Supplementary Information

Rapid and Modular 1,2-Carboheterofunctionalization of Diverse Alkenes *via* Photoredox and RLT Catalysis

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List of the Contents

I. General methods--- S4

II. Synthetic procedures for substrates--- S5

Preparation of Alkylated-malonate, -cyanoacetate and -nitroacetate------------------------ S6
General procedure 1 for the formation of Bromo malonate----------------------------------- S8
General procedure 2 for the formation of Bromo Cyanoacetate or Bromo Nitroacetate- S8
The formation of Bromo Phosphonoacetate--- S22
General procedure 3 for the formation of Alkene--- S26
General procedure 4 for the formation of Alkene--- S26
The formation of S'28--- S32
The formation of S'29--- S33
The formation of S'30--- S34
The formation of S'34--- S35
General procedure 5 for the formation of complexed molecules contained Alkene------ S36
The formation of S′45 for radical clock experiment--- S40
General procedure 6 for formation of S'46-47 for carbocation trapping experiment--- S41

III. Optimization of 1,2-Carboheterofunctionalization-- S43

Optimization of 1,2-Carboheterofunctionalization of styrenes ----------------------------- S43
Optimization of 1,2-Carboheterofunctionalization of unreactive alkenes----------------- S50

IV. General procedures for 1,2-Carboheterofunctionalization-------------------------------- S52

V. Limited Scope-- S54

VI. Application--- S56

Gram-Scale experiment--- S56
Click reaction--- S57
Staudinger reaction & Boc protection-- S59
Staudinger reaction (N-P bond)---S60

Lactamization--- S61
Ullmann reaction--- S65

VII. Mechanism Studies--- S67

Radical Scavenger Trapping experiment-- S67
Radical Clock Reaction--- S68
Carbocation trapping experiment-- S69
Tracking of Reaction intermediate--- S71
Synthesis of 91-- S72
Reaction of Iron(III)-Azide complex (92) with for verification experiment--------------- S73
Synthesis of 92-- S75
Light ON-OFF experiment--- S78
Stern-Volmer luminescence quenching experiment-- S78
Quantum Yield measurement-- S80
Determination of the Reaction Quantum Yield--- S82
Hammett plot analysis-- S84
Cyclic voltammetry measurements--- S86
Window of Compatibility-- S87

VIII. X-Ray Crystallography Data for 83 and 83'--- S88

IX. Computational details-- S91

Energy correlation-- S91
Cartesian coordinates of computed structures--- S92
Calculated spin-density plots for ^{3}TS-2--- S103

X. Characterization of Products-- S107

XI. Reference--- S160

XII. NMR Spectra-- S163

I. General methods

All commercially available reagents and solvents (purchased from Sigma-Aldrich, TCI, Alfa-Aesar, Acros, Combi-block) were used without further purification unless otherwise noted. All reactions were carried out in oven-dried round bottom flask & seal tube. Reactions were monitored by thin layer chromatography on silica gel 60 F254 plate (Merck, Darmstadt, Germany) using UV illumination at 254 nm (VL-4.LC, Vilber Lourmat, Eberhardzell, Germany). Column chromatography was performed on silica gel (230~400 mesh; Zeochem, Lake Zurich, Switzerland), using mixture of hexane and EtOAc as eluents. Melting points were measured on a Büchi B-540 melting point apparatus and were not corrected. Nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR) spectra were measured on JEOL JNM-ECZ400s [400 MHz (^{1}H), 100 MHz (^{13}C), and 376 MHz (^{19}F)] spectrometer. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm. Coupling constants (*J*) are expressed in hertz (Hz). IR spectra were recorded on a JASCO, FT/IR-4200 Infrared spectrophotometer and are reported as cm^{-1}. All high-resolution mass spectra (HR-MS) were acquired using Chemical Ionization (CI) method on a JMS-700 MStation mass spectrometer and GC-6890 Series (JEOL + Agilent), fast atom bombardments (FAB) method on a JMS-700 MStation mass spectrometer (JEOL, Tokyo, Japan), and Electrospray Ionization (ESI) method on an Agilent 6530 Q-TOF mass spectrometer and Agilent 1290 Infinity system. X-ray crystallographic data was collected by Agilent SuperNova, Bruker D8-Venture and Bruker APEX-II CCD X-ray Diffractometer using graphite-monochromated Mo Kα radiation.

Light Sources. Reactions were carried out using 40 W Blue LED lamps (Kessil PR160L-427 nm, λmax = 427 nm). The lamp was positioned approximately 1.0 cm away from an 8.0 mL vial. A cooling fan was positioned 10.0 cm directly opposite the vial.

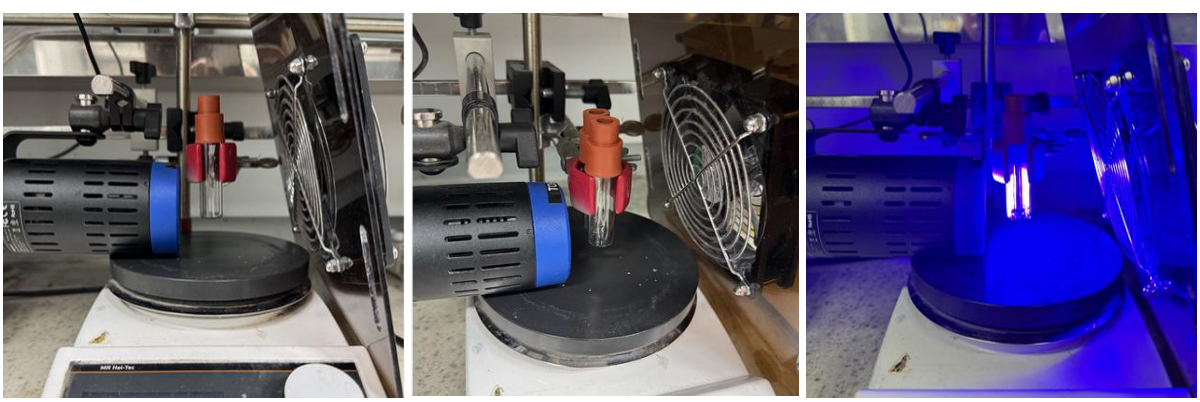
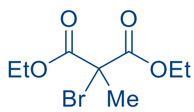


Figure 1. Photograph of the photochemical reaction setup.

II. Synthetic procedures for substrates

List of Bromo malonates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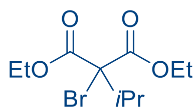
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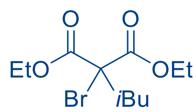
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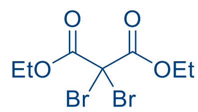
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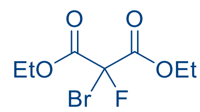
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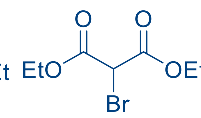
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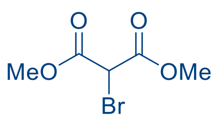
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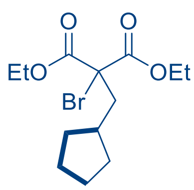
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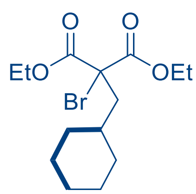
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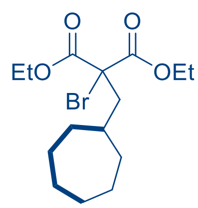
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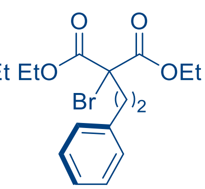
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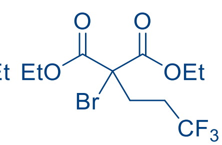
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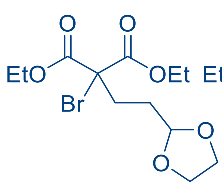
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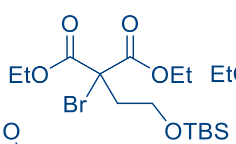
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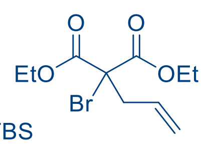
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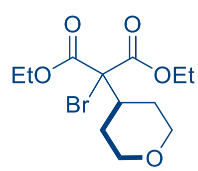
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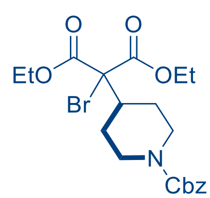
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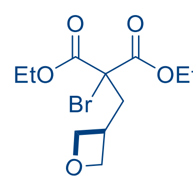
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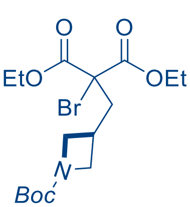
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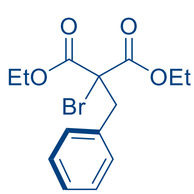
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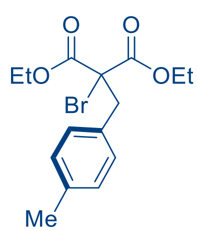
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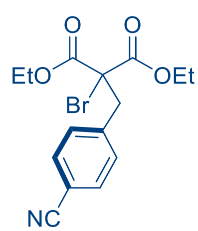
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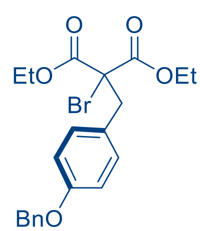
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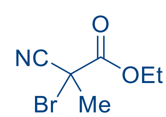
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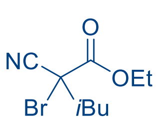
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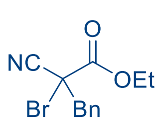
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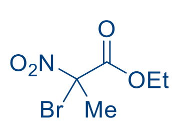
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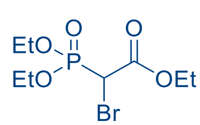
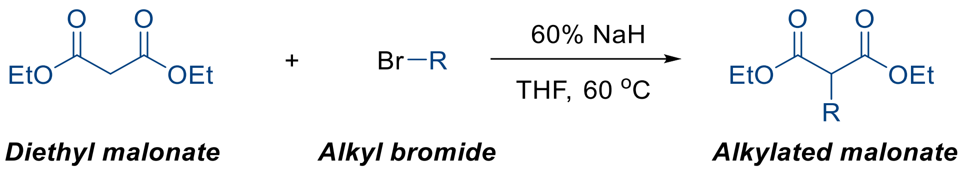
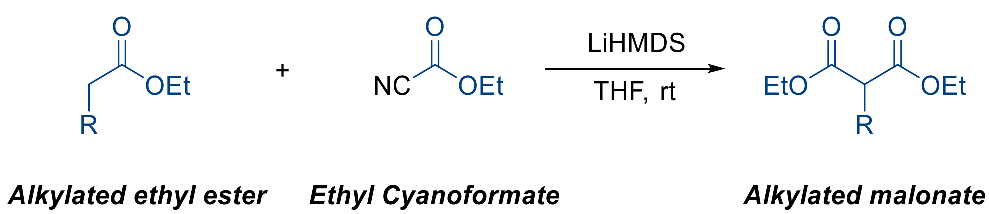

S28

S1, S4, **S6** and **S7** are commercially available. Other substrates are synthesized following the known method or modified method in literature.

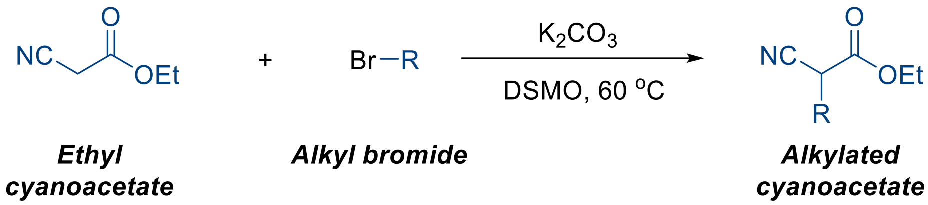
Preparation of Alkylated-malonate, -cyanoacetate and -nitroacetate. [1-3]



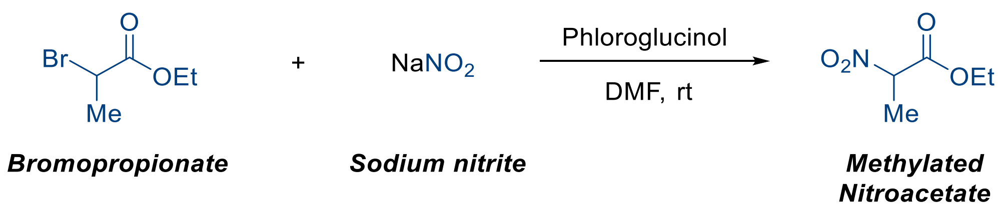
To an oven-dried round bottom flask was added diethyl malonate (1.0 equiv.) and dry THF (0.5 M) under argon gas. The reaction vessel was cooled to 0 °C and 60% NaH (1.1 equiv.) was added to a reaction. After resulting mixture was stirred at 0 °C for 20 min, alkyl bromide (1.1 equiv.) was added to the reaction. The reaction was heated to 70 °C for 12 h in a heat block. Upon the completion of reaction, to a mixture was added H_2O (30 mL) and extracted with EtOAc (2 x 30 mL). The combine extracts were washed with brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired alkylated malonates.



To an oven-dried round bottom flask was added alkylated ethyl ester (1.0 equiv.) and dry THF (0.5 M) under argon gas. The reaction vessel was cooled to -78 °C and 1 M Lithium bis(trimethylsilyl)amide in THF (2.0 equiv.) added to a reaction. After resulting mixture was stirred at -78 °C for 30 min, ethyl cyanoformate (2.0 equiv.) was then added dropwise. The reaction was further stirred at -78 °C for 30 min, allowed to warm to rt, and further stirred for 12 h. The reaction mixture was then quenched with sat. NH_4Cl (30.0 mL), extracted with EtOAc (2 x 20 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired alkylated malonates.

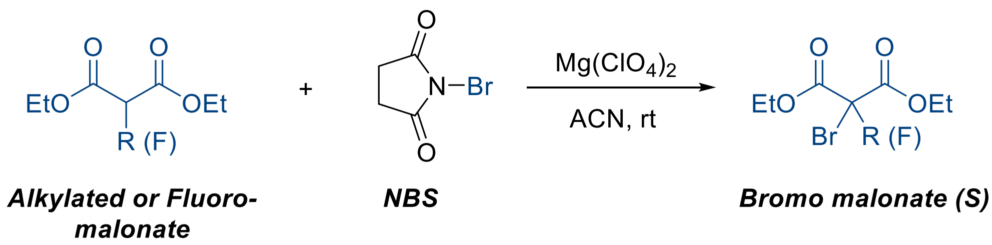


To an oven-dried round bottom flask was added Cyanoacetate (1.5 equiv.), K_2CO_3 (1.5 equiv.) and dry DMSO (0.1 M) under argon gas. After resulting mixture was stirred for 30 min and then alkyl bromide (1.0 equiv.) was added to the reaction. The reaction was heated to 60 °C for 12 h in a heat block. Upon the completion of reaction, to a mixture was added H_2O (20 mL) and extracted with EtOAc (2 x 20 mL). The combine extracts were washed with brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired alkylated cyanoacetate.



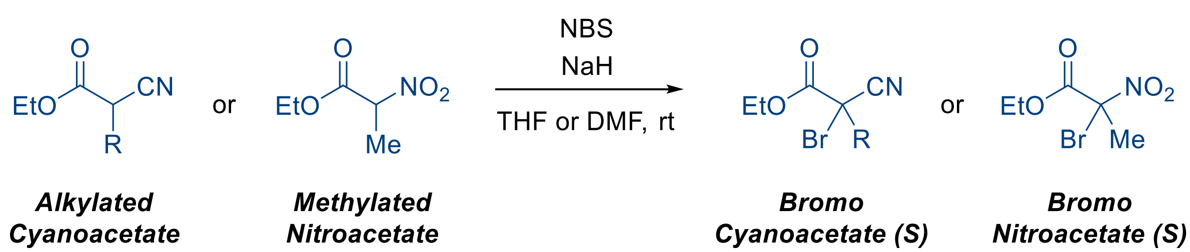
To an oven-dried round bottom flask was added sodium nitrite (2.0 equiv.), phloroglucinol (0.9 equiv.) and dry DMF (0.5 M) under argon gas. Ethyl 2-bromopropionate (1.0 equiv.) was added to reaction mixture, and then the reaction was stirred at room temperature for overnight. Upon the completion of reaction, to a mixture was added H_2O (20 mL) and extracted with EtOAc (2 x 20 mL). The combine extracts were washed with brine (3 x 30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired methylated nitroacetate.

General procedure 1 for the formation of Bromo malonate from Alkylated or Fluoro-malonate and NBS.[4]



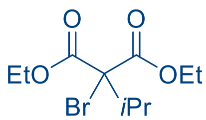
To an oven-dried round bottom flask was added Alkylated malonate (1.0 equiv.), $Mg(ClO_4)_2$ (0.3 equiv.), and dry ACN (0.2 M) under argon gas. After resulting mixture was stirred at rt for 30 min, N-bromosuccinimide (1.5 equiv.) was then added portionwise. The reaction was further stirred at rt for 18 h, and then the reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired bromo malonates (**S**).

General procedure 2 for the formation of Bromo Cyanoacetate or Bromo Nitroacetate from Alkylated Cyanoacetate or Methylated Nitroacetate and NBS.[1]



To an oven-dried round bottom flask was added Alkylated Cyanoacetate or Methylated Nitroacetate (1.0 equiv.) and dry THF or DMF (0.5 M) under argon gas. The reaction vessel was cooled to 0 °C and 60% NaH (1.1 equiv.) was added to a reaction. After resulting mixture was stirred at 0 °C for 30 min, N-bromosuccinimide (1.1 equiv.) was added to the reaction. Upon the completion of reaction, to a mixture was added H_2O (30 mL) and extracted with EtOAc (2 x 30 mL). The combine extracts were washed with brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired Bromo Cyanoacetate or Bromo Nitroacetate.

Diethyl 2-bromo-2-isopropylmalonate (S2)

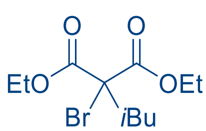


S2

S2 was synthesized according to general procedure 1. Alkylated malonate (625.6 mg, 3.0 mmol, 1.0 equiv.), N-bromosuccinimide (809.0 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a colorless oil (571.3 mg, 68% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.26 (q, *J* = 7.2 Hz, 4H), 2.59-2.49 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 6H), 1.08 (d, *J* = 6.4 Hz, 6H).
^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.7, 71.1, 62.9, 35.3, 19.3, 14.0.
IR (neat) ν 2979, 2940, 1744, 1467, 1249, 1049, 861 cm^{-1}.
HRMS (ESI) calcd for $C_{10}H_{18}BrO_4$ $[M+H]^+$ 281.0383, found 281.0381.

Diethyl 2-bromo-2-isobutylmalonate (S3)

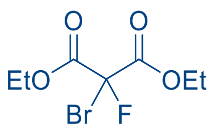


S3

S3 was synthesized according to general procedure 1. Alkylated malonate (662.1 mg, 3.0 mmol, 1.0 equiv.), N-bromosuccinimide (809.0 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a colorless oil (842.5 mg, 95% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.32-4.19 (m, 4H), 2.25 (d, *J* = 6.4 Hz, 2H), 1.95 (qd, *J* = 13.1, 6.5 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 6H), 0.93 (d, *J* = 6.9 Hz, 6H).
^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.4, 63.4, 63.1, 45.6, 26.0, 23.2, 14.0
IR (neat) ν 2981, 2962, 1745, 1469, 1267, 1029, 860 cm^{-1}.
HRMS (ESI) calcd for $C_{11}H_{20}BrO_4$ $[M+H]^+$ 295.0539, found 295.0544.

Diethyl 2-bromo-2-fluoromalonate (S5)

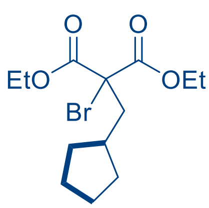


S5

S5 was synthesized according to general procedure 1. Fluorinated malonate (937.7 mg, 5.0 mmol, 1.0 equiv.), N-bromosuccinimide (1.35 g, 7.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), the title compound was isolated as a colorless oil (1.01 g, 79% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 4.33-4.21 (m, 4H), 3.68 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.5 (q, $J_{C\text{-}F}$ = 25.8), 90.1 (q, $J_{C\text{-}F}$ = 268.3), 64.4, 13.9.
^{19}F-NMR (376 MHz, $CDCl_3$): δ -122.3.
IR (neat) ν 2987, 2943, 1769, 1469, 1240, 1028, 859 cm^{-1}.
HRMS (ESI) calcd for $C_7H_{11}BrFO_4$ $[M+H]^+$ 258.9804, found 258.9791.

Diethyl 2-bromo-2-(cyclopentylmethyl)malonate (S8)

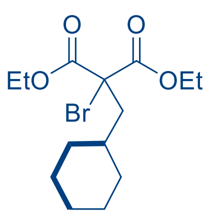


S8

S8 was synthesized according to general procedure 1. Alkylated malonate (484.6 mg, 1.9 mmol, 1.0 equiv.), N-bromosuccinimide (512.4 mg, 2.85 mmol, 1.5 equiv.) were used as a starting material and reaction was heated to 60 ºC for 4 h in a heat block. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a colorless oil (471.3 mg, 77% yield).

^{1}H-NMR (401 MHz, $CDCl_3$) δ 4.32-4.20 (m, 4H), 2.40 (d, J = 6.4 Hz, 2H), 2.06-1.94 (m, 1H), 1.83-1.76 (m, 2H), 1.65-1.42 (m, 4H), 1.28 (t, J = 7.1 Hz, 6H), 1.17-1.06 (m, 2H).
^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.4, 63.8, 63.0, 43.6, 37.4, 33.7, 33.2, 24.9, 14.0.
IR (neat) ν 2980, 2955, 1744, 1464, 1240, 1028, 859 cm^{-1}.
HRMS (ESI) calcd for $C_{13}H_{22}BrO_4$ $[M+H]^+$ 321.0696, found 321.0678.

Diethyl 2-bromo-2-(cyclohexylmethyl)malonate (S9)

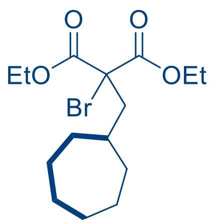


S9

S9 was synthesized according to general procedure 1. Alkylated malonate (566.7 mg, 2.1 mmol, 1.0 equiv.), N-bromosuccinimide (566.3 mg, 3.2 mmol, 1.5 equiv.) were used as a starting material and reaction was heated to 60 ºC for 4 h in a heat block. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a colorless oil (636.6 mg, 90% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.31-4.20 (m, 4H), 2.23 (d, J = 5.9 Hz, 2H), 1.70-1.58 (m, 6H), 1.28 (t, J = 7.3 Hz, 6H), 1.25-1.06 (m, 3H), 1.03-0.93 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.5, 63.2, 63.1, 44.5, 35.1, 33.8, 26.3, 26.2, 14.0.
IR (neat) ν 2982, 2925, 1744, 1465, 1248, 1056, 861 cm^{-1}.
HRMS (ESI) calcd for $C_{14}H_{24}BrO_4$ $[M+H]^+$ 335.0858, found 335.0871.

Diethyl 2-bromo-2-(cycloheptylmethyl)malonate (S10)



S10

S10 was synthesized according to general procedure 1. Alkylated malonate (300.4 mg, 1.1 mmol, 1.0 equiv.), N-bromosuccinimide (296.6 mg, 1.7 mmol, 1.5 equiv.) were used as a starting material and reaction was heated to 60 ºC for 4 h in a heat block. After purification by column chromatography (hexane : EtOAc = 30 : 1), the title compound was isolated as a colorless oil (356.1 mg, 93% yield).

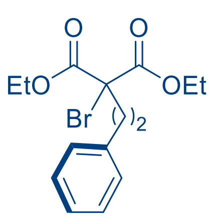
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.31-4.20 (m, 4H), 2.27 (d, J = 5.5 Hz, 2H), 1.84-1.75 (m, 1H), 1.72-1.64 (m, 2H), 1.62-1.55 (m, 4H), 1.50-1.34 (m, 4H), 1.29 (t, J = 7.1 Hz, 7H), 1.25-1.21 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.5, 63.6, 63.2, 63.1, 62.9, 45.1, 36.8, 35.4, 28.5, 26.1, 14.0

IR (neat) ν 2981, 2925, 1745, 1445, 1255, 1068, 860 cm^{-1}.

HRMS (ESI) calcd for $C_{15}H_{26}BrO_4$ $[M+H]^+$ 349.1009, found 349.1004.

Diethyl 2-bromo-2-phenethylmalonate (S11)

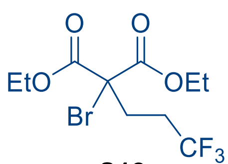


S11

S11 was synthesized according to general procedure 1. Alkylated malonate (973.8 mg, 3.5 mmol, 1.0 equiv.), N-bromosuccinimide (943.8 mg, 5.25 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 30 : 1), the title compound was isolated as a colorless oil (518.4 mg, 72% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.21 (dd, *J* = 7.3, 5.5 Hz, 3H), 4.27 (q, *J* = 7.0 Hz, 4H), 2.78-2.74 (m, 2H), 2.60-2.56 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.9, 140.3, 128.7, 128.6, 126.5, 63.2, 63.1, 40.0, 31.8, 14.0.
IR (neat) ν 2982, 2938, 17453 14454, 1254, 1098, 859 cm^{-1}.
HRMS (ESI) calcd for $C_{15}H_{20}BrO_4$ $[M+H]^+$ 343.0539, found 343.0554.

Diethyl 2-bromo-2-(3,3,3-trifluoropropyl)malonate (S12)

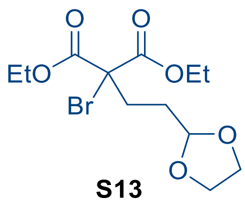


S12

S12 was synthesized according to general procedure 1. Alkylated malonate (768.7 mg, 3.0 mmol, 1.0 equiv.), N-bromosuccinimide (809.0 mg, 4.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a colorless oil (896.5 mg, 89% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.30 (q, *J* = 7.2 Hz, 4H), 2.55-2.51 (m, 2H), 2.35-2.23 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 6H)
^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.3, 126.5 (q, J_{C-F} = 275.0), 63.6, 61.0, 31.1 (q , J_{C-F} = 3.8), 30.1 (q , J_{C-F} = 59.0), 14.0.
^{19}F-NMR (376 MHz, $CDCl_3$): δ -66.2, -66.2, -66.3.
IR (neat) ν 2986, 2943, 1746, 1468, 1252, 1059, 858 cm^{-1}.
HRMS (ESI) calcd for $C_{10}H_{15}BrF_3O_4$ $[M+H]^+$ 335.0100, found 335.0106.

Diethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)-2-bromomalonate (S13)

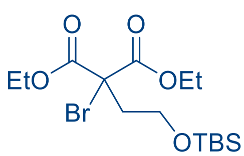


S13

S13 was synthesized according to general procedure 1. Alkylated malonate (584.3mg, 2.2mmol, 1.0 equiv.), N-bromosuccinimide (593.3 g, 3.3 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 8 : 1) and further purification by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−48% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a bright yellow oil (213.1 mg, 29% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.40 (t, *J* = 6.2 Hz, 2H), 4.32-4.25 (m, 4H), 3.51 (t, *J* = 6.2 Hz, 2H), 2.66-2.55 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 6H)
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.7, 166.6, 64.2, 63.4, 61.9, 33.2, 30.6, 28.6, 14.0.
IR (neat) ν 2984, 2940, 1745, 1443, 1256, 1075, 858 cm^{-1}.
HRMS (CI) calcd for $C_{12}H_{18}BrO_6$ $[M-H]^-$ 337.0292, found 337.0277.

Diethyl 2-bromo-2-(2-((tert-butyldimethylsilyl)oxy)ethyl)malonate (S14)



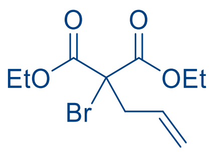
S14

S14 was synthesized according to general procedure 1. Alkylated malonate (965.1 mg, 3.0 mmol, 1.0 equiv.), N-bromosuccinimide (809.0 mg, 4.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 50 : 1), the title compound was isolated as a colorless oil (1.1 g, 94% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.31-4.19 (m, 4H), 3.84 (t, *J* = 6.2 Hz, 2H), 2.52 (t, *J* = 6.4 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H), 0.88 (t, *J* = 2.7 Hz, 9H), 0.05 (t, *J* = 3.0 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 63.0, 61.6, 60.1, 40.3, 26.1, 18.6, 14.0, -5.3.

IR (neat) ν 2981, 2956, 1745, 1471, 1235, 1079, 836 cm^{-1}.
HRMS (ESI) calcd for $C_{15}H_{30}BrO_5Si$ $[M+H]^+$ 399.1025, found 399.1045.

Diethyl 2-allyl-2-bromomalonate (S15)

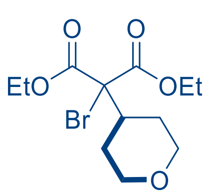


S15

S15 was synthesized according to general procedure 1. Alkylated malonate (441.3 mg, 3.0 mmol, 1.0 equiv.), N-bromosuccinimide (593.3 mg, 3.3 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 40 : 1), the title compound was isolated as a colorless oil (244.9 mg, 29% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.86-5.76 (m, 1H), 5.19 (m, 2H), 4.27 (q, J = 7.0 Hz, 4H), 3.04 (d, J = 7.3 Hz, 2H), 1.28 (t, J = 7.1 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.7, 71.1, 62.9, 35.3, 19.3, 14.0.
IR (neat) ν 2983, 2939, 1745, 1445, 1267, 1096, 857 cm^{-1}.
HRMS (ESI) calcd for $C_{10}H_{16}BrO_4$ $[M+H]^+$ 279.0232, found 279.0219.

Diethyl 2-bromo-2-(tetrahydro-2H-pyran-4-yl)malonate (S16)



S16

S16 was synthesized according to general procedure 1. Alkylated malonate (548.4 mg, 2.2 mmol, 1.0 equiv.), N-bromosuccinimide (593.3 mg, 3.3 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 5 : 1), the title compound was isolated as a colorless oil (604.5 mg, 85% yield).

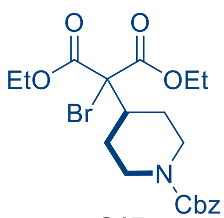
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.30-4.23 (m, 4H), 4.00 (dd, J = 11.2, 3.9 Hz, 2H), 3.44 (td, J = 11.8, 2.0 Hz, 2H), 2.45 (tt, J = 11.7, 3.4 Hz, 1H), 1.77 (d, J = 12.8 Hz, 2H), 1.66 (qd, J = 12.3, 4.2 Hz, 2H), 1.29 (t, J = 7.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.2, 68.4, 67.8, 63.1, 42.6, 29.3, 14.0.

IR (neat) ν 2980, 2962, 1741, 1445, 1297, 1092, 891 cm^{-1}.

HRMS (ESI) calcd for $C_{12}H_{20}BrO_5$ $[M+H]^+$ 323.0489, found 323.0498.

Diethyl 2-(1-((benzyloxy)carbonyl)piperidin-4-yl)-2-bromomalonate (S17)



S17

S17 was synthesized according to general procedure 1. Alkylated malonate (377.4 mg, 1.0 mmol, 1.0 equiv.), N-bromosuccinimide (269.7 mg, 1.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 6 : 1), the title compound was isolated as a colorless oil (274.4 mg, 60% yield).

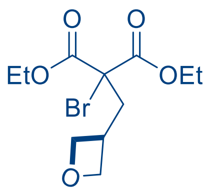
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.12 (s, 2H), 4.32-4.21 (m, 6H), 2.81 (s, 2H), 2.36 (tt, J = 11.7, 3.1 Hz, 1H), 1.87 (d, J = 12.9 Hz, 2H), 1.48 (qd, J = 12.4, 3.4 Hz, 2H), 1.28 (t, J = 7.1 Hz, 6H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.2, 155.2, 136.9, 128.6, 128.1, 128.0, 68.1, 67.2, 63.2, 43.9, 43.5, 28.4, 14.0.

IR (neat) ν 2984, 2940, 1745, 1471, 1280, 1095, 860 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{27}BrNO_6$ $[M+H]^+$ 456.1016, found 456.1007.

Diethyl 2-bromo-2-(oxetan-3-ylmethyl)malonate (S18)

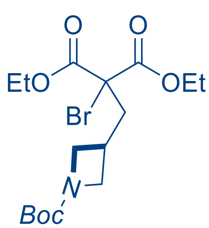


S18

S18 was synthesized according to general procedure 1. Alkylated malonate (604.7 mg, 2.6 mmol, 1.0 equiv.), N-bromosuccinimide (701.1 mg, 3.9 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 4: 1), the title compound was isolated as a colorless oil (498.1 mg, 62% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.31-4.20 (m, 4H), 2.23 (d, J = 5.9 Hz, 2H), 1.70-1.58 (m, 6H), 1.28 (t, J = 7.3 Hz, 6H), 1.25-1.06 (m, 3H), 1.03-0.93 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.5, 63.2, 63.1, 44.5, 35.1, 33.8, 26.3, 26.2, 14.0.
IR (neat) ν 2981, 2939, 1745, 1446, 1252, 1054, 854 cm^{-1}.
HRMS (ESI) calcd for $C_{11}H_{18}BrO_5$ $[M+H]^+$ 311.0317, found 311.0306.

Diethyl 2-bromo-2-((1-(tert-butoxycarbonyl)azetidin-3-yl)methyl)malonate (S19)



S19

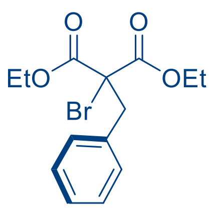
S19 was synthesized according to general procedure 1. Alkylated malonate (415.9 mg, 1.25 mmol, 1.0 equiv.), N-bromosuccinimide (338.0 mg, 1.88 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 6 : 1), the title compound was isolated as a colorless oil (391.4 mg, 77% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.32-4.20 (m, 4H), 4.02 (t, J = 8.5 Hz, 2H), 3.63 (dd, J = 8.7, 5.9 Hz, 2H), 2.84-2.74 (m, 1H), 2.60 (d, J = 6.4 Hz, 2H), 1.42 (s, 9H), 1.29 (t, J = 7.1 Hz, 6H)
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.7, 156.2, 79.6, 63.4, 61.3, 54.9, 42.4, 28.5, 26.5, 13.9.

IR (neat) ν 2978, 29437 1745, 1446, 1255, 1066, 859 cm^{-1}.

HRMS (ESI) calcd for $C_{16}H_{26}BrNNaO_6$ $[M+Na]^+$ 430.0836, found 430.0816.

Diethyl 2-benzyl-2-bromomalonate (S20)



S20

S20 was synthesized according to general procedure 1. Alkylated malonate (774.1 mg, 3.0 mmol, 1.0 equiv.), N-bromosuccinimide (809.0 mg, 4.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 40 : 1), the title compound was isolated as a colorless oil (768.3 mg, 78% yield).

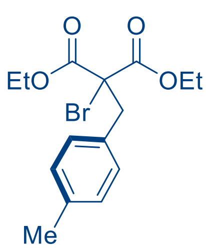
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 5H), 4.32-4.21 (m, 4H), 3.64 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 134.5, 130.6, 128.3, 127.8, 63.4, 63.2, 43.7, 13.9.

IR (neat) ν 2983, 2938, 1746, 1445, 1259, 1037, 862 cm^{-1}.

HRMS (ESI) calcd for $C_{14}H_{18}BrO_4$ $[M+H]^+$ 331.0363, found 331.0361.

Diethyl 2-bromo-2-(4-methylbenzyl)malonate (S21)

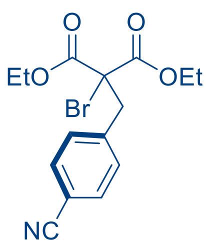


S21

S21 was synthesized according to general procedure 1. Alkylated malonate (634.4 mg, 2.4 mmol, 1.0 equiv.), N-bromosuccinimide (647.2 mg, 3.6 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 40 : 1), the title compound was isolated as a colorless oil (793.6 mg, 96% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.32-4.21 (m, 4H), 3.60 (s, 2H), 2.32 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 137.4, 131.4, 130.4, 129.0, 63.7, 63.2, 43.3, 21.2, 14.0.
IR (neat) ν 2982, 2937, 1745, 1445, 1257, 1038, 851 cm^{-1}.
HRMS (ESI) calcd for $C_{15}H_{20}BrO_4$ $[M+H]^+$ 343.0545, found 343.0520.

Diethyl 2-bromo-2-(4-cyanobenzyl)malonate (S22)

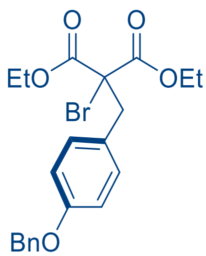


S22

S22 was synthesized according to general procedure 1. Alkylated malonate (1.02 g, 3.7 mmol, 1.0 equiv.), N-bromosuccinimide (1.01 g, 5.6 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 6 : 1), the title compound was isolated as a White solid (946.1 mg, 72% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 4.33-4.21 (m, 4H), 3.68 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.4, 140.0, 132.0, 131.4, 118.7, 111.8, 63.6, 62.1, 43.5, 14.0.
IR (neat) ν 2983, 2939, 1743, 1449, 1273, 1079, 855 cm^{-1}.
HRMS (ESI) calcd for $C_{15}H_{17}BrNO_4$ $[M+H]^+$ 356.0320, found 356.0305.
m.p. 81-83 °C

Diethyl 2-(4-(benzyloxy)benzyl)-2-bromomalonate (S23)



S23

S23 was synthesized according to general procedure 1. Alkylated malonate (213.9 mg, 0.6 mmol, 1.0 equiv.), N-bromosuccinimide (161.8 mg, 0.9 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a White solid (162.4 mg, 62% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43-7.30 (m, 5H), 7.12 (dd, J = 11.4, 2.7 Hz, 2H), 6.89 (dd, J = 11.7, 3.0 Hz, 2H), 5.03 (s, 2H), 4.21-4.10 (m, 4H), 3.60 (t, J = 7.8 Hz, 1H), 3.16 (d, J = 7.8 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H).

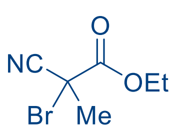
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 158.5, 137.1, 131.7, 128.7, 128.1, 127.6, 126.8, 114.6, 70.1, 63.8, 63.2, 42.9, 14.0.

IR (neat) ν 2981, 2942, 1744, 1449, 1257, 1018, 866 cm^{-1}.

HRMS (ESI) calcd for $C_{21}H_{24}BrO_5$ $[M+H]^+$ 435.0807, found 435.0807.

m.p. 77-79 °C

Ethyl 2-bromo-2-cyanopropanoate (S24)



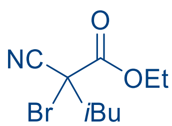
S24

S24 was synthesized according to general procedure 2. Alkylated malonate (526.5 mg, 4.1 mmol, 1.0 equiv.), N-bromosuccinimide (810.8 mg, 4.51 mmol, 1.5 equiv.) were used as a starting material and THF (0.25 M) as a solvent. After purification by column chromatography (hexane : EtOAc = 25 : 1), the title compound was isolated as a colorless oil (186.2 mg, 22% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.43-4.31 (m, 1H), 2.21 (s, 2H), 1.38 (t, J = 7.1 Hz, 2H).

^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 164.6, 116.7, 64.6, 36.7, 28.1, 13.9.
IR (neat) ν 2987, 2940, 1755, 1446, 1296, 1056, 861 cm^{-1}.
HRMS (CI) calcd for $C_6H_9BrNO_2$ $[M+H]^+$ 205.9811, found 205.9818.

Ethyl 2-bromo-2-cyano-4-methylpentanoate (S25)

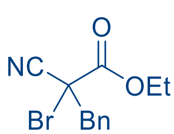


S25

S25 was synthesized according to general procedure 2. Alkylated malonate (1.03 g, 6.0 mmol, 1.0 equiv.), N-bromosuccinimide (1.19 g, 6.6 mmol, 1.5 equiv.) were used as a starting material and THF (0.25 M) as a solvent. After purification by column chromatography (hexane : EtOAc = 50 : 1), the title compound was isolated as a colorless oil (904.4 mg, 61% yield).

^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 4.36 (q, J = 7.0 Hz, 2H), 2.37 (q, J = 7.2 Hz, 1H), 2.26 (dd, J = 14.2, 5.5 Hz, 1H), 2.03-1.90 (m, 1H), 1.37 (t, J = 7.1 Hz, 3H), 1.07 (d, J = 6.9 Hz, 3H), 0.96 (d, J = 6.4 Hz, 3H).
^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 164.8, 116.1, 64.5, 47.9, 41.9, 27.6, 23.3, 22.1, 13.8.
IR (neat) ν 2966, 2938, 1755, 1447, 1276, 1065, 855 cm^{-1}.
HRMS (CI) calcd for $C_9H_{15}BrNO_2$ $[M+H]^+$ 248.0281, found 248.0283.

Ethyl 2-bromo-2-cyano-3-phenylpropanoate (S26)



S26

S26 was synthesized according to general procedure 2. Alkylated malonate (431.1 mg, 2.1 mmol, 1.0 equiv.), N-bromosuccinimide (415.3 mg, 2.31 mmol, 1.5 equiv.) were used as a starting material and THF (0.25 M) as a solvent. After purification by column chromatography (hexane : EtOAc = 25 : 1), the title compound was isolated as a colorless oil (375.4 mg, 64% yield).

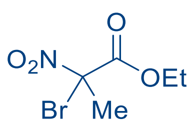
^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.35 (s, 5H), 4.36-4.24 (m, 2H), 3.73 (d, *J* = 13.7 Hz, 1H), 3.52 (d, *J* = 13.7 Hz, 1H), 1.28 (*t*, J = 7.1 Hz, 3H).

^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 164.1, 132.9, 130.6, 128.9, 128.8, 115.6, 64.6, 45.6, 42.7, 13.8.

IR (neat) ν 2985, 2940, 1747, 1455, 1219, 1036, 855 cm^{-1}.

HRMS (ESI) calcd for $C_{12}H_{13}BrNO_2$ $[M+H]^+$ 282.0124, found 282.0117.

Ethyl 2-bromo-2-nitropropanoate (S27)



S27

S27 was synthesized according to general procedure 2. Alkylated malonate (1.02 g, 3.7 mmol, 1.0 equiv.), N-bromosuccinimide (1.01 g, 5.6 mmol, 1.5 equiv.) were used as a starting material and DMF (0.25 M) as a solvent. After purification by column chromatography (hexane : EtOAc = 25 : 1), the title compound was isolated as a colorless oil (946.1 mg, 72% yield).

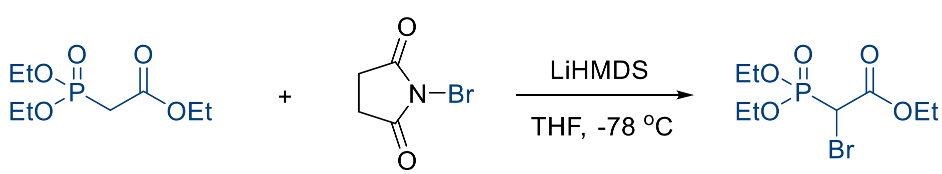
^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 4.36 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 163.7, 89.1, 64.6, 29.1, 13.8.

IR (neat) ν 2987, 2941, 1759, 1573, 1260, 1012, 856 cm^{-1}.

HRMS (CI) calcd for $C_5H_9BrNO_4$ $[M+H]^+$ 225.9709, found 225.9713.

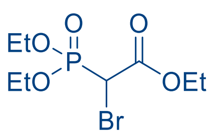
The formation of Bromo Phosphonoacetate from Phosphonoacetate and NBS.[5]



Phosphonoacetate ***NBS*** ***Bromo Phosphonoacetate (S)***

To an oven-dried round bottom flask was added triethyl phosphonoacetate (1.13 g, 5.0 mmol, 1.0 equiv.) and dry THF (10 mL) and then the reaction vessel was cooled to -78 ^{o}C under argon gas. Lithium bis(trimethylsilyl)amide, 1M solution in THF (10 mL, 2.0 equiv.) was added dropwise for 10 min by syringe pump to the reaction vessel. A solution of N-bromosuccinimide (1.08 g, 6.0 mmol, 1.2 equiv.) in THF (10 mL) was added dropwise for 20 min by syringe pump to the reaction mixture. After resulting mixture was stirred at -78 ^{o}C for 30 min, the reaction was warmed to 0 ^{o}C. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with EtOAc (2 x 20 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired bromo phosphonoacetate.

Ethyl 2-bromo-2-(diethoxyphosphoryl)acetate (S28)

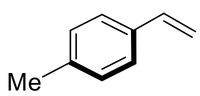


S28

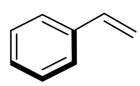
S28 was synthesized according to above procedure. After purification by column chromatography (hexane : EtOAc = 1 : 1), the title compound was isolated as a yellow oil (172.1 mg, 11% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.35 (d, J = 13.7 Hz, 1H), 4.30-4.23 (m, 7H), 1.37 (t, J = 7.1 Hz, 6H), 1.31 (t, J = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.0, 64.7, 64.6, 63.1, 36.5, 35.1, 16.4, 16.3, 13.9.
IR (neat) ν 2981, 2942, 1744, 1449, 1257, 1018, 866 cm^{-1}.
HRMS (ESI) calcd for $C_8H_{17}BrO_5P$ $[M+H]^+$ 302.9992, found 302.9978.

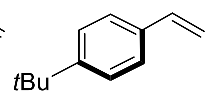
List of Substrate – Alkene



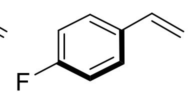
S'1



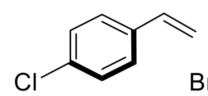
S'2



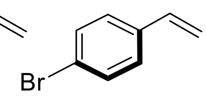
S'3



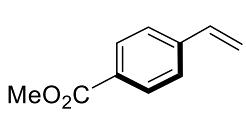
S'4



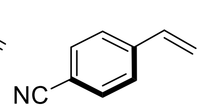
S'5



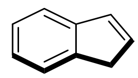
S'6



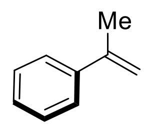
S'7



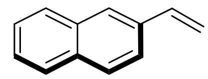
S'8



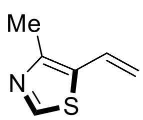
S'9



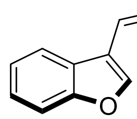
S'10



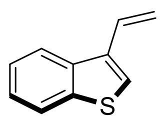
S'11



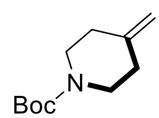
S'12



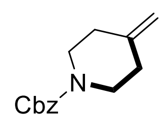
S'13



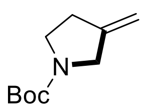
S'14



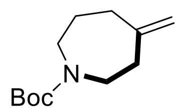
S'15



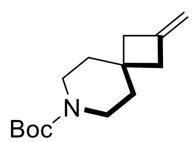
S'16



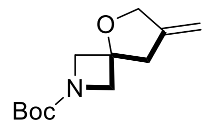
S'17



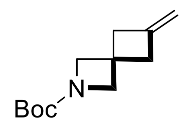
S'18



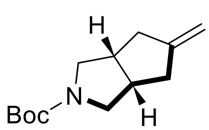
S'19



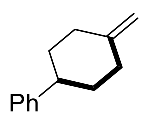
S'20



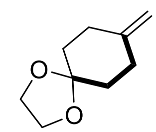
S'21



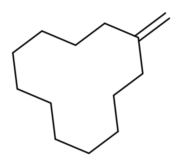
S'22



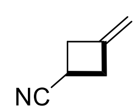
S'23



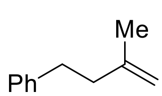
S'24



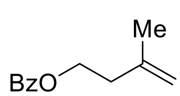
S'25



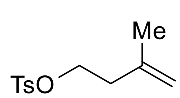
S'26



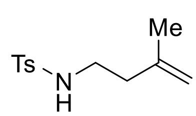
S'27



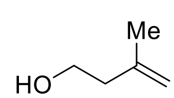
S'28



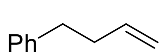
S'29



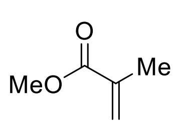
S'30



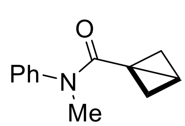
S'31



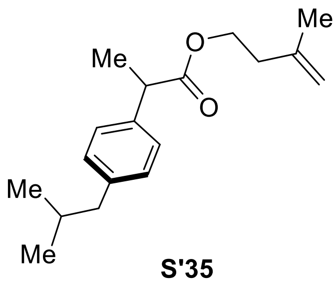
S'32



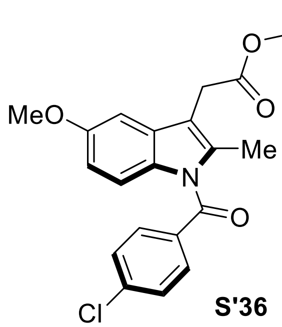
S'33



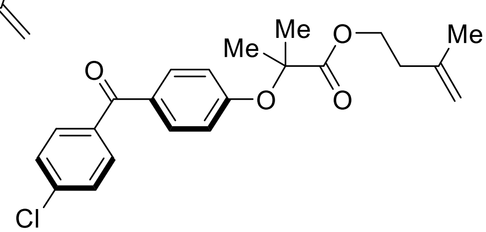
S'34



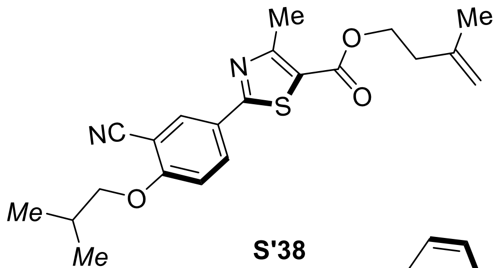
S'35



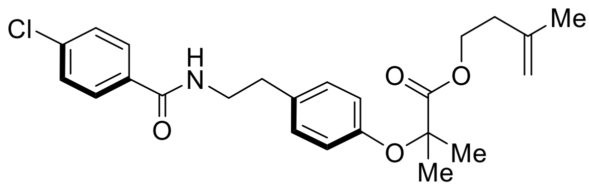
S'36



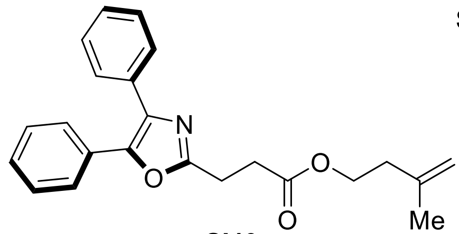
S'37



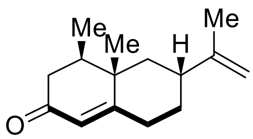
S'38

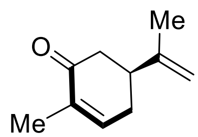


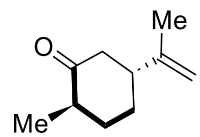
S'39

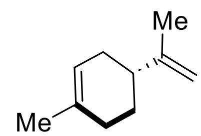


S'40

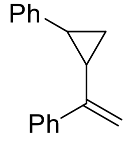


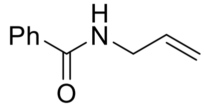


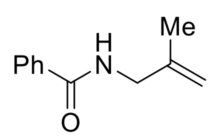




S'41 **S'42** **S'43** **S'44**



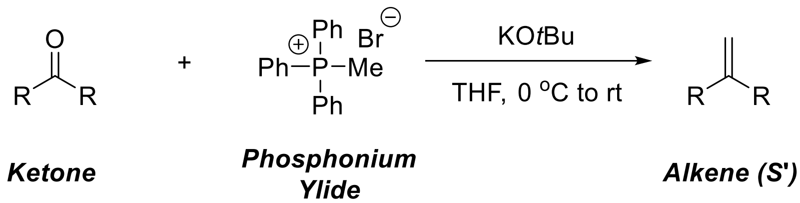




S'45 **S'46** **S'47**

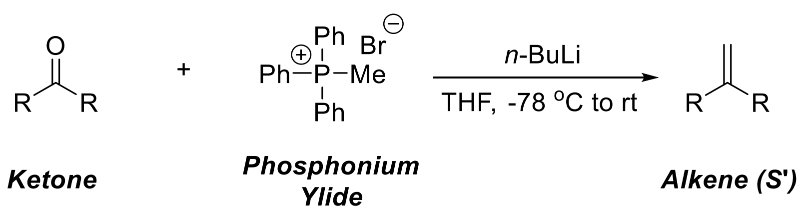
S'1-S'12, **S'15-S'16**, **S'24**, **S'26**, **S'31-S'33** and **S'41-S'44** are commercially available. Other substrates are synthesized following the known method or modified method in literature.

General procedure 3 for the formation of Alkene from Ketone and Phosphonium ylide.[6]



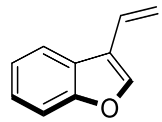
To an oven-dried round bottom flask was added Methyltriphenylphosphonium bromide (1.5 equiv.), KO^{t}Bu (1.5 equiv.), and dry THF (0.5 M) at 0 ^{o}C under argon gas. After resulting mixture was stirred at 0 ^{o}C for 30 min, Ketone (1.0 equiv.) in THF (0.5 M) was then added to a reaction. The reaction was further stirred at room temperature for 12 h. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with EtOAc (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired Alkene (**S'**)

General procedure 4 for the formation of Alkene from Ketone and Phosphonium ylide.[6]



To an oven-dried round bottom flask was added Methyltriphenylphosphonium bromide (1.5 equiv.), and dry THF (0.1 M) under argon gas. After resulting mixture was cooled to -78 ^{o}C, 2.5 M *n*-BuLi in hexane was added dropwise to a reaction. The solution was allowed to warm to room temperature and stirred for 30 min before ketone (1.0 equiv.) was added. The reaction was further stirred at room temperature for 12 h and quenched with H_2O (30 mL) cautiously. The mixture was extracted with EtOAc (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford desired Alkene (**S'**)

3-Vinylbenzo[b]thiophene (S'13)

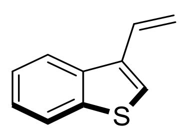


S'13

S'13 was synthesized according to general procedure 3. ketone (820.1 g, 5.5 mmol, 1.0 equiv.), phosphonium ylide (2.98 g, 8.25 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane = 100%), the title compound was isolated as a colorless oil (713.1 mg, 90% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.31-7.26 (m, 1H), 7.23-7.19 (m, 1H), 6.69-6.64 (m, 1H), 6.61 (s, 1H), 5.98 (d, *J* = 17.5 Hz, 1H), 5.40 (d, *J* = 11.0 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.0, 154.9, 128.9, 125.4, 124.8, 122.9, 121.1, 115.9, 111.1, 104.9.

3-Vinylbenzofuran (S'14)

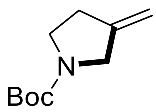


S'14

S'14 was synthesized according to general procedure 3. ketone (919.8 g, 5.5 mmol, 1.0 equiv.), phosphonium ylide (2.98 g, 8.25 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane = 100%), the title compound was isolated as a white solid (786.3 mg, 89% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78-7.74 (m, 1H), 7.71-7.67 (m, 1H), 7.34-7.27 (m, 2H), 7.17 (s, 1H), 6.92 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.67 (d, *J* = 17.5 Hz, 1H), 5.31 (d, *J* = 11.0 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.2, 140.1, 139.0, 130.7, 124.9, 124.5, 123.7, 123.2, 122.4, 116.1.

tert-Butyl 3-methylenepyrrolidine-1-carboxylate (S'17)

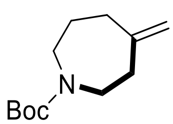


S'17

S'17 was synthesized according to general procedure 3. ketone (1.05 g, 5.5 mmol, 1.0 equiv.), phosphonium ylide (2.98 g, 8.25 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 15 : 1), the title compound was isolated as a colorless solid (494.7 mg, 49% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.96 (d, *J* = 7.3 Hz, 2H), 3.92 (s, 2H), 3.49-3.42 (m, 2H), 2.54 (t, *J* = 7.3 Hz, 2H), 1.46 (s, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.6, 145.9, 106.8, 79.4, 50.4, 45.8, 32.0, 28.7.

tert-Butyl 4-methyleneazepane-1-carboxylate (S'18)

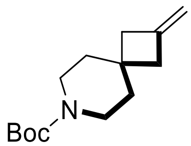


S'18

S'18 was synthesized according to general procedure 3. ketone (1.10 g, 5.0 mmol, 1.0 equiv.), phosphonium ylide (2.71 g, 7.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 15 : 1), the title compound was isolated as a colorless solid (201.5 mg, 19% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.76 (d, *J* = 14.2 Hz, 2H), 3.40-3.36 (m, 4H), 2.40 (t, *J* = 6.2 Hz, 2H), 2.23-2.20 (m, 2H), 1.68 (td, *J* = 12.3, 5.9 Hz, 2H), 1.44 (s, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.4, 148.9, 112.9, 79.2, 48.2, 46.6, 36.7, 34.8, 29.0, 28.6.

tert-Butyl 2-methylene-7-azaspiro[3.5]nonane-7-carboxylate (S'19)

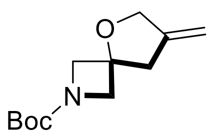


S'19

S'19 was synthesized according to general procedure 3. ketone (2.47 g, 10.0 mmol, 1.0 equiv.), phosphonium ylide (5.41 g, 15.0 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 10 : 1), the title compound was isolated as a colorless solid (1.91 g, 80% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.83-4.81 (m, 2H), 3.31 (t, *J* = 5.5 Hz, 4H), 2.41 (t, *J* = 2.5 Hz, 4H), 1.54 (t, *J* = 5.5 Hz, 4H), 1.44 (s, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.1, 144.6, 107.8, 79.4, 41.9, 41.3, 36.7, 33.8, 28.6.

tert-Butyl 7-methylene-5-oxa-2-azaspiro[3.4]octane-2-carboxylate (S'20)

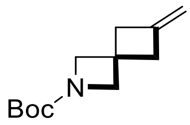


S'20

S'20 was synthesized according to general procedure 3. ketone (1.05 g, 4.5 mmol, 1.0 equiv.), phosphonium ylide (2.44 g, 8.25 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 10 : 1), the title compound was isolated as a colorless solid (781.5 mg, 77% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.03 (t, *J* = 2.3 Hz, 1H), 4.94 (t, *J* = 2.1 Hz, 1H), 4.33 (s, 2H), 3.98 (d, *J* = 9.1 Hz, 2H), 3.87 (d, *J* = 9.1 Hz, 2H), 2.72 (s, 2H), 1.42 (d, *J* = 0.9 Hz, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.5, 145.7, 106.0, 77.2, 76.8, 70.6, 61.2, 42.2, 28.5.

tert-Butyl 6-methylene-2-azaspiro[3.3]heptane-2-carboxylate (S'21)

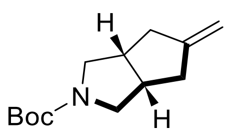


S'21

S'21 was synthesized according to general procedure 3. ketone (1.09 g, 5.0 mmol, 1.0 equiv.), phosphonium ylide (2.71 g, 7.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 15 : 1), the title compound was isolated as a colorless solid (616.5 mg, 59% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.81-4.79 (m, 2H), 3.92 (s, 4H), 2.84 (t, *J* = 2.3 Hz, 4H), 1.43 (s, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.4, 143.0, 107.3, 79.5, 61.2, 43.0, 33.2, 28.5.

tert-Butyl (3aR,6aR)-5-methylenehexahydrocyclopenta[c]pyrrole-2(1H)-carboxylate (S'22)

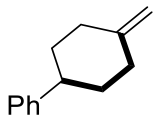


S'22

S'22 was synthesized according to general procedure 3. ketone (1.26 g, 5.5 mmol, 1.0 equiv.), phosphonium ylide (2.98 g, .5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 15 : 1), the title compound was isolated as a colorless oil (616.5 mg, 59% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.88-4.86 (m, 2H), 3.51 (dd, *J* = 11.2, 7.5 Hz, 2H), 3.10 (dd, *J* = 11.0, 4.6 Hz, 2H), 2.71-2.62 (m, 2H), 2.58-2.50 (m, 2H), 2.20-2.14 (m, 2H), 1.44 (s, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.8, 151.3, 107.2, 79.2, 51.1, 42.7, 37.5, 28.7.

(4-Methylenecyclohexyl)benzene (S'23)

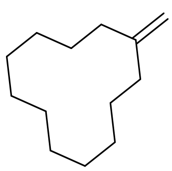


S'23

S'23 was synthesized according to general procedure 3. ketone (898.1 mg, 5.0 mmol, 1.0 equiv.), phosphonium ylide (2.89 g, 8.0 mmol, 1.6 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a colorless oil (780.9 mg, 91% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.23-7.18 (m, 3H), 4.70 (d, J = 1.4 Hz, 2H), 2.69 (t, J = 12.1 Hz, 1H), 2.44 (dd, J = 13.3, 1.8 Hz, 2H), 2.24-2.17 (m, 2H), 2.00 (d, J = 12.8 Hz, 2H), 1.57 (qd, J = 12.8, 2.9 Hz, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.0, 147.0, 128.5, 128.5, 127.0, 126.1, 107.5, 44.3, 35.7, 35.3.

Methylenecyclododecane (S'25)

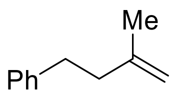


S'25

S'25 was synthesized according to general procedure 4. ketone (1.88 g, 10.0 mmol, 1.0 equiv.), phosphonium ylide (5.41 g, 15.0 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane = 100%), the title compound was isolated as a colorless oil (1.98 g, 99% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.23-7.18 (m, 3H), 4.70 (d, J = 1.4 Hz, 2H), 2.69 (t, J = 12.1 Hz, 1H), 2.44 (dd, J = 13.3, 1.8 Hz, 2H), 2.24-2.17 (m, 2H), 2.00 (d, J = 12.8 Hz, 2H), 1.57 (qd, J = 12.8, 2.9 Hz, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.7, 110.5, 33.2, 24.6, 24.3, 23.9, 23.4, 22.8.

(3-Methylbut-3-en-1-yl)benzene (S'27)



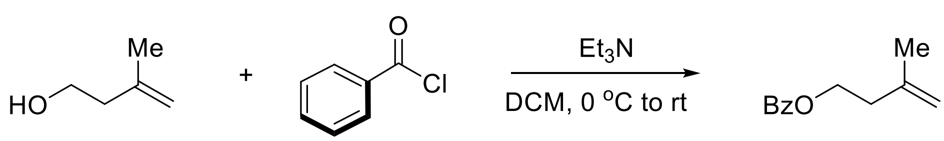
S'27

S'27 was synthesized according to general procedure 4. ketone (1.51 g, 10.0 mmol, 1.0 equiv.), phosphonium ylide (5.77 g, 16.0 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane = 100%), the title compound was isolated as a colorless solid (1.11 g, 76% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.23-7.18 (m, 3H), 4.75 (dt, J = 11.1, 1.1 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.34 (t, *J* = 8.2 Hz, 2H), 1.79 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.5, 142.4, 128.5, 128.4, 125.9, 110.3, 77.5, 77.2, 76.8, 39.7, 34.4, 22.7.

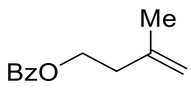
The formation of S'28 from S'31 and Benzyl Chloride.[7]



S'*31** ***Benzoyl Chloride ***S'*28**

To an oven-dried round bottom flask was added 3-Methyl-3-buten-1-ol (2.30 mL, 22.0 mmol, 1.1 equiv.), Et_3N (5.63 mL, 40.0 mmol, 2.0 equiv.), and dry DCM (40.0 mL, 0.5 M) under argon gas. After resulting mixture was stirred at 0 °C for 5 min, benzyl chloride (1.0 equiv.) was then added dropwise to a reaction. The reaction was further stirred at room temperature for 3 h. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with DCM (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum.

3-Methylbut-3-en-1-yl benzoate (S'28)

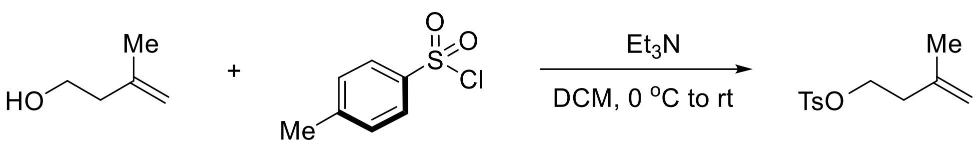


S'28

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 (dt, J = 8.8, 2.2 Hz, 1H), 7.37 (dd, J = 7.1, 1.6 Hz, 1H), 7.08 (d, J = 8.7 Hz, 1H), 6.81 (d, J = 8.7 Hz, 1H), 6.06 (s, 1H), 4.73 (d, J = 32.0 Hz, 1H), 4.29 (t, J = 6.9 Hz, 1H), 3.66 (q, J = 6.6 Hz, 1H), 2.86 (t, J = 6.9 Hz, 1H), 2.34 (t, J = 6.6 Hz, 1H), 1.72 (s, 2H), 1.57 (s, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.3, 166.5, 154.3, 141.4, 137.8, 133.2, 132.5, 129.6, 129.0, 128.4, 119.8, 112.7, 79.3, 63.6, 41.4, 36.7, 34.9, 25.6, 22.5.

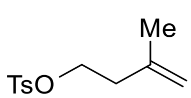
The formation of S'29 from S'31 and Tosyl Chloride.[7]



S*'31** ***Tosyl Chloride ***S*'29**

To an oven-dried round bottom flask was added 3-Methyl-3-buten-1-ol (2.61 mL, 22.0 mmol, 1.0 equiv.), Et_3N (4.22 mL, 30.0 mmol, 1.2 equiv.), and dry DCM (50.0 mL, 0.5 M) under argon gas. After resulting mixture was stirred at 0 °C for 5 min, tosyl chloride (1.1 equiv.) was then added portionwise to a reaction. The reaction was further stirred at room temperature for 3 h. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with DCM (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. After purification by column chromatography (hexane : EtOAc = 30 : 1), **S'29** was isolated as a colorless oil (3.80 g, 63% yield).

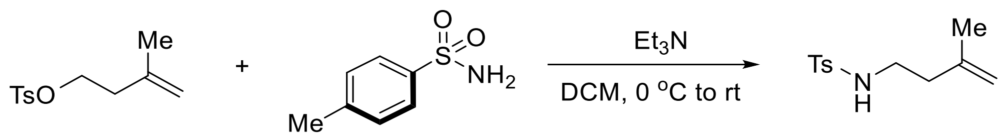
4-Methyl-N-(3-methylbut-3-en-1-yl)benzenesulfonamide (S'29)



S'29

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.73 (d, *J* = 45.5 Hz, 2H), 4.12 (t, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), 2.34 (t, *J* = 6.9 Hz, 2H), 1.65 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.9, 140.2, 133.3, 129.9, 128.0, 113.2, 68.6, 36.9, 22.4, 21.7.

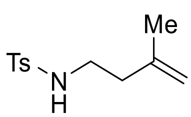
The formation of S'30 from S'29 and Tosylamide.[7]



S'29 ***Tosylamide*** **S'30**

To an oven-dried round bottom flask was added **S'29** (721.0 mg, 3.0 mmol, 1.0 equiv.), *p*-toluenesulfonamide (616.4 mg, 3.6 mmol, 1.2 equiv.), K_2CO_3 (497.6 mg, 3.6 mmol, 1.2 euiqv.) and dry DMF (6.0 mL, 0.5 M) under argon gas. The reaction mixture was heated to 80 °C for 12 h. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with EtOAc (3 x 30 mL), washed with brine (2 x 30 mL), dried over $MgSO_4$, and concentrated under vacuum. After purification by column chromatography (hexane : EtOAc = 30 : 1), **S'30** was isolated as a white solid (675.3 mg, 94% yield).

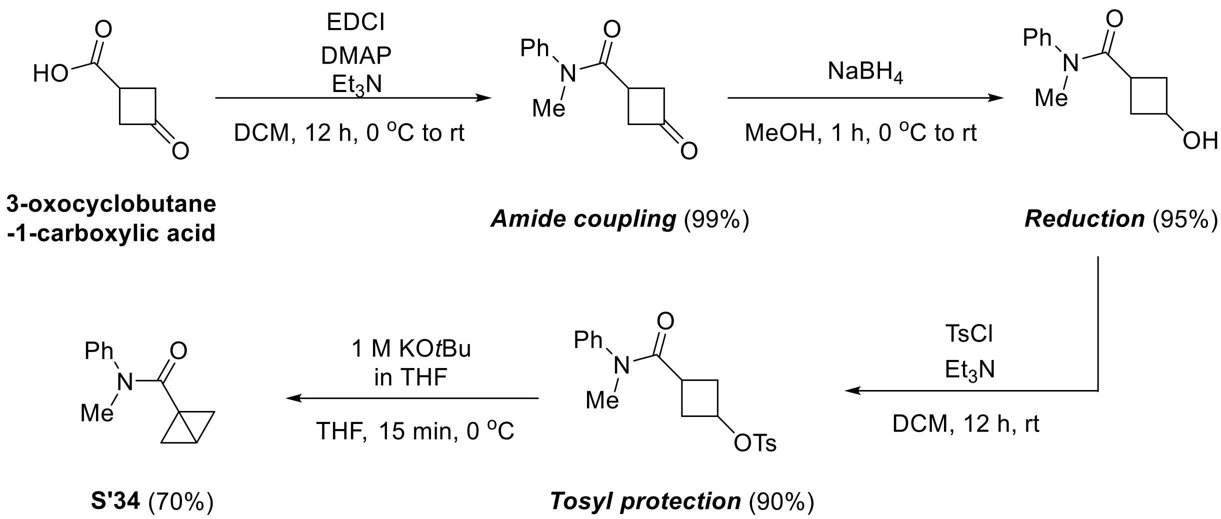
4-Methyl-N-(3-methylbut-3-en-1-yl)benzenesulfonamide (S'30)



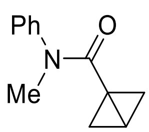
S'30

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.79 (s, 1H), 4.64 (s, 1H), 4.53 (s, 1H), 3.04 (q, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 2.14 (t, *J* = 6.6 Hz, 2H), 1.59 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.5, 141.6, 136.9, 129.8, 127.2, 113.3, 40.6, 37.3, 21.8, 21.6.

The formation of S'34 from 3-oxocyclobutane-1-carboxylic acid.[8]



To an oven-dried round bottom flask was added tosyl protection product (7.19 g, 20.0 mmol ,1.0 equiv.), 1.0 M KO^{t}Bu in THF (22.0 mL, 22.0 mmol, 1.1 equiv.), and dry THF (133.0 mL) at 0 °C under argon gas. After the reaction was further stirred at 0 °C for 15 min, the reaction mixture was then quenched with sat.NH_4Cl (50.0 mL), extracted with EtOAc (2 x 50 mL), washed with brine (40 mL), dried over $MgSO_4$, and concentrated under vacuum. After purification by column chromatography (hexane : EtOAc = 8 : 1), **S'34** was isolated as a colorless oil (2.63 g, 70% yield).

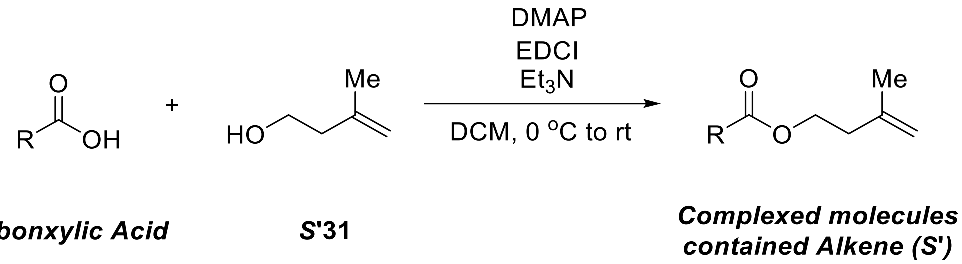


S'34

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37 (td, *J* = 6.7, 1.8 Hz, 2H), 7.27-7.22 (m, 3H), 3.35 (s, 3H), 2.04-2.01 (m, 1H), 1.81 (d, *J* = 3.2 Hz, 2H), 0.78 (d, *J* = 2.3 Hz, 2H).

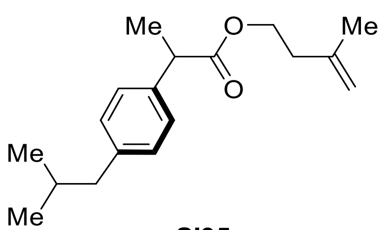
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 145.2, 129.2, 127.0, 126.6, 38.1, 37.2, 17.0, 10.1.

General procedure 5 for the formation of complexed molecules contained Alkene from Carboxylic Acids and S'31.[9]



To an oven-dried round bottom flask was added carboxylic acid (1.0 equiv.), 4-dimethylamino pyridine (0.5 equiv.), and dry DCM (0.5 M) at 0 °C under argon gas. After resulting mixture was stirred at 0 °C for 30 min, 3-Methyl-3-buten-1-ol (1.5 equiv.) and Et_3N (1.5 equiv.) were then added to a reaction at 0 °C. The solution was allowed to warm to room temperature and was further stirred for 12 h. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with DCM (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford complexed molecules contained alkenes (**S′35- S′39**).

3-Methylbut-3-en-1-yl 2-(4-isobutylphenyl)propanoate (S'35)



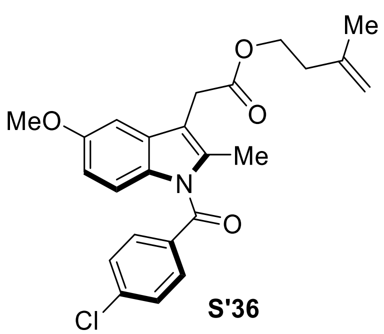
S'35

S'35 was synthesized according to general procedure 5. Ibuprofen (625.1 mg, 3.0 mmol, 1.0 equiv.) and 3-Methyl-3-buten-1-ol (0.46 mL, 4.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 15 : 1), the title compound was isolated as a colorless oil (818.7 mg, 99% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.69 (d, *J* = 38.1 Hz, 2H), 4.20-4.16 (m, 2H), 3.68 (q, *J* = 7.0 Hz, 1H), 2.45 (d, *J* = 7.4 Hz, 2H), 2.29 (t, *J* =

6.9 Hz, 2H), 1.85 (tt, *J* = 20.3, 6.7 Hz, 1H), 1.69 (s, 3H), 1.48 (d, *J* = 7.4 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.9, 141.8, 140.6, 137.9, 129.4, 127.3, 112.4, 63.0, 45.3, 45.2, 36.8, 30.3, 22.5, 18.6.

3-Methylbut-3-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (S'36)

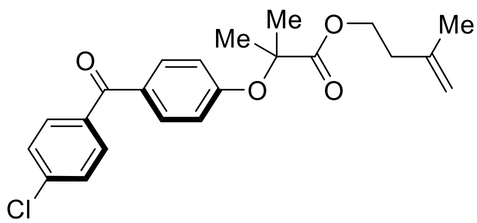


S'36

S'36 was synthesized according to general procedure 5. Indomethacin (1.08 g, 3.0 mmol, 1.0 equiv.) and 3-Methyl-3-buten-1-ol (0.46 mL, 4.5 mmol, 1.1 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 8 : 1), the title compound was isolated as a white solid (1.01 g, 79% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 6.6, 2.1 Hz, 2H), 7.47 (dd, *J* = 6.6, 2.1 Hz, 2H), 6.96 (d, *J* = 2.3 Hz, 1H), 6.86 (d, *J* = 9.1 Hz, 1H), 6.67 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.72 (d, *J* = 32.5 Hz, 2H), 4.22 (t, *J* = 6.9 Hz, 2H), 3.84 (s, 3H), 3.65 (s, 2H), 2.38 (s, 3H), 2.33 (t, *J* = 6.9 Hz, 2H), 1.71 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 168.4, 156.2, 141.6, 139.4, 136.1, 134.1, 131.3, 130.9, 130.8, 129.2, 115.1, 112.8, 112.5, 111.8, 101.5, 63.3, 55.8, 36.8, 30.5, 22.5, 13.5.

3-Methylbut-3-en-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (S'37)

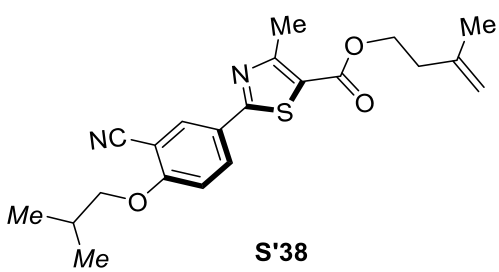


S'37

S'37 was synthesized according to general procedure 5. Fenofibric acid (965.9 mg, 3.0 mmol, 1.0 equiv.) and 3-Methyl-3-buten-1-ol (0.46 mL, 4.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 8 : 1), the title compound was isolated as a white solid (975.2 mg, 84% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (tt, J = 8.9, 2.2 Hz, 4H), 7.44 (dt, J = 8.9, 2.2 Hz, 2H), 6.86 (dt, J = 9.3, 2.3 Hz, 2H), 4.76-4.68 (m, 2H), 4.29 (t, J = 6.9 Hz, 2H), 2.32 (t, J = 6.7 Hz, 2H), 1.71 (s, 3H), 1.66 (s, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.3, 173.7, 159.8, 141.3, 138.5, 136.5, 132.1, 131.3, 130.5, 128.7, 117.5, 112.8, 79.5, 63.8, 36.7, 25.6, 22.4

3-Methylbut-3-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (S'38)

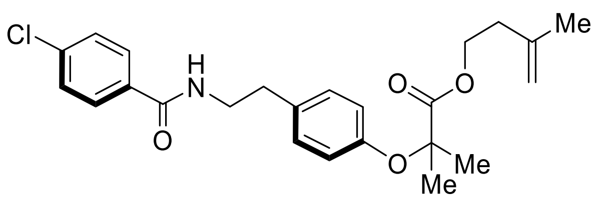


S'38

S'38 was synthesized according to general procedure 5. Febuxostat (968.5 mg, 3.0 mmol, 1.0 equiv.) and 3-Methyl-3-buten-1-ol (0.46 mL, 4.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 5 : 1 : 1), the title compound was isolated as a white solid (914.6 mg, 79% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.5 Hz, 1H), 8.09 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 4.83 (d, *J* = 19.8 Hz, 2H), 4.41 (t, *J* = 6.7 Hz, 2H), 3.90 (d, *J* = 6.4 Hz, 2H), 2.75 (s, 3H), 2.46 (t, *J* = 6.7 Hz, 2H), 2.25-2.15 (m, 1H), 1.81 (s, 3H), 1.09 (d, *J* = 6.9 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.4, 162.6, 162.1, 161.3, 141.5, 132.7, 132.3, 126.2, 122.0, 115.5, 112.8, 112.7, 103.1, 75.8, 63.6, 36.9, 28.3, 22.6, 19.2, 17.6.

3-Methylbut-3-en-1-yl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate (S'39)

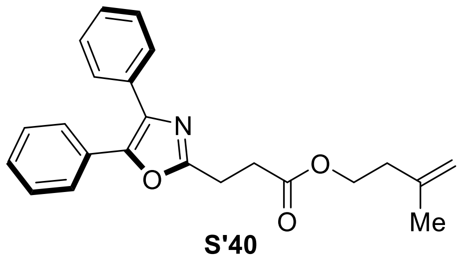


S'39

S'39 was synthesized according to general procedure 5. Bezafibrate (886.1 mg, 2.4 mmol, 1.0 equiv.) and 3-Methyl-3-buten-1-ol (0.37 mL, 3.6 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 5 : 1 : 1), the title compound was isolated as a white solid (895.5 mg, 87% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 8.8, 2.2 Hz, 1H), 7.37 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 6.06 (s, 1H), 4.73 (d, *J* = 32.0 Hz, 1H), 4.29 (t, *J* = 6.9 Hz, 1H), 3.66 (q, *J* = 6.6 Hz, 1H), 2.86 (t, *J* = 6.9 Hz, 1H), 2.34 (t, *J* = 6.6 Hz, 1H), 1.72 (s, 2H), 1.57 (s, 4H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.3, 166.5, 154.3, 141.4, 137.8, 133.2, 132.5, 129.6, 129.0, 128.4, 119.8, 112.7, 79.3, 63.6, 41.4, 36.7, 34.9, 25.6, 22.5.

3-Methylbut-3-en-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (S'40)

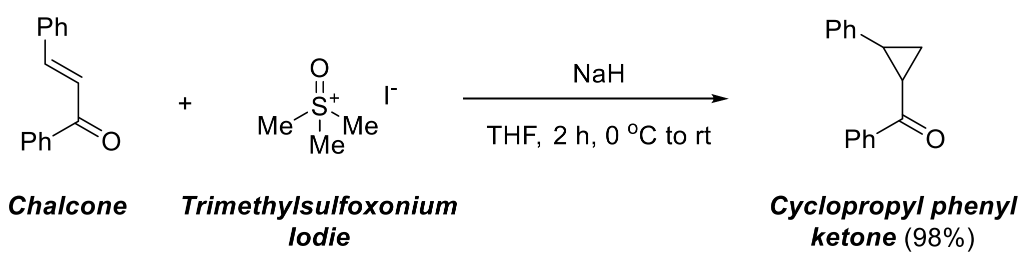


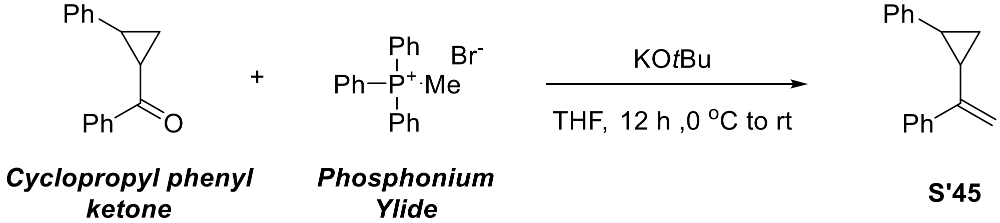
S'40

S'40 was synthesized according to general procedure 5. Oxaprozin (880.0 mg, 3.0 mmol, 1.0 equiv.) and 3-Methyl-3-buten-1-ol (0.46 mL, 4.5 mmol, 1.5 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 15 : 1), the title compound was isolated as a colorless oil (1.05 g, 97% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (dt, J = 8.2, 1.8 Hz, 2H), 7.58-7.56 (m, 2H), 7.39-7.30 (m, 6H), 4.76 (d, J = 24.7 Hz, 2H), 4.25 (t, J = 6.9 Hz, 2H), 3.19 (t, J = 7.5 Hz, 2H), 2.91 (t, J = 7.5 Hz, 2H), 2.35 (t, J = 6.9 Hz, 2H), 1.74 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.1, 161.9, 145.6, 141.7, 135.2, 132.5, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 126.6, 112.4, 63.1, 36.8, 31.3, 23.7, 22.6.

The formation of S′45 for radical clock experiment.[10]

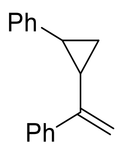




S'45

To an oven-dried round bottom flask was added Methyltriphenylphosphonium bromide (3.25 g, 2.0 equiv.), KO^{t}Bu (1.03 g, 2.0 equiv.), and dry THF (18.0 mL) at 0 °C under argon gas. After resulting mixture was stirred at 0 °C for 30 min, cyclopropyl phenyl ketone[7] (1.02 g, 1.0 equiv.) in THF (4.5 mL) was then added to a reaction. The reaction was further stirred at room temperature for 12 h. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with EtOAc (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. After purification by column chromatography (hexane : EtOAc : DCM= 20 : 1 : 1), **S'45** was isolated as a colorless oil (911.4 mg, 92% yield).

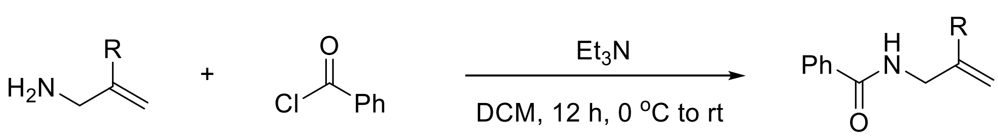
(1-(2-Phenylcyclopropyl)vinyl)benzene (S'45)



S'45

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.34-7.26 (m, 5H), 7.23-7.16 (m, 3H), 5.39 (s, 1H), 5.06 (s, 1H), 2.05-1.96 (m, 2H), 1.45-1.40 (m, 1H), 1.32-1.27 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 142.7, 141.2, 128.6, 128.4, 127.7, 126.2, 125.9, 109.5, 28.0, 26.6, 16.0.

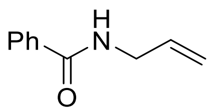
General procedure 6 for formation of S'46-47 for carbocation trapping experiment.[6]



Allylamine R = H, Me ***Benzoyl Chloride*** **S'46**, R = H **S'47**, R = Me

To an oven-dried round bottom flask was added allylamine (1.0 equiv.), Et_3N (3.0 equiv.), and dry DCM (0.25 M) at 0 °C under argon gas. After resulting mixture was stirred at 0 °C for 5 min, benzoyl chloride (1.1 equiv.) was added to a reaction. The reaction was further stirred at room temperature for 12 h. The reaction mixture was then quenched with H_2O (30.0 mL), extracted with EtOAc (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford **S'46** and **S'47**.

N-Allylbenzamide (S'46)

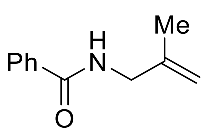


S'46

S'46 was synthesized according to general procedure 6. Allylamine hydrochloride (472.5 mg, 5.0 mmol, 1.0 equiv.) and benzoyl chloride (0.43 mL, 5.5 mmol, 1.1 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 2 : 1), the title compound was isolated as a colorless solid (692.0 mg, 86% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.52-7.48 (m, 1H), 7.44-7.41 (m, 2H), 6.27 (s, 1H), 5.99-5.89 (m, 1H), 5.26 (dd, J = 17.5, 1.4 Hz, 1H), 4.09 (t, J = 5.7 Hz, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.5, 134.6, 134.3, 131.6, 128.7, 127.0, 116.8, 42.6.

N-(2-Methylallyl)benzamide (S'47)



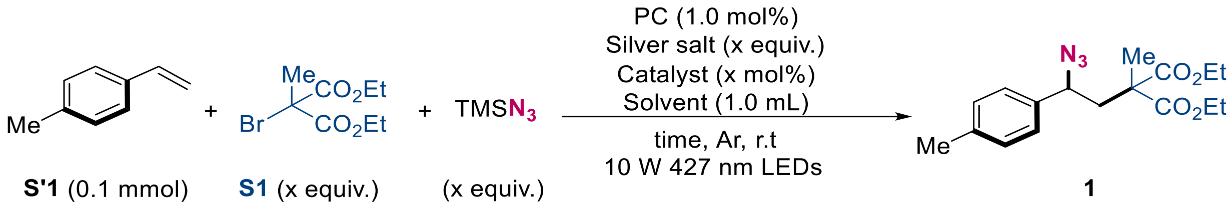
S'47

S'47 was synthesized according to general procedure 6. 2-Methylallylamine (359.2 mg, 5.0 mmol, 1.0 equiv.) and benzoyl chloride (0.43 mL, 5.5 mmol, 1.1 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 3 : 1 : 1), the title compound was isolated as a white solid (663.3 mg, 76% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.52-7.42 (m, 3H), 6.25 (s, 1H), 4.90 (d, J = 9.1 Hz, 2H), 4.03 (d, J = 5.9 Hz, 2H), 1.80 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.5, 142.2, 134.7, 131.6, 128.7, 127.0, 111.3, 45.6, 20.6.

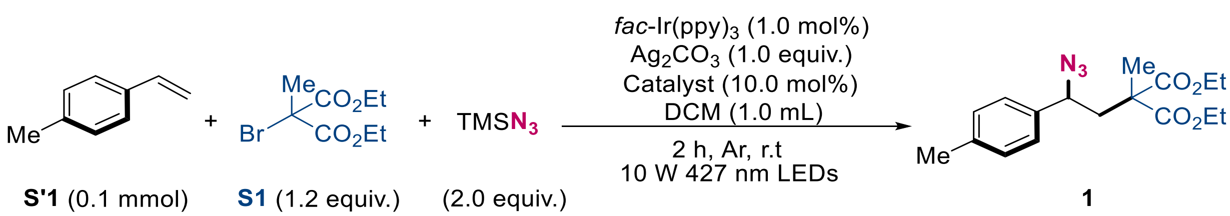
III. Optimization of 1,2-Carboheterofunctionalization

Optimization of 1,2-Carboheterofunctionalization of styrenes



To an oven-dried 8 mL vial was added Photocatalyst (1.0 mol%), silver salt (x equiv.), **S** (x equiv.), and catalyst (10.0 mol%) under Ar condition (The vial was capped with rubber septum and Ar balloon). The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'1** (13.3 µL, 0.1 mmol, 1.0 equiv.) and fresh $TMSN_3$ (x equiv.) to a reaction mixture (If the styrene is a volatile, it should be subjected to Ar purging prior to use.). The vial was charged with anhydrous solvent (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 2 h under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (10 mL), and concentrated under vacuum. To evaluate yield of the products, CH_2Br_2 (7.0 µL) as internal standard was added to the residue. The mixture was diluted with $CDCl_3$ and analyzed by ^{1}H-NMR.

Table 1. Optimization of diverse Catalysts.

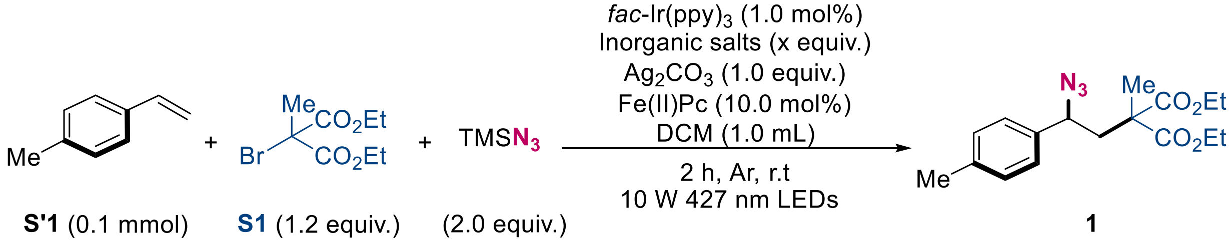


Entry	Catalyst (10.0 mol%)	Yield (%)[a]
1	$FeCl_2$	33
2	$FeBr_2$	56
3	FeI_2	25

4	Fe(OTf)$_2$	45
5	**Fe(OAc)$_2$**	**75**
6	FeCl$_3$ 6H$_2$O	42
7	Fe(acac)$_3$	40
8	**Fe(II)Pc**	**81**
9	MnCl$_2$	21
10	Mn(OAc)$_2$ 4H$_2$O	48
11	CoCl$_2$	15
12	Co(OAc)2 4H$_2$O	41

[a]Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard.

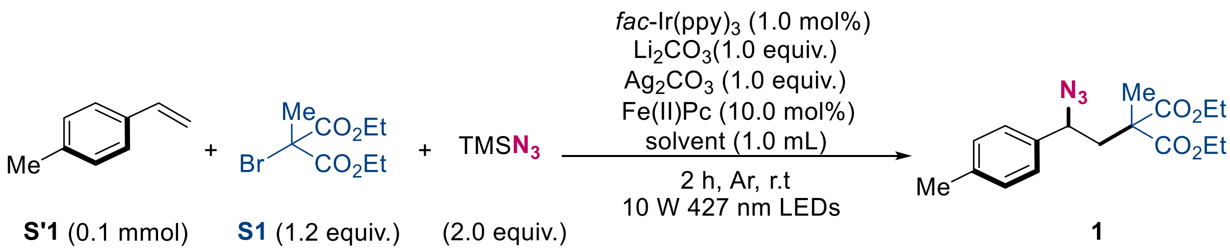
Table 2. Optimization of Inorganic salts.



Entry	Inorganic salts (Equiv.)	Yield (%)[a]
1	**Li$_2$CO$_3$ (1.0)**	**98 (96)[b]**
2	Li$_2$BF$_4$ (1.0)	87
3	LiOTf (1.0)	55
4	LiPF$_6$ (1.0)	84
5	LiNO$_3$ (1.0)	5
6	LiCl (1.0)	62
7	Na$_2$CO$_3$ (1.0)	50
8	K$_2$CO$_3$ (1.0)	73
9	Cs$_2$CO$_3$ (1.0)	66
10	Li$_2$CO$_3$ (0.5)	90
11	Li$_2$CO$_3$ (0.25)	87

[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] Isolated yield.

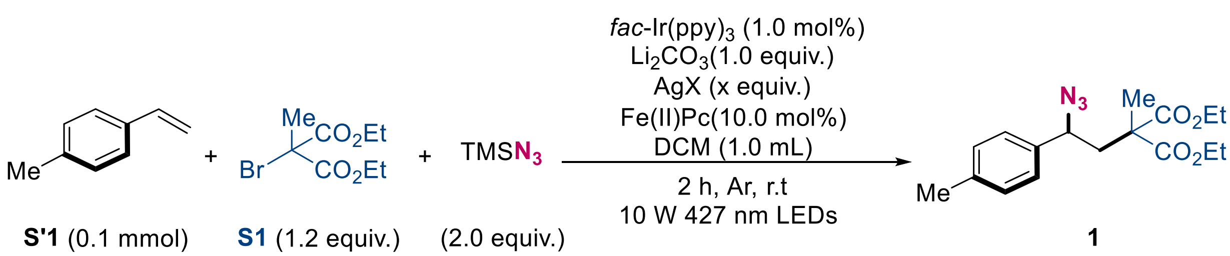
Table 3. Optimization of Solvent.



Entry	Solvent (1.0 mL)	Yield (%)[a]
1	**DCM**	**98 (96)[b]**
2	DCE	73
3	Ether	44
4	Dioxane	49
5	ACN	57
6	DMF	5
7	THF	9

[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] Isolated yield.

Table 4. Optimization of Silver salts.

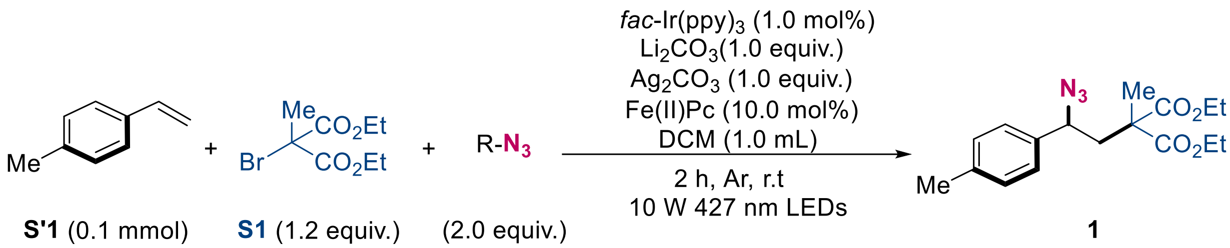


Entry	Silver salts (Equiv.)	Yield (%)[a]
1	**Ag_2CO_3 (1.0)**	**98 (96)[b]**
2	$AgPF_6$ (1.0)	N.D
3	$AgBF_4$ (1.0)	49

4	AgOTf (1.0)	18
5	AgF (1.0)	22
6	$AgNO_3$ (1.0)	5
7	Ag_2O (1.0)	14
8	Ag_2CO_3 (0.5)	72
9	X	0

[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] Isolated yield.

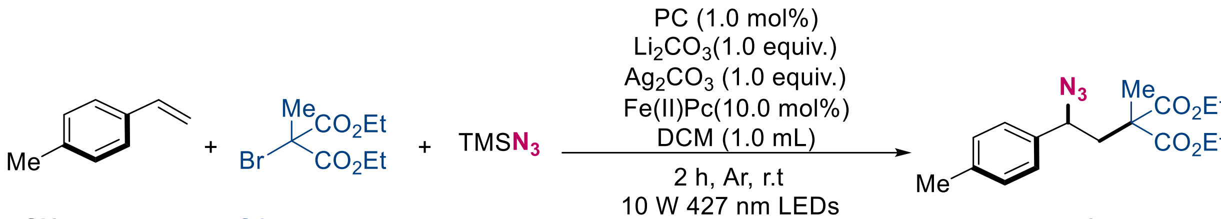
Table 5. Optimization of Azide sources or substrate equivalent.



Entry	Azide sources	Yield (%)[a]
1	**$TMSN_3$**	**98 (96)**[b]
2	NaN_3	75%
3	$ABSN_3$	8%
Entry	**Substrate equiv. (equiv.)**	**Yield (%)[a]**
1	**S1** (1.0)	87
2	**S1** (1.5)	90
3	**$TMSN_3$** (1.5)	68
4	**$TMSN_3$** (2.5)	93

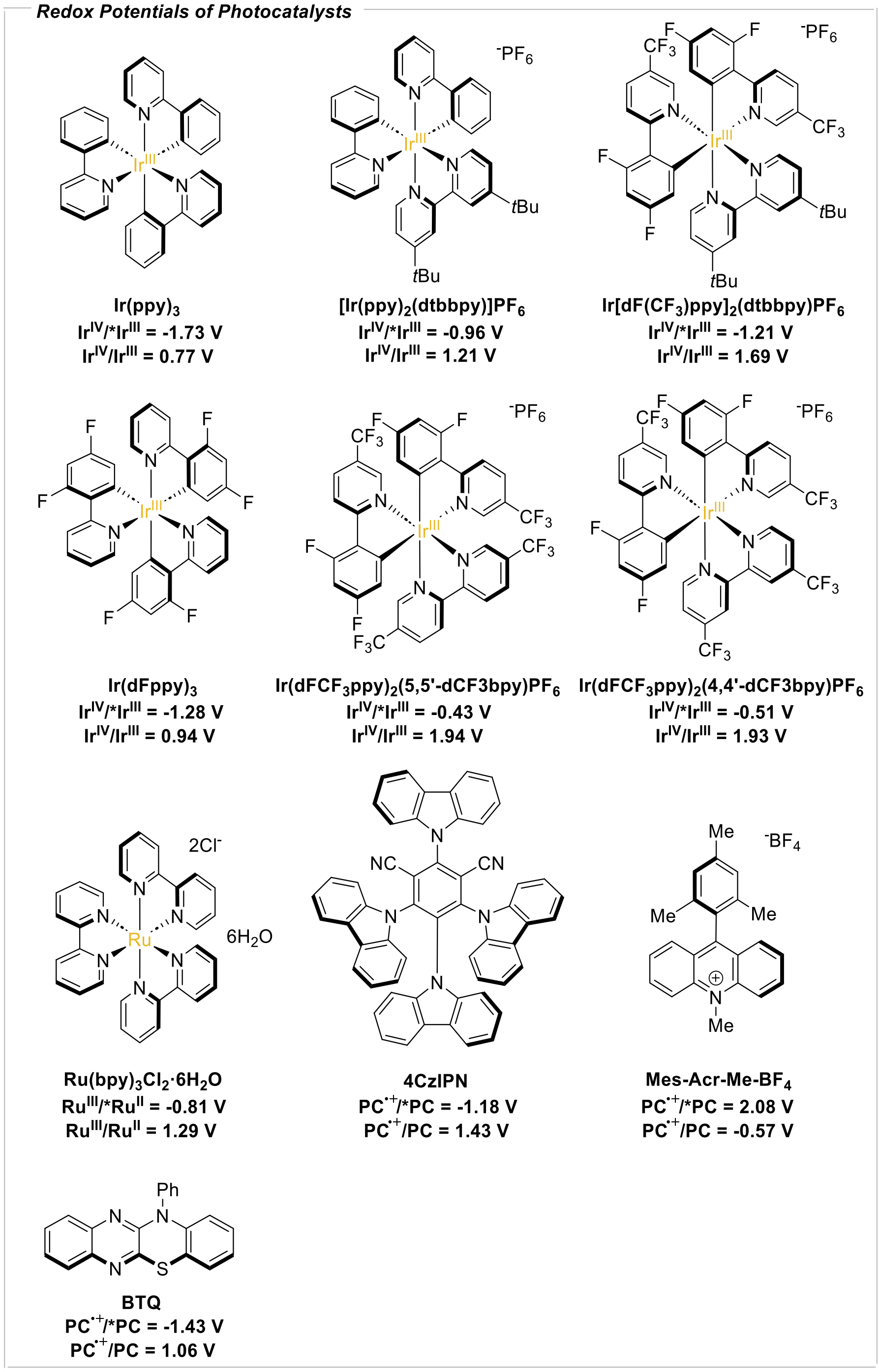
[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] Isolated yield.

Table 6. Optimization of Photocatalyst catalysts



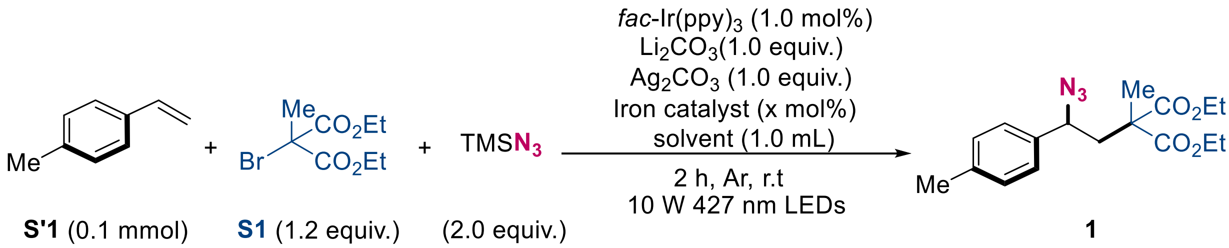
Entry	Iron catalyt (1.0 mol%)	Yield (%)[a]
1	***fac*-Ir(ppy)$_3$**	**98 (96)[b]**
2	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	N.D
3	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	N.D
4	Ir(dFppy)$_3$	12
5	[Ir(dFCF$_3$ppy)$_2$-(5,5'-dCF$_3$bpy)]PF$_6$	7
6	[Ir(dFCF$_3$ppy)$_2$-(4,4'-dCF$_3$bpy)]PF$_6$	Trace
7	Ru(bpy)$_3$Cl$_2$·6H$_2$O	Trace
8	4CzPIN	15
9	Mes-Acr-BF$_4$	N.D
10	BTQ[11]	21

[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] Isolated yield.



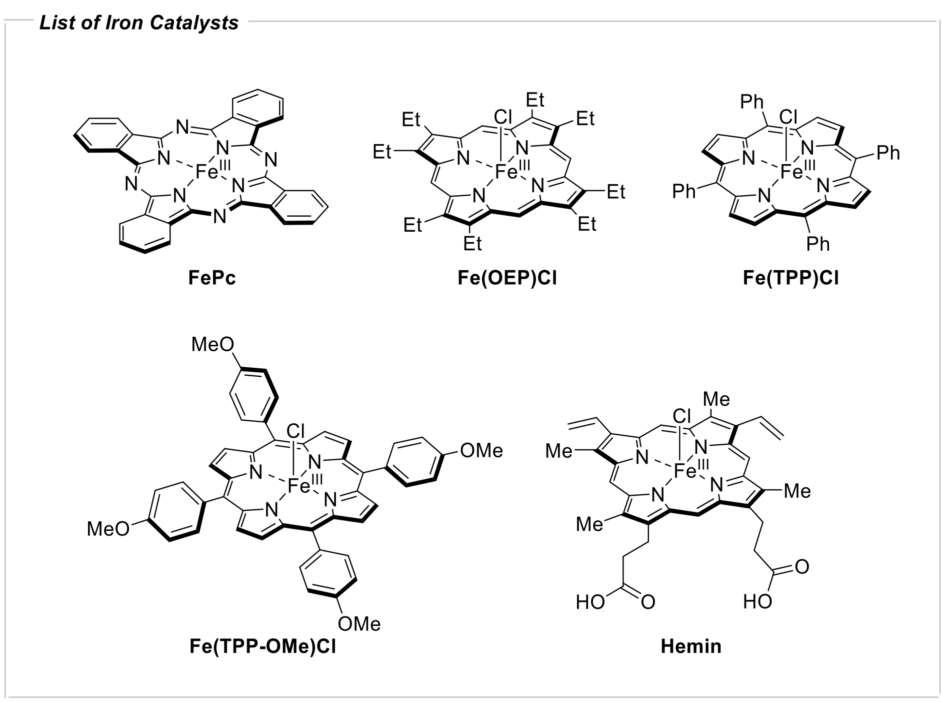
Scheme 1. List of Photocatalysts

Table 7. Optimization of Iron catalysts



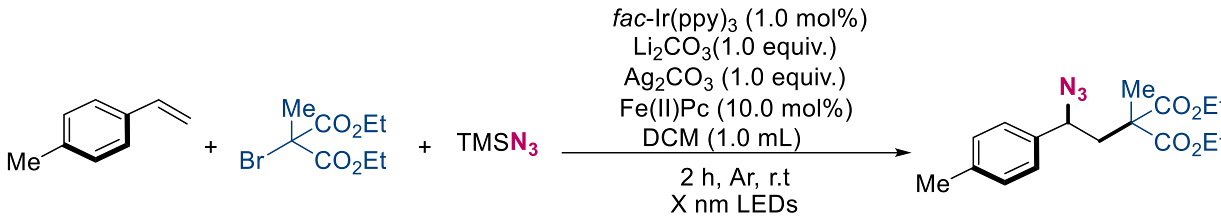
Entry	Iron catalyt (mol%)	Yield (%)[a]
1	**Fe(II)Pc (10.0 mol%)**	**98 (96)[b]**
2	Fe(OEP)Cl (10.0 mol%)	45
3	Fe(TPP)Cl (10.0 mol%)	N.D
4	Fe(TPP-OMe) (10.0 mol%)	Trace
5	Hemin (10.0 mol%)	12
6	**$Fe(OAc)_2$ (10 mol%)**	**95 (93)[b]**
7	Fe(II)Pc (7.5 mol%)	82
8	X	12

[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] Isolated yield.



Scheme 2. List of Iron Catalysts

Table 8. Optimization of LEDs.

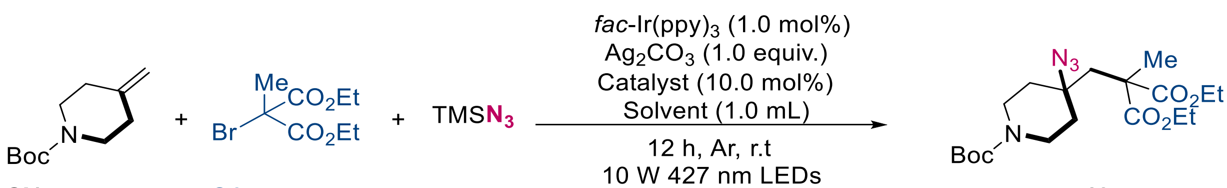


S'1 (0.1 mmol) **S1** (1.2 equiv.) (2.0 equiv.) **1**

Entry	x LEDs	Yield (%)[a]
1	10 W 427 nm	**98 (96)[b]**
2	20 W 427 nm	83
3	30 W 427 nm	57
4	10 W 390 nm	87
5	10 W 440 nm	91
6	10 W 456 nm	90

[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] Isolated yield.

Optimization of 1,2-Carboheterofunctionalization of unreactive alkenes



S'15 (x equiv.) **S1** (x equiv.) (2.0 equiv.) **42**

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S1** (x euqiv.), **S'15** (x equiv.), and Fe(II)Pc or Fe(OAc)$_2$ (x mol%) under Ar condition (The vial was capped with rubber septum and Ar balloon). The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of fresh $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) to a reaction mixture (If the styrene is volatile, it should be subjected to Ar purging prior to use.). The vial was charged with anhydrous ACN (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (10 mL), and concentrated under vacuum. To evaluate yield of the products, CH_2Br_2 (7.0 µL) as internal standard was added to the residue. The mixture was diluted with $CDCl_3$ and analyzed by ^{1}H-NMR.

Table 9. Optimization of 1,2-Carboheterofunctionalization of unreactive alkenes.

Entry	Catalyst (mol%)	Solvent (mL)	S1 (equiv.)	S'15 (equiv.)	Yield (%)[a]
1	Fe(II)Pc (10.0)	DCM (1.0)	1.2	1.0	7
2	Fe(II)Pc (10.0)	ACN (1.0)	1.2	1.0	21
3	$Fe(OAc)_2$ (10.0)	ACN (1.0)	1.2	1.0	50
4	$Fe(OAc)_2$ (10.0)	ACN (1.0)	1.2	1.0	N.D[b]
5	$Fe(OAc)_2$ (20.0)	ACN (1.0)	1.2	1.0	42
6	$Fe(OAc)_2$ (5.0)	ACN (1.0)	1.2	1.0	41
7	$Fe(OAc)_2$ (10.0)	ACN (1.0)	1.5	1.0	49
8	$Fe(OAc)_2$ (10.0)	ACN (1.0)	1.0	1.0	50
9	$Fe(OAc)_2$ (10.0)	ACN (1.0)	1.0	2.0	69
10	**$Fe(OAc)_2$ (10.0)**	**ACN (1.0)**	**1.0**	**3 .0**	**84 (75)[c]**

[a] Yields determined by analysis of the ^{1}H-NMR spectra of crude reaction mixtures using CH_2Br_2 as an internal standard, [b] NaN_3 instead of $TMSN_3$ [c] Isolated yield.

IV. General procedures for 1,2-Carboheterofunctionalization

General procedure A for 1,2-Carboazidofunctionalization of Styrenes

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S** (0.12 mmol, 1.2 equiv.), and Fe(II)Pc or Fe(OAc)$_2$ (0.01 mmol, 10.0 mol%) under Ar condition (The vial was capped with rubber septum and Ar balloon). The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'** (0.1 mmol, 1.0 equiv.) and fresh TMS**N$_3$** (28.1 μL, 0.2 mmol, 2.0 equiv.) to a reaction mixture (If the styrene is a volatile, it should be subjected to Ar purging prior to use.). The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the residue was directly purified by flash column chromatography on silica gel, using hexane, EtOAc, and DCM to afford the carboazidofunctionalized products. (If further purification is required, reverse-phase column chromatography should be employed.)

General procedure B for 1,2-Carboazidofunctionalization of Unreactive Alkenes

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S** (0.1 mmol, 1.0 equiv.), and Fe(OAc)$_2$ (1.8 mg, 0.01 mmol, 10.0 mol%) under Ar condition (The vial was capped with rubber septum and Ar balloon). The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'** (0.3 mmol, 3.0 equiv.) and fresh $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) to a reaction mixture (If the styrene is a volatile, it should be subjected to Ar purging prior to use.). The vial was charged with anhydrous ACN (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the reaction mixture was concentrated under vacuum. The residue was directly purified by flash column chromatography on silica gel, using hexane, EtOAc, and DCM to afford the carboazidofunctionalized products (If further purification is required, reverse-phase column chromatography should be employed.)

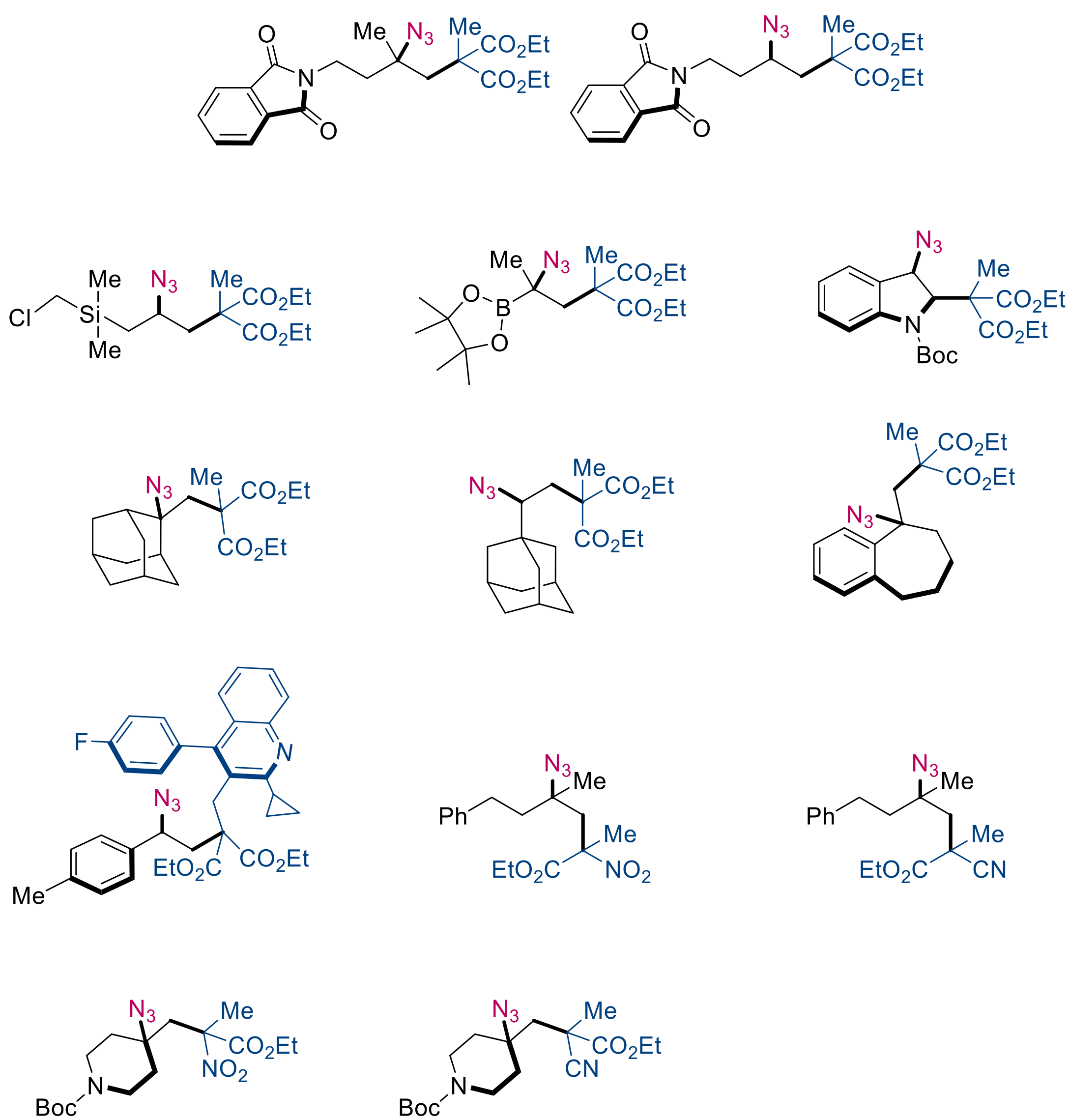
General procedure C for 1,2-Carboheterofunctionalization of Styrenes

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S** (0.12 mmol, 1.2 equiv.), and Fe(II)Pc (5.9 mg, 0.01 mmol, 10.0 mol%) under Ar condition (The vial was capped with rubber septum and Ar balloon). The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'** (0.1 mmol, 1.0 equiv.) and pseudohalogens (2.0 equiv.) to a reaction mixture (If the styrene is a volatile, it should be subjected to Ar purging prior to use.). The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the residue was directly purified by flash column chromatography on silica gel, using hexane, EtOAc, and DCM to afford the carboheterofunctionalized products. (If further purification is required, reverse-phase column chromatography should be employed.)

General procedure D for 1,2-Carboheterofunctionalization of Unreactive Alkenes

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S** (0.1 mmol, 1.0 equiv.), and Fe(II)Pc (5.9 mg, 0.01 mmol, 10.0 mol%) under Ar condition (The vial was capped with rubber septum and Ar balloon). The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'** (0.3 mmol, 3.0 equiv.) and pseudohalogens (2.0 equiv.) to a reaction mixture (If the styrene is a volatile, it should be subjected to Ar purging prior to use.). The vial was charged with anhydrous ACN (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel, using hexane, EtOAc, and DCM to afford the carboheterofunctionalized products. (If further purification is required, reverse-phase column chromatography should be employed.)

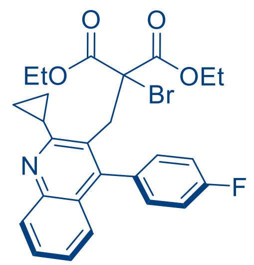
V. Limited Scope



Scheme 3. Unsuccessful substrate scope

Comment: While the reaction proved broadly applicable to a wide range of alkenes, several substrate-dependent limitations were identified. Notably, alkenes bearing a phthalimide moiety preferentially underwent diazidation, with no desired product formation observed. Substrates incorporating silane or boron functionalities led to complex and poorly defined reaction mixtures, suggesting incompatibility under the standard conditions. Furthermore, steric effects appeared to play a significant role, as alkenes containing sterically demanding indole or adamantyl groups, as well as malonates with bulky substituents, failed to undergo the transformation. Nitroacetate and cyanoacetate substrates exhibited no reactivity, with quantitative recovery of the starting materials. This outcome is likely associated with their relatively low redox potentials, which may hinder efficient radical formation under the reaction conditions, thus preventing productive reaction with unactivated alkenes.

Diethyl 2-bromo-2-((2-cyclopropyl-4-(4-fluorophenyl)quinolin-3-yl)methyl)malonate (S29)



S29

S29 was synthesized according to general procedure 1. Alkylated malonate (659.9 mg, 1.5 mmol, 1.0 equiv.), N-bromosuccinimide (404.5 mg, 2.25 mmol, 1.5 equiv.) were used as a starting material and reaction was heated to 60 °C for 4 h in a heat block. After purification by column chromatography (hexane : EtOAc : DCM = 25 : 1 : 1), the title compound was isolated as a White solid (617.5 mg, 80% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.1 Hz, 1H), 7.61-7.56 (m, 1H), 7.30-7.14 (m, 6H), 4.20 (s, 2H), 4.14-3.96 (m, 4H), 2.52-2.45 (m, 1H), 1.34-1.29 (m, 2H), 1.15 (t, J = 7.1 Hz, 6H), 1.08 (dd, J = 8.0, 3.0 Hz, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.0, 163.1, 162.6 (d, $J_{C\text{-}F}$ = 246.3), 147.0 (d, $J_{C\text{-}F}$ = 10.5), 132.8 (d, $J_{C\text{-}F}$ = 3.8), 132.3, 132.2, 129.1, 128.9, 127.6, 126.4, 126.3, 125.5, 115.4 (d, $J_{C\text{-}F}$ = 22.0), 63.5, 62.5, 34.7, 16.0, 13.8, 11.0.

^{19}F-NMR (376 MHz, $CDCl_3$): δ -113.9, -113.9, -113.9, -113.9, -114.0.

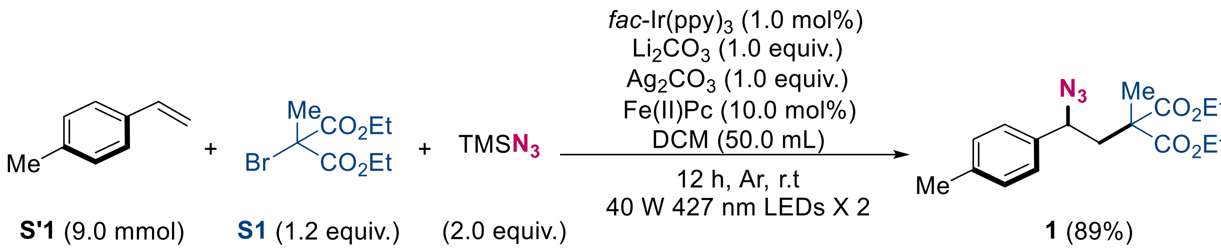
IR (neat) ν 2970, 2939, 1739, 1511, 1228, 1034, 769 cm^{-1}.

HRMS (ESI) calcd for $C_{26}H_{26}BrFNO_4$ $[M+H]^+$ 516.1004, found 516.0997.

m.p. 93-95 °C

VI. Application

1. Gram-Scale experiment



To an oven-dried 100 mL round bottom flask was added *fac*-Ir(ppy)3 (59.5 mg, 0.09 mmol, 1.0 mol%), Ag_2CO_3 (2.5 g, 9.0 mmol, 1.0 equiv.), Li_2CO_3 (678.6 mg, 9.0 mmol, 1.0 equiv.), **S1** (2.8 g, 10.8 mmol, 1.2 equiv.), and Fe(II)Pc (532.8 mg, 0.9 mmol, 10.0 mol%) under Ar condition (round bottom flask was capped with rubber septum and Ar balloon). The flask was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'1** (1.2 mL, 9.0 mmol, 1.0 equiv.) and fresh $TMSN_3$ (2.5 mL, 18.0 mmol, 2.0 equiv.) to a reaction mixture. The flask was charged with anhydrous DCM (50.0 mL, 0.2 M). After stirring for 10 min at room temperature, the reaction was irradiated with Two 40 W 427 nm LED Kessil lamps (100% intensity) for 12 h under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (50 mL), and concentrated under vacuum. A mixture was diluted with EtOAc (40 mL) and H_2O (20 mL), and extracted with EtOAc (2 x 20 mL). The combine extracts were washed with brine (3 x 30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, using hexane and EtOAc (30 : 1) After purification by column chromatography, the title compound was isolated as a colorless oil (2.67 g, 89% yield).

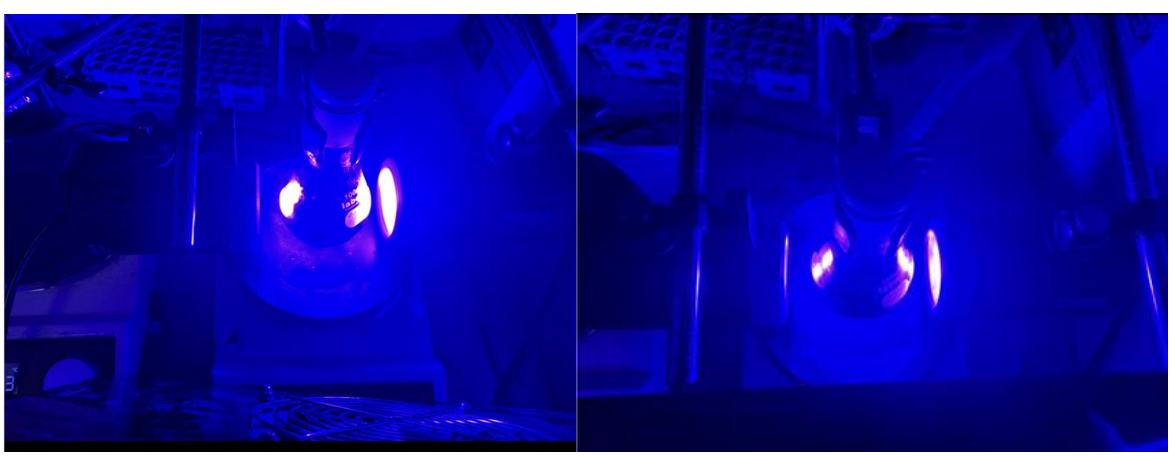
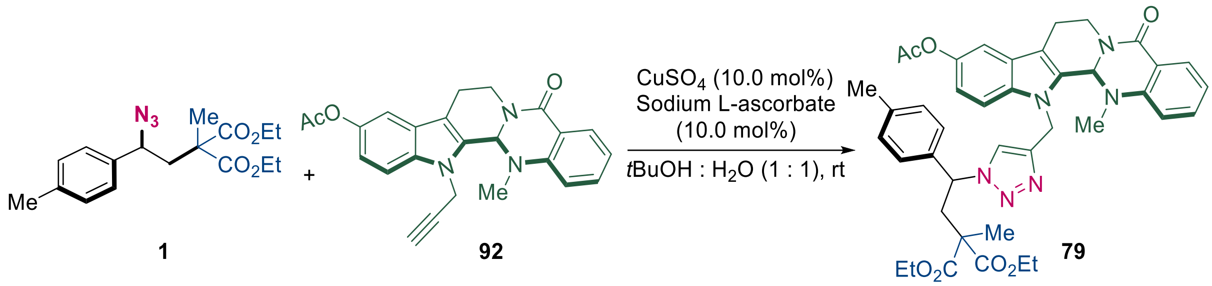


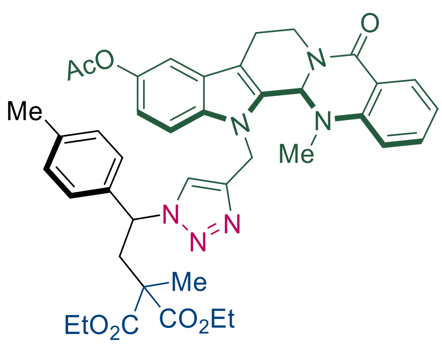
Figure 2. Photograph of the gram-scale photochemical reaction setup

2. Click reaction[12,13]



To an oven-dried 8 mL vial was added **1** (24.3 mg, 0.072 mmol, 1.2 equiv.), **92** (24.3 mg, 0.06 mmol, 1.0 equiv.), $CuSO_4$ (0.8 mg, 0.06 mmol, 10.0 mol%), and Sodium L-ascorbate (1.2 mg 0.06 mmol, 10.0 mol%). The vial was charged with *t*BuOH and H_2O (0.5 + 0.5 mL, 1:1) and sealed with cap. After stirring for 24 h at room temperature, the reaction mixture was checked by TLC. Upon the completion of reaction, the residue was directly purified by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−70% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min). **79** was isolated as a brown oil (36.4 mg, 83% yield, d.r. = 1:1.3).

Diethyl 2-(2-(4-(((R)-10-acetoxy-14-methyl-5-oxo-7,8,13b,14-tetrahydroindolo[2',3':3,4]pyrido[2,1-b]quinazolin-13(5H)-yl)methyl)-1H-1,2,3-triazol-1-yl)-2-(p-tolyl)ethyl)-2-methylmalonate (79)



79

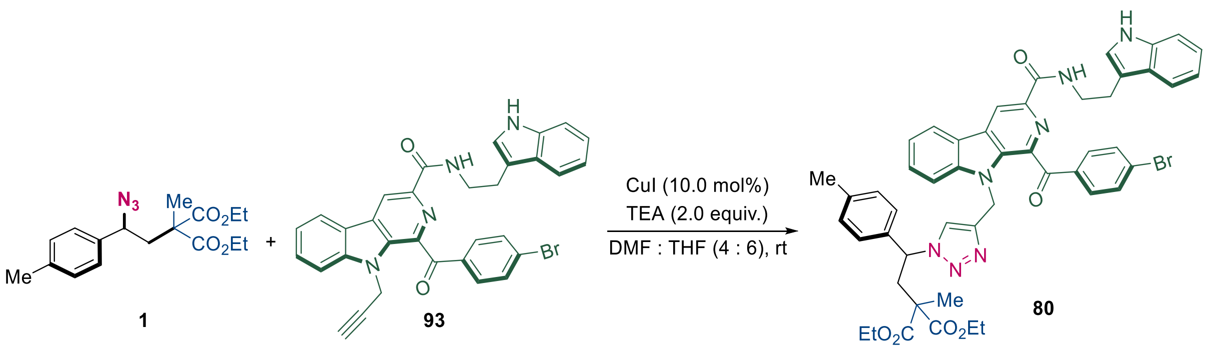
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.8, 1.8 Hz, 1H), 7.50-7.43 (m, 2H), 7.27-6.95 (m, 13H), 6.03 (d, J = 16.0 Hz, 1H), 5.73-5.65 (m, 2H), 5.37 (dd, J = 16.0, 5.0 Hz, 1H), 4.90-4.86 (m, 1H), 4.55 (q, J = 4.6 Hz, 1H), 4.23-4.05 (m, 3H), 3.92-3.66 (m, 4H), 3.20-3.09 (m, 2H), 2.94-

2.69 (m, 3H), 2.38-2.33 (m, 5H), 2.31-2.24 (m, 6H), 1.50 (d, *J* = 4.1 Hz, 2H), 1.32 (d, *J* = 1.4 Hz, 3H), 1.29-1.20 (m, 5H), 1.11-1.01 (m, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 171.8, 171.4, 171.4, 171.3, 171.2, 170.5, 164.6, 150.8, 144.7, 144.2, 138.7, 138.7, 138.4, 136.7, 136.4, 136.3, 135.3, 135.3, 133.0, 129.8, 129.7, 129.7, 129.6, 129.0, 127.0, 127.0, 126.9, 126.2, 126.2, 124.6, 124.3, 124.3, 123.4, 123.4, 122.0, 121.7, 117.2, 117.2, 114.0, 114.0, 111.3, 110.8, 110.7, 68.0, 62.5, 61.9, 61.6, 61.6, 61.5, 52.6, 52.5, 52.5, 41.7, 40.6, 40.5, 39.5, 39.5, 39.3, 36.8, 21.3, 21.3, 21.2, 20.5, 20.4, 20.4, 14.1, 14.1, 13.9, 13.9, 13.8.

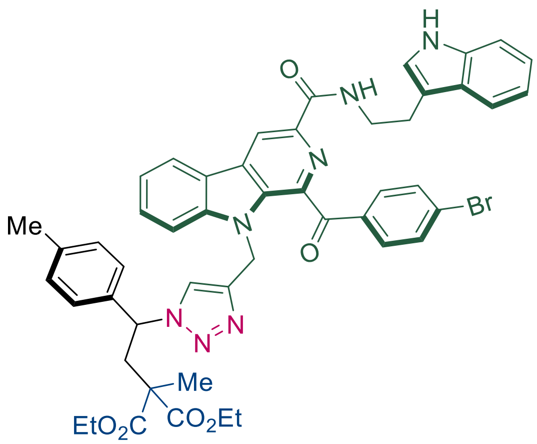
IR (neat) ν 2982, 2926, 2104., 1731, 1658, 1465, 1216, 1108, 1021 cm^{-1}.

HRMS (ESI) calcd for $C_{41}H_{45}N_6O_7$ $[M+H]^+$ 733.3344, found 733.3368.



To an oven-dried 8 mL vial was added **1** (15.5 mg, 0.046 mmol, 1.2 equiv.), **93** (22.1 mg, 0.038 mmol, 1.0 equiv.), CuI (0.73 mg, 0.0038 mmol, 10.0 mol%), and TEA (10.7 μL, 0.076 mmol, 2.0 equiv.). The vial was charged with DMF and THF (0.4 + 0.6 mL, 4:6) and sealed with cap. After stirring for 24 h at room temperature, the reaction mixture was checked by TLC. Upon the completion of reaction, the residue was directly purified by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−80% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min). **80** was isolated as a yellow solid (24.5 mg, 71% yield).

Diethyl 2-(2-(4-((3-((2-(1H-indol-3-yl)ethyl)carbamoyl)-1-(4-bromobenzoyl)-9H-pyrido[3,4-b]indol-9-yl)methyl)-1H-1,2,3-triazol-1-yl)-2-(p-tolyl)ethyl)-2-methylmalonate (80)



80

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.01 (s, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.80-7.74 (m, 3H), 7.68 (t, J = 7.5 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.7 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.22-7.19 (m, 1H), 7.16 (s, 1H), 7.11-7.07 (m, 1H), 7.05 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 2.3 Hz, 1H), 5.65 (s, 2H), 5.53 (dd, J = 7.8, 5.0 Hz, 1H), 3.81-3.60 (m, 6H), 3.48 (q, J = 7.0 Hz, 1H), 3.05 (t, J = 6.4 Hz, 2H), 2.91 (q, J = 7.6 Hz, 1H), 2.61 (dd, J = 14.9, 5.3 Hz, 1H), 2.28 (d, J = 7.3 Hz, 3H), 1.25-1.18 (m, 5H), 0.99 (td, J = 7.2, 2.9 Hz, 6H).

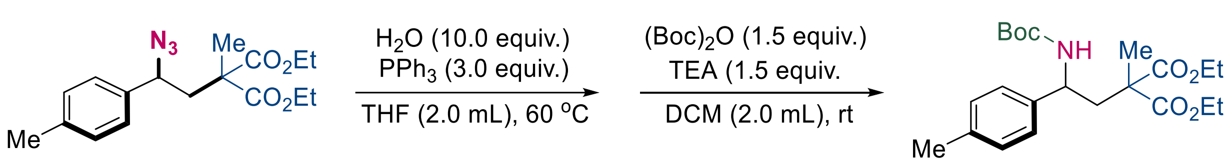
^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.7, 171.2, 164.5, 142.9, 138.7, 138.5, 136.9, 136.5, 135.8, 135.7, 133.4, 132.8, 131.8, 130.0, 129.6, 128.7, 127.3, 127.0, 122.3, 122.1, 121.9, 121.8, 121.6, 119.5, 118.9, 116.4, 113.1, 111.4, 66.0, 61.8, 61.5, 52.4, 40.6, 39.6, 25.4, 21.2, 20.2, 15.4, 13.8.

IR (neat) ν 3393, 3298, 2975, 1729, 1659, 1459, 1228, 1109, 741 cm^{-1}.

HRMS (ESI) calcd for $C_{49}H_{47}BrN_7O_6$ $[M+H]^+$ 910.2746, found 910.2792.

m.p. 109-111 °C

3. Staudinger reaction & Boc protection[10]



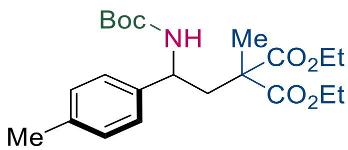
1 **81**

Step 1 : To an oven-dried 8 mL vial was added **1** (67.4 mg, 0.2 mmol, 1.0 equiv.), PPh_3 (159.0 mg, 0.6 mmol, 3.0 equiv.). To the mixture was additionally added H_2O (36.4 μL, 2.0 mmol, 10.0

equiv.) and THF (2.0 mL). The solution was heated in a heat block at 60 °C for 12 h, and then solvent was removed by high vacuum.

Step 2 : Without further purification, $(Boc)_2O$ (83.7 μL, 0.3 mmol, 1.5 equiv.) Et_3N (42.2 μL, 0.3 mmol, 1.5 equiv.), and DCM (2.0 mL) were added to the vial, and then the mixture was stirred for 24 h. Upon the completion of reaction, the solution was directly purified by column chromatography (hexane : EtOAc = 10 : 1). **81** was isolated as a white solid (31.5 mg, 39% yield).

Diethyl 2-(2-((tert-butoxycarbonyl)amino)-2-(p-tolyl)ethyl)-2-methylmalonate (81)



81

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 19.4, 8.0 Hz, 4H), 4.94 (d, *J* = 8.7 Hz, 1H), 4.80-4.78 (m, 1H), 4.23 (ddd, *J* = 18.2, 7.0, 4.2 Hz, 2H), 4.12-3.99 (m, 2H), 2.48 (dd, *J* = 14.3, 11.3 Hz, 1H), 2.32 (s, 3H), 2.19 (dd, *J* = 14.6, 4.1 Hz, 1H), 1.54 (s, 3H), 1.38 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

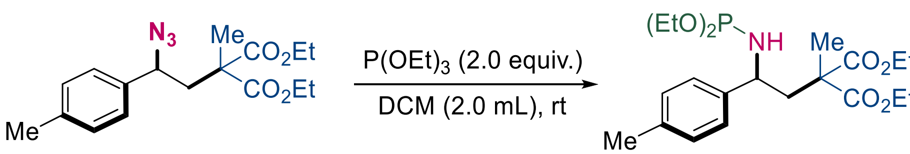
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 154.8, 140.3, 137.0, 129.4, 126.1, 79.5, 61.7, 52.7, 50.9, 41.8, 28.5, 21.2, 19.6, 14.2, 14.0.

IR (neat) ν 3384, 2980, 2934, 1730, 1514, 1365, 1231, 1173, 1021 cm^{-1}.

HRMS (ESI) calcd for $C_{22}H_{33}NNaO_6$ $[M+Na]^+$ 430.2200, found 430.2188.

m.p. 36-38 °C

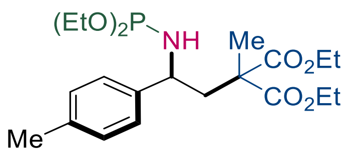
4. Staudinger reaction (N-P bond)[14]



1 **82**

To an oven-dried 8 mL vial was added **1** (67.4 mg, 0.2 mmol, 1.0 equiv.), $P(OEt)_3$ (67.1 mg, 0.4 mmol, 2.0 equiv.) and DCM (2.0 mL). The solution was stirred at room temperature for 24 h. Upon the completion of reaction, the solution was directly purified by column chromatography (hexane : EtOAc = 1 : 1). **82** was isolated as a colorless oil (59.0 mg, 69% yield).

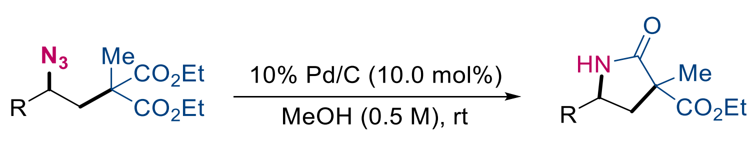
Diethyl 2-(2-((diethoxyphosphaneyl)amino)-2-(p-tolyl)ethyl)-2-methylmalonate (82)



82

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 4.27-4.16 (m, 3H), 4.05-3.78 (m, 5H), 3.57-3.46 (m, 1H), 3.25 (t, J = 10.1 Hz, 1H), 2.51 (dd, J = 14.6, 9.1 Hz, 1H), 2.31 (s, 3H), 2.14 (ddd, J = 14.8, 5.6, 4.0 Hz, 1H), 1.53 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.3 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.6, 172.1, 141.3, 137.1, 129.2, 126.5, 62.5, 62.4, 62.1, 62.1, 61.7, 61.6, 52.8, 43.4, 43.3, 21.2, 19.1, 16.2, 16.2, 16.0, 15.9, 14.1, 14.0.
IR (neat) ν 3205, 2982, 2937, 1732, 1457, 1232, 1032, 967 cm^{-1}.
HRMS (CI) calcd for $C_{17}H_{23}O_4$ [M-$C_4H_{11}NO_2P$] 291.1591, found 291.1601.

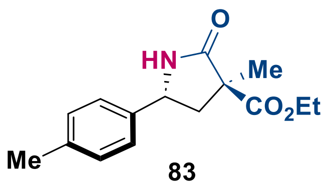
5. Lactamization[15]



Lactam Product

To an oven-dried 10 mL round-bottom flask was added **1** (1.0 equiv.), 10% Pd/C (10.0 mol%) and MeOH (0.5 M). Purge the reaction with H_2 (1 atm) for 10 min, and hold under a H_2 atmosphere at room temperature. Upon the completion of reaction, filtrate the reaction mixture over Celite, and then remove the solvent under reduced pressure thoroughly. the residue was purified by column chromatography (hexane : EtOAc).

Ethyl (3S,5R)-3-methyl-2-oxo-5-(p-tolyl)pyrrolidine-3-carboxylate (83)



83

83 was synthesized according to above procedure. **1** (101.0 mg, 0.3 mmol, 1.0 equiv.) was used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 3 : 1 : 1), the title compound was isolated as a white solid (57.5 mg, 73% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 9.1 Hz, 4H), 5.83 (s, 1H), 4.82 (dd, *J* = 8.7, 6.9 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.94 (q, *J* = 6.7 Hz, 1H), 2.35 (s, 3H), 1.85 (dd, *J* = 13.3, 8.7 Hz, 1H), 1.50 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H).

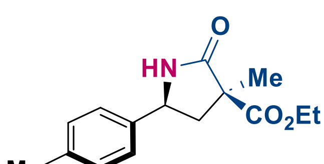
^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.9, 172.2, 138.6, 138.3, 129.8, 126.0, 61.9, 55.7, 52.3, 45.0, 21.2, 21.0, 14.3.

IR (neat) ν 3223, 2987, 1736, 1687, 1447, 1398, 1260, 1191, 818 cm^{-1}.

HRMS (ESI) calcd for $C_{15}H_{20}NO_3$ $[M+H]^+$ 262.1438, found 262.1430.

m.p. 122-124 °C

Ethyl (3S,5S)-3-methyl-2-oxo-5-(p-tolyl)pyrrolidine-3-carboxylate (83')



83'

83' was synthesized according to above procedure. **1** (101.0 mg, 0.3 mmol, 1.0 equiv.) was used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 1 : 1 : 1), the title compound was isolated as a white solid (18.9 mg, 24% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 7.17 (d, J = 7.8 Hz, 2H), 6.34 (s, 1H), 4.69 (t, *J* = 7.8 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 2.56 (dd, *J* = 13.0, 8.0 Hz, 1H), 2.39 (dd, *J* = 12.8, 7.8 Hz, 1H), 2.34 (s, 3H), 1.51 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).

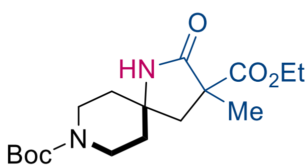
^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.8, 172.3, 138.5, 138.2, 129.7, 126.2, 77.5, 77.2, 76.8, 61.8, 55.2, 52.0, 43.8, 21.2, 20.0, 14.2.

IR (neat) ν 3178, 2986, 1729, 1703, 1342, 1214, 1105, 1020, 773 cm^{-1}.

HRMS (ESI) calcd for $C_{15}H_{19}NNaO_3$ $[M+Na]^+$ 284.1263, found 284.1253.

m.p. 108-110 °C

8-(tert-butyl) 3-ethyl 3-methyl-2-oxo-1,8-diazaspiro[4.5]decane-3,8-dicarboxylate (84)



84

84 was synthesized according to above procedure. **42** (29.2 mg, 0.07 mmol, 1.0 equiv.) was used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 4), the title compound was isolated as a white solid (20.5 mg, 86% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.54-3.44 (m, 2H), 3.42-3.35 (m, 2H), 2.59 (d, *J* = 13.7 Hz, 1H), 1.82 (d, *J* = 13.7 Hz, 1H), 1.72-1.58 (m, 4H), 1.49 (s, 3H), 1.44 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H).

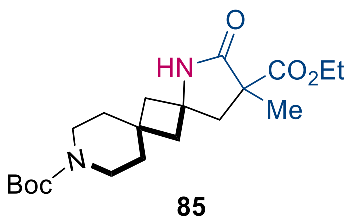
^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.4, 172.8, 154.6, 80.0, 61.9, 55.2, 51.6, 44.7, 40.9, 40.4, 39.5, 38.1, 28.5, 22.9, 14.2.

IR (neat) ν 3257, 2971, 1742, 1689, 1424, 1364, 1216, 1162 cm^{-1}.

HRMS (ESI) calcd for $C_{17}H_{29}N_2O_5$ $[M+H]^+$ 341.2071, found 341.2060.

m.p. 125-127 °C

10-(tert-butyl) 3-ethyl 3-methyl-2-oxo-1,10-diazadispiro[4.1.57.15]tridecane-3,10-dicarboxylate (85)

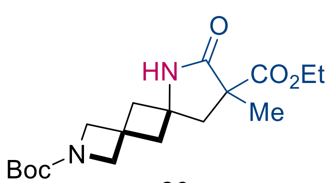


85

85 was synthesized according to above procedure. **46** (34.3 mg, 0.075 mmol, 1.0 equiv.) was used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 1), the title compound was isolated as a white solid (11.4 mg, 40% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1H), 4.18 (dq, J = 18.2, 3.7 Hz, 2H), 3.33-3.27 (m, 4H), 2.76 (d, J = 13.3 Hz, 1H), 2.23 (d, J = 13.3 Hz, 1H), 2.11 (d, J = 5.0 Hz, 3H), 2.09-2.06 (m, 1H), 1.55-1.50 (m, 4H), 1.44 (s, 9H), 1.43 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.1, 172.3, 155.0, 79.6, 61.8, 53.2, 52.3, 49.6, 47.2, 47.1, 40.8, 38.8, 37.0, 30.0, 28.6, 21.0, 14.2.
IR (neat) ν 3253, 2975, 2920, 1740, 1696, 1423, 1273, 1147 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{32}NO_5$ $[M+H]^+$ 381.2384, found 381.2393.
m.p. 111-113 °C

2-(tert-butyl) 9-ethyl 9-methyl-8-oxo-2,7-diazadispiro[3.1.46.14]undecane-2,9-dicarboxylate (86)

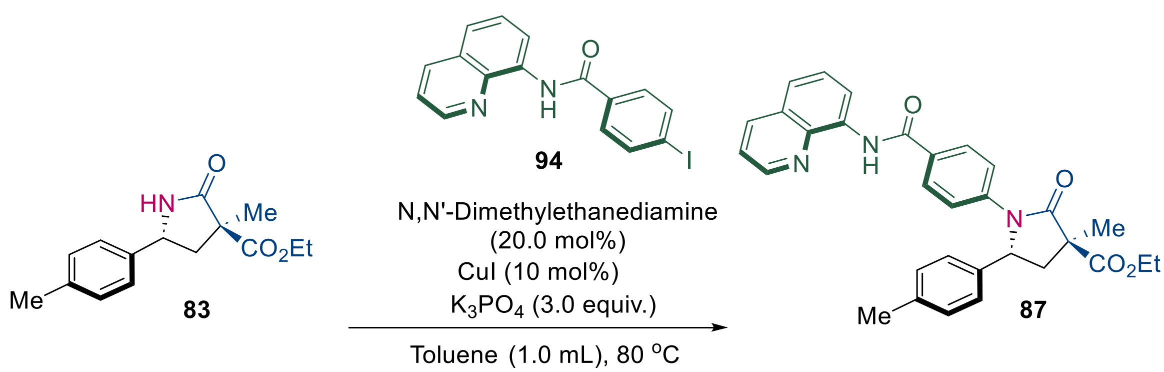


86

86 was synthesized according to above procedure. **48** (32.2 mg, 0.075 mmol, 1.0 equiv.) was used as a starting material. After purification by column chromatography (hexane : EtOAc = 1 : 2), the title compound was isolated as a white solid (8.2 mg, 31% yield).

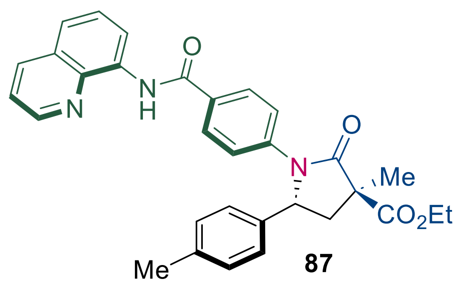
^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 4.18 (q, J = 7.0 Hz, 2H), 3.99-3.92 (m, 2H), 3.87 (s, 2H), 2.68 (d, J = 12.9 Hz, 1H), 2.48 (dt, J = 12.2, 4.6 Hz, 2H), 2.43-2.32 (m, 2H), 2.02 (d, J = 13.3 Hz, 1H), 1.44 (s, 3H), 1.42 (s, 9H), 1.27 (t, J = 7.4 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.3, 172.2, 156.2, 79.7, 61.9, 59.9, 53.7, 52.3, 47.5, 46.9, 30.2, 28.5, 21.2, 14.2.
IR (neat) ν 3264, 2972, 2931, 1740, 1703, 1398, 1365, 1176, 1142 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{29}N_2O_5$ $[M+H]^+$ 353.2076, found 353.2076.
m.p. 121-123 °C

6. Ullmann reaction[16]



To an oven-dried 8 mL vial was added **83** (26.40 mg, 0.1 mmol, 1.0 equiv.), **94**[17] (37.8 mg, 1.0 mmol, 1.0 equiv.), K_3PO_4 (64.3 mg, 0.3 mmol, 3.0 equiv.), and N,N'-dimethylethanediamine (2.2 μL, 0.02 mmol, 20.0 mol%), and CuI (1.8 mg, 0.01 mmol, 10.0 mol%). To the mixture was added dry Toluene (1.0 mL), and then charged with Ar gas. The reaction mixture was heated to 80 ºC for 18 h in a heat block. Upon the completion of reaction, A mixture was diluted with EtOAc (4.0 mL) and H_2O (3.0 mL), and extracted with EtOAc (2 x 3.0 mL). The combine extracts were washed with brine (3 x 2.0 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, using hexane, EtOAc and DCM (3 : 1 :1) After purification by column chromatography, **87** was isolated as a white solid (26.4 mg, 52% yield).

Ethyl (3S,5R)-3-methyl-2-oxo-1-(4-(quinolin-8-ylcarbamoyl)phenyl)-5-(p-tolyl)pyrrolidine-3-carboxylate (87)



87

^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.87-8.81 (m, 2H), 8.17 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.58-7.50 (m, 4H), 7.46 (q, *J* = 4.3 Hz, 1H), 7.10 (dd, *J* = 11.0, 8.7 Hz, 4H), 5.41 (t, *J* = 7.8 Hz, 1H), 4.24 (qd, *J* = 7.0, 1.4 Hz, 2H), 3.06 (q, *J* = 6.9 Hz, 1H), 2.28 (s, 3H), 1.94 (dd, *J* = 13.3, 8.7 Hz, 1H), 1.63 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.4, 172.0, 164.9, 148.3, 141.2, 138.7, 138.1, 137.3, 136.6, 134.6, 131.6, 129.9, 128.1, 127.9, 127.6, 126.5, 122.9, 121.8, 116.8, 62.1, 61.3, 52.9, 42.8, 30.4, 21.3, 21.2, 14.3.

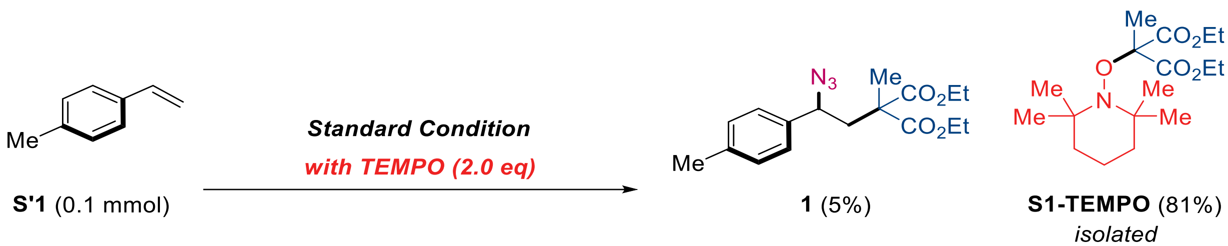
IR (neat) ν 2987, 1737, 1704, 1457, 1365, 1217, 1134, 1109 cm^{-1}.

HRMS (ESI) calcd for $C_{31}H_{30}N_3O_4$ $[M+H]^+$ 508.2231, found 508.2242. 23-22

m.p. 95-97 °C

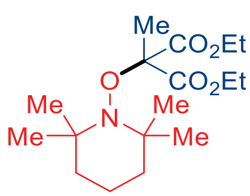
VII. Mechanism Studies

Radical Scavenger Trapping experiment



To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), TEMPO (31.6 mg, 0.2 mmol, 2.0 equiv.) and Fe(II)Pc (5.9 mg, 0.01 mmol, 10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'1** (13.3 µL, 0.1 mmol, 1.0 equiv.) and fresh $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) to a reaction mixture. The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 2 h under fan cooling. Upon the completion of reaction, the residue was directly purified by flash column chromatography on silica gel, using hexane and EtOAc to afford **S1-TEMPO**.

Diethyl 2-methyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)malonate



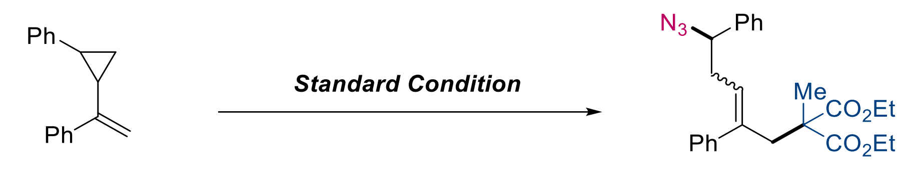
S1-TEMPO

S1-TEMPO was captured according to above procedure. After purification by column chromatography (hexane : EtOAc = 40 : 1), the title compound was isolated as a yellow solid (32.2 mg, 81% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.30-4.14 (m, 4H), 1.73 (s, 3H), 1.63-1.38 (m, 6H), 1.27 (t, *J* = 7.1 Hz, 6H), 1.22 (s, 6H), 1.02 (s, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.5, 85.7, 61.7, 60.5, 40.9, 33.2, 29.8, 20.8, 18.1, 17.1, 14.2.
IR (neat) ν 2970, 2918, 1759, 1737, 1374, 1363, 1217, 1110 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{32}NO_5$ $[M+H]^+$ 330.2275, found 330.2278.
m.p. 72-74 °C

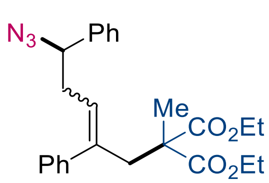
Radical Clock Reaction



S'44 (0.1 mmol) **88** (59%, E/Z = 6.3 : 1)

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′44** (22.3 mg, 0.1 mmol, 1.0 equiv.) and FePc (5.9 mg, 0.01 mmol, 10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of fresh $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) to a reaction mixture. The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm LED lamp (25% intensity) for 2 h under fan cooling. Upon the completion of reaction, the residue was directly purified by flash column chromatography on silica gel, using hexane, EtOAc and DCM to afford **88**.

Diethyl 2-(5-azido-2,5-diphenylpent-2-en-1-yl)-2-methylmalonate (88)



88

88 was synthesized according to above procedure. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (25.9 mg, 59% yield, E/Z ratio = 6.3 : 1).

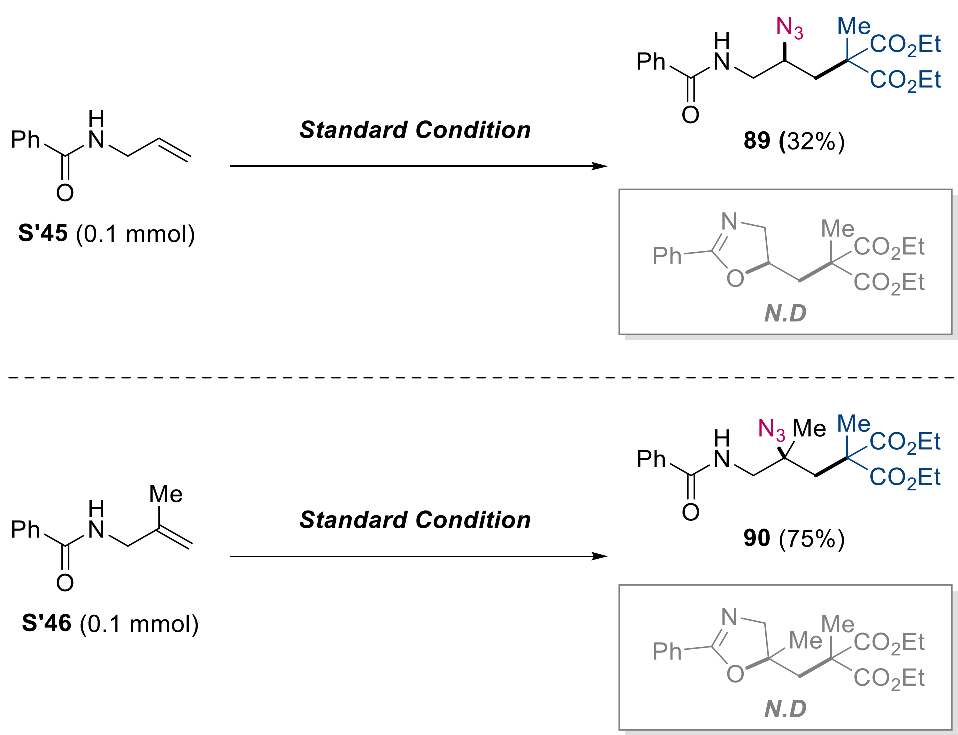
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.30 (m, 6H), 7.26-7.17 (m, 6H), 5.62 (t, J = 7.1 Hz, 1H), 5.48 (t, J = 7.1 Hz, 0.16H), 4.52 (dd, J = 7.8, 6.4 Hz, 1H), 4.40 (t, J = 7.1 Hz, 0.16H), 3.94-3.82 (m, 2H), 3.76-3.65 (m, 2H), 3.17 (s, 0.34H), 3.13 (s, 2H), 2.74-2.58 (m, 2H), 2.43 (tt, J = 21.6, 7.2 Hz, 0.34H), 1.24 (s, 0.75H), 1.21 (s, 3H), 1.13-1.05 (m, 8H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 171.8, 143.2, 143.1, 141.6, 139.5, 139.3, 139.2, 139.2, 139.1, 138.8, 130.4, 129.3, 129.0, 128.9, 128.9, 128.8, 128.6, 128.5, 128.4, 128.0, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 66.2, 61.3, 61.2, 61.1, 61.1, 54.3, 53.5, 53.4, 53.3, 44.4, 39.6, 36.4, 35.8, 35.0, 34.8, 19.9, 19.8, 19.8, 13.9.

IR (neat) ν 2983, 2938, 2096, 1739, 1455, 1376, 1229, 1107, 699 cm^{-1}.

HRMS (ESI) calcd for $C_{25}H_{29}N_3NaO_4$ $[M+Na]^+$ 458.2050, found 458.2062.

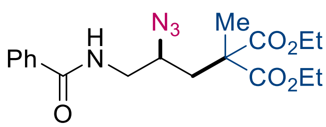
Carbocation trapping experiment[6]



To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S1** (31.0 mg, 0.1 mmol, 1.0 equiv.), and $Fe(OAc)_2$ (1.8 mg, 0.01 mmol, 10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S′45 or 46** (49.4 or 53.1 mg, 0.3 mmol, 3.0 equiv.) and fresh $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0

equiv.) to a reaction mixture. The vial was charged with anhydrous ACN (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the reaction mixture was concentrated under vacuum. the residue was purified by flash column chromatography on silica gel, using hexane, EtOAc and DCM to afford **89** and **90**.

Diethyl 2-(2-azido-3-benzamidopropyl)-2-methylmalonate (89)



89

89 was synthesized according to above procedure. After purification by column chromatography (hexane : EtOAc : DCM = 5 : 1 : 1), the title compound was isolated as a colorless oil (12.2 mg, 34% yield).

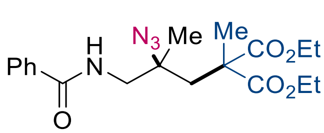
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.54-7.50 (m, 1H), 7.46-7.42 (m, 2H), 6.61 (d, *J* = 5.1 Hz, 1H), 4.28-4.16 (m, 4H), 3.85-3.74 (m, 2H), 3.45-3.37 (m, 1H), 2.15 (dd, *J* = 14.9, 3.0 Hz, 1H), 2.07-2.01 (m, 1H), 1.51 (s, 3H), 1.27 (td, *J* = 7.1, 2.8 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.0, 171.9, 167.9, 134.2, 131.9, 128.8, 127.1, 62.0, 61.8, 58.8, 52.4, 44.8, 38.1, 20.6, 14.1.

IR (neat) ν 3326, 2982, 2935, 2107, 1730, 1646, 1535, 1113, 659 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{25}N_4O_5$ $[M+H]^+$ 377.1819, found 377.1826.

Diethyl 2-(2-azido-3-benzamido-2-methylpropyl)-2-methylmalonate (90)



90

90 was synthesized according to above procedure. After purification by column chromatography (hexane : EtOAc : DCM = 3 : 1 : 1), the title compound was isolated as a white solid (29.2 mg, 75% yield).

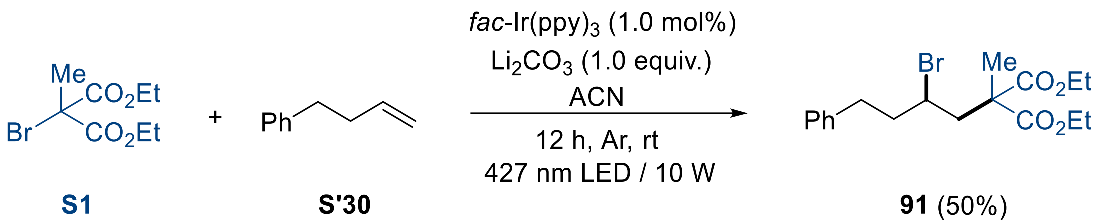
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, J = 6.7, 1.6 Hz, 2H), 7.53-7.41 (m, 3H), 6.89 (t, J = 5.9 Hz, 1H), 4.27-4.15 (m, 4H), 3.54 (ddd, J = 21.6, 13.8, 6.3 Hz, 2H), 2.38 (d, J = 15.1 Hz, 1H), 2.17 (d, J = 15.1 Hz, 1H), 1.59 (s, 3H), 1.38 (s, 3H), 1.26 (td, J = 7.1, 2.3 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.7, 172.2, 167.7, 134.3, 131.8, 128.8, 127.1, 63.4, 62.0, 62.0, 52.7, 47.2, 41.9, 22.9, 21.9, 14.1, 14.0.
IR (neat) ν 3317, 2982, 2938, 2107, 1731, 1648, 1535, 1253, 694 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{27}N_4O_5$ $[M+H]^+$ 391.1976, found 391.1988.
m.p. 79-81 ℃

Tracking of Reaction intermediate

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **91** (38.9 mg, 0.1 mmol, 1.0 equiv.), and $Fe(OAc)_2$ (1.8 mg, 0.01 mmol, 10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of fresh $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) to a reaction mixture. The vial was charged with anhydrous ACN (1.0 mL, 0.1 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (10 mL), and concentrated under vacuum.

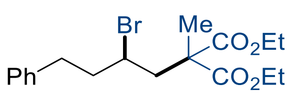
To evaluate yield of the products, CH_2Br_2 (7.0 µL) as internal standard was added to the residue. The mixture was diluted with $CDCl_3$ and analyzed by ^{1}H-NMR.

Synthesis of 91



To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (6.6 mg, 0.01 mmol, 1.0 mol%), Li_2CO_3 (75.4 mg, 1.0 mmol, 1.0 equiv.), and S1 (258.3 mg, 1.0 mmol, 1.0 equiv.) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'30** (0.46 mL, 3.0 mmol, 3.0 equiv.) to a reaction mixture. The vial was charged with anhydrous ACN (2.0 mL, 0.5 M) and a rubber septum was coated with vacuum grease. After stirring for 5 min at room temperature, the reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 12 h under fan cooling. Upon the completion of reaction, the reaction mixture was concentrated under vacuum. the residue was purified by flash column chromatography on silica gel, using hexane and EtOAc to afford **91**.

Diethyl 2-(2-bromo-4-phenylbutyl)-2-methylmalonate (91)



91

91 was captured according to above procedure. After purification by column chromatography (hexane : EtOAc = 15 : 1), the title compound was isolated as a colorless oil (194.9 mg, 50% yield).

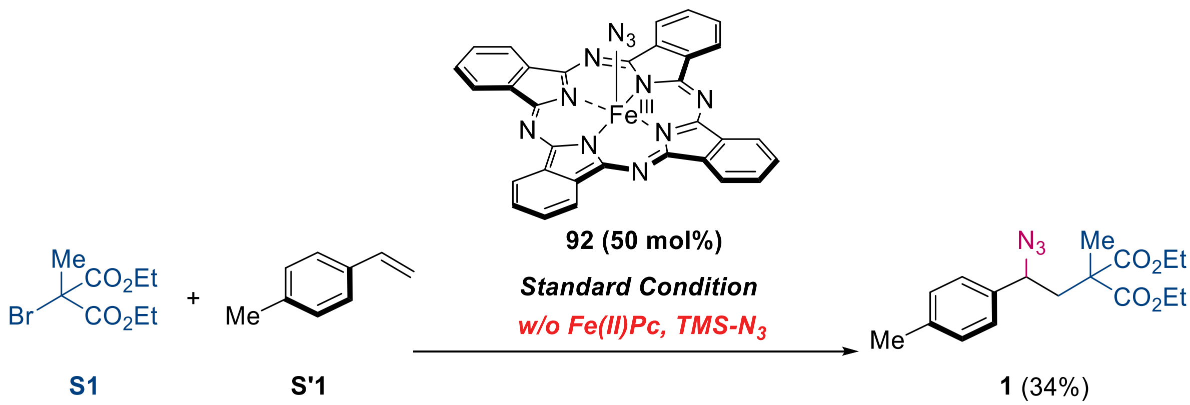
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.19 (q, J = 2.8 Hz, 3H), 4.22-4.10 (m, 4H), 4.03-3.97 (m, 1H), 2.92-2.85 (m, 1H), 2.78-2.71 (m, 1H), 2.62 (q, J = 8.0 Hz, 1H), 2.53 (dd, J = 15.6, 3.7 Hz, 1H), 2.19-2.03 (m, 2H), 1.42-1.46 (3H), 1.25-1.19 (m, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 171.8, 140.8, 128.7, 128.6, 126.3, 61.8, 61.7, 53.3, 51.1, 44.5, 42.1, 33.7, 20.0, 14.2, 14.1.

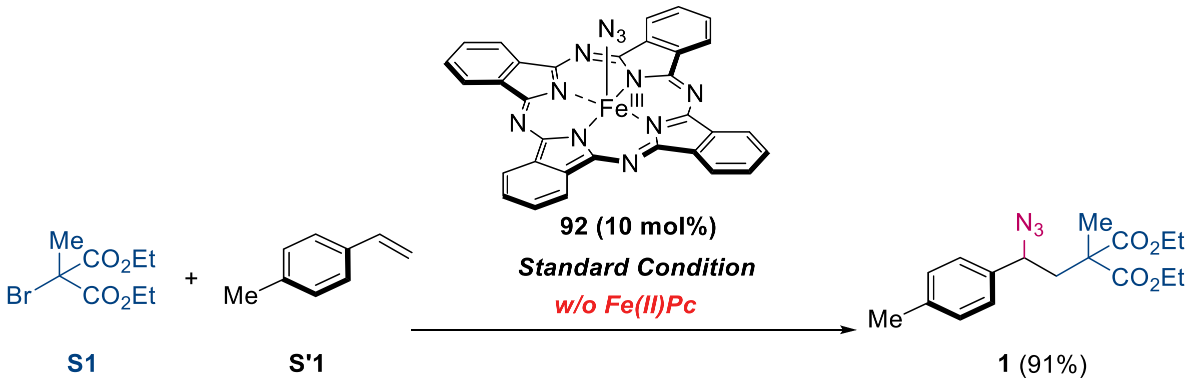
IR (neat) ν 2983, 2939, 1739, 1455, 1379, 1217, 1111, 701 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{26}BrO_4$ $[M+H]^+$ 385.1009, found 385.1016.

Reaction of Iron(III)-Azide complex (92) with for verification experiment[18,19]

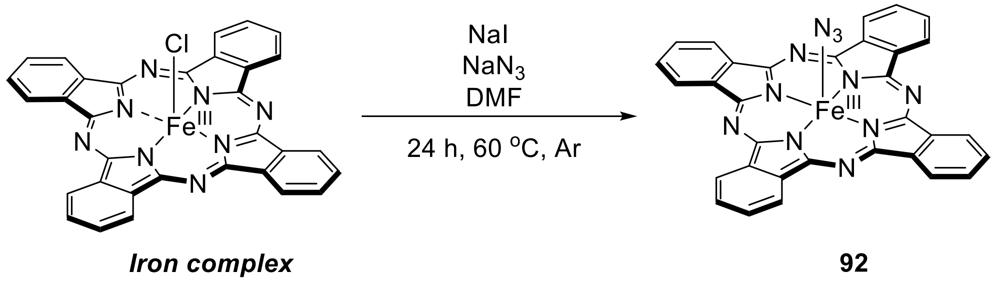


To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), and **95** (30.8 mg, 0.05 mmol, 50.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'1** (0.1 mmol, 1.0 equiv.) to a reaction mixture. The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and then the reaction was stirred for 5 min at room temperature. The reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 2 h under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (10 mL), and concentrated under vacuum. To evaluate yield of the products, CH_2Br_2 (7.0 µL) as internal standard was added to the residue. The mixture was diluted with $CDCl_3$ and analyzed by ^{1}H-NMR.



To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), and **95** (6.2 mg, 0.01 mmol, 10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'1** (13.3 µL, 0.1 mmol, 1.0 equiv.) and fresh $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) to a reaction mixture. The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and then the reaction was stirred for 5 min at room temperature. The reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 2 h under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (10 mL), and concentrated under vacuum. To evaluate yield of the products, CH_2Br_2 (7.0 µL) as internal standard was added to the residue. The mixture was diluted with $CDCl_3$ and analyzed by ^{1}H-NMR.

Synthesis of 92



To an oven-dried 30 mL vial was added Iron complex (188.7 mg, 0.3 mmol, 1.0equiv.), NaI (13.6 mg, 0.09 mmol, 0.3 equiv.), NaN_3 (23.6 mg, 0.36 mmol, 1.2 equiv.) and dry DMF (9 mL, 0.033 M) under argon gas. The reaction was heated to 60 °C for 24 h in the heat block. After the reaction was cooled to room temperature, the mixture was poured into H_2O (30 mL) and stirred for 10 min. The formed dark blue solids were filtered, washed with H_2O (3 x 10 mL), and concentrated on high vacuum. The title compound was collected as a dark blue solid (181.3 mg, 99%). The crude product was used in subsequent experiment.

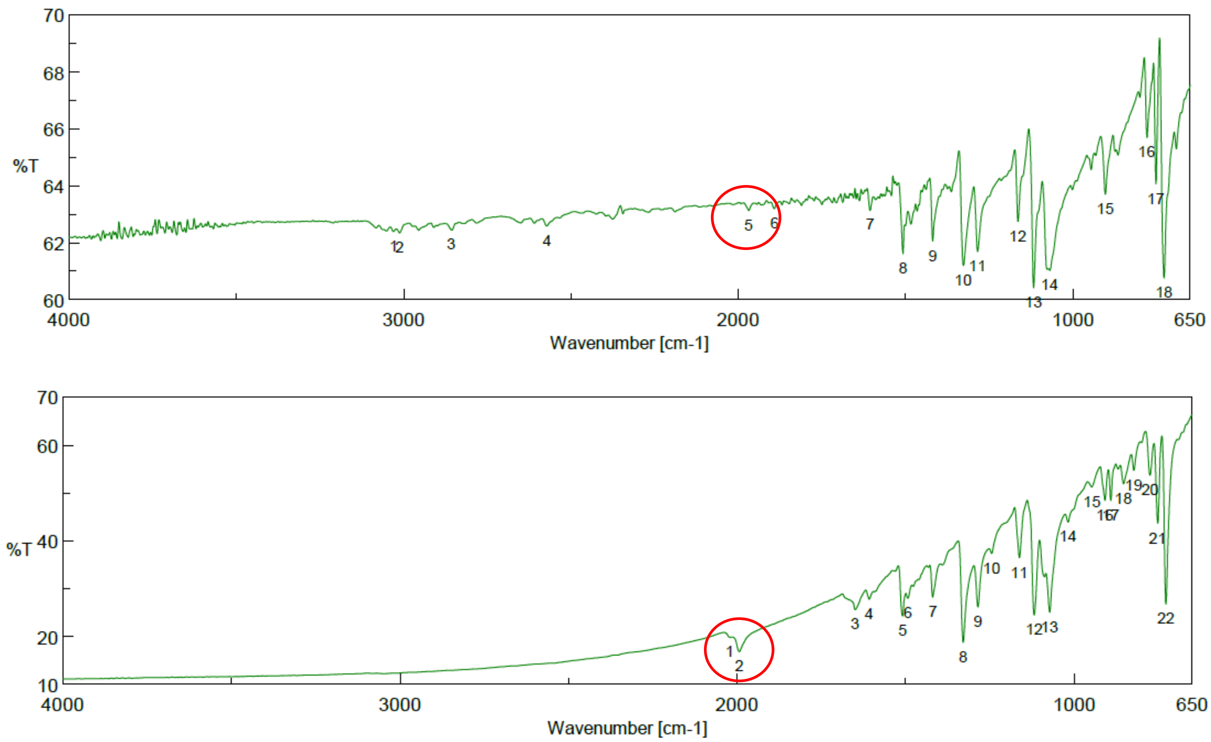
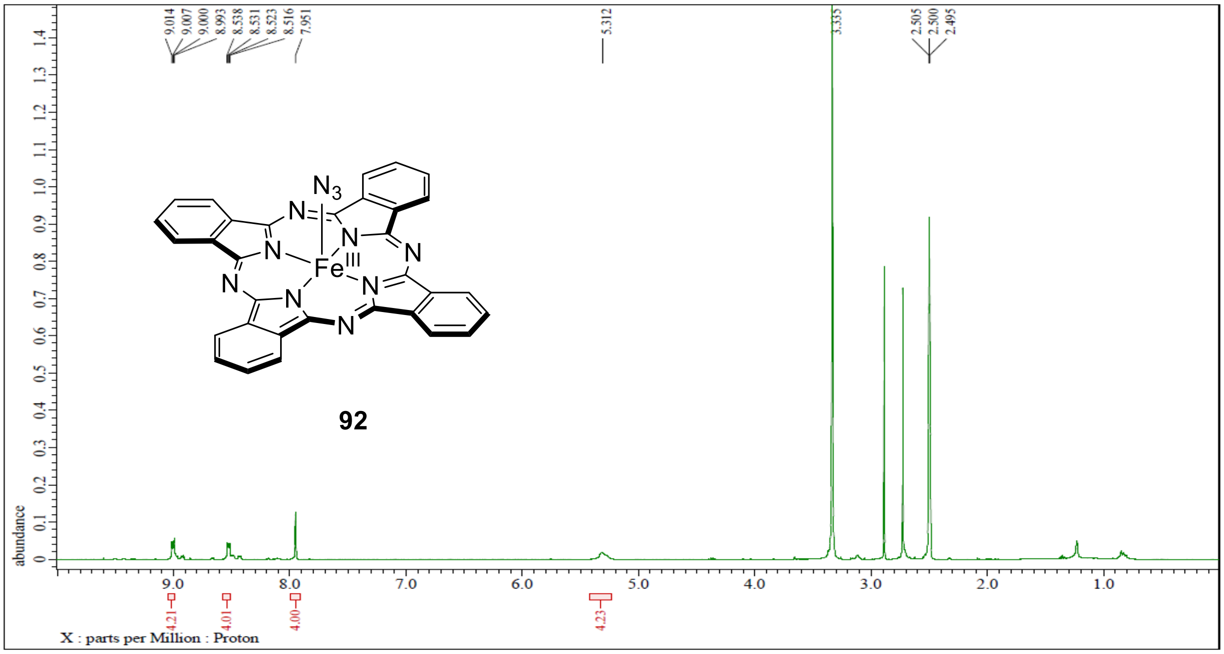


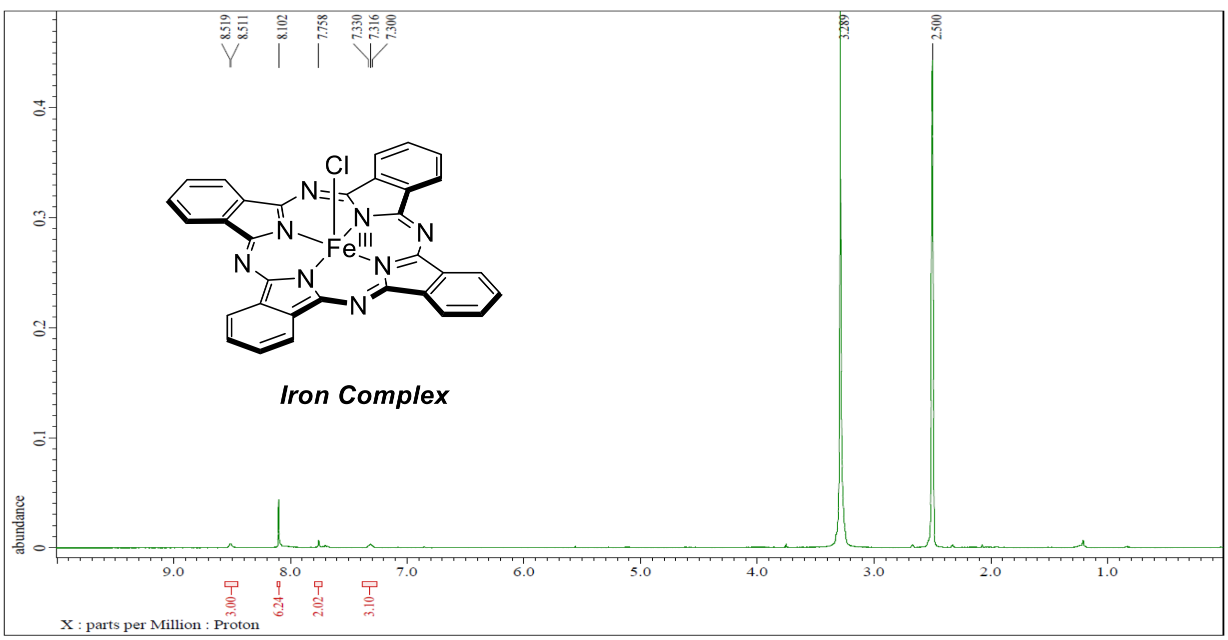
Figure 3. IR spectral comparison between the iron complex and **95**.

Comment: To verify the formation of the iron–azide complex, IR spectroscopy, a commonly employed analytical method, was conducted. Since the introduction of an azide group typically gives rise to a new absorption band around 2000 cm^{-1}, the presence of this characteristic peak was used as diagnostic evidence for complex formation.

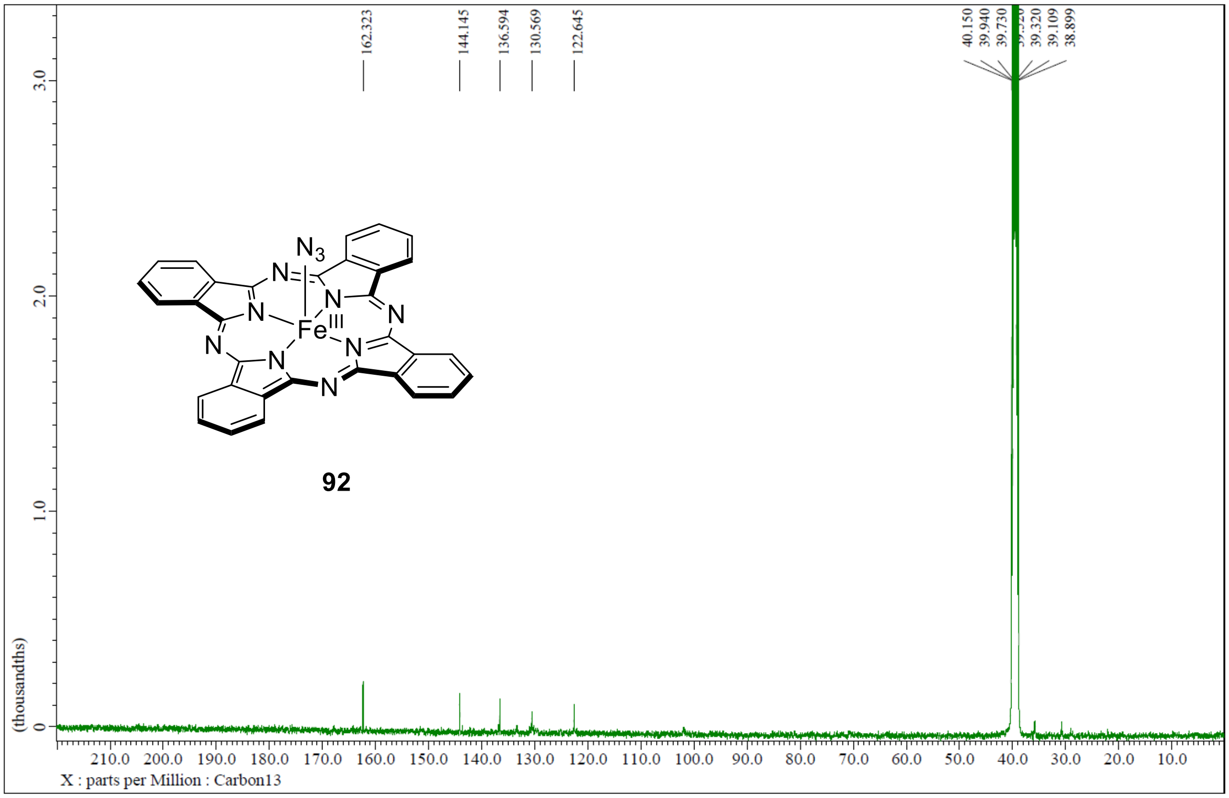
92 ^{1}H NMR (400 MHz, DMSO-d_6)



Iron Complex ^{1}H NMR (400 MHz, DMSO-d_6)



92 ^{13}C NMR (100 MHz, DMSO-d_6)



Light ON-OFF experiment[10,20,22]

To an oven-dried 8 mL vial was added Photocatalyst (1.0 mol%), silver salt (x equiv.), **S1** (x equiv.), and catalyst (10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S'1** (0.1 mmol, 1.0 equiv.) and fresh $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) to a reaction mixture via a micro syringe. The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and then the reaction was stirred for 5 min at room temperature. The reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for indicated time under fan cooling and the samples were checked by HPLC analysis.

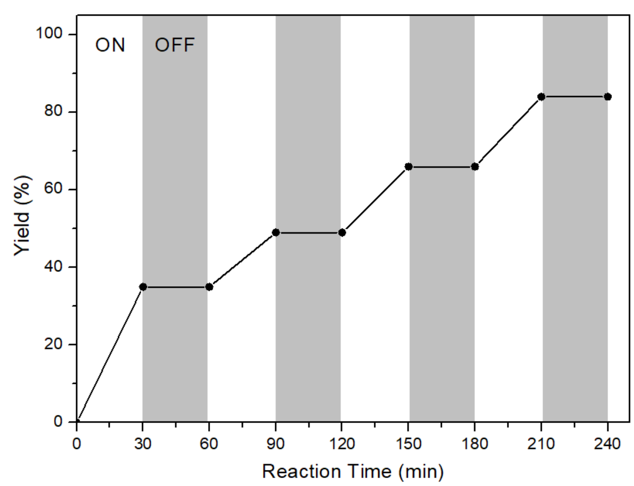


Figure 4. Photograph of Light ON-OFF experiment

Stern-Volmer luminescence quenching experiment[10,20,22]

A stock solution of *fac*-Ir(ppy)$_3$ (3.1 mg, 0.005 mmol, 0.5 mM) was prepared in degassed, anhydrous ACN (10 mL). Solutions of **S1** (25.8 mg, 0.1 mmol, 100.0 mM), **S'1** (13.3 μL, 0.1 mmol, 24.0 mM) and $TMSN_3$ (14.1 μL, 0.1 mmol, 100.0 mM) were analogously prepared in ACN (1 mL each). For quenching experiments, 1 cm × 1 cm quartz cuvette were charged with photocatalyst solution (0.5 mL) under Ar using rubber septa, and quencher solutions (3, 5, 10, and 20 μL) were introduced using a micro syringe (final quencher concentration = 0.6, 1.0, 2.0, 4.0 mM). Fluorescence changes were subsequently monitored. All experiments were conducted under exclusion of light and air. Samples were kept light-protected until measurement. Fluorescence spectra were recorded immediately after preparation (λ_{ex} = 390 nm, Ex bandwidth = 5 nm, Em bandwidth = 2.5 nm, Wavelength range = 400 to 800 nm).

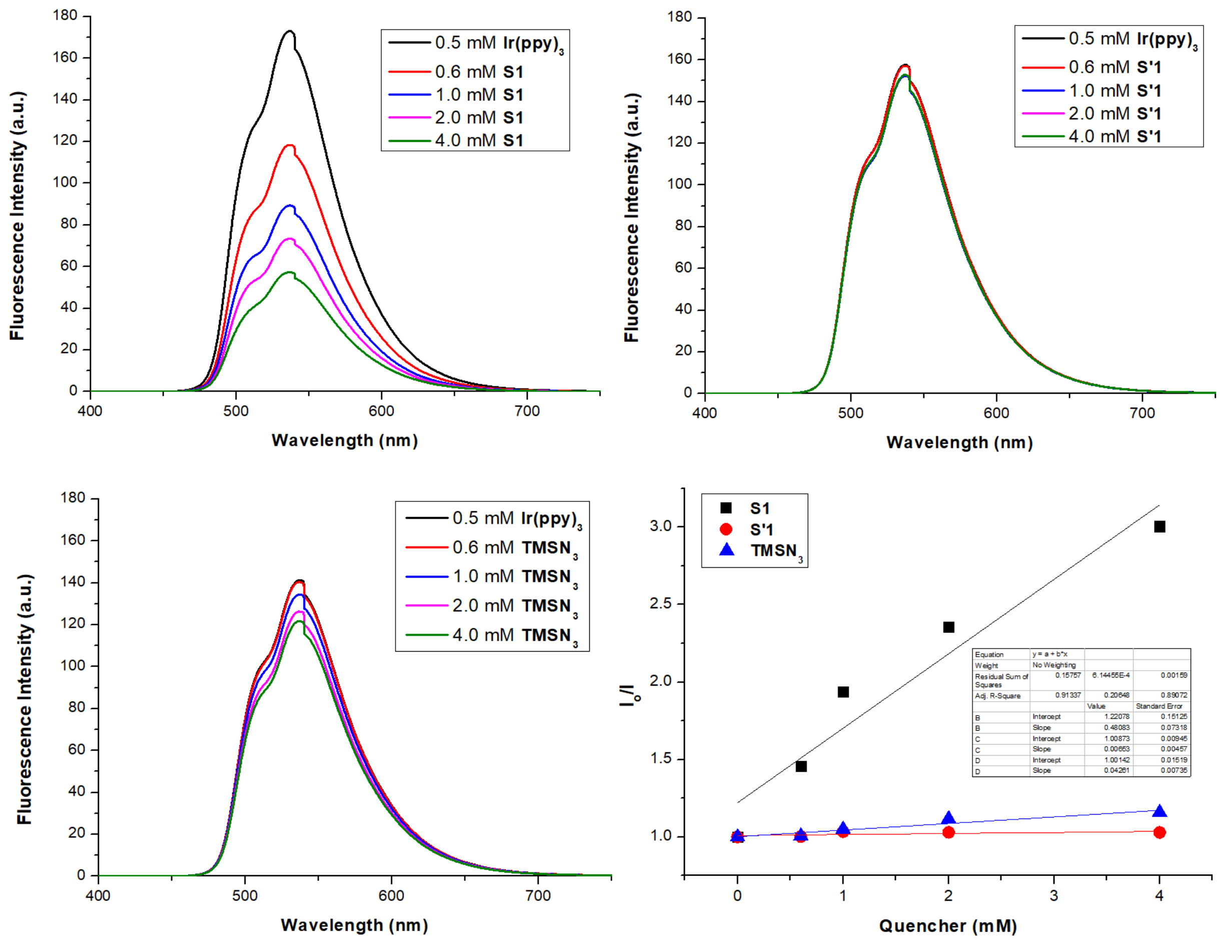


Figure 5. Stern–Volmer analysis of the fluorescence quenching of *fac*-Ir(ppy)$_3$ by **S1**, **S′1** and TMSN$_3$.

Comment: The interactions between the excited-state photocatalyst and the individual reaction components were examined by fluorescence quenching experiments. No significant quenching was detected upon addition of TMSN$_3$ or **S′1**. In contrast, a substantial reduction in the photocatalyst emission intensity was observed in the presence of **S1**. These results suggest that S1 efficiently quenches the excited photocatalyst via an oxidative pathway, consistent with electron transfer from the photocatalyst to **S1** to generate carbon-centered radicals.

Quantum Yield measurement[10,21-23]

Part 1: Determination of Photon Flux of the Reactor

Photon flux can be determined by chemical actinometry using potassium ferrioxalate in a setup using Blue LEDs as a source of irradiation. Blue LEDs (427 nm) were used because their emission profile lines up with known photochemical data for the actinometer. Great care is taken to ensure that the compound is kept in the dark when not in use.

Procedure for Photon Flux

The following solutions must be prepared ahead of time:

1. 0.5 M sulfuric acid stock solution

In a 500 mL volumetric flask, 14.1 mL of concentrated sulfuric acid (17.8 M) was added to 400 mL deionized H_2O. Then, water was added until the 100 mL graduation mark was reached. (0.05 M H_2SO_4 in deionized H_2O was prepared by combining 100 mL of 0.5 M H_2SO_4 with 400 mL of deionized H_2O in a 500 mL volumetric flask and mixing thoroughly.)

2. Ferrioxalate solution

A 0.15 M solution of potassium ferrioxolate was prepared by dissolving potassium ferrioxolate ($K_3FeC_2O_4$*$3H_2O$, MW 491.243) (1.842 g, 3.75 mmol) with the 0.05 M sulfuric acid solution prepared in a 25 mL volumetric flask. Make every precaution to prepare and store the solution in the dark.

3. Developer solution

5.82 g of NaOAc was dissolved in 25 mL of 0.5 M sulfuric acid. 25.9 mg of 1,10-phenantroline was added to this solution. Store in the dark.

A 1 cm × 1 cm quartz cuvette was filled with 2.0 mL of a 0.15 M aqueous potassium ferrioxalate solution. Two sides of the cuvette were covered with black electrical tape to ensure a minimum light path length of 1 cm. To maintain sufficient agitation, the solution was continuously sparged with a steady stream of nitrogen gas. To determine the photon flux of the LED, 2.0 mL of the ferrioxalate solution was transferred to a cuvette and irradiated for 60 seconds at λmax= 427 nm. Immediately after irradiation, 10 μL of the solution was added to 5 mL of developer solution, and the resulting mixture was wrapped in aluminum foil to protect it from light. A non-irradiated control sample was prepared by adding 10 μL of the ferrioxalate solution to 5 mL of the developer solution under identical conditions. Both samples were left in the dark for 1 h, during which they developed a bright red color. The solutions were then transferred to separate cuvettes, and the absorbance spectra of the $Fe(phen)_3^{2+}$ complex was recorded. The absorbance at 510 nm (ε = 11,100 $M^{-1}\cdot cm^{-1}$) was measured for both the irradiated and non-irradiated samples. Each sample preparation and measurement were repeated two additional times. The average absorbance values for both the irradiated and non-irradiated samples were calculated and used to determine the photon flux.

$$\text{mol of Fe}^{2+} = \frac{V^1 \text{ x } V^3 \text{ x } \Delta A \text{ (510 nm)}}{V_2 \text{ x } l \text{ x } \varepsilon} \qquad (1)$$

Where :

$\Delta A_{510\ nm}$ = the absorbance difference between the sample and the blank at 510 nm.

$\mathbf{A}_{sample}$	$\mathbf{A}_{blank}$
0.381	0.041
0.376	0.046
0.405	0.058
Average = 0.387	Average = 0.0483

l = the cuvette path length (1.0 cm).

ε = the molar extinction coefficient of the $Fe(phen)_3^{2+}$ complex at 510 nm (11,100 $M^{-1}\cdot cm^{-1}$).

V_1 = the total volume of the irradiated solution, is 2.0 mL (2×10^{-3} L).

V_2 = the volume of the aliquot taken from the solution, is 10.0 μL (10×10^{-6} L).

V_3 = the volume used to dilute the aliquot, is 5.0 mL (5×10^{-5} L).

$$\text{mol of Fe}^{2+} = \frac{0.002 \text{ L x } 0.005 \text{ L x } 0.339}{0.00001 \text{ L x } 1.0 \text{ cm x } 11{,}100 \text{ M}^{-1}\cdot\text{cm}^{-1}} = 3.05 \text{ x}10^{-5}$$

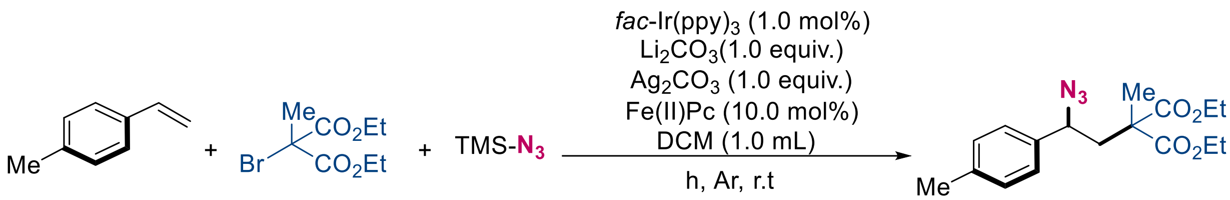
Photon flux can be determined by

$$\text{Photon flux} = \frac{\text{mol of Fe}^{2+}}{\Phi \text{ x } t \text{ x } f} \qquad (2)$$

Where Φ is the quantum yield of the ferrioxalate actinometer (1.14 for a 0.15 M solution at λ = 427 nm), t is the irradiation time (60 s), and *f* is obtained from $f = 1\text{-}10^{-A}$ denoting the absorbance of the ferrioxalate solution at 427 nm (A = 0.387, *f* = 0.59).

$$\text{Photon flux} = \frac{3.05 \times 10^{-5}}{1.14 \times 60\ \text{s} \times 0.59} = 7.76 \times 10^{-7}\ \text{einsteins}\cdot\text{s}^{-1}$$

Determination of the Reaction Quantum Yield.



S'1 (0.1 mmol) **S1** (1.2 equiv.) (2.0 equiv.) **1**

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), and Fe(II)Pc (5.9 mg, 0.01 mmol, 10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S1**ʹ (13.3 μL, 0.1 mmol, 1.0 equiv.) and fresh $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) to a reaction mixture. The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and then the reaction was stirred for 5 min at room temperature. The reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) at each time point (150 s, 300 s, 600 s) under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (10 mL), and concentrated under vacuum. To evaluate yield of the products, CH_2Br_2 (7.0 μL) as internal standard was added to the residue. The mixture was diluted with $CDCl_3$ and analyzed by ^{1}H-NMR.

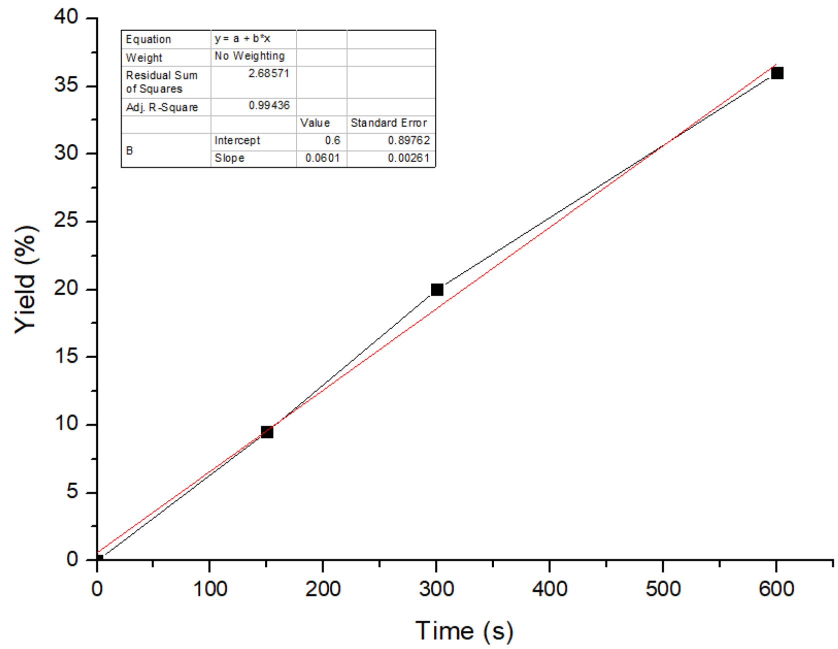


Figure 6. Determination of Product formation rate

The Quantum Yield (Φ) can be determined with the following equation:

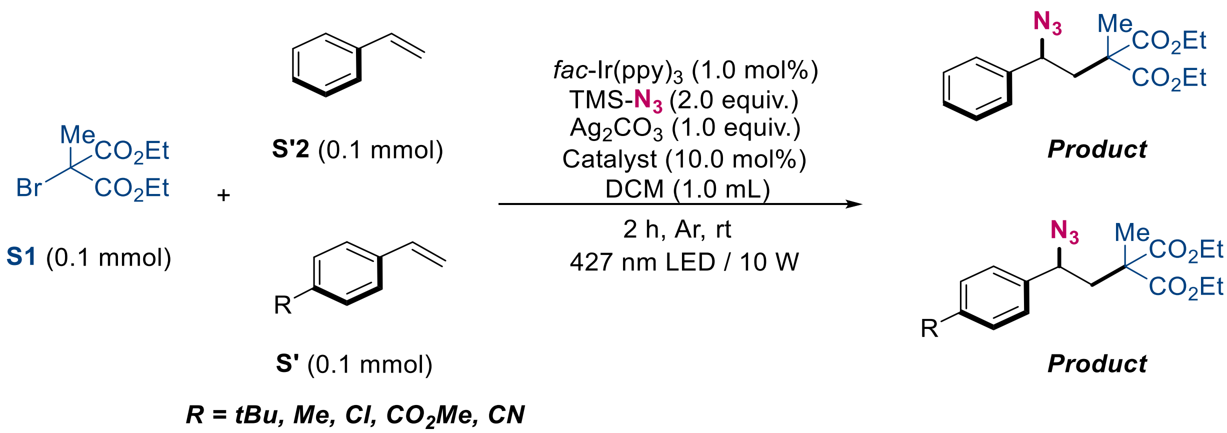
$$\text{Quantum yield} = \frac{\text{mole of product formation rate}}{\text{Photon flux}} \qquad (3)$$

Product formation rate = (0.0601%/s) × (1 × 10^{-6} mol/%) = 6.01×10^{-8} mol/s

Photon flux = 7.76 x 10^{-7} einsteins·s^{-1}

$$\text{Quantum Yield} = \frac{6.01\times10^{-8}\ \text{mol/s}}{7.76\ \text{x}\ 10^{-7}\ \text{einsteins}\cdot\text{s}^{-1}} = 0.08$$

Hammett plot analysis[20]



Hammett studies were performed through competition experiments between styrene (**S′2**) and para-substituted styrene derivatives (R = ***t*Bu**, **Me**, **Cl**, **CO_2Me**, **CN**). Relative reactivities were determined based on the product ratios (**1**, **30**, **32**, **34**, and **35**). The competition experiments were conducted as follows.

To an oven-dried 8 mL vial was added *fac*-Ir(ppy)$_3$ (0.7 mg, 0.001 mmol, 1.0 mol%), Ag_2CO_3 (27.9 mg, 0.1 mmol, 1.0 equiv.), Li_2CO_3 (7.5 mg, 0.1 mmol, 1.0 equiv.), and Fe(II)Pc (5.9 mg, 0.01 mmol, 10.0 mol%) under Ar condition. The vial was evacuated and backfilled with Ar (repeated for 3 times), subsequently followed by addition of **S′2** (0.1 mmol, 1.0 equiv.), **S′** (0.1 mmol, 1.0 equiv.), and fresh $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) to a reaction mixture. The vial was charged with anhydrous DCM (1.0 mL, 0.1 M) and then the reaction was stirred for 5 min at room temperature. The reaction was irradiated with a 40 W 427 nm Kessil lamp (25% intensity) for 10 min under fan cooling. Upon the completion of reaction, the reaction mixture was filtered on a celite, washed with DCM (10 mL), and concentrated under vacuum. To evaluate yield of the products, CH_2Br_2 (7.0 µL) as internal standard was added to the residue. The mixture was diluted with $CDCl_3$ and analyzed by ^{1}H-NMR. Each set of competition reactions was performed in duplicate, and the relative yields (X/H^1, X/H^2) were averaged to provide the final X/H values. The summarized results are shown below.

Table 10. The original data of Hammett study experiments

X	X/H[1]	X/H[2]	Average X/H	Log(X/H)
***t*Bu** (δ = -0.20)	2.50	2.43	2.47	1.0
Me (δ = -0.17)	1.80	1.76	1.78	1.0
Cl (δ = 0.23)	0.76	0.71	0.735	-0.13
CO_2Me (δ = 0.45)	0.56	0.56	0.560	-0.25
CN (δ = 0.66)	0.42	0.41	0.415	-0.38

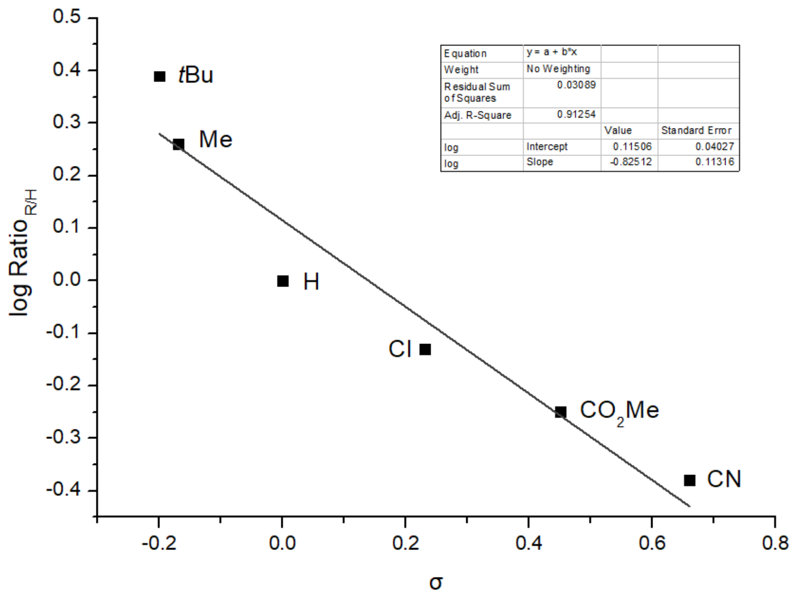


Figure 7. Hammett plot analysis

Comment: A Hammett analysis employing styrene derivatives with systematically varied electronic properties revealed a clear electronic effect on the reaction rate. Specifically, electron-rich styrenes bearing electron-donating substituents reacted markedly faster than their electron-deficient counterparts containing electron-withdrawing groups, indicating a strong dependence of the reaction kinetics on the electronic nature of the aromatic substituent.

Cyclic voltammetry measurements[11,24,25]

Cyclic voltammetry (CV) experiments were performed using a three-electrode cell setup comprising an Ag/AgCl (3 M NaCl) reference electrode, a 3 mm glassy carbon disk working electrode, and a Pt wire counter electrode. Samples were prepared at a substrate concentration of 5.0 mM in ACN with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. Before measurements, the sample solution was bubbled with argon for 5 min. All experiments were conducted at a scan rate of 100 mV/s within the selected potential window. The working electrode was polished, and all electrodes were rinsed thoroughly between each measurement. Reduction potential values were referenced to Saturated Calomel Electrode (SCE) by converting the Ag/AgCl (3 M NaCl) reference values, subtracting 0.035 V to all potentials. The reduction potential was estimated as the half-peak potential ($E_{p/2}$) where the current is half of the value of the peak current.

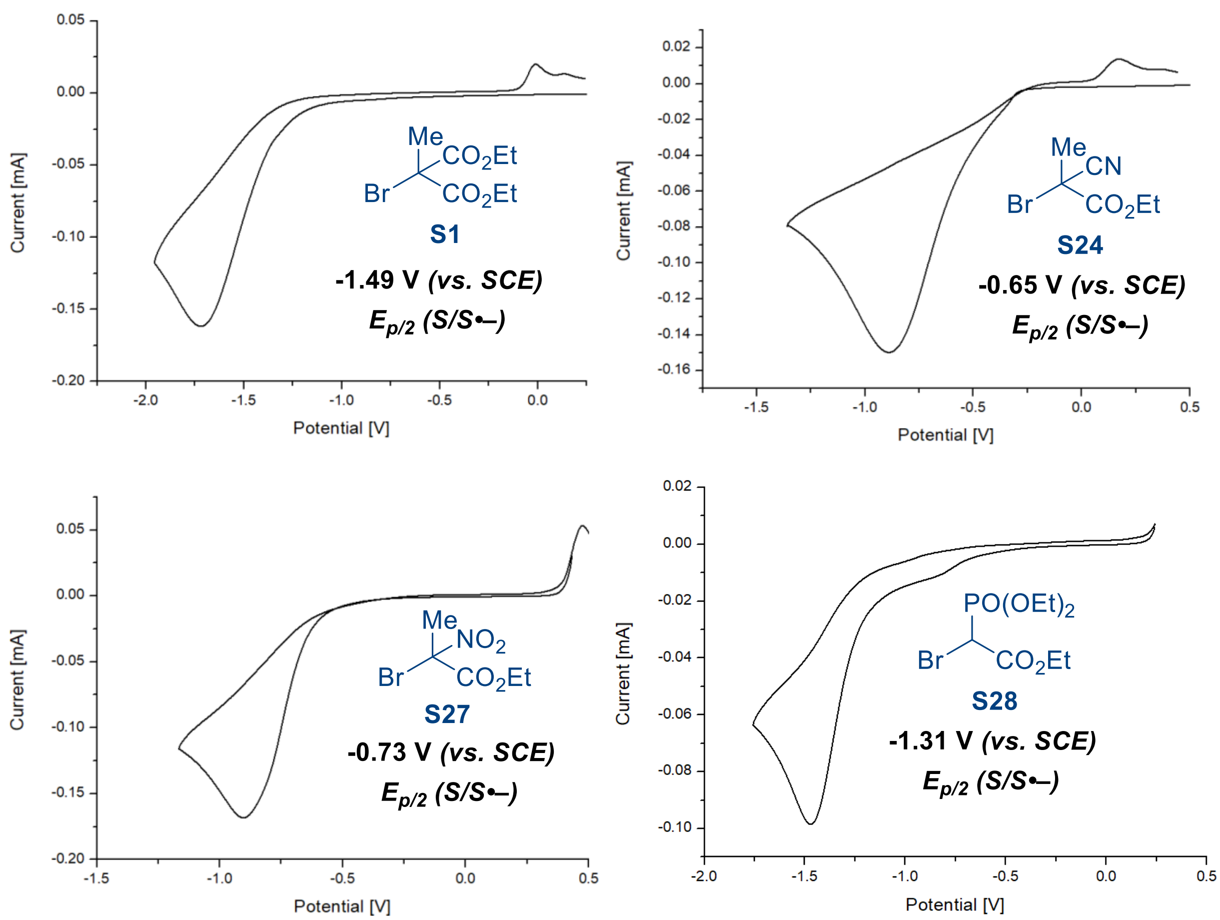


Figure 8. Cyclic voltammogram (CV)

Window of Compatibility

Table 11. Nucleophile-dependent reaction outcomes

Entry	*Nucleophile*	*Desired Product*	*Elimination Product*
1	**$^{-}N_3$**	**O**	**X**
2	**$^{-}$SCN**	**O**	**X**
3	**$^{-}$SeCN**	**O**	**X**
4	**$^{-}ONO_2$**	**O**	**X**
5	**$^{-}$OAc**	**X**	**O**
6	**$^{-}$Cl**	**O**	**X**
7	**$^{-}$Br**	**X**	**O**

Comment: We explored the compatibility of a variety of heteroatom-containing nucleophiles under the developed reaction conditions and observed that most nucleophiles, upon coordination to the iron center, efficiently engaged with the vicinal carbon-centered radical generated via the RLT pathway. In contrast, substrates bearing good leaving groups such as bromine and OAc preferentially underwent elimination under the standard conditions, which was verified by the formation of the corresponding elimination byproducts.

VIII. X-Ray Crystallography Data for 83 and 83'

[Method for crystal growth : vapor diffusion] In a 4.0 mL vial, products were dissolved in a minimum amount of DCM to obtain a concentrated solution. The 4.0 mL vial was placed into a 30.0 mL vial and n-hexane was added to the 30.0 mL vial. The vial was sealed and allowed over 2 days at -20 ℃ for crystal growth. The single crystal of **83** and **83'**were obtained as a transparent solid.

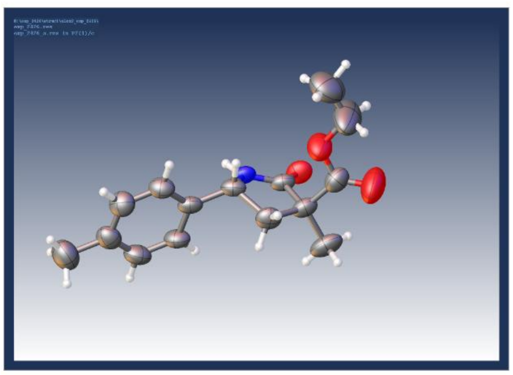


Table 11. Crystal data and structure refinement for 83.

Identification code	**83**
Empirical formula	$C_{15}H_{19}NO_3$
Formula weight	261.31
Temperature/K	293.1(7)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9009(3)
b/Å	6.2017(2)
c/Å	23.7192(8)
α/°	90
β/°	91.975(3)
γ/°	90
Volume/Å^3	1455.56(8)
Z	4

ρ_{calc}g/cm^3	1.192
μ/mm^{-1}	0.672
F(000)	560.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.458 to 147.734
Index ranges	-8 ≤ h ≤ 12, -7 ≤ k ≤ 7, -29 ≤ l ≤ 26
Reflections collected	5452
Independent reflections	2865 [R_{int} = 0.0550, R_{sigma} = 0.0459]
Data/restraints/parameters	2865/0/175
Goodness-of-fit on F^2	1.180
Final R indexes [I>=2σ (I)]	R_1 = 0.0882, wR_2 = 0.2785
Final R indexes [all data]	R_1 = 0.1205, wR_2 = 0.2918
Largest diff. peak/hole / e Å^{-3}	0.36/-0.30

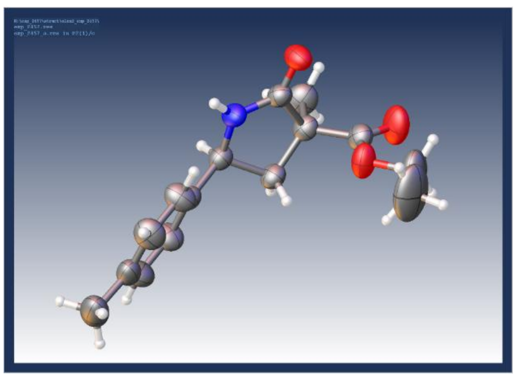


Table 12. Crystal data and structure refinement for 83'.

Identification code	**83'**
Empirical formula	$C_{15}H_{19}NO_3$
Formula weight	261.31
Temperature/K	292.5(4)
Crystal system	monoclinic
Space group	P2$_1$/c
a/Å	6.39809(16)
b/Å	11.3852(3)

c/Å	20.1220(5)
α/°	90
β/°	93.180(2)
γ/°	90
Volume/$Å^3$	1463.50(7)
Z	4
ρ_{calc}g/cm^3	1.186
μ/mm^{-1}	0.669
F(000)	560.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.802 to 147.586
Index ranges	-7 ≤ h ≤ 5, -13 ≤ k ≤ 14, -24 ≤ l ≤ 22
Reflections collected	5443
Independent reflections	2867 [R_{int} = 0.0156, R_{sigma} = 0.0193]
Data/restraints/parameters	2867/0/175
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1505
Final R indexes [all data]	R_1 = 0.0591, wR_2 = 0.1570
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.25

IX. Computational details

General methods All DFT computations were carried out using Gaussian

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package.[26] Geometry optimizations and frequency calculations were carried out at the unrestricted B3LYP/def2-SVP level in the gas phase.[27] Frequency analyses confirmed the nature of each stationary point (no imaginary frequencies for minima and one imaginary frequency for transition states) and provided thermal corrections to Gibbs free energies at 298.15 K. Intrinsic reaction coordinate (IRC) calculations were performed to verify the connectivity of transition states. Single-point energies were calculated at the level with solvation effects (DCM) included using the SMD model. Reported energies correspond to Gibbs free energies computed at the unrestricted B3LYP/def2-TZVP level in DCM with thermal corrections[28] from unrestricted B3LYP/def2-SVP calculations. The unrestricted formalism was applied to open-shell species. Structural graphics were generated using CYLview.[29] Spin density analyses were performed using the wavefunction analysis program Multiwfn (version 3.8). The wavefunction file (.fchk) was generated from the Gaussian output and used as input for Multiwfn.[30,31]

Energy correlation

	E (sol) (SCF/TZ, Hartree)	Thermal correction (Hartree)	G (sol) (kcal/mol)
S'2	-309.80445483	0.101434	-309.70302083
Int-1	-495.83964668	0.081519	-495.75812768
TS-1	-805.64678332	0.205585	-805.44119832
Int-2	-805.68671095	0.207740	-805.47897095
^{4}95	-3096.07958661	0.370704	-3095.70888261
^{3}TS-2	-3901.76230862	0.602938	-3901.15937062
P	-969.97809189	0.227082	-969.75100989
^{3}Fe(II)Pc	-2931.82087856	0.358019	-2931.46285956

Cartesian coordinates of computed structures

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S'2

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C	1.956648	-0.420409	-0.001631
C	3.344496	-0.366029	0.000234
C	3.992078	0.863084	0.000733
C	3.272816	2.063878	-0.000616
C	1.873043	1.989962	-0.002526
C	1.224891	0.765141	-0.003026
H	3.924790	-1.280273	0.001310
H	5.075368	0.898457	0.002209
H	1.284851	2.898422	-0.003689
H	0.142417	0.731754	-0.004524
C	4.011373	3.333410	0.000033
H	5.092315	3.223847	0.000973
C	3.509573	4.568179	-0.000434
H	2.445748	4.769627	-0.001322
H	4.161992	5.430958	0.000059
H	1.446831	-1.375454	-0.002046

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Int-1

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C	-0.755214	3.316211	-0.059850
H	-0.726865	4.391242	-0.161858
C	0.371546	2.663164	0.605282
C	-1.918009	2.673489	-0.670131
O	0.586328	1.475993	0.675006
O	-2.671799	3.295803	-1.392702
O	1.187417	3.605134	1.139636
O	-2.072452	1.381790	-0.359346
C	2.348149	3.105565	1.819202
H	2.057495	2.459679	2.647521
H	2.977463	2.539147	1.132967

C	-3.203195	0.726606	-0.954239
H	-3.129215	0.751415	-2.041036
H	-4.130136	1.212233	-0.649854
H	2.873434	3.983570	2.184322
H	-3.167133	-0.296148	-0.590688

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TS-1

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C	-0.852621	-0.265518	1.703627
H	-1.205482	-1.189823	1.247679
C	0.614341	-0.163797	1.764815
C	-1.839024	0.825904	1.657303
O	1.355080	-0.984124	1.263245
O	-3.040519	0.624970	1.640469
O	1.065070	0.886138	2.483278
O	-1.309349	2.061762	1.640721
C	2.480938	1.026007	2.561289
H	2.941075	0.144443	3.034382
H	2.920880	1.146213	1.559328
C	-2.238184	3.142486	1.603185
H	-2.903224	3.121088	2.480324
H	-2.862010	3.094926	0.697294
C	-4.068962	-5.266921	2.633310
C	-2.876154	-5.669904	3.243871
C	-1.934447	-4.717713	3.629869
C	-2.166642	-3.338404	3.428130
C	-3.372816	-2.948537	2.797313
C	-4.307740	-3.904760	2.407572
H	-2.679176	-6.731203	3.415253
H	-1.001198	-5.035632	4.103059
H	-3.562860	-1.893993	2.582696
H	-5.230163	-3.586608	1.915172
C	-1.163073	-2.376458	3.862063
H	-0.195265	-2.798849	4.154304

C	-1.310980	-1.012840	3.889818
H	-2.295949	-0.558878	3.777189
H	-0.529381	-0.385275	4.321321
H	-4.807125	-6.011781	2.325377
H	-1.637258	4.060363	1.603490
H	2.666696	1.922560	3.166062

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Int-2

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C	-0.554134	1.111250	0.802790
C	0.803040	0.419094	0.779120
H	1.219758	0.560423	-0.221160
C	1.751150	1.095115	1.759635
O	-0.961025	1.821974	1.682690
O	2.199165	0.593819	2.757324
O	-1.262801	0.788746	-0.293488
O	2.056084	2.332107	1.338955
C	2.899377	3.105502	2.208968
H	3.860406	2.611420	2.346689
H	2.419878	3.236670	3.178025
C	-2.600086	1.316804	-0.353854
H	-3.188733	0.951159	0.486179
H	-2.578813	2.405504	-0.332183
C	0.657967	-1.106754	1.030761
H	0.225490	-1.544303	0.132962
H	1.674904	-1.504271	1.121603
C	-0.125193	-1.470251	2.247431
H	0.255803	-1.091376	3.187410
C	-1.286850	-2.266935	2.290937
C	-1.908112	-2.836593	1.145364
C	-1.897070	-2.535803	3.549128
C	-3.046293	-3.611709	1.259852
H	-1.489735	-2.662456	0.163444
C	-3.033185	-3.310765	3.650460

H	-1.448161	-2.114141	4.440376
C	-3.621063	-3.858492	2.507394
H	-3.495782	-4.032964	0.368704
H	-3.471469	-3.495089	4.623655
H	3.028228	4.063610	1.713541
H	-4.512086	-4.467413	2.588127
H	-3.011412	0.959923	-1.293810

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^{4}95

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N	-12.101814	-4.413534	0.221121
N	-11.853028	-4.943803	1.202334
N	-11.585766	-5.517528	2.227067
Fe	-11.774349	-4.766427	4.001849
N	-12.624209	-6.268328	4.937755
C	-13.963223	-6.555262	4.920812
C	-14.189329	-7.855294	5.534216
C	-15.351330	-8.592718	5.765803
C	-15.209527	-9.825386	6.392561
C	-13.943815	-10.307330	6.780125
C	-12.788398	-9.568883	6.550838
C	-12.933715	-8.333122	5.919234
C	-11.969382	-7.314855	5.528514
N	-10.679605	-7.435219	5.745444
C	-9.811409	-6.504265	5.414244
C	-8.386594	-6.624230	5.679453
C	-7.796323	-5.451708	5.198294
C	-6.420648	-5.235795	5.297502
C	-5.659811	-6.235409	5.891769
C	-6.254713	-7.417311	6.376710
C	-7.624849	-7.628660	6.279180
C	-8.875273	-4.643588	4.653124
N	-8.677428	-3.455181	4.124252
C	-9.653394	-2.707511	3.663466

C	-9.437106	-1.377065	3.114206
C	-10.694797	-0.893436	2.743764
C	-10.850236	0.371808	2.176378
C	-9.701569	1.132871	1.992612
C	-8.433745	0.645815	2.366448
C	-8.282528	-0.614575	2.933162
C	-11.651252	-1.938625	3.075967
N	-10.989669	-3.006112	3.624601
N	-12.942319	-1.814008	2.870959
C	-13.809926	-2.748512	3.192995
N	-13.552662	-3.967636	3.760712
C	-14.745148	-4.619188	3.933952
C	-15.831494	-3.778426	3.456897
C	-15.242379	-2.599697	2.990216
C	-16.010773	-1.563420	2.457936
C	-17.387159	-1.750975	2.409560
C	-17.981214	-2.938511	2.880799
C	-17.213607	-3.968369	3.411747
N	-14.940300	-5.809729	4.456537
N	-10.063141	-5.306246	4.802689
H	-16.325289	-8.207267	5.460488
H	-16.093462	-10.435562	6.589911
H	-13.873532	-11.281009	7.269703
H	-11.802327	-9.930513	6.846230
H	-5.972990	-4.315975	4.918119
H	-4.579441	-6.107206	5.986647
H	-5.622460	-8.179614	6.836956
H	-8.097763	-8.539023	6.650623
H	-11.838008	0.735606	1.889702
H	-9.778631	2.127612	1.548633
H	-7.554963	1.273709	2.204821
H	-7.306469	-1.003990	3.226418
H	-15.537834	-0.649822	2.094785
H	-18.024549	-0.965747	1.997576

H	-19.066317	-3.047981	2.824459
H	-17.660719	-4.893252	3.779216

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^{3}TS-2

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C	-2.715432	-8.285446	-0.510143
C	-3.366018	-6.956469	-0.859022
H	-2.601328	-6.337874	-1.349413
C	-4.439163	-7.187522	-1.908177
O	-3.197741	-9.373062	-0.697492
O	-4.214828	-7.237876	-3.090905
O	-1.526255	-8.084786	0.082696
O	-5.665211	-7.327618	-1.379443
C	-6.716886	-7.607597	-2.303072
H	-6.524355	-8.555192	-2.827470
H	-6.803150	-6.804681	-3.050143
C	-0.855985	-9.247024	0.571520
H	-1.470456	-9.751295	1.331338
H	-0.650812	-9.950008	-0.249014
C	-3.816261	-6.212031	0.429904
H	-2.906411	-5.894787	0.942737
H	-4.341255	-5.295938	0.122728
C	-4.675095	-6.984844	1.371665
H	-5.735191	-7.064036	1.124560
C	-4.223195	-7.699551	2.502806
C	-5.165142	-8.429189	3.288469
C	-2.866949	-7.685005	2.950958
C	-4.777159	-9.107531	4.435344
H	-6.210044	-8.443517	2.969816
C	-2.494647	-8.353941	4.107116
H	-2.116207	-7.139059	2.383244
C	-3.441908	-9.071319	4.856049
H	-5.520035	-9.655316	5.019514
H	-1.456181	-8.315497	4.440456

H	-7.635447	-7.678946	-1.708316
H	0.079604	-8.889264	1.017911
H	-3.137595	-9.590441	5.767496
N	-5.036452	-5.734073	4.873823
N	-4.672696	-5.140140	3.961788
N	-4.313671	-4.555568	2.959941
Fe	-2.992312	-3.148434	3.163956
N	-2.022269	-3.491108	1.488229
C	-1.012336	-4.413489	1.329885
C	-0.717454	-4.573677	-0.089278
C	0.159920	-5.413065	-0.778804
C	0.128184	-5.374524	-2.173649
C	-0.755868	-4.517795	-2.862540
C	-1.629681	-3.675373	-2.173093
C	-1.600210	-3.717455	-0.776555
C	-2.398323	-3.046229	0.242029
N	-3.343443	-2.170592	-0.045163
C	-4.084857	-1.582992	0.872396
C	-5.113567	-0.598924	0.556412
C	-5.695468	-0.225297	1.783050
C	-6.727318	0.714077	1.838238
C	-7.160944	1.268467	0.632261
C	-6.578102	0.894344	-0.596226
C	-5.545882	-0.043980	-0.650483
C	-5.010076	-0.995723	2.816341
N	-5.313156	-0.908132	4.097672
C	-4.709249	-1.605976	5.038963
C	-5.045579	-1.492692	6.455030
C	-4.210694	-2.398161	7.136999
C	-4.281111	-2.546517	8.523902
C	-5.211466	-1.763734	9.210010
C	-6.047791	-0.856859	8.527115
C	-5.976088	-0.709031	7.140401
C	-3.379792	-3.036520	6.123224

N	-3.701521	-2.530520	4.881917
N	-2.477805	-3.956293	6.402854
C	-1.710289	-4.515917	5.487601
N	-1.694036	-4.252158	4.135350
C	-0.728919	-5.040087	3.551398
C	-0.084670	-5.854114	4.574372
C	-0.714158	-5.535079	5.793045
C	-0.359014	-6.177994	6.981512
C	0.641259	-7.149258	6.916842
C	1.276273	-7.464467	5.696680
C	0.923725	-6.818766	4.510211
N	-0.415239	-5.117671	2.272324
N	-4.045079	-1.783088	2.235000
H	0.824488	-6.085579	-0.235499
H	0.790747	-6.026610	-2.747282
H	-0.761661	-4.525164	-3.954650
H	-2.326723	-3.016961	-2.693997
H	-7.170910	0.994995	2.794979
H	-7.966939	2.006106	0.636092
H	-6.944085	1.349159	-1.519728
H	-5.086218	-0.342407	-1.594302
H	-3.629709	-3.254185	9.039438
H	-5.297524	-1.853760	10.295416
H	-6.764979	-0.261466	9.097096
H	-6.619127	-0.011990	6.600357
H	-0.859802	-5.926589	7.917948
H	0.941385	-7.677355	7.824900
H	2.057158	-8.228565	5.685106
H	1.404148	-7.055534	3.559211

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P

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O	1.492028	2.592631	-2.103684
C	1.507495	2.686612	-0.909659

O	2.679696	2.773811	-0.274828
C	2.796798	2.614165	1.129463
C	0.208945	2.769833	-0.097748
C	-0.240974	1.439360	0.523473
C	-0.072955	0.222526	-0.386635
N	1.364198	-0.120902	-0.360155
N	1.770202	-0.743355	-1.335643
N	2.237301	-1.309655	-2.181145
C	-0.955994	-0.920021	0.069389
C	-2.272032	-0.967373	-0.378927
C	-3.124909	-1.968929	0.054284
C	-2.670266	-2.935625	0.939796
C	-1.359858	-2.893093	1.388484
C	-0.505872	-1.888969	0.956016
C	-0.858699	3.313909	-1.037186
O	-0.636439	4.597168	-1.306274
C	-1.509372	5.195602	-2.263002
O	-1.788844	2.685448	-1.461416
H	3.833053	2.841864	1.365239
H	2.578520	1.583753	1.411634
H	2.152373	3.303425	1.678833
H	0.332244	3.509302	0.695338
H	-1.294690	1.536167	0.780098
H	0.301135	1.247535	1.450380
H	-0.362509	0.502529	-1.402531
H	-2.625808	-0.208662	-1.068185
H	-4.145790	-1.998619	-0.305161
H	-3.334674	-3.722084	1.274539
H	-0.997300	-3.646548	2.076451
H	0.520157	-1.861594	1.301057
H	-2.541325	5.159813	-1.914875
H	-1.432010	4.674884	-3.216851
H	-1.175573	6.224391	-2.363327

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[3]Fe(II)Pc

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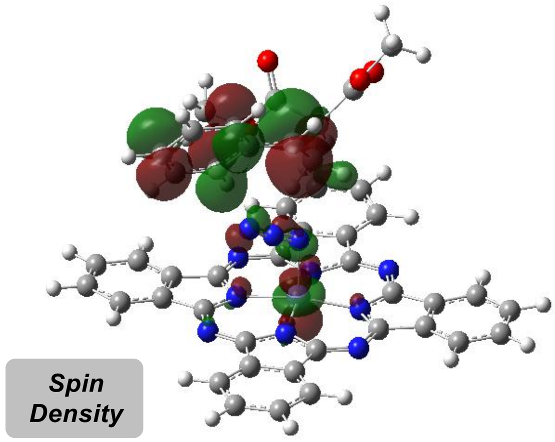
Fe	-11.814964	-4.608276	4.339378
N	-12.634201	-6.238810	4.995960
C	-13.967095	-6.530546	4.970089
C	-14.186369	-7.841972	5.551475
C	-15.336553	-8.590536	5.759076
C	-15.190833	-9.831087	6.351730
C	-13.930292	-10.313078	6.727932
C	-12.785729	-9.565926	6.520331
C	-12.934065	-8.320847	5.925181
C	-11.977045	-7.291607	5.563739
N	-10.685656	-7.411788	5.775644
C	-9.818003	-6.479903	5.448743
C	-8.392661	-6.615249	5.683630
C	-7.803853	-5.445209	5.212848
C	-6.431896	-5.248140	5.287064
C	-5.672419	-6.258704	5.846563
C	-6.265203	-7.436514	6.320546
C	-7.631695	-7.631076	6.245858
C	-8.882544	-4.620145	4.700431
N	-8.686143	-3.433898	4.174947
C	-9.663062	-2.684785	3.709752
C	-9.443978	-1.375061	3.130103
C	-10.697126	-0.895830	2.756004
C	-10.844475	0.350758	2.161184
C	-9.700647	1.097533	1.954667
C	-8.439175	0.615141	2.331287
C	-8.293458	-0.624848	2.922810
C	-11.652560	-1.923914	3.116056
N	-10.995357	-2.976540	3.683107
N	-12.945838	-1.804928	2.904462
C	-13.812571	-2.734769	3.230334

N	-13.560056	-3.940924	3.819085
C	-14.746011	-4.595176	3.979459
C	-15.825998	-3.772077	3.468524
C	-15.238842	-2.601433	2.997056
C	-16.002761	-1.587353	2.435956
C	-17.369093	-1.784617	2.363381
C	-17.960070	-2.963093	2.838110
C	-17.197881	-3.971946	3.396510
N	-14.943519	-5.783463	4.506064
N	-10.069968	-5.275343	4.860259
H	-16.305311	-8.209391	5.464890
H	-16.064350	-10.445119	6.530516
H	-13.855988	-11.289538	7.189504
H	-11.807903	-9.929059	6.807211
H	-5.983516	-4.335274	4.918360
H	-4.598705	-6.142346	5.922100
H	-5.637309	-8.205510	6.752311
H	-8.099411	-8.536559	6.608748
H	-11.822150	0.714209	1.874108
H	-9.774616	2.074338	1.493698
H	-7.565855	1.229663	2.153060
H	-7.324624	-1.005827	3.217048
H	-15.537495	-0.680962	2.072222
H	-17.998704	-1.016544	1.932362
H	-19.033672	-3.080990	2.763995
H	-17.643829	-4.885665	3.766102

Calculated spin-density plots for ^{3}TS-2



Population of atoms:

Atom	Alpha pop.	Beta pop.	Spin pop.	Atomic charge
1(C)	2.91111	2.91229	-0.00118	0.17660
2(C)	3.01888	2.99079	0.02809	-0.00967
3(H)	0.47300	0.47121	0.00180	0.05579
4(C)	2.91118	2.91254	-0.00136	0.17628
5(O)	4.10727	4.10705	0.00022	-0.21431
6(O)	4.11122	4.11060	0.00061	-0.22182
7(O)	4.15546	4.15458	0.00088	-0.31003
8(O)	4.15173	4.15075	0.00098	-0.30247
9(C)	2.90371	2.90365	0.00007	0.19264
10(H)	0.48131	0.48132	-0.00001	0.03738
11(H)	0.48545	0.48536	0.00009	0.02918
12(C)	2.90770	2.90751	0.00019	0.18479
13(H)	0.47971	0.47974	-0.00003	0.04055
14(H)	0.48268	0.48270	-0.00002	0.03462
15(C)	2.91090	2.96651	-0.05560	0.12259
16(H)	0.47859	0.47204	0.00655	0.04936
17(H)	0.49025	0.47745	0.01280	0.03231

18(C)	3.34433	2.71939	0.62493	-0.06372
19(H)	0.48536	0.51285	-0.02749	0.00179
20(C)	2.86928	3.04815	-0.17888	0.08257
21(C)	3.09839	2.90115	0.19724	0.00046
22(C)	3.12464	2.91206	0.21258	-0.03670
23(C)	2.92267	3.03513	-0.11246	0.04220
24(H)	0.50777	0.51643	-0.00866	-0.02420
25(C)	2.93284	3.04828	-0.11545	0.01888
26(H)	0.49509	0.50439	-0.00930	0.00053
27(C)	3.09769	2.87110	0.22660	0.03121
28(H)	0.51013	0.50603	0.00410	-0.01617
29(H)	0.50765	0.50336	0.00429	-0.01101
30(H)	0.48542	0.48530	0.00012	0.02928
31(H)	0.48481	0.48481	0.00001	0.03038
32(H)	0.50250	0.51302	-0.01053	-0.01552
33(N)	3.59764	3.65470	-0.05707	-0.25234
34(N)	3.34736	3.30061	0.04675	0.35202
35(N)	3.58458	3.74138	-0.15680	-0.32597
36(Fe)	13.41013	11.94564	1.46449	0.64423
37(N)	3.63443	3.65674	-0.02231	-0.29118
38(C)	2.97771	2.98532	-0.00761	0.03697
39(C)	2.96632	2.96192	0.00440	0.07177
40(C)	3.01449	3.01883	-0.00434	-0.03332
41(C)	2.99161	2.98678	0.00483	0.02160
42(C)	2.97933	2.98393	-0.00460	0.03673
43(C)	3.03015	3.02586	0.00430	-0.05601
44(C)	2.96152	2.96722	-0.00570	0.07126
45(C)	2.98187	2.97358	0.00829	0.04456
46(N)	3.50469	3.50860	-0.00390	-0.01329
47(C)	2.97272	2.96491	0.00780	0.06237
48(C)	2.96151	2.96490	-0.00339	0.07360

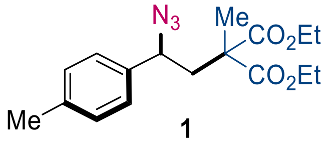
49(C)	2.96378	2.95998	0.00381	0.07624
50(C)	3.02190	3.02464	-0.00274	-0.04653
51(C)	2.98699	2.98275	0.00424	0.03026
52(C)	2.98428	2.98683	-0.00255	0.02888
53(C)	3.02433	3.02115	0.00317	-0.04548
54(C)	2.96952	2.97159	-0.00207	0.05888
55(N)	3.50439	3.50797	-0.00358	-0.01236
56(C)	2.97161	2.97115	0.00046	0.05725
57(C)	2.96327	2.95919	0.00408	0.07754
58(C)	2.95798	2.96281	-0.00483	0.07921
59(C)	3.02295	3.01845	0.00450	-0.04141
60(C)	2.98431	2.98648	-0.00217	0.02921
61(C)	2.98757	2.98165	0.00593	0.03078
62(C)	3.02185	3.02456	-0.00271	-0.04641
63(C)	2.98147	2.96629	0.01517	0.05224
64(N)	3.63008	3.67007	-0.03998	-0.30015
65(N)	3.49721	3.50661	-0.00940	-0.00381
66(C)	2.97951	2.96451	0.01500	0.05597
67(N)	3.63009	3.66569	-0.03560	-0.29577
68(C)	2.97277	2.97395	-0.00118	0.05328
69(C)	2.96695	2.96180	0.00515	0.07125
70(C)	2.95689	2.96147	-0.00458	0.08163
71(C)	3.02344	3.01918	0.00426	-0.04261
72(C)	2.98534	2.98753	-0.00219	0.02713
73(C)	2.98920	2.98314	0.00606	0.02767
74(C)	3.02531	3.02847	-0.00315	-0.05378
75(N)	3.51567	3.51933	-0.00365	-0.03500
76(N)	3.63431	3.66126	-0.02695	-0.29557
77(H)	0.51144	0.51126	0.00018	-0.02270
78(H)	0.50423	0.50443	-0.00020	-0.00866
79(H)	0.50255	0.50237	0.00018	-0.00492

80(H)	0.50713	0.50730	-0.00017	-0.01442
81(H)	0.50794	0.50784	0.00011	-0.01578
82(H)	0.50476	0.50495	-0.00019	-0.00971
83(H)	0.50499	0.50491	0.00008	-0.00989
84(H)	0.50786	0.50799	-0.00014	-0.01585
85(H)	0.50773	0.50792	-0.00019	-0.01564
86(H)	0.50506	0.50502	0.00004	-0.01007
87(H)	0.50484	0.50513	-0.00029	-0.00997
88(H)	0.50819	0.50809	0.00010	-0.01629
89(H)	0.50664	0.50682	-0.00019	-0.01346
90(H)	0.50459	0.50454	0.00005	-0.00913
91(H)	0.50493	0.50522	-0.00029	-0.01015
92(H)	0.50938	0.50926	0.00012	-0.01864

Total net charge: 0.00000009 Total spin electrons: 1.99999998

X. Characterization of Products

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-methylmalonate (1)

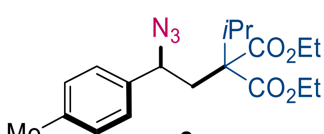


1

1 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc = 30 : 1), the title compound was isolated as a colorless oil (31.7 mg, 95% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 4.56 (q, J = 4.6 Hz, 1H), 4.23-4.05 (m, 4H), 2.42 (dd, J = 14.7, 9.7 Hz, 1H), 2.35 (s, 3H), 2.26 (dd, J = 14.7, 4.1 Hz, 1H), 1.50 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$) δ 171.9, 171.8, 138.4, 136.6, 129.6, 127.0, 62.4, 61.7, 61.6, 52.5, 41.7, 21.3, 20.4, 14.1, 14.1.
IR (neat) ν 2984, 2941, 2107, 1731, 1447, 1380, 1240, 1108, 861 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{23}N_3NaO_4$ $[M+Na]^+$ 356.1581, found 356.1574.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-isopropylmalonate (2)

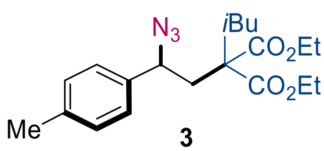


2

2 was synthesized according to general procedure A. **S2** (34.4 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 50 : 1 : 1), the title compound was isolated as a colorless oil (23.4 mg, 65% yield).

^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.64 (dd, J = 9.1, 3.7 Hz, 1H), 4.31-4.11 (m, 4H), 2.39-2.33 (m, 4H), 2.23 (dd, *J* = 14.6, 9.1 Hz, 1H), 1.28 (td, *J* = 7.1, 5.3 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 1H), 0.98 (dd, *J* = 6.9, 4.6 Hz, 6H).
^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.7, 138.2, 137.5, 129.6, 126.9, 62.9, 61.3, 61.1, 60.4, 40.6, 33.1, 21.3, 19.3, 18.9, 18.6, 14.2, 14.2, 14.0.
IR (neat) ν 2977, 2936, 2104, 1726, 1465, 1330, 1243, 1052, 819 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{27}N_3NaO_4$ $[M+Na]^+$ 384.1894, found 384.1903.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-isobutylmalonate (3)

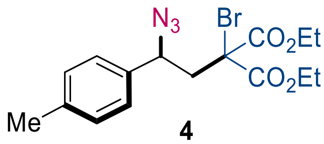


3

3 was synthesized according to general procedure A. **S3** (35.8 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (32.7 mg, 87% yield).

^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.47 (q, *J* = 4.4 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.13-4.02 (m, 2H), 2.45-2.32 (m, 5H), 2.05-1.95 (m, 2H), 1.65-1.55 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.87 (q, *J* = 3.2 Hz, 6H).
^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 171.8, 171.7, 138.4, 136.8, 129.6, 127.0, 62.5, 61.5, 61.5, 55.6, 41.1, 39.0, 24.3, 23.8, 23.6, 21.3, 14.1, 14.0.
IR (neat) ν 2979, 2959, 2106, 1731, 1466, 1389, 1223, 1048, 818 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{29}N_3NaO_4$ $[M+Na]^+$ 398.2050, found 398.2048.

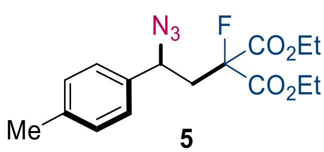
Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-bromomalonate (4)


4

4 was synthesized according to general procedure A. **S4** (39.7 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (27.1 mg, 68% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.84 (dd, *J* = 9.8, 3.9 Hz, 1H), 4.39-4.26 (m, 2H), 4.20-4.09 (m, 2H), 2.79 (dd, *J* = 15.3, 9.8 Hz, 1H), 2.63 (dd, *J* = 15.1, 4.1 Hz, 1H), 2.36 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.3 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 166.1, 138.8, 135.6, 129.7, 127.2, 63.6, 63.2, 63.2, 61.5, 44.0, 21.3, 14.0, 13.8.
IR (neat) ν 2982, 2923, 2111, 1743, 1465, 1390, 1257, 1045, 818 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{23}N_3NaO_4$ $[M+Na]^+$ 356.1581, found 356.1574.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-fluoromalonate (5)


5

5 was synthesized according to general procedure A. **S5** (31.2 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 20 : 1 : 1), the title compound was isolated as a white solid (23.8 mg, 71% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23-7.18 (m, 4H), 4.71 (dd, J = 10.1, 4.1 Hz, 1H), 4.39-4.31 (m, 2H), 4.17 (qd, J = 7.1, 3.4 Hz, 2H), 2.76 (ddd, J = 28.3, 15.2, 9.9 Hz, 1H), 2.54-2.46 (m, 1H), 2.36 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.7 (q, $J_{C\text{-}F}$ = 36.8), 138.7, 135.2, 129.6, 128.4 (d, $J_{C\text{-}F}$ = 165.2), 126.9, 92.4 (d , $J_{C\text{-}F}$ = 198.6), 77.3, 77.2, 77.0, 76.7, 62.9, 62.8, 60.2, 60.2, 40.3 (d , $J_{C\text{-}F}$ = 21.0), 21.1, 13.9, 13.8.

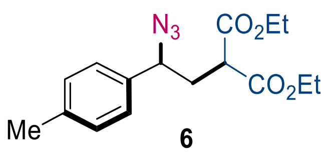
^{19}F-NMR (376 MHz, $CDCl_3$) δ -167.5, -167.6, -167.6, -167.6

IR (neat) ν 2986, 2940, 2107, 1751, 1446, 1370, 1243, 1021, 823 cm^{-1}.

HRMS (ESI) calcd for $C_{16}H_{24}FN_4O_4$ $[M+NH_4]^+$ 355.1776, found 355.1769.

m.p. 33-35 °C

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)malonate (6)



6

6 was synthesized according to general procedure A. **S6** (31.9 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (29.4 mg, 92% yield).

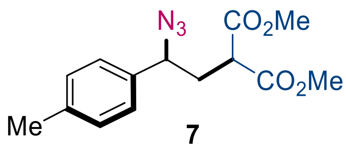
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 8.7 Hz, 4H), 4.51 (dd, J = 8.7, 6.0 Hz, 1H), 4.26-4.14 (m, 4H), 3.47 (dd, J = 7.8, 6.9 Hz, 1H), 2.37-2.29 (m, 5H), 1.27 (td, J = 7.1, 2.9 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.0, 169.0, 138.6, 135.6, 129.8, 127.0, 63.9, 61.8, 49.3, 35.3, 21.3, 14.2.

IR (neat) ν 2982, 2935, 2102, 1748, 1446, 1370, 1254, 1030, 819 cm^{-1}.

HRMS (CI) calcd for $C_{16}H_{22}NO_4$ $[M+H-N_2]^+$ 292.1543, found 292.1550.

Dimethyl 2-(2-azido-2-(p-tolyl)ethyl)malonate (7)

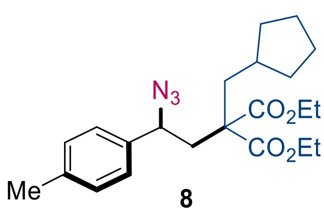


7

7 was synthesized according to general procedure A. **S15** (26.7 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 15 : 1 : 1), the title compound was isolated as a colorless oil (23.3 mg, 81% yield).

^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.20 (s, 4H), 4.50 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.74 (d, *J* = 3.2 Hz, 6H), 3.52 (dd, *J* = 7.8, 6.9 Hz, 1H), 2.38-2.26 (m, 5H).
^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 169.4, 169.3, 138.7, 135.4, 129.8, 127.0, 63.8, 52.9, 48.9, 35.3, 21.3.
IR (neat) ν 2954, 2847, 2102, 1747, 1436, 1339, 1231, 1021, 820 cm^{-1}.
HRMS (ESI) calcd for $C_{14}H_{17}N_3NaO_4$ $[M+Na]^+$ 314.1111, found 314.1137.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(cyclopentylmethyl)malonate (8)



8

8 was synthesized according to general procedure A. **S7** (39.3 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (36.1 mg, 90% yield).

^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.48 (q, *J* = 4.4 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 4.13-4.02 (m, 2H), 2.41-2.39 (m, 2H), 2.35 (s, 3H), 2.15

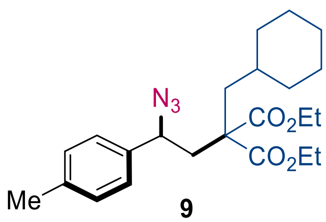
(ddd, J = 24.9, 14.6, 6.2 Hz, 2H), 1.74-1.53 (m, 5H), 1.52-1.38 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.13-0.99 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 171.6, 138.4, 136.7, 129.6, 127.0, 62.4, 61.5, 61.4, 56.0, 38.9, 38.5, 36.1, 33.7, 33.6, 24.9, 24.9, 21.3, 14.1, 14.0.

IR (neat) ν 2978, 2954, 2105, 1731, 1447, 1389, 1221, 1048, 818 cm^{-1}.

HRMS (ESI) calcd for $C_{22}H_{31}N_3NaO_4$ $[M+Na]^+$ 424.2207, found 424.2208.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(cyclohexylmethyl)malonate (9)



9

9 was synthesized according to general procedure A. **S8** (40.6 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a white solid (39.6 mg, 95% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 4.64 (dd, J = 9.1, 3.7 Hz, 1H), 4.31-4.11 (m, 4H), 2.39-2.33 (m, 4H), 2.23 (dd, J = 14.6, 9.1 Hz, 1H), 1.28 (td, J = 7.1, 5.3 Hz, 6H), 1.09 (d, J = 6.9 Hz, 1H), 0.98 (dd, J = 6.9, 4.6 Hz, 6H).

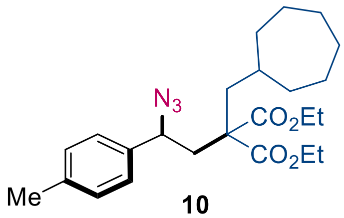
^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 138.2, 137.5, 129.6, 126.9, 62.9, 61.3, 61.1, 60.4, 40.6, 33.1, 21.3, 19.3, 18.9, 18.6, 14.2, 14.2, 14.0.

IR (neat) ν 2981, 2926, 2105, 1731, 1448, 1367, 1238, 1036, 819 cm^{-1}.

HRMS (ESI) calcd for $C_{23}H_{33}N_3NaO_4$ $[M+Na]^+$ 438.2363, found 438.2370.

m.p. 34-36 ℃

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(cycloheptylmethyl)malonate (10)



10 was synthesized according to general procedure A. **S9** (42.8 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc = 40 : 1), the title compound was isolated as a colorless oil (39.3 mg, 91% yield).

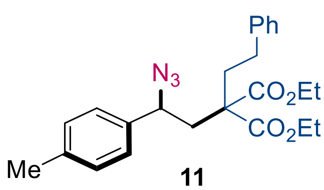
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24-7.16 (m, 4H), 4.47 (q, J = 4.6 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 4.12-4.01 (m, 2H), 2.44-2.31 (m, 5H), 2.01 (ddd, J = 27.7, 14.9, 5.9 Hz, 2H), 1.61-1.30 (m, 11H), 1.29-1.16 (m, 8H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 171.7, 138.4, 136.8, 129.6, 127.0, 62.5, 61.5, 61.4, 55.8, 40.6, 39.2, 35.9, 35.6, 35.1, 28.5, 26.1, 26.0, 21.3, 14.1, 14.0.

IR (neat) ν 2981, 2925, 2104, 1730, 1446, 1367, 1217, 1039, 818 cm^{-1}.

HRMS (ESI) calcd for $C_{24}H_{35}N_3NaO_4$ $[M+Na]^+$ 452.2520, found 452.2510.

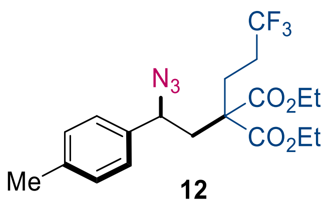
Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-phenethylmalonate (11)



11 was synthesized according to general procedure A. **S13** (41.6 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (33.9 mg, 80% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.24-7.18 (m, 5H), 7.16-7.13 (m, 2H), 4.53 (q, J = 4.6 Hz, 1H), 4.28-4.07 (m, 4H), 2.60-2.20 (m, 9H), 1.30 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.3 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 171.0, 141.2, 138.5, 136.7, 129.7, 128.6, 128.5, 127.0, 126.3, 62.5, 61.7, 61.6, 56.4, 39.0, 34.8, 30.8, 21.3, 14.2, 14.2.
IR (neat) ν 2980, 2936, 2103, 1730, 1455, 1386, 1231, 1030, 818 cm^{-1}.
HRMS (ESI) calcd for $C_{24}H_{29}N_3NaO_4$ $[M+Na]^+$ 446.2050, found 446.2035.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(3,3,3-trifluoropropyl)malonate (12)

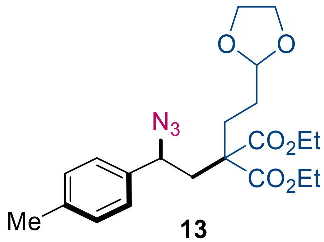


12

12 was synthesized according to general procedure A. **S10** (34.4 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a white solid (32.5 mg, 78% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 4H), 4.50 (q, J = 4.6 Hz, 1H), 4.28-4.10 (m, 4H), 2.41-2.35 (m, 4H), 2.33-2.10 (m, 4H), 2.04-1.86 (m, 1H), 1.27 (dt, J = 13.8, 6.2 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 170.3, 138.7, 136.3, 129.8, 126.9, 126.8 (q, J_{C-F} = 275.0), 62.2, 62.1, 62.0, 55.4, 39.3, 29.6 (q, J_{C-F} = 28.7), 25.6 (q, J_{C-F} = 3.8), 21.3, 14.1.
^{19}F-NMR (376 MHz, $CDCl_3$): δ -66.5, -66.6, -66.6.
IR (neat) ν 2977, 2949, 2107, 1747, 1449, 1396, 1228, 1144, 859 cm^{-1}.
HRMS (CI) calcd for $C_{19}H_{25}F_3NO_4$ $[M+H-N_2]^+$ 388.1730, found 388.1737.
m.p. 37-39 °C

Diethyl 2-(2-(1,3-dioxolan-2-yl)ethyl)-2-(2-azido-2-(p-tolyl)ethyl)malonate (13)

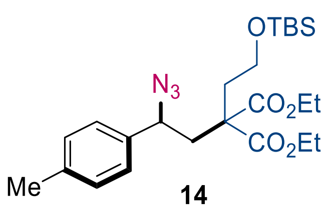


13

13 was synthesized according to general procedure A. **S11** (41.1 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 10 : 1 : 1), the title compound was isolated as a colorless oil (27.5 mg, 66% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 11.2, 8.5 Hz, 4H), 4.54 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.37 (t, *J* = 6.2 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.16-4.06 (m, 2H), 3.49 (t, *J* = 6.2 Hz, 2H), 2.46-2.22 (m, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H)
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 170.7, 170.6, 138.6, 136.5, 129.7, 127.0, 64.1, 62.2, 61.9, 61.8, 55.7, 39.4, 29.5, 28.7, 28.1, 21.3, 14.1, 14.1.
IR (neat) ν 2981, 2939, 2104, 1715, 1463, 1368, 1217, 1021, 819 cm^{-1}.
HRMS (CI) calcd for $C_{21}H_{28}N_3O_6$ $[M-H]^-$ 418.1984, found 418.1969.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(2-((tert-butyldimethylsilyl)oxy)ethyl)malonate (14)

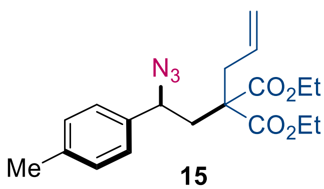


14

14 was synthesized according to general procedure A. **S12** (48.7 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (44.8 mg, 94% yield).

^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.55 (q, *J* = 4.4 Hz, 1H), 4.22-4.03 (m, 4H), 3.68-3.57 (m, 2H), 2.43-2.21 (m, 7H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H).
^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 171.2, 171.0, 138.8, 138.4, 138.2, 136.6, 129.6, 127.0, 62.4, 61.6, 61.5, 59.5, 54.8, 38.9, 35.3, 26.0, 21.3, 18.5, 14.1, 14.1, -5.3.
IR (neat) ν 2981, 2939, 2104, 1746, 1463, 1387, 1229, 1021, 819 cm^{-1}.
HRMS (ESI) calcd for $C_{24}H_{39}N_3NaO_5Si$ $[M+Na]^+$ 500.2551, found 500.2555.

Diethyl 2-allyl-2-(2-azido-2-(p-tolyl)ethyl)malonate (15)

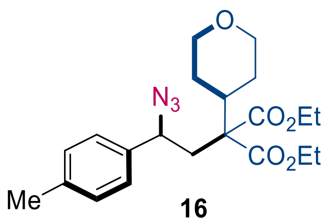


15

15 was synthesized according to general procedure A. **S14** (33.8 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a white solid (22.7 mg, 65% yield).

^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 11.4, 8.2 Hz, 4H), 5.65-5.55 (m, 1H), 5.17-5.09 (m, 2H), 4.55 (q, *J* = 4.6 Hz, 1H), 4.24-4.05 (m, 4H), 2.78 (ddd, *J* = 31.0, 14.5, 7.4 Hz, 2H), 2.40-2.34 (m, 4H), 2.27 (dd, *J* = 14.9, 3.9 Hz, 1H), 1.25 (dt, *J* = 18.9, 7.1 Hz, 6H).
^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 170.9, 170.8, 138.4, 136.7, 132.2, 129.6, 126.9, 119.7, 62.2, 61.7, 61.6, 56.0, 38.8, 37.5, 21.3, 14.1.
IR (neat) ν 2981, 2936, 2122, 1731, 1464, 1368, 1232, 1025, 817 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{25}NO_4$ $[M+H-N_2]^+$ 332.1784, found 332.1834.
m.p. 35-37 °C

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(tetrahydro-2H-pyran-4-yl)malonate (16)

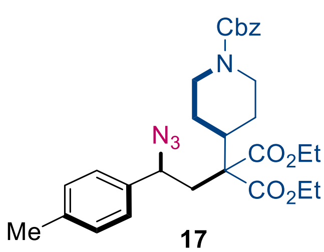


16

16 was synthesized according to general procedure A. **S16** (39.2 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 µL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 15 : 1 : 1), the title compound was isolated as a colorless oil (23.9 mg, 59% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 12.8, 8.2 Hz, 4H), 4.58 (q, *J* = 4.1 Hz, 1H), 4.27-4.10 (m, 4H), 3.99-3.94 (m, 2H), 3.45-3.31 (m, 2H), 2.36 (dd, *J* = 14.4, 3.9 Hz, 4H), 2.31-2.22 (m, 2H), 1.79 (d, *J* = 15.1 Hz, 1H), 1.59-1.49 (m, 2H), 1.37 (td, *J* = 12.5, 4.4 Hz, 1H), 1.28 (td, *J* = 7.1, 2.5 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.3, 170.2, 138.4, 137.1, 129.7, 126.9, 68.5, 68.4, 62.7, 61.5, 61.4, 59.6, 40.4, 39.8, 28.9, 28.9, 21.3, 14.2, 14.2.
IR (neat) ν 2979, 2956, 2103, 1725, 1466, 1367, 1223, 1023, 820 cm^{-1}.
HRMS (ESI) calcd for $C_{21}H_{29}N_3NaO_5$ $[M+Na]^+$ 426.1999, found 426.2006.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(1-((benzyloxy)carbonyl)piperidin-4-yl)malonate (17)



17

17 was synthesized according to general procedure A. **S17** (55.4 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 µL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 7 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−96% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (40.6 mg, 76% yield).

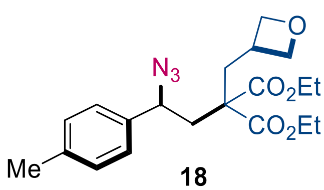
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 7.22-7.17 (m, 4H), 5.11 (s, 2H), 4.57 (dd, *J* = 8.9, 3.4 Hz, 1H), 4.26-4.10 (m, 6H), 2.73 (d, *J* = 11.4 Hz, 2H), 2.38-2.31 (m, 4H), 2.27 (dd, *J* = 14.9, 8.9 Hz, 1H), 2.19-2.13 (m, 1H), 1.90 (d, *J* = 12.8 Hz, 1H), 1.67 (s, 1H), 1.40-1.30 (m, 1H), 1.29-1.23 (m, 6H), 1.21-1.08 (m, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.2, 155.2, 138.4, 137.1, 136.9, 129.7, 128.6, 128.1, 128.0, 126.8, 67.1, 62.7, 61.6, 61.4, 59.5, 44.5, 41.2, 40.0, 27.9, 21.2, 14.2, 14.1.

IR (neat) ν 2980, 2937, 2104, 1724, 1469, 1366, 1238, 1027, 820 cm^{-1}.

HRMS (ESI) calcd for $C_{29}H_{36}N_4NaO_6$ $[M+Na]^+$ 559.2527, found 559.2533.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(oxetan-3-ylmethyl)malonate (18)



18

18 was synthesized according to general procedure A. **S18** (37.5 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 7 : 1 : 1), the title compound was isolated as a colorless oil (32.3 mg, 83% yield).

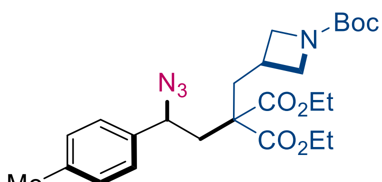
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 4H), 4.65 (qd, *J* = 8.1, 6.0 Hz, 2H), 4.46 (q, *J* = 4.4 Hz, 1H), 4.36 (dt, *J* = 16.5, 6.4 Hz, 2H), 4.21-4.14 (m, 2H), 4.12-4.07 (m, 2H), 3.17-3.06 (m, 1H), 2.42 (q, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 2.34-2.29 (m, 2H), 2.22 (dd, *J* = 14.7, 4.1 Hz, 1H), 1.29-1.22 (m, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.8, 138.6, 136.4, 129.7, 126.9, 77.7, 77.6, 62.2, 61.8, 61.7, 55.4, 39.6, 37.2, 31.6, 21.3, 14.1, 14.0.

IR (neat) ν 2970, 2869, 2099, 1740, 1445, 1366, 1217, 1022, 819 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{28}N_3O_5$ $[M+H]^+$ 390.2023, found 390.2029.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-((1-(tert-butoxycarbonyl)azetidin-3-yl)methyl)malonate (19)

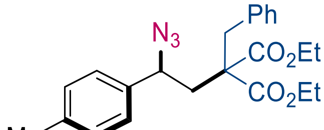


19

19 was synthesized according to general procedure A. **S19** (49.5 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 µL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 6 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−87% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (32.5 mg, 67% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 4H), 4.45 (q, J = 4.4 Hz, 1H), 4.22-4.08 (m, 4H), 3.96-3.88 (m, 2H), 3.50 (qd, J = 8.2, 6.2 Hz, 2H), 2.65-2.53 (m, 1H), 2.37-2.31 (m, 5H), 2.27-2.19 (m, 2H), 1.41 (s, 9H), 1.29-1.22 (m, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.8, 156.2, 138.6, 136.4, 129.7, 126.9, 79.5, 62.3, 61.8, 61.8, 55.5, 55.0, 39.6, 37.9, 28.5, 25.3, 21.3, 14.1, 14.0.
IR (neat) ν 2981, 2958, 2114, 1750, 1446, 1390, 1256, 1031, 814 cm^{-1}.
HRMS (ESI) calcd for $C_{25}H_{36}N_4NaO_6$ $[M+Na]^+$ 511.2527, found 511.2541.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-benzylmalonate (20)

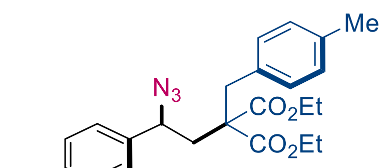


20

20 was synthesized according to general procedure A. **S20** (39.5 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a white solid (32.7 mg, 83% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.25-7.16 (m, 7H), 7.10 (dd, *J* = 7.5, 1.6 Hz, 2H), 4.66 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.22-4.05 (m, 4H), 3.39 (dd, *J* = 30.2, 14.2 Hz, 2H), 2.34 (d, *J* = 2.7 Hz, 3H), 2.31-2.27 (m, 1H), 2.11-2.21 (1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.9, 138.4, 136.7, 135.8, 130.1, 129.6, 128.5, 127.2, 127.0, 62.5, 61.7, 61.6, 57.5, 39.0, 38.7, 21.3, 14.1, 14.1.
IR (neat) ν 2981, 2939, 2106, 1732, 1454, 1389, 1244, 1022, 815 cm^{-1}.
HRMS (ESI) calcd for $C_{23}H_{27}N_3NaO_4$ $[M+Na]^+$ 432.1894, found 432.1897.
m.p. 68-70 °C

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(4-methylbenzyl)malonate (21)



21

21 was synthesized according to general procedure A. **S21** (41.7 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (29.3 mg, 69% yield).

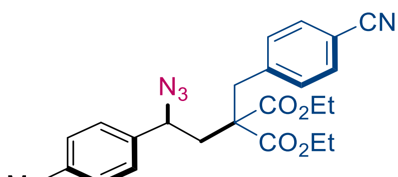
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 11.4, 8.2 Hz, 4H), 7.00 (dd, *J* = 25.8, 8.0 Hz, 4H), 4.66 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.23-4.05 (m, 4H), 3.34 (q, J = 13.7 Hz, 2H), 2.34 (s, 3H), 2.32-2.26 (m, 4H), 2.14 (dd, *J* = 15.1, 3.7 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.3 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 138.4, 136.8, 136.7, 132.6, 129.9, 129.6, 129.2, 127.0, 62.5, 61.6, 61.6, 57.5, 38.6, 21.3, 21.1, 14.1, 14.1.

IR (neat) ν 2980, 2926, 2106, 1732, 1446, 1390, 1243, 1022, 816 cm^{-1}.

HRMS (ESI) calcd for $C_{24}H_{29}N_3NaO_4$ $[M+Na]^+$ 446.2050, found 446.2039.

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(4-cyanobenzyl)malonate (22)



22

22 was synthesized according to general procedure A. **S21** (42.9 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 15 : 1 : 1), the title compound was isolated as a white solid (34.7 mg, 69% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53 (dt, J = 8.2, 1.8 Hz, 2H), 7.25 (dd, J = 6.6, 2.1 Hz, 2H), 7.18 (t, J = 9.1 Hz, 4H), 4.59 (dd, J = 9.6, 3.7 Hz, 1H), 4.23-4.06 (m, 4H), 3.47 (d, J = 14.2 Hz, 1H), 3.37 (d, J = 14.2 Hz, 1H), 2.35 (s, 3H), 2.29 (dd, J = 14.6, 9.6 Hz, 1H), 2.14 (dd, J = 14.6, 3.7 Hz, 1H), 1.27-1.20 (m, 6H).

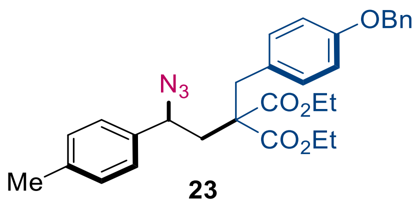
^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 170.3, 141.8, 138.7, 136.4, 132.2, 131.0, 129.8, 126.9, 118.8, 111.2, 62.4, 62.0, 61.9, 57.5, 39.2, 39.2, 21.3, 14.1, 14.0.

IR (neat) ν 2970, 2940, 2107, 1736, 1446, 1366, 1216, 1021, 821 cm^{-1}.

HRMS (CI) calcd for $C_{24}H_{27}N_2O_4$ $[M+H-N_2]^+$ 407.1965, found 407.1972.

m.p. 111-113 °C

Diethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-(4-(benzyloxy)benzyl)malonate (23)

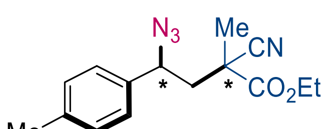


23

23 was synthesized according to general procedure A. **S23** (52.8 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 20 : 1 : 1), the title compound was isolated as a colorless oil (44.1 mg, 86% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 7.21-7.17 (m, 4H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.01 (s, 2H), 4.65 (dd, *J* = 9.2, 3.7 Hz, 1H), 4.22-4.17 (m, 2H), 4.16-4.05 (m, 2H), 3.33 (q, *J* = 14.1 Hz, 2H), 2.35 (s, 3H), 2.30 (dd, *J* = 15.2, 9.7 Hz, 1H), 2.17 (dd, *J* = 15.2, 3.7 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 158.0, 138.4, 137.1, 136.7, 131.1, 129.6, 128.7, 128.1, 128.0, 127.6, 127.0, 114.9, 70.1, 62.5, 61.6, 61.6, 57.6, 38.7, 38.3, 21.3, 14.1, 14.1.
IR (neat) ν 2981, 2927, 2106, 1731, 1454, 1367, 1217, 1025, 820 cm^{-1}.
HRMS (ESI) calcd for $C_{30}H_{33}N_3NaO_5$ $[M+Na]^+$ 538.2312, found 538.2323.

Ethyl 4-azido-2-cyano-2-methyl-4-(p-tolyl)butanoate (24)



24

24 was synthesized according to general procedure A. **S24** (25.8 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (18.9 mg, 66% yield, d.r = 1:1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 4H), 4.77 (dd, *J* = 11.2, 3.4 Hz, 1H), 4.38-4.23 (m, 2H), 2.53 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.37-2.32 (m, 4H), 1.66 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

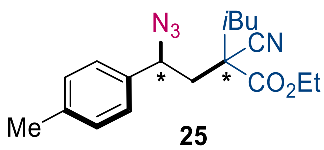
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 4H), 4.67 (t, *J* = 7.1 Hz, 1H), 4.38-4.23 (m, 2H), 2.34 (s, 3H), 2.24 (dd, *J* = 14.4, 8.0 Hz, 1H), 1.94 (dd, *J* = 14.4, 3.4 Hz, 1H), 1.61 (s, 3H), 1.21 (*t*, J = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.3, 168.7, 139.1, 135.2, 134.6, 129.9, 129.7, 127.4, 127.0, 119.4, 119.3, 63.3, 63.2, 63.1, 63.1, 44.2, 43.5, 43.0, 42.2, 25.1, 24.8, 21.3, 14.1, 13.9.

IR (neat) ν 2986, 2940, 2102, 1747, 1455, 1384, 1246, 1020, 820 cm^{-1}.

HRMS (ESI) calcd for $C_{15}H_{19}N_4O_2$ $[M+H]^+$ 287.1503, found 287.1494.

Ethyl 2-(2-azido-2-(p-tolyl)ethyl)-2-cyano-4-methylpentanoate (25)



25

25 and 25′ were synthesized according to general procedure A. **S25** (30.1 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (15.8 mg, 48% yield, d.r = 1:1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.7 Hz, 4H), 4.82 (dd, *J* = 11.7, 3.0 Hz, 1H), 4.40-4.28 (m, 2H), 2.49 (dd, *J* = 14.4, 11.7 Hz, 1H), 2.36 (s, 3H), 1.94-1.79 (m, 3H), 1.63 (q, *J* = 6.3 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H).

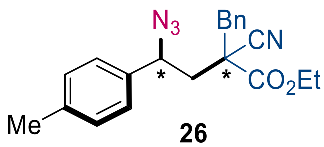
^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.1, 139.0, 135.4, 129.9, 126.9, 119.0, 63.1, 63.0, 47.5, 47.2, 45.1, 26.2, 23.3, 23.0, 21.3, 14.1.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 12.8, 8.2 Hz, 4H), 4.66 (t, *J* = 7.3 Hz, 1H), 3.92-3.72 (m, 2H), 2.39-2.34 (m, 4H), 2.21 (q, *J* = 7.0 Hz, 1H), 1.90-1.75 (m, 3H), 1.18 (t, *J* = 7.3 Hz, 3H), 1.03 (d, *J* = 5.9 Hz, 3H), 0.87 (d, *J* = 5.9 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.6, 139.0, 134.4, 129.6, 127.7, 118.9, 63.1, 62.8, 47.1, 46.7, 44.1, 26.1, 23.4, 22.8, 21.3, 13.8.

IR (neat) ν 2961, 2933, 2102, 1746, 1471, 1371, 1223, 1021, 816 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{25}N_4O_2$ $[M+H]^+$ 329.1972, found 329.1962.

Ethyl 4-azido-2-benzyl-2-cyano-4-(p-tolyl)butanoate (26)

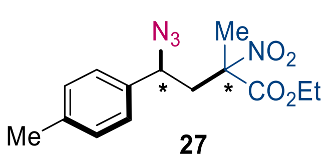


26

26 was synthesized according to general procedure A. **S26** (34.2 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (26.1 mg, 72% yield, d.r = 1:1.25).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.17 (m, 9H), 4.80 (dd, *J* = 11.9, 3.2 Hz, 1H), 4.27-4.11 (m, 2H), 3.16 (dd, *J* = 21.8, 14.5 Hz, 2H), 2.49 (q, *J* = 7.4 Hz, 1H), 2.37 (s, 3H), 2.02 (dd, *J* = 14.2, 3.2 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). *Minor Product*
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.17 (m, 9H), 4.72 (t, *J* = 7.4 Hz, 1H), 3.78-3.61 (m, 2H), 3.19 (d, *J* = 15.2 Hz, 3H), 3.00 (d, *J* = 13.3 Hz, 1H), 2.49 (q, *J* = 7.4 Hz, 1H), 2.34 (s, 3H), 2.29 (q, *J* = 7.0 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). *Major Product*
^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.4, 167.7, 139.1, 139.0, 135.2, 134.2, 133.6, 133.6, 130.2, 130.2, 129.9, 129.6, 128.7, 128.7, 128.2, 127.8, 127.0, 118.3, 63.3, 63.2, 63.0, 62.8, 50.2, 49.3, 44.4, 44.3, 43.1, 42.4, 21.3, 13.9, 13.7.
IR (neat) ν 2982, 2928, 2103, 1741, 1455, 1369, 1232, 1095, 702 cm^{-1}.
HRMS (ESI) calcd for $C_{21}H_{26}N_5O_2$ $[M+NH_4]^+$ 380.2087, found 380.2068.

Ethyl 4-azido-2-methyl-2-nitro-4-(p-tolyl)butanoate (27)

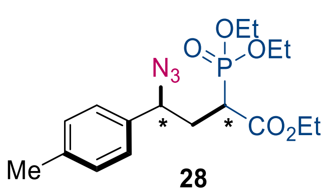


27

27 was synthesized according to general procedure A. **S27** (27.4 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc = 30 : 1), the title compound was isolated as a colorless oil (23.3 mg, 76% yield, d.r = 1:1.1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 4H), 4.52 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.71 (dd, *J* = 14.6, 9.6 Hz, 1H), 2.59 (dd, *J* = 14.9, 3.9 Hz, 1H), 2.37 (s, 3H), 1.89 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). *Major Product*
^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 139.0, 135.4, 129.9, 126.9, 91.6, 63.2, 61.6, 42.1, 21.8, 21.3, 13.9. *Major Product*
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 2.8 Hz, 4H), 4.64 (dd, *J* = 9.7, 3.7 Hz, 1H), 4.29-4.17 (m, 2H), 2.71 (dd, *J* = 15.2, 9.7 Hz, 1H), 2.58 (dd, *J* = 15.2, 4.1 Hz, 1H), 2.37 (s, 3H), 1.87 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). *Minor Product*
^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.1, 139.0, 135.5, 129.9, 126.9, 91.1, 63.3, 61.6, 42.5, 22.1, 21.3, 13.9. *Minor Product*
IR (neat) ν 2984, 2927, 2110, 1740, 1454, 1366, 1217, 1021, 819 cm^{-1}.
HRMS (ESI) calcd for $C_{14}H_{19}N_2O_4$ $[M+H-N_2]^+$ 279.1345, found 279.1349.

Ethyl 4-azido-2-(diethoxyphosphoryl)-4-(p-tolyl)butanoate (28)

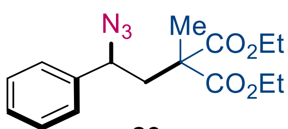


28

28 was synthesized according to general procedure A. **S28** (27.4 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (30.2 mg, 79% yield, d.r = 1:1.1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 4H), 4.51 (t, J = 7.5 Hz, 1H), 4.31-4.05 (m, 6H), 2.90 (ddd, J = 23.6, 9.8, 4.1 Hz, 1H), 2.40-2.31 (m, 8H), 1.34-1.25 (m, 9H). *Minor Product*
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 4H), 4.46 (dd, J = 10.1, 4.1 Hz, 1H), 4.31-4.05 (m, 6H), 3.26 (ddd, J = 23.9, 11.1, 3.1 Hz, 1H), 2.35 (s, 3H), 2.26-2.14 (m, 2H), 1.34-1.25 (m, 9H). *Major Product*
^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.8, 168.7, 168.7, 168.6, 138.7, 138.5, 135.7, 135.1, 129.8, 129.7, 127.1, 126.9, 64.8, 64.7, 64.3, 64.2, 63.1, 63.0, 63.0, 62.9, 61.8, 61.7, 43.7, 43.2, 42.4, 41.9, 33.8, 33.8, 33.4, 33.4, 30.4, 29.8, 21.3, 16.5, 16.5, 16.4, 16.4, 14.2.
IR (neat) ν 2982, 2933, 2103, 1735, 1444, 1368, 1255, 1048, 819 cm^{-1}.
HRMS (FAB) calcd for $C_{17}H_{27}N_3O_5P$ $[M+H]^+$ 384.1683, found 384.1698.

Diethyl 2-(2-azido-2-phenylethyl)-2-methylmalonate (29)

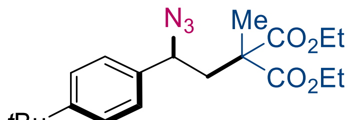


29

29 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′2** (11.6 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (22.4 mg, 70% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 5H), 4.60 (q, J = 4.4 Hz, 1H), 4.25-4.05 (m, 4H), 2.42 (dd, J = 14.7, 9.2 Hz, 1H), 2.29 (dd, J = 14.7, 4.1 Hz, 1H), 1.51 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 171.8, 139.8, 129.0, 128.6, 127.1, 62.8, 61.7, 61.6, 52.5, 41.8, 20.5, 14.1, 14.1.
IR (neat) ν 2982, 2932, 2105, 1731, 1455, 1381, 1210, 1023, 702 cm^{-1}.
HRMS (CI) calcd for $C_{16}H_{22}NO_4$ $[M+H-N_2]^+$ 292.1543, found 292.1554.

Diethyl 2-(2-azido-2-(4-(tert-butyl)phenyl)ethyl)-2-methylmalonate (30)

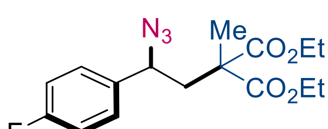


30

30 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′3** (20.1 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (36.5 mg, 97% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.25 (dt, *J* = 8.7, 1.9 Hz, 2H), 4.56 (q, *J* = 4.6 Hz, 1H), 4.19 (dq, *J* = 18.2, 3.7 Hz, 2H), 4.14-4.02 (m, 2H), 2.42 (dd, *J* = 14.9, 9.4 Hz, 1H), 2.29 (dd, *J* = 14.6, 4.1 Hz, 1H), 1.51 (s, 3H), 1.32 (s, 9H), 1.29-1.25 (m, 3H), 1.22 (t, *J* = 7.3 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 171.9, 151.5, 136.7, 126.8, 125.9, 62.4, 61.6, 61.6, 52.5, 41.7, 34.7, 31.4, 20.4, 14.1, 14.1.
IR (neat) ν 2964, 2907, 2105, 1732, 1465, 1365, 1239, 1109, 833 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{29}N_3NaO_4$ $[M+Na]^+$ 398.2050, found 398.2065.

Diethyl 2-(2-azido-2-(4-fluorophenyl)ethyl)-2-methylmalonate (31)



31

31 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′4** (12.2 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (25.6 mg, 76% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (qd, J = 5.7, 3.0 Hz, 2H), 7.10-7.04 (m, 2H), 4.61 (q, J = 4.6 Hz, 1H), 4.22-4.06 (m, 4H), 2.37 (dd, J = 14.6, 9.3 Hz, 1H), 2.25 (dd, J = 14.7, 4.1 Hz, 1H), 1.50 (s, 3H), 1.29-1.22 (m, 6H)

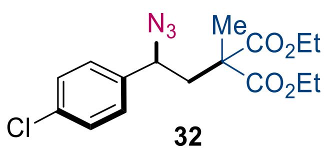
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 171.7, 162.7 (d, J_{C-F} = 244.4), 135.6, 128.8 (d, J_{C-F} = 8.6), 115.9 (q , J_{C-F} = 21.0), 115.8, 77.4, 77.1, 76.8, 61.8 (q , J_{C-F} = 39.2), 61.7, 52.4, 41.9, 20.4, 14.1, 14.0.

^{19}F-NMR (376 MHz, $CDCl_3$): δ -113.18.

IR (neat) ν 2984, 2940, 2106, 1731, 1448, 1366, 1235, 1022, 837 cm^{-1}.

HRMS (ESI) calcd for $C_{16}H_{20}FN_3NaO_4$ $[M+Na]^+$ 360.1330, found 360.1327.

Diethyl 2-(2-azido-2-(4-chlorophenyl)ethyl)-2-methylmalonate (32)



32

32 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′5** (13.0 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. The reaction was stirred for 4 h. The reaction was stirred for 4 h. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (23.0 mg, 65% yield).

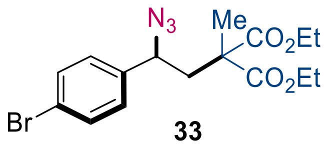
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36 (dt, J = 8.8, 2.2 Hz, 2H), 7.29-7.27 (m, 2H), 4.61 (dd, J = 9.4, 3.9 Hz, 1H), 4.23-4.06 (m, 4H), 2.35 (dd, J = 14.6, 9.6 Hz, 1H), 2.23 (dd, J = 14.9, 3.9 Hz, 1H), 1.50 (s, 3H), 1.29-1.22 (m, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 138.4, 134.4, 129.2, 128.4, 77.5, 77.2, 76.8, 62.1, 61.8, 61.7, 52.5, 42.0, 20.6, 14.1, 14.1.

IR (neat) ν 2983, 2936, 2106, 1731, 1492, 1381, 1240, 1016, 829 cm^{-1}.

HRMS (ESI) calcd for $C_{16}H_{20}ClN_3NaO_4$ $[M+Na]^+$ 376.1035, found 376.1027.

Diethyl 2-(2-azido-2-(4-bromophenyl)ethyl)-2-methylmalonate (33)



33

33 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′6** (13.1 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. The reaction was stirred for 4 h. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (20.6 mg, 52% yield). 21-17 (4시간 반응)

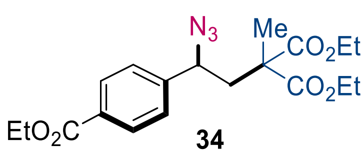
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 8.9, 2.3 Hz, 2H), 7.22 (dt, *J* = 8.7, 2.2 Hz, 2H), 4.60 (dd, *J* = 9.4, 3.9 Hz, 1H), 4.23-4.07 (m, 4H), 2.34 (dd, *J* = 14.7, 9.7 Hz, 1H), 2.23 (dd, *J* = 14.7, 4.1 Hz, 1H), 1.50 (s, 3H), 1.29-1.26 (m, 3H), 1.25-1.22 (m, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 171.8, 138.9, 132.2, 128.7, 122.5, 62.2, 61.8, 61.7, 52.5, 42.0, 20.6, 14.1, 14.1.

IR (neat) ν 2982, 2926, 2111, 1743, 1445, 1367, 1204, 1022, 818 cm^{-1}.

HRMS (CI) calcd for $C_{16}H_{21}BrN_3O_4$ $[M+H]^+$ 398.0710, found 398.0719.

Diethyl 2-(2-azido-2-(4-(ethoxycarbonyl)phenyl)ethyl)-2-methylmalonate (34)

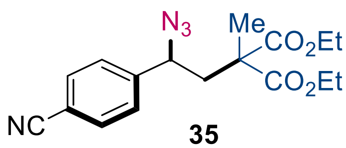


34

34 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′7** (16.6 mg 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. The reaction was stirred for 4 h. After purification by column chromatography (hexane : EtOAc : DCM = 15 : 1 : 1), the title compound was isolated as a colorless oil (13.4 mg, 36% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 4.69 (dd, *J* = 9.4, 3.9 Hz, 1H), 4.24-4.07 (m, 4H), 3.92 (s, 3H), 2.36 (dd, *J* = 14.7, 9.2 Hz, 1H), 2.26 (dd, *J* = 14.7, 4.1 Hz, 1H), 1.51 (s, 3H), 1.29-1.26 (m, 3H), 1.23 (d, *J* = 7.4 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 171.8, 166.7, 144.9, 130.4, 127.0, 62.5, 61.8, 61.7, 52.5, 52.4, 42.0, 20.6, 14.1, 14.1.
IR (neat) ν 2984, 2954, 2107, 1729, 1437, 1366, 1282, 1020, 710 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{24}NO_6$ $[M+H-N_2]^+$ 350.1598, found 350.1586.

Diethyl 2-(2-azido-2-(4-cyanophenyl)ethyl)-2-methylmalonate (35)

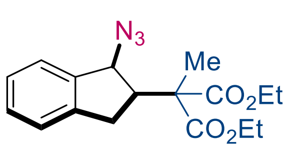


35

35 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′8** (12.1 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. The reaction was stirred for 4 h. After purification by column chromatography (hexane : EtOAc : DCM = 15 : 1 : 1), the title compound was isolated as a colorless oil (7.8mg, 23yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.49-7.47 (m, 2H), 4.73 (dd, *J* = 9.1, 3.7 Hz, 1H), 4.23-4.10 (m, 4H), 2.31-2.17 (m, 2H), 1.51 (s, 3H), 1.27 (q, *J* = 7.2 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.7, 171.6, 145.4, 132.9, 127.7, 118.5, 112.5, 62.4, 61.9, 61.8, 52.5, 42.3, 20.8, 14.1, 14.1.
IR (neat) ν 2984, 2939, 2107, 1730, 1466, 1366, 1242, 1050, 837 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{20}KN_2O_4$ $[M+K]^+$ 355.1055, found 355.1352.

Diethyl 2-((2R)-1-azido-2,3-dihydro-1H-inden-2-yl)-2-methylmalonate (36)



36

36 was synthesized according to general procedure B. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S′9** (12.1 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and $Fe(OAc)_2$ (1.8 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (23.0 mg, 65% yield, d.r. > 20:1).

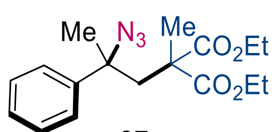
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.33 (m, 1H), 7.30-7.15 (m, 4H), 4.89 (d, *J* = 5.5 Hz, 1H), 4.26-4.08 (m, 4H), 3.31 (q, *J* = 8.4 Hz, 1H), 3.06-3.01 (m, 1H), 2.87 (dd, *J* = 16.5, 6.4 Hz, 1H), 1.45 (s, 3H), 1.26-1.20 (m, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.5, 171.3, 142.0, 140.0, 129.1, 127.3, 124.9, 124.6, 67.9, 61.8, 61.7, 55.9, 50.5, 33.9, 18.9, 14.1, 14.0.

IR (neat) ν 2981, 2941, 2106, 1744, 1454, 1366, 1216, 1020, 818 cm^{-1}.

HRMS (CI) calcd for $C_{17}H_{22}NO_4$ $[M+H-N_2]^+$ 304.1543, found 304.1546.

Diethyl 2-(2-azido-2-phenylpropyl)-2-methylmalonate (37)



37

37 was synthesized according to general procedure B. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'10** (13.1 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and $Fe(OAc)_2$ (1.8 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (12.2 mg, 37% yield).

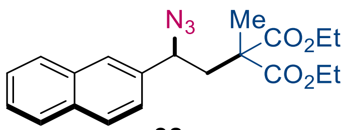
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (dt, *J* = 8.4, 1.7 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27-7.23 (m, 1H), 4.26-4.12 (m, 2H), 4.04-3.93 (m, 2H), 2.67 (q, *J* = 15.2 Hz, 2H), 1.72 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 6.4 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.1, 172.1, 143.7, 128.5, 127.5, 125.7, 77.5, 77.2, 76.8, 65.3, 61.6, 61.5, 53.0, 45.6, 28.4, 20.3, 14.1, 14.0.

IR (neat) ν 2982, 2937, 2112, 1730, 1446, 1383, 1260, 1023, 702 cm^{-1}.

HRMS (ESI) calcd for $C_{17}H_{23}N_3NaO_4$ $[M+Na]^+$ 356.1581, found 356.1566.

Diethyl 2-(2-azido-2-(naphthalen-2-yl)ethyl)-2-methylmalonate (38)

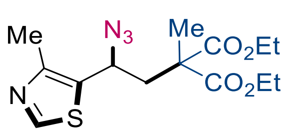


38

38 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'11** (15.6 mg 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (26.5 mg, 72% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89-7.82 (m, 3H), 7.78 (d, J = 0.9 Hz, 1H), 7.54-7.46 (m, 3H), 4.80 (q, J = 4.6 Hz, 1H), 4.25-4.17 (m, 2H), 4.15-4.04 (m, 2H), 2.51 (dd, J = 14.6, 9.6 Hz, 1H), 2.38 (dd, J = 15.1, 4.1 Hz, 1H), 1.55 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.3 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 171.9, 137.1, 133.3, 133.3, 129.1, 128.2, 127.8, 126.6, 126.5, 126.2, 124.6, 63.0, 61.7, 61.7, 52.6, 41.8, 20.5, 14.1, 14.1.
IR (neat) ν 2982, 2938, 2106, 1730, 1465, 1365, 1107, 1021, 750 cm^{-1}.
HRMS (FAB) calcd for $C_{20}H_{24}N_3O_4$ $[M+H]^+$ 370.1761, found 370.1760.

Diethyl 2-(2-azido-2-(4-methylthiazol-5-yl)ethyl)-2-methylmalonate (39)



39

39 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'12** (11.5 μL 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 5 : 1 : 1), the title compound was isolated as a colorless oil (20.7 mg, 61% yield).

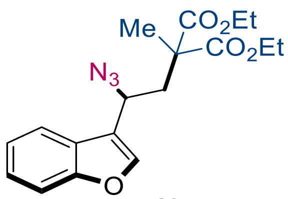
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 0H), 5.04 (dd, *J* = 9.4, 3.9 Hz, 0H), 4.21-4.10 (m, 2H), 2.49 (s, 2H), 2.40 (dd, *J* = 14.7, 9.2 Hz, 0H), 2.27 (dd, *J* = 14.7, 4.1 Hz, 0H), 1.51 (s, 1H), 1.26 (q, J = 7.0 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.6, 171.5, 151.7, 61.9, 61.8, 55.4, 52.4, 42.9, 20.7, 15.5, 14.1.

IR (neat) ν 2983, 2938, 2108, 1731, 1447, 1380, 1206, 1022, 862 cm^{-1}.

HRMS (ESI) calcd for $C_{14}H_{21}N_4O_4S$ $[M+H]^+$ 341.1278, found 341.1286.

Diethyl 2-(2-azido-2-(benzofuran-3-yl)ethyl)-2-methylmalonate (40)



40

40 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'13** (14.6 mg 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 40 : 1 : 1), the title compound was isolated as a colorless oil (20.6 mg, 57% yield).

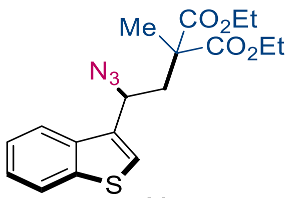
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.31 (td, *J* = 7.8, 1.4 Hz, 1H), 7.26-7.22 (m, 1H), 6.71 (s, 1H), 4.74 (dd, *J* = 7.8, 5.9 Hz, 1H), 4.23-4.09 (m, 4H), 2.62-2.53 (m, 2H), 1.52 (s, 3H), 1.28-1.21 (m, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.7, 171.6, 155.1, 154.5, 127.7, 125.0, 123.2, 121.5, 111.5, 104.7, 61.9, 61.8, 55.9, 52.2, 38.2, 20.3, 14.1.

IR (neat) ν 2982, 2940, 2104, 1715, 1454, 1366, 1223, 1020, 752 cm^{-1}.

HRMS (FAB) calcd for $C_{18}H_{22}N_3O_5$ $[M+H]^+$ 360.1554, found 360.1565.

Diethyl 2-(2-azido-2-(benzo[b]thiophen-3-yl)ethyl)-2-methylmalonate (41)

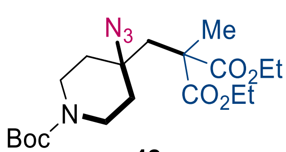


41

41 was synthesized according to general procedure A. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'14** (16.2 mg 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material and Fe(II)Pc (5.9 mg, 0.01 mmol, 0.1 equiv.) was used as a catalyst. After purification by column chromatography (hexane : EtOAc : DCM = 30 : 1 : 1), the title compound was isolated as a colorless oil (19.6 mg, 52% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82 (td, J = 6.9, 4.6 Hz, 1H), 7.75 (td, J = 6.8, 4.6 Hz, 1H), 7.39-7.32 (m, 2H), 7.29 (s, 1H), 4.94 (q, J = 4.4 Hz, 1H), 4.27-4.10 (m, 4H), 2.57-2.46 (m, 2H), 1.54 (s, 3H), 1.28 (t, J = 6.4 Hz, 3H), 1.26-1.23 (m, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 171.6, 143.4, 139.7, 139.1, 125.0, 124.7, 124.0, 122.6, 122.3, 61.9, 61.8, 58.6, 52.5, 41.9, 20.5, 14.1, 14.1.
IR (neat) ν 2982, 2939, 2107, 1715, 1462, 1366, 1223, 1020, 748 cm^{-1}.
HRMS (FAB) calcd for $C_{18}H_{21}NO_4S$ $[M-N_2]^+$ 347.1191, found 347.1178.

Diethyl 2-((4-azido-1-(tert-butoxycarbonyl)piperidin-4-yl)methyl)-2-methylmalonate (42)



42

42 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'15** (60.4 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 8 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−76% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a white solid (31.0 mg, 75% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.26-4.13 (m, 4H), 3.87 (s, 2H), 2.97 (t, *J* = 11.7 Hz, 2H), 2.29 (s, 2H), 1.71 (d, *J* = 11.9 Hz, 2H), 1.59 (s, 3H), 1.55-1.47 (m, 2H), 1.44 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 6H).

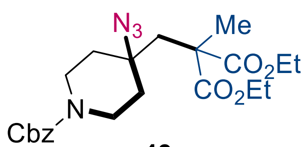
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 154.7, 79.9, 61.8, 61.5, 52.4, 43.9, 39.8, 35.0, 28.5, 21.0, 14.1.

IR (neat) ν 2980, 2934, 2108, 1732, 1462, 1366, 1249, 1021, 863 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{32}N_4NaO_6$ $[M+Na]^+$ 435.2214, found 435.2233.

m.p. 35-37 °C

Diethyl 2-((4-azido-1-((benzyloxy)carbonyl)piperidin-4-yl)methyl)-2-methylmalonate (43)



43

43 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'16** (70.8 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 8 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0–80% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (31.4 mg, 70% yield).

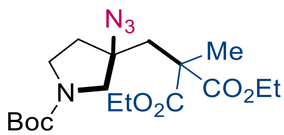
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 5H), 5.12 (s, 2H), 4.26-4.12 (m, 4H), 3.97 (s, 2H), 3.05 (s, 2H), 2.30 (s, 2H), 1.73 (d, *J* = 13.6 Hz, 2H), 1.59 (s, 3H), 1.57-1.51 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.1, 155.2, 136.8, 128.6, 128.2, 128.0, 67.3, 61.8, 61.4, 52.4, 43.9, 40.0, 34.8, 21.0, 14.0.

IR (neat) ν 2982, 2939, 2109, 1731, 1467, 1365, 1282, 1022, 764 cm^{-1}.

HRMS (ESI) calcd for $C_{22}H_{31}N_4O_6$ $[M+H]^+$ 447.2238, found 447.2226.

Diethyl 2-((3-azido-1-(tert-butoxycarbonyl)pyrrolidin-3-yl)methyl)-2-methylmalonate (44)



44

44 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'17** (63.4 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 7 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−78% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (19.0 mg, 48% yield).

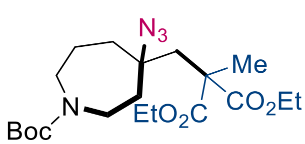
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.28-4.15 (m, 4H), 3.70-3.32 (m, 3H), 3.20 (dd, J = 11.7, 8.5 Hz, 1H), 2.52-2.34 (m, 2H), 2.13 (q, J = 6.3 Hz, 1H), 1.98-1.89 (m, 1H), 1.53 (d, J = 2.8 Hz, 3H), 1.48-1.44 (m, 9H), 1.26 (t, J = 7.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.0, 171.9, 171.9, 171.8, 154.3, 80.1, 79.9, 68.7, 67.9, 61.9, 55.9, 55.9, 52.7, 44.1, 43.9, 41.4, 37.4, 36.7, 28.7, 28.6, 20.7, 20.5, 14.1.

IR (neat) ν 2980, 2937, 2108, 1733, 1404, 1366, 1258, 1022, 771 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{30}N_4NaO_6$ $[M+Na]^+$ 421.2058, found 421.2043.

Diethyl 2-((4-azido-1-(tert-butoxycarbonyl)azepan-4-yl)methyl)-2-methylmalonate (45)

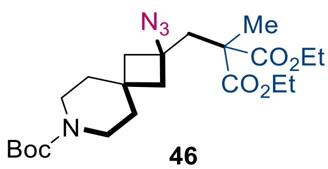


45

45 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'18** (64.0 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 7 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−78% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (20.6 mg, 48% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.25-4.12 (m, 4H), 3.72-3.43 (m, 2H), 3.29-3.18 (m, 1H), 3.06 (dd, J = 14.5, 10.3 Hz, 1H), 2.36-2.25 (m, 2H), 1.95-1.66 (m, 4H), 1.59-1.49 (m, 5H), 1.45-1.41 (m, 9H), 1.28-1.23 (m, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.3, 172.2, 155.6, 79.6, 65.1, 65.1, 61.8, 61.7, 52.7, 46.3, 45.2, 44.2, 44.1, 40.2, 39.7, 39.0, 38.8, 37.2, 36.8, 28.6, 21.7, 21.3, 20.9, 20.6, 14.1.
IR (neat) ν 2979, 2935, 2105, 1733, 1412, 1365, 1255, 1022, 772 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{34}N_4NaO_6$ $[M+Na]^+$ 449.2371, found 449.2355.

Diethyl 2-((2-azido-7-(tert-butoxycarbonyl)-7-azaspiro[3.5]nonan-2-yl)methyl)-2-methylmalonate (46)

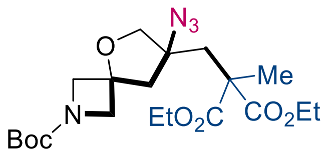


46

46 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'19** (72.7 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 6 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−78% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (36.2 mg, 80% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.24-4.11 (m, 4H), 3.32-3.27 (m, 4H), 2.42 (s, 2H), 2.10 (d, J = 13.7 Hz, 2H), 1.99 (d, J = 14.2 Hz, 2H), 1.57 (dt, J = 31.6, 5.5 Hz, 4H), 1.43 (s, 9H), 1.41 (d, J = 9.6 Hz, 3H), 1.24 (t, J = 7.1 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.1, 155.0, 79.6, 61.7, 59.4, 53.0, 45.3, 43.8, 40.6, 38.5, 37.0, 31.2, 28.6, 19.8, 14.1.
IR (neat) ν 2979, 2927, 2106, 1733, 1422, 1366, 1151, 1021, 863 cm^{-1}.
HRMS (ESI) calcd for $C_{22}H_{37}N_2O_6$ $[M+H-N_2]^+$ 425.2646, found 425.2658.

Diethyl 2-((7-azido-2-(tert-butoxycarbonyl)-5-oxa-2-azaspiro[3.4]octan-7-yl)methyl)-2-methylmalonate (47)



47

47 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'20** (68.3 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 5 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−77% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a white solid (24.5 mg, 57% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.27-4.15 (m, 4H), 4.09 (d, J = 9.1 Hz, 1H), 3.99 (q, J = 9.3 Hz, 3H), 3.91 (d, J = 9.6 Hz, 1H), 3.69 (d, J = 9.6 Hz, 1H), 2.50 (dd, J = 13.7, 0.9 Hz, 1H), 2.39 (dd, J = 37.0, 15.1 Hz, 2H), 2.14 (d, J = 14.2 Hz, 1H), 1.49 (s, 3H), 1.42 (s, 9H), 1.25 (td, J = 7.2, 2.9 Hz, 6H).

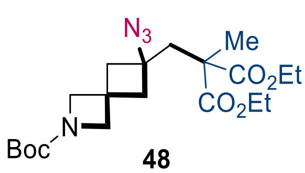
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 171.7, 156.3, 79.9, 78.2, 77.0, 70.3, 63.2, 62.0, 61.7, 52.5, 47.8, 40.3, 28.5, 20.7, 14.1.

IR (neat) ν 2980, 2943, 2111, 1732, 1450, 1397, 1258, 1112, 772 cm^{-1}.

HRMS (FAB) calcd for $C_{20}H_{33}N_4O_7$ $[M+H]^+$ 441.2344, found 441.2354.

m.p. 36-38 ℃

Diethyl 2-((6-azido-2-(tert-butoxycarbonyl)-2-azaspiro[3.3]heptan-6-yl)methyl)-2-methylmalonate (48)



48

48 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'21** (63.4 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 6 : 1 : 1), the title compound was isolated as a white solid (33.5 mg, 79% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.24-4.11 (m, 4H), 3.95 (s, 2H), 3.90 (s, 2H), 2.41-2.32 (m, 6H), 1.41 (s, 12H), 1.28-1.20 (m, 6H).

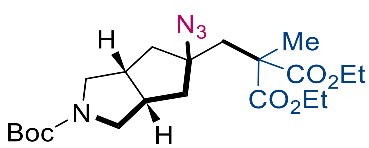
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.9, 156.1, 79.7, 61.8, 60.5, 52.8, 44.5, 43.2, 32.1, 28.5, 19.9, 14.0.

IR (neat) ν 2980, 2934, 2108, 1732, 1396, 1316, 1252, 1024, 862 cm^{-1}.

HRMS (FAB) calcd for $C_{20}H_{33}N_4O_6$ $[M+H]^+$ 425.2395, found 425.2402.

m.p. 35-37 °C

Diethyl 2-(((3aR,6aR)-5-azido-2-(tert-butoxycarbonyl)octahydrocyclopenta[c]pyrrol-5-yl)methyl)-2-methylmalonate (49)



49

49 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'22** (67.7 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 6 : 1 : 1), the title compound was isolated as a colorless oil (25.8 mg, 59% yield).

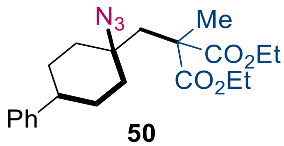
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.25-4.12 (m, 4H), 3.41-3.35 (m, 2H), 3.26 (d, J = 11.0 Hz, 2H), 2.80-2.71 (m, 2H), 2.41 (s, 2H), 2.20 (dd, J = 13.6, 7.6 Hz, 2H), 1.52 (s, 3H), 1.48-1.42 (m, 11H), 1.25 (t, J = 7.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 155.0, 79.6, 73.6, 61.8, 52.9, 51.6, 44.7, 43.0, 41.4, 28.6, 20.8, 14.1.

IR (neat) ν 2977, 2933, 2104, 1732, 1399, 1365, 1254, 1022, 773 cm^{-1}.

HRMS (ESI) calcd for $C_{21}H_{35}N_4O_6$ $[M+H]^+$ 439.2551, found 439.2548.

Diethyl 2-((1-azido-4-phenylcyclohexyl)methyl)-2-methylmalonate (50)



50

50 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'23** (52.2 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 20 : 1), the title compound was isolated as a white solid (23.9 mg, 62% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.20 (td, J = 7.7, 1.7 Hz, 3H), 4.28-4.15 (m, 4H), 2.51-2.42 (m, 1H), 2.34 (s, 2H), 1.95 (dd, J = 14.0, 2.5 Hz, 2H), 1.76-1.71 (m, 4H), 1.63 (s, 3H), 1.56-1.47 (m, 2H), 1.28 (t, J = 7.1 Hz, 6H).

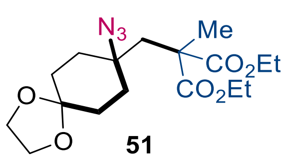
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 146.5, 128.6, 126.9, 126.3, 62.6, 61.7, 52.6, 44.9, 43.3, 35.9, 29.5, 21.0, 14.1.

IR (neat) ν 2983, 2937, 2105, 1732, 1449, 1381, 1261, 1022, 701 cm^{-1}.

HRMS (ESI) calcd for $C_{21}H_{30}NO_4$ $[M+H-N_2]^+$ 360.2169, found 360.2180.

m.p. 69-71 °C

Diethyl 2-((8-azido-1,4-dioxaspiro[4.5]decan-8-yl)methyl)-2-methylmalonate (51)



51

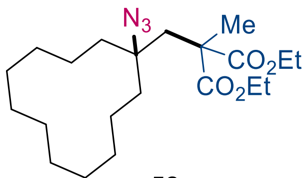
51 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'24** (46.7 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 10 : 1 : 1), the title compound was isolated as a colorless oil (26.1 mg, 71% yield). 23-83.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.27-4.11 (m, 4H), 3.92 (ddd, J = 16.8, 9.3, 4.0 Hz, 4H), 2.30 (s, 2H), 1.82-1.62 (m, 6H), 1.58 (dd, J = 13.7, 9.1 Hz, 5H), 1.24 (t, J = 7.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.3, 107.7, 64.5, 64.4, 62.2, 61.7, 52.6, 43.5, 33.1, 30.8, 20.9, 14.0.

IR (neat) ν 2980, 2958, 2109, 1732, 1447, 1365, 1259, 1027, 862 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{28}NO_6$ $[M+H-N_2]^+$ 342.1911, found 342.1936.

Diethyl 2-((1-azidocyclododecyl)methyl)-2-methylmalonate (52)

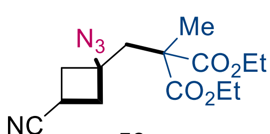


52

52 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'25** (66.8 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 50 : 1 : 1), the title compound was isolated as a colorless oil (26.1 mg, 66% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.23-4.12 (m, 4H), 2.25 (s, 2H), 1.71-1.64 (m, 2H), 1.58 (s, 3H), 1.56-1.49 (m, 2H), 1.44-1.29 (m, 18H), 1.25 (t, *J* = 7.1 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.5, 65.7, 61.6, 53.0, 41.8, 33.7, 26.5, 26.0, 22.8, 22.4, 20.6, 19.7, 14.1.
IR (neat) ν 2968, 2938, 2101, 1739, 1446, 1365, 1228, 1023, 729 cm^{-1}.
HRMS (ESI) calcd for $C_{21}H_{38}NO_4$ $[M+H-N_2]^+$ 368.2795, found 368.2758.

Diethyl 2-(((1s,3r)-1-azido-3-cyanocyclobutyl)methyl)-2-methylmalonate (53)



53

53 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'26** (28.2 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 7 : 1 : 1), the title compound was isolated as a colorless oil (24.1 mg, 78% yield).

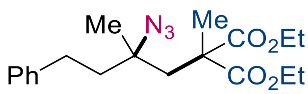
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.24-4.14 (m, 4H), 3.30-3.21 (m, 1H), 2.62-2.49 (m, 4H), 2.49 (d, *J* = 6.6 Hz, 2H), 1.42 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.6, 121.1, 63.2, 61.9, 52.6, 43.7, 38.5, 19.9, 17.6, 14.0.

IR (neat) ν 2984, 2926, 2110, 1731, 1465, 1379, 1253, 1020, 860 cm^{-1}.

HRMS (ESI) calcd for $C_{14}H_{21}N_2O_4$ $[M+H-N_2]^+$ 281.1496, found 281.1521.

Diethyl 2-(2-azido-2-methyl-4-phenylbutyl)-2-methylmalonate (54)



54

54 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'27** (44.3 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 20 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0–78% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (19.8 mg, 55% yield).

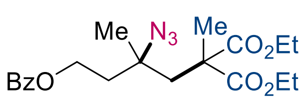
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.8 Hz, 2H), 7.21-7.17 (m, 3H), 4.23-4.15 (m, 4H), 2.70 (t, *J* = 8.5 Hz, 2H), 2.31 (dd, *J* = 20.0, 14.9 Hz, 2H), 1.86 (tdd, *J* = 22.3, 13.6, 5.4 Hz, 2H), 1.60 (s, 3H), 1.35 (s, 3H), 1.28-1.22 (m, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 172.3, 141.5, 128.7, 128.4, 126.2, 62.8, 61.7, 52.9, 44.2, 43.2, 30.5, 28.7, 23.6, 20.9, 14.1.

IR (neat) ν 2982, 2938, 2103, 1732, 1455, 1383, 1252, 1022, 700 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{27}N_3NaO_4$ $[M+Na]^+$ 384.1894, found 384.1902.

Diethyl 2-(2-azido-4-(benzoyloxy)-2-methylbutyl)-2-methylmalonate (55)



55

55 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'28** (57.7 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 10 : 1 : 1), the title compound was isolated as a colorless oil (25.5 mg, 63% yield).

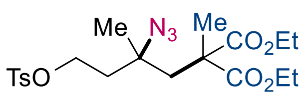
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05-8.02 (m, 2H), 7.58-7.54 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.45 (t, *J* = 6.7 Hz, 2H), 4.25-4.13 (m, 4H), 2.35 (s, 2H), 2.12-1.99 (m, 2H), 1.60 (s, 3H), 1.40 (s, 3H), 1.25 (td, *J* = 7.1, 2.8 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 172.2, 166.6, 133.2, 130.2, 129.7, 128.5, 61.8, 61.8, 61.0, 52.8, 43.6, 40.1, 24.0, 20.9, 14.1.

IR (neat) ν 2982, 2940, 2105, 1738, 1452, 1383, 1275, 1025, 714 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{28}N_3O_6$ $[M+H]^+$ 406.1973, found 406.1957.

Diethyl 2-(2-azido-2-methyl-4-(tosyloxy)butyl)-2-methylmalonate (56)



56

56 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'29** (72.8 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 7 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−80% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (24.5 mg, 54% yield).

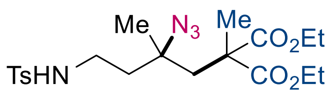
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 4.23-4.08 (m, 6H), 2.45 (s, 3H), 2.20 (dd, *J* = 21.6, 15.2 Hz, 2H), 1.97-1.84 (m, 2H), 1.51 (s, 3H), 1.27 (s, 3H), 1.24 (td, *J* = 7.1, 4.2 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.0, 172.0, 145.1, 133.0, 130.1, 128.1, 66.3, 61.8, 61.5, 52.7, 43.6, 39.9, 24.0, 21.8, 20.9, 14.0.

IR (neat) ν 2986, 2941, 2105, 1739, 1462, 1365, 1228, 1021, 667 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{33}N_4O_7S$ $[M+NH_4]^+$ 473.2064, found 473.2052.

Diethyl 2-(2-azido-2-methyl-4-((4-methylphenyl)sulfonamido)butyl)-2-methylmalonate (57)

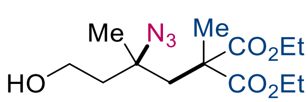


57

57 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'30** (75.5 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 5 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−75% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (29.8 mg, 66% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 4.85 (t, J = 5.7 Hz, 1H), 4.22-4.09 (m, 4H), 3.10-2.96 (m, 2H), 2.42 (s, 3H), 2.17 (s, 2H), 1.77-1.61 (m, 2H), 1.50 (s, 3H), 1.23 (td, J = 7.1, 4.7 Hz, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.1, 172.1, 143.7, 136.9, 129.9, 127.2, 61.9, 61.8, 52.7, 43.3, 40.6, 39.0, 23.9, 21.6, 20.9, 14.0.
IR (neat) ν 3288, 2982, 2939, 2104, 1730, 1447, 1366, 1256, 1020, 816 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{31}N_4O_6S$ $[M+H]^+$ 455.1959, found 455.1946.

Diethyl 2-(2-azido-4-hydroxy-2-methylbutyl)-2-methylmalonate (58)



58

58 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'31** (26.1 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 4 : 1 : 1), the title compound was isolated as a colorless oil (13.8 mg, 46% yield).

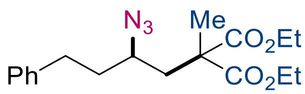
^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 4.24-4.13 (m, 4H), 3.82-3.76 (m, 2H), 2.29 (dd, *J* = 27.1, 15.2 Hz, 2H), 1.88-1.74 (m, 3H), 1.57 (s, 3H), 1.35 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H)

^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 172.3, 172.3, 62.2, 61.8, 58.9, 52.9, 43.5, 43.4, 24.3, 20.9, 14.1.

IR (neat) ν 3456, 2984, 2941, 2103, 1739, 1463, 1365, 1228, 1049, 861 cm^{-1}.

HRMS (ESI) calcd for $C_{13}H_{24}NO_5$ $[M+H-N_2]^+$ 274.1649, found 274.1658.

Diethyl 2-(2-azido-4-phenylbutyl)-2-methylmalonate (59)



59

59 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'30** (46.0 µL 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 20 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−78% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (11.7 mg, 34% yield).

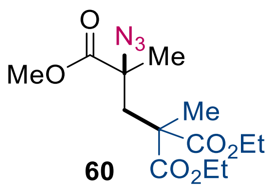
^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 3H), 4.26-4.13 (m, 4H), 3.36-3.32 (m, 1H), 2.83-2.67 (m, 2H), 2.19-2.06 (m, 2H), 1.99-1.82 (m, 2H), 1.44 (s, 3H), 1.28-1.22 (m, 6H).

^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 172.2, 171.9, 140.9, 128.7, 128.5, 126.3, 61.8, 61.7, 58.4, 52.5, 40.2, 37.4, 32.3, 20.3, 15.4, 14.1.

IR (neat) ν 2982, 2937, 2104, 1732, 1455, 1365, 1254, 1022, 700 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{26}NO_4$ $[M+H-N_2]^+$ 320.1856, found 320.1862.

2,2-Diethyl 4-methyl-4-azidopentane-2,2,4-tricarboxylate (60)

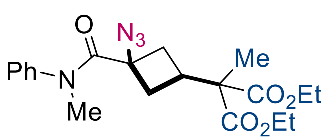


60

60 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'33** (30.7 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 10 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−72% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (14.5 mg, 46% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.26-4.12 (m, 5H), 3.78 (s, 4H), 2.70 (d, *J* = 14.6 Hz, 1H), 2.47 (d, *J* = 15.1 Hz, 1H), 1.58 (s, 4H), 1.36 (s, 4H), 1.28-1.21 (m, 8H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.5, 172.0, 171.4, 64.2, 61.8, 61.6, 53.1, 52.4, 41.9, 25.2, 18.9, 14.1, 14.1
IR (neat) ν 2987, 2970, 2122, 1740, 1455, 1365, 1228, 1022, 659 cm^{-1}.
HRMS (ESI) calcd for $C_{13}H_{22}N_3O_6$ $[M+H]^+$ 316.1503, found 316.1506.

Diethyl 2-(3-azido-3-(methyl(phenyl)carbamoyl)cyclobutyl)-2-methylmalonate (61)

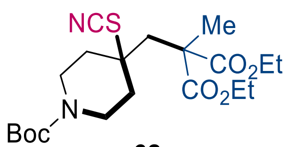


61

61 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'34** (57.3 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 , 0.2 mmol, 2.0 euiqv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 7 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−75% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (17.1 mg, 42% yield, d.r. = 4:1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.23-7.21 (m, 2H), 4.18 (dq, *J* = 42.0, 7.0 Hz, 4H), 3.28 (d, *J* = 13.7 Hz, 3H), 3.16 (d, *J* = 7.8 Hz, 1H), 2.76 (t, *J* = 8.9 Hz, 1H), 2.38 (s, 1H), 1.78 (s, 2H), 1.27 (d, *J* = 4.6 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.5, 171.2, 169.8, 129.4, 128.1, 128.0, 127.5, 122.7, 122.1, 107.9, 63.8, 61.5, 61.4, 55.0, 39.0, 35.1, 34.0, 33.7, 33.6, 17.8, 17.3, 14.2, 14.2.
IR (neat) ν 3000, 2970, 2106, 1739, 1435, 1365, 1217, 1015, 697 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{27}N_4O_5$ $[M+H]^+$ 403.1976, found 403.1972.

Diethyl 2-((1-(tert-butoxycarbonyl)-4-thiocyanatopiperidin-4-yl)methyl)-2-methylmalonate (62)

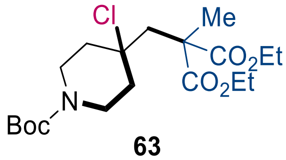


62

62 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'15** (70.8 mg 0.3 mmol, 3.0 equiv.) and KSCN (19.8 mg, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 8 : 1), the title compound was isolated as a white solid (25.4 mg, 63% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.27-4.14 (m, 4H), 3.94 (d, *J* = 10.1 Hz, 2H), 3.07 (s, 2H), 2.57 (s, 2H), 1.91 (d, *J* = 13.3 Hz, 2H), 1.85-1.77 (m, 2H), 1.61 (s, 3H), 1.45 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 7H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.8, 154.5, 110.3, 80.3, 62.0, 57.9, 53.0, 46.5, 39.6, 35.8, 28.5, 22.2, 14.0.
IR (neat) ν 2980, 2931, 1731, 1697, 1424, 1366, 1240, 1020, 669 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{32}KN_2O_6S$ $[M+K]^+$ 467.1613, found 467.1641.
m.p. 59-61 °C

Diethyl 2-((1-(tert-butoxycarbonyl)-4-chloropiperidin-4-yl)methyl)-2-methylmalonate (63)

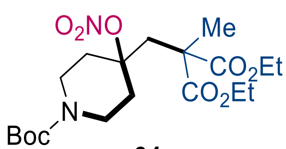


63

63 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'15** (70.8 mg 0.3 mmol, 3.0 equiv.) and Tetrabutylammonium chloride (58.5 mg, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 6 : 1), the title compound was isolated as a colorless oil (22.6 mg, 53% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.23-4.12 (m, 4H), 3.95 (d, *J* = 12.8 Hz, 2H), 3.11 (t, *J* = 12.3 Hz, 2H), 2.56 (s, 2H), 1.91 (d, *J* = 12.3 Hz, 2H), 1.69 (dd, *J* = 12.3, 4.6 Hz, 2H), 1.63 (s, 3H), 1.44 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 154.7, 79.8, 70.9, 61.8, 53.3, 48.9, 39.6, 28.5, 21.5, 14.0.
IR (neat) ν 2979, 2932, 1733, 1697, 1423, 1366, 1242, 1021, 863 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{32}ClNNaO_6$ $[M+Na]^+$ 428.1810, found 428.1796.

Diethyl 2-((1-(tert-butoxycarbonyl)-4-(nitrooxy)piperidin-4-yl)methyl)-2-methylmalonate (64)



64

64 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'15** (70.8 mg 0.3 mmol, 3.0 equiv.) and Tetrabutylammonium nitrate (58.5 mg, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 8 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−88% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as an white solid (18.9 mg, 44% yield).
mp

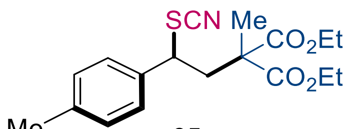
^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 4.25-4.13 (m, 4H), 3.98 (d, J = 13.3 Hz, 2H), 3.14 (t, J = 11.9 Hz, 2H), 2.74 (s, 2H), 2.01 (d, J = 12.3 Hz, 2H), 1.66 (s, 3H), 1.64-1.56 (m, 2H), 1.44 (s, 9H), 1.25 (t, J = 7.3 Hz, 6H).

^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 172.0, 154.6, 79.7, 69.2, 61.7, 53.7, 49.8, 40.5, 40.3, 28.4, 28.4, 21.5, 13.9.

IR (neat) ν 2980, 2937, 1775, 1732, 1448, 1366, 1227, 1020, 770 cm^{-1}.

HRMS (CI) calcd for $C_{19}H_{32}NO_6$ $[M+H-HNO_3]^+$ 370.2224, found 370.2230.

Diethyl 2-methyl-2-(2-thiocyanato-2-(p-tolyl)ethyl)malonate (**65**)



65

65 was synthesized according to general procedure C. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and KSCN (19.8 mg, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 8 : 1), the title compound was isolated as a brown oil (23.0 mg, 66% yield).

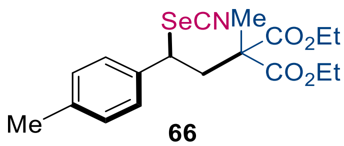
^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 4.55 (q, J = 4.4 Hz, 1H), 4.11-4.01 (m, 2H), 4.00-3.92 (m, 1H), 3.87-3.79 (m, 1H), 2.84 (dd, J = 14.6, 9.1 Hz, 1H), 2.72 (dd, J = 14.6, 4.6 Hz, 1H), 2.33 (s, 3H), 1.37 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H).

^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 171.2, 171.0, 139.3, 134.9, 129.8, 127.9, 111.7, 61.9, 61.7, 53.1, 50.0, 40.9, 21.3, 20.5, 14.0, 13.9.

IR (neat) ν 2985, 2940, 1731, 1515, 1447, 1381, 1272, 1108, 1021 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{27}N_2O_4S$ $[M+NH_4]^+$ 367.1686, found 367.1672.

Diethyl 2-methyl-2-(2-selenocyanato-2-(p-tolyl)ethyl)malonate (**66**)

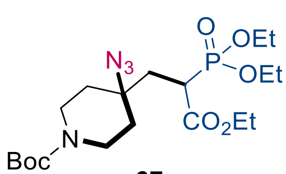


66

66 was synthesized according to general procedure C. **S1** (31.0 mg, 0.12 mmol, 1.2 equiv.), **S'1** (13.2 μL 0.1 mmol, 1.0 equiv.) and KSeCN (29.4 mg, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 7 : 1), the title compound was isolated as a red solid (25.6 mg, 65% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 4.86 (dd, J = 10.1, 4.1 Hz, 1H), 4.10-3.99 (m, 2H), 3.98-3.91 (m, 1H), 3.86-3.78 (m, 1H), 2.97 (dd, J = 14.6, 10.1 Hz, 1H), 2.85 (dd, J = 14.6, 4.1 Hz, 1H), 2.32 (s, 3H), 1.36 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.3, 171.1, 139.2, 135.3, 129.8, 127.9, 102.9, 61.9, 61.7, 53.7, 46.9, 41.6, 21.3, 20.4, 14.0, 13.9.
IR (neat) ν 2983, 2939, 1730, 1514, 1464, 1380, 1195, 1021, 861 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{27}N_2O_4Se$ $[M+NH_4]^+$ 415.1131, found 415.1143.
m.p. 65-67 ℃

tert-Butyl 4-azido-4-(2-(diethoxyphosphoryl)-3-ethoxy-3-oxopropyl)piperidine-1-carboxylate (67)



67

67 was synthesized according to general procedure D. **S28** (30.9 mg, 0.10 mmol, 1.0 equiv.), **S'15** (60.4 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 2 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−56% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a yellow oil (37.5 mg, 81% yield).

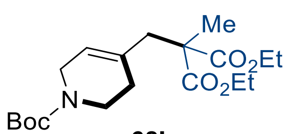
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.28-4.09 (m, 6H), 3.83 (s, 2H), 3.17-3.08 (m, 1H), 3.01 (d, J = 11.9 Hz, 2H), 2.45-2.37 (m, 1H), 2.02 (td, J = 15.0, 1.2 Hz, 1H), 1.62 (dd, J = 32.0, 13.7 Hz, 2H), 1.49-1.43 (m, 11H), 1.34-1.27 (m, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.2, 169.2, 154.6, 80.0, 63.3, 63.3, 63.1, 63.0, 62.0, 61.9, 41.5, 40.2, 39.8, 36.8, 36.7, 33.7, 28.5, 16.5, 16.4, 14.1.

IR (neat) ν 2980, 2931, 2106, 1736, 1423, 1366, 1256, 1024, 866 cm^{-1}.

HRMS (FAB) calcd for $C_{19}H_{36}N_4O_7P$ $[M+H]^+$ 463.2316, found 463.2334.

Diethyl 2-((1-(tert-butoxycarbonyl)-1,2,3,6-tetrahydropyridin-4-yl)methyl)-2-methylmalonate (68′)



68'

68′ was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'15** (70.8 mg 0.3 mmol, 3.0 equiv.) and Tetrabutylammonium bromide or acetate (65.8 mg, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 6 : 1), the title compound was isolated as a yellow oil (23.9 mg, 65% yield).

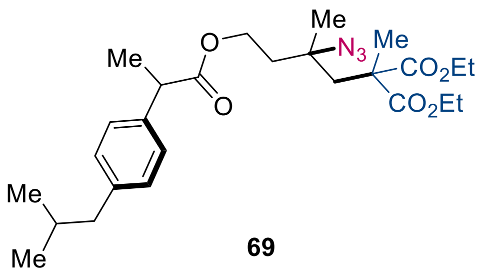
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.25-4.13 (m, 4H), 3.98 (d, J = 13.3 Hz, 2H), 3.14 (t, J = 11.9 Hz, 2H), 2.74 (s, 2H), 2.01 (d, J = 12.3 Hz, 2H), 1.66 (s, 3H), 1.64-1.56 (m, 2H), 1.44 (s, 9H), 1.25 (t, J = 7.3 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.0, 154.6, 79.7, 69.2, 61.7, 53.7, 49.8, 40.5, 40.3, 28.4, 28.4, 21.5, 13.9.

IR (neat) ν 2980, 2935, 1732, 1699, 1419, 1366, 1242, 1109, 862 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{31}NNaO_6$ $[M+Na]^+$ 392.2044, found 392.2033.

Diethyl 2-(2-azido-4-((2-(4-isobutylphenyl)propanoyl)oxy)-2-methylbutyl)-2-methylmalonate (69)



69

69 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'35** (83.2 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 15 : 1 : 1), the title compound was isolated as a colorless oil (24.5 mg, 51% yield, d.r. = 1:1).

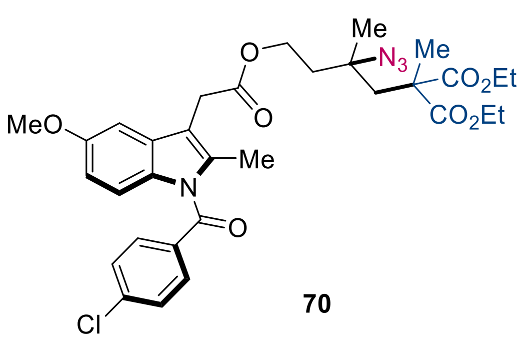
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 8.0, 2.1 Hz, 4H), 7.08 (d, J = 7.8 Hz, 4H), 4.23-4.09 (m, 12H), 3.68 (td, J = 14.8, 7.8 Hz, 2H), 2.44 (d, J = 7.3 Hz, 4H), 2.23 (d, J = 1.8 Hz, 4H), 1.90-1.76 (m, 6H), 1.53 (s, 6H), 1.48 (d, J = 7.3 Hz, 6H), 1.26-1.21 (m, 17H), 0.89 (d, J = 6.4 Hz, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.7, 172.2, 172.1, 140.7, 137.7, 129.5, 127.3, 61.7, 60.7, 52.7, 45.2, 45.2, 43.5, 43.5, 39.8, 39.8, 30.3, 23.9, 23.8, 22.5, 20.9, 18.5, 14.1.

IR (neat) ν 2970, 2952, 2105, 1739, 1455, 1365, 1217, 1022, 781 cm^{-1}.

HRMS (ESI) calcd for $C_{26}H_{43}N_4O_6$ $[M+NH_4]^+$ 507.3177, found 507.3146.

Diethyl 2-(2-azido-4-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxy)-2-methylbutyl)-2-methylmalonate (70)

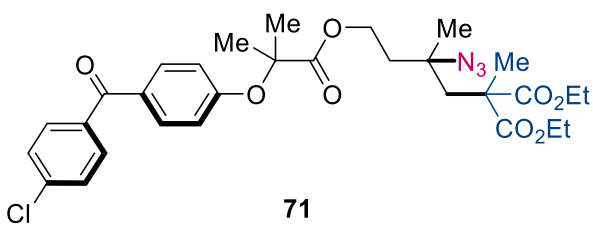


70

70 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'36** (130.4 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 5 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−74% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (31.8 mg, 50% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 2.8 Hz, 1H), 6.86 (d, *J* = 9.2 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.24-4.11 (m, 6H), 3.83 (s, 3H), 3.67 (s, 2H), 2.38 (s, 3H), 2.25 (s, 2H), 1.96-1.81 (m, 2H), 1.55 (s, 3H), 1.27 (s, 3H), 1.23 (t, *J* = 6.4 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 172.1, 170.8, 168.4, 156.2, 139.4, 136.1, 134.0, 131.3, 130.9, 130.7, 129.3, 115.1, 112.5, 111.8, 101.4, 61.8, 61.7, 61.0, 55.9, 52.7, 43.6, 39.9, 30.4, 23.8, 20.9, 14.1, 13.5.
IR (neat) ν 2979, 2935, 2105, 1732, 1685, 1593, 1478, 1323, 1258, 1016, 755 cm^{-1}.
HRMS (ESI) calcd for C32H41ClN5O8 $[M+NH_4]^+$ 658.2638, found 658.2646.

Diethyl 2-(2-azido-4-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)-2-methylbutyl)-2-methylmalonate (71)



71

71 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'37** (117.2 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 8 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−78% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a colorless oil (34.2 mg, 57% yield).

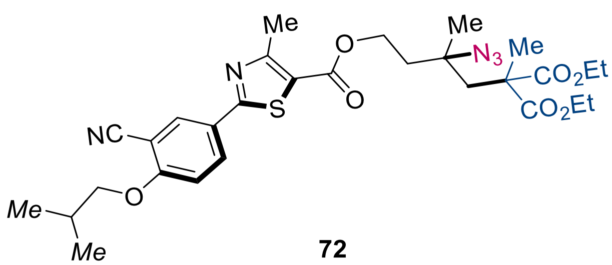
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 13.1, 8.5 Hz, 4H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.28 (t, *J* = 6.7 Hz, 2H), 4.23-4.10 (m, 4H), 2.23 (s, 2H), 1.85 (tt, *J* = 21.2, 7.0 Hz, 2H), 1.67 (s, 6H), 1.53 (s, 3H), 1.27 (s, 3H), 1.23 (td, *J* = 7.1, 4.1 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.3, 173.7, 172.1, 172.0, 159.7, 138.5, 136.5, 132.2, 131.3, 130.6, 128.7, 117.4, 79.4, 61.8, 61.6, 52.7, 43.5, 39.7, 25.5, 25.5, 23.9, 20.9, 14.1.

IR (neat) ν 2988, 2971, 2104, 1739, 1599, 1506, 1379, 1229, 1140, 1015, 763 cm^{-1}.

HRMS (ESI) calcd for $C_{30}H_{37}ClN_3O_8$ $[M+H]^+$ 602.2264, found 602.2283.

Diethyl 2-(2-azido-4-((2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)oxy)-2-methylbutyl)-2-methylmalonate (72)



72

72 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'38** (116.5 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 5 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−85% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a white solid (28.4 mg, 47% yield).

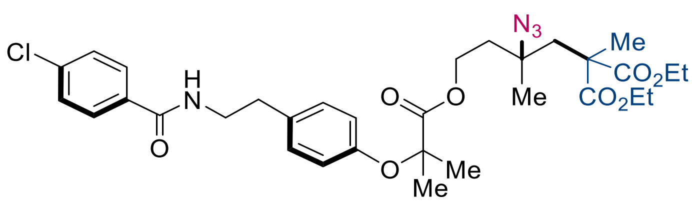
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.3 Hz, 1H), 8.09 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 4.42 (t, *J* = 6.7 Hz, 2H), 4.26-4.14 (m, 4H), 3.89 (d, *J* = 6.4 Hz, 2H), 2.75 (s, 3H), 2.33 (s, 2H), 2.24-2.15 (m, 1H), 2.08-1.95 (m, 2H), 1.59 (s, 3H), 1.39 (s, 3H), 1.26 (td, *J* = 7.1, 2.3 Hz, 6H), 1.08 (d, *J* = 6.4 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 172.1, 167.6, 162.7, 161.9, 161.8, 132.7, 132.3, 126.1, 121.4, 115.5, 112.7, 103.1, 75.8, 61.8, 61.7, 61.3, 52.8, 43.6, 40.1, 28.3, 24.0, 20.9, 19.2, 17.6, 14.1.

IR (neat) ν 2970, 2940, 2105, 1730, 1696, 1510, 1434, 1336, 1100, 1012, 760 cm^{-1}.

HRMS (ESI) calcd for $C_{29}H_{38}N_5O_7S$ $[M+H]^+$ 600.2486, found 600.2480.
m.p. 74-76 °C

Diethyl 2-(2-azido-4-((2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoyl)oxy)-2-methylbutyl)-2-methylmalonate (73)

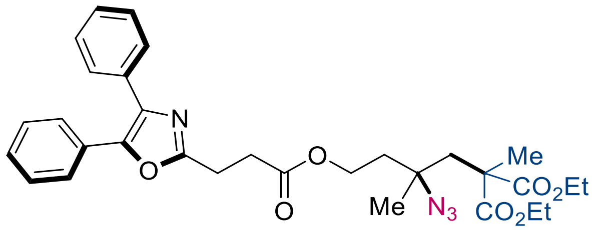


73

73 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'39** (130.3 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 µL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 3 : 1 : 1), followed by reverse phase MPLC column (Biotage SNAP Ultra C18, 30 g) using a gradient condition (0−78% H_2O/ACN, UV detection at 280 nm, flow rate = 25 mL/min), the title compound was isolated as a white solid (26.1 mg, 40% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62 (dt, J = 8.8, 2.3 Hz, 2H), 7.37 (dt, J = 9.0, 2.3 Hz, 2H), 7.08 (dt, J = 9.1, 2.4 Hz, 2H), 6.78 (td, J = 5.7, 3.7 Hz, 2H), 6.18 (t, J = 5.3 Hz, 1H), 4.27 (t, J = 6.9 Hz, 2H), 4.23-4.08 (m, 4H), 3.65 (q, J = 6.6 Hz, 2H), 2.89-2.82 (m, 2H), 2.23 (s, 2H), 1.93-1.79 (m, 2H), 1.58 (s, 6H), 1.53 (s, 3H), 1.27 (s, 3H), 1.24 (td, J = 7.1, 3.5 Hz, 6H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.3, 172.1, 172.1, 166.5, 154.2, 137.7, 133.1, 132.6, 129.7, 128.9, 128.4, 119.5, 79.1, 61.8, 61.6, 61.4, 52.7, 43.5, 41.4, 39.7, 34.8, 25.4, 25.4, 23.9, 20.9, 14.1.
IR (neat) ν 3330, 2983, 2939, 2106, 1732, 1569, 1508, 1235, 1140, 1015, 850 cm^{-1}.
HRMS (ESI) calcd for $C_{32}H_{42}ClN_4O_8$ $[M+H]^+$ 645.2686, found 645.2674.
m.p. 38-40 °C

Diethyl 2-(2-azido-4-((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)-2-methylbutyl)-2-methylmalonate (74)



74

74 was synthesized according to general procedure D. **S1** (25.8 mg, 0.10 mmol, 1.0 equiv.), **S'40** (109.5 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 6 : 1 : 1), the title compound was isolated as a colorless oil (34.7 mg, 60% yield).

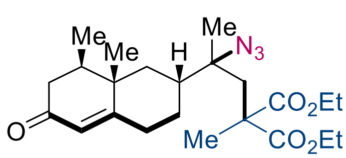
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62 (dt, *J* = 6.6, 1.6 Hz, 2H), 7.57 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.38-7.29 (m, 6H), 4.25 (t, *J* = 6.9 Hz, 2H), 4.22-4.12 (m, 4H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.26 (s, 2H), 1.91 (tt, *J* = 21.6, 7.2 Hz, 2H), 1.56 (s, 3H), 1.31 (s, 3H), 1.25 (td, *J* = 7.1, 3.4 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.2, 172.1, 172.0, 161.8, 145.6, 135.2, 132.4, 129.0, 128.8, 128.7, 128.6, 128.2, 128.0, 126.6, 61.8, 61.7, 60.8, 52.7, 43.5, 39.9, 31.2, 23.9, 23.5, 20.9, 14.1.

IR (neat) ν 2982, 2940, 2104, 1739, 1580, 1445, 1365, 1228, 1024, 861, 765 cm^{-1}.

HRMS (ESI) calcd for $C_{31}H_{37}N_4O_7$ $[M+H]^+$ 577.2657, found 577.2641.

Diethyl 2-(2-azido-2-((2R,8R,8aS)-8,8a-dimethyl-6-oxo-1,2,3,4,6,7,8,8a-octahydronaphthalen-2-yl)propyl)-2-methylmalonate (75)

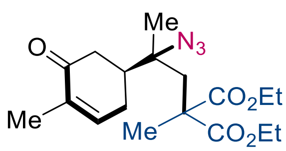


75

75 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'41** (66.8 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc = 6 : 1), the title compound was isolated as a colorless oil (24.7 mg, 57% yield, d.r. = 1:1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.75 (s, 1H), 4.24-4.12 (m, 4H), 2.52-2.36 (m, 2H), 2.32-2.19 (m, 3H), 2.17 (s, 1H), 2.05-1.92 (m, 3H), 1.86 (tt, *J* = 12.4, 2.5 Hz, 1H), 1.77 (s, 1H), 1.57 (d, *J* = 5.5 Hz, 3H), 1.30 (s, 2H), 1.25 (tt, *J* = 7.1, 1.8 Hz, 8H), 1.09 (s, 3H), 0.98 (dd, *J* = 6.9, 2.3 Hz, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.5, 199.4, 172.4, 172.2, 169.5, 169.5, 124.9, 64.9, 64.8, 61.7, 61.7, 52.9, 44.6, 43.9, 42.1, 41.1, 40.6, 40.6, 40.3, 39.4, 39.3, 32.8, 32.8, 27.8, 27.5, 21.0, 20.9, 20.8, 20.2, 17.0, 16.9, 15.1, 15.1, 14.1.
IR (neat) ν 2970, 2939, 2103, 1739, 1668, 1463, 1380, 1228, 1135, 1021, 669 cm^{-1}.
HRMS (ESI) calcd for $C_{23}H_{36}N_3O_5$ $[M+H]^+$ 434.2649, found 434.2666.

Diethyl 2-(2-azido-2-((S)-4-methyl-5-oxocyclohex-3-en-1-yl)propyl)-2-methylmalonate (76)

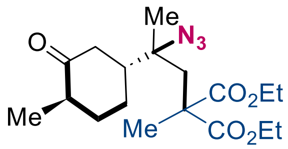


76

76 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'42** (46.0 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 8 : 1 : 1), the title compound was isolated as a colorless oil (26.5 mg, 72% yield, d.r. = 1:1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.75-6.73 (m, 0H), 4.23-4.11 (m, 1H), 2.63-2.57 (m, 0H), 2.50-2.42 (m, 0H), 2.31-2.14 (m, 1H), 1.77 (s, 1H), 1.56 (s, 1H), 1.32 (d, J = 9.6 Hz, 0H), 1.28-1.23 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.0, 198.9, 172.3, 172.1, 144.3, 144.2, 135.7, 135.6, 63.9, 63.8, 61.8, 52.8, 52.8, 46.5, 46.2, 40.8, 40.5, 39.6, 39.5, 27.3, 27.3, 20.9, 20.9, 20.7, 20.1, 15.7, 14.1.
IR (neat) ν 2986, 2945, 2104, 1740, 1682, 1463, 1365, 1216, 1021, 705 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{28}NO_5$ $[M+H-N_2]^+$ 338.1962, found 338.1959.

Diethyl 2-(2-azido-2-((1R,4R)-4-methyl-3-oxocyclohexyl)propyl)-2-methylmalonate (77)



77

77 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'43** (46.1 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 12 : 1 : 1), the title compound was isolated as a colorless oil (21.4 mg, 58% yield, d.r. = 1:1).

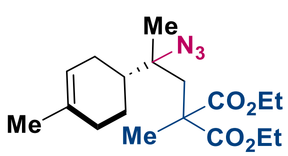
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.25-4.11 (m, 4H), 2.56-2.47 (m, 1H), 2.34 (qt, *J* = 9.2, 3.1 Hz, 1H), 2.22-2.12 (m, 4H), 2.05-1.94 (m, 1H), 1.89-1.81 (m, 1H), 1.71-1.51 (m, 4H), 1.31-1.22 (m, 10H), 1.02 (d, *J* = 6.4 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ δ 211.7, 211.7, 172.3, 172.3, 172.1, 172.1, 64.3, 61.8, 52.9, 50.9, 50.7, 45.0, 44.9, 43.1, 43.0, 40.7, 40.6, 34.2, 34.1, 30.4, 26.5, 26.3, 20.9, 20.8, 20.6, 20.5, 14.3, 14.1, 14.0.

IR (neat) ν 2970, 2934, 2108, 1730, 1713, 1457, 1383, 1258, 1135, 1020 cm^{-1}.

HRMS (ESI) calcd for C18H33N4O5 $[M+NH_4]^+$ 385.2445, found 385.2449.

Diethyl 2-(2-azido-2-((R)-4-methylcyclohex-3-en-1-yl)propyl)-2-methylmalonate (78)



78

78 was synthesized according to general procedure D. **S1** (25.8 mg, 0.1 mmol, 1.0 equiv.), **S'44** (41.3 mg 0.3 mmol, 3.0 equiv.) and $TMSN_3$ (28.1 μL, 0.2 mmol, 2.0 equiv.) were used as a starting material. After purification by column chromatography (hexane : EtOAc : DCM = 50 : 1 : 1), the title compound was isolated as a colorless oil (18.4 mg, 52% yield, d.r. = 1:1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.36 (t, *J* = 1.6 Hz, 1H), 4.24-4.11 (m, 4H), 2.30-2.16 (m, 2H), 2.11-1.94 (m, 3H), 1.94-1.81 (m, 2H), 1.73-1.64 (m, 4H), 1.57 (d, *J* = 2.3 Hz, 3H), 1.40-1.19 (m, 10H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.6, 172.6, 172.4, 172.3, 134.2, 134.2, 120.2, 120.1, 77.5, 77.2, 76.8, 65.3, 65.2, 61.6, 53.0, 52.9, 45.4, 45.3, 41.0, 40.4, 31.0, 31.0, 26.9, 26.6, 24.3, 24.1, 23.4, 23.3, 20.9, 20.4, 20.1, 14.1.

IR (neat) ν 2981, 2929, 2105, 1733, 1447, 1381, 1249, 1132, 1022, 861 cm^{-1}.

HRMS (FAB) calcd for $C_{18}H_{30}N_3O_4$ $[M+H]^+$ 352.2231, found 352.2233.

XI. Reference

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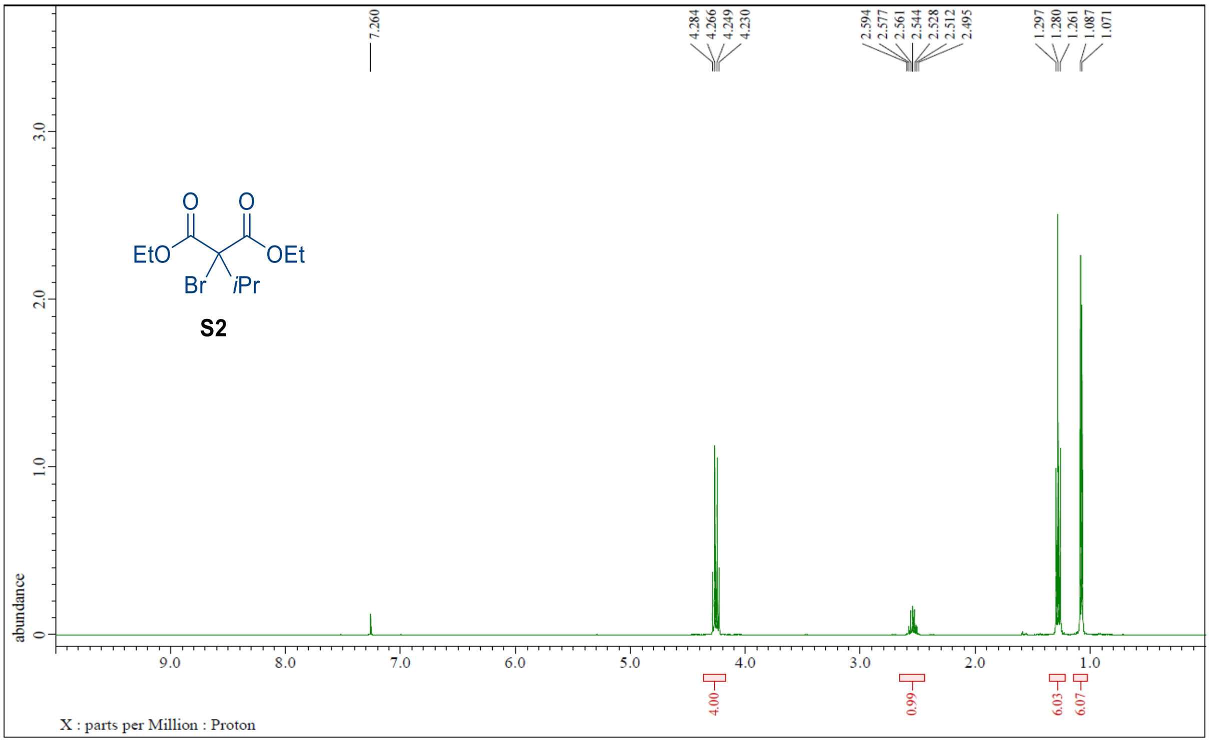
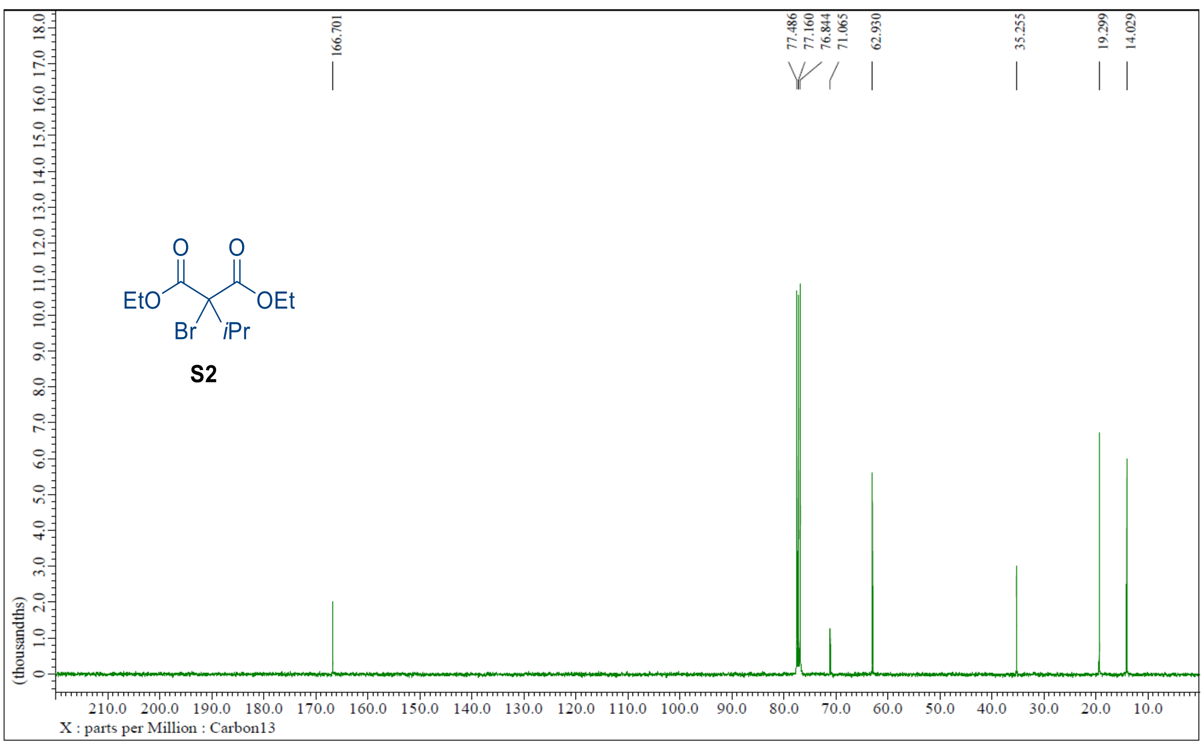
XII. NMR Spectra

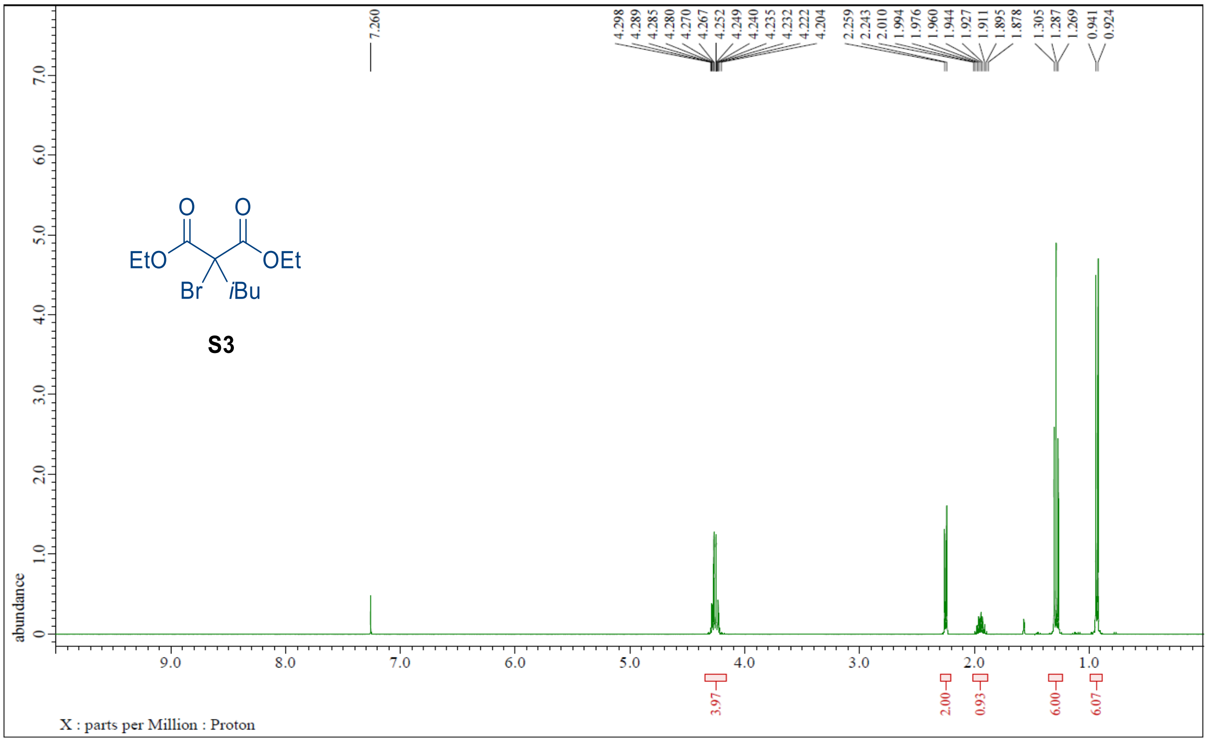
S2 ^{1}H NMR (400 MHz, $CDCl_3$)



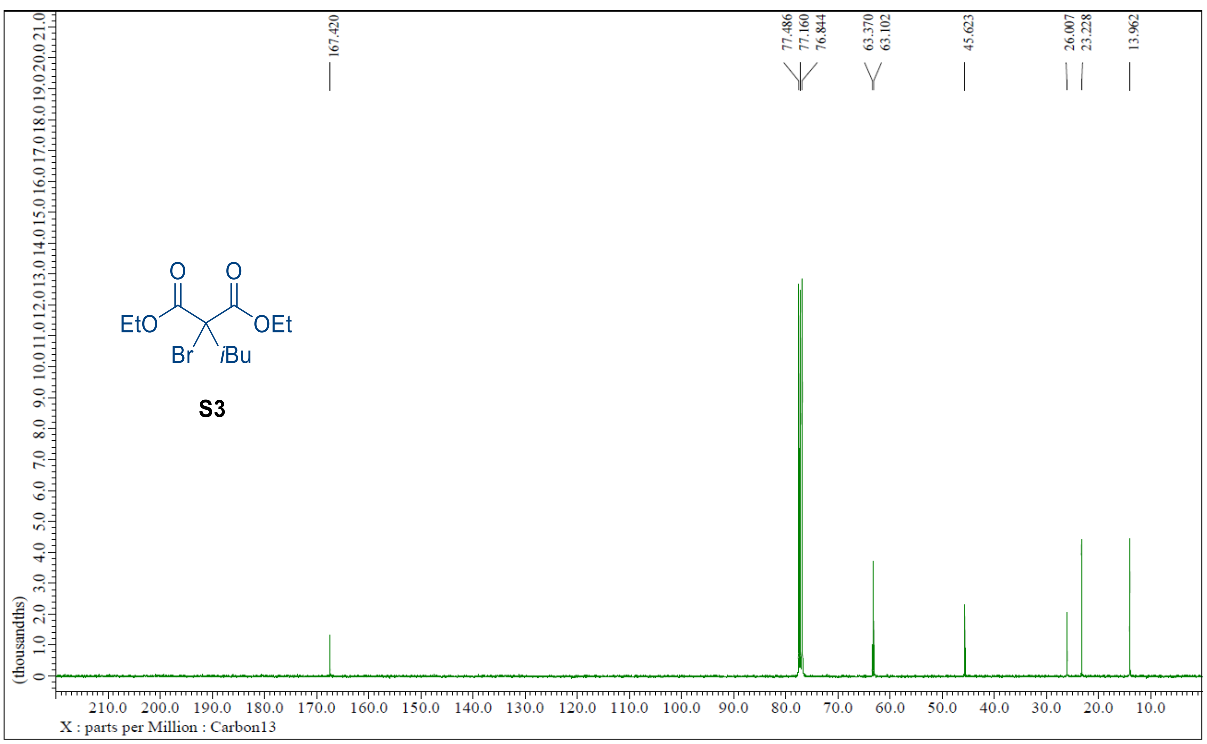
S2 ^{13}C NMR (100 MHz, $CDCl_3$)



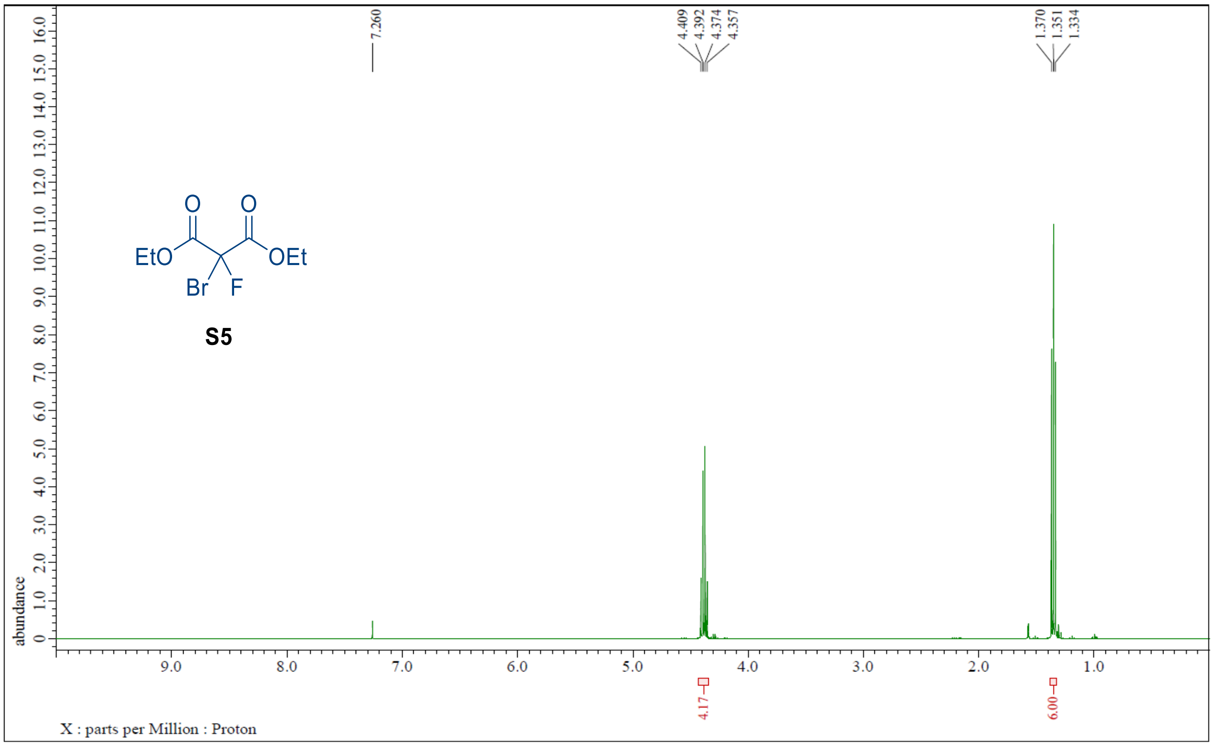
S3 ^{1}H NMR (400 MHz, $CDCl_3$)



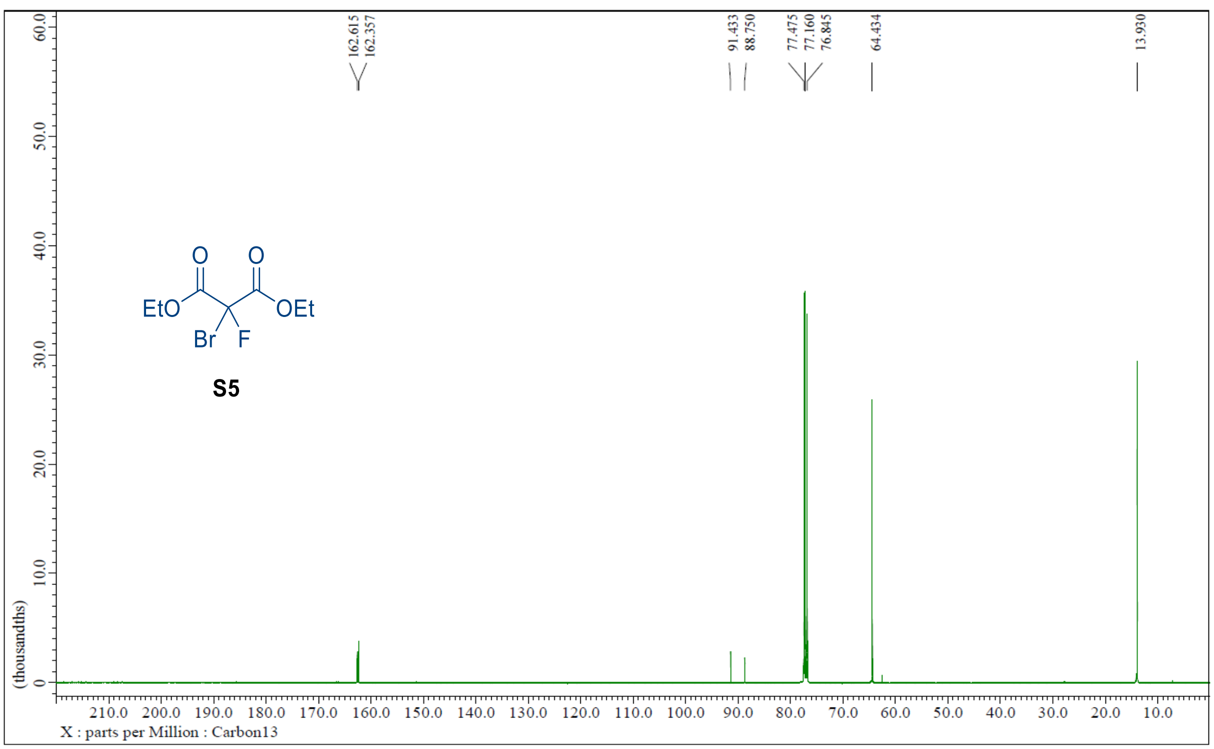
S3 ^{13}C NMR (100 MHz, $CDCl_3$)



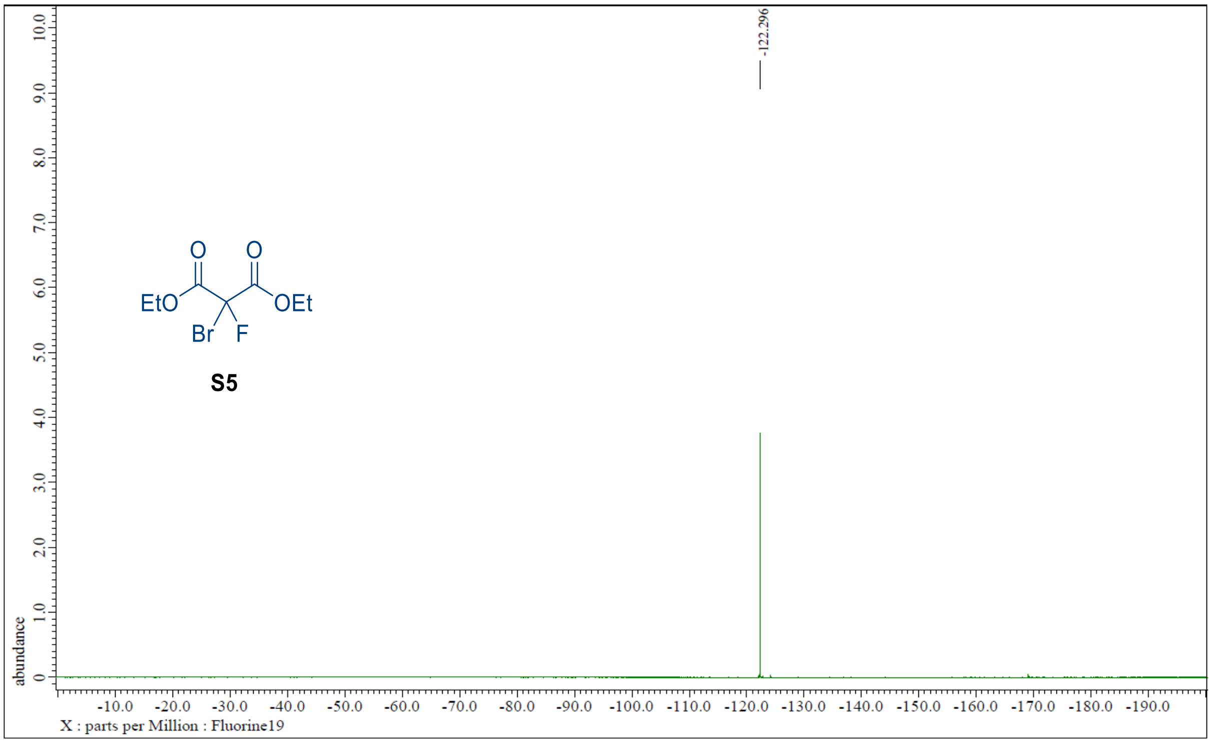
S5 ^{1}H NMR (400 MHz, $CDCl_3$)



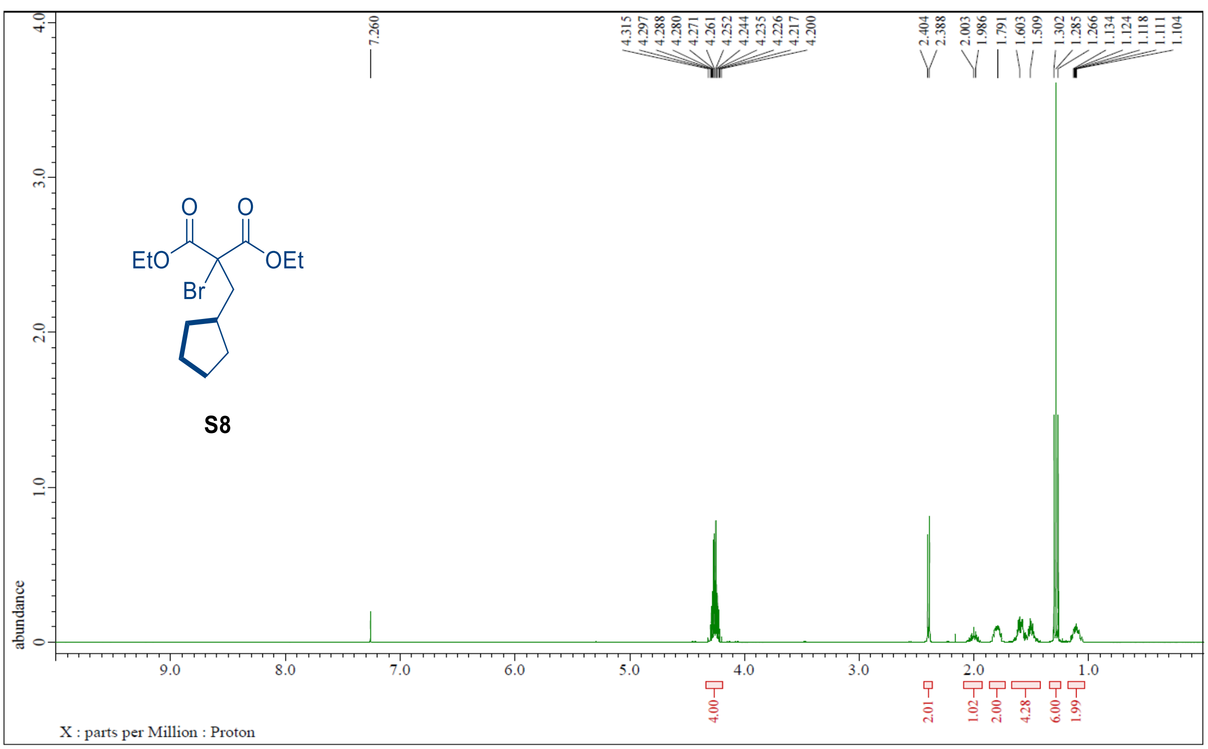
S5 ^{13}C NMR (100 MHz, $CDCl_3$)



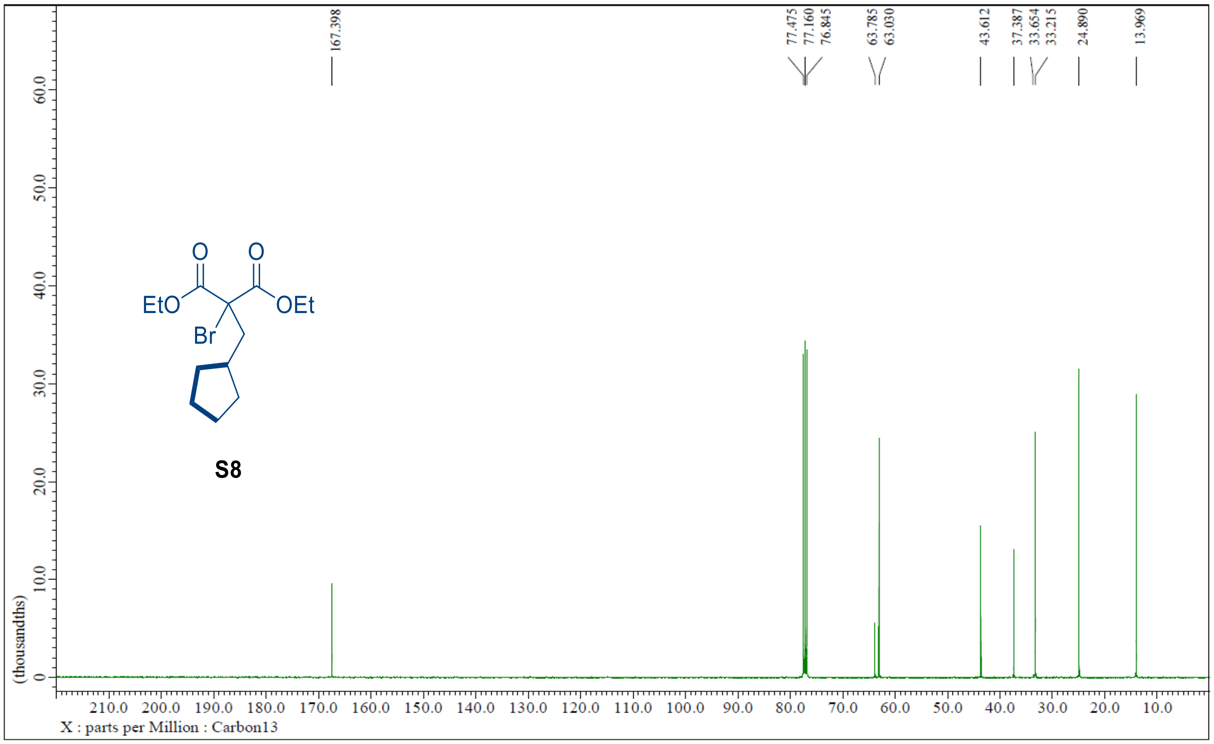
S5 ^{19}F NMR (376 MHz, $CDCl_3$)



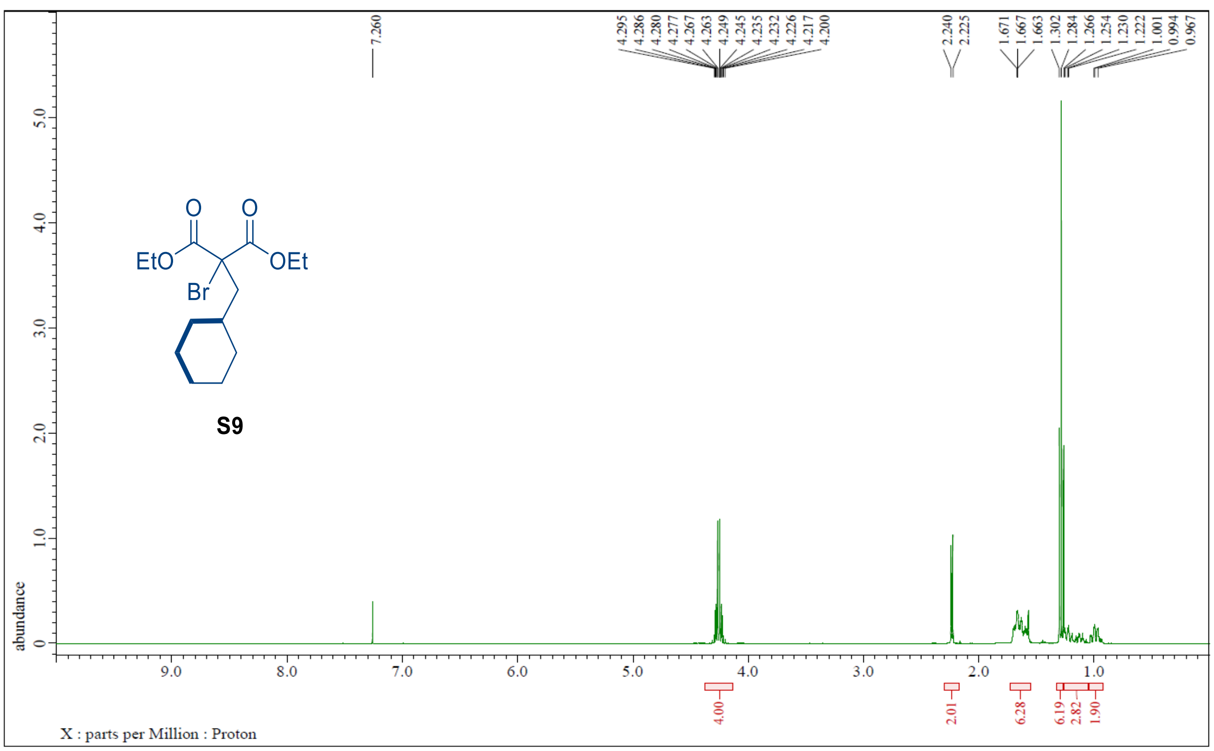
S8 ^{1}H NMR (400 MHz, $CDCl_3$)



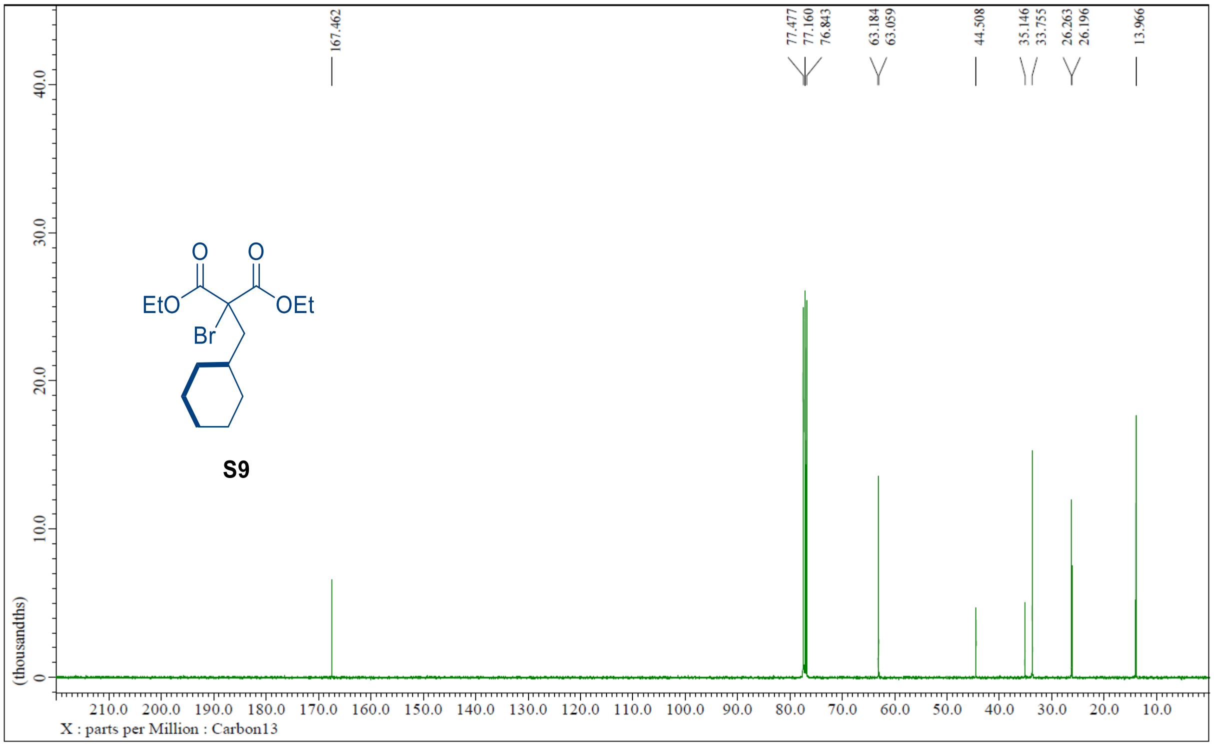
S8 ^{13}C NMR (100 MHz, $CDCl_3$)



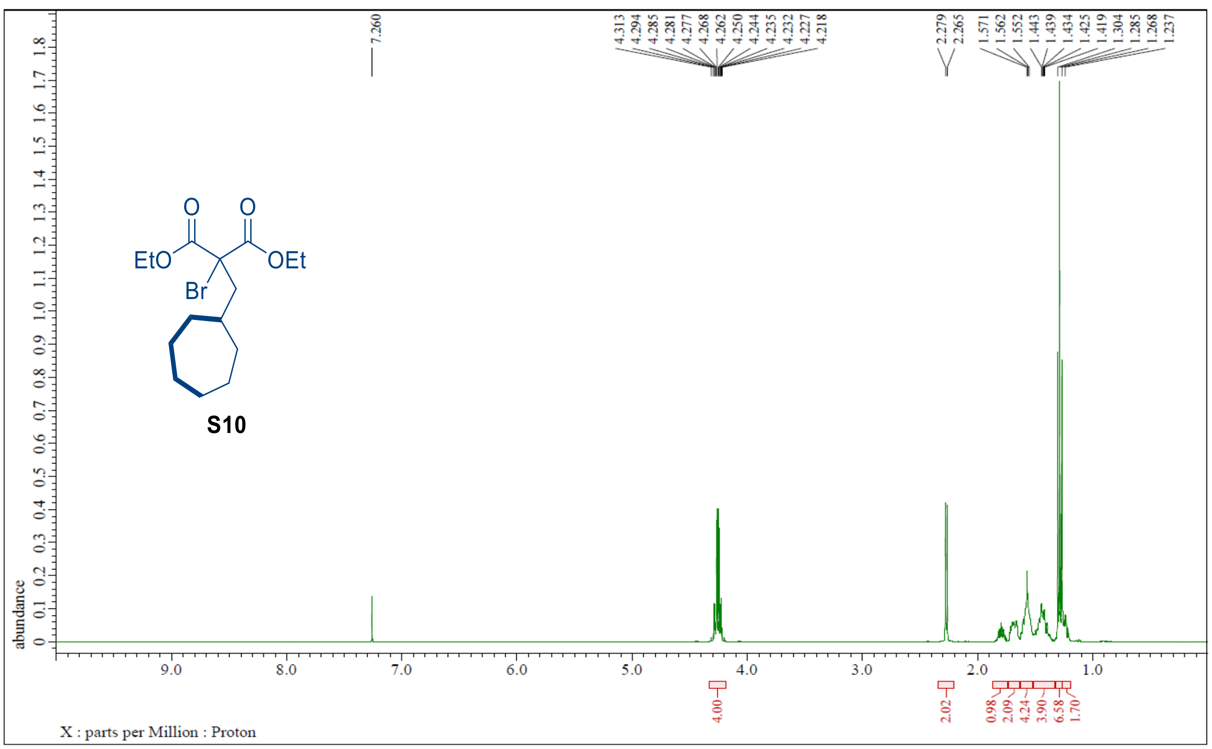
S9 ^{1}H NMR (400 MHz, $CDCl_3$)



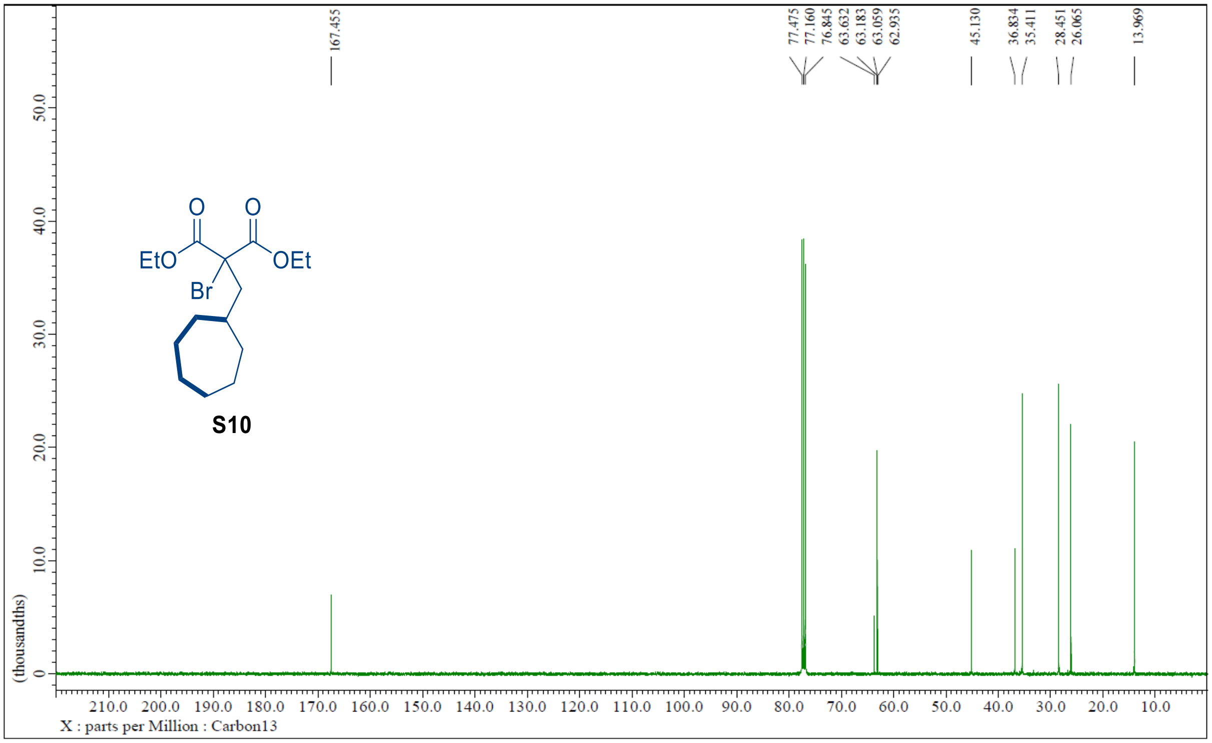
S9 ^{13}C NMR (100 MHz, CDCl$_3$)



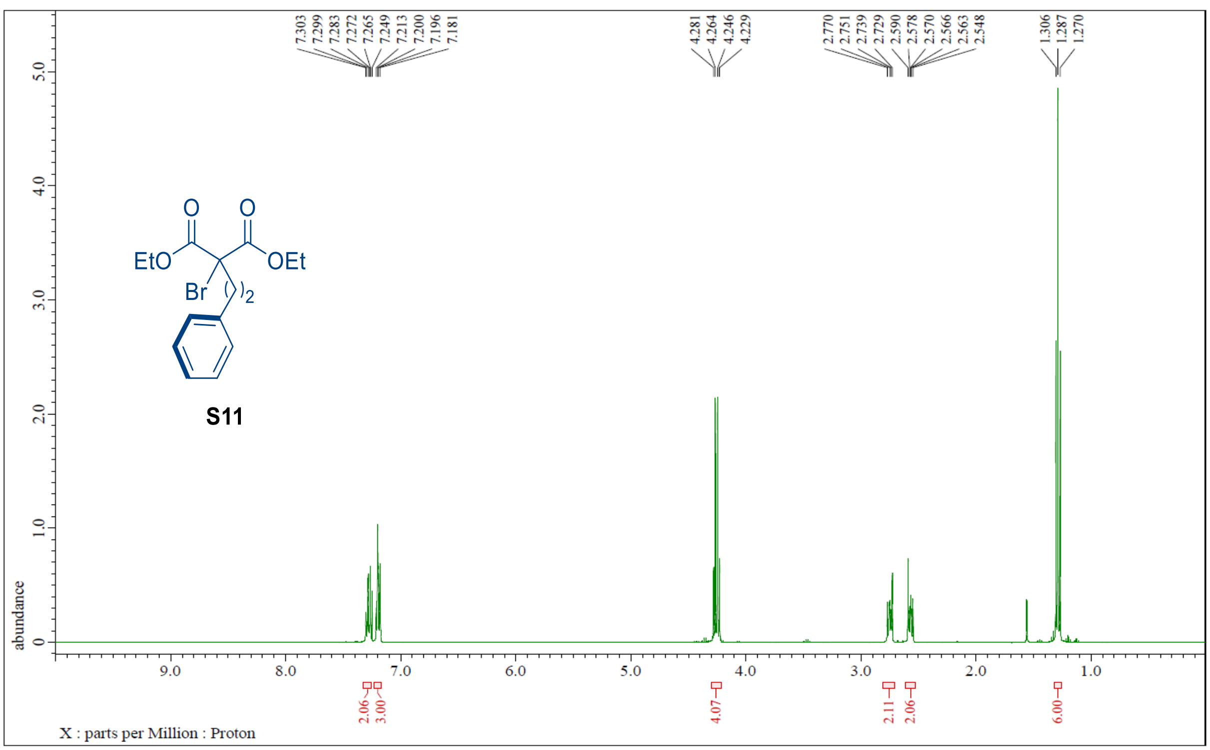
S10 ^{1}H NMR (400 MHz, CDCl$_3$)



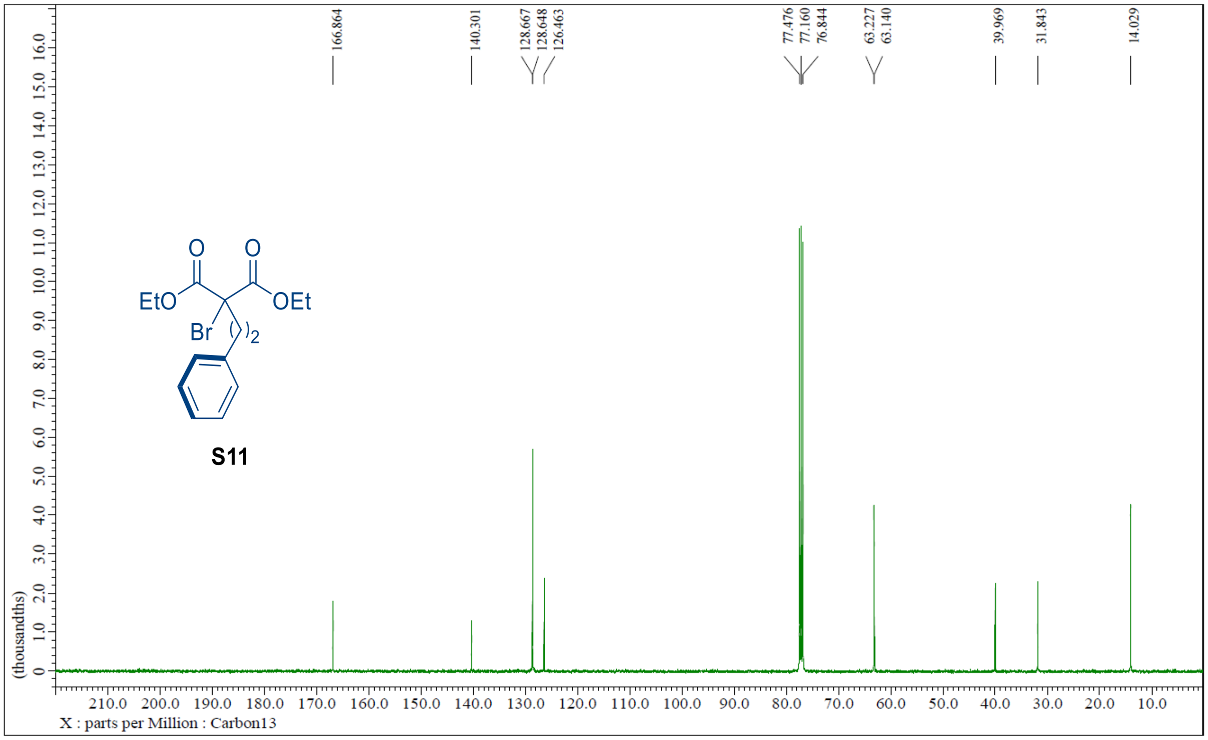
S10 ^{13}C NMR (100 MHz, $CDCl_3$)



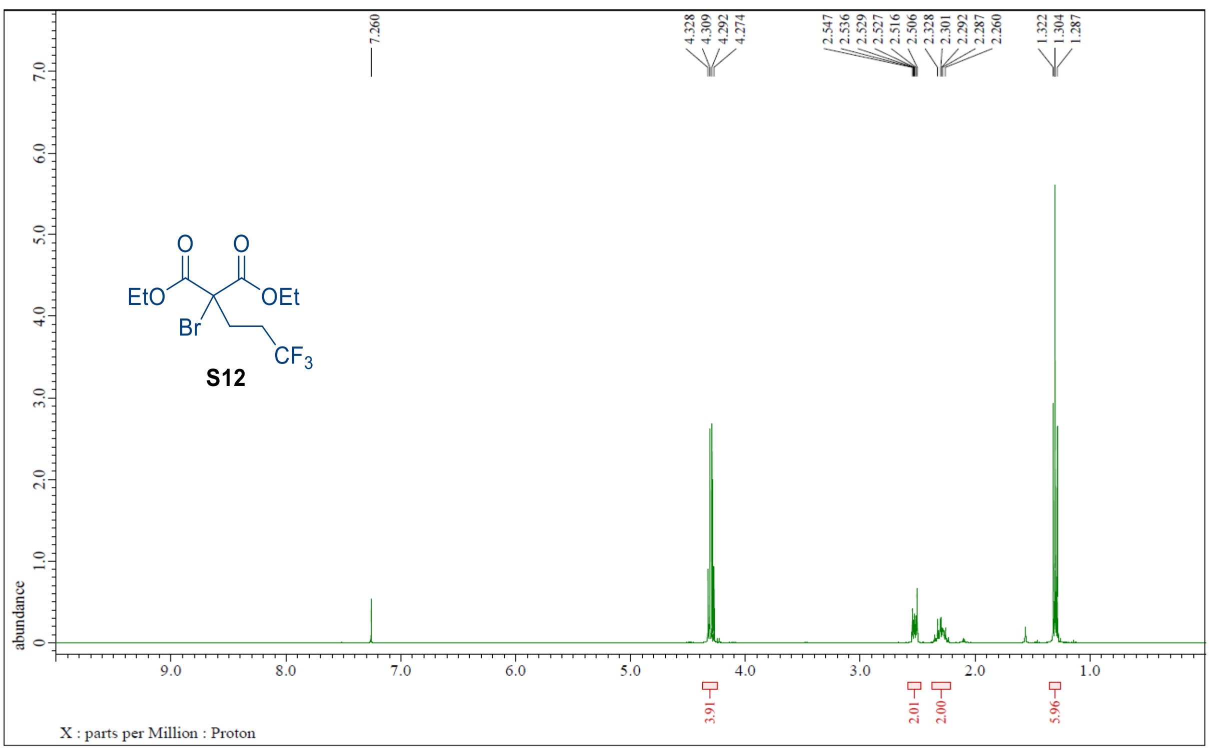
S11 ^{1}H NMR (400 MHz, $CDCl_3$)



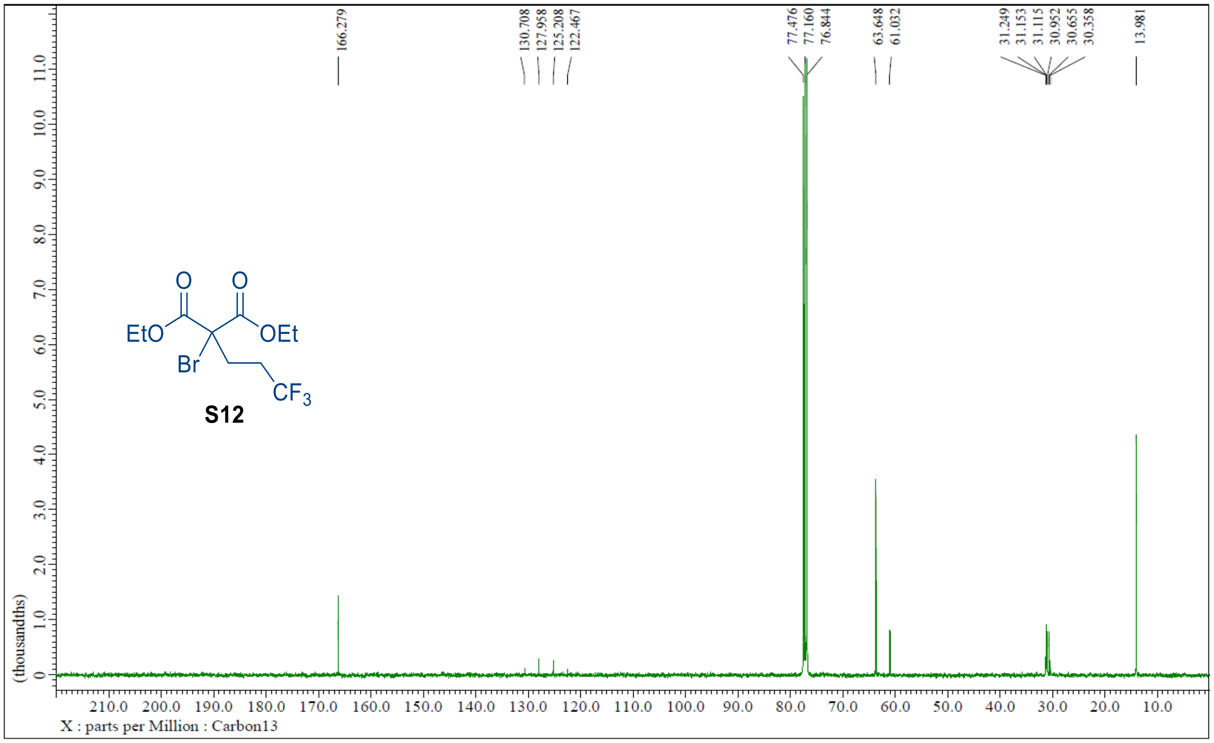
S11 ^{13}C NMR (100 MHz, $CDCl_3$)



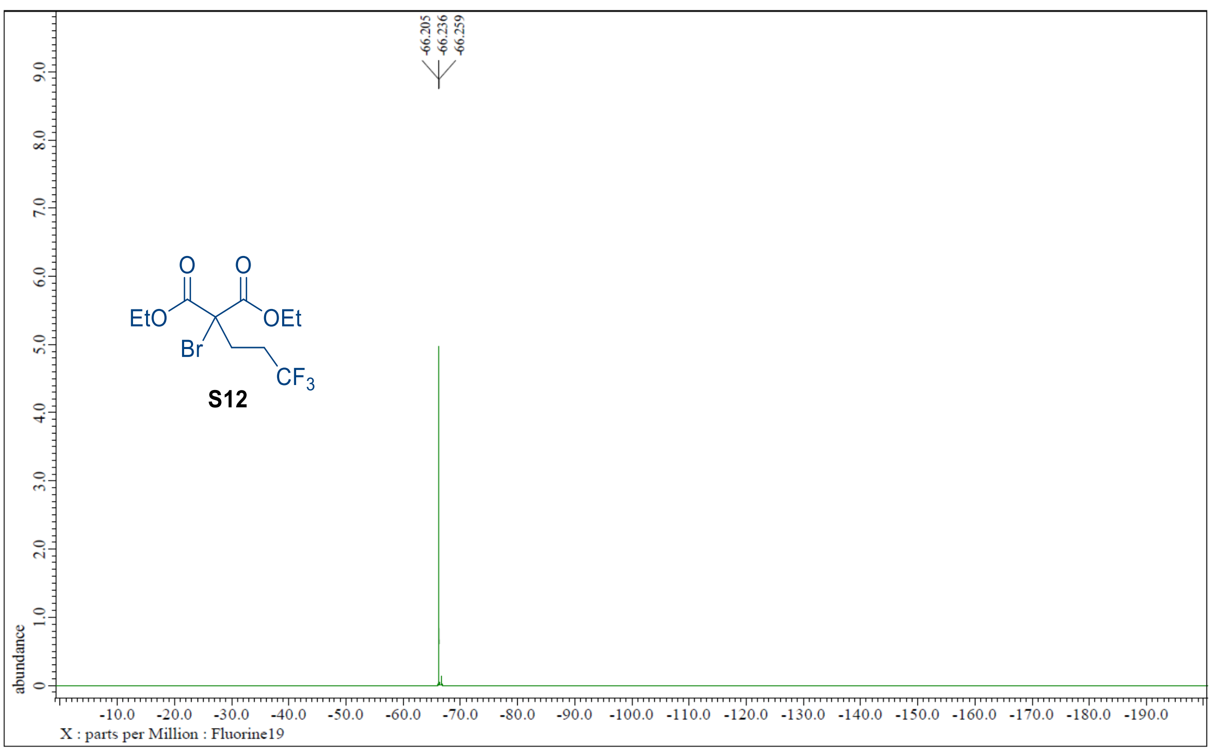
S12 ^{1}H NMR (400 MHz, $CDCl_3$)



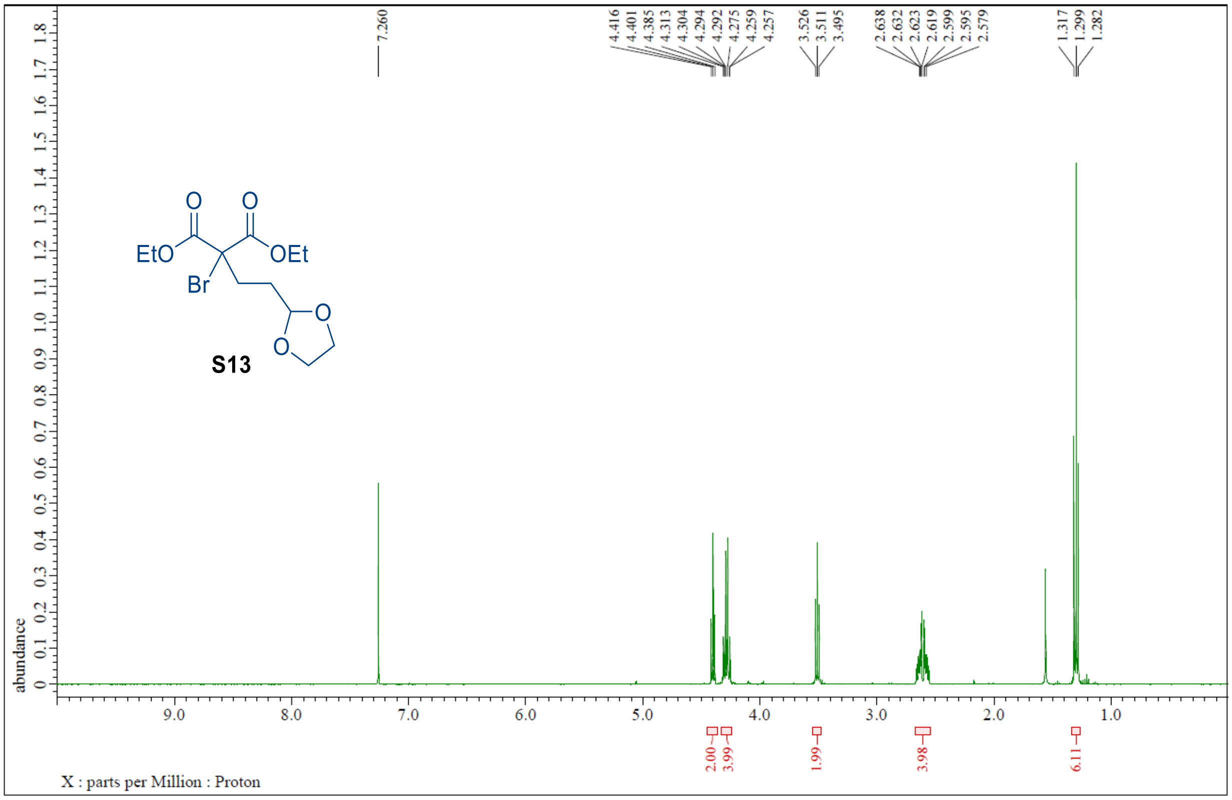
S12 ^{13}C NMR (100 MHz, $CDCl_3$)



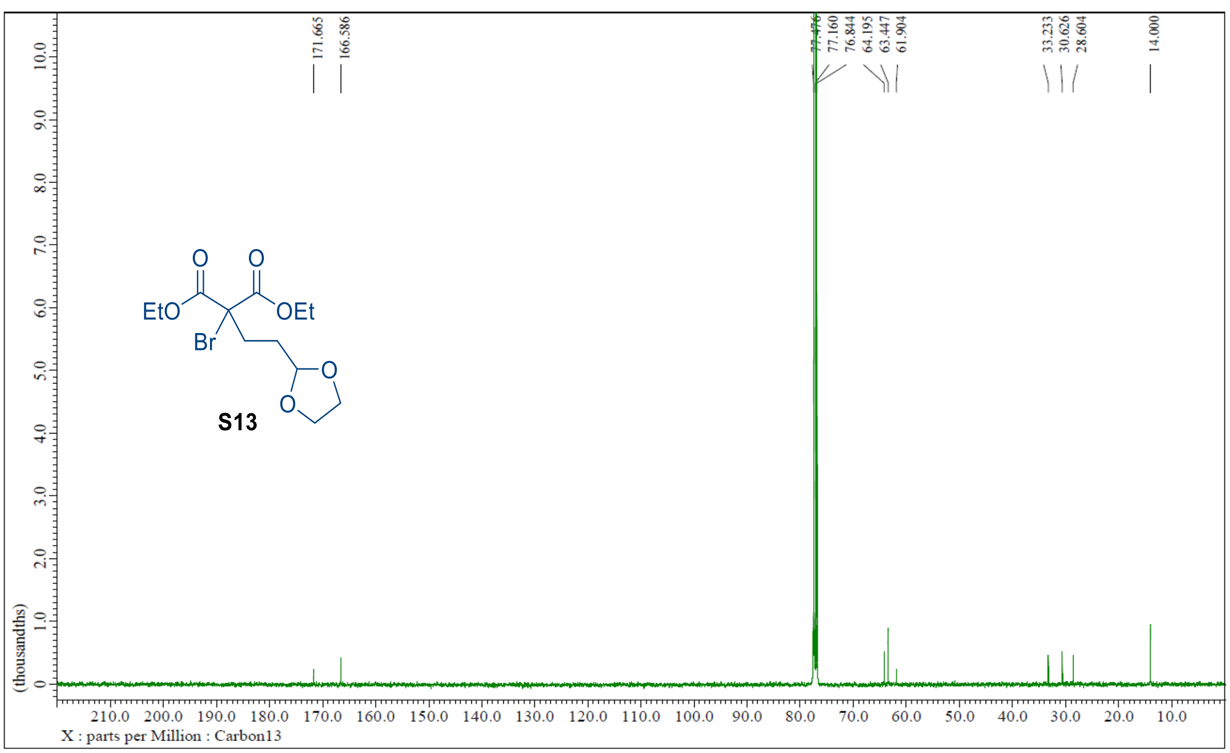
S12 ^{19}F NMR (376 MHz, $CDCl_3$)



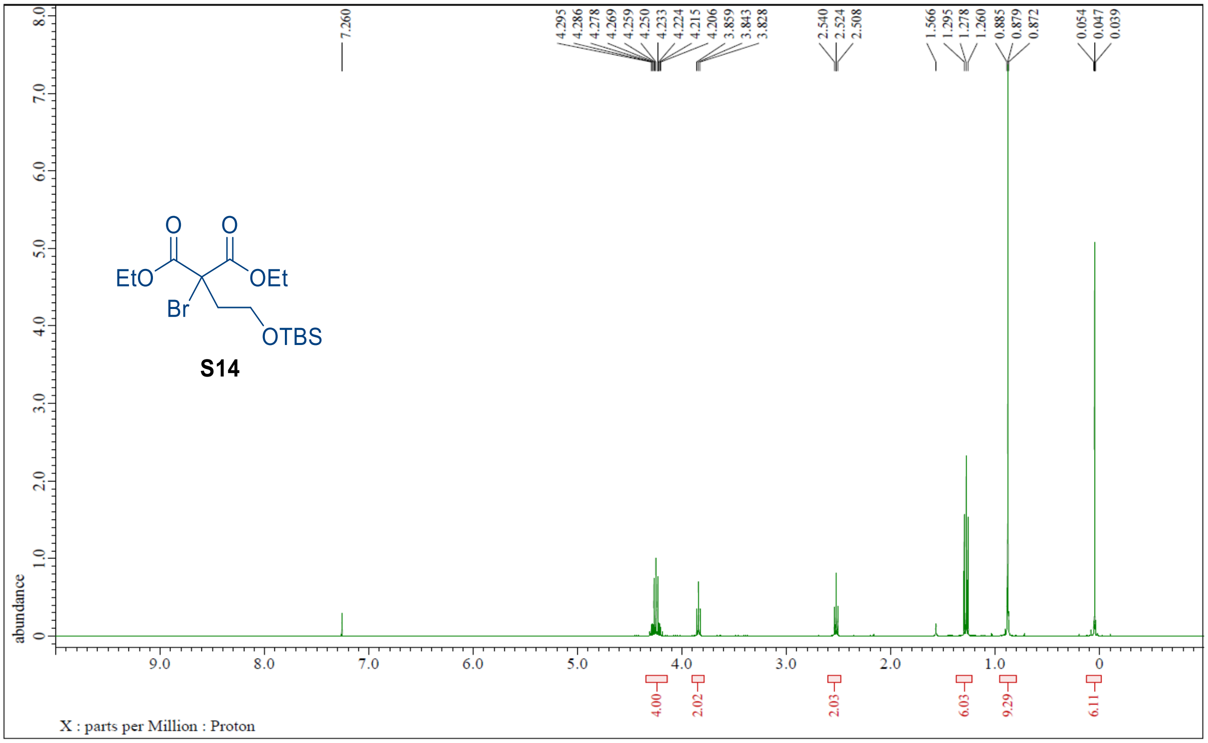
S13 ^{1}H NMR (400 MHz, $CDCl_3$)



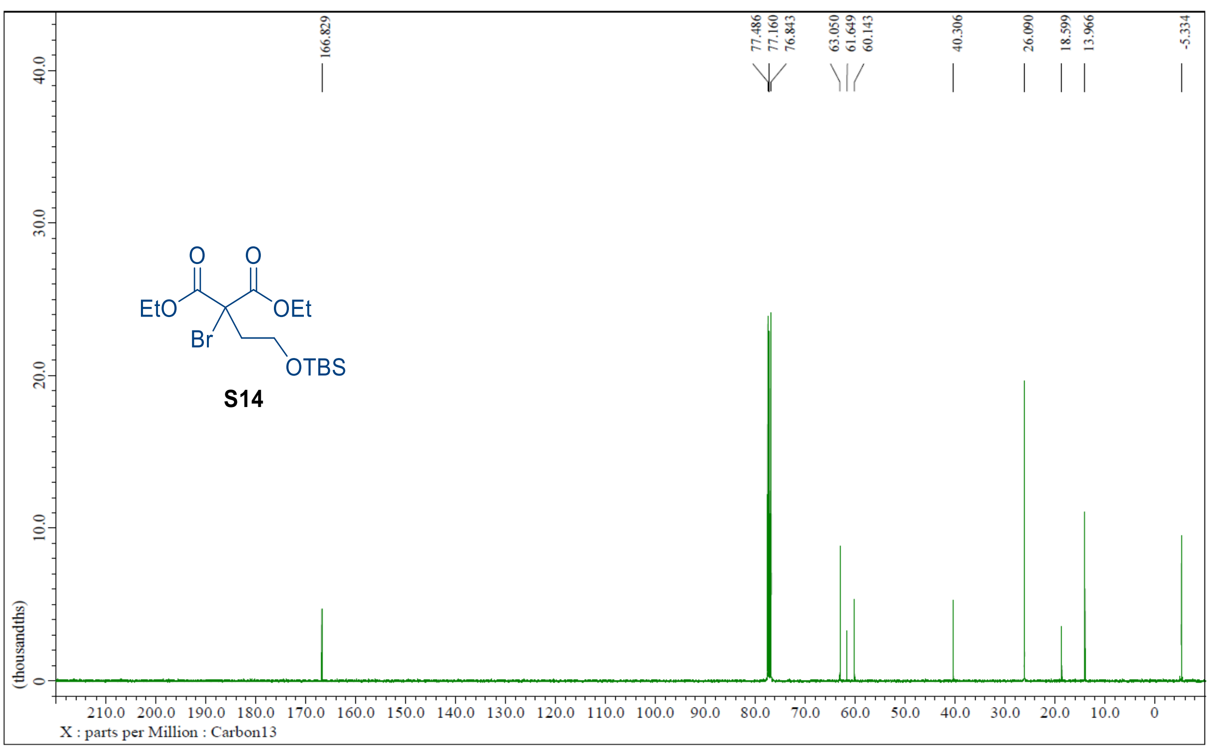
S13 ^{13}C NMR (100 MHz, $CDCl_3$)



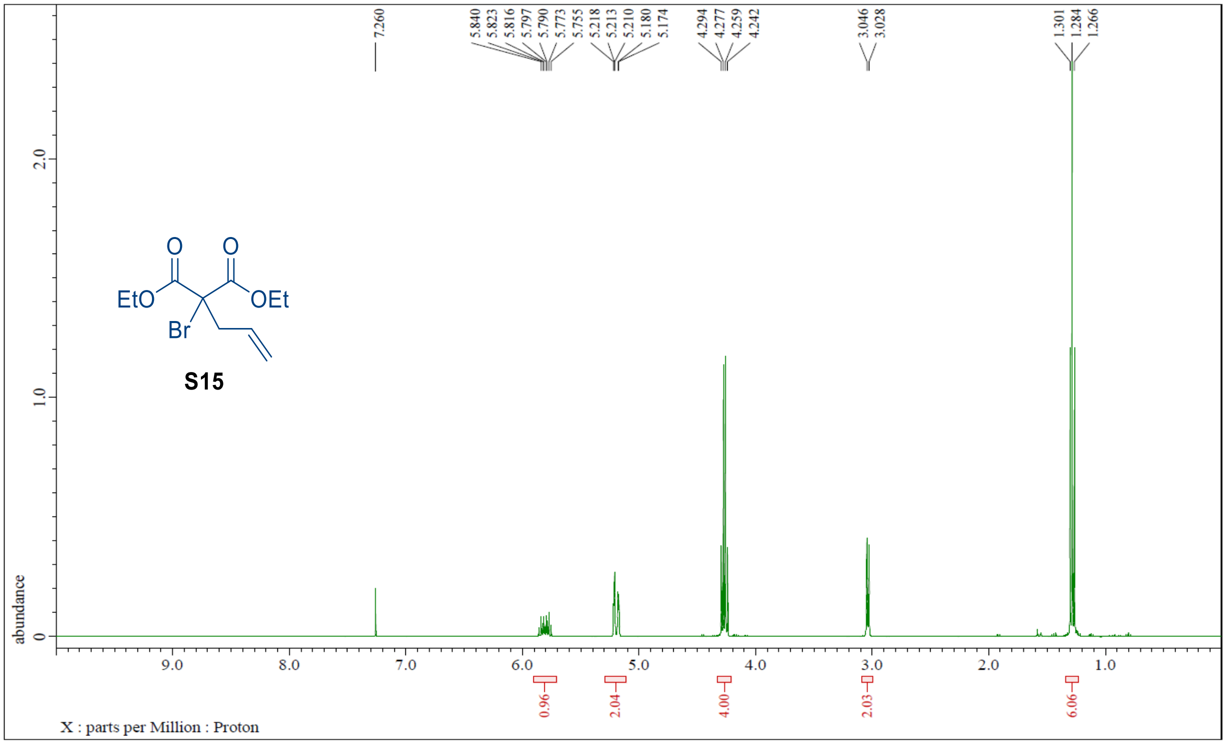
S14 ^{1}H NMR (400 MHz, $CDCl_3$)



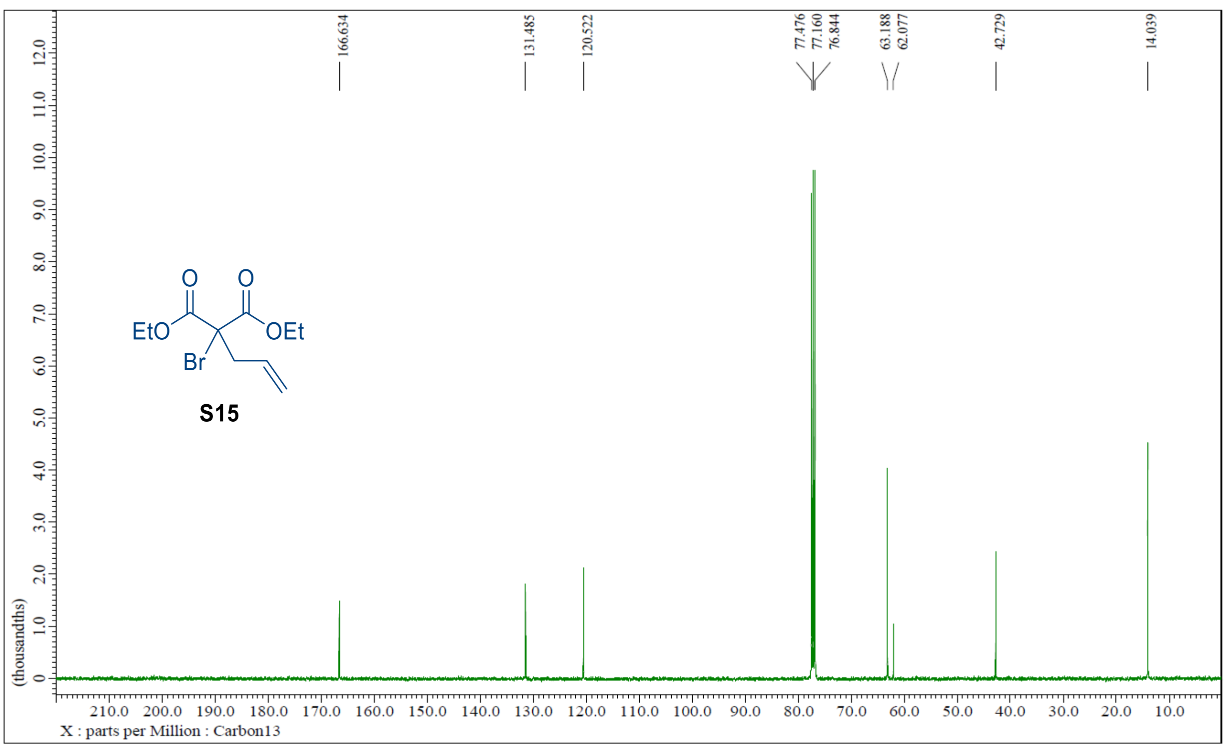
S14 ^{13}C NMR (100 MHz, $CDCl_3$)



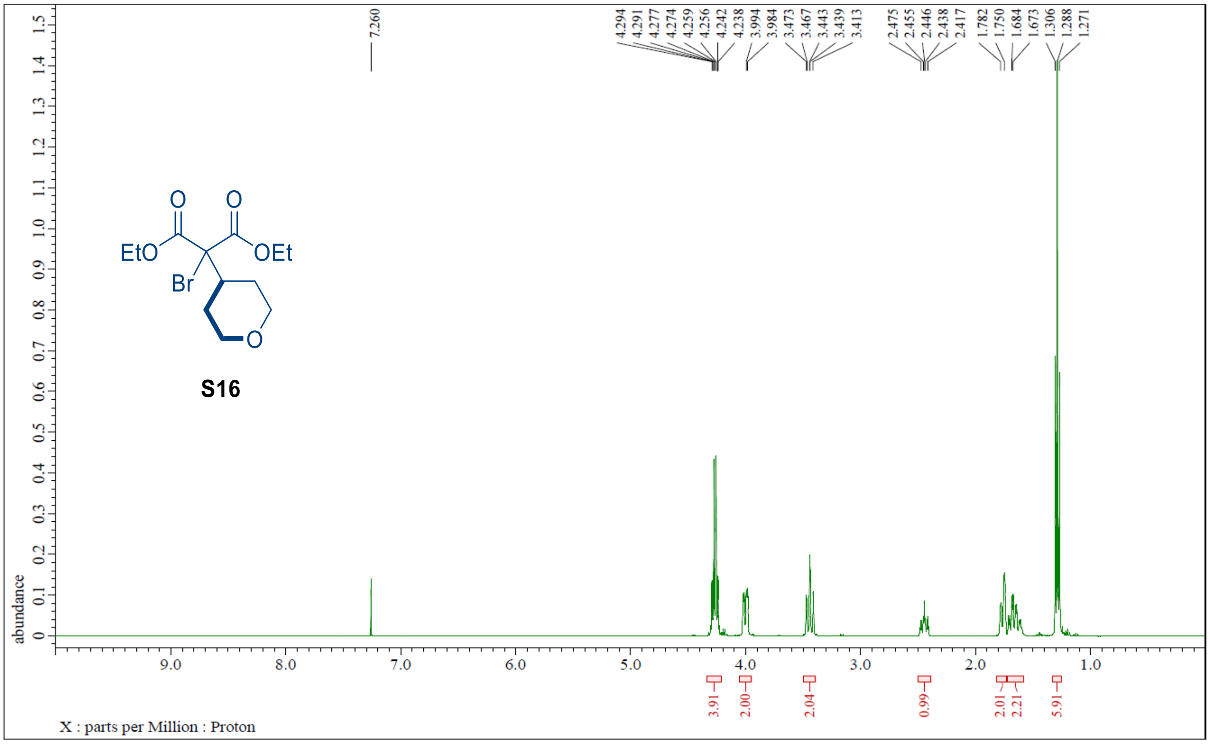
S15 ^{1}H NMR (400 MHz, CDCl$_3$)



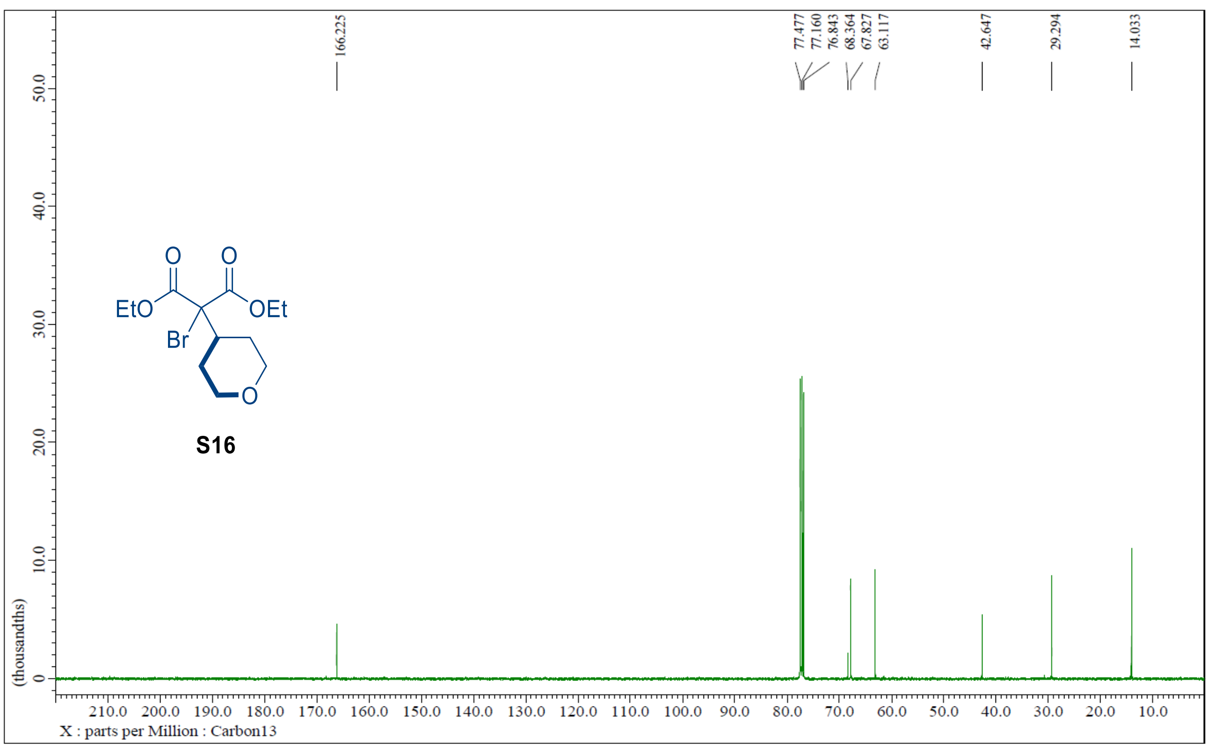
S15 ^{13}C NMR (100 MHz, CDCl$_3$)



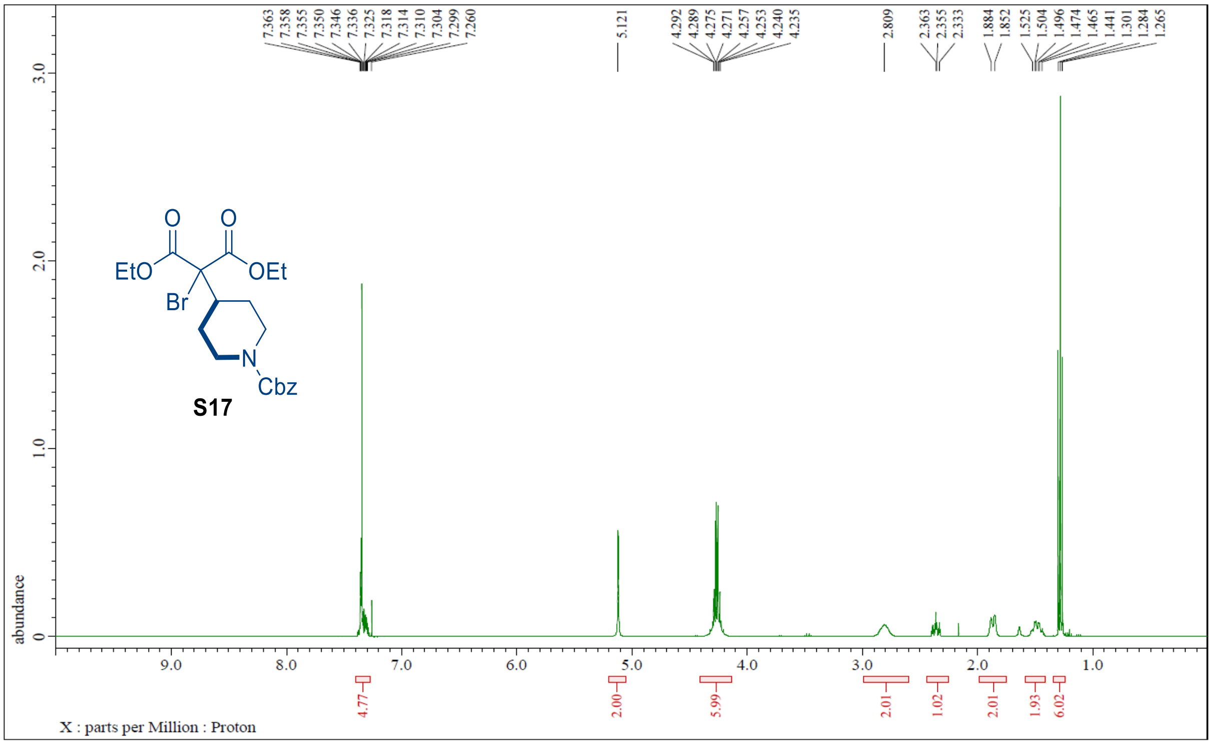
S16 ^{1}H NMR (400 MHz, $CDCl_3$)



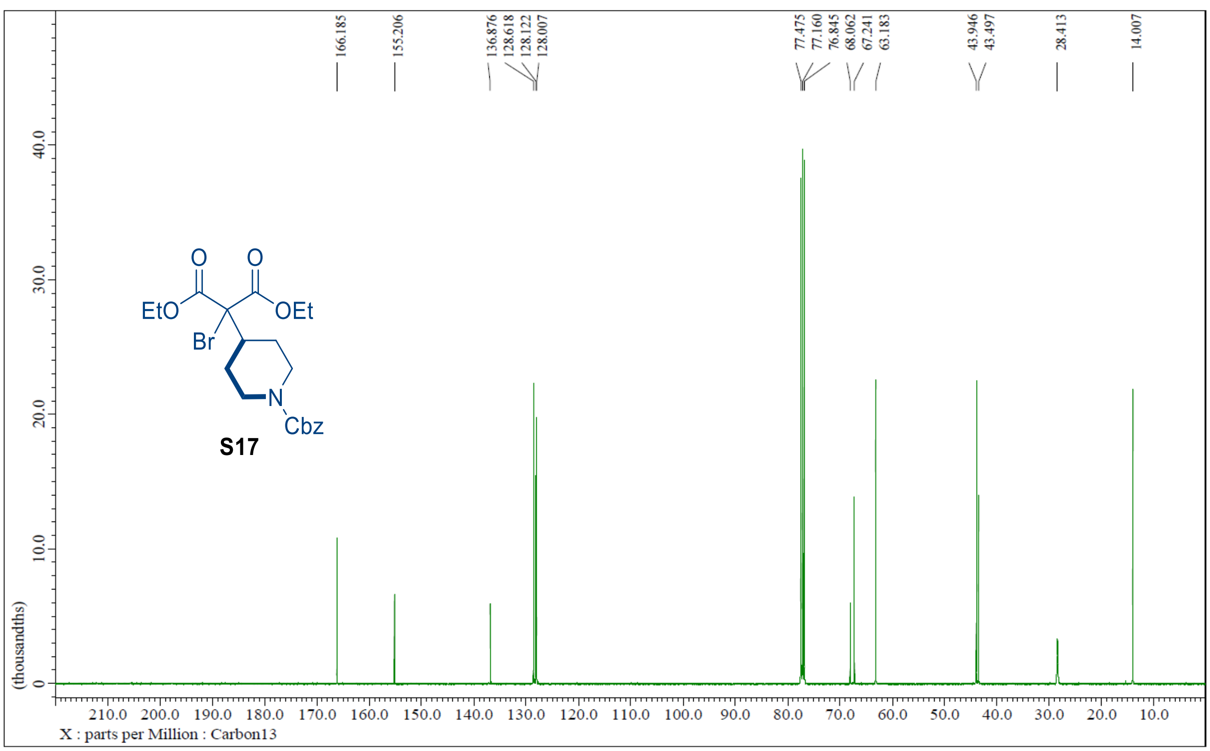
S16 ^{13}C NMR (100 MHz, $CDCl_3$)



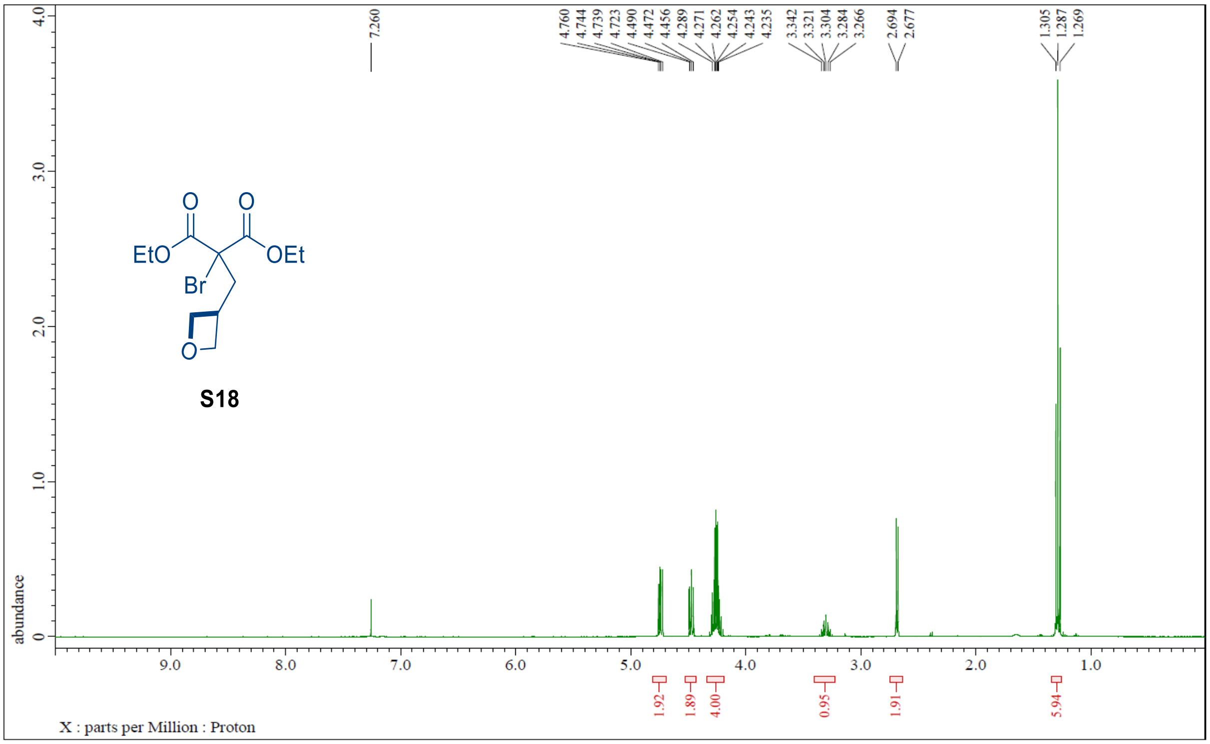
S17 ^{1}H NMR (400 MHz, $CDCl_3$)



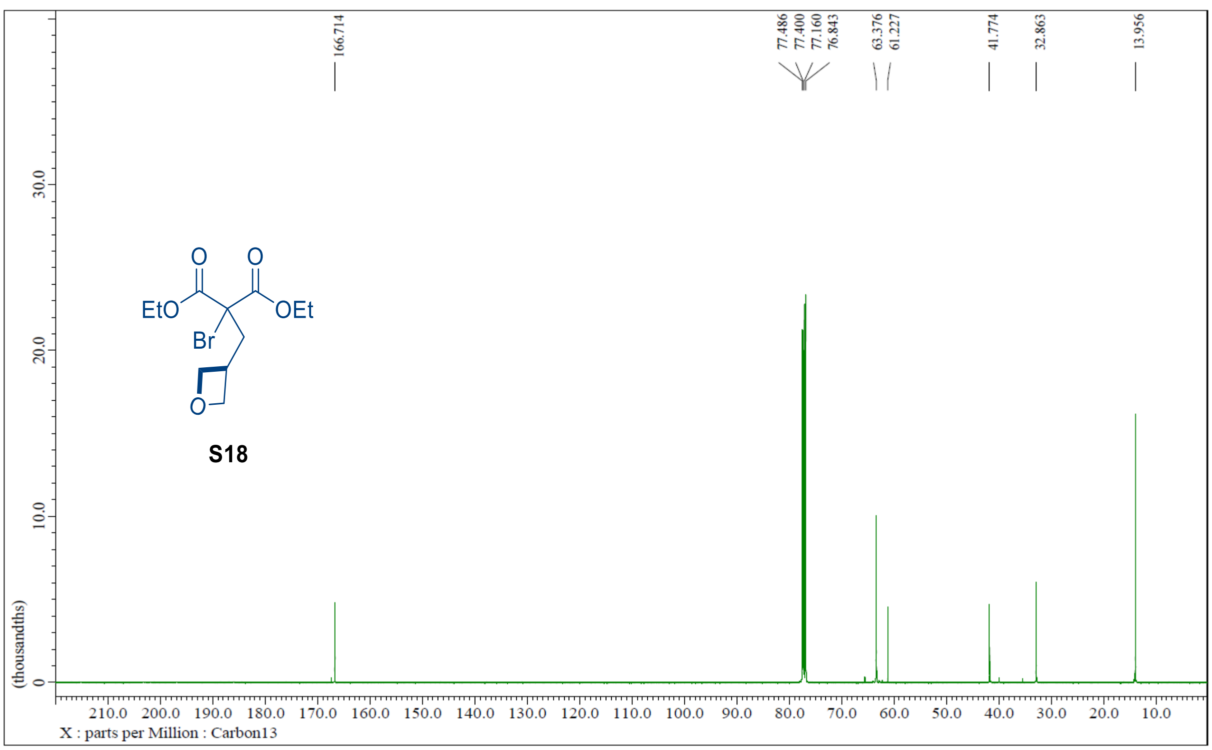
S17 ^{13}C NMR (100 MHz, $CDCl_3$)



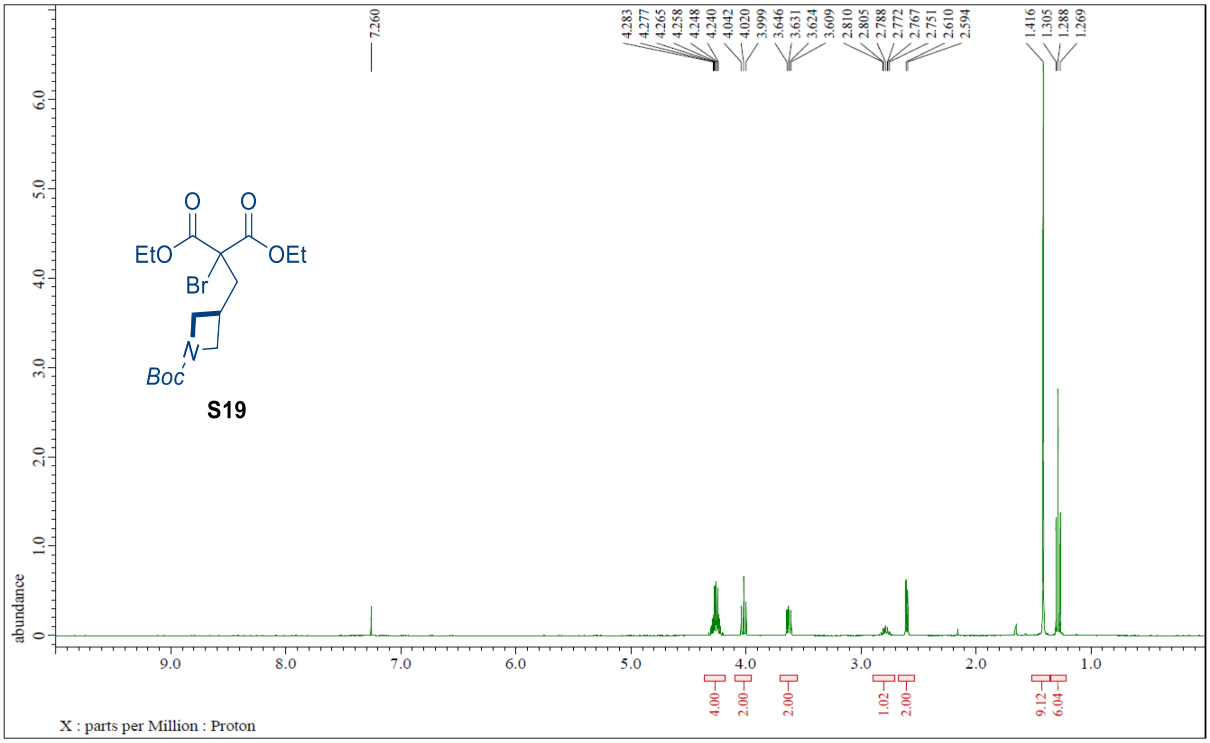
S18 ^{1}H NMR (400 MHz, $CDCl_3$)



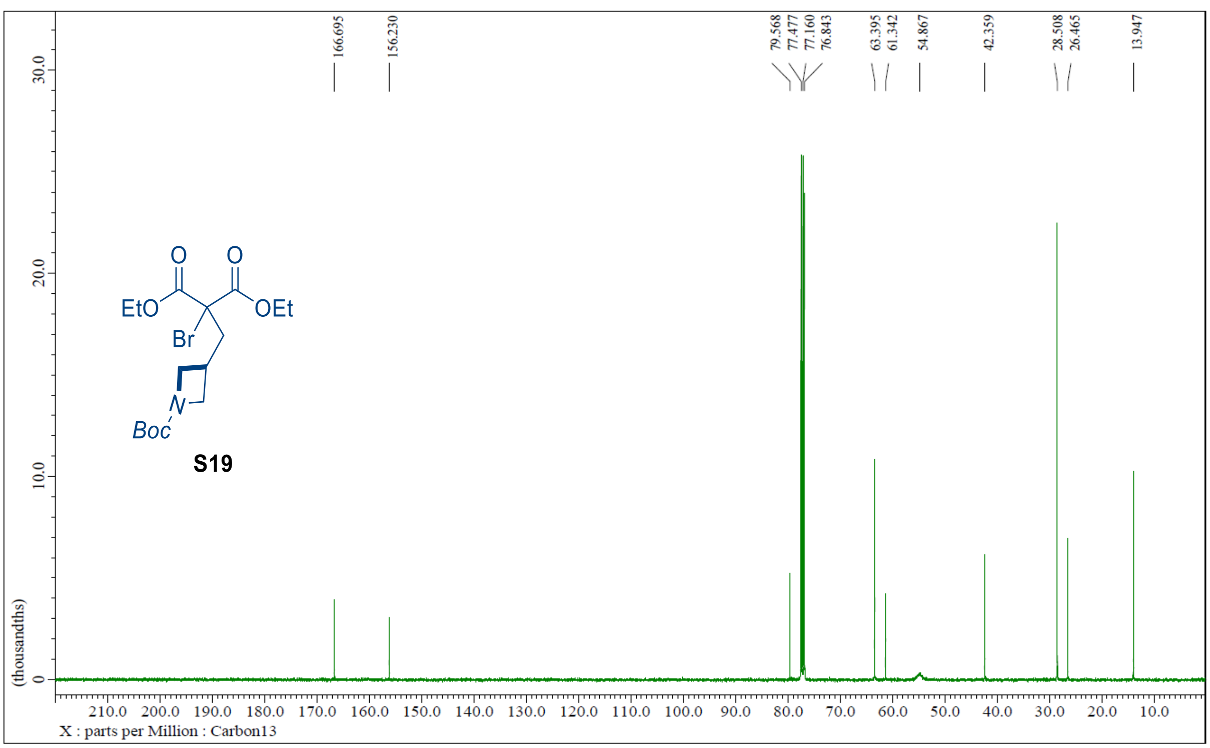
S18 ^{13}C NMR (100 MHz, $CDCl_3$)



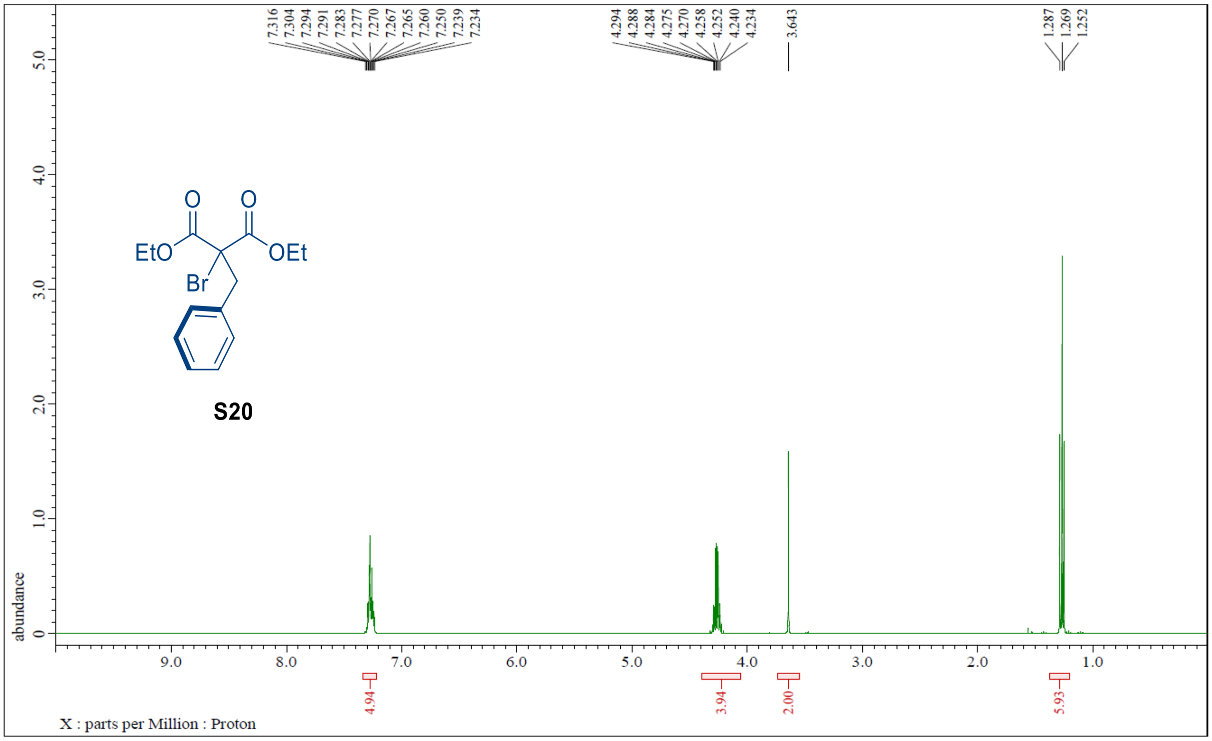
S19 ^{1}H NMR (400 MHz, $CDCl_3$)



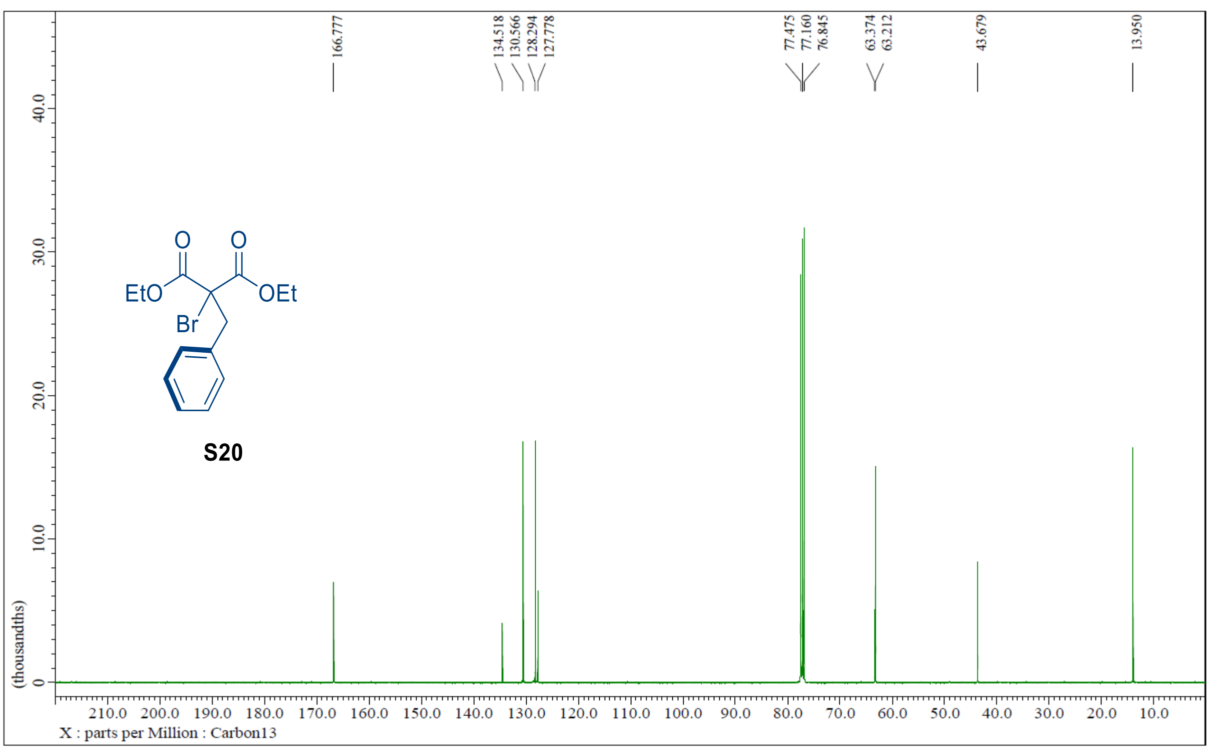
S19 ^{13}C NMR (100 MHz, $CDCl_3$)



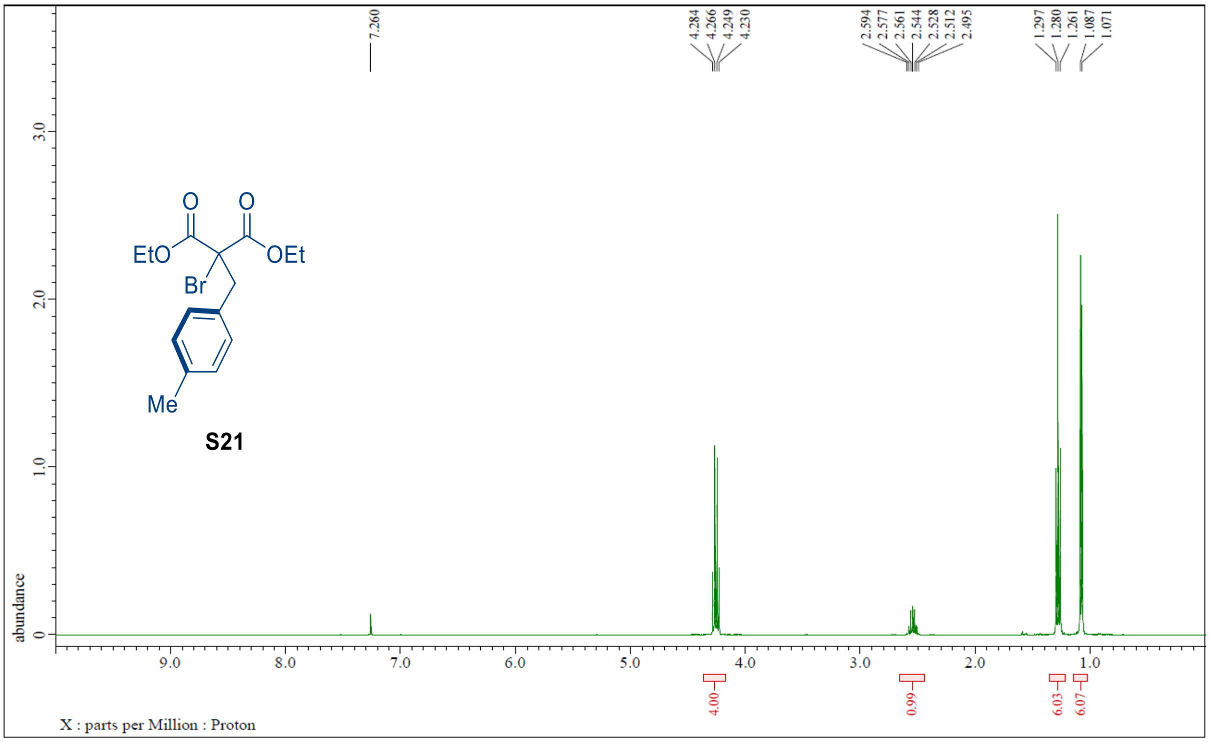
S20 ^{1}H NMR (400 MHz, $CDCl_3$)



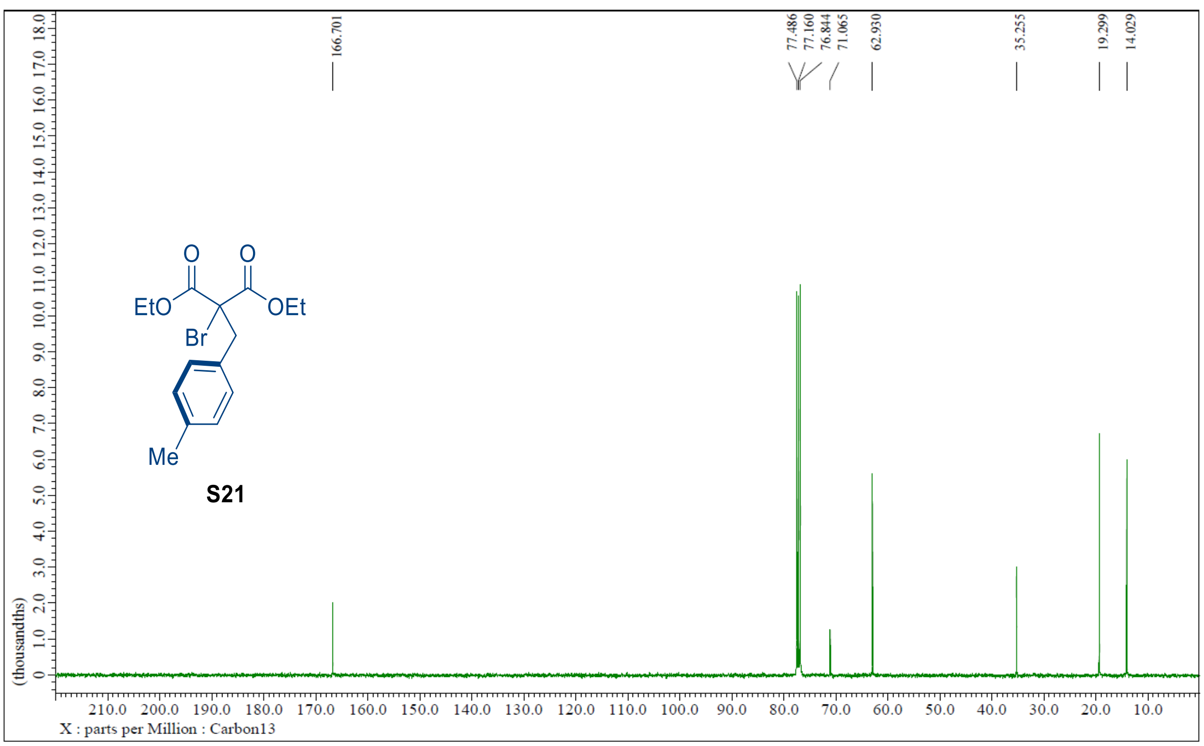
S20 ^{13}C NMR (100 MHz, $CDCl_3$)



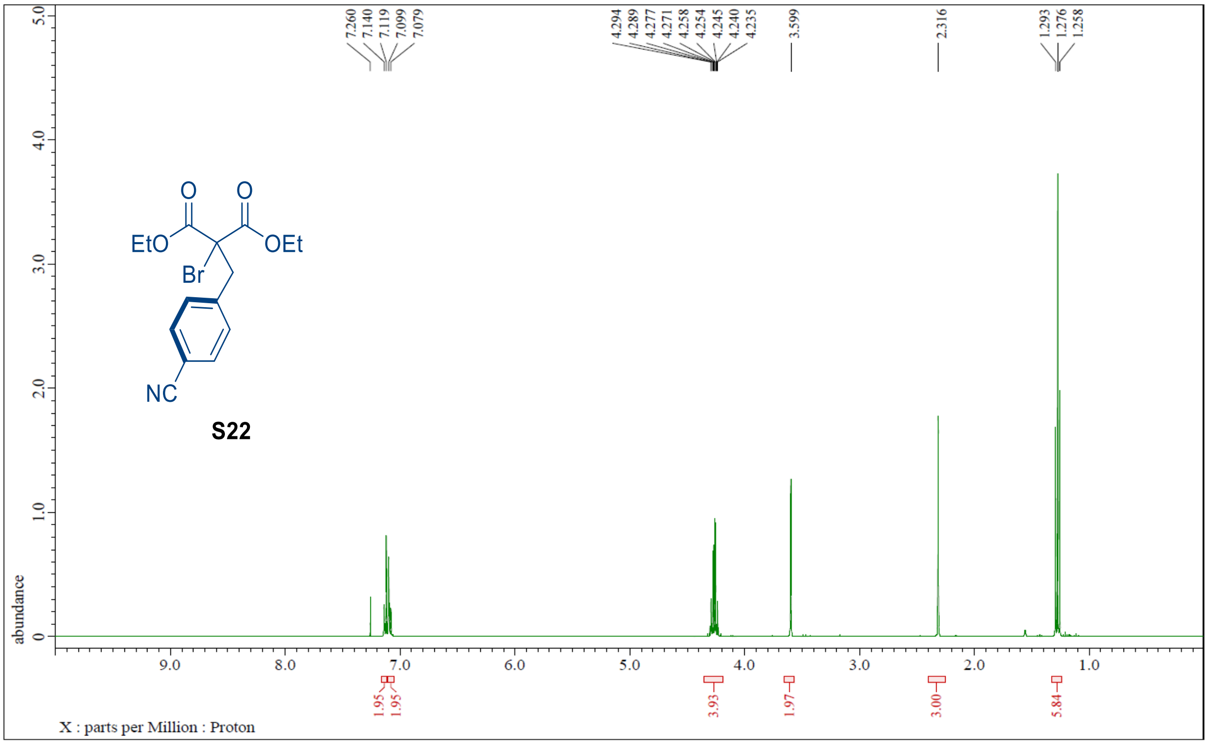
S21 ^{1}H NMR (400 MHz, $CDCl_3$)



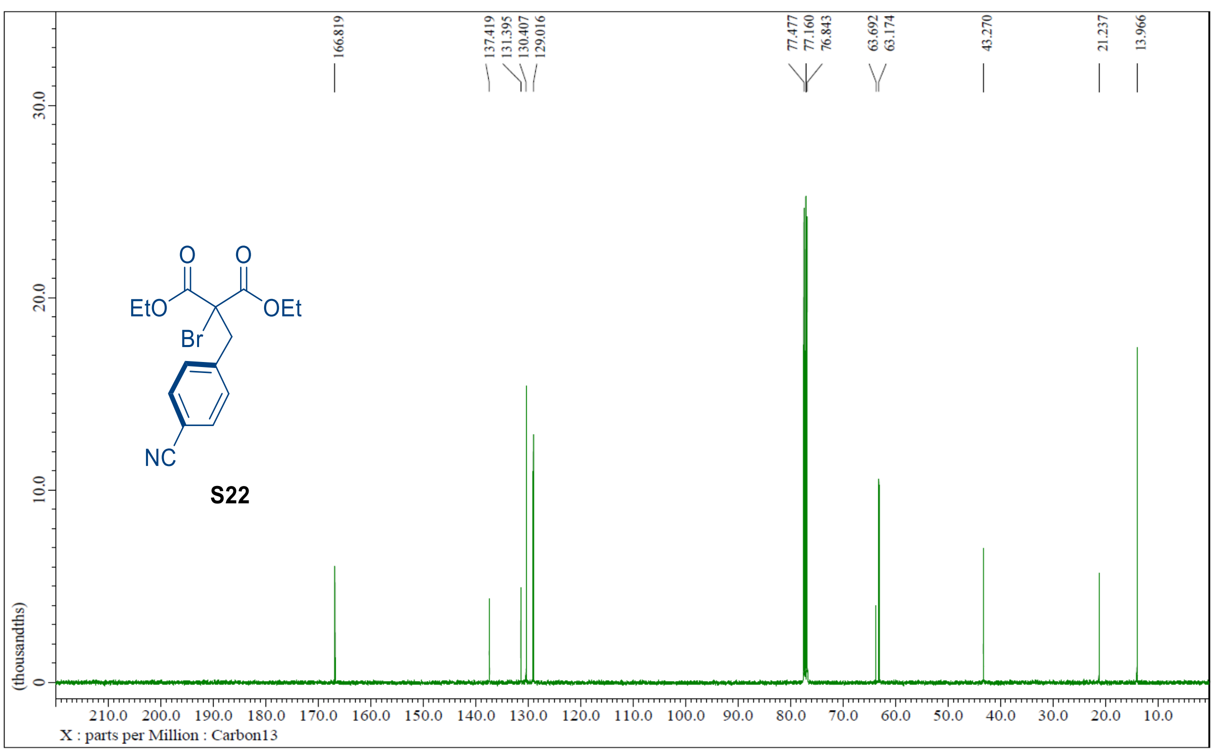
S21 ^{13}C NMR (100 MHz, $CDCl_3$)



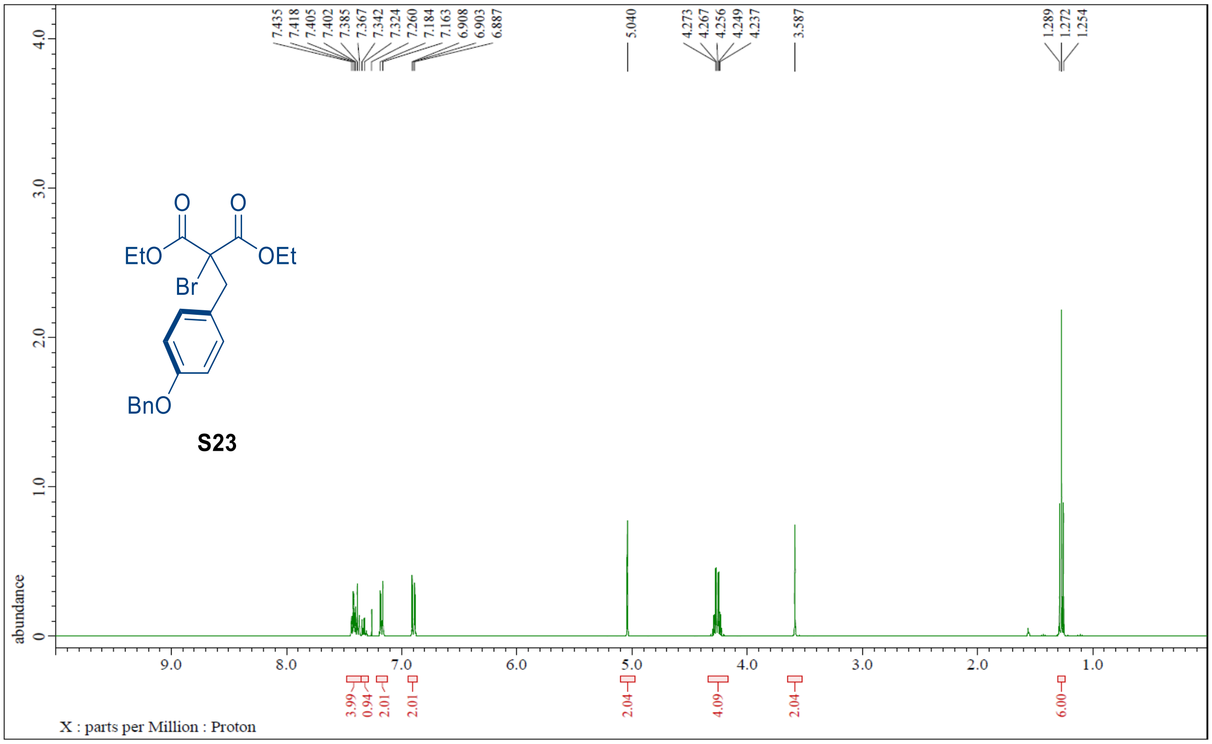
S22 ^{1}H NMR (400 MHz, CDCl$_3$)



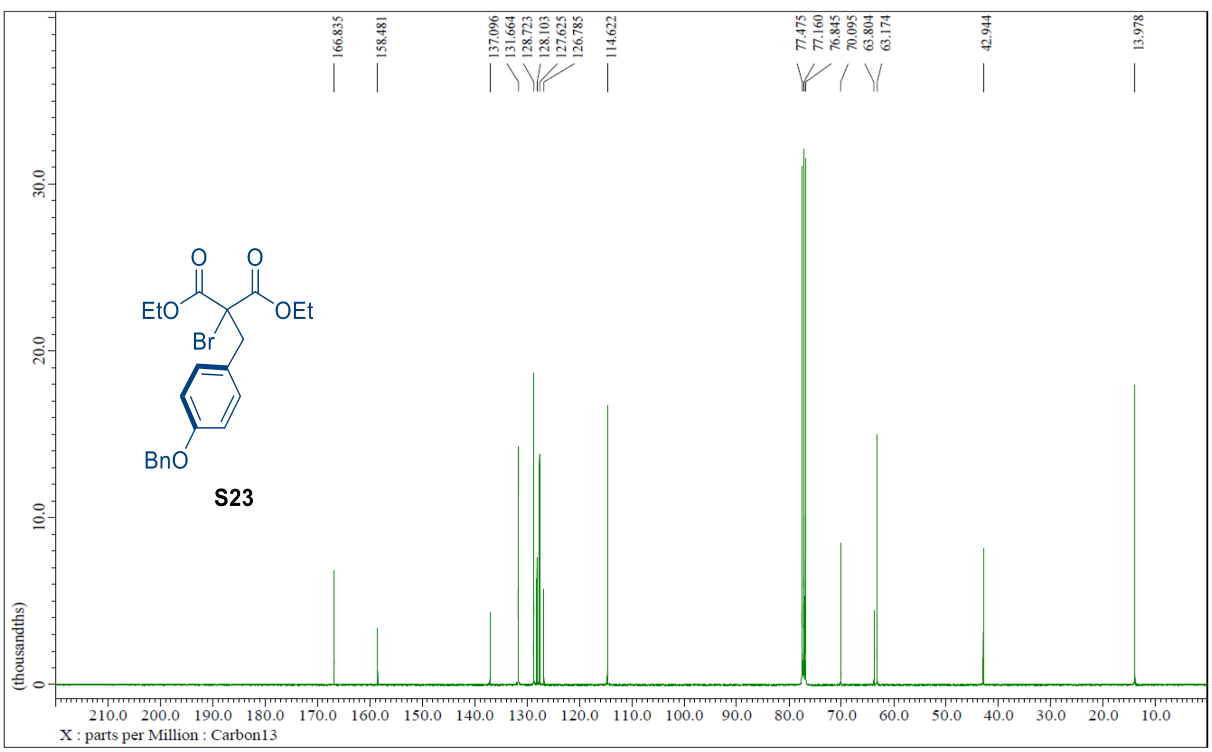
S22 ^{13}C NMR (100 MHz, CDCl$_3$)



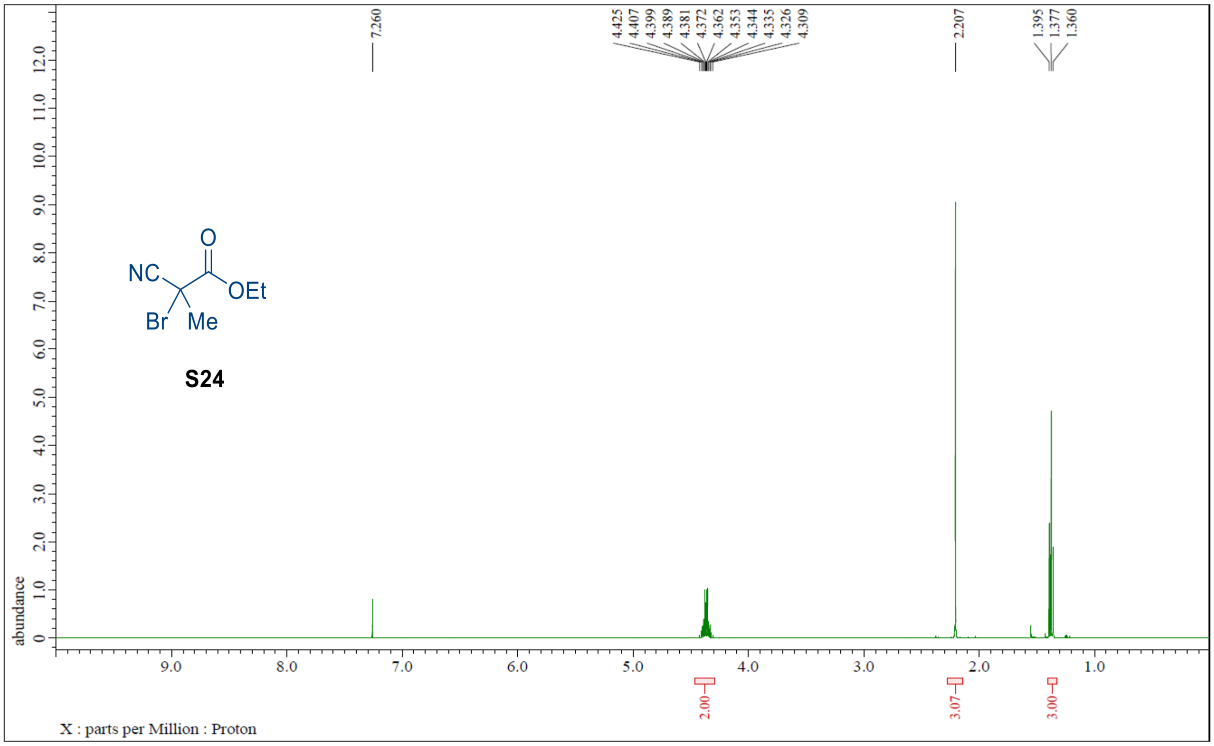
S23 ^{1}H NMR (400 MHz, $CDCl_3$)



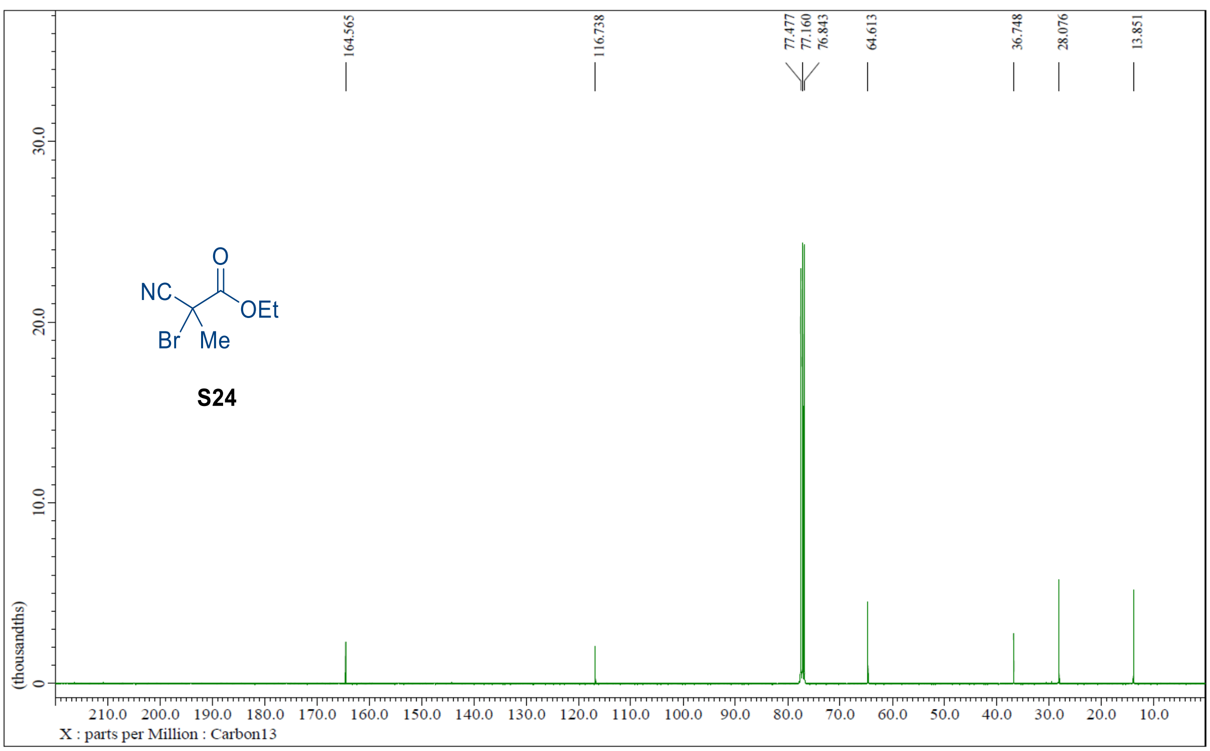
S23 ^{13}C NMR (100 MHz, $CDCl_3$)



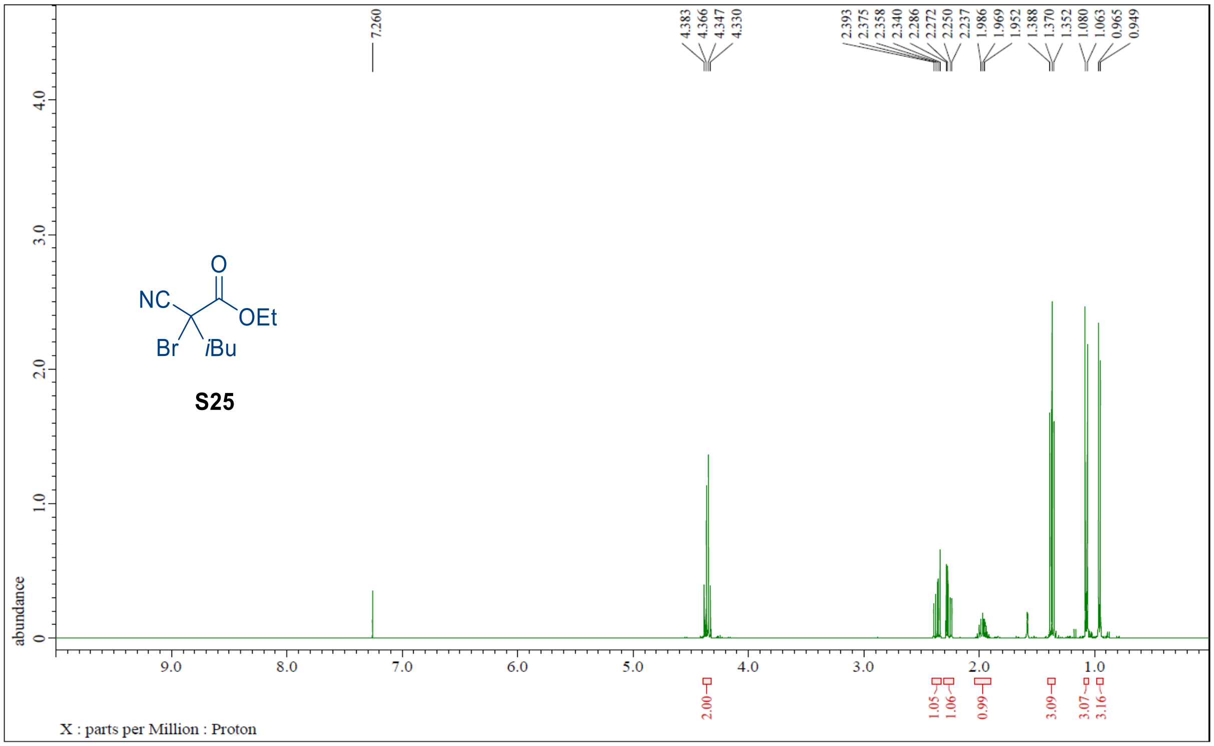
S24 ^{1}H NMR (400 MHz, $CDCl_3$)



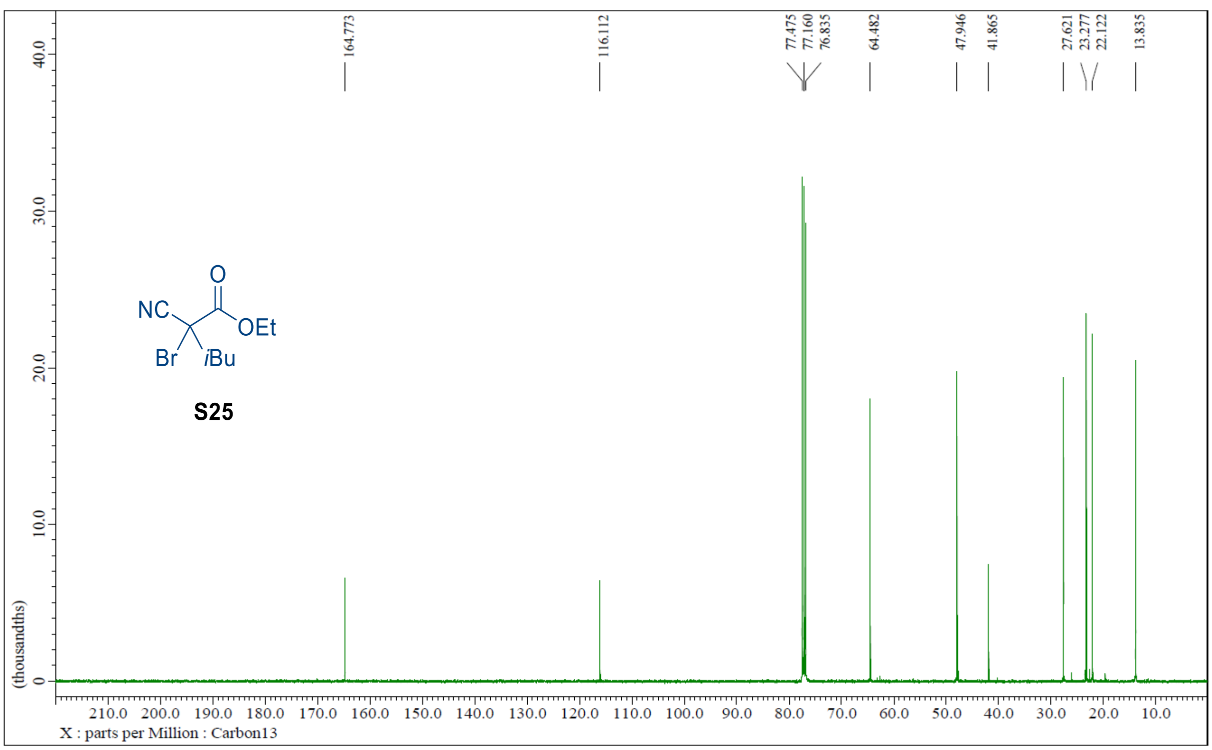
S24 ^{13}C NMR (100 MHz, $CDCl_3$)



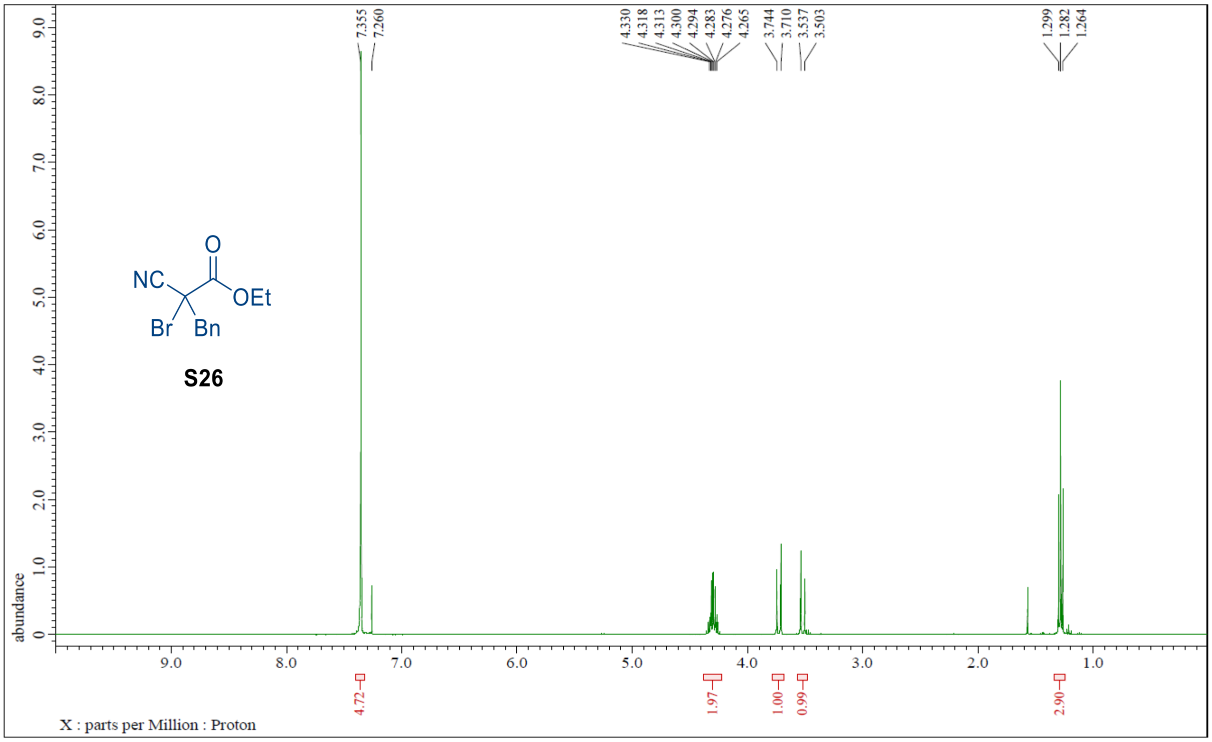
S25 ^{1}H NMR (400 MHz, $CDCl_3$)



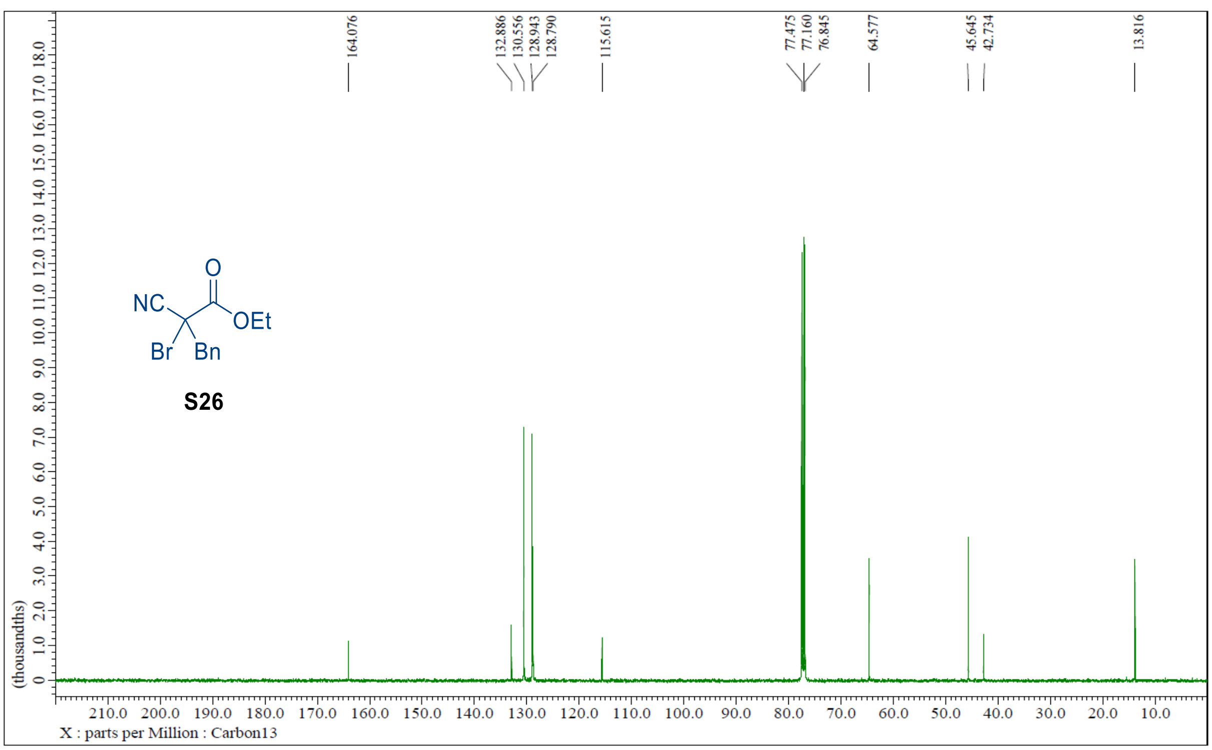
S25 ^{13}C NMR (100 MHz, $CDCl_3$)



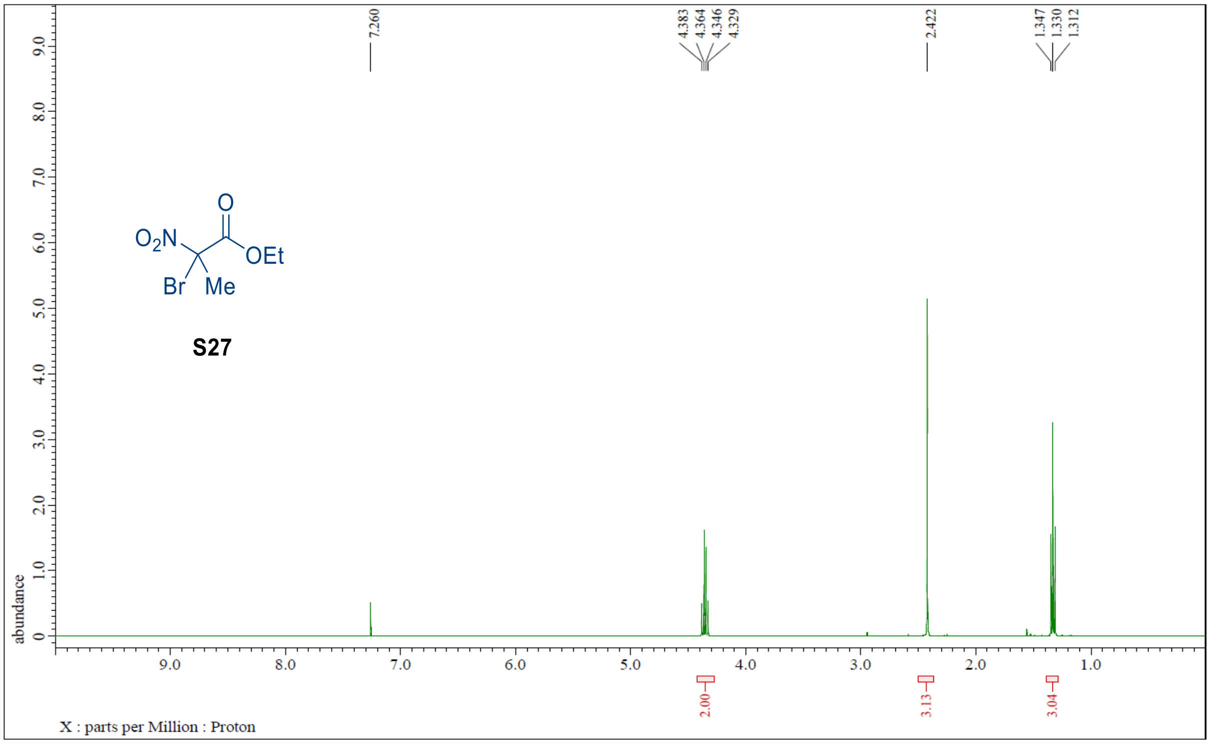
S26 ^{1}H NMR (400 MHz, $CDCl_3$)



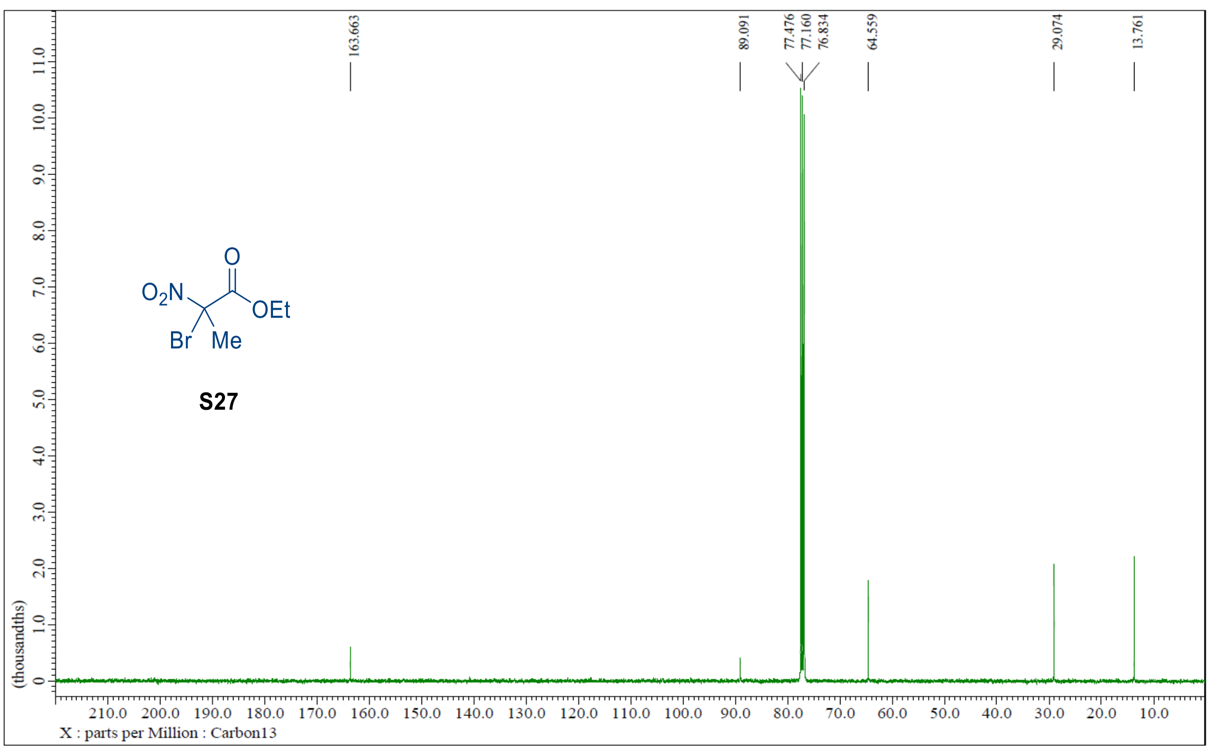
S26 ^{13}C NMR (100 MHz, $CDCl_3$)



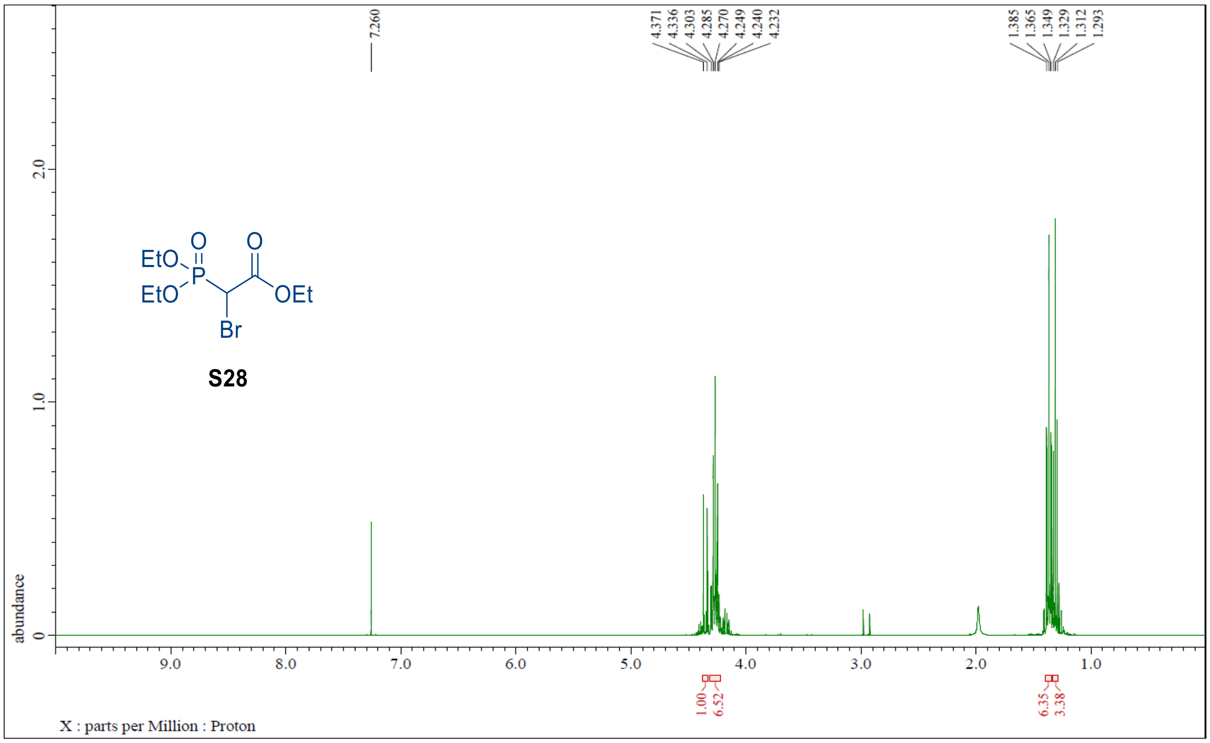
S27 ^{1}H NMR (400 MHz, $CDCl_3$)



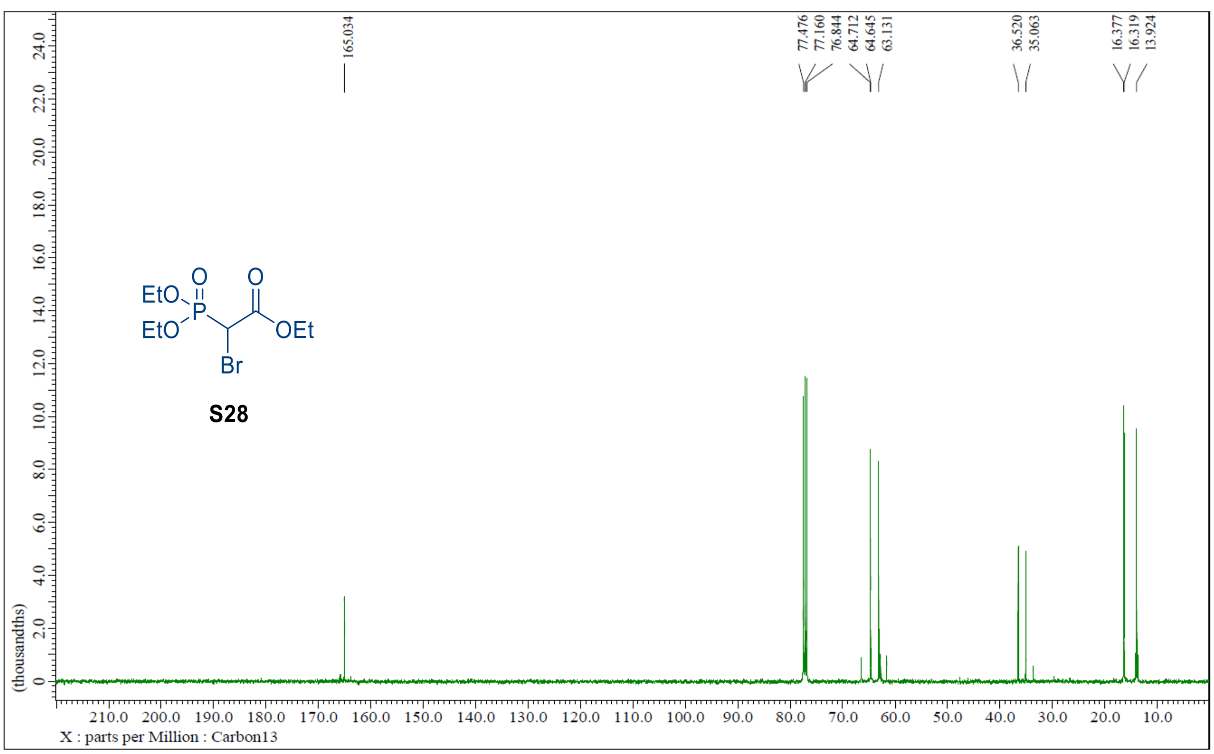
S27 ^{13}C NMR (100 MHz, $CDCl_3$)



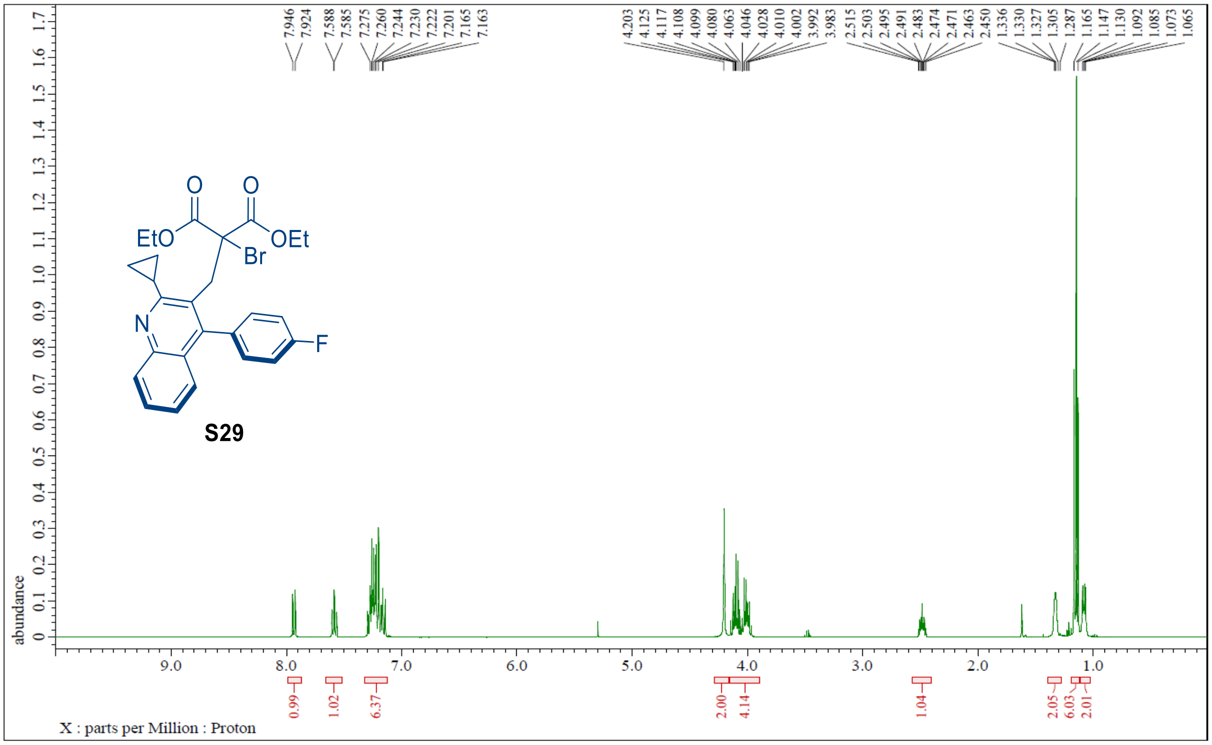
S28 ^{1}H NMR (400 MHz, $CDCl_3$)



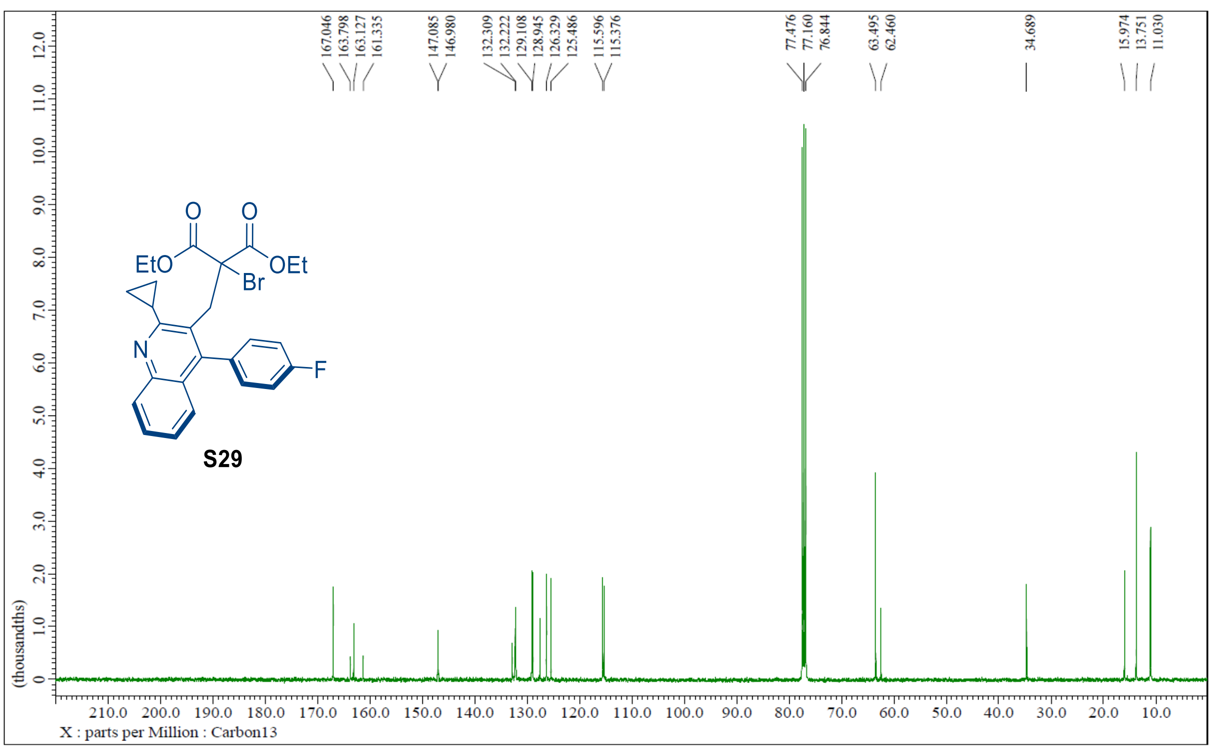
S28 ^{13}C NMR (100 MHz, $CDCl_3$)



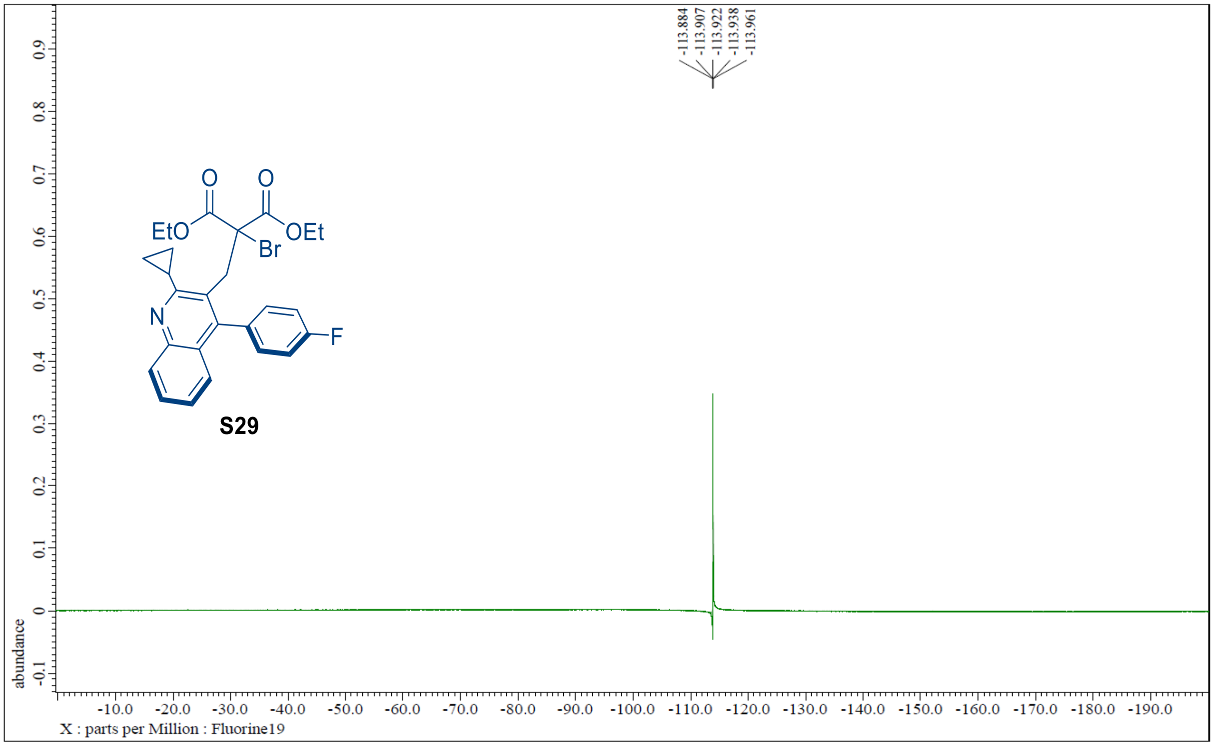
S29 [1]H NMR (400 MHz, CDCl$_3$)



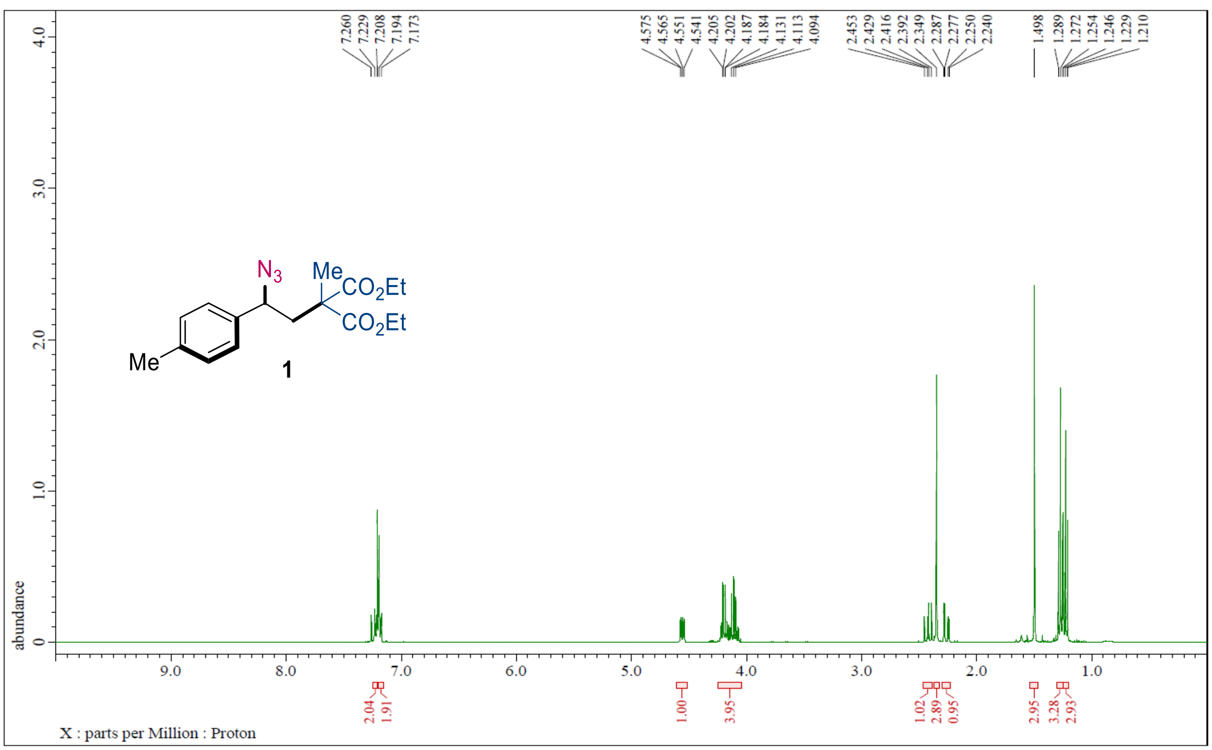
S29 [13]C NMR (100 MHz, CDCl$_3$)



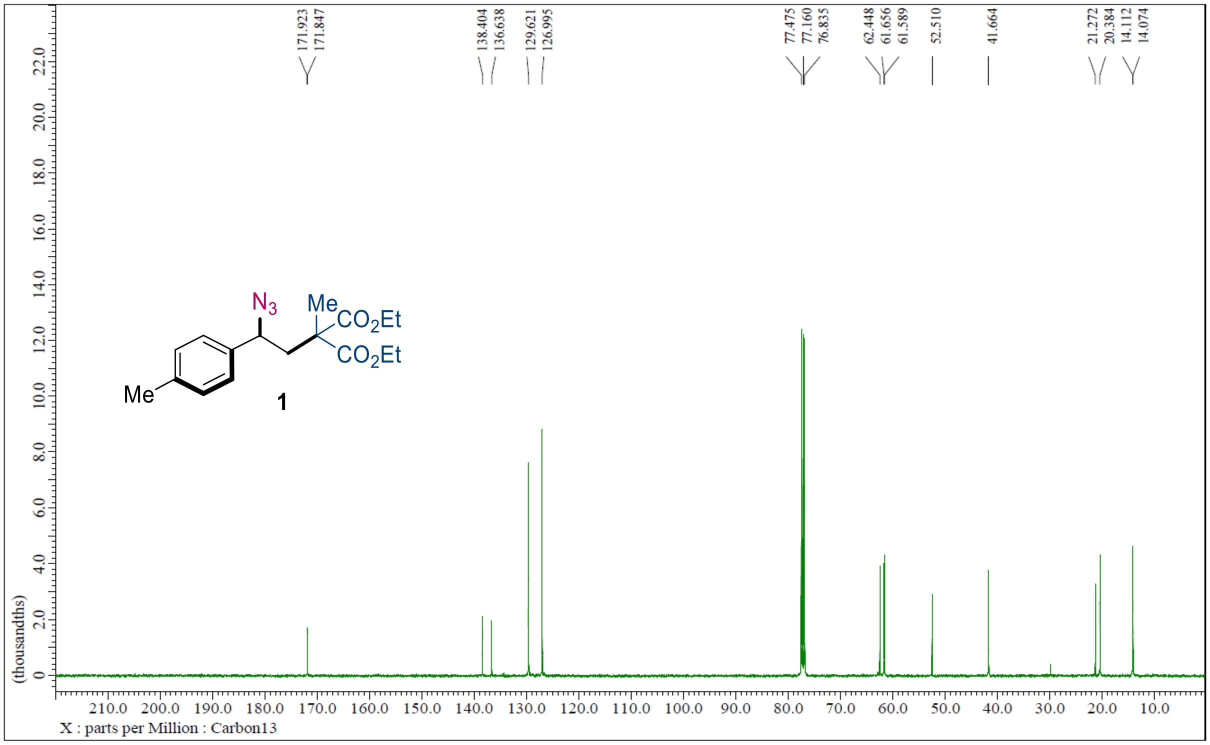
S29 ^{19}F NMR (376 MHz, CDCl$_3$)



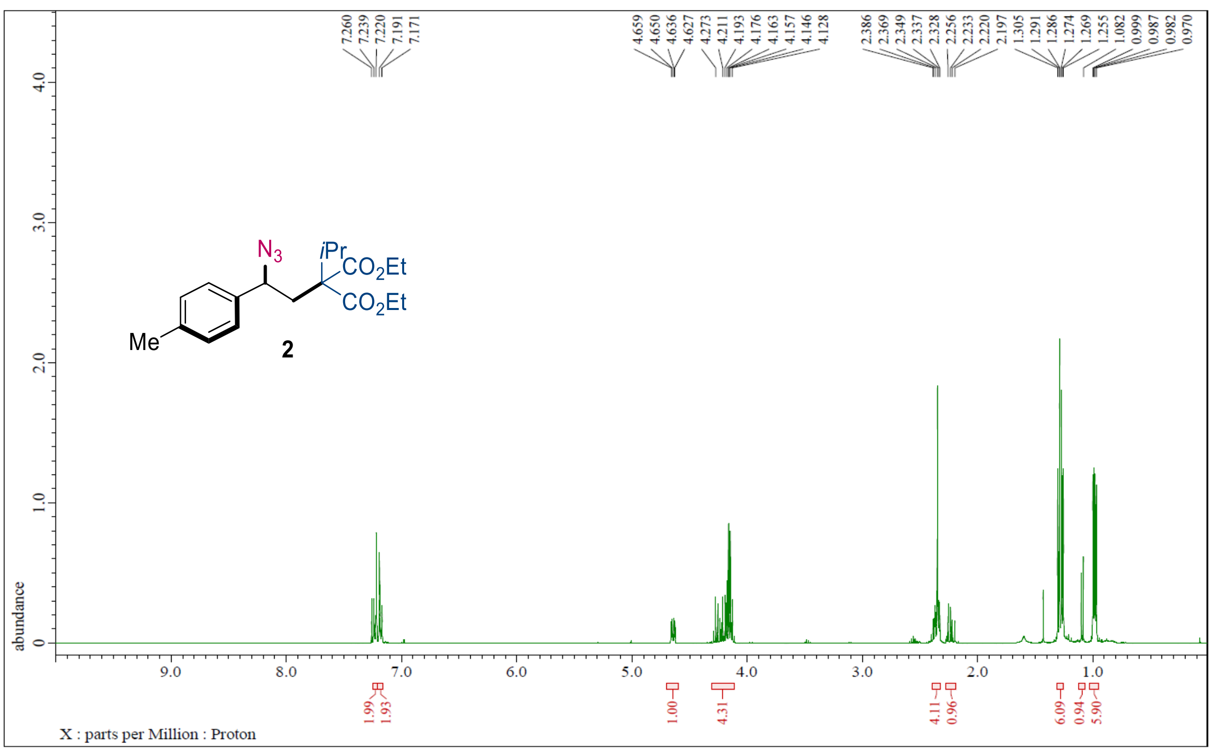
1 ^{1}H NMR (400 MHz, CDCl$_3$)



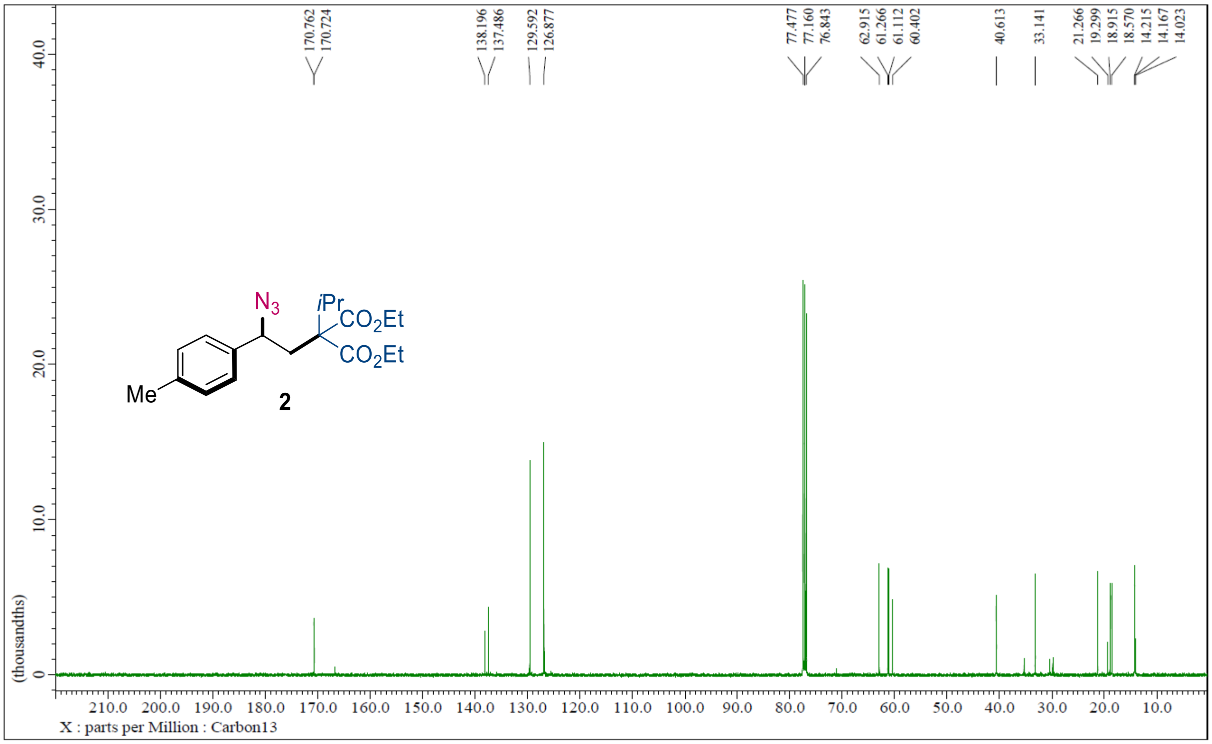
1 ^{13}C NMR (100 MHz, $CDCl_3$)



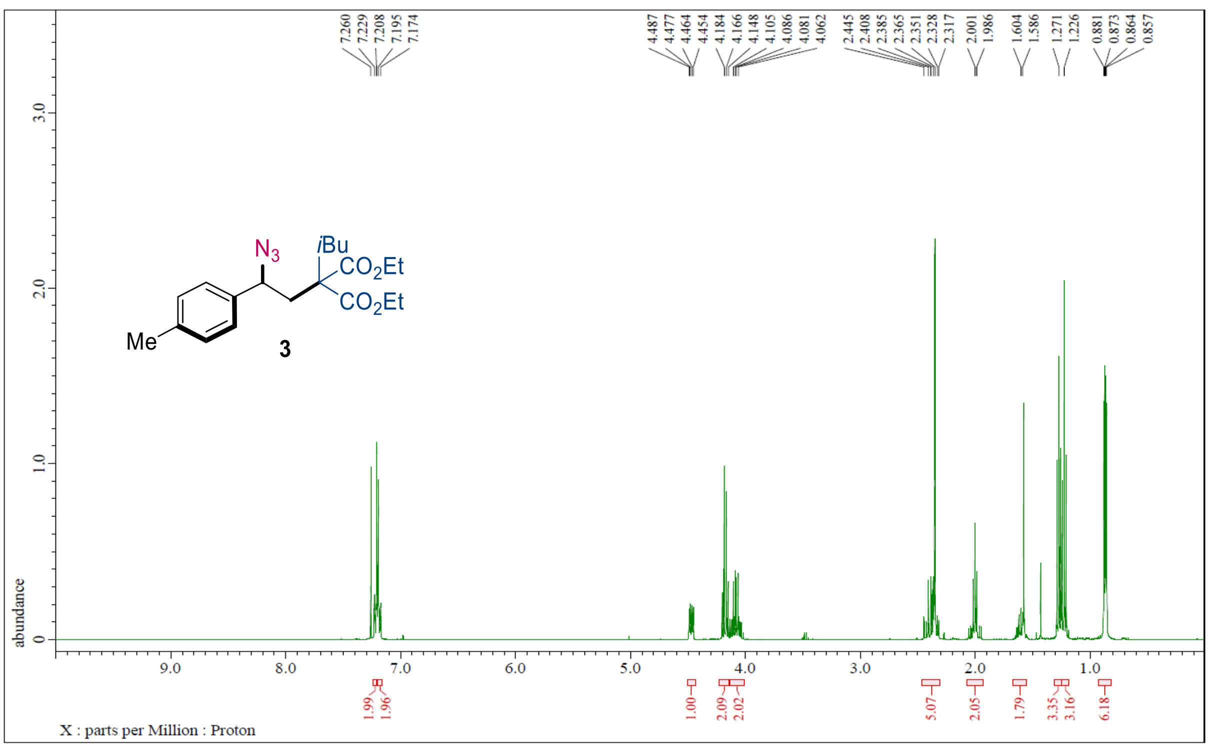
2 ^{1}H NMR (400 MHz, $CDCl_3$)



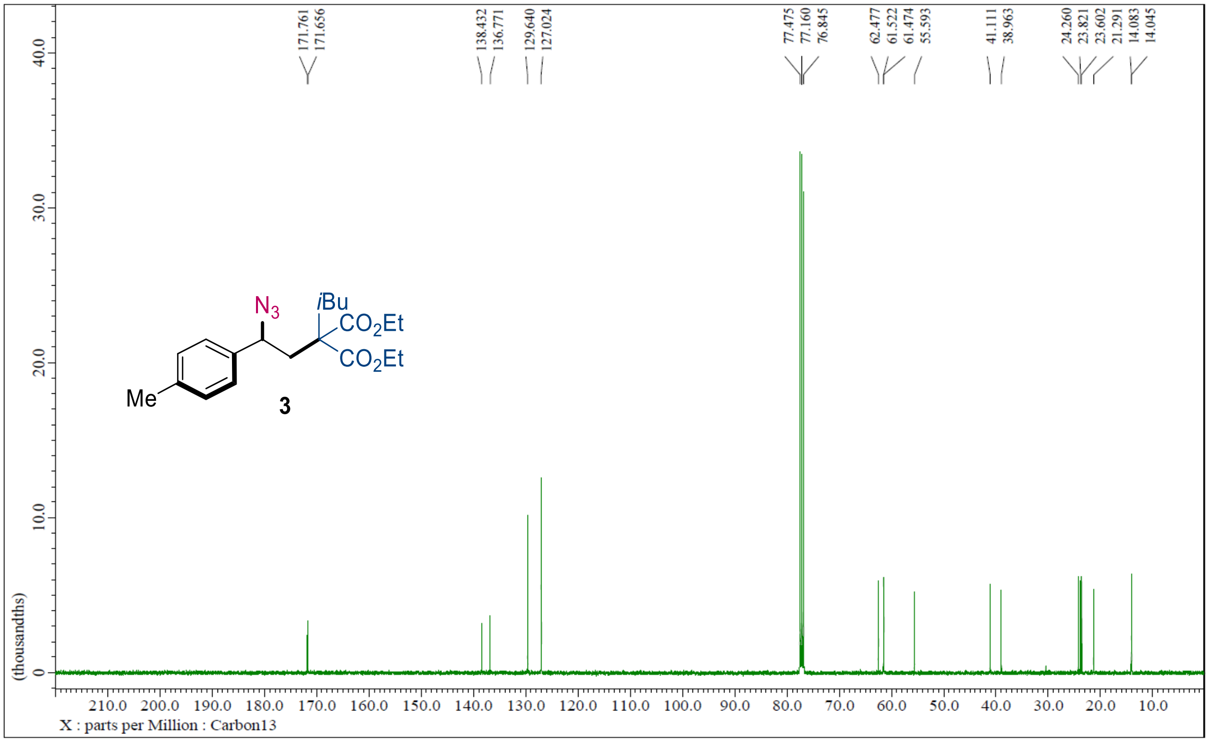
2 ^{13}C NMR (100 MHz, $CDCl_3$)



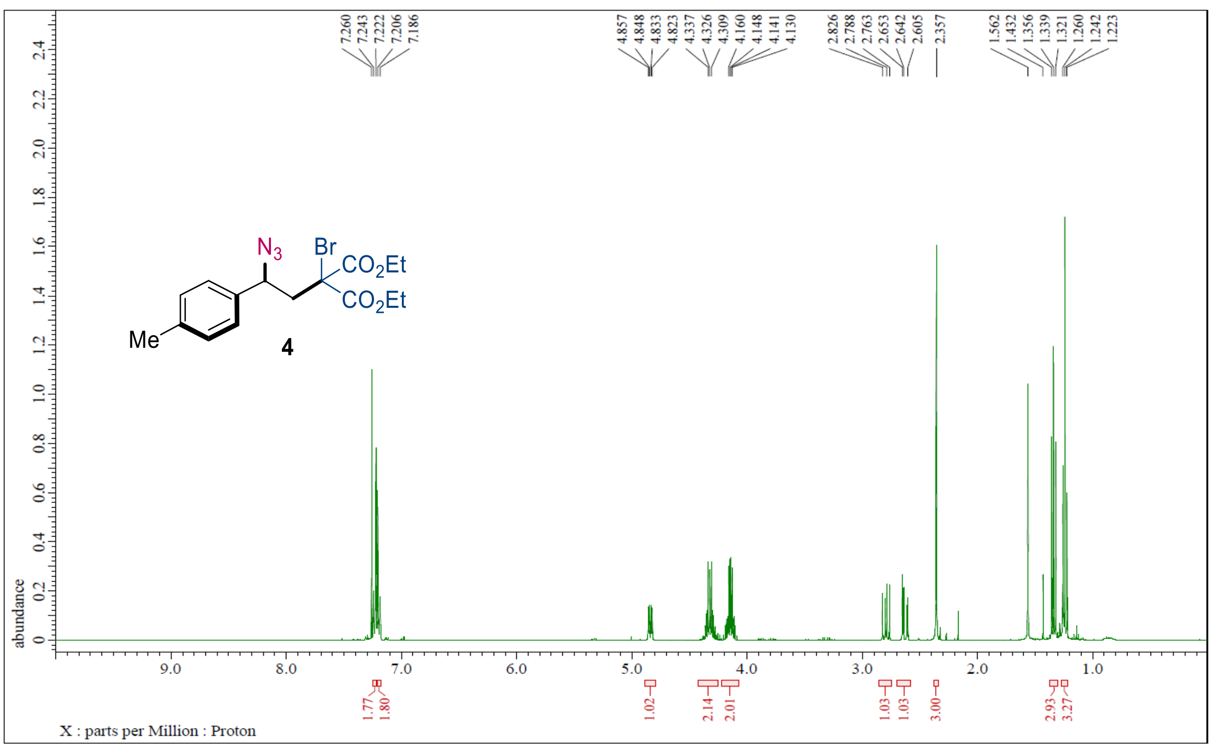
3 ^{1}H NMR (400 MHz, $CDCl_3$)



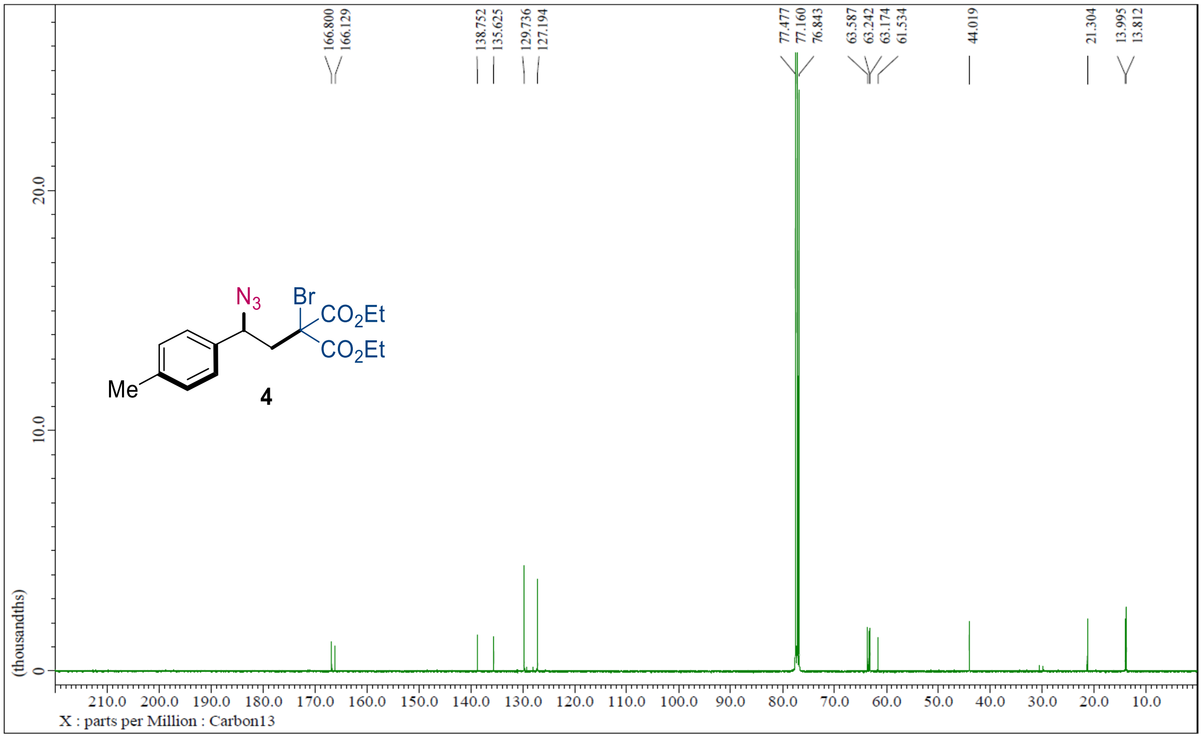
3 ^{13}C NMR (100 MHz, $CDCl_3$)



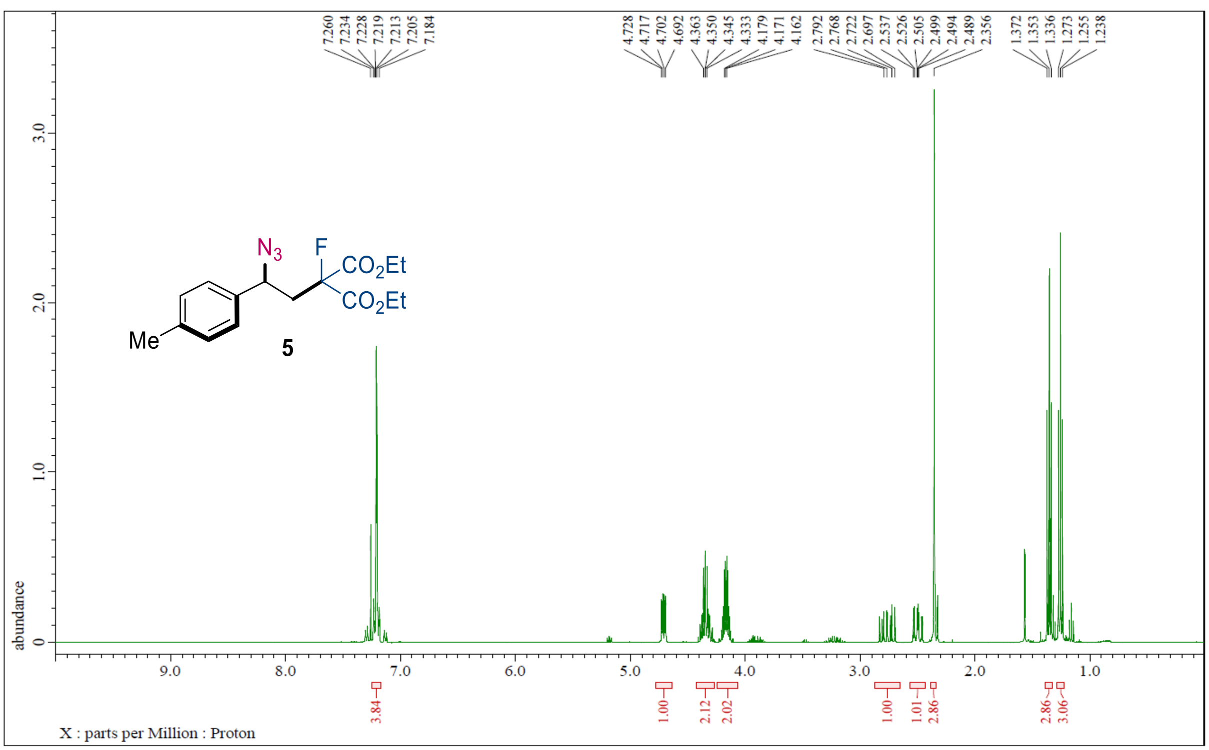
4 ^{1}H NMR (400 MHz, $CDCl_3$)



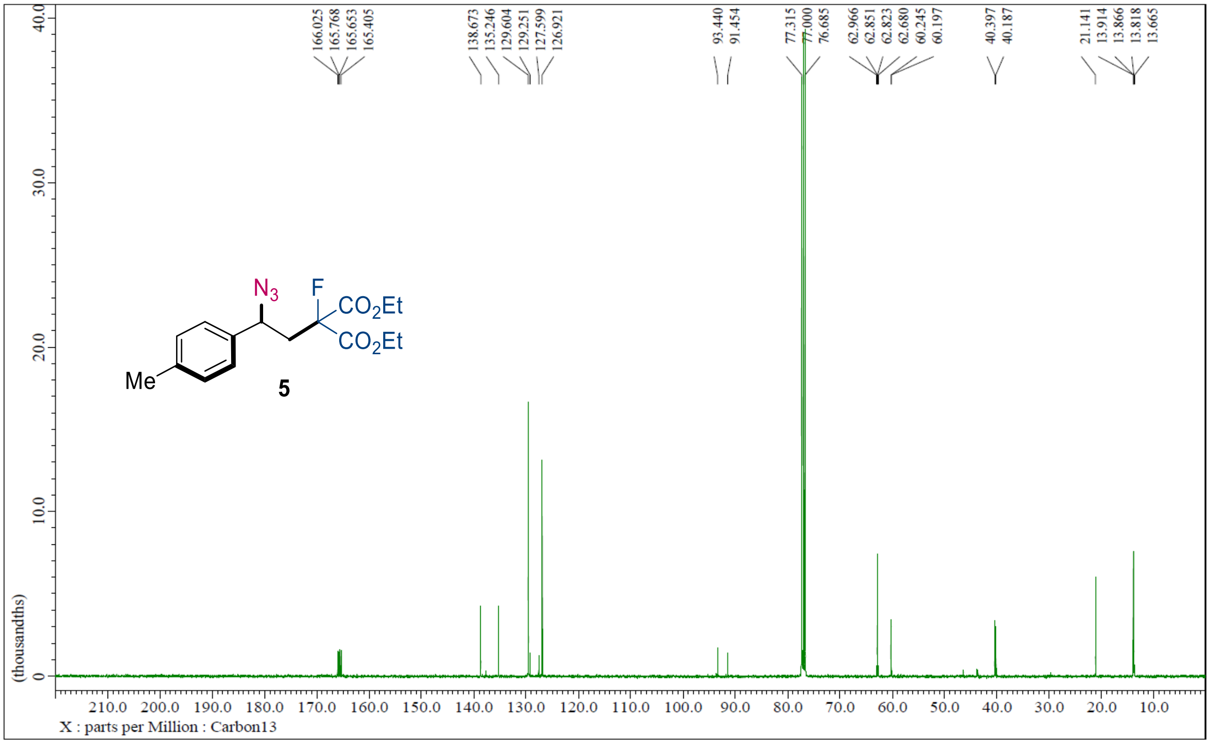
4 ^{13}C NMR (100 MHz, $CDCl_3$)



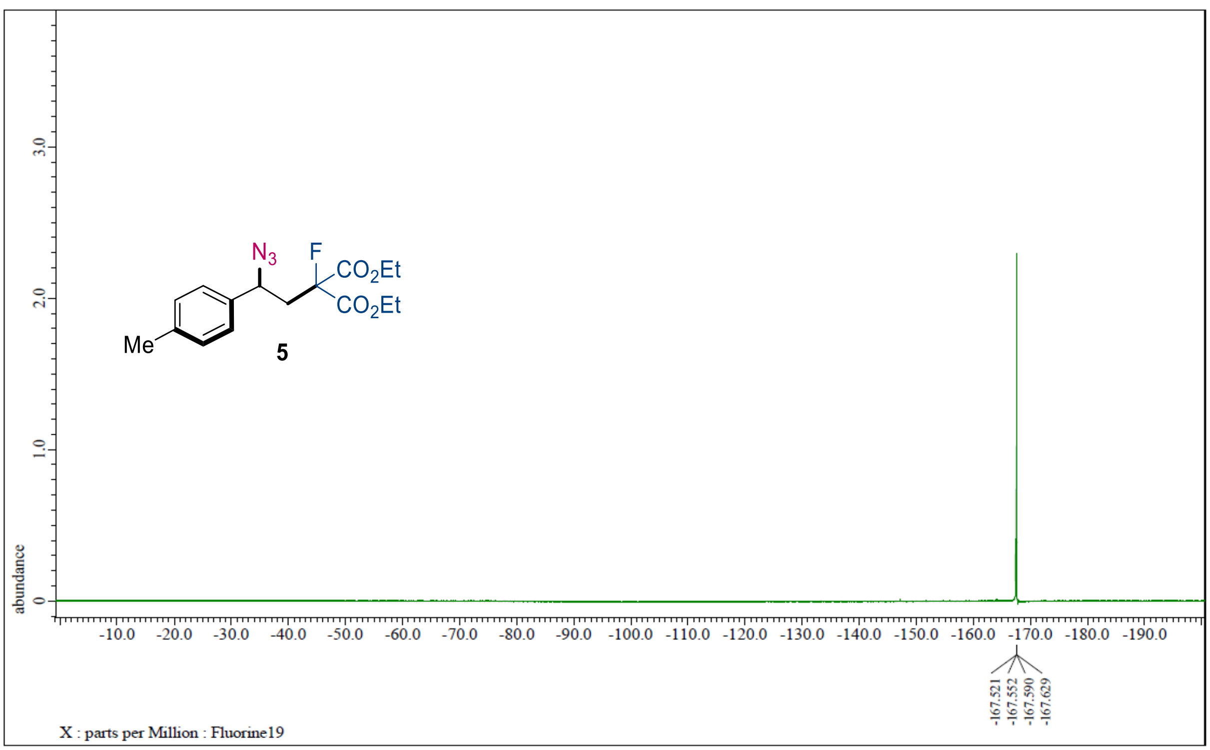
5 ^{1}H NMR (400 MHz, $CDCl_3$)



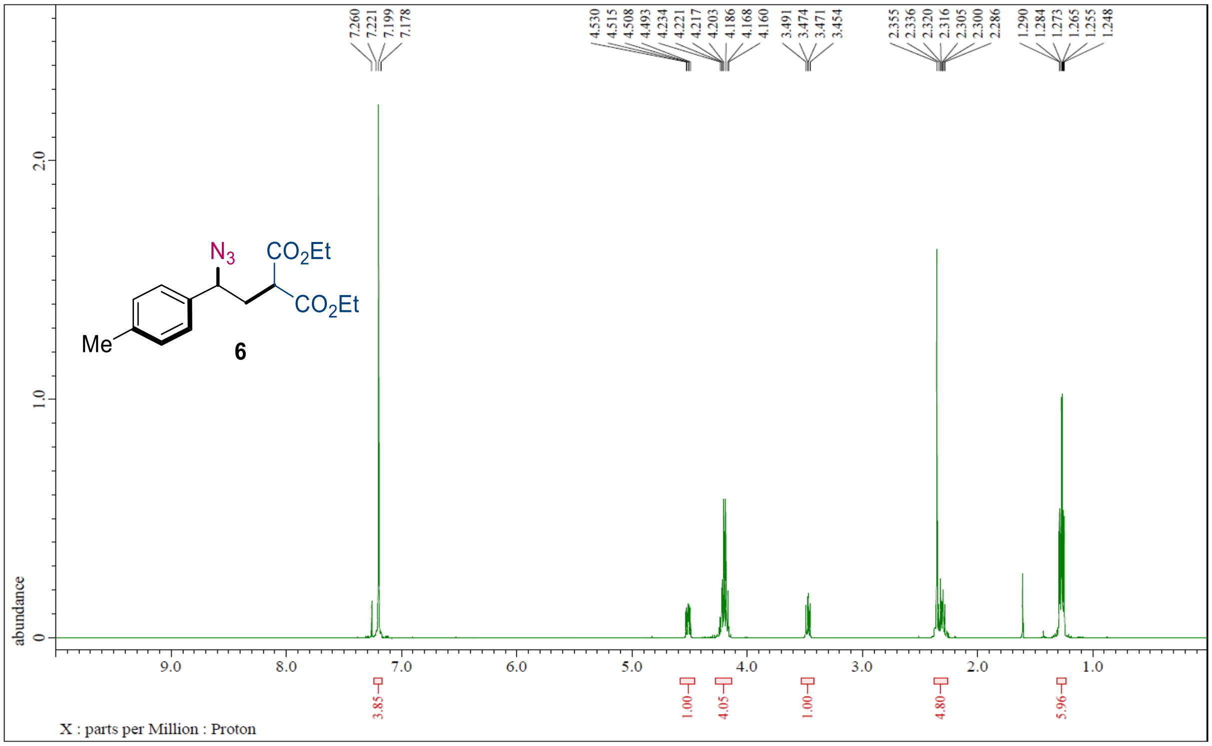
5 ^{13}C NMR (100 MHz, $CDCl_3$)



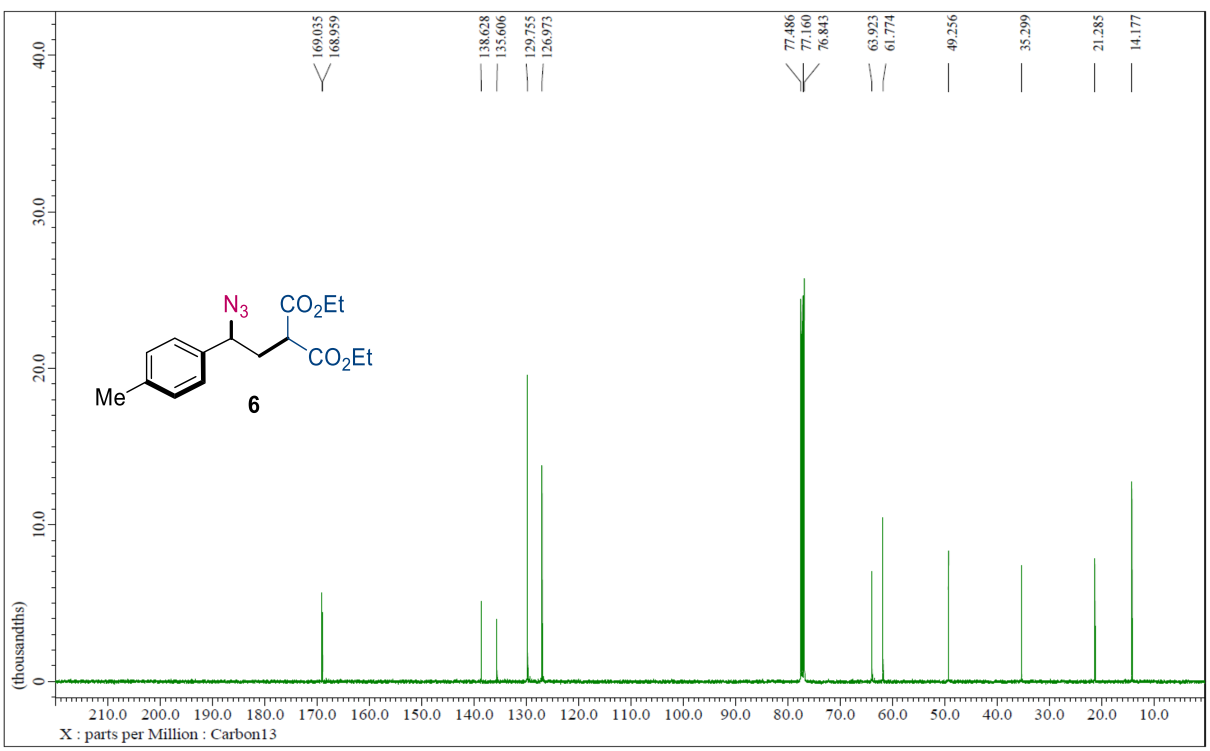
5 ^{19}F NMR (376 MHz, $CDCl_3$)



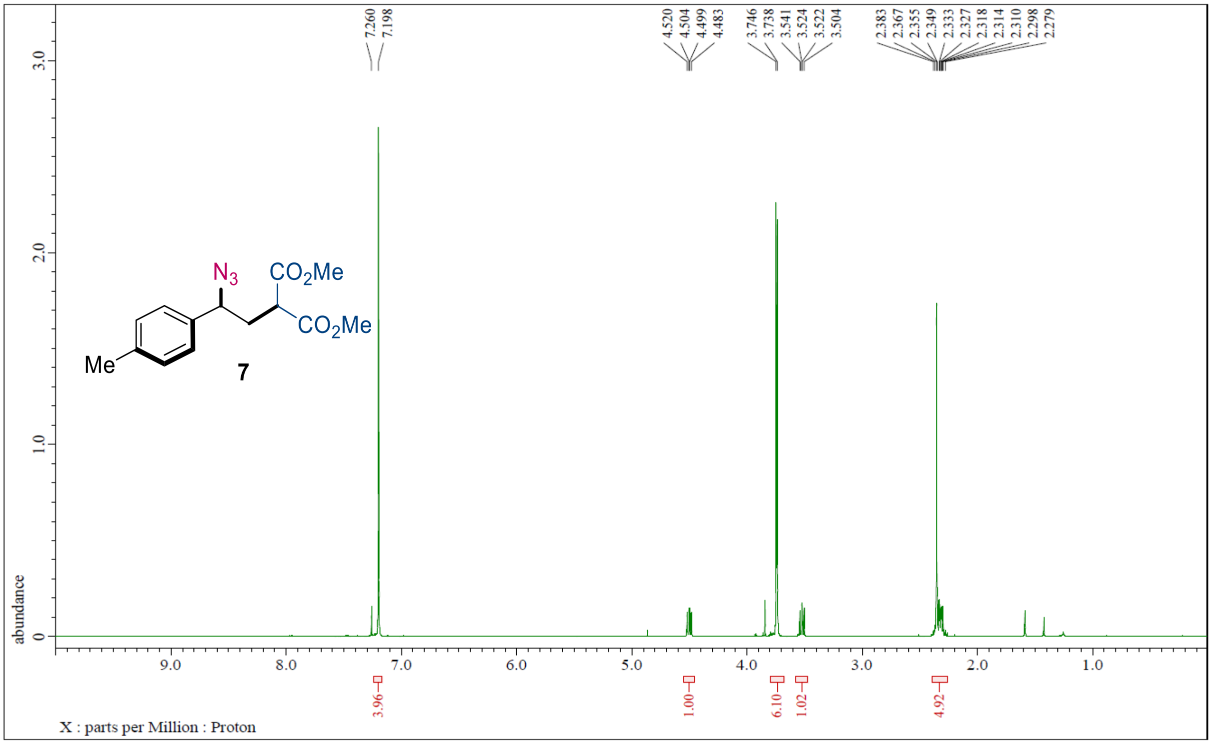
6 [1]H NMR (400 MHz, $CDCl_3$)



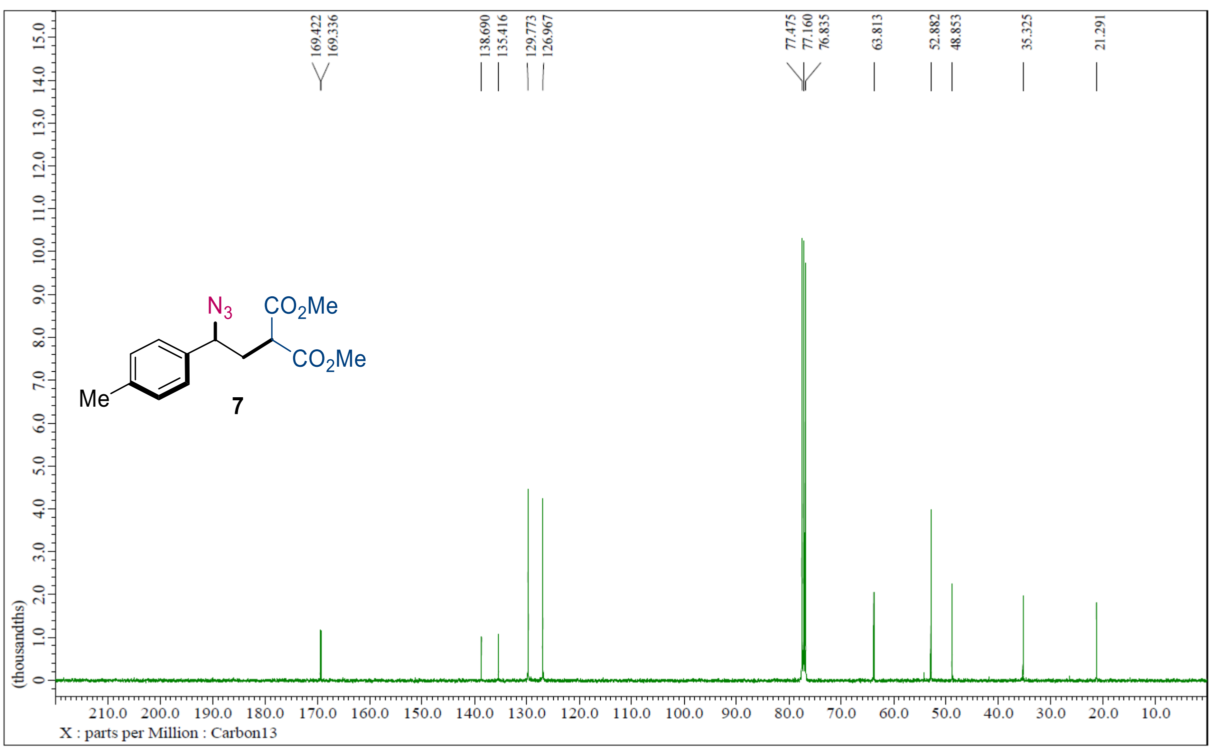
6 [13]C NMR (100 MHz, $CDCl_3$)



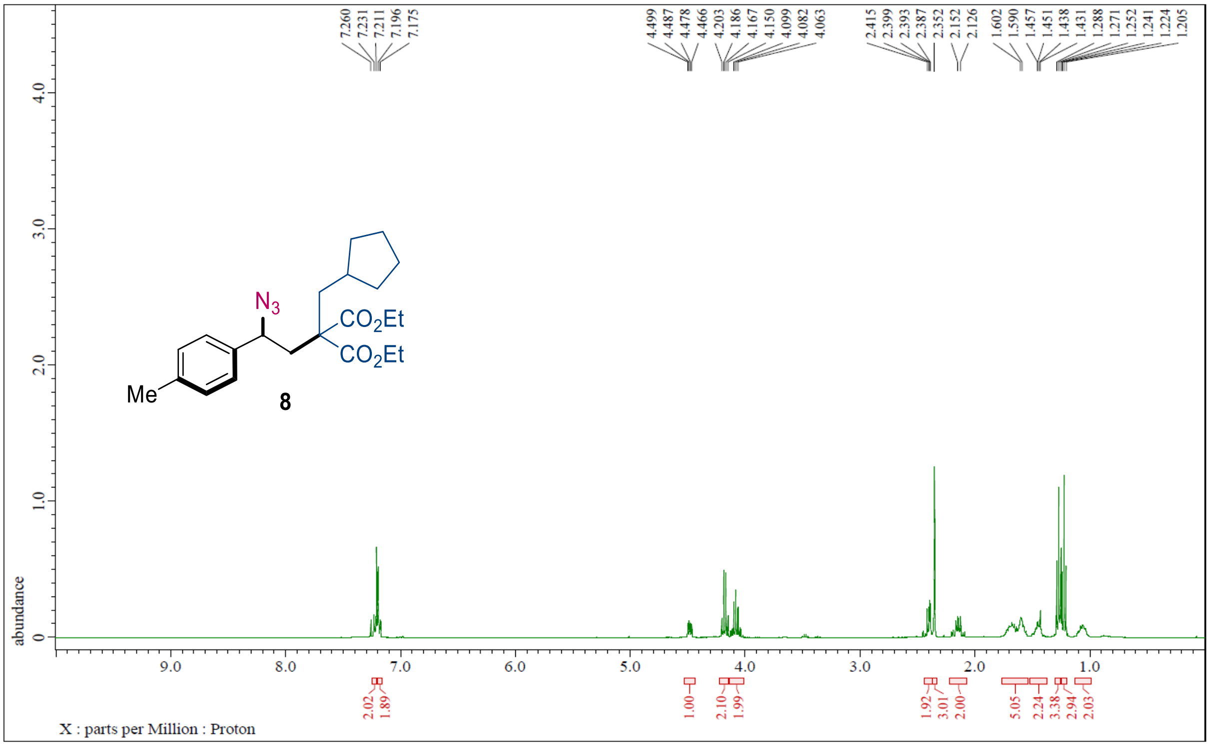
7 ^{1}H NMR (400 MHz, $CDCl_3$)



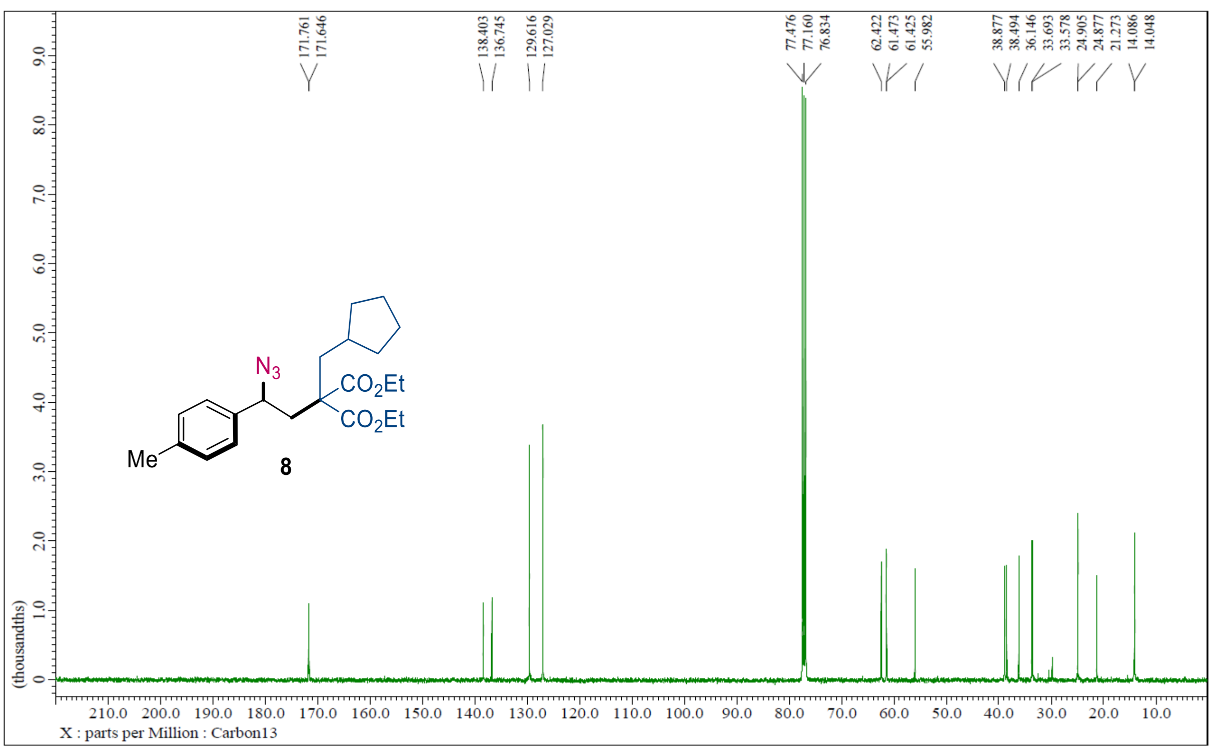
7 ^{13}C NMR (100 MHz, $CDCl_3$)



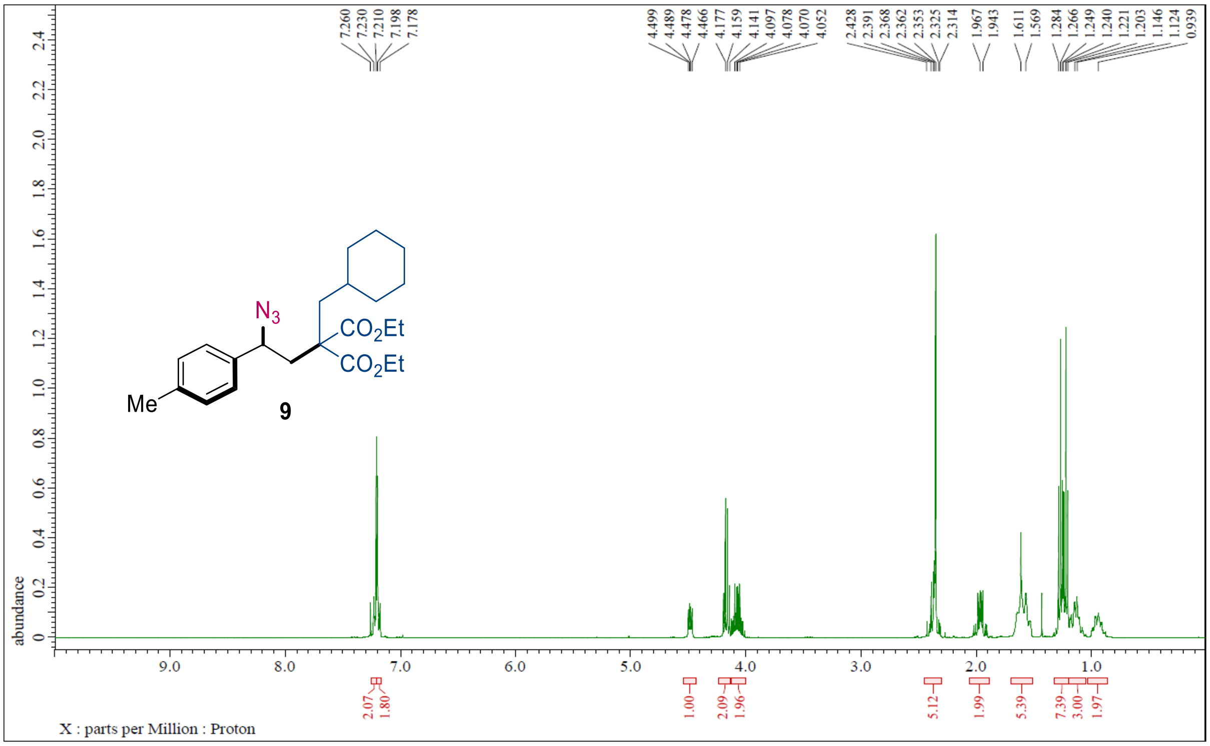
8 ^{1}H NMR (400 MHz, $CDCl_3$)



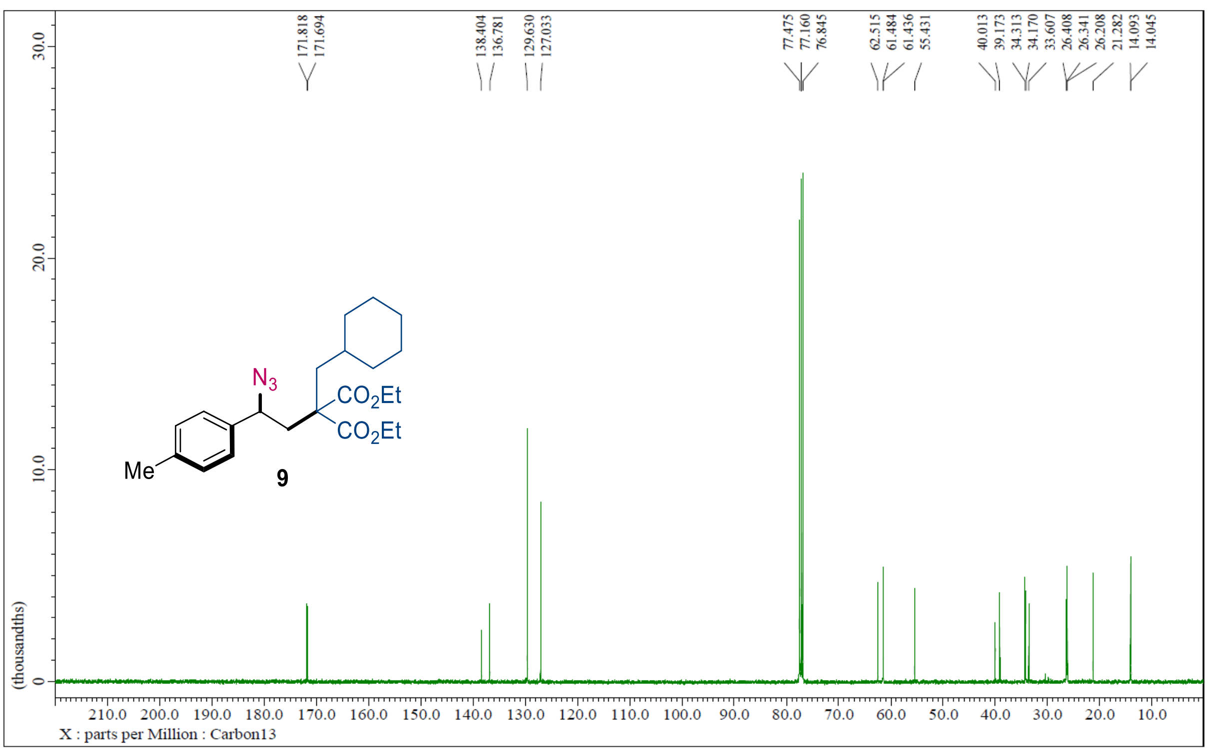
8 ^{13}C NMR (100 MHz, $CDCl_3$)



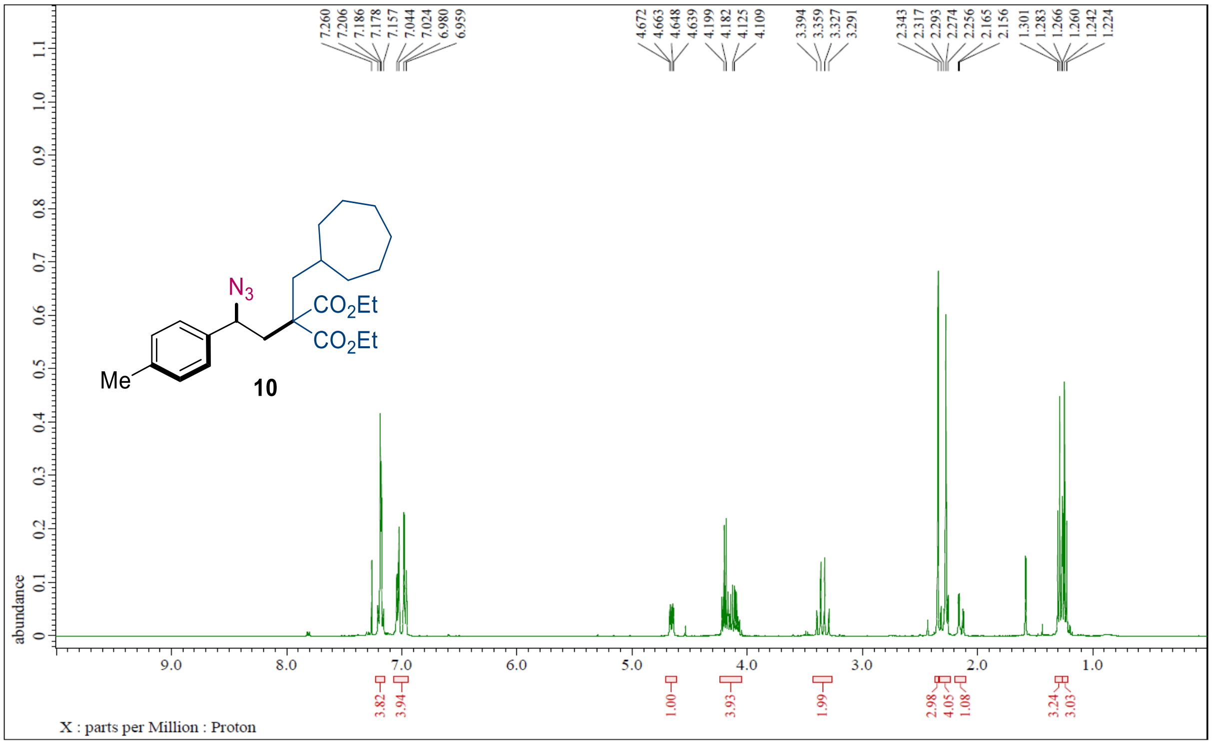
9 ^{1}H NMR (400 MHz, $CDCl_3$)



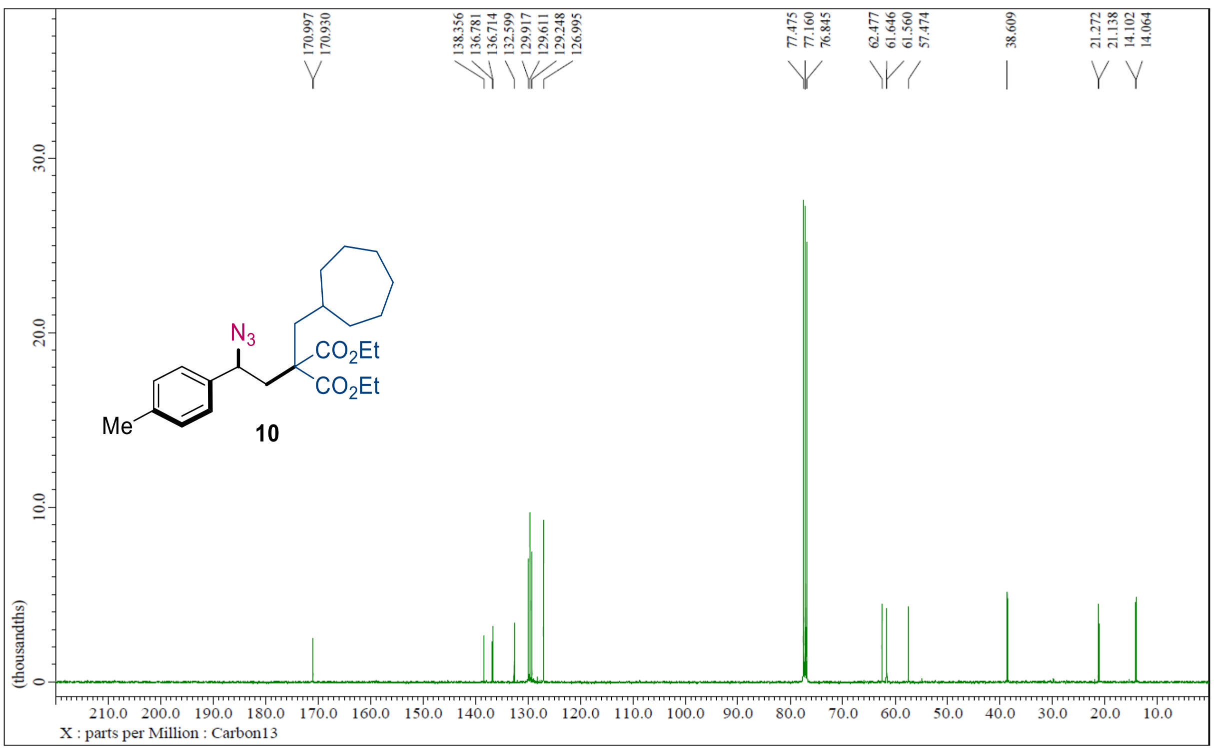
9 ^{13}C NMR (100 MHz, $CDCl_3$)



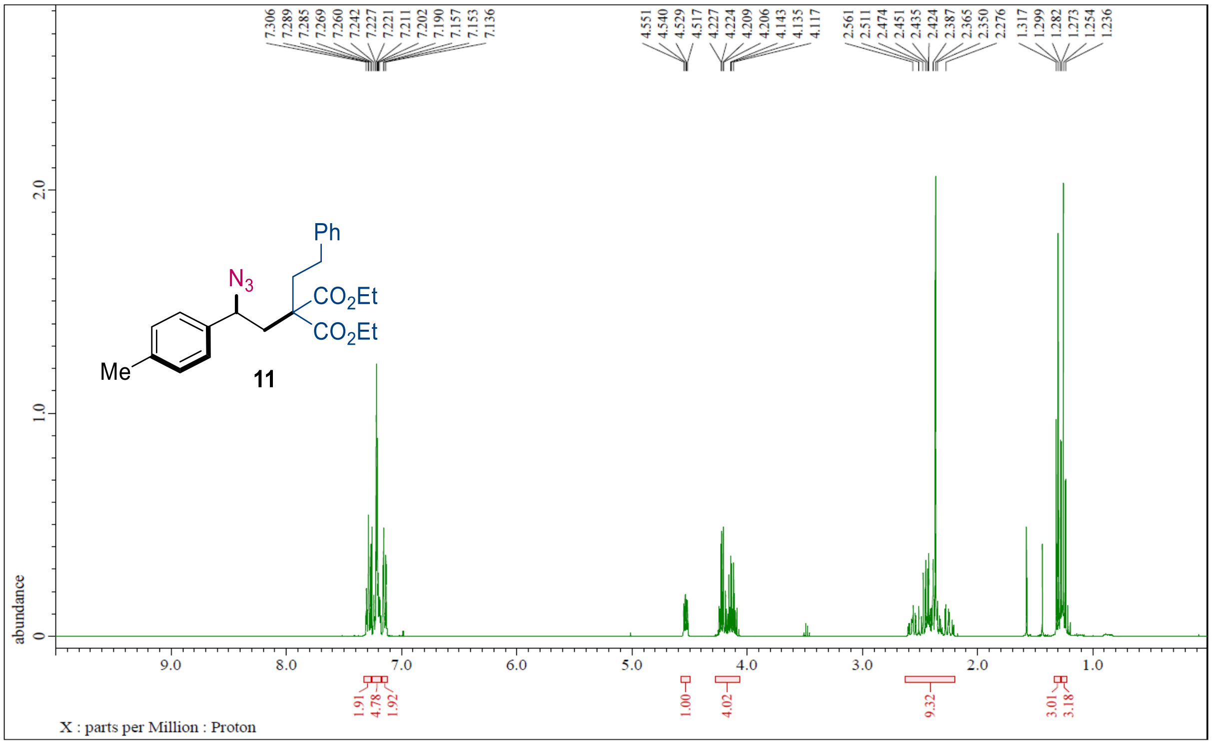
10 ^{1}H NMR (400 MHz, CDCl$_3$)



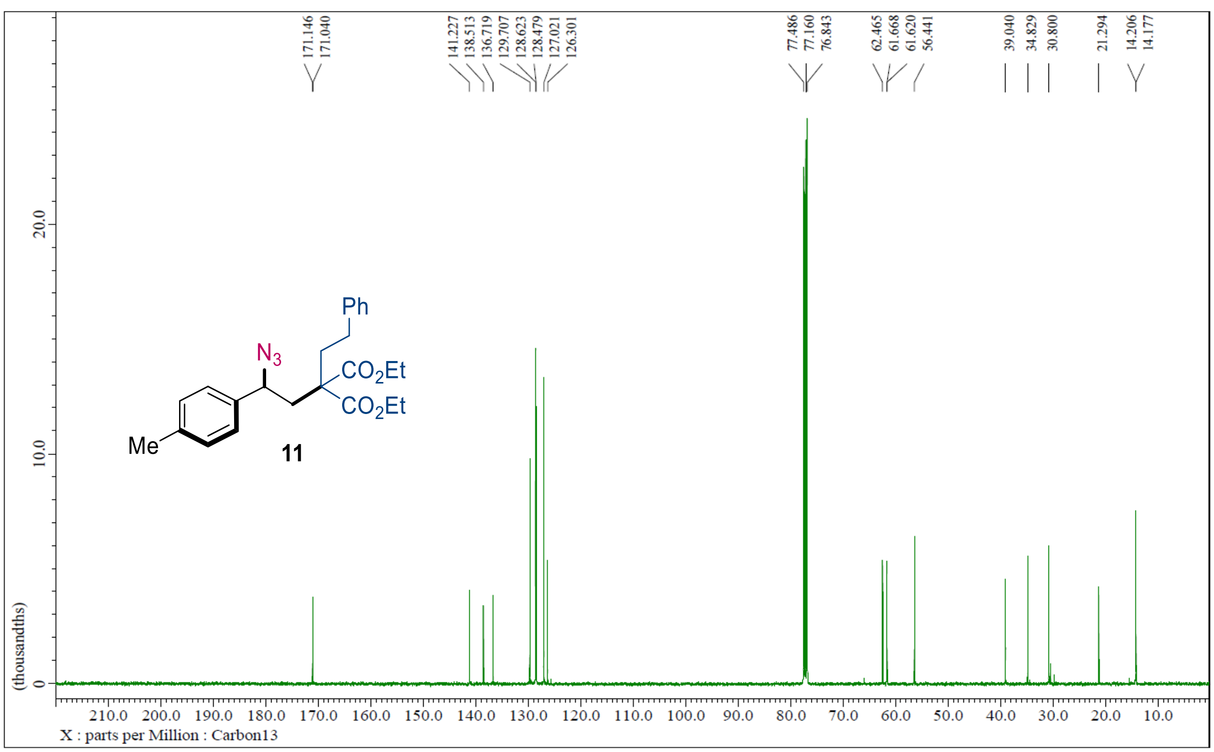
10 ^{13}C NMR (100 MHz, CDCl$_3$)



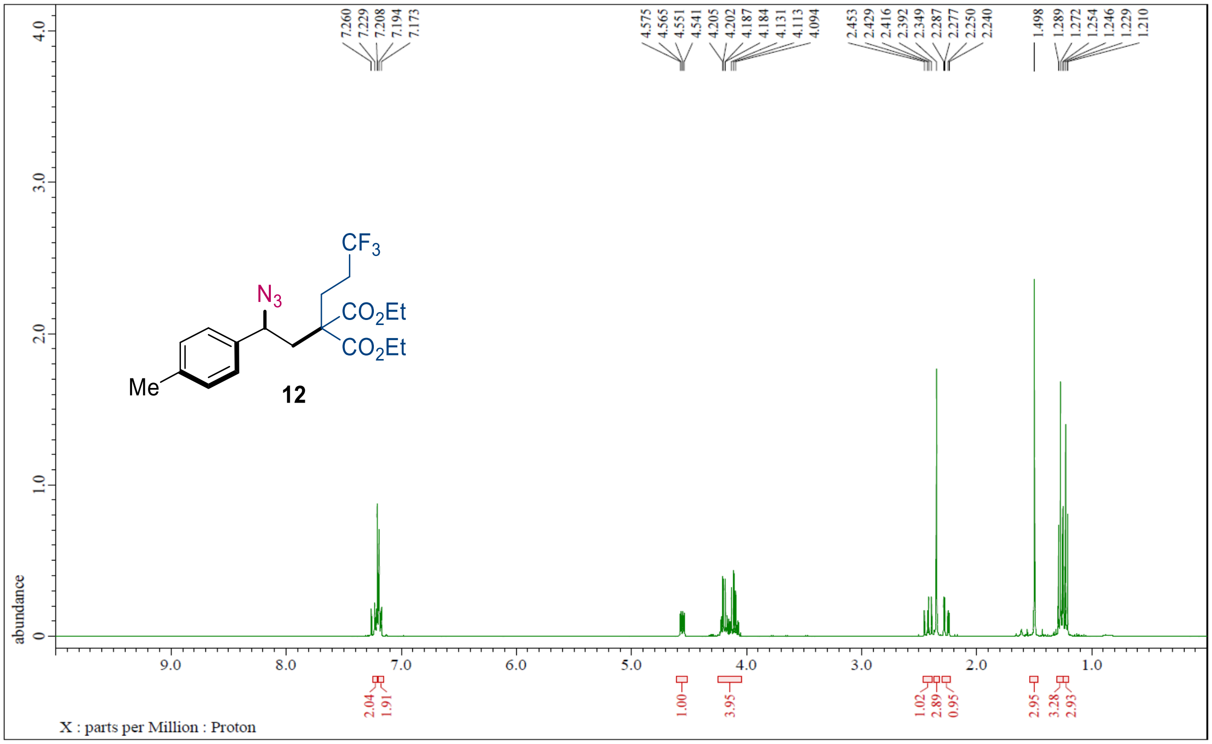
11 ^{1}H NMR (400 MHz, CDCl$_3$)



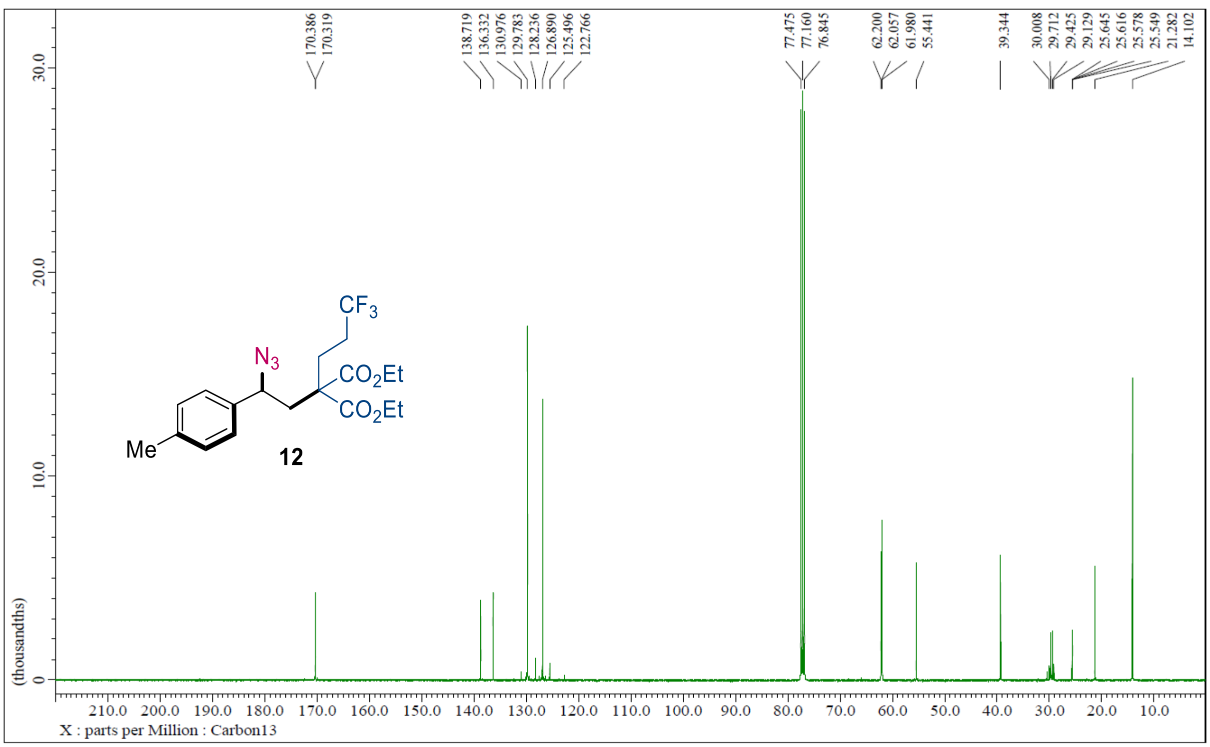
11 ^{13}C NMR (100 MHz, CDCl$_3$)



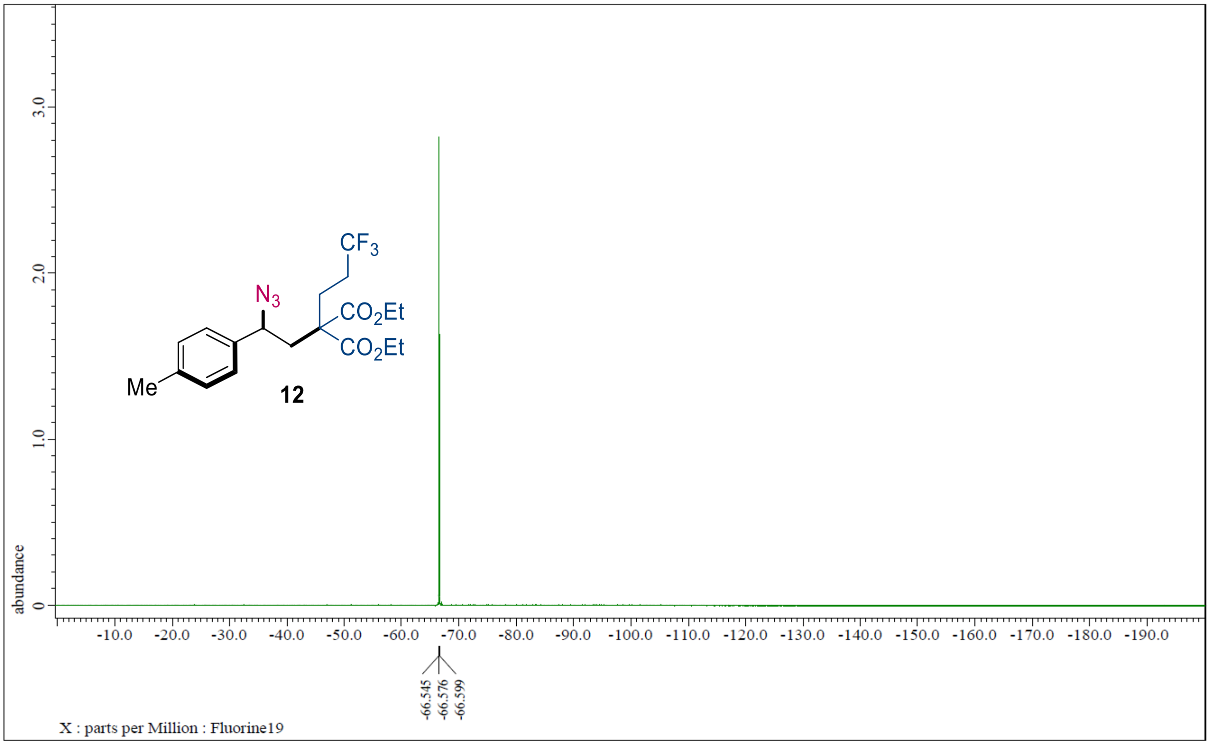
12 ^{1}H NMR (400 MHz, $CDCl_3$)



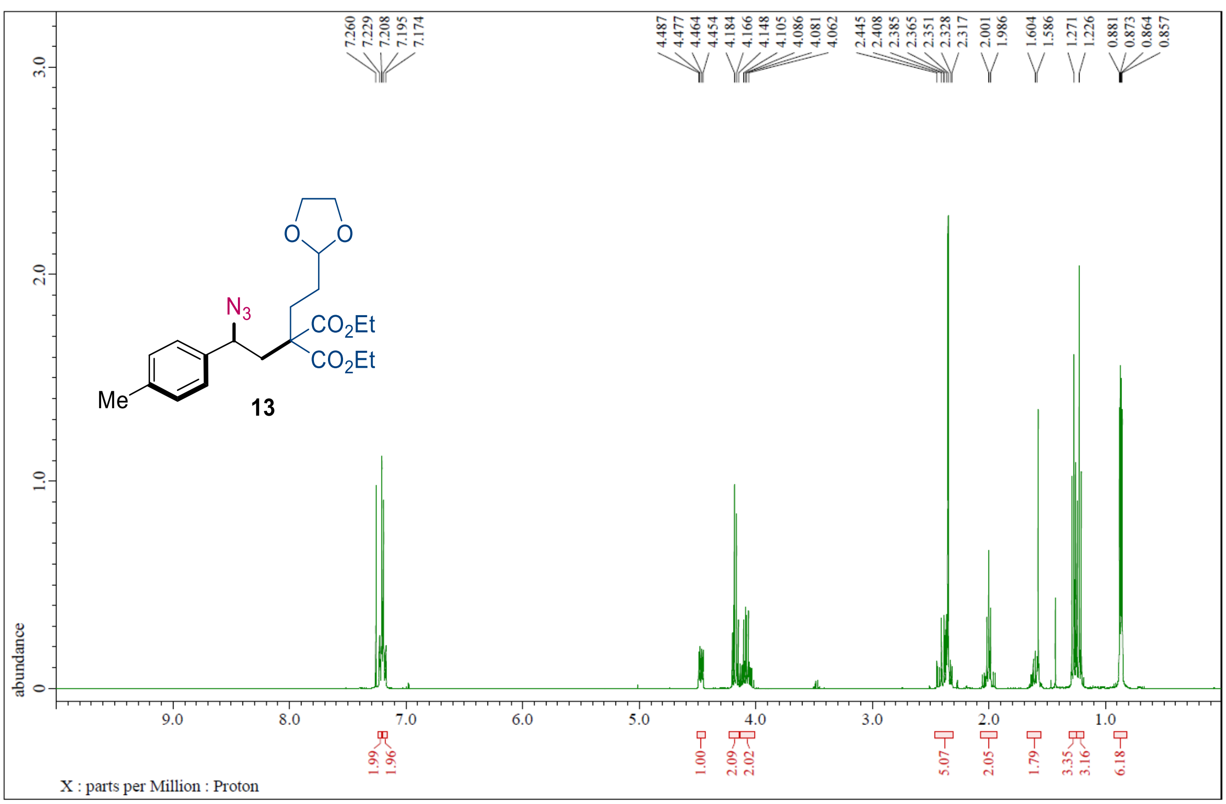
12 ^{13}C NMR (100 MHz, $CDCl_3$)



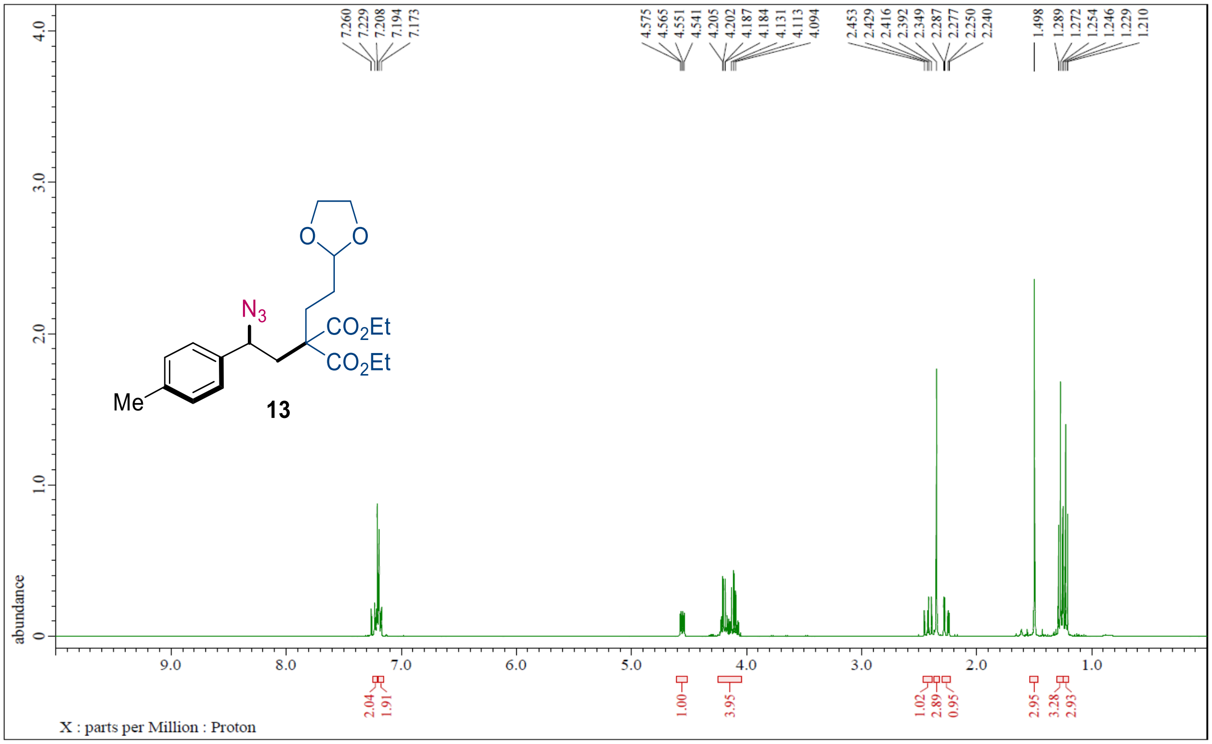
12 ^{19}F NMR (376 MHz, $CDCl_3$)



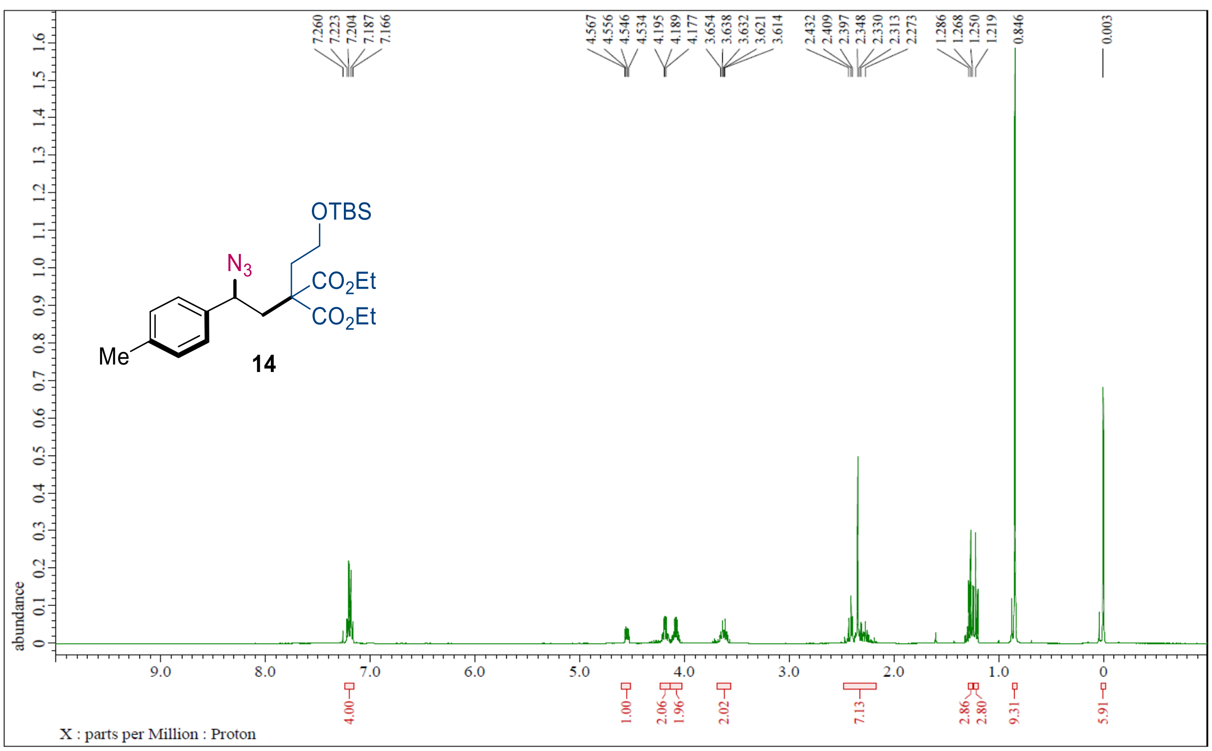
13 ^{1}H NMR (400 MHz, $CDCl_3$)



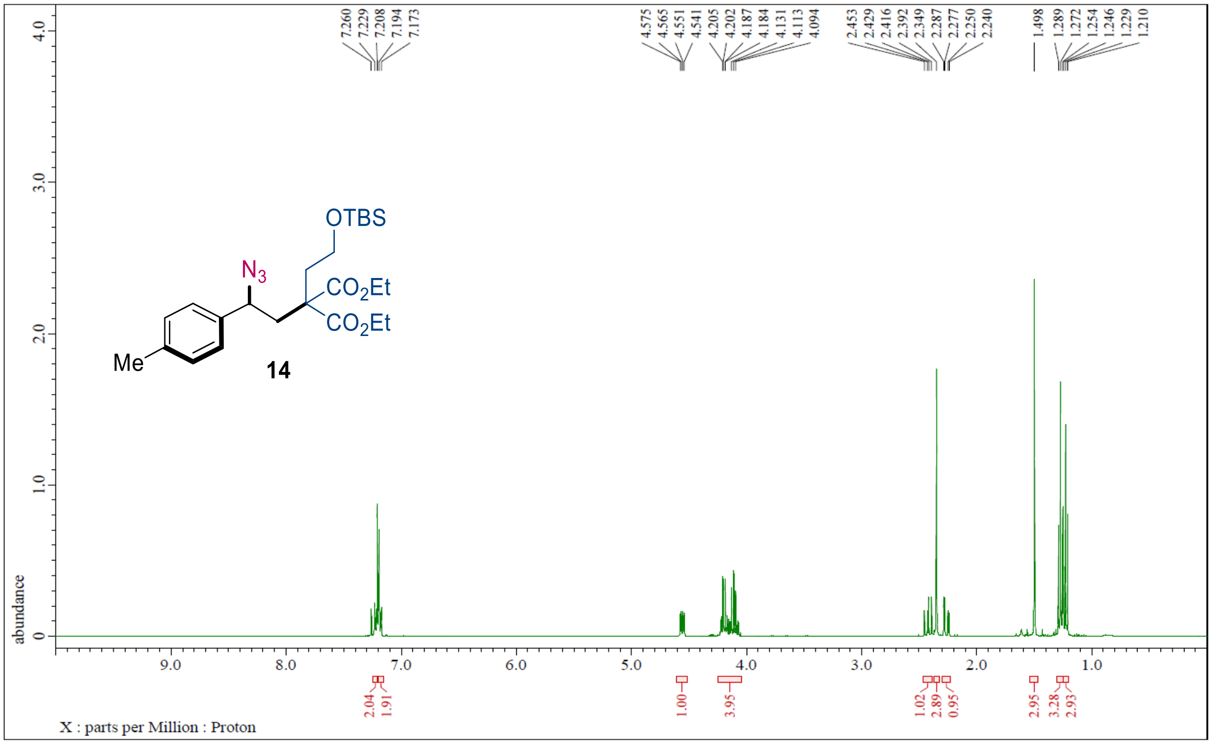
13 ^{13}C NMR (100 MHz, $CDCl_3$)



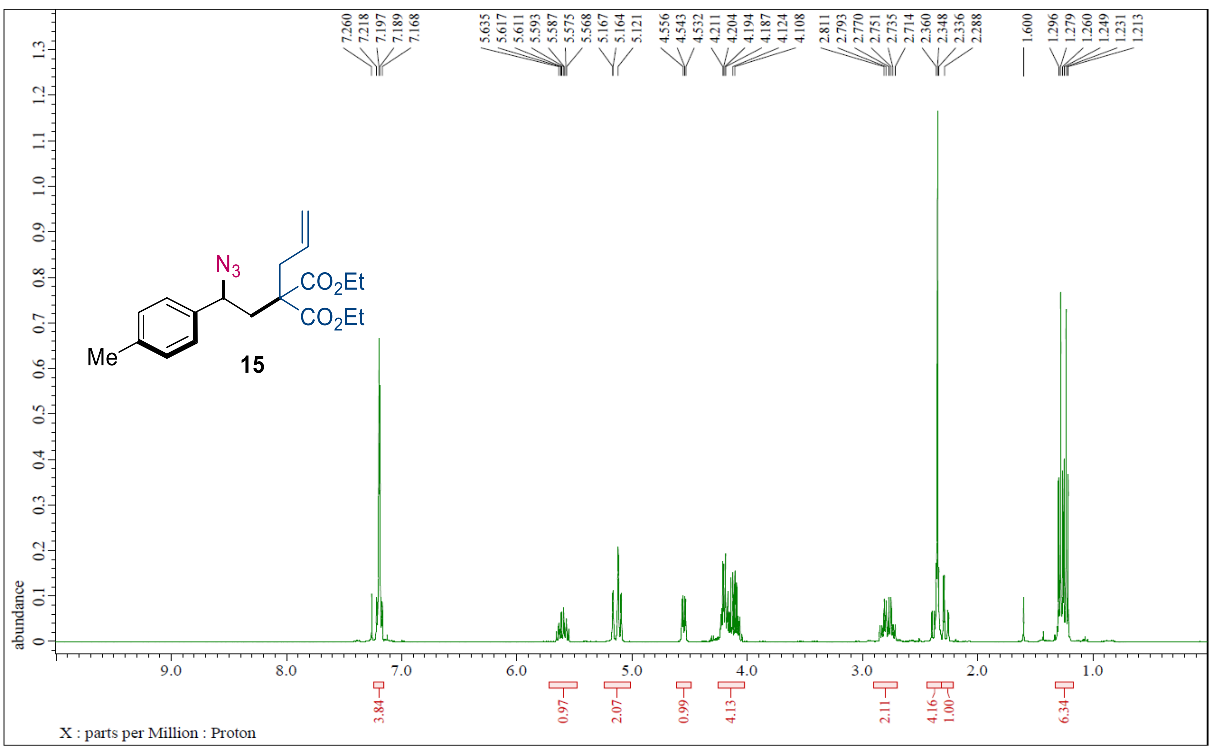
14 ^{1}H NMR (400 MHz, $CDCl_3$)



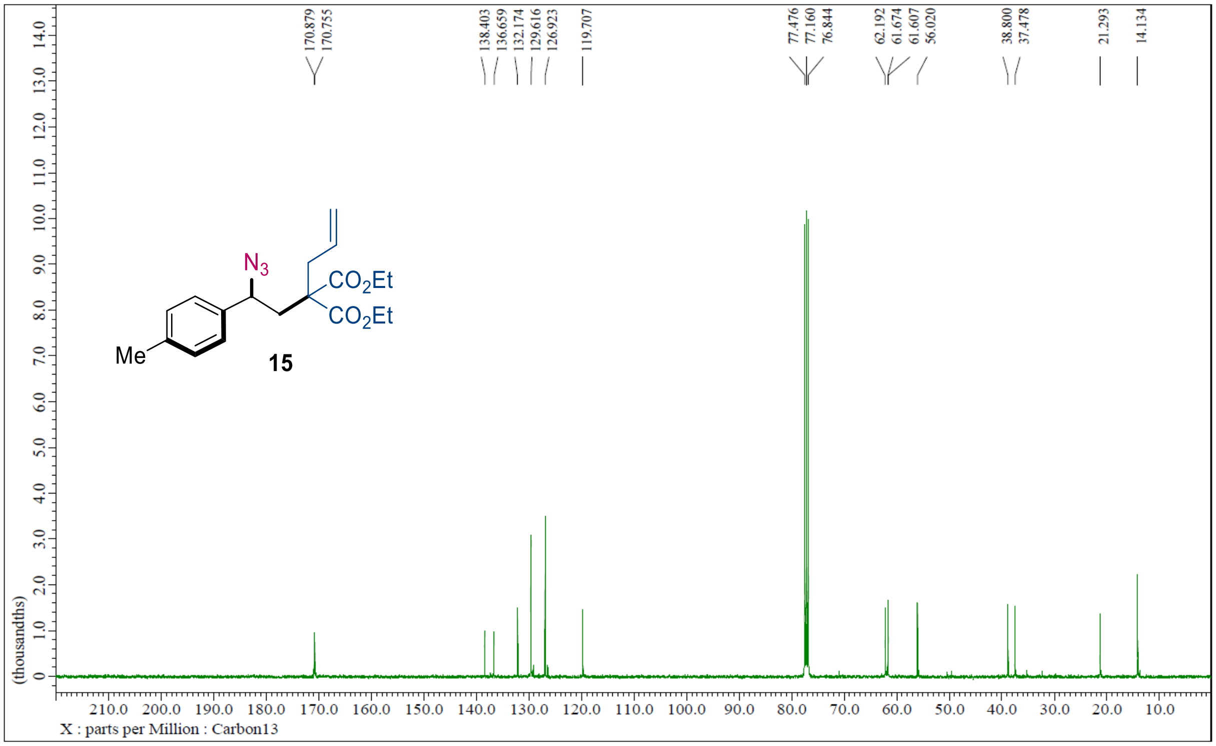
14 ^{13}C NMR (100 MHz, $CDCl_3$)



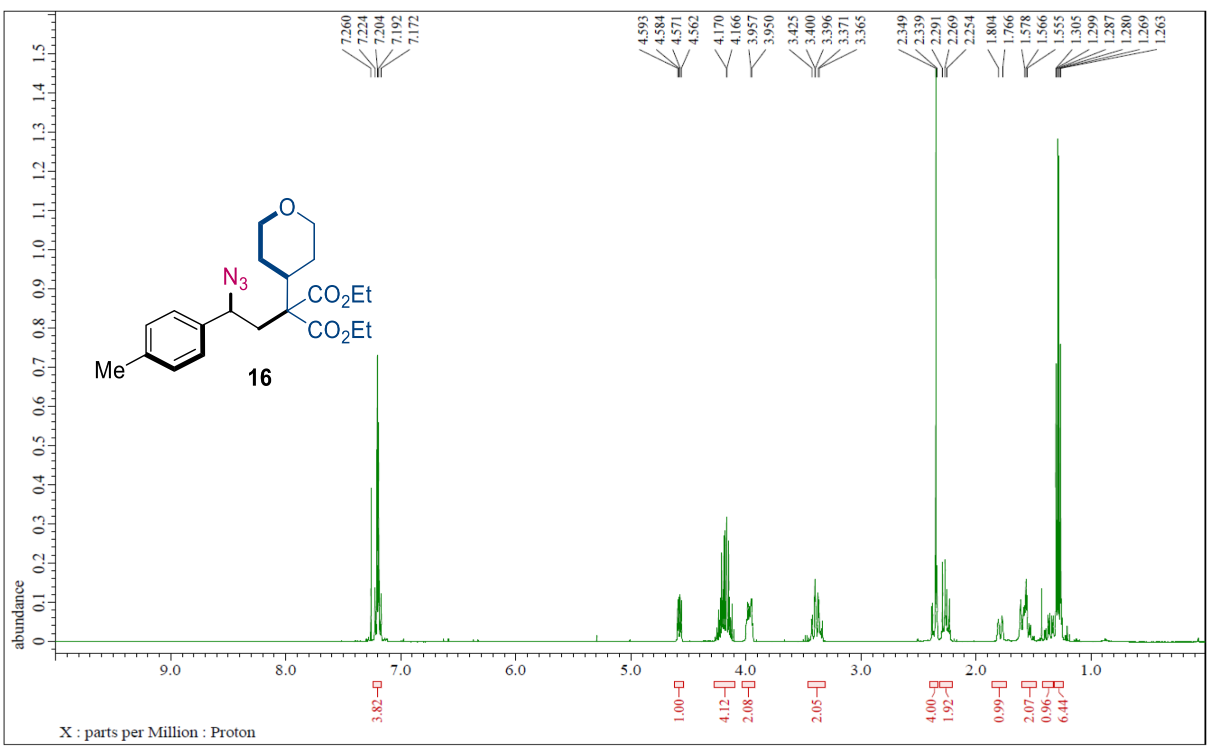
15 ^{1}H NMR (400 MHz, $CDCl_3$)



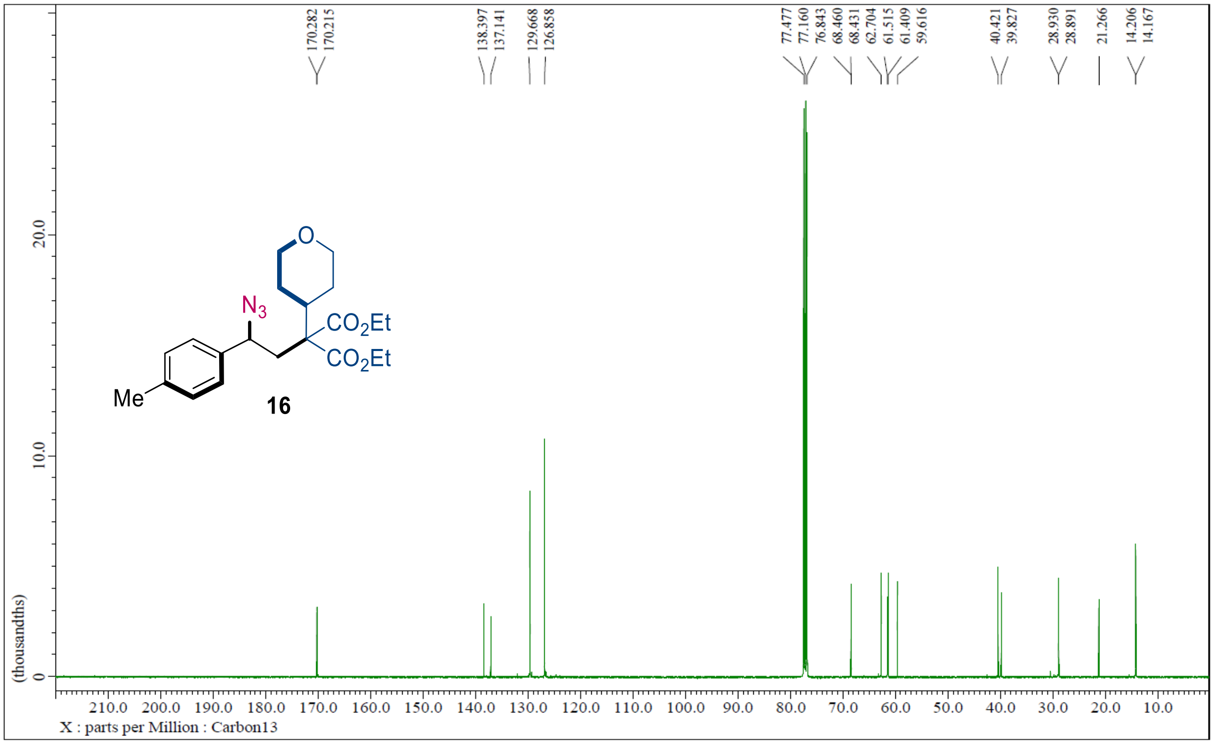
15 ^{13}C NMR (100 MHz, $CDCl_3$)



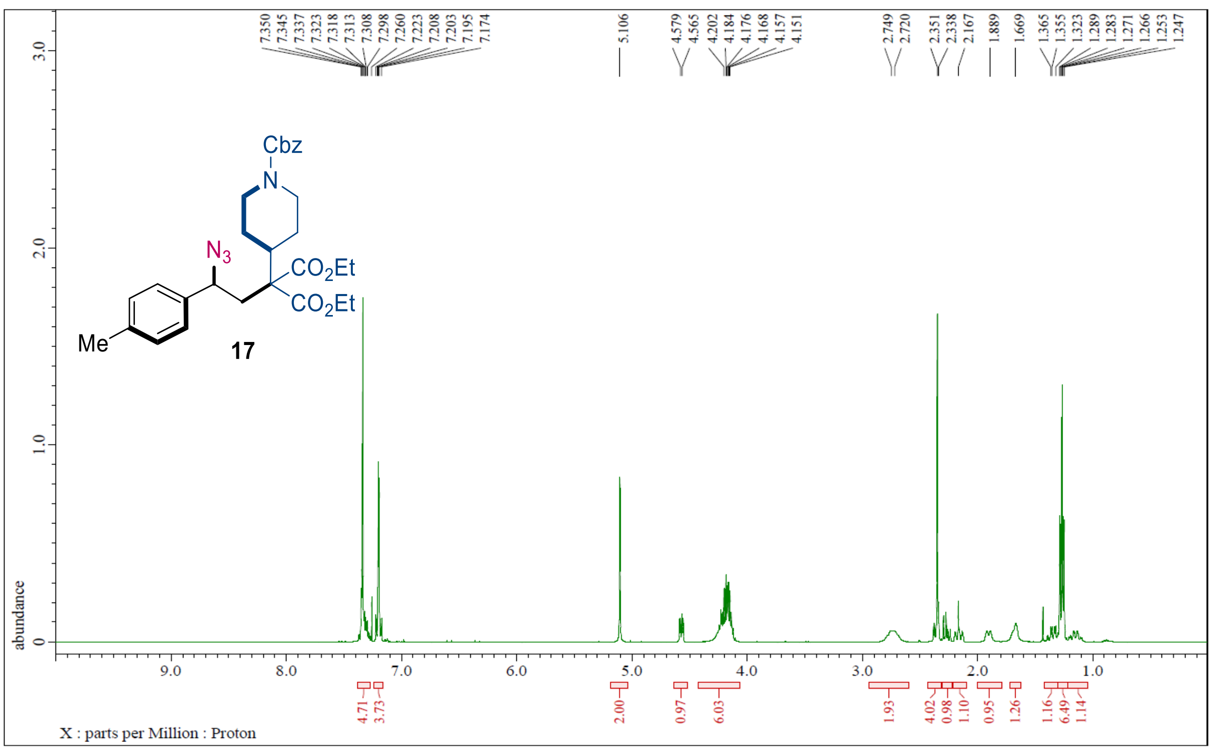
16 ^{1}H NMR (400 MHz, $CDCl_3$)



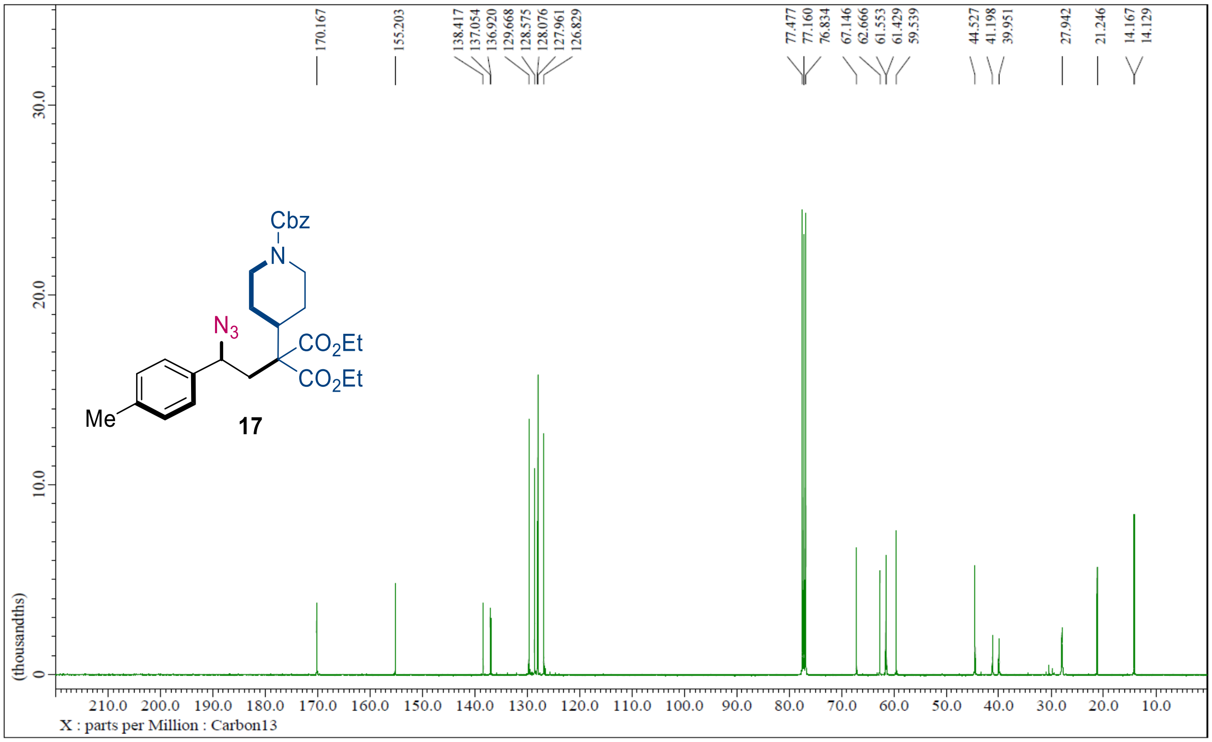
16 ^{13}C NMR (100 MHz, $CDCl_3$)



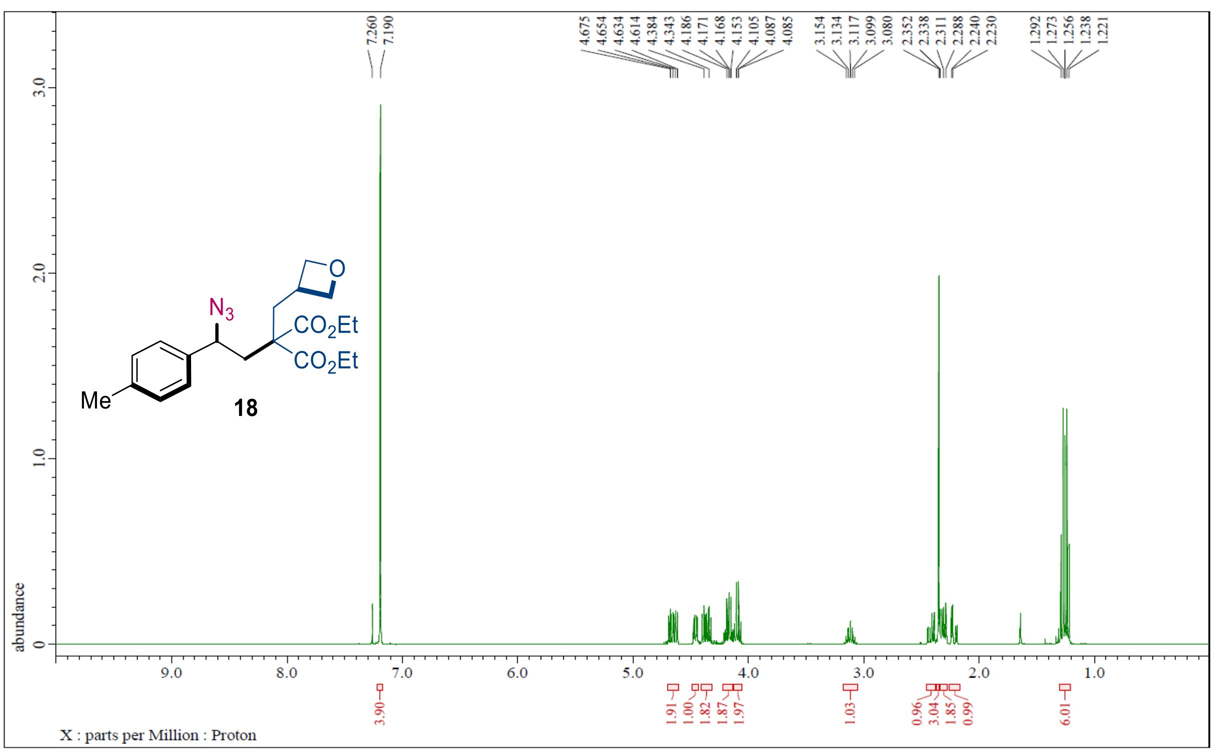
17 ^{1}H NMR (400 MHz, $CDCl_3$)



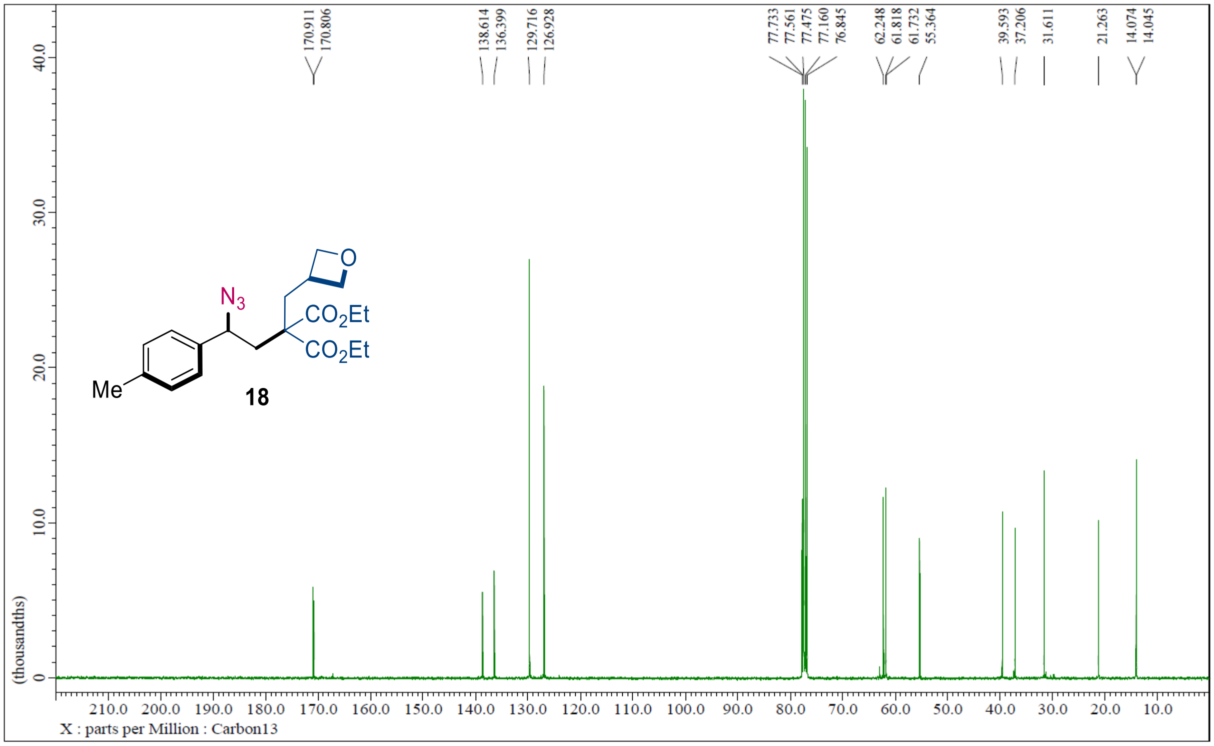
17 ^{13}C NMR (100 MHz, $CDCl_3$)



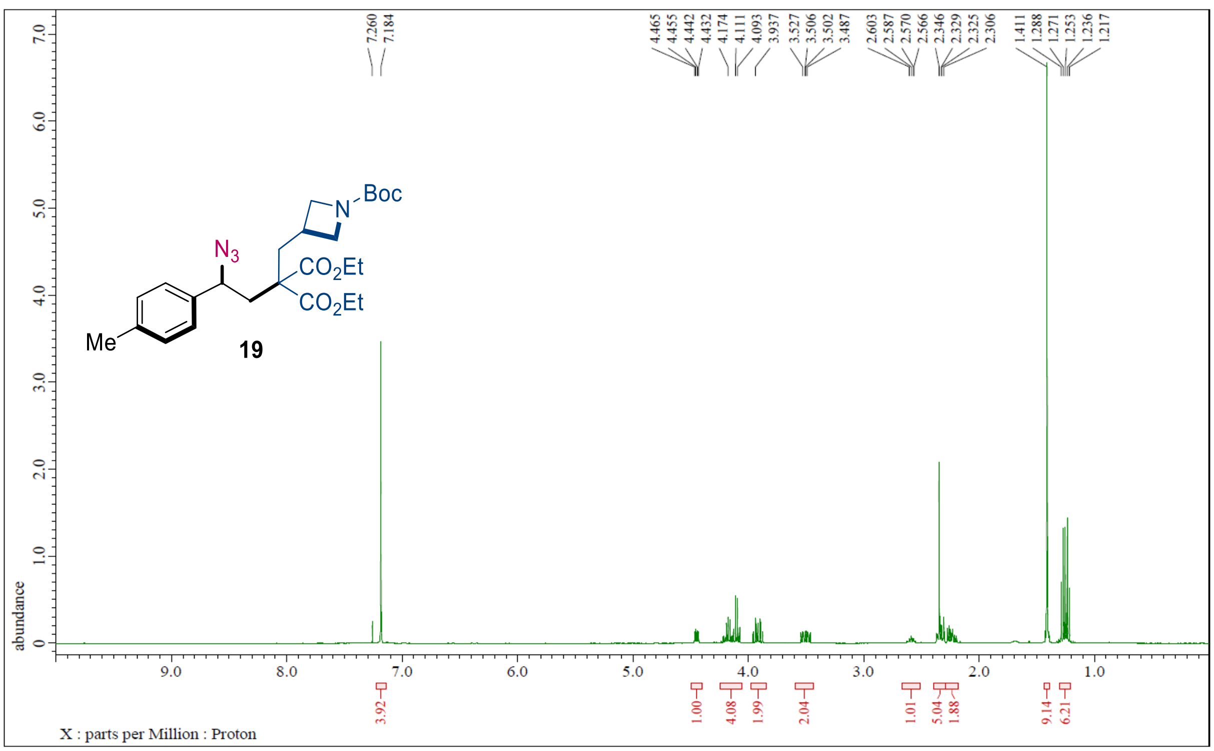
18 ^{1}H NMR (400 MHz, $CDCl_3$)



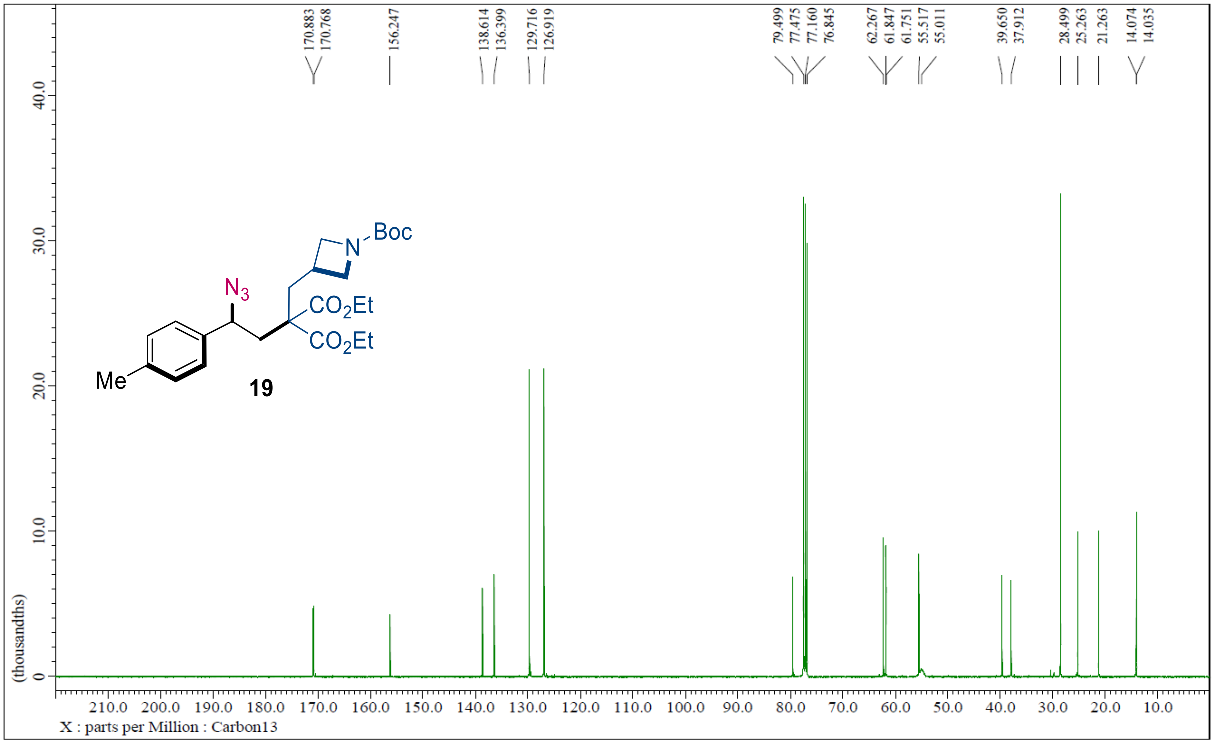
18 ^{13}C NMR (100 MHz, $CDCl_3$)



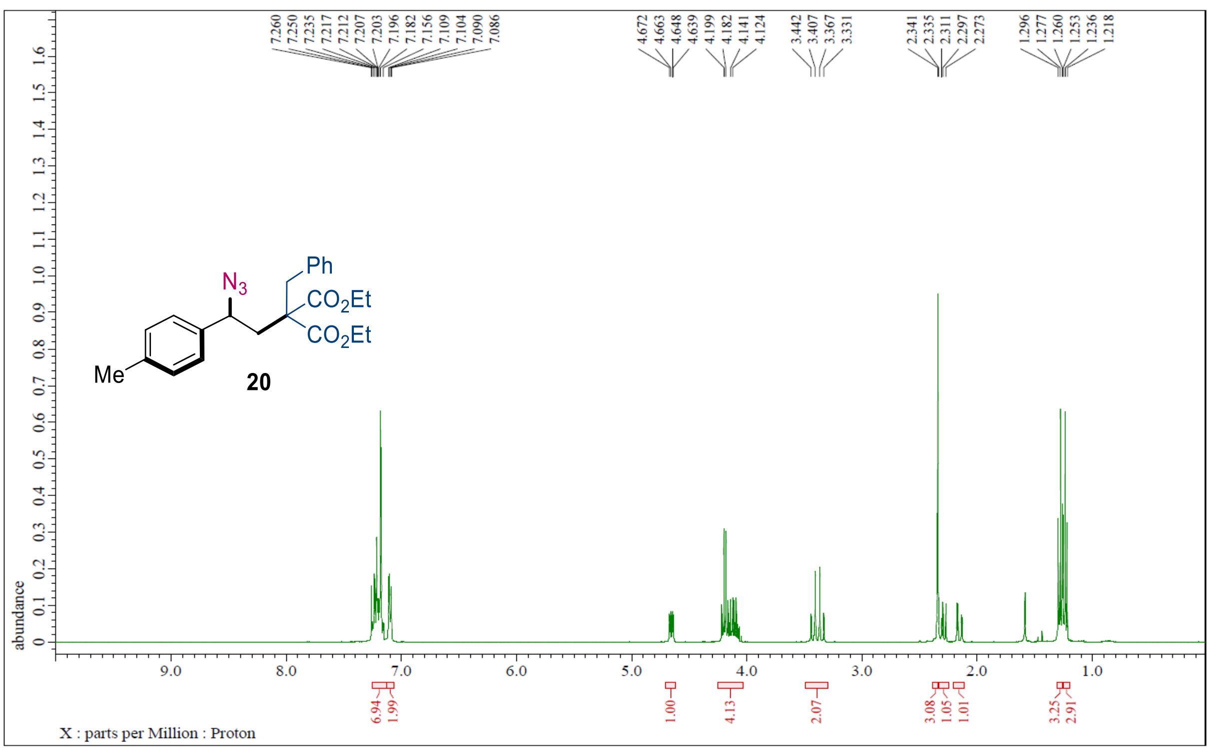
19 ^{1}H NMR (400 MHz, $CDCl_3$)



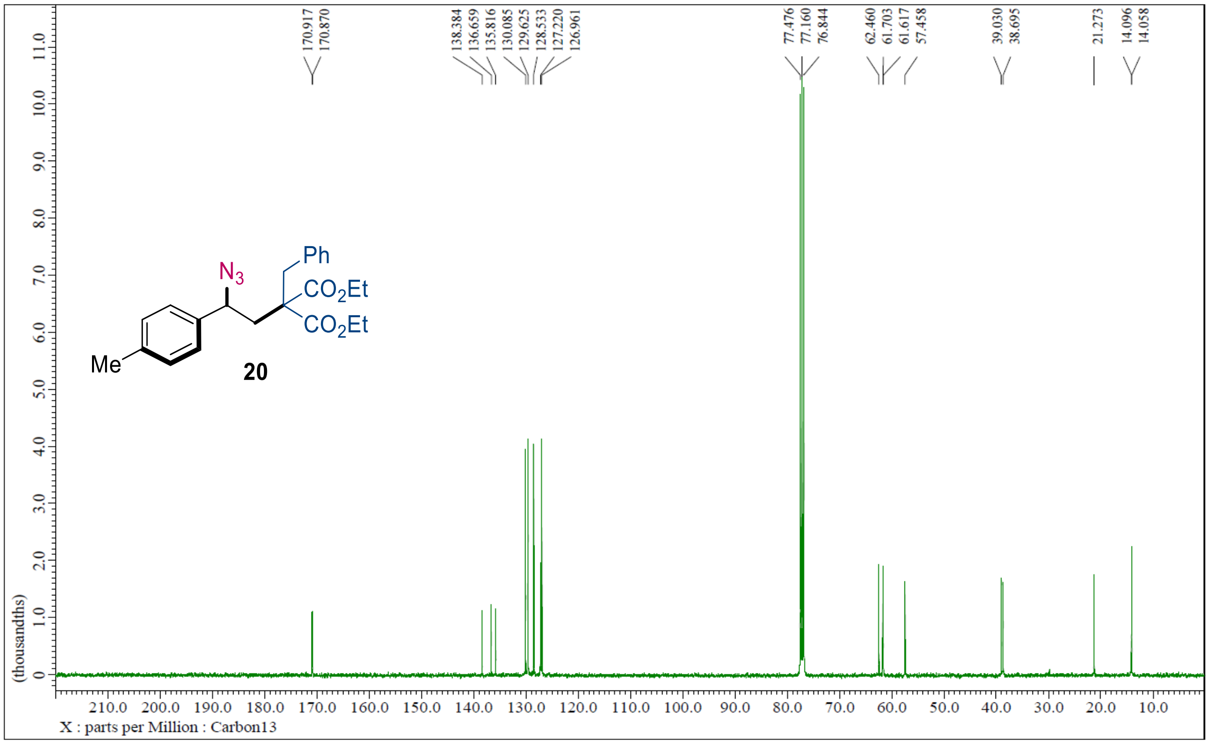
19 ^{13}C NMR (100 MHz, $CDCl_3$)



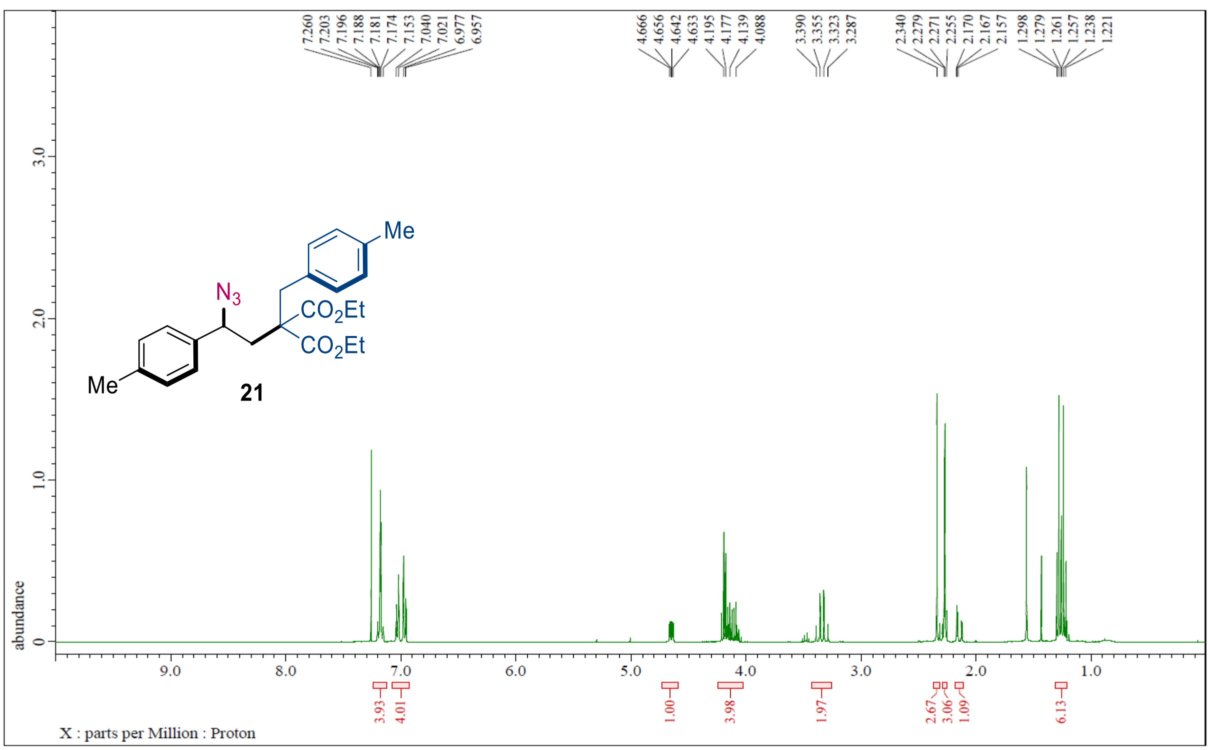
20 ^{1}H NMR (400 MHz, $CDCl_3$)



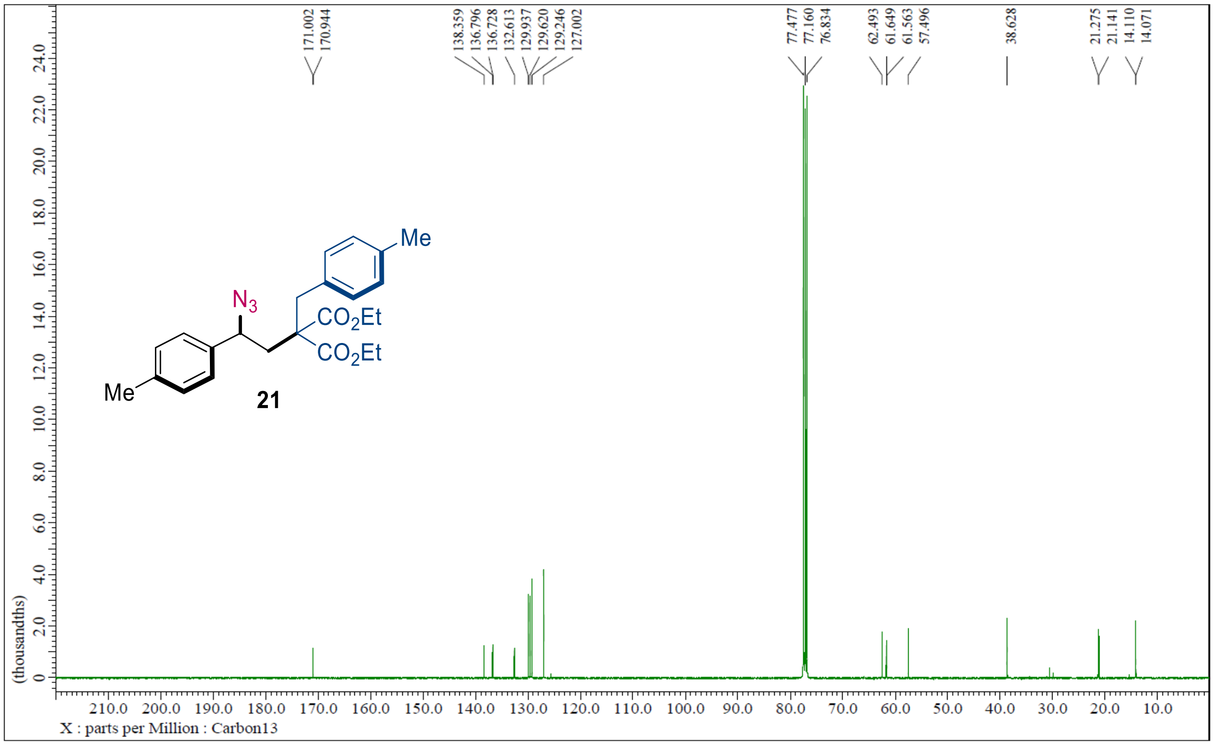
20 ^{13}C NMR (100 MHz, $CDCl_3$)



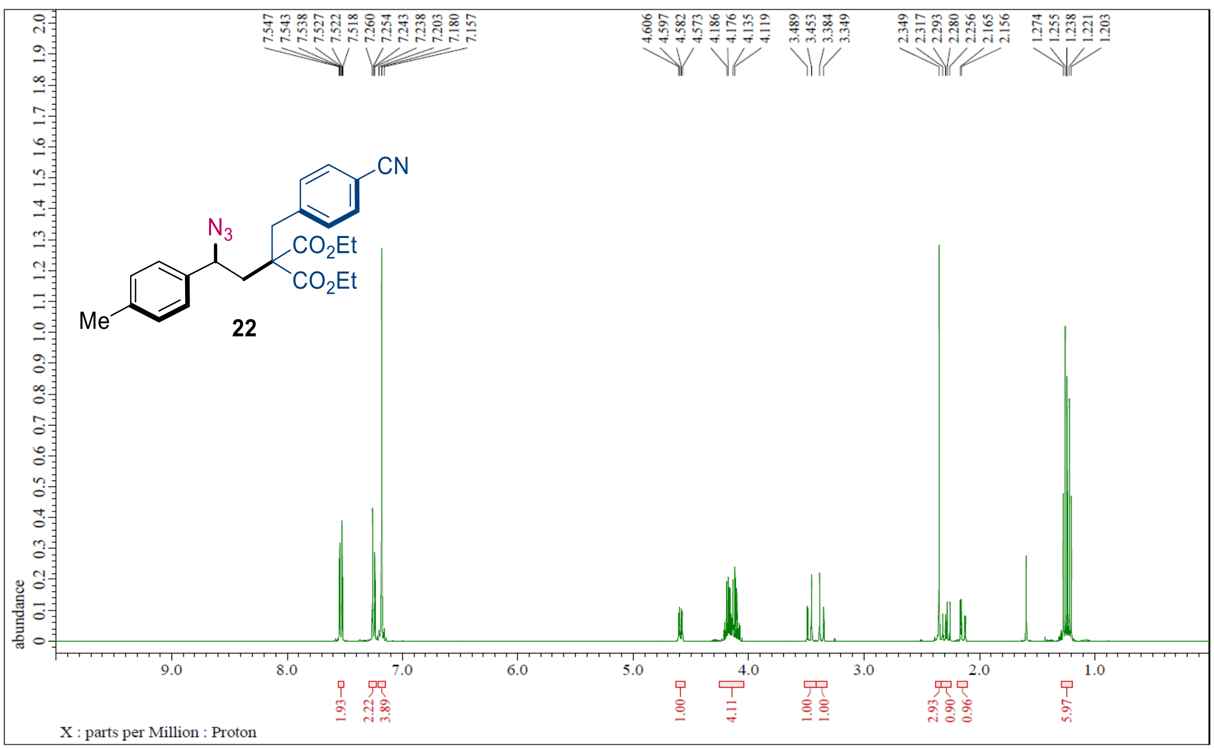
21 ^{1}H NMR (400 MHz, $CDCl_3$)



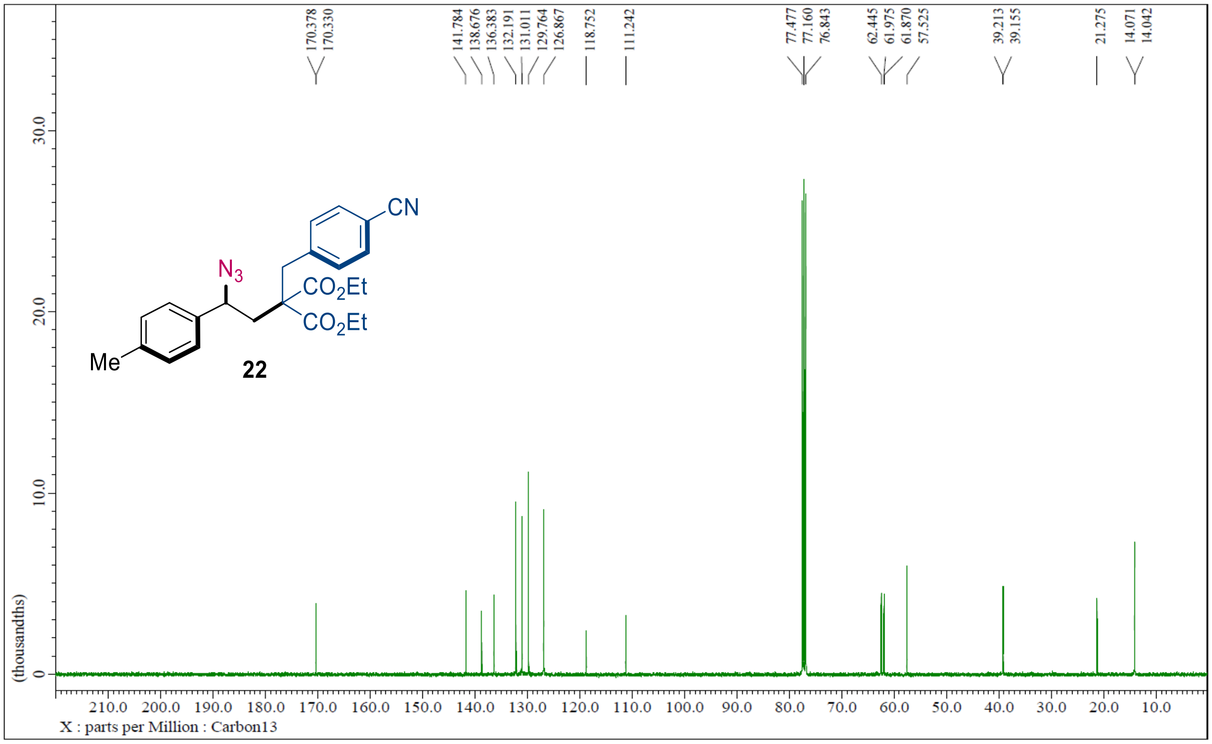
21 ^{13}C NMR (100 MHz, $CDCl_3$)



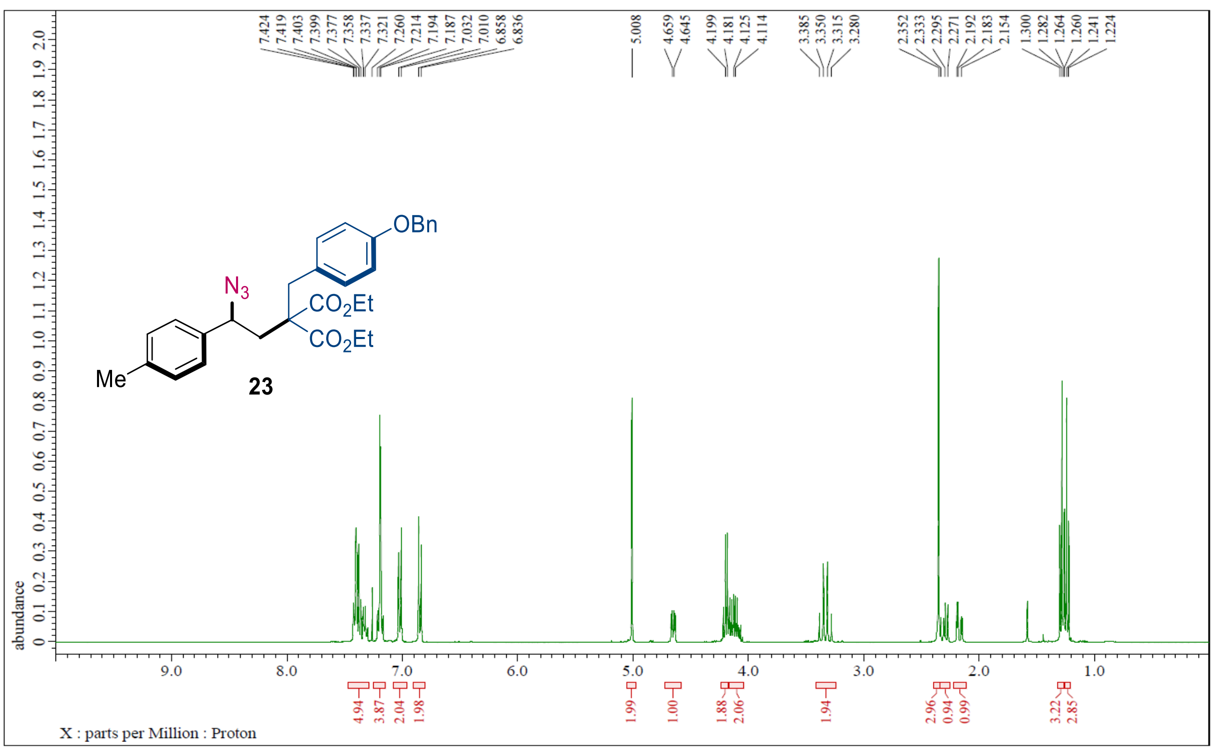
22 ^{1}H NMR (400 MHz, $CDCl_3$)



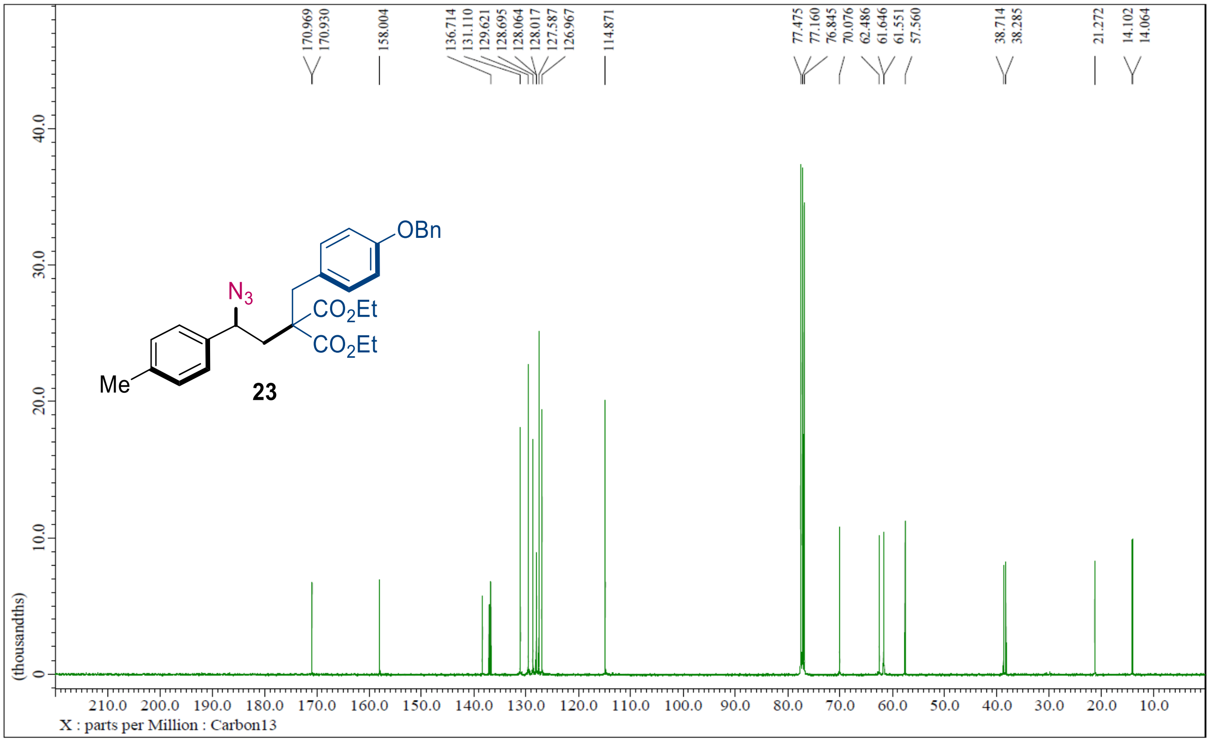
22 ^{13}C NMR (100 MHz, $CDCl_3$)



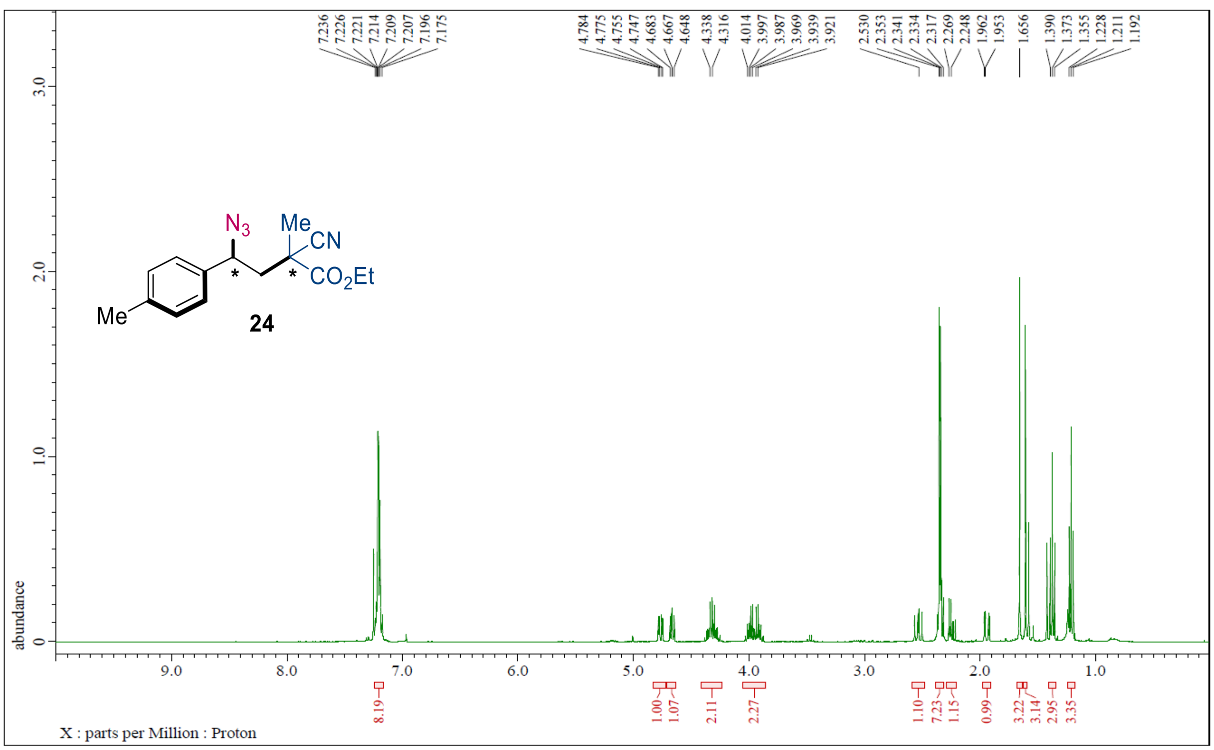
23 ^{1}H NMR (400 MHz, $CDCl_3$)



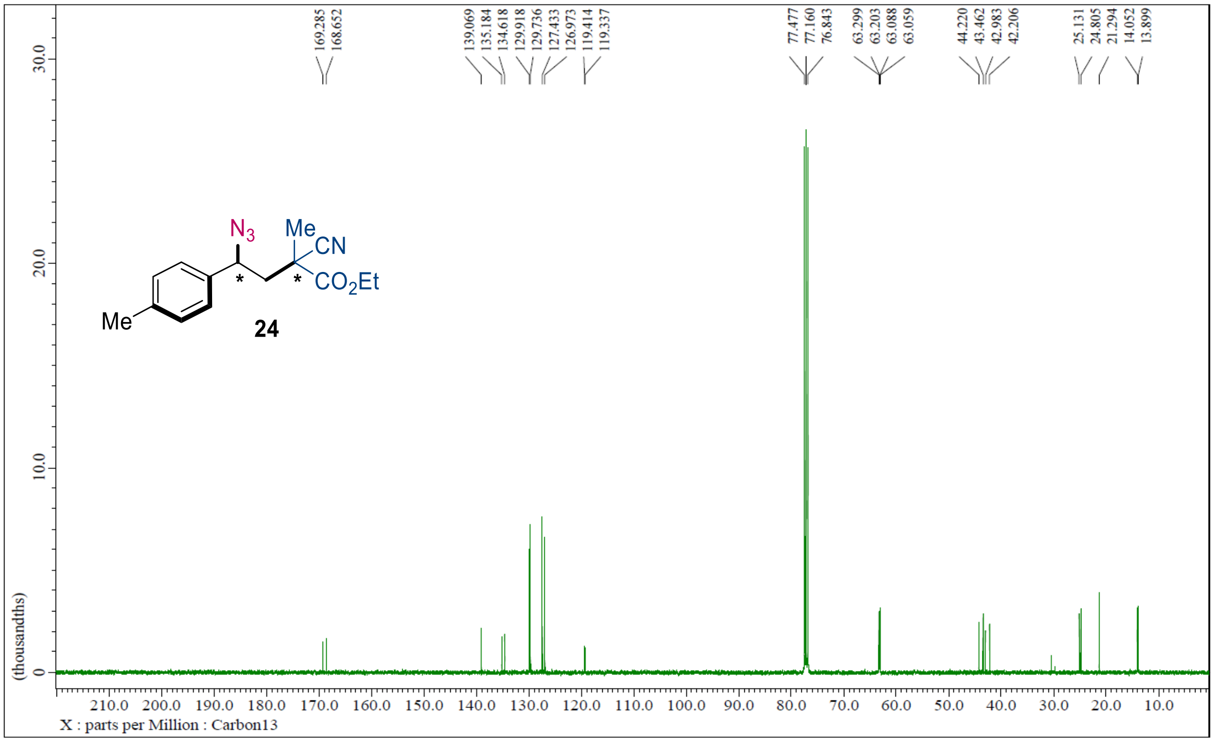
23 ^{13}C NMR (100 MHz, $CDCl_3$)



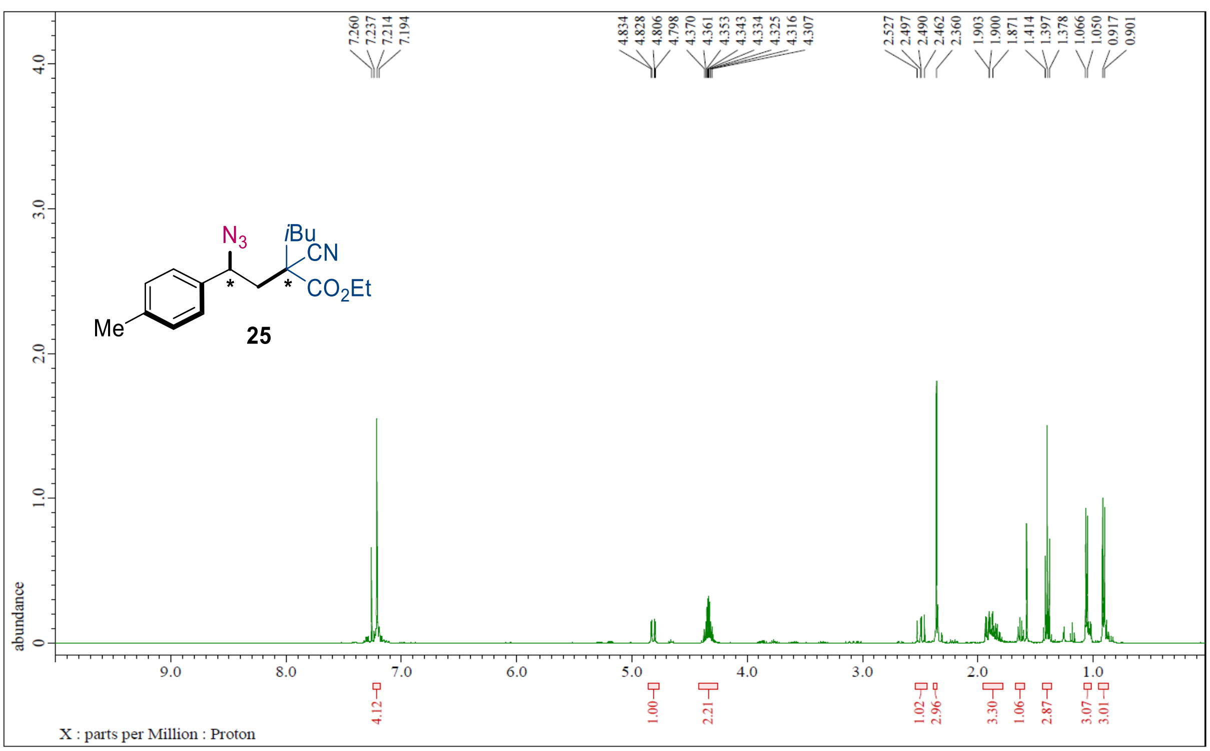
24 ^{1}H NMR (400 MHz, $CDCl_3$)



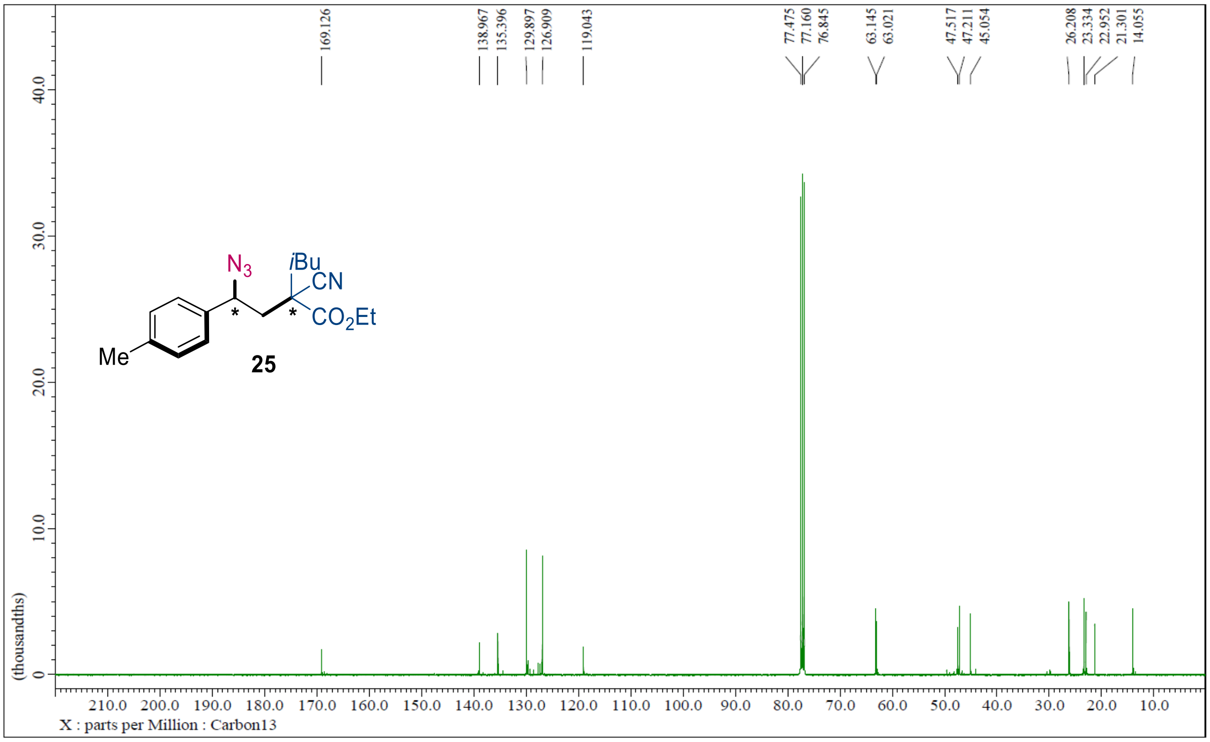
24 ^{13}C NMR (100 MHz, $CDCl_3$)



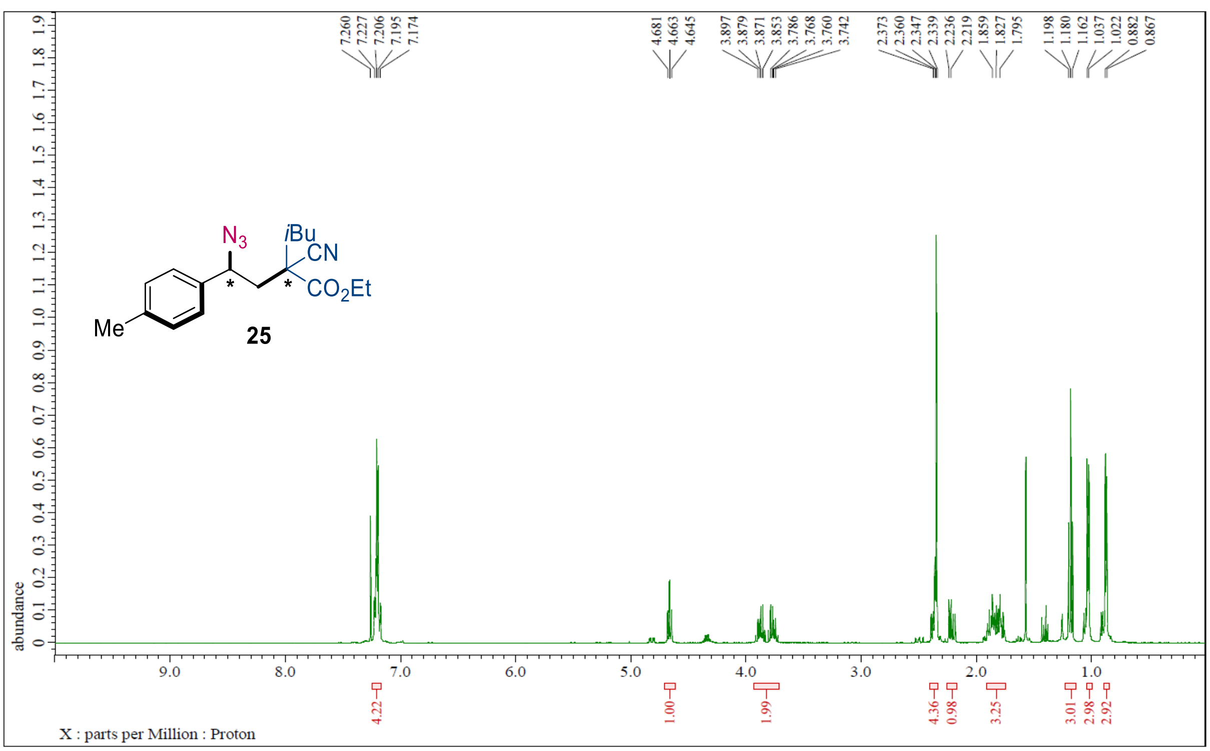
25 ^{1}H NMR (400 MHz, $CDCl_3$)



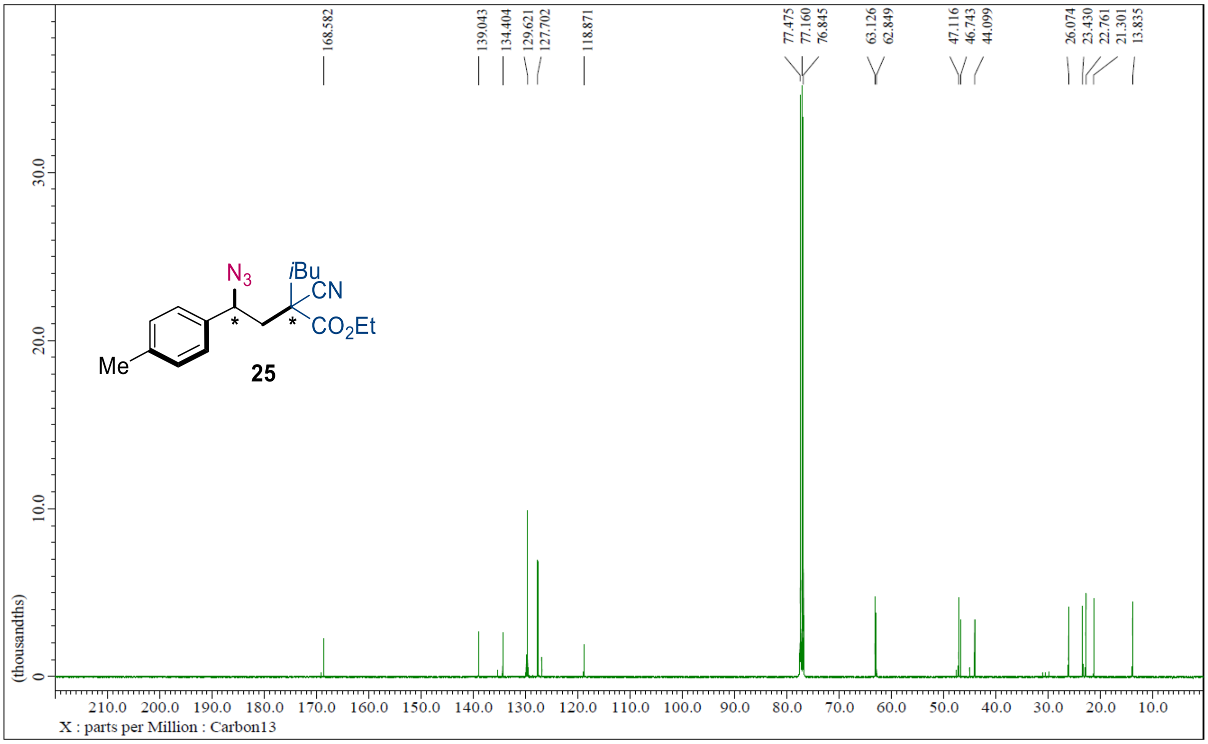
25 ^{13}C NMR (100 MHz, $CDCl_3$)



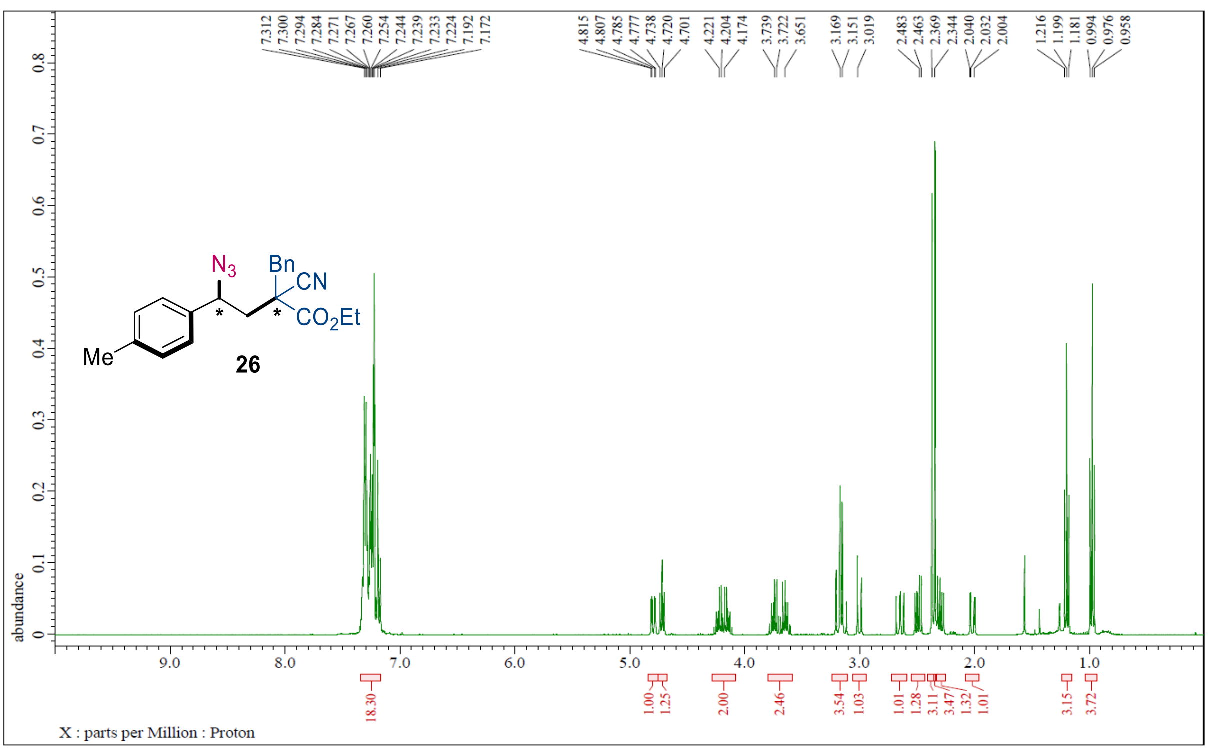
25 ^{1}H NMR (400 MHz, $CDCl_3$)



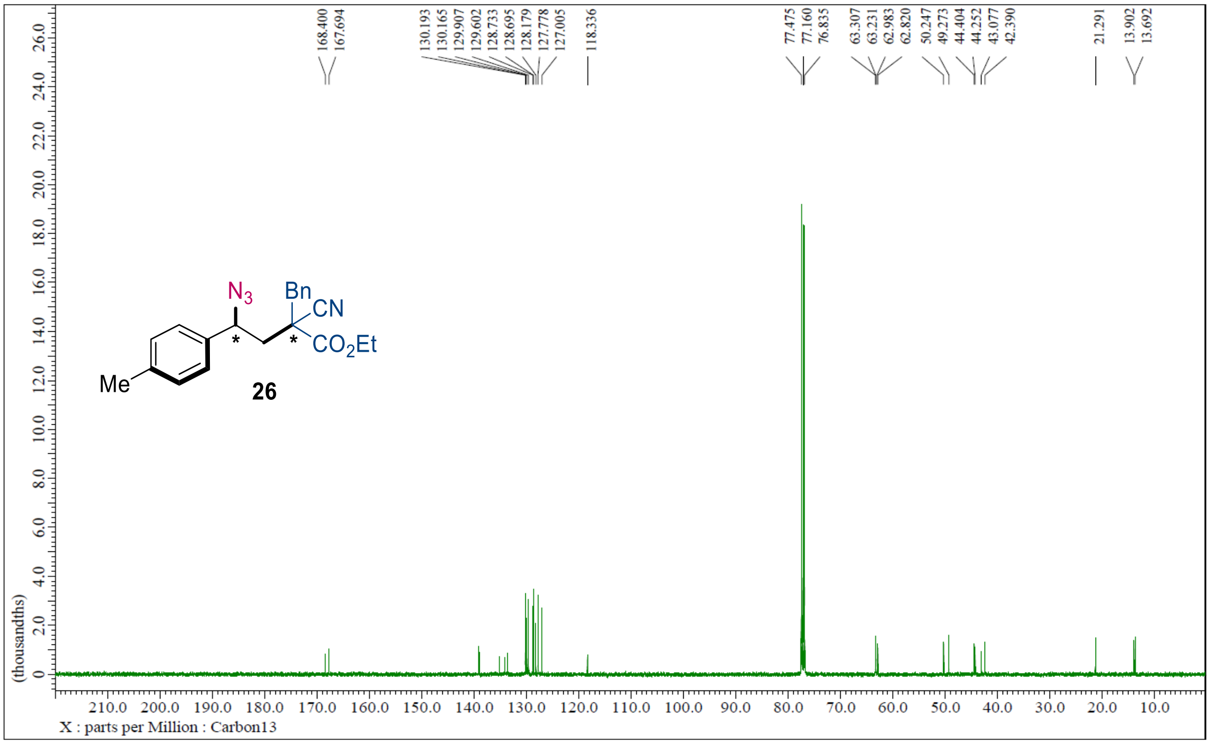
25 ^{13}C NMR (100 MHz, $CDCl_3$)



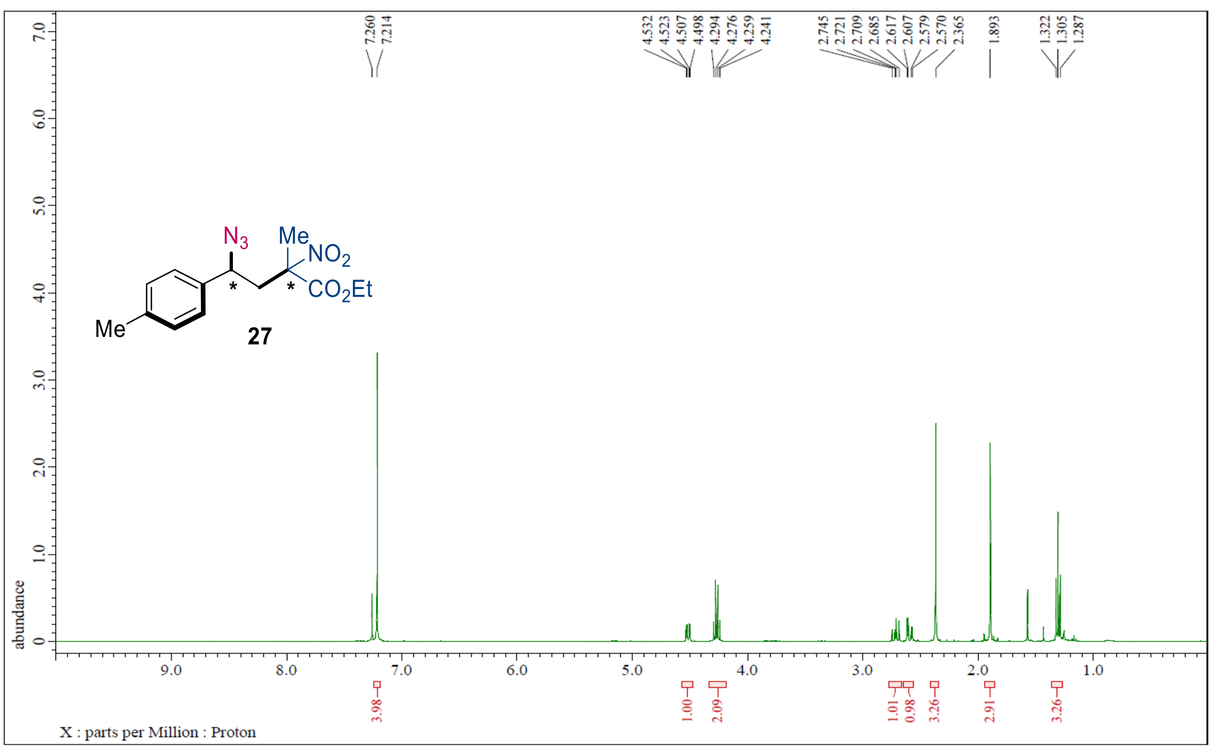
26 ^{1}H NMR (400 MHz, $CDCl_3$)



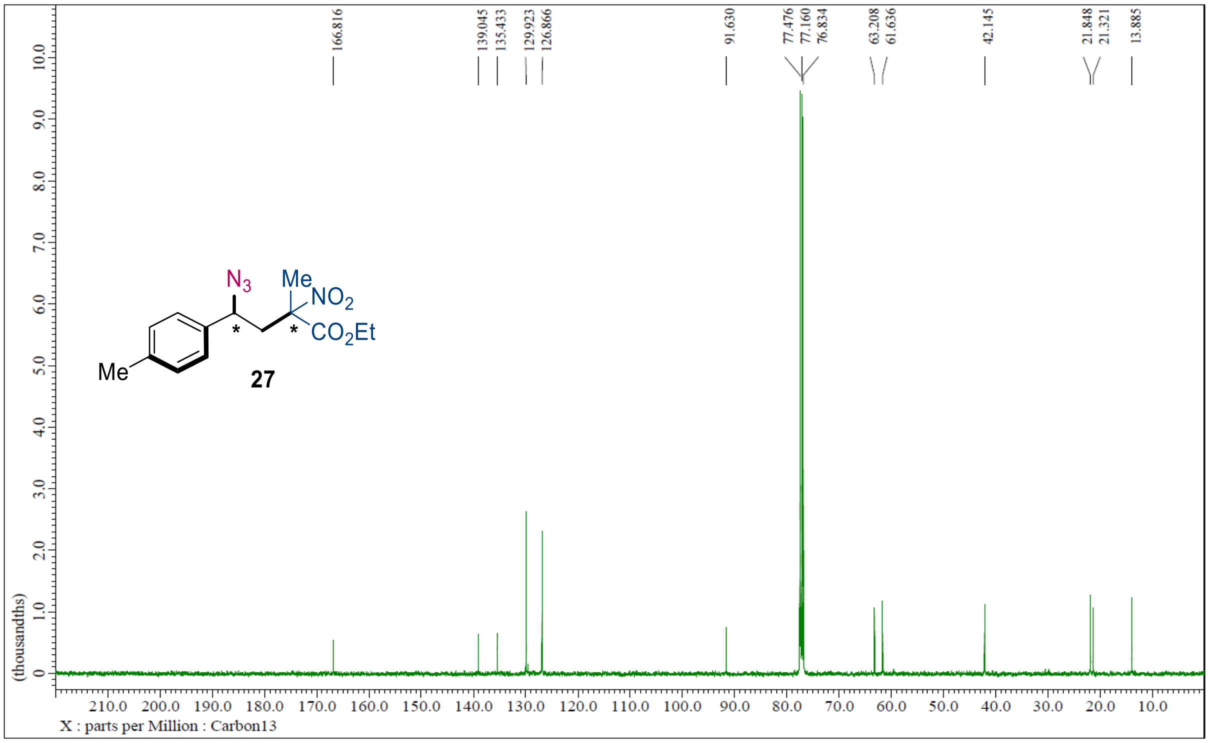
26 ^{13}C NMR (100 MHz, $CDCl_3$)



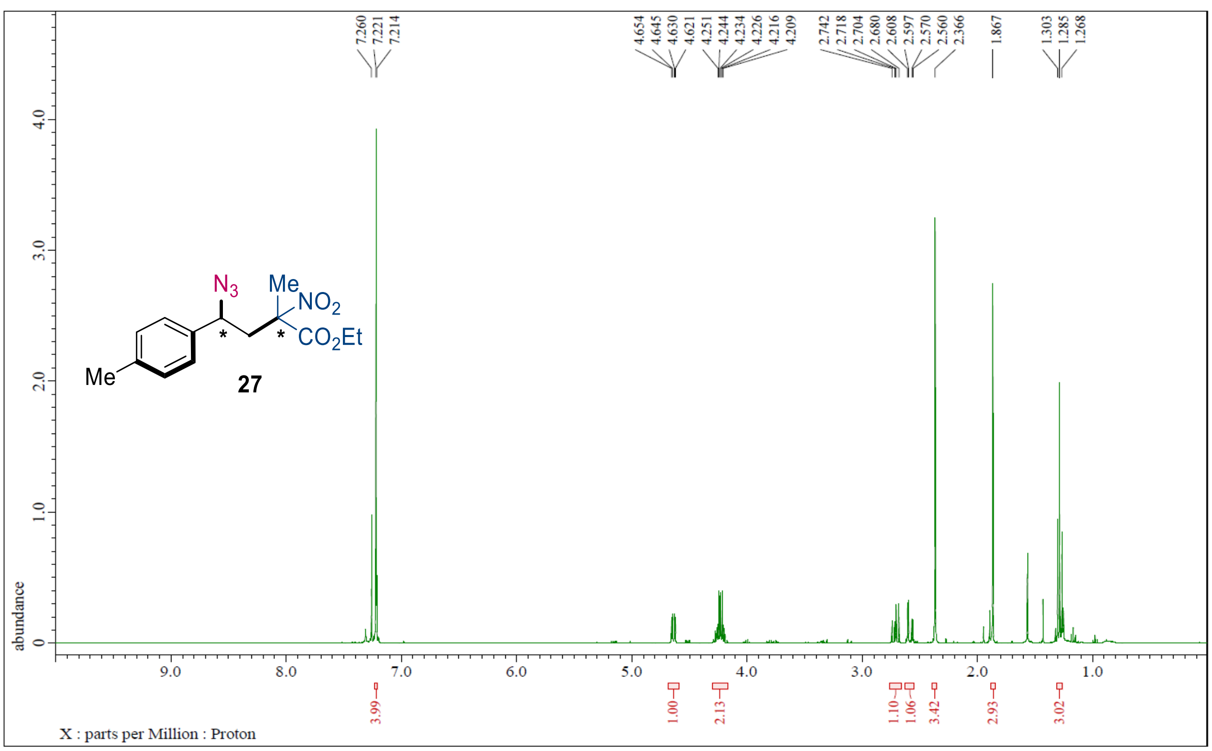
27 ^{1}H NMR (400 MHz, $CDCl_3$)



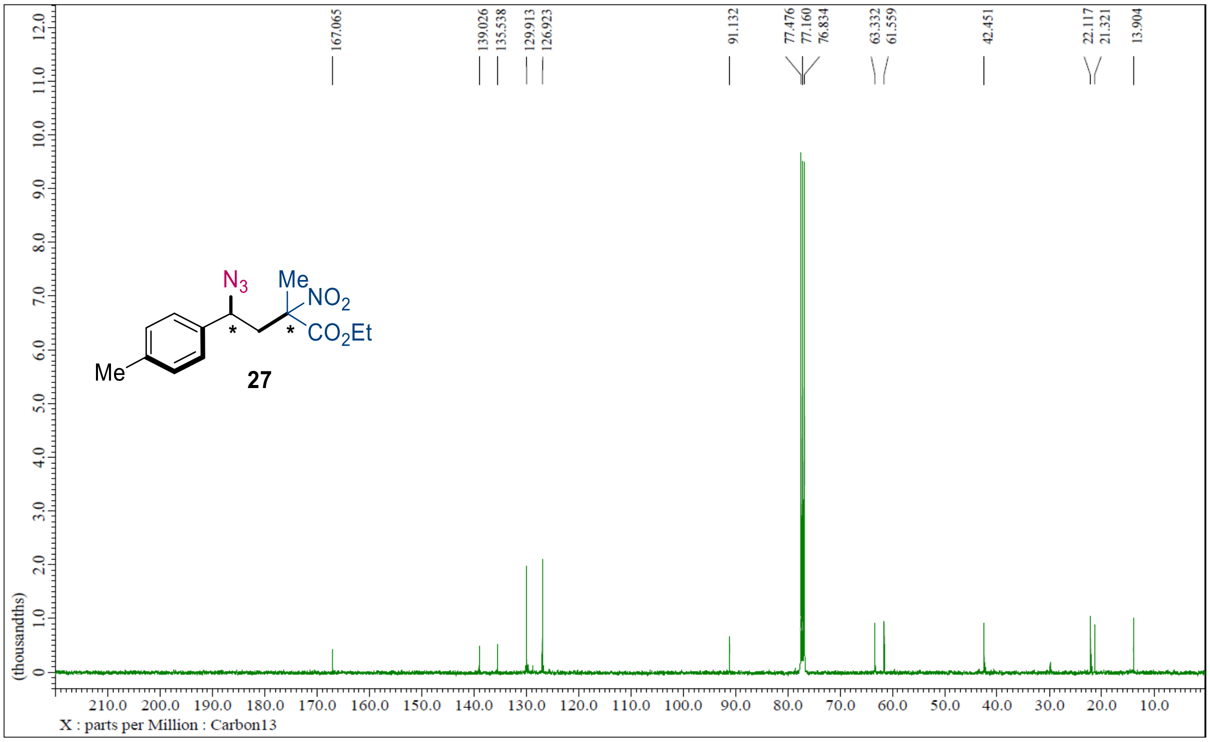
27 ^{13}C NMR (100 MHz, $CDCl_3$)



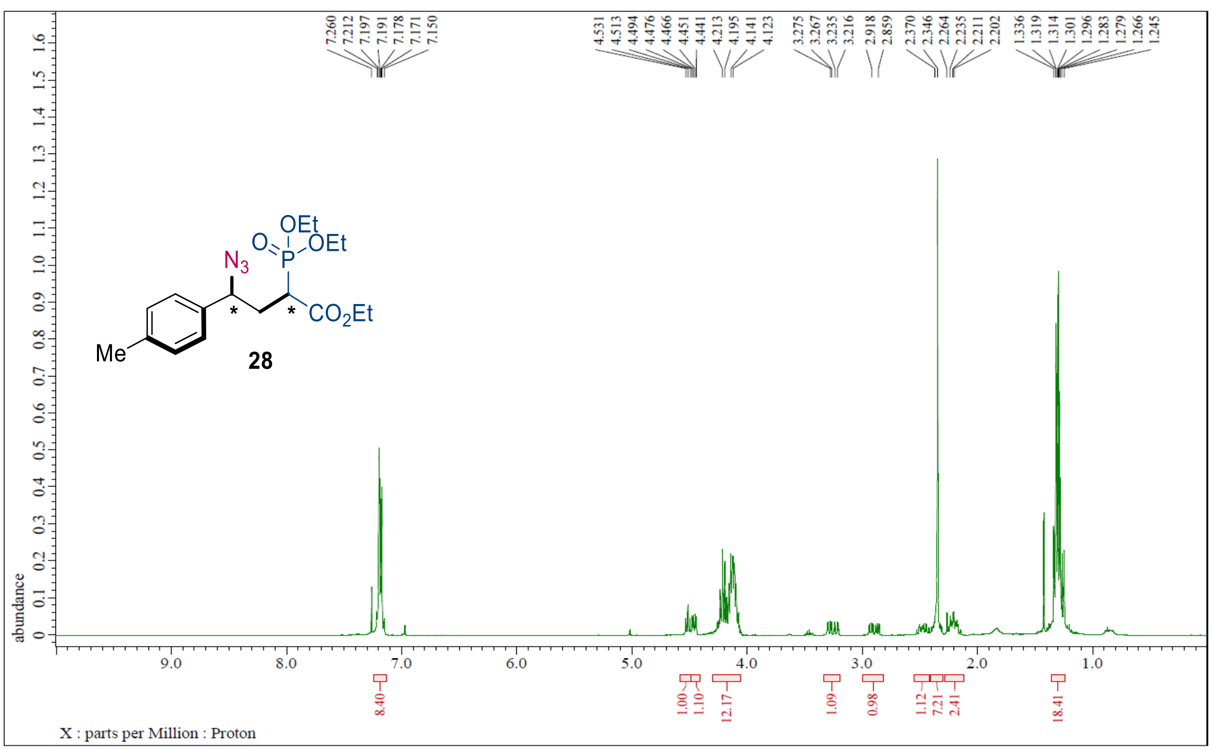
27 ^{1}H NMR (400 MHz, $CDCl_3$)



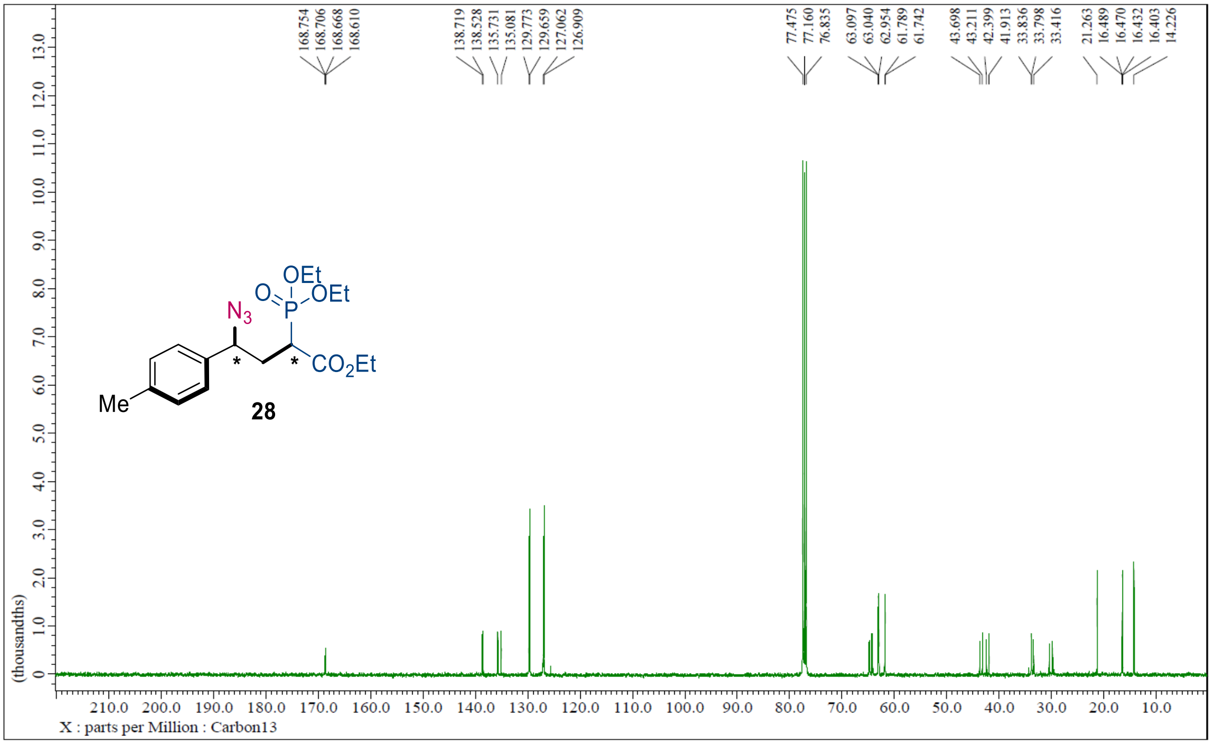
27 ^{13}C NMR (100 MHz, $CDCl_3$)



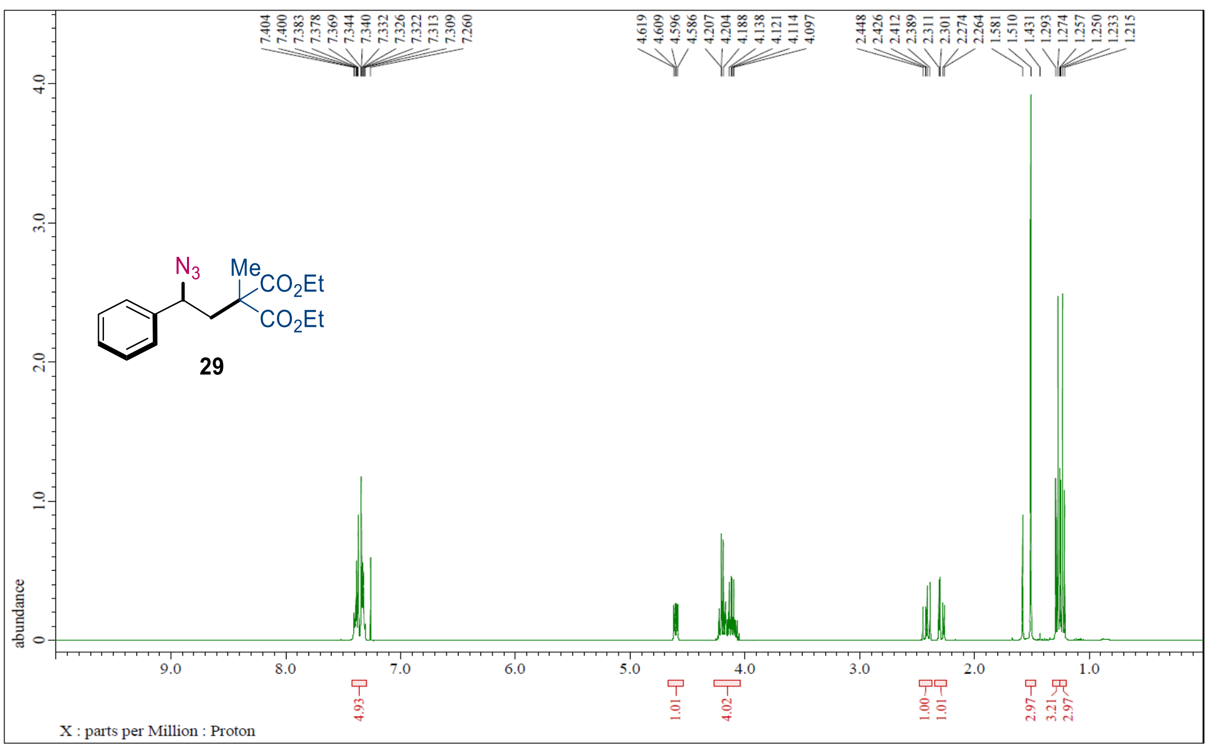
28 ^{1}H NMR (400 MHz, $CDCl_3$)



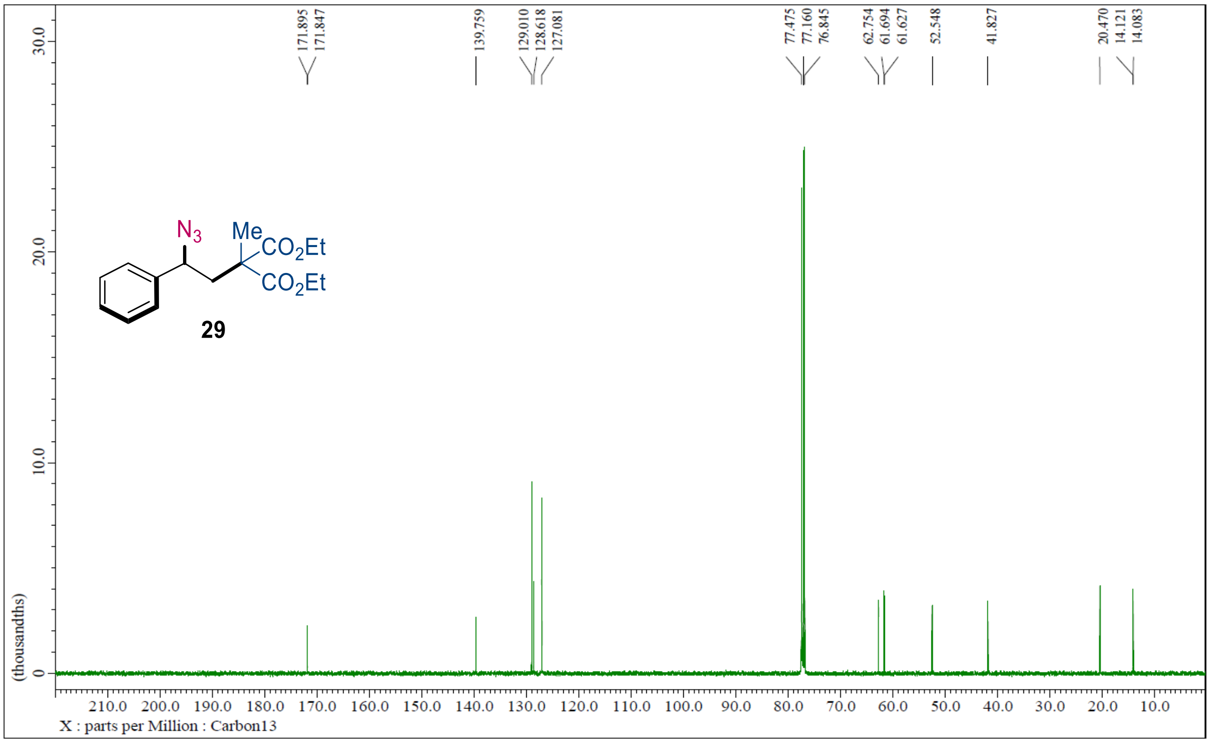
28 ^{13}C NMR (100 MHz, $CDCl_3$)



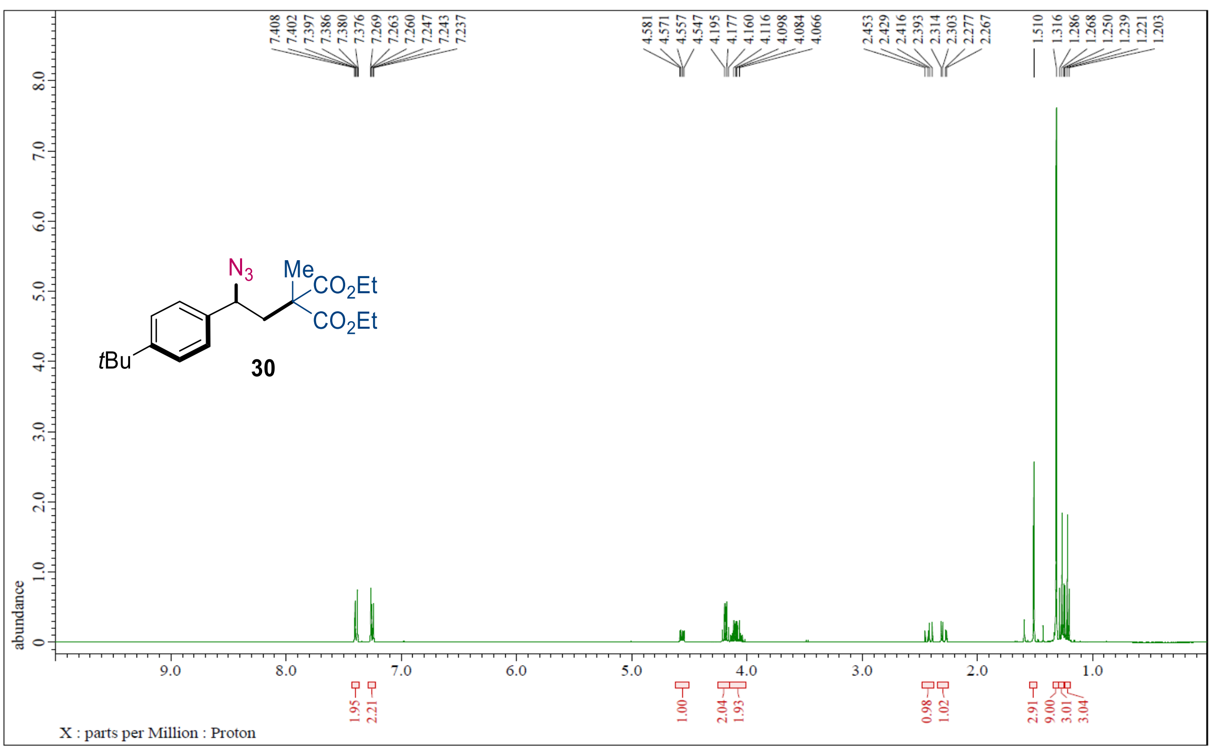
29 ^{1}H NMR (400 MHz, $CDCl_3$)



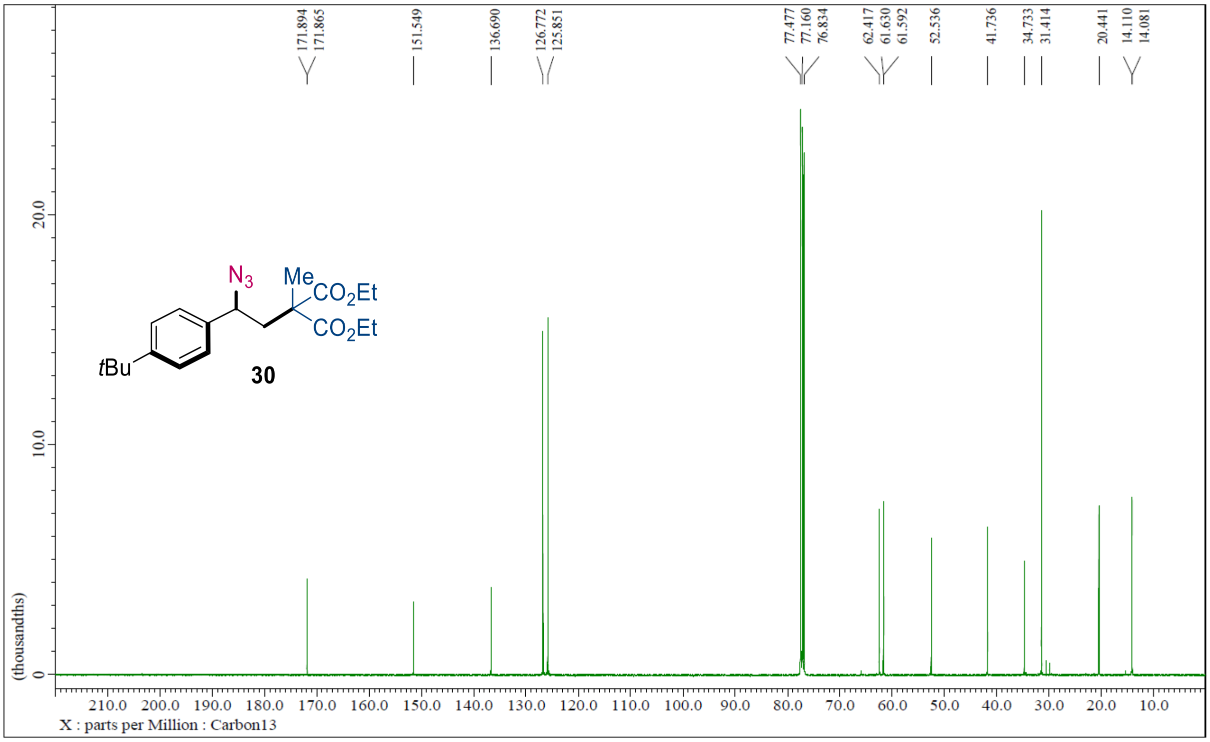
29 ^{13}C NMR (100 MHz, $CDCl_3$)



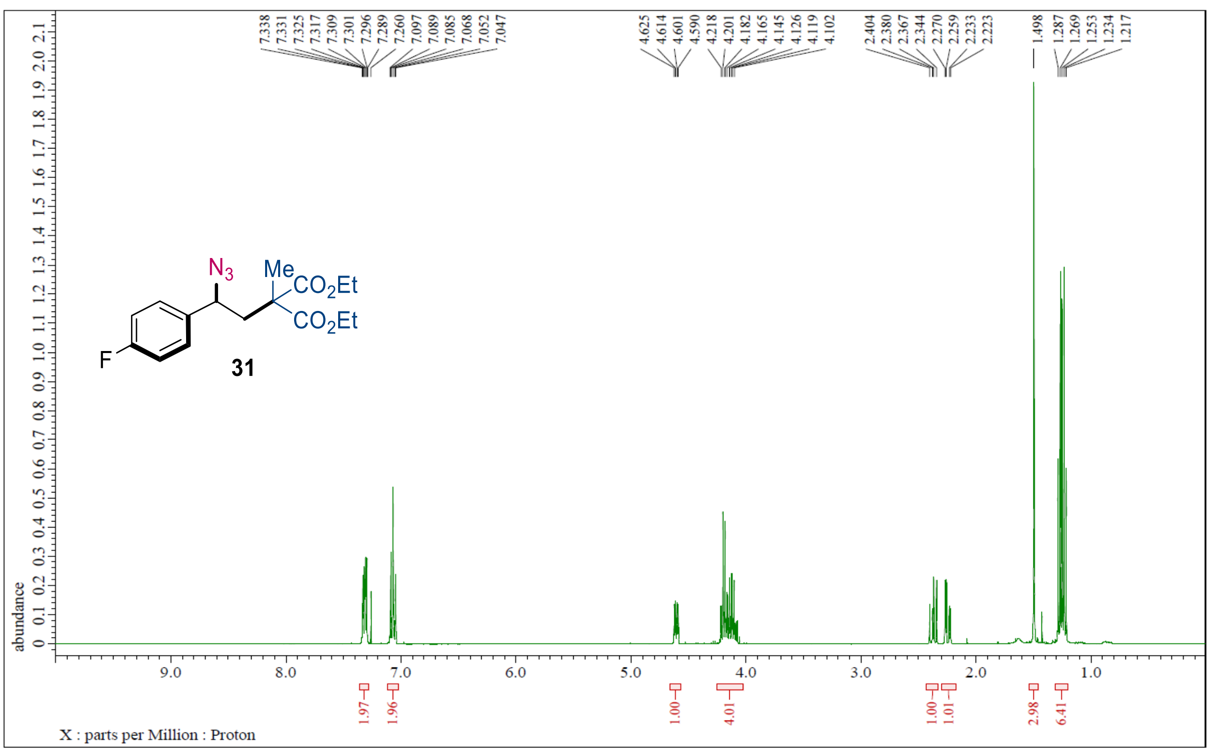
30 ^{1}H NMR (400 MHz, $CDCl_3$)



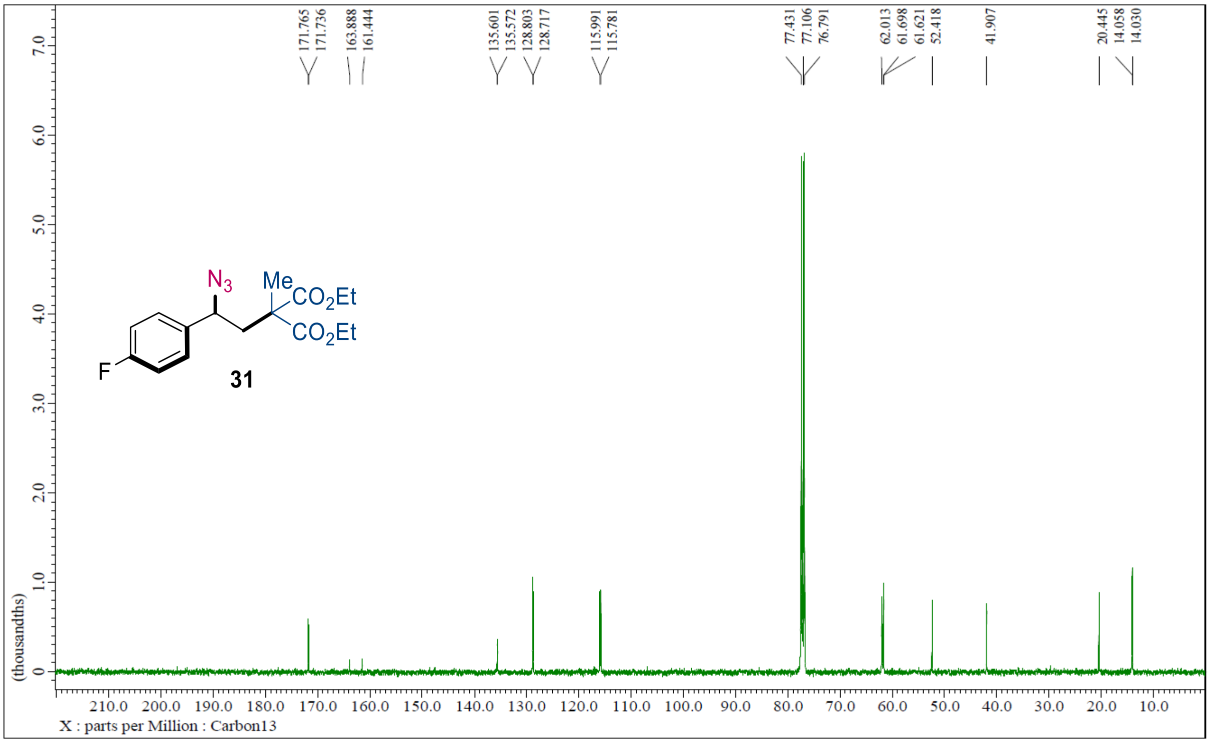
30 ^{13}C NMR (100 MHz, $CDCl_3$)



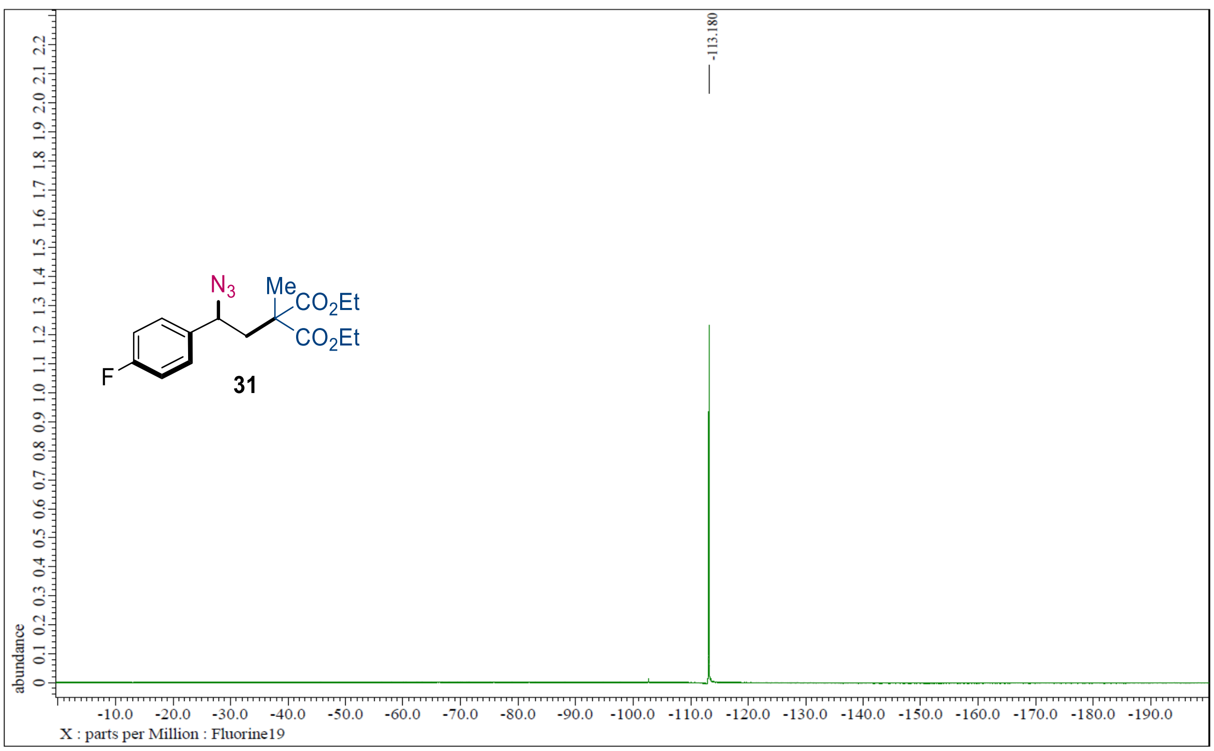
31 ^{1}H NMR (400 MHz, $CDCl_3$)



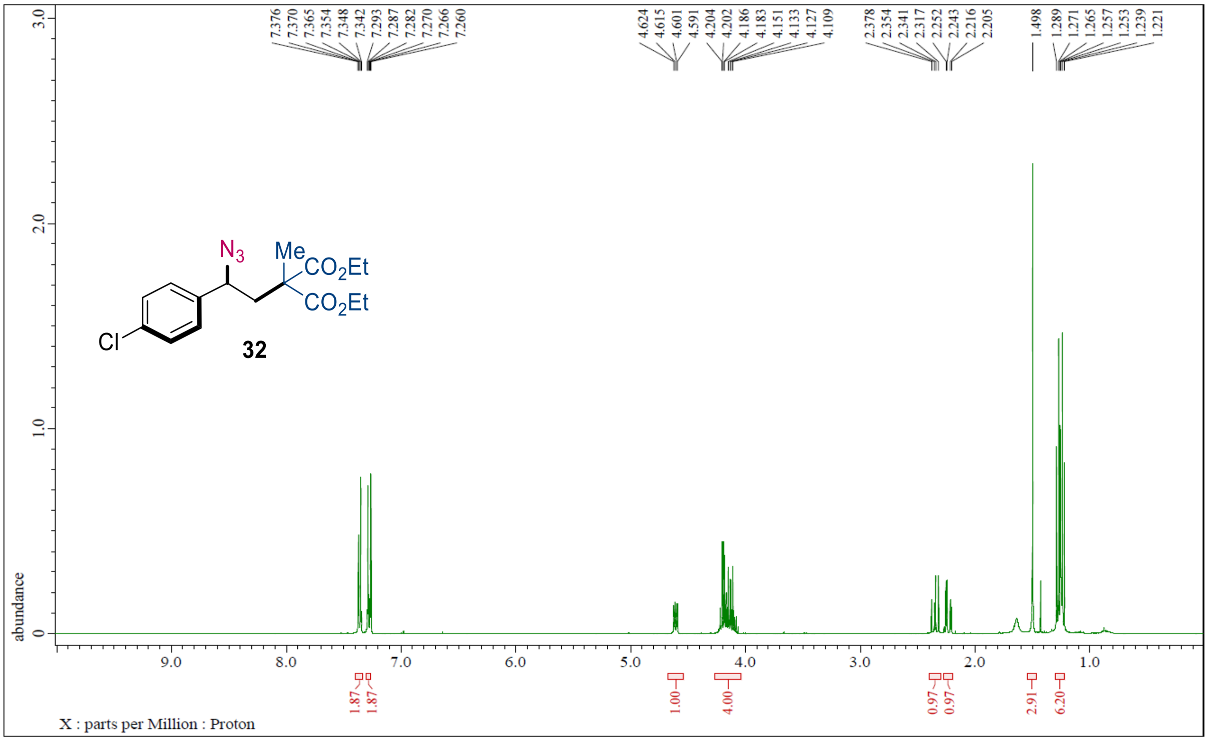
31 ^{13}C NMR (100 MHz, $CDCl_3$)



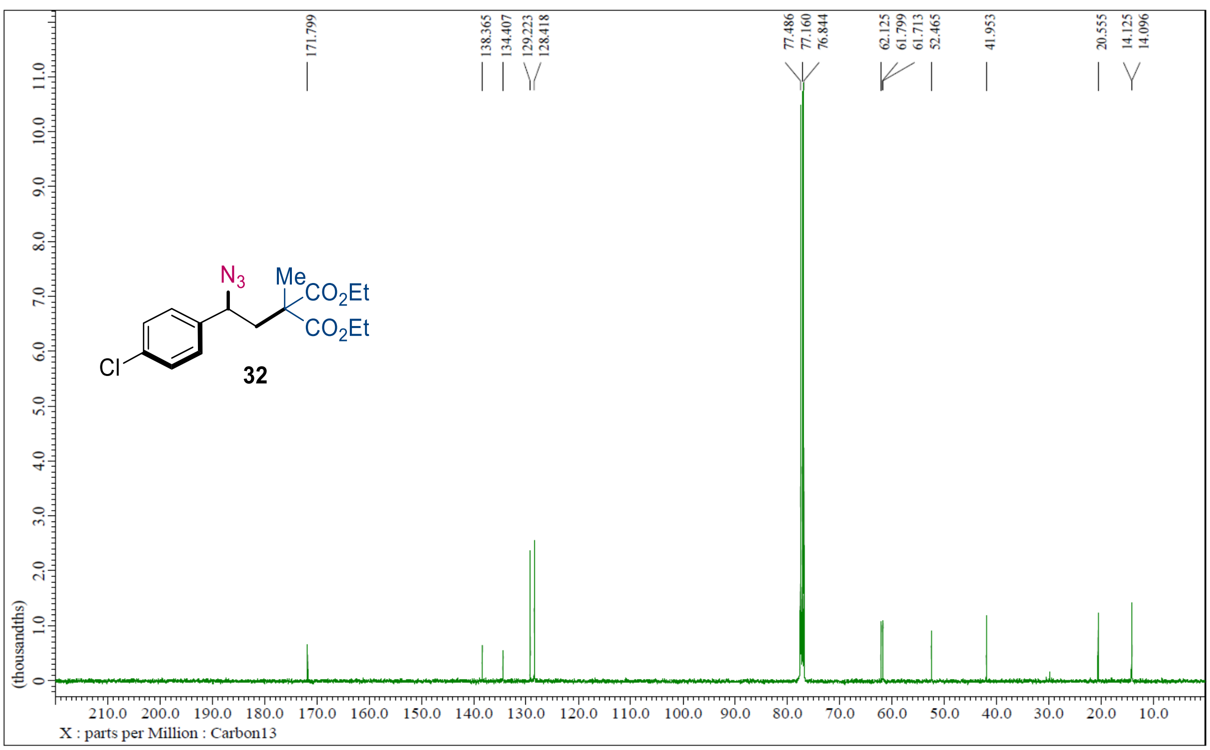
31 ^{19}F NMR (376 MHz, $CDCl_3$)



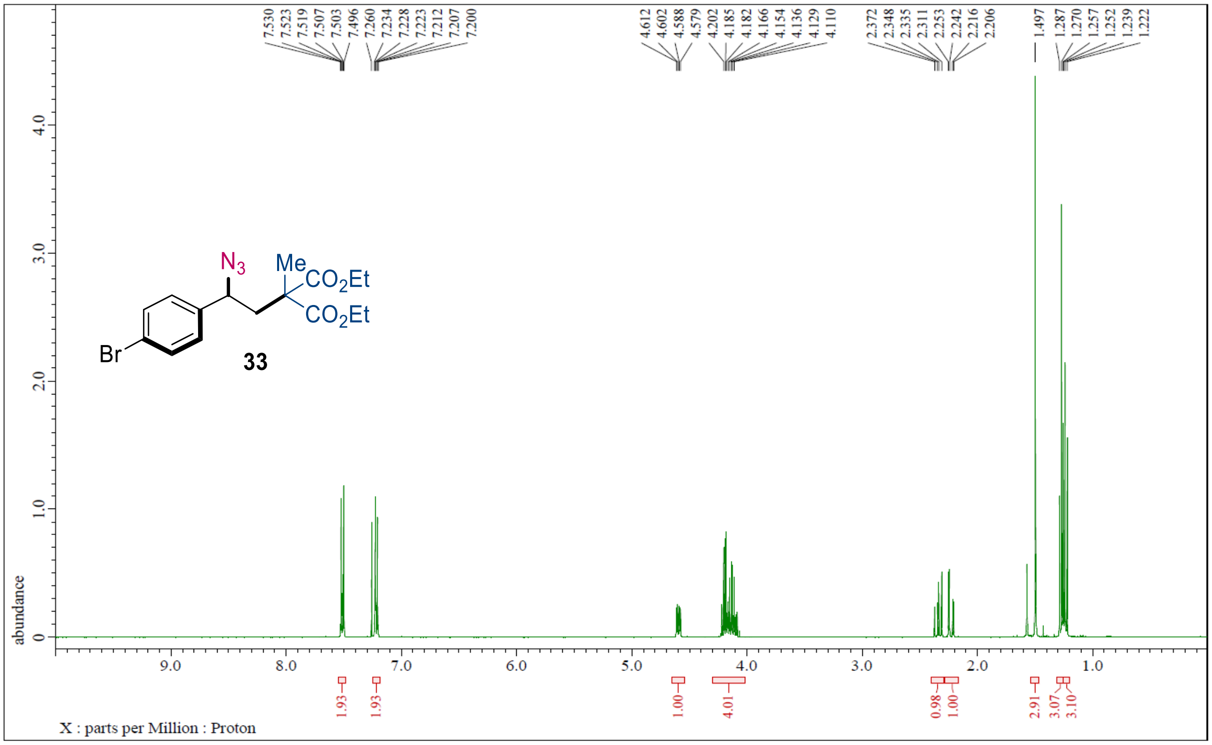
32 ^{1}H NMR (400 MHz, $CDCl_3$)



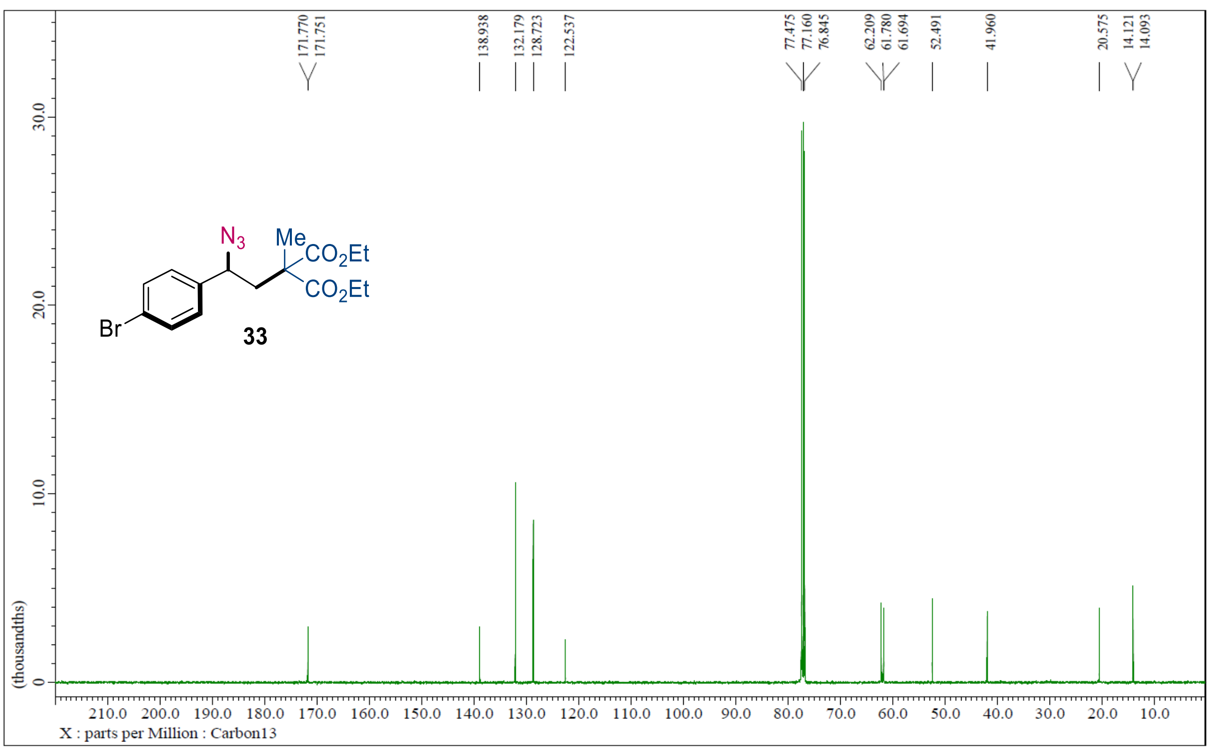
32 ^{13}C NMR (100 MHz, $CDCl_3$)



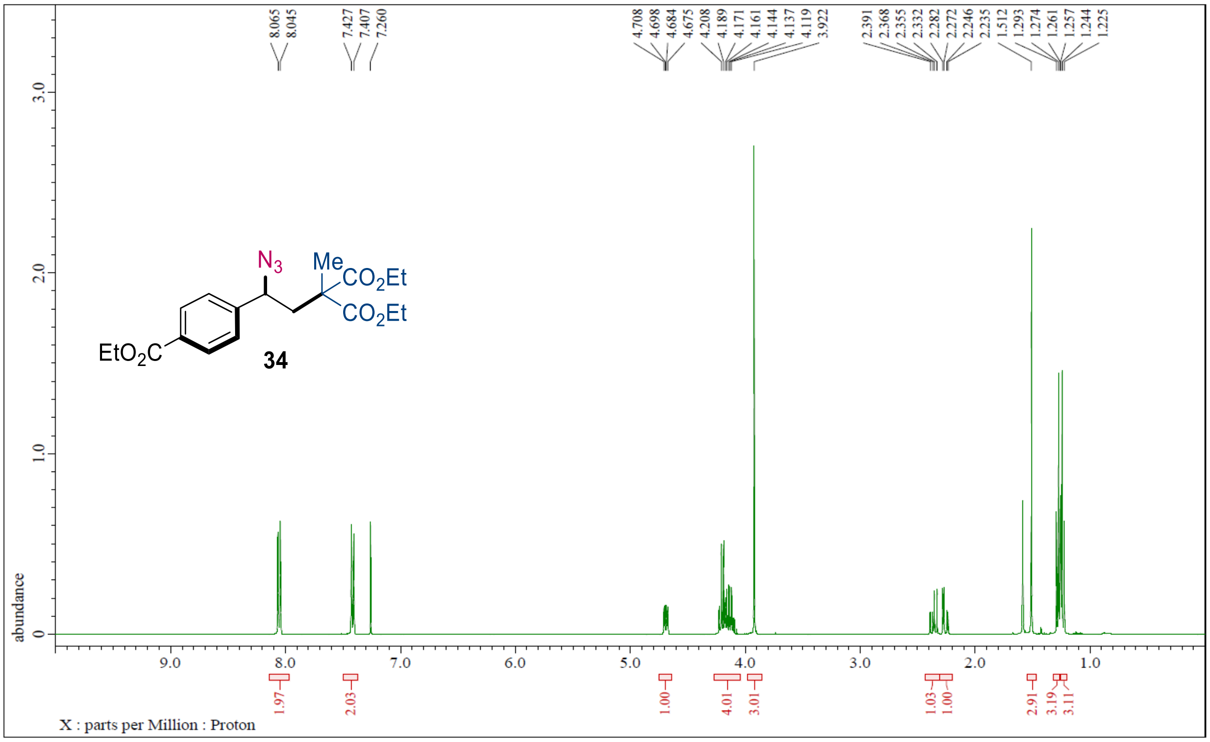
33 ^{1}H NMR (400 MHz, $CDCl_3$)



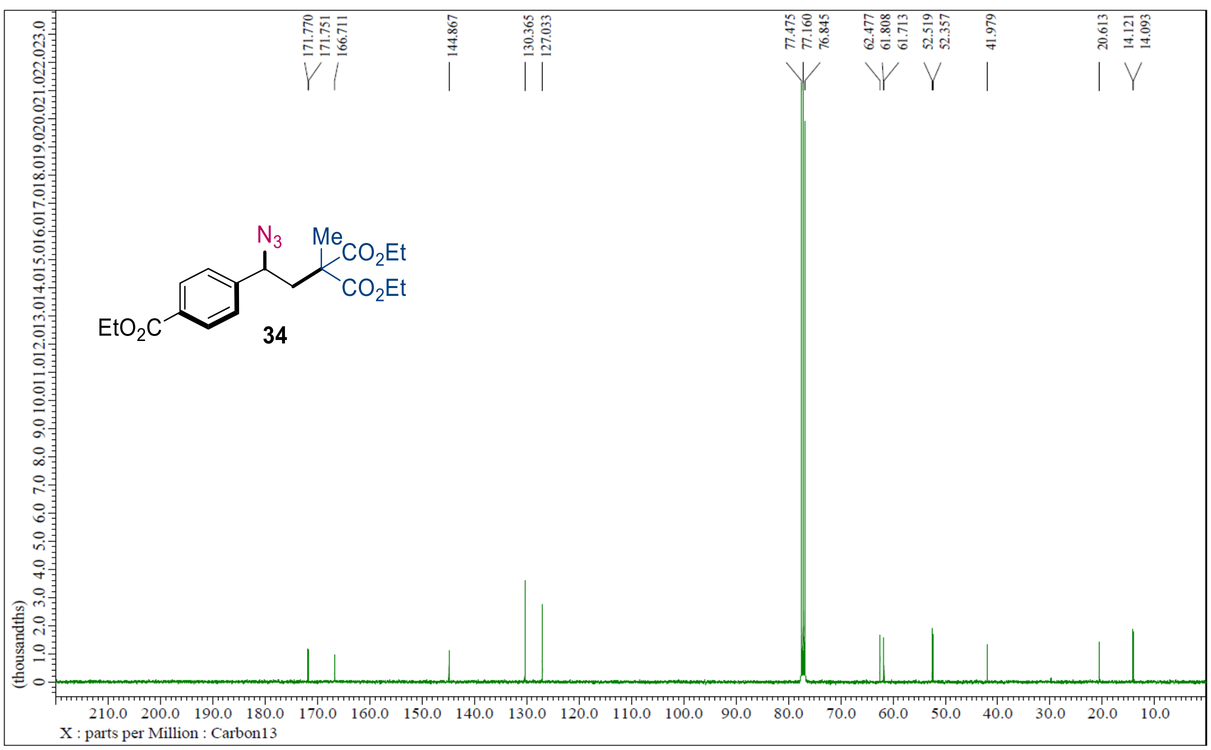
33 ^{13}C NMR (100 MHz, $CDCl_3$)



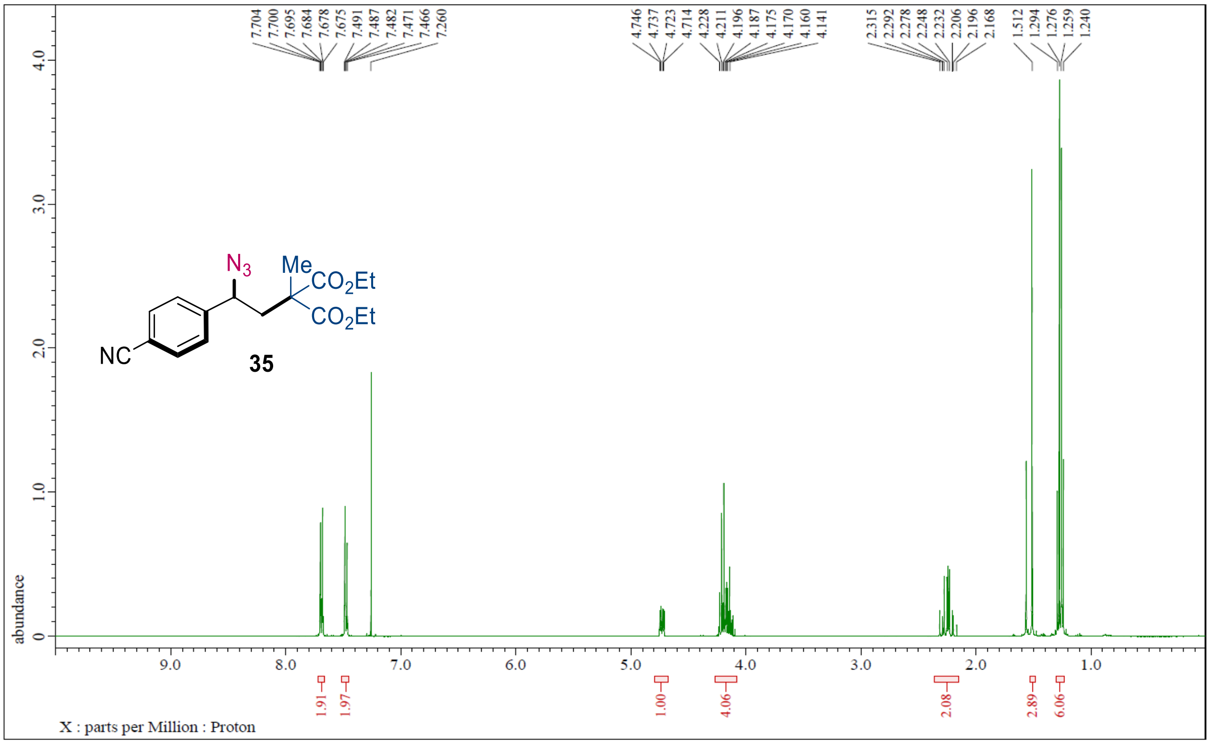
34 ^{1}H NMR (400 MHz, $CDCl_3$)



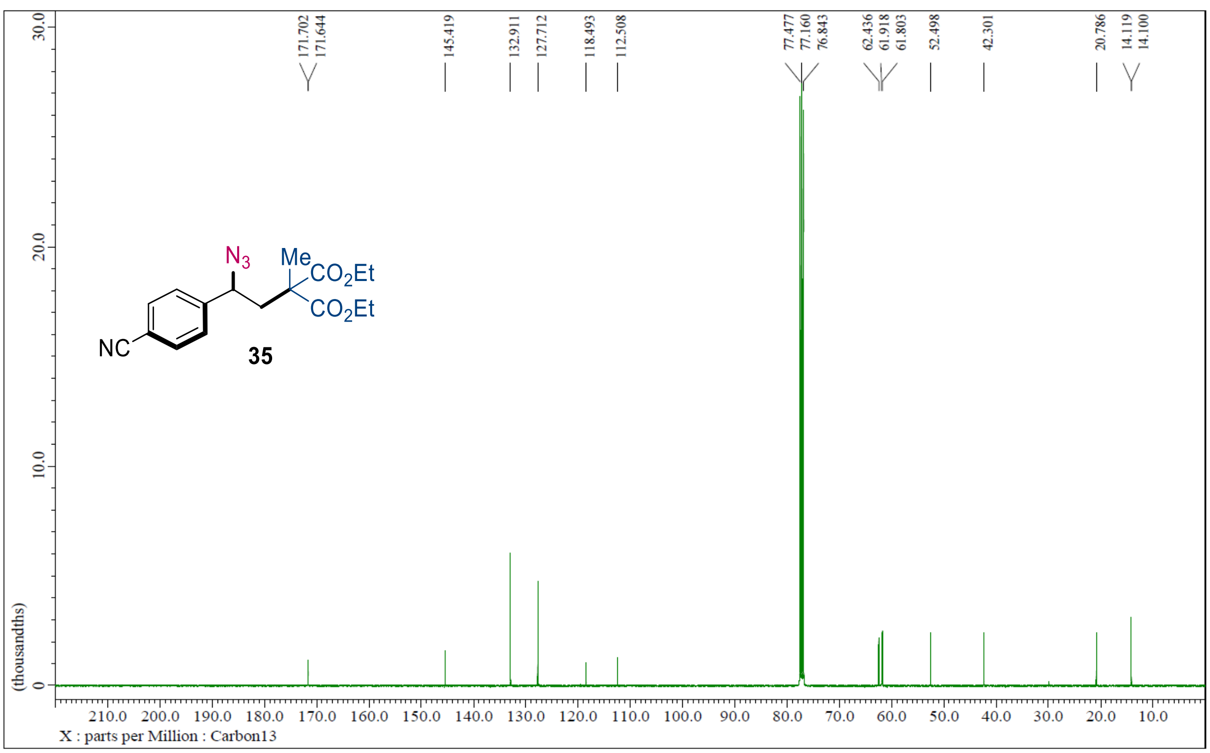
34 ^{13}C NMR (100 MHz, $CDCl_3$)



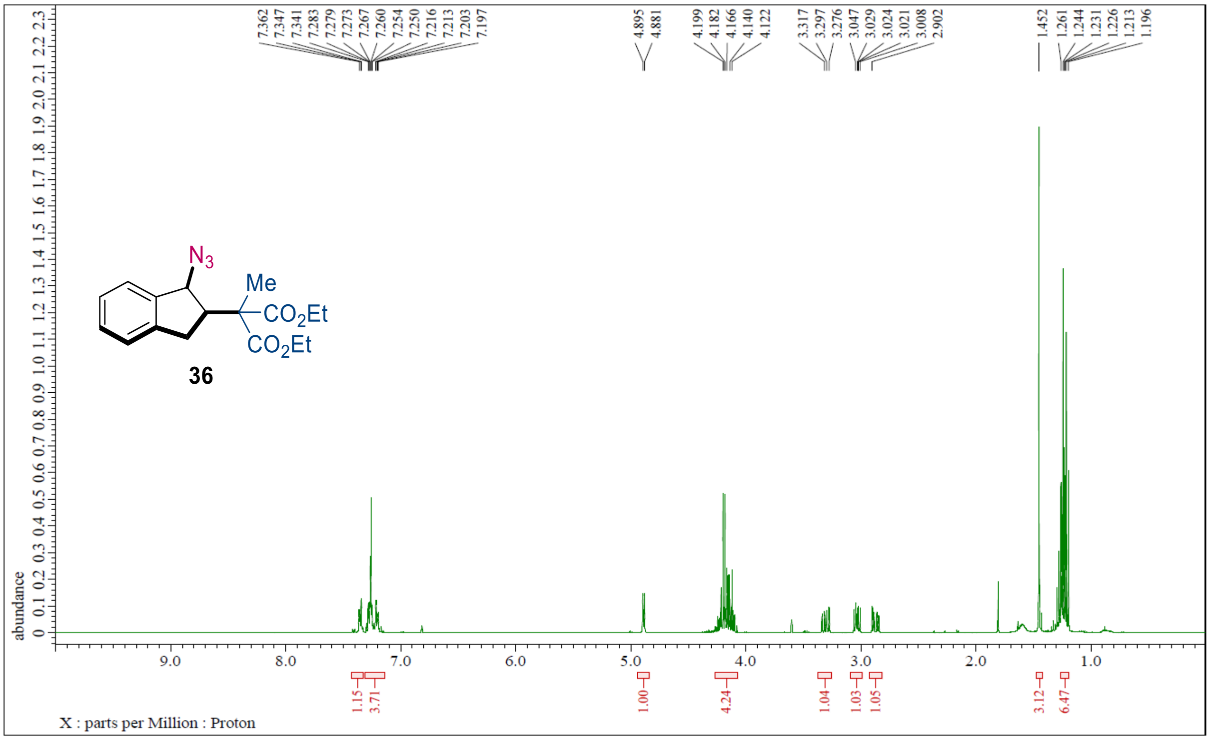
35 ^{1}H NMR (400 MHz, $CDCl_3$)



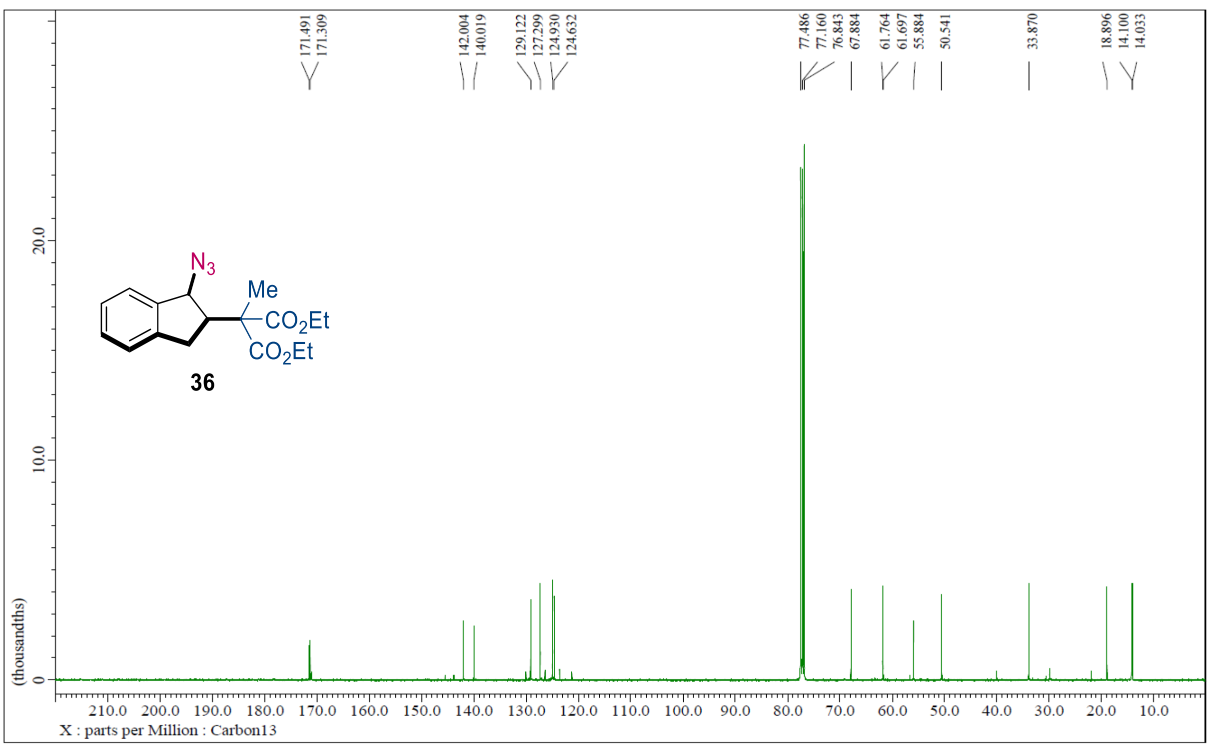
35 ^{13}C NMR (100 MHz, $CDCl_3$)



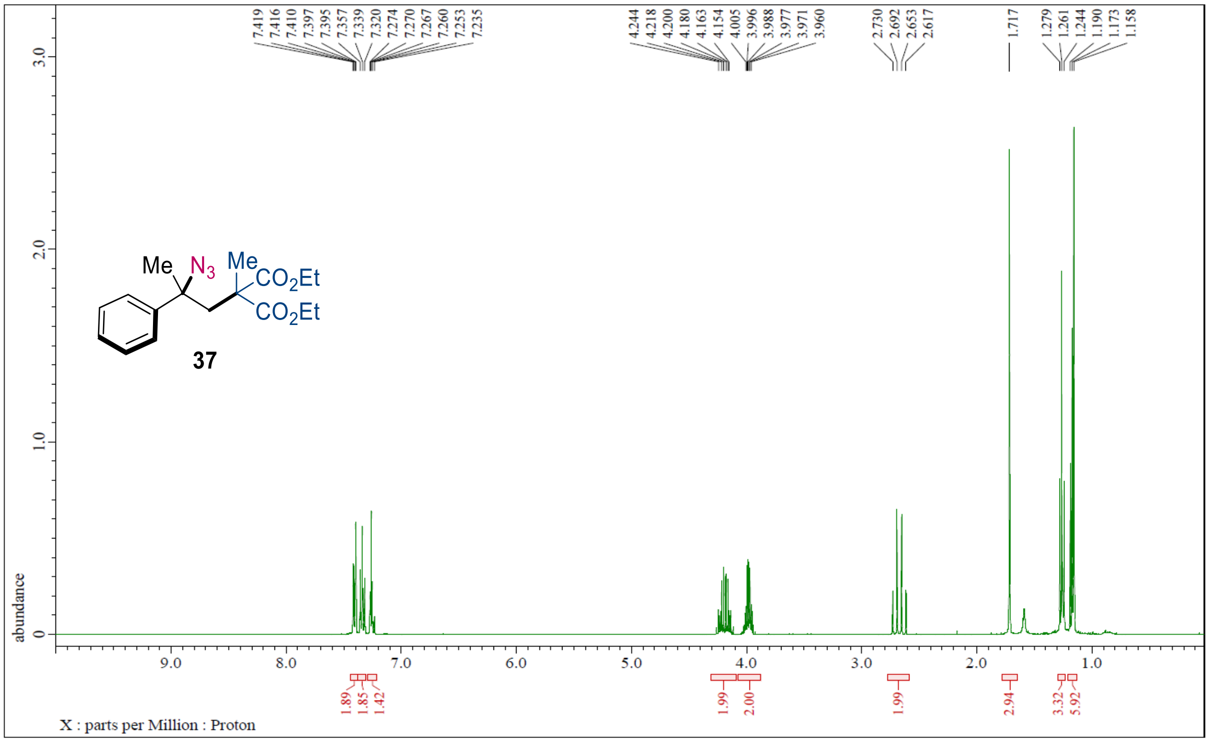
36 ^{1}H NMR (400 MHz, $CDCl_3$)



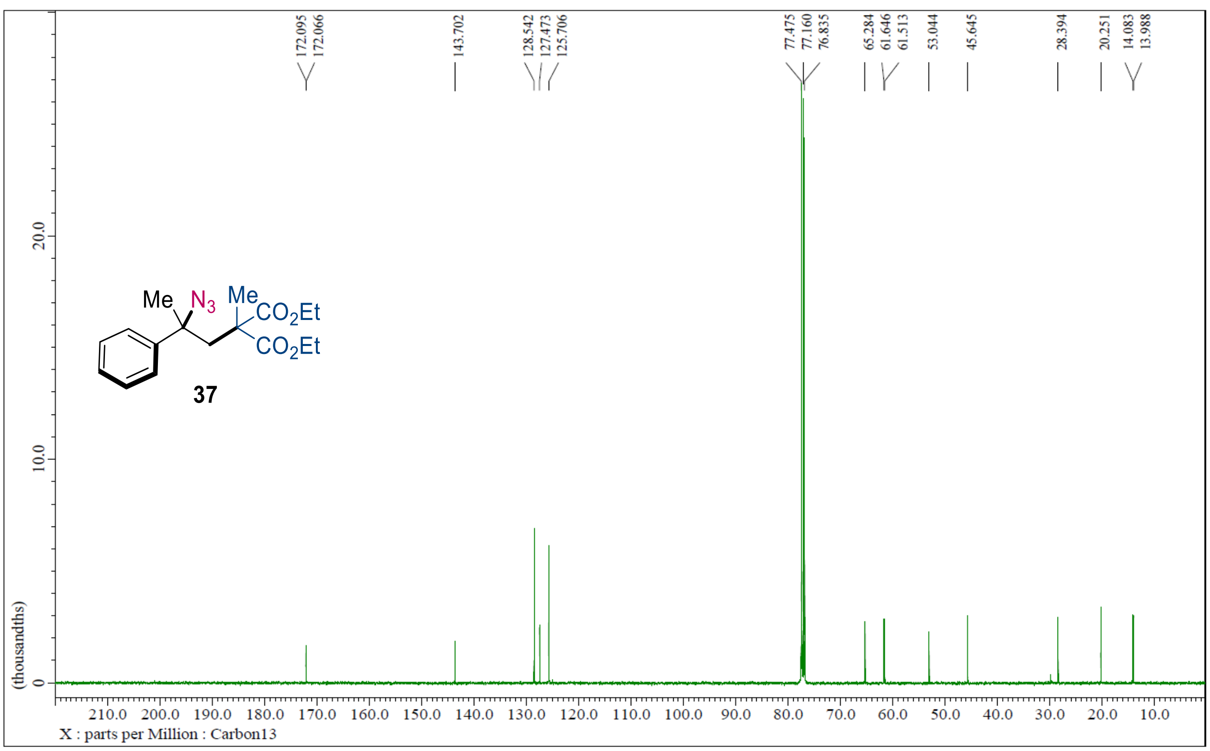
36 ^{13}C NMR (100 MHz, $CDCl_3$)



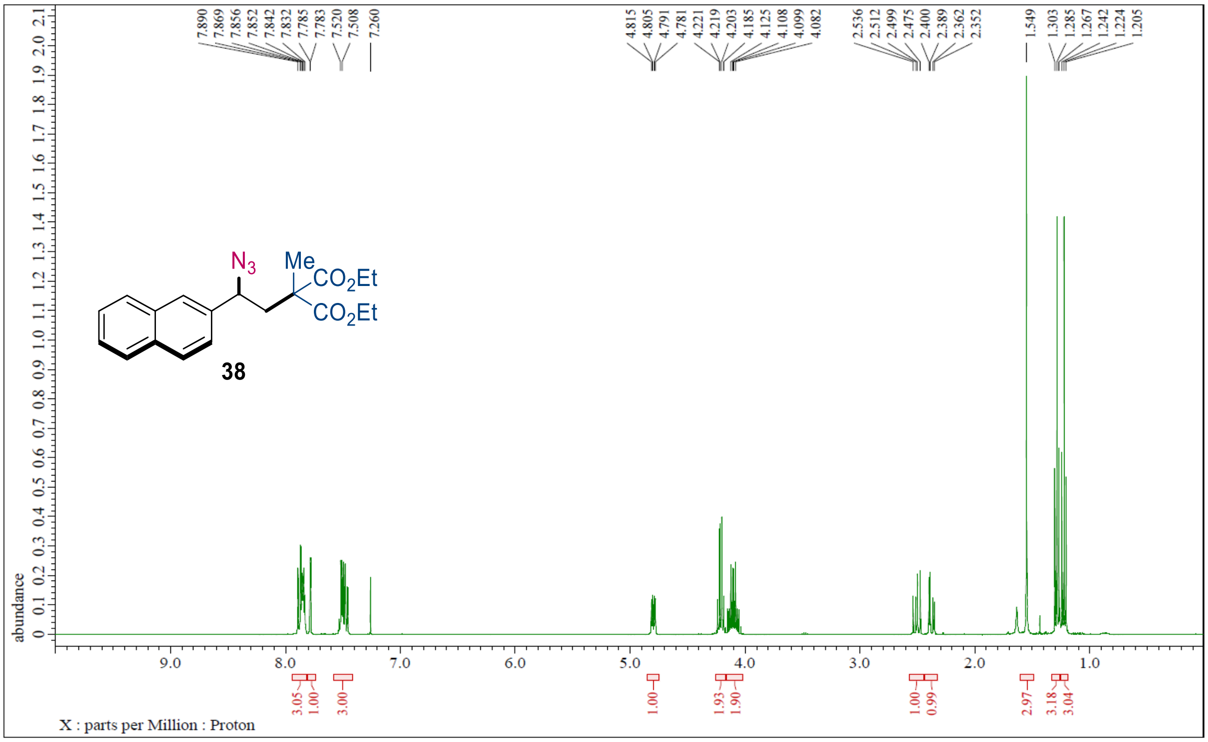
37 ^{1}H NMR (400 MHz, $CDCl_3$)



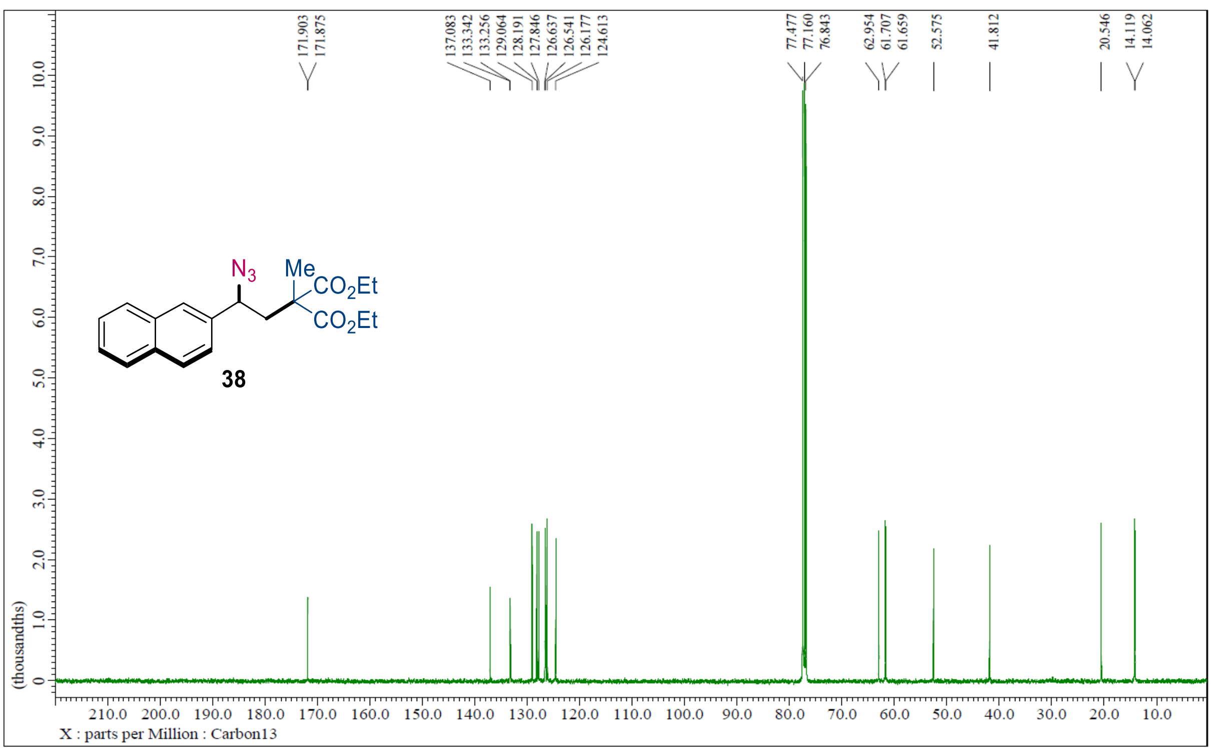
37 ^{13}C NMR (100 MHz, $CDCl_3$)



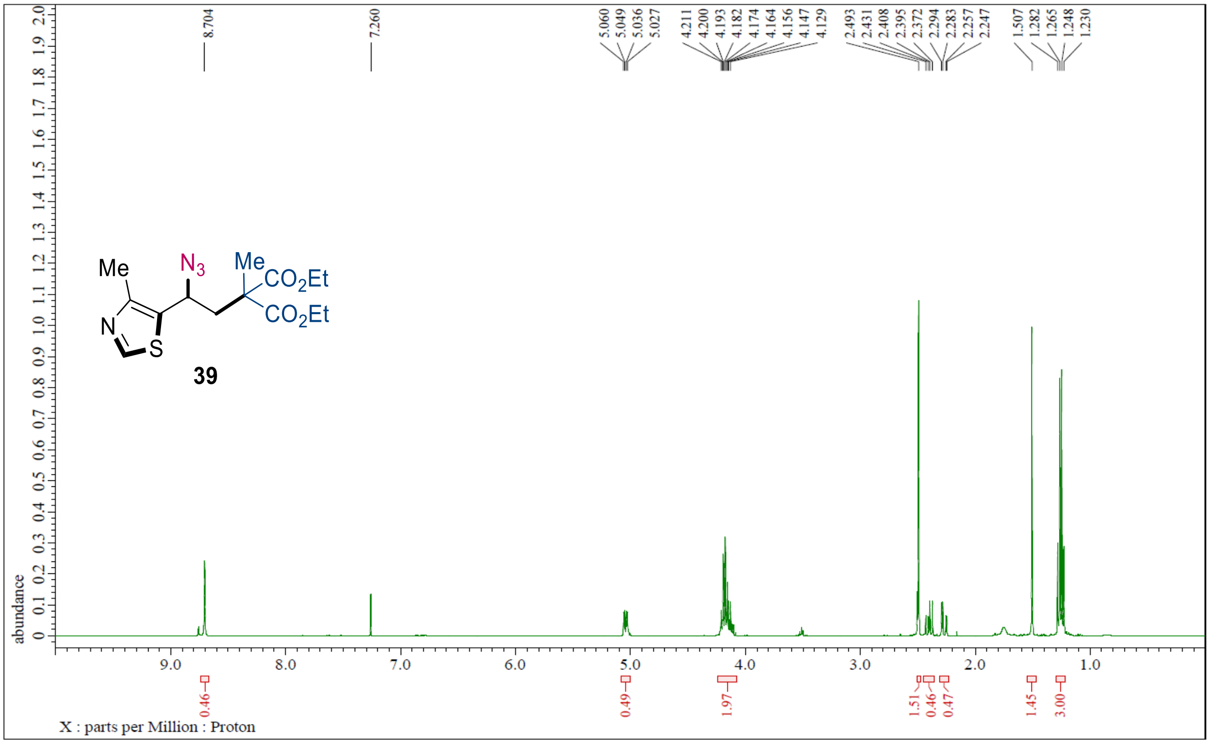
38 ^{1}H NMR (400 MHz, $CDCl_3$)



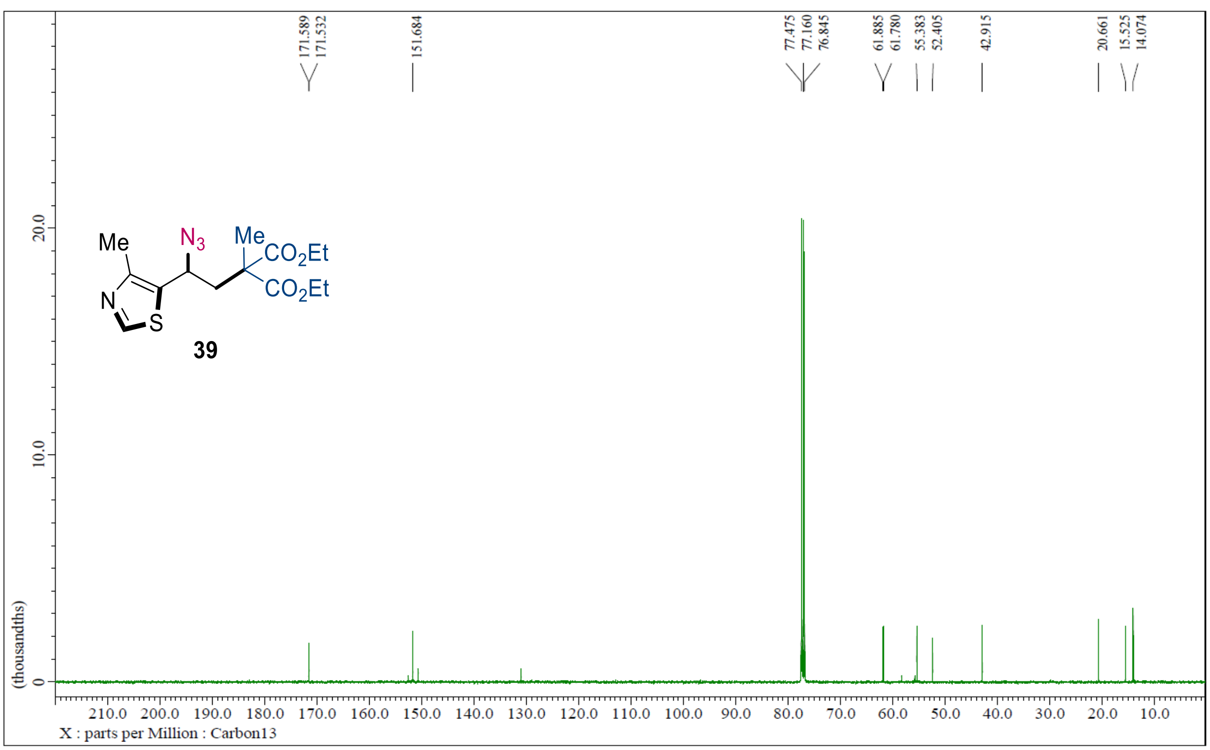
38 ^{13}C NMR (100 MHz, $CDCl_3$)



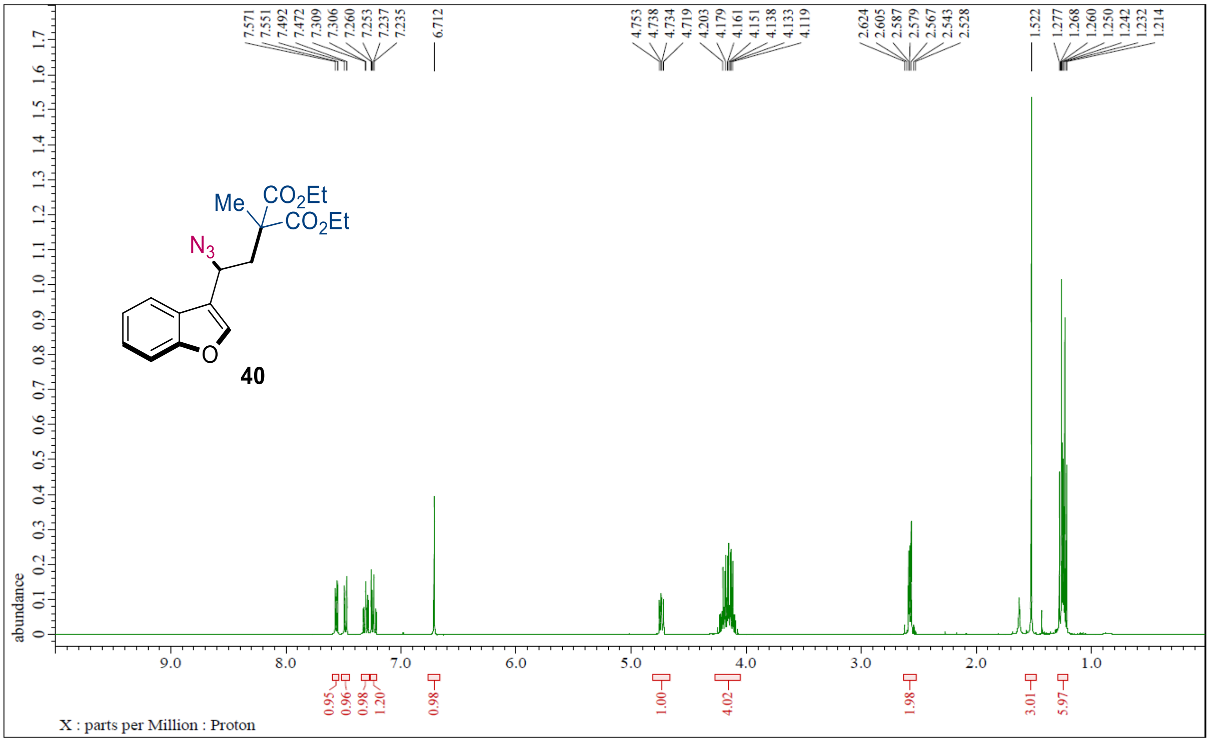
39 ^{1}H NMR (400 MHz, $CDCl_3$)



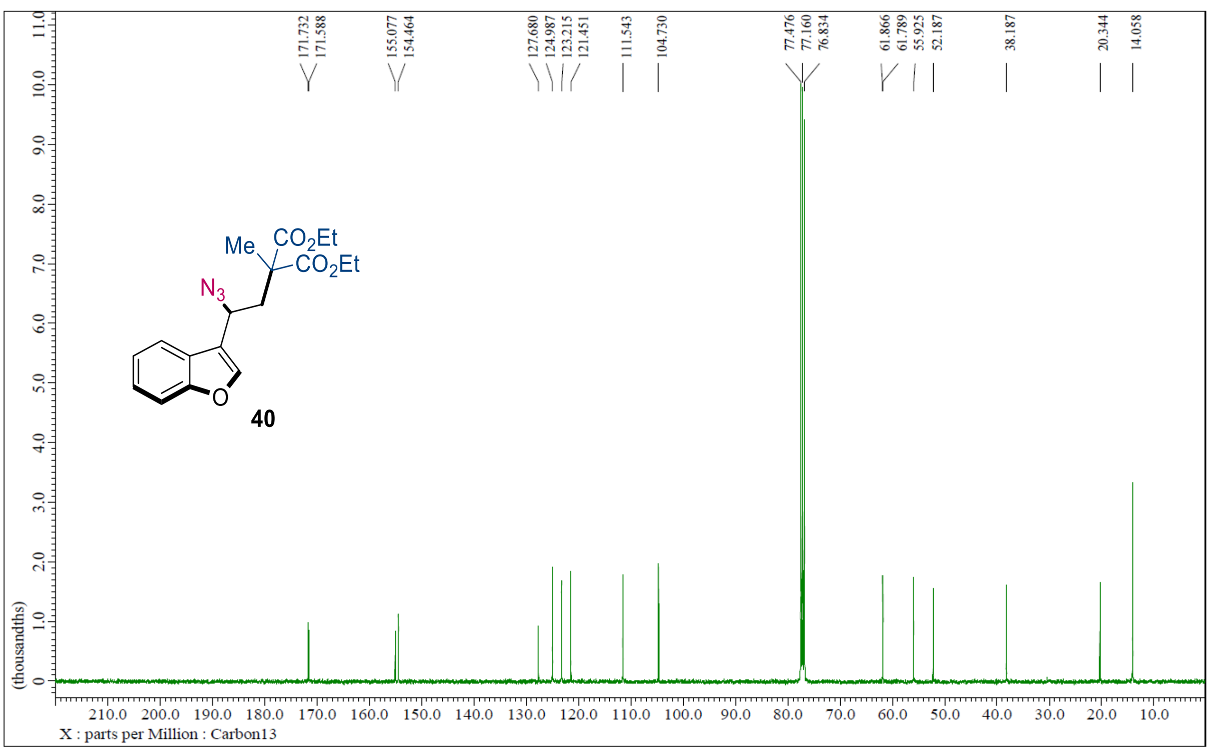
39 ^{13}C NMR (100 MHz, $CDCl_3$)



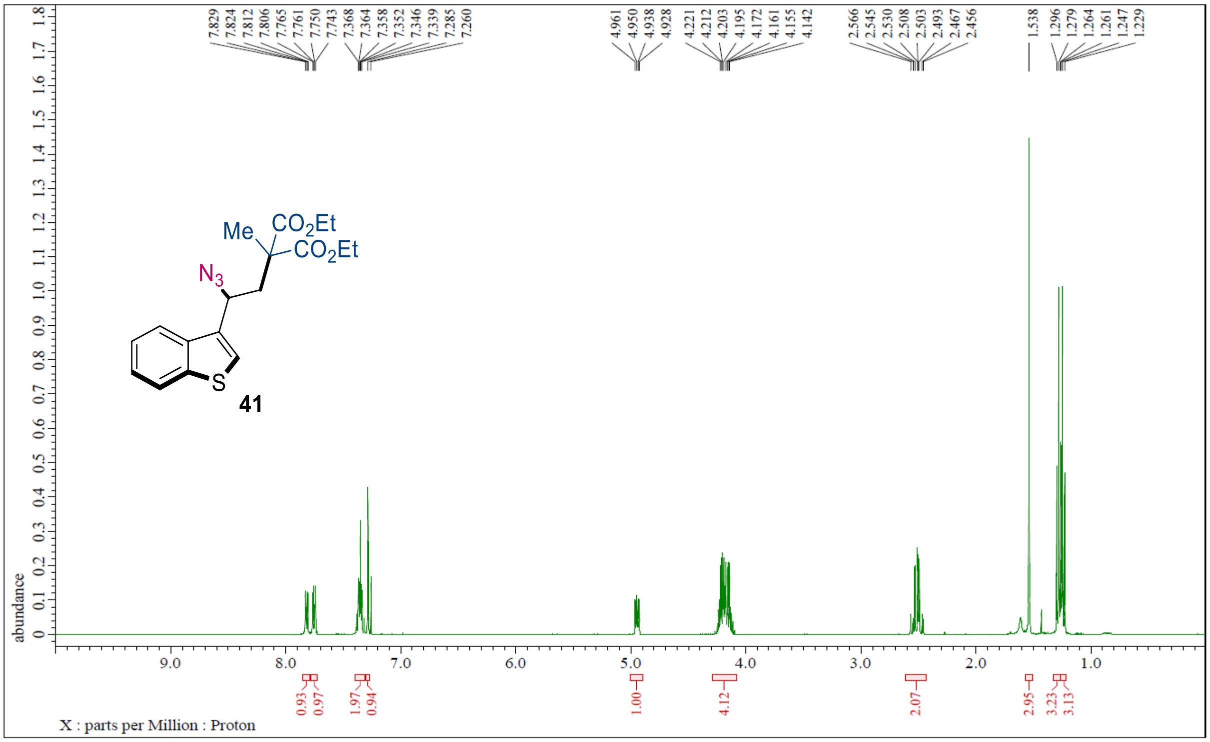
40 ^{1}H NMR (400 MHz, $CDCl_3$)



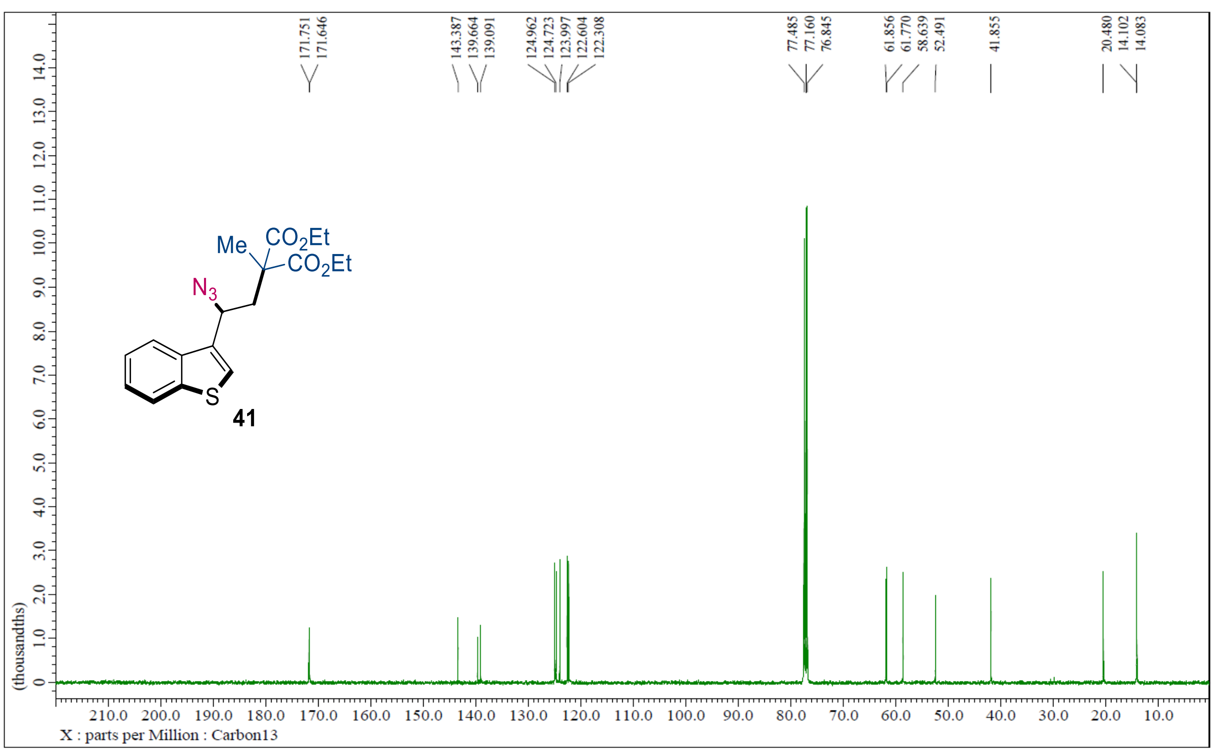
40 ^{13}C NMR (100 MHz, $CDCl_3$)



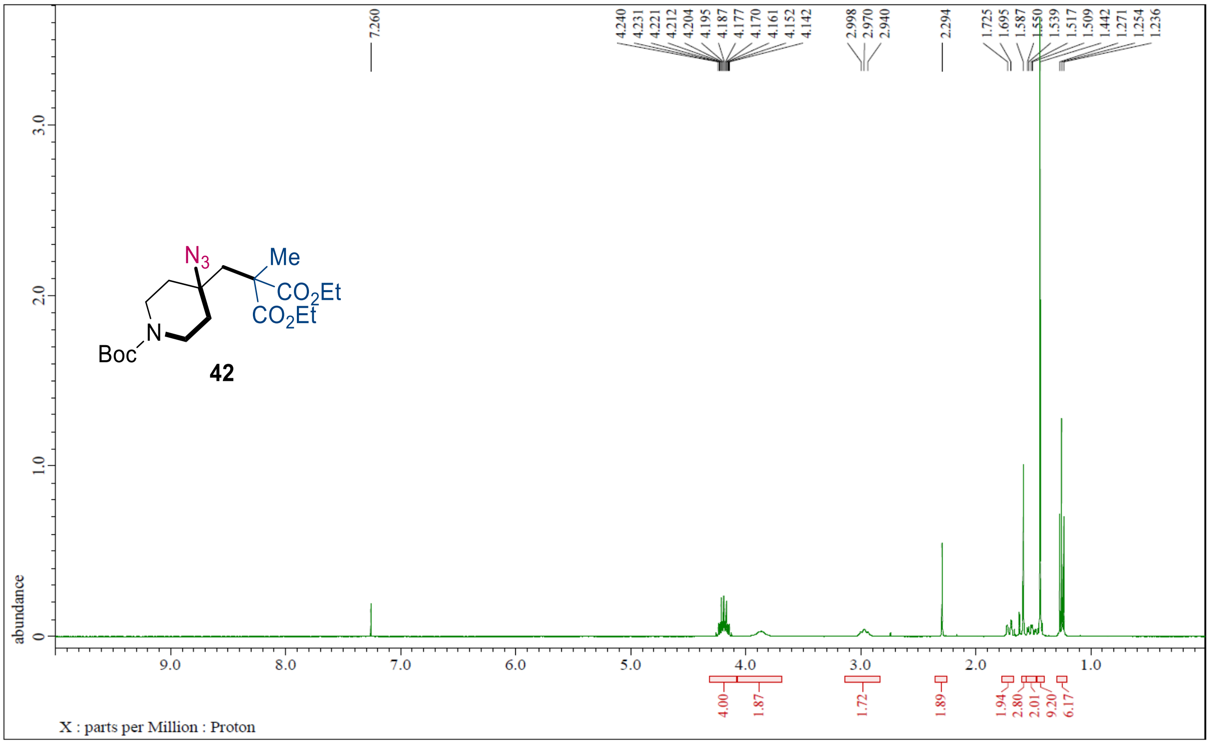
41 ^{1}H NMR (400 MHz, $CDCl_3$)



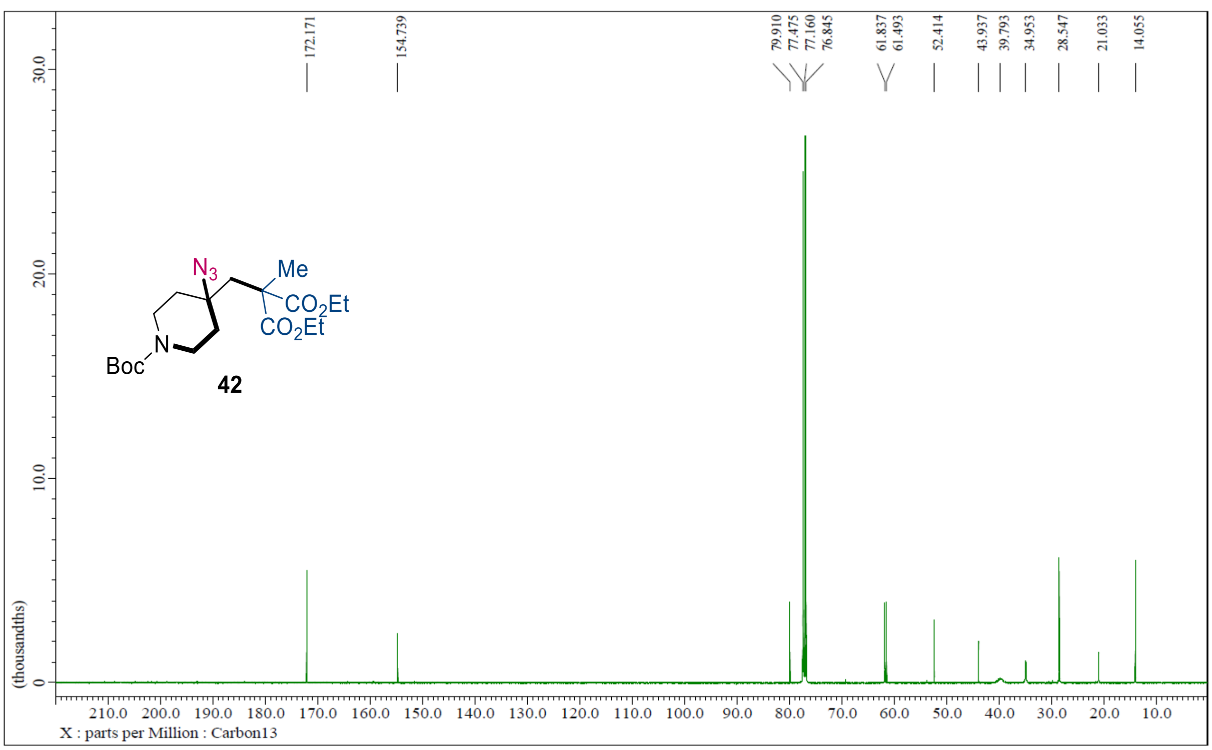
41 ^{13}C NMR (100 MHz, $CDCl_3$)



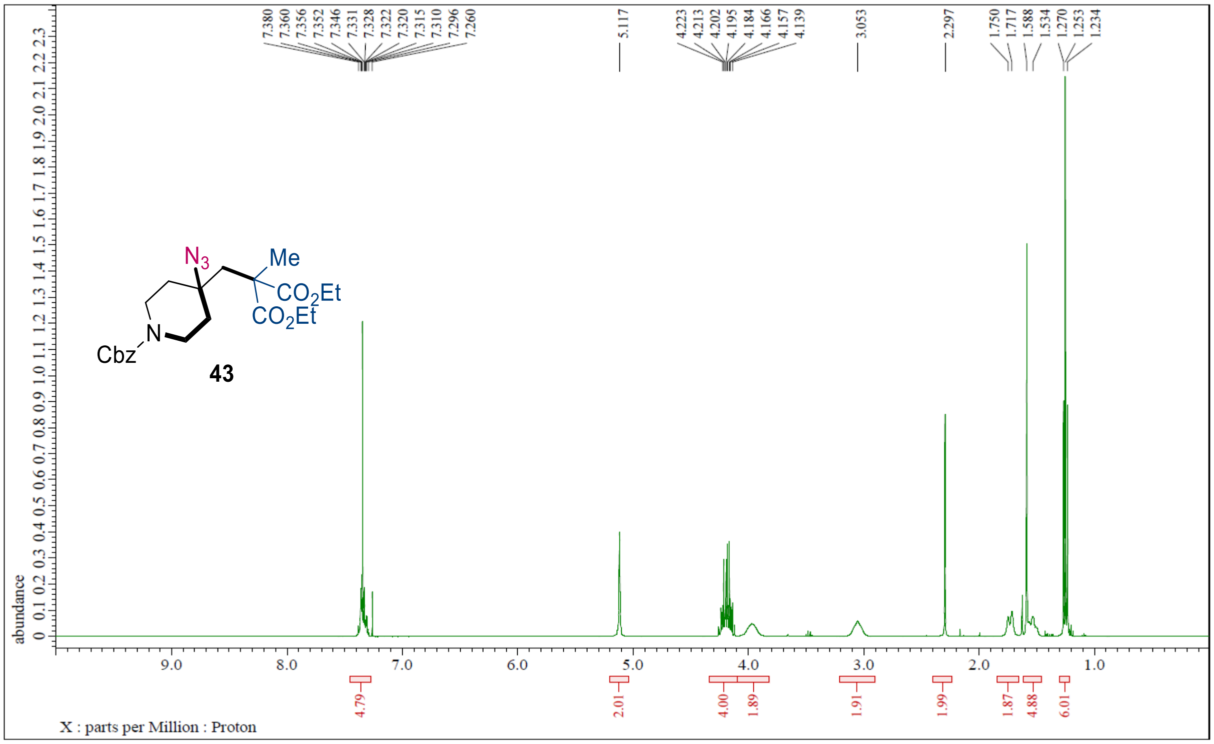
42 ^{1}H NMR (400 MHz, $CDCl_3$)



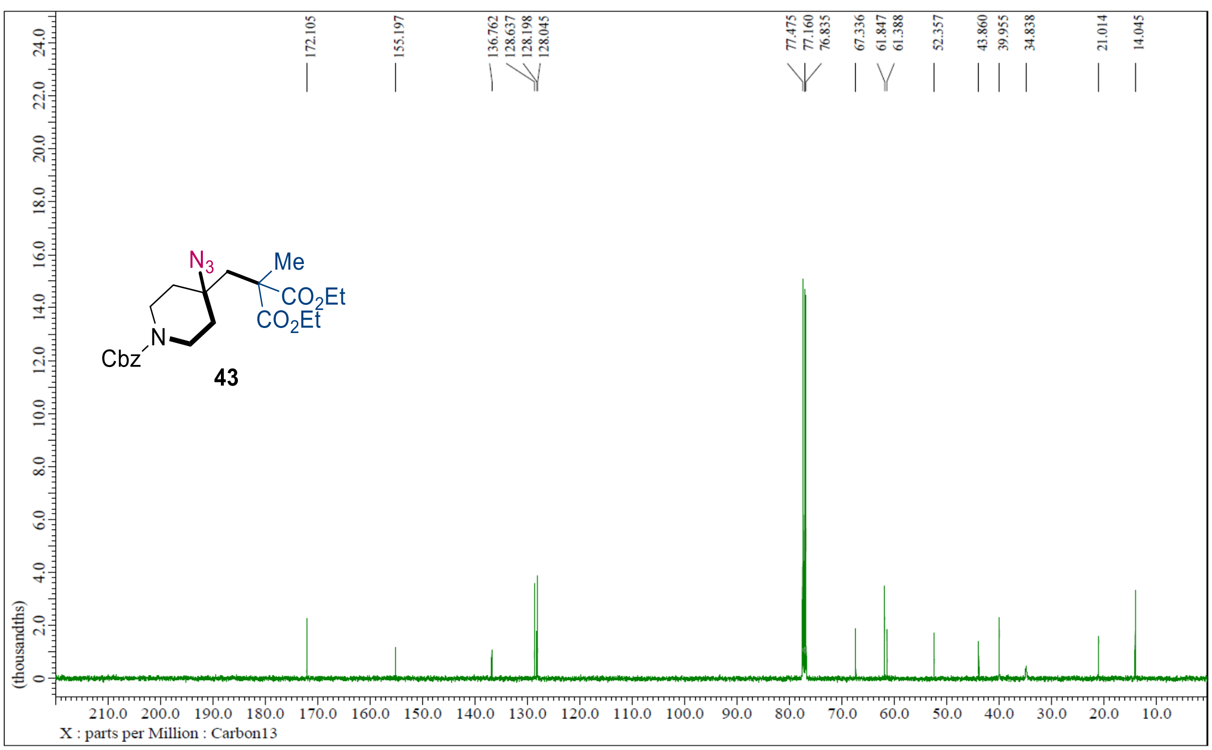
42 ^{13}C NMR (100 MHz, $CDCl_3$)



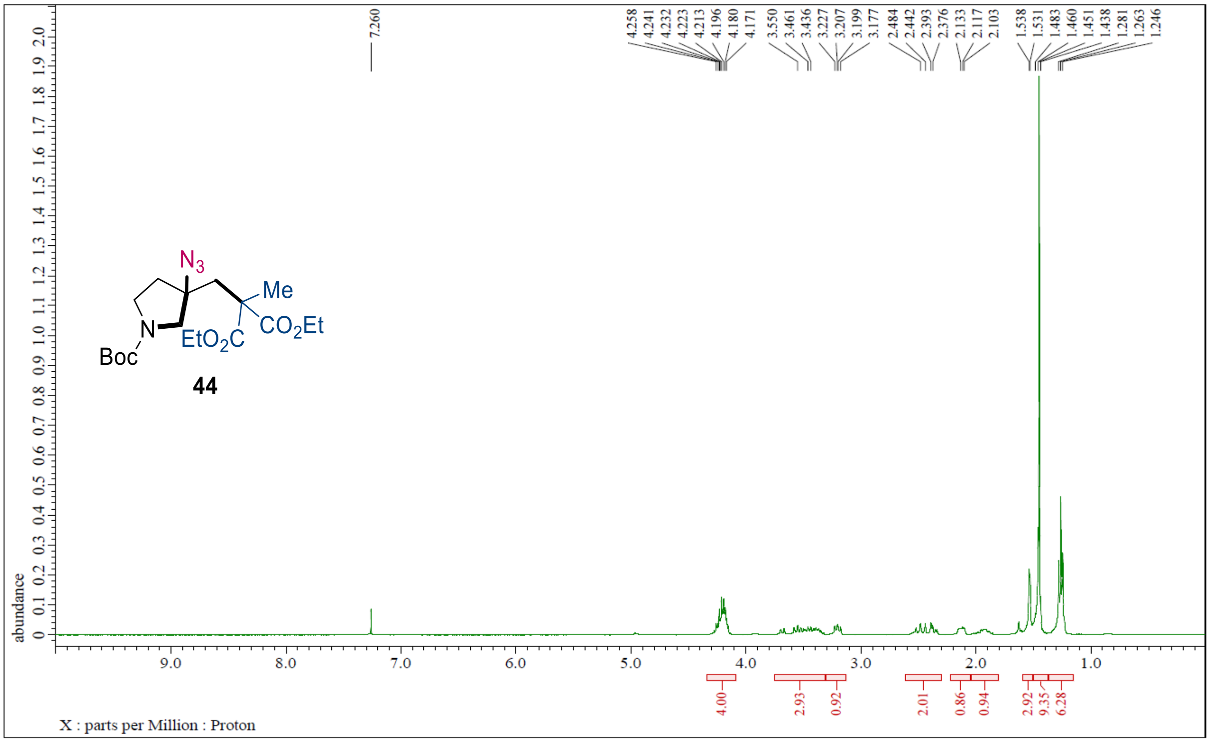
43 ^{1}H NMR (400 MHz, $CDCl_3$)



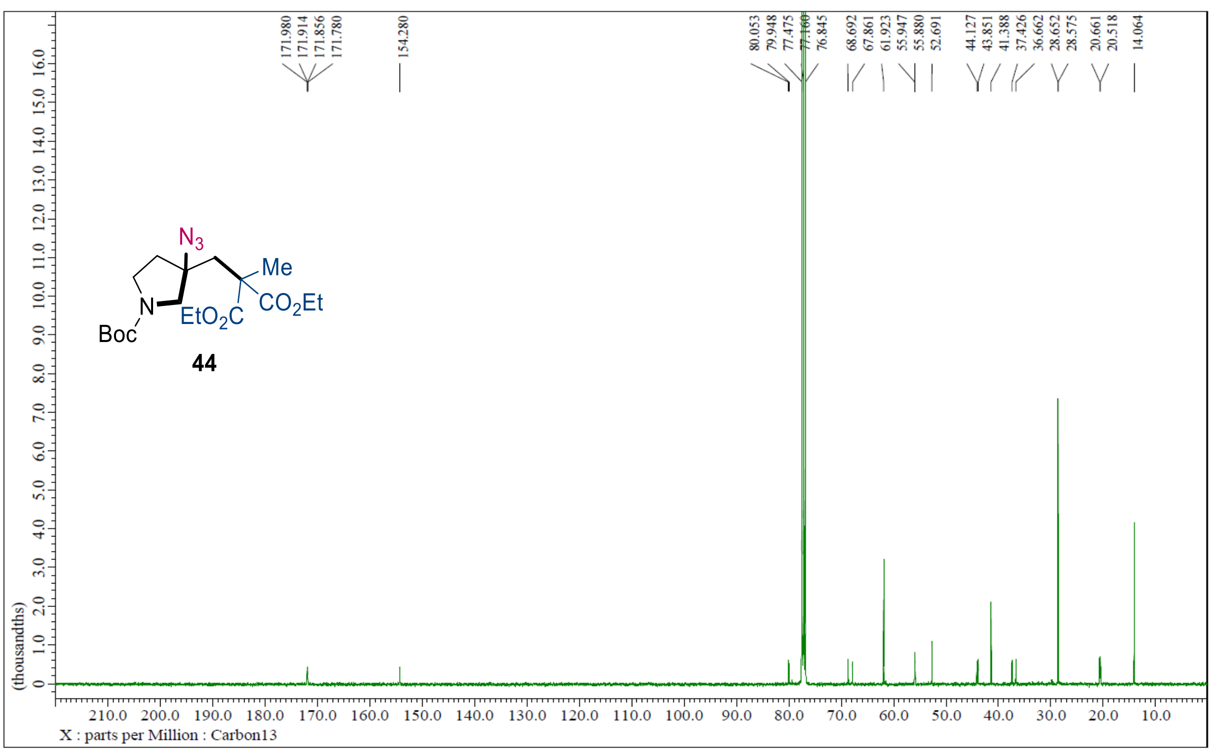
43 ^{13}C NMR (100 MHz, $CDCl_3$)



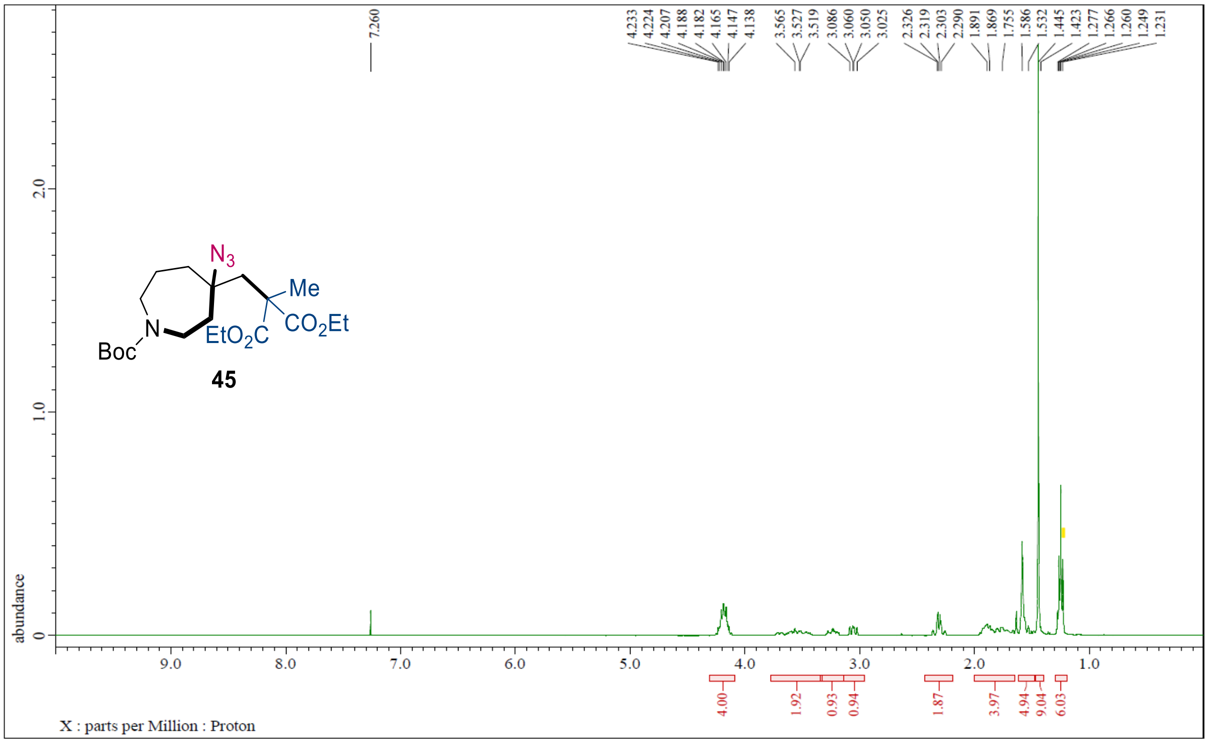
44 ^{1}H NMR (400 MHz, $CDCl_3$)



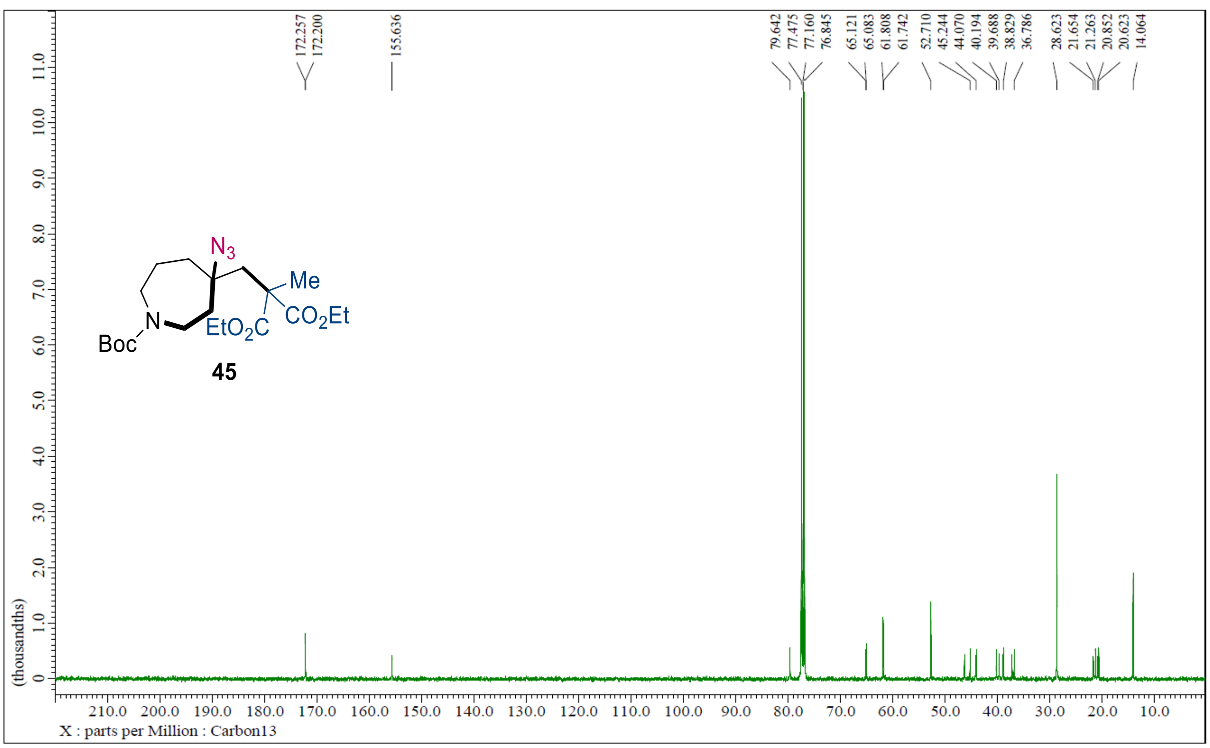
44 ^{13}C NMR (100 MHz, $CDCl_3$)



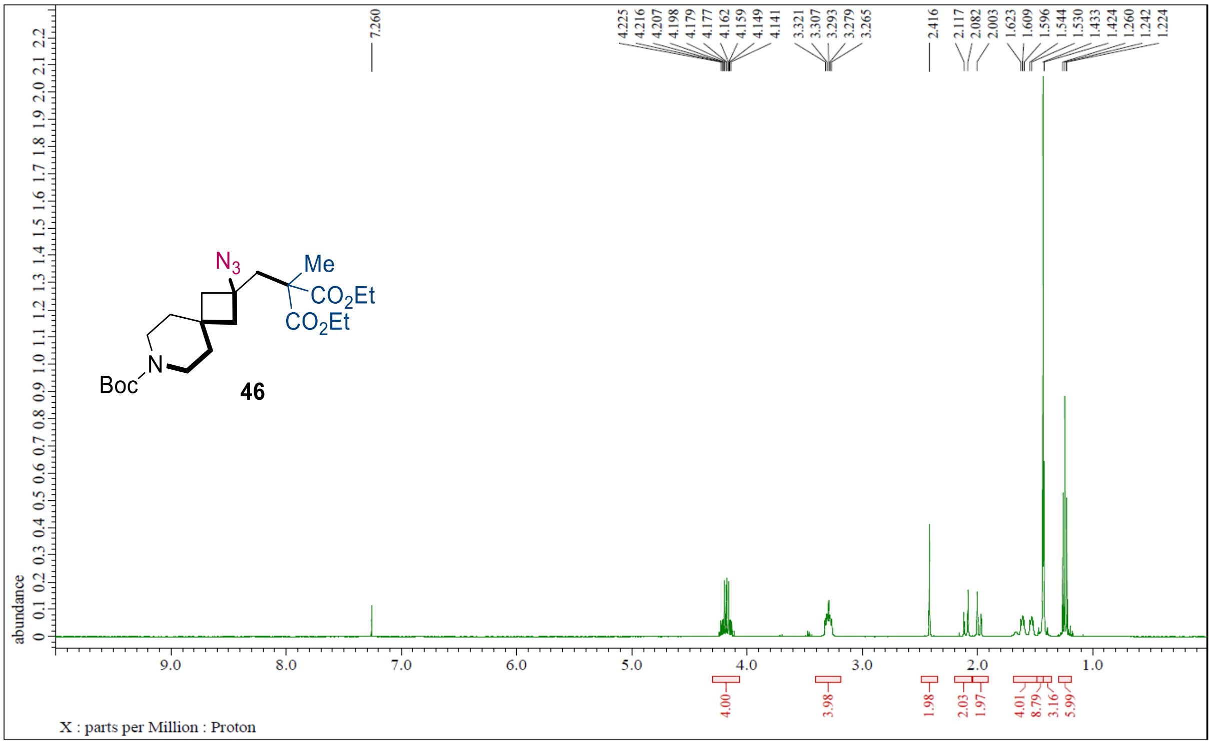
45 ^{1}H NMR (400 MHz, $CDCl_3$)



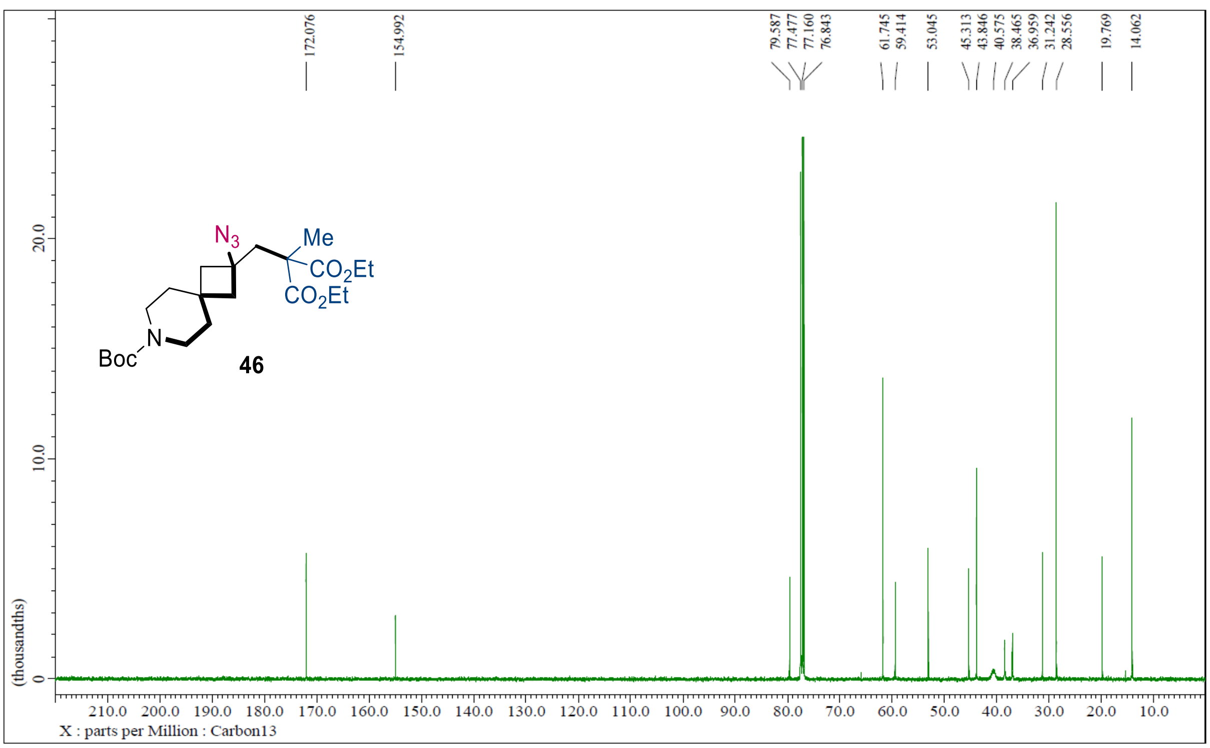
45 ^{13}C NMR (100 MHz, $CDCl_3$)



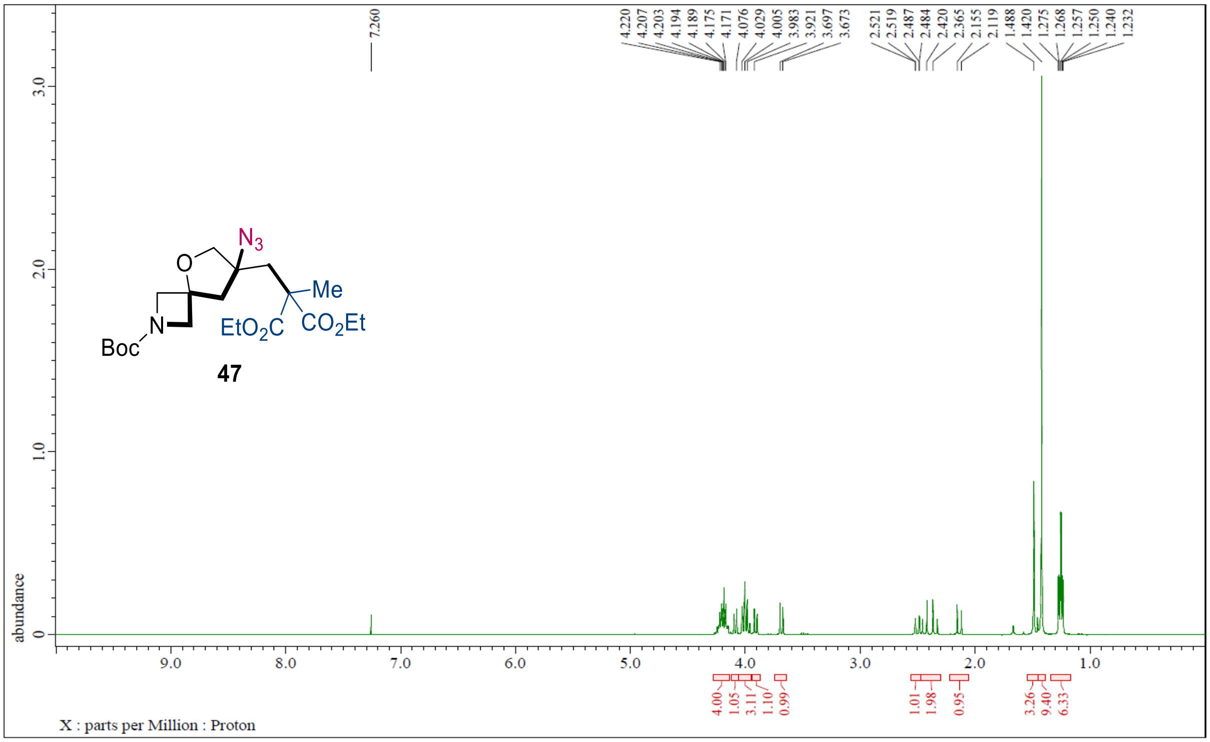
46 ^{1}H NMR (400 MHz, $CDCl_3$)



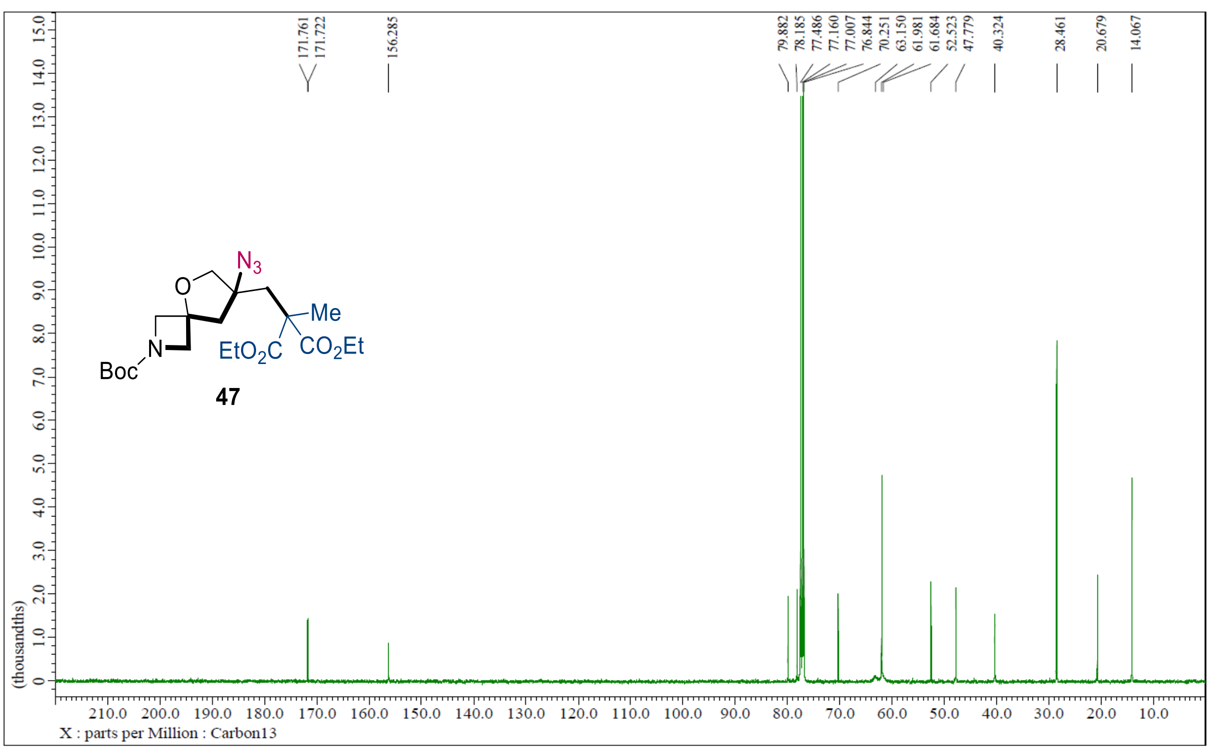
46 ^{13}C NMR (100 MHz, $CDCl_3$)



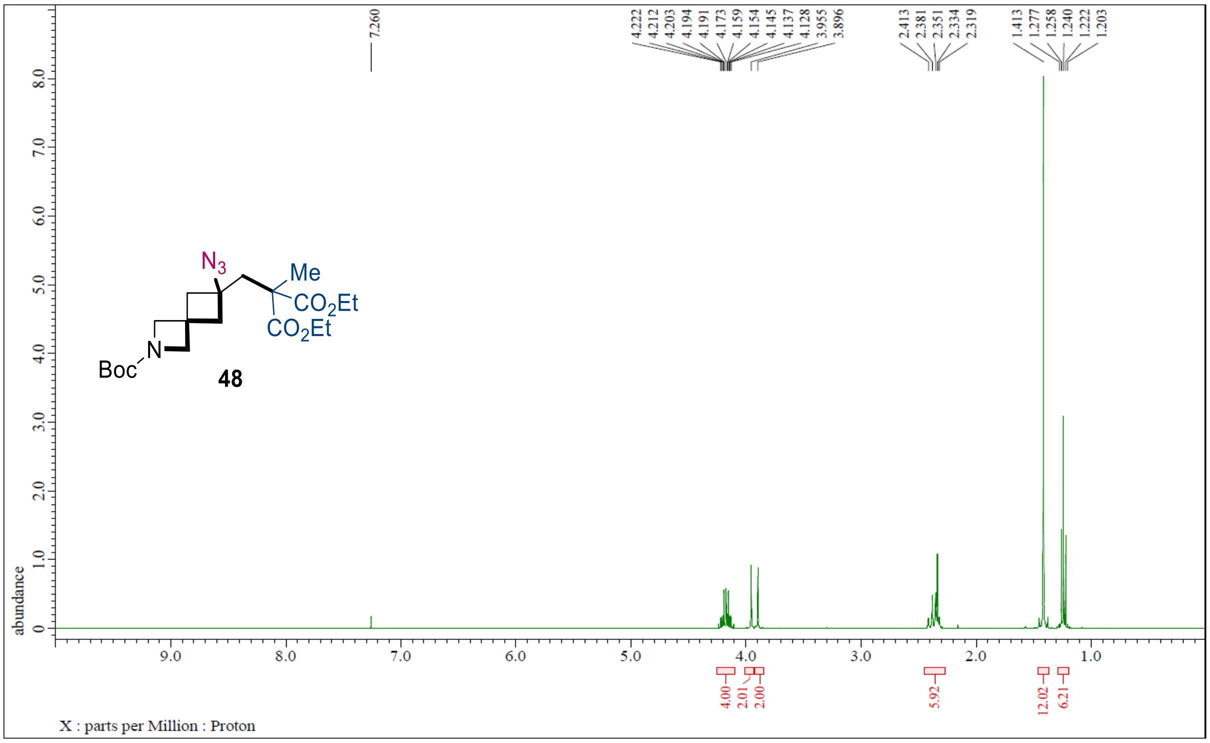
47 ^{1}H NMR (400 MHz, $CDCl_3$)



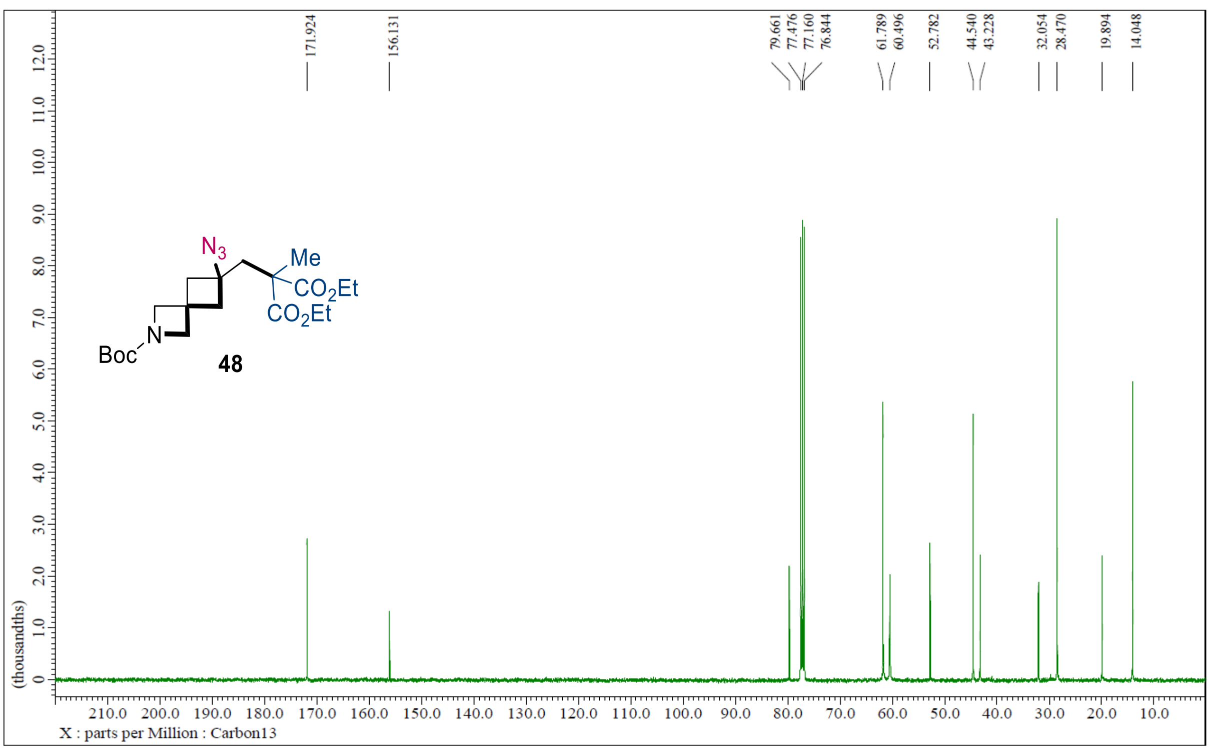
47 ^{13}C NMR (100 MHz, $CDCl_3$)



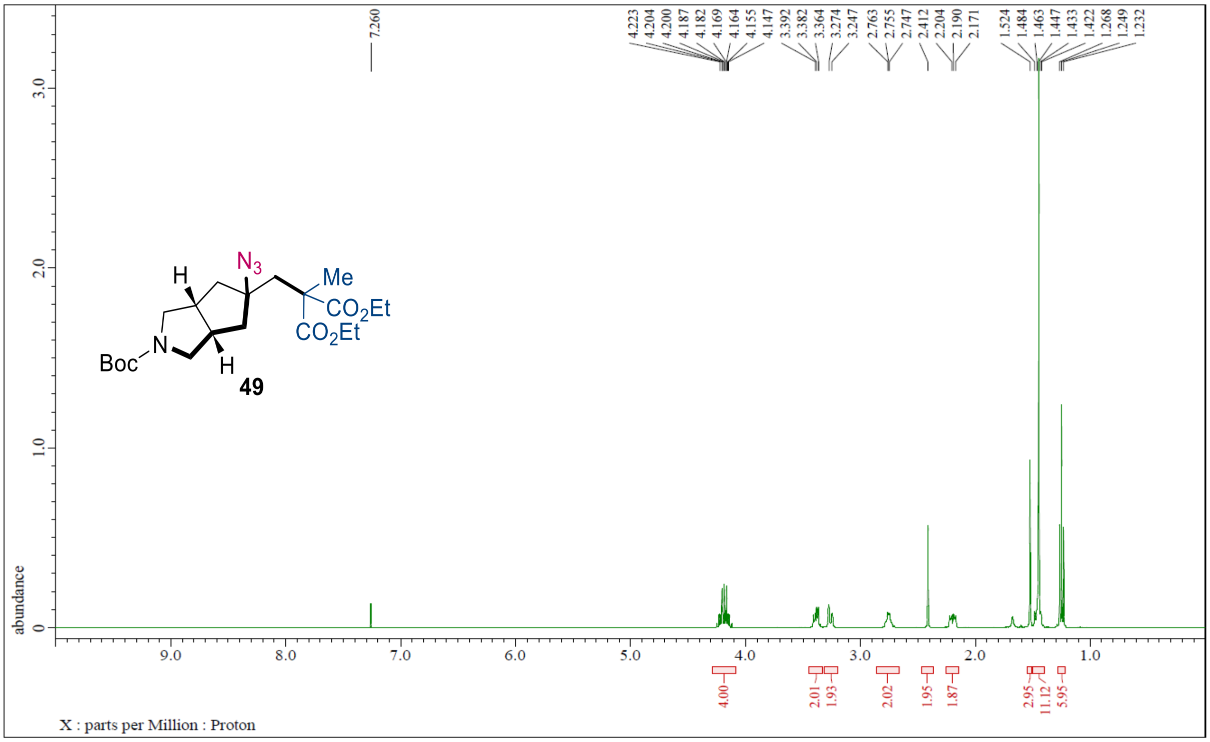
48 ^{1}H NMR (400 MHz, CDCl$_3$)



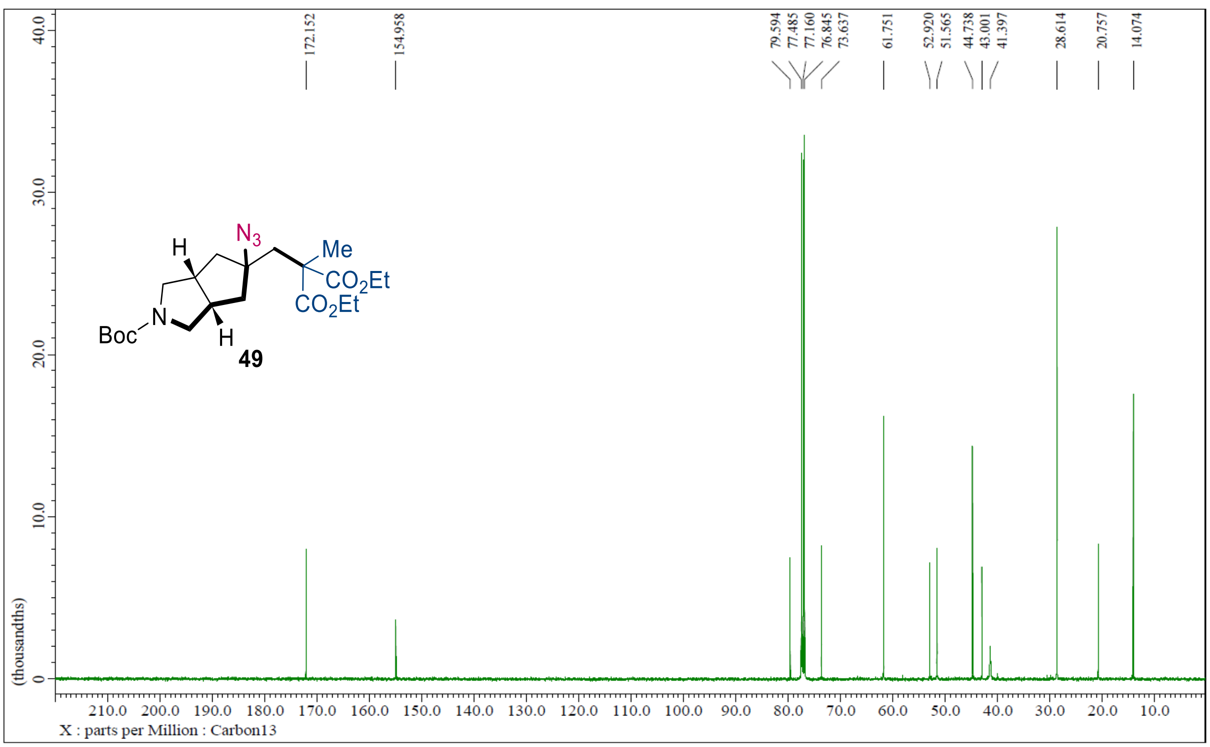
48 ^{13}C NMR (100 MHz, CDCl$_3$)



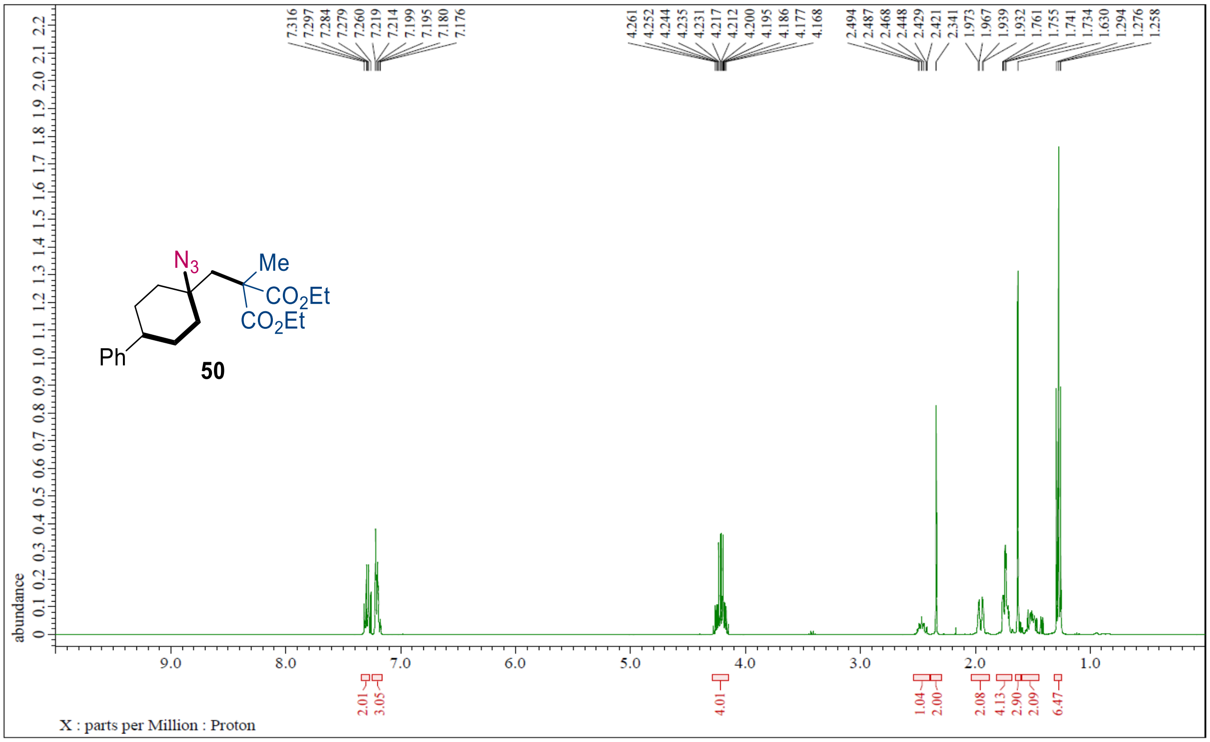
49 ^{1}H NMR (400 MHz, $CDCl_3$)



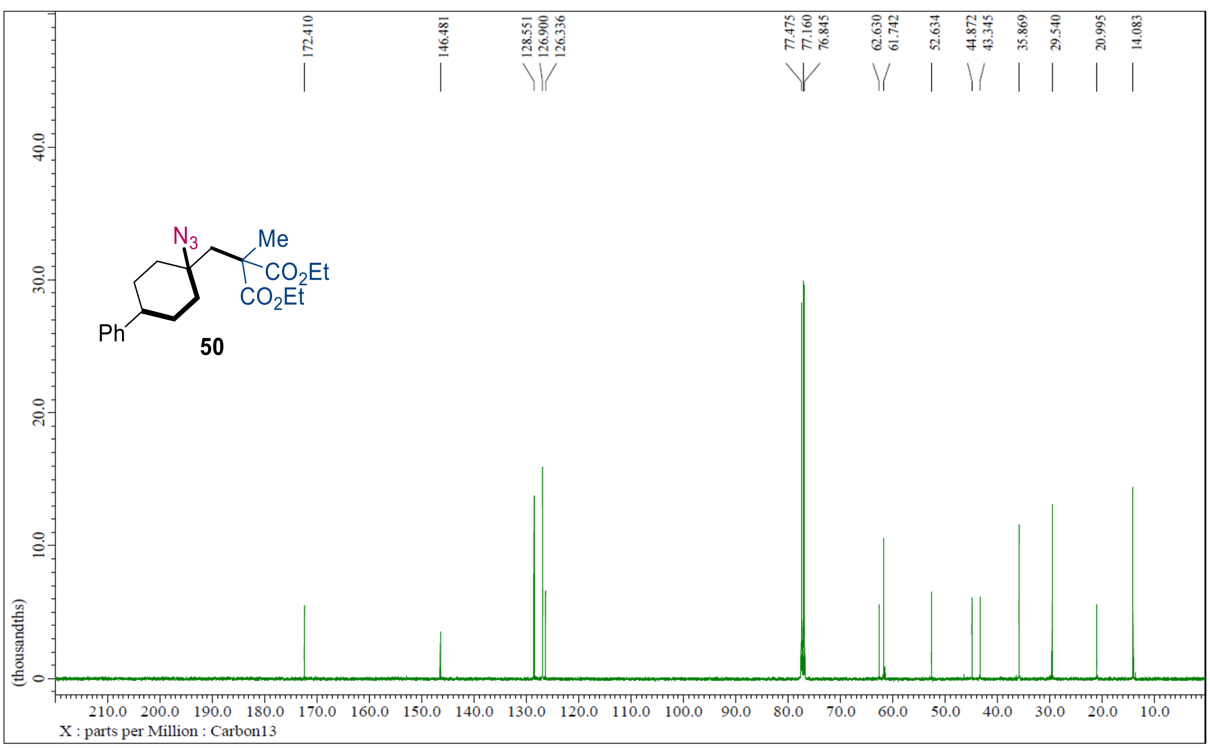
49 ^{13}C NMR (100 MHz, $CDCl_3$)



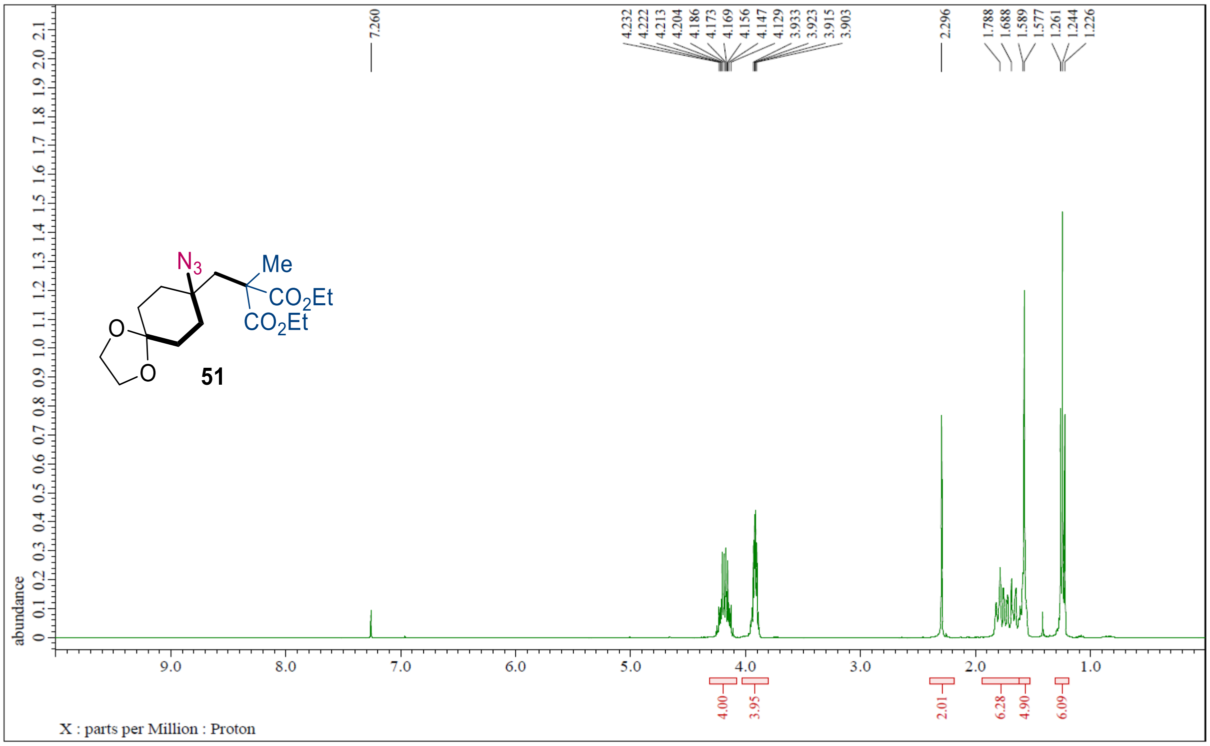
50 ^{1}H NMR (400 MHz, $CDCl_3$)



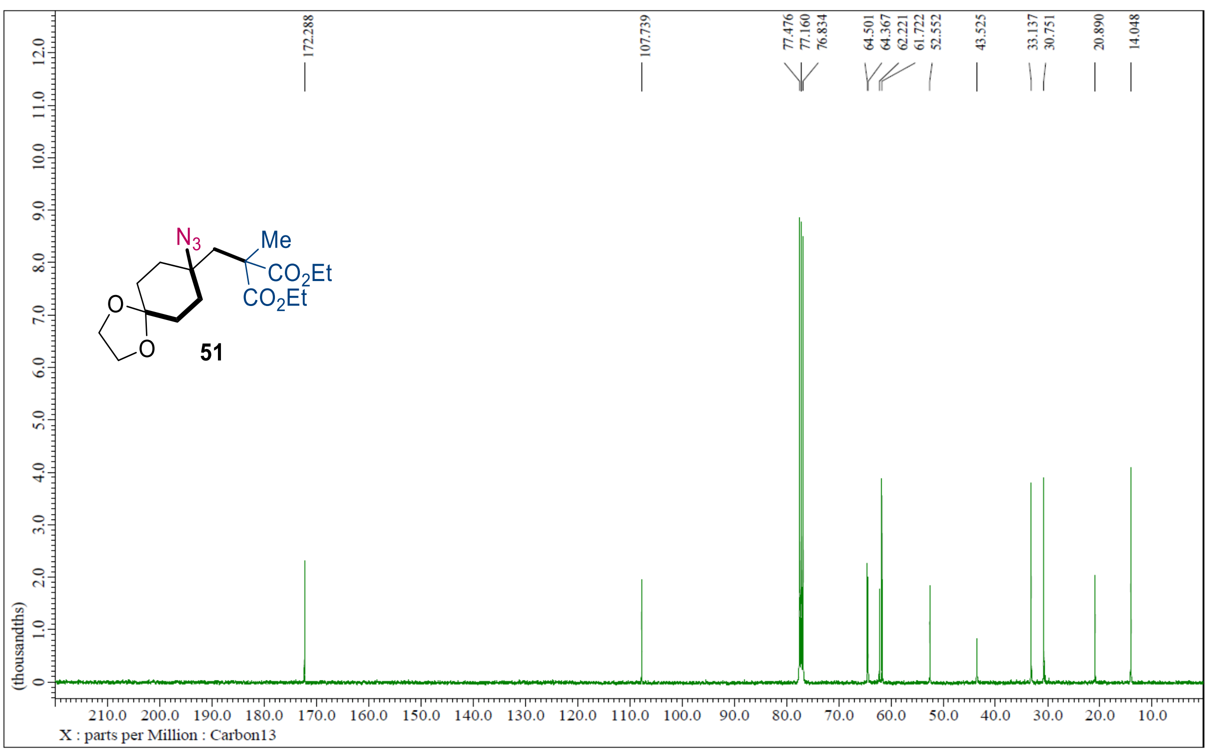
50 ^{13}C NMR (100 MHz, $CDCl_3$)



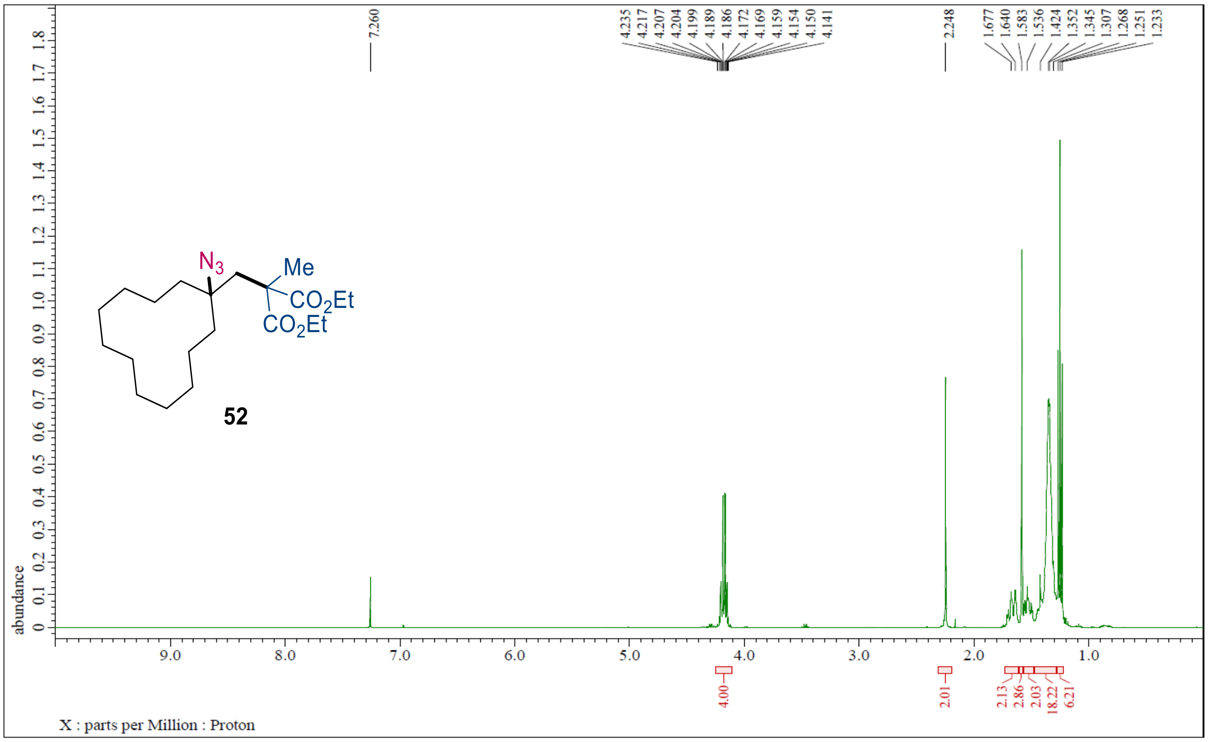
51 ^{1}H NMR (400 MHz, $CDCl_3$)



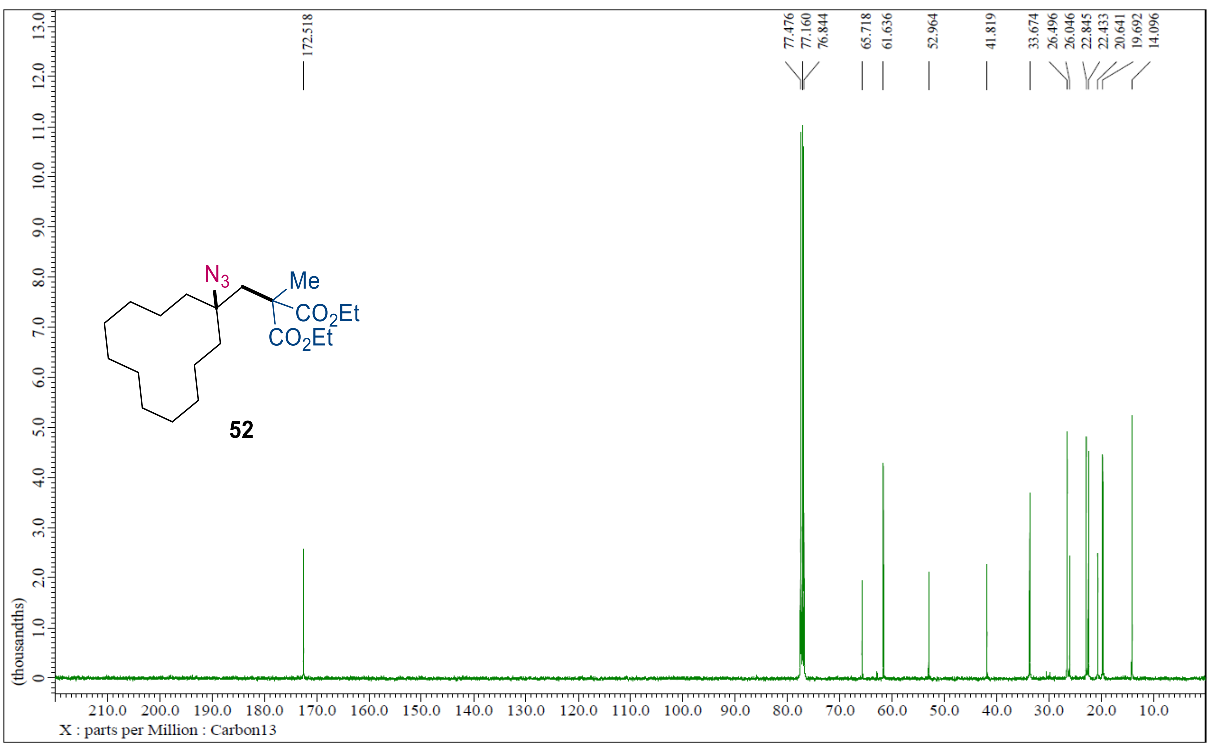
51 ^{13}C NMR (100 MHz, $CDCl_3$)



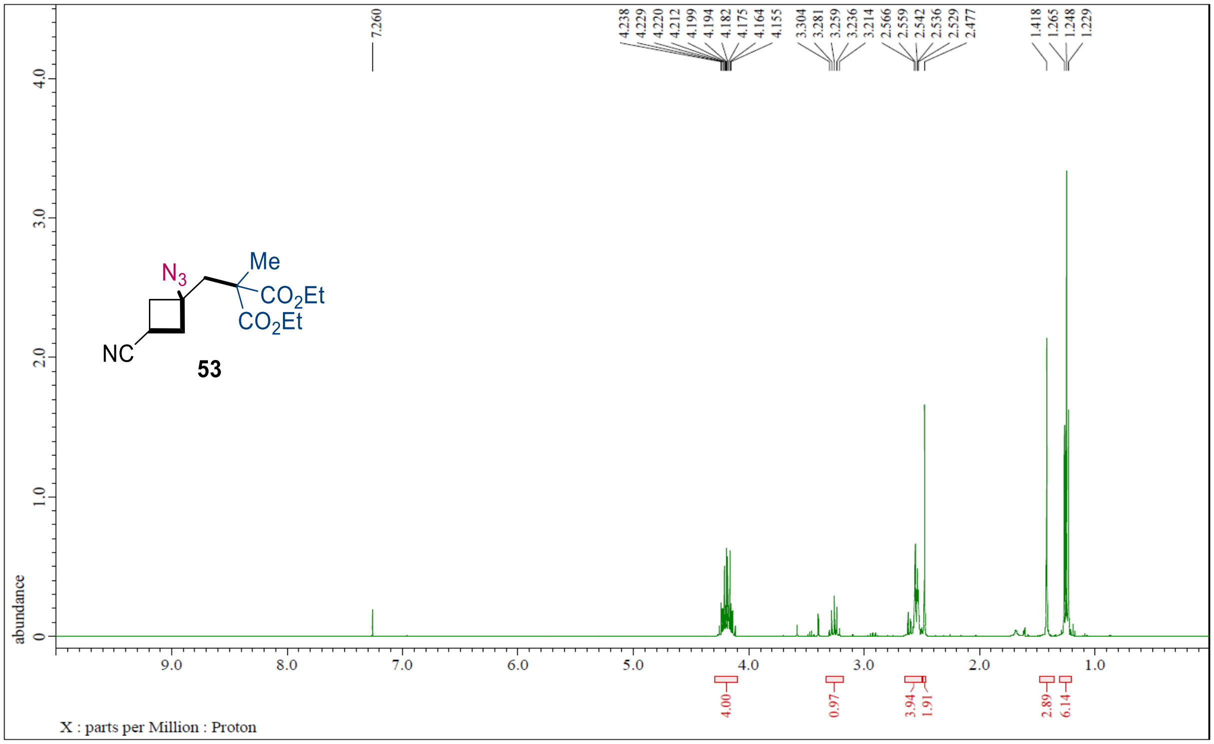
52 ^{1}H NMR (400 MHz, $CDCl_3$)



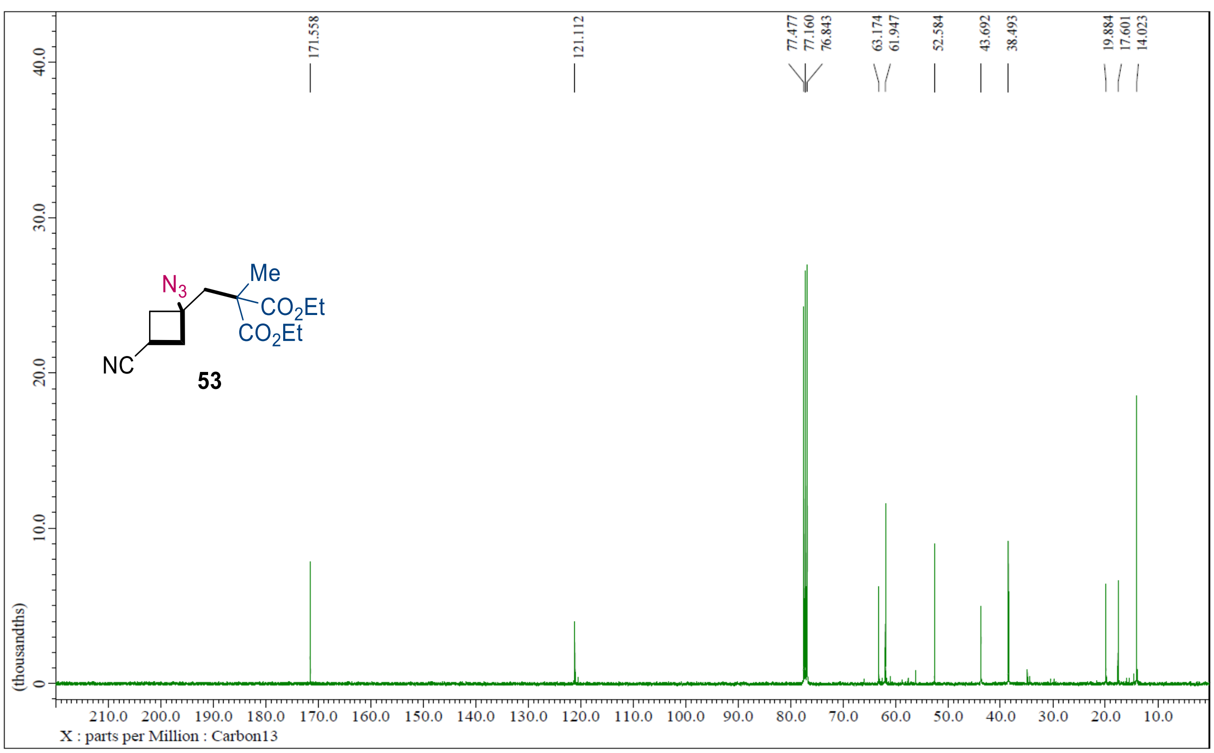
52 ^{13}C NMR (100 MHz, $CDCl_3$)



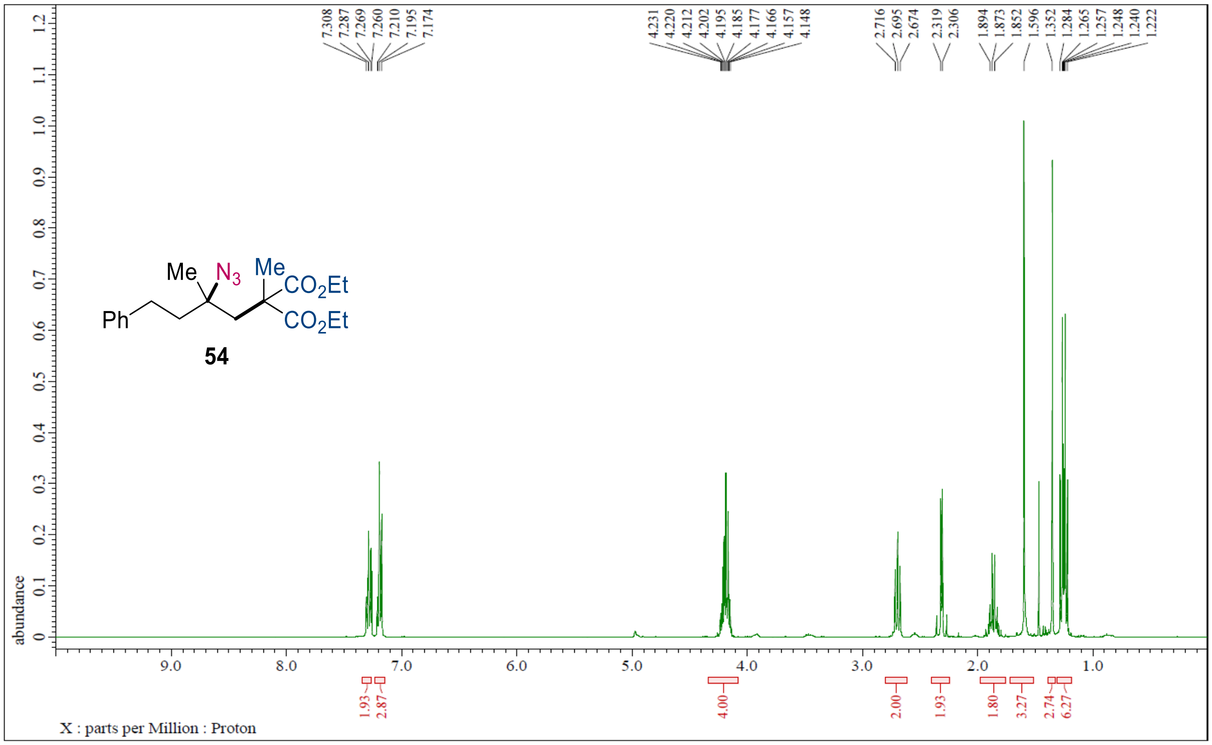
53 ^{1}H NMR (400 MHz, $CDCl_3$)



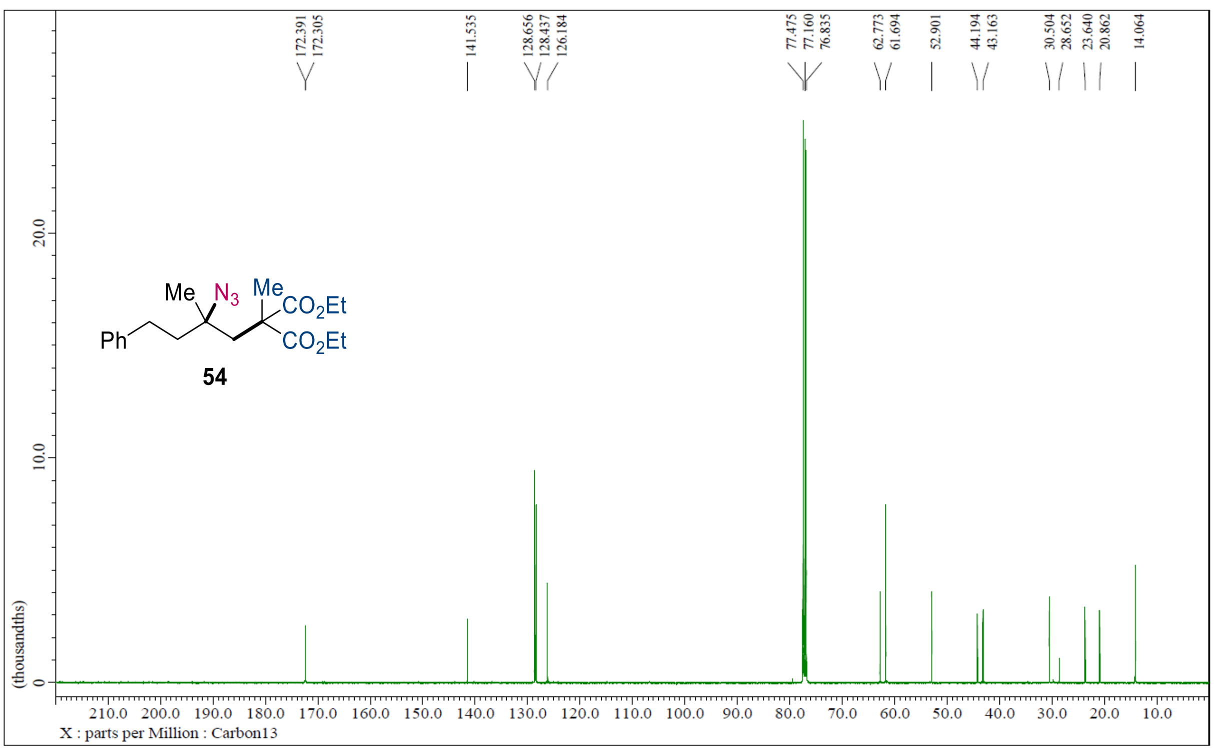
53 ^{13}C NMR (100 MHz, $CDCl_3$)



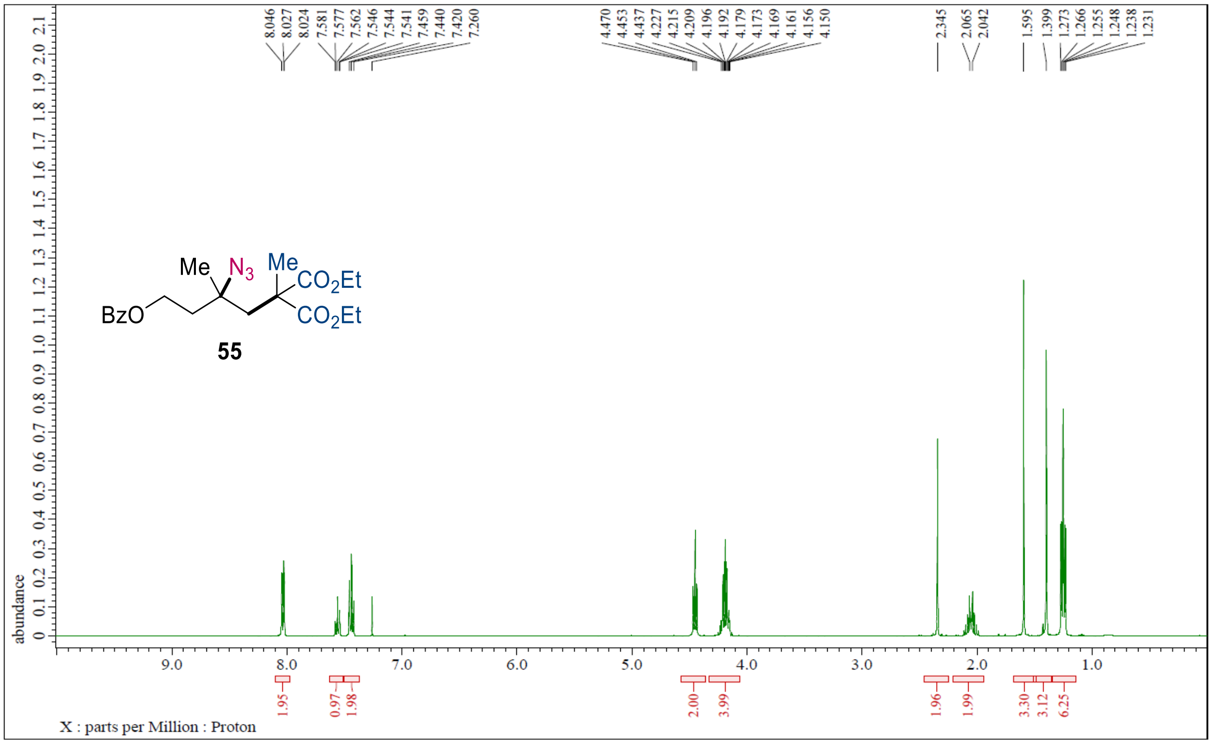
54 ^{1}H NMR (400 MHz, $CDCl_3$)



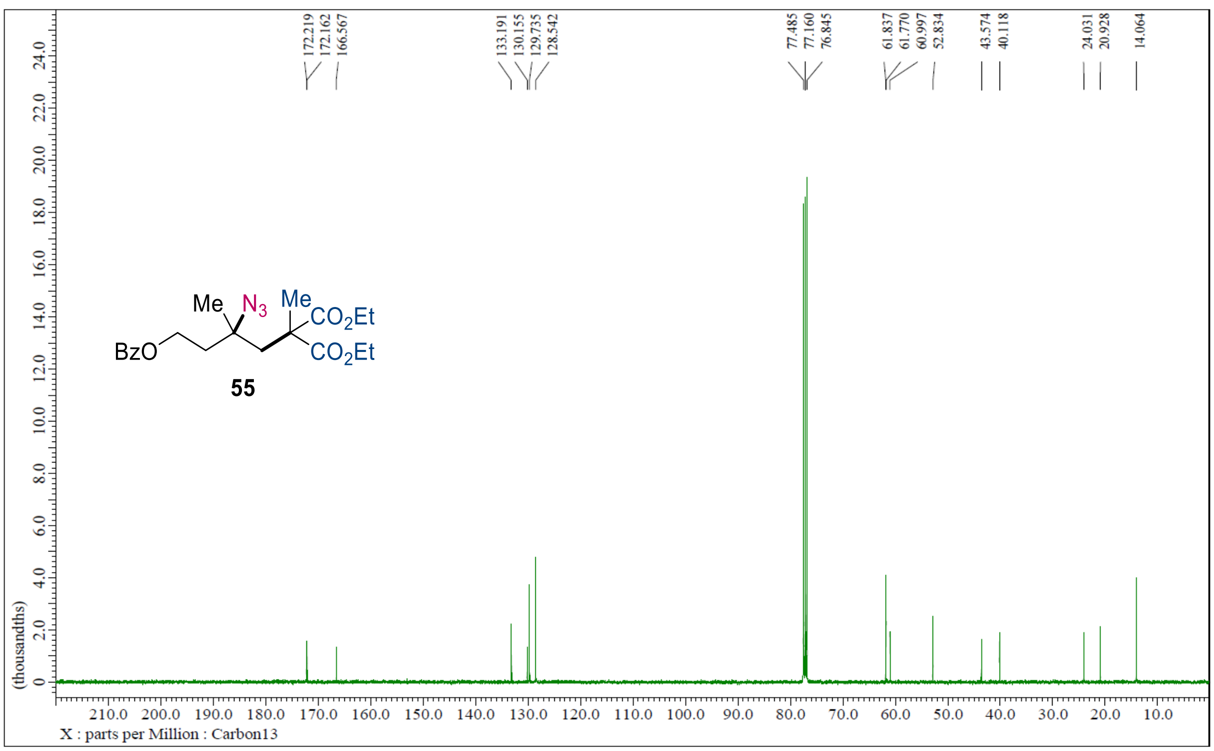
54 ^{13}C NMR (100 MHz, $CDCl_3$)



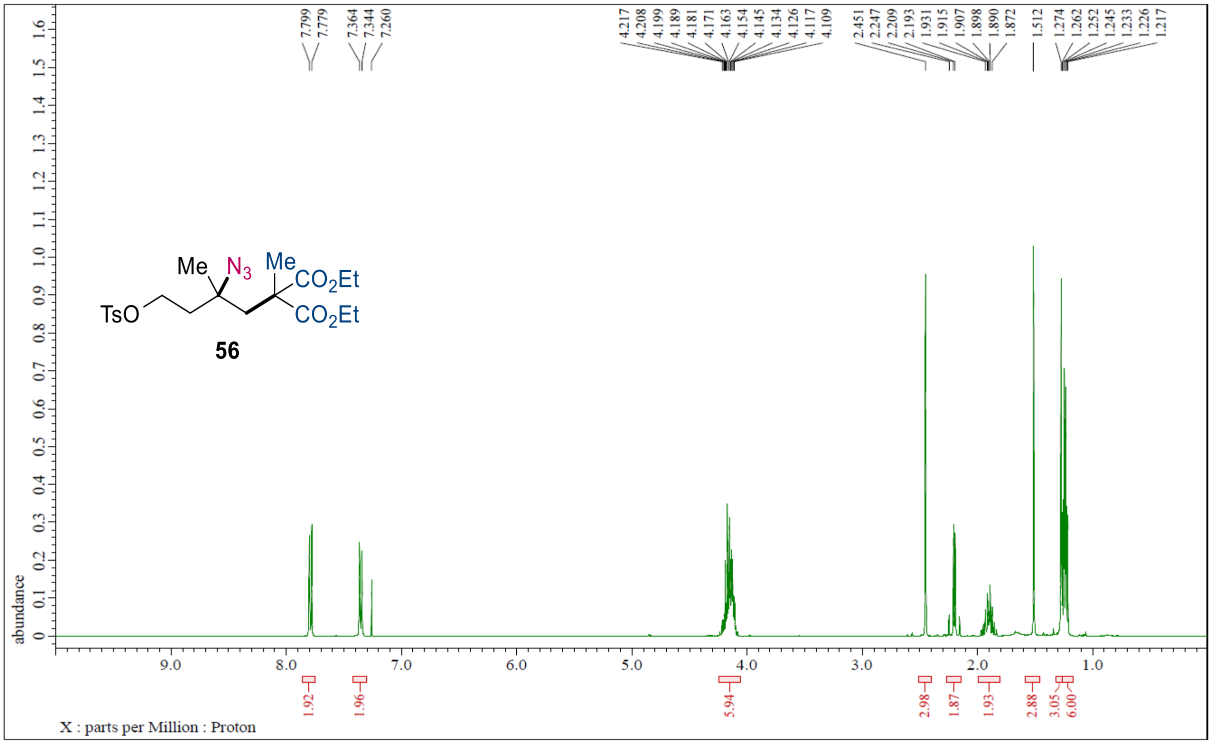
55 ^{1}H NMR (400 MHz, $CDCl_3$)



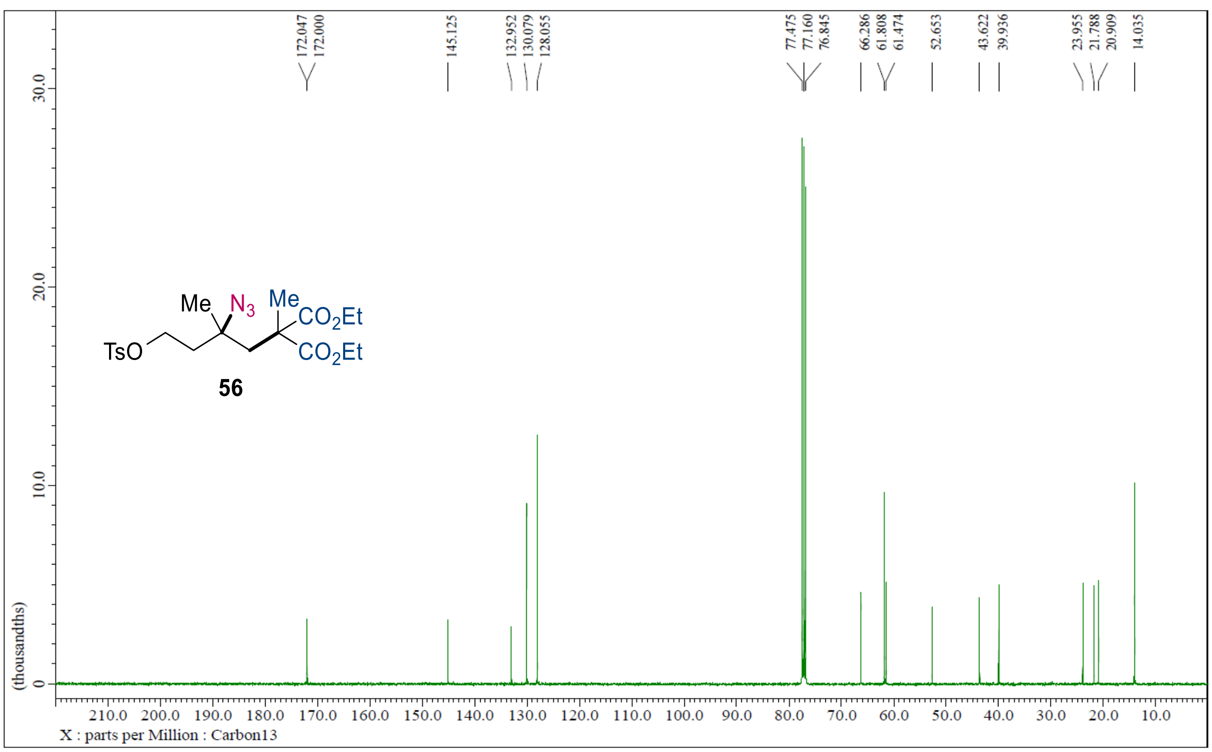
55 ^{13}C NMR (100 MHz, $CDCl_3$)



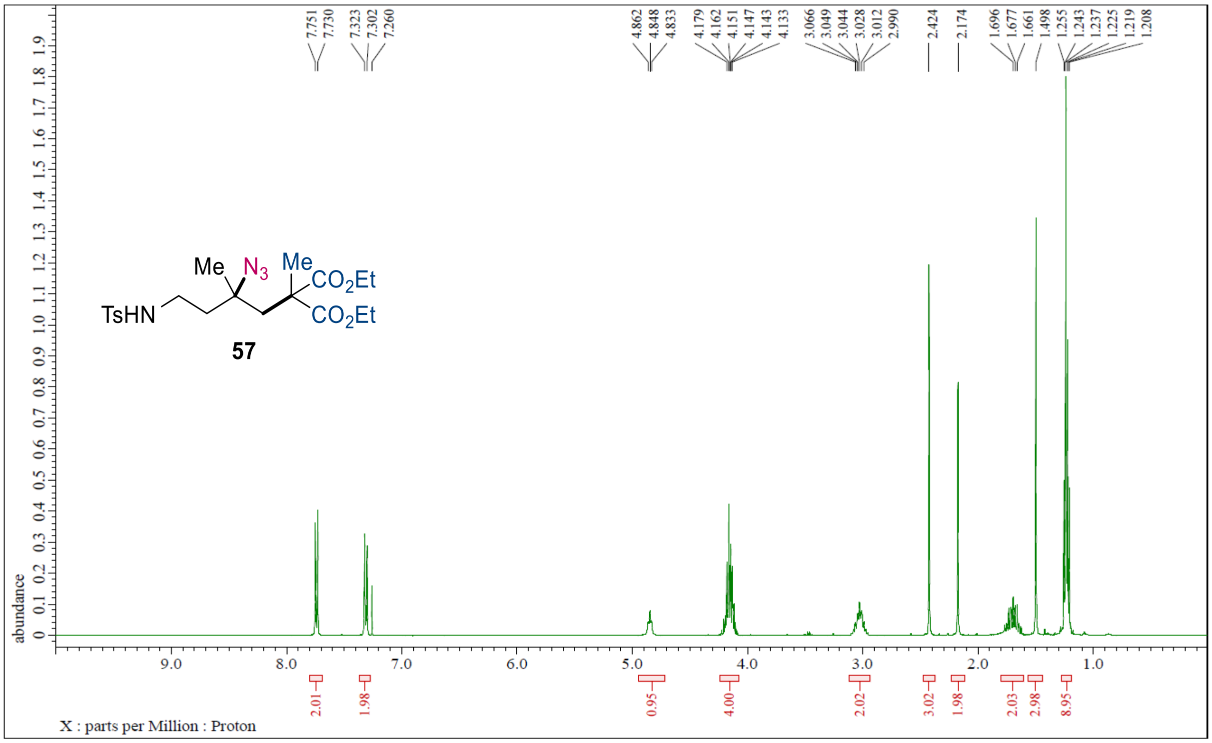
56 ^{1}H NMR (400 MHz, $CDCl_3$)



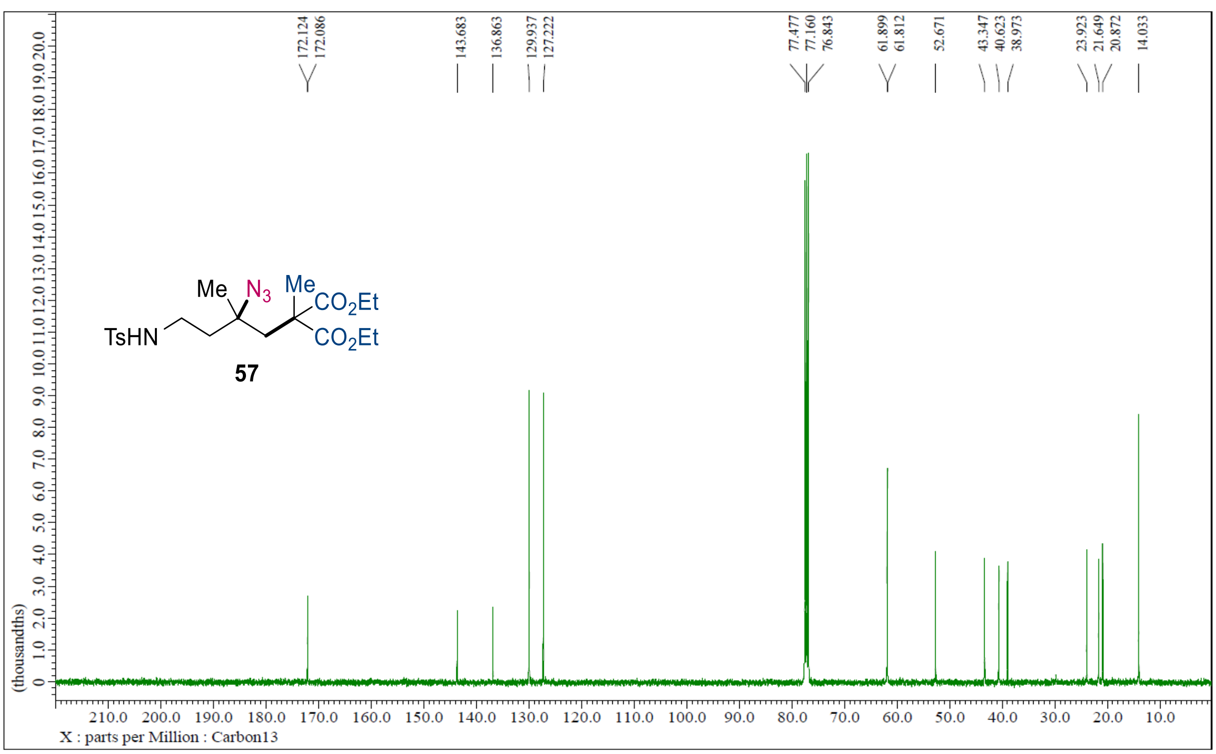
56 ^{13}C NMR (100 MHz, $CDCl_3$)



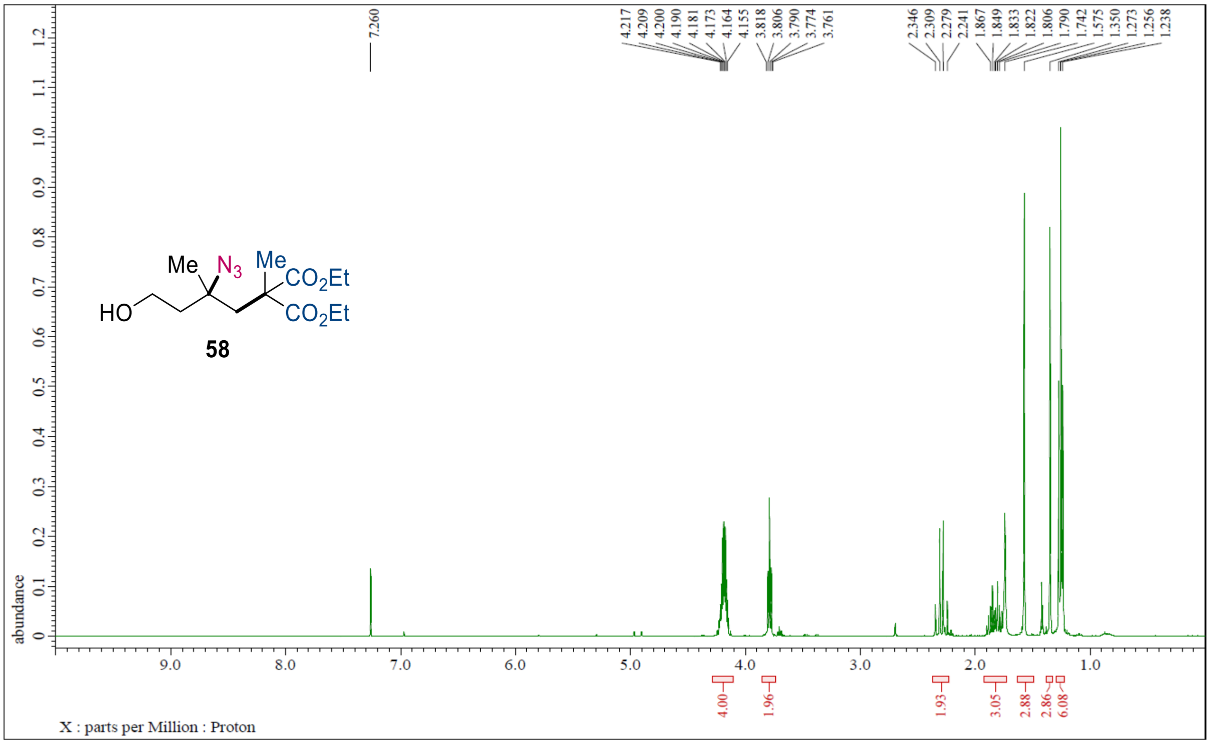
57 ^{1}H NMR (400 MHz, $CDCl_3$)



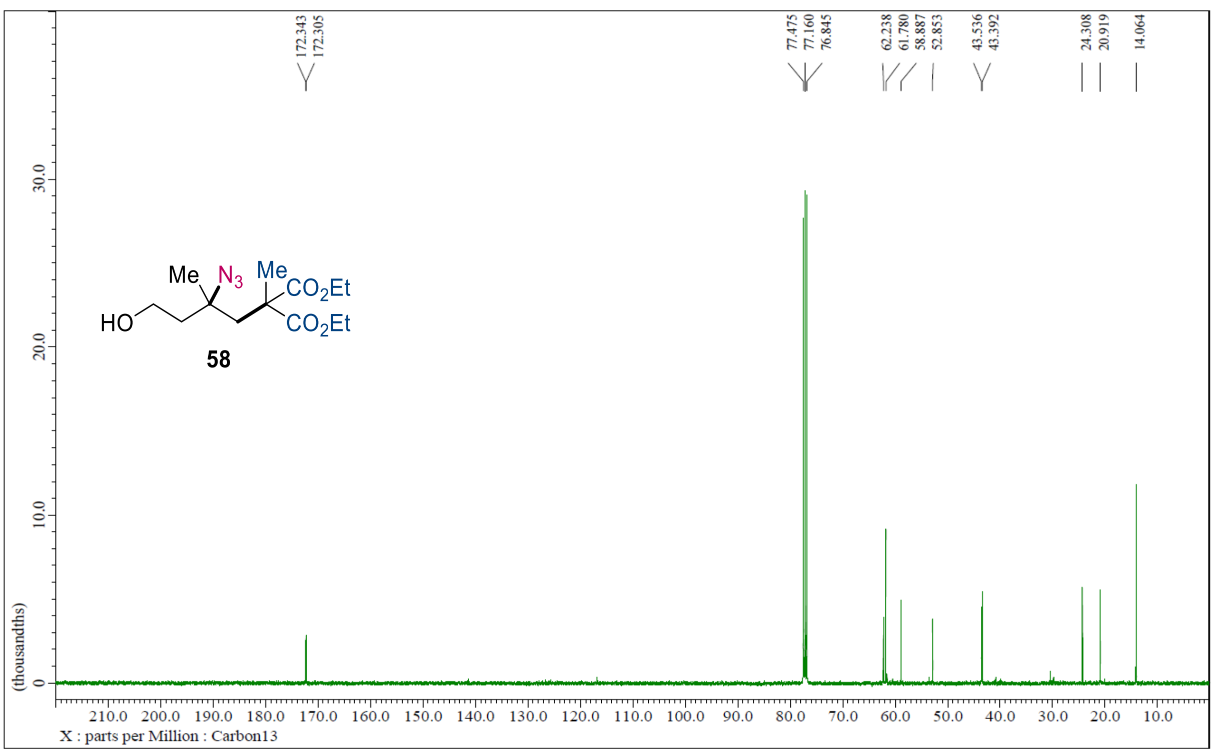
57 ^{13}C NMR (100 MHz, $CDCl_3$)



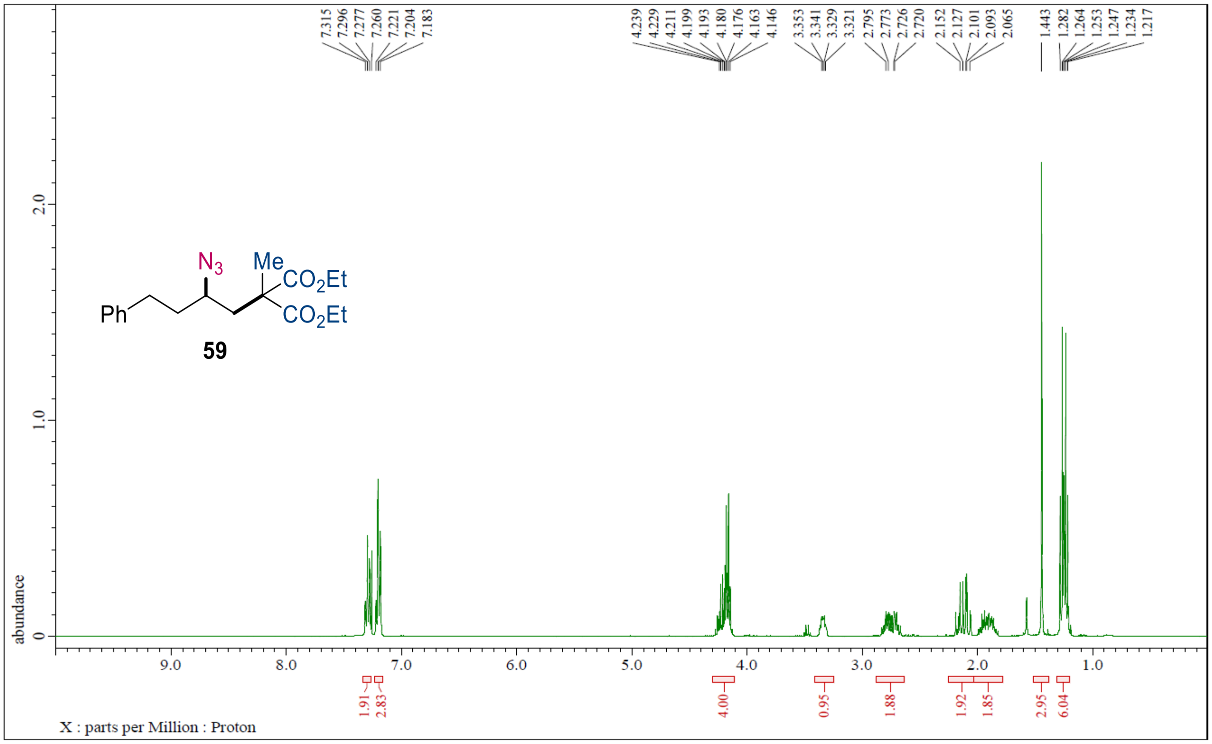
58 ^{1}H NMR (400 MHz, $CDCl_3$)



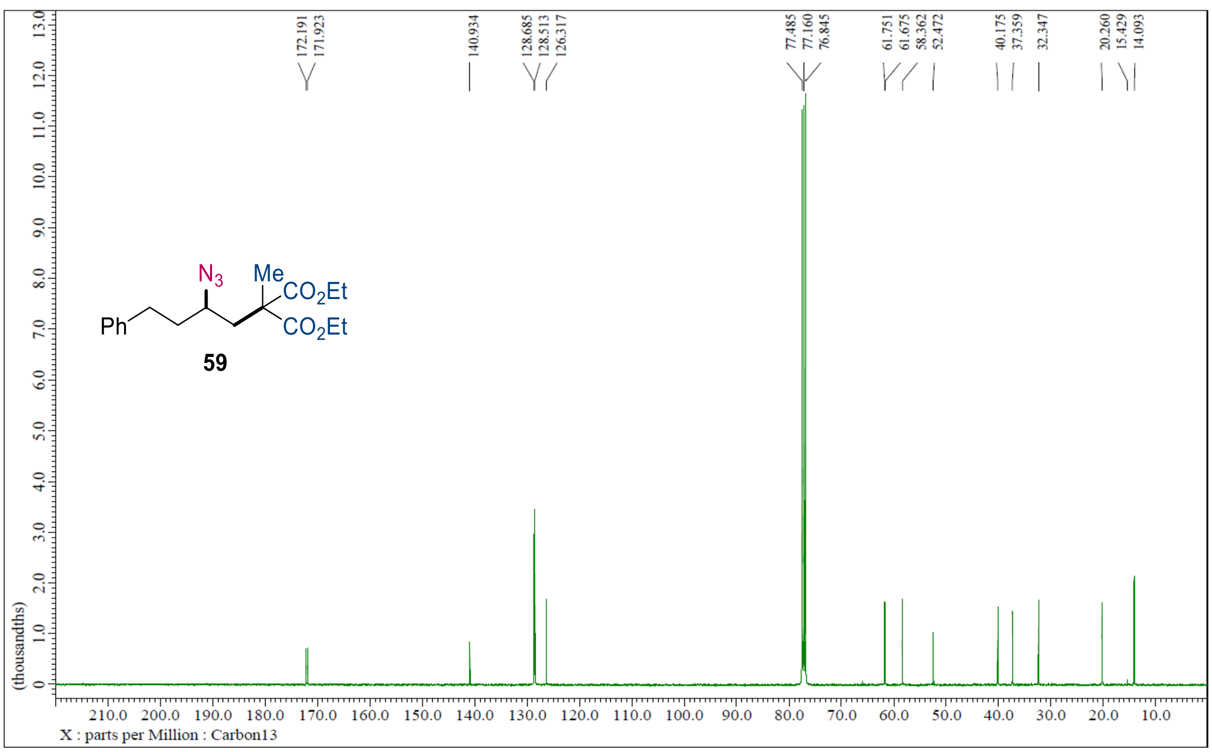
58 ^{13}C NMR (100 MHz, $CDCl_3$)



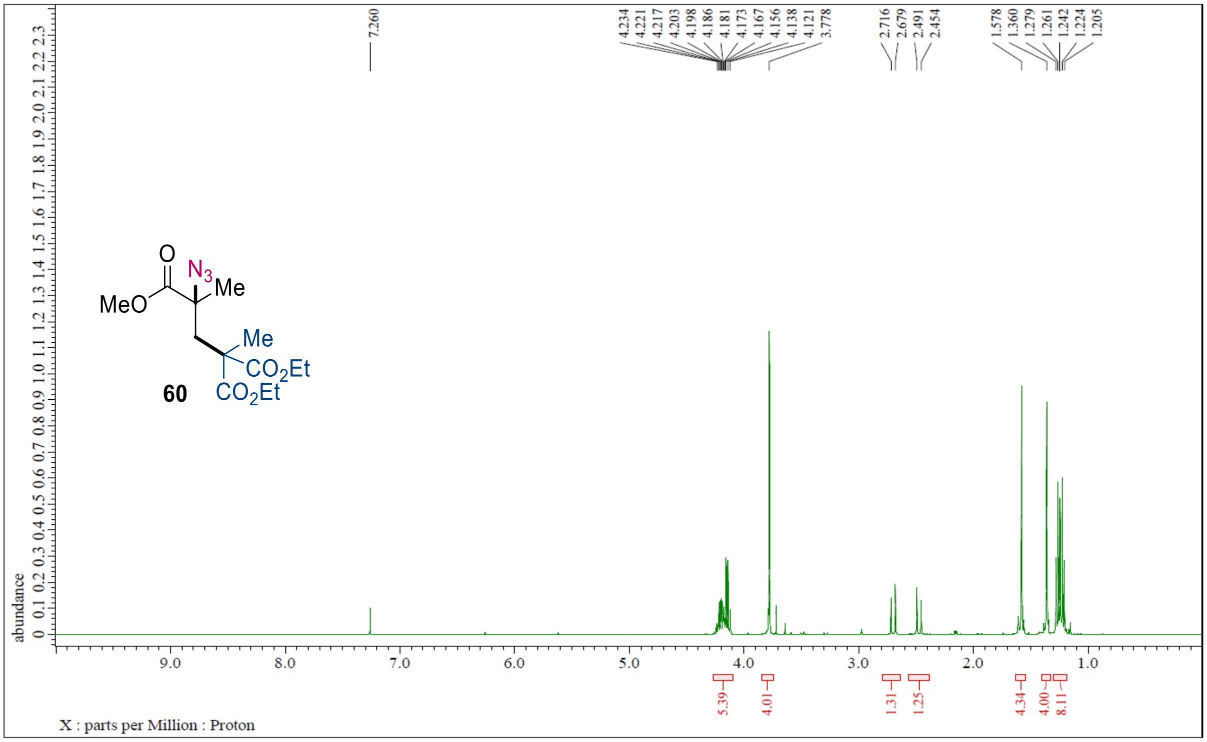
59 ^{1}H NMR (400 MHz, $CDCl_3$)



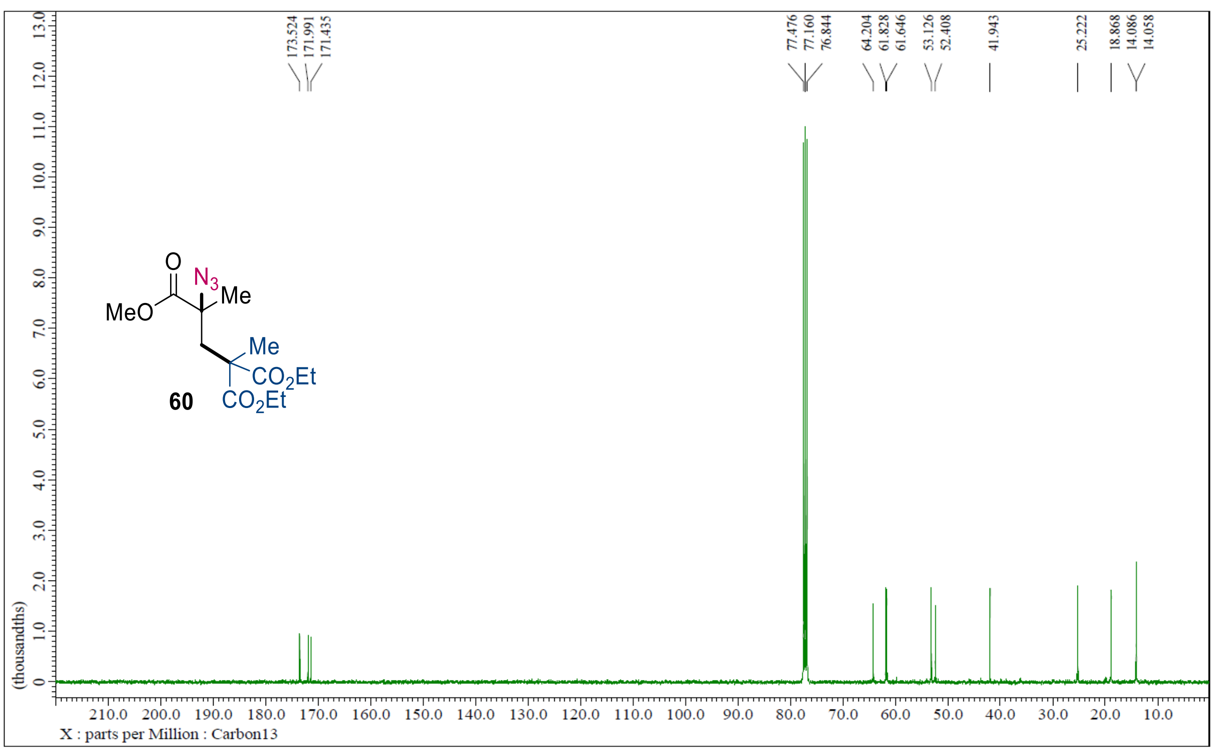
59 ^{13}C NMR (100 MHz, $CDCl_3$)



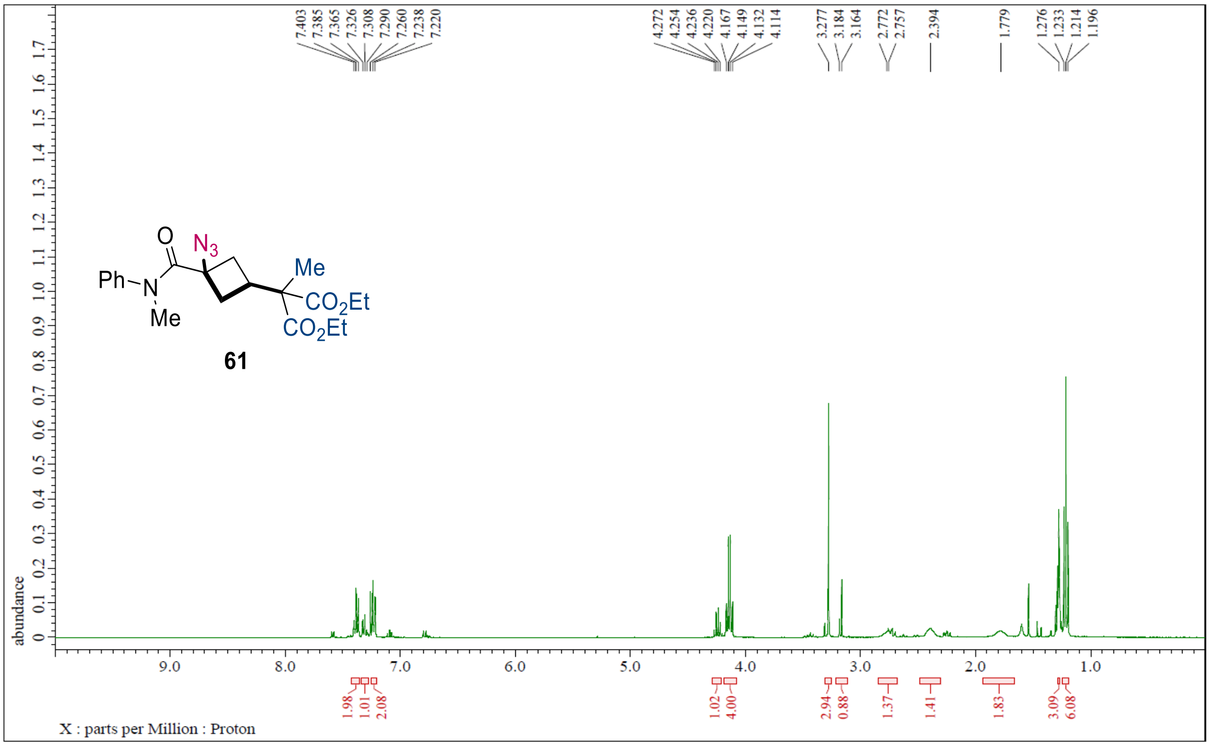
60 ^{1}H NMR (400 MHz, $CDCl_3$)



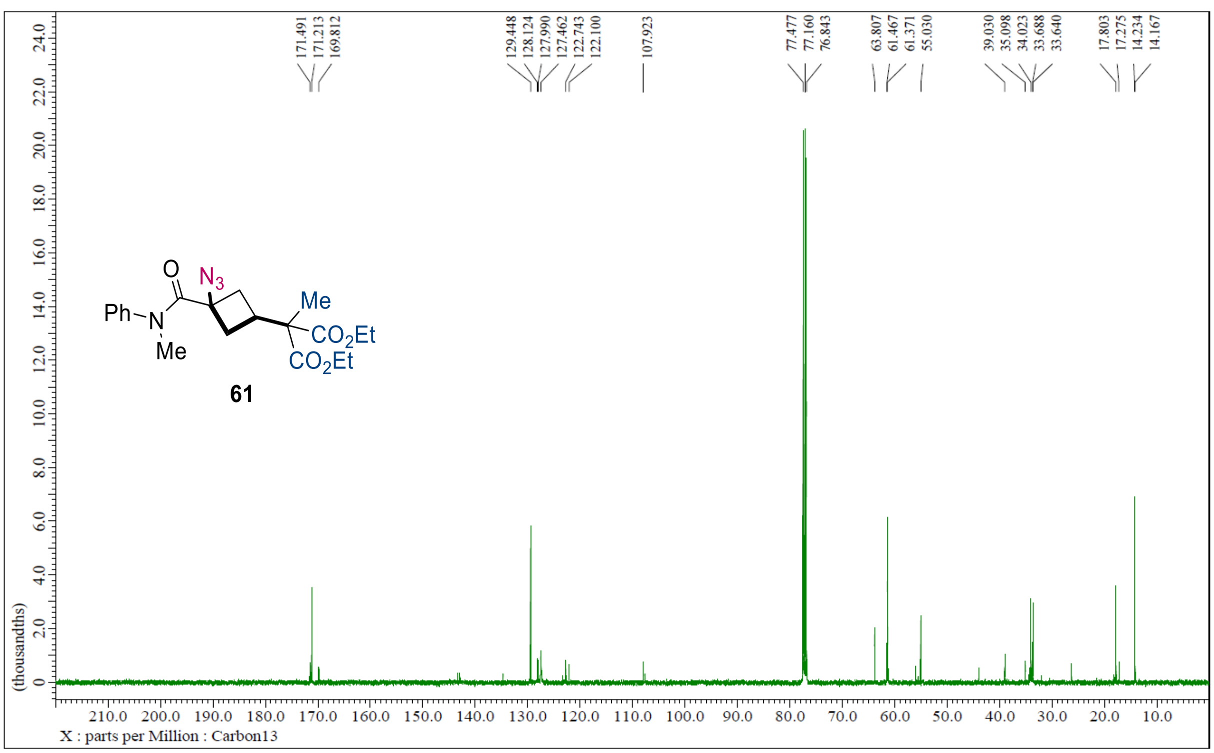
60 ^{13}C NMR (100 MHz, $CDCl_3$)



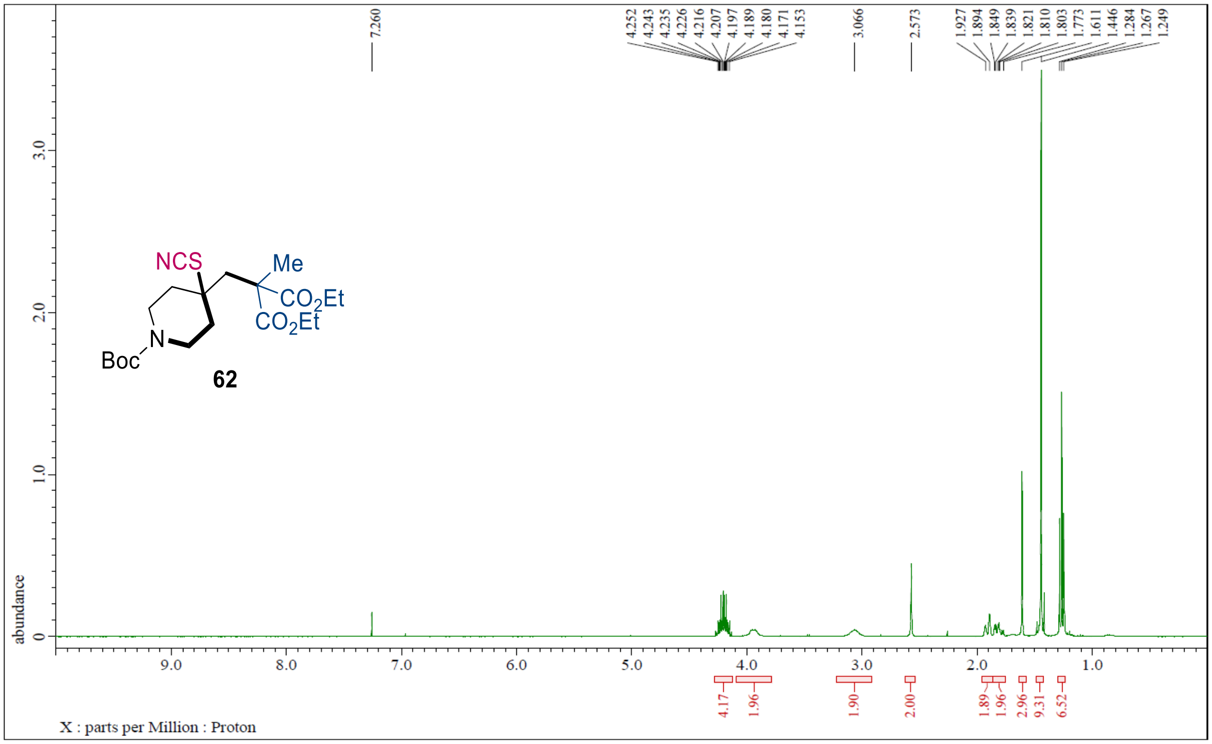
61 ^{1}H NMR (400 MHz, $CDCl_3$)



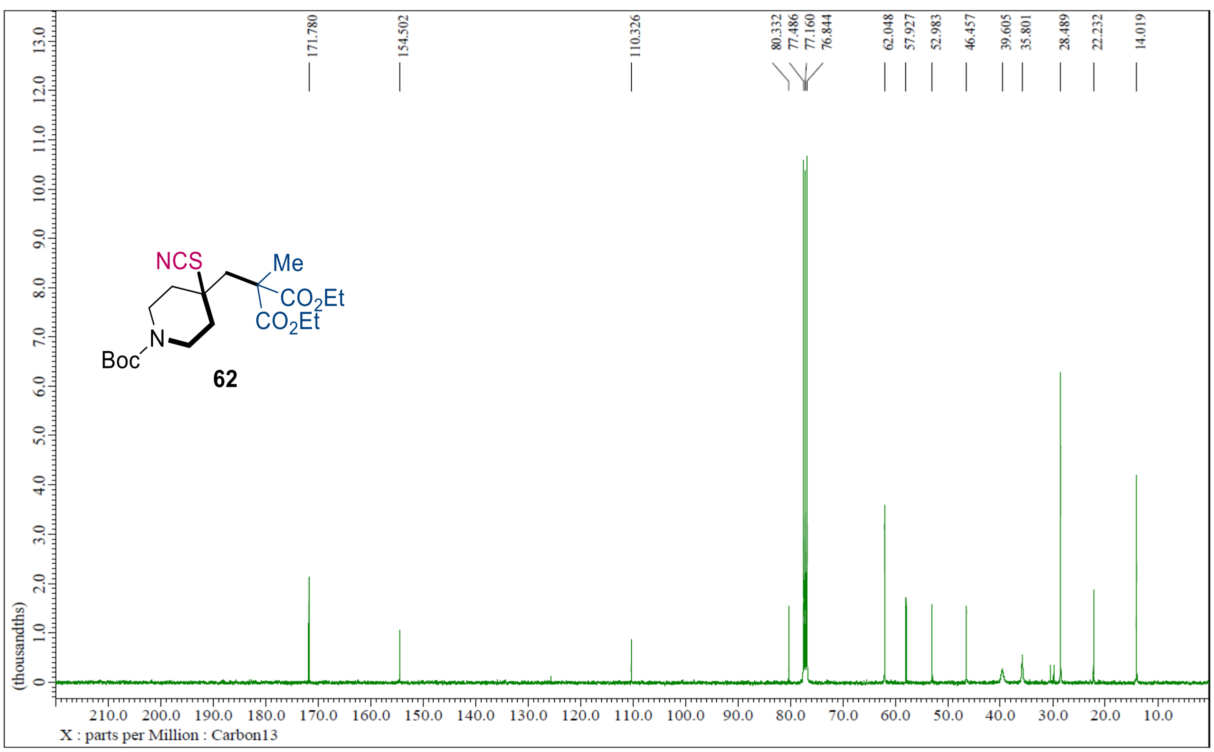
61 ^{13}C NMR (100 MHz, $CDCl_3$)



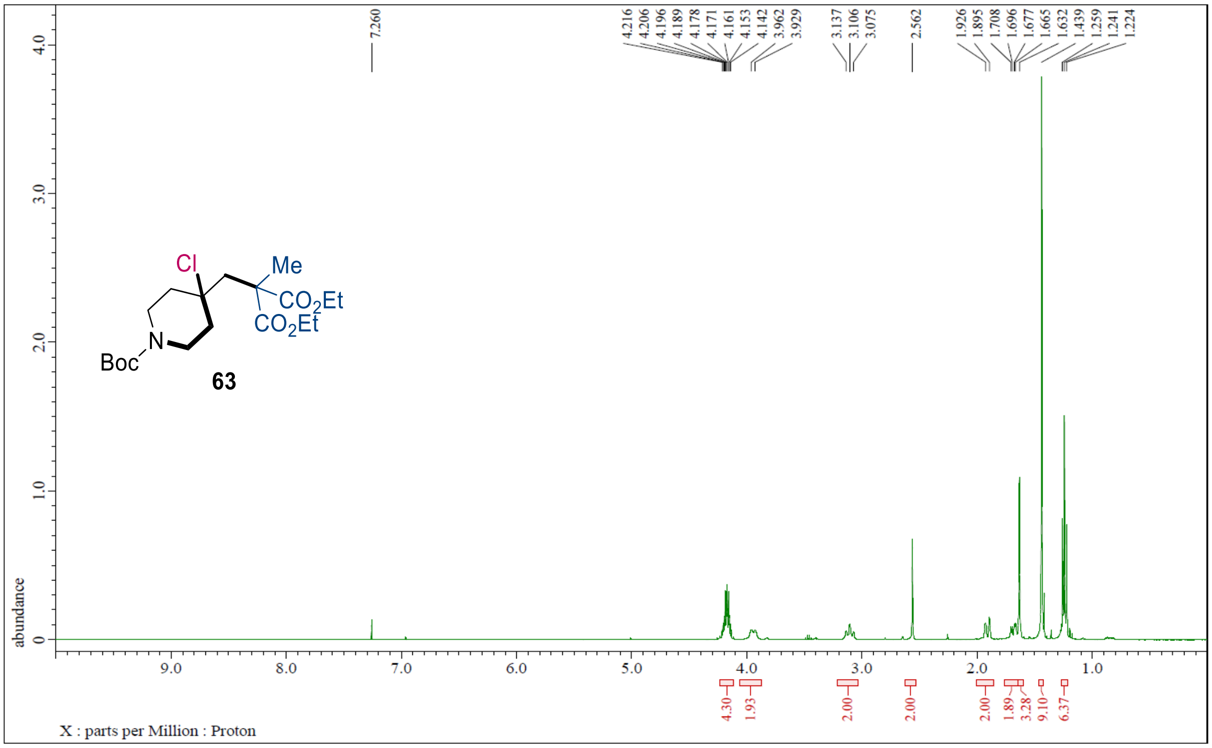
62 ^{1}H NMR (400 MHz, $CDCl_3$)



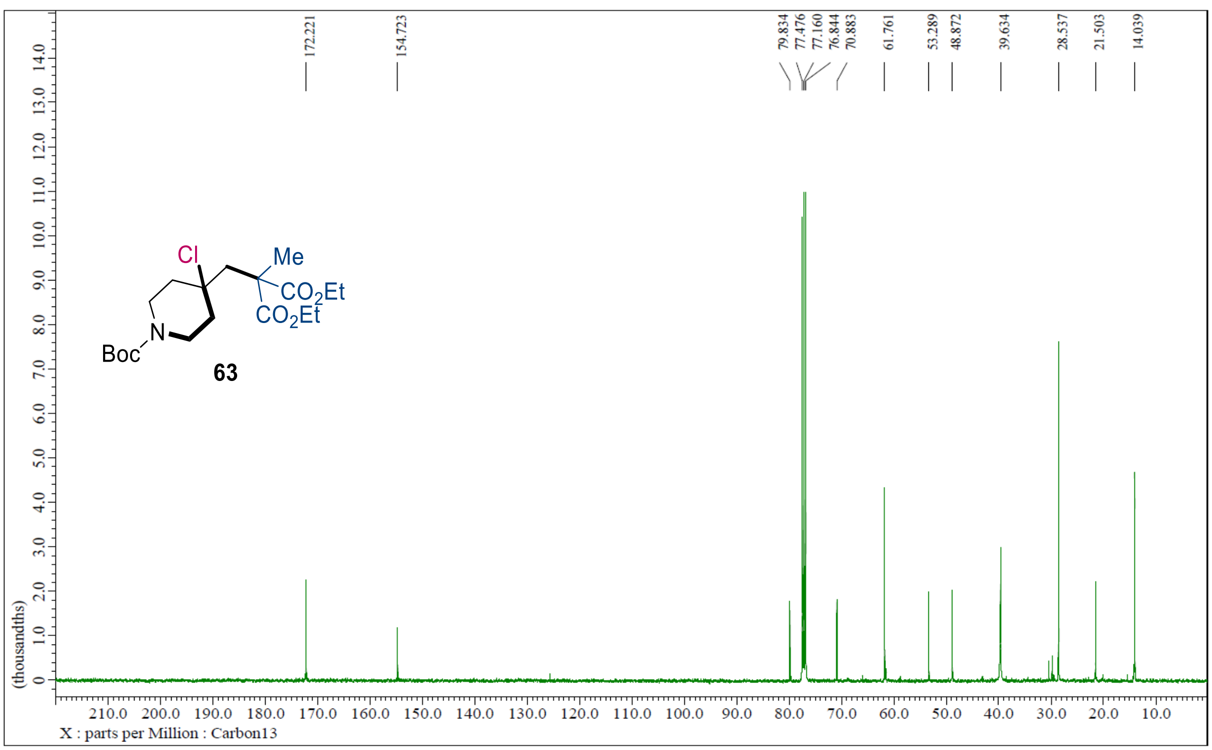
62 ^{13}C NMR (100 MHz, $CDCl_3$)



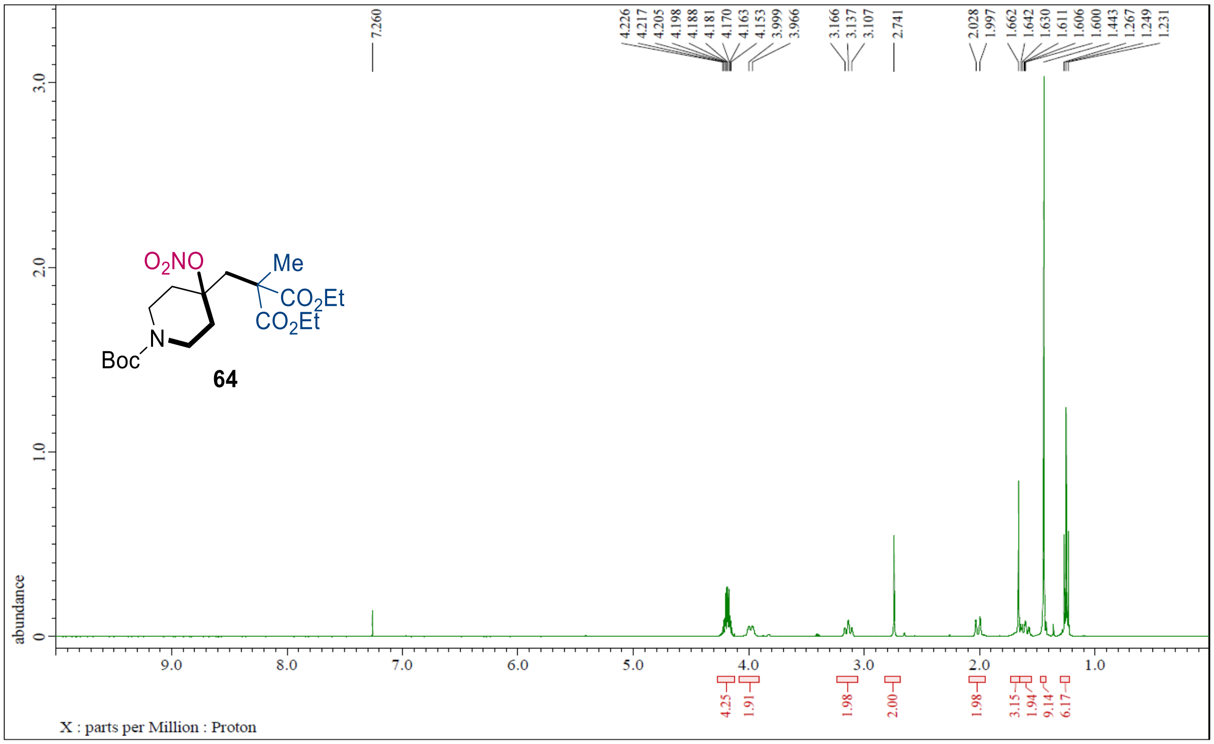
63 ^{1}H NMR (400 MHz, $CDCl_3$)



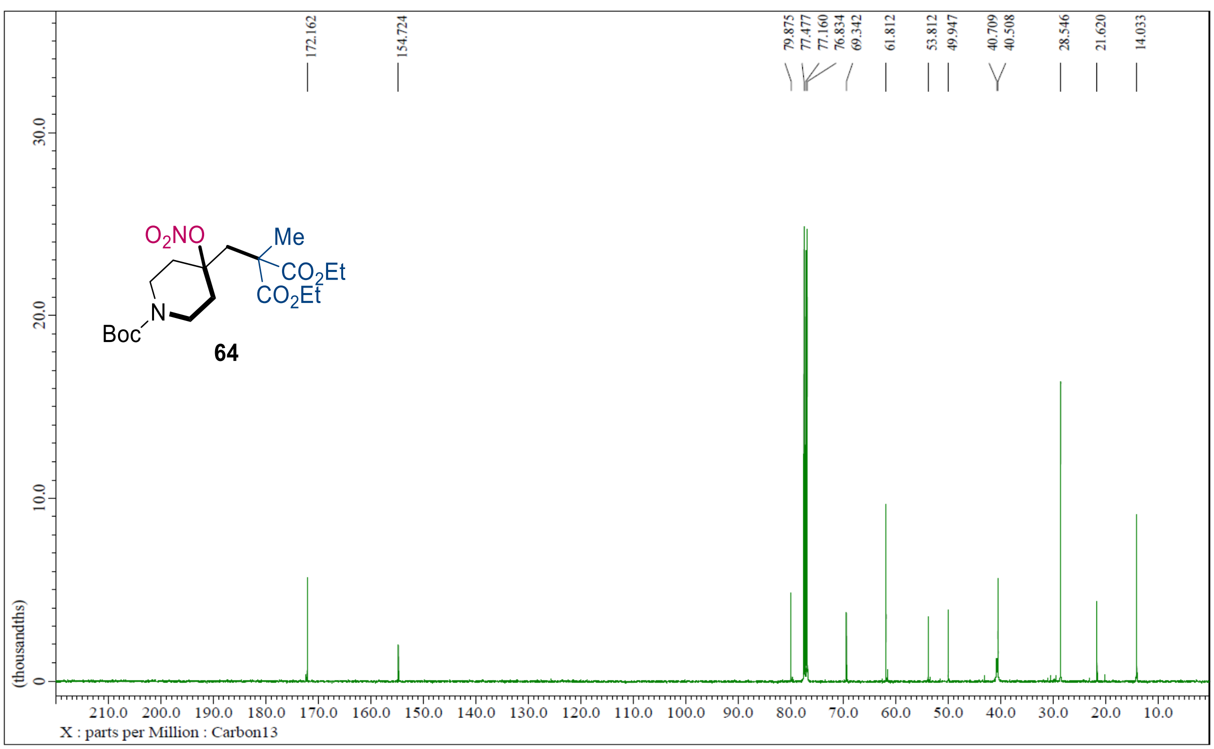
63 ^{13}C NMR (100 MHz, $CDCl_3$)



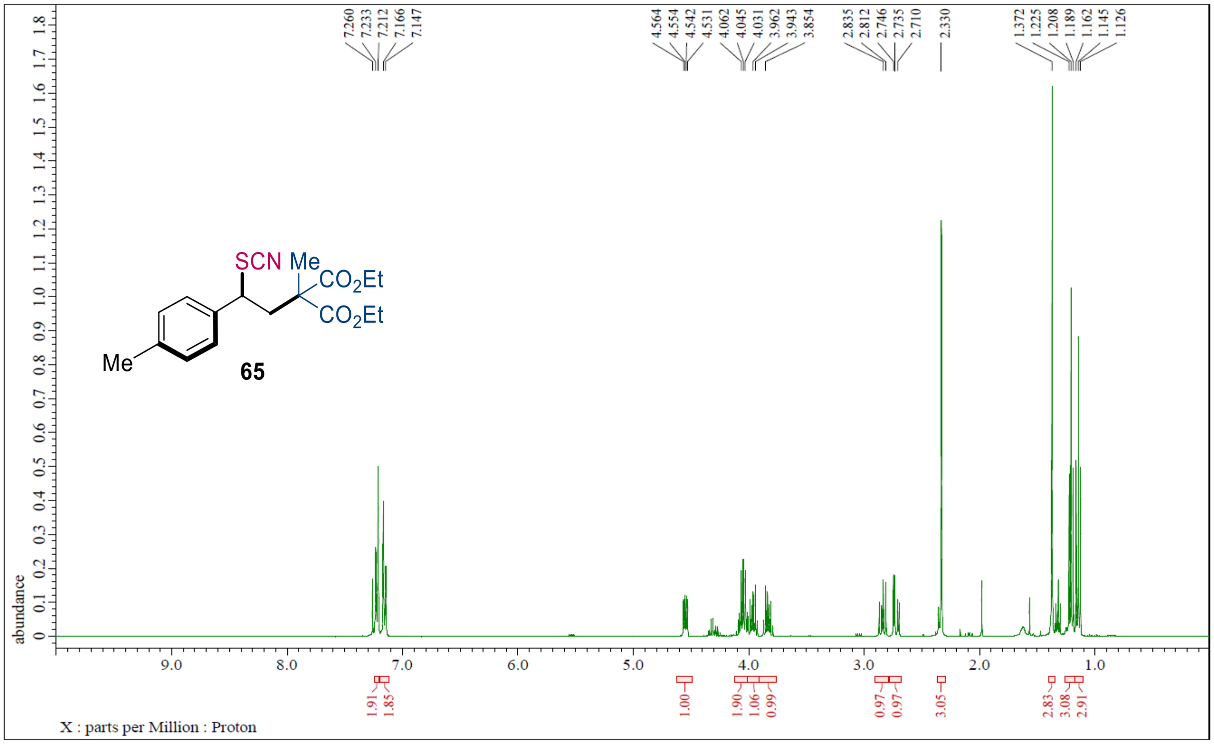
64 ^{1}H NMR (400 MHz, $CDCl_3$)



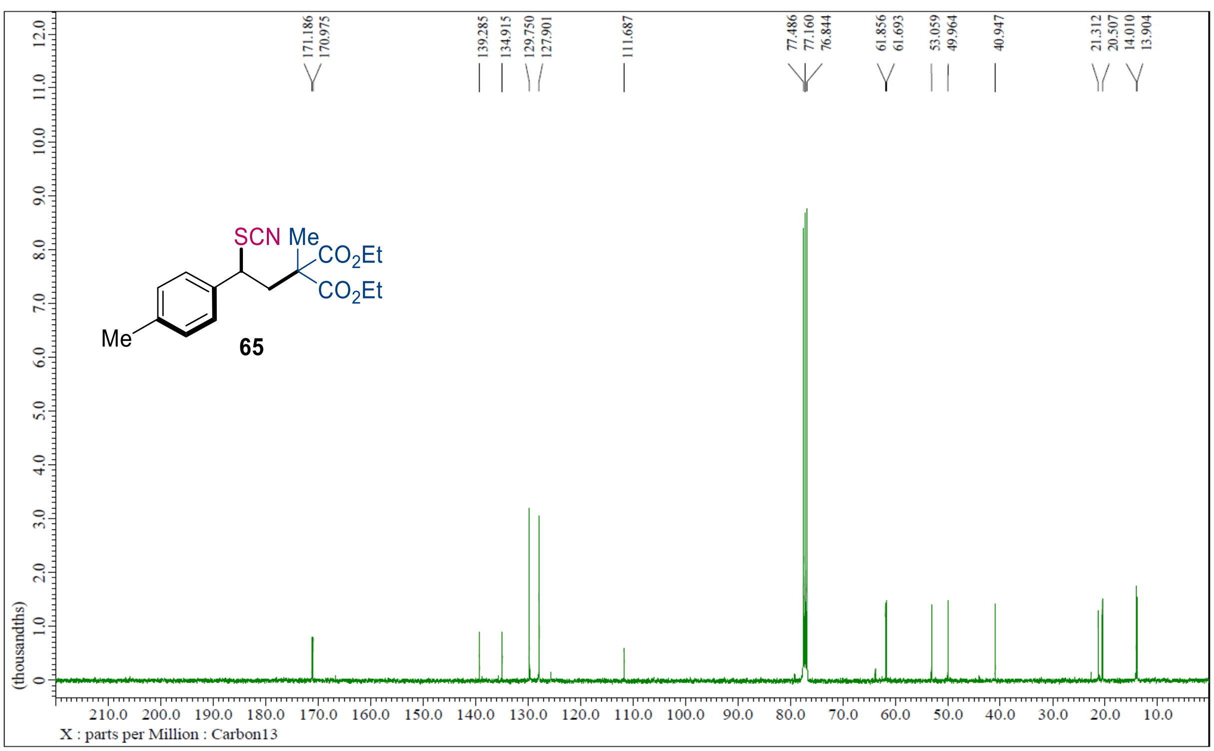
64 ^{13}C NMR (100 MHz, $CDCl_3$)



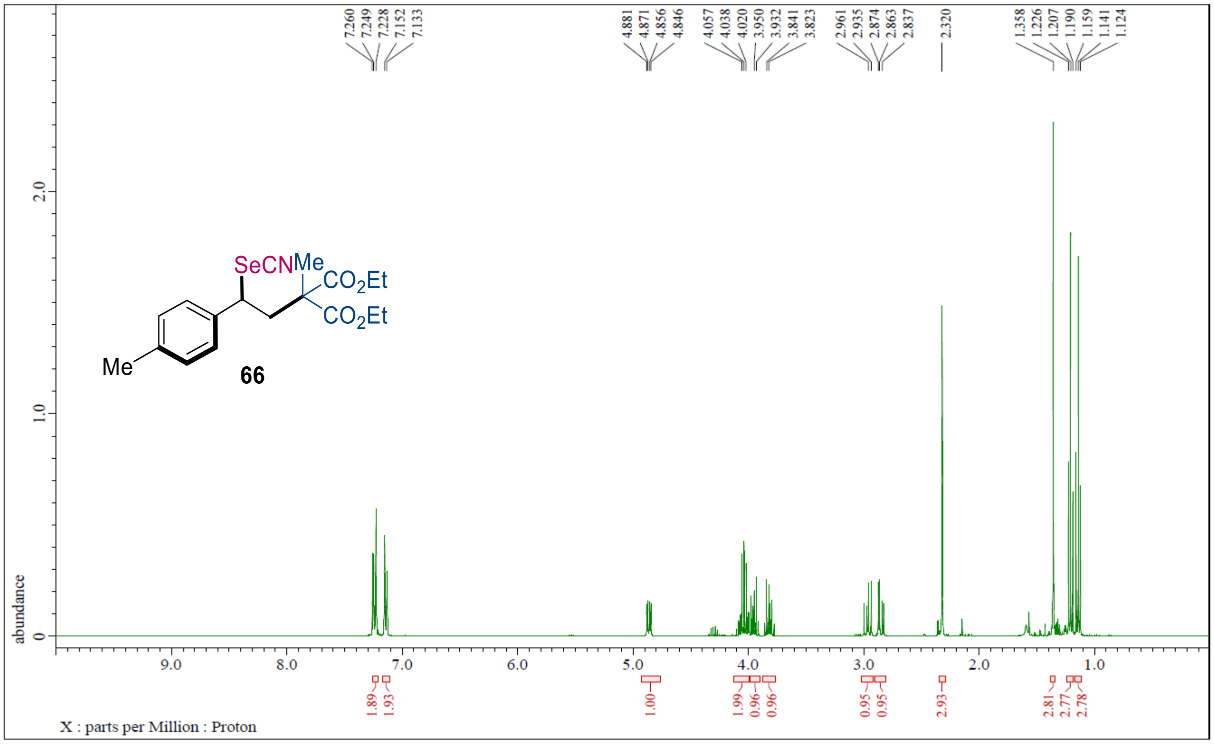
65 ^{1}H NMR (400 MHz, $CDCl_3$)



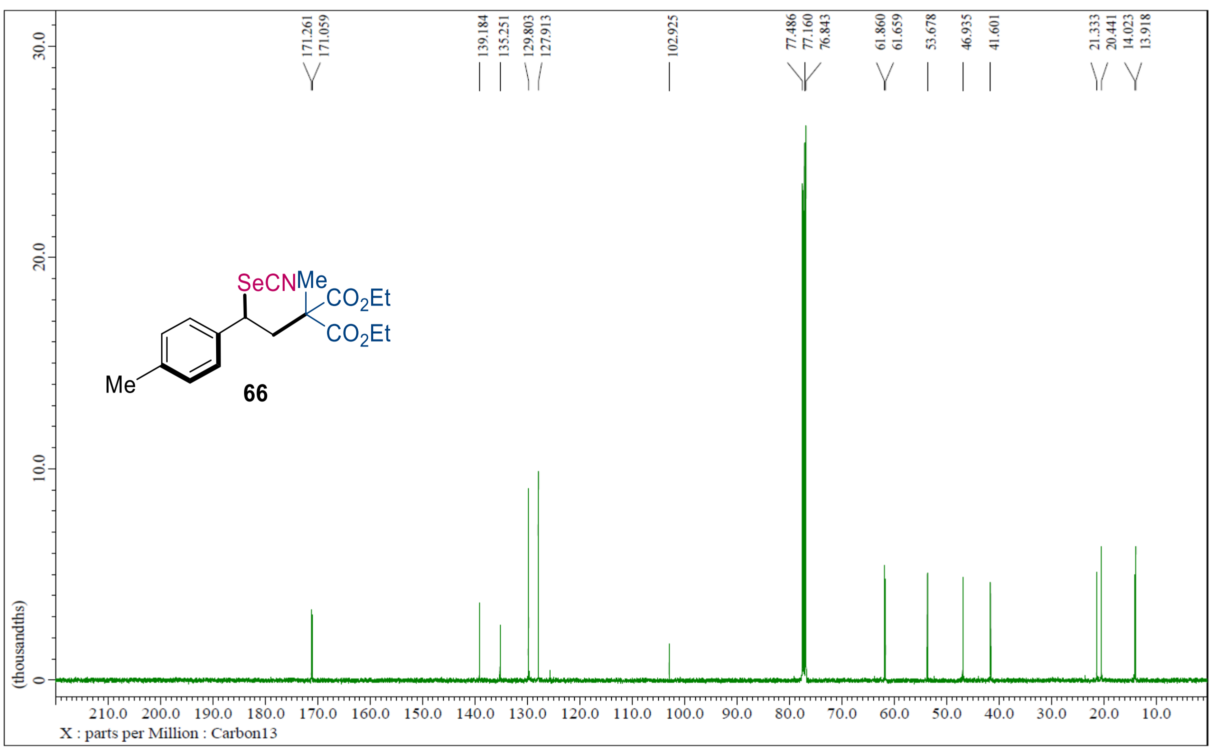
65 ^{13}C NMR (100 MHz, $CDCl_3$)



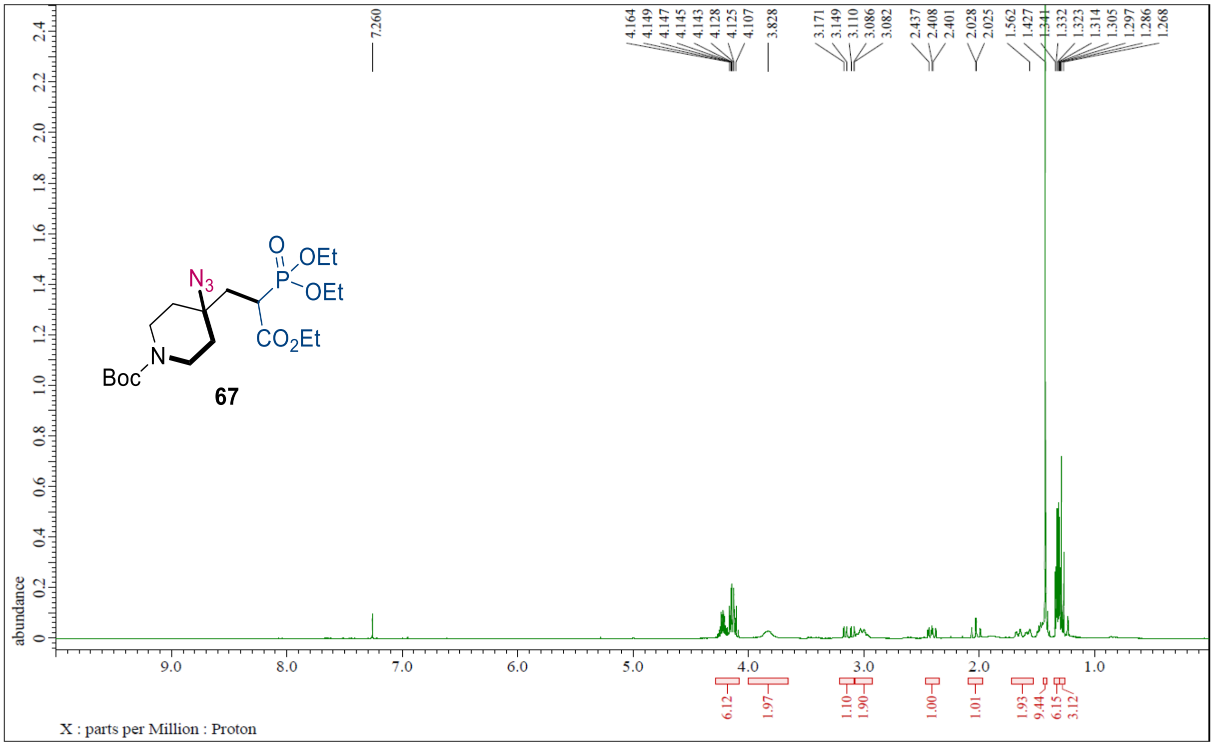
66 ^{1}H NMR (400 MHz, $CDCl_3$)



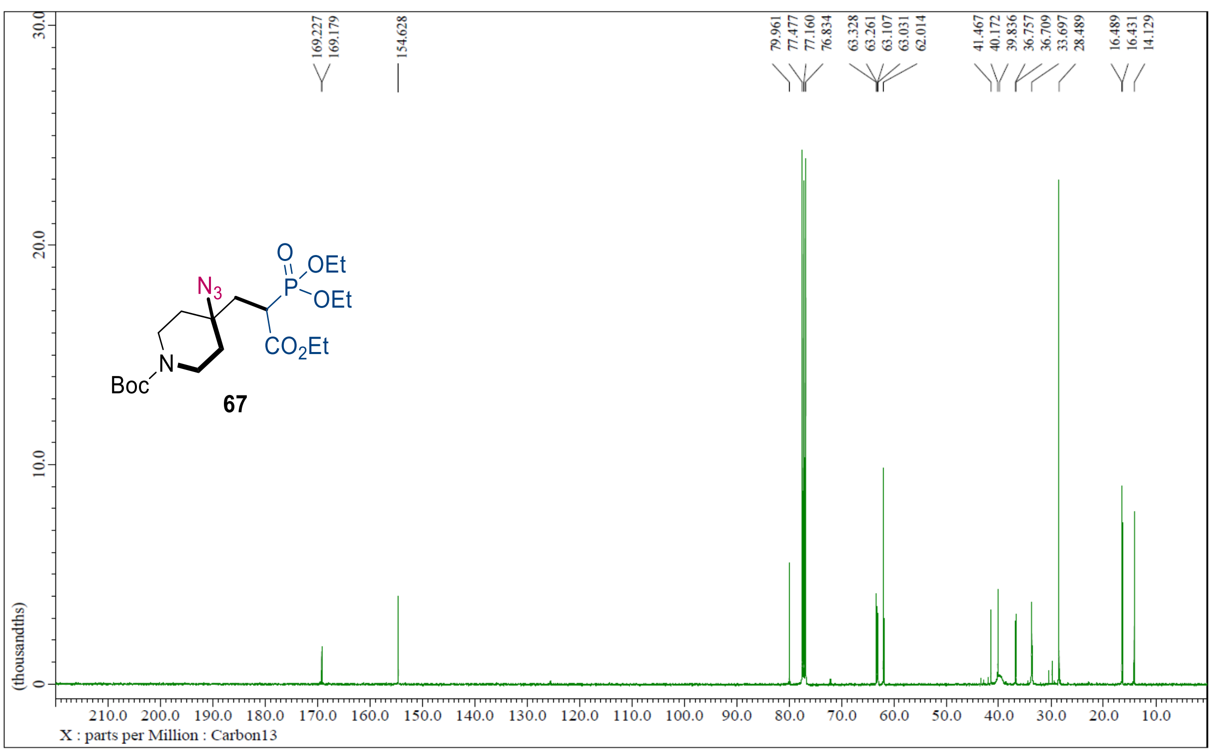
66 ^{13}C NMR (100 MHz, $CDCl_3$)



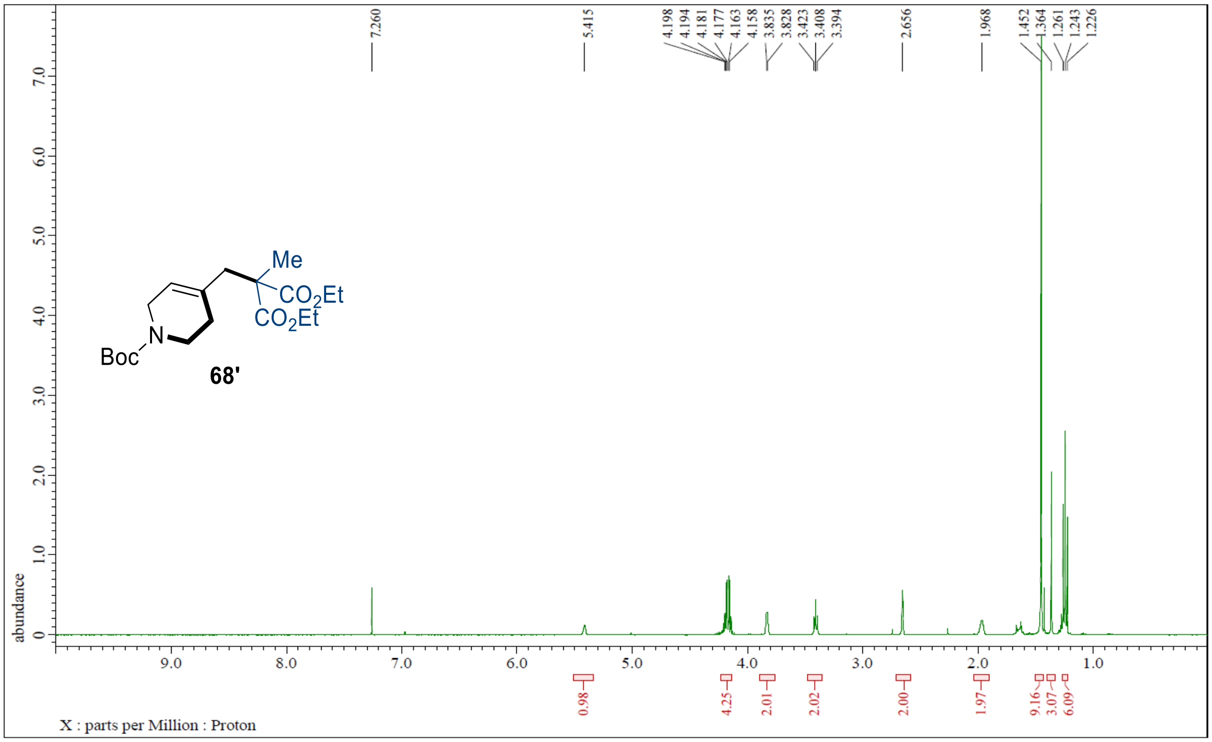
67 ^{1}H NMR (400 MHz, $CDCl_3$)



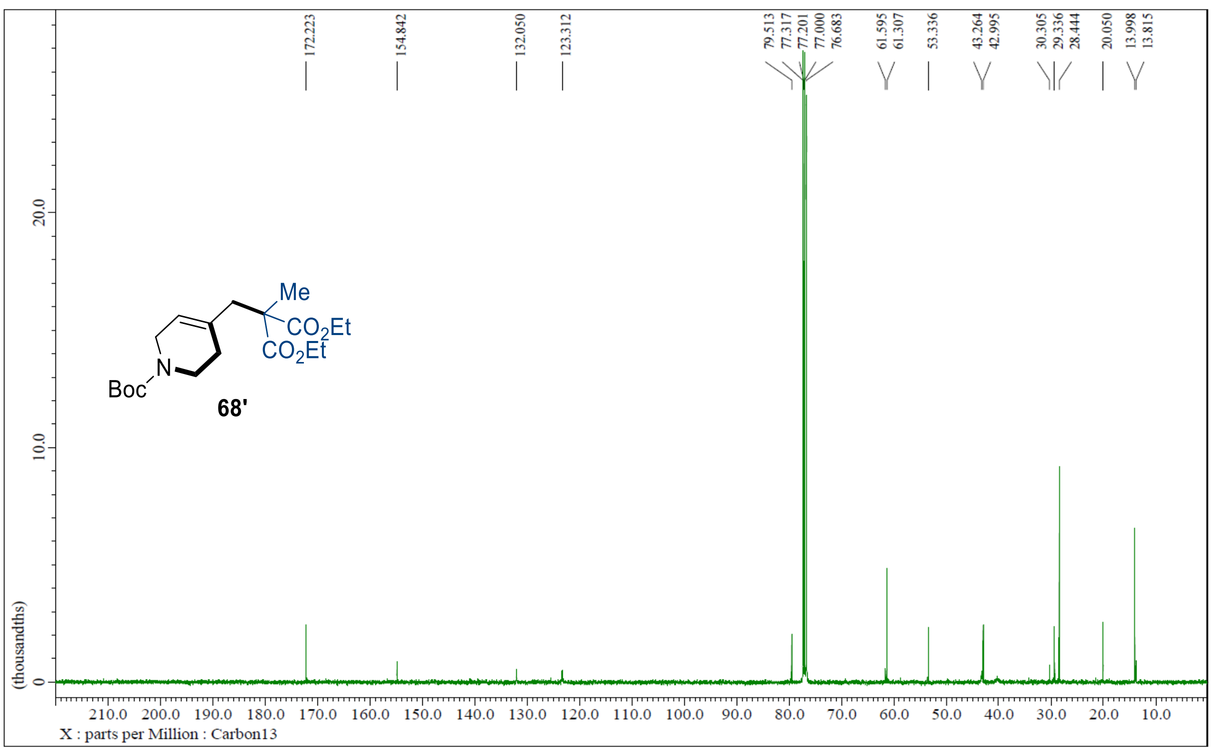
67 ^{13}C NMR (100 MHz, $CDCl_3$)



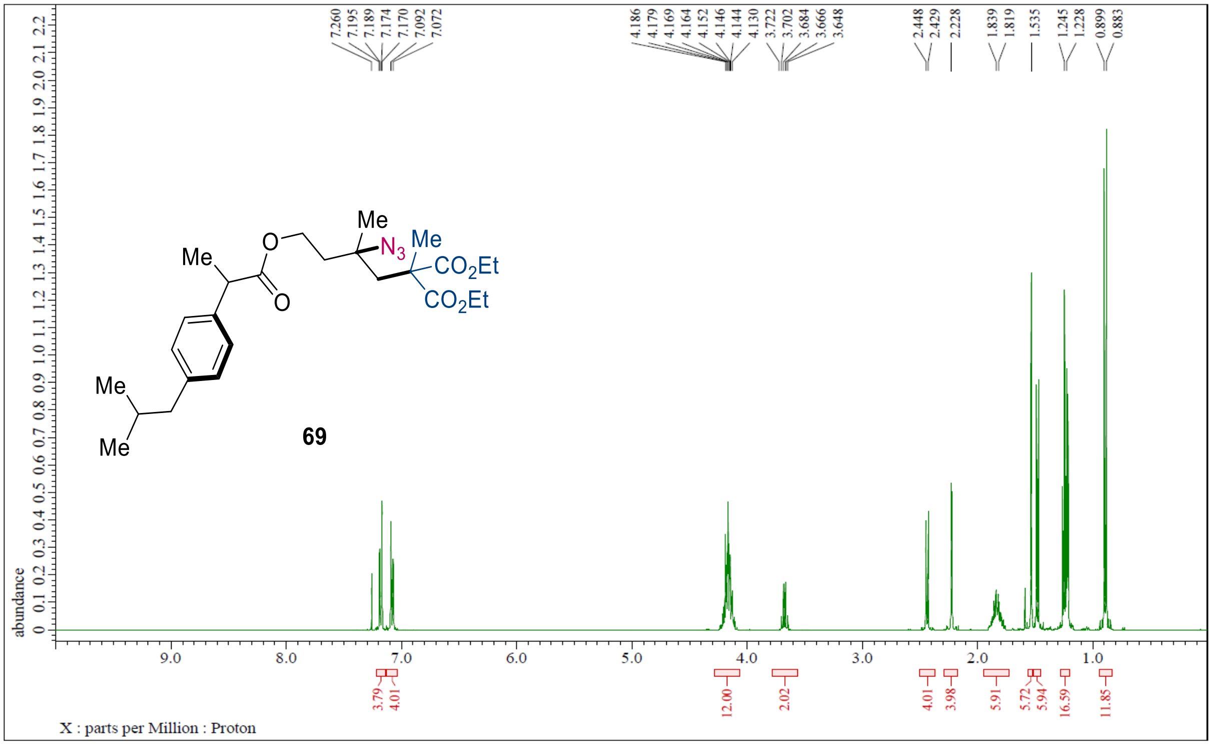
68' ^{1}H NMR (400 MHz, $CDCl_3$)



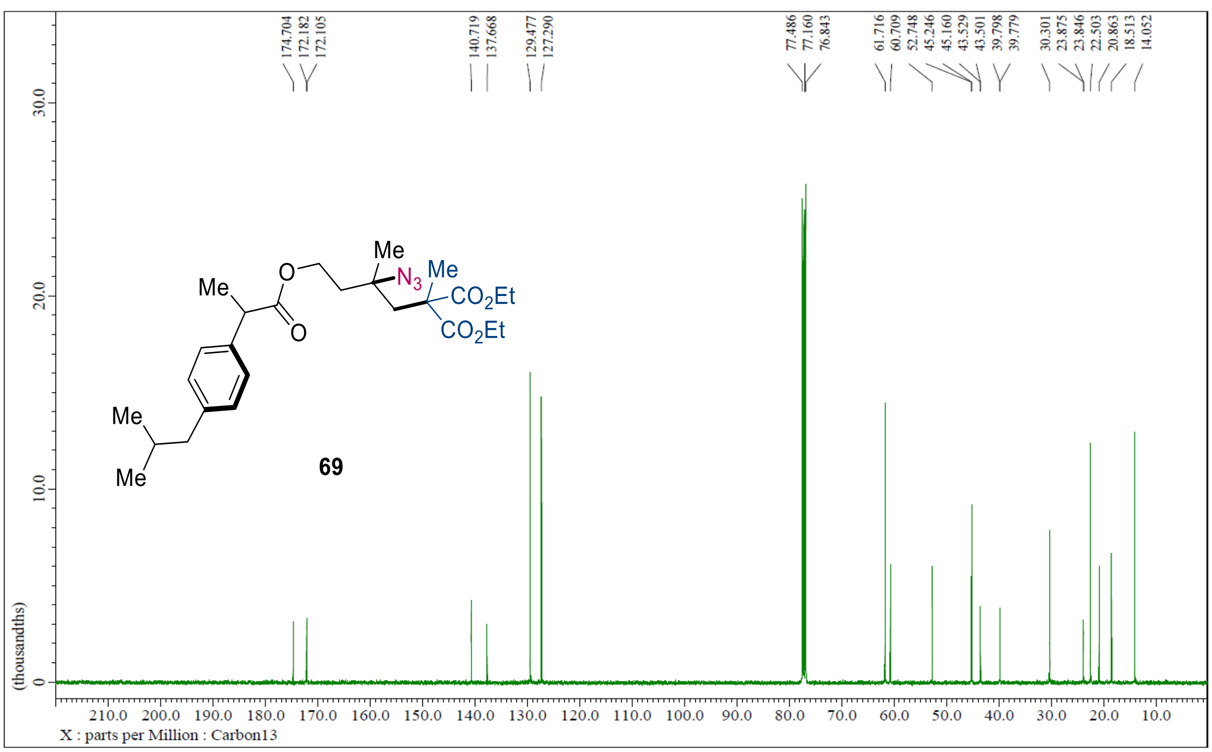
68' ^{13}C NMR (100 MHz, $CDCl_3$)



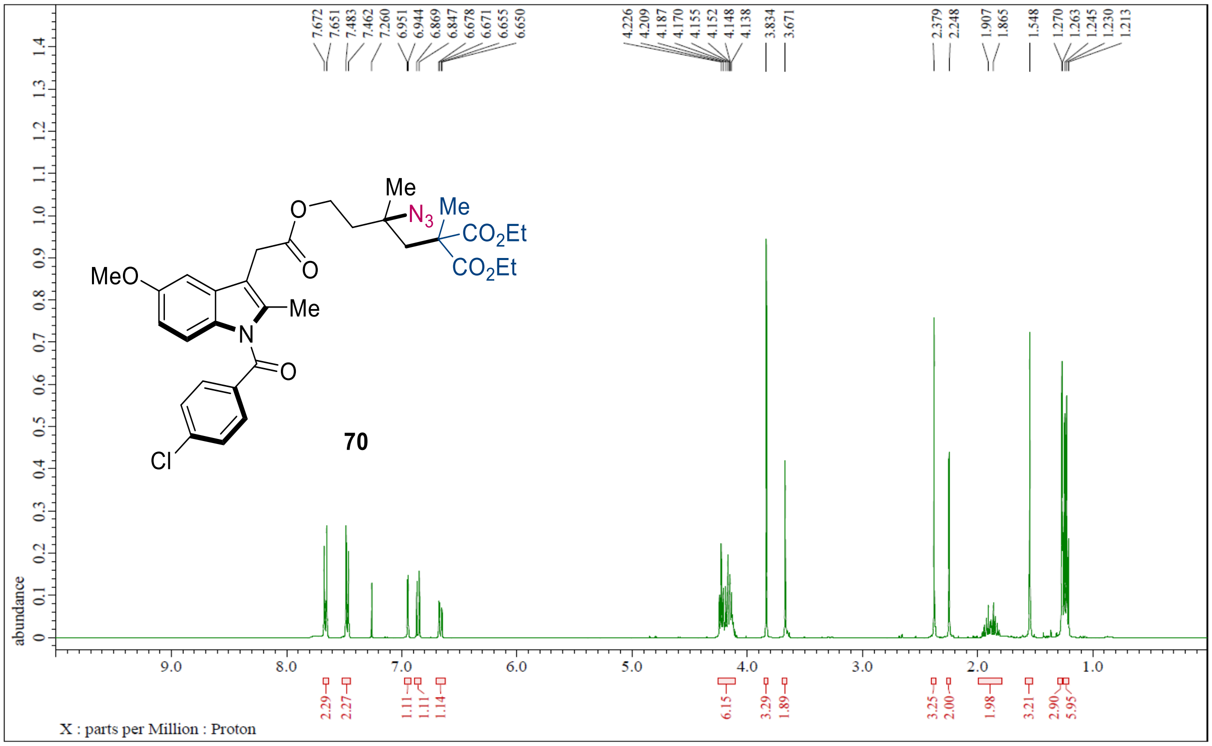
69 ^{1}H NMR (400 MHz, $CDCl_3$)



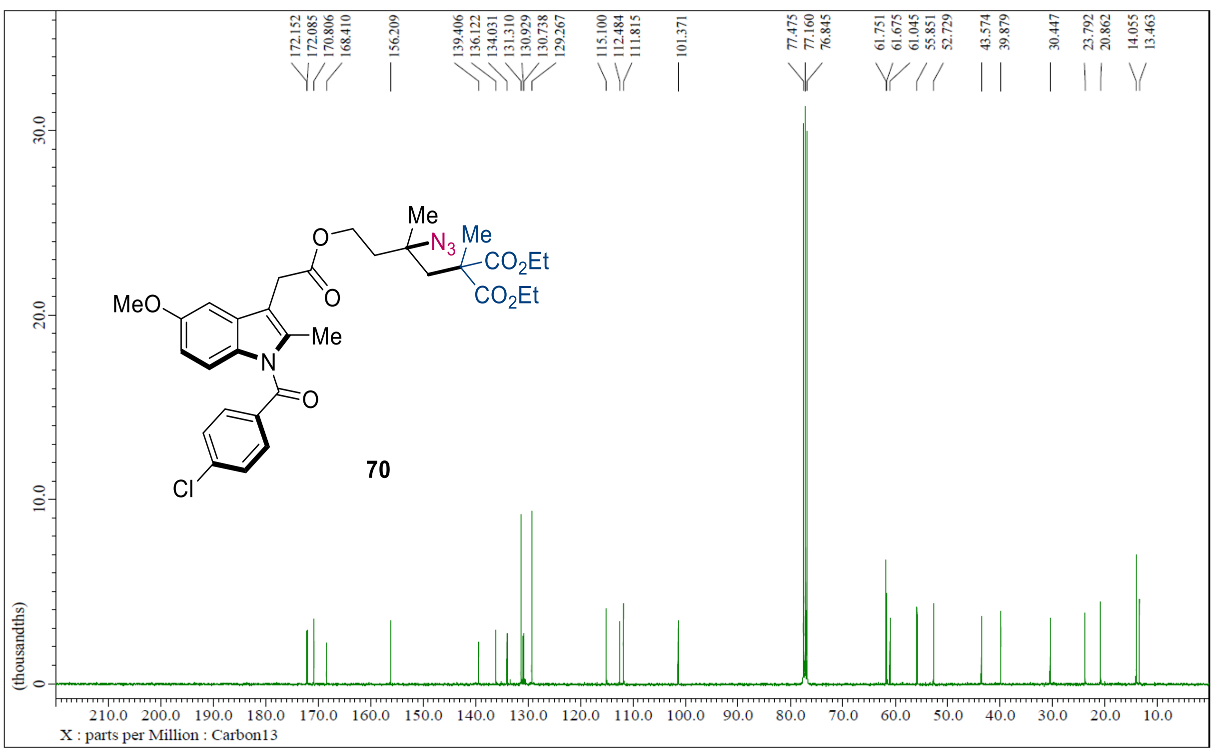
69 ^{13}C NMR (100 MHz, $CDCl_3$)



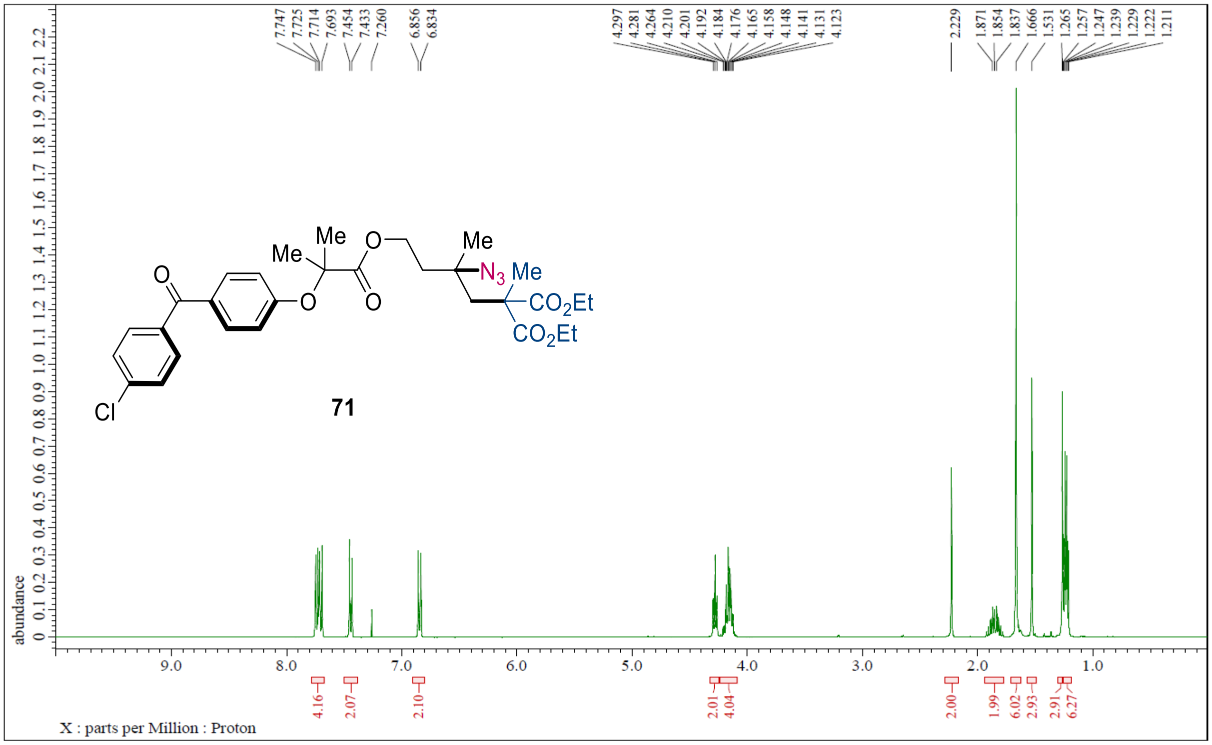
70 ^{1}H NMR (400 MHz, $CDCl_3$)



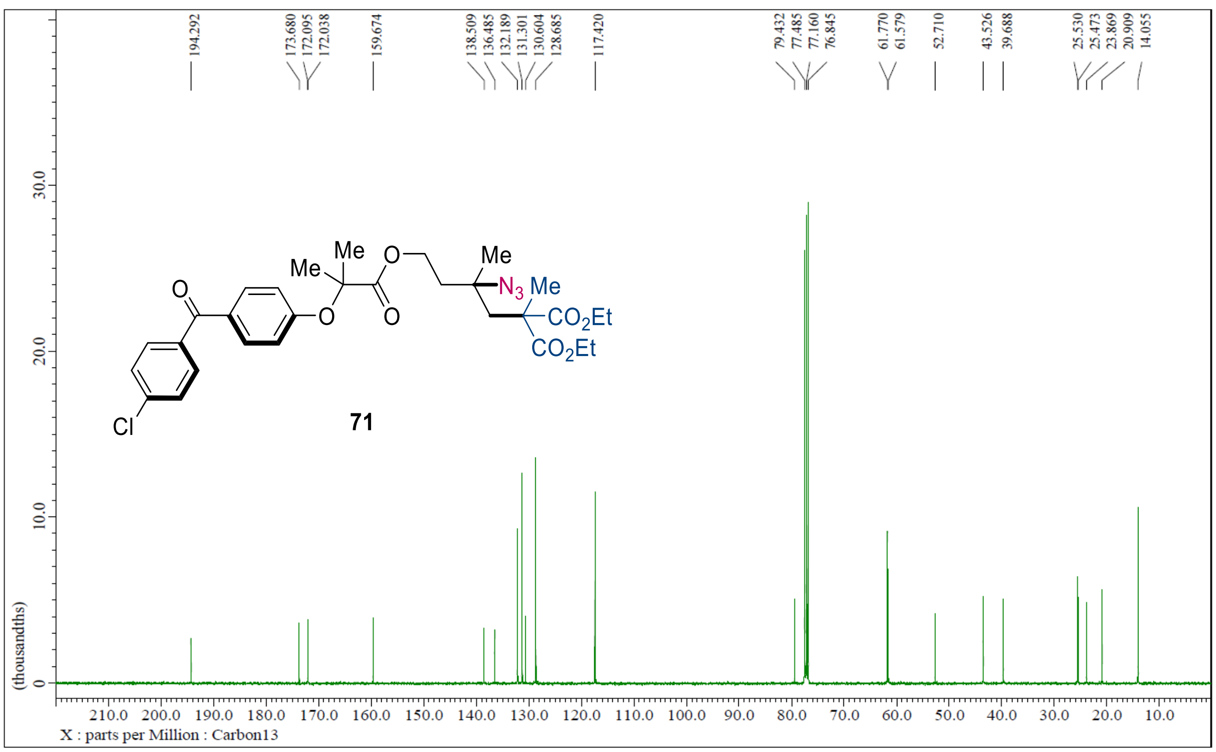
70 ^{13}C NMR (100 MHz, $CDCl_3$)



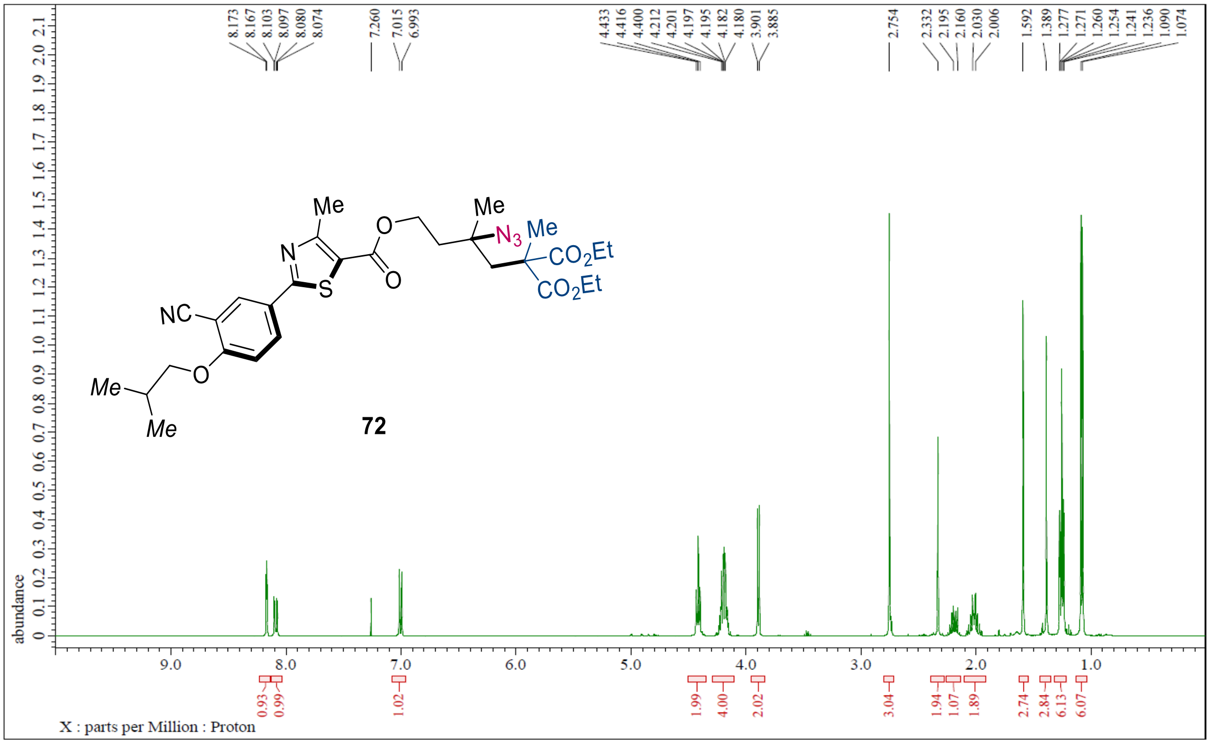
71 ^{1}H NMR (400 MHz, $CDCl_3$)



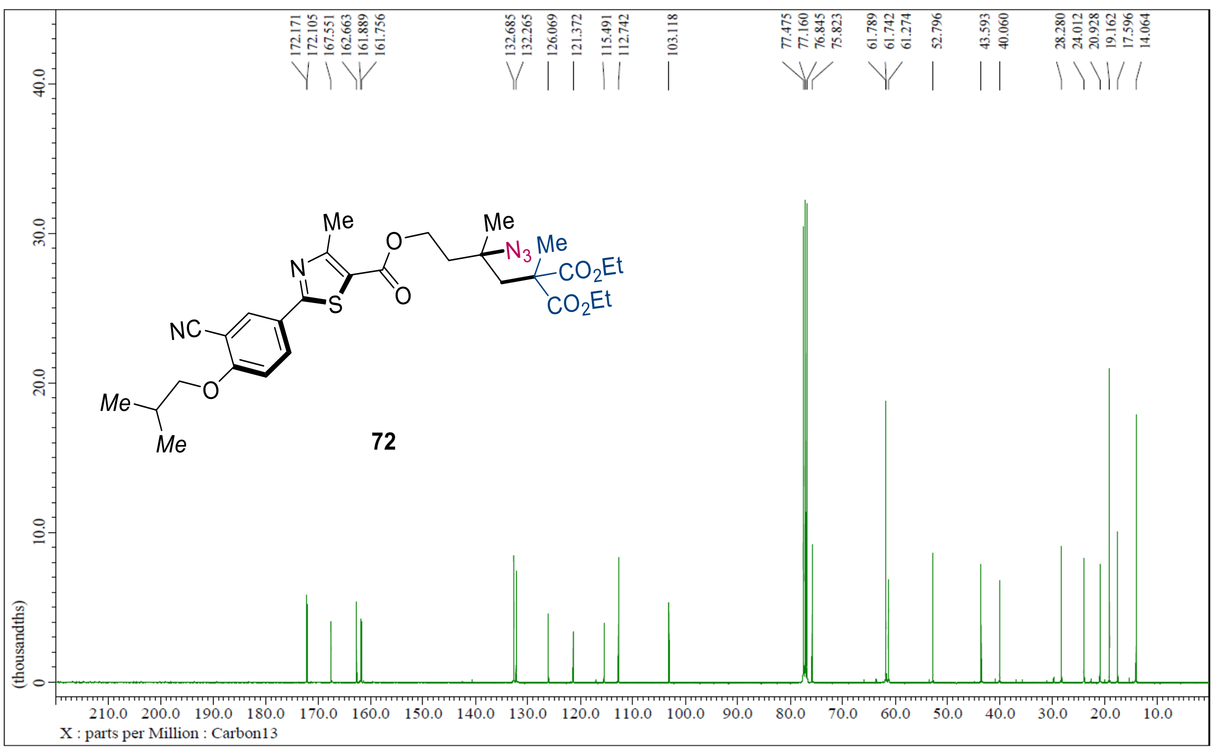
71 ^{13}C NMR (100 MHz, $CDCl_3$)



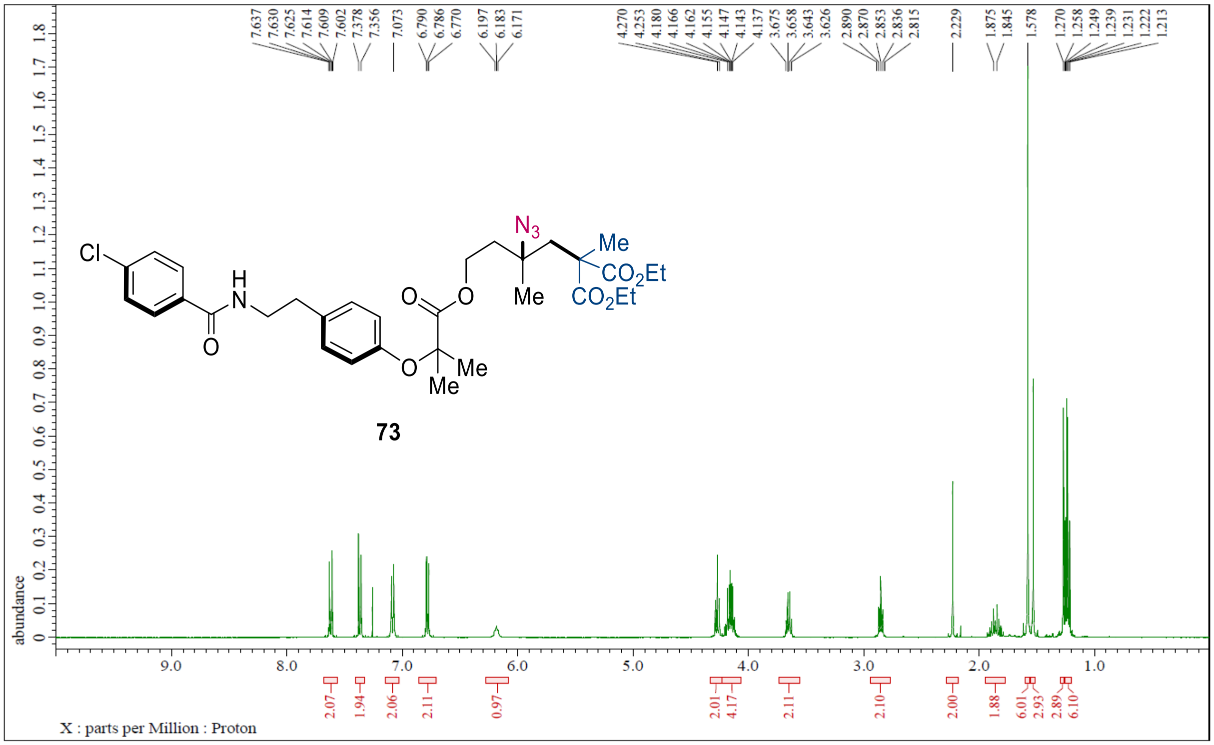
72 ^{1}H NMR (400 MHz, CDCl$_3$)



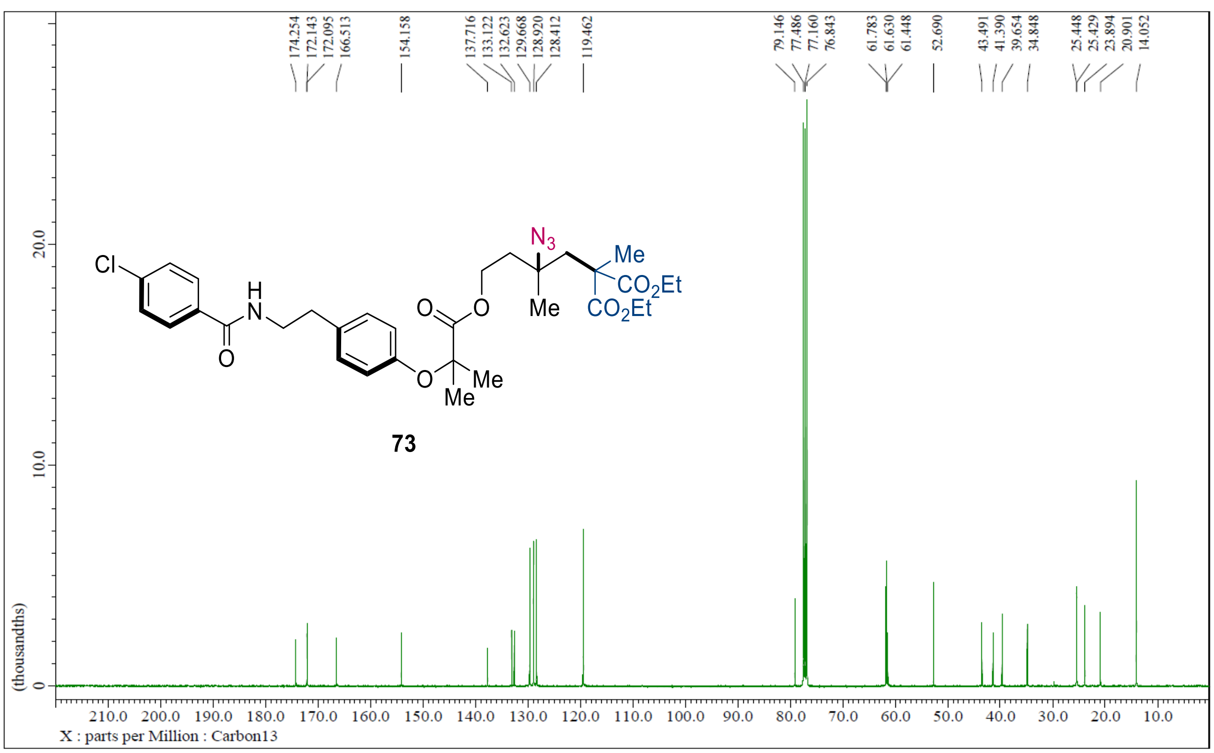
72 ^{13}C NMR (100 MHz, CDCl$_3$)



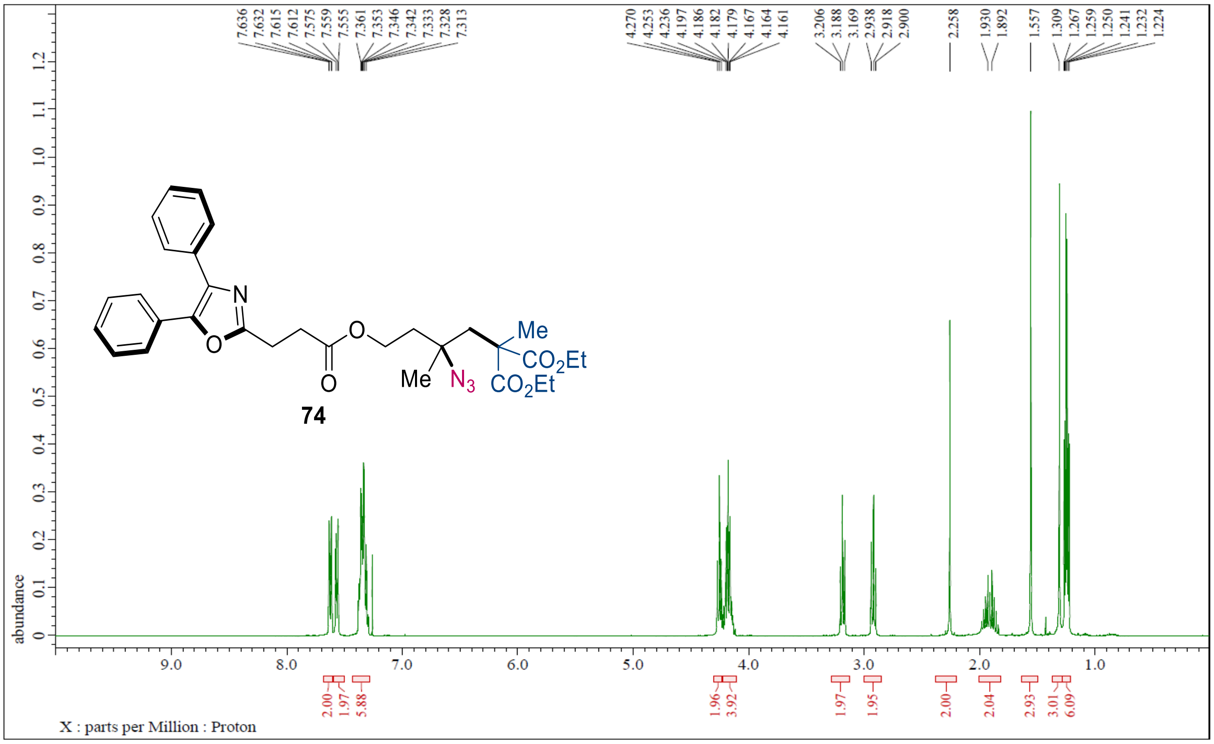
73 [1]H NMR (400 MHz, $CDCl_3$)



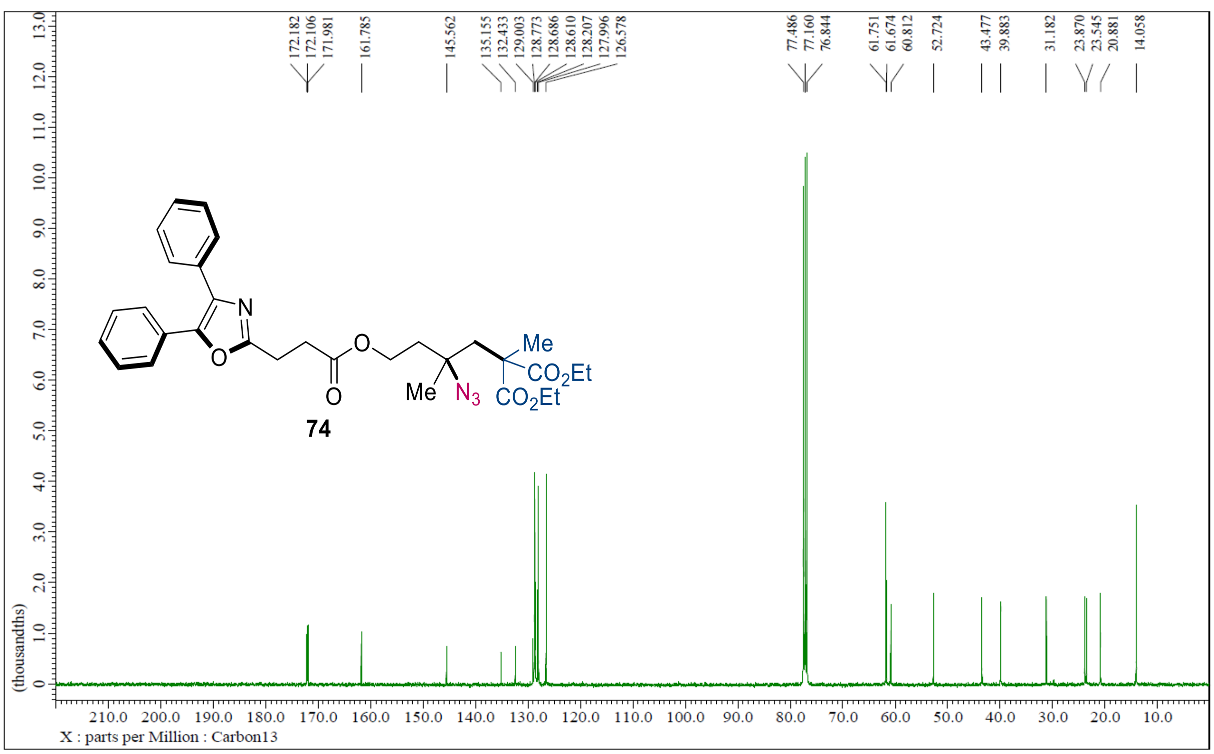
73 [13]C NMR (100 MHz, $CDCl_3$)



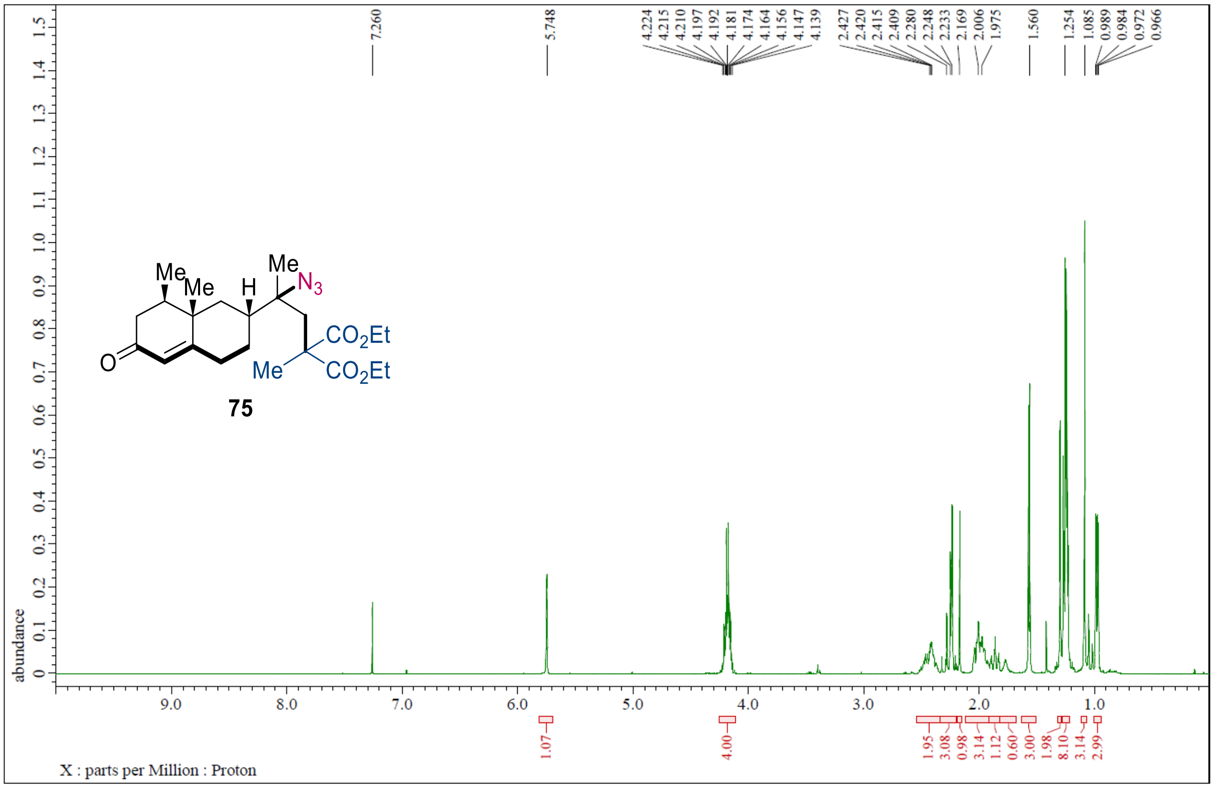
74 ^{1}H NMR (400 MHz, $CDCl_3$)



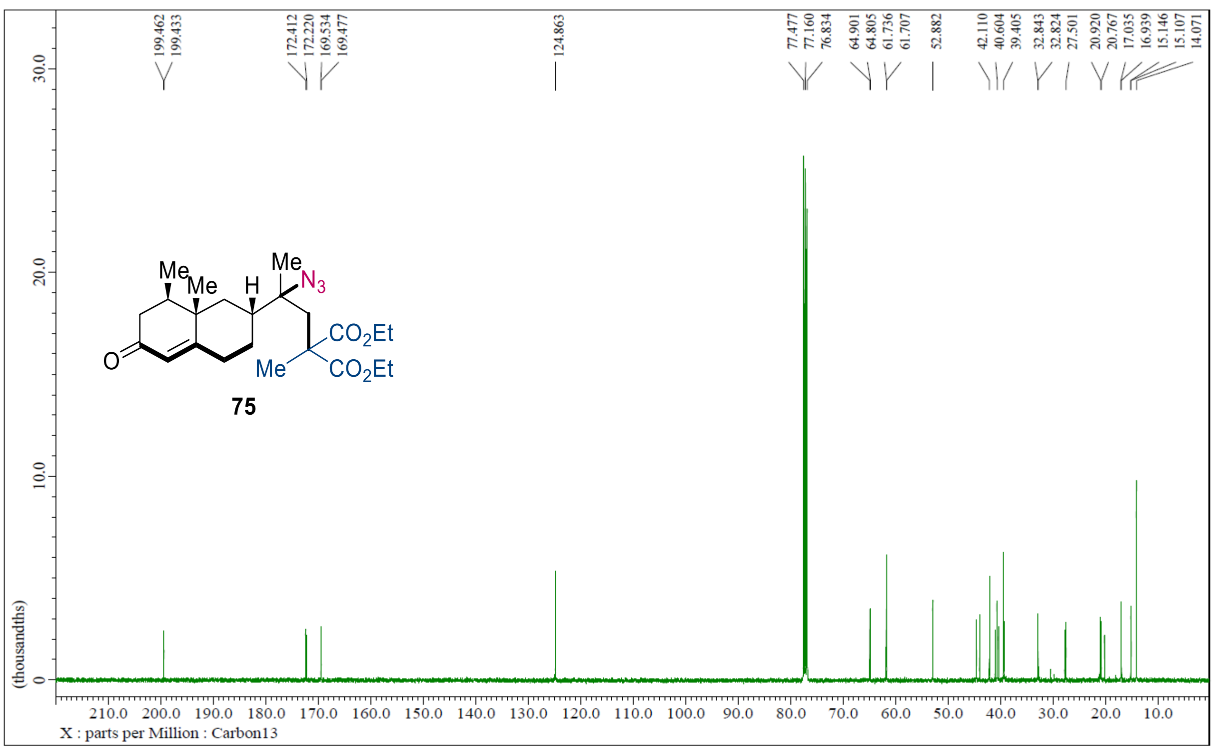
74 ^{13}C NMR (100 MHz, $CDCl_3$)



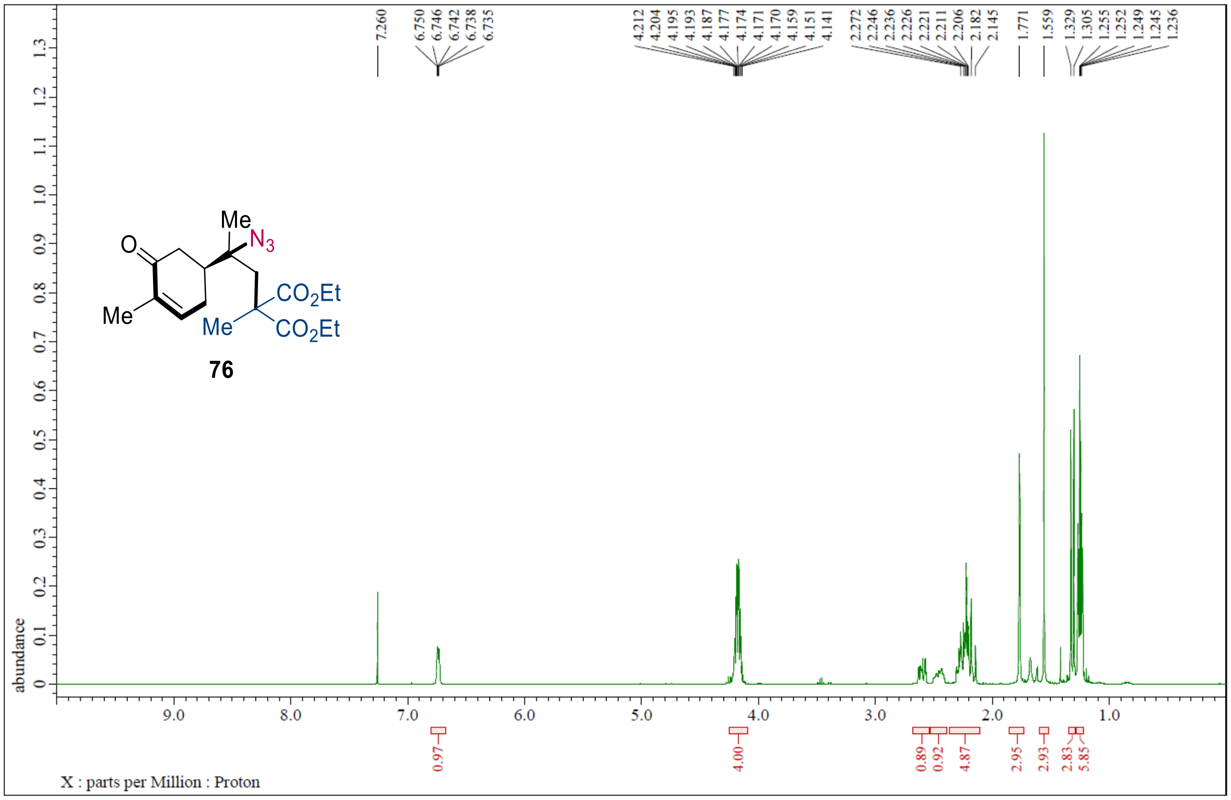
75 ^{1}H NMR (400 MHz, $CDCl_3$)



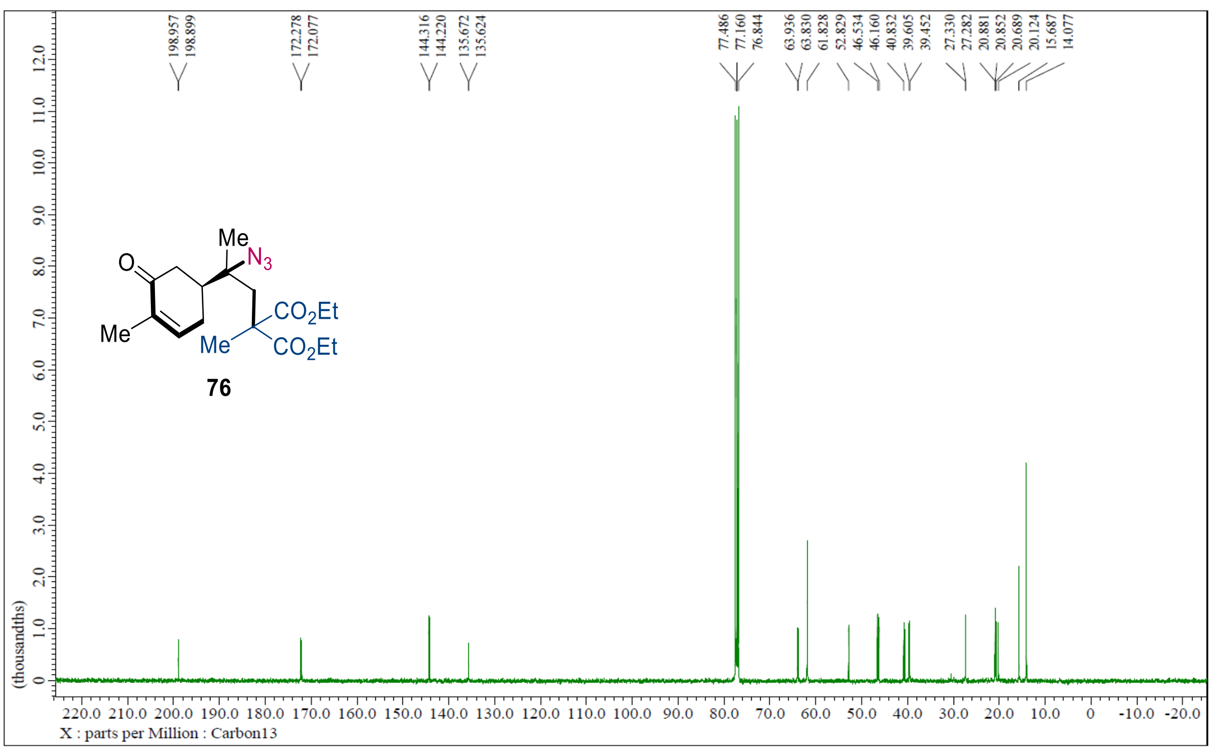
75 ^{13}C NMR (100 MHz, $CDCl_3$)



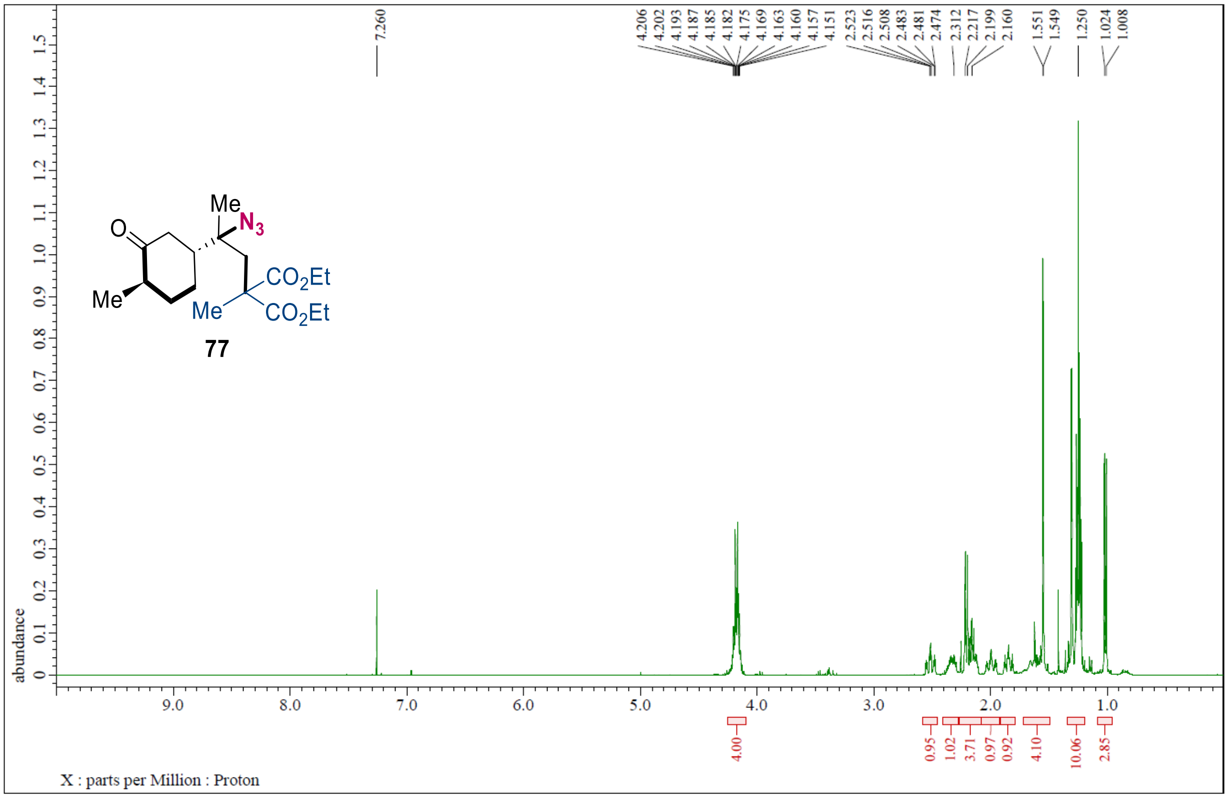
76 ^{1}H NMR (400 MHz, $CDCl_3$)



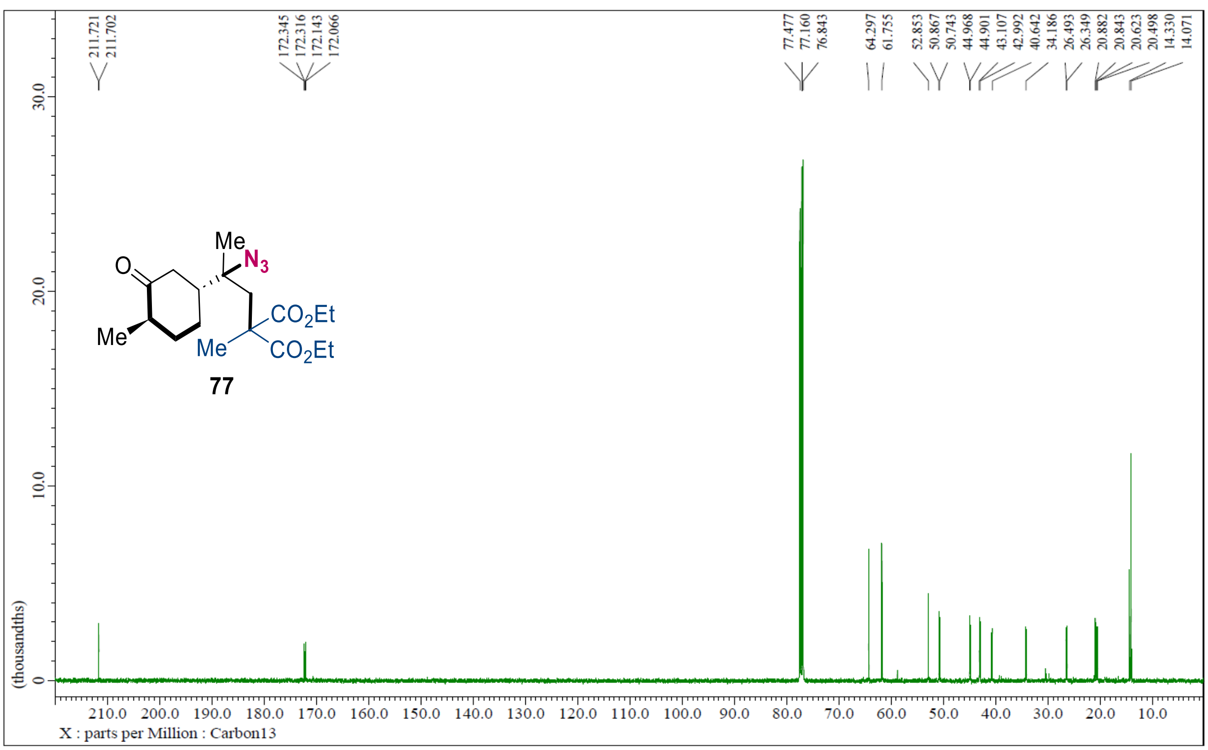
76 ^{13}C NMR (100 MHz, $CDCl_3$)



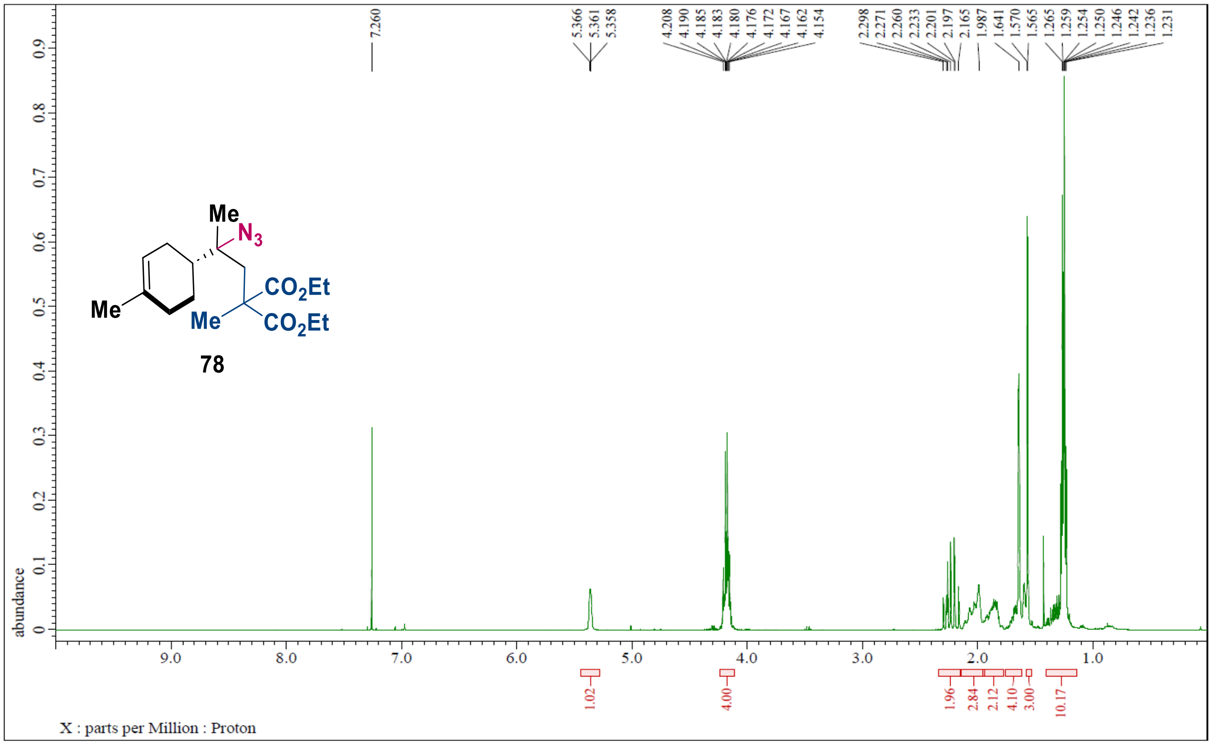
77 ^{1}H NMR (400 MHz, $CDCl_3$)



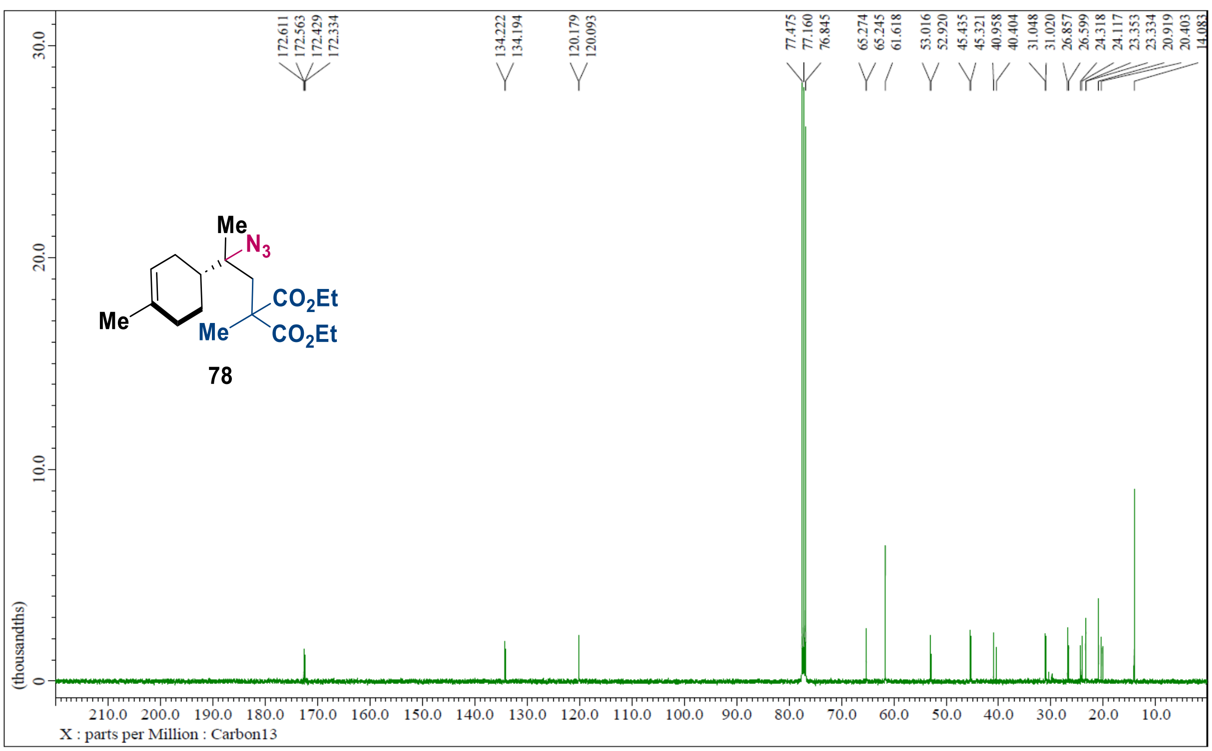
77 ^{13}C NMR (100 MHz, $CDCl_3$)



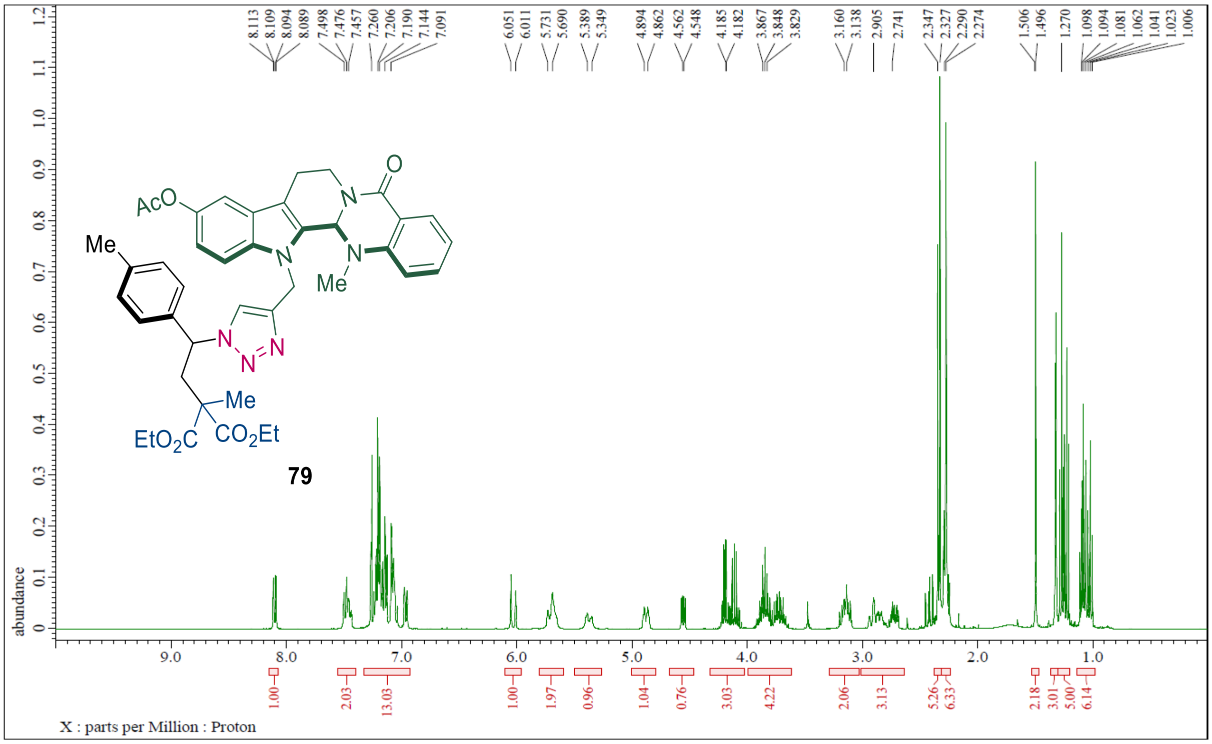
78 ^{1}H NMR (400 MHz, $CDCl_3$)



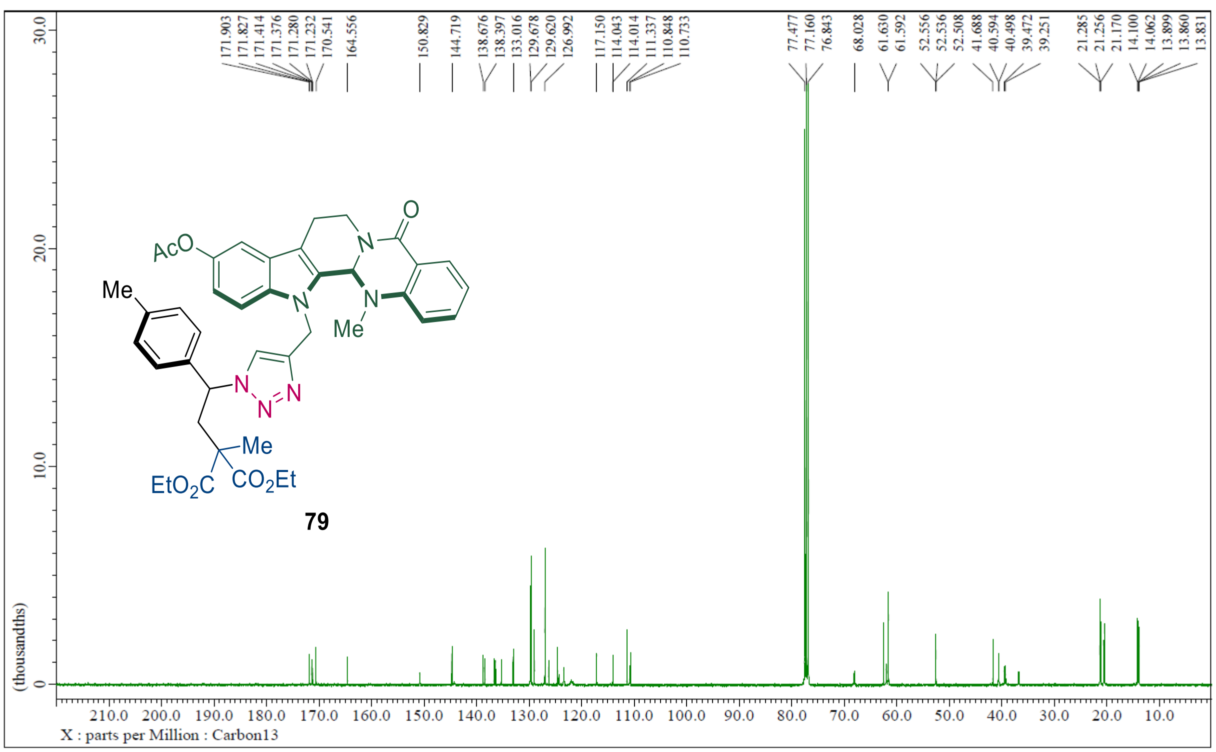
78 ^{13}C NMR (100 MHz, $CDCl_3$)



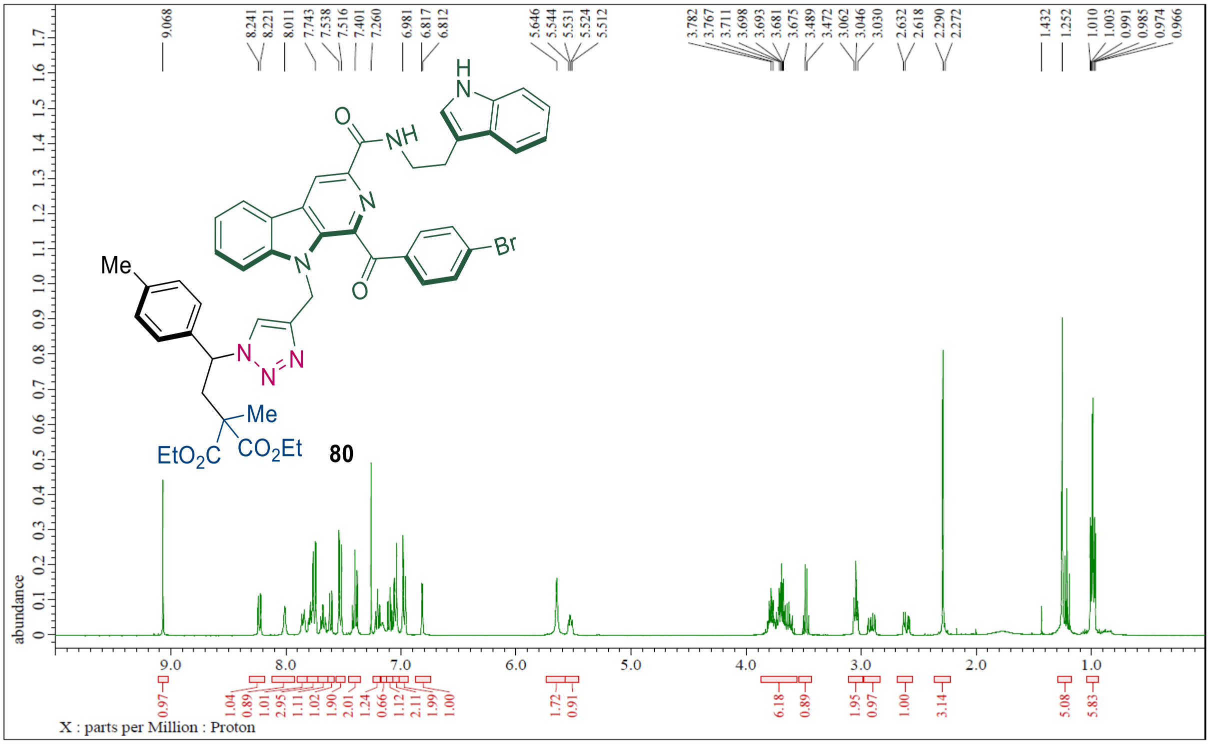
79 ^{1}H NMR (400 MHz, $CDCl_3$)



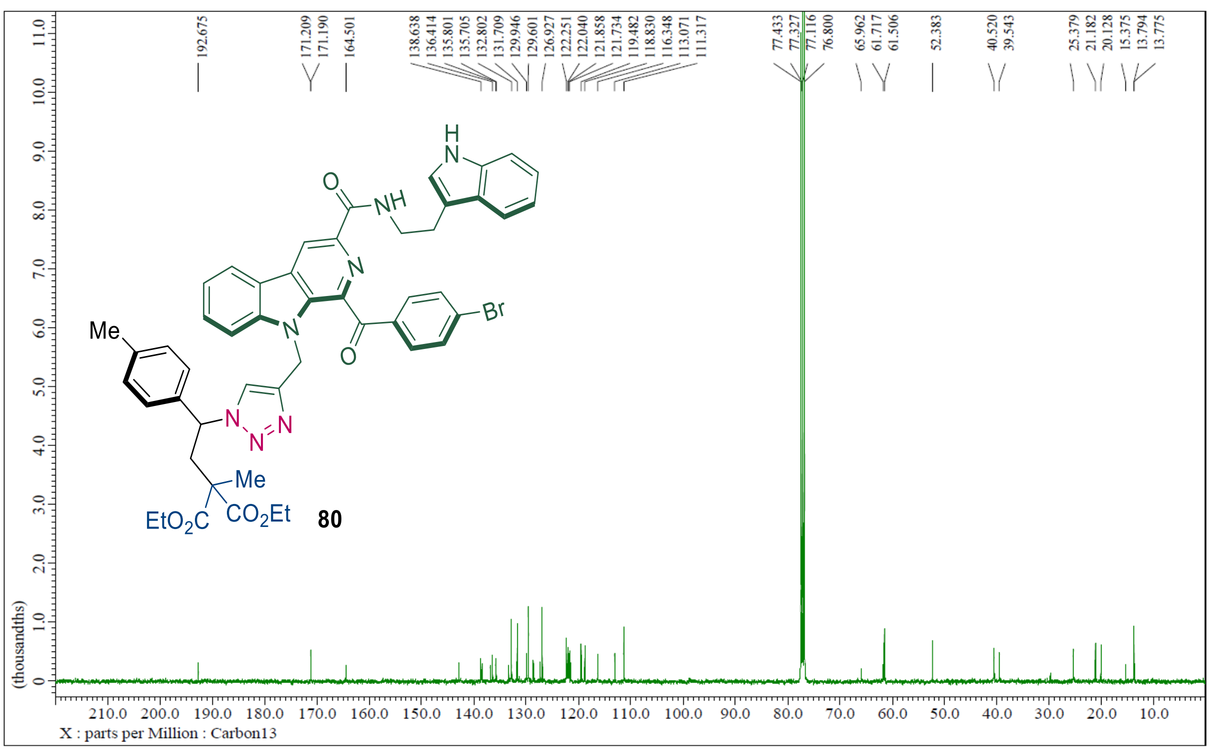
79 ^{13}C NMR (100 MHz, $CDCl_3$)



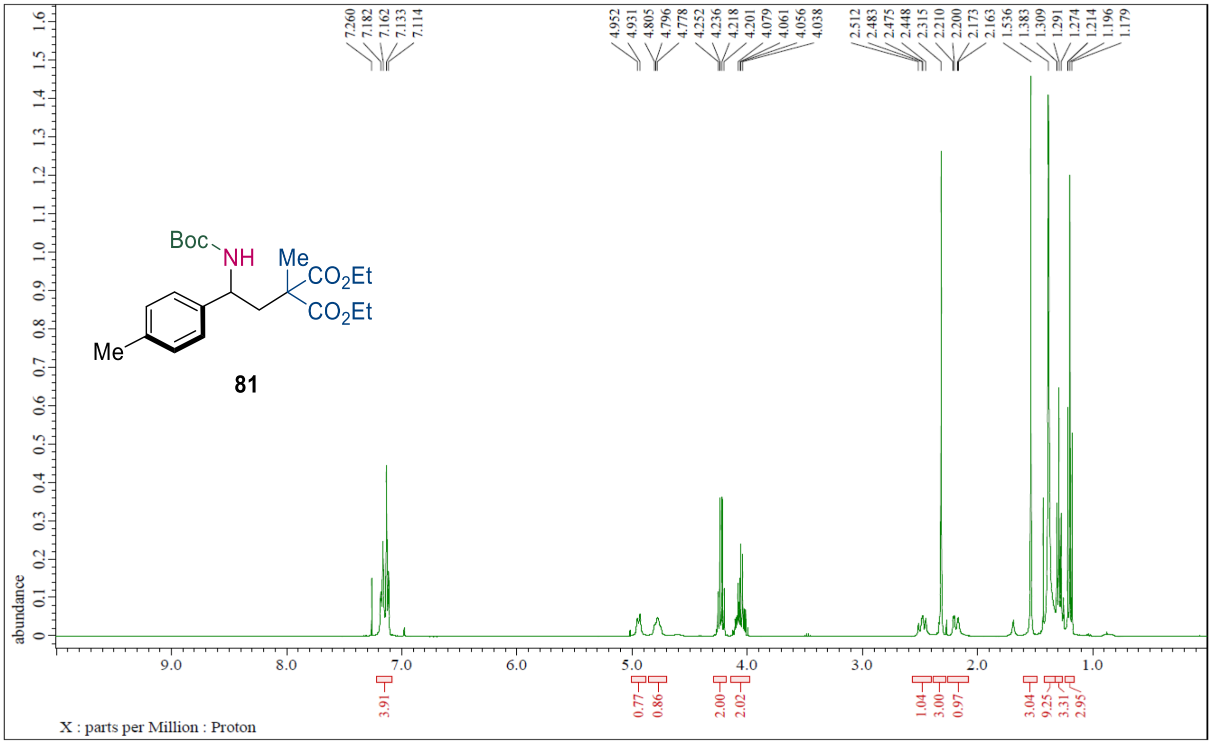
80 ^{1}H NMR (400 MHz, $CDCl_3$)



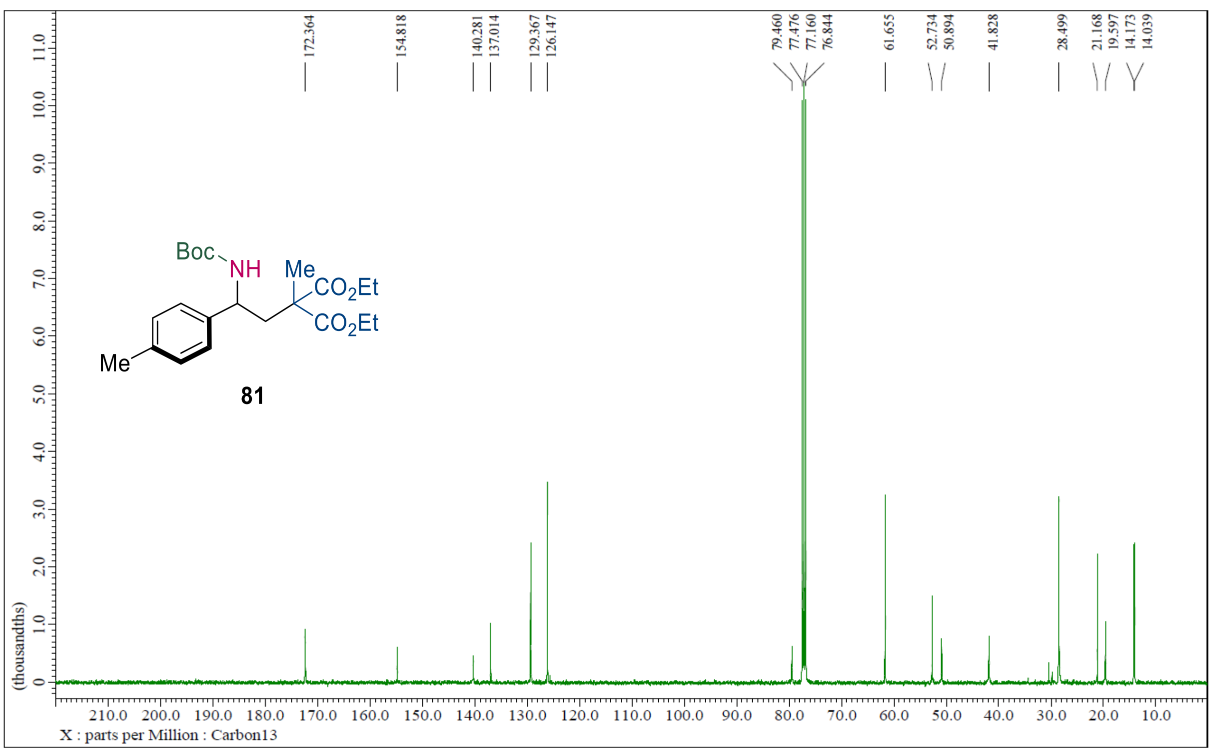
80 ^{13}C NMR (100 MHz, $CDCl_3$)



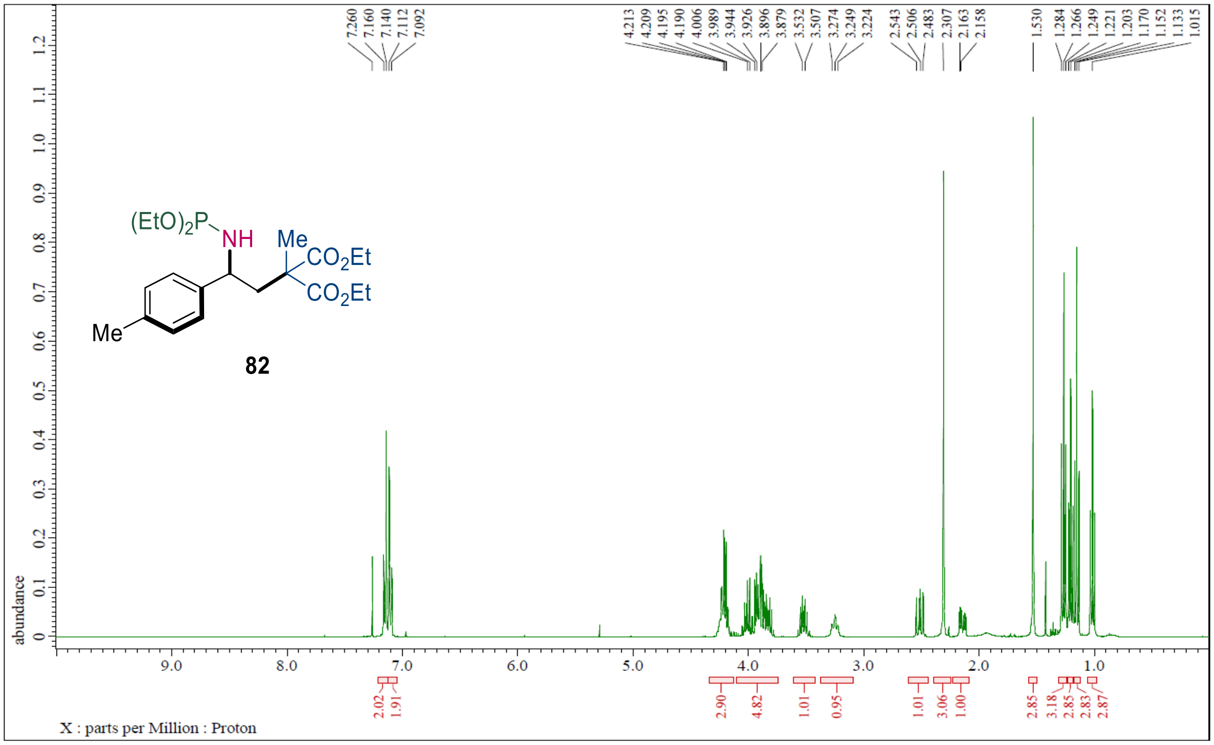
81 ^{1}H NMR (400 MHz, $CDCl_3$)



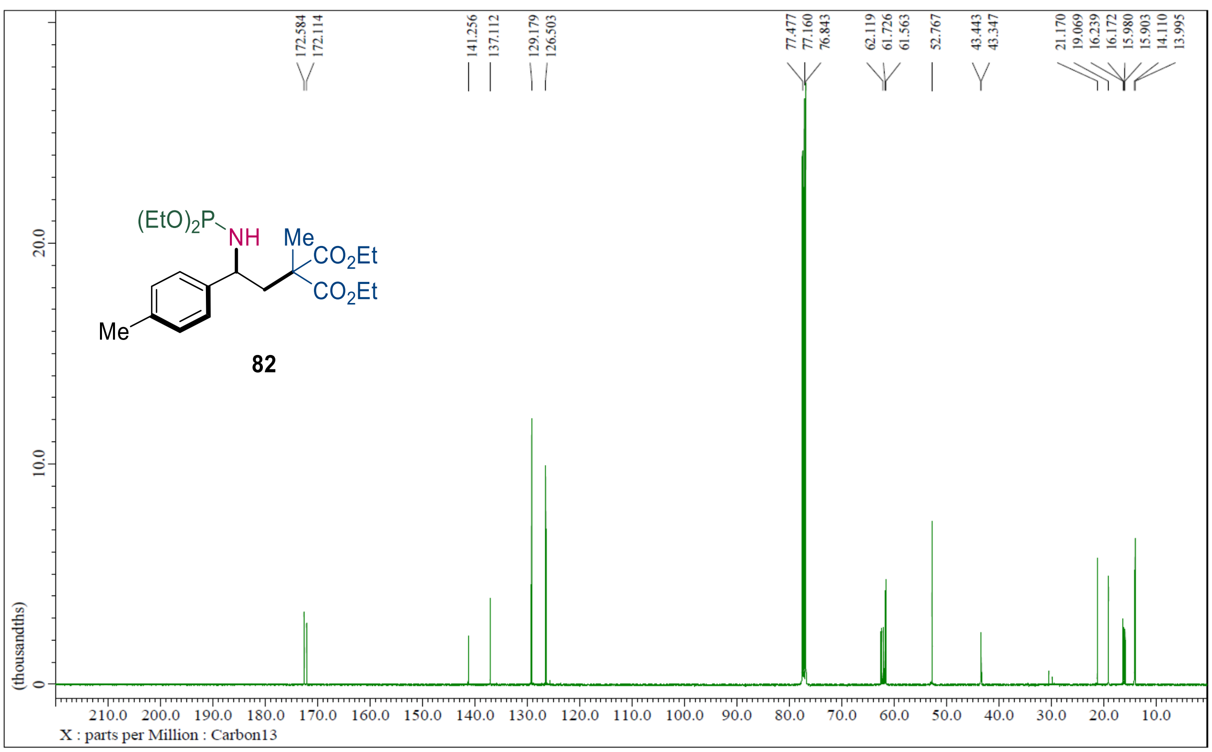
81 ^{13}C NMR (100 MHz, $CDCl_3$)



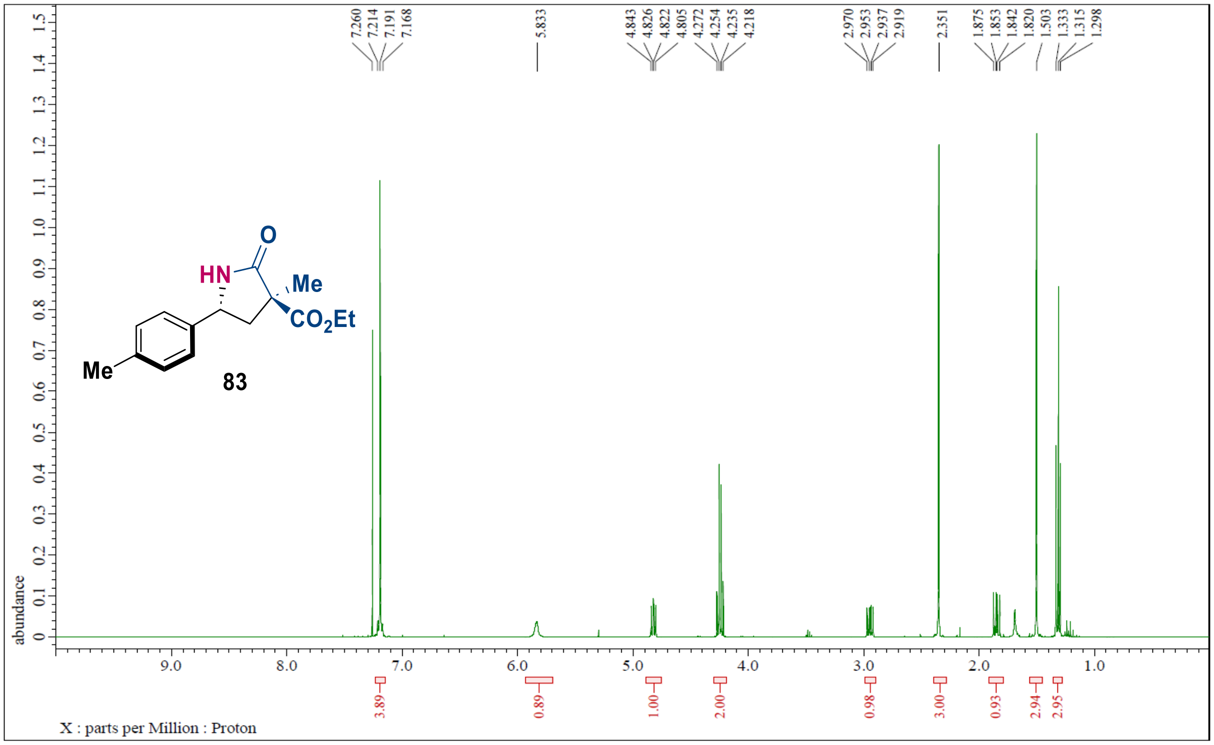
82 ^{1}H NMR (400 MHz, $CDCl_3$)



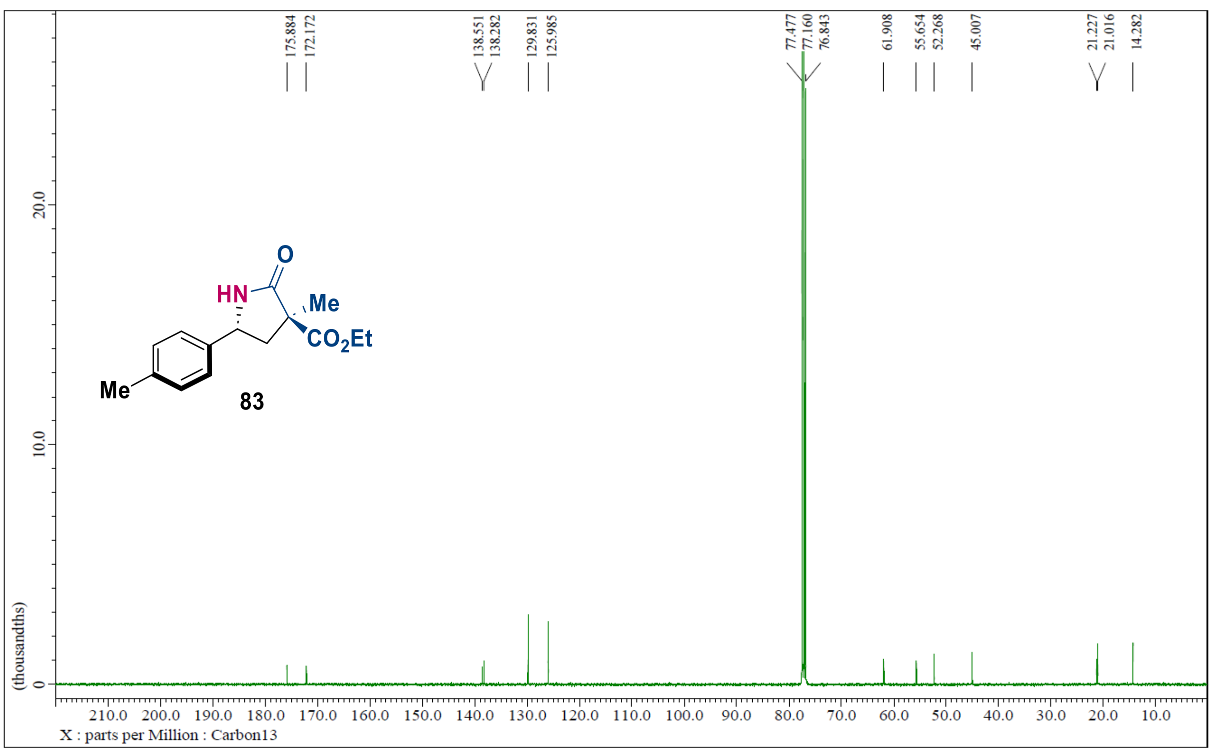
82 ^{13}C NMR (100 MHz, $CDCl_3$)



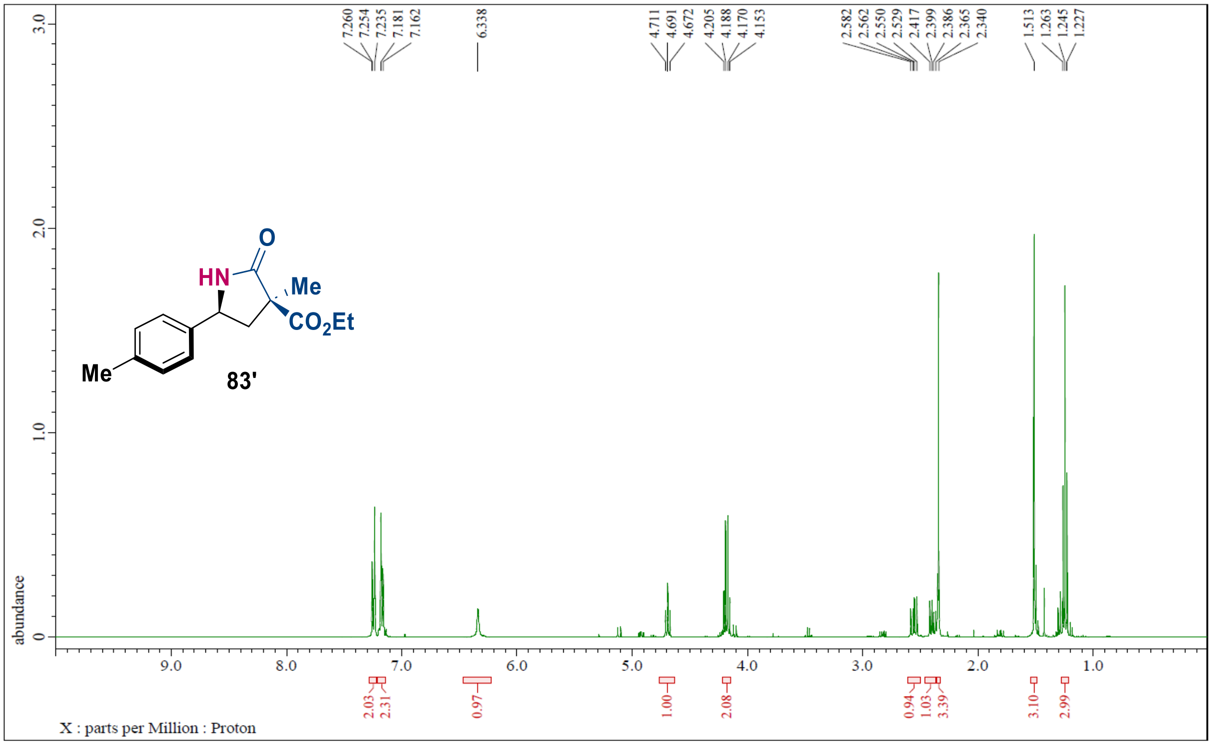
83 [1]H NMR (400 MHz, $CDCl_3$)



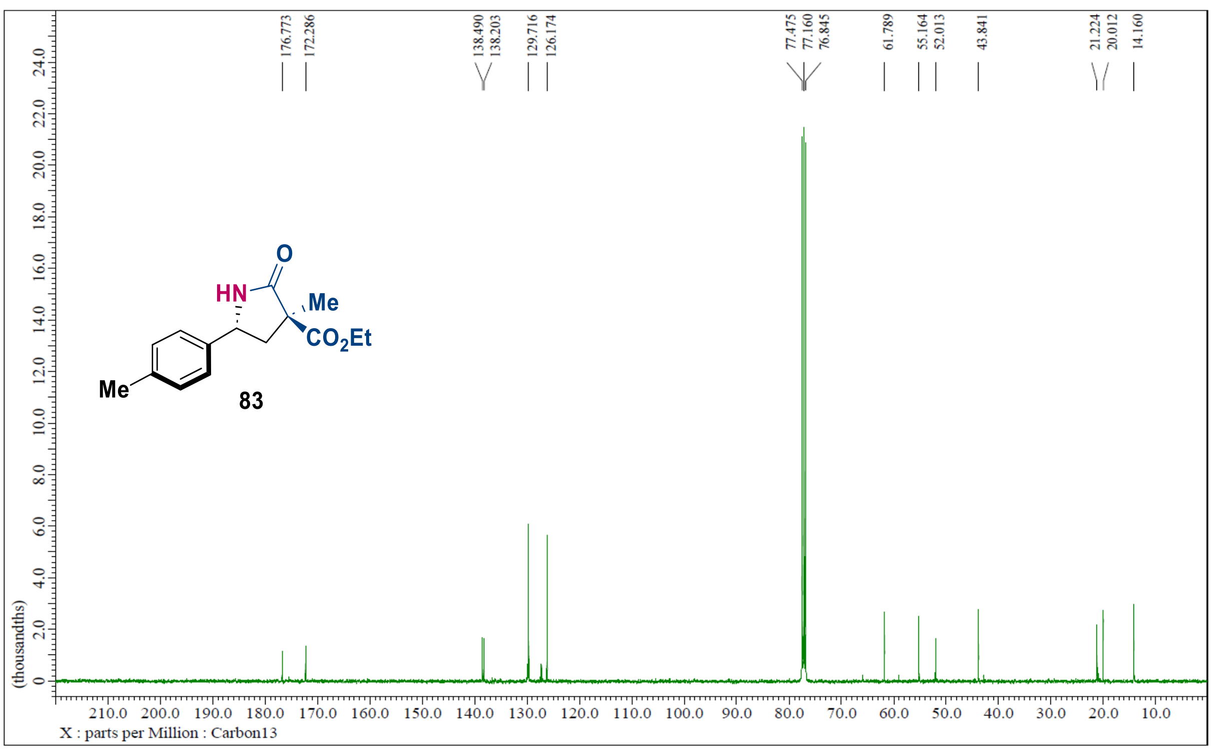
83 [13]C NMR (100 MHz, $CDCl_3$)



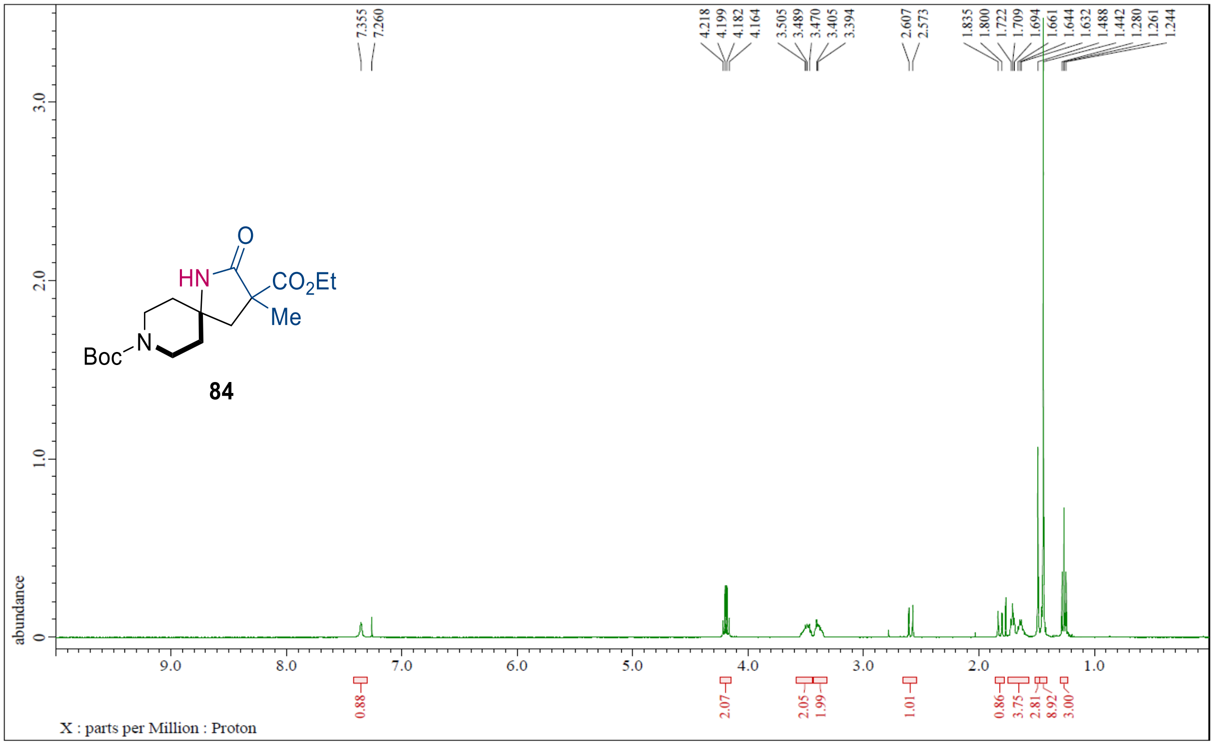
83' ^{1}H NMR (400 MHz, $CDCl_3$)



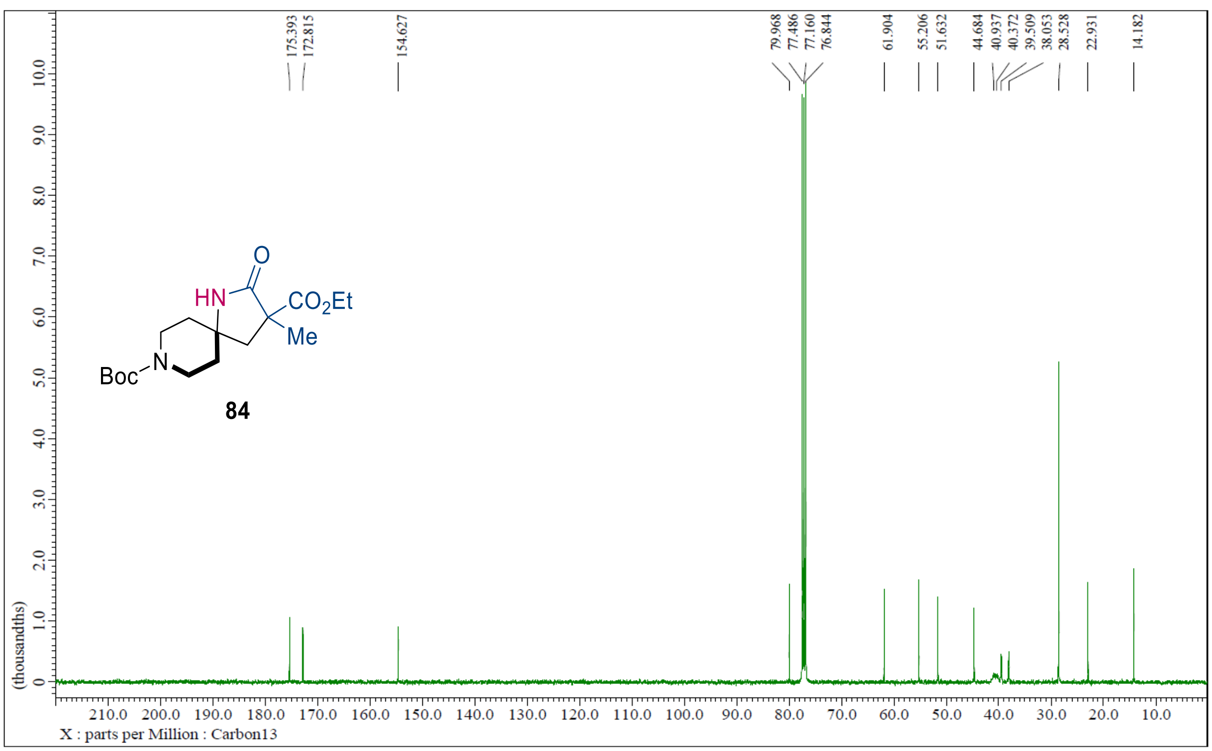
83' ^{13}C NMR (100 MHz, $CDCl_3$)



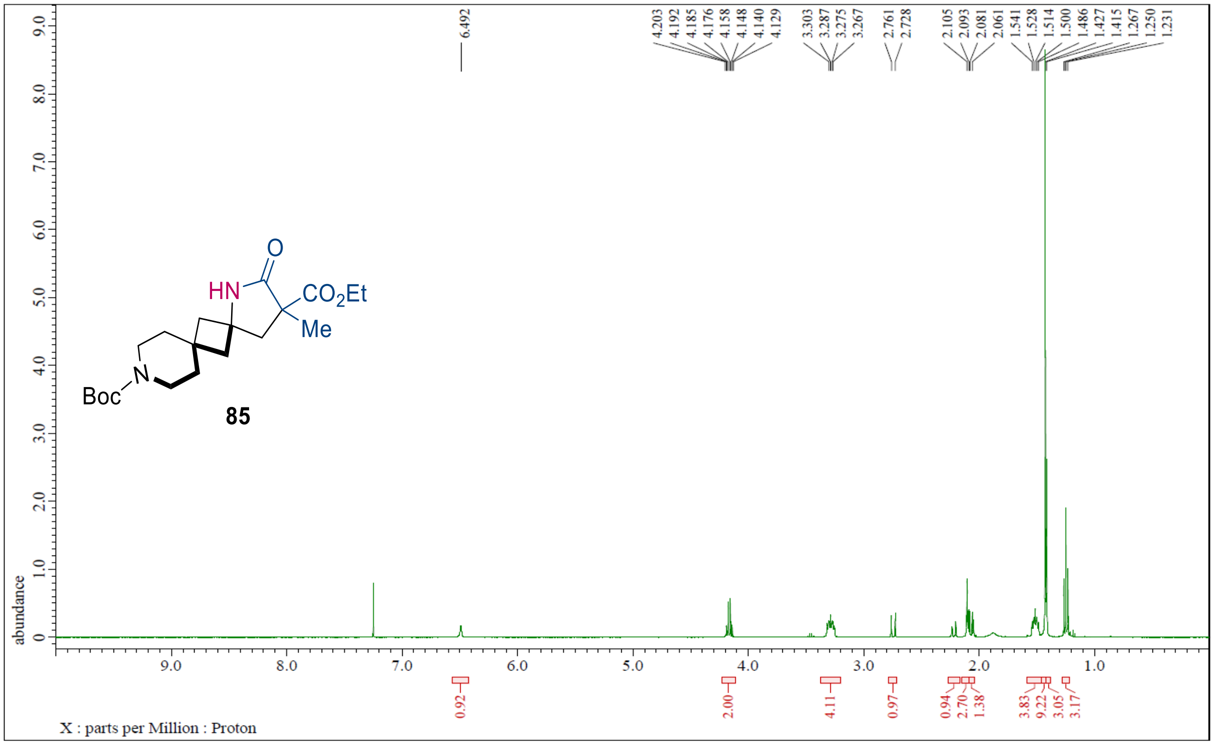
84 ^{1}H NMR (400 MHz, $CDCl_3$)



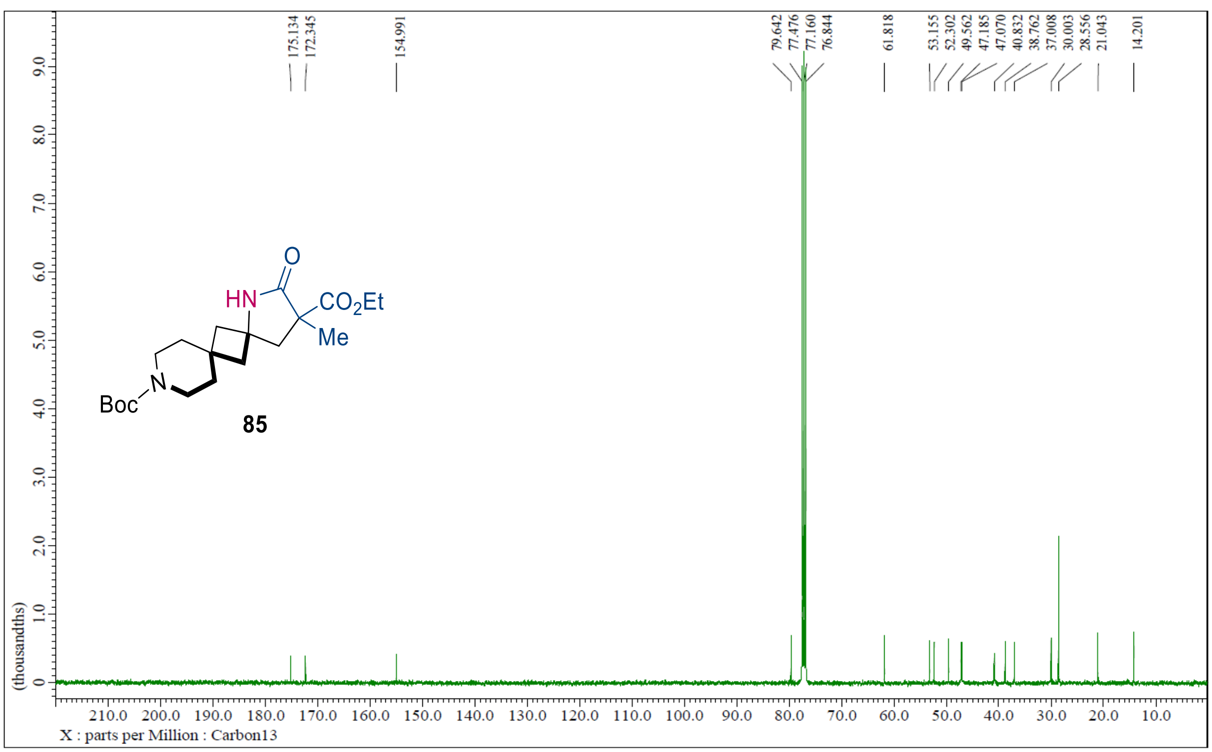
84 ^{13}C NMR (100 MHz, $CDCl_3$)



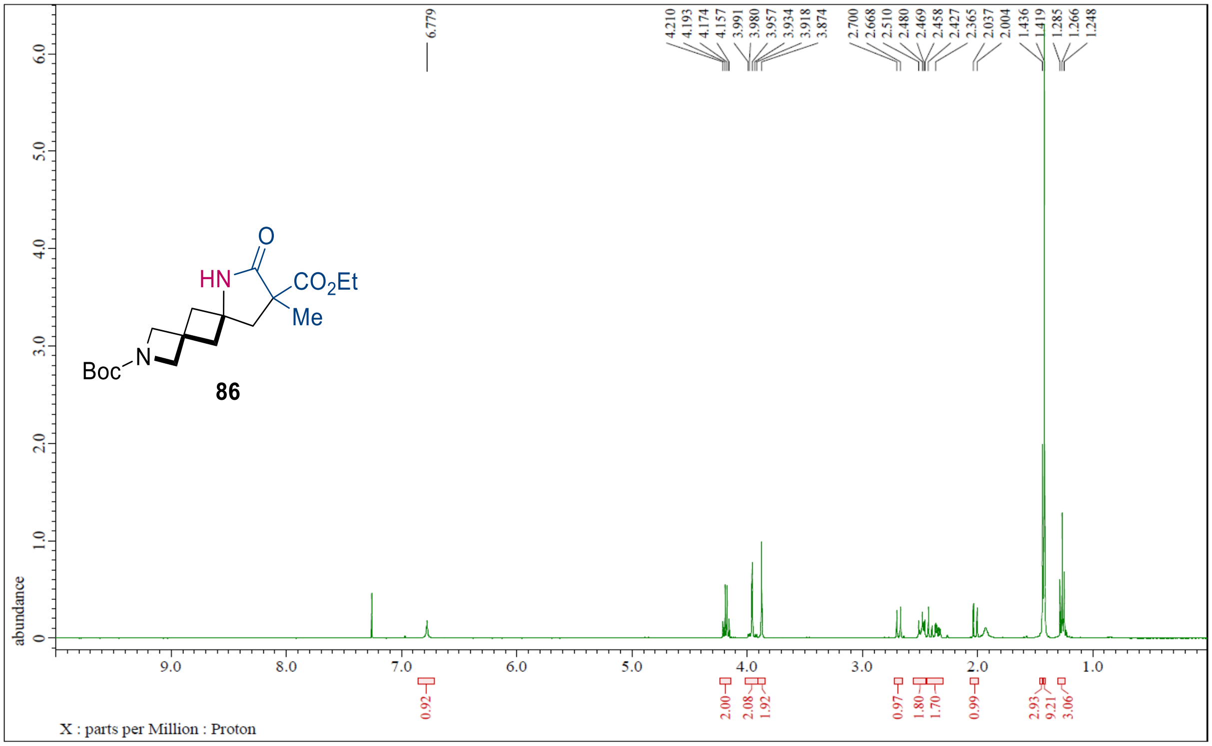
85 ^{1}H NMR (400 MHz, $CDCl_3$)



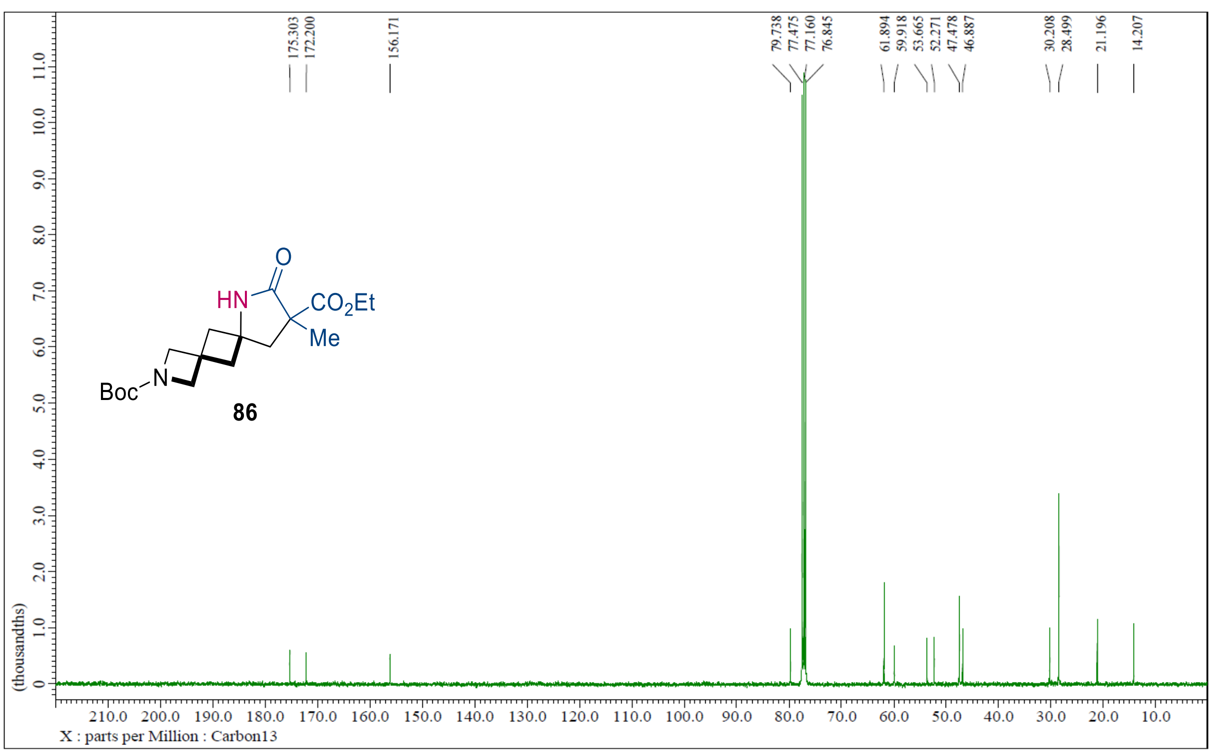
85 ^{13}C NMR (100 MHz, $CDCl_3$)



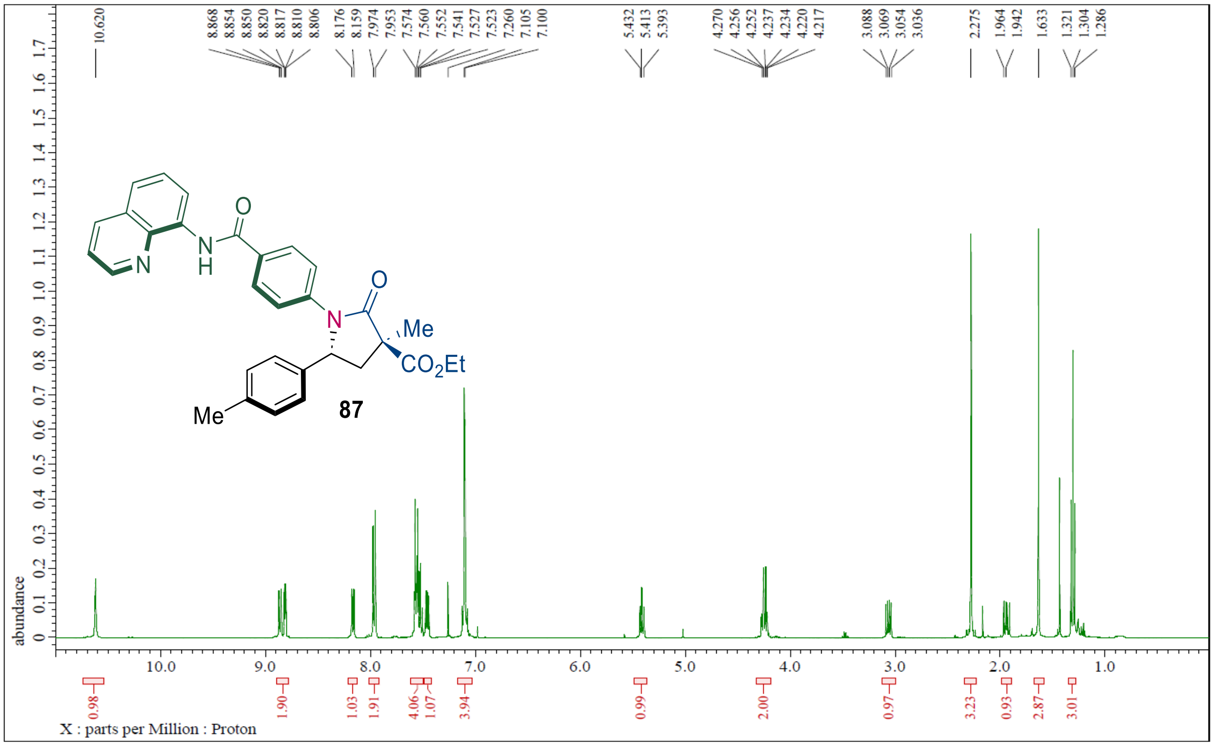
86 ^{1}H NMR (400 MHz, $CDCl_3$)



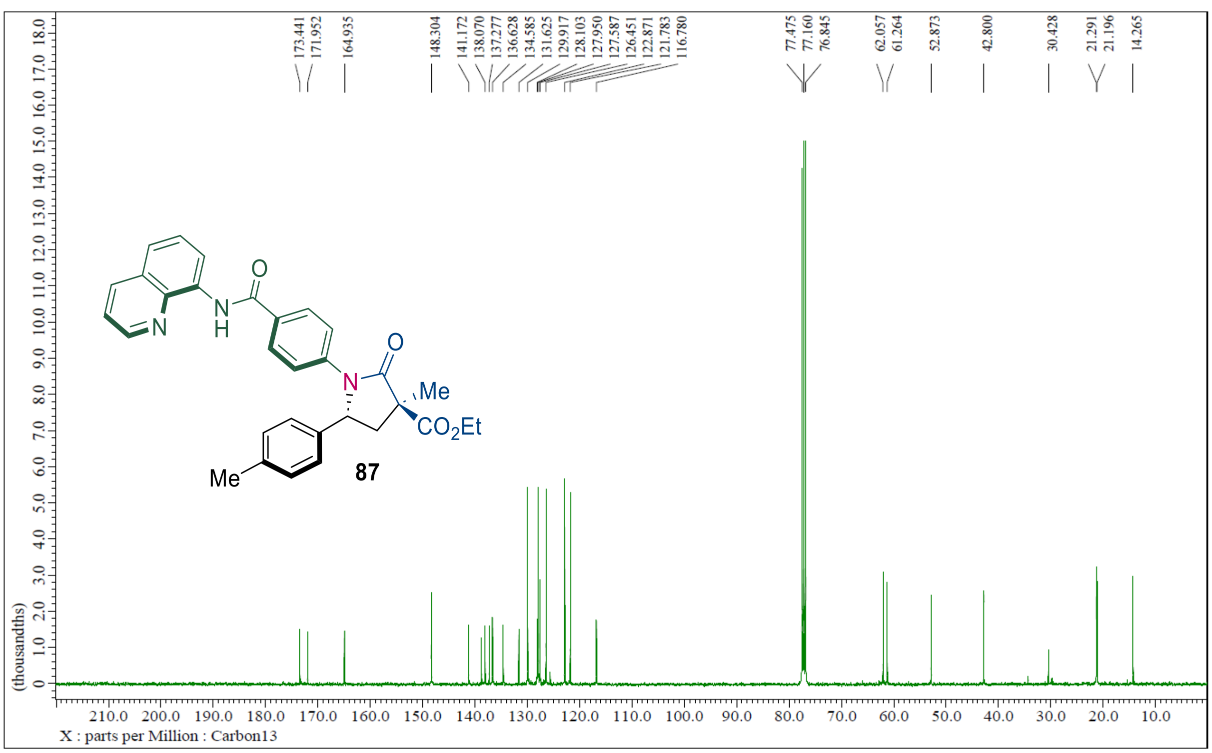
86 ^{13}C NMR (100 MHz, $CDCl_3$)



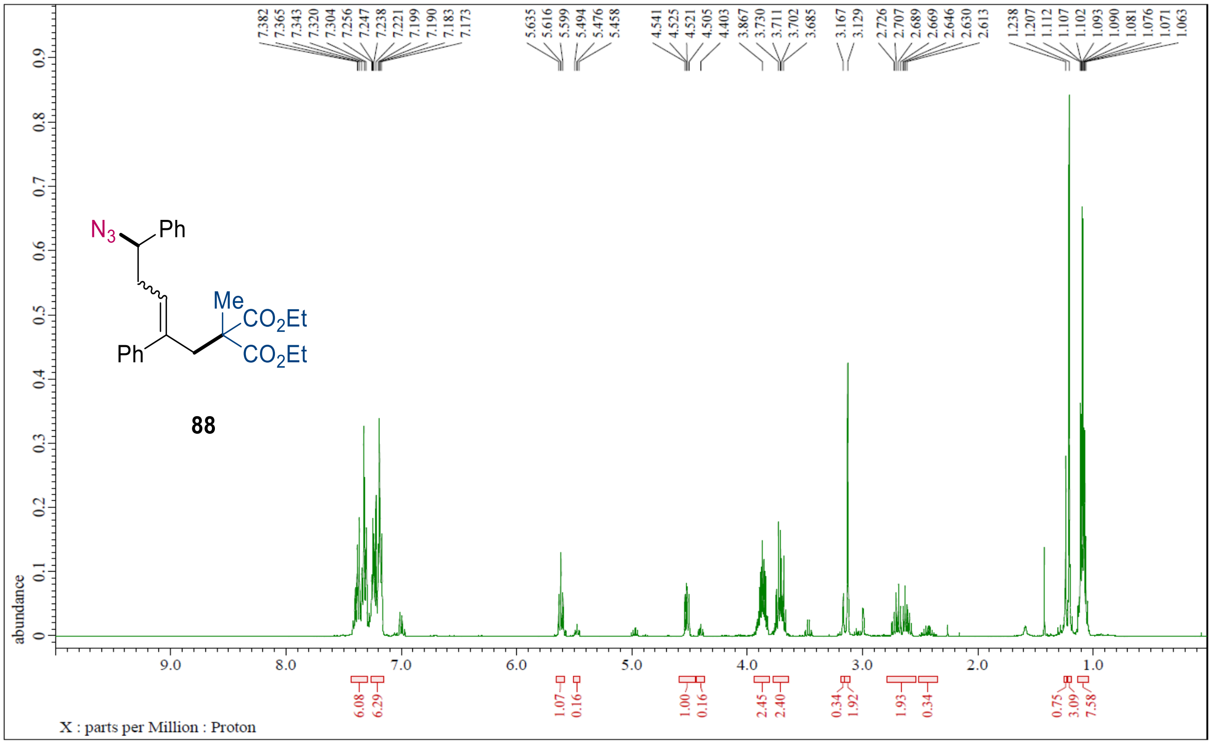
87 ^{1}H NMR (400 MHz, $CDCl_3$)



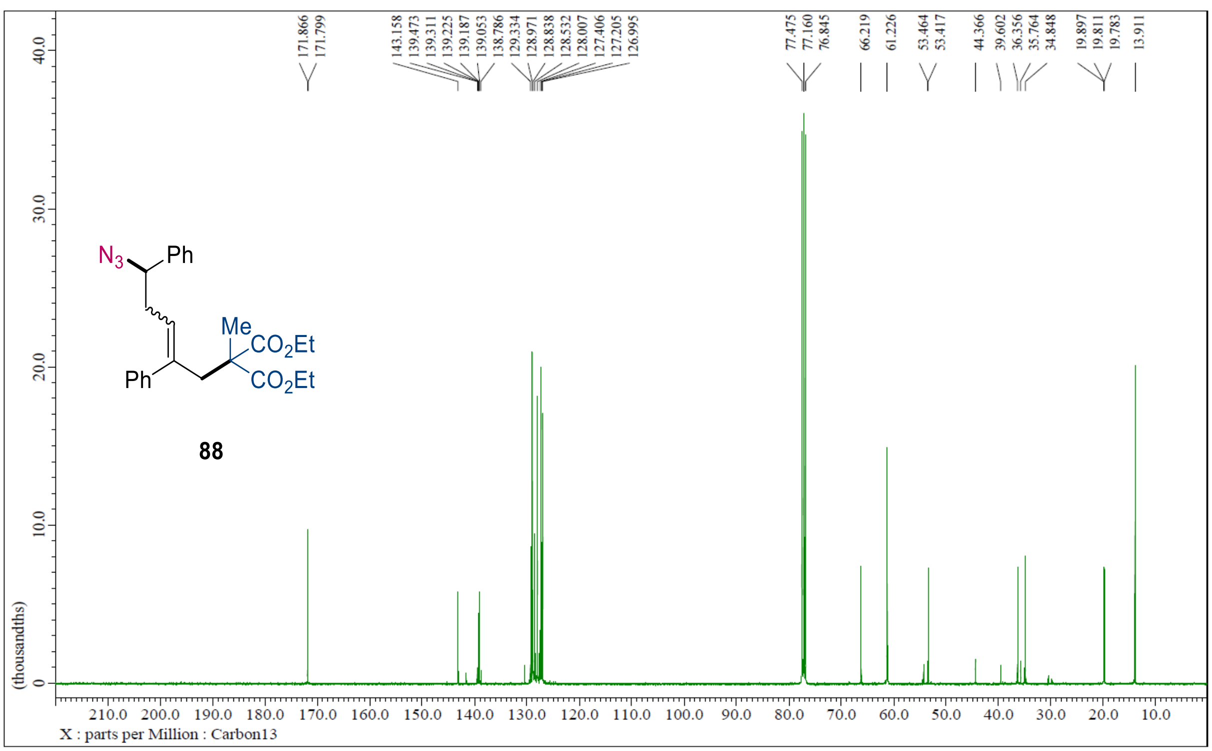
87 ^{13}C NMR (100 MHz, $CDCl_3$)



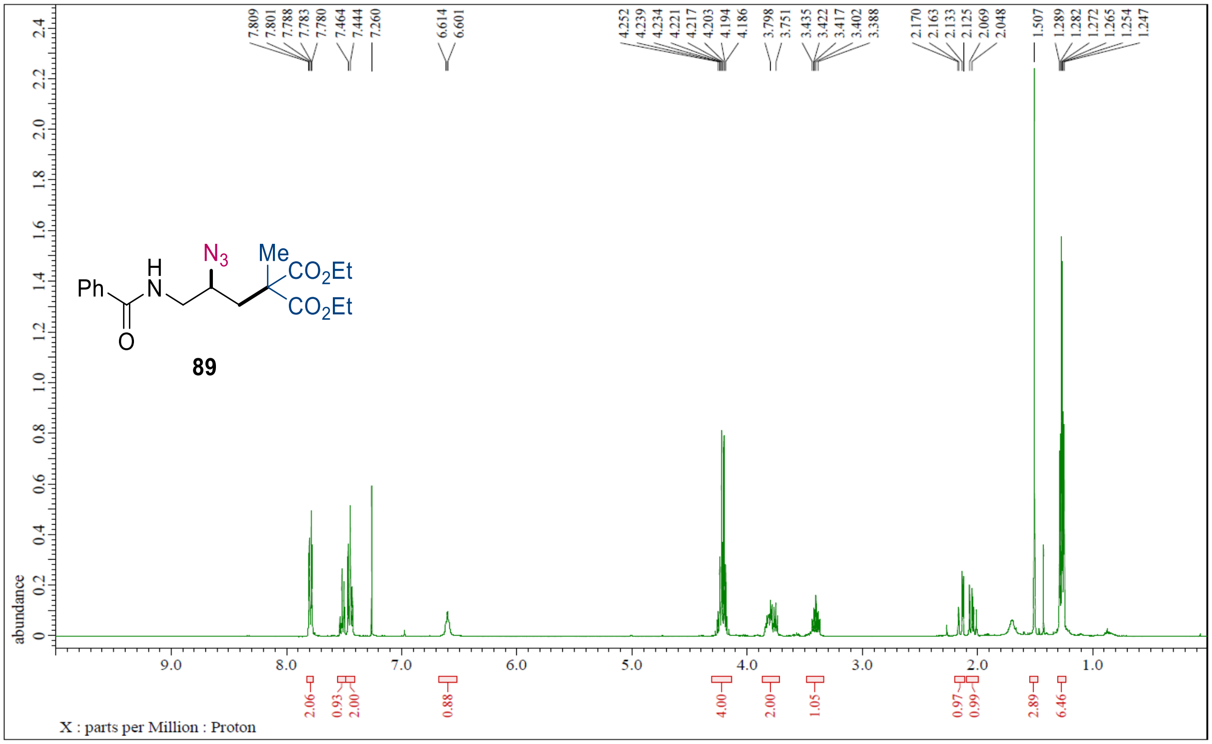
88 ^{1}H NMR (400 MHz, $CDCl_3$)



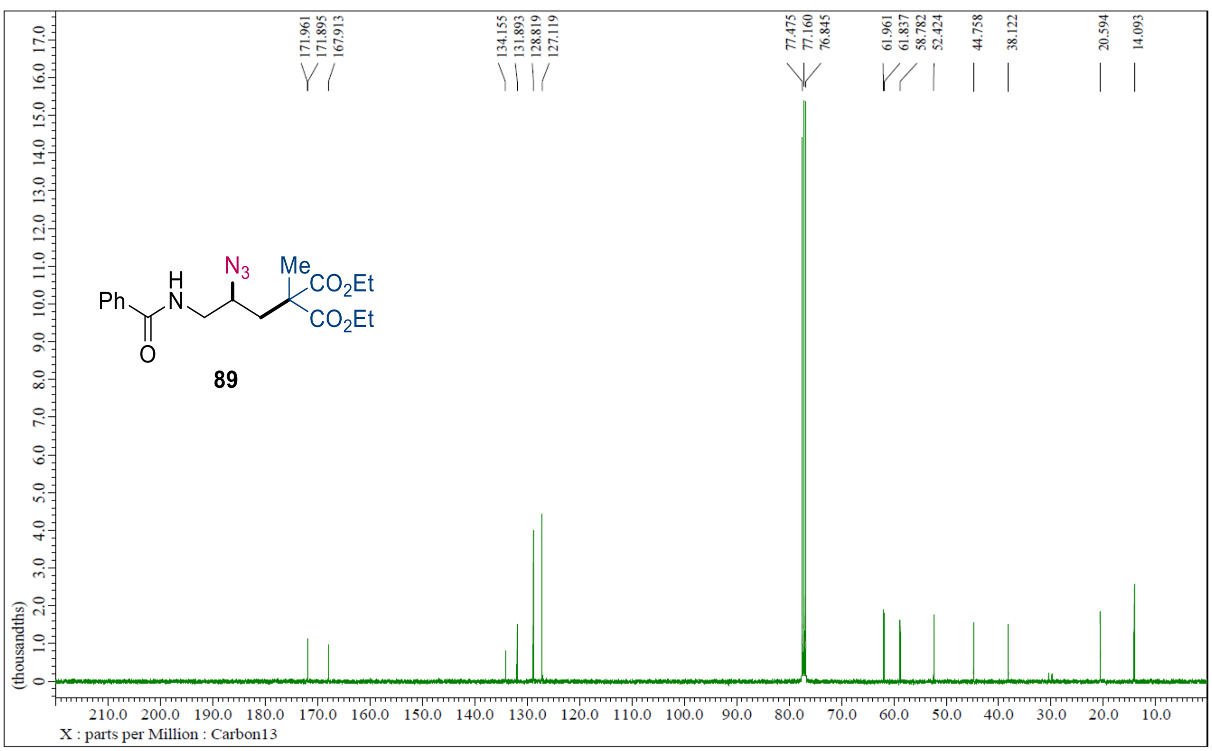
88 ^{13}C NMR (100 MHz, $CDCl_3$)



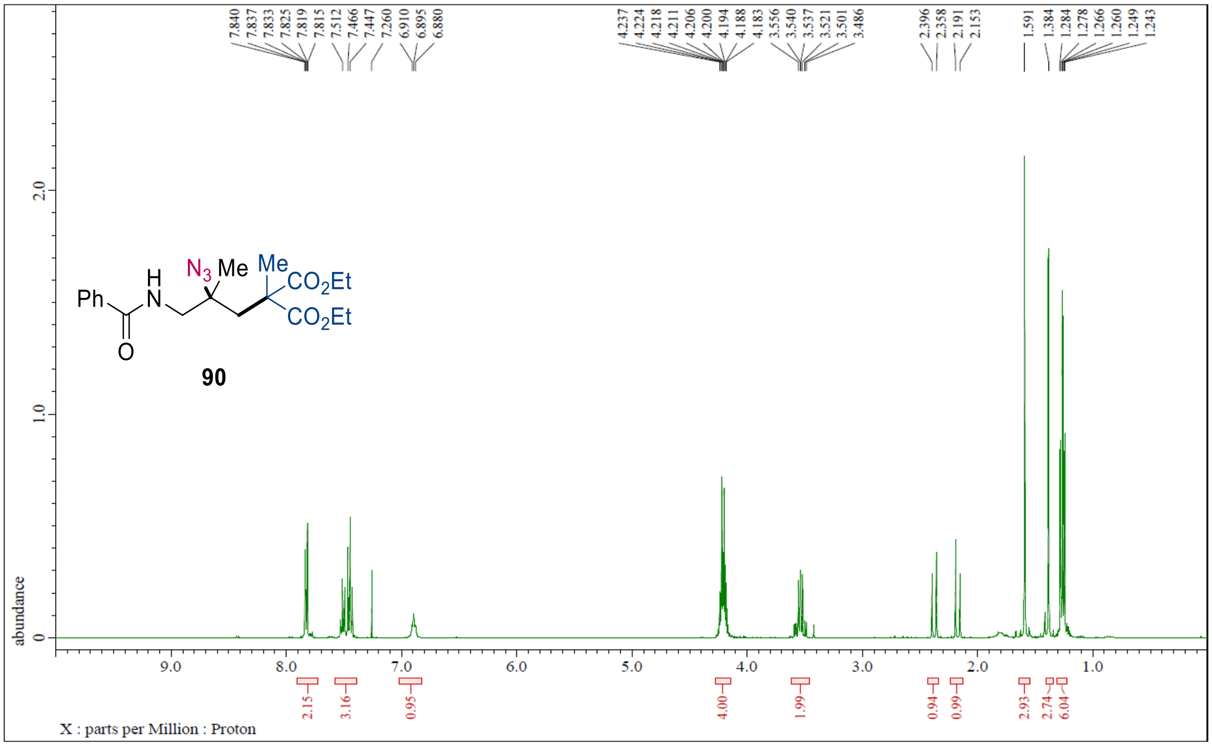
89 ^{1}H NMR (400 MHz, $CDCl_3$)



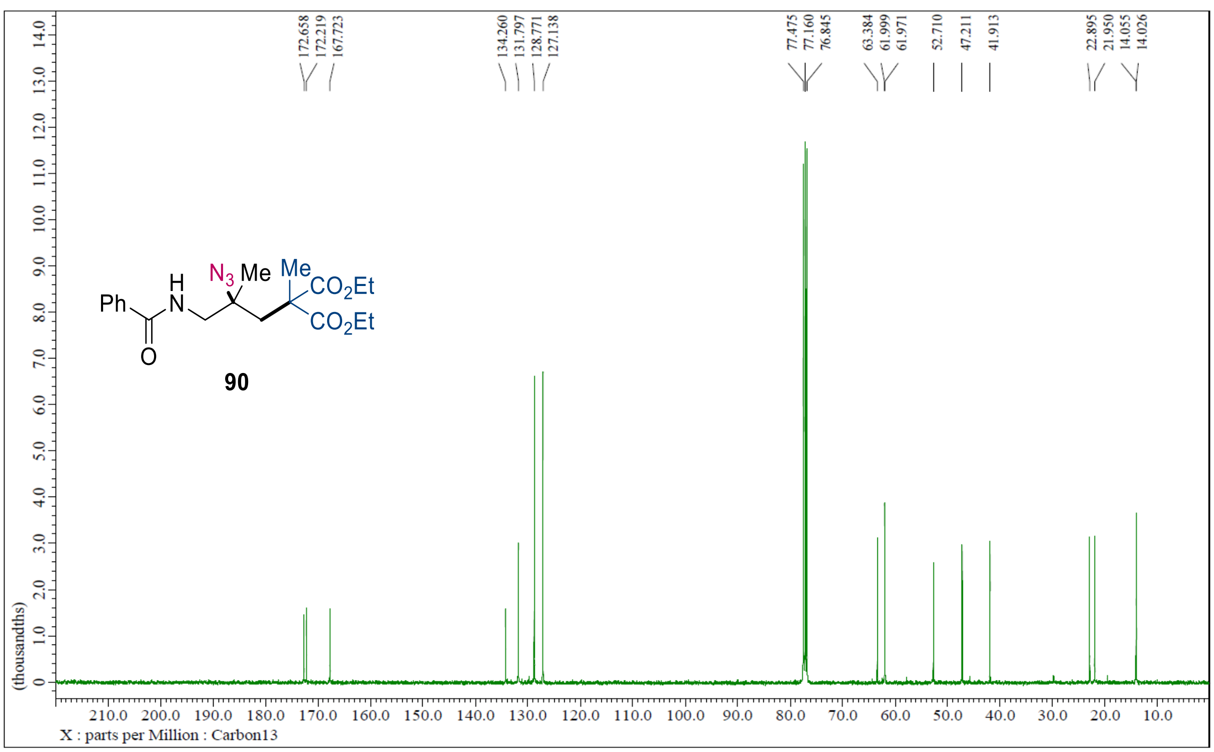
89 ^{13}C NMR (100 MHz, $CDCl_3$)



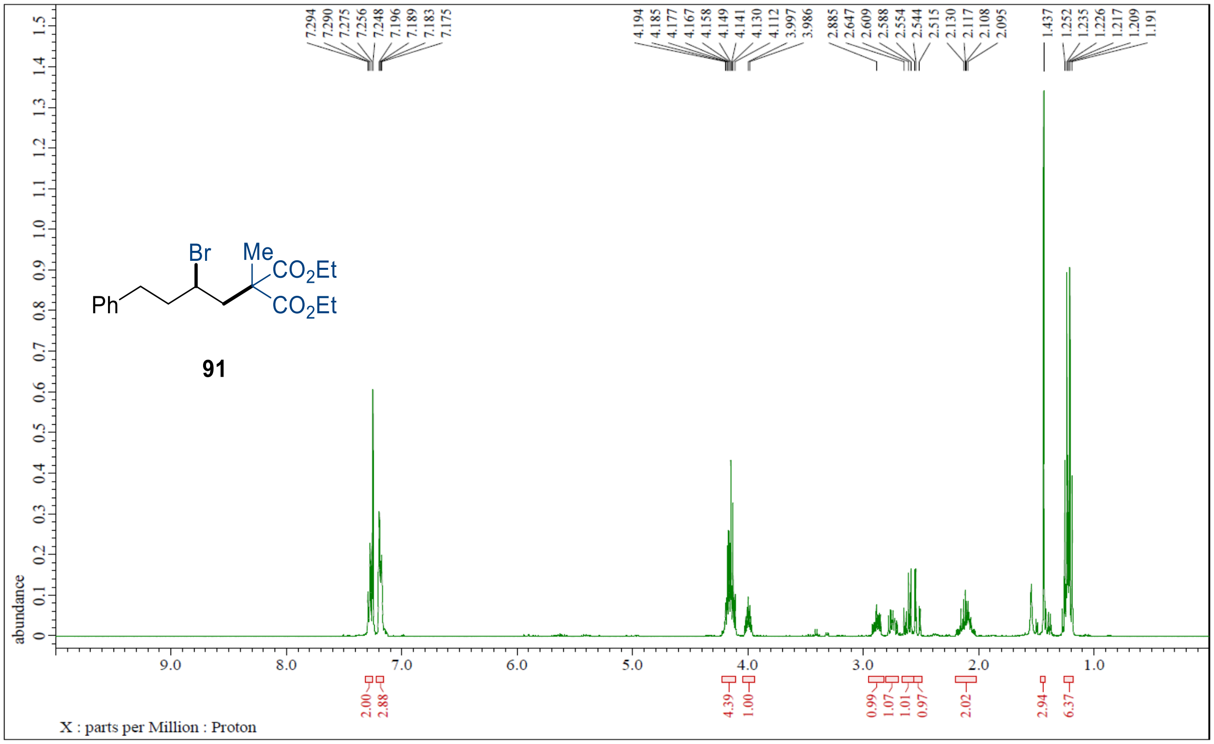
90 ^{1}H NMR (400 MHz, $CDCl_3$)



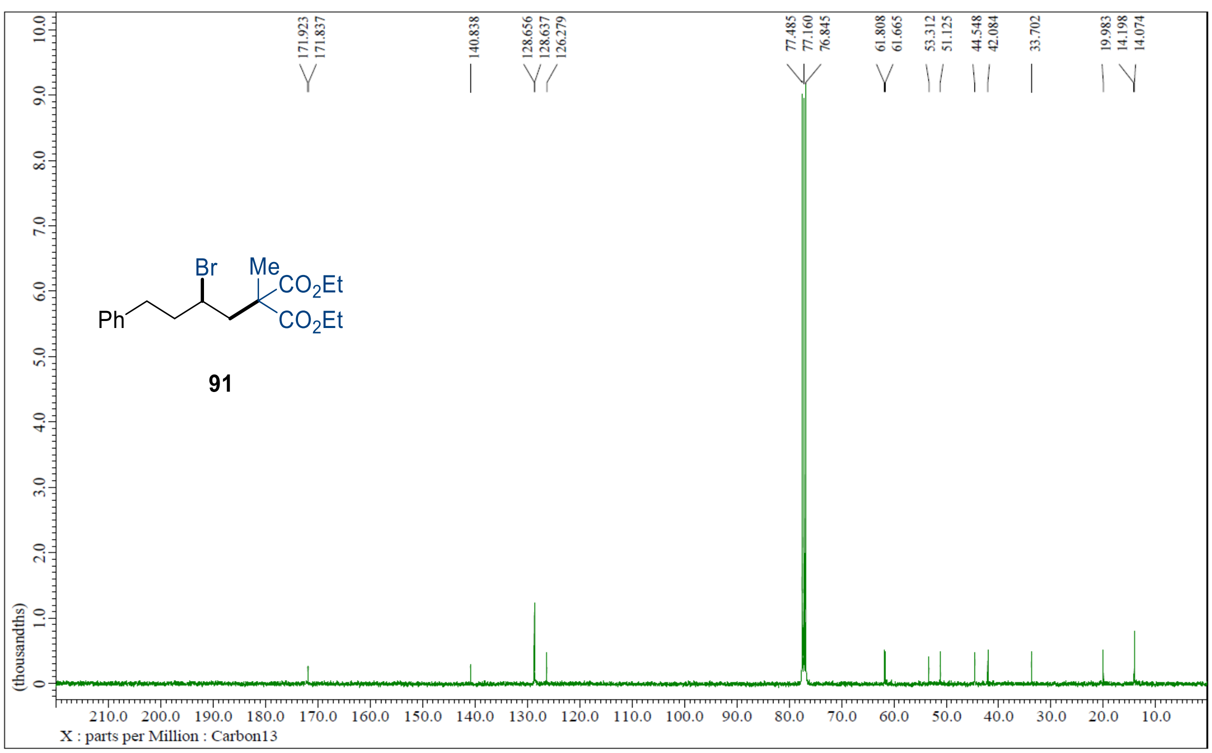
90 ^{13}C NMR (100 MHz, $CDCl_3$)



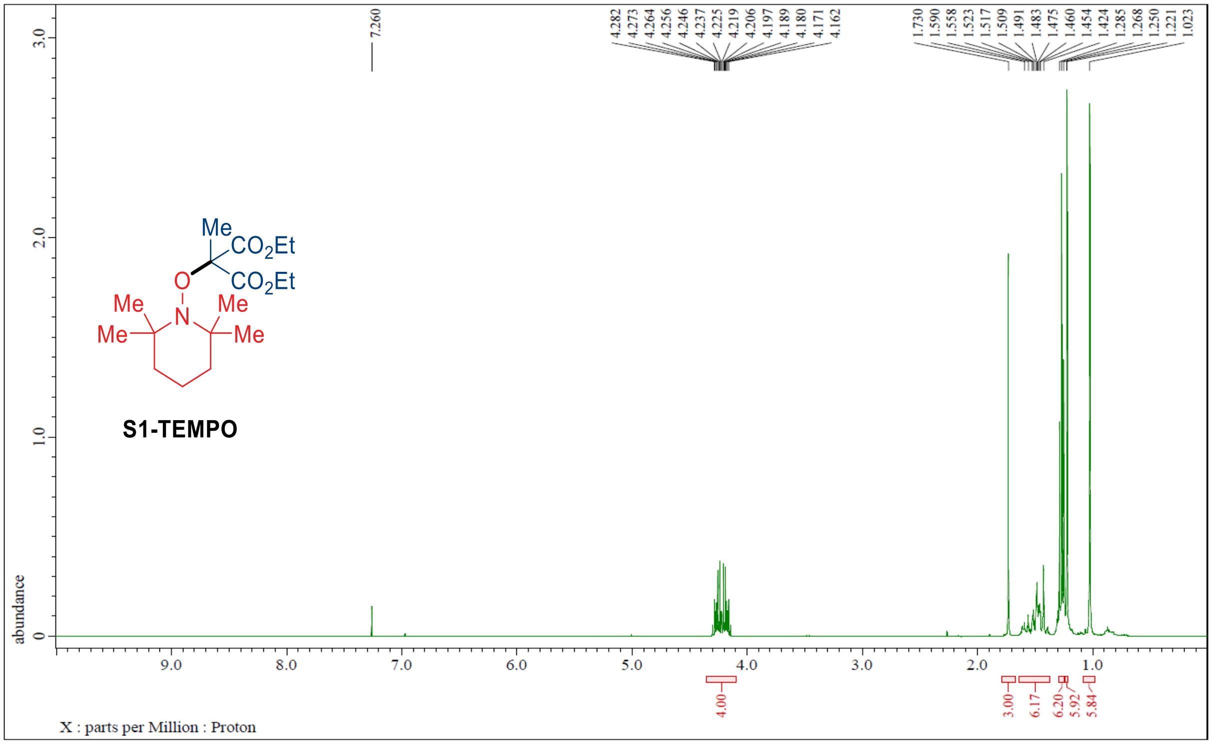
91 ^{1}H NMR (400 MHz, CDCl$_3$)



91 ^{13}C NMR (100 MHz, CDCl$_3$)



S1-TEMPO ^{1}H NMR (400 MHz, $CDCl_3$)



S1-TEMPO ^{13}C NMR (100 MHz, $CDCl_3$)