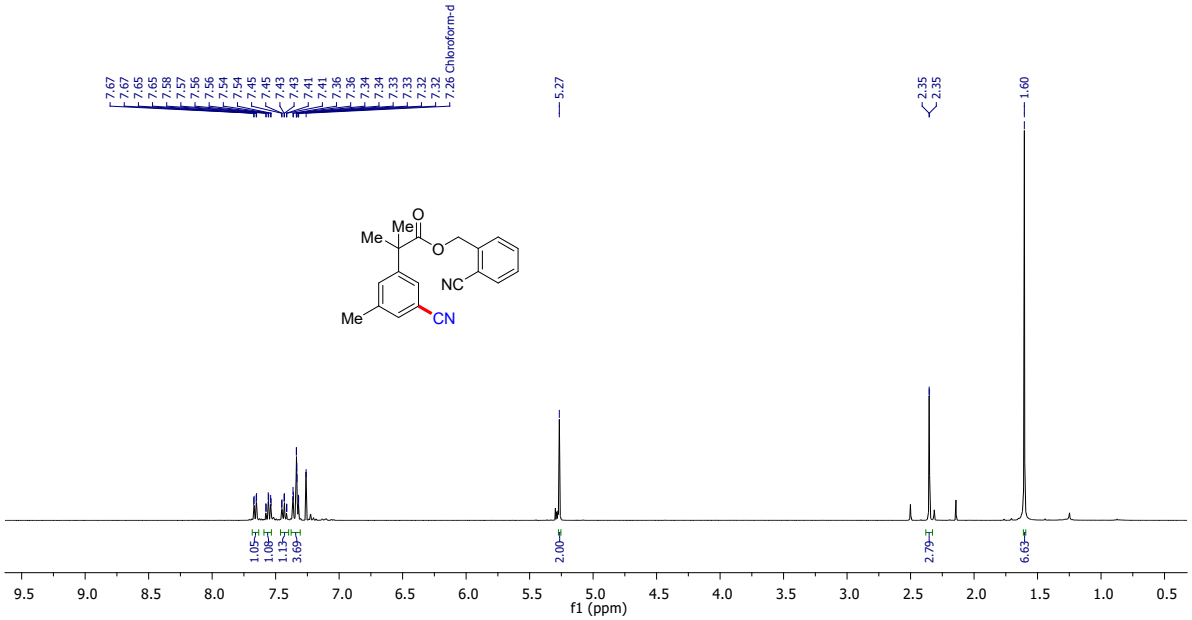
^{13}C NMR (100 MHz) spectrum of **5g** in $CDCl_3$



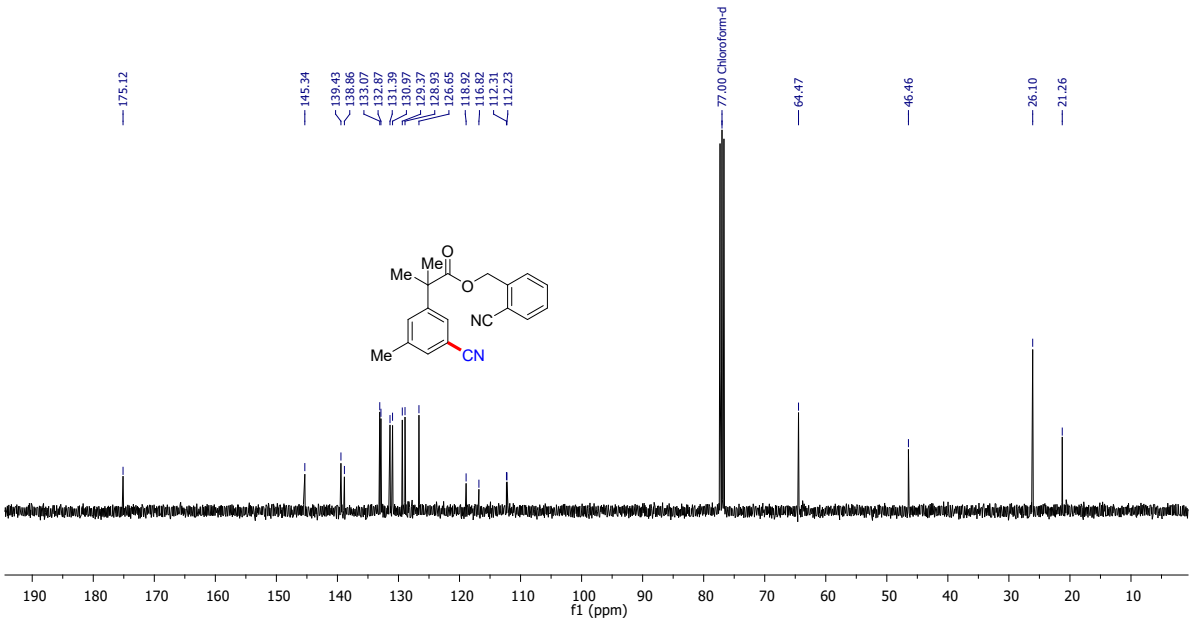
^{1}H NMR (400 MHz) spectrum of **6a** in $CDCl_3$



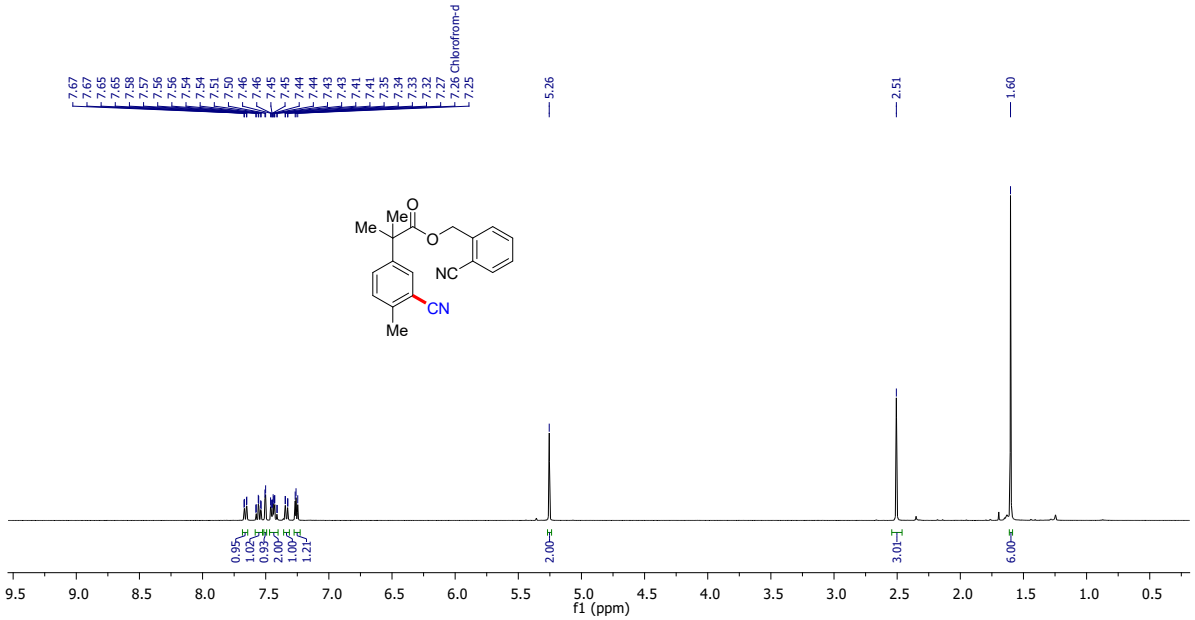
^{13}C NMR (100 MHz) spectrum of **6a** in $CDCl_3$



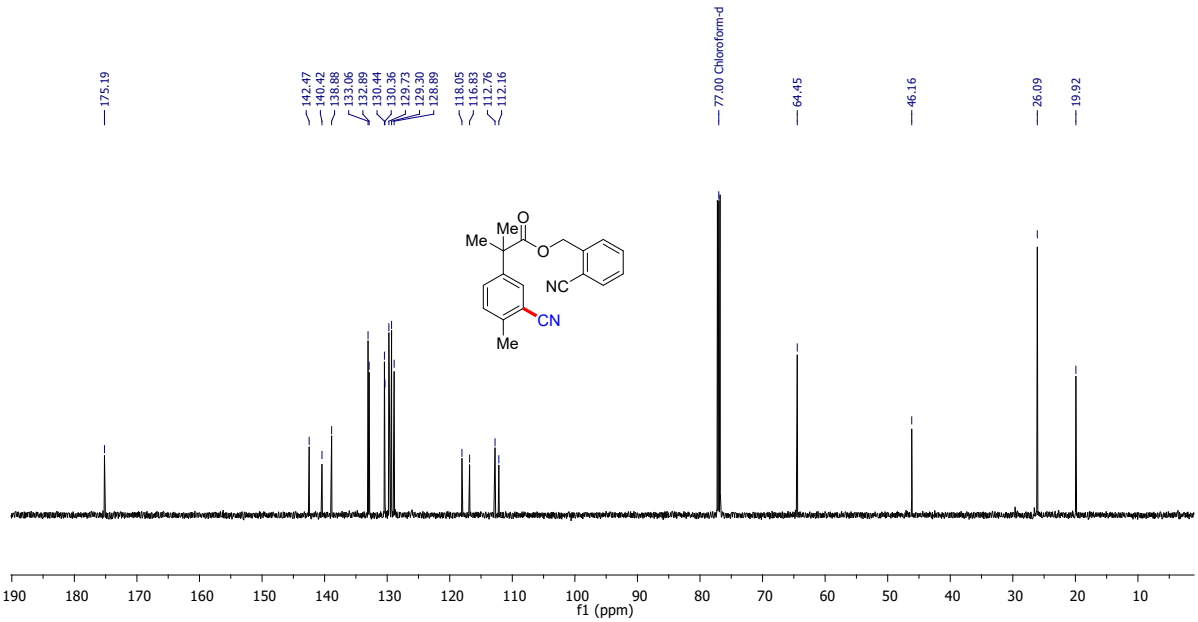
^{1}H NMR (400 MHz) spectrum of **6b** in $CDCl_3$



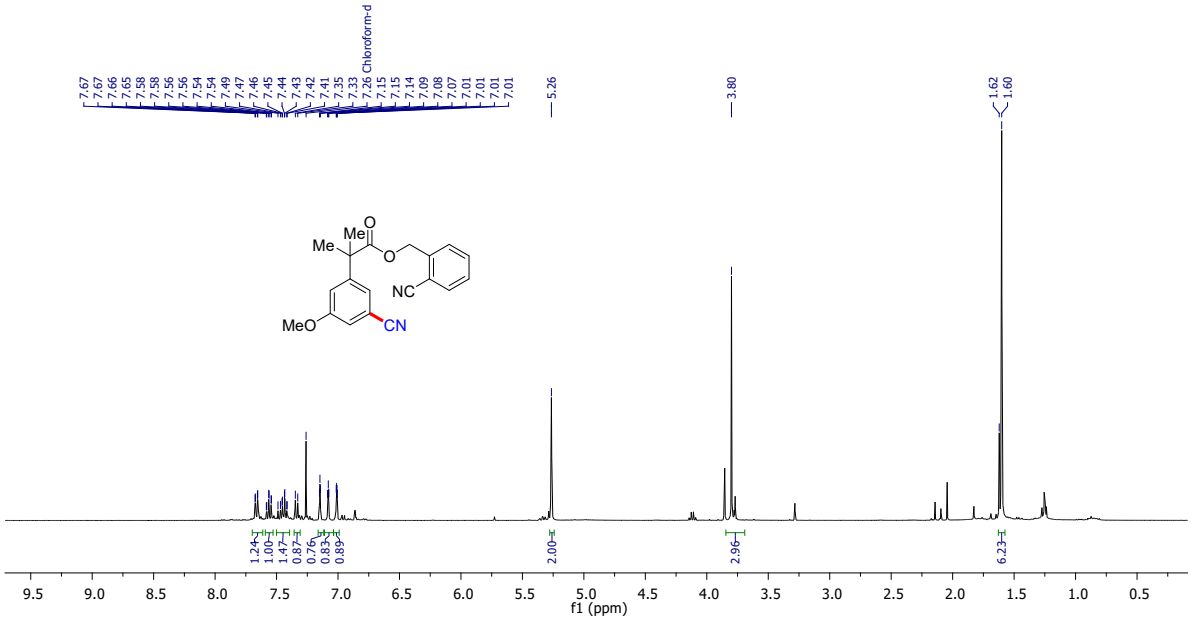
^{13}C NMR (100 MHz) spectrum of **6b** in $CDCl_3$



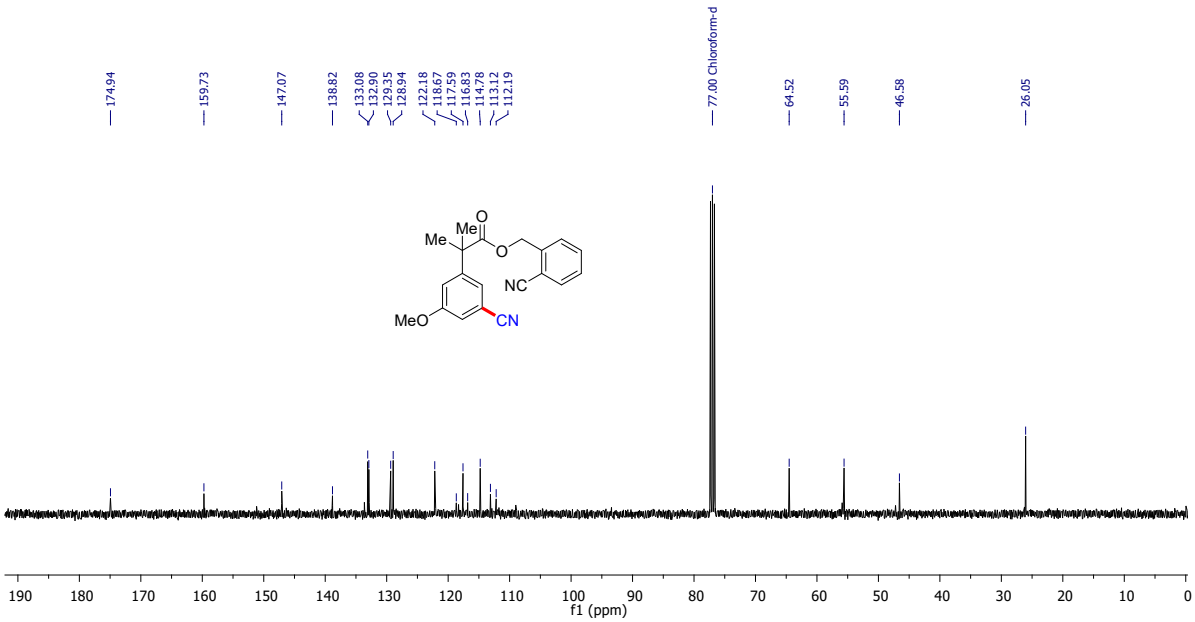
^{1}H NMR (400 MHz) spectrum of **6c** in $CDCl_3$



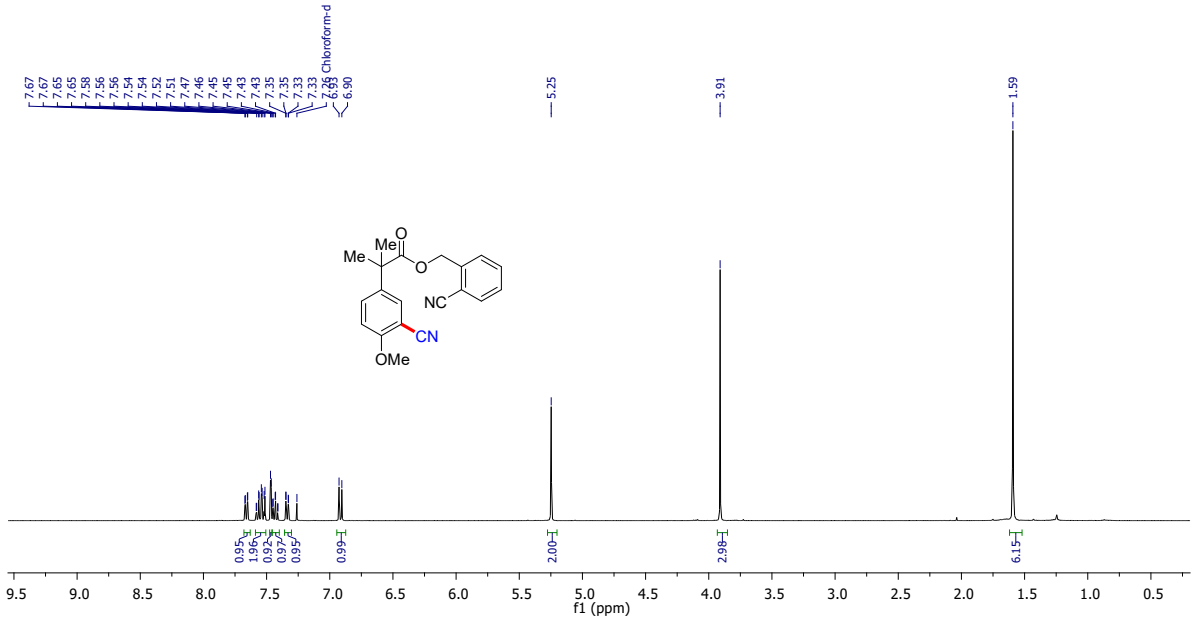
^{13}C NMR (151 MHz) spectrum of **6c** in $CDCl_3$



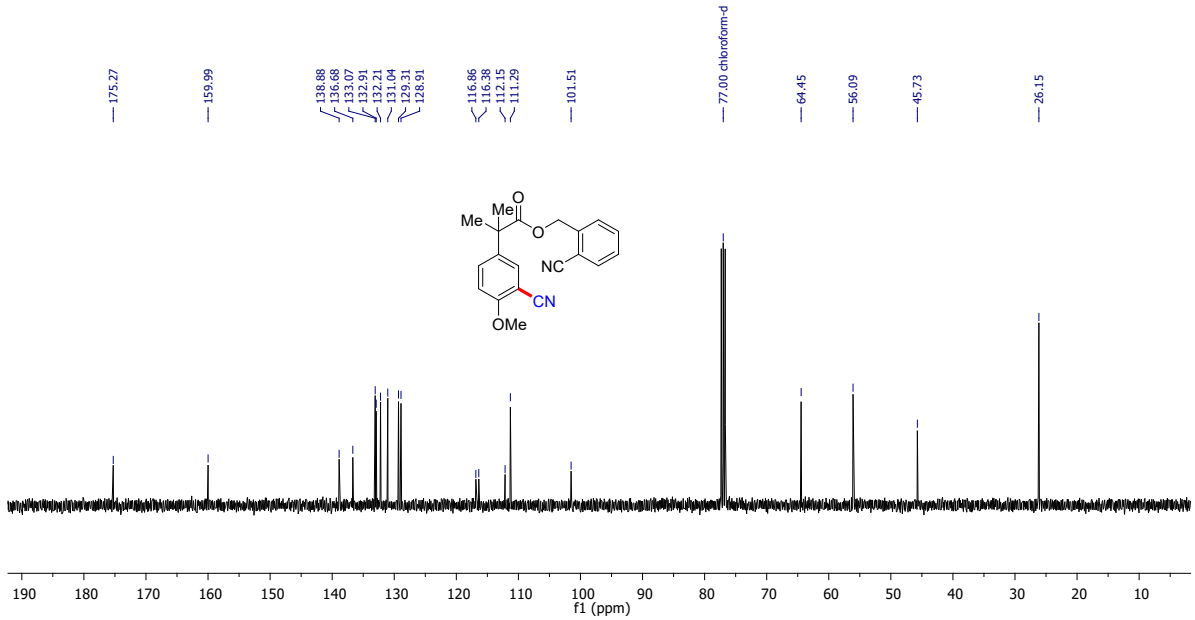
^{1}H NMR (400 MHz) spectrum of **6d** in $CDCl_3$



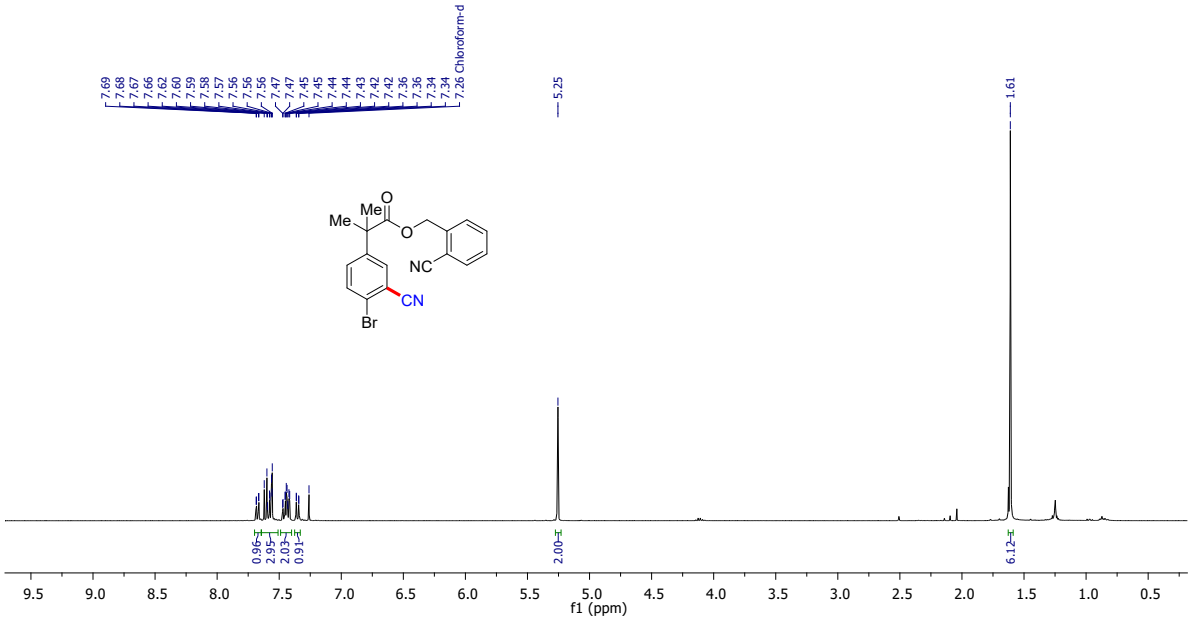
^{13}C NMR (100 MHz) spectrum of **6d** in $CDCl_3$



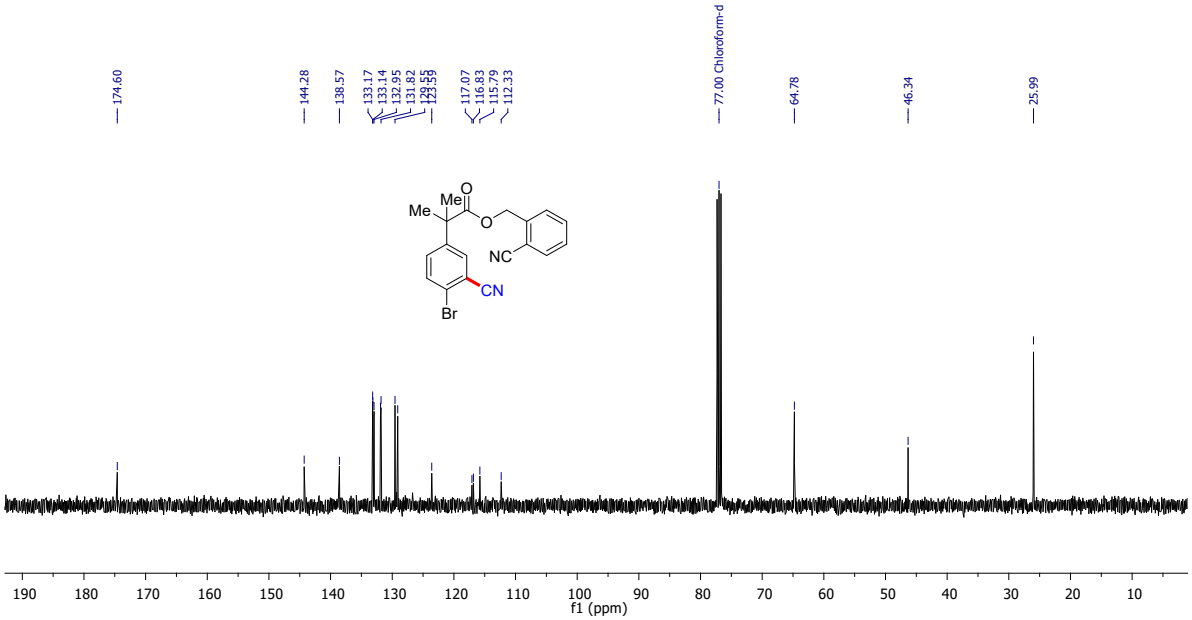
^{1}H NMR (400 MHz) spectrum of **6e** in $CDCl_3$



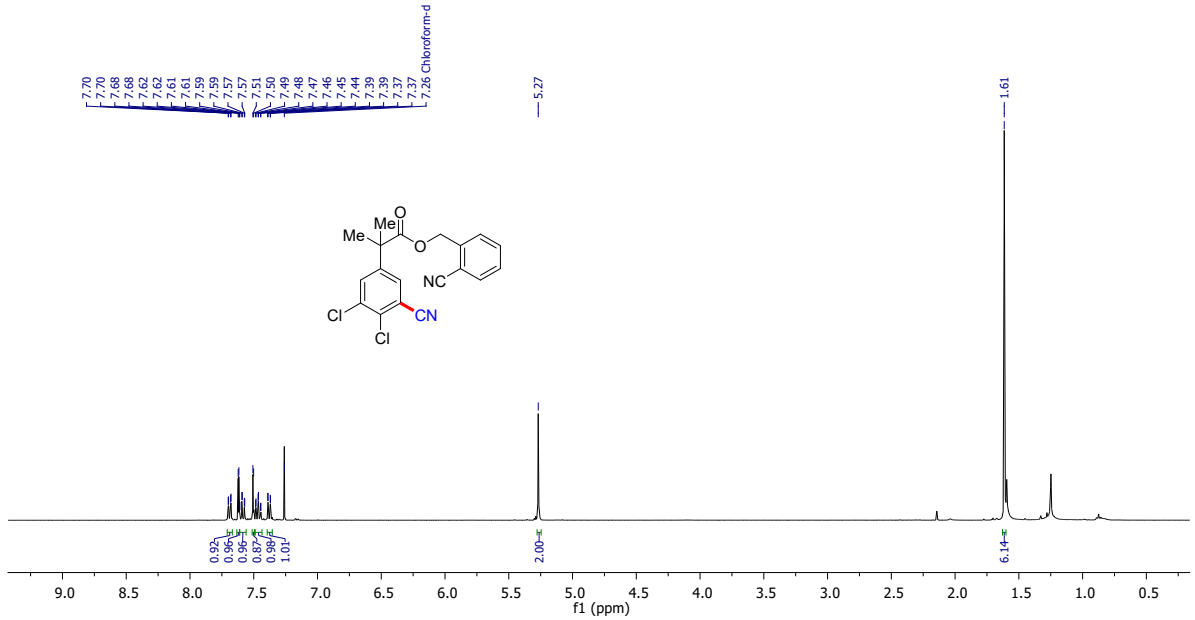
^{13}C NMR (100 MHz) spectrum of **6e** in $CDCl_3$



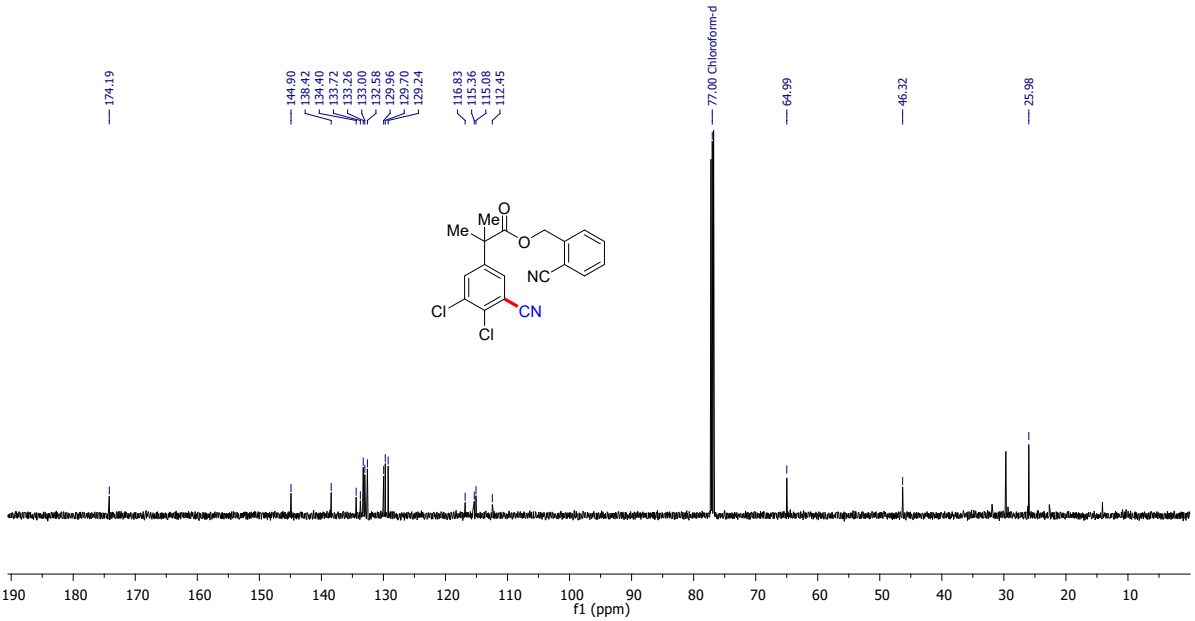
^{1}H NMR (400 MHz) spectrum of **6f** in $CDCl_3$



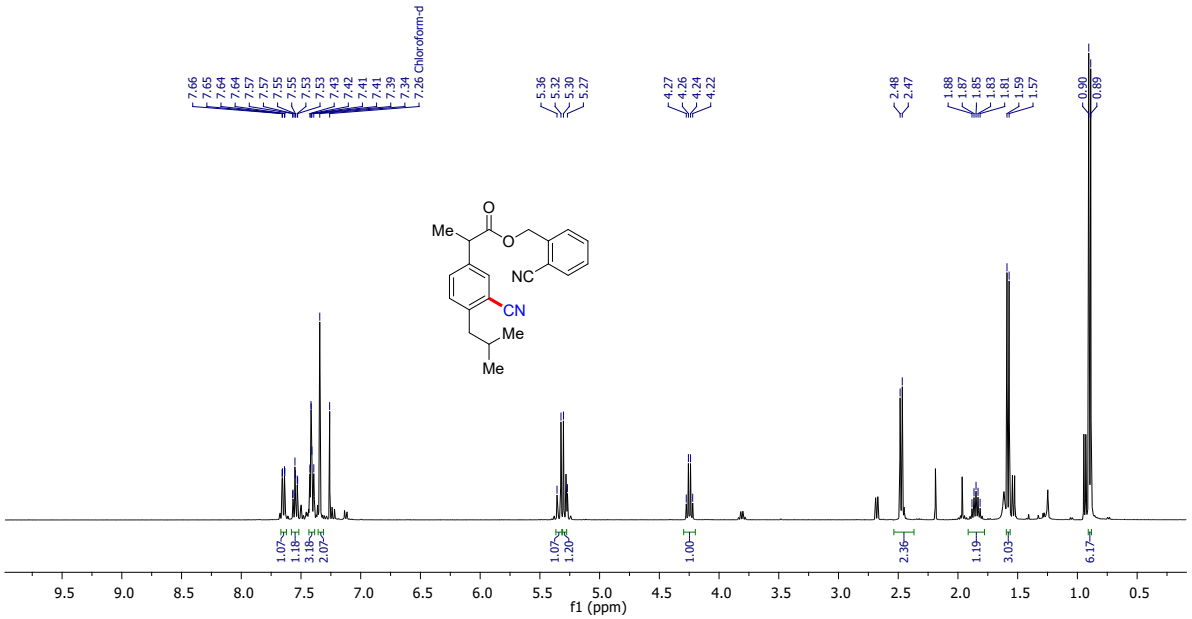
^{13}C NMR (100 MHz) spectrum of **6f** in $CDCl_3$



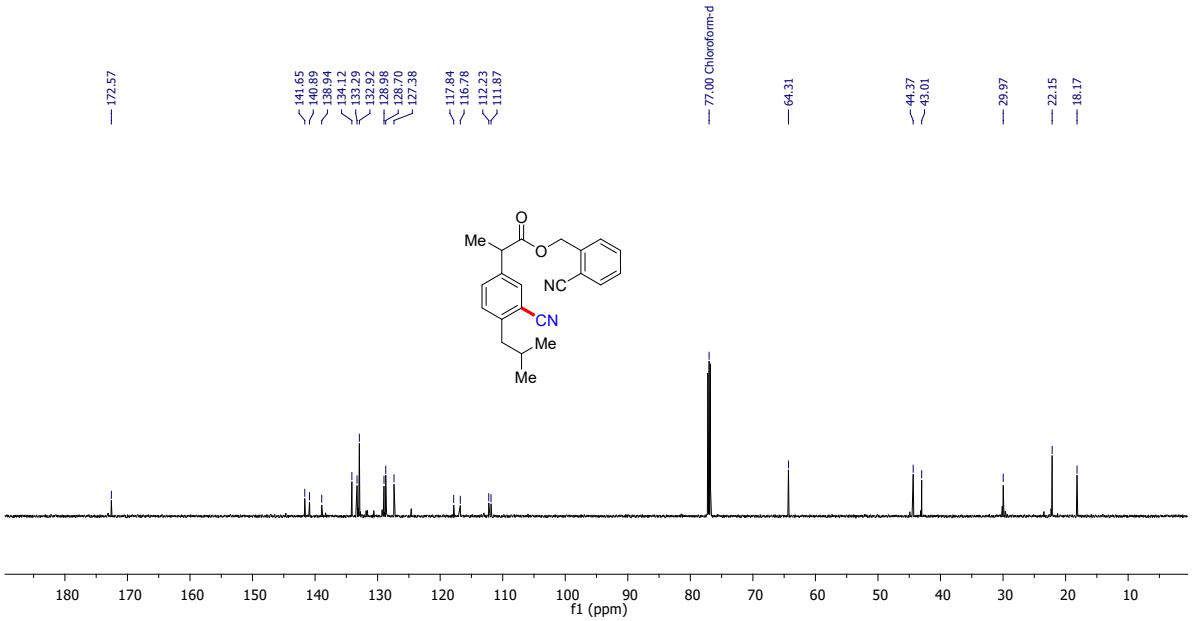
^{1}H NMR (400 MHz) spectrum of **6g** in $CDCl_3$



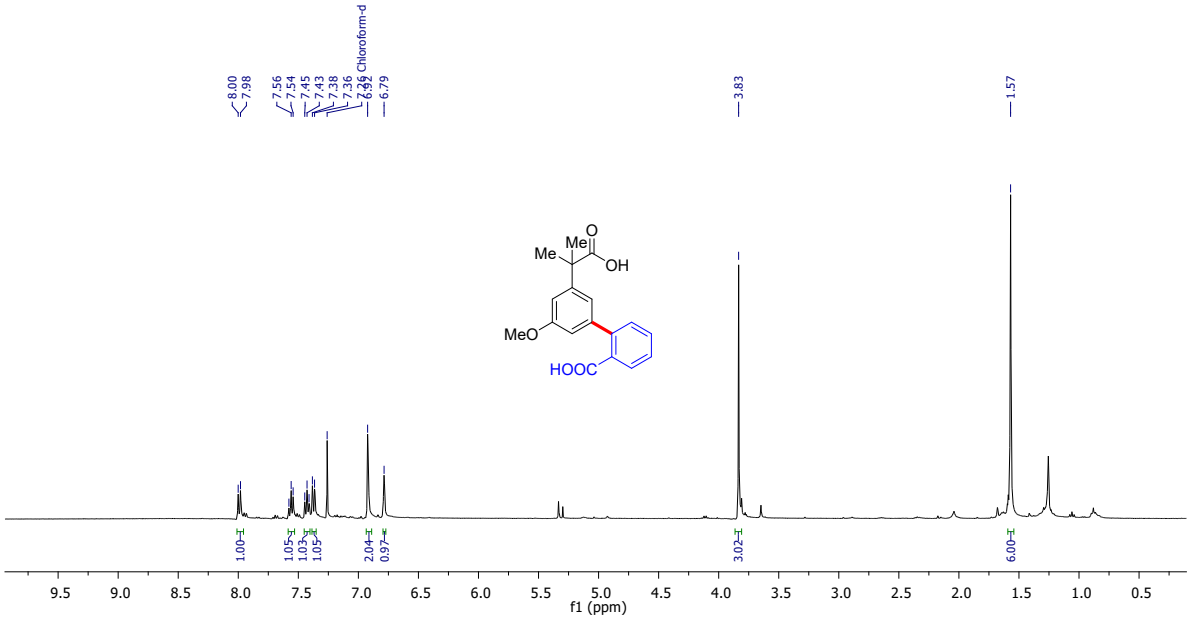
^{13}C NMR (151 MHz) spectrum of **6g** in $CDCl_3$



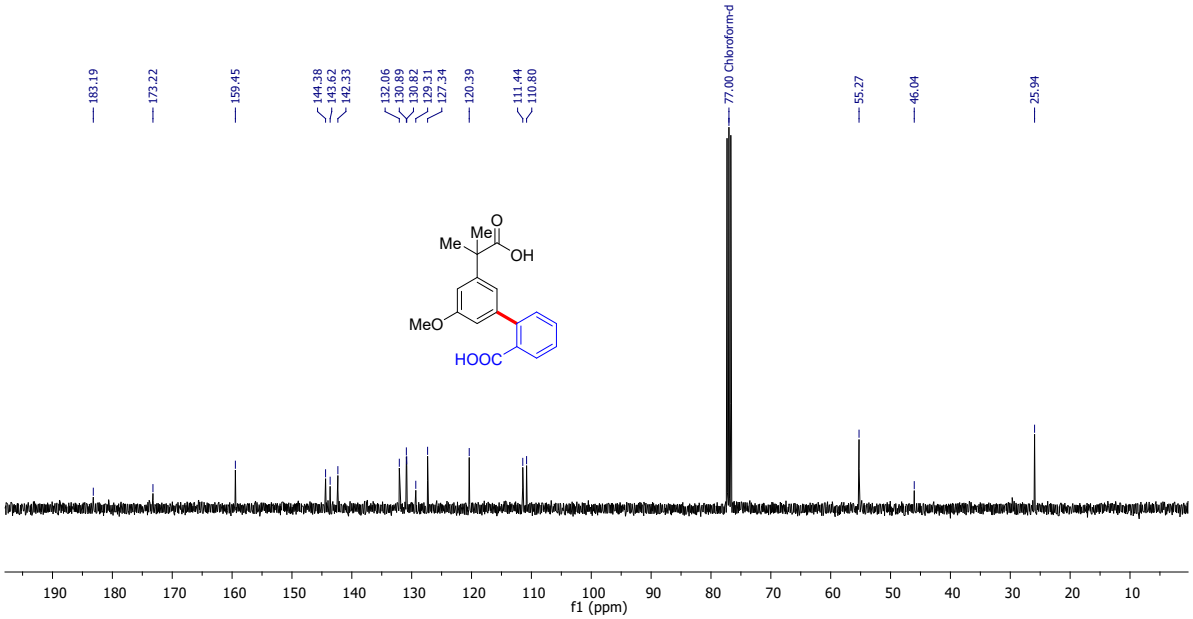
^{1}H NMR (400 MHz) spectrum of **6h** in $CDCl_3$



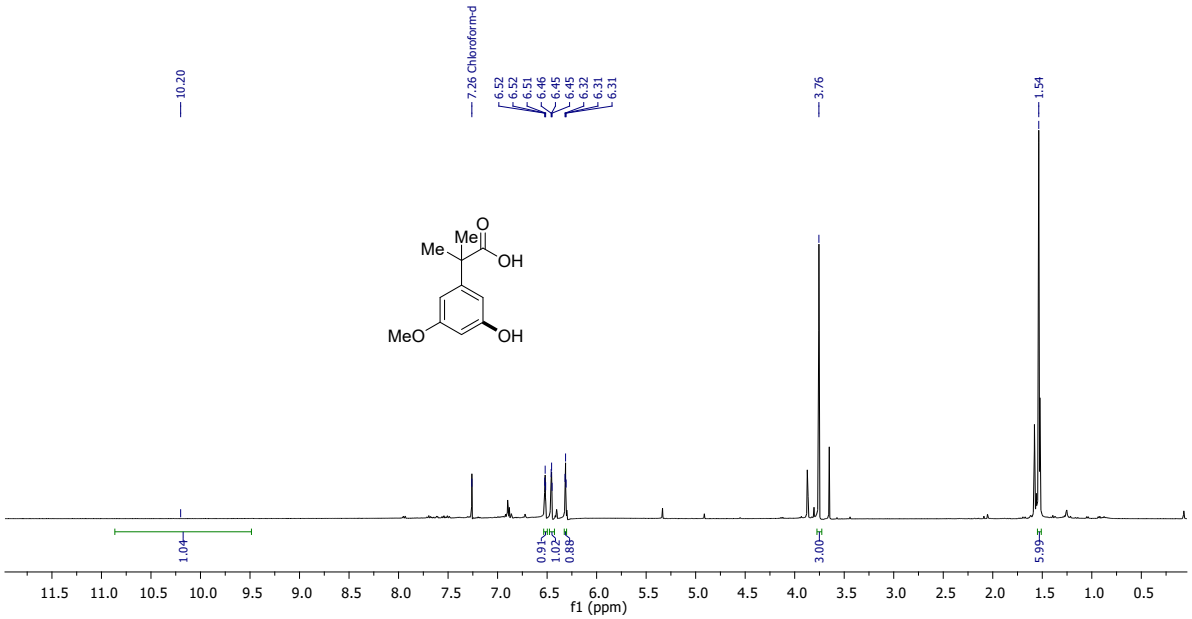
^{13}C NMR (151 MHz) spectrum of **6h** in $CDCl_3$



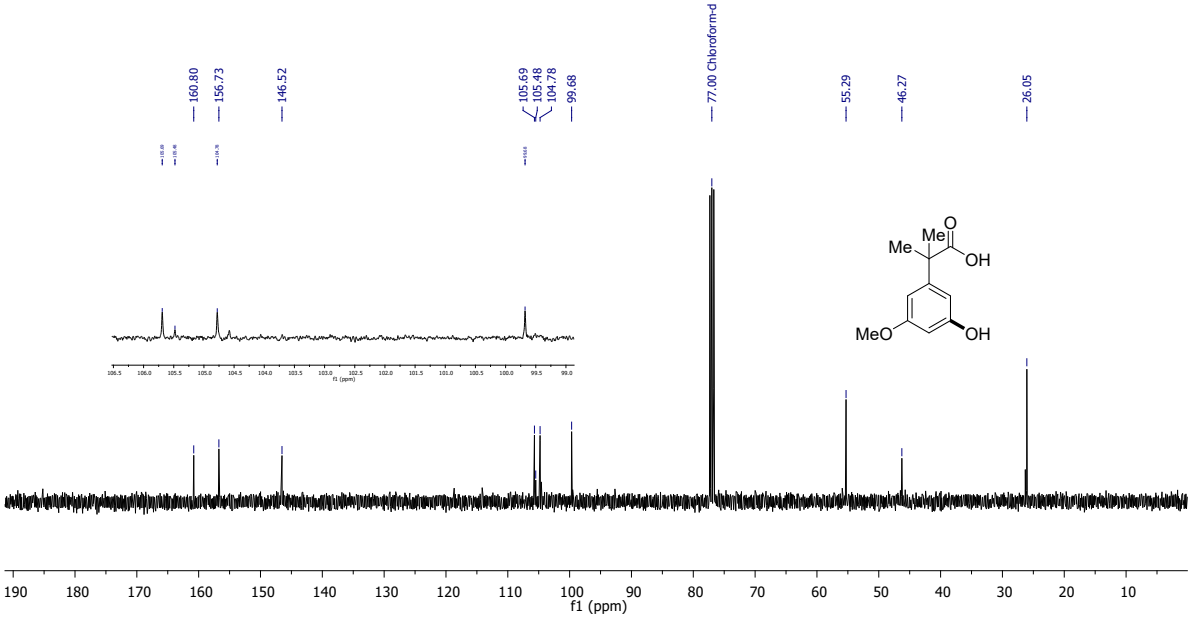
^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$



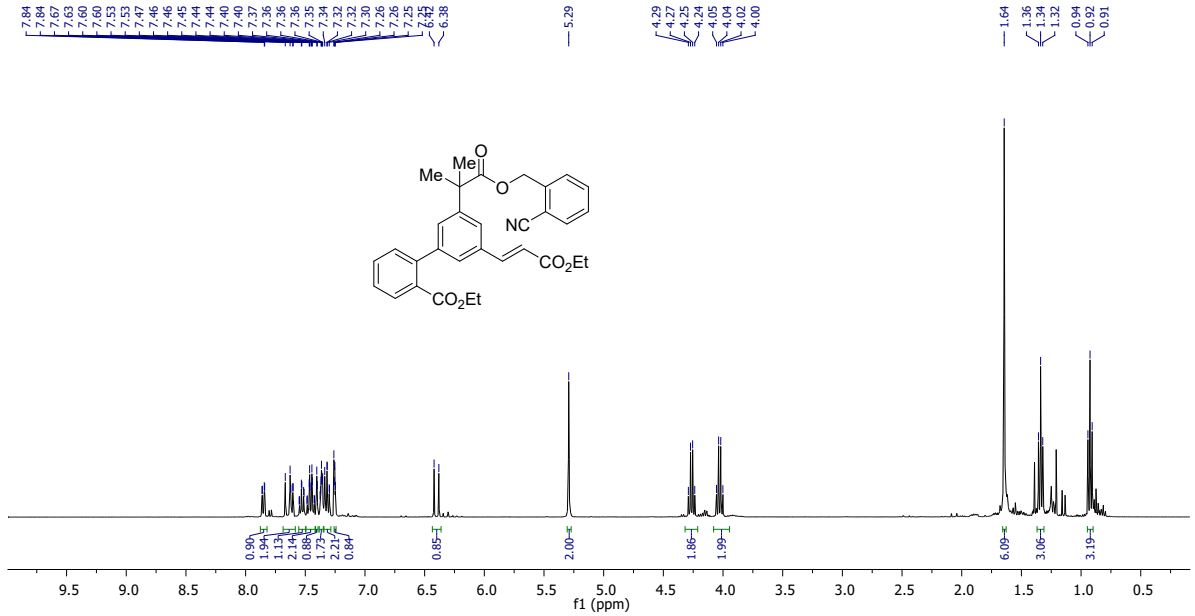
^{13}C NMR (100 MHz) spectrum of **7** in $CDCl_3$



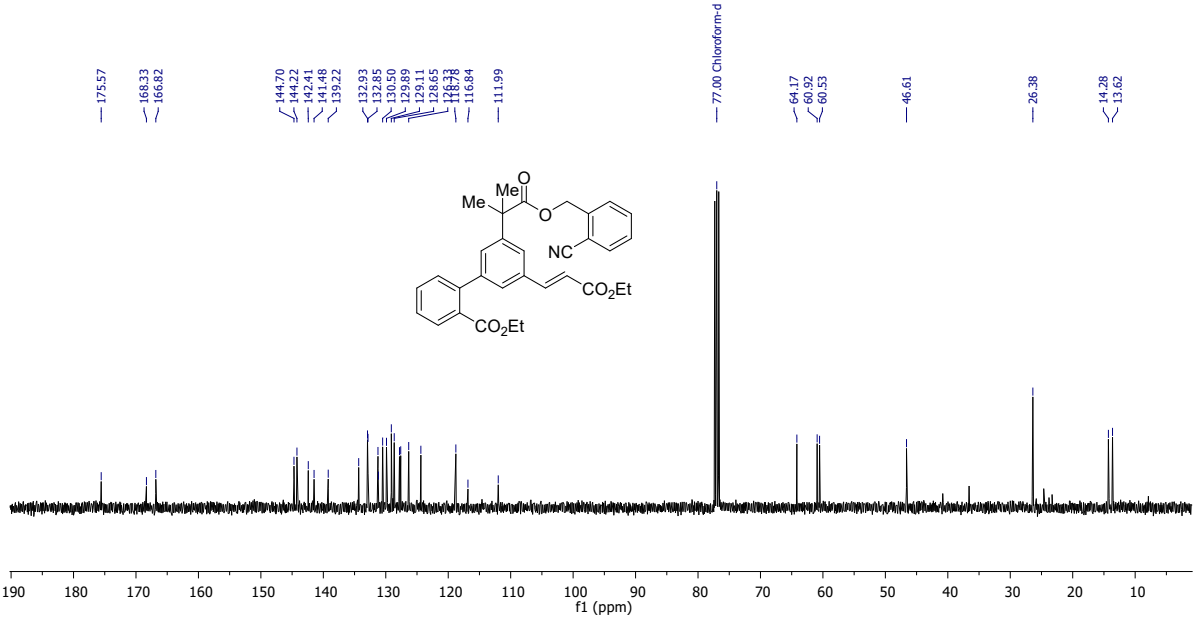
^{1}H NMR (400 MHz) spectrum of **8** in $CDCl_3$



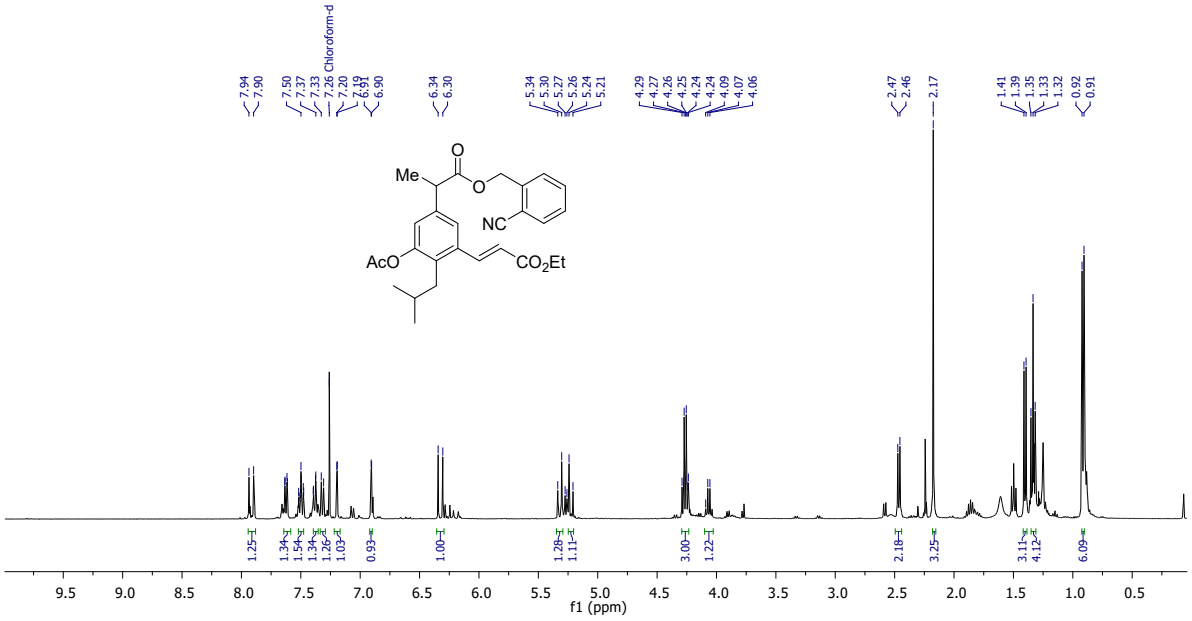
^{13}C NMR (100 MHz) spectrum of **8** in $CDCl_3$



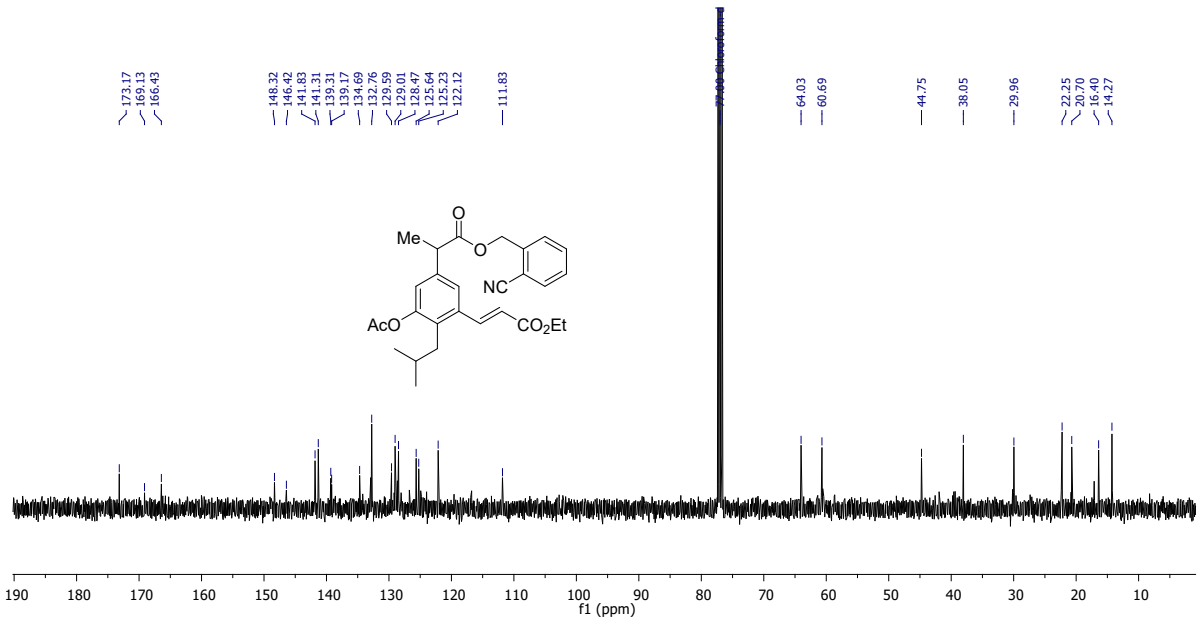
^{1}H NMR (400 MHz) spectrum of **10** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **10** in $CDCl_3$



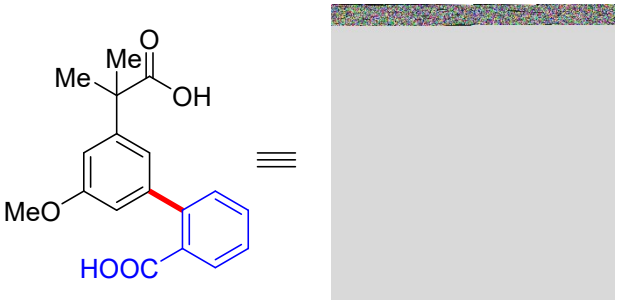
^{1}H NMR (400 MHz) spectrum of **11** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **11** in $CDCl_3$

X-ray Diffraction Analysis of Compound 7:

Crystal of compound **7** was obtained by dissolving product in mixture of MeOH and hexane in 3:1 ratio, allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. **CCDC No. (2245703)** contains the crystal structure information of this compound and can be obtained free of charge *via* http://www.ccdc.cam.ac.uk



7

Figure S1. X-ray structure of the product **7** with the ellipsoids drawn at the 50% probability level.

Crystal data and structure refinement for mo_GS_DS_2_469_0m.

Identification code	mo_GS_DS_2_469_0m
Empirical formula	$C_{18}H_{18}O_5$
Formula weight	314.32
Temperature/K	297
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.8205(4)
b/Å	18.7330(11)
c/Å	19.9045(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3288.9(3)
Z	8
ρ_{calc}g/cm^3	1.270
μ/mm^{-1}	0.093
F(000)	1328.0
Crystal size/mm^3	0.5 × 0.5 × 0.214
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.092 to 54.884
Index ranges	-11 ≤ h ≤ 10, -23 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	27161
Independent reflections	3692 [R_{int} = 0.0527, R_{sigma} = 0.0320]

Data/restraints/parameters	3692/0/212
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	$R_1 = 0.0524$, $wR_2 = 0.1374$
Final R indexes [all data]	$R_1 = 0.0824$, $wR_2 = 0.1580$
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.36

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