Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tandem Pd-catalyzed annulation/coupling of acetylenic enamines with aryl triflates.

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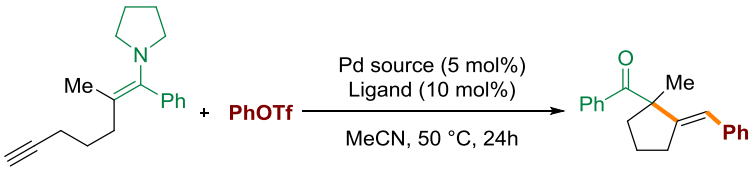
General Information

All the manipulations were performed in a nitrogen-filled glovebox or under an argon atmosphere using Schlenk techniques, unless mentioned otherwise. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates and visualized with cerium molybdate stain (Hanessian's stain). ^{1}H, $^{13}C\{1H\}$, and ^{19}F NMR spectra were recorded with a Bruker AV 400 spectrometer. ^{1}H and ^{13}C chemical shifts are given in ppm relative to TMS. The solvent signals were used as references ($CDCl_3\delta_H$ = 7.26 ppm, δ_C = 77.0 ppm) and the chemical shift converted to the TMS scale. Coupling constants (J) are reported in Hz, and the following abbreviations were used to denote multiplets: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet (denotes complex pattern), dd = doublet of doublets, dt = doublet of triplets and br = broad signal. Infrared spectra were recorded with a Jasco FTIR-6200 spectometer. Electron ionization high-resolution mass spectra (EI-HR) were recorded with an Autospec Premier (Waters Inc) mass spectrometer using the narrow-range high-voltage scan technique with low-boiling perfluorokerosene (PFK) as internal standard. Samples were introduced by using a heated direct insertion probe. Electrospray ionization high-resolution mass spectra (ESI-HR) were recorded with MALDISynapt G2-S HDMS (Waters Inc) mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyzer. ESI-MS spectra were recorded in the positive ion mode (the source parameters: capillary voltage 3.15 kV, sampling cone 25 V, source temperature 120 °C, desolvation temperature 150 °C). GC analyses were performed on Agilent 9890B Gas Chromatograph equipped with FID detector and INERTCAP 5MS/Sil (30 m, 0.32 mm ID, 0.50 μm df) The following temperature program was used: 100 °C (2 min), 20 °C/min to 310 °C (2 min). Unless otherwise noted, all commercially available compounds (ABCR, Acros, Fluorochem, TCI, Sigma-Aldrich, Strem) were used as received. Phosphine ligands were purchased from Aldrich, $Pd(OAc)_2$ was purchased Strem. Precatalyst RuPhos Pd G3 was prepared following Buchwald's procedure,[1] and showed similar reactivity to the commercial sample purchased from Strem.

Evaluation of reaction conditions for Pd-catalyzed cyclization/coupling of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine with phenyl trifluoromethanesulfonate.

General procedure for evaluation of reaction conditions: In a glovebox, to a 4-mL screw-capped vial containing catalyst (typically 5 mol%) following reagents were added: 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (25.3 mg, 0.100 mmol), phenyl trifluoromethanesulfonate (32.0 mg, 0.150 mmol), base (0.150 mmol) and solvent (0.25 ml or 0.5 ml). Then, magnetic stirring bar was placed and the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 50 or 80 °C for 24 h and then cooled to room temperature. The mixture was diluted with MTBE (2 mL) quenched with sat. aqueous NH_4Cl (0.5 mL) and mesitylene (25 µl) was added as a internal standard. An aliquot (200 µl) of the organic layer was diluted with MTBE and analyzed by GC.

Table S1. Effect of catalyst

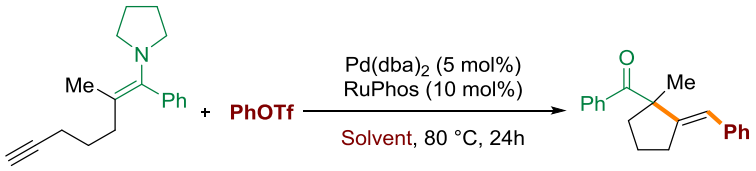


Entry	Palladium source	Ligand	Yield
1	$Pd(dba)_2$	XPhos	0%
2	$Pd(dba)_2$	RuPhos	47%
3	$Pd(dba)_2$	APhos	0%
4	$Pd(dba)_2$	SPhos	0%
5	$Pd(dba)_2$	DavePhos	38%
6	$Pd(dba)_2$	XantPhos	0%
7	$Pd(dba)_2$	CyJohnPhos	0%
8	$Pd(dba)_2$	JackiePhos	0%
9	$Pd(dba)_2$	DPEPhos	0%
10	$Pd(dba)_2$	MonoPhos	0%
11	$Pd(dba)_2$	PPh_3	0%
12	$Pd(dba)_2$	PCy_3	0%
13	$Pd(dba)_2$	$P(o\text{-}tol)_3$	0%
14	$Pd(dba)_2$	DPPF	0%
15	$Pd(dba)_2$	DPPM	0%
16	$Pd(dba)_2$	DPPP	0%
17	$Pd(dba)_2$	DPPPy	0%
18	$Pd(dba)_2$	t-BuXPhos	0%
19	$Pd(dba)_2$	BrettPhos	0%
20	$Pd(dba)_2$	(*R*)-BINAP	0%
21	$Pd(dba)_2$	(*R*)-tol-BINAP	0%
22	$Pd(dba)_2$	(*R*)-DM-BINAP	0%
23	$Pd(dba)_2$	(*R*)-SEGPhos 0%	0%
24	$Pd(dba)_2$	(*R*)-(-)-DTBM-SEGPhos	0%
25	$Pd(dba)_2$	(*R*,*S*)-O PINAP	0%
26	$Pd(dba)_2$	(R,R)-DACH-phenyl	0%
27	$Pd(dba)_2$	(*S*)-5,5-(Dimethyl)-i-Pr-PHOX	0%
28	$Pd(dba)_2$	(1S,2S)-(2-Amino-1-phenylpropyl)diphenylphosphine	0%

29	$Pd(PPh_3)_4$	XPhos	0%
30	$Pd(PPh_3)_4$	RuPhos	13%
31	$Pd(PPh_3)_4$	APhos	0%
32	$Pd(PPh_3)_4$	SPhos	10%
33	$Pd(PPh_3)_4$	DavePhos	23%
34	$Pd(PPh_3)_4$	t-BuXPhos	4%
35	$Pd(PPh_3)_4$	CyJohnPhos	0%
36	$Pd(PPh_3)_4$	JackiePhos	4%
37	$Pd(PPh_3)_4$	DPEPhos	4%
38	$Pd(PPh_3)_4$	MonoPhos	0%
39	$Pd(PPh_3)_4$	PPh_3	0%
40	$Pd(PPh_3)_4$	PCy_3	0%
41	$Pd(PPh_3)_4$	$P(o\text{-}tol)_3$	0%
42	$Pd(PPh_3)_4$	BINAP	0%
43	RuPhos PdG3	—	19%
44	DavePhos PdG3	—	10%

[a]Conditions: L (10 mol%), $Pd(dba)_2$ or $Pd(PPh_3)_4$ (5 mol%), 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (0.100 mmol, 1 equiv.), phenylmethanesulphonate (0.150 mmol, 1.5 equiv.), MeCN (0.5 mL), 50°C, 24h. [b]Yield was determined by GC with mesitylene as an internal standard.

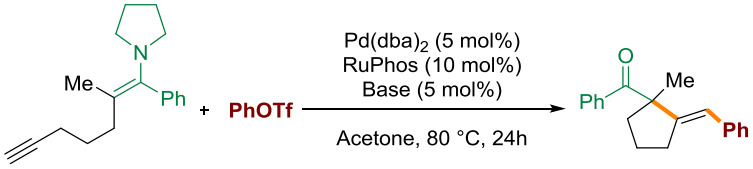
Table S2. Effect of solvent.



Entry	Solvent	Yield
1	THF	16%
2	DMF	4%
3	NMP	5%
4	DMSO	9%
5	DCM	37%
6	Acetone	79%
7	DMPU	8%
8	Dioxane	56%
9	AcOEt	17%
10	MeCN	65%

[a]Conditions: RuPhos (10 mol%), $Pd(dba)_2$ (5 mol%), 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (0.100 mmol, 1 equiv.), phenylmethanesulphonate (0.150 mmol, 1.5 equiv.), solvent (0.5 mL), 80°C, 24h. [b]Yield was determined by GC with mesitylene as an internal standard.

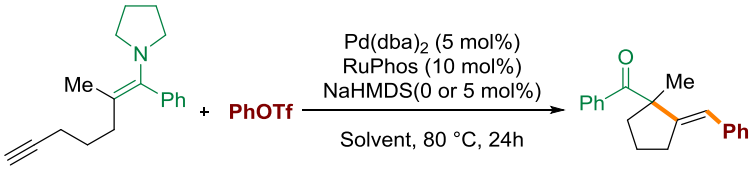
Table S3. Effect of base/additive.



Entry	Base	Yield
1	Cs_2CO_3	34%
2	CsF	14%
3	K_2CO_3	11%
4	Li_2CO_3	16%
5	t-BuOLi	11%
6	$BaCO_3$	16%
7	DMAP	6%
8	KHMDS	77%
9	**NaHMDS**	**90%**
10	LiHMDS	85%
11	AcONa	21%
12	K_3PO_4	10%

[a]Conditions: RuPhos (10 mol%), $Pd(dba)_2$ (5 mol%), 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (0.100 mmol, 1 equiv.), phenylmethanesulphonate (0.150 mmol, 1.5 equiv.), acetone (0.25 mL), base (5 mol%). 80°C, 24h. [b]Yield was determined by GC with mesitylene as an internal standard.

Table S4. Effect of NaHMDS in various solvents.



Entry	Solvent	NaHMDS	Yield
1	Acetone	-	79%
2	Acetone	5 mol%	90%
3	MeCN	-	65%
4	MeCN	5 mol%	79%
5	Dioxane	-	56%
6	Dioxane	5 mol%	65%
7	DCM	-	37%
8	DCM	5 mol%	48%

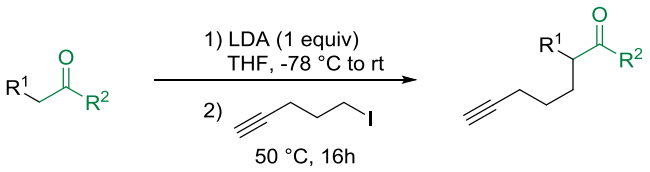
[a]Conditions: RuPhos (10 mol%), $Pd(dba)_2$ (5 mol%), 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (0.100 mmol, 1 equiv.), phenylmethanesulphonate (0.150 mmol, 1.5 equiv.), acetone (0.25 mL), NaHMDS (0 or 5 mol%). 80°C, 24h. [b] Yield was determined by GC with mesitylene as an internal standard.

Comment on influence of NaHMDS on reactivity.

The positive impact of NaHMDS on the reaction performance is not fully understood, however some conclusions can be drawn. One can consider that added base could neutralize traces of acids (e.g. HCl) present in crude enamine. From this perspective, however, detrimental effect of other tested bases is unclear. Generally, presence of bases, in particular in greater amounts favors Sonogashira coupling. Furthermore, crude enamine was shown by NMR to be acceptably pure (e.g. no parent ketone was present) and elemental analysis shown no chlorine in a sample of crude enamine (which excludes traces of HCl). Furthermore enamine purified by Kugelrohr distillation showed similar reactivity (also positive effect of NaHMDS) to a crude substrate. Hydrolysis of enamine and reaction of the resulting ketone under strongly basic conditions can also be ruled out. The reaction is carried out under anhydrous conditions, which excludes hydrolysis. Moreover ketone **1** was independently shown to be uncreative under variety of conditions tested, including presence of NaHMDS. It's probable that acetone (solvent) can directly react with strong base triggering aldol-type reaction. If this side reaction has influence on the reactivity of enamie, the effect should be specific only to reactions run in acetone. In fact addition of enamine is also beneficial in other solvent, including acetionitrile, but also dioxane and dichloromethane, both lacking sufficiently C-H acidic centers.
It could be speculated that NaHMDS can modulate reactivity and/or stability of the palladium catalyst before its reaction towards weekly coordinating alkynes moiety. Reversible coordination of organic base to Pd-centre (dissociation facilitated by steric hindrance) was postulated to enable efficient Buchwald-Hartwig reaction of aryl triflates with weakly binding amines (e.g. secondary aryl amines).[2,3]

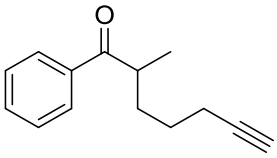
General procedure for substrates synthesis – ketone and enamines

General procedure for the synthesis of acetylenic ketones



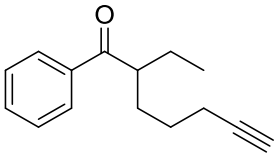
Solution of diisopropyl amine (1.70 g, 16.5 mmol) in THF (100 ml) was cooled to -78 °C, then n-BuLi (6 mL, 2.5M in hexanes, 15 mmol) was added dropwise and mixture was allowed to reach slowly room temperature, left for 30 min. Next ketone (15 mmol) was added at -78 °C, mixture was again allowed to reach room temperature and 5-iodopent-1-yne (12 mmol) was added dropwise. Reaction was carried out overnight (16h) at 50 °C, cooled to room temperature, quenched with 50 ml of sat. aqueous NH_4Cl, washed with Et_2O and extracted with Et_2O (3 x 50 ml). Combined organic phases were dried over Na_2SO_4, filtered and concentrated. Crude ketone was purified via column chromatography.

2-methyl-1-phenylhept-6-yn-1-one



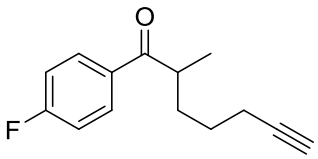
Prepared under general conditions in reaction of propiophenone (2.02 g, 15.1 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated after column chromatography as pale yellow oil (2.09 g, 10.4 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.43 (m, 2H), 3.54 – 3.45 (m, 1H), 2.19 (td, *J* = 6.8, 2.6 Hz, 2H), 1.97 – 1.88 (m, 2H), 1.63 – 1.51 (m, 3H), 1.21 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 136.6, 132.9, 128.6, 128.2, 84.0, 68.6, 40.1, 32.6, 26.2, 18.5, 17.3. HRMS (ESI): m/z calcd for $C_{14}H_{16}ONa$ 223.1009; found 223.1011.

2-ethyl-1-phenylhept-6-yn-1-one



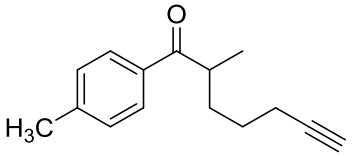
Prepared under general conditions in reaction of phenyl-1-butan-1-one (2.22 g, 15.0 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated after column chromatography as pale yellow oil (1.47 g, 6.9 mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.58 – 7.52 (m, 1H), 7.51 – 7.42 (m, 2H), 3.39 (tt, *J* = 7.7, 5.5 Hz, 1H), 2.16 (td, *J* = 7.0, 2.6 Hz, 2H), 1.92 (t, *J* = 2.7 Hz, 1H), 1.90 – 1.74 (m, 2H), 1.71 – 1.44 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 137.6, 132.9, 128.6, 128.1, 84.0, 68.5, 47.1, 30.7, 26.3, 25.4, 18.5, 11.7. HRMS (ESI): m/z calcd for $C_{15}H_{18}ONa$ 237.1255; found 237.1254.

1-(4-fluorophenyl)-2-methylhept-6-yn-1-one



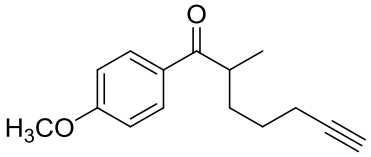
Prepared under general conditions in reaction of 1-(4-fluorophenyl)propan-1-one (2.29 g, 15.0 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated after column chromatography as pale yellow oil (675 mg, 3.09, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.17 – 7.09 (m, 2H), 3.49 – 3.39 (m, 1H), 2.19 (td, *J* = 6.9, 2.6 Hz, 2H), 1.97 – 1.87 (m, 2H), 1.63 – 1.49 (m, 3H), 1.20 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 166.9, 164.4, 132.9, 130.9, 130.8, 115.8, 115.6, 84.0, 68.6, 40.1, 32.5, 26.2, 18.4, 17.3. HRMS (ESI): m/z calcd for $C_{14}H_{15}FONa$ 241.1005; found 241.1007.

2-methyl-1-(p-tolyl)hept-6-yn-1-one



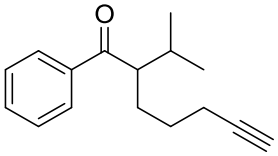
Prepared under general conditions in reaction of 1-(p-tolyl)propan-1-one (2.22 g, 15.0 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated after column chromatography as pale yellow oil (790 mg, 3.69 mmol, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.29 – 7.23 (m, 2H), 3.51 – 3.41 (m, 1H), 2.41 (s, 3H), 2.22 – 2.13 (m, 2H), 1.96 – 1.86 (m, 2H), 1.62 – 1.49 (m, 3H), 1.19 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 143.6, 134.1, 129.3, 128.4, 84.1, 68.5, 40.0, 32.7, 26.3, 21.6, 18.5, 17.4. HRMS (ESI): m/z calcd for $C_{15}H_{18}ONa$ 237.1255; found 237.1257.

1-(4-methoxyphenyl)-2-methylhept-6-yn-1-one



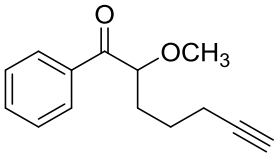
Prepared under general conditions in reaction of 1-(4-methoxyphenyl)propan-1-one (2.46 g, 15.0 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated after column chromatography as pale yellow oil (1.13 g, 4.91 mmol, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 6.96 – 6.90 (m, 2H), 3.86 (s, 3H), 3.45 (h, *J* = 6.6 Hz, 1H), 2.18 (td, *J* = 6.8, 2.6 Hz, 2H), 1.96 – 1.84 (m, 2H), 1.60 – 1.49 (m, 3H), 1.19 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 163.4, 130.5, 129.6, 113.8, 84.1, 68.5, 55.4, 39.7, 32.7, 26.3, 18.5, 17.5. HRMS (ESI): m/z calcd for $C_{15}H_{18}O_2Na$ 253.1204; found 253.1202.

2-isopropyl-1-phenylhept-6-yn-1-one



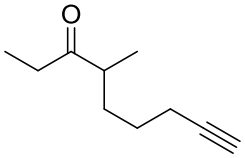
Prepared under general conditions in reaction of 3-methyl-1-phenylbutan-1-one (2.43 g, 15 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated after column chromatography as pale yellow oil (1.99 g, 8.72 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.43 (m, 2H), 3.28 (ddd, *J* = 10.0, 6.5, 3.4 Hz, 1H), 2.15 (tdd, *J* = 7.0, 2.7, 1.0 Hz, 2H), 2.04 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.69 (dddd, *J* = 13.5, 10.7, 5.8, 3.4 Hz, 1H), 1.53 – 1.32 (m, 2H), 0.93 (dd, *J* = 11.6, 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 138.3, 132.8, 128.6, 128.1, 84.1, 68.5, 52.0, 30.7, 27.7, 26.6, 21.3, 19.3, 18.6. HRMS (ESI): m/z calcd for $C_{16}H_{20}ONa$ 251.1412; found 251.1413.

2-methoxy-1-phenylhept-6-yn-1-one



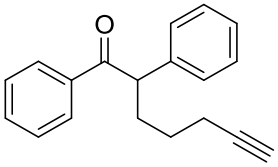
Prepared under general conditions in reaction of 2-methoxy-1-phenylethan-1-one (2.25 g, 15.0 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated after column chromatography on silica gel as oil (1.17g, 5.41 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.61 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 4.48 (dd, *J* = 8.2, 4.7 Hz, 1H), 3.36 (s, 3H), 2.28 – 2.17 (m, 2H), 2.00 – 1.84 (m, 3H), 1.77 – 1.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 135.0, 133.4, 128.7, 128.6, 84.2, 83.7, 68.8, 57.7, 31.8, 24.4, 18.0. HRMS (ESI): m/z calcd for $C_{14}H_{16}O_2Na$ 239.1048; found 239.1051.

4-methylnon-8-yn-3-one



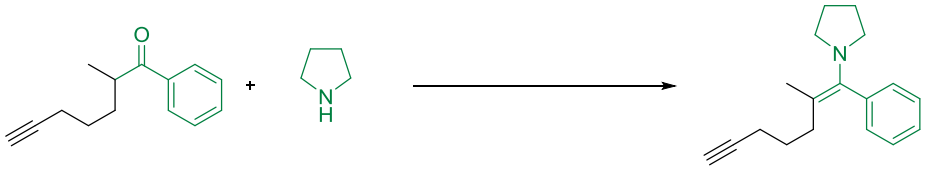
Prepared under general conditions in reaction of pentan-3-one (1.29 g, 15.0 mmol) and 5-iodopent-1-yne (2.33 g, 12.0 mmol). Product was isolated as oil after column chromatography on silica gel (1.11 g, 7.29, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 – 2.49 (m, 1H), 2.49 – 2.38 (m, 1H), 2.23 – 2.10 (m, 2H), 1.81 – 1.66 (m, 1H), 1.57 – 1.35 (m, 4H), 1.13 – 0.98 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.9, 68.5, 45.6, 34.2, 32.0, 31.7, 26.1, 18.4, 16.4, 7.8. HRMS (ESI): m/z calcd for $C_{10}H_{16}ONa$ 175.1099; found 175.1098.

1,2-diphenylhept-6-yn-1-one



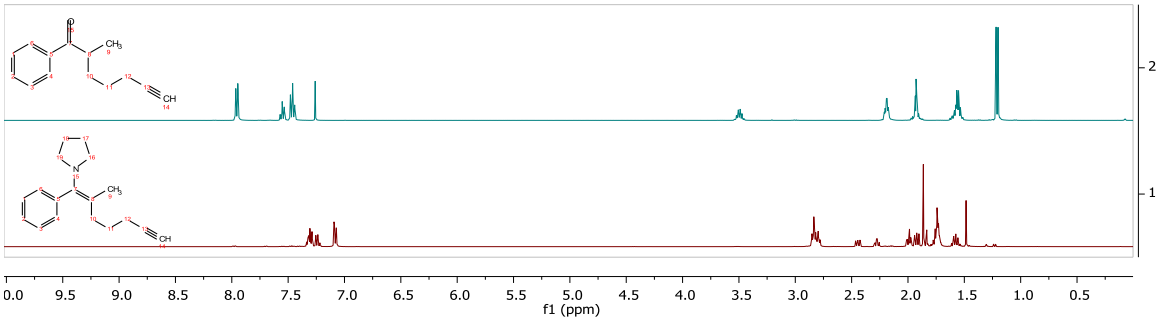
Prepared in reaction of 1,2-diphenylethan-1-one (3.92 g, 20.0 mmol) and 5-iodopent-1-yne (3.50 g, 18.0 mmol) under general conditions. Product was isolated as yellow solid after column chromatography on silica gel (1.45 g, 5.53 mmol, 31%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.50 – 7.44 (m, 1H), 7.41 – 7.26 (m, 5H), 7.22 – 7.16 (m, 1H), 4.59 (t, J = 7.3 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.21 (td, J = 7.2, 2.5 Hz, 2H), 2.04 – 1.92 (m, 2H), 1.62 – 1.42 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 139.3, 136.7, 132.8, 128.9, 128.6, 128.4, 128.1, 127.0, 84.0, 68.6, 53.1, 33.0, 26.4, 18.4. HRMS (EI): m/z calcd for $C_{19}H_{18}O$ 262.1436; found 262.1438.

Synthesis of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (3). General procedure for the synthesis of acetylenic enamines.



To solution of 2-methyl-1-phenylhept-6-yn-1-one **1** (1.00 g, 5.0 mmol, 1.0 equiv) and pyrrolidine (1.78 g, 25 mmol, 5.0 equiv) in 50 ml toluene at 0 °C, $TiCl_4$ (5 ml, 5.0 mmol, 1.0 M solution in toluene) was added dropwise, then ice bath was removed, reaction was allowed to reach room temperature and ran overnight. Next mixture was diluted with 200 ml of Et_2O and filtered through 5G funnel to remove all precipitated TiO_2, concentrated and dried under reduced pressure to provide crude **3** (1.27, 5.0 mmol, quant). Enamine was formed as a 1:2 mixture of *E*/*Z* isomers. Dry product was used without any further purification. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 7.11 – 7.06 (m, 2H), 2.87 – 2.77 (m, 4H), 2.48 – 2.42 (m, ⅓ · 1H), 2.28 (td, *J* = 7.3, 2.7 Hz, ⅓ · 1H), 2.02 – 1.96 (m, ⅔ · 2H), 1.95 – 1.89 (m, ⅔ · 2H), 1.86 (s, ⅔ · 3H), 1.83 (t, *J* = 2.7 Hz, 1H), 1.79 – 1.70 (m, 5H), 1.62 – 1.53 (m, ⅔ · 2H), 1.48 (s, ⅓ · 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ major isomer:142.9, 138. 8, 129.5, 127.71, 126.5, 121.2, 84.5, 68.0, 51.0, 33. 7, 27.8, 24.9, 18.0, 17.2; minor isomer: 142.2, 138. 8, 129.6, 127.67, 126.4, 123.9, 84.8, 68.1, 51.3, 32.1, 27.1, 24.8, 18.4, 18.3;

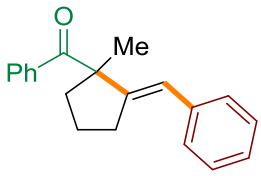
No chlorine in crude enamine **3** was detected by elemental analysis. No significant amount of ketone **1** in crude enamine **3** was detected by ^{1}H NMR.



General procedure for Pd-catalyzed cyclization/coupling of acetylenic enamines and aryl triflates

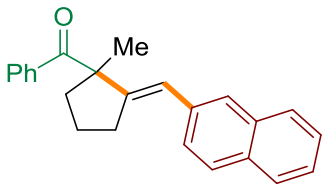
In a glovebox, to a 4-mL screw-capped vial containing $Pd(dba)_2$ (11.5 mg, 20 μmol, 5 mol%) and RuPhos (18.7 mg, 40 μmol, 10 mol%) following reagents were added: crude acetylenic enamine (0.400 mmol, 1 eqiuv), aryl trifluoromethanesulfonate (0.500 mmol, 1.25 equiv), NaHMDS (3.7 mg, 20 μmol, 5 mol%) and dry acetone (0.5 ml). Then, magnetic stirring bar was placed and the vial was sealed with a cap containing a PTFE seal. The reaction mixture was stirred at 80 °C for 24 h and then cooled to room temperature, quenched with sat. aqueous NH_4Cl (10 mL), extracted with MTBE (3 x 10 mL). Combined organic phase were dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel.

(E)-(2-benzylidene-1-methylcyclopentyl)(phenyl)methanone (4)



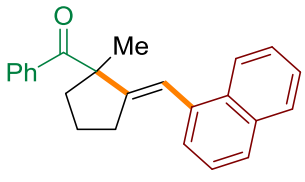
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.2 mg, 0.400 mmol) and phenyl trifluoromethanesulfonate (113.1 mg, 0.500 mmol) under general conditions (96.1 mg, 0.348 mmol, 87%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.47 – 7.40 (m, 1H), 7.38 – 7.29 (m, 6H), 7.24 – 7.18 (m, 1H), 6.23 (t, *J* = 2.6 Hz, 1H), 3.06 – 2.91 (m, 2H), 2.44 – 2.34 (m, 1H), 2.13 – 2.03 (m, 1H), 2.02 – 1.88 (m, 1H), 1.77 – 1.70 (m, 1H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 150.4, 137.9, 137.2, 131.2, 128.9, 128.3, 128.2, 128.0, 126.5, 123.9, 60.4, 38.6, 32.3, 26.0, 24.9. IR (CH_2Cl_2): 2965, 1671, 1596, 1445, 1265, 1176, 1007, 963, 759, 695 cm^{-1}. MS (EI): m/z (%) = 276(4)[M$^+$], 226(2), 202(1), 184(4), 173(7), 172(16), 171(100), 170(11), 155(4), 143(5), 129(15), 122(64), 115(3), 106(9), 105(89), 97(4), 91(20), 77(34), 43(3). HRMS (EI): m/z calcd for $C_{20}H_{20}O$ 276.1514; found 276.1502.

(E)-(1-methyl-2-(naphthalen-2-ylmethylene)cyclopentyl)(phenyl)methanone (5)



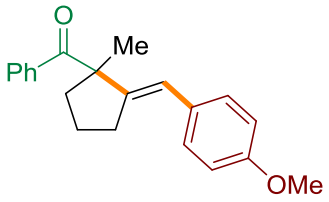
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.4 mg, 0.400 mmol) and naphthalen-2-yl trifluoromethanesulfonate (138.7 mg, 0.502 mmol) under general conditions (53.5 mg, 0.164 mmol, 41%). Product was isolated as oil after column chromatography on silica gel (15, hex/AcOEt 95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 6H), 7.51 – 7.41 (m, 4H), 7.40 – 7.33 (m, 2H), 6.39 (t, *J* = 2.7 Hz, 1H), 3.16 – 3.02 (m, 2H), 2.48 – 2.38 (m, 1H), 2.17 – 2.07 (m, 1H), 2.05 – 1.92 (m, 1H), 1.81 – 1.73 (m, 1H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 151.1, 137.4, 135.6, 133.5, 132.1, 131.3, 129.0, 128.1, 128.0, 127.8, 127.6, 127.0, 126.7, 126.2, 125.8, 124.1, 60.6, 38.7, 32.5, 26.1, 25.0. IR (CH_2Cl_2): 2962, 1670, 1596, 1445, 1263, 1175, 1007, 963, 816, 706 cm^{-1}. HRMS (ESI): m/z calcd for $C_{24}H_{22}ONa$ 349.1568; found 349.1568.

(E)-(1-methyl-2-(naphthalen-1-ylmethylene)cyclopentyl)(phenyl)methanone (6)



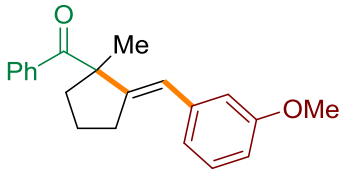
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.4 mg, 0.400 mmol) and naphthalen-1-yl trifluoromethanesulfonate (138.2 mg, 0.501 mmol) under general conditions (82.2 mg, 0.252 mmol, 63%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.87 – 7.82 (m, 1H), 7.79 – 7.71 (m, 2H), 7.54 – 7.37 (m, 7H), 6.78 (t, *J* = 2.6 Hz, 1H), 2.86 – 2.79 (m, 2H), 2.55 – 2.45 (m, 1H), 2.07 – 1.96 (m, 1H), 1.96 – 1.86 (m, 1H), 1.85 – 1.78 (m, 1H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 204.9, 152.5, 137.2, 135.1, 133.5, 131.7, 131.3, 129.0, 128.3, 128.0, 127.1, 125.8, 125.7, 125.4, 125.2, 124.4, 121.4, 59.7, 39.0, 31.6, 26.6, 24.3. IR (CH_2Cl_2): 2963, 1671, 1594, 1445, 1263, 1175, 1006, 963, 781, 705, cm^{-1}. MS (EI): m/z (%) = 327(2), 326(7)[M$^+$], 222(31), 221(100), 206(16), 205(6), 179(10), 165(6), 141(4), 105(9); HRMS (ESI): m/z calcd for $C_{24}H_{22}ONa$ 349.1568; found 349.1566.

***(E)*-(2-(4-methoxybenzylidene)-1-methylcyclopentyl)(phenyl)methanone (7)**



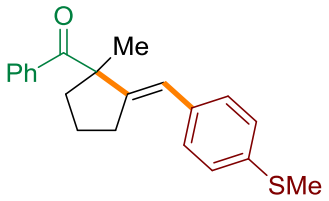
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.8 mg, 0.402 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (128.1 mg, 0.500 mmol) under general conditions (101.2 mg, 0.331 mmol, 82%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 98:2→97:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.44 – 7.38 (m, 1H), 7.36 – 7.30 (m, 2H), 7.28 – 7.22 (m, 2H), 6.91 – 6.85 (m, 2H), 6.15 (t, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 3.01 – 2.86 (m, 2H), 2.41 – 2.31 (m, 1H), 2.11 – 2.01 (m, 1H), 1.98 – 1.88 (m, 1H), 1.74 – 1.66 (m, 1H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.1, 158.2, 148.0, 137.4, 131.1, 130.8, 129.4, 128.9, 127.9, 123.3, 113.7, 60.3, 55.2, 38.6, 32.2, 25.9, 24.9. IR (CH_2Cl_2): 2961, 1670, 1606, 1511, 1251, 1177, 1034, 707 cm^{-1}. MS (EI): m/z (%) = 306(1)[M^+], 281(1), 221(1), 215(3), 202(25), 201(100), 200(2), 173(3), 159(7), 145(3), 135(4), 121(17), 105(8), 93(3), 84(1), 77(2), 55(2); HRMS (ESI): m/z calcd for $C_{21}H_{22}O_2Na$ 329.1517; found 329.1514.

(*E*)-(2-(3-methoxybenzylidene)-1-methylcyclopentyl)(phenyl)methanone (8)



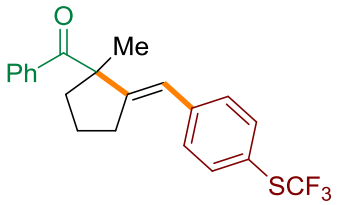
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (103.9 mg, 0.400 mmol) and 3-methoxyphenyl trifluoromethanesulfonate (128.1 mg, 0.500 mmol) under general conditions (83.8 mg, 0.273 mmol, 68%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 98:2→95:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.47 – 7.40 (m, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.23 (m, 1H), 6.91 (dd, 1H), 6.86 (t, *J* = 2.1 Hz, 1H), 6.78 (dt, *J* = 8.2, 1.7 Hz, 1H), 6.18 (t, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 3.07 – 2.90 (m, 2H), 2.43 – 2.32 (m, 1H), 2.12 – 2.02 (m, 1H), 2.02 – 1.89 (m, 1H), 1.77 – 1.67 (m, 1H), 1.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 159.6, 150.9, 139.4, 137.2, 131.2, 129.2, 128.9, 128.0, 123.8, 120.9, 113.9, 112.0, 60.5, 55.2, 38.7, 32.4, 26.0, 24.9. IR (CH_2Cl_2): 2961, 1670, 1597, 1577, 1263, 1174, 780, 707, 690 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{22}O_2Na$ 329.1517; found 329.1516.

***(E)*-(1-methyl-2-(4-(methylthio)benzylidene)cyclopentyl)(phenyl)methanone (9)**



Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.1 mg, 0.399 mmol) and 4-(methylthio)phenyl trifluoromethanesulfonate (136.3 mg, 0.501 mmol) under general conditions (41.3 mg, 0.128 mmol, 32%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.45 – 7.39 (m, 1H), 7.37 – 7.31 (m, 2H), 7.22 (s, 4H), 6.14 (t, *J* = 2.6 Hz, 1H), 2.99 – 2.87 (m, 2H), 2.48 (s, 3H), 2.40 – 2.31 (m, 1H), 2.13 – 2.00 (m, 1H), 2.01 – 1.88 (m, 1H), 1.75 – 1.67 (m, 1H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 150.1, 137.3, 136.6, 135.0, 131.2, 128.9, 128.7, 128.0, 127.6, 126.6, 123.3, 121.7, 60.5, 38.7, 32.4, 26.0, 24.9, 15.9. IR (CH_2Cl_2): 2962, 2924, 1671, 1493, 1263, 1213, 1175, 1141, 1093, 1008, 963, 885, 809, 706 cm^{-1}. MS (EI): m/z (%) = 322(4), 278(1), 237(1), 219(10), 218(28), 217(100), 205(2), 175(2), 170(8), 155(4), 137(30), 128(2), 105(11), 93(1), 71(1); HRMS (ESI): m/z calcd for $C_{21}H_{22}ONaS$ 345.1289; found 345.1284.

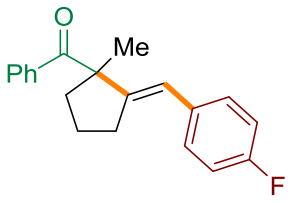
***(E)*-(1-methyl-2-(4-((trifluoromethyl)thio)benzylidene)cyclopentyl)(phenyl)methanone (10)**



Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.9 mg, 0.402 mmol) and 4-((trifluoromethyl)thio)phenyl trifluoromethanesulfonate (163.70 mg, 0.502 mmol) under general conditions (133.2 mg, 0.354 mmol, 88%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.40 (m, 1H), 7.39 – 7.31 (m, 4H), 6.20 (t, *J* = 2.6 Hz, 1H), 3.01 – 2.93 (m, 2H), 2.45 – 2.36 (m, 1H), 2.15 – 2.05 (m, 1H), 2.03 – 1.90 (m, 1H), 1.78 – 1.71 (m, 1H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 153.5, 140.5,

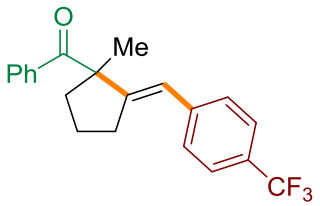
136.9, 136.3, 131.4, 131.1, 129.1, 128.9, 128.1, 128.0, 122.7, 121.8, 121.8, 60.6, 38.6, 32.4, 26.0, 24.8. IR (CH_2Cl_2): 2966, 1673, 1593, 1264, 1118, 1009, 963, 706 cm^{-1}. MS (EI): m/z (%) = 377(1), 376(4), 273(6), 272(18), 271(79), 270(5), 229(3), 202(4), 191(16), 170(11), 155(4), 142(3), 128(2), 106(13), 105(100), 93(1), 77(4), 55(2); HRMS (EI): m/z calcd for $C_{21}H_{20}OSF_3$ 377.1187; found 377.1185.

***(E)*-(2-(4-fluorobenzylidene)-1-methylcyclopentyl)(phenyl)methanone (11)**



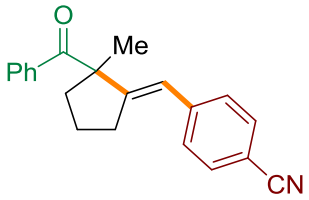
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.7 mg, 0.401 mmol) and 4-fluorophenyl trifluoromethanesulfonate (122.6 mg, 0.502 mmol) under general conditions (63.6 mg, 0.216 mmol, 54%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.47 – 7.39 (m, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.21 (m, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.16 (t, *J* = 2.6 Hz, 1H), 2.98 – 2.85 (m, 2H), 2.43 – 2.32 (m, 1H), 2.12 – 2.01 (m, 1H), 2.01 – 1.86 (m, 1H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 162.6, 160.1, 150.1, 150.0, 137.2, 134.10, 134.07, 131.2, 129.8, 129.7, 128.9, 128.0, 122.8, 115.3, 115.0, 60.3, 38.6, 32.1, 26.0, 24.9. IR (CH_2Cl_2): 2965, 1671, 1599, 1508, 1229, 1007, 963, 825, 705 cm^{-1}. MS (EI): m/z (%) = 294(3), 277(3), 190(22), 189(100), 172(4), 161(3), 147(9), 109(17), 105(47), 97(3), 83(3), 71(4), 57(5); HRMS (APCI): m/z calcd for $C_{20}H_{20}OF$ 295.1498; found 295.1507.

***(E)*-(1-methyl-2-(4-(trifluoromethyl)benzylidene)cyclopentyl)(phenyl)methanone (12)**



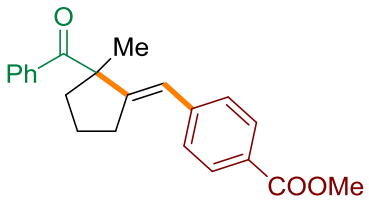
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.0 mg, 0.399 mmol) and 4-(trifluoromethyl)phenyl trifluoromethanesulfonate (147.2 mg, 0.501 mmol) under general conditions (60.6 mg, 0.176 mmol, 44%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.41 – 7.32 (m, 4H), 6.22 (t, *J* = 2.6 Hz, 1H), 3.01 – 2.93 (m, 2H), 2.45 – 2.36 (m, 1H), 2.15 – 2.04 (m, 1H), 2.02 – 1.90 (m, 1H), 1.79 – 1.72 (m, 1H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 153.5, 141.4, 137.0, 131.4, 128.9, 128.3, 128.1, 125.3, 125.2, 125.2, 122.8, 60.6, 38.6, 32.4, 26.0, 24.8. IR (CH_2Cl_2): 2965, 1673, 1614, 1326, 1166, 1122, 1068, 706 cm^{-1}. HRMS (EI): m/z calcd for $C_{21}H_{19}OF_3$ 344.1388; found 344.1390.

***(E)*-4-((2-benzoyl-2-methylcyclopentylidene)methyl)benzonitrile (13)**



Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.8 mg, 0.402 mmol) and 4-cyanophenyl trifluoromethanesulfonate (125.6 mg, 0.500 mmol) under general conditions (116.3 mg, 0.385 mmol, 96%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 95:5→9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.61 – 7.56 (m, 2H), 7.47 – 7.41 (m, 1H), 7.38 – 7.32 (m, 4H), 6.19 (t, *J* = 2.7 Hz, 1H), 2.99 – 2.92 (m, 2H), 2.41 (ddd, *J* = 12.8, 10.5, 7.4 Hz, 1H), 2.15 – 2.05 (m, 1H), 2.02 – 1.90 (m, 1H), 1.75 (ddd, *J* = 12.9, 7.1, 3.1 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1, 155.1, 142.4, 136.8, 132.1, 131.5, 128.8, 128.6, 128.1, 122.6, 119.0, 109.7, 60.8, 38.5, 32.5, 26.0, 24.8. IR (CH_2Cl_2): 2967, 2225, 1672, 1602, 1264, 1175, 963, 706, 554cm^{-1}. MS (EI): m/z (%) = 301(2), 286(1), 258(1), 197(2), 196(13), 168(1), 158(8), 154(3), 134(2), 116(4), 106(15), 105(100), 97(1), 77(4); HRMS (APCI): m/z calcd for $C_{21}H_{20}NO$ 302.1545; found 302.1549.

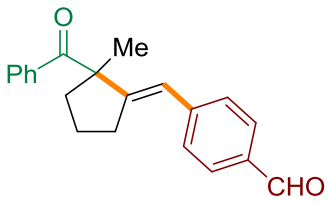
Methyl *(E)*-4-((2-benzoyl-2-methylcyclopentylidene)methyl)benzoate (14)



Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.6 mg, 0.401 mmol) and methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (142.3 mg, 0.501 mmol) under general conditions (93.4 mg, 0.280 mmol, 70%). Product was isolated as oil after column chromatography on silica gel (15g,

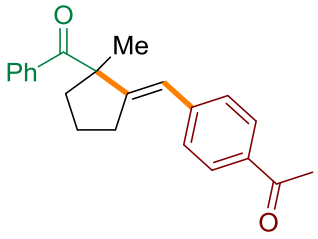
hex/AcOEt 95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.30 (m, 4H), 6.22 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 3H), 3.02 – 2.93 (m, 2H), 2.44 – 2.34 (m, 1H), 2.13 – 2.02 (m, 1H), 1.76 – 1.69 (m, 1H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 166.8, 153.5, 142.4, 136.9, 131.3, 129.6, 128.8, 128.0, 127.8, 123.2, 60.6, 51.9, 38.6, 32.5, 25.9, 24.8. IR (CH_2Cl_2): 2953, 1720, 1672, 1605, 1436, 1280, 1180, 1110, 707 cm^{-1}. MS (EI): m/z (%) = 355(1), 327(1), 307(1), 305(7), 292(3), 269(1), 230(3), 229(18), 222(5), 181(2), 180(7), 164(13), 149(14), 133(14), 122(100), 105(93), 97(6), 86(12), 84(19), 77(19), 71(9), 57(11), 43(7); HRMS (ESI): m/z calcd for $C_{22}H_{22}O_3Na$ 357.1467; found 357.1465.

***(E)*-4-((2-benzoyl-2-methylcyclopentylidene)methyl)benzaldehyde (15)**



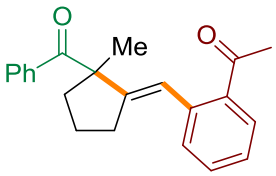
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.5 mg, 0.401 mmol) and 4-formylphenyl trifluoromethanesulfonate (126.8 mg, 0.499 mmol) under general conditions (88.9 mg, 0.292 mmol, 73 %). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.87 – 7.80 (m, 2H), 7.73 – 7.67 (m, 2H), 7.47 – 7.40 (m, 3H), 7.38 – 7.32 (m, 2H), 6.24 (t, *J* = 2.6 Hz, 1H), 3.03 – 2.97 (m, 2H), 2.46 – 2.35 (m, 1H), 2.16 – 2.06 (m, 1H), 2.04 – 1.89 (m, 1H), 1.80 – 1.70 (m, 1H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 191.6, 154.8, 144.0, 136.9, 134.3, 131.5, 129.8, 128.9, 128.7, 128.1, 123.2, 60.8, 38.6, 32.6, 26.0, 24.9. IR (CH_2Cl_2): 2963, 2928, 1694, 1673, 1601, 1263, 1214, 1172, 707 cm^{-1}. MS (EI): m/z (%) = 305(1), 304(22), 303(11), 287(7), 276(2), 229(2), 215(9), 199(25), 198(24), 171(14), 155(6), 141(7), 129 (15), 115(11), 106(16), 105(100), 91(22), 77(29), 51(8).

***(E)*-1-(4-((2-benzoyl-2-methylcyclopentylidene)methyl)phenyl)ethan-1-one (16)**



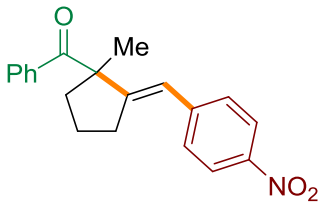
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.9 mg, 0.402 mmol) and 4-acetylphenyl trifluoromethanesulfonate (134.6 mg, 0.502 mmol) under general conditions (105.6mg, 0.332 mmol, 83 %). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.73 – 7.67 (m, 2H), 7.47 – 7.40 (m, 1H), 7.39 – 7.31 (m, 4H), 6.23 (t, *J* = 2.6 Hz, 1H), 3.03 – 2.95 (m, 2H), 2.58 (s, 3H), 2.44 – 2.35 (m, 1H), 2.15 – 2.04 (m, 1H), 2.02 – 1.89 (m, 1H), 1.78 – 1.70 (m, 1H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 197.5, 153.9, 142.6, 137.0, 134.9, 131.4, 128.9, 128.4, 128.3, 128.1, 123.2, 60.7, 38.6, 32.6, 26.5, 26.0, 24.9. IR (CH_2Cl_2): 2965, 1680, 1600, 1359, 1268, 1177, 961, 709cm^{-1}. MS (EI): m/z (%) = 319(4), 318(12)[M^+], 276(2), 213(48), 212(21), 198(2), 171(7), 169(10), 155(5), 141(7), 106(10), 105(100), 91(5), 77(38), 51(10), 43(65); HRMS (EI): m/z calcd for $C_{22}H_{22}O_2$ 318.1620; found 318.1624.

(*E*)-1-(2-((2-benzoyl-2-methylcyclopentylidene)methyl)phenyl)ethan-1-one (17)



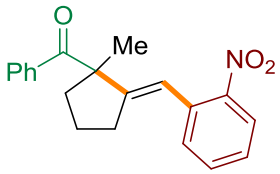
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (103.9 mg, 0.401 mmol) and 2-acetylphenyl trifluoromethanesulfonate (134.1 mg, 0.500 mmol) under general conditions (63.9 mg, 0.201 mmol, 50%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 98:2→90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.62 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.26 (m, 2H), 6.49 (t, *J* = 2.6 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.46 (s, 3H), 2.45 – 2.38 (m, 1H), 2.02 – 1.92 (m, 1H), 1.90 – 1.80 (m, 1H), 1.77 – 1.70 (m, 1H), 1.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 201.9, 151.1, 138.3, 137.3, 131.3, 131.0, 129.3, 128.8, 128.6, 128.0, 126.6, 123.2, 59.6, 38.9, 31.7, 29.9, 25.6, 24.4. IR (CH_2Cl_2): 2964, 1680, 1596, 1426, 1248, 768, 706cm^{-1}. HRMS (EI): m/z calcd for $C_{22}H_{22}O_2$ 318.1620; found 318.1622.

***(E)*-(1-methyl-2-(4-nitrobenzylidene)cyclopentyl)(phenyl)methanone (18)**



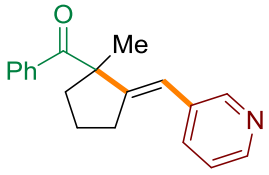
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.3 mg, 0.400 mmol) and 4-nitrophenyl trifluoromethanesulfonate (134.2 mg, 0.495 mmol) under general conditions (111.7 mg, 0.348 mmol, 87 %). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 2H), 7.72 – 7.66 (m, 2H), 7.48 – 7.32 (m, 5H), 6.25 (t, *J* = 2.6 Hz, 1H), 3.04 – 2.95 (m, 2H), 2.48 – 2.38 (m, 1H), 2.17 – 2.06 (m, 1H), 2.05 – 1.91 (m, 1H), 1.81 – 1.73 (m, 1H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 156.0, 145.9, 144.4, 136.7, 131.6, 128.8, 128.7, 128.1, 123.7, 122.3, 60.9, 38.6, 32.6, 26.0, 24.8. IR (CH_2Cl_2): 2965, 1671, 1594, 1514, 1343, 1262, 1175, 1109, 709cm^{-1}. MS (EI): m/z (%) = 321(3), 305(2), 216(7), 200(22), 170(9), 155(10), 142(8), 128(9), 115(9), 106(17), 105(100), 91(4), 78(7), 77(30), 51(9); HRMS (EI): m/z calcd for $C_{20}H_{19}NO_3$ 321.1365; found 321.1380.

***(E)*-(1-methyl-2-(2-nitrobenzylidene)cyclopentyl)(phenyl)methanone (19)**



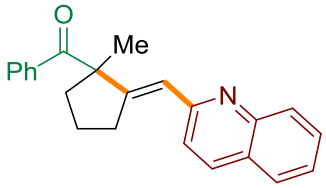
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.6 mg, 0.401 mmol) and 2-nitrophenyl trifluoromethanesulfonate (135.1 mg, 0.498 mmol) under general conditions (127.2 mg, 0.396 mmol, 99%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.55 (td, *J* = 7.6, 1.4 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.42 – 7.32 (m, 4H), 6.47 (t, *J* = 2.6 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.69 – 2.59 (m, 1H), 2.49 – 2.38 (m, 1H), 2.04 – 1.92 (m, 1H), 1.92 – 1.80 (m, 1H), 1.80 – 1.71 (m, 1H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1, 153.4, 147.9, 136.9, 133.2, 132.6, 131.4, 130.5, 128.8, 128.0, 127.4, 124.4, 119.6, 59.7, 38.9, 31.5, 25.8, 24.2. IR (CH_2Cl_2): 2967, 1671, 1523, 1343, 1264, 1175, 708 cm^{-1}. MS (EI): m/z (%) = 304(1), 287(1), 235(5), 234(31), 216(7), 215(23), 200(25), 199(9), 182(13), 170(5), 156(4), 131(7), 128(2), 106(8), 105(100), 91(4), 84(6), 57(3). HRMS (ESI): m/z calcd for $C_{20}H_{19}NO_3Na$ 344.1263; found 344.1265.

***(E)*-(1-methyl-2-(pyridin-3-ylmethylene)cyclopentyl)(phenyl)methanone (20)**



Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.5 mg, 0.401 mmol) and pyridin-3-yl trifluoromethanesulfonate (141.1 mg, 0.500 mmol) under general conditions (102.8 mg, 0.370 mmol, 93%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.3 Hz, 1H), 8.38 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.54 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.34 – 7.28 (m, 2H), 7.20 (ddd, *J* = 7.9, 4.8, 0.8 Hz, 1H), 6.12 (t, *J* = 2.6 Hz, 1H), 2.95 – 2.88 (m, 2H), 2.43 – 2.32 (m, 1H), 2.10 – 2.00 (m, 1H), 1.98 – 1.86 (m, 1H), 1.74 – 1.67 (m, 1H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 153.2, 149.4, 147.2, 136.8, 134.7, 133.5, 131.3, 128.7, 128.0, 123.1, 120.3, 60.4, 38.6, 32.3, 25.9, 24.7. IR (CH_2Cl_2): 2964, 1671, 1264, 1175, 1007, 962, 708cm^{-1}. MS (EI): m/z (%) = 278(13) [M^{+}], 277958), 269(1), 219(2), 173(10), 172(68), 171(5), 157(2), 144(3), 130(5), 122(2), 106(13), 105(100), 92(8), 71(3), 69(5), 57(4); HRMS (EI): m/z calcd for $C_{19}H_{20}NO$ 278.1545; found 278.1540.

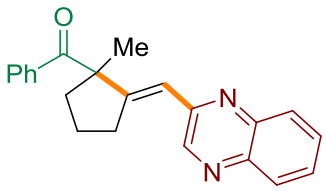
***(E)*-(1-methyl-2-(quinolin-2-ylmethylene)cyclopentyl)(phenyl)methanone (21)**



Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.5 mg, 0.400 mmol) and quinolin-2-yl trifluoromethanesulfonate (139.7 mg, 0.504 mmol) under general conditions (99.5 mg, 0.304 mmol, 76%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 85:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (ddd, *J* = 16.4, 8.5, 0.9 Hz, 2H), 7.80 – 7.71 (m, 3H), 7.70 – 7.64 (m, 1H), 7.50 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 6.42 (t, *J* = 2.6 Hz, 1H), 3.68 – 3.58 (m, 1H), 3.39 – 3.25 (m, 1H), 2.48 –

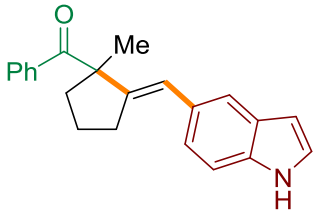
2.35 (m, 1H), 2.20 – 2.09 (m, 2H), 2.07 – 1.94 (m, 1H), 1.81 – 1.72 (m, 1H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 158.6, 156.8, 148.2, 136.9, 135.7, 131.4, 129.4, 129.3, 129.1, 128.0, 127.4, 126.3, 125.9, 123.2, 122.3, 61.0, 38.7, 33.6, 26.0, 24.9. IR (CH_2Cl_2): 3059, 2964, 1671, 1597, 1504, 1215, 1137, 960, 913, 845 cm^{-1}. . MS (EI): m/z (%) = 328(4)[M^{+1}], 327(20)[M$^+$], 223(17), 222(100), 206(6), 194(5), 180(4), 143(14), 129(2), 105(15), 77(3). HRMS (EI): m/z calcd for $C_{23}H_{21}NO$ 327.1701; found 327.1705.

***(E)*-(1-methyl-2-(quinoxalin-2-ylmethylene)cyclopentyl)(phenyl)methanone (22)**



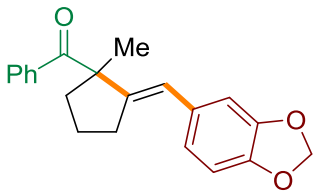
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.4 mg, 0.400 mmol) and quinoxalin-2-yl trifluoromethanesulfonate (137.7 mg, 0.495 mmol) under general conditions (110.3 mg, 0.336 mmol, 84%). Product was isolated as oil after column chromatography on silica gel (15g, 9:1→75:25). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.02 (ddd, *J* = 17.5, 8.2, 1.6 Hz, 2H), 7.78 – 7.62 (m, 4H), 7.45 – 7.37 (m, 1H), 7.37 – 7.29 (m, 2H), 6.44 (t, *J* = 2.6 Hz, 1H), 3.69 – 3.57 (m, 1H), 3.41 – 3.29 (m, 1H), 2.52 – 2.40 (m, 1H), 2.22 – 2.11 (m, 1H), 2.08 – 1.95 (m, 1H), 1.83 – 1.74 (m, 1H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 162.5, 151.8, 146.4, 142.4, 140.3, 136.5, 131.6, 129.9, 129.3, 129.1, 129.1, 129.0, 128.1, 119.4, 61.3, 38.8, 34.0, 26.0, 24.8. IR (CH_2Cl_2): 3060, 2966, 1672, 1640, 1544, 1261, 1175, 763, 707cm^{-1}. MS (EI): m/z (%) = 329(6), 328(26)[M$^+$], 224(24), 223(90), 221(8), 207(13), 195(17), 181(16), 168(4), 144(10), 129(6), 106(13), 105(100), 77(50), 51(12); HRMS (EI): m/z calcd for $C_{22}H_{20}N_2O$ 328.1576; found 328.1569.

***(E)*-(2-((1H-indol-5-yl)methylene)-1-methylcyclopentyl)(phenyl)methanone (23)**



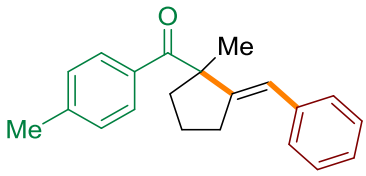
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.1 mg, 0.399 mmol) and 1H-indol-5-yl trifluoromethanesulfonate (132.3 mg, 0.499 mmol) under general conditions (60.2 mg, 0.191 mmol, 48%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.82 – 7.76 (m, 2H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.38 – 7.30 (m, 3H), 7.19 – 7.14 (m, 2H), 6.58 – 6.52 (m, 1H), 6.35 (t, *J* = 2.6 Hz, 1H), 3.13 – 2.95 (m, 2H), 2.43 – 2.34 (m, 1H), 2.14 – 2.02 (m, 1H), 2.01 – 1.89 (m, 1H), 1.77 – 1.70 (m, 1H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7, 147.2, 137.6, 134.6, 131.0, 130.0, 128.9, 128.0, 124.9, 124.7, 123.2, 120.2, 110.8, 102.7, 60.3, 38.7, 32.4, 26.0, 25.0. IR (CH_2Cl_2): 3409, 2963, 1665, 1467, 1265, 1176, 1008, 964, 894, 726 cm^{-1}. MS (EI): m/z (%) = 315(2), 295(1), 265(4), 211(26), 210(100), 195(4), 182(5), 168(5), 155(2), 132(7), 117(1), 105(5), 93(2), 84(7); HRMS (ESI): m/z calcd for $C_{22}H_{21}NONa$ 338.1521; found 338.1515.

***(E)*-(2-(benzo[d][1,3]dioxol-5-ylmethylene)-1-methylcyclopentyl)(phenyl)methanone (24)**



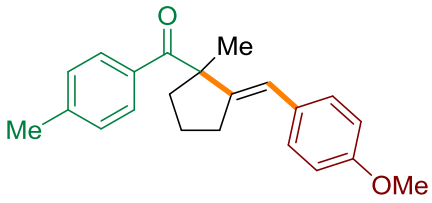
Prepared in reaction of 1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (101.3 mg, 0.400 mmol) and benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (135.9 mg, 0.503 mmol) under general conditions (96.0 mg, 0.300 mmol, 75%).Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 95:5→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.38 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 1.7 Hz, 1H), 6.79 – 6.71 (m, 2H), 6.10 (t, *J* = 2.7 Hz, 1H), 5.94 (s, 2H), 3.00 – 2.83 (m, 2H), 2.40 – 2.30 (m, 1H), 2.11 – 2.00 (m, 1H), 1.98 – 1.86 (m, 1H), 1.74 – 1.66 (m, 1H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 148.6, 147.6, 146.1, 137.3, 132.3, 131.1, 128.9, 128.0, 123.6, 122.4, 108.2, 108.2, 101.0, 60.3, 38.6, 32.3, 26.0, 24.9. IR (CH_2Cl_2): 2964, 1670, 1503, 1489, 1444, 1257, 1039, 934, 707cm^{-1}. MS (EI): m/z (%) = 320(4)[M$^+$], 216(27), 215(100), 185(11), 173(1), 157(4), 143(2), 135(6), 105(5), 93(2); HRMS (ESI): m/z calcd for $C_{21}H_{20}O_3Na$ 343.1310; found 343.1316.

***(E)*-(2-benzylidene-1-methylcyclopentyl)(p-tolyl)methanone (25)**



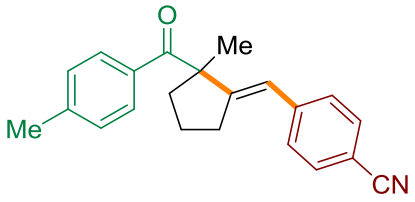
Prepared in reaction of 1-(2-methyl-1-(p-tolyl)hept-1-en-6-yn-1-yl)pyrrolidine (107.2 mg, 0.401 mmol) and phenyl trifluoromethanesulfonate (113.5 mg, 0.501 mmol) under general conditions (64.7 mg, 0.223 mmol, 55%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 98:2→95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.37 – 7.28 (m, 4H), 7.24 – 7.12 (m, 3H), 6.18 (t, *J* = 2.6 Hz, 1H), 3.03 – 2.94 (m, 2H), 2.45 – 2.37 (m, 1H), 2.35 (s, 3H), 2.16 – 2.04 (m, 1H), 2.03 – 1.88 (m, 1H), 1.77 – 1.68 (m, 1H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 150.8, 141.8, 138.1, 134.1, 129.3, 128.7, 128.3, 128.2, 126.4, 123.8, 60.3, 38.8, 32.3, 26.1, 24.9, 21.4. IR (CH_2Cl_2): 2962, 1667, 1606, 1266, 1173, 1007, 962, 758, 694 cm^{-1}. MS (EI): m/z (%) = 291(1) [M^{+1}], 290(5) [M^{+}], 172(14), 171(65), 170(12), 155(4), 141(6), 129(21), 119(100), 115(13), 93(3), 92(7), 91(57), 89(4), 77(8), 65(15), 55(11), 41(11). HRMS (EI): m/z calcd for $C_{21}H_{22}O$ 290.1671; found 290.1667.

***(E)*-(2-(4-methoxybenzylidene)-1-methylcyclopentyl)(p-tolyl)methanone (26)**



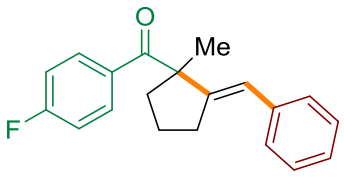
Prepared in reaction of 1-(2-methyl-1-(p-tolyl)hept-1-en-6-yn-1-yl)pyrrolidine (107.9 mg, 0.403 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (128.7 mg, 0.502 mmol) under general conditions (63.4 mg, 0.198 mmol, 49%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 95:5→9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.25 – 7.21 (m, 2H), 7.15 – 7.11 (m, 2H), 6.90 – 6.83 (m, 2H), 6.11 (t, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 2.98 – 2.89 (m, 2H), 2.43 – 2.36 (m, 1H), 2.34 (s, 3H), 2.13 – 2.03 (m, 1H), 2.01 – 1.87 (m, 1H), 1.74 – 1.65 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 158.2, 148.4, 141.7, 134.3, 130.9, 129.4, 129.3, 128.6, 123.2, 113.8, 60.3, 55.3, 38.9, 32.2, 26.1, 25.0, 21.4. IR (CH_2Cl_2): 2960, 1667, 1606, 1510, 1251, 1175, 1035, 825 cm^{-1}. MS (EI): m/z (%) = 320(2) [M^{+}], 203(2), 202(27), 201(100), 173(3), 160(4), 159(8), 145(5), 128(5), 121(27), 119(33), 115(6), 93(4), 91(25), 77(5), 65(9), 55(9), 41(5). HRMS (EI): m/z calcd for $C_{22}H_{24}O_2$ 320.1776; found 320.1784.

***(E)*-4-((2-methyl-2-(4-methylbenzoyl)cyclopentylidene)methyl)benzonitrile (27)**



Prepared in reaction of 1-(2-methyl-1-(p-tolyl)hept-1-en-6-yn-1-yl)pyrrolidine (107.4 mg, 0.402 mmol) and 4-cyanophenyl trifluoromethanesulfonate (125.3 mg, 0.499 mmol) under general conditions (79.5 mg, 0.252 mmol, 63%). Product was isolated as oil after column chromatography on silica gel (25 g, hex/AcOEt 98:2→9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 4H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.16 (t, *J* = 2.7 Hz, 1H), 3.01 – 2.93 (m, 2H), 2.47 – 2.37 (m, 1H), 2.35 (s, 3H), 2.17 – 2.06 (m, 1H), 2.03 – 1.91 (m, 1H), 1.79 – 1.71 (m, 1H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 155.4, 142.4, 142.1, 133.6, 132.0, 129.1, 128.7, 128.5, 122.4, 118.9, 109.5, 60.6, 38.6, 32.4, 26.0, 24.7, 21.3. IR (CH_2Cl_2): 2965, 2226, 1667, 1604, 1266, 1174, 553 cm^{-1}. MS (EI): m/z (%) = 315(1)[M^{+}], 196(3), 180(3), 154(3), 140(3), 127(3), 120(14), 119(100), 116(11), 91(31), 77(3), 65(10), 63(2), 39(4).). HRMS (EI): m/z calcd for $C_{22}H_{21}NO$ 315.1623; found 315.1622.

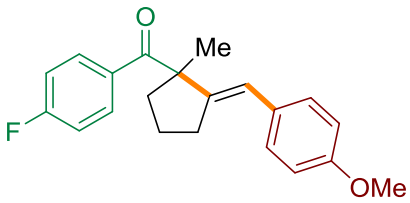
***(E)*-(2-benzylidene-1-methylcyclopentyl)(4-fluorophenyl)methanone (28)**



Prepared in reaction of 1-(1-(4-fluorophenyl)-2-methylhept-1-en-6-yn-1-yl)pyrrolidine (108.8 mg, 0.401 mmol) and phenyl trifluoromethanesulfonate (113.6 mg, 0502 mmol) under general conditions (61.2 mg, 0.208 mmol, 52%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 98:2→9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.37 – 7.27 (m, 4H), 7.24 – 7.17 (m, 1H), 7.07 – 6.98 (m, 2H), 6.17 (t, *J* = 2.6 Hz, 1H), 3.07 – 2.88 (m, 2H),

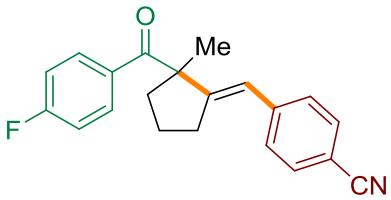
2.40 – 2.29 (m, 1H), 2.15 – 2.05 (m, 1H), 2.03 – 1.90 (m, 1H), 1.77 – 1.68 (m, 1H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 165.7, 163.2, 150.4, 137.8, 133.0, 133.0, 131.7, 131.6, 128.3, 128.2, 126.6, 124.1, 115.1, 114.9, 60.4, 38.8, 32.2, 26.1, 24.9. IR (CH_2Cl_2): 2964, 1672, 1598, 1503, 1236, 1155, 843, 694 cm^{-1}. MS (EI): m/z (%) = 294(7) [M$^+$], 172(23), 171(100), 155(5), 143(9), 129(32), 123(34), 115(17), 105(4), 95(23), 91(54), 77(9), 69(7), 55(10), 41(7). HRMS (EI): m/z calcd for $C_{20}H_{19}OF$ 294.1420, found 294.1427.

***(E)*-(4-fluorophenyl)(2-(4-methoxybenzylidene)-1-methylcyclopentyl)methanone (29)**



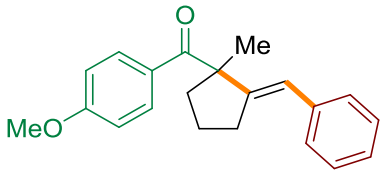
Prepared in reaction of 1-(1-(4-fluorophenyl)-2-methylhept-1-en-6-yn-1-yl)pyrrolidine (108.3 mg, 0.399 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (under general conditions (60.9 mg, 0.188 mmol, 47%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 95:5→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.27 – 7.18 (m, 2H), 7.05 – 6.97 (m, 2H), 6.91 – 6.84 (m, 2H), 6.10 (t, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 3.04 – 2.84 (m, 2H), 2.38 – 2.27 (m, 1H), 2.13 – 2.03 (m, 1H), 2.02 – 1.89 (m, 1H), 1.75 – 1.66 (m, 1H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 165.7, 163.1, 158.3, 148.0, 133.1, 131.7, 131.6, 130.7, 129.5, 123.5, 122.3, 115.1, 115.0, 114.9, 113.8, 60.3, 55.3, 38.8, 32.1, 26.0, 24.9. IR (CH_2Cl_2): 2961, 1671, 1598, 1510, 1251, 1035, 843, 611 cm^{-1}. MS (EI): m/z (%) = 324(1)[M$^+$], 202(23),201(100), 173(3), 160(4), 159(10), 123(12), 121(28), 115(6), 103(1), 95(12), 91(6), 77(5), 55(3), 41(2). HRMS (EI): m/z calcd for $C_{21}H_{21}O_2F$ 324.1526; found 324.1524.

***(E)*-4-((2-(4-fluorobenzoyl)-2-methylcyclopentylidene)methyl)benzonitrile (30)**



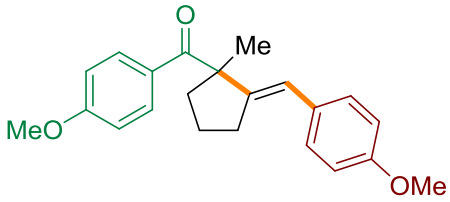
Prepared in reaction of 1-(1-(4-fluorophenyl)-2-methylhept-1-en-6-yn-1-yl)pyrrolidine (108.1 mg, 0.398 mmol) and 4-cyanophenyl trifluoromethanesulfonate (125.2 mg, 0.499 mmol) under general conditions (86.8 mg, 0.272 mmol, 68%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 98:2→9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.62 – 7.55 (m, 2H), 7.38 – 7.32 (m, 2H), 7.07 – 6.99 (m, 2H), 6.15 (t, *J* = 2.6 Hz, 1H), 3.01 – 2.93 (m, 2H), 2.44 – 2.32 (m, 1H), 2.18 – 2.07 (m, 1H), 2.05 – 1.93 (m, 1H), 1.80 – 1.72 (m, 1H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 165.8, 163.3, 155.0, 142.2, 132.5, 132.4, 132.1, 131.6, 131.5, 128.6, 122.7, 118.9, 115.3, 115.0, 109.8, 60.7, 38.6, 32.4, 26.0, 24.7. IR (CH_2Cl_2): 2966, 2225, 1672, 1599, 1503, 1236, 1156, 845, 553cm^{-1}. MS (EI): m/z (%) = 319(2)[M$^+$], 197(4), 196(26), 180(3), 166(33), 154(9), 140(6), 124(14), 123(100), 116(24), 95(27), 77(4), 75(7), 69(5), 41(5). HRMS (EI): m/z calcd for $C_{21}H_{18}NOF$ 319.1372; found 319.1385.

***(E)*-(2-benzylidene-1-methylcyclopentyl)(4-methoxyphenyl)methanone (31)**



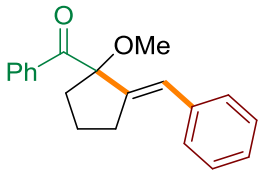
Prepared in reaction of 1-(1-(4-methoxyphenyl)-2-methylhept-1-en-6-yn-1-yl)pyrrolidine and phenyl trifluoromethanesulfonate (113.5 mg, 0.500 mmol) under general conditions (83.7 mg, 0.273 mmol, 68%).Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.35 – 7.27 (m, 4H), 7.22 – 7.16 (m, 1H), 6.87 – 6.81 (m, 2H), 6.15 (t, *J* = 2.6 Hz, 1H), 3.81 (s, 3H), 3.04 – 2.96 (m, 2H), 2.47 – 2.36 (m, 1H), 2.16 – 2.08 (m, 1H), 1.72 (ddd, *J* = 12.7, 7.2, 2.6 Hz, 1H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 162.1, 151.1, 138.1, 131.6, 129.0, 128.3, 128.2, 126.4, 123.7, 113.2, 60.2, 55.3, 39.1, 32.2, 26.2, 24.9. IR (CH_2Cl_2): 2964, 1660, 1600, 1508, 1256, 1167, 1032, 839, 695 cm^{-1}. MS (EI): m/z (%) = 306(1), 252(1), 185(1), 171(13), 152(7), 136(17), 135(100), 129(7), 107(5), 92(9), 91(15), 77(5), 64(3), 55(3). HRMS (EI): m/z calcd for $C_{21}H_{22}O_2$ 3061620; found 306.1608.

***(E)*-(2-(4-methoxybenzylidene)-1-methylcyclopentyl)(4-methoxyphenyl)methanone (32)**



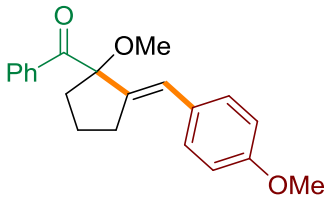
Prepared in reaction of 1-(1-(4-methoxyphenyl)-2-methylhept-1-en-6-yn-1-yl)pyrrolidine and 4-methoxyphenyl trifluoromethanesulfonate (128.5 mg, 0.502 mmol) under general conditions (72.2 mg, 0.216 mmol, 54%).Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 9:1→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.26 – 7.19 (m, 3H), 6.91 – 6.80 (m, 4H), 6.09 (t, *J* = 2.6 Hz, 1H), 3.80 (d, *J* = 4.3 Hz, 6H), 3.02 – 2.88 (m, 2H), 2.45 – 2.32 (m, 1H), 2.16 – 2.06 (m, 1H), 2.03 – 1.87 (m, 1H), 1.75 – 1.64 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 162.0, 158.1, 148.7, 131.5, 130.9, 129.4, 129.1, 123.1, 113.7, 113.1, 60.1, 55.3, 55.3, 39.1, 32.1, 26.2, 24.9. IR (CH_2Cl_2): 2960, 1660, 1601, 1510, 1253, 1167, 1034, 835 cm^{-1}. MS (EI): m/z (%) = 336(7)[M^+], 307(3), 202(28), 201(100), 200(9), 160(4), 159(8), 136(9), 135(57), 121(28), 115(7), 92(10), 77(16), 55(5), 41(4). HRMS (EI): m/z calcd for $C_{22}H_{24}O_3$ 336.1725; found 336.1719.

***(E)*-(2-benzylidene-1-methoxycyclopentyl)(phenyl)methanone (33)**



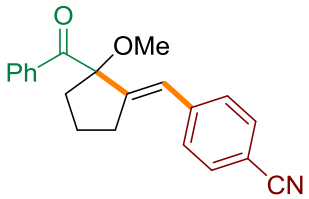
Prepared in reaction of 1-(2-methoxy-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (107.8 mg, 0.400 mg) and phenyl trifluoromethanesulfonate under general conditions (87.1 mg, 0.298 mmol, 75%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.12 (m, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.39 (m, 2H), 7.33 (d, *J* = 5.0 Hz, 4H), 7.26 – 7.20 (m, 1H), 6.59 (t, *J* = 2.6 Hz, 1H), 3.36 (s, 3H), 2.91 – 2.80 (m, 1H), 2.79 – 2.67 (m, 1H), 2.46 (dt, *J* = 12.8, 7.3 Hz, 1H), 2.15 – 2.06 (m, 1H), 2.03 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 143.4, 137.2, 136.2, 132.3, 129.7, 128.8, 128.2, 128.1, 127.3, 126.9, 94.8, 52.6, 34.5, 29.9, 22.8. IR (CH_2Cl_2): 2953, 1676, 1596, 1447, 1239, 1174, 1078, 694 cm^{-1}. MS (EI): m/z (%) = 292(3)[M^+], 260(1), 217(1), 189(2), 188(22), 187(100), 172(3), 171(9), 155(8), 143(3), 130(4), 129(12), 115(20), 105(24), 91(29), 77(28), 65(3), 55(6), 51(11), 41(5). HRMS (EI): m/z calcd for $C_{20}H_{20}O_2$ 292.1463; found 292.1458.

***(E)*-(1-methoxy-2-(4-methoxybenzylidene)cyclopentyl)(phenyl)methanone (34)**



Prepared in reaction of 1-(2-methoxy-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (108.0 mg, 0.401 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (128.3 mg, 0.501 mmol) under general conditions (88.3 mg, 0.273 mmol, 68%). Product was isolated as oil after column chromatography on silica gel(15g, hex/AcOEt 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 2H), 7.54 – 7.46 (m, 1H), 7.43 – 7.37 (m, 2H), 7.30 – 7.23 (m, 2H), 6.89 – 6.83 (m, 2H), 6.50 (t, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 3.33 (s, 3H), 2.88 – 2.77 (m, 1H), 2.76 – 2.64 (m, 1H), 2.43 (dt, *J* = 12.8, 7.3 Hz, 1H), 2.13 – 2.03 (m, 1H), 2.03 – 1.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 158.6, 141.1, 136.3, 132.2, 130.1, 130.0, 129.7, 128.1, 127.0, 113.7, 94.9, 55.2, 52.6, 34.7, 30.0, 22.9. IR (CH_2Cl_2): 2955, 1676, 1606, 1512, 1251,1177, 1034, 706 cm^{-1}. MS (EI): m/z (%) = 322(2)[M^+], 291(7), 256(1),219(4), 218(25), 217(100), 201(8), 185(5), 159(7), 146(8), 131(5), 123(12), 121(21), 105(26), 103(7), 91(5), 77(26), 69(2)(, 57(6), 51(10). HRMS (EI): m/z calcd for $C_{21}H_{22}O_3$ 322.1569; found 322.1560.

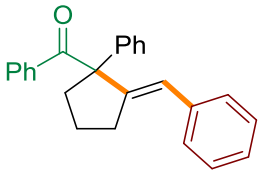
***(E)*-4-((2-benzoyl-2-methoxycyclopentylidene)methyl)benzonitrile (35)**



Prepared in reaction of 1-(2-methoxy-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (107.8 mg, 0.400 mmol) and 4-cyanophenyl trifluoromethanesulfonate (125.7 mg, 0.500 mmol) under general conditions (77.1 mg, 0.243 mmol, 91%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1→8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 2H), 7.60 – 7.55 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.34 (m, 4H), 6.58 (t, *J* = 2.7 Hz, 1H), 3.32 (s, 3H), 2.84 – 2.63 (m, 2H), 2.48 – 2.40 (m, 1H), 2.15 – 2.05 (m, 1H), 2.03 – 1.92 (m, 2H). ^{13}C NMR (101

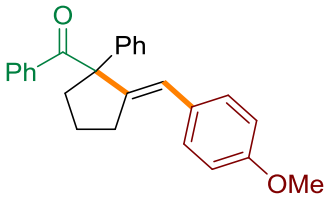
MHz, $CDCl_3$) δ 200.5, 147.6, 141.7, 135.7, 132.5, 131.9, 129.7, 129.1, 128.1, 125.3, 118.8, 110.1, 94.8, 52.6, 33.9, 30.0, 22.5. IR (CH_2Cl_2): 2955, 2226, 1680, 1603, 1177, 887, 706, 555 cm^{-1}. MS (EI): m/z (%) = 317(1)[M^+], 286(1), 228(1), 213(27), 212(100), 196(3), 180(5), 155(3), 154(9), 140(11), 127(6), 116(16), 105(21), 96(2), 77(21), 51(7), 41(4). HRMS (EI): m/z calcd for $C_{21}H_{19}NO_2$ 317.1416; found 317.1427.

(*E*)-(2-benzylidene-1-phenylcyclopentyl)(phenyl)methanone (36)



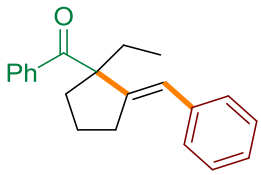
Prepared in reaction of 1-(1,2-diphenylhept-1-en-6-yn-1-yl)pyrrolidine (126.5 mg, 0.401 mmol) and phenyl trifluoromethanesulfonate (113.7 mg, 0.500 mmol) under general conditions (63 mg, 0.186 mmol, 47%). Product was isolated as yellow oil after column chromatography on silica gel (15g, hex/AcOEt 98:2→95:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.36 – 7.27 (m, 3H), 7.26 – 7.17 (m, 9H), 7.14 – 7.09 (m, 1H), 6.07 (t, *J* = 2.6 Hz, 1H), 2.77 (td, *J* = 7.4, 2.5 Hz, 2H), 2.67 (dt, *J* = 13.2, 6.8 Hz, 1H), 2.25 (dt, *J* = 12.7, 7.0 Hz, 1H), 1.76 – 1.65 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.0, 146.8, 142.9, 137.9, 137.1, 131.6, 130.0, 128.6, 128.6, 128.1, 127.9, 127.8, 127.8, 126.9, 126.5, 39.2, 31.6, 23.5. IR (CH_2Cl_2): 2957, 2926, 1674, 1596, 1446, 1225, 757, 699 cm^{-1}. HRMS (ESI): m/z calcd for $C_{26}H_{24}O_2Na$ 361.1568; found 361.1566.

(*E*)-(2-(4-methoxybenzylidene)-1-phenylcyclopentyl)(phenyl)methanone (37)



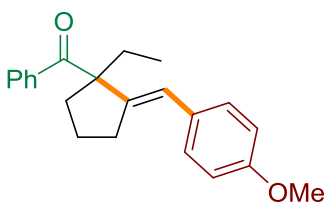
Prepared in reaction of 1-(1,2-diphenylhept-1-en-6-yn-1-yl)pyrrolidine (126.4 mg, 0.400 mmol) and 4-metoxyphenyl trifluoromethanesulfonate (128.3 mg, 0.501 mmol) under general conditions (110 mg, 0.299 mmol, 75%). Product was isolated as yellow oil after column chromatography on silica gel (15g, hex/AcOEt 98:2→85:15).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.43 – 7.31 (m, 5H), 7.32 – 7.25 (m, 3H), 7.25 – 7.20 (m, 2H), 6.89 – 6.84 (m, 2H), 6.11 (t, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 2.83 (td, *J* = 7.4, 2.5 Hz, 2H), 2.75 (dt, *J* = 12.7, 6.9 Hz, 1H), 2.31 (dt, *J* = 12.6, 6.9 Hz, 1H), 1.86 – 1.73 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 158.2, 144.5, 143.0, 137.2, 131.5, 130.7, 129.9, 129.8, 128.5, 127.9, 127.8, 127.2, 126.8, 113.6, 69.9, 55.2, 39.3, 31.5, 23.5. IR (CH_2Cl_2): 2956, 1673, 1605, 1510, 1251, 1177, 1034, 702 cm^{-1}. HRMS (ESI): m/z calcd for $C_{26}H_{24}O_2Na$ 391.1674; found 391.1675.

***(E)*-(2-benzylidene-1-ethylcyclopentyl)(phenyl)methanone (38)**



Prepared in reaction of 1-(2-ethyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (107.2 mg, 0.401 mmol) and phenyl trifluoromethanesulfonate (113.1 mg, 0.500 mmol) under general conditions (72 mg, 0.248 mmol, 62%). Product was isolated as oil after column chromatography on silica gel (25g, hex/AcOEt 95:5→9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.44 – 7.38 (m, 1H), 7.38 – 7.29 (m, 6H), 7.25 – 7.19 (m, 1H), 6.25 (t, *J* = 2.6 Hz, 1H), 2.90 (td, *J* = 7.5, 2.5 Hz, 2H), 2.36 – 2.25 (m, 1H), 2.17 – 2.06 (m, 1H), 2.01 – 1.72 (m, 4H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3, 148.7, 138.8, 138.0, 130.7, 128.4, 128.3, 128.2, 127.9, 126.5, 124.5, 64.5, 34.3, 32.1, 31.0, 24.5, 9.7. IR (CH_2Cl_2): 2963, 1672, 1597, 1445, 1256, 1173, 517 cm^{-1}. MS (EI): m/z (%) = 290(6)[M^+], 186(25), 185(100), 184(7), 155(6), 143(19), 129(32), 128(14), 115(15), 91(52), 77(37), 51(11). HRMS (ESI): m/z calcd for $C_{21}H_{22}O$ 290.1671; found 290.1680.

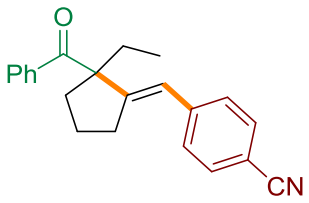
***(E)*-(1-ethyl-2-(4-methoxybenzylidene)cyclopentyl)(phenyl)methanone (39)**



Prepared in reaction of 1-(2-ethyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (107.9 mg, 0.403 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (128.5 mg, 0.502 mmol) under general conditions (77.9 mg, 0.243 mmol, 61%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 8:2).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 3H), 7.42 – 7.36 (m, 1H), 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 6.93 – 6.85 (m, 2H), 6.18 (t, *J*

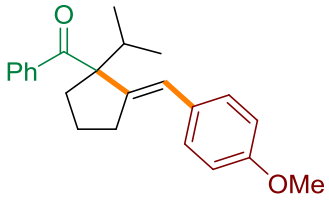
= 2.6 Hz, 1H), 3.81 (s, 3H), 2.93 – 2.81 (m, 2H), 2.34 – 2.23 (m, 1H), 2.15 – 2.05 (m, 1H), 1.99 – 1.81 (m, 3H), 1.81 – 1.69 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5, 158.2, 146.4, 138.9, 130.8, 130.6, 129.6, 128.2, 127.8, 123.9, 113.7, 64.4, 55.2, 34.3, 32.0, 30.9, 24.5, 9.7. IR (CH_2Cl_2): 2961, 1670, 1605, 1510, 1250, 1176, 1032, 826, 705 cm^{-1}. MS (EI): m/z (%) = 320(1)[M$^+$], 216(22), 215(100), 185(2), 173(5), 159(9), 141(3), 123(5), 121(27), 105(14), 91(6), 77(20), 69(8), 51(5). HRMS (ESI): m/z calcd for 320.1776; found 320.1772.

***(E)*-4-((2-benzoyl-2-ethylcyclopentylidene)methyl)benzonitrile (40)**



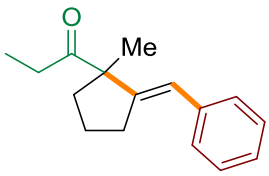
Prepared in reaction of 1-(2-ethyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (106.7 mg, 0.399 mmol) and 4-cyanophenyl trifluoromethanesulfonate (125.8 mg, 0.500 mmol) under general conditions (103.4 mg, 0.328 mmol, 82%). Product was isolated after column chromatography on silica gel (25g, hex/AcOEt 95:5→9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.6 Hz, 4H), 7.46 – 7.30 (m, 6H), 6.21 (t, *J* = 2.6 Hz, 1H), 2.91 – 2.83 (m, 2H), 2.38 – 2.27 (m, 1H), 2.16 – 2.04 (m, 1H), 2.01 – 1.84 (m, 3H), 1.82 – 1.70 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 153.2, 142.3, 138.2, 132.0, 130.9, 128.7, 128.0, 128.0, 123.1, 118.9, 109.6, 64.9, 34.2, 32.3, 31.0, 24.4, 9.7. IR (CH_2Cl_2): 2965, 2226, 1671, 1603, 1256, 1175, 704, 555 cm^{-1}. MS (EI): m/z (%) = 315(1)[M$^+$], 286(1), 210(11), 180(3), 168(6), 154(7), 140(6), 127(4), 116(14), 105(100), 78(4), 77(34), 55(3), 51(8), 41(5). HRMS (EI): m/z calcd for $C_{22}H_{21}NO$ 315.1623; found 315.1625.

***(E)*-(1-isopropyl-2-(4-methoxybenzylidene)cyclopentyl)(phenyl)methanone (41)**



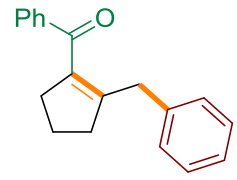
Prepared in reaction of 1-(2-isopropyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (112.6 mg, 0.400 mg) and 4-methoxyphenyl trifluoromethanesulfonate under general conditions (60.2 mg, 0.180 mmol, 45%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 3H), 7.32 – 7.21 (m, 4H), 6.92 – 6.85 (m, 2H), 6.24 (t, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 2.91 – 2.78 (m, 1H), 2.74 (p, *J* = 6.7 Hz, 1H), 2.69 – 2.56 (m, 1H), 2.11 – 2.01 (m, 1H), 1.90 – 1.77 (m, 2H), 1.67 – 1.52 (m, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 158.3, 145.3, 141.2, 130.9, 129.8, 129.6, 127.7, 126.9, 124.5, 113.8, 68.2, 55.3, 34.6, 32.8, 28.7, 24.9, 19.4, 17.3. IR (CH_2Cl_2): 2959, 1677, 1606, 1510, 1251, 1177, 1035, 827, 701 cm^{-1}. MS (EI): m/z (%) = 334(1)[M$^+$], 291(2), 230(30), 229(100), 214(2), 199(3), 187(6), 173(17) 159(10), 147(6), 135(10), 128(3), 121(34), 115(5), 95(4), 69(9), 55(3), 41(3). HRMS (EI): m/z calcd for $C_{23}H_{26}O_2$ 334.1933; found 334.1937.

***(E)*-1-(2-benzylidene-1-methylcyclopentyl)propan-1-one (42)**



Prepared in a reaction of 1-(4-methylnon-3-en-8-yn-3-yl)pyrrolidine (0.400 mmol, 82.93 mg) and phenyl trifluoromethanesulfonate (107.1 mg, 0.399 mmol) under general conditions (34.7 mg, 0.152 mmol, 38%). Product was isolated as oil after column chromatography on silica gel(15g, hex/AcOEt 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.23 – 7.18 (m, 1H), 6.16 (t, *J* = 2.6 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.76 – 2.65 (m, 1H), 2.62 – 2.53 (m, 1H), 2.51 – 2.40 (m, 1H), 2.29 – 2.19 (m, 1H), 1.98 – 1.86 (m, 1H), 1.86 – 1.75 (m, 1H), 1.62 – 1.53 (m, 1H), 1.34 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 149.7, 128.3, 128.3, 126.5, 123.3, 96.8, 60.9, 37.2, 32.3, 30.9, 24.5, 23.9, 8.9. IR (CH_2Cl_2): 2972, 2937, 1711, 1599, 1490, 1459, 1377, 758, 692 cm^{-1}. HRMS (APCI): m/z calcd for $C_{16}H_{21}O$ 229.1592; found 229.1593.

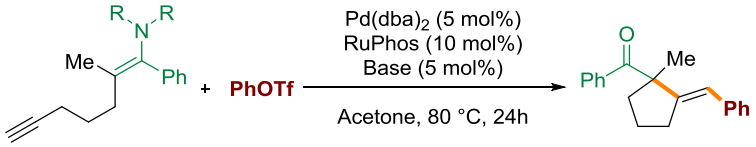
(2-benzylcyclopent-1-en-1-yl)(phenyl)methanone



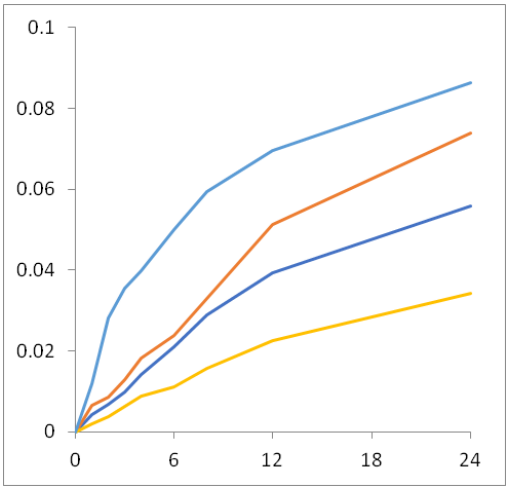
Prepared in reaction of 1-(1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (95.8 mg, 0.401 mmol) and phenyl trifluoromethanesulfonate (113.09 mg, 0.500 mmol) under general conditions (38.8 mg, 0.148 mmol, 37%). Product was isolated as oil after column chromatography on silica gel (15g, hex/AcOEt 98:2→95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.57 – 7.52 (m, 1H), 7.48 –

7.42 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H), 3.46 (s, 2H), 2.77 (ddt, *J* = 7.8, 5.9, 1.9 Hz, 2H), 2.43 (dddd, *J* = 7.8, 5.8, 2.2, 1.1 Hz, 2H), 1.96 – 1.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 150.5, 138.8, 138.7, 137.3, 132.6, 128.9, 128.8, 128.5, 128.4, 126.2, 37.1, 36.4, 36.2, 22.4. IR (CH_2Cl_2): 2962, 1670, 1445, 1596, 1263, 1175, 963, 816, 706 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{18}ONa$ 285.1255; found 285.1255.

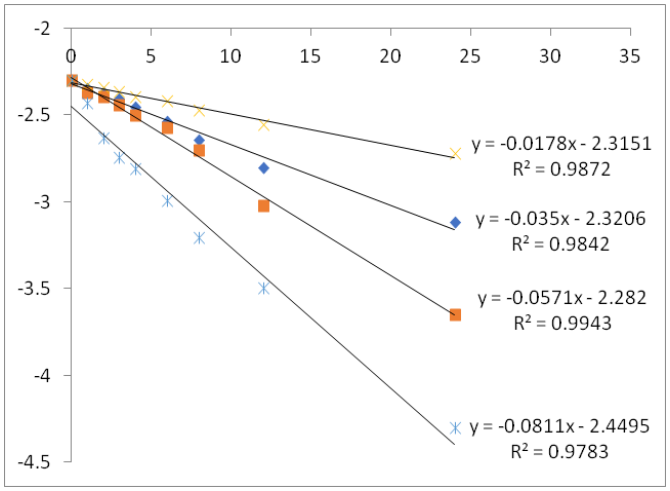
Kinetic profiles for the reaction of various enamines with phenyl triflate.



Entry	Time	Concentration of product [mol/L]			
		Pyrrolidine	Piperidine	Morfoline	Et2NH
1	1 h	0.012	0.006	0.004	0.002
2	2 h	0.028	0.009	0.007	0.004
3	3 h	0.036	0.013	0.010	0.006
4	4 h	0.040	0.018	0.014	0.009
5	6 h	0.05	0.024	0.021	0.011
6	8 h	0.059	0.033	0.029	0.016
7	12 h	0.070	0.051	0.039	0.023
8	24 h	0.086	0.074	0.056	0.034

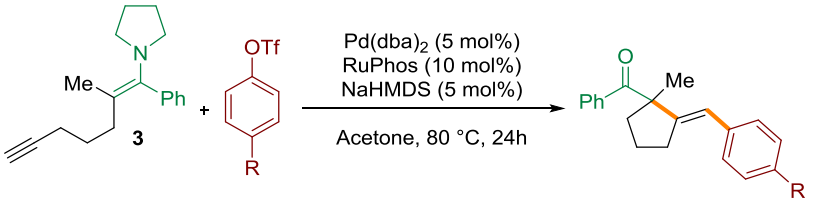


[product] *vs* time

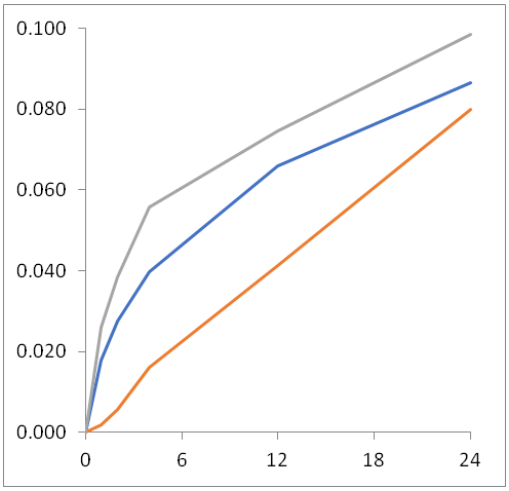


log(0.1-[product]) vs time

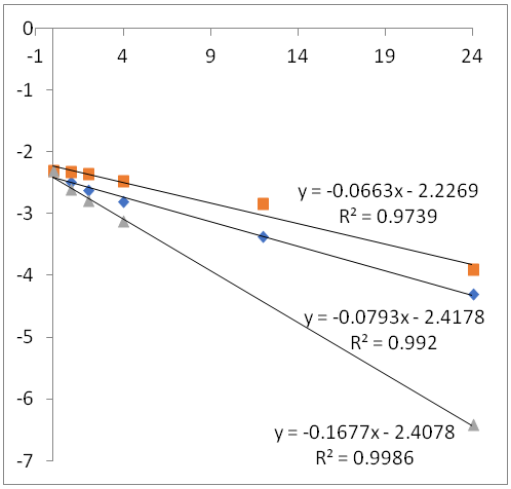
Kinetic profiles for the reaction of 3 with electronically varied aryl triflates.



Entry	Time	Concentration of product [mol/L]		
		R= CN	R= H	R= OMe
1	1 h	0.026	0.018	0.002
2	2 h	0.039	0.028	0.006
3	4 h	0.056	0.040	0.016
4	12 h	0.075	0.066	0.041
5	24 h	0.098	0.086	0.080



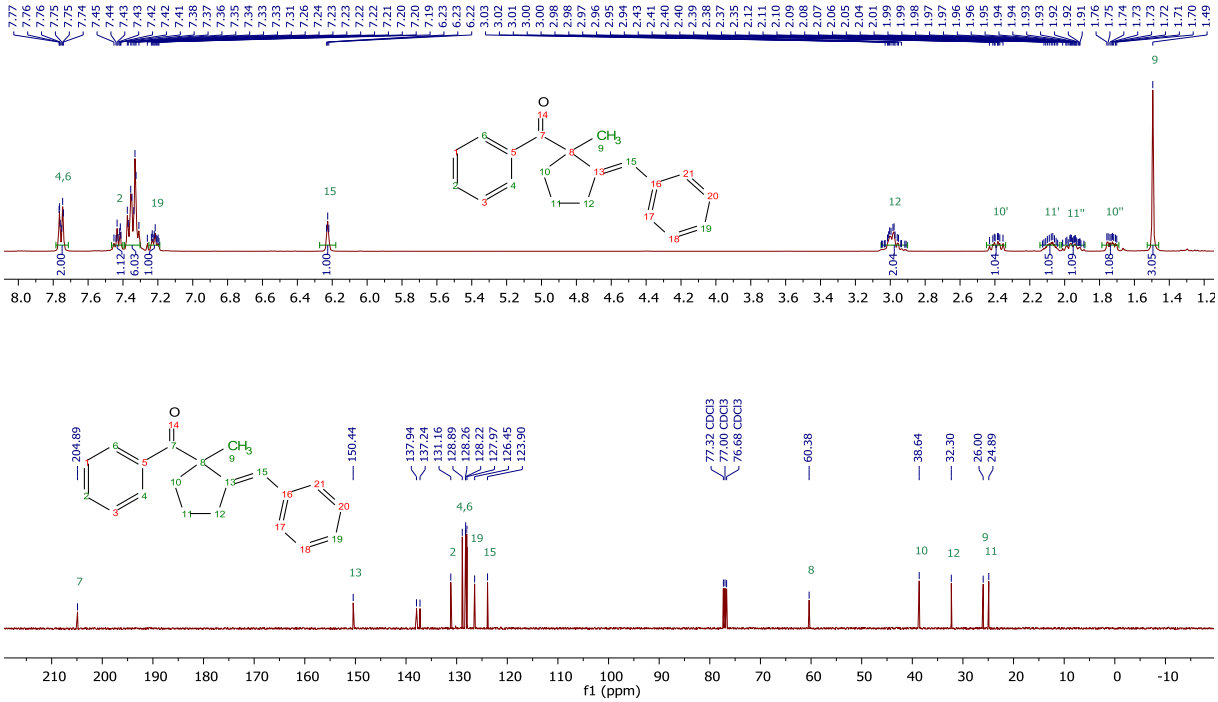
[product] *vs* time



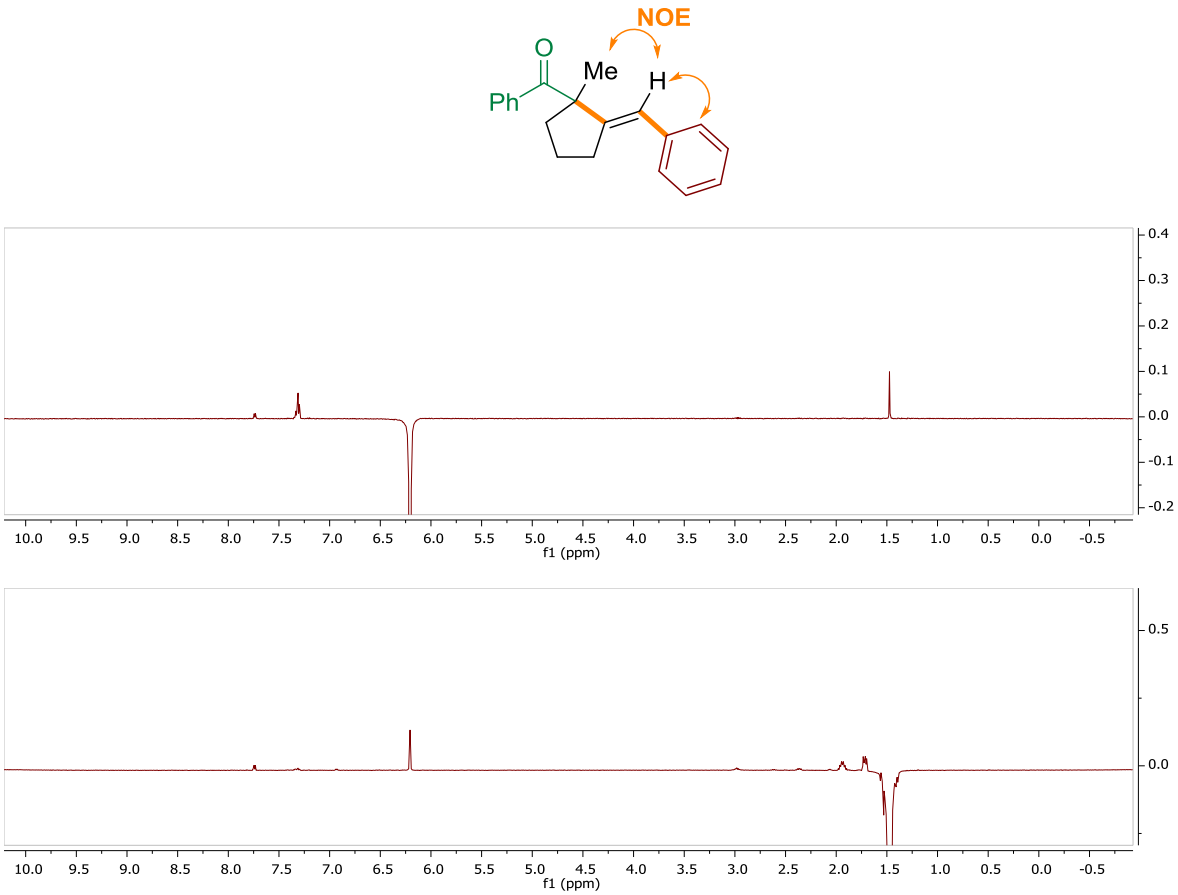
log(0.1-[product]) vs time

Structure elucidation of compound 4

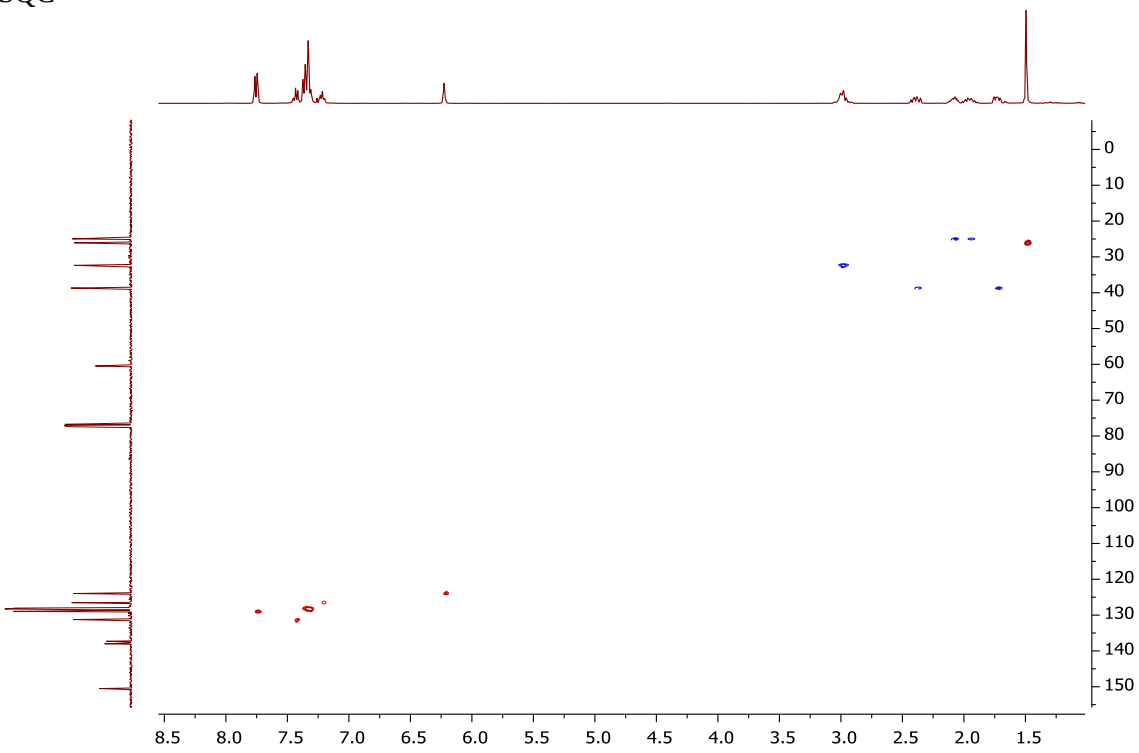
1D ^{1}H and ^{13}C NMR Spectra



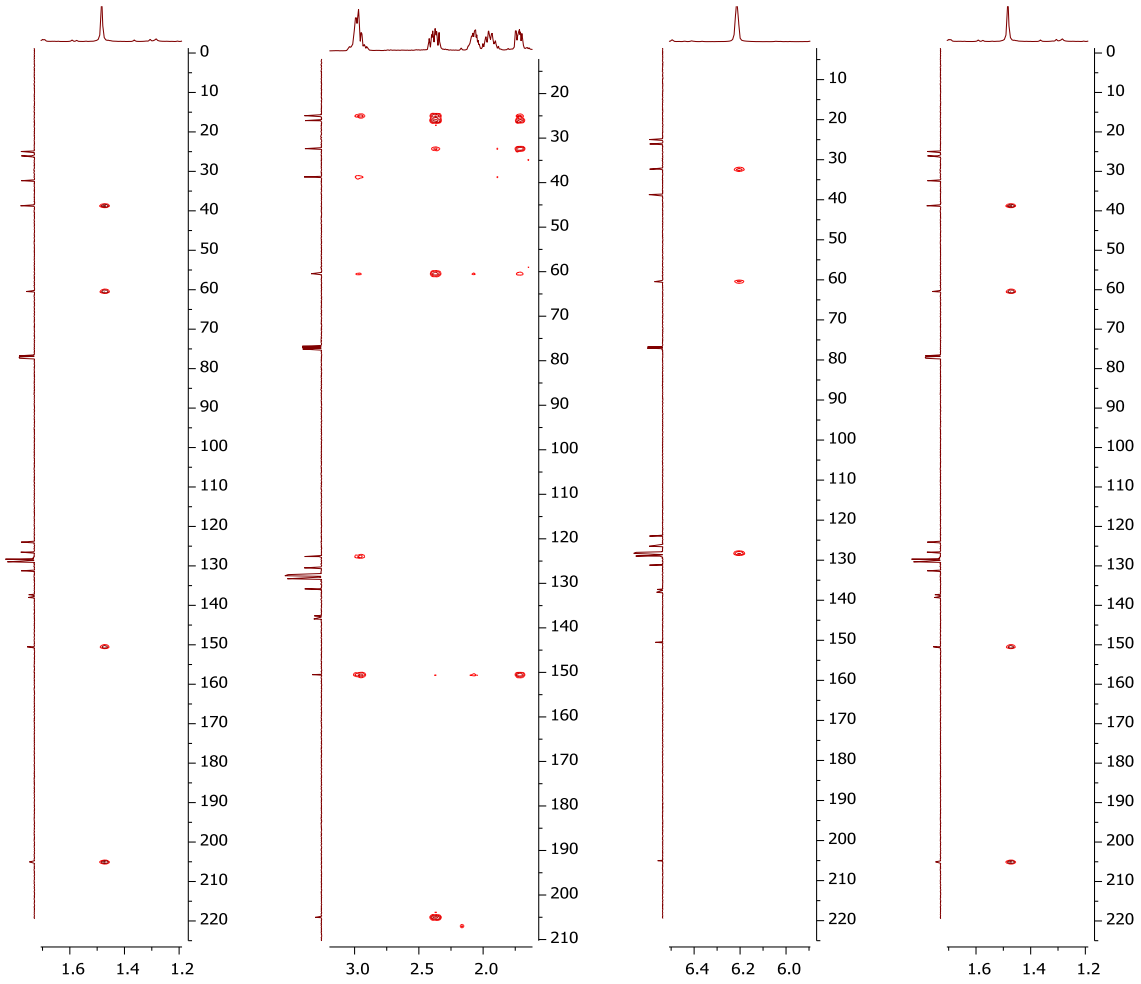
1D ^{1}H NOESY



HSQC


0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
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

HMBC


1.6
1.4
1.2
3.0
2.5
2.0
6.4
6.2
6.0
1.6
1.4
1.2

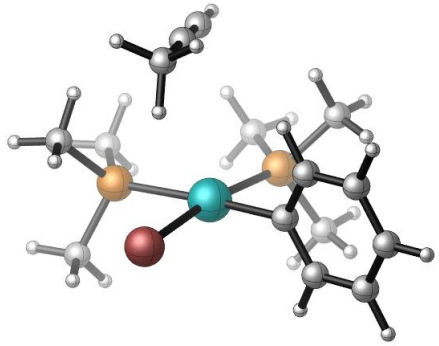
Computational studies

All calculations were performed using Gaussian 09 package.[4] Structures of minima and transition states were optimized employing B3LYP functional with the D3 version of Grimme's empirical dispersion correction[5] Def2-SVP bases set[6] and SMD solvation model.[7] Frequency calculations were then performed at the same level of theory to confirm the nature of stationary points and provide corrections to thermodynamic functions. Single point energies were calculated at M06 level of theory using Def2-TZVPP basis set and SMD solvation model. Various conformers of intermediates and transition states were investigated and only the lowest energy conformers are shown in the work. Structures were visualized using: CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

Optimized geometries, energies and corrections to thermodynamic functions.

Model studies (Scheme 2)

[$(PMe_3)_2$PdPhBr] [Propyn]



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -3971.898152
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -3972.394484

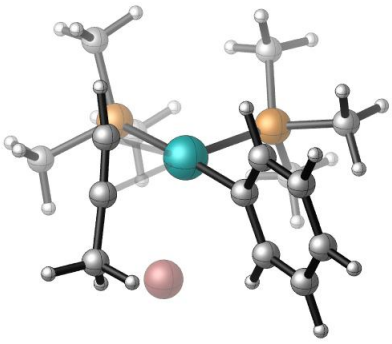
Zero-point correction=	0.376302 (Hartree/Particle)
Thermal correction to Energy=	0.405252
Thermal correction to Enthalpy=	0.406197
Thermal correction to Gibbs Free Energy=	0.315467

Charge = 0 Multiplicity = 1

Pd	-0.09384700	-0.01336900	-0.33290800
P	0.37620600	2.23990500	-0.33017700
C	-1.01732400	3.42702100	-0.23486500
H	-0.61624900	4.45223000	-0.20044200
H	-1.65374600	3.31989300	-1.12310700
H	-1.61499600	3.23849600	0.66698800
C	1.23615200	2.78310200	-1.85656400
H	1.39206500	3.87332500	-1.83038400
H	2.20760600	2.27631300	-1.93508500
H	0.62320900	2.52069400	-2.73234500
C	1.47711500	2.83309400	1.01253300
H	2.47110300	2.37870900	0.90914000
H	1.56490800	3.92940300	0.95509200
H	1.05517600	2.54902600	1.98769700
P	-2.52304800	-0.06553200	-0.51658300
C	-3.30292900	-1.15780100	0.74163300

H	-3.21029000	-0.68603500	1.73112700
H	-4.36980100	-1.30461300	0.50816500
H	-2.78343600	-2.12551200	0.75277300
C	-3.02774400	-0.82934100	-2.11114800
H	-4.12061600	-0.96250800	-2.15755900
H	-2.70348500	-0.17971000	-2.93958700
H	-2.52521900	-1.80266000	-2.20739800
C	-3.64245200	1.39394900	-0.43362600
H	-3.43358800	2.08760000	-1.25973800
H	-4.68766500	1.05341300	-0.50994600
H	-3.50616000	1.91917200	0.52271000
C	1.93675200	-0.22035400	-0.16231900
C	2.52338800	-0.37347300	1.10742600
C	2.77649400	-0.31071300	-1.28642500
C	3.89688600	-0.61258300	1.25017400
H	1.90456800	-0.30326900	2.00665900
C	4.15239100	-0.54726700	-1.15018000
H	2.35844300	-0.19970200	-2.29165500
C	4.71992500	-0.69878900	0.12029100
H	4.32622500	-0.72958600	2.25040200
H	4.78260400	-0.61338200	-2.04286900
H	5.79271600	-0.88211900	0.22932000
C	-1.28833000	1.38769100	3.07132500
C	-0.97878900	0.21937000	3.18769100
H	-1.56219000	2.42387300	2.97364500
C	-0.61896600	-1.18837800	3.30580400
H	0.29276500	-1.31326800	3.91254500
H	-1.42858700	-1.76093400	3.78783500
H	-0.43279400	-1.62849000	2.31140800
Br	-0.19023900	-2.57611800	-0.44659200

$[(PMe_3)_2PdPh(Propyn)]^+$ Br^-



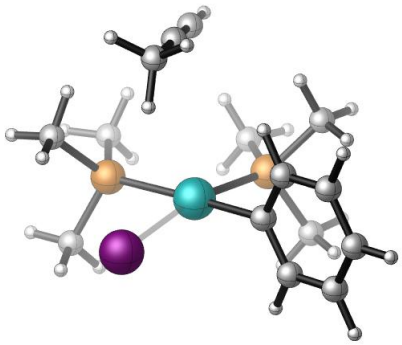
E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -3971.880329
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -3972.379189

Zero-point correction=	0.375839 (Hartree/Particle)
Thermal correction to Energy=	0.404765
Thermal correction to Enthalpy=	0.405709
Thermal correction to Gibbs Free Energy=	0.315537

Charge = 0 Multiplicity = 1

Pd	-0.03271300	-0.08786800	-0.52611200
P	0.12442100	-2.12182500	0.56552200
C	-0.90908300	-3.46688900	-0.13753000
H	-0.75765900	-4.39141500	0.44253500
H	-1.97303900	-3.19743300	-0.11244400
H	-0.60971000	-3.64052000	-1.18229100
C	-0.37605500	-2.01714300	2.32129600
H	-0.27554000	-3.00425800	2.80045800
H	0.26325200	-1.27794600	2.82387500
H	-1.41203700	-1.66289000	2.39091600
C	1.76753200	-2.93079500	0.65821200
H	2.46928500	-2.28820900	1.20738700
H	1.66545500	-3.89679900	1.17775500
H	2.15861200	-3.09669300	-0.35583100
P	-2.44481400	-0.10968800	-0.73831800
C	-3.11747900	1.57572300	-1.01426300
H	-2.70532100	1.99652400	-1.94241200
H	-4.21672000	1.54275900	-1.08276800
H	-2.80663700	2.19964900	-0.16289900
C	-3.45695200	-0.69415800	0.67574000
H	-4.52857100	-0.56658900	0.45313800
H	-3.25733500	-1.75468400	0.88362900
H	-3.17637300	-0.09145700	1.55219800
C	-3.10814500	-1.05886600	-2.16739100
H	-2.84849100	-2.12246900	-2.05761100
H	-4.20314600	-0.95640100	-2.23839300
H	-2.64939900	-0.68160000	-3.09467700
C	2.00536000	0.02987200	-0.34625800
C	2.86392200	-0.42372800	-1.36367900
C	2.57972800	0.64740900	0.77998600
C	4.25372700	-0.26614100	-1.26326000
H	2.45215200	-0.91158500	-2.25312100
C	3.96984100	0.80504300	0.88326800
H	1.92565300	1.02047400	1.57438100
C	4.81351400	0.34662900	-0.13584100
H	4.90111900	-0.62703000	-2.06887200
H	4.39593800	1.29059700	1.76736300
H	5.89749900	0.46772200	-0.05359500
C	-0.03358500	1.13382500	-2.53069100
C	0.26716900	2.04973100	-1.76975700
H	-0.28909600	0.49872200	-3.36504900
C	0.65036200	3.21084800	-0.97886800
H	1.72843800	3.17533500	-0.75328100
H	0.43555100	4.13717000	-1.53689500
H	0.10549300	3.21099100	-0.01883500
Br	-0.83993700	1.67127200	2.00950400

[$(PMe_3)_2$PdPhI] [Propyn]



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1695.824172
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1696.098331

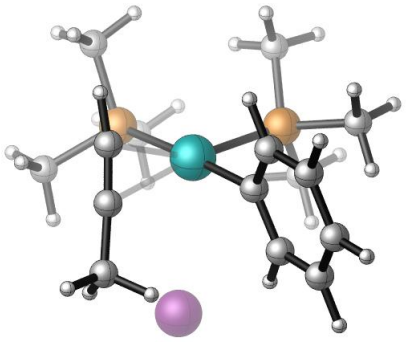
Zero-point correction=	0.376079 (Hartree/Particle)
Thermal correction to Energy=	0.405284
Thermal correction to Enthalpy=	0.406228
Thermal correction to Gibbs Free Energy=	0.313996

Charge = 0 Multiplicity = 1

Pd	-0.09449300	0.14154600	-0.29920000
P	0.26833900	2.39463200	-0.63595300
C	-1.18271500	3.49506100	-0.83203900
H	-0.82516400	4.52538400	-0.98615700
H	-1.76741900	3.18212900	-1.70735400
H	-1.81394600	3.46058600	0.06512000
C	1.19477300	2.72205200	-2.18411600
H	1.27116000	3.80919100	-2.34433800
H	2.20186900	2.28991900	-2.11699800
H	0.66221300	2.26336100	-3.03107700
C	1.24283800	3.26621600	0.64897300
H	2.26394500	2.86521600	0.68381200
H	1.27649100	4.34030900	0.40790400
H	0.76712300	3.12499600	1.63038500
P	-2.52323400	-0.04797400	-0.47324300
C	-3.26411000	-1.04067000	0.88899500
H	-3.18950600	-0.46988400	1.82631100
H	-4.32616900	-1.23843700	0.67218100
H	-2.72802000	-1.99223600	1.00412300
C	-3.02289300	-0.96270300	-1.98843600
H	-4.11374200	-1.11655000	-2.00945400
H	-2.71912400	-0.38258300	-2.87400900
H	-2.51202000	-1.93629200	-2.01291700
C	-3.69203600	1.37351800	-0.50227300
H	-3.53876200	1.98315900	-1.40245200
H	-4.72374500	0.98698100	-0.50537500
H	-3.54683100	1.99870300	0.39022400
C	1.94562000	0.10522300	-0.06665000
C	2.50004900	0.20870800	1.22214600
C	2.82074700	-0.12983900	-1.14227200
C	3.87962200	0.07432900	1.43130600

H	1.85317600	0.40136600	2.08270000
C	4.20179500	-0.26103500	-0.93862100
H	2.42671200	-0.21895000	-2.15909700
C	4.73788300	-0.15939600	0.35037700
H	4.28442800	0.15663000	2.44485200
H	4.86046500	-0.44564000	-1.79300900
H	5.81483800	-0.26124700	0.51113500
C	-1.64068600	2.18296700	2.78449800
C	-1.20801200	1.08956400	3.08636400
H	-2.02132100	3.15528700	2.52383200
C	-0.69472700	-0.22971100	3.43506300
H	0.22559900	-0.14985100	4.03594800
H	-1.43558700	-0.79898400	4.02000700
H	-0.45959800	-0.80796000	2.52668200
I	0.05800300	-2.65738300	-0.16305100

[$(PMe_3)_2$PdPh(Propyn)]$^+$ I^-



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1695.822354
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1696.091996

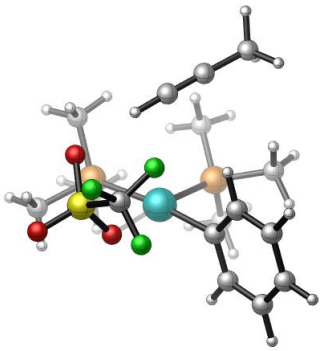
Zero-point correction=	0.375771 (Hartree/Particle)
Thermal correction to Energy=	0.404859
Thermal correction to Enthalpy=	0.405804
Thermal correction to Gibbs Free Energy=	0.314443

Charge = 0 Multiplicity = 1

Pd	-0.33278600	-0.67252000	0.45789400
P	-0.63278000	-1.43217900	-1.70432500
C	-0.20627400	-3.20637200	-1.88252900
H	-0.40857900	-3.52661800	-2.91696700
H	0.85245400	-3.38135700	-1.65086200
H	-0.82705300	-3.79512800	-1.19044800
C	0.37274700	-0.56523400	-2.96002900
H	0.21797900	-1.03980400	-3.94221000
H	0.05763400	0.48738600	-3.00247600
H	1.43539100	-0.60326300	-2.68905900
C	-2.31962200	-1.37073700	-2.41262700
H	-2.66124600	-0.32892400	-2.47889700
H	-2.29923000	-1.82013500	-3.41804200
H	-3.01227200	-1.93201700	-1.76965500

P	1.90812400	-1.57840600	0.75094800
C	2.86459000	-0.67933700	2.03512400
H	2.32651000	-0.71210400	2.99280900
H	3.85835700	-1.13903600	2.15635500
H	2.98078600	0.37005400	1.72496800
C	3.09920900	-1.62099200	-0.64538800
H	4.05940600	-2.03715100	-0.30113400
H	2.71481300	-2.23925900	-1.46829100
H	3.25615200	-0.59529500	-1.01081900
C	1.90157600	-3.30834500	1.36655700
H	1.42404200	-3.96113800	0.62075000
H	2.92719000	-3.66131600	1.56002600
H	1.31851700	-3.35564900	2.29918400
C	-2.19384900	0.16024500	0.29474900
C	-3.33556100	-0.49935700	0.78204700
C	-2.34650100	1.45614700	-0.22966900
C	-4.59341300	0.11931400	0.75386800
H	-3.25327900	-1.51114300	1.19163600
C	-3.60344100	2.07852600	-0.25610200
H	-1.47892700	1.99364200	-0.62437600
C	-4.73211900	1.41169100	0.23374200
H	-5.46872600	-0.41258600	1.13963800
H	-3.69862800	3.08910200	-0.66541300
H	-5.71297000	1.89478800	0.20964100
C	-0.51776400	-0.80373300	2.78994300
C	-0.36924600	0.41150800	2.71558100
H	-0.65597300	-1.83686700	3.07174300
C	-0.21803400	1.85808300	2.74462900
H	-0.35888900	2.22581800	3.77432900
H	0.78139100	2.15490200	2.39122600
H	-0.96642300	2.33493500	2.09247000
I	1.81048600	2.39215800	-0.69505700

[(PMe_3)$_2$PdPhOTf] [Propyn]



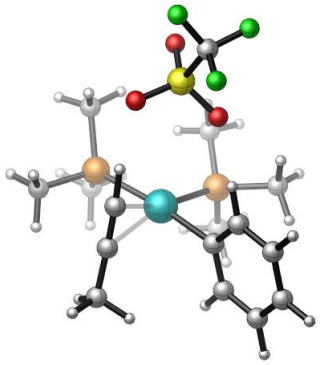
E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2358.909296
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2359.837864

Zero-point correction=	0.404558 (Hartree/Particle)
Thermal correction to Energy=	0.440089
Thermal correction to Enthalpy=	0.441033
Thermal correction to Gibbs Free Energy=	0.335245

Charge = 0 Multiplicity = 1

Pd	-0.61485500	-0.12485000	-0.56311700
P	-2.64659700	0.74582800	-0.07650200
C	-3.61647300	-0.20316300	1.15491600
H	-4.54250000	0.34696000	1.38389800
H	-3.87653400	-1.19584200	0.76668400
H	-3.02153000	-0.32235500	2.07070900
C	-3.71471000	0.83324600	-1.55792000
H	-4.70413300	1.23515000	-1.28742200
H	-3.23897800	1.49278800	-2.29919300
H	-3.82664400	-0.17110900	-1.99082800
C	-2.70640800	2.44331400	0.60585000
H	-2.35878700	3.16023600	-0.14968400
H	-3.74395100	2.67653200	0.89178300
H	-2.05427600	2.51159700	1.48724000
P	-1.24655700	-2.47131000	-0.50416200
C	-1.40122700	-3.24004000	1.15393300
H	-2.15809800	-2.70750400	1.74732800
H	-1.68204700	-4.30197000	1.06625800
H	-0.42787000	-3.15623700	1.65894500
C	-0.05142300	-3.57600200	-1.35984900
H	-0.45763600	-4.59929900	-1.40026400
H	0.11817600	-3.21108300	-2.38393000
H	0.90475400	-3.59182000	-0.82228900
C	-2.80931500	-2.91503400	-1.36622800
H	-2.73024600	-2.60264600	-2.41904100
H	-2.97365600	-4.00362700	-1.32392900
H	-3.67022500	-2.40426600	-0.91369600
C	0.00429400	1.80665300	-0.80695700
C	0.61923300	2.53087000	0.22891400
C	-0.05818900	2.39528900	-2.08288100
C	1.17755300	3.79406200	-0.00802000
H	0.67124200	2.10966900	1.23549700
C	0.49482200	3.66237300	-2.32220400
H	-0.54264900	1.86717900	-2.91088800
C	1.11616500	4.36623700	-1.28448100
H	1.66036800	4.33553700	0.81161000
H	0.43643000	4.10012200	-3.32367700
H	1.54726000	5.35446100	-1.46824400
C	-0.03989800	-0.20955200	2.84643900
C	-0.78254700	0.52998100	3.46037700
H	0.63328400	-0.84539900	2.28892000
C	-1.68550900	1.42372900	4.17713300
H	-1.34760300	2.47016400	4.09885400
H	-2.70610900	1.36704400	3.76403900
H	-1.73818600	1.16411600	5.24753300
O	1.46557500	-0.71464800	-1.09408900
S	2.44421700	-1.39926100	-0.17130200
O	3.43326200	-2.21186400	-0.88886700
O	1.81904800	-2.00756800	1.02442200
C	3.44278100	0.03361500	0.52708500
F	2.76632500	0.65261400	1.49866000
F	3.72704800	0.92191200	-0.42647500
F	4.58722200	-0.42405100	1.03888100

[$(PMe_3)_2$PdPh(Propyn)]$^+$ TfO$^-$



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2358.904602
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2359.838679

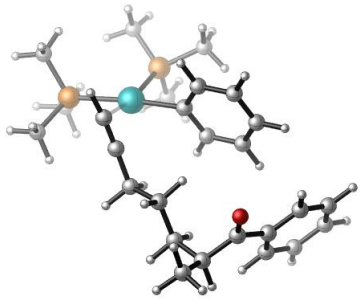
Zero-point correction=	0.404494 (Hartree/Particle)
Thermal correction to Energy=	0.439904
Thermal correction to Enthalpy=	0.440848
Thermal correction to Gibbs Free Energy=	0.335139

Charge = 0 Multiplicity = 1

Pd	1.10145300	0.27543600	-0.23273200
P	1.10050700	0.14147600	2.06606200
C	-0.06634300	1.28603700	2.89145400
H	-0.07905700	1.06933500	3.97132200
H	0.24491200	2.32788400	2.74111800
H	-1.06923700	1.13495400	2.46869300
C	2.73747100	0.53293800	2.78474600
H	2.69142700	0.48970100	3.88471500
H	3.47160000	-0.20117900	2.41977200
H	3.04889000	1.53823900	2.46635000
C	0.66459200	-1.46909000	2.81541200
H	1.40910000	-2.22882900	2.54384900
H	0.63389300	-1.35409000	3.91043200
H	-0.32253200	-1.77108400	2.44102400
P	0.80922200	2.68731100	-0.37901800
C	1.14501700	3.33364500	-2.06623400
H	0.39991400	2.93596900	-2.77000700
H	1.09522500	4.43414200	-2.06428500
H	2.14560100	3.01384700	-2.39423900
C	1.98176200	3.67019800	0.63993700
H	1.85303400	4.74680000	0.44406000
H	1.81649000	3.47658400	1.70931400
H	3.01129900	3.37552600	0.38413200
C	-0.83036900	3.41931800	-0.00644500
H	-1.12110700	3.20264500	1.02949500
H	-0.80163400	4.50956700	-0.16392600
H	-1.57709100	2.95767900	-0.66651100
C	1.54332500	-1.72221100	-0.18122500
C	0.53633100	-2.68661500	-0.36717200

C	2.87425900	-2.15998300	-0.06491600
C	0.85572100	-4.04851700	-0.44908700
H	-0.50779700	-2.36961600	-0.42744400
C	3.19537100	-3.52421300	-0.14541200
H	3.68117600	-1.43756000	0.09533600
C	2.18611700	-4.47365700	-0.33795500
H	0.05817100	-4.78410800	-0.59501600
H	4.23838800	-3.84304600	-0.05329100
H	2.43298300	-5.53746500	-0.39802600
C	0.41257500	0.08554600	-2.45955600
C	1.62039600	0.06093800	-2.66729200
H	-0.66816100	0.12520300	-2.35394300
C	3.03472000	0.00816800	-3.01082800
H	3.51621700	-0.85267900	-2.52018000
H	3.15657800	-0.09642700	-4.10136300
H	3.55218500	0.92561800	-2.68824400
O	-1.73389400	-0.68714500	0.75700000
S	-2.68607000	0.22224900	0.07559700
O	-2.28323900	0.67503100	-1.28257700
O	-3.27920200	1.26818800	0.93362400
C	-4.11736700	-0.92171700	-0.30301300
F	-3.70698100	-1.94761300	-1.06279000
F	-4.63994200	-1.42257000	0.82303600
F	-5.08829000	-0.27856600	-0.96263800

[$(PMe_3)_2$PdPh(acetylenic ketone)]$^+$



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1899.149165
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1899.601159

Zero-point correction=	0.581498 (Hartree/Particle)
Thermal correction to Energy=	0.619250
Thermal correction to Enthalpy=	0.620194
Thermal correction to Gibbs Free Energy=	0.509500

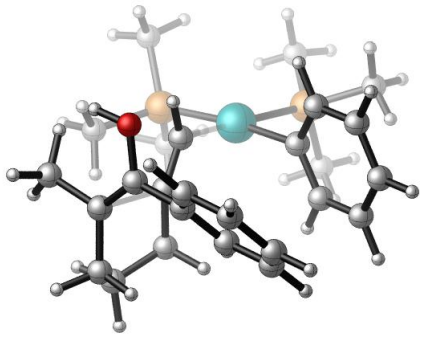
Charge = 1 Multiplicity = 1

P	-2.86783500	-2.02172800	0.25615200
C	-4.64828500	-2.31360900	-0.05703900
H	-4.89294200	-3.35168100	0.21842900
H	-5.27429400	-1.62956400	0.52909900
H	-4.85280200	-2.16362300	-1.12771800

C	-2.61636500	-2.35965500	2.03459600
H	-3.01705900	-3.35387500	2.28860200
H	-1.53742100	-2.33302000	2.24905700
H	-3.12075800	-1.58955500	2.63485300
C	-2.09981100	-3.45692400	-0.58049600
H	-1.03411600	-3.51956500	-0.32488400
H	-2.61574100	-4.37368200	-0.25439100
H	-2.20169100	-3.34403100	-1.66966400
P	-4.06232700	1.30446800	0.48302600
C	-3.73478700	3.09600200	0.71956200
H	-3.48783000	3.56405600	-0.24393200
H	-4.62387800	3.58593700	1.14727500
H	-2.88185600	3.22537000	1.40322700
C	-4.71837400	0.82416500	2.13010500
H	-5.56182300	1.47656900	2.40680400
H	-5.05677500	-0.22104300	2.12500800
H	-3.91679500	0.93200300	2.87690700
C	-5.53442900	1.29821500	-0.61150300
H	-5.90378900	0.27052400	-0.73811900
H	-6.33488300	1.92623100	-0.18864400
H	-5.24514100	1.69202400	-1.59824600
C	-0.38218400	-0.86754900	-0.84837600
C	-0.08489900	-1.11400600	-2.19897300
C	0.58431100	-1.19269300	0.11883800
C	1.14908800	-1.66315100	-2.57440200
H	-0.81653100	-0.87428400	-2.97701400
C	1.82175100	-1.73683500	-0.25350300
H	0.38262900	-1.02152700	1.18098100
C	2.10636000	-1.97609700	-1.60255000
H	1.36321000	-1.84494600	-3.63209300
H	2.56849400	-1.96922500	0.51075000
H	3.07055500	-2.40013800	-1.89226300
Pd	-2.11284200	0.08307500	-0.30836700
C	-1.52188300	2.01888700	-1.51261500
C	-0.70769300	2.09595100	-0.59900900
H	-2.16780100	2.12293200	-2.37160500
C	0.33806000	2.27813900	0.40811100
C	4.28143500	2.43619300	0.44712100
C	1.75967500	2.24949000	-0.18319000
H	0.15773100	3.23844100	0.92251500
H	0.23635400	1.49222000	1.17411400
C	2.80792700	2.35573000	0.92594100
C	4.65311700	1.19524100	-0.36586600
C	4.57239300	3.71317600	-0.34474300
H	1.86371700	3.07616400	-0.90351800
H	1.89478500	1.31293900	-0.74717800
H	2.68614700	1.49570400	1.60433700
H	2.60890500	3.25685000	1.53175200
C	4.95600200	-0.09687800	0.34221600
H	4.27676600	4.59997000	0.23803100
H	4.03139500	3.72709200	-1.30150200
H	5.64652800	3.79658200	-0.57429900
C	4.88879600	-0.24915000	1.73921400
C	5.29925500	-1.21197700	-0.44519800

C	5.13791700	-1.49210500	2.32864700
H	4.63824900	0.59615700	2.38120200
C	5.55602000	-2.44943600	0.14213600
H	5.34814700	-1.08732200	-1.52808700
C	5.46871100	-2.59428400	1.53306000
H	5.07481500	-1.59915500	3.41451500
H	5.81796500	-3.30708800	-0.48287600
H	5.66253000	-3.56531800	1.99655500
O	4.68258400	1.24172400	-1.58608400
H	4.90484900	2.44350600	1.35540300

[$(PMe_3)_2$PdPh(acetylenic enol)]$^+$ (TS for cyclization)



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1899.115943
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1899.563297

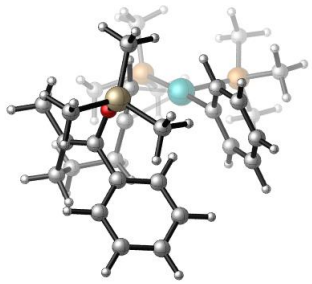
Zero-point correction=	0.580603 (Hartree/Particle)
Thermal correction to Energy=	0.617261
Thermal correction to Enthalpy=	0.618206
Thermal correction to Gibbs Free Energy=	0.510804

Charge = 1 Multiplicity = 1

P	3.37674100	1.52508600	0.08184400
C	4.96670800	1.07919700	-0.71801400
H	5.72422000	1.84450400	-0.48566100
H	5.31930100	0.10315600	-0.35922400
H	4.82253700	1.03061600	-1.80792600
C	3.79180900	1.66162200	1.86182700
H	4.64503700	2.34306200	2.00871800
H	2.91540600	2.04992200	2.40253500
H	4.04110700	0.66559800	2.25674000
C	3.16905700	3.26965500	-0.44281600
H	2.33927400	3.73019900	0.11018800
H	4.09929000	3.82606400	-0.24683800
H	2.94123900	3.30461500	-1.51879500
P	2.78512300	-1.95946500	-0.26286100
C	1.73923600	-3.46448400	-0.14343500
H	1.06765200	-3.51779900	-1.01222500
H	2.37393400	-4.36435600	-0.11215900
H	1.12655400	-3.41577700	0.76871600
C	3.94562700	-2.19219000	1.14277300

H	4.42367200	-3.18346500	1.08970600
H	4.72186200	-1.41426300	1.13172000
H	3.38103200	-2.11176300	2.08468100
C	3.80447300	-2.30750900	-1.75012900
H	4.56354200	-1.52337100	-1.87997200
H	4.30095400	-3.28694800	-1.65896000
H	3.14953300	-2.31267500	-2.63539900
C	0.35388600	1.76597900	-0.11659900
C	-0.17711800	2.40208100	-1.25441300
C	-0.03536900	2.25557900	1.14540600
C	-1.06279200	3.48278000	-1.13857300
H	0.09674800	2.05253500	-2.25528600
C	-0.92001700	3.33699100	1.26733000
H	0.35441100	1.79271700	2.05793000
C	-1.43854400	3.95614400	0.12402400
H	-1.46341800	3.95537500	-2.04092900
H	-1.20721400	3.69458000	2.26118400
H	-2.13236900	4.79631500	0.21615400
Pd	1.55382300	0.10221200	-0.24882100
C	-0.27370100	-0.90687200	-0.63082300
C	-0.86089700	-1.30678800	0.42580400
H	-0.60932100	-0.91330800	-1.67105100
C	-0.92268600	-1.44088900	1.89654100
C	-2.78774000	-2.47268300	0.07546800
C	-1.80630900	-2.60728900	2.35352000
H	0.11589800	-1.57275100	2.24387000
H	-1.28433000	-0.49329100	2.33140100
C	-3.11524300	-2.58605400	1.54521200
C	-3.25177800	-1.45254500	-0.73537500
C	-2.22279600	-3.72026600	-0.57666100
H	-2.00466100	-2.53602600	3.43345400
H	-1.27386600	-3.55681200	2.18420000
H	-3.74745800	-1.75096300	1.87635400
H	-3.68026300	-3.51696000	1.72417100
C	-4.02093800	-0.23835900	-0.36193000
H	-1.62715400	-4.30433600	0.13768400
H	-1.55485400	-3.50819700	-1.42790500
H	-3.04113000	-4.37132900	-0.93356700
C	-3.66191700	0.62123900	0.69047900
C	-5.14271200	0.08935500	-1.15091600
C	-4.41742900	1.76499600	0.96120300
H	-2.77072900	0.42283300	1.28026600
C	-5.90083400	1.22721800	-0.87143100
H	-5.42185700	-0.55997700	-1.98308400
C	-5.54138000	2.06948900	0.18725700
H	-4.11233300	2.42822700	1.77398600
H	-6.77415300	1.45983700	-1.48626800
H	-6.13003700	2.96527000	0.40161200
O	-3.02588100	-1.47786100	-2.06006500
H	-2.64839700	-2.33259200	-2.33286400

[$(PMe_3)_2$PdPh(acetylenic TMS-enolate)]$^+$



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2307.694184
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2308.237937

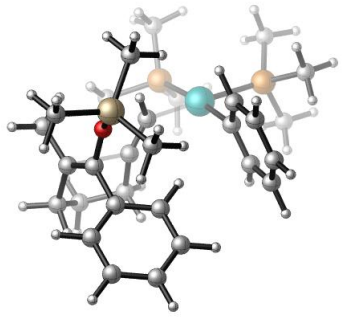
Zero-point correction=	0.680786 (Hartree/Particle)
Thermal correction to Energy=	0.726396
Thermal correction to Enthalpy=	0.727341
Thermal correction to Gibbs Free Energy=	0.599955

Charge = 1 Multiplicity = 1

P	3.89714200	-1.55781300	0.10107000
C	5.30901200	-1.14850600	1.19481700
H	6.04711500	-1.96439100	1.14281800
H	5.79099200	-0.21068500	0.89126500
H	4.94628900	-1.05206600	2.22902700
C	4.61497900	-1.73420900	-1.57153200
H	5.45398200	-2.44782400	-1.54833800
H	3.83612200	-2.10543500	-2.25450200
H	4.96842800	-0.75622100	-1.92736400
C	3.52548300	-3.27803400	0.60610800
H	2.80318400	-3.73021800	-0.08566100
H	4.46085400	-3.85941600	0.59955800
H	3.09898200	-3.27810400	1.61985900
P	3.55076400	1.96571200	0.17012600
C	2.68205200	3.52408600	-0.26520800
H	1.83049500	3.67720700	0.41212400
H	3.37898700	4.37237000	-0.17552100
H	2.31149800	3.46930100	-1.29879000
C	5.00880600	2.01889800	-0.94490100
H	5.54245800	2.97584100	-0.83027800
H	5.69673200	1.19166300	-0.72142100
H	4.66316700	1.91860800	-1.98533400
C	4.22729000	2.35077600	1.83250600
H	4.86783000	1.52948900	2.18276300
H	4.80977300	3.28557400	1.80690900
H	3.38706800	2.46465500	2.53525100
C	0.92277600	-1.66466800	-0.01185900
C	0.21001800	-2.12786000	1.10774400
C	0.72643000	-2.31814000	-1.24113300
C	-0.66795900	-3.21573500	1.00415200
H	0.33229100	-1.64030500	2.07972200

C	-0.14762400	-3.40952100	-1.34696600
H	1.26945300	-1.98945500	-2.13299300
C	-0.84735800	-3.86364800	-0.22378200
H	-1.21399500	-3.55728400	1.88859900
H	-0.28210200	-3.90478300	-2.31318500
H	-1.53289200	-4.71136100	-0.30552600
Pd	2.14986100	-0.02945000	0.10671300
C	0.33148400	1.15896100	0.83036500
C	0.18427800	1.38515700	-0.36738300
H	0.21815600	1.07078700	1.90006900
C	-0.06997100	1.77082600	-1.75673600
C	-2.60731000	2.48268700	-0.18695800
C	-0.82142600	3.11592700	-1.89294200
H	0.89974100	1.83906300	-2.27632000
H	-0.63475000	0.96149700	-2.25052300
C	-2.32953300	3.04108500	-1.56457500
C	-3.00905000	1.20291700	-0.00074900
C	-2.25177700	3.37301400	0.97424800
H	-0.70684600	3.45453600	-2.93543300
H	-0.32143400	3.86936700	-1.26341700
H	-2.81731000	2.43429300	-2.33983100
H	-2.74521300	4.06093200	-1.65115500
C	-3.44858400	0.27935200	-1.08926200
H	-1.18840900	3.66695100	0.95117000
H	-2.44520400	2.88712800	1.93955400
H	-2.83517700	4.31068600	0.93059200
C	-2.74087900	-0.90892200	-1.34045400
C	-4.60685400	0.55021200	-1.83803300
C	-3.17318100	-1.79429600	-2.33103900
H	-1.84829400	-1.13772000	-0.75545000
C	-5.04358600	-0.33963700	-2.82502600
H	-5.16929000	1.46554900	-1.63719000
C	-4.32589900	-1.51434900	-3.07522500
H	-2.60796100	-2.70973500	-2.51894000
H	-5.94871600	-0.11616100	-3.39634700
H	-4.66499800	-2.21197800	-3.84578300
O	-2.95638100	0.63701600	1.24431000
Si	-4.14160900	-0.21973600	2.12267300
C	-5.69533100	0.83230200	2.16447700
H	-6.09659100	0.97232700	1.14634100
H	-6.48105600	0.35392800	2.77416800
H	-5.48858000	1.82833100	2.59096400
C	-4.48996300	-1.89946100	1.36038800
H	-5.13273200	-2.48540200	2.04101100
H	-5.00716500	-1.81397600	0.39200000
H	-3.55632400	-2.46354000	1.20303400
C	-3.35182000	-0.41937500	3.80896000
H	-3.13314700	0.55945300	4.26767500
H	-4.01662800	-0.97699300	4.49040900
H	-2.40442400	-0.97912600	3.72576100

[$(PMe_3)_2$PdPh(acetylenic TMS-enolate)]$^+$ (TS for cyclization)



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2307.686493
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -2308.224103

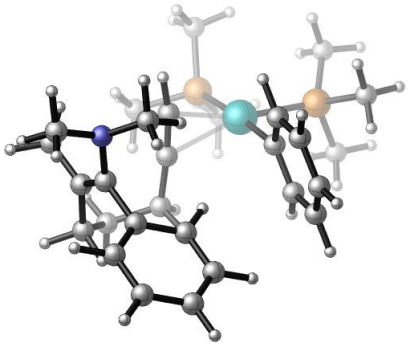
Zero-point correction=	0.680142 (Hartree/Particle)
Thermal correction to Energy=	0.723883
Thermal correction to Enthalpy=	0.724827
Thermal correction to Gibbs Free Energy=	0.602140

Charge = 1 Multiplicity = 1

P	-3.94914200	1.39157000	-0.02403500
C	-5.41814300	0.87738700	0.94968200
H	-6.22896600	1.60951500	0.80769600
H	-5.76572900	-0.11208800	0.62348700
H	-5.15277600	0.83209200	2.01660200
C	-4.58550700	1.50520800	-1.73874000
H	-5.46541400	2.16709400	-1.78152000
H	-3.79436100	1.90405700	-2.39166000
H	-4.86397100	0.49963700	-2.08720100
C	-3.75824200	3.14374400	0.48120600
H	-3.02115900	3.64078200	-0.16403300
H	-4.72857500	3.65853600	0.40016100
H	-3.40487100	3.18802200	1.52230200
P	-3.16724900	-2.05973200	0.26051300
C	-2.09407400	-3.53439600	0.05204400
H	-1.32063300	-3.54130600	0.83315000
H	-2.69922800	-4.45225300	0.12253700
H	-1.60142200	-3.49666900	-0.92956400
C	-4.47454700	-2.36029500	-0.99663600
H	-4.92591700	-3.35538100	-0.85578600
H	-5.25689700	-1.59164500	-0.92433500
H	-4.02171100	-2.30576500	-1.99887000
C	-3.99154900	-2.41322800	1.86400300
H	-4.76079900	-1.65749000	2.07435000
H	-4.45457000	-3.41293400	1.84826400
H	-3.23533300	-2.37594700	2.66373400
C	-0.92928000	1.77067400	-0.11696300
C	-0.30343800	2.40327300	0.97367600
C	-0.71514400	2.31836900	-1.39686100
C	0.50254500	3.53678300	0.79583900
H	-0.43510400	2.00852500	1.98619300

C	0.09022600	3.45137500	-1.58139000
H	-1.18138600	1.85934800	-2.27488400
C	0.70345500	4.06718800	-0.48414700
H	0.97834600	4.00491000	1.66294500
H	0.24082600	3.85256400	-2.58839800
H	1.33579500	4.94802100	-0.62514900
Pd	-2.03423500	0.05069600	0.10742700
C	-0.13154400	-0.83423200	0.33057000
C	0.41834300	-1.39953200	-0.67202500
H	0.34198500	-0.62722900	1.29590800
C	0.42211700	-1.87575700	-2.06337700
C	2.40309700	-2.47284400	-0.19092400
C	1.11877600	-3.23393600	-2.19007000
H	-0.63391600	-1.93369700	-2.37820200
H	0.91965200	-1.12881700	-2.70679400
C	2.51739200	-3.11114400	-1.55575600
C	2.82909800	-1.18138300	0.06011100
C	1.98837300	-3.37220800	0.94601600
H	1.19196500	-3.53467200	-3.24641800
H	0.52612000	-4.00191300	-1.66741600
H	3.15662400	-2.51549000	-2.22053600
H	2.97951400	-4.10732200	-1.45845200
C	3.43895600	-0.26960700	-0.95288400
H	1.24064400	-4.10792500	0.61495000
H	1.57685700	-2.80816200	1.79263500
H	2.86698200	-3.93654800	1.30804500
C	2.76837300	0.90090400	-1.34402300
C	4.71852400	-0.53724300	-1.46549000
C	3.36415500	1.78070500	-2.24996500
H	1.77870000	1.11899700	-0.94003800
C	5.31840500	0.35333000	-2.36148400
H	5.24567800	-1.44220800	-1.15326000
C	4.64071100	1.51176300	-2.75790600
H	2.82789700	2.68311500	-2.55287300
H	6.31753900	0.14103300	-2.75077300
H	5.10802100	2.20551300	-3.46181000
O	2.65154500	-0.67715900	1.28249300
Si	3.53813900	0.35273200	2.34889600
C	5.01864600	-0.65115300	2.90160500
H	5.67320900	-0.88090500	2.04366800
H	5.61541600	-0.09306300	3.64327700
H	4.70250200	-1.60335600	3.35930400
C	4.05923900	1.94771900	1.52243700
H	4.53136700	2.59599200	2.28179100
H	4.78945300	1.77947000	0.71598300
H	3.19394900	2.48547600	1.10548400
C	2.29461400	0.65360100	3.71066200
H	1.93604300	-0.29819000	4.13646800
H	2.74563200	1.24550700	4.52516900
H	1.42491900	1.21182500	3.32530400

[$(PMe_3)_2$PdPh(acetylenic enamine)]$^+$



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1957.834498
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1958.268732

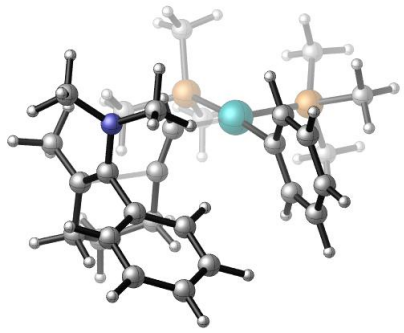
Zero-point correction=	0.648334 (Hartree/Particle)
Thermal correction to Energy=	0.689201
Thermal correction to Enthalpy=	0.690145
Thermal correction to Gibbs Free Energy=	0.573870

Charge = 1 Multiplicity = 1

P	-3.68653200	1.44489400	0.12442600
C	-5.20165400	0.85544600	0.96805500
H	-5.96782100	1.64515300	0.91654800
H	-5.59102900	-0.05328600	0.49172000
H	-4.96929700	0.64251700	2.02213600
C	-4.20290000	1.80166500	-1.59301200
H	-5.06840100	2.48321100	-1.59201900
H	-3.36411300	2.27363200	-2.12601800
H	-4.46893500	0.86328500	-2.10059400
C	-3.45420700	3.09811000	0.87559800
H	-2.67947100	3.65498800	0.33272400
H	-4.40794700	3.64703200	0.83039300
H	-3.14481200	2.98328800	1.92487500
P	-3.16034700	-2.05855400	-0.09951600
C	-2.12811100	-3.51108400	-0.54486600
H	-1.39726300	-3.70904400	0.25178600
H	-2.77029700	-4.39533900	-0.68259500
H	-1.58530300	-3.30645400	-1.47959500
C	-4.41946700	-2.06685100	-1.43594600
H	-4.90070300	-3.05556600	-1.50323200
H	-5.18641300	-1.30245400	-1.24983300
H	-3.92096800	-1.84016700	-2.39105100
C	-4.05690200	-2.65322300	1.38740000
H	-4.80381200	-1.91233500	1.70446700
H	-4.55746200	-3.61216800	1.17824000
H	-3.33085200	-2.79214200	2.20365500
C	-0.72739100	1.68635600	0.24769700
C	-0.13472200	2.09605700	1.45428500
C	-0.44154000	2.41941800	-0.91712200
C	0.71584800	3.20971600	1.49748700
H	-0.33082500	1.54536200	2.37945900

C	0.40602600	3.53598100	-0.87624600
H	-0.88999200	2.13266500	-1.87352900
C	0.98628600	3.93635400	0.33222900
H	1.16973300	3.50899900	2.44712000
H	0.61390700	4.09309400	-1.79471700
H	1.65095500	4.80380400	0.36424600
Pd	-1.87862400	-0.00426400	0.15405400
C	-0.03500300	-1.22715900	0.82558800
C	0.18433800	-1.17729700	-0.38088100
H	-0.01821600	-1.37596500	1.89471100
C	0.53215300	-1.21454400	-1.80265200
C	3.04377400	-2.21379300	-0.17292500
C	1.44953900	-2.39424700	-2.18750500
H	-0.40448700	-1.27894900	-2.38091400
H	1.00259400	-0.25469300	-2.07477900
C	2.89957400	-2.28636300	-1.67758200
C	3.57656100	-1.13807100	0.45447700
C	2.59706000	-3.43126900	0.59360600
H	1.47280000	-2.44072900	-3.28813900
H	0.98380600	-3.33333100	-1.84801600
H	3.37414000	-1.41422400	-2.15043000
H	3.44237000	-3.17770000	-2.04468500
C	4.08577000	0.07084700	-0.27584800
N	3.73087000	-1.12255700	1.88012000
H	1.66857600	-3.85227700	0.17731400
H	2.43398200	-3.19817000	1.65492100
H	3.35768700	-4.23176900	0.53633500
C	3.23320700	1.10409200	-0.70023000
C	5.46931600	0.20935500	-0.49687500
C	3.48316500	0.15344800	2.53052000
C	4.90957100	-1.80363500	2.39759500
C	3.74713800	2.23205300	-1.35009100
H	2.15990000	1.02901100	-0.51307300
C	5.98420600	1.33791100	-1.14258000
H	6.14501800	-0.58572400	-0.17172100
H	4.30155600	0.89311400	2.39514100
H	3.35931100	-0.00868600	3.61443000
H	2.55500800	0.60396600	2.14835700
H	5.84803500	-1.22899800	2.23868300
H	5.02736100	-2.78560700	1.91709300
H	4.80185800	-1.96687000	3.48365500
C	5.12247300	2.35249100	-1.57530000
H	3.06620200	3.02135400	-1.67579800
H	7.06108800	1.42227300	-1.31361000
H	5.52169200	3.23424800	-2.08391600

[$(PMe_3)_2$PdPh(acetylenic enamine)]$^+$ (TS for cyclization)



E (SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1957.826873
E (SMD(Acetonitrile)/M06/Def2-TZVPP//SMD(Acetonitrile)/B3LYP-D3/Def2-SVP) = -1958.255849

Zero-point correction=	0.648238 (Hartree/Particle)
Thermal correction to Energy=	0.688076
Thermal correction to Enthalpy=	0.689021
Thermal correction to Gibbs Free Energy=	0.575500

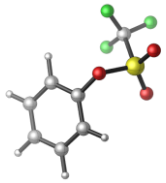
Charge = 1 Multiplicity = 1

P	-3.71852000	1.29608700	-0.01053500
C	-5.21938900	0.62702800	0.80442900
H	-6.05593100	1.33104300	0.67003400
H	-5.49355500	-0.34445700	0.37236400
H	-5.02074700	0.49959300	1.87928600
C	-4.21512200	1.53101200	-1.75842400
H	-5.13504300	2.13444400	-1.81874800
H	-3.40292700	2.04644300	-2.29312100
H	-4.38421900	0.55043500	-2.22660900
C	-3.65984400	3.00500400	0.64979300
H	-2.90339500	3.58886900	0.10829400
H	-4.64796100	3.47688900	0.53126800
H	-3.39141000	2.97797500	1.71640200
P	-2.80945100	-2.13313600	-0.03257100
C	-1.63591800	-3.50487300	-0.36844300
H	-0.92507200	-3.59550100	0.46483400
H	-2.18646200	-4.45138000	-0.48890700
H	-1.07132600	-3.28909700	-1.28753100
C	-4.02163800	-2.32825400	-1.39942100
H	-4.40211600	-3.36173900	-1.43197400
H	-4.86490300	-1.63604700	-1.26814400
H	-3.52093800	-2.09649800	-2.35229600
C	-3.70653700	-2.73261800	1.45323900
H	-4.52398600	-2.04206600	1.70458400
H	-4.11767100	-3.73987600	1.27859200
H	-3.00408700	-2.76833500	2.30056100
C	-0.74243500	1.80714800	0.22101200
C	-0.25389500	2.34685700	1.42494100
C	-0.42240200	2.47763500	-0.97449600
C	0.52889600	3.51029500	1.43556900
H	-0.47487200	1.85378600	2.37684800

C	0.35711100	3.64348200	-0.96941400
H	-0.78339200	2.09281300	-1.93392200
C	0.83734700	4.16497200	0.23740400
H	0.90191900	3.90447700	2.38600300
H	0.59240000	4.14386700	-1.91385300
H	1.45004300	5.07062400	0.24352500
Pd	-1.76800500	0.02950000	0.16095500
C	0.15216500	-0.86156200	0.49119500
C	0.72865900	-1.07016200	-0.60973800
H	0.47602800	-0.95782300	1.53041500
C	0.96066300	-1.12262600	-2.05424400
C	2.87784600	-2.21775100	-0.20452000
C	1.83194100	-2.31296500	-2.48454100
H	-0.03207700	-1.18034700	-2.53371300
H	1.42557600	-0.17708600	-2.38145300
C	3.15128600	-2.31690500	-1.68864500
C	3.24795400	-1.11151500	0.53373700
C	2.27248100	-3.45091000	0.42386800
H	2.03085100	-2.24750000	-3.56551500
H	1.27671700	-3.24949700	-2.31594900
H	3.77934100	-1.48211000	-2.02958100
H	3.70220000	-3.24852300	-1.90915100
C	3.89618100	0.08689100	-0.10617400
N	3.05655400	-1.03052600	1.91071500
H	1.58863300	-3.94888500	-0.27881300
H	1.70411300	-3.21683100	1.33462000
H	3.04850100	-4.19132000	0.68807100
C	3.17363500	1.17972000	-0.60968800
C	5.30123200	0.12637200	-0.15246800
C	2.94023400	0.27794300	2.54144000
C	3.60741600	-2.04230900	2.80961500
C	3.84016100	2.27621300	-1.16705000
H	2.08471800	1.18592800	-0.55126300
C	5.96746500	1.22019200	-0.71360900
H	5.87454600	-0.71444900	0.24732600
H	3.92191000	0.76728500	2.69357700
H	2.46923400	0.15023700	3.52860400
H	2.30090000	0.94662400	1.95255500
H	4.49812900	-1.64031300	3.33006100
H	3.92583100	-2.93507400	2.26285900
H	2.87201700	-2.33912600	3.57622700
C	5.23723500	2.29876900	-1.22592600
H	3.25785600	3.11758800	-1.55054800
H	7.06024200	1.22943400	-0.75029800
H	5.75593000	3.15544700	-1.66452300

Gibbs free energy profile for model reaction with PhOTf (Figure 2)

PhOTf



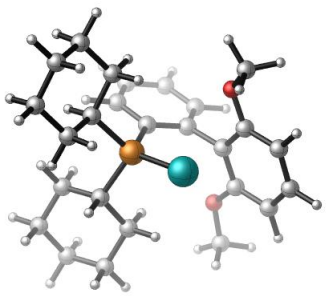
E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -1192.368827
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -1193.052361

Zero-point correction=	0.119172 (Hartree/Particle)
Thermal correction to Energy=	0.131410
Thermal correction to Enthalpy=	0.132354
Thermal correction to Gibbs Free Energy=	0.078306

Charge = 0 Multiplicity = 1

S	1.20889100	-0.91349100	0.05393400
O	0.74280400	-1.40803200	-1.23085700
O	2.19838100	-1.59618600	0.86282300
O	-0.04482200	-0.60317600	1.05776600
C	1.83572600	0.84254900	-0.22686600
F	2.02489300	1.43834900	0.94045700
F	2.98057500	0.77319800	-0.88960600
F	0.94434700	1.51887600	-0.93894400
C	-1.30627600	-0.24893400	0.53819000
C	-2.11764700	-1.23126800	-0.02737800
C	-1.71719300	1.07694100	0.66756900
C	-3.38792700	-0.86447500	-0.48144100
H	-1.75618400	-2.25764000	-0.10598100
C	-2.99236300	1.42667200	0.21382400
H	-1.04714800	1.81140700	1.11818700
C	-3.82533200	0.45987300	-0.36153700
H	-4.03835100	-1.62054500	-0.92803700
H	-3.33335100	2.46039400	0.31013300
H	-4.82037700	0.73943500	-0.71642500

LPd



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -1630.790621
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -1631.212952

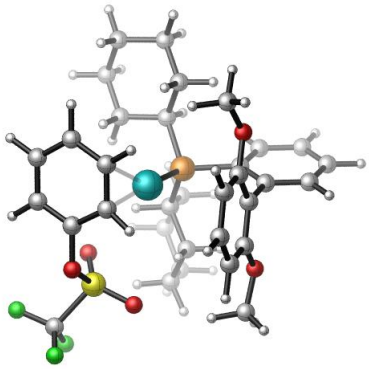
Zero-point correction=	0.559179 (Hartree/Particle)
Thermal correction to Energy=	0.589016
Thermal correction to Enthalpy=	0.589960
Thermal correction to Gibbs Free Energy=	0.498251

Charge = 0 Multiplicity = 1

C	-0.02936200	0.23579100	1.49755200
C	-0.74561600	0.74508000	2.60007600
H	-1.76612200	1.10465000	2.46710700
C	-0.18875000	0.80789800	3.87895300
H	-0.77703000	1.20990700	4.70829400
C	1.11765100	0.35903600	4.08686800
H	1.57018200	0.40563200	5.08110500
C	1.83920100	-0.16083600	3.01246100
H	2.85771900	-0.52590900	3.16740600
C	1.28732900	-0.24026900	1.72129300
C	2.13335700	-0.85663600	0.65513000
C	1.92628400	-2.20255100	0.28270000
C	2.69958300	-2.79167400	-0.73569300
H	2.54046000	-3.82820500	-1.03077000
C	3.68358500	-2.02523400	-1.36671200
H	4.28476700	-2.47821500	-2.15990500
C	3.92475000	-0.69915700	-1.00202300
H	4.70452900	-0.12973900	-1.50641300
C	3.15177100	-0.12016600	0.02113300
C	4.17558900	2.02963600	-0.25421600
H	5.22958600	1.70889000	-0.17656100
C	0.49472800	-4.10709300	0.49726500
H	0.13455100	-4.02614700	-0.54407800
C	-2.62871200	-0.09357700	0.20311300
H	-2.95530500	0.63180200	0.96552600
C	-3.51987000	0.10255200	-1.03624400
H	-3.43457100	1.13416400	-1.41474000
H	-3.16089900	-0.56193900	-1.84383100
C	-4.98951600	-0.21563800	-0.72615500
H	-5.37366500	0.52161000	0.00307400
H	-5.59689600	-0.09967700	-1.64019700
C	-5.15375000	-1.62616800	-0.14924000
H	-4.86814500	-2.36671800	-0.91942700
H	-6.21155300	-1.81987400	0.09846400
C	-4.26877500	-1.82360900	1.08656500
H	-4.36087700	-2.85564900	1.46653200
H	-4.62012900	-1.15708700	1.89605800
C	-2.79854900	-1.51135100	0.77968200
H	-2.41279100	-2.24179400	0.04447400
H	-2.18714200	-1.63017300	1.68890800
C	-0.78473500	2.06644700	-0.67238700
H	-1.32672200	2.06933900	-1.63512400
C	-1.48476200	3.05444400	0.27431900
H	-0.97882200	3.04298800	1.25422600
H	-2.53109300	2.75701000	0.44924400

C	-1.43648800	4.48460500	-0.28551800
H	-2.01451100	4.52562700	-1.22735600
H	-1.92967800	5.17773000	0.41766100
C	0.00413300	4.93215700	-0.55658300
H	0.55125400	4.98469700	0.40326300
H	0.01833300	5.94931400	-0.98460300
C	0.72066100	3.94775500	-1.48755200
H	1.77270000	4.24918700	-1.63155000
H	0.24322700	3.97877900	-2.48462600
C	0.66248500	2.51372000	-0.94639500
H	1.24349000	2.44962200	-0.01168500
H	1.14353700	1.81832300	-1.65455300
O	3.30735600	1.15845600	0.44885600
O	0.96636100	-2.86051700	0.97629900
P	-0.82595600	0.24068500	-0.19896800
Pd	0.01660800	-1.10141800	-1.75058800
H	1.26846200	-4.89303700	0.55569600
H	-0.34713500	-4.39048700	1.14417800
H	3.90212000	2.10816300	-1.32071000
H	4.07045900	3.01769300	0.21488000

I



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2823.204623
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2824.297547

Zero-point correction=	0.678754 (Hartree/Particle)
Thermal correction to Energy=	0.722747
Thermal correction to Enthalpy=	0.723692
Thermal correction to Gibbs Free Energy=	0.598071

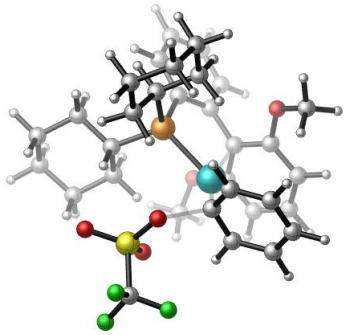
Charge = 0 Multiplicity = 1

C	-2.70291500	-1.24072400	0.32837900
C	-3.68919800	-1.67351800	1.23729800
H	-3.69720200	-1.28536700	2.25661800
C	-4.67280400	-2.59382100	0.87023700
H	-5.42326000	-2.90923200	1.60015500
C	-4.68798000	-3.10663500	-0.42981100
H	-5.44892100	-3.83147300	-0.73163000
C	-3.72911400	-2.67692000	-1.34749600
H	-3.74463200	-3.06217000	-2.37030900

C	-2.73781900	-1.74344100	-0.99456300
C	-1.79706000	-1.31044700	-2.07386100
C	-2.06453100	-0.13371700	-2.80486400
C	-1.23236400	0.25501500	-3.86949100
H	-1.43332300	1.16393100	-4.43511300
C	-0.12232400	-0.53308500	-4.18169000
H	0.53396500	-0.22886200	-5.00167900
C	0.17420700	-1.69644600	-3.46818800
H	1.05245100	-2.28564900	-3.72909900
C	-0.67561100	-2.08984700	-2.41859400
C	0.71793200	-3.94177800	-1.80807900
H	0.81184700	-4.39604800	-2.81054200
C	-3.38718800	1.85856400	-2.92933500
H	-2.52899300	2.52870500	-2.74952600
C	-2.30269700	1.13358900	1.98589300
H	-2.87963300	0.55978400	2.73004700
C	-1.32107900	2.04644300	2.74342500
H	-0.65647300	1.44870200	3.38799100
H	-0.67174700	2.55877900	2.00971600
C	-2.06200000	3.09301300	3.58715900
H	-2.62478500	2.58031200	4.38925200
H	-1.33212900	3.75272700	4.08709900
C	-3.03560700	3.91760100	2.73775500
H	-2.46018800	4.50913100	2.00131800
H	-3.57971600	4.64099600	3.36902200
C	-4.01992700	3.01043300	1.99087700
H	-4.68868500	3.61089600	1.35036400
H	-4.66603500	2.49291500	2.72415100
C	-3.28414900	1.96732800	1.14072000
H	-2.71563300	2.48000100	0.34293300
H	-4.00683100	1.30744900	0.63385100
C	-0.33818800	-1.10441900	2.06243500
H	0.45491600	-0.39312100	2.34863500
C	-0.99142000	-1.63660500	3.34592900
H	-1.78677400	-2.35569900	3.08622900
H	-1.46700000	-0.82267600	3.91646200
C	0.05403300	-2.34653300	4.22220700
H	0.80553800	-1.60658000	4.55474900
H	-0.42549700	-2.74057600	5.13495100
C	0.76045200	-3.47605700	3.46155700
H	0.02288900	-4.26719700	3.23001000
H	1.53272900	-3.94189300	4.09791600
C	1.37516200	-2.97056000	2.15088800
H	1.81698100	-3.80807500	1.58358400
H	2.20123800	-2.27092500	2.37098900
C	0.33411800	-2.24993600	1.28702700
H	-0.43579000	-2.96827900	0.95844200
H	0.80292100	-1.86576900	0.37166600
O	-0.48750200	-3.20735700	-1.67472700
O	-3.15396100	0.56482800	-2.40233700
P	-1.37519300	-0.06721900	0.89007000
Pd	-0.02973400	1.01383800	-0.64545400
C	2.59337000	2.04819300	-0.95408700
C	1.53602000	1.93187700	-1.88944500

C	2.74548200	3.13851100	-0.11058100
C	0.55995500	2.96036900	-1.89179900
H	1.59586900	1.18723400	-2.68871600
C	1.78482000	4.16489900	-0.15659400
H	3.59320900	3.17071800	0.57610100
C	0.69192300	4.06540100	-1.01680400
H	-0.20528200	2.97505700	-2.67076700
H	1.89105100	5.03113400	0.50066900
H	-0.05974700	4.85811400	-1.04274300
O	3.56996800	1.03366500	-0.94159700
S	3.36080300	-0.24043200	0.07393800
O	2.97987100	-1.41853900	-0.68984400
O	2.67742400	0.16427800	1.29296500
H	-3.60574800	1.83045600	-4.01162200
H	-4.26542100	2.25524300	-2.40142000
H	1.60083800	-3.31196500	-1.60910700
H	0.67409200	-4.74582500	-1.06059100
C	5.18015900	-0.41826700	0.49765300
F	5.60827600	0.69613300	1.07026300
F	5.87983400	-0.66460000	-0.59765100
F	5.29337200	-1.43288000	1.34473800

TS1



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2823.187944
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2824.275696

Zero-point correction=	0.676778 (Hartree/Particle)
Thermal correction to Energy=	0.720457
Thermal correction to Enthalpy=	0.721401
Thermal correction to Gibbs Free Energy=	0.597338

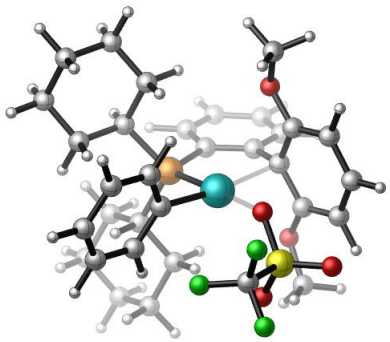
Charge = 0 Multiplicity = 1

C	2.77874300	0.96125700	0.24897200
C	3.65644800	1.90349600	0.81701700
H	3.28323600	2.62710200	1.54365600
C	5.00887000	1.92676200	0.47223300
H	5.67413800	2.66721100	0.92409200
C	5.50419600	1.00003800	-0.45082500
H	6.56105700	1.01033500	-0.73035100
C	4.64644600	0.05062900	-1.00785100

H	5.03434600	-0.68397600	-1.71815100
C	3.28367000	0.01103500	-0.66496500
C	2.45782800	-1.08194800	-1.28414800
C	2.39261900	-2.36038000	-0.66437200
C	1.87253600	-3.47205900	-1.35983600
H	1.81845900	-4.44914500	-0.88204600
C	1.42503400	-3.30375200	-2.66970700
H	1.02023300	-4.16491200	-3.20770900
C	1.45673500	-2.05892300	-3.30569300
H	1.08865600	-1.95812400	-4.32583600
C	1.98646300	-0.95245300	-2.61972200
C	1.46935700	0.57768100	-4.38509700
H	1.91372900	0.01160800	-5.22184300
C	2.54573500	-3.52427900	1.41716400
H	1.44941400	-3.63933300	1.47297300
C	0.94105800	1.10232300	2.52181600
H	1.59899200	1.94585800	2.79275200
C	-0.47972400	1.41655400	3.02713400
H	-0.82781900	2.37890600	2.62018200
H	-1.18198700	0.65475400	2.65262100
C	-0.53030800	1.45876800	4.56051400
H	0.07096000	2.31469900	4.91932300
H	-1.56696200	1.64143700	4.89124900
C	0.01348900	0.16928300	5.18503300
H	-0.64257600	-0.67527400	4.90266800
H	-0.01198600	0.23484800	6.28615400
C	1.43780200	-0.11814500	4.69754600
H	1.81001700	-1.06532900	5.12406900
H	2.11388500	0.67885900	5.05869300
C	1.50006500	-0.18104000	3.16691200
H	0.90891700	-1.04382700	2.81371300
H	2.53495800	-0.35427300	2.83039200
C	0.25681000	2.50368300	-0.02032100
H	-0.79933500	2.42177500	0.28529400
C	0.80791200	3.82952900	0.52817100
H	1.86395600	3.93864200	0.22858200
H	0.78168600	3.84458500	1.62937400
C	0.00553900	5.01434300	-0.03220800
H	-1.03361800	4.95220400	0.33916400
H	0.42200100	5.96214800	0.35012900
C	-0.00398400	5.01468700	-1.56581700
H	1.02450200	5.19436000	-1.93125500
H	-0.62299400	5.84636700	-1.94421400
C	-0.50543500	3.67669500	-2.12185800
H	-0.45268600	3.67425900	-3.22438200
H	-1.56717600	3.53648500	-1.85212500
C	0.29361300	2.49503900	-1.55919300
H	1.34190200	2.54941100	-1.89949100
H	-0.11720900	1.55000600	-1.94110900
O	2.10818600	0.28011700	-3.15275400
O	2.90221900	-2.42827700	0.58578900
P	0.98349500	0.93242000	0.66806900
Pd	0.06442300	-1.00133300	-0.22259500
C	-1.66534200	-1.55524200	0.53049800

C	-1.86545200	-2.30534500	-0.66112700
C	-1.68438600	-2.18541500	1.80260700
C	-1.97855300	-3.71500900	-0.55571000
H	-2.07449300	-1.80553200	-1.60800600
C	-1.77817900	-3.56814600	1.85649800
H	-1.58560300	-1.58706200	2.70896700
C	-1.92142200	-4.34309200	0.68060500
H	-2.13770800	-4.29824900	-1.46713100
H	-1.73190600	-4.06417400	2.83046300
H	-2.00763100	-5.42995300	0.75340600
O	-2.71361500	-0.06219200	0.75416800
S	-3.12888900	0.86083500	-0.40447900
O	-2.41927800	0.60545500	-1.66389500
O	-3.29061400	2.24653200	0.04834800
H	2.99662000	-4.46867000	1.06740600
H	2.93659100	-3.29426300	2.41746800
H	0.38702300	0.36830000	-4.33844500
H	1.62124100	1.65099900	-4.56051500
C	-4.87128400	0.24966700	-0.72045800
F	-5.63056000	0.42524700	0.35930600
F	-4.85024100	-1.04933200	-1.02575900
F	-5.40642700	0.92164600	-1.73980100

II



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2823.254646
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2824.338853

Zero-point correction=	0.679754 (Hartree/Particle)
Thermal correction to Energy=	0.722622
Thermal correction to Enthalpy=	0.723566
Thermal correction to Gibbs Free Energy=	0.603594

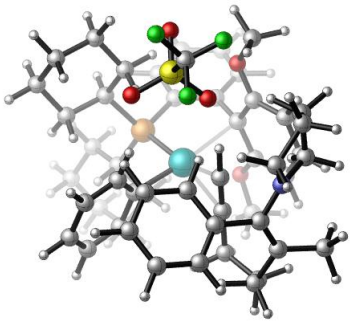
Charge = 0 Multiplicity = 1

C	-2.65183900	-1.26310400	-0.10959300
C	-4.05211000	-1.34043400	0.01615600
H	-4.63730300	-0.44537600	0.23051200
C	-4.71458800	-2.55918300	-0.13297800
H	-5.80179400	-2.60278700	-0.03004000
C	-3.98244800	-3.71840100	-0.41136300
H	-4.49239200	-4.67870000	-0.52433300

C	-2.59793800	-3.64396900	-0.56300100
H	-2.02508800	-4.54241800	-0.80596600
C	-1.91835100	-2.42094100	-0.42562800
C	-0.44195900	-2.43073900	-0.70413700
C	-0.00856200	-2.31934600	-2.06039000
C	1.27701100	-2.73323800	-2.43777300
H	1.61698400	-2.63399900	-3.46738900
C	2.12552300	-3.26581100	-1.46715600
H	3.13578900	-3.56453700	-1.75290100
C	1.74613600	-3.38696500	-0.13030300
H	2.45533700	-3.76716800	0.60140900
C	0.46064400	-2.97924200	0.25373900
C	0.87649500	-3.35271000	2.57631900
H	1.27422200	-4.38066600	2.52144800
C	-0.52178100	-1.41209100	-4.21253600
H	0.28998900	-0.66724800	-4.14977100
C	-2.66628500	1.55369700	-0.86990800
H	-3.73297700	1.33312400	-0.69425700
C	-2.42256100	3.02147400	-0.47465900
H	-2.70267100	3.19045500	0.57656400
H	-1.35212900	3.25763800	-0.56317400
C	-3.22185300	3.96502300	-1.38474900
H	-4.30310700	3.80477600	-1.21746800
H	-3.01004000	5.01110200	-1.10585900
C	-2.90021800	3.72937400	-2.86505200
H	-1.83819500	3.97767200	-3.04716400
H	-3.49784700	4.40523400	-3.50010300
C	-3.14881400	2.26868300	-3.25730300
H	-2.87634800	2.09824700	-4.31274800
H	-4.22820300	2.04615900	-3.16881200
C	-2.36092200	1.30651100	-2.36065100
H	-1.27985600	1.44926500	-2.53021300
H	-2.58182400	0.26058700	-2.62556800
C	-1.97172900	0.75749000	1.94953600
H	-1.48594900	1.74524800	2.01362600
C	-3.42416400	0.91346400	2.43056900
H	-3.93610700	-0.06071100	2.37251000
H	-3.98068200	1.61189300	1.78568400
C	-3.45359400	1.39523000	3.88857200
H	-3.00565400	2.40420100	3.94714800
H	-4.49947500	1.49251900	4.22586500
C	-2.68148900	0.44040200	4.80664200
H	-3.19677500	-0.53797500	4.82201200
H	-2.68628500	0.81654900	5.84382400
C	-1.24211600	0.24092100	4.31830600
H	-0.71606400	-0.49160300	4.95376800
H	-0.69079500	1.19464700	4.41228200
C	-1.19452500	-0.21682700	2.85530100
H	-1.63153400	-1.22570900	2.76186900
H	-0.15031600	-0.30350800	2.51580400
O	-0.02395900	-3.08570800	1.50491100
O	-0.92953600	-1.83390300	-2.91761500
P	-1.74277000	0.31070300	0.15898400
Pd	0.43404800	-0.07997100	-0.32491400

C	0.82987900	1.85922900	-0.08045800
C	1.13704200	2.60300300	-1.23087300
C	0.93137300	2.46936200	1.17608100
C	1.52794500	3.94372600	-1.12250700
H	1.07332700	2.14566000	-2.22177300
C	1.31878800	3.81243700	1.28145200
H	0.72591600	1.90398900	2.08706500
C	1.61190000	4.55578800	0.13390200
H	1.76361500	4.51220300	-2.02721200
H	1.39448600	4.27528400	2.26999600
H	1.91087800	5.60429500	0.21712300
O	2.54806700	-0.34787900	-0.75865400
S	3.58204800	-0.64526200	0.30991600
O	4.53630900	-1.69357400	-0.07671600
O	3.03308100	-0.69330300	1.67764400
H	-0.19216400	-2.26175200	-4.83413000
H	-1.40218400	-0.94964300	-4.67814800
H	1.70915800	-2.63076200	2.57740300
H	0.29297900	-3.24587200	3.50059300
C	4.63319800	0.90833200	0.27524000
F	3.95471600	1.97500400	0.69942200
F	5.06569900	1.14941800	-0.96618900
F	5.69663500	0.74447600	1.06919100

III



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.231572
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.482956

Zero-point correction=	1.048520 (Hartree/Particle)
Thermal correction to Energy=	1.111862
Thermal correction to Enthalpy=	1.112806
Thermal correction to Gibbs Free Energy=	0.948536

Charge = 0 Multiplicity = 1

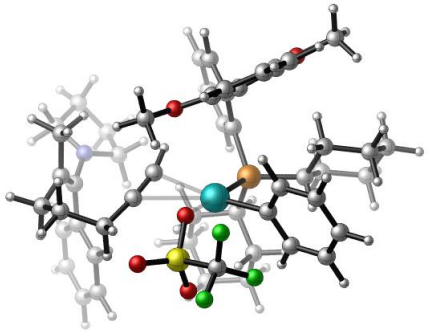
C	-3.76530000	0.75726100	-1.44998200
C	-4.93026000	1.52566300	-1.64429500
H	-5.41396500	2.01415100	-0.79791600
C	-5.47620300	1.68956900	-2.91701600
H	-6.38128000	2.28812700	-3.04762800
C	-4.85711400	1.08970900	-4.01873600

H	-5.27684900	1.20950900	-5.02097000
C	-3.68993000	0.34913700	-3.83771200
H	-3.19098600	-0.10139900	-4.69930500
C	-3.12442000	0.17762300	-2.56077400
C	-1.83518100	-0.59417100	-2.50383300
C	-0.65164200	0.03639300	-2.99497000
C	0.46444100	-0.72985000	-3.36451100
H	1.37667000	-0.25235600	-3.71663200
C	0.39477600	-2.12078500	-3.26729500
H	1.26894100	-2.71311700	-3.54992800
C	-0.74343300	-2.77951000	-2.80052400
H	-0.75677900	-3.86596400	-2.73139000
C	-1.86520900	-2.01706400	-2.43391900
C	-3.15548900	-3.94151700	-1.82207400
H	-2.99960900	-4.51482500	-2.75174600
C	0.38736400	2.10292000	-3.62852000
H	1.27401900	1.98794300	-2.99080500
C	-2.88289600	2.27498800	0.86243900
H	-3.81250600	2.78689300	0.55914900
C	-2.75415400	2.39300700	2.39129300
H	-3.63908700	1.96740400	2.88959900
H	-1.88405400	1.81505900	2.73417900
C	-2.57537400	3.86008500	2.80947800
H	-3.49820700	4.42134500	2.57129100
H	-2.44648200	3.91486100	3.90401000
C	-1.38827200	4.51562600	2.09406700
H	-0.45068300	4.01391000	2.39365900
H	-1.29642700	5.57278100	2.39775700
C	-1.52772800	4.40579600	0.57216300
H	-0.63701000	4.81606300	0.07285200
H	-2.40284200	4.99326800	0.23642000
C	-1.69647400	2.94529900	0.14150900
H	-0.77189500	2.39863200	0.38748200
H	-1.81700500	2.87244400	-0.95136600
C	-4.32774300	-0.34430800	1.27136700
H	-3.83755600	-0.35865200	2.25978500
C	-5.69335800	0.34577700	1.43054100
H	-6.21133500	0.36182100	0.45796600
H	-5.57348100	1.39221200	1.75187500
C	-6.56207600	-0.42530600	2.43543900
H	-6.08303900	-0.38958200	3.43103800
H	-7.54193300	0.07121800	2.53695600
C	-6.74460900	-1.88674800	2.00896200
H	-7.32039600	-1.91593000	1.06534000
H	-7.33948500	-2.43465300	2.75937500
C	-5.39344100	-2.57819100	1.79162000
H	-5.54182200	-3.60847900	1.42589800
H	-4.86509900	-2.65823300	2.75949700
C	-4.50919700	-1.80183800	0.80772100
H	-4.96884200	-1.80703700	-0.19528100
H	-3.53204400	-2.29719100	0.69721500
O	-3.04395900	-2.54327400	-2.04626500
O	-0.72080700	1.37368000	-3.10390400
P	-3.06085900	0.53223700	0.23323300

C	-0.82697300	-0.56983900	2.01547500
C	0.12239700	0.31233700	2.55166500
C	-1.48943400	-1.47223300	2.85984200
C	0.38445100	0.30278200	3.92809800
H	0.66433100	1.01624200	1.91716700
C	-1.21846900	-1.47764200	4.23639400
H	-2.21940100	-2.17965400	2.46123100
C	-0.28601100	-0.58608500	4.77579900
H	1.12473200	0.99718300	4.33438300
H	-1.74360300	-2.18563600	4.88450900
H	-0.07785100	-0.58821600	5.84922300
H	-2.43917700	-4.28575900	-1.05717300
H	-4.17776500	-4.11439500	-1.46122000
H	0.08326700	3.15698100	-3.62333200
H	0.60885500	1.79034600	-4.66353500
S	2.10377900	2.89917200	-0.21866200
O	2.12605500	1.55640500	-0.86827600
O	1.83669000	2.88138900	1.23728400
O	1.41664600	3.94515300	-0.99949500
Pd	-1.08626500	-0.64325300	0.03152600
C	1.13131400	-1.14496300	-0.27555400
C	0.75744500	-2.25344000	0.09302300
H	1.58232700	-0.20178600	-0.57104300
C	0.47744000	-3.59395800	0.60547600
C	1.58564800	-4.63109500	0.33414500
H	-0.47340900	-3.95070700	0.17700200
H	0.31326300	-3.49989400	1.69322400
C	2.99355300	-4.24027000	0.84599700
H	1.26461400	-5.55885200	0.83484100
H	1.61497900	-4.85848200	-0.74333400
C	3.83369300	-3.45114300	-0.14145500
H	2.88127500	-3.70900000	1.80176300
H	3.52865600	-5.18052000	1.07606000
C	4.32940900	-2.19665400	0.08650700
C	4.07950800	-4.15169600	-1.45813900
C	4.29601300	-1.54066000	1.43311300
H	4.09042600	-5.24529300	-1.31267500
H	3.30933500	-3.94564300	-2.22374500
H	5.04798900	-3.85757300	-1.88971400
C	3.78169000	-0.23798700	1.57073500
C	4.80561800	-2.17625300	2.57978600
C	3.75455500	0.40093300	2.81110000
H	3.40159100	0.28575300	0.69543200
C	4.77592600	-1.54161700	3.82666100
H	5.23702200	-3.17638000	2.48833900
C	4.24837900	-0.25075900	3.94780600
H	3.33812900	1.40911000	2.87343900
H	5.17539400	-2.05512900	4.70590300
H	4.22692200	0.24613100	4.92176000
N	4.85401300	-1.41359000	-0.94914300
C	5.96619800	-0.47366100	-0.76632500
C	4.20378100	-1.22832600	-2.25011900
H	5.75897400	0.25447500	0.03588900
H	6.89921300	-0.99902600	-0.49300800

C	6.07734200	0.24461400	-2.11998600
H	4.53180500	-1.97023600	-3.00399600
H	3.11324000	-1.32911300	-2.15192500
C	4.64787300	0.17285800	-2.67328500
H	6.44759200	1.27544000	-2.01160700
H	6.76949300	-0.29681600	-2.78704200
H	4.59537700	0.32282000	-3.76327000
H	4.01079000	0.92600800	-2.18826600
C	3.90594100	3.41228000	-0.32039000
F	4.07326500	4.64137300	0.17789900
F	4.32526800	3.41626700	-1.59352400
F	4.69058000	2.57264000	0.36925600

IV



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.208171
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.461176

Zero-point correction=	1.048190 (Hartree/Particle)
Thermal correction to Energy=	1.111623
Thermal correction to Enthalpy=	1.112567
Thermal correction to Gibbs Free Energy=	0.946837

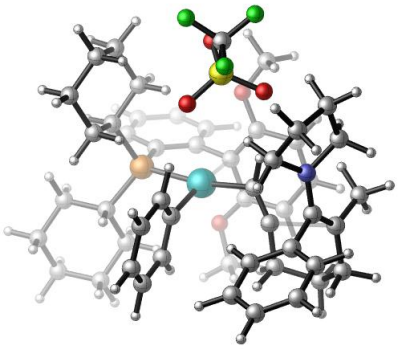
Charge = 0 Multiplicity = 1

C	0.08815200	-2.56549700	-0.19595100
C	-0.99431500	-3.35584700	0.24395400
H	-1.34957100	-3.27677400	1.26981600
C	-1.65198200	-4.25257900	-0.59939900
H	-2.49014100	-4.83945600	-0.21620800
C	-1.23792200	-4.37958600	-1.92509300
H	-1.75202000	-5.06109300	-2.60774300
C	-0.13963100	-3.64266100	-2.36719300
H	0.21675100	-3.76888800	-3.39230200
C	0.55212000	-2.74577100	-1.53261500
C	1.78954700	-2.14436100	-2.13668500
C	1.76984200	-0.94140500	-2.87579700
C	2.94541400	-0.43759400	-3.46237300
H	2.94090200	0.51544100	-3.98830500
C	4.12500300	-1.17525200	-3.36838100
H	5.04073300	-0.77873200	-3.81495300
C	4.15448600	-2.41891200	-2.73687400
H	5.07736500	-2.99643000	-2.71218800

C	2.97514900	-2.91495900	-2.15674700
C	4.03729100	-4.96994500	-1.51209300
H	4.43084000	-5.22714300	-2.51079300
C	0.46279100	0.87892100	-3.72570700
H	1.02160200	1.68449800	-3.22340100
C	-0.55738200	-1.11631600	2.35014900
H	-0.67750000	-2.13167900	2.75791800
C	-0.04023400	-0.21514800	3.49193700
H	0.95028900	-0.53634500	3.84477800
H	0.07356600	0.81269100	3.10482500
C	-1.01986500	-0.21912000	4.67506300
H	-1.03967800	-1.23297400	5.11541500
H	-0.64739500	0.45860400	5.46190400
C	-2.43871400	0.17522400	4.25282300
H	-2.44281300	1.23479500	3.93834900
H	-3.13076300	0.09808500	5.10873900
C	-2.92701600	-0.68514400	3.08382100
H	-3.92227000	-0.35216500	2.75293500
H	-3.03444200	-1.73524400	3.41341100
C	-1.94373600	-0.62072600	1.90833800
H	-1.86118400	0.41964200	1.56199500
H	-2.32989300	-1.20022100	1.06018700
C	2.15984600	-2.07114400	1.92566200
H	2.49228300	-1.26327500	2.59475800
C	1.75523500	-3.28428300	2.78639000
H	1.37800100	-4.08723400	2.12831400
H	0.94356600	-3.03191500	3.48339300
C	2.95510200	-3.80004300	3.59775700
H	3.24254100	-3.02569900	4.33267700
H	2.65004100	-4.68723000	4.17855000
C	4.16413300	-4.12477800	2.71478900
H	3.91578600	-4.97905300	2.05755000
H	5.01871400	-4.44079900	3.33726900
C	4.53962300	-2.92311800	1.84308100
H	5.37254300	-3.17927000	1.16631400
H	4.89518900	-2.09433000	2.48220200
C	3.33535900	-2.45291900	1.01982900
H	3.00821800	-3.27638800	0.37509000
H	3.61841200	-1.61943900	0.36705400
O	2.88304900	-4.14939200	-1.60107400
O	0.56433800	-0.34573100	-3.01181700
P	0.73585000	-1.28000200	0.99579000
C	2.85291300	0.89602600	0.74024700
C	3.13103500	1.15778800	2.08836200
C	3.90979900	0.83999100	-0.17954700
C	4.45370300	1.34987200	2.51169600
H	2.32531300	1.21682500	2.82148500
C	5.22970500	1.03091300	0.24670800
H	3.71228300	0.63858300	-1.23323000
C	5.50767400	1.28055900	1.59528200
H	4.65592100	1.55523900	3.56727400
H	6.04327300	0.97915900	-0.48319900
H	6.53900500	1.42524100	1.92897200
H	0.81351000	0.76641600	-4.76586000

H	-0.60251900	1.13980200	-3.73380900
H	3.72065100	-5.89131100	-1.00440800
H	4.83613700	-4.49058900	-0.92087900
S	1.41544300	4.05870900	-0.30368100
O	1.40950100	2.69345300	-0.96361200
O	0.95236900	4.04835500	1.09320600
O	0.88077600	5.10175100	-1.19521800
Pd	0.99622100	0.79032400	0.01884100
C	-1.22841700	0.39605400	-1.01927700
C	-1.46545000	1.59296000	-1.01301700
H	-1.27394700	-0.66704700	-1.16799500
C	-1.84351300	2.99809200	-1.11295600
C	-2.92469300	3.25946500	-2.18629000
H	-0.95663900	3.58601600	-1.38410300
H	-2.17476900	3.36977800	-0.12883900
C	-4.31360000	2.63129700	-1.95557400
H	-3.05120400	4.35277500	-2.24608000
H	-2.52355700	2.94688700	-3.16376500
C	-4.37858500	1.11676100	-1.93557400
H	-4.75687700	3.05868100	-1.04596200
H	-4.94886900	2.97750400	-2.79461900
C	-4.91440600	0.38083300	-0.91743500
C	-3.90189100	0.44034200	-3.19580100
C	-5.34142300	0.95321600	0.39958400
N	-5.16076000	-0.99833100	-1.08879400
H	-3.01498500	0.94471500	-3.60803400
H	-3.64237100	-0.61219100	-3.01306600
H	-4.67137400	0.46519900	-3.99024700
C	-4.52337200	1.80639400	1.16161900
C	-6.59161000	0.58748700	0.94003200
C	-4.85936800	-1.98967100	-0.05105400
C	-6.15873300	-1.50065700	-2.03710800
C	-4.94874700	2.30848100	2.39533000
H	-3.52920000	2.05658900	0.79744100
C	-7.01698700	1.08008700	2.17570600
H	-7.23512400	-0.09418800	0.37896200
H	-3.83718100	-2.39384400	-0.18254200
H	-4.90262100	-1.55600300	0.96032400
H	-7.15540500	-1.05041100	-1.84839600
H	-5.89850000	-1.27473800	-3.08409100
C	-6.19875400	1.94942200	2.90878700
H	-4.28882900	2.96726900	2.96618000
H	-7.99390500	0.78532100	2.56928400
H	-6.52997100	2.33405900	3.87714300
C	-5.90654200	-3.08797500	-0.26041200
H	-5.55909300	-4.07844300	0.07177800
H	-6.82431900	-2.84431900	0.30177000
C	-6.18271500	-3.00813300	-1.76717000
H	-7.13232900	-3.47623200	-2.06838100
H	-5.36800400	-3.50135000	-2.32500200
C	3.24585900	4.49540600	-0.20850600
F	3.82909400	3.93472700	0.84711500
F	3.88398500	4.09865900	-1.31299100
F	3.37234400	5.82182800	-0.10129400

TS2



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.215942
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.46362

Zero-point correction=	1.047331 (Hartree/Particle)
Thermal correction to Energy=	1.110289
Thermal correction to Enthalpy=	1.111233
Thermal correction to Gibbs Free Energy=	0.946693

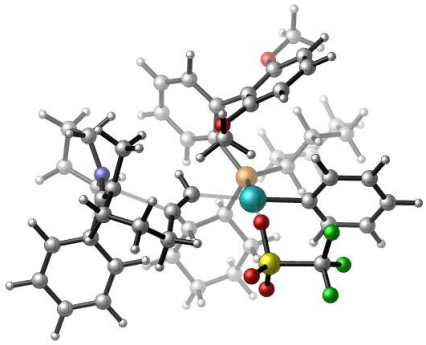
Charge = 0 Multiplicity = 1

C	4.04220400	0.44877600	0.83458000
C	5.35630600	0.91491300	0.63887300
H	5.74471500	1.04365800	-0.37215600
C	6.17164700	1.23830300	1.72331600
H	7.18973200	1.59748800	1.55213800
C	5.67449000	1.11051200	3.02501700
H	6.30179800	1.36586500	3.88319400
C	4.37005500	0.66089600	3.22667300
H	3.97744700	0.56604400	4.24220700
C	3.53773000	0.32502400	2.14265400
C	2.15918400	-0.16844300	2.48875600
C	1.19756000	0.74292100	3.01554200
C	0.09147400	0.27246000	3.74646700
H	-0.65389300	0.96262000	4.13712500
C	-0.03649800	-1.09522700	3.97831200
H	-0.88778500	-1.45463700	4.55936400
C	0.87903000	-2.02386700	3.47809600
H	0.73879700	-3.08589900	3.67085000
C	1.97693800	-1.56102300	2.73988800
C	2.81094500	-3.76875600	2.33534700
H	2.78214300	-4.12140300	3.38058300
C	0.53661900	3.02865700	3.27190300
H	-0.45484100	2.89334400	2.81562200
C	2.96859300	1.73414400	-1.50901200
H	4.03007900	1.91298600	-1.75689600
C	2.15441300	1.68566500	-2.81224400
H	2.52631000	0.88891500	-3.47722400
H	1.11223600	1.44251100	-2.56455400
C	2.18243900	3.03999400	-3.53407100
H	3.21649000	3.26296300	-3.85845500
H	1.57040700	2.98031100	-4.45069300

C	1.67761700	4.16599500	-2.62371400
H	0.62095700	3.98182000	-2.36830400
H	1.72674200	5.13555400	-3.14957100
C	2.48459000	4.22193500	-1.32223200
H	2.06756800	4.99040300	-0.65141100
H	3.52847300	4.51333600	-1.54642300
C	2.47514200	2.87135500	-0.59618800
H	1.44698700	2.65841300	-0.27221100
H	3.09087400	2.92987800	0.31453100
C	3.74998400	-1.15864100	-1.67874500
H	2.95045500	-1.37744200	-2.40732100
C	4.99738300	-0.73327800	-2.47190300
H	5.82161000	-0.50370300	-1.77680500
H	4.80087100	0.17850800	-3.05653500
C	5.44261000	-1.86798000	-3.40751700
H	4.65345400	-2.04294800	-4.16175200
H	6.34648600	-1.56093100	-3.96072800
C	5.70350300	-3.16715500	-2.63604100
H	6.56416900	-3.01637200	-1.95811100
H	5.98680600	-3.97596200	-3.33102000
C	4.48093400	-3.57839700	-1.80717500
H	4.70336900	-4.48155400	-1.21349700
H	3.65025200	-3.84180700	-2.48734200
C	4.02322900	-2.44617000	-0.88011600
H	4.80526500	-2.24372500	-0.12761200
H	3.12770300	-2.74503900	-0.31642900
O	2.95368700	-2.35825900	2.26101200
O	1.45835100	2.04547500	2.80863200
P	2.93189800	0.11205600	-0.59236300
C	0.24847100	-1.21287200	-1.55176200
C	-0.57499300	-0.48617900	-2.42558200
C	0.59122700	-2.53435300	-1.88257200
C	-1.01306500	-1.06147700	-3.62623000
H	-0.88367400	0.52668400	-2.16345500
C	0.14361800	-3.10856200	-3.08171300
H	1.21477100	-3.13340200	-1.21550300
C	-0.65242900	-2.37088900	-3.96395700
H	-1.65270400	-0.47948000	-4.29677300
H	0.42398600	-4.13862300	-3.32200500
H	-0.99739300	-2.81595600	-4.90121000
H	1.90141600	-4.10847200	1.81102600
H	3.69265900	-4.19453300	1.83886500
H	0.93651800	3.99624400	2.94675000
H	0.46043700	3.01007900	4.37302900
S	-1.40984000	3.22287600	-0.04184100
O	-2.16732700	2.46254000	0.98682000
O	-0.99843700	2.42658800	-1.22284300
O	-0.40472400	4.16704900	0.48707200
Pd	0.83695000	-0.50343900	0.23067000
C	-1.20522300	-0.67282000	0.82300600
C	-1.52196100	-1.87443400	1.02430400
H	-1.71172100	0.29746400	0.82367900
C	-1.40241800	-3.33341800	1.09171700
C	-2.29008000	-3.96165800	2.17598500

H	-0.34160200	-3.56196200	1.28773300
H	-1.65170000	-3.76190300	0.10627000
C	-3.75308600	-3.51319500	1.98888200
H	-2.20927800	-5.05938100	2.12667900
H	-1.91706200	-3.65672600	3.16716300
C	-3.83945000	-2.00359000	1.88976200
H	-4.16068700	-3.99917800	1.09208200
H	-4.35022400	-3.87301400	2.84675000
C	-4.23922400	-1.37463700	0.71969300
C	-3.58901200	-1.27650100	3.19571900
C	-4.55777000	-2.19869100	-0.50116100
H	-3.01122200	-1.91412000	3.87896000
H	-3.01613500	-0.35131900	3.06056100
H	-4.52629900	-1.02429700	3.71956900
C	-3.60568000	-2.52786000	-1.47738200
C	-5.88446200	-2.62875900	-0.67481900
C	-3.96936000	-3.29089300	-2.59249700
H	-2.58221200	-2.16556000	-1.37923900
C	-6.24744600	-3.39343100	-1.78769100
H	-6.63516900	-2.36666300	0.07569000
C	-5.28784500	-3.73037100	-2.74919700
H	-3.21407400	-3.53373800	-3.34355700
H	-7.28234500	-3.72713400	-1.90333300
H	-5.56848300	-4.32849700	-3.62040500
N	-4.40410200	-0.02089000	0.56797300
C	-4.50541800	0.64971800	-0.73951500
C	-4.90958000	0.88949400	1.62101000
H	-3.58408400	1.22568700	-0.92462600
H	-4.62829100	-0.06995000	-1.55549400
C	-5.69696800	1.58762100	-0.56923800
H	-5.67427200	0.36130900	2.21046200
H	-4.11336100	1.22119100	2.29767000
C	-5.49956000	2.09450900	0.86335800
H	-5.71339900	2.39470800	-1.31519300
H	-6.63471400	1.01193300	-0.65548900
H	-6.42788800	2.45600600	1.33091600
H	-4.77114800	2.91743100	0.86873300
C	-2.68701400	4.38305700	-0.78188600
F	-2.09568500	5.25106200	-1.61263300
F	-3.31475900	5.08307600	0.17367200
F	-3.61590000	3.71562300	-1.48129700

TS3



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.199064
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.448017

Zero-point correction=	1.049025 (Hartree/Particle)
Thermal correction to Energy=	1.110962
Thermal correction to Enthalpy=	1.111907
Thermal correction to Gibbs Free Energy=	0.951546

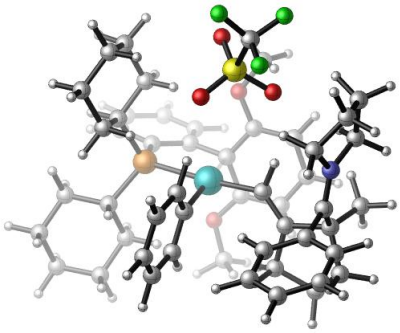
Charge = 0 Multiplicity = 1

C	0.19169300	-2.54253400	0.06344600
C	-0.77681600	-3.36608800	0.67198200
H	-1.01945100	-3.23976400	1.72540200
C	-1.45461400	-4.36309100	-0.03003300
H	-2.19412000	-4.97932400	0.48623900
C	-1.19301500	-4.54793900	-1.38687200
H	-1.73303900	-5.30416300	-1.96214500
C	-0.21170800	-3.76943400	-1.99930300
H	0.03433400	-3.94165400	-3.04989300
C	0.51193600	-2.78288100	-1.30344600
C	1.66709600	-2.19817800	-2.06538100
C	1.58635600	-1.01762800	-2.83425400
C	2.69608400	-0.56926200	-3.57677600
H	2.64603400	0.35708100	-4.14582100
C	3.86625300	-1.32568200	-3.58853500
H	4.72776900	-0.96991400	-4.16008800
C	3.95290400	-2.53750700	-2.90229100
H	4.86743300	-3.12693500	-2.94738300
C	2.84194800	-2.98055200	-2.16825100
C	3.96841000	-4.99391700	-1.50101800
H	4.23260500	-5.32916700	-2.51920800
C	0.28481300	0.86940900	-3.51011700
H	1.02012700	1.59921200	-3.13903700
C	-0.17618500	-1.02744000	2.62562100
H	-0.21081800	-2.03962500	3.05787400
C	0.45549200	-0.09496500	3.68071500
H	1.48363300	-0.39849700	3.92408700
H	0.50975600	0.92502400	3.26207400
C	-0.37824600	-0.08117800	4.97090200
H	-0.34005900	-1.08648300	5.42968600
H	0.08003800	0.61301600	5.69566100

C	-1.83975100	0.29961900	4.71405600
H	-1.88586700	1.35081000	4.37411900
H	-2.42178300	0.24303900	5.64980500
C	-2.45779900	-0.59513900	3.63567100
H	-3.48667400	-0.27107600	3.40762400
H	-2.52678500	-1.63407900	4.00832500
C	-1.61774500	-0.56699800	2.35434700
H	-1.58606900	0.46200100	1.96600300
H	-2.09334300	-1.17522200	1.57650500
C	2.51006800	-1.79773500	1.81726100
H	2.80283100	-0.98010500	2.49291700
C	2.33869400	-3.08185700	2.65227700
H	2.02351200	-3.90508500	1.98686600
H	1.55275500	-2.96735900	3.41319900
C	3.65617000	-3.45667000	3.34963700
H	3.89836300	-2.67436600	4.09244100
H	3.52060700	-4.39538100	3.91373500
C	4.81957400	-3.58757000	2.36121000
H	4.63026800	-4.44746300	1.69180700
H	5.75746800	-3.80574800	2.90023600
C	4.96278900	-2.32082200	1.51121800
H	5.76287100	-2.44605200	0.76159200
H	5.26118400	-1.47191700	2.15335000
C	3.64419400	-1.98721800	0.80334300
H	3.38017400	-2.82697900	0.15364900
H	3.75805400	-1.10052000	0.16859300
O	2.81670500	-4.16632100	-1.50507000
O	0.39799700	-0.37568500	-2.83596600
P	0.90799800	-1.15505300	1.08700800
C	2.76466400	1.25374000	0.48103000
C	3.27822600	1.48774700	1.76740700
C	3.63923100	1.40288800	-0.61101800
C	4.61922300	1.85031400	1.95872500
H	2.63211400	1.39497200	2.64257300
C	4.97971400	1.76275700	-0.42575600
H	3.27816100	1.22902700	-1.62744400
C	5.47877300	1.98355800	0.86346400
H	4.99177200	2.02895200	2.97253800
H	5.63759600	1.86726200	-1.29455900
H	6.52643700	2.26081700	1.01213100
H	0.39493300	0.74402000	-4.60147600
H	-0.71528700	1.24972200	-3.28263900
H	3.71446600	-5.87106300	-0.89029500
H	4.83845500	-4.48429600	-1.05223700
S	0.67466500	4.17456500	-0.21521600
O	0.78695700	2.84442900	-0.92445200
O	0.38885300	4.07489000	1.22609200
O	-0.10673100	5.15157200	-0.99431100
Pd	0.81609000	0.85904900	0.03994000
C	-1.27849200	0.42971400	-0.59690200
C	-2.11896100	1.31668400	-0.97018800
H	-1.50253500	-0.64024000	-0.61621100
C	-2.52188800	2.71358800	-1.19616900
C	-3.36923600	2.86862200	-2.46018900

H	-1.60019500	3.30593300	-1.27495300
H	-3.08269400	3.09084700	-0.32344800
C	-4.50810300	1.83897800	-2.39145600
H	-3.76247600	3.89424900	-2.53948700
H	-2.74138900	2.69361800	-3.34932500
C	-3.95176600	0.47003400	-2.04653500
H	-5.24224400	2.16846600	-1.64366500
H	-5.03591800	1.79039600	-3.36078500
C	-4.39830500	-0.21397800	-0.90986600
C	-3.22012900	-0.21151900	-3.18625300
C	-5.18188200	0.50579700	0.15324700
N	-4.19141100	-1.54549400	-0.68730600
H	-2.70082100	0.53895800	-3.79737000
H	-2.45969300	-0.91981400	-2.83537400
H	-3.90956200	-0.74358800	-3.86202500
C	-4.57842400	1.25334000	1.17405500
C	-6.58260100	0.38554500	0.13348200
C	-4.44932900	-2.20076000	0.60886500
C	-4.29820400	-2.57619400	-1.75526100
C	-5.35967600	1.87766900	2.15240100
H	-3.49283800	1.32836600	1.21275600
C	-7.36331100	1.01554300	1.10667700
H	-7.06105700	-0.20074400	-0.65541700
H	-3.51197300	-2.65567900	0.96735600
H	-4.78508500	-1.48466100	1.36453100
H	-4.94017000	-2.18823100	-2.55541200
H	-3.31746800	-2.81967500	-2.18474200
C	-6.75306000	1.76376900	2.12042300
H	-4.87201800	2.45104600	2.94522400
H	-8.45201600	0.92070000	1.07367800
H	-7.36271000	2.25387900	2.88418900
C	-5.46361800	-3.28726600	0.26883900
H	-5.52721300	-4.06716300	1.04240200
H	-6.46232900	-2.83503200	0.14863700
C	-4.93078900	-3.80893400	-1.07270900
H	-5.71200900	-4.26043900	-1.70172400
H	-4.16125500	-4.57472300	-0.89675900
C	2.41926800	4.88384500	-0.31001600
F	3.20570000	4.39755700	0.64687000
F	2.36004800	6.21257200	-0.16332500
F	2.97431400	4.61779700	-1.49657000

V



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.251058
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.496409

Zero-point correction=	1.051907 (Hartree/Particle)
Thermal correction to Energy=	1.113968
Thermal correction to Enthalpy=	1.114912
Thermal correction to Gibbs Free Energy=	0.951791

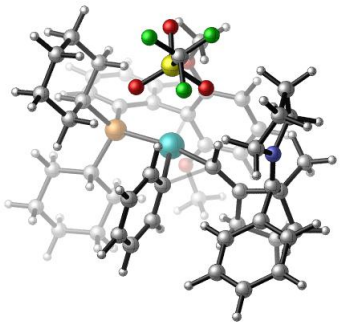
Charge = 0 Multiplicity = 1

C	4.02978200	0.61168400	0.84245700
C	5.31662400	1.15260600	0.65728000
H	5.67646000	1.36882000	-0.34957300
C	6.14185800	1.43650800	1.74563700
H	7.13857000	1.85439400	1.58104400
C	5.68218000	1.19085900	3.04432100
H	6.31757200	1.41174200	3.90623900
C	4.40287200	0.67057600	3.23815000
H	4.03710300	0.48846900	4.25203300
C	3.56111900	0.37747400	2.14847000
C	2.20209100	-0.17112500	2.49301300
C	1.20209100	0.70891700	2.99391600
C	0.12581600	0.21257100	3.75274500
H	-0.64235300	0.88256600	4.13545700
C	0.06477300	-1.15218900	4.02972800
H	-0.75563700	-1.53169200	4.64113700
C	1.00887000	-2.05381500	3.53310300
H	0.91564700	-3.11668600	3.75002000
C	2.07378400	-1.56343900	2.76336300
C	2.98824900	-3.74309600	2.37805600
H	3.00805800	-4.07938800	3.42926000
C	0.42785900	2.97042400	3.14032800
H	-0.54412900	2.76270000	2.66895600
C	2.89061400	1.91602600	-1.45502200
H	3.94601800	2.16940000	-1.65953800
C	2.13188300	1.85869900	-2.79133800
H	2.57302900	1.10238800	-3.46113300
H	1.09541300	1.54889600	-2.59641600
C	2.11726600	3.23155600	-3.47856600
H	3.15106100	3.51253500	-3.75578500
H	1.54571600	3.16637800	-4.42084600

C	1.52164300	4.30965100	-2.56452500
H	0.46421400	4.07138900	-2.36262400
H	1.54989600	5.29374100	-3.06481000
C	2.26432400	4.36915900	-1.22498700
H	1.77608600	5.09596400	-0.55578100
H	3.30132400	4.71894200	-1.39061000
C	2.29107500	2.99837100	-0.53862600
H	1.26000900	2.72035900	-0.27558700
H	2.85087500	3.05751600	0.40777900
C	3.76093000	-0.93861700	-1.68798200
H	2.97492000	-1.14601600	-2.43585600
C	5.01597500	-0.47368000	-2.44388100
H	5.82469600	-0.26107000	-1.72504600
H	4.82102900	0.45869000	-2.99630100
C	5.49265000	-1.56714900	-3.41258100
H	4.71892400	-1.72439600	-4.18663600
H	6.40245900	-1.23096100	-3.93890600
C	5.75591300	-2.89045900	-2.68352300
H	6.60398400	-2.75410800	-1.98675800
H	6.06026700	-3.67091000	-3.40189600
C	4.52554200	-3.34496500	-1.88894500
H	4.75021700	-4.26634100	-1.32441200
H	3.70921400	-3.59438700	-2.59149900
C	4.03864400	-2.25104100	-0.93099500
H	4.80748100	-2.06588700	-0.16029800
H	3.13958400	-2.58092800	-0.38904300
O	3.07216300	-2.33055700	2.27678000
O	1.40839800	2.01649800	2.74629000
P	2.89649900	0.27484700	-0.56738900
C	0.19702500	-1.16326400	-1.57099800
C	-0.57297900	-0.37769100	-2.44836500
C	0.59568200	-2.44154700	-2.00871800
C	-0.89200100	-0.83746100	-3.73374800
H	-0.92756500	0.60432200	-2.13093000
C	0.26846400	-2.90364000	-3.29155400
H	1.17615400	-3.09379500	-1.35303100
C	-0.47041500	-2.09958000	-4.16668300
H	-1.48578500	-0.20164800	-4.39825300
H	0.59710700	-3.89965100	-3.60483500
H	-0.72290500	-2.45679700	-5.16904900
H	2.07657500	-4.12856400	1.89053400
H	3.86972800	-4.14271900	1.85911700
H	0.78503700	3.94159500	2.77728700
H	0.32410200	3.00351000	4.23918600
S	-1.62963500	3.20366700	-0.13368900
O	-2.18807800	2.27491800	0.88290700
O	-1.24751200	2.56530500	-1.41459100
O	-0.70011900	4.22463100	0.38988700
Pd	0.79608600	-0.52064200	0.23672100
C	-1.09868000	-1.00429300	0.81179500
C	-1.70855200	-2.17974700	1.03315200
H	-1.69368100	-0.08991400	0.95916000
C	-1.14412000	-3.57109800	0.81003100
C	-2.02906100	-4.50314600	1.64445600

H	-0.07571200	-3.61343400	1.07041600
H	-1.22411200	-3.83477700	-0.25993100
C	-3.42297100	-3.87337900	1.50627400
H	-2.01159700	-5.54809100	1.29820400
H	-1.70166300	-4.49994500	2.69763300
C	-3.16955100	-2.33615400	1.60965700
H	-3.83499800	-4.14806000	0.52755800
H	-4.13972200	-4.21043500	2.27098700
C	-3.99739400	-1.51709100	0.63772600
C	-3.21397700	-1.95468300	3.09916100
C	-4.35467800	-2.16831700	-0.66372900
H	-2.62176200	-2.69268300	3.65739700
H	-2.77150200	-0.97577500	3.30074600
H	-4.24103900	-1.98730900	3.49344700
C	-3.43048000	-2.37476500	-1.69461300
C	-5.67892500	-2.62064000	-0.81105700
C	-3.82976700	-3.02972500	-2.86475400
H	-2.40915300	-2.01500500	-1.58625400
C	-6.06787800	-3.27944600	-1.97861000
H	-6.40011900	-2.45923600	-0.00571300
C	-5.14278500	-3.48619800	-3.00911800
H	-3.10189700	-3.17628000	-3.66563600
H	-7.09722700	-3.63193900	-2.08320200
H	-5.44781000	-4.00041000	-3.92426200
N	-4.39712300	-0.28520400	0.80384100
C	-4.90724800	0.57242800	-0.30490300
C	-4.44586000	0.51746800	2.06823300
H	-4.03309400	1.12450500	-0.68245700
H	-5.33167700	-0.02691000	-1.11353700
C	-5.89195400	1.50338600	0.38156900
H	-4.98622200	-0.07107100	2.81629400
H	-3.42786000	0.71780600	2.41328600
C	-5.19113400	1.81098100	1.70890400
H	-6.08386600	2.40156800	-0.22065200
H	-6.84836000	0.97978100	0.54602600
H	-5.89035200	2.09906000	2.50689100
H	-4.46518300	2.62144700	1.57162700
C	-3.11178500	4.23763900	-0.64572100
F	-4.03197400	3.49528000	-1.28357300
F	-3.70505000	4.79587400	0.42006500
F	-2.73455500	5.21925800	-1.47259300

TS4



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.235678
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.49099

Zero-point correction=	1.050881 (Hartree/Particle)
Thermal correction to Energy=	1.112589
Thermal correction to Enthalpy=	1.113533
Thermal correction to Gibbs Free Energy=	0.951008

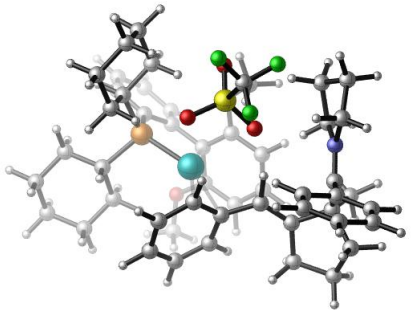
Charge = 0 Multiplicity = 1

C	-4.22434800	0.40025400	-0.70323900
C	-5.47398400	0.99348800	-0.43897400
H	-5.64192300	1.51118100	0.50671500
C	-6.51390700	0.94181800	-1.36862700
H	-7.47503700	1.40947000	-1.13858600
C	-6.31702700	0.29052600	-2.59050200
H	-7.12386200	0.23932500	-3.32666400
C	-5.07796600	-0.28472800	-2.87316400
H	-4.91488000	-0.78114000	-3.83324400
C	-4.01886800	-0.23228900	-1.94820700
C	-2.71715100	-0.83450500	-2.38066700
C	-1.71108300	-0.02145600	-2.95650200
C	-0.59341500	-0.60542000	-3.58438800
H	0.17934300	0.01621000	-4.03466000
C	-0.49167300	-1.99549000	-3.62970000
H	0.36003500	-2.45052200	-4.13633500
C	-1.44518300	-2.82291100	-3.03189500
H	-1.32276300	-3.90479300	-3.06375300
C	-2.55740500	-2.23885400	-2.40520700
C	-3.36340600	-4.33330400	-1.57427400
H	-3.34503000	-4.90478700	-2.51893900
C	-0.84420400	2.20099600	-3.13474100
H	0.02125200	1.96461900	-2.49698400
C	-2.92602300	2.16935700	1.19730900
H	-3.96765500	2.36817900	1.50333000
C	-2.02013700	2.35954500	2.42688500
H	-2.29145000	1.65137000	3.22688700
H	-0.97800600	2.14731400	2.13988400
C	-2.11992200	3.80044100	2.95191800
H	-3.14543500	3.97531100	3.32953500
H	-1.44249100	3.92888100	3.81422300

C	-1.79261800	4.83256100	1.86400900
H	-0.73199600	4.72989400	1.58600100
H	-1.93808400	5.85538600	2.25416500
C	-2.64769000	4.61699400	0.60857700
H	-2.33746300	5.31699700	-0.18663900
H	-3.70670300	4.84428200	0.83519100
C	-2.54253200	3.17440500	0.09481700
H	-1.50496300	2.97998700	-0.22208800
H	-3.18142900	3.03749900	-0.79222900
C	-3.46576700	-0.66674900	1.93596800
H	-2.61071800	-0.63584300	2.63598800
C	-4.72466500	-0.22905500	2.69920300
H	-5.58983100	-0.23716000	2.01484900
H	-4.61916900	0.80191600	3.07272000
C	-5.01184600	-1.18278400	3.86927500
H	-4.18632200	-1.11400900	4.60172900
H	-5.92842000	-0.86551000	4.39583200
C	-5.14467600	-2.63403300	3.39257500
H	-6.03459600	-2.71858000	2.74119600
H	-5.31616800	-3.30691000	4.25035900
C	-3.90547200	-3.07503900	2.60474300
H	-4.03676600	-4.10191300	2.22177000
H	-3.03283100	-3.09913200	3.28335500
C	-3.60625800	-2.11979000	1.44318400
H	-4.41906000	-2.17511200	0.69879200
H	-2.69091100	-2.43225100	0.91557100
O	-3.54168600	-2.94563400	-1.79899400
O	-1.92783000	1.31219800	-2.89367000
P	-2.85812600	0.42596700	0.54025500
C	0.44364500	-0.77998500	1.45058800
C	1.18824600	0.25564100	2.06720700
C	0.05960500	-1.87842600	2.26427200
C	1.51602800	0.20160700	3.42425500
H	1.49060500	1.12241400	1.48221100
C	0.39128200	-1.92299700	3.62222000
H	-0.52836800	-2.69261100	1.84049500
C	1.12359100	-0.88627400	4.21498600
H	2.08387800	1.02546800	3.86782200
H	0.06638200	-2.77790600	4.22336300
H	1.38243600	-0.92590900	5.27645600
H	-2.43508300	-4.53739800	-1.01224600
H	-4.22378900	-4.66440000	-0.97665900
H	-1.20043800	3.20508600	-2.87557800
H	-0.53838000	2.19109600	-4.19597400
S	1.56952200	3.36641300	-0.38214100
O	2.05900400	2.08679100	-0.96209800
O	0.93656800	3.23894500	0.95014100
O	0.90247200	4.27681800	-1.33342700
Pd	-0.76189600	-0.39639600	-0.16548500
C	1.18127300	-1.06632500	-0.33248500
C	1.68853100	-2.28712700	-0.63058400
H	1.78794500	-0.18486100	-0.57273600
C	1.12032300	-3.63170800	-0.23883200
C	1.93237800	-4.66587000	-1.02719100

H	0.03509800	-3.68454800	-0.41293600
H	1.27845000	-3.77847300	0.84716400
C	3.32978300	-4.03394100	-1.09153600
H	1.94835600	-5.65714900	-0.54937900
H	1.51163400	-4.79510400	-2.03773800
C	3.05603900	-2.51965100	-1.36036000
H	3.82855300	-4.18519500	-0.12632900
H	3.97758700	-4.46501200	-1.87003900
C	4.02327800	-1.59537300	-0.63312500
C	2.91426200	-2.34759400	-2.88541000
C	4.57619900	-2.08039400	0.67121200
H	2.30372100	-3.17603200	-3.26694300
H	2.40585700	-1.42174200	-3.16712400
H	3.89332600	-2.40335500	-3.38426700
C	3.79787600	-2.18127300	1.83129900
C	5.92106300	-2.49188100	0.69476500
C	4.36359700	-2.68404400	3.00749600
H	2.75870700	-1.86258400	1.81866100
C	6.47641900	-3.00074200	1.87018500
H	6.52713600	-2.41698700	-0.21177700
C	5.69894400	-3.09637600	3.03073700
H	3.74905100	-2.74952600	3.90848400
H	7.52060500	-3.32347800	1.87894700
H	6.13573200	-3.49204500	3.95132700
N	4.37077800	-0.39599600	-1.01232300
C	5.04248700	0.59390800	-0.11727300
C	4.16966200	0.24951300	-2.35002500
H	4.23018700	1.15595500	0.36779500
H	5.64513700	0.09869100	0.64739200
C	5.82754000	1.48007300	-1.06936800
H	4.61140100	-0.40682500	-3.10633300
H	3.09875200	0.36874800	-2.53747400
C	4.88833300	1.60157100	-2.27353200
H	6.06112700	2.45053700	-0.60981100
H	6.77381300	0.98726500	-1.34733700
H	5.41946100	1.82032100	-3.21082800
H	4.14999300	2.39124400	-2.09797400
C	3.15656000	4.27409300	0.04486300
F	2.88537100	5.43243600	0.65598400
F	3.88216500	4.54591200	-1.05101300
F	3.92237700	3.54085600	0.87039700

VI



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.287275
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.546353

Zero-point correction=	1.053995 (Hartree/Particle)
Thermal correction to Energy=	1.115914
Thermal correction to Enthalpy=	1.116859
Thermal correction to Gibbs Free Energy=	0.954965

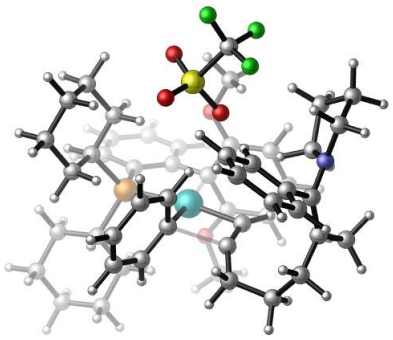
Charge = 0 Multiplicity = 1

C	-4.11423800	0.42184900	-1.31450600
C	-5.20931400	1.26012200	-1.60264600
H	-5.37855100	2.15853000	-1.00784900
C	-6.10046400	0.97592300	-2.63977400
H	-6.93966900	1.64894500	-2.83573600
C	-5.91446000	-0.17060500	-3.41689800
H	-6.60751500	-0.41028200	-4.22794700
C	-4.82537500	-1.00326500	-3.15822900
H	-4.66222900	-1.89246700	-3.77257700
C	-3.91287500	-0.72016700	-2.12612800
C	-2.73946300	-1.63192000	-1.97744700
C	-1.47314900	-1.22420300	-2.44990400
C	-0.36960100	-2.09190300	-2.36992100
H	0.60339200	-1.78132200	-2.74078200
C	-0.53480600	-3.35732300	-1.80648900
H	0.32718100	-4.02499700	-1.73630900
C	-1.77116400	-3.77904700	-1.31401100
H	-1.86981200	-4.76620800	-0.86421500
C	-2.87561200	-2.91262800	-1.40694400
C	-4.28644400	-4.36567300	-0.12842400
H	-4.11321600	-5.30367400	-0.68524500
C	-0.15144700	0.65699200	-3.10757900
H	0.36250400	0.71105300	-2.13439600
C	-2.93021200	2.65217400	0.14947400
H	-3.95995100	3.04465000	0.10872700
C	-2.27541800	3.16915800	1.44305500
H	-2.85729900	2.85141600	2.32402500
H	-1.26834000	2.73218100	1.53749600
C	-2.14565100	4.69941000	1.43033600
H	-3.15467000	5.15412800	1.43973500
H	-1.64107800	5.03451500	2.35337100

C	-1.37725200	5.18898900	0.19713000
H	-0.34375300	4.80969100	0.24527800
H	-1.32407900	6.29209400	0.19156900
C	-2.02834400	4.67946700	-1.09395300
H	-1.43650800	4.99509800	-1.97043100
H	-3.03032700	5.13596000	-1.20676800
C	-2.16106600	3.15093700	-1.08733400
H	-1.15092200	2.71229700	-1.08337200
H	-2.65940600	2.80739700	-2.00892000
C	-4.09561600	0.33802200	1.60512100
H	-3.44829500	0.59839200	2.46184500
C	-5.42237400	1.09637600	1.76122200
H	-6.07733700	0.86994500	0.90295300
H	-5.25537100	2.18549300	1.75875700
C	-6.14415900	0.68269500	3.05332900
H	-5.53153900	0.98525400	3.92286800
H	-7.10171600	1.22513800	3.13834800
C	-6.38066100	-0.83118800	3.10516400
H	-7.07562800	-1.11451700	2.29256500
H	-6.87140300	-1.11249400	4.05296200
C	-5.06685400	-1.60121900	2.93032200
H	-5.25518100	-2.68893100	2.91417900
H	-4.41258500	-1.40721000	3.80034000
C	-4.33171500	-1.18282700	1.65153600
H	-4.92036200	-1.48842600	0.77000600
H	-3.36932200	-1.71341600	1.57695300
O	-4.11525100	-3.22407400	-0.94974900
O	-1.41354500	0.01722200	-2.98859700
P	-3.00019400	0.78269600	0.13589500
C	0.59324100	-1.52340600	1.52141300
C	0.41376000	-0.29090700	2.23905900
C	-0.22610300	-2.62854800	1.93261700
C	-0.38357400	-0.25169100	3.41169900
H	1.05711300	0.56196800	2.01277700
C	-1.02508500	-2.55856300	3.06954200
H	-0.20697400	-3.54845000	1.35100700
C	-1.07676800	-1.37798300	3.84108100
H	-0.43893400	0.68295000	3.97679200
H	-1.62299600	-3.42700700	3.35964100
H	-1.68534000	-1.34119800	4.74849200
H	-3.61732600	-4.34026600	0.74921600
H	-5.32971500	-4.34728500	0.21608300
H	-0.35171800	1.67824000	-3.45575200
H	0.49558700	0.15236700	-3.84515500
S	1.83867000	2.69072700	0.06729000
O	2.42937600	1.33424700	-0.08041100
O	1.10856100	2.92115100	1.33135400
O	1.22739500	3.23075600	-1.16688900
Pd	-0.99316300	-0.32826900	0.43306800
C	1.74710700	-1.64403800	0.60467500
C	2.47523800	-2.74500800	0.32741200
H	2.06296400	-0.69000100	0.18003800
C	2.29600500	-4.14254500	0.89932700
C	3.61929700	-4.89418700	0.63632200

H	1.44320900	-4.66084200	0.43220000
H	2.06322500	-4.07674900	1.97455400
C	4.61075200	-3.80041500	0.21650700
H	3.97779800	-5.43274500	1.52606800
H	3.49406100	-5.64452000	-0.15854700
C	3.74047700	-2.75904500	-0.55944800
H	5.02489200	-3.34047800	1.12225800
H	5.45115900	-4.17047800	-0.39001500
C	4.43554900	-1.39360700	-0.61175500
C	3.43370300	-3.35667900	-1.95629000
C	5.37733600	-1.01130000	0.48651200
H	3.22216300	-4.42887100	-1.85427700
H	2.55653400	-2.90913300	-2.43158000
H	4.30216000	-3.25641800	-2.62551900
C	4.92687600	-0.13595900	1.48769900
C	6.70289600	-1.47213900	0.49928700
C	5.79873200	0.25534500	2.50773200
H	3.91141700	0.25993400	1.44713600
C	7.57014600	-1.06619400	1.51612100
H	7.05325700	-2.14341100	-0.28741400
C	7.11828400	-0.20756000	2.52507300
H	5.44286300	0.93628100	3.28502600
H	8.60258900	-1.42454100	1.52055500
H	7.79807000	0.10507700	3.32195400
N	4.26916300	-0.49633800	-1.53612200
C	5.09032100	0.75658100	-1.60173200
C	3.25754100	-0.47260100	-2.63235800
H	4.76967400	1.40323400	-0.77952600
H	6.14796900	0.50207700	-1.46914600
C	4.74936800	1.36453700	-2.95653600
H	3.57671500	-1.17414000	-3.41321800
H	2.29223400	-0.78155900	-2.22559900
C	3.28668800	0.96243700	-3.15329500
H	4.90435300	2.45205100	-2.94948800
H	5.38457100	0.92722300	-3.74409700
H	2.95864900	1.00612400	-4.20110800
H	2.63104500	1.60237000	-2.54946000
C	3.35407900	3.77301300	0.28185300
F	3.00278900	5.03988500	0.52485800
F	4.11702000	3.76013500	-0.82419300
F	4.10865400	3.34332300	1.30328700

TS5



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3577.199645
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -3578.452322

Zero-point correction=	1.046599 (Hartree/Particle)
Thermal correction to Energy=	1.109514
Thermal correction to Enthalpy=	1.110458
Thermal correction to Gibbs Free Energy=	0.947387

Charge = 0 Multiplicity = 1

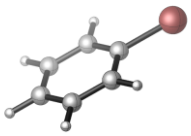
C	-3.90120400	0.85370000	-1.20362500
C	-5.00830600	1.71694300	-1.31390900
H	-5.35347600	2.27767000	-0.44433100
C	-5.67043400	1.88167400	-2.53060500
H	-6.52850800	2.55551500	-2.59700900
C	-5.22787900	1.18511800	-3.66054100
H	-5.73967800	1.30582900	-4.61896000
C	-4.11942200	0.34432500	-3.56538400
H	-3.75987500	-0.18694100	-4.45040800
C	-3.43984800	0.17350400	-2.34547500
C	-2.22932300	-0.72353600	-2.38453600
C	-1.01557100	-0.20595500	-2.94360900
C	-0.04499600	-1.07498300	-3.47420500
H	0.87891700	-0.68615400	-3.89611600
C	-0.29229100	-2.44813900	-3.47795800
H	0.45697700	-3.11701200	-3.90913700
C	-1.45412500	-3.00007100	-2.92921600
H	-1.60299000	-4.07865200	-2.93768500
C	-2.42450800	-2.14144400	-2.39108900
C	-3.83851100	-3.93363900	-1.67482400
H	-3.85631700	-4.50592700	-2.61772100
C	0.26807500	1.75441100	-3.44255500
H	1.13725900	1.42039900	-2.86055800
C	-2.70740100	2.35681200	0.97113000
H	-3.67632500	2.88059200	0.89826800
C	-2.23719000	2.40938500	2.43456600
H	-2.99851200	1.97574100	3.10204000
H	-1.33038400	1.79841600	2.54359100
C	-1.92207300	3.84657300	2.87176600
H	-2.85882600	4.43466800	2.88989600
H	-1.53579100	3.83644300	3.90570100

C	-0.92057500	4.52226600	1.92849200
H	0.05024400	3.99716100	1.97171300
H	-0.73631500	5.56232200	2.24974400
C	-1.41865800	4.48853900	0.48005800
H	-0.66366400	4.92626500	-0.18959700
H	-2.34236500	5.09092600	0.38984500
C	-1.70152800	3.05031100	0.03360300
H	-0.75398900	2.48733500	0.02960600
H	-2.07011800	3.03330700	-1.00457900
C	-4.18701000	-0.16509200	1.58573600
H	-3.59084700	-0.18487700	2.51457500
C	-5.48560900	0.60333400	1.87758700
H	-6.09745700	0.64898900	0.96144900
H	-5.26837400	1.64182000	2.17376800
C	-6.29601200	-0.10234600	2.97496800
H	-5.72159900	-0.08200500	3.91951000
H	-7.23200300	0.45109500	3.16185700
C	-6.60046700	-1.55655400	2.59668200
H	-7.26030200	-1.56664000	1.70924000
H	-7.15497600	-2.05753200	3.40844800
C	-5.31541500	-2.32750200	2.27356100
H	-5.55263400	-3.35598800	1.95179600
H	-4.70508300	-2.41595600	3.19148700
C	-4.48636000	-1.62340700	1.19180300
H	-5.03309900	-1.63576600	0.23339200
H	-3.54640400	-2.17168300	1.01507800
O	-3.61060600	-2.54983300	-1.90590500
O	-0.92858800	1.13024200	-2.97567100
P	-3.00050800	0.61735300	0.38005900
C	-0.35209100	-0.75142100	1.89891200
C	0.69446100	0.17116500	2.08488500
C	-1.13201800	-1.15069100	3.00270000
C	0.93946900	0.70685800	3.35303800
H	1.30823200	0.48142600	1.24024800
C	-0.87943600	-0.61528400	4.26656200
H	-1.92685800	-1.88816800	2.87164400
C	0.15814000	0.31234400	4.44460600
H	1.74360200	1.43587700	3.47309600
H	-1.49241500	-0.92335400	5.11802400
H	0.35583500	0.72445500	5.43775800
H	-3.07145300	-4.35725000	-1.00437700
H	-4.82186500	-4.00717700	-1.19199000
H	0.13659500	2.82912200	-3.27091400
H	0.41834800	1.56030400	-4.51826600
S	2.21655100	2.83383200	-0.29046500
O	2.03040000	1.41942700	-0.71509000
O	2.34381900	3.02755300	1.17266100
O	1.38248800	3.81738400	-1.01130900
Pd	-1.15355000	-0.80302500	-0.05656600
C	0.34446000	-2.21078900	-0.24919200
C	0.53957600	-2.39782000	0.99146400
H	0.63020000	-2.59417100	-1.22588100
C	1.00910900	-3.19410900	2.14453200
C	1.86983300	-4.41173600	1.74876300

H	0.11526600	-3.54138800	2.68740800
H	1.56136700	-2.54510900	2.84330800
C	3.35334100	-4.09999600	1.47038600
H	1.82677800	-5.10720300	2.60333200
H	1.40774100	-4.94036800	0.89863500
C	3.66432200	-3.46472500	0.13260000
H	3.72937800	-3.48961700	2.30238400
H	3.89802200	-5.06182200	1.52120900
C	4.22950600	-2.23118000	-0.01524800
C	3.30801200	-4.29972300	-1.07208200
C	4.71254900	-1.40752500	1.14036300
H	3.39263400	-5.37436500	-0.83762700
H	2.27286500	-4.13689200	-1.42322000
H	3.97414300	-4.07401500	-1.91896000
C	4.21223900	-0.10342800	1.30341500
C	5.67830200	-1.87097900	2.05151300
C	4.63571100	0.70395700	2.36135700
H	3.49119500	0.28540400	0.58496700
C	6.10570200	-1.06491500	3.11278600
H	6.10083500	-2.87094100	1.92211400
C	5.58202100	0.22361900	3.27498400
H	4.21956800	1.71049400	2.45090800
H	6.85682200	-1.44295400	3.81233400
H	5.91851300	0.85296400	4.10378200
N	4.35327200	-1.62880800	-1.28011800
C	5.50047400	-0.78715100	-1.62120200
C	3.19573600	-1.32315200	-2.13686200
H	5.55445300	0.13205200	-1.00725900
H	6.44688900	-1.33520400	-1.47628200
C	5.23423300	-0.42112800	-3.08154600
H	2.84718100	-2.21351600	-2.69063400
H	2.34810900	-0.95204600	-1.54187100
C	3.71051600	-0.23738600	-3.09547100
H	5.78135700	0.48098800	-3.39660100
H	5.53245900	-1.25302100	-3.74260400
H	3.27222900	-0.32015200	-4.10188600
H	3.45276900	0.75123900	-2.69278200
C	3.93633300	3.24726800	-0.92223600
F	4.24475500	4.51882600	-0.64204700
F	4.00713300	3.08893700	-2.25358300
F	4.87207400	2.46426600	-0.36677600

Gibbs free energy profile for model reaction with PhBr (Figure 2)

PhBr



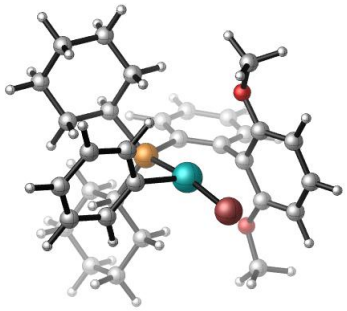
E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2805.369671
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -2805.618447

Zero-point correction=	0.090434 (Hartree/Particle)
Thermal correction to Energy=	0.096127
Thermal correction to Enthalpy=	0.097071
Thermal correction to Gibbs Free Energy=	0.059548

Charge = 0 Multiplicity = 1

C	-0.10214600	-0.00000600	-0.00036000
C	-0.78618300	1.21954300	-0.00009100
C	-0.78619200	-1.21955100	-0.00011000
C	-2.18545300	1.21042300	0.00011800
H	-0.23810600	2.16361000	-0.00023400
C	-2.18545800	-1.21041800	0.00013800
H	-0.23812100	-2.16362300	-0.00027000
C	-2.88704200	0.00000600	-0.00005800
H	-2.72639300	2.16040500	0.00023900
H	-2.72640300	-2.16039700	0.00027000
H	-3.97992800	0.00001100	0.00025800
Br	1.81439400	0.00000100	0.00005500

IIa



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -4436.239576
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -4436.890229

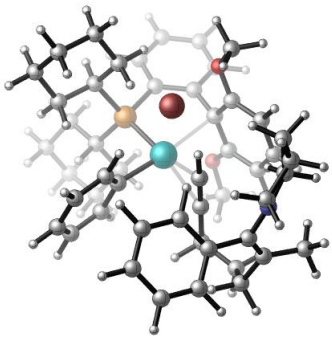
Zero-point correction=	0.651439 (Hartree/Particle)
Thermal correction to Energy=	0.688747
Thermal correction to Enthalpy=	0.689691
Thermal correction to Gibbs Free Energy=	0.580377

Charge = 0 Multiplicity = 1

C	0.27122100	2.12812300	1.05308900
C	-0.24843000	3.33272500	1.56647800
H	-1.31819300	3.53824300	1.51169800
C	0.58841200	4.28279400	2.15193900
H	0.16661500	5.21242000	2.54257300
C	1.96376400	4.03925300	2.23243200
H	2.63004500	4.77873500	2.68456300
C	2.48259300	2.83957700	1.74711100
H	3.55326200	2.63558000	1.82784100
C	1.64854900	1.86778000	1.16375700
C	2.30767400	0.58039600	0.75919800
C	2.44823400	-0.44842000	1.73406600
C	3.41887500	-1.44951200	1.58276200
H	3.52050400	-2.24587600	2.31812800
C	4.24420800	-1.42472700	0.45935600
H	4.99395700	-2.21010800	0.33711300
C	4.12834600	-0.44338600	-0.52776300
H	4.77519300	-0.47335300	-1.40322300
C	3.16682300	0.56247700	-0.37499200
C	3.66982400	1.57944900	-2.48318700
H	4.76375900	1.65329000	-2.35585400
C	1.48105000	-1.44856000	3.68061300
H	1.17721400	-2.35499900	3.12940800
C	-2.28043600	0.77306500	1.33788400
H	-2.48981100	1.80753400	1.65799600
C	-3.55948100	0.23374400	0.67156100
H	-3.85237600	0.87408300	-0.17471300
H	-3.37638300	-0.77033400	0.26429100
C	-4.70887300	0.16074200	1.68708900
H	-4.97542800	1.18383700	2.01162700
H	-5.60456500	-0.25959900	1.19892100
C	-4.32763700	-0.67336400	2.91548000
H	-4.15017800	-1.71834200	2.60098300
H	-5.16164600	-0.69674400	3.63752100
C	-3.05959100	-0.12687900	3.58126500
H	-2.77056500	-0.75610100	4.44035500
H	-3.26583400	0.88232900	3.98336900
C	-1.89561800	-0.04469400	2.58662500
H	-1.60731300	-1.06198800	2.27258200
H	-1.00621500	0.39401300	3.06651000
C	-1.37568900	1.70804300	-1.36555500
H	-2.11102100	0.98282000	-1.75280800
C	-2.08115900	3.06559600	-1.21217700
H	-1.36709800	3.80568400	-0.81538500
H	-2.91120900	2.99927900	-0.49106000
C	-2.59583100	3.56361700	-2.57069600
H	-3.36601100	2.86511800	-2.94650400
H	-3.08967900	4.54224200	-2.44512100
C	-1.45785900	3.66479400	-3.59277300
H	-0.74236500	4.43890100	-3.25822900
H	-1.84674200	3.99518000	-4.57108100
C	-0.72036800	2.32865500	-3.73503600

H	0.12985200	2.42866700	-4.43118800
H	-1.40541800	1.58222400	-4.17792700
C	-0.22194900	1.80362800	-2.38260600
H	0.56042100	2.47185000	-1.98372500
H	0.25547300	0.81854300	-2.51128700
O	2.99365000	1.58903400	-1.23538100
O	1.62899400	-0.34141700	2.80399700
P	-0.80051100	0.89316000	0.21066300
Pd	0.42380800	-1.00375100	-0.27043300
C	-1.25402700	-1.92376800	-0.83200700
C	-1.83337300	-2.86455000	0.03556500
C	-1.86330100	-1.67923100	-2.07115400
C	-3.01928700	-3.52091800	-0.31685500
H	-1.36690900	-3.08917000	0.99753500
C	-3.05192300	-2.33641600	-2.42112500
H	-1.41961800	-0.97207600	-2.77569600
C	-3.64031800	-3.25249600	-1.54290000
H	-3.46108900	-4.24378700	0.37581500
H	-3.51847800	-2.12593200	-3.38839900
H	-4.57003700	-3.76006400	-1.81439200
H	2.40856100	-1.65499800	4.24182000
H	0.68888600	-1.17691300	4.39123800
H	3.43170300	0.67150600	-3.06334100
H	3.31446000	2.46107000	-3.03371900
Br	1.66197400	-3.02639400	-1.09919600

IIIa



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -5190.19896
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -5191.021723

Zero-point correction=	1.019515 (Hartree/Particle)
Thermal correction to Energy=	1.075446
Thermal correction to Enthalpy=	1.076390
Thermal correction to Gibbs Free Energy=	0.928549

Charge = 0 Multiplicity = 1

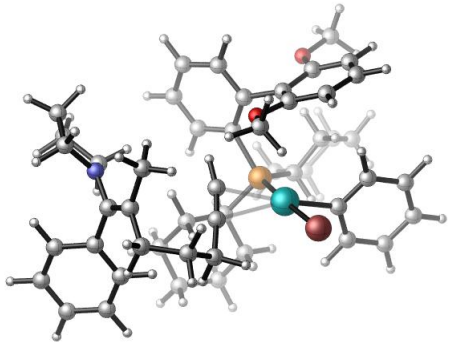
C	3.70432400	-1.26927900	0.64891300
C	5.02258600	-1.31673100	1.14331900
H	5.57644500	-0.39436400	1.32048500
C	5.63740800	-2.53612900	1.42655100

H	6.66181200	-2.55332300	1.80707700
C	4.93584000	-3.72936700	1.22388400
H	5.40912500	-4.69112500	1.43856100
C	3.62041500	-3.68865400	0.76343100
H	3.06017900	-4.61744700	0.62961800
C	2.98472800	-2.46627500	0.47896700
C	1.54183300	-2.54628500	0.06445500
C	0.56413700	-2.78028600	1.07766000
C	-0.70785700	-3.27157200	0.74219000
H	-1.46576100	-3.42820800	1.50755400
C	-0.98979100	-3.56281200	-0.59260600
H	-1.97992900	-3.94695800	-0.84977700
C	-0.06081200	-3.35699400	-1.61480400
H	-0.32439700	-3.58474000	-2.64627500
C	1.20939000	-2.85757200	-1.28525900
C	1.97382800	-2.88451700	-3.55749300
H	1.72097700	-3.93781400	-3.76742100
C	0.05527500	-2.63423900	3.41657300
H	-0.75442500	-1.89304700	3.30599900
C	3.10285000	1.32788900	1.80060300
H	4.14436000	1.15714500	2.12501500
C	2.90389400	2.84188900	1.61511200
H	3.63114500	3.24417500	0.89238800
H	1.90326200	3.03296000	1.20160400
C	3.03632100	3.57575600	2.95723900
H	4.07358500	3.47602600	3.32796800
H	2.85765700	4.65388000	2.80515100
C	2.06927900	3.01382000	4.00594200
H	1.02944800	3.18706400	3.67354800
H	2.19127900	3.54713600	4.96435200
C	2.27880800	1.50793300	4.19874100
H	1.54073600	1.10666800	4.91340600
H	3.28027100	1.32933100	4.63322100
C	2.15001600	0.75534500	2.87012300
H	1.10498000	0.83349200	2.52246200
H	2.34261500	-0.31971300	3.01529400
C	3.92160700	1.12860600	-1.10483500
H	3.38732400	2.08132600	-1.26000500
C	5.38792900	1.45995600	-0.77749300
H	5.95236700	0.52534600	-0.62908100
H	5.46396500	2.03795100	0.15679200
C	6.02523500	2.23726300	-1.93899700
H	5.50915100	3.20831900	-2.05172600
H	7.07833000	2.46366000	-1.70080100
C	5.93132400	1.45358200	-3.25365600
H	6.54029300	0.53455800	-3.16773800
H	6.36112900	2.04111800	-4.08266200
C	4.48244700	1.06501300	-3.57119400
H	4.43999800	0.44909100	-4.48559100
H	3.89653300	1.97958300	-3.77730400
C	3.82880900	0.30981200	-2.40706100
H	4.33473800	-0.65996100	-2.25932700
H	2.77929400	0.07308000	-2.64361200
O	2.20666600	-2.67058800	-2.17270300

O	0.97828700	-2.54595400	2.33322100
P	2.91163900	0.33750800	0.23782200
C	0.44395000	1.87569100	-0.77334300
C	-0.31163500	2.64943000	0.12042600
C	0.87254100	2.43636900	-1.98472200
C	-0.61143500	3.98193100	-0.19191200
H	-0.68248800	2.21776900	1.05632000
C	0.56438500	3.77074500	-2.29148500
H	1.44660000	1.84760300	-2.70303900
C	-0.17209400	4.54948300	-1.39380600
H	-1.19890100	4.57716300	0.51321100
H	0.90595000	4.19649800	-3.23975200
H	-0.40891900	5.59008700	-1.63202500
H	1.16838300	-2.23460600	-3.93826600
H	2.91179800	-2.63138700	-4.06929300
H	0.63184900	-2.39825300	4.32129900
H	-0.35472000	-3.65458100	3.51029400
Pd	0.73050700	-0.07140100	-0.38918200
C	-1.54859200	-0.35072200	-0.28032800
C	-1.42407100	-0.38066300	-1.50149600
H	-1.77981100	-0.24814500	0.78507500
C	-1.40209000	-0.34494800	-2.96557600
C	-2.56676800	-1.06647300	-3.67005700
H	-0.44922000	-0.77683000	-3.31108900
H	-1.38759300	0.71720400	-3.26745100
C	-3.97593900	-0.52629100	-3.33315100
H	-2.38796100	-0.94750000	-4.75122200
H	-2.50555900	-2.14735100	-3.46529700
C	-4.61279100	-1.13567700	-2.09920100
H	-3.91877300	0.56907500	-3.26576400
H	-4.62640400	-0.74939400	-4.19937800
C	-4.94728000	-0.43668700	-0.97226100
C	-4.83437800	-2.62842100	-2.17803900
C	-4.92891700	1.06069900	-0.91374300
H	-5.00340500	-2.93558400	-3.22406500
H	-3.97910400	-3.22428300	-1.81136500
H	-5.71268500	-2.93114400	-1.58803900
C	-4.22038500	1.72335100	0.10712200
C	-5.63336300	1.84030600	-1.84912800
C	-4.19077700	3.11830300	0.16704500
H	-3.68144600	1.15162900	0.86683200
C	-5.60374100	3.23792300	-1.79065300
H	-6.21380100	1.34070200	-2.62912100
C	-4.87698000	3.88360700	-0.78409600
H	-3.62338300	3.60552800	0.96442300
H	-6.15587500	3.82398200	-2.53093800
H	-4.85213000	4.97589300	-0.73623800
N	-5.28090600	-1.08568600	0.22231300
C	-6.25308000	-0.54942700	1.18024100
C	-4.49180600	-2.17413000	0.81286800
H	-5.97485200	0.46152600	1.52963000
H	-7.25957100	-0.47047900	0.73199400
C	-6.20302600	-1.54333900	2.34747600
H	-4.82135800	-3.17388600	0.46986800

H	-3.43145500	-2.07375700	0.53973900
C	-4.74732800	-2.02703900	2.31469900
H	-6.49224200	-1.07888500	3.30277400
H	-6.88838400	-2.38818000	2.16070900
H	-4.58750700	-2.96890400	2.86346500
H	-4.07406200	-1.25928700	2.73286700
Br	-1.87874200	0.66844200	3.03275000

IVa



E (SMD(Acetone)/B3LYP-D3/Def2-SVP) = -5190.198108
E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -5191.019611

Zero-point correction=	1.019607 (Hartree/Particle)
Thermal correction to Energy=	1.076520
Thermal correction to Enthalpy=	1.077464
Thermal correction to Gibbs Free Energy=	0.925561

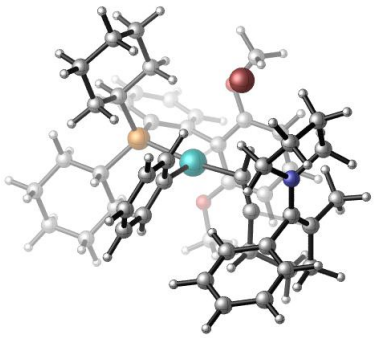
Charge = 0 Multiplicity = 1

C	-0.75858500	2.06403600	-0.25303100
C	0.08665400	3.10555800	0.18547700
H	0.41916700	3.13918900	1.22162300
C	0.53235400	4.11463200	-0.66919100
H	1.19334900	4.89580000	-0.28551000
C	0.13556900	4.10789300	-2.00660400
H	0.48843600	4.87776700	-2.69775200
C	-0.74044300	3.11758200	-2.44912600
H	-1.09030700	3.13081300	-3.48416700
C	-1.21734700	2.09900400	-1.60279900
C	-2.25832300	1.20376300	-2.21393000
C	-1.92399200	0.02178200	-2.90914500
C	-2.92108900	-0.77387800	-3.50271400
H	-2.66659900	-1.71416900	-3.98839600
C	-4.24625300	-0.34240000	-3.46731100
H	-5.02391300	-0.96372000	-3.91953400
C	-4.59663800	0.87763600	-2.88737600
H	-5.63130900	1.21595700	-2.91184900
C	-3.59331900	1.66411900	-2.29631800
C	-5.14142500	3.42298800	-1.78003100
H	-5.54671400	3.54666100	-2.79946700
C	-0.18016400	-1.41660900	-3.70430600

H	-0.53072200	-2.33618800	-3.20831700
C	0.16245600	0.86478100	2.32749400
H	0.01946700	1.87960000	2.72769300
C	-0.13196200	-0.12945800	3.47145000
H	-1.18312100	-0.08070300	3.79189600
H	0.03795700	-1.15581500	3.10022800
C	0.77891200	0.14784100	4.67732100
H	0.51134100	1.13238800	5.10309500
H	0.58521500	-0.59875100	5.46631600
C	2.26359700	0.15131600	4.29530700
H	2.56445400	-0.87120900	4.00232300
H	2.88367400	0.42389700	5.16642700
C	2.53415100	1.09672100	3.12017700
H	3.59276900	1.04559600	2.82261200
H	2.33955400	2.14047900	3.42946700
C	1.64065500	0.74286500	1.92473800
H	1.85154600	-0.28895100	1.61451700
H	1.88285900	1.37846900	1.06331100
C	-2.68259900	1.23857700	1.89127100
H	-2.91728400	0.35486600	2.50482700
C	-2.51503000	2.45109600	2.82797300
H	-2.23745700	3.33799300	2.23045000
H	-1.71027500	2.29173800	3.55898800
C	-3.81704500	2.72992400	3.59744600
H	-4.01291500	1.87939100	4.27620200
H	-3.68139500	3.61831100	4.23786100
C	-5.02113400	2.91510000	2.66902300
H	-4.88174900	3.83612400	2.07282700
H	-5.94238300	3.05623700	3.25999500
C	-5.16119100	1.72418200	1.71704200
H	-5.99064200	1.88923700	1.00870000
H	-5.41356800	0.81431800	2.29159100
C	-3.85977600	1.49091900	0.94230900
H	-3.63447100	2.38513700	0.34667700
H	-3.98084000	0.66002600	0.23833600
O	-3.82106800	2.90613400	-1.80269400
O	-0.60519400	-0.25642500	-3.00238100
P	-1.13071800	0.69958400	0.97157000
C	-2.86446100	-1.84268700	0.82314100
C	-3.03699400	-2.21509400	2.16548700
C	-3.98867100	-1.79537200	-0.01501700
C	-4.31193900	-2.52550900	2.66139600
H	-2.17964000	-2.26110400	2.84118900
C	-5.26208200	-2.09968400	0.48254700
H	-3.87758300	-1.51578000	-1.06338500
C	-5.43130600	-2.46424200	1.82400100
H	-4.42658900	-2.81230000	3.71136700
H	-6.12683200	-2.04780400	-0.18628900
H	-6.42606900	-2.70029200	2.21224100
H	-0.52114300	-1.39496600	-4.75394900
H	0.91601400	-1.39803700	-3.68521400
H	-5.07801400	4.40876400	-1.29892100
H	-5.82350500	2.78280000	-1.19531300
Pd	-1.03500600	-1.48027200	0.09945400

C	1.14054300	-0.76094600	-0.85675000
C	1.63567500	-1.83416600	-0.54997600
H	0.94969400	0.22642100	-1.23603900
C	2.30527200	-3.09577800	-0.24922400
C	3.39208700	-3.48168900	-1.27647700
H	1.53170300	-3.88065900	-0.24148200
H	2.72752000	-3.05726100	0.76916400
C	4.65043400	-2.58748600	-1.33506300
H	3.71634900	-4.50693700	-1.03346000
H	2.91979000	-3.54039500	-2.27056100
C	4.40834200	-1.13168900	-1.67664500
H	5.20718800	-2.68636800	-0.39357400
H	5.30011600	-3.01817300	-2.12182800
C	4.76893400	-0.07834500	-0.88732200
C	3.79573400	-0.89016500	-3.03308400
C	5.38359200	-0.21457900	0.47348400
N	4.64534300	1.24645300	-1.36232500
H	3.11955400	-1.70835000	-3.31900900
H	3.23125400	0.05331000	-3.05764200
H	4.56927000	-0.83663700	-3.82176100
C	4.84249700	-1.02240700	1.48860900
C	6.54057100	0.53321500	0.77798400
C	4.11813100	2.32543900	-0.51942500
C	5.46295100	1.77268000	-2.45837400
C	5.45198800	-1.11678300	2.74403000
H	3.91672700	-1.56255700	1.30234200
C	7.14814600	0.44775900	2.03232400
H	6.96718300	1.18892100	0.01564600
H	3.02292100	2.42431000	-0.64945000
H	4.29453500	2.13659400	0.55208200
H	6.54590700	1.63831100	-2.25608000
H	5.25324000	1.27508800	-3.41914800
C	6.60994200	-0.38486400	3.02223800
H	5.00479200	-1.75100100	3.51410800
H	8.04889000	1.03262600	2.23909300
H	7.08422100	-0.45247000	4.00501600
C	4.83844100	3.58243000	-1.01709500
H	4.25061700	4.50046100	-0.86367800
H	5.79838800	3.70075100	-0.48588400
C	5.09773400	3.25996400	-2.49419800
H	5.88665600	3.87761500	-2.94999900
H	4.17230300	3.40425800	-3.07804600
Br	-1.11963900	-3.86238700	-0.78241400

TS2a



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Zero-point correction=	1.018267 (Hartree/Particle)
Thermal correction to Energy=	1.074742
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Charge = 0 Multiplicity = 1

C	-3.97698200	-0.42734500	0.64323000
C	-5.33985700	-0.63339400	0.35459500
H	-5.71252500	-0.49615300	-0.66132900
C	-6.23045700	-1.02719200	1.35362400
H	-7.28564300	-1.18071300	1.11314800
C	-5.76512900	-1.22554100	2.65833100
H	-6.45507600	-1.53031100	3.44969600
C	-4.41142000	-1.05134000	2.94502100
H	-4.04023300	-1.23077000	3.95730900
C	-3.50103100	-0.66135200	1.94606500
C	-2.05337600	-0.58431500	2.34999600
C	-1.31231100	-1.80097600	2.43289700
C	-0.13973000	-1.87431400	3.20679500
H	0.44097600	-2.79395800	3.25299300
C	0.26752800	-0.75071000	3.92313400
H	1.17258400	-0.81200300	4.53135800
C	-0.42889000	0.46047300	3.87231700
H	-0.06924300	1.32019900	4.43472400
C	-1.58896200	0.54255500	3.08986500
C	-1.97442600	2.84374400	3.63711200
H	-1.92440400	2.72622200	4.73324100
C	-1.15449500	-4.08114400	1.70734100
H	-0.19510000	-3.95523000	1.17667700
C	-3.03845000	-1.08546800	-2.02531400
H	-4.13152200	-1.17645500	-2.15290900
C	-2.43612100	-0.62485400	-3.36405700
H	-2.89085700	0.32427600	-3.68959100
H	-1.36108700	-0.43403200	-3.23306800
C	-2.62326000	-1.69493700	-4.44868800
H	-3.70198500	-1.81566200	-4.66156500
H	-2.15264500	-1.35418400	-5.38681000

C	-2.04044900	-3.04504400	-4.01507200
H	-0.94785700	-2.94504100	-3.88053200
H	-2.19829100	-3.80187200	-4.80269800
C	-2.65675800	-3.50959600	-2.69108400
H	-2.19585500	-4.45745100	-2.36510700
H	-3.73447800	-3.71097100	-2.83890500
C	-2.47403100	-2.45496800	-1.59394800
H	-1.39621800	-2.36130000	-1.37037900
H	-2.95288200	-2.78516000	-0.65852600
C	-3.36293200	1.80104600	-1.22349800
H	-2.60031500	2.05393200	-1.98045400
C	-4.74281100	1.87466700	-1.89817500
H	-5.52584200	1.63555600	-1.16026500
H	-4.82624200	1.13520000	-2.70992600
C	-4.99534300	3.28996700	-2.43936000
H	-4.25786200	3.51090600	-3.23280100
H	-5.99161600	3.33671400	-2.91115000
C	-4.88029000	4.34190900	-1.32948300
H	-5.69141900	4.17922200	-0.59558600
H	-5.02700100	5.35432500	-1.74290100
C	-3.52961800	4.25044800	-0.60918900
H	-3.48796500	4.97202100	0.22458300
H	-2.72239500	4.52995400	-1.31109100
C	-3.26184300	2.83409600	-0.08483100
H	-3.99858200	2.58138200	0.69753600
H	-2.27417800	2.78233500	0.39975800
O	-2.36980200	1.63829700	2.99964700
O	-1.85937600	-2.84468300	1.78863000
P	-2.78675600	0.13265600	-0.63990700
C	0.13536500	0.92495600	-1.38004200
C	0.87050100	0.12544200	-2.27143600
C	0.04597100	2.30502200	-1.62049100
C	1.47979500	0.69736900	-3.39578400
H	0.98363600	-0.94712300	-2.08116200
C	0.65959500	2.87328100	-2.74786600
H	-0.50302100	2.95563800	-0.93617300
C	1.37351000	2.07133700	-3.64352600
H	2.04917500	0.05984200	-4.07935900
H	0.57774000	3.95099500	-2.91915800
H	1.85358500	2.51493600	-4.52009500
H	-0.99814400	3.19730600	3.26500800
H	-2.74311500	3.58827000	3.39073700
H	-1.79743100	-4.75466300	1.12436100
H	-0.99731100	-4.51703100	2.70936900
Pd	-0.65689600	0.13371800	0.28869000
C	1.38422400	-0.15206600	0.83422400
C	1.86718700	0.86606400	1.39114800
H	1.70080600	-1.12796000	0.43883600
C	1.94092500	2.21953700	1.94951400
C	2.92691200	2.32943600	3.12045900
H	0.92363700	2.49047000	2.27631400
H	2.22674900	2.92629700	1.15161500
C	4.31477600	1.81824600	2.68591400
H	2.98514900	3.37671500	3.45833400

H	2.54476900	1.73956600	3.96956900
C	4.21226600	0.44416900	2.05086000
H	4.75692300	2.54945100	1.99626700
H	4.97534500	1.77809500	3.57182600
C	4.51546900	0.24429300	0.70880000
C	3.91946000	-0.66655300	3.04145000
C	4.86319100	1.43106700	-0.15319400
H	3.39806900	-0.25948000	3.91965400
H	3.27364000	-1.44950300	2.62862600
H	4.84013800	-1.14468400	3.41836000
C	3.90382600	2.12852200	-0.90269700
C	6.20750800	1.83179000	-0.22887000
C	4.27960600	3.22090200	-1.69182600
H	2.86325000	1.80283800	-0.88526000
C	6.58318200	2.92388700	-1.01741100
H	6.96251200	1.28550400	0.34303200
C	5.61755900	3.62522900	-1.74850600
H	3.51854900	3.75080100	-2.26953800
H	7.63270500	3.22792100	-1.05988300
H	5.90816000	4.48052400	-2.36461000
N	4.54014000	-0.95769800	0.05597500
C	4.58582400	-1.10531600	-1.40962900
C	4.80967300	-2.27315700	0.67781000
H	3.59242400	-1.42942800	-1.76612000
H	4.85243600	-0.16636700	-1.90520200
C	5.60820400	-2.21779200	-1.62026400
H	5.58942500	-2.15432400	1.44417300
H	3.90909800	-2.69255800	1.14439600
C	5.26447200	-3.18362200	-0.48091100
H	5.53019100	-2.67914900	-2.61691700
H	6.62894900	-1.81298400	-1.50545100
H	6.10431600	-3.83226800	-0.18811300
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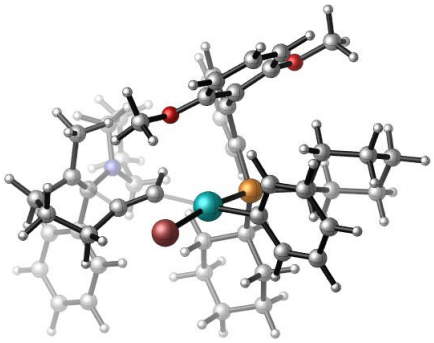
Br	1.49555700	-3.35460800	-0.93275600

TS3a



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E (SMD(Acetone)/M06/Def2-TZVPP//SMD(Acetone)/B3LYP-D3/Def2-SVP) = -5191.001946

Zero-point correction=	1.020770 (Hartree/Particle)
Thermal correction to Energy=	1.076131
Thermal correction to Enthalpy=	1.077075
Thermal correction to Gibbs Free Energy=	0.930860

Charge = 0 Multiplicity = 1

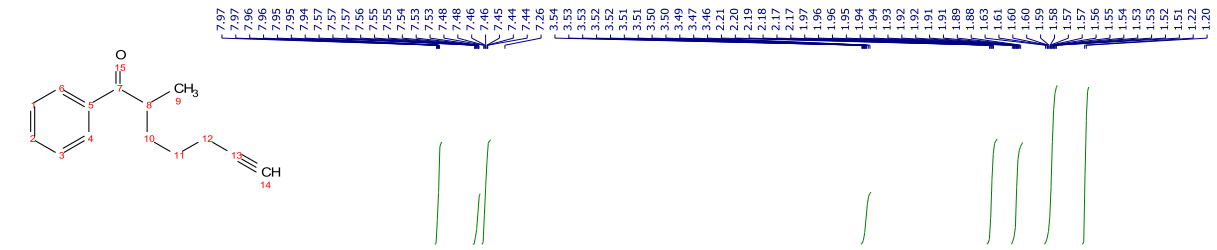
C	-0.72181100	2.01387200	0.18366100
C	0.07356500	2.95914000	0.86413700
H	0.32974500	2.80387100	1.91061300
C	0.55867500	4.11247100	0.24666500
H	1.17037200	4.81481100	0.81787000
C	0.27078200	4.34537700	-1.09758300
H	0.66272900	5.22823700	-1.60889100
C	-0.54838300	3.44646400	-1.77896500
H	-0.82081500	3.64813000	-2.81778200
C	-1.07873600	2.29432500	-1.16774700
C	-2.10746200	1.56967000	-1.98947900
C	-1.81404700	0.47016900	-2.82413500
C	-2.82282800	-0.12261700	-3.60941800
H	-2.60675000	-0.99234700	-4.22667800
C	-4.10811100	0.41518600	-3.59872200
H	-4.88988500	-0.05408100	-4.20215700
C	-4.41036700	1.55340100	-2.85060900
H	-5.41341600	1.97612200	-2.88090800
C	-3.39898600	2.14327700	-2.07644700
C	-4.87165400	3.87910300	-1.31142200
H	-5.20578600	4.21743800	-2.30784700
C	-0.19291200	-1.08988900	-3.62082200
H	-0.78918200	-1.96754100	-3.32984300
C	-0.06217500	0.41811800	2.62305700
H	-0.22432500	1.38180500	3.13022800
C	-0.48953800	-0.69709000	3.60116900
H	-1.56058900	-0.63894400	3.84254100
H	-0.32525800	-1.67474900	3.11546800
C	0.32480700	-0.62508400	4.90185900
H	0.07611000	0.31598700	5.42638800
H	0.02213000	-1.44771200	5.57207400
C	1.83462800	-0.67326100	4.64323800
H	2.10098500	-1.66770300	4.23931700
H	2.39041100	-0.55679500	5.58944900
C	2.25543800	0.39742500	3.63159700
H	3.33008300	0.30967900	3.40238100
H	2.10544800	1.40198200	4.06920800
C	1.44075400	0.27739700	2.33884000
H	1.61896800	-0.70958000	1.88799600
H	1.78155300	1.01504000	1.60300300
C	-2.84748200	0.74746600	1.87674300
H	-3.05195800	-0.21302700	2.37588700
C	-2.88125300	1.86977900	2.93225000
H	-2.64219500	2.83203500	2.44457900
H	-2.12635100	1.71360300	3.71594500
C	-4.26570400	1.95597600	3.59559400
H	-4.43822700	1.02855600	4.17240200
H	-4.27475900	2.78525200	4.32378400

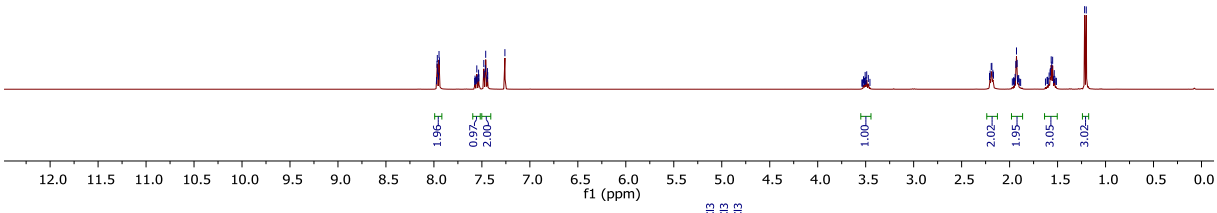
C	-5.39482700	2.12641900	2.57411800
H	-5.29017100	3.10986700	2.07857000
H	-6.37434800	2.13007100	3.08256400
C	-5.33698900	1.02758700	1.50847100
H	-6.11210600	1.19147100	0.74009900
H	-5.55240600	0.04672900	1.97035600
C	-3.95557600	0.98814500	0.84573000
H	-3.76904600	1.95987900	0.37458500
H	-3.92990800	0.22950400	0.05550800
O	-3.58531500	3.28473800	-1.36382900
O	-0.53099800	0.05252200	-2.84698400
P	-1.16656700	0.44005000	1.09430300
C	-2.64200300	-2.20186900	0.39392400
C	-2.97011600	-2.75065100	1.64711500
C	-3.65322600	-2.17952100	-0.58585900
C	-4.25515300	-3.24566800	1.91686300
H	-2.21760800	-2.79542800	2.43870700
C	-4.93956400	-2.66759500	-0.32263800
H	-3.44143800	-1.76507200	-1.57443300
C	-5.25102500	-3.20119300	0.93459000
H	-4.47788300	-3.66444500	2.90384100
H	-5.70431900	-2.62581500	-1.10527600
H	-6.25548900	-3.58039900	1.14420200
H	-0.30955900	-0.88634700	-4.70020600
H	0.85338500	-1.31169400	-3.39527800
H	-4.78072400	4.75188800	-0.65029500
H	-5.62509400	3.18931900	-0.89352400
Pd	-0.76946400	-1.52167000	-0.06685300
C	1.24182100	-0.71196300	-0.64726900
C	2.27728400	-1.39355800	-0.98209100
H	1.24388600	0.38157400	-0.67075900
C	2.91492400	-2.70963600	-1.16384900
C	3.79247900	-2.72717000	-2.41422100
H	2.08283900	-3.43487900	-1.22460800
H	3.52376700	-2.96676800	-0.27939600
C	4.71653100	-1.49944700	-2.33634400
H	4.37499100	-3.65990600	-2.47881600
H	3.15714200	-2.67855400	-3.31451300
C	3.90348900	-0.26258400	-1.98687100
H	5.49493800	-1.68876400	-1.58502900
H	5.23277000	-1.34254200	-3.30019100
C	4.22568600	0.49415700	-0.84672200
C	3.11439000	0.29592800	-3.15636000
C	5.12614000	-0.08642500	0.20945800
N	3.79641600	1.76341100	-0.60957000
H	2.75719400	-0.52935200	-3.78669300
H	2.23125200	0.86505200	-2.84274100
H	3.73598500	0.93665200	-3.80306000
C	4.66917500	-0.94387600	1.21889500
C	6.48315900	0.28122900	0.18890300
C	3.93916900	2.44450600	0.69101600
C	3.64097200	2.80572300	-1.65910400
C	5.55259500	-1.43312100	2.18714200
H	3.61479600	-1.21201500	1.25547300

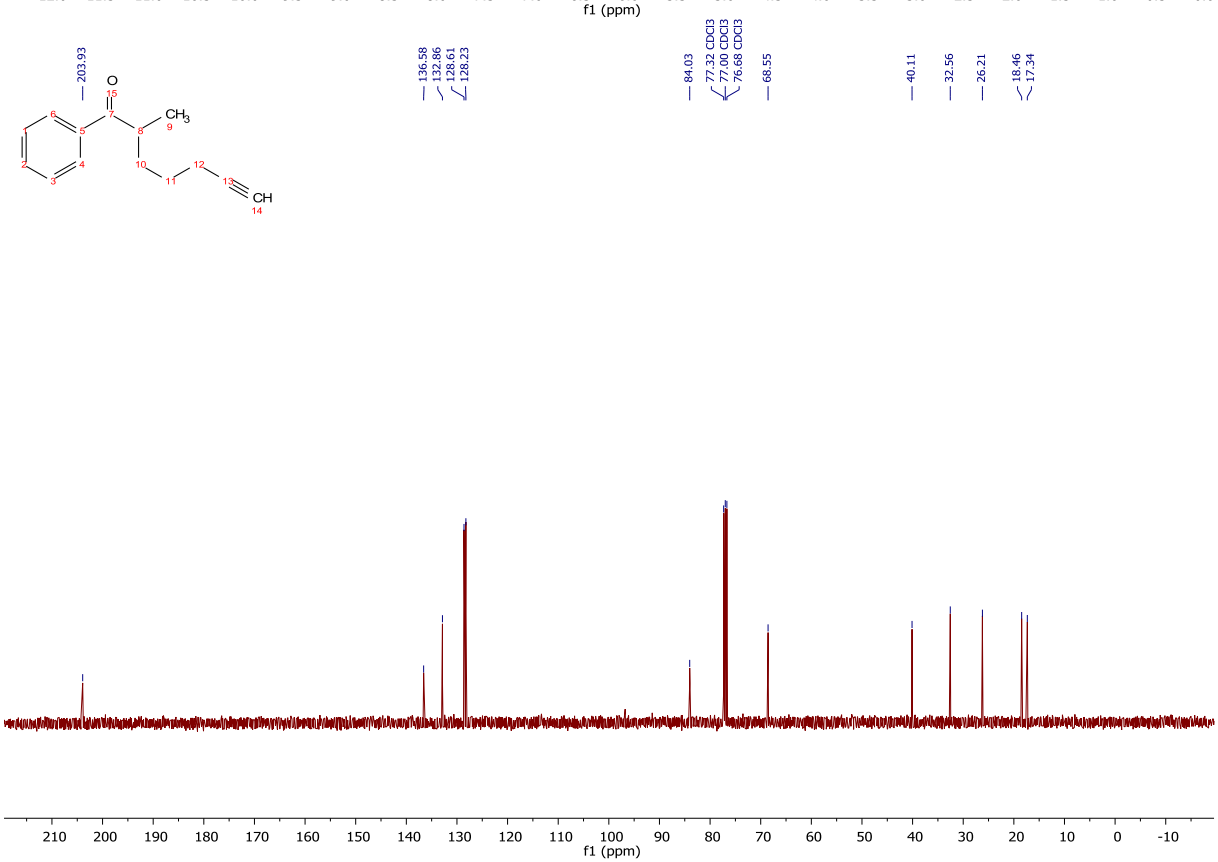
C	7.36694400	-0.21327500	1.15197500
H	6.84659500	0.95460600	-0.59185400
H	2.93471800	2.69187300	1.07096800
H	4.43054100	1.80692200	1.43144800
H	4.30803200	2.56733100	-2.49494500
H	2.61042400	2.84853200	-2.03623300
C	6.90327500	-1.07261200	2.15534100
H	5.17766200	-2.09525800	2.97210500
H	8.42122100	0.07436000	1.11915500
H	7.59331700	-1.45733100	2.91100600
C	4.70007000	3.71928200	0.34533700
H	4.61813400	4.48790300	1.12831600
H	5.76769100	3.48357400	0.20066100
C	4.04208400	4.13388200	-0.97817700
H	4.70568200	4.73093800	-1.62071700
H	3.14430400	4.73557600	-0.77613100
Br	-0.43097800	-3.84969200	-1.08059200

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of isolated compounds

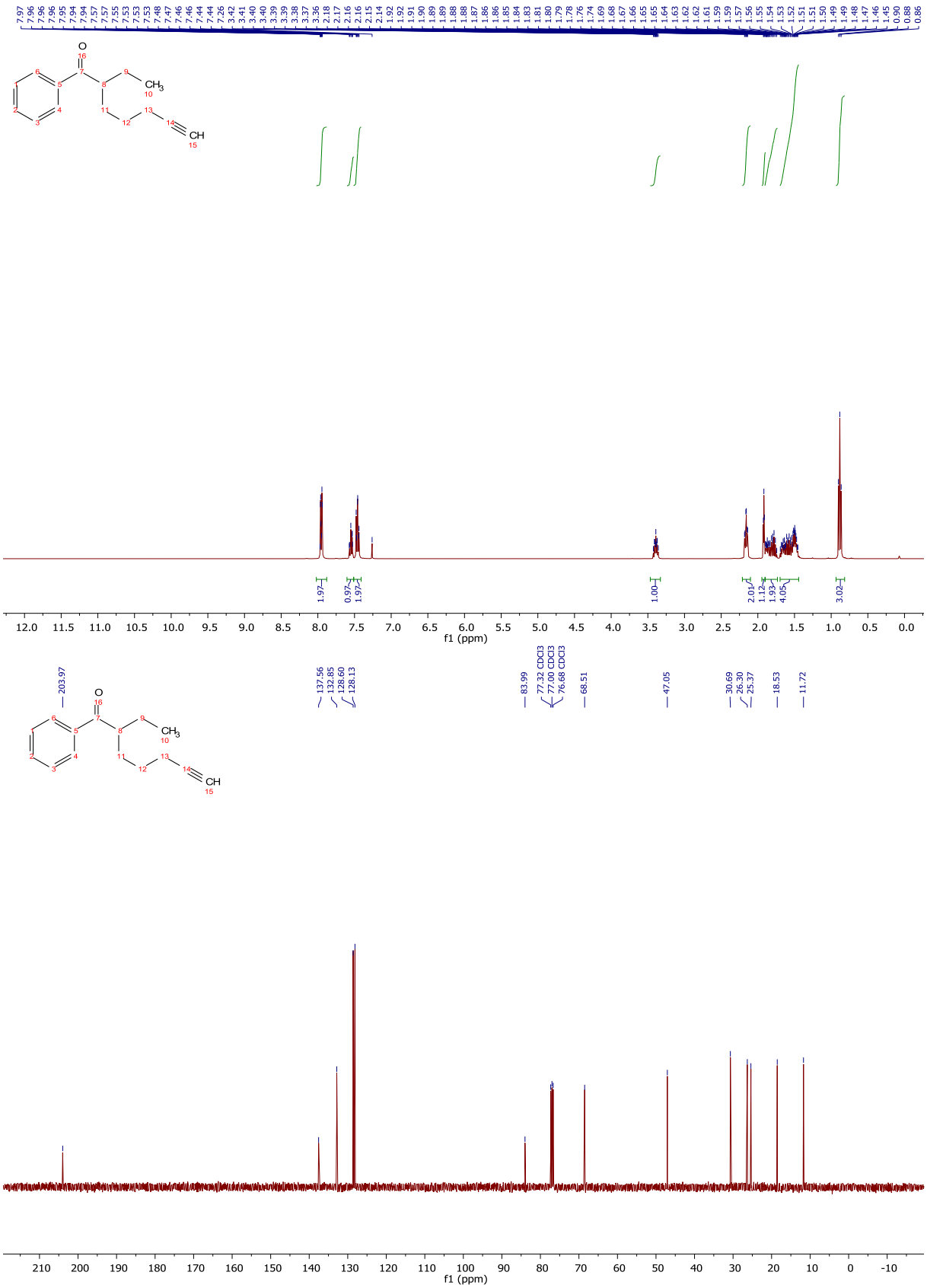
2-methyl-1-phenylhept-6-yn-1-one



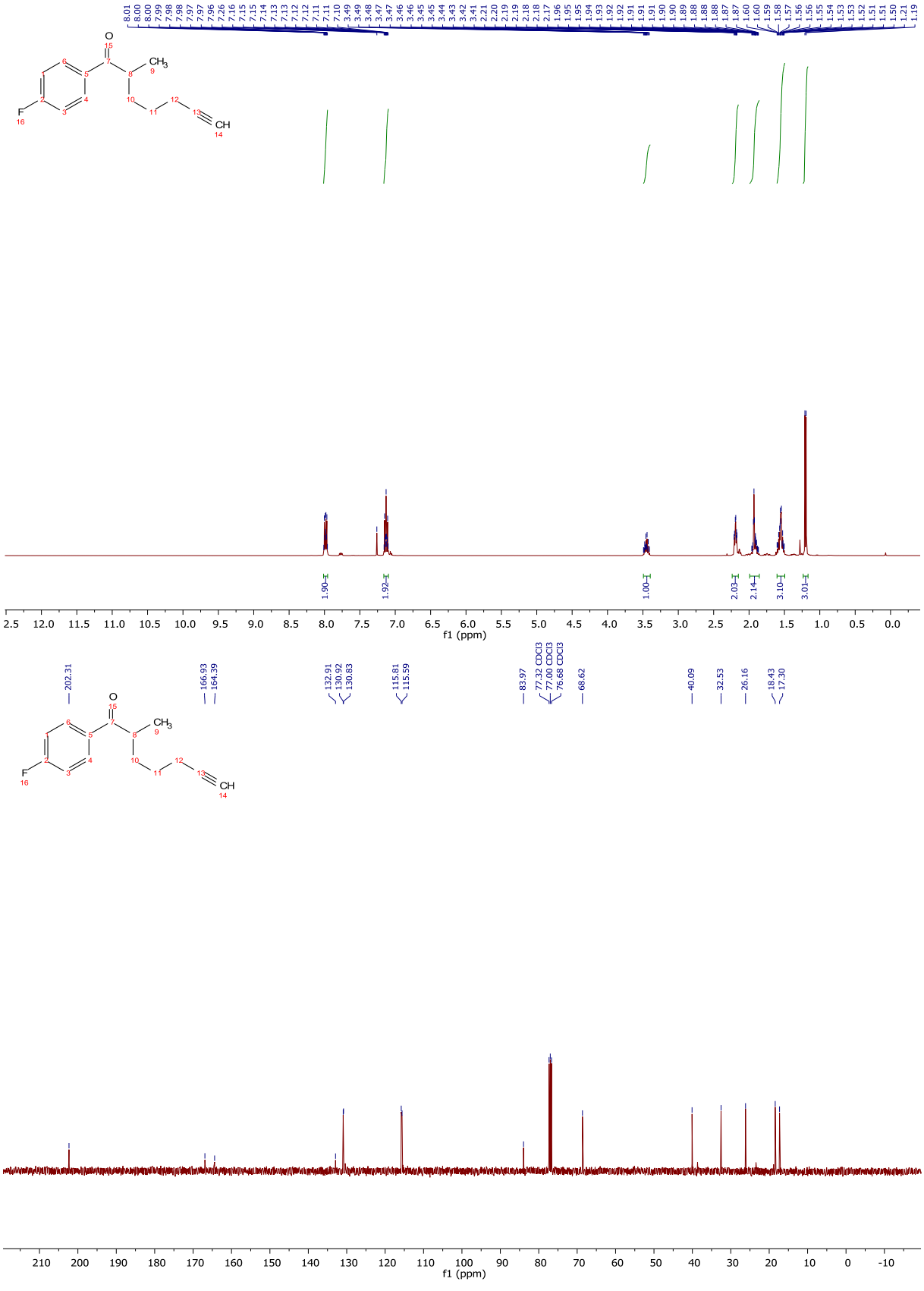




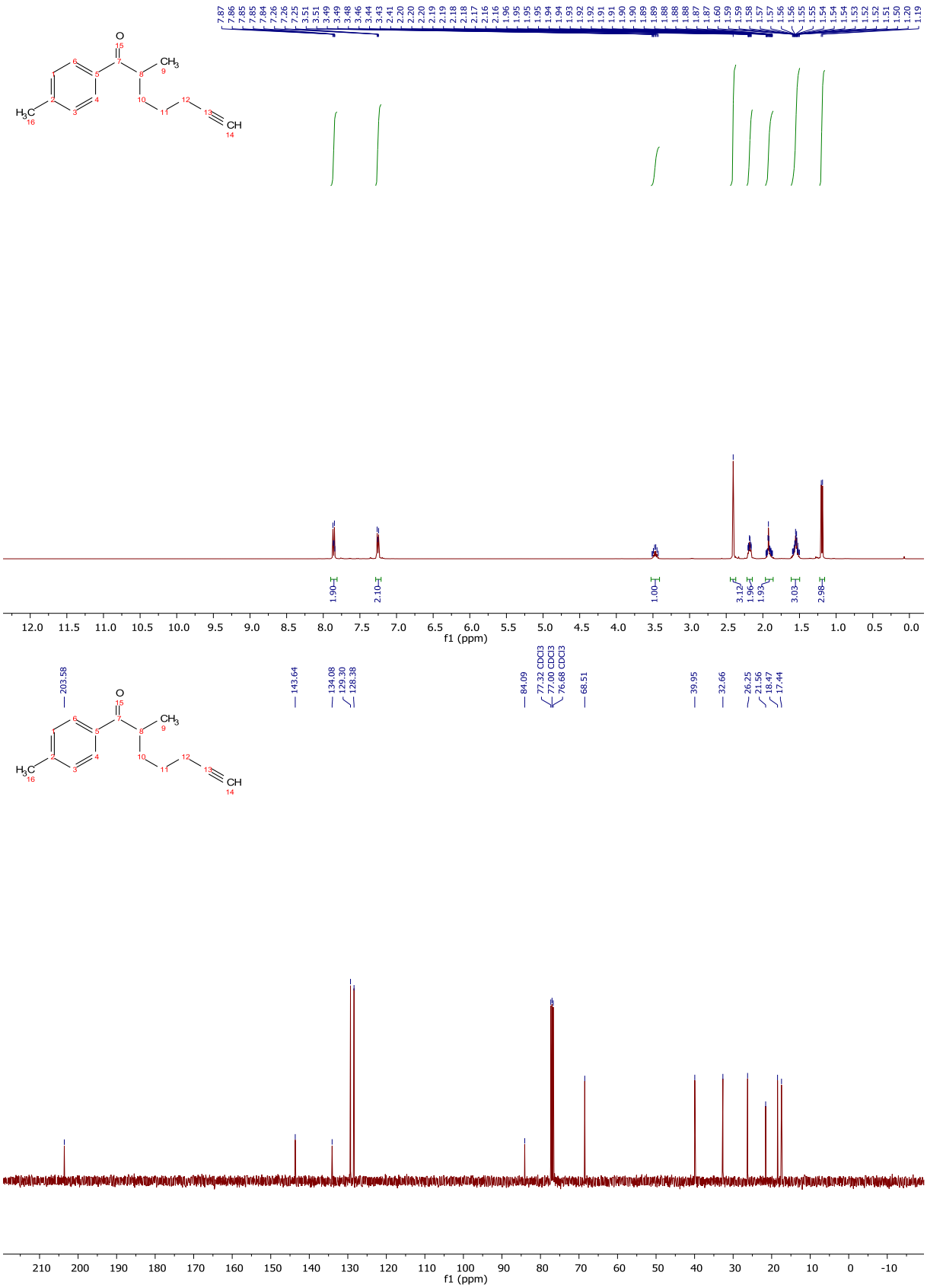
2-ethyl-1-phenylhept-6-yn-1-one



1-(4-fluorophenyl)-2-methylhept-6-yn-1-one

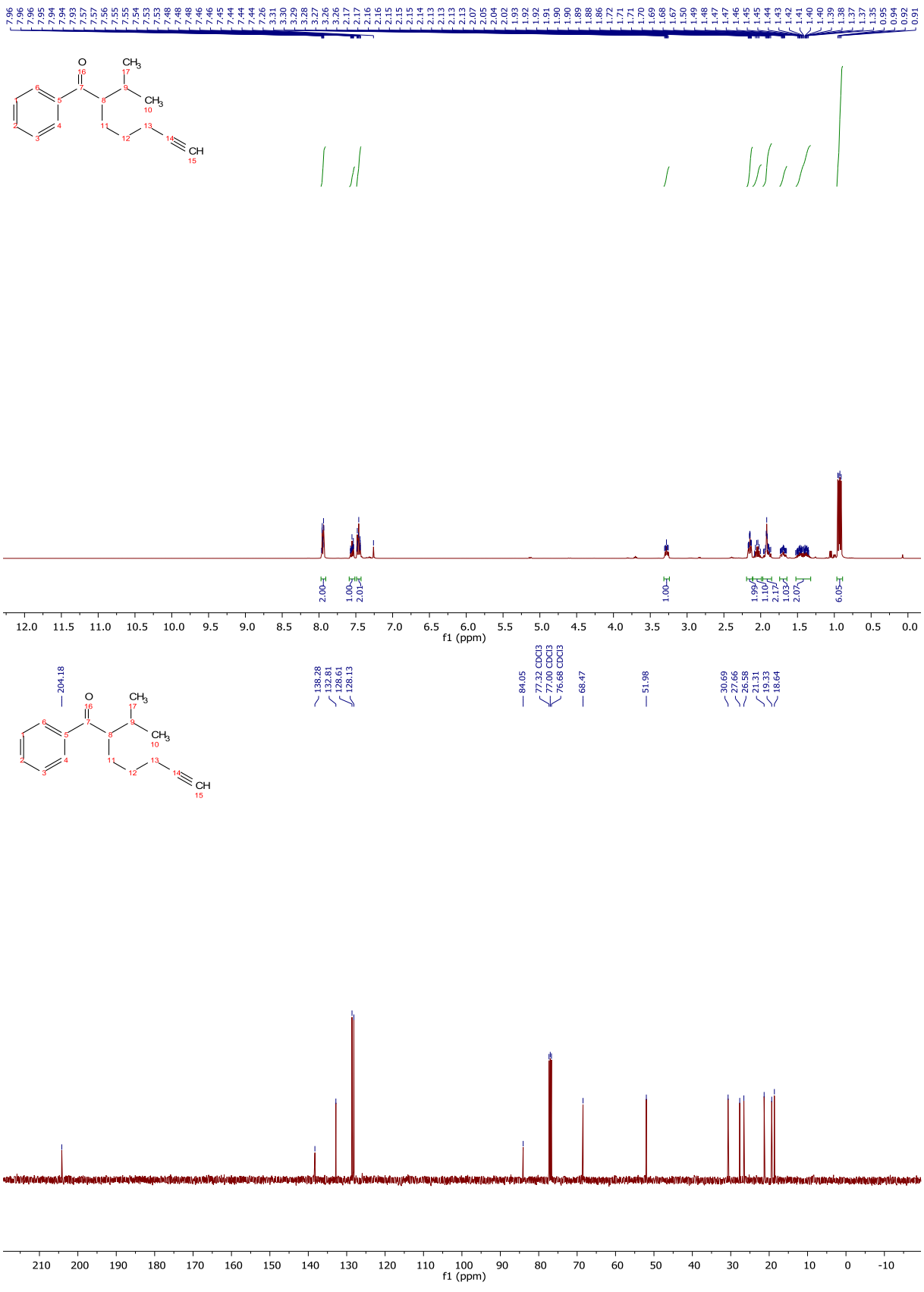


2-methyl-1-(p-tolyl)hept-6-yn-1-one

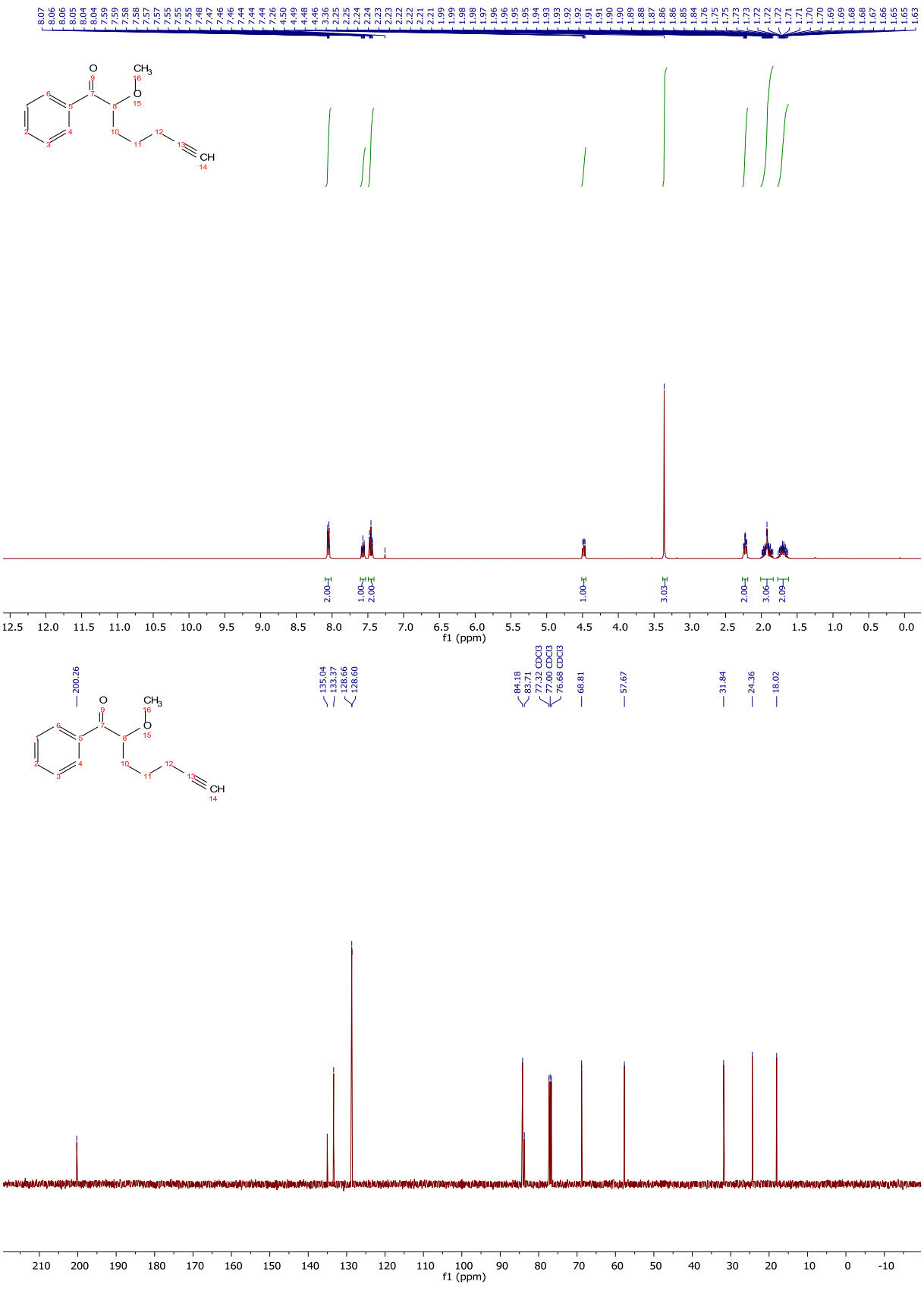


1-(4-methoxyphenyl)-2-methylhept-6-yn-1-one

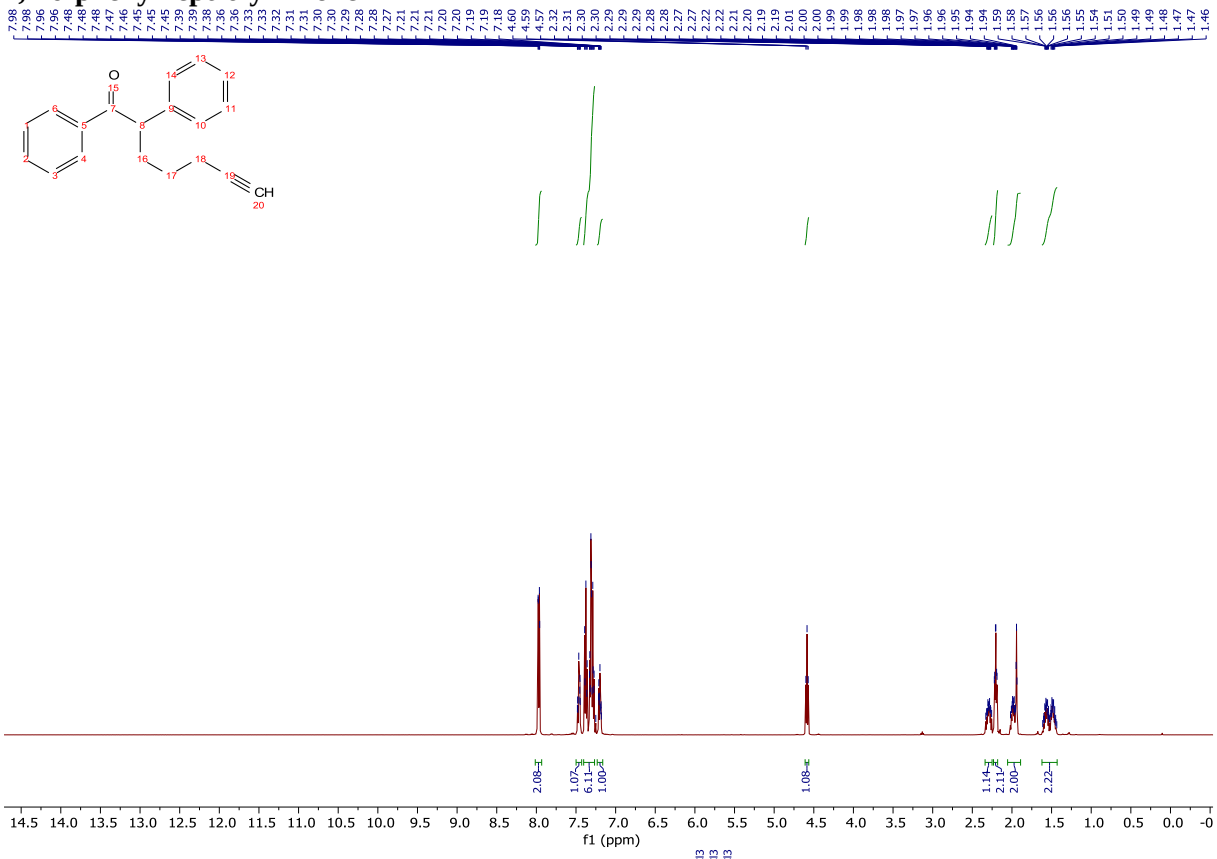
2-isopropyl-1-phenylhept-6-yn-1-one

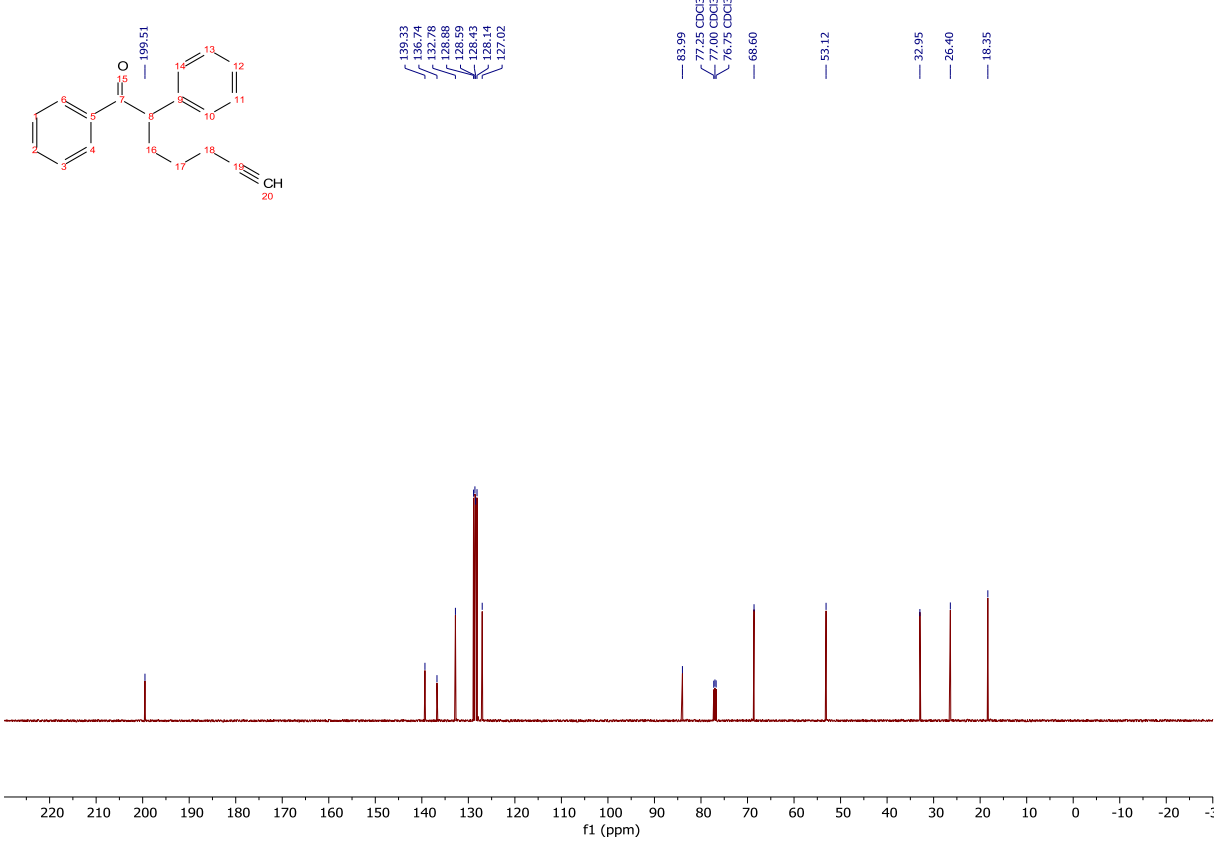


2-methoxy-1-phenylhept-6-yn-1-one

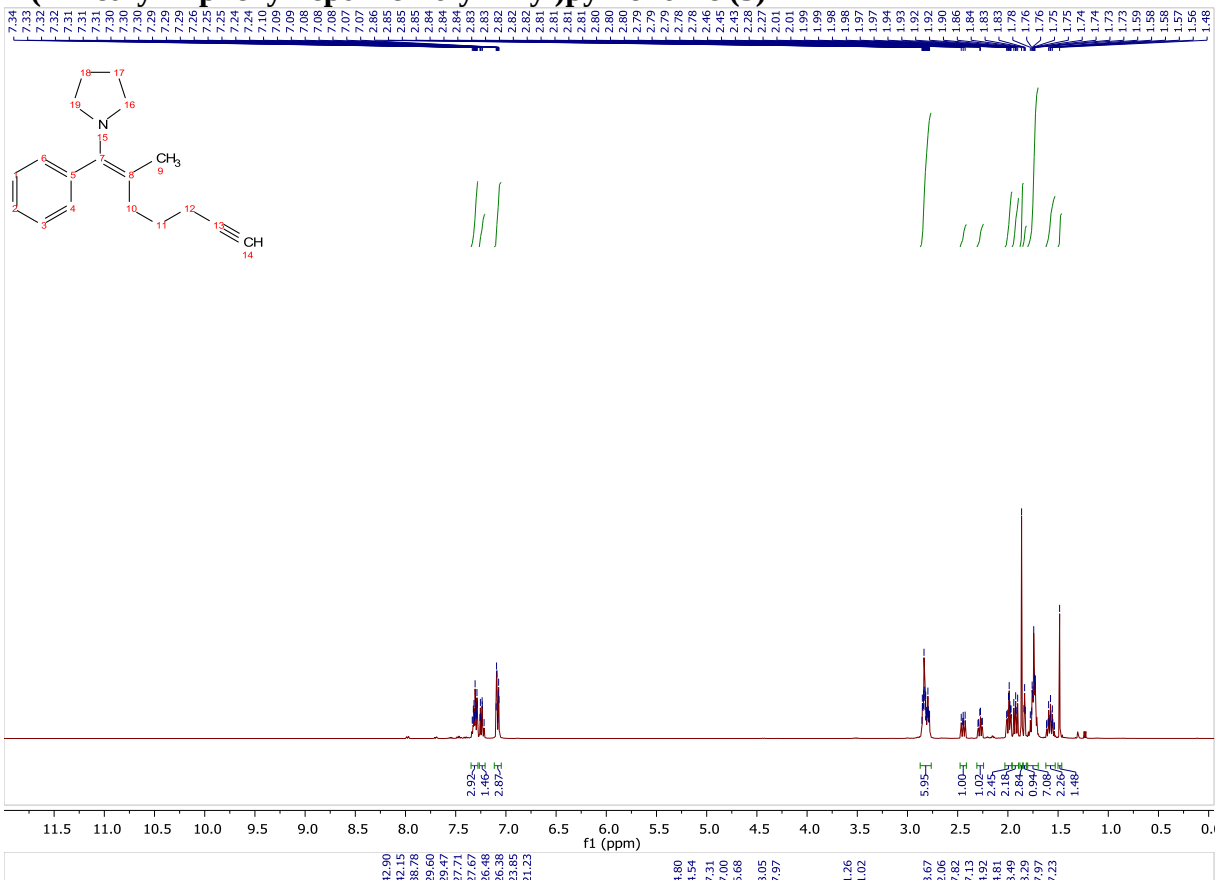


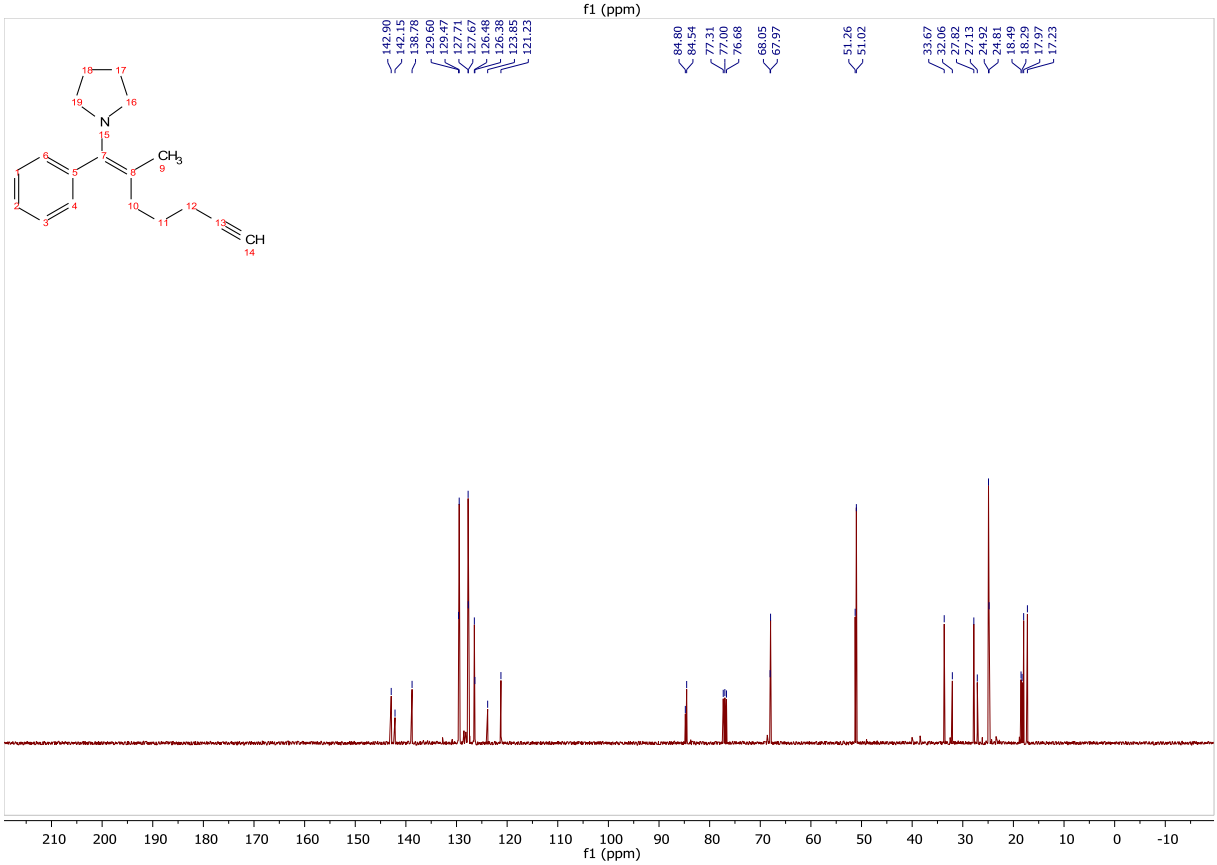
1,2-diphenylhept-6-yn-1-one



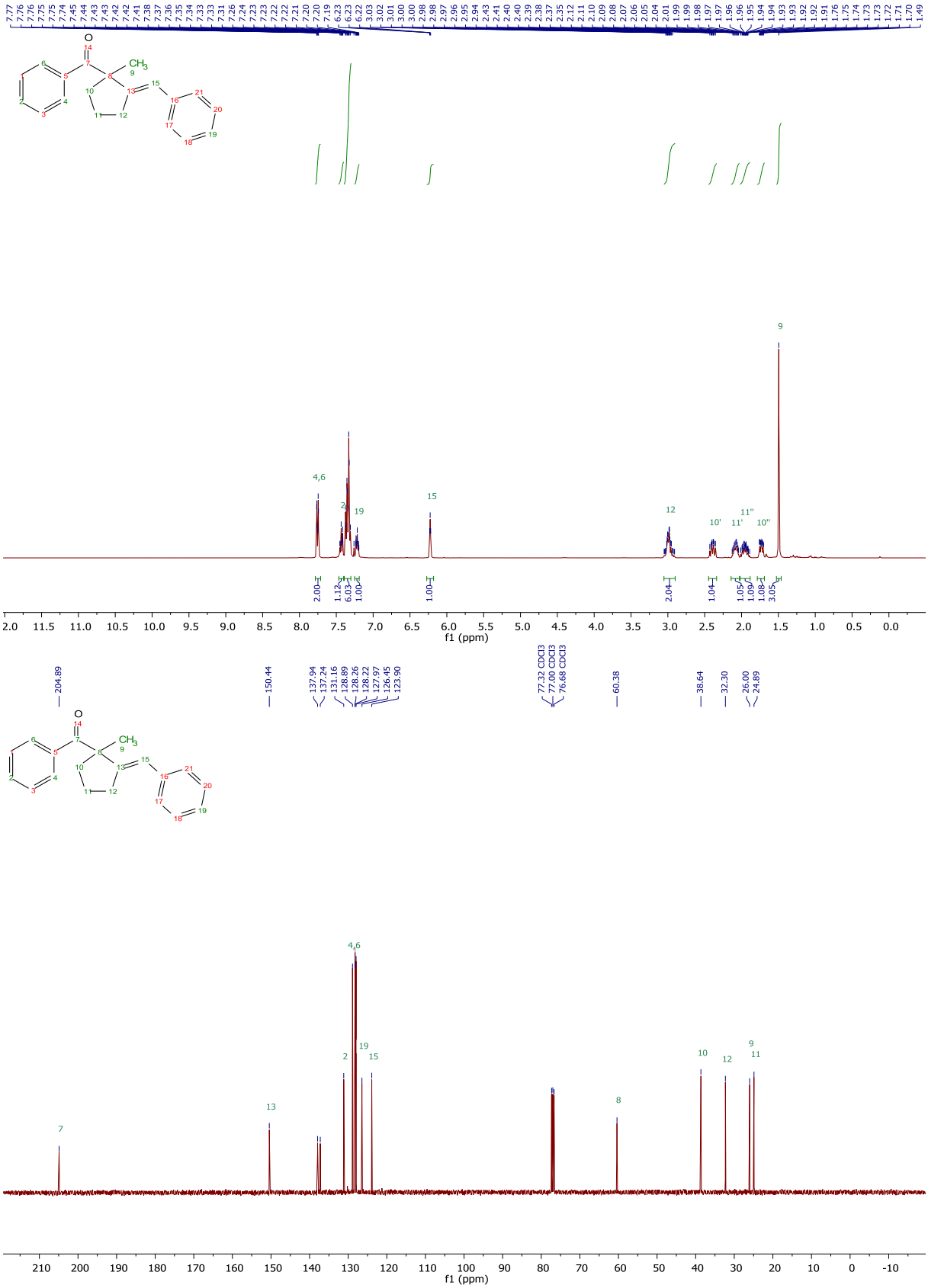


1-(2-methyl-1-phenylhept-1-en-6-yn-1-yl)pyrrolidine (3)

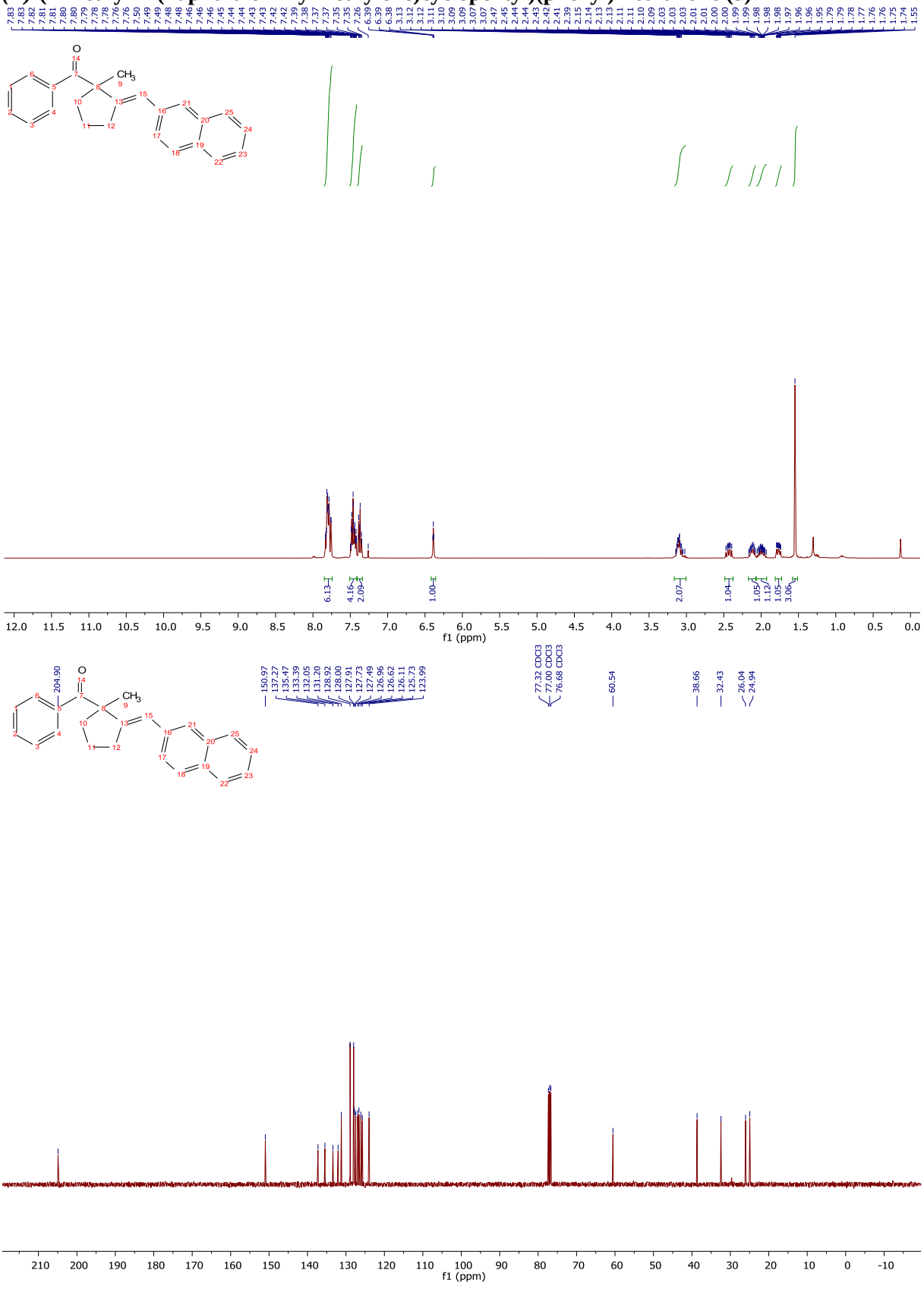




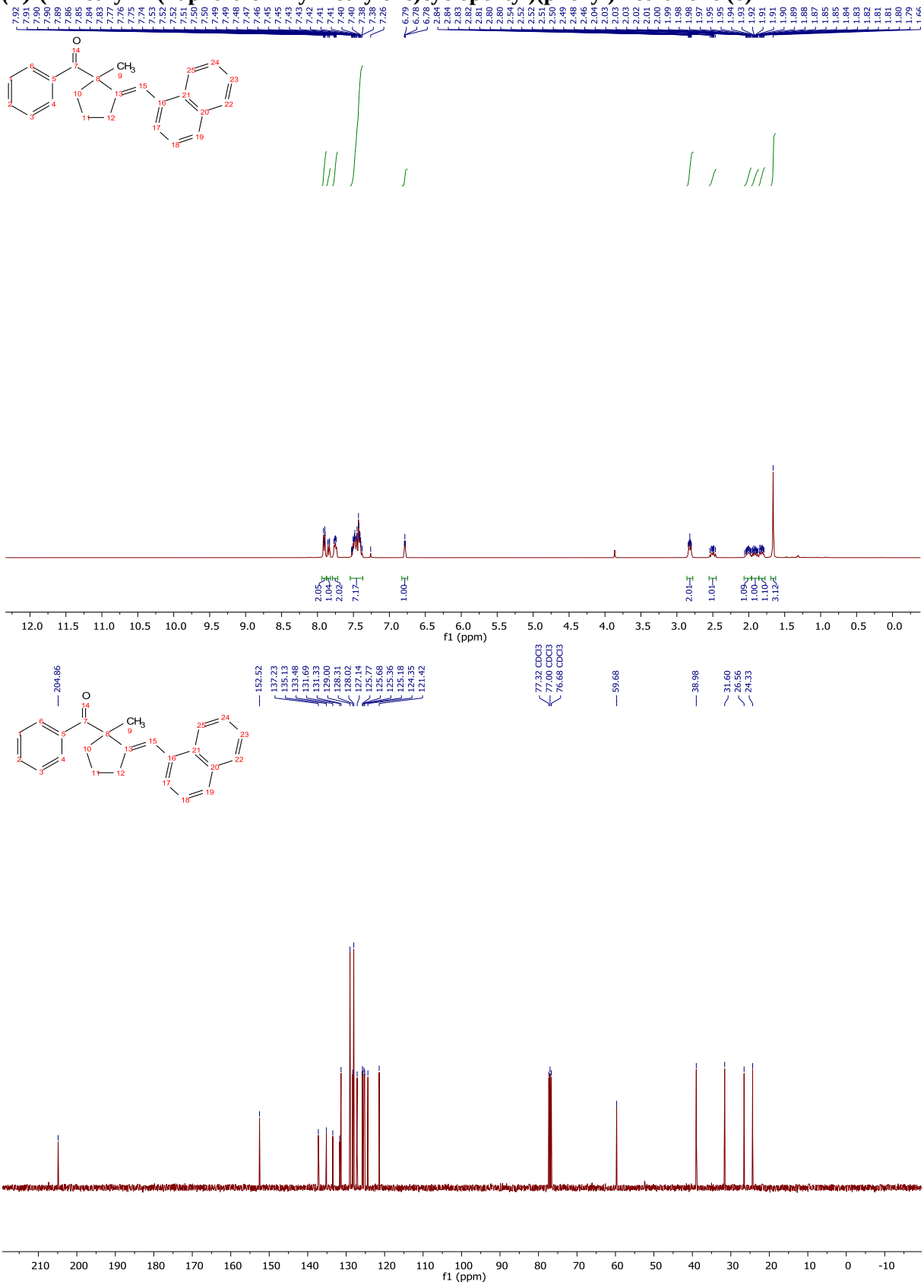
(E)-(2-benzylidene-1-methylcyclopentyl)(phenyl)methanone (4)



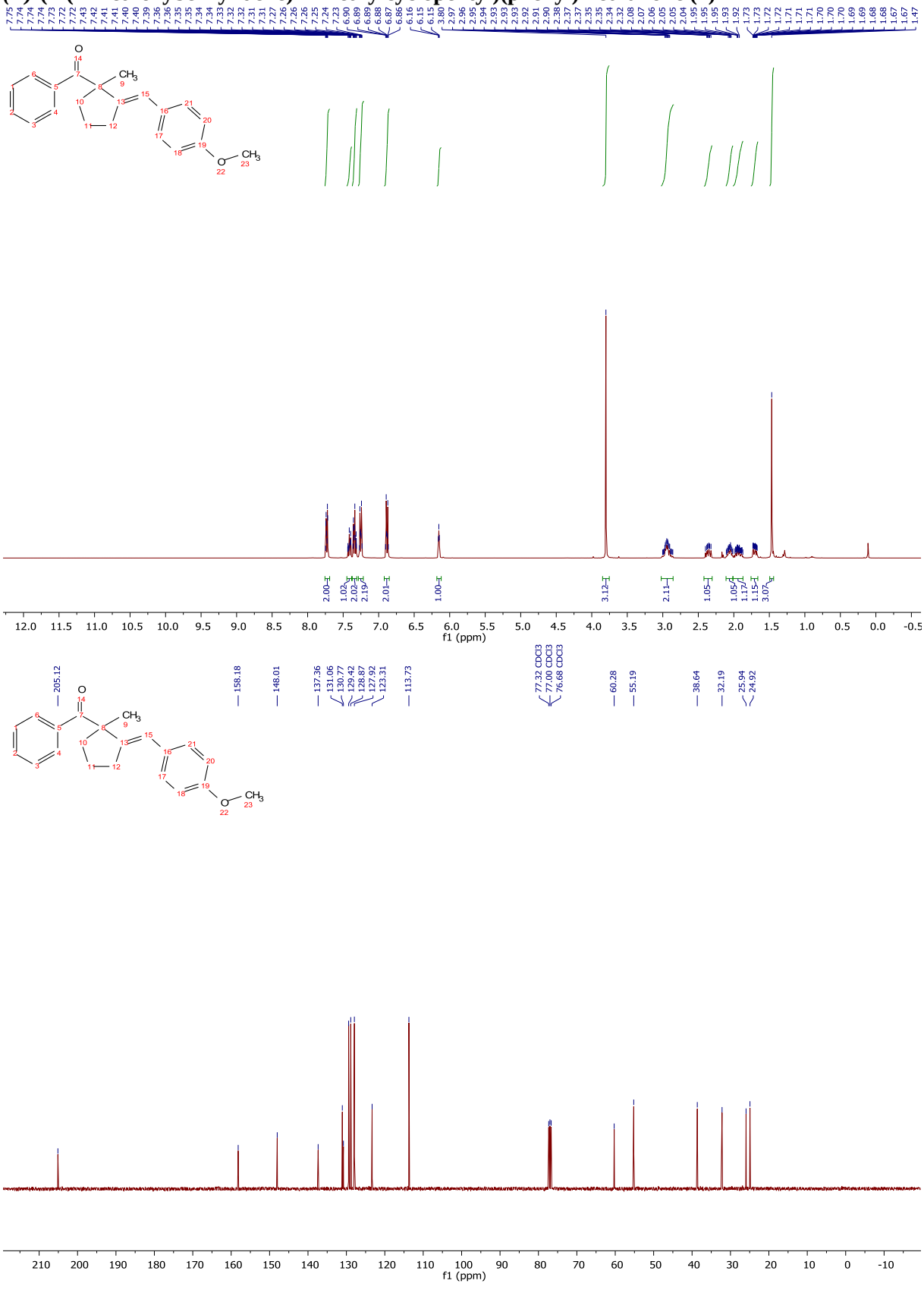
(E)-(1-methyl-2-(naphthalen-2-ylmethylene)cyclopentyl)(phenyl)methanone (5)



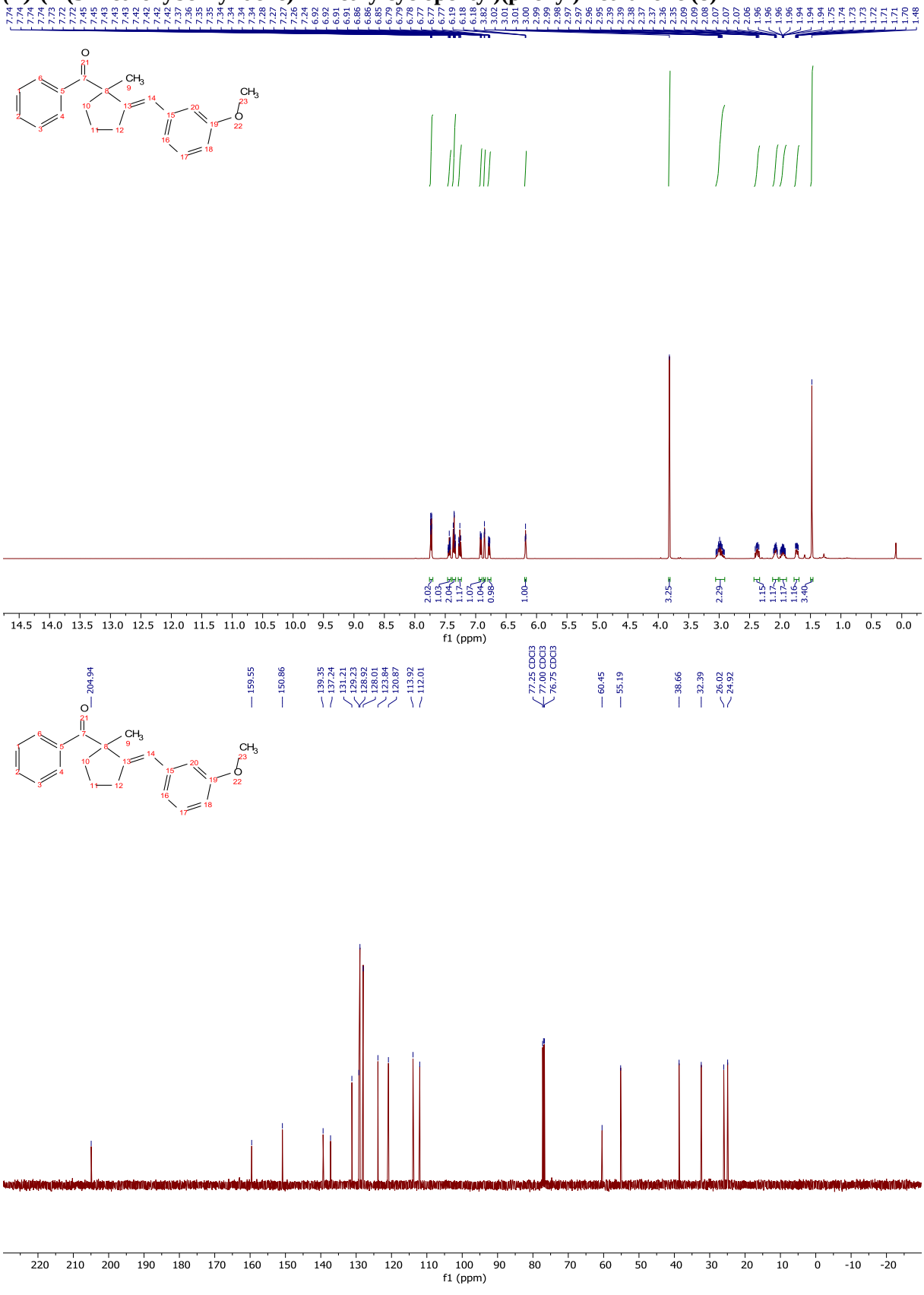
(E)-(1-methyl-2-(naphthalen-1-ylmethylene)cyclopentyl)(phenyl)methanone (6)



(*E*)-(2-(4-methoxybenzylidene)-1-methylcyclopentyl)(phenyl)methanone (7)

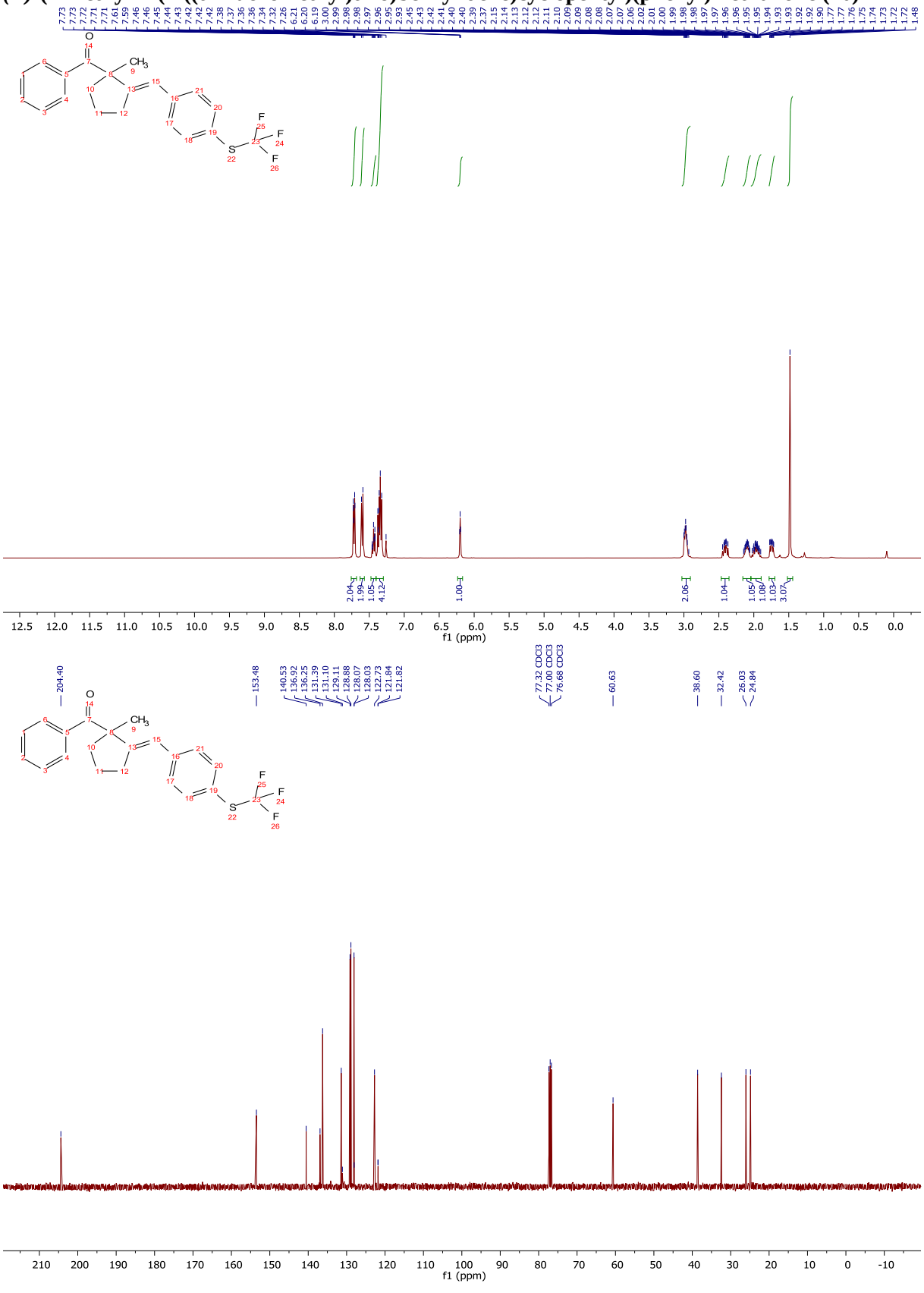


(E)-(2-(3-methoxybenzylidene)-1-methylcyclopentyl)(phenyl)methanone (8)

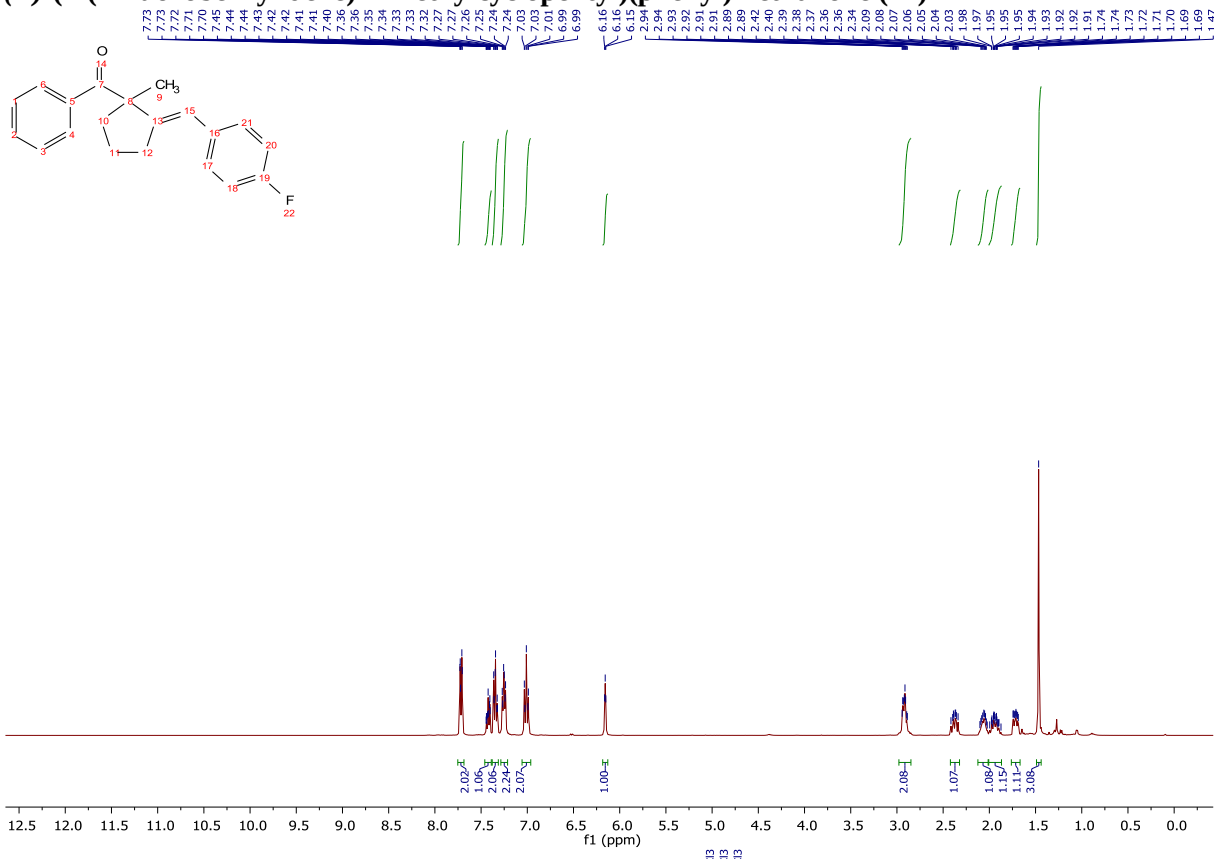


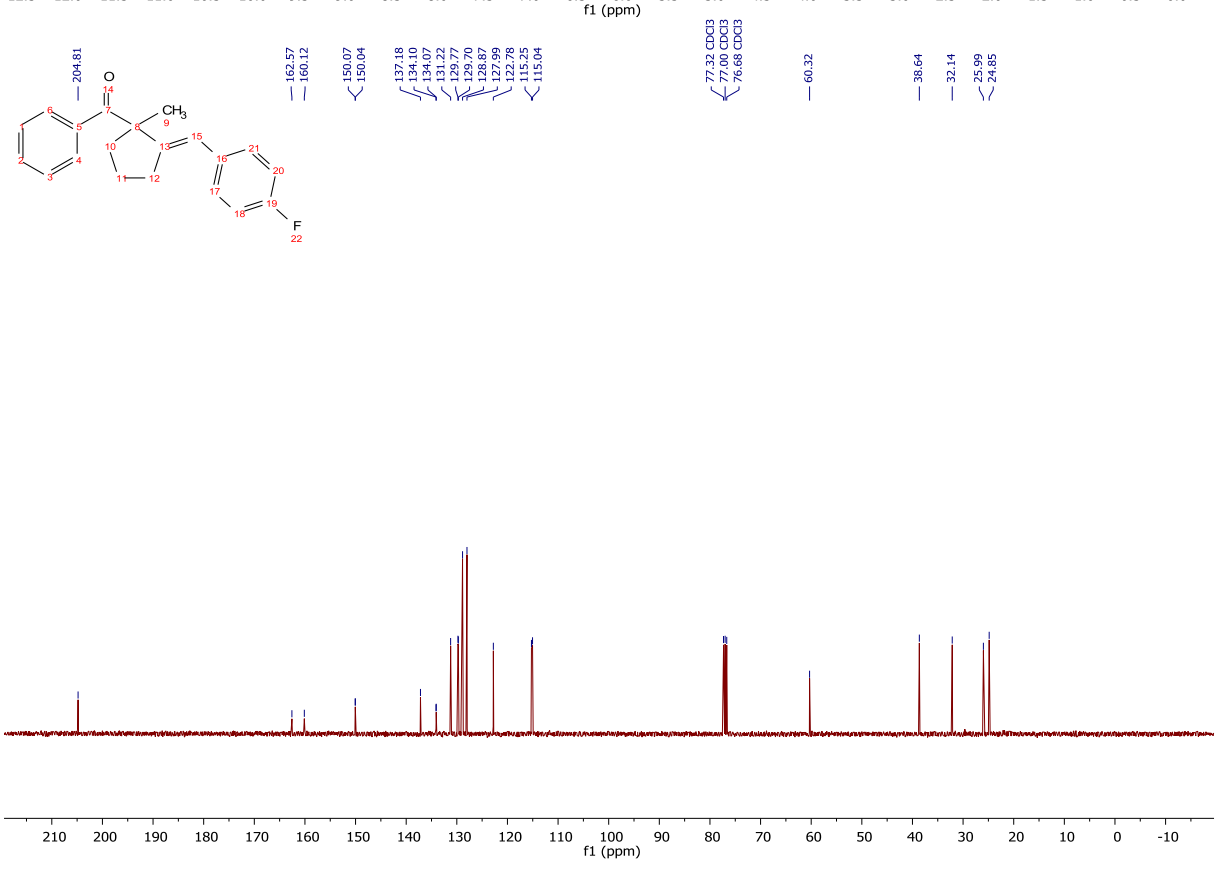
(E)-(1-methyl-2-(4-(methylthio)benzylidene)cyclopentyl)(phenyl)methanone (9)

(*E*)-(1-methyl-2-(4-((trifluoromethyl)thio)benzylidene)cyclopentyl)(phenyl)methanone (10)

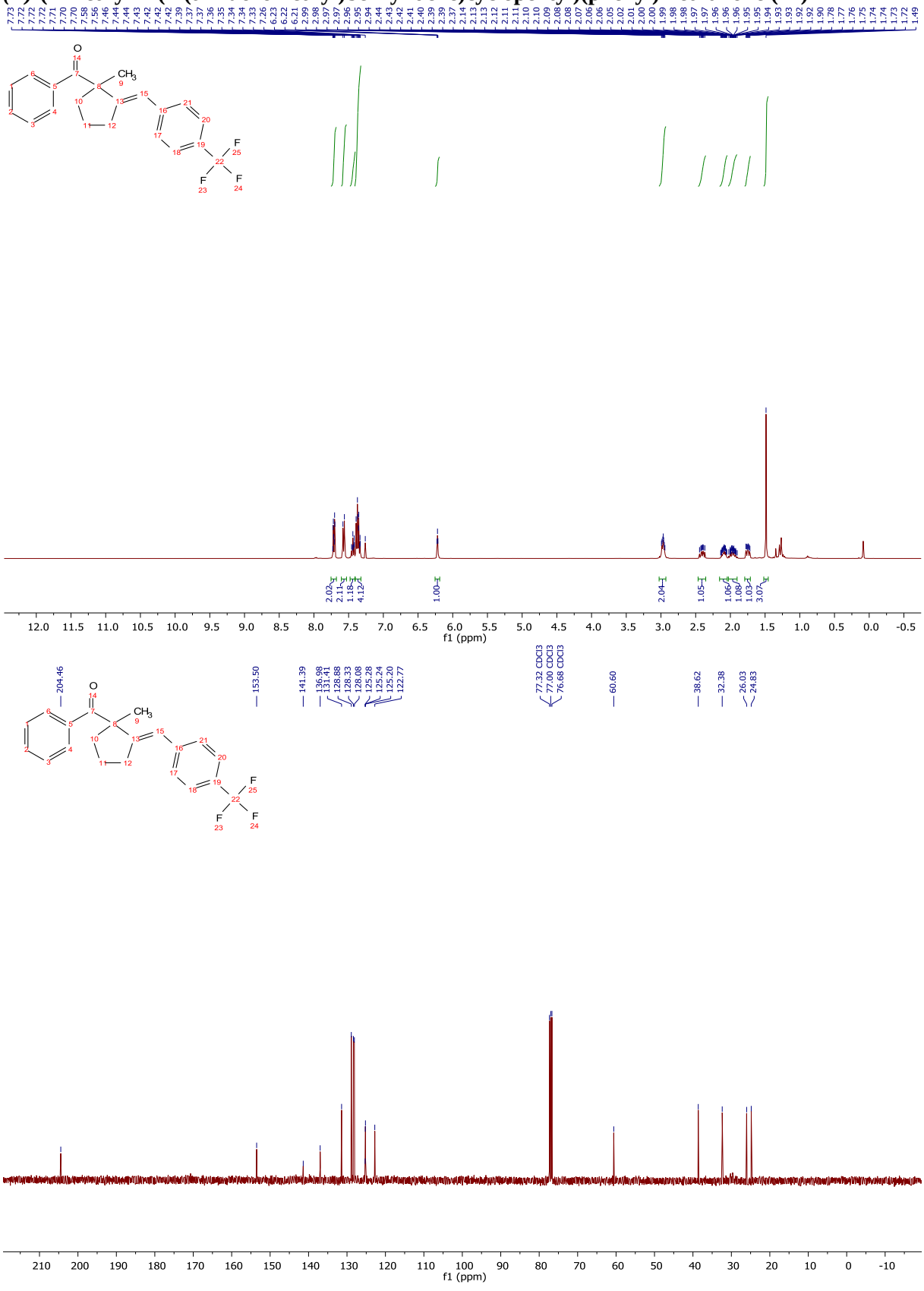


(*E*)-(2-(4-fluorobenzylidene)-1-methylcyclopentyl)(phenyl)methanone (11)

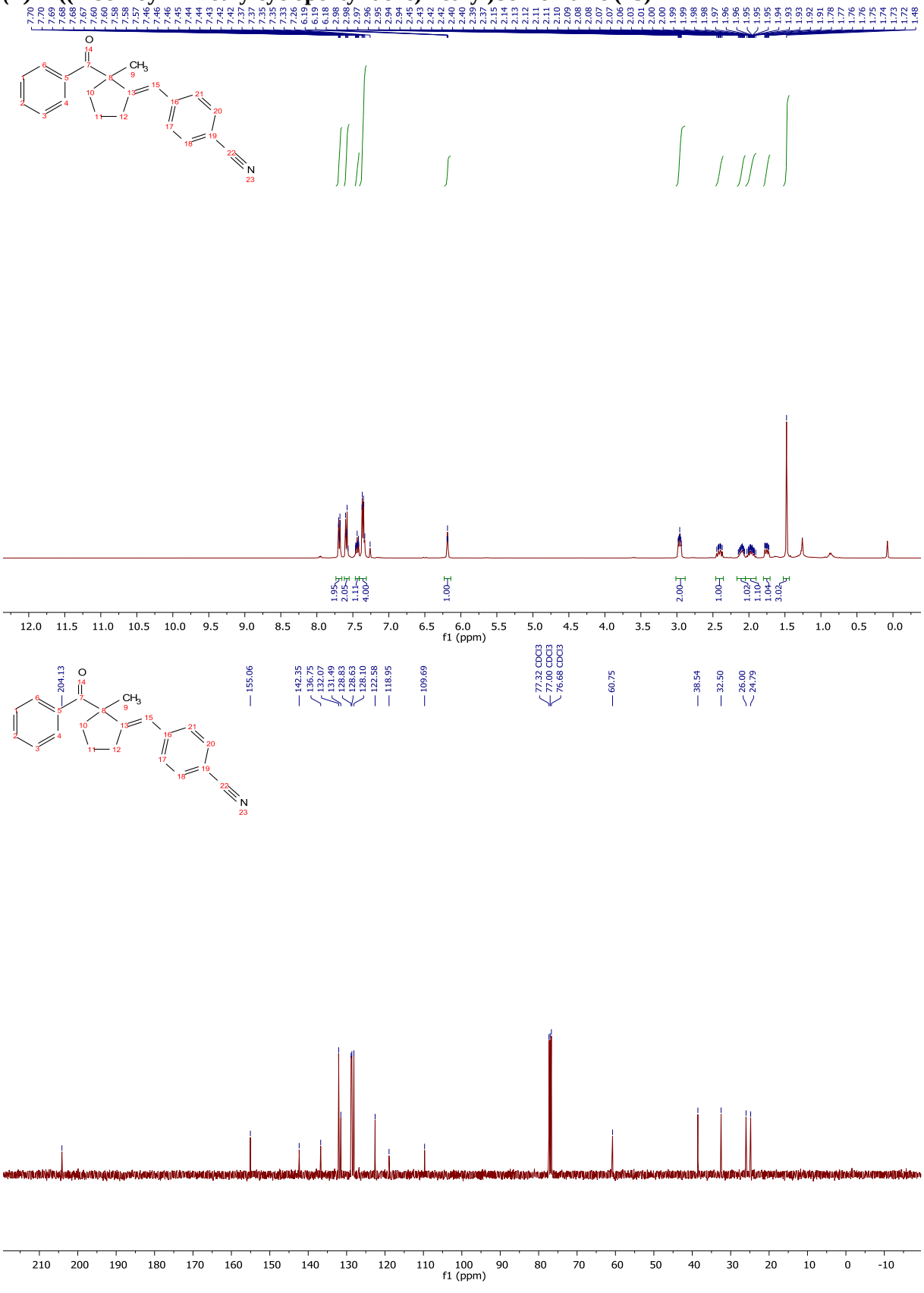




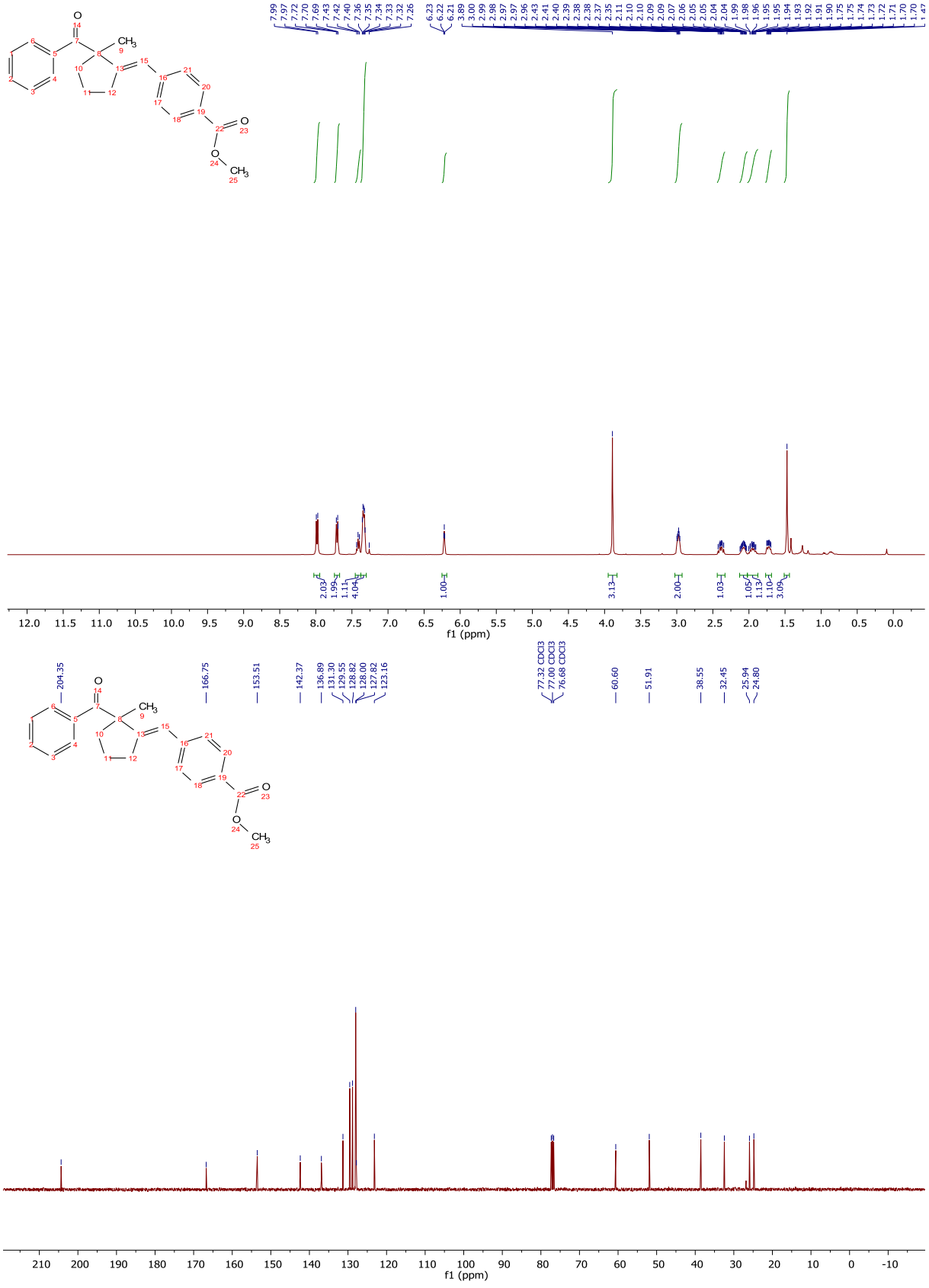
(E)-(1-methyl-2-(4-(trifluoromethyl)benzylidene)cyclopentyl)(phenyl)methanone (12)



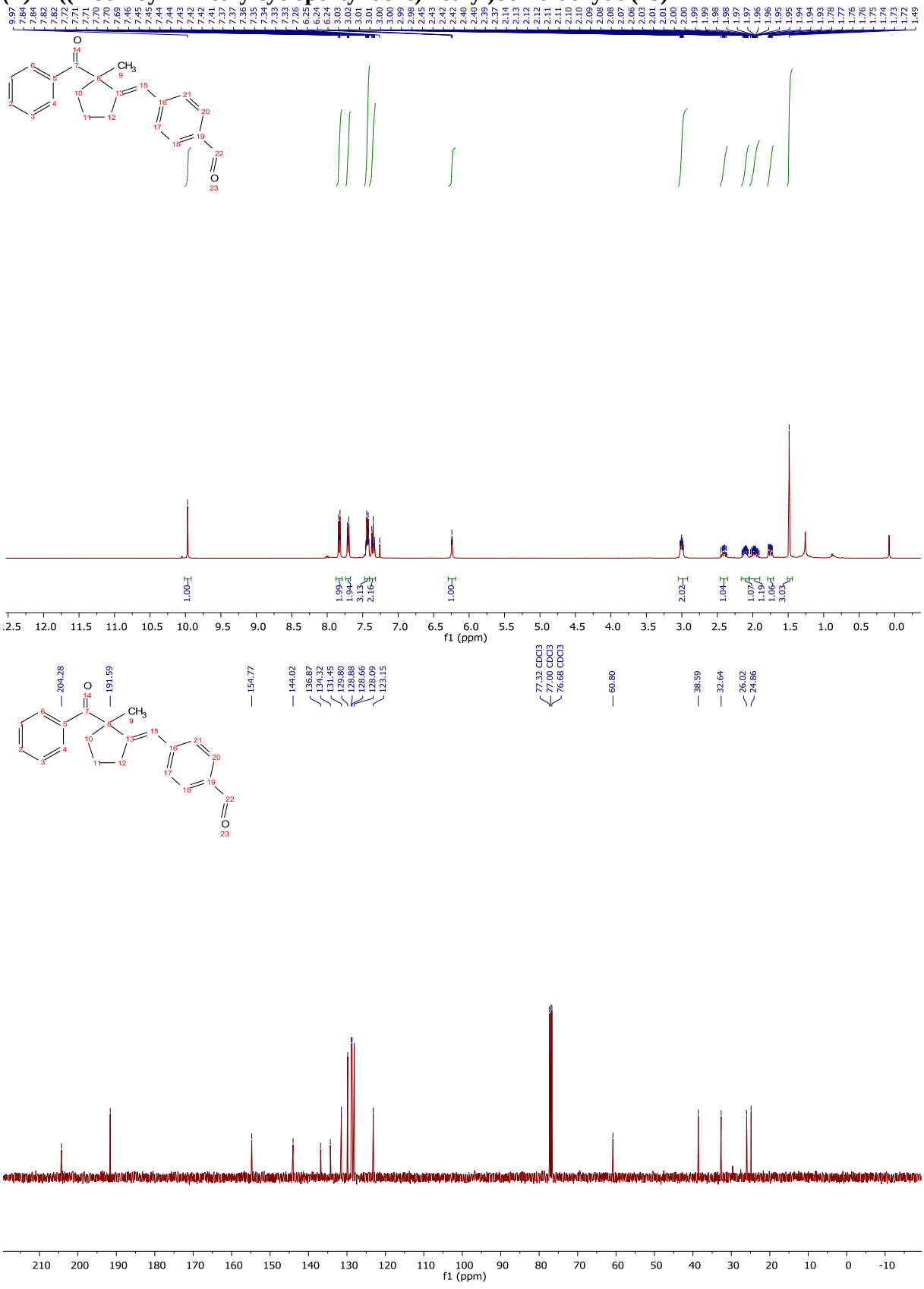
(E)-4-((2-benzoyl-2-methylcyclopentylidene)methyl)benzonitrile (13)



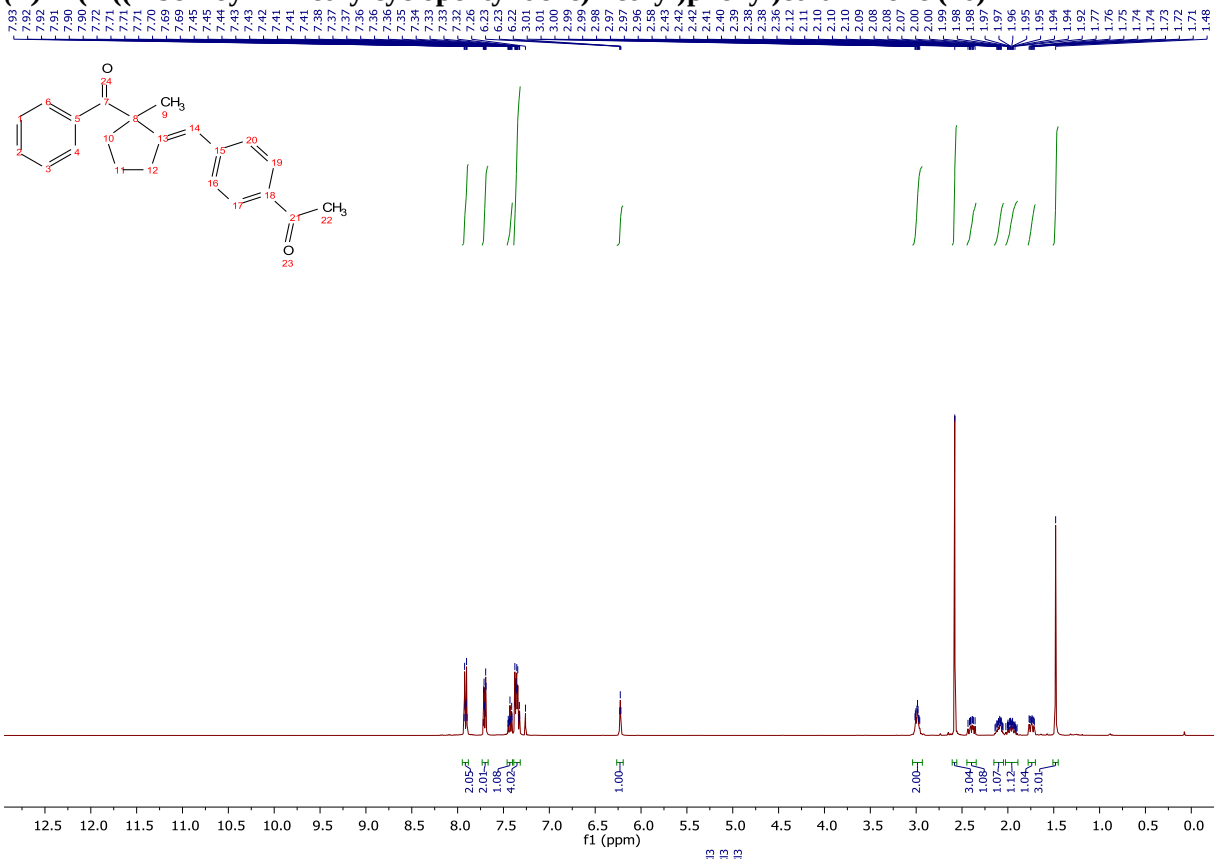
Methyl *(E)*-4-((2-benzoyl-2-methylcyclopentylidene)methyl)benzoate (14)

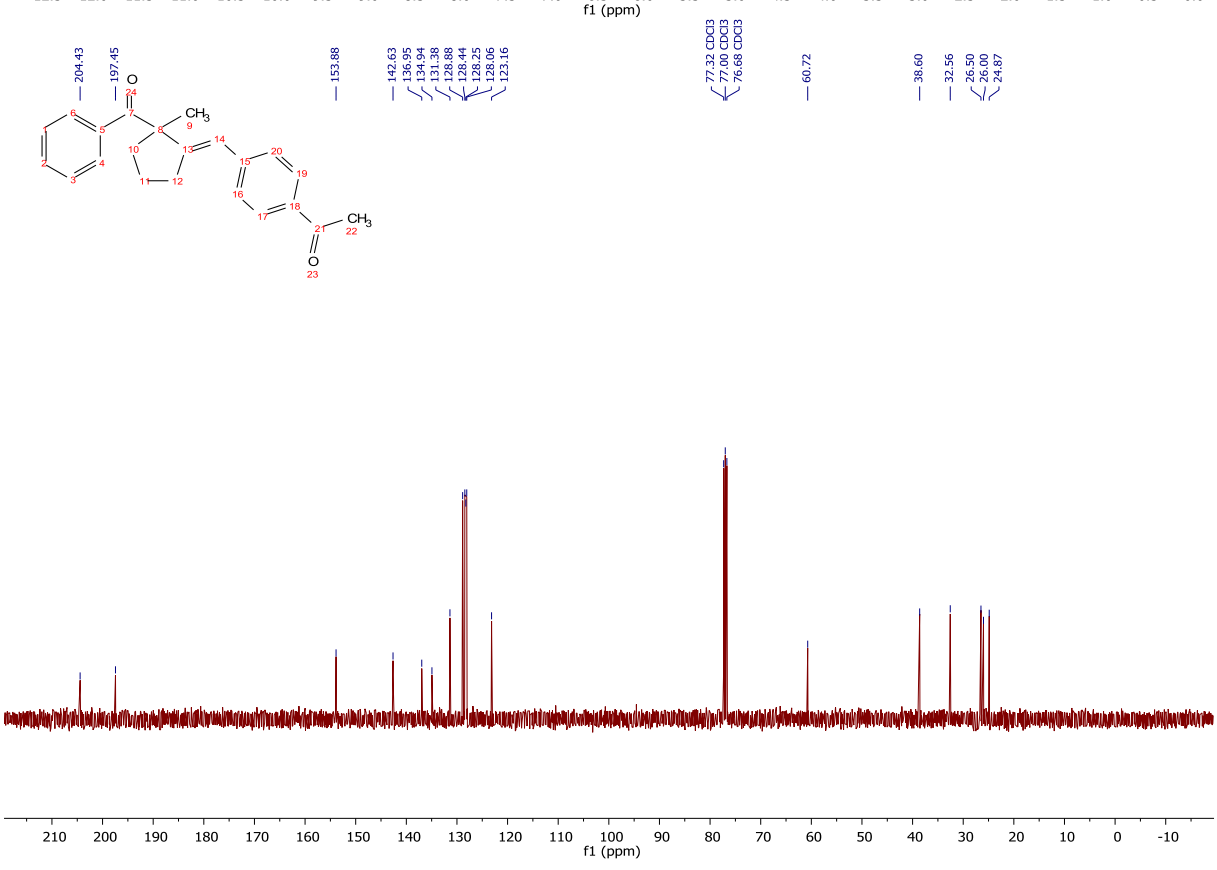


(E)-4-((2-benzoyl-2-methylcyclopentylidene)methyl)benzaldehyde (15)

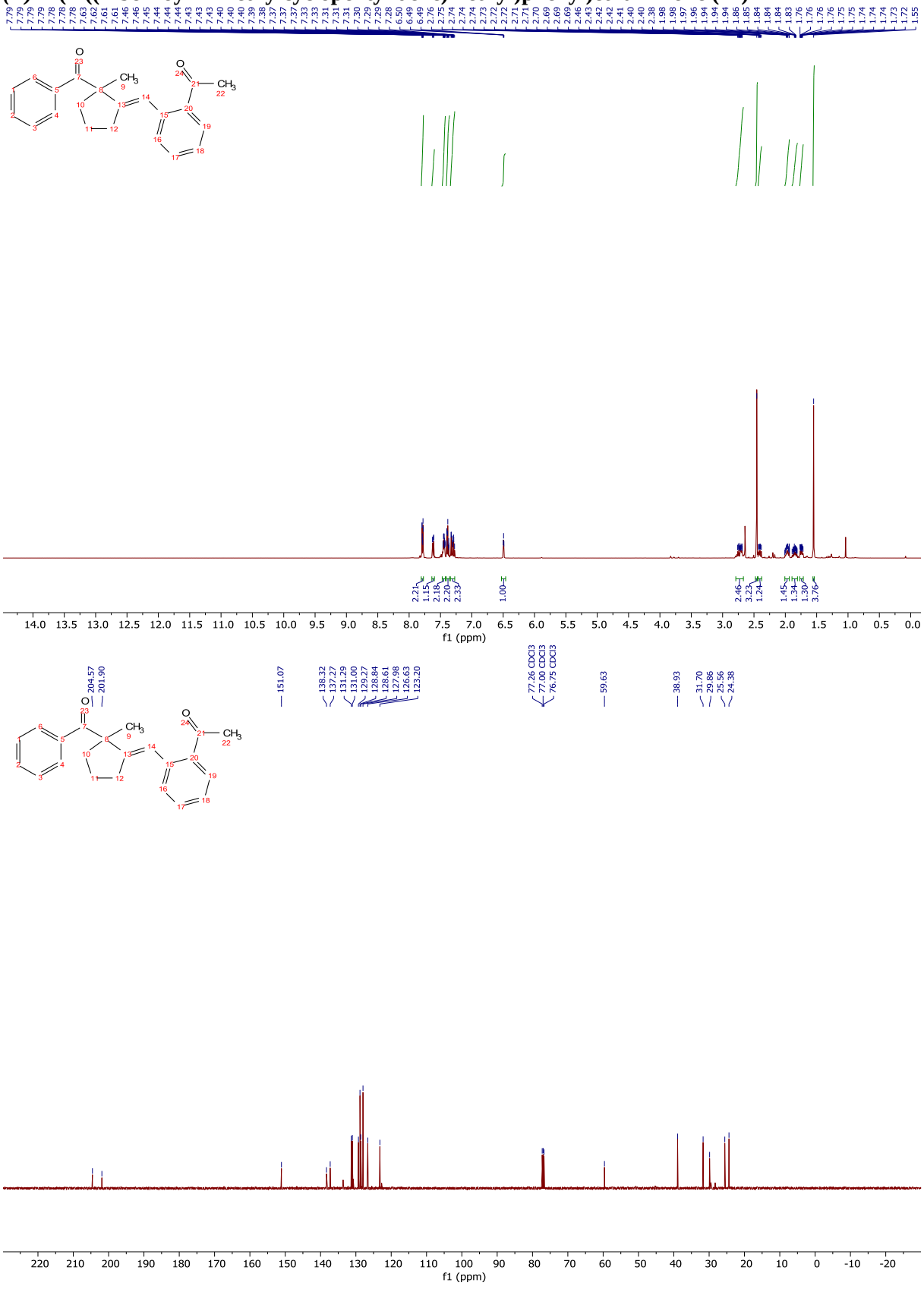


(E)-1-(4-((2-benzoyl-2-methylcyclopentylidene)methyl)phenyl)ethan-1-one (16)

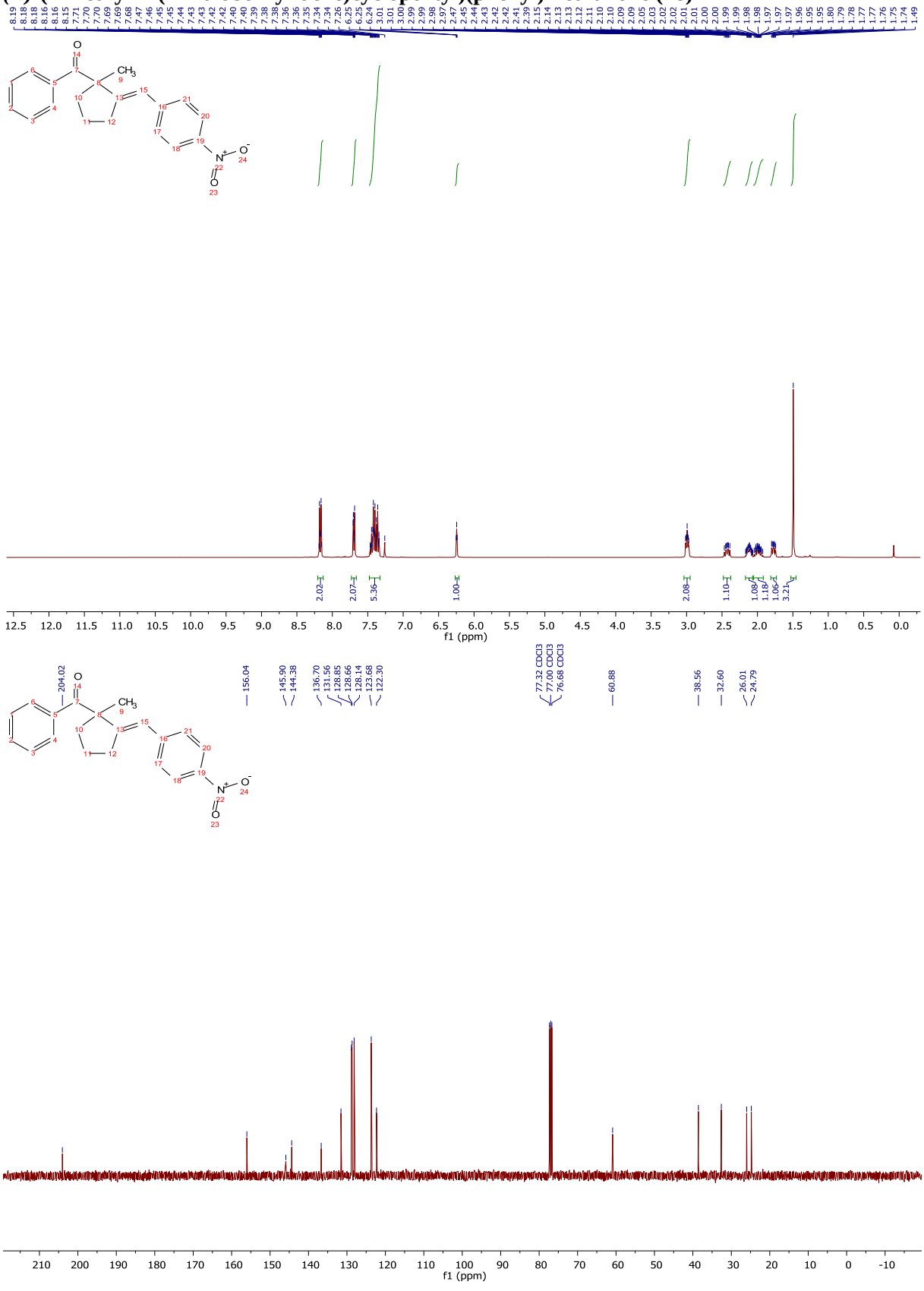




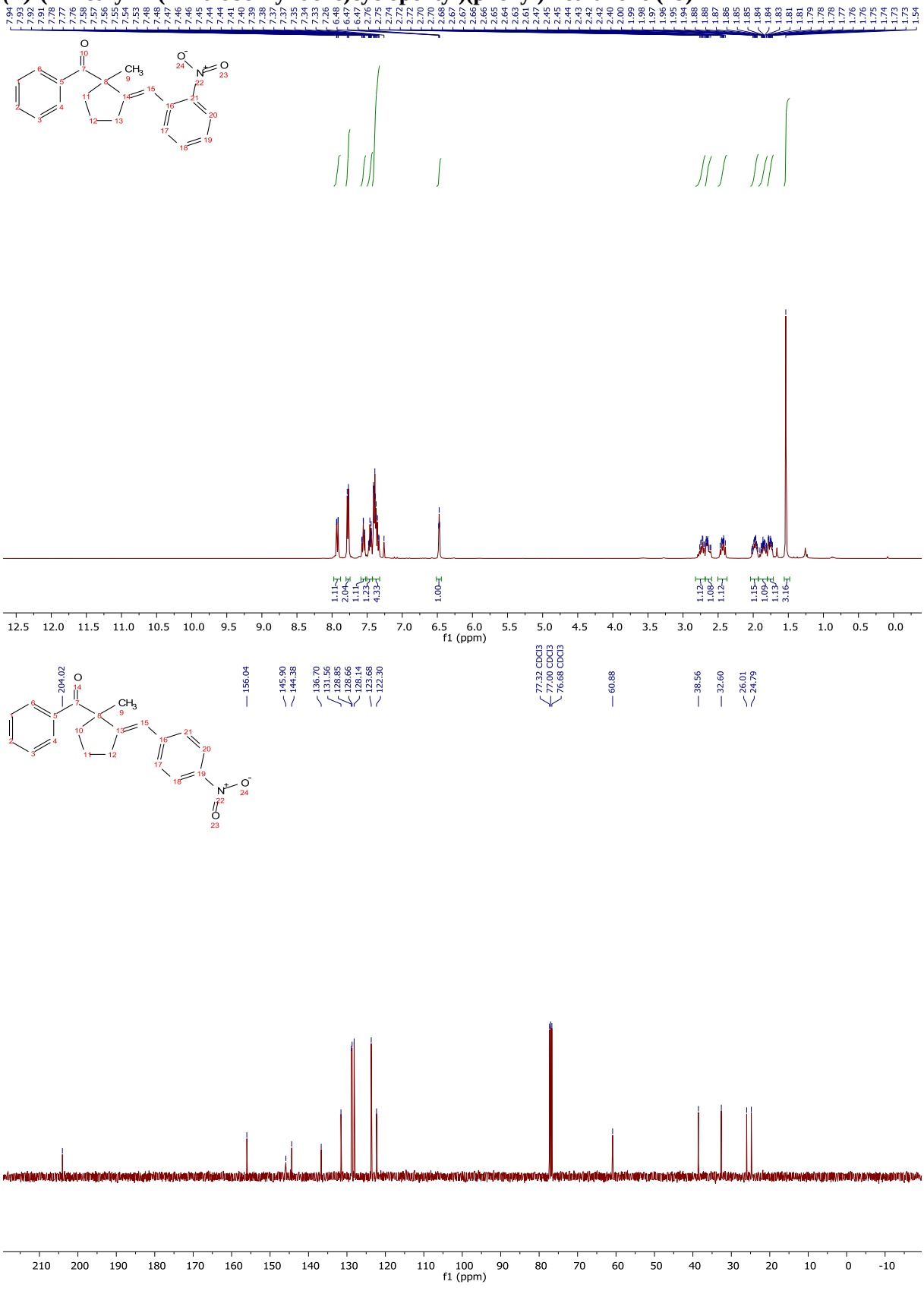
(E)-1-(4-((2-benzoyl-2-methylcyclopentylidene)methyl)phenyl)ethan-1-one (17)



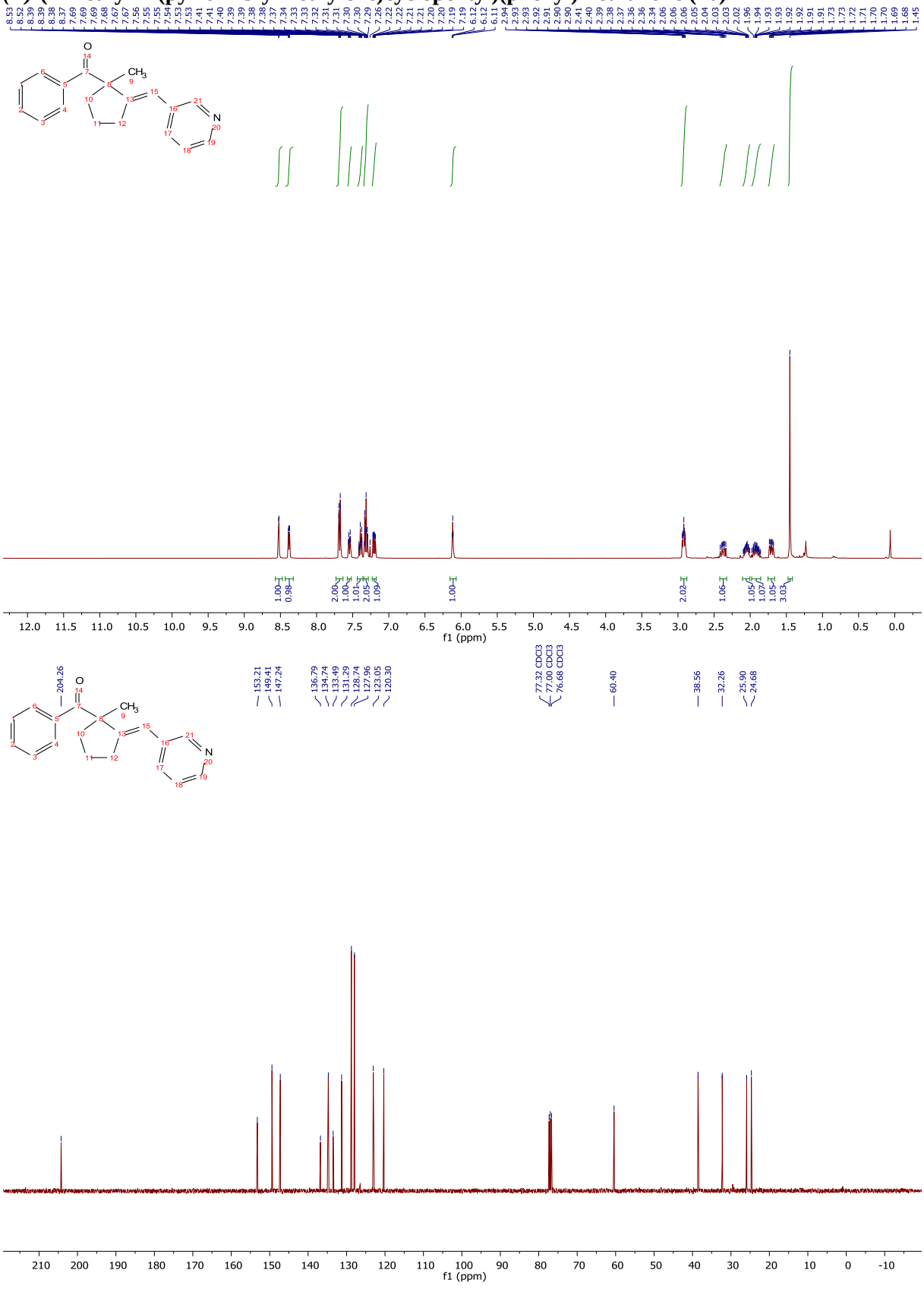
(E)-(1-methyl-2-(4-nitrobenzylidene)cyclopentyl)(phenyl)methanone (18)



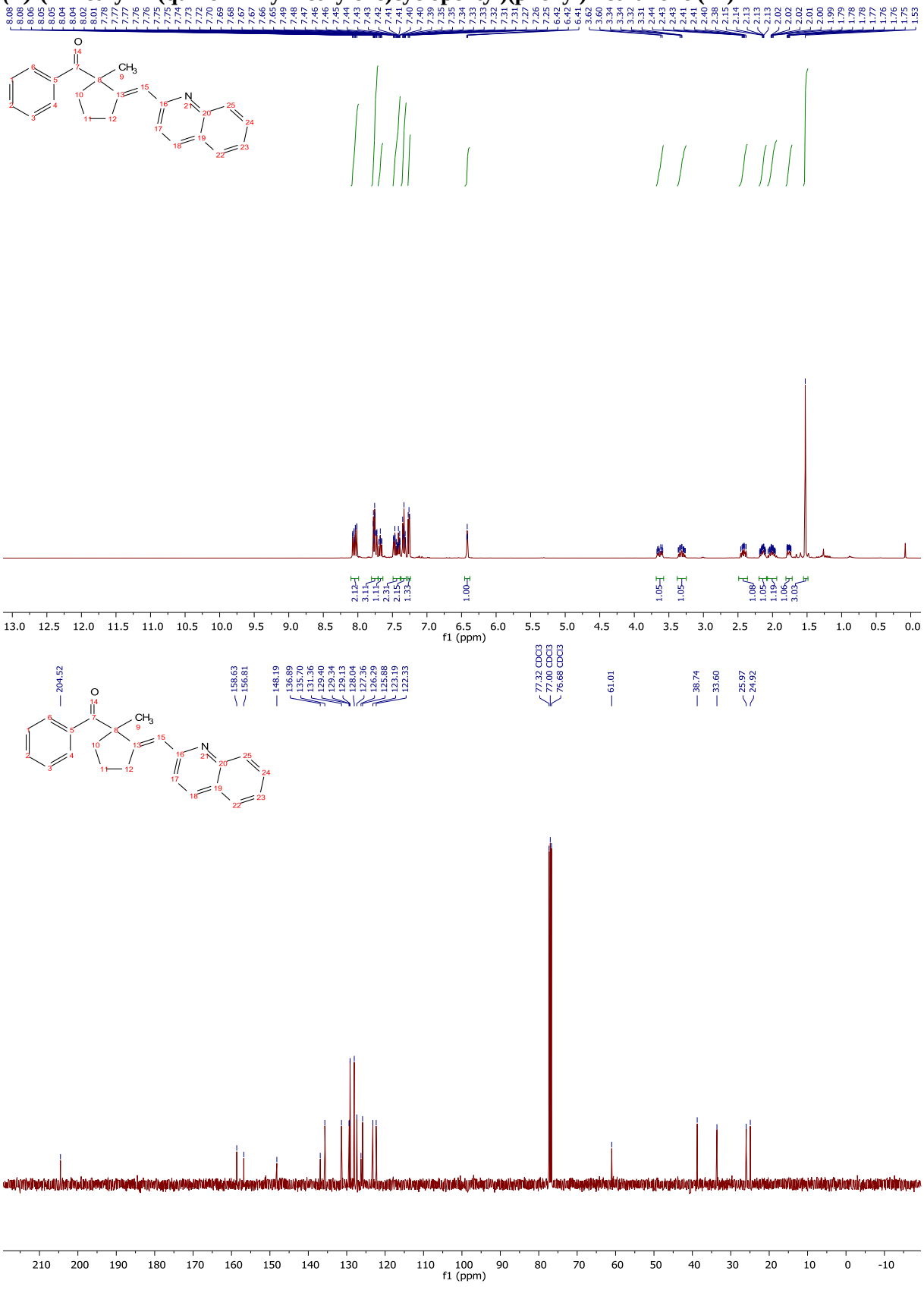
(E)-(1-methyl-2-(2-nitrobenzylidene)cyclopentyl)(phenyl)methanone (19)



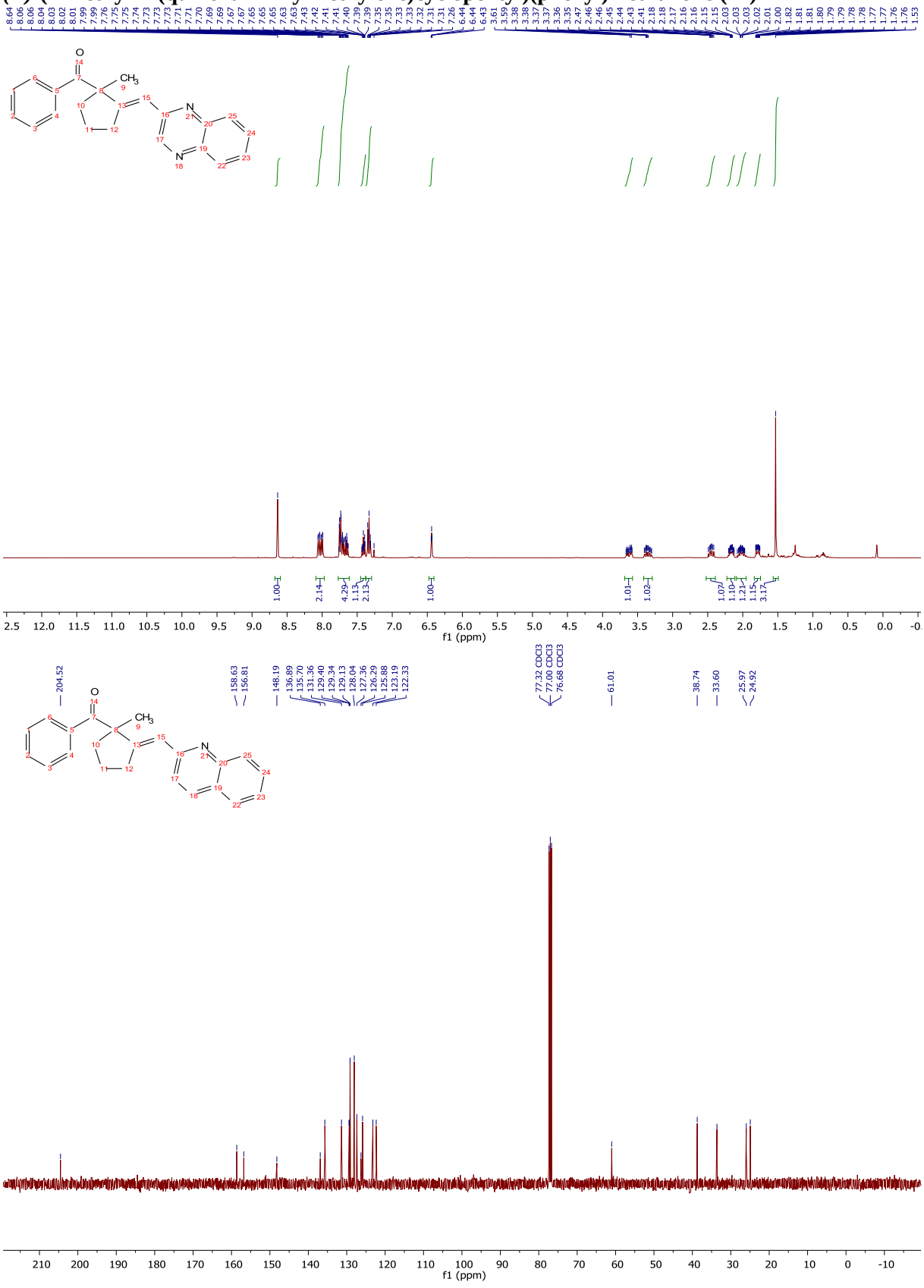
(E)-(1-methyl-2-(pyridin-3-ylmethylene)cyclopentyl)(phenyl)methanone (20)



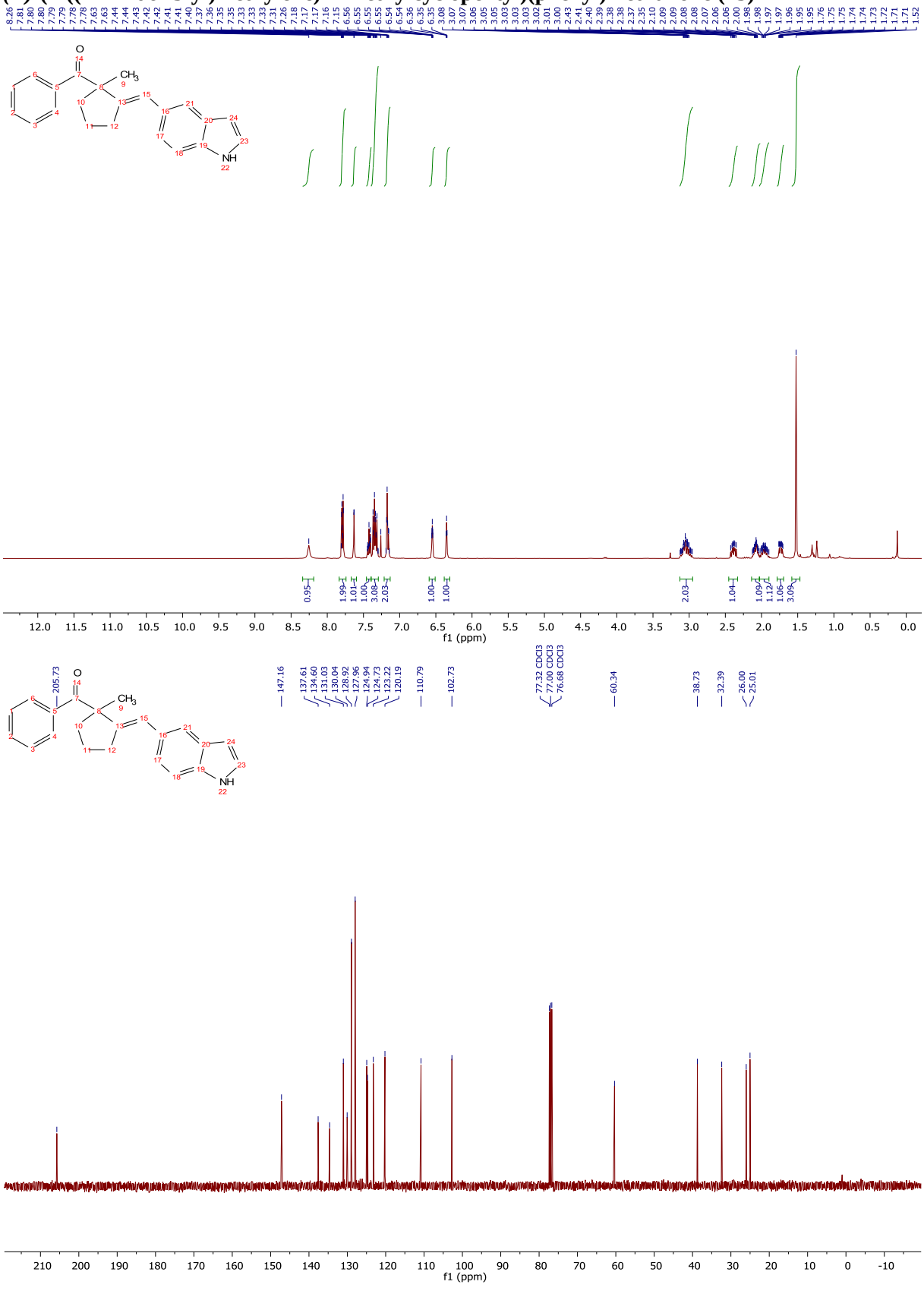
(E)-(1-methyl-2-(quinolin-2-ylmethylene)cyclopentyl)(phenyl)methanone (21)



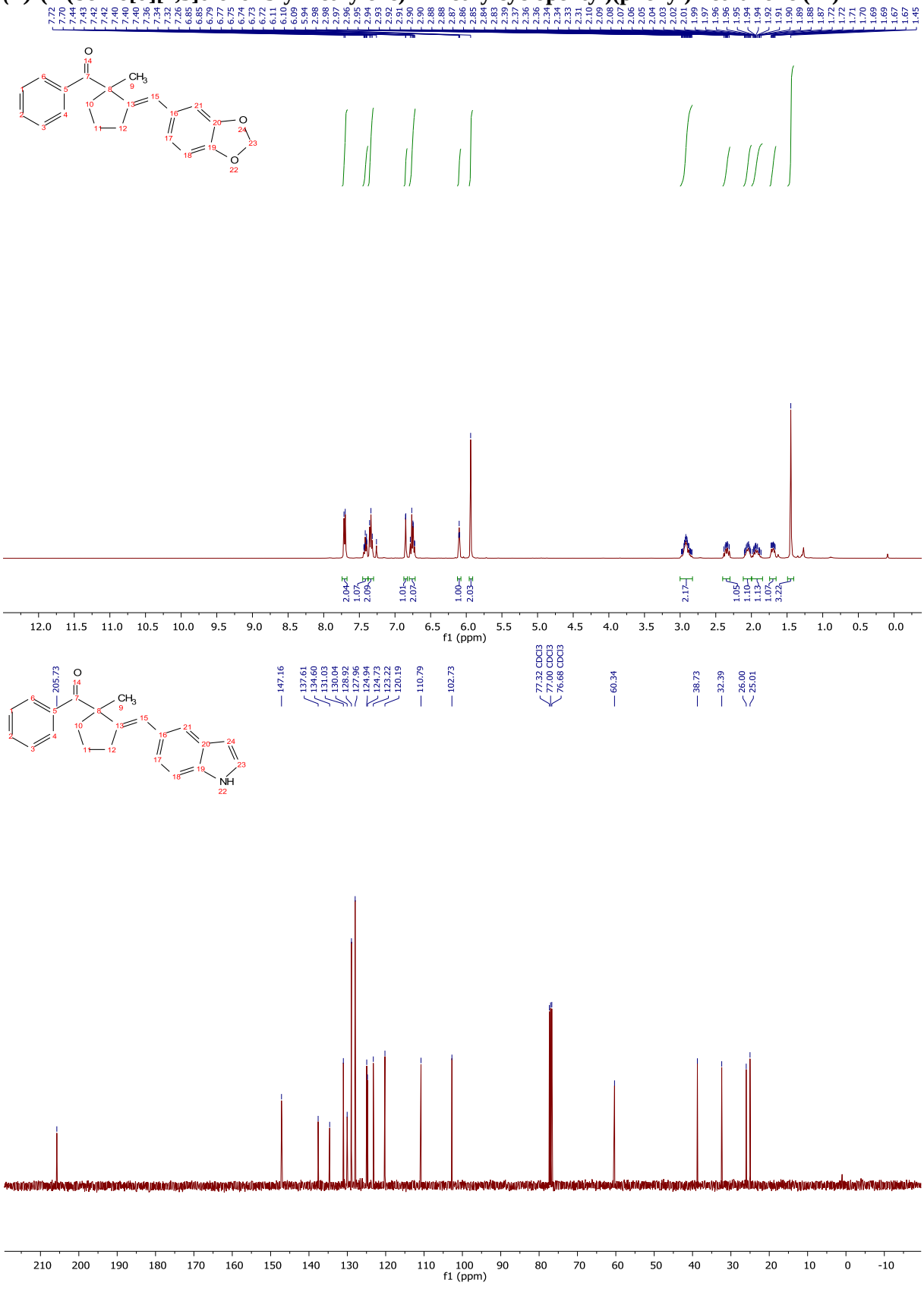
(E)-(1-methyl-2-(quinoxalin-2-ylmethylene)cyclopentyl)(phenyl)methanone (22)



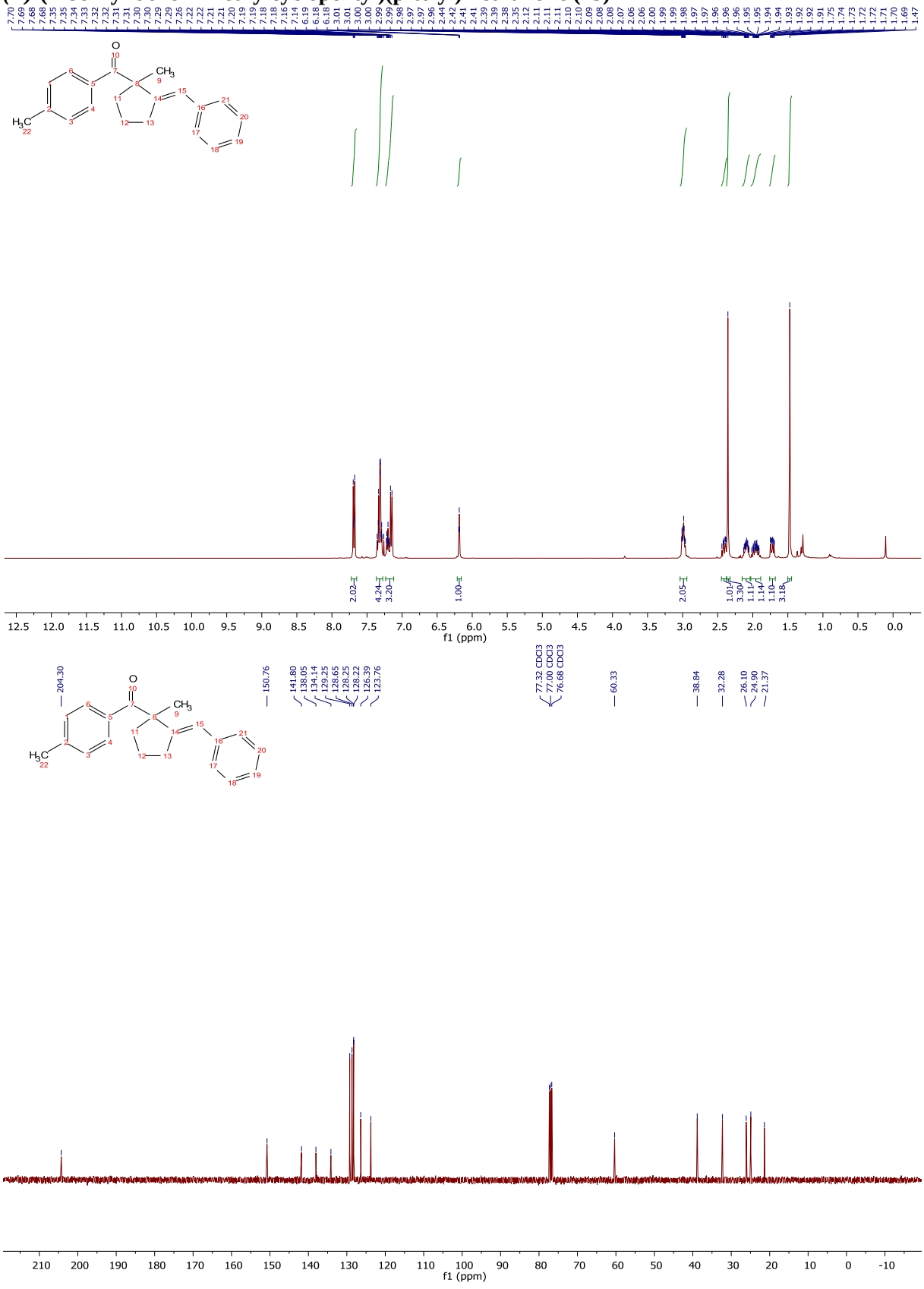
(E)-(2-((1H-indol-5-yl)methylene)-1-methylcyclopentyl)(phenyl)methanone (23)



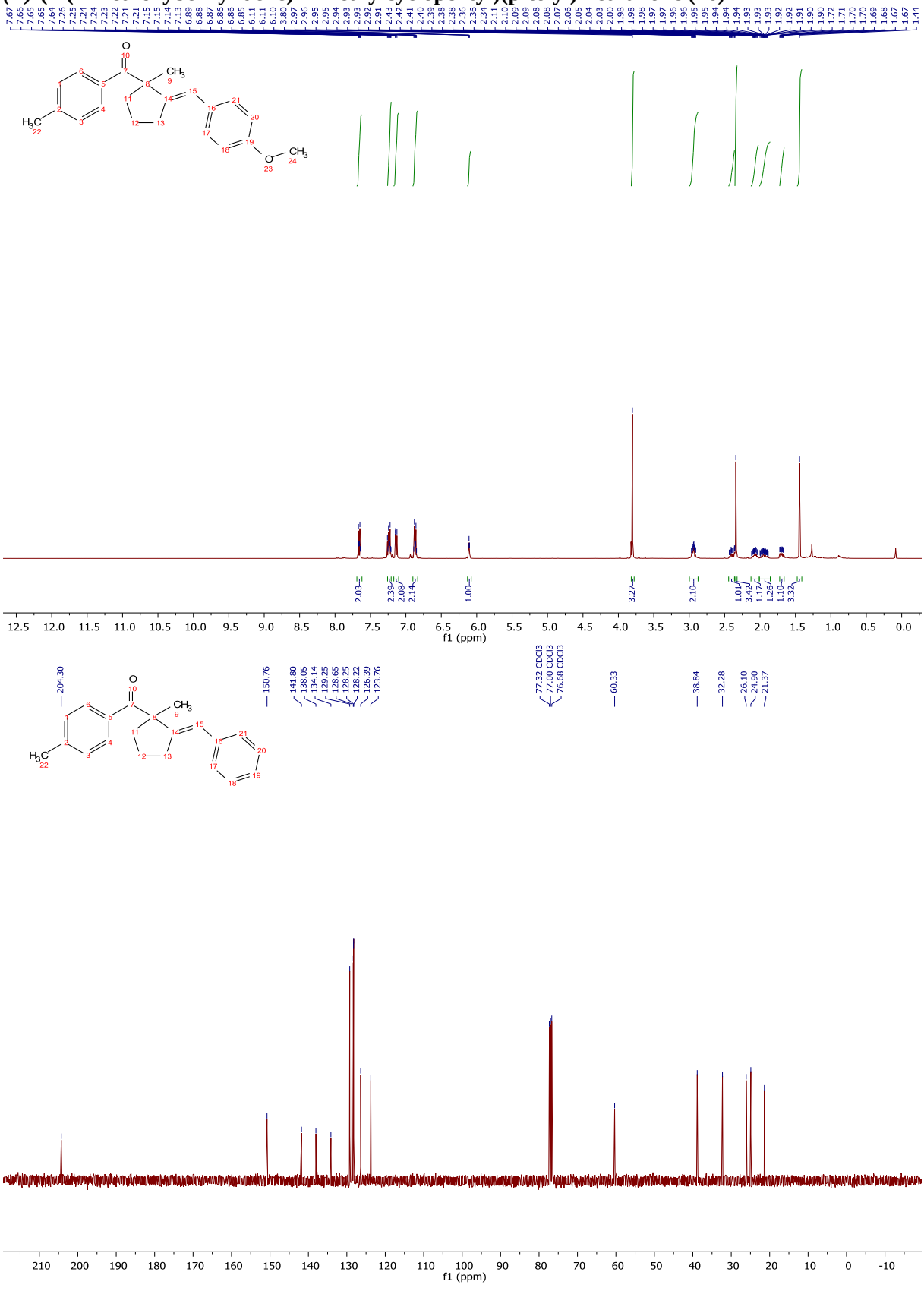
***(E)*-(2-(benzo[d][1,3]dioxol-5-ylmethylene)-1-methylcyclopentyl)(phenyl)methanone (24)**



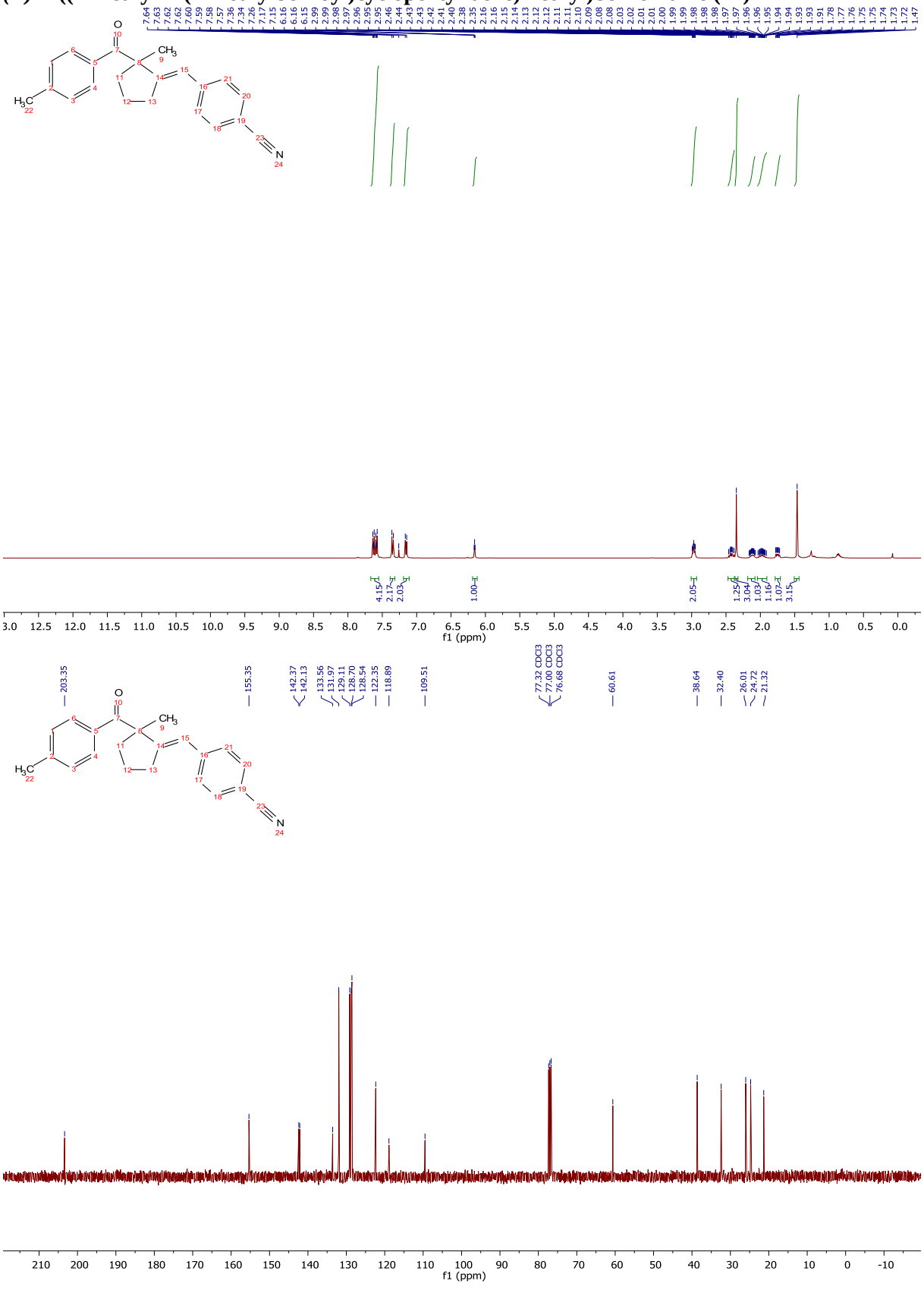
(E)-(2-benzylidene-1-methylcyclopentyl)(p-tolyl)methanone (25)



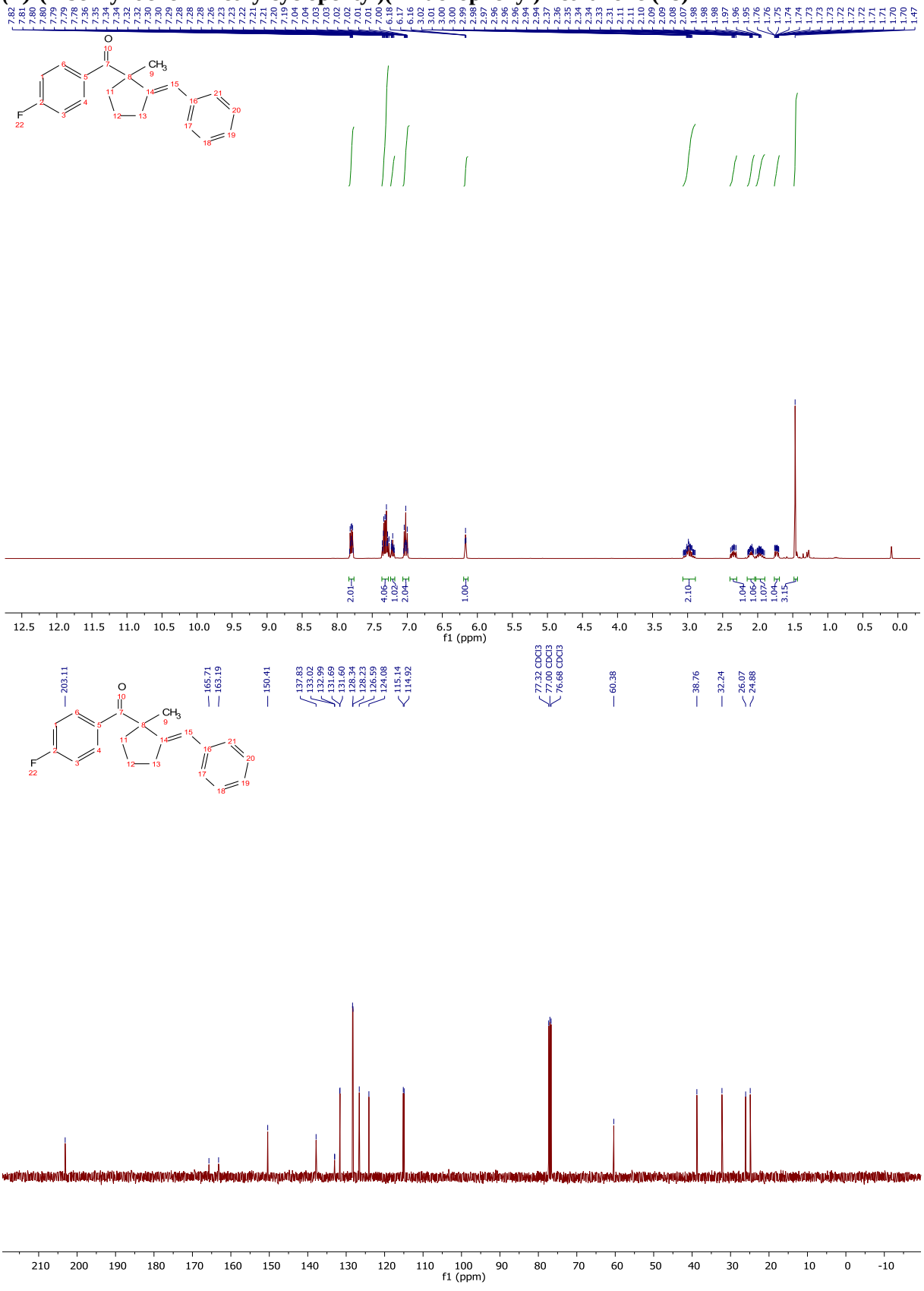
(E)-(2-(4-methoxybenzylidene)-1-methylcyclopentyl)(p-tolyl)methanone (26)



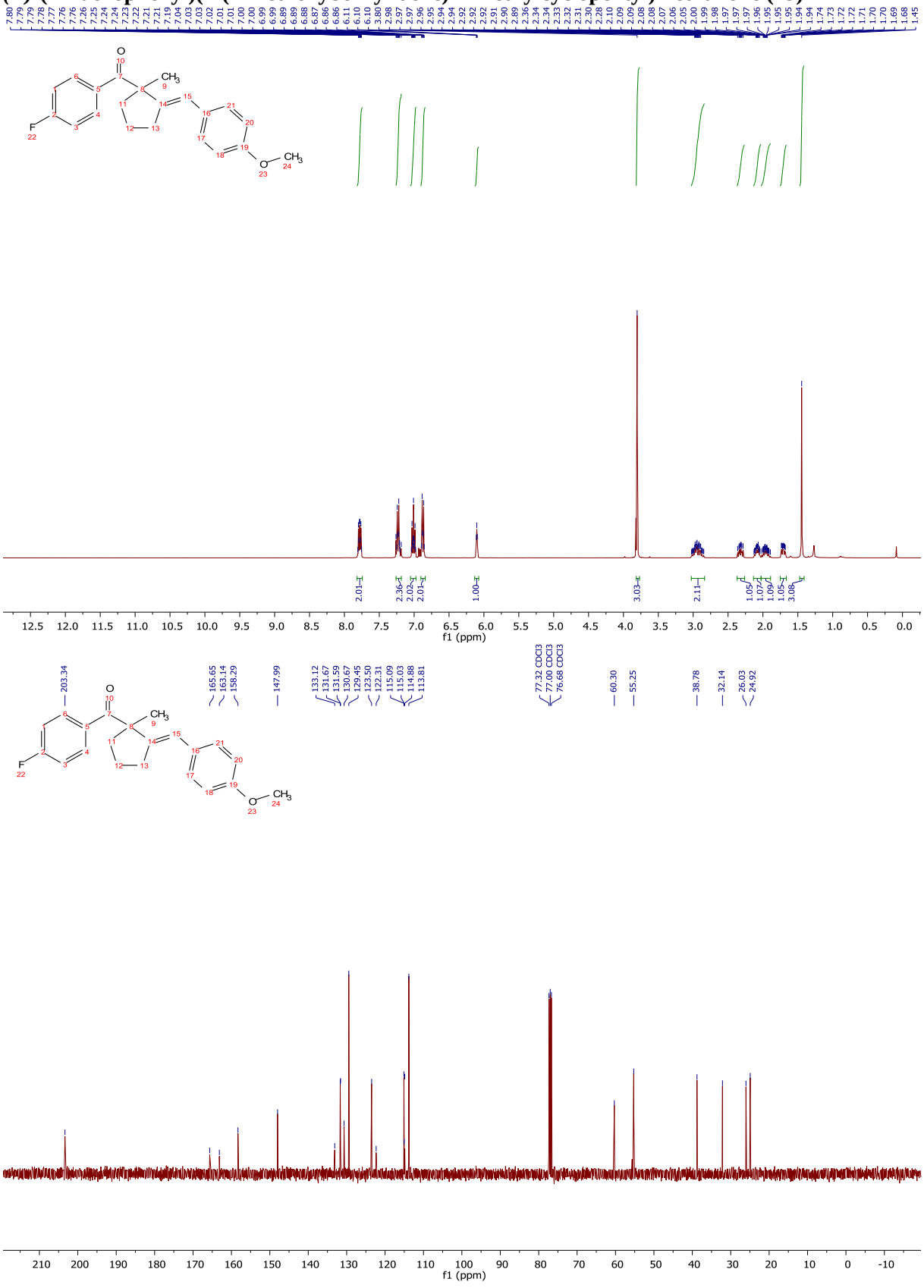
(*E*)-4-((2-methyl-2-(4-methylbenzoyl)cyclopentylidene)methyl)benzonitrile (27)



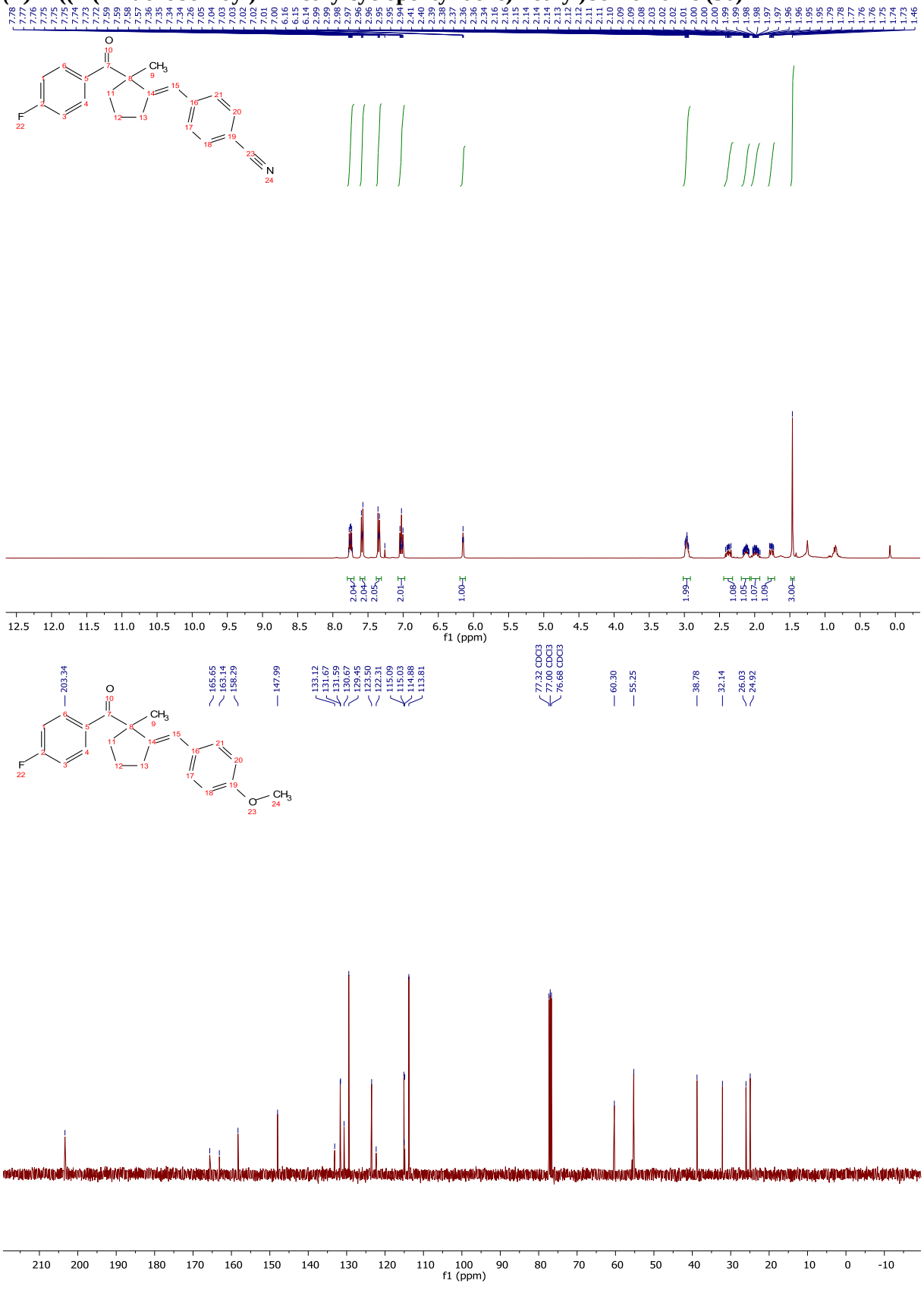
(E)-(2-benzylidene-1-methylcyclopentyl)(4-fluorophenyl)methanone (28)



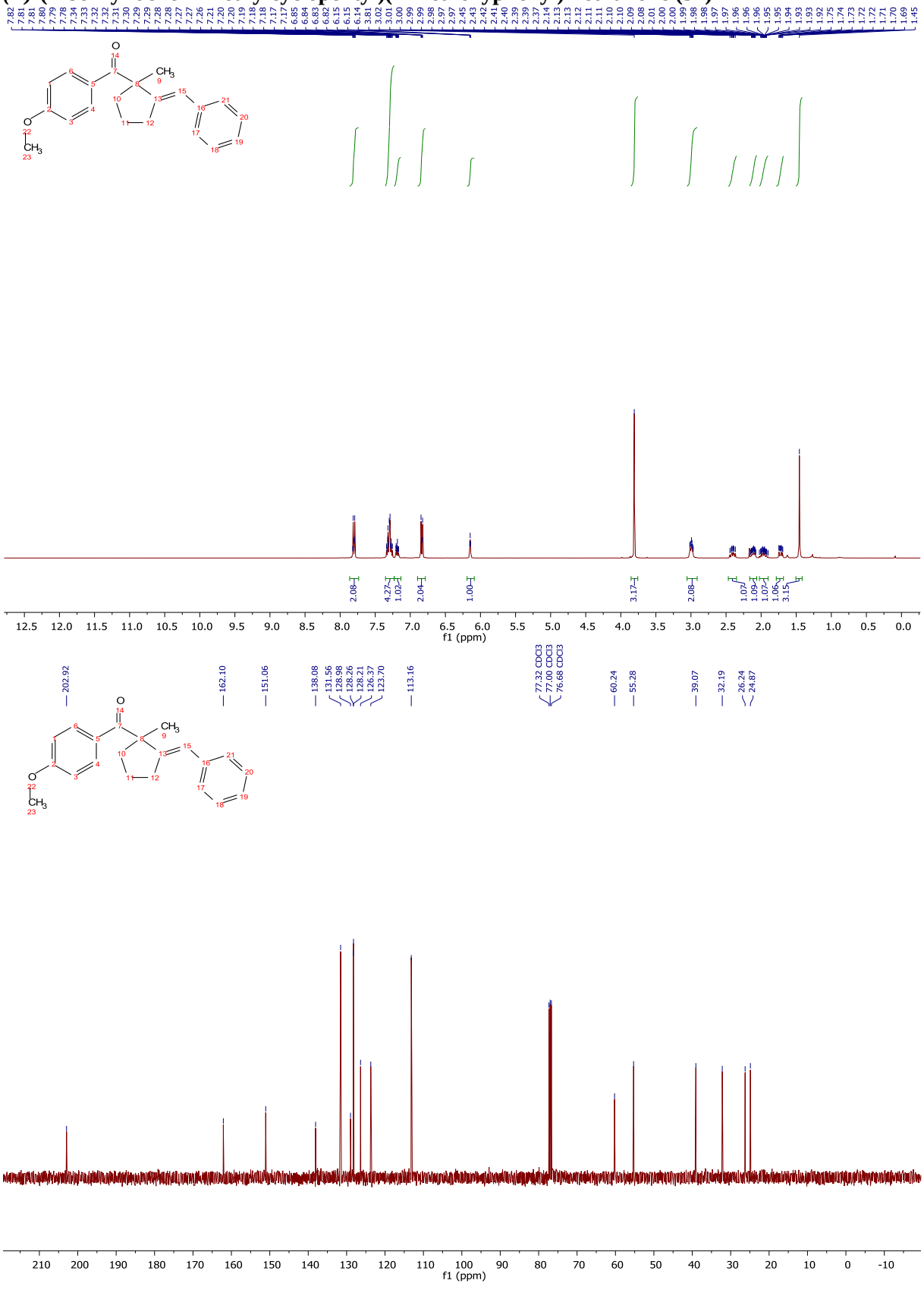
(E)-(4-fluorophenyl)(2-(4-methoxybenzylidene)-1-methylcyclopentyl)methanone (29)



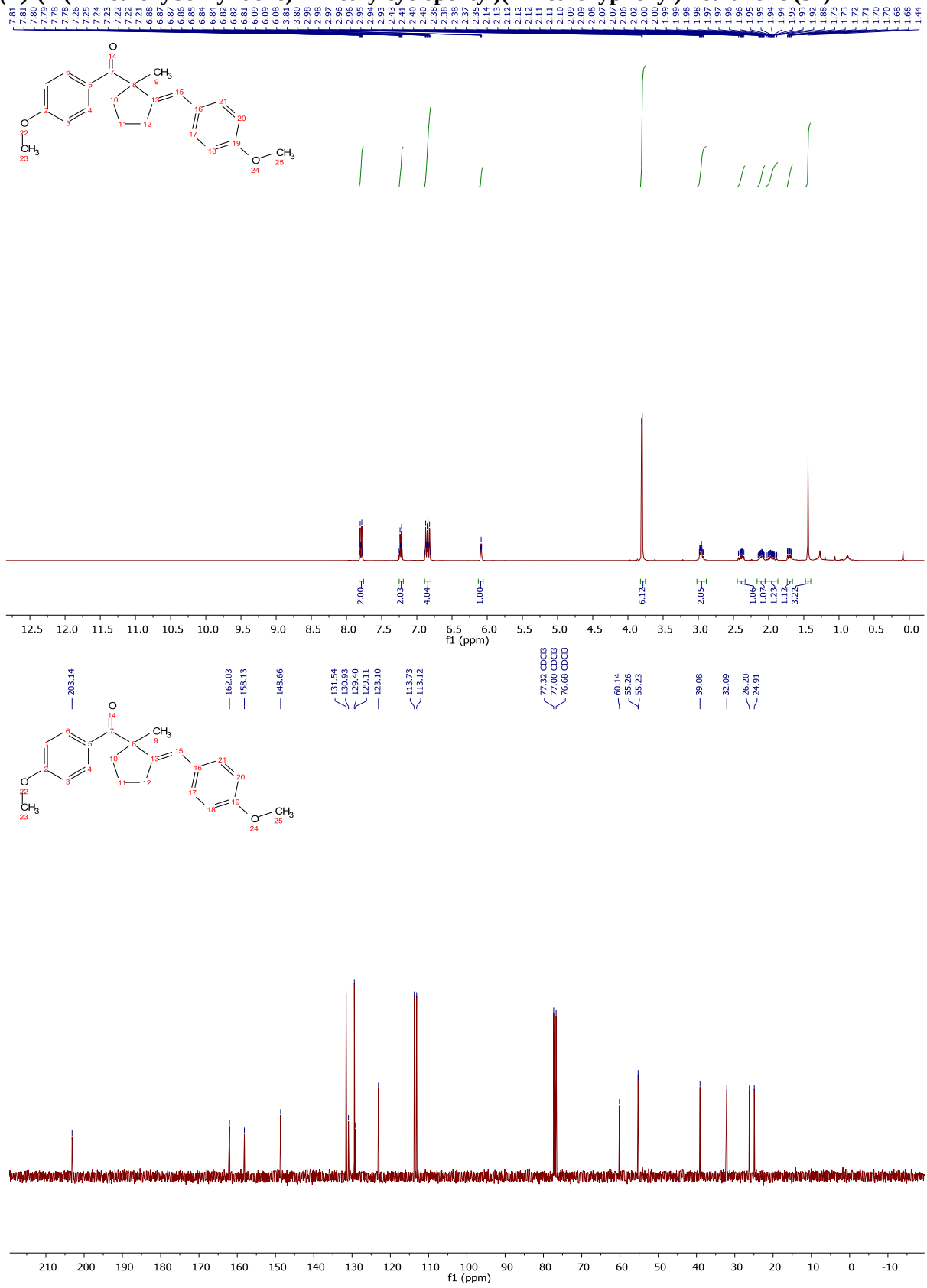
(E)-4-((2-(4-fluorobenzoyl)-2-methylcyclopentylidene)methyl)benzonitrile (30)



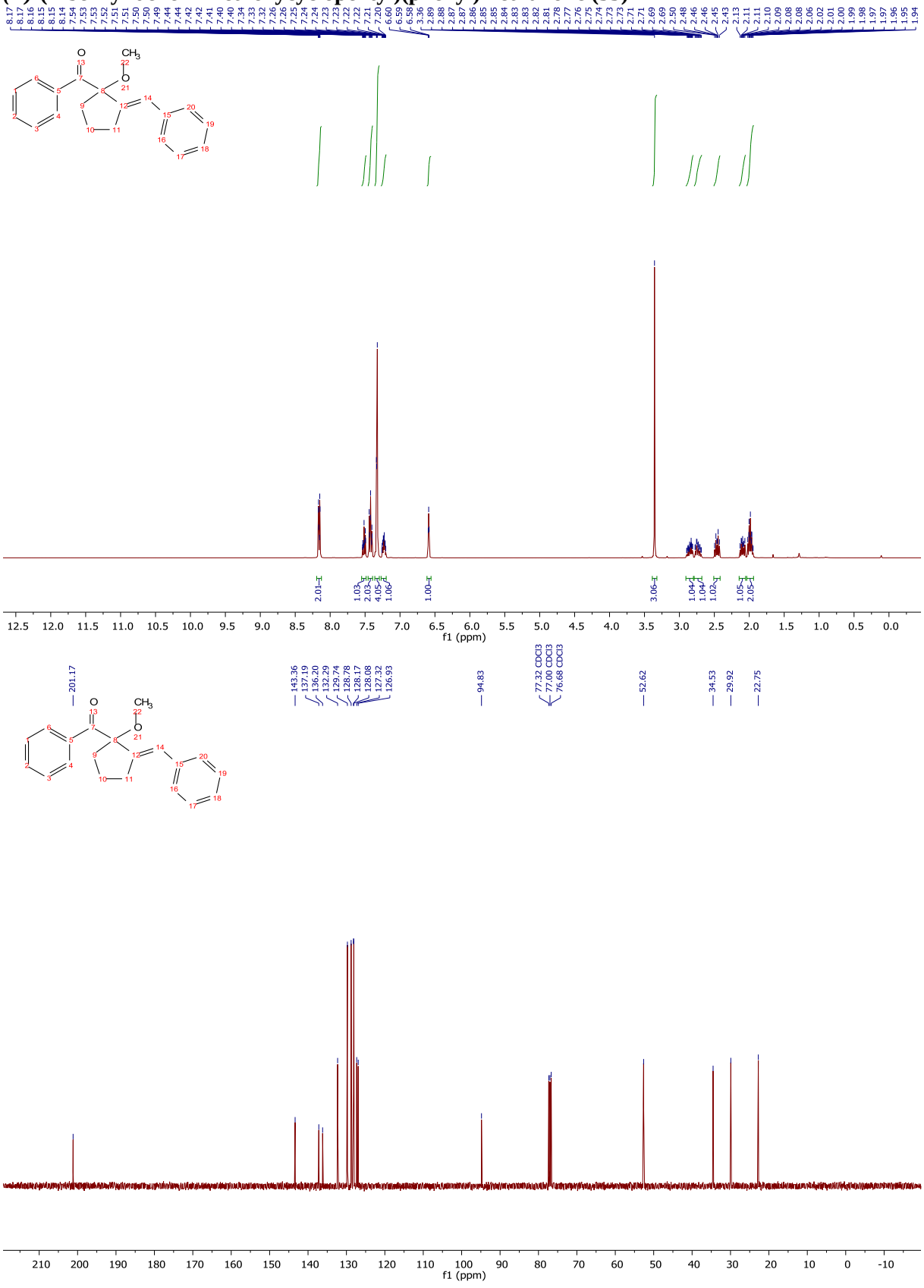
(E)-(2-benzylidene-1-methylcyclopentyl)(4-methoxyphenyl)methanone (31)



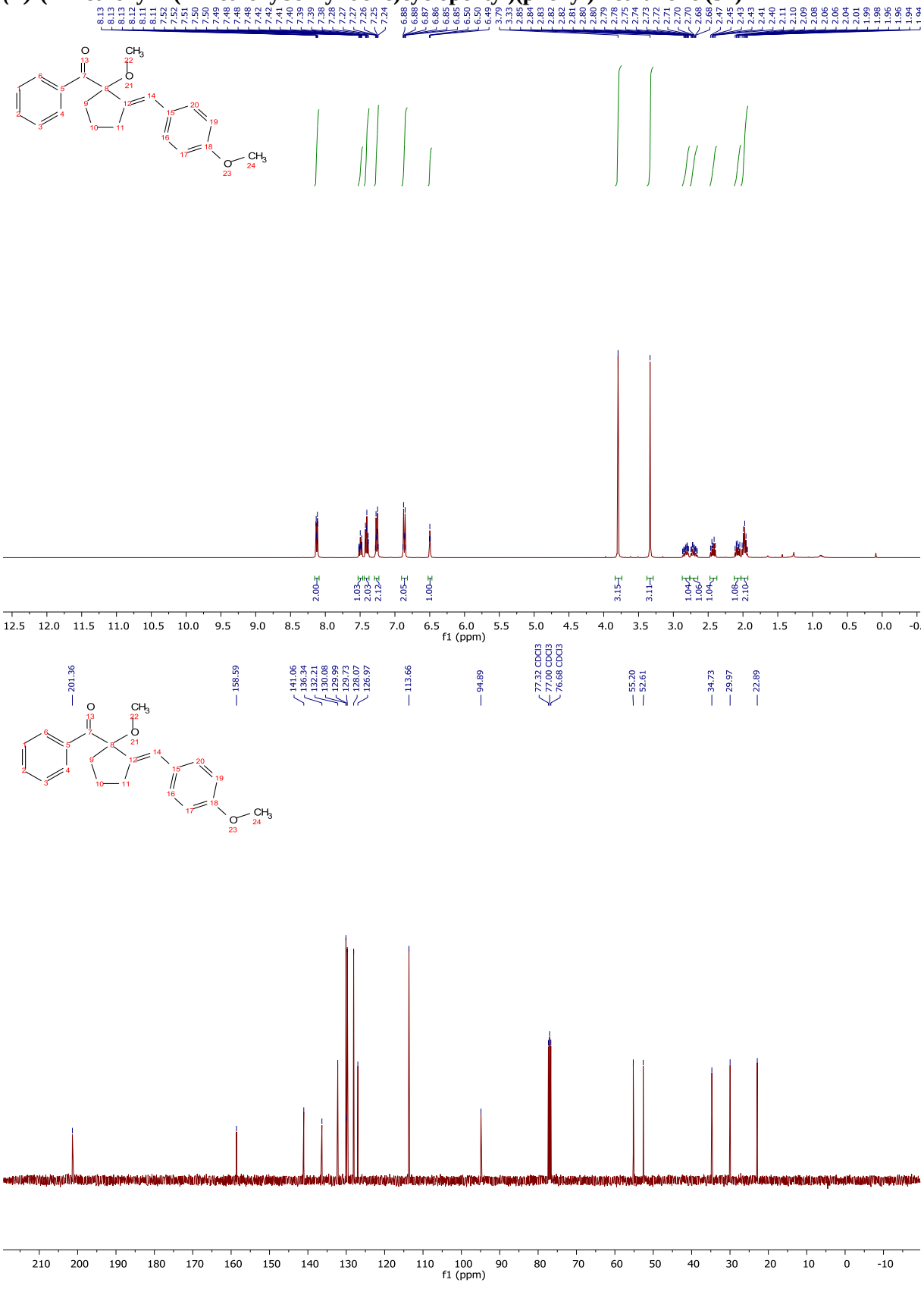
(E)-(2-(4-methoxybenzylidene)-1-methylcyclopentyl)(4-methoxyphenyl)methanone (32)



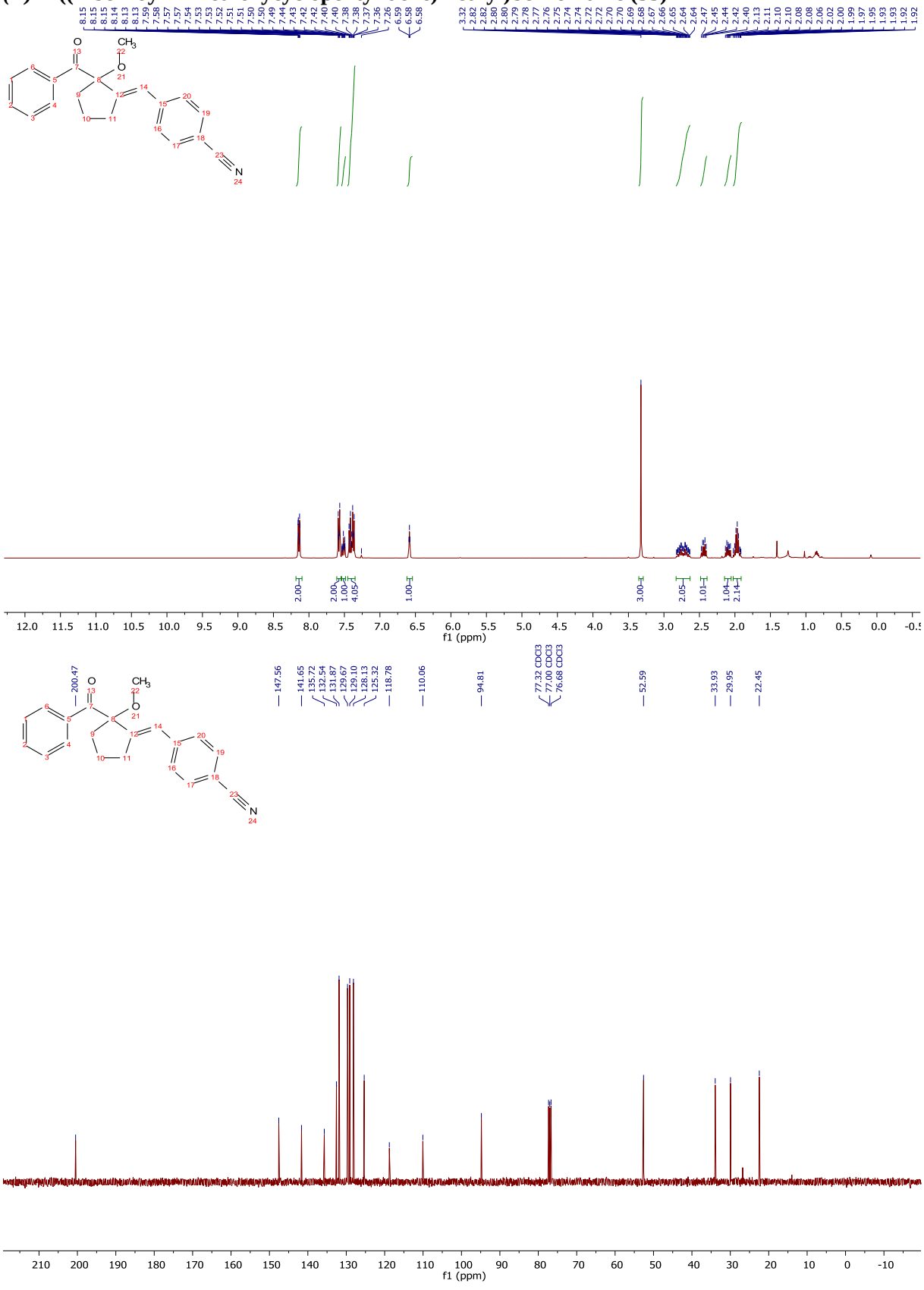
(E)-(2-benzylidene-1-methoxycyclopentyl)(phenyl)methanone (33)



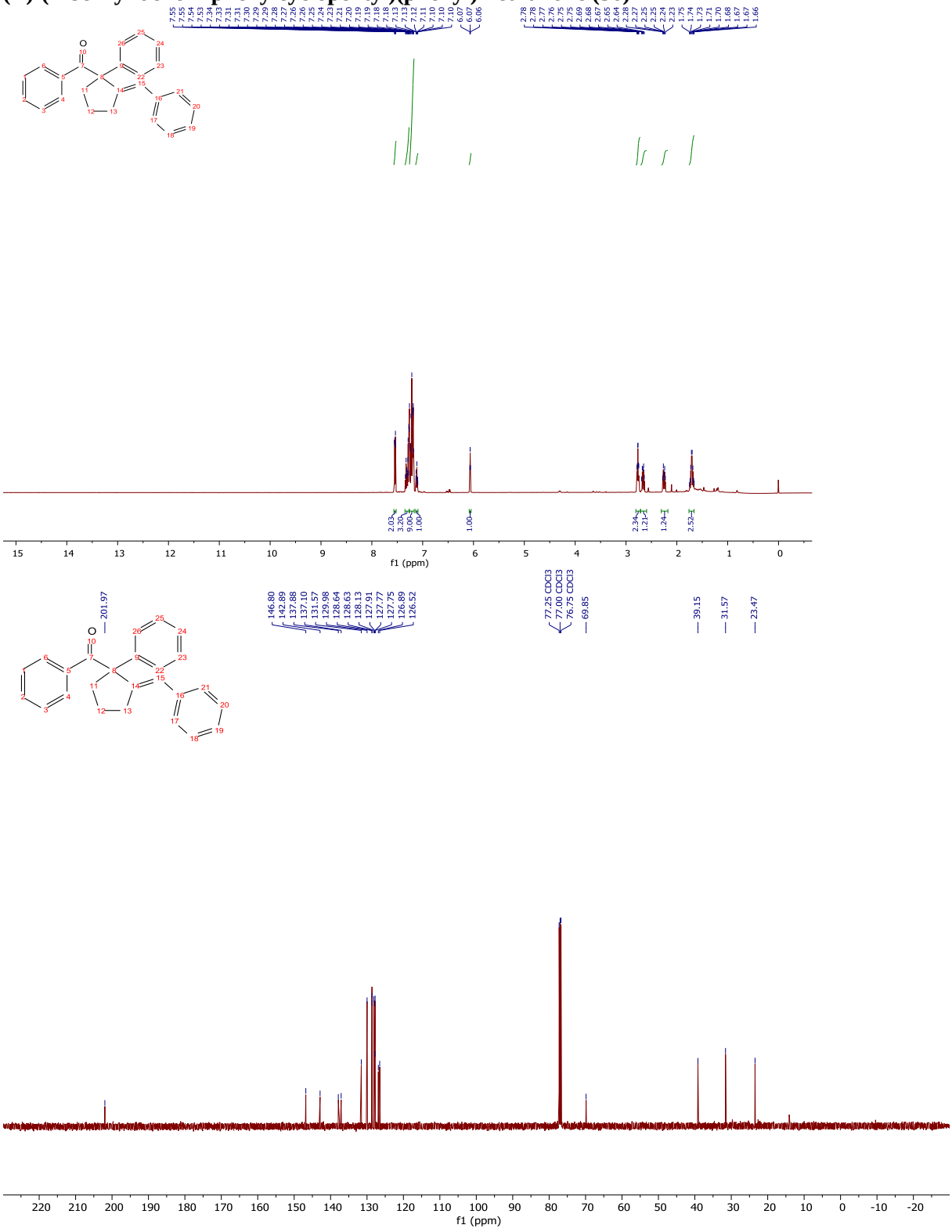
(*E*)-(1-methoxy-2-(4-methoxybenzylidene)cyclopentyl)(phenyl)methanone (34)



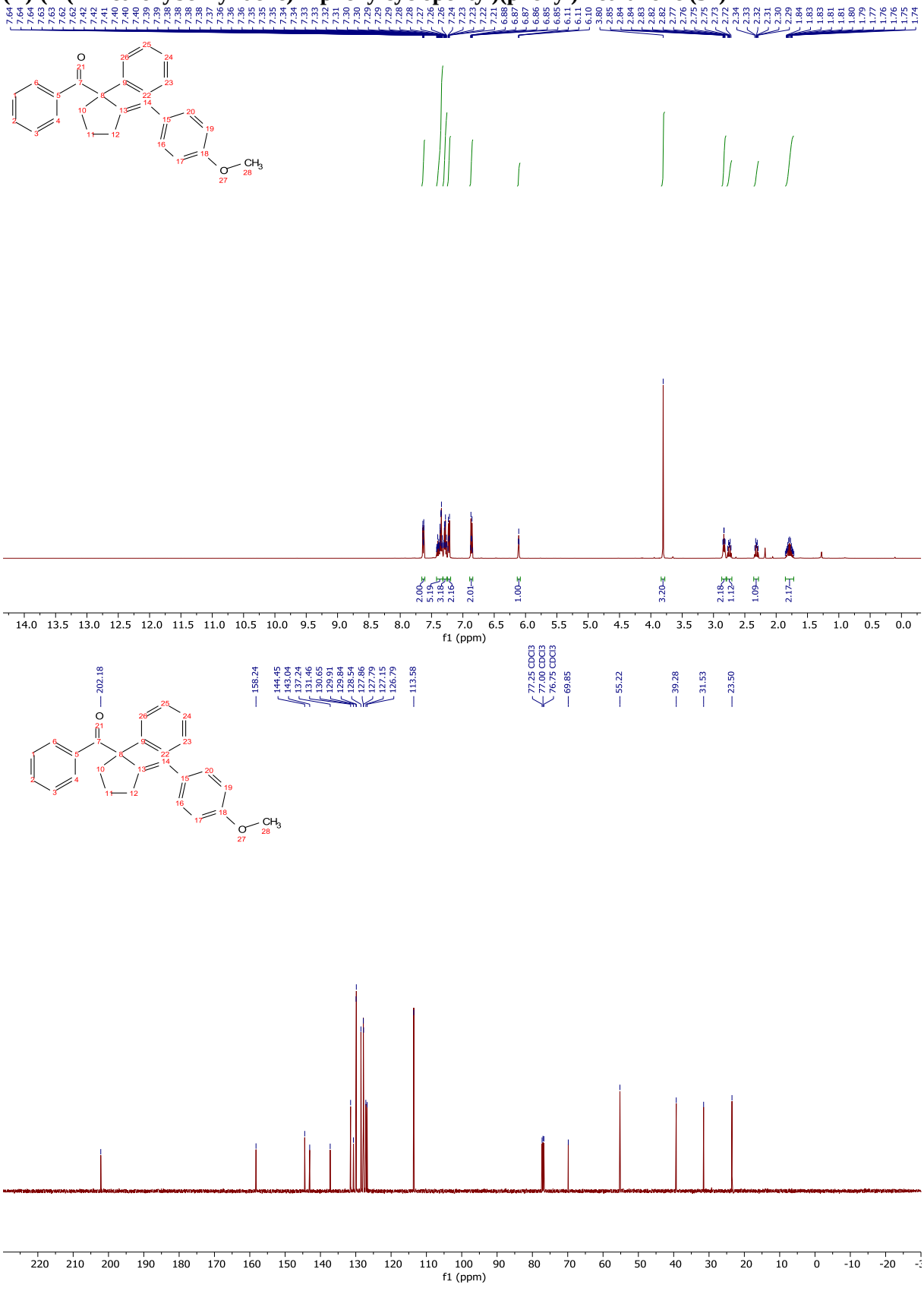
(*E*)-4-((2-benzoyl-2-methoxycyclopentylidene)methyl)benzonitrile (35)



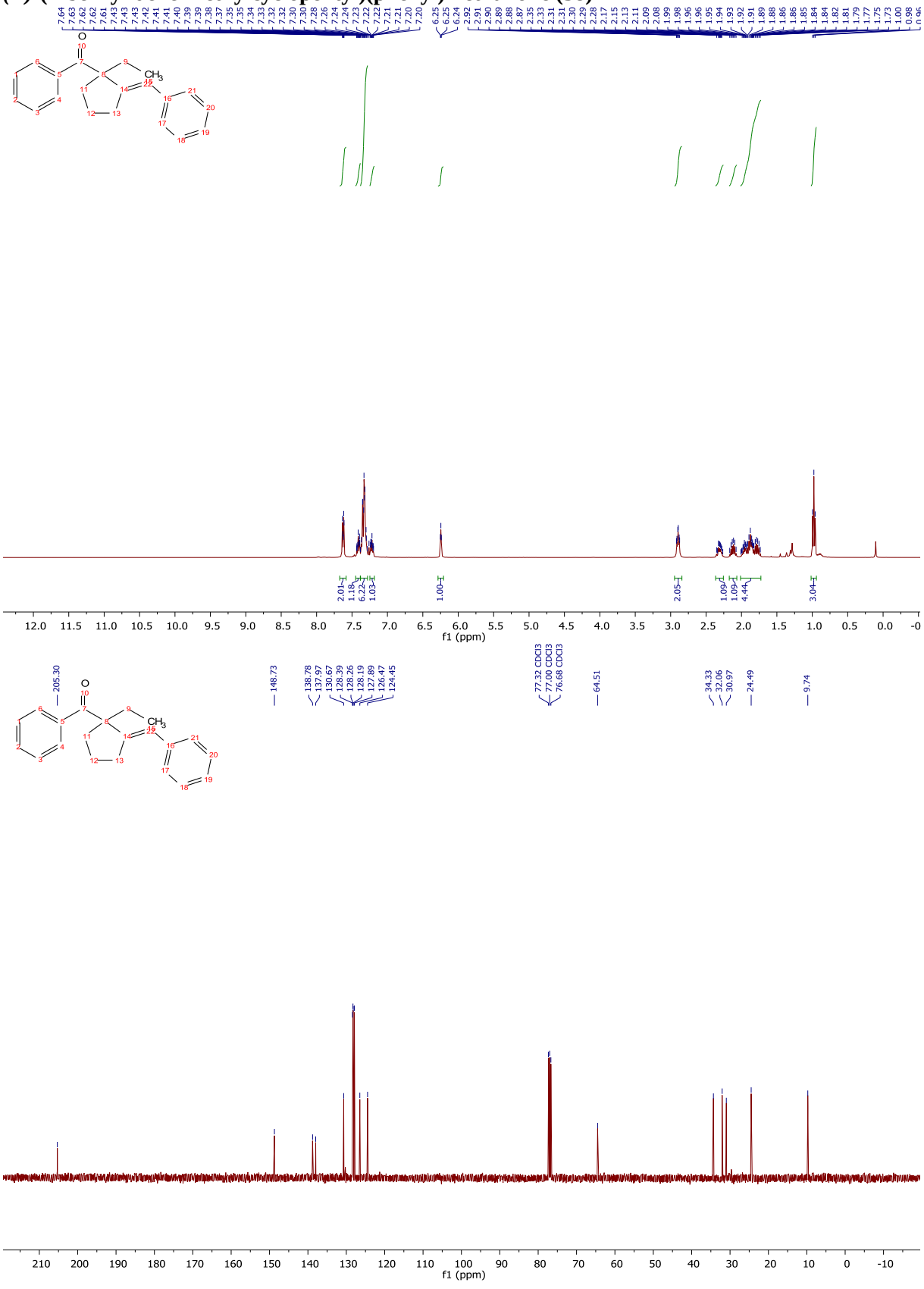
(*E*)-(2-benzylidene-1-phenylcyclopentyl)(phenyl)methanone (36)



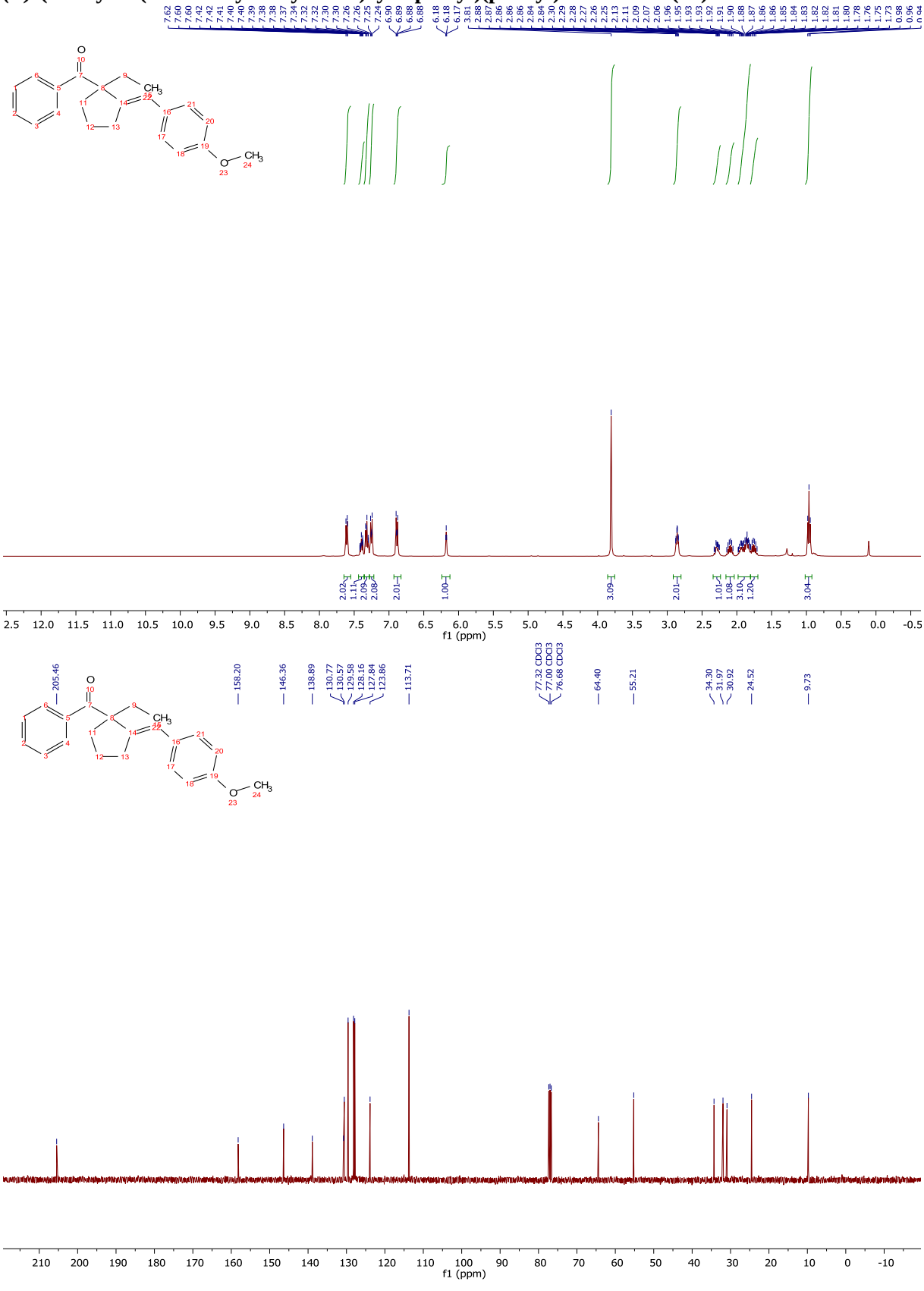
(*E*)-(2-(4-methoxybenzylidene)-1-phenylcyclopentyl)(phenyl)methanone (37)



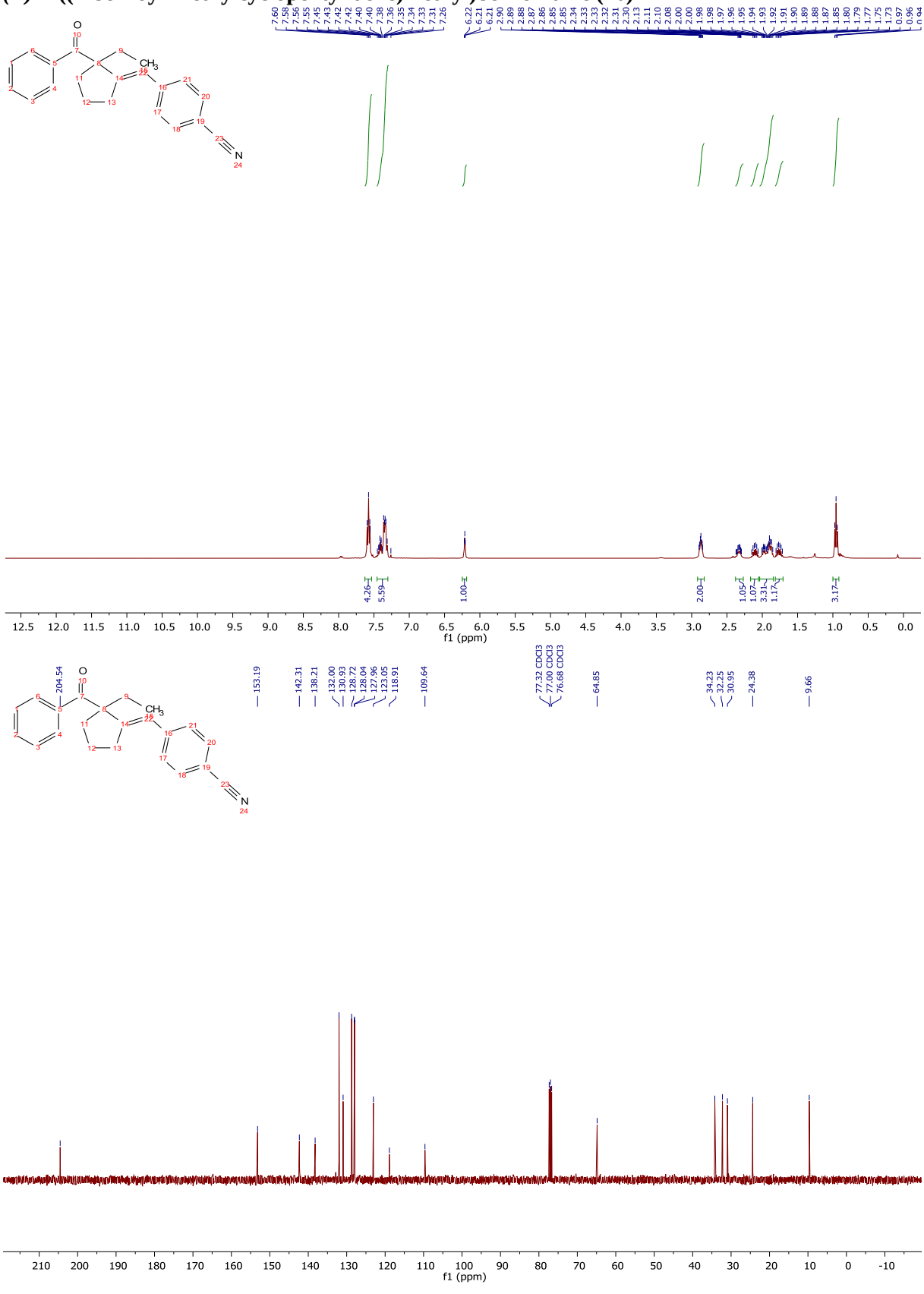
(*E*)-(2-benzylidene-1-ethylcyclopentyl)(phenyl)methanone (38)



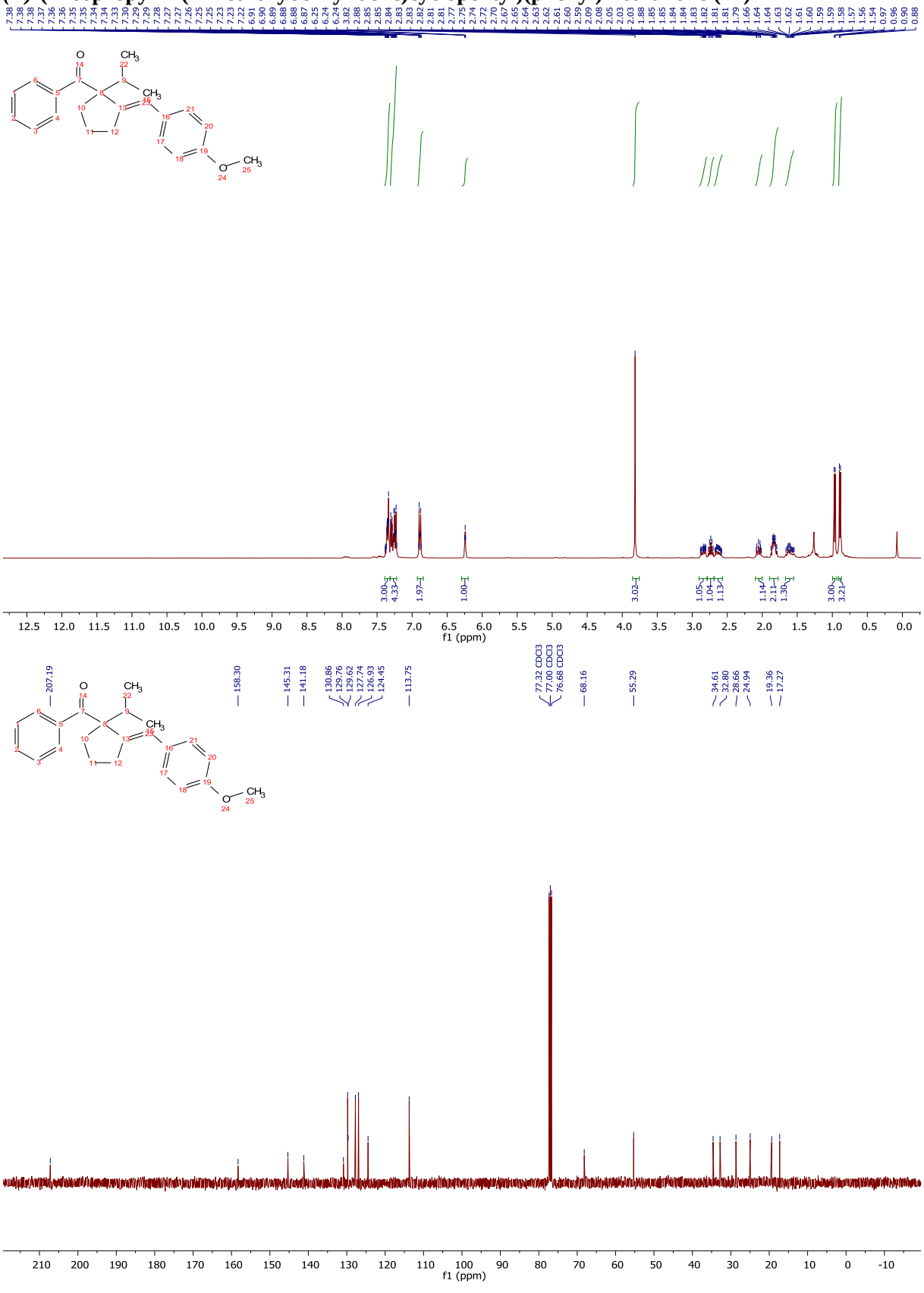
(E)-(1-ethyl-2-(4-methoxybenzylidene)cyclopentyl)(phenyl)methanone (39)



(E)-4-((2-benzoyl-2-ethylcyclopentylidene)methyl)benzonitrile (40)

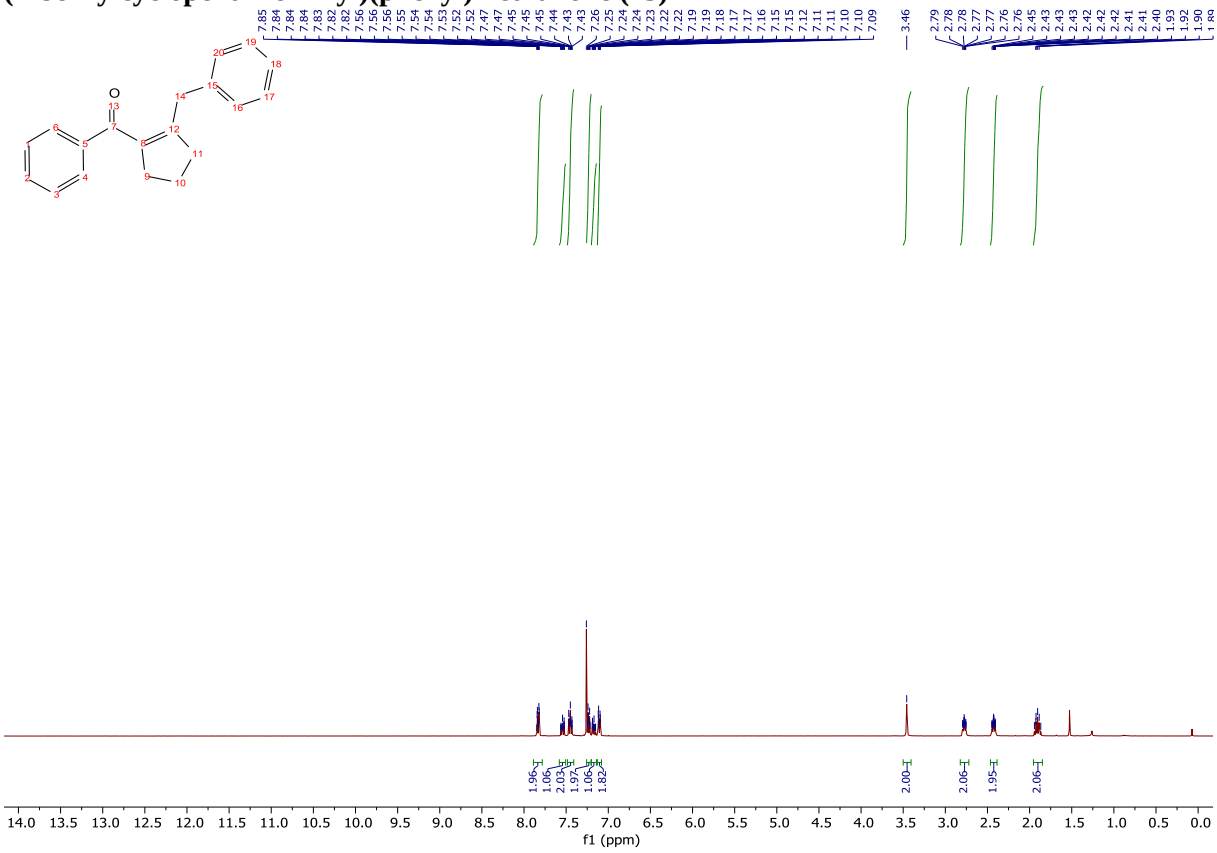


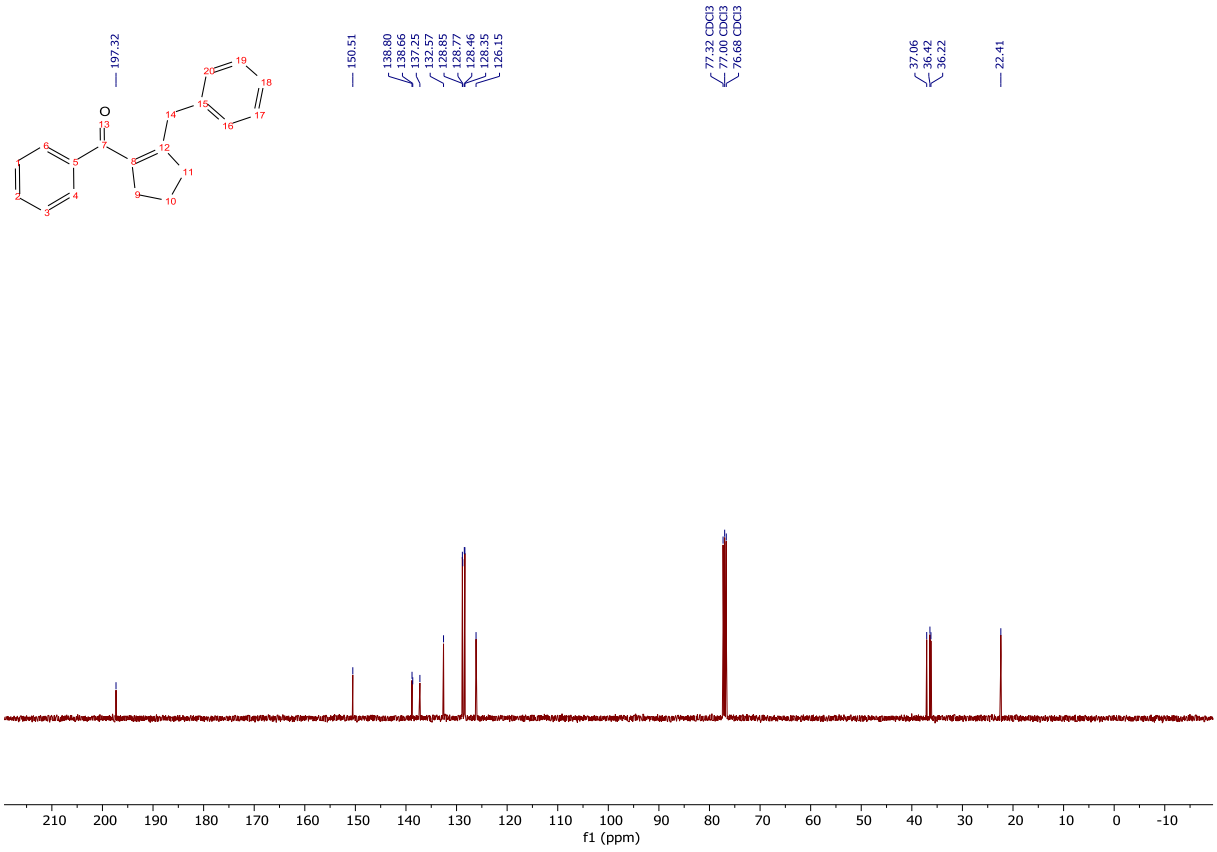
(E)-(1-isopropyl-2-(4-methoxybenzylidene)cyclopentyl)(phenyl)methanone (41)



(E)-1-(2-benzylidene-1-methylcyclopentyl)propan-1-one (42)

(2-benzylcyclopent-1-en-1-yl)(phenyl)methanone (43)





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