Redox-Neutral Decarboxylative Cross-Coupling of Oxamates with Arylbromides

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General Considerations

Chemicals

All the chemicals were purchased from commercial sources (Sigma-Aldrich, Merck, TCI, ACROS Organics, Spectrochem, Carbanio, BLDpharm) and directly used as received without additional purification. Anhydrous solvents (DMA, DMF, DMSO, CH_3CN, $CHCl_3$, THF, 1,4-dioxane, NMP) dry over Molecular Sieves were purchased Extra AcroSeal™, Thermo Scientific™ directly used as received without additional purification.

Chromatography

Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum 60 F-254 plates. Visualization of TLC was achieved by using a UV lamp (254 nm). Column chromatography was carried out with silica gel (60-120 mesh, 100-200 mesh and 230-400 mesh) to purify products using proper solvents as the eluent system. All the yields of the products are referred to chromatography pure compounds.

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra were recorded at 500 MHz for ^{1}H NMR spectra and 125 MHz for ^{13}C NMR spectra. ^{19}F NMR spectra were recorded in chloroform-*d* at 471 M Hz. The sample to be analyze was dissolved in chloroform-*d* and DMSO solvent. Chemical shifts are quoted in parts per million referenced to the appropriate solvent peak. For ^{13}C NMR and ^{1}H NMR, chemical shifts are reported in parts per million referenced to the center of a triplet at 77.16 ppm and 7.26 ppm of chloroform-*d* respectively. For ^{13}C NMR and ^{1}H NMR, chemical shifts are reported in parts per million referenced to the center of a septet at 39.52 ppm and 2.50 ppm of DMSO respectively. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet; d = doublet; t = triplet; q = quartet; quin = quintet; sext = sextet; sept = septet; m = multiplet; brs = broad singlet. Coupling constants, *J* are reported in hertz.

Fourier Transform Infrared Spectroscopy

FT-IR spectra were recorded on the IR Prestige-21 SHIMADZU instrument using a KBr disc or pellet and are reported in terms of frequency of absorption (cm^{-1}).

High-Resolution Mass Spectrometry (HRMS)

HRMS was recorded on the Thermo Scientific Q Exactive TM Benchtop LC-HRMS (ESI) instrument.

UV instrument

The optical absorption spectra were recorded on a Shimadzu (Model UV3600) spectrophotometer.

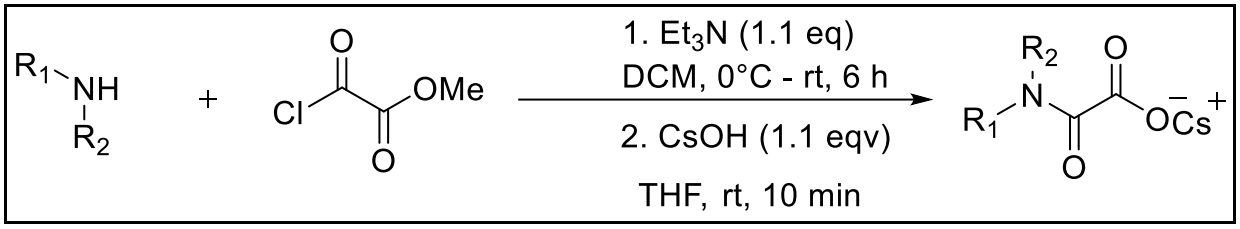
Melting point apparatus

Melting points (MP) are uncorrected and were recorded on a Thomas-Hoover Unimelt capillary melting point apparatus.

Description of Light Source and reaction vessels

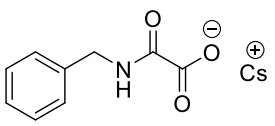
The blue lights were purchased from Kessil (Kessil® PR160-456 nm). All the reactions were conducted in 10 ml crimp glass vials made up of borosilicate glass material. The reaction vessels were placed 5 cm away from the light sources (see, Figure 1).

General procedure for synthesis of Cesium Oxamates (A):

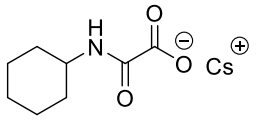


Et_3N (11 mmol, 1.1 equiv) was added to a DCM (30 mL) solution containing the appropriate amine (10 mmol, 1.0 equiv). The solution is cooled down to 0°C, and then methyl oxalyl monochloride (11 mmol, 1.1 equiv) solution of DCM (10 mL) was slowly added to the stirred mixture. The mixture was brought to room temperature before it was stirred for 6 hours. The reaction was then quenched with 1.0 M HCl (20 ml). The layers were separated, and the aqueous layer was extracted three times with DCM (20 ml). Then the combined organic phase was drying over Na_2SO_4, and evaporation in a vacuum. The concentrated residue (1 eq.) was dissolved in THF. Then 1.1eq of CsOH was added to the solution and stirred under room temperature for 10 min. The progress of the reaction was checked by checking the TLC of the resultant mixture. The mixture was dried under reduced pressure until dry solid salt was obtained. Good to excellent yields were observed in each case.

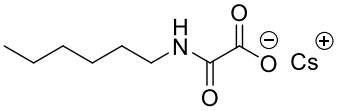
The following salts were prepared using the above-mentioned procedure:



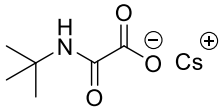
1a



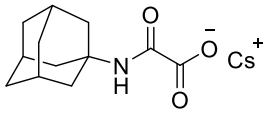
1b



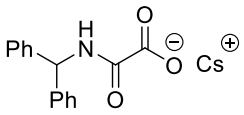
1c



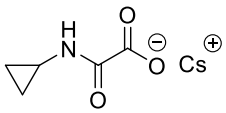
1d



1e



1f



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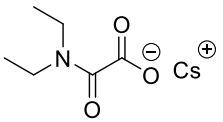
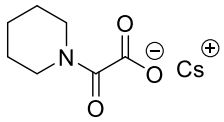
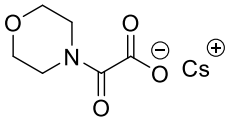


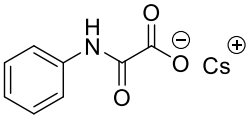
1h



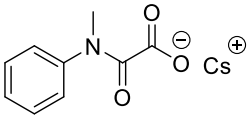
1i



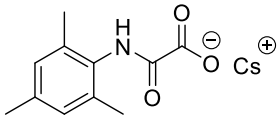
1j



1k

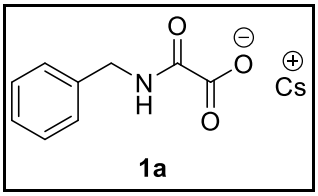


1l



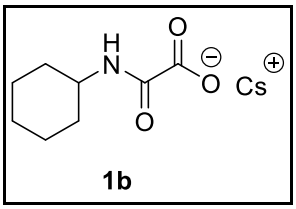
1m

Characterisation of Cesium Oxamates derivatives:



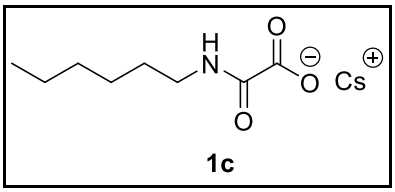
1a

Cesium 2-(benzylamino)-2-oxoacetate (1a) was prepared following the general procedure (A), the product **1a** was obtained as a white solid (910 mg, 91% yield). **MP**:105-112°C.**^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.30-7.19 (m, 5H), 4.21 (s, 2H). **^{13}C{^{1}H} NMR** (125 MHz DMSO-d_6) δ 166.3, 163.1, 140.0, 128.1, 127.2, 126.5, 41.9. **IR (neat, cm^{-1}):** 3398, 1674, 1627, 1514, 1394, 1247, 860, 740, 700. **HRMS (ESI)**: m/z calculated for $C_9H_{10}NO_3^+(M+2H)^+$: 180.0655, found: 180.0654.



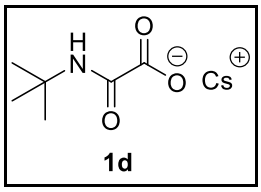
1b

Cesium 2-(cyclohexylamino)-2-oxoacetate (1b) was prepared following the general procedure (A), the product **1b** was obtained as a white solid (910 mg, 91% yield). **MP**: 268-272°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 3.43-3.39 (m, 1H), 1.68-1.63 (m, 4H), 1.55-1.52 (m, 1H), 1.26-1.10 (m, 5H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 165.0, 163.3, 47.1, 32.3, 25.1, 24.6. **IR (neat, cm^{-1}):** 3290, 2924, 2848, 1635, 1510, 1392, 1367, 1313, 1203, 1095, 889, 765. **HRMS (APCI)**: m/z calculated for $C_8H_{14}NO_3^+(M+2H)^+$: 172.0968, found: 172.0965.



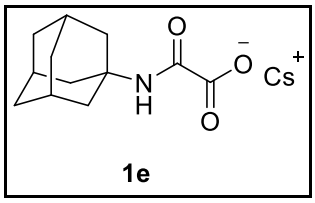
1c

Cesium 2-(hexylamino)-2-oxoacetate (1c) was prepared following the general procedure (A), the product **1c** was obtained as a brownish semi-solid (900 mg, 90% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.93 (s, 1H), 3.40 (s, 2H), 3.01, 3.00, 2.98, 2.97, 2.50, 1.39, 1.37, 1.36, 1.26, 1.25, 1.23, 0.86, 0.85, 0.84. **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 166.1, 163.4, 40.0, 39.8, 39.6, 39.5, 39.3, 39.1, 39.0, 38.4, 31.0, 29.2, 26.1, 22.0, 13.9. **IR (neat, cm^{-1}):** 3373, 2943, 2868, 1647, 1514, 1463,1400, 1311, 771. **HRMS (APCI)**: m/z calculated for $C_8H_{16}NO_3^+(M+2H)^+$: 174.1125, found: 174.1123.



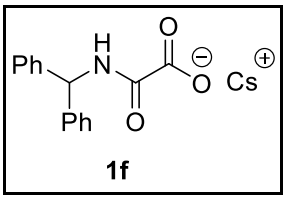
1d

Cesium 2-(tert-butylamino)-2-oxoacetate (1d): was prepared following the general procedure (A), the product **1d** was obtained as a white solid (820 mg, 82% yield). **MP**: 91-95°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.61 (s, 1H), 1.24 (s, 9H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 165.3, 163.6, 49.1, 28.3. **IR (neat, cm^{-1}):** 3373, 2968, 2914, 1683, 1629, 1512, 1450, 1371, 1263, 1220, 794, 754. **HRMS (ESI)**: m/z calculated for $C_6H_{10}NO_3^-$(M): 144.0655, found: 144.0650.



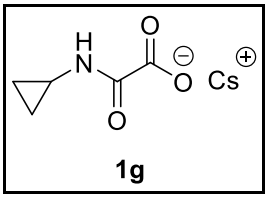
1e

Cesium 2-(((3s,5s,7s)-adamantan-1-yl) amino)-2-oxoacetate (1e) was prepared following the general procedure (A), the product **1e** was obtained as a white solid (880 mg, 88% yield). **MP**: 304-309°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 2.00 (s, 3H), 1.90 (s, 5H), 1.61 (s, 5H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 164.9, 163.5, 49.5, 36.0, 28.7. **IR (neat, cm^{-1}):** 3354, 2904, 2848,1664, 1643, 1620, 1510, 1375, 1099, 810, 781. **HRMS (APCI)**: m/z calculated for $C_{12}H_{18}NO_3^+$(M+2H)$^+$: 224.1281, found: 224.1279.



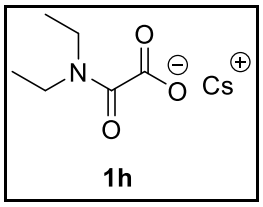
1f

Cesium 2-(benzhydrylamino)-2-oxoacetate (1f) was prepared following the general procedure (A), the product **1f** was obtained as a white solid (920 mg, 92% yield). **MP**: 186-191°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.33-7.21 (m, 10H), 5.98 (s, 1H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 165.3, 162.8, 142.6, 128.4, 127.1, 126.9, 55.9. **IR (neat, cm^{-1}):** 3367, 3037, 1643, 1500, 1446, 1375, 761, 702. **HRMS (APCI)**: m/z calculated for $C_{15}H_{12}NO_3^-$(M): 254.0812, found: 254.0807.



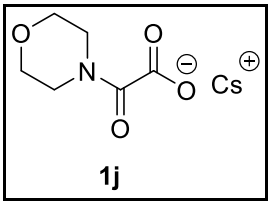
1g

Cesium 2-(cyclopropylamino)-2-oxoacetate (1g) was prepared following the general procedure (A), the product **1g** was obtained as a yellowish solid (900 mg, 90% yield). **MP**: 215-221°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.86 (s, 1h), 2.61-2.55 (m, 1H), 0.57-0.53 (m, 2H), 0.46-0.43 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 167.7, 163.0, 22.1, 5.6. **IR (neat, cm^{-1}):** 3373, 1653, 1516, 1386, 1342, 1315, 1232, 1020, 983, 840, 765. **HRMS (APCI)**: m/z calculated for $C_5H_8NO_3^+$(M+2H)$^+$:130.0499, found: 130.0499.



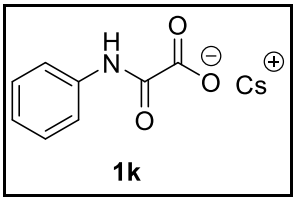
1h

Cesium 2-(diethylamino)-2-oxoacetate (1h) was prepared following the general procedure (A), the product **1h** was obtained as a brownish solid (870 mg, 87% yield). **MP**: 157-164°C.^{1}H NMR (500 MHz, DMSO-d_6) δ 3.22-3.13 (m, 4H), 1.05 (t, J=6.95 Hz, 3H), 0.97 (t, J=6.95 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 170.7, 167.8, 41.1, 36.4, 14.4, 13.0. **IR (neat, cm^{-1}):** 3456, 1604, 1382, 1274, 1151, 794. **HRMS (APCI)**: m/z calculated for $C_6H_{12}NO_3^+$(M+2H)$^+$: 146.0812, found: 146.0811.



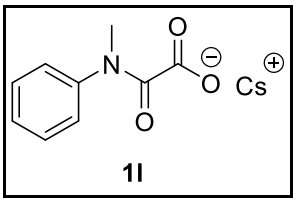
1j

Cesium 2-morpholino-2-oxoacetate (1j) was prepared following the general procedure (A), the product **1j** was obtained as an offwhite solid (890 mg, 89% yield). **MP**: 284-289°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 3.50-3.48 (m, 4H), 3.31-3.27 (m, 4H). **^{13}C{^{1}H} NMR** (125 MHz DMSO-d_6) δ 169.6, 166.4, 66.4, 66.0, 45.6. **IR (neat, cm^{-1}):** 3373, 2986, 2918, 1608, 1496, 1436, 1379, 1313, 1274, 1107, 1037, 943, 842, 775, 709. **HRMS (ESI)**: m/z calculated for $C_6H_{10}NO_4^+$(M+2H)$^+$: 160.0604, found: 160.0602.



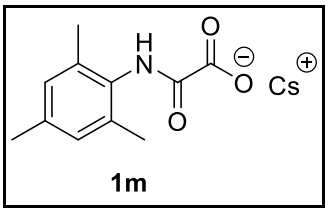
1k

Cesium 2-oxo-2-(phenylamino) acetate (1k) was prepared following the general procedure (A), the product **1k** was obtained as a white solid (850 mg, 85% yield). **MP**: 247-253°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.06 (s, 1H), 7.73 (d, J=8 Hz, 2H), 7.26 (t, J=7.7 Hz, 2H), 7.00 (t, J=7.7 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 165.2, 163.1, 139.5, 129.0, 123.2, 119.3. **IR (neat, cm^{-1}):** 3367, 3062, 1664, 1591, 1512, 1354, 1303, 765, 754. **HRMS (ESI)**: m/z calculated for $C_9H_9CsNO_3$(M): 311.9631, found: 311.9634.



1l

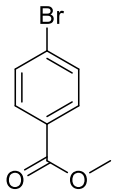
Cesium 2-(methyl(phenyl)amino)-2-oxoacetate (1l) was prepared following the general procedure (A), the product **1l** was obtained as a white solid (890 mg, 89% yield). **MP:** 98-106°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.35 (s, 5H), 7.18 (s, 1H), 3.26-3.14 (m, 3H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 170.8, 166.7, 143.9, 128.5, 124.9, 111.6, 34.1. **IR (neat, cm^{-1}):**3290, 3120, 1442, 1402, 1344, 1120, 825, 773. **HRMS (APCI)**: m/z calculated for $C_9H_{10}NO_3^+(M+2H)^+$: 180.0655, found: 180.0654.



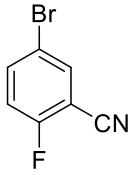
1m

Cesium 2-(mesitylamino)-2-oxoacetate (1m): was prepared following the general procedure (A), the product **1m** was obtained as a white solid (830 mg, 83% yield). **MP**: 117-123°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.28 (s, 1H), 6.83 (s, 2H), 2.20 (s, 3H), 2.06 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 164.8, 162.9, 134.6, 134.3, 133.2, 128.0, 20.4, 18.2. **IR (neat, cm^{-1}):** 3456, 3361, 2918, 1689, 1647, 1514, 1377, 844, 769. **HRMS (ESI)**: m/z calculated for $C_{12}H_{15}CsNO_3$(M): 354.0101, found: 354.0102.

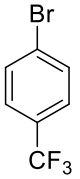
Synthesis and scope of aryl bromide



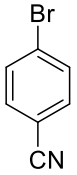
2a



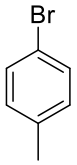
2b



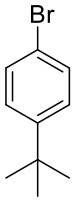
2c



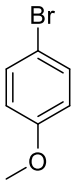
2d



2e



2f



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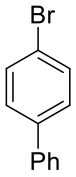
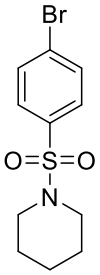
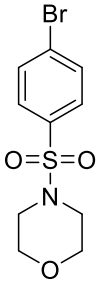


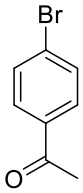
2h



2i



2j



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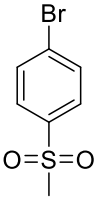
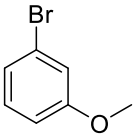
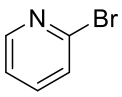


2l



2m



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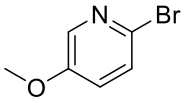
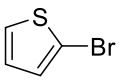
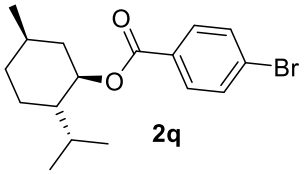


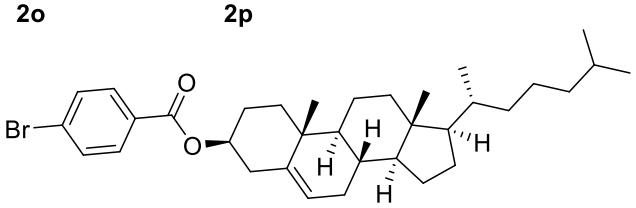
2o



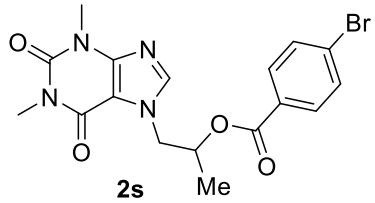
2p



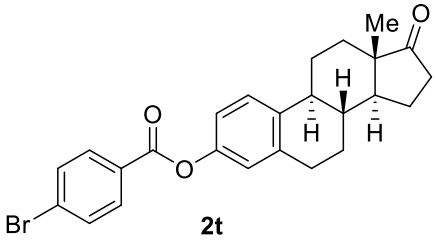
2q



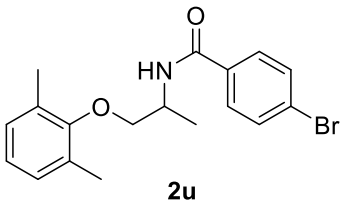
2r



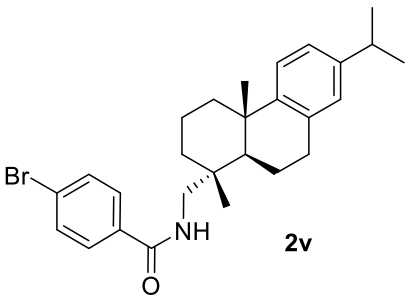
2s



2t



2u

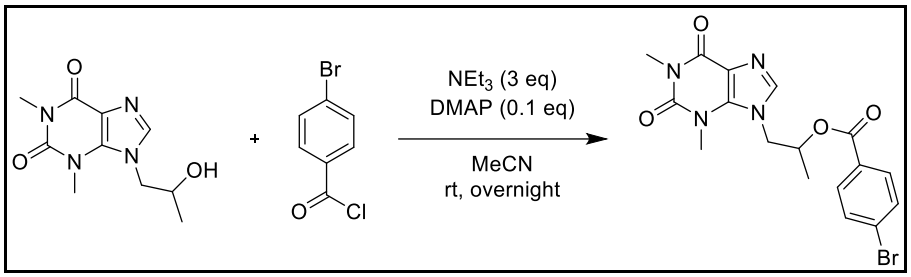


2v

Aryl Bromides **2a, 2b, 2c, 2d, 2e, 2f, 2g, 2h, 2k, 2l, 2m, 2n, 2o, 2p**, were purchased from commercial suppliers. Aryl Bromides **2i**[1], **2j**[1], **2q**[2], **2r**[2], **2t**[3], **2v**[4] were prepared according to known literature procedure.

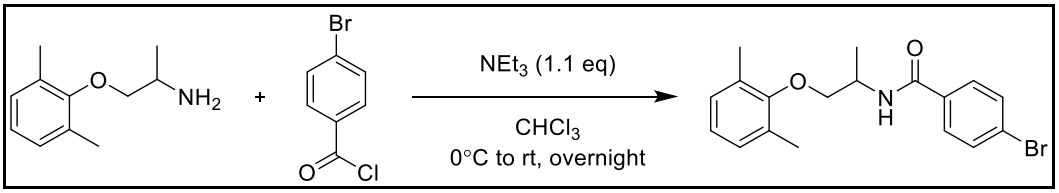
Preparation and characterization of starting material:

1-(1,3-dimethyl-2,6-dioxo-1,2,3,4,5,6-hexahydro-7H-purin-7-yl) propan-2-yl 4-bromobenzoate (2s):



The alcohol (1.3 g, 5.5 mmol, 1.2 eq) was dissolved in MeCN (20 ml) followed by the addition of NEt_3 (1.9 ml, 13.5 mmol, 3 eq) and DMAP (55 mg, 0.45 mmol, 0.1 eq). Then 4-bromo benzoyl chloride (1 g, 4.5 mmol, 1 eq) was added dropwise to the reaction mixture. Then the reaction was stirred overnight at rt. After completion of the reaction, the reaction mixture was quenched by $NaHCO_3$ and extracted with EtOAC. The organic layer was separated by sat. NaCl and filtered over Na_2SO_4. The organic layer was concentrated under reduced pressure and The product **2s** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 1:1) and afforded as white solid. **MP :** 96-100°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.57-7.53 (m, 3H), 5.53-5.50 (m, 1H), 4.69-4.66 (m, 1H), 4.48-4.44 (m, 1H), 3.55 (s, 3H), 3.37 (s, 3H), 1.43 (d, J= 6.45 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 164.8, 155.4, 151.7, 148.8, 141.5, 132.0, 131.0, 128.6, 128.5, 107.2, 70.3, 50.8, 29.9, 28.0, 17.3. **IR (neat, cm^{-1})**: 2937, 2366, 1728, 1651, 1581, 1550, 1475, 1268, 1101, 1018, 844, 759. **HRMS (ESI)**: m/z calculated for $C_{17}H_{18}BrN_4O_4$+(M+H)$^+$: 421.0506, found: 421.0506.

4-bromo-N-(1-(2,6-dimethyl phenoxy) propan-2-yl) benzamide (2u):

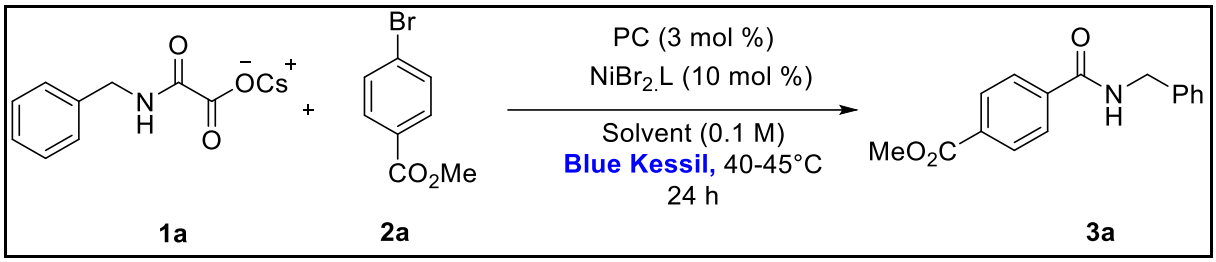


The amine (1 g, 5.6 mmol, 1 eq) was dissolved in $CHCl_3$(15 ml) followed by the addition of NEt_3 (0.87 ml, 6.2 mmol, 1.1 eq). Then 4-bromo benzoyl chloride (1.35 g, 6.16 mmol, 1.1 eq) was added dropwise to the reaction mixture. Then the reaction was slowly brought to rt and was stirred overnight. After completion of the reaction, the reaction mixture was quenched by water and extracted with $CHCl_3$. The organic layer was washed with 1M HCl solution and separated by sat. NaCl and filtered over Na_2SO_4. The organic layer was concentrated under reduced pressure and The product **2u** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 8:1) and afforded as white solid white solid. **MP:** 138-143°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, J=8.35 Hz, 2H), 7.59 (d, J=8.35 Hz, 2H), 7.01 (d, J=7.45 Hz, 2H), 6.95-6.92 (m, 1H), 6.62-6.61 (m, 1H), 4.56-4.53 (m, 1H), 3.94-3.91 (m, 1H), 3.82-3.80 (m, 1H), 2.26 (s, 6H), 1.52 (d, J=6.85 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 165.9, 154.8, 133.5, 132.0, 130.8, 129.2, 128.6, 126.3, 124.3, 73.9, 46.1, 17.9, 16.3. **IR (neat,**

cm^{-1}): 3273, 3095, 2929, 1645, 1595, 1554, 1481, 1303, 1203, 1037, 833, 765, 731. **HRMS (ESI)**: m/z calculated for $C_{18}H_{21}BrNO_2$+(M+H)$^+$: 362.0750, found: 362.0750.

Optimization details

General procedure for the optimization



All the reaction set up were performed inside the glovebox with an argon atmosphere. An oven-dried 10 mL glass vial was charged with **1a** (46.6 mg, 0.15 mmol, 1.5 eq), **2a** (21.5 mg, 0.1 mmol, 1 eq), Photocatalyst (3 mol%), $NiBr_2$.L (10 mol%) and a PTFE coated magnetic bar. Then solvent (0.1 M) was added to the glass vial and sealed with a PTFE septum. The reaction vials were placed on the magnetic stirrer under irradiation with a Kessil® PR160-456 nm light (40 W) at 45-50 °C (the temperature mentioned in the reaction condition is produced by the light source itself not by an external heat source) and after 24 h, benzyl benzoate (0.1 mmol) was added as an internal standard. The reaction mixture was extracted with EtOAc, followed by washing with brine solution. The organic layer was concentrated under reduced pressure and was analyzed by ^{1}H NMR to determine the yield of the reaction.

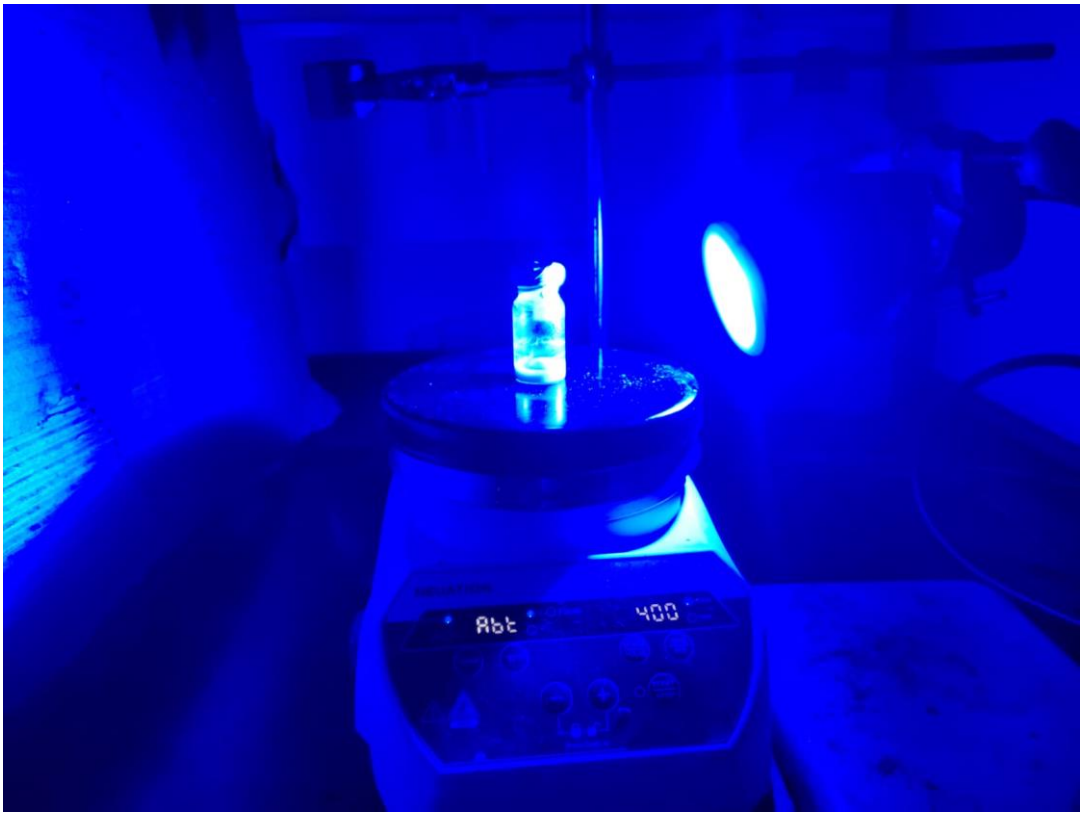
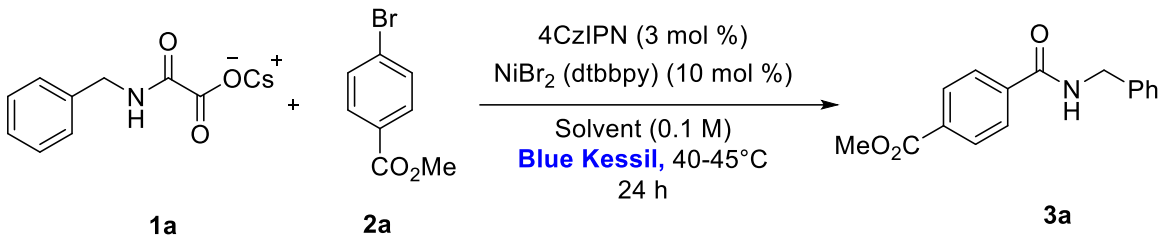


Figure S1: Reaction setup with Kessil® PR160-456 nm light (40 W)

Optimisation

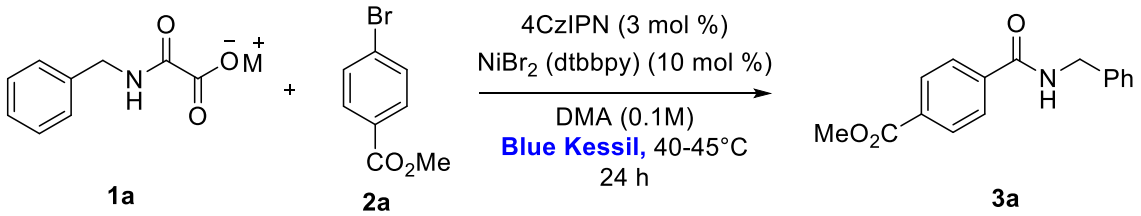
Table S1: Screening of Solvents:



Entry	Variation in solvents	Yield (%)
1	DMF	67
2	DMA	75 (71)[b]
3	DMSO	49
4	CH_3CN	0
5	DCM	0
6	Dioxane	0
7	DMF + DMA	71

Optimization of the Reaction Conditions. **1a** (0.15 mmol), **2a** (0.1 mmol). NMR yields using benzyl benzoate as internal standard.[b]isolated yield.

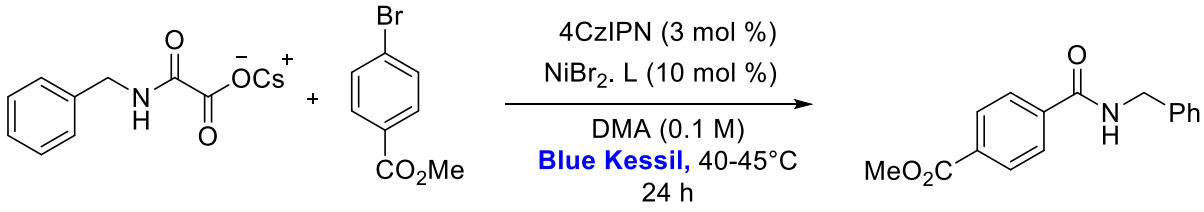
Table S2: Screening of Counter ions



Entry	Counter Ion M	Yield (%)
1	Cs	75 (71)[b]
2	Li	27
3	Na	33
4	K	52

Optimization of the Reaction Conditions. **1a** (0.15 mmol), **2a** (0.1 mmol). NMR yields using benzyl benzoate as internal standard. [b]isolated yield.

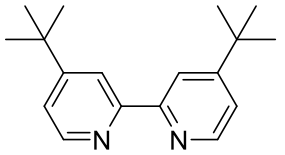
Table S3. Screening of other conditions:



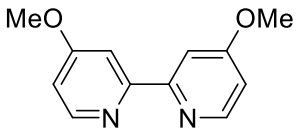
1a **2a** **3a**

Entry	Deviation from standard condition	Yield
1	Ir-I	46
2	Ir-II	38
3	$NiBr_2$.L2 instead of $NiBr_2$.L1	62
4	$NiBr_2$.L3 instead of $NiBr_2$.L1	40
5	$NiBr_2$.L4 instead of $NiBr_2$.L1	36
6	$NiCl_2$ glyme.L1 instead of $NiBr_2$.L1	61
7	Blue LED	65
8	Purple LED	67
9	Green LED	0
10	without photocatalyst	0
11	without nickel	0
12	without ligand	12
13	without light	0

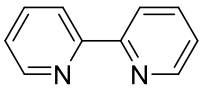
Optimization of the Reaction Conditions. **1a** (0.15 mmol), **2a** (0.1 mmol). NMR yields using benzyl benzoate as internal standard.



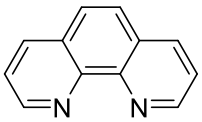
L1



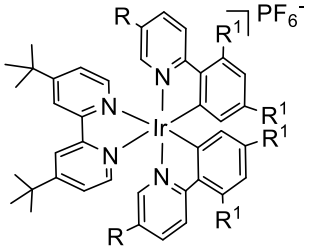
L2



L3

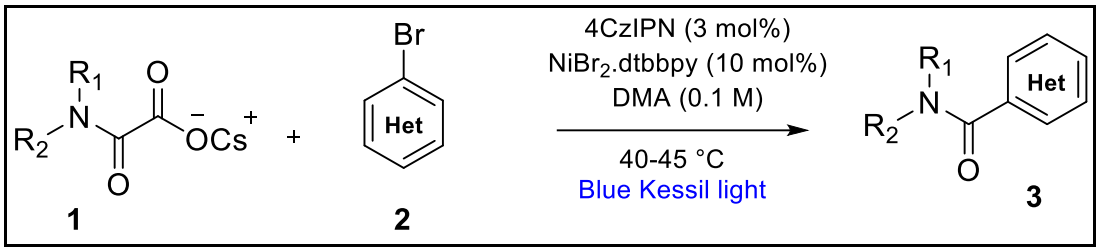


L4



Ir-I, R = CF_3, R_1 = F
Ir-II, R = R_1 = H

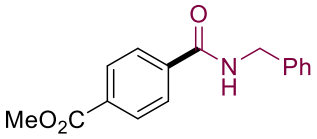
General procedure for Carbamoylation of (Hetero)Aryl Bromides



In an argon atmosphere glove box, a 10 mL glass vial was charged with **1** (0.15 mmol, 1.5 eq), **2** (0.1 mmol, 1 eq), 4CzIPN (3 mol%), $NiBr_2$.dtbbpy (10 mol%) and a PTFE coated magnetic bar. Then DMA (0.1 M) was added to the glass vial and sealed with a PTFE septum. The reaction vial was placed on the magnetic stirrer under irradiation with a Kessil® PR160-456 nm light (40 W) at 45-50 °C (the temperature mentioned in the reaction condition is produced by the light source itself not by an external heat source). After 24 h, the product was confirmed by TLC and extracted with EtOAc, followed by washing with brine solution. The organic layer was concentrated under reduced pressure. Product **3** was purified by column chromatography on silica using hexane and EtOAc.

Note*: At the same time, we run two independent reactions for each substrate, and the obtained yield was the combined average yield of these two independent runs.*

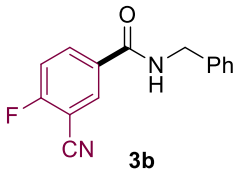
Characterisation of products



3a

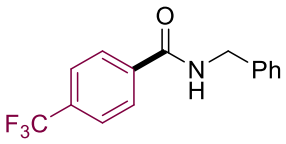
methyl 4-(benzylcarbamoyl)benzoate (3a): Following the general procedure two independent reactions of **1a** (0.15 mmol, 46.6 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3a** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 4:1) and afforded as white crystalline solid (71%, 38 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, J=8.35 Hz, 2H), 7.83 (d, J=8.35 Hz, 2H), 7.36-7.28 (m, 5H), 6.76 (brs, 1H), 4.62 (d, J=5.7 Hz, 2H), 3.92 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.7, 166.4, 138.4, 137.9, 132.8, 129.9, 128.9, 128.0, 127.8, 127.1, 52.4, 44.3. The analytical data are consistent with published ones.[5]

Scale-up reaction: Large-scale reaction (one independent reaction) was conducted using **1a** (1.5 mmol, 466 mg) and **2a** (1 mmol, 215 mg) in DMA (10 mL) for 72 h afforded **3a** as white crystalline solid (57%, 153.5 mg).



3b

N-benzyl-3-cyano-4-fluorobenzamide (3b): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2b** (0.1 mmol, 20 mg) for 24 h. The product **3b** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 5:1) and afforded as off-white semisolid (56%, 28.4 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71-7.63 (m, 3H), 7.38-7.33 (5H), 6.55 (brs, 1H), 4.63 (d, J=5.6 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 164.4, 163.5 ($^{1}J_{C-F}$ = 259.53 Hz), 141.1 ($^{4}J_{C-F}$ = 6.96 Hz), 137.34, 134.03, 129.09, 128.16, 128.13, 123.14 ($^{5}J_{C-F}$ = 3.7 Hz), 115.7 ($^{2}J_{C-F}$ = 20.97 Hz), 113.30, 104.3 ($^{3}J_{C-F}$ = 15.68 Hz), 44.65. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -104.58. **IR (neat, cm^{-1})**: 3294, 1639, 1531, 1492, 1230, 763, 700. **HRMS (ESI):** m/z calculated for $C_{15}H_{12}N_2OF^+(M+H)^+$: 255.0934, found: 255.0930.

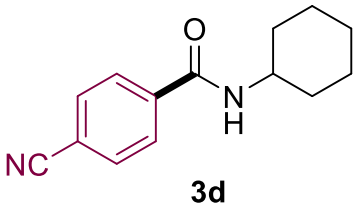


3c

N-benzyl-4-(trifluoromethyl) benzamide (3c): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2c** (0.1 mmol, 22.5 mg) for 24 h. The product **3c** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 4:1) and afforded as white solid (63%, 35.1 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, J=8.2 Hz, 2H), 7.69 (d, J=8.2 Hz, 2H), 7.38-7.31 (m, 5H), 6.52 (brs, 1H), 4.66

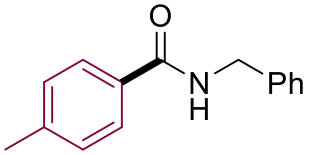
(d, J=5.65 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.0, 137.7, 137.6, 132.3 (q, $^{2}J_{C-F}$ =32.46 Hz), 128.9, 127.9, 127.8, 127.4, 125.6 (q, $^{3}J_{C-F}$ =3.7 Hz), 123.2 (q, $^{1}J_{C-F}$=270.73 Hz), 44.4**. ^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.95. The analytical data are consistent with published ones. [6]

Scale-up reaction: Large-scale reaction (one independent reaction) was conducted using **1a** (1.5 mmol, 466 mg) and **2c** (1 mmol, 225 mg) in DMA (10 mL) for 72 h afforded **3c** as white solid (45%, 112 mg).



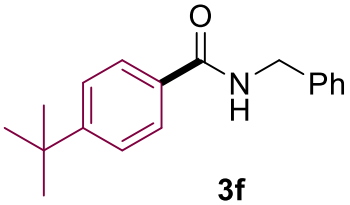
3d

4-cyano-N-cyclohexylbenzamide (3d): Following the general procedure two independent reactions of **1b** (0.15 mmol, 45.4 mg) and **2d** (0.1 mmol, 18.2 mg) for 24 h. The product **3d** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 5:1) and afforded as white solid (53%, 24.1 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, J=8.2 Hz, 2H), 7.71 (d, J=8.2 Hz, 2H), 6.07 (brs, 1H), 3.99-3.92 (m, 1H), 2.03-2.00 (m, 2H), 1.78-1.74 (m, 2H), 1.67-1.65 (m, 1H), 1.46-1.37 (m, 2H), 1.28-1.18 (m, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 164.8, 139.0, 132.3, 127.6, 118.0, 114.8, 49.1, 33.1, 25.4, 24.8. The analytical data are consistent with published ones. [7]



3e

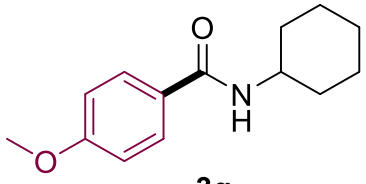
N-benzyl-4-methyl benzamide (3e):- Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2e** (0.1 mmol, 17.1 mg) for 30 h. The product **3e** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as white solid (54%, 24.3 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, J=7.95, 2H), 7.35-7.28 (m, 5H), 7.22 (d, J=7.9, 2H), 6.44 (brs, 1H), 4.64 (d, J=5.65, 2H), 2.39 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 167.4, 142.1, 138.4, 131.6, 129.4, 128.9, 128.0, 127.7, 127.1, 44.2, 21.5. The analytical data are consistent with published ones. [6]



3f

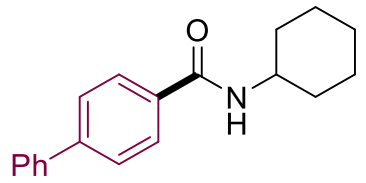
N-benzyl-4-(tert-butyl)benzamide (3f): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2f** (0.1 mmol, 21.3 mg) for 30 h.The product **3f** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as white solid (51%, 27.2 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d,

J=8.3 Hz, 2H), 7.44 (d, J=8.3 Hz, 2H), 7.36-7.28 (m, 5H), 6.38 (brs, 1H), 4.66 (d, J=5.65 Hz, 2H), 1.33 (s, 9H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 167.4, 155.2, 138.4, 131.6, 128.9, 128.0, 127.7, 126.9, 125.6, 44.2, 35.0, 31.3. The analytical data are consistent with published ones. [8]



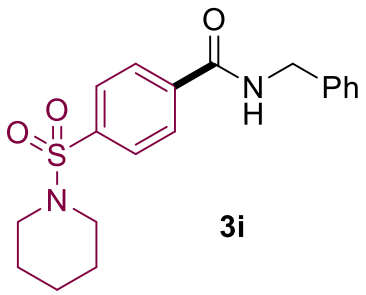
3g

***N*-cyclohexyl-4-methoxy benzamide (3g)**:- Following the general procedure two independent reactions of **1b** (0.15 mmol, 45.4 mg) and **2g** (0.1 mmol, 18.7 mg) for 30 h. The product **3g** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as white solid (48%, 22.3 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, J=8.6 Hz, 2H), 6.91 (d, J=8.65 Hz, 2H), 5.88 (brs, 1H), 4.00-3.92 (m, 1H), 3.84 (s, 3H), 2.03-2.01 (m, 2H), 1.76-1.65 (m, 3H), 1.46-1.39 (m, 2H), 1.29-1.19 (m, 3H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 166.3, 162.1, 128.7, 127.5, 113.8, 55.5, 48.7, 33.5, 25.7, 25.1. The analytical data are consistent with published ones.[6]



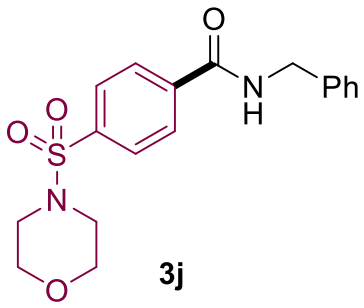
3h

N-cyclohexyl-[1,1'-biphenyl]-4-carboxamide (3h):- Following the general procedure two independent reactions of **1b** (0.15 mmol, 45.4 mg) and **2h** (0.1 mmol, 23.3 mg) for 30 h. The product **3h** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 13:1) and afforded as white amorphous solid (61%, 34 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, J=8.1 Hz, 2H), 7.64 (d, J=8.1 Hz, 2H), 7.60 (d, J=7.4 Hz, 2H), 7.46 (t, J=7.4 Hz, 2H), 7.40-7.37 (m, 1H), 6.06 (brs, 1H), 4.04-3.98 (m, 1H), 2.06-2.04 (m, 2H), 1.78-1.75 (m, 2H), 1.68-1.65 (m, 1H), 1.48-1.40 (m, 2H), 1.29-1.21 (m, 3H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 166.4, 144.2, 140.2, 133.9, 129.0, 128.0, 127.5, 127.3, 127.3, 48.8, 33.4, 25.7, 25.0. The analytical data are consistent with published ones. [6]



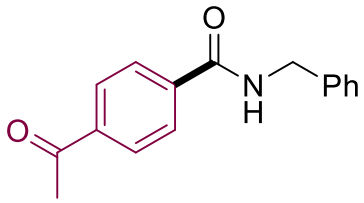
3i

N-benzyl-4-(piperidin-1-ylsulfonyl) benzamide (3i):-Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2i** (0.1 mmol, 30.4 mg) for 24 h. The product **3i** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 3:1) and afforded as white solid (69%, 49 mg). MP : 159-164°C.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, J=8.4 Hz, 2H), 7.78 (d, J=8.4 Hz, 2H), 7.38-7.29 (m, 5H), 6.62 (brs, 1H), 4.66 (d, J=5.6 Hz, 2H), 2.97 (t, J=5.35 Hz, 4H), 1.64-1.60 (m, 4H), 1.43-1.39 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.1, 139.3, 138.4, 137.8, 129.0, 128.1, 128.0, 127.9, 127.8, 47.0, 44.5, 25.2, 23.5. **IR (neat, cm^{-1})**: 3340, 2933, 2852, 1639, 1543, 1454, 1338, 1165, 1087, 927, 756. **HRMS (ESI)**: m/z calculated for $C_{19}H_{23}N_2O_3S$+(M+H)+: 359.1424, found: 359.1426.



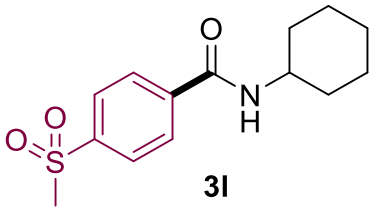
3j

N-benzyl-4-(morpholinosulfonyl)benzamide (3j): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2j** (0.1 mmol, 30.6 mg) for 24 h. The product **3j** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 2:1) and afforded as white solid (67%, 48.2 mg).**MP :** 174-177°C.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, J=8.15 Hz, 2H), 7.77 (d, J=8.15 Hz, 2H), 7.36-7.30 (m, 5H), 6.68 (brs, 1H), 4.64 (d, J=5.6 Hz, 2H), 3.73-3.71 (m, 2H), 2.98-2.97 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 165.9, 138.8, 138.0, 137.7, 129.0, 128.1, 128.1, 128.0, 127.9, 66.1, 46.0, 44.5. **IR (neat, cm^{-1})**: 3332, 2920, 2860, 1645, 1539, 1448, 1355, 1261, 1166, 1111, 943, 854, 743. **HRMS (ESI):** m/z calculated for $C_{18}H_{21}N_2O_4S$+(M+H)+: 361.1217, found: 361.1213.



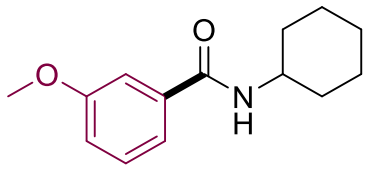
3k

4-acetyl-N-benzylbenzamide (3k):- Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2k** (0.1 mmol, 19.9 mg) for 24 h.The product **3k** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 3:1) and afforded as white solid (59%, 29.8 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, J=7.95 Hz, 2H), 7.87 (d, J=8.2 Hz, 2H), 7.38-7.29 (m, 5H), 6.51 (brs, 1H), 4.66-4.65 (m, 2H), 2.63 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 197.5, 166.5, 139.4, 138.4, 137.9, 129.0, 128.7, 128.1, 127.9, 127.4, 44.4, 26.9. The analytical data are consistent with published ones. [5]



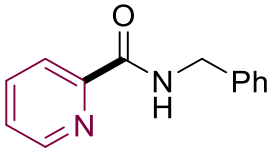
3l

N-cyclohexyl-4-(methyl sulfonyl) benzamide (3l): Following the general procedure two independent reactions of **1b** (0.15 mmol, 45.4 mg) and **2l** (0.1 mmol, 23.5 mg) for 24 h. The product **3l** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as white solid (57%, 32 mg). **MP :** 143-147°C.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, 8.3 Hz, 2H), 7.91 (d, 8.3 Hz, 2H), 6.10-6.09 (m, 1H), 4.01-3.94 (m, 1H), 3.06 (s, 3H), 2.06-2.03 (m, 2H), 1.79-1.76 (m, 2H), 1.68-1.65 (m, 1H), 1.48-1.39 (m, 2H), 1.30-1.20 (m, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 165.1, 142.9, 140.3, 128.1, 127.8, 49.3, 44.5, 33.2, 25.6, 25.0. **IR (neat, cm^{-1})**: 3354, 3313, 2900, 2852, 1629, 1548, 1458, 1317, 1294, 1143, 1091, 786, 756. **HRMS (ESI):** m/z calculated for $C_{14}H_{20}NO_3S^+(M+H)^+$: 282.1158, found: 282.1153.



3m

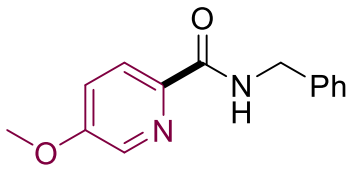
N-cyclohexyl-3-methoxybenzamide (3m): Following the general procedure two independent reactions of **1b** (0.15 mmol, 45.4 mg) and **2m** (0.1 mmol, 18.7 mg) for 24 h. The product **3m** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as white amorphous solid (51%, 23.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.28-7.27 (m, 1H), 7.04-7.02 (m, 1H), 6.01-6.00 (m, 1H), 4.01-3.96 (m, 1H), 3.86 (s, 3H), 2.06-2.03 (m, 2H), 1.78-1.75 (m, 2H), 1.69-1.65 (m, 1H), 1.48-1.41 (m, 2H), 1.28-1.21 (m, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.6, 159.9, 136.7, 129.6, 118.6, 117.5, 112.5, 55.5, 48.8, 33.3, 25.7, 25.0. The analytical data are consistent with published ones. [9]



3n

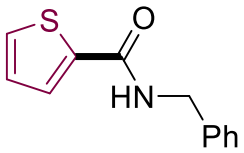
N-benzylpicolinamide (3n) :- Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2n** (0.1 mmol, 15.8 mg) for 24 h. The product **3n** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as off white semi solid (52%, 22 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53-8.52 (m, 1H), 8.39 (brs, 1H), 8.24 (d, J=7.8 Hz, 1H), 7.87-7.84 (m, 1H), 7.43-7.41 (m, 1H), 7.38-7.28 (m, 5H), 4.68 (d, J=6.1 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 164.4, 149.5, 148.2, 138.3,

137.5, 128.8, 127.9, 127.6, 126.3, 122.5, 43.6. The analytical data are consistent with published ones. [10]



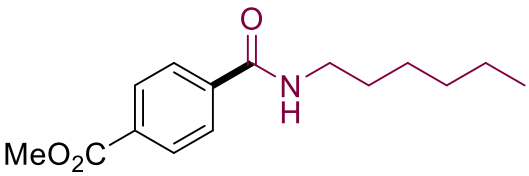
3o

N-benzyl-5-methoxypicolinamide (3o):- Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2o** (0.1 mmol, 18.8 mg) for 24 h. The product **3o** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 8:1) and afforded as off-white semi solid (65%, 31.4 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (brs, 1H), 7.85 (d, J=7.25 Hz, 1H), 7.73 (t, J=7.75 Hz, 1H), 7.38-7.28 (m, 5H), 6.90 (d, J=8,25 Hz, 1H), 4.69 (d, J=6.15 Hz, 2H), 3.92 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 164.4, 162.9, 147.2, 139.8, 138.5, 128.8, 127.7, 127.5, 115.8, 114.4, 53.6, 43.4. **IR (neat, cm^{-1})**: 3361, 1658, 1598, 1525, 1467, 1431, 1332, 1273, 1028, 825, 702. **HRMS (ESI)**: m/z calculated for $C_{14}H_{14}N_2O_2K^+$(M+K)$^+$: 281.0687, found: 281.0683.



3p

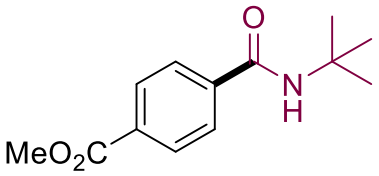
N-benzylthiophene-2-carboxamide (3p):- Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2p** (0.1 mmol, 16.3 mg) for 24 h. The product **3p** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 8:1) and afforded as white solid (44%, 19 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.36-7.30 (m, 5H), 7.08-7.06 (m, 1H), 6.31 (brs, 1H), 4.63 (d, J=5.7 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 161.9, 138.8, 138.1, 130.2, 128.9, 128.3, 128.1, 127.8, 127.8, 44.1. The analytical data are consistent with published ones. [11]



3q

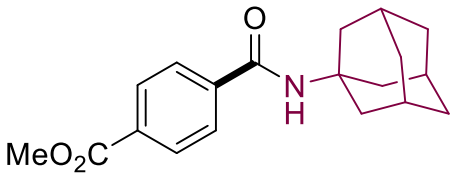
methyl 4-(hexylcarbamoyl)benzoate (3q): Following the general procedure two independent reactions of **1c** (0.15 mmol, 45.7 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3q** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 8:1) and afforded as off-white semi solid (57%, 30 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, J=8.2 Hz, 2H), 7.81 (d, J=8.2 Hz, 2H), 6.20 (brs, 1H), 3.94 (s, 3H), 3.45 (q, J=6.4 Hz,

2H), 1.63-1.59 (m, 2H), 1.41-1.37 (m, 2H), 1.33-1.31 (m, 4H), 0.90-0.88 (m, 3H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 166.7, 166.4, 138.9, 132.7, 129.9, 127.0, 52.5, 40.4, 31.6, 29.7, 26.8, 22.6, 14.1. **IR (neat, cm^{-1})**:3340, 2974, 2933, 2852, 1722, 1635, 1543, 1468, 1442, 1280, 1107, 868, 740. **HRMS (ESI)**: m/z calculated for $C_{15}H_{22}NO_3$+(M+H)+: 264.1594, found: 264.1592.



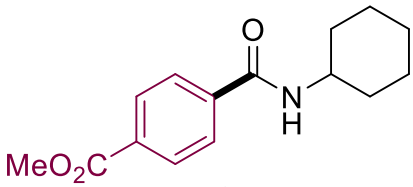
3r

methyl 4-(tert-butylcarbamoyl) benzoate (3r): Following the general procedure two independent reactions of **1d** (0.15 mmol, 41.5 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3r** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as white solid (54%, 25 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J=8.25 Hz, 2H), 7.76 (d, J=8.25 Hz, 2H), 6.00 (brs, 1H), 3.93 (s, 3H), 1.47 (s, 9H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 166.5, 166.1, 139.9, 132.4, 129.9, 126.9, 52.4, 52.0, 29.7, 28.9. The analytical data are consistent with published ones. [12]



3s

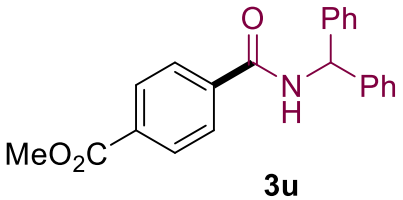
methyl 4-(((3s,5s,7s)-adamantan-1-yl) carbamoyl) benzoate (3s): Following the general procedure two independent reactions of **1e** (0.15 mmol, 53.2 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3s** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 12:1) and afforded as white crystaline solid (65%, 40.6 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, J=8.2 Hz, 2H), 7.76 (d, J=8.2 Hz, 2H), 5.82 (brs, 1H), 3.93 (s, 3H), 2.13 (s, 9H), 1.75-1.70 (m, 6H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 166.5, 165.8, 140.1, 132.4, 129.9, 126.9, 52.7, 52.4, 41.7, 36.4, 29.6. The analytical data are consistent with published ones. [13]



3t

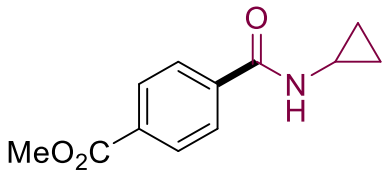
methyl 4-(cyclohexyl carbamoyl) benzoate (3t): Following the general procedure two independent reactions of **1b** (0.15 mmol, 45.4 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3t** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 12:1) and afforded as white solid (55%, 28.5 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, J=8.3 Hz, 2H), 7.80 (d, J=8.3 Hz, 2H), 6.09-6.07 (m, 1H), 4.00-3.96 (m, 1H),

3.93 (s, 3H), 2.04-2.02 (m, 2H), 1.77-1.74 (m, 2H), 1.67-1.64 (m, 1H), 1.46-1.38 (m, 2H), 1.28-1.18 (m, 3H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 166.4, 165.9, 139.1, 132.6, 129.9, 127.0, 52.5, 49.0, 33.2, 25.6, 25.0. The analytical data are consistent with published ones. [13]



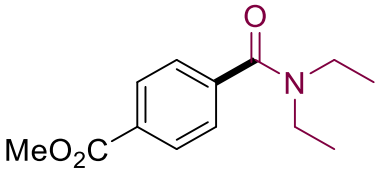
3u

methyl 4-(benzhydryl carbamoyl) benzoate (3u): Following the general procedure two independent reactions of **1f** (0.15 mmol, 58 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3u** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 8:1) and afforded as white solid (73%, 50.3 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, J=8.05, 2H), 7.87 (d, J=8.15, 2H), 7.37-7.30 (m, 10H), 6.81-6.79 (m, 1H), 6.45 (d, J=7.7 Hz, 2H), 3.94 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 166.3, 165.8, 141.2, 138.2, 133.0, 130.0, 128.9, 127.8, 127.6, 127.2, 57.7, 52.5. The analytical data are consistent with published ones.[14]



3v

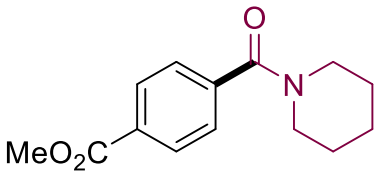
methyl 4-(cyclopropyl carbamoyl) benzoate (3v): Following the general procedure two independent reactions of **1g** (0.15 mmol, 39.2 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3v** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 4:1) and afforded as white solid (63%, 27.6 mg). **MP:** 144-147°C.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, J=8.15 Hz, 2H), 7.79 (d, J=8.15 Hz, 2H), 6.41-6.38 (m, 1H), 3.93 (s, 3H), 2.93-2.89 (m, 1H), 0.89-0.88 (m, 2H), 0.65-0.62 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ 168.1, 166.4, 138.4, 132.8, 129.9, 127.0, 52.5, 23.3, 6.9. **IR (neat, cm^{-1})**:3365, 1730, 1631, 1531, 1442, 1317, 1274, 1107, 1015, 873, 742. **HRMS (ESI):** m/z calculated for $C_{12}H_{14}NO_3^+(M+H)^+$: 220.0968, found: 220.0963.



3w

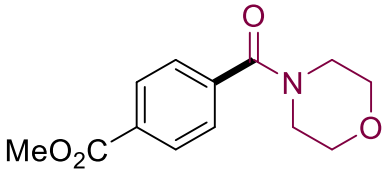
methyl 4-(diethyl carbamoyl) benzoate (3w): Following the general procedure two independent reactions of **1h** (0.15 mmol, 41.5 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3w** was purified by column chromatography of reaction mixture on silica gel

(Gradient, hexane: ethyl acetate = 9:1) and afforded as thick liquid (61%, 28.6 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J=8.05 Hz, 2H), 7.42 (d, J=8.05 Hz, 2H), 3.92 (s, 3H), 3.55-3.53 (m, 2H), 3.20-3.19 (m, 2H), 1.26-1.24 (m, 3H), 1.09-1.07 (m, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 170.3, 166.5, 141.6, 130.7, 129.9, 126.4, 52.3, 43.3, 39.4, 14.3, 12.9. The analytical data are consistent with published ones. [13]



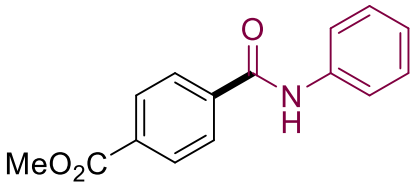
3x

methyl 4-(piperidine-1-carbonyl)benzoate (3x):- Following the general procedure two independent reactions of **1i** (0.15 mmol, 43.4 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3x** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 5:1) and afforded as off-white thick liquid (66%, 32.6 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J=8.1 Hz, 2H), 7.44 (d, J=8.1 Hz, 2H), 3.92 (s, 3H), 3.71 (brs, 2H), 3.28 (brs, 2H), 1.67 (brs, 4H), 1.50 (brs, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 169.3, 166.5, 140.9, 130.9, 129.9, 126.8, 52.4, 48.7, 43.2, 26.6, 25.6, 24.6. The analytical data are consistent with published ones. [13]



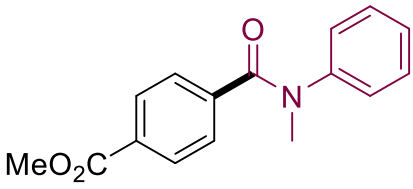
3y

methyl 4-(morpholine-4-carbonyl)benzoate (3y): Following the general procedure two independent reactions of **1j** (0.15 mmol, 43.6 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3y** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 2:1) and afforded as off-white semi solid (60%, 30 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, J=8.15 Hz, 2H), 7.47 (d, J=8.1 Hz, 2H), 3.93 (s, 3H), 3.78 (brs, 4H), 3.61 (brs, 2H), 3.39 (brs, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 169.4, 166.2, 139.5, 131.3, 129.9, 127.0, 66.8, 52.3, 48.0, 42.5. The analytical data are consistent with published ones. [13]



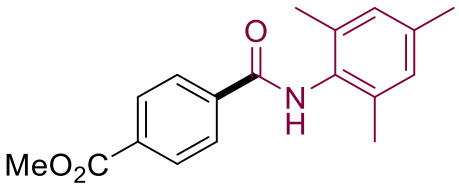
3z

methyl 4-(phenyl carbamoyl) benzoate (3z): Following the general procedure two independent reactions of **1k** (0.15 mmol, 44.5 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3z** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 9:1) and afforded as white solid (51%, 26 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, J=8.05 Hz, 2H), 7.93-7.91 (m, 3H), 7.65 (d, J=7.7 Hz, 2H), 7.38 (t, J=7.65 Hz, 2H), 7.18 (t, J=7.3 Hz, 1H), 3.96 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.3, 164.9, 139.0, 137.7, 133.1, 130.1, 129.3, 127.2, 125.0, 120.4, 52.6. The analytical data are consistent with published ones. [13]



3aa

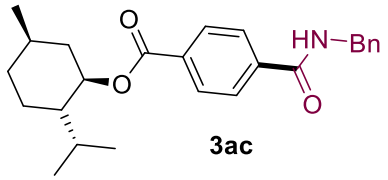
methyl 4-(methyl(phenyl)carbamoyl)benzoate (3aa): Following the general procedure two independent reactions of **1l** (0.15 mmol, 46.6 mg) and **2a** (0.1 mmol, 21.5 mg) for 24 h. The product **3aa** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 8:1) and afforded as white solid (58%, 31.2 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, J=8.1 Hz, 2H), 7.34 (d, J=8.15 Hz, 2H), 7.23-7.20 (m, 2H), 7.15-7.13 (m, 1H), 7.02 (d, J=7.7 Hz, 2H), 3.86 (s, 3H), 3.50 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 169.8, 166.5, 144.4, 140.4, 130.9, 129.4, 129.1, 128.7, 127.0, 52.3, 38.4. The analytical data are consistent with published ones.[15]



3ab

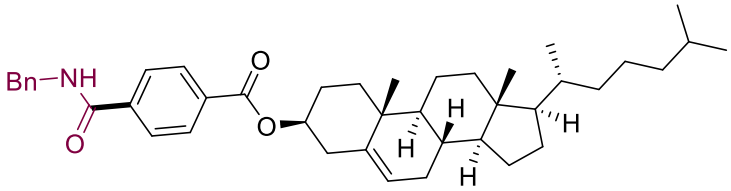
methyl 4-(mesityl carbamoyl) benzoate (3ab): Following the general procedure two independent reactions of **1m** (0.15 mmol, 50.8 mg) and **2a** (0.1 mmol, 21.5 mg) for 30 h. The product **3ab** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 6:1) and afforded as white solid (56%, 33.2 mg). **MP:** 195-198^{o}C.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, J=8.25 Hz, 2H), 7.95 (d, J=8.25 Hz, 2H), 7.49 (brs, 1H), 6.93 (s, 2H), 3.96 (s, 3H), 2.30 (s, 3H), 2.23 (s, 6H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.4,

165.4, 138.6, 137.5, 135.3, 133.0, 131.0, 130.1, 129.2, 127.3, 52.5, 21.1, 18.4. **IR (neat, cm^{-1})**:3288, 2966, 2926, 1726, 1649, 1525, 1494, 1431, 1274, 1114, 798, 731. **HRMS (ESI)**: m/z calculated for $C_{18}H_{19}NO_3K^+(M+K)^+$: 336.0997, found: 336.0995.



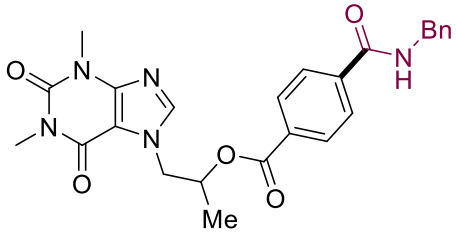
3ac

2-isopropyl-5-methylcyclohexyl 4-(benzyl carbamoyl) benzoate (3ac): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2q** (0.1 mmol, 33.9 mg) for 24 h. The product **3ac** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 19:1) and afforded as white amorphous solid (64%, 50.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, J=8.2 Hz, 2H), 7.84 (d, J=8.2 Hz, 2H), 7.34-7.30 (m, 5H), 6.65 (brs, 1H), 4.93 (dt, J=4.35 Hz, 10.87 Hz, 1H), 4.64-4.63 (m, 2H), 2.12-2.10 (m, 1H), 1.96-1.90 (m, 1H), 1.74-1.72 (m, 2H), 1.58-1.54 (m, 2H), 1.16-1.07 (m, 2H), 0.92 (t, J=6.85 Hz, 7H), 0.79 (d, J=6.95 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.6, 165.4, 138.1, 138.0, 133.6, 129.9, 128.9, 128.0, 127.8, 127.1, 75.5, 47.3, 44.3, 41.0, 34.3, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6. The analytical data are consistent with published ones.[16]



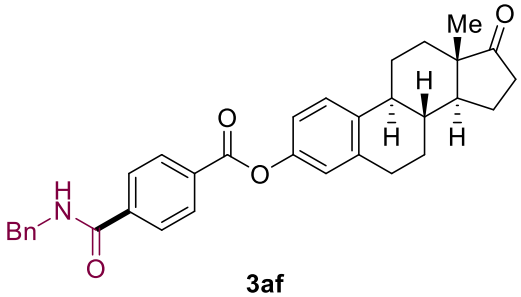
3ad

(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 4-(benzyl carbamoyl) benzoate (3ad): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2r** (0.1 mmol, 56.9 mg) for 35 h. The product **3ad** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 14:1) and afforded as colourless semi-solid (54%, 67.2 mg).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, J=8.2Hz, 2H), 7.84 (d, J=8.2Hz, 2H), 7.37-7.30 (m, 5H), 6.48-6.46 (m, 1H), 5.42-5.42 (m, 1H), 4.91-4.83 (m, 1H), 4.67 (d, J=5.5 Hz, 2H), 2.47-2.46 (m, 2H), 2.04-1.98 (m, 3H), 1.93-1.91 (m, 1H), 1.86-1.71 (m, 2H), 1.57-1.46 (m, 5H), 1.40-1.33 (m, 3H), 1.29-1.23 (m, 2H), 1.21-1.17 (m, 2H), 1.16-1.09 (m, 4H), 1.07-0.96 (m, 7H), 0.93-0.91 (m, 3H), 0.87-0.86 (m, 6H), 0.69 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.6, 165.3, 139.6, 138.2, 138.0, 133.6, 129.9, 129.0, 128.1, 127.9, 127.0, 123.0, 75.2, 56.8, 56.3, 50.2, 44.4, 42.4, 39.8, 39.6, 38.3, 37.1, 36.8, 36.3, 35.9, 32.0, 32.0, 31.06, 28., 28.1, 27.9, 24.4, 23.9, 22.9, 22.7, 21.2, 19.5, 18.8, 12.0. **IR (neat, cm^{-1})**:2918, 1708, 1635, 1541, 1279, 1050, 886, 734. **HRMS (APCI)**: m/z calculated for $C_{42}H_{58}NO_3^+(M+H)^+$: 624.4411, found: 624.4410.



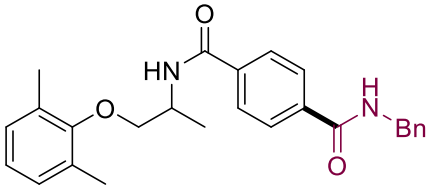
3ae

1-(1,3-dimethyl-2,6-dioxo-1,2,3,4,5,6-hexahydro-7H-purin-7-yl) propan-2-yl 4-(benzyl carbamoyl) benzoate (3ae): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2s** (0.1 mmol, 42.3 mg) for 35 h. The product **3ae** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 1:2) and afforded as off-white semisolid (61%, 58.2 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, J=8.1 Hz, 2H), 7.83 (d, J=8.1 Hz, 2H), 7.53 (s, 1H), 7.34-7.27 (m, 5H), 6.83-6.81 (m, 1H), 5.53-5.51 (m, 1H), 4.68-4.65 (m, 1H), 4.62 (d, J=5.6 Hz, 2H), 4.47-4.43 (m, 1H), 3.50 (s, 3H), 3.33 (s, 3H), 1.43 (d, J=6.35, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.4, 164.7, 155.3, 151.6, 148.7, 141.5, 138.7, 137.9, 132.2, 129.7, 128.8, 128.0, 127.8, 127.3, 107.2, 70.4, 50.7, 44.3, 29.8, 28.0, 17.3. **IR (neat, cm^{-1})**: 2929, 2868, 1708, 1658, 2546, 1458, 1274, 1105, 1076, 750. **HRMS (ESI)**: m/z calculated for $C_{25}H_{26}N_5O_5H^+(M+H)^+$: 476.1928, found: 476.1926.



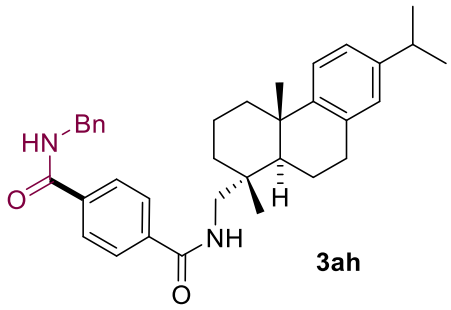
3af

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a] phenanthren-3-yl 4-(benzyl carbamoyl) benzoate: Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2t** (0.1 mmol, 45.3 mg) for 35 h. The product **3af** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 8:1) and afforded as colourless semisolid (47%, 47 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (d, J=7.75 Hz, 2H), 7.91 (d, J=8.2 Hz, 2H), 7.38-7.29 (m, 6H), 6.99-6.95 (m, 2H), 6.59 (s, 1H), 4.67 (d, J=5.4 Hz, 2H), 2.94-2.93 (m, 2H), 2.54-2.48 (m, 1H), 2.44-2.41 (m, 1H), 2.34-2.29 (m, 1H), 2.19-2.13 (m, 1H), 2.08-1.96 (m, 3H), 1.66-1.62 (m, 2H), 1.56-1.47 (m, 4H), 0.92 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.5, 164.7, 148.7, 138.9, 138.3, 137.9, 137.8, 132.4, 130.5, 129.0, 128.9, 128.1, 127.9, 127.3, 126.6, 121.7, 118.8, 50.5, 48.0, 44.4, 44.3, 38.1, 35.9, 31.6, 29.5, 26.4, 25.9, 21.7, 13.9. **IR (neat, cm^{-1})**: 3334, 2924, 2860, 1734, 1643, 1544, 1259, 1145, 1070, 702. **HRMS (APCI)**: m/z calculated for $C_{33}H_{34}NO_4^+(M+H)^+$:508.2482 , found: 508.2475 .



3ag

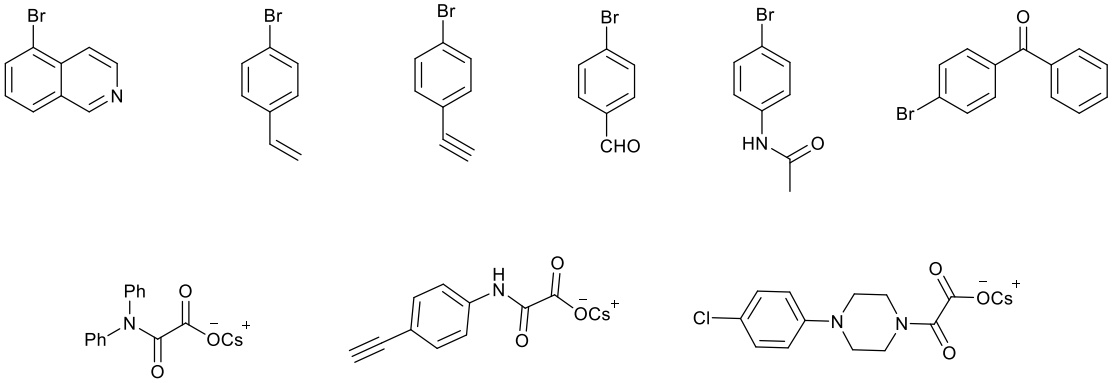
N1-benzyl-N4-(1-(2,6-dimethylphenoxy) propan-2-yl) terephthalamide (3ag): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2u** (0.1 mmol, 36.2 mg) for 24 h. The product **3ag** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 2:1) and afforded as white amorphous solid (59%, 49 mg). **MP**: 180-186°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 4H), 7.36-7.29 (m, 5H), 7.01-6.99 (m, 2H), 6.94-6.92 (m, 1H), 6.76-6.74 (m, 1H), 6.66 (brs, 1H), 4.65 (d, J=5.55, 2H), 4.54-4.52 (m, 1H), 3.93-3.90 (m, 1H), 3.82-3.80 (m, 1H), 2.25 (s, 6H), 1.52 (d, J=6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 166.6, 166.1, 154.8, 138.0, 137.4, 137.1, 130.8, 129.2, 128.9, 128.1, 127.8, 127.5, 127.3, 124.3, 73.8, 46.2, 44.4, 17.9, 16.3. **IR (neat, cm^{-1})**: 3309, 1643, 1541, 1317, 1205, 1031.**HRMS (APCI)**: m/z calculated for $C_{26}H_{29}N_2O_3^+$(M+H)$^+$: 417.2173 , found: 417.2169.



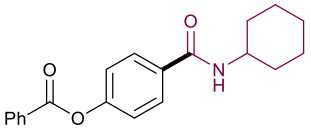
3ah

N1-benzyl-N4-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydro phenanthren-1-yl) methyl) terephthalamide (3ah): Following the general procedure two independent reactions of **1a** (0.15 mmol, 45.5 mg) and **2v** (0.1 mmol, 46.8 mg) for 24 h. The product **3ah** was purified by column chromatography of reaction mixture on silica gel (Gradient, hexane: ethyl acetate = 2:1) and afforded as white amorphous solid (65%, 67.8 mg). **MP**: 225-230°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, J=8.1 Hz, 2H), 7.69 (d, J=8.1 Hz, 2H), 7.34-7.27 (m, 5H), 7.17 (d, J=8.1 Hz, 1H), 6.99 (d, J=8.1 Hz, 1H), 6.88 (s, 1H), 6.81-6.80 (m, 1H), 6.37-6.34 (m, 1H), 4.62 (d, J=5.5 Hz, 2H), 3.43-3.39 (m, 1H), 3.33-3.29 (m, 1H), 2.94-2.89 (m, 1H), 2.83-2.78 (m, 2H), 2.31-2.29 (m, 1H), 1.98-1.94 (m, 1H), 1.78-1.75 (m, 2H), 1.70-1.67 (m, 1H), 1.53-1.46 (m, 2H), 1.40-1.34 (m, 2H), 1.23-1.20 (m, 9H), 1.00 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 167.0, 166.7, 147.1, 145.7, 138.1, 137.6, 137.0, 134.7, 128.9, 128.0, 127.7, 127.4, 127.2, 127.0, 124.3, 124.0, 50.6, 45.9, 44.2, 38.4, 37.8, 37.6, 36.5, 33.5, 30.4, 25.5, 24.0, 19.2, 18.8, 18.7. **IR (neat, cm^{-1})**:2860, 1639, 1544, 1450, 1386, 1284, 1259, 1022, 860, 813, 721. **HRMS (APCI)**: m/z calculated for $C_{35}H_{43}N_2O_2^+$(M+H)$^+$: 523.3319 , found: 523.3317.

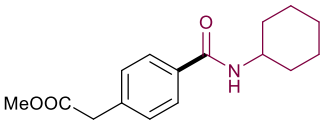
Unsuccessful Aryl bromides and Cesium oxamates



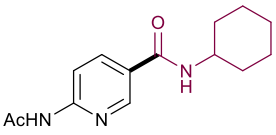
List of products that are difficult to isolate through coloumn chromatography



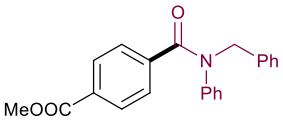
41% (^{1}HNMR yield)



32% (^{1}HNMR yield)



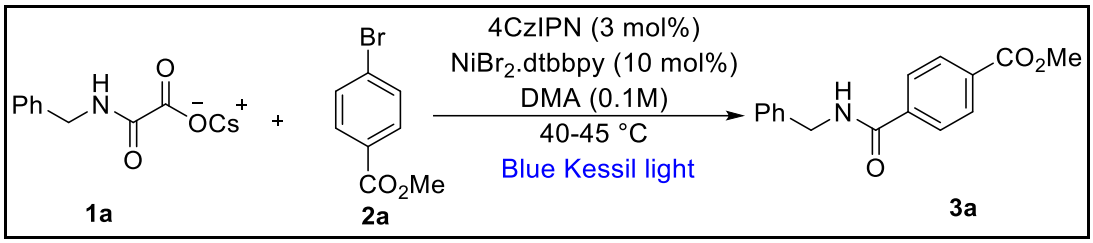
47% (^{1}HNMR yield)



39% (^{1}HNMR yield)

Mechanistic Studies

ON/OFF experiment:



In an argon atmosphere glovebox, a 10 mL glass vial was charged with **1a** (93 mg, 0.3 mmol, 1.5 eq), **2a** (43 mg, 0.2 mmol, 1 eq), 4CzIPN (3 mol%), $NiBr_2$.dtbbpy (10 mol%), benzyl benzoate (42.4 mg, 0.2 mmol) (as the internal standard to determine the yield of the reaction) and a PTFE coated magnetic bar. Then DMA (0.1 M) was added to the glass vial and sealed with a PTFE septum. The reaction vial was placed on the magnetic stirrer under irradiation with a Kessil® PR160-456 nm light (40 W) at 45-50 °C (the temperature mentioned in the reaction condition is produced by the light source itself not by an external heat source). After selected time interval, a small aliquot was taken from the reaction mixture and extracted with EtOAc, followed by washing with brine solution. The organic layer was concentrated under reduced pressure and was analysed by ^{1}HNMR to determine the yield of the reaction.

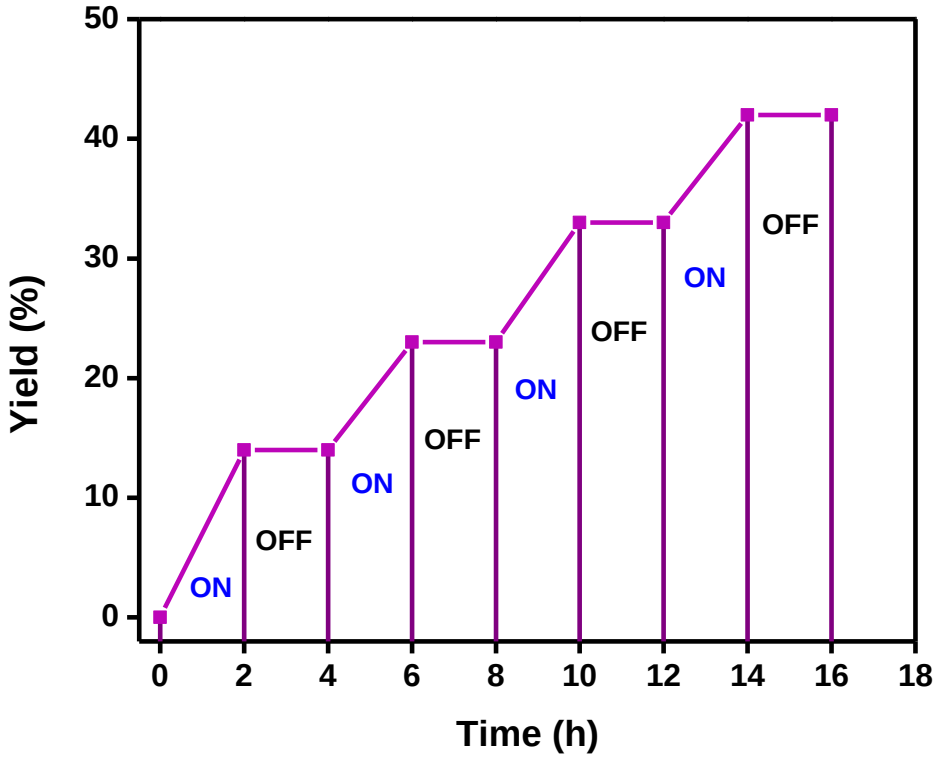
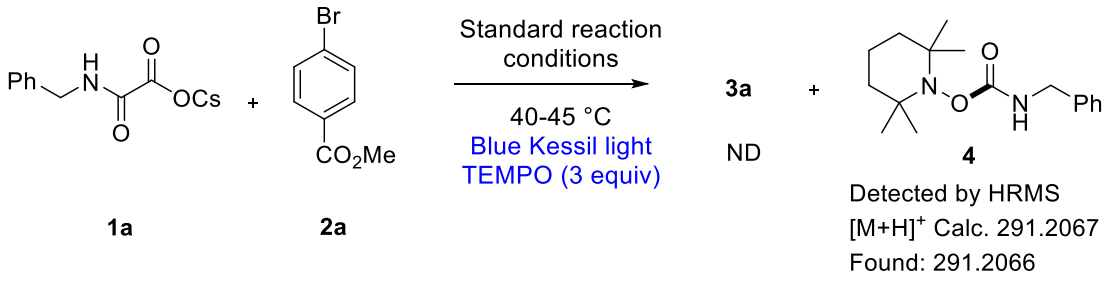


Figure S2: The reaction profile of the on/off experiment showing continuous irradiation of light is essential throughout the reaction.

Reaction with TEMPO:



In an argon atmosphere glovebox, a 10 mL glass vial was charged with **1a** (93 mg, 0.3 mmol, 1.5 eq), **2a** (43 mg, 0.2 mmol, 1 eq), 4CzIPN (3 mol%), $NiBr_2$.dtbbpy (10 mol%), TEMPO (93 mg, 0.6 mmol, 3 eq) and a PTFE coated magnetic bar. Then DMA (0.1M) was added to the glass vial and sealed with a PTFE septum. The reaction vial were placed on the magnetic stirrer under irradiation with a Kessil® PR160-456 nm light (40 W) at 45-50 °C (the temperature mentioned in the reaction condition is produced by the light source itself not by an external heat source). After 24 h, the reaction mixture was filtered with cotton and an aliquot of the mixture was analysed by HRMS to observe 2,2,6,6-tetramethylpiperidin-1-yl benzylcarbamate (**4**).

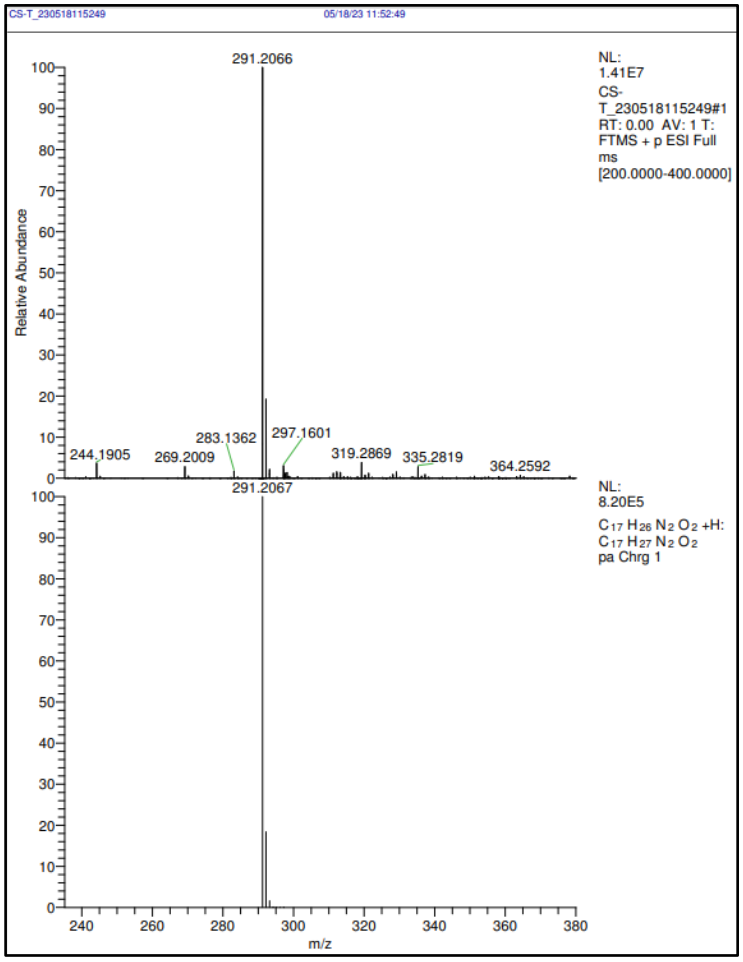


Figure S3: HRMS spectrum of reaction mixture.

Fluorescence quenching experiments

On a Fluorolog Horiba Jobin Yvon spectrofluorometer, fluorescence spectra were recorded using a 4 mL glass cuvette with a septum screw on top having 1 cm path length. All of the stock solutions were prepared inside the glovebox. To make sure our solvent is degassed, we did freeze-pump-thaw process several times, followed by degassing with argon balloon throughout our experiment. With an excitation wavelength of 405 nm, the spectra were recorded between from 380 nm to 700 nm. For the excitation and emission spectra, the slit widths were maintained at 2 nm. The observed λ_{max} for 4CzIPN was recorded as 530 nm.

Stock solution preparation of photocatalyst:

A sample solution of photocatalyst with concentration 1.25 X 10^{-5} M is prepared and used the same for the quenching studies.

Sample preparation of cesium 2-(benzylamino)-2-oxoacetate (1a):

A stock solution of **1a** containing 0.04 M is prepared. Concentrations in the range of 0.5 mM, 1.0 mM, 1.5 mM, 2.0 mM, and 2.5 mM are obtained by adding 25 µl of 1a to 2 ml of stock solution of 4CzIPN.

Sample preparation of methyl 4-bromobenzoate (2a):

A stock solution of **2a** containing 0.04 M is prepared. Concentrations in the range of 0.5 mM, 1.0 mM, 1.5 mM, 2.0 mM, and 2.5 mM are obtained by adding 25 µl of 1a to 2 ml of stock solution of 4CzIPN.

Fluorescence quenching experiment of cesium 2-(benzylamino)-2-oxoacetate (1a):

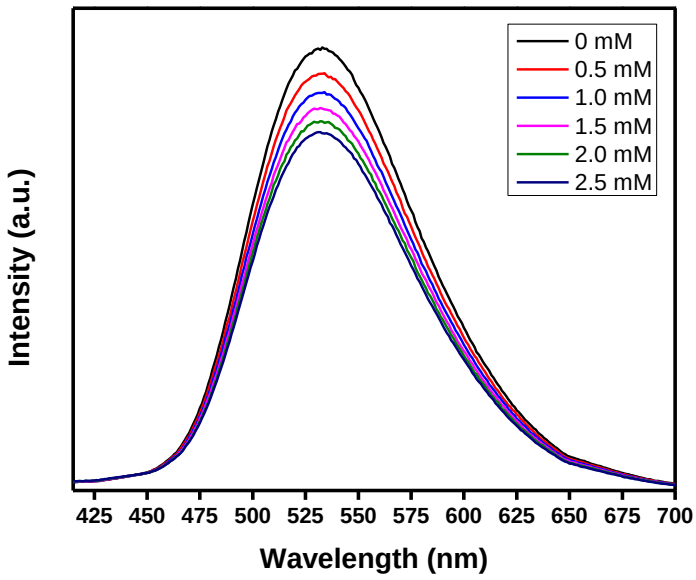


Figure S4. Luminescence quenching experiment of **1a** in presence of **4CzIPN.**

As shown above, a significant decrease of photocatalyst luminescence was observed in the presence of **1a**, suggesting that the mechanism might operate via a canonical photoredox cycle consisting of an reductive quenching with 4CzIPN.

Fluorescence quenching experiment of methyl 4-bromobenzoate (2a):

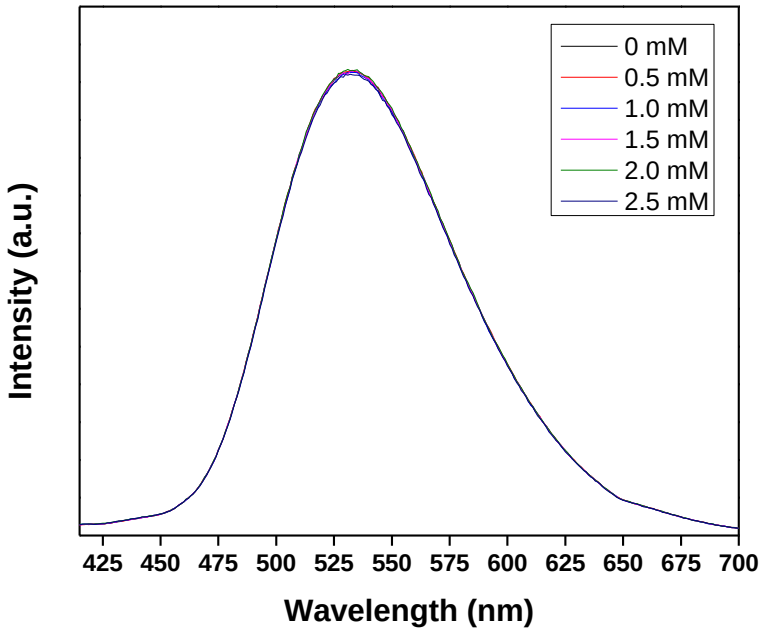


Figure S5. Luminescence quenching experiment of **2a** in presence of **4CzIPN.**

As shown below, there is negligible change in the luminescence graph by increasing the amount of **methyl 4-bromobenzoate (2a)** to the cuvette containing a stock solution of 4CzIPN (2ml) indicates that there is no quenching of 4CzIPN with **2a.**

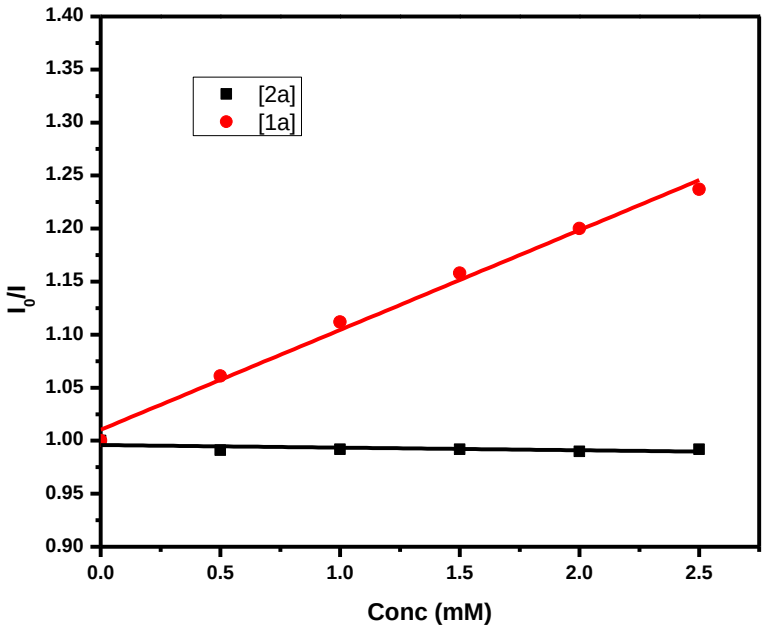


Figure S6. Stern Volmer plot of **1a** and **2a** in presence of **4CzIPN.**

Cyclic Voltammetry Analysis: -

Cyclic voltammetry was performed using a three-electrode set-up consisting of a glassy carbon as working electrode and a platinum electrode as counter electrode. The reference electrode was an Ag/AgCl electrode (containing 3.0 M NaCl saturated with AgCl). Electrochemical measurements were carried out in a bespoke glass cell using a CHI600E Electrochemical workstation (CH Instruments). The surface area of the glassy carbon electrode is 3 mm and the surface of the electrode is round shaped. The electrode is polished with figure-eight motions on a cloth polishing pad in a water-alumina slurry. For the cyclic voltametric measurement, IUPAC convention was followed. The starting point for the CV curve was at -0.95 V (for 1b Cs salt), -0.43 volt (for 1a Cs salt) and measured in the positive direction. For the CV experiments, initial potential was 0.0 V, the switching potential was +1.58 V (for 1b Cs salt), +1.4 V (for 1a Cs salt) and the scan rate was 0.1 V.s-1. Before any experiment, the chemical was completely degassed by Ar gas bubbling and sonicated with 0.01 M NBu_4PF_6/DMA supporting electrolyte solution. As an internal benchmark, Ferrocene was introduced, and all potential was indicated by V vs. Fc/Fc+.

The analyte sample (**1a** and **1b**) was dissolved in 5ml DMA containing 0.01 M tetrabutylammonium hexafluorophosphate electrolyte. The CV cell was filled with this solution and voltage scans were performed at room temperature.

The cesium oxamate **1a** shows oxidation event at +0.76 V vs Fc/Fc+ in DMA.

The cesium oxamate **1b** shows oxidation event at +0.94 V vs Fc/Fc+ in DMA.

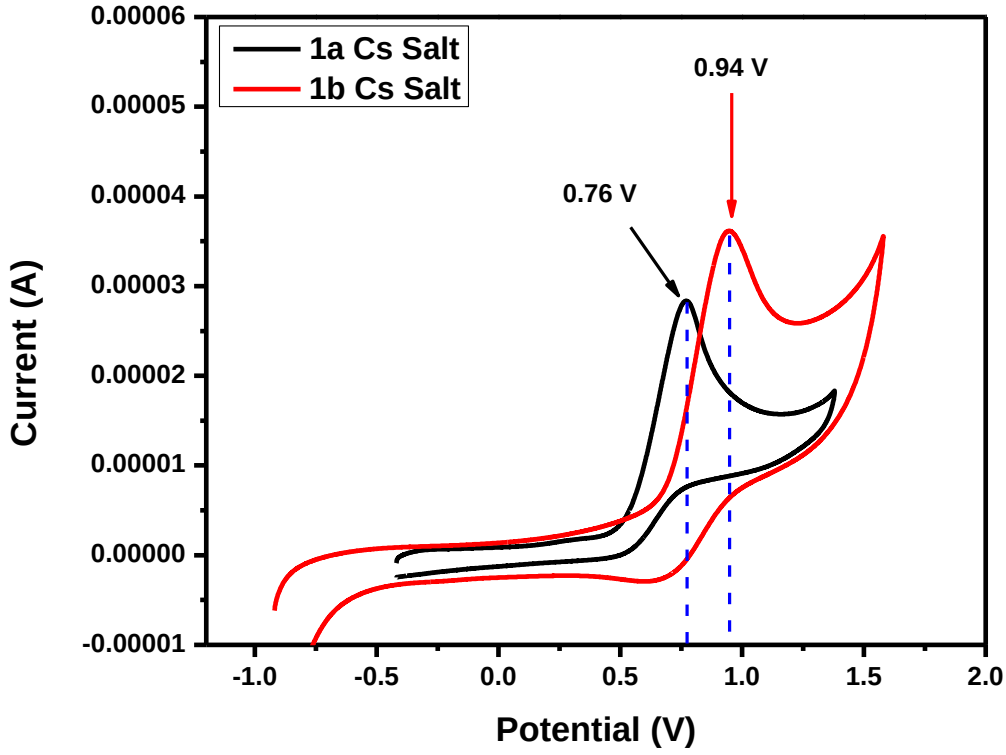


Figure S7: cyclic voltammetry of cesium oxamate **1a** and cesium oxamate **1b** vs Fc/Fc+.

NMR Spectra:

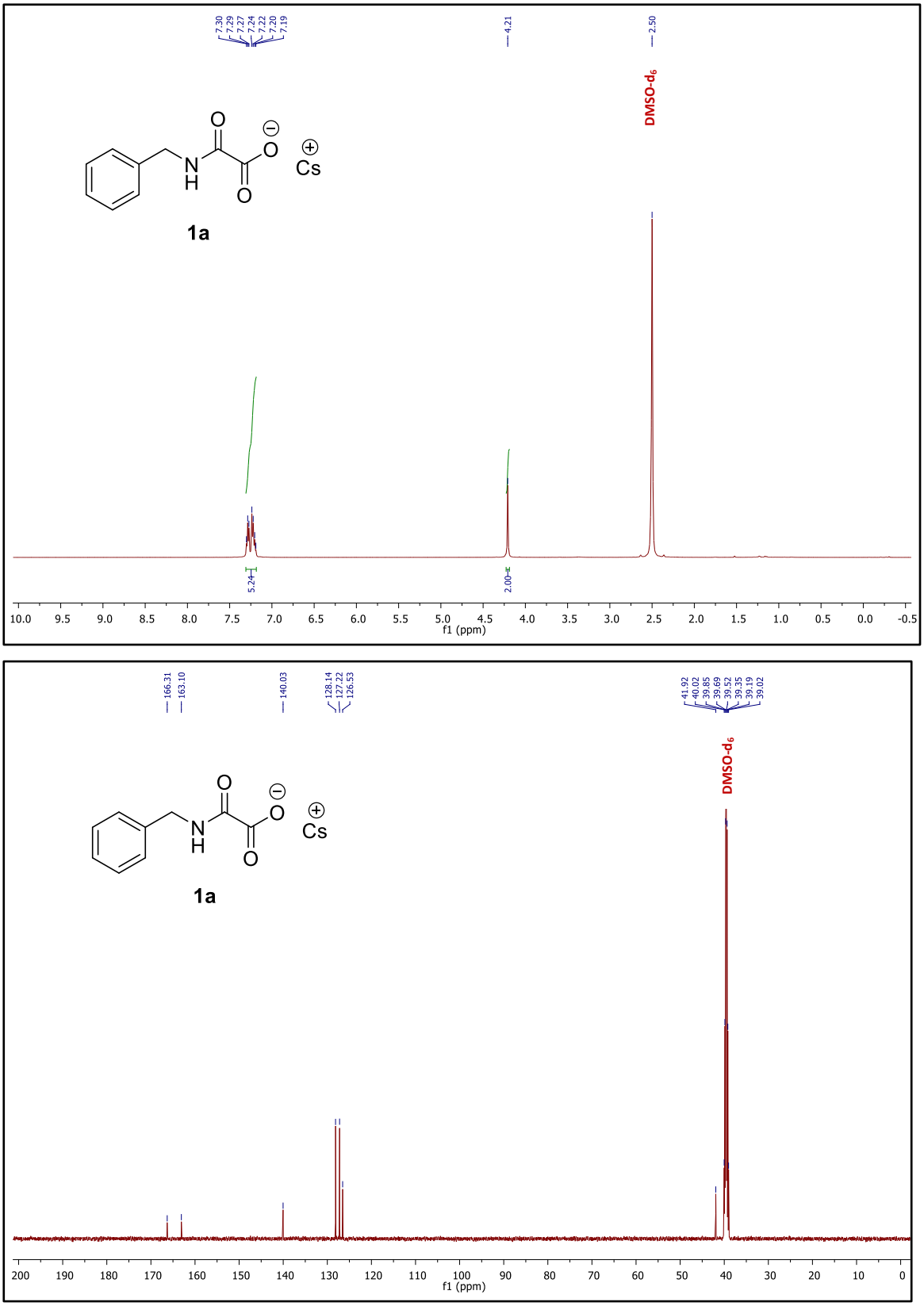


Figure S8. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **1a** in DMSO-d_6 at 298K.

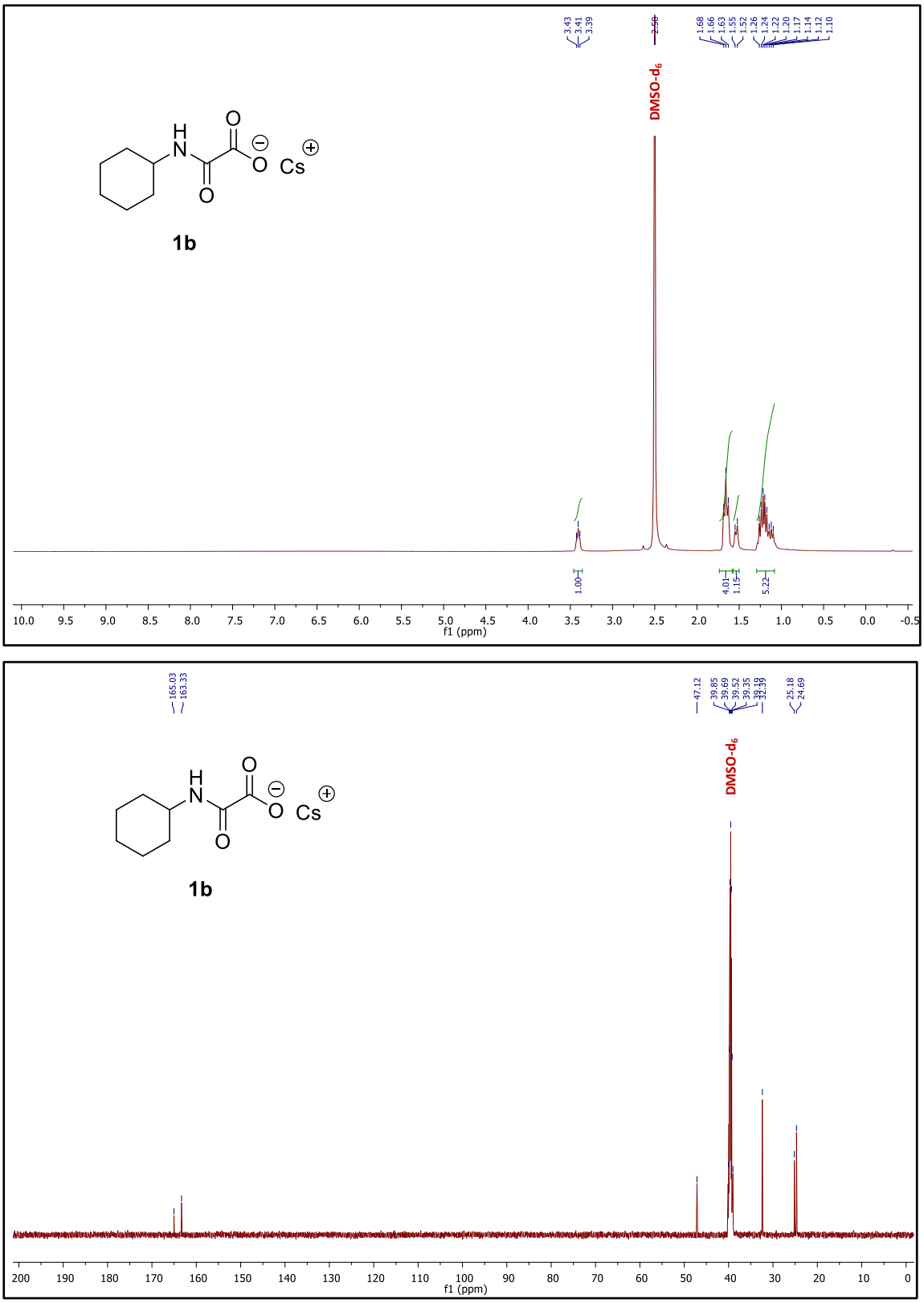


Figure S9. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1b** in DMSO-d_6 at 298K.

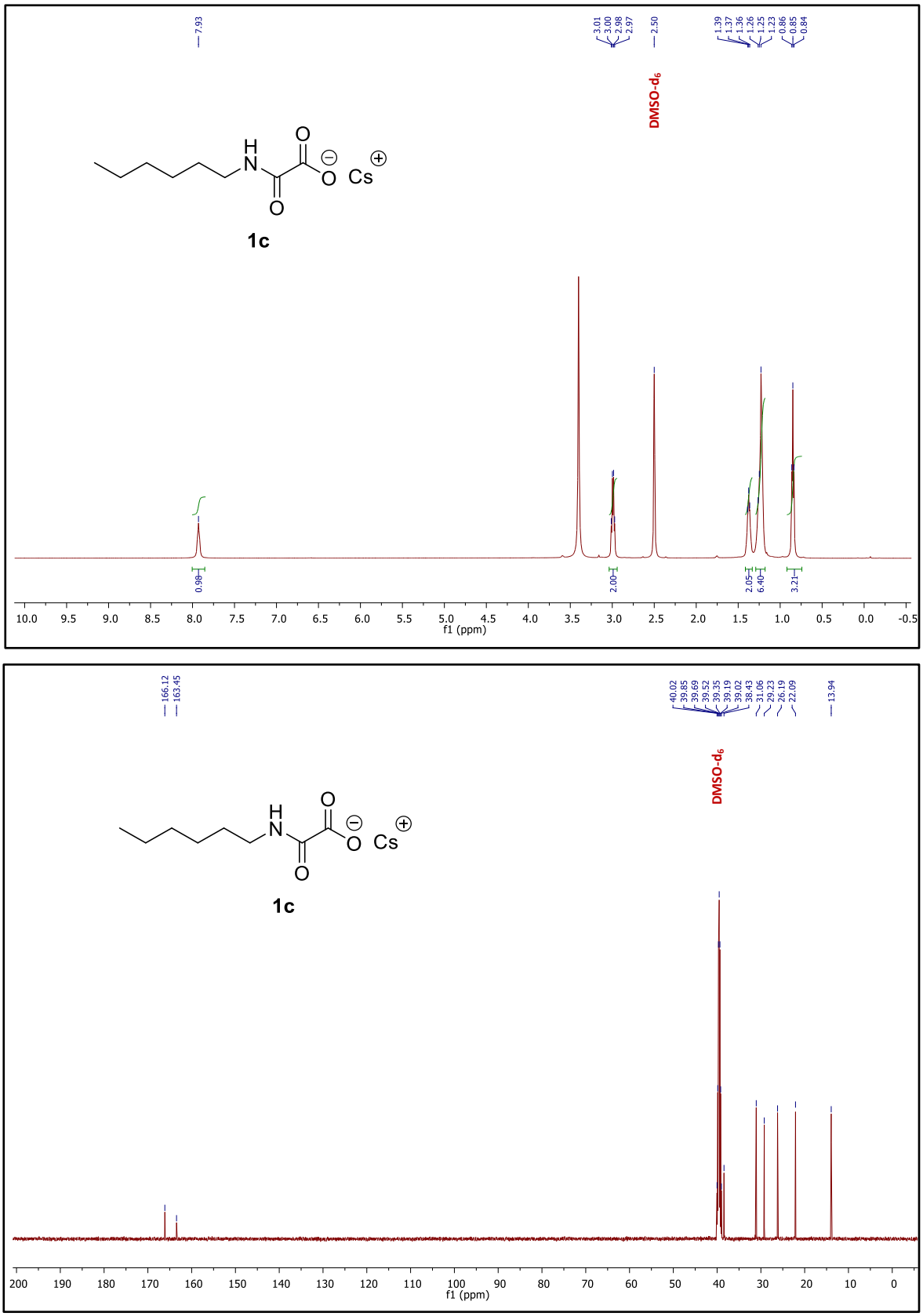
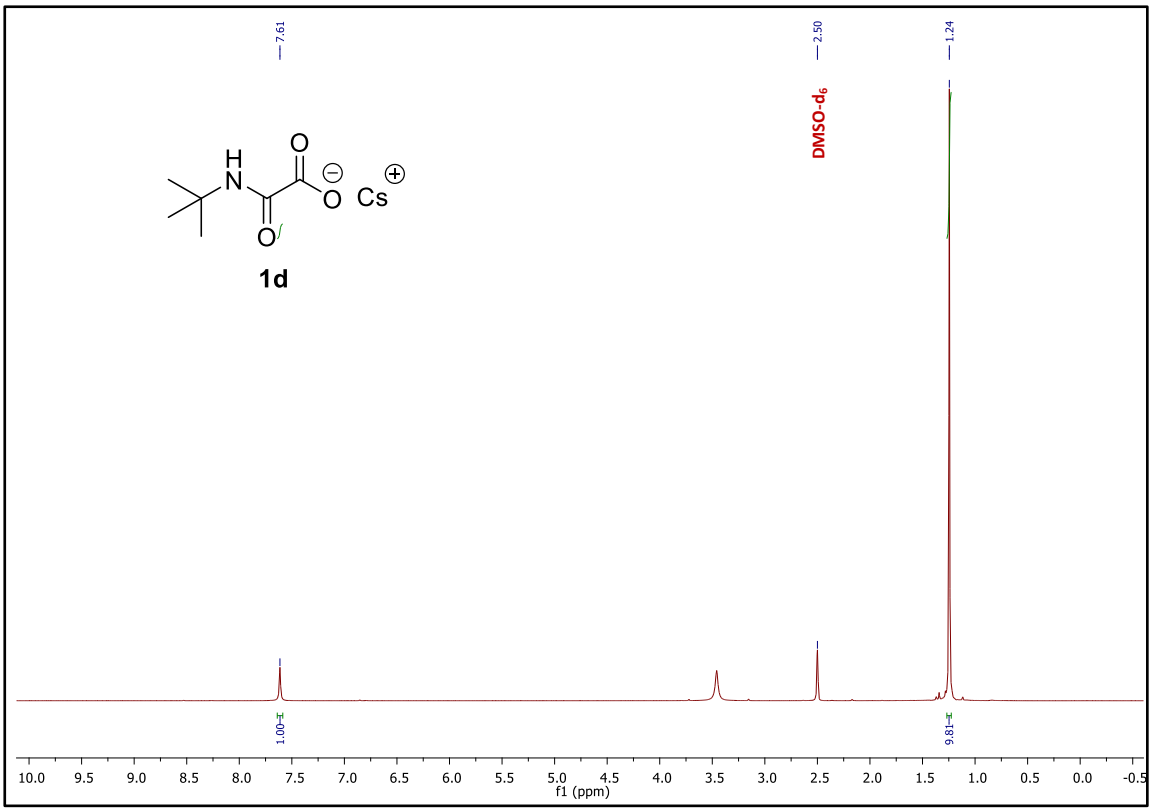


Figure S10. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1c** in DMSO-d_6 at 298K.



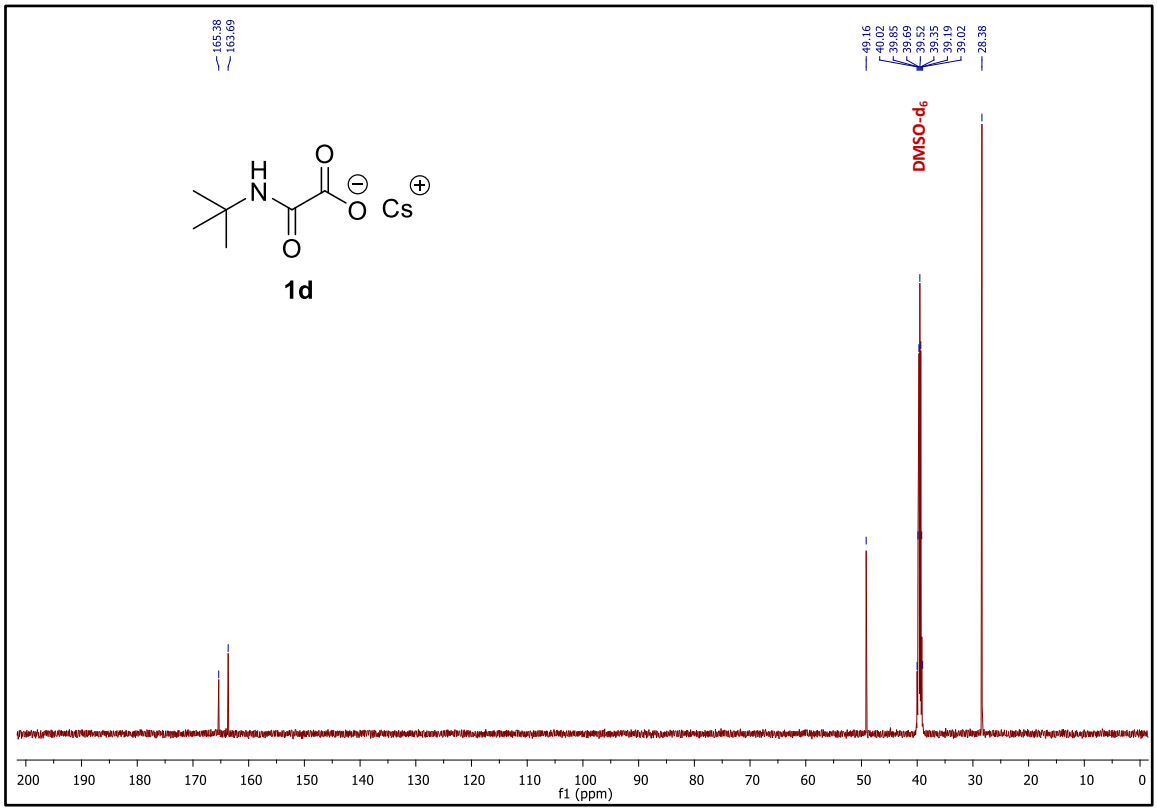


Figure S11. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1d** in DMSO-d_6 at 298K.

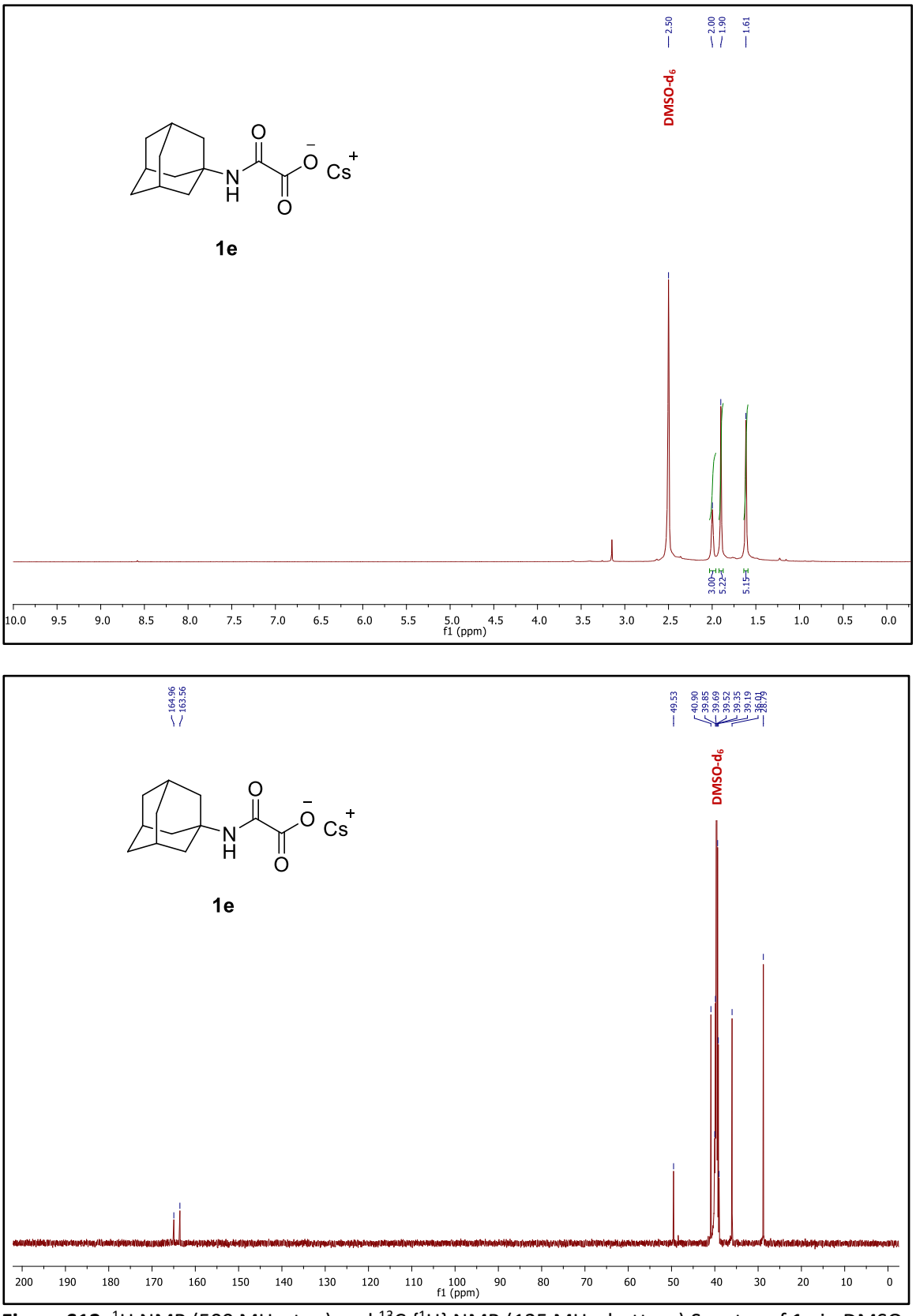


Figure S12. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1e** in DMSO-d_6 at 298K.

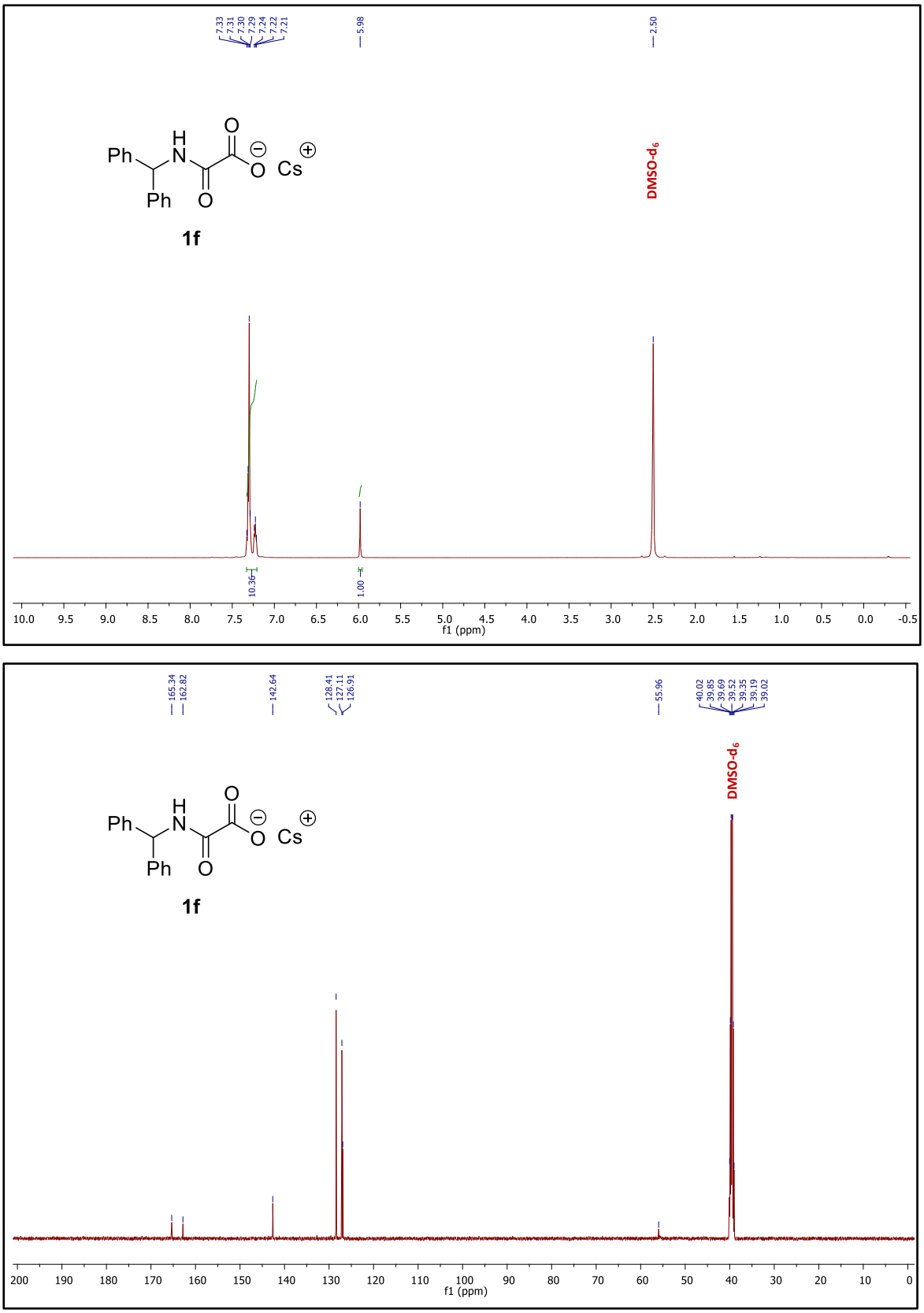


Figure S13. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1f** in DMSO-d_6 at 298K.

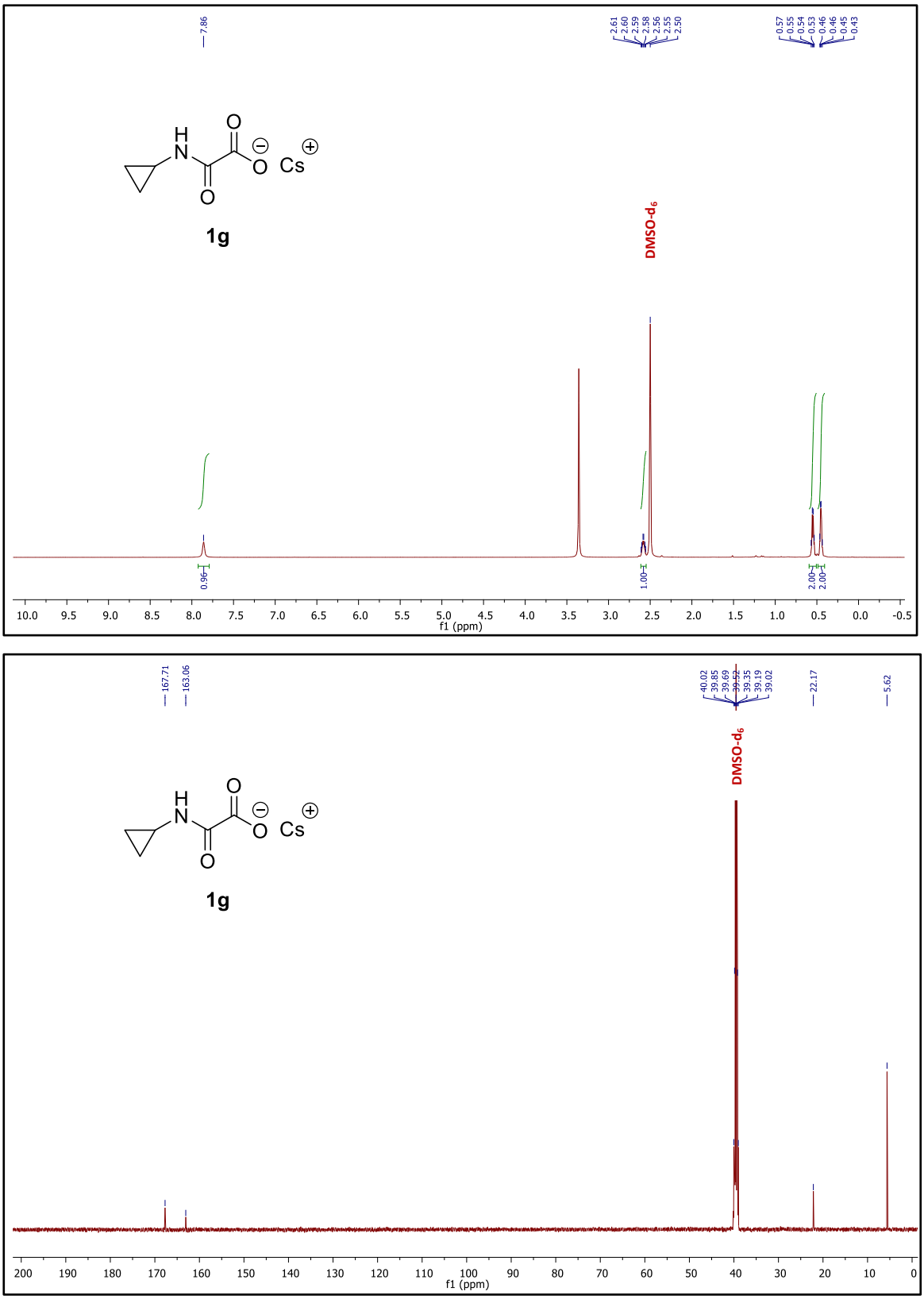


Figure S14. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **1g** in DMSO-d_6 at 298K.

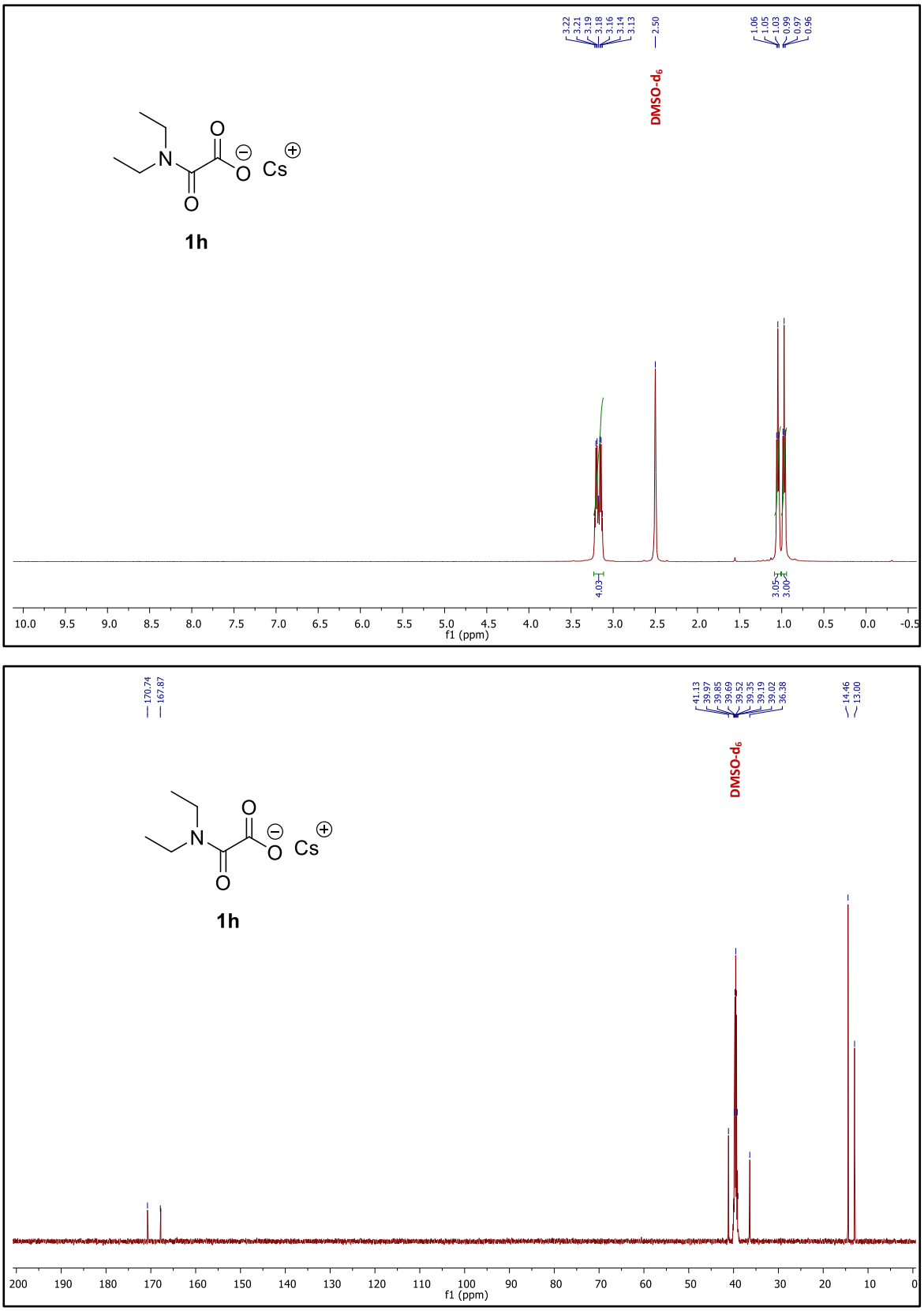


Figure S15. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **1h** in DMSO-d_6 at 298K.

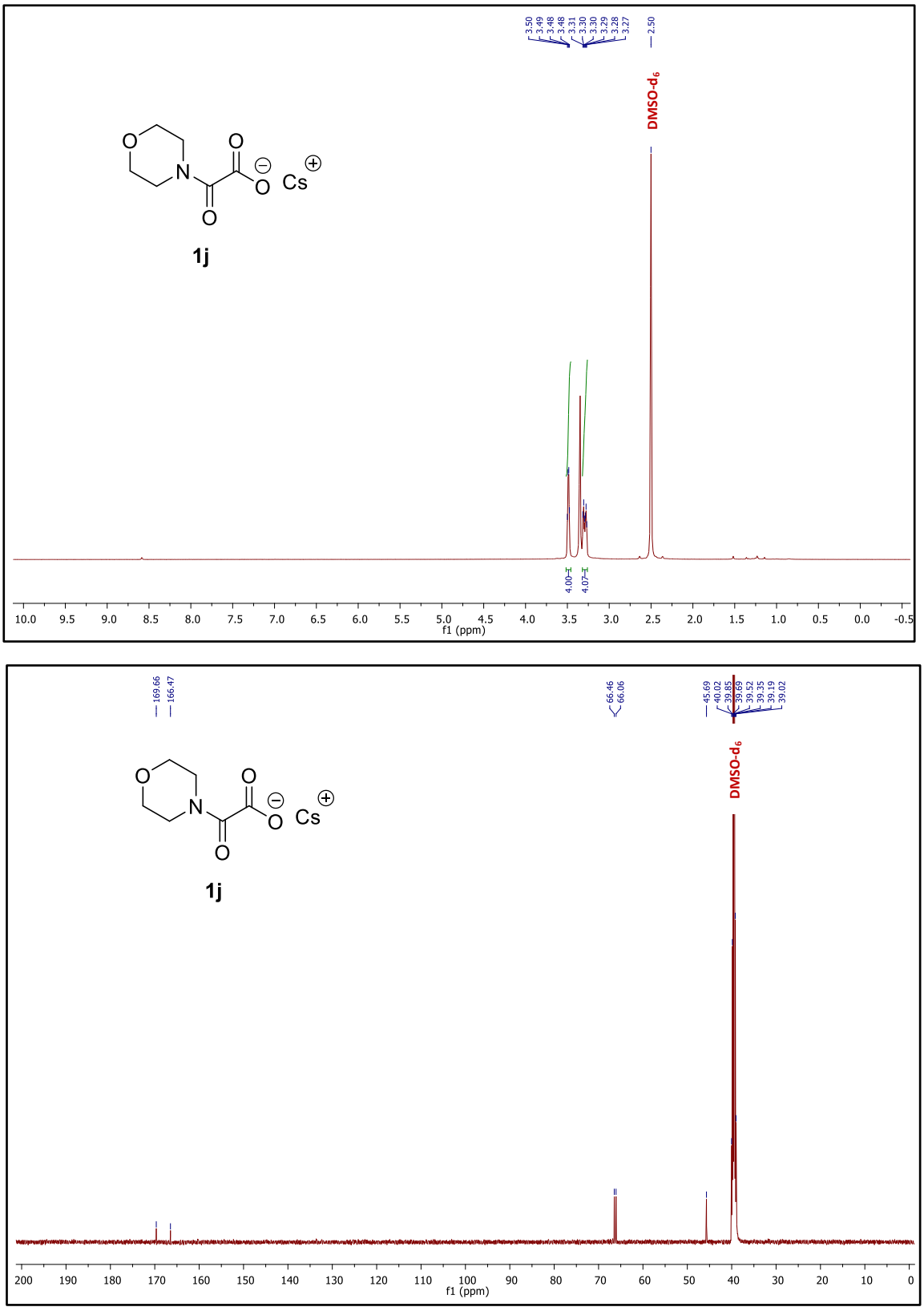


Figure S16. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **1j** in DMSO-d_6 at 298K.

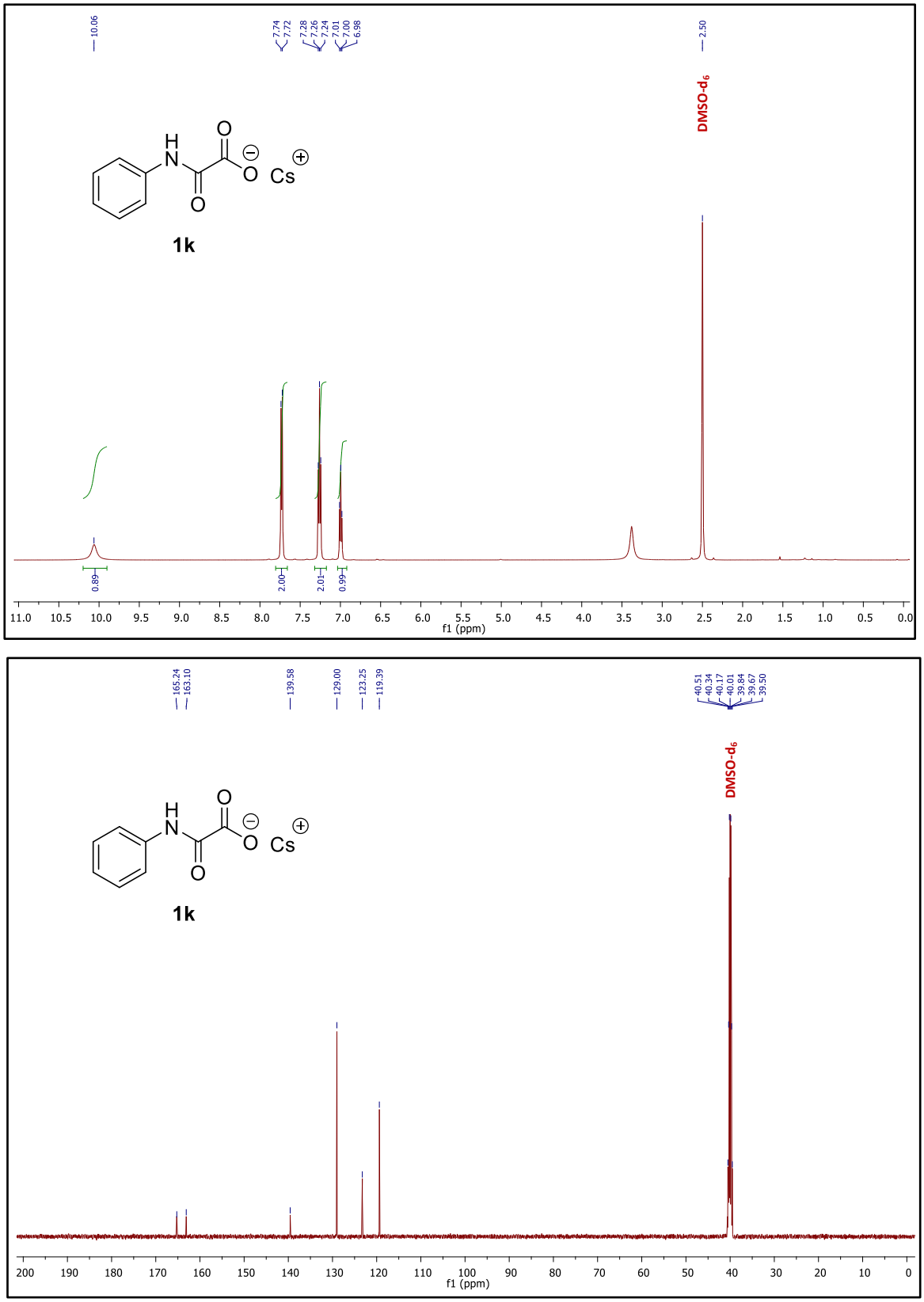


Figure S17. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1k** in DMSO-d_6 at 298K.

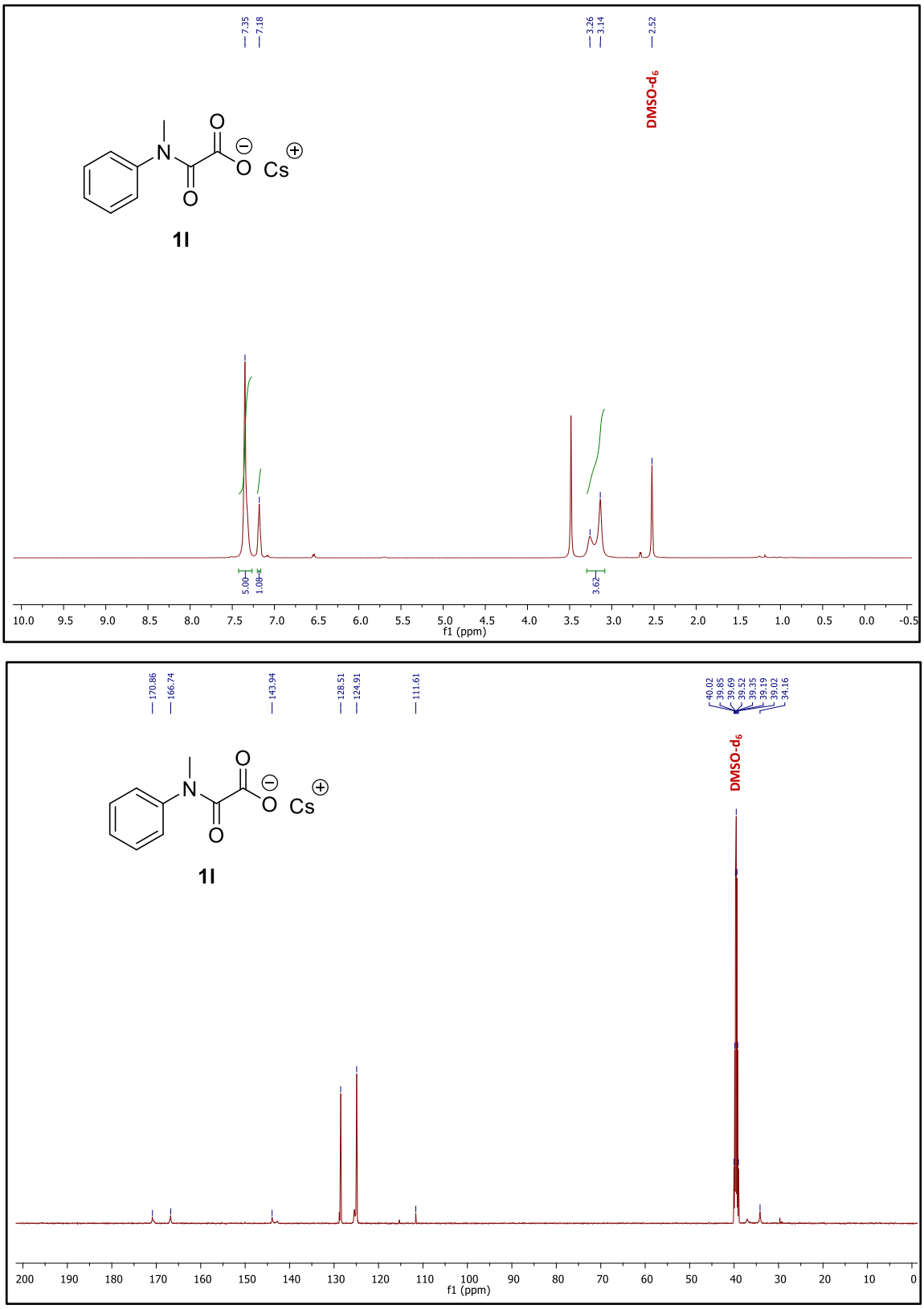


Figure S18. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1l** in DMSO-d_6 at 298K.

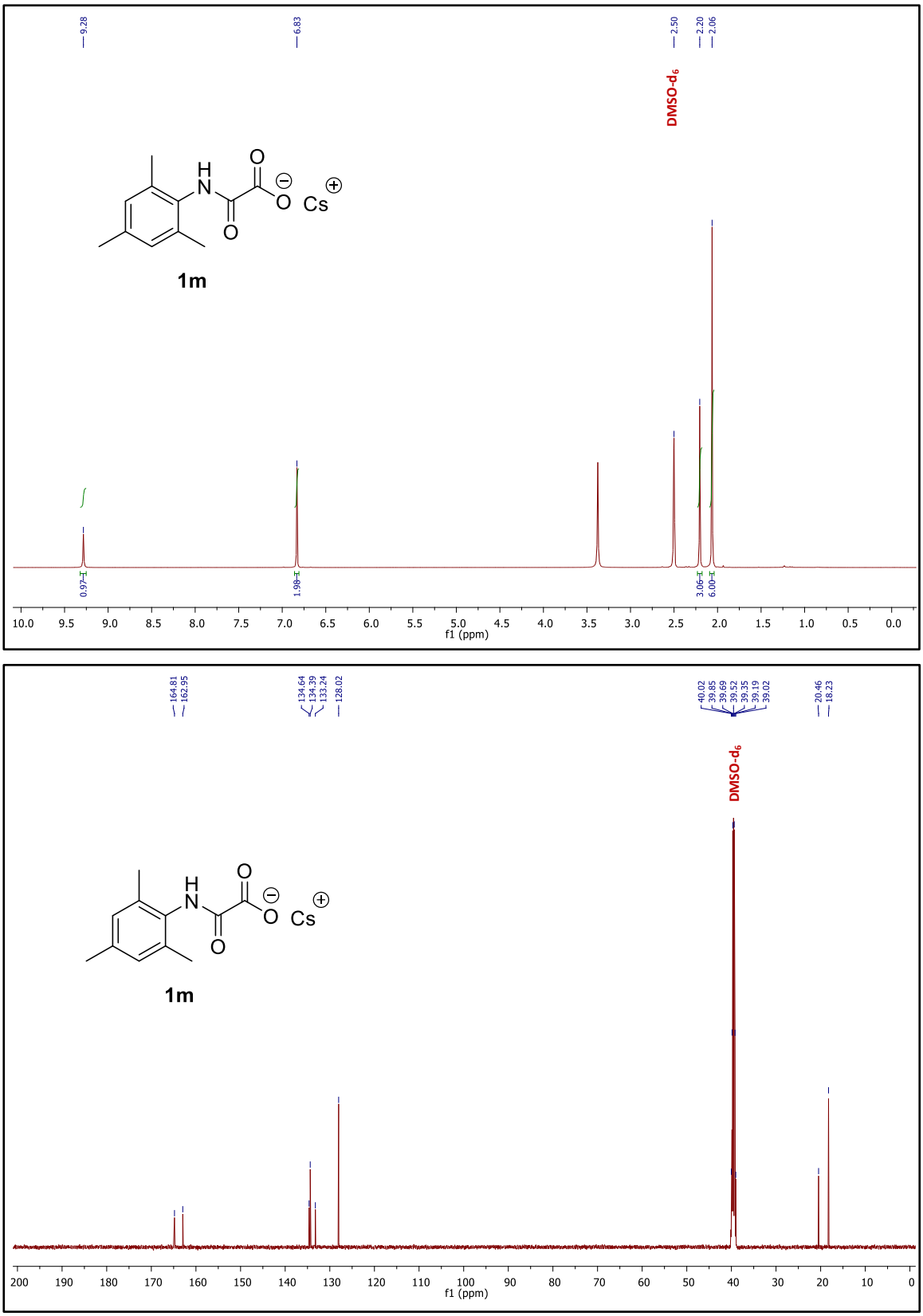


Figure S19. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **1m** in DMSO-d_6 at 298K.

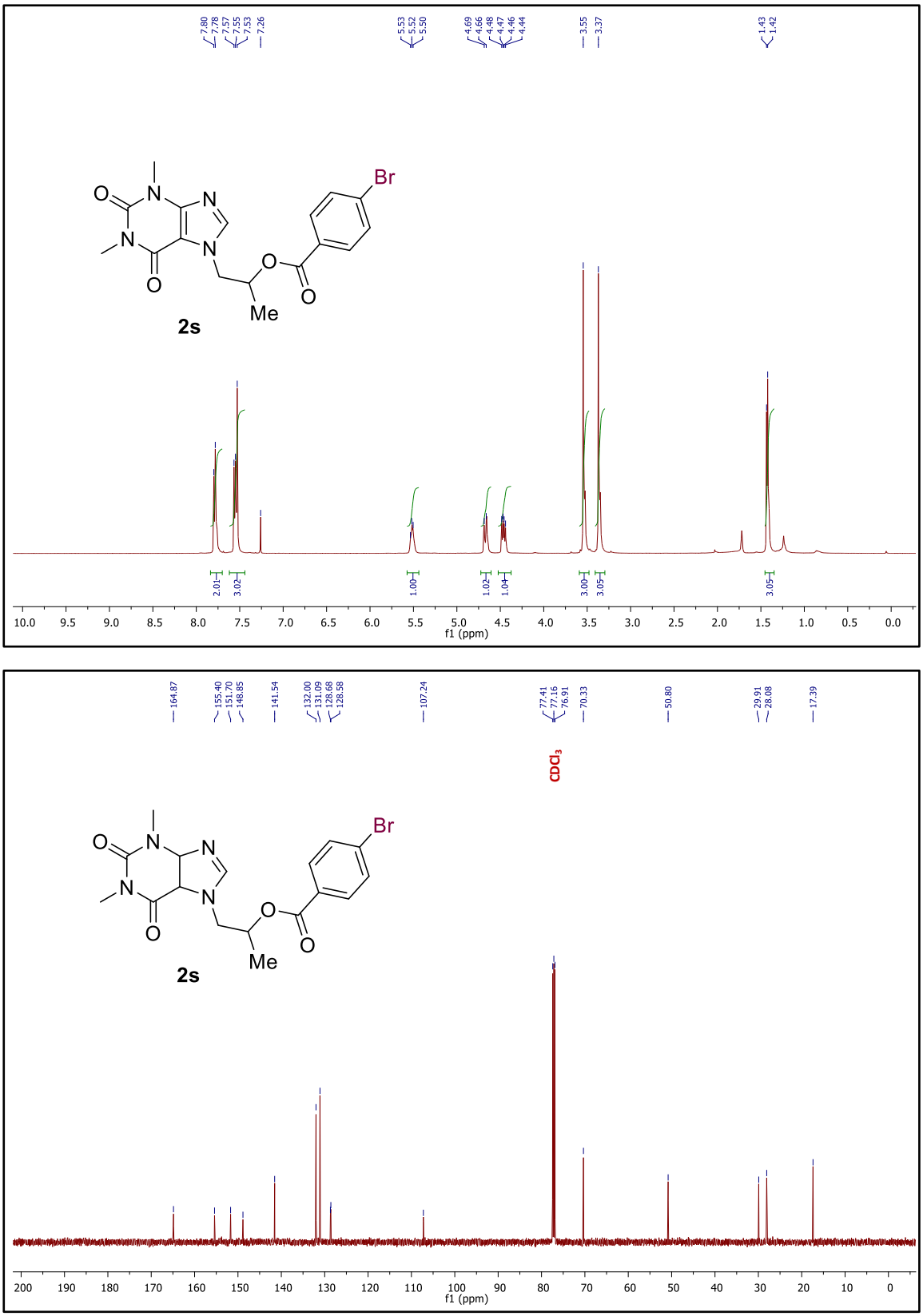


Figure S20. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **2s** in $CDCl_3$ at 298K.

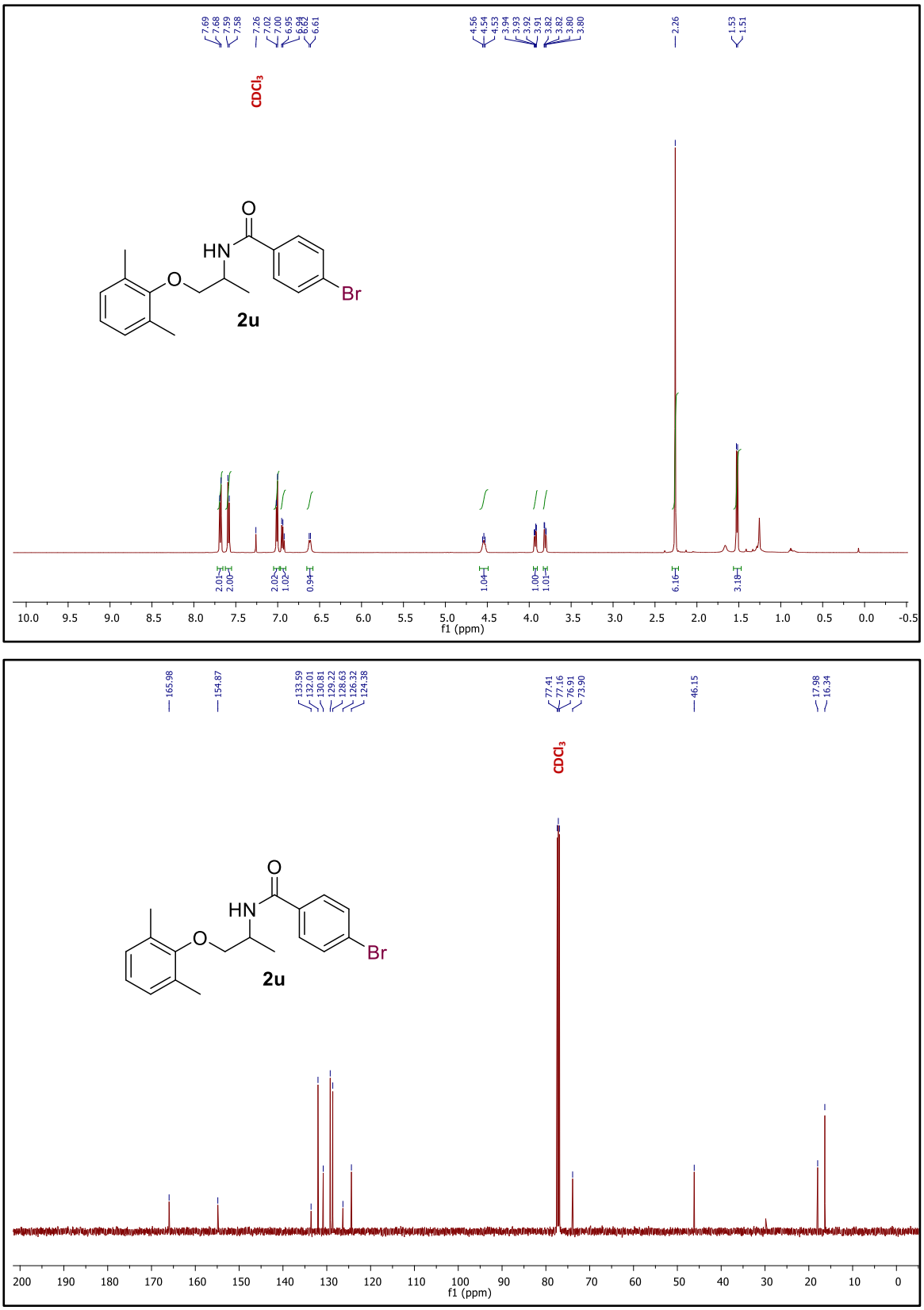
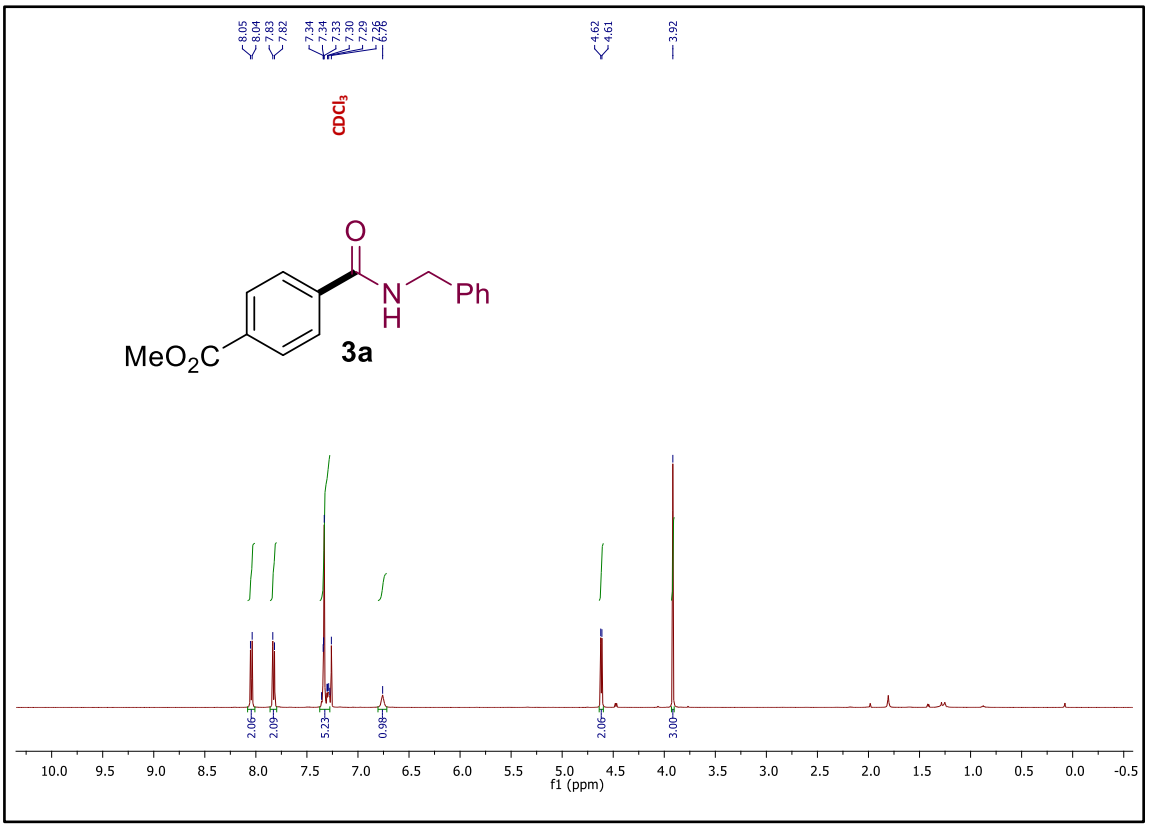


Figure S21. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **2u** in $CDCl_3$ at 298K.



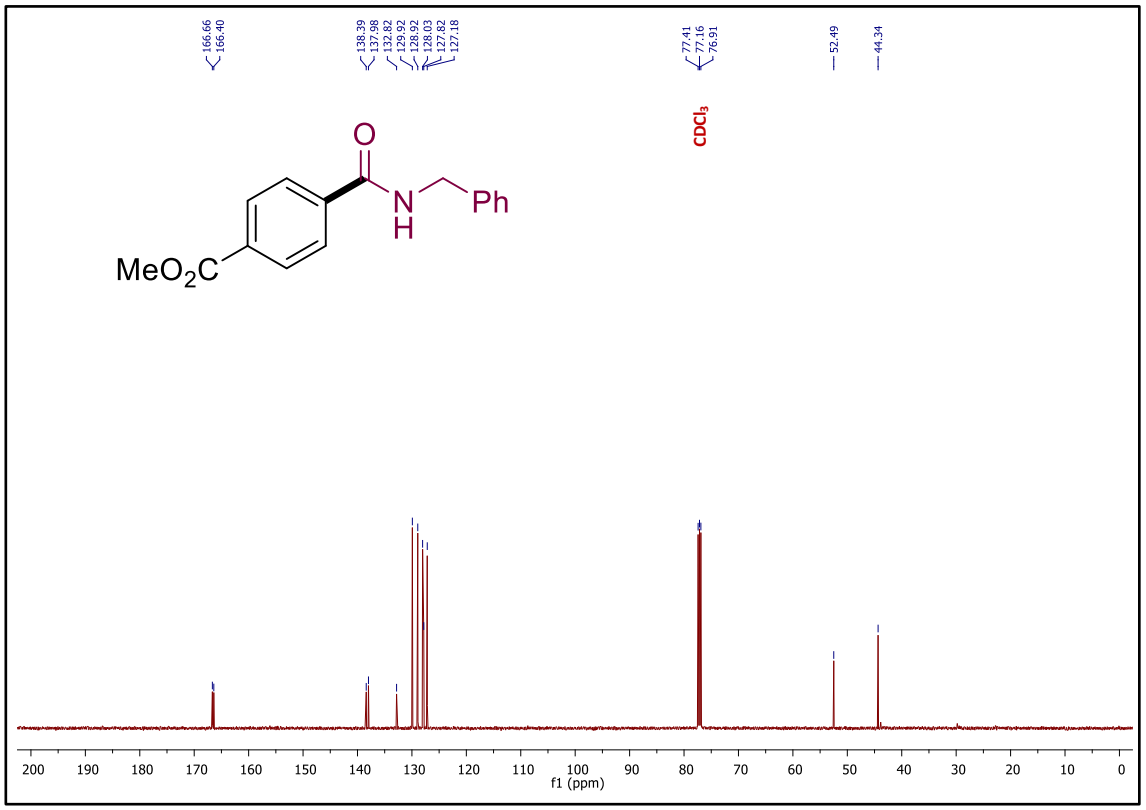


Figure S22. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3a** in $CDCl_3$ at 298K.

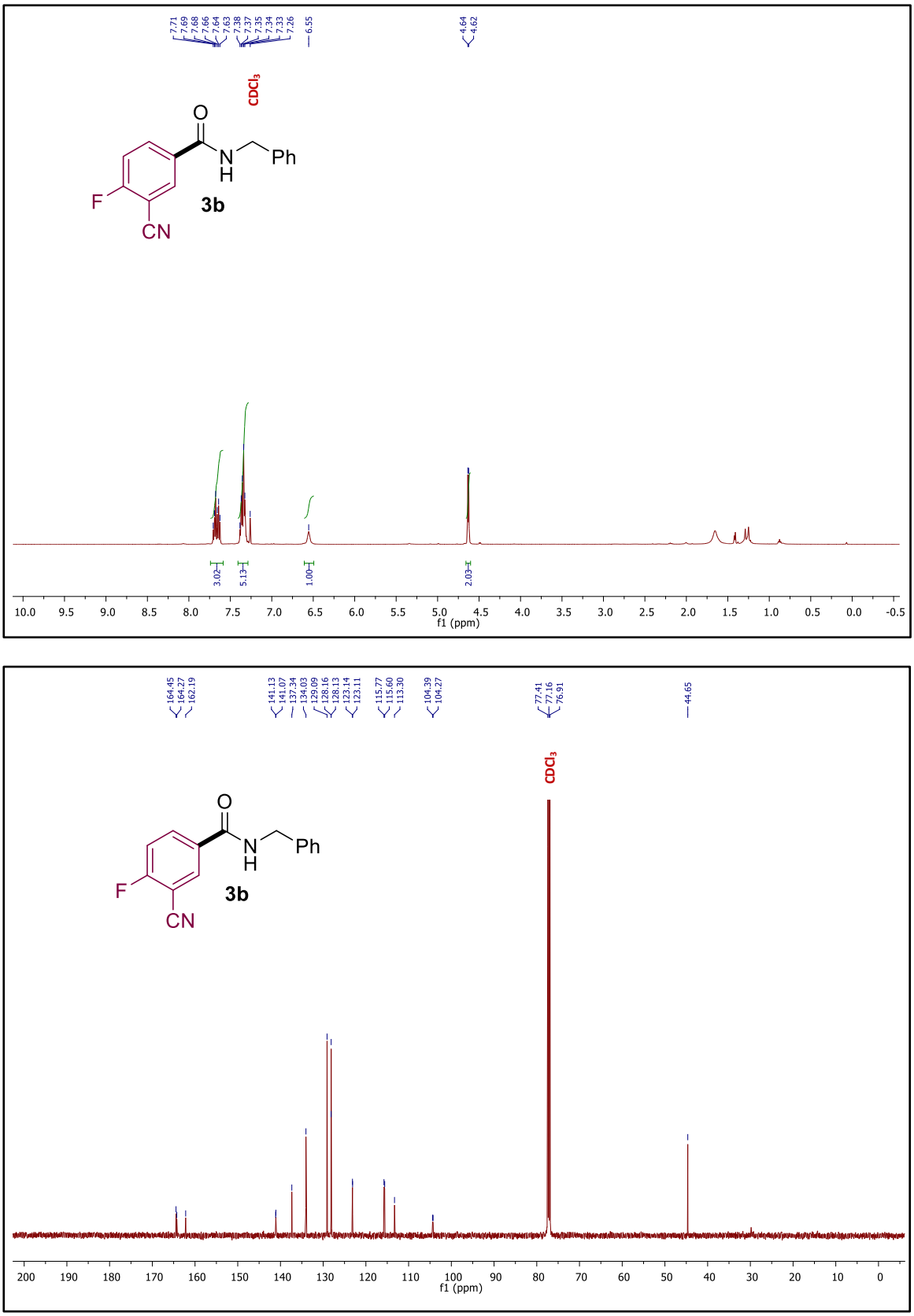


Figure S23. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3b** in $CDCl_3$ at 298K.

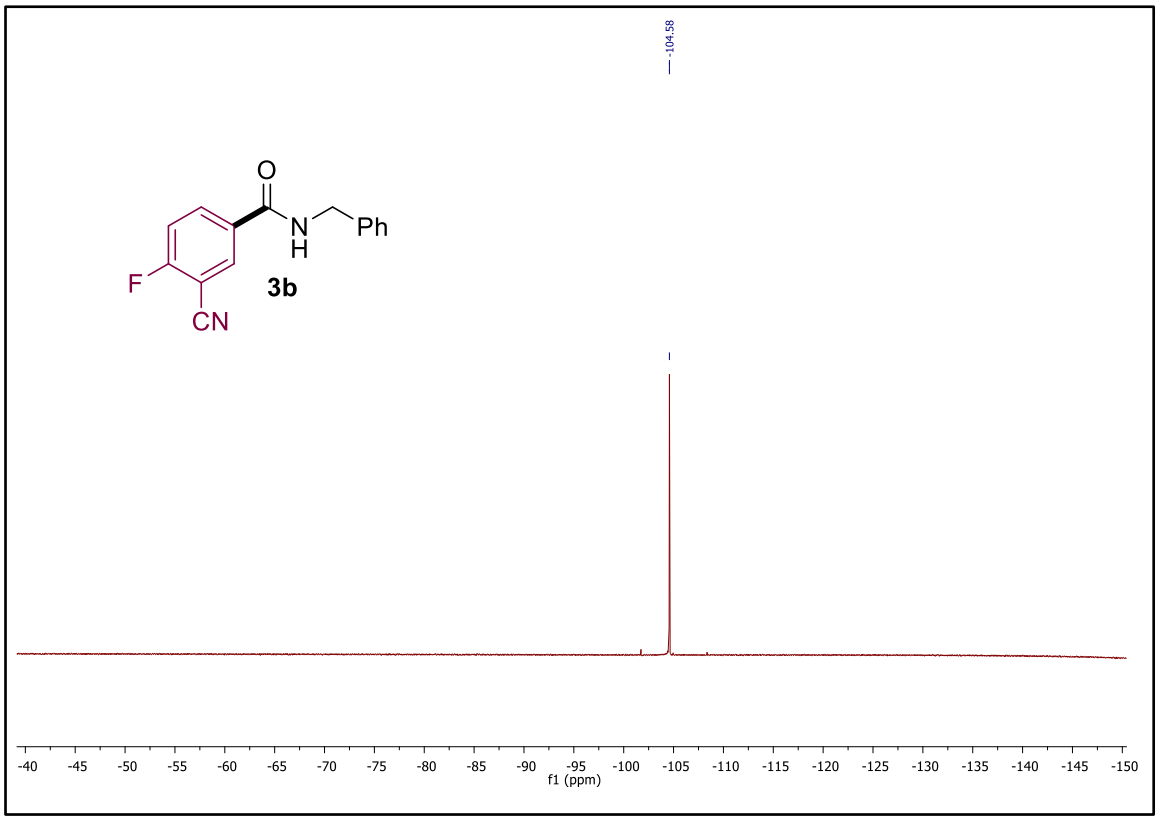
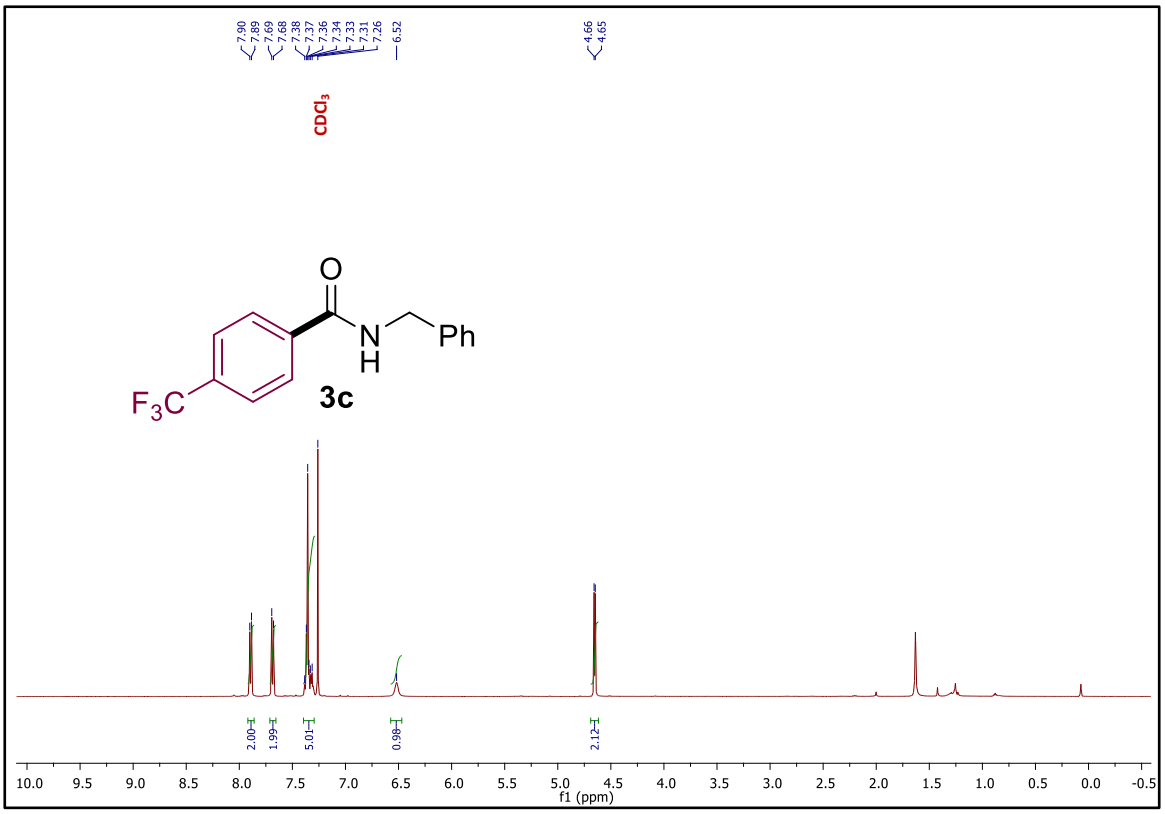


Figure S24. ^{19}F NMR (471 MHz) Spectra of **3b** in $CDCl_3$ at 298K



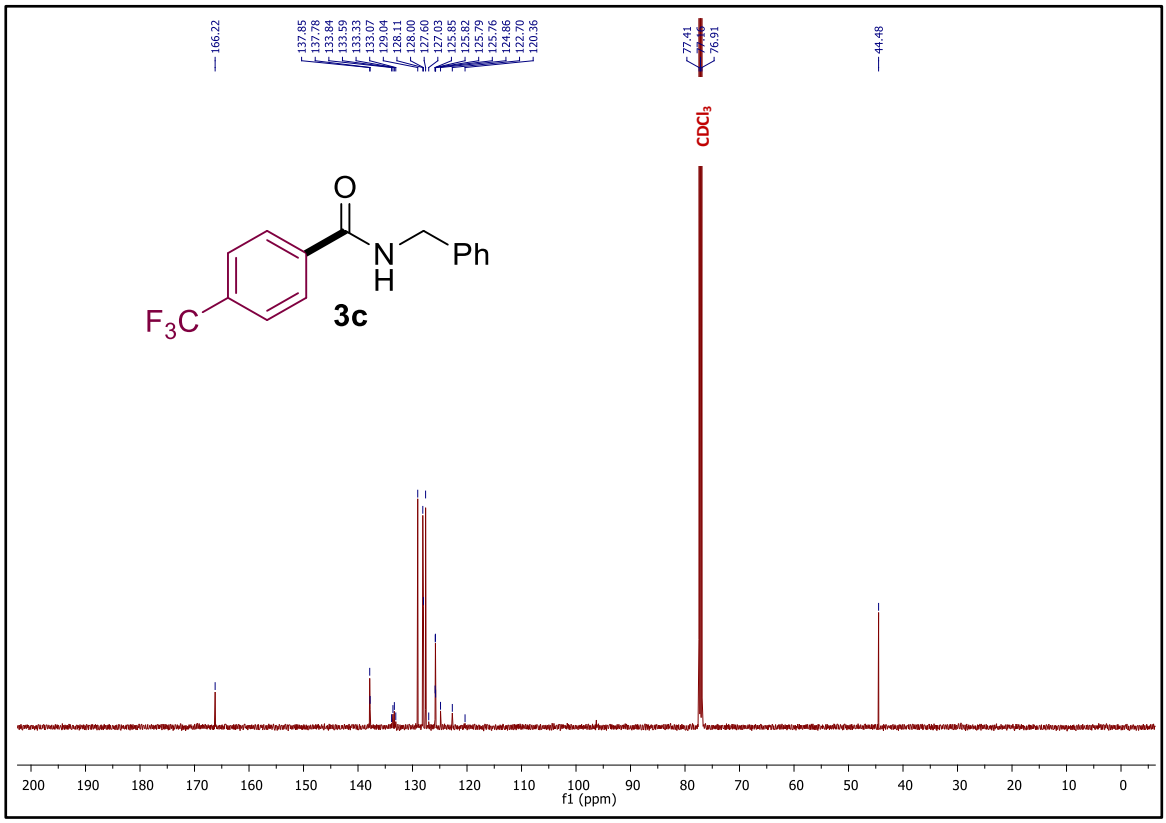


Figure S25. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3c** in $CDCl_3$ at 298K.

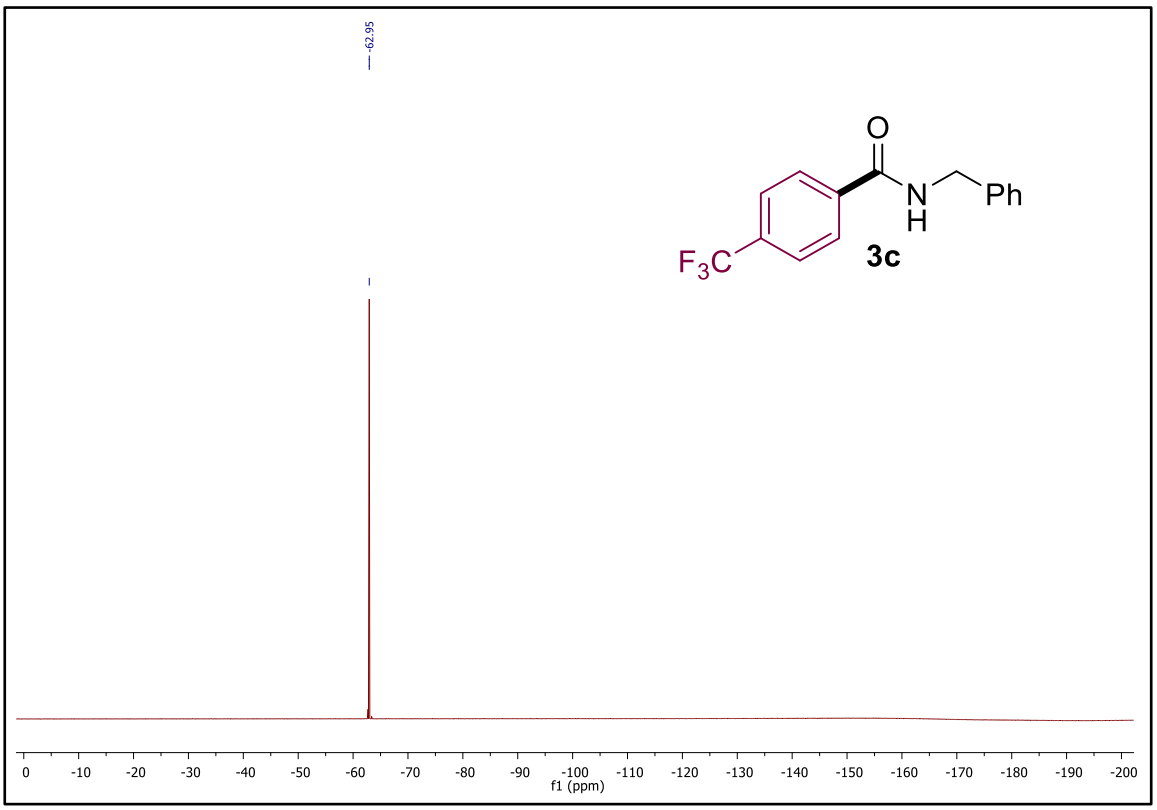


Figure S26. ^{19}F NMR (471 MHz) Spectra of **3c** in $CDCl_3$ at 298K

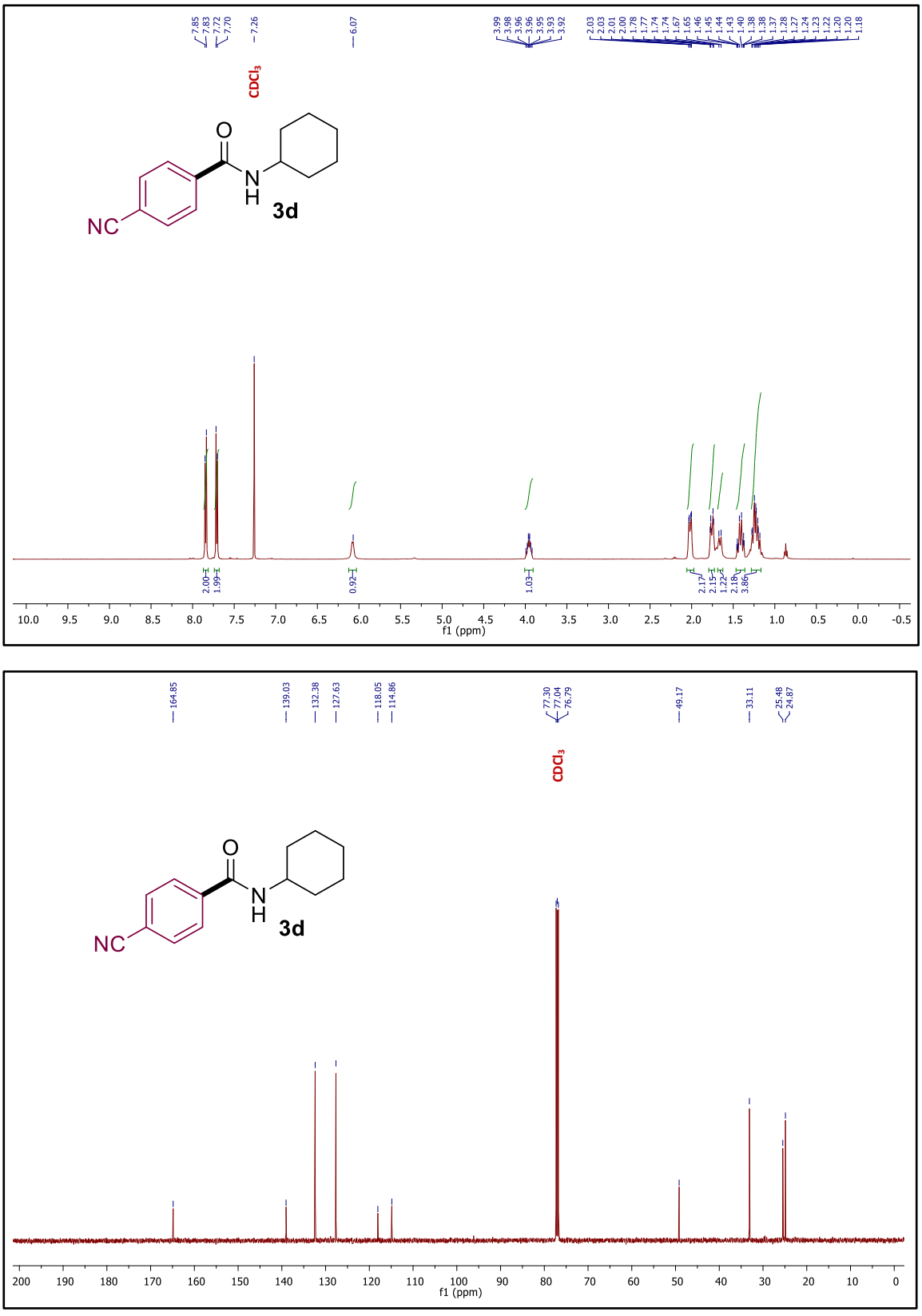


Figure S27. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3d** in $CDCl_3$ at 298K.

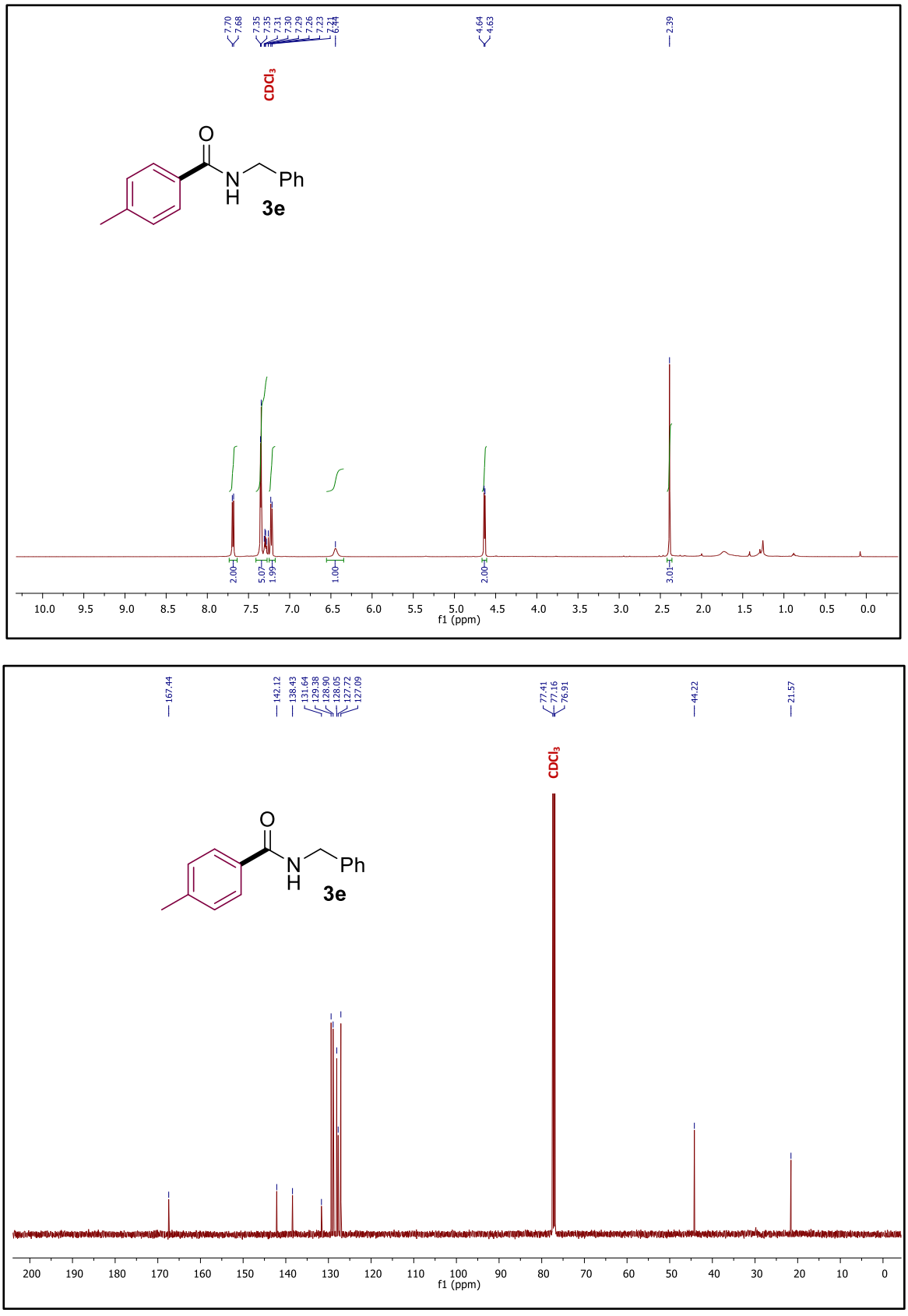


Figure S28. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3e** in $CDCl_3$ at 298K.

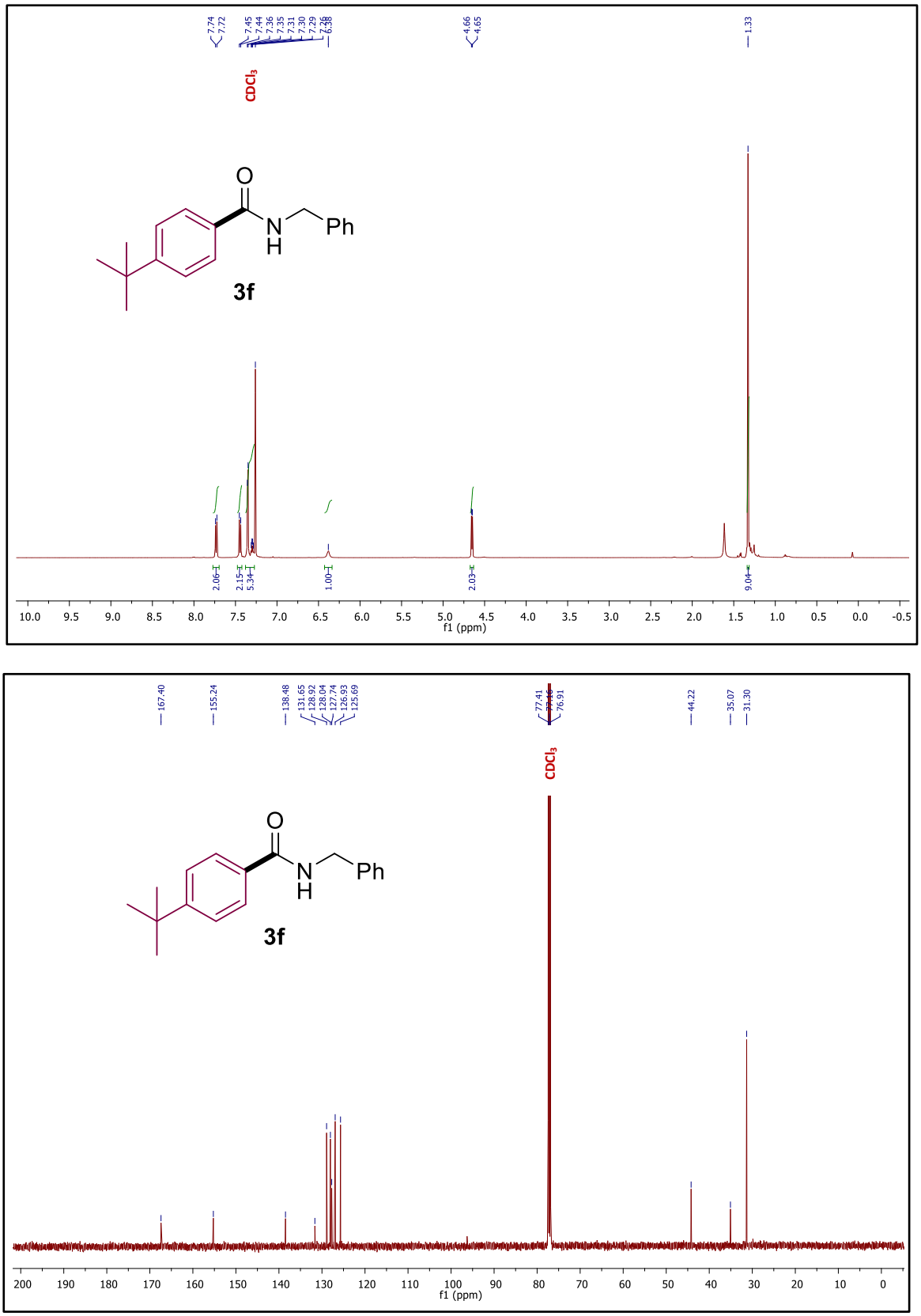
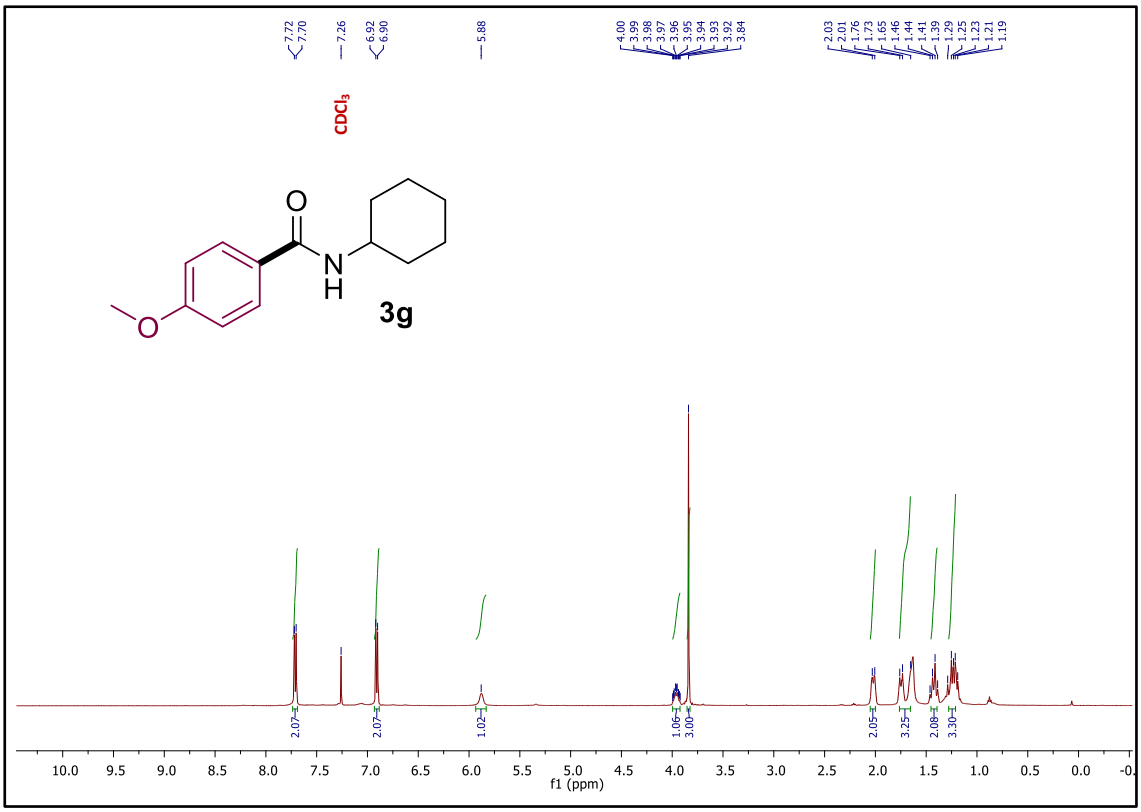


Figure S29. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3f** in $CDCl_3$ at 298K.



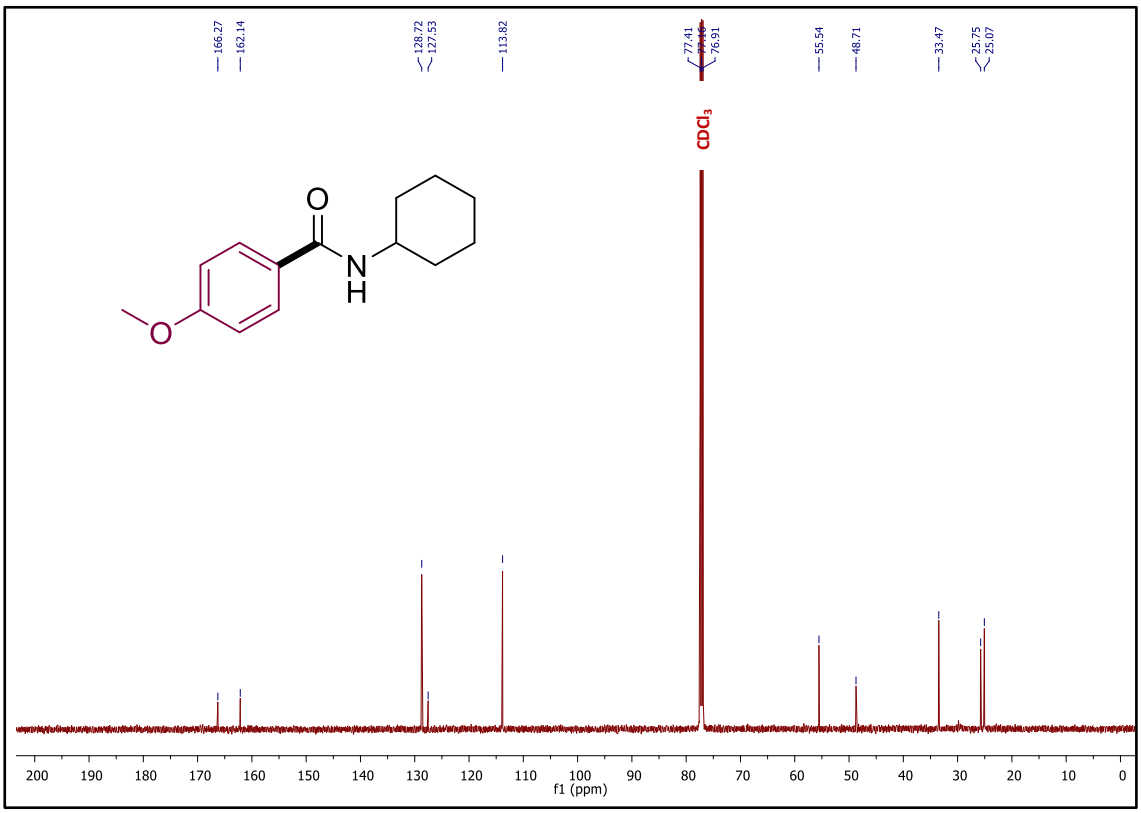


Figure S30. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3g** in $CDCl_3$ at 298K.

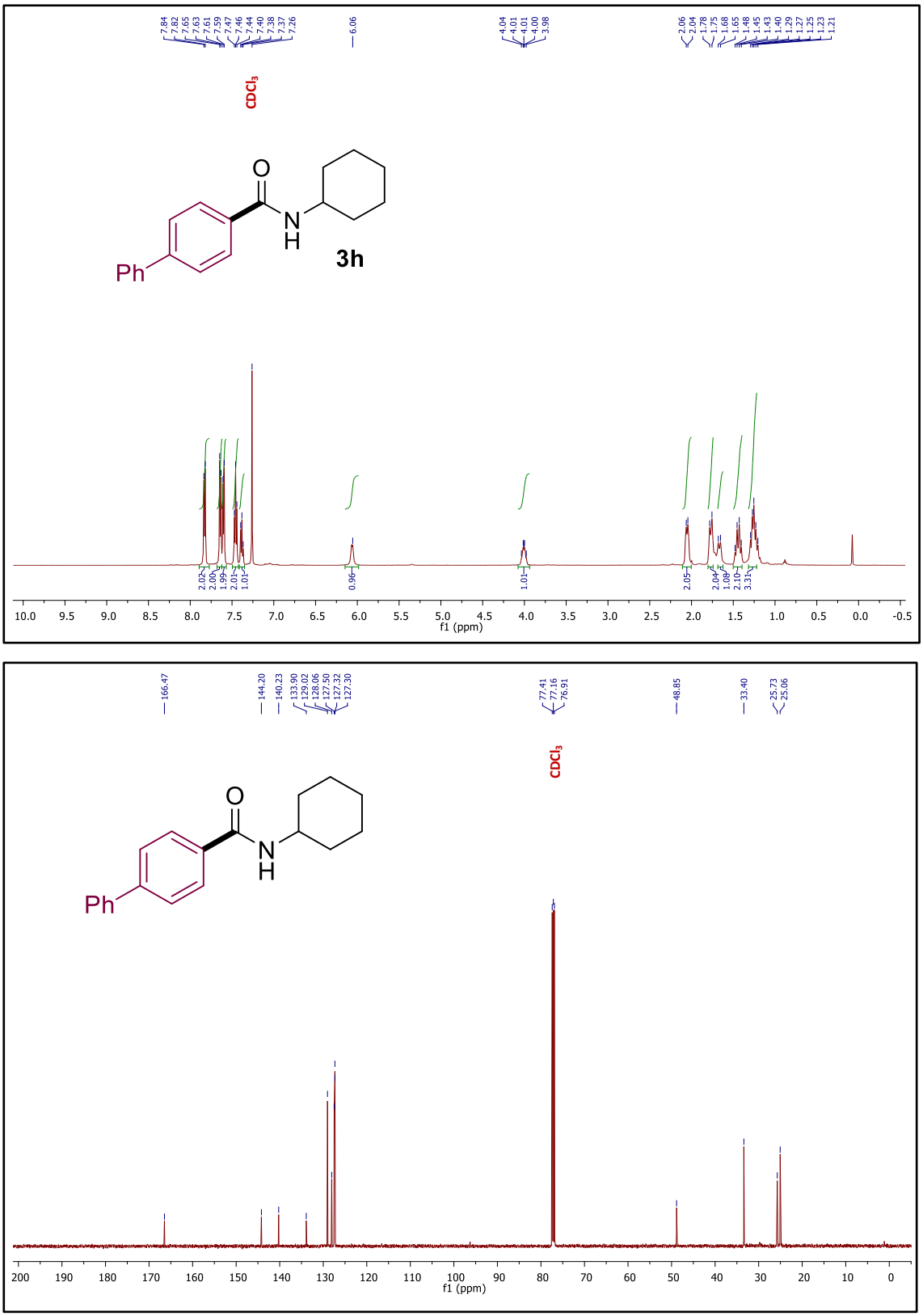


Figure S31. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3h** in $CDCl_3$ at 298K.

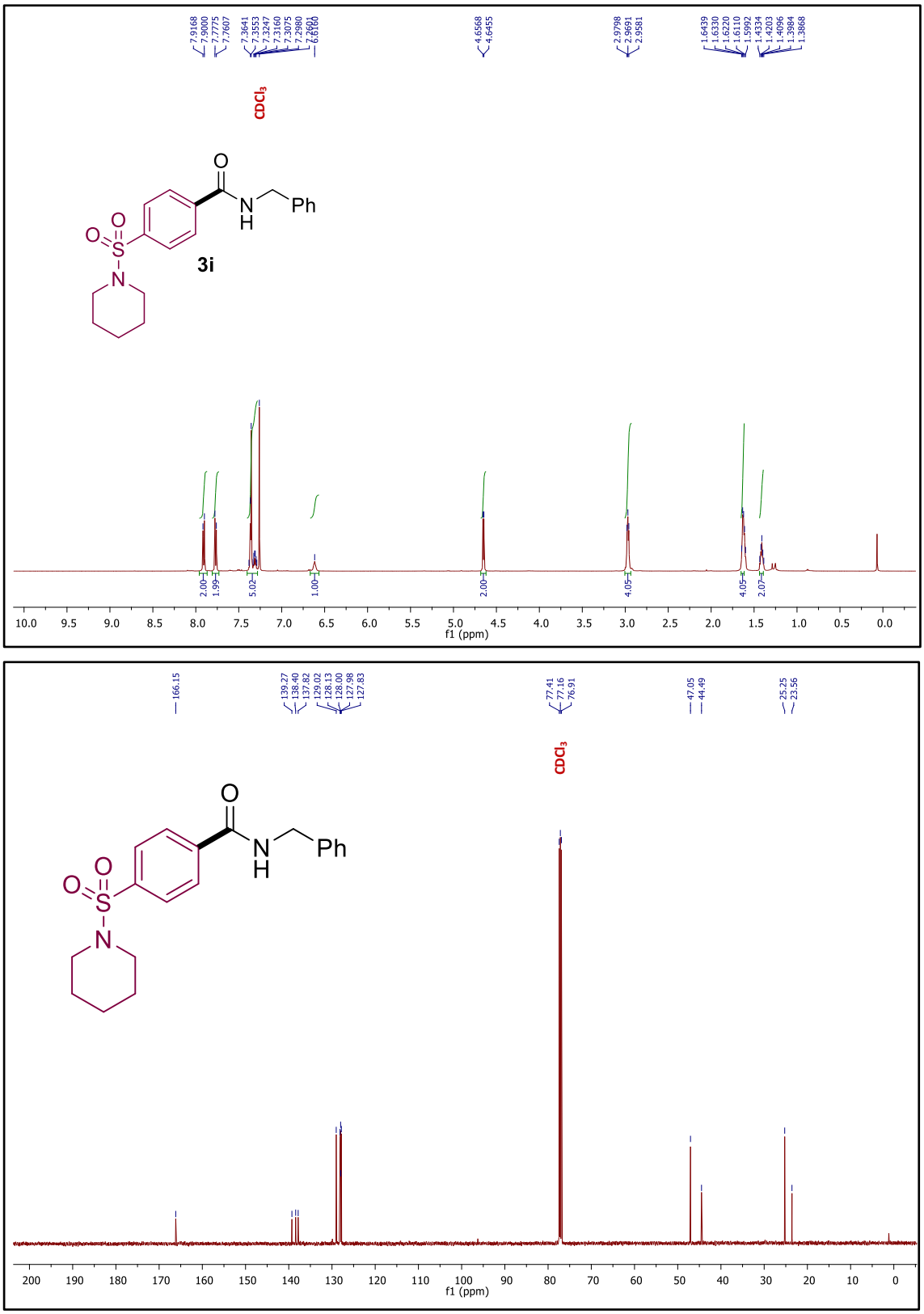


Figure S32. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3i** in $CDCl_3$ at 298K.

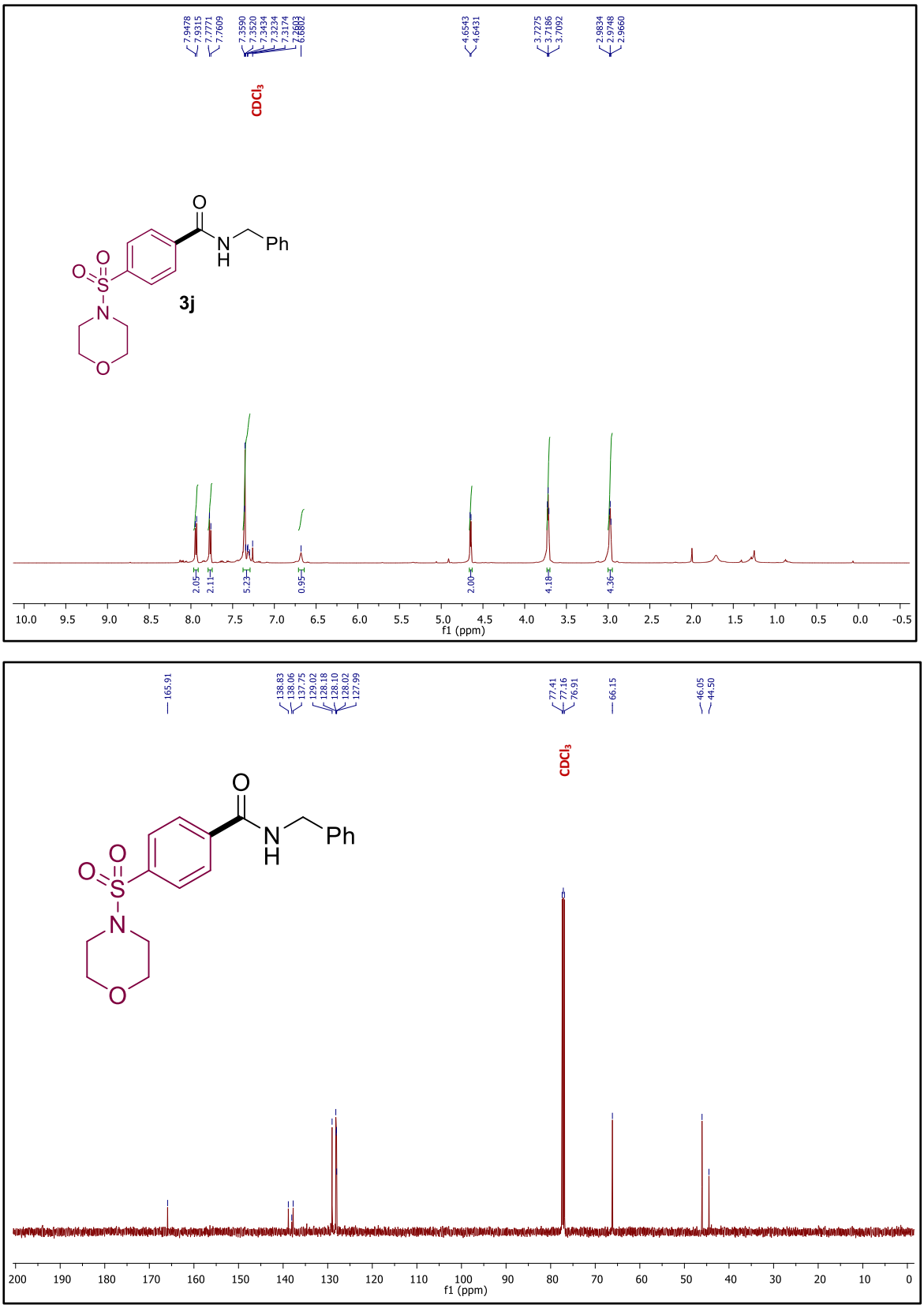


Figure S33. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3j** in $CDCl_3$ at 298K.

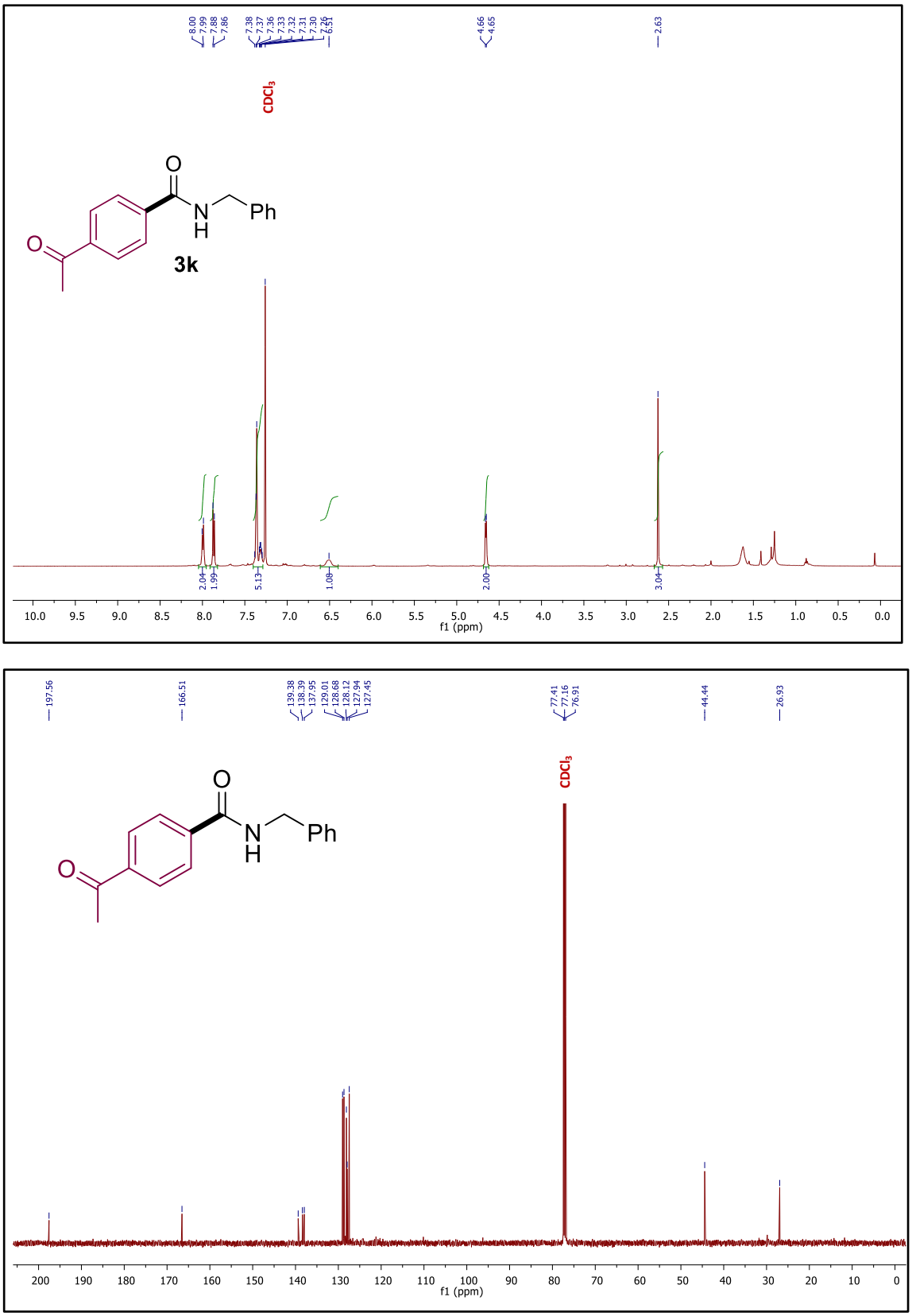


Figure S34. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3k** in $CDCl_3$ at 298K.

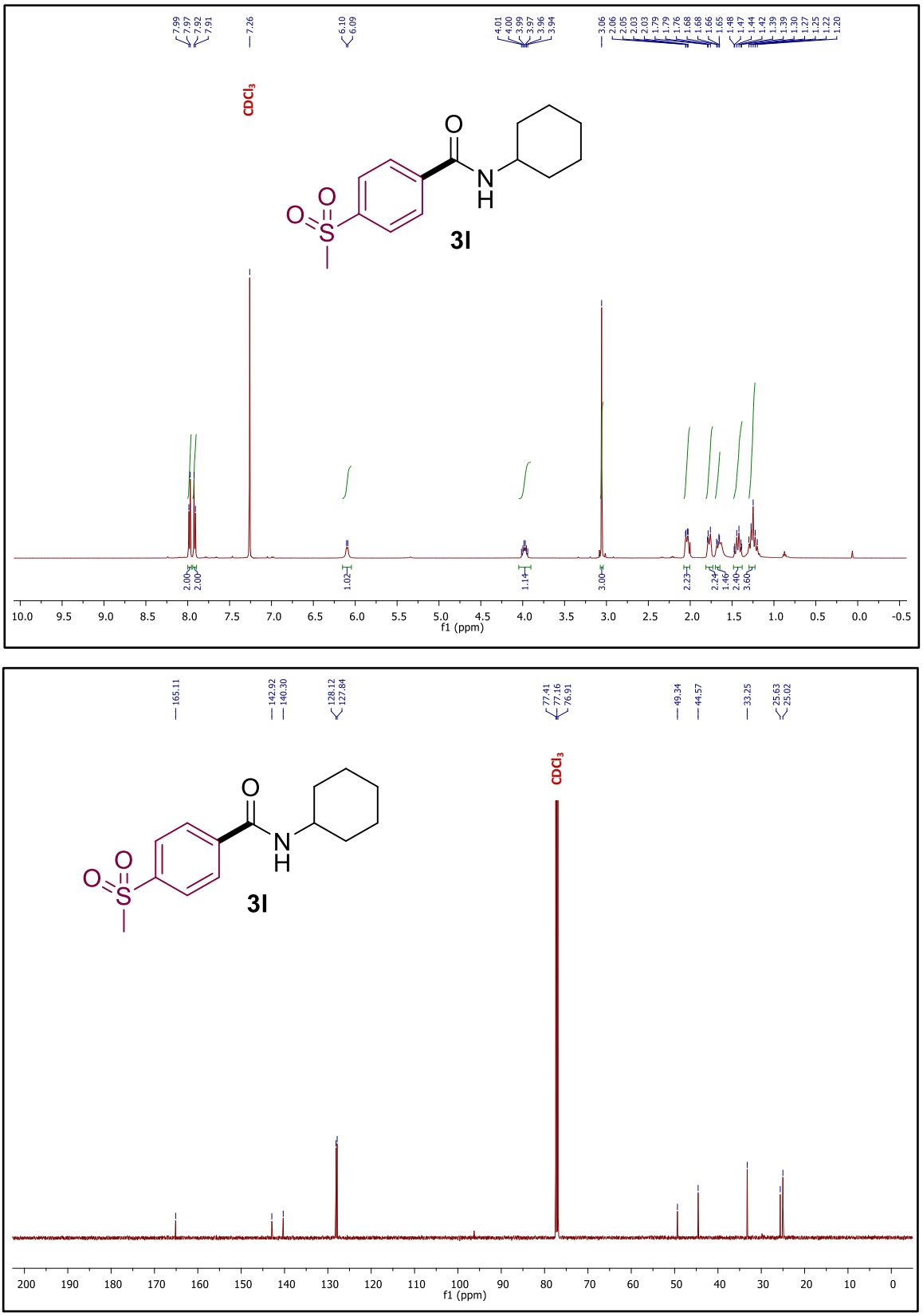


Figure S35. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3l** in $CDCl_3$ at 298K.

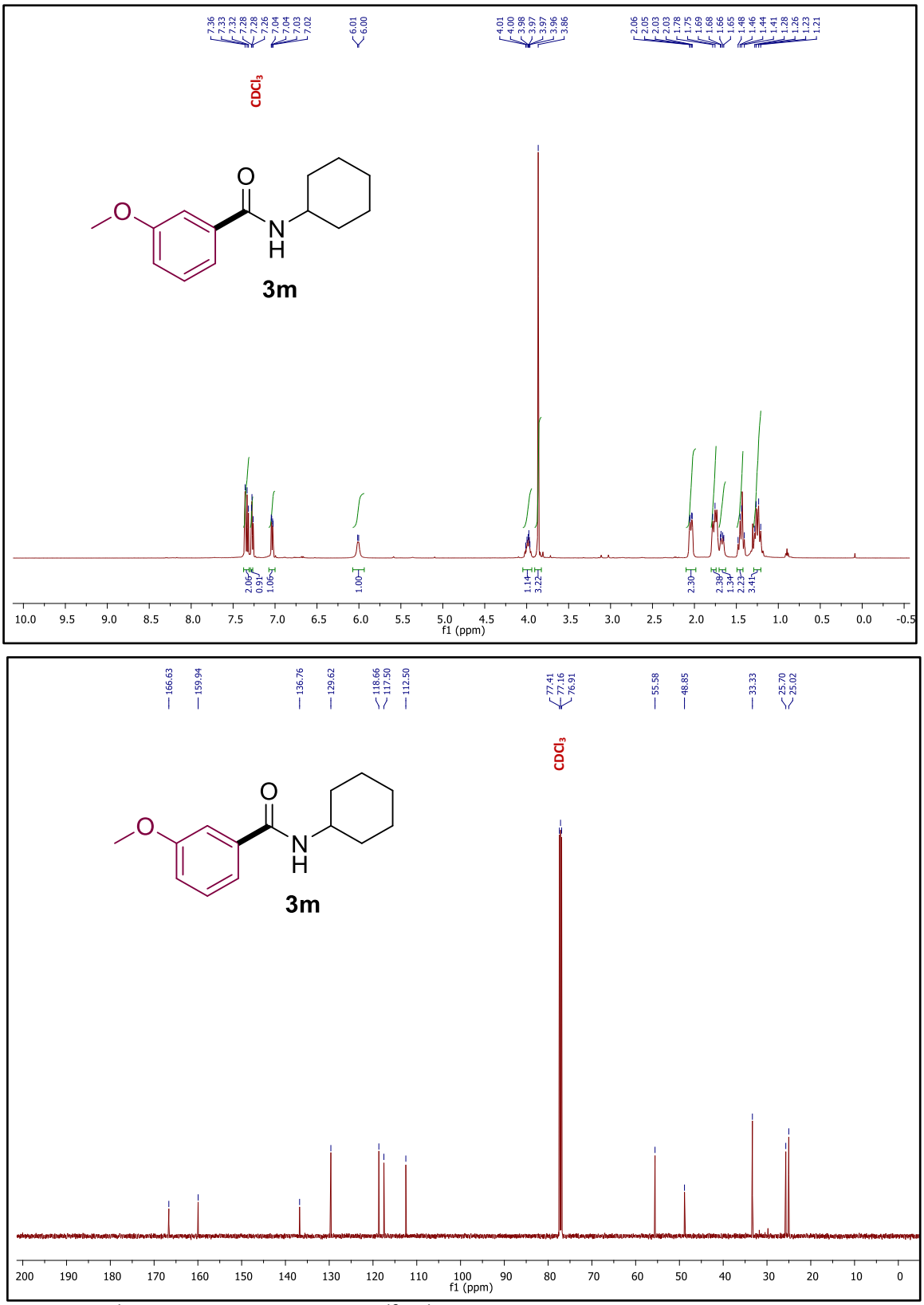


Figure S36. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3m** in $CDCl_3$ at 298K.

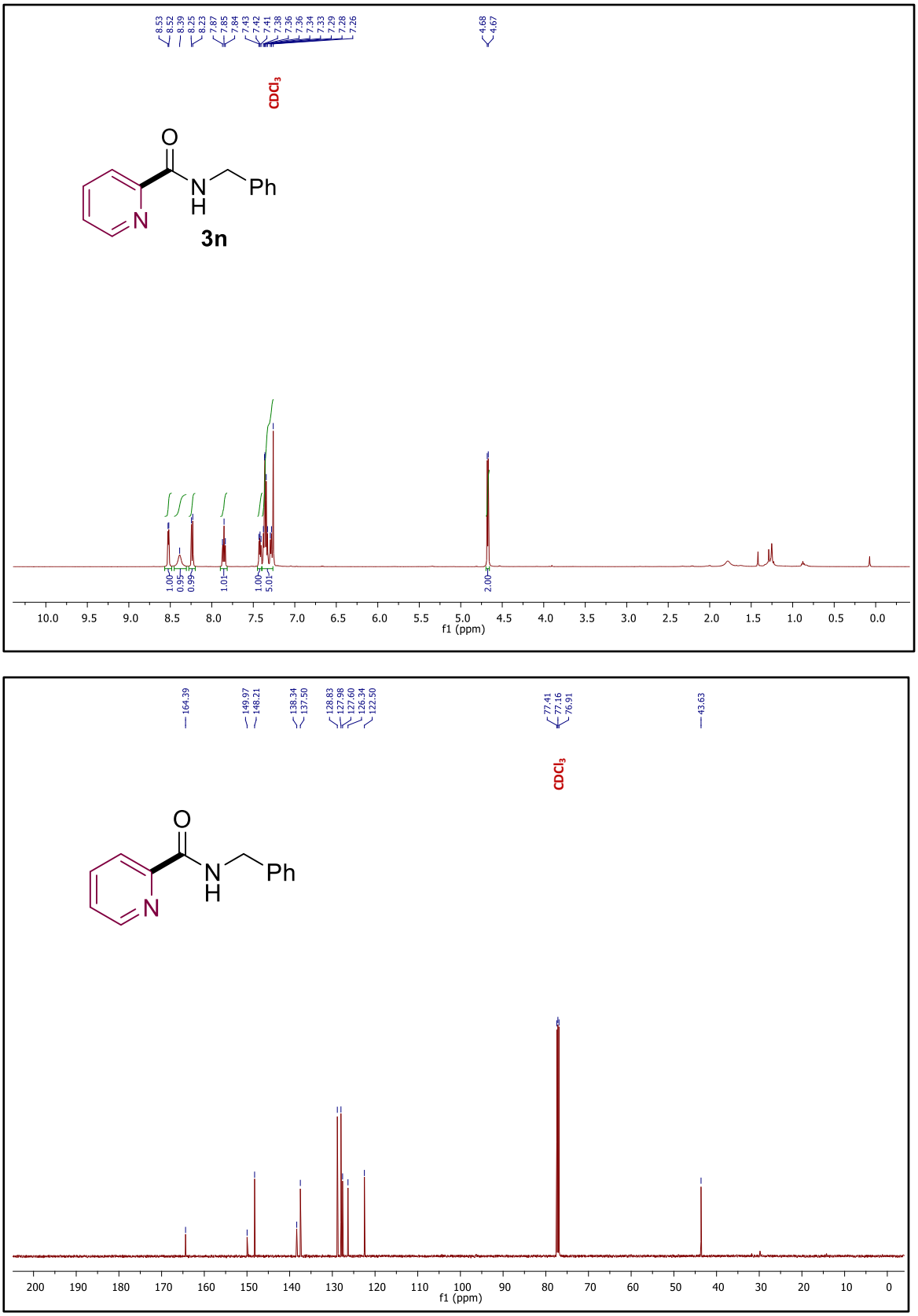


Figure S37. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3n** in $CDCl_3$ at 298K.

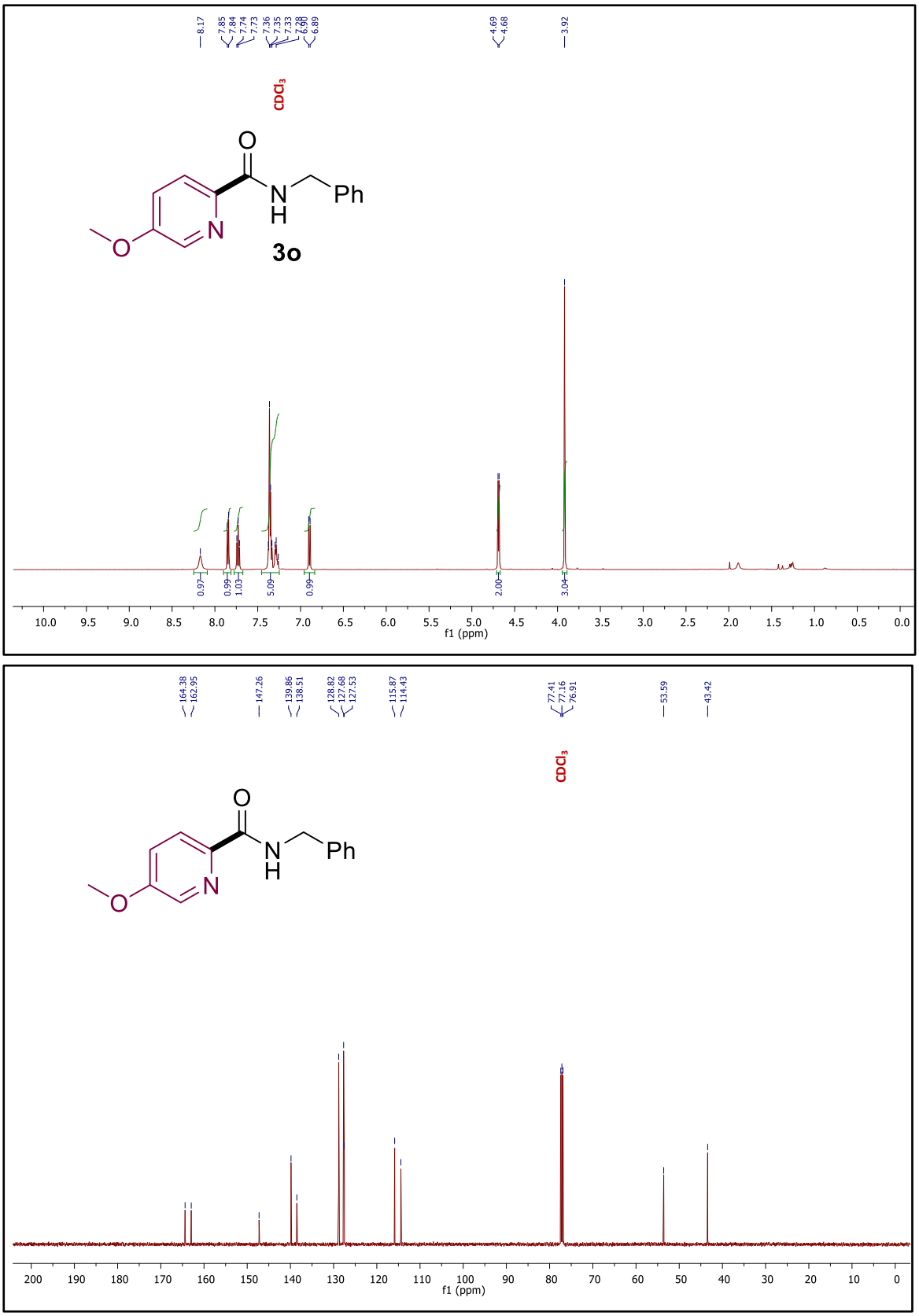


Figure S38. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3o** in $CDCl_3$ at 298K.

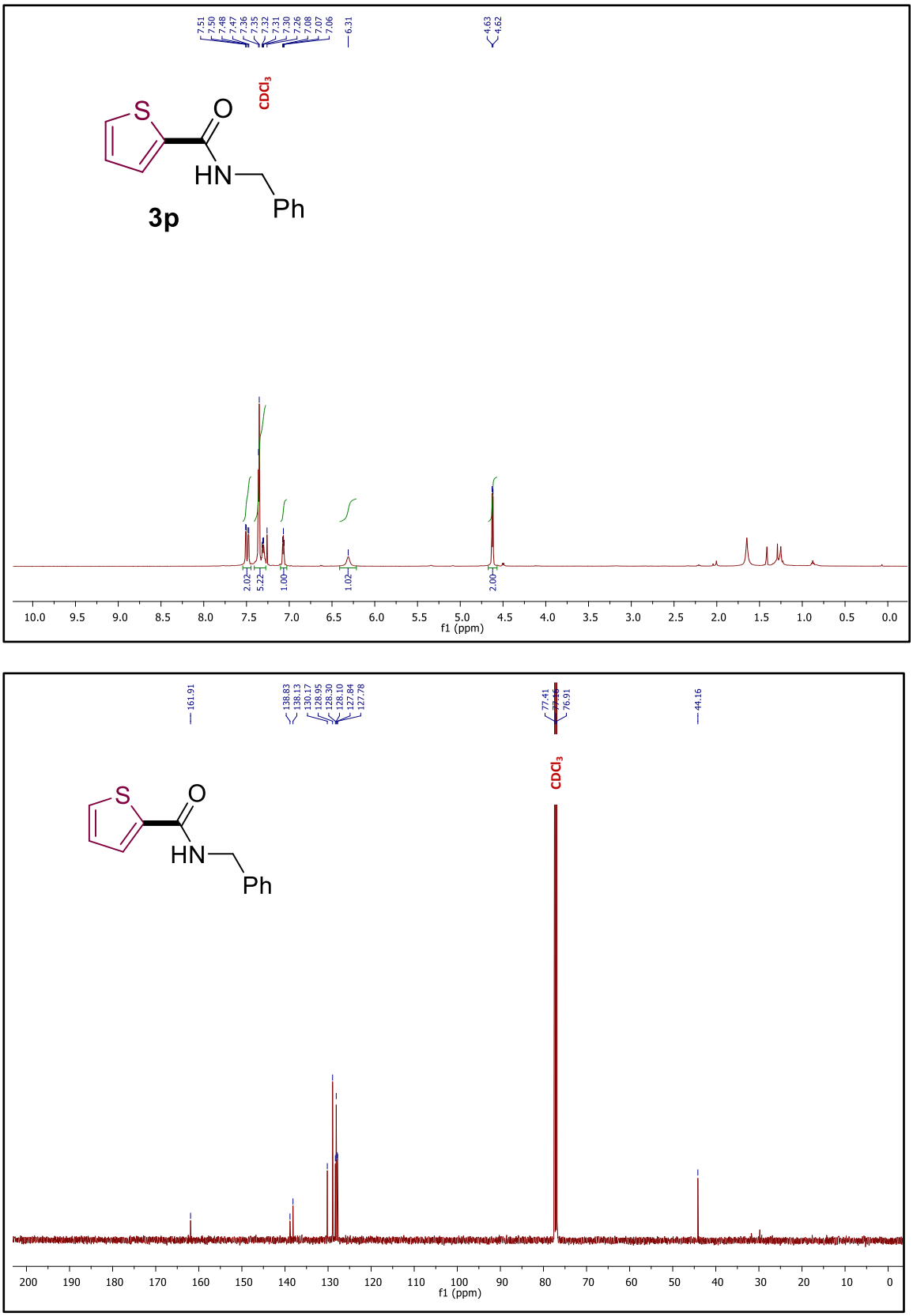


Figure S39. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3p** in $CDCl_3$ at 298K.

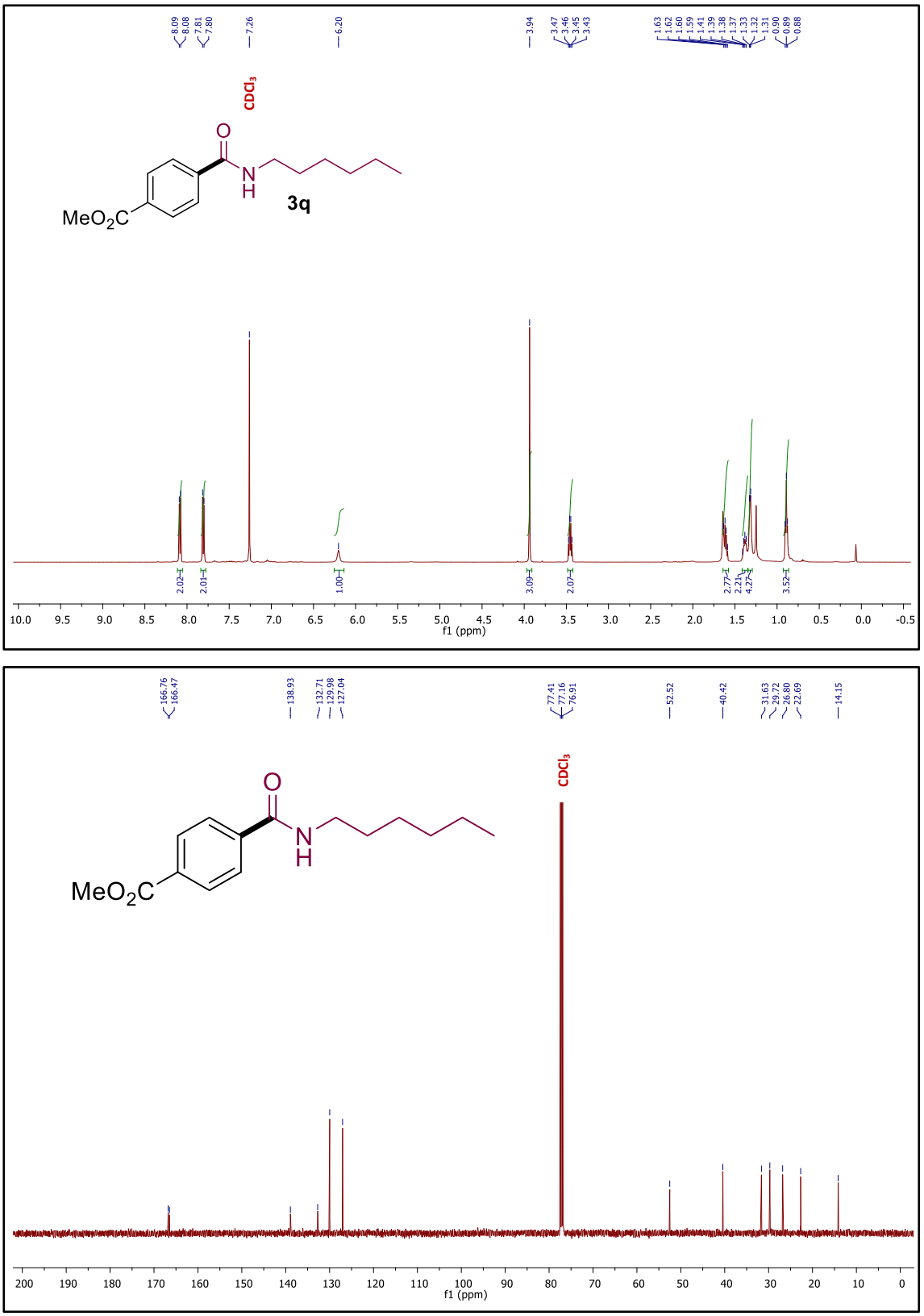


Figure S40. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3q** in $CDCl_3$ at 298K.

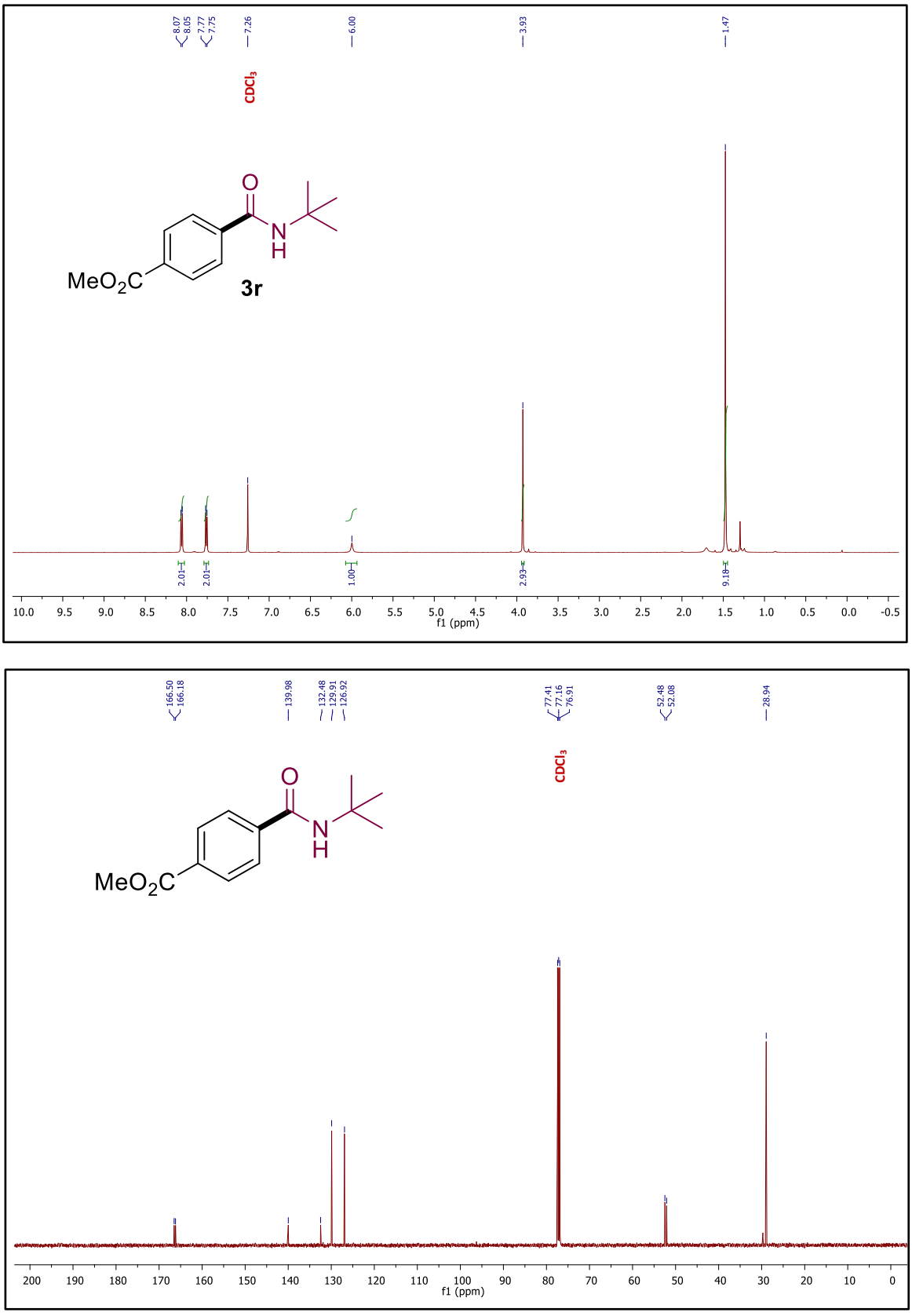


Figure S41. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3r** in $CDCl_3$ at 298K.

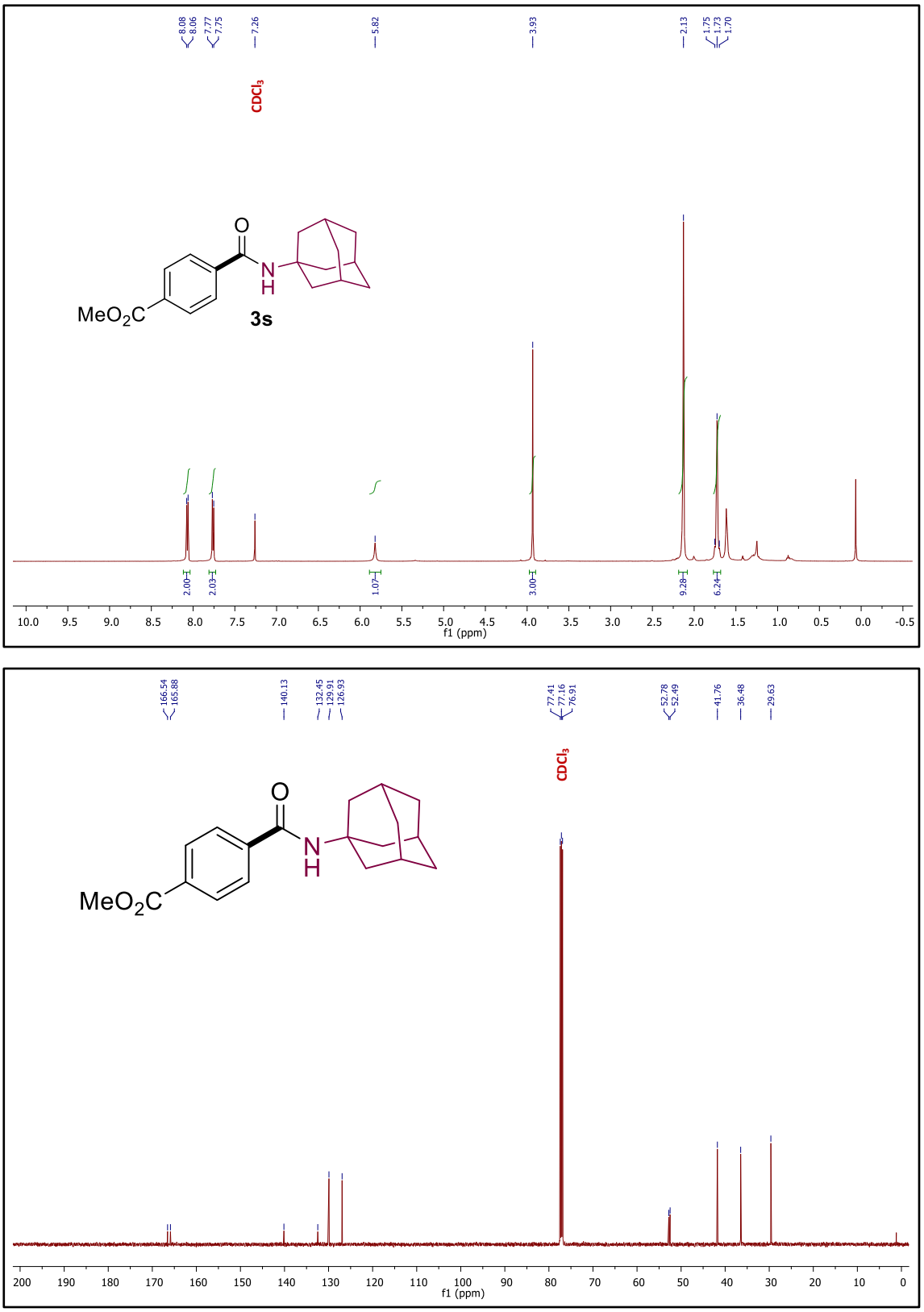
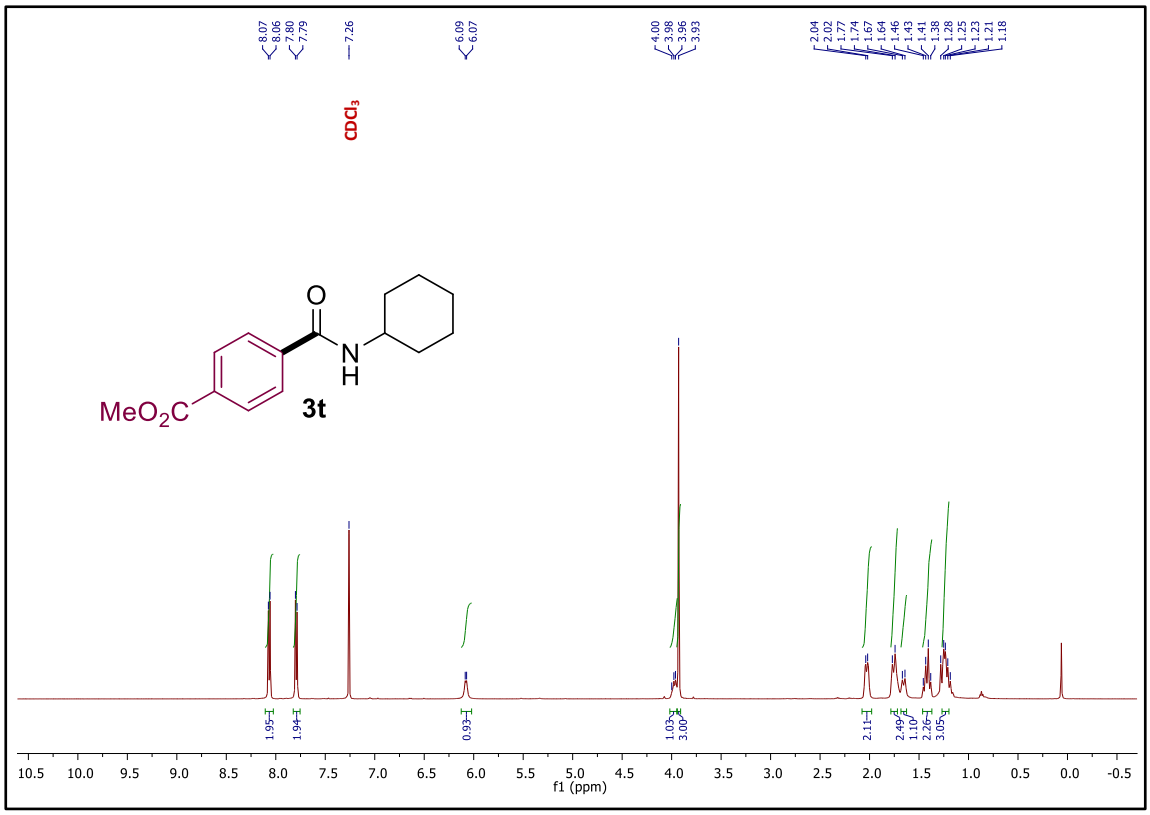


Figure S42. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3s** in $CDCl_3$ at 298K.



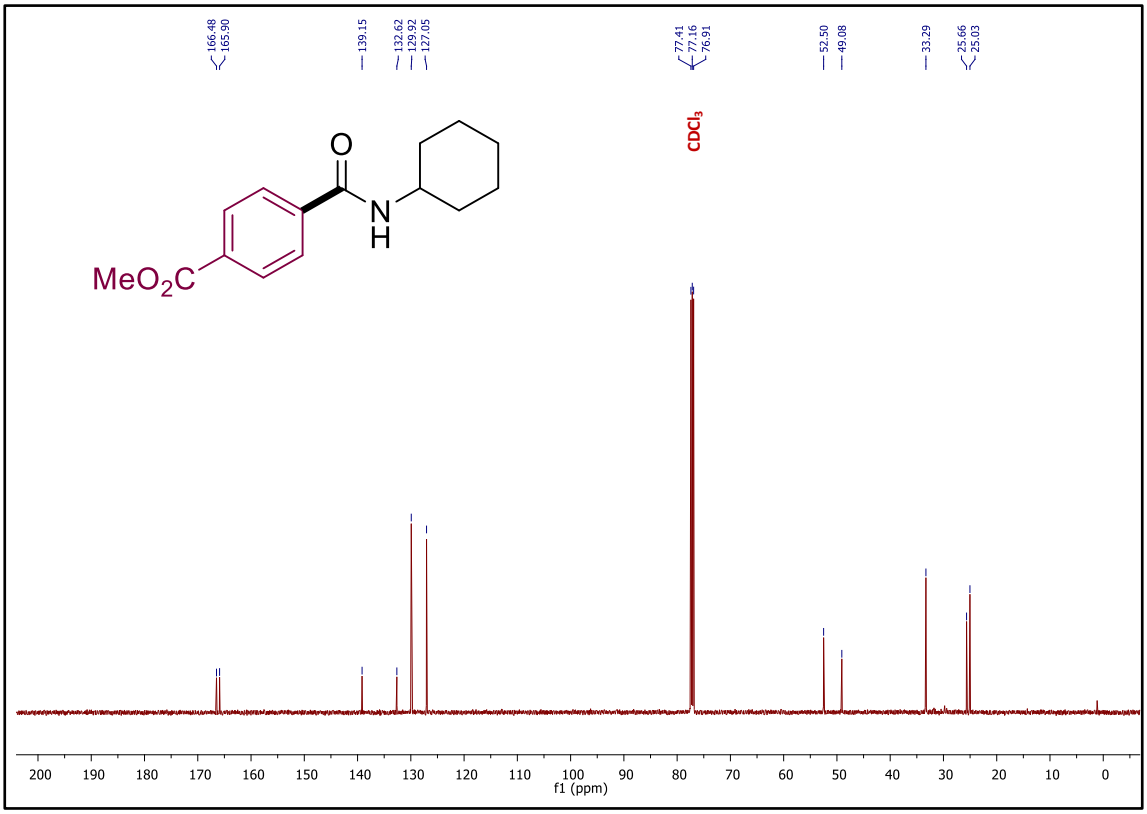


Figure S43. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3t** in $CDCl_3$ at 298K.

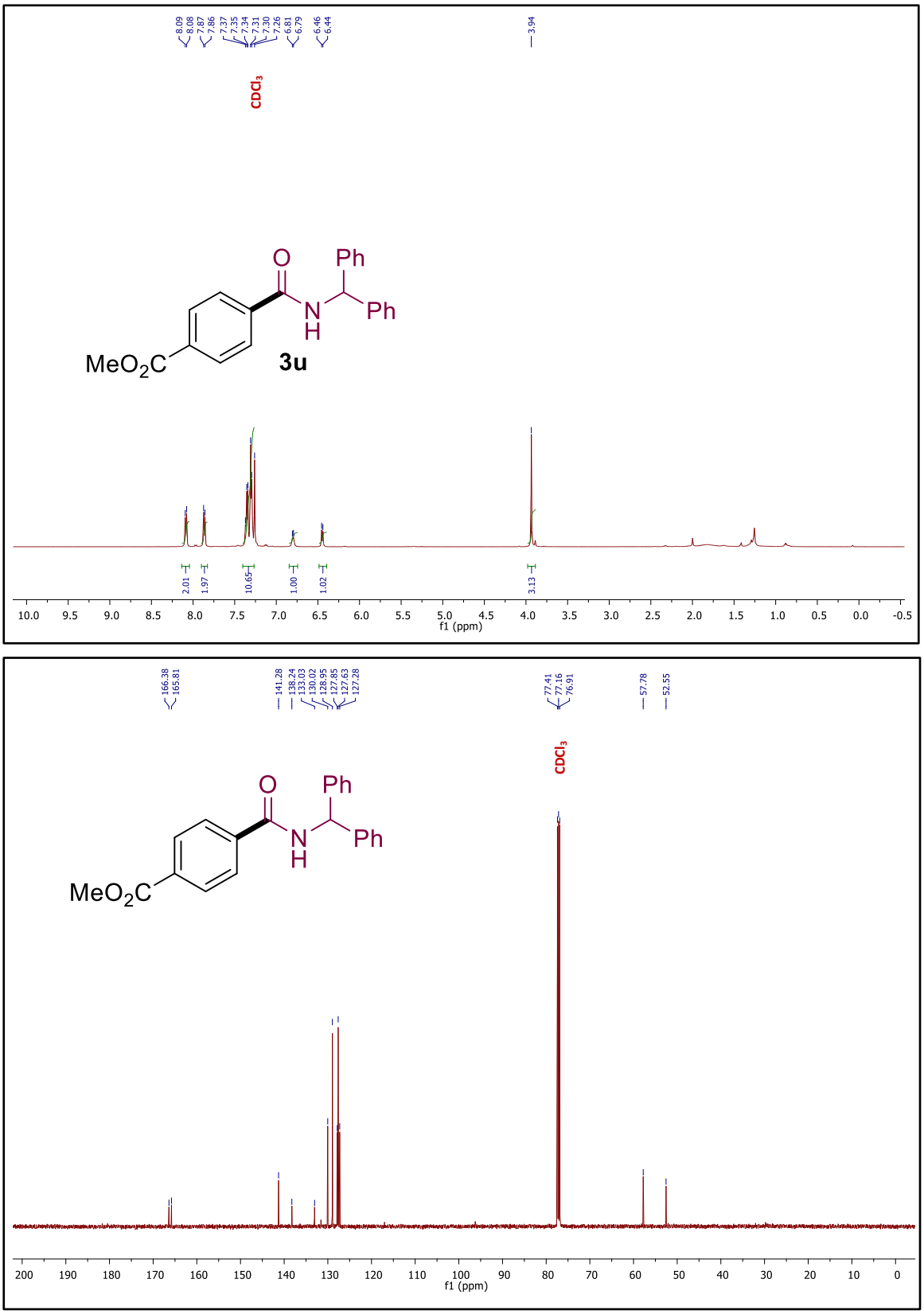


Figure S44. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3u** in $CDCl_3$ at 298K.

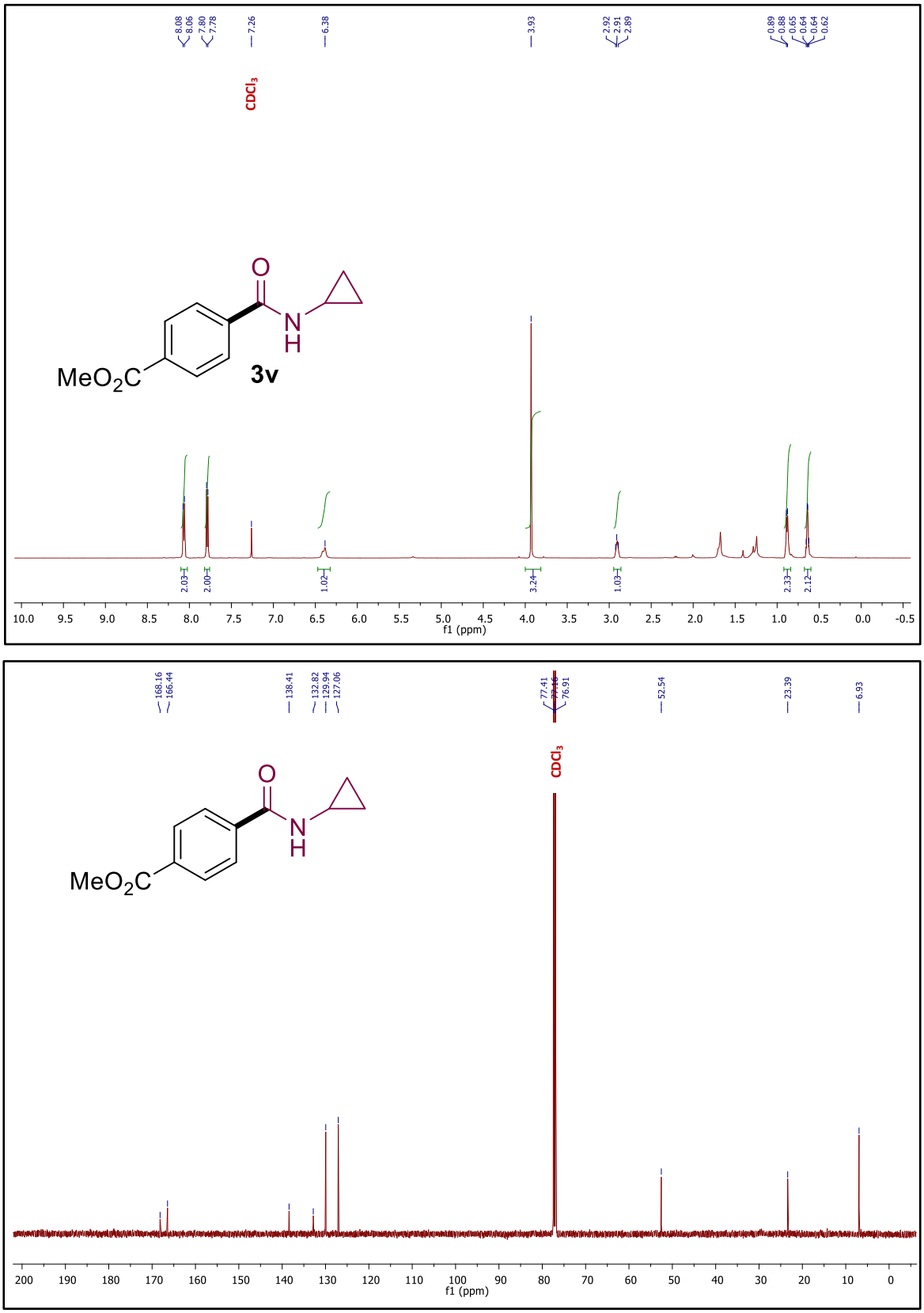


Figure S45. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3v** in $CDCl_3$ at 298K.

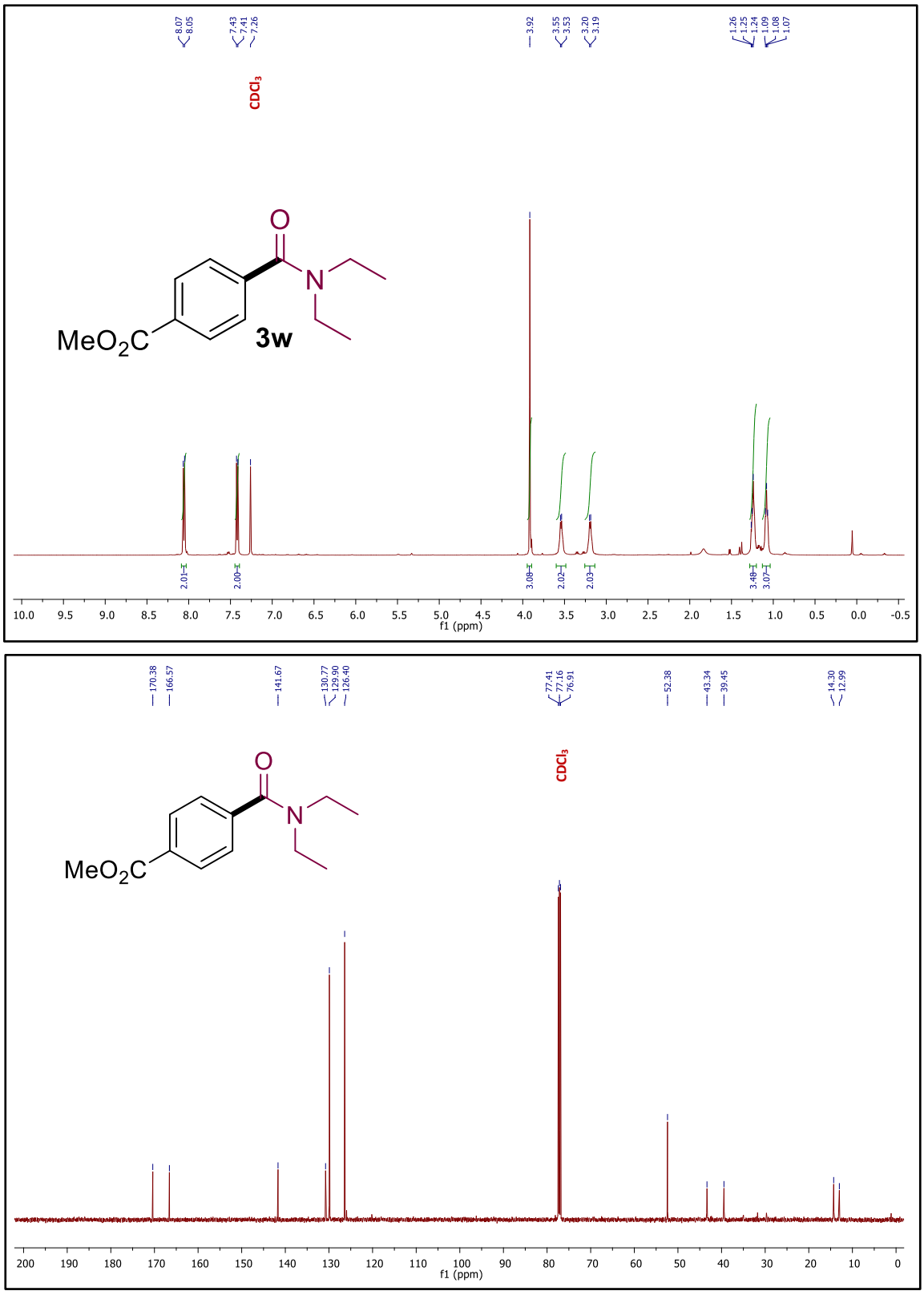


Figure S46. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3w** in $CDCl_3$ at 298K.

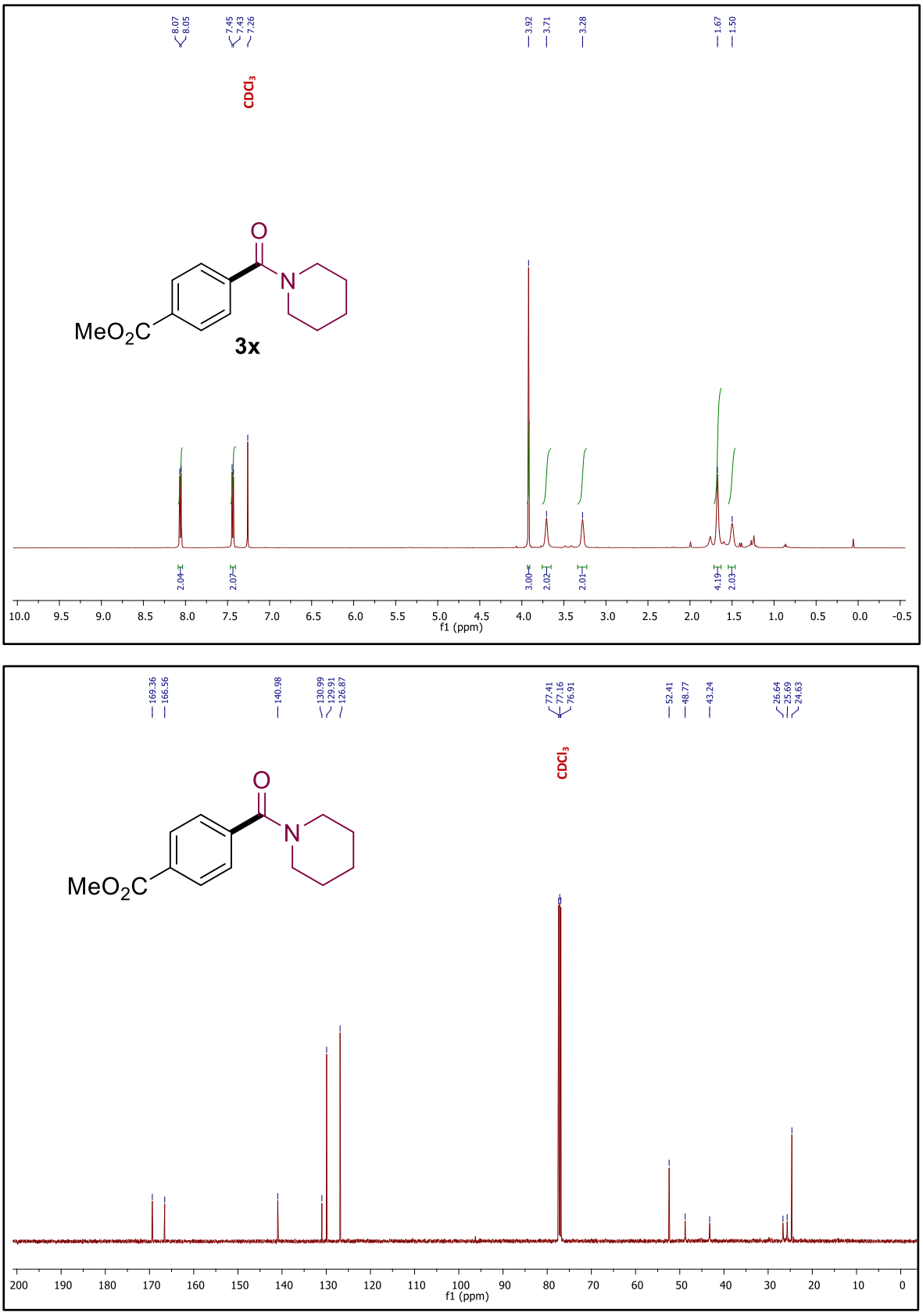
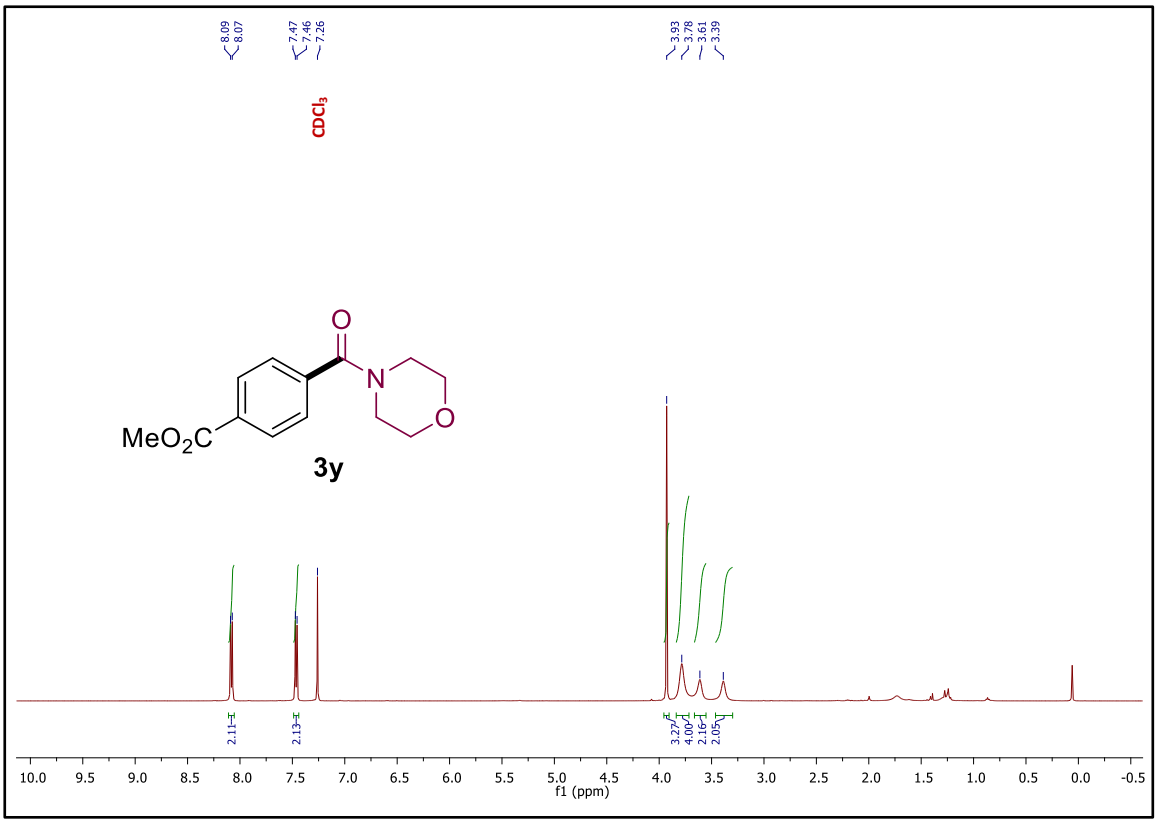


Figure S47. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3x** in $CDCl_3$ at 298K.



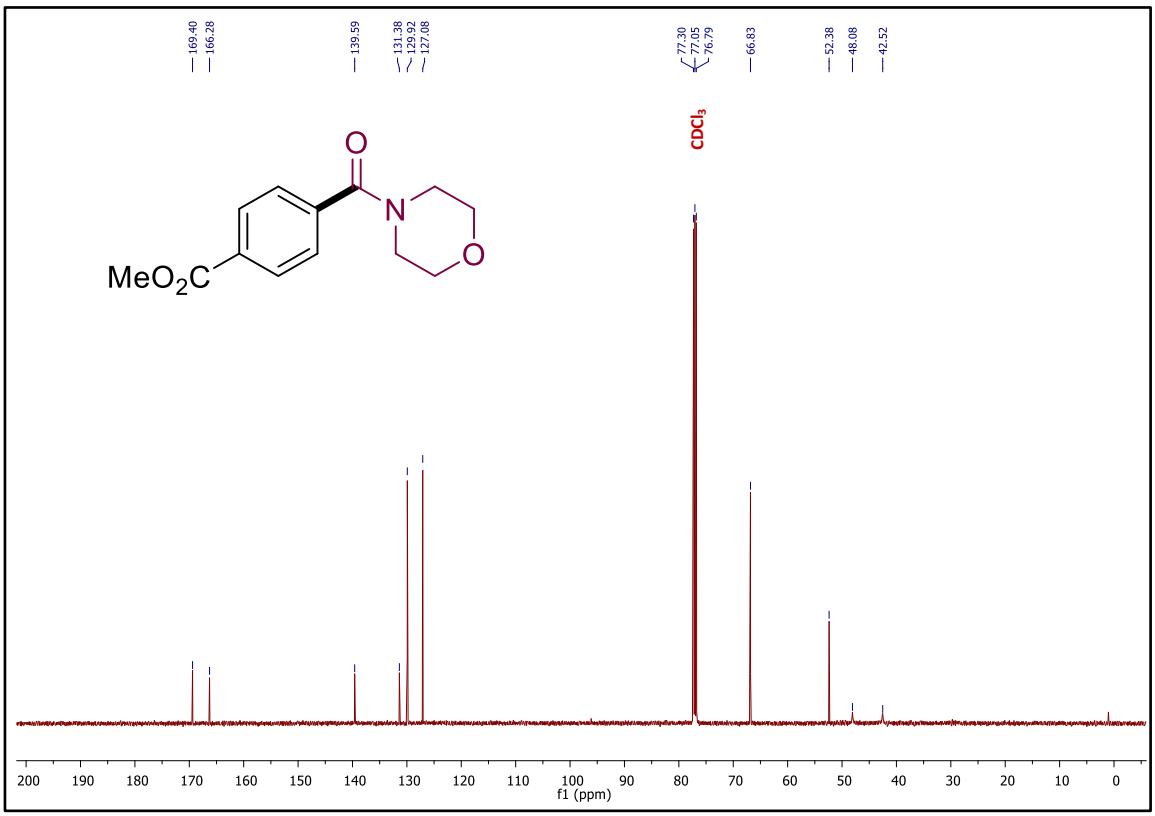


Figure S48. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3y** in $CDCl_3$ at 298K.

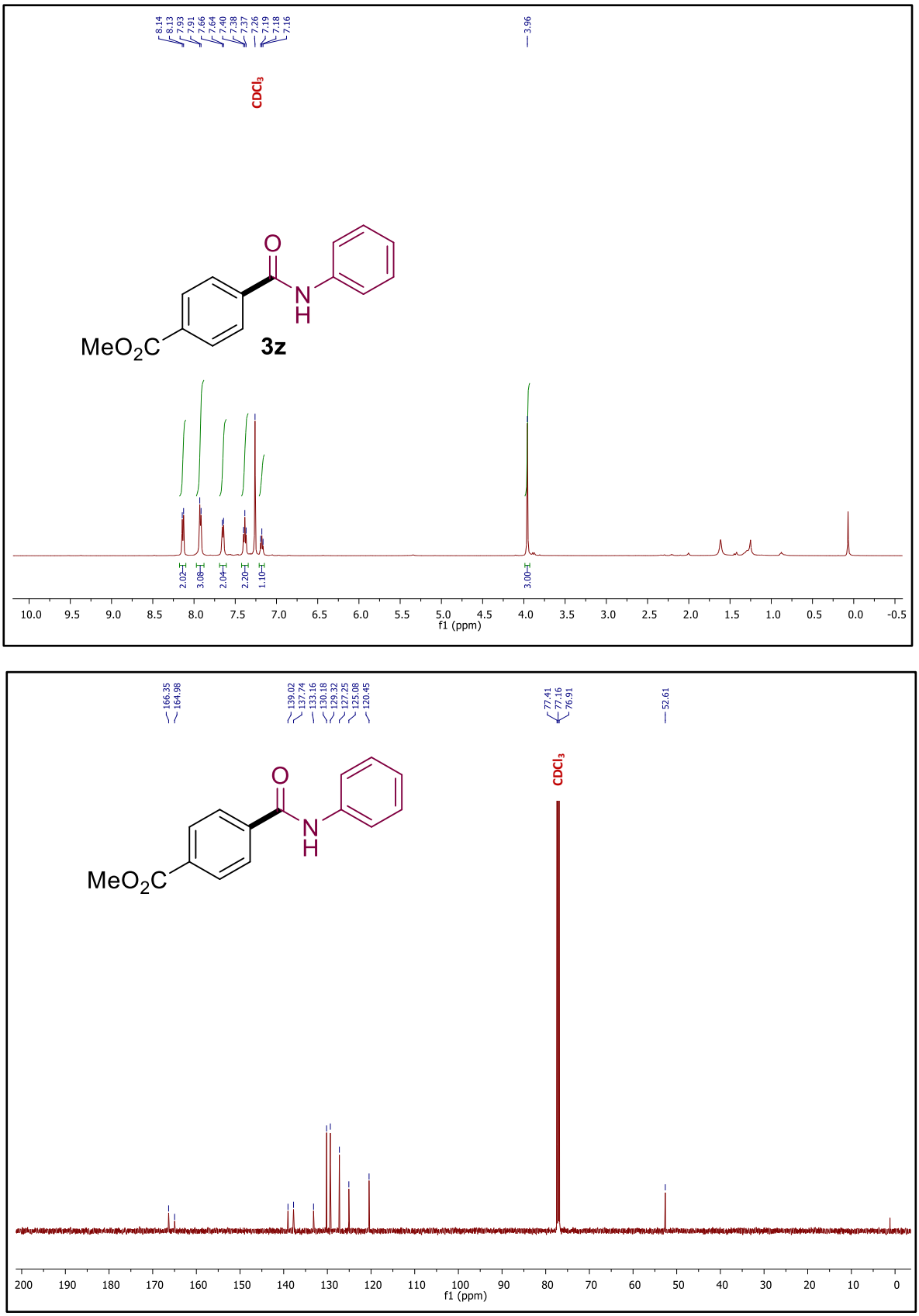


Figure S49. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3z** in $CDCl_3$ at 298K.

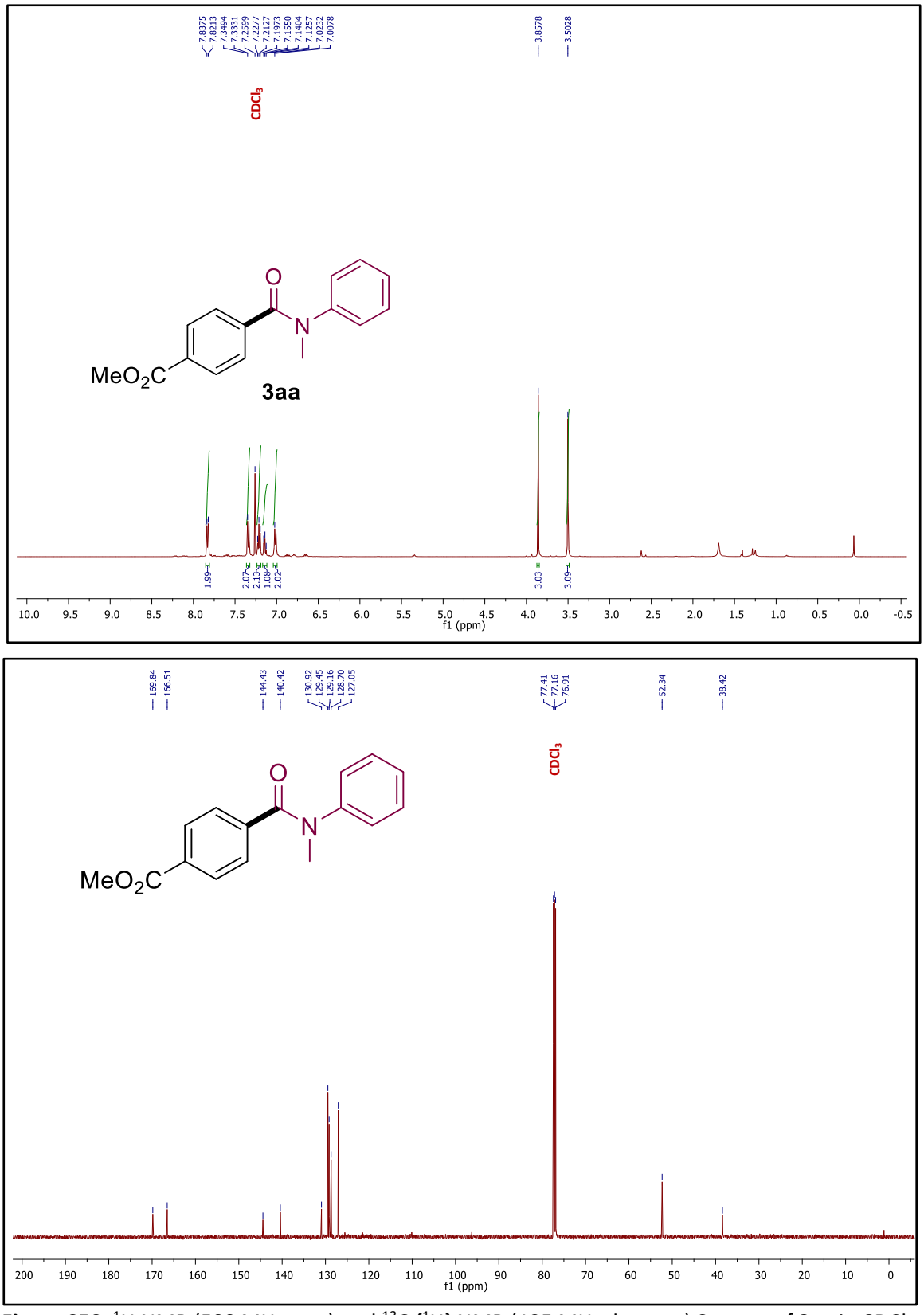


Figure S50. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3aa** in $CDCl_3$ at 298K.

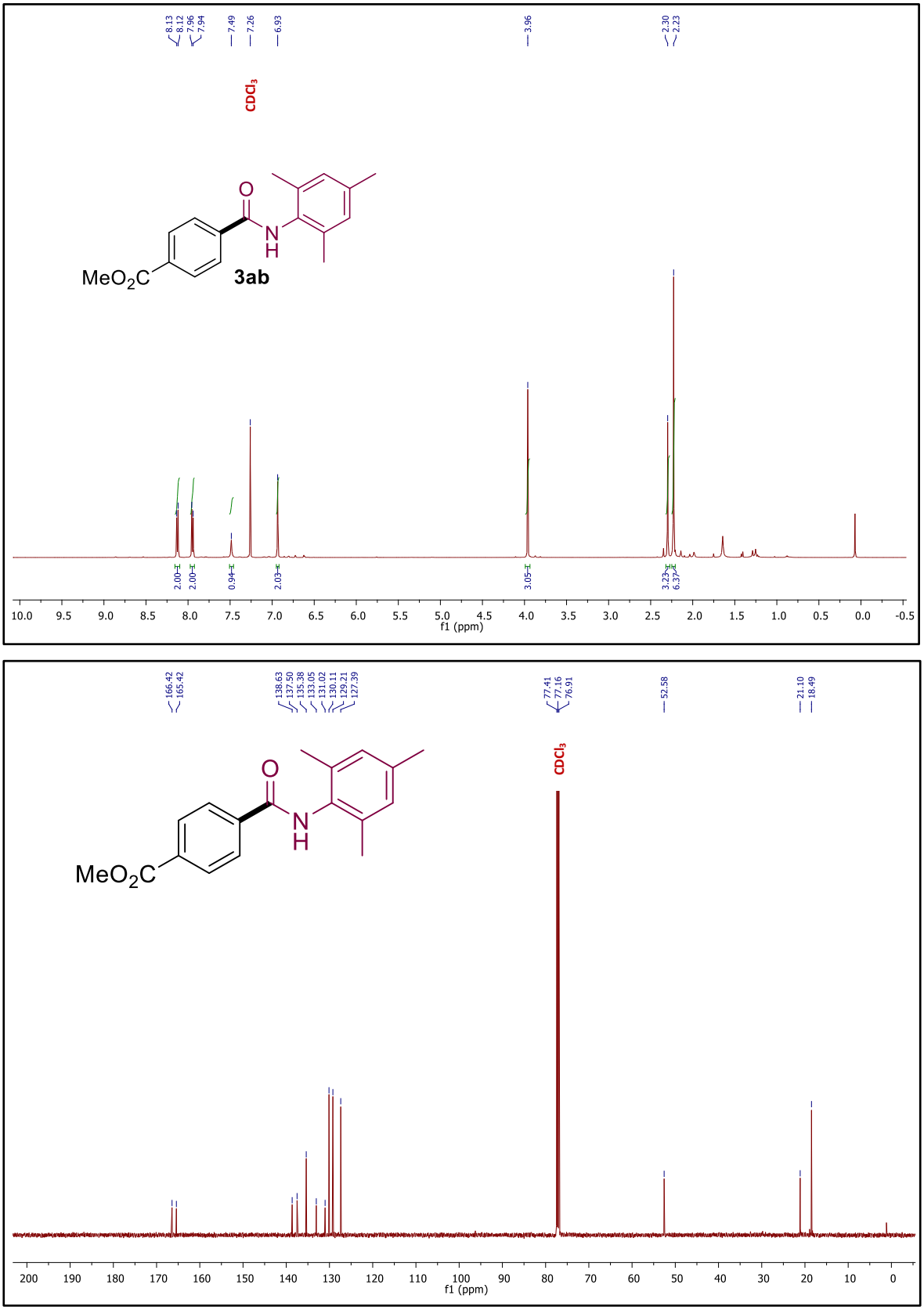
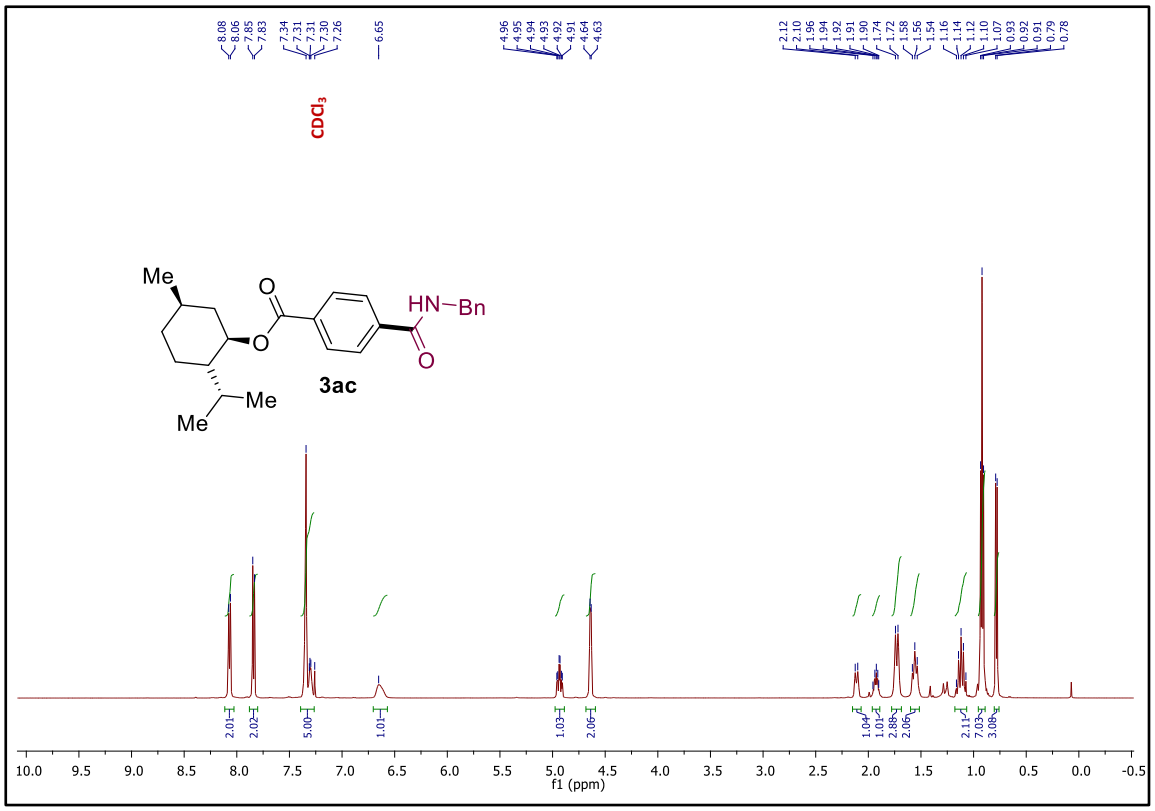


Figure S51. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3ab** in $CDCl_3$ at 298K.



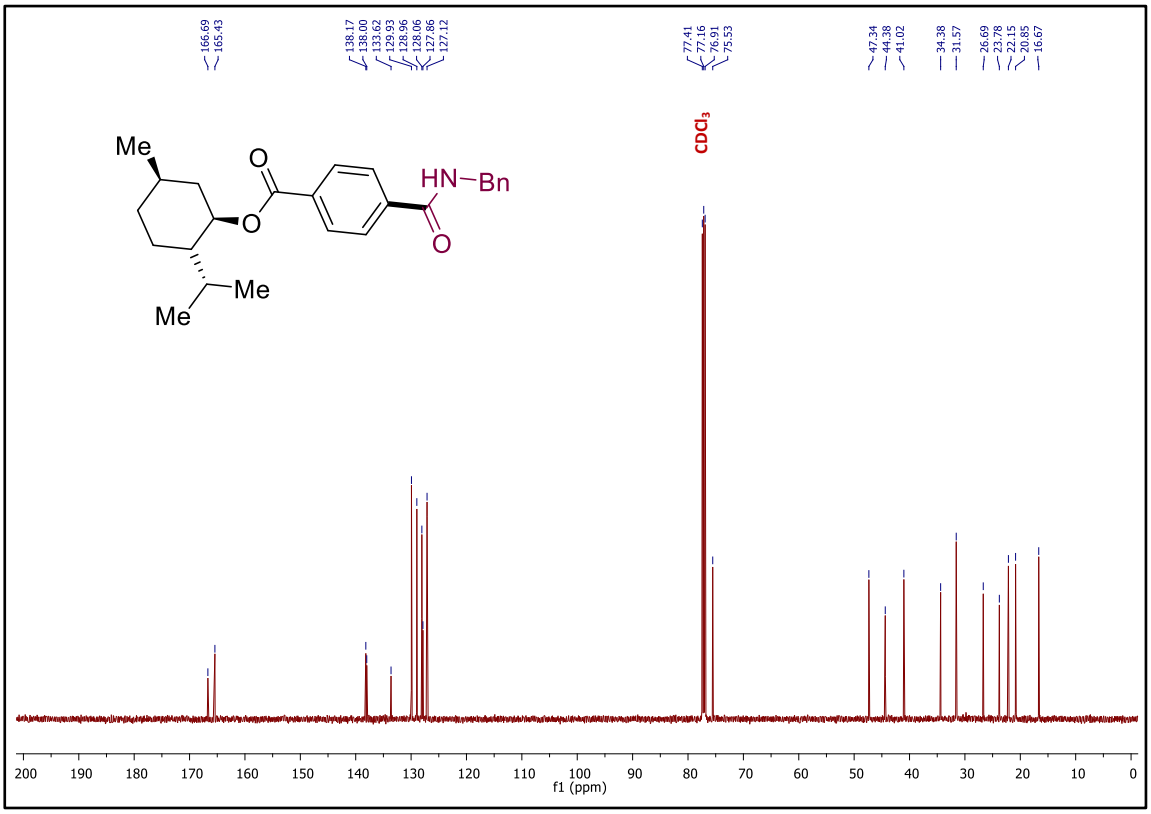


Figure S52. ^{1}H NMR (500 MHz, top) and ^{13}C $\{^{1}H\}$ NMR (125 MHz, bottom) Spectra of **3ac** in $CDCl_3$ at 298K.

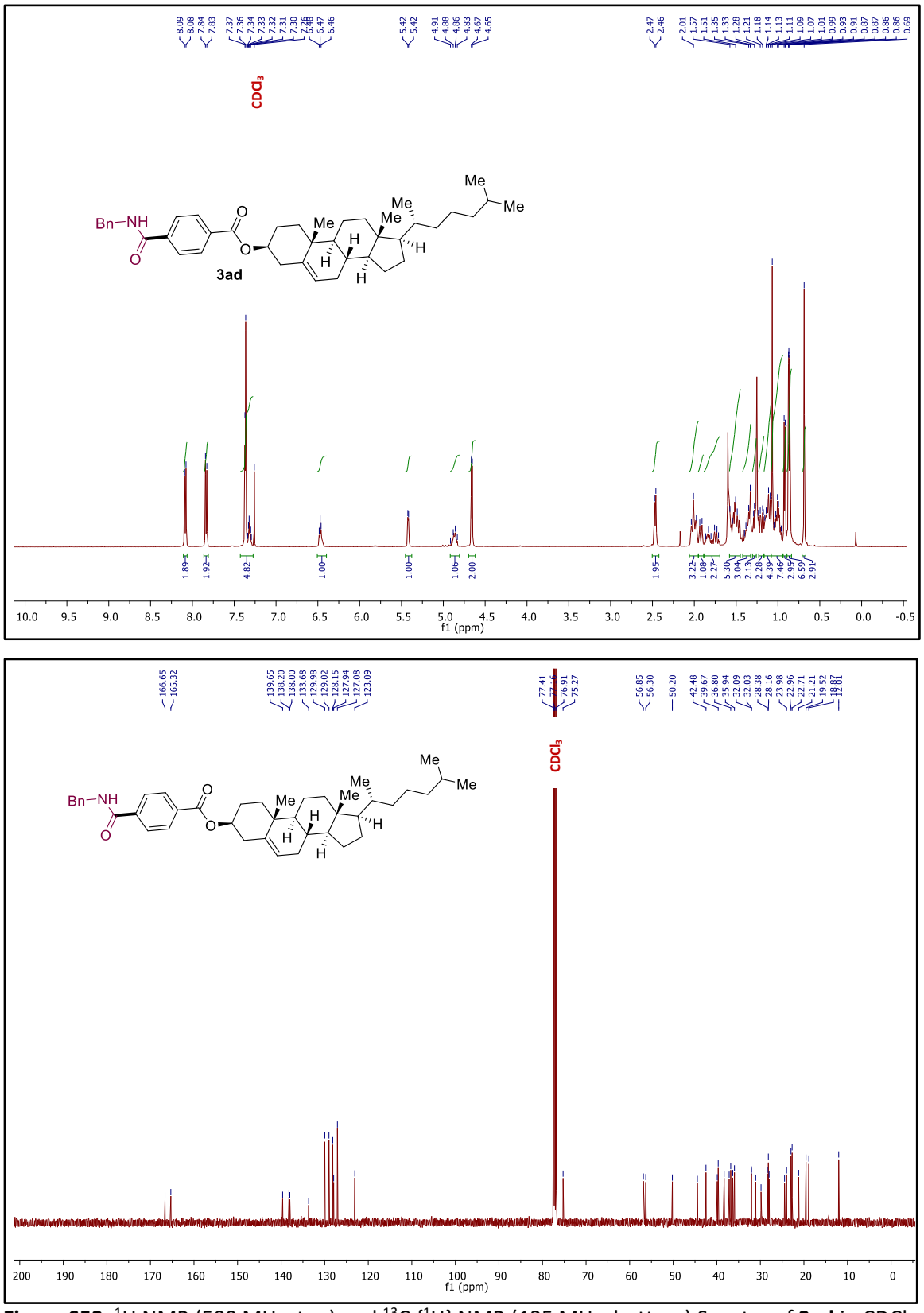
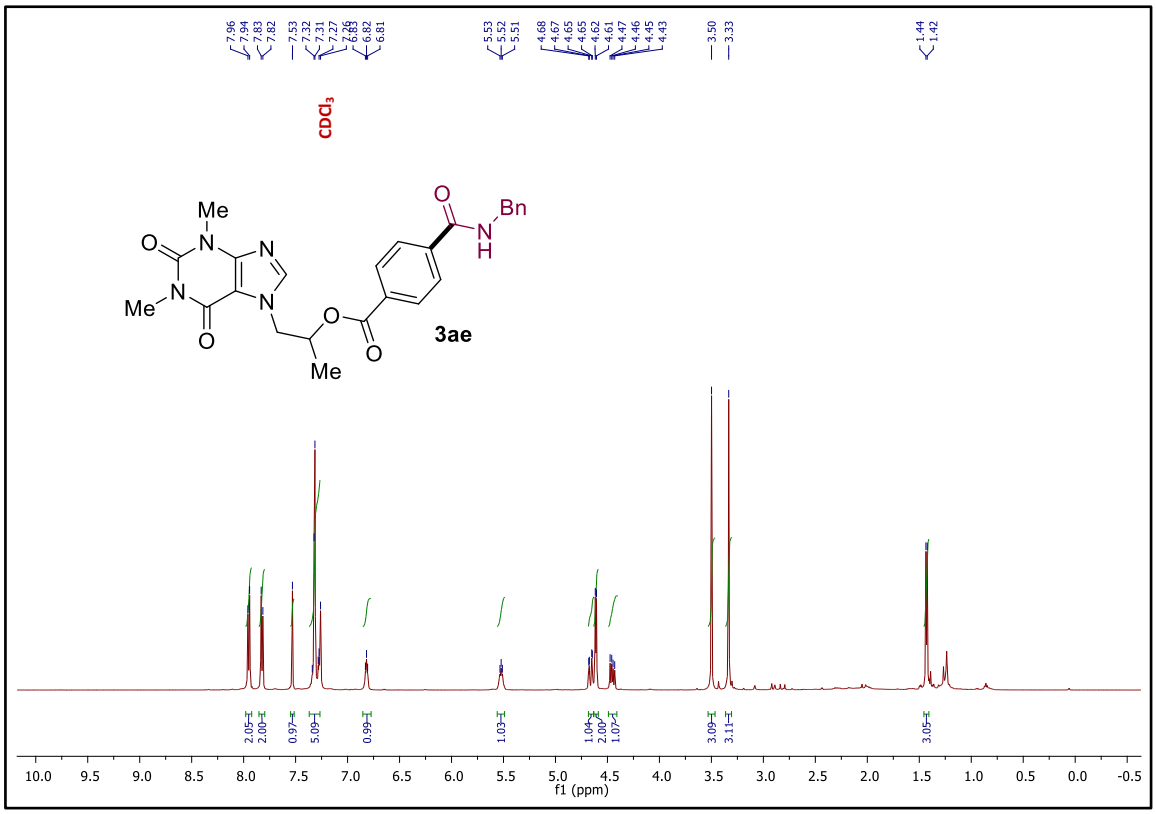


Figure S53. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3ad** in $CDCl_3$ at 298K.



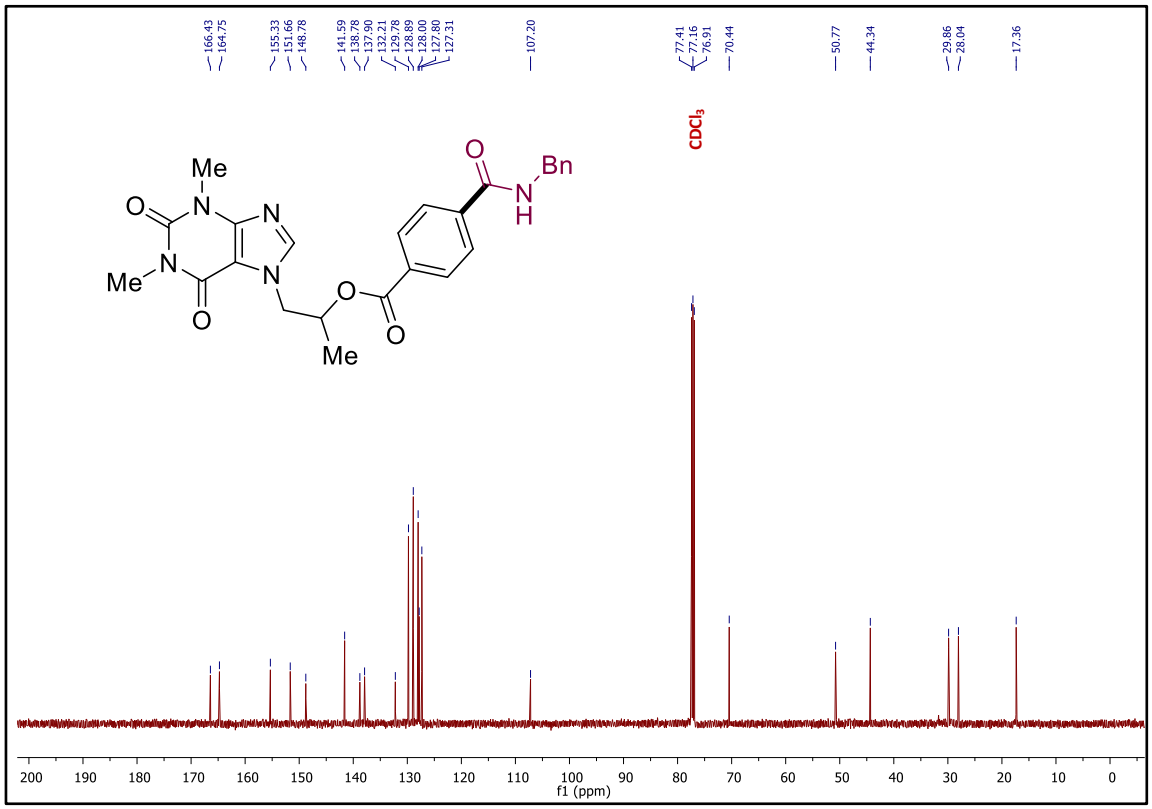


Figure S54. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3ae** in $CDCl_3$ at 298K.

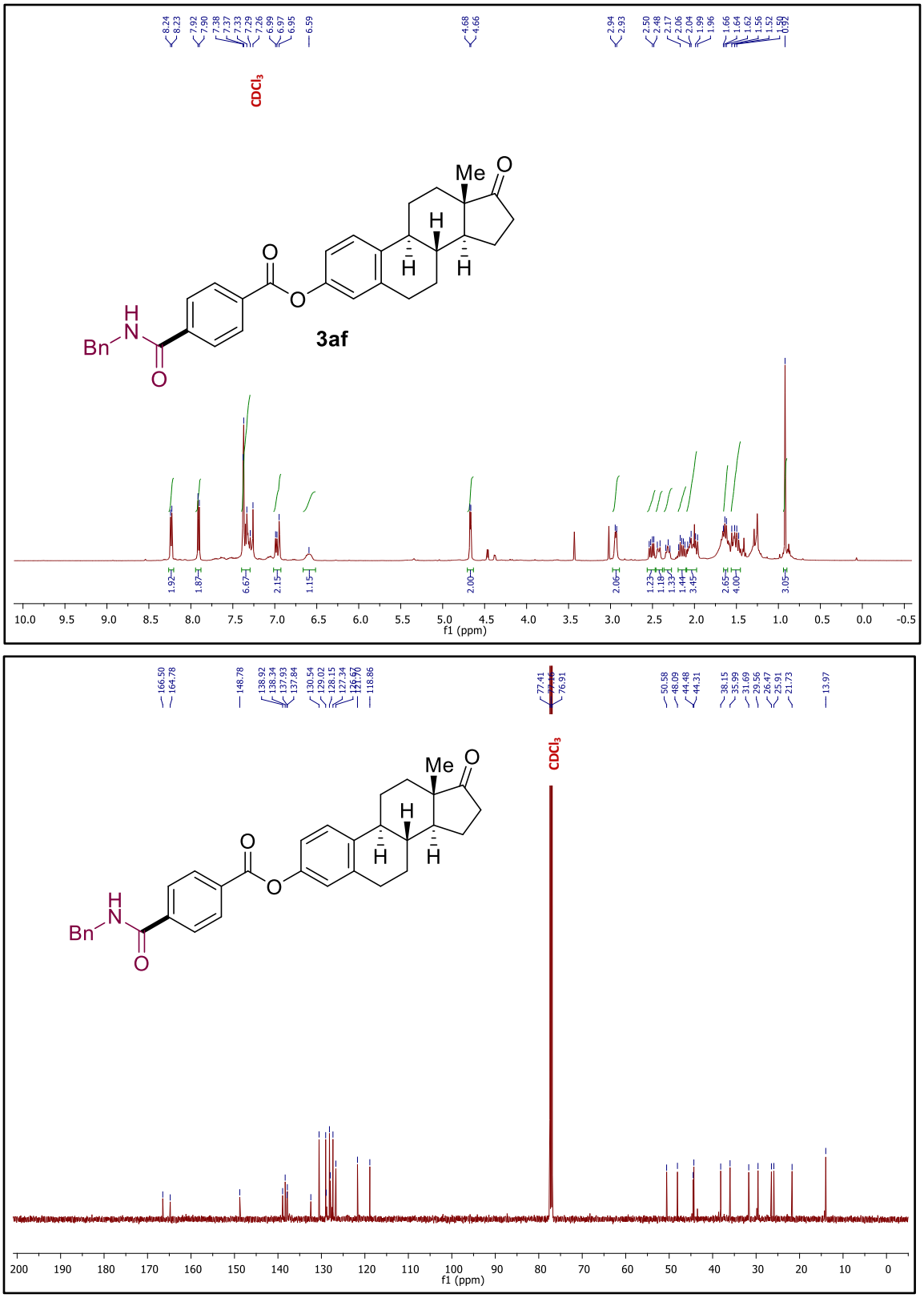


Figure S55. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3af** in $CDCl_3$ at 298K.

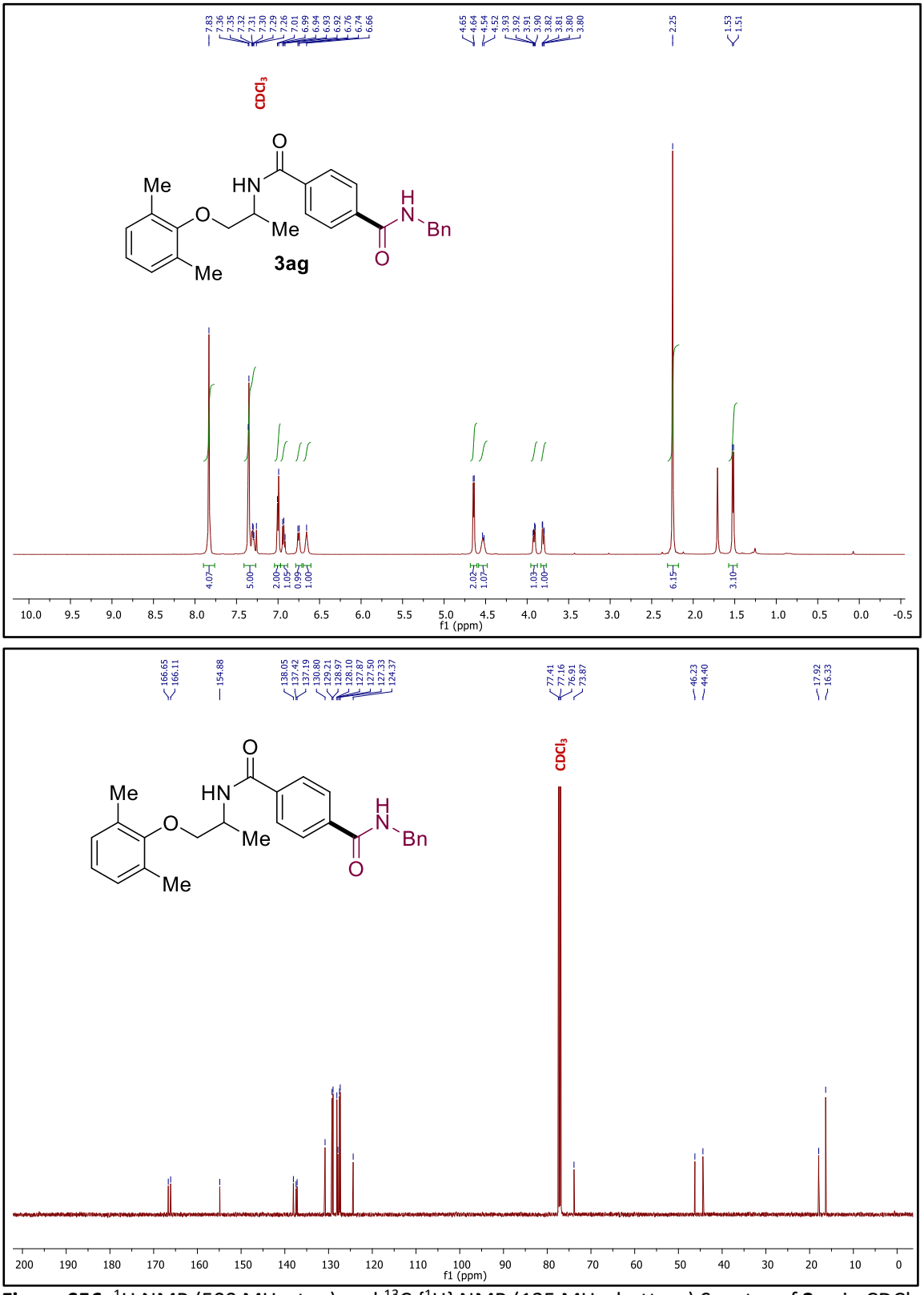


Figure S56. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3ag** in $CDCl_3$ at 298K.

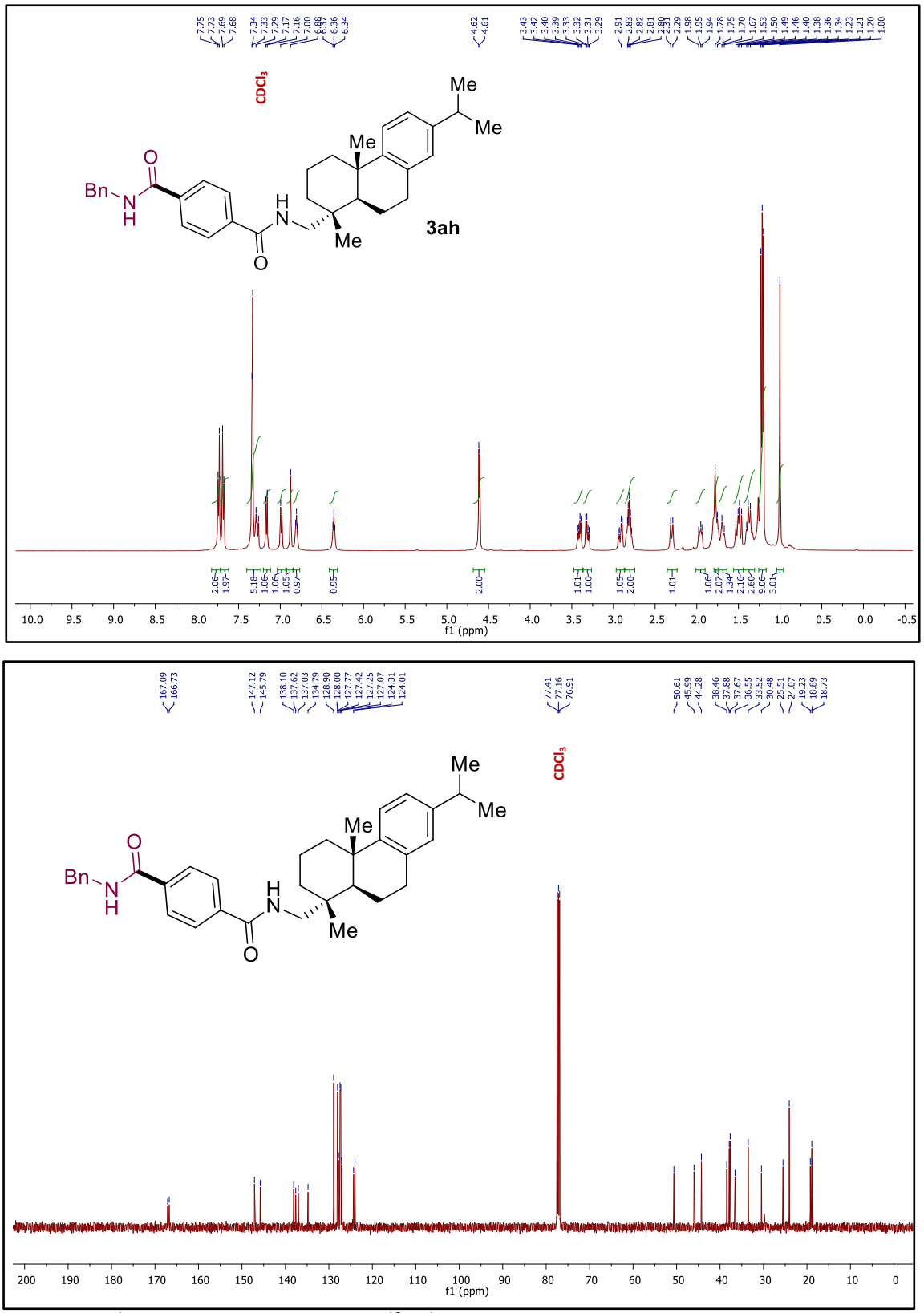


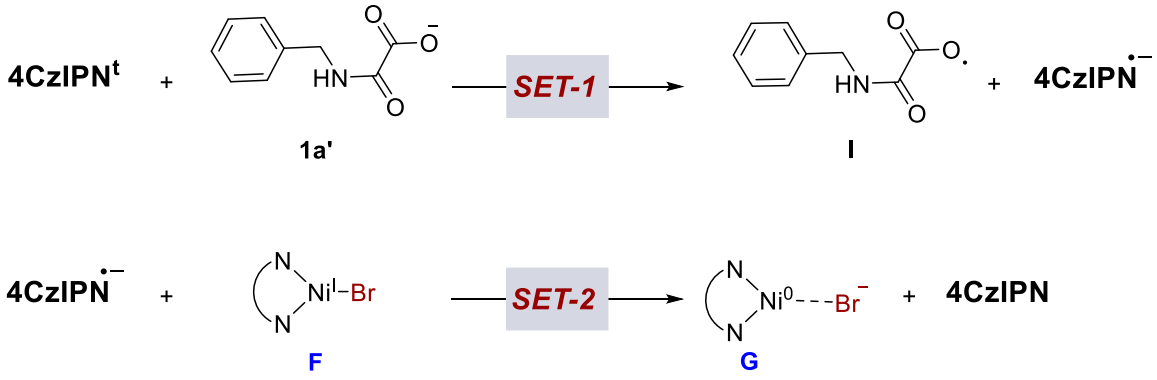
Figure S57. ^{1}H NMR (500 MHz, top) and ^{13}C {^{1}H} NMR (125 MHz, bottom) Spectra of **3ah** in $CDCl_3$ at 298K.

Computational Details

All the DFT computations were carried out using the Gaussian16 program.[17] The geometries of all the stationary points were optimized using the B3LYP-D3[18-20] functional except the open-shell systems for which UB3LYP-D3 functional was used along with the Becke and Johnson damping scheme[21]. The basis set LANL2DZ[22] was used for Nickel and 6-31G*[23] for all other atoms. All the transition states are identified as having a single imaginary frequency and all the intermediates by the absence of imaginary frequencies. The single-point energies were calculated by incorporating the solvent for all the stationary points whose geometries were optimized in gas phase, using the same functional and 6-31G** basis set, for all atoms except Ni. For Ni, LANL2DZ was employed. The SMD implicit solvent model was used for the solvent *N*,*N*-Dimethyl formamide (dielectric constant = 36.7).[24] The geometries of transition states are graphically represented using CYLView software.[25]

Calculation of energy barrier for single electron transfer (SET) process:

We have used the Marcus theory[26-32] to calculate the activation barrier for the following SET steps.



From the Marcus Theory, the activation barrier for the single electron transfer $\Delta G_{ET}^{\ddagger}$ can be calculated from reaction energy ΔG_r and intrinsic barrier $\Delta G_0^{\ddagger}$ using the equation **1** given below:

$$\Delta G_{ET}^{\ddagger} = \Delta G_0^{\ddagger} \left(1 + \frac{\Delta G_r}{4\Delta G_0^{\ddagger}}\right)^2 \qquad \text{(Equation 1)}$$

The intrinsic barrier $\Delta G_0^{\ddagger}$ can be calculated from reorganisation energy λ using the equation 2 shown below:

$$\Delta G_0^{\ddagger} = \frac{\lambda}{4} \qquad \text{(Equation 2)}$$

The reorganisation energy λ can be written as the sum of solvent reorganisation energy λ_0 and internal reorganisation energy λ_i.

$$\lambda = \lambda_0 + \lambda_i$$

Internal reorganisation energy λ_i was calculated using Nelsen's four-point method.[33]

$$\lambda_i = \frac{\lambda_1 + \lambda_2}{2}$$

where $\lambda_1 = G_\alpha(\chi_\beta) - G_\alpha(\chi_\alpha)$,

$\lambda_2 = G_\beta(\chi_\alpha) - G_\beta(\chi_\beta)$,

$G_\alpha(\chi_\beta)$ = sum of gibbs free energies of reactants in product's geoemtries,

$G_\beta(\chi_\alpha)$ = sum of gibbs free energies of products in reactant's geometries,

$G_\alpha(\chi_\alpha)$ = sum of gibbs free energies of reactants in equilibrium geometries,

$G_\beta(\chi_\beta)$ = sum of gibbs free energies of products in equilibrium geometries, as shown in Figure 58.

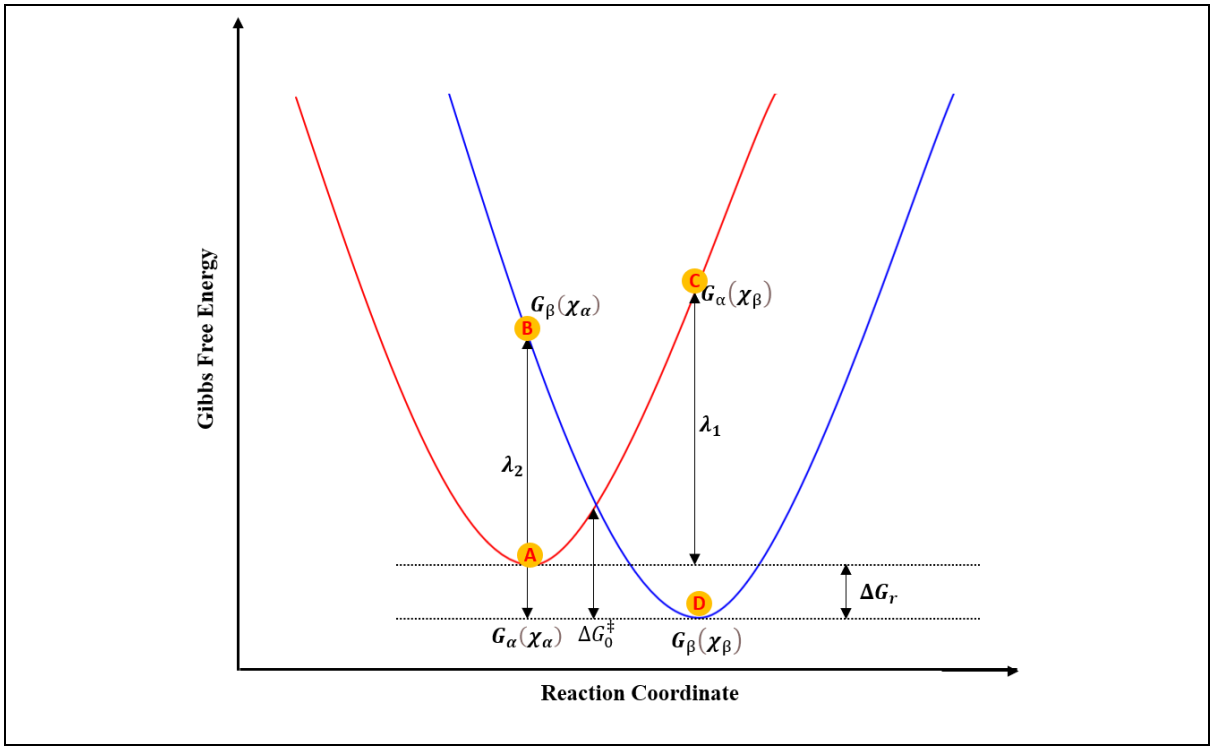


Figure S58. Nelsen's four-point method for calculation of intrinsic reorganization energy.

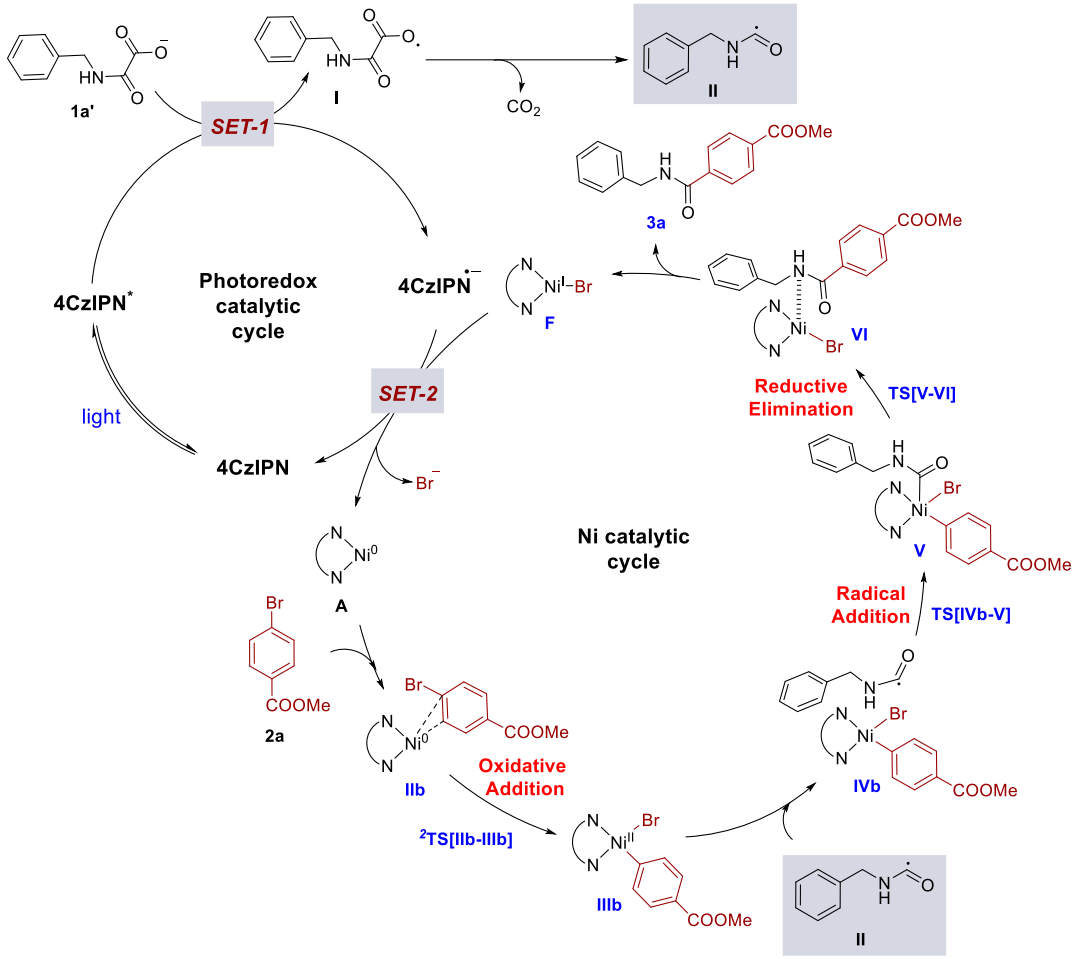
The solvent reorganization energy λ_0 is calculated by using the equation **3**.

$$\lambda_0 = (332 \text{ kcal/mol}) \left\{\frac{1}{2r_d} + \frac{1}{2r_a} - \frac{1}{r_{ad}}\right\}\left\{\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right\} \qquad \text{(Equation 3)}$$

where ε_{op} = 2.05 and ε_s = 37.22 are optical and static dielectric constants of solvent DMF, r_d and r_a are radii of electron donor and acceptor respectively. The distance between the donor and acceptor is $r_{ad} = (r_a + r_d)$.

Table 4. The values for reorganisation energies (λ_i and λ_s), free energies of reaction (ΔG_r), radius of electron acceptor (r_a) and donor (r_d) and activation barrier for SET-1 and SET-2.

SET	λ_i	λ_s	ΔG_r	r_a	r_d	$\Delta G_{ET}^{\ddagger}$
SET-1	10.7	12.5	3.3	8.67	5.21	8.0
SET-2	14.0	10.1	-38.4	7.0	9.0	2.1



Scheme S1. Pathway B considered for the reaction of mechanism of dual nickel-photo catalyzed redox-neutral decarboxylative cross-coupling reaction of oxamate anion **1a'** with aryl bromide **2a** to form amide **3a.**

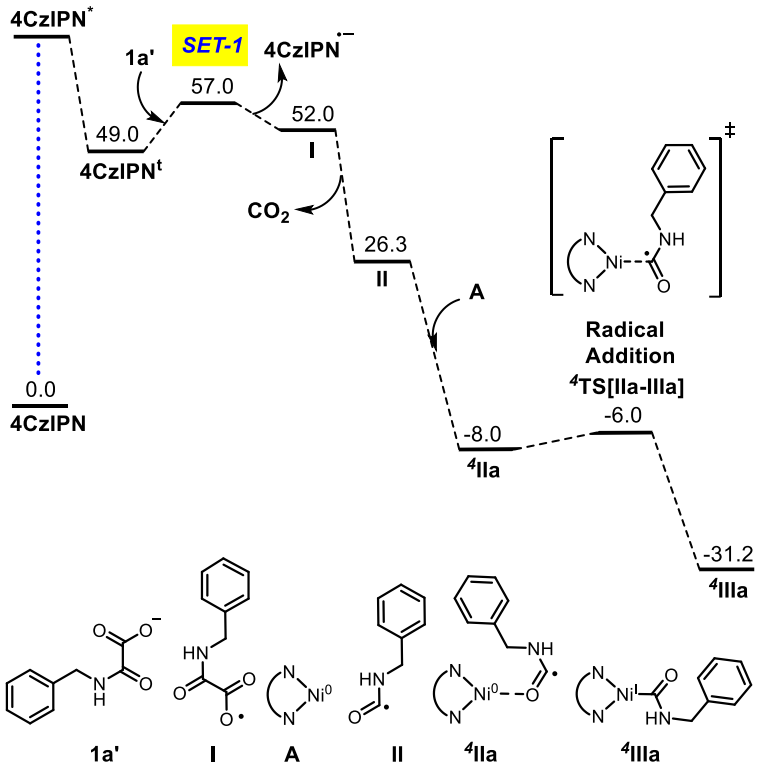


Figure S59. Computed Gibbs free energy profile diagram for the pathway with an alternative radical addition transition state in quartet spin state **^{4}TS[IIa-IIIa]** obtained at the UB3LYP-D3(BJ)/6-31G**,LANL2DZ(Ni)+SMD(DMF)//UB3LYP-D3(BJ)/6-31G*,LANL2DZ(Ni) level of theory. The relative Gibbs free energies (in kcal/mol) of all intermediates and transition states are with respect to the oxamate anion **1a'**, **4CzIPN** in singlet state, Ni(0) species **A**, and the aryl bromide **2a**. The calculations suggest this pathway is of higher energy compared to the pathway A.

Optimized Cartesian Coordinates of Various Stationary Points

Coordinates of geometries of all stationary points obtained at the UB3LYP-D3(BJ)/6-31G**, LANL2DZ(Ni)+SMD(DMF)//UB3LYP-D3(BJ)/6-31G*,LANL2DZ(Ni) level of theory.

2a

Charge = 0, Multiplicity = 1
Number of imaginary frequencies = 0
SCF Energy = -3030.97999
Thermal correction to Gibbs Free Energy = 0.096657

.....

Cartesian Coordinates

.....

6	0.652456	-1.158822	0.000134
6	-0.575536	1.354165	0.000317
1	1.141847	-2.125894	0.000060
1	-1.074213	2.317256	0.000400

35	3.315680	-0.115961	-0.000478
6	0.812928	1.270159	0.000021
1	1.424669	2.164848	-0.000138
6	1.413207	0.010441	-0.000068
6	-0.736663	-1.063066	0.000429
1	-1.342650	-1.961390	0.000593
6	-1.357584	0.192455	0.000537
6	-2.836689	0.350722	0.000889
8	-3.413360	1.420817	0.000320
8	-3.480963	-0.837434	0.000293
6	-4.913259	-0.751969	-0.000251
1	-5.264542	-0.221973	-0.889447
1	-5.267227	-1.782966	-0.000876
1	-5.265249	-0.222817	0.889171

3a

Charge = 0, Multiplicity = 1
Number of imaginary frequencies = 0
SCF Energy = -899.287004
Thermal correction to Gibbs Free Energy = 0.232615

.....

Cartesian Coordinates

.....

6	0.905414	0.530208	1.386410
6	2.117521	0.957361	-1.091771
6	2.142720	-0.044639	1.116071
1	0.430551	0.402012	2.353388
1	2.617611	1.123618	-2.039602
1	2.644338	-0.648265	1.863161
6	0.871494	1.514928	-0.825525
1	0.385811	2.141911	-1.566713
6	0.251430	1.294532	0.412062
1	-2.892725	2.370759	0.196273
6	-1.064118	1.918528	0.778823
7	-2.045012	1.965329	-0.190371
6	2.753643	0.165711	-0.127722
6	4.078965	-0.417963	-0.474361
8	4.643314	-0.257517	-1.538988
8	4.595177	-1.156368	0.532669
6	5.875313	-1.744390	0.261144
1	6.615693	-0.968331	0.050166
1	6.140925	-2.295349	1.163485
1	5.812987	-2.417017	-0.598345
8	-1.235314	2.410990	1.887819
6	-2.289480	0.924927	-1.199731
1	-1.324165	0.561133	-1.553015

1	-2.791618	1.394492	-2.052057
6	-3.122319	-0.223828	-0.668853
6	-4.472641	-0.345319	-1.008219
6	-2.553317	-1.162404	0.202471
6	-5.246792	-1.384685	-0.487808
1	-4.921002	0.376913	-1.686961
6	-3.322902	-2.200207	0.723541
1	-1.503391	-1.077546	0.471192
6	-4.672925	-2.313404	0.379911
1	-6.294919	-1.467929	-0.761095
1	-2.870183	-2.923605	1.395804
1	-5.272276	-3.123081	0.786250

4CzIPN

Charge = 0, Multiplicity = 1
Number of imaginary frequencies = 0
SCF Energy = -2482.13381723
Thermal correction to Gibbs Free Energy = 0.645986

.....

Cartesian Coordinates

.....

6	0.498851	0.000030	0.000005
6	-0.214911	1.151425	0.409176
6	-1.627085	1.132546	0.435568
6	-2.337187	-0.000023	0.000006
6	-1.627042	-1.132564	-0.435564
6	-0.214867	-1.151392	-0.409171
6	-2.339373	2.227451	1.014495
6	-2.339288	-2.227486	-1.014513
7	-2.921697	3.109591	1.497265
7	-2.921575	-3.109636	-1.497308
6	-5.908098	0.543328	-0.480922
6	-4.556122	0.857914	-0.755414
6	-4.193974	1.840561	-1.672484
6	-5.220797	2.537462	-2.306530
6	-6.569066	2.252583	-2.037961
6	-6.919618	1.255194	-1.131694
6	-5.908068	-0.543646	0.480844
6	-4.556074	-0.858099	0.755400
6	-4.193873	-1.840708	1.672490
6	-5.220657	-2.537710	2.306487
6	-6.568941	-2.252963	2.037854
6	-6.919548	-1.255610	1.131570
1	-3.153368	2.052899	-1.893939
1	-4.969456	3.314656	-3.021941
1	-7.345785	2.814448	-2.547467

1	-7.963461	1.028235	-0.935363
1	-3.153256	-2.052939	1.893998
1	-4.969274	-3.314878	3.021912
1	-7.345629	-2.814904	2.547323
1	-7.963405	-1.028752	0.935191
7	-3.737163	-0.000051	0.000015
6	4.074643	-0.559158	0.461625
6	2.722556	-0.877702	0.730590
6	2.366360	-1.873283	1.635346
6	3.393882	-2.594731	2.240573
6	4.741066	-2.312856	1.966409
6	5.087897	-1.290211	1.086414
6	4.074640	0.559139	-0.461757
6	2.722552	0.877759	-0.730627
6	2.366351	1.873353	-1.635366
6	3.393872	2.594727	-2.240683
6	4.741060	2.312772	-1.966619
6	5.087893	1.290120	-1.086632
1	1.331051	-2.094558	1.862163
1	3.138952	-3.391415	2.932685
1	5.519631	-2.893461	2.451828
1	6.130919	-1.059621	0.889484
1	1.331040	2.094688	-1.862115
1	3.138939	3.391414	-2.932790
1	5.519623	2.893319	-2.452107
1	6.130915	1.059465	-0.889780
7	1.901694	0.000054	0.000016
6	2.131225	3.633804	1.658410
6	1.508354	2.368732	1.754530
6	1.908523	1.416743	2.686225
6	3.000655	1.725271	3.494220
6	3.652889	2.964212	3.394133
6	3.215632	3.928071	2.488892
6	1.424629	4.382309	0.635856
6	0.390054	3.551083	0.146231
6	-0.450913	3.953974	-0.887584
6	-0.250521	5.225072	-1.425526
6	0.763835	6.067769	-0.947012
6	1.604854	5.651893	0.082414
1	1.402756	0.463574	2.777791
1	3.349206	0.988582	4.211332
1	4.500983	3.175879	4.038125
1	3.708303	4.894012	2.427070
1	-1.239913	3.313494	-1.264366
1	-0.899173	5.566474	-2.226550
1	0.892621	7.053052	-1.384359
1	2.397954	6.299307	0.445030

7	0.451179	2.312492	0.824593
6	1.424895	-4.382161	-0.635753
6	0.390233	-3.551011	-0.146183
6	-0.450725	-3.953944	0.887623
6	-0.250232	-5.225005	1.425614
6	0.764214	-6.067626	0.947158
6	1.605222	-5.651710	-0.082262
6	2.131456	-3.633627	-1.658310
6	1.508476	-2.368614	-1.754489
6	1.908587	-1.416619	-2.686200
6	3.000777	-1.725070	-3.494147
6	3.653121	-2.963948	-3.393997
6	3.215920	-3.927821	-2.488744
1	-1.239798	-3.313527	1.264359
1	-0.898874	-5.566438	2.226633
1	0.893078	-7.052882	1.384542
1	2.398390	-6.299064	-0.444834
1	1.402735	-0.463499	-2.777811
1	3.349288	-0.988369	-4.211265
1	4.501259	-3.175555	-4.037950
1	3.708677	-4.893714	-2.426875
7	0.451265	-2.312435	-0.824587

4CzIPN^{t}

Charge = 0, Multiplicity = 3
Number of imaginary frequencies = 0
SCF Energy = -2482.04953891
Thermal correction to Gibbs Free Energy = 0.639433

.....

Cartesian Coordinates

.....

6	-0.454939	0.019071	-0.065310
6	0.158953	-1.192949	0.290920
6	1.608196	-1.271344	0.330953
6	2.357707	-0.142245	-0.029353
6	1.734191	1.064837	-0.414712
6	0.283061	1.151844	-0.401831
6	2.235845	-2.430181	0.831025
6	2.493797	2.136738	-0.918144
7	2.728969	-3.408777	1.239967
7	3.105748	3.046845	-1.328328
6	5.921248	-0.825845	-0.469525
6	4.558799	-1.076613	-0.771785
6	4.174157	-2.024550	-1.720658
6	5.185951	-2.741659	-2.358860
6	6.542296	-2.516528	-2.064026

6	6.917646	-1.557980	-1.123983
6	5.948952	0.233540	0.522385
6	4.602723	0.593614	0.782685
6	4.265704	1.571851	1.719113
6	5.311687	2.208953	2.386190
6	6.654101	1.875010	2.133127
6	6.980396	0.886146	1.206226
1	3.129822	-2.197283	-1.956434
1	4.916048	-3.488876	-3.099474
1	7.304782	-3.093771	-2.578642
1	7.965831	-1.376266	-0.904218
1	3.231612	1.827635	1.922780
1	5.080228	2.978375	3.117017
1	7.444227	2.391575	2.670039
1	8.017009	0.621070	1.018745
7	3.763822	-0.208207	-0.007159
6	-4.034182	0.536899	0.497484
6	-2.670522	0.846522	0.753181
6	-2.284559	1.738548	1.758038
6	-3.298502	2.368951	2.478982
6	-4.649704	2.094260	2.220968
6	-5.027296	1.167980	1.237872
6	-4.046687	-0.478732	-0.546770
6	-2.693623	-0.737430	-0.881009
6	-2.332101	-1.613013	-1.905554
6	-3.362719	-2.292337	-2.561751
6	-4.703414	-2.075400	-2.220706
6	-5.057375	-1.156126	-1.220966
1	-1.242251	1.924617	1.978594
1	-3.031369	3.076693	3.257121
1	-5.417176	2.595932	2.802148
1	-6.074916	0.942097	1.065073
1	-1.297646	-1.745853	-2.194321
1	-3.112648	-2.994039	-3.350885
1	-5.483995	-2.614232	-2.748658
1	-6.100680	-0.974580	-0.982105
7	-1.872517	0.064138	-0.078989
6	-2.343286	-3.339385	1.859927
6	-1.502209	-2.199727	1.869048
6	-1.574303	-1.229560	2.865402
6	-2.554789	-1.391174	3.849349
6	-3.415411	-2.498224	3.842828
6	-3.309490	-3.485537	2.856526
6	-1.943608	-4.144938	0.717416
6	-0.878246	-3.449303	0.078286
6	-0.257737	-3.934908	-1.078998
6	-0.723057	-5.140632	-1.595408

6	-1.779306	-5.838081	-0.979612
6	-2.395123	-5.347354	0.175823
1	-0.890872	-0.388823	2.880753
1	-2.646161	-0.642734	4.630552
1	-4.167841	-2.596081	4.619442
1	-3.967099	-4.349751	2.865386
1	0.549894	-3.388353	-1.553489
1	-0.264429	-5.547475	-2.491293
1	-2.122097	-6.773424	-1.411397
1	-3.214301	-5.889033	0.638890
7	-0.637350	-2.262215	0.761336
6	-1.258729	4.451350	-0.641381
6	-0.341704	3.538348	-0.056644
6	0.389662	3.854419	1.091335
6	0.191155	5.114973	1.651541
6	-0.710918	6.034743	1.084688
6	-1.438675	5.710590	-0.059786
6	-1.843104	3.782748	-1.789483
6	-1.252416	2.495235	-1.859745
6	-1.560566	1.596085	-2.879528
6	-2.510378	1.990652	-3.821866
6	-3.123602	3.254434	-3.757208
6	-2.788977	4.158930	-2.749613
1	1.081435	3.144841	1.532883
1	0.745603	5.390546	2.543914
1	-0.841209	7.008744	1.547024
1	-2.138916	6.420325	-0.491039
1	-1.076055	0.628811	-2.939946
1	-2.776350	1.305421	-4.621583
1	-3.860288	3.530745	-4.505793
1	-3.252221	5.140730	-2.709207
7	-0.354068	2.348121	-0.791754

4CzIPN$^{\bullet -}$

Charge = -1, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -2482.23259461
Thermal correction to Gibbs Free Energy = 0.639564

.....

Cartesian Coordinates

.....

6	0.515210	0.000149	-0.000035
6	-0.172348	1.158140	0.392886
6	-1.629070	1.141363	0.446811
6	-2.310269	-0.000342	-0.000082
6	-1.628657	-1.141826	-0.446913

6	-0.171935	-1.158076	-0.392891
6	-2.335641	2.220162	1.024425
6	-2.334817	-2.220886	-1.024540
7	-2.909294	3.126081	1.491160
7	-2.908137	-3.127002	-1.491302
6	-5.899542	0.525171	-0.498061
6	-4.541525	0.826787	-0.776249
6	-4.178681	1.793663	-1.712796
6	-5.201918	2.471351	-2.369617
6	-6.553977	2.192152	-2.104396
6	-6.907957	1.220893	-1.172064
6	-5.899389	-0.527160	0.497613
6	-4.541285	-0.828262	0.775928
6	-4.178163	-1.794997	1.712513
6	-5.201204	-2.473071	2.369239
6	-6.553345	-2.194384	2.103889
6	-6.907605	-1.223261	1.171524
1	-3.135410	2.008998	-1.913564
1	-4.946538	3.234890	-3.099328
1	-7.328356	2.741687	-2.632552
1	-7.953425	1.001531	-0.970759
1	-3.134829	-2.009931	1.913383
1	-4.945604	-3.236511	3.098976
1	-7.327565	-2.744211	2.631974
1	-7.953136	-1.004295	0.970120
7	-3.728069	-0.000582	-0.000120
6	4.109821	-0.522706	0.500526
6	2.751911	-0.817456	0.785592
6	2.393228	-1.760231	1.747299
6	3.416576	-2.438584	2.403748
6	4.767602	-2.173033	2.123169
6	5.119081	-1.212328	1.178391
6	4.109757	0.523300	-0.500915
6	2.751808	0.817876	-0.785996
6	2.393025	1.760418	-1.747892
6	3.416295	2.438805	-2.404426
6	4.767351	2.173497	-2.123765
6	5.118939	1.212961	-1.178856
1	1.354230	-1.968626	1.967557
1	3.157403	-3.192757	3.141403
1	5.543381	-2.721476	2.650475
1	6.163928	-0.997521	0.969263
1	1.354012	1.968635	-1.968219
1	3.157033	3.192827	-3.142206
1	5.543067	2.721957	-2.651145
1	6.163810	0.998278	-0.969722
7	1.936609	0.000267	-0.000085

6	2.059211	3.767371	1.669235
6	1.468521	2.479782	1.757555
6	1.847119	1.565684	2.739241
6	2.856785	1.941599	3.620098
6	3.466518	3.205968	3.538136
6	3.066739	4.124145	2.570758
6	1.411155	4.448251	0.567191
6	0.461007	3.541772	0.030413
6	-0.329476	3.871753	-1.070672
6	-0.157112	5.132702	-1.636105
6	0.779412	6.044678	-1.119018
6	1.563888	5.708154	-0.018441
1	1.377742	0.592117	2.804673
1	3.180464	1.237061	4.381155
1	4.255577	3.467462	4.237991
1	3.531327	5.105344	2.513105
1	-1.055497	3.169081	-1.463773
1	-0.764967	5.416457	-2.491051
1	0.888300	7.021834	-1.581674
1	2.292007	6.411743	0.377374
7	0.511409	2.344162	0.748997
6	1.413146	-4.447444	-0.566747
6	0.462503	-3.541383	-0.030136
6	-0.327939	-3.871665	1.070888
6	-0.155052	-5.132503	1.636409
6	0.781948	-6.044075	1.119472
6	1.566397	-5.707245	0.018971
6	2.061069	-3.766293	-1.668704
6	1.469815	-2.478973	-1.757139
6	1.848263	-1.564652	-2.738676
6	2.858288	-1.940100	-3.619323
6	3.468531	-3.204218	-3.537288
6	3.068945	-4.122600	-2.570023
1	-1.054345	-3.169318	1.463857
1	-0.762876	-5.416497	2.491298
1	0.891239	-7.021154	1.582195
1	2.294903	-6.410509	-0.376710
1	1.378495	-0.591273	-2.804154
1	3.181841	-1.235390	-4.380275
1	4.257860	-3.465343	-4.236974
1	3.533969	-5.103588	-2.512282
7	0.512369	-2.343822	-0.748840

1a'

Charge = -1, Multiplicity = 1
Number of imaginary frequencies = 0

SCF Energy = -628.394330659
Thermal correction to Gibbs Free Energy = 0.119685
.....
Cartesian Coordinates
.....

1	0.840433	-1.797187	1.313625
6	2.123647	-0.369683	0.682209
7	1.103898	-1.289623	0.475736
8	2.757365	-0.400240	1.735831
6	0.161026	-1.254214	-0.626863
1	-0.071806	-2.283074	-0.936964
1	0.687371	-0.780553	-1.461041
6	-1.133551	-0.524352	-0.309740
6	-1.105663	0.830979	0.058819
6	-2.362918	-1.187785	-0.364999
6	-2.295050	1.492195	0.360999
1	-0.146577	1.351092	0.100011
6	-3.554707	-0.522272	-0.063456
1	-2.386999	-2.239371	-0.647429
6	-3.522434	0.823014	0.301767
1	-2.264368	2.542494	0.642067
1	-4.502227	-1.055295	-0.110551
1	-4.445524	1.347866	0.538859
8	1.937008	1.795800	-0.237914
6	2.353671	0.636065	-0.481693
8	2.877913	0.154153	-1.511790

II

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -439.645145749
Thermal correction to Gibbs Free Energy = 0.107695
.....
Cartesian Coordinates
.....

1	-1.871406	-0.448424	-1.357778
6	-2.994031	0.163793	0.229684
7	-1.968947	-0.487805	-0.343570
8	-3.902967	0.766326	-0.281068
6	-0.898498	-1.116850	0.419927
1	-0.841391	-2.182974	0.168933
1	-1.200076	-1.047196	1.470761
6	0.451885	-0.464875	0.201049
6	0.590956	0.926259	0.282652
6	1.579586	-1.245619	-0.067120
6	1.837705	1.522578	0.104252

1	-0.283363	1.539921	0.481471
6	2.830594	-0.651008	-0.243273
1	1.478378	-2.326138	-0.139063
6	2.961708	0.734925	-0.158584
1	1.933524	2.602685	0.170124
1	3.698456	-1.269844	-0.452949
1	3.932797	1.200780	-0.299494

CO_2

Charge = 0, Multiplicity = 1
Number of imaginary frequencies = 0
SCF Energy = -188.580984712
Thermal correction to Gibbs Free Energy = -0.009095
.....
Cartesian Coordinates
.....

6	0.000000	0.000000	0.000000
8	0.000000	0.000000	1.169393
8	0.000000	0.000000	-1.169393

A

Charge = 0, Multiplicity = 1
Number of imaginary frequencies = 0
SCF Energy = -979.304952552
Thermal correction to Gibbs Free Energy = 0.334458
.....
Cartesian Coordinates
.....

6	0.723328	0.554541	0.124641
6	2.599964	1.833794	0.627397
6	3.444231	0.753783	0.416011
6	2.917919	-0.503450	0.074504
6	1.527115	-0.564124	-0.075681
6	-0.723319	0.554530	-0.124731
6	-2.599973	1.833731	-0.627551
6	-3.444224	0.753718	-0.416111
6	-2.917896	-0.503490	-0.074543
6	-1.527088	-0.564137	0.075641
1	2.996364	2.791998	0.946664
1	4.509125	0.898023	0.553074
1	1.054060	-1.485552	-0.398134
1	-2.996388	2.791910	-0.946877
1	-4.509120	0.897936	-0.553185
1	-1.054021	-1.485543	0.398136
7	1.250934	1.767061	0.516658

7	-1.250940	1.767032	-0.516796
28	-0.000067	3.112562	0.000077
6	-3.777211	-1.747706	0.160841
6	-3.322354	-2.871213	-0.796530
6	-3.603223	-2.218010	1.622094
6	-5.269496	-1.473582	-0.087081
1	-3.438528	-2.563414	-1.841484
1	-2.271489	-3.135427	-0.639567
1	-3.922311	-3.774836	-0.635902
1	-3.919744	-1.437286	2.322290
1	-4.208576	-3.113161	1.808753
1	-2.560368	-2.465418	1.845357
1	-5.845910	-2.389780	0.080641
1	-5.659050	-0.707647	0.592535
1	-5.455075	-1.146884	-1.116353
6	3.777253	-1.747667	-0.160812
6	3.322390	-2.871136	0.796600
6	3.603297	-2.218035	-1.622047
6	5.269531	-1.473515	0.087126
1	3.438546	-2.563293	1.841543
1	2.271529	-3.135364	0.639632
1	3.922357	-3.774761	0.636018
1	3.919815	-1.437335	-2.322271
1	4.208670	-3.113183	-1.808659
1	2.560450	-2.465473	-1.845316
1	5.845959	-2.389711	-0.080558
1	5.659086	-0.707596	-0.592507
1	5.455089	-1.146783	1.116391

I

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -628.2039833
Thermal correction to Gibbs Free Energy = 0.117487

.....

Cartesian Coordinates

.....

1	-0.689631	-2.157669	-0.526233
6	-2.031795	-0.699522	-0.424851
7	-0.946965	-1.350445	0.032110
8	-2.739019	-1.073709	-1.359438
6	-0.000668	-0.930006	1.077472
1	0.232171	-1.817021	1.675064
1	-0.511924	-0.217700	1.725272
6	1.263006	-0.330819	0.499769
6	1.275216	0.998278	0.058271

6	2.418868	-1.106018	0.367584
6	2.427077	1.539223	-0.509734
1	0.382678	1.607261	0.171014
6	3.573458	-0.565481	-0.201311
1	2.418250	-2.136486	0.716422
6	3.577916	0.757871	-0.642416
1	2.428983	2.572435	-0.844730
1	4.466718	-1.176083	-0.296720
1	4.475343	1.181512	-1.083898
8	-3.584591	1.054430	-0.306636
6	-2.509759	0.605258	0.210445
8	-1.993109	1.267298	1.119531

---

^{2}IIa

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -1419.06522882
Thermal correction to Gibbs Free Energy = 0.466288
.....
Cartesian Coordinates
.....

6	1.670997	-0.274823	-0.413513
6	2.801484	-2.279426	-0.125922
6	3.957032	-1.626167	0.265650
6	3.986791	-0.220809	0.328029
6	2.809309	0.438172	-0.023803
6	0.398128	0.363899	-0.798048
6	-1.731256	-0.021860	-1.632122
6	-2.046189	1.326656	-1.555893
6	-1.114812	2.242884	-1.039682
6	0.128238	1.730630	-0.663394
1	2.759326	-3.362878	-0.174486
1	4.830010	-2.216448	0.520878
1	2.766612	1.518496	-0.010833
1	-2.445292	-0.786722	-1.935019
1	-3.031083	1.651415	-1.871852
1	0.881690	2.383011	-0.243598
7	1.667418	-1.634425	-0.463362
7	-0.531818	-0.494668	-1.262758
28	-0.033910	-2.450650	-1.005014
7	-3.033649	-3.222657	0.219061
1	-2.464246	-3.738473	0.899765
6	-2.541570	-3.054407	-1.040821
8	-1.417350	-3.686821	-1.224862
6	-4.072895	-2.356765	0.727484
6	5.259073	0.510147	0.760632

6	5.634794	0.060927	2.190184
6	6.403649	0.148903	-0.211876
6	5.081096	2.037093	0.759796
1	4.836274	0.305005	2.899277
1	5.813906	-1.017556	2.243147
1	6.549549	0.569000	2.515925
1	6.158718	0.455219	-1.234649
1	7.326416	0.658929	0.087167
1	6.604090	-0.927090	-0.221582
1	6.013604	2.514931	1.077335
1	4.837848	2.417284	-0.238632
1	4.293926	2.354633	1.452788
6	-1.479630	3.723415	-0.908736
6	-0.369496	4.537821	-0.224975
6	-1.717282	4.300536	-2.321788
6	-2.769751	3.858814	-0.070738
1	-0.164074	4.169557	0.786583
1	0.564477	4.517309	-0.797926
1	-0.680709	5.584261	-0.140965
1	-2.522546	3.771764	-2.841436
1	-1.995856	5.358629	-2.255486
1	-0.812453	4.221801	-2.934641
1	-3.030560	4.917145	0.045066
1	-3.617785	3.354914	-0.543791
1	-2.639340	3.418318	0.921900
1	-4.727010	-2.912825	1.412859
1	-4.680853	-2.069146	-0.136933
6	-3.567450	-1.095819	1.422607
6	-4.489272	-0.163843	1.918019
6	-2.203154	-0.825031	1.565919
6	-4.060284	1.008324	2.538598
1	-5.554831	-0.358670	1.812349
6	-1.768456	0.348111	2.186133
1	-1.476116	-1.526458	1.172452
6	-2.693736	1.268001	2.678154
1	-4.790777	1.719344	2.915648
1	-0.702943	0.540789	2.278284
1	-2.357497	2.177225	3.169756

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^{2}TS[IIa-IIIa]

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 1
SCF Energy = -1419.06301202
Thermal correction to Gibbs Free Energy = 0.466551
.....
Cartesian Coordinates

.....

6	1.686630	-0.277445	-0.320781
6	2.629428	-2.385623	-0.125917
6	3.867057	-1.853918	0.196878
6	4.040297	-0.459565	0.258728
6	2.912917	0.317346	-0.008680
6	0.452245	0.481605	-0.599423
6	-1.770402	0.289066	-1.238562
6	-1.953701	1.660450	-1.147250
6	-0.893370	2.491617	-0.748084
6	0.326098	1.868869	-0.473205
1	2.477162	-3.458723	-0.185421
1	4.691887	-2.529820	0.393045
1	2.977654	1.396468	0.016211
1	-2.558423	-0.412415	-1.500018
1	-2.931545	2.071480	-1.369626
1	1.176477	2.453708	-0.149855
7	1.549171	-1.627558	-0.387591
7	-0.589354	-0.287377	-0.974217
28	-0.264288	-2.264940	-0.893130
7	-3.387817	-3.347786	-0.068179
1	-3.135053	-4.134069	0.539233
6	-2.504840	-2.957870	-1.033234
8	-1.476685	-3.750262	-1.130123
6	-4.398959	-2.415978	0.391682
6	5.405799	0.137883	0.604238
6	5.831475	-0.358030	2.004023
6	6.439444	-0.327438	-0.445182
6	5.381800	1.674928	0.617664
1	5.110935	-0.042384	2.766426
1	5.906498	-1.449274	2.043026
1	6.811871	0.054987	2.267223
1	6.156969	0.010236	-1.448207
1	7.426800	0.085733	-0.209572
1	6.530035	-1.417901	-0.470294
1	6.377329	2.054737	0.869545
1	5.108725	2.085530	-0.360789
1	4.680631	2.063744	1.364579
6	-1.100469	4.004104	-0.631109
6	0.177885	4.736603	-0.192339
6	-1.533207	4.557205	-2.007010
6	-2.206119	4.286386	0.408994
1	0.519536	4.401229	0.793409
1	0.994481	4.593770	-0.909064
1	-0.019425	5.811632	-0.125449
1	-2.467805	4.103224	-2.350276
1	-1.688366	5.640498	-1.945617

1	-0.766509	4.363002	-2.765038
1	-2.391629	5.364537	0.477398
1	-3.147209	3.794889	0.145796
1	-1.909411	3.924070	1.398345
1	-5.071660	-2.949308	1.075782
1	-5.006277	-2.100151	-0.463804
6	-3.846361	-1.172744	1.081754
6	-4.603496	0.004137	1.114460
6	-2.583289	-1.170074	1.684114
6	-4.115080	1.154874	1.735015
1	-5.582174	0.021690	0.638870
6	-2.089343	-0.021809	2.302979
1	-1.971429	-2.063953	1.634234
6	-2.853290	1.145344	2.332804
1	-4.716426	2.060420	1.746693
1	-1.099734	-0.037767	2.752125
1	-2.469250	2.040110	2.814266

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^{2}IIIa

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -1419.0933388
Thermal correction to Gibbs Free Energy = 0.467096

.....

Cartesian Coordinates

.....

6	1.747272	-0.168823	-0.319905
6	2.732708	-2.258107	-0.151278
6	3.972813	-1.700288	0.118035
6	4.121180	-0.303346	0.172541
6	2.970618	0.453821	-0.054576
6	0.487664	0.560633	-0.570552
6	-1.696589	0.375936	-1.293208
6	-1.927400	1.728336	-1.094131
6	-0.906729	2.545992	-0.583406
6	0.319861	1.928345	-0.330453
1	2.588287	-3.333293	-0.186129
1	4.817922	-2.358891	0.284836
1	3.017573	1.534223	-0.041698
1	-2.478557	-0.277149	-1.658042
1	-2.911578	2.126135	-1.310652
1	1.144369	2.498628	0.075748
7	1.632319	-1.517170	-0.369577
7	-0.522830	-0.212630	-1.027268
28	-0.209233	-2.213999	-0.646076
7	-2.895166	-3.594712	-0.016158

1	-3.252727	-4.403120	0.488153
6	-1.536876	-3.510190	-0.206949
8	-0.809800	-4.450417	0.192214
6	-3.806987	-2.565863	-0.451216
6	5.487578	0.320020	0.466549
6	5.974298	-0.166560	1.849563
6	6.490052	-0.126465	-0.620525
6	5.435576	1.856405	0.480860
1	5.276821	0.136289	2.638117
1	6.070443	-1.256148	1.886061
1	6.956109	0.264666	2.076006
1	6.164109	0.205032	-1.612437
1	7.477618	0.305393	-0.422048
1	6.600022	-1.215024	-0.648860
1	6.432213	2.254826	0.697259
1	5.120360	2.261482	-0.487231
1	4.754172	2.232466	1.252206
6	-1.167149	4.029192	-0.312141
6	0.081817	4.753783	0.215063
6	-1.612992	4.713300	-1.622971
6	-2.288987	4.152068	0.742339
1	0.423829	4.332978	1.167173
1	0.910139	4.708305	-0.501099
1	-0.151216	5.809986	0.385801
1	-2.527879	4.265897	-2.023480
1	-1.810425	5.776430	-1.444152
1	-0.834981	4.633800	-2.390217
1	-2.503174	5.208220	0.943246
1	-3.213422	3.673080	0.407324
1	-1.992437	3.674394	1.682164
1	-4.806693	-3.002279	-0.561009
1	-3.500838	-2.250722	-1.458854
6	-3.894436	-1.320377	0.424460
6	-4.878590	-0.361938	0.148467
6	-2.973299	-1.063332	1.443282
6	-4.937638	0.832081	0.866514
1	-5.603062	-0.552205	-0.641768
6	-3.029260	0.131555	2.164152
1	-2.204056	-1.796809	1.653112
6	-4.007870	1.083775	1.879135
1	-5.711965	1.561726	0.642776
1	-2.301846	0.317850	2.949955
1	-4.052284	2.011015	2.443291

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^{4}IIa

Charge = 0, Multiplicity = 4

Number of imaginary frequencies = 0

SCF Energy = -1419.02728435
Thermal correction to Gibbs Free Energy = 0.464758
.....
Cartesian Coordinates
.....

6	1.655245	-0.243000	-0.501381
6	2.988727	-2.168443	-0.232119
6	4.011467	-1.454179	0.344767
6	3.873216	-0.039689	0.511112
6	2.694499	0.529267	0.080044
6	0.411884	0.291195	-0.963013
6	-1.633649	-0.190693	-2.029229
6	-2.048891	1.119767	-1.960062
6	-1.204061	2.088797	-1.336224
6	0.014441	1.651689	-0.857588
1	3.073531	-3.243257	-0.372887
1	4.907534	-1.973863	0.662247
1	2.541871	1.595995	0.175319
1	-2.265412	-0.959339	-2.467179
1	-3.015864	1.393138	-2.364280
1	0.690375	2.348413	-0.379903
7	1.831123	-1.615641	-0.657185
7	-0.455140	-0.620883	-1.539944
28	0.266308	-2.460085	-1.438712
7	-2.404298	-2.950477	0.392621
1	-1.532136	-2.885969	0.927395
6	-2.334094	-3.345989	-0.876308
8	-1.209911	-3.639831	-1.361443
6	-3.615758	-2.473694	1.042962
6	5.011532	0.762663	1.141234
6	5.280828	0.227106	2.565239
6	6.284733	0.596627	0.281915
6	4.686731	2.261584	1.241360
1	4.392659	0.340940	3.196552
1	5.551173	-0.833439	2.555126
1	6.105917	0.780026	3.029875
1	6.119958	0.976795	-0.732263
1	7.118999	1.152550	0.726205
1	6.585101	-0.452794	0.201670
1	5.528305	2.792320	1.699636
1	4.511975	2.703838	0.254279
1	3.801539	2.442355	1.861336
6	-1.672025	3.541389	-1.234576
6	-0.687603	4.420109	-0.446518
6	-1.811679	4.119448	-2.660714
6	-3.044038	3.594387	-0.525719
1	-0.554457	4.056795	0.578981

1	0.296073	4.460147	-0.927161
1	-1.070509	5.444804	-0.390137
1	-2.521706	3.540916	-3.260240
1	-2.169059	5.155400	-2.619364
1	-0.847079	4.108673	-3.180113
1	-3.385330	4.633157	-0.444019
1	-3.807357	3.035138	-1.075030
1	-2.984011	3.169241	0.481131
1	-3.988717	-3.228369	1.747946
1	-4.367444	-2.371835	0.252990
6	-3.402714	-1.161031	1.774288
6	-4.245474	-0.826178	2.841557
6	-2.391915	-0.268400	1.402618
6	-4.090075	0.383090	3.517362
1	-5.027280	-1.518705	3.145993
6	-2.225198	0.935243	2.089898
1	-1.729756	-0.507942	0.580552
6	-3.074777	1.267752	3.144814
1	-4.752825	0.629256	4.342321
1	-1.428295	1.607520	1.787456
1	-2.945014	2.205225	3.678289

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^{4}TS[IIa-IIIa]

Charge = 0, Multiplicity = 4
Number of imaginary frequencies = 1
SCF Energy = -1419.0236259
Thermal correction to Gibbs Free Energy = 0.464558
.....
Cartesian Coordinates
.....

6	1.563910	-0.282575	-0.592597
6	2.959749	-2.131200	-0.183725
6	4.000329	-1.333599	0.236429
6	3.832066	0.086155	0.249449
6	2.613646	0.575944	-0.168307
6	0.277488	0.166480	-1.024953
6	-1.826661	-0.458950	-1.861740
6	-2.295640	0.835283	-1.830983
6	-1.444575	1.873708	-1.342893
6	-0.165580	1.515819	-0.974993
1	3.065925	-3.213408	-0.201949
1	4.930051	-1.794665	0.548186
1	2.438525	1.643288	-0.191288
1	-2.457622	-1.272415	-2.209783
1	-3.304874	1.044352	-2.165772
1	0.517523	2.264948	-0.597685

7	1.764182	-1.658548	-0.591848
7	-0.596045	-0.821472	-1.450770
28	0.131874	-2.625635	-1.044376
7	-2.680261	-3.053709	0.746882
1	-2.150460	-3.402067	1.548912
6	-2.217665	-3.322321	-0.468127
8	-1.248400	-4.046447	-0.736032
6	-3.657815	-1.996563	0.998560
6	4.982720	0.981287	0.710354
6	5.353728	0.620355	2.166021
6	6.206228	0.746075	-0.203072
6	4.620958	2.474243	0.659891
1	4.502594	0.787828	2.835478
1	5.651764	-0.428613	2.259526
1	6.189820	1.240210	2.511601
1	5.968897	1.002548	-1.241387
1	7.049488	1.367957	0.120854
1	6.531332	-0.298814	-0.182338
1	5.472216	3.073202	1.001669
1	4.374343	2.795726	-0.358008
1	3.768808	2.705087	1.308990
6	-1.985180	3.298211	-1.223284
6	-0.956942	4.264236	-0.613969
6	-2.375853	3.815852	-2.624764
6	-3.233181	3.284205	-0.311517
1	-0.662954	3.951032	0.394084
1	-0.053518	4.336493	-1.229739
1	-1.390073	5.267815	-0.539956
1	-3.127206	3.174191	-3.096106
1	-2.792273	4.828174	-2.556242
1	-1.501486	3.847840	-3.284288
1	-3.637307	4.298515	-0.206446
1	-4.025226	2.648898	-0.720070
1	-2.982494	2.903839	0.683776
1	-4.505121	-2.409752	1.557719
1	-4.029367	-1.691623	0.014776
6	-3.073054	-0.805568	1.734980
6	-3.913750	-0.000753	2.512916
6	-1.723691	-0.461408	1.613511
6	-3.416386	1.137674	3.146069
1	-4.963952	-0.263565	2.619808
6	-1.224199	0.676432	2.247009
1	-1.060169	-1.063313	1.005432
6	-2.067685	1.479381	3.014922
1	-4.079656	1.754627	3.745756
1	-0.176032	0.931305	2.124763
1	-1.679676	2.365379	3.509529

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^{4}IIIa

Charge = 0, Multiplicity = 4
Number of imaginary frequencies = 0
SCF Energy = -1419.06679287
Thermal correction to Gibbs Free Energy = 0.467231

.....

Cartesian Coordinates

.....

6	0.613890	0.379574	-0.900342
6	2.713357	-0.680684	-1.035963
6	3.383160	0.483301	-0.733572
6	2.640723	1.685517	-0.524050
6	1.267719	1.606133	-0.622375
6	-0.802563	0.189664	-0.908489
6	-2.561106	-1.369818	-1.060955
6	-3.508224	-0.421624	-0.756208
6	-3.099939	0.933696	-0.541289
6	-1.753050	1.206346	-0.640429
1	3.240313	-1.617531	-1.196883
1	4.463981	0.469007	-0.658104
1	0.659504	2.484127	-0.454385
1	-2.845165	-2.403640	-1.244620
1	-4.549908	-0.712769	-0.691833
1	-1.390078	2.211896	-0.477646
7	1.372500	-0.750607	-1.135672
7	-1.240104	-1.106114	-1.144974
28	0.261662	-2.338673	-1.412035
7	0.510299	-4.020180	0.999208
1	1.121927	-4.609210	1.558067
6	0.910476	-3.749315	-0.269502
8	1.900614	-4.267215	-0.796973
6	-0.528881	-3.246883	1.663776
6	3.377452	2.977803	-0.170270
6	4.148360	2.768200	1.152371
6	4.374832	3.323891	-1.297465
6	2.420211	4.166063	0.013696
1	3.456300	2.536509	1.969818
1	4.866852	1.945992	1.077122
1	4.701938	3.676121	1.419754
1	3.848469	3.482768	-2.245052
1	4.924235	4.240467	-1.051798
1	5.106580	2.524639	-1.450789
1	2.991834	5.066724	0.262528
1	1.852544	4.372650	-0.900305
1	1.708492	3.987901	0.827697

6	-4.145197	1.991616	-0.190263
6	-3.524413	3.383069	0.010926
6	-5.187168	2.081009	-1.326965
6	-4.850722	1.580754	1.121807
1	-2.796450	3.385429	0.830020
1	-3.021812	3.736004	-0.896328
1	-4.308794	4.105800	0.260400
1	-5.687576	1.122019	-1.494200
1	-5.956067	2.823295	-1.081778
1	-4.709940	2.378692	-2.267067
1	-5.614973	2.319098	1.391956
1	-5.341743	0.606835	1.030640
1	-4.130212	1.516958	1.945266
1	-0.814853	-3.799034	2.566736
1	-1.413930	-3.227983	1.018989
6	-0.150536	-1.816589	2.019649
6	1.181388	-1.406667	2.119673
6	-1.165212	-0.882720	2.254638
6	1.494908	-0.088522	2.450011
1	1.977380	-2.112541	1.906515
6	-0.855141	0.434650	2.587580
1	-2.205239	-1.178411	2.140276
6	0.478024	0.836462	2.686366
1	2.534876	0.219266	2.497202
1	-1.655757	1.151450	2.746994
1	0.722874	1.866784	2.929492

IVa

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -4450.10769426
Thermal correction to Gibbs Free Energy = 0.588735

.....

Cartesian Coordinates

.....

6	0.755063	0.818752	0.860996
6	2.897722	0.240581	0.212162
6	3.343472	1.546021	0.350485
6	2.449029	2.555169	0.734270
6	1.137800	2.154955	0.996880
6	-0.619805	0.336975	1.121952
6	-2.022106	-1.503915	1.049993
6	-3.099482	-0.750219	1.510735
6	-2.941242	0.613999	1.775468
6	-1.661870	1.147221	1.566511
1	3.564627	-0.550425	-0.105526

1	4.380338	1.771333	0.127159
1	0.398319	2.884086	1.295950
1	-2.122702	-2.541927	0.749707
1	-4.058654	-1.236197	1.633215
1	-1.485079	2.200074	1.747445
28	0.825894	-1.937349	0.095215
6	-0.284938	-0.251836	-2.433557
6	-2.330596	1.589016	-1.931061
6	-1.563406	-0.709081	-2.112603
1	0.515998	-0.961424	-2.600029
1	-3.137489	2.285534	-1.733246
1	-1.723989	-1.776551	-1.984371
35	1.701732	1.750949	-2.927210
6	-1.057735	2.051659	-2.243131
1	-0.845447	3.113466	-2.294670
6	-0.050201	1.119026	-2.496328
1	0.340035	-5.556548	-1.028411
6	0.017693	-3.564369	-0.652772
7	0.766539	-4.738018	-0.597501
6	-2.589614	0.212329	-1.868407
7	1.630612	-0.131179	0.453610
7	-0.807281	-0.977018	0.872610
8	-4.110059	-1.556441	-1.568773
6	-3.961271	-0.221034	-1.503838
8	-4.865371	0.533050	-1.178443
6	-5.398778	-2.060992	-1.207069
1	-5.339481	-3.138710	-1.356595
1	-6.176298	-1.620776	-1.836858
1	-5.620838	-1.831959	-0.160594
8	-1.168665	-3.683201	-1.024761
6	2.910369	4.010765	0.823424
6	1.771687	4.956847	1.237414
6	4.045262	4.120086	1.864636
6	3.431778	4.451186	-0.562773
1	0.948446	4.939251	0.514541
1	1.370887	4.703980	2.225479
1	2.147687	5.984025	1.285984
1	4.899800	3.489271	1.599927
1	4.399688	5.155211	1.928783
1	3.696208	3.815464	2.857503
1	3.749475	5.499628	-0.529362
1	4.289711	3.850568	-0.881201
1	2.651736	4.346129	-1.323532
6	-4.075833	1.512861	2.274037
6	-3.726116	1.996162	3.698788
6	-4.228488	2.727911	1.332696
6	-5.421742	0.770540	2.312442

1	-3.615004	1.148807	4.384642
1	-2.790457	2.565659	3.713402
1	-4.521683	2.645377	4.082296
1	-4.491928	2.394050	0.325682
1	-5.024862	3.383918	1.702876
1	-3.310521	3.322657	1.277029
1	-6.203809	1.451724	2.664500
1	-5.703675	0.421636	1.314240
1	-5.397709	-0.084145	2.998009
6	2.213293	-4.709543	-0.522654
1	2.679283	-4.423353	-1.480570
1	2.558522	-5.729660	-0.305785
6	2.745019	-3.780437	0.556240
6	4.016489	-3.207556	0.409658
6	2.041567	-3.554734	1.755302
6	4.579143	-2.435391	1.428211
1	4.569945	-3.376081	-0.511609
6	2.602571	-2.771897	2.769251
1	1.075978	-4.026935	1.894435
6	3.868734	-2.206669	2.608373
1	5.568447	-2.005201	1.295160
1	2.042209	-2.603925	3.684683
1	4.299488	-1.595586	3.396439

TS[IVa-V]

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 1
SCF Energy = -4450.09224995
Thermal correction to Gibbs Free Energy = 0.590421
.....
Cartesian Coordinates
.....

6	1.105238	1.354289	-0.008640
6	2.707695	0.260737	-1.260541
6	3.413267	1.438634	-1.472836
6	2.965203	2.634743	-0.895209
6	1.779704	2.569332	-0.157391
6	-0.203007	1.241146	0.684145
6	-1.731032	-0.195921	1.660282
6	-2.689633	0.815403	1.740170
6	-2.395128	2.098537	1.271439
6	-1.105388	2.298806	0.754380
1	3.034235	-0.684914	-1.679471
1	4.318669	1.408780	-2.068696
1	1.376750	3.452828	0.319484
1	-1.926882	-1.219524	1.971835

1	-3.666693	0.572867	2.137816
1	-0.828305	3.263021	0.345238
28	0.589514	-1.661883	0.197609
6	-1.974190	-2.685112	-0.800244
6	-2.394906	-0.129488	-1.883268
6	-3.249227	-2.135029	-0.818042
1	-1.799809	-3.648144	-0.343081
1	-2.578256	0.856911	-2.296333
1	-4.077789	-2.694146	-0.398557
35	0.952152	-2.994836	-2.022839
6	-1.119667	-0.673458	-1.894012
1	-0.287083	-0.127783	-2.318939
6	-0.900956	-1.896240	-1.233895
1	0.877955	-4.482293	2.814578
6	0.078407	-3.087995	1.536567
7	1.119743	-3.780953	2.119539
6	-3.467330	-0.837170	-1.313942
7	1.585572	0.212532	-0.537615
7	-0.521432	0.013457	1.137435
8	-5.748198	-0.976103	-0.736571
6	-4.771931	-0.162107	-1.208214
8	-4.981760	1.011464	-1.481636
6	-7.032616	-0.365096	-0.580082
1	-7.700714	-1.166035	-0.261728
1	-7.372439	0.069761	-1.523581
1	-6.996998	0.423678	0.177692
8	-1.067368	-3.295544	1.963945
6	3.767784	3.926474	-1.068777
6	3.091948	5.128548	-0.389533
6	5.164555	3.727908	-0.439219
6	3.916800	4.234085	-2.574707
1	2.097604	5.323780	-0.806351
1	2.991244	4.981535	0.691487
1	3.698680	6.026466	-0.545468
1	5.706381	2.900659	-0.908311
1	5.765645	4.636275	-0.559553
1	5.082001	3.512741	0.631957
1	4.494489	5.154733	-2.714104
1	4.435681	3.430325	-3.105996
1	2.936752	4.370768	-3.044542
6	-3.402487	3.250680	1.277239
6	-2.886748	4.349537	2.231996
6	-3.539712	3.818317	-0.153587
6	-4.794969	2.794648	1.742205
1	-2.790804	3.969154	3.255232
1	-1.907083	4.727435	1.919591
1	-3.584592	5.194515	2.244702

1	-3.890992	3.043682	-0.841220
1	-4.266187	4.639184	-0.155018
1	-2.591591	4.218463	-0.528307
1	-5.480076	3.648899	1.730549
1	-5.201001	2.032837	1.069342
1	-4.778504	2.398550	2.763676
6	2.481511	-3.707786	1.633365
1	2.562538	-4.105629	0.611750
1	3.094268	-4.354901	2.272750
6	3.069641	-2.302669	1.650348
6	4.205709	-2.024808	0.876588
6	2.541798	-1.284487	2.456004
6	4.809790	-0.770224	0.920380
1	4.615457	-2.802603	0.236060
6	3.136588	-0.020189	2.485204
1	1.662001	-1.488912	3.054886
6	4.274254	0.240186	1.723876
1	5.690471	-0.573487	0.314739
1	2.703840	0.759862	3.105450
1	4.735065	1.223444	1.743048

V

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -4450.14508553
Thermal correction to Gibbs Free Energy = 0.590384

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Cartesian Coordinates

.....

6	-1.925590	-0.417339	-0.471322
6	-1.445119	-2.682912	-0.456642
6	-2.790755	-3.011965	-0.537846
6	-3.759782	-1.998403	-0.582764
6	-3.293775	-0.683474	-0.545752
6	-1.356439	0.946071	-0.454038
6	0.580914	2.204014	-0.370952
6	-0.129215	3.394757	-0.493804
6	-1.524609	3.363991	-0.593805
6	-2.124082	2.099982	-0.591983
1	-0.666324	-3.436032	-0.402690
1	-3.072289	-4.058488	-0.566765
1	-3.992272	0.139595	-0.559046
1	1.663226	2.194866	-0.316256
1	0.419685	4.327354	-0.516793
1	-3.198147	2.014750	-0.691304
28	0.937870	-0.866073	-0.371528

6	3.749148	-1.340936	-0.560684
6	4.623580	0.812187	0.980491
6	5.111954	-1.092284	-0.426186
1	3.416761	-2.175476	-1.168340
1	4.981498	1.638066	1.587123
1	5.834781	-1.733534	-0.918285
35	1.110559	-0.860268	-2.798482
6	3.261054	0.551164	0.847098
1	2.563251	1.184243	1.386345
6	2.804523	-0.506254	0.051721
1	0.955559	-1.948176	3.291734
6	1.120274	-1.768697	1.300802
7	0.937647	-1.257630	2.546906
6	5.560392	-0.005336	0.339805
7	-1.024508	-1.414567	-0.426443
7	-0.014661	1.010060	-0.317816
6	6.996909	0.313833	0.515195
8	7.430056	1.242552	1.173522
8	7.806055	-0.551059	-0.145232
6	9.206737	-0.288757	-0.014894
1	9.513701	-0.340484	1.033574
1	9.705845	-1.062628	-0.599294
1	9.451448	0.703957	-0.403100
8	1.320539	-2.954992	1.077961
6	0.318949	0.023305	2.816437
6	-5.246871	-2.346009	-0.683157
6	-5.642604	-3.271813	0.487214
6	-6.138504	-1.094545	-0.631740
6	-5.490035	-3.075487	-2.023224
1	-5.057516	-4.196378	0.495064
1	-5.495459	-2.769579	1.448810
1	-6.699908	-3.546964	0.404818
1	-5.946783	-0.422918	-1.475810
1	-7.191028	-1.391819	-0.680712
1	-5.991766	-0.534038	0.298506
1	-6.550118	-3.334871	-2.123384
1	-5.209649	-2.440479	-2.870331
1	-4.908482	-4.000353	-2.090232
6	-2.391196	4.620795	-0.698201
6	-3.207802	4.568888	-2.007969
6	-3.351861	4.659313	0.511651
6	-1.548481	5.906181	-0.696221
1	-2.546057	4.526440	-2.879377
1	-3.867264	3.695913	-2.043895
1	-3.833378	5.464307	-2.094838
1	-2.792599	4.695341	1.453424
1	-3.988956	5.549191	0.458893

1	-4.003835	3.780234	0.540372
1	-2.208026	6.777131	-0.767494
1	-0.964108	6.007665	0.224935
1	-0.860346	5.940672	-1.547682
1	0.686992	0.381695	3.785550
1	0.672677	0.729085	2.065128
6	-1.202905	0.021163	2.809730
6	-1.885078	1.241741	2.741609
6	-1.944036	-1.161637	2.871696
6	-3.278331	1.281348	2.737271
1	-1.318471	2.167442	2.667915
6	-3.338782	-1.125676	2.878019
1	-1.430147	-2.116981	2.892842
6	-4.011851	0.094431	2.809763
1	-3.790142	2.237668	2.675304
1	-3.897141	-2.055391	2.929443
1	-5.098096	0.121505	2.813042

TS[V-VI]

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 1
SCF Energy = -4450.13884053
Thermal correction to Gibbs Free Energy = 0.589886

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Cartesian Coordinates

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6	-1.954877	-0.382831	-0.501564
6	-1.540956	-2.657991	-0.399844
6	-2.892082	-2.952496	-0.520974
6	-3.828046	-1.913978	-0.641292
6	-3.326278	-0.611546	-0.627710
6	-1.344033	0.964090	-0.487003
6	0.626616	2.169679	-0.376327
6	-0.047051	3.379460	-0.512981
6	-1.441703	3.386863	-0.631079
6	-2.075688	2.140025	-0.636104
1	-0.785459	-3.430491	-0.297258
1	-3.204179	-3.990872	-0.524853
1	-3.999892	0.229040	-0.702313
1	1.707546	2.131159	-0.299514
1	0.527630	4.296585	-0.528515
1	-3.150924	2.085192	-0.744286
28	0.885483	-0.884962	-0.342700
6	3.680433	-1.590582	-0.046266
6	4.546354	0.834157	1.027667
6	5.025711	-1.247660	-0.113701

1	3.338248	-2.539883	-0.442305
1	4.906631	1.765535	1.452148
1	5.738592	-1.918508	-0.578999
35	1.343177	-1.085806	-2.719205
6	3.199916	0.486945	1.088021
1	2.513749	1.162762	1.585588
6	2.746663	-0.711759	0.519666
1	0.769081	-1.921365	3.295072
6	1.279756	-1.690141	1.381446
7	0.951870	-1.185727	2.619692
6	5.466572	-0.025807	0.416837
7	-1.085446	-1.402231	-0.393236
7	-0.001494	0.991136	-0.329880
6	6.888807	0.398544	0.375217
8	7.312750	1.446977	0.825898
8	7.684227	-0.516102	-0.226650
6	9.068560	-0.157646	-0.306697
1	9.487928	-0.015753	0.693211
1	9.557513	-0.989641	-0.814288
1	9.193776	0.767720	-0.875584
8	1.340954	-2.898478	1.162664
6	0.279265	0.078357	2.839474
6	-5.319812	-2.223725	-0.789502
6	-5.791148	-3.078777	0.406601
6	-6.175139	-0.946980	-0.835809
6	-5.531250	-3.010762	-2.101908
1	-5.230771	-4.015235	0.487012
1	-5.673599	-2.531401	1.347509
1	-6.850675	-3.332752	0.290603
1	-5.925021	-0.320340	-1.698962
1	-7.232797	-1.216931	-0.920393
1	-6.054834	-0.348470	0.074427
1	-6.594009	-3.243518	-2.234359
1	-5.196626	-2.426684	-2.965804
1	-4.976958	-3.954518	-2.100200
6	-2.272737	4.666942	-0.741574
6	-3.083148	4.637652	-2.055817
6	-3.238549	4.731597	0.463188
6	-1.395090	5.928727	-0.735039
1	-2.417979	4.576902	-2.923566
1	-3.766427	3.783390	-2.095625
1	-3.683176	5.550063	-2.146176
1	-2.683429	4.753903	1.407811
1	-3.852315	5.637531	0.406475
1	-3.912838	3.869375	0.489294
1	-2.029802	6.817437	-0.812492
1	-0.815067	6.015684	0.190339

1	-0.699839	5.942728	-1.581333
1	0.596592	0.475030	3.812729
1	0.629904	0.780018	2.084161
6	-1.241632	0.033828	2.781901
6	-1.950022	1.239917	2.717612
6	-1.957191	-1.165628	2.801021
6	-3.343028	1.249001	2.676414
1	-1.402989	2.179497	2.678767
6	-3.352201	-1.160683	2.772021
1	-1.425634	-2.111338	2.810444
6	-4.050853	0.044892	2.709099
1	-3.874521	2.194935	2.617850
1	-3.889790	-2.103666	2.786573
1	-5.137142	0.047494	2.683280

VI

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -4450.19315995
Thermal correction to Gibbs Free Energy = 0.592362

.....

Cartesian Coordinates

.....

6	-0.553904	-0.299490	-1.202205
6	0.116941	-2.485142	-1.550527
6	-1.195172	-2.915152	-1.669771
6	-2.250050	-1.994085	-1.577728
6	-1.897135	-0.663290	-1.335658
6	-0.096372	1.069182	-0.875888
6	1.687494	2.331818	-0.104980
6	0.920041	3.493587	-0.112281
6	-0.402643	3.460444	-0.571896
6	-0.904422	2.203945	-0.941569
1	0.948760	-3.177102	-1.629747
1	-1.385608	-3.970008	-1.826084
1	-2.664618	0.089520	-1.220125
1	2.718400	2.333479	0.235404
1	1.378633	4.415825	0.220367
1	-1.916805	2.109422	-1.315416
28	2.287885	-0.465735	-1.020374
6	1.611401	-2.289038	1.492973
6	1.973805	0.216791	2.648945
6	2.866452	-1.690258	1.453889
1	1.444998	-3.260864	1.044757
1	2.127970	1.197908	3.085228
1	3.702822	-2.180003	0.971609

35	4.481032	-0.810521	-1.698354
6	0.726403	-0.396266	2.702009
1	-0.067977	0.100219	3.241014
6	0.516183	-1.635957	2.076200
1	-2.766449	-2.267045	1.958845
6	-0.802790	-2.338918	1.942743
7	-1.980933	-1.668630	2.178197
6	3.042174	-0.412908	2.006789
7	0.442538	-1.205747	-1.318557
7	1.204454	1.148298	-0.504650
6	4.312800	0.340136	1.819380
8	4.370451	1.559065	1.791039
8	5.366291	-0.469148	1.666743
6	6.578252	0.160042	1.216092
1	6.835224	1.002575	1.861738
1	7.341385	-0.616406	1.263041
1	6.438230	0.494711	0.185644
8	-0.854445	-3.521679	1.602046
6	-2.260780	-0.238314	2.242617
6	-3.699429	-2.464966	-1.721773
6	-4.062625	-3.340045	-0.500843
6	-4.687063	-1.289461	-1.796477
6	-3.838119	-3.300077	-3.013893
1	-3.316856	-4.118666	-0.315929
1	-4.136548	-2.720902	0.397851
1	-5.036841	-3.817645	-0.656583
1	-4.470122	-0.635734	-2.649430
1	-5.704493	-1.674538	-1.922319
1	-4.677365	-0.687063	-0.884993
1	-4.881281	-3.608270	-3.145048
1	-3.540908	-2.716547	-3.892145
1	-3.226958	-4.207159	-2.987903
6	-1.258428	4.720414	-0.737386
6	-1.422904	4.988252	-2.251035
6	-2.650877	4.518555	-0.104347
6	-0.604984	5.950341	-0.085223
1	-0.449327	5.141729	-2.728230
1	-1.915352	4.149262	-2.753978
1	-2.030609	5.886165	-2.412596
1	-2.573058	4.278420	0.961625
1	-3.241221	5.436055	-0.203065
1	-3.211347	3.717318	-0.596057
1	-1.261747	6.818738	-0.200773
1	-0.435899	5.797729	0.986571
1	0.352839	6.199479	-0.553283
1	-2.109829	0.132470	3.267302
1	-1.566939	0.309103	1.598402

6	-3.679086	0.084531	1.826776
6	-3.916319	1.231529	1.062357
6	-4.771082	-0.694517	2.227567
6	-5.211656	1.589363	0.689425
1	-3.074845	1.847125	0.763710
6	-6.067742	-0.347943	1.843637
1	-4.617979	-1.570620	2.852602
6	-6.292618	0.793332	1.072267
1	-5.374857	2.484353	0.095465
1	-6.903447	-0.967740	2.155078
1	-7.302145	1.061575	0.775628

F

Charge = 0, Multiplicity = 1
Number of imaginary frequencies = 0
SCF Energy = -3550.87773778
Thermal correction to Gibbs Free Energy = 0.330808
.....
Cartesian Coordinates
.....

6	0.348279	0.748385	-0.001813
6	-1.135626	2.525044	-0.002660
6	-0.099834	3.447283	-0.001219
6	1.234662	3.008038	-0.000053
6	1.435797	1.626039	-0.000403
6	0.472668	-0.725621	-0.001740
6	-0.695371	-2.724111	-0.001469
6	0.482120	-3.466101	-0.000358
6	1.719499	-2.811339	-0.000276
6	1.685329	-1.410382	-0.001002
1	-2.175649	2.835240	-0.003626
1	-0.339894	4.504542	-0.001030
1	2.439493	1.223924	0.000693
1	-1.667933	-3.206104	-0.001924
1	0.415609	-4.546519	0.000307
1	2.612710	-0.850656	-0.001023
28	-2.342645	-0.219266	-0.001160
35	-4.624001	-0.368944	0.001955
7	-0.926038	1.199314	-0.002960
7	-0.712109	-1.385656	-0.002149
6	2.383682	4.018946	0.001057
6	2.272849	4.904480	1.262044
6	3.760683	3.335127	0.004037
6	2.276579	4.901626	-1.262366
1	1.325154	5.450925	1.293294
1	2.343149	4.299673	2.172626

1	3.084516	5.640588	1.276262
1	3.906653	2.710933	-0.884710
1	4.547345	4.096414	0.005368
1	3.902911	2.711454	0.893761
1	3.088153	5.637847	-1.275874
1	2.349631	4.294676	-2.171299
1	1.328754	5.447633	-1.297553
6	3.062007	-3.547066	0.000705
6	3.856920	-3.147643	-1.262374
6	3.857741	-3.142926	1.261716
6	2.883740	-5.073907	0.003645
1	3.310343	-3.420456	-2.171477
1	4.052447	-2.071004	-1.297297
1	4.823574	-3.663612	-1.276200
1	3.312042	-3.412847	2.172215
1	4.824639	-3.658408	1.276516
1	4.052789	-2.066071	1.292791
1	3.865969	-5.557461	0.003740
1	2.344929	-5.417892	0.893218
1	2.343448	-5.421171	-0.883758

G

Charge = -1, Multiplicity = 1
Number of imaginary frequencies = 0
SCF Energy = -3550.92065236
Thermal correction to Gibbs Free Energy = 0.336792

.....

Cartesian Coordinates

.....

6	0.727724	0.584830	-0.000093
6	2.672885	1.860746	-0.000331
6	3.471647	0.728405	-0.000142
6	2.883417	-0.545855	-0.000040
6	1.484139	-0.587081	-0.000045
6	-0.762183	0.588848	0.000123
6	-2.697012	1.880423	0.000400
6	-3.509247	0.751599	0.000244
6	-2.930890	-0.521756	0.000095
6	-1.526943	-0.571927	0.000088
1	3.109784	2.853933	-0.000593
1	4.548381	0.848526	-0.000085
1	0.981082	-1.542666	-0.000035
1	-3.128536	2.876163	0.000670
1	-4.583087	0.883858	0.000249
1	-1.034492	-1.534864	0.000083
28	-0.008001	3.231967	-0.000029

7	1.330446	1.799641	-0.000299
7	-1.359041	1.811300	0.000323
6	3.751898	-1.803142	0.000088
6	4.641931	-1.790532	1.264290
6	2.911956	-3.090654	0.000119
6	4.642095	-1.790715	-1.263999
1	5.300535	-0.916933	1.293737
1	4.034423	-1.790360	2.175571
1	5.274550	-2.683804	1.276932
1	2.278291	-3.166205	-0.890911
1	3.578467	-3.957852	0.000209
1	2.278186	-3.166096	0.891083
1	5.274690	-2.684005	-1.276447
1	4.034701	-1.790643	-2.175357
1	5.300722	-0.917135	-1.293476
6	-3.744512	-1.815466	-0.000086
6	-3.385596	-2.629374	-1.264653
6	-3.384956	-2.630278	1.263689
6	-5.257492	-1.544027	0.000404
1	-3.621974	-2.069191	-2.175428
1	-2.324221	-2.896919	-1.294992
1	-3.962051	-3.559834	-1.278215
1	-3.620941	-2.070794	2.174997
1	-3.961351	-3.560780	1.276824
1	-2.323559	-2.897818	1.293360
1	-5.796840	-2.495632	0.000195
1	-5.572630	-0.988755	0.890643
1	-5.573097	-0.988111	-0.889268

IIb

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -4010.37871555
Thermal correction to Gibbs Free Energy = 0.453125

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Cartesian Coordinates

.....

6	1.490263	1.007831	-0.334030
6	-0.194793	2.395134	-1.103486
6	0.622923	3.518998	-1.012211
6	1.939380	3.386295	-0.558893
6	2.355444	2.092208	-0.215143
6	1.856102	-0.384642	0.023380
6	1.077455	-2.552699	0.266167
6	2.338673	-3.010432	0.640798
6	3.414167	-2.118849	0.708577

6	3.140831	-0.782641	0.382652
1	-1.223981	2.471789	-1.438552
1	0.216095	4.481992	-1.293087
1	3.359116	1.933943	0.160171
1	0.228770	-3.224109	0.179938
1	2.461548	-4.061298	0.869945
1	3.940104	-0.051668	0.401137
7	0.218784	1.164713	-0.780501
7	0.831236	-1.271413	-0.030437
28	-0.924187	-0.511190	-0.666765
6	-2.947358	-1.690983	0.836126
6	-3.670154	0.473608	-0.822047
1	-2.708561	-2.546656	1.460369
1	-4.023347	1.282226	-1.455993
35	-2.203234	-3.465056	-1.356002
6	-2.814298	-0.525558	-1.358724
1	-2.731852	-0.614382	-2.439595
6	-2.417147	-1.646290	-0.507413
6	4.832791	-2.537117	1.103682
6	5.793439	-2.230841	-0.066622
6	5.265837	-1.736314	2.351639
6	4.923121	-4.036562	1.430255
1	5.502252	-2.783578	-0.966271
1	5.805505	-1.164775	-0.315712
1	6.815286	-2.523706	0.199841
1	4.595020	-1.933097	3.194883
1	6.281386	-2.022338	2.647808
1	5.263783	-0.657566	2.164504
1	5.950989	-4.289261	1.710411
1	4.273918	-4.308815	2.269576
1	4.652384	-4.656698	0.568838
6	2.905760	4.565321	-0.419801
6	3.338529	4.690107	1.057893
6	4.146823	4.307200	-1.302607
6	2.264074	5.892644	-0.855041
1	2.472932	4.867393	1.705143
1	3.844363	3.786106	1.412245
1	4.032496	5.529947	1.175926
1	3.864088	4.209458	-2.356329
1	4.851275	5.141771	-1.213120
1	4.673024	3.393096	-1.008982
1	2.989996	6.704578	-0.742983
1	1.953463	5.868047	-1.905284
1	1.391092	6.141889	-0.242120
6	-3.714663	-0.667849	1.324407
1	-4.062531	-0.693865	2.350764
6	-4.090751	0.439032	0.494742

6	-4.928663	1.546453	0.980813
8	-5.243983	2.535334	0.337913
8	-5.333447	1.365697	2.269388
6	-6.151002	2.412850	2.795187
1	-7.067055	2.523091	2.207594
1	-6.387062	2.117121	3.818621
1	-5.615466	3.366901	2.786156

TS[IIb-IIIb]

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 1
SCF Energy = -4010.36770243
Thermal correction to Gibbs Free Energy = 0.453533
.....
Cartesian Coordinates
.....

6	1.871907	0.879832	-0.075508
6	0.803117	2.742522	-0.938947
6	1.897041	3.557666	-0.667061
6	3.035527	3.015503	-0.060043
6	2.993253	1.646281	0.232508
6	1.771923	-0.573262	0.186215
6	0.378566	-2.417718	0.138582
6	1.410570	-3.263709	0.535447
6	2.689891	-2.745880	0.765250
6	2.850692	-1.367864	0.568195
1	-0.091644	3.144887	-1.402463
1	1.842533	4.605892	-0.931337
1	3.839547	1.174037	0.715992
1	-0.608091	-2.798708	-0.097160
1	1.200735	-4.319630	0.648323
1	3.827497	-0.916809	0.694180
7	0.774411	1.433467	-0.653471
7	0.541554	-1.100857	-0.014465
28	-0.801848	0.220438	-0.761523
6	-3.110134	-1.280629	0.266537
6	-4.128382	1.257981	-0.415887
1	-2.720801	-2.258838	0.529386
1	-4.575394	2.207853	-0.692334
35	-1.692696	-1.691719	-2.660151
6	-3.031623	0.745165	-1.121265
1	-2.698422	1.229694	-2.035336
6	-2.463875	-0.498145	-0.717252
6	3.883741	-3.605453	1.188577
6	4.983825	-3.506921	0.108548
6	4.430838	-3.080773	2.534444

6	3.498905	-5.083773	1.360619
1	4.615441	-3.865989	-0.858302
1	5.332527	-2.477748	-0.025354
1	5.847095	-4.118025	0.395355
1	3.665735	-3.136393	3.316375
1	5.289180	-3.683558	2.851796
1	4.762464	-2.039855	2.461247
1	4.378603	-5.657652	1.669887
1	2.729379	-5.215897	2.129068
1	3.131468	-5.519066	0.425079
6	4.278334	3.838370	0.287498
6	4.515048	3.772651	1.812665
6	5.498183	3.245494	-0.452051
6	4.127712	5.312550	-0.121339
1	3.659276	4.182757	2.359594
1	4.673768	2.745534	2.156735
1	5.403504	4.355883	2.079467
1	5.350870	3.275168	-1.537008
1	6.398454	3.822416	-0.212701
1	5.682303	2.205030	-0.165503
1	5.037778	5.860671	0.143094
1	3.977602	5.421143	-1.201075
1	3.289796	5.793713	0.394867
6	-4.202984	-0.763260	0.933409
1	-4.671934	-1.330243	1.730054
6	-4.715065	0.518793	0.611233
6	-5.880566	1.102685	1.304928
8	-6.361179	2.198199	1.072007
8	-6.381322	0.279081	2.264213
6	-7.512940	0.795671	2.970305
1	-8.340918	0.992405	2.283382
1	-7.788005	0.023549	3.690163
1	-7.257037	1.726501	3.484587

IIIb

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -4010.43911964
Thermal correction to Gibbs Free Energy = 0.454986

.....

Cartesian Coordinates

.....

6	-2.300413	0.144709	0.013275
6	-2.431879	2.454295	0.022946
6	-3.824354	2.415344	0.049474
6	-4.491911	1.187321	0.058319

6	-3.688066	0.038717	0.039385
6	-1.380338	-1.009986	-0.007979
6	0.832896	-1.689913	-0.055430
6	0.464606	-3.031715	-0.049338
6	-0.885303	-3.390857	-0.021459
6	-1.805544	-2.334689	-0.000158
1	-1.872664	3.384872	0.015230
1	-4.366540	3.352098	0.062616
1	-4.150690	-0.940278	0.044756
1	1.873211	-1.394331	-0.078448
1	1.248573	-3.777689	-0.067354
1	-2.866709	-2.547973	0.022633
7	-1.682415	1.348294	0.005203
7	-0.058973	-0.688653	-0.036077
28	0.348805	1.242047	-0.040443
6	2.948981	0.831167	1.096041
6	4.211464	0.397441	-1.350720
1	2.470505	1.011364	2.055358
1	4.723011	0.228973	-2.293291
35	0.740249	3.520891	-0.026641
6	2.869802	0.768563	-1.313675
1	2.329072	0.896411	-2.248187
6	2.211208	0.973972	-0.089979
6	-1.375315	-4.839966	-0.013361
6	-2.201642	-5.083584	1.269020
6	-2.263205	-5.077464	-1.255131
6	-0.210460	-5.842480	-0.044496
1	-1.594142	-4.914392	2.164529
1	-3.073981	-4.424215	1.323691
1	-2.562486	-6.117874	1.290513
1	-1.700217	-4.903306	-2.178331
1	-2.624154	-6.111899	-1.264300
1	-3.137656	-4.418662	-1.263927
1	-0.606093	-6.863224	-0.038643
1	0.399302	-5.728522	-0.947312
1	0.441485	-5.734853	0.829173
6	-6.016521	1.055640	0.086526
6	-6.478280	0.285493	-1.170522
6	-6.430879	0.275349	1.353771
6	-6.714072	2.425326	0.105099
1	-6.188427	0.816560	-2.083521
1	-6.047538	-0.720140	-1.214340
1	-7.569063	0.181922	-1.166334
1	-6.107223	0.799317	2.259495
1	-7.521034	0.171259	1.389515
1	-5.998635	-0.730419	1.373490
1	-7.799386	2.282837	0.125213

1	-6.439802	3.008695	0.990700
1	-6.473647	3.015507	-0.785798
6	4.292644	0.461933	1.067395
1	4.851721	0.349041	1.990086
6	4.933384	0.233715	-0.159557
6	6.352784	-0.174720	-0.254586
8	6.947416	-0.407959	-1.291600
8	6.949945	-0.273424	0.962216
6	8.327770	-0.656020	0.927706
1	8.916954	0.070533	0.361093
1	8.651760	-0.682708	1.969016
1	8.445909	-1.639373	0.463319

IVb

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 0
SCF Energy = -4450.14149268
Thermal correction to Gibbs Free Energy = 0.590791

.....

Cartesian Coordinates

.....

6	2.024432	-0.597685	-0.391746
6	1.728079	-2.869889	-0.048388
6	3.097109	-3.107061	-0.126698
6	3.976771	-2.039947	-0.338156
6	3.403585	-0.769833	-0.474414
6	1.352262	0.713676	-0.503447
6	-0.640544	1.861485	-0.338325
6	-0.024848	3.075185	-0.629113
6	1.348085	3.111947	-0.888648
6	2.028654	1.891935	-0.809933
1	1.014383	-3.664367	0.137155
1	3.455381	-4.122099	-0.014742
1	4.039421	0.092623	-0.625156
1	-1.706323	1.807793	-0.147538
1	-0.631155	3.971426	-0.657425
1	3.093172	1.859425	-1.000372
7	1.209254	-1.646876	-0.170690
7	0.020318	0.704119	-0.283729
28	-0.793759	-1.275309	-0.148239
6	-3.576841	-1.625209	0.936110
6	-4.629108	0.312871	-0.768217
6	-4.936812	-1.323039	0.978373
1	-3.201536	-2.404680	1.589118
1	-5.041606	1.047115	-1.451856
1	-5.601033	-1.841243	1.662863

35	-0.877950	-1.738045	-2.530138
6	-3.272596	-0.001413	-0.812238
1	-2.655594	0.459721	-1.574862
6	-2.713571	-0.953906	0.057176
7	-0.807427	-1.063880	2.795949
1	-0.720988	-1.571724	3.671028
6	-0.797598	-1.829728	1.680766
6	-5.473484	-0.339726	0.139941
8	-0.747468	-3.054421	1.712591
6	-0.762275	0.380237	2.819123
6	5.497318	-2.201270	-0.403150
6	6.131662	-1.384084	0.744757
6	5.929977	-3.668954	-0.257140
6	6.007087	-1.671138	-1.761235
1	5.885138	-0.319725	0.671278
1	5.783759	-1.745206	1.719155
1	7.222972	-1.478461	0.716203
1	5.516504	-4.294114	-1.055857
1	7.021274	-3.736672	-0.313627
1	5.621660	-4.089869	0.706110
1	7.095558	-1.781755	-1.821716
1	5.558858	-2.227686	-2.590998
1	5.770860	-0.611383	-1.900906
6	2.099366	4.387835	-1.275771
6	3.296942	4.601162	-0.325577
6	2.612752	4.227197	-2.724644
6	1.197218	5.630474	-1.206407
1	2.959051	4.723868	0.707413
1	3.996760	3.760074	-0.348829
1	3.847530	5.501906	-0.618515
1	1.781365	4.066946	-3.419145
1	3.151148	5.130026	-3.034575
1	3.296668	3.377372	-2.818377
1	1.777316	6.520264	-1.471678
1	0.357541	5.563833	-1.906403
1	0.795966	5.782525	-0.198087
6	-6.922023	-0.044647	0.240710
8	-7.693345	-0.582331	1.013851
8	-7.319305	0.914699	-0.634491
6	-8.714094	1.231009	-0.589573
1	-8.995202	1.602369	0.400087
1	-8.865077	2.002403	-1.345872
1	-9.317963	0.347866	-0.816143
1	-1.301796	0.722722	3.709911
1	-1.331407	0.737450	1.957604
6	0.637312	0.975978	2.804806
6	0.783223	2.368861	2.822728

6	1.783745	0.180059	2.758882
6	2.047269	2.951750	2.788286
1	-0.102171	2.999642	2.857731
6	3.053188	0.762007	2.719114
1	1.683087	-0.899463	2.734149
6	3.190290	2.148890	2.730002
1	2.142070	4.033747	2.810390
1	3.932638	0.125843	2.674327
1	4.176042	2.604417	2.699630

TS[IVb-V]

Charge = 0, Multiplicity = 2
Number of imaginary frequencies = 1
SCF Energy = -4450.11050331
Thermal correction to Gibbs Free Energy = 0.588180
.....
Cartesian Coordinates
.....

6	1.952354	-0.230174	-0.824922
6	2.009709	-2.543480	-0.866023
6	3.401818	-2.546150	-0.907635
6	4.107031	-1.338946	-0.903747
6	3.341698	-0.165372	-0.864343
6	1.073088	0.950822	-0.734355
6	-1.086997	1.699698	-0.373970
6	-0.688200	3.028166	-0.477168
6	0.644220	3.342978	-0.758064
6	1.525255	2.260084	-0.863290
1	1.424496	-3.456480	-0.849864
1	3.913357	-3.499540	-0.927560
1	3.831206	0.799593	-0.832761
1	-2.120275	1.436878	-0.189394
1	-1.438467	3.798799	-0.355859
1	2.573074	2.434942	-1.069209
7	1.298461	-1.413102	-0.823258
7	-0.240547	0.671091	-0.523197
28	-0.721431	-1.256436	-0.606594
6	-3.200238	-1.087744	0.868846
6	-4.656223	-0.058397	-1.277121
6	-4.522061	-0.691087	1.053758
1	-2.661446	-1.529773	1.702223
1	-5.229132	0.329824	-2.112465
1	-5.007986	-0.787647	2.019761
35	-1.217299	-3.496507	-0.889062
6	-3.329289	-0.447290	-1.450069
1	-2.876849	-0.354028	-2.434649

6	-2.569073	-0.947055	-0.378354
7	0.418986	-1.793133	3.040365
1	0.752092	-1.973324	3.987434
6	0.779363	-2.658472	2.073321
6	-5.260383	-0.164577	-0.015578
8	1.385283	-3.693620	2.164174
6	-0.095849	-0.470013	2.738067
6	5.635147	-1.255992	-0.926551
6	6.117771	-0.506240	0.334859
6	6.288911	-2.646935	-0.947986
6	6.077972	-0.482391	-2.187943
1	5.729607	0.516704	0.372725
1	5.796742	-1.025136	1.244845
1	7.211927	-0.448397	0.342285
1	5.999263	-3.217234	-1.837073
1	7.378423	-2.539441	-0.963408
1	6.024792	-3.232843	-0.061081
1	7.170830	-0.408276	-2.219019
1	5.743600	-0.993300	-3.097188
1	5.672571	0.534649	-2.204378
6	1.134740	4.770236	-1.013118
6	2.358787	5.090816	-0.130881
6	1.537189	4.871669	-2.502781
6	0.043445	5.813822	-0.724153
1	2.094587	5.062225	0.929395
1	3.180044	4.385244	-0.288872
1	2.730489	6.094000	-0.366718
1	0.687733	4.641402	-3.154641
1	1.879983	5.887244	-2.730905
1	2.347993	4.177790	-2.748131
1	0.442676	6.818744	-0.895357
1	-0.824997	5.689007	-1.379519
1	-0.298049	5.762891	0.315796
6	-6.657806	0.251463	0.238269
8	-7.218569	0.202401	1.318271
8	-7.275953	0.713256	-0.880395
6	-8.635176	1.118370	-0.693812
1	-8.700948	1.932669	0.033623
1	-8.980020	1.451166	-1.673765
1	-9.242544	0.281773	-0.337156
1	-0.873365	-0.210966	3.464911
1	-0.587054	-0.542444	1.762173
6	0.956452	0.621723	2.690970
6	0.563899	1.956256	2.852013
6	2.304000	0.339129	2.448344
6	1.498075	2.986554	2.777187
1	-0.482122	2.185829	3.041027

6	3.242325	1.370365	2.375409
1	2.622005	-0.689425	2.314615
6	2.844270	2.696379	2.540823
1	1.177142	4.015331	2.915494
1	4.286848	1.131985	2.197703
1	3.575583	3.497946	2.493000

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