Supporting Information

Redox-enabled cooperative catalysis by activating secondary alcohols using low-valent Zn complexes

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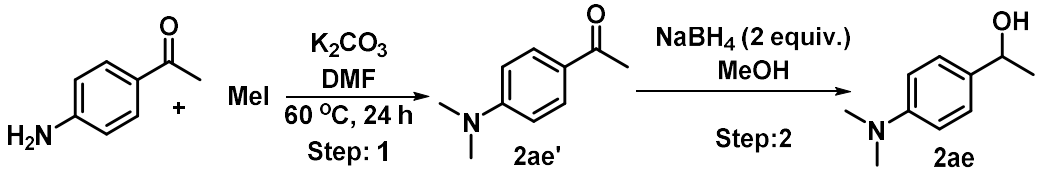
1. General considerations:

Unless otherwise stated, all chemicals were purchased from common commercial sources such as Sigma-Aldrich, Alfa Aesar, TCI, Thermo Fisher Scientific, BLD pharm and used as received. All solvents were dried by using standard protocol. The synthesis of catalyst was performed under argon atmosphere with freshly distilled dry THF. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600, 500 and 400 spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ and DMSO-d_6 as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (*J*) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, and brs = broad singlet. X-ray crystallographic data were collected using Agilent Super Nova (Single source at offset, Eos) diffractometer. Q-Tof ESIMS instrument (model HAB 273) was used for recording mass spectra. SRL silica gel (100- 200 mesh) was used for column chromatography.

2. Procedure for synthesis of starting materials:

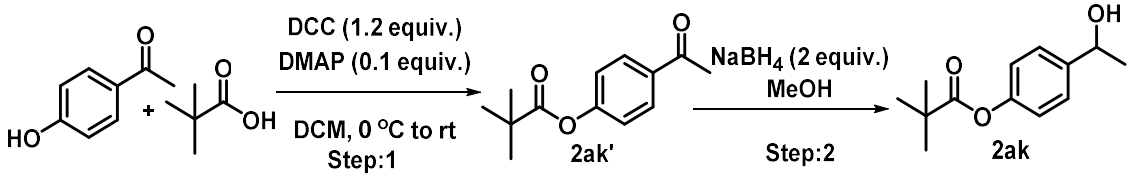
2.a) Preparation of 1-(4-(dimethylamino)phenyl)ethan-1-ol (2ae):



Step 1: 1-(4-(dimethylamino)phenyl)ethan-1-ol was prepared from previous literature method.[1a] To a DMF solution of 4-aminoacetophenone (1.35 g, 10 mmol, 1 equiv.), iodomethane (4.3 g, 30 mmol, 3 equiv.) and K_2CO_3 (4.2 g, 30 mmol, 3 equiv.) were added. The resultant mixture was stirred at 60 °C for 24 h, cooled at room temperature and quenched with a mixture of ice and water. The product was filtered and washed with water to afford the compound as a white solid (1.06 g, 65%).

Step 2: To an oven dried 25 mL round bottomed flask, **2ae′** (408.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol **2ae** in 87% (359.0 mg) yield.

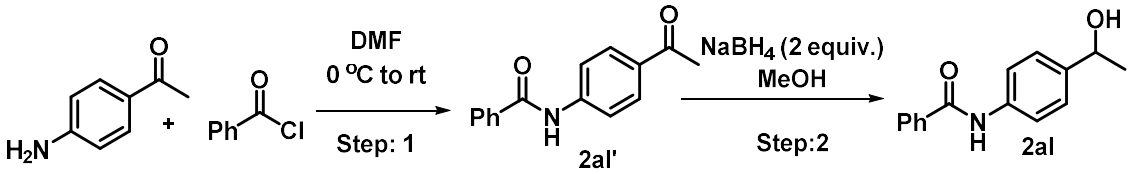
2.b) Preparation of 4-(1-hydroxyethyl)phenyl pivalate (2ak):



Step 1: 4-(1-hydroxyethyl)phenyl pivalate was prepared according to reported literature method.[1b] A solution of Pivalic acid (1.020 g, 10 mmol, 1.0 equiv.), dicyclohexylcarbodiimide (2.472 g, 12 mmol, 1.2 equiv), and 4-(dimethylamino)pyridine (122 mg, 0.1 equiv) in DCM (25 mL) was stirred at 0 □ for 30 min. 1-(4-hydroxyphenyl)ethan-1-one (1.36 g, 10 mmol, 1.0 equiv) was then added. The reaction was warmed to room temperature gradually and stirred for 24 h. The resulting mixture was diluted with ethyl acetate and filtered. The filtrate was concentrated, and the residue was purified by column chromatography (Petroleum ether:ethylacetate = 90:10) to give **2ak′** (1.54 g, 70% yield) as a white solid.

Step 2: To an oven dried 25 mL round bottomed flask, **2ak′** (550.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol **2ak** in 82% (455.0 mg, 2.05 mmol) yield.

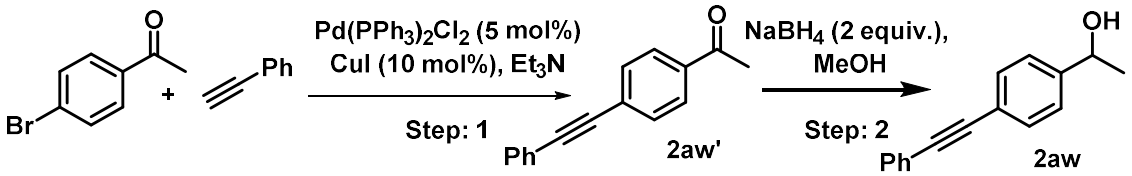
2.c) Preparation of N-(4-(1-hydroxyethyl)phenyl)benzamide (2al):



Step 1: N-(4-(1-hydroxyethyl)phenyl)benzamide was prepared according to previous literature method.[1c] To a solution of *p*-aminoacetophenone (1.35 g, 10 mmol) in dimethyl formamide (20 ml) an equimolar amount of benzoyl chloride (1.16 mL, 10 mol) was added. The mixture was stirred at 0 °C for 3 h, after which crushed ice was added with continuous stirring. A heavy precipitate was obtained, which was filtered, washed with water for several times and then oven dried to get **2al′** (1.793g, 75%) as white solid.

Step 2: To an oven dried 25 mL round bottomed flask, **2al′** (598.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol **2al** in 80% (482.0 mg) yield.

2.d) Preparation of 1-(4-(phenylethynyl)phenyl)ethan-1-ol (2aw):

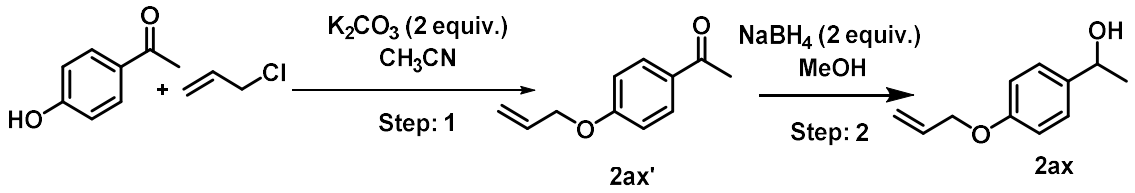


Step 1: 1-(4-(phenylethynyl)phenyl)ethan-1-one (**2aw′**) was prepared according to the reported literature procedure.[1d] An oven dried Schlenk tube was charged with the selected

ketone (5.0 mmol, 995 mg), bis(triphenylphosphine)palladium(II) chloride (176.0 mg, 0.25 mmol), copper iodide (95.0 mg, 0.5 mmol) and Et_3N (25 mL). The tube was evacuated and backfilled with Ar (this process was repeated three times) and then phenylacetylene (0.8 mL, 7.5 mmol) was added by syringe. The reaction mixture was stirred at 80 ºC for 12 h until the consumption of ketone, indicated by TLC. The reaction mixture was filtered through celite pad and concentrated in vacuo to give the crude product, which was purified by common column chromatography petroleum ether: ethyl acetate (95:5) to give desired compound **2aw′** as white solid with 78% (858 mg, 3.9 mmol) yield.

Step 2: To an oven dried 25 mL round bottomed flask, **2aw′** (550.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol **2aw** in 85% (472.0 mg, 2.13 mmol) yield.

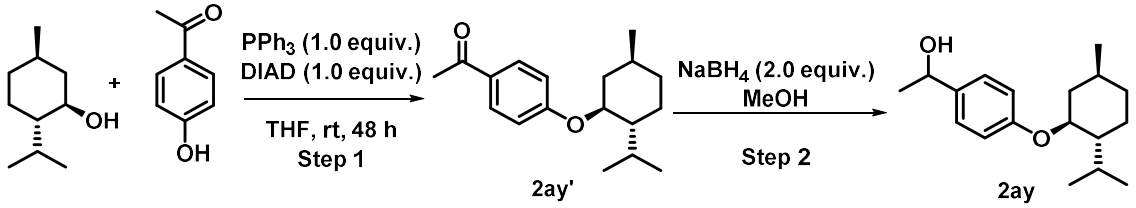
2.e) Preparation of 1-(4-(allyloxy)phenyl)ethan-1-ol (2ax):



Step 1: 1-(4-(allyloxy)phenyl)ethan-1-one was prepared by modified literature procedure.[2] To an oven dried 50 mL round bottomed flask 4′-hydroxyacetophenone (544 mg, 4.0 mmol, 1 equiv.), allylchloride (0.65 mL, 8.0 mmol, 2 equiv.) and K_2CO_3 (1.104 g, 8.0 mmol) was refluxed for overnight in acetonitrile (20 mL) solvent. Then, solvent was evaporated under reduced pressure and extracted in DCM (3×15 mL) and the combined organic phase was dried over Na_2SO_4. After column chromatography gave the title product with 92% (648 mg, 3.68 mmol) yield.

Step 2: To an oven dried 25 mL round bottomed flask, **2ax′** (440.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol **2ax** in 87% (387.0 mg, 2.17 mmol) yield.

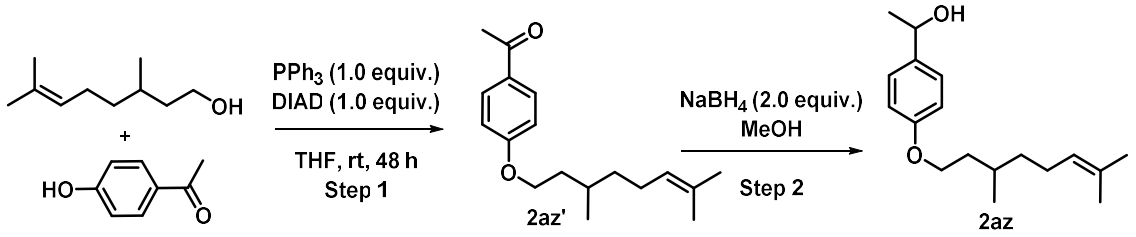
2.f) Preparation of 1-(4-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)ethan-1-ol (2ay):



Step 1: 1-(4-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)ethan-1-one was prepared according to reported literature procedure.[3] PPh_3 (3.672 g, 14.0 mmol, 1 equiv.) and DIAD (2.831 g, 14.0 mmol, 1 equiv.) were added sequentially to a solution of the 4′-hydroxy acetophenone (1.902 g, 14.0 mmol, 1.0 equiv.) and menthol (2.188 g, 14.0 mmol, 1 equiv.) in THF. The resulting suspension was stirred vigorously at room temperature for 48 h. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (petroleum-ether/EtOAc) afforded the desired **2ay′** with 22% (844 mg, 3.1 mmol).

Step 2: To an oven dried 25 mL round bottomed flask, **2ay′** (685.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol **2ay** in 80% (552.0 mg, 2.0 mmol) yield.

2.g) Preparation of 1-(4-((3,7-dimethyloct-6-en-1-yl)oxy)phenyl)ethan-1-ol (2az):



Step 1: This compound was prepared according to literature method.[4] PPh_3 (1.836 g, 7.0 mmol, 1 equiv.) and DIAD (1.416 g, 7.0 mmol, 1 equiv.) were added sequentially to a solution of the 4′-hydroxy acetophenone (951 mg, 7.0 mmol, 1.0 equiv.) and citronellol (1.094 g, 7.0 mmol, 1 equiv.) in THF. The resulting suspension was stirred vigorously at room temperature for 48 h. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (petroleum-ether/EtOAc) afforded the desired **2az′** with 48% (921 mg, 3.36 mmol).

Step 2: To an oven dried 25 mL round bottomed flask, **2az′** (685.0 mg, 2.5 mmol, 1.0 equiv.) was dissolved in 15 mL of methanol and $NaBH_4$ (190 mg, 5.0 mmol, 2.0 equiv.) was added in a portion wise manner under stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 15 mL of water was added. After that, it was extracted by (3×15 mL) CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the desired alcohol **2az** in 86% (593.0 mg, 2.14 mmol) yield.

3. Synthesis of Ligands:

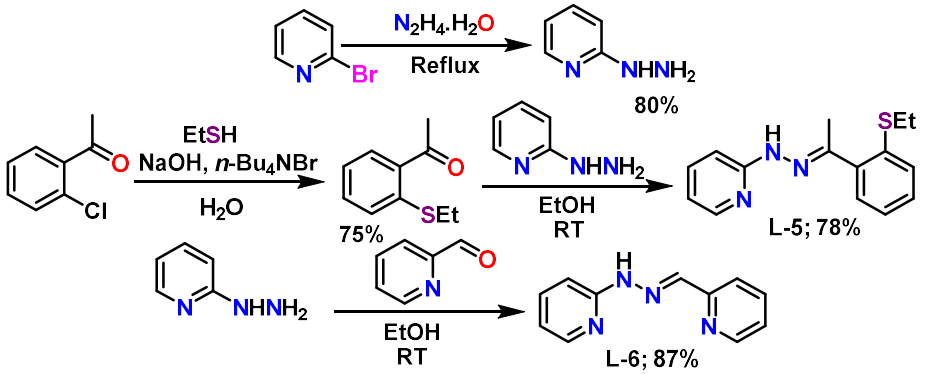


Figure S1. Synthesis of ligands

2-hydrazinopyridine was prepared using previous literature method.[5]

A mixture of NaOH (7.0 mmol, 1.4 equiv.), H_2O (5.0 mL) and ethanethiol (7.0 mmol, 1.4 equiv.) was stirred at room temperature for 30 min, the corresponding 2′-Chloroacetophenone (5.0 mmol, 1.0 equiv.) and tetrabutylammonium bromide (50.0 mg) were added, and the reaction mixture was stirred at 82 °C for a period of 12 h. After being cooled to room temperature, the reaction mixture was poured into 30 mL of water and extracted three times with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash chromatography using a mixture of ethyl acetate and hexane as the elutent to afford the corresponding 2-(ethylthio)-acetaldehyde.[6]

2-hydrazinopyridine (2.0 mmol) and substituted Carbonyl compounds (2.2 mmol) were dissolved in ethanol (10 mL). The resulting solution was stirred for 12 h at room temperature. Then, it was filtered and the filter residue was washed thoroughly with ethanol. After that, residue was dissolved by CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the crude product, which was further purified by silica gel column chromatography using 10-50 % ethyl acetate in hexane to get the desired compound.

4. Synthesis and Characterization of Zn-NN Complexes:

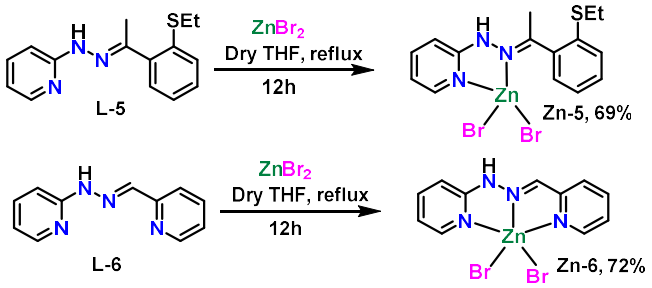


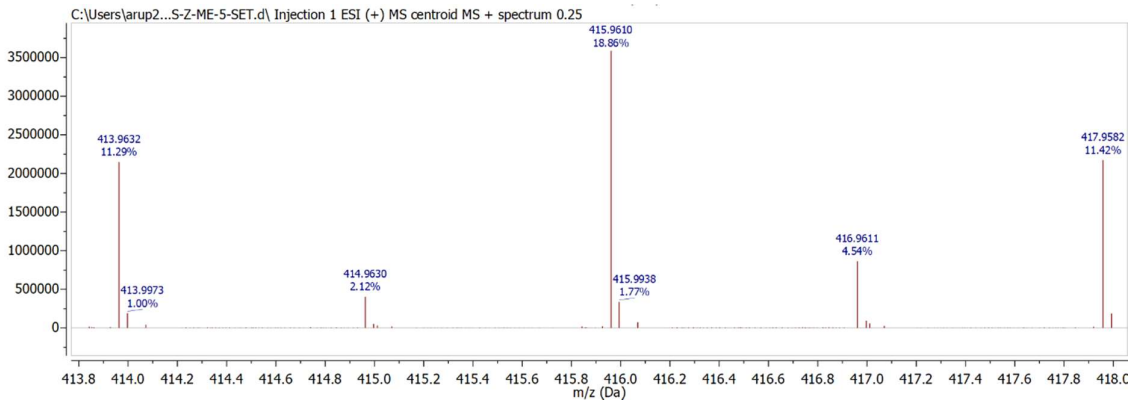
Figure S2. Zinc complexes preparation.

Complexes Zn-1 to Zn-4 were prepared from reported procedure.[5]

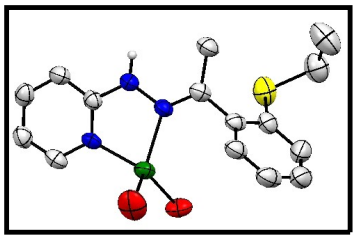
In an oven dried two-neck round bottom flask L- 5 and L-6 (1.0 mmol) was taken in 4 mL of dry THF and was added dropwise to the suspension of $ZnBr_2$ (0.225g, 1.0 mmol) in 8 mL

degassed dry THF. Then, the suspension was refluxed overnight under argon atmosphere. After being cooled to room temperature, the solvent was evaporated to obtain the residue, which was further washed with ether and dried under vacuum to get light yellow powder of Zn-complex. The single crystal was grown by slow diffusion of ether in the methanol solution of the complex.

4.1 HRMS of Zn-5:



4.2 SC-XRD data of Zn-5:

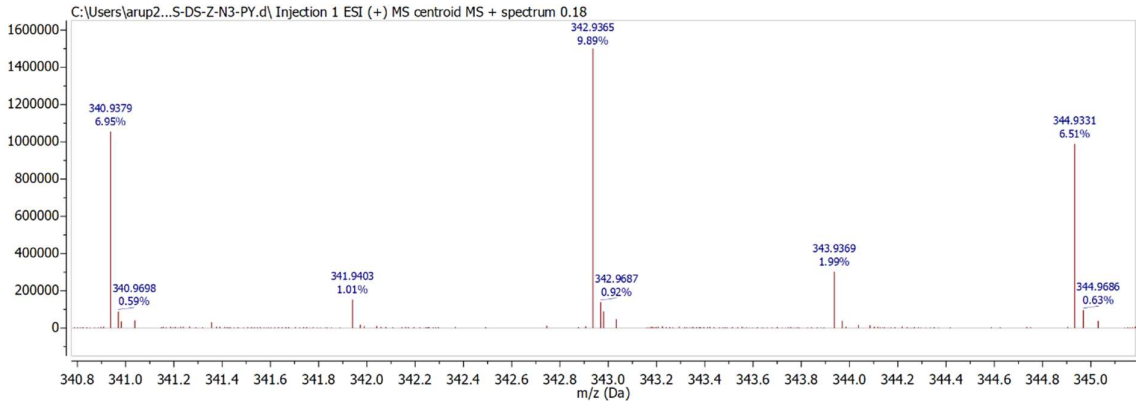


CCDC	2357528
Empirical formula	C15 H17 Br2 N3 S Zn
Formula weight	496.57
Temperature, T	297(2) K
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a=7.5800(18) Å α=90° b=12.603(3) Å β=92.335(7)° c=19.172(5) Å γ=90°
Volume, V ($Å^3$)	1830.1(8)
Z	1
Density (calculated), g cm^{-3}	1.802
Absorption coefficient, μ (mm^{-1})	5.821
F (000)	976.0
Crystal size, mm^3	0.38 × 0.32 × 0.28
Theta range for data collection	1.934 to 25.000
Index ranges	-9 ≤ h ≤ 9 -14 ≤ k ≤ 14 -22 ≤ l ≤ 22
Reflections collected	3209

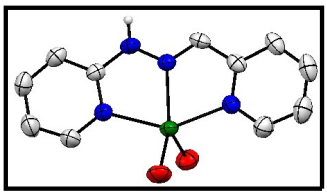
Independent reflections	2220
Completeness to theta	1.000
Absorption correction	none
Refinement method	'SHELXL-2018/3 (Sheldrick, 2018)'
Data / restraints / parameters	3209/1/205
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0792, wR2 = 0.1539
R indices (all data)	R1 = 0.0424, wR2 = 0.1134
Largest diff. peak and hole	0.815 and -0.687 e·Å^{-3}

Bond Distances [Å]	Bond angles [°]
Br01 Zn02 2.3470(10)	N005 Zn02 N006 78.31(17)
Zn02 N005 2.039(5)	N005 Zn02 Br03 110.90(12)
Zn02 N006 2.103(4)	N006 Zn02 Br03 119.76(13)
Zn02 Br03 2.3224(11)	N005 Zn02 Br01 113.70(13)
S004 C00H 1.771(7)	N006 Zn02 Br01 111.88(13)
S004 C00L 1.822(7)	Br03 Zn02 Br01 116.41(4)
N005 C008 1.325(7)	C00H S004 C00L 102.8(3)
N005 C00A 1.361(7)	C008 N005 C00A 117.7(5)
N006 C009 1.292(7)	C008 N005 Zn02 115.9(4)
N006 N007 1.381(7)	C00A N005 Zn02 126.4(4)
N007 C008 1.401(7)	C009 N006 N007 119.2(5)
C008 C00E 1.377(9)	C009 N006 Zn02 130.0(4)
C009 C00B 1.487(8)	N007 N006 Zn02 110.6(3)
C009 C00G 1.495(8)	N006 N007 C008 116.3(5)
C00A C00D 1.348(9)	N005 C008 C00E 123.2(5)
C00B C00F 1.389(8)	N005 C008 N007 116.3(5)
C00B C00H 1.397(9)	C00E C008 N007 120.6(5)
C00C C00D 1.366(9)	N006 C009 C00B 116.1(5)
C00C C00E 1.373(9)	N006 C009 C00G 123.5(5)
C00F C00I 1.388(10)	C00B C009 C00G 120.4(5)
C00H C00J 1.403(9)	C00D C00A N005 122.1(6)
C00I C00K 1.378(11)	C00F C00B C00H 119.9(6)
C00J C00K 1.388(10)	C00F C00B C009 119.1(6)
C00L C00M 1.504(11)	C00H C00B C009 121.0(5)
	C00D C00C C00E 119.9(6)
	C00A C00D C00C 119.4(6)
	C00C C00E C008 117.7(6)
	C00I C00F C00B 120.7(7)
	C00B C00H C00J 119.6(6)
	C00B C00H S004 119.7(5)
	C00J C00H S004 120.5(6)
	C00K C00I C00F 119.0(7)
	C00K C00J C00H 118.9(7)
	C00I C00K C00J 121.9(7)
	C00M C00L S004 113.5(6)

4.3 HRMS of Zn-6:



4.4 SC-XRD data of Zn-6:



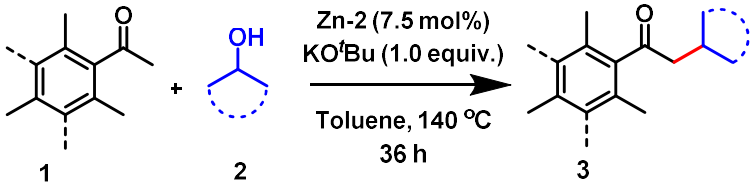
CCDC	2357530
Empirical formula	C11 H10 Br2 N4 Zn
Formula weight	423.42
Temperature, T	296(2)
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a=7.6960(6) Å α=76.839(2)° b=7.9855(6) Å β=84.112(2)° c=11.6761(8) Å γ=81.127(2)°
Volume, V ($Å^3$)	688.66(9)
Z	2
Density (calculated), g cm^{-3}	2.042
Absorption coefficient, μ (mm^{-1})	7.572
F (000)	408.0
Crystal size, mm^3	0.35 × 0.28 × 0.24
Theta range for data collection	1.796 to 24.996
Index ranges	$-9 \le h \le 9$ $-9 \le k \le 9$ $-13 \le l \le 13$
Reflections collected	2410
Independent reflections	2217
Completeness to theta	0.993
Absorption correction	Multi-scan
Refinement method	SHELXL 2018/3 (Sheldrick, 2015)

Data / restraints / parameters	2410/0/163
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0233, wR2 = 0.0541
R indices (all data)	R1 = 0.0207, wR2 = 0.0528
Largest diff. peak and hole	0.457 and -0.475 e·Å^{-3}

Bond Distances [Å]	Bond angles [°]
Zn1 Br2 2.3730(4)	Br2 Zn1 Br1 117.476(16)
Zn1 Br1 2.4079(4)	N3 Zn1 Br2 111.64(6)
Zn1 N3 2.133(2)	N3 Zn1 Br1 130.83(6)
Zn1 N1 2.186(2)	N3 Zn1 N1 73.59(7)
Zn1 N4 2.229(2)	N3 Zn1 N4 72.75(8)
N3 N2 1.338(3)	N1 Zn1 Br2 102.86(6)
N3 C6 1.290(3)	N1 Zn1 Br1 97.03(5)
N1 C5 1.334(3)	N1 Zn1 N4 144.21(8)
N1 C1 1.341(3)	N4 Zn1 Br2 100.51(6)
N4 C7 1.347(3)	N4 Zn1 Br1 95.78(6)
N4 C11 1.332(3)	N2 N3 Zn1 116.44(15)
N2 H2 0.8600	C6 N3 Zn1 120.08(17)
N2 C5 1.387(3)	C6 N3 N2 123.3(2)
C6 H6 0.9300	C5 N1 Zn1 115.44(16)
C6 C7 1.442(4)	C5 N1 C1 117.6(2)
C7 C8 1.385(3)	C1 N1 Zn1 126.91(17)
C5 C4 1.390(3)	C7 N4 Zn1 115.03(16)
C4 H4 0.9300	C11 N4 Zn1 126.63(18)
C4 C3 1.366(4)	C11 N4 C7 118.1(2)
C1 H1 0.9300	N3 N2 H2 121.5
C1 C2 1.369(4)	N3 N2 C5 117.1(2)
C3 H3 0.9300	C5 N2 H2 121.5
C3 C2 1.383(4)	N3 C6 H6 121.8
C8 H8 0.9300	N3 C6 C7 116.4(2)
C8 C9 1.375(4)	C7 C6 H6 121.8
C11 H11 0.9300	N4 C7 C6 115.2(2)
C11 C10 1.385(4)	N4 C7 C8 122.4(2)
C9 H9 0.9300	C8 C7 C6 122.4(2)
C9 C10 1.374(5)	N1 C5 N2 116.2(2)
C2 H2A 0.9300	N1 C5 C4 123.2(2)
C10 H10 0.9300	N2 C5 C4 120.6(2)
	C5 C4 H4 121.2
	C3 C4 C5 117.7(3)
	C3 C4 H4 121.2
	N1 C1 H1 118.4
	N1 C1 C2 123.2(3)
	C2 C1 H1 118.4
	C4 C3 H3 119.9
	C4 C3 C2 120.3(3)
	C2 C3 H3 119.9
	C7 C8 H8 120.8
	C9 C8 C7 118.3(3)

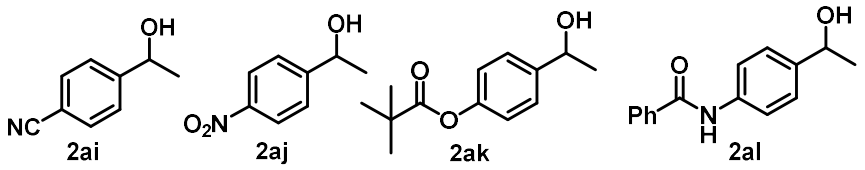
	C9 C8 H8 120.8 N4 C11 H11 118.6 N4 C11 C10 122.9(3) C10 C11 H11 118.6 C8 C9 H9 120.0 C10 C9 C8 119.9(3) C10 C9 H9 120.0 C1 C2 C3 118.1(3) C1 C2 H2A 120.9 C3 C2 H2A 120.9 C11 C10 H10 120.9 C9 C10 C11 118.3(3) C9 C10 H10 120.9

5. General procedure for α-alkylation of ketones with secondary alcohols:

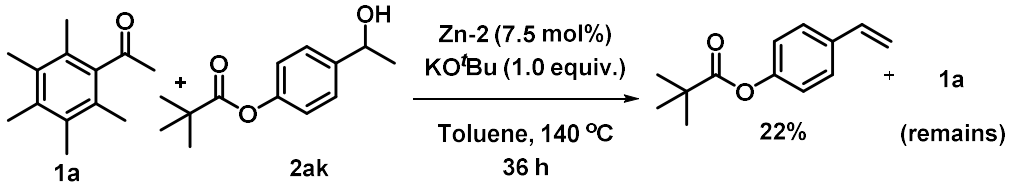


In an oven dried well-capped 100 mL ace pressure tube secondary alcohol 2 (1.0-1.5 mmol), ketone 1 (0.5 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (2 mL) were added in a gentle stream of argon. The tube was then closed and stirred in a preheated oil bath at 140 °C for 36 h. After that, reaction mixture was cooled to room temperature and it was filtered through celite and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether/ethyl acetate mixture as eluent.

5. Incompatible substrates:

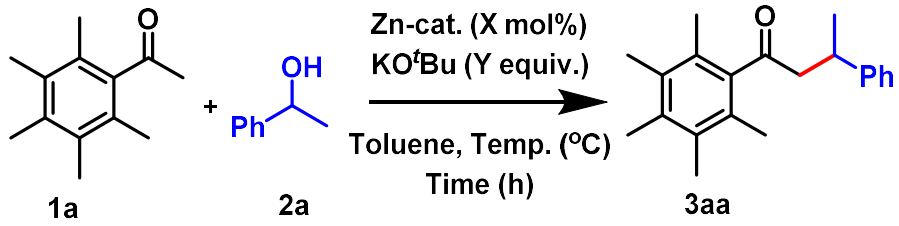


Dehydration product of the alcohol is isolated



6. Optimization Table:

6.a) For aromatic secondary alcohols:

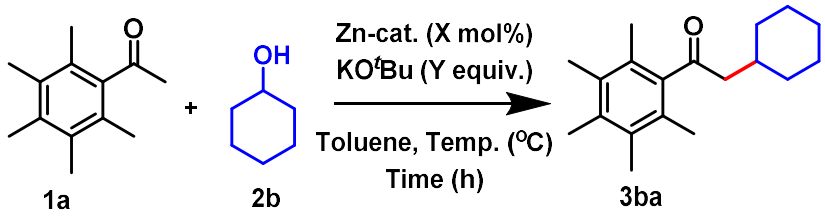


1a 2a 3aa

Entry	1a: 2a	Zn-cat. (mol%)	Base (equiv.)	Time (h)	Yield of 3aa (%)
1.	1:1.2	Zn-2 (5)	KO^{t}Bu (2)	24	31
2.	1:1.5	Zn-2 (5)	KO^{t}Bu (2)	24	55
3.	1:1.5	Zn-2 (5)	KO^{t}Bu (1)	24	52
4.	1:1.5	Zn-2 (7.5)	KO^{t}Bu (1)	24	68
5.	1:2	Zn-2 (7.5)	KO^{t}Bu (1)	24	76
6.	1:2	Zn-2 (7.5)	KO^{t}Bu (1)	30	86
7.	1:2	Zn-2 (7.5)	KO^{t}Bu (1)	36	94
8.[b]	1:2	Zn-2 (7.5)	KO^{t}Bu (1)	36	65
9.[c]	1:2	Zn-2 (7.5)	KO^{t}Bu (1)	36	71
10.	1:2	Zn-2 (7.5)	NaO^{t}Bu (1)	36	58
11.	1:2	Zn-2 (7.5)	Cs_2CO_3 (1)	36	>10
12.	1:2	Zn-2 (7.5)	KOH (1)	36	54
13.	1:2	Zn-2 (7.5)	Na_2CO_3 (1)	36	>5
14.	1:2	Zn-2 (7.5)	NaOH (1)	36	48
15.[d]	1:2	Zn-2 (7.5)	KO^{t}Bu (1)	36	23
16.	1:2	-	KO^{t}Bu (1)	36	trace
17.	1:2	Zn-2 (7.5)	-	36	-
18.	1:2	$ZnBr_2$ (7.5)	KO^{t}Bu (1)	36	-
19.	1:2	Zn-1 (7.5)	KO^{t}Bu (1)	36	68
20.	1:2	Zn-3 (7.5)	KO^{t}Bu (1)	36	70
21.	1:2	Zn-4 (7.5)	KO^{t}Bu (1)	36	20
22.	1:2	Zn-5 (7.5)	KOtBu (1)	36	44
23.	1:2	Zn-6 (7.5)	KO^{t}Bu (1)	36	62

[a]**Conditions:** 1a (0.5 mmol), 2a (0.6-1.0 mmol), Base (1.0-2.0 equiv.), Zn-catalyst (5.0-7.5 mol%), Toluene (2.0 mL), Under argon, Temperature: 140 □, Time: 24-36 h; [b]Temperature: 120 □; [c]Solvent: Xylene; [d]Solvent: 1,4-dioxane.

6.b) For cyclic and aliphatic secondary alcohols:

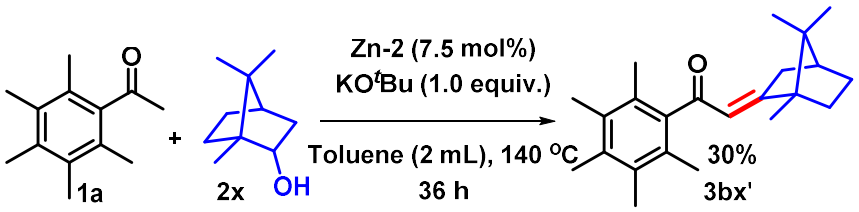


Entry	1a: 2b	Zn-cat. (mol%)	Base (equiv.)	Time (h)	Yield of 3ba (%)
1.	1:1.2	Zn-2 (7.5)	KO^{t}Bu (1)	36	28
2.	1:2	Zn-2 (7.5)	KO^{t}Bu (1)	36	62
3.	1:2.5	Zn-2 (7.5)	KO^{t}Bu (1)	36	75
4.	1:3	Zn-2 (7.5)	KO^{t}Bu (1)	36	96
5.	1:3	Zn-2 (7.5)	KO^{t}Bu (1)	24	68
6.[e]	1:3	Zn-2 (7.5)	KO^{t}Bu (1)	36	25

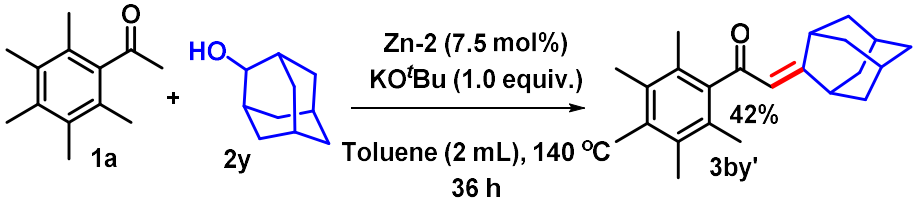
[a]**Conditions:** 1a (0.5 mmol), 2b (0.6-1.5 mmol), Base (1.0-2.0 equiv.), Zn-catalyst (7.5 mol%), Toluene (2.0 mL), Under argon, Temperature: 140 □, Time: 24-36 h; [e]Solvent: THF.

7. Control experiments for mechanistic investigation:

7.1. (a) Involvement of enone intermediacy:



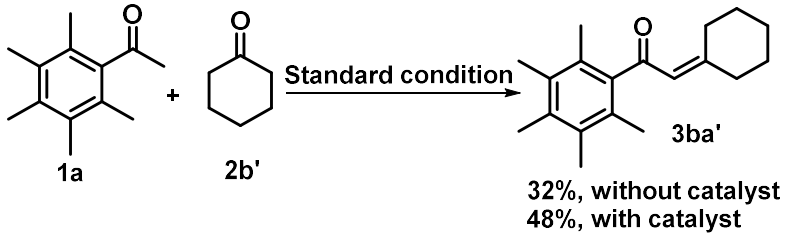
In an oven dried well-capped 100 mL ace pressure tube secondary alcohol 2x (1.5 mmol), ketone 1a (0.5 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (2 mL) were added in a gentle stream of argon. The tube was then closed and stirred in a preheated oil bath at 140 ^{o}C for 36 h. After that, reaction mixture was cooled to room temperature and it was filtered through celite and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether:ethyl acetate (98:2) mixture as eluent.



In an oven dried well-capped 100 mL ace pressure tube secondary alcohol 2y (1.5 mmol), ketone 1a (0.5 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (2 mL) were added in a gentle stream of argon. The tube was then closed and stirred in a preheated oil bath at 140 ^{o}C for 36 h. After that, reaction mixture was cooled to room temperature and it was

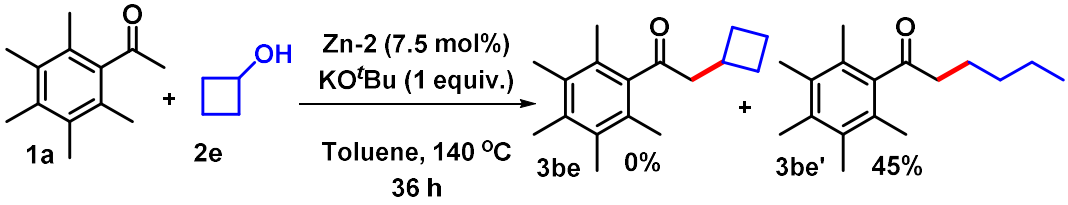
filtered through celite and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether:ethyl acetate (98:2) mixture as eluent.

7.1. (b) Importance of aryl group in ketone part for alkylation:



In an oven dried well-capped 100 mL ace pressure tube secondary alcohol 2b′ (1.5 mmol), ketone 1a (0.5 mmol), KO^{t}Bu (1.0 equiv.) and toluene (2 mL) were added in a gentle stream of argon in two different reactions set up. One in presence of catalyst and another without catalyst were set. The tube was then closed and stirred in a preheated oil bath at 140 °C for 36 h. After that, reaction mixture was cooled to room temperature and it was filtered through celite and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether/ethyl acetate (99:1) mixture as eluent.

7.1. (c) Experiment with Cyclobutanol:



In an oven dried well-capped 100 mL ace pressure tube secondary alcohol 2e (1.5 mmol), ketone 1a (0.5 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (2 mL) were added in a gentle stream of argon. The tube was then closed and stirred in a preheated oil bath at 140 °C for 36 h. After that, reaction mixture was cooled to room temperature and it was filtered through celite and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether as eluent.

7.2. Synthesis of deuterated secondary alcohol 2a-D:

Deuterated secondary alcohol was prepared from the previous literature method.[7] To a stirred solution of acetophenone (240.0 mg, 2.0 mmol) in 3.0 mL of anhydrous methanol, cooled at 0 °C, sodium borodeuteride 98 D□atom % (42.0 mg, 1.0 mmol) was added portion□wise. Reaction temperature must not exceed 25 °C along this process. The reaction mixture was allowed to stand under stirring for 1 h. The solvent was removed under vacuum and the residue was suspended in 10 mL of diethyl ether and treated with 2 mL of 0.6 M hydrochloric acid, under stirring. The organic layer was separated, washed with several portions of distilled water until the aqueous phase had neutral pH, and dried over anhydrous Na_2SO_4. The solvent was

removed under vacuum to give 98% yield (241.0 mg) of colourless 1□deutero□1□ phenylethanol which was used without further purification.

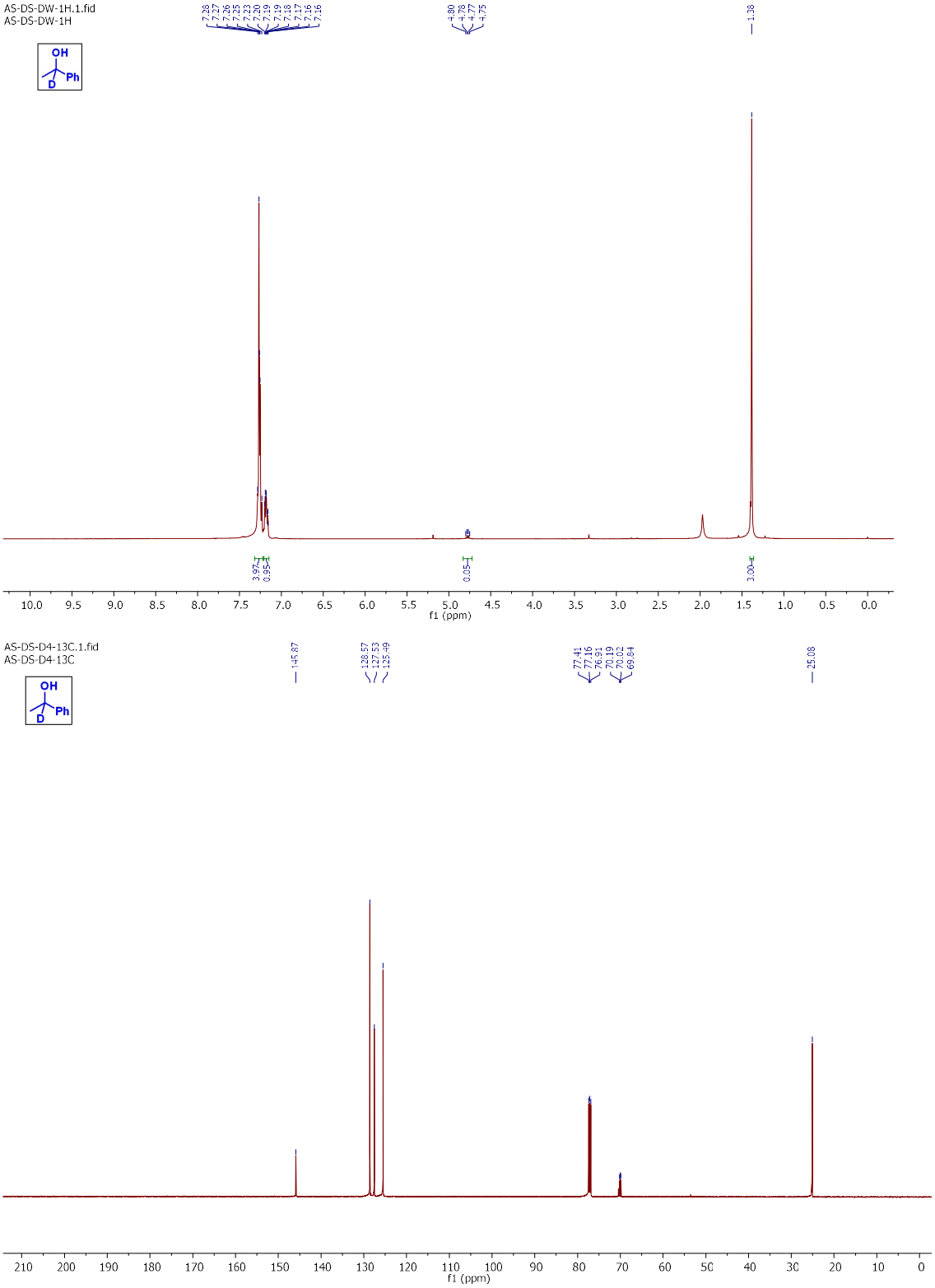
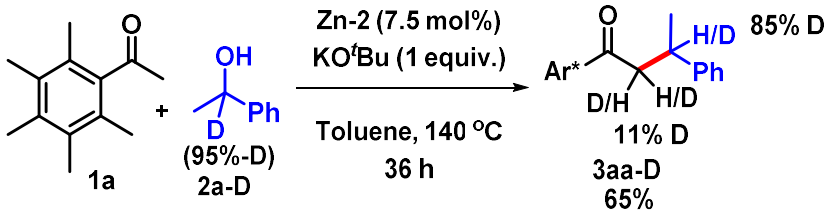
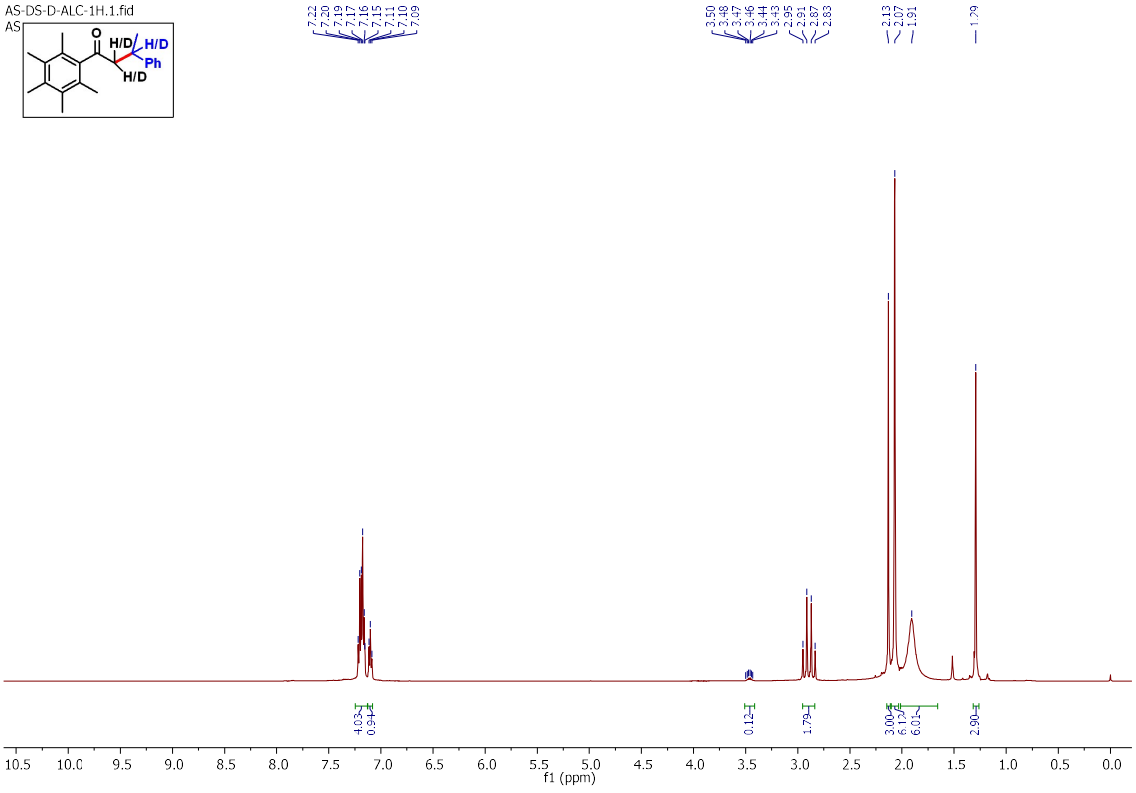


Figure S3. ^{1}H NMR (400 MHz) and ^{13}C {^{1}H} NMR (125 MHz) spectrum of Compound 2a-D in $CDCl_3$.

7.2. (a) Deuterium labelling experiment:



In an oven dried well-capped 100 mL ace pressure tube secondary alcohol 2a-D (1.5 mmol), ketone 1a (0.5 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (2 mL) were added in a gentle stream of argon. The tube was then closed and stirred in a preheated oil bath at 140 °C for 36 h. After that, reaction mixture was cooled to room temperature and it was filtered through celite and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether and ethyl acetate as eluent. The product was characterized through ^{1}H NMR spectroscopy.



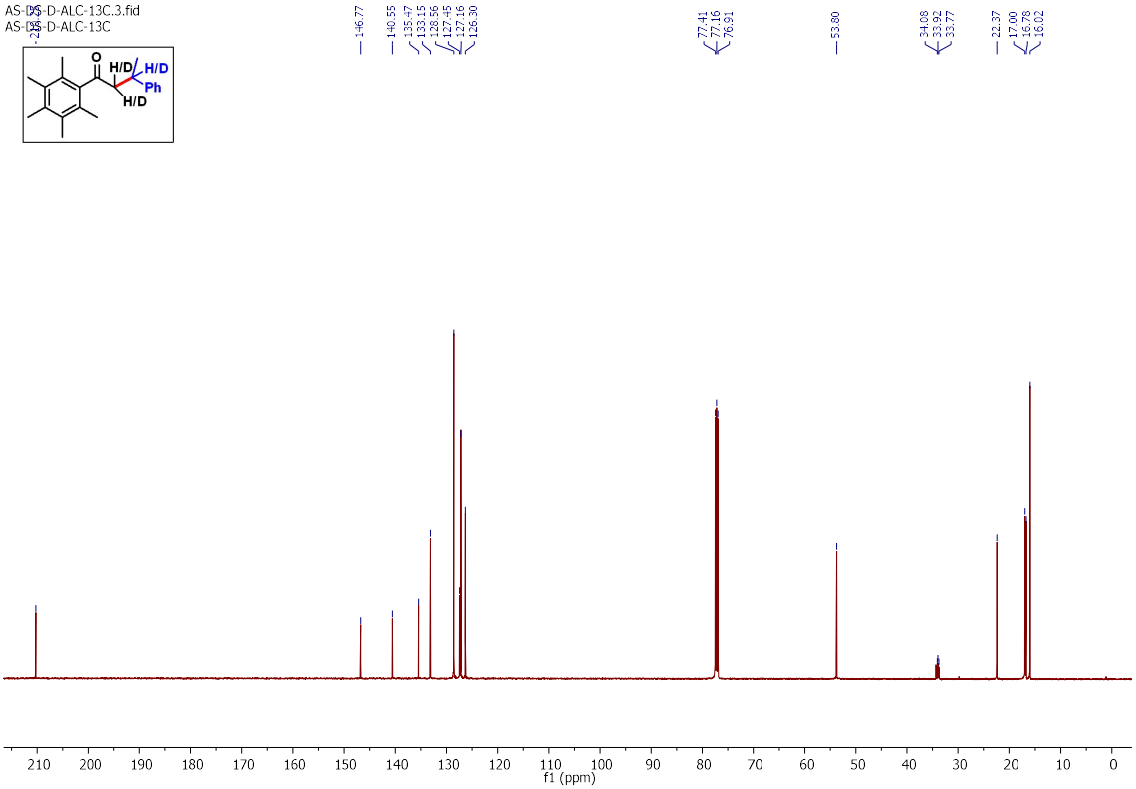
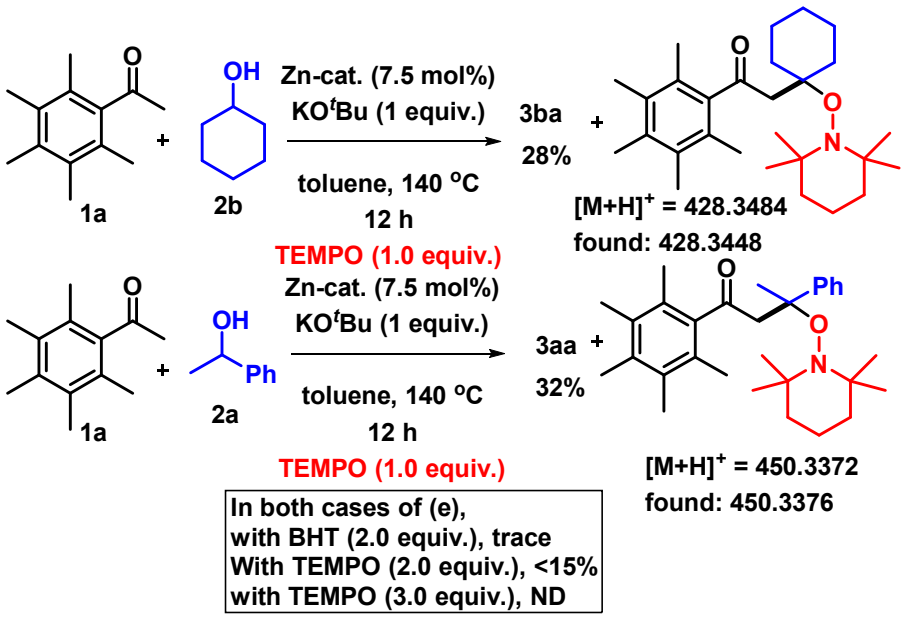


Figure S4. ^{1}H NMR (500 MHz) and ^{13}C {^{1}H} NMR (125 MHz) spectrum of Compound 2a-D in $CDCl_3$.

7.3. Radical quenching experiments:



In an oven dried well-capped 100 mL ace pressure tube secondary alcohol 2 (1.5 mmol), ketone 1a (0.5 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%), radical inhibitor (TEMPO or BHT) and toluene (2 mL) were added in a gentle stream of argon. The tube was then closed and stirred in a preheated oil bath at 140 °C for 36 h. After that, reaction mixture was cooled to

room temperature and one portion was characterized through HRMS spectrometry and the corresponding mass of TEMPO trapped ketyl radical were found and another portion was filtered through celite and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with petroleum-ether and ethyl acetate as eluent. The product was characterized through ^{1}H NMR spectroscopy.

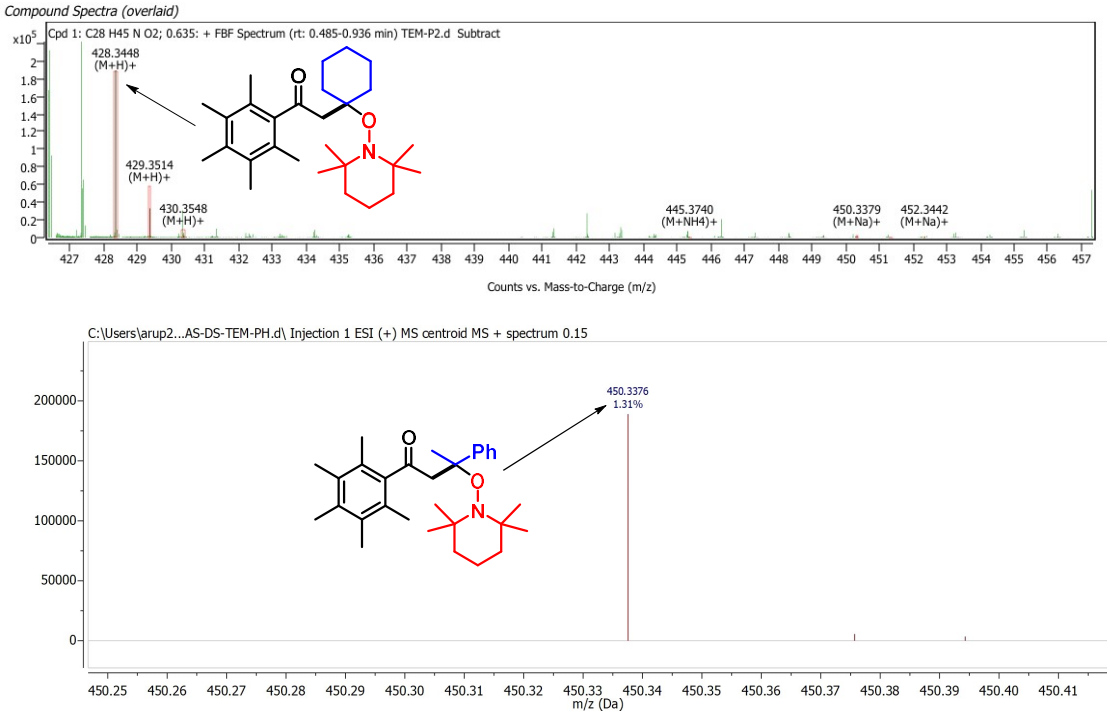


Figure S5. HRMS data of TEMPO-Ketyl adduct.

8. Kinetic experiments:

8.1 Experimental Procedure:

To an oven dried 100 mL ace pressure tube, Cyclohexanol 2b (3.0 mmol, 3 equiv.), Ketone 1a (1.0 mmol, 1.0 equiv.), KO^{t}Bu (1 equiv.) and Zn-2 (0.075mmol, 7.5 mol%), mesitylene (1.0 mmol, 1.0 equiv.) as an internal standard and toluene as a solvent were added under argon to make up the total volume of the reaction mixture to 5 ml. Afterwards, the reaction mixture was kept in a preheated oil bath for stirring at 140 °C. At regular intervals (1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 10 h, 14 h, 18 h, 22 h, 26 h, 30 h, 34 h, 36 h) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with toluene and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of the product (mmol) vs time (h) plot.

Time (h)	Concentration of Pentamethyl ketone **1a** (mmolar)	Concentration of Cyclohexanol **2b** (mmolar)	Concentration of Cyclohexanone **2b′**(mmolar)	Concentration of Eneone **3ba′** (mmolar)	Concentration of Product **3ba** (mmolar)
0	1	3	0	0	0
1	0.928	2.896	0.008	0.021	0.088
2	0.853	2.785	0.016	0.042	0.139

3	0.782	2.674	0.026	0.064	0.187
4	0.719	2.572	0.038	0.088	0.245
5	0.652	2.496	0.051	0.104	0.297
6	0.561	2.375	0.065	0.121	0.369
10	0.481	2.251	0.082	0.158	0.422
14	0.385	2.089	0.101	0.190	0.504
18	0.305	1.965	0.094	0.179	0.566
22	0.196	1.799	0.072	0.154	0.645
26	0.105	1.667	0.051	0.131	0.726
30	0.017	1.526	0.024	0.111	0.801
34	0.005	1.398	0.008	0.086	0.885
36	0.002	1.275	0.003	0.044	0.967

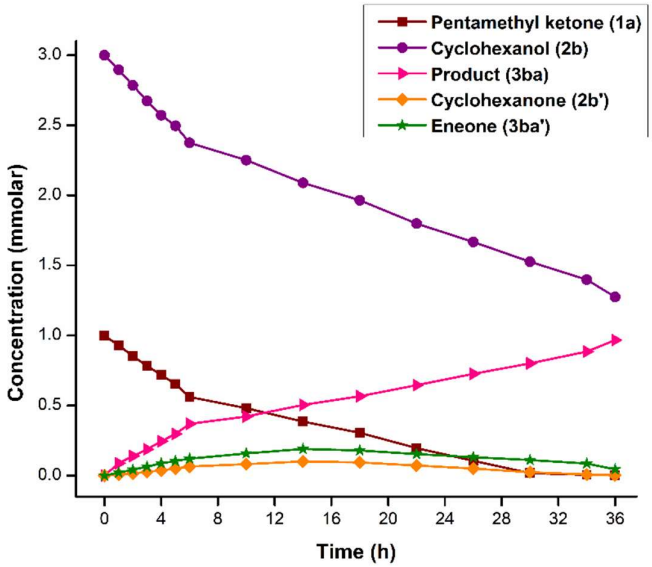


Figure S6. Overall kinetics of reaction progress.

8.2 Rate order determination w.r.t 1a and 2b:

The initial rate method was used to determine the rate order of the α-alkylation reaction with respect to various components of the reaction. The data of the concentration (mM) vs time (min.) plot was fitted to linear using origin pro 9. The slope of the linear fitted curve represents the initial rate of the reaction. The order of the reaction was determined by plotting initial rate (mM/min.) vs concentration (mM) of that particular component.

Rate order determination with respect to ketone (1a):

To determine the order of the reaction, initial rates at different concentration of ketone **1a** were recorded.

Experimental procedure: To an oven dried 100 mL ace pressure tube, cyclohexanol 2b (3.0 equiv.), KO^{t}Bu (1 equiv.) and Zn-2 (7.5 mol%), mesitylene (1.0 equiv.) as an internal standard, specific amount of ketone **1a** and toluene as a solvent were added under argon to make up the total volume of the reaction mixture 5 mL. Afterwards, the reaction mixture was kept in an oil bath of 140 °C for stirring. At regular intervals (30 min., 60 min., 90 min., 120 min., 150 min., 180 min.) the reaction mixture was cooled to ambient temperature and an aliquot of mixture

was taken in a GC vial. The GC sample was diluted with toluene and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of the product (mM) vs time (min.) plot (Figure S7). The rate of the reaction at different initial concentration of ketone **1a** was given below and used to plot the initial rate (mM/min.) vs concentration of ketone **1a** (mM) to determine the order of the reaction with respect to ketone **1a**.

Time (min.)	Conc. of **1a**, (0.09 mM)	Conc. of **1a**, (0.10 mM)	Conc. of **1a**, (0.11 mM)	Conc. of **1a**, (0.12 mM)
0	0.09	0.10	0.11	0.12
30	0.0889	0.0968	0.1037	0.1098
60	0.086	0.0936	0.1002	0.1059
90	0.0829	0.0901	0.0964	0.1018
120	0.0797	0.0866	0.0925	0.0976
150	0.0762	0.0827	0.0882	0.0929
180	0.0727	0.0788	0.0839	0.0882

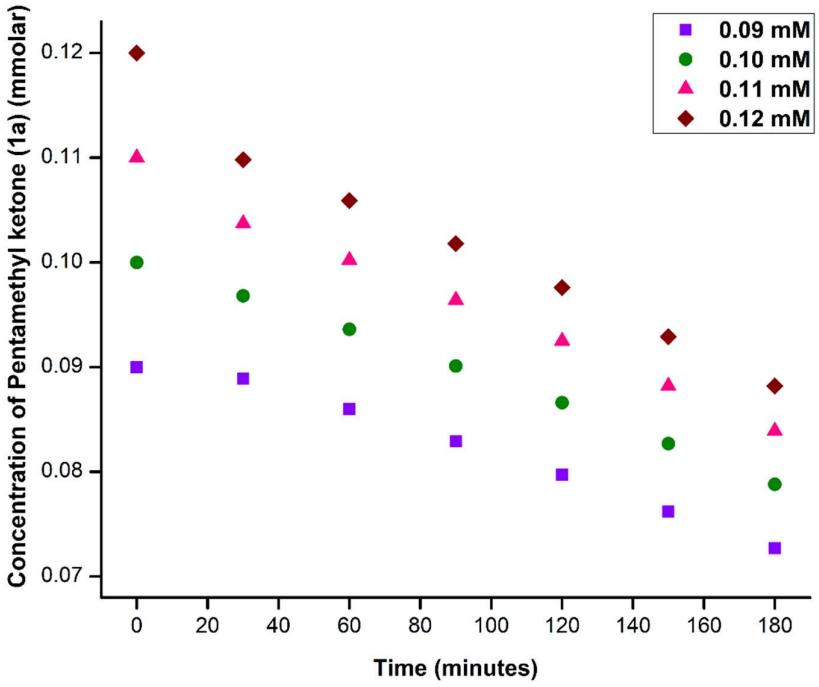


Figure S7. Concentration versus time plot at various concentration of Ketone (**1a**).

log(concentration of **1a**)	log(rate)
-1.046	-4.0022
-1	-3.9296
-0.9586	-3.8564
-0.9208	-3.7859

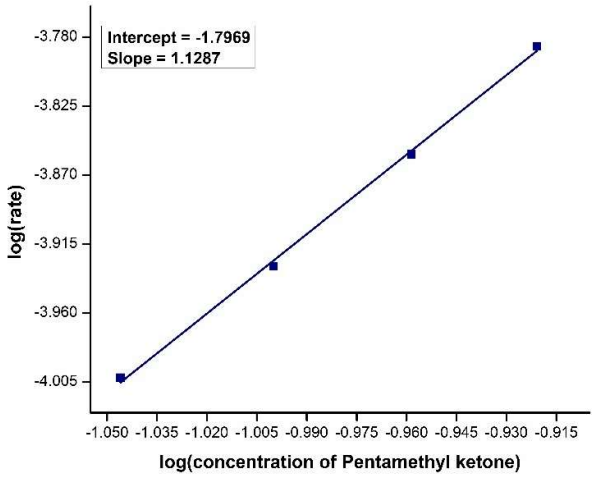


Figure S8. Plot for determining the order of the reaction with respect to log (Conc. Of **1a**).

Rate order determination with respect to cyclohexanol (2b):

To determine the order of the reaction, initial rates at different concentration of cyclohexanol **2b** were recorded.

Experimental procedure: To an oven dried 100 mL ace pressure tube, ketone **1a** (1.0 equiv.), KO^{t}Bu (1 equiv.) and Zn-2 (7.5 mol%), mesitylene (1.0 equiv.) as an internal standard, specific amount of cyclohexanol **2b** and toluene as a solvent were added under argon to make up the total volume of the reaction mixture 5 mL. Afterwards, the reaction mixture was kept in an oil bath of 140 °C for stirring. At regular intervals (30 min., 60 min., 90 min., 120 min., 150 min., 180 min.) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with toluene and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was accomplished to draw the concentration of the product (mM) vs time (min.) plot (Figure S9). The rate of the reaction at different initial concentration of cyclohexanol **2b** was given below and used to plot the initial rate (mM/min.) vs concentration of cyclohexanol **2b** (mM) to determine the order of the reaction with respect to cyclohexanol **2b**.

Time (min.)	Conc. of **2b**, (0.29 mM)	Conc. of **2b**, (0.30 mM)	Conc. of **2b**, (0.31 mM)	Conc. of **2b**, (0.32 mM)
0	0.29	0.30	0.31	0.32
30	0.2886	0.2956	0.3016	0.3068
60	0.2843	0.2911	0.2969	0.302
90	0.2793	0.2859	0.2916	0.2966
120	0.2744	0.2809	0.2864	0.2911
150	0.2689	0.2752	0.2805	0.285
180	0.2634	0.2695	0.2746	0.2789

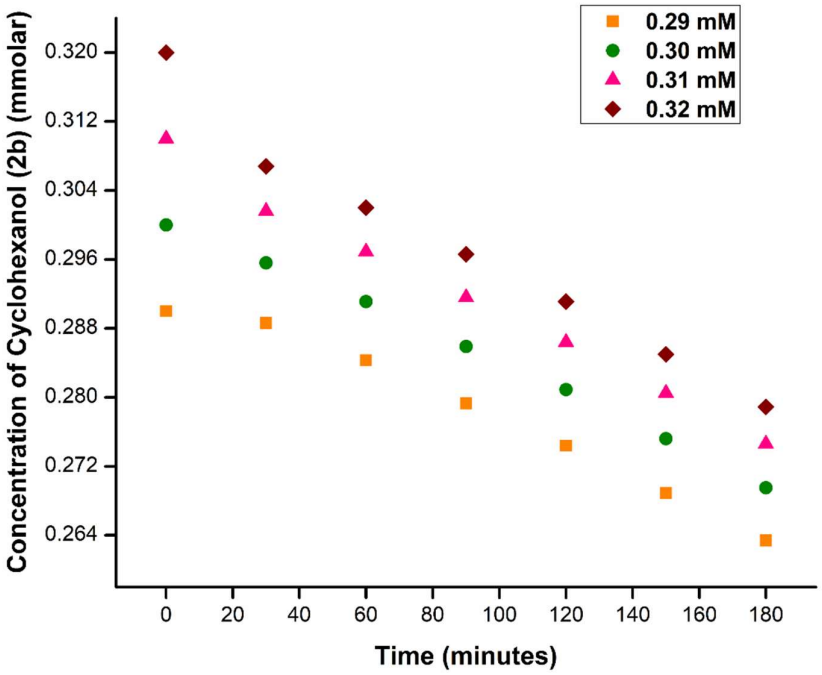


Figure S9. Concentration versus time plot at various concentration of cyclohexanol (**2b**).

log(concentration of **2b**)	log(rate)
-0.5376	-3.8133
-0.5228	-3.7705
-0.5086	-3.7232
-0.4948	-3.6743

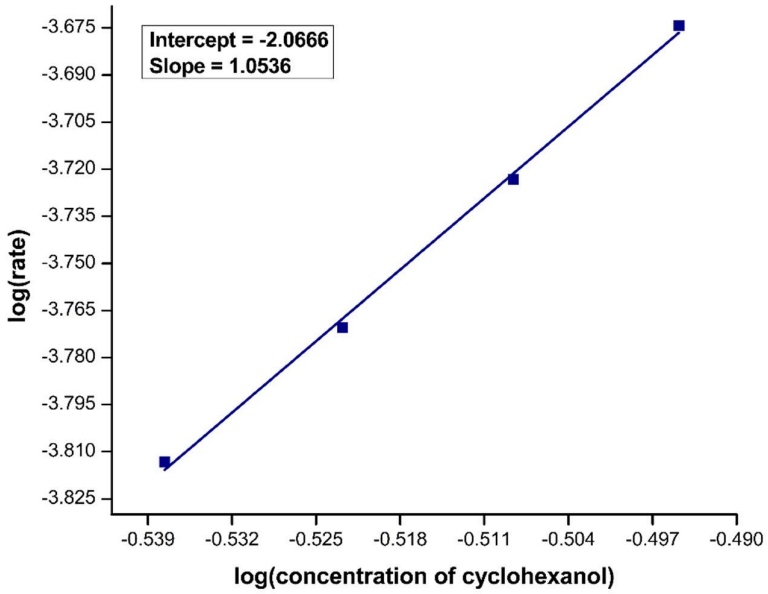
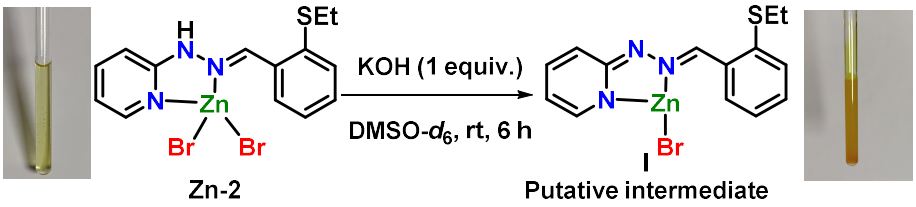


Figure S10. Plot for determining the order of the reaction with respect to log (Conc. Of **2b**).

9. Mechanistic study:



An oven dried NMR tube was taken and charged with Zn-2 complex (0.2 mmol), KOH (0.2 mmol) and 0.5 mL DMSO-d_6 was added inside a nitrogen-filled glovebox and kept for 6 h at RT. After that, reaction mixture was analysed with ^{1}H NMR.

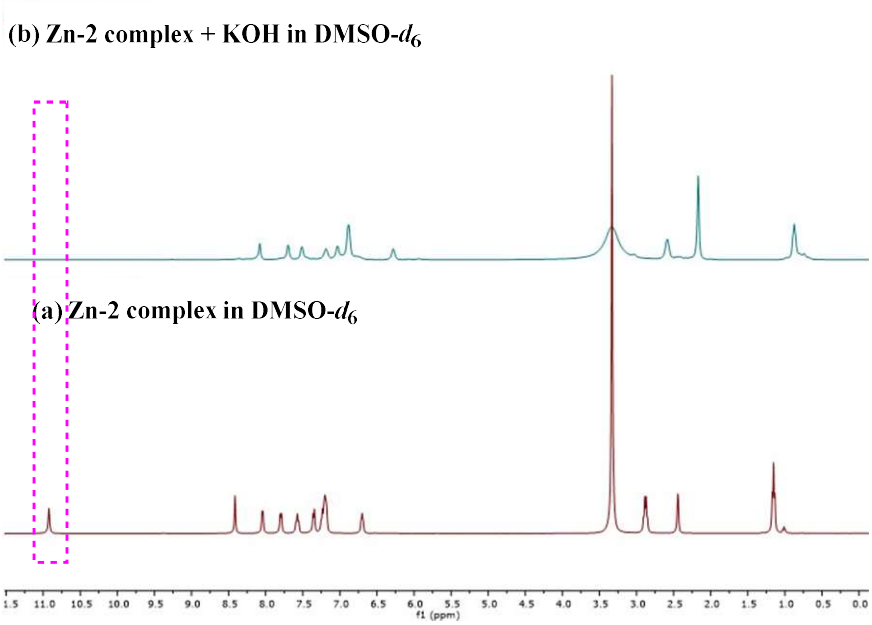
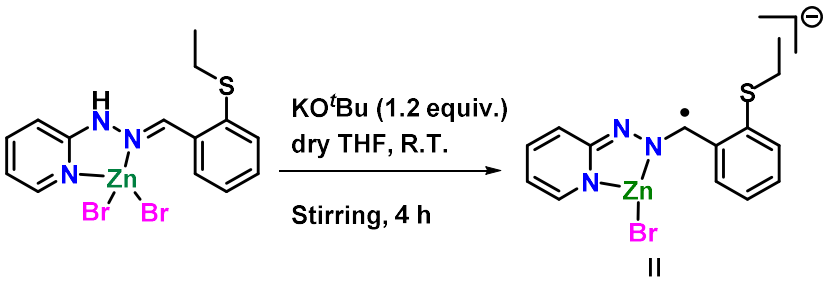


Figure S11. ^{1}H NMR (400 MHz) stacking of Zn-2 complex before and after addition of KOH in DMSO-d_6.

9.1. EPR study:

Sample preparation:



In 25 mL glass vial Zn-2 (0.5 mmol) in dry THF solution, KO^{t}Bu (0.6 mmol) in 5 mL dry THF were added dropwise inside a nitrogen-filled glovebox. The reaction mixture was stirred for 4

h at RT. The colour of the solution changed from bright yellow to orange. Then, it was filtered and dried in vacuo.

EPR details:

The one-electron reduced paramagnetic product II was analysed by X-band EPR on solid state at room temperature. The parameters during the data collection were following. Microwave frequency 9.44 GHz; Microwave Power 0.9950 MW; Modulation frequency 100 kHz; Modulation amplitude 2.0 mT.

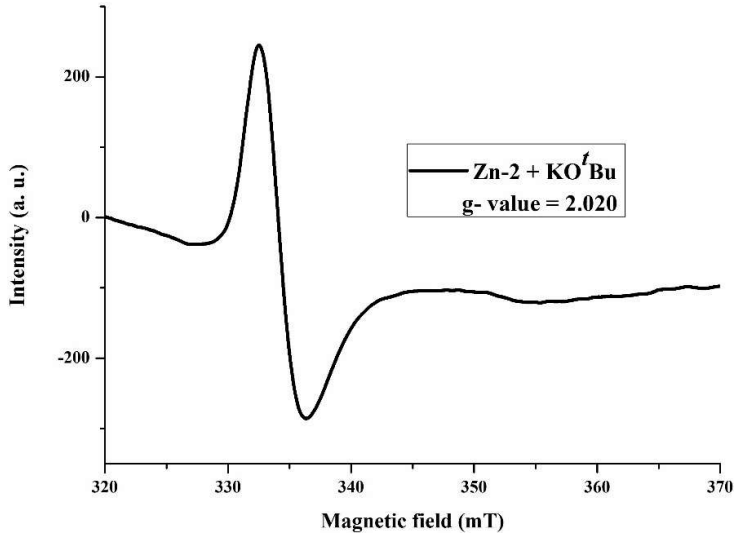
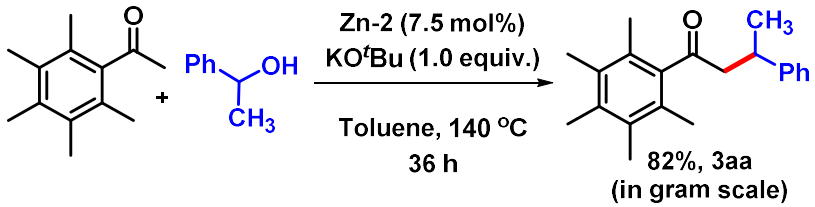
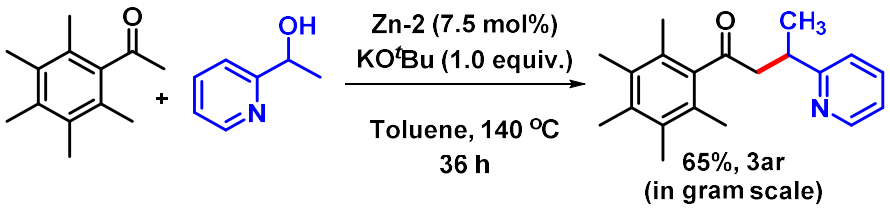


Figure S12. ESR spectra of II.

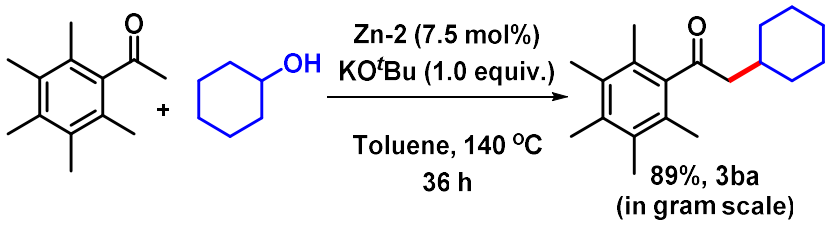
10. Experimental procedure for gram scale synthesis of compound 3aa, 3ar and 3ba:



In an oven dried 100 mL ace pressure tube, 1-Phenylethanol (1.220 g, 10.0 mmol), ketone (0.950 g, 5.0 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (20 mL) were added in a gentle stream of argon. Then the reaction mixture was refluxed and stirred with a magnetic stirring bar at 140 °C (oil-bath temperature) for 36 h. After completion of the reaction the crude mixture was filtered through celite filter and washed with ethyl acetate (3×5 mL), followed by the solvent was removed under vacuum and finally the residue was purified by silica gel column chromatography (100- 200 mesh size) using petroleum-ether and ethyl acetate (99:1) as an eluent to give **3aa** in 82% yield (1.205 g).



In an oven dried 100 mL ace pressure tube, 1-(pyridin-2-yl)ethan-1-ol (1.476 g, 12.0 mmol), ketone (1.140 g, 6.0 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (24 mL) were added in a gentle stream of argon. Then the reaction mixture was refluxed and stirred with a magnetic stirring bar at 140 °C (oil-bath temperature) for 36 h. After completion of the reaction the crude mixture was filtered through celite filter and washed with ethyl acetate (3×5 mL), followed by the solvent was removed under vacuum and finally the residue was purified by silica gel column chromatography (100- 200 mesh size) using petroleum-ether and ethyl acetate (98:2) as an eluent to give **3ar** in 65% yield (1.150 g).



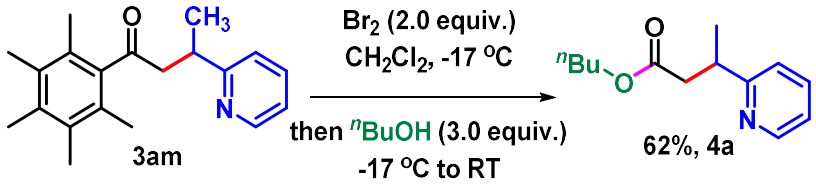
In an oven dried 100 mL ace pressure tube, cyclohexanol (1.500 g, 15.0 mmol), ketone (0.950 g, 5.0 mmol), KO^{t}Bu (1.0 equiv.), Zn-2 catalyst (7.5 mol%) and toluene (24 mL) were added in a gentle stream of argon. Then the reaction mixture was refluxed and stirred with a magnetic stirring bar at 140 °C (oil-bath temperature) for 36 h. After completion of the reaction the crude mixture was filtered through celite filter and washed with ethyl acetate (3×5 mL), followed by the solvent was removed under vacuum and finally the residue was purified by silica gel column chromatography (100- 200 mesh size) using petroleum-ether and ethyl acetate (98:2) as an eluent to give **3ba** in 89% yield (1.210 g).

11. Post-synthetic modification:

11.1 General procedure for cleavage of Pentamethylphenyl Group with Br_2:[8]

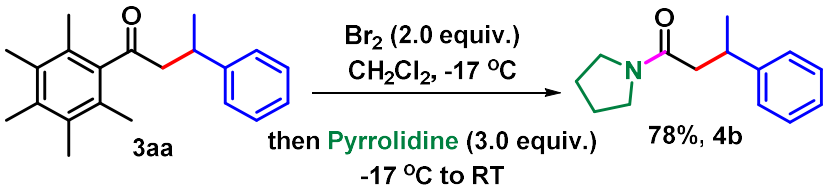
To an oven dried 10 mL round bottom flask equipped with a stirrer bar was added substrate (1.0 equiv.) and CH_2Cl_2 (2 mL) sequentially in the open atmosphere. The reaction setup was cooled to –17 °C (ice/NaCl bath). Following this, Br_2 (2.0 equiv.) was added dropwise and the mixture stirred until TLC analysis indicated complete consumption of the substrate (typically 15 min). To this, was added ^{n}BuOH, Pyrrolidine and morpholine (3.0 equiv.) dropwise at –17 °C, and the reaction warmed to RT and stirred for 16 h. The reaction was diluted with Et_2O (15 mL per mmol substrate) and H_2O (7 mL per mmol substrate). The layers were separated and the aqueous layer extracted with Et_2O (× 3). The combined organics were washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, brine, dried (Na_2SO_4) and concentrated in vacuo. Purification by column chromatography provided the corresponding ester or amide.

11.1.(a) Synthesis of Butyl 3-(pyridin-2-yl)butanoate (4a):[8]



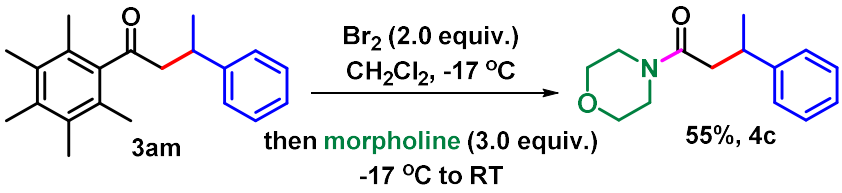
To an oven dried 10 mL round bottom flask equipped with a stirrer bar was added substrate **3am** (0.25 mmol, 1.0 equiv.) and CH_2Cl_2 (2 mL) sequentially in the open atmosphere. The reaction setup was cooled to –17 °C (ice/NaCl bath). Following this, Br_2 (0.5 mmol, 2.0 equiv.) was added dropwise and the mixture stirred until TLC analysis indicated complete consumption of the substrate (typically 15 min). To this, ^{n}BuOH (0.75 mmol, 3.0 equiv.) was added dropwise at –17 °C, and the reaction warmed to RT and stirred for 16 h. The reaction was diluted with Et_2O (15 mL per mmol substrate) and H_2O (7 mL per mmol substrate). The layers were separated and the aqueous layer extracted with Et_2O (× 3). The combined organics were washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, brine, dried (Na_2SO_4) and concentrated in vacuo. Purification by column chromatography provided the corresponding ester **4a** in 62% yield.

11.1.(b) Synthesis of 3-phenyl-1-(pyrrolidin-1-yl)butan-1-one (4b):[8]



To an oven dried 10 mL round bottom flask equipped with a stirrer bar was added substrate **3aa** (1.0 equiv.) and CH_2Cl_2 (2 mL) sequentially in the open atmosphere. The reaction setup was cooled to –17 °C (ice/NaCl bath). Following this, Br_2 (2.0 equiv.) was added dropwise and the mixture stirred until TLC analysis indicated complete consumption of the substrate (typically 15 min). To this, pyrrolidine (3.0 equiv.) was added dropwise at –17 °C, and the reaction warmed to RT and stirred for 16 h. The reaction was diluted with Et_2O (15 mL per mmol substrate) and H_2O (7 mL per mmol substrate). The layers were separated and the aqueous layer extracted with Et_2O (× 3). The combined organics were washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, brine, dried (Na_2SO_4) and concentrated in vacuo. Purification by column chromatography provided the corresponding amide **4b** in 78% yield.

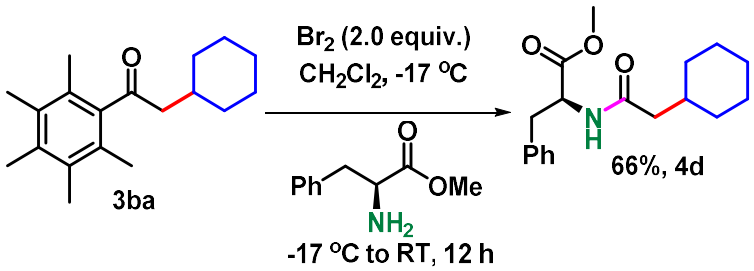
11.1.(c) Synthesis of 1-morpholino-3-phenylbutan-1-one (4c):[8]



To an oven dried 10 mL round bottom flask equipped with a stirrer bar was added substrate **3aa** (1.0 equiv.) and CH_2Cl_2 (2 mL) sequentially in the open atmosphere. The reaction setup was cooled to –17 °C (ice/NaCl bath). Following this, Br_2 (2.0 equiv.) was added dropwise and the mixture stirred until TLC analysis indicated complete consumption of the substrate

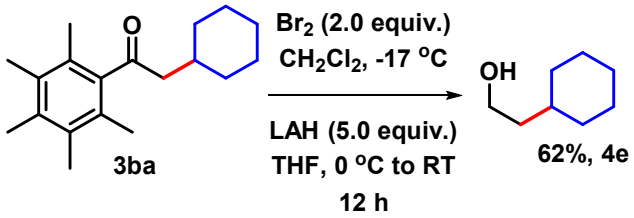
(typically 15 min). To this, morpholine (3.0 equiv.) was added dropwise at –17 °C, and the reaction warmed to RT and stirred for 16 h. The reaction was diluted with Et_2O (15 mL per mmol substrate) and H_2O (7 mL per mmol substrate). The layers were separated and the aqueous layer extracted with Et_2O (× 3). The combined organics were washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, brine, dried (Na_2SO_4) and concentrated in vacuo. Purification by column chromatography provided the corresponding amide **4c** in 55% yield.

11.1.(d) Synthesis of 4d:[9]



To an oven dried 10 mL round bottom flask equipped with a stirrer bar was added substrate **3ba** (1.0 equiv.) and CH_2Cl_2 (2 mL) sequentially in the open atmosphere. The reaction setup was cooled to –17 °C (ice/NaCl bath). Following this, Br_2 (2.0 equiv.) was added dropwise and the mixture stirred until TLC analysis indicated complete consumption of the substrate (typically 15 min). To this, acid protected phenylalanine (3.0 equiv.) was added dropwise at –17 °C, and the reaction warmed to RT and stirred for 12 h. The reaction was diluted with Et_2O (15 mL per mmol substrate) and H_2O (7 mL per mmol substrate). The layers were separated and the aqueous layer extracted with Et_2O. The combined organics were washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, brine, dried with Na_2SO_4 and concentrated in vacuo. Purification by column chromatography provided the corresponding amide **4d** in 66% yield.

11.1.(e) Synthesis of 2-cyclohexylethan-1-ol:[10]

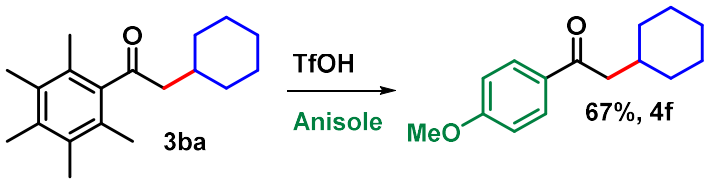


A stirred solution of ketone **3ba** (0.5 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) was cooled to –17 °C (ice/NaCl bath). Following this, Br_2 (1.0 mmol, 2 equiv.) was added dropwise and the resulting solution was stirred at –17 °C for 15 min. The reaction mixture was then warmed to RT and the majority of the volatiles were removed under a stream of nitrogen and the resulting solid was dried in vacuo. The residue was dissolved in THF (2 mL) and the resulting stirred solution was cooled to 0 °C. $LiAlH_4$ (95 mg, 2.5 mmol) was added in a single portion and the reaction mixture was warmed to RT and stirred for 12 h and then diluted with Et_2O (2 mL) and then quenched by sequential dropwise addition of H_2O, aq. NaOH and H_2O. Na_2SO_4 was added and the resulting suspension was stirred vigorously for 30 min and then filtered and concentrated in vacuo. Purification by column chromatography (Petroleum-ether:ethyl acetate, 85:15) afforded 62% of the title compound **4e** as a colourless oil.

11.2. General procedure for cleavage of Pentamethylphenyl Group with TfOH:[11]

In a 15 mL oven-dried ace pressure tube equipped with a stirring bar, substrate (1.0 equiv.), anisole (2 equiv.), and TfOH (1.2 equiv.) were poured in. The solution was then stirred for 90 min at 100 °C. The reaction was then cooled to room temperature and diluted in water (20 mL). The mixture was then extracted with CH_2Cl_2 and the organic phase was washed with sat. aq. $NaHCO_3$ (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography provided the corresponding compound.

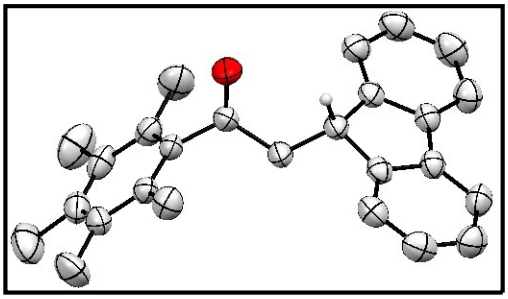
11.2. (a) Synthesis of 2-cyclohexyl-1-(4-methoxyphenyl)ethan-1-one (4f):



In a 15 mL oven-dried ace pressure tube equipped with a stirring bar, substrate **3ba** (1.0 equiv.), anisole (2 equiv.), and TfOH (1.2 equiv.) were poured in. The solution was then stirred for 90 min at 100 °C. The reaction was then cooled to room temperature and diluted in water (20 mL). The mixture was then extracted with CH_2Cl_2 and the organic phase was washed with sat. aq. $NaHCO_3$ (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography provided the corresponding **4f** compound in 67% of yield.

12. SC-XRD data of substrate 3aq and 3bk:

12.1. Crystal data of substrate 3aq:

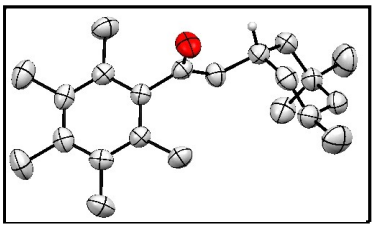


CCDC	2357526
Empirical formula	C26 H26 O
Formula weight	354.47
Temperature, T	299(2)
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a=5.3391(2)Å α=80.9430(10)° b=11.8521(5) Å β=87.1840(10)° c=15.6974(6) Å γ=84.8440(10)°
Volume, V ($Å^3$)	976.35(7)
Z	2
Density (calculated), g cm^{-3}	1.206
Absorption coefficient, μ (mm^{-1})	0.071

F (000)	380.0
Crystal size, mm^3	0.40 × 0.36 × 0.30
Theta range for data collection	1.314 to 24.999
Index ranges	$-6 \leq h \leq 6$ $-14 \leq k \leq 14$ $-18 \leq l \leq 18$
Reflections collected	3413
Independent reflections	2853
Completeness to theta	0.993
Absorption correction	none
Refinement method	SHELXL-2018/3 (Sheldrick, 2018)
Data / restraints / parameters	3413/0/249
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1320
R indices (all data)	R1 = 0.0591, wR2 = 0.1519
Largest diff. peak and hole	0.235 and -0.158 $e \cdot Å^{-3}$

Bond Distances [Å]	Bond angles [°]
O001 C002 1.209(2)	O001 C002 1.209(2)
C002 C004 1.504(2)	C002 C004 1.504(2)
C002 C005 1.505(2)	C002 C005 1.505(2)
C003 C00C 1.385(2)	C003 C00C 1.385(2)
C003 C009 1.397(2)	C003 C009 1.397(2)
C003 C006 1.513(2)	C003 C006 1.513(2)
C004 C007 1.394(2)	C004 C007 1.394(2)
C004 C00E 1.398(2)	C004 C00E 1.398(2)
C005 C006 1.539(2)	C005 C006 1.539(2)
C006 C00A 1.512(2)	C006 C00A 1.512(2)
C007 C00B 1.395(2)	C007 C00B 1.395(2)
C007 C00G 1.509(2)	C007 C00G 1.509(2)
C008 C00J 1.390(3)	C008 C00J 1.390(3)
C008 C00A 1.400(2)	C008 C00A 1.400(2)
C008 C009 1.463(2)	C008 C009 1.463(2)
C009 C00I 1.387(3)	C009 C00I 1.387(3)
C00A C00D 1.381(3)	C00A C00D 1.381(3)
C00B C00H 1.391(3)	C00B C00H 1.391(3)
C00B C00P 1.518(3)	C00B C00P 1.518(3)
C00C C00M 1.383(3)	C00C C00M 1.383(3)
C00D C00K 1.385(3)	C00D C00K 1.385(3)
C00E C00F 1.406(3)	C00E C00F 1.406(3)
C00E C00O 1.505(3)	C00E C00O 1.505(3)
C00F C00H 1.398(3)	C00F C00H 1.398(3)
C00F C00Q 1.516(3)	C00F C00Q 1.516(3)
C00H C00R 1.518(3)	C00H C00R 1.518(3)
C00I C00L 1.379(3)	C00I C00L 1.379(3)
C00J C00N 1.381(3)	C00J C00N 1.381(3)
C00K C00N 1.378(3)	C00K C00N 1.378(3)
C00L C00M 1.380(3)	C00L C00M 1.380(3)

12.2 Crystal data of substrate 3bk:

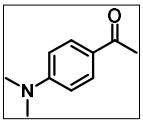


CCDC	2357527
Empirical formula	C22 H34O
Formula weight	314.49
Temperature, T	297(2)
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a=11.736(4)Å α=90° b=6.162(2) Å β=92.424(11)° c=27.346(10) Å γ=90°
Volume, V ($Å^3$)	1976.0(13)
Z	4
Density (calculated), g cm^{-3}	1.057
Absorption coefficient, μ (mm^{-1})	0.062
F (000)	696.0
Crystal size, mm^3	0.42 × 0.36 × 0.28
Theta range for data collection	1.491 to 25.000
Index ranges	-13 ≤ h ≤ 13 -7 ≤ k ≤ 7 -32 ≤ l ≤ 32
Reflections collected	3487
Independent reflections	1906
Completeness to theta	1.000
Absorption correction	none
Refinement method	SHELXL-2018/3 (Sheldrick, 2018)
Data / restraints / parameters	3487/0/216
Goodness-of-fit on F^2	1.162
Final R indices [I>2sigma(I)]	R1 = 0.0792, wR2 = 0.1902
R indices (all data)	R1 = 0.1639, wR2 = 0.2566
Largest diff. peak and hole	0.265 and -0.212 e·$Å^{-3}$
The R indices of structural refinement for 3bk is high due to the quality of crystal	

Bond Distances [Å]	Bond angles [°]
O001 C004 1.210(4)	C003 C002 C005 121.3(3)
C002 C003 1.399(5)	C003 C002 C004 119.9(3)
C002 C005 1.407(5)	C005 C002 C004 118.7(3)
C002 C004 1.503(5)	C002 C003 C006 119.2(3)
C003 C006 1.400(5)	C002 C003 C00C 120.2(3)
C003 C00C 1.509(5)	C006 C003 C00C 120.6(3)
C004 C007 1.514(5)	O001 C004 C002 121.3(3)

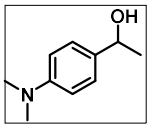
C005 C009 1.401(5) C005 C00H 1.514(5) C006 C00A 1.406(5) C006 C00K 1.512(5) C007 C008 1.531(5) C008 C00E 1.520(5) C008 C00F 1.543(5) C009 C00A 1.400(5) C009 C00J 1.522(5) C00A C00L 1.513(5) C00B C00G 1.529(5) C00B C00F 1.530(5) C00B C00I 1.532(5) C00B C00M 1.534(6) C00D C00E 1.519(6) C00D C00G 1.530(6) C00D C00N 1.531(6)	O001 C004 C007 121.5(3) C002 C004 C007 117.2(3) C009 C005 C002 119.0(3) C009 C005 C00H 120.9(3) C002 C005 C00H 120.1(3) C003 C006 C00A 120.0(3) C003 C006 C00K 118.6(3) C00A C006 C00K 121.3(4) C004 C007 C008 114.4(3) C00E C008 C007 112.5(3) C00E C008 C00F 110.0(3) C007 C008 C00F 115.2(3) C00A C009 C005 120.1(3) C00A C009 C00J 121.0(4) C005 C009 C00J 118.9(4) C009 C00A C006 120.3(3) C009 C00A C00L 119.6(4) C006 C00A C00L 120.1(4) C00G C00B C00F 109.2(3) C00G C00B C00I 110.5(3) C00F C00B C00I 112.1(3) C00G C00B C00M 108.9(3) C00F C00B C00M 108.3(4) C00I C00B C00M 107.8(4) C00E C00D C00G 109.5(3) C00E C00D C00N 111.5(4) C00G C00D C00N 111.3(4) C00D C00E C008 114.0(3) C00B C00F C008 117.0(3) C00B C00G C00D 114.6(3)

13. Characterization data:



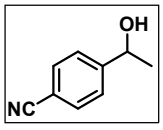
1-(4-(dimethylamino)phenyl)ethan-1-one (2ae′):[1a] Isolated as white solid, Yield: 1.06 g (65%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.06 (s, 6H), 2.51 (s, 3H).

1-(4-(dimethylamino)phenyl)ethan-1-ol (2ae):[22] Isolated as colorless liquid, Yield: 359 mg (87%).



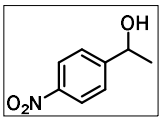
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.81 (q, *J* = 6.4 Hz, 1H), 2.93 (s, 6H), 1.76 (brs, 1H), 1.47 (d, *J* = 6.4 Hz, 3H).

4-(1-hydroxyethyl)benzonitrile (2ai):[26] Isolated as colourless liquid, Yield: 308 mg (85%).

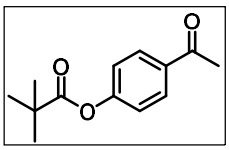


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.92 (q, *J* = 7.3, 5.6 Hz, 1H), 2.59 (s, 1H), 1.46 (d, *J* = 6.5 Hz, 3H).

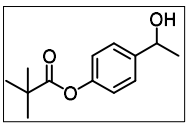
1-(4-nitrophenyl)ethan-1-ol (2aj):[26] Isolated as light yellow oil, Yield: 338 mg (82**%**). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 4.99 (q, *J* = 7.0 Hz, 6.3 Hz, 1H), 2.48 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H).



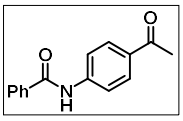
4-acetylphenyl pivalate (2ak′):[23] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 10:90 (v/v)). Yield: 1.54 g (70%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 2.60 (s, 3H), 1.37 (s, 9H).



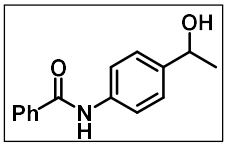
4-(1-hydroxyethyl)phenyl pivalate (2ak): Isolated as colorless liquid, Yield: 455 mg (82%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 4.87 (q, *J* = 6.0 Hz, 1H), 1.47 (d, *J* = 6.5 Hz, 3H), 1.35 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 177.3, 150.4, 143.3, 126.5, 121.5, 70.0, 39.2, 27.2, 25.3. **HRMS (ESI+):** m/z calcd. for $C_{13}H_{18}O_3$ $[M+Na]^+$: 245.1154; Found: 245.1130.



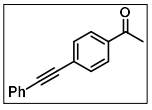
N-(4-acetylphenyl)benzamide (2al′):[24] Isolated as white solid, Yield: 1.793 g (75%).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 8.7 Hz, 3H), 7.90 – 7.88 (m, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 2.60 (s, 3H).



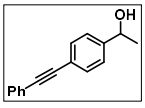
N-(4-(1-hydroxyethyl)phenyl)benzamide (2al):[25] Isolated as white solid, Yield: 482 mg (80%).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.82 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 4.91 (q, *J* = 6.0 Hz, 1H), 1.82 (s, 1H), 1.50 (d, *J* = 6.5 Hz, 3H).



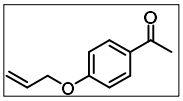
1-(4-(phenylethynyl)phenyl)ethan-1-one (2aw′):[12] Isolated as a white amorphous solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 5:95 (v/v)). Yield: 858.0 mg (78%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.55 (m, 2H), 7.38 – 7.36 (m, 3H), 2.62 (s, 3H).

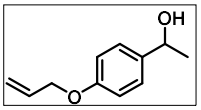


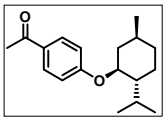
1-(4-(phenylethynyl)phenyl)ethan-1-ol (2aw):[13] Isolated as a white amorphous solid. Yield: 472.0 mg (85%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.50 (m, 4H), 7.37 – 7.33 (m, 5H), 4.89 (q, *J* = 6.3 Hz, 1H), 1.96 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H).

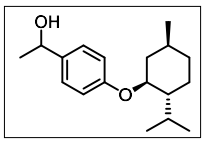


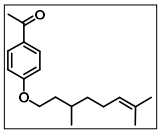
1-(4-(allyloxy)phenyl)ethan-1-one (2ax′):[14] Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 10:90 (v/v)). Yield: 648.0 mg (92%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.81 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 5.99 – 5.89 (m, 1H), 5.32 (d, *J* = 17.3 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 4.48 (d, *J* = 4.28 Hz, 2H), 2.43 (s, 3H).

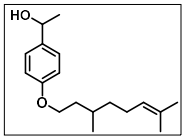


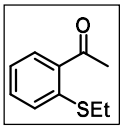
1-(4-(allyloxy)phenyl)ethan-1-ol (2ax):[15] Isolated as a colourless liquid. Yield: 387.0 mg (87%).  **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.19 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.02 – 5.92 (m, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 4.75 (q, *J* = 6.4 Hz, 1H), 4.44 (d, *J* = 5.3 Hz, 2H), 1.96 (brs, 1H), 1.38 (d, *J* = 6.4 Hz, 3H).

1-(4-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)ethan-1-one (2ay′):[3]  Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 3:97 (v/v)). Yield: 844.0 mg (22%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.84 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.66 (q, *J* = 2.8 Hz, 1H), 2.47 (s, 3H), 2.05 – 1.98 (m, 1H), 1.75 – 1.66 (m, 2H), 1.62 – 1.44 (m, 4H), 1.03- 0.97 (m, 2H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 6.7 Hz, 6H).

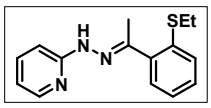
1-(4-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)ethan-1-ol (2ay):[16] Isolated as a colourless liquid. Yield: 552.0 mg (80%).  **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.19 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.76 (q, *J* = 6.4 Hz, 1H), 4.54 (q, *J* = 2.8 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.72 – 1.49 (m, 5H), 1.40 (d, *J* = 6.4 Hz, 3H), 0.88 – 0.83 (m, 6H), 0.79 (d, *J* = 7.3 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H).

1-(4-((3,7-dimethyloct-6-en-1-yl)oxy)phenyl)ethan-1-one (2az′):[4] Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 10:90 (v/v)). Yield: 921.0 mg (48%).  **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.10 (t, *J* = 7.0 Hz, 1H), 4.09 – 4.02 (m, 2H), 2.55 (s, 3H), 2.07 – 1.95 (m, 2H), 1.90 – 1.82 (m, 1H), 1.69 (s, 3H), 1.61 (s, 3H), 1.45 – 1.35 (m, 1H), 1.28 – 1.18 (m, 2H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.84 (m, 1H).

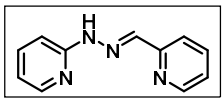
1-(4-((3,7-dimethyloct-6-en-1-yl)oxy)phenyl)ethan-1-one (2az):[16] Isolated as a colourless liquid. Yield: 593.0 mg (86%).  **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.13 – 5.07 (m, 1H), 4.83 (q, *J* = 6.4 Hz, 1H), 4.03 – 3.94 (m, 2H), 2.09 – 1.93 (m, 2H), 1.87 – 1.78 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.46 (d, *J* = 6.4 Hz, 3H), 1.44 – 1.34 (m, 1H), 1.28 – 1.18 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.93 – 0.84 (m, 1H).

1-(2-(ethylthio)phenyl)ethan-1-one:[6] Isolated as a yellow liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 675.0 mg (75%).  **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.83 (q, *J* = 7.4 Hz, 2H), 2.52 (s, 3H), 1.27 (t, *J* = 7.4 Hz, 3H).

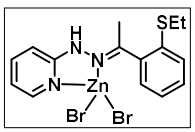
(E)-2-(2-(1-(2-(ethylthio)phenyl)ethylidene)hydrazineyl)pyridine (L-5): Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 35:65 (v/v)). Yield: 423.0 mg (78%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 8.02 (d, *J* = 4.8 Hz, 1H), 7.66 (s, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.71 – 6.67 (m, 1H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 1.31 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.9, 147.6, 145.7, 138.0, 135.6, 135.1, 129.7, 128.7, 127.9, 126.6, 115.3, 107.3, 27.1, 24.2, 14.3. **HRMS (ESI+):** m/z calcd. for $C_{15}H_{17}N_3S$ $[M+H]^+$: 272.1221; Found: 272.1233.



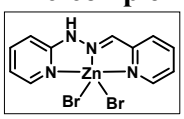
(E)-2-((2-(pyridin-2-yl)hydrazineylidene)methyl)pyridine (L-6): Isolated as a faded yellow solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 50:50 (v/v)). Yield: 345.0 mg (87%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.08 (s, 1H), 8.50 (d, *J* = 4.6 Hz, 1H), 8.12 (d, *J* = 4.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.78 – 6.74 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 156.5, 154.3, 149.5, 147.8, 139.5, 138.3, 136.4, 123.1, 119.9, 116.5, 107.8. **HRMS (ESI+):** m/z calcd. for $C_{11}H_{10}N_4$ $[M+H]^+$: 199.0984; Found: 199.0989.



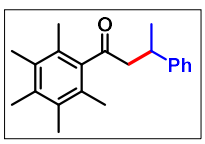
Zinc complex (Zn-5): Obtained as white powder**.** Yield: 342.0 mg (69%). **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.67 (s, 1H), 8.07 (s, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.28 – 7.22 (m, 2H), 7.16 – 7.12 (m, 1H), 6.72 (t, *J* = 5.5 Hz, 1H), 2.87 (q, *J* = 6.9 Hz, 2H), 2.22 (s, 3H), 1.14 (t, J = 7.14 Hz, 3H). **^{13}C NMR (150 MHz, DMSO)** δ 158.9, 157.7, 147.4, 139.5, 138.0, 135.4, 128.6, 128.2, 127.0, 124.7, 115.3, 107.0, 26.4, 16.9, 13.7. **HRMS (ESI+):** m/z calcd. for $C_{15}H_{17}N_3SZnBr_2$ $[M-Br]^+$: 415.9598; Found: 415.9610.



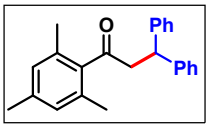
Zinc complex (Zn-6): Obtained as light-yellow powder**.** Yield: 305.0 mg (72%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 12.90 (s, 1H), 8.58 (s, 1H), 8.30 (s, 1H), 8.18 (s, 1H), 8.08 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.63 (s, 1H), 7.15 – 6.97 (m, 2H). **^{13}C NMR (125 MHz, DMSO)** δ 150.9, 148.6, 146.7, 146.0, 141.2, 140.5, 134.2, 126.2, 125.1, 117.8, 109.8. **HRMS (ESI+):** m/z calcd. for $C_{11}H_{10}N_4ZnBr_2$ $[M-Br]^+$: 342.9360; Found: 342.9365.



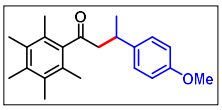
1-(2,3,4,5,6-pentamethylphenyl)-3-phenylbutan-1-one (3aa):[11] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 138.0 mg (94%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.30 – 7.24 (m, 4H), 7.20 – 7.17 (m, 1H), 3.57 – 3.51 (m, 1H), 3.04 – 2.91 (m, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 1.99 (s, 6H), 1.38 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.3, 146.8, 140.6, 135.5, 133.2, 128.6, 127.5, 127.2, 126.3, 53.9, 34.3, 22.5, 17.0, 16.8, 16.0.



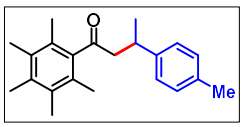
1-mesityl-3,3-diphenylpropan-1-one (3ab):[11] Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 125.0 mg (76%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.22 – 7.15 (m, 8H), 7.10 – 7.07 (m, 2H), 6.68 (s, 2H), 4.73 (t, *J* = 7.2 Hz, 1H), 3.41 (d, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 1.82 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 207.9, 144.2, 139.3, 138.6, 133.1, 128.7, 128.6, 128.1, 126.6, 51.1, 45.5, 21.1, 19.0.



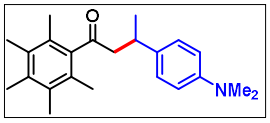
3-(4-methoxyphenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3ac):[17] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 4:96 (v/v)). Yield: 133.0 mg (82%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 3.68 (s, 3H), 3.44 – 3.37 (m, 1H), 2.92 – 2.79 (m, 2H), 2.12 (s, 3H), 2.06 (s, 6H), 1.89 (s, 6H), 1.26 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.3, 158.0, 140.6, 138.9, 135.4, 133.1, 128.0, 127.4, 113.9, 55.3, 54.1, 33.5, 22.6, 17.0, 16.7, 16.0.



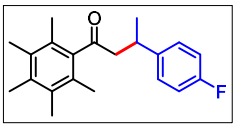
1-(2,3,4,5,6-pentamethylphenyl)-3-(p-tolyl)butan-1-one (3ad):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 128.0 mg (83%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.19 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 3.58 – 3.53 (m, 1H), 3.07 – 2.96 (m, 2H), 2.36 (s, 3H), 2.26 (s, 3H), 2.20 (s, 6H), 2.05 (s, 6H), 1.41 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 210.4, 143.8, 140.6, 135.7, 135.5, 133.1, 129.2, 127.5, 127.0, 53.9, 33.9, 22.7, 21.1, 17.0, 16.8, 16.0.



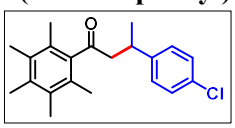
3-(4-(dimethylamino)phenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3ae): Isolated as light yellow solid by column chromatography (SiO2; ethyl acetate:petroleum-ether, 5:95(v/v)). Yield: 128.0 mg (76%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.13 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.51 – 3.43 (m, 1H), 3.09 – 2.94 (m, 2H), 2.92 (s,6H), 2.23 (s, 3H), 2.17 (s, 6H), 2.02 (s, 6H), 1.36 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 210.7, 149.4, 140.7, 135.4, 135.1, 133.1, 127.7, 127.5, 113.1, 54.2, 41.0, 33.3, 22.7, 17.0, 16.8, 16.0. **HRMS (ESI+):** m/z calcd. for $C_{23}H_{32}NO$ $[M+H]^+$: 338.2484; Found: 338.2476.



3-(4-fluorophenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3af):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 106.0 mg (68%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.15 – 7.13 (m, 2H), 6.91 – 6.88 (m, 2H), 3.49 – 3.43 (m, 1H), 2.92 – 2.81 (m, 2H), 2.14 (s, 3H), 2.08 (s, 6H), 1.90 (s, 6H), 1.28 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.1, 161.5 (*J* = 242.2 Hz), 142.4 (*J* = 3.1 Hz), 140.4, 135.6, 133.2, 128.6 (*J* = 7.76 Hz), 127.4, 115.3 (*J* = 20.9 Hz), 54.1, 33.6, 22.6, 17.0, 16.8, 16.0. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -117.2.

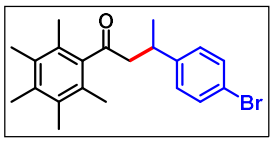


3-(4-chlorophenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3ag): Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 149.0 mg (91%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 3.56 – 3.47 (m, 1H), 3.00 – 2.87 (m, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 1.97 (s, 6H), 1.34 (d, *J* = 7.0 Hz, 3H). **^{13}C**

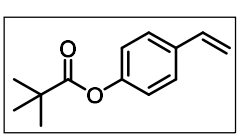


NMR (125 MHz, $CDCl_3$) δ 209.9, 145.2, 140.3, 135.6, 1332, 131.9, 128.6, 128.6, 127.4, 53.8, 33.8, 22.4, 17.0, 16.8, 16.0. **HRMS (ESI+):** m/z calcd. for $C_{21}H_{25}ClO$ $[M+H]^+$: 329.1672; Found: 329.1674.

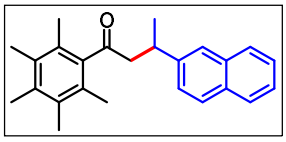
3-(4-bromophenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3ah):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 132.0 mg (71%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.57 – 3.46 (m, 1H), 3.00 – 2.87 (m, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 1.97 (s, 6H), 1.34 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 209.9, 145.7, 140., 135.6, 133.2, 131.6, 129.0, 127.4, 119.9, 53.7, 33.9, 22.4, 17.0, 16.8, 16.0.



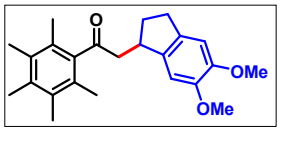
4-vinylphenyl pivalate (3ak): Isolated as colourless liquid by column chromatography (SiO2; hexane). Yield: 22 mg (22%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 18.3 Hz, 1H), 5.24 (d, *J* = 11.6 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 150.9, 136.1, 135.3, 127.2, 121.7, 114.0, 39.2, 27.3. **HRMS (ESI+):** m/z calcd. for $C_{13}H_{16}O_2$ $[M+H]^+$: 205.1229; Found: 205.1209.



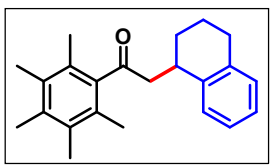
3-(naphthalen-2-yl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3am):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 157.0 mg (91%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.83 – 7.80 (m, 3H), 7.70 (s, 1H), 7.49 – 7.42 (m, 3H), 3.77 – 3.71 (m, 1H), 3.18 – 3.05 (m, 2H), 2.24 (s, 3H), 2.18 (s, 6H), 2.03 (s, 6H), 1.50 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 210.2, 144.2, 140.5, 135.5, 133.7, 133.2, 132.3, 128.2, 127.7, 127.7, 127.5, 126.1, 125.9, 125.4, 125.3, 53.7, 34.5, 22.6, 17.1, 16.8, 16.0.



2-(5,6-dimethoxy-2,3-dihydro-1H-inden-1-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3an): Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 5:95 (v/v)). Yield: 141.0 mg (77%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 6.79 (d, *J* = 12.2 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.78 – 3.68 (m, 1H), 3.14 – 3.09 (m, 1H), 2.91 – 2.81 (m, 3H), 2.61 – 2.54 (m, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.12 (s, 6H), 1.81 – 1.74 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.2, 148.4, 148.1, 140.6, 138.0, 135.6, 135.6, 133.3, 127.5, 107.9, 107.5, 56.2, 56.1, 51.9, 39.8, 33.5, 31.5, 17.3, 16.8, 16.1. **HRMS (ESI+):** m/z calcd. for $C_{24}H_{30}O_3$ $[M+Na]^+$: 389.2093; Found: 389.2087.

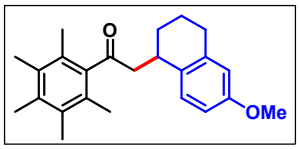


1-(2,3,4,5,6-pentamethylphenyl)-2-(1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (3ao):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 130.0 mg (81%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.16 (d, *J* = 7.1 Hz, 1H), 7.11 – 7.04 (m, 3H), 3.67 – 3.63 (m, 1H), 3.01 (d, *J* = 6.2 Hz, 2H), 2.78 –

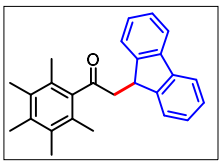


2.75 (m, 2H), 2.22 (s, 3H), 2.17 (s, 6H), 2.12 (s, 6H), 2.09 – 2.04 (m, 1H), 1.86 – 1.78 (m, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.6, 140.5, 140.3, 137.3, 135.5, 133.2, 129.3, 128.5, 127.4, 125.9, 125.8, 53.6, 32.3, 29.7, 28.68, 19.8, 17.1, 16.8, 16.0.

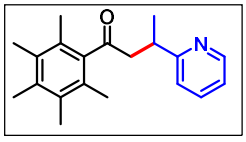
2-(6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3ap):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 5:95 (v/v)). Yield: 136.0 mg (78%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.13 (d, *J* = 8.5 Hz, 1H), 6.73 – 6.72 (m, 1H), 6.63 (s, 1H), 3.80 (s, 3H), 3.64 – 3.61 (m, 1H), 3.02 (d, *J* = 6.3 Hz, 2H), 2.79 – 2.78 (m, 2H), 2.25 (s, 3H), 2.21 (s, 6H), 2.15 (s, 6H), 2.12 – 2.08 (m, 1H), 1.86 – 1.80 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 210.8, 157.6, 140.6, 138.5, 135.5, 133.2, 132.4, 129.5, 127.4, 113.7, 112.4, 55.3, 53.7, 31.6, 30.0, 28.9, 19.8, 17.2, 16.8, 16.1.



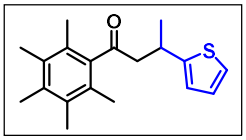
2-(9H-fluoren-9-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3aq):[11] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 115.0 mg (65%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 4.70 (t, *J* = 6.3 Hz, 1H), 3.19 (d, *J* = 6.4 Hz, 2H), 2.21 (s, 3H), 2.16 (s, 6H), 2.14 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.4, 147.2, 141.0, 139.9, 135.7, 133.3, 127.5, 127.4, 127.3, 125.0, 119.9, 50.5, 42.2, 17.3, 16.8, 16.0.



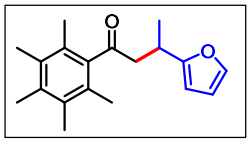
1-(2,3,4,5,6-pentamethylphenyl)-3-(pyridin-2-yl)butan-1-one (3ar):[18] Isolated as a light yellow solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 10:90 (v/v)). Yield: 124.0 mg (84%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.51 (d, *J* = 4.7 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.28 – 7.25 (m, 1H), 7.10 – 7.07 (m, 1H), 3.66 – 3.59 (m, 1H), 3.41 – 3.35 (m, 1H), 2.98 – 2.93 (m, 1H), 2.20 (s, 3H), 2.14 (s, 6H), 2.00 (s, 6H), 1.38 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.6, 165.2, 149.2, 140.4, 136.5, 135.3, 133.0, 127.5, 122.8, 121.4, 52.0, 36.3, 21.2, 16.9, 16.7, 16.0.



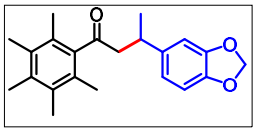
1-(2,3,4,5,6-pentamethylphenyl)-3-(thiophen-2-yl)butan-1-one (3as):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 132.0 mg (88%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.11 (d, *J* = 5.0 Hz, 1H), 6.91 – 6.88 (m, 2H), 3.90 – 3.83 (m, 1H), 3.10 – 2.91 (m, 2H), 2.21 (s, 3H), 2.16 (s, 6H), 2.02 (s, 6H), 1.46 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 209.6, 150.8, 140.2, 135.6, 133.2, 127.5, 126.6, 123.2, 122.9, 54.7, 29.9, 23.3, 17.0, 16.8, 16.0.



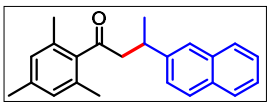
3-(furan-2-yl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3at):[18] Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 92.0 mg (65%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.29 (s, 1H), 6.27 (s, 1H), 6.04 – 6.03 (m, 1H), 3.65 – 3.58 (m, 1H), 3.16 – 3.11 (m, 1H), 2.84 – 2.79 (m, 1H), 2.22 (s, 3H), 2.17 (s, 6H), 2.06 (s, 6H), 1.39 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 209.8, 159.3, 140.9, 140.4, 135.6, 133.2, 127.5, 110.1, 104.1, 51.1, 28.1, 19.3, 17.0, 16.8, 16.0.



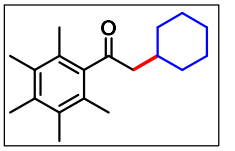
3-(benzo[d][1,3]dioxol-5-yl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3au):[11] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 3:97 (v/v)). Yield: 134.0 mg (79%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 6.73 – 6.71 (m, 3H), 5.89 (s, 2H), 3.50 – 3.43 (m, 1H), 2.99 – 2.85 (m, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 2.00 (s, 6H), 1.33 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.2, 147.7, 145.8, 140.8, 140.5, 135.4, 133.1, 127.4, 120.0, 108.2, 107.6, 100.9, 54.1, 34.1, 22.6, 17.0, 16.7, 16.0.



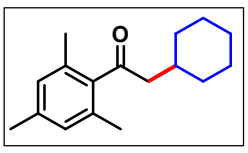
1-mesityl-3-(naphthalen-2-yl)butan-1-one (3av):[11] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 114.0 mg (72%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.69 (t, *J* = 7.5 Hz, 3H), 7.58 (s, 1H), 7.37 – 7.29 (m, 3H), 6.70 (s, 2H), 3.65 – 3.58 (m, 1H), 3.08 – 2.94 (m, 2H), 2.16 (s, 3H), 1.98 (s, 6H), 1.36 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 209.1, 144.0, 139.6, 138.4, 133.7, 132.7, 132.4, 128.7, 128.3, 127.7, 127.7, 126.1, 125.9, 125.4, 125.3, 53.1, 34.7, 22.4, 21.1, 19.1.



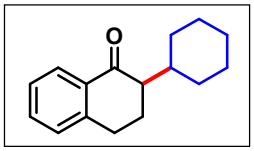
2-cyclohexyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3ba):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 131.0 mg (96%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 2.59 (d, *J* = 6.4 Hz, 2H), 2.25 (s, 3H), 2.20 (s, 6H), 2.12 (s, 6H), 2.07 – 2.06 (m, 1H), 1.90 – 1.87 (m, 2H), 1.74 – 1.69 (m, 3H), 1.41 – 1.34 (m, 2H), 1.23 – 1.16 (m, 1H), 1.04 – 0.98 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.2, 141.0, 135.4, 133.2, 127.4, 53.3, 33.5, 32.5, 26.5, 26.3, 17.1, 16.8, 16.1.



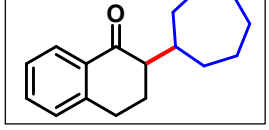
2-cyclohexyl-1-mesitylethan-1-one (3bb):[11] Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 104.0 mg (85%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.82 (s, 2H), 2.58 (d, *J* = 6.5 Hz, 2H), 2.27 (s, 3H), 2.19 (s, 6H), 2.07 – 1.97 (m, 1H), 1.84 – 1.80 (m, 2H), 1.72 – 1.65 (m, 3H), 1.39 – 1.29 (m, 2H), 1.22 – 1.10 (m, 1H), 1.03 – 0.93 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.1, 140.1, 138.2, 132.6, 128.6, 52.6, 33.5, 32.8, 26.4, 26.3, 21.1, 19.2.



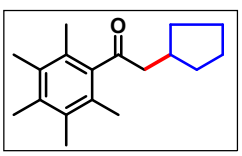
2-cyclohexyl-3,4-dihydronaphthalen-1(2H)-one (3bc):[19] Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 86.0 mg (75%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 2.97 – 2.92 (m, 1H), 2.87 – 2.81 (m, 1H), 2.26 – 2.22 (m, 1H), 2.09 – 2.06 (m, 2H), 1.96 – 1.88 (m, 1H), 1.70 – 1.64 (m, 3H), 1.51 – 1.48 (m, 1H), 1.28 – 1.15 (m, 4H), 1.11 – 1.05 (m, 1H), 1.00 – 0.91 (m, 1H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ 200.1, 144.1, 133.2, 133.1, 128.7, 127.6, 126.6, 53.4, 36.3, 31.3, 29.3, 28.5, 26.8, 26.6, 26.5, 24.4.



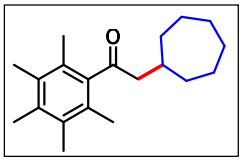
2-cycloheptyl-3,4-dihydronaphthalen-1(2H)-one (3bd): Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 82.0 mg (68%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 3.03 – 2.91 (m, 2H), 2.45 – 2.37 (m, 2H), 2.19 – 2.14 (m, 1H), 2.01 – 1.93 (m, 1H), 1.72 – 1.66 (m, 3H), 1.60 – 1.59 (m, 1H), 1.56 – 1.49 (m, 7H), 1.29 – 1.23 (m, 1H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ 200.1, 144.1, 133.3, 133.1, 128.7, 127.6, 126.7, 55.0, 37.9, 33.2, 30.8, 29.3, 28.5, 27.9, 27.5, 27.4, 24.2. **HRMS (ESI+):** m/z calcd. for $C_{17}H_{22}O$ $[M+H]^+$: 243.1749; Found: 243.1750.



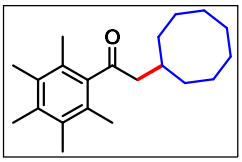
2-cyclopentyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bf):[18] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 120.0 mg (93%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.72 (d, *J* = 6.8 Hz, 2H), 2.43 – 2.37 (m, 1H), 2.22 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H), 1.98 – 1.92 (m, 2H), 1.64 – 1.57 (m, 4H), 1.19 – 1.14 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.9, 141.0, 135.3, 133.1, 127.4, 52.1, 34.8, 32.9, 25.1, 17.2, 16.8, 16.1.



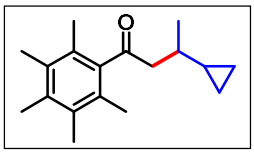
2-cycloheptyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bg):[19] Isolated as a gummy liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 132.0 mg (92%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.62 (d, *J* = 6.5 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 6H), 2.10 (s, 6H), 1.85 – 1.82 (m, 2H), 1.64 – 1.50 (m, 9H), 1.29 – 1.23 (m, 2H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.3, 140.9, 135.3, 133.1, 127.4, 54.1, 35.0, 34.2, 28.4, 26.5, 17.1, 16.8, 16.0.



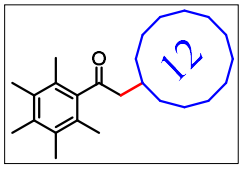
2-cyclooctyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bh):[17] Isolated as a viscous liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 50:50 (v/v)). Yield: 144.0 mg (96%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.61 (d, *J* = 6.4 Hz, 2H), 2.33 – 2.22 (m, 1H), 2.22 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H), 1.77 – 1.72 (m, 2H), 1.69 – 1.66 (m, 2H), 1.61 – 1.52 (m, 8H), 1.39 – 1.33 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.4, 140.9, 135.3, 133.1, 127.4, 54.1, 32.6, 32.2, 27.3, 26.3, 25.4, 17.2, 16.8, 16.1.



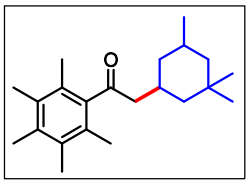
3-cyclopropyl-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3bi):[20] Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 50:50 (v/v)). Yield: 117.0 mg (91%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 2.93 – 2.89 (m, 1H), 2.71 – 2.66 (m, 1H), 2.27 (s, 3H), 2.22 (s, 6H), 2.15 (s, 6H), 1.54 – 1.49 (m, 1H), 1.16 (d, *J* = 6.7 Hz, 3H), 0.70 – 0.64 (m, 1H), 0.50 – 0.42 (m, 2H), 0.24 – 0.17 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 211.3, 140.9, 135.3, 133.1, 127.4, 53.0, 33.5, 20.0, 18.2, 17.1, 16.8, 16.1, 4.3, 4.1.



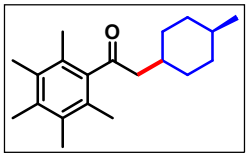
2-cyclododecyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bj):[17] Isolated as a gummy liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 50:50 (v/v)). Yield: 93.0 mg (52%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 2.53 (d, *J* = 6.3 Hz, 2H), 2.15 (s, 4H), 2.11 (s, 6H), 2.03 (s, 6H), 1.44 – 1.27 (m, 22H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 211.7, 141.0, 135.3, 133.2, 127.4, 51.3, 29.4, 29.2, 29.1, 24.8, 24.3, 24.2, 24.0, 23.5, 23.4, 23.3, 21.9, 21.0, 17.2, 16.8, 16.1.



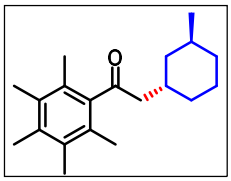
1-(2,3,4,5,6-pentamethylphenyl)-2-(3,3,5-trimethylcyclohexyl)ethan-1-one (3bk): Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 101.0 mg (64%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.73 – 2.53 (m, 2H), 2.51 – 2.45 (m, 1H), 2.15 (s, 3H), 2.11 (s, 6H), 2.03 (s, 6H), 1.73 – 1.64 (m, 1H), 1.43 – 1.37 (m, 2H), 1.29 – 1.23 (m, 2H), 1.09 – 1.06 (m, 1H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.87 (s, 3H), 0.82 (s, 3H), 0.79 – 0.69 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.3, 141.0, 135.4, 133.2, 127.5, 52.1, 47.2, 44.6, 38.8, 32.3, 31.2, 30.9, 26.4, 25.5, 22.4, 17.2, 16.8, 16.0. **HRMS (ESI+):** m/z calcd. for $C_{22}H_{34}O$ $[M+H]^+$: 315.2688; Found: 315.2673.



2-((1s,4s)-4-methylcyclohexyl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bl):[18] Isolated as a off white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 113.0 mg (79%), d.r. = 80:20. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.67 (d, *J* = 6.6 Hz, 2H), 2.35 – 2.31 (m, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H), 1.97 – 1.86 (m, 1H), 1.74 – 1.60 (m, 2H), 1.58 – 1.52 (m, 2H), 1.48 – 1.33 (m, 2H), 1.21 – 1.18 (m, 1H), 1.06 – 0.97 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.4, 141.0, 135.4, 133.2, 127.42, 53.3, 50.2, 35.2, 33.4, 30.9, 29.2, 17.1, 16.8, 16.1.

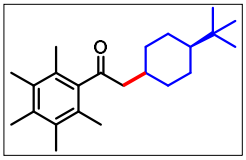


2-((1S,3S)-3-methylcyclohexyl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bm):[8]



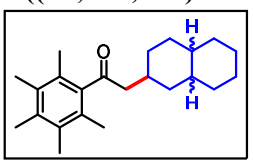
Isolated as a off white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 116.0 mg (81%), d.r. = 80:20. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 2.68 (dd, *J* = 6.6, 1.3 Hz, 2H), 2.53 – 2.44 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.12 (s, 6H), 1.72 – 1.69 (m, 2H), 1.59 – 1.54 (m, 2H), 1.50 – 1.32 (m, 4H), 1.13 (q, *J* = 8.4 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.3, 141.1, 135.4, 133.2, 127.4, 50.7, 39.4, 33.9, 31.7, 27.7, 27.4, 21.2, 21.0, 17.1, 16.8, 16.1.

2-((1s,4s)-4-(tert-butyl)cyclohexyl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bn):[18]



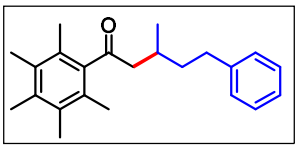
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.75 (d, *J* = 6.6 Hz, 1H), 2.57 – 2.56 (m, 1H), 2.24 (s, 3H), 2.20 (s, 6H), 2.12 (s, 6H), 1.74 (d, *J* = 12.1 Hz, 2H), 1.61 – 1.56 (m, 4H), 1.10 – 1.04 (m, 2H), 1.01 – 0.96 (m, 1H), 0.83 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.4, 141.1, 135.4, 133.3, 127.4, 48.4, 47.8, 32.7, 31.0, 27.6, 26.9, 22.1, 17.1, 16.8, 16.1.

2-((2S,4aS,8aS)-decahydronaphthalen-2-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3bo):



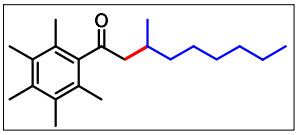
Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 135.0 mg (83%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.56 – 2.44 (m, 2H), 2.15 (s, 3H), 2.10 (s, 6H), 2.02 (s, 6H), 1.87 – 1.85 (m, 1H), 1.66 – 1.53 (m, 6H), 1.49 – 1.38 (m, 3H), 1.36 – 1.23 (m, 3H), 1.22 – 1.10 (m, 3H), 0.99 – 0.84 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.3, 141.0, 135.3, 133.2, 127.5, 53.6, 48.5, 43.8, 38.3, 38.1, 36.1, 35.7, 33.4, 32.8, 32.3, 30.4, 29.0, 27.1, 25.9, 21.1, 17.2, 16.8, 16.1. **HRMS (ESI+):** m/z calcd. for $C_{23}H_{34}O$ $[M+Na]^+$: 349.2507; Found: 349.2513.

3-methyl-1-(2,3,4,5,6-pentamethylphenyl)-5-phenylpentan-1-one (3bp):[8]



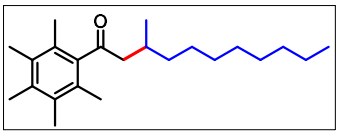
Isolated as a viscous liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 132.0 mg (82%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.26 (t, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 3H), 2.72 (dd, *J* = 18.6 Hz, 4.7 Hz, 1H), 2.68 – 2.61 (m, 2H), 2.56 (dd, *J* = 18.8 Hz, 7.8 Hz, 1H), 2.27 – 2.24 (m, 1H), 2.22 (s, 3H), 2.17 (s, 6H), 2.09 (s, 6H), 1.78 – 1.71 (m, 1H), 1.57 – 1.49 (m, 1H), 1.10 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.1, 142.6, 140.8, 135.4, 133.2, 128.5, 127.4, 125.8, 52.9, 38.9, 33.6, 28.0, 20.1, 17.2, 16.8, 16.0.

3-methyl-1-(2,3,4,5,6-pentamethylphenyl)nonan-1-one (3bq):[11]

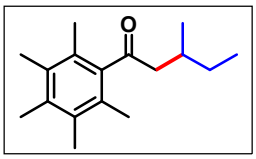


Isolated as a viscous liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 118.0 mg (78%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.67 (dd, *J* = 18.9 Hz, 5.0 Hz, 1H), 2.50 (dd, *J* = 18.8 Hz, 7.9 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H), 1.38 – 1.20 (m, 11H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 6.2 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.5, 141.0, 135.3, 133.1, 127.4, 53.1, 37.0, 32.0, 29.6, 28.0, 27.0, 22.8, 20.2, 17.1, 16.8, 16.0, 14.2.

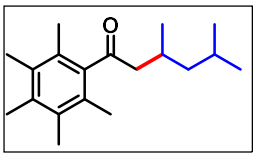
3-methyl-1-(2,3,4,5,6-pentamethylphenyl)undecan-1-one (3br): Isolated as a gummy liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 106.0 mg (64%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.67 (dd, *J* = 18.8 Hz, 4.8 Hz, 1H), 2.50 (dd, *J* = 18.8 Hz, 7.9 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H), 1.41 – 1.20 (m, 15H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.5, 141.0, 135.3, 133.1, 127.4, 53.1, 37.0, 32.0, 29.9, 29.8, 29.4, 28.0, 27.1, 22.8, 20.2, 17.1, 16.8, 16.0, 14.2. **HRMS (ESI+):** m/z calcd. for $C_{23}H_{38}O$ $[M+H]^+$: 331.3001; Found: 331.3012.



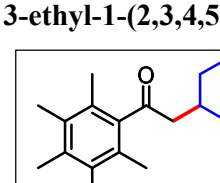
3-methyl-1-(2,3,4,5,6-pentamethylphenyl)pentan-1-one (3bs):[8] Isolated as a liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 40.0 mg (32%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 2.72 (dd, *J* = 18.8 Hz, 4.7 Hz, 1H), 2.55 (dd, *J* = 18.7 Hz, 7.8 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 6H), 2.18 – 2.16 (m, 1H), 2.14 (s, 6H), 1.53 – 1.46 (m, 1H), 1.32 – 1.25 (m, 1H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 211.5, 141.0, 135.4, 133.2, 127.4, 52.7, 29.6, 19.7, 17.1, 16.8, 16.1, 11.4.



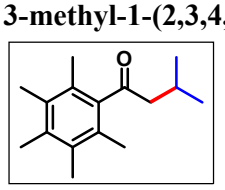
3,5-dimethyl-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one (3bt):[18] Isolated as a liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 77.0 mg (56%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.65 (dd, *J* = 18.9 Hz, 4.5 Hz, 1H), 2.50 (dd, *J* = 18.9 Hz, 8.2 Hz, 1H), 2.29 – 2.26 (m, 1H), 2.22 (s, 3H), 2.17 (s, 6H), 2.10 (s, 6H), 1.68 – 1.62 (m, 1H), 1.24 – 1.20 (m, 1H), 1.12 – 1.06 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.91 – 0.89 (m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.4, 141.0, 135.3, 133.1, 127.4, 53.4, 46.5, 25.8, 25.4, 23.4, 22.2, 20.27, 17.1, 16.8, 16.0.



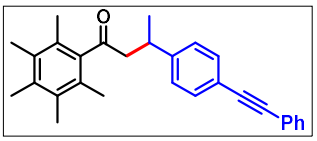
3-ethyl-1-(2,3,4,5,6-pentamethylphenyl)pentan-1-one (3bu):[8] Isolated as a liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 1:99 (v/v)). Yield: 66.0 mg (51%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 2.62 (d, *J* = 6.4 Hz, 2H), 2.23 (s, 3H), 2.18 (s, 6H), 2.11 (s, 6H), 2.02 – 1.99 (m, 1H), 1.49 – 1.37 (m, 4H), 0.89 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.7, 141.1, 135.3, 133.2, 127.4, 49.7, 35.2, 25.7, 17.1, 16.8, 16.1, 10.9.



3-methyl-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3bv):[18] Isolated as a liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 0:100 (v/v)). Yield: 33.0 mg (28%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 2.57 (d, *J* = 6.5 Hz, 2H), 2.35 – 2.29 (m, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H), 1.02 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 211.4, 140.9, 135.4, 133.2, 127.4, 54.6, 23.5, 22.9, 17.1, 16.8, 16.1.

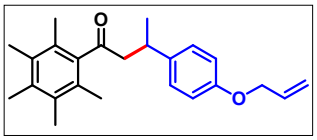


1-(2,3,4,5,6-pentamethylphenyl)-3-(4-(phenylethynyl)phenyl)butan-1-one (3aw):[18]



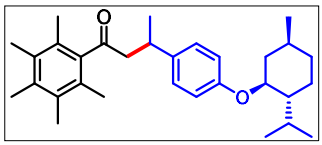
Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 146.0 mg (74%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.53 – 7.49 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.31 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.59 – 3.52 (m, 1H), 3.03 – 2.90 (m, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 1.99 (s, 6H), 1.37 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.0, 147.2, 140.4, 135.6, 133.2, 131.8, 131.7, 128.4, 128.3, 127.5, 127.3, 123.5, 121.2, 89.6, 89.1, 53.7, 34.3, 22.3, 17.0, 16.8, 16.0.

3-(4-(allyloxy)phenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3ax):



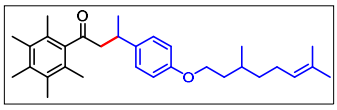
Isolated as a white solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 4:96 (v/v)). Yield: 137.0 mg (78%).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.09 – 6.00 (m, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 4.50 (d, *J* = 5.3 Hz, 2H), 3.53 – 3.45 (m, 1H), 3.01 – 2.86 (m, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 1.98 (s, 6H), 1.34 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.3, 157.1, 140.6, 139.1, 135.4, 133.6, 133.1, 128.0, 127.4, 117.6, 114.8, 69.0, 54.1, 33.5, 22.6, 17.0, 16.8, 16.0. **HRMS (ESI+):** m/z calcd. for $C_{24}H_{30}O_2$ $[M+H]^+$: 351.2324; Found: 351.2313.

(R)-3-(4-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3ay):



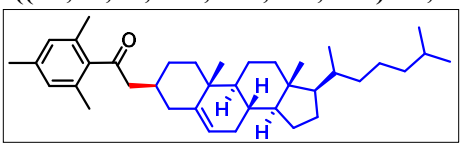
Isolated as a gummy liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 5:95 (v/v)). Yield: 139.0 mg (62%).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.05 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 4.50 (q, *J* = 2.8 Hz, 1H), 3.45 – 3.36 (m, 1H), 2.94 – 2.78 (m, 2H), 2.13 (s, 3H), 2.07 (s, 6H), 2.01 - 1.97 (m, 1H), 1.90 (s, 6H), 1.71 – 1.57 (m, 4H), 1.51 – 1.44 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 0.99 – 0.90 (m, 3H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.7 Hz, 3H), 0.73 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.5, 156.76, 156.74, 140.7, 138.4, 135.4, 133.1, 128.1, 127.5, 115.8, 73.40, 73.38, 54.28, 54.26, 48.0, 37.8, 35.2, 33.5, 29.4, 26.3, 25.0, 22.6, 22.5, 22.4, 21.2, 21.0, 17.0, 16.8, 16.0. **HRMS (ESI+):** m/z calcd. for $C_{31}H_{44}O_2$ $[M+H]^+$: 449.3420; Found: 449.3417.

3-(4-((3,7-dimethyloct-6-en-1-yl)oxy)phenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (3az):



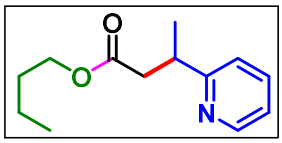
Isolated as a gummy liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 4:96 (v/v)). Yield: 128.0 mg (57%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.14 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 5.10 (t, *J* = 6.6 Hz, 1H), 4.00 – 3.92 (m, 2H), 3.52 – 3.45 (m, 1H), 3.00 – 2.87 (m, 2H), 2.20 (s, 3H), 2.14 (s, 6H), 2.04 – 1.98 (m, 8H), 1.85 – 1.78 (m, 1H), 1.68 (s, 4H), 1.60 (s, 3H), 1.58 – 1.54 (m, 1H), 1.42 – 1.37 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 3H), 1.25 – 1.18 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.3, 157.6, 140.6, 138.7, 135.4, 133.1, 131.3, 128.0, 127.4, 124.8, 114.5, 66.4, 54.1, 37.3, 36.3, 33.5, 29.6, 25.8, 25.6, 22.6, 19.7, 17.8, 17.0, 16.8, 16.0. **HRMS (ESI+):** m/z calcd. for $C_{31}H_{44}O_2$ $[M+H]^+$: 449.3420; Found: 449.3425.

2-((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-

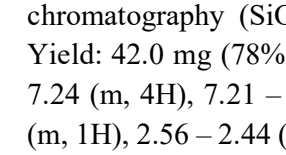


2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)-1-mesitylethan-1-one (3bw):[11] Isolated as a faded yellow solid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 2:98 (v/v)). Yield: 109.0 mg (41%).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 6.82 (s, 2H), 5.16 (s, 1H), 2.70 (s, 1H), 2.63 (d, *J* = 6.8 Hz, 2H), 2.27 (s, 3H), 2.20 (s, 6H), 2.00 – 1.95 (m, 2H), 1.85 – 1.80 (m, 2H), 1.73 – 1.68 (m, 2H), 1.39 – 1.31 (m, 7H), 1.15 – 1.07 (m, 7H), 1.04 – 0.97 (m, 7H), 0.91 – 0.86 (m, 12H), 0.80 – 0.74 (m, 1H), 0.68 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 210.2, 146.1, 139.9, 138.3, 132.7, 128.7, 123.0, 56.4, 56.3, 54.7, 52.0, 42.7, 40.1, 39.7, 37.9, 37.3, 36.3, 36.2, 35.9, 33.4, 32.8, 32.0, 28.4, 28.2, 26.7, 24.4, 24.0, 23.0, 22.7, 21.5, 21.3, 19.6, 19.3, 12.1.

Butyl 3-(pyridin-2-yl)butanoate (4a): Isolated as a liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 40:60 (v/v)). Yield: 34.0 mg (62%).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.53 (d, *J* = 4.8 Hz, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.12 – 7.09 (m, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.41 (h, *J* = 7.1 Hz, 1H), 2.88 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.60 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.56 – 1.49 (m, 2H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.32 – 1.25 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.8, 164.5, 149.3, 136.5, 122.0, 121.5, 64.2, 41.0, 38.3, 30.7, 20.9, 19.2, 13.8. **HRMS (ESI+):** m/z calcd. for $C_{13}H_{19}NO_2$ $[M+H]^+$: 222.1494; Found: 222.1503.



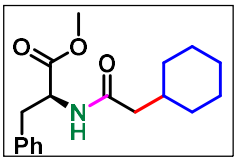
3-phenyl-1-(pyrrolidin-1-yl)butan-1-one (4b):[11] Isolated as a faded yellow liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 30:70 (v/v)). Yield: 42.0 mg (78%).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.31 – 7.24 (m, 4H), 7.21 – 7.17 (m, 1H), 3.44 – 3.29 (m, 4H), 3.15 – 3.09 (m, 1H), 2.56 – 2.44 (m, 2H), 1.88 – 1.75 (m, 4H), 1.34 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.4, 146.6, 128.5, 127.0, 126.3, 46.7, 45.6, 43.7, 36.5, 26.1, 24.4, 21.5.



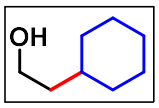
1-morpholino-3-phenylbutan-1-one (4c): Isolated as a liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 30:70 (v/v)). Yield: 32.0 mg (55%).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.19 (m, 3H), 3.66 – 3.61 (m, 2H), 3.52 – 3.44 (m, 3H), 3.36 – 3.30 (m, 2H), 3.25 – 3.21 (m, 2H), 2.62 (dd, *J* = 14.5, 7.1 Hz, 1H), 2.50 (dd, *J* = 14.5, 7.4 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.5, 146.1, 128.6, 127.0, 126.5, 66.9, 66.5, 46.2, 41.9, 41.4, 37.0, 21.7. **HRMS (ESI+):** m/z calcd. for $C_{31}H_{44}O_2$ $[M+H]^+$: 234.1494; Found: 234.1487.

Methyl (2-cyclohexylacetyl)-L-phenylalaninate (4d): Isolated as a faded yellow liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 25:75 (v/v)). Yield: 50.0 mg

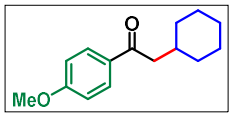
(66%).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.23 – 7.16 (m, 3H), 7.03 (d, *J* = 7.3 Hz, 2H), 5.76 (d, *J* = 7.2 Hz, 1H), 4.85 (q, *J* = 6.0 Hz, 1H), 3.66 (s, 3H), 3.10 – 2.99 (m, 2H), 1.96 (d, *J* = 7.0 Hz, 2H), 1.61 – 1.55 (m, 6H), 1.20 – 1.13 (m, 2H), 1.07 – 1.03 (m, 1H), 0.86 – 0.77 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.4, 172.1, 136.0, 129.4, 128.7, 127.2, 53.0, 52.4, 44.7, 38.2, 35.4, 33.20, 33.16, 26.3, 26.2. **HRMS (ESI+):** m/z calcd. for $C_{18}H_{25}NO_3$ $[M+H]^+$: 326.1732; Found: 326.1743.



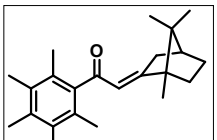
2-cyclohexylethan-1-ol (4e):[21] Isolated as a colourless oil by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 15:85 (v/v)). Yield: 40.0 mg (62%).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 3.61 (t, *J* = 6.8 Hz, 2H), 1.65 – 1.56 (m, 5H), 1.40 (q, *J* = 6.8 Hz, 2H), 1.36 – 1.29 (m, 1H), 1.22 – 1.07 (m, 3H), 0.89 – 0.81 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 61.0, 40.5, 34.4, 33.5, 26.7, 26.4.



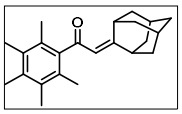
2-cyclohexyl-1-(4-methoxyphenyl)ethan-1-one (4f): Isolated as a light yellow liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 10:90 (v/v)). Yield: 39.0 mg (67%).**^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.86 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 2.69 (d, *J* = 6.8 Hz, 2H), 1.91 – 1.84 (m, 1H), 1.68 – 1.66 (m, 2H), 1.63 – 1.56 (m, 3H), 1.24 – 1.16 (m, 2H), 1.11 – 1.04 (m, 1H), 0.96 – 0.90 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 199.1, 163.4, 130.7, 130.5, 113.8, 55.5, 46.0, 35.0, 33.6, 26.4, 26.3. **HRMS (ESI+):** m/z calcd. for $C_{15}H_{20}O_2$ $[M+H]^+$: 233.1542; Found: 233.1542.



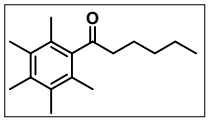
(E)-1-(2,3,4,5,6-pentamethylphenyl)-2-((1R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)ethan-1-one (3bx′): Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 3:97 (v/v)). Yield: 49.0 mg (30%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 6.15 (s, 1H), 2.59 – 2.55 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.14 – 2.13 (m,1H), 2.09 (s, 6H), 1.82 – 1.69 (m, 3H), 1.29 – 1.24 (m, 1H), 1.19 – 1.14 (m, 1H), 0.95 (s, 3H), 0.92 (s, 3H), 0.73 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 201.6, 175.3, 141.8, 135.1, 133.0, 127.9, 119.1, 54.2, 48.2, 44.6, 38.6, 34.3, 27.4, 19.7, 19.0, 17.1, 16.8, 16.1, 12.7. **HRMS (ESI+):** m/z calcd. for $C_{23}H_{32}O$ $[M+H]^+$: 325.2531; Found: 325.2529.



2-((1r,3r,5R,7S)-adamantan-2-ylidene)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3by′): Isolated as a light yellow liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 3:97 (v/v)). Yield: 68.0 mg (42%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 6.14 (s, 1H), 3.71 (s, 1H), 2.39 (s, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.14 (s, 6H), 2.00 – 1.98 (m, 1H), 1.97 – 1.95 (m, 3H), 1.91 – 1.85 (m, 6H), 1.81 – 1.78 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 202.3, 171.2, 141.8, 135.1, 133.0, 127.9, 120.4, 41.9, 40.5, 39.5, 36.9, 33.2, 28.0, 17.3, 16.8, 16.1. **HRMS (ESI+):** m/z calcd. for $C_{23}H_{30}O$ $[M+H]^+$: 323.2375; Found: 323.2363.



1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one (3be′):[9] Isolated as a colourless liquid by column chromatography (SiO_2; ethyl acetate:petroleum-ether, 3:97 (v/v)). Yield: 49.0 mg (45%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 2.67 (t, *J* = 7.4 Hz, 2H), 2.23 (s, 3H), 2.18 (s, 6H), 2.09 (s, 6H), 1.74 – 1.69 (m, 2H), 1.37 – 1.34 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 212.4, 141.0, 135.4, 133.2, 127.4, 45.8, 31.5, 23.0, 22.7, 17.3, 16.8, 16.1, 14.1.



14. Copy of NMR spectra of starting materials, Zn-complexes and products:

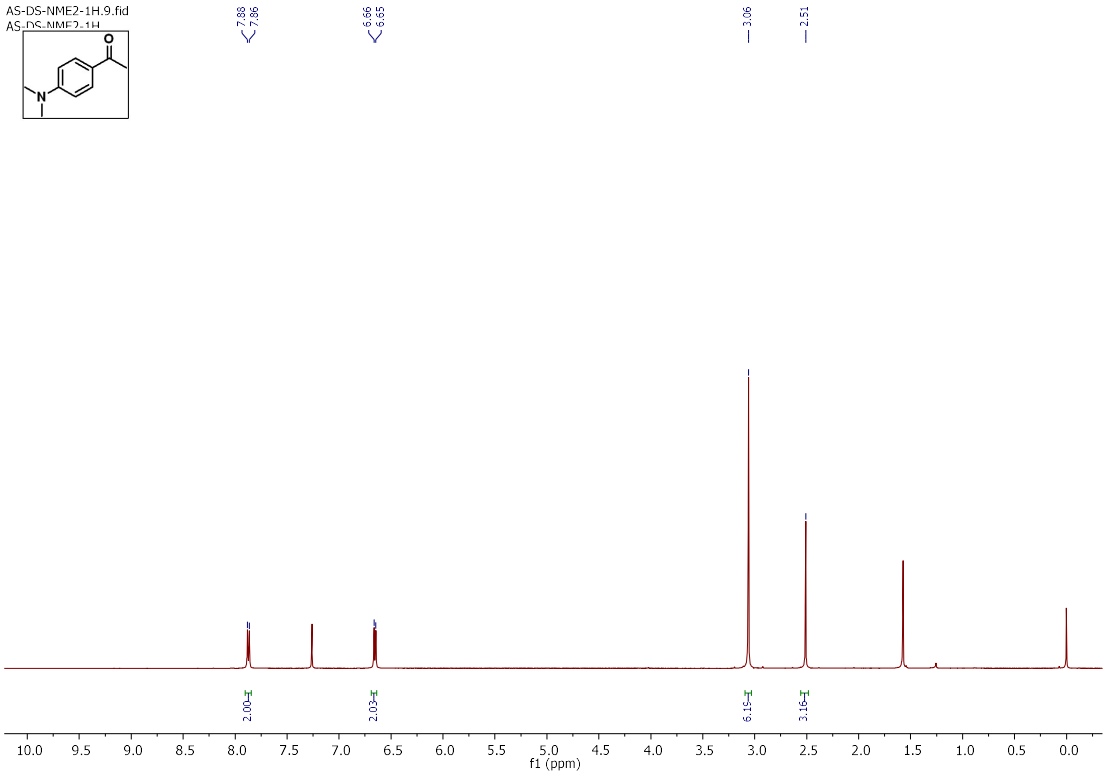


Figure S13. ^{1}H NMR (500 MHz) spectrum of Compound **2ae′** in $CDCl_3$.

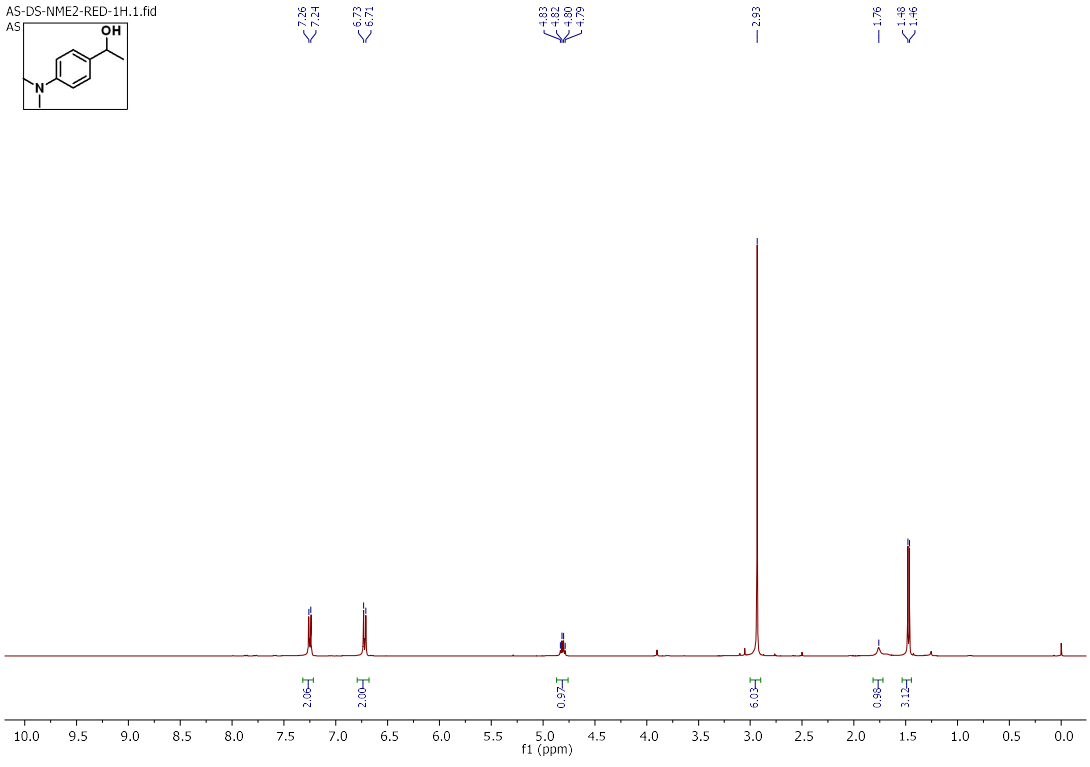


Figure S14. ^{1}H NMR (400 MHz) spectrum of Compound **2ae** in $CDCl_3$.

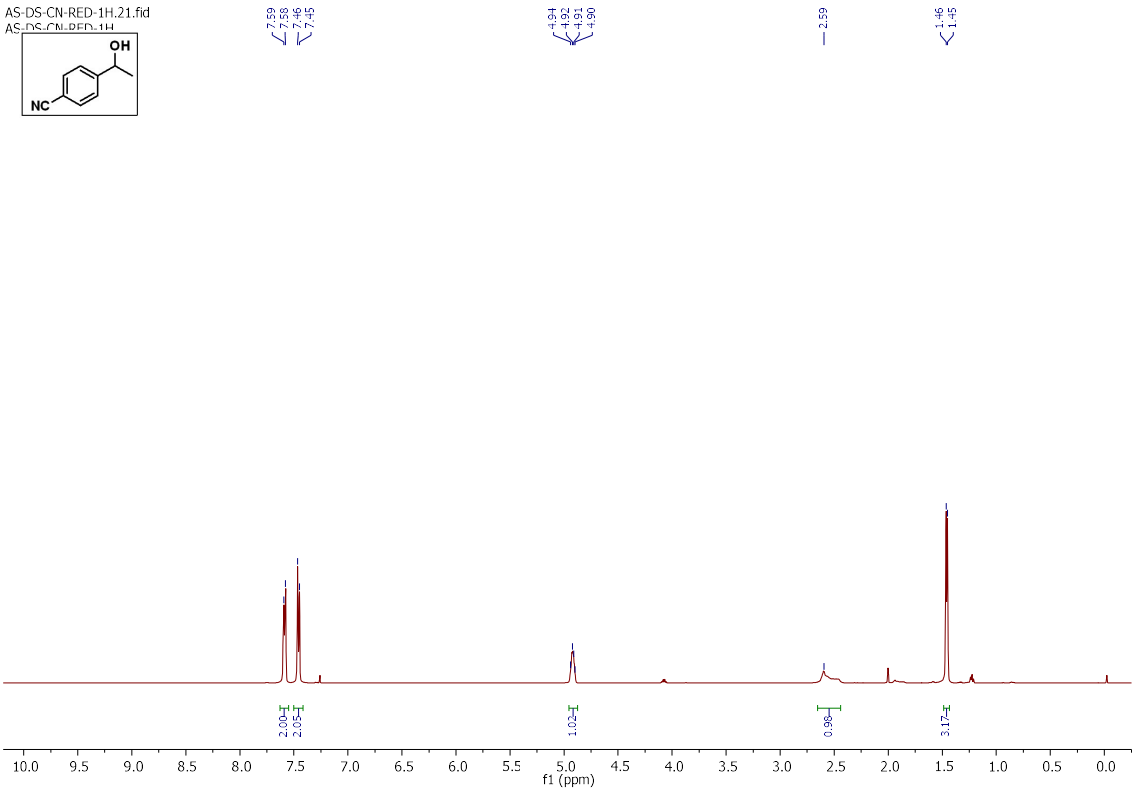


Figure S15. ^{1}H NMR (500 MHz) spectrum of Compound **2ai** in $CDCl_3$.

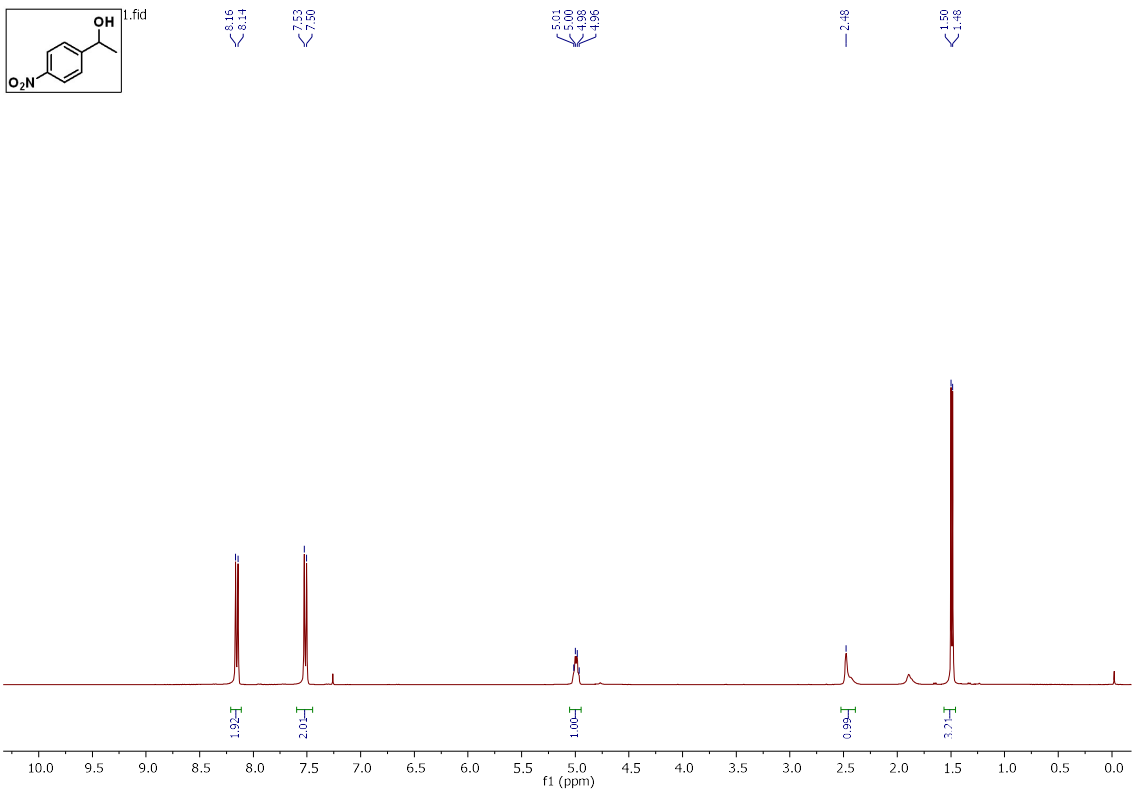


Figure S16. ^{1}H NMR (400 MHz) spectrum of Compound **2aj** in $CDCl_3$.

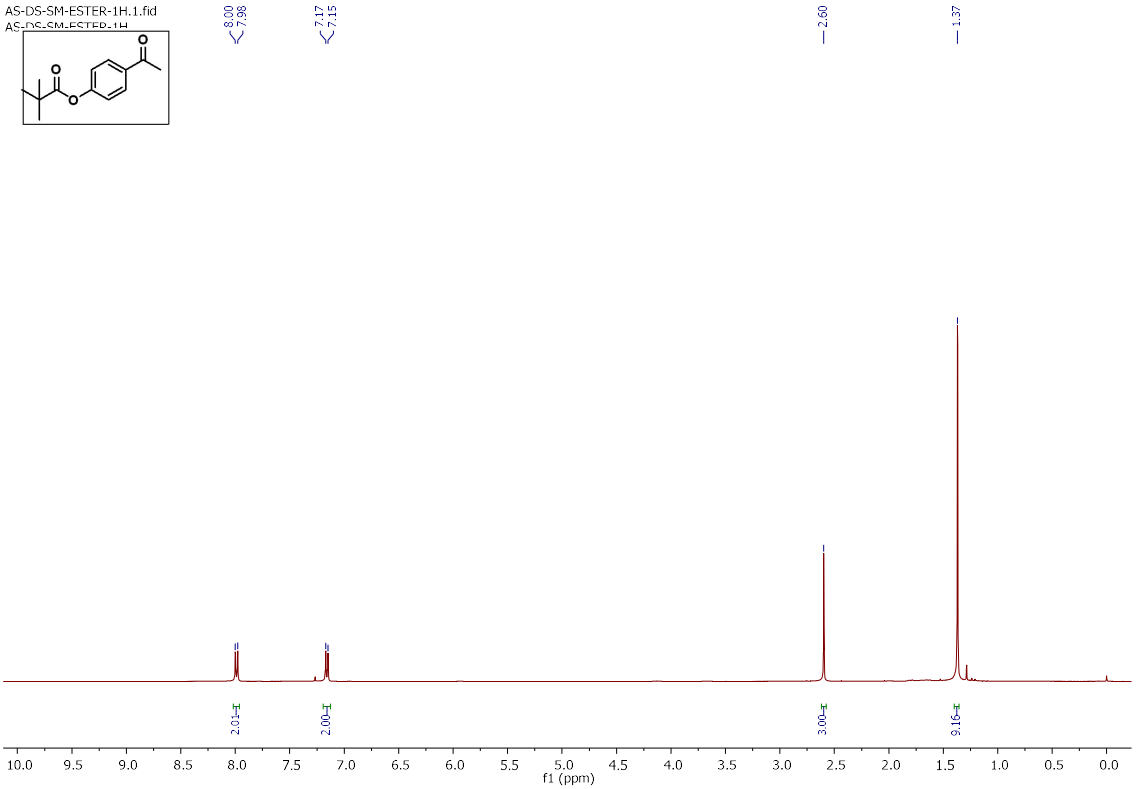
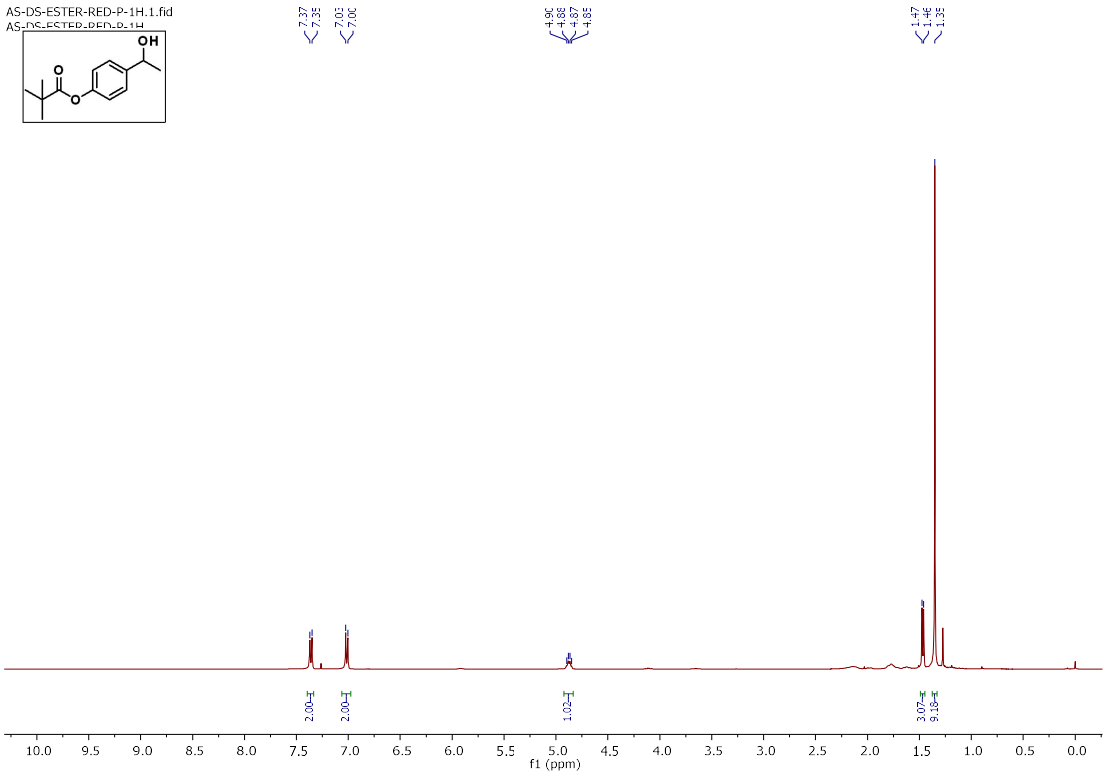


Figure S17. ^{1}H NMR (400 MHz) spectrum of Compound **2ak′** in $CDCl_3$.



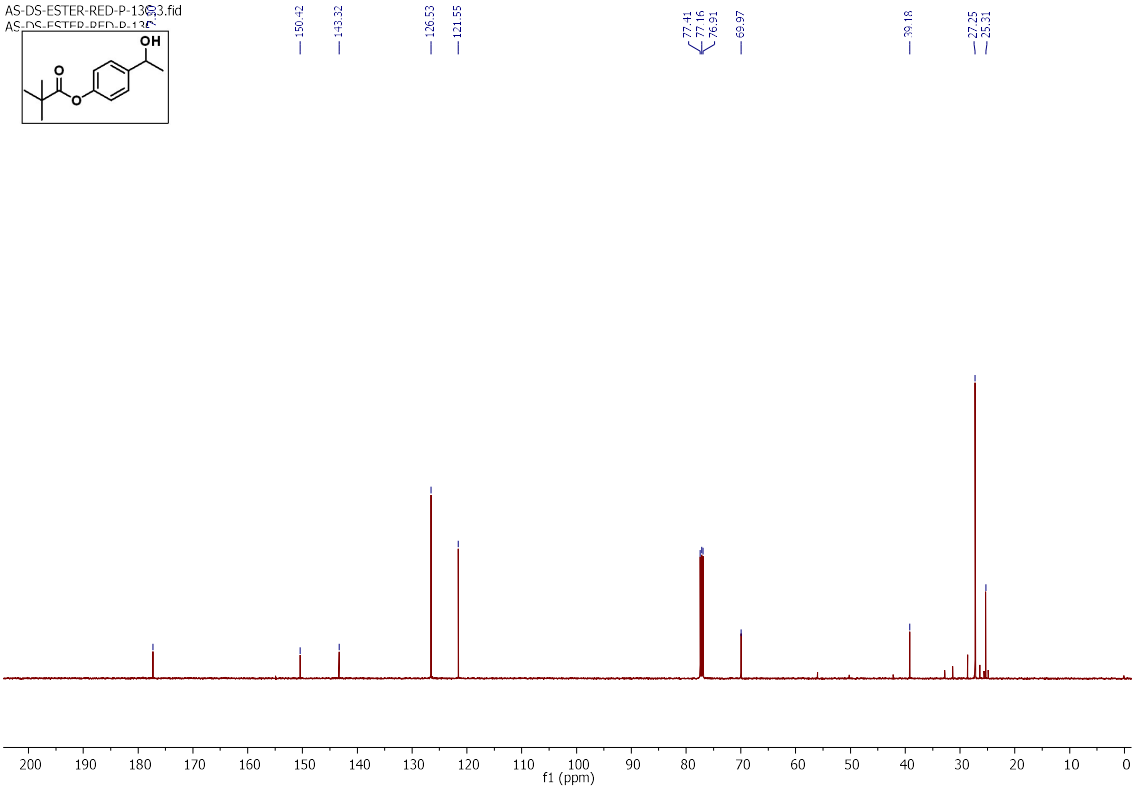


Figure S18. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum spectrum of Compound **2ak** in $CDCl_3$.

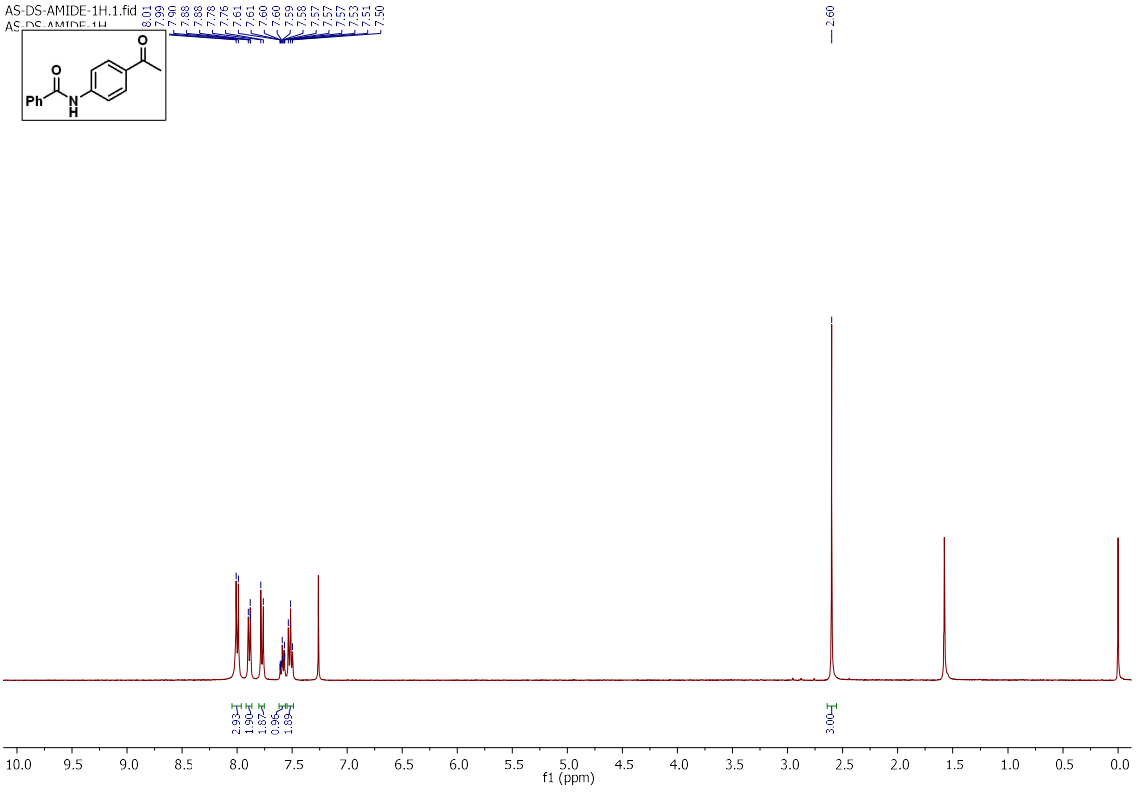


Figure S19. ^{1}H NMR (400 MHz) spectrum of Compound **2al′** in $CDCl_3$.

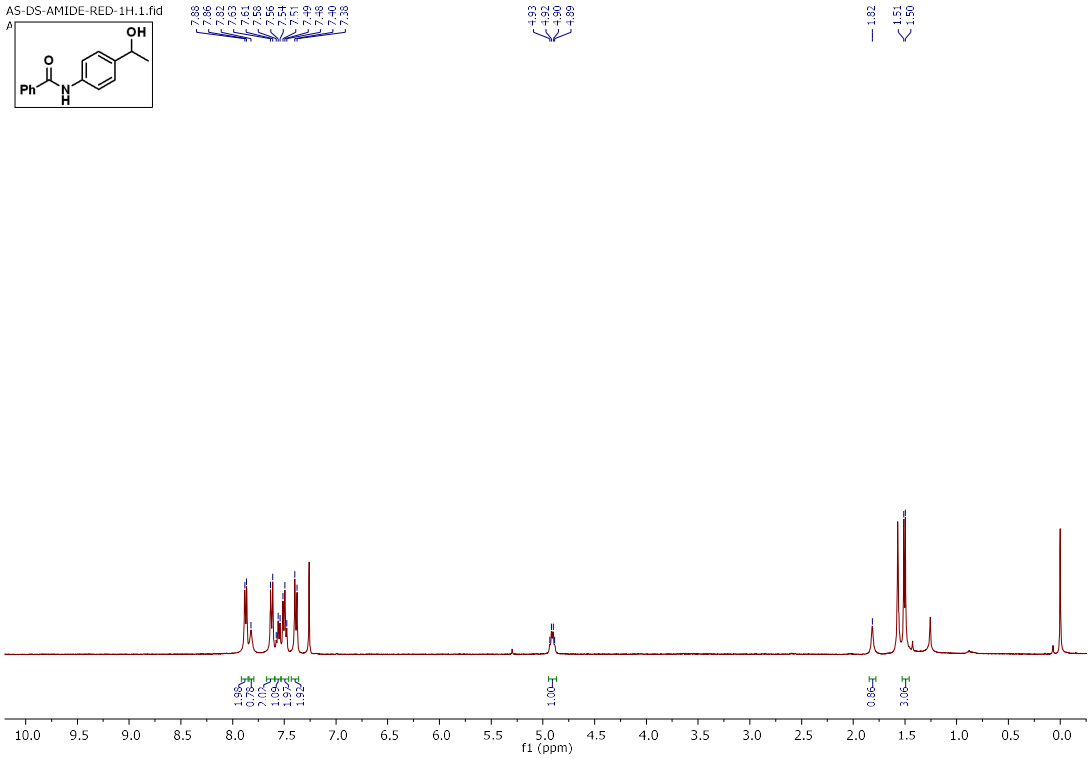


Figure S20. ^{1}H NMR (400 MHz) spectrum of Compound **2al** in $CDCl_3$.

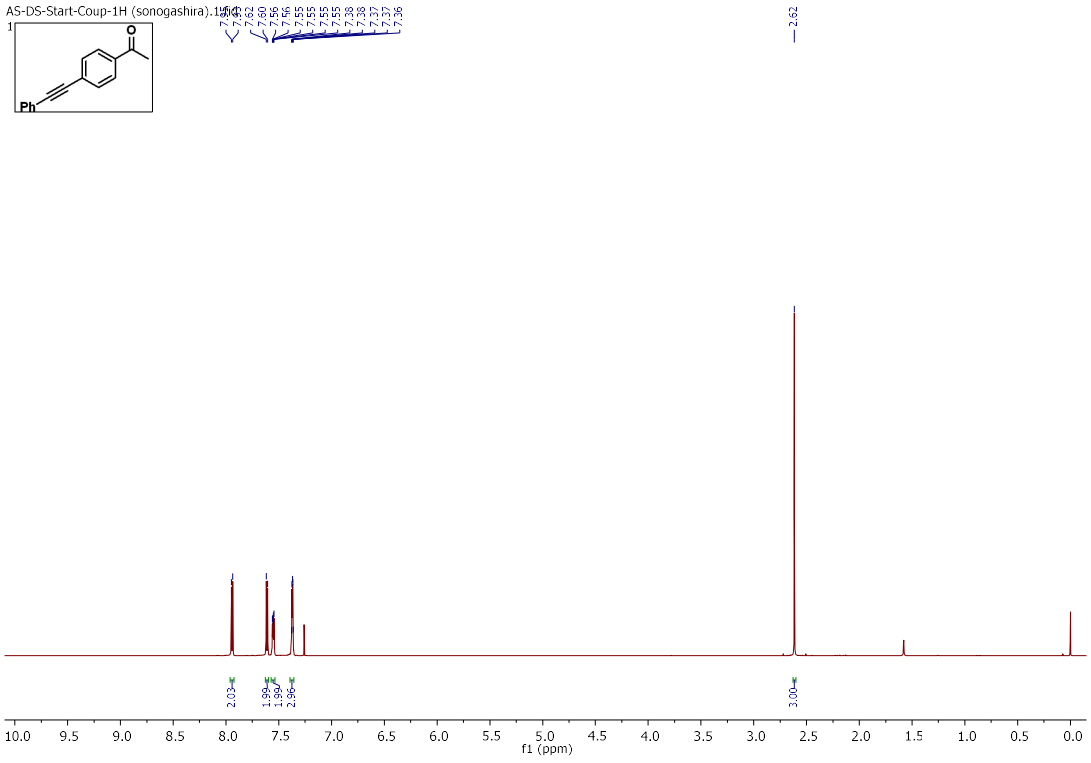


Figure S21. ^{1}H NMR (600 MHz) spectrum of Compound **2aw′** in $CDCl_3$.

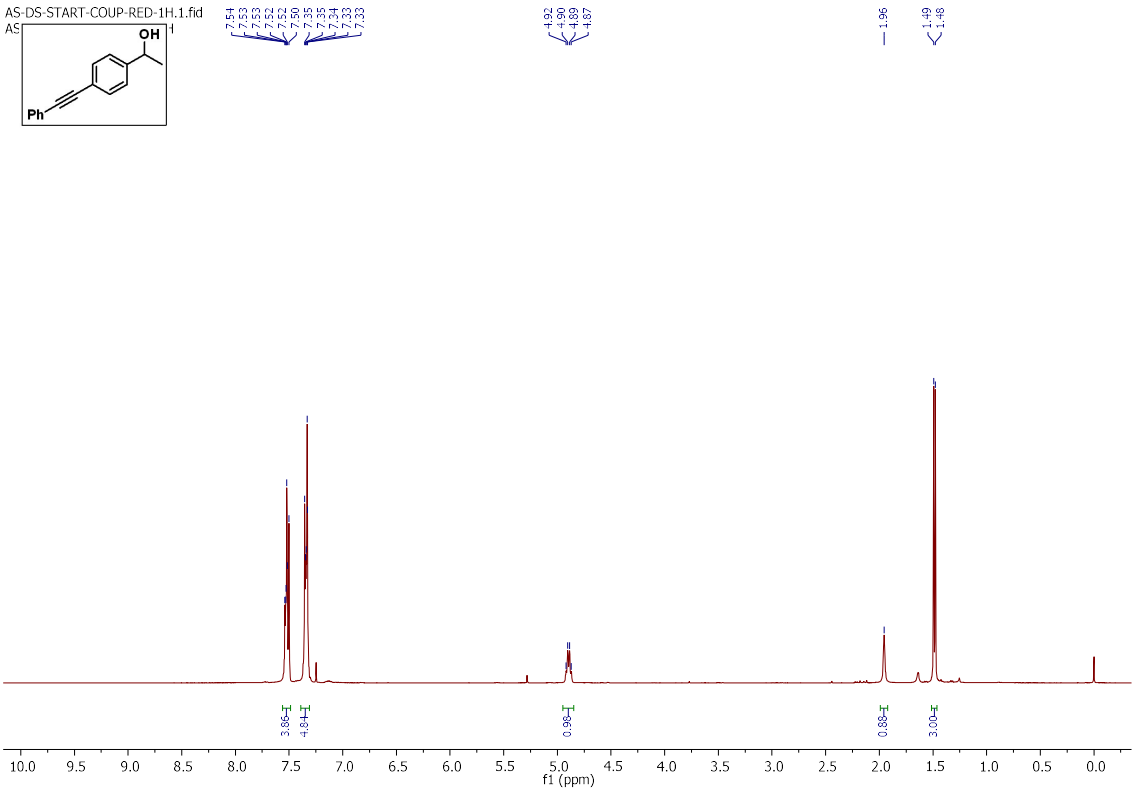


Figure S22. ^{1}H NMR (400 MHz) spectrum of Compound **2aw** in $CDCl_3$.

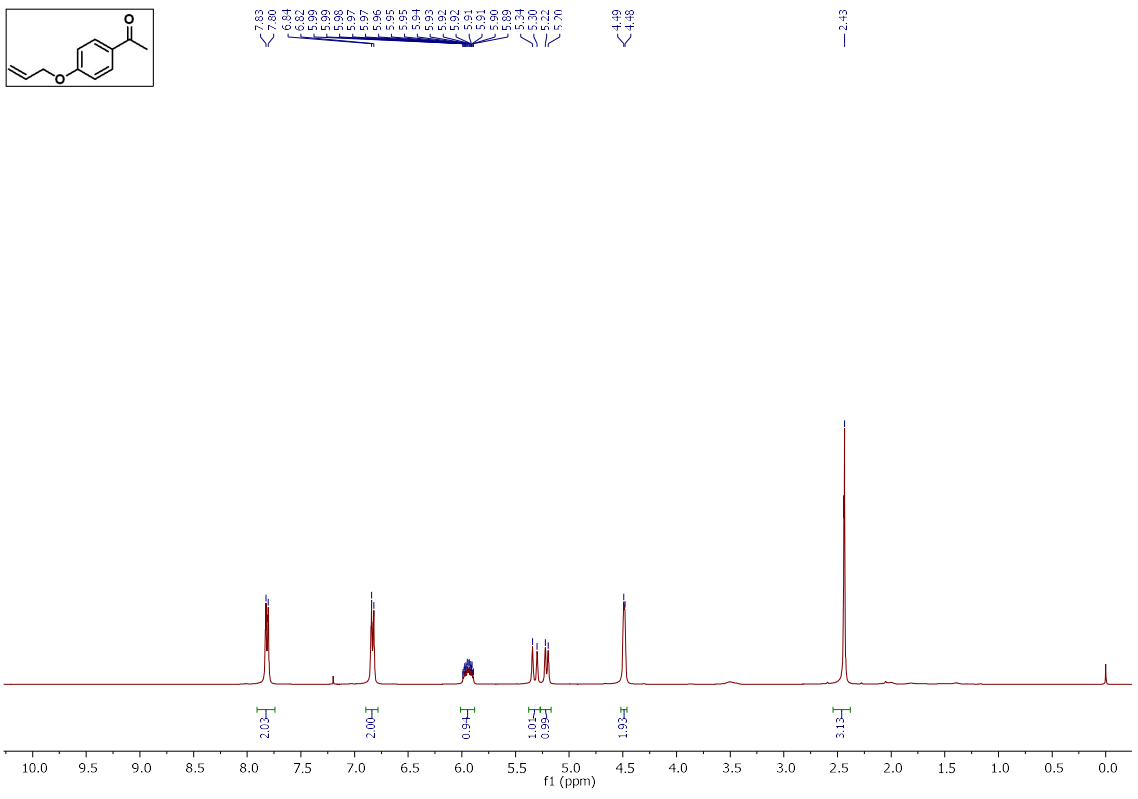


Figure S23. ^{1}H NMR (400 MHz) spectrum of Compound **2ax′** in $CDCl_3$.

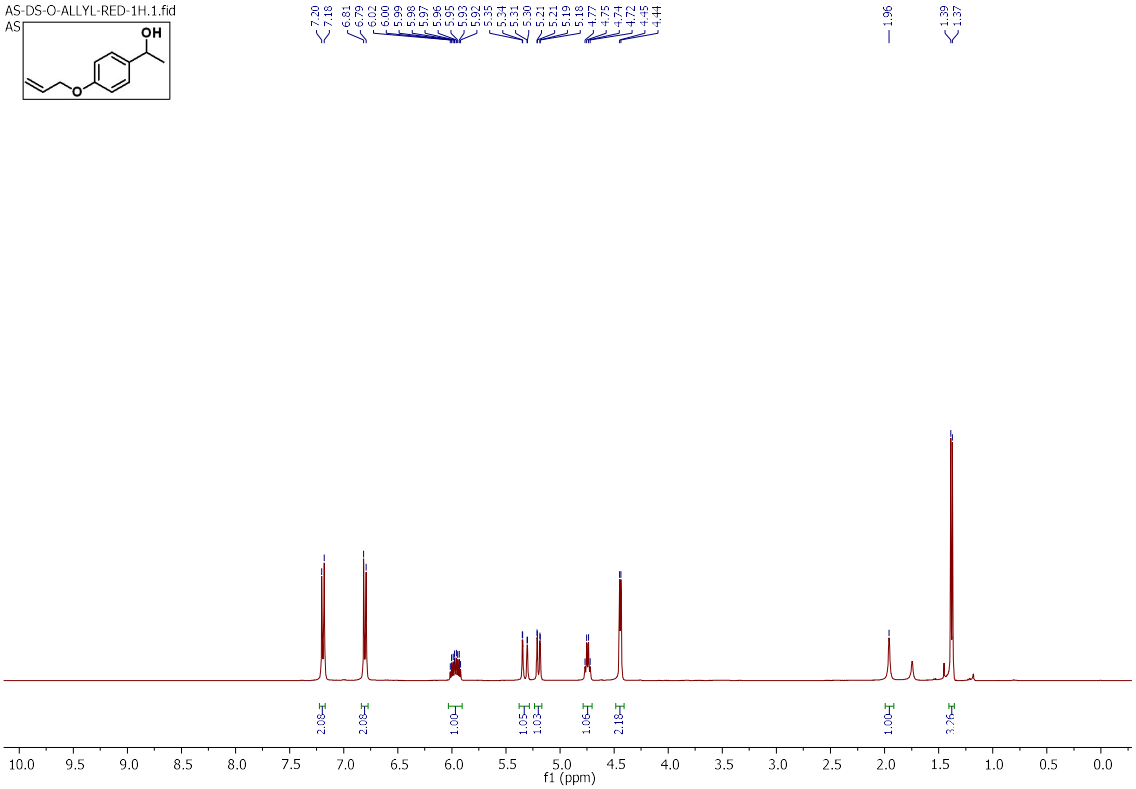


Figure S24. ^{1}H NMR (400 MHz) spectrum of Compound **2ax** in $CDCl_3$.

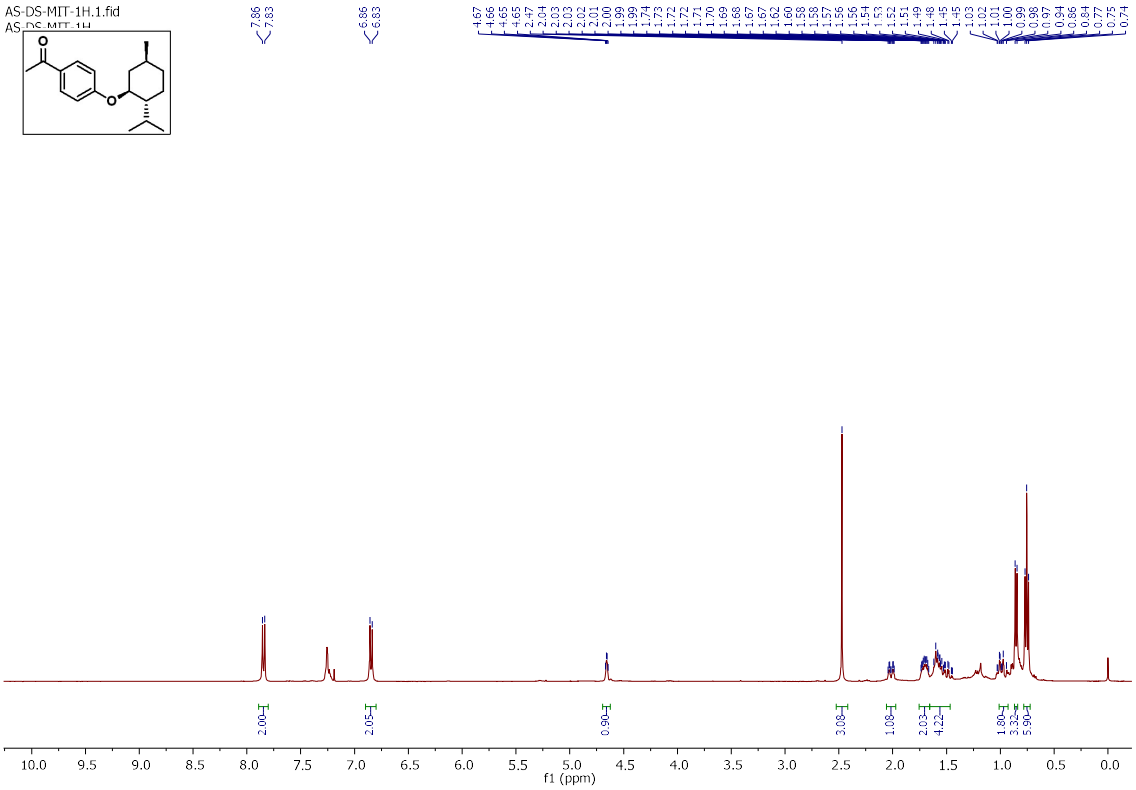


Figure S25. ^{1}H NMR (400 MHz) spectrum of Compound **2ay′** in $CDCl_3$.

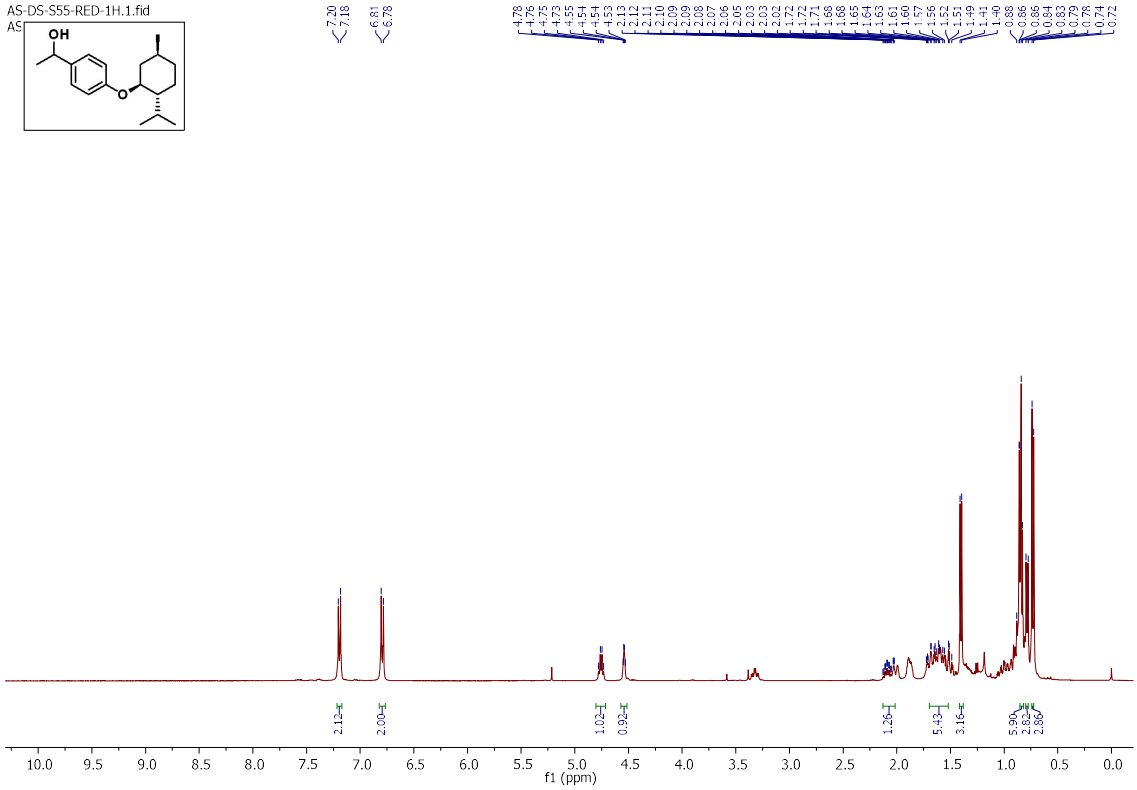


Figure S26. ^{1}H NMR (400 MHz) spectrum of Compound **2ay** in $CDCl_3$.

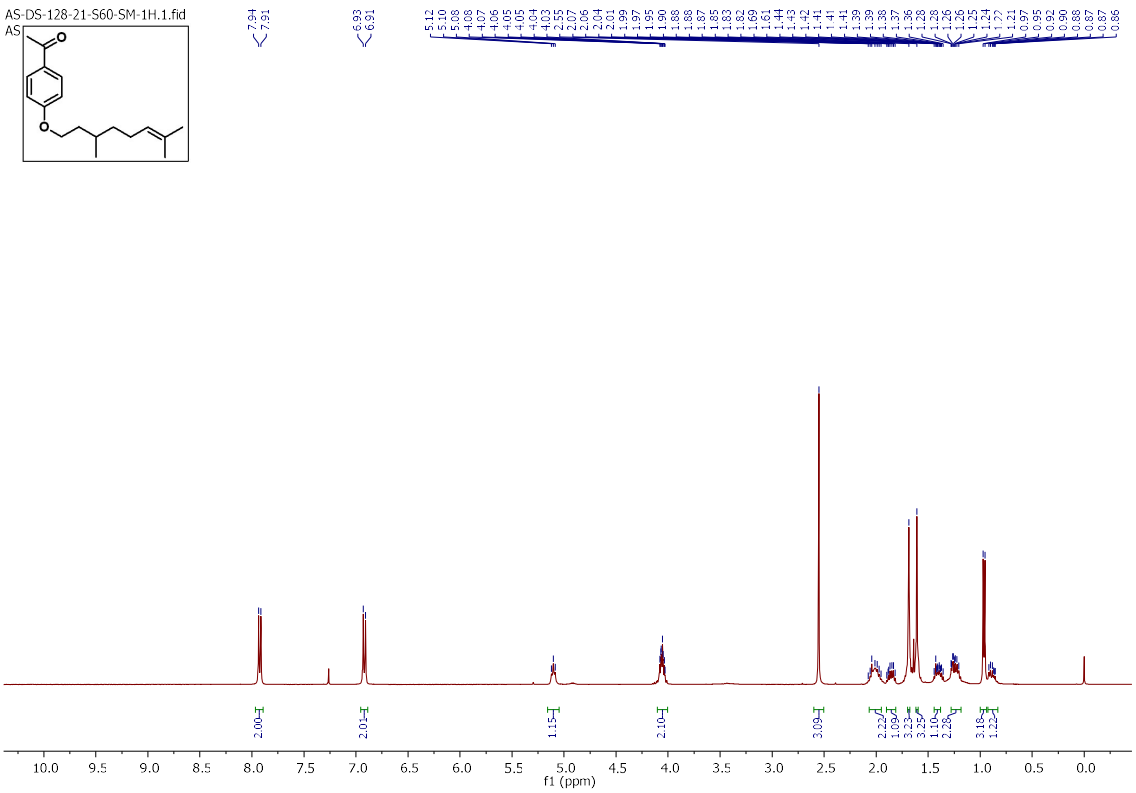


Figure S27. ^{1}H NMR (400 MHz) spectrum of Compound **2az′** in $CDCl_3$.

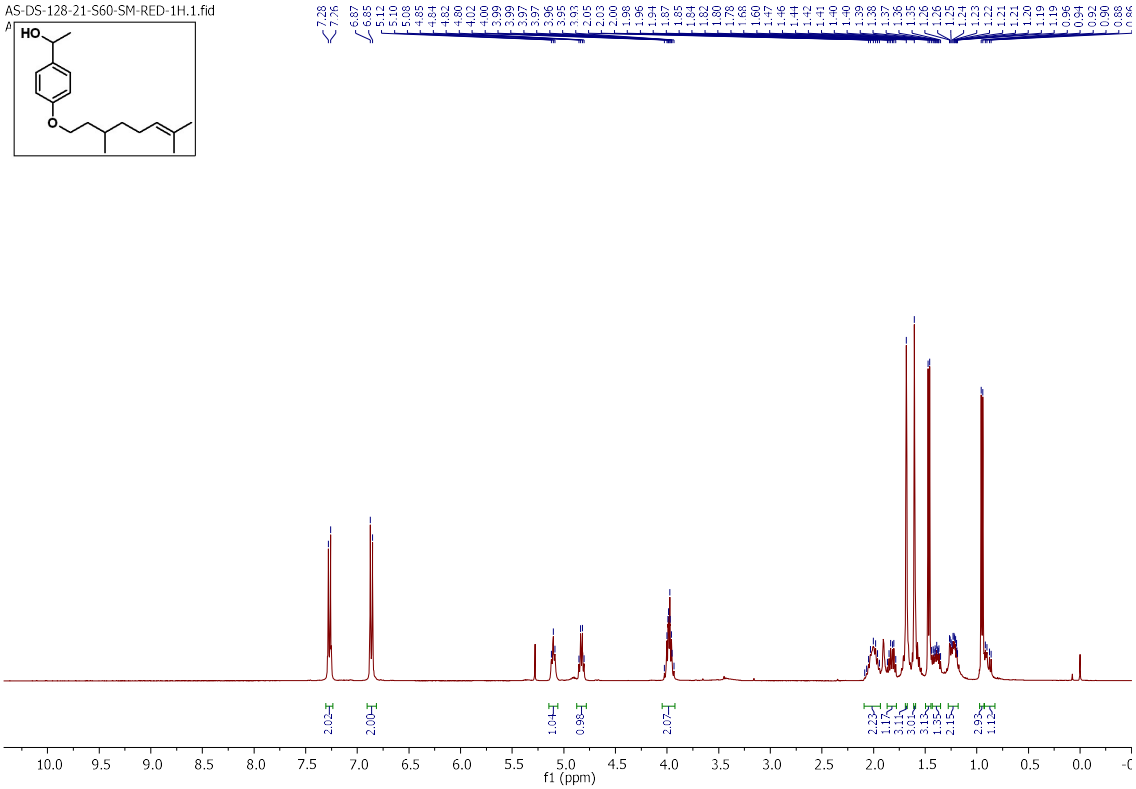


Figure S28. ^{1}H NMR (400 MHz) spectrum of Compound **2az** in $CDCl_3$.

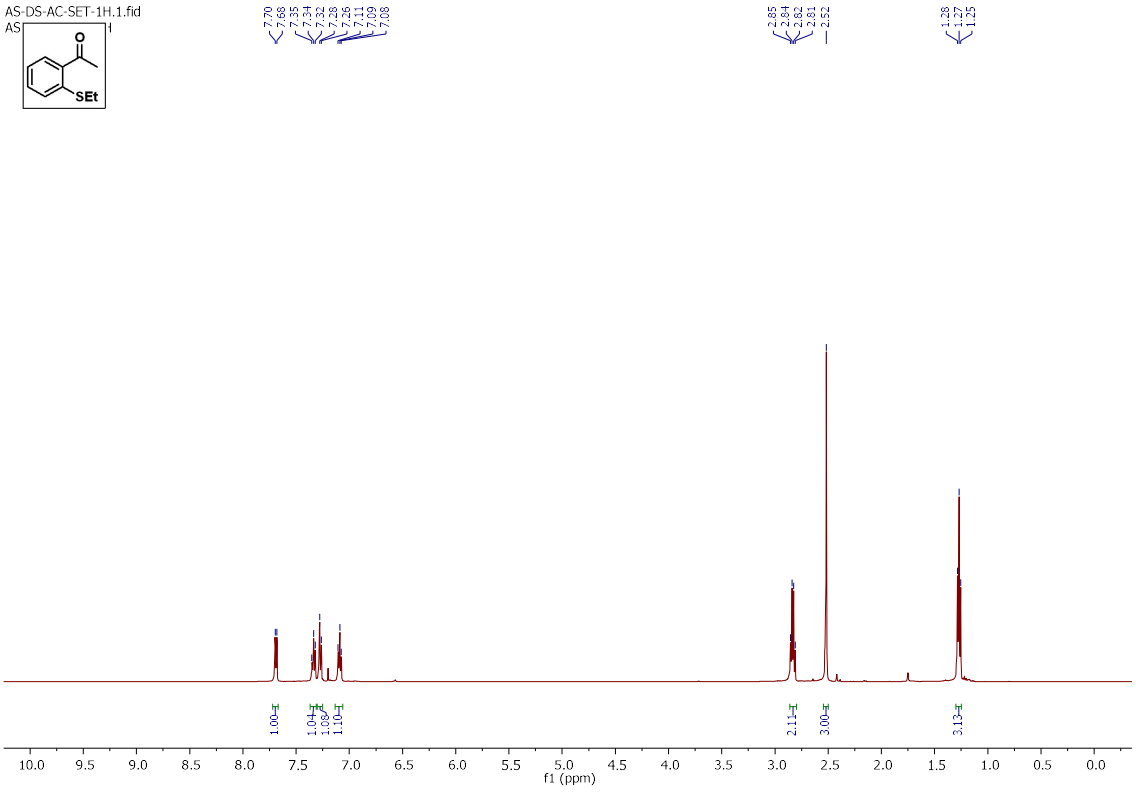


Figure S29. ^{1}H NMR (400 MHz) spectrum of Compound **1-(2-(ethylthio)phenyl)ethan-1-one** in $CDCl_3$.

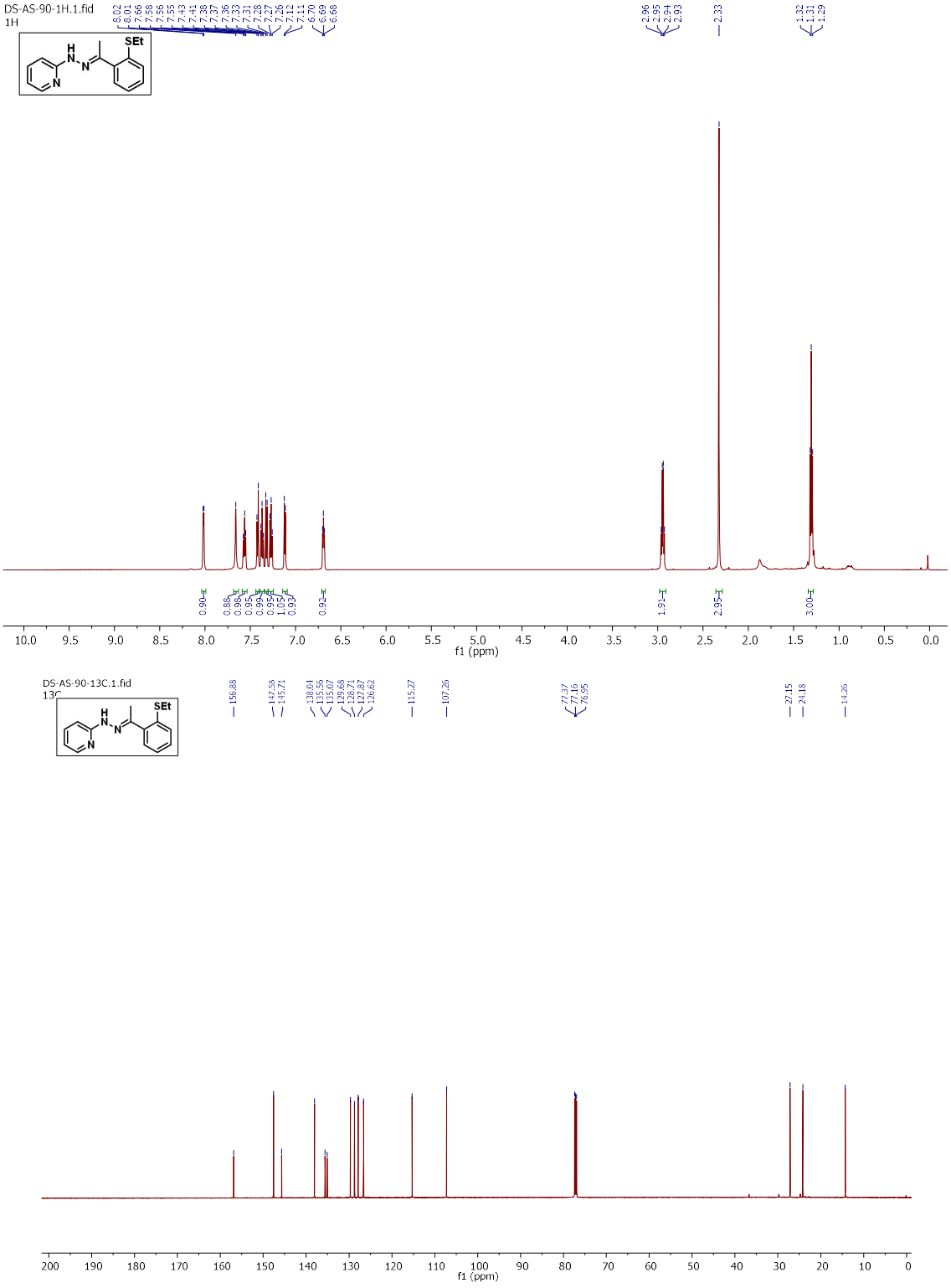


Figure S30. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **L-5** in $CDCl_3$.

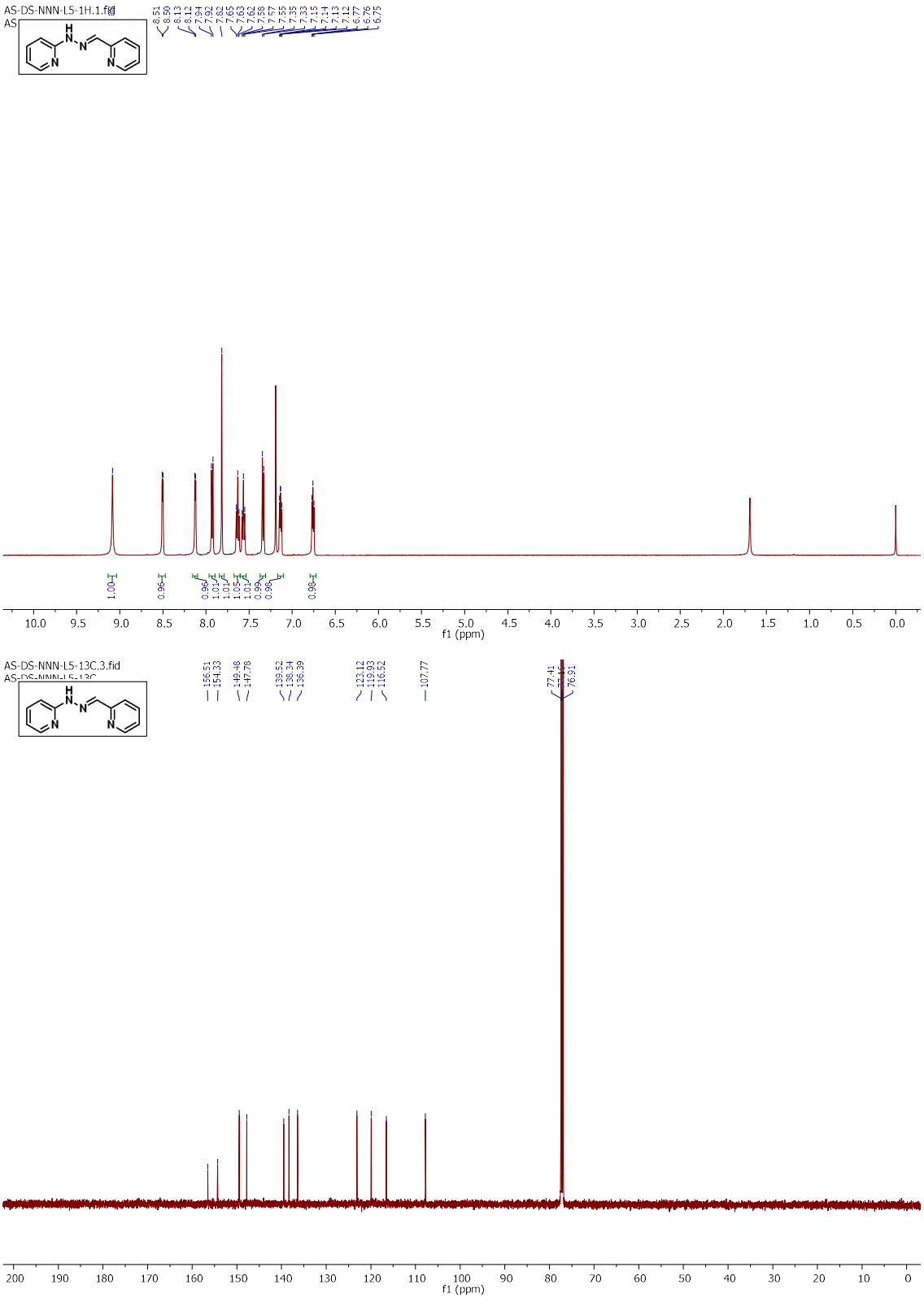


Figure S31. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **L-6** in $CDCl_3$.

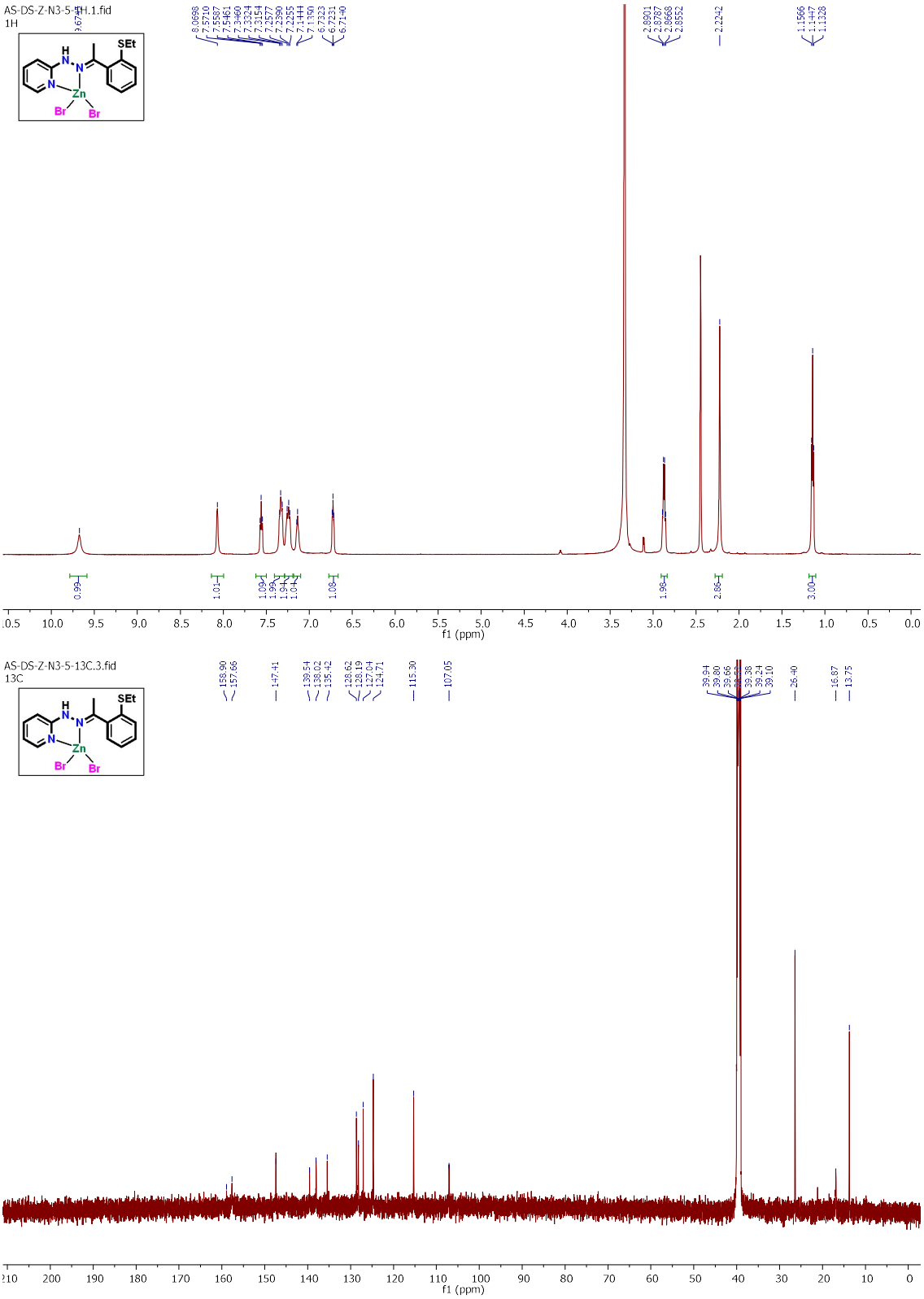


Figure S32. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **Zn-5** in DMSO-d_6.

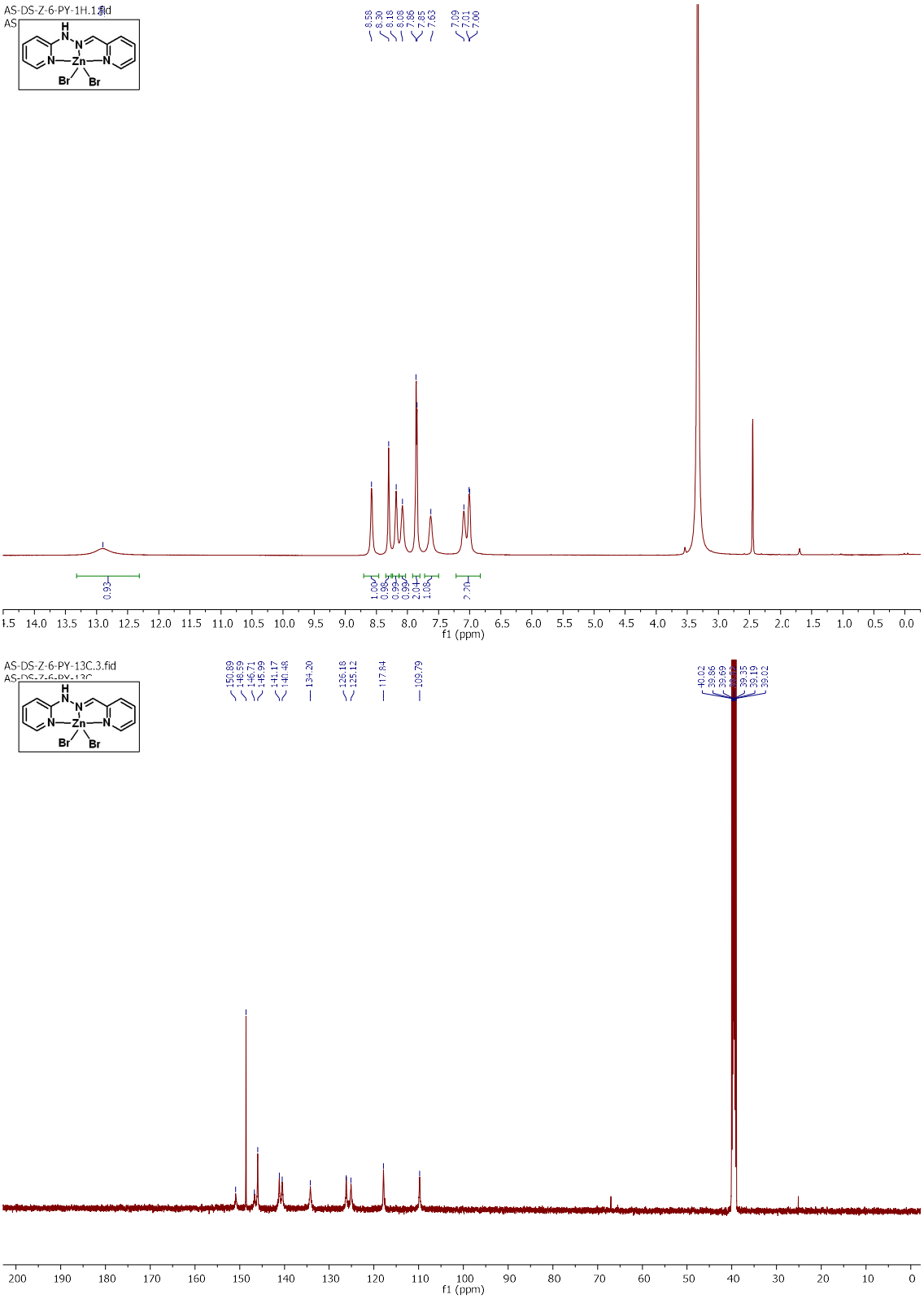


Figure S33. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **Zn-6** in DMSO-d_6.

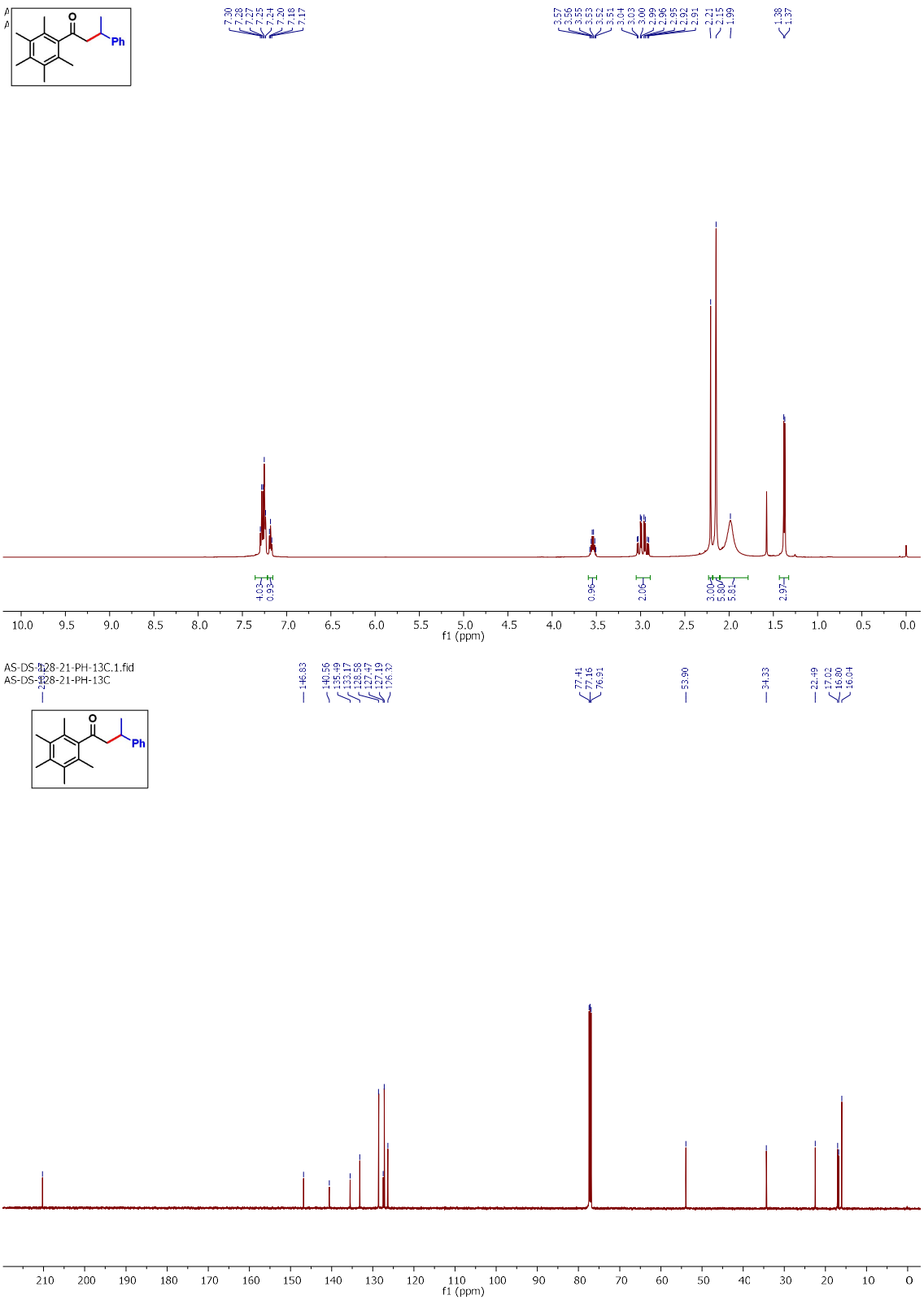


Figure S34. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3aa** in $CDCl_3$.

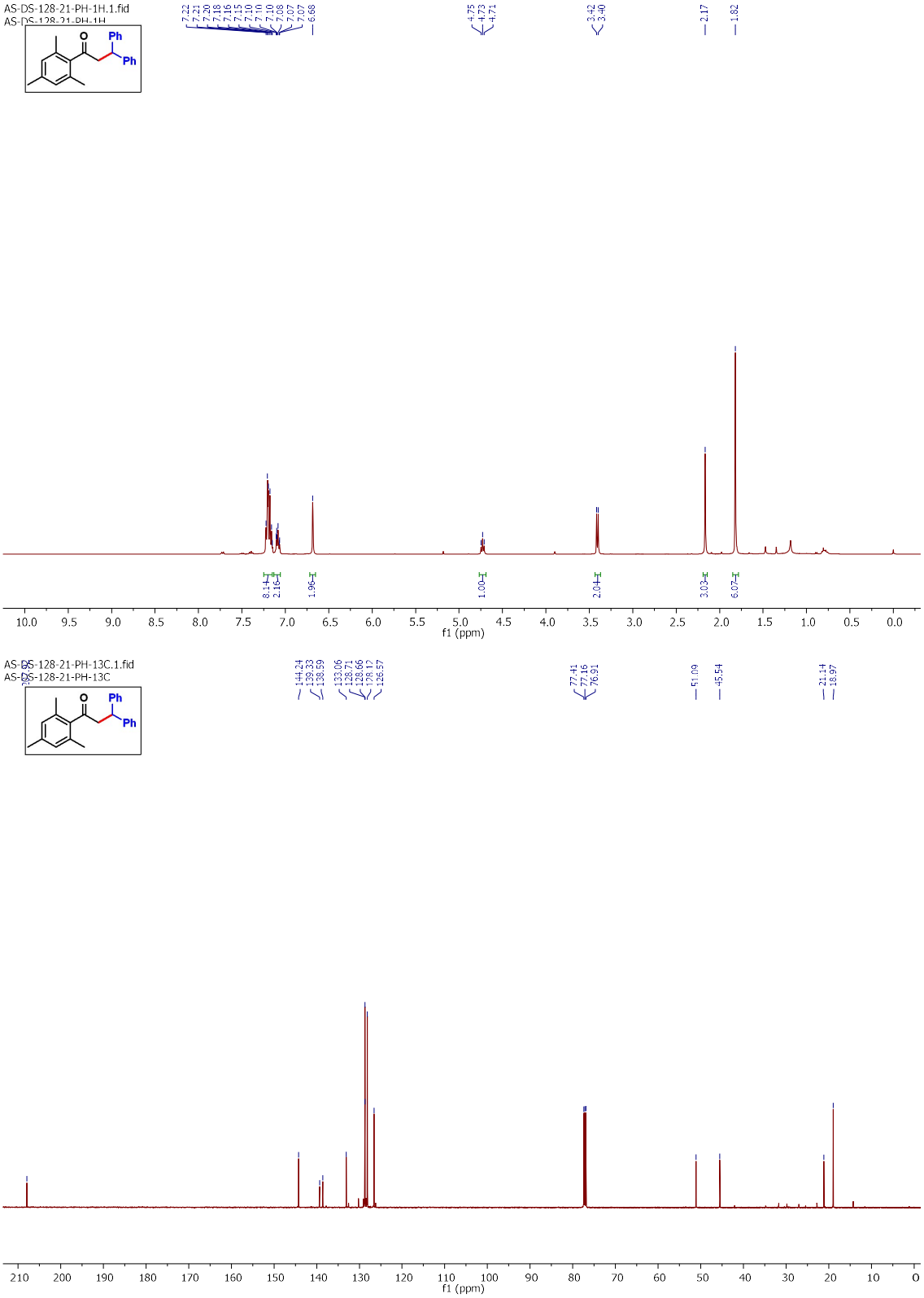


Figure S35. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ab** in $CDCl_3$.

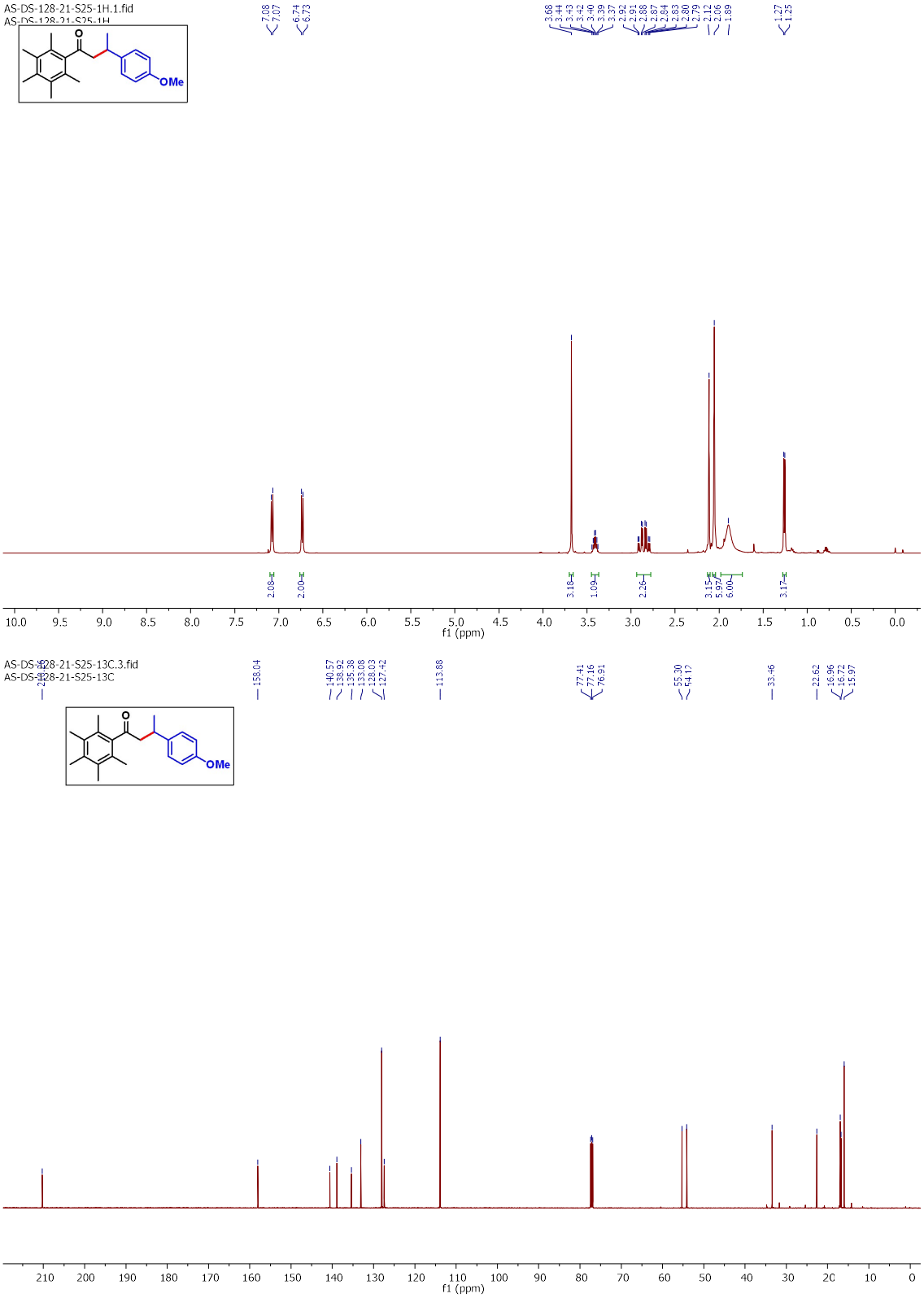


Figure S36. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ac** in $CDCl_3$.

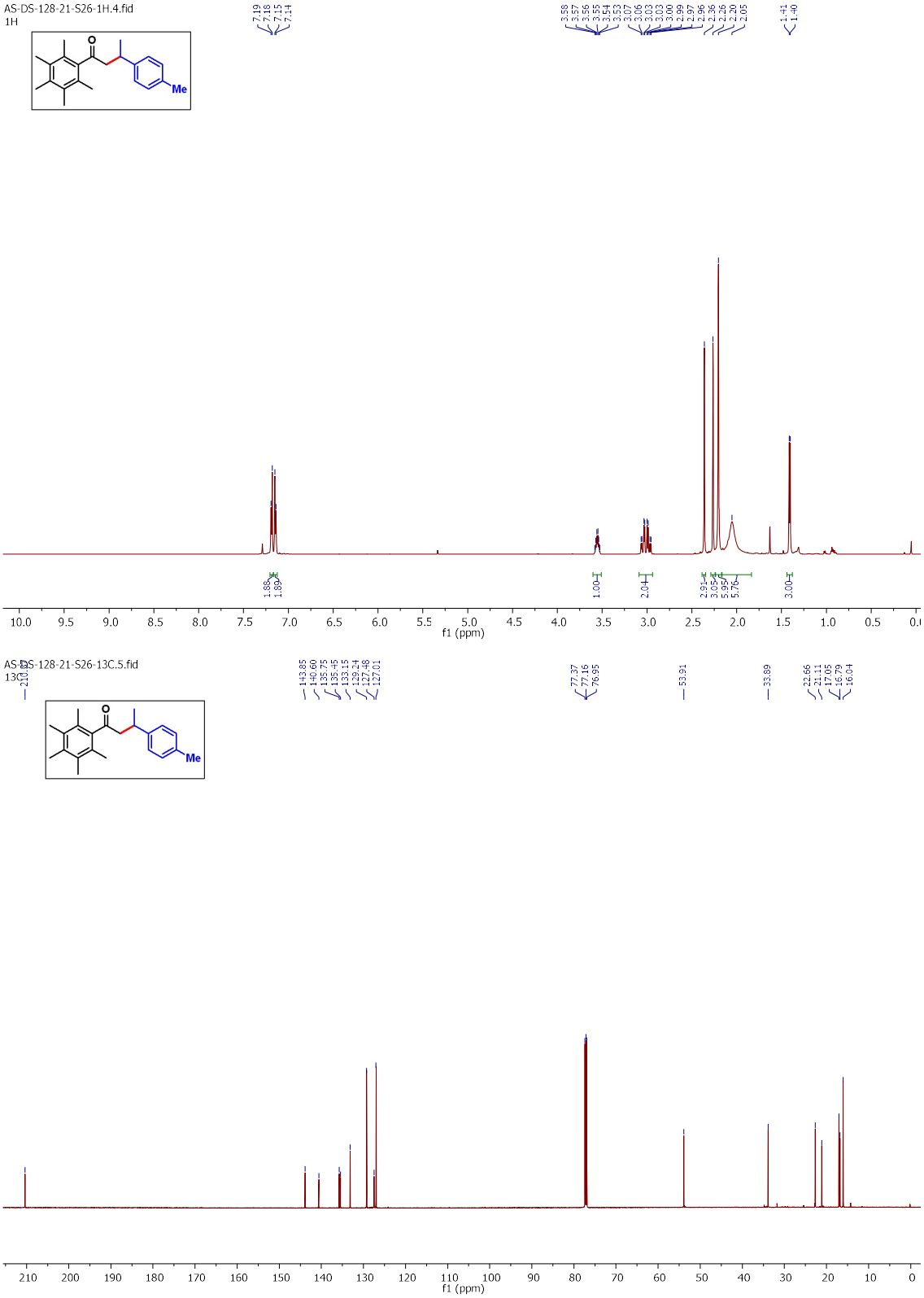


Figure S37. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3ad** in $CDCl_3$.

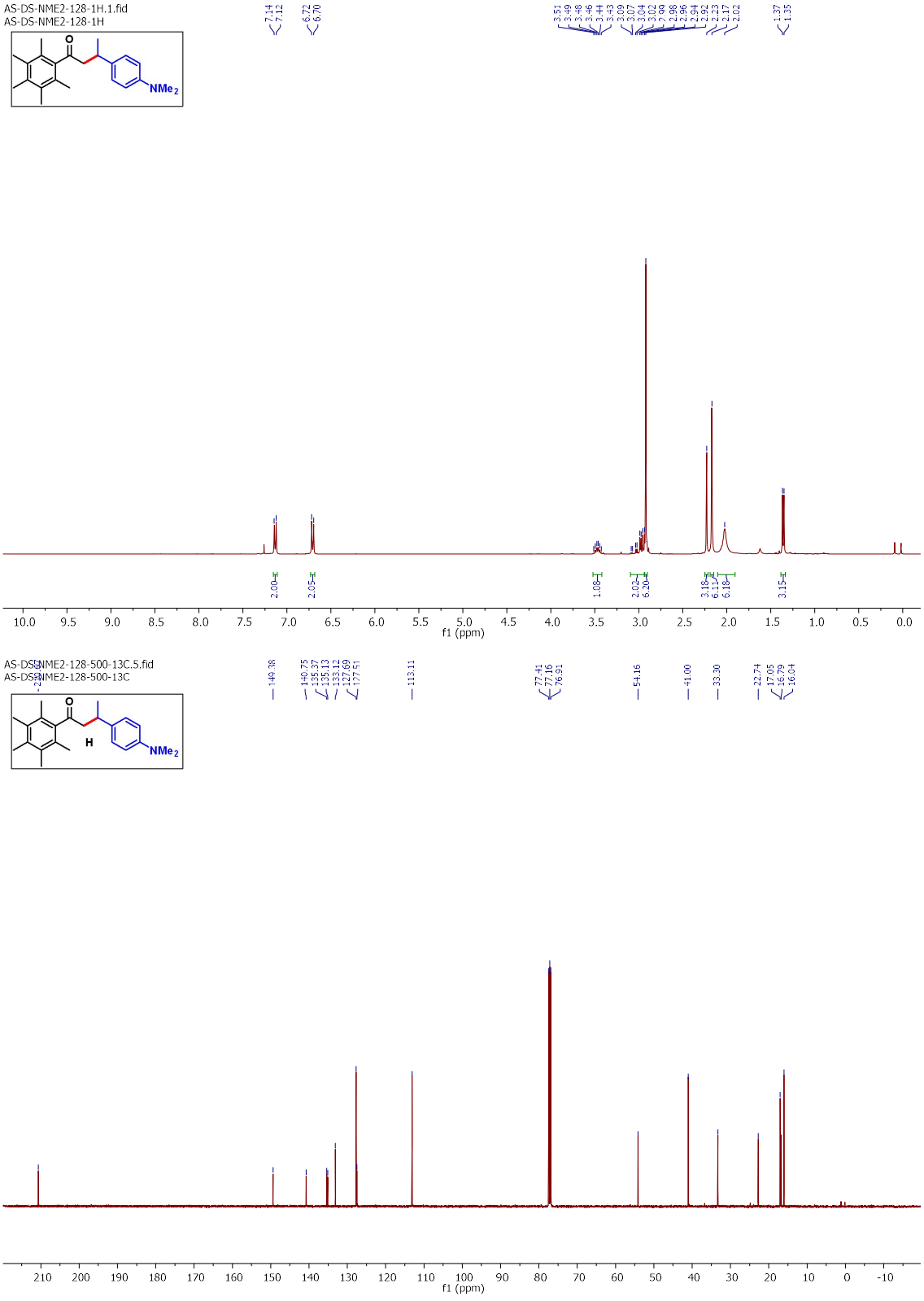
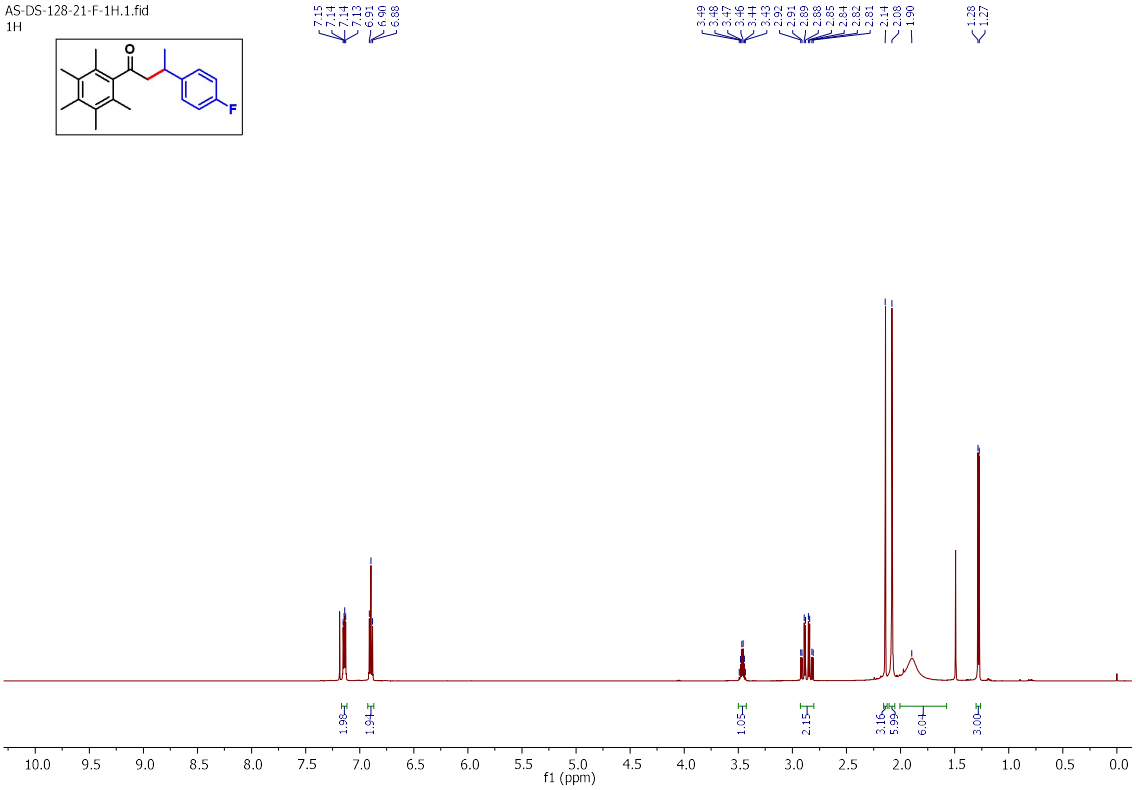
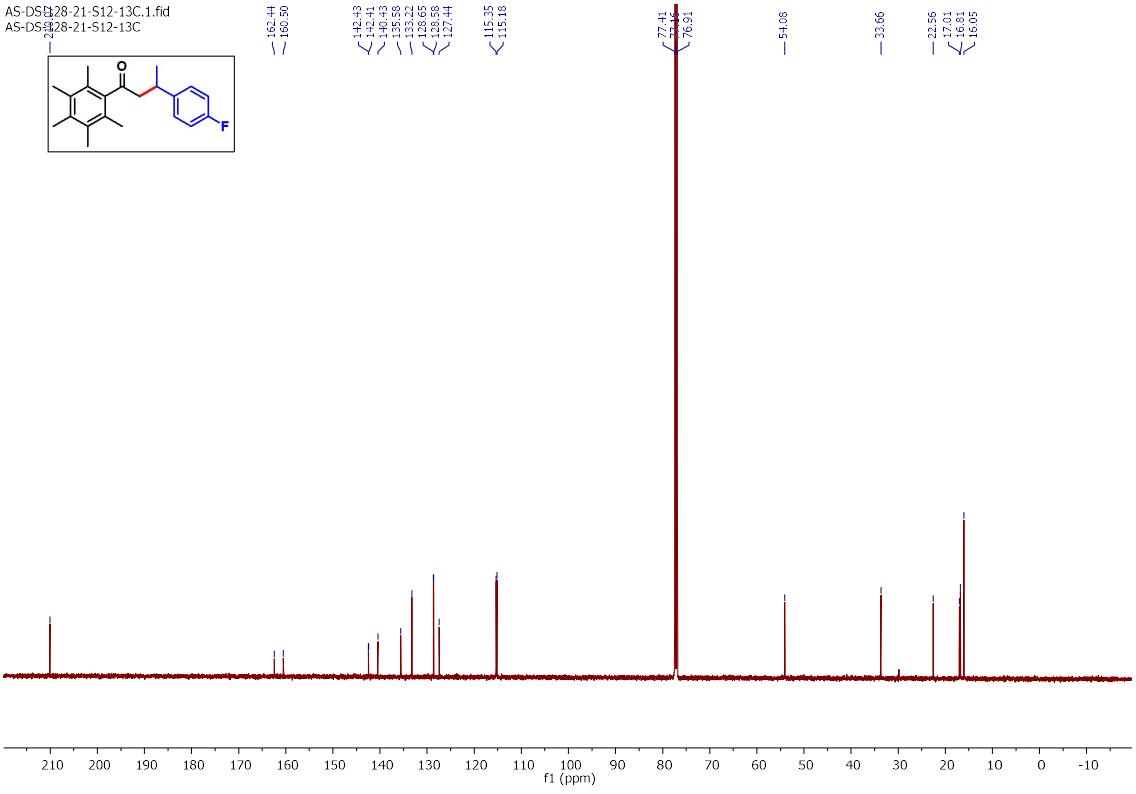


Figure S38. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3ad** in $CDCl_3$.


AS-DS-128-21-F-1H.1.fid
1H
7.15
7.14
7.14
7.13
6.91
6.90
6.88
3.49
3.48
3.47
3.46
3.44
3.43
2.92
2.91
2.89
2.88
2.85
2.84
2.82
2.81
2.14
2.08
1.90
1.28
1.27
F
1.96
1.94
1.05
2.15
3.16
5.99
6.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


AS-DS-128-21-S12-13C.1.fid
AS-DS-128-21-S12-13C
162.44
160.50
142.43
142.41
140.43
135.58
133.22
128.65
128.58
127.44
115.35
115.18
77.41
77.16
76.91
54.08
33.66
22.56
17.01
16.81
16.05
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

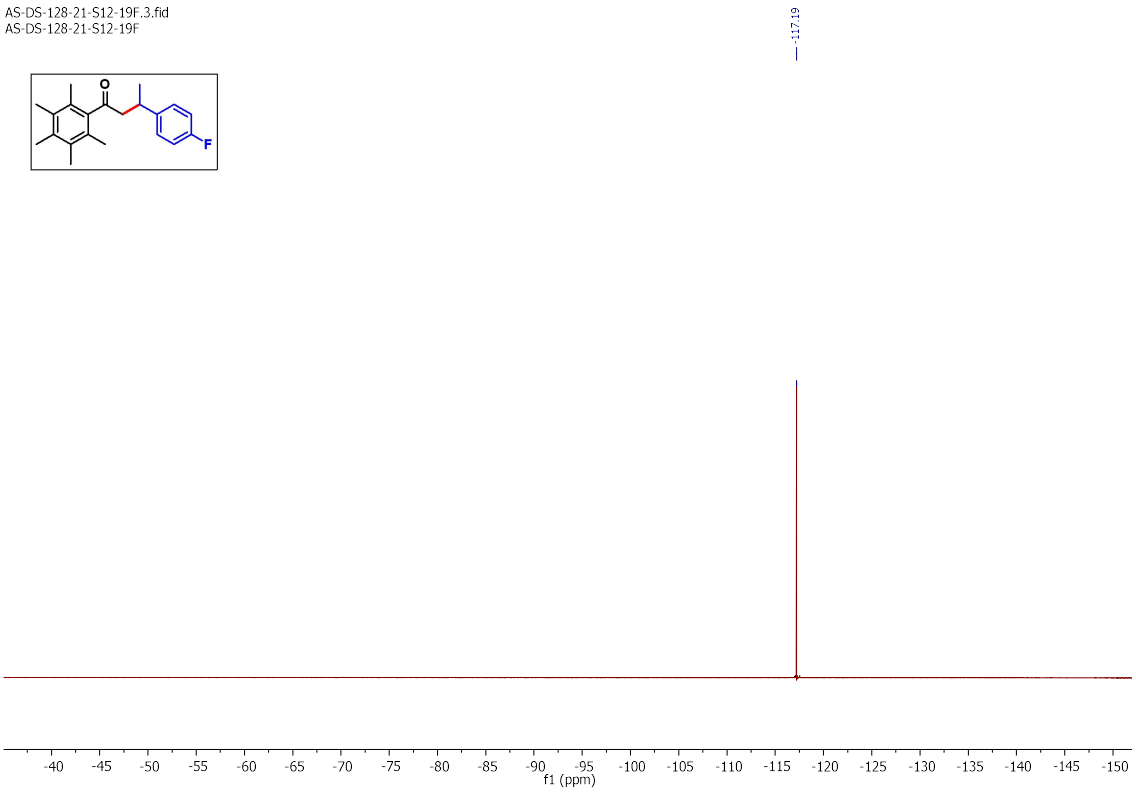


Figure S39. ^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ NMR (125 MHz) and ^{19}F $\{^{1}H\}$ NMR (470 MHz) spectrum of Compound **3af** in $CDCl_3$.

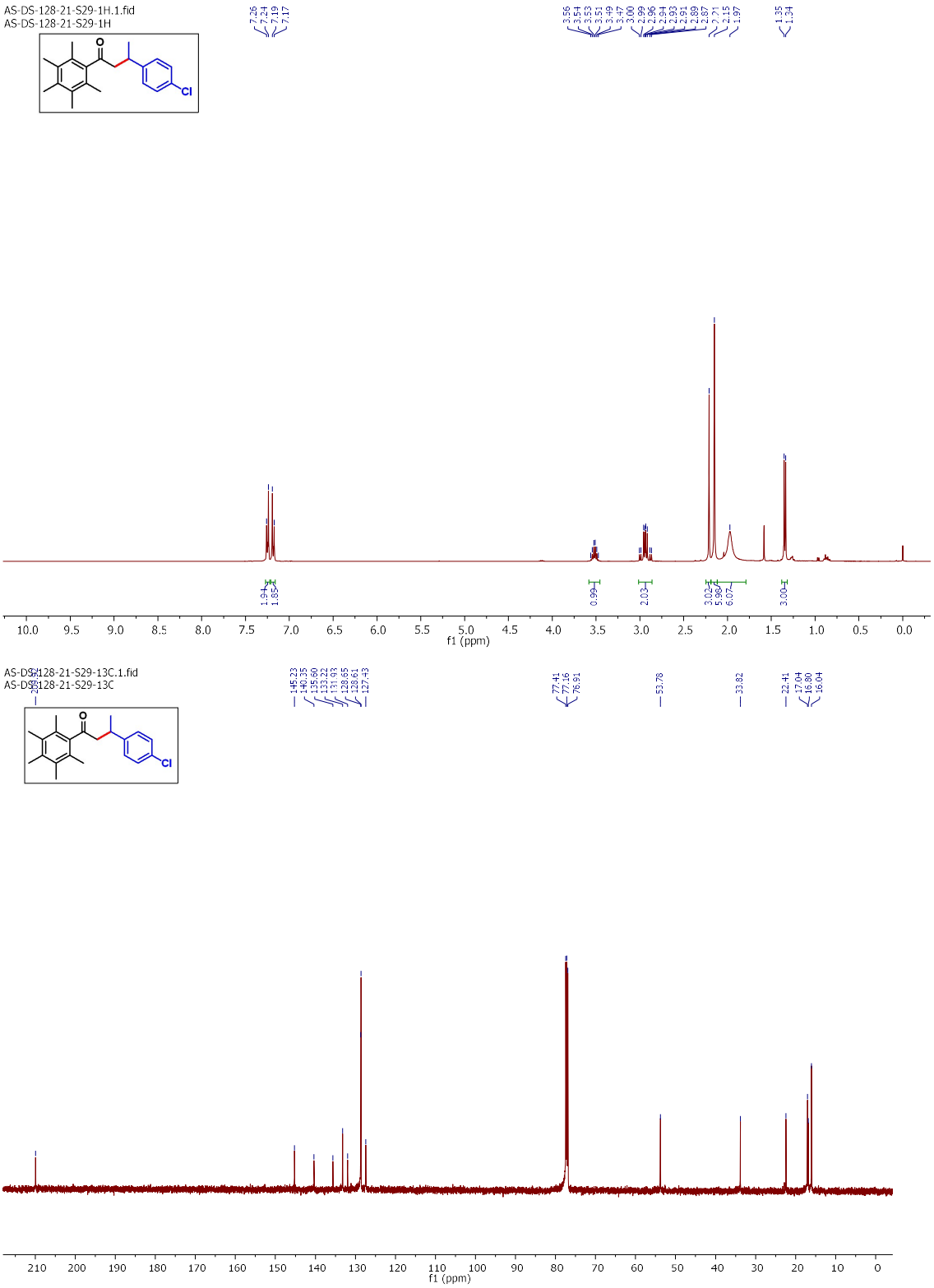


Figure S40. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ag** in $CDCl_3$.

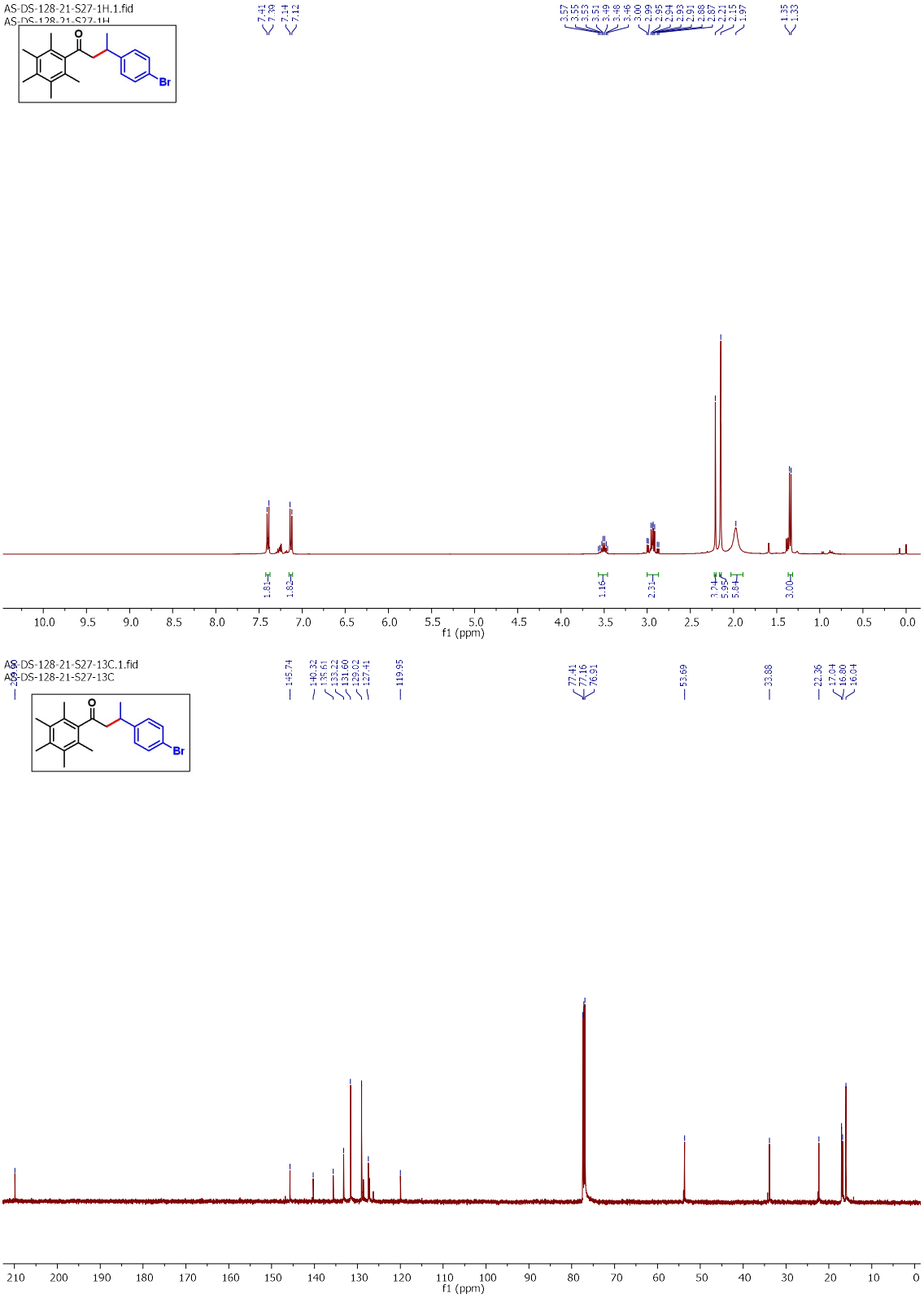


Figure S41. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ah** in $CDCl_3$.

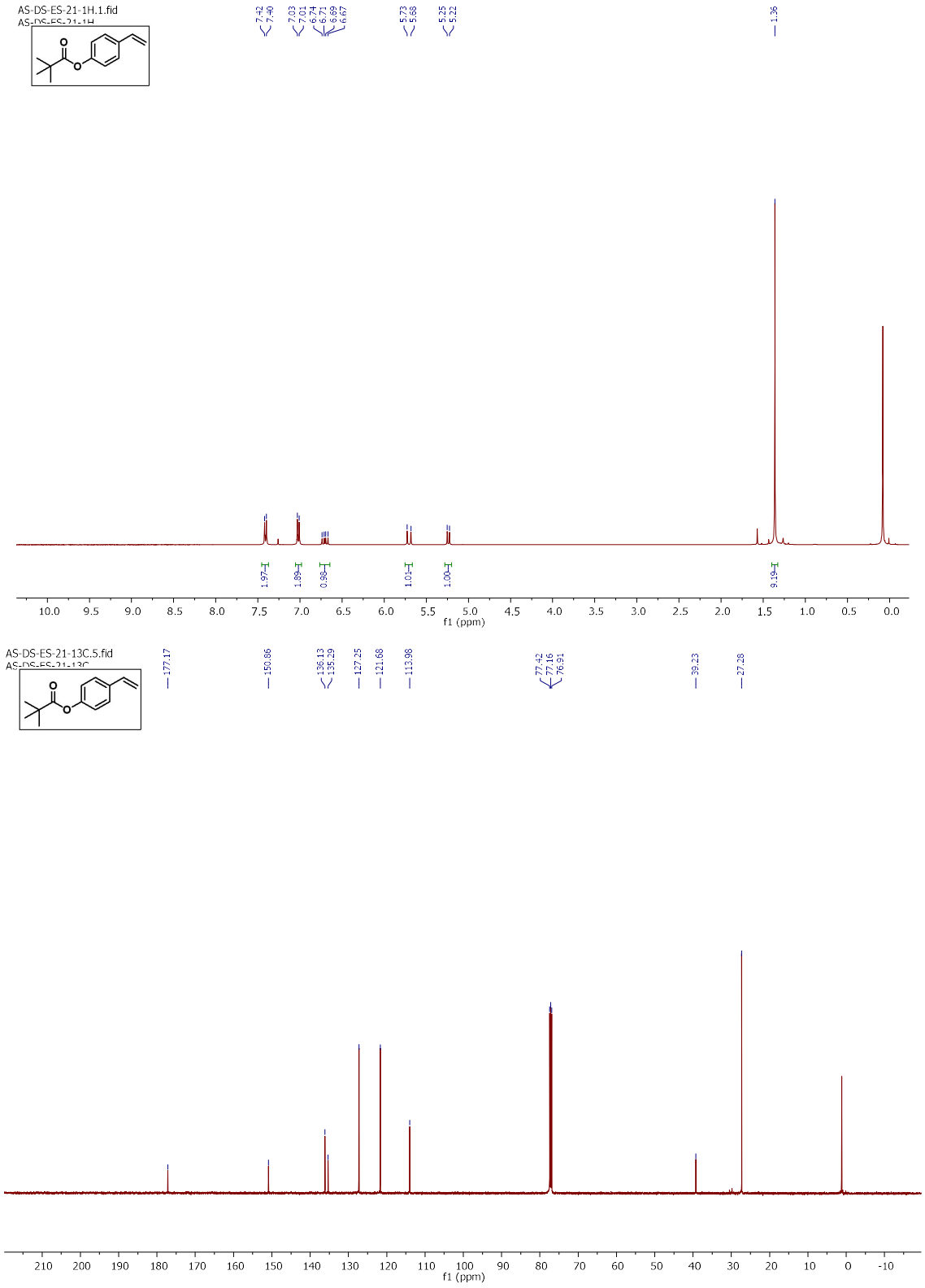


Figure S42. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ak** in $CDCl_3$.

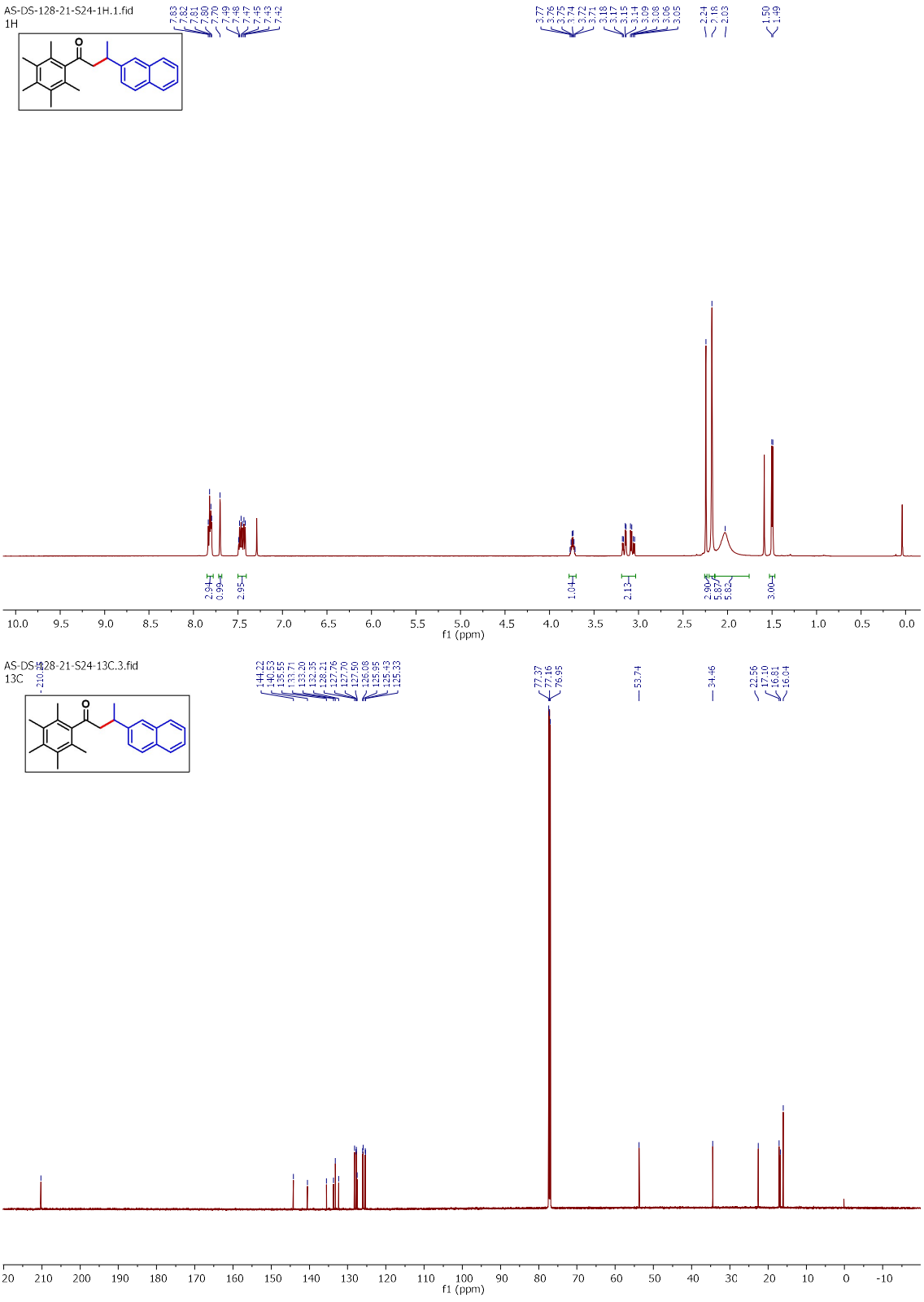


Figure S43. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3am** in $CDCl_3$.

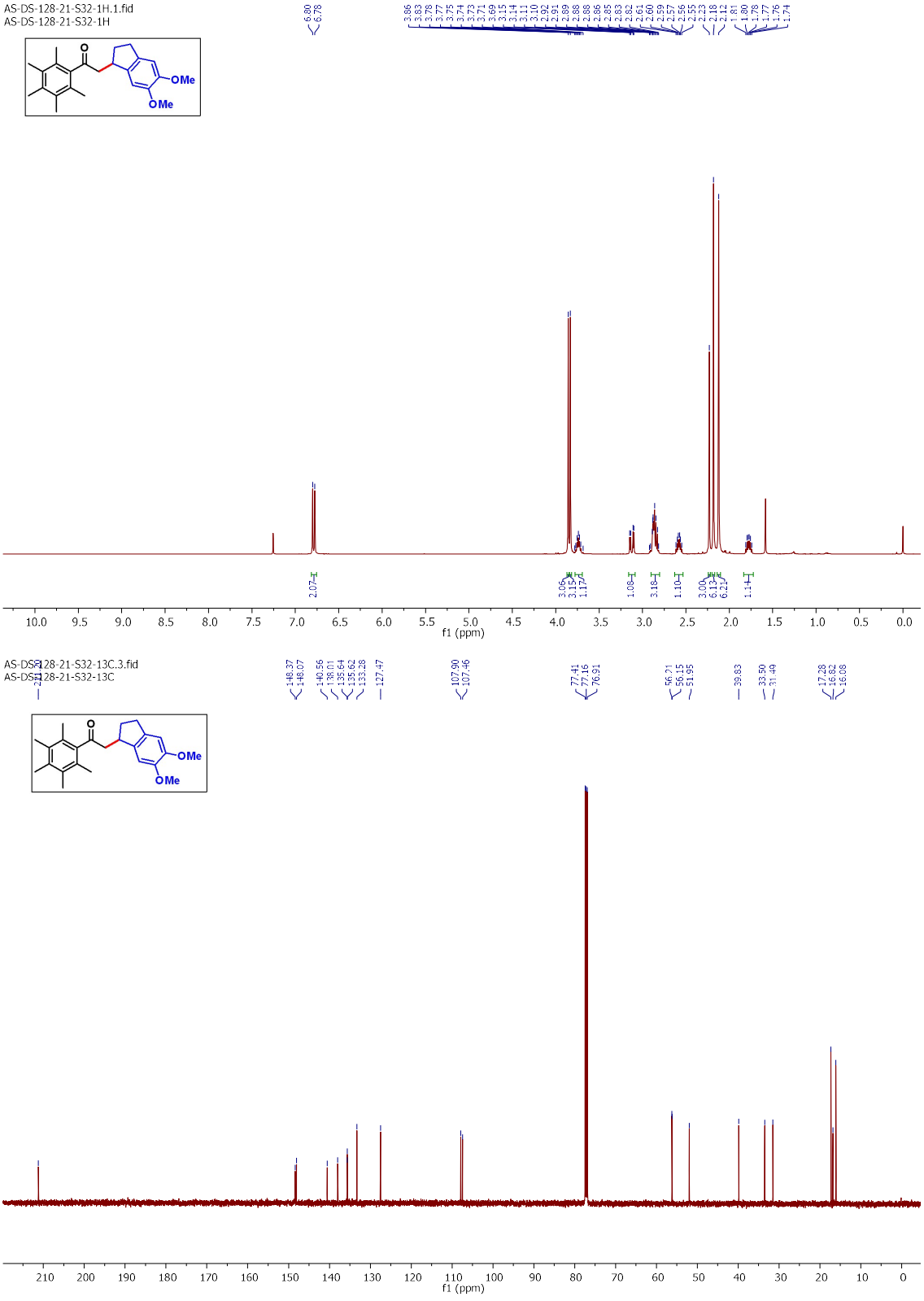


Figure S44. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3an** in $CDCl_3$.

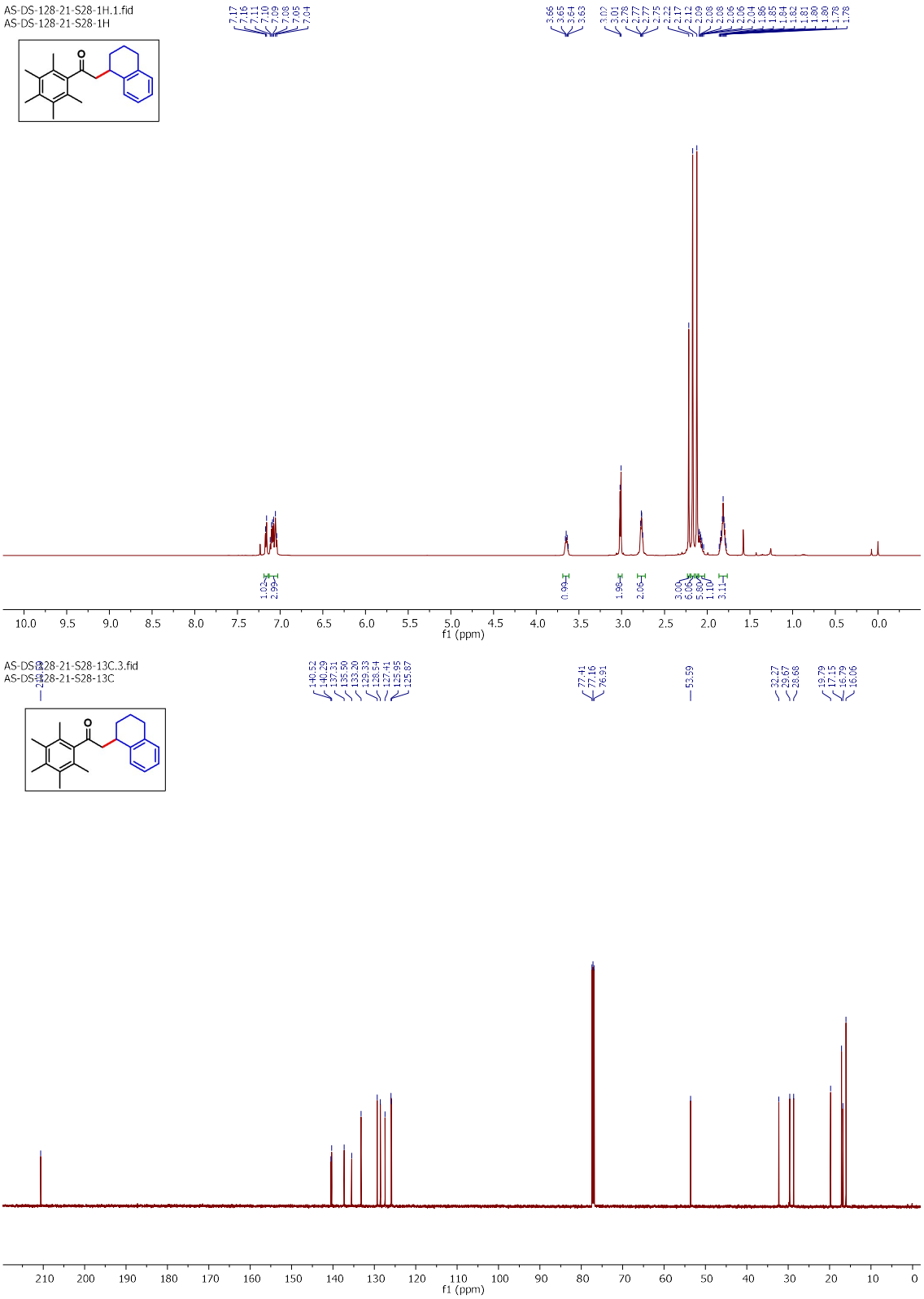


Figure S45. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ao** in $CDCl_3$.

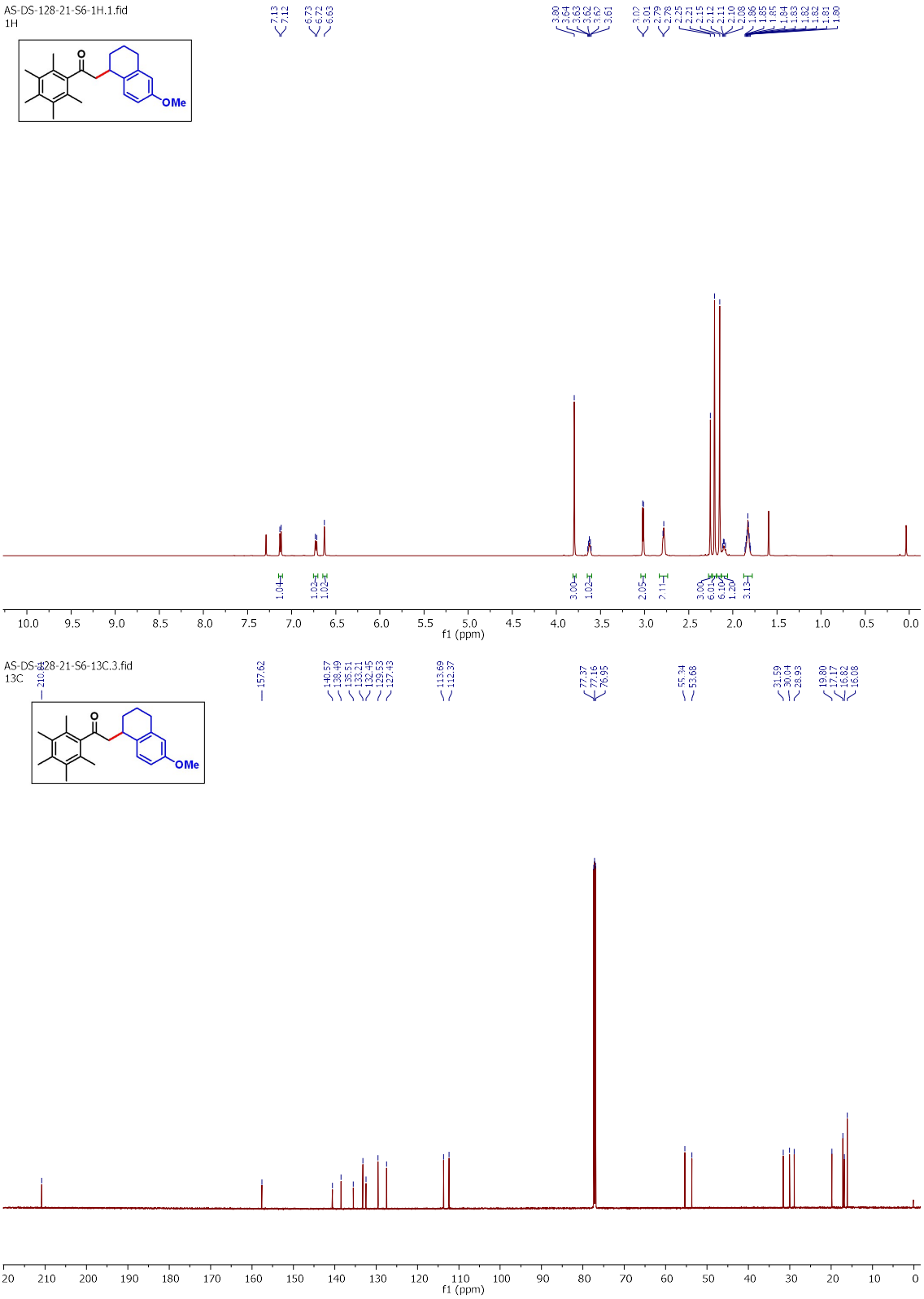


Figure S46. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3ap** in $CDCl_3$.

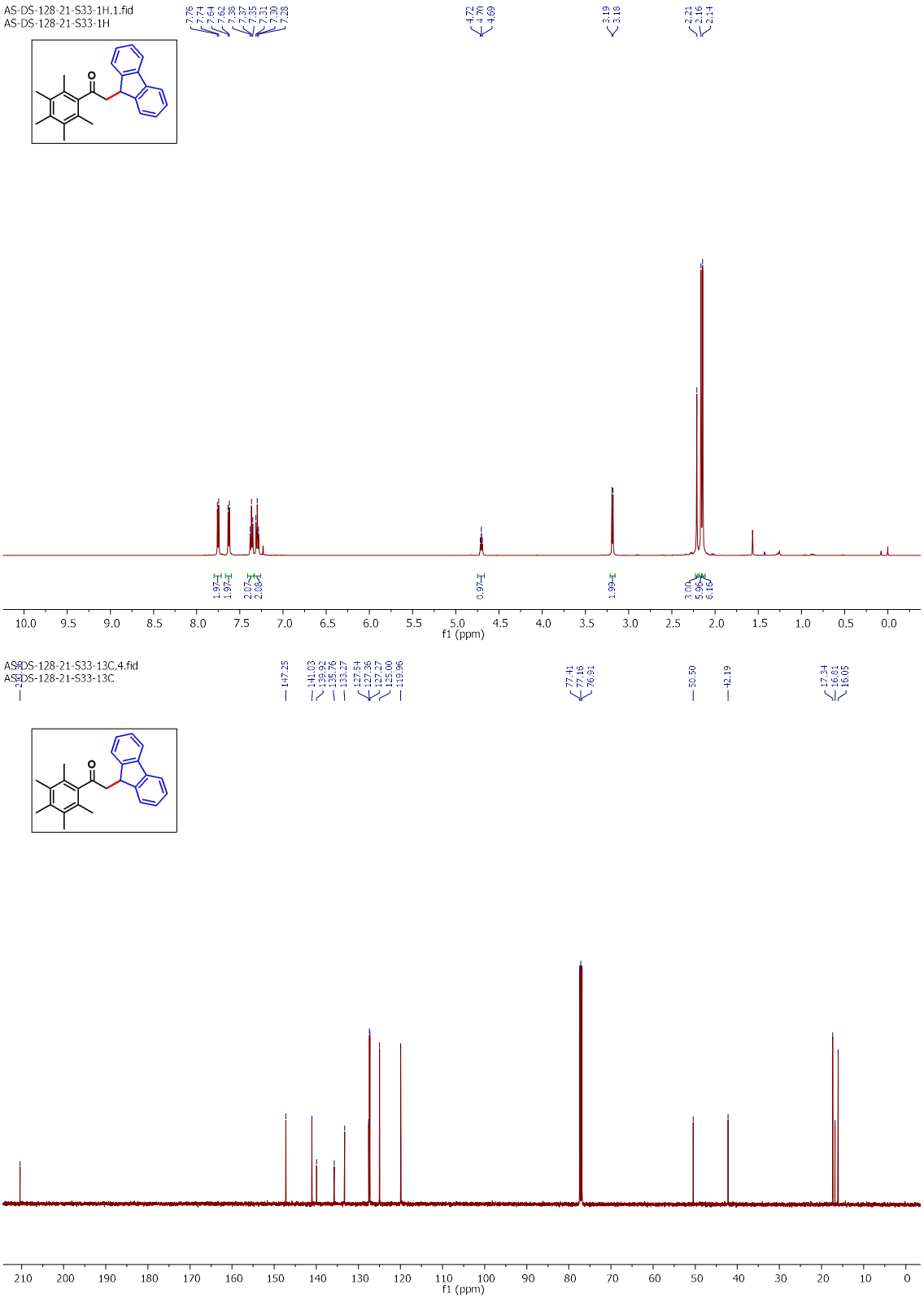


Figure S47. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3aq** in $CDCl_3$.

Figure S48. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ar** in $CDCl_3$.

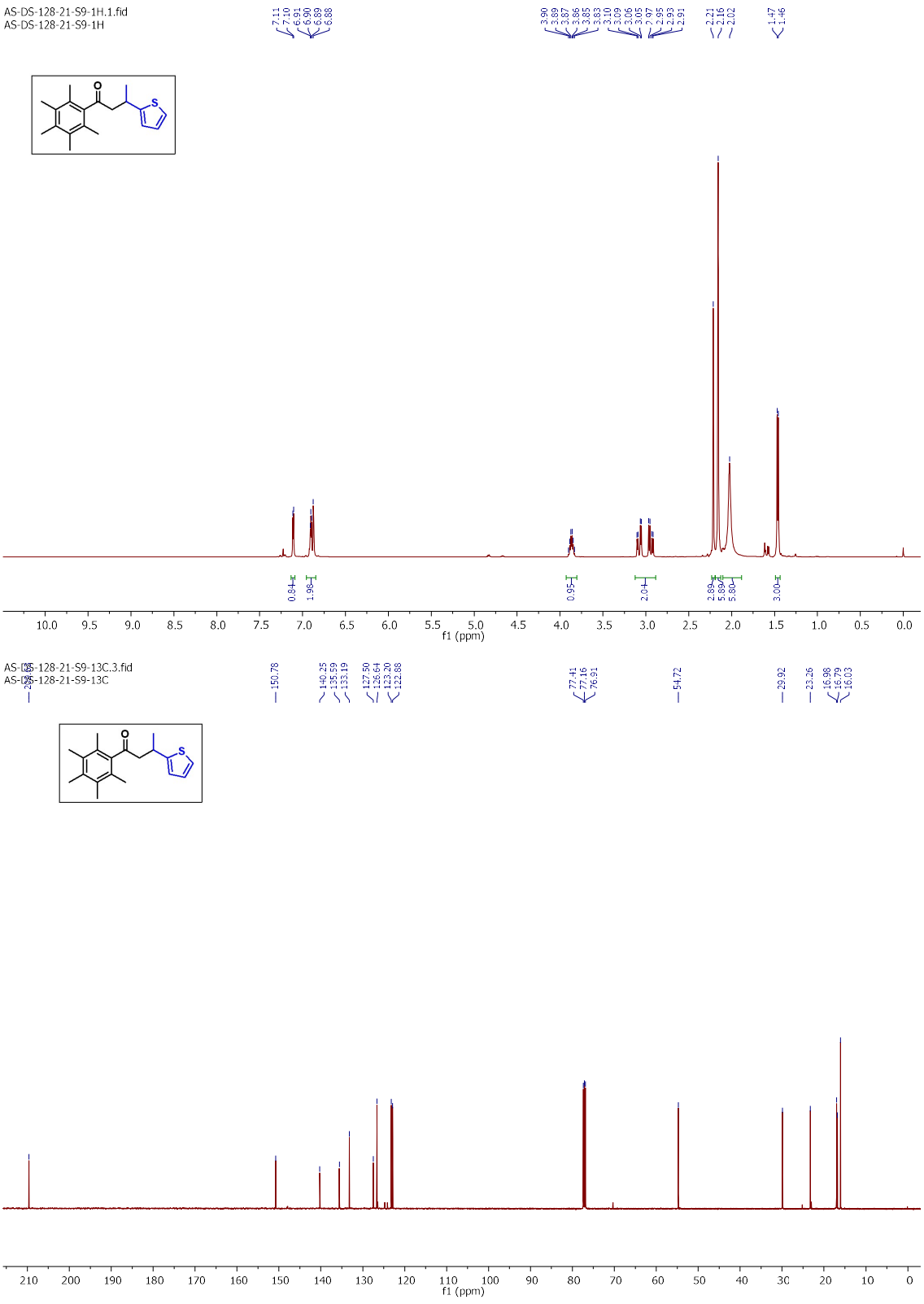


Figure S49. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3as** in $CDCl_3$.

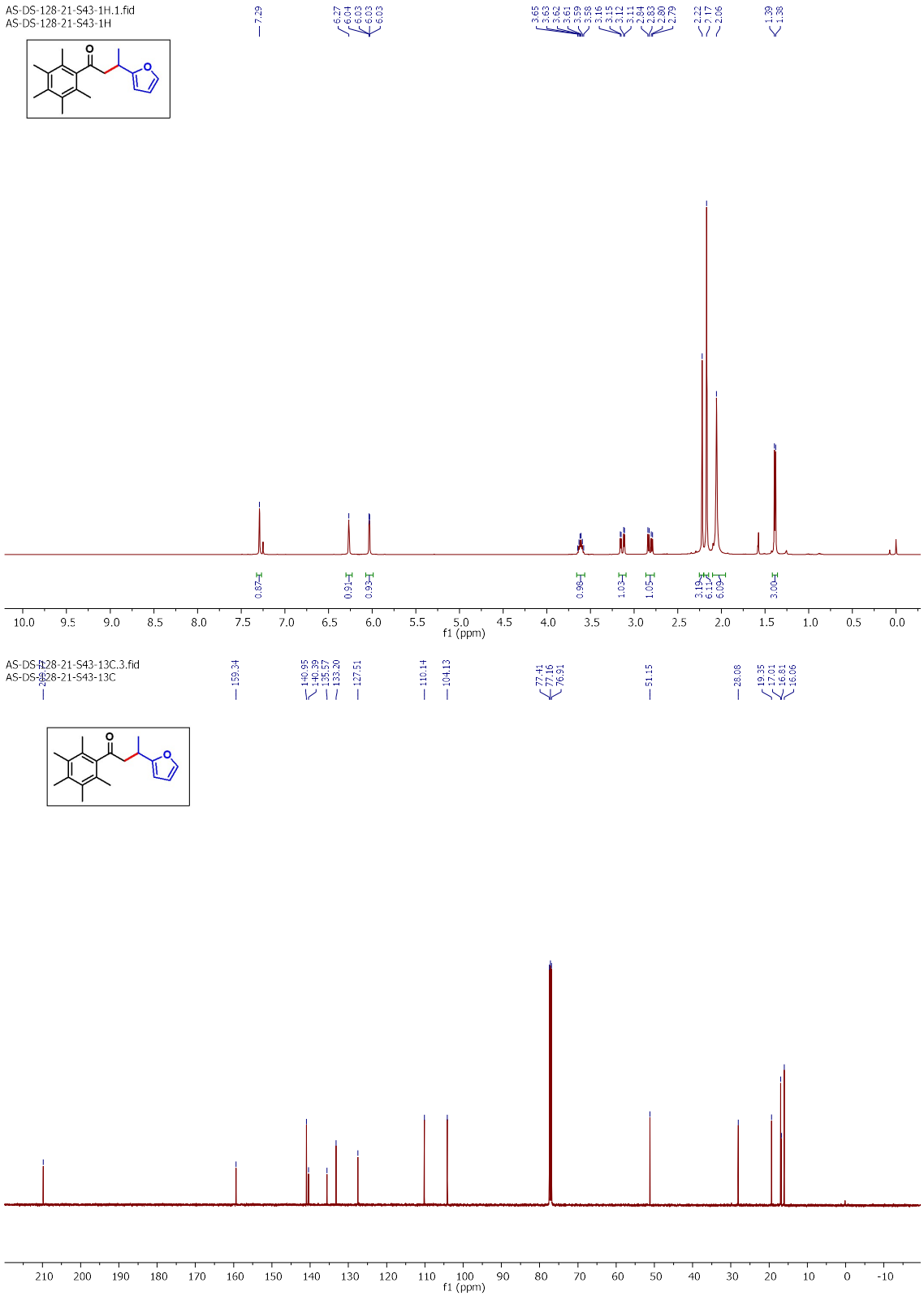


Figure S50. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3at** in $CDCl_3$.

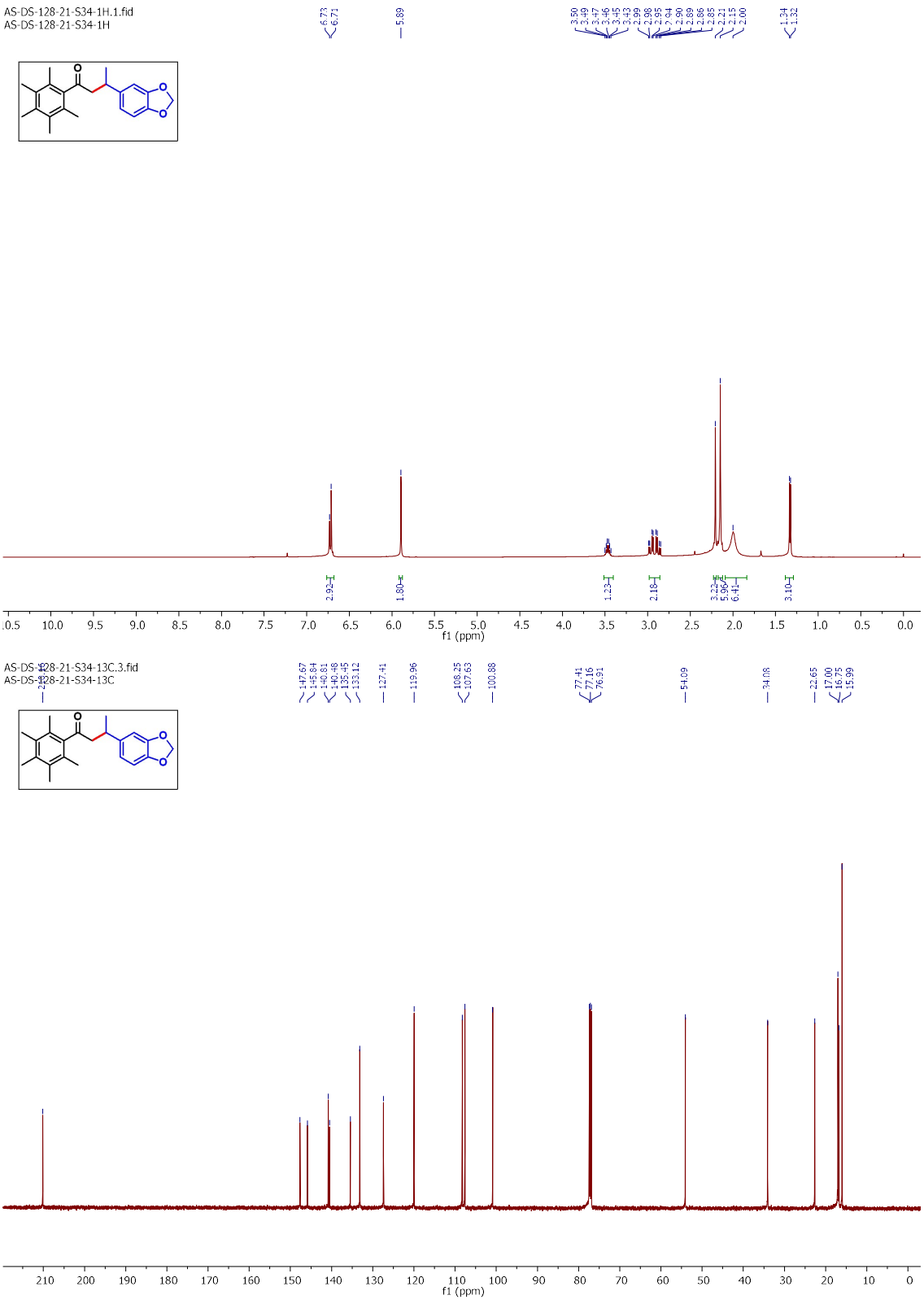


Figure S51. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3au** in $CDCl_3$.

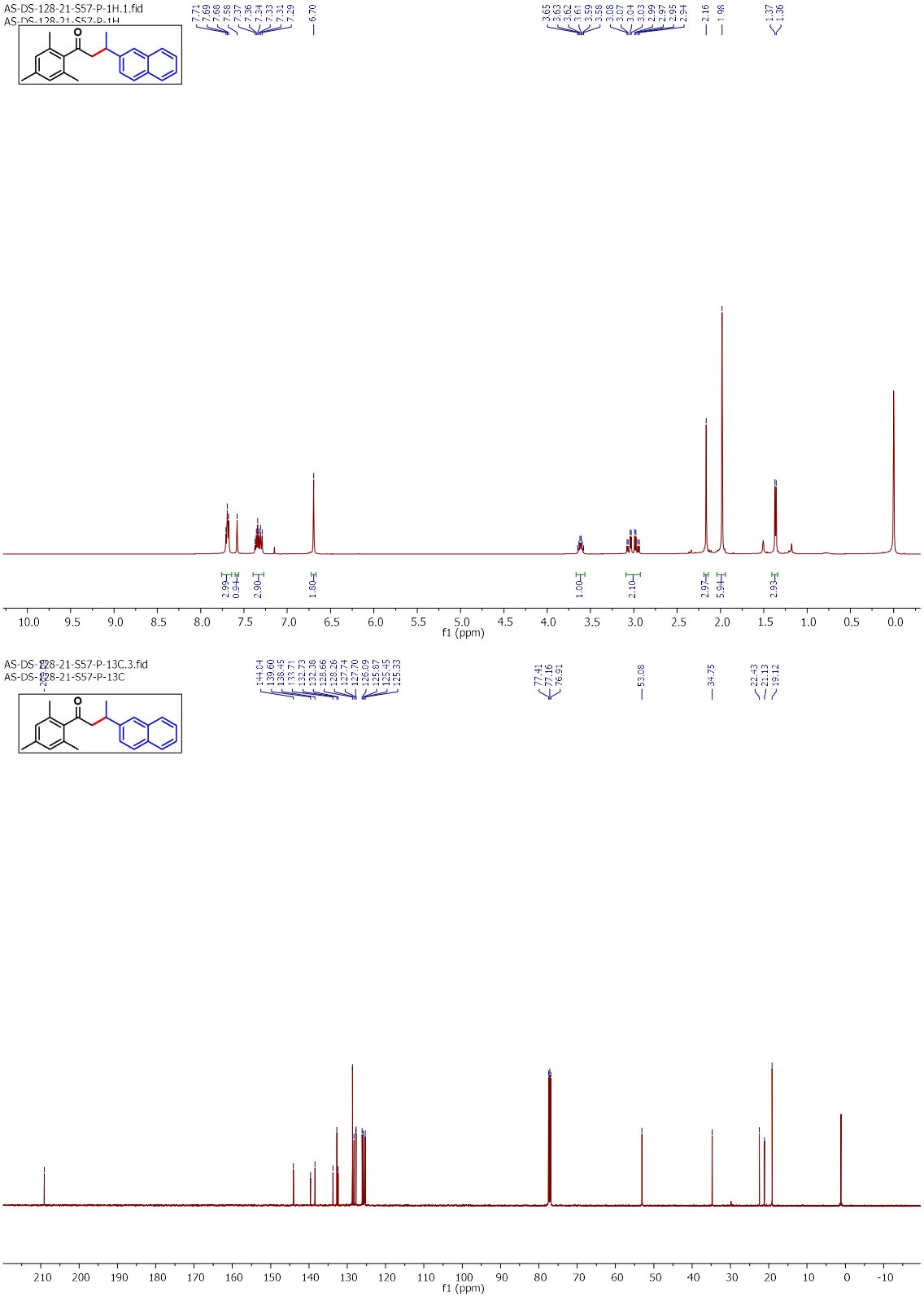


Figure S52. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3av** in $CDCl_3$.

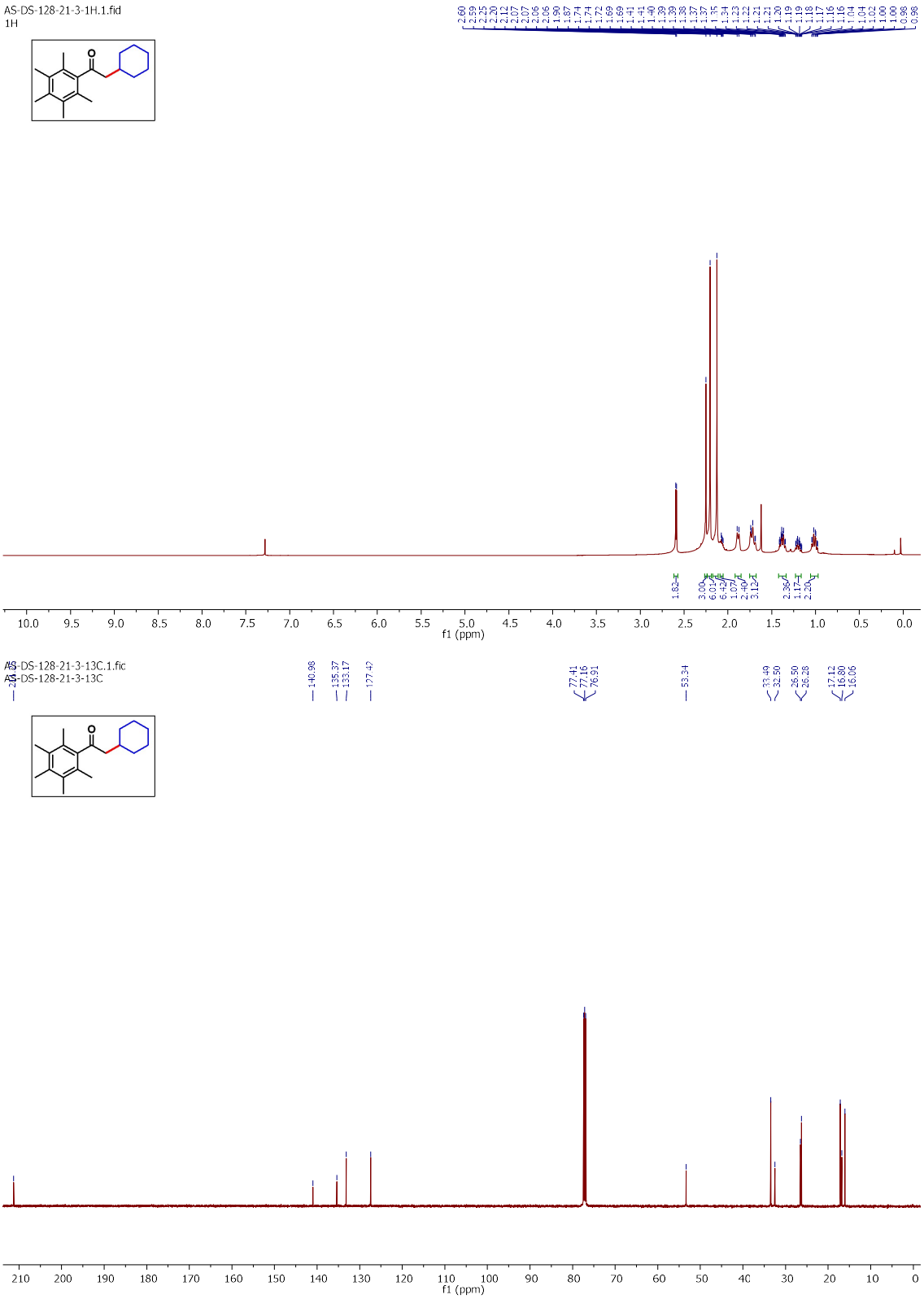


Figure S53. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ba** in $CDCl_3$.

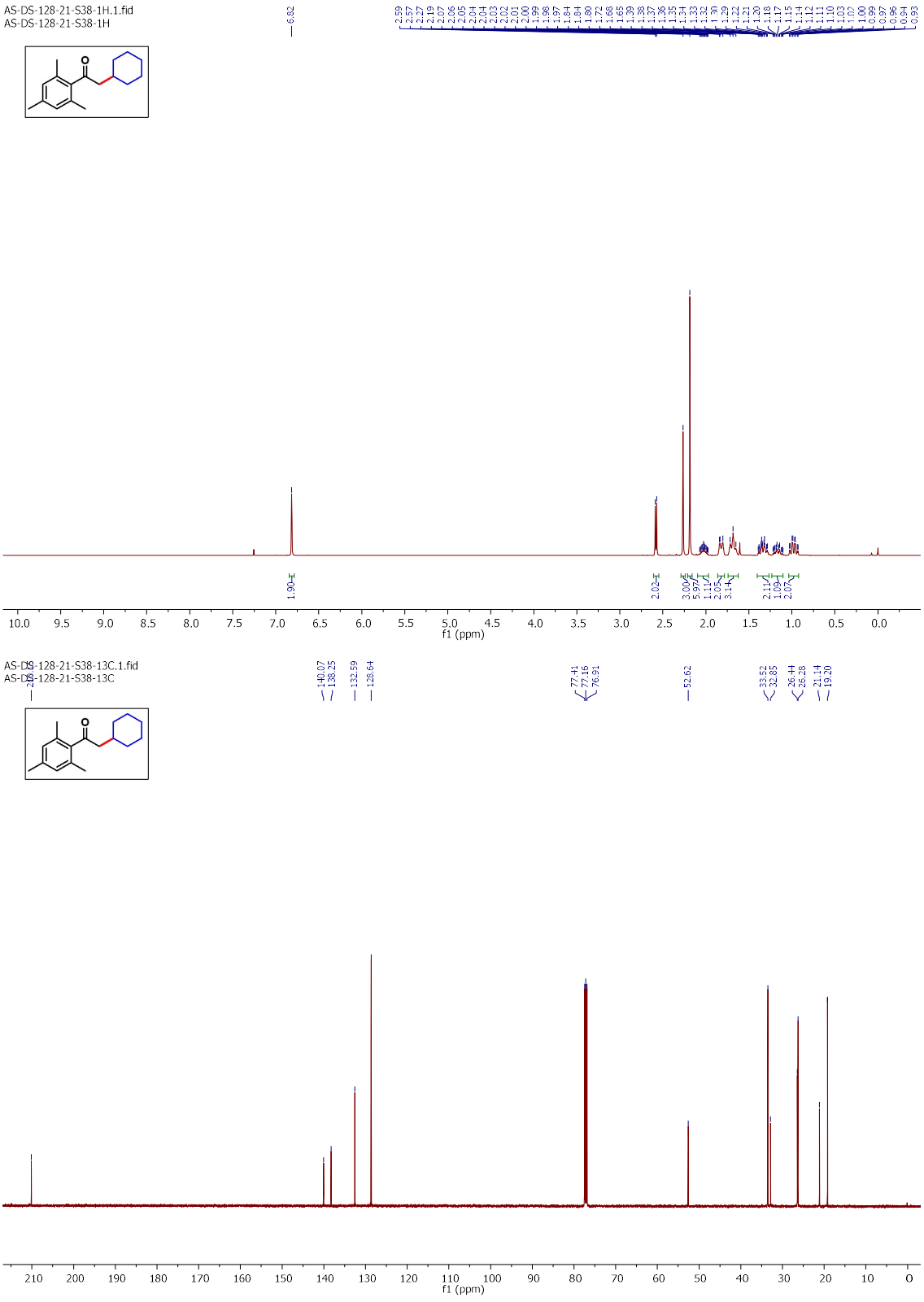


Figure S54. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bb** in $CDCl_3$.

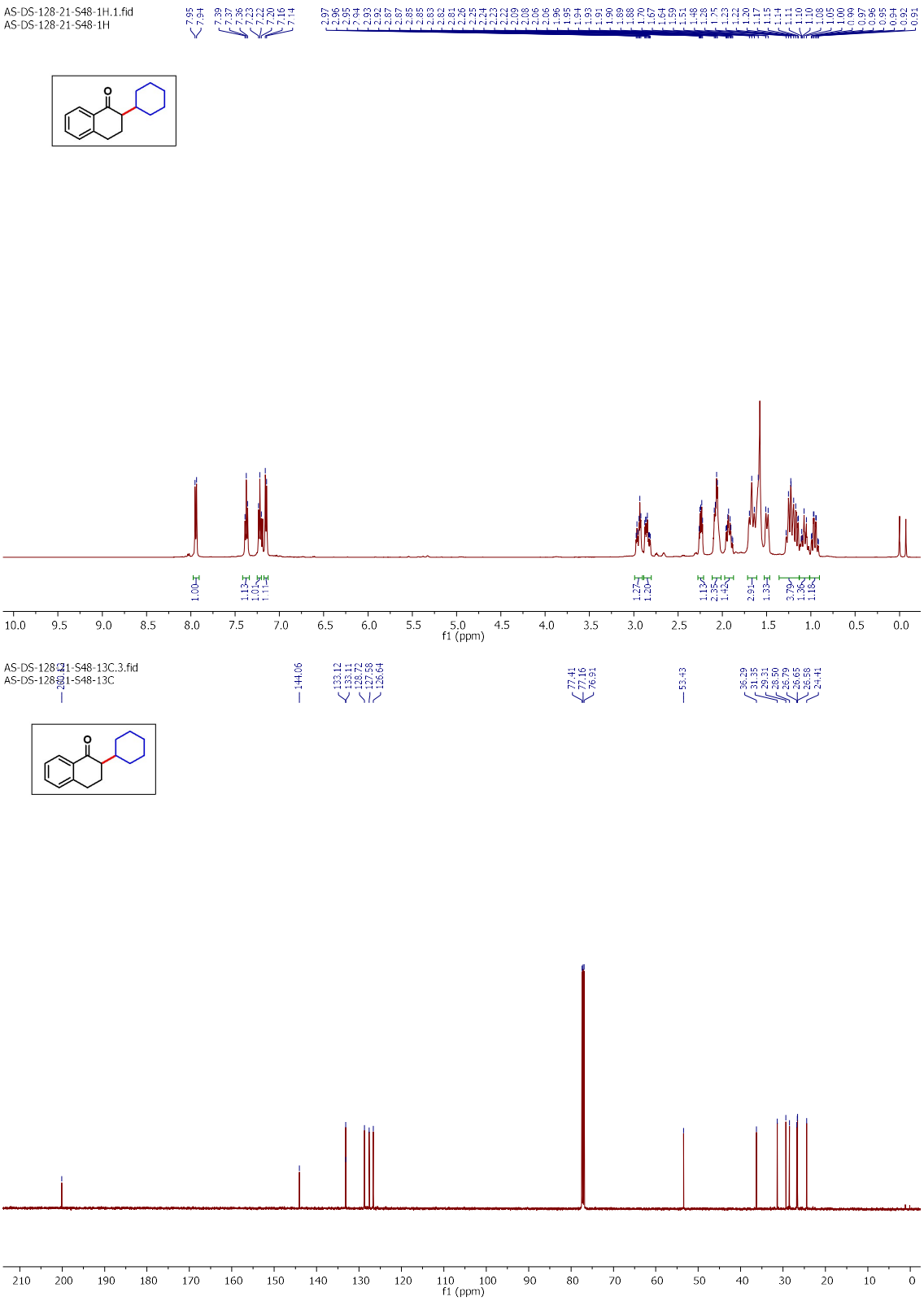


Figure S55. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bc** in $CDCl_3$.

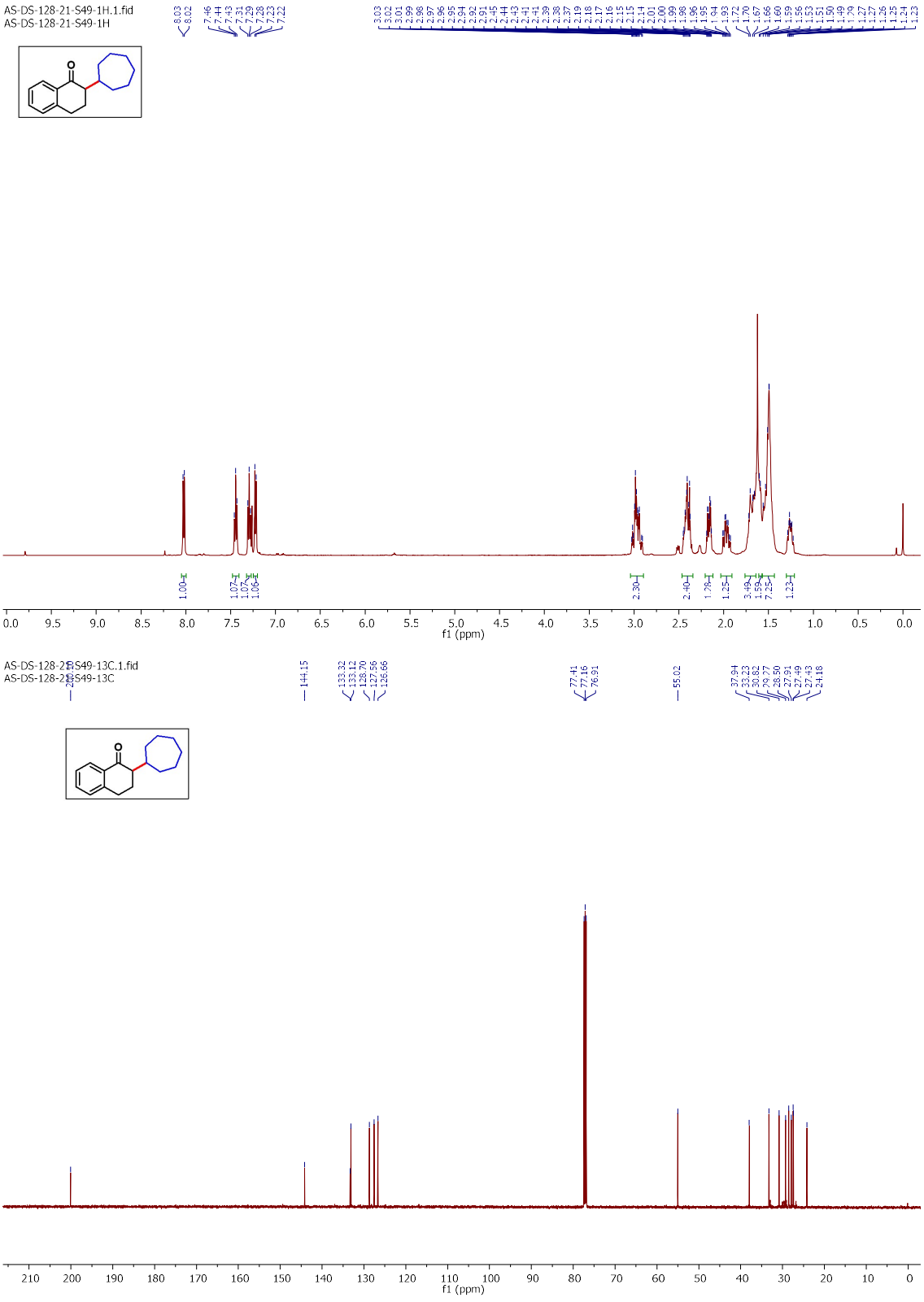


Figure S56. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bd** in $CDCl_3$.

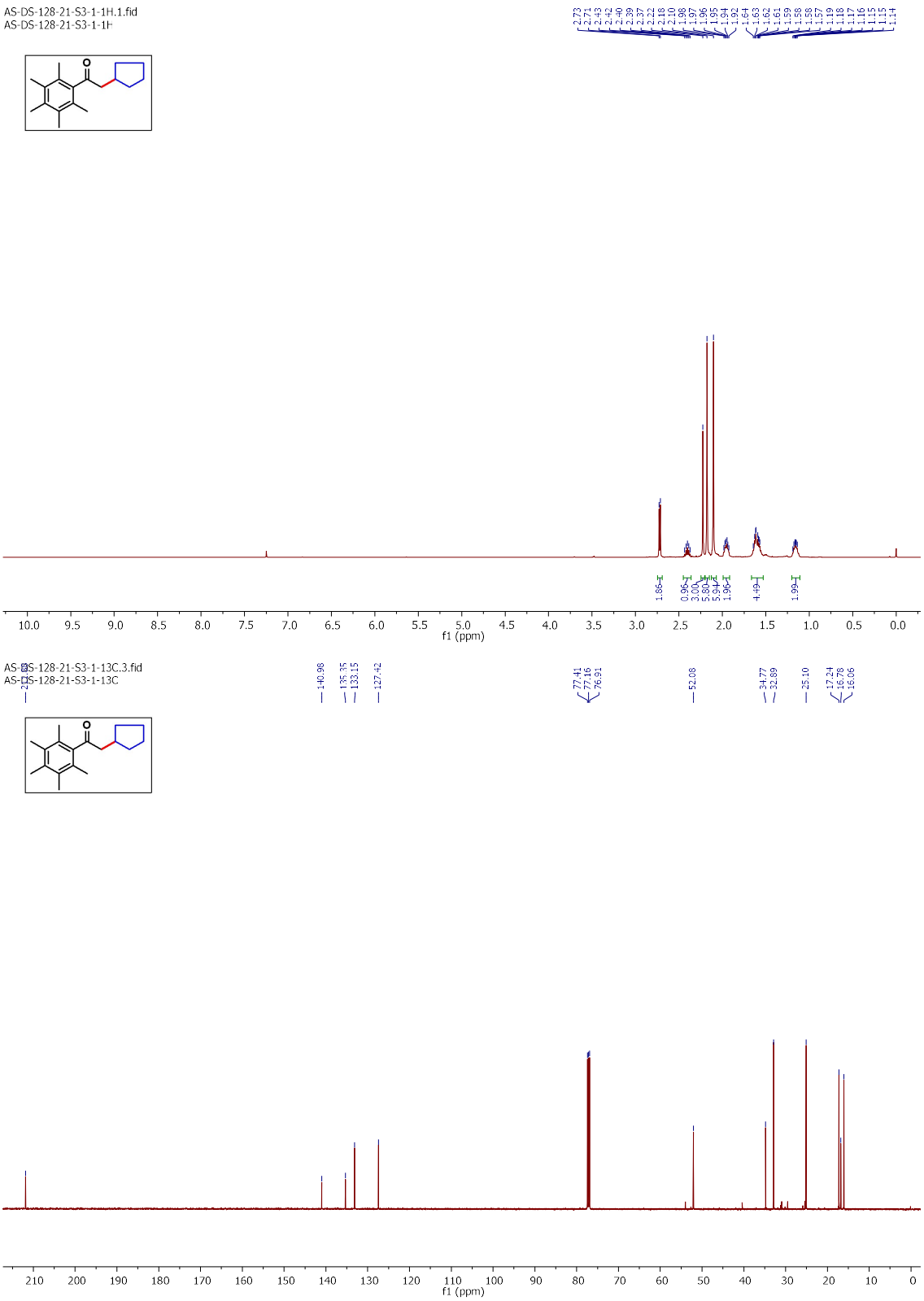


Figure S57. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bf** in $CDCl_3$.

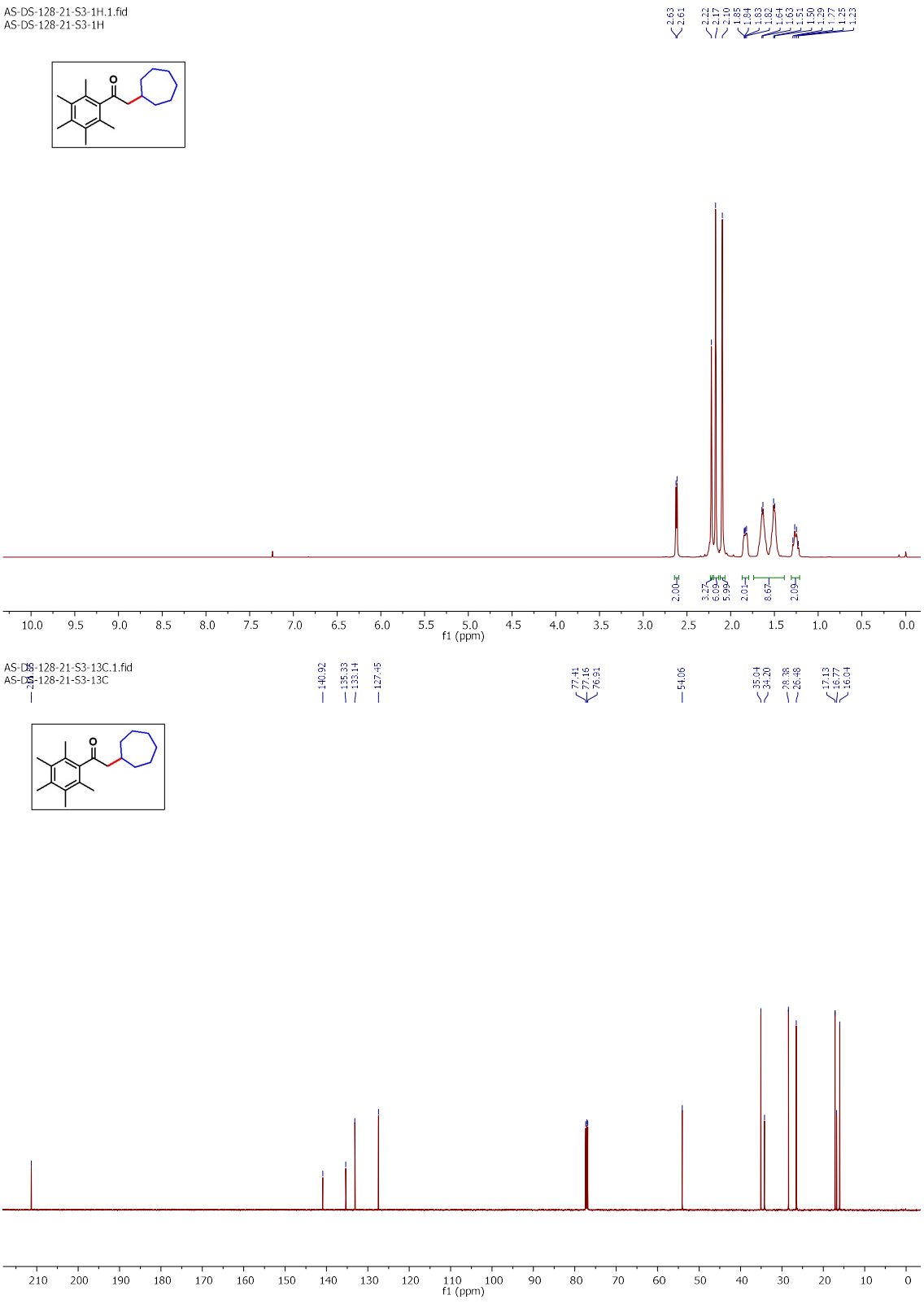


Figure S58. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bg** in $CDCl_3$.

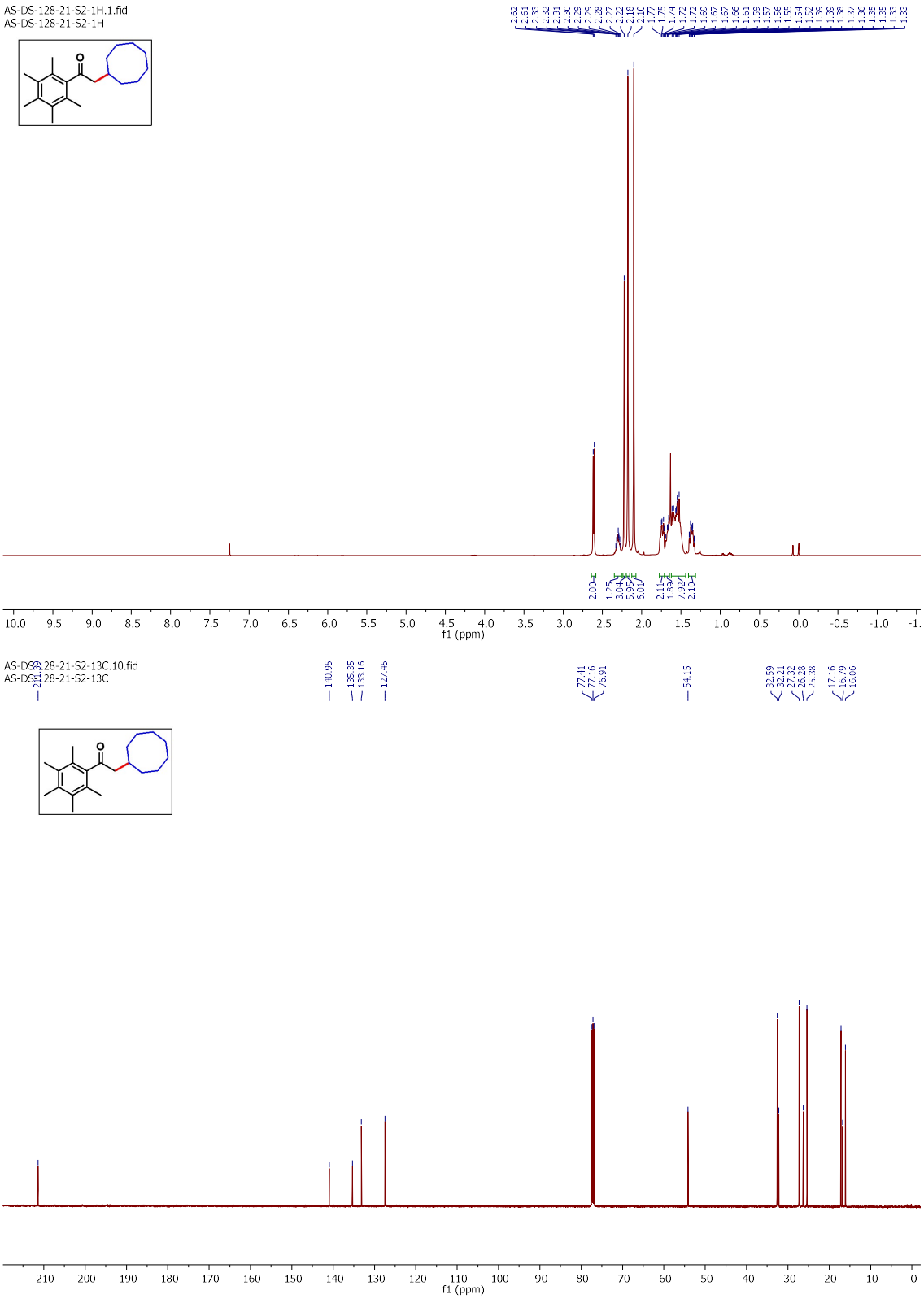


Figure S59. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bh** in $CDCl_3$.

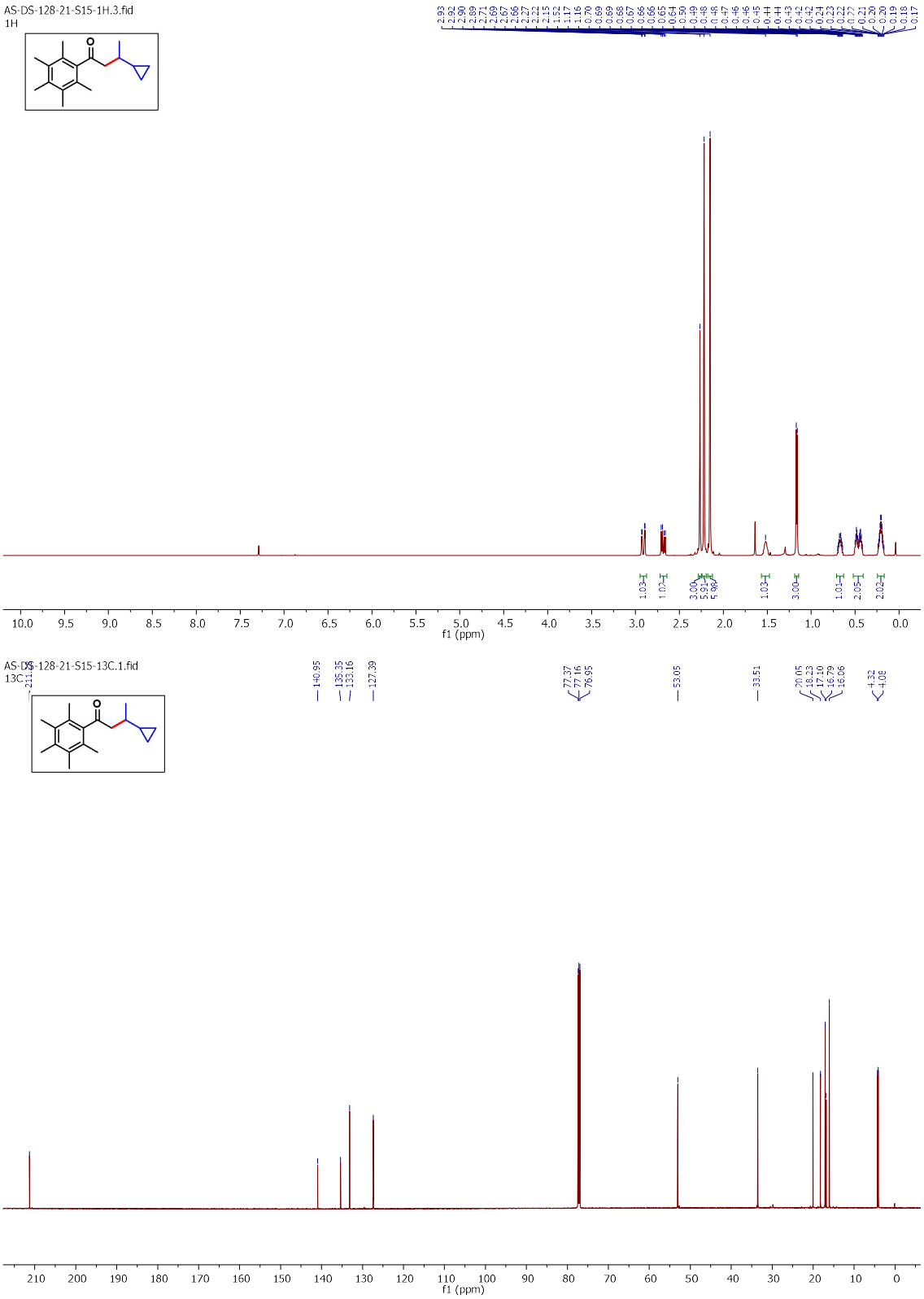


Figure S60. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3bi** in $CDCl_3$.

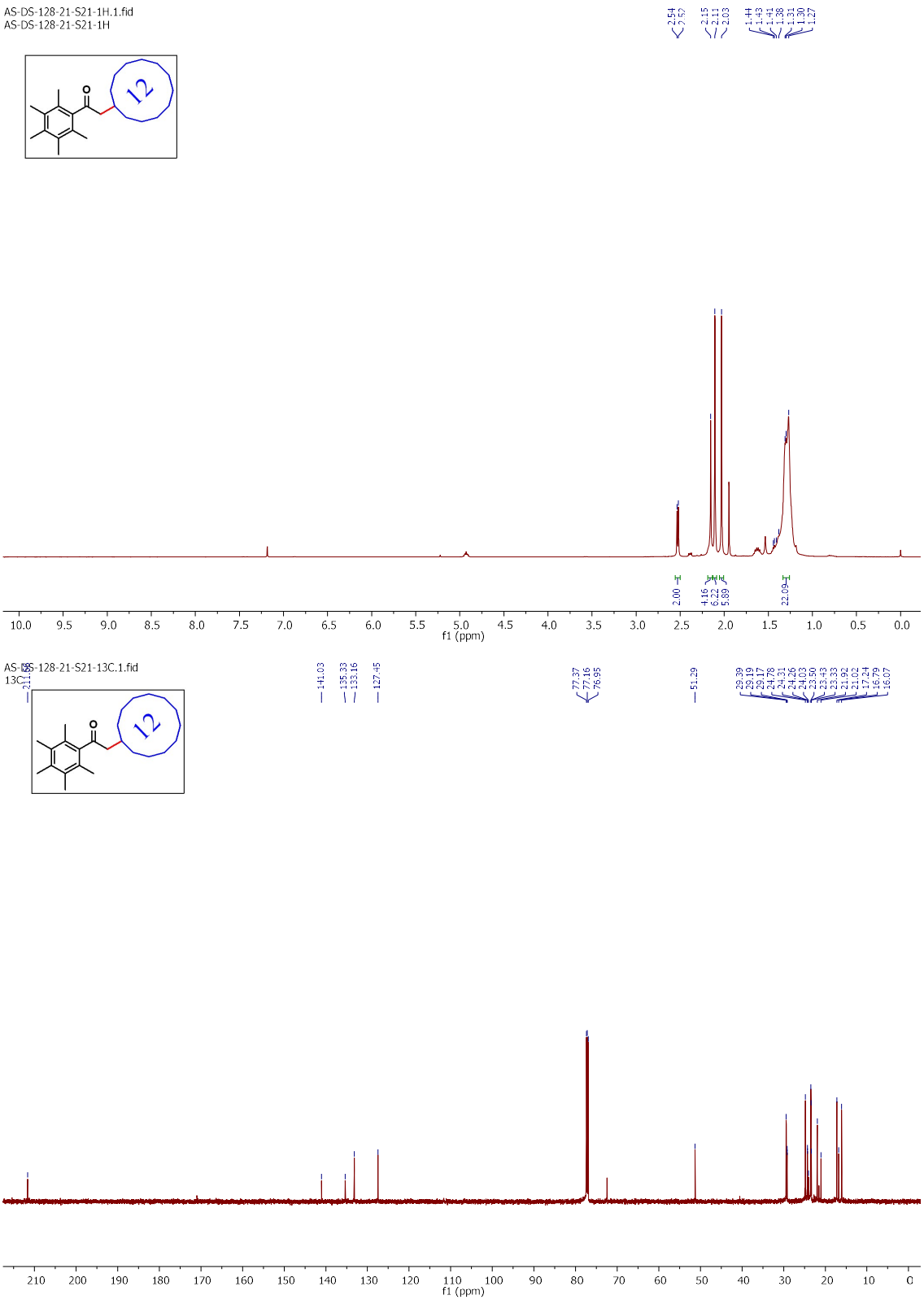


Figure S61. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3bj** in $CDCl_3$.

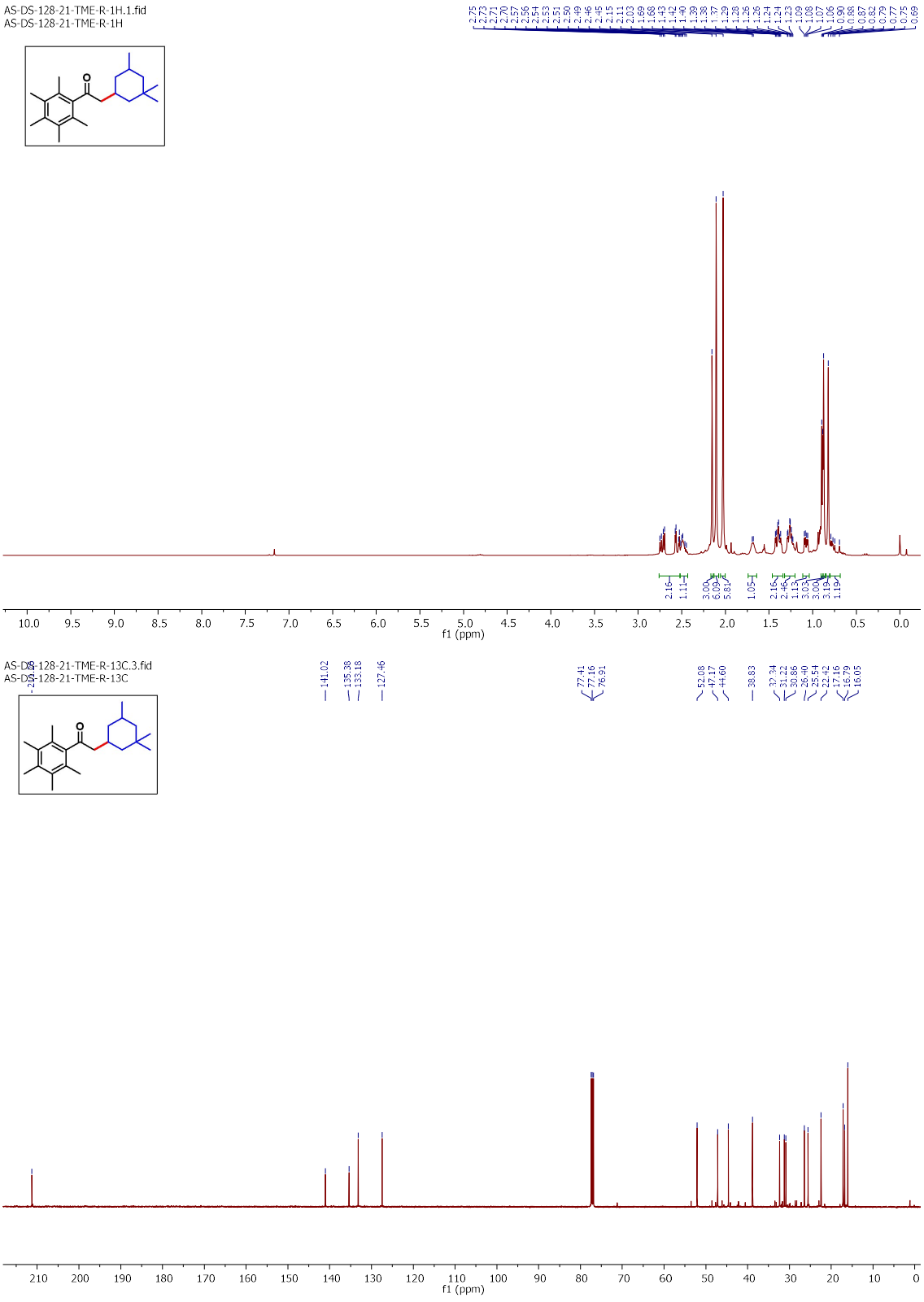


Figure S62. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bk** in $CDCl_3$.

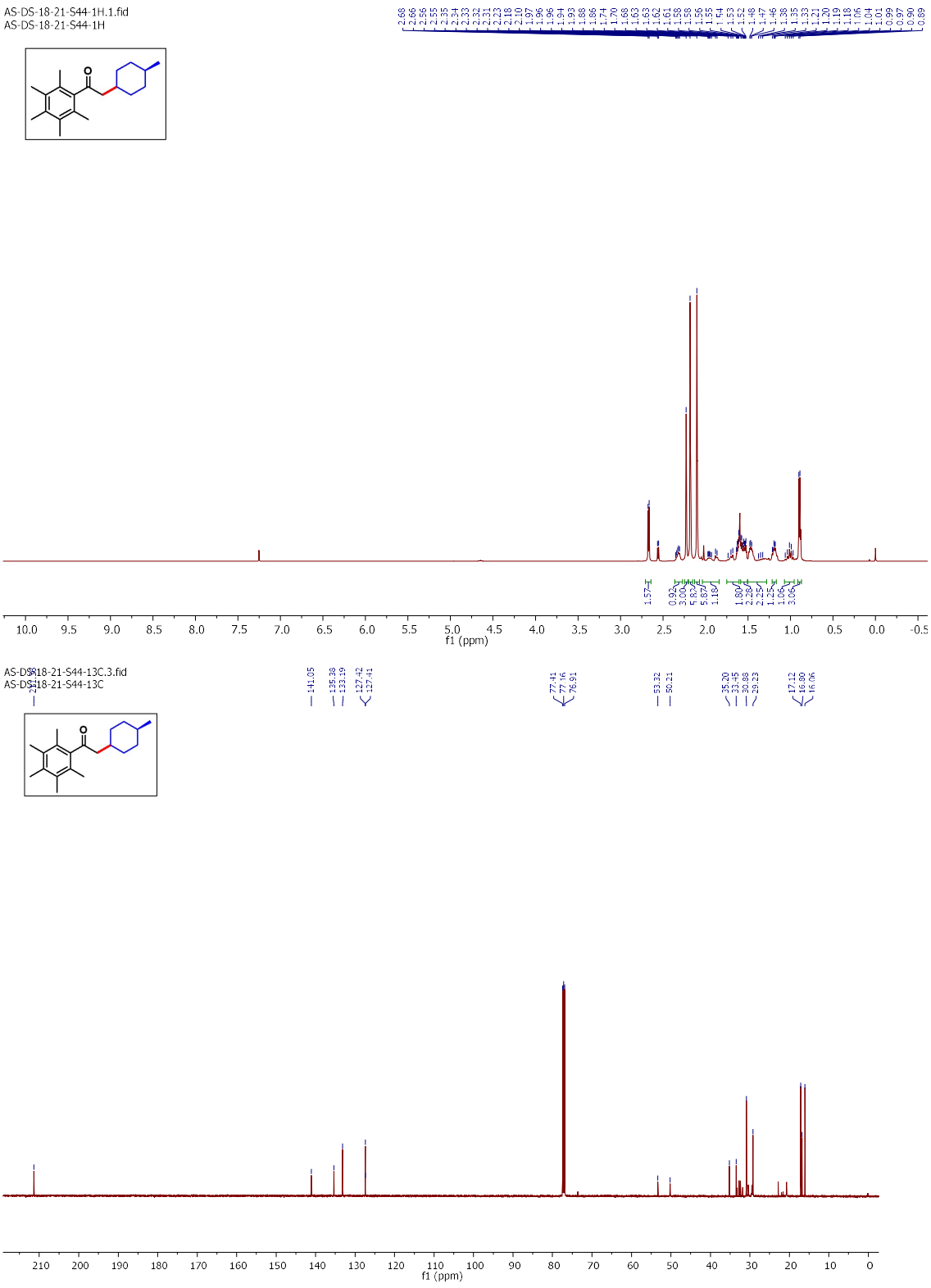


Figure S63. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bl** in $CDCl_3$.

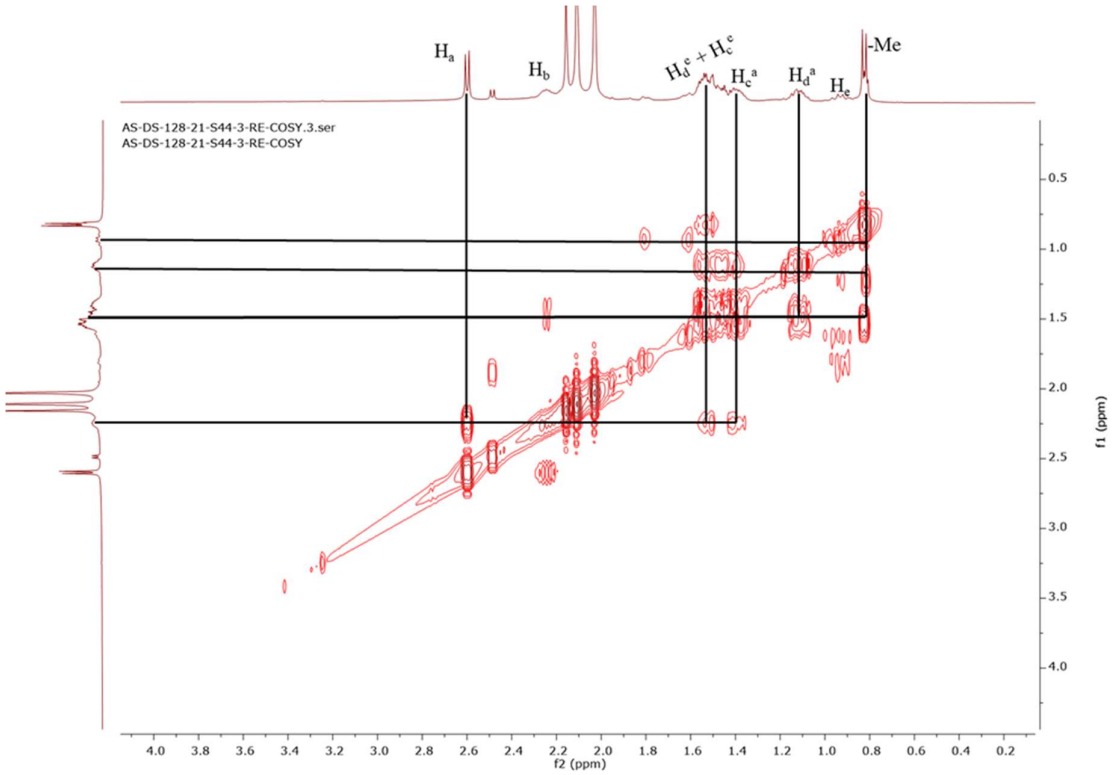
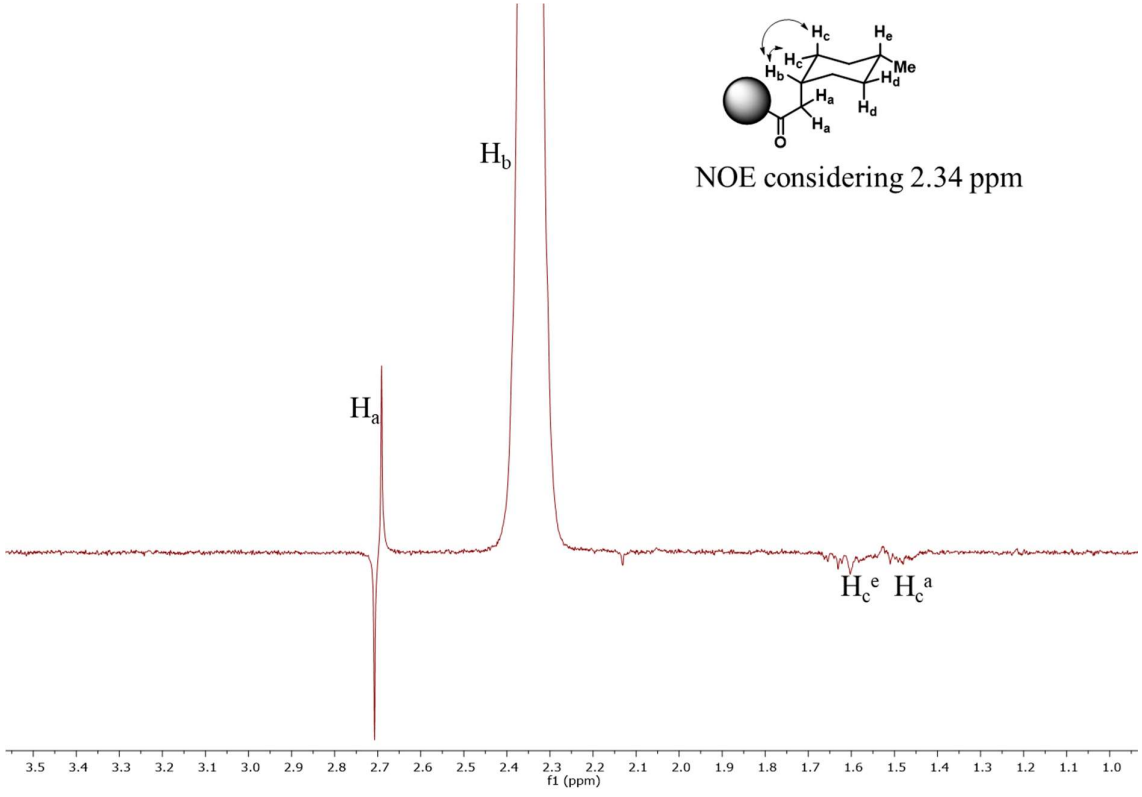


Figure S64. COSY of Compound **3bl** in $CDCl_3$.



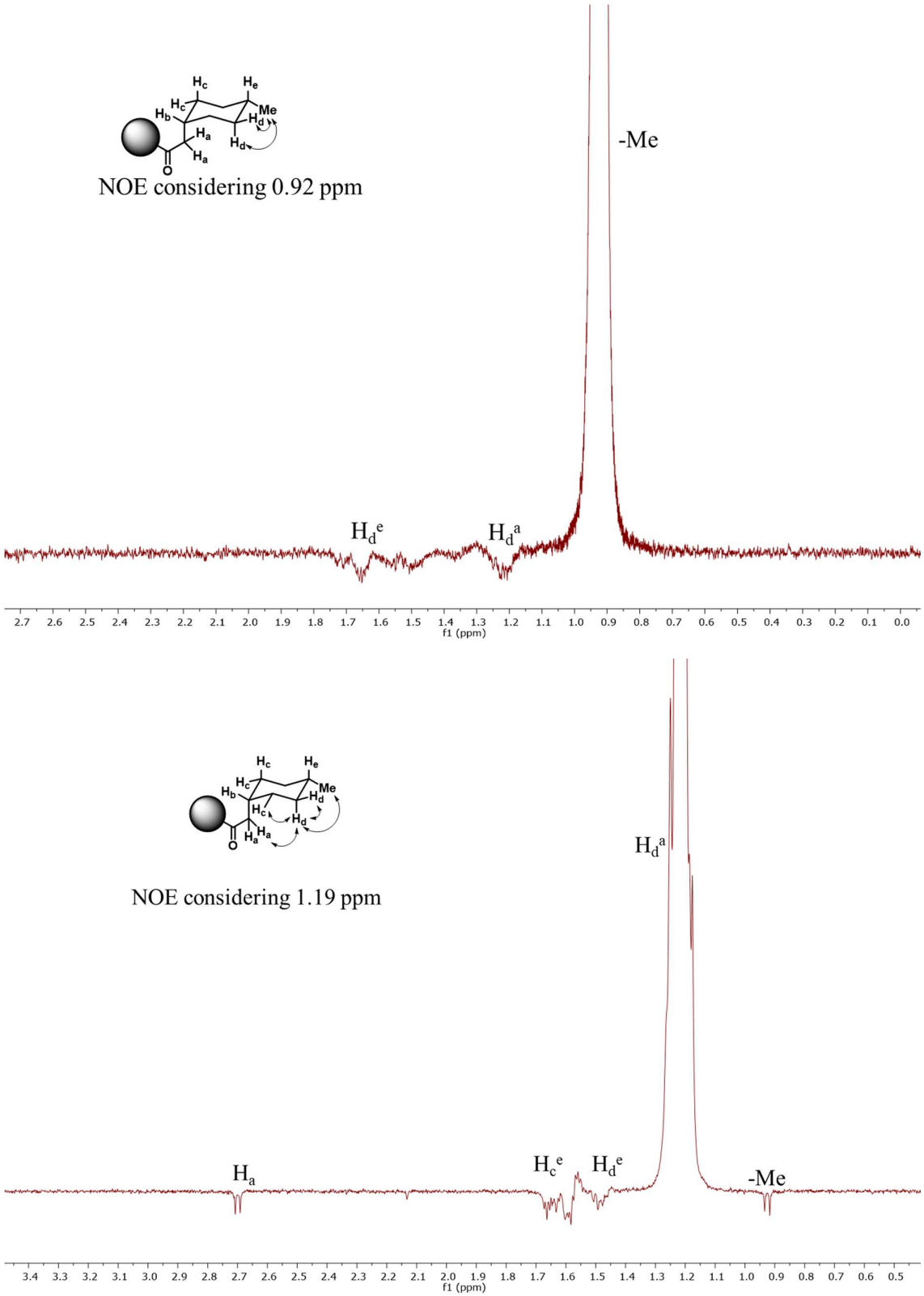


Figure S65. NOE of Compound **3bl** at different δ (ppm) value in $CDCl_3$.

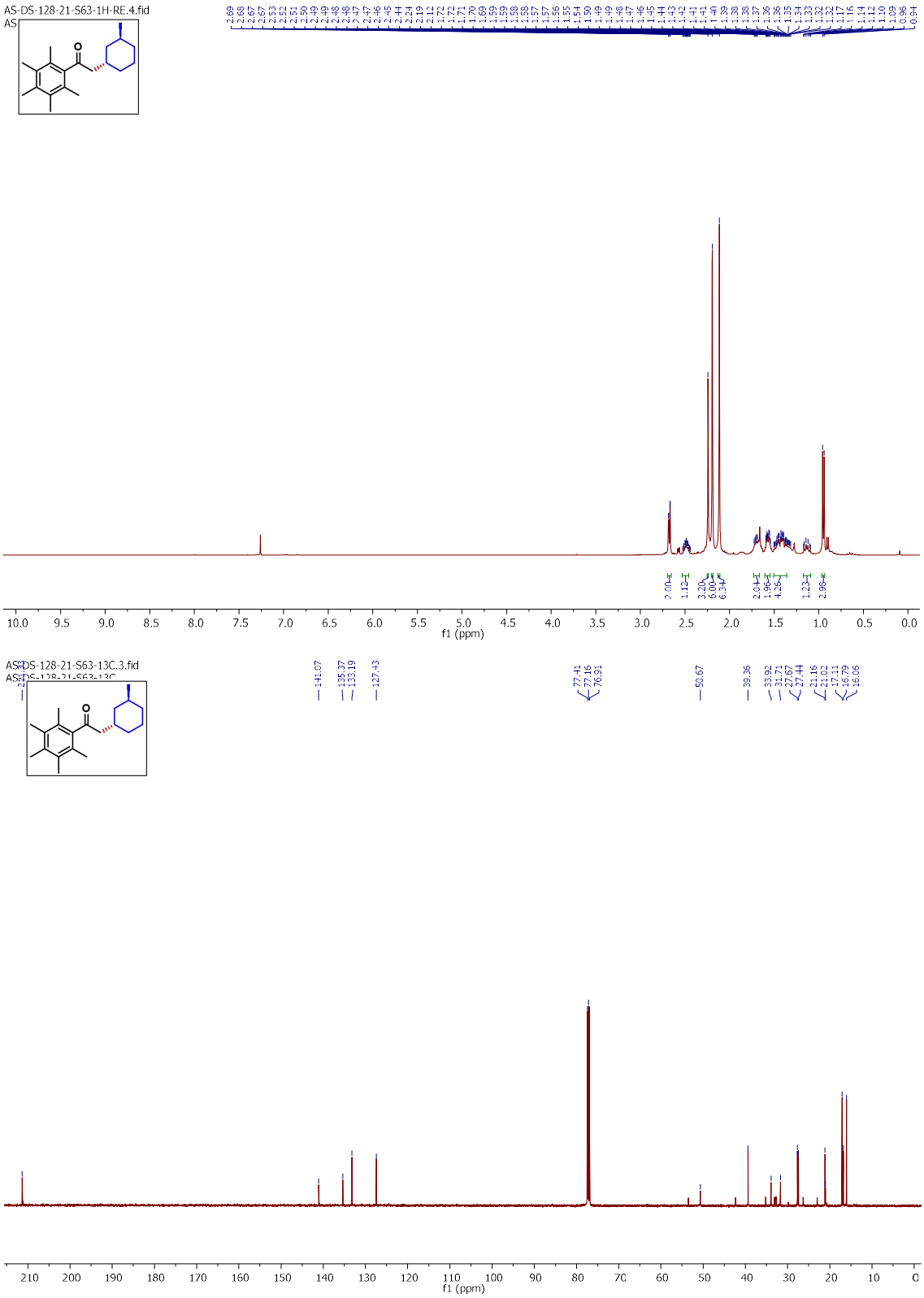


Figure S66. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bm** in $CDCl_3$.

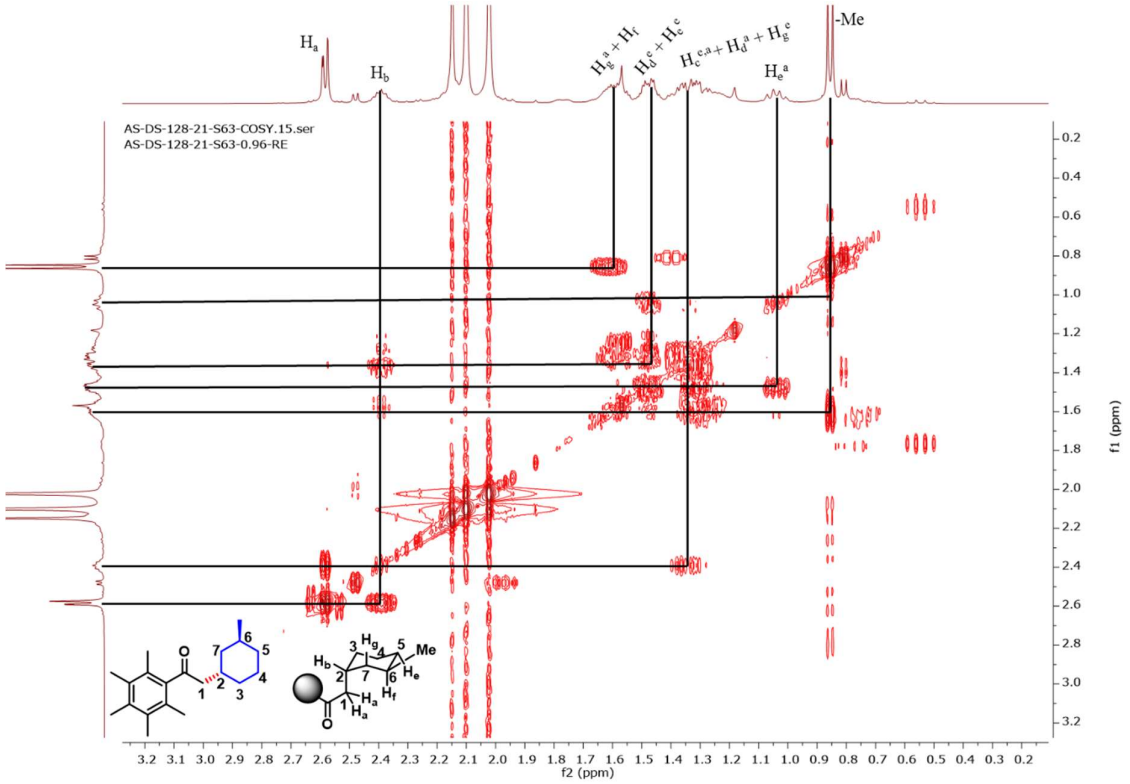
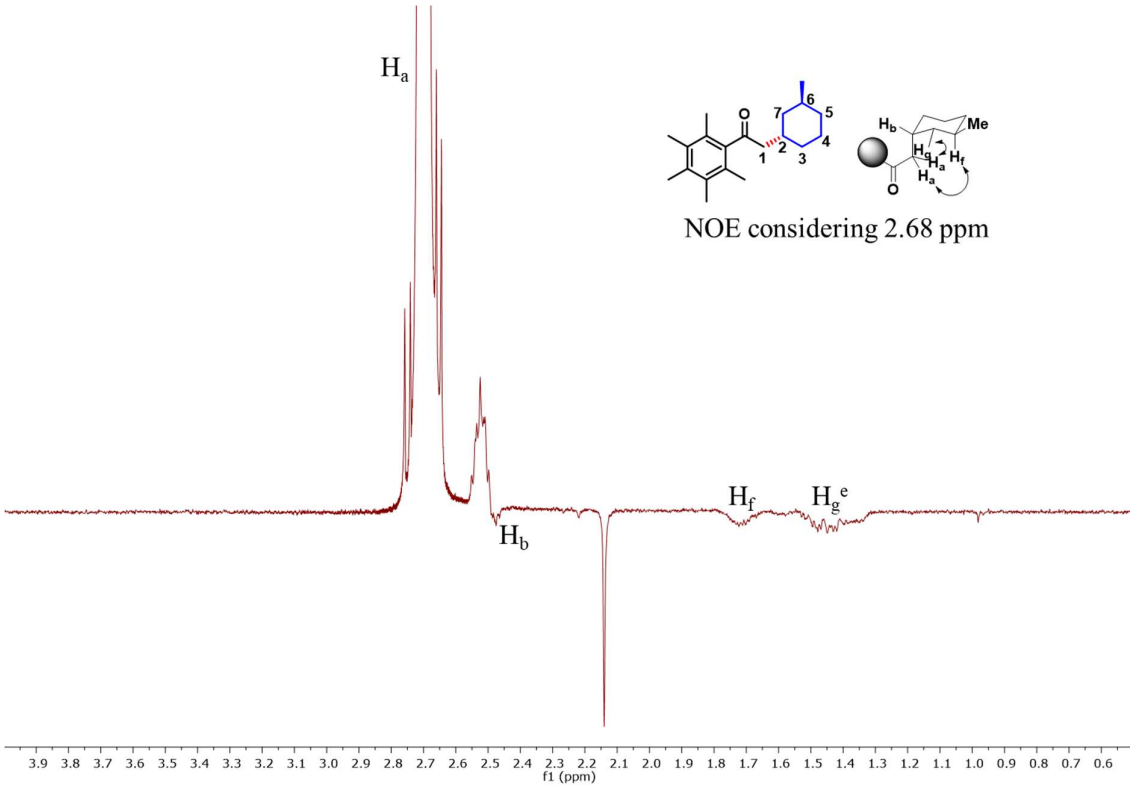
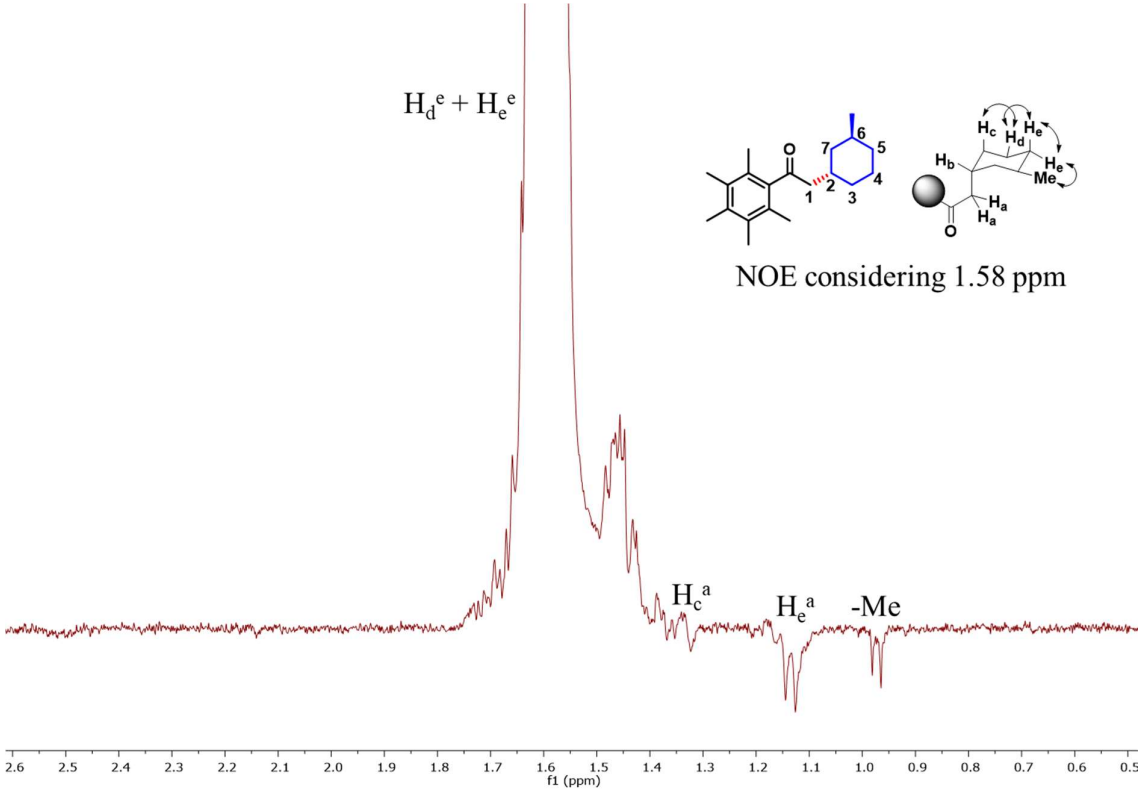
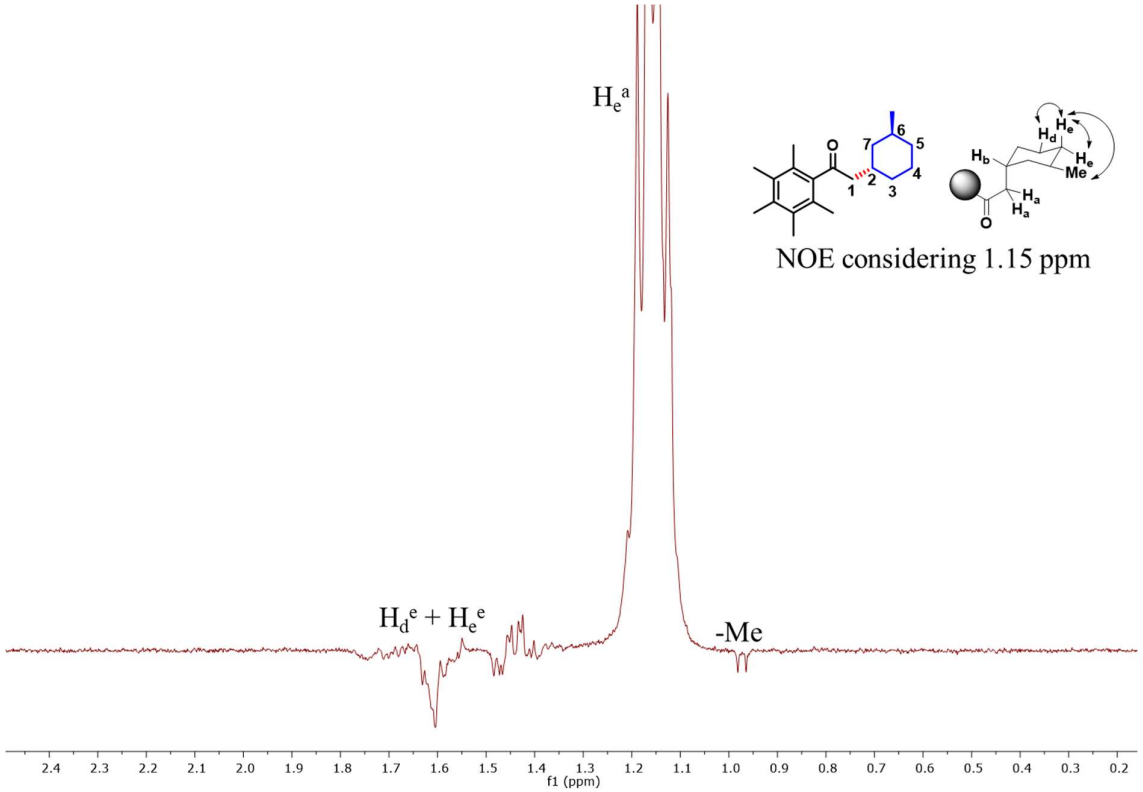


Figure S67. COSY of Compound **3bm** in $CDCl_3$.





NOE considering 1.58 ppm



NOE considering 1.15 ppm

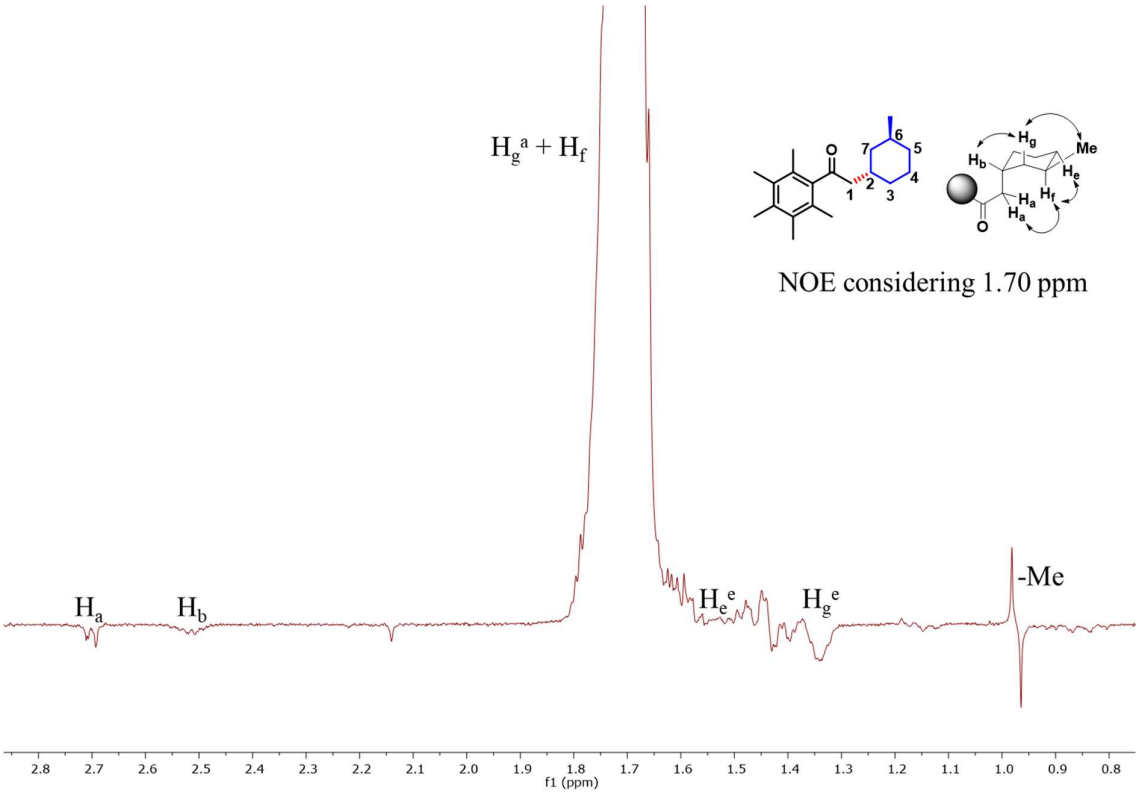


Figure S68. NOE of Compound **3bm** at different δ (ppm) value in $CDCl_3$.

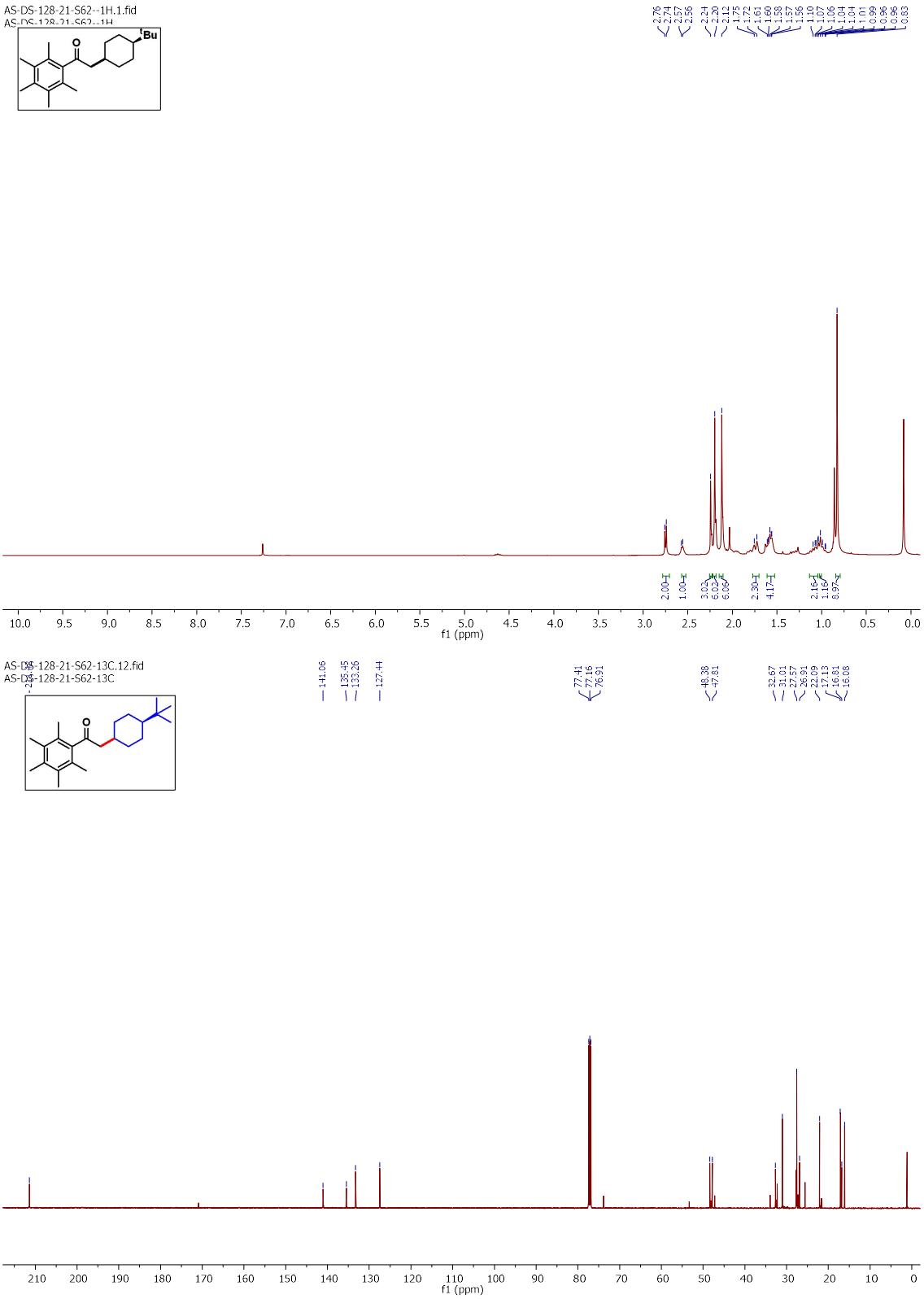


Figure S69. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bn** in $CDCl_3$.

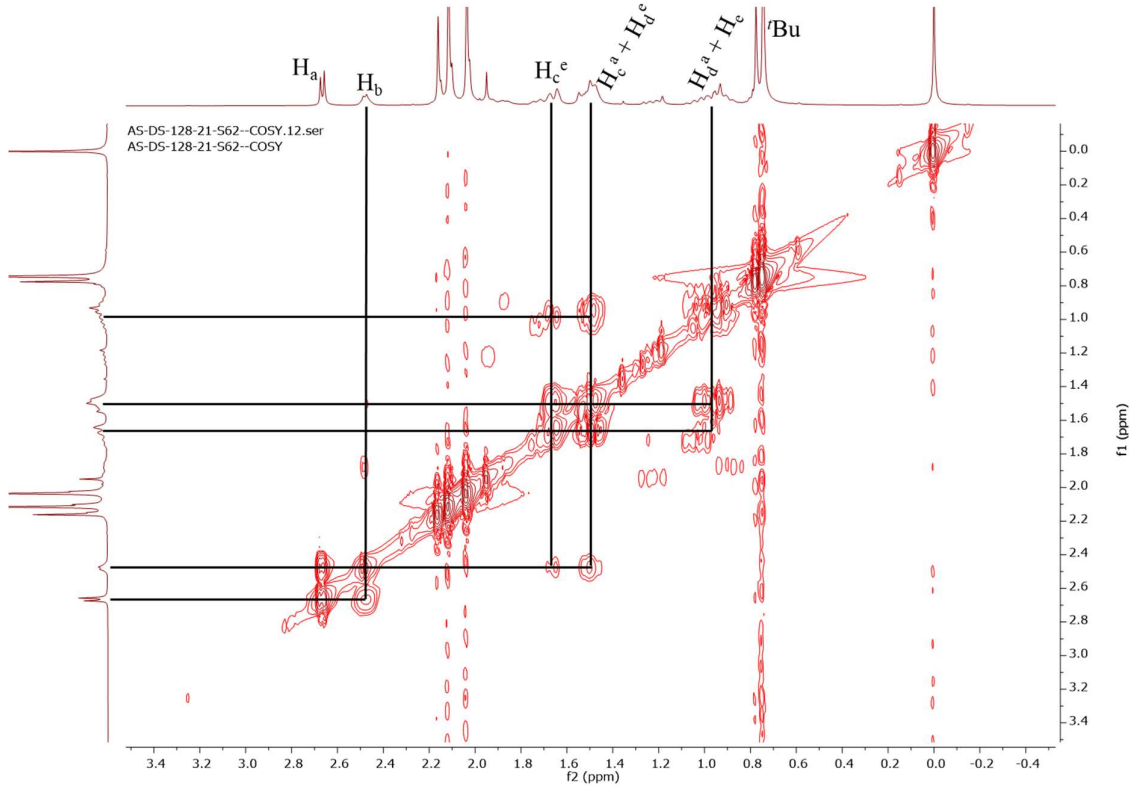
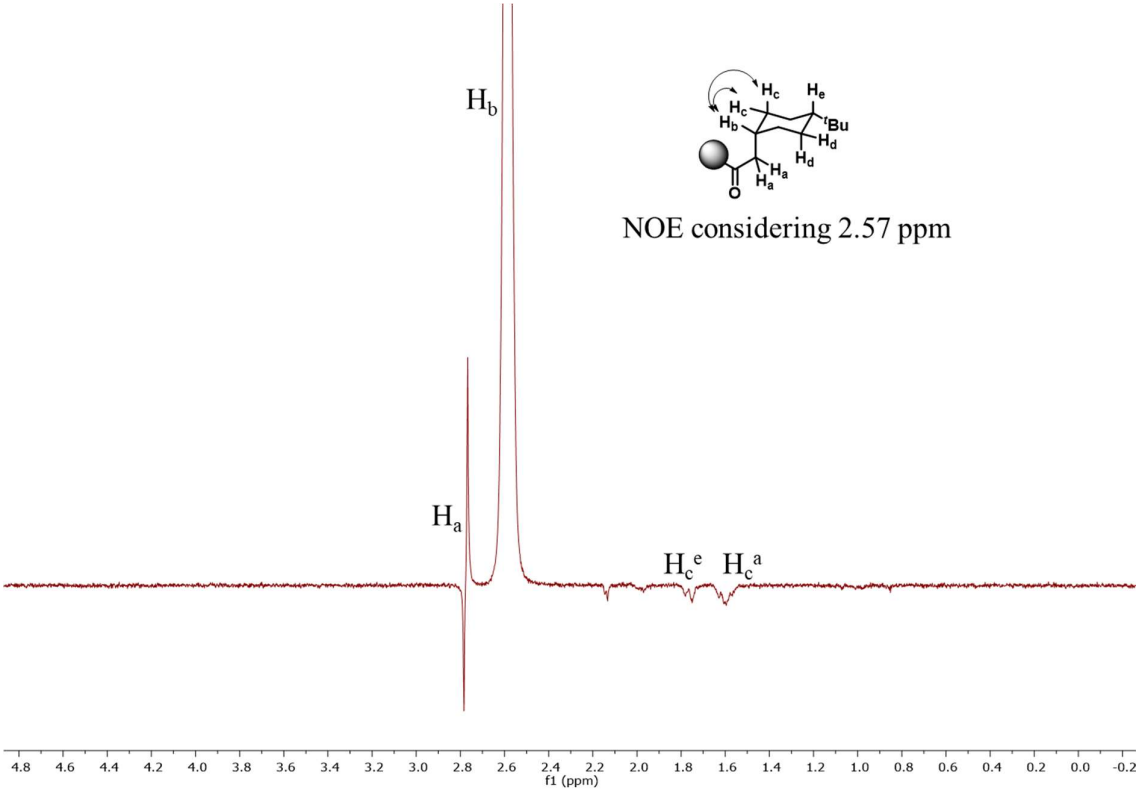
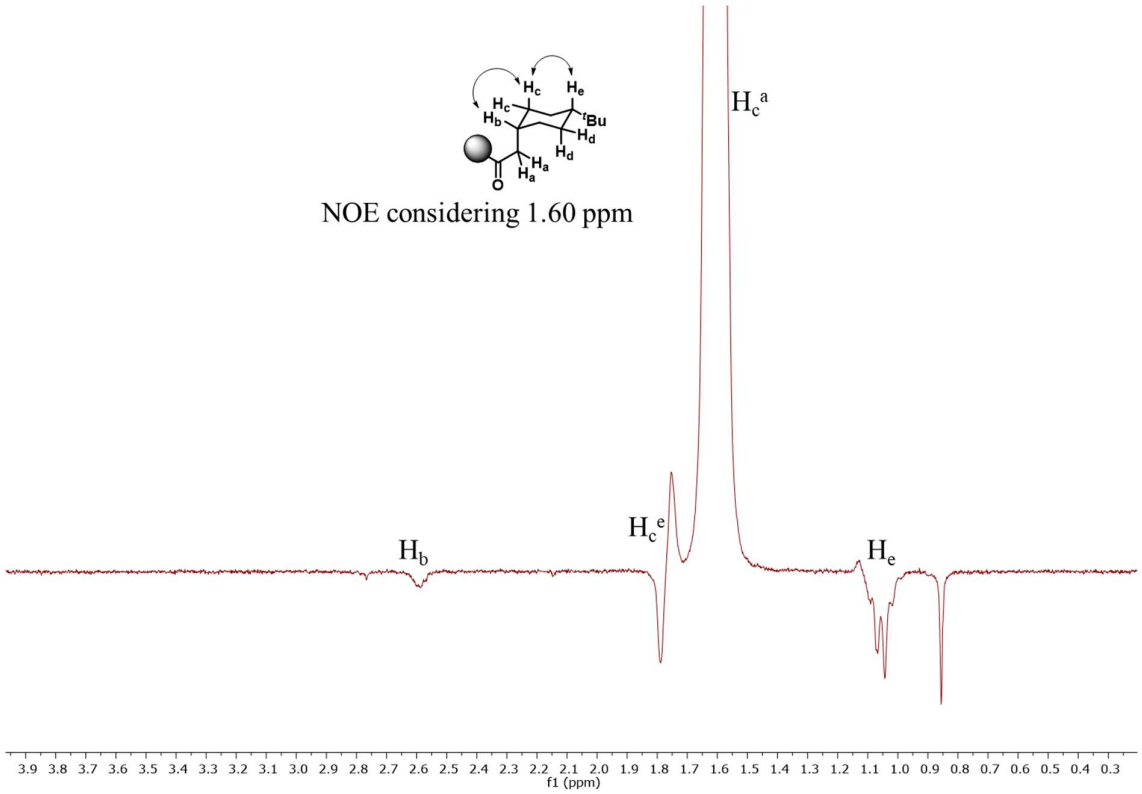


Figure S70. COSY of Compound **3bn** in $CDCl_3$.





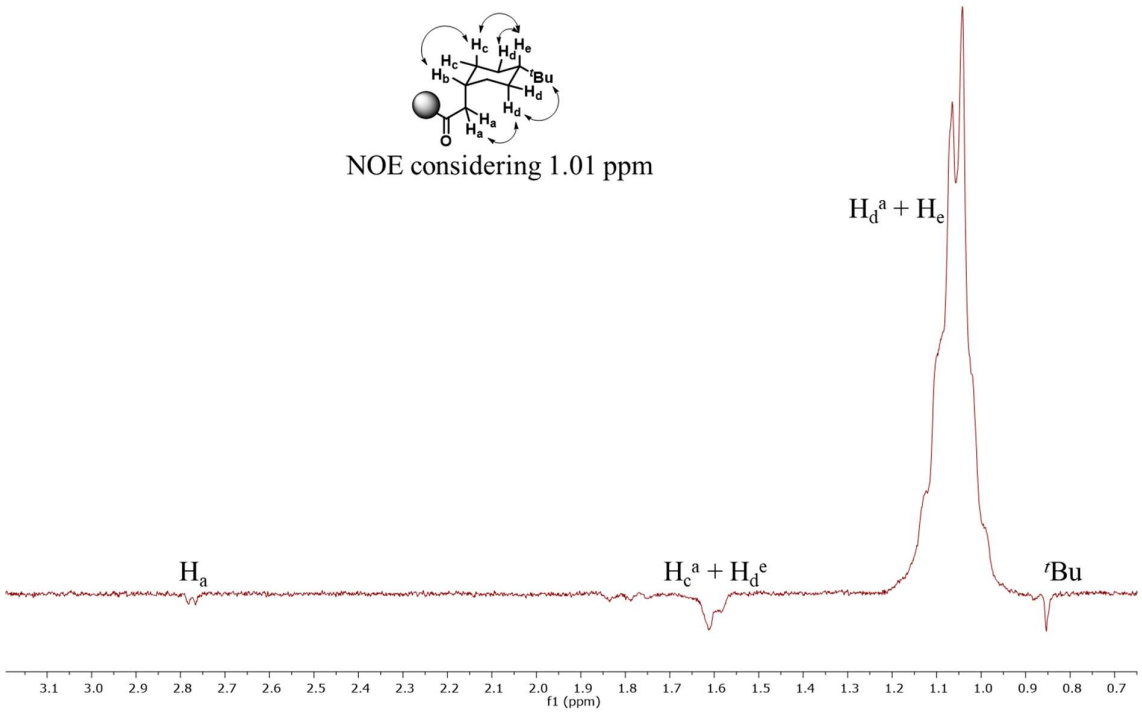


Figure S71. NOE of Compound **3bn** at different δ (ppm) value in $CDCl_3$.

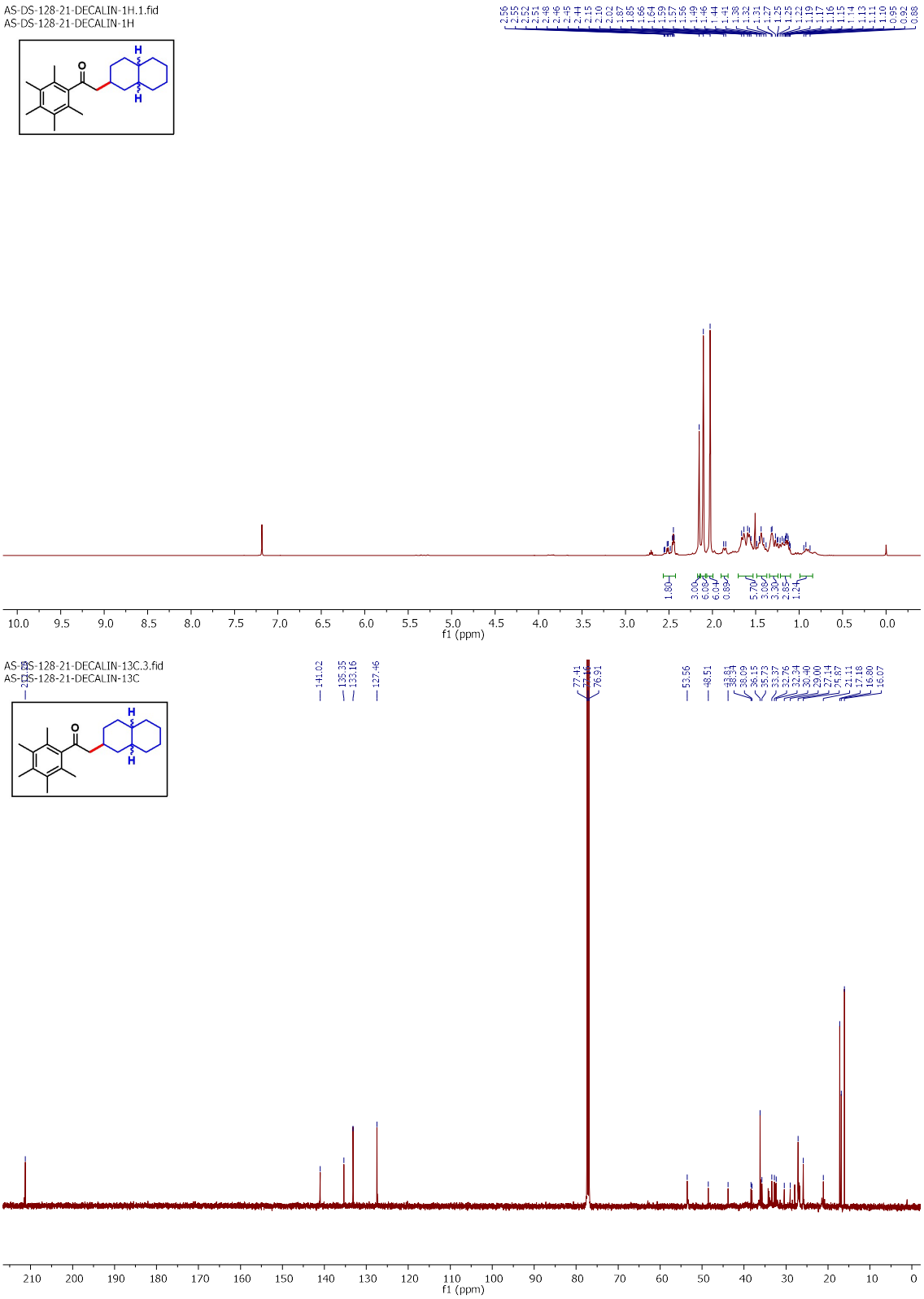


Figure S72. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bo** in $CDCl_3$.

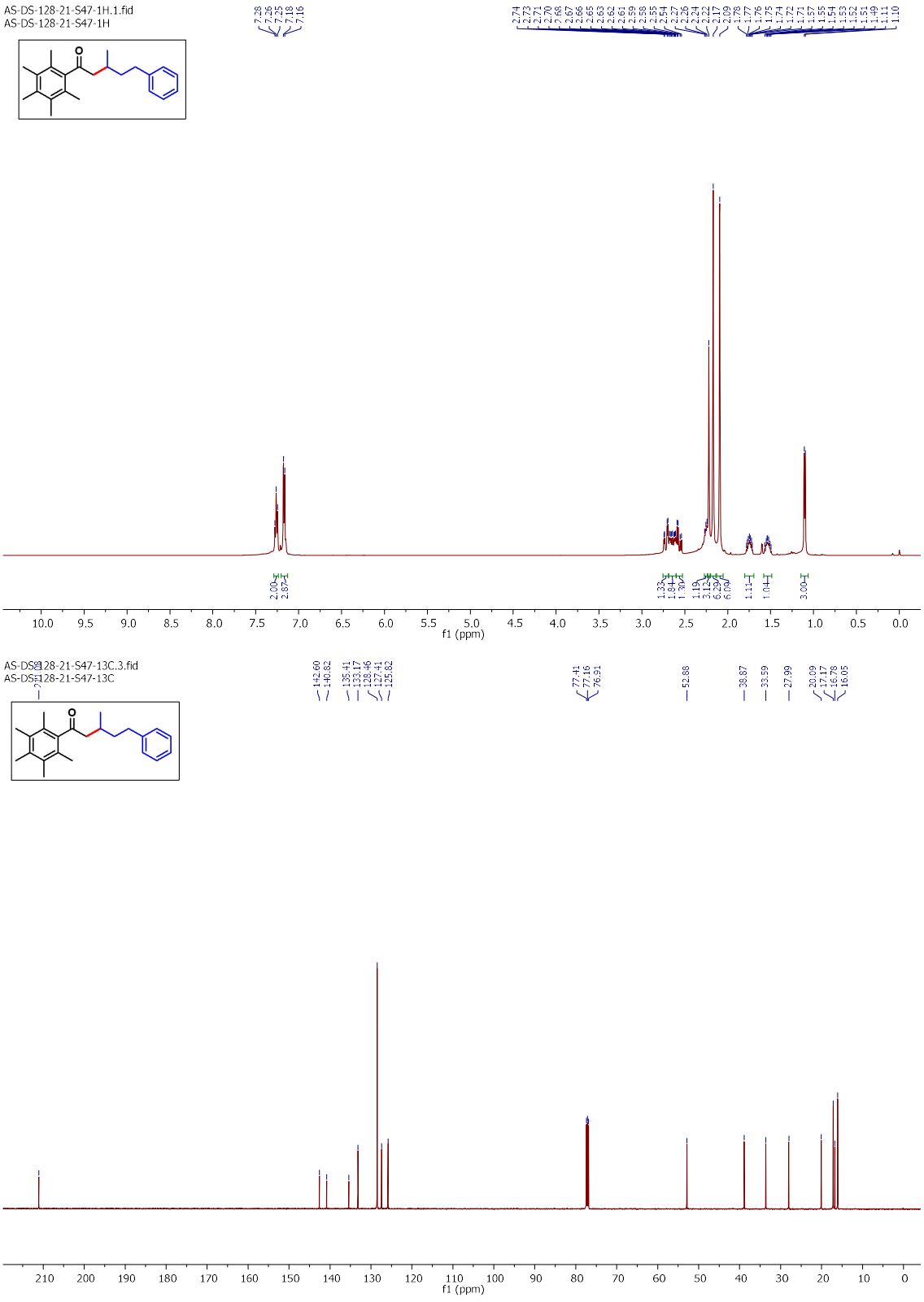


Figure S73. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bp** in $CDCl_3$.

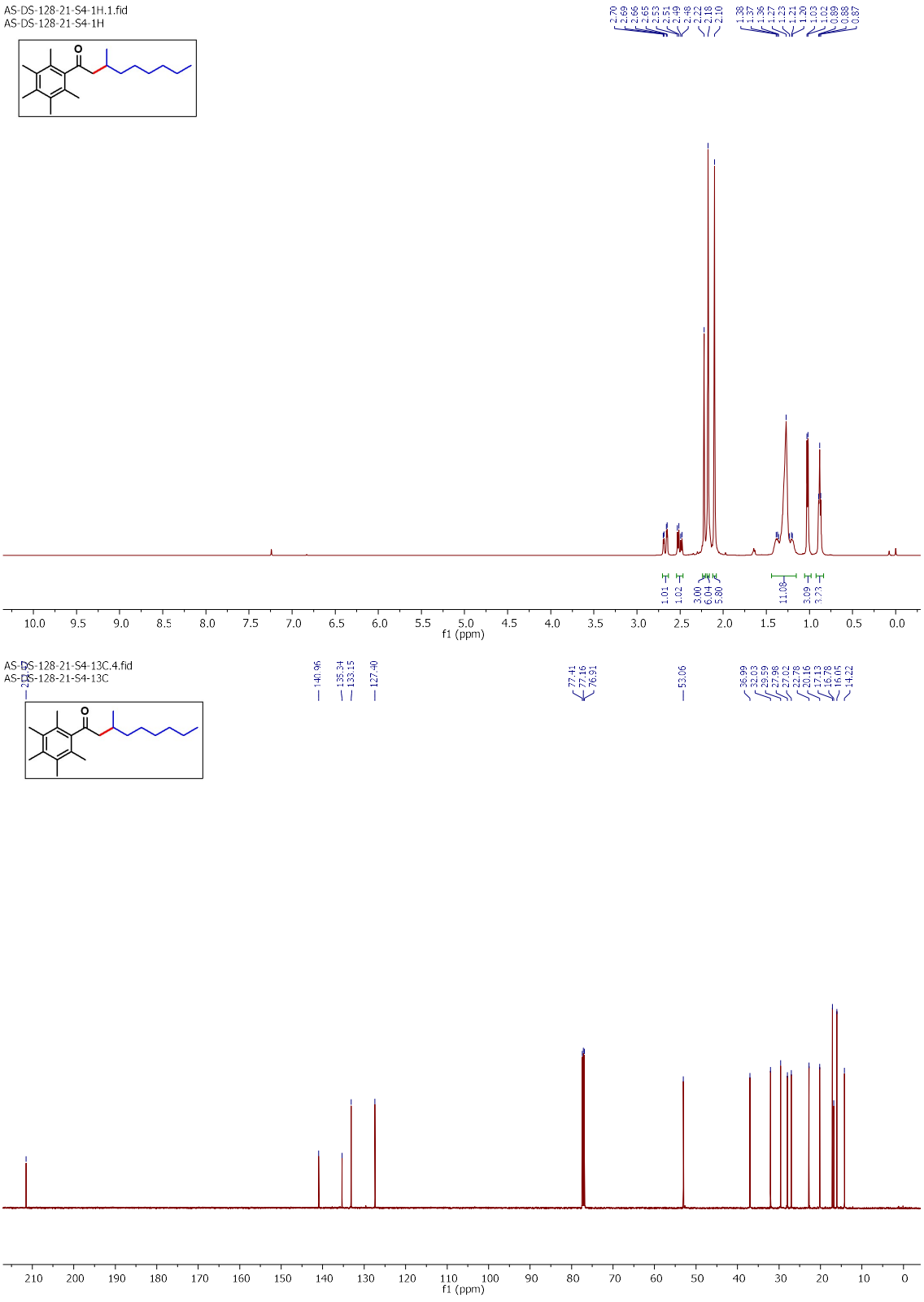


Figure S74. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bq** in $CDCl_3$.

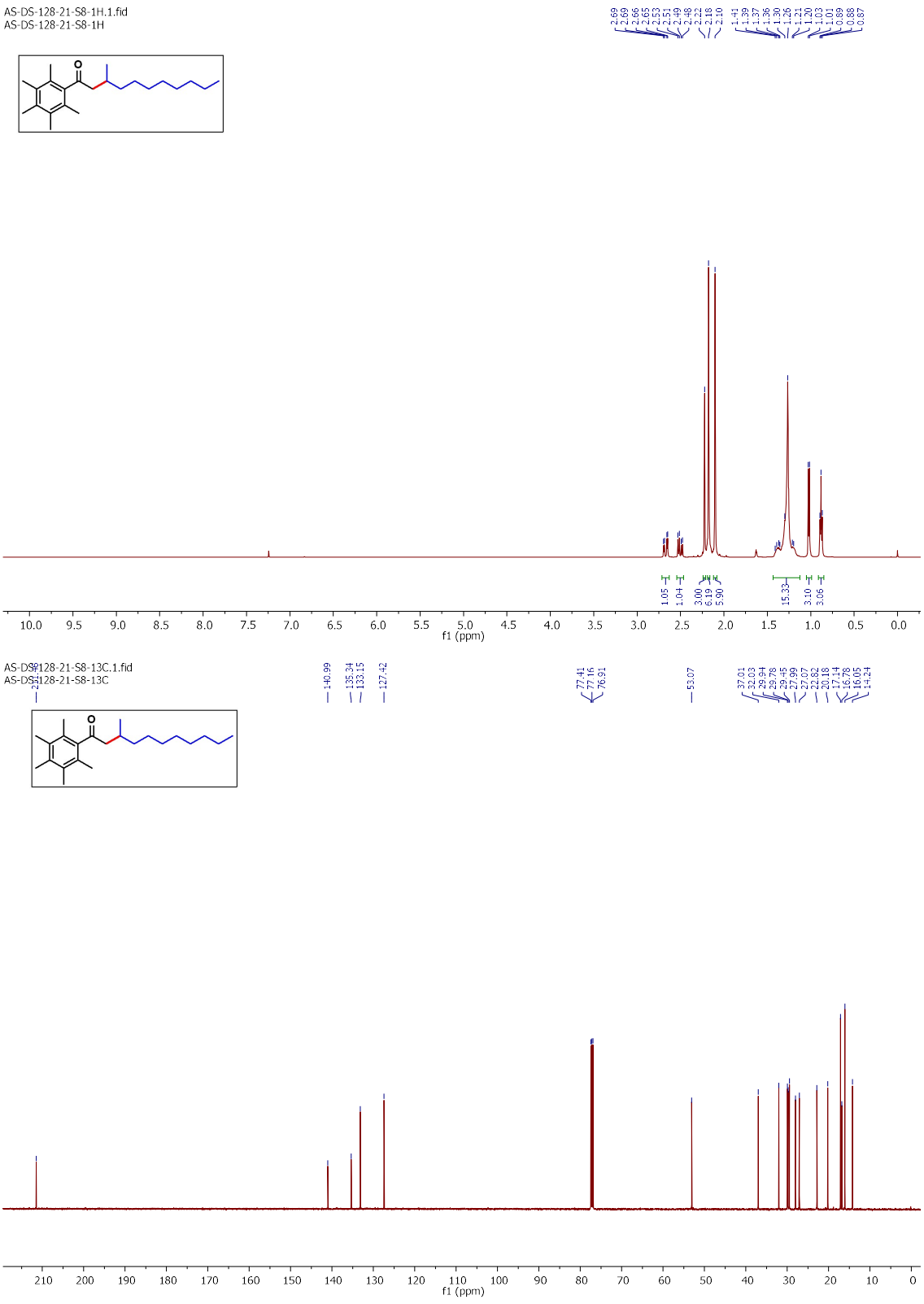


Figure S75. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3br** in $CDCl_3$.

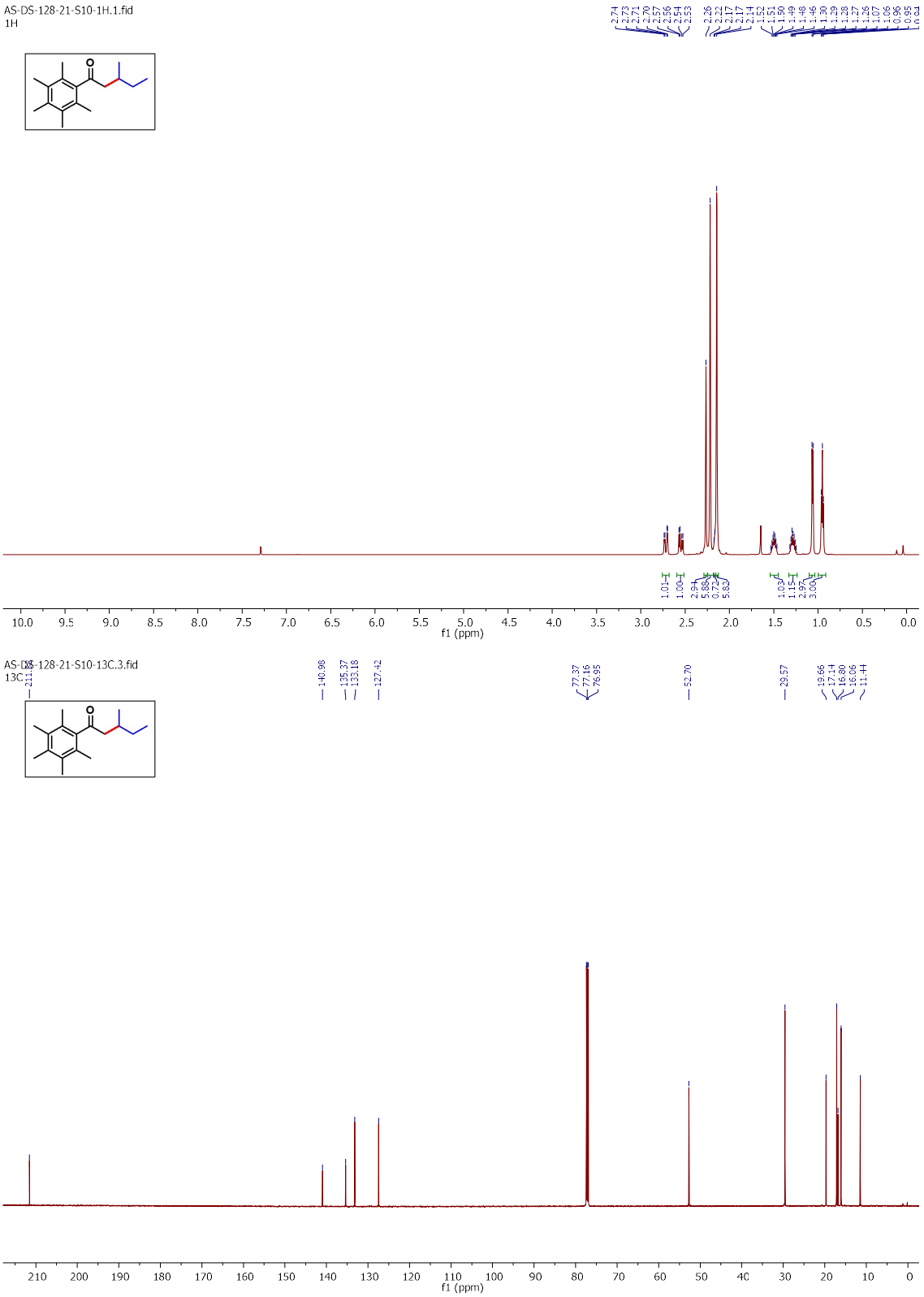


Figure S76. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3bs** in $CDCl_3$.

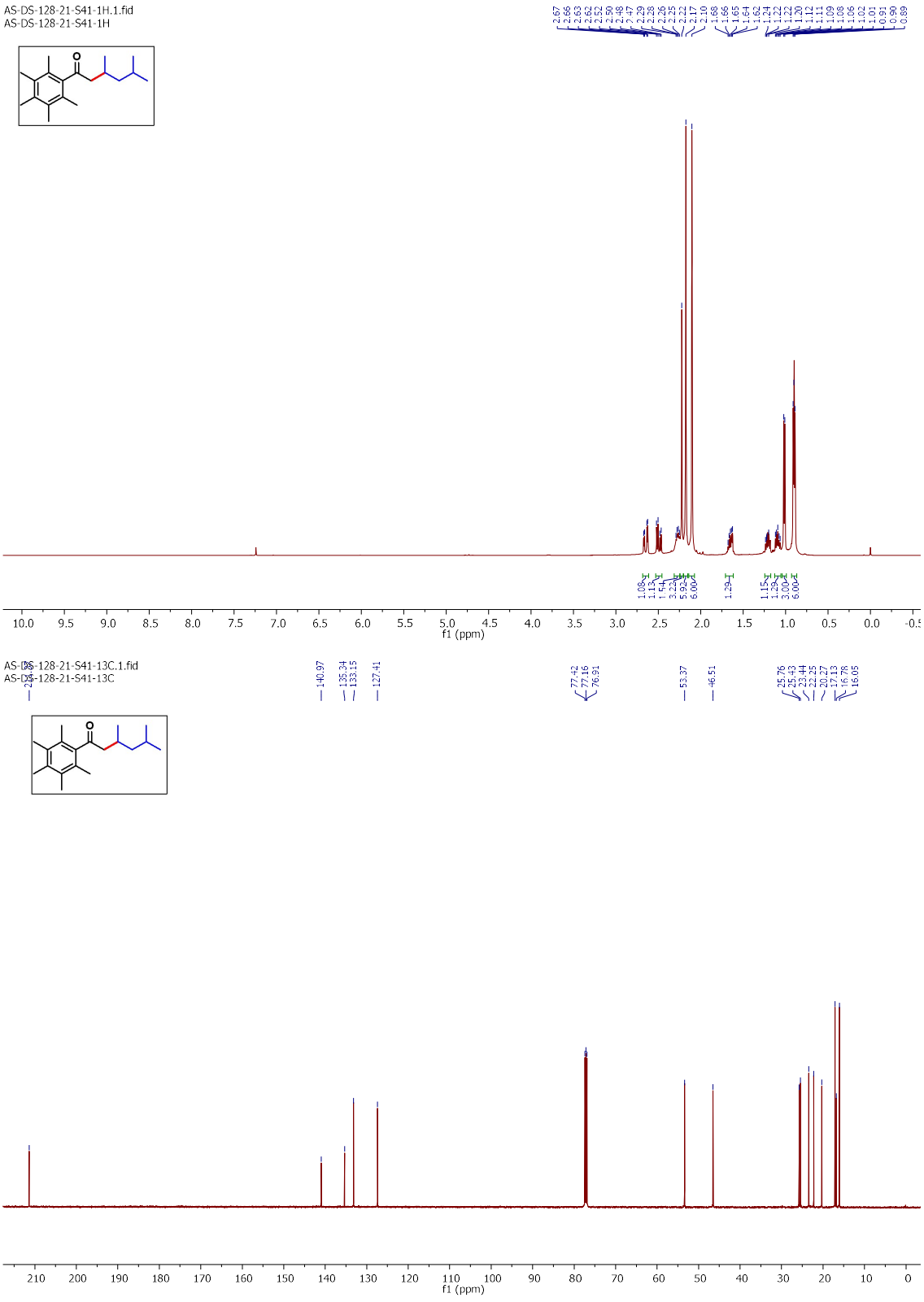


Figure S77. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bt** in $CDCl_3$.

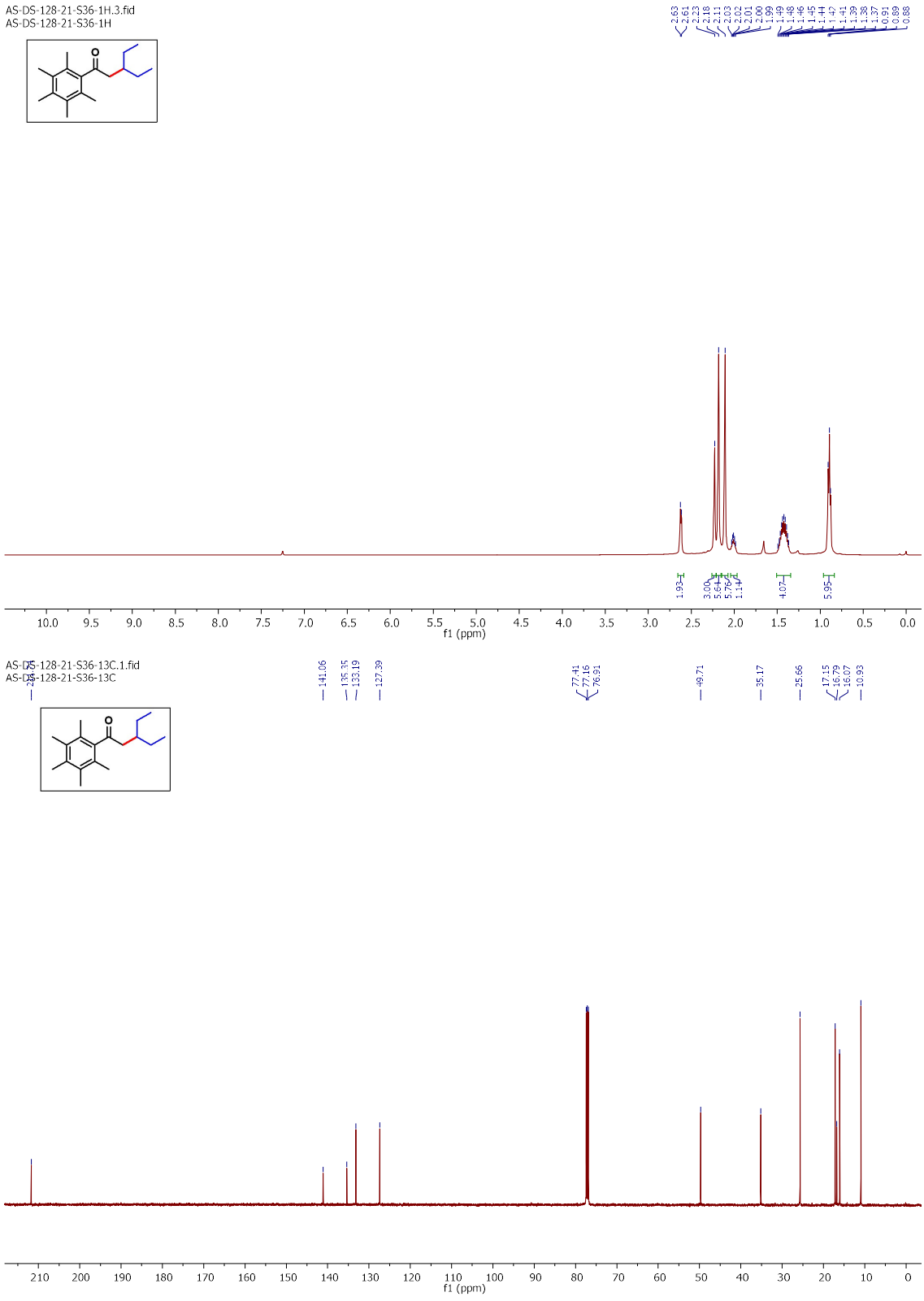


Figure S78. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bu** in $CDCl_3$.

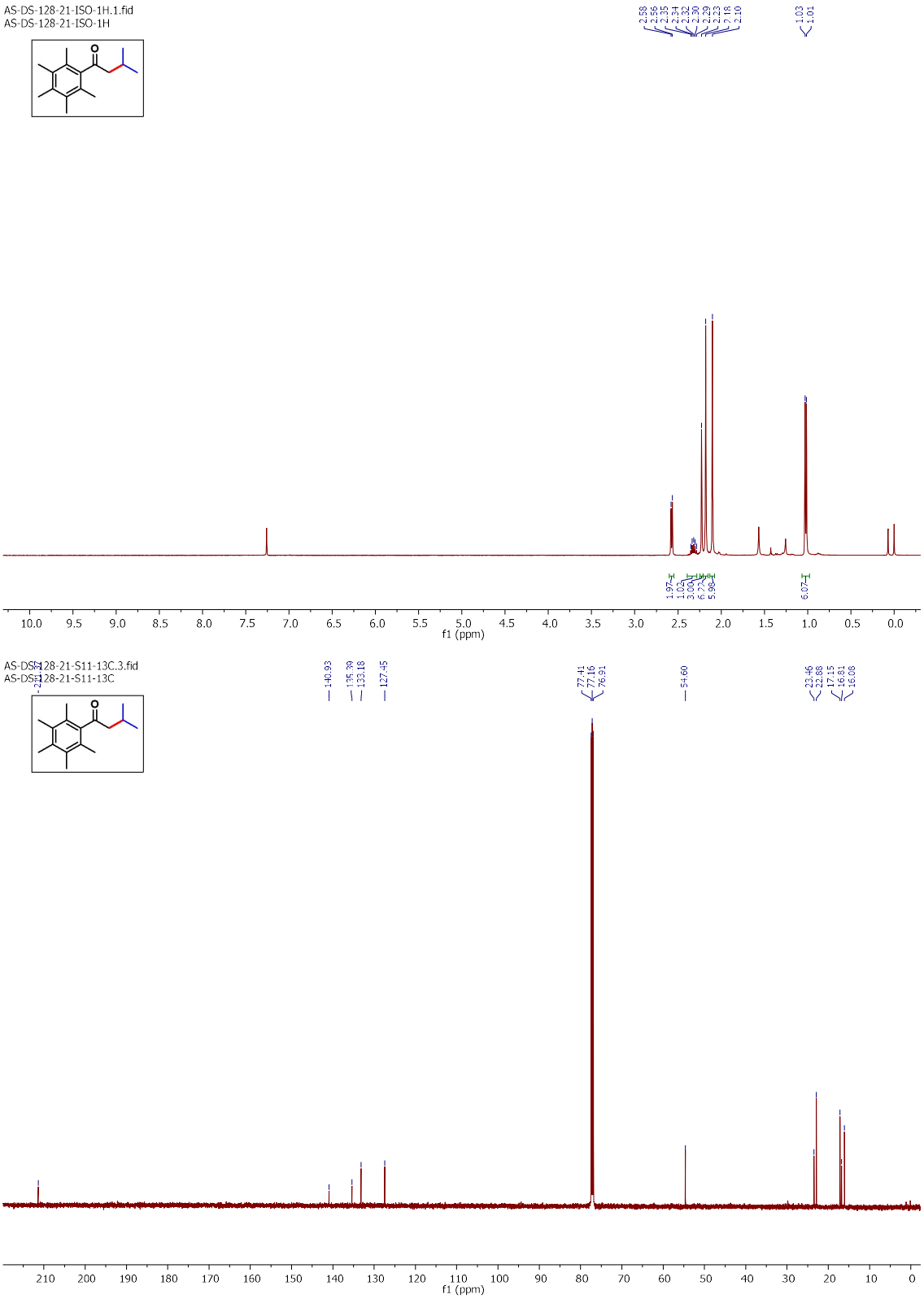


Figure S79. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3bv** in $CDCl_3$.

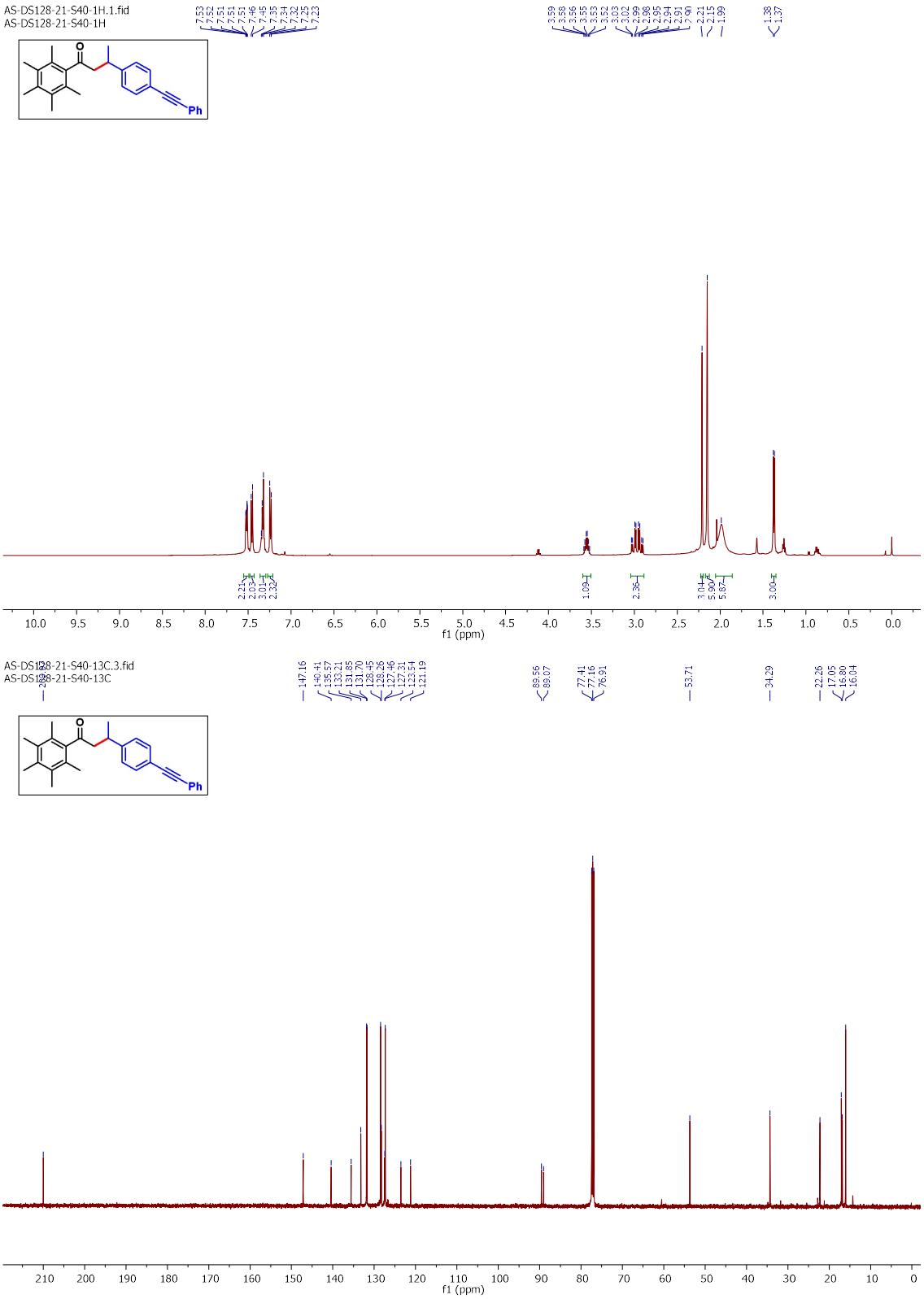


Figure S80. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3aw** in $CDCl_3$.

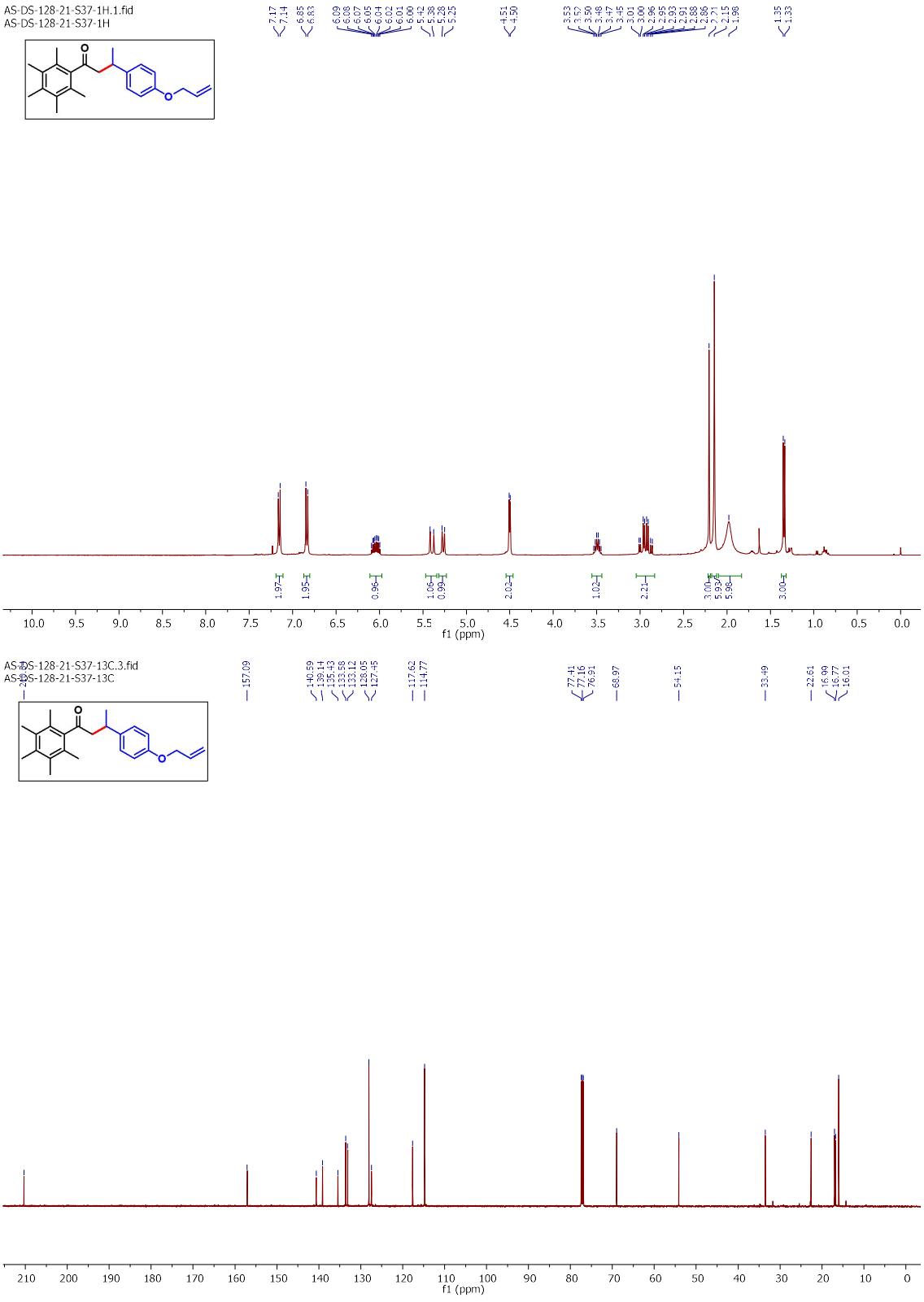


Figure S81. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ax** in $CDCl_3$.

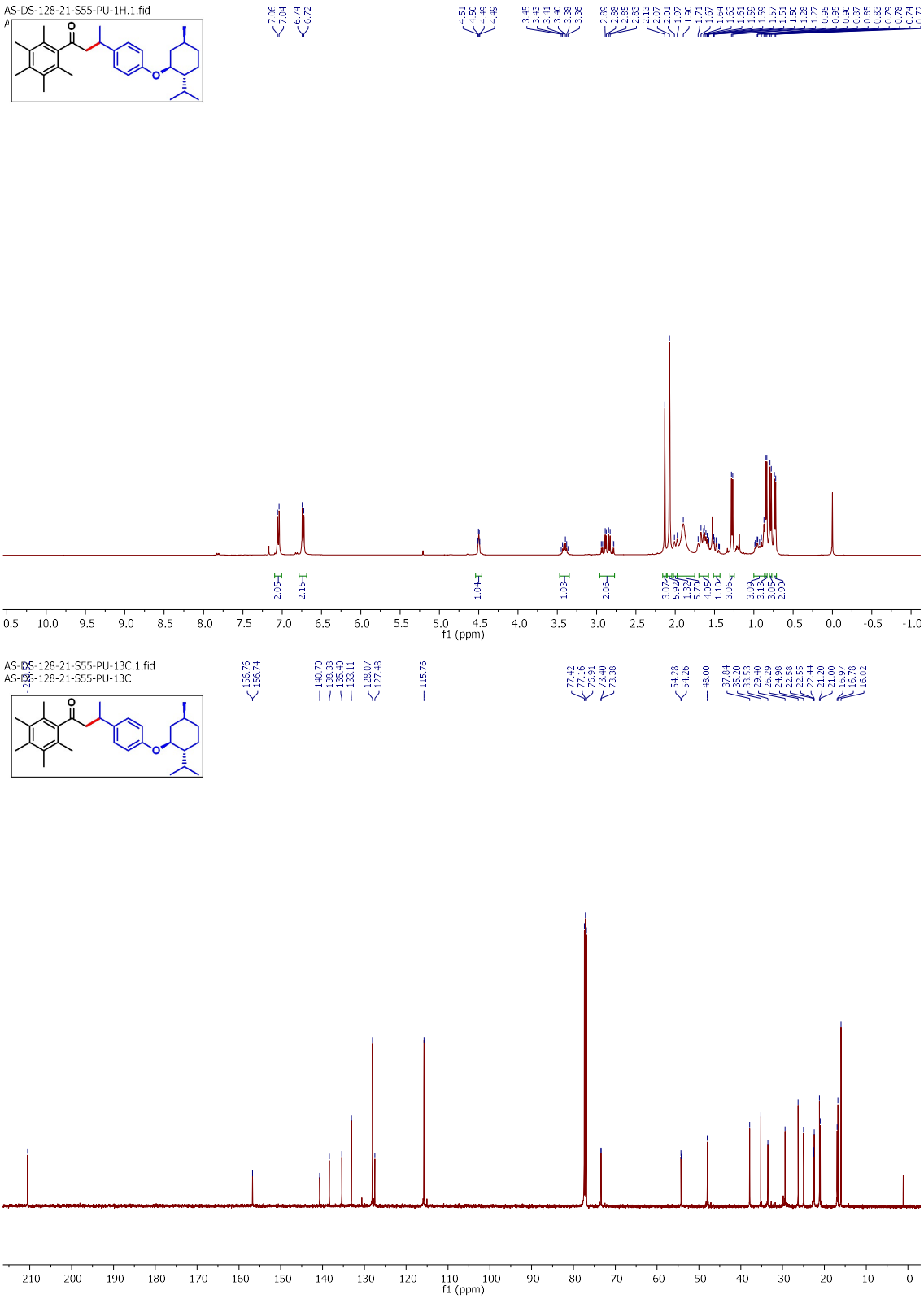


Figure S82. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3ay** in $CDCl_3$.

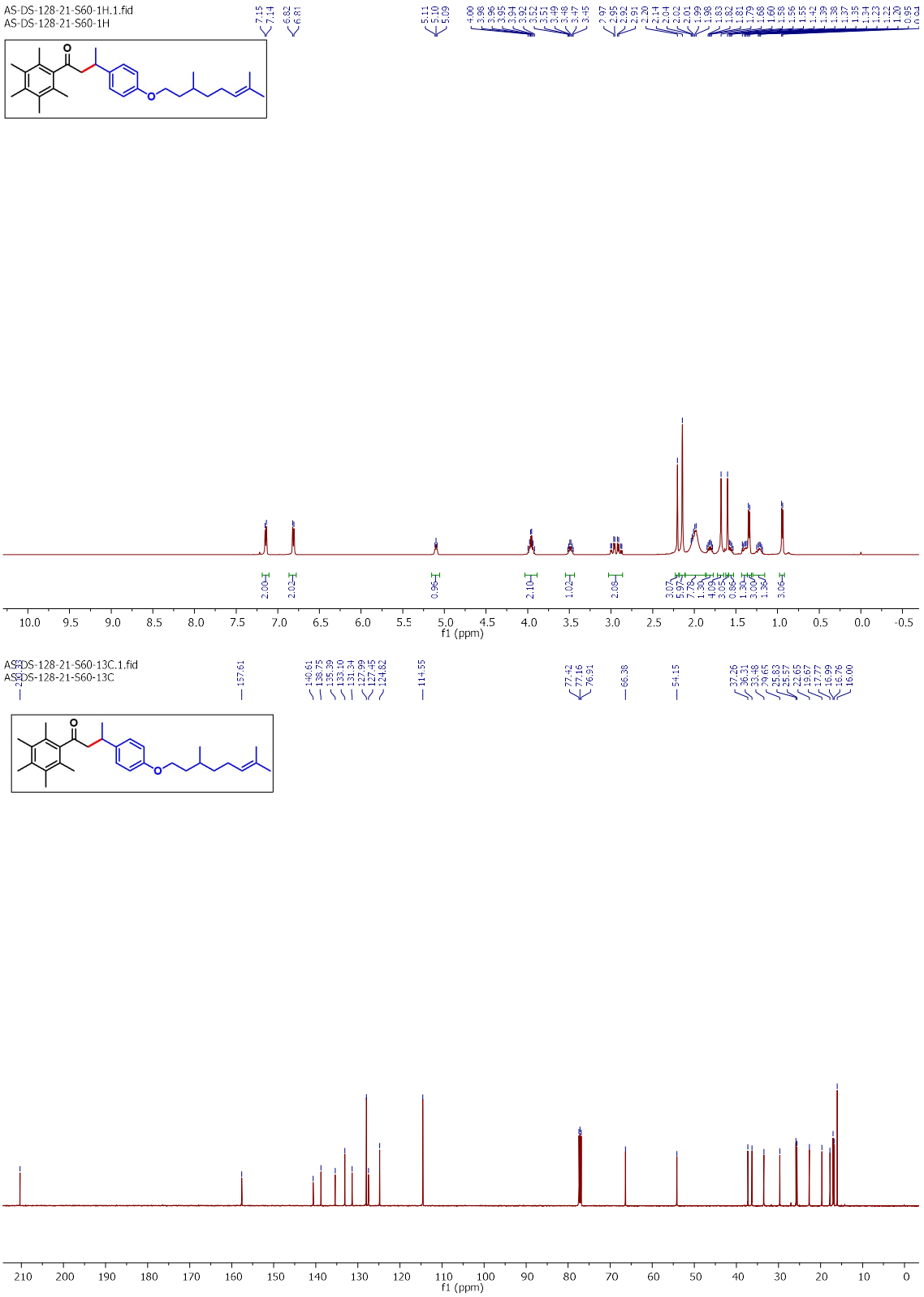


Figure S83. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3az** in $CDCl_3$.

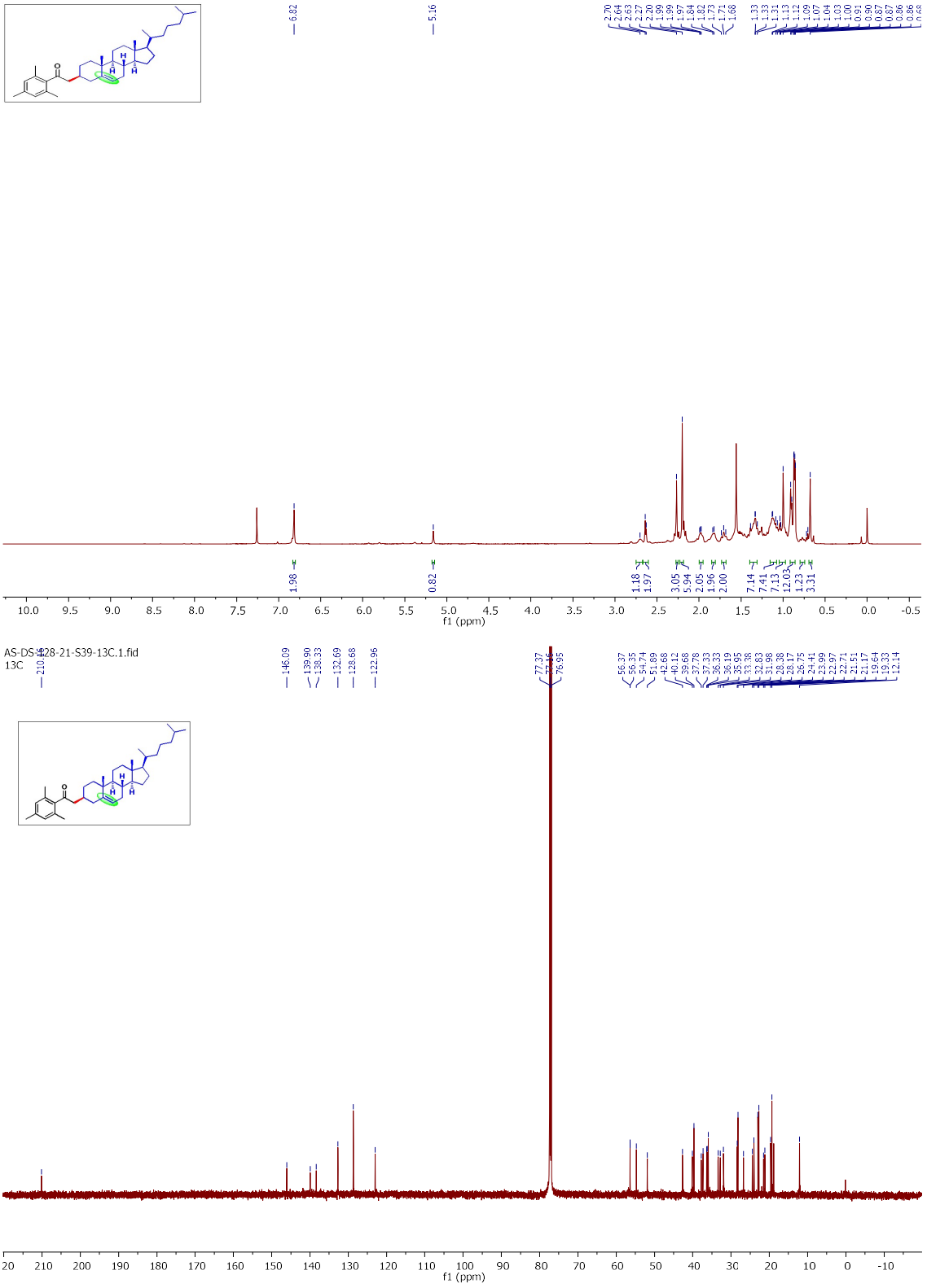


Figure S84. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3bw** in $CDCl_3$.

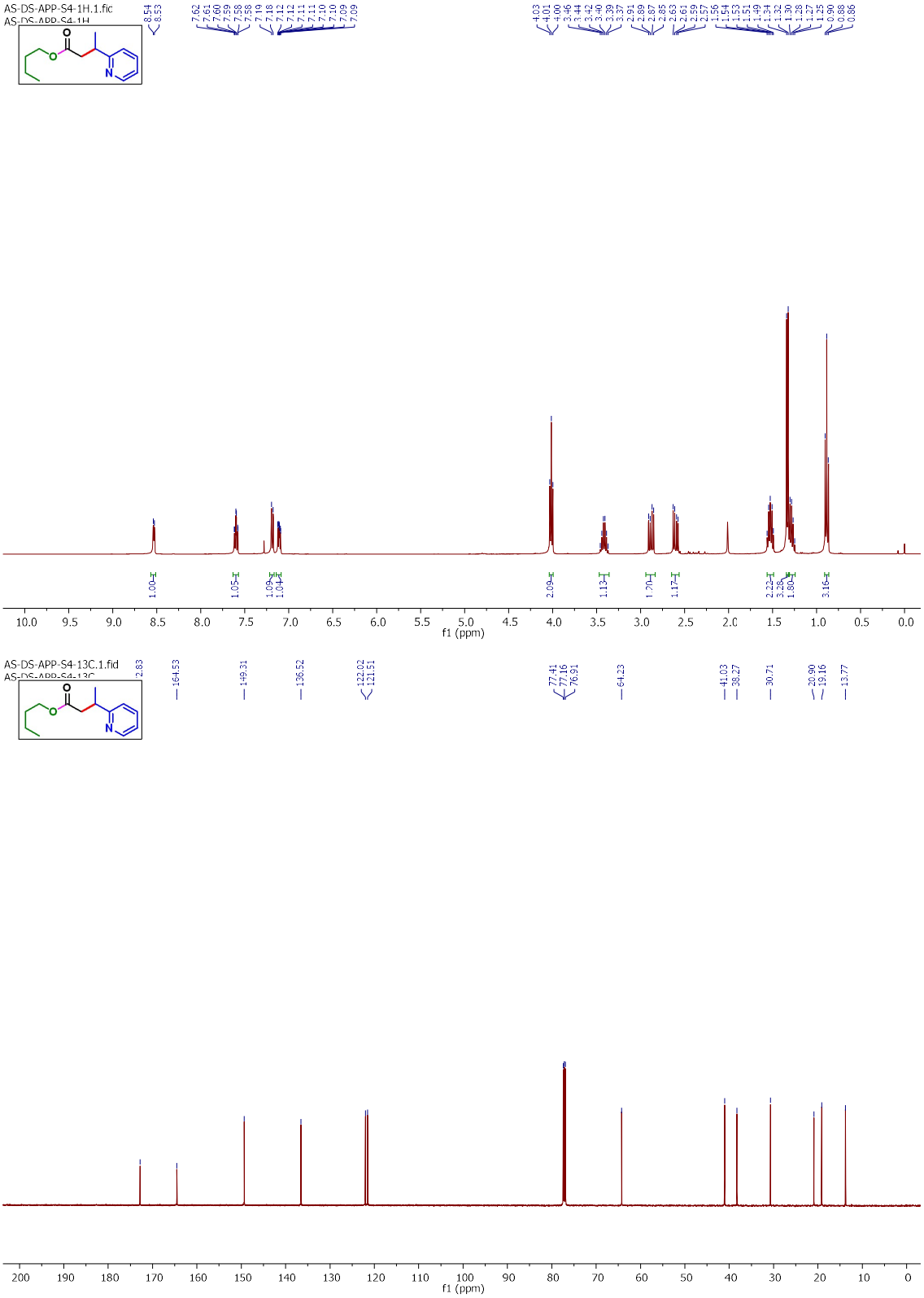


Figure S85. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **4a** in $CDCl_3$.

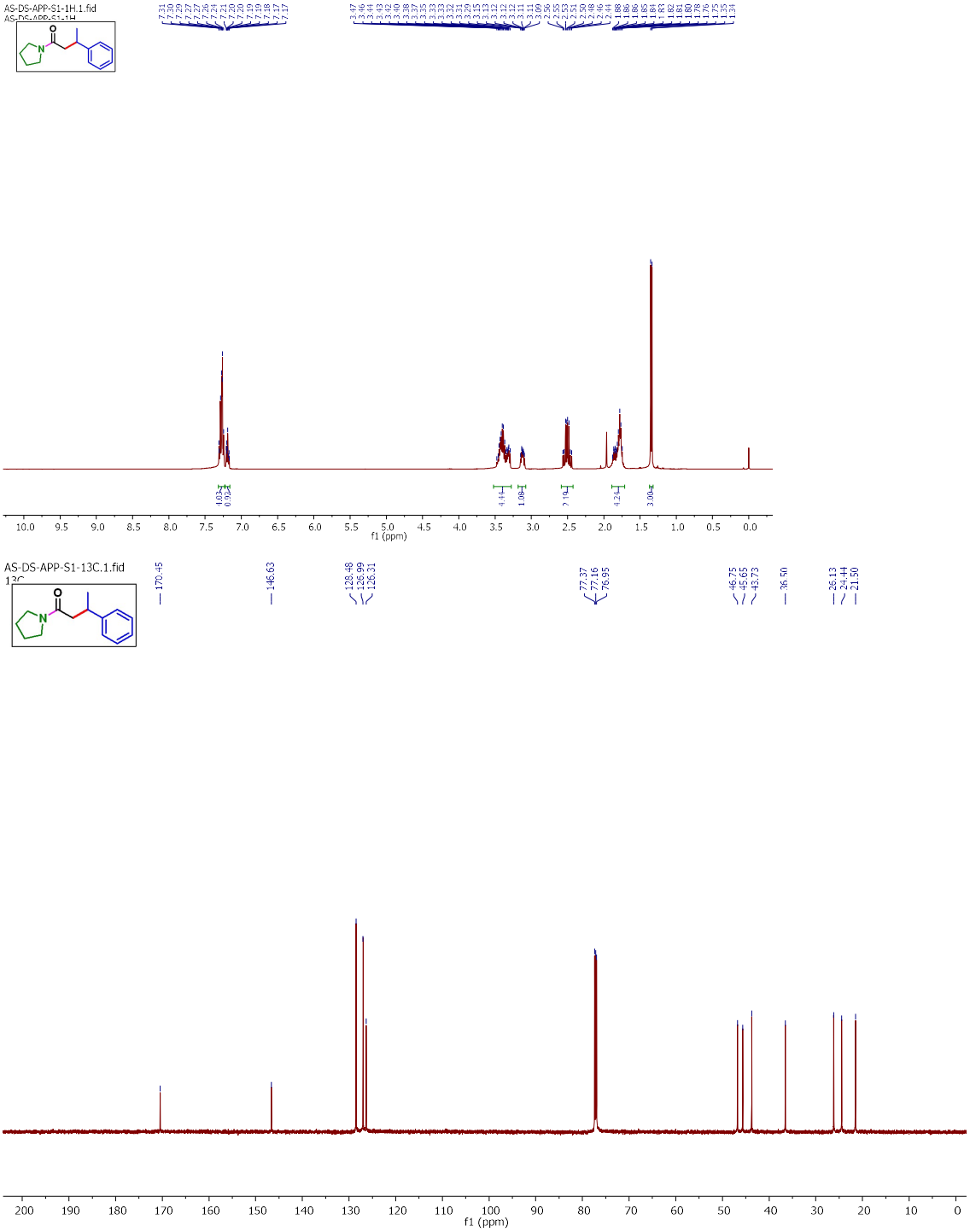


Figure S86. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **4b** in $CDCl_3$.

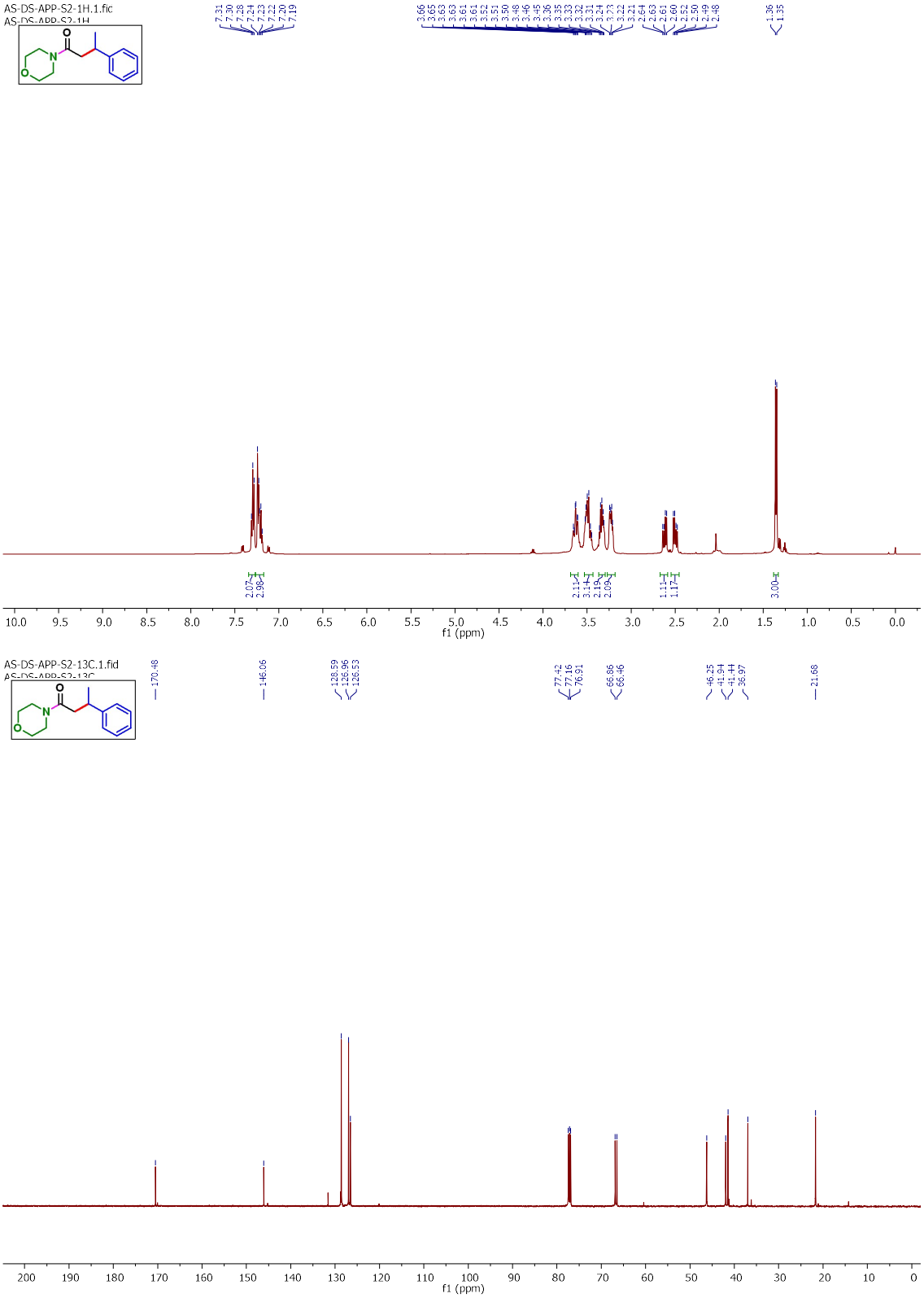


Figure S87. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **4c** in $CDCl_3$.

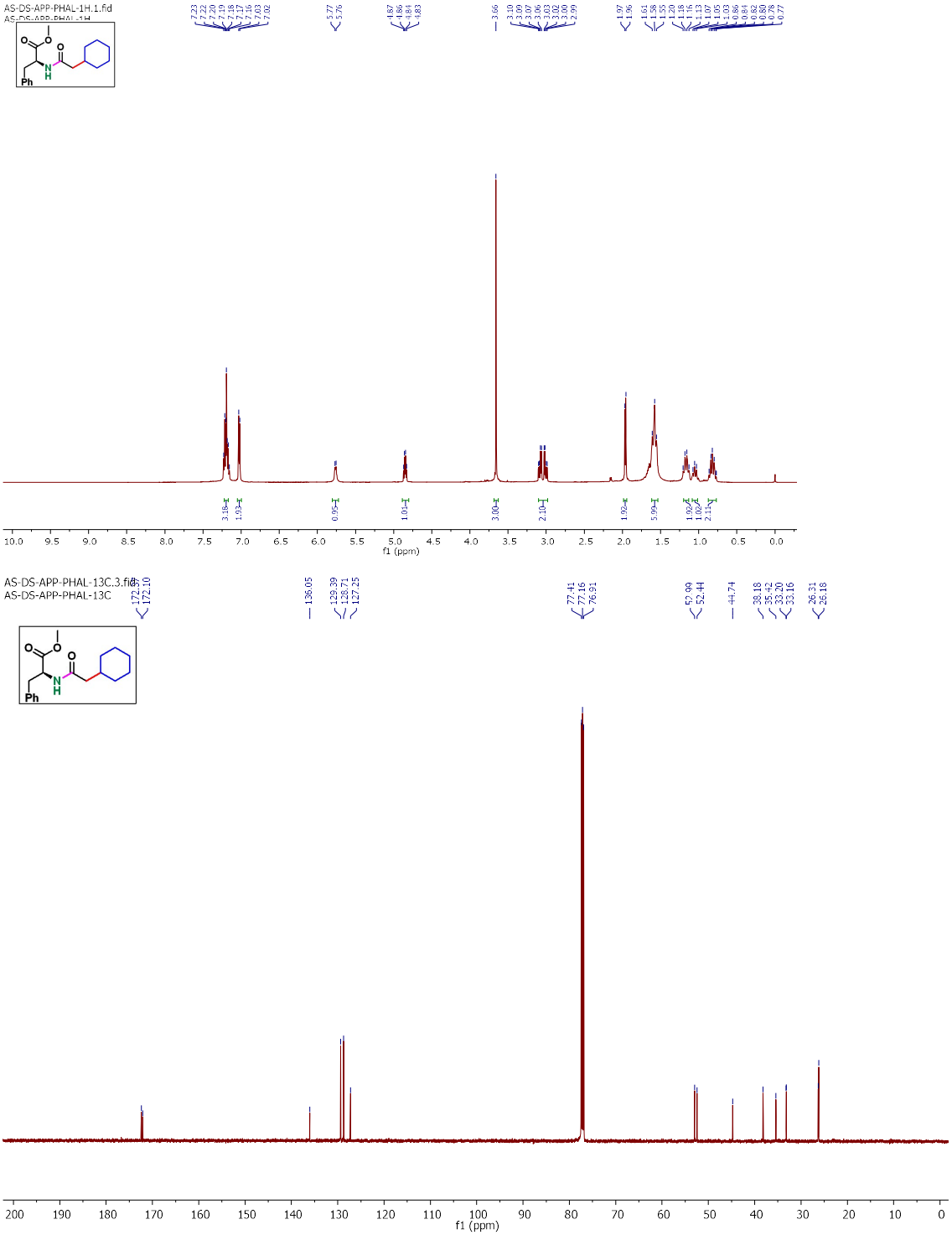


Figure S88. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **4d** in $CDCl_3$.

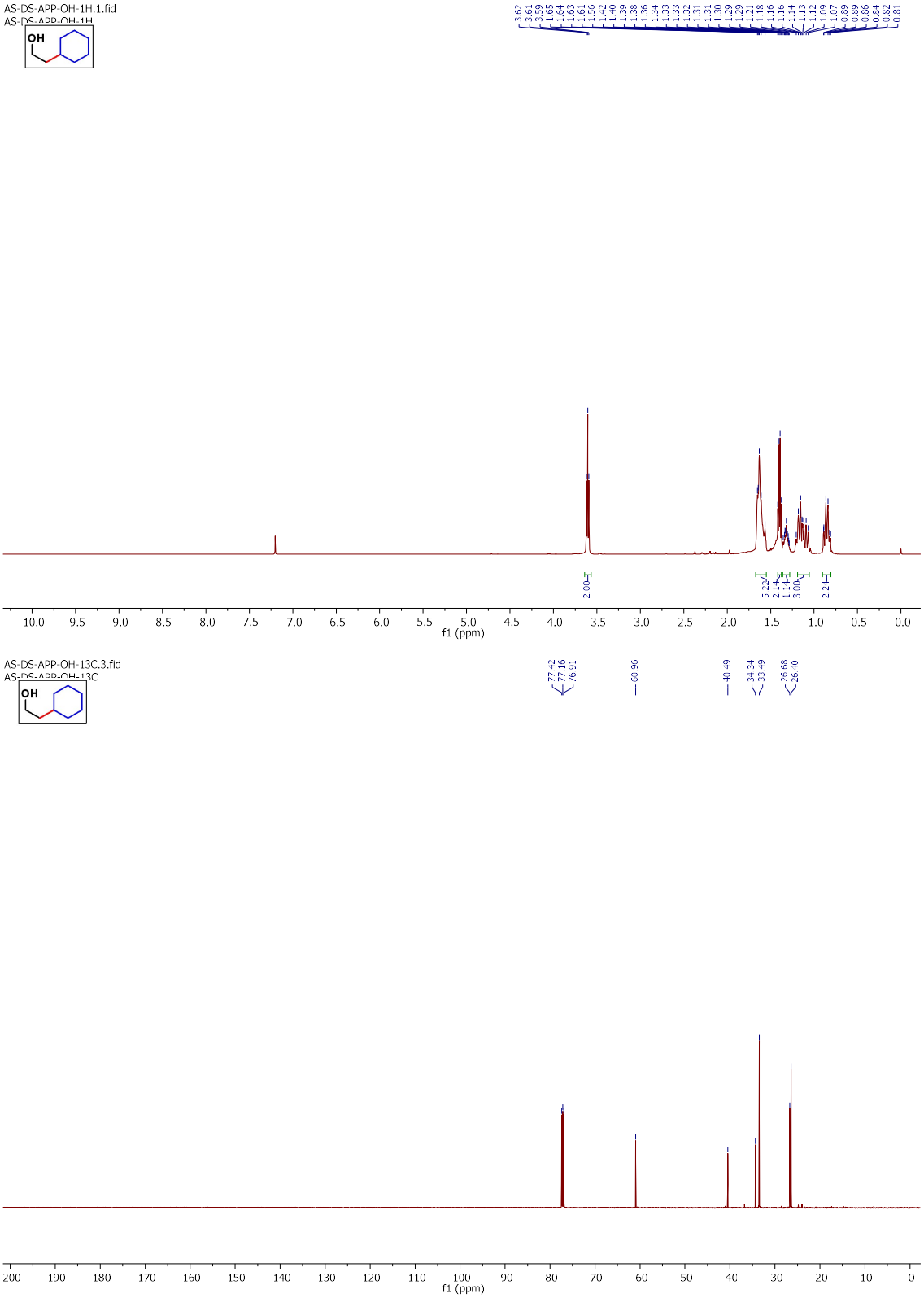


Figure S89. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **4e** in $CDCl_3$.

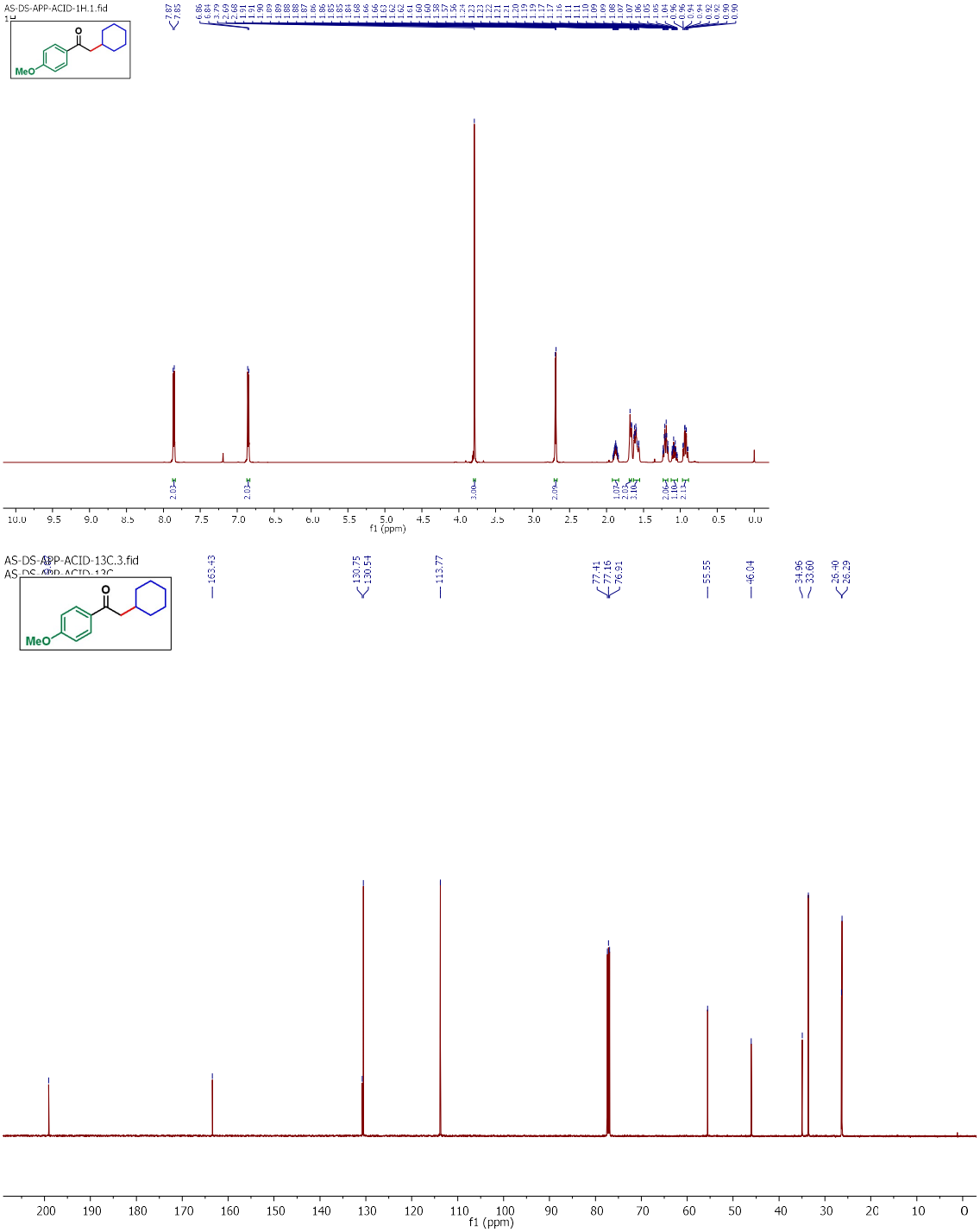


Figure S90. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **4f** in $CDCl_3$.

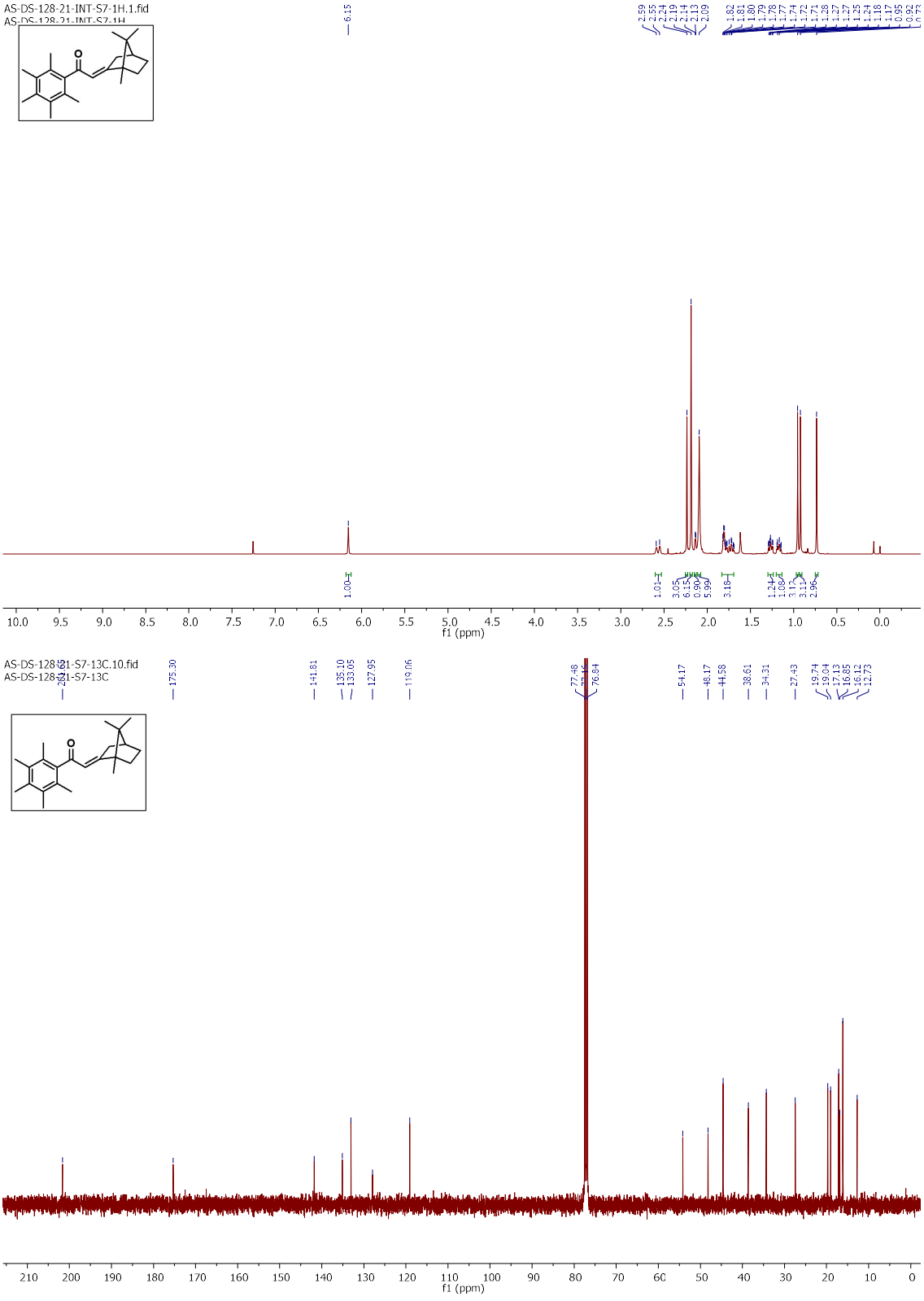


Figure S91. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of Compound **3bx′** in $CDCl_3$.

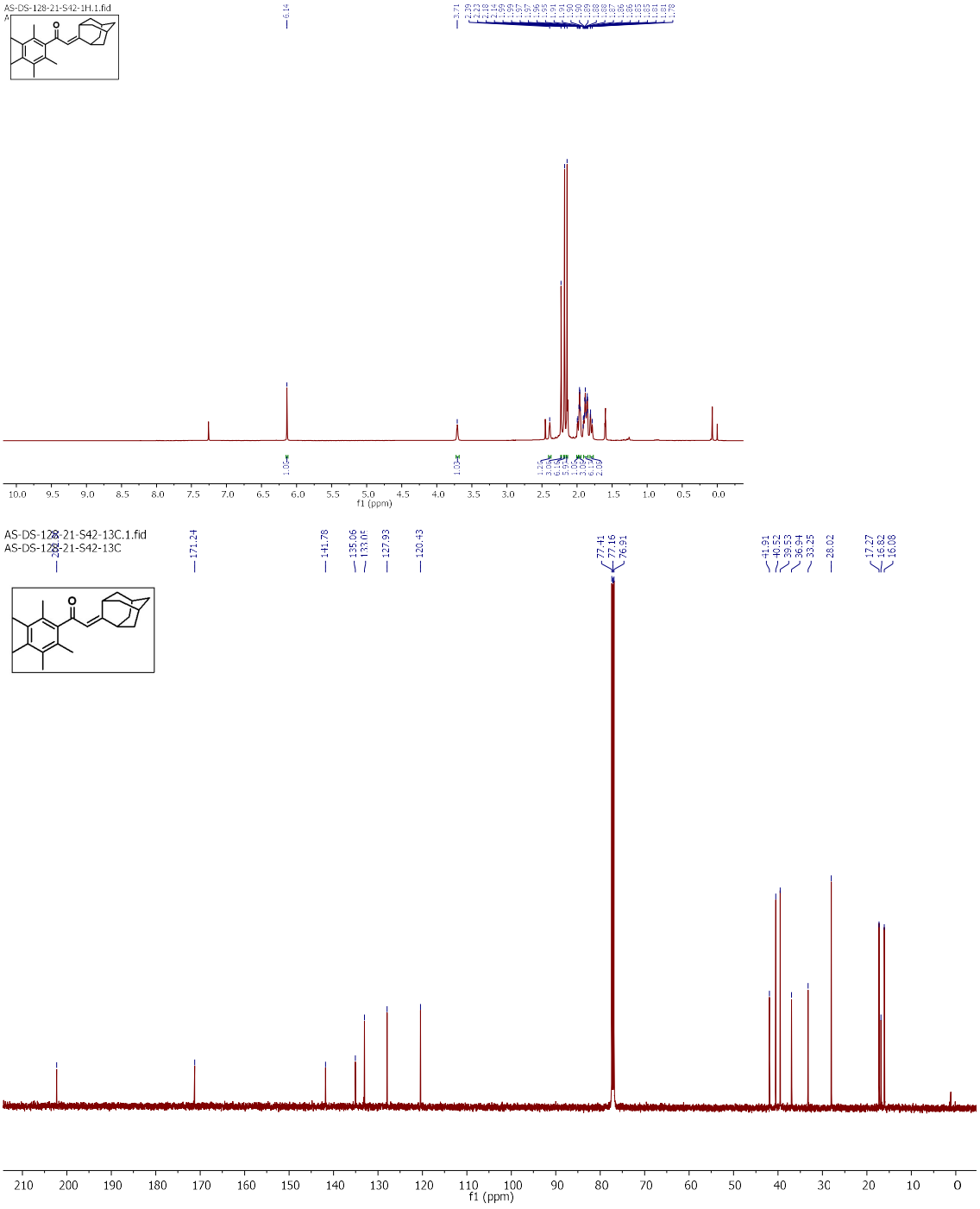


Figure S92. ^{1}H NMR (500 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of Compound **3by′** in $CDCl_3$.

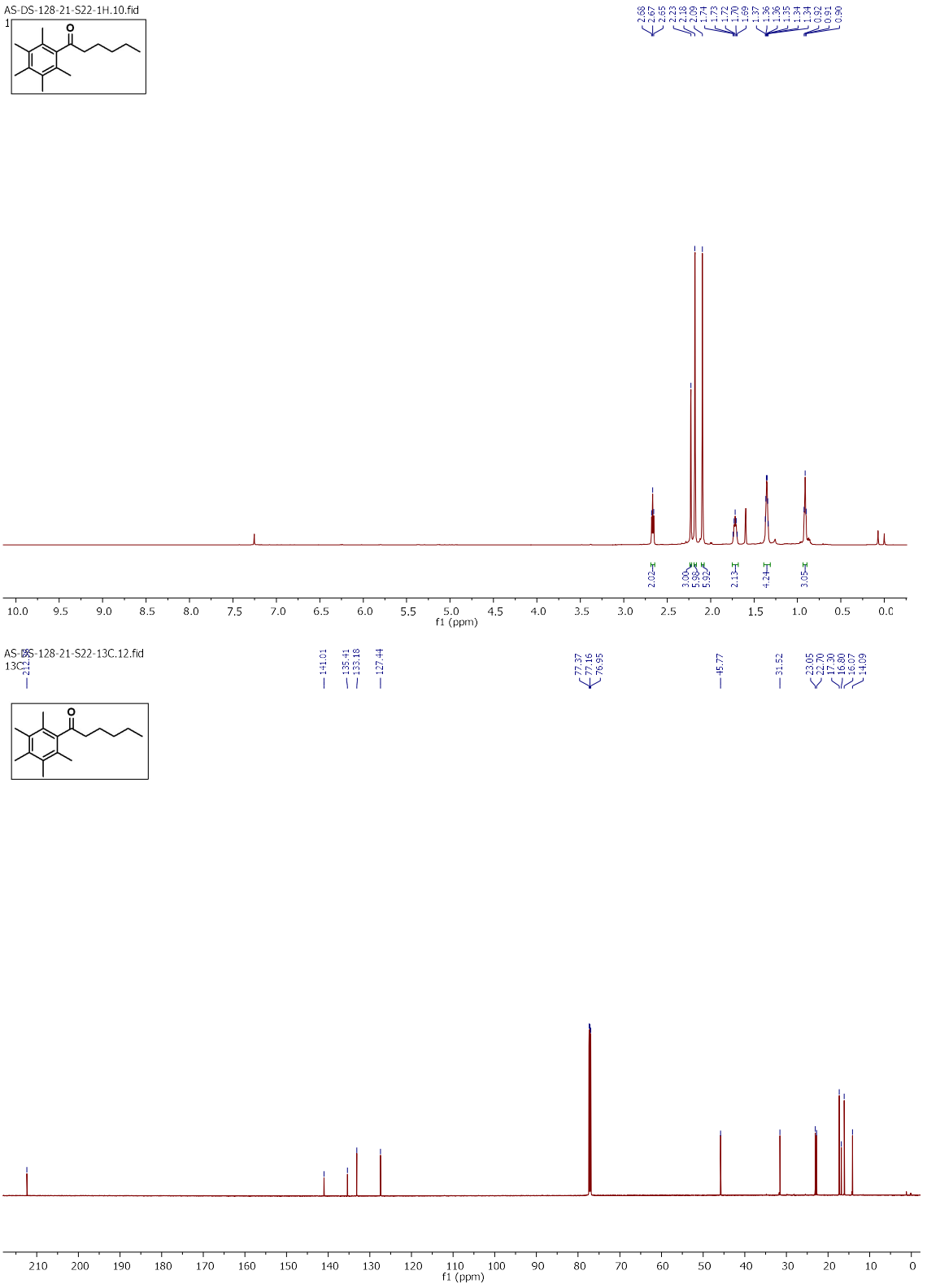


Figure S93. ^{1}H NMR (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectrum of Compound **3be′** in $CDCl_3$.

15. References:

1. (a) T. V. U. Gangan and M. L. P. Reddy *Dalton Trans.* **2015**, *44*, 15924. (b) X. Zeng, Y. Li, Q. -Q. Min, X. -S. Xue and X. Zhang *Nature Chemistry* **2023**, *15*, 1064–1073. (c) A. M. Farrag, M. H. Ibrahim, A. B. M. Mehany, M. M. F. Ismail *Bioorganic Chemistry* **2020**, *105*, 104378. (d) J. Dong, X. Wang, Z. Wang, H. Song, Y. Liu and Q. Wang *Chem. Sci.* **2020**, *11*, 1026-1031.
2. R. Sharma, A. Mondal, A. Samanta, N. Biswas and Srimani *Adv. Synth. Catal.* **2022**, *364*, 2429–2437.
3. K. Maji, P. R. Thorve and B. Maji *Chem. Commun.* **2022**, *58*, 9516-9519.
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