Supporting Information

Employment of a C(sp^3)-Based Nucleophile for the Photoinduced Palladium-Catalysed Cross-Coupling

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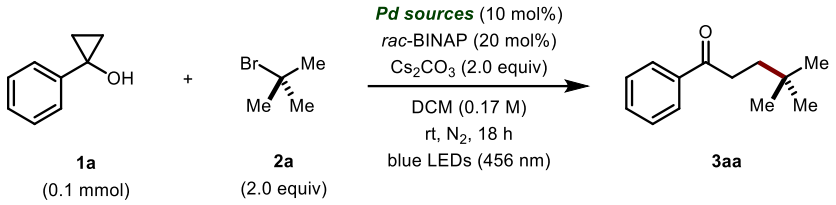
Table of Contents

1. General Information

All chemical reagents were purchased from commercial sources including Sigma-Aldrich, Acros Organics, Alfa Aesar, TCI and Strem, and used without further purification. Tetrahydrofuran (THF) and dichloromethane (DCM) were dried by passing through an activated alumina column of solvent purification system. Other solvents and dichloromethane for photochemical reactions were purchased as anhydrous grade from commercial sources, and were degassed by bubbling nitrogen gas from Schlenk line for more than half an hour. Yield represent isolated yield of chromatographically homogeneous product or/and NMR yield using 1,1,2,2-tetrachloroethane (TCE) or 1,3,5-trimethoxybenzene (TMB) as internal standard. All reactions were monitored by thin-layers chromatography (TLC) using 0.25 mm E. Merck silica gel plates (60 F_{254}), and visualized under UV light or staining with potassium permanganate and heating. Blue LED lamps (456 nm, 34 W) were purchased from Kessil (Kessil H150 Grow Light-Blue) and were used for all the photocatalytic reactions. NMR spectra were recorded on an Agilent 400-MR DD2 Magnetic Resonance System, Varian/Oxford As-500 instrument and Brucker 500MHz NMR spectrometer and calibrated using residual undeuterated solvent ($CHCl_3$ at δ7.26 ppm for ^{1}H NMR and δ77.16 ppm for ^{13}C NMR) as internal reference. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (*J*) are reported in hertz (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, ddt = doublet of doublet of triplets, dt = doublet of triplets, dtt = doublet of triplet of triplets, td = triplet of doublets, tt = triplet of triplets, qd = quartet of doublets, m = multiplet, br = broad. Enantiomeric excess (*ee*) was determined by using High-Performance Liquid Chromatography (HPLC) with columns packed with chiral stationary phase and HPLC grade solvents (*n*-hexane and isopropanol) as eluents. HPLC equipment employed for measuring enantiomeric excess was C196-E061W (Shimadzu, degassing unit: DGU-20A5R, pump: LC-20AD, auto sampler: SIL-20A, communication bus module: CBM-20A, UV/Vis detector: SPD-20A, and column oven: CTO-20A). Optical rotations were recorded on JASCO P1030 polarimeter (D line of sodium vapor lamp) with a cylindrical glass cell (JASCO). High-resolution mass spectrometry (HRMS) was performed using ThermoFisher Scientific mass spectrometer (Orbitrap Exploris 120) at Department of Chemistry in Seoul National University.

2. Optimization of Reaction Conditions

Table S1. Effect of Pd source as precatalyst on the reactions

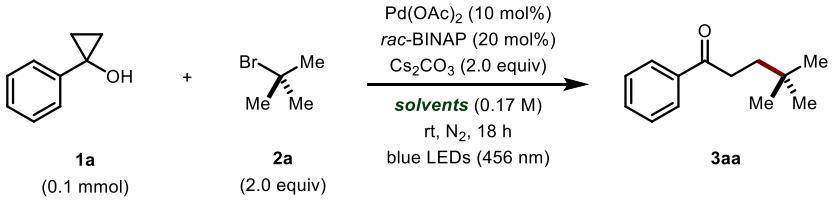


1a (0.1 mmol) + **2a** (2.0 equiv) → **3aa**

entry[a]	deviation from standard conditions	**3aa** (%)[b]
1	none	90
2	PdI_2	74
3	$PdBr_2$	47
4	$PdCl_2$	39
5	$Pd(acac)_2$	34
6	$PdCl_2(PPh_3)_2$	44
7	$Pd(dppf)Cl_2$-DCM	9
8	$PdCl_2(PhCN)_2$	60
9	$Pd(PPh_3)_4$	17
10	$Pd_2(dba)_3$	6

[a]***Reaction conditions***: phenyl cyclopropanol **1a** (0.1 mmol, 1.0 equiv), **2a** (2.0 equiv), Pd source (10 mol%), *rac*-BINAP (20 mol%) and Cs_2CO_3 (2.0 equiv) in 0.6 mL of DCM, rt, N_2, 18 h, irradiated with blue LEDs (456 nm). [b]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. Effect of solvent identity on the reactions

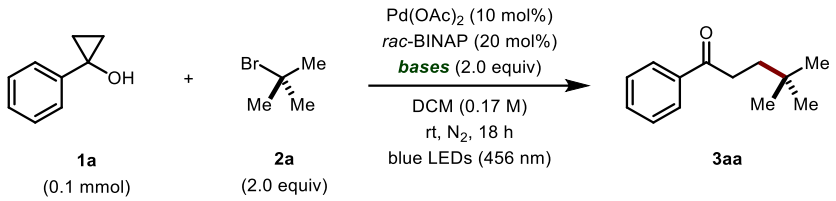


1a (0.1 mmol) + **2a** (2.0 equiv) → **3aa**

entry[a]	deviation from standard conditions	**3aa** (%)[b]
1	none	90
2	DME	21
3	diisopropyl ether	33
4	pentane	38
5	DMF	ND
6	MeCN	24
7	1,4-dioxane	15
8	THF	14
9	DCE	78
10	toluene	60
11	DMA	ND
12	DMSO	2

[a]***Reaction conditions***: phenyl cyclopropanol **1a** (0.1 mmol, 1.0 equiv), **2a** (2.0 equiv), $Pd(OAc)_2$ (10 mol%), *rac*-BINAP (20 mol%) and Cs_2CO_3 (2.0 equiv) in solvent, rt, N_2, 18 h, irradiated with blue LEDs (456 nm). [b]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. ND denotes not detected.

Table S3. Effect of bases on the reactions

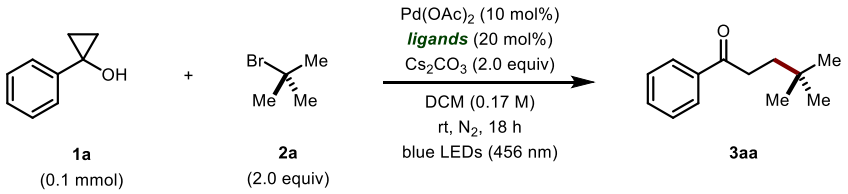


1a (0.1 mmol) | **2a** (2.0 equiv) | **3aa**

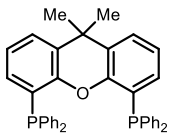
entry[a]	deviation from standard conditions	**3aa** (%)[b]
1	none	90
2	Li_2CO_3	30
3	Na_2CO_3	7
4	K_2CO_3	7
5	CsOAc	54
6	CsOPiv	36
7	K_3PO_4	86
8	K_2HPO_4	44
9	NaH_2PO_4	9
10	Na_2HPO_4	8
11	*t*-BuOK	ND
12	MeONa	ND
13	MeOLi	9
14	DIPEA	28
15	TEA	28
16	DBU	47
17	pyr	16

[a]***Reaction conditions***: phenyl cyclopropanol **1a** (0.1 mmol, 1.0 equiv), **2a** (2.0 equiv), $Pd(OAc)_2$ (10 mol%), *rac*-BINAP (20 mol%) and bases (2.0 equiv) in 0.6 mL of DCM, rt, N_2, 18 h, irradiated with blue LEDs (456 nm). [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. ND denotes not detected.

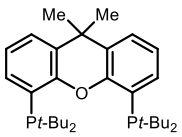
Table S4. Ligand evaluation[a]



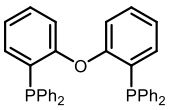
ligand evaluation



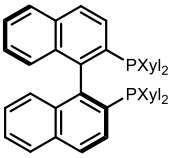
L2: Xantphos, 41%



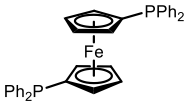
L3: *t*-Bu-Xantphos, 15%



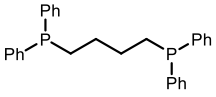
L4: DPEPhos, 28%



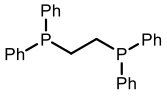
L5: (*R*)-(+)-XylBINAP, 63%



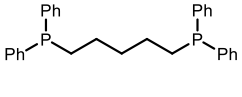
L6: dppf, 10%



L7: dppb, 37%

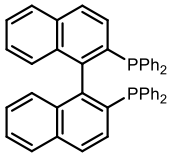


L8: dppe, 45%

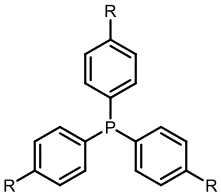


L9: dppppe, 44%

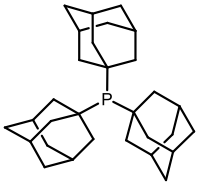
optimal ligand



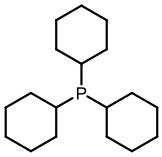
L1: *rac*-BINAP, 90%



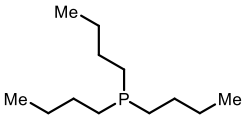
L10: R = H, 12%
L11: R = CF_3, 21%
L12: R = OMe, 19%



L13: PAd_3, ND



L14: PCy_3, 10%

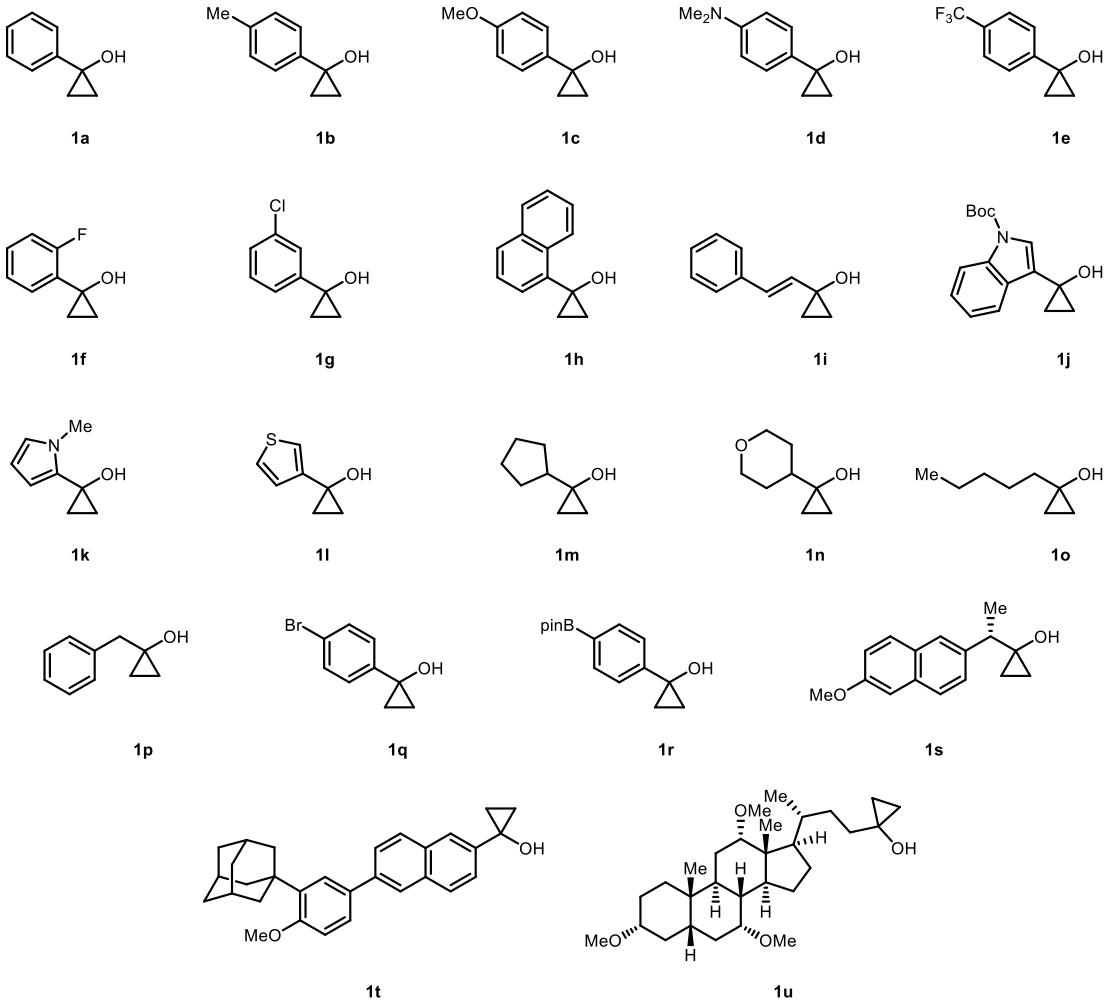


L15: P(*n*-Bu)$_3$, 14%

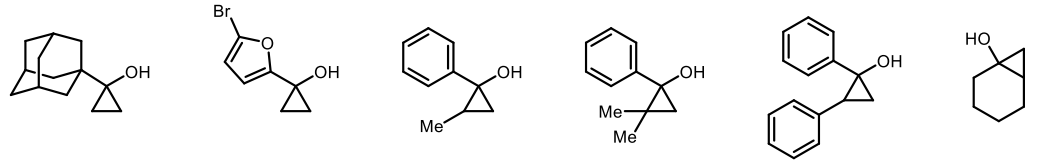
[a]***Reaction conditions***: phenyl cyclopropanol **1a** (0.1 mmol, 1.0 equiv), **2a** (2.0 equiv), $Pd(OAc)_2$ (10 mol%), ligands (20 mol%) and Cs_2CO_3 (2.0 equiv) in 0.6 mL of DCM, rt, N_2, 18 h, irradiated with blue LEDs (456 nm). [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. ND denotes not detected.

3. Preparation of Starting Materials

Table S5. Aryl, heteroaryl, alkenyl and alkyl cyclopropanols **1a**–**1u**

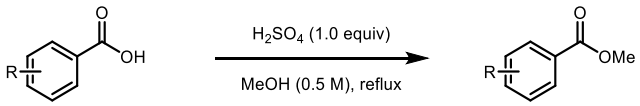


Unsuccessful cyclopropanols (n.d. or <5%)



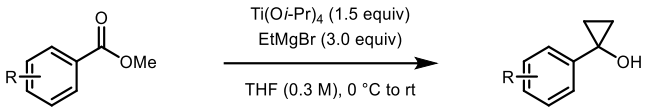
Cyclopropanols **1a**[1], **1b**[1], **1c**[1], **1e**[1], **1f**[3], **1g**[3], **1h**[4], **1l**[6], **1n**[7], **1o**[4], **1p**[1] and **1q**[1] were prepared from the corresponding commercially available methyl esters *General Procedure B*. Cyclopropanols **1d**[2], **1m**[7], **1s**[8] and **1t** were prepared from the corresponding commercially available carboxylic acid according to *General Procedure A* and *General Procedure B*. The corresponding methyl ester of **1i**, **1j**, **1k**, **1r** and **1u** were prepared according to the literature procedures[9,10,11,12,13] and cyclopropanols **1i**[4], **1j**[5], **1k**, **1r** and **1u** were prepared according to *General Procedure B*. The NMR spectra of cyclopropanols were consistent with the previous literatures.

General Procedure A



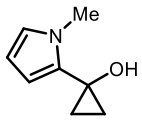
A 100 mL two-neck round-bottom flask was charged with a magnetic stir bar and the corresponding carboxylic acid was added to the flask, followed by reflux condenser placed on top of the round-bottom flask. The reflux condenser and another neck of round-bottom flask were sealed with a rubber septum, and a ballon filled with inert gas was placed on top of the reflux condenser. Anhydrous methanol (0.5 M) was added to the flask, and concentrated sulfuric acid (1.0 equiv) was added to the flask. Then, the reaction mixture was heated to reflux overnight. After then, the resulting mixture was cooled to room temperature, and was quenched with sat. $NaHCO_3$ solution. The resulting solution was transferred to separatory funnel and the layers were separated. The mixture was extracted with dichloromethane three times, and the organic layer was washed with water and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting mixture was purified by silica gel column chromatography (ethyl acetate/hexane) to give the corresponding carboxylic acid methyl ester products.

General Procedure B



An oven-dried 100 mL round-bottom flask was charged with a magnetic stir bar and the corresponding carboxylic acid methyl ester was added to the flask. The reaction vessel was sealed with a rubber septum, and was evacuated and backfilled with nitrogen gas three times by using Schlenk line, then ballon filled with inert gas was placed. Anhydrous tetrahydrofuran (0.3 M) was added to the flask and the resulting solution was cooled to 0 °C. Then, titanium isopropoxide (1.5 equiv) was added to the solution. After stirring for 5 min, ethyl magnesium bromide (3.0 M in diethyl ether, 3.0 equiv) was added dropwise by syringe to the reaction mixture. Then, the reaction mixture was allowed to stir at room temperature overnight. After then, the resulting mixture was cooled to 0 °C under ice bath, and was quenched with water. The solution was filtered through Celite and the filter cake was eluted with diethyl ether. The filtrate was transferred to separatory funnel and the layers were separated. The organic layer was washed with water and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting mixture was purified by silica gel column chromatography (ethyl acetate/hexane) to give the corresponding cyclopropanol products.

1-(1-methyl-1H-pyrrol-2-yl)cyclopropan-1-ol (*Table S5*, 1k).



1k

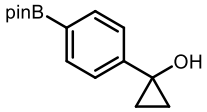
Following *General Procedure B* from methyl 1-methyl-1H-pyrrole-2-carboxylate, the desired product was isolated by silica gel chromatography (10% ethyl acetate in hexane) to provide **1k** in 49% yield as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (t, *J* = 2.3 Hz, 1H), 6.04 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.01 (t, *J* = 3.1 Hz, 1H), 3.78 (s, 3H), 1.11–1.08 (m, 2H), 0.95–0.92 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.15, 123.14, 107.35, 106.30, 50.51, 34.30, 13.61 ppm.

HRMS (ESI) calculated for $[C_8H_{11}NO+H]^+$: 138.0913, found: 138.0915.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropan-1-ol (*Table S5*, 1r).



1r

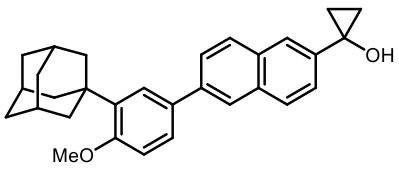
Following *General Procedure B* from methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate, the desired product was isolated by silica gel chromatography (20% ethyl acetate in hexane) to provide **1r** in 55% yield as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 11.5, 8.0 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 1.34 (s, 12H), 1.31–1.28 (m, 1H), 1.27–1.21 (m, 1H), 1.10–1.06 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.06, 135.00, 125.41, 123.43, 83.88, 56.64, 24.99, 18.79 ppm.

HRMS (ESI) calculated for $[C_{15}H_{21}BO_3+H]^+$: 261.1657, found: 261.1661.

1-(6-(3-((3*R*,5*R*,7*R*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)cyclopropan-1-ol (*Table S5*, 1t).



1t

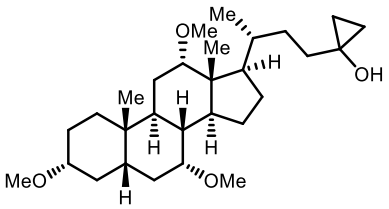
Following *General Procedure A and B* from 6-(3-((*3R*,*5R*,*7R*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid, the desired product was isolated by silica gel chromatography (10% ethyl acetate in hexane) to provide **1t** in 62% yield as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 2H), 7.73 (dd, *J* = 6.1, 2.5 Hz, 1H), 7.59 (d, *J* = 2.3 Hz, 2H), 7.53 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H), 1.37–1.34 (m, 2H), 1.20–1.16 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.67, 141.39, 138.99, 138.82, 133.26, 132.17, 128.48, 128.24, 126.18, 125.97, 125.66, 124.82, 124.64, 123.40, 122.88, 112.21, 76.32, 55.31, 40.75, 37.32, 37.28, 29.26, 17.93, 10.30 ppm.

HRMS (ESI) calculated for $[C_{30}H_{32}O_2+H]^+$: 425.2475, found: 425.2481.

1-((*R*)-3-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)butyl)cyclopropan-1-ol (*Table S5*, 1u).



1u

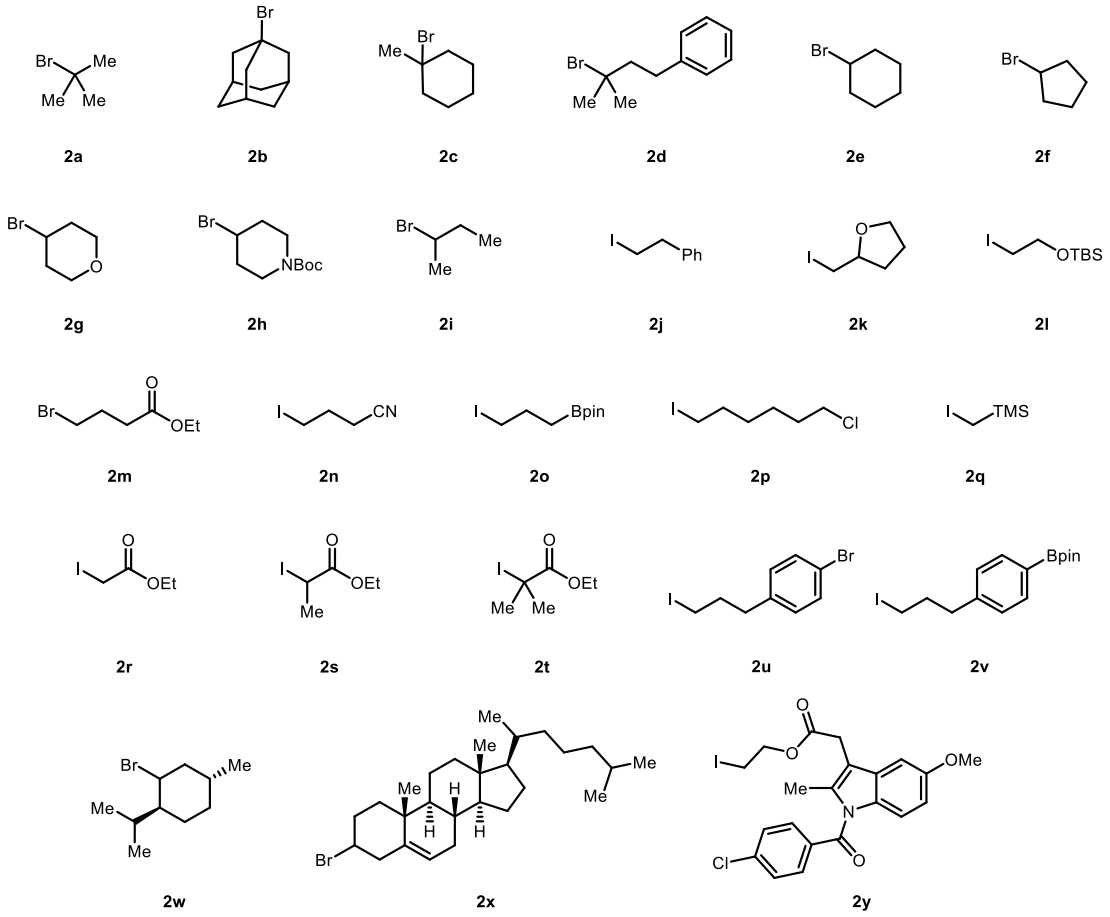
Following *General Procedure B* from methyl (*R*)-4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate, the desired product was isolated by silica gel chromatography (20% ethyl acetate in hexane) to provide **1u** in 66% yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (d, *J* = 2.9 Hz, 1H), 3.32 (s, 3H), 3.24 (s, 3H), 3.20 (s, 3H), 3.14–3.11 (m, 1H), 2.98 (m, 1H), 2.22–2.14 (m, 1H), 2.11–2.02 (m, 2H), 1.92 (t, *J* = 9.8 Hz, 1H), 1.81 (m, 4H), 1.76–1.70 (m, 2H), 1.67 (dq, *J* = 13.1, 2.8, 1.7 Hz, 1H), 1.62–1.55 (m, 3H), 1.54–1.46 (m, 2H), 1.46–1.36 (m, 3H), 1.34–1.14 (m, 6H), 1.06–0.95 (m, 2H), 0.92 (d, *J* = 3.1 Hz, 1H), 0.91–0.87 (m, 6H), 0.64 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 82.13, 80.86, 77.08, 55.98, 55.79, 55.52, 46.23, 46.19, 42.80, 42.08, 39.74, 39.04, 35.97, 35.39, 35.03, 34.55, 29.97, 28.10, 27.89, 27.47, 26.85, 23.26, 22.98, 22.07, 17.69, 12.59, 8.04 ppm.

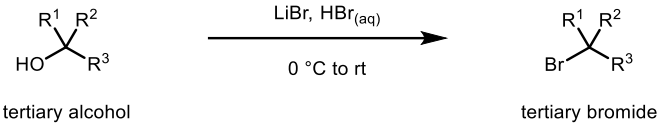
HRMS (ESI) calculated for $[C_{29}H_{50}O_4+H]^+$: 463.3782, found: 463.3790.

Table S6. Tertiary, secondary, primary bromides and iodides **2a**–**2y**



Halides **2a**, **2b**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2m**, **2p**, **2q**, **2r**, **2s** and **2t** were purchased from commercial sources. Halides **2c**[14] and **2d**[15] were prepared from the corresponding commercially available alcohol according to *General Procedure C*. Halides **2w**[16] and **2x**[17] were prepared from the corresponding commercially available alcohol according to *General Procedure D*. Halides **2k**[18], **2u**[19] and **2v** were prepared from the corresponding commercially available alcohol according to *General Procedure E*. Halides **2n**[20] and **2o**[21] were prepared from the corresponding commercially available bromide according to *General Procedure F*. Halides **2l**[22] and **2y**[23] were prepared according to previous literatures.

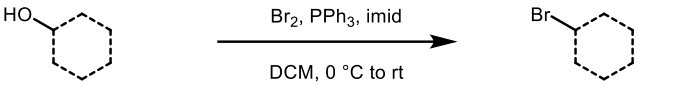
General Procedure C



tertiary alcohol — tertiary bromide

The tertiary bromides **2c** and **2d** were prepared according to the procedure of precedent literature.[24]

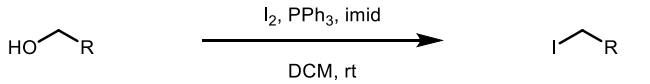
General Procedure D



secondary alcohol — secondary bromide

The secondary bromides **2w** and **2x** were prepared according to the procedure of precedent literature.[25]

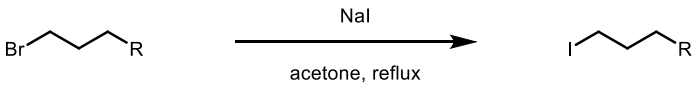
General Procedure E



primary alcohol — primary iodide

The primary iodides **2k**, **2u** and **2v** were prepared according to the procedure of precedent literature.[26]

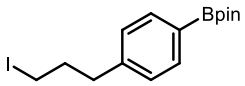
General Procedure F



primary bromide — primary iodide

The primary iodides **2n** and **2o** were prepared according to the procedure of precedent literature.[27]

2-(4-(3-iodopropyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*Table S6*, 2v).



2v

Following *General Procedure E* from 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol, the desired product was isolated by silica gel chromatography (10% ethyl acetate in hexane) to provide **2v** in 72% yield as a white solid.

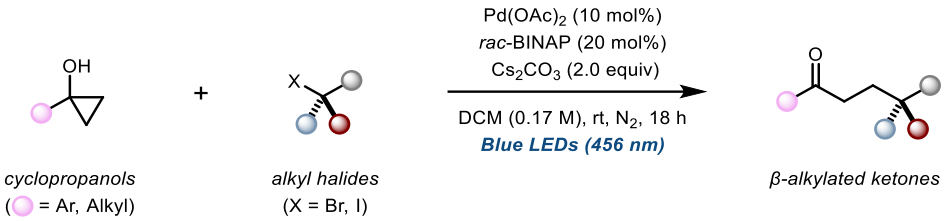
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.13 (p, *J* = 6.9 Hz, 2H), 1.34 (s, 12H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.90, 135.16, 128.14, 83.82, 36.54, 34.82, 24.99, 6.35 ppm.

HRMS (ESI) calculated for $[C_{15}H_{22}BIO_2+H]^+$: 373.0830, found: 373.0836.

4. General Procedure for Photoinduced Palladium-Catalysed C(sp^3)–C(sp^3) Cross-Coupling

General Procedure G

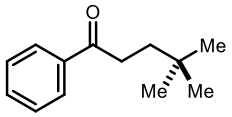


In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with a magnetic stir bar. $Pd(OAc)_2$ (0.02 mmol, 10 mol%, 4.4 mg), *rac*-BINAP (0.04 mmol, 20 mol%, 25 mg) and Cs_2CO_3 (0.4 mmol, 2.0 equiv, 130 mg). was added into the reaction vessel. In a separate 4mL vial, cyclopropanol (0.2 mmol, 1.0 equiv) was dissolved in 1.2 mL of dichloromethane (DCM) and the solution of cyclopanol was added to the mixture via syringe or Pasteur pipette. Halides (0.4 mmol, 2.0 equiv) was added to the mixture via syringe. The reaction mixture was sealed with screw cap, and was taken out of the glovebox. The reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours. The resulting mixture was diluted with dichloromethane, filtered through silica by eluting with ethyl acetate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to give the corresponding ketone products.

Figure S1. Reaction set-ups

5. Characterization of Isolated Products

4,4-dimethyl-1-phenylpentan-1-one (Table 2, 3aa).



3aa

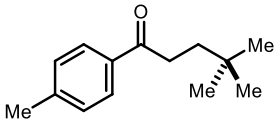
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3aa** as a colorless liquid (32.3 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.57–7.53 (m, 1H), 7.48–7.44 (m, 2H), 2.96–2.92 (m, 2H), 1.66–1.63 (m, 2H), 0.96 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.20, 137.22, 132.99, 128.69, 128.21, 38.27, 34.44, 30.35, 29.36 ppm.

HRMS (ESI) calculated for $[C_{13}H_{18}O+H]^+$: 191.1430, found: 191.1432.

4,4-dimethyl-1-(*p*-tolyl)pentan-1-one (Table 2, 3ab).



3ab

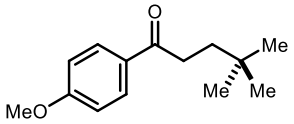
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3ab** as a colorless solid (33.9 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.93–2.88 (m, 2H), 2.41 (s, 3H), 1.65–1.61 (m, 2H), 0.95 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.90, 143.71, 134.73, 129.37, 128.35, 38.41, 34.34, 30.36, 29.36, 21.75 ppm.

HRMS (ESI) calculated for $[C_{14}H_{20}O+H]^+$: 205.1587, found: 205.1588.

1-(4-methoxyphenyl)-4,4-dimethylpentan-1-one (Table 2, 3ac).



3ac

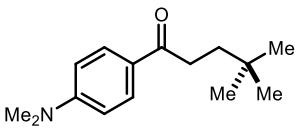
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3ac** as a white solid (30.4 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 2H), 6.95–6.91 (m, 2H), 3.86 (s, 3H), 2.90–2.86 (m, 2H), 1.64–1.60 (m, 2H), 0.95 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.85, 163.42, 130.47, 130.28, 113.80, 55.57, 38.56, 34.11, 30.37, 29.36 ppm.

HRMS (ESI) calculated for $[C_{14}H_{20}O_2+H]^+$: 221.1536, found: 221.1535.

1-(4-(dimethylamino)phenyl)-4,4-dimethylpentan-1-one (Table 2, 3ad).



3ad

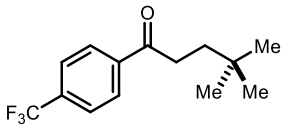
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3ad** as a white solid (12.6 mg, 27%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.86 (m, 2H), 6.68–6.64 (m, 2H), 3.05 (s, 6H), 2.86–2.81 (m, 2H), 1.64–1.60 (m, 2H), 0.95 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.58, 153.38, 130.43, 125.20, 110.80, 40.17, 39.07, 33.78, 30.46, 29.38 ppm.

HRMS (ESI) calculated for $[C_{15}H_{23}NO+H]^+$: 234.1852, found: 234.1853.

4,4-dimethyl-1-(4-(trifluoromethyl)phenyl)pentan-1-one (Table 2, 3ae).



3ae

Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3ae** as a white solid (21.2 mg, 41%).

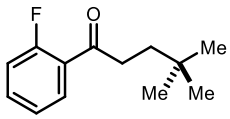
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 2.98–2.93 (m, 2H), 1.67–1.63 (m, 2H), 0.96 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.09, 139.87, 134.36 (q, *J* = 32.7 Hz), 128.54, 125.81 (q, *J* = 3.7 Hz), 123.78 (q, *J* = 272.6 Hz), 38.01, 34.76, 30.33, 29.33 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.12 ppm.

HRMS (ESI) calculated for $[C_{14}H_{17}F_3O+H]^+$: 259.1304, found: 259.1308.

1-(2-fluorophenyl)-4,4-dimethylpentan-1-one (Table 2, 3af).



3af

Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3af** as a colorless liquid (23.7 mg, 57%).

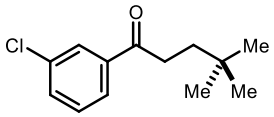
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 1H), 7.53–7.47 (m, 1H), 7.24–7.20 (m, 1H), 7.13 (ddd, *J* = 11.2, 8.3, 0.9 Hz, 1H), 2.94 (ddd, *J* = 10.5, 5.9, 2.8 Hz, 2H), 1.64–1.60 (m, 2H), 0.94 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.78 (d, *J* = 4.1 Hz), 162.89, 160.87, 134.35 (d, *J* = 8.9 Hz), 130.81 (d, *J* = 2.8 Hz), 126.17 (d, *J* = 13.3 Hz), 124.54 (d, *J* = 3.3 Hz), 116.75 (d, *J* = 24.0 Hz), 39.54 (d, *J* = 7.1 Hz), 37.83 (d, *J* = 1.7 Hz), 30.23, 29.34 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.86 ppm.

HRMS (ESI) calculated for $[C_{13}H_{17}FO+H]^+$: 209.1336, found: 209.1340.

1-(3-chlorophenyl)-4,4-dimethylpentan-1-one (Table 2, 3ag).



3ag

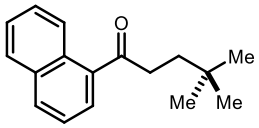
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3ag** as a colorless solid (28.3 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 1.8 Hz, 1H), 7.83 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 2.92–2.88 (m, 2H), 1.65–1.61 (m, 2H), 0.95 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.73, 138.77, 135.04, 132.92, 130.04, 128.33, 126.28, 38.00, 34.53, 30.30, 29.33 ppm.

HRMS (ESI) calculated for $[C_{13}H_{17}ClO+H]^+$: 225.1041, found: 225.1044.

4,4-dimethyl-1-(naphthalen-1-yl)pentan-1-one (Table 2, 3ah).



3ah

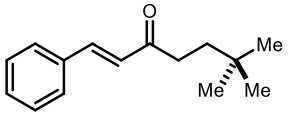
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3ah** as a beige solid (24.0 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.90–7.84 (m, 2H), 7.59 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.55–7.48 (m, 2H), 3.05–3.01 (m, 2H), 1.74–1.69 (m, 2H), 0.97 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.63, 136.74, 134.10, 132.37, 130.28, 128.52, 127.90, 127.10, 126.53, 125.91, 124.51, 38.46, 38.24, 30.34, 29.36 ppm.

HRMS (ESI) calculated for $[C_{17}H_{20}O+H]^+$: 241.1587, found: 241.1591.

(*E*)-6,6-dimethyl-1-phenylhept-1-en-3-one (Table 2, 3ai).



3ai

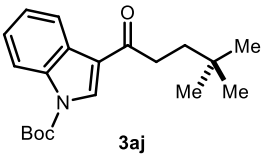
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3ai** as a colorless liquid (25.5 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 3H), 7.41–7.38 (m, 3H), 6.76 (d, *J* = 16.2 Hz, 1H), 2.66–2.61 (m, 2H), 1.61–1.57 (m, 2H), 0.94 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.15, 142.39, 134.79, 130.51, 129.08, 128.40, 127.83, 126.39, 38.18, 36.98, 30.32, 29.35 ppm.

HRMS (ESI) calculated for $[C_{15}H_{20}O+H]^+$: 217.1587, found: 217.1589.

***tert*-butyl 3-(4,4-dimethylpentanoyl)-1*H*-indole-1-carboxylate (Table 2, 3aj).**



3aj

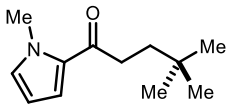
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3aj** as a white solid (30.3 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.0 Hz, 1H), 8.25 (s, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.39–7.33 (m, 2H), 2.88–2.83 (m, 2H), 1.72 (s, 9H), 1.69 (d, *J* = 8.2 Hz, 2H), 0.98 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.44, 149.44, 135.66, 131.77, 127.83, 125.56, 124.49, 122.94, 120.38, 115.06, 85.52, 38.69, 35.97, 30.42, 29.38, 28.27 ppm.

HRMS (ESI) calculated for $[C_{20}H_{27}NO_3+H]^+$: 330.2064, found: 330.2069.

4,4-dimethyl-1-(1-methyl-1*H*-pyrrol-2-yl)pentan-1-one (Table 2, 3ak).



3ak

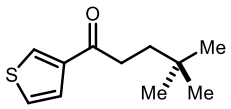
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3ak** as a pale brown liquid (21.3 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 4.1, 1.6 Hz, 1H), 6.78 (t, *J* = 1.9 Hz, 1H), 6.12 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.93 (s, 3H), 2.75–2.70 (m, 2H), 1.62–1.59 (m, 2H), 0.94 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.42, 130.88, 130.87, 118.93, 107.88, 39.44, 37.80, 35.13, 30.43, 29.34 ppm.

HRMS (ESI) calculated for $[C_{12}H_{19}NO+H]^+$: 194.1539, found: 194.1540.

4,4-dimethyl-1-(thiophen-3-yl)pentan-1-one (Table 2, 3al).



3al

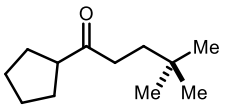
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3al** as a colorless liquid (13.7 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.55 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.31 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.86–2.82 (m, 2H), 1.65–1.61 (m, 2H), 0.95 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.56, 142.52, 131.78, 127.20, 126.40, 38.31, 35.84, 30.35, 29.34 ppm.

HRMS (ESI) calculated for $[C_{11}H_{16}OS+H]^+$: 197.0995, found: 197.0996.

1-cyclopentyl-4,4-dimethylpentan-1-one (Table 2, 3am).



3am

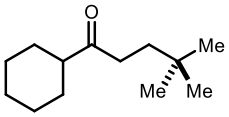
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3am** as a white solid (19.7 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (p, *J* = 8.0 Hz, 1H), 2.43–2.37 (m, 2H), 1.82–1.77 (m, 2H), 1.76–1.70 (m, 2H), 1.65 (ddt, *J* = 7.9, 6.3, 2.3 Hz, 2H), 1.59–1.54 (m, 2H), 1.49–1.44 (m, 2H), 0.88 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.16, 51.61, 37.64, 30.09, 29.28, 29.18, 28.89, 26.12 ppm.

HRMS (ESI) calculated for $[C_{12}H_{22}O+H]^+$: 183.1743, found: 183.1747.

4,4-dimethyl-1-(tetrahydro-2*H*-pyran-4-yl)pentan-1-one (Table 2, 3an).



3an

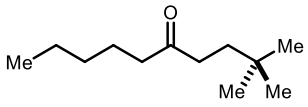
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to provide **3an** as a colorless liquid (30.0 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01–3.96 (m, 2H), 3.41 (td, *J* = 11.4, 2.8 Hz, 2H), 2.56 (tt, *J* = 11.0, 4.3 Hz, 1H), 2.42–2.37 (m, 2H), 1.74–1.64 (m, 4H), 1.48–1.43 (m, 2H), 0.87 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.62, 67.41, 47.76, 37.34, 36.04, 30.05, 29.24, 28.41 ppm.

HRMS (ESI) calculated for $[C_{12}H_{22}O_2+H]^+$: 199.1693, found: 199.1694.

2,2-dimethyldecan-5-one (Table 2, 3ao).



3ao

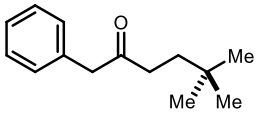
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3ao** as a colorless liquid (25.1 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (t, *J* = 7.5 Hz, 2H), 2.37–2.33 (m, 2H), 1.59–1.54 (m, 2H), 1.49–1.44 (m, 2H), 1.33–1.24 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.11, 42.94, 38.64, 37.62, 31.62, 30.09, 29.27, 23.78, 22.60, 14.05 ppm.

HRMS (ESI) calculated for $[C_{12}H_{24}O+H]^+$: 185.1900, found: 185.1901.

5,5-dimethyl-1-phenylhexan-2-one (Table 2, 3ap).



3ap

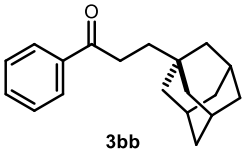
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3ap** as a colorless liquid (35.1 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.29–7.26 (m, 1H), 7.22–7.20 (m, 2H), 3.70 (s, 2H), 2.44–2.39 (m, 2H), 1.48–1.44 (m, 2H), 0.84 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.07, 134.57, 129.55, 128.83, 127.10, 50.24, 37.92, 37.54, 30.09, 29.21 ppm.

HRMS (ESI) calculated for $[C_{14}H_{20}O+H]^+$: 205.1587, found: 205.1588.

3-(adamantan-1-yl)-1-phenylpropan-1-one (Table 2, 3bb).



3bb

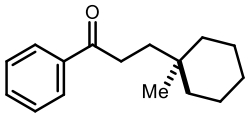
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ether in hexanes) to provide **3bb** as a colorless liquid (17.7 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 2.95–2.90 (m, 2H), 1.98 (s, 3H), 1.74–1.63 (m, 6H), 1.53 (s, 6H), 1.51 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.58, 137.19, 132.99, 128.69, 128.25, 42.40, 38.66, 37.25, 32.42, 32.24, 28.79 ppm.

HRMS (ESI) calculated for $[C_{19}H_{24}O+H]^+$: 269.1900, found: 269.1904.

3-(1-methylcyclohexyl)-1-phenylpropan-1-one (Table 2, 3bc).



3bc

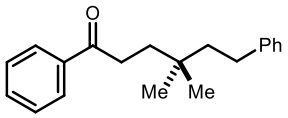
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3bc** as a colorless liquid (40.1 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 2.94–2.88 (m, 2H), 1.67 (dd, *J* = 9.5, 7.0 Hz, 2H), 1.51–1.41 (m, 5H), 1.31 (t, *J* = 5.8 Hz, 5H), 0.93 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.45, 137.22, 132.97, 128.68, 128.22, 37.82, 33.26, 32.60, 26.57, 22.14 ppm.

HRMS (ESI) calculated for $[C_{16}H_{22}O+H]^+$: 231.1743, found: 231.1745.

4,4-dimethyl-1,6-diphenylhexan-1-one (Table 2, 3bd).



3bd

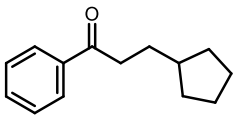
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3bd** as a colorless liquid (38.7 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.95 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (dd, *J* = 7.9, 3.4 Hz, 3H), 2.99–2.94 (m, 2H), 2.63–2.57 (m, 2H), 1.77–1.72 (m, 2H), 1.60–1.56 (m, 2H), 1.02 (s, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.04, 143.32, 137.18, 133.06, 128.72, 128.50, 128.43, 128.20, 125.77, 44.32, 36.04, 33.85, 32.92, 30.83, 27.08 ppm.

HRMS (ESI) calculated for $[C_{20}H_{24}O+H]^+$: 281.1900, found: 281.1903.

3-cyclopentyl-1-phenylpropan-1-one (Table 2, 3be).



3be

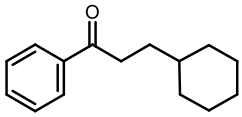
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3be** as a yellow liquid (26.3 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.00–2.95 (m, 2H), 1.88–1.77 (m, 3H), 1.74 (q, *J* = 7.2 Hz, 2H), 1.65–1.59 (m, 2H), 1.56–1.48 (m, 2H), 1.18–1.10 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.92, 137.17, 133.00, 128.68, 128.21, 39.95, 38.07, 32.72, 30.77, 25.28 ppm.

HRMS (ESI) calculated for $[C_{14}H_{18}O+H]^+$: 203.1430, found: 203.1429.

3-cyclohexyl-1-phenylpropan-1-one (Table 2, 3bf).



3bf

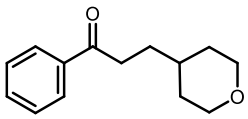
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3bf** as a colorless liquid (19.9 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.00–2.95 (m, 2H), 1.78–1.69 (m, 4H), 1.66–1.60 (m, 3H), 1.31 (ddt, *J* = 11.1, 7.6, 3.8 Hz, 1H), 1.19 (dtt, *J* = 27.2, 12.4, 3.3 Hz, 3H), 0.95 (qd, *J* = 12.0, 3.1 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.03, 137.23, 132.98, 128.68, 128.20, 37.58, 36.31, 33.35, 31.93, 26.71, 26.43 ppm.

HRMS (ESI) calculated for $[C_{15}H_{20}O+H]^+$: 217.1587, found: 217.1587.

1-phenyl-3-(tetrahydro-2*H*-pyran-4-yl)propan-1-one (Table 2, 3bg).



3bg

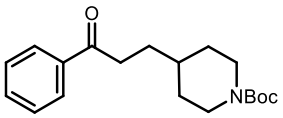
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to provide **3bg** as a colorless liquid (23.6 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.93 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.98–3.92 (m, 2H), 3.36 (td, *J* = 11.8, 2.1 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 1.70 (q, *J* = 7.1 Hz, 2H), 1.66–1.61 (m, 2H), 1.60–1.53 (m, 1H), 1.32 (qd, *J* = 12.3, 4.4 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.25, 136.95, 133.03, 128.63, 128.03, 68.00, 35.38, 34.59, 32.98, 31.11 ppm.

HRMS (ESI) calculated for $[C_{14}H_{18}O_2+H]^+$: 219.1380, found: 219.1379.

***tert*-butyl 4-(3-oxo-3-phenylpropyl)piperidine-1-carboxylate (Table 2, 3bh).**



3bh

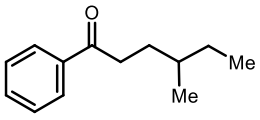
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 15% ethyl acetate in hexane) to provide **3bh** as a white solid (45.7 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.16–3.99 (m, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 12.1 Hz, 2H), 1.73–1.67 (m, 4H), 1.53–1.48 (m, 1H), 1.45 (s, 9H), 1.14 (qd, *J* = 12.4, 4.4 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.30, 155.01, 137.09, 133.15, 128.75, 128.16, 79.40, 35.79, 35.76, 30.85, 28.61 ppm.

HRMS (ESI) calculated for $[C_{19}H_{27}NO_3+Na]^+$: 340.1883, found: 340.1884.

4-methyl-1-phenylhexan-1-one (Table 2, 3bi).



3bi

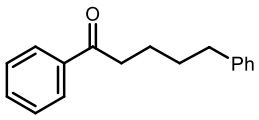
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3bi** as a colorless liquid (19.8 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H), 7.57–7.53 (m, 1H), 7.46 (dd, *J* = 8.4, 7.1 Hz, 2H), 3.02–2.90 (m, 2H), 1.82–1.74 (m, 1H), 1.59–1.53 (m, 1H), 1.46–1.37 (m, 2H), 1.24–1.18 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.98, 137.30, 132.98, 128.69, 128.21, 36.54, 34.40, 31.15, 29.46, 19.20, 11.48 ppm.

HRMS (ESI) calculated for $[C_{13}H_{18}O+H]^+$: 191.1430, found: 191.1430.

1,5-diphenylpentan-1-one (Table 2, 3bj).



3bj

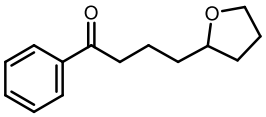
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3bj** as a colorless liquid (24.8 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22–7.17 (m, 3H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.85–1.79 (m, 2H), 1.77–1.71 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.35, 142.36, 137.20, 133.01, 128.67, 128.51, 128.42, 128.15, 125.86, 38.51, 35.92, 31.20, 24.11 ppm.

HRMS (ESI) calculated for $[C_{17}H_{18}O+H]^+$: 239.1430, found: 239.1430.

1-phenyl-4-(tetrahydrofuran-2-yl)butan-1-one (Table 2, 3bk).



3bk

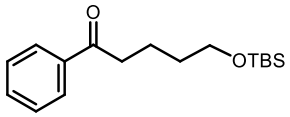
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to provide **3bk** as a colorless liquid (26.6 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 3.88–3.82 (m, 2H), 3.71 (q, *J* = 7.3 Hz, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.03–1.96 (m, 1H), 1.91–1.80 (m, 4H), 1.65–1.56 (m, 2H), 1.48 (m, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.37, 137.24, 133.03, 128.69, 128.18, 79.25, 67.82, 38.60, 35.28, 31.48, 25.84, 21.26 ppm.

HRMS (ESI) calculated for $[C_{14}H_{18}O_2+H]^+$: 219.1380, found: 219.1378.

5-((*tert*-butyldimethylsilyl)oxy)-1-phenylpentan-1-one (Table 2, 3bl).



3bl

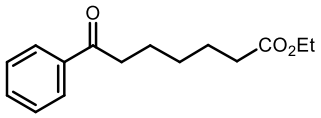
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3bl** as a colorless liquid (24.0 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 3.69 (t, *J* = 6.3 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 1.83 (p, *J* = 7.4 Hz, 2H), 1.66–1.62 (m, 2H), 0.92 (s, 9H), 0.07 (s, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.23, 133.00, 128.69, 128.19, 63.04, 38.50, 32.51, 26.10, 21.04, 18.47, -5.16 ppm.

HRMS (ESI) calculated for $[C_{17}H_{28}O_2Si+H]^+$: 293.1931, found: 293.1932.

ethyl 7-oxo-7-phenylheptanoate (Table 2, 3bm).



3bm

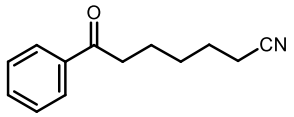
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to provide **3bm** as a colorless liquid (24.8 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.76 (q, *J* = 7.5 Hz, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.43 (p, *J* = 7.8 Hz, 2H), 1.24 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.34, 173.82, 137.21, 133.07, 128.72, 128.18, 60.37, 38.46, 34.33, 28.96, 24.94, 24.05, 14.39 ppm.

HRMS (ESI) calculated for $[C_{15}H_{20}O_3+H]^+$: 249.1485, found: 249.1487.

7-oxo-7-phenylheptanenitrile (Table 2, 3bn).



3bn

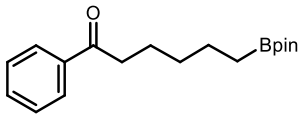
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 15% ethyl acetate in hexane) to provide **3bn** as a colorless liquid (29.4 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.58–7.53 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.81–1.75 (m, 2H), 1.74–1.69 (m, 2H), 1.57–1.50 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.84, 136.96, 133.19, 128.73, 128.08, 119.75, 38.13, 28.41, 25.41, 23.31, 17.13 ppm.

HRMS (ESI) calculated for $[C_{13}H_{15}NO+H]^+$: 202.1226, found: 202.1227.

1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (Table 2, 3bo).



3bo

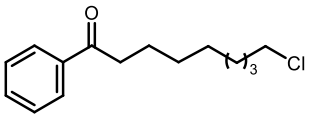
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **3bo** as a colorless liquid (32.6 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.95 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.00–2.95 (m, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.52–1.46 (m, 2H), 1.45–1.38 (m, 2H), 1.26 (s, 12H), 0.81 (t, *J* = 7.6 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.74, 137.31, 132.93, 128.65, 128.20, 83.04, 38.72, 32.21, 24.95, 24.34, 23.94 ppm.

HRMS (ESI) calculated for $[C_{18}H_{27}BO_3+H]^+$: 303.2126, found: 303.2127.

9-chloro-1-phenylnonan-1-one (Table 2, 3bp).



3bp

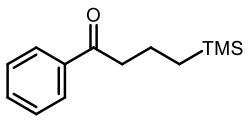
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3bp** as a colorless solid (21.7 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.79–1.70 (m, 4H), 1.45–1.32 (m, 8H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.59, 137.24, 132.99, 128.68, 128.16, 45.24, 38.67, 32.73, 29.41, 29.35, 28.84, 26.94, 24.41 ppm.

HRMS (ESI) calculated for $[C_{15}H_{21}ClO+H]^+$: 253.1354, found: 253.1353.

1-phenyl-4-(trimethylsilyl)butan-1-one (Table 2, 3bq).



3bq

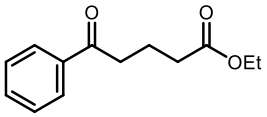
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **3bq** as a colorless liquid (23.8 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.57–7.53 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 7.3 Hz, 2H), 1.79–1.72 (m, 2H), 0.61–0.56 (m, 2H), 0.00 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.75, 137.36, 132.99, 128.70, 128.19, 42.46, 19.30, 16.85, -1.59 ppm.

HRMS (ESI) calculated for $[C_{13}H_{20}OSi+H]^+$: 221.1356, found: 221.1355.

ethyl 5-oxo-5-phenylpentanoate (Table 2, 3br).



3br

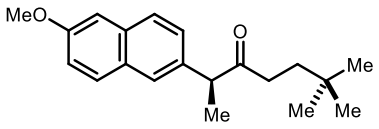
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to provide **3br** as a colorless liquid (26.0 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H), 7.58–7.54 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.08 (p, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.59, 173.41, 137.03, 133.20, 128.75, 128.18, 60.51, 37.64, 33.58, 19.59, 14.38 ppm.

HRMS (ESI) calculated for $[C_{13}H_{16}O_3+H]^+$: 221.1172, found: 221.1172.

(*S*)-2-(6-methoxynaphthalen-2-yl)-6,6-dimethylheptan-3-one (Scheme 1A, 4a).



4a

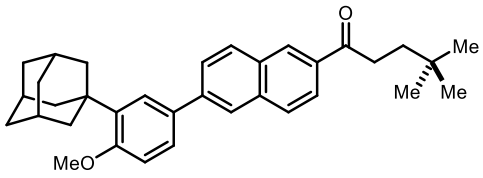
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **4a** as a beige solid (46.6 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.62–7.60 (m, 1H), 7.30 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.16 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 3.92 (q, *J* = 6.9 Hz, 1H), 3.91 (s, 3H), 2.35 (t, *J* = 8.3 Hz, 2H), 1.51–1.47 (m, 1H), 1.46 (d, *J* = 7.0 Hz, 3H), 1.38–1.31 (m, 1H), 0.77 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.84, 157.79, 136.06, 133.77, 129.31, 129.23, 127.58, 126.56, 126.55, 119.22, 105.74, 55.44, 53.02, 37.76, 37.01, 30.03, 29.15, 17.81 ppm.

HRMS (ESI) calculated for $[C_{20}H_{26}O_2+H]^+$: 299.2006, found: 299.2008.

1-(6-(3-((3*R*,5*R*,7*R*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-4,4-dimethylpentan-1-one (Scheme 1A, 4b).



4b

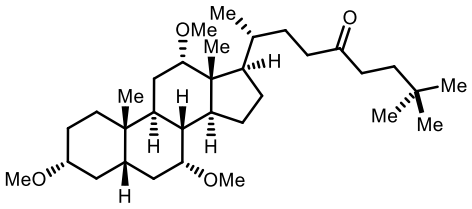
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **4b** as a beige solid (49.0 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.06–8.00 (m, 3H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.11–3.06 (m, 2H), 2.19 (d, *J* = 2.0 Hz, 6H), 2.11 (br s, 3H), 1.81 (br s, 6H), 1.74–1.70 (m, 2H), 1.01 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.10, 159.07, 141.61, 139.14, 136.07, 134.12, 132.61, 131.41, 130.04, 129.52, 128.60, 126.65, 126.08, 125.86, 124.84, 124.51, 112.22, 55.30, 40.72, 38.43, 37.34, 37.25, 34.48, 30.42, 29.43, 29.23 ppm.

HRMS (ESI) calculated for $[C_{34}H_{40}O_2+H]^+$: 481.3101, found: 481.3088.

(*R*)-2,2-dimethyl-8-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)nonan-5-one (Scheme 1A, 4c).



4c

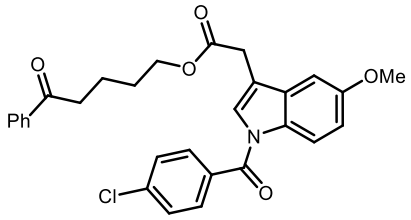
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **4c** as a colorless liquid (79.9 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (t, *J* = 2.9 Hz, 1H), 3.32 (s, 3H), 3.25 (s, 3H), 3.20 (s, 3H), 3.13 (q, *J* = 3.0 Hz, 1H), 3.02–2.94 (m, 1H), 2.46 (ddd, *J* = 15.3, 10.4, 4.6 Hz, 1H), 2.41–2.26 (m, 3H), 2.18 (q, *J* = 12.9 Hz, 1H), 2.05 (ddd, *J* = 24.0, 12.4, 8.1 Hz, 2H), 1.92 (q, *J* = 9.7 Hz, 1H), 1.84–1.72 (m, 6H), 1.70–1.64 (m, 2H), 1.58 (ddd, *J* = 14.9, 5.2, 3.1 Hz, 1H), 1.53–1.42 (m, 4H), 1.37–1.16 (m, 6H), 1.04–0.97 (m, 1H), 0.91–0.85 (m, 15H), 0.64 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.84, 82.12, 80.86, 77.07, 55.98, 55.80, 55.53, 46.20, 46.17, 42.80, 42.06, 39.72, 39.38, 38.61, 37.61, 35.38, 35.02, 34.97, 34.54, 30.08, 29.93, 29.27, 28.08, 27.87, 27.46, 26.84, 23.26, 22.98, 22.05, 17.70, 12.60 ppm.

HRMS (ESI) calculated for $[C_{33}H_{58}O_4+Na]^+$: 541.4227, found: 541.4238.

5-oxo-5-phenylpentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-1*H*-indol-3-yl)acetate (Scheme 1A, 4d).



4d

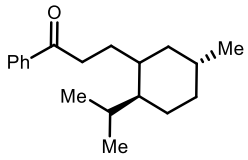
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 20% ethyl acetate in hexane) to provide **4d** as a white solid (46.4 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.91 (m, 2H), 7.67–7.64 (m, 2H), 7.58–7.54 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 4H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.15 (t, *J* = 6.2 Hz, 2H), 3.82 (s, 3H), 3.66 (s, 2H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.38 (s, 3H), 1.81–1.70 (m, 4H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.71, 171.07, 168.43, 156.14, 139.34, 136.95, 136.04, 134.02, 133.20, 131.30, 130.91, 130.76, 129.24, 128.74, 128.09, 115.09, 112.76, 111.75, 64.83, 55.82, 37.87, 30.50, 28.29, 20.57, 13.50 ppm.

HRMS (ESI) calculated for $[C_{29}H_{26}ClNO_5+H]^+$: 518.1729, found: 518.1736.

3-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-1-phenylpropan-1-one (Scheme 1A, 4e).



4e

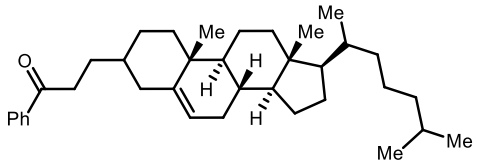
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **4e** as a colorless liquid (16.3 mg, 30%, dr = 1.3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H), 7.57–7.53 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.01 (dddd, *J* = 18.5, 15.9, 10.0, 5.7 Hz, 1H), 2.93–2.82 (m, 1H), 2.06–1.97 (m, 1H), 1.79–1.66 (m, 3H), 1.68–1.60 (m, 1H), 1.52–1.42 (m, 1H), 1.39–1.29 (m, 2H), 1.02–0.94 (m, 2H), 0.91–0.83 (m, 8H), 0.78–0.67 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.10, 137.32, 132.99, 132.97, 128.71, 128.69, 128.20, 48.55, 46.79, 41.32, 38.62, 38.37, 37.36, 36.02, 35.49, 35.42, 32.98, 27.40, 26.59, 26.13, 25.29, 24.46, 22.96, 22.94, 21.81, 21.75, 20.91, 20.18, 15.39 ppm.

HRMS (ESI) calculated for $[C_{19}H_{28}O+H]^+$: 273.2213, found: 273.2215.

3-((8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)-1-phenylpropan-1-one (Scheme 1A, 4f).



4f

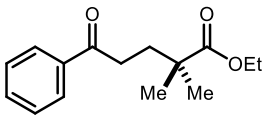
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **4f** as a white solid (46.3 mg, 46%, dr = 1.6:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.29 (s, 1H), 2.97 (ddd, *J* = 15.8, 9.5, 6.6 Hz, 1.37H), 2.85 (ddd, *J* = 15.8, 9.5, 5.8 Hz, 0.62H), 2.51 (d, *J* = 13.3 Hz, 0.61H), 2.02–0.98 (m, 36H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.2 Hz, 3H), 0.86 (d, *J* = 2.2 Hz, 3H), 0.68 (d, *J* = 3.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.02, 140.45, 133.00, 132.98, 128.70, 128.69, 128.27, 128.22, 121.64, 119.75, 57.02, 56.99, 56.35, 56.32, 50.65, 50.59, 42.48, 40.02, 39.99, 39.69, 39.67, 39.38, 37.60, 37.09, 36.89, 36.37, 36.29, 35.97, 35.95, 34.39, 34.15, 32.07, 31.72, 29.21, 28.40, 28.16, 26.49, 25.85, 24.44, 24.01, 23.99, 22.96, 22.71, 21.10, 20.91, 19.65, 19.61, 18.88, 12.01 ppm.

HRMS (ESI) calculated for $[C_{36}H_{54}O+Na]^+$: 525.4067, found: 525.4097.

ethyl 2,2-dimethyl-5-oxo-5-phenylpentanoate (Scheme 1B, 5aa).



5aa

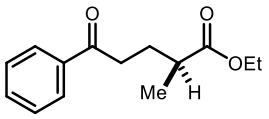
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **5aa** as a colorless liquid (37.7 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.96–2.91 (m, 2H), 2.00–1.95 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.97, 177.58, 136.95, 133.14, 128.70, 128.19, 60.60, 41.81, 34.75, 34.60, 25.37, 14.35 ppm.

HRMS (ESI) calculated for $[C_{15}H_{20}O_3+H]^+$: 249.1485, found: 249.1488.

ethyl 2-methyl-5-oxo-5-phenylpentanoate (Scheme 1B, 5ba).



5ba

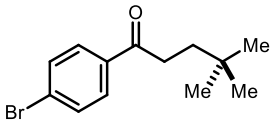
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **5ba** as a colorless liquid (29.5 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.92 (m, 2H), 7.57–7.53 (m, 1H), 7.47–7.42 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.07–2.93 (m, 2H), 2.59–2.51 (m, 1H), 2.09–2.01 (m, 1H), 1.95–1.87 (m, 1H), 1.25–1.20 (m, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.65, 176.37, 136.92, 133.16, 128.70, 128.13, 60.46, 39.01, 36.17, 28.03, 17.47, 14.35 ppm.

HRMS (ESI) calculated for $[C_{14}H_{18}O_3+H]^+$: 235.1329, found: 235.1331.

1-(4-bromophenyl)-4,4-dimethylpentan-1-one (Scheme 1C, 6aa).



6aa

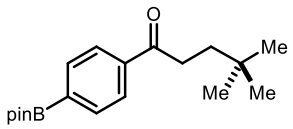
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to provide **6aa** as a white solid (34.5 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 2.92–2.87 (m, 2H), 1.64–1.60 (m, 2H), 0.95 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.11, 135.92, 132.02, 129.78, 128.13, 38.16, 34.41, 30.34, 29.35 ppm.

HRMS (ESI) calculated for $[C_{13}H_{17}BrO+H]^+$: 269.0536, found: 269.0539.

4,4-dimethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pentan-1-one (Scheme 1C, 6ba).



6ba

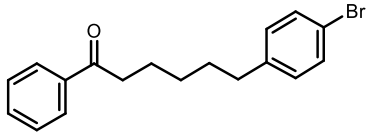
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **6ba** as a white solid (36.1 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (q, *J* = 8.0 Hz, 4H), 2.97–2.91 (m, 2H), 1.65–1.61 (m, 2H), 1.35 (s, 12H), 0.95 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.53, 139.14, 135.05, 127.20, 84.32, 38.22, 34.64, 30.34, 29.36, 25.01 ppm.

HRMS (ESI) calculated for $[C_{19}H_{29}BO_3+Na]^+$: 339.2102, found: 339.2154.

6-(4-bromophenyl)-1-phenylhexan-1-one (Scheme 1C, 6ca).



6ca

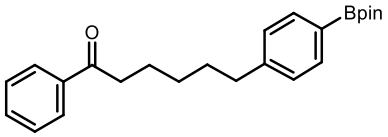
Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **6ca** as a white solid (45.1 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 2H), 7.58–7.54 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40–7.37 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.44–1.37 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.48, 141.61, 137.13, 133.08, 131.43, 130.31, 128.71, 128.16, 119.49, 38.58, 35.27, 31.28, 28.95, 24.19 ppm.

HRMS (ESI) calculated for $[C_{18}H_{19}BrO+H]^+$: 331.0692, found: 331.0696.

1-phenyl-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hexan-1-one (Scheme 1C, 6da).



6da

Following *General Procedure G*, the crude product was purified by silica gel chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to provide **6da** as a colorless liquid (43.9 mg, 58%).

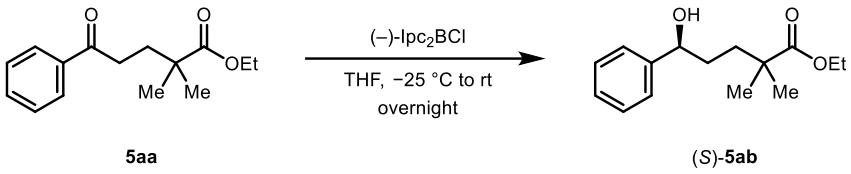
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 1.77 (p, *J* = 7.5 Hz, 2H), 1.68 (p, *J* = 7.7 Hz, 2H), 1.42 (p, *J* = 7.7 Hz, 2H), 1.34 (s, 12H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.53, 146.15, 137.23, 135.00, 133.01, 128.69, 128.18, 128.04, 83.76, 38.64, 36.11, 31.25, 29.10, 25.00, 24.31 ppm.

HRMS (ESI) calculated for $[C_{24}H_{31}BO_3+H]^+$: 379.2439, found: 379.2445.

6. Synthetic Applications

6.1. Enantioselective carbonyl reduction to access enantio-enriched alcohol[28]



5aa (*S*)-**5ab**

Ethyl (*S*)-5-hydroxy-2,2-dimethyl-5-phenylpentanoate (Scheme 1B (a), 5ab)

A flame-dried 25 mL round-bottom flask was equipped with a magnetic stir bar and phenone **5aa** (0.81 mmol) was added to the flask. The reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous tetrahydrofuran (5 mL) was added to the flask and magnetic stir bar was allowed to stir. The resulting solution was cooled to –25°C for 5 minutes. (–)-Ipc_2BCl (0.52 mL, 1.1 equiv, 60% in hexane) was added to the reaction solution via a syringe at –25°C, and the reaction mixture was allowed to stir at room temperature for overnight. After then, additional (–)-Ipc_2BCl (0.52 mL, 1.1 equiv, 60% in hexane) was added to the reaction solution and the mixture was stirred for a while. Then, the reaction mixture was quenched with diethanolamine (0.55 ml, 7.0 equiv) and the mixture was filtered through silica gel and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 15% ethyl acetate in hexane) to afford the desired product (*S*)-**5ab** as a colorless liquid (157.3 mg, 78% yield, 94% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 7.29–7.26 (m, 1H), 4.61 (dd, *J* = 7.2, 4.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.77–1.65 (m, 3H), 1.52–1.45 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 2.0 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.01, 144.65, 128.58, 127.69, 125.99, 74.86, 60.45, 42.01, 36.58, 34.57, 25.42, 25.11, 14.32 ppm.

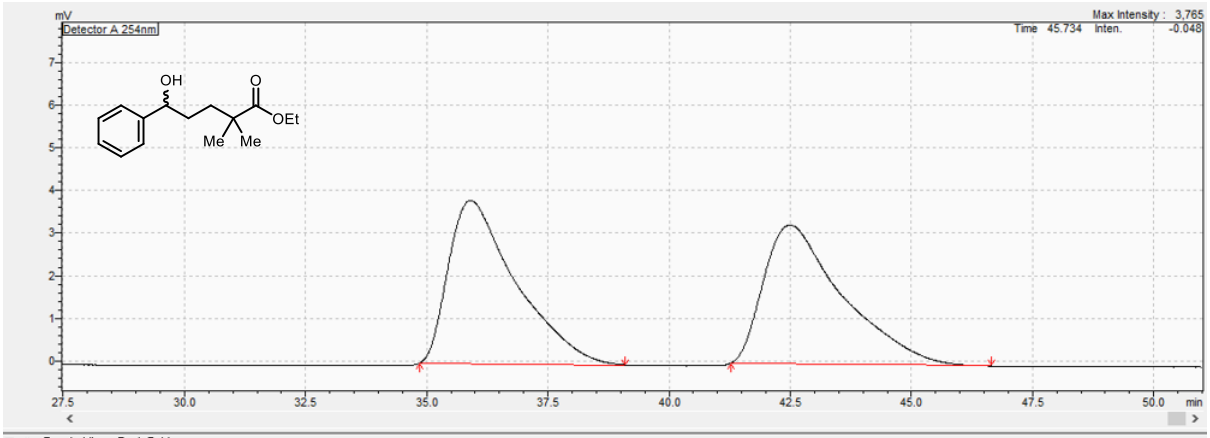
HRMS (ESI) calculated for $[C_{15}H_{22}O_3+Na]^+$: 273.1461, found: 273.1464.

Optical rotation, $[\alpha]_D^{22}$ = –22.7 (c = 0.45, $CHCl_3$).

The absolute stereochemistry of enantio-enriched alcohol was determined by comparing the optical rotation to literature values.[29]

Enantiomeric excess, 94% *ee* was measured by HPLC (CHIRALPAK OD-H, *n*-hexane : *i*-PrOH = 99 : 1, 1.0 mL/min, wavelength = 254 nm, 30 °C); t_R = 35.108 min (minor), t_R = 41.839 min (major).

[Racemic alcohol for **5ab**]

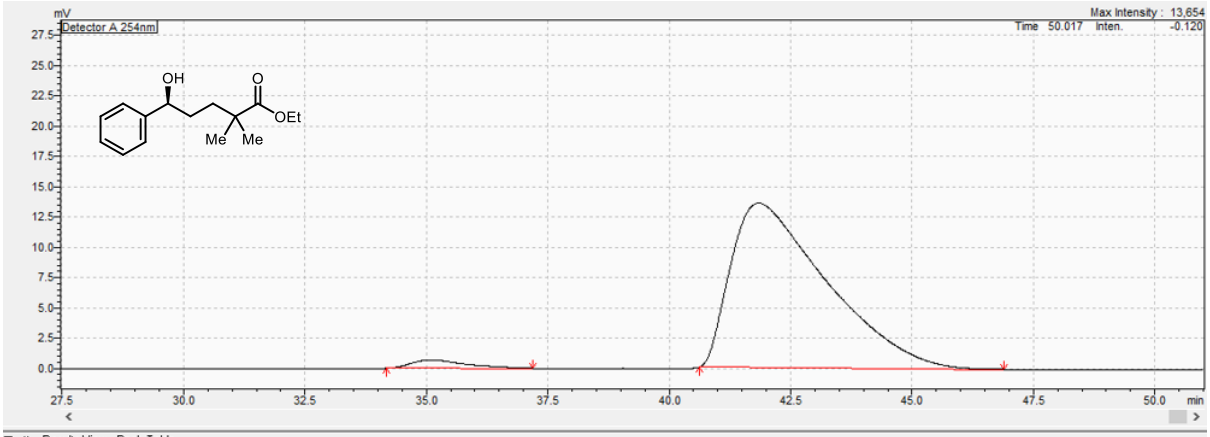


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Mark	USP Width	Area	Height	Area%
1	35,906	M	2,608	369885	3828	50,136
2	42,492	M	2,918	367877	3251	49,864
Total				737762	7080	100,000

[Enantioenriched alcohol for **5ab**]

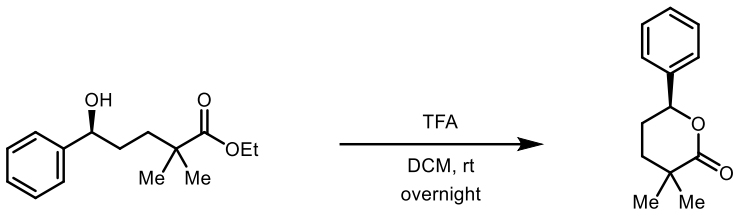


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Mark	USP Width	Area	Height	Area%
1	35,108	M	1,989	53465	692	2,791
2	41,839	M	3,831	1862149	13584	97,209
Total				1915614	14276	100,000

6.2. Acid-mediated lactonization to access α,α-dimethyl lactone[30]



(*S*)-**5ab** (*S*)-**5ac**

(*S*)-3,3-dimethyl-6-phenyltetrahydro-2*H*-pyran-2-one (Scheme 1B (a), 5ac)

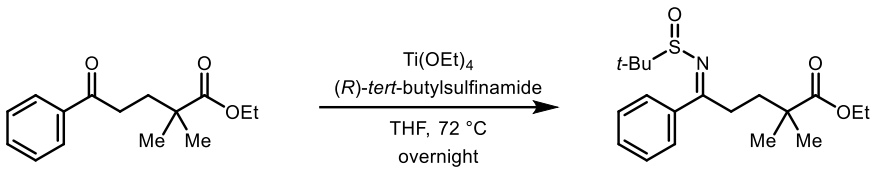
A flame-dried 25 mL round-bottom flask was equipped with a magnetic stir bar and (*S*)-**5ab** (0.19 mmol) was added to the flask. The reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous dichloromethane (2 mL) was added to the flask and magnetic stir bar was allowed to stir. Five drops of trifluoroacetic acid were added to the reaction solution via a syringe and the reaction mixture was allowed to stir at room temperature for overnight. After then, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ solution, and the two layers were separated. The aqueous layer was extracted with dichloromethane for two times, washed with water and brine, dried with $MgSO_4$, filtered and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to afford the desired product (*S*)-**5ac** as a white solid (24.5 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 5.37 (dd, *J* = 10.2, 3.8 Hz, 1H), 2.15–2.09 (m, 1H), 2.07–1.98 (m, 1H), 1.89 (td, *J* = 12.7, 11.8, 3.7 Hz, 1H), 1.82–1.76 (m, 1H), 1.37 (d, *J* = 9.4 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.32, 140.37, 128.70, 128.28, 125.65, 82.70, 38.35, 34.53, 28.77, 28.05, 27.92 ppm.

HRMS (ESI) calculated for $[C_{13}H_{16}O_2+H]^+$: 205.1223, found: 205.1223.

6.3. Installation of Ellman auxiliary to access *tert*-butylsulfinimine[31]



5aa (*R*)-**5ad**

Ethyl (*R*)-5-((tert-butylsulfinyl)imino)-2,2-dimethyl-5-phenylpentanoate (Scheme 1B (b), 5ad)

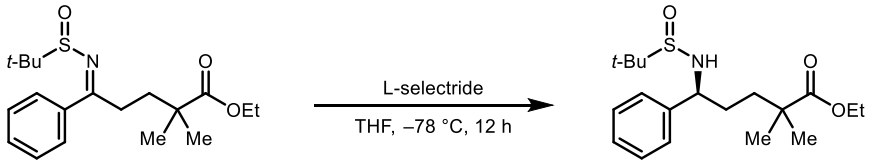
A flame-dried 25 mL round-bottom flask was equipped with a magnetic stir bar, and reflux condenser was placed on top of the round-bottom flask. **5aa** (1.21 mmol) and (*R*)-*tert*-butylsulfinamide (147 mg, 1.0 equiv) were added to the flask. Then, the reflux condenser and another neck of round-bottom flask were sealed with a rubber septum, and the reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous tetrahydrofuran (4 mL) was added to the flask and magnetic stir bar was allowed to stir. $Ti(OEt)_4$ (0.51 mL, 2.0 equiv) was added to the flask, and the reaction mixture was allowed to stir overnight at 72 °C. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, and the resulting solution was poured onto brine. The resulting suspension was filtered through a pad of celite, and the filter cake was washed with ethyl acetate. After concentration *in vacuo*, the crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to afford the desired product (*R*)-**5ad** as a yellow liquid (290 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.44 (dt, *J* = 27.2, 7.2 Hz, 3H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.18 (dtd, *J* = 60.1, 12.1, 5.8 Hz, 2H), 1.92–1.83 (m, 2H), 1.33–1.22 (m, 18H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.51, 177.51, 137.72, 131.73, 128.67, 127.62, 60.69, 57.61, 42.43, 38.50, 28.69, 25.57, 24.75, 22.75, 14.33 ppm.

HRMS (ESI) calculated for $[C_{19}H_{29}NO_3S+H]^+$: 352.1941, found: 352.1945.

6.4. Enantioselective hydride addition to access enantio-enriched amine[32]



(*R*)-**5ad** (*R*,*S*)-**5ae**

Ethyl (5*S*)-5-(((*R*)-tert-butylsulfinyl)amino)-2,2-dimethyl-5-phenylpentanoate (Scheme 1B (b), 5ae)

A flame-dried 10 mL round-bottom flask was equipped with a magnetic stir bar and (*R*)-**5ad** (0.28 mmol) was added to the flask. The reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous tetrahydrofuran (2 mL) was added to the flask and magnetic stir bar was allowed to stir. The resulting solution was cooled to –78 °C for 5 minutes. L-selectride (0.34 mL, 1.2 equiv, 1.0 M in tetrahydrofuran) was added dropwise via a syringe, and the reaction mixture was allowed to stir at –78 °C for 12 hours. After then, the reaction mixture was quenched with aqueous saturated NH_4Cl solution, and the two layers were separated. The aqueous layer was extracted with ethyl acetate for two times, washed with water and brine, dried with $MgSO_4$, filtered and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 30% ethyl acetate in hexane) to afford the desired product (*R*,*S*)-**5ae** as a white solid (92.4 mg, 92% yield) as a sole diastereomer.

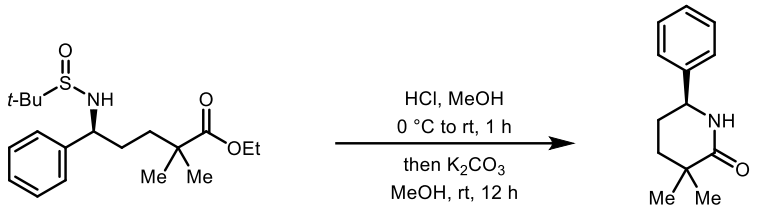
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.29–7.26 (m, 3H), 4.30 (td, *J* = 7.0, 1.8 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 1H), 1.74–1.69 (m, 2H), 1.59–1.51 (m, 1H), 1.35–1.28 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.17 (s, 9H), 1.10 (d, *J* = 16.3 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.66, 141.86, 128.58, 127.78, 60.53, 59.35, 55.62, 42.04, 36.60, 34.41, 25.47, 25.08, 22.67, 14.32 ppm.

HRMS (ESI) calculated for $[C_{19}H_{31}NO_3S+H]^+$: 354.2097, found: 354.2102.

The absolute stereochemistry of sulfonamide was determined by comparing the optical rotation to literature values.[33]

6.5. Auxiliary removal and lactamization to access α,α-dimethyl lactam[32]



(*R*,*S*)-**5ae** (*S*)-**5af**

(*S*)-3,3-dimethyl-6-phenylpiperidin-2-one (Scheme 1B (b), 5af)

A flame-dried 10 mL round-bottom flask was equipped with a magnetic stir bar and (*R,S*)-**5ae** (0.14 mmol) was added to the flask. The reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous methanol (1 mL) was added to the flask and magnetic stir bar was allowed to stir. The resulting solution was cooled to 0 °C for 5 minutes. A solution of hydrogen chloride in methanol (0.85 mL, 3.0 equiv, 0.5 M in methanol) was added to the flask via a syringe, and the reaction mixture was allowed to stir at room temperature for 1 hour. After then, the solvents were removed under reduced pressure. The residue was dissolved in anhydrous methanol (1 mL), and K_2CO_3 was added to the flask. The reaction mixture was allowed to stir at room temperature for 12 hours. After then, the resulting suspension was filtered through a pad of celite, and the filter cake was washed with ethyl acetate. After concentration *in vacuo*, the crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 25% ethyl acetate in hexane) to afford the desired product (*S*)-**5af** as a white solid (25.5 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.4 Hz, 2H), 7.31–7.26 (m, 3H), 5.75 (s, 1H), 4.54 (dd, *J* = 8.8, 4.9 Hz, 1H), 2.09–2.03 (m, 1H), 1.86–1.78 (m, 1H), 1.76–1.68 (m, 2H), 1.29 (d, *J* = 11.8 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.61, 142.81, 128.92, 128.00, 126.11, 58.35, 37.75, 34.73, 29.31, 27.38, 27.30 ppm.

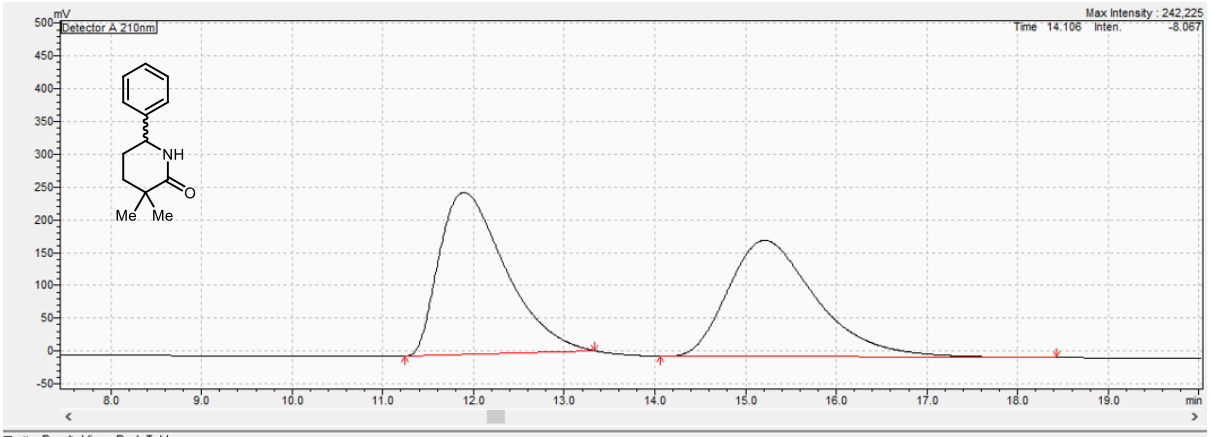
HRMS (ESI) calculated for $[C_{13}H_{17}NO+H]^+$: 204.1383, found: 204.1382.

Optical rotation, $[\alpha]_D^{22} = -12.5$ (c = 1.02, $CHCl_3$).

The absolute stereochemistry of enantio-enriched lactam was determined by comparing the optical rotation to literature values.[34]

Enantiomeric excess, >99% *ee* was measured by HPLC (CHIRALPAK OJ-H, *n*-hexane : *i*-PrOH = 97 : 3, 1.0 mL/min, wavelength = 210 nm, 28 °C); t_R = 11.838 min (major), t_R = 15.212 min (minor).

[Racemic lactam for **5af**]

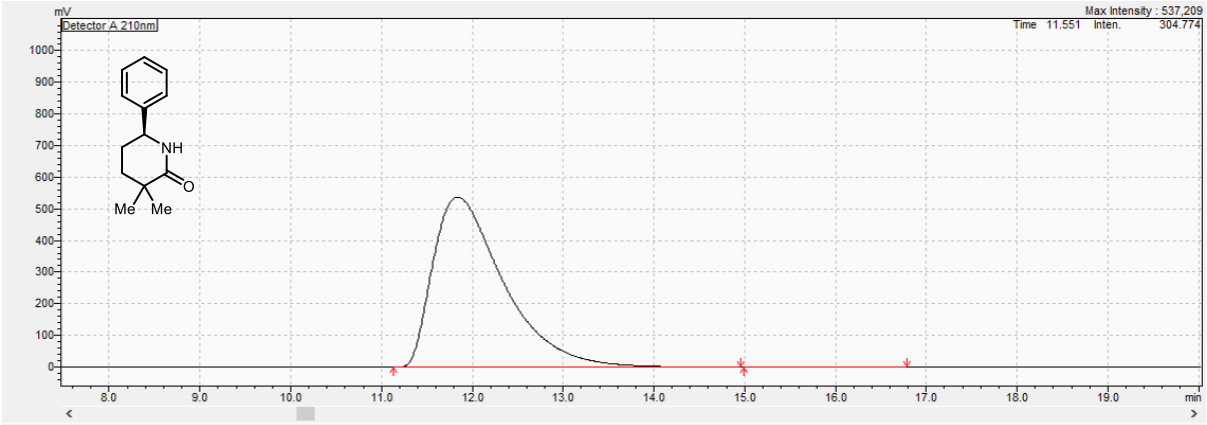


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Mark	USP Width	Area	Height	Area%
1	11,896	M	1,331	12600243	247730	51,269
2	15,212	M	1,736	11976638	177414	48,731
Total				24576881	425144	100,000

[Enantioenriched lactam for **5af**]

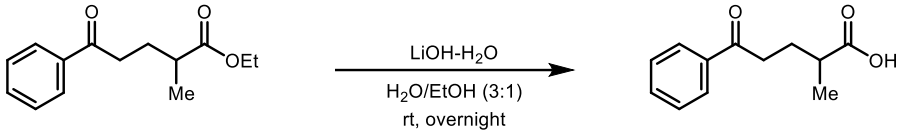


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Mark	USP Width	Area	Height	Area%
1	11,838	M	1,374	29164720	537917	99,973
2	15,667	M	1,228	7821	171	0,027
Total				29172541	538088	100,000

6.6. Hydrolysis of ethyl ester to access carboxylic acid[33]



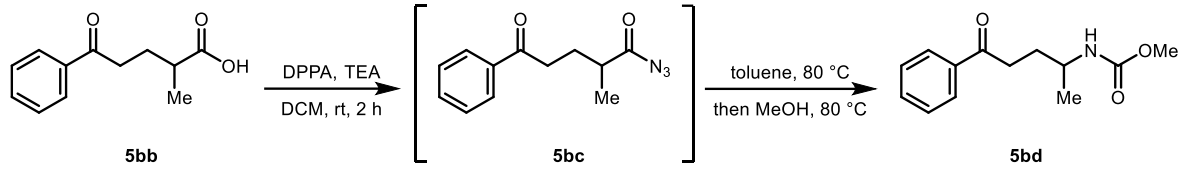
5ba **5bb**

2-methyl-5-oxo-5-phenylpentanoic acid (Scheme 1B, 5bb)

A 20 mL vial was equipped with a magnetic stir bar and **5ba** (0.24 mmol) was added to the vial. Ethanol (0.5 mL) was added to the reaction vessel, and was allowed to stir to dissolve the substrate. Then, water (1.5 mL) was added to the vial, and white cloudy solution appeared. To the resulting solution, lithium hydroxide monohydrate (49.5 mg, 5.0 equiv) was added in one portion and the reaction mixture was allowed to stir at room temperature for overnight. After then, the solution was acidified with aqueous 1.0 M HCl to pH 1.0 – 2.0, and the two layers were separated. The aqueous layer was extracted with diethyl ether three times, washed with water, dried with $MgSO_4$, filtered and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 40% ethyl acetate in hexane) to afford the desired product **5bb** as a white solid (48.8 mg, 99% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 3.13–2.99 (m, 2H), 2.61 (dq, *J* = 14.1, 7.0 Hz, 1H), 2.13–2.04 (m, 1H), 1.95 (ddt, *J* = 12.0, 8.9, 6.0 Hz, 1H), 1.26 (d, *J* = 7.1 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ 199.63, 182.75, 136.82, 133.25, 128.71, 128.15, 38.83, 36.09, 27.69, 17.31 ppm.
HRMS (ESI) calculated for $[C_{12}H_{14}O_3\text{-}H]^-$: 205.0870, found: 205.0866.

6.7. Acyl substitution, Curtius rearrangement and nucleophilic addition to access methyl carbamate[34]



5bb **5bc** **5bd**

Methyl (5-oxo-5-phenylpentan-2-yl)carbamate (Scheme 1B (c), 5bd)

A 20 mL vial was equipped with a magnetic stir bar and **5bb** (0.4 mmol) was added to the vial. The reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous dichloromethane (3.0 mL) was added to the reaction vessel, and was allowed to stir to dissolve the substrate. Then, triethylamine (70 µL, 1.2 equiv) and diphenylphosphoryl azide (95 µL, 1.1 equiv) were added to the vial, and the reaction mixture was allowed to stir at room temperature for 2 hours. After then, the solution was quenched with aqeous saturated $NaHCO_3$ solution, and the two layers were separated. The aqueous layer was extracted with dichloromethane three times, washed with water and brine, dried with $MgSO_4$, filtered and concentrated *in vacuo* to give crude acyl azide (**5bc**) product, and was used for the next reaction without further purification.

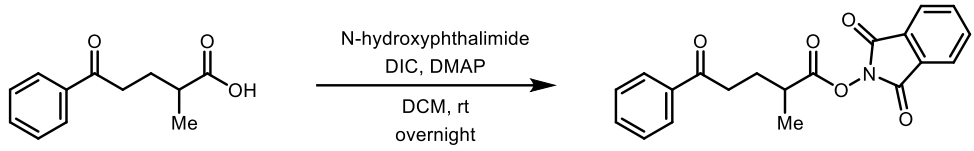
To a 20 mL vial equipped with a magnetic stir bar was added crude acyl azide (**5bc**) mixture and the reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous toluene (2.5 mL) was added to dissolve the substrate and methanol (0.5 mL) was added to the solution. The reaction mixture was heated at 80 °C for overnight. After then, solvents were removed *in vacuo*, and the crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes, 10% ethyl acetate in hexane to 30% ethyl acetate in hexane) to afford the desired product **5bd** as a white solid (43.4 mg, 46% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.61 (s, 1H), 3.84–3.73 (m, 1H), 3.60 (s, 3H), 3.06 (t, *J* = 7.2 Hz, 2H), 1.99–1.81 (m, 2H), 1.21 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.14, 156.75, 136.95, 133.24, 128.73, 128.18, 52.07, 47.39, 35.58, 31.24, 21.92 ppm.

HRMS (ESI) calculated for $[C_{13}H_{17}NO_3+H]^+$: 236.1281, found: 236.1285.

6.8. Esterification to access redox-active ester[35]



5bb **5be**

1,3-dioxoisoindolin-2-yl 2-methyl-5-oxo-5-phenylpentanoate (Scheme 1B (d), 5be)

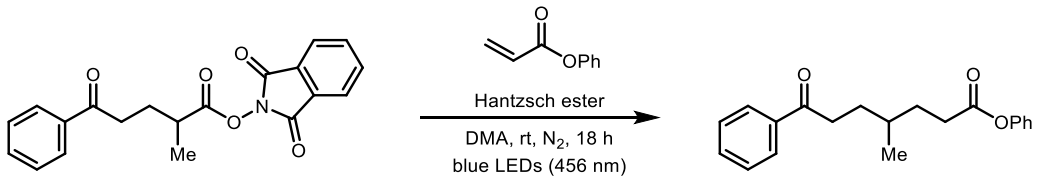
A 20 mL vial was equipped with a magnetic stir bar, and **5bb** (0.16 mmol), N-hydroxyphthalimide (29 mg, 1.1 equiv), and 4-(dimethylamino)pyridine (2.0 mg, 0.1 equiv) were added to the vial. The reaction vessel was evacuated and backfilled with inert gas three times and was kept under inert atmosphere by adding balloon containing inert gas. Anhydrous dichloromethane (2 mL) was added to the vessel and magnetic stir bar was allowed to stir. Diisopropylcarbodiimide (30 µL, 1.1 equiv) was added dropwise via a syringe, and the reaction mixture was allowed to stir at room temperature for overnight. After then, the reaction mixture was concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 20% ethyl acetate in hexane) to afford the desired product **5be** as a white solid (51 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.01 (m, 2H), 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.58–7.54 (m, 1H), 7.47 (dd, *J* = 8.4, 7.0 Hz, 2H), 3.30–3.18 (m, 2H), 3.05–2.97 (m, 1H), 2.24–2.08 (m, 2H), 1.43 (d, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.23, 172.62, 162.11, 136.83, 134.90, 133.26, 129.02, 128.74, 128.25, 124.08, 36.69, 35.59, 28.20, 17.48 ppm.

HRMS (ESI) calculated for $[C_{20}H_{17}NO_5+H]^+$: 352.1180, found: 352.1186.

6.9. Photochemical Giese addition to access 1,4-adduct[36]



5be **5bf**

Phenyl 4-methyl-7-oxo-7-phenylheptanoate (Scheme 1B (d), 5bf)

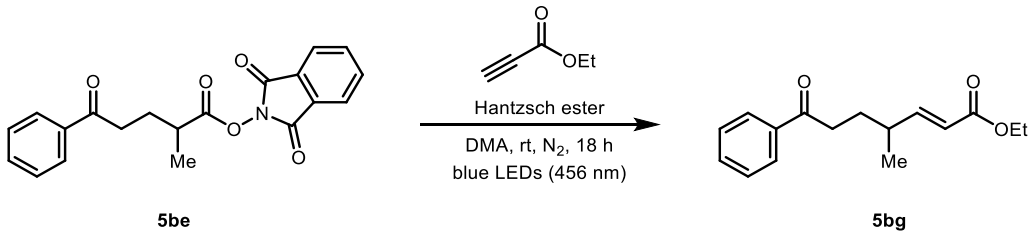
In a glovebox, a 4 mL vial was equipped with a magnetic stir bar, and Hantzsch ester (40 mg, 1.5 equiv) and **5be** (0.1 mmol) were added to the vial. Anhydrous *N*,*N*-dimethylacetamide (1 mL) and phenyl acrylate (21 μL, 1.5 equiv) were added via a syringe and a gastight syringe, respectively, and the reaction mixture was sealed with a screw cap. The reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours. The resulting mixture was diluted with sat. aqueous sodium chloride and 1.0 M HCl, and was extracted with diethyl ether three times. The organic layer was washed with 1.0 M HCl three times and water, dried with $MgSO_4$, filtered and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to afford the desired product **5bf** as a beige liquid (18.4 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 3.08–2.97 (m, 2H), 2.68–2.55 (m, 2H), 1.86 (ddt, *J* = 15.3, 11.6, 5.9 Hz, 2H), 1.68–1.60 (m, 3H), 1.02 (d, *J* = 5.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.46, 172.51, 150.82, 137.08, 133.11, 129.53, 128.72, 128.16, 125.87, 121.68, 36.21, 32.31, 32.18, 31.72, 30.92, 19.37 ppm.

HRMS (ESI) calculated for $[C_{20}H_{22}O_3+H]^+$: 311.1642, found: 311.1649.

6.10. Photochemical Giese addition to access α,β-unsaturated ester[36]



5be **5bg**

Ethyl (E)-4-methyl-7-oxo-7-phenylhept-2-enoate (Scheme 1B (d), 5bg)

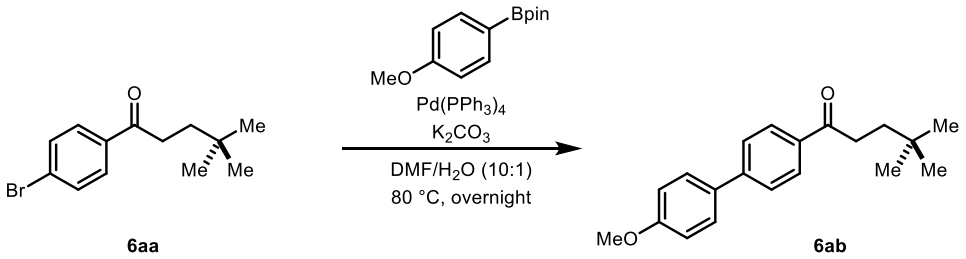
In a glovebox, a 4 mL vial was equipped with a magnetic stir bar, and Hantzsch ester (40 mg, 1.5 equiv) and **5be** (0.1 mmol) were added to the vial. Anhydrous *N*,*N*-dimethylacetamide (1 mL) and ethyl propiolate (15 μL, 1.5 equiv) were added via a syringe and a gastight syringe, respectively, and the reaction mixture was sealed with a screw cap. The reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours. The resulting mixture was diluted with sat. aqueous sodium chloride and 1.0 M HCl, and was extracted with diethyl ether three times. The organic layer was washed with 1.0 M HCl three times and water, dried with $MgSO_4$, filtered and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to afford the desired product (*E*)-**5bg** as a colorless liquid (10.4 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.86 (dd, *J* = 15.7, 8.1 Hz, 1H), 5.81 (d, *J* = 15.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.99–2.91 (m, 2H), 2.46–2.39 (m, 1H), 1.92–1.84 (m, 1H), 1.84–1.76 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.87, 166.84, 153.54, 137.02, 133.20, 128.74, 128.13, 120.71, 60.43, 36.29, 36.15, 30.18, 19.78, 14.40 ppm.

HRMS (ESI) calculated for $[C_{16}H_{20}O_3+H]^+$: 261.1485, found: 261.1492.

6.11. Palladium-catalysed Suzuki-Miyaura cross-coupling to access biaryls[37]



1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4-dimethylpentan-1-one (Scheme 1C (a), 6ab)

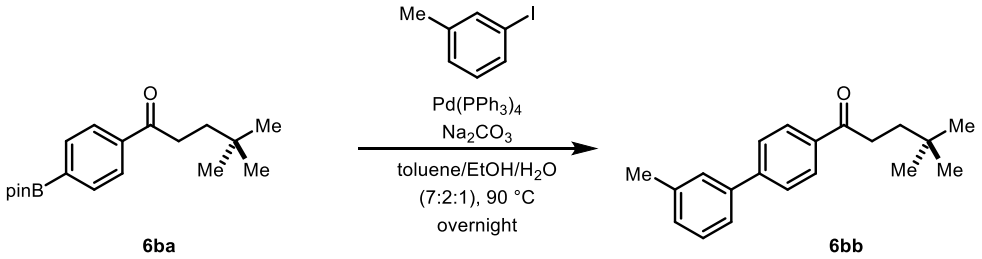
In a glovebox, an oven-dried 20 mL vial was equipped with a magnetic stir bar. $Pd(PPh_3)_4$ (2.2 mg, 0.05 equiv), K_2CO_3 (10.5 mg, 2.0 equiv), and **6aa** (0.038 mmol) were added to the vial. Anhydrous *N*,*N*-dimethylformamide (2 mL) was added, followed by 4-methoxyphenylboronic acid pinacol ester (13 µL, 1.5 equiv). The vial was sealed with a rubber cap and kept under inert atmosphere by adding balloon containing inert gas. Water (0.2 mL) was added to the vial, and the reaction mixture was allowed to stir overnight at 80 °C. After then, the resulting suspension was filtered through a pad of celite, and the filter cake was washed with ethyl acetate. The resulting mixture was transferred to separatory funnel and the organic layer was washed with water for four times and brine. The mixture was dried with $MgSO_4$, filtered, and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to afford the desired product **6ab** as a white solid (5.5 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 2.98–2.93 (m, 2H), 1.68–1.64 (m, 2H), 0.97 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.84, 160.01, 145.28, 135.32, 132.47, 128.87, 128.50, 126.77, 114.54, 55.53, 38.43, 34.47, 30.40, 29.38 ppm.

HRMS (ESI) calculated for $[C_{20}H_{24}O_2+H]^+$: 297.1849, found: 297.1850.

6.12. Palladium-catalysed Suzuki-Miyaura cross-coupling to access biaryls[38]



6ba **6bb**

4,4-dimethyl-1-(3'-methyl-[1,1'-biphenyl]-4-yl)pentan-1-one (Scheme 1C (a), 6bb)

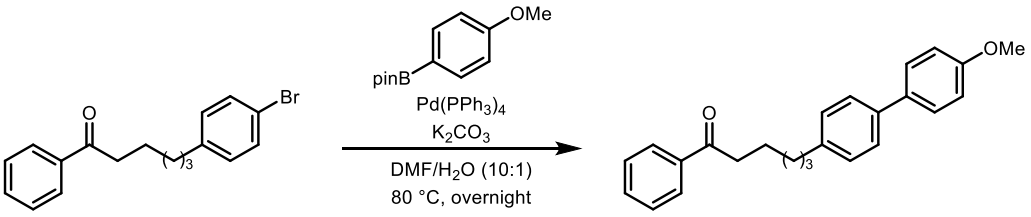
In a glovebox, an oven-dried 20 mL vial was equipped with a magnetic stir bar. $Pd(PPh_3)_4$ (6.4 mg, 0.05 equiv), Na_2CO_3 (23.3 mg, 2.0 equiv), and **6ba** (0.11 mmol) were added to the vial. Anhydrous toluene (1.4 mL) was added, followed by 3-iodotoluene (17 µL, 1.2 equiv). The vial was sealed with a rubber cap and kept under inert atmosphere by adding balloon containing inert gas. Ethanol (0.4 mL) and water (0.2 mL) was added to the vial, and the reaction mixture was allowed to stir overnight at 90 °C. After then, the resulting suspension was filtered through a pad of celite, and the filter cake was washed with ethyl acetate. The resulting mixture was transferred to separatory funnel and the organic layer was washed with water and brine. The mixture was dried with $MgSO_4$, filtered, and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 3% ethyl acetate in hexane) to afford the desired product **6bb** as a white solid (16.8 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.01 (m, 2H), 7.70–7.66 (m, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 2.99–2.94 (m, 2H), 2.44 (s, 3H), 1.70–1.65 (m, 2H), 0.98 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.85, 145.84, 140.08, 138.72, 135.84, 129.06, 128.98, 128.77, 128.15, 127.36, 124.51, 38.39, 34.50, 30.39, 29.38, 21.66 ppm.

HRMS (ESI) calculated for $[C_{20}H_{24}O+H]^+$: 281.1900, found: 281.1902.

6.13. Palladium-catalysed Suzuki-Miyaura cross-coupling to access biaryls[37]



6ca **6cb**

6-(4'-methoxy-[1,1'-biphenyl]-4-yl)-1-phenylhexan-1-one (Scheme 1C (b), 6cb)

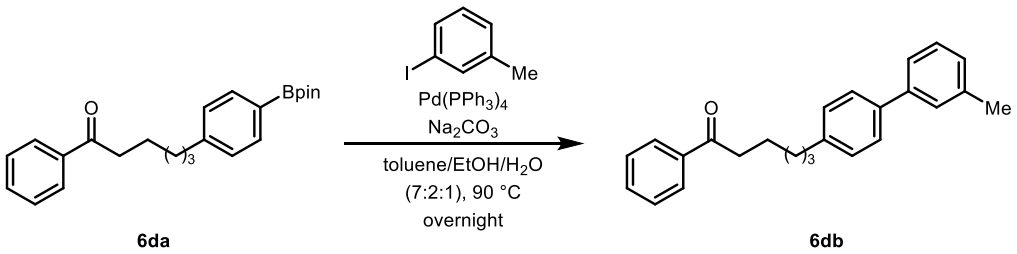
In a glovebox, an oven-dried 20 mL vial was equipped with a magnetic stir bar. $Pd(PPh_3)_4$ (6.4 mg, 0.05 equiv), K_2CO_3 (30.4 mg, 2.0 equiv), and **6ca** (0.11 mmol) were added to the vial. Anhydrous *N*,*N*-dimethylformamide (3 mL) was added, followed by 4-methoxyphenylboronic acid pinacol ester (38 µL, 1.5 equiv). The vial was sealed with a rubber cap and kept under inert atmosphere by adding balloon containing inert gas. Water (0.3 mL) was added to the vial, and the reaction mixture was allowed to stir overnight at 80 °C. After then, the resulting suspension was filtered through a pad of celite, and the filter cake was washed with ethyl acetate. The resulting mixture was transferred to separatory funnel and the organic layer was washed with water for four times and brine. The mixture was dried with $MgSO_4$, filtered, and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 10% ethyl acetate in hexane) to afford the desired product **6cb** as a white solid (24.1 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.95 (m, 2H), 7.58–7.51 (m, 3H), 7.48–7.44 (m, 4H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.98–6.96 (m, 2H), 3.85 (s, 3H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.80 (p, *J* = 7.5 Hz, 2H), 1.72 (p, *J* = 7.7 Hz, 2H), 1.50–1.44 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.59, 159.04, 141.19, 138.37, 137.16, 133.83, 133.04, 128.92, 128.69, 128.18, 128.09, 126.73, 114.27, 55.46, 38.65, 35.49, 31.46, 29.14, 24.31 ppm.

HRMS (ESI) calculated for $[C_{25}H_{26}O_2+H]^+$: 359.2006, found: 359.2011.

6.14. Palladium-catalysed Suzuki-Miyaura cross-coupling to access biaryls[38]



6da **6db**

6-(3'-methyl-[1,1'-biphenyl]-4-yl)-1-phenylhexan-1-one (Scheme 1C (b), 6db)

In a glovebox, an oven-dried 20 mL vial was equipped with a magnetic stir bar. $Pd(PPh_3)_4$ (5.2 mg, 0.05 equiv), Na_2CO_3 (19 mg, 2.0 equiv), and **6da** (0.09 mmol) were added to the vial. Anhydrous toluene (2.1 mL) was added, followed by 3-iodotoluene (14 µL, 1.2 equiv). The vial was sealed with a rubber cap and kept under inert atmosphere by adding balloon containing inert gas. Ethanol (0.6 mL) and water (0.3 mL) was added to the vial, and the reaction mixture was allowed to stir overnight at 90 °C. After then, the resulting suspension was filtered through a pad of celite, and the filter cake was washed with ethyl acetate. The resulting mixture was transferred to separatory funnel and the organic layer was washed with water and brine. The mixture was dried with $MgSO_4$, filtered, and concentrated *in vacuo* to give crude product mixture. The crude mixture was purified by silica gel flash column chromatography (gradient elution: full hexanes to 5% ethyl acetate in hexane) to afford the desired product **6db** as a white solid (24 mg, 78% yield).

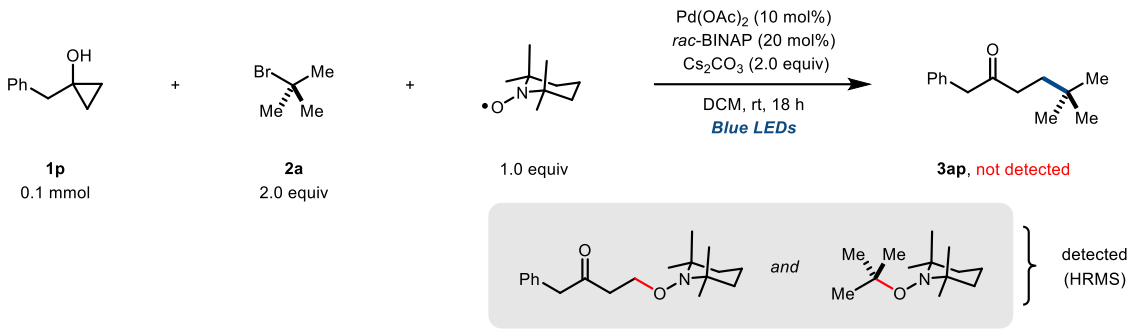
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.62–7.45 (m, 6H), 7.44–7.38 (m, 2H), 7.35–7.31 (m, 1H), 7.24 (d, *J* = 5.8 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.43 (s, 3H), 1.81 (p, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.7 Hz, 2H), 1.48 (p, *J* = 7.7 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.56, 141.73, 141.27, 138.89, 138.37, 137.21, 133.03, 128.96, 128.89, 128.83, 128.73, 128.69, 128.18, 127.94, 127.85, 127.16, 127.11, 124.23, 38.65, 35.53, 31.42, 29.15, 24.32, 21.68 ppm.

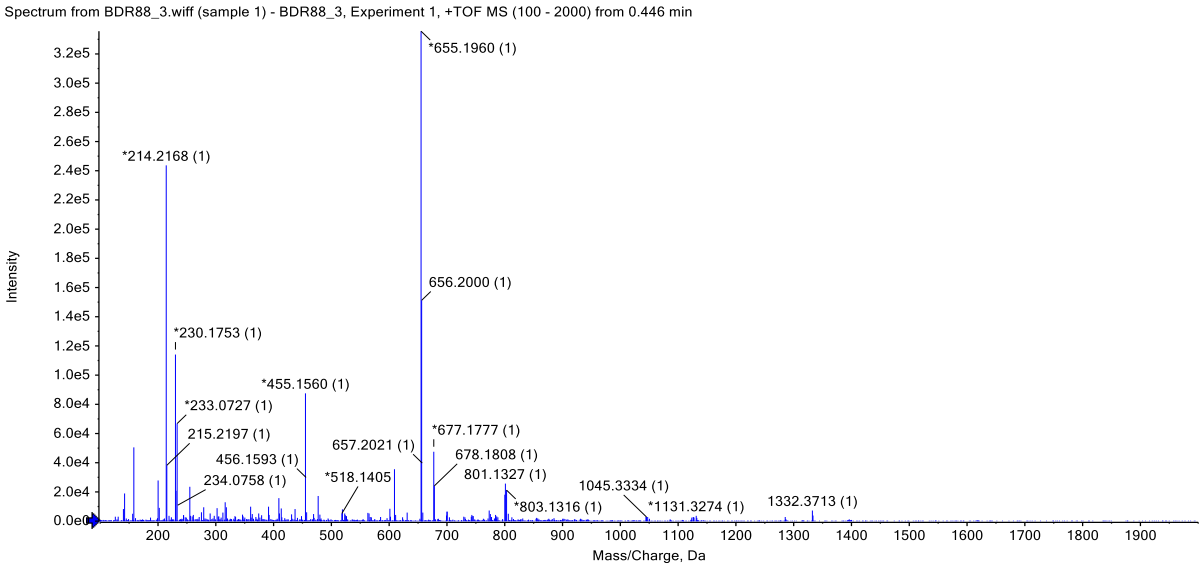
HRMS (ESI) calculated for $[C_{25}H_{26}O+H]^+$: 343.2056, found: 343.2059.

7. Mechanistic Investigations

7.1. Control experiment with radical scavanger (**Scheme 2A**).



In a nitrogen-filled glovebox, to the 4 mL oven-dried vial with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.2 mg), *rac*-BINAP (0.02 mmol, 20 mol%, 12 mg), Cs_2CO_3 (0.2 mmol, 2.0 equiv, 65 mg), TEMPO (0.1 mmol, 1.0 equiv, 15.6 mg), and anhydrous dichloromethane (DCM) (0.4 mL). In a separate 4 mL vial, **1p** (0.1 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (0.2 mL) and then, the solution of **1p** and **2a** (0.2 mmol, 2.0 equiv, 22.5 µL) was added to the reaction mixture sequentially using a gastight syringe. The vial was then sealed with screw cap and then, the reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours outside the glovebox. The crude mixture was then diluted with ethyl acetate and filtered through a short pad of silica. After evaporation of the remaining solvent, the filtrate was diluted in methanol for HRMS analysis.



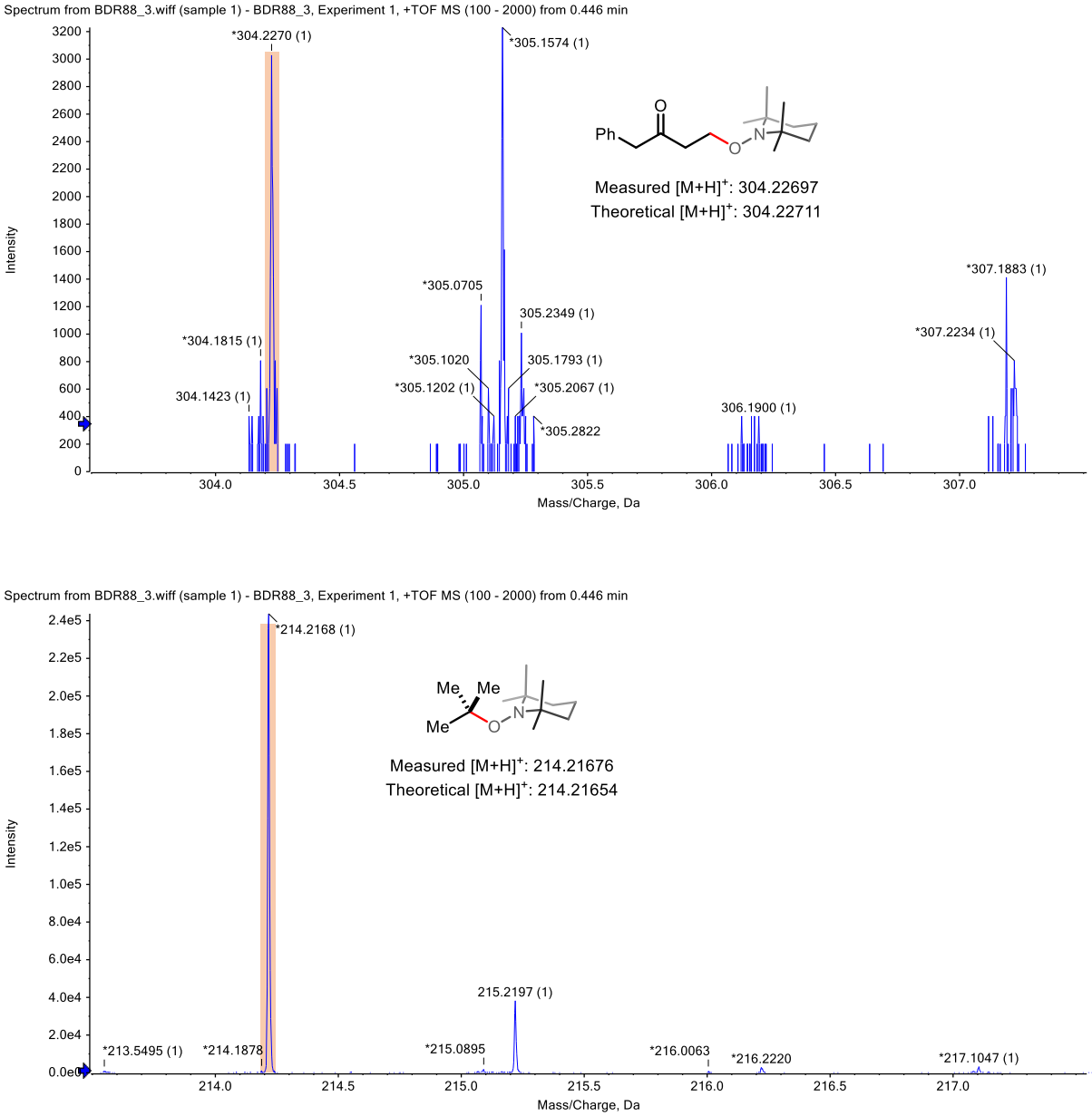
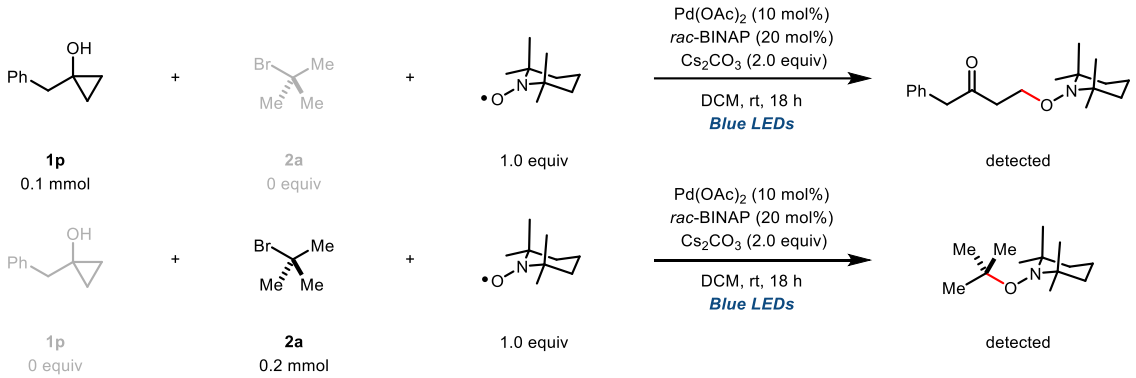
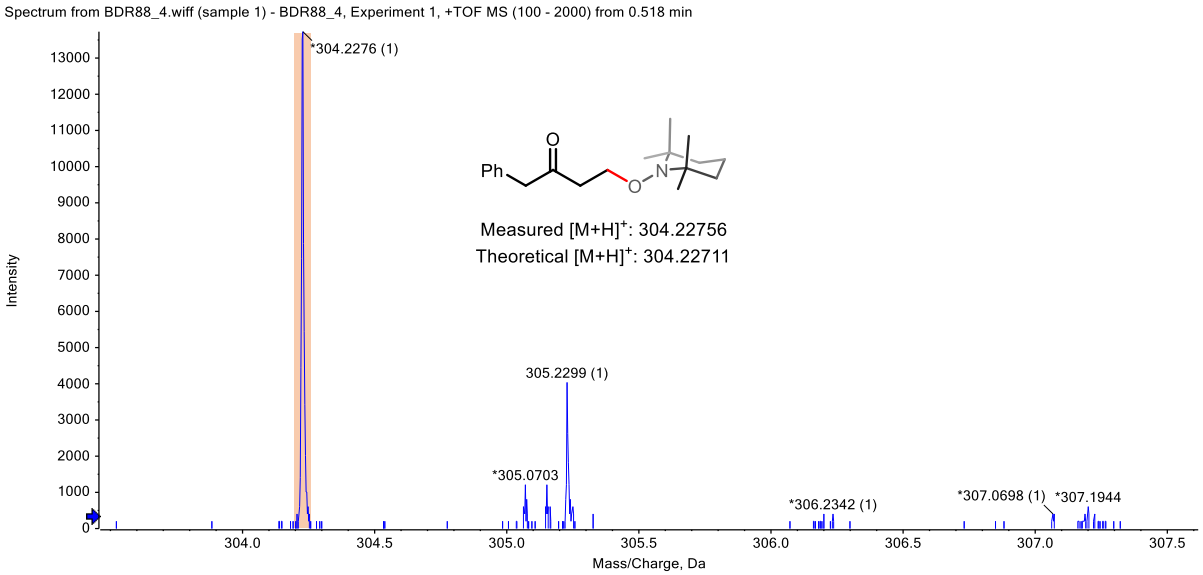


Figure S2. High Resolution Mass Spectrometry (HRMS) data of crude mixture in MeOH.

7.2. Control experiment with radical scavenger.



In a nitrogen-filled glovebox, to the 4 mL oven-dried vial with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.2 mg), *rac*-BINAP (0.02 mmol, 20 mol%, 12 mg), Cs_2CO_3 (0.2 mmol, 2.0 equiv, 65 mg), TEMPO (0.1 mmol, 1.0 equiv, 15.6 mg), and anhydrous dichloromethane (DCM) (0.4 mL). Then, either the solution of **1p** (0.1 mmol, 1.0 equiv) dissolved in anhydrous dichloromethane (0.2 mL), or **2a** (0.2 mmol, 2.0 equiv, 22.5 µL) was added to the reaction mixture using a gastight syringe. The vial was then sealed with screw cap and then, the reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours outside the glovebox. The crude mixture was then diluted with ethyl acetate and filtered through a short pad of silica. After evaporation of the remaining solvent, the filtrate was diluted in methanol for HRMS analysis.



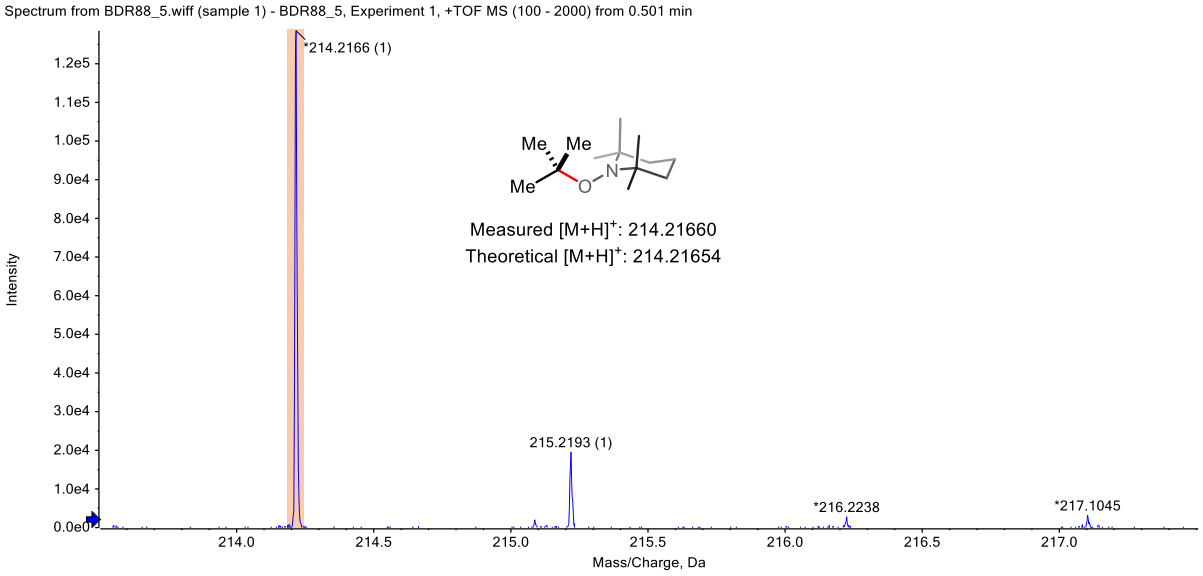
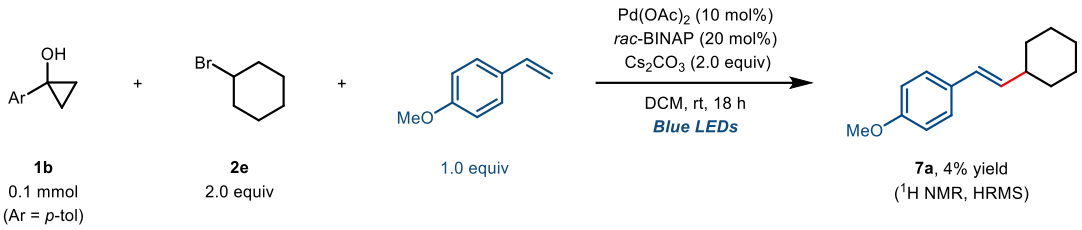


Figure S3. High Resolution Mass Spectrometry (HRMS) data of crude mixture in MeOH.

7.3. Control experiment with styrene as additives (**Scheme 2B**).



In a nitrogen-filled glovebox, to the 4 mL oven-dried vial with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.2 mg), *rac*-BINAP (0.02 mmol, 20 mol%, 12 mg), Cs_2CO_3 (0.2 mmol, 2.0 equiv, 65 mg), and anhydrous dichloromethane (DCM) (0.4 mL). In a separate 4 mL vial, **1b** (0.1 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (0.2 mL). Then, the solution of **1b**, **2e** (0.2 mmol, 2.0 equiv, 24.6 µL), and 4-methoxystyrene (0.1 mmol, 1.0 equiv, 13.5 µL) was added to the reaction mixture sequentially using a gastight syringe. The vial was then sealed with screw cap and then, the reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours outside the glovebox. The crude mixture was then diluted with ethyl acetate and filtered through a short pad of silica. After evaporation of the remaining solvent, the crude mixture was dissolved with 1,1,2,2-tetrachloroethane (0.19 mmol, 1.9 equiv, 20 µL) as an internal standard in $CDCl_3$ for ^1H NMR analysis or MeOD for HRMS analysis, respectively.

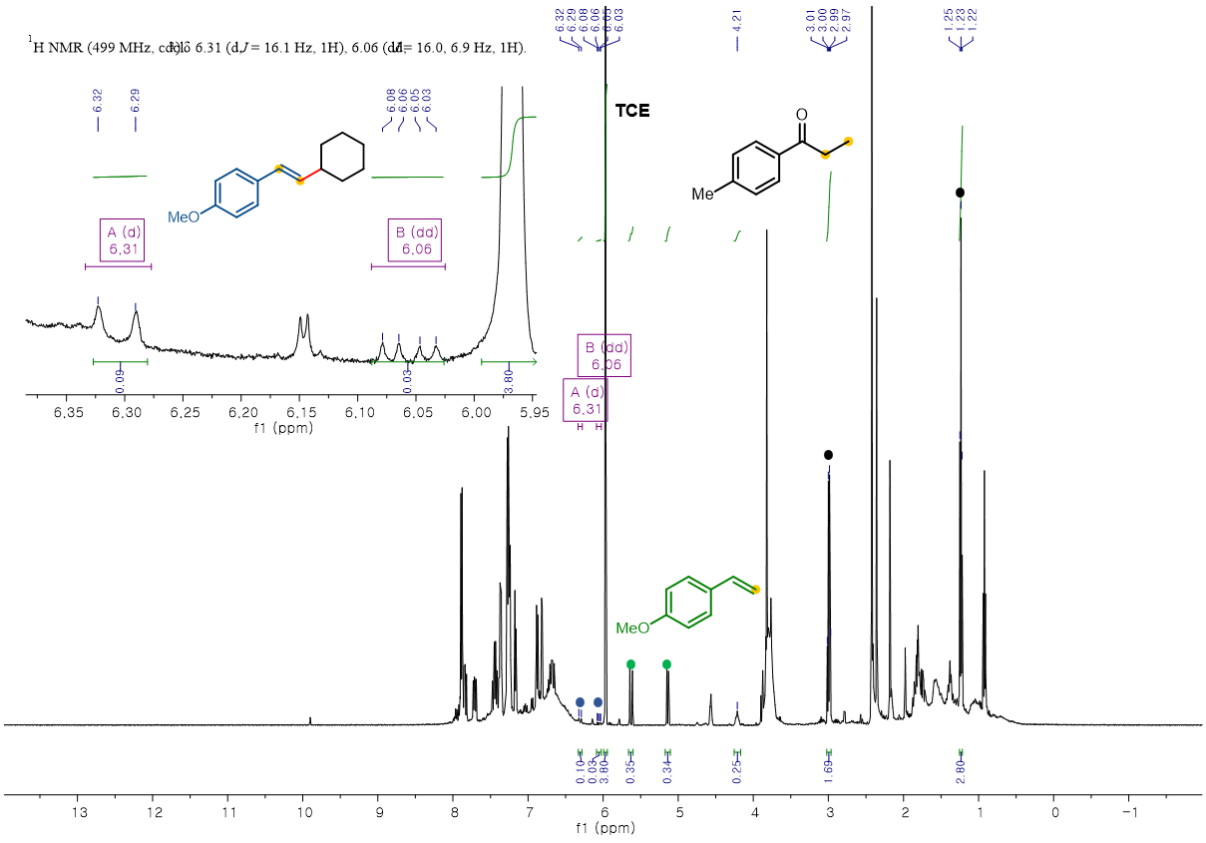


Figure S4. ^1H NMR spectra of crude mixture in $CDCl_3$.

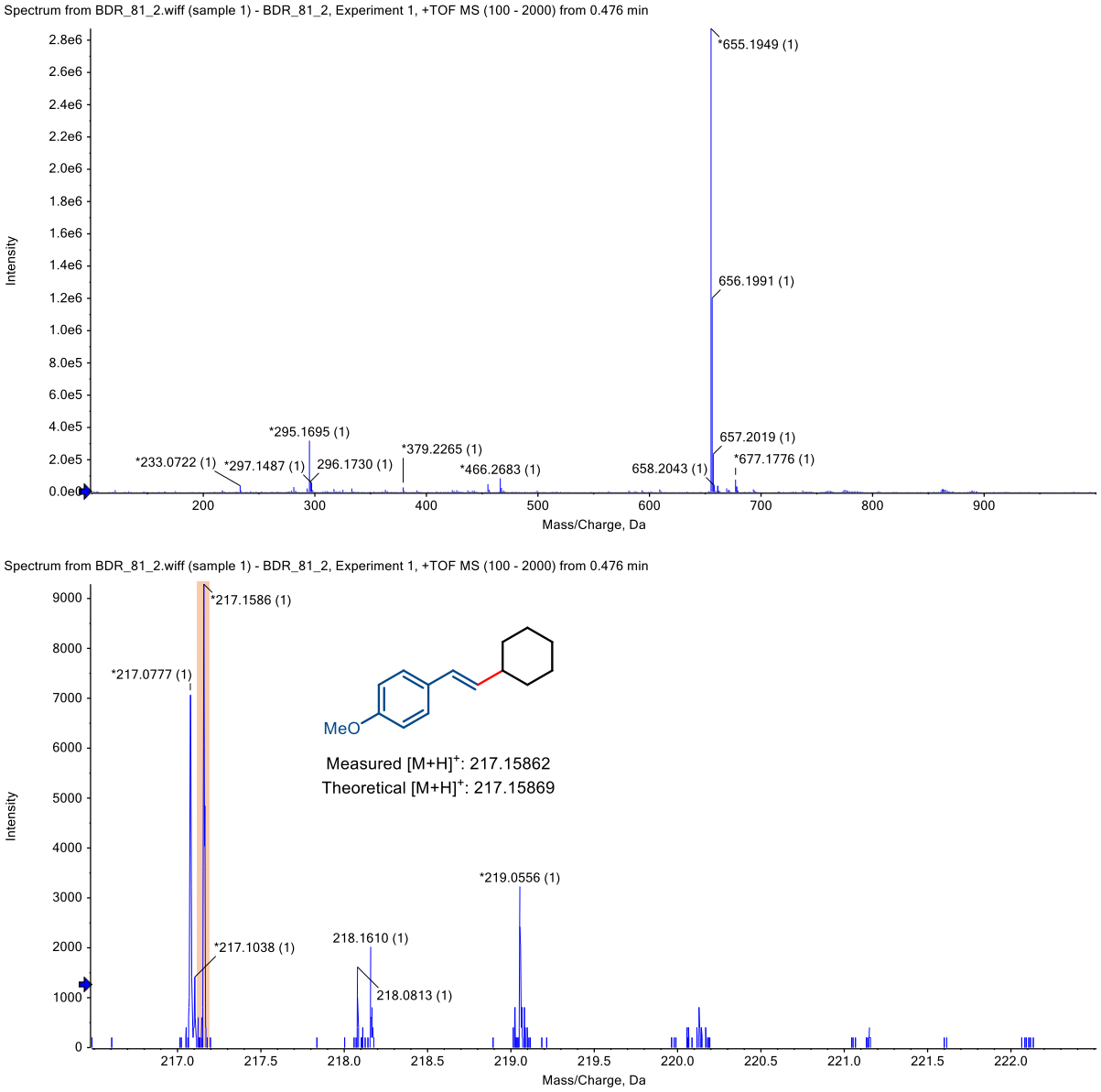
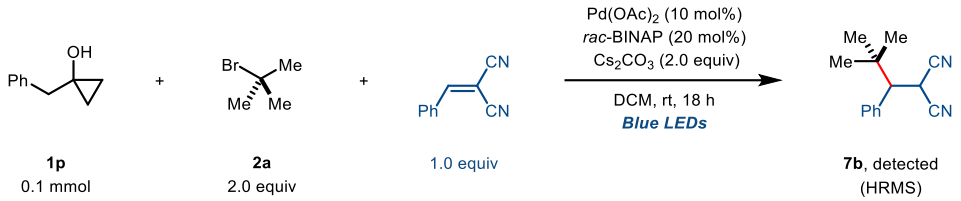
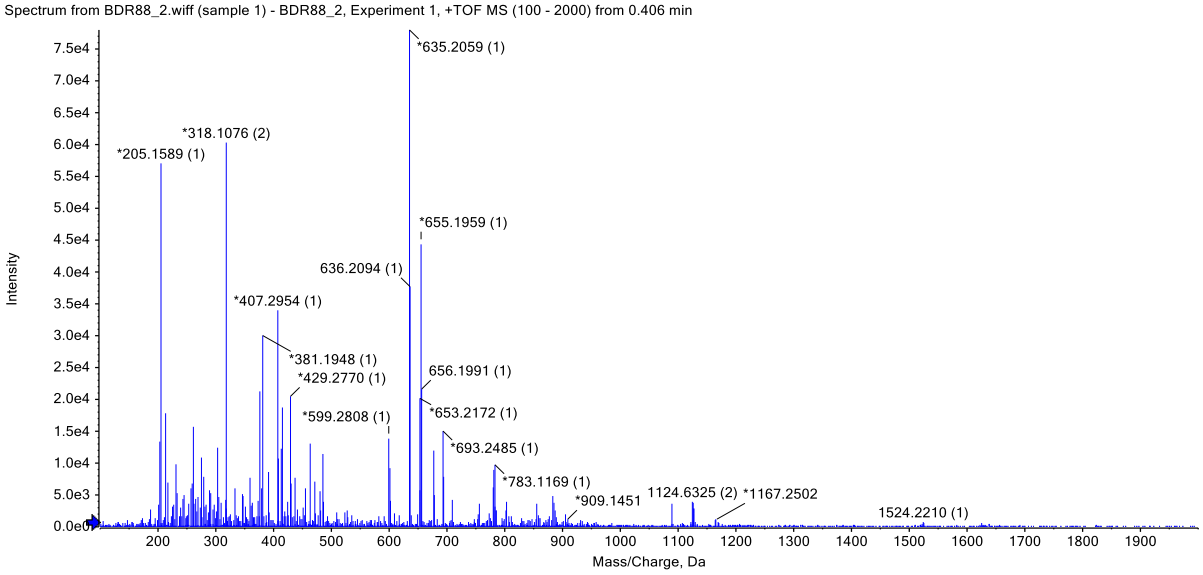


Figure S5. High Resolution Mass Spectrometry (HRMS) data of crude mixture in MeOH.

7.4. Control experiment with benzylidenemalononitrile as radical acceptor (**Scheme 2B**).



In a nitrogen-filled glovebox, to the 4 mL oven-dried vial with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.2 mg), *rac*-BINAP (0.02 mmol, 20 mol%, 12 mg), Cs_2CO_3 (0.2 mmol, 2.0 equiv, 65 mg), benzylidenemalononitrile (0.01 mmol, 1.0 equiv, 15.5 mg), and anhydrous dichloromethane (DCM) (0.4 mL). In a separate 4 mL vial, **1p** (0.1 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (0.2 mL) and then, the solution of **1p** and **2a** (0.2 mmol, 2.0 equiv, 22.5 µL) was added to the reaction mixture sequentially using a gastight syringe. The vial was then sealed with screw cap and then, the reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours outside the glovebox. The crude mixture was then diluted with ethyl acetate and filtered through a short pad of silica. After evaporation of the remaining solvent, the crude mixture was diluted with MeOD for HRMS analysis.



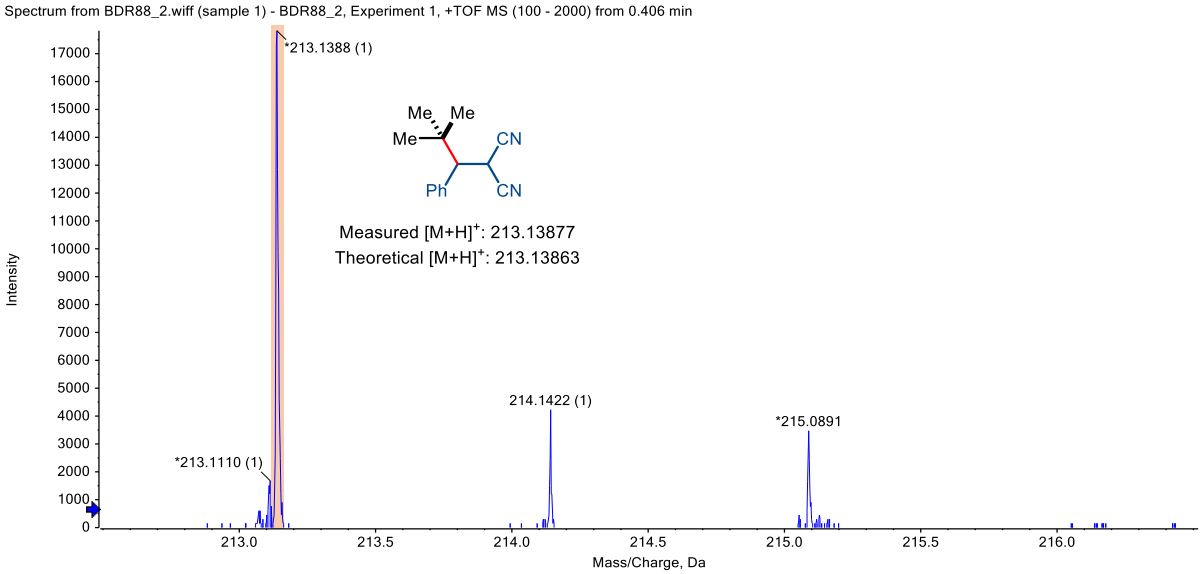
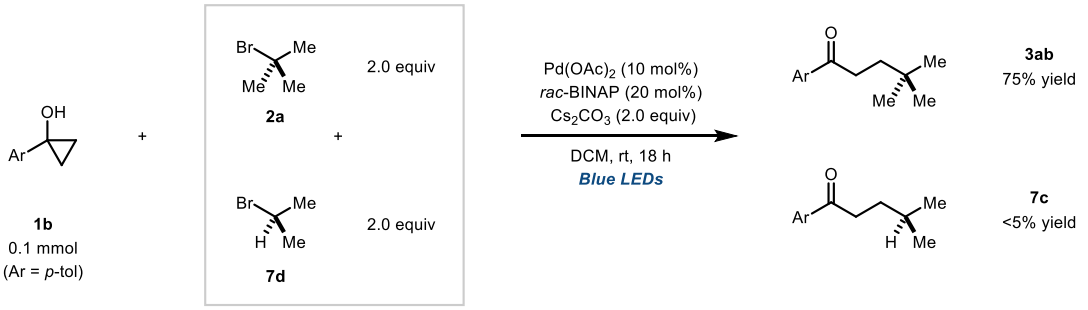


Figure S6. High Resolution Mass Spectrometry (HRMS) data of crude mixture in MeOH.

7.5. Competition experiments (3° vs 2° alkyl halide) (**Scheme 2C**).



In a nitrogen-filled glovebox, to the 4 mL oven-dried vial with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.2 mg), *rac*-BINAP (0.02 mmol, 20 mol%, 12 mg), Cs_2CO_3 (0.2 mmol, 2.0 equiv, 65 mg), benzylidenemalononitrile (0.01 mmol, 1.0 equiv, 15.5 mg), and anhydrous dichloromethane (DCM) (0.4 mL). In a separate 4 mL vial, **1b** (0.1 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (0.2 mL) and then, the solution of **1b**, **2a** (0.2 mmol, 2.0 equiv, 22.5 µL), and **7d** (0.2 mmol, 2.0 equiv, 18.8 µL) was added to the reaction mixture sequentially using a gastight syringe. The vial was then sealed with screw cap and then, the reaction mixture was stirred under irradiation of blue light (456 nm) from Kessil lamp with fan-cooling for 18 hours outside the glovebox. The crude mixture was then diluted with ethyl acetate and filtered through a short pad of silica. After evaporation of the remaining solvent, the crude mixture was dissolved in $CDCl_3$ with 1,1,2,2-tetrachloroethane (0.2 mmol, 2.0 equiv, 21 µL) as an internal standard for ^1H NMR analysis.

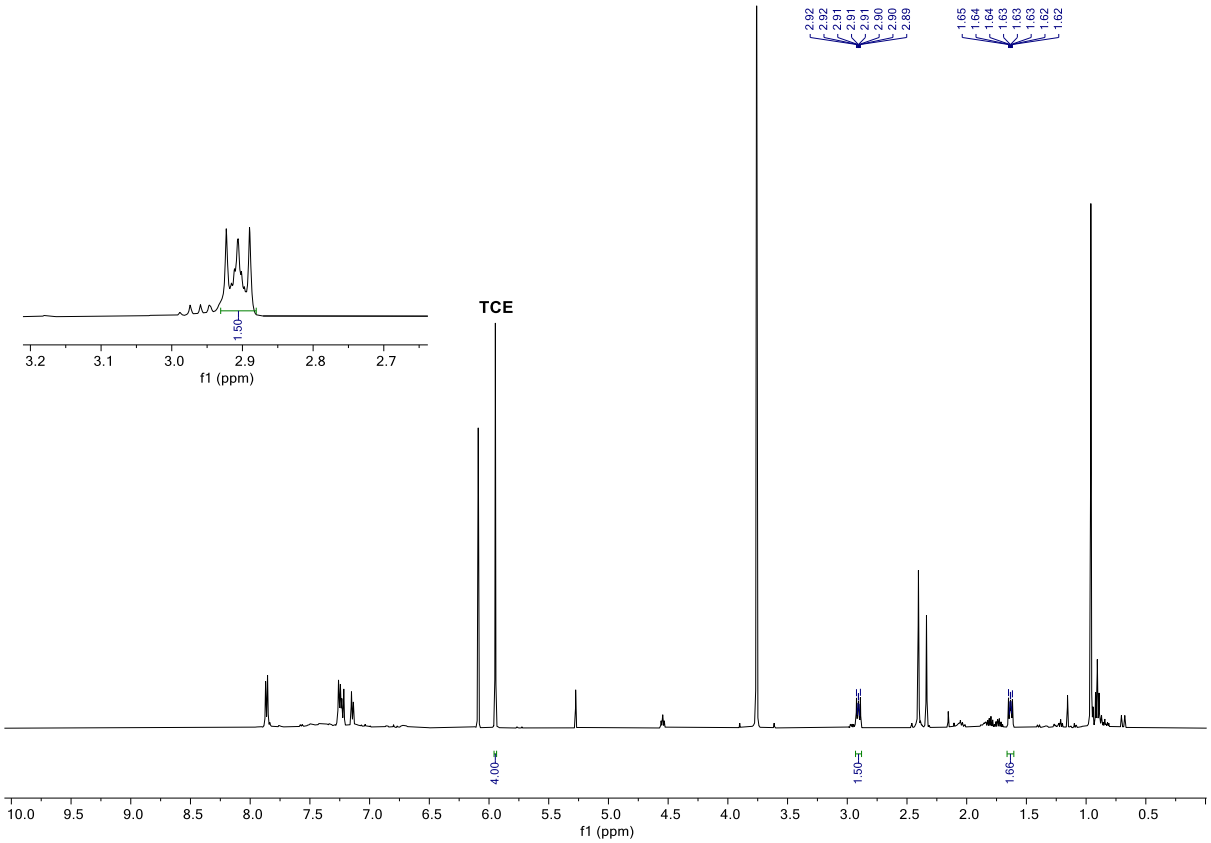


Figure S7. ^1H NMR spectra of crude mixture in $CDCl_3$.

8. References

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9. NMR spectra

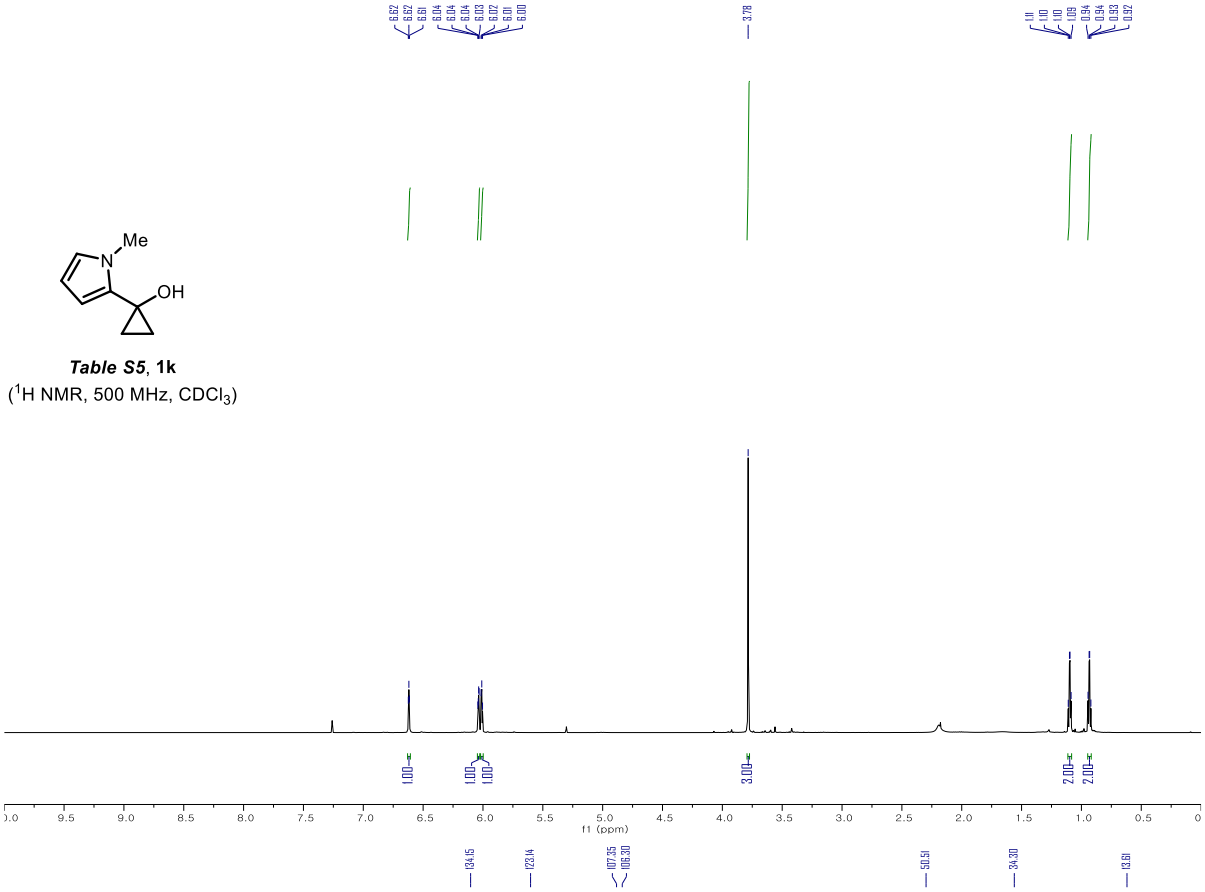
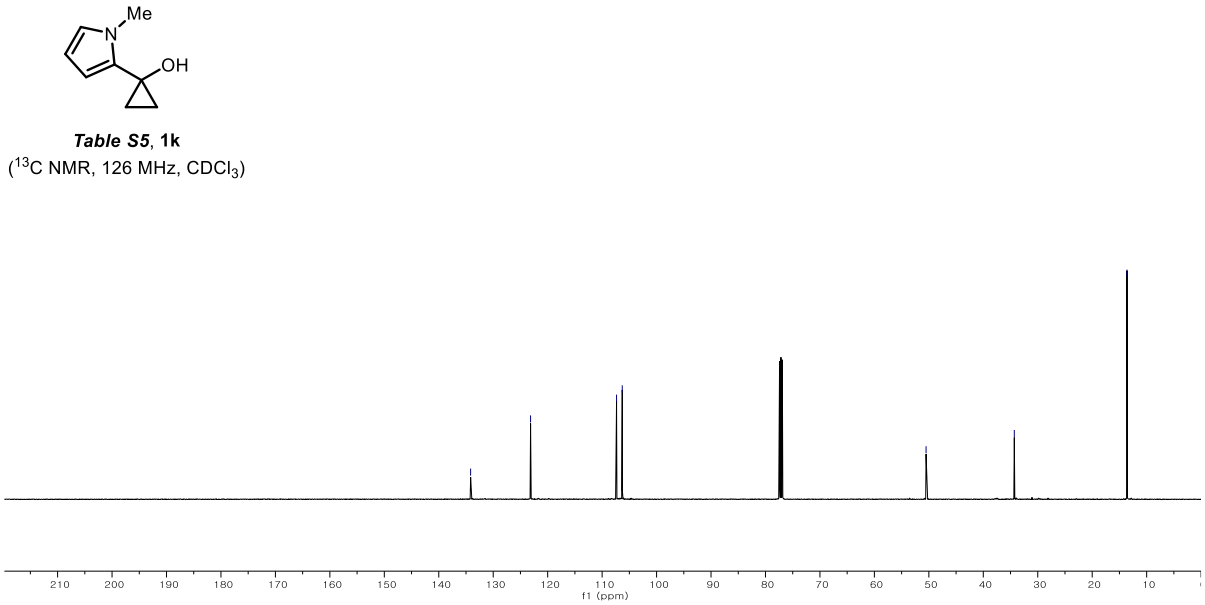


Table S5, **1k**
(^{1}H NMR, 500 MHz, $CDCl_3$)



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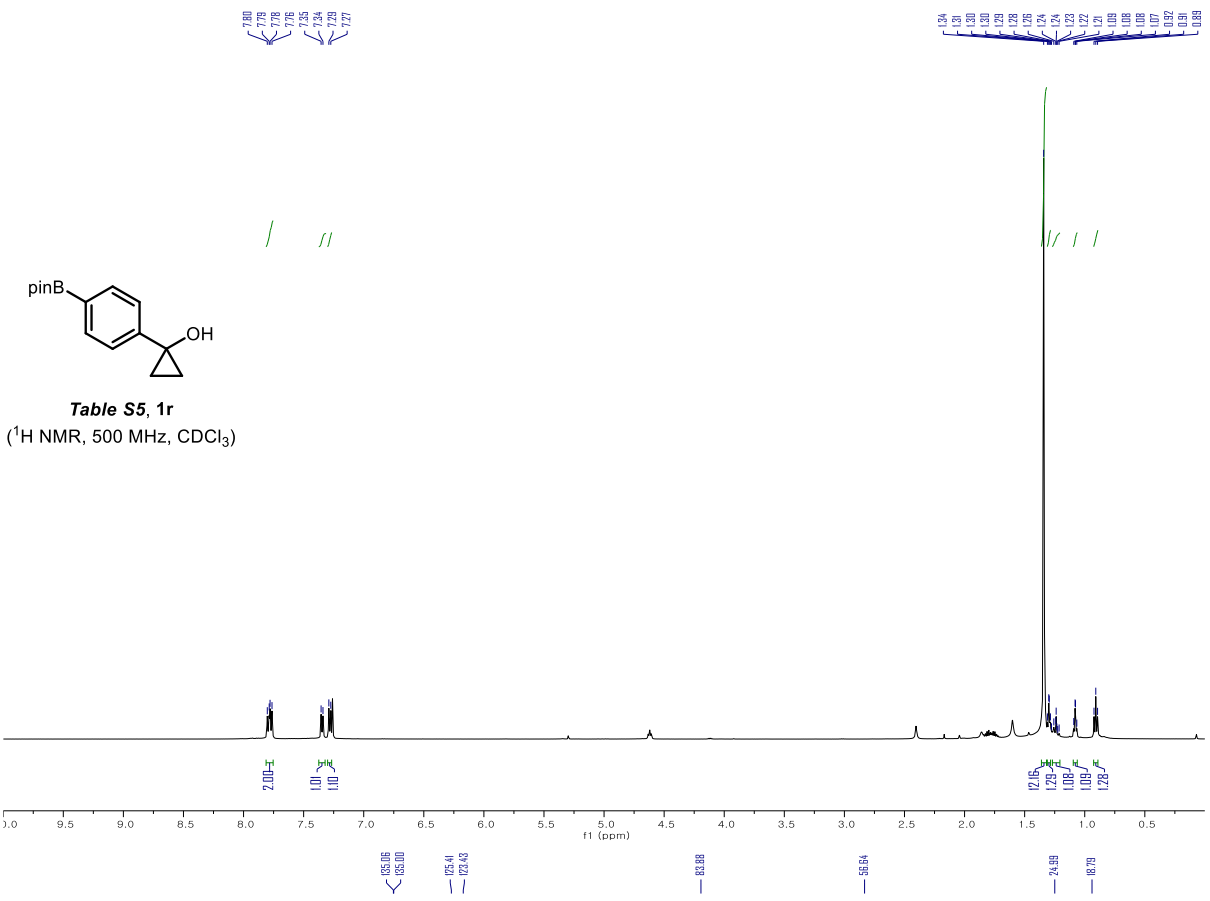

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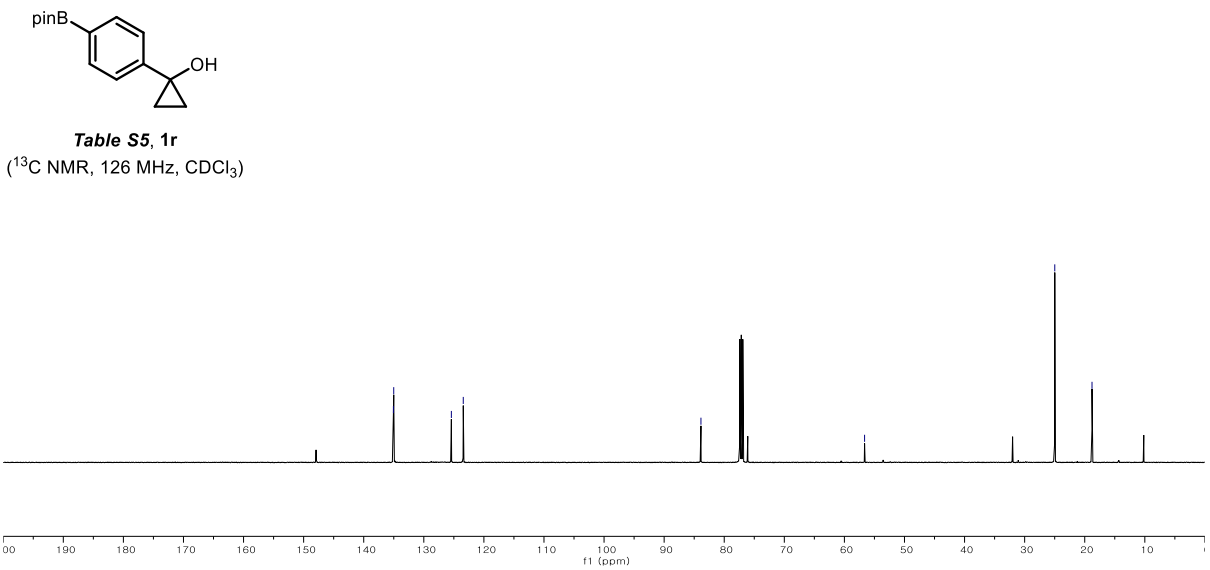

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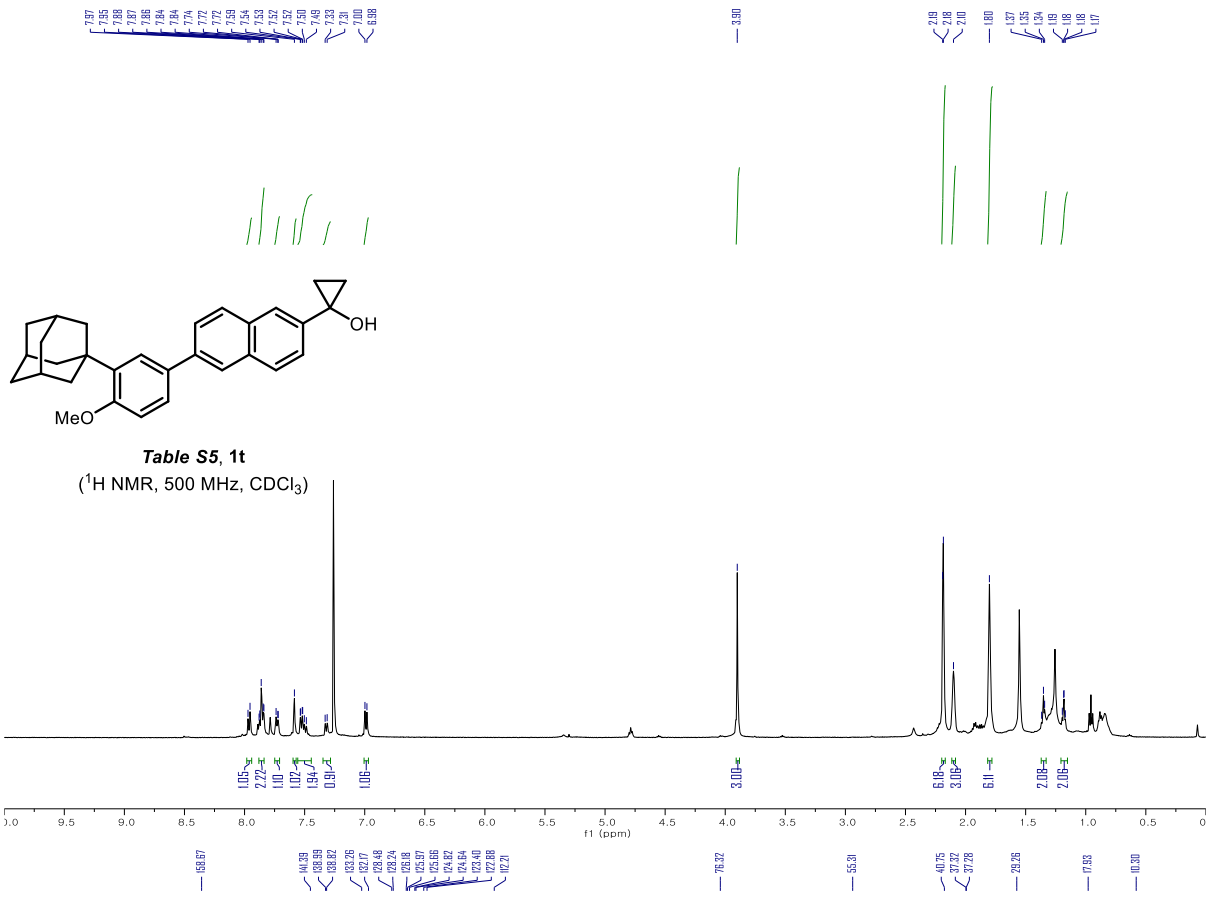

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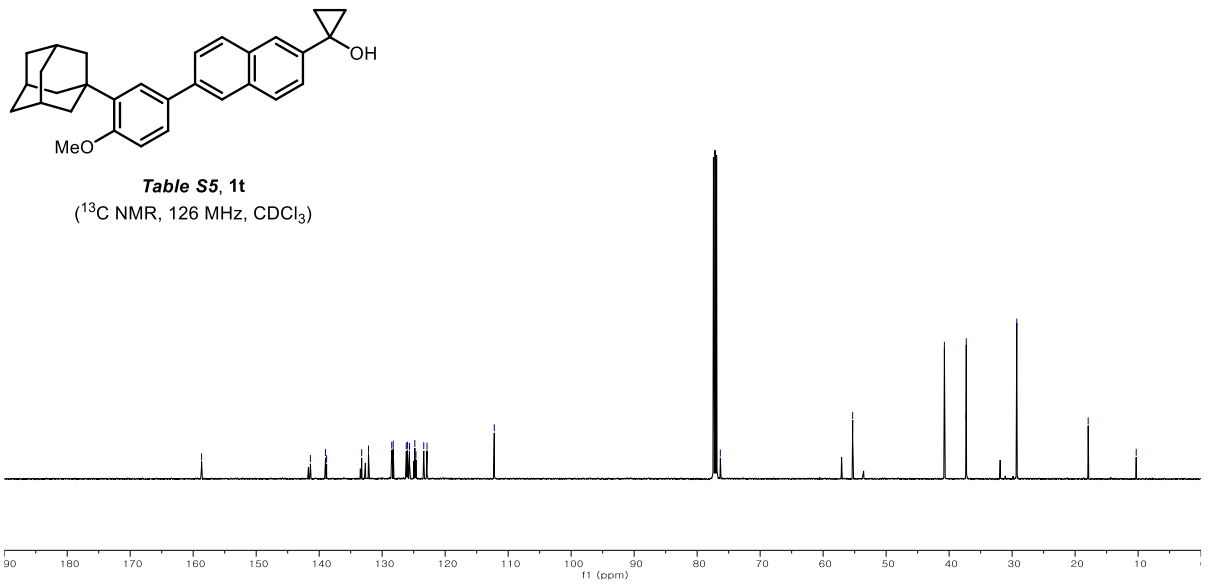

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(^{13}C NMR, 126 MHz, $CDCl_3$)

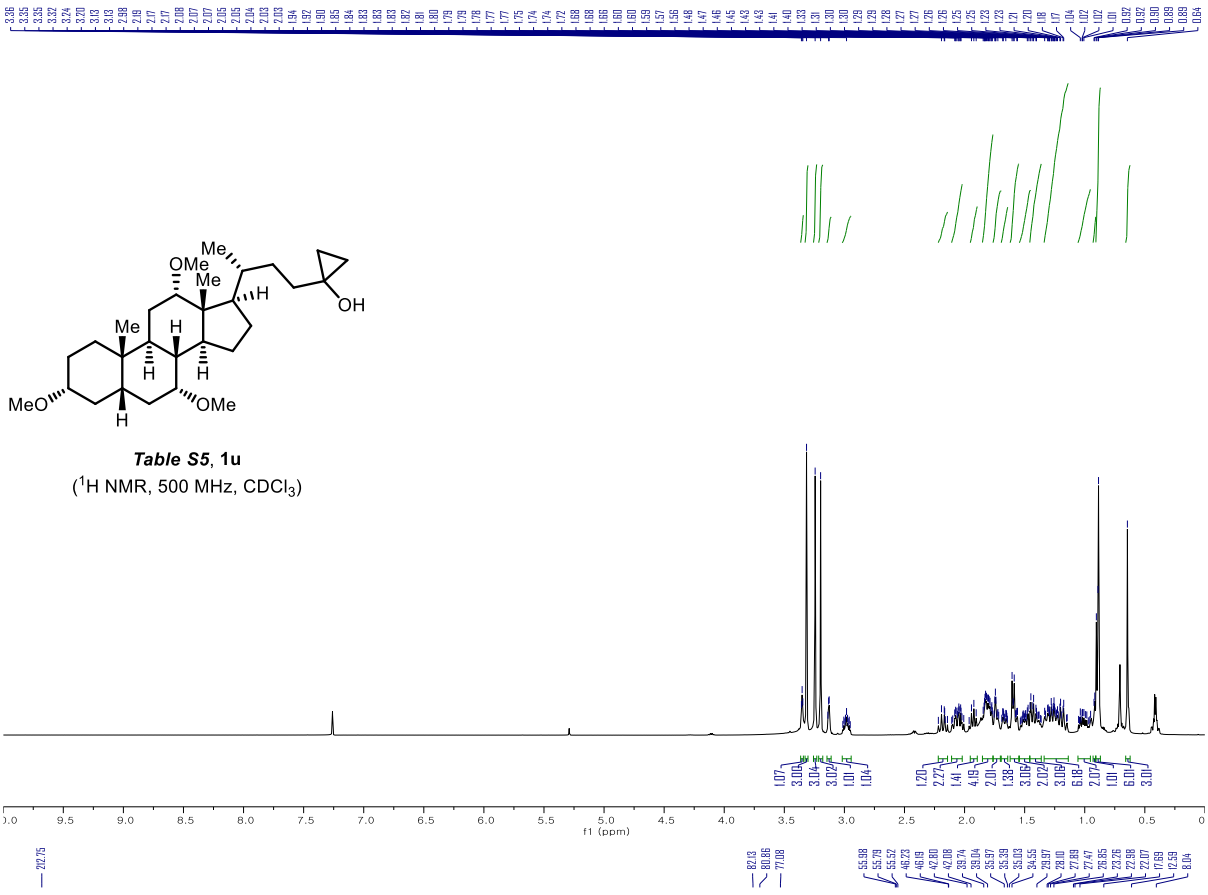
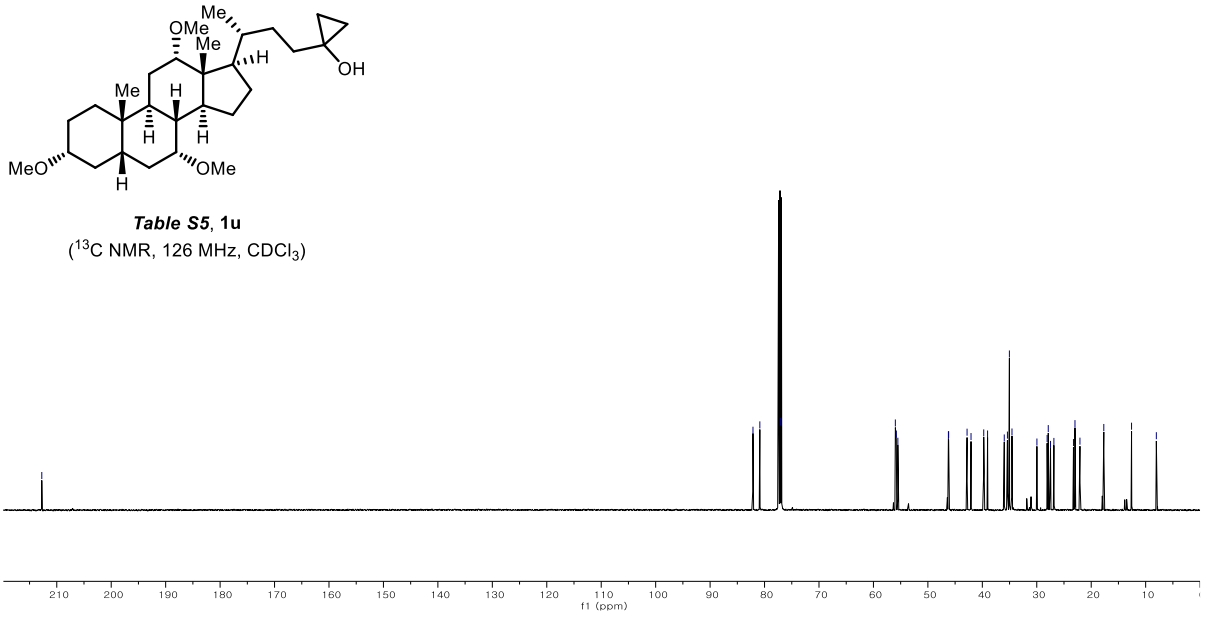


Table S5, **1u**

(^{1}H NMR, 500 MHz, $CDCl_3$)



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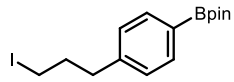

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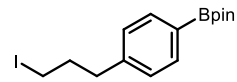
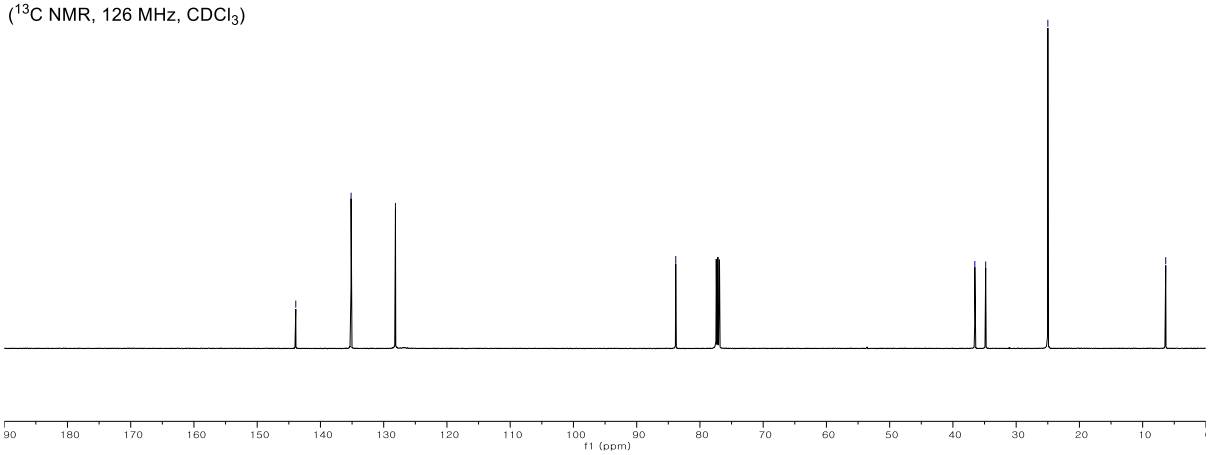
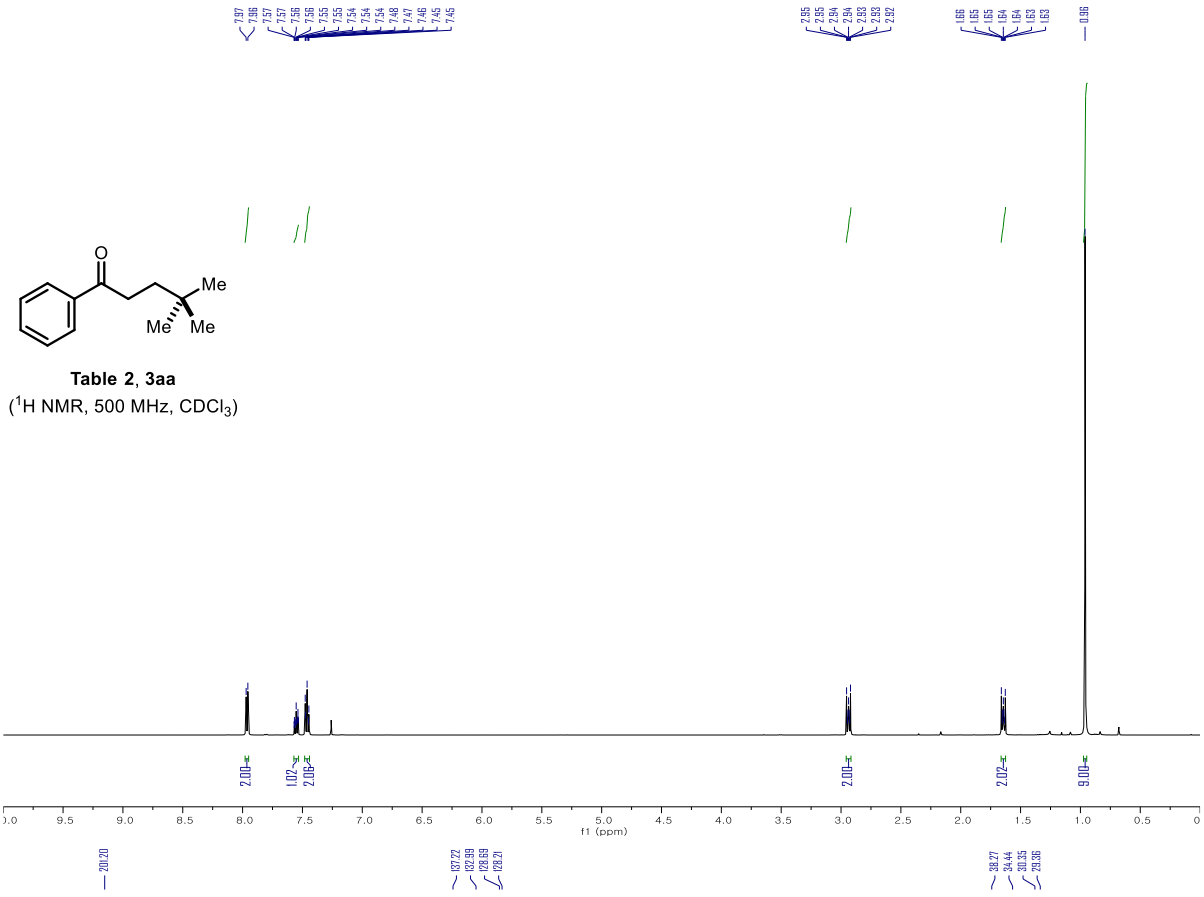


Table *S*6, 2v
(^{13}C NMR, 126 MHz, $CDCl_3$)





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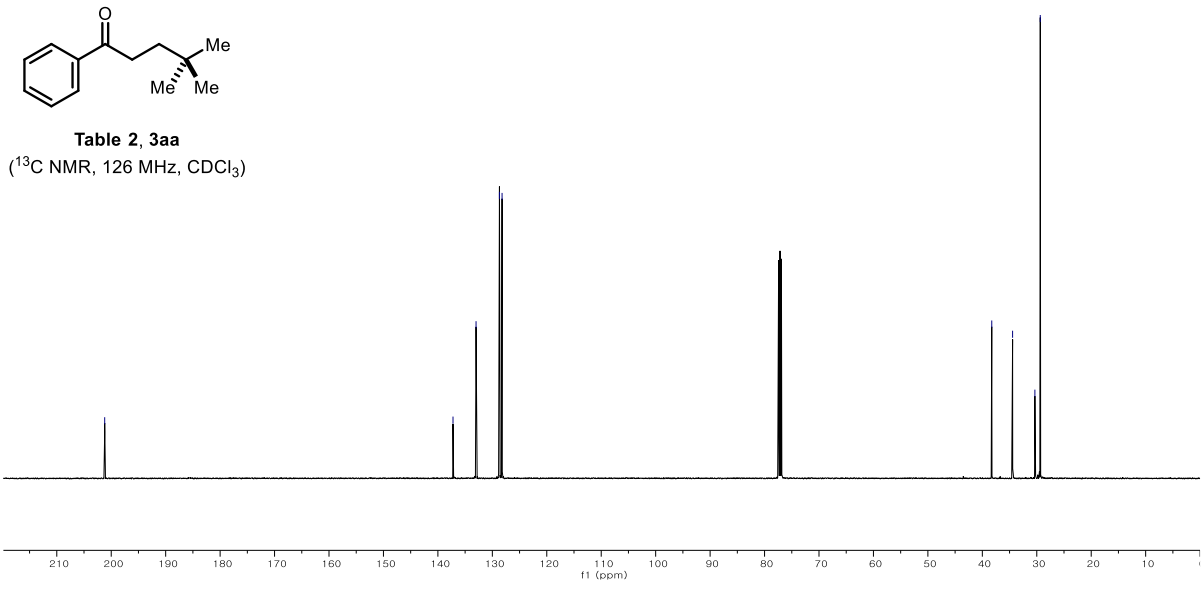

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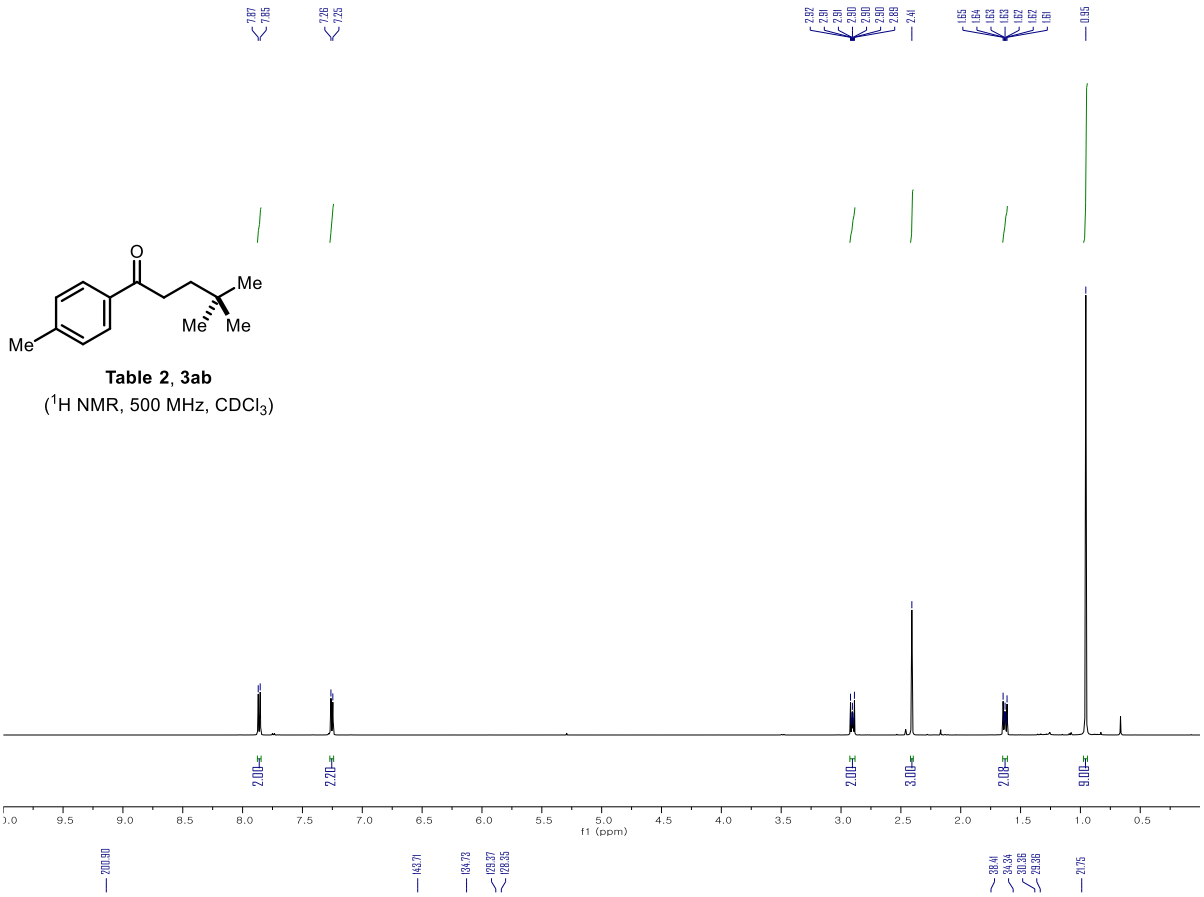

Table 2, **3ab**

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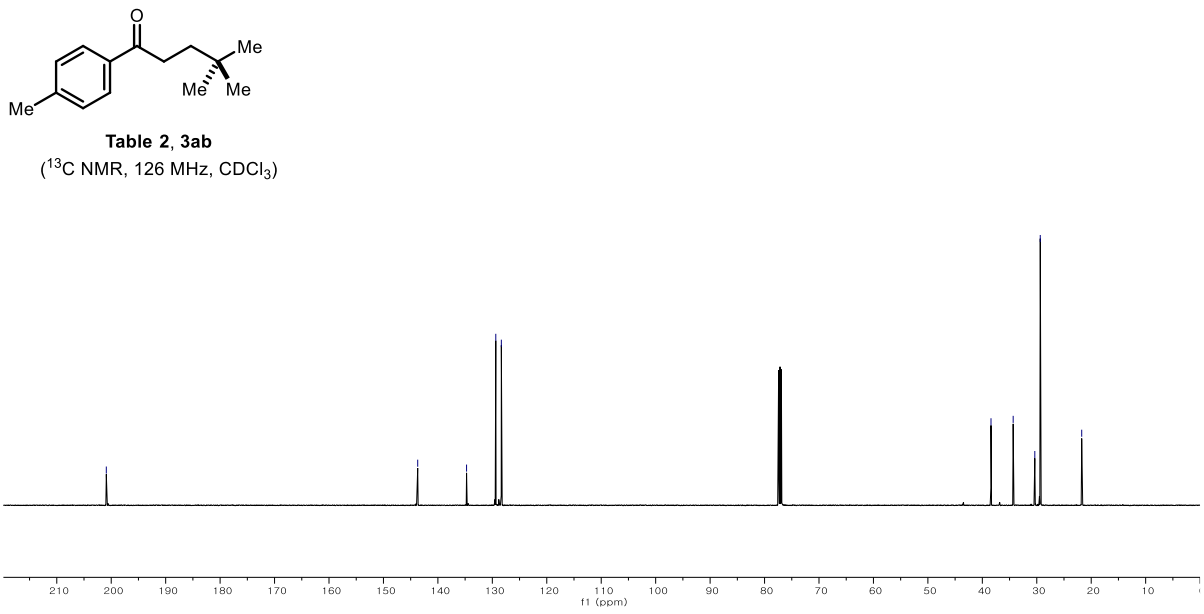
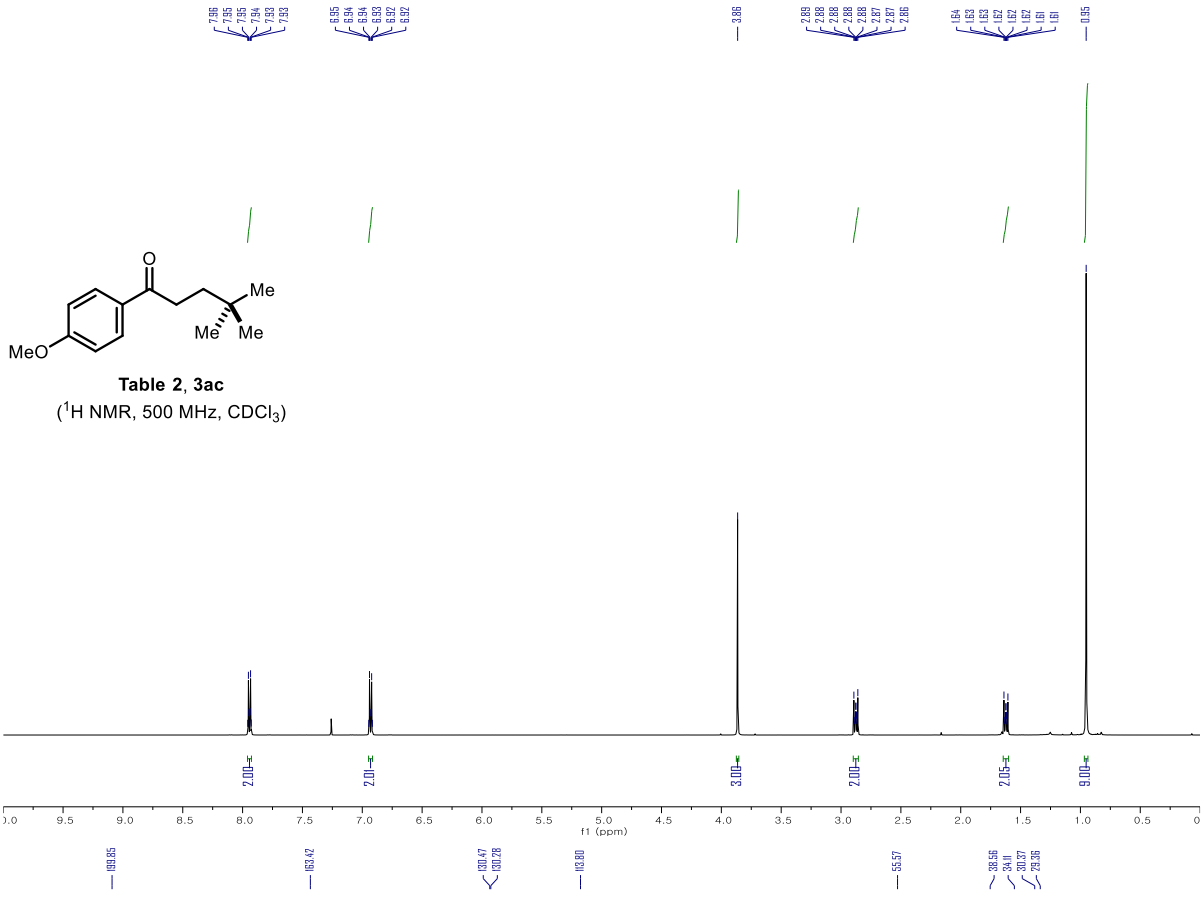


Table 2, **3ab**

(^{13}C NMR, 126 MHz, $CDCl_3$)



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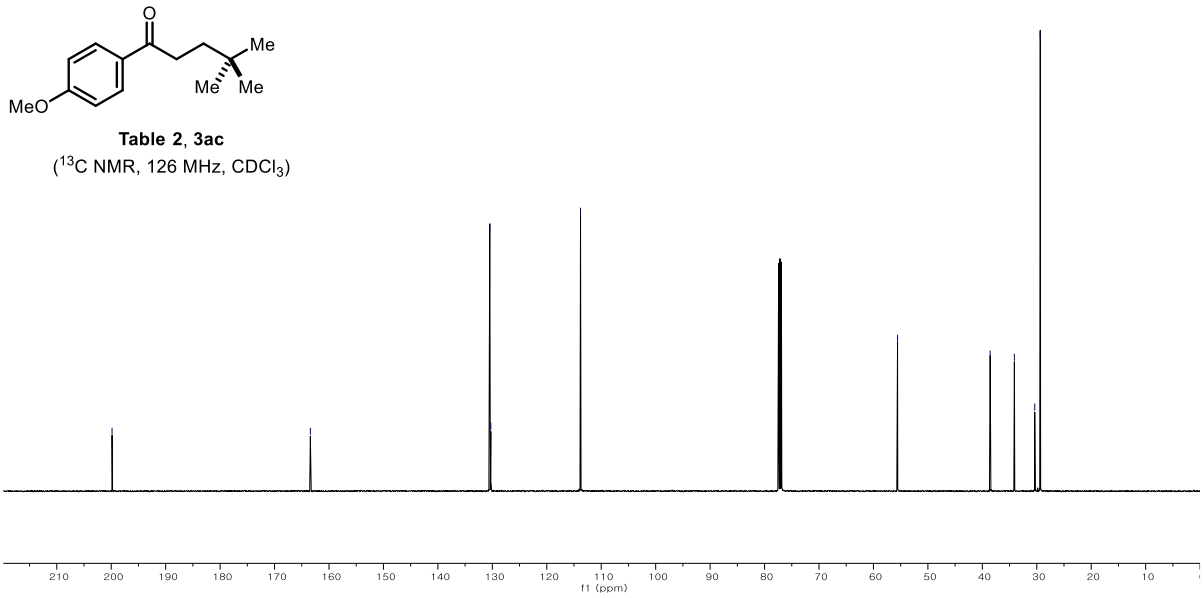

Table 2, **3ac**
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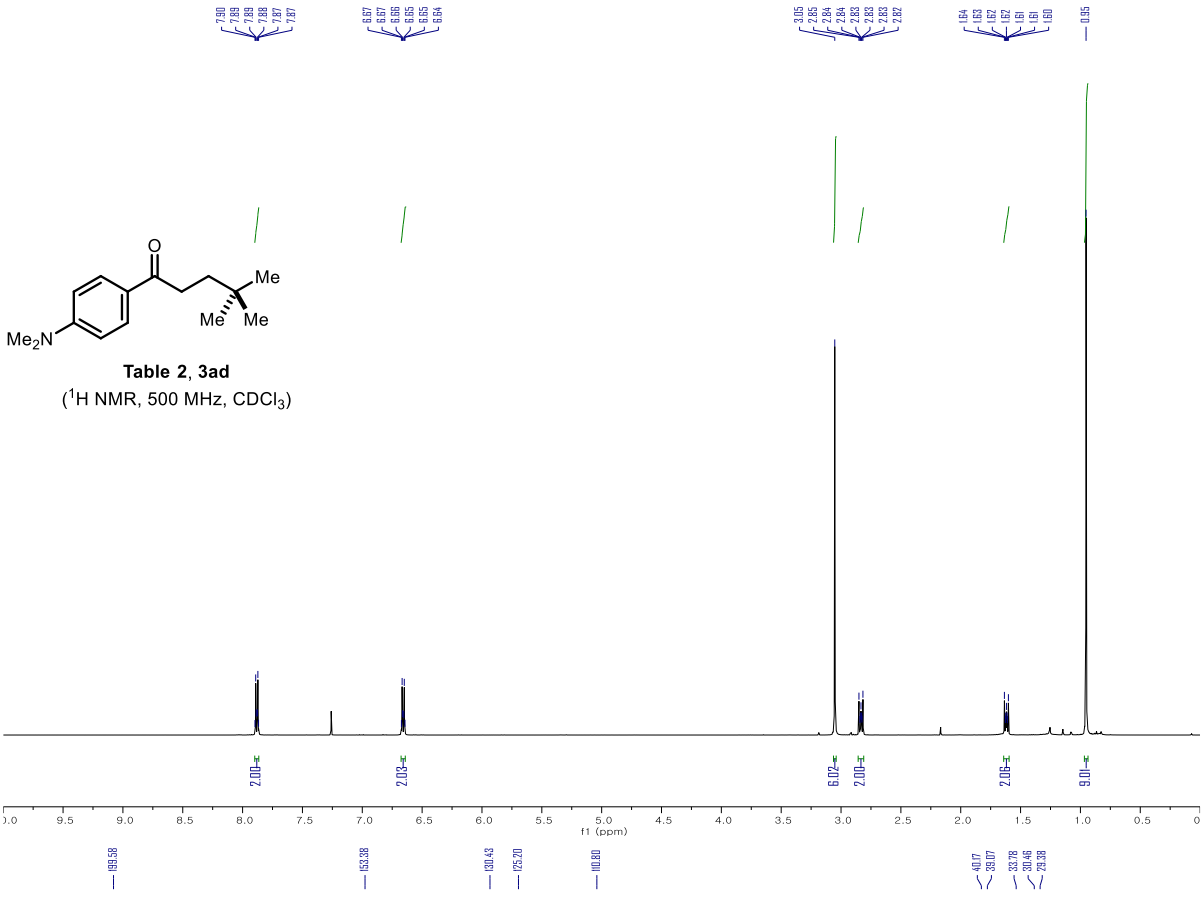

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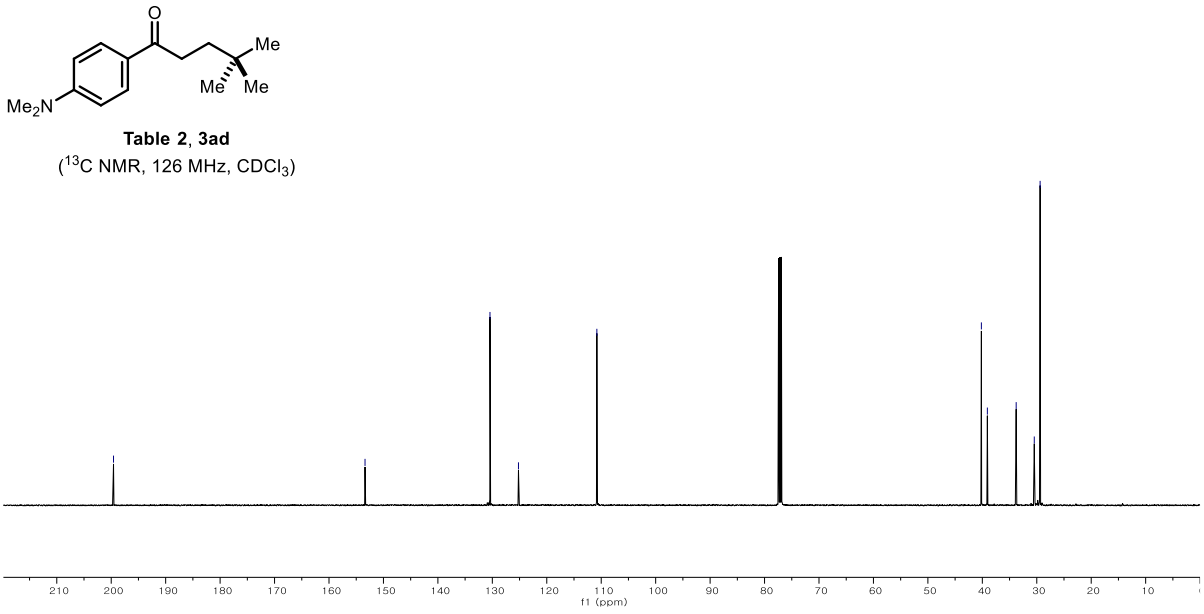

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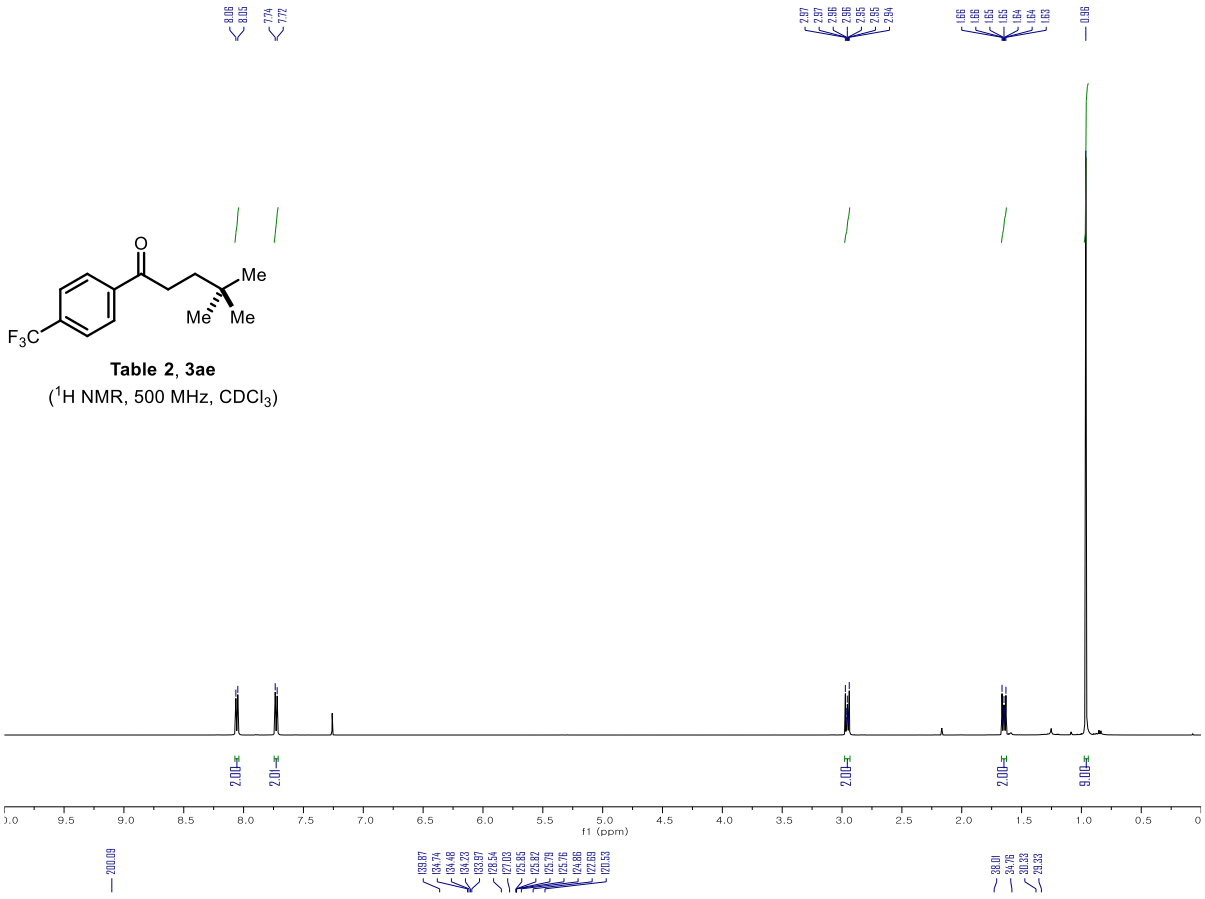


Table 2, **3ae**

(^{1}H NMR, 500 MHz, $CDCl_3$)

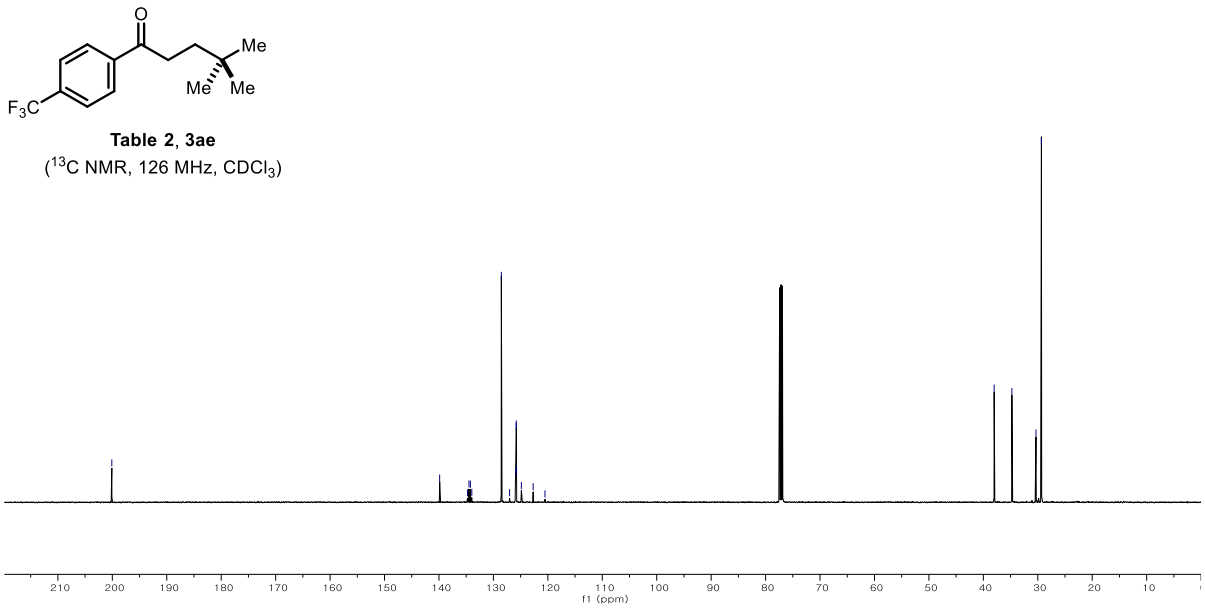


Table 2, **3ae**

(^{13}C NMR, 126 MHz, $CDCl_3$)

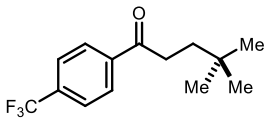
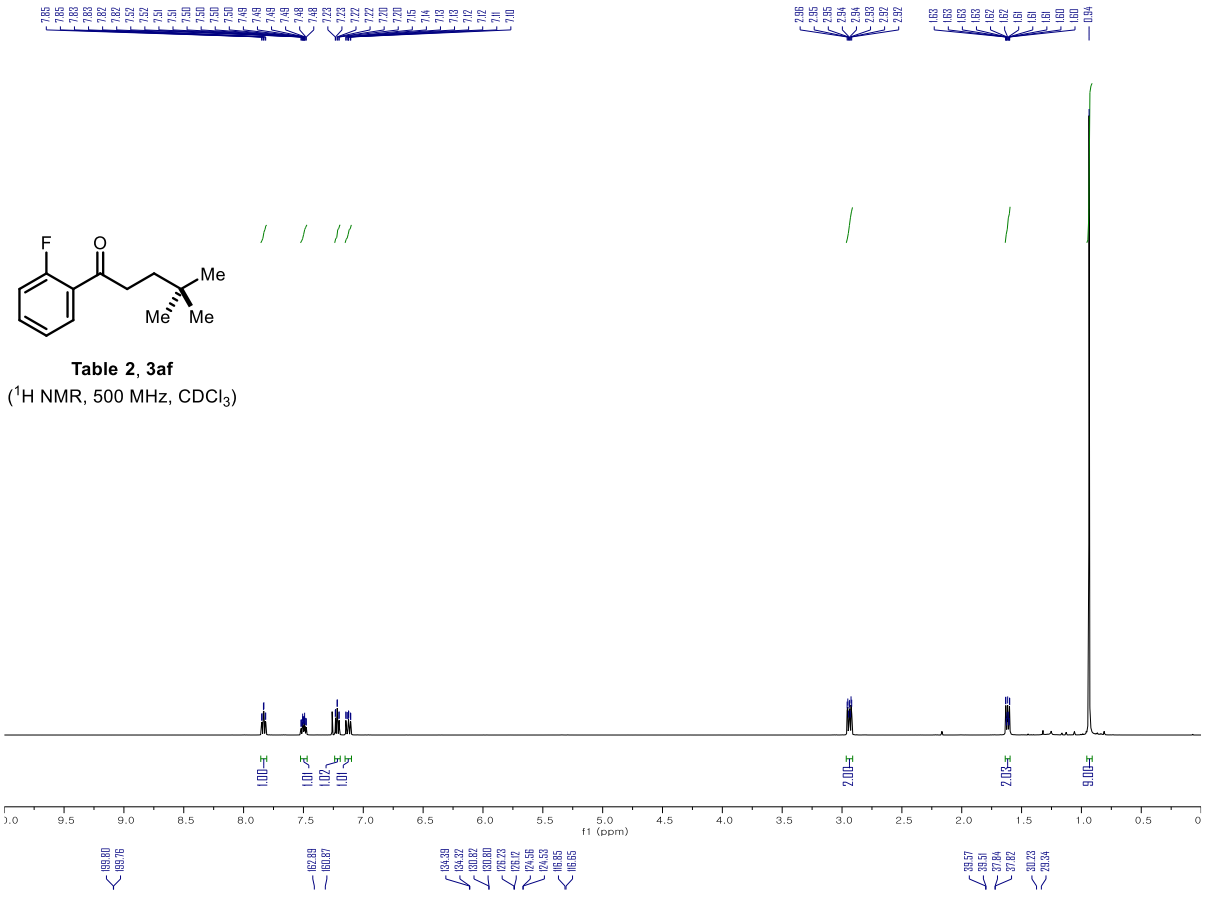


Table 2, **3ae**

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



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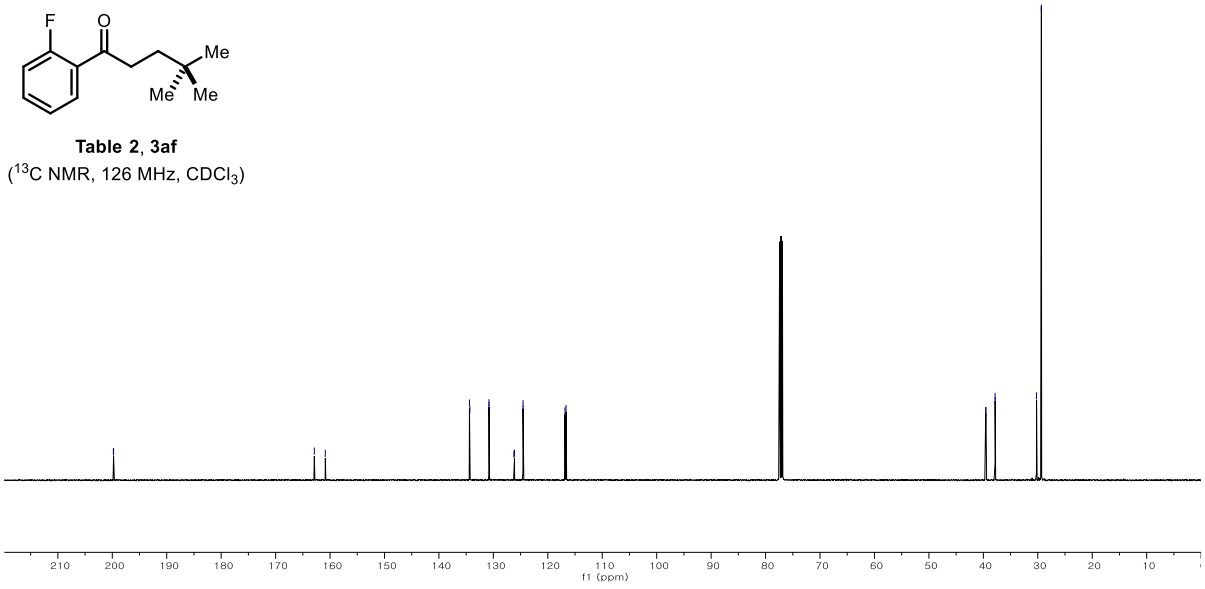

Table 2, **3af**
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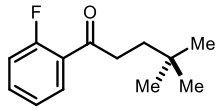

Table 2, **3af**

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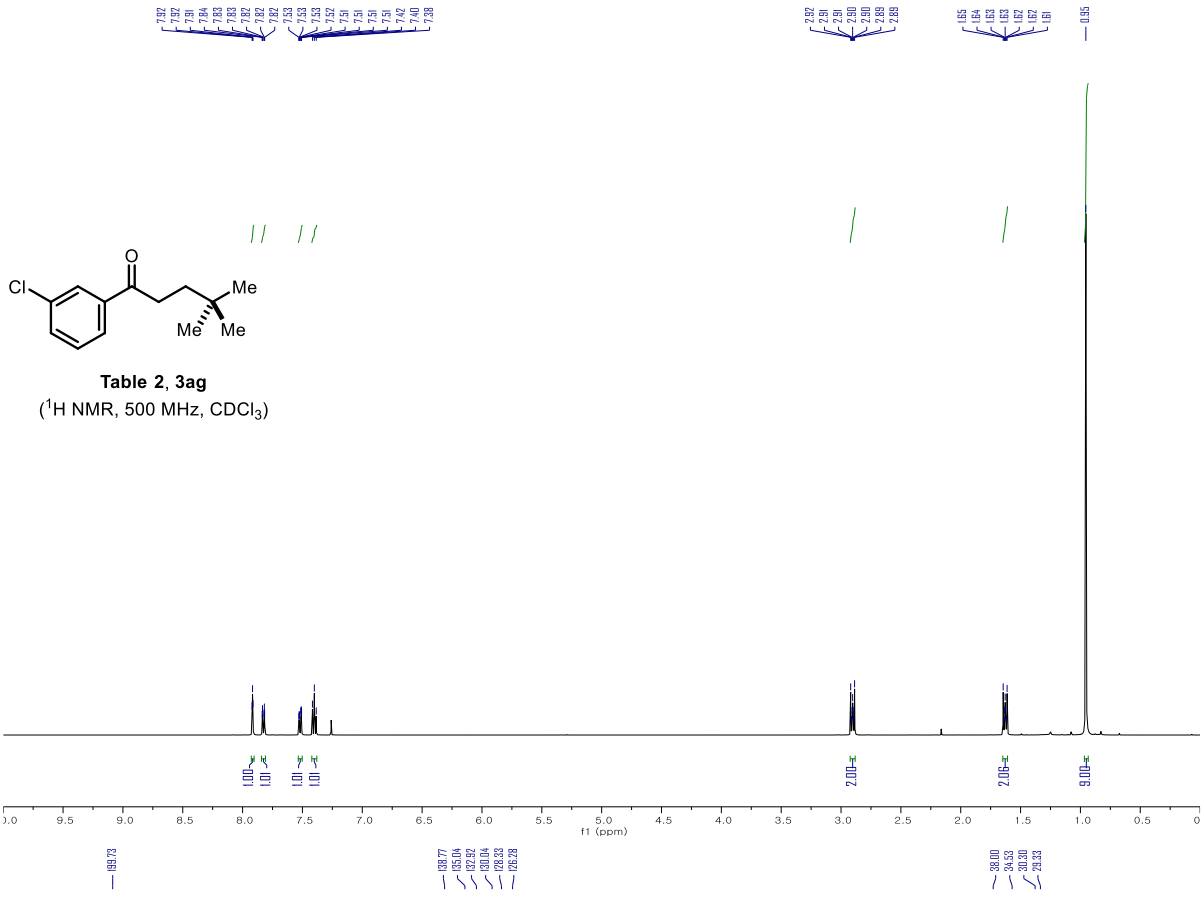

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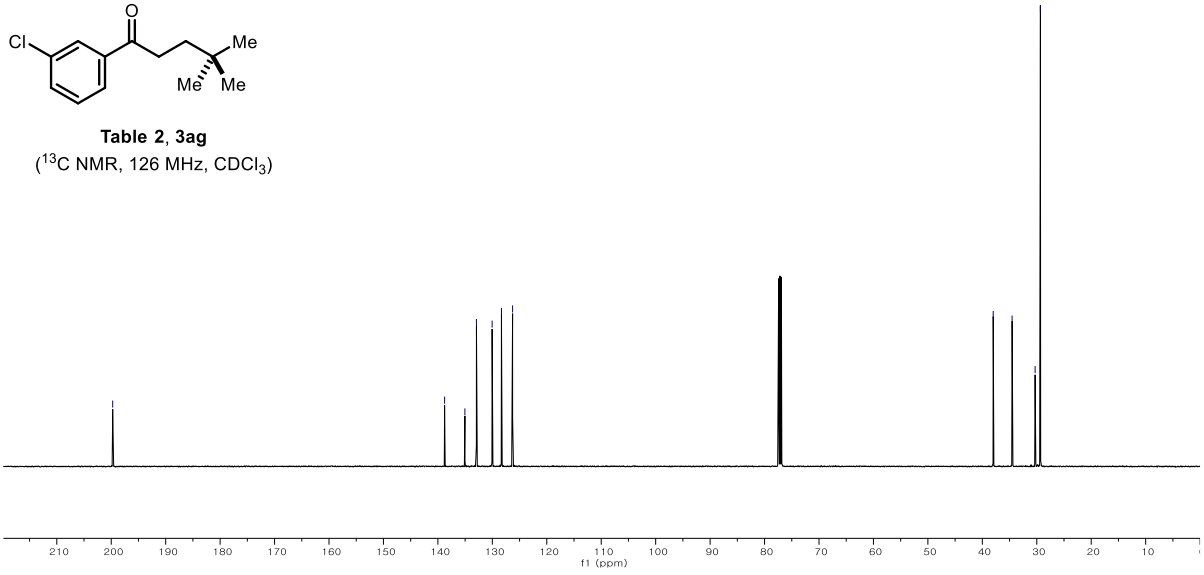

Table 2, **3ag**
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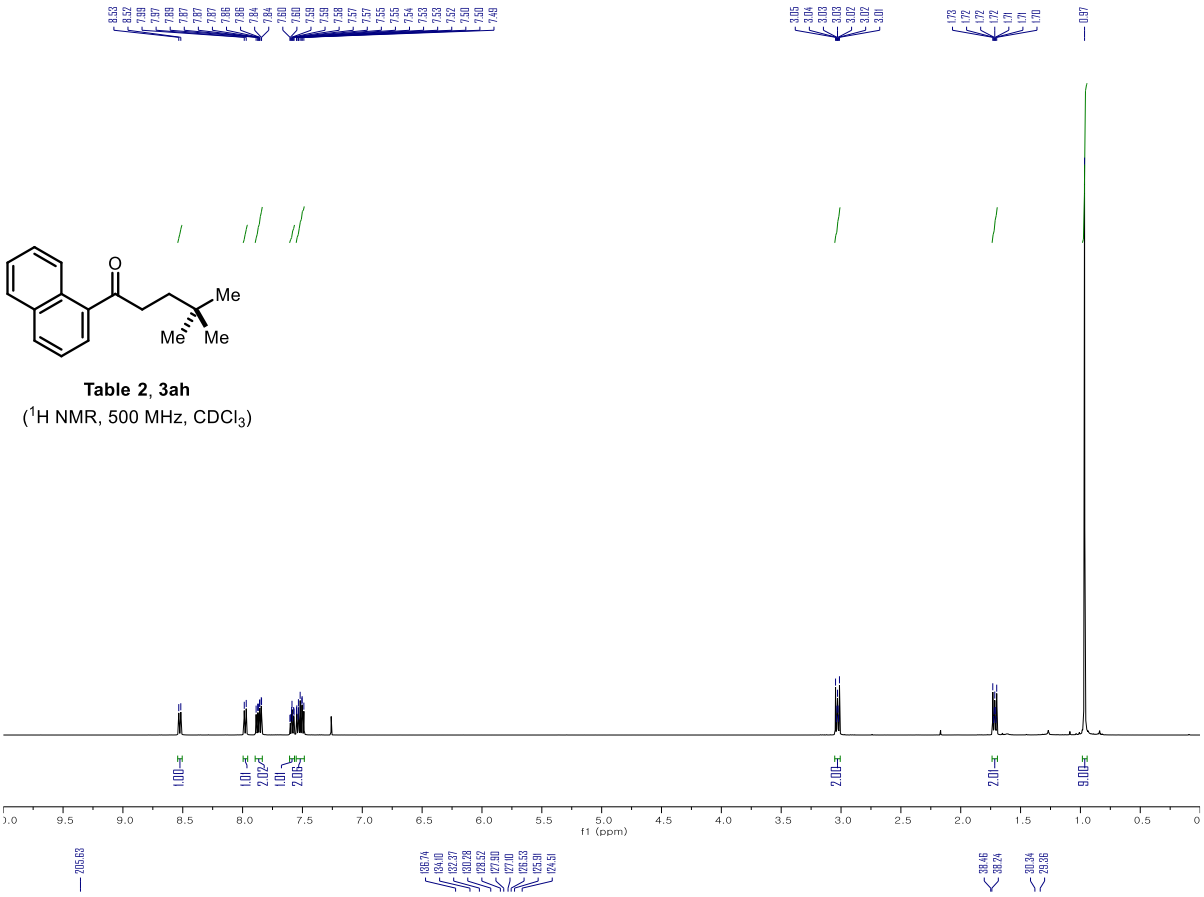

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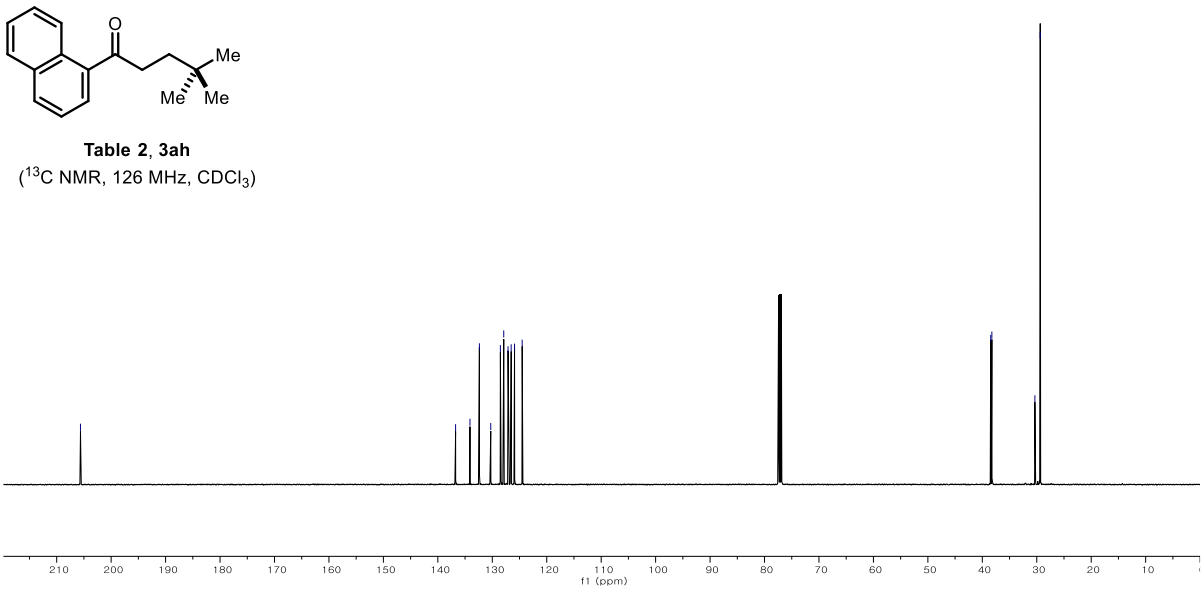

Table 2, **3ah**
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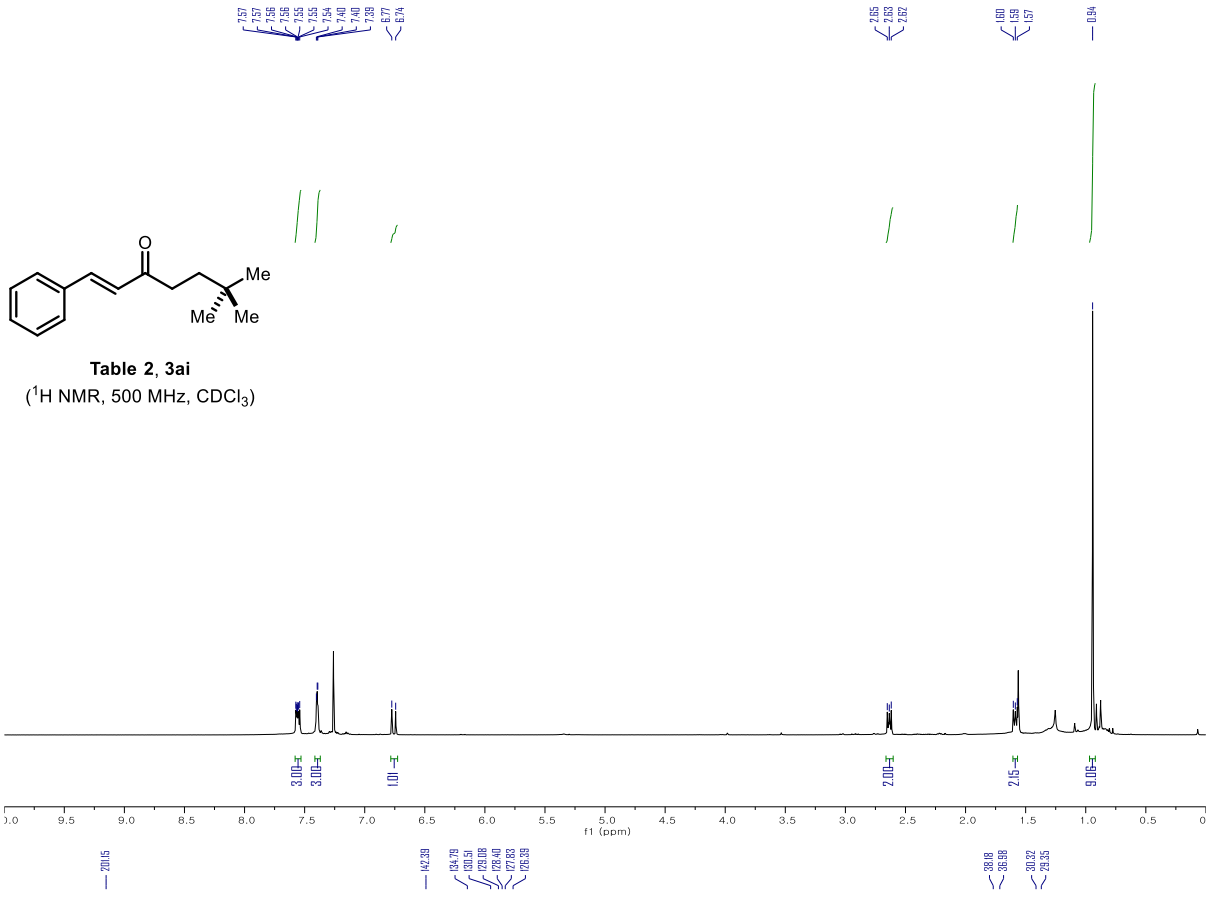


Table 2, **3ai**
(^{1}H NMR, 500 MHz, $CDCl_3$)

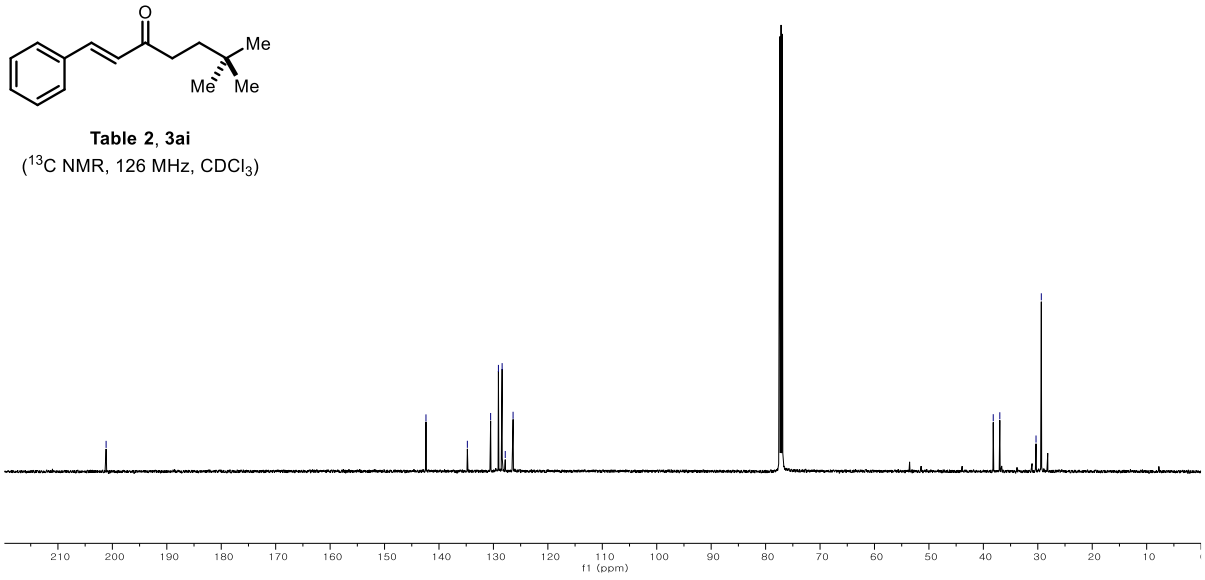


Table 2, **3ai**
(^{13}C NMR, 126 MHz, $CDCl_3$)

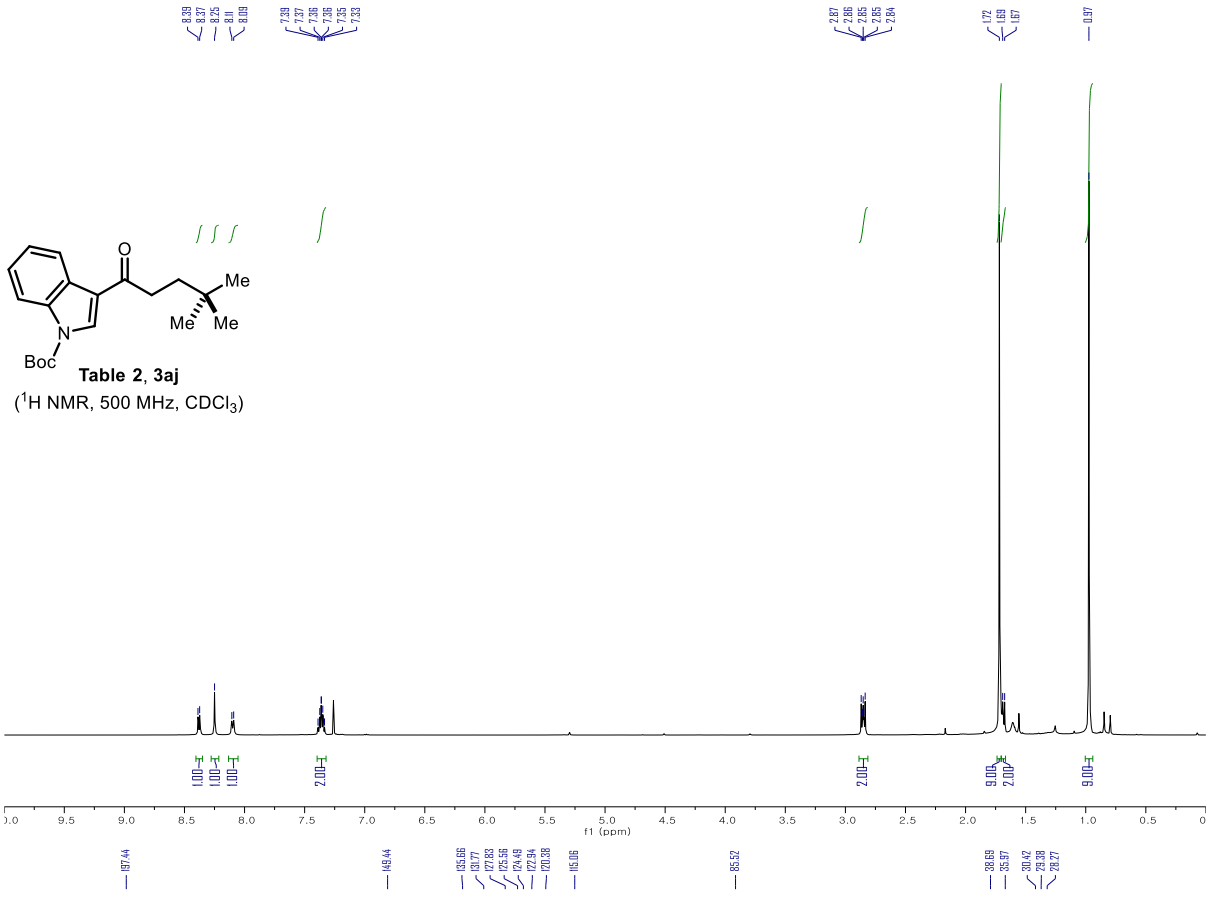


Table 2, **3aj**

(^{1}H NMR, 500 MHz, $CDCl_3$)

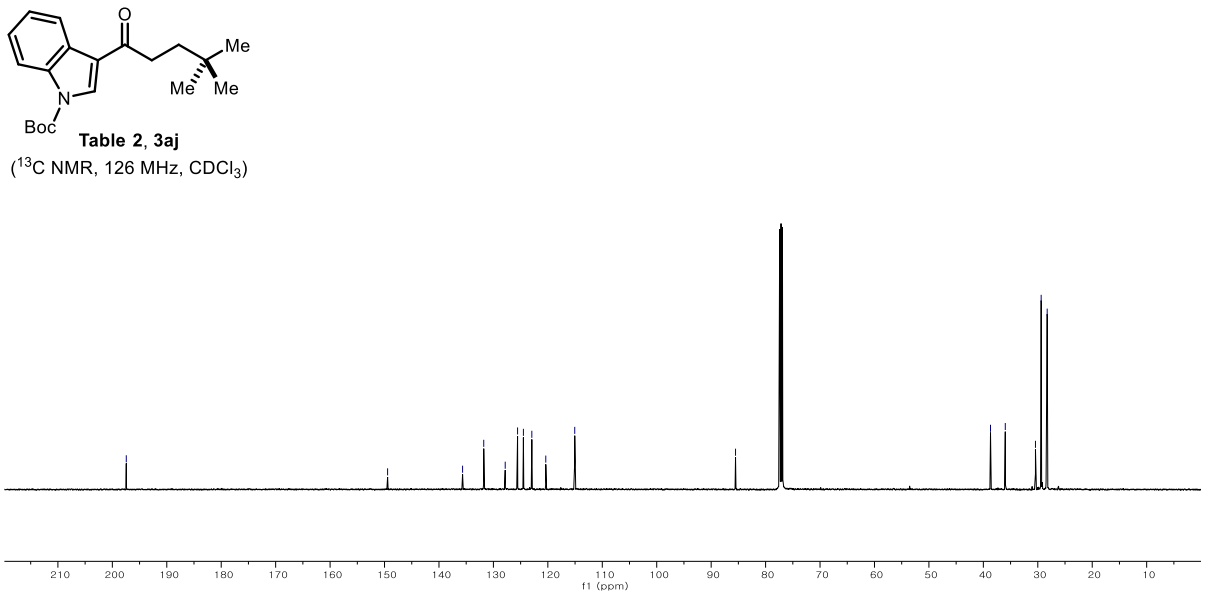


Table 2, **3aj**

(^{13}C NMR, 126 MHz, $CDCl_3$)

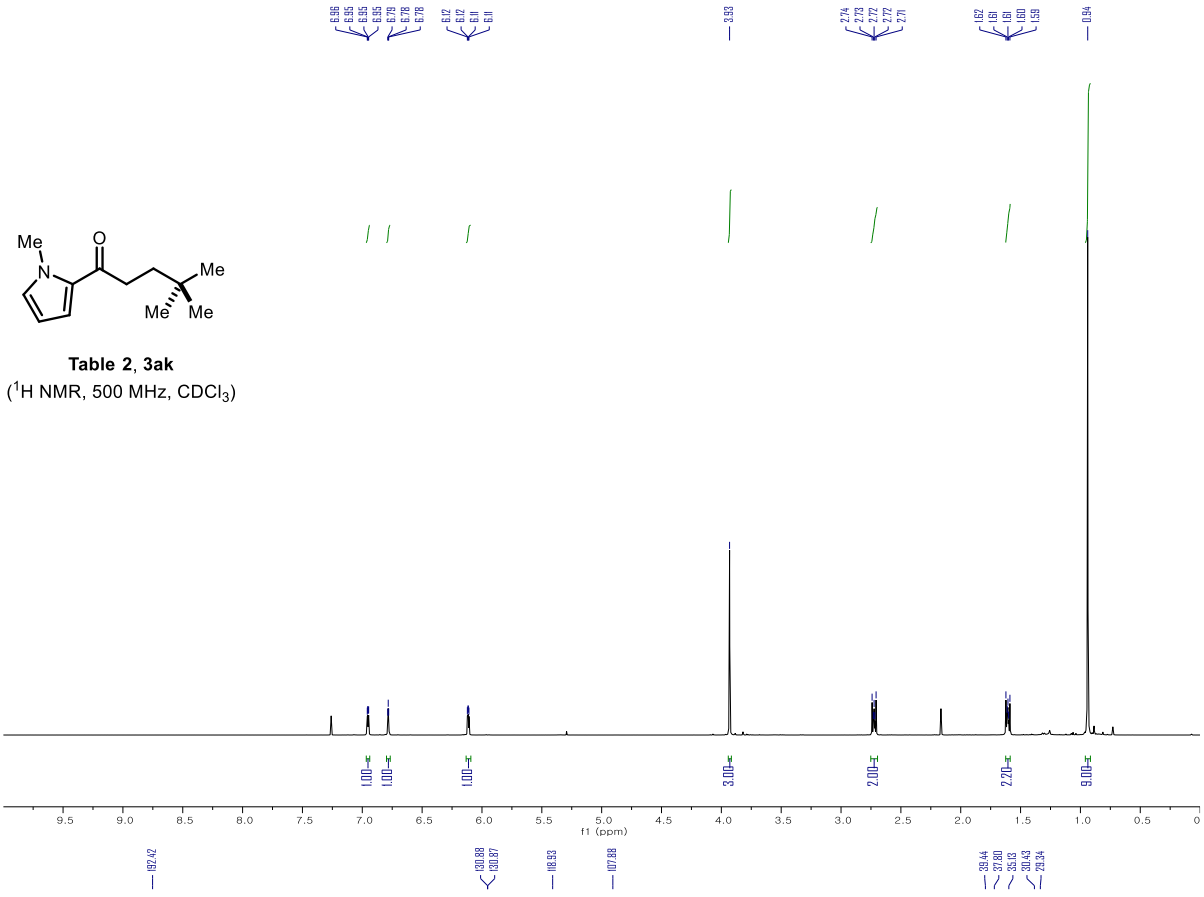


Table 2, **3ak**
(^{1}H NMR, 500 MHz, $CDCl_3$)

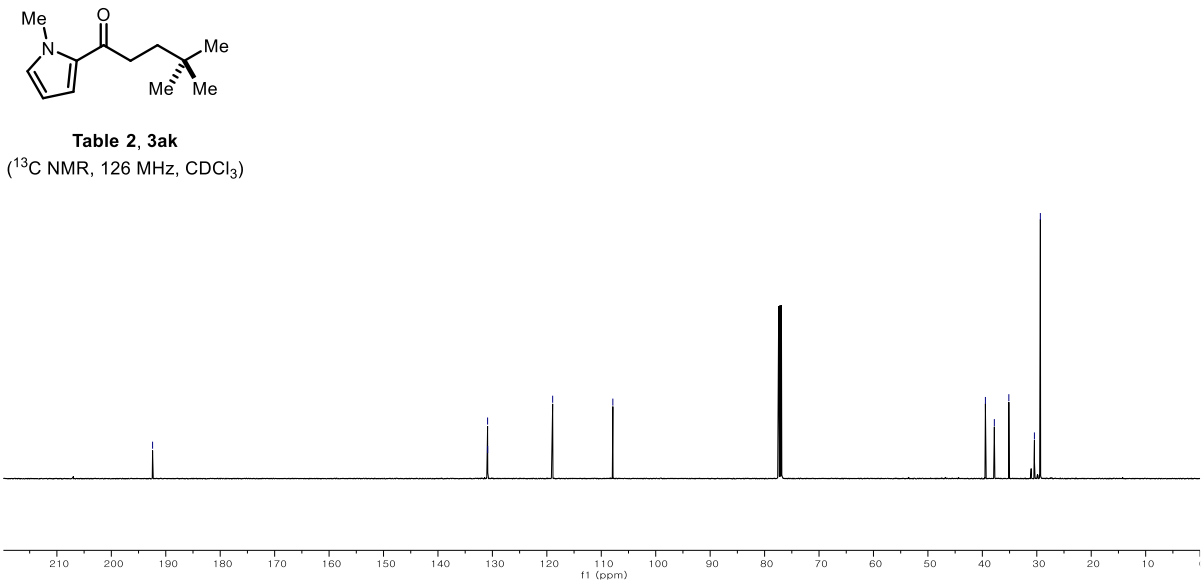


Table 2, **3ak**
(^{13}C NMR, 126 MHz, $CDCl_3$)

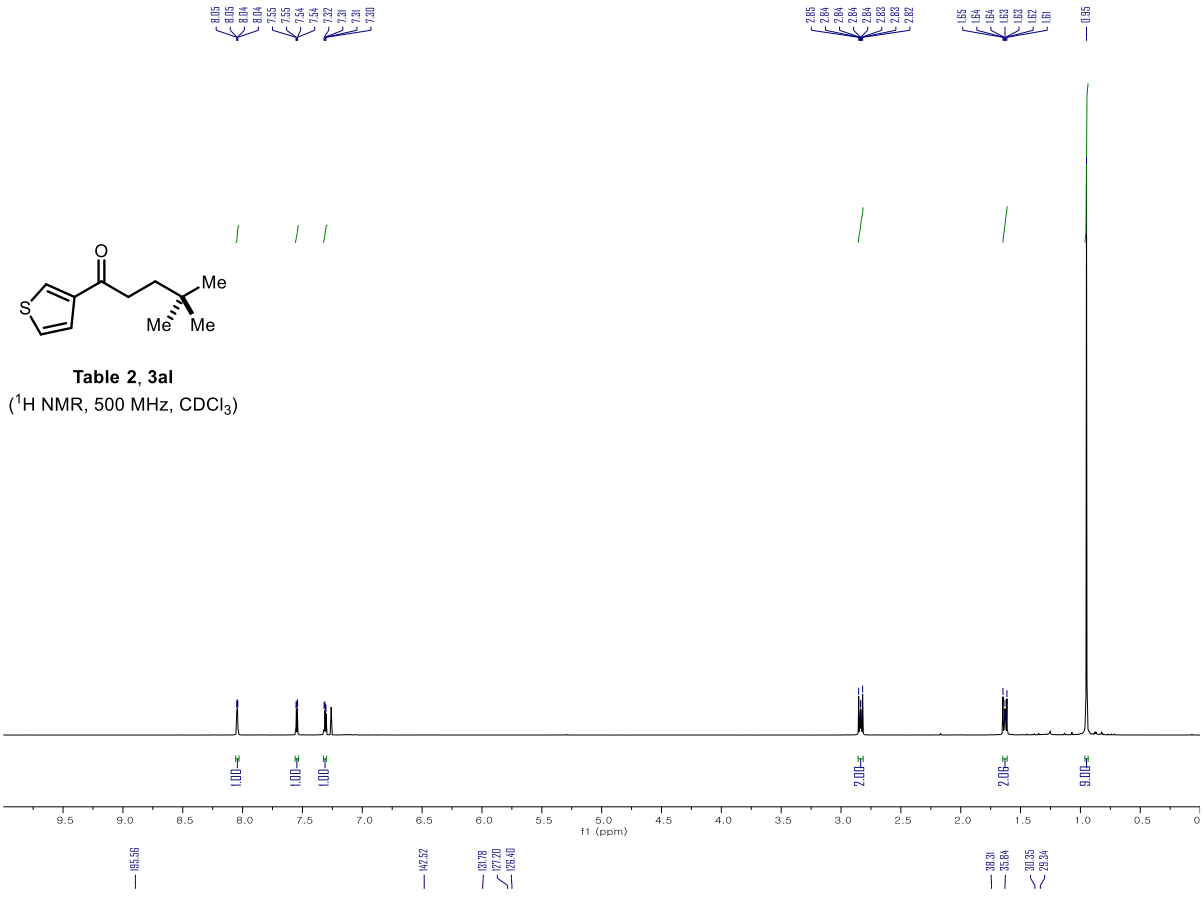


Table 2, **3al**
(^{1}H NMR, 500 MHz, $CDCl_3$)

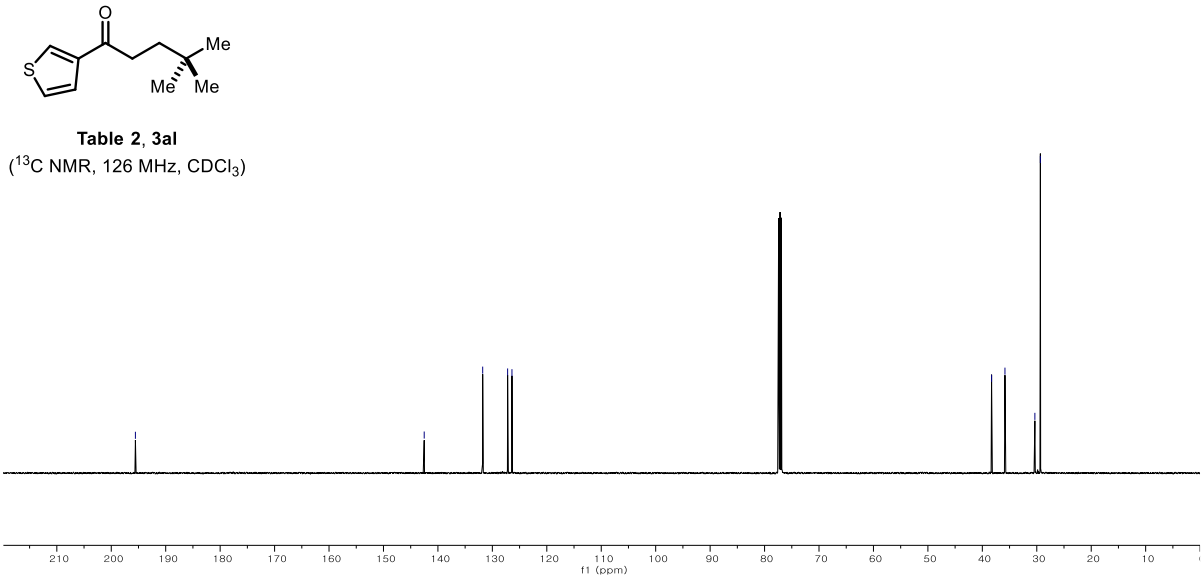


Table 2, **3al**
(^{13}C NMR, 126 MHz, $CDCl_3$)

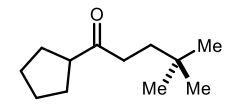


Table 2, **3am**
(^{1}H NMR, 500 MHz, $CDCl_3$)

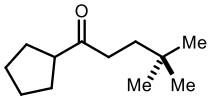
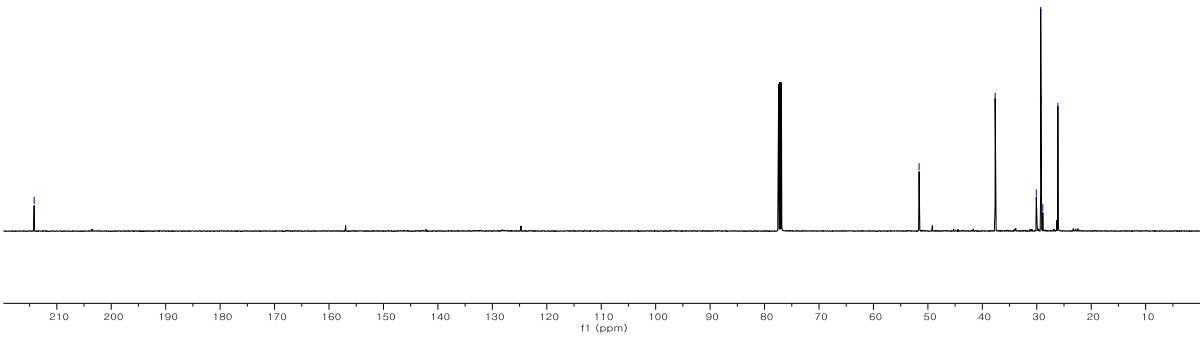


Table 2, **3am**
(^{13}C NMR, 126 MHz, $CDCl_3$)



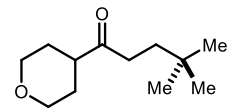


Table 2, **3an**
(^{1}H NMR, 500 MHz, $CDCl_3$)

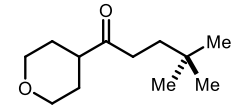
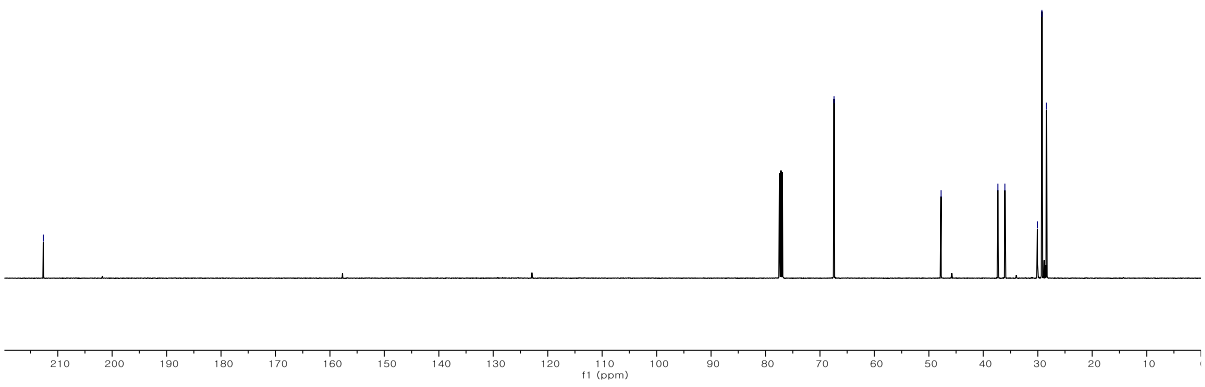


Table 2, **3an**
(^{13}C NMR, 126 MHz, $CDCl_3$)



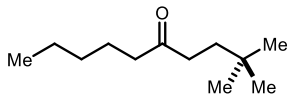


Table 2, **3ao**
(^{1}H NMR, 500 MHz, $CDCl_3$)

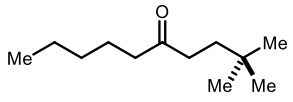
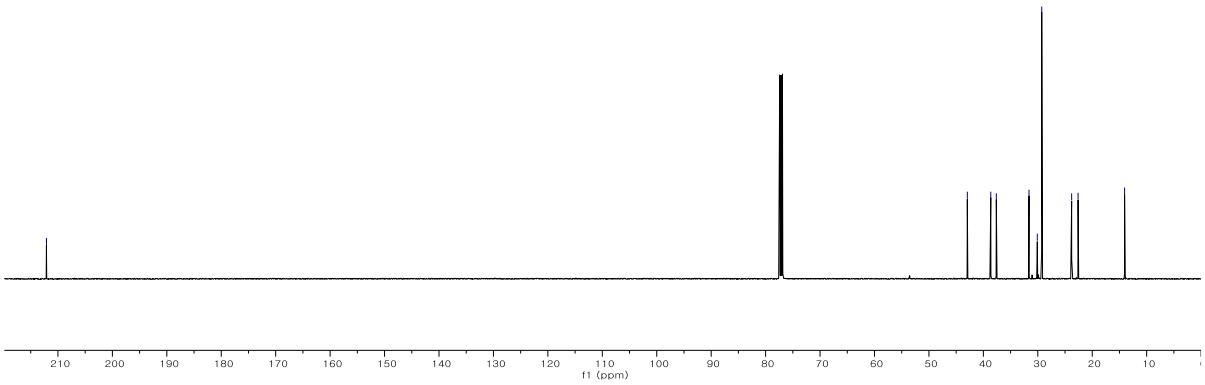


Table 2, **3ao**
(^{13}C NMR, 126 MHz, $CDCl_3$)



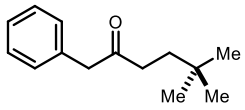


Table 2, **3ap**
(^{1}H NMR, 500 MHz, $CDCl_3$)

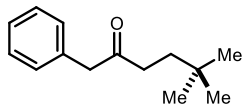
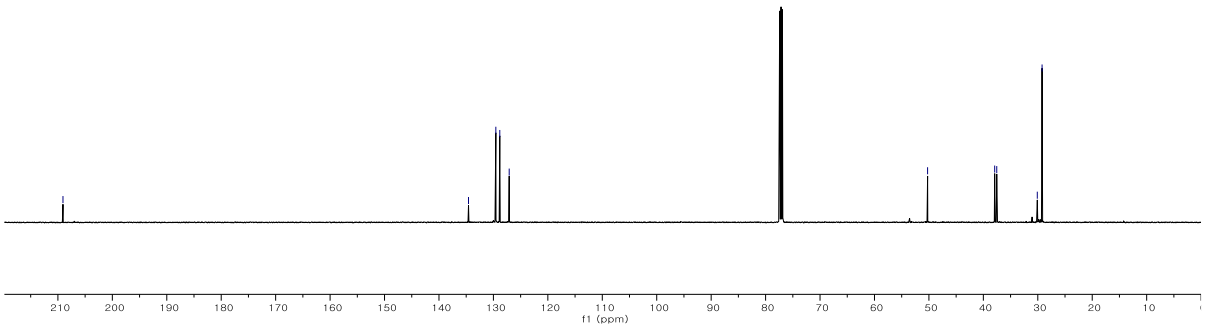


Table 2, **3ap**
(^{13}C NMR, 126 MHz, $CDCl_3$)



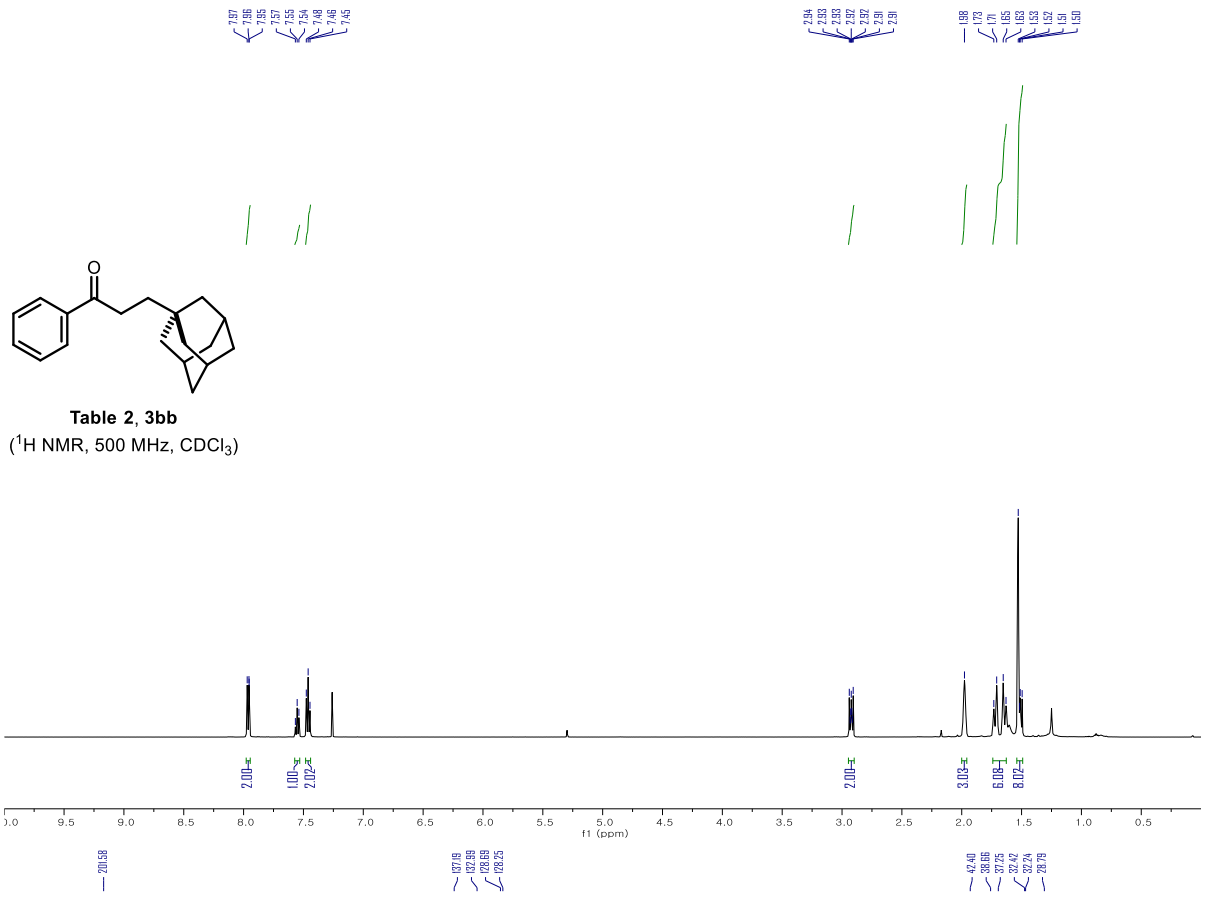


Table 2, **3bb**
(^{1}H NMR, 500 MHz, $CDCl_3$)

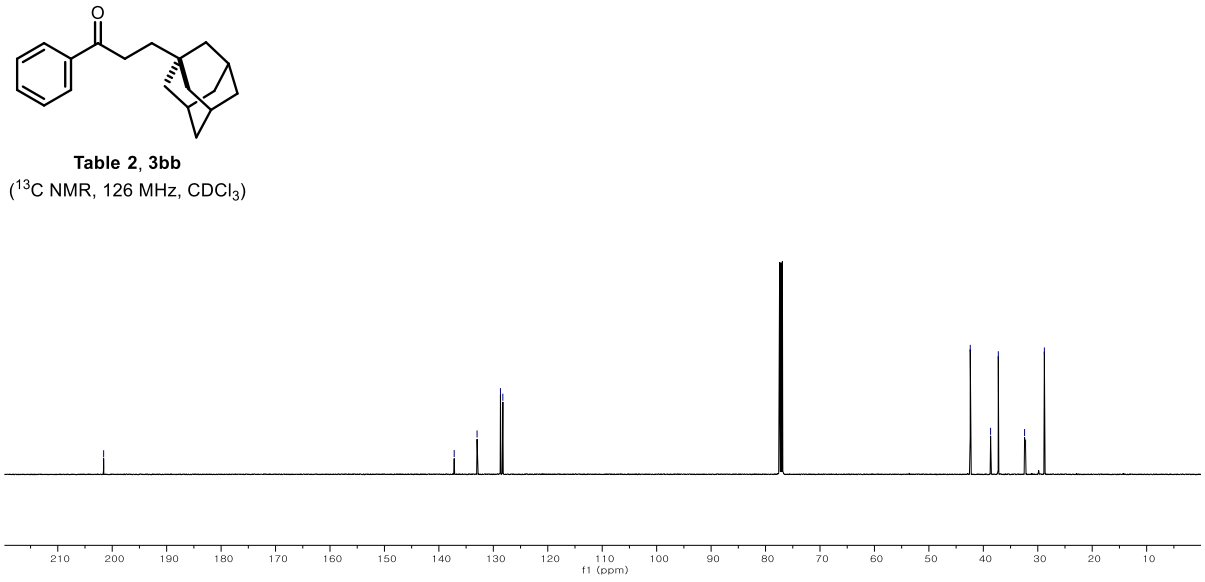
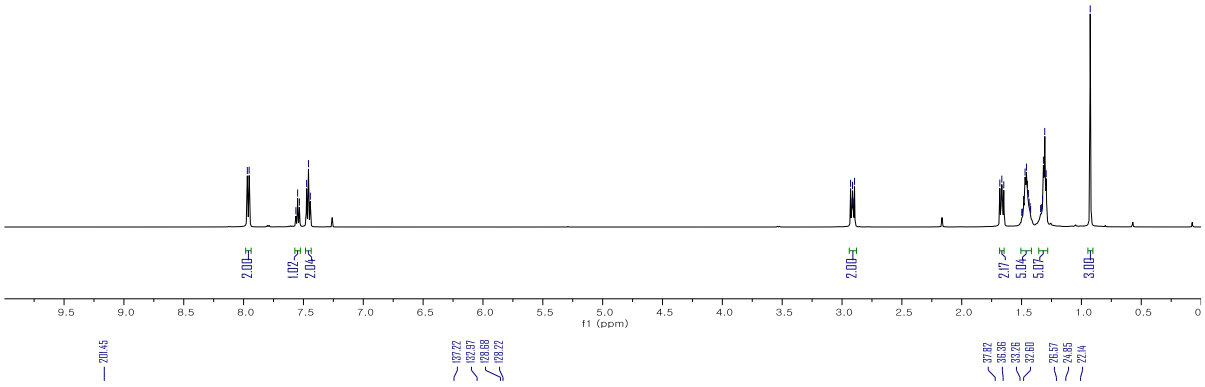


Table 2, **3bb**
(^{13}C NMR, 126 MHz, $CDCl_3$)

Table 2, **3bc**
(^{1}H NMR, 500 MHz, $CDCl_3$)



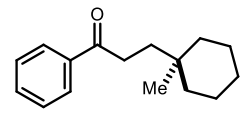
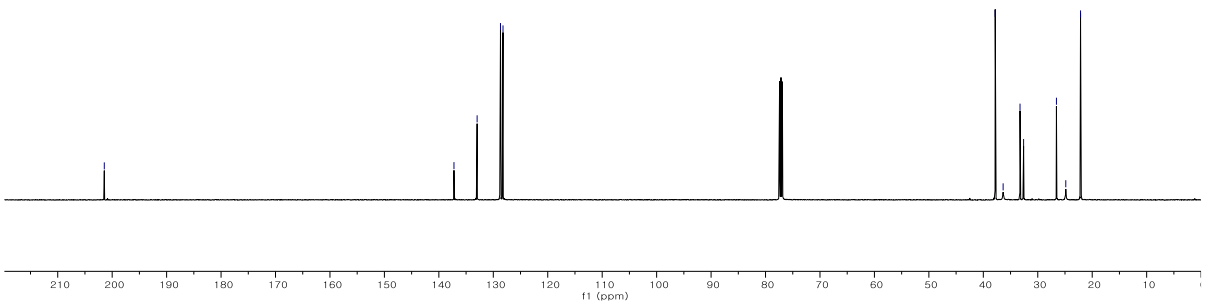


Table 2, **3bc**
(^{13}C NMR, 126 MHz, $CDCl_3$)



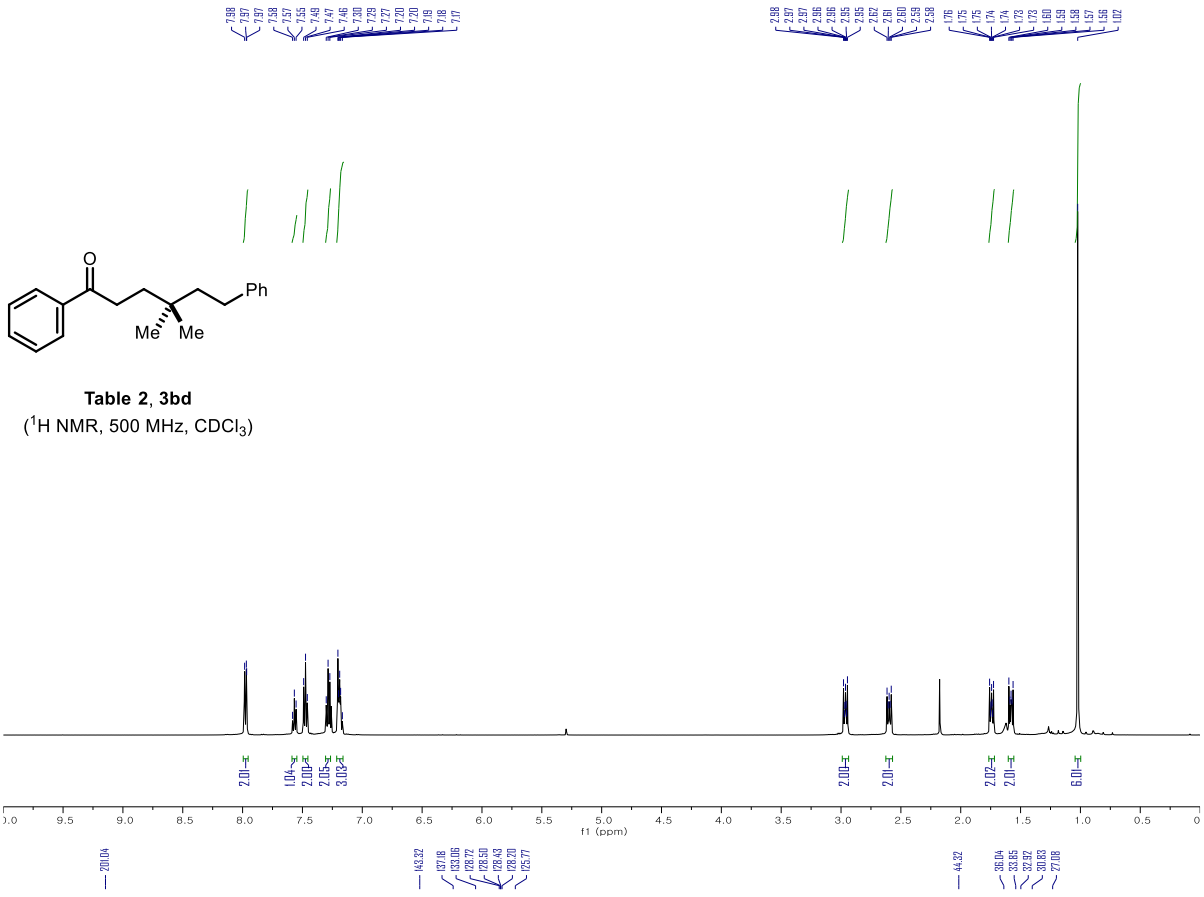


Table 2, **3bd**
(^{1}H NMR, 500 MHz, $CDCl_3$)

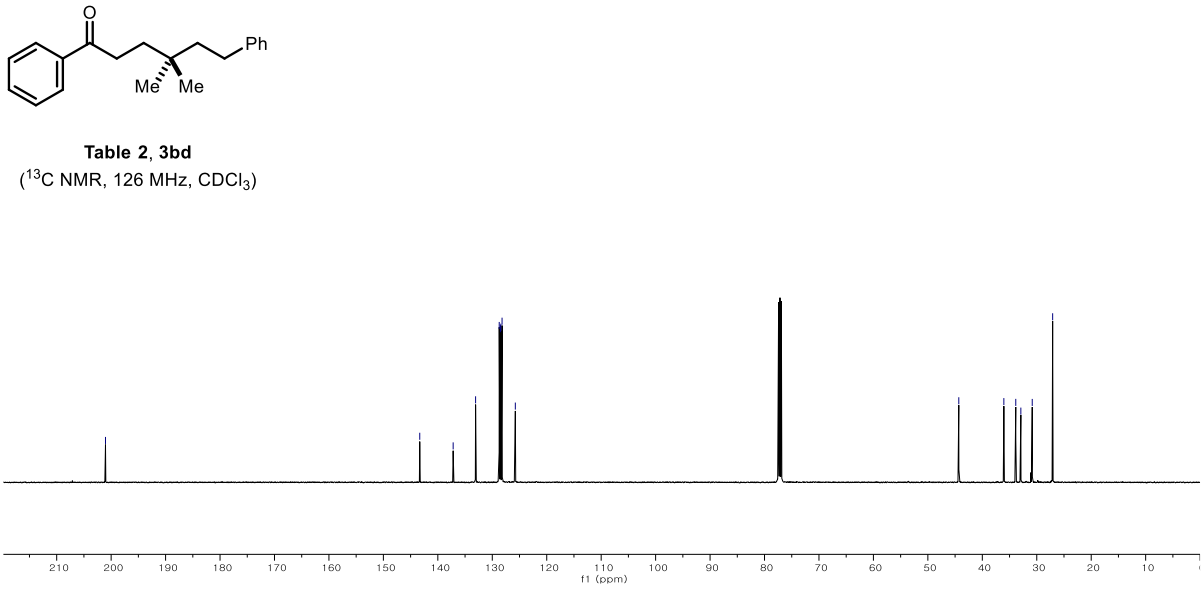
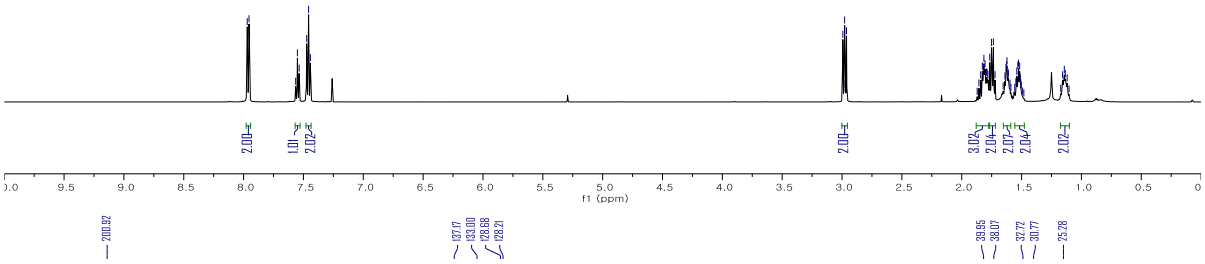


Table 2, **3bd**
(^{13}C NMR, 126 MHz, $CDCl_3$)

Table 2, **3be**
(^{1}H NMR, 500 MHz, $CDCl_3$)



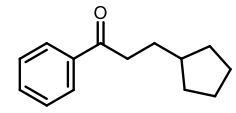


Table 2, **3be**
(^{13}C NMR, 126 MHz, $CDCl_3$)

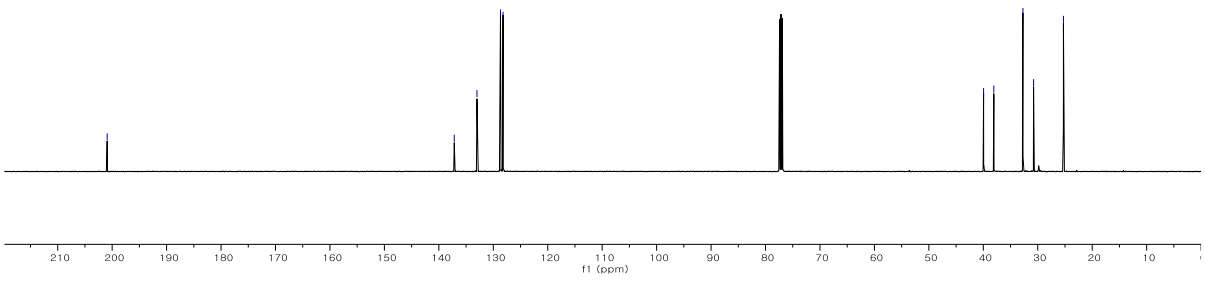


Table 2, **3bf**
(^{1}H NMR, 500 MHz, $CDCl_3$)

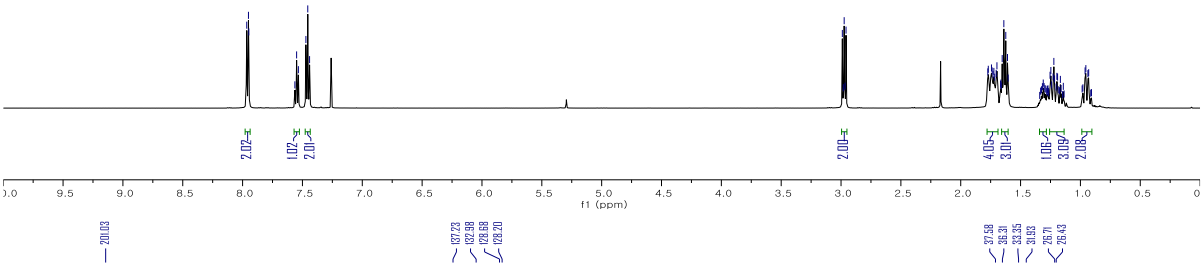
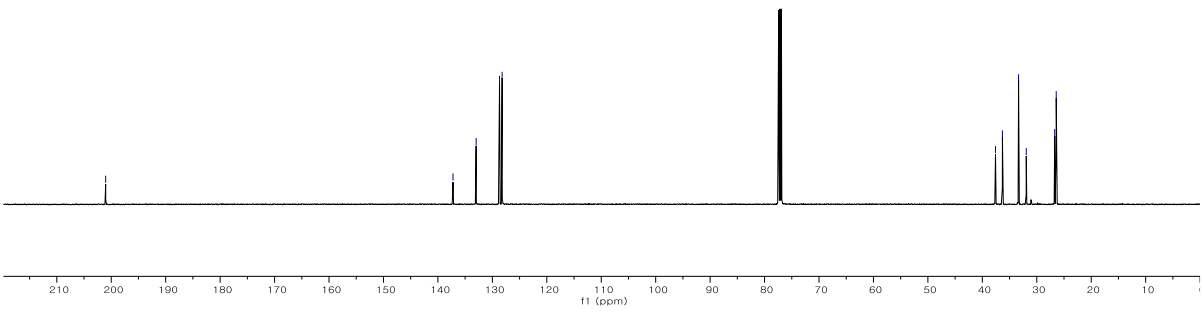


Table 2, **3bf**
(^{13}C NMR, 126 MHz, $CDCl_3$)



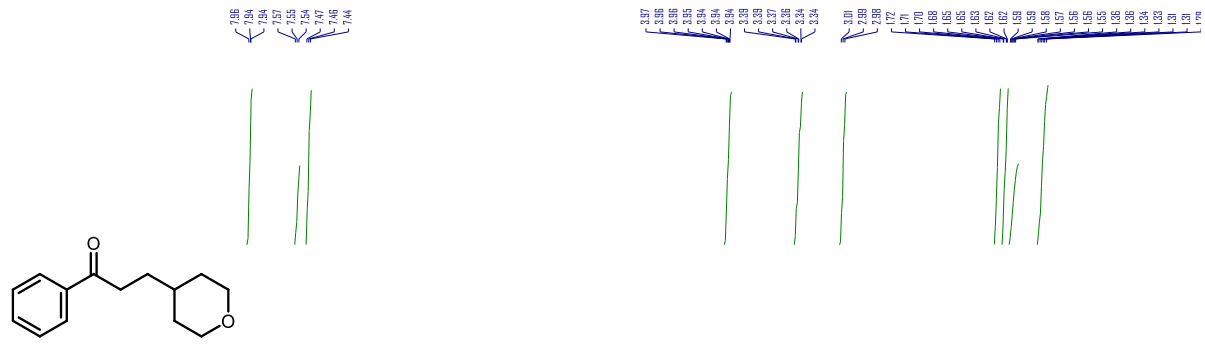
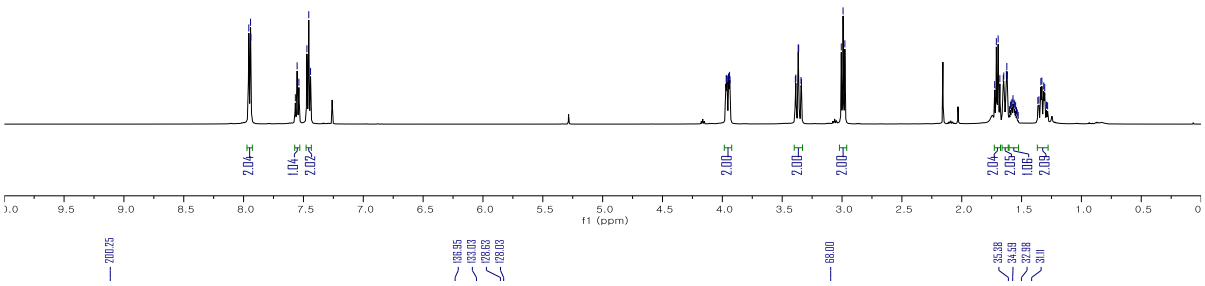


Table 2, **3bg**
(^{1}H NMR, 500 MHz, $CDCl_3$)



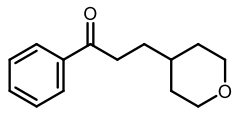
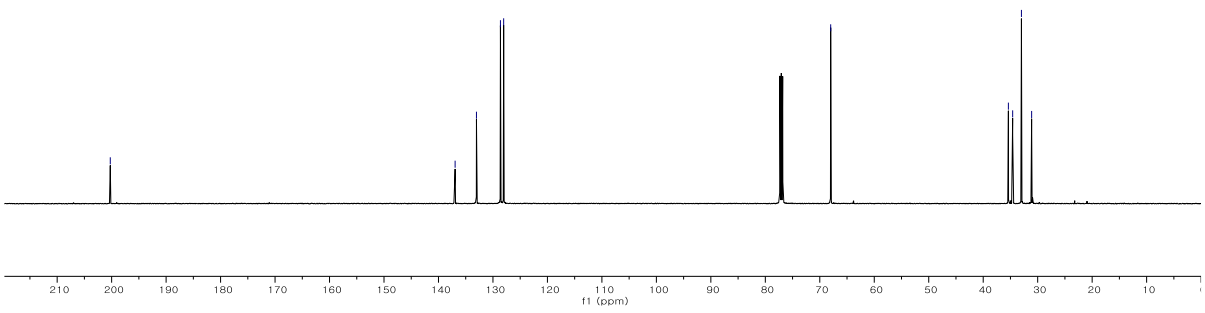


Table 2, **3bg**
(^{13}C NMR, 125 MHz, $CDCl_3$)



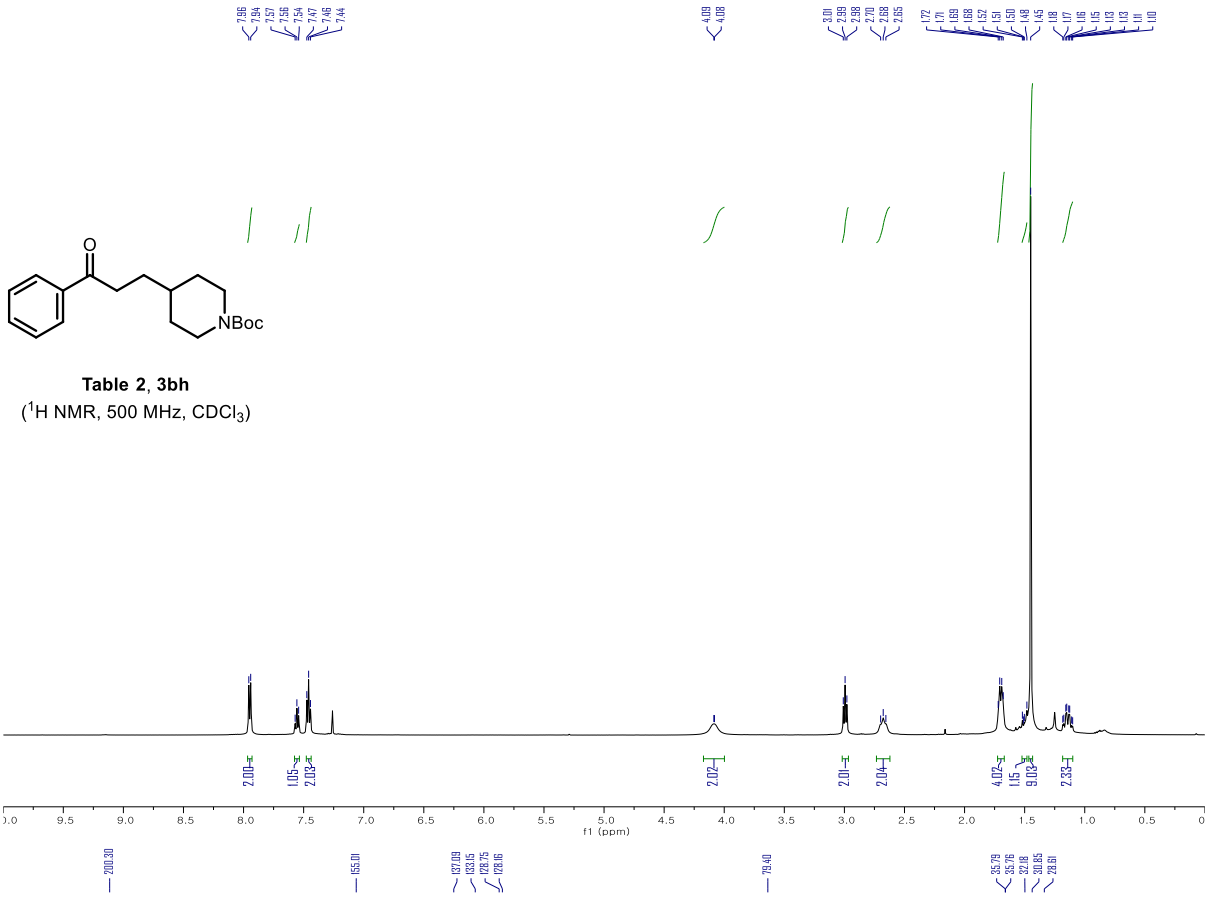


Table 2, **3bh**
(^{1}H NMR, 500 MHz, $CDCl_3$)

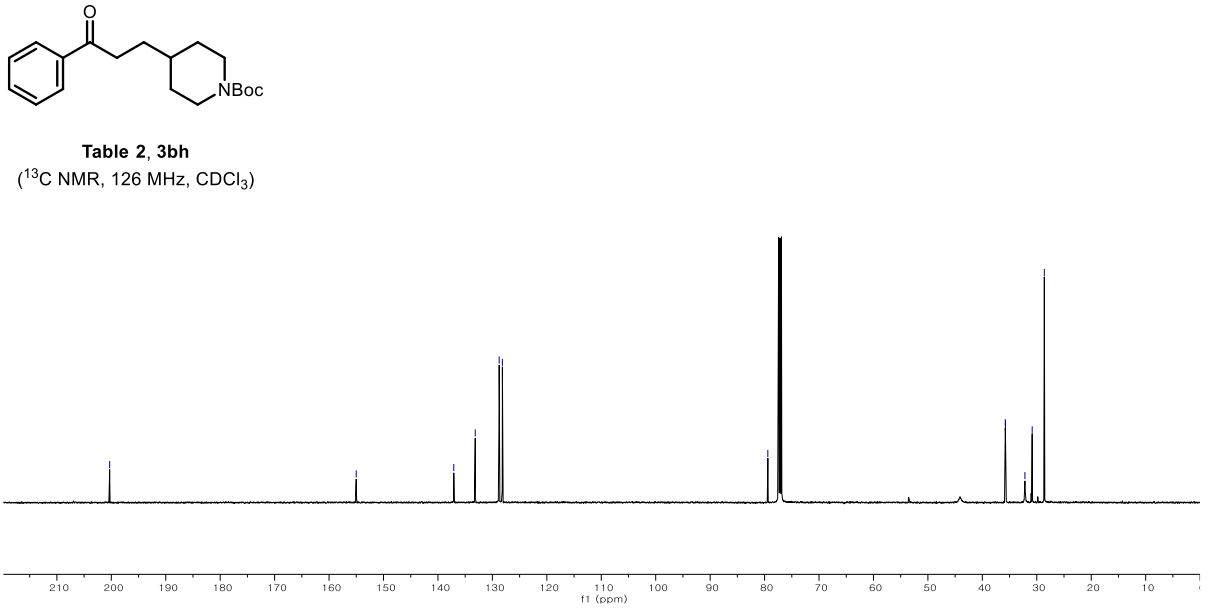


Table 2, **3bh**
(^{13}C NMR, 126 MHz, $CDCl_3$)

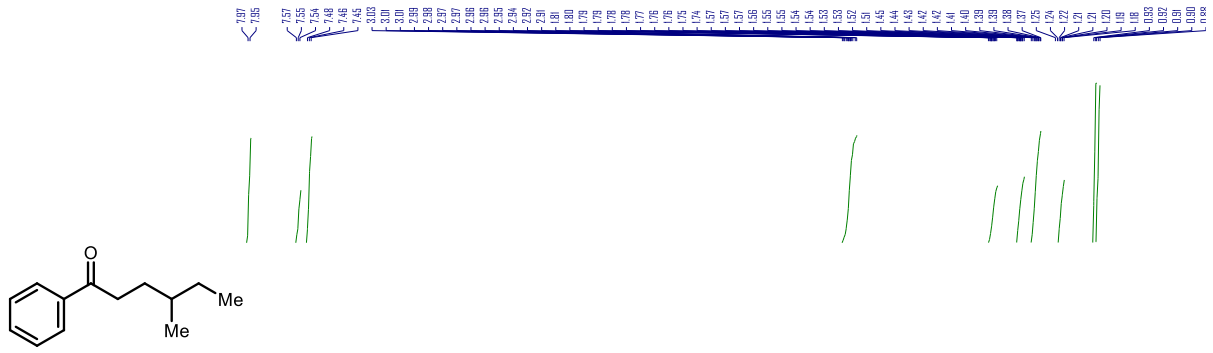
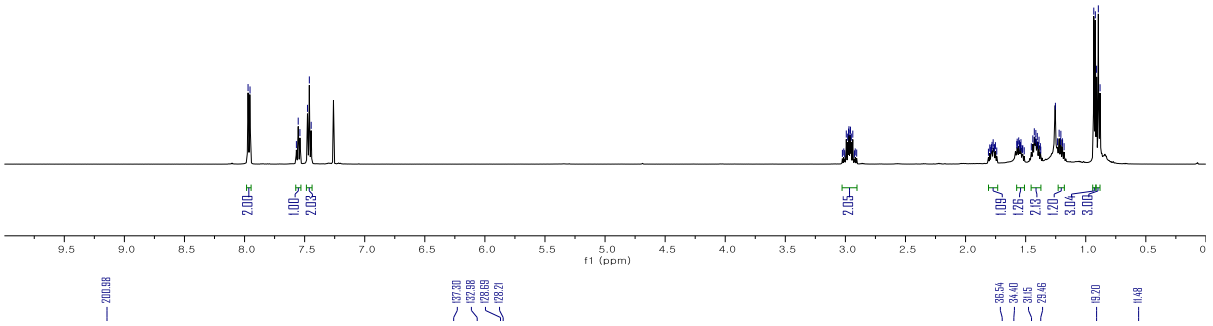


Table 2, **3bi**
(^{1}H NMR, 500 MHz, $CDCl_3$)



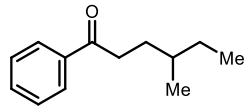


Table 2, **3bi**
(^{13}C NMR, 126 MHz, $CDCl_3$)

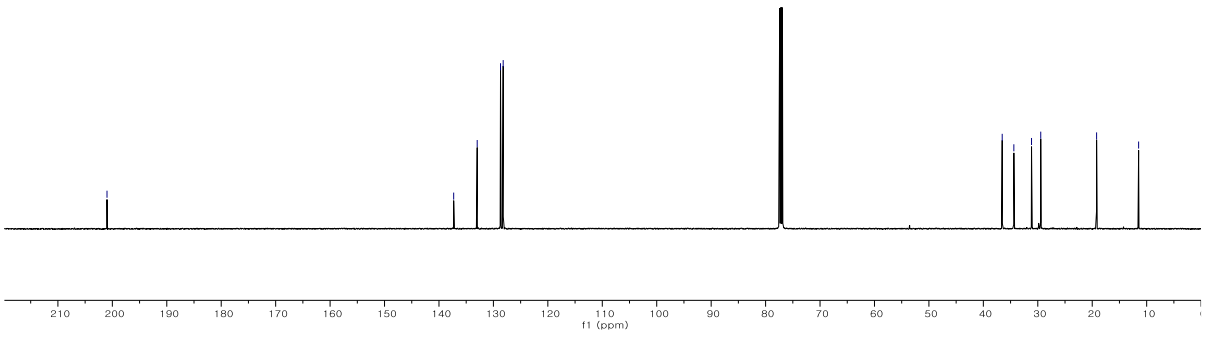
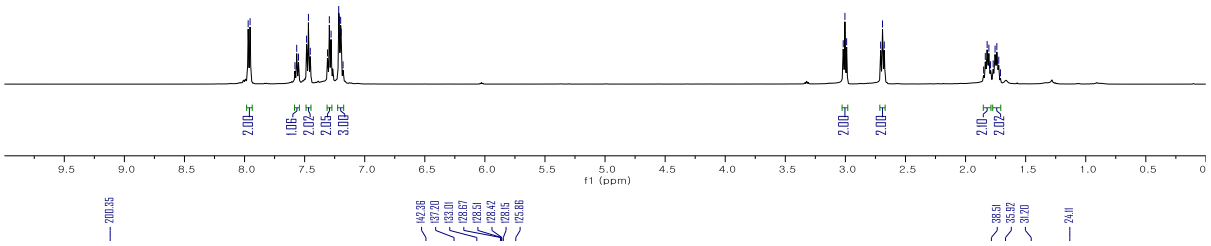


Table 2, **3bj**
(^{1}H NMR, 500 MHz, $CDCl_3$)



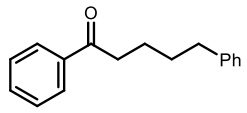
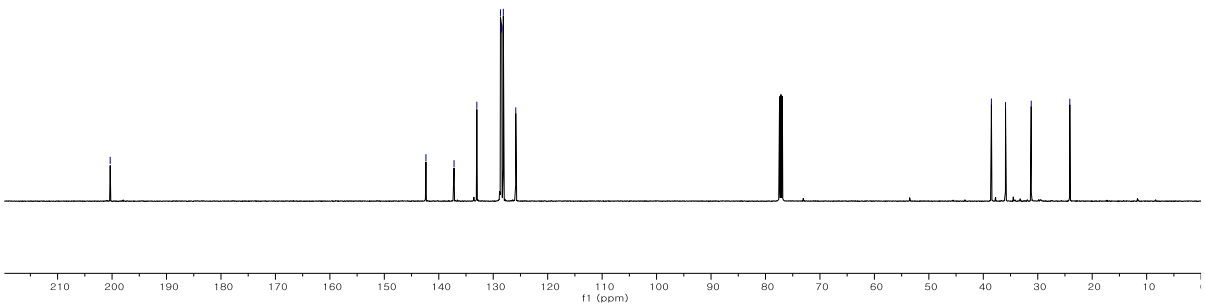


Table 2, **3bj**
(^{13}C NMR, 126 MHz, $CDCl_3$)



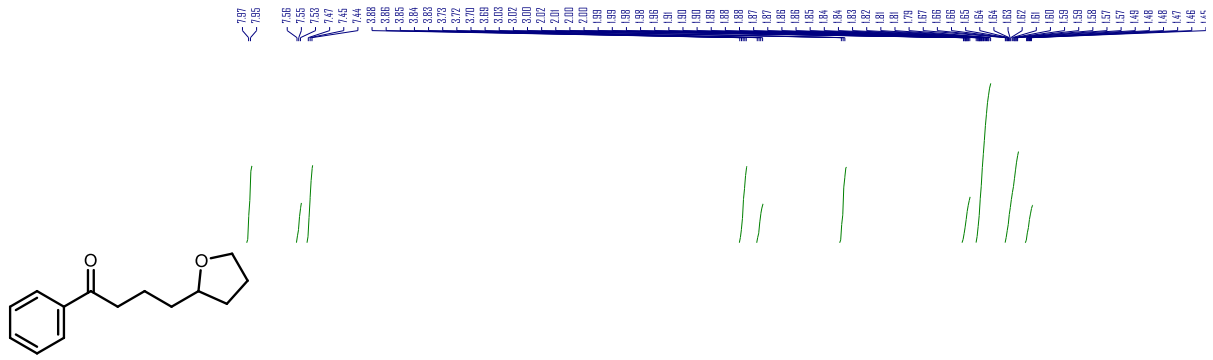
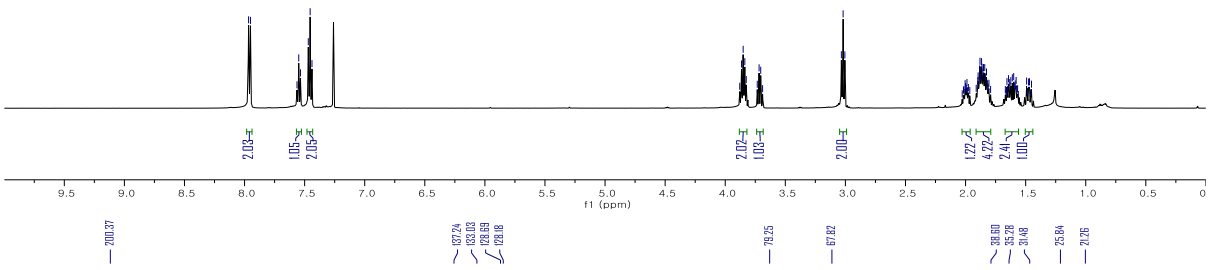


Table 2, **3bk**
(^{1}H NMR, 500 MHz, $CDCl_3$)



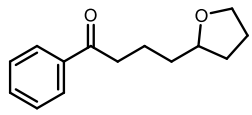
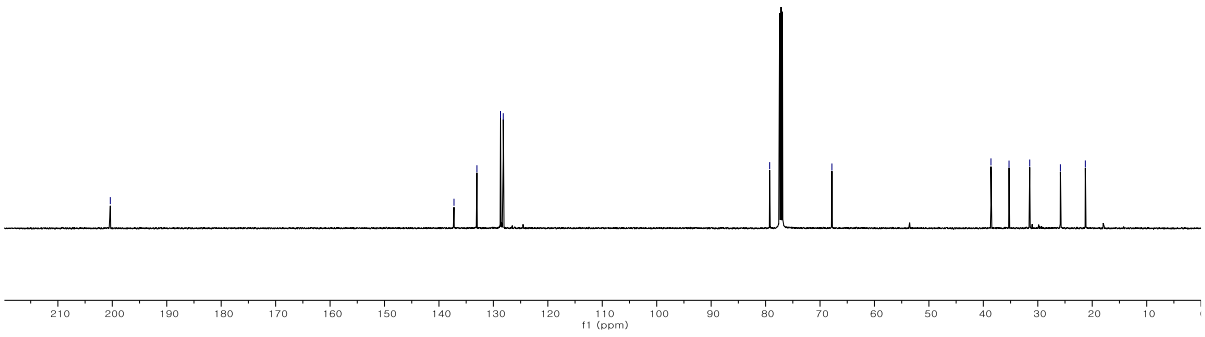


Table 2, **3bk**
(^{13}C NMR, 126 MHz, $CDCl_3$)



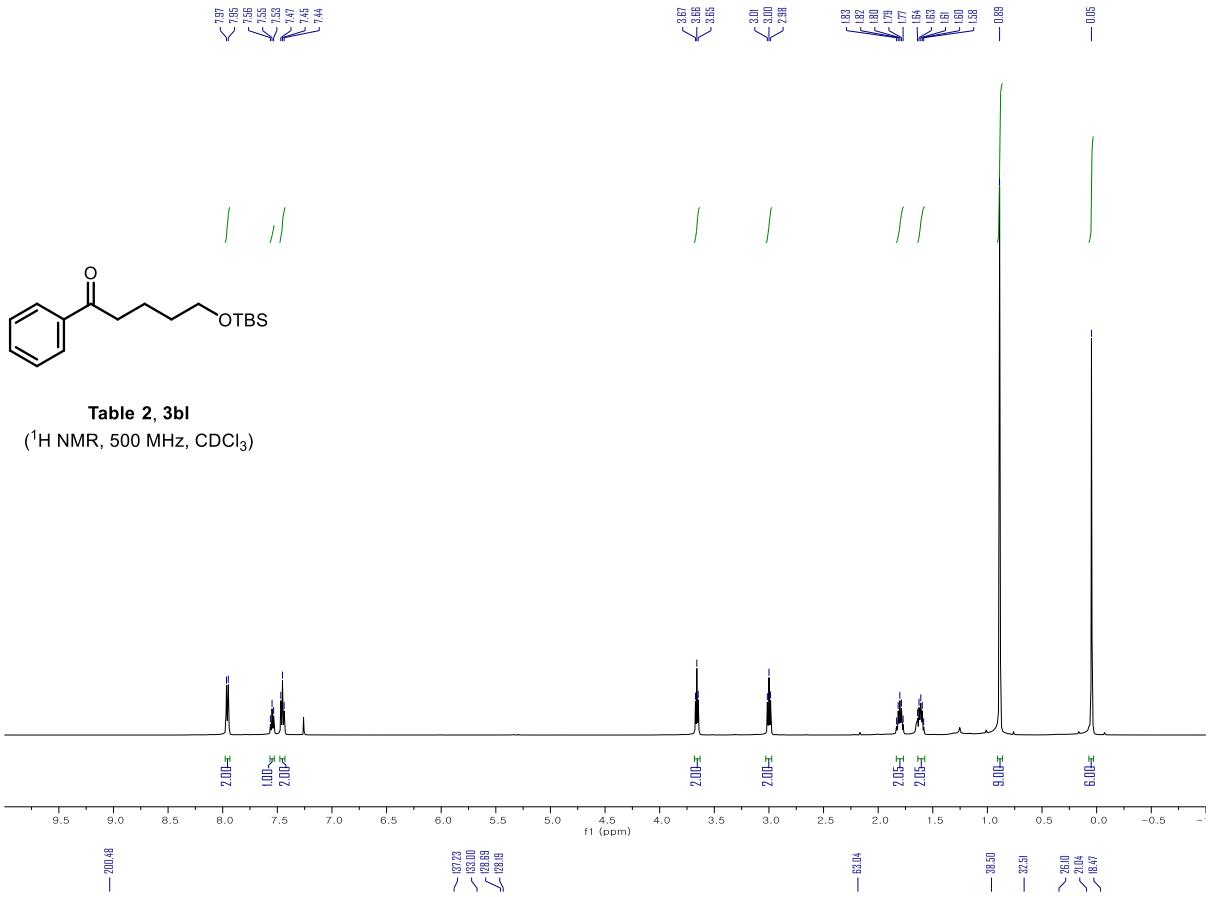


Table 2, **3bl**
(^{1}H NMR, 500 MHz, $CDCl_3$)

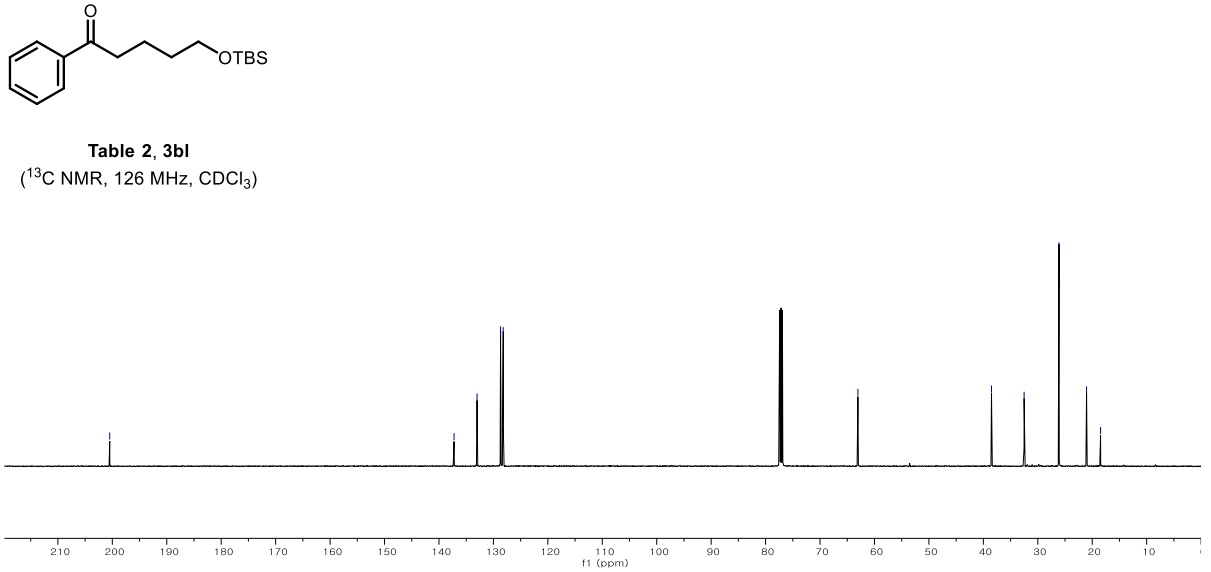


Table 2, **3bl**
(^{13}C NMR, 126 MHz, $CDCl_3$)

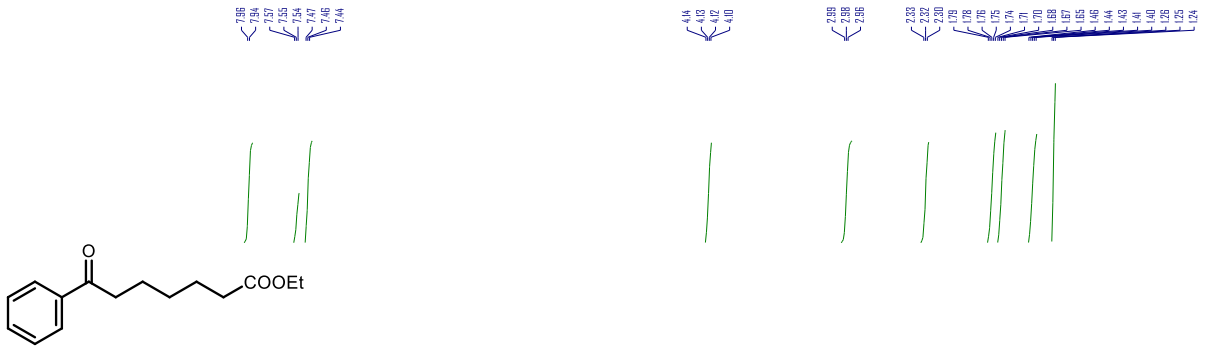
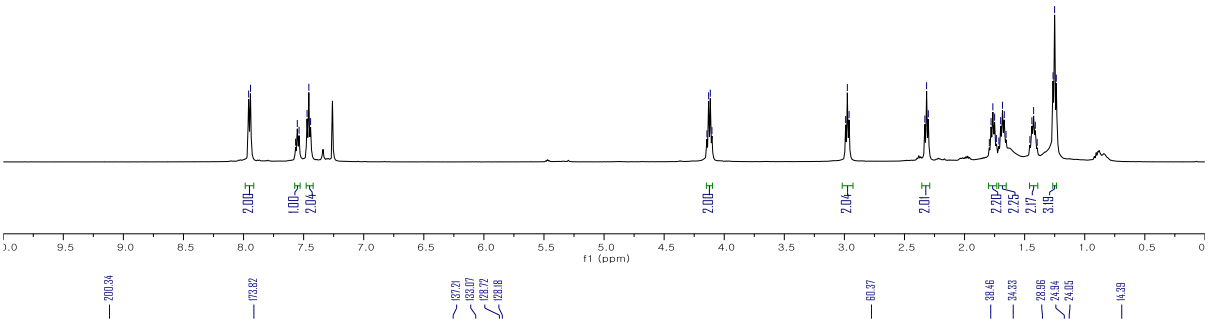


Table 2, **3bm**
(^{1}H NMR, 500 MHz, $CDCl_3$)



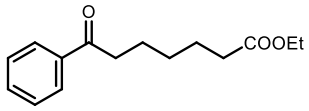
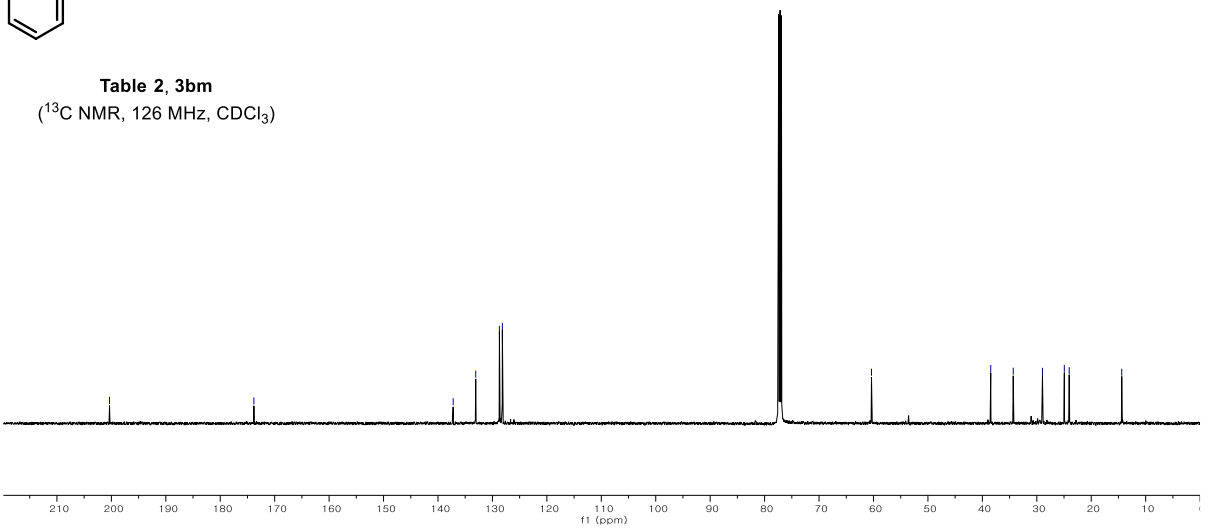


Table 2, **3bm**
(^{13}C NMR, 126 MHz, $CDCl_3$)



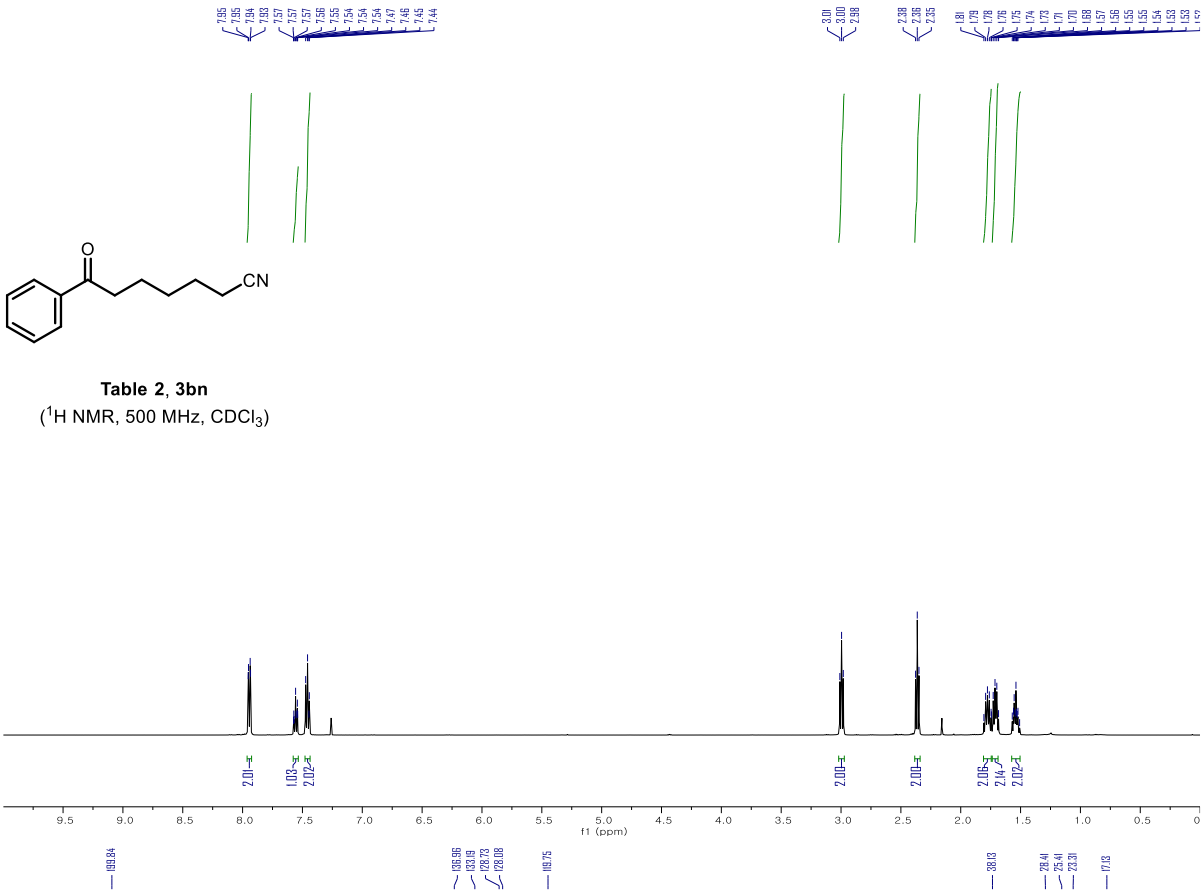


Table 2, **3bn**
(^{1}H NMR, 500 MHz, $CDCl_3$)

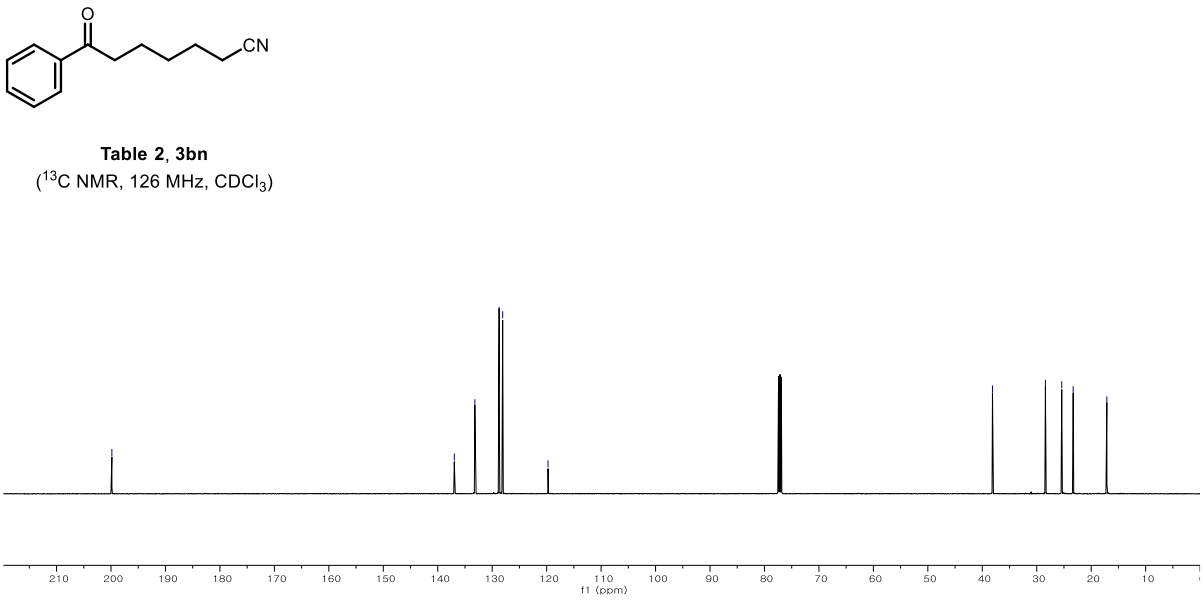


Table 2, **3bn**
(^{13}C NMR, 126 MHz, $CDCl_3$)

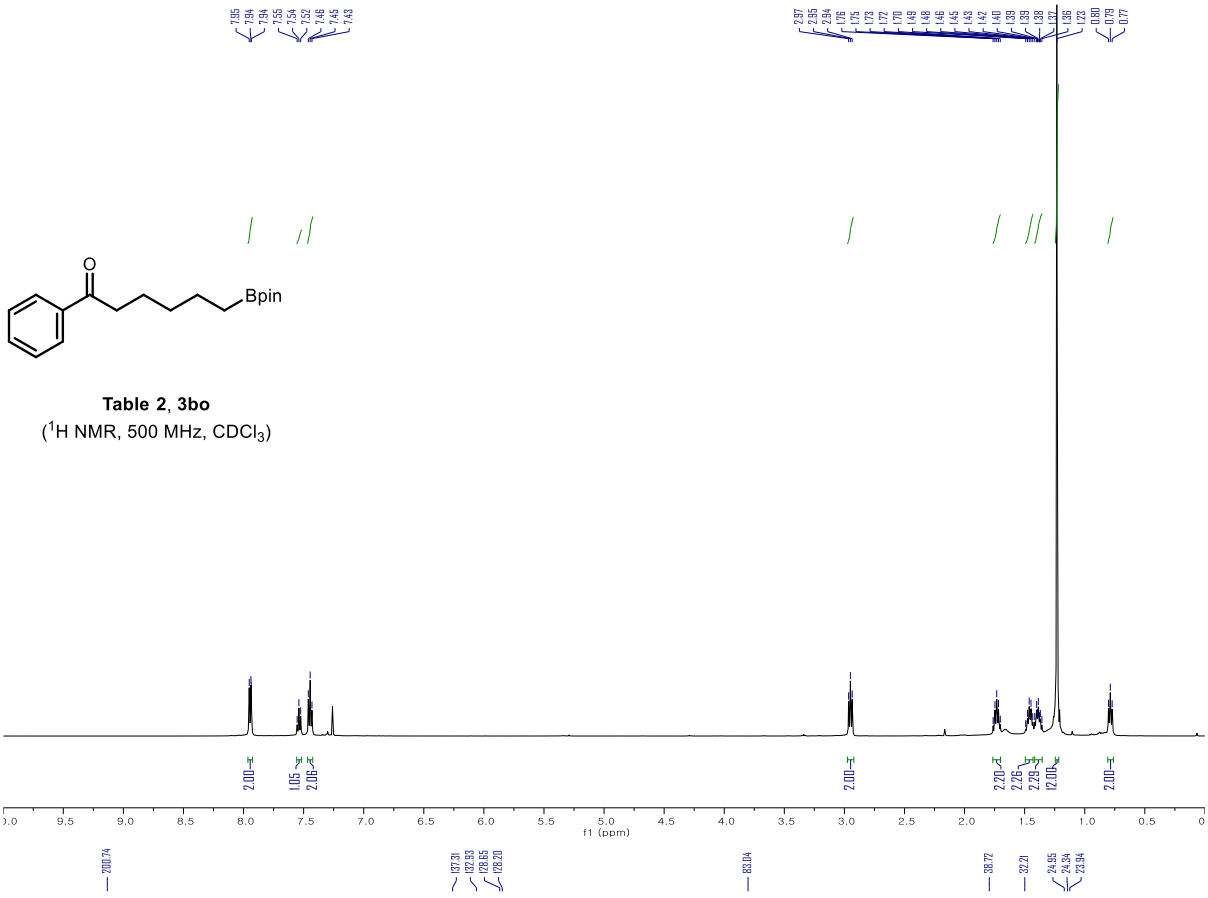


Table 2, **3bo**
(^{1}H NMR, 500 MHz, $CDCl_3$)

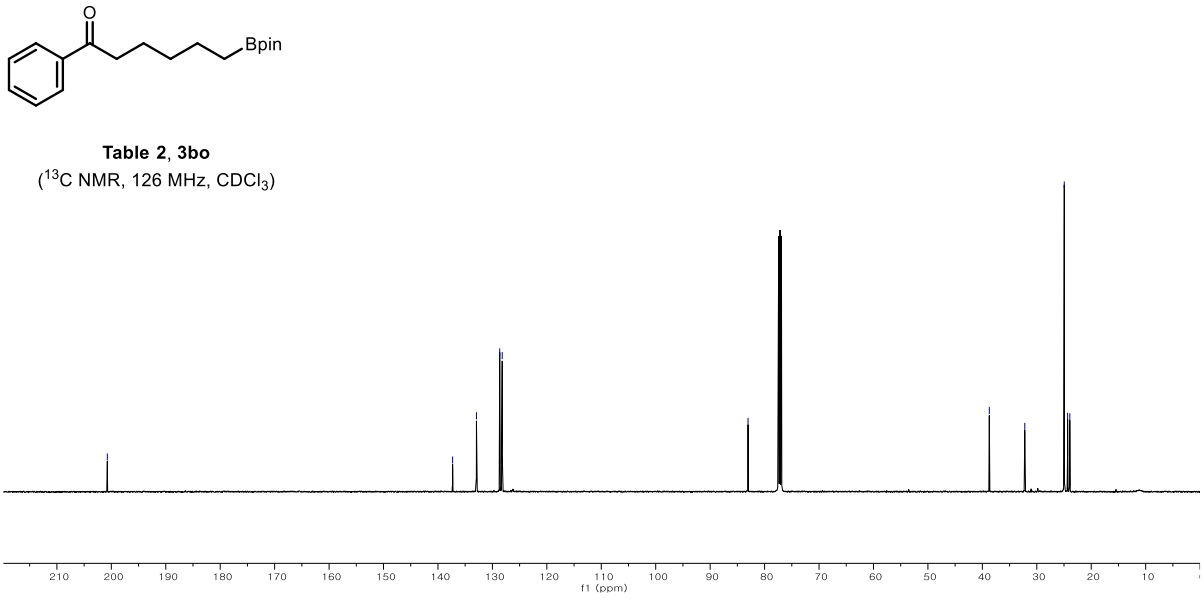


Table 2, **3bo**
(^{13}C NMR, 126 MHz, $CDCl_3$)

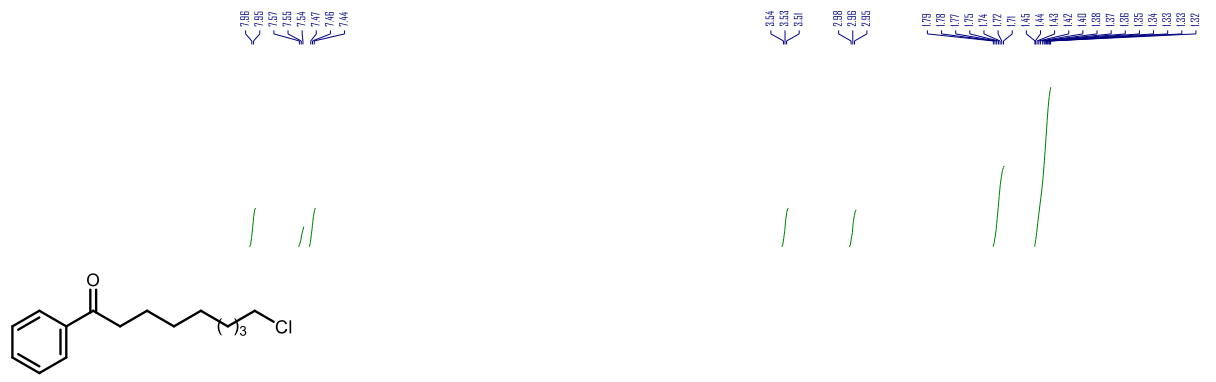


Table 2, **3bp**
(^{1}H NMR, 500 MHz, $CDCl_3$)

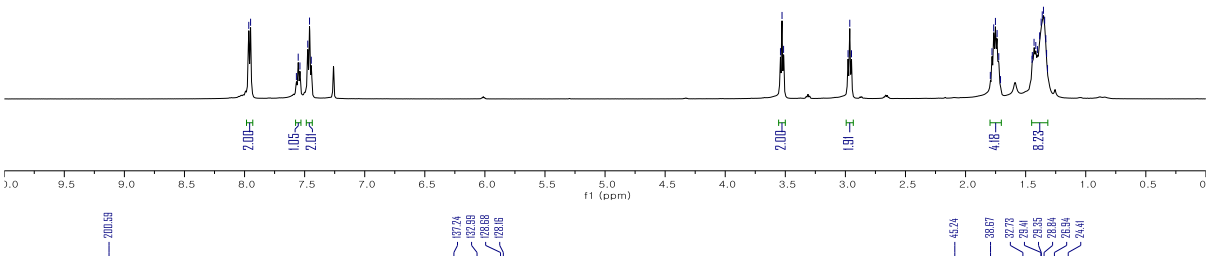
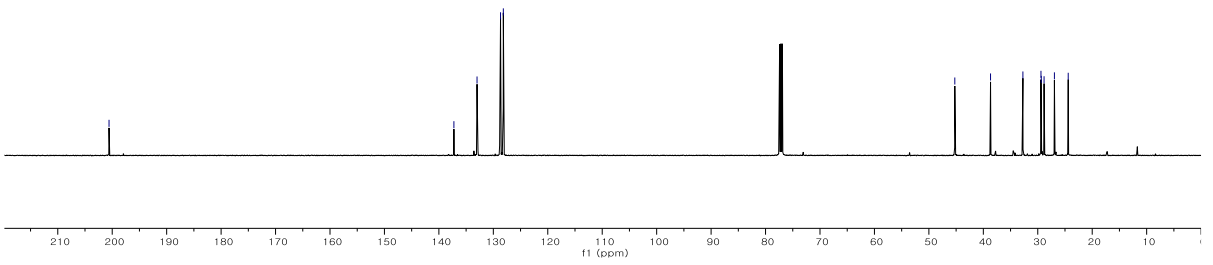


Table 2, **3bp**
(^{13}C NMR, 126 MHz, $CDCl_3$)



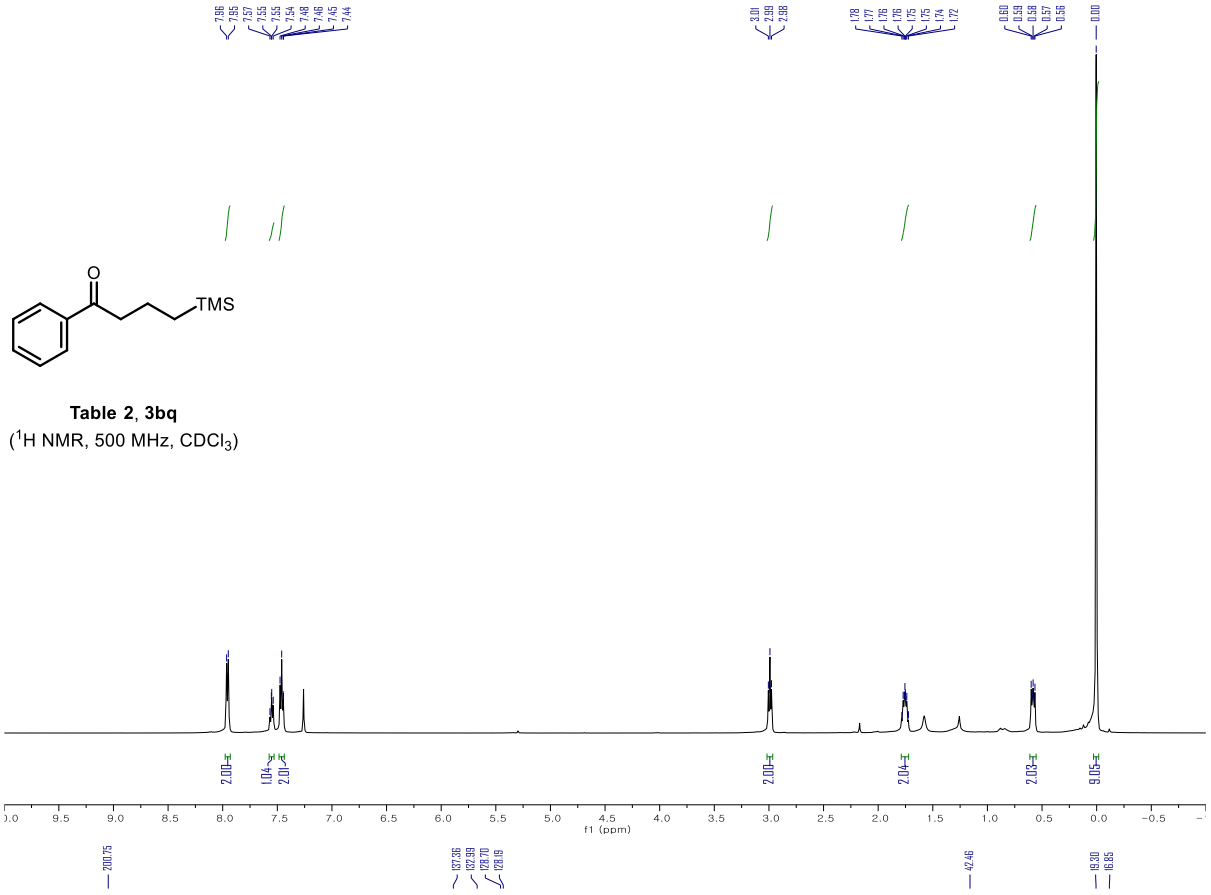


Table 2, **3bq**
(^{1}H NMR, 500 MHz, $CDCl_3$)

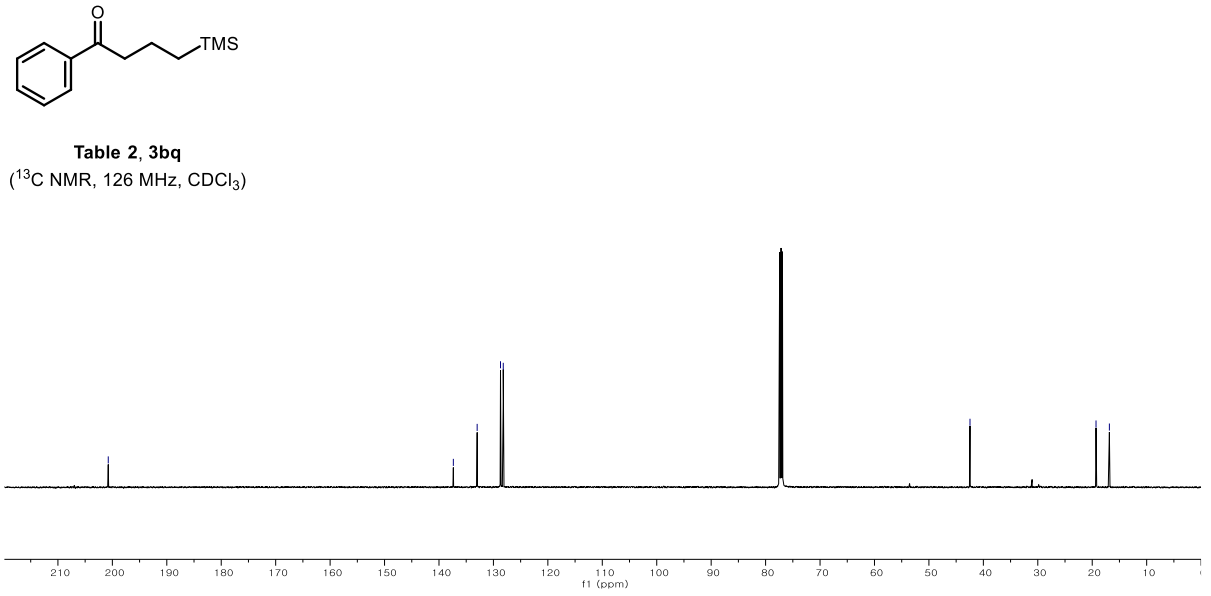


Table 2, **3bq**
(^{13}C NMR, 126 MHz, $CDCl_3$)

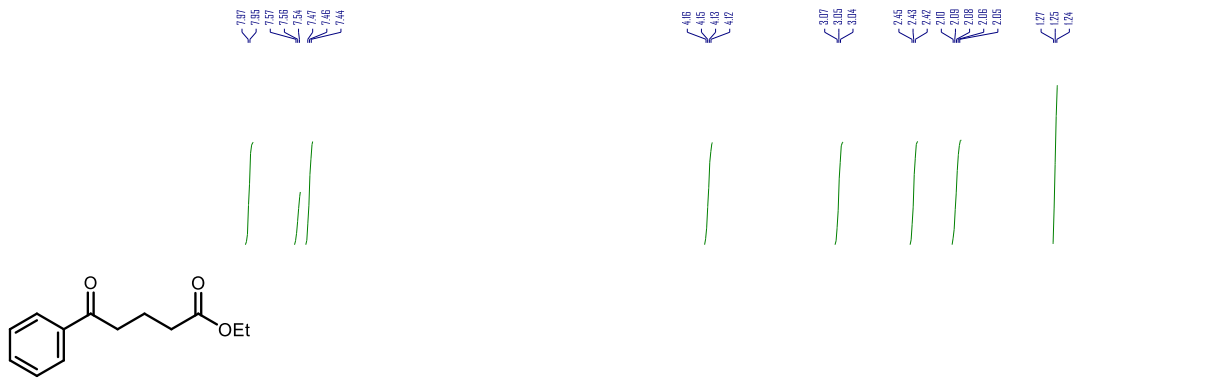
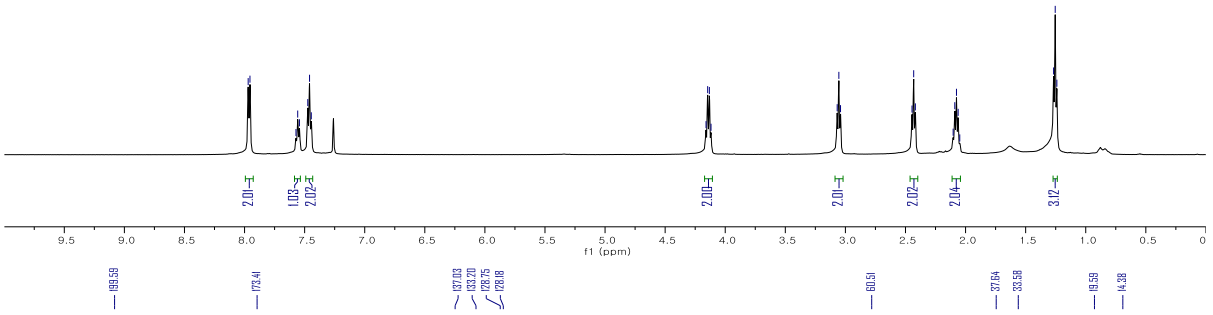


Table 2, **3br**
(^{1}H NMR, 500 MHz, $CDCl_3$)



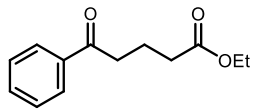
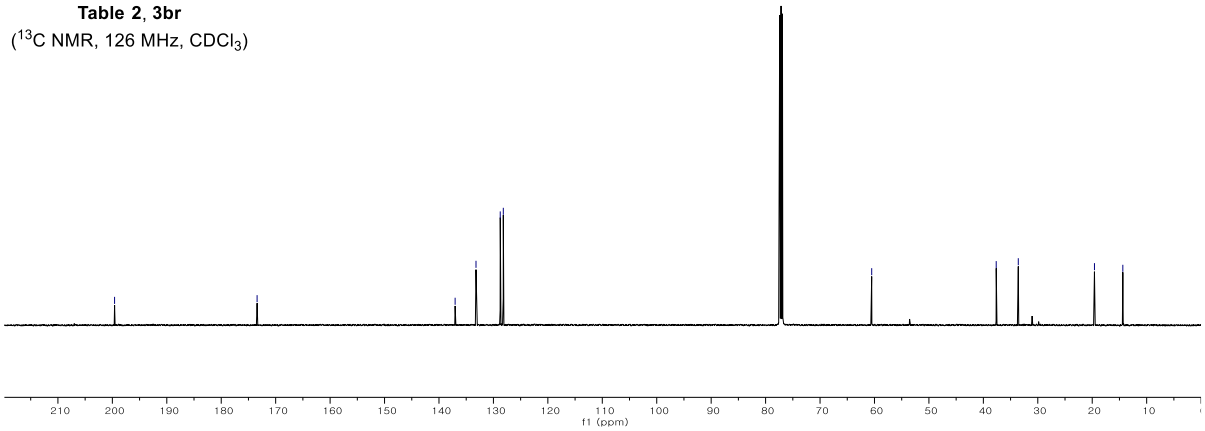
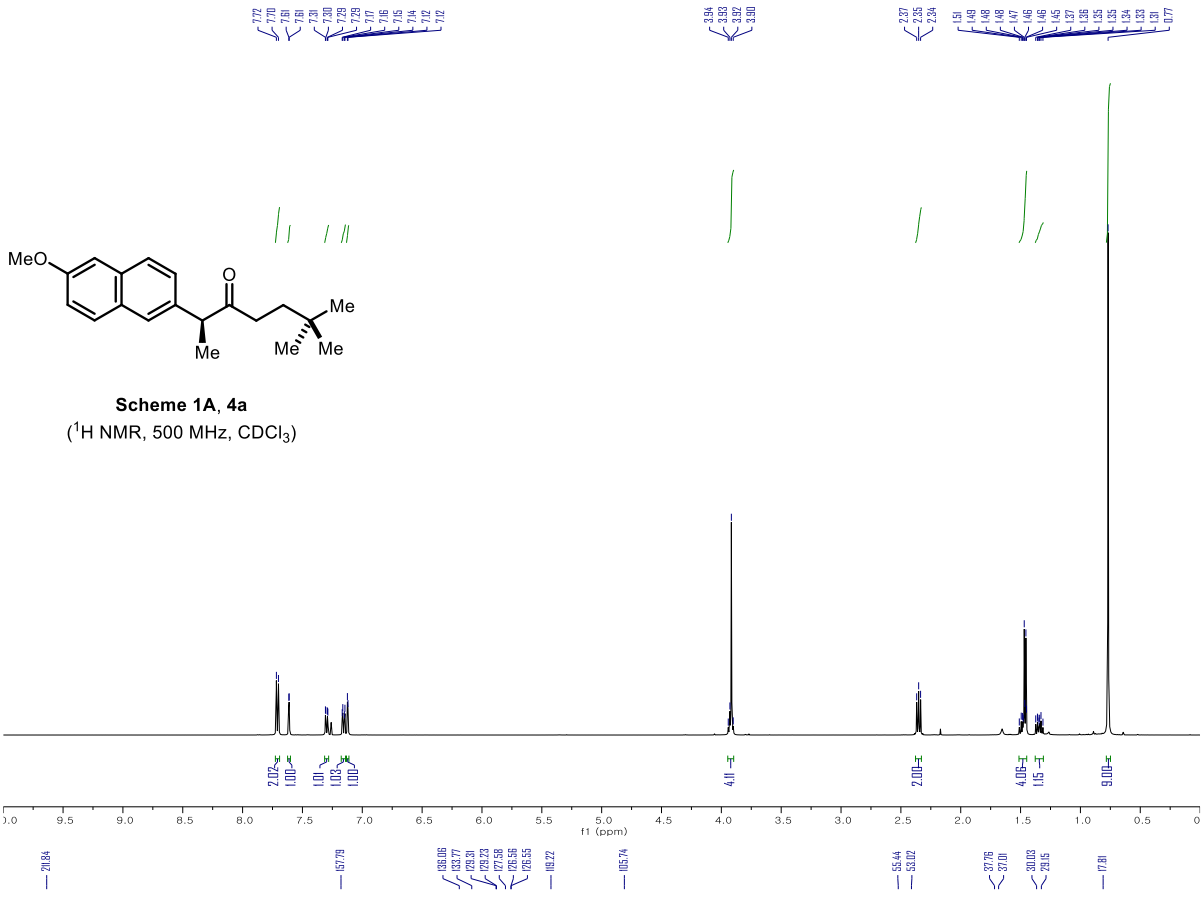
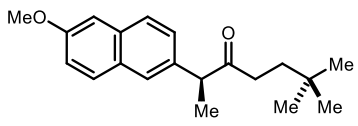


Table 2, **3br**
(^{13}C NMR, 126 MHz, $CDCl_3$)

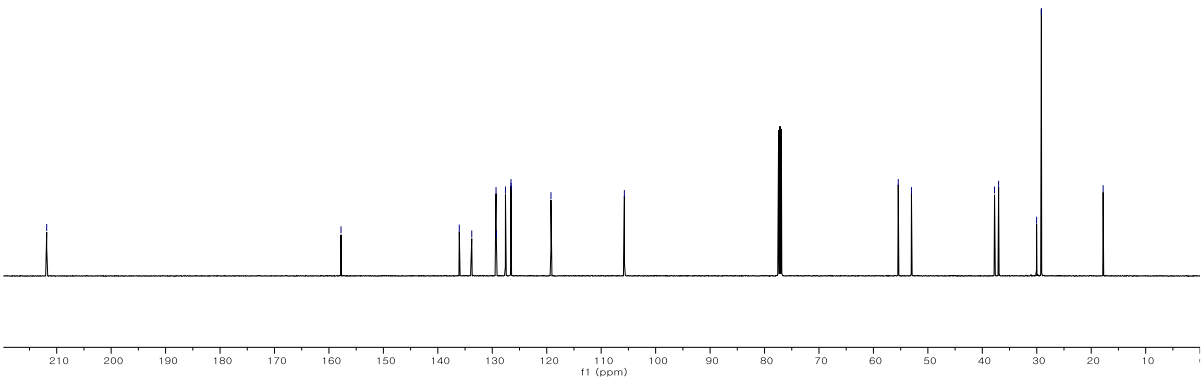


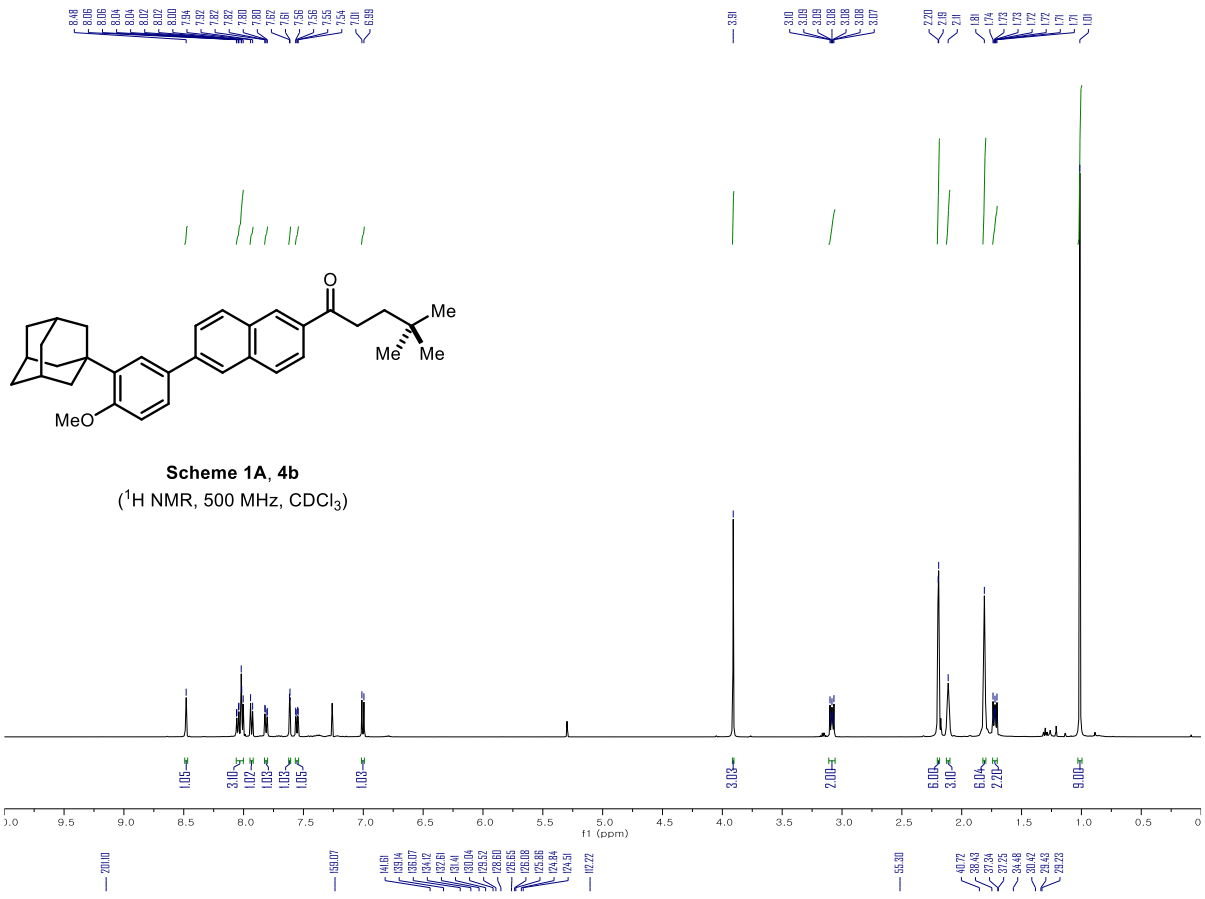


Scheme 1A, **4a**
(^{1}H NMR, 500 MHz, $CDCl_3$)



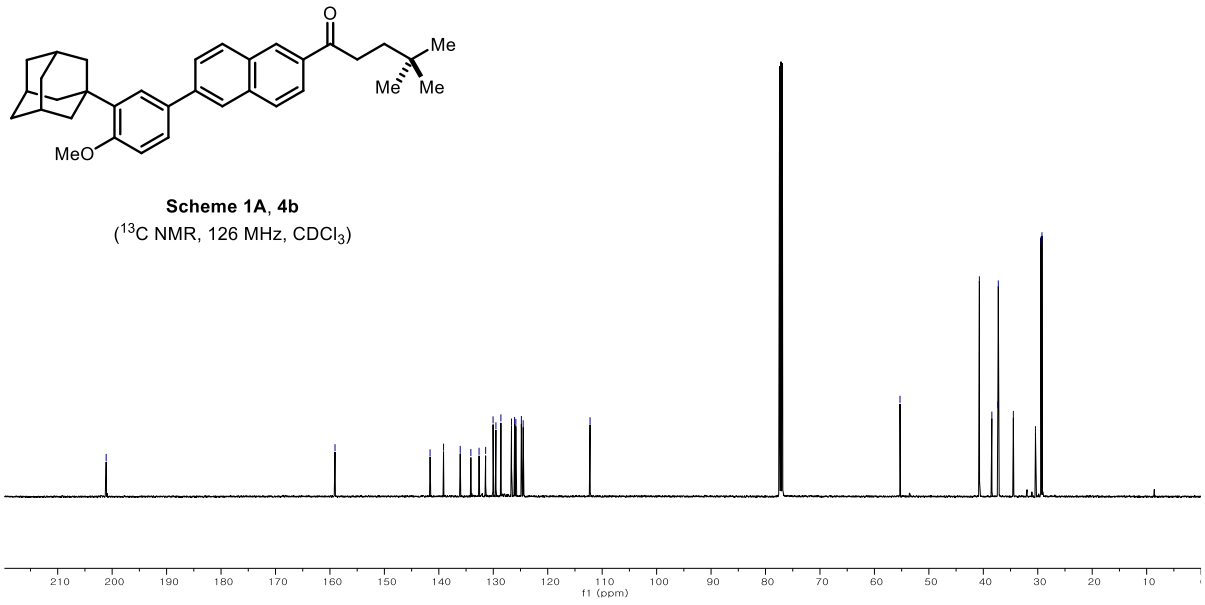
Scheme 1A, **4a**
(^{13}C NMR, 126 MHz, $CDCl_3$)





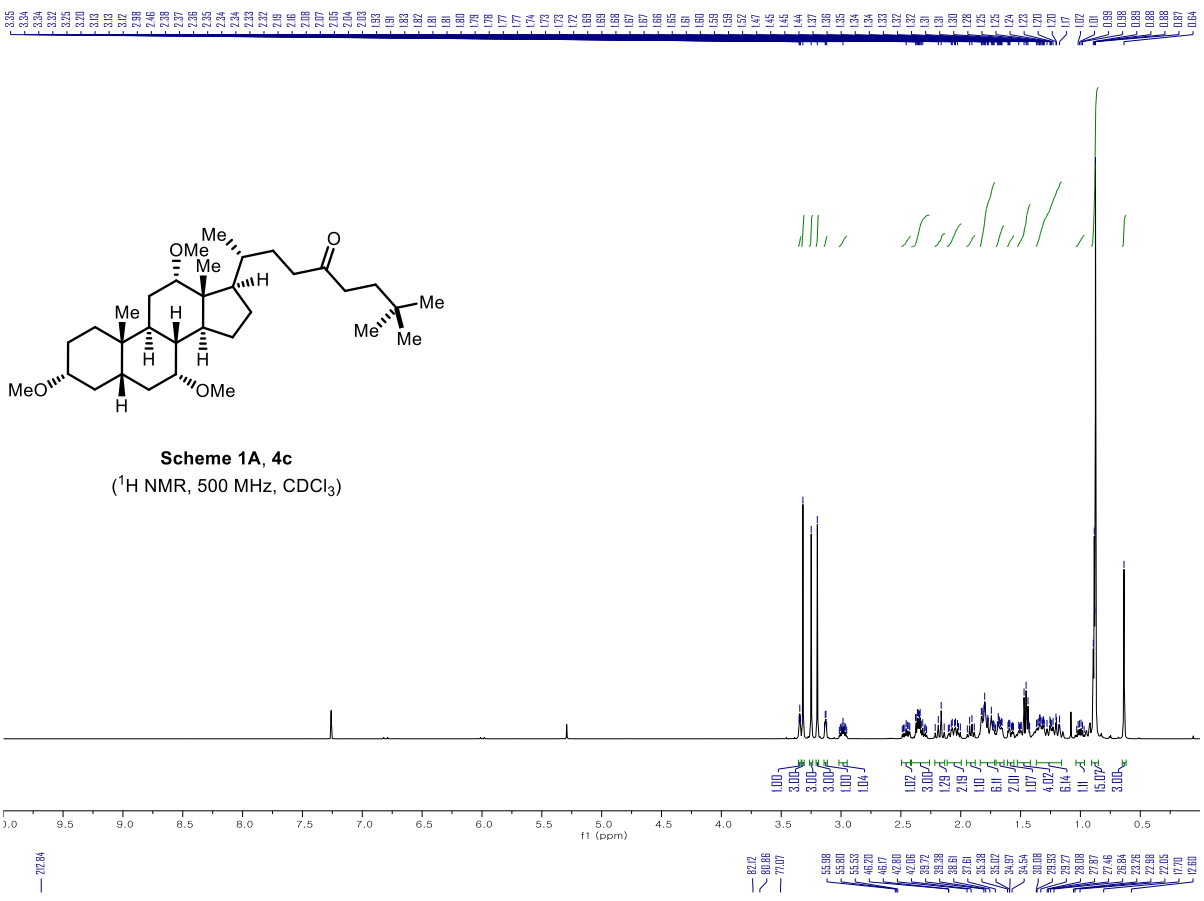
Scheme 1A, **4b**

(^{1}H NMR, 500 MHz, $CDCl_3$)

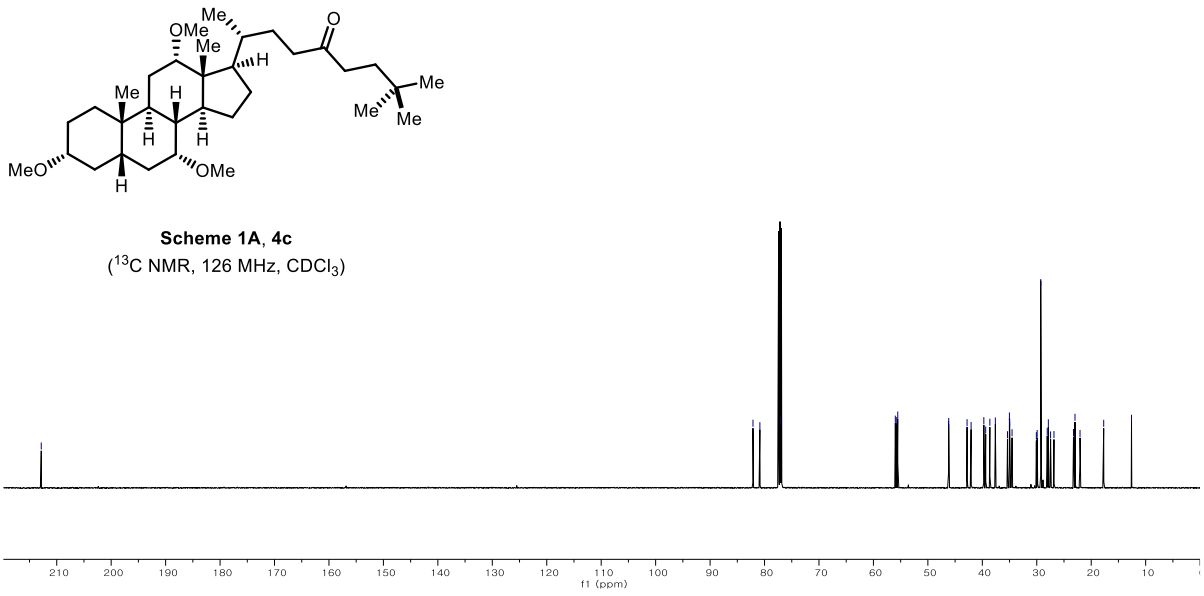


Scheme 1A, **4b**

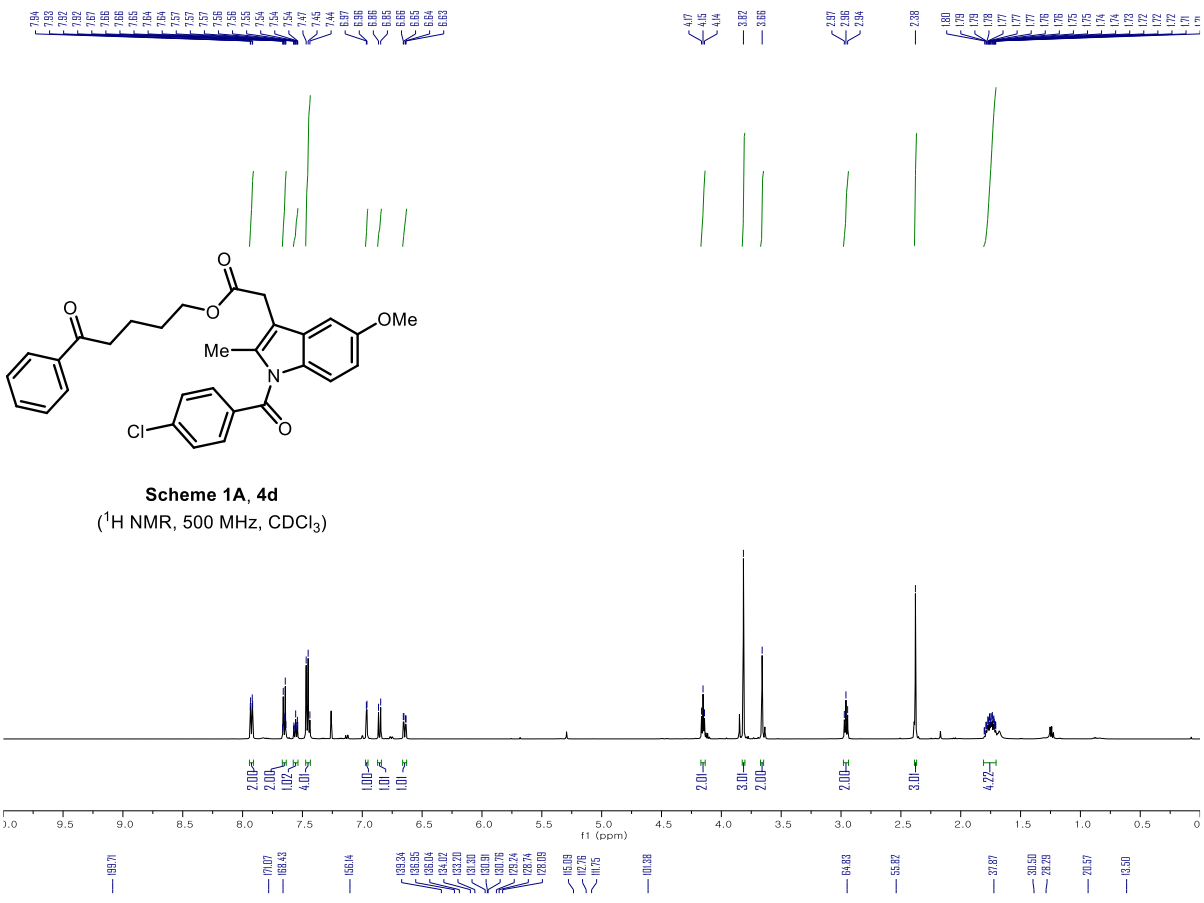
(^{13}C NMR, 126 MHz, $CDCl_3$)



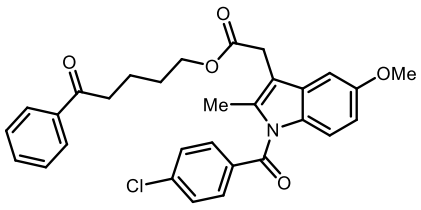
Scheme 1A, **4c**
(^{1}H NMR, 500 MHz, $CDCl_3$)



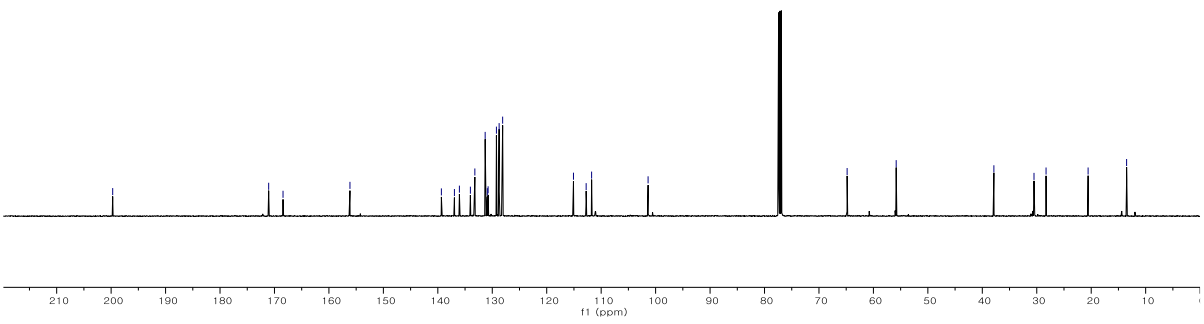
Scheme 1A, **4c**
(^{13}C NMR, 126 MHz, $CDCl_3$)

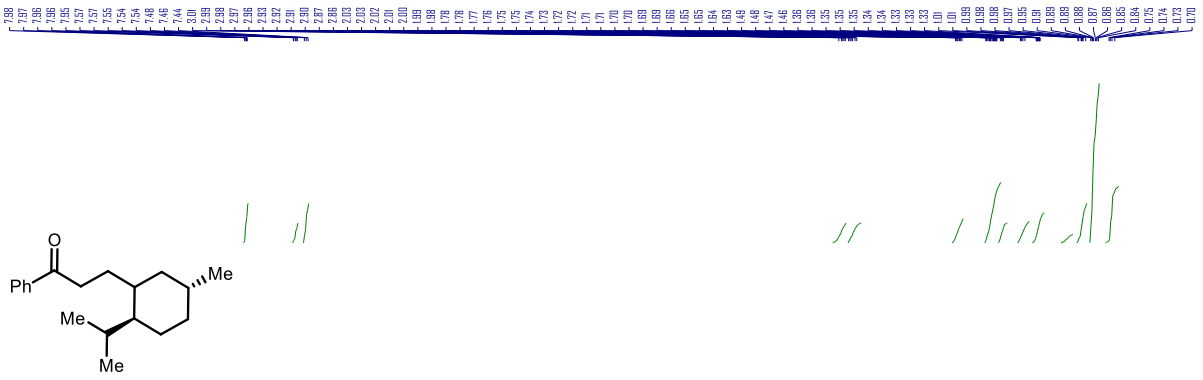


Scheme 1A, **4d**
(^{1}H NMR, 500 MHz, $CDCl_3$)

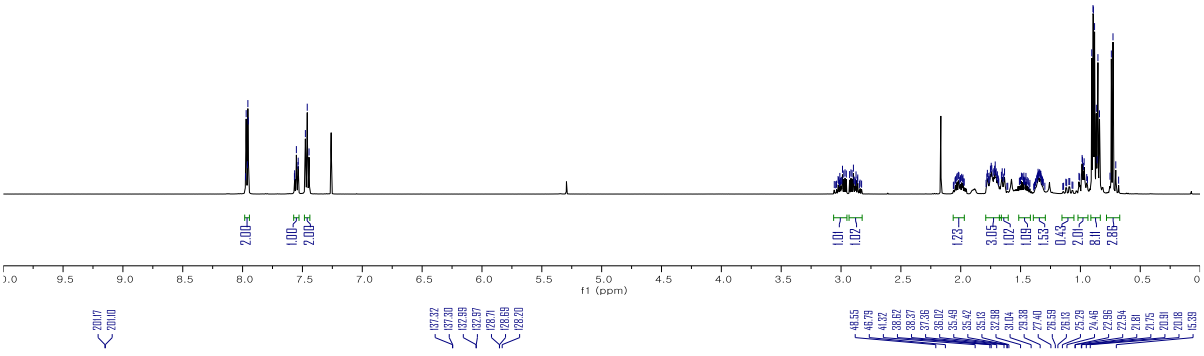


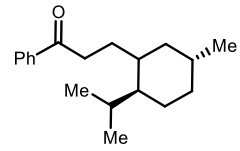
Scheme 1A, **4d**
(^{13}C NMR, 126 MHz, $CDCl_3$)



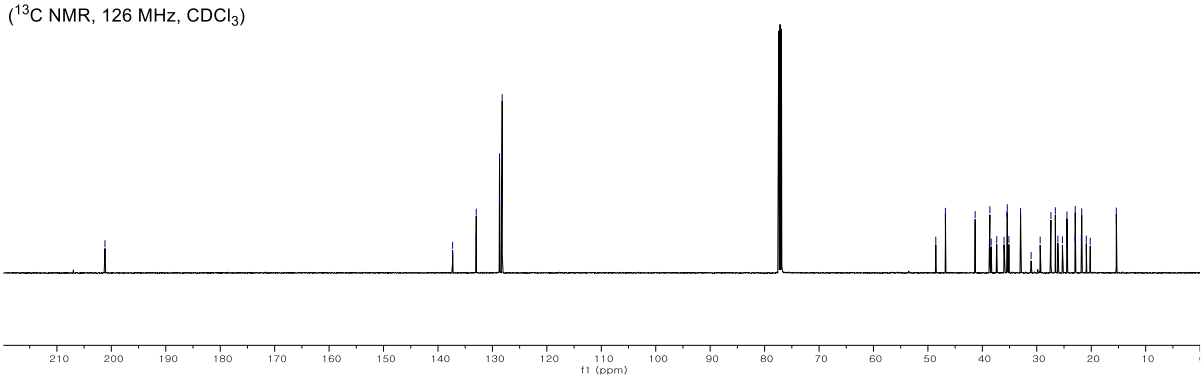


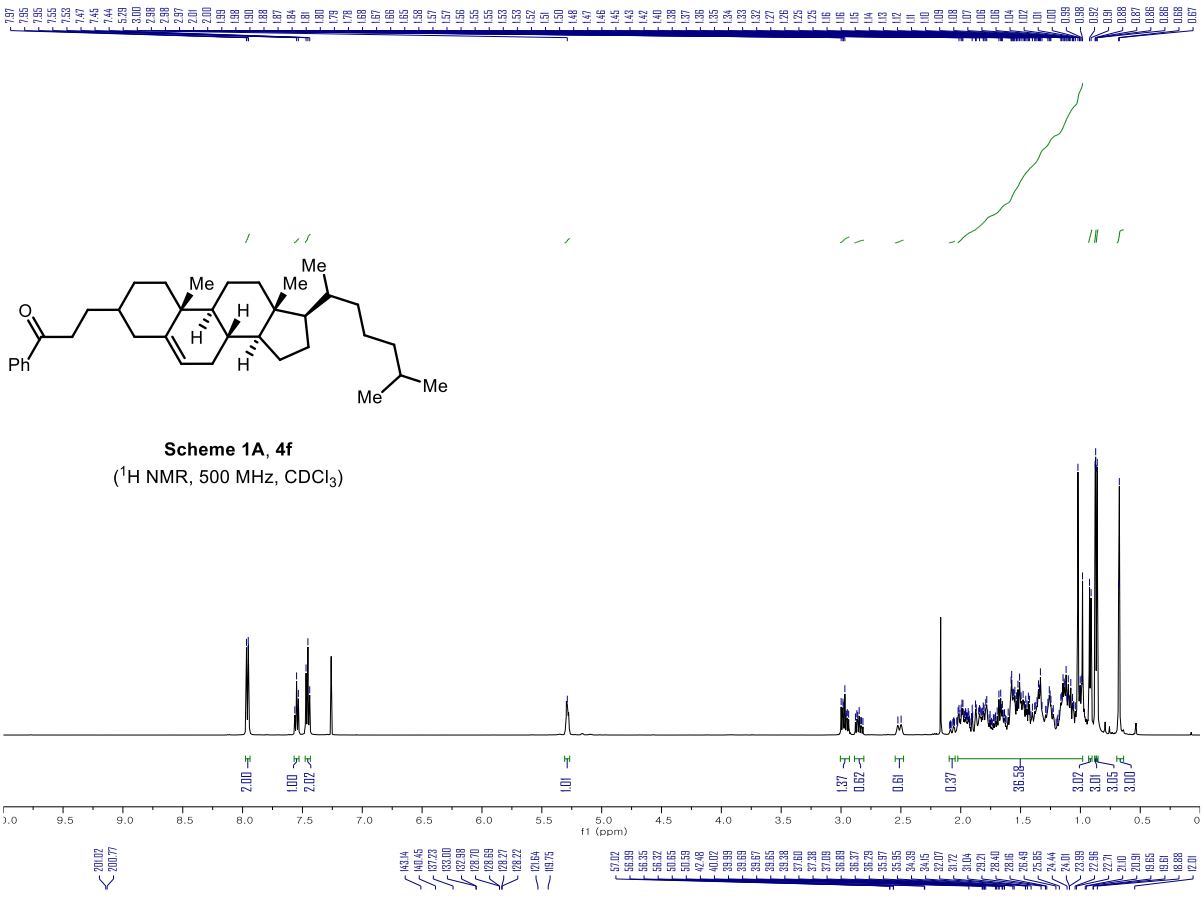
Scheme 1A, **4e**
(^{1}H NMR, 500 MHz, $CDCl_3$)





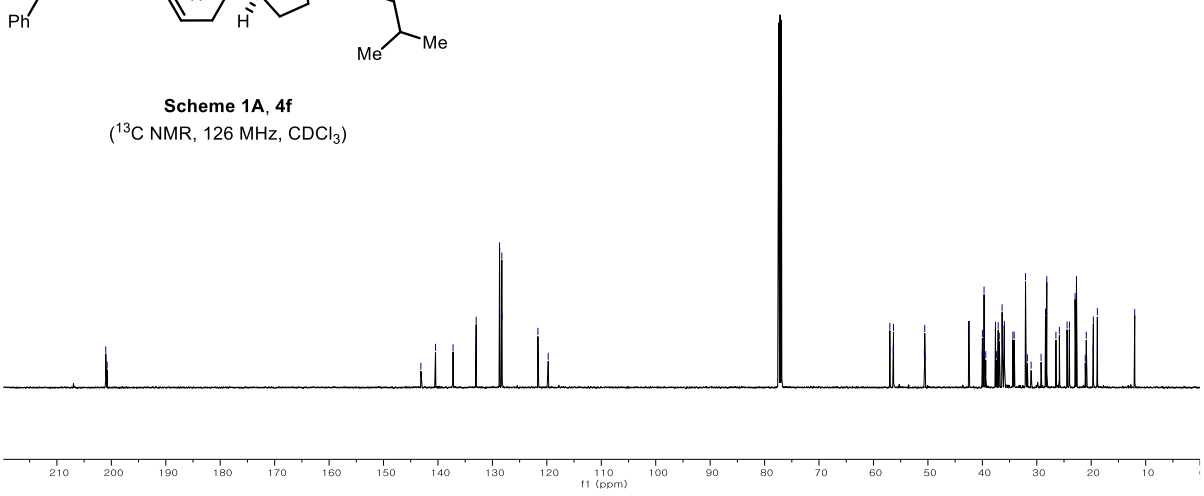
Scheme 1A, **4e**
(^{13}C NMR, 126 MHz, $CDCl_3$)

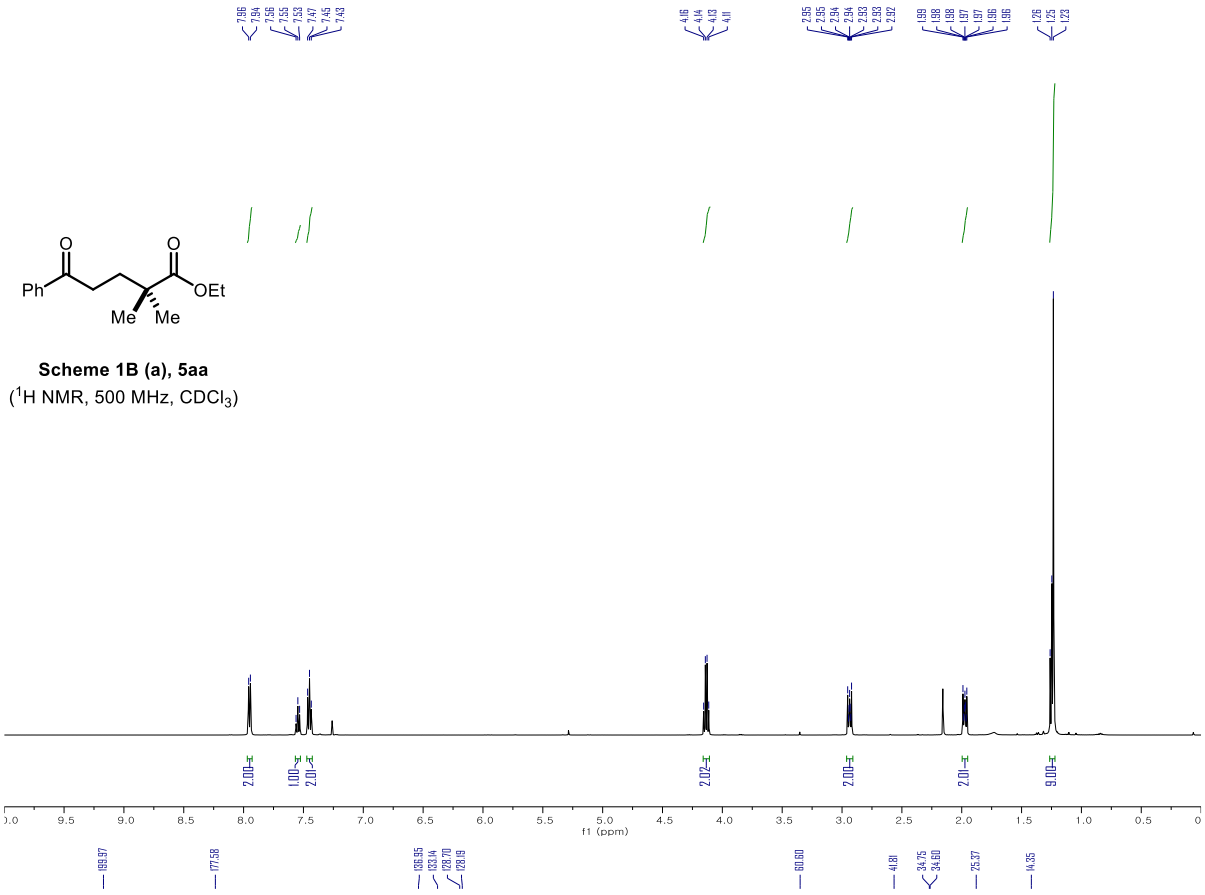




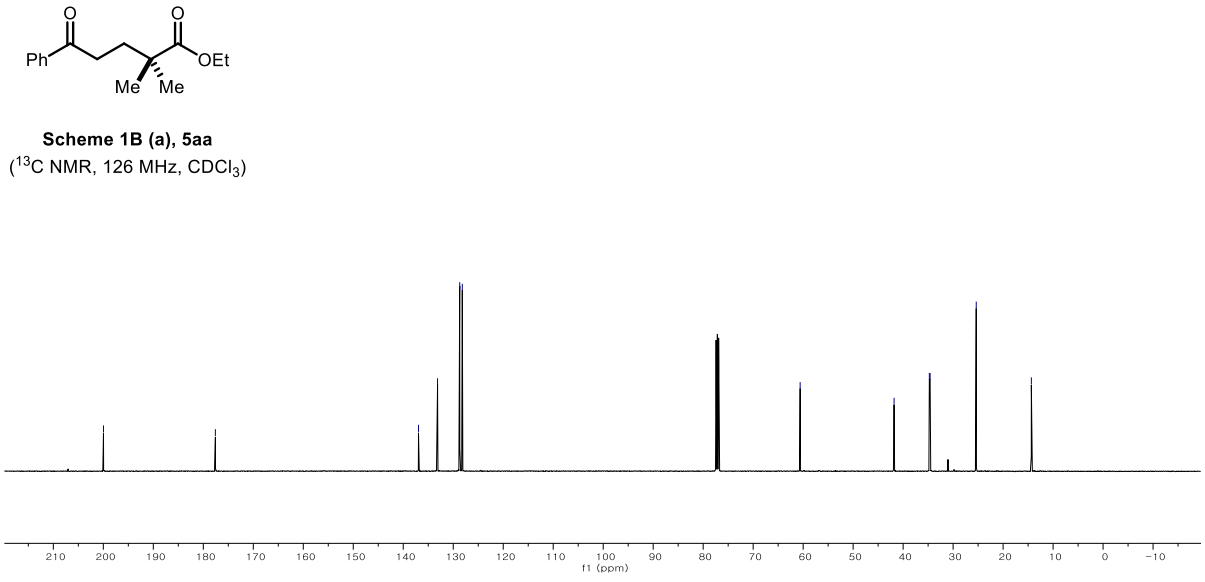
Scheme 1A, **4f**
(^{1}H NMR, 500 MHz, $CDCl_3$)

Scheme 1A, **4f**
(^{13}C NMR, 126 MHz, $CDCl_3$)

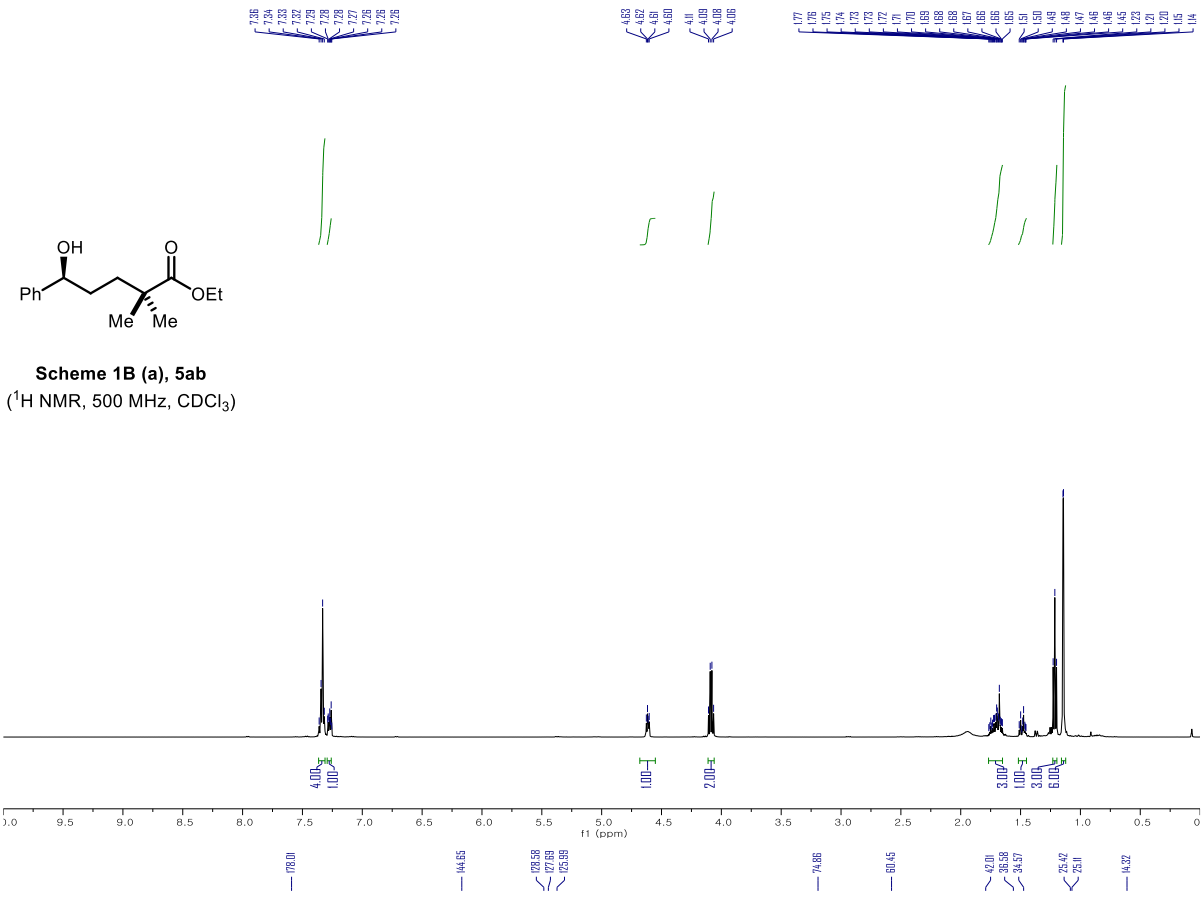




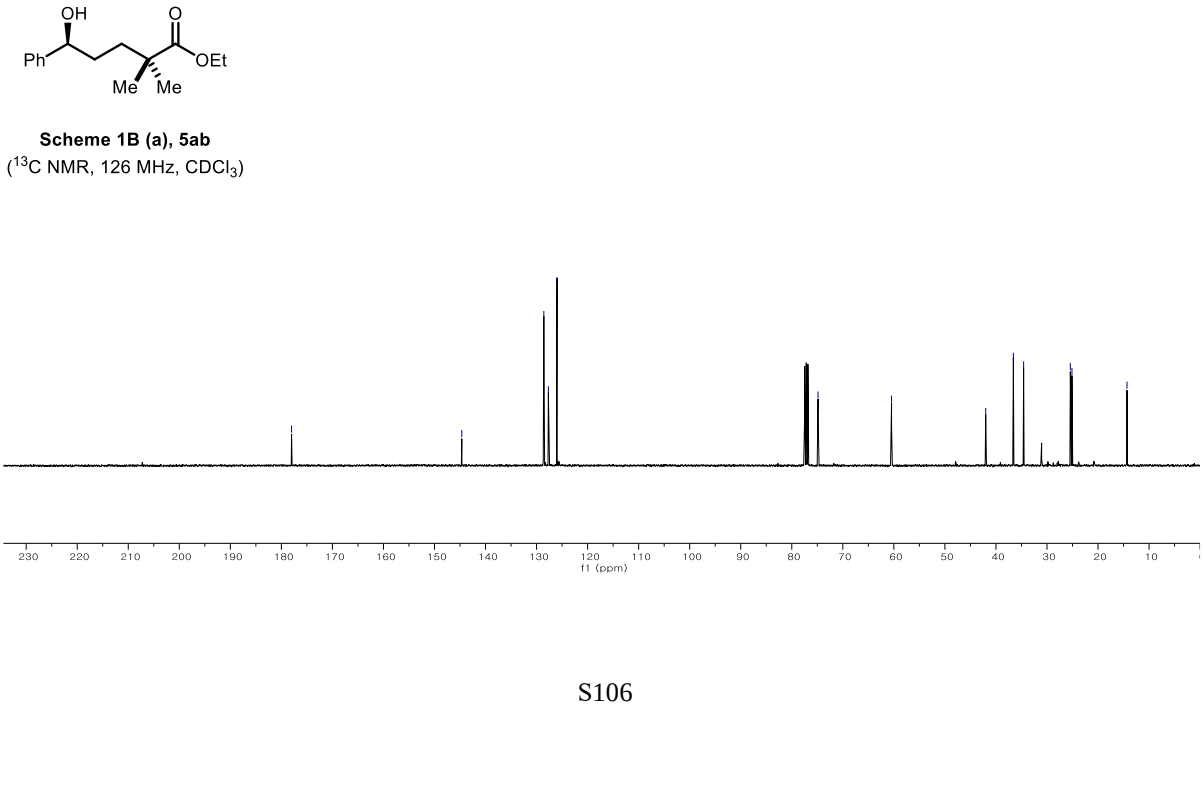
Scheme 1B (a), 5aa
(^{1}H NMR, 500 MHz, $CDCl_3$)



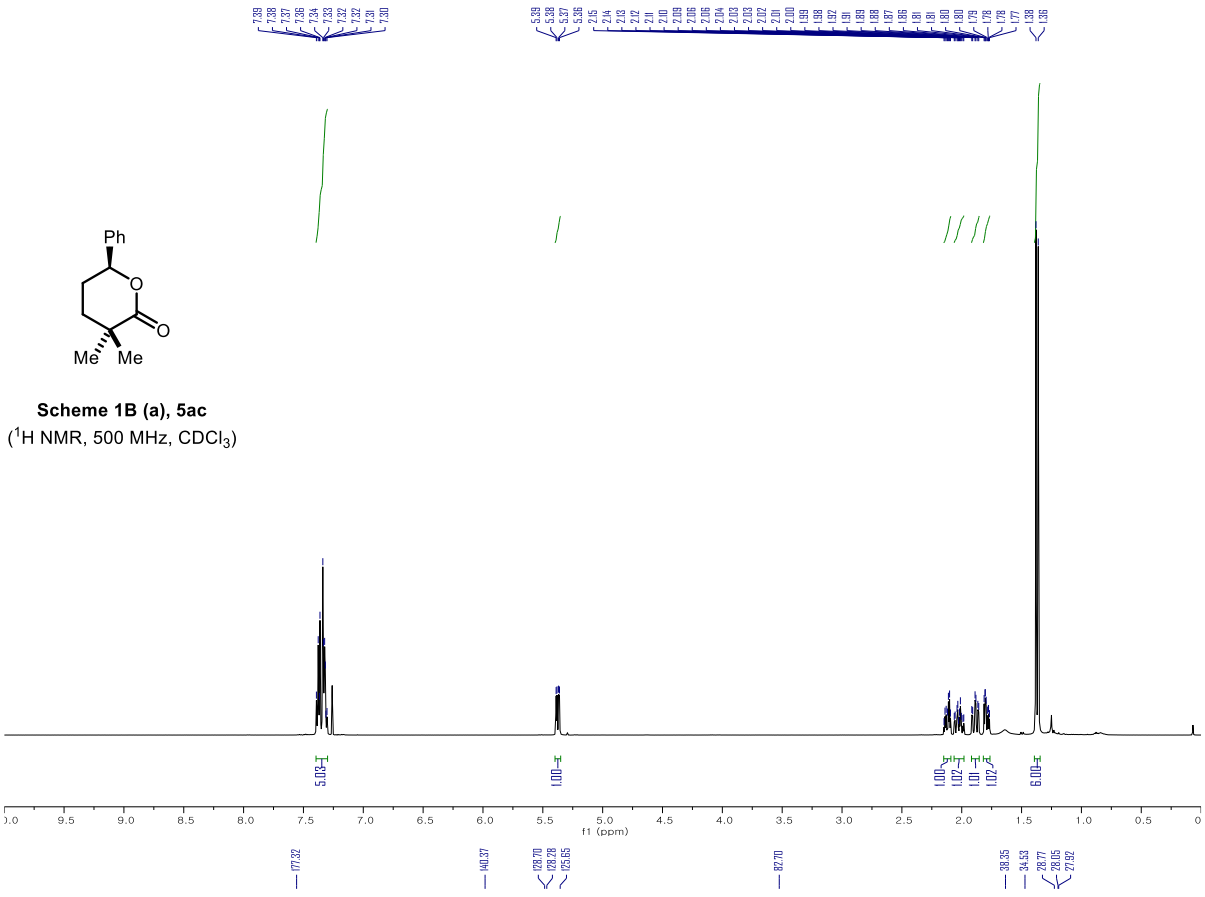
Scheme 1B (a), 5aa
(^{13}C NMR, 126 MHz, $CDCl_3$)



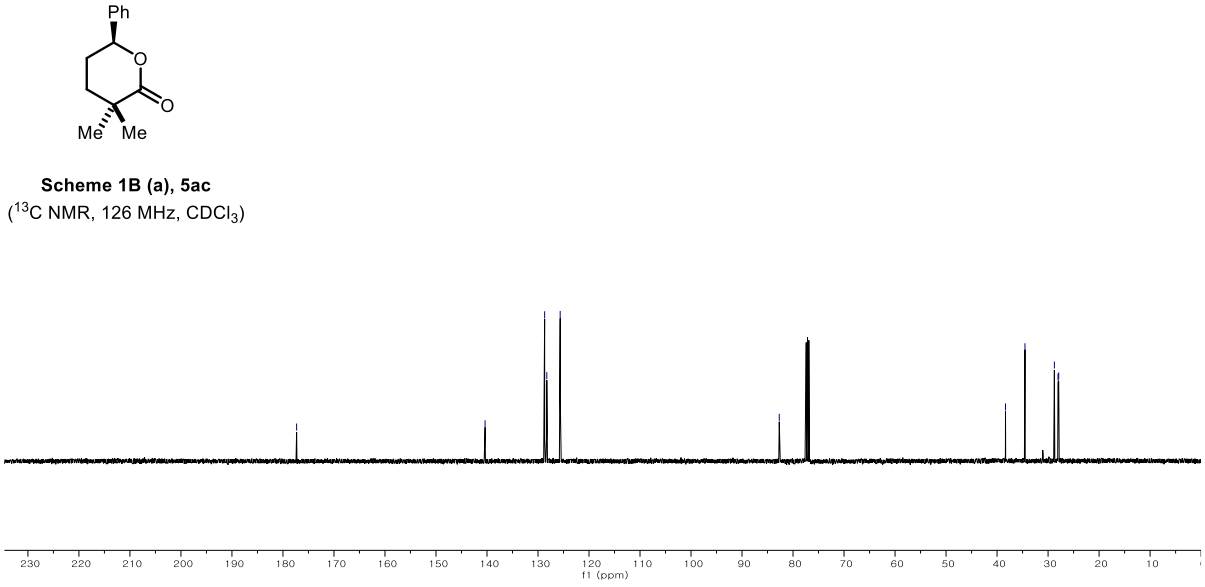
Scheme 1B (a), 5ab
(^{1}H NMR, 500 MHz, $CDCl_3$)



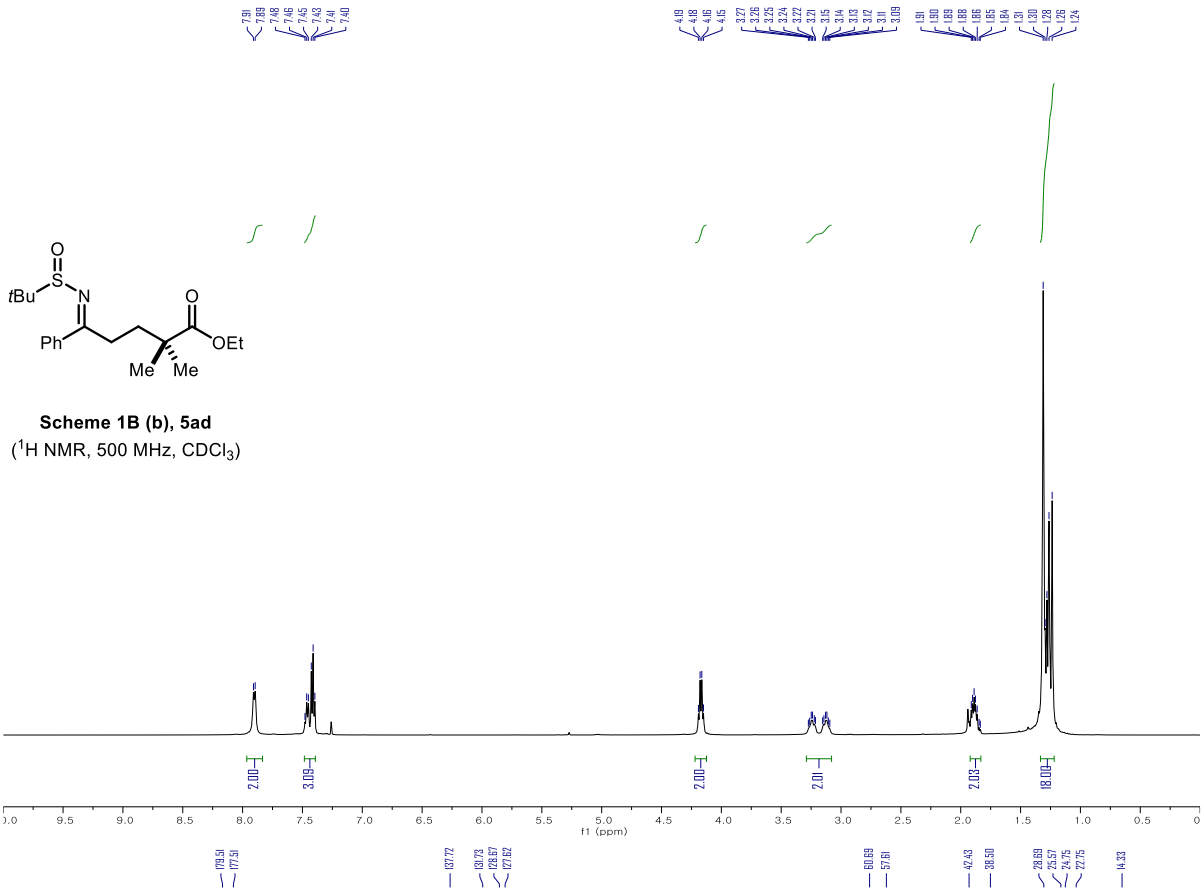
Scheme 1B (a), 5ab
(^{13}C NMR, 126 MHz, $CDCl_3$)



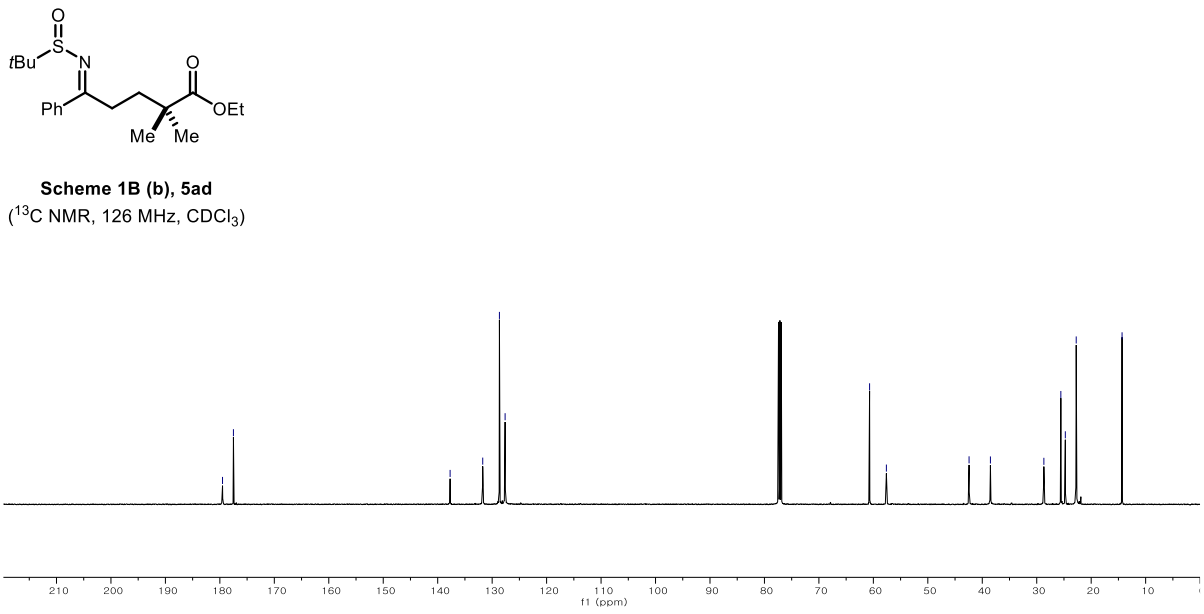
Scheme 1B (a), 5ac
(^{1}H NMR, 500 MHz, $CDCl_3$)



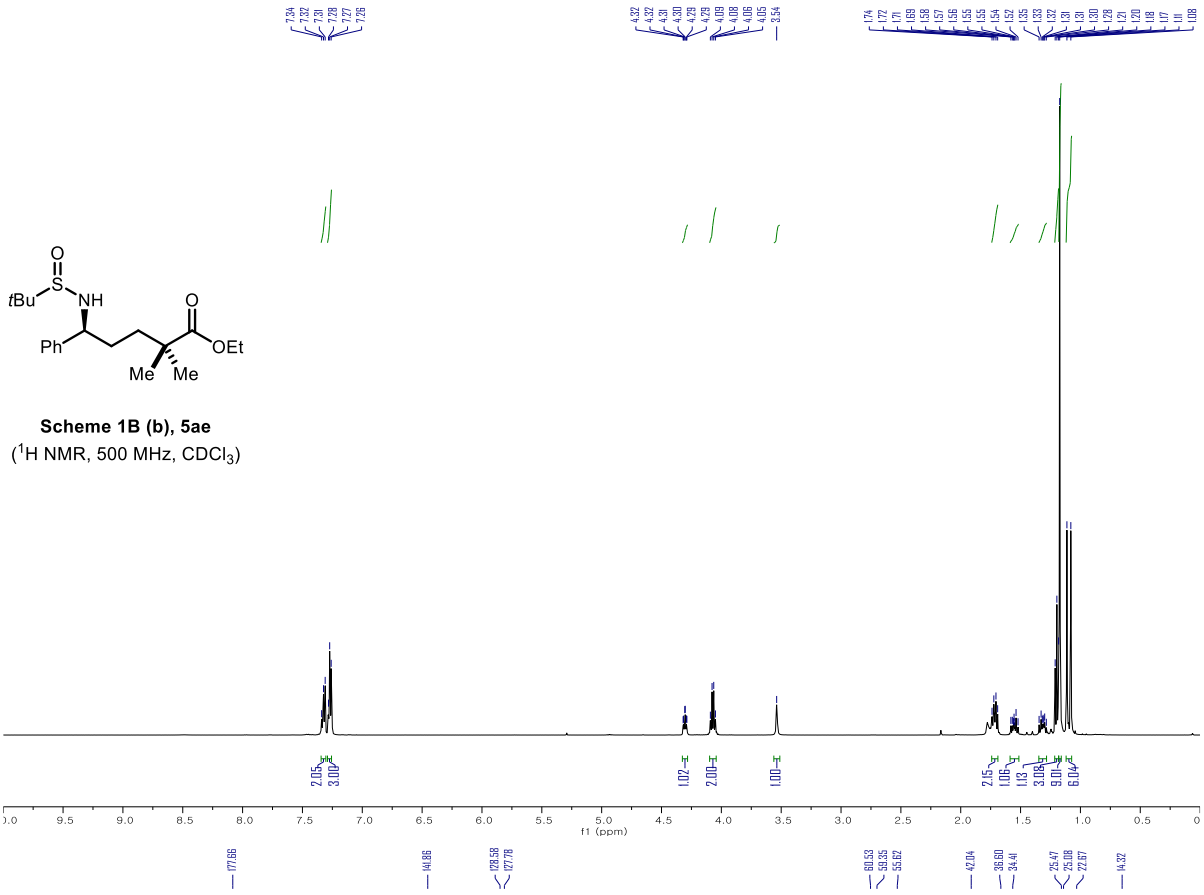
Scheme 1B (a), 5ac
(^{13}C NMR, 126 MHz, $CDCl_3$)



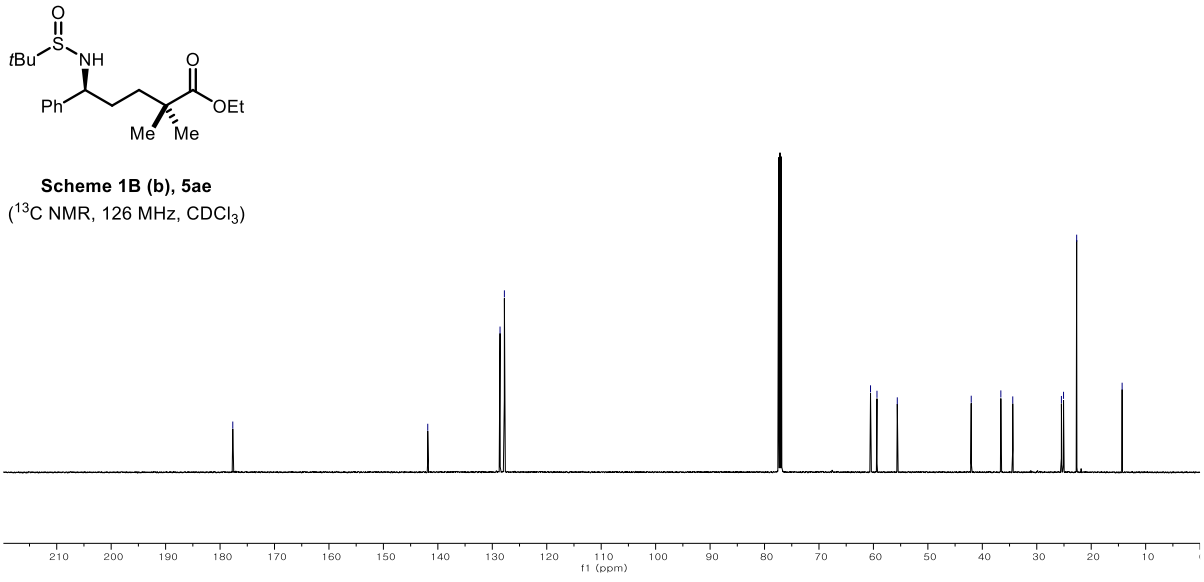
Scheme 1B (b), 5ad
(^{1}H NMR, 500 MHz, $CDCl_3$)



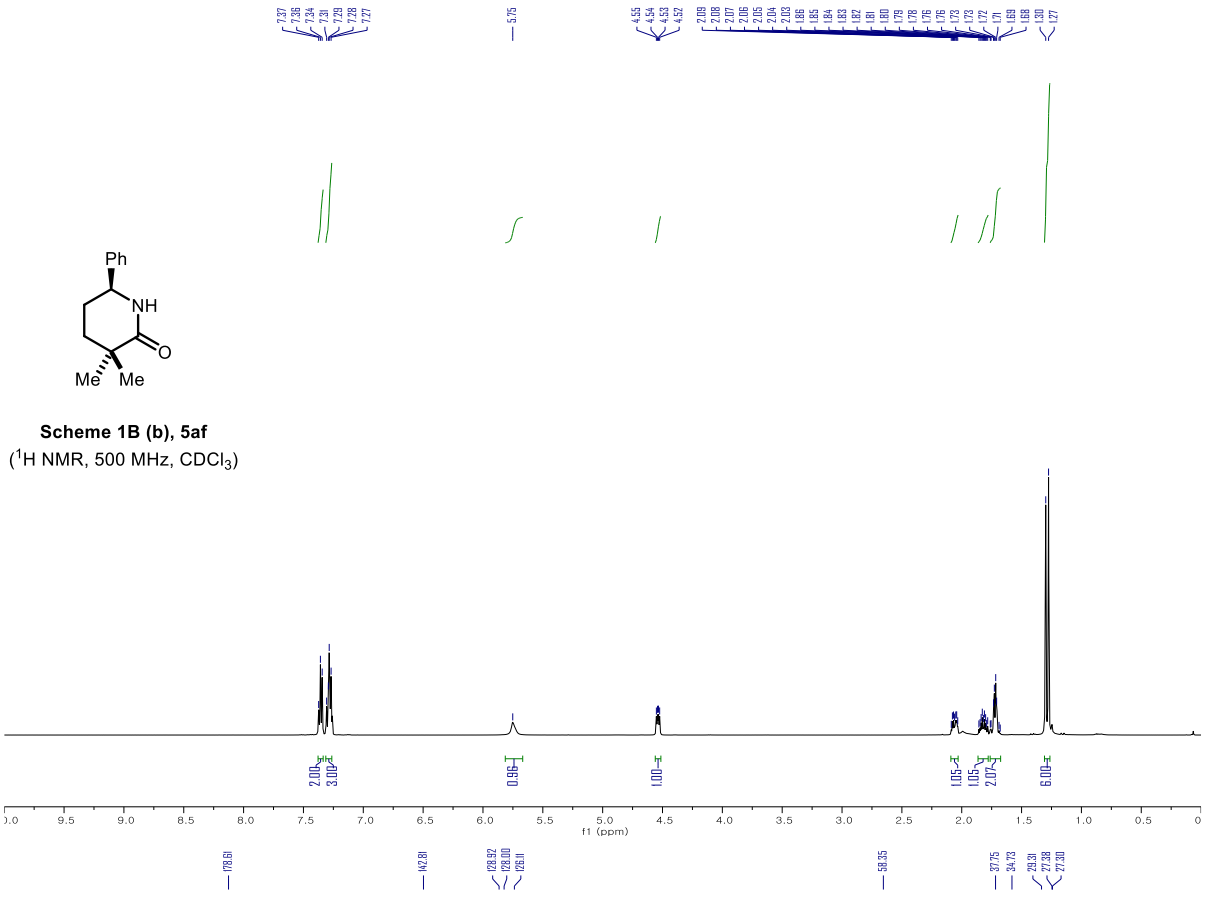
Scheme 1B (b), 5ad
(^{13}C NMR, 126 MHz, $CDCl_3$)



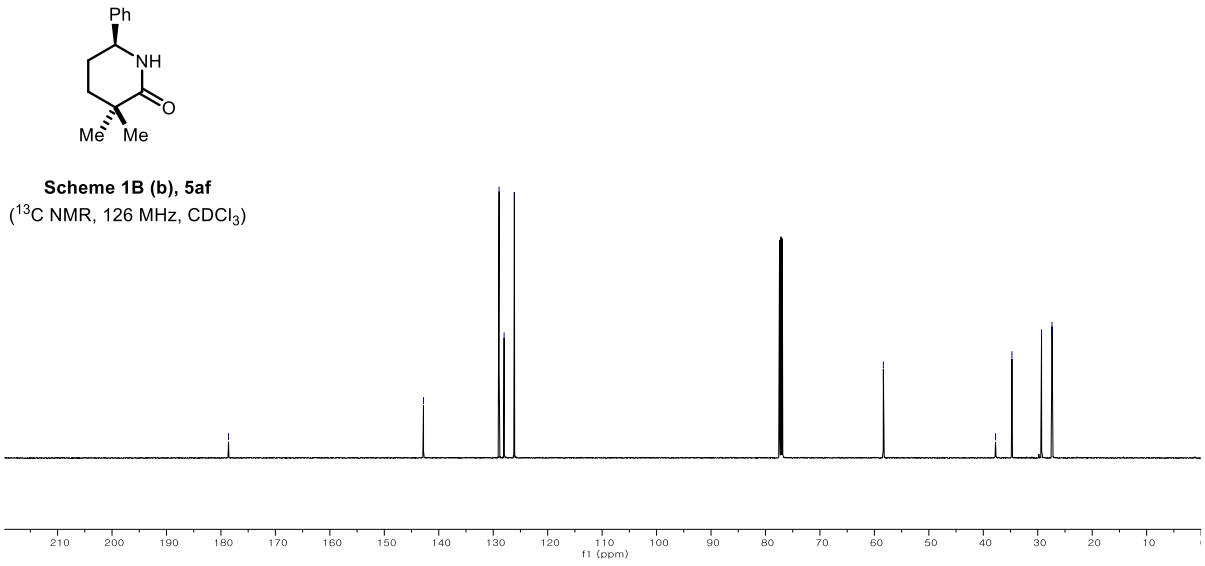
Scheme 1B (b), 5ae
(^{1}H NMR, 500 MHz, $CDCl_3$)



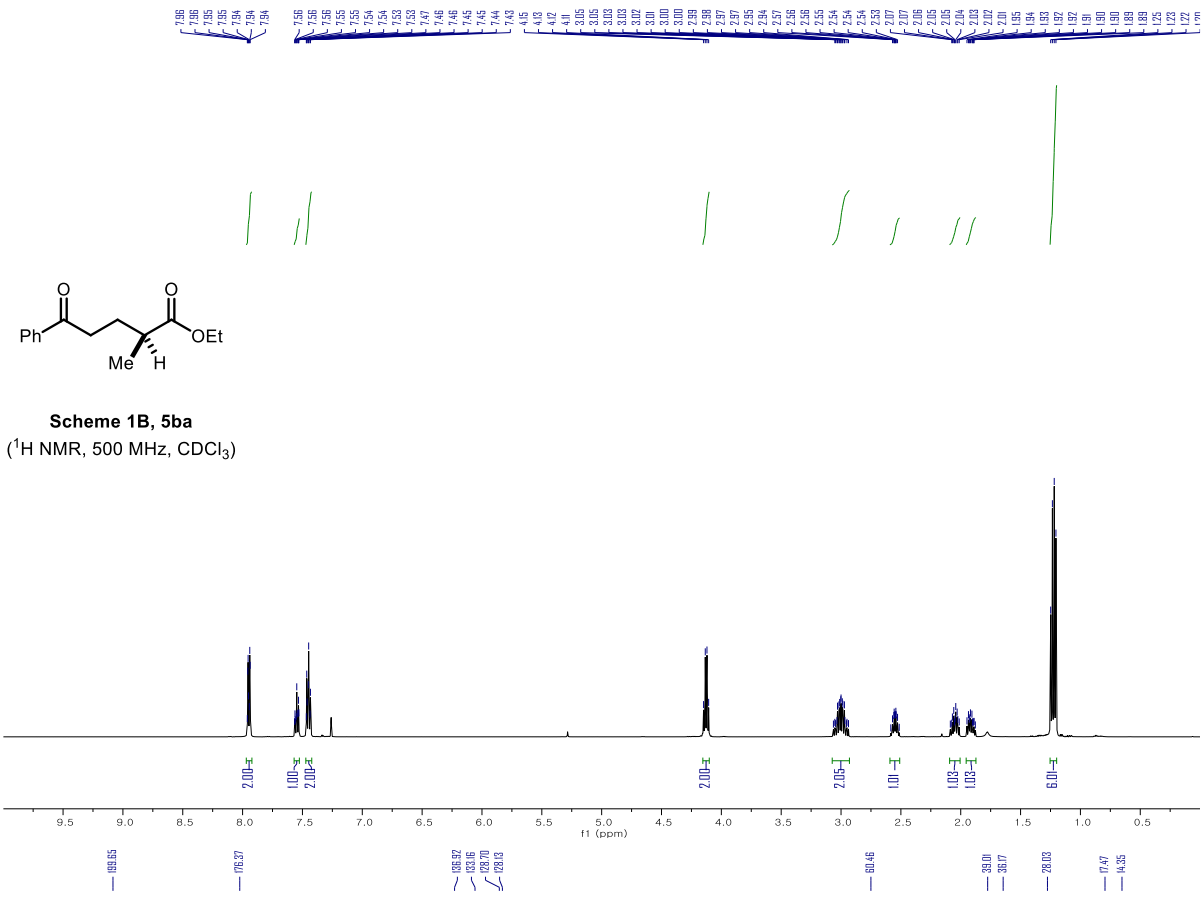
Scheme 1B (b), 5ae
(^{13}C NMR, 126 MHz, $CDCl_3$)



Scheme 1B (b), 5af
(^{1}H NMR, 500 MHz, $CDCl_3$)

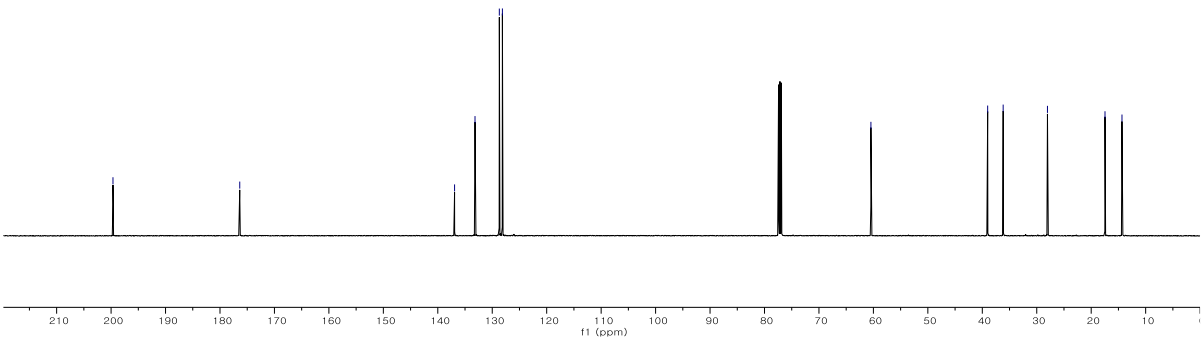


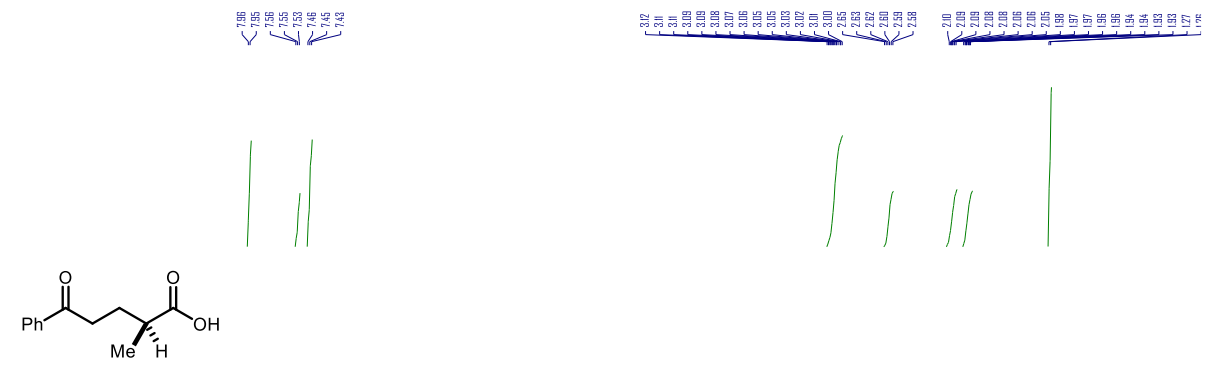
Scheme 1B (b), 5af
(^{13}C NMR, 126 MHz, $CDCl_3$)



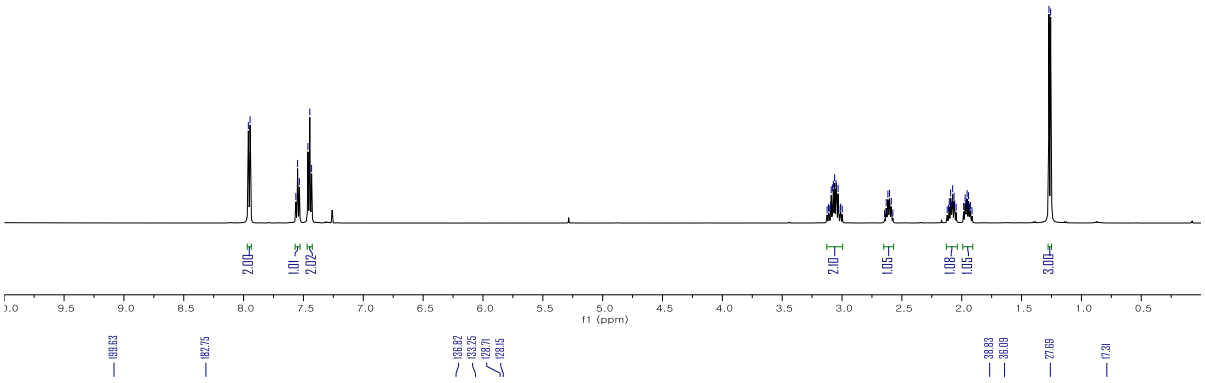
Scheme 1B, 5ba
(^{1}H NMR, 500 MHz, $CDCl_3$)

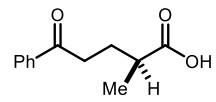
Scheme 1B, 5ba
(^{13}C NMR, 126 MHz, $CDCl_3$)



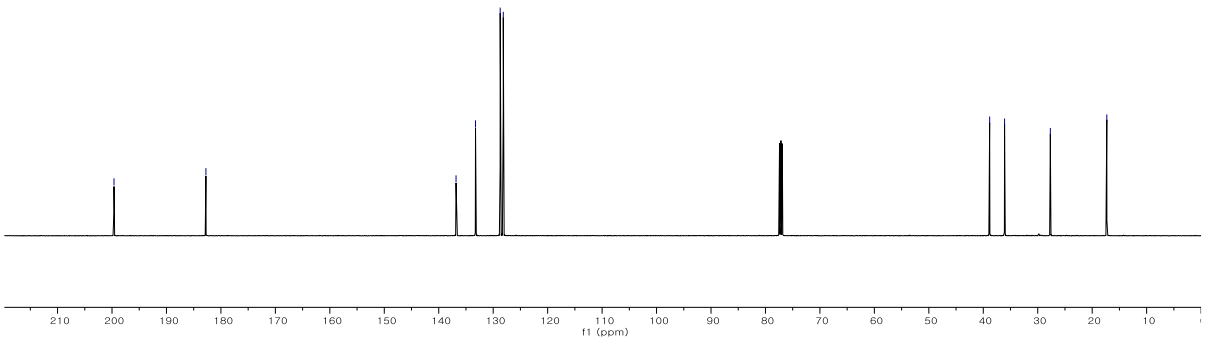


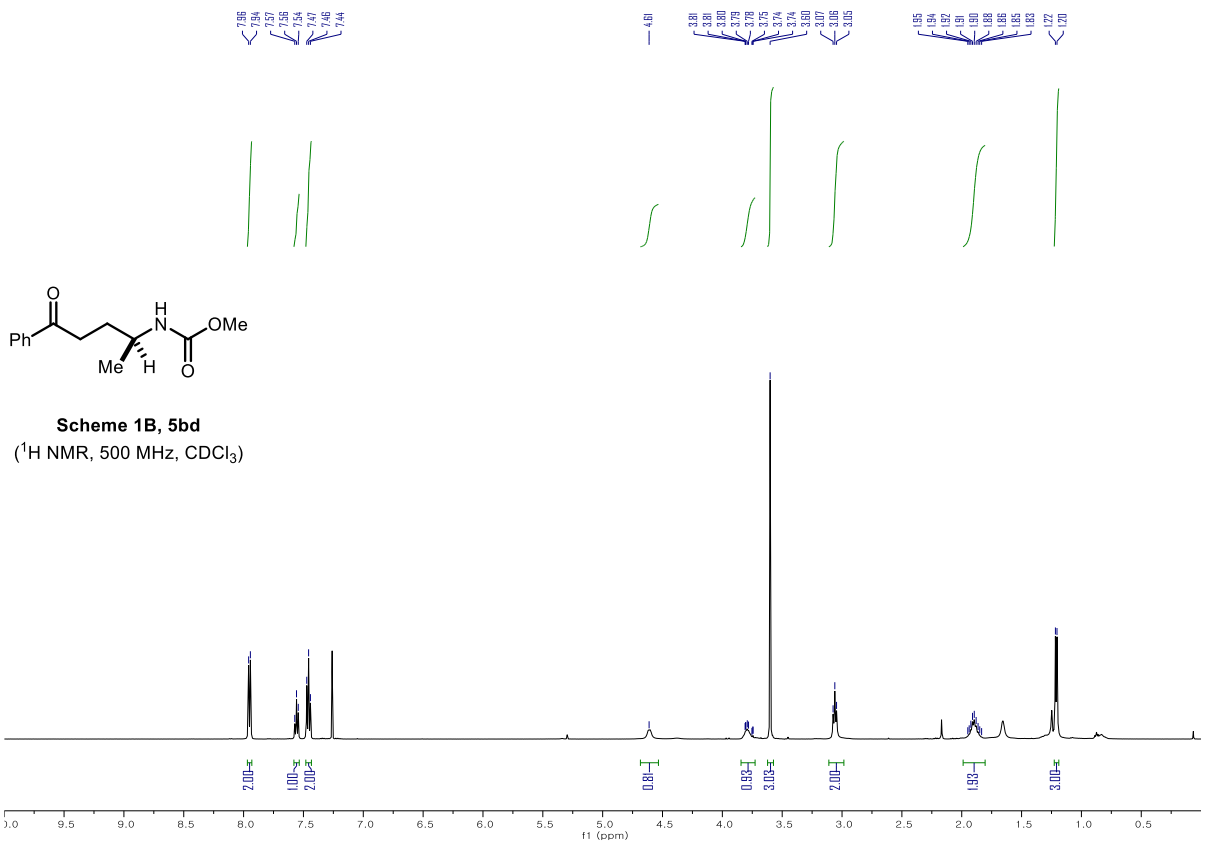
Scheme 1B, 5bb
(^{1}H NMR, 500 MHz, $CDCl_3$)



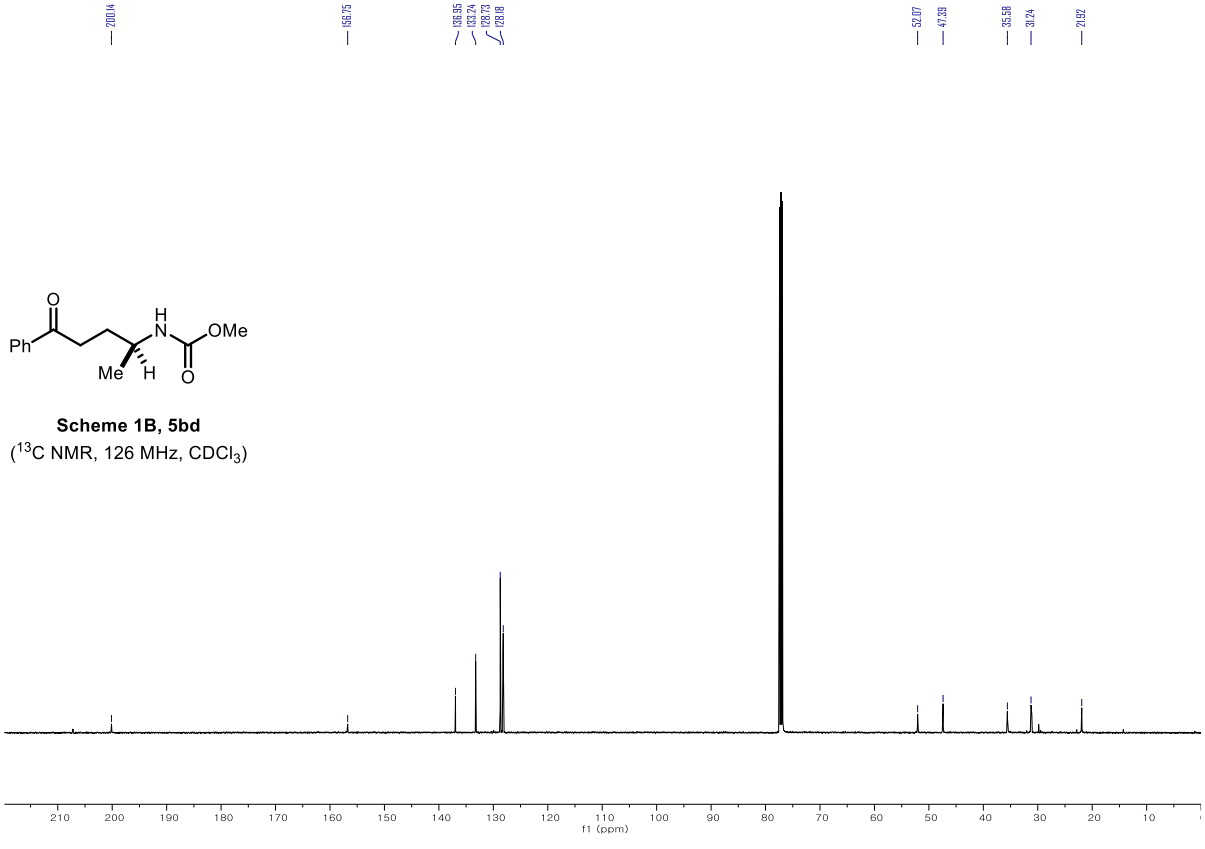


Scheme 1B, 5bb
(^{13}C NMR, 126 MHz, $CDCl_3$)

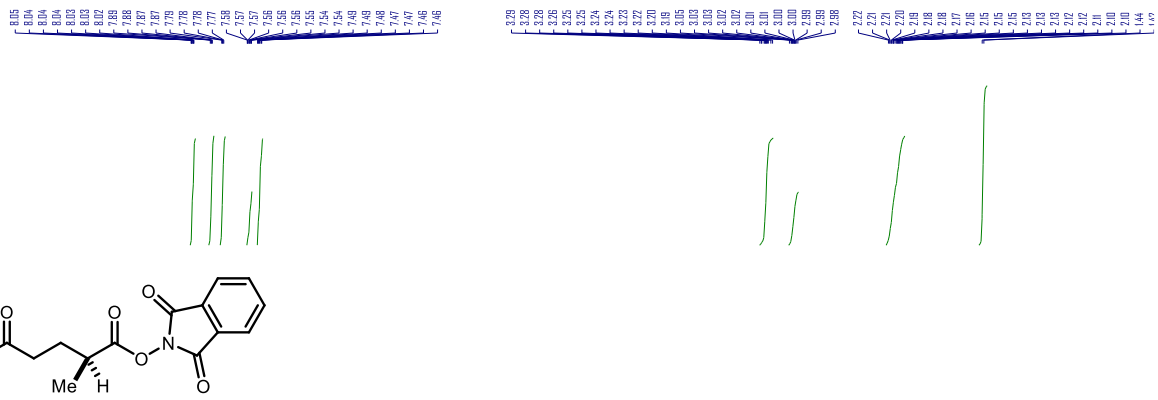




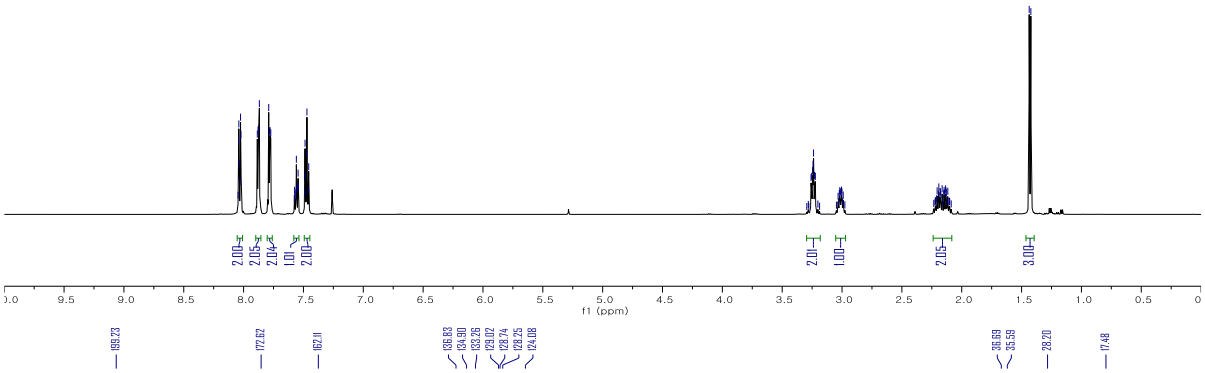
Scheme 1B, 5bd
(^{1}H NMR, 500 MHz, $CDCl_3$)

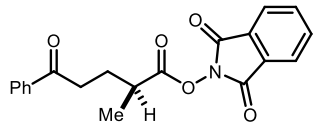


Scheme 1B, 5bd
(^{13}C NMR, 126 MHz, $CDCl_3$)

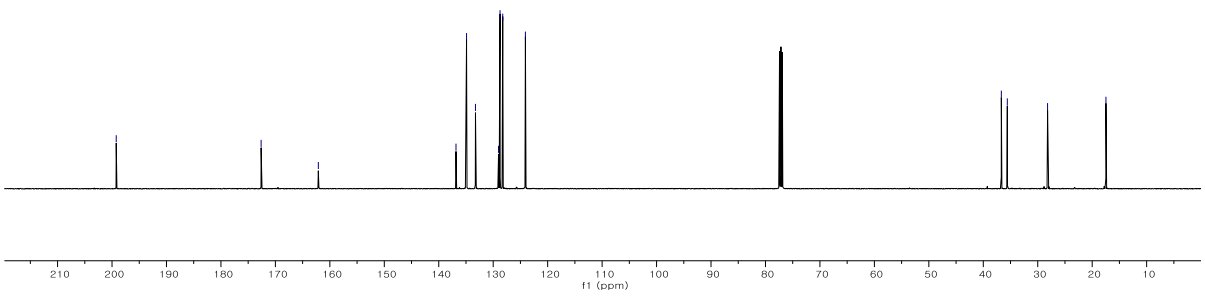


Scheme 1B (d), 5be
(^{1}H NMR, 500 MHz, $CDCl_3$)

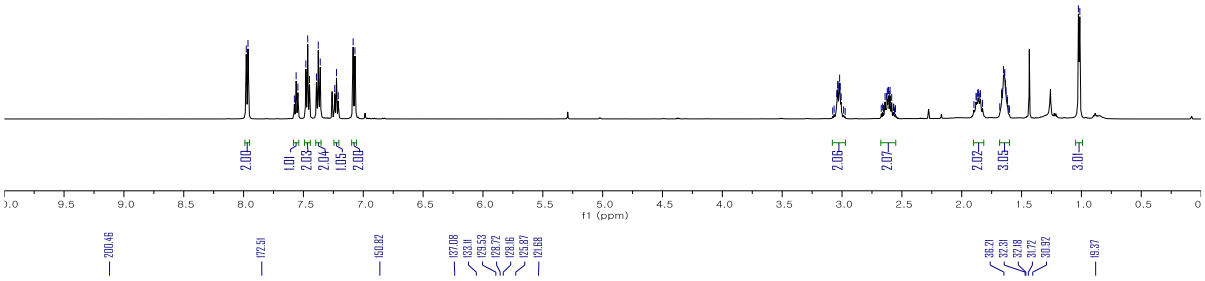


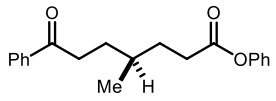


Scheme 1B (d), 5be
(^{13}C NMR, 126 MHz, $CDCl_3$)

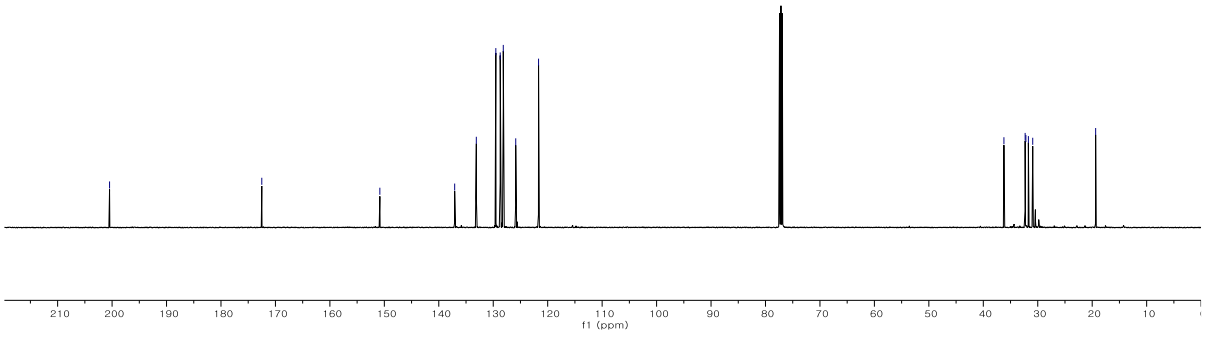


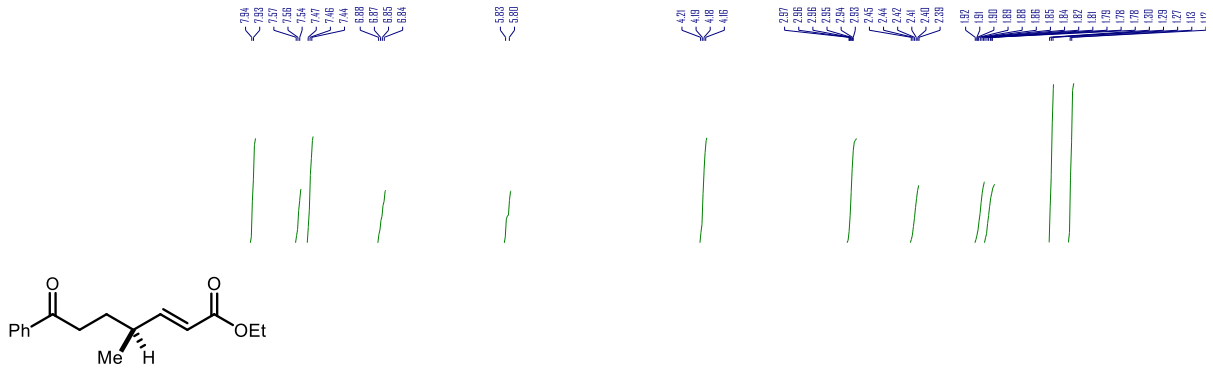
Scheme 1B (d), 5bf
(^{1}H NMR, 500 MHz, $CDCl_3$)



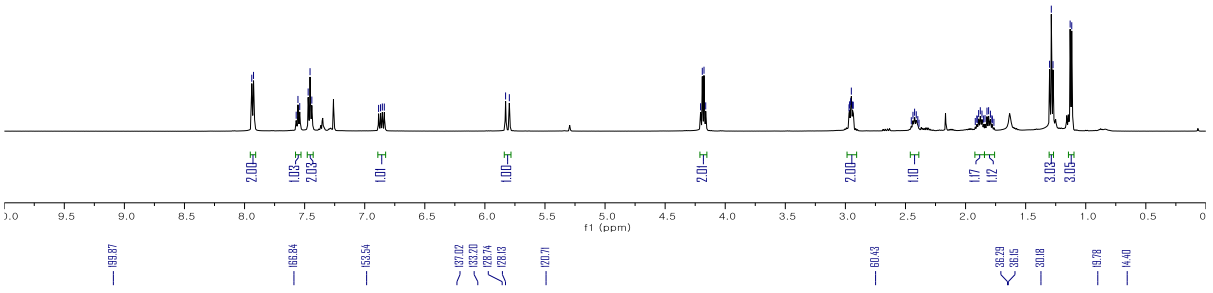


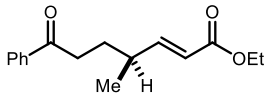
Scheme 1B (d), 5bf
(^{13}C NMR, 126 MHz, $CDCl_3$)



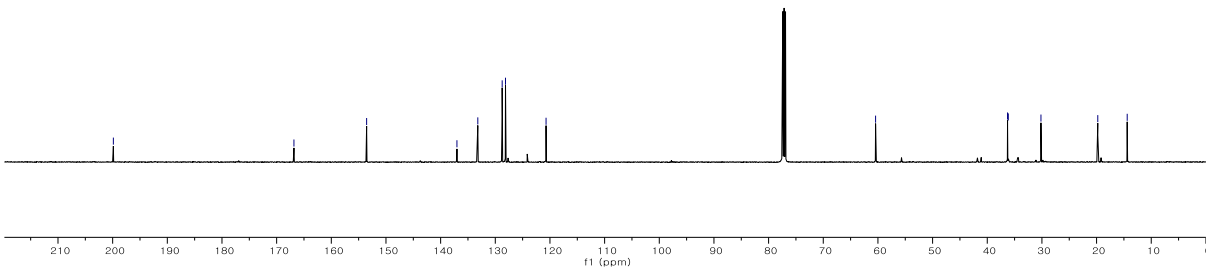


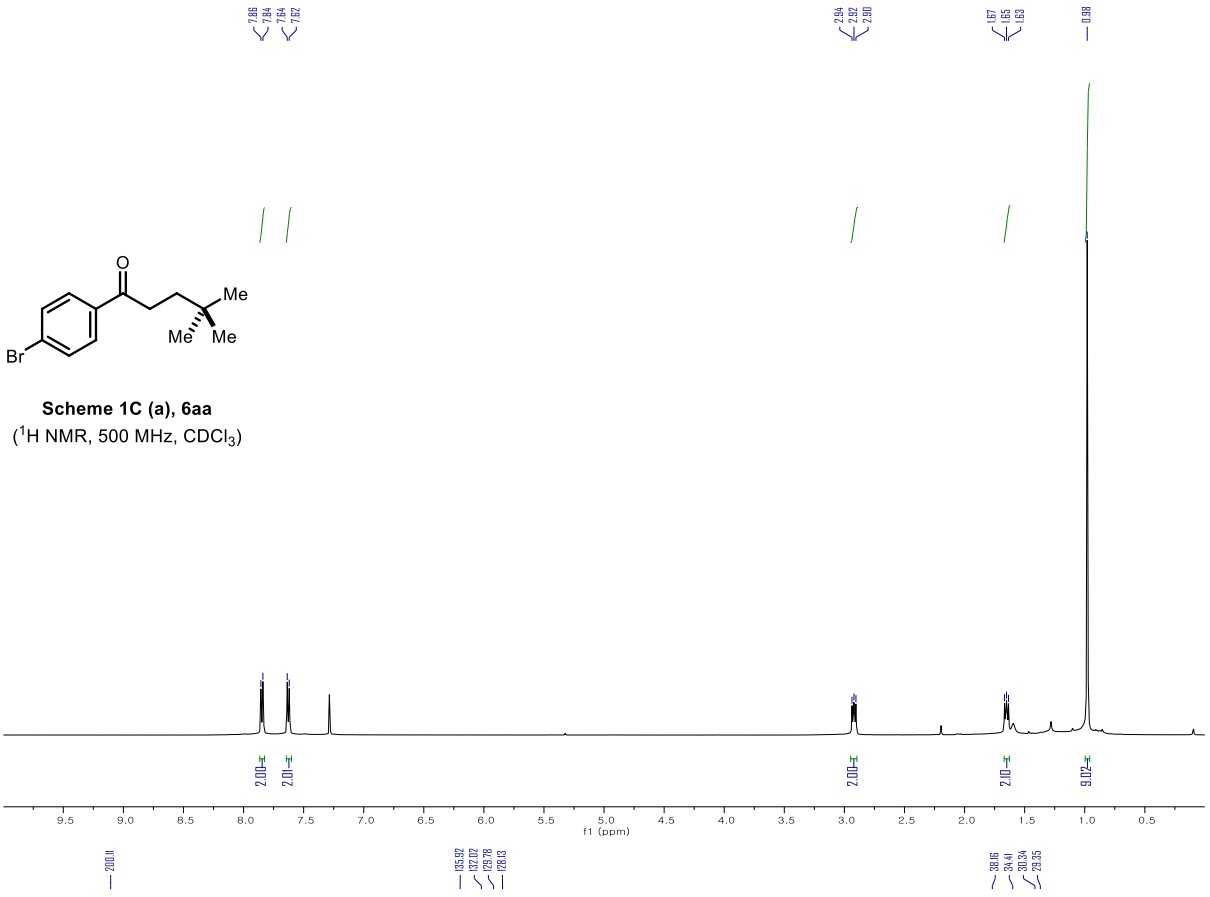
Scheme 1B (d), 5bg
(^{1}H NMR, 500 MHz, $CDCl_3$)



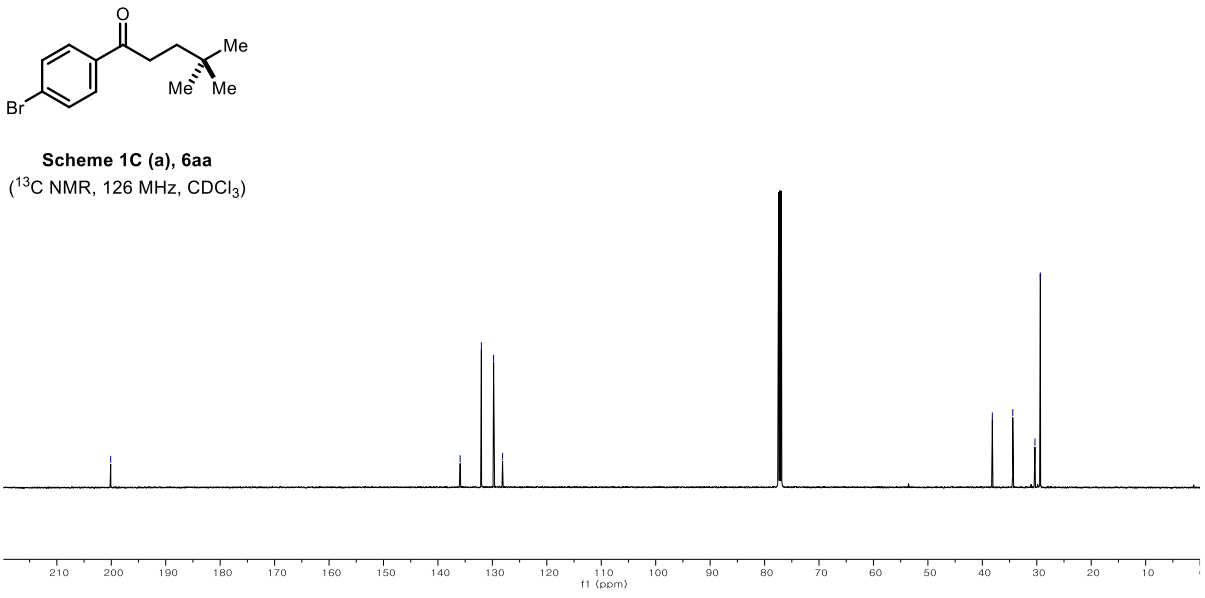


Scheme 1B (d), 5bg
(^{13}C NMR, 126 MHz, $CDCl_3$)

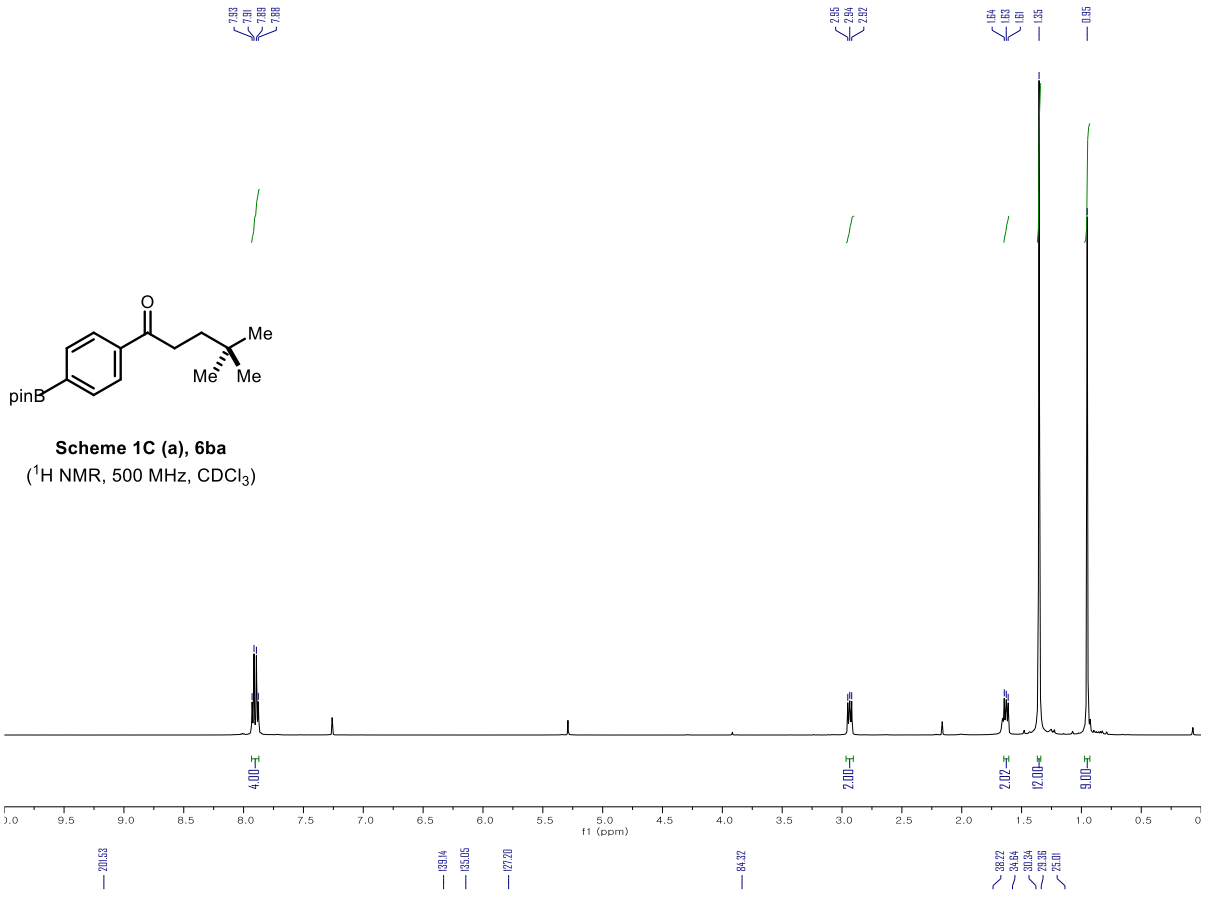




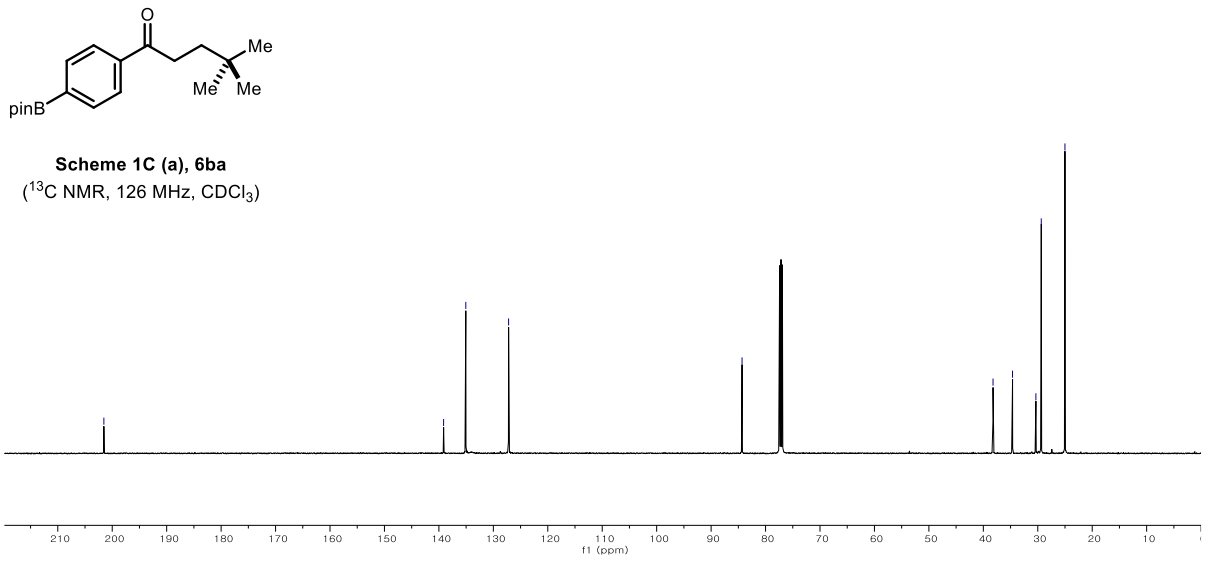
Scheme 1C (a), 6aa
(^{1}H NMR, 500 MHz, $CDCl_3$)



Scheme 1C (a), 6aa
(^{13}C NMR, 126 MHz, $CDCl_3$)

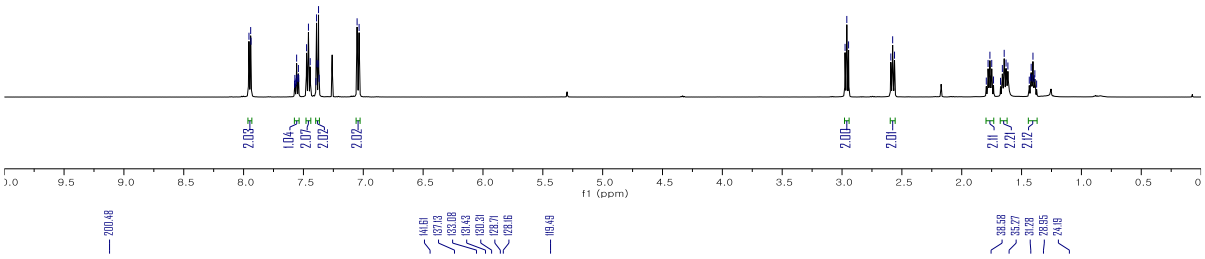


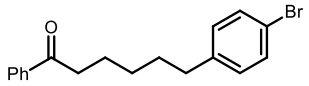
Scheme 1C (a), 6ba
(^{1}H NMR, 500 MHz, $CDCl_3$)



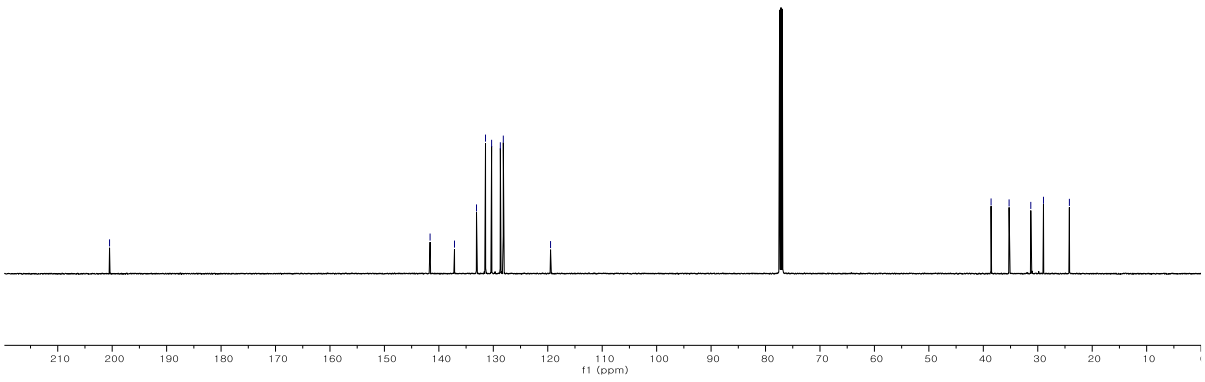
Scheme 1C (a), 6ba
(^{13}C NMR, 126 MHz, $CDCl_3$)

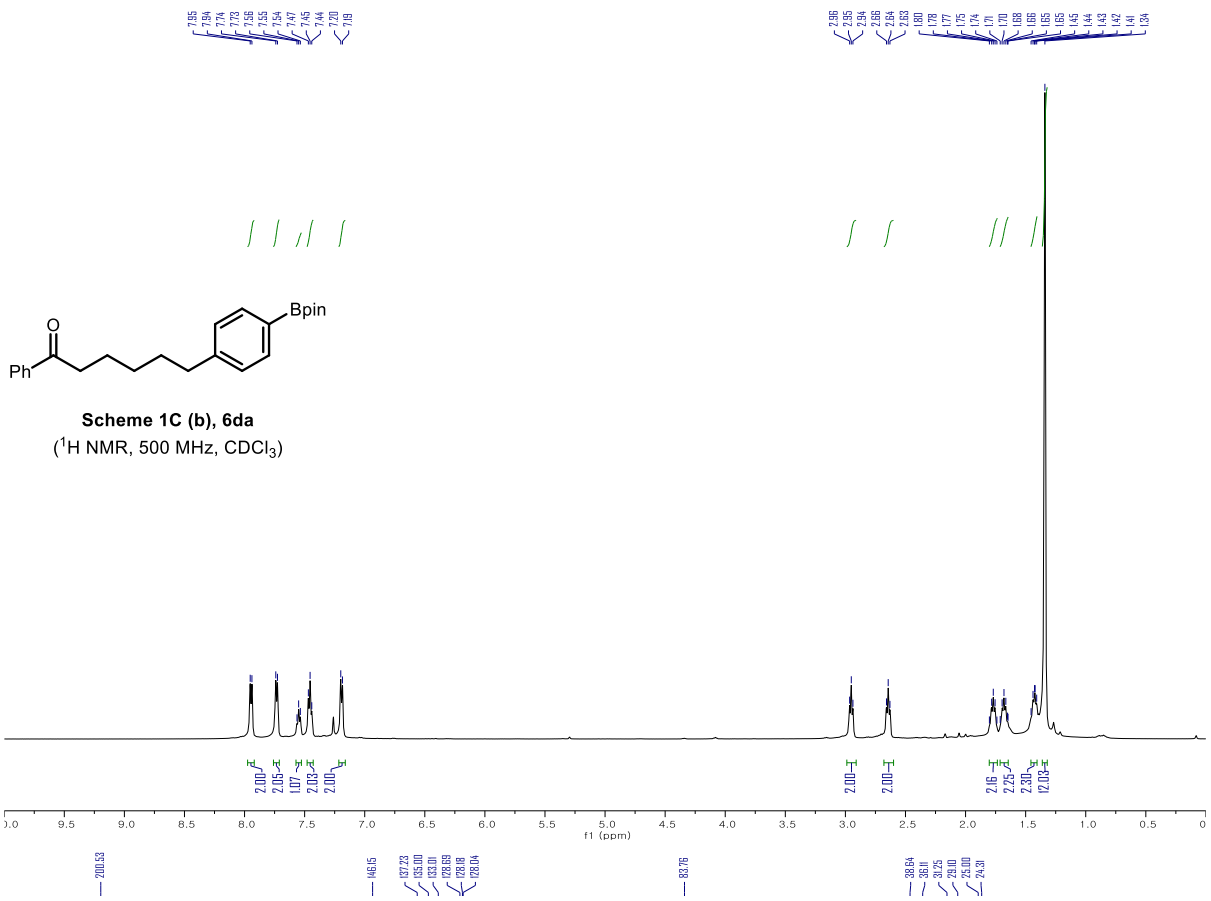
Scheme 1C (b), 6ca
(^{1}H NMR, 500 MHz, $CDCl_3$)



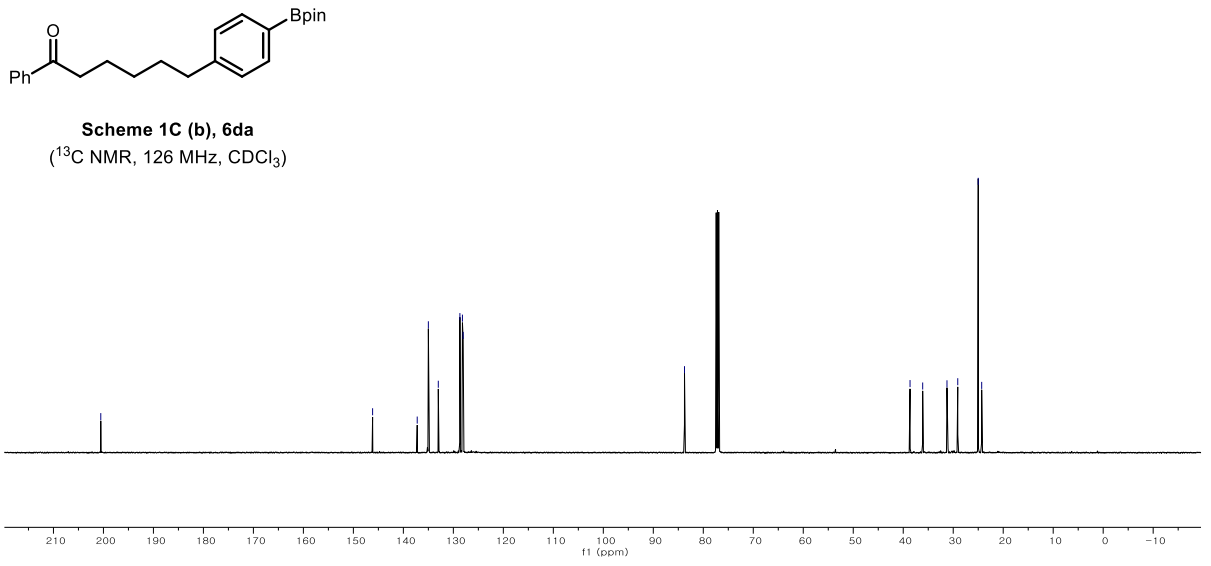


Scheme 1C (b), 6ca
(^{13}C NMR, 126 MHz, $CDCl_3$)

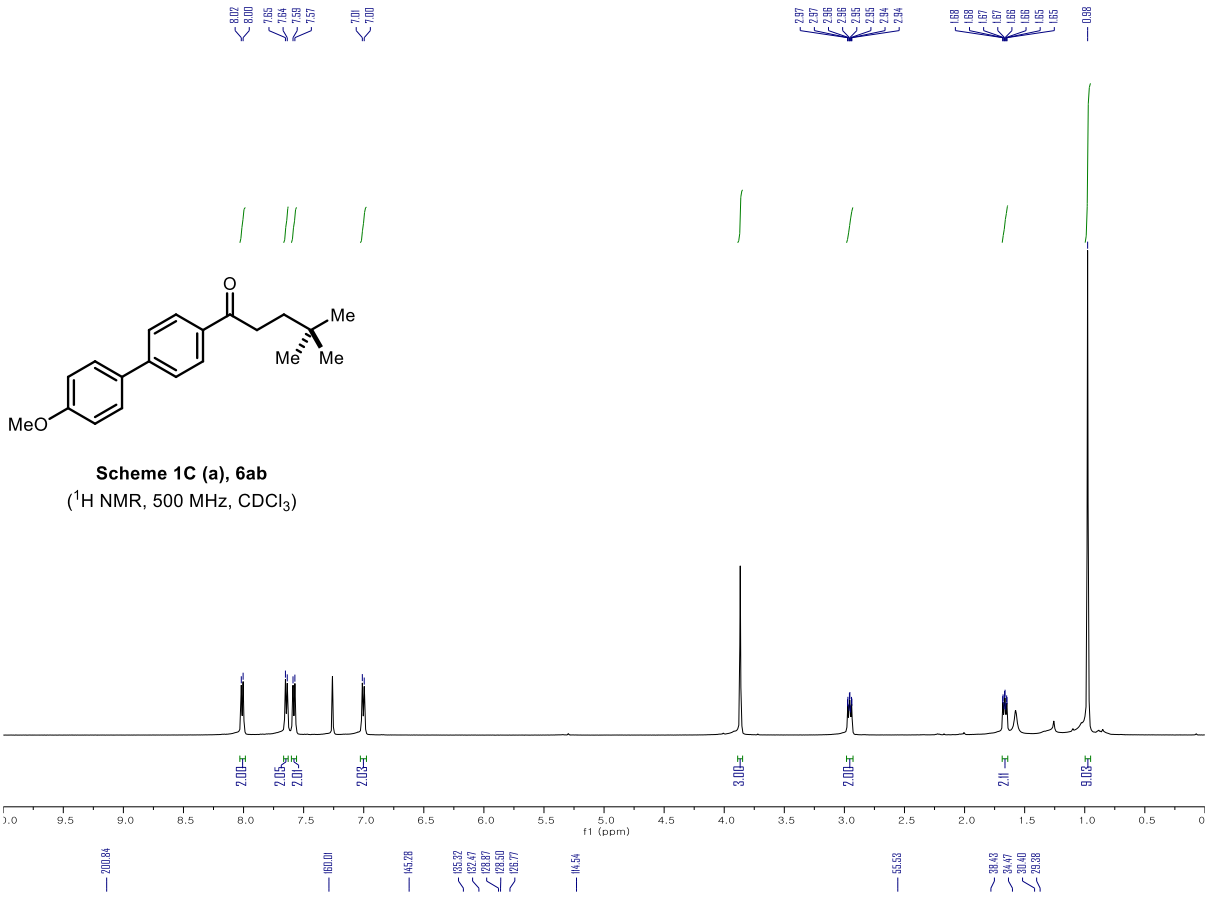




Scheme 1C (b), 6da
(^{1}H NMR, 500 MHz, $CDCl_3$)

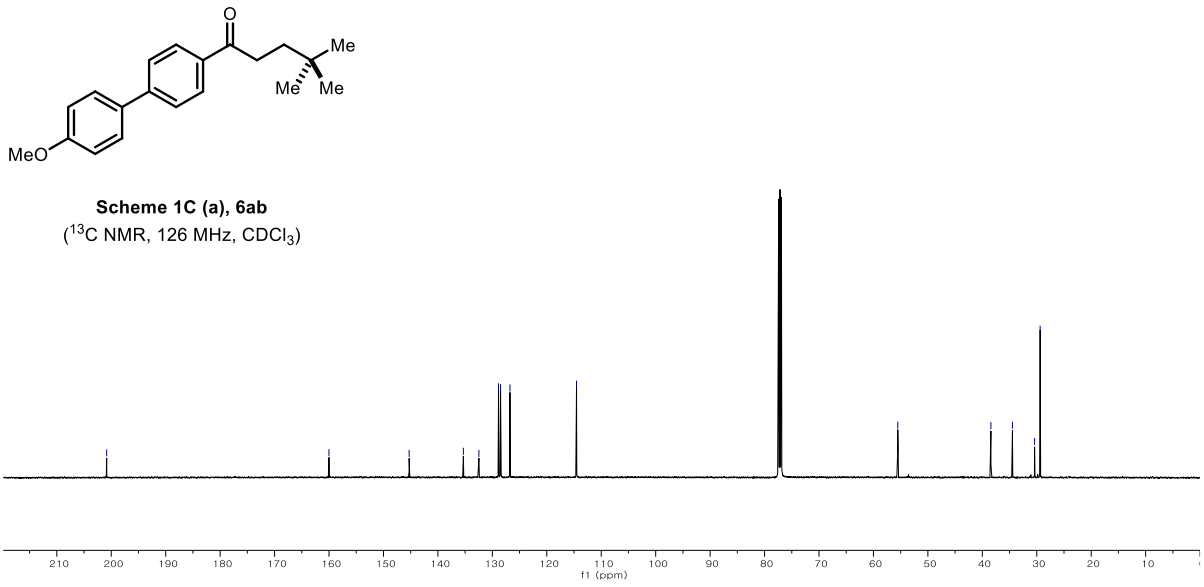


Scheme 1C (b), 6da
(^{13}C NMR, 126 MHz, $CDCl_3$)



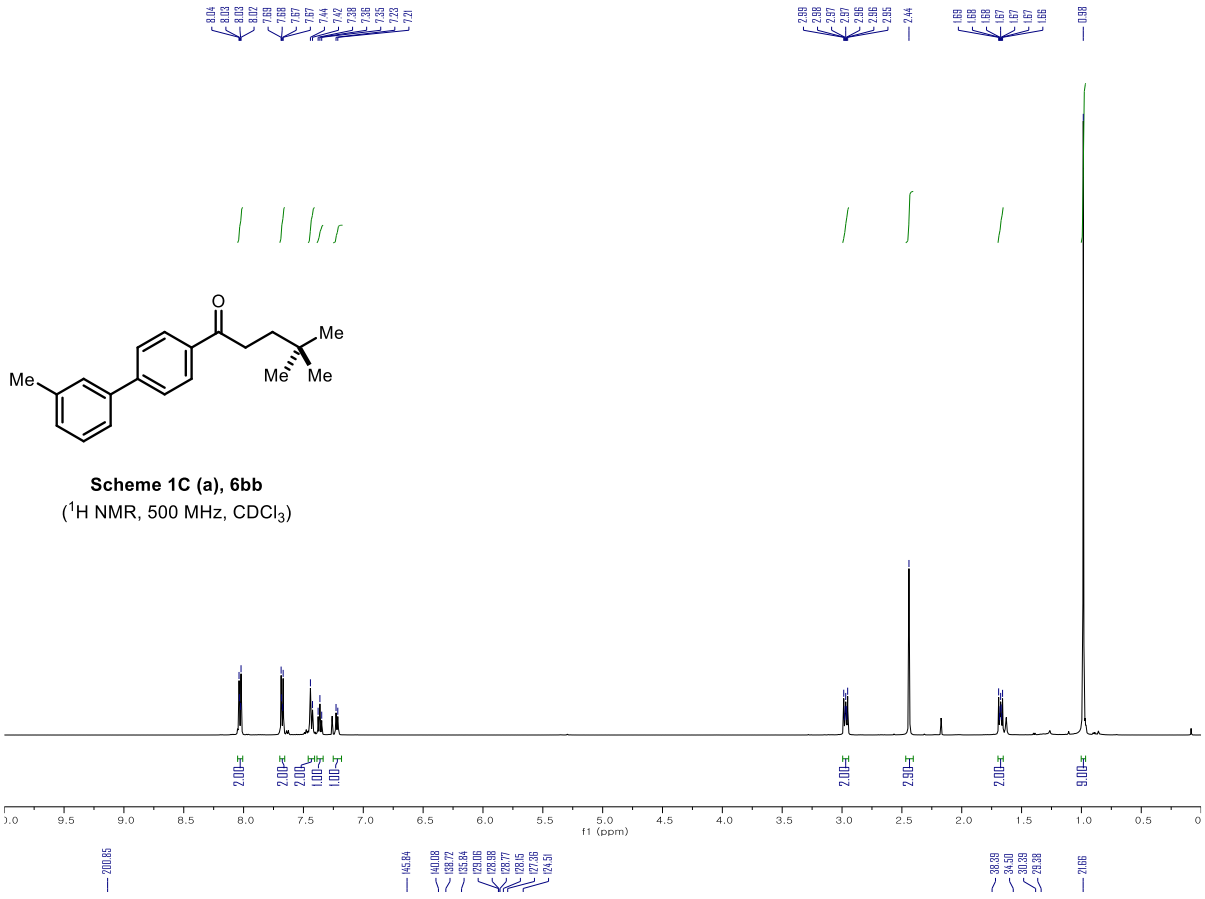
Scheme 1C (a), 6ab

(^{1}H NMR, 500 MHz, $CDCl_3$)

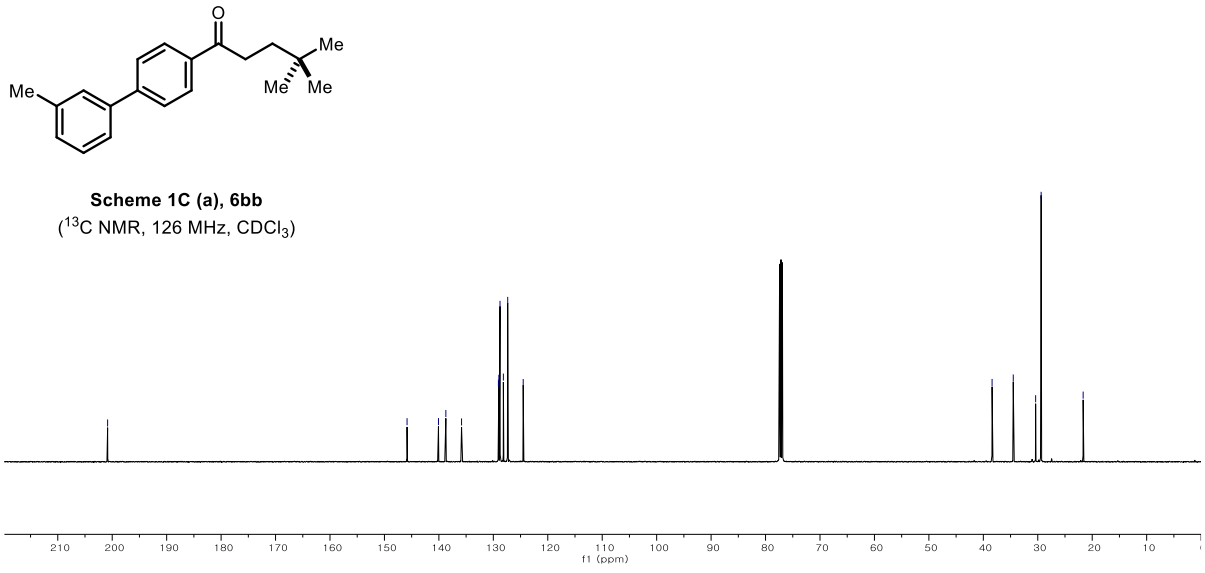


Scheme 1C (a), 6ab

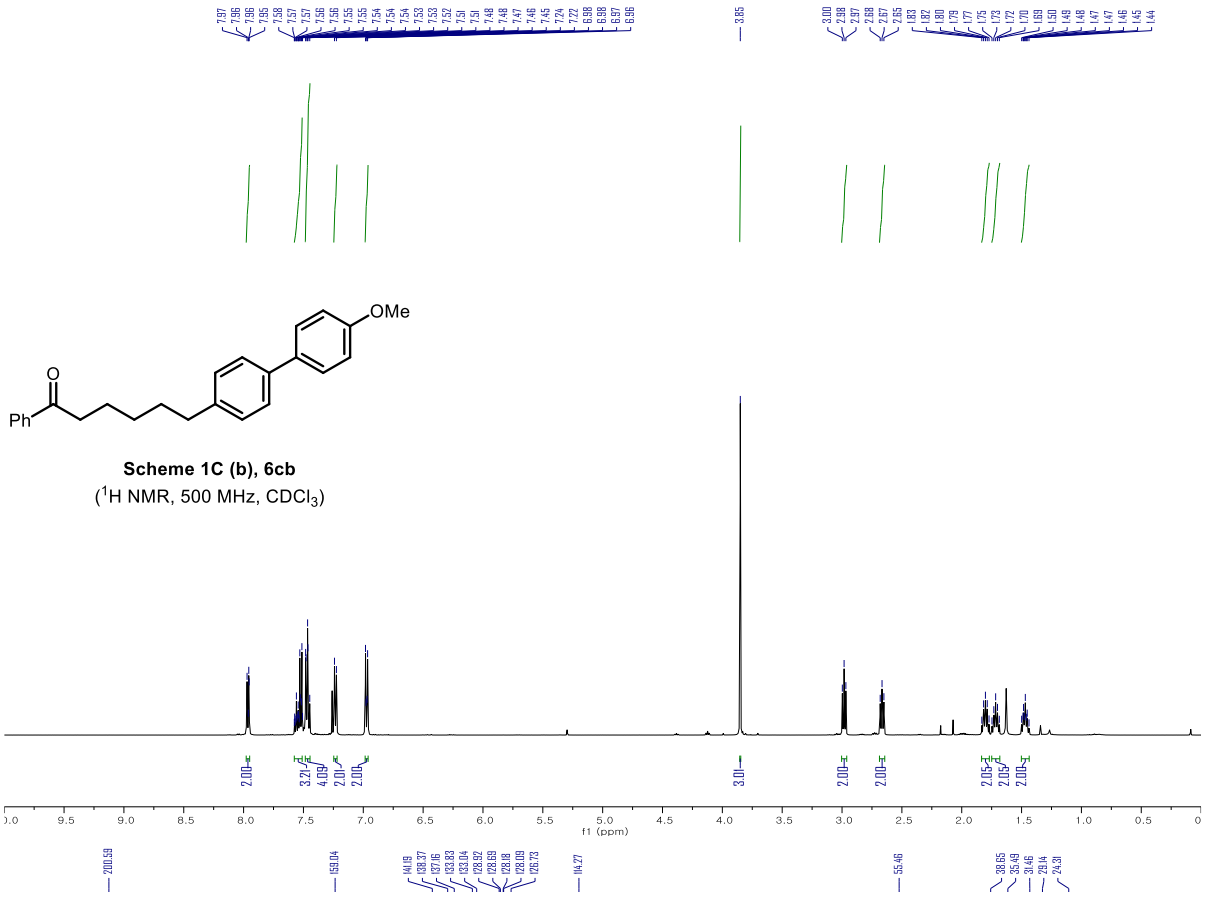
(^{13}C NMR, 126 MHz, $CDCl_3$)



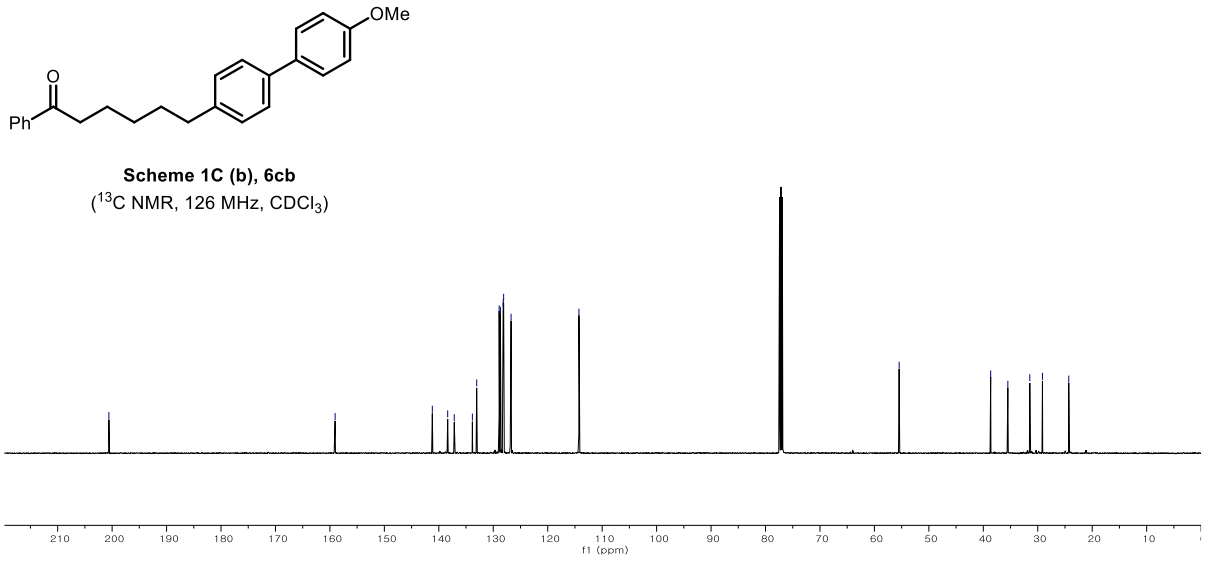
Scheme 1C (a), 6bb
(^{1}H NMR, 500 MHz, $CDCl_3$)



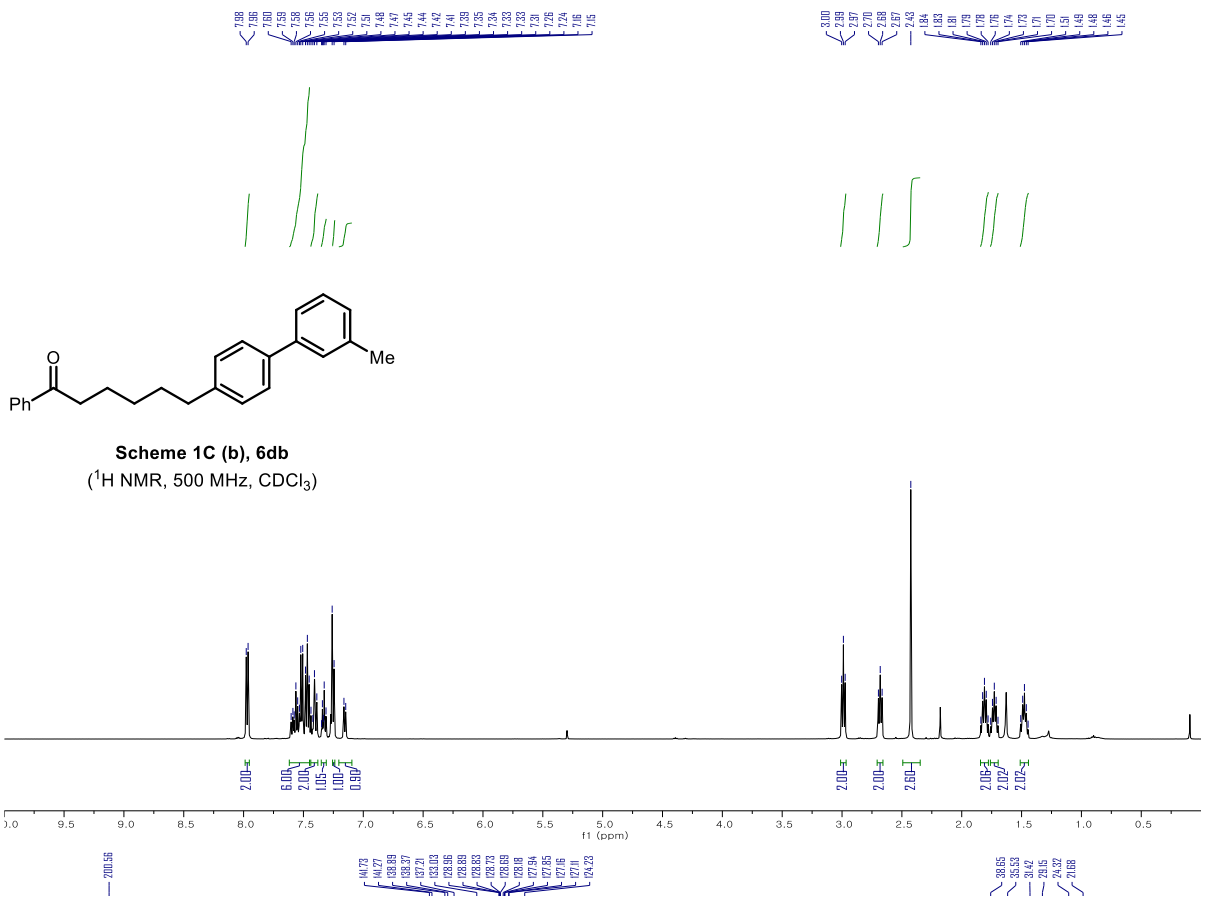
Scheme 1C (a), 6bb
(^{13}C NMR, 126 MHz, $CDCl_3$)



Scheme 1C (b), 6cb
(^{1}H NMR, 500 MHz, $CDCl_3$)

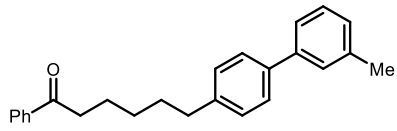


Scheme 1C (b), 6cb
(^{13}C NMR, 126 MHz, $CDCl_3$)



Scheme 1C (b), 6db

(^{1}H NMR, 500 MHz, $CDCl_3$)



Scheme 1C (b), 6db

(^{13}C NMR, 126 MHz, $CDCl_3$)