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Supporting Information

Direct Acylation and Alkynylation of Hydrocarbons via Synergistic Decatungstate Photo-HAT/Nickel Catalysis

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Contents

1. General Information

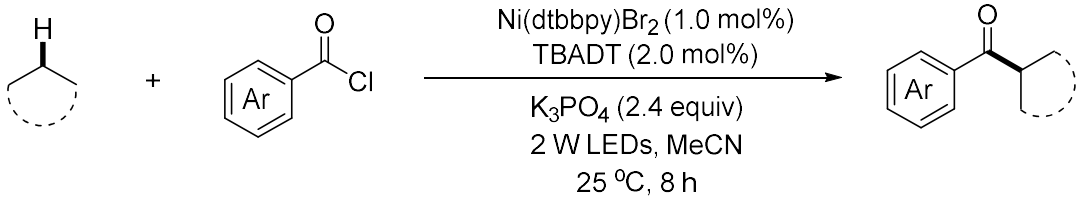
Nuclear magnetic resonance (NMR) spectroscopy measurements were carried out at room temperature. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, HSQC and HMBC experiments were carried out using Bruker ADVANCE III (600 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak with corresponding coupling constants (*J*) in Hertz (Hz) and multiplicities (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet and combinations of these and app.: apparent multiplicities). Gas chromatography was determined with a SHIMADZU Nexis GC 2030 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Orbitrap Elite mass spectrometer. The photoreaction instrument (WPTEC-1020L) was purchased from WATTCAS, China.

Materials and Methods:

Commercially available reagents and ligands were purchased from Sigma Aldrich, Alfa Aesar, and Strem Chemicals and unless otherwise stated were used without further purification. $NiBr_2{\cdot}DME$, NiI_2 and $Ni(OAc)_2$ were bought from Strem Chemicals. All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over 4 Å activated molecular sieves. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

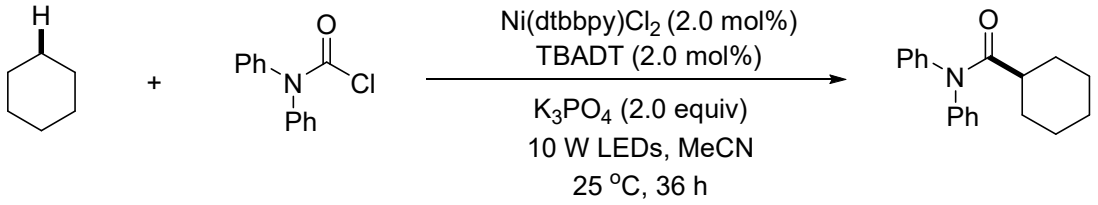
2. General Procedure

2.1 Synthesis of ketones via direct and selective acylation of hydrocarbons



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mol%), tetrabutylammonium decatungstate (0.004 mmol, 2.0 mol%), acyl chlorides (0.2 mmol, 1.0 equiv.), hydrocarbons (2.0 mmol, 10.0 equiv.), anhydrous K_3PO_4 (0.48 mmol, 2.4 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 2 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25 °C for 8 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding ketone products.

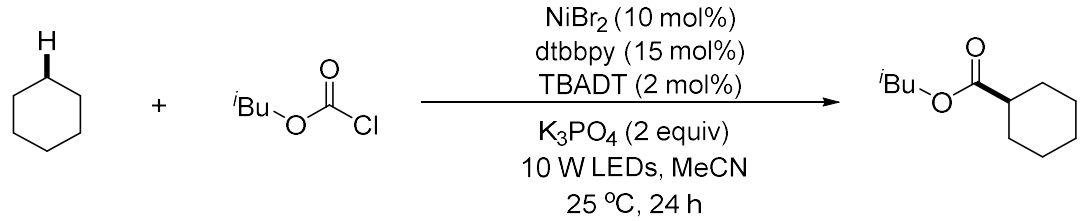
2.2 Synthesis of amides via direct and selective acylation of hydrocarbons



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiCl_2$•dtbbpy (0.004 mmol, 2.0 mol%), tetrabutylammonium decatungstate (0.004 mmol, 2.0 mol%), carbamic chloride (0.2 mmol, 1.0 equiv.), hydrocarbons (2.0 mmol, 10.0 equiv.), anhydrous K_3PO_4 (0.4 mmol, 2.0 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25 °C for 36 hours. The resulting mixture was

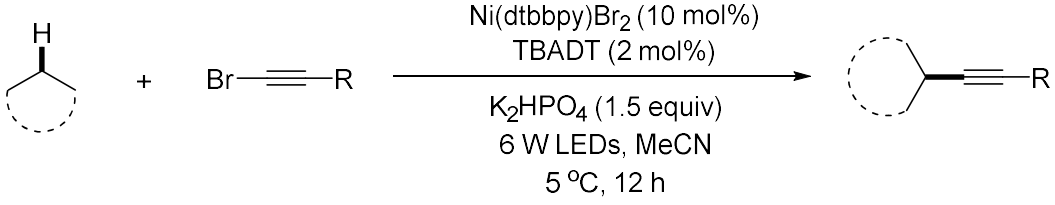
diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding amide products.

2.3 Synthesis of esters via direct and selective acylation of hydrocarbons



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$ (0.02 mmol, 10 mol%), dtbbpy (0.03 mmol, 15 mol%), tetrabutylammonium decatungstate (0.004 mmol, 2.0 mol%), chloroformates (0.2 mmol, 1.0 equiv.), hydrocarbons (2.0 mmol, 10.0 equiv.), anhydrous K_3PO_4 (0.4 mmol, 2.0 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25 °C for 24 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding ester products.

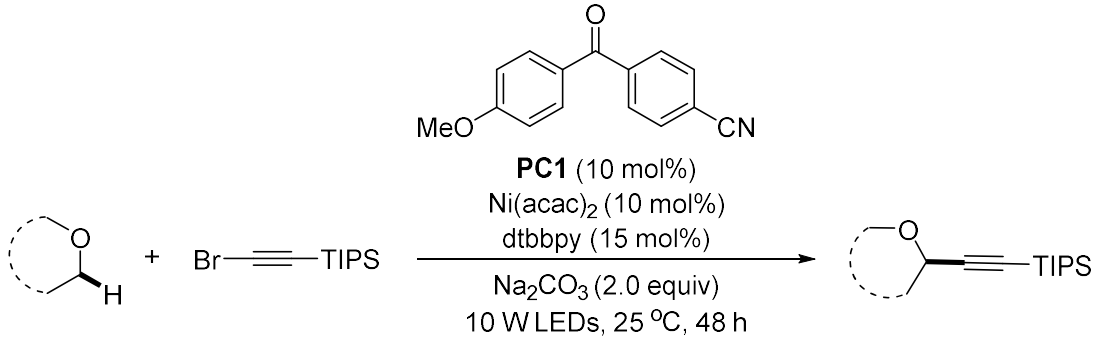
2.4 Synthesis of alkyl-substituted alkynes via direct and selective alkynylation of hydrocarbons



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$•dtbbpy (0.02 mmol, 10 mol%), tetrabutylammonium decatungstate (0.004

mmol, 2 mol%), alkynyl bromides (0.2 mmol, 1.0 equiv.), anhydrous K_2HPO_4 (0.3 mmol, 1.5 equiv.), hydrocarbon (2.0 mmol, 10.0 equiv.) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 6 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 5 °C for 12 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding alkyne products.

2.5 Synthesis of alkyl-substituted alkynes via direct and selective alkynylation of ethers



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (0.02 mmol, 10 mol%), dtbbpy (0.03 mmol, 15 mol%), **PC1** (0.02 mmol, 10 mol%), alkynyl bromides (0.2 mmol, 1.0 equiv.), anhydrous Na_2CO_3 (0.4 mmol, 2.0 equiv.) and ether (1.0 mL) as both C-H partners and solvent in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp (WATTCAS: WP-TEC-1020LC) at 25 °C for 48 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with EtOAc/hexane to afford the corresponding alkyne products.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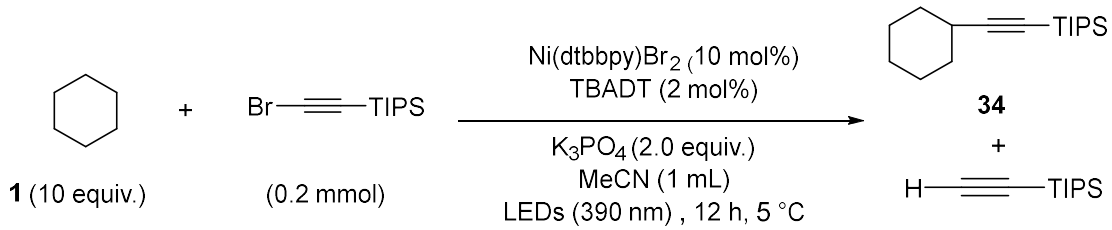
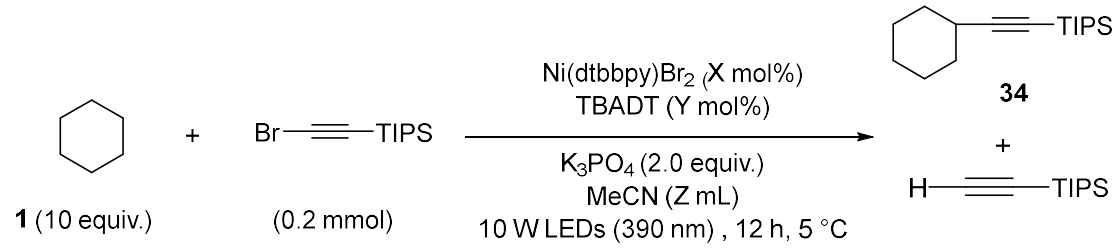
3. Optimization of Reaction Conditions

Table S1: Optimization of the reaction conditions for C(sp^3)-H alkynylation of hydrocarbons.



entry	Power value of LED lamp (W)	yield of **34** (%)
1	10	50
2	8	56
3	6	65
4	4	59

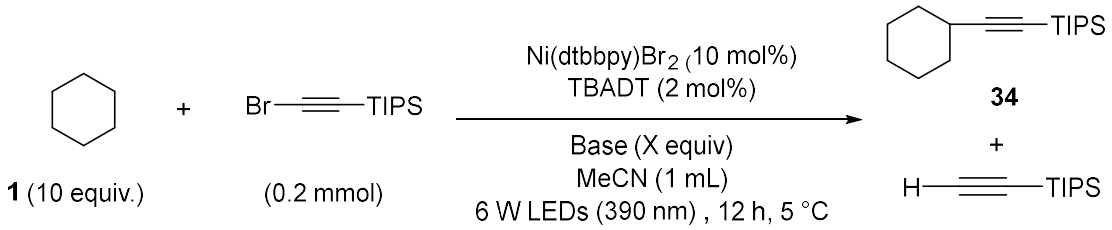
Table S2: optimization of the equivalents of Ni and TBADT, concentration for C(sp^3)−H alkynylation of hydrocarbons with alkynyl bromides



1 (10 equiv.) (0.2 mmol)

entry	X	Y	Z	yield of **34** (%)
1	10	2	0.5	60
2	10	2	1.0	75
3	5	2	0.5	45
4	10	1	0.5	64
5	10	2	2	62

Table S3: optimization of the base for C(sp^3)−H alkynylation of hydrocarbons with alkynyl bromides

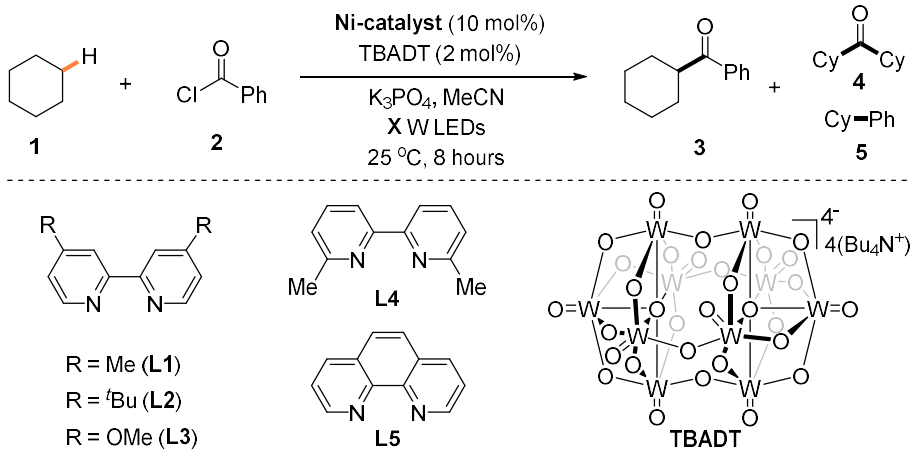


1 (10 equiv.) (0.2 mmol)

entry	Base	Eq.	yield of **34** (%)[a]
1	K_3PO_4	2.0	75
2	K_2HPO_4	2.0	86
3	Na_2CO_3	2.0	72
4	K_2HPO_4	1.5	96(76)[b]
5	K_2HPO_4	1.1	90
6	K_2HPO_4[c]	1.5	67(57)[b]

[a]GC yield, [b]isolated yield, [c]This reaction was performed at 25 °C.

Table S4: Optimization of the Reaction Conditions

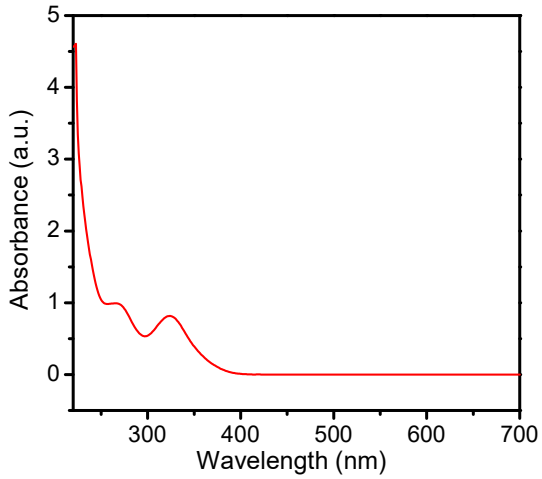


entry		nickel catalyst	Power value of LEDs (W)	yield of **3** (%)[b]	yield of **4** (%)[b]
1	**L1**	$NiBr_2$	10	15	-
2	**L2**	$NiBr_2$	10	45	8
3	**L3**	$NiBr_2$	10	10	13
4	**L4**	$NiBr_2$	10	42	10
5	**L5**	$NiBr_2$	10	trace	-
6	**L2**	$NiCl_2$	10	trace	-
7	**L2**	NiI_2	10	39	5
8	**L2**	$NiOAc_2{\cdot}4H_2O$	10	44	15
9	**L2**	$NiBr_2{\cdot}dme$	10	62	8
10		Ni(**L2**)Br_2	10	66	7
11		Ni(**L2**)Br_2	6	68	5
12		Ni(**L2**)Br_2	2	78	< 2
13[d]		**Ni(L2)Br_2**	**2**	**83 (71)[c]**	**< 2**
14[d,e]		Ni(**L2**)Br_2	2	69	6
15[d]		-	2	no reaction	
16[d,f]		Ni(**L2**)Br_2	2	no reaction	
17[d,g]		Ni(**L2**)Br_2	2	no reaction	

[a]Reaction conditions: **1** (2 mmol), **2** (0.2 mmol), [Ni]/**L** (10 mol%), TBADT (2 mol%), K_3PO_4 (0.48 mmol) in MeCN (0.5 mL) at 25 °C under irradiation of LEDs (X W, 390 nm) for 8 hours. [b]Yields determined by GC analysis using adamantane as an internal standard. [c]Isolated yield. [d]1 mol% Ni(**L2**)Br_2 was used. [e]5 equivalents of cyclohexane were used. [f]Without TBADT. [g]Without light.

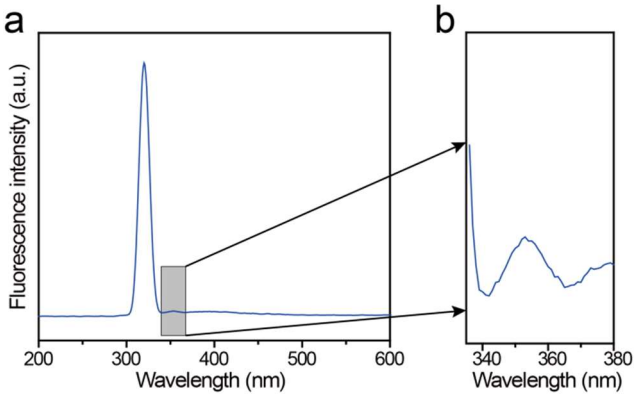
4. Mechanistic studies

4.1 UV-VIS absorption spectra



The UV-visible absorption spectra for TBADT in MeCN (10^{-4} M) is shown above.

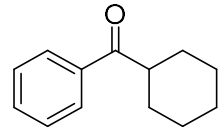
4.2 Emission spectra



The emission spectra for TBADT irradiated under 320 nm light in MeCN (10^{-5} M) is shown above.

5. Characterization Data of Products

Cyclohexyl(phenyl)methanone (3)



Chemical Formula: $C_{13}H_{16}O$
Exact Mass: 188.1201

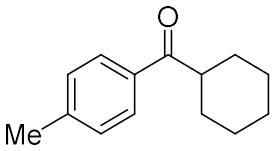
3 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and benzoyl chloride (0.2 mmol, 28.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **3** as colorless oil (28.9 mg, 71% yield).

The NMR data matched those reported in the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97-7.91 (m, 2H), 7.56-7.52 (m, 1H), 7.48-7.42 (m, 2H), 3.26 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.96-1.81 (m, 4H), 1.79-1.70 (m, 1H), 1.56-1.45 (m, 2H), 1.45-1.35 (m, 2H), 1.31-1.24 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 204.0, 136.5, 132.8, 128.7, 128.4, 45.8, 29.5, 26.1, 26.0.

Cyclohexyl(*p*-tolyl)methanone (6)



Chemical Formula: $C_{14}H_{18}O$
Exact Mass: 202.1358

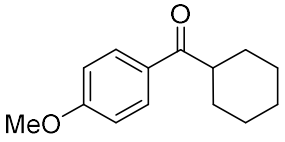
6 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **6** as colorless oil (32.2 mg, 73% yield).

The NMR data matched those reported in the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.24 (tt, *J* = 11.6, 3.3 Hz, 1H), 2.40 (s, 3H), 1.92-1.81 (m, 4H), 1.78-1.69 (m, 1H), 1.53-1.45 (m, 2H), 1.44-1.34 (m, 2H), 1.31-1.24 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 203.7, 143.6, 133.9, 129.4, 128.5, 45.6, 29.6, 26.1, 26.0, 21.7.

Cyclohexyl(4-methoxyphenyl)methanone (7)



Chemical Formula: $C_{14}H_{18}O_2$
Exact Mass: 218.1307

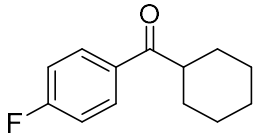
7 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methoxybenzoyl chloride (0.2 mmol, 34.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **7** as colorless oil (28.8 mg, 66% yield).

The NMR data matched those reported in the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.89 (m, 2H), 6.97-6.89 (m, 2H), 3.86 (s, 3H), 3.21 (tt, *J* = 11.6, 3.2 Hz, 1H), 1.92-1.80 (m, 4H), 1.77-1.70 (m, 1H), 1.55-1.45 (m, 2H), 1.43-1.34 (m, 2H), 1.31-1.22 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.6, 163.3, 130.6, 129.4, 113.8, 55.6, 45.4, 29.7, 26.1, 26.1.

Cyclohexyl(4-fluorophenyl)methanone (8)



Chemical Formula: $C_{13}H_{15}FO$
Exact Mass: 206.1107

8 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2

mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-fluorobenzoyl chloride (0.2 mmol, 31.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **8** as colorless oil (29.7 mg, 72% yield).

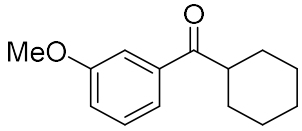
The NMR data matched those reported in the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00-7.94 (m, 2H), 7.15-7.08 (m, 2H), 3.21 (tt, *J* = 11.6, 3.2 Hz, 1H), 1.90-1.81 (m, 4H), 1.76-1.71 (m, 1H), 1.53-1.44 (m, 2H), 1.43-1.34 (m, 2H), 1.29-1.24 (m, 1H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -106.00 (m);

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.3, 165.6 (d, *J* = 254.0 Hz), 132.7 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 9.2 Hz), 115.7 (d, *J* = 21.8 Hz), 45.6, 29.4, 25.9, 25.8.

Cyclohexyl(3-methoxyphenyl)methanone (9)



Chemical Formula: $C_{14}H_{18}O_2$
Exact Mass: 218.1307

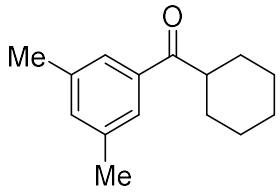
9 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 3-methoxybenzoyl chloride (0.2 mmol, 34.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **9** as colorless oil (27.9 mg, 64% yield).

The NMR data matched those reported in the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.50 (m, 1H), 7.49-7.44 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.11-7.07 (m, 1H), 3.85 (s, 3H), 3.23 (tt, *J* = 11.5, 3.3 Hz, 1H), 1.90-1.82 (m, 4H), 1.76-1.72 (m, 1H), 1.53-1.45 (m, 2H), 1.43-1.35 (m, 2H), 1.29-1.24 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 203.8, 159.9, 137.8, 129.5, 120.8, 119.0, 112.8, 55.4, 45.8, 29.5, 26.0, 25.9.

Cyclohexyl(3,5-dimethylphenyl)methanone (10)



Chemical Formula: $C_{15}H_{20}O$
Exact Mass: 216.1514

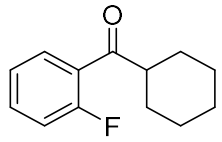
10 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 3,5-dimethylbenzoyl chloride (0.2 mmol, 33.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **10** as colorless oil (27.2 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.18 (s, 1H), 3.24 (tt, *J* = 11.5, 3.3 Hz, 1H), 2.37 (s, 6H), 1.90-1.81 (m, 4H), 1.77-1.70 (m, 1H), 1.53-1.44 (m, 2H), 1.44-1.35 (m, 2H), 1.31-1.23 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 204.3, 138.1, 136.5, 134.3, 125.9, 45.6, 29.4, 25.9, 25.8, 21.2;

HRMS: (ESI) calcd for $C_{15}H_{21}O^+[M+H]^+$ 217.1587; found 217.1583.

Cyclohexyl(2-fluorophenyl)methanone (11)



Chemical Formula: $C_{13}H_{15}FO$
Exact Mass: 206.1107

11 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 2-fluorobenzoyl chloride (0.2 mmol, 31.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain **11** as colorless oil (12.8 mg, 31% yield).

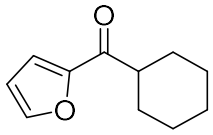
The NMR data matched those reported in the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.70 (m, 1H), 7.51-7.44 (m, 1H), 7.24-7.19 (m, 1H), 7.14-7.08 (m, 1H), 3.15-3.08 (m, 1H), 1.97-1.91 (m, 2H), 1.84-1.78 (m, 2H), 1.73-1.68 (m, 1H), 1.45-1.34 (m, 4H), 1.27-1.23 (m, 1H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.69 (m);

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.9 (d, *J* = 4.2 Hz), 161.1 (d, *J* = 253.1 Hz), 133.8 (d, *J* = 8.8 Hz), 130.8 (d, *J* = 2.9 Hz), 126.1 (d, *J* = 13.6 Hz), 124.4 (d, *J* = 3.6 Hz), 116.4 (d, *J* = 23.8 Hz), 50.1 (d, *J* = 6.1 Hz), 28.8, 26.0, 25.8.

Cyclohexyl(furan-2-yl)methanone (12)



Chemical Formula: $C_{11}H_{14}O_2$
Exact Mass: 178.0994

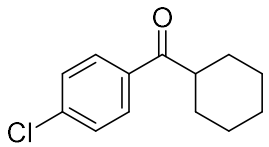
12 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and furan-2-carbonyl chloride (0.2 mmol, 26.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **12** as colorless oil (15.3 mg, 43% yield).

The NMR data matched those reported in the literature.[4]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60-7.55 (m, 1H), 7.18 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.06 (tt, *J* = 11.7, 3.3 Hz, 1H), 1.91-1.80 (m, 4H), 1.75-1.69 (m, 1H), 1.55-1.46 (m, 2H), 1.40-1.32 (m, 2H), 1.30-1.25 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 152.3, 146.1, 117.0, 112.1, 46.3, 28.9, 25.8, 25.7.

(4-chlorophenyl)(cyclohexyl)methanone (13)



Chemical Formula: $C_{13}H_{15}ClO$
Exact Mass: 222.0811

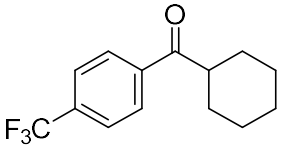
13 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-chlorobenzoyl chloride (0.2 mmol, 35.0 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain **13** as colorless oil (29.8 mg, 67% yield).

The NMR data matched those reported in the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00-7.78 (m, 2H), 7.53-7.35 (m, 2H), 3.20 (tt, J = 11.5, 3.2 Hz, 1H), 1.94-1.80 (m, 4H), 1.80-1.71 (m, 1H), 1.54-1.42 (m, 2H), 1.42 -1.32 (m, 2H), 1.31-1.21 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.6, 139.1, 134.6, 129.7, 128.9, 45.6, 29.3, 25.9, 25.8.

cyclohexyl(4-(trifluoromethyl)phenyl)methanone (14)



Chemical Formula: $C_{14}H_{15}F_3O$
Exact Mass: 256.1075

14 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-(trifluoromethyl)benzoyl chloride (0.2 mmol, 41.7 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain **14** as colorless oil (17.9 mg, 35% yield).

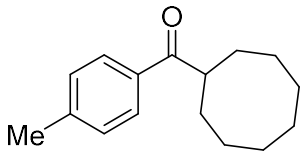
The NMR data matched those reported in the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06-7.99 (m, 2H), 7.76-7.69 (m, 2H), 3.24 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.92-1.83 (m, 4H), 1.78-1.72 (m, 1H), 1.55-1.44 (m, 2H), 1.44-1.35 (m, 2H), 1.30-1.25 (m, 1H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.08(s);

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.9, 139.1, 134.0 (q, *J* = 32.7 Hz), 128.5, 125.6 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.6 Hz), 45.9, 29.2, 25.8, 25.7.

Cyclooctyl(*p*-tolyl)methanone (15)



Chemical Formula: $C_{16}H_{22}O$
Exact Mass: 230.1671

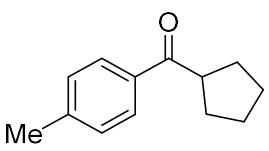
15 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclooctane (2 mmol, 224.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **15** as colorless oil (33.0 mg, 69% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 3.46 (tt, *J* = 8.8, 3.5 Hz, 1H), 2.41 (s, 3H), 1.88-1.81 (m, 2H), 1.80-1.70 (m, 4H), 1.69-1.63 (m, 3H), 1.63-1.53 (m, 5H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 204.2, 143.4, 133.9, 129.3, 128.4, 44.8, 29.1, 26.7, 26.6, 25.6, 21.6;

HRMS: (ESI) calcd for $C_{16}H_{23}O^+[M+H]^+$ 217.1743; found 217.1736.

Cyclopentyl(*p*-tolyl)methanone (16)



Chemical Formula: $C_{13}H_{16}O$
Exact Mass: 188.1201

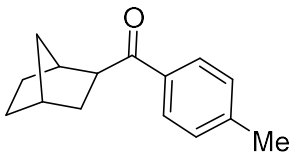
16 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclopentane (2 mmol, 140.0 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **16** as colorless oil (20.7 mg, 66% yield).

The NMR data matched those reported in the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 3.74-3.65 (m, 1H), 2.41 (s, 3H), 1.96-1.85 (m, 4H), 1.77-1.69 (m, 2H), 1.69-1.61 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.5, 143.4, 134.5, 129.2, 128.6, 46.3, 30.1, 26.4, 21.6.

((*1S,4R*)-Bicyclo[2.2.1]heptan-2-yl)(*p*-tolyl)methanone (17)



Chemical Formula: $C_{15}H_{18}O$
Exact Mass: 214.1358

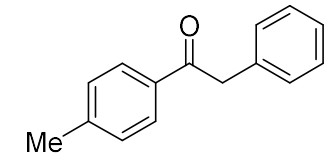
17 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), (*1s,4s*)-bicyclo[2.2.1]heptane (2 mmol, 192.4 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **17** as colorless oil (26.6 mg, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.26-7.22 (m, 2H), 3.19 (dd, *J* = 8.9, 5.5 Hz, 1H), 2.52-2.48 (m, 1H), 2.40 (s, 3H), 2.34 (s, 1H), 2.03-1.97 (m, 1H), 1.65-1.55 (m, 2H), 1.50-1.44 (m, 1H), 1.44-1.39 (m, 2H), 1.33-1.27 (m, 1H), 1.17-1.11 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.2, 143.4, 134.2, 129.3, 128.7, 49.5, 41.2, 36.4, 36.3, 33.8, 29.9, 29.2, 21.7;

HRMS: (ESI) calcd for $C_{15}H_{19}O^+[M+H]^+$ 215.1430; found 215.1428.

2-phenyl-1-(*p*-tolyl)ethan-1-one (18)



Chemical Formula: $C_{15}H_{14}O$
Exact Mass: 210.1045

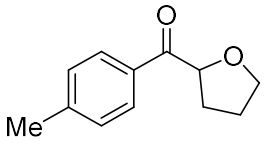
18 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), toluene (2.0 mmol, 184.3 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **18** as colorless oil (15.0 mg, 35% yield).

The NMR data matched those reported in the literature.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.88 (m, 2H), 7.36-7.29 (m, 2H), 7.29-7.23 (m, 5H), 4.26 (s, 2H), 2.40 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 144.1, 134.9, 134.2, 129.6, 129.5, 128.9, 128.8, 126.9, 45.6, 21.8.

(tetrahydrofuran-2-yl)(*p*-tolyl)methanone (19)



Chemical Formula: $C_{12}H_{14}O_2$
Exact Mass: 190.0994

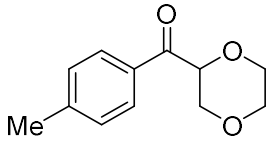
19 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tetrahydrofuran (2 mmol, 144.2 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **19** as colorless oil (22.3 mg, 57% yield).

The NMR data matched those reported in the literature.[8]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.27-7.25 (m, 2H), 5.24 (dd, *J* = 8.5, 5.8 Hz, 1H), 4.04 (dt, *J* = 8.3, 6.8 Hz, 1H), 3.97 (dt, *J* = 8.2, 6.7 Hz, 1H), 2.41 (s, 3H), 2.32-2.24 (m, 1H), 2.16-2.07 (m, 1H), 2.00-1.93 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.5, 144.3, 132.7, 129.4, 129.0, 80.0, 69.5, 29.5, 25.8, 21.8.

(1,4-dioxan-2-yl)(*p*-tolyl)methanone (20)



Chemical Formula: $C_{12}H_{14}O_3$
Exact Mass: 206.0943

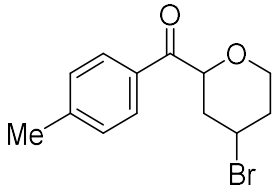
20 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), 1,4-dioxane (2 mmol, 176.2 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **20** as colorless oil (26.6 mg, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.29-7.25 (m, 2H), 4.97 (dd, *J* = 9.5, 2.9 Hz, 1H), 4.08 (dd, *J* = 11.8, 2.9 Hz, 1H), 4.00-3.95 (m, 1H), 3.92-3.86 (m, 1H), 3.81-3.76 (m, 1H), 3.74-3.67 (m, 2H), 2.42 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.5, 144.8, 132.4, 129.5, 129.0, 77.6, 68.4, 66.9, 66.5, 21.9.

HRMS: (ESI) calcd for $C_{12}H_{15}O_3^+$[M+H]$^+$ 207.1016; found 207.1014.

(4-bromotetrahydro-2*H*-pyran-2-yl)(*p*-tolyl)methanone (21)



Chemical Formula: $C_{13}H_{15}BrO_2$
Exact Mass: 282.0255

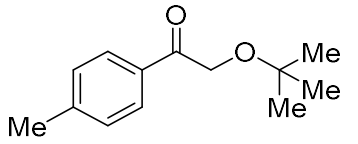
21 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), 4-bromotetrahydro-2*H*-pyran (2.0 mmol, 330.1 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **21** as colorless oil (30.6 mg, 54% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.29-7.25 (m, 2H), 5.29 (dd, *J* = 10.1, 2.6 Hz, 1H), 4.83-4.77 (m, 1H), 4.16-4.09 (m, 1H), 4.05-3.99 (m, 1H), 2.41 (s, 3H), 2.35-2.28 (m, 1H), 2.26-2.17 (m, 2H), 2.01-1.95 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 144.7, 132.1, 129.5, 129.1, 74.6, 63.7, 49.3, 37.1, 34.2, 21.9;

HRMS: (ESI) calcd for $C_{13}H_{16}BrO_2^+$[M+H]$^+$ 283.0823; found 283.0325.

2-(*tert*-butoxy)-1-(*p*-tolyl)ethan-1-one (22)



Chemical Formula: $C_{13}H_{18}O_2$
Exact Mass: 206.1307

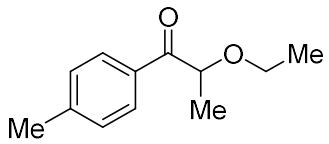
22 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), 2-methoxy-2-methylpropane (2.0 mmol, 176.4 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **22** as colorless oil (26.4 mg, 64% yield).

The NMR data matched those reported in the literature.[9]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.26-7.23 (m, 2H), 4.63 (s, 2H), 2.40 (s, 3H), 1.27 (s, 9H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 144.1, 133.0, 129.3, 128.4, 74.6, 66.3, 27.6, 21.8.

2-ethoxy-1-(*p*-tolyl)propan-1-one (23)



Chemical Formula: $C_{12}H_{16}O_2$
Exact Mass: 192.1150

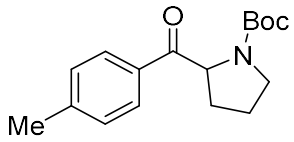
23 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), ethoxyethane (2.0 mmol, 148.2 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **23** as colorless oil (9.6 mg, 27% yield).

The NMR data matched those reported in the literature.[10]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.27-7.25 (m, 2H), 4.65 (q, *J* = 6.9 Hz, 1H), 3.54 (dq, *J* = 9.1, 7.0 Hz, 1H), 3.47 (dq, *J* = 9.0, 7.0 Hz, 1H), 2.41 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.9, 144.3, 132.4, 129.4, 129.1, 79.3, 65.3, 21.8, 19.2, 15.5.

Tert-butyl 2-(4-methylbenzoyl)pyrrolidine-1-carboxylate (24)



Chemical Formula: $C_{17}H_{23}NO_3$
Exact Mass: 289.1678

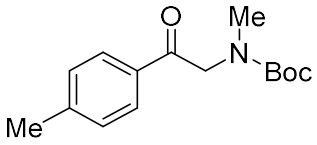
24 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tert-butyl pyrrolidine-1-carboxylate (1.0 mmol, 171.2 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **24** as colorless oil (26.5 mg, 45% yield); a 3:2 mixture of rotamers.

The NMR data matched those reported in the literature.[11]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91-7.82 (m, 2H), 7.29-7.22 (m, 2H), 5.31 (dd, *J* = 9.3, 3.1 Hz, 0.4H), 5.17 (dd, *J* = 8.9, 3.9 Hz, 0.6H), 3.70-3.64 (m, 0.6H), 3.64-3.58 (m, 0.4H), 3.56-3.51 (m, 0.6H), 3.49-3.43 (m, 0.4H), 2.41 (s, 1.8H), 2.39 (s, 1.2H), 2.35-2.23 (m, 1H), 1.97-1.85 (m, 3H), 1.46 (s, 3.6H), 1.25 (s, 5.4H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.5, 198.0, 154.5, 153.9, 144.0, 144.0, 132.7, 132.5, 129.4, 129.3, 128.7, 128.3, 79.7, 79.6, 61.3, 61.0, 46.8, 46.6, 31.0, 29.9, 28.5, 28.2, 24.2, 23.6, 21.7.

Tert-butyl methyl(2-oxo-2-(*p*-tolyl)ethyl)carbamate (25)



Chemical Formula: $C_{15}H_{21}NO_3$
Exact Mass: 263.1521

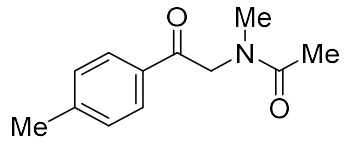
25 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tert-butyl dimethylcarbamate (1.0 mmol, 145.2 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **25** as colorless oil (35.8 mg, 69% yield); a 1.2:1 mixture of rotamers.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.29-7.22 (m, 2H), 4.65 (s, 1.1H), 4.55 (s, 0.9H), 2.96 (s, 1.35H), 2.92 (s, 1.65H), 2.41 (s, 1.35H), 2.40 (s, 1.65H), 1.48 (s, 5H), 1.37 (s, 4H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.9, 194.5, 156.4, 155.9, 144.5, 144.4, 132.91, 132.88, 129.6, 129.5, 128.1, 127.9, 80.1, 80.0, 55.7, 55.1, 35.8, 35.7, 28.5, 28.3, 21.8.

HRMS: (ESI) calcd for $C_{15}H_{22}NO_3^+$[M+H]$^+$ 264.1594; found 264.1601.

N-methyl-N-(2-oxo-2-phenylethyl)acetamide (26)



Chemical Formula: $C_{12}H_{15}NO_2$
Exact Mass: 205.1103

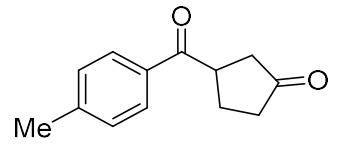
26 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), N,N-dimethylacetamide (2.0 mmol, 174.2 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **26** as colorless oil (15.7 mg, 41% yield); a 4.7:1 mixture of rotamers.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.80 (m, 2H), 7.27-7.24 (m, 2H), 4.82 (s, 1.65H), 4.72 (s, 0.35H), 3.09 (s, 2.5H), 2.99 (s, 0.5H), 2.43 (s, 0.5H), 2.40 (s, 2.5H), 2.19 (s, 2.5H), 1.98 (s, 0.5H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.1, 193.1, 171.6, 171.5, 145.3, 144.6, 132.8, 132.3, 129.8, 129.5, 128.2, 128.0, 57.0, 54.0, 37.4, 35.3, 21.9, 21.8, 21.5, 21.3;

HRMS: (ESI) calcd for $C_{12}H_{16}NO_2^+[M+H]^+$ 206.1176; found 206.1170.

3-(4-methylbenzoyl)cyclopentan-1-one (27)



Chemical Formula: $C_{13}H_{14}O_2$
Exact Mass: 202.0994

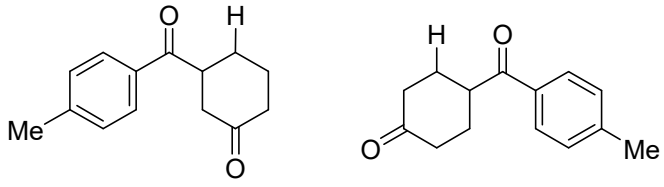
27 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclopentanone (2.0 mmol, 168.2 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **27** as colorless oil (19.9 mg, 47% yield).

The NMR data matched those reported in the literature.[12]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.32-7.27 (m, 2H), 4.14-4.06 (m, 1H), 2.74-2.65 (m, 1H), 2.48-2.43 (m, 1H), 2.43 (s, 3H), 2.42-2.37 (m, 1H), 2.37-2.32 (m, 1H), 2.31-2.24 (m, 1H), 2.20-2.12 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 217.2, 200.0, 144.6, 133.2, 129.7, 128.7, 43.1, 41.2, 37.5, 27.2, 21.8.

3-(4-methylbenzoyl)cyclohexan-1-one (28)



Chemical Formula: $C_{14}H_{16}O_2$
Exact Mass: 216.1150

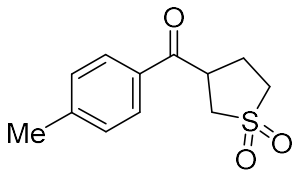
28 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexanone (2.0 mmol, 196.3 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **28** as colorless oil (29.7 mg, 68% yield, r.r. = 3:2).

The NMR data matched those reported in the literature.[12]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 0.8H), 7.85 (d, *J* = 8.3 Hz, 1.2H), 7.31-7.27 (m, 2H), 3.85-3.75 (m, 0.6H), 3.69 (tt, *J* = 10.2, 3.8 Hz, 0.4H), 2.75-2.69 (m, 0.6H), 2.61-2.51 (m, 0.9H), 2.50-2.44 (m, 1.1H), 2.43-2.36 (m, 4.4H), 2.24-2.19 (m, 1H), 2.13-2.00 (m, 2H), 1.89-1.80 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.6, 210.4, 200.1, 144.5, 144.3, 132.9, 129.7, 129.6, 128.6, 128.5, 45.2, 43.3, 42.7, 41.1, 40.1, 29.0, 28.6, 25.0, 21.8.

(1,1-dioxidotetrahydrothiophen-3-yl)(p-tolyl)methanone (29)



Chemical Formula: $C_{12}H_{14}O_3S$
Exact Mass: 238.0664

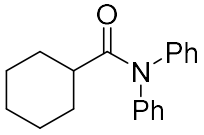
29 was prepared according to general procedure **2.1** using $NiBr_2$•dtbbpy (0.002 mmol, 1.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), tetrahydrothiophene 1,1-dioxide (2.0 mmol, 240.3 mg), anhydrous K_3PO_4 (0.48 mmol, 101.8 mg) and 4-methylbenzoyl chloride (0.2 mmol, 30.9 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **29** as colorless oil (25.8 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.34-7.30 (m, 2H), 4.35-4.23 (m, 1H), 3.52-3.42 (m, 1H), 3.30-3.21 (m, 2H), 3.17-3.10 (m, 1H), 2.60-2.50 (m, 1H), 2.44 (s, 3H), 2.41-2.33 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.3, 145.5, 132.2, 130.0, 128.8, 52.5, 50.8, 41.8, 25.9, 21.9;

HRMS: (ESI) calcd for $C_{12}H_{15}O_3S^+[M+H]^+$ 239.0736; found 239.0733.

***N, N*-diphenylcyclohexanecarboxamide (31)**



Chemical Formula: $C_{19}H_{21}NO$
Exact Mass: 279.1623

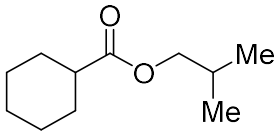
31 was prepared according to general procedure **2.2** using $NiCl_2$•dtbbpy (0.004 mmol, 1.6 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.4 mmol, 84.8 mg) and diphenylcarbamic chloride (0.2 mmol, 46.3 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **31** as colorless oil (34.1 mg, 61% yield).

The NMR data matched those reported in the literature.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.31 (m, 5H), 7.28-7.20 (m, 5H), 2.38 (tt, *J* = 11.6, 3.4 Hz, 1H), 1.86-1.76 (m, 2H), 1.73-1.68 (m, 2H), 1.65-1.53 (m, 3H), 1.26-1.17 (m, 1H), 1.07-0.95 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 143.1, 129.6, 128.9, 126.7, 42.3, 29.4, 25.6, 25.5.

Isobutyl cyclohexanecarboxylate (33)



Chemical Formula: $C_{11}H_{20}O_2$
Exact Mass: 184.1463

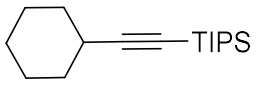
33 was prepared according to general procedure **2.3** using $NiBr_2$ (0.02 mmol, 4.4 mg), dtbbpy (0.03 mmol, 8.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_3PO_4 (0.4 mmol, 84.8 mg) and isobutyl carbonochloridate (0.2 mmol, 27.3 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain **33** as colorless oil (14.4 mg, 39% yield).

The NMR data matched those reported in the literature.[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.81 (d, *J* = 6.6 Hz, 2H), 2.27 (tt, *J* = 11.3, 3.7 Hz, 1H), 1.91-1.85 (m, 3H), 1.74-1.68 (m, 2H), 1.63-1.58 (m, 1H), 1.45-1.37 (m, 2H), 1.29-1.16 (m, 3H), 0.89 (d, *J* = 6.7 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 70.1, 43.3, 29.0, 27.8, 25.8, 25.4, 19.0.

(cyclohexylethynyl)triisopropylsilane (34)



Chemical Formula: $C_{17}H_{32}Si$
Exact Mass: 264.2273

34 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2

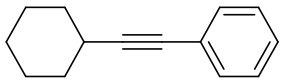
mmol, 168.0 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE) to obtain **34** as colorless oil (40.3 mg, 76% yield).

The NMR data matched those reported in the literature.[15]

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.50-42 (m, 1H), 1.80-1.70 (m, 4H), 1.53-1.44 (m, 3H), 1.39-1.28 (m, 3H), 1.13-1.03 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 113.6, 79.5, 32.7, 29.8, 26.0, 24.5, 18.6, 11.3

(cyclohexylethynyl)benzene (35)



Chemical Formula: $C_{14}H_{16}$
Exact Mass: 184.2820

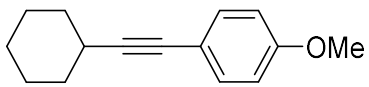
35 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and (bromoethynyl)benzene (0.2 mmol, 36.2 mg) and was purified by silica gel column chromatography (PE) to obtain **35** as colorless oil (18.8 mg, 51% yield).

The NMR data matched those reported in the literature.[16]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.29-7.23 (m, 3H), 2.62-2.55 (m, 1H), 1.92-1.86 (m, 2H), 1.79-1.74 (m, 2H), 1.57-1.51 (m, 3H), 1.39-1.32 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 131.6, 128.2, 127.4, 124.1, 94.5, 80.5, 32.7, 29.7, 26.0, 24.9.

1-(cyclohexylethynyl)-4-methoxybenzene (36)



Chemical Formula: $C_{15}H_{18}O$
Exact Mass: 214.1358

36 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2

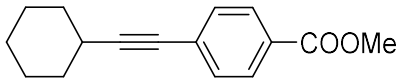
mmol, 168.0 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and 1-(bromoethynyl)-4-methoxybenzene (0.2 mmol, 42.2 mg) and was purified by silica gel column chromatography (PE) to obtain **36** as colorless oil (26.9 mg, 63% yield).

The NMR data matched those reported in the literature.[17]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 6.83-6.78 (m, 2H), 3.79 (s, 3H), 2.59-2.53 (m, 1H), 1.90-1.84 (m, 2H), 1.79-1.72 (m, 2H), 1.55-1.48 (m, 3H), 1.37-1.30 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 132.9, 116.3, 113.7, 92.8, 80.1, 55.2, 32.8, 29.7, 25.9, 24.9.

methyl 4-(cyclohexylethynyl)benzoate (37)



Chemical Formula: $C_{16}H_{18}O_2$
Exact Mass: 242.1307

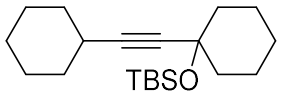
37 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and methyl 4-(bromoethynyl)benzoate (0.2 mmol, 47.8 mg) and was purified by silica gel column chromatography (PE/EtOAc = 100/1) to obtain **37** as colorless oil (22.3 mg, 46% yield).

The NMR data matched those reported in the literature.[17]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.92 (m, 2H), 7.47-7.39 (m, 2H), 3.90 (s, 3H), 2.66-2.56 (m, 1H), 1.92-1.86 (m, 2H), 1.78-1.73 (m, 2H), 1.58-1.50 (m, 3H), 1.39-1.30 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 131.5, 129.3, 129.0, 128.7, 97.9, 80.0, 52.1, 32.5, 29.7, 25.8, 24.8.

tert-butyl((1-(cyclohexylethynyl)cyclohexyl)oxy)dimethylsilane (38)



Chemical Formula: $C_{20}H_{36}OSi$
Exact Mass: 320.2535

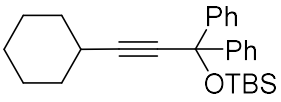
38 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and ((1-(bromoethynyl)cyclohexyl)oxy)(tert-butyl)dimethylsilane (0.2 mmol, 63.5 mg) and was purified by silica gel column chromatography (PE) to obtain **38** as colorless oil (51.5 mg, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.45-2.33 (m, 1H), 1.84-1.76 (m, 2H), 1.75-1.68 (m, 4H), 1.66-1.57 (m, 3H), 1.55-1.49 (m, 3H), 1.48-1.37 (m, 4H), 1.35-1.25 (m, 4H), 0.87 (s, 9H), 0.16 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 89.0, 84.5, 69.2, 41.5, 32.8, 29.1, 25.9, 25.9, 25.5, 25.0, 23.0, 18.1, -2.8.

HRMS: (ESI) calcd for $C_{20}H_{37}OSi^+[M+H]^+$ 321.2608; found 321.2600.

tert-butyl((3-cyclohexyl-1,1-diphenylprop-2-yn-1-yl)oxy)dimethylsilane (39)



Chemical Formula: $C_{27}H_{36}OSi$
Exact Mass: 404.2535

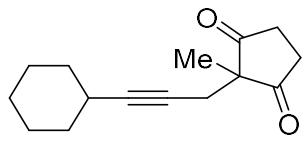
39 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and ((3-bromo-1,1-diphenylprop-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (0.2 mmol, 80.3 mg) and was purified by silica gel column chromatography (PE) to obtain **39** as colorless oil (41.5 mg, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60-7.57 (m, 4H), 7.28-7.24 (m, 4H), 7.20-7.17 (m, 2H), 2.56-2.50 (m, 1H), 1.94-1.87 (m, 2H), 1.77-1.73 (m, 2H), 1.58-1.53 (m, 3H), 1.37-1.31 (m, 3H), 0.97 (s, 9H), 0.02 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 127.7, 126.8, 126.0, 93.2, 82.9, 75.4, 32.5, 29.4, 26.1, 25.8, 25.1, 18.5, -3.1.

HRMS: (APCI) calcd for $C_{27}H_{37}OSi^+[M+H]^+$ 405.2608; found 405.2608.

2-(3-cyclohexylprop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (40)



Chemical Formula: $C_{15}H_{20}O_2$
Exact Mass: 232.1463

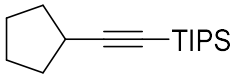
40 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclohexane (2 mmol, 168.0 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and 2-(3-bromoprop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (0.2 mmol, 45.8 mg) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **40** as colorless oil (23.0 mg, 50% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.77 (s, 4H), 2.41 (d, 2H), 2.26-2.20 (m, 1H), 1.73-1.67 (m, 2H), 1.64-1.59 (m, 2H), 1.51-1.44 (m, 1H), 1.31-1.20 (m, 5H), 1.07 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 216.0, 87.3, 74.2, 55.7, 36.1, 32.8, 28.8, 25.8, 25.7, 24.8, 18.6.

HRMS: (ESI) calcd for $C_{15}H_{21}O_2^+[M+H]^+$ 233.1536; found 233.1538.

(cyclopentylethynyl)triisopropylsilane (41)



Chemical Formula: $C_{16}H_{30}Si$
Exact Mass: 250.2117

41 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclopentane (2 mmol, 140.3 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and

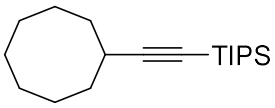
(bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE) to obtain **41** as colorless oil (32.5 mg, 65% yield).

The NMR data matched those reported in the literature.[15]

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70-2.64 (m, 1H), 1.93-1.86 (m, 2H), 1.76-1.70 (m, 2H), 1.67-1.61 (m, 2H), 1.57-1.53 (m, 2H), 1.09-1.02 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 114.1, 79.0, 34.2, 31.2, 24.9, 18.6, 11.3.

(cyclooctylethynyl)triisopropylsilane (42)



Chemical Formula: $C_{19}H_{36}Si$
Exact Mass: 292.2586

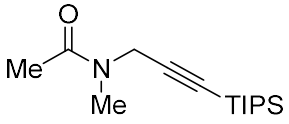
42 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), cyclooctane (2 mmol, 224.4mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE) to obtain **42** as colorless oil (24.5 mg, 42% yield).

The NMR data matched those reported in the literature.[15]

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.65-2.60 (m, 1H), 1.89-1.83 (m, 2H), 1.79-1.73 (m, 2H), 1.73-1.65 (m, 3H), 1.55-1.51 (m, 4H), 1.50-1.46 (m, 3H), 1.07-1.04 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 114.5, 79.4, 31.7, 31.2, 27.5, 25.4, 24.4, 18.7, 11.3.

N-methyl-N-(3-(triisopropylsilyl)prop-2-yn-1-yl)acetamide (43)



Chemical Formula: $C_{15}H_{29}NOSi$
Exact Mass: 267.2018

43 was prepared according to general procedure **2.4** using $NiBr_2$•dtbbpy (0.02 mmol, 10.0 mg), tetrabutylammonium decatungstate (0.004 mmol, 14.0 mg), N,N-dimethylacetamide (2.0 mmol, 174.2 mg), anhydrous K_2HPO_4 (0.3 mmol, 52.3 mg) and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by

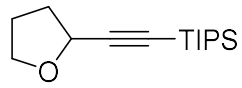
silica gel column chromatography (PE/EtOAc = 10/1) to obtain **43** as colorless oil (27.3 mg, 51% yield); a 1.2:1 mixture of rotamers.

The NMR data matched those reported in the literature.[18]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.29 (s, 1.1H), 4.06 (s, 0.9H), 3.07 (s, 1.7H), 2.99 (s, 1.3H), 2.16 (s, 1.3H), 2.09 (s, 1.7H), 1.05 (s, 3H), 1.05 (s, 18H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 170.1, 102.2, 101.2, 86.0, 85.0, 41.3, 36.7, 34.7, 33.1, 21.7, 21.4, 18.5, 18.5, 11.1, 11.0.

triisopropyl((tetrahydrofuran-2-yl)ethynyl)silane (44)



Chemical Formula: $C_{15}H_{28}OSi$
Exact Mass: 252.1909

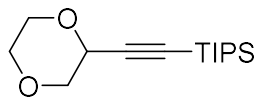
44 was prepared according to general procedure **2.5** using $Ni(acac)_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na_2CO_3 (0.4 mmol, 42.0 mg), tetrahydrofuran (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **44** as colorless oil (41.9 mg, 83% yield).

The NMR data matched those reported in the literature.[18]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.62 (dd, J = 7.3, 4.6 Hz, 1H), 3.97-3.94 (m, 1H), 3.84-3.80 (m, 1H), 2.17-2.11 (m, 1H), 2.06-1.97 (m, 2H), 1.92-1.86 (m, 1H), 1.07-1.05 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 107.8, 85.0, 68.6, 67.5, 33.7, 25.1, 18.6, 11.1.

((1,4-dioxan-2-yl)ethynyl)triisopropylsilane (45)



Chemical Formula: $C_{15}H_{28}O_2Si$
Exact Mass: 268.1859

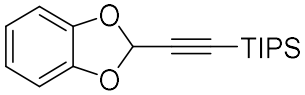
45 was prepared according to general procedure **2.5** using $Ni(acac)_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na_2CO_3 (0.4 mmol, 42.0 mg), 1,4-dioxane (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **45** as colorless oil (17.2 mg, 32% yield).

The NMR data matched those reported in the literature.[18]

^1H NMR (600 MHz, $CDCl_3$) δ 4.37 (dd, *J* = 8.3, 2.9 Hz, 1H), 3.92-3.88 (m, 1H), 3.84 (dd, *J* = 11.5, 2.9 Hz, 1H), 3.69-3.66 (m, 3H), 3.59 (dd, *J* = 11.5, 8.3 Hz, 1H), 1.07-1.06 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 102.5, 87.9, 70.6, 66.5, 66.3, 65.6, 18.5, 11.0.

(benzo[d][1,3]dioxol-2-ylethynyl)triisopropylsilane (46)



Chemical Formula: $C_{18}H_{26}O_2Si$
Exact Mass: 302.1702

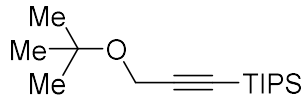
46 was prepared according to general procedure **2.5** using $Ni(acac)_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na_2CO_3 (0.4 mmol, 42.0 mg), benzo[d][1,3]dioxole (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **46** as colorless oil (21.8 mg, 36% yield).

The NMR data matched those reported in the literature.[18]

^1H NMR (600 MHz, $CDCl_3$) δ 6.85 (s, 4H), 6.58 (s, 1H), 1.08-1.07 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 121.8, 108.9, 99.6, 98.1, 90.9, 18.4, 10.9.

(3-(tert-butoxy)prop-1-yn-1-yl)triisopropylsilane (47)



Chemical Formula: $C_{16}H_{32}OSi$
Exact Mass: 268.2222

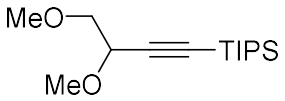
47 was prepared according to general procedure **2.5** using $Ni(acac)_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na_2CO_3 (0.4 mmol, 42.0 mg), 2-methoxy-2-methylpropane (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **47** as colorless oil (22.1 mg, 41% yield).

The NMR data matched those reported in the literature.[18]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.14 (s, 2H), 1.25 (s, 9H), 1.08-1.05 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 106.2, 85.4, 74.6, 51.2, 27.8, 18.6, 11.2.

(3,4-dimethoxybut-1-yn-1-yl)triisopropylsilane (48)



Chemical Formula: $C_{15}H_{30}O_2Si$
Exact Mass: 270.2015

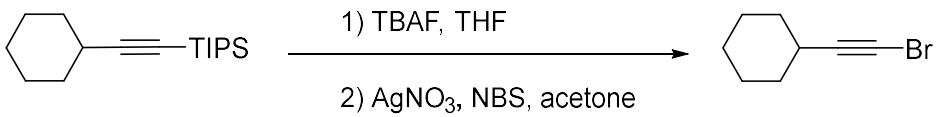
48 was prepared according to general procedure **2.5** using $Ni(acac)_2$ (0.02 mmol, 5.1 mg), dtbbpy (0.03 mmol, 8.0 mg), 4-(4-methoxybenzoyl)benzonitrile (0.02 mmol, 4.7 mg), anhydrous Na_2CO_3 (0.4 mmol, 42.0 mg), 1,2-dimethoxyethane (1 mL) as sovlent and (bromoethynyl)triisopropylsilane (0.2 mmol, 52.1 mg) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **48** as colorless oil (22.7 mg, 42% yield).

The NMR data matched those reported in the literature.[18]

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.22 (dd, J = 8.0, 3.4 Hz, 1H), 3.61-3.53 (m, 2H), 3.47 (s, 3H), 3.41 (s, 3H), 1.08-1.06 (m, 21H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 103.0, 88.1, 75.0, 71.0, 59.2, 56.5, 18.5, 11.1.

6. Synthetic Applications



34 **50**, 78% y

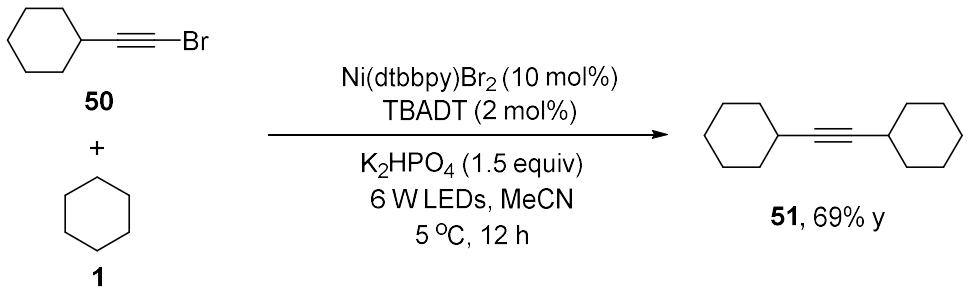
To the solution of **34** (211.6 mg, 0.8 mmol) in THF (2.0 mL) and 2 mL TBAF (1.0 M in THF) was added under Ar atmosphere, and was stirred at room temperature for 2 h. Saturated NH_4Cl aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with AcOEt (10 mL × 3). The combined extracts were washed by brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the terminal alkyne, which was used in the next step without further purification.

The terminal alkyne was dissolved in acetone (2.0 mL). Then, $AgNO_3$ (13.6 mg, 0.1 equiv.), NBS (156.6 mg, 1.1 equiv.) were added. The mixture was stirred at room temperature for 4 h. After the reaction was completed, concentrated the mixture and purified by chromatography on silica gel (PE) to afford the bromide alkyne **50** as color less liquid (116.7 mg, 78% yield).

The NMR data matched those reported in the literature.[19]

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.45-2.34 (m, 1H), 1.83-1.74 (m, 2H), 1.73-1.64 (m, 2H), 1.53-1.41 (m, 3H), 1.34-1.26 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 84.4, 37.7, 32.3, 30.1, 25.8, 24.8.

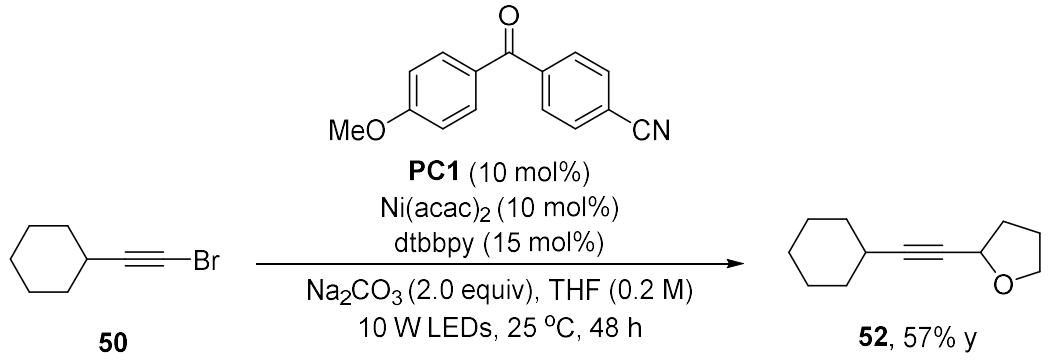


An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$•dtbbpy (9.8 mg, 0.02 mmol), tetrabutylammonium decatungstate (14.0 mg, 0.004 mmol), **50** (37.4 mg, 0.2 mmol), anhydrous K_2HPO_4 (50 mg, 0.3 mmol), cyclohexane (168 mg, 2.0 mmol) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 6 W 390 nm LED lamp at 5 °C for 12 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (PE) to afford **51** as color less liquid (26.3 mg, 69% yield).

The NMR data matched those reported in the literature.[20]

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.38-2.29 (m, 2H), 1.82-1.73 (m, 4H), 1.72-1.65 (m, 4H), 1.53-1.44 (m, 2H), 1.45-1.35 (m, 4H), 1.33-1.23 (m, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 84.5, 33.2, 29.0, 26.0, 24.9.



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $Ni(acac)_2$ (5.6 mg, 0.02 mmol), dtbbpy (7.7 mg, 0.03 mmol), **PC1** (5.6 mg, 0.02 mmol), **50** (37.4 mg, 0.2 mmol), anhydrous Na_2CO_3 (42.3 mg, 0.4 mmol) and THF (1.0 mL) as both C-H partners and solvent in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp at 25 ºC for 48 hours. The resulting mixture was diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (PE/EA = 50/1) to afford **52** as color less liquid (20.3 mg, 57% yield).

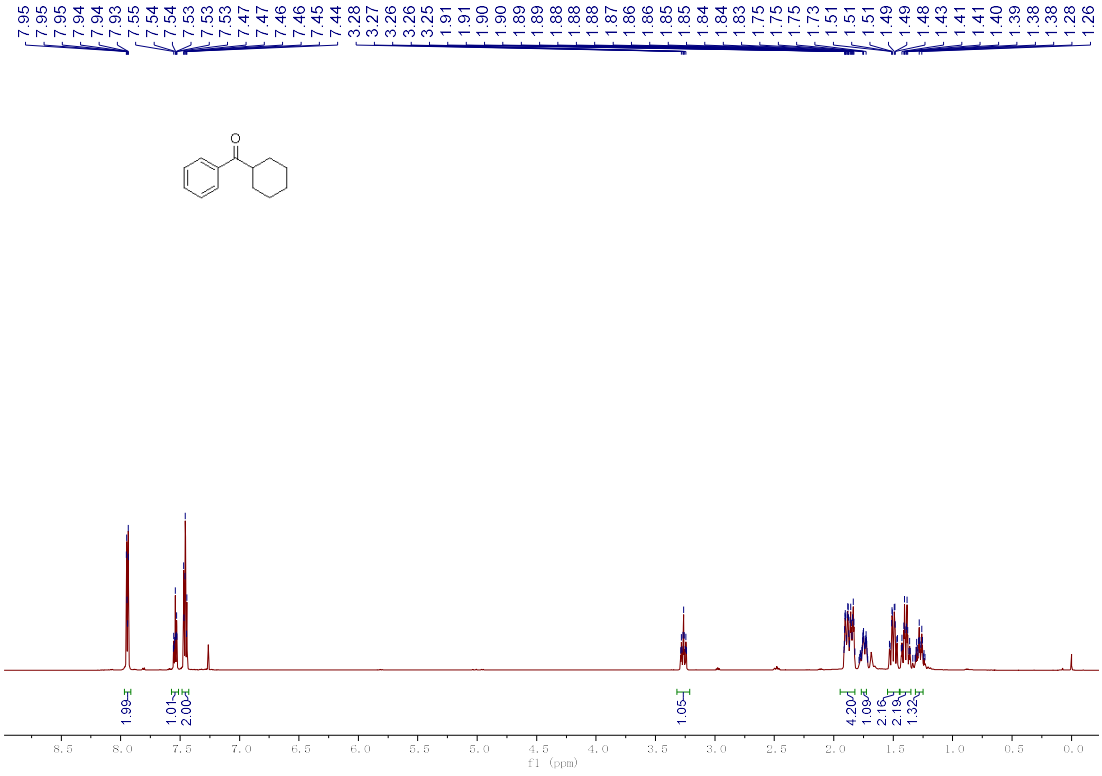
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.56 (ddd, *J* = 7.3, 5.7, 1.8 Hz, 1H), 3.97-3.92 (m, 1H), 3.80-3.74 (m, 1H), 2.42-2.34 (m, 1H), 2.15-2.09 (m, 1H), 2.04-1.98 (m, 1H), 1.94-1.86 (m, 2H), 1.80-1.74 (m, 2H), 1.72-1.67 (m, 2H), 1.52-1.47 (m, 1H), 1.44-1.38 (m, 2H), 1.30-1.25 (m, 3H);

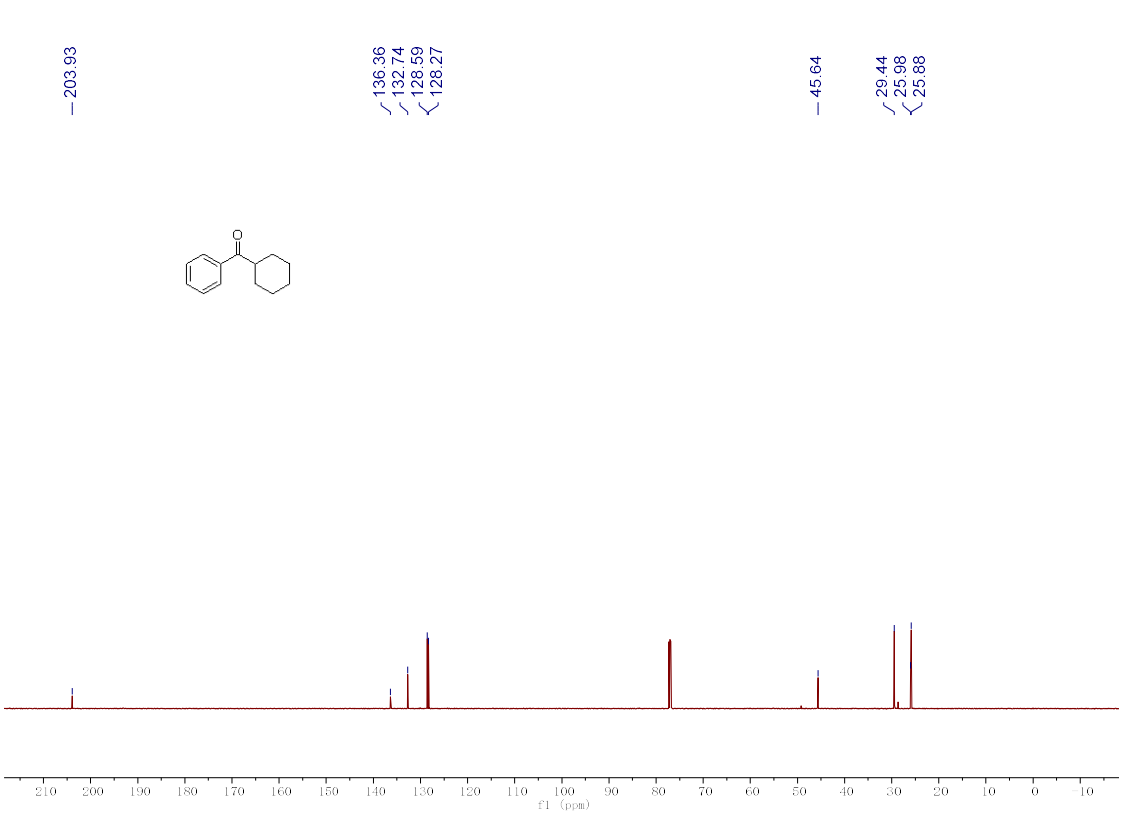
^{13}C NMR (151 MHz, $CDCl_3$) δ 89.3, 79.8, 68.5, 67.6, 33.7, 32.6, 29.1, 25.9, 25.4, 24.9;

HRMS: (ESI) calcd for $C_{12}H_{19}O^+[M+H]^+$ 179.1430; found 179.1424.

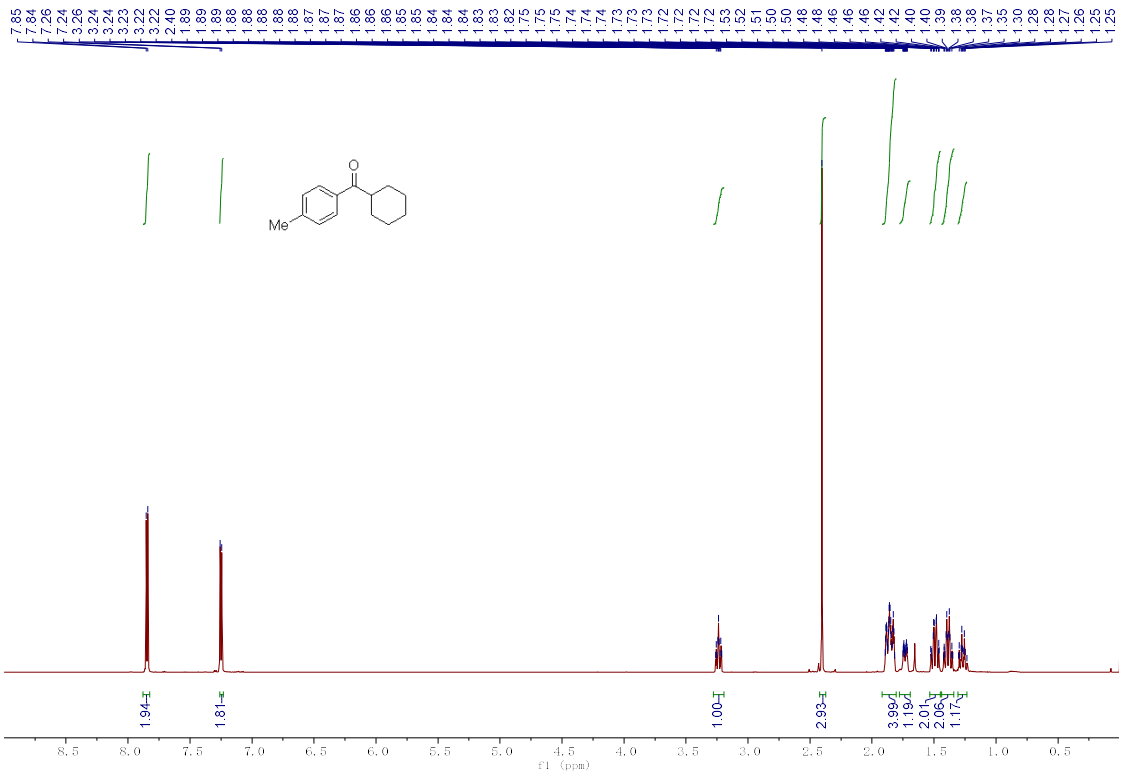
7. NMR Spectra

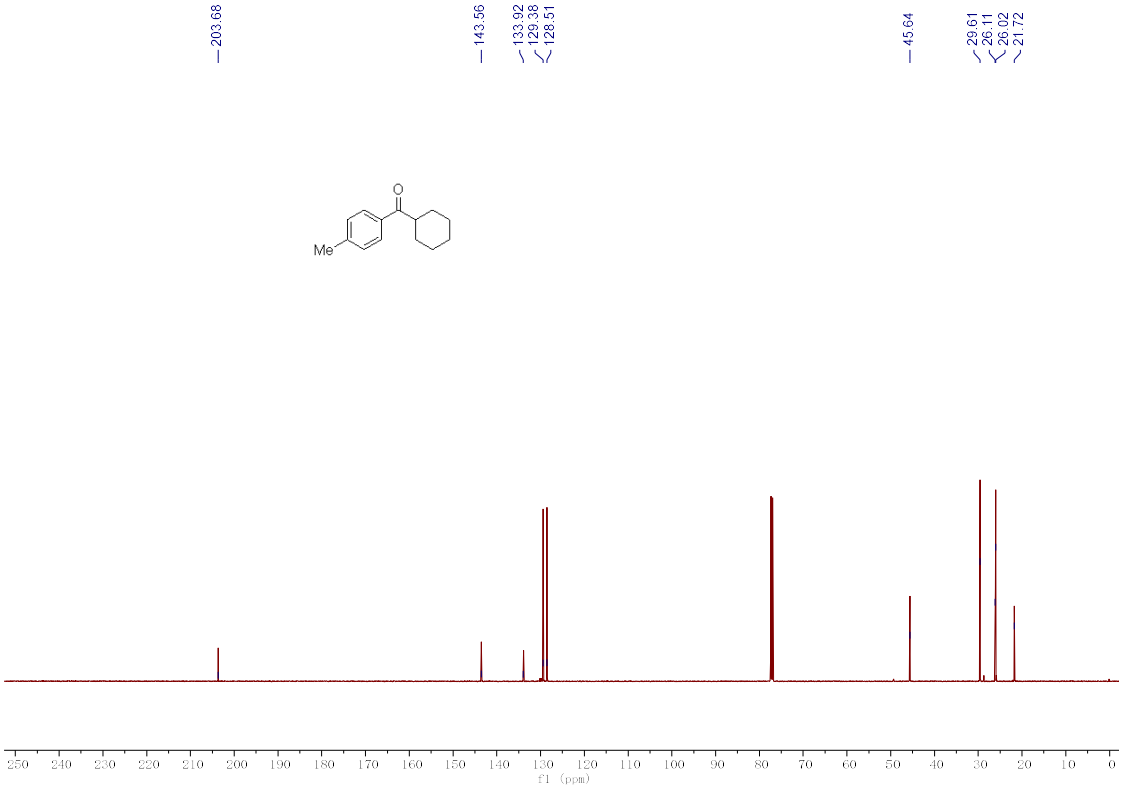
3





6


7.85 7.84 7.26 7.24 3.26 3.24 3.24 3.23 3.22 3.22 2.40 1.89 1.89 1.89 1.88 1.88 1.88 1.88 1.88 1.87 1.87 1.87 1.86 1.86 1.86 1.85 1.85 1.84 1.84 1.84 1.83 1.82 1.75 1.75 1.75 1.74 1.74 1.74 1.73 1.73 1.73 1.72 1.72 1.72 1.72 1.53 1.52 1.51 1.50 1.50 1.48 1.46 1.46 1.42 1.42 1.40 1.40 1.39 1.38 1.38 1.37 1.35 1.30 1.28 1.28 1.27 1.26 1.25 1.25
O
Me
1.94
1.81
1.00
2.93
3.99
1.19
2.01
2.06
1.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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129.38
128.51
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26.02
21.72
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Me
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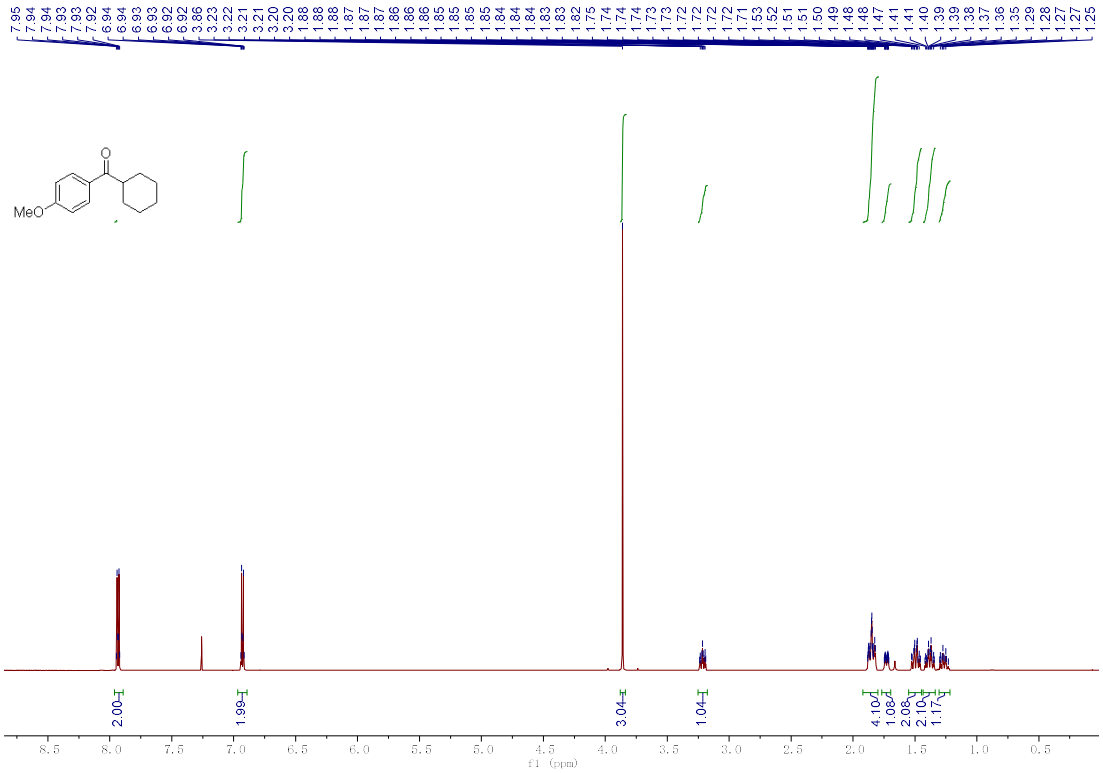
f1 (ppm)

7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1.04
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2.08
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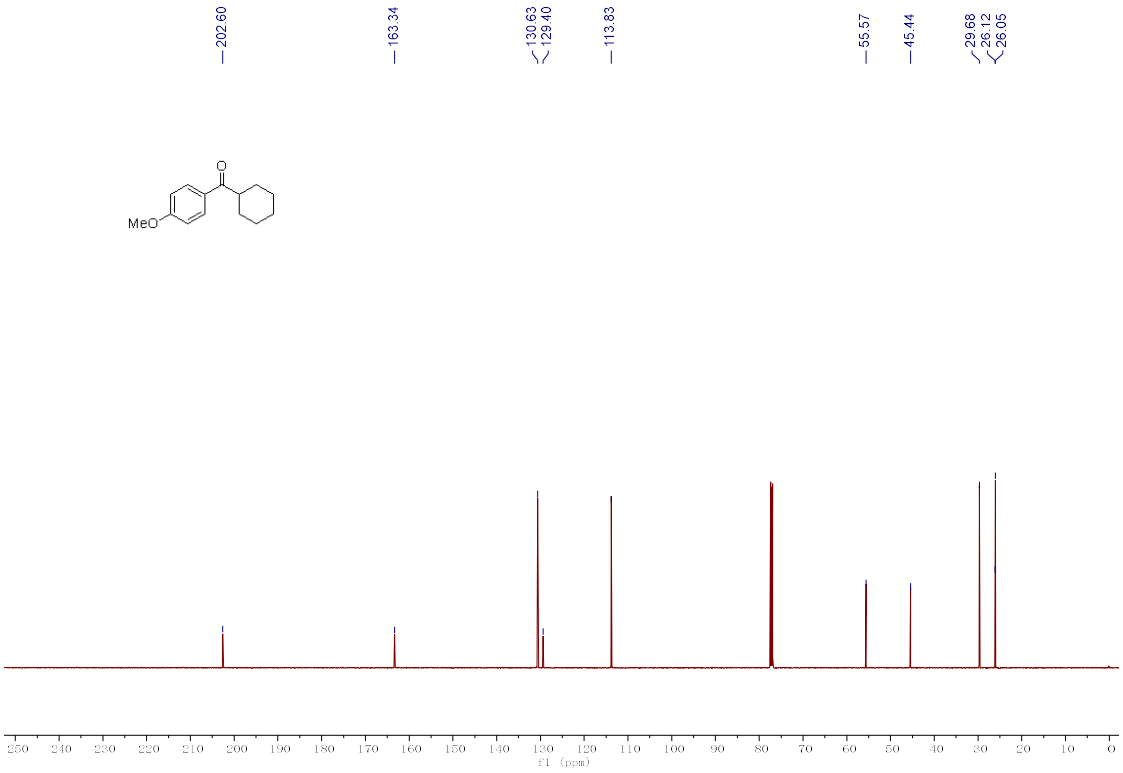
1.17
f1 (ppm)


202.60
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130.63
129.40
113.83
55.57
45.44
29.68
26.12
26.05
MeO
f1 (ppm)

8


7.98
7.97
7.97
7.96
7.96
7.96
7.95
7.13
7.13
7.12
7.12
7.11
7.10
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3.19
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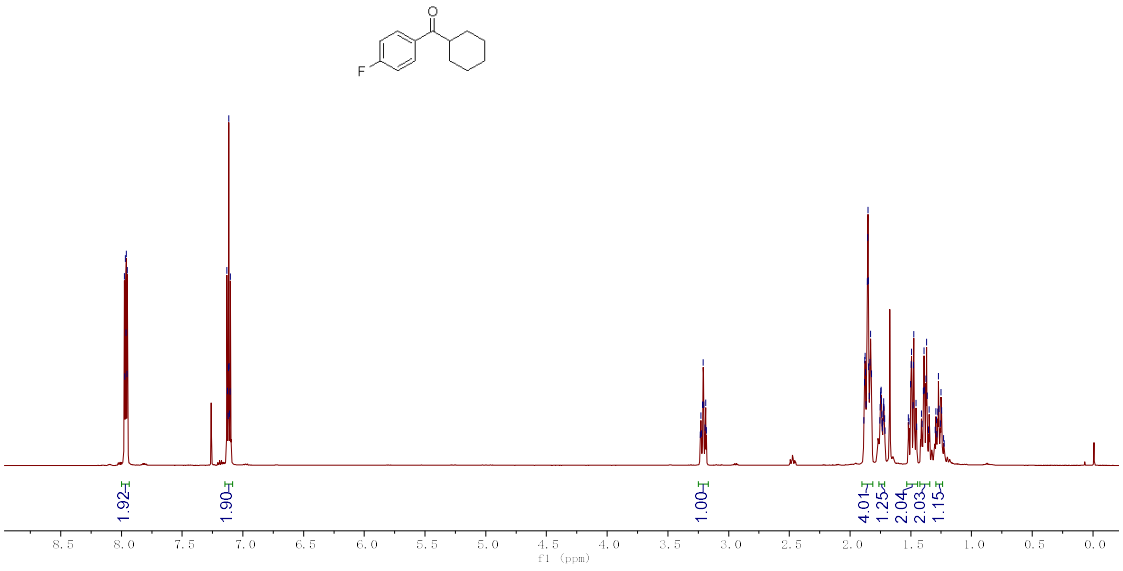
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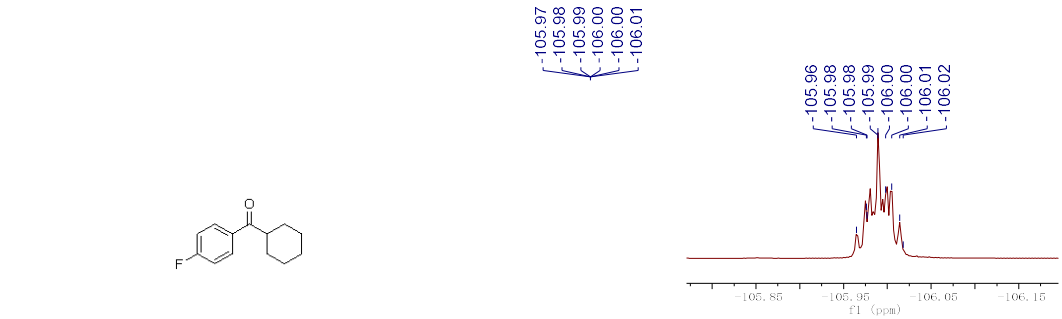
f1 (ppm)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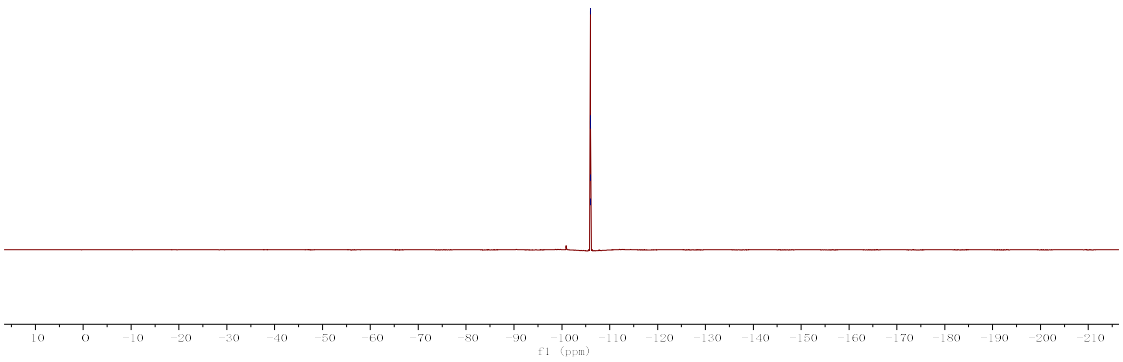
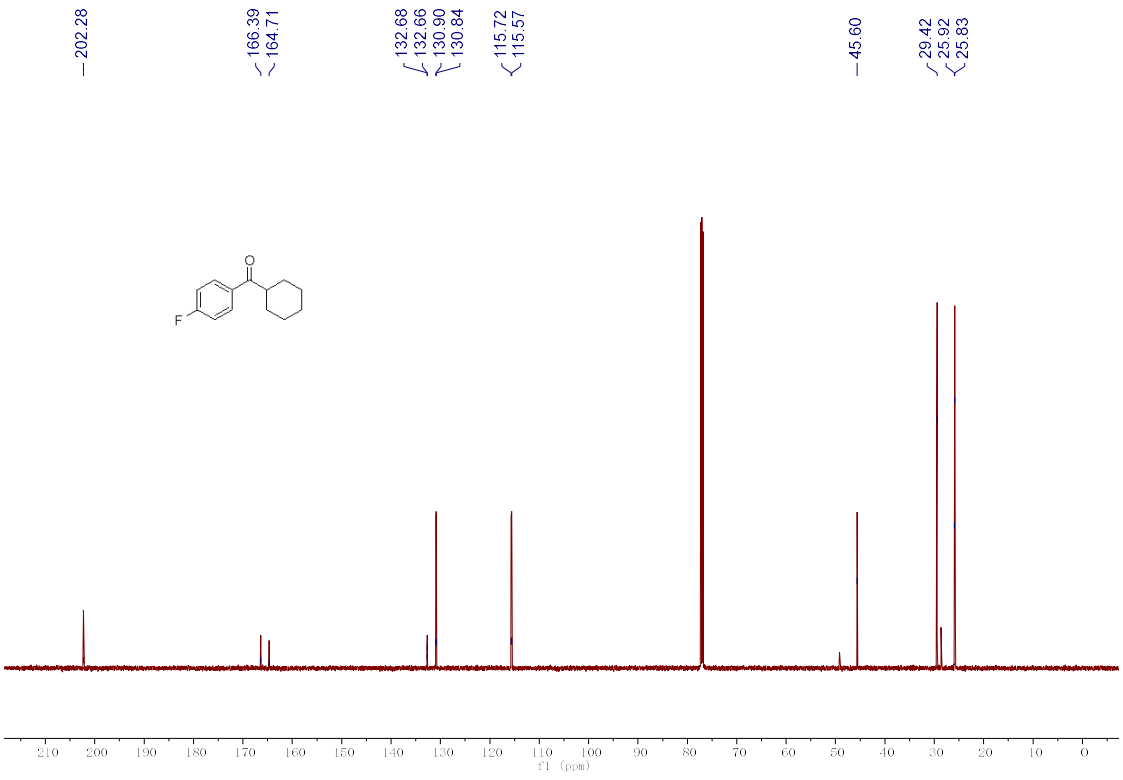
O
F
f1 (ppm)


f1 (ppm)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29.42
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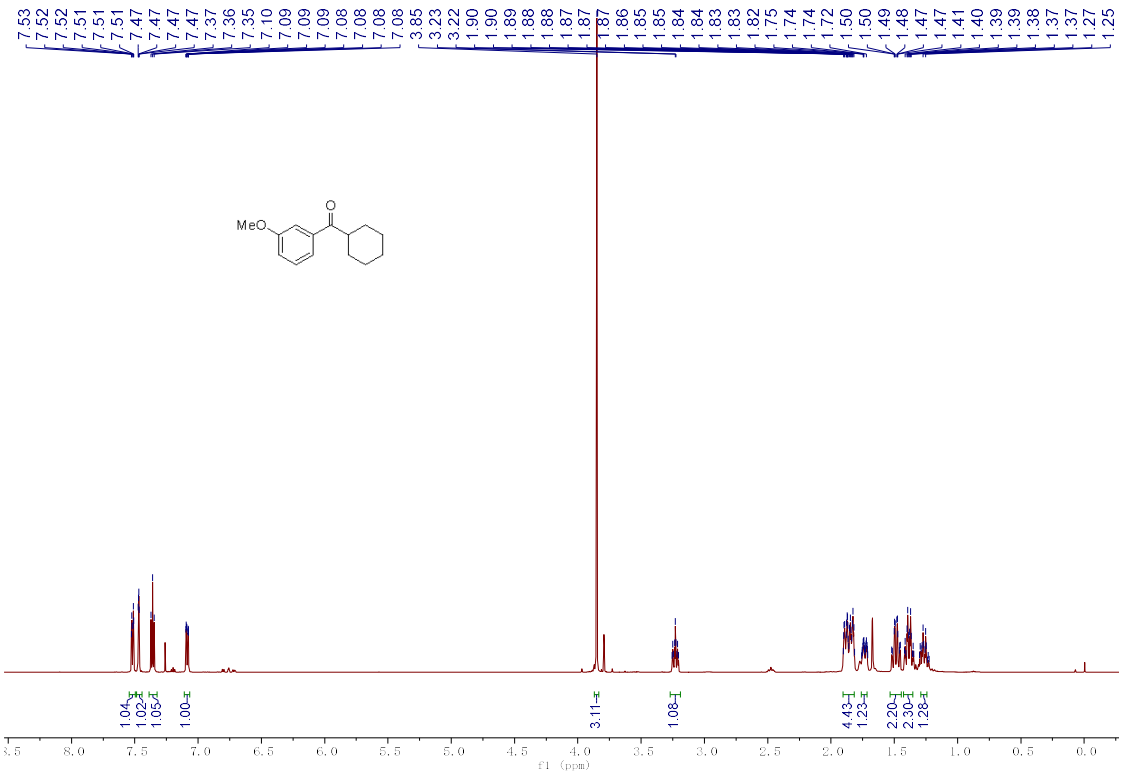
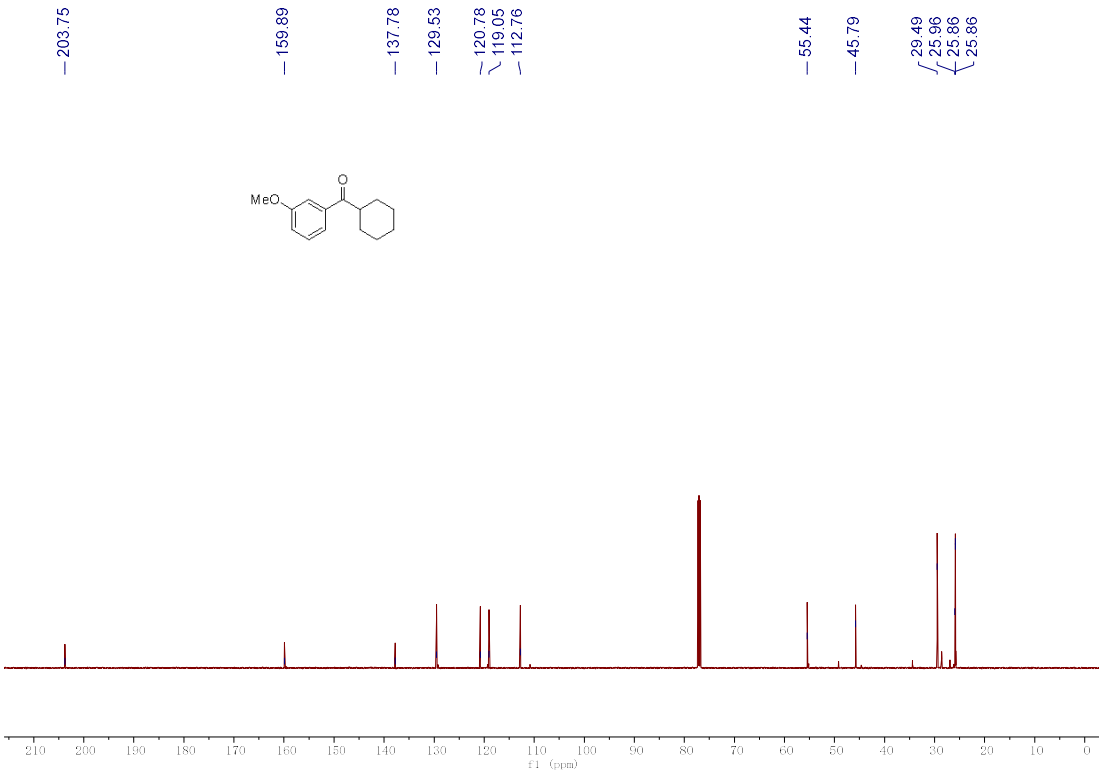
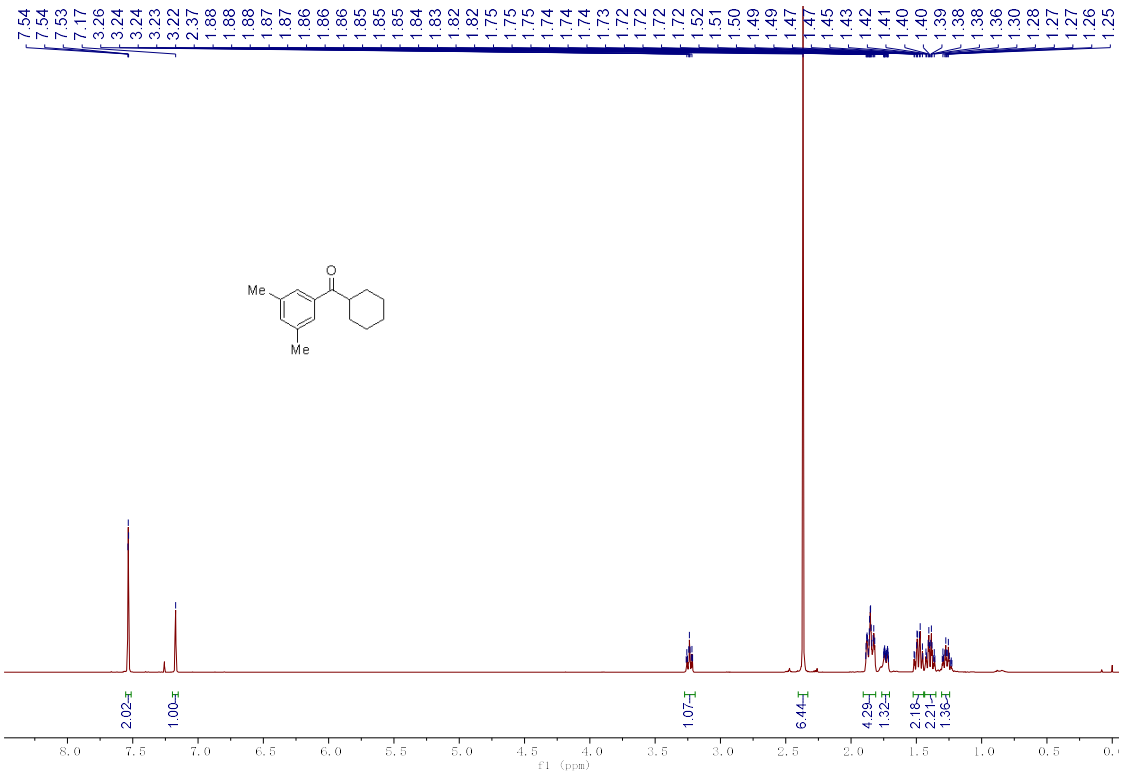
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

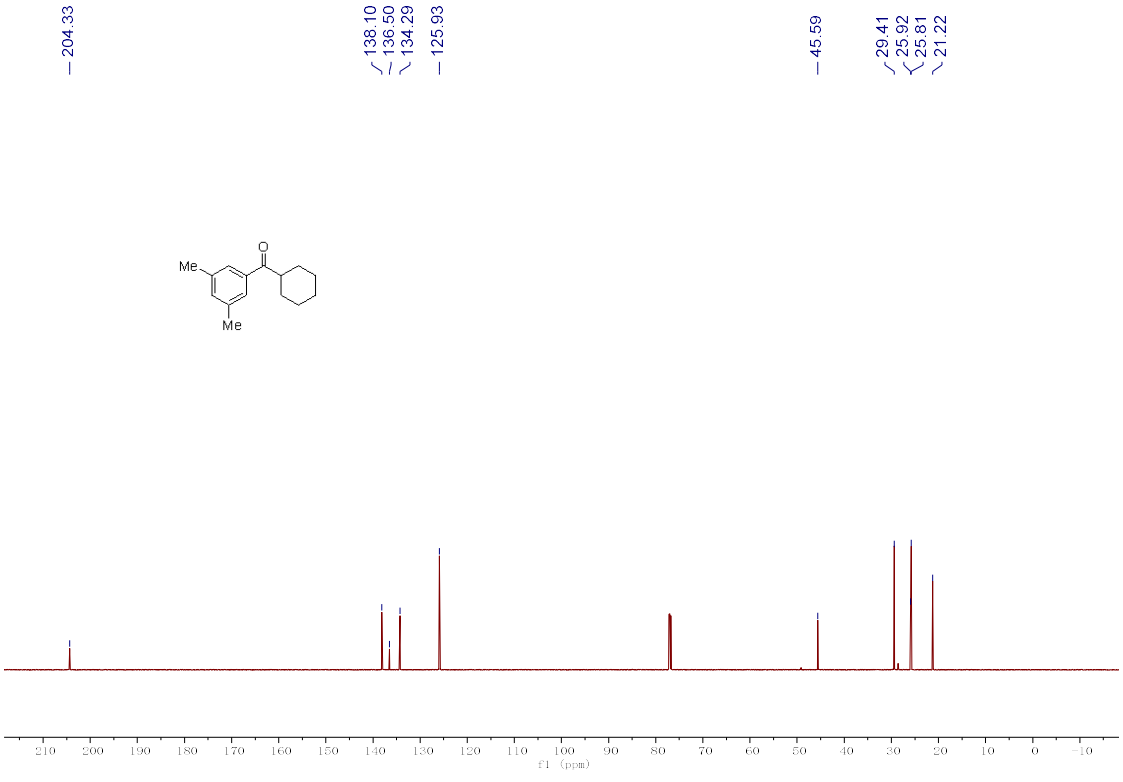
9


7.53 7.52 7.52 7.51 7.51 7.51 7.47 7.47 7.47 7.47 7.37 7.36 7.35 7.10 7.09 7.09 7.09 7.08 7.08 7.08 7.08
3.85 3.23 3.22 1.90 1.90 1.89 1.88 1.88 1.87 1.87 1.87 1.86 1.85 1.85 1.84 1.84 1.83 1.83 1.82 1.75 1.74 1.74 1.72 1.50 1.50 1.49 1.48 1.47 1.47 1.41 1.40 1.39 1.39 1.38 1.37 1.37 1.27 1.25
MeO
O
1.04 1.02 1.05 1.00 3.11 1.08 4.43 1.23 2.20 2.30 1.28
f1 (ppm)

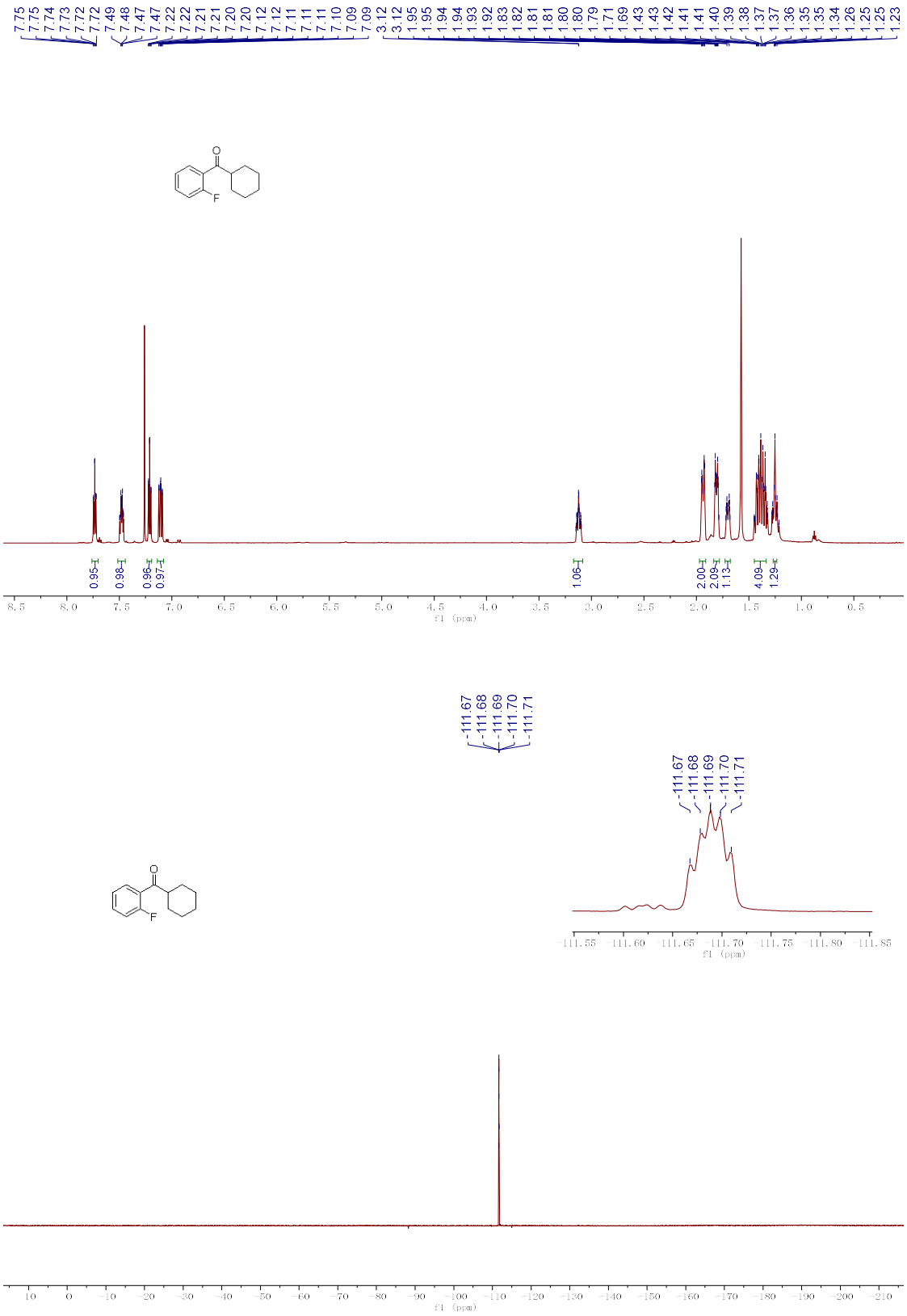

203.75 159.89 137.78 129.53 120.78 119.05 112.76 55.44 45.79 29.49 25.96 25.86 25.86
MeO
O
f1 (ppm)

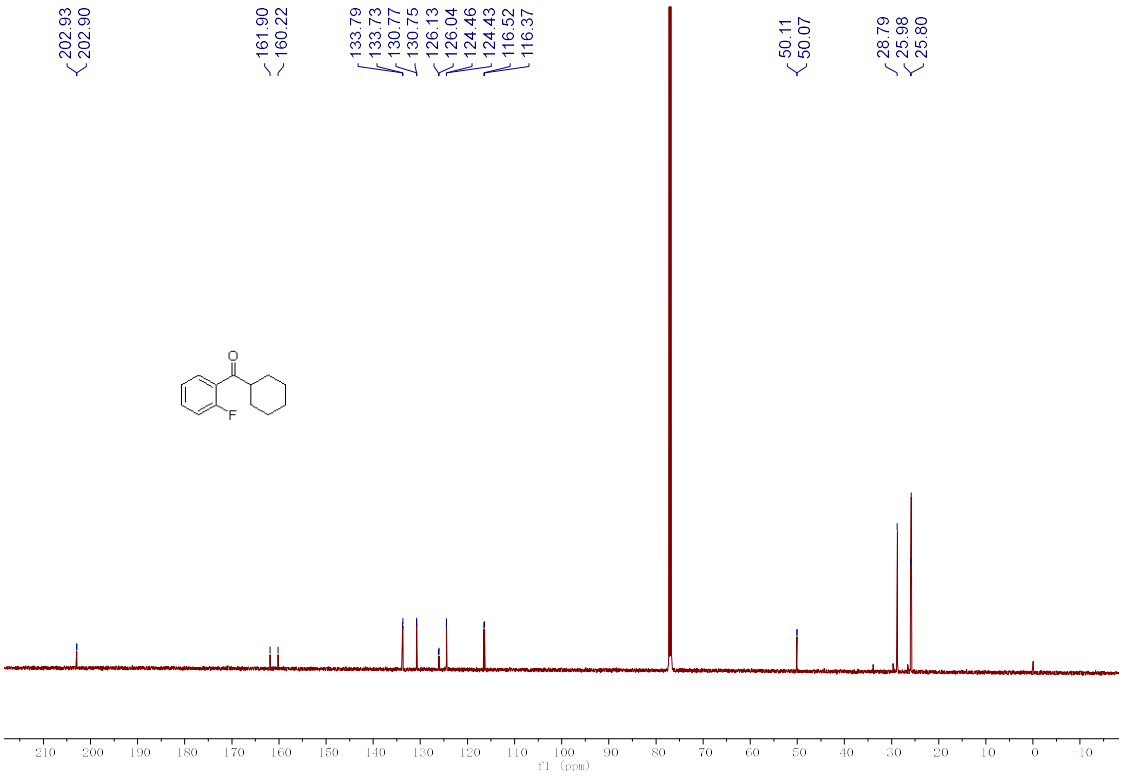
10


7.54 7.54 7.53 7.17 3.26 3.24 3.24 3.23 3.22 2.37 1.88 1.88 1.88 1.87 1.87 1.86 1.86 1.86 1.85 1.85 1.85 1.84 1.83 1.82 1.82 1.75 1.75 1.75 1.74 1.74 1.74 1.73 1.72 1.72 1.72 1.72 1.52 1.51 1.50 1.49 1.49 1.47 1.47 1.45 1.43 1.42 1.41 1.40 1.40 1.39 1.38 1.38 1.36 1.30 1.28 1.27 1.27 1.26 1.25
O
Me
Me
2.02
1.00
1.07
6.44
4.29
1.32
2.18
2.21
1.36
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

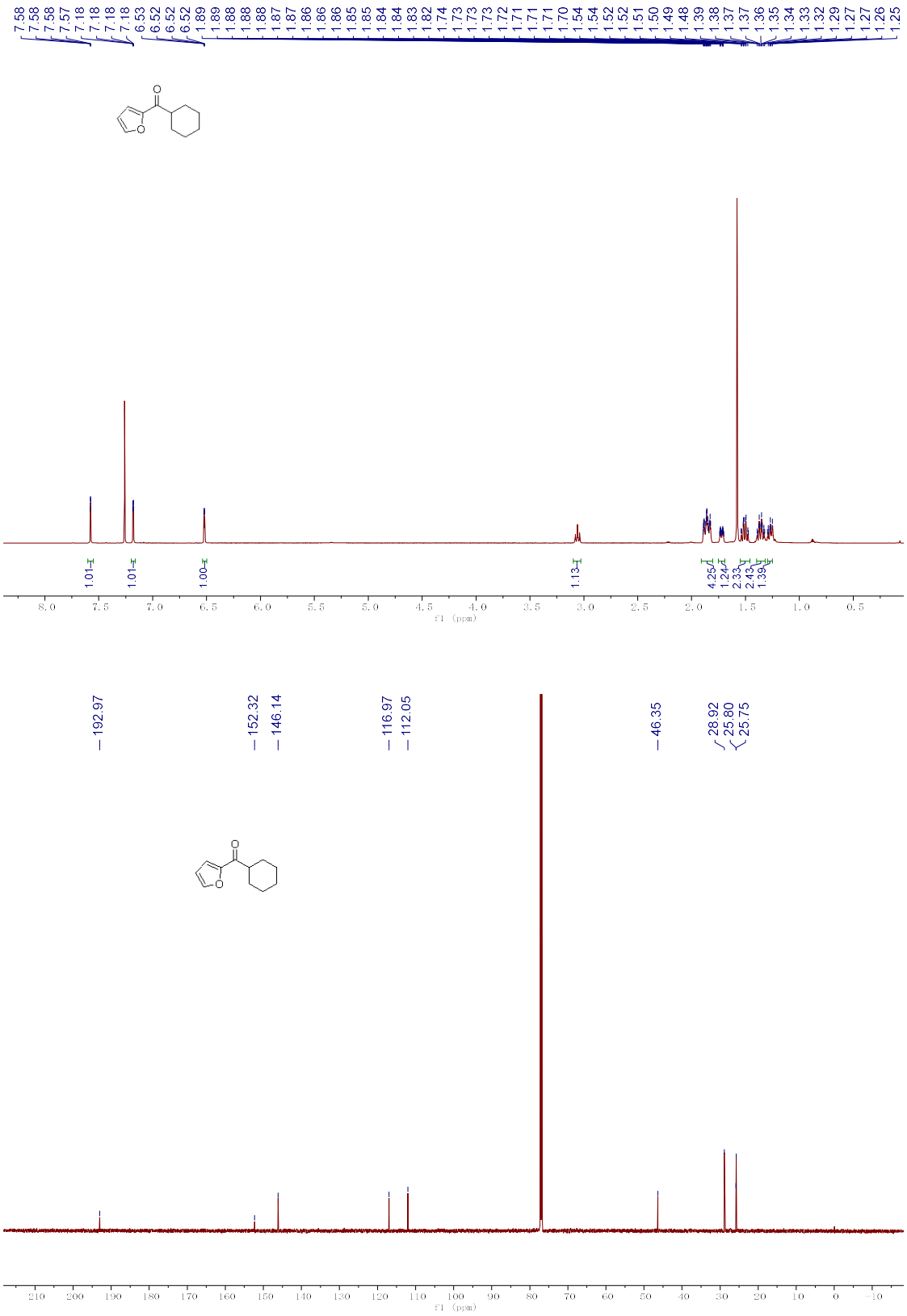

204.33
138.10
136.50
134.29
125.93
45.59
29.41
25.92
25.81
21.22
O
Me
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

11


7.75 7.75 7.74 7.73 7.72 7.72 7.49 7.48 7.47 7.47 7.22 7.22 7.21 7.21 7.20 7.20 7.12 7.12 7.11 7.11 7.11 7.10 7.09 7.09 3.12 3.12 1.95 1.95 1.94 1.94 1.93 1.92 1.83 1.82 1.81 1.81 1.80 1.80 1.79 1.71 1.69 1.43 1.43 1.42 1.41 1.41 1.40 1.39 1.38 1.37 1.37 1.36 1.35 1.35 1.34 1.26 1.25 1.25 1.23
O
F
0.95 0.98 0.96 0.97 1.06 2.00 2.09 1.13 4.09 1.29
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
-111.67 -111.68 -111.69 -111.70 -111.71
-111.55 -111.60 -111.65 -111.70 -111.75 -111.80 -111.85
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


202.93
202.90
161.90
160.22
133.79
133.73
130.77
130.75
126.13
126.04
124.46
124.43
116.52
116.37
50.11
50.07
28.79
25.98
25.80
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

12


7.58
7.58
7.58
7.57
7.18
7.18
7.18
6.53
6.52
6.52
6.52
1.89
1.89
1.88
1.88
1.88
1.87
1.87
1.86
1.86
1.86
1.85
1.85
1.84
1.84
1.83
1.82
1.74
1.73
1.73
1.73
1.72
1.71
1.71
1.71
1.70
1.54
1.54
1.52
1.52
1.51
1.50
1.49
1.48
1.39
1.38
1.37
1.37
1.36
1.35
1.34
1.33
1.32
1.29
1.27
1.27
1.26
1.25
1.01
1.01
1.00
1.13
4.25
1.24
2.33
2.43
1.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
192.97
152.32
146.14
116.97
112.05
46.35
28.92
25.80
25.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

13


7.88
7.87
7.43
7.41
3.22
3.20
3.20
3.19
3.18
1.88
1.88
1.88
1.87
1.87
1.86
1.86
1.86
1.85
1.85
1.85
1.85
1.85
1.84
1.84
1.84
1.83
1.82
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.72
1.50
1.49
1.49
1.49
1.48
1.47
1.47
1.47
1.45
1.41
1.40
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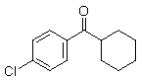
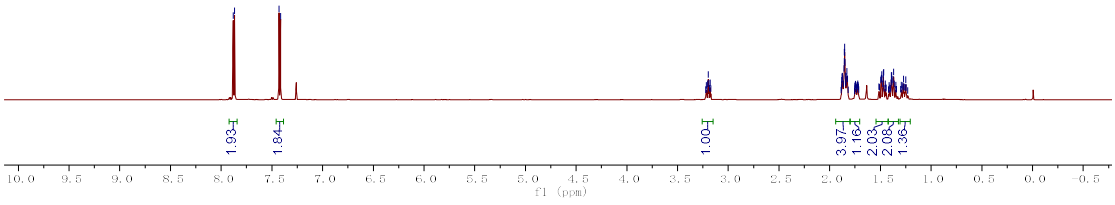
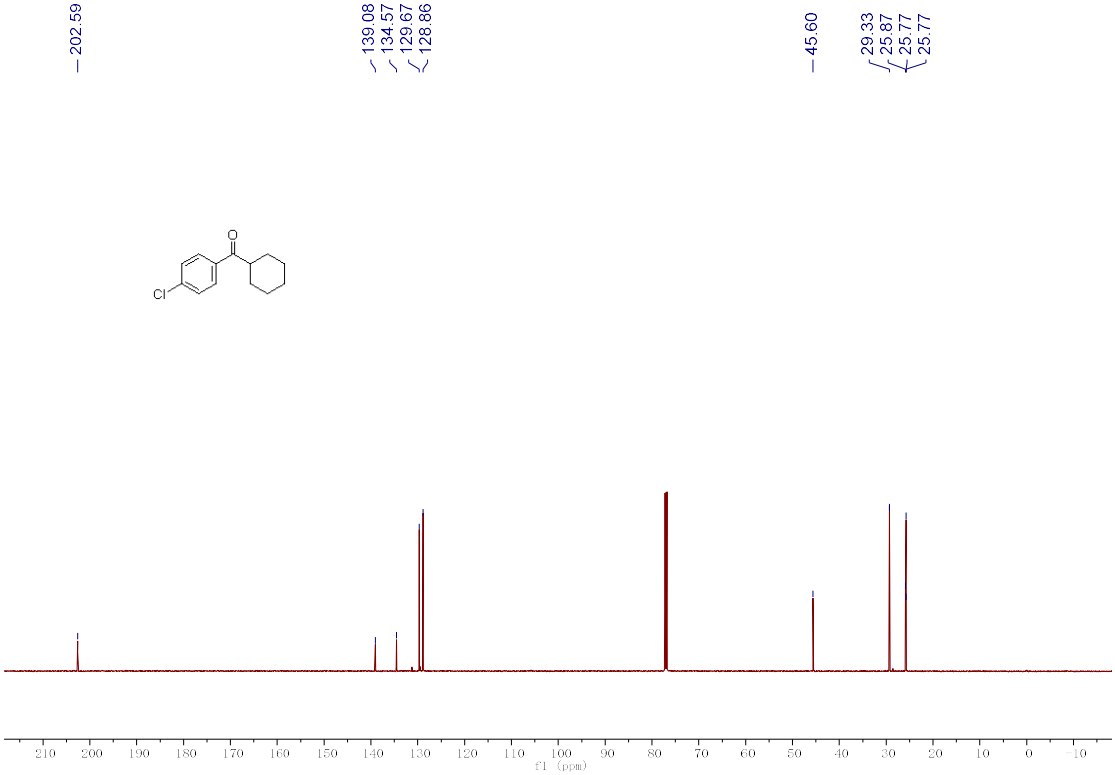
1.36
1.35
1.29
1.28
1.27
1.25

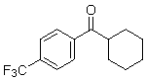

O
Cl

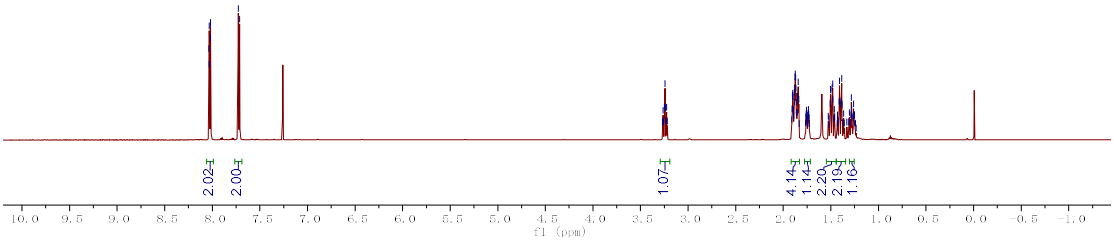

1.93
1.84
1.00
3.97
1.16
2.03
2.08
1.36
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


202.59
139.08
134.57
129.67
128.86
45.60
29.33
25.87
25.77
25.77
O
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

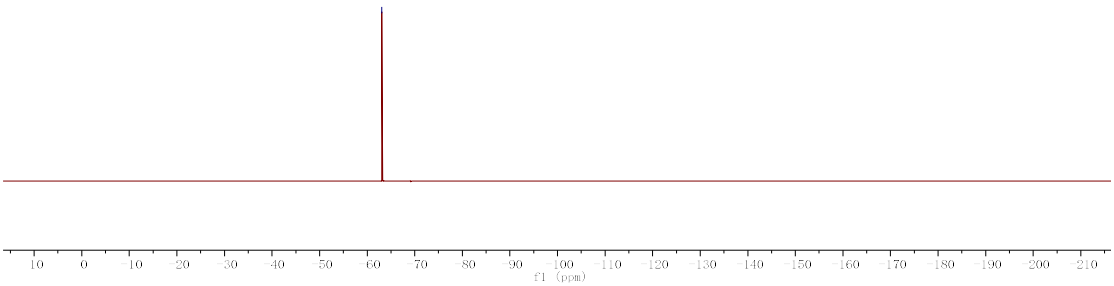
14

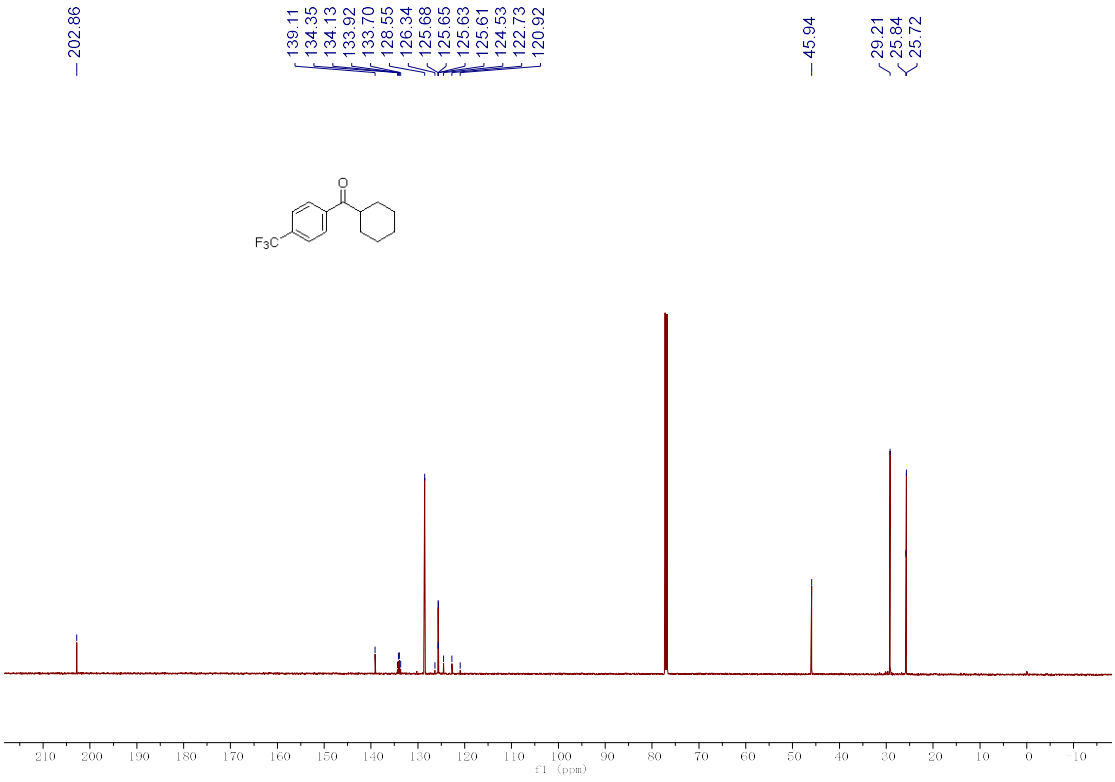

8.03 8.03 8.03 8.02 8.02 7.73 7.71 3.26 3.25 3.24 3.24 3.23 1.91 1.90 1.90 1.90 1.90 1.89 1.89 1.88 1.88 1.88 1.88 1.87 1.87 1.87 1.86 1.86 1.85 1.85 1.84 1.84 1.76 1.76 1.74 1.74 1.73 1.51 1.50 1.50 1.49 1.48 1.48 1.46 1.43 1.41 1.41 1.40 1.39 1.39 1.38 1.37 1.30 1.29 1.28 1.28 1.26 1.26


O
F3C

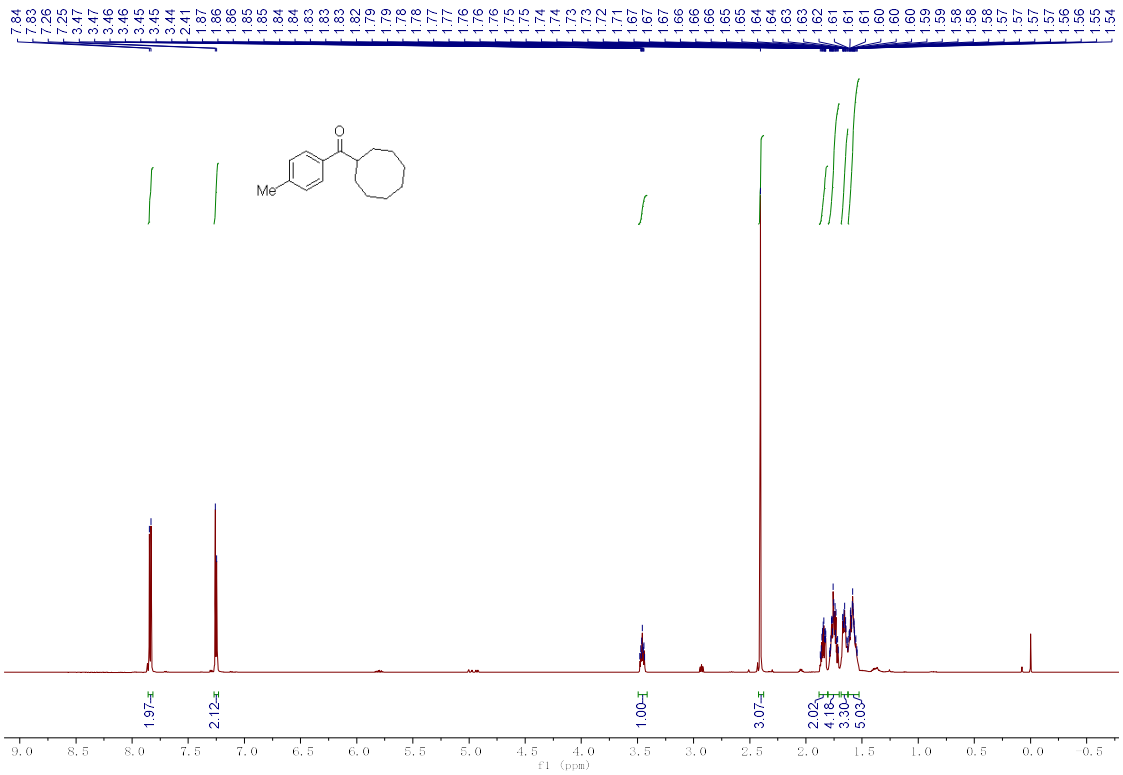

2.02
2.00
1.07
4.14
1.14
2.20
2.19
1.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

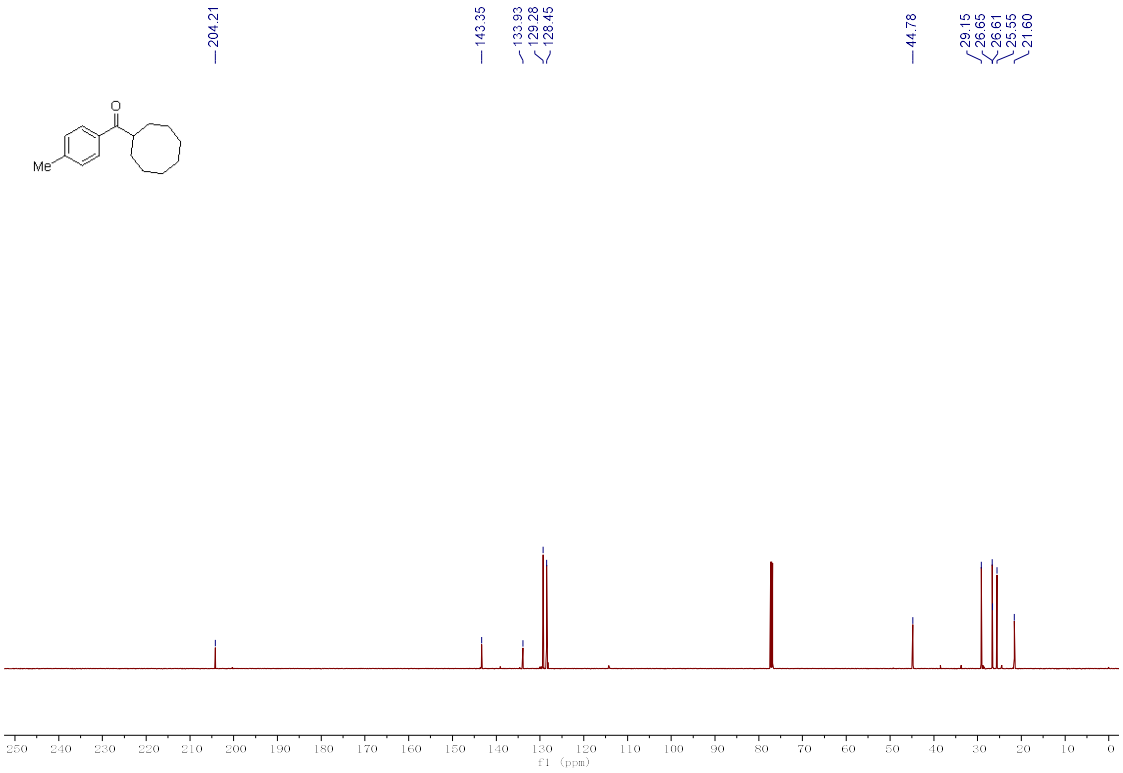

-63.08
-63.08
O
F3C
-63.04 -63.06 -63.08 -63.10 -63.12
f1 (ppm)


10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

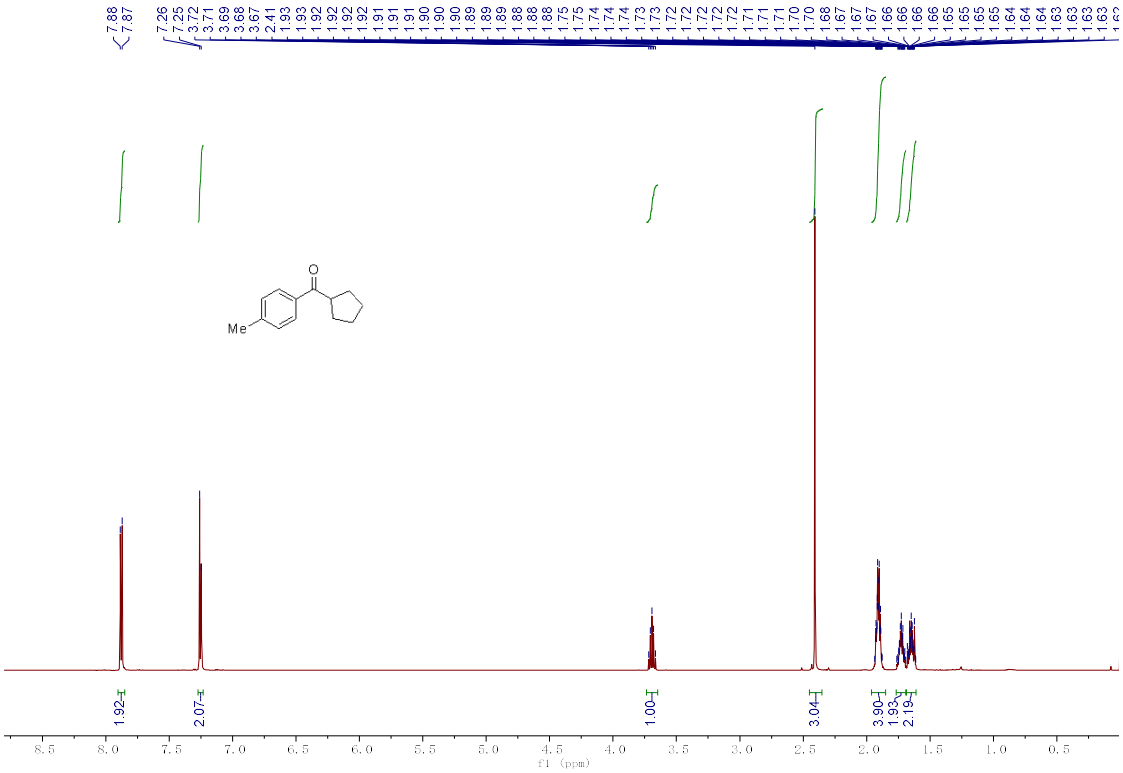

202.86
139.11
134.35
134.13
133.92
133.70
128.55
126.34
125.68
125.65
125.63
125.61
124.53
122.73
120.92
45.94
29.21
25.84
25.72
O
F3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

15


7.84 7.83 7.26 7.25 3.47 3.47 3.46 3.46 3.45 3.45 3.44 2.41 1.87 1.86 1.86 1.85 1.85 1.84 1.84 1.83 1.83 1.82 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.72 1.71 1.67 1.67 1.67 1.66 1.66 1.66 1.65 1.65 1.64 1.64 1.63 1.63 1.62 1.61 1.61 1.61 1.60 1.60 1.60 1.59 1.59 1.58 1.58 1.57 1.57 1.57 1.56 1.56 1.55 1.54
O
Me
1.97 2.12 1.00 3.07 2.02 4.18 3.30 5.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


204.21
143.35
133.93
129.28
128.45
44.78
29.15
26.65
26.61
25.55
21.60
O
Me
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

16


7.88
7.87
7.26
7.25
3.72
3.71
3.69
3.68
3.67
2.41
1.93
1.92
1.92
1.92
1.92
1.91
1.91
1.91
1.90
1.90
1.90
1.89
1.89
1.89
1.88
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1.88
1.75
1.75
1.74
1.74
1.74
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1.73
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1.71
1.71
1.71
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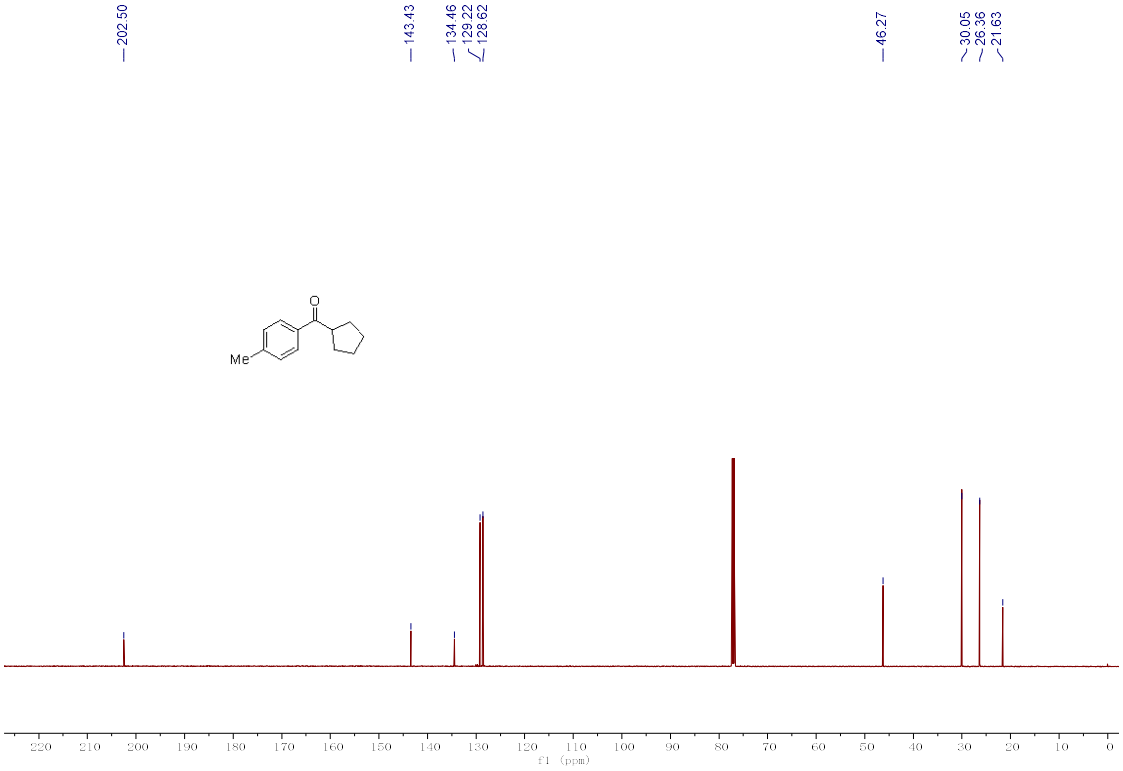
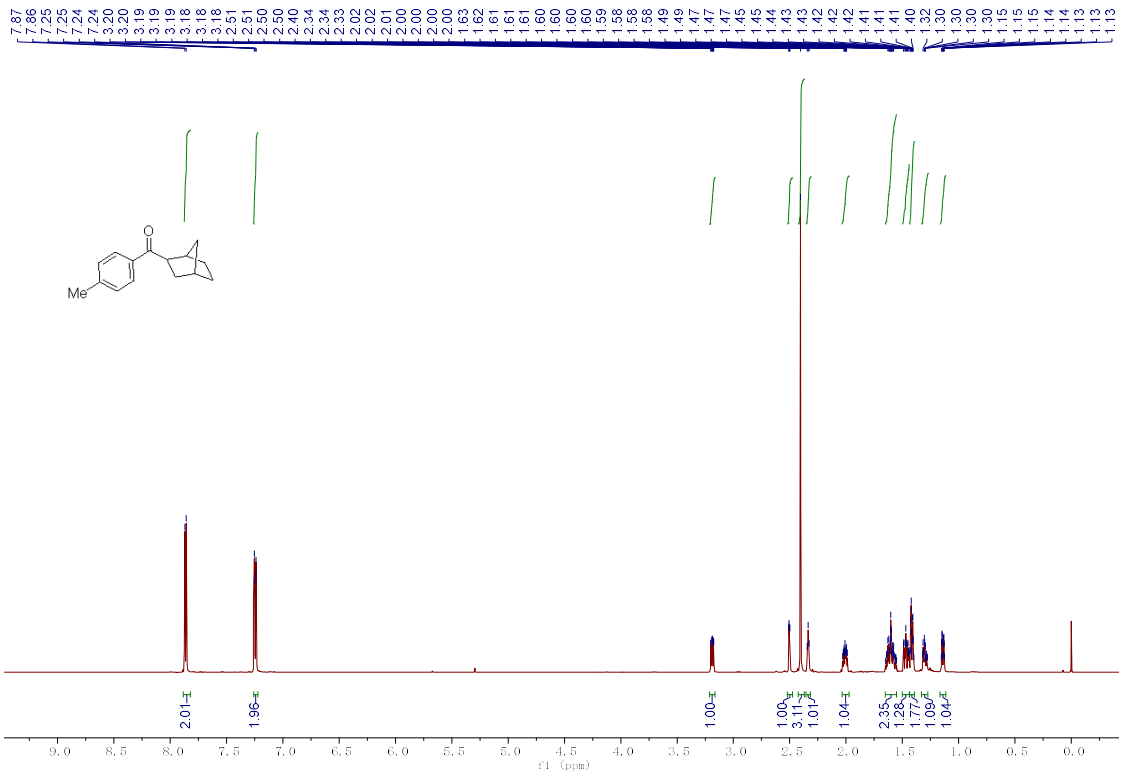
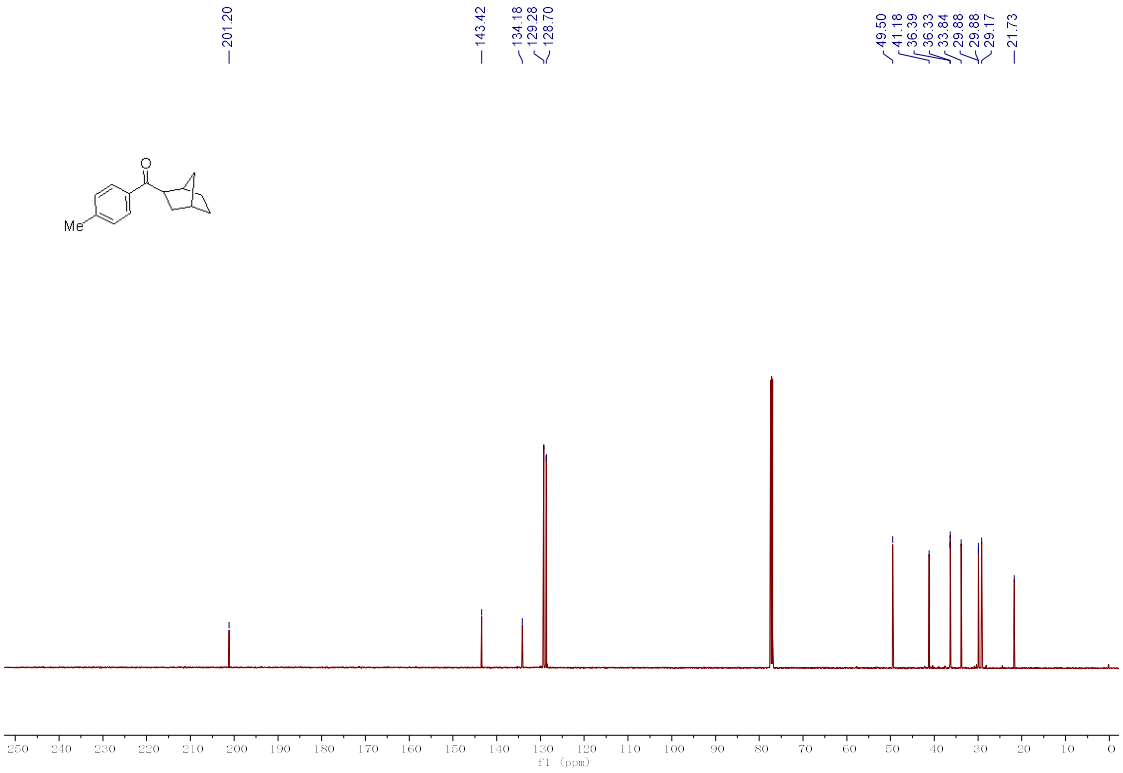
1.66
1.65
1.65
1.65
1.65
1.64
1.64
1.64
1.63
1.63
1.63
1.63
O
Me
1.92
2.07
1.00
3.04
3.90
1.93
2.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

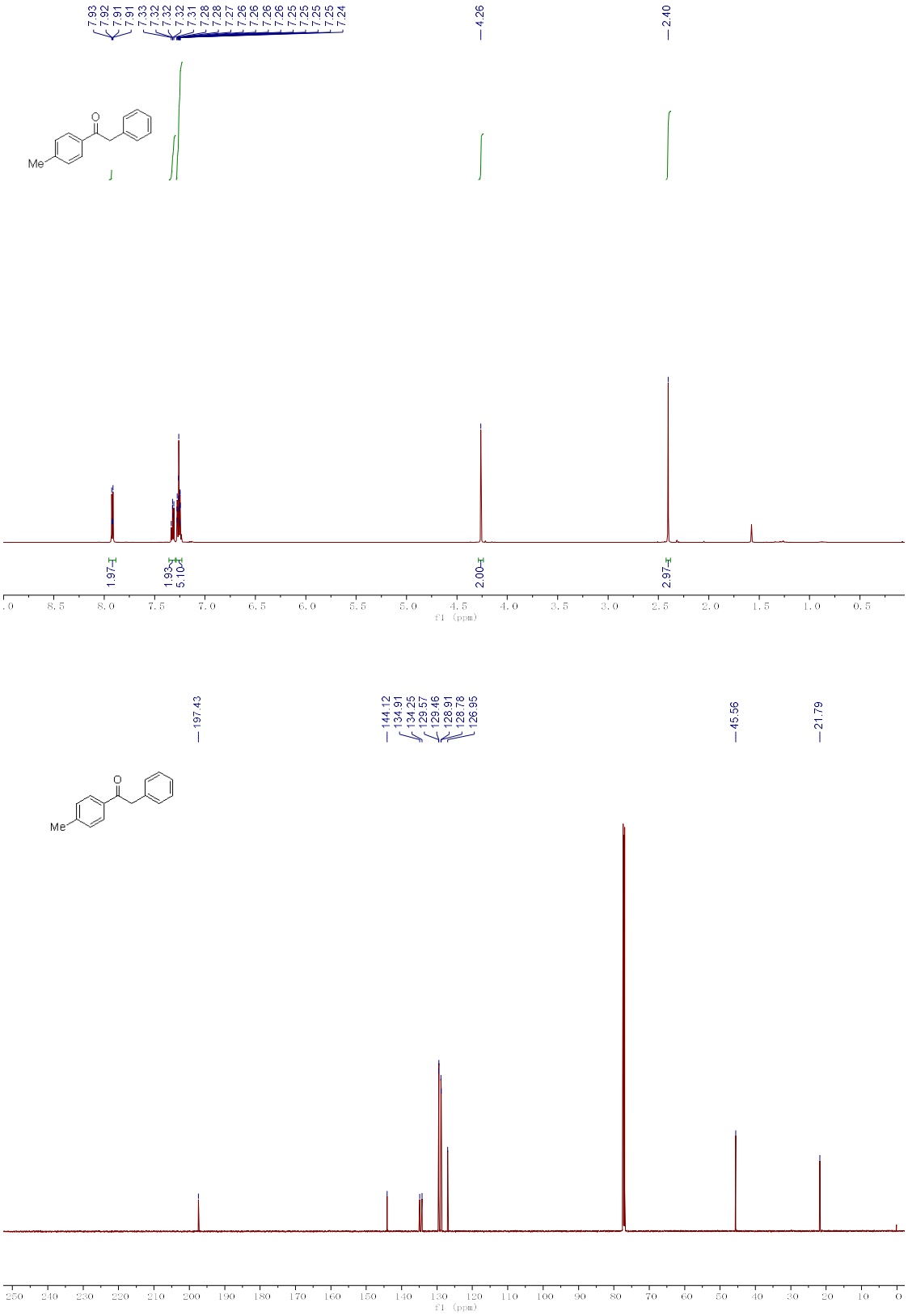

202.50
143.43
134.46
129.22
128.62
46.27
30.05
26.36
21.63
O
Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

17

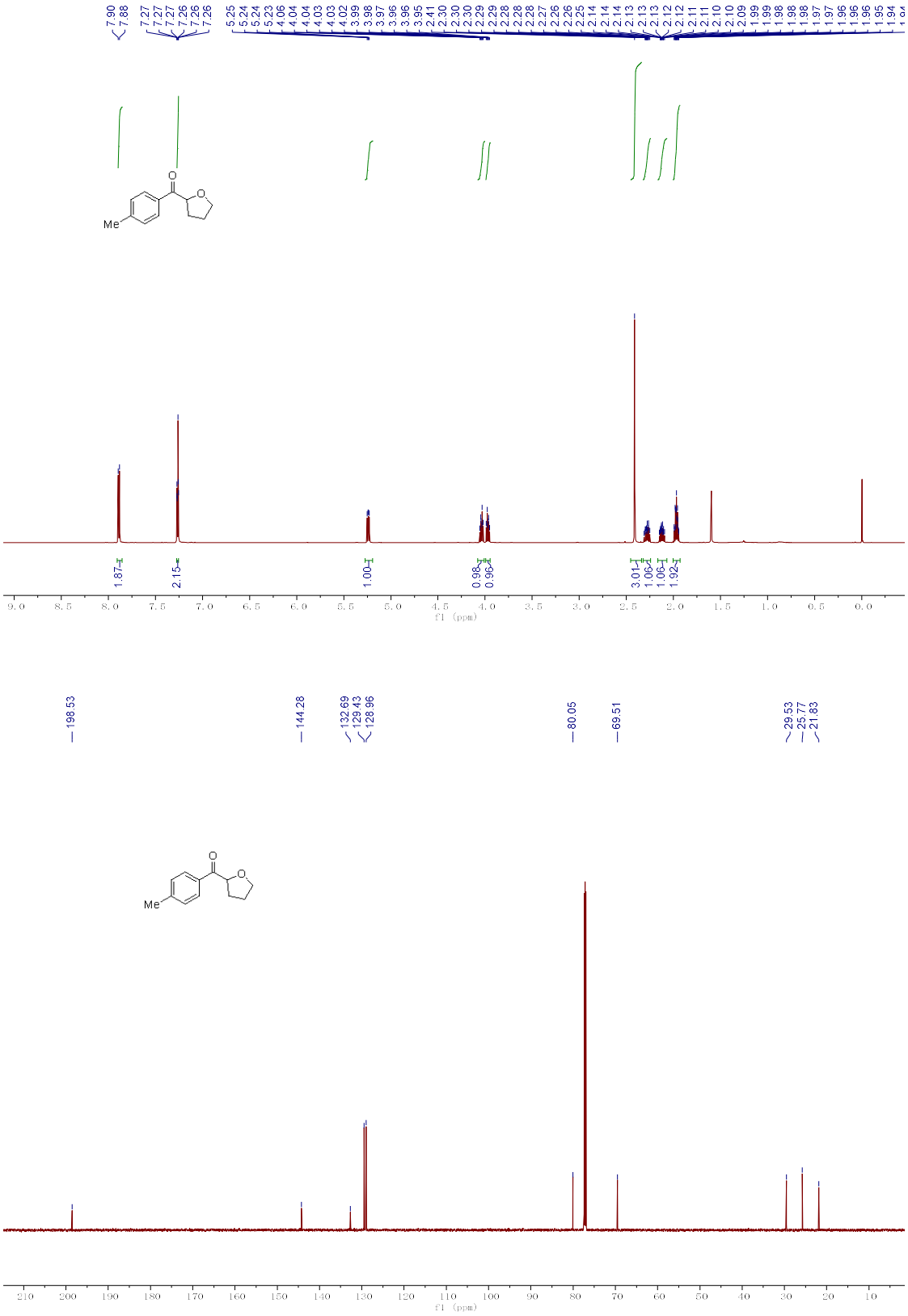

7.87 7.86 7.25 7.25 7.24 7.24 3.20 3.20 3.19 3.19 3.19 3.18 3.18 3.18 2.51 2.51 2.50 2.50 2.40 2.34 2.34 2.33 2.02 2.02 2.01 2.00 2.00 2.00 2.00 1.63 1.62 1.61 1.61 1.61 1.60 1.60 1.60 1.60 1.59 1.58 1.58 1.58 1.49 1.49 1.47 1.47 1.47 1.45 1.45 1.44 1.43 1.43 1.42 1.42 1.42 1.41 1.41 1.41 1.40 1.32 1.30 1.30 1.30 1.30 1.15 1.15 1.15 1.14 1.14 1.13 1.13 1.13
Me
2.01 1.96 1.00 1.00 3.11 1.01 1.04 2.35 1.28 1.77 1.09 1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


201.20
143.42
134.18
129.28
128.70
49.50
41.18
36.39
36.33
33.84
29.88
29.88
29.17
21.73
Me
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

18


7.93
7.92
7.91
7.91
7.33
7.32
7.32
7.32
7.31
7.28
7.28
7.27
7.26
7.26
7.26
7.26
7.25
7.25
7.25
7.25
7.24
4.26
2.40
Me
1.97
1.93
5.10
2.00
2.97
f1 (ppm)
197.43
144.12
134.91
134.25
129.57
129.46
128.91
128.78
126.95
45.56
21.79
Me
f1 (ppm)

19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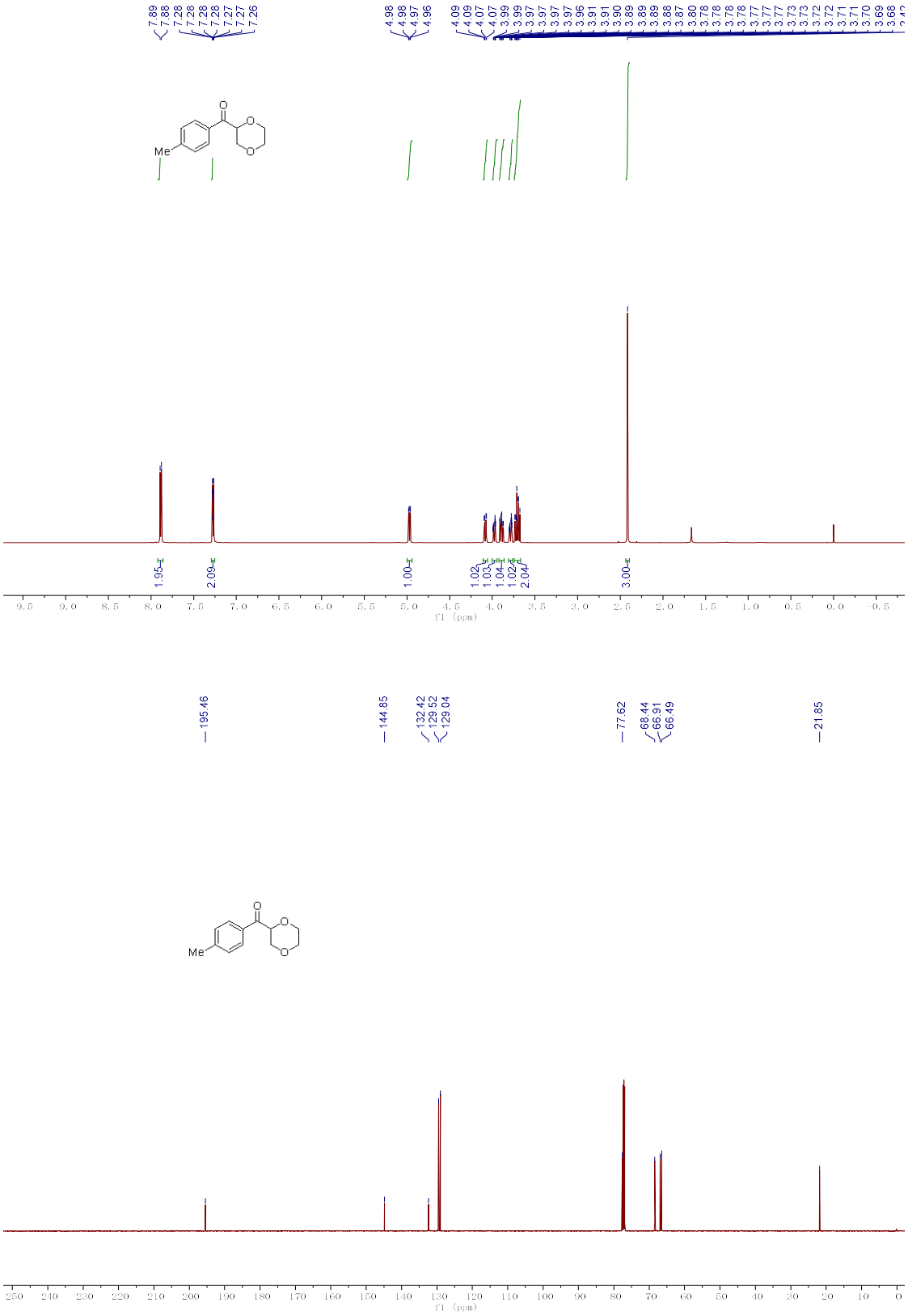
7.88
7.27
7.27
7.27
7.26
7.26
7.26
5.25
5.24
5.24
5.23
4.06
4.04
4.04
4.03
4.03
4.02
3.99
3.98
3.97
3.96
3.96
3.95
2.41
2.30
2.30
2.30
2.29
2.29
2.28
2.28
2.28
2.27
2.26
2.26
2.25
2.14
2.14
2.13
2.13
2.12
2.12
2.11
2.11
2.10
2.10
2.09
1.99
1.99
1.98
1.98
1.98
1.97
1.97
1.96
1.96
1.96
1.95
1.94
O
O
Me
1.87
2.15
1.00
0.98
0.96
3.01
1.06
1.06
1.92
f1 (ppm)
198.53
144.28
132.69
129.43
128.96
80.05
69.51
29.53
25.77
21.83
O
O
Me
f1 (ppm)

20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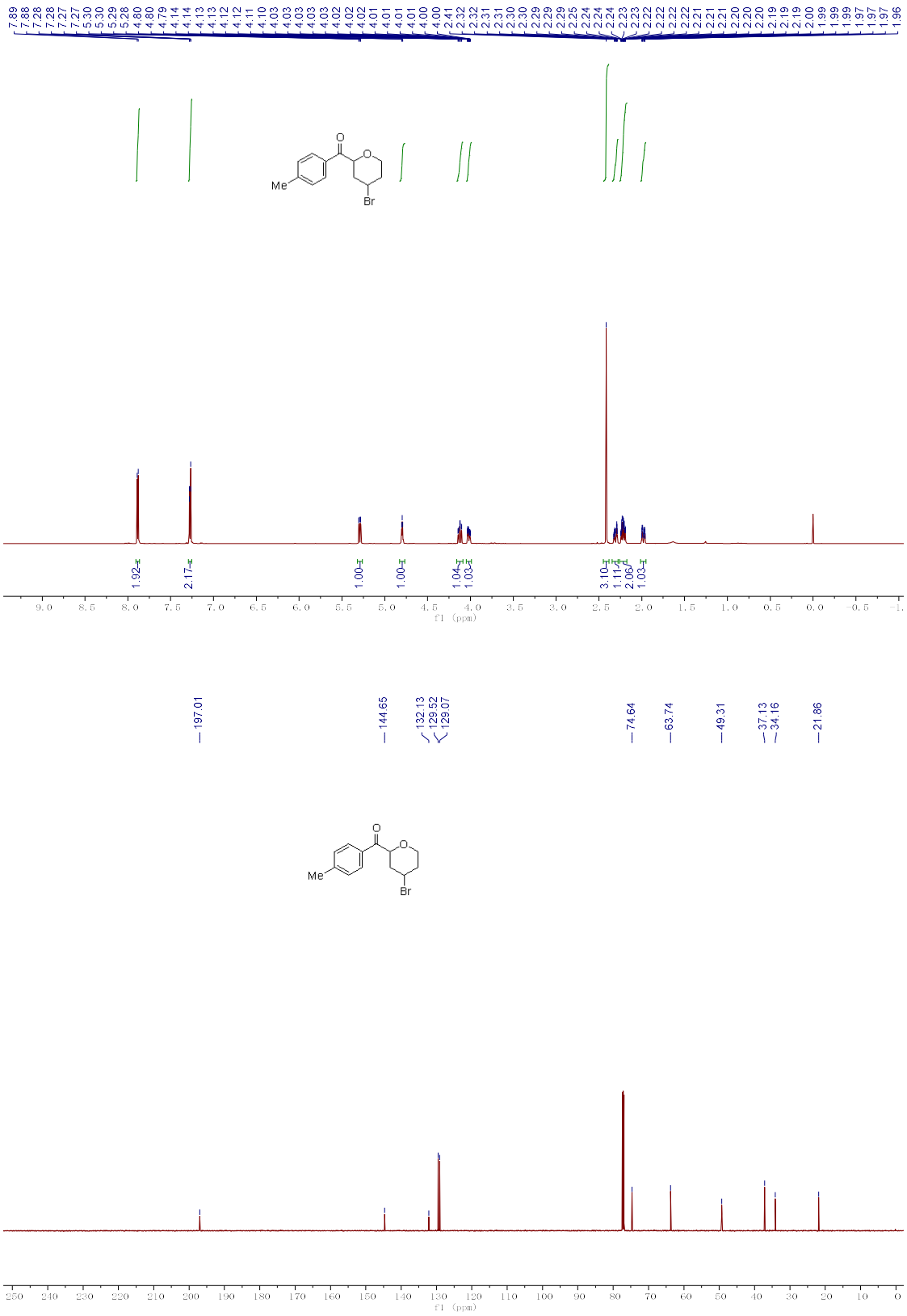
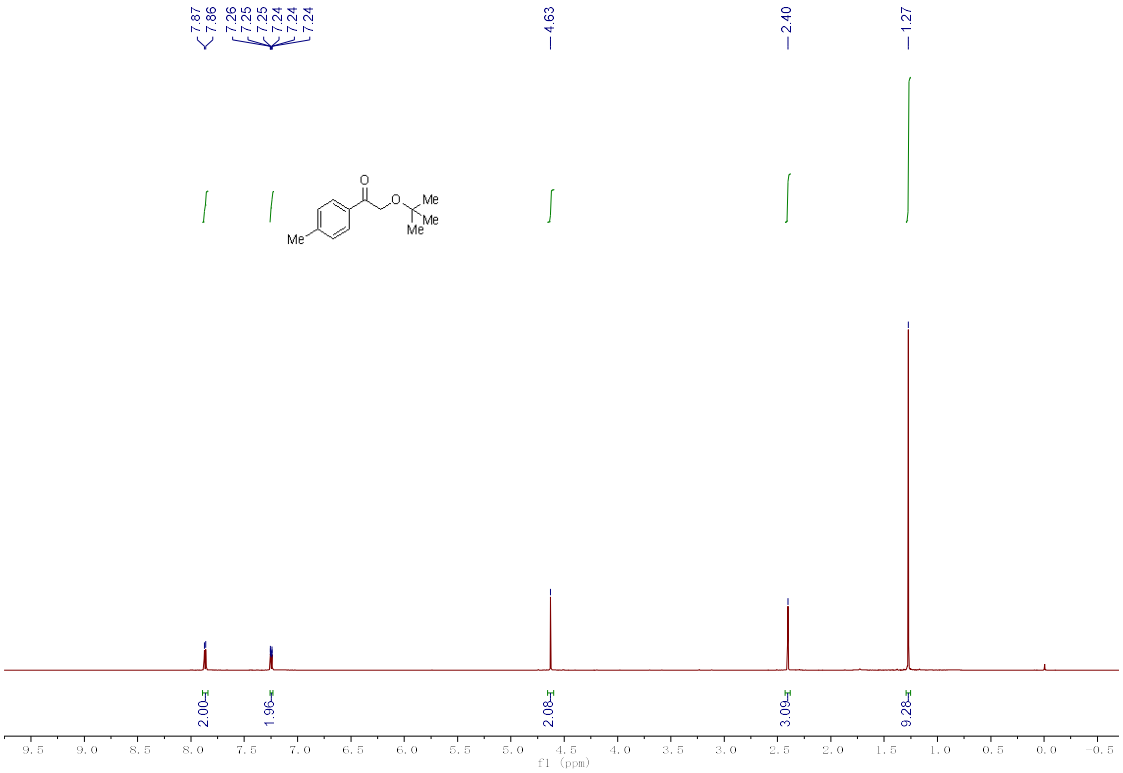
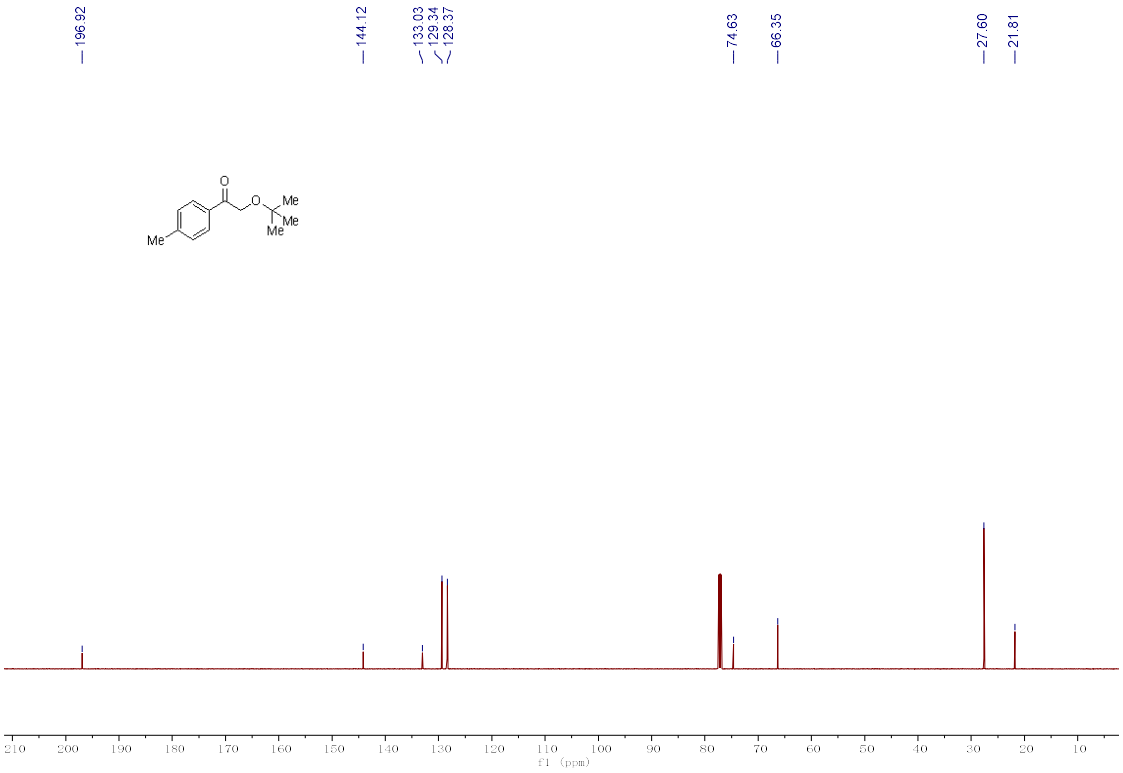
7.28
7.28
7.28
7.27
7.27
7.26
4.98
4.98
4.97
4.96
4.09
4.09
4.07
4.07
3.99
3.99
3.97
3.97
3.97
3.97
3.96
3.91
3.91
3.90
3.89
3.89
3.89
3.88
3.87
3.80
3.78
3.78
3.78
3.77
3.77
3.77
3.73
3.73
3.72
3.72
3.71
3.71
3.70
3.69
3.68
Me
1.95
2.09
1.00
1.02
1.03
1.04
1.02
2.04
3.00
f1 (ppm)
195.46
144.85
132.42
129.52
129.04
77.62
68.44
66.91
66.49
21.85
Me
f1 (ppm)

21

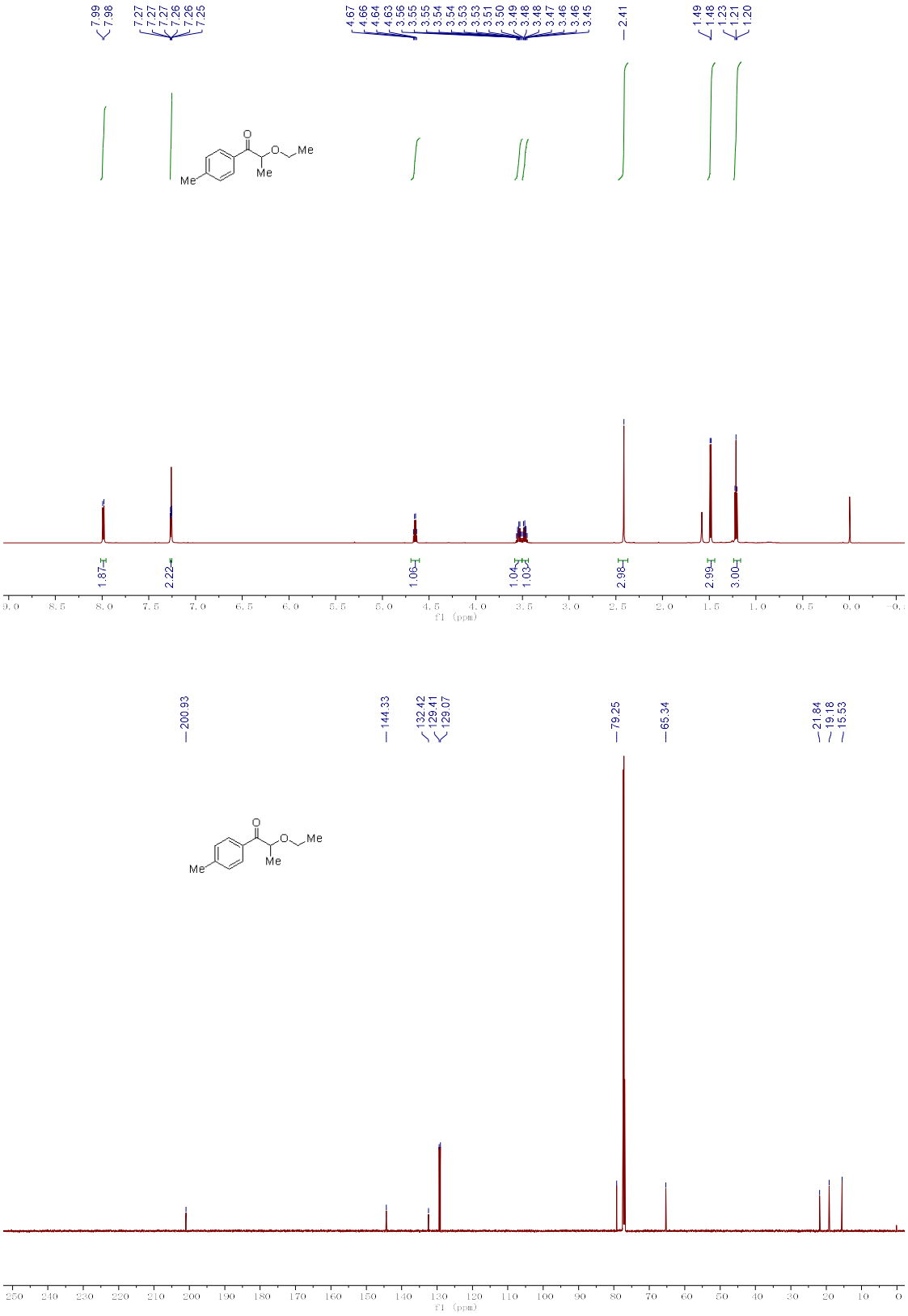

7.89 7.88 7.28 7.28 7.27 7.27 5.30 5.30 5.29 5.28 4.80 4.80 4.79 4.14 4.14 4.13 4.13 4.12 4.12 4.11 4.10 4.03 4.03 4.03 4.03 4.02 4.02 4.02 4.01 4.01 4.01 4.01 4.00 4.00 2.41 2.32 2.32 2.31 2.31 2.30 2.30 2.29 2.29 2.29 2.25 2.24 2.24 2.24 2.23 2.23 2.22 2.22 2.22 2.22 2.21 2.21 2.20 2.20 2.20 2.19 2.19 2.19 2.00 1.99 1.99 1.99 1.97 1.97 1.97 1.96
O
O
Me
Br
1.92
2.17
1.00
1.00
1.04
1.03
3.10
1.11
2.06
1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
197.01
144.65
132.13
129.52
129.07
74.64
63.74
49.31
37.13
34.16
21.86
O
O
Me
Br
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

22

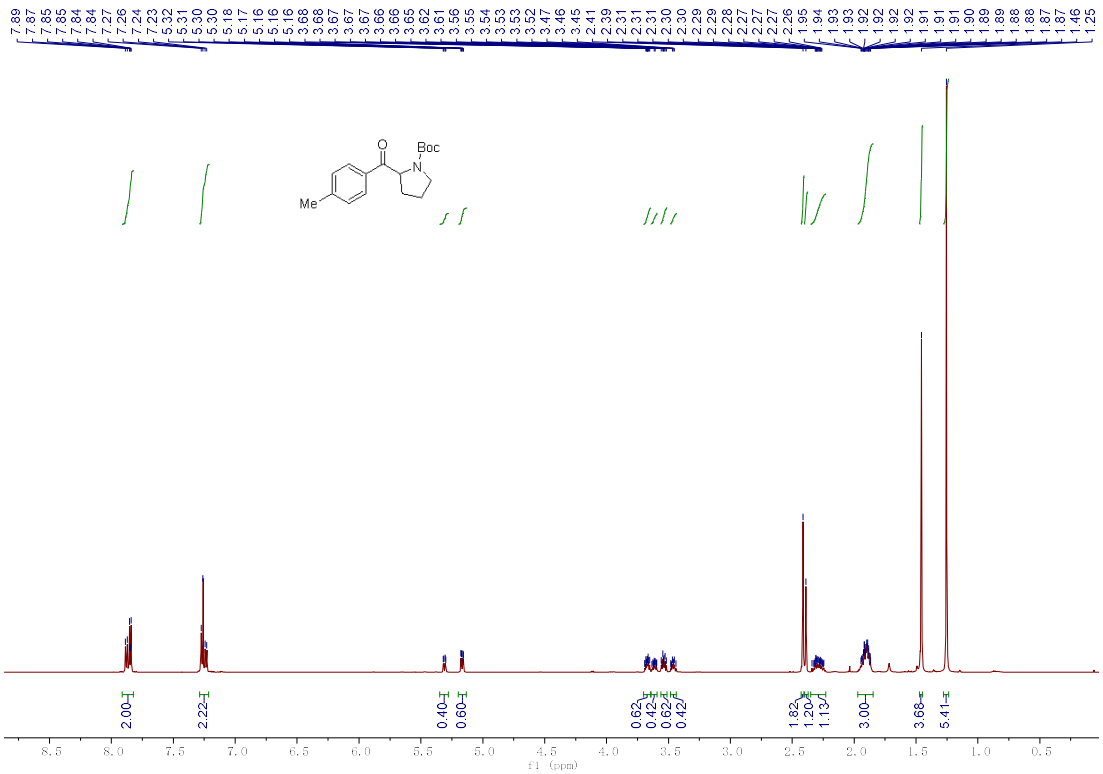

7.87
7.86
7.26
7.25
7.25
7.24
7.24
7.24
4.63
2.40
1.27
Me
O
O
Me
Me
Me
2.00
1.96
2.08
3.09
9.28
f1 (ppm)

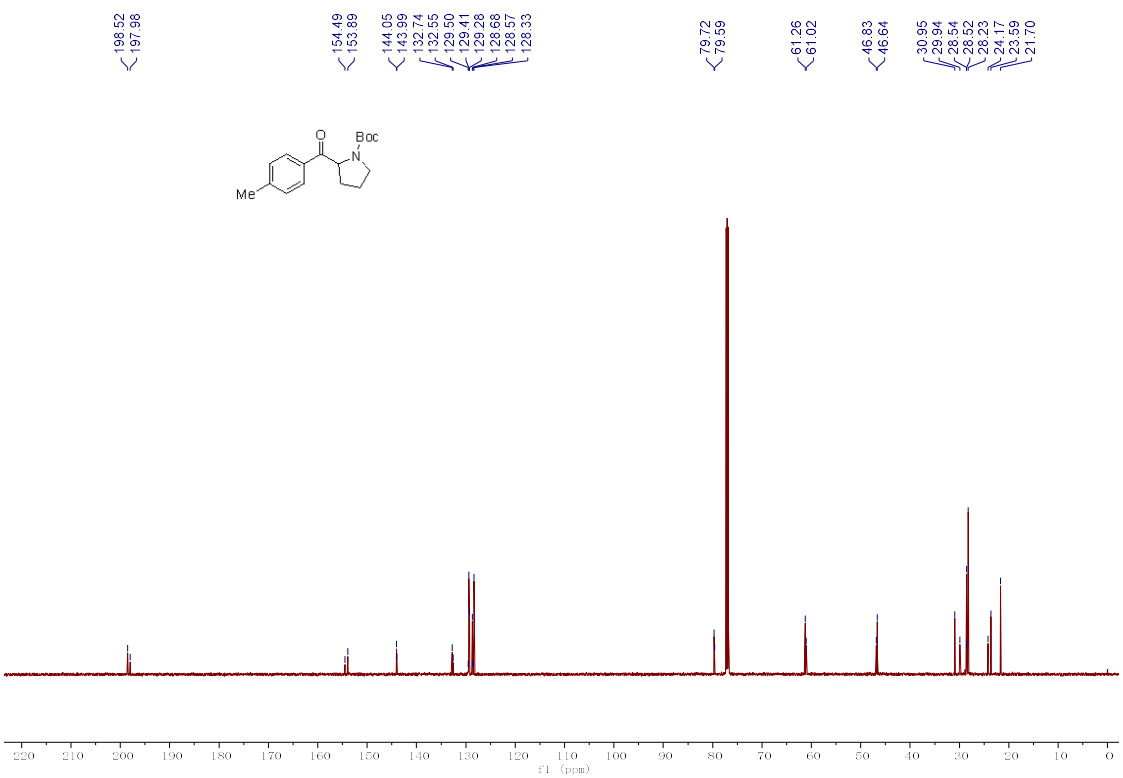

196.92
144.12
133.03
129.34
128.37
74.63
66.35
27.60
21.81
Me
O
O
Me
Me
Me
f1 (ppm)

23

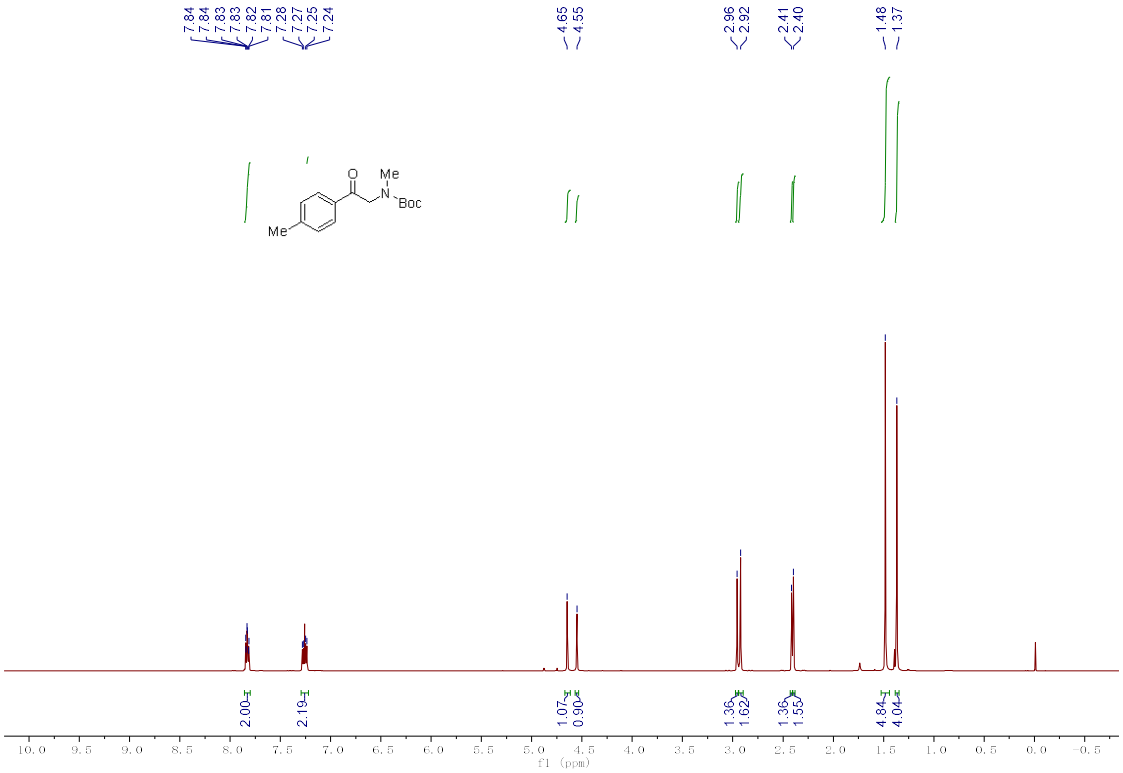

7.99
7.98
7.27
7.27
7.27
7.26
7.26
7.25
4.67
4.66
4.64
4.63
3.56
3.55
3.55
3.54
3.54
3.53
3.53
3.51
3.50
3.49
3.48
3.48
3.47
3.46
3.46
3.45
2.41
1.49
1.48
1.23
1.21
1.20
O
O
Me
Me
Me
1.87
2.22
1.06
1.04
1.03
2.98
2.99
3.00
f1 (ppm)
200.93
144.33
132.42
129.41
129.07
79.25
65.34
21.84
19.18
15.53
O
O
Me
Me
Me
f1 (ppm)

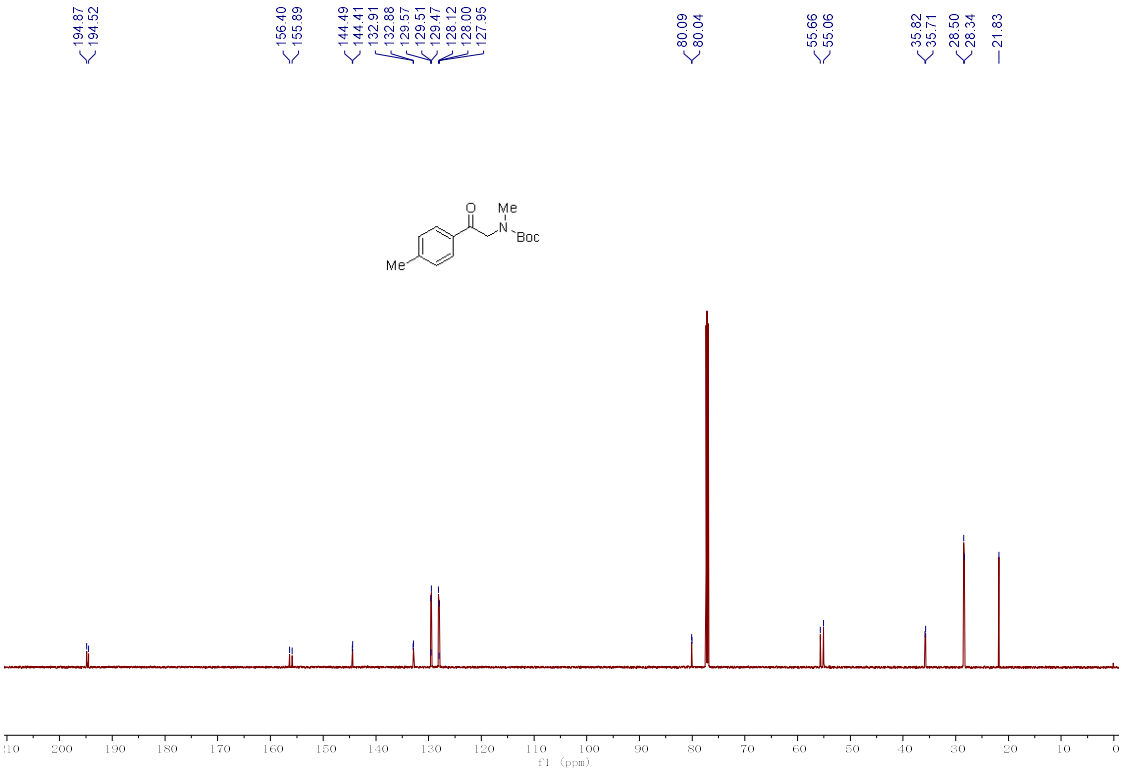
24



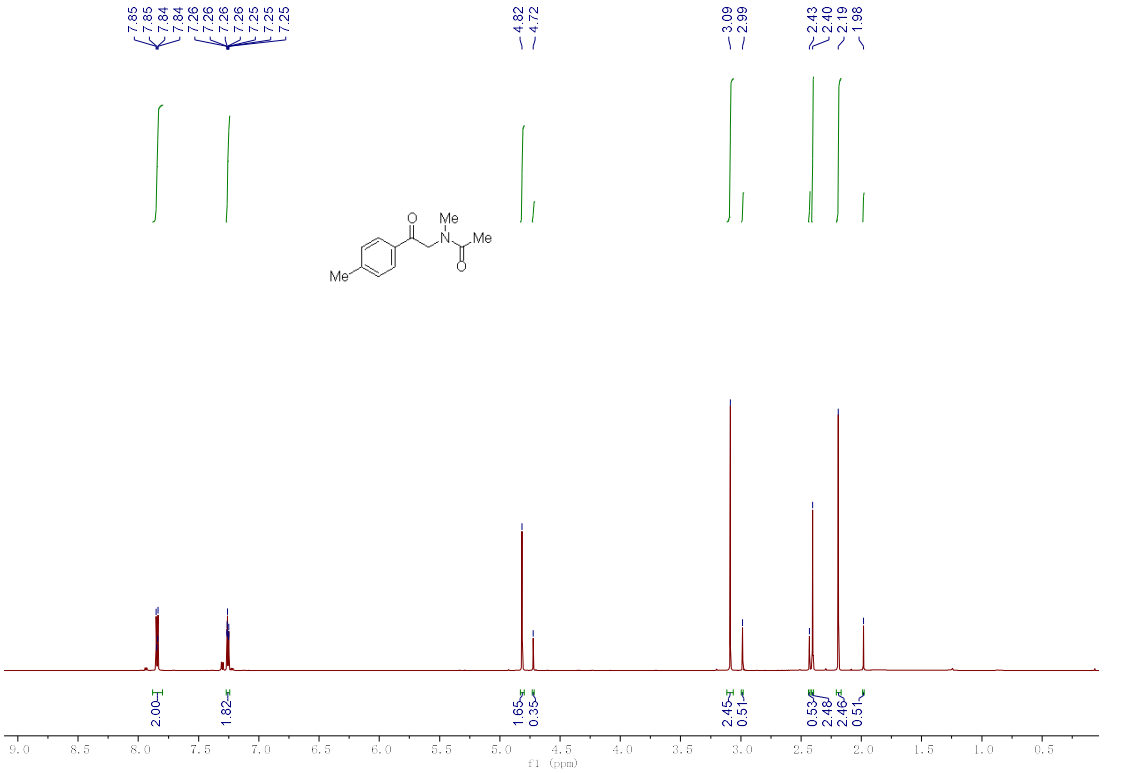


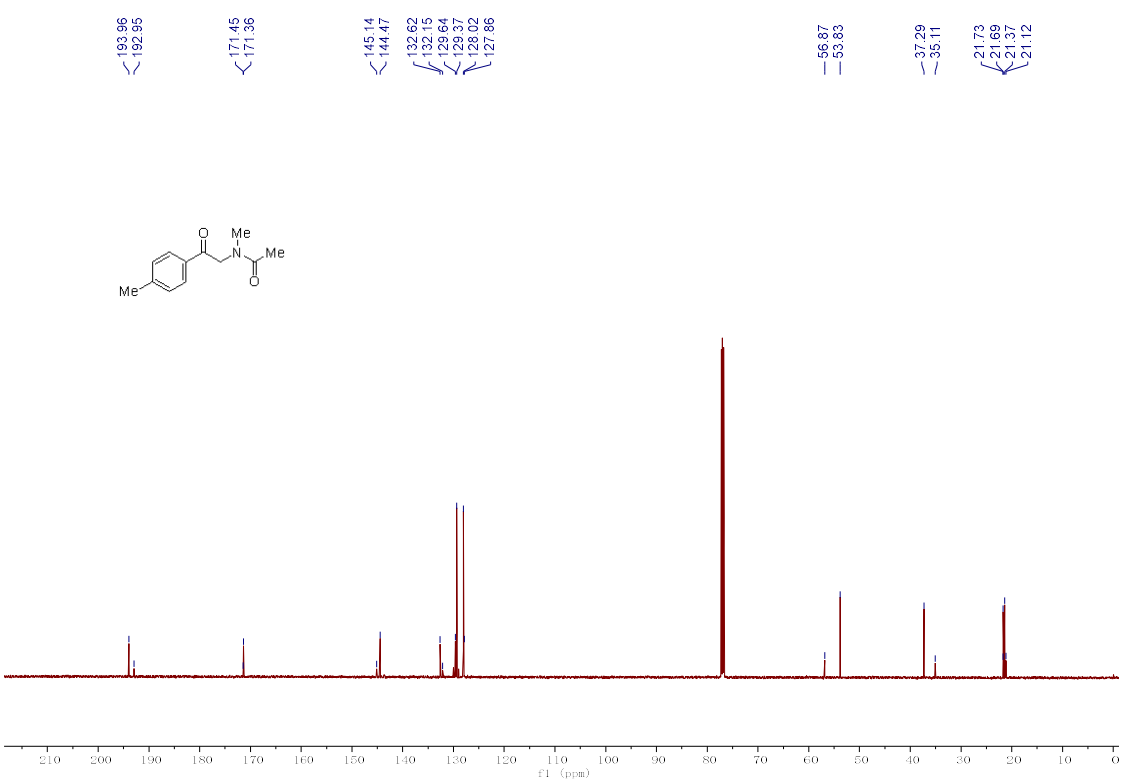
25


7.84
7.84
7.83
7.83
7.82
7.81
7.28
7.27
7.25
7.24
4.65
4.55
2.96
2.92
2.41
2.40
1.48
1.37
Me
O
N
Boc
Me
2.00
2.19
1.07
0.90
1.36
1.62
1.36
1.55
4.84
4.04
f1 (ppm)

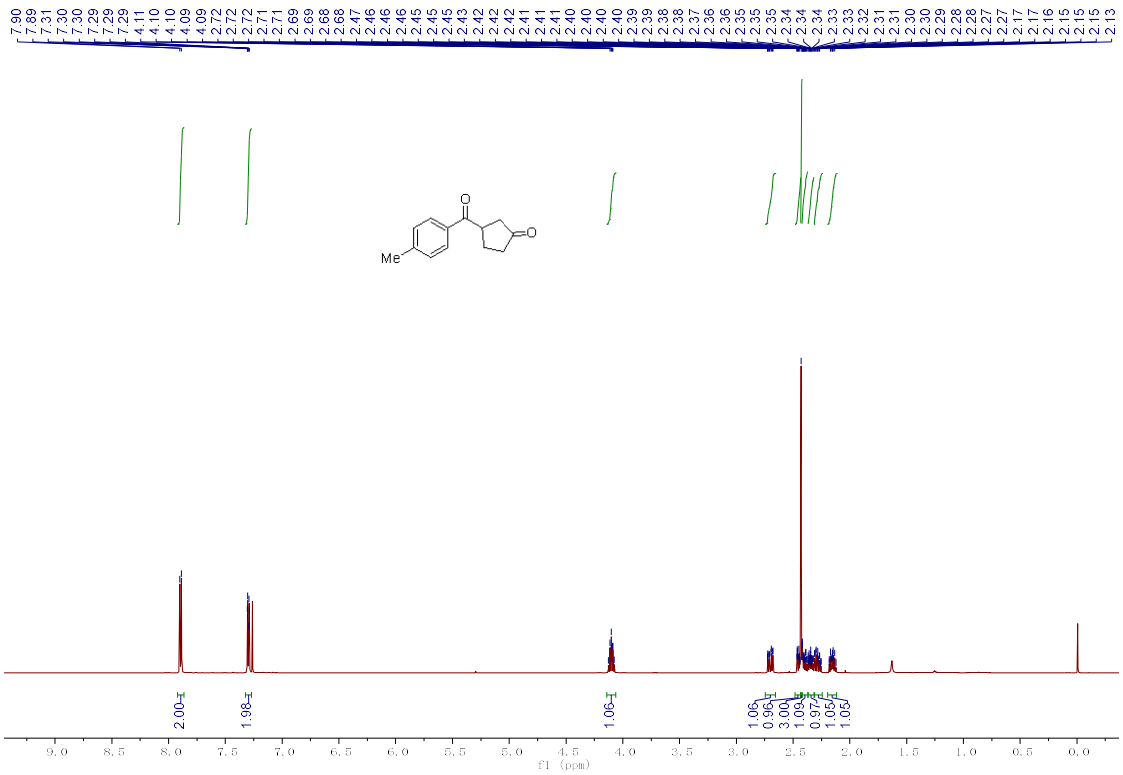

194.87
194.52
156.40
155.89
144.49
144.41
132.91
132.88
129.57
129.51
129.47
128.12
128.00
127.95
80.09
80.04
55.66
55.06
35.82
35.71
28.50
28.34
21.83
Me
O
N
Me
Boc
f1 (ppm)

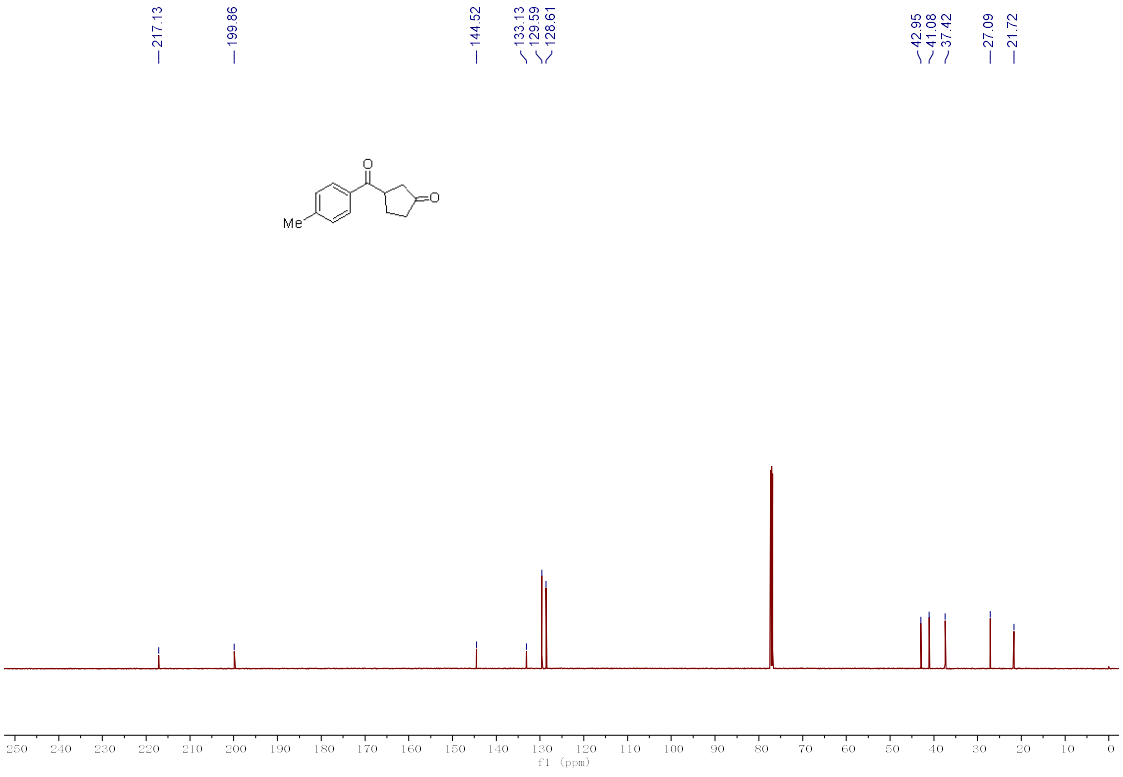
26


7.85
7.85
7.84
7.84
7.26
7.26
7.26
7.26
7.25
7.25
7.25
4.82
4.72
3.09
2.99
2.43
2.40
2.19
1.98
Me
O
N
Me
O
Me
2.00
1.82
1.65
0.35
2.45
0.51
0.53
2.48
2.46
0.51
f1 (ppm)

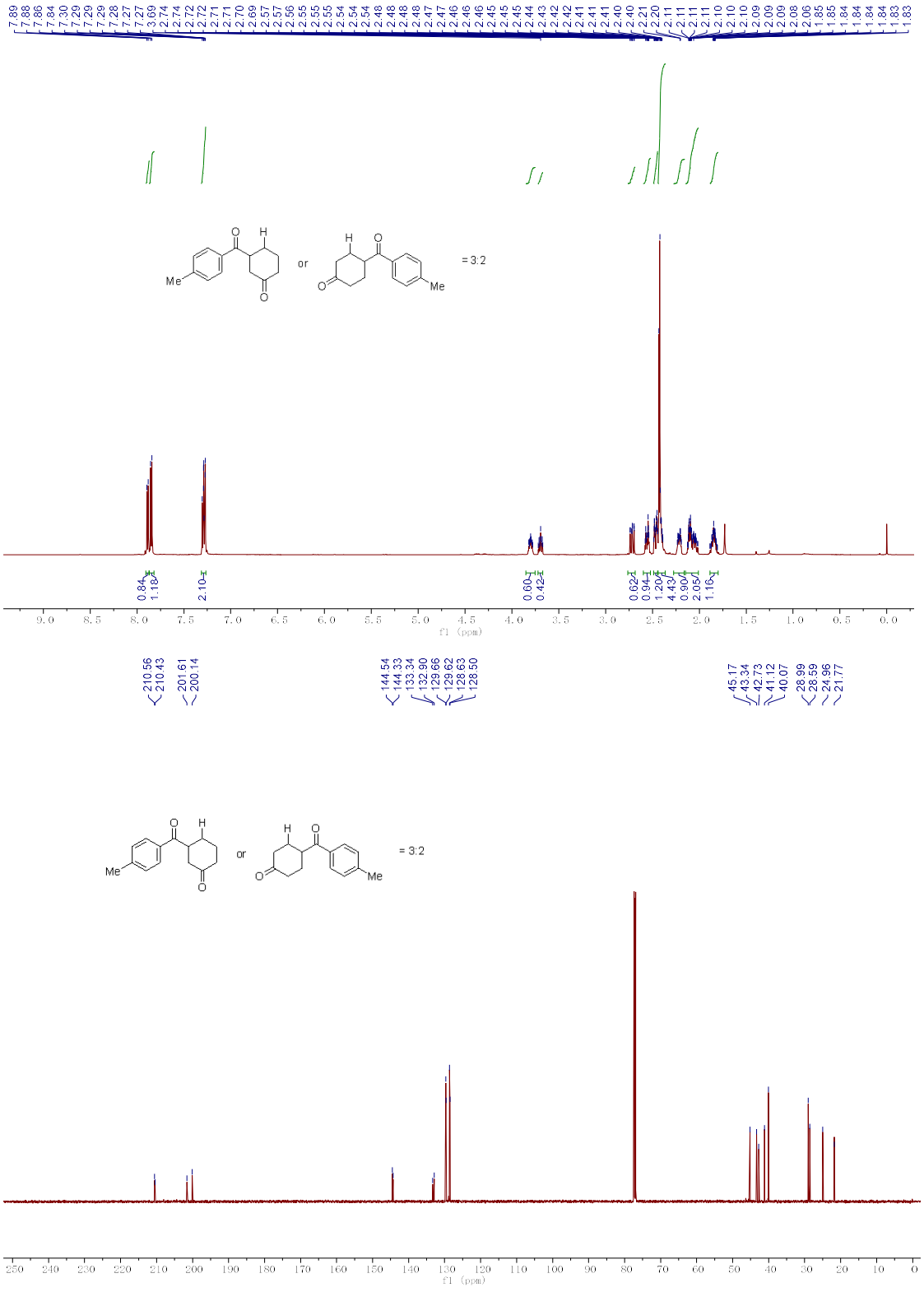

193.96
192.95
171.45
171.36
145.14
144.47
132.62
132.15
129.64
129.37
128.02
127.86
56.87
53.83
37.29
35.11
21.73
21.69
21.37
21.12
O
Me
N
Me
O
Me
f1 (ppm)

27

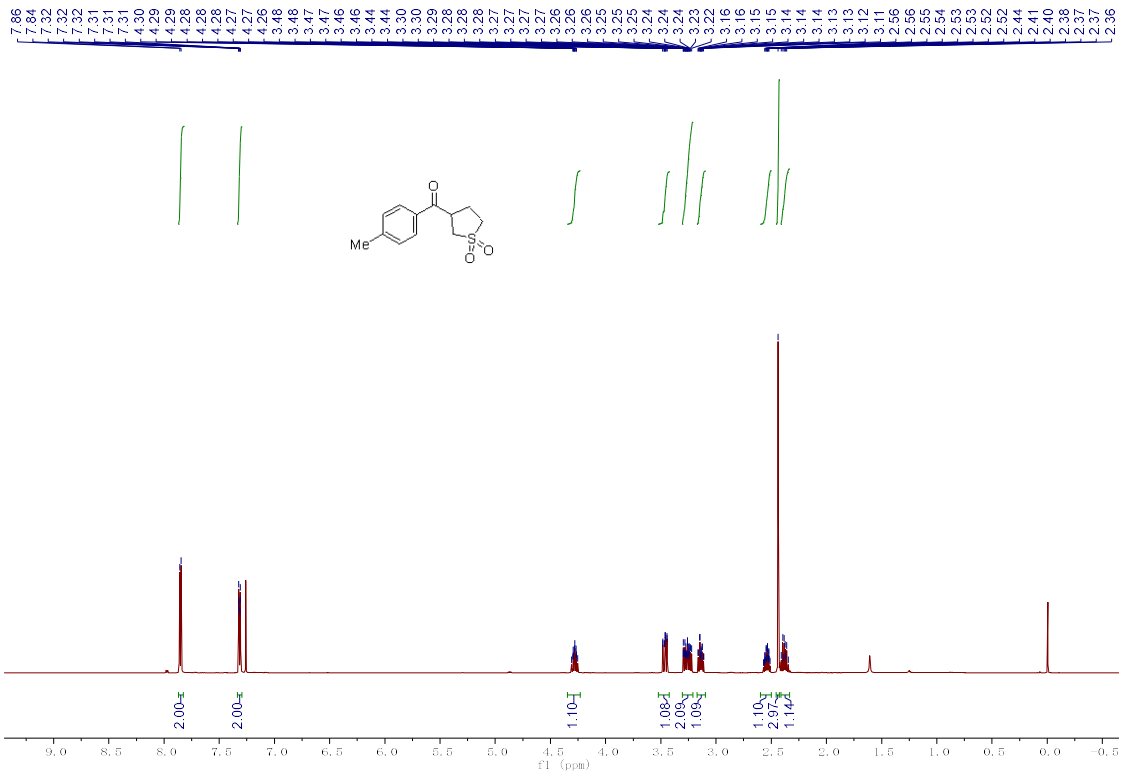

7.90 7.89 7.31 7.30 7.30 7.29 7.29 7.29 4.11 4.10 4.10 4.09 4.09 2.72 2.72 2.72 2.71 2.69 2.68 2.68 2.47 2.46 2.46 2.46 2.45 2.45 2.45 2.43 2.42 2.42 2.42 2.41 2.41 2.41 2.40 2.40 2.40 2.40 2.39 2.39 2.39 2.38 2.38 2.37 2.36 2.36 2.35 2.35 2.35 2.34 2.34 2.34 2.33 2.33 2.32 2.31 2.31 2.30 2.30 2.29 2.28 2.28 2.27 2.27 2.17 2.16 2.15 2.15 2.15 2.13
O
O
Me
2.00
1.98
1.06
1.06
0.96
3.00
1.09
0.97
1.05
1.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

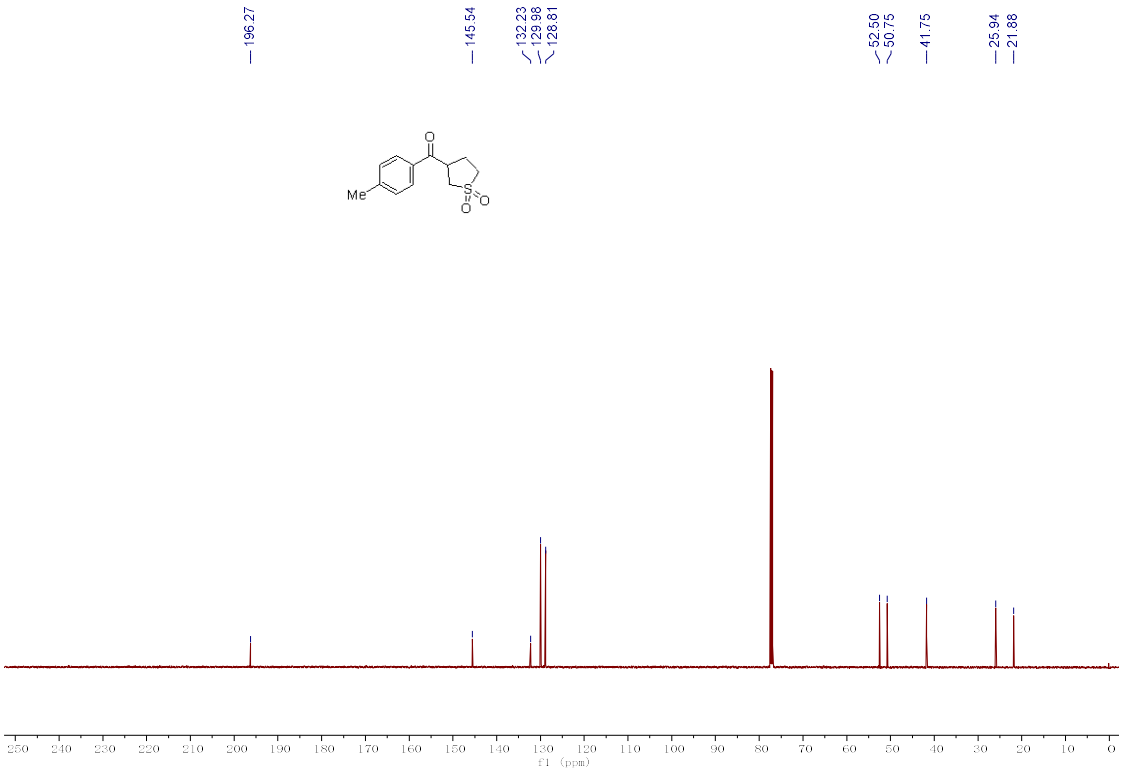

217.13
199.86
144.52
133.13
129.59
128.61
42.95
41.08
37.42
27.09
21.72
O
O
Me
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

28

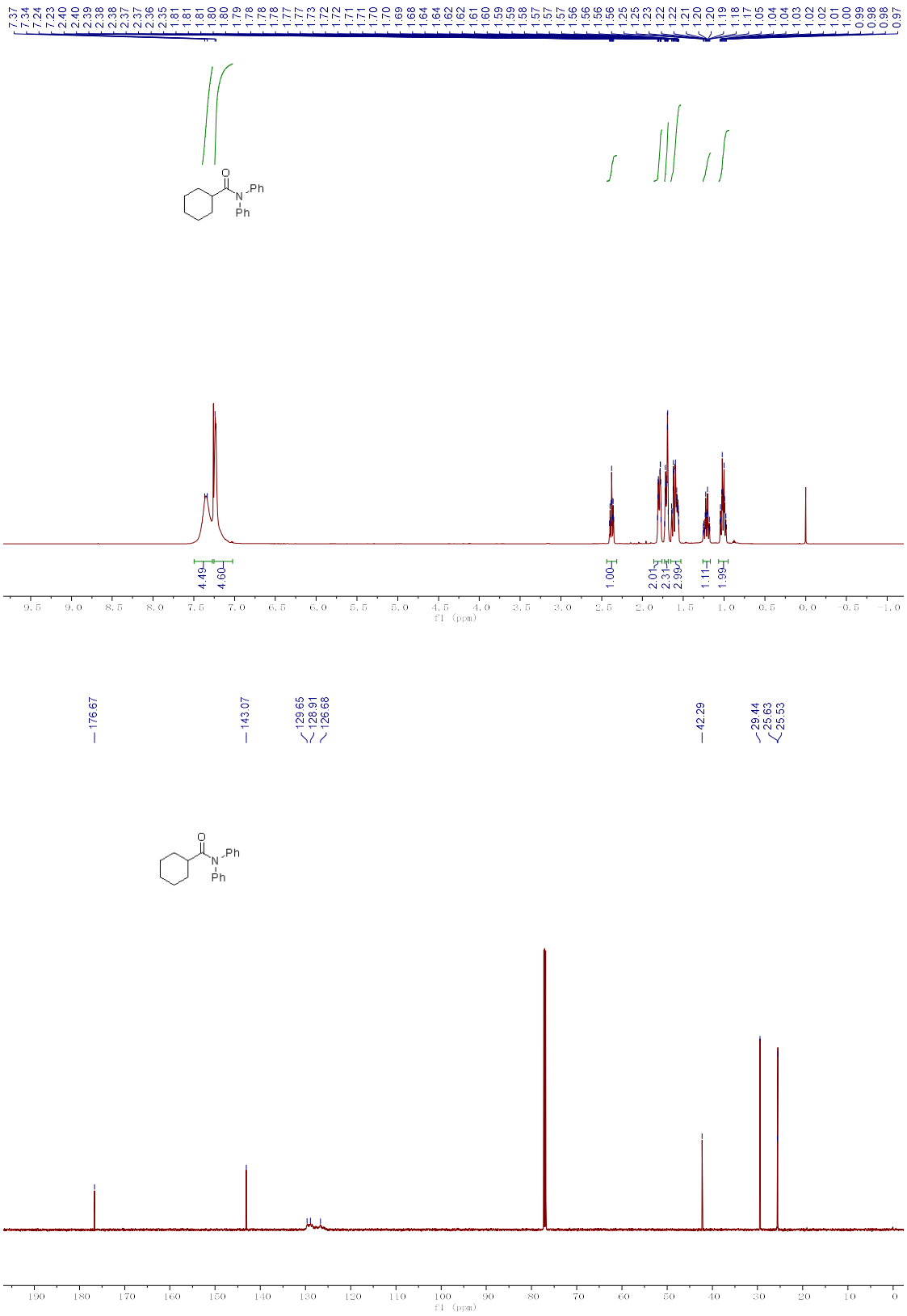


29

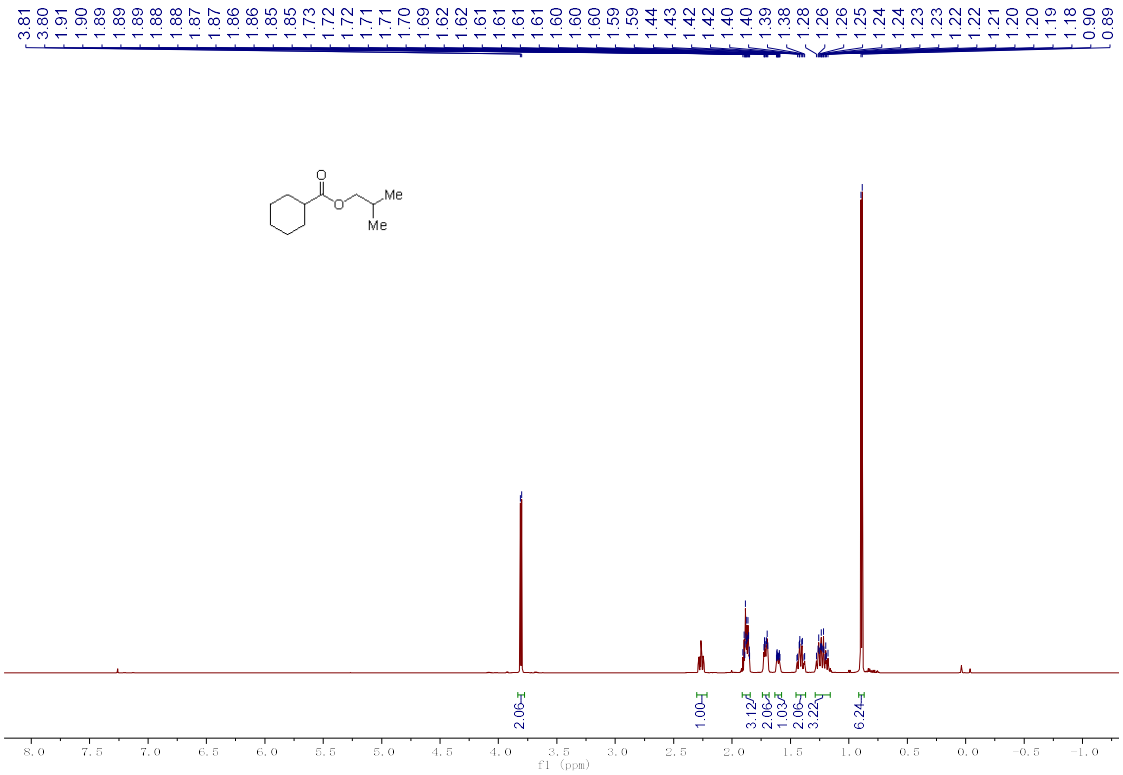

7.86 7.84 7.32 7.32 7.32 7.31 7.31 7.31 7.31 4.30 4.29 4.29 4.28 4.28 4.28 4.27 4.27 4.26 3.48 3.48 3.47 3.47 3.46 3.46 3.44 3.44 3.30 3.30 3.29 3.28 3.28 3.28 3.27 3.27 3.27 3.27 3.26 3.26 3.26 3.25 3.25 3.25 3.24 3.24 3.24 3.23 3.22 3.16 3.16 3.15 3.15 3.14 3.14 3.14 3.13 3.13 3.12 3.11 2.56 2.56 2.55 2.54 2.53 2.53 2.52 2.52 2.44 2.41 2.40 2.38 2.37 2.37 2.36
Me
O
S
O
O
2.00 2.00 1.10 1.08 2.09 1.09 1.10 2.97 1.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

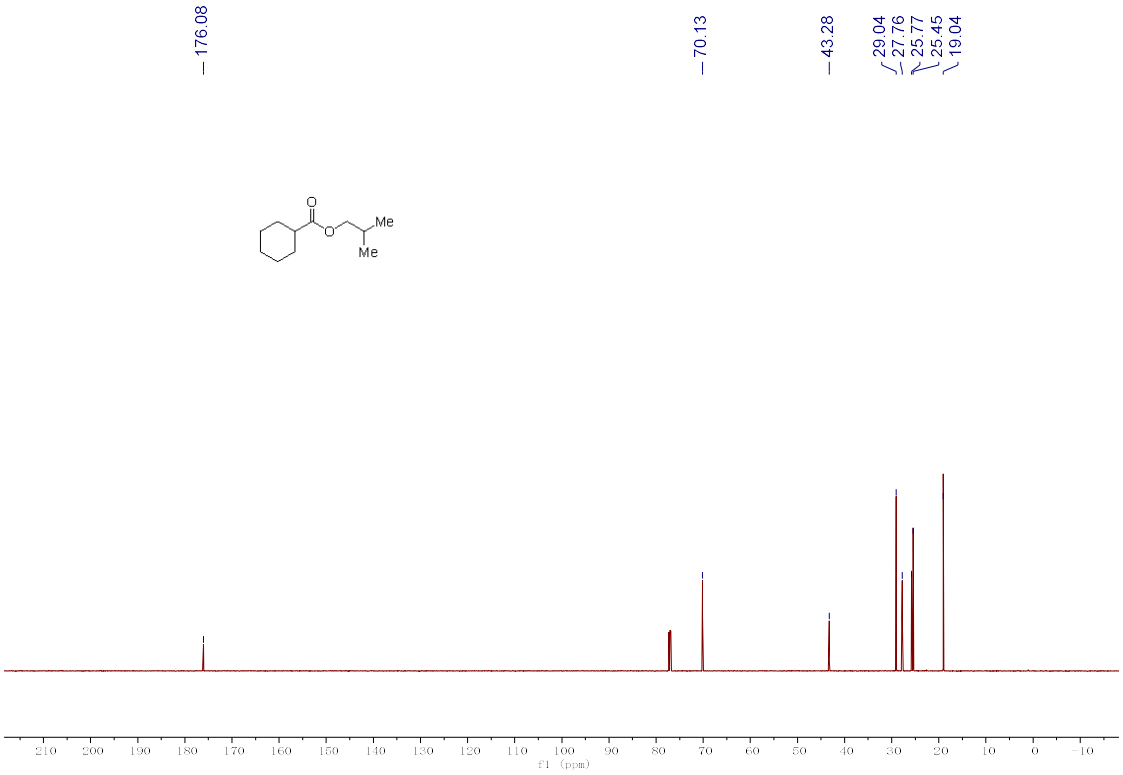

196.27
145.54
132.23
129.98
128.81
52.50
50.75
41.75
25.94
21.88
Me
O
S
O
O
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

31

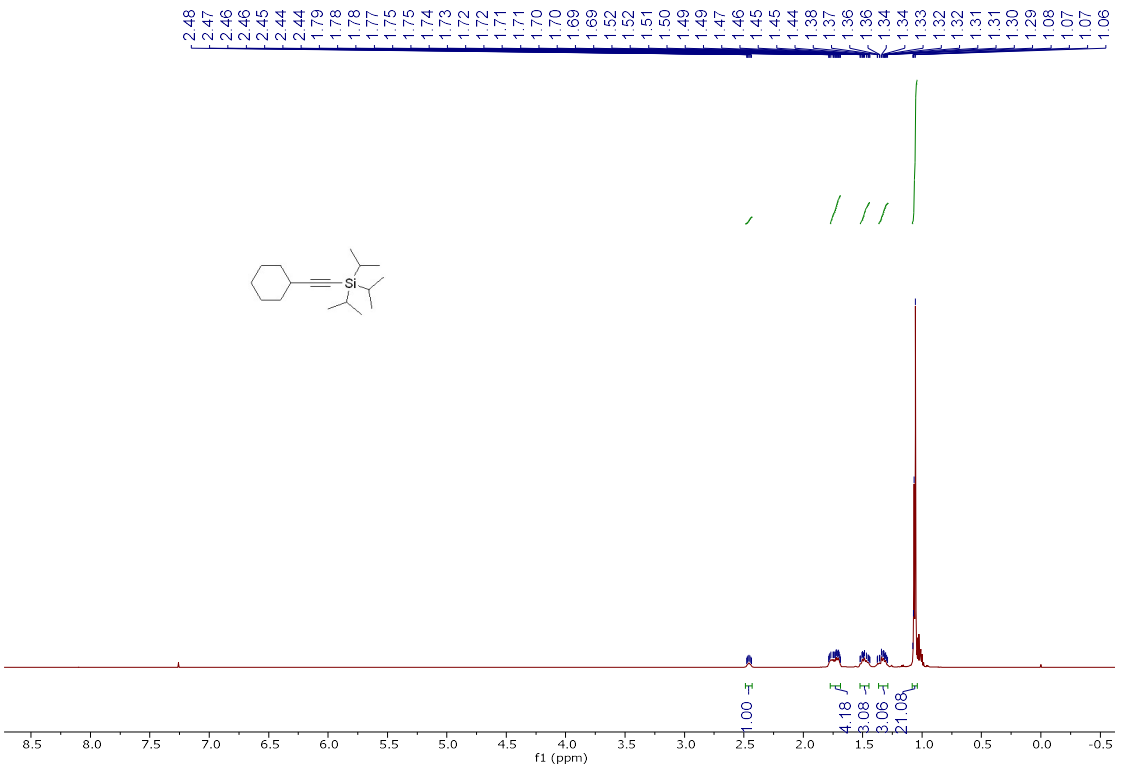

7.37 7.34 7.24 7.23 2.40 2.40 2.39 2.38 2.38 2.37 2.37 2.36 2.35 1.81 1.81 1.81 1.80 1.80 1.79 1.78 1.78 1.78 1.77 1.77 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.68 1.64 1.64 1.62 1.62 1.61 1.60 1.59 1.59 1.58 1.57 1.57 1.57 1.56 1.56 1.56 1.56 1.25 1.25 1.23 1.22 1.22 1.21 1.20 1.20 1.19 1.18 1.17 1.05 1.04 1.04 1.03 1.02 1.02 1.01 1.00 0.99 0.98 0.98 0.97
O
N
Ph
Ph
4.49
4.60
1.00
2.01
2.31
2.99
1.11
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
176.67
143.07
129.65
128.91
126.68
42.29
29.44
25.63
25.53
O
N
Ph
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

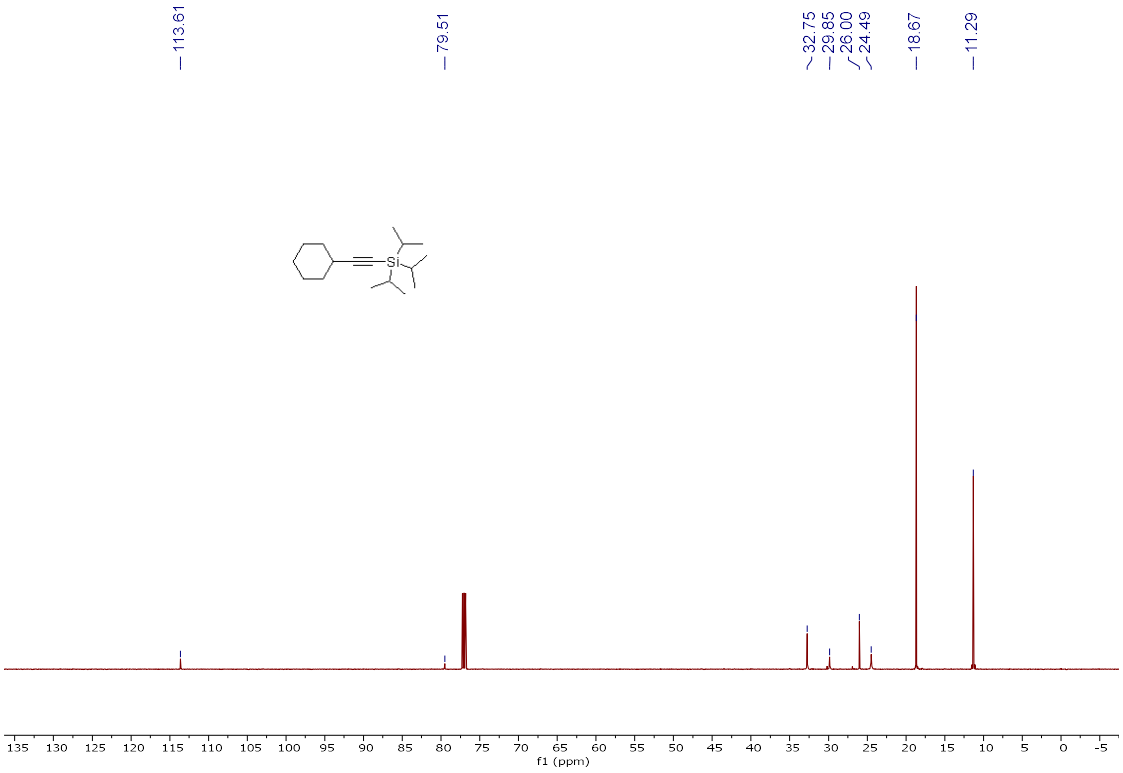
33


3.81 3.80 1.91 1.90 1.89 1.89 1.89 1.88 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.73 1.72 1.72 1.71 1.71 1.70 1.69 1.62 1.62 1.61 1.61 1.61 1.61 1.60 1.60 1.60 1.59 1.59 1.44 1.43 1.42 1.42 1.40 1.40 1.39 1.38 1.28 1.26 1.26 1.25 1.24 1.24 1.23 1.23 1.22 1.22 1.21 1.20 1.20 1.19 1.18 0.90 0.89
O
O
Me
Me
2.06
1.00
3.12
2.06
1.03
2.06
3.22
6.24
f1 (ppm)

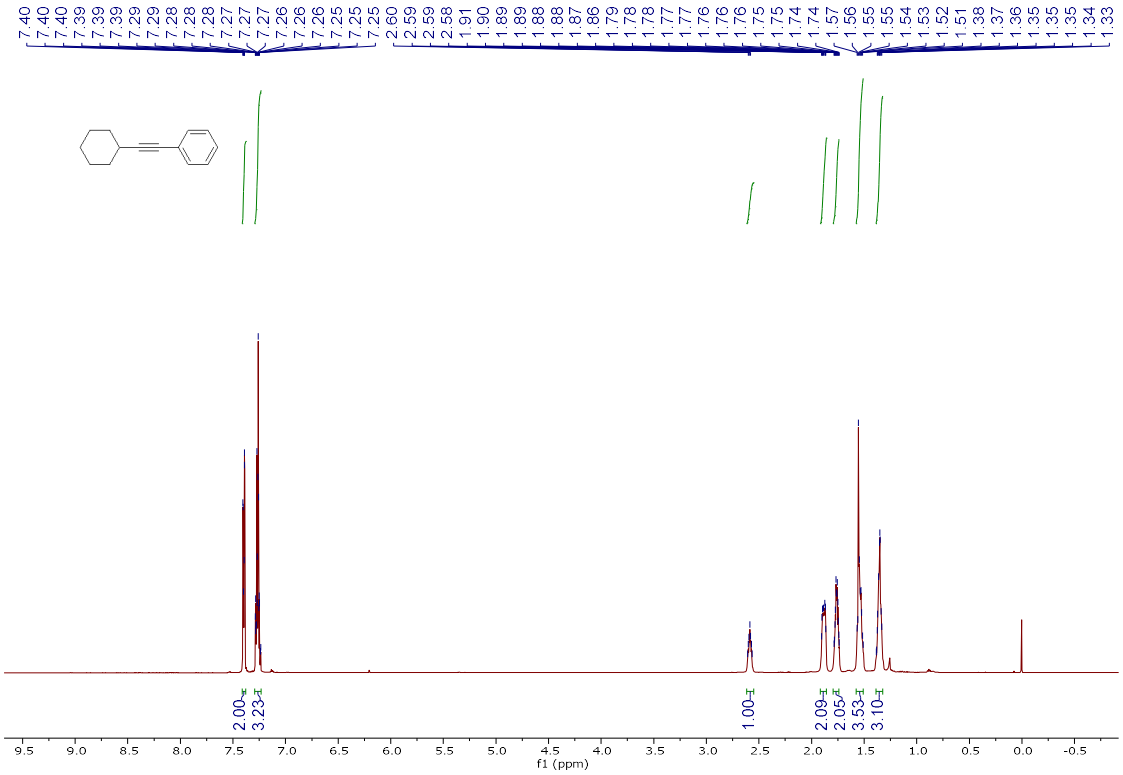

176.08
70.13
43.28
29.04
27.76
25.77
25.45
19.04
O
O
Me
Me
f1 (ppm)

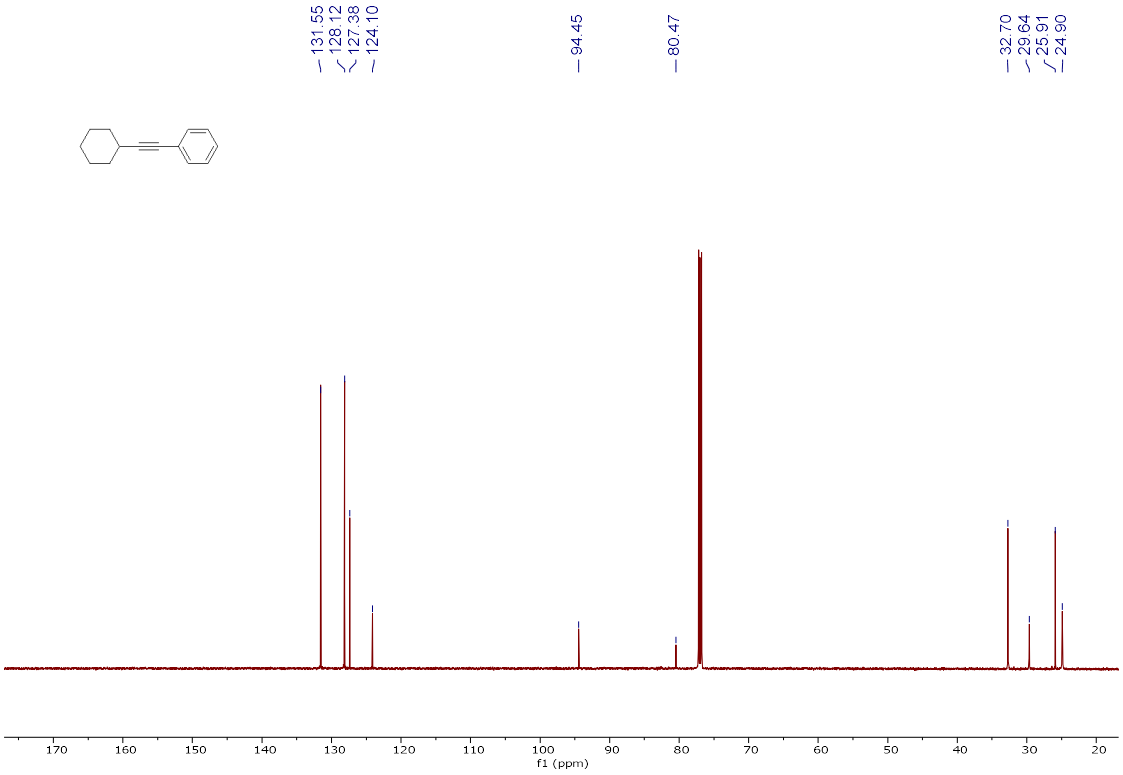
34


2.48
2.47
2.46
2.46
2.45
2.44
2.44
1.79
1.78
1.78
1.77
1.75
1.75
1.74
1.73
1.72
1.72
1.71
1.71
1.70
1.70
1.69
1.69
1.52
1.52
1.51
1.50
1.49
1.49
1.47
1.46
1.45
1.45
1.44
1.38
1.37
1.36
1.36
1.34
1.34
1.33
1.32
1.32
1.31
1.31
1.30
1.29
1.08
1.07
1.07
1.06
Si
1.00
4.18
3.08
3.06
21.08
f1 (ppm)

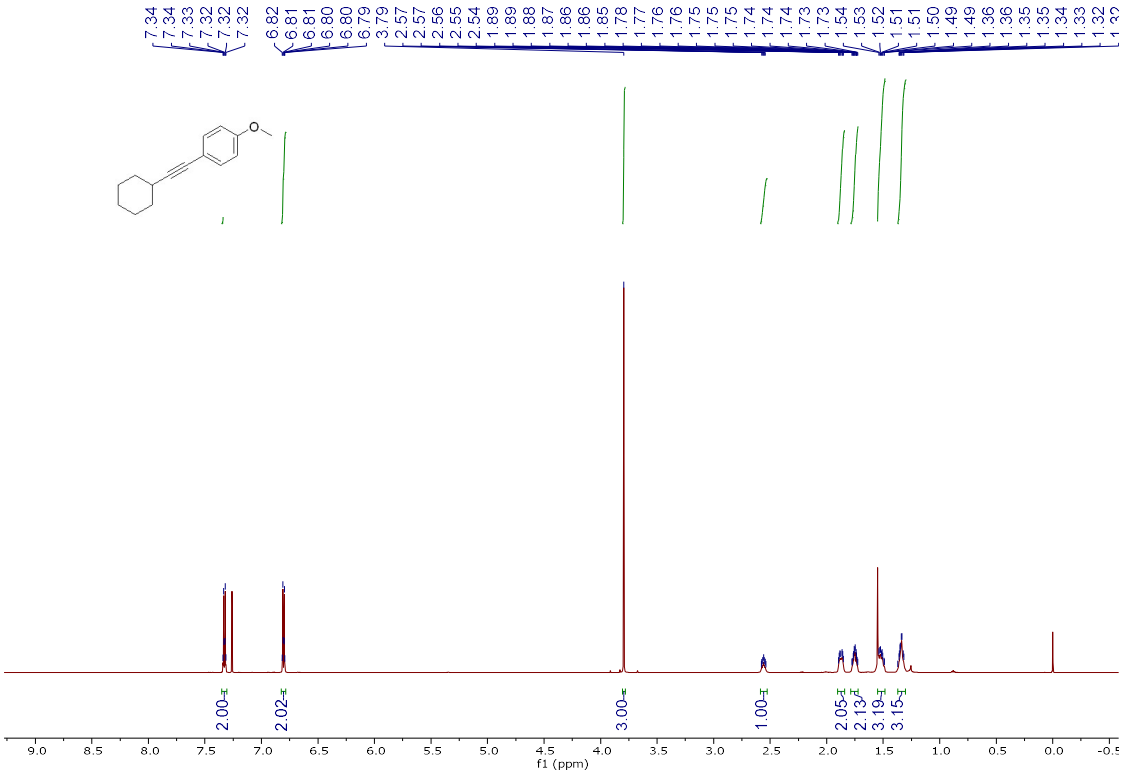

113.61
79.51
32.75
29.85
26.00
24.49
18.67
11.29
Si
f1 (ppm)

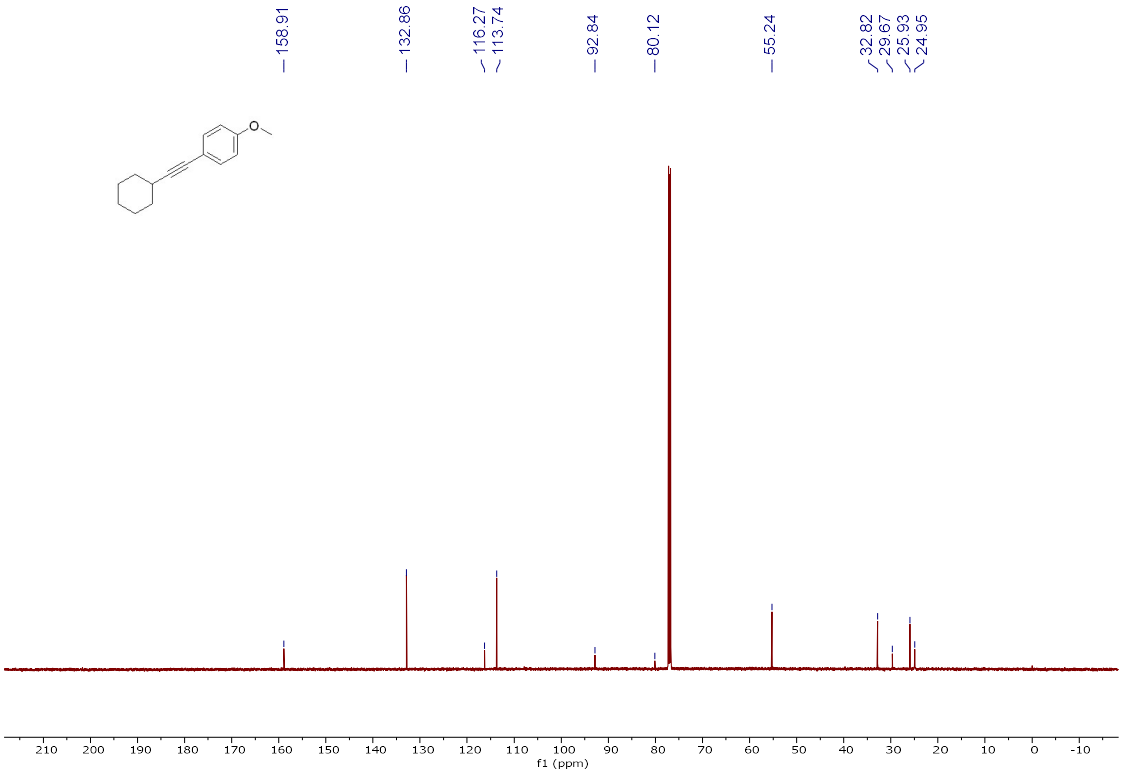
35


7.40 7.40 7.40 7.39 7.39 7.39 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25
2.60 2.59 2.59 2.58 1.91 1.90 1.89 1.89 1.88 1.88 1.87 1.86 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.76 1.75 1.75 1.74 1.74 1.57 1.56 1.55 1.55 1.54 1.53 1.52 1.51 1.38 1.37 1.36 1.35 1.35 1.35 1.34 1.33
2.00
3.23
1.00
2.09
2.05
3.53
3.10
f1 (ppm)

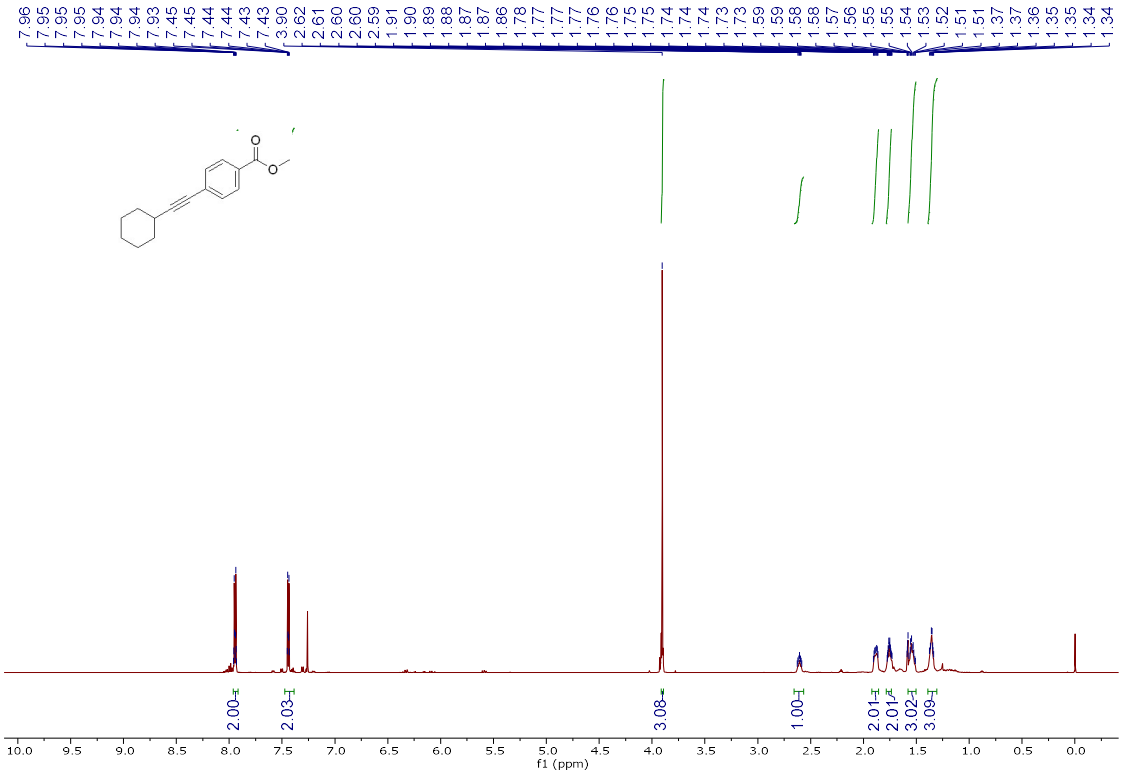

131.55
128.12
127.38
124.10
94.45
80.47
32.70
29.64
25.91
24.90
f1 (ppm)

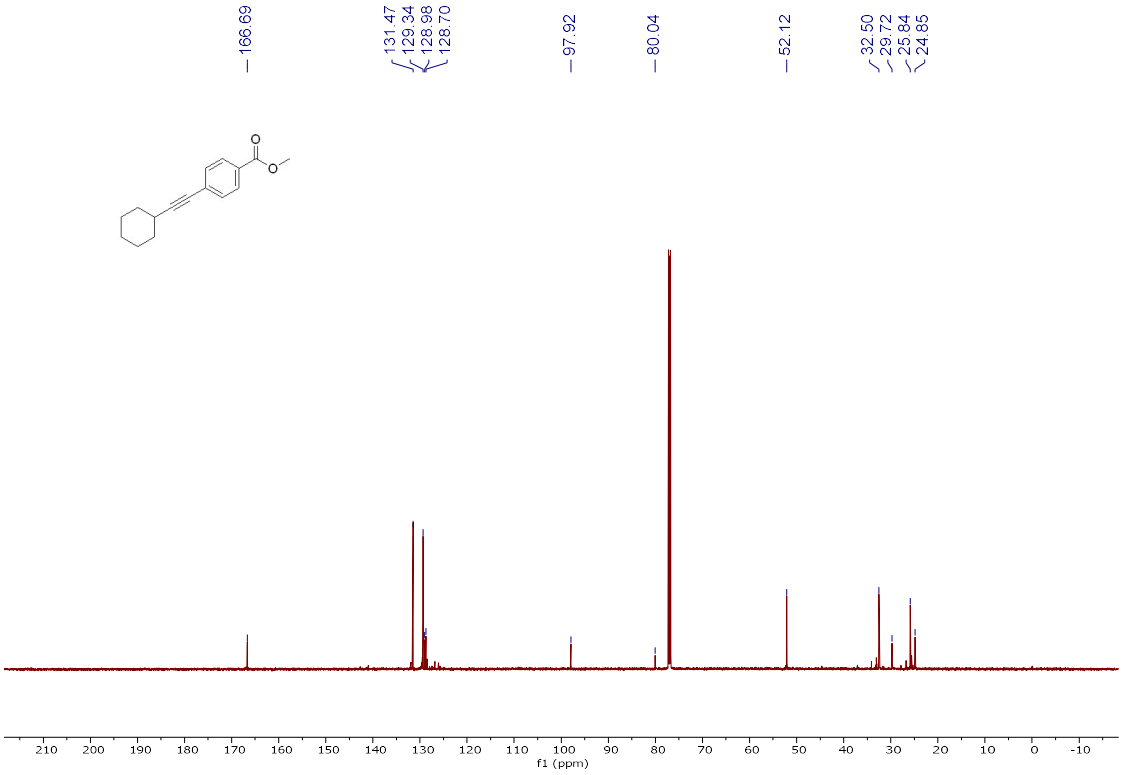
36


7.34
7.34
7.33
7.32
7.32
7.32
6.82
6.81
6.81
6.80
6.80
6.79
3.79
2.57
2.57
2.56
2.55
2.54
1.89
1.89
1.88
1.87
1.86
1.86
1.85
1.78
1.77
1.76
1.76
1.75
1.75
1.75
1.74
1.74
1.74
1.73
1.73
1.54
1.53
1.52
1.51
1.51
1.50
1.49
1.49
1.36
1.36
1.35
1.35
1.34
1.33
1.32
2.00
2.02
3.00
1.00
2.05
2.13
3.19
3.15
f1 (ppm)

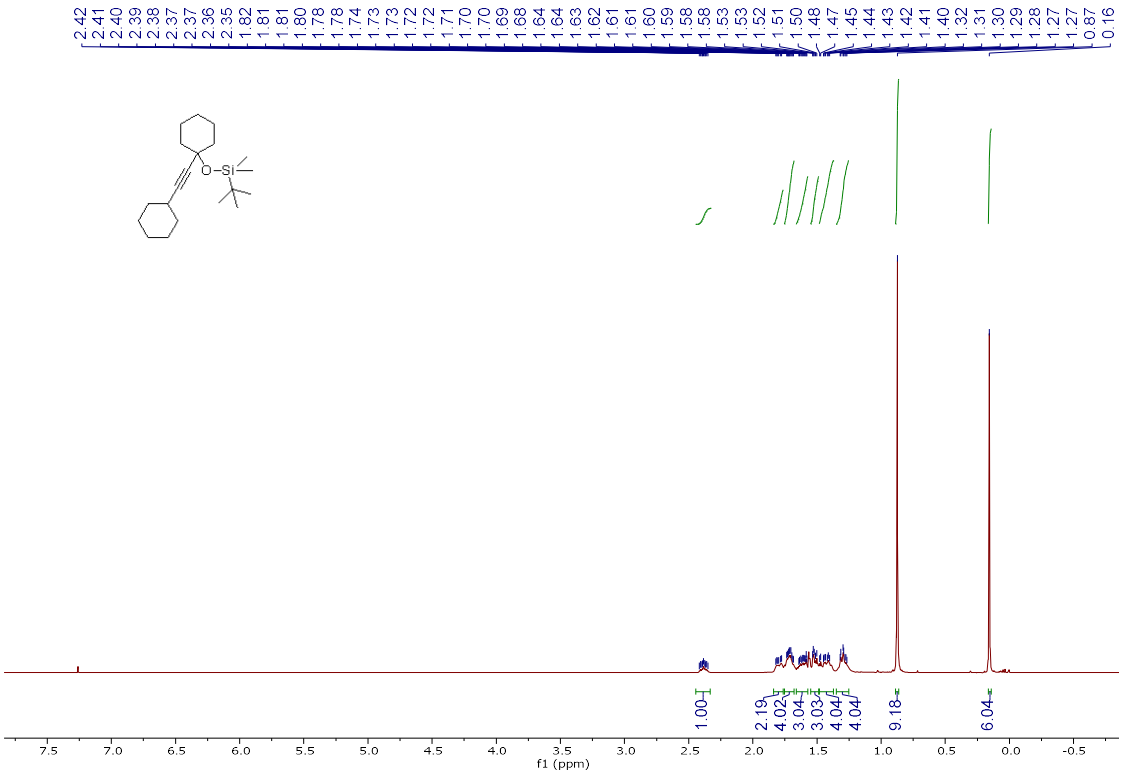

158.91
132.86
116.27
113.74
92.84
80.12
55.24
32.82
29.67
25.93
24.95
f1 (ppm)

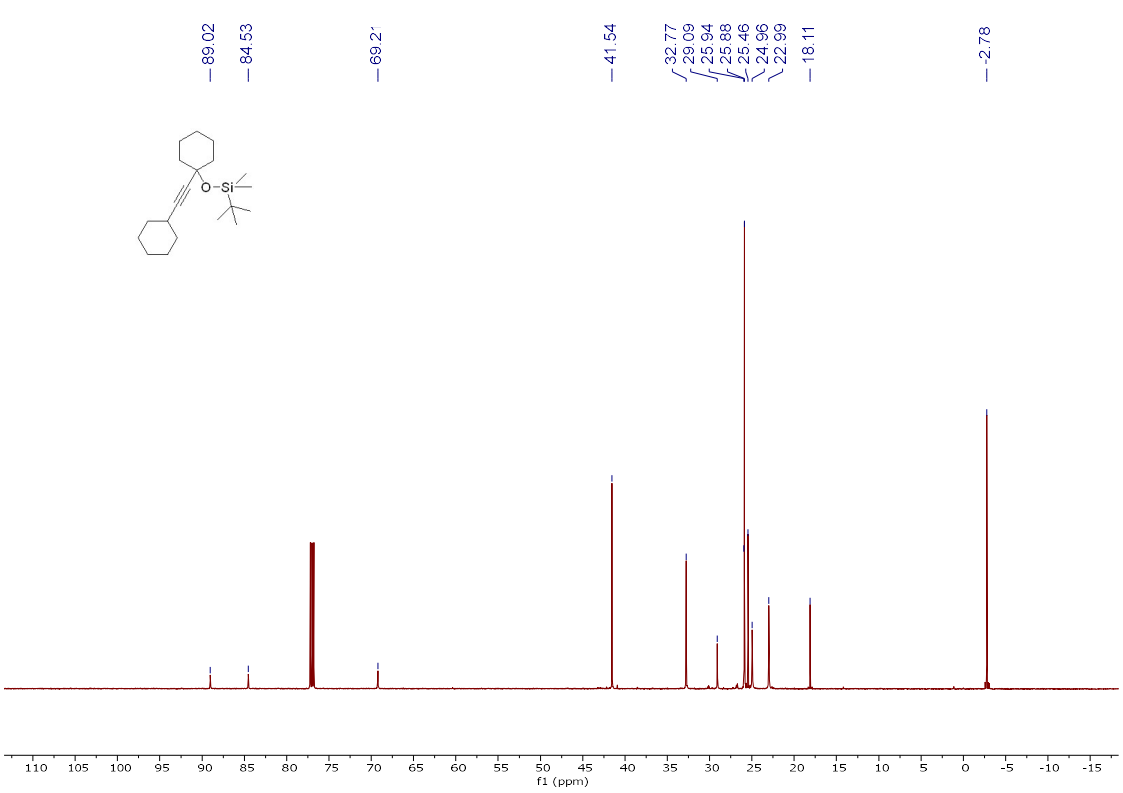
37


7.96 7.95 7.95 7.95 7.94 7.94 7.94 7.93 7.45 7.45 7.44 7.44 7.43 7.43 3.90 2.62 2.61 2.60 2.60 2.59 1.91 1.90 1.89 1.88 1.87 1.87 1.86 1.78 1.77 1.77 1.77 1.76 1.76 1.75 1.75 1.74 1.74 1.74 1.73 1.73 1.59 1.59 1.58 1.58 1.57 1.56 1.55 1.55 1.54 1.53 1.52 1.51 1.51 1.37 1.37 1.36 1.35 1.35 1.34 1.34
2.00 2.03 3.08 1.00 2.01 2.01 3.02 3.09
f1 (ppm)

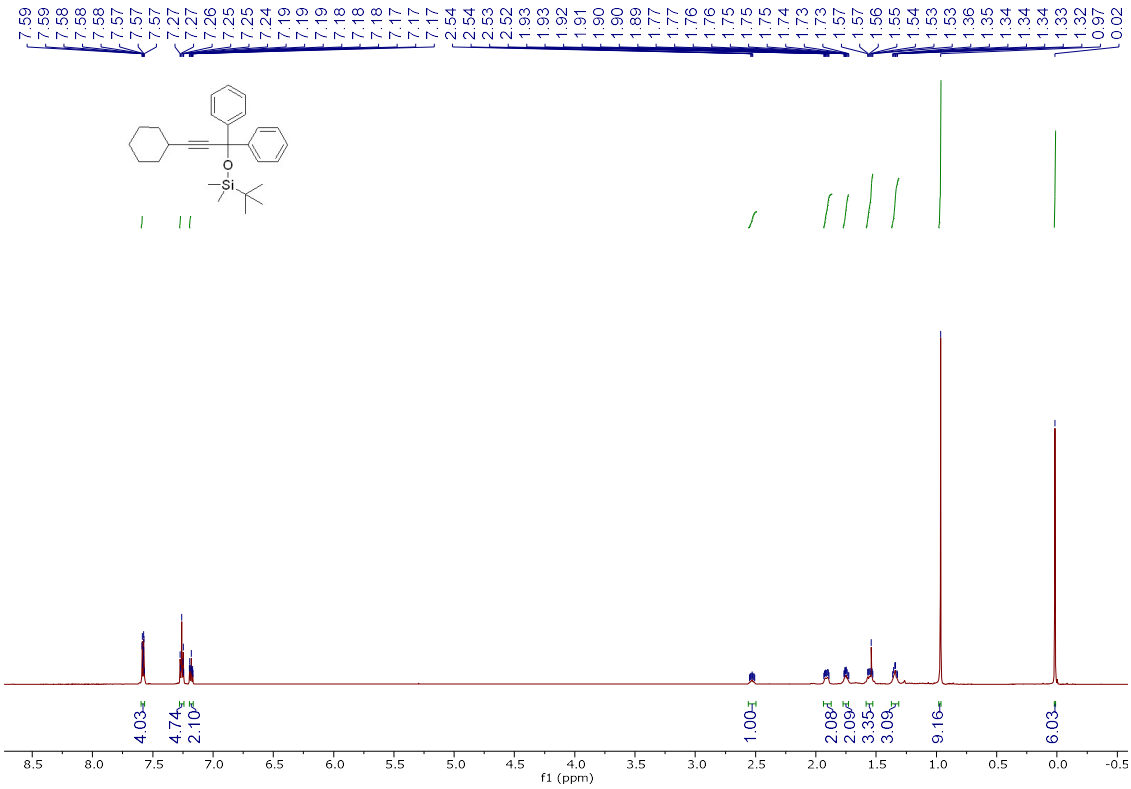

166.69
131.47
129.34
128.98
128.70
97.92
80.04
52.12
32.50
29.72
25.84
24.85
f1 (ppm)

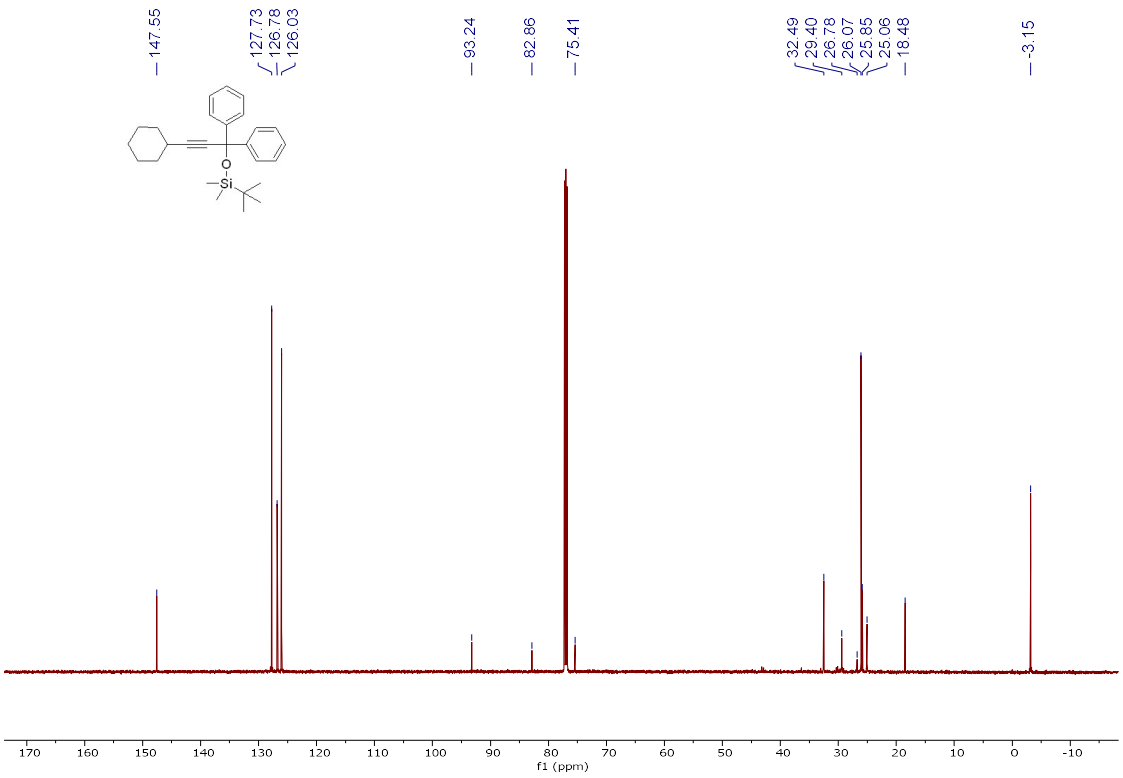
38


2.42 2.41 2.40 2.39 2.38 2.37 2.37 2.36 2.35 1.82 1.81 1.81 1.80 1.78 1.78 1.74 1.73 1.73 1.72 1.72 1.71 1.70 1.70 1.69 1.68 1.64 1.64 1.63 1.62 1.61 1.61 1.60 1.59 1.58 1.58 1.53 1.53 1.52 1.51 1.50 1.48 1.47 1.45 1.44 1.43 1.42 1.41 1.40 1.32 1.31 1.30 1.29 1.28 1.27 1.27 0.87 0.16
O–Si
1.00 2.19 4.02 3.04 3.03 4.04 4.04 9.18 6.04
f1 (ppm)

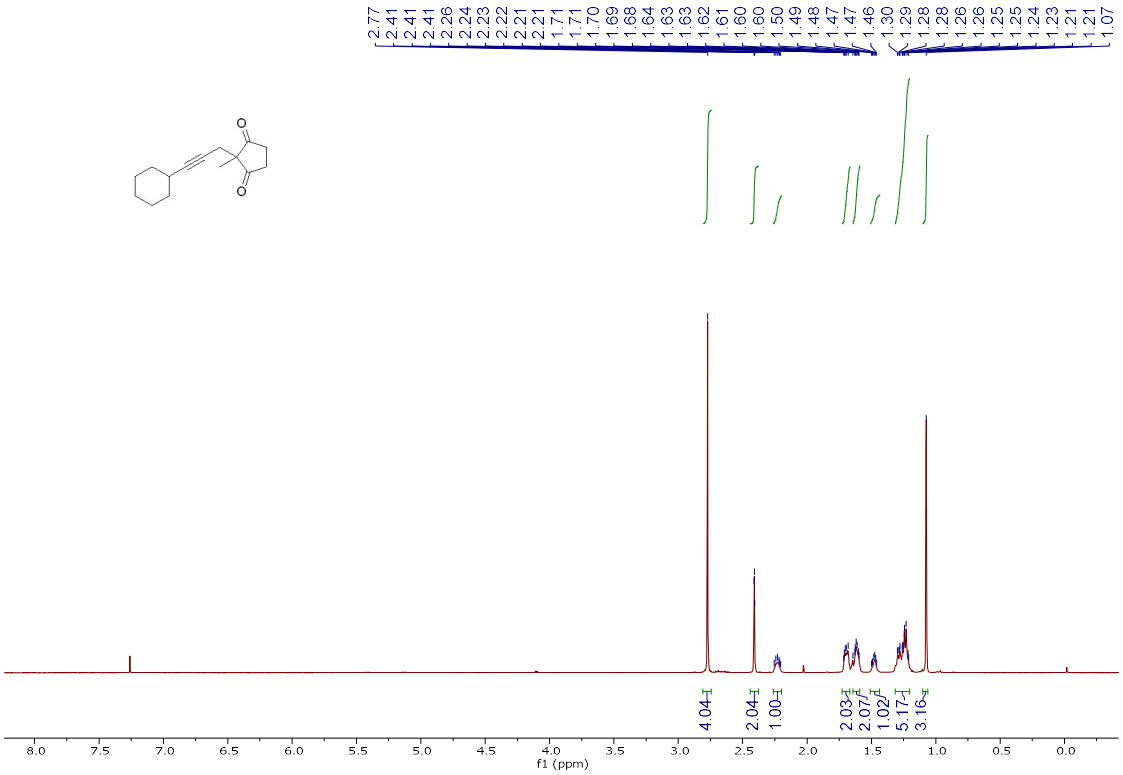

89.02 84.53 69.2 41.54 32.77 29.09 25.94 25.88 25.46 24.96 22.99 18.11 -2.78
O–Si
f1 (ppm)

39


7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.57 7.27 7.27 7.26 7.25 7.25 7.24 7.19 7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.17 2.54 2.54 2.53 2.52 1.93 1.93 1.92 1.91 1.90 1.90 1.89 1.77 1.77 1.76 1.76 1.75 1.75 1.74 1.73 1.73 1.57 1.56 1.55 1.54 1.53 1.53 1.36 1.35 1.34 1.34 1.34 1.33 1.32 0.97 0.02
O
Si
4.03 4.74 2.10 1.00 2.08 2.09 3.35 3.09 9.16 6.03
f1 (ppm)


147.55 127.73 126.78 126.03 93.24 82.86 75.41 32.49 29.40 26.78 26.07 25.85 25.06 18.48 -3.15
O
Si
f1 (ppm)

40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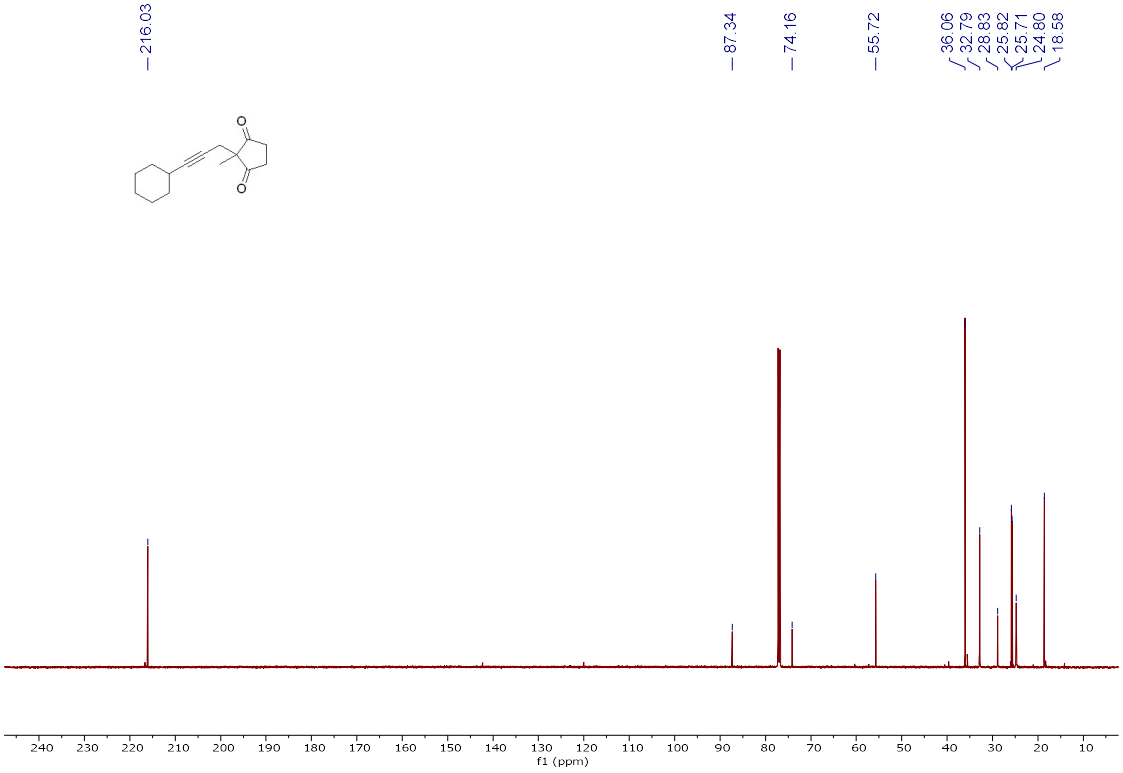
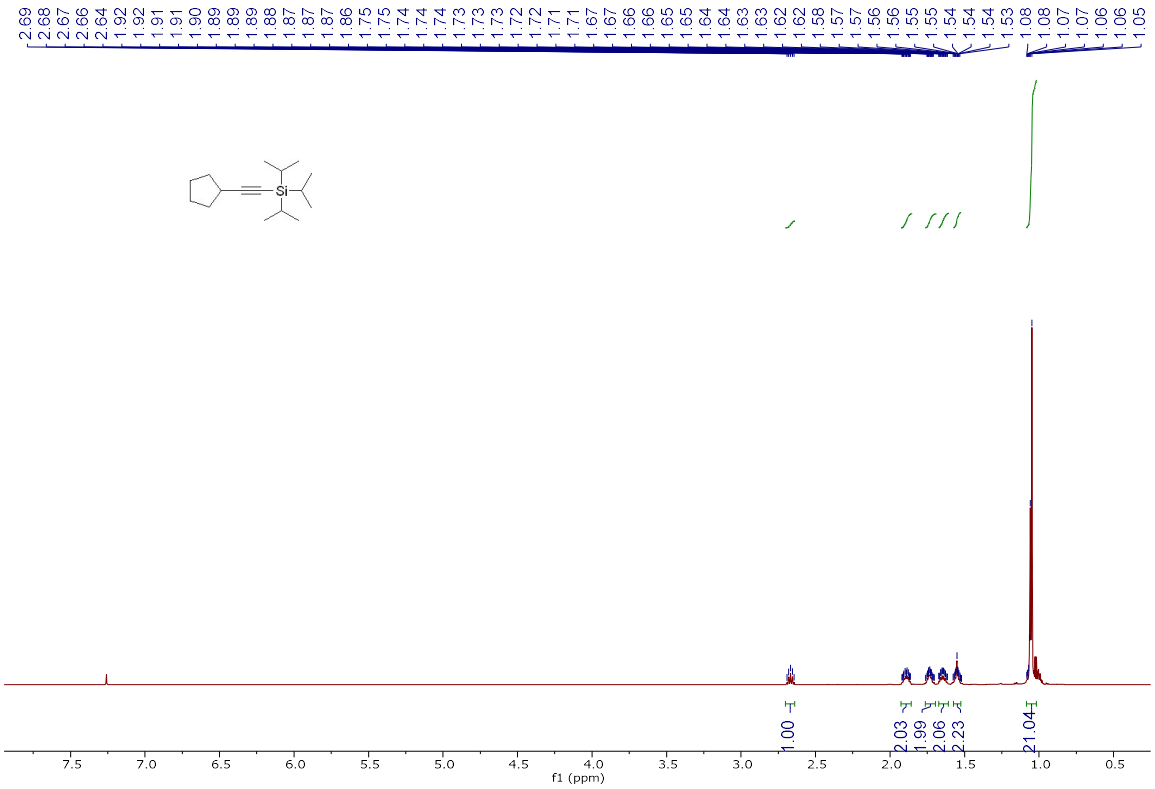
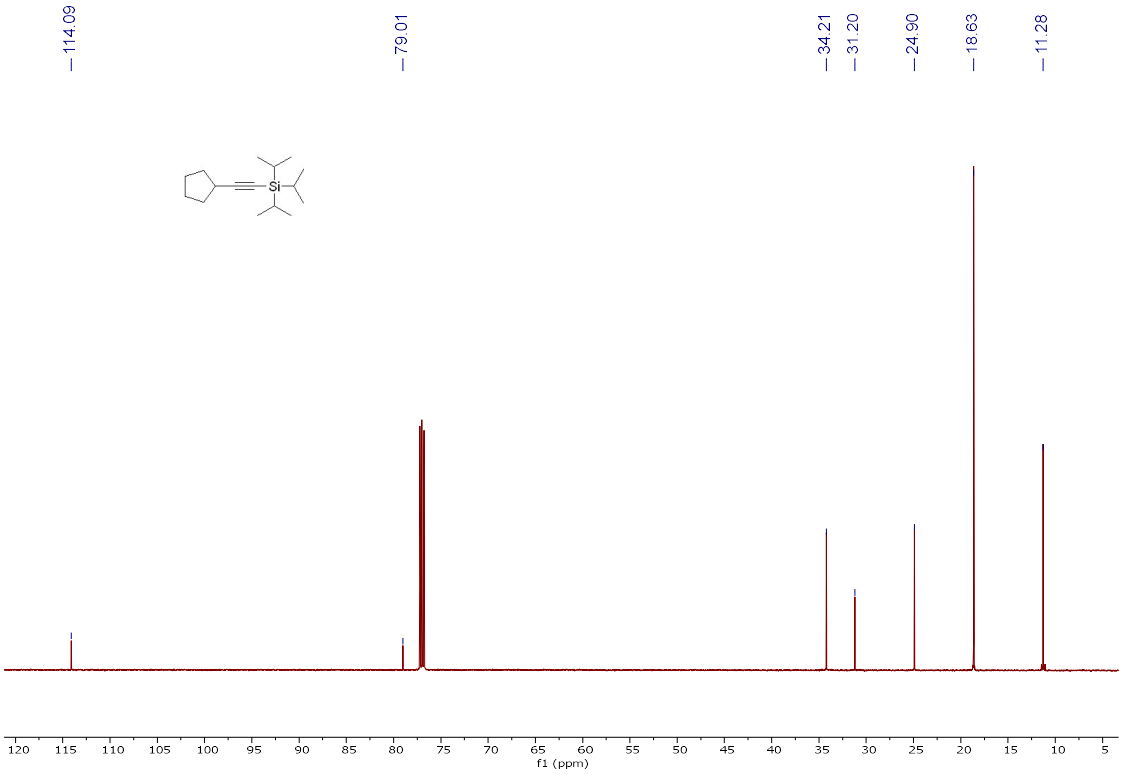
2.41
2.41
2.26
2.24
2.23
2.22
2.21
2.21
1.71
1.71
1.70
1.69
1.68
1.64
1.63
1.63
1.62
1.61
1.60
1.60
1.50
1.49
1.48
1.47
1.47
1.46
1.30
1.29
1.28
1.28
1.26
1.26
1.25
1.25
1.24
1.23
1.21
1.21
1.07
O
O
4.04
2.04
1.00
2.03
2.07
1.02
5.17
3.16
f1 (ppm)

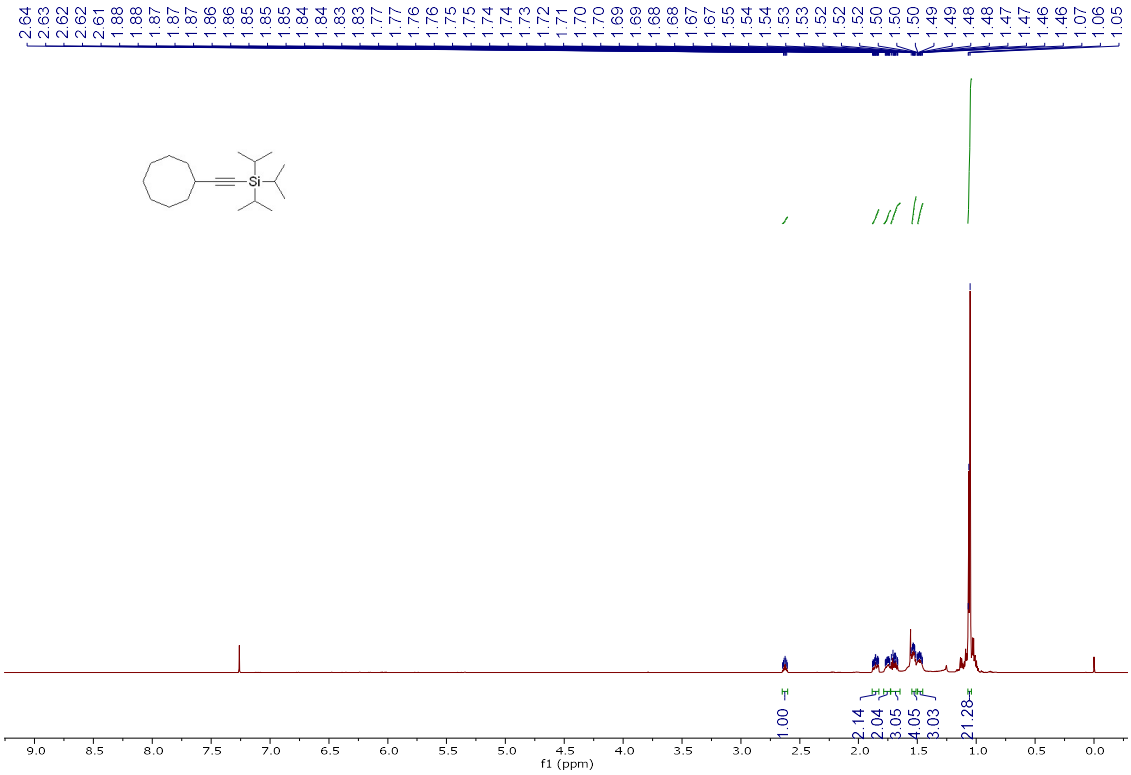

216.03
87.34
74.16
55.72
36.06
32.79
28.83
25.82
25.71
24.80
18.58
O
O
f1 (ppm)

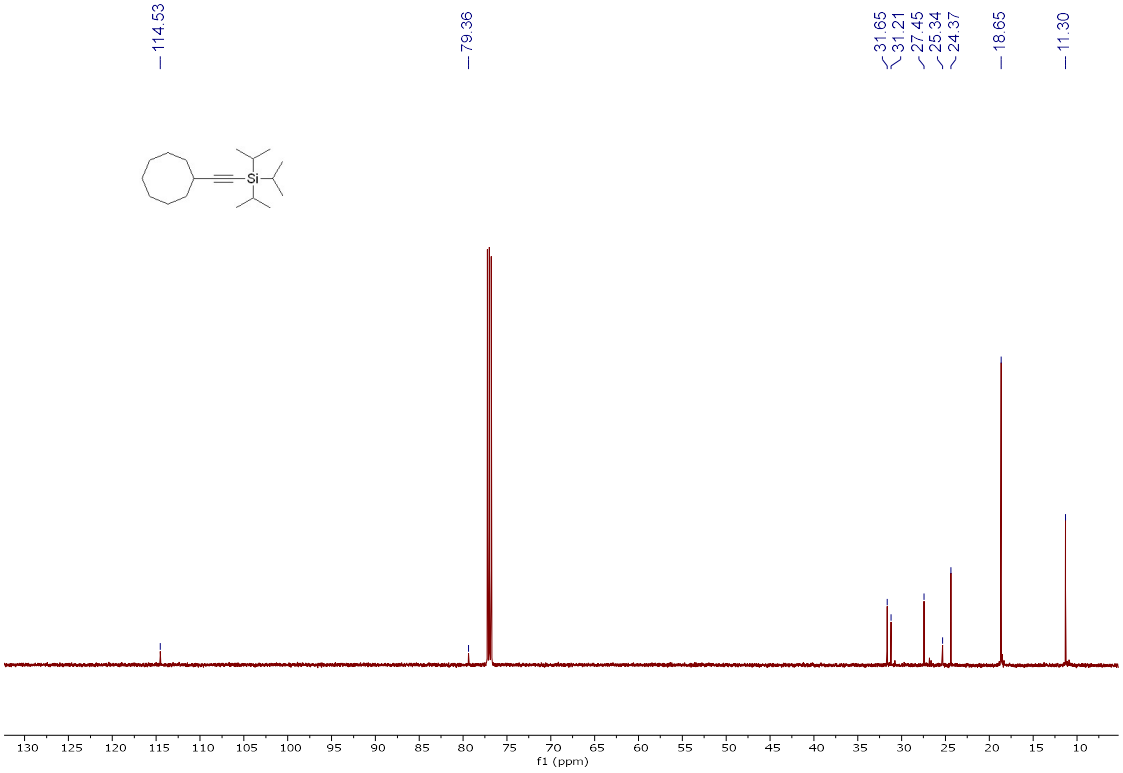
41


2.69 2.68 2.67 2.66 2.64 1.92 1.92 1.91 1.91 1.90 1.89 1.89 1.89 1.88 1.87 1.87 1.87 1.86 1.75 1.75 1.74 1.74 1.74 1.73 1.73 1.73 1.72 1.72 1.71 1.71 1.67 1.67 1.66 1.66 1.65 1.65 1.64 1.64 1.63 1.63 1.62 1.62 1.58 1.57 1.57 1.56 1.56 1.55 1.55 1.54 1.54 1.54 1.53 1.08 1.08 1.07 1.07 1.06 1.06 1.05
Si
1.00
2.03
1.99
2.06
2.23
21.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

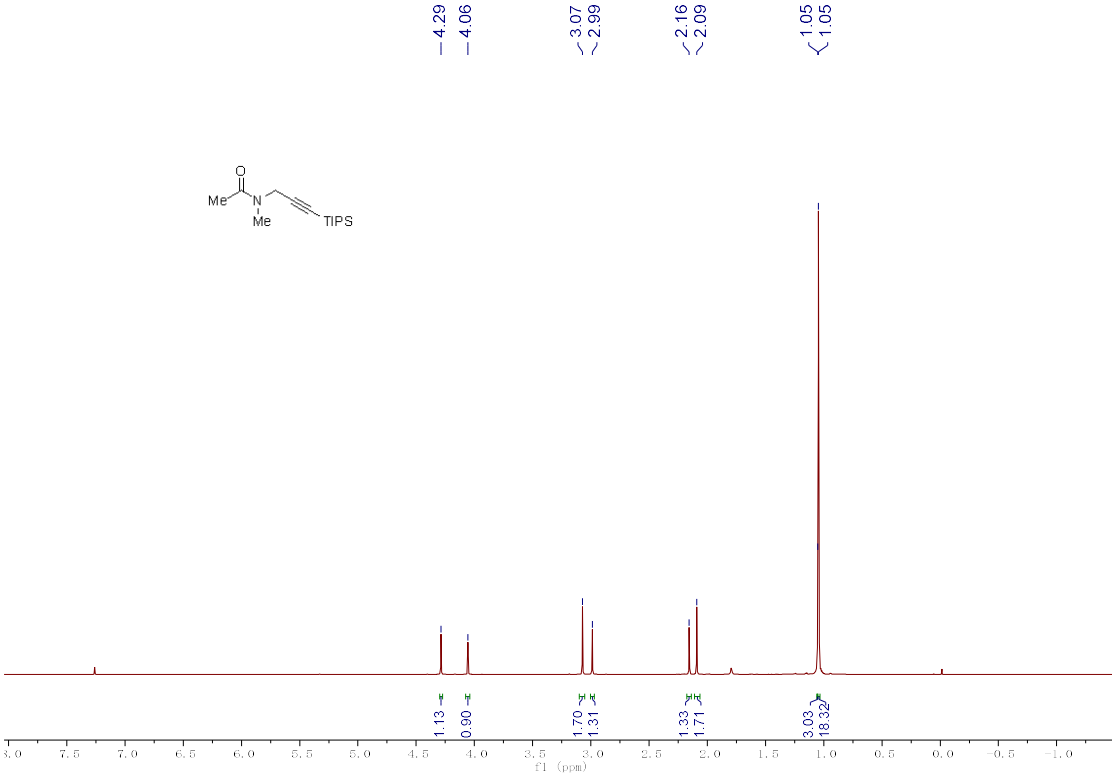

114.09
79.01
34.21
31.20
24.90
18.63
11.28
Si
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

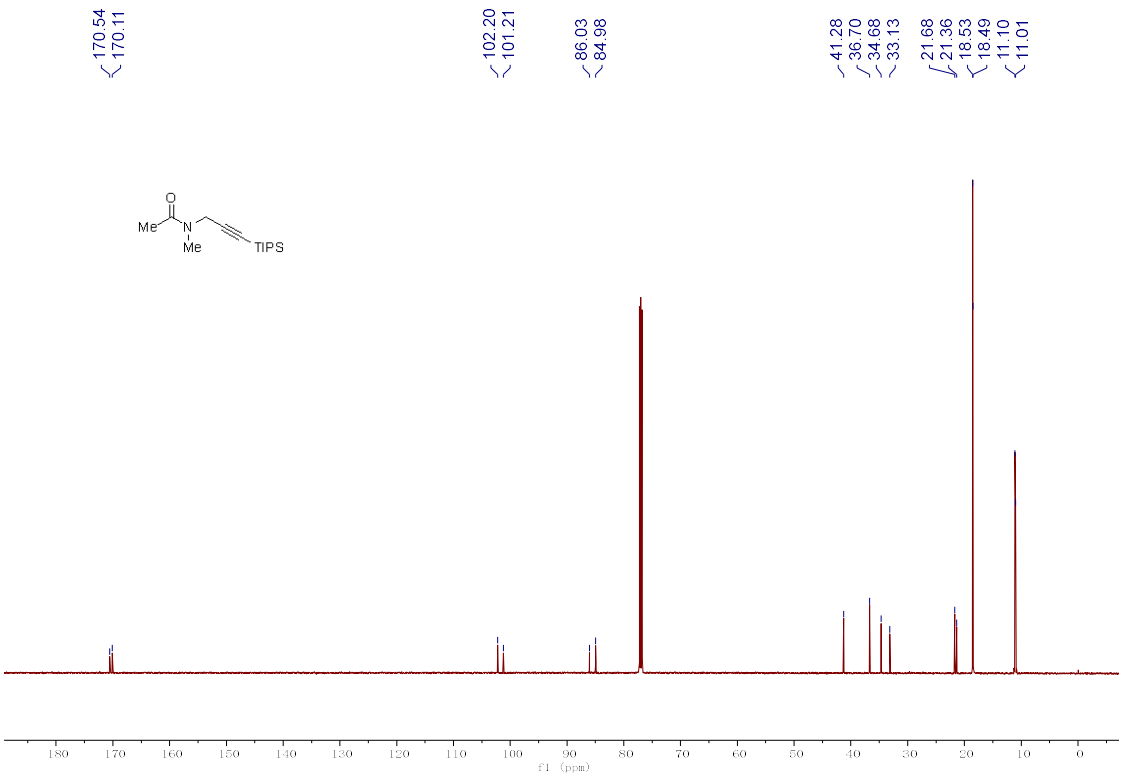
42


2.64 2.63 2.62 2.62 2.61 1.88 1.87 1.87 1.87 1.86 1.86 1.85 1.85 1.85 1.84 1.84 1.83 1.83 1.77 1.77 1.76 1.76 1.75 1.75 1.74 1.74 1.73 1.72 1.71 1.70 1.70 1.69 1.69 1.68 1.68 1.67 1.67 1.55 1.54 1.54 1.53 1.53 1.52 1.52 1.52 1.50 1.50 1.50 1.49 1.49 1.48 1.48 1.47 1.47 1.46 1.46 1.07 1.06 1.05
Si
1.00 2.14 2.04 3.05 4.05 3.03 21.28
f1 (ppm)

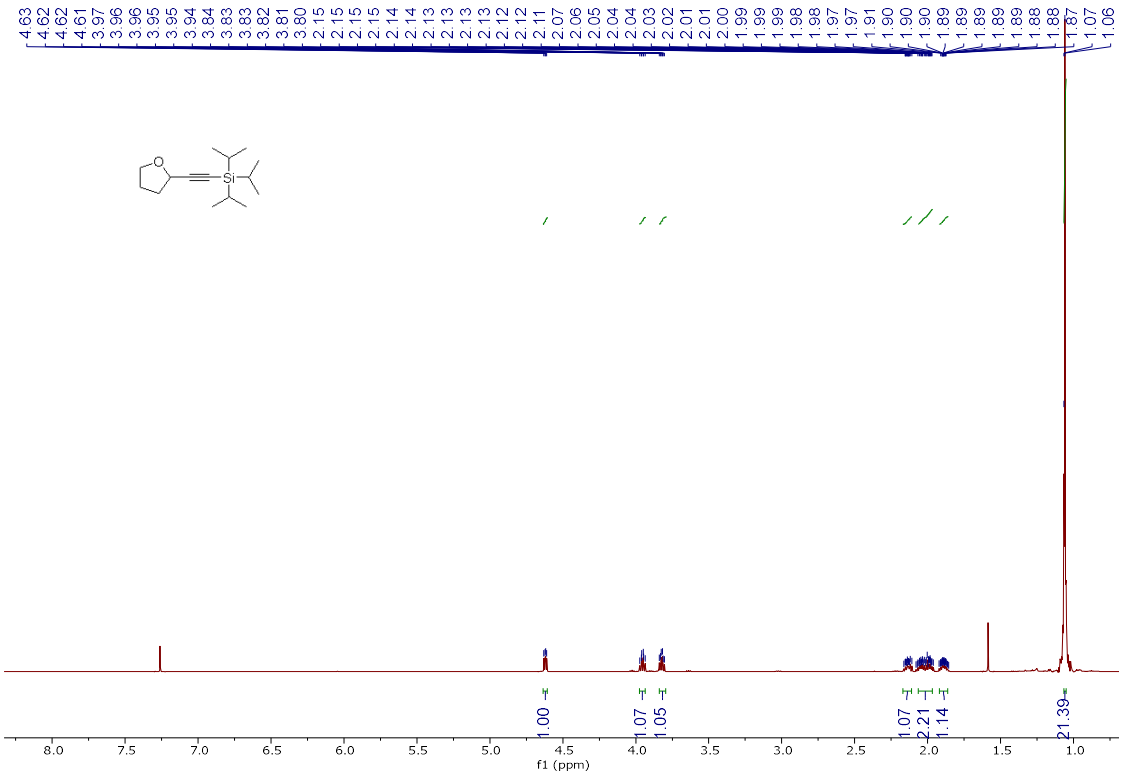

114.53
79.36
31.65
31.21
27.45
25.34
24.37
18.65
11.30
Si
f1 (ppm)

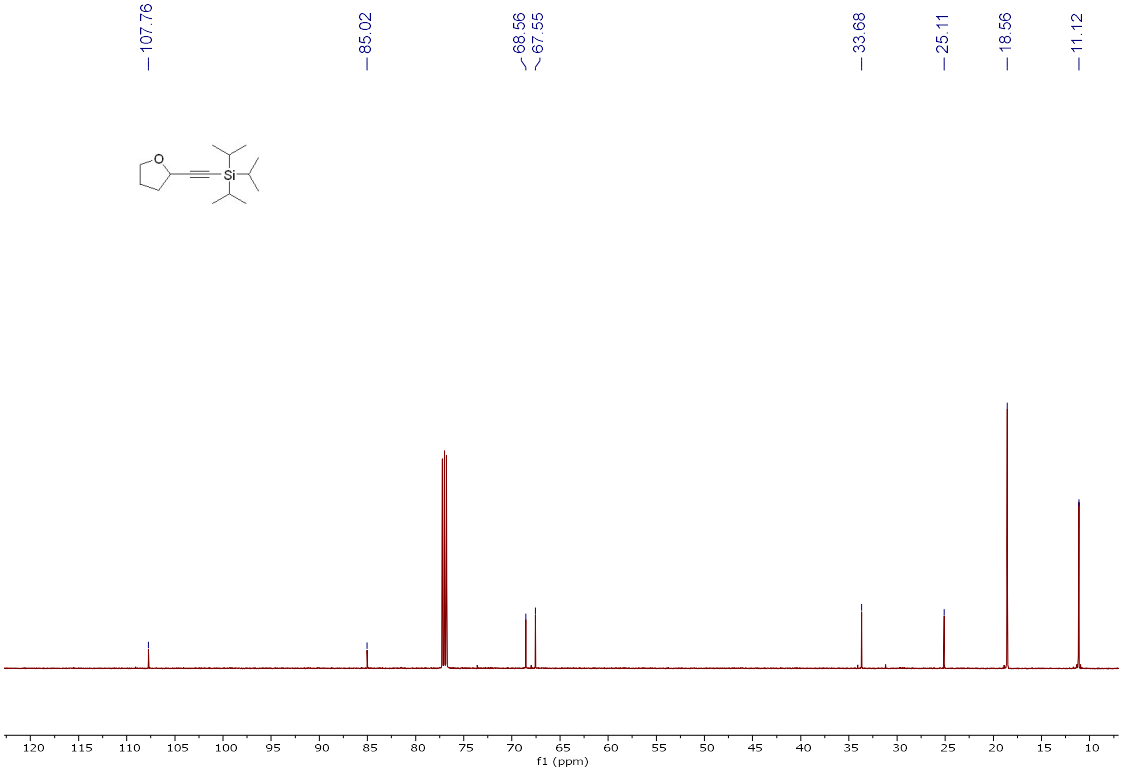
43


4.29
4.06
3.07
2.99
2.16
2.09
1.05
1.05
Me
N
Me
TIPS
1.13
0.90
1.70
1.31
1.33
1.71
3.03
18.32
f1 (ppm)

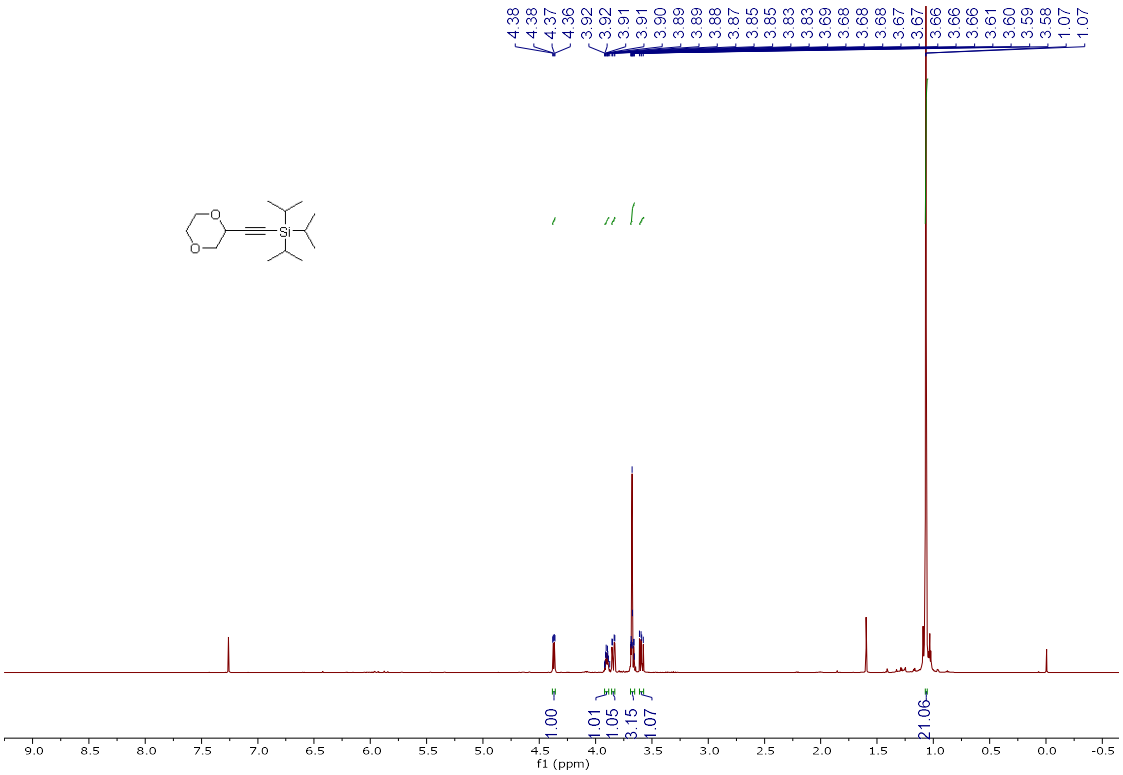

170.54
170.11
102.20
101.21
86.03
84.98
41.28
36.70
34.68
33.13
21.68
21.36
18.53
18.49
11.10
11.01
Me
N
Me
TIPS
f1 (ppm)

44


4.63 4.62 4.62 4.61 3.97 3.96 3.96 3.95 3.95 3.94 3.84 3.83 3.83 3.82 3.81 3.80 2.15 2.15 2.15 2.14 2.14 2.13 2.13 2.13 2.12 2.12 2.11 2.07 2.06 2.05 2.04 2.04 2.03 2.02 2.01 2.01 2.00 1.99 1.99 1.99 1.98 1.98 1.97 1.97 1.91 1.90 1.90 1.90 1.89 1.89 1.89 1.89 1.88 1.88 1.87 1.07 1.06
O
Si
1.00
1.07
1.05
1.07
2.21
1.14
21.39
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


107.76
85.02
68.56
67.55
33.68
25.11
18.56
11.12
O
Si
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

45


4.38
4.38
4.37
4.36
3.92
3.92
3.91
3.91
3.90
3.89
3.89
3.88
3.87
3.85
3.85
3.83
3.83
3.69
3.68
3.68
3.67
3.67
3.66
3.66
3.66
3.61
3.60
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Si
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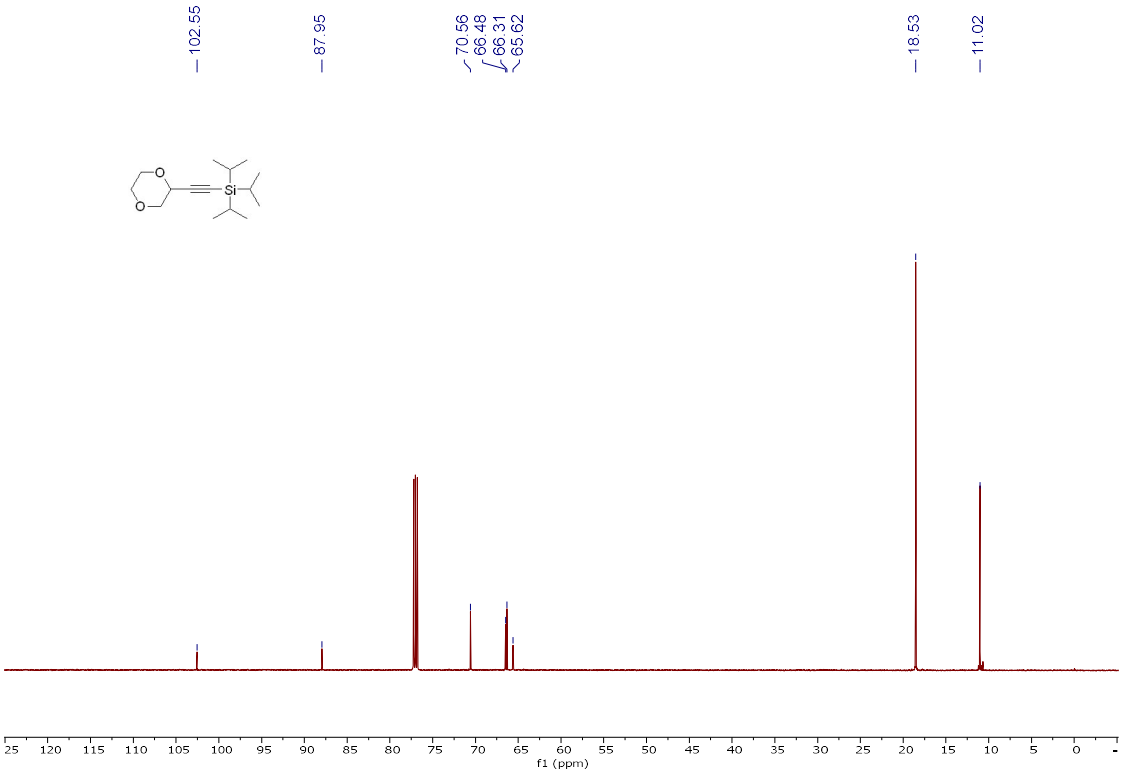
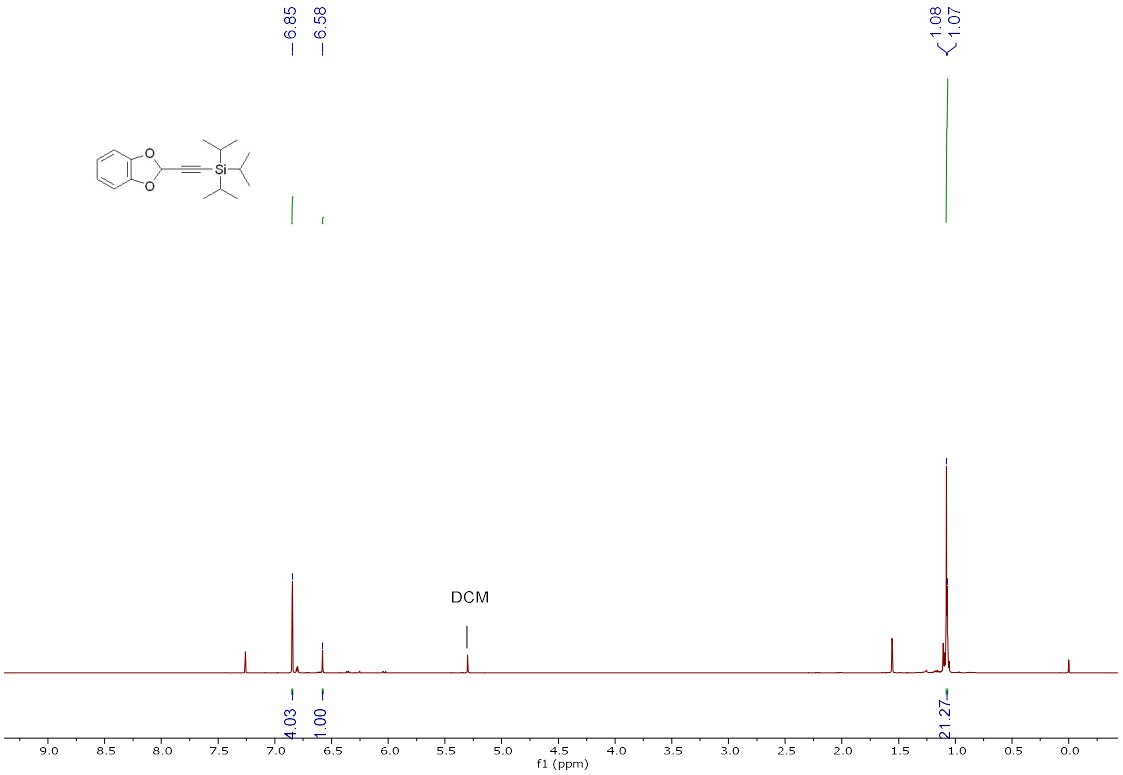
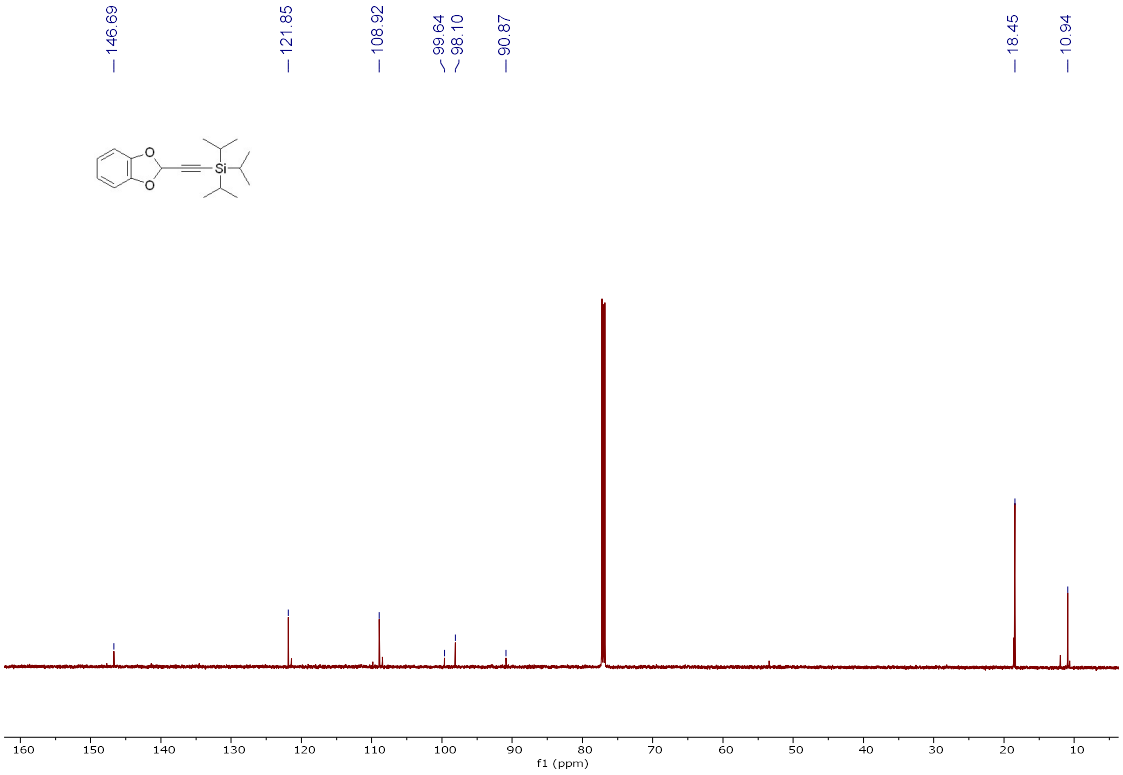
1.05
3.15
1.07
21.06
f1 (ppm)

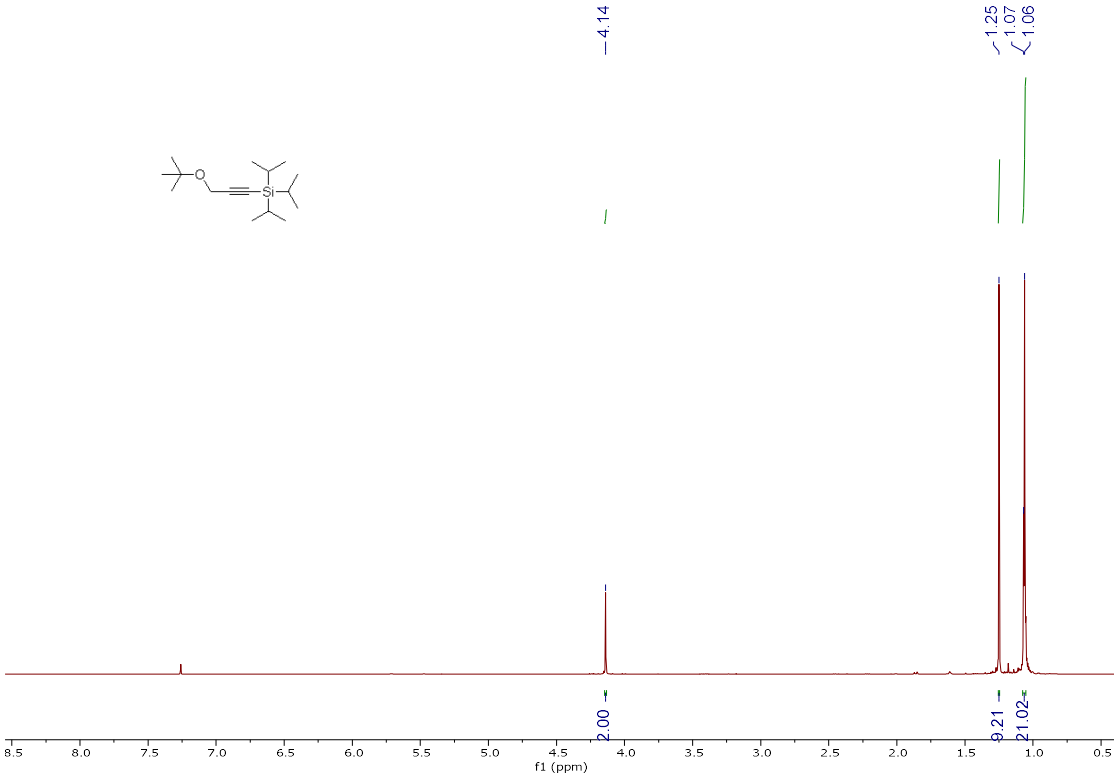

102.55
87.95
70.56
66.48
66.31
65.62
18.53
11.02
Si
f1 (ppm)

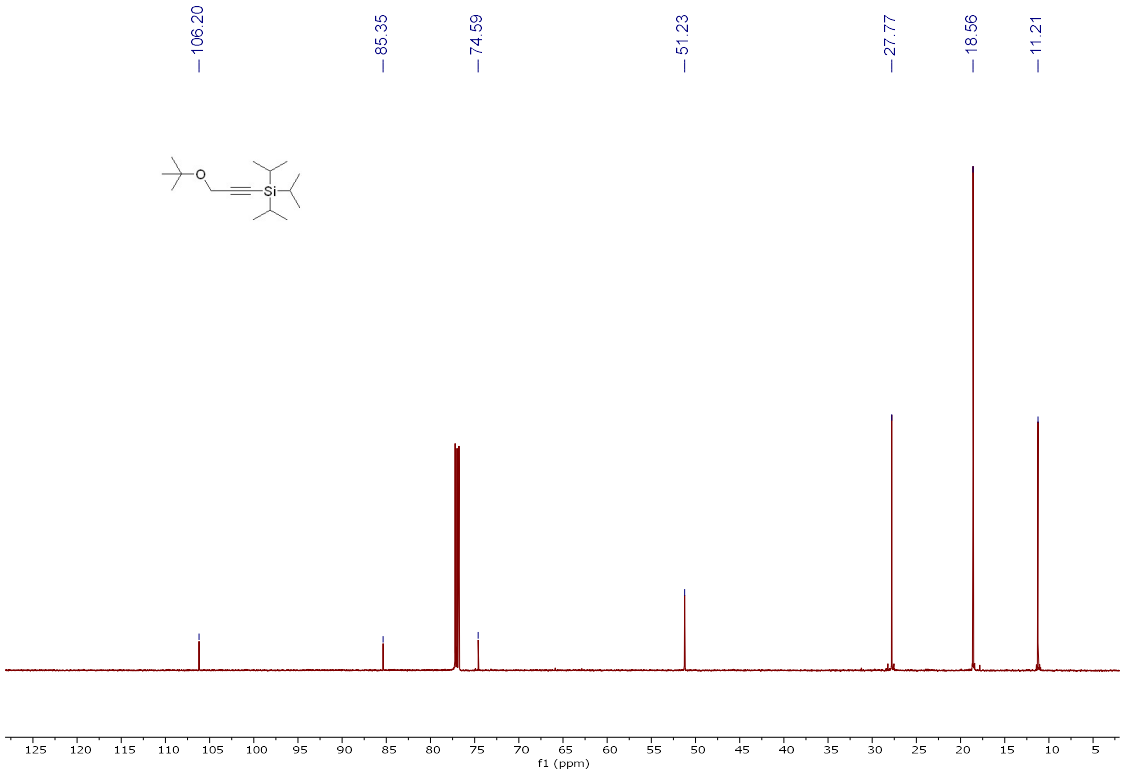
46


6.85
6.58
1.08
1.07
DCM
4.03
1.00
21.27
f1 (ppm)

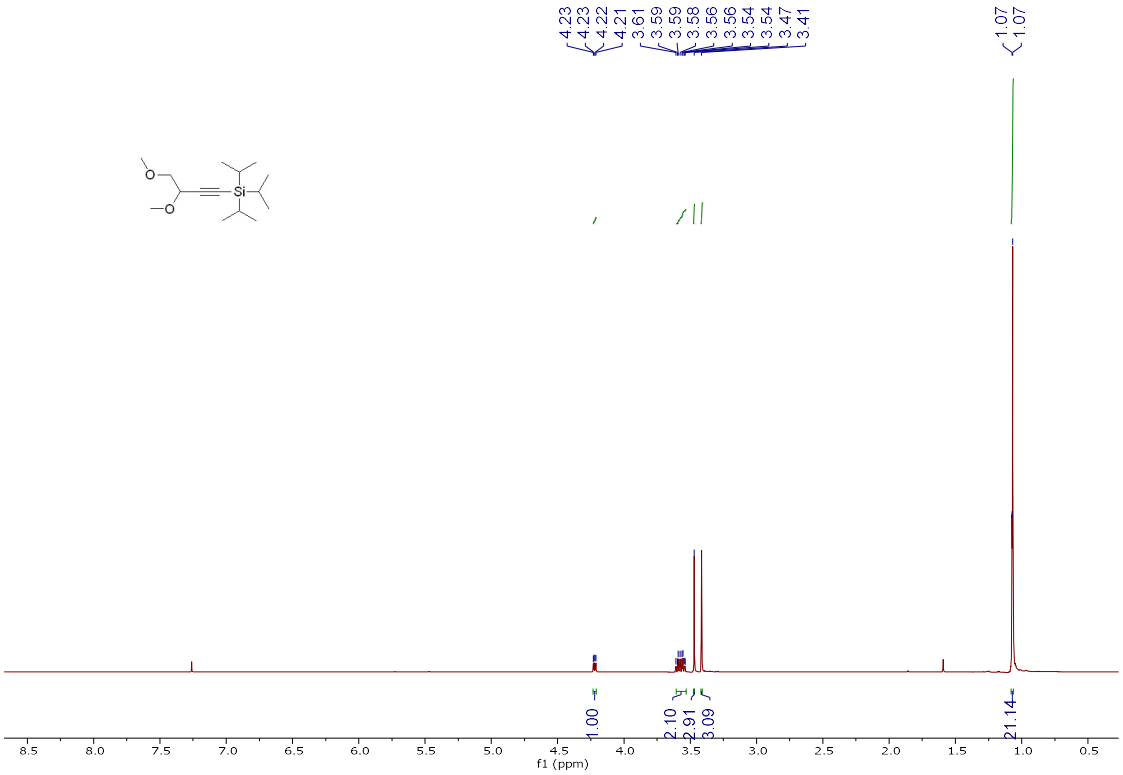

146.69
121.85
108.92
99.64
98.10
90.87
18.45
10.94
f1 (ppm)

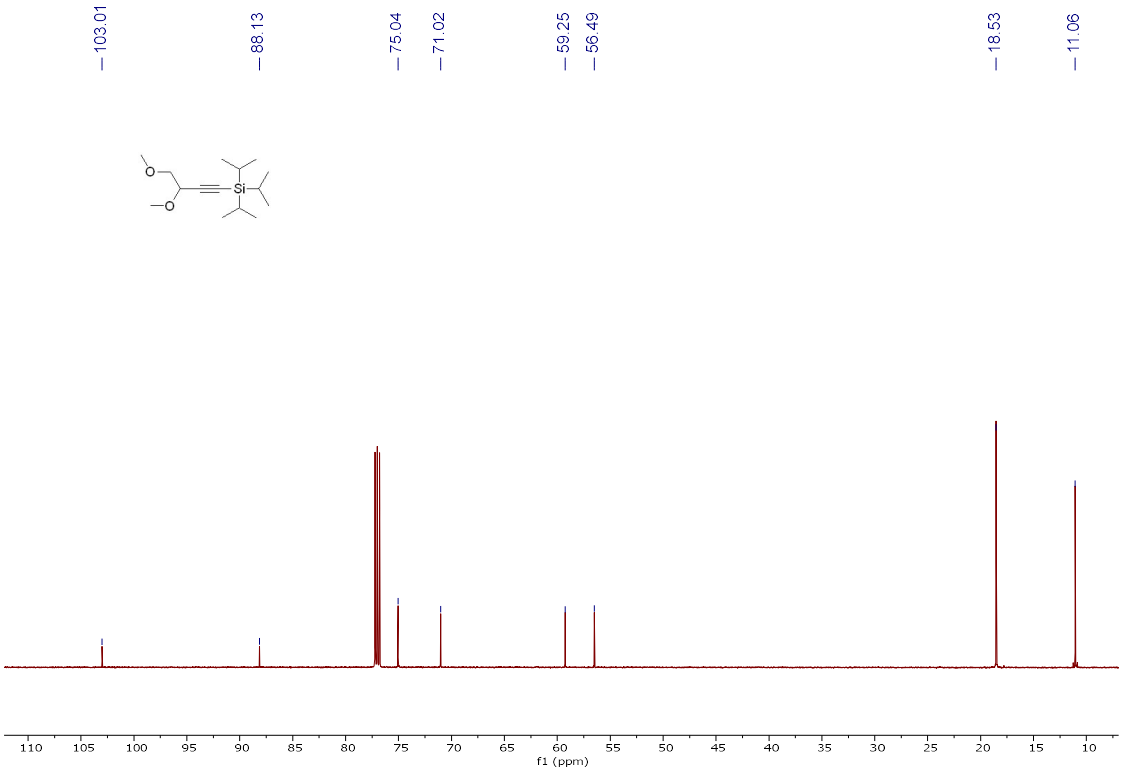
47


4.14
1.25
1.07
1.06
2.00
9.21
21.02
f1 (ppm)


106.20
85.35
74.59
51.23
27.77
18.56
11.21
f1 (ppm)

48


4.23
4.23
4.22
4.21
3.61
3.59
3.59
3.58
3.56
3.56
3.54
3.54
3.47
3.41
1.07
1.07
O
O
Si
1.00
2.10
2.91
3.09
21.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


103.01
88.13
75.04
71.02
59.25
56.49
18.53
11.06
O
O
Si
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

50


2.41
2.41
2.40
2.39
2.39
2.38
1.80
1.80
1.79
1.79
1.78
1.78
1.77
1.77
1.76
1.71
1.71
1.70
1.70
1.69
1.69
1.68
1.67
1.67
1.66
1.52
1.51
1.51
1.50
1.50
1.49
1.47
1.47
1.46
1.45
1.44
1.44
1.43
1.43
1.42
1.41
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1.31
1.30
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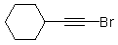
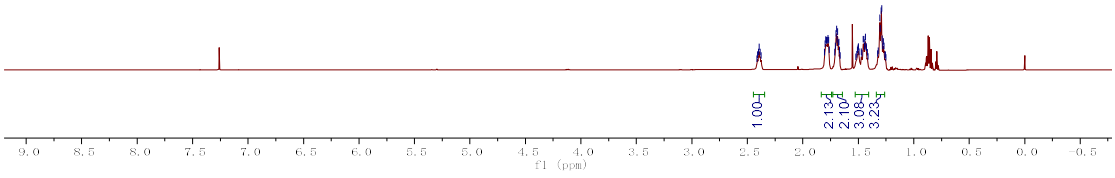
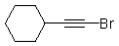
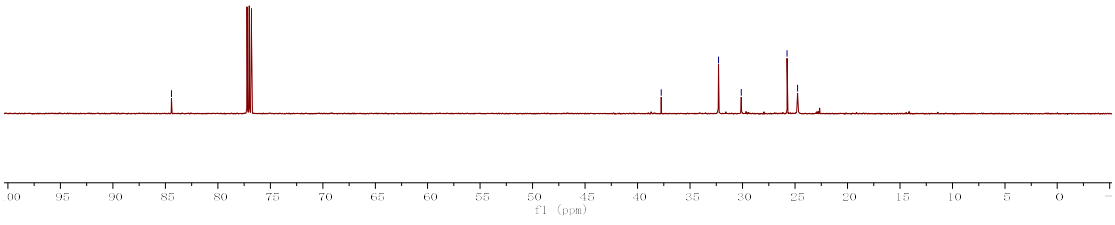
1.28
1.28
1.27
1.27
1.26
1.26
1.25


Br

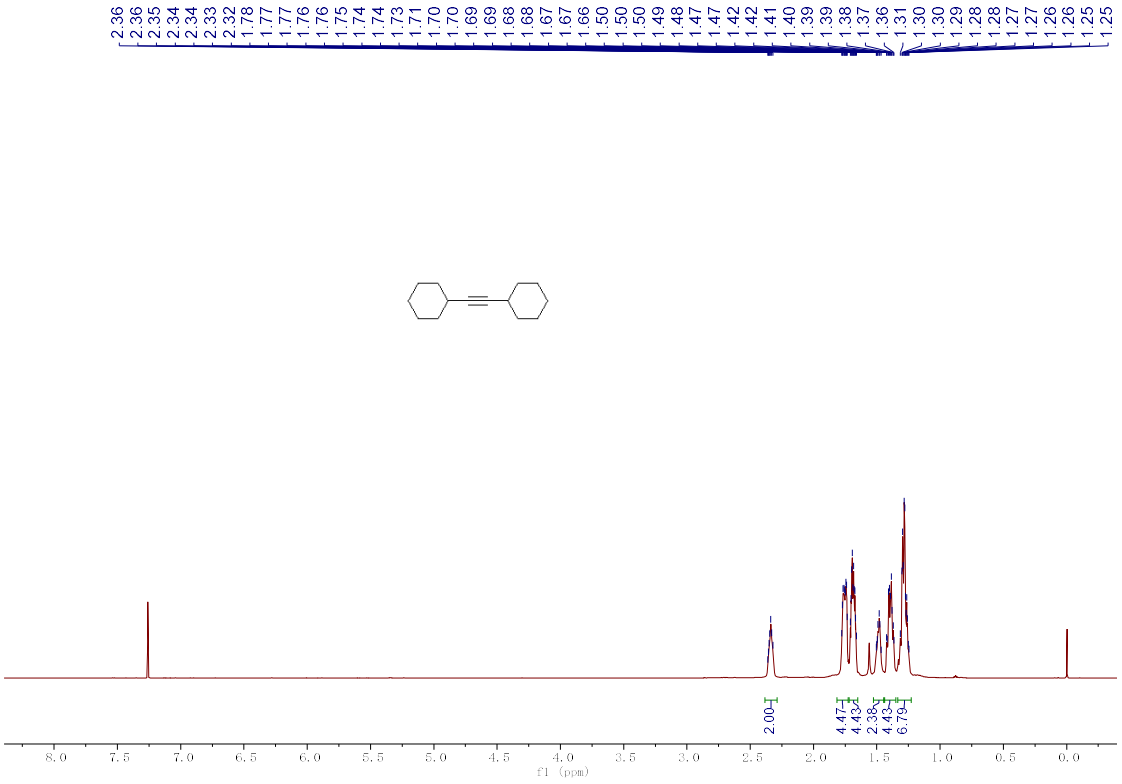

1.00
2.13
2.10
3.08
3.23
f1 (ppm)


84.42
37.75
32.29
30.13
25.75
24.75


Br


f1 (ppm)

51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2.35
2.34
2.34
2.33
2.32
1.78
1.77
1.77
1.76
1.76
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1.74
1.74
1.73
1.71
1.70
1.70
1.69
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1.68
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1.40
1.39
1.39
1.38
1.37
1.36
1.31
1.30
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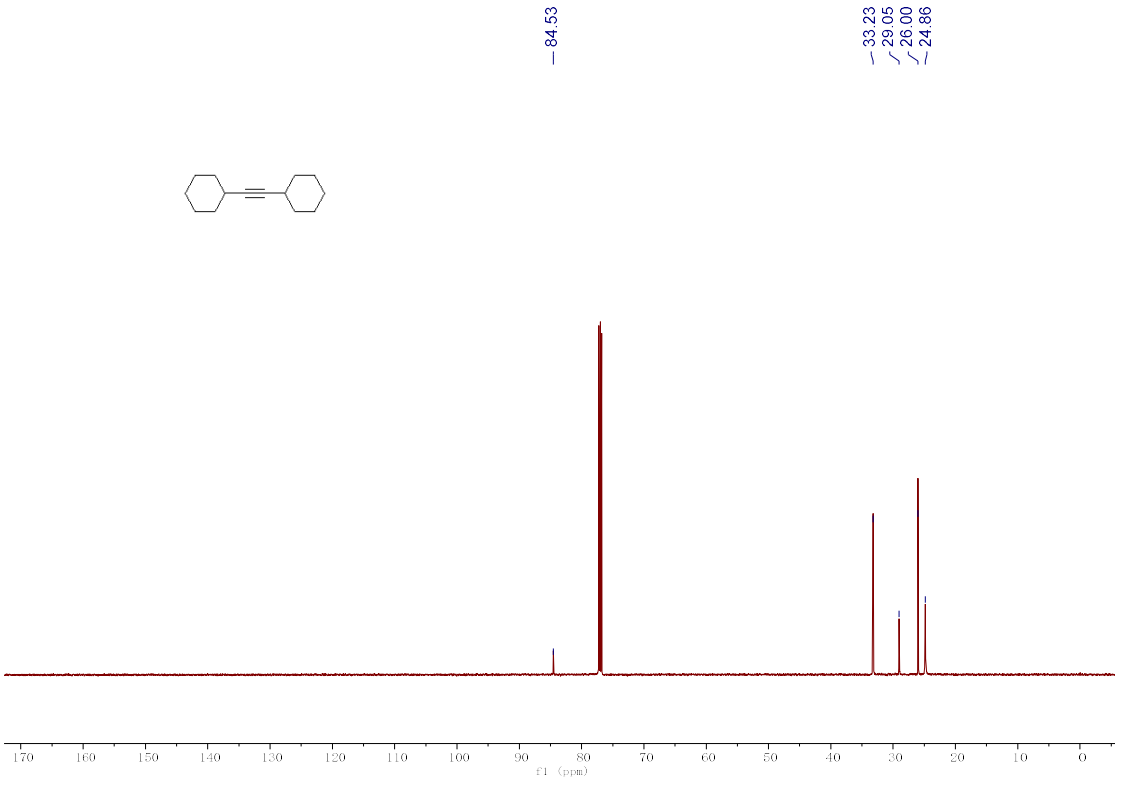
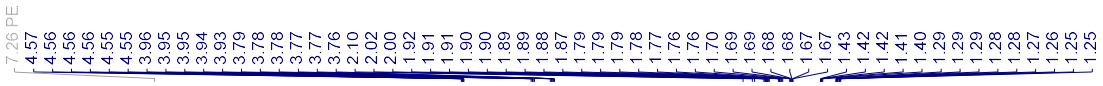
1.29
1.28
1.28
1.27
1.27
1.26
1.26
1.25
1.25
2.00
4.47
4.43
2.38
4.43
6.79
f1 (ppm)


84.53
33.23
29.05
26.00
24.86
f1 (ppm)

52


7.26 PE
4.57
4.56
4.56
4.56
4.55
4.55
3.96
3.95
3.95
3.94
3.93
3.79
3.78
3.78
3.77
3.77
3.76
2.10
2.02
2.00
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1.91
1.90
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1.89
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1.88
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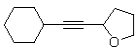
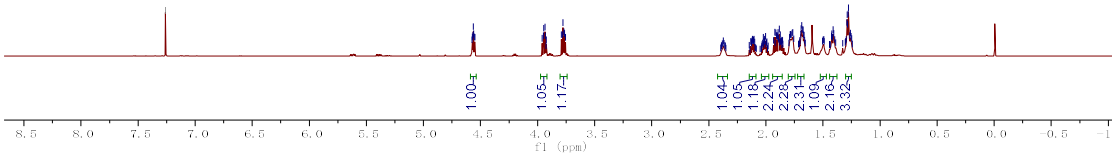
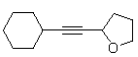
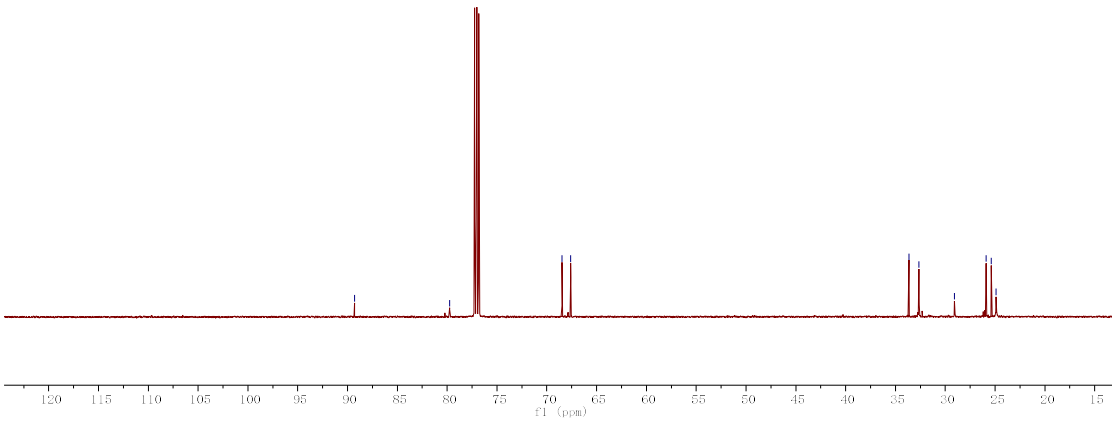
1.28
1.28
1.27
1.26
1.25
1.25




1.00
1.05
1.17
1.04
1.05
1.18
2.24
2.28
2.31
1.08
2.16
3.32
f1 (ppm)


89.31
79.76
68.48
67.61
33.66
32.64
29.07
25.89
25.38
24.90




f1 (ppm)

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