Supporting Information

Intramolecular cycloaddition/- rearrangement cascade from gold(III)-catalysed reactions of propargyl aryldiazoesters with cinnamyl imines

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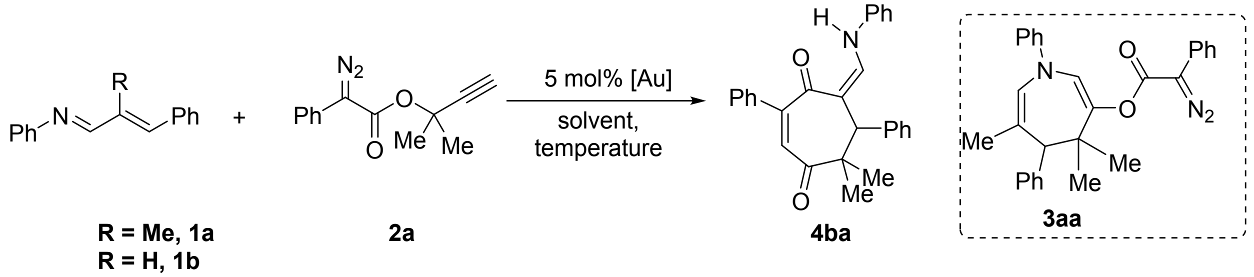
General Experimental Information

General: Unless noted all reactions were carried out under an inert atmosphere of dinitrogen in oven-dried glassware with magnetic stirring using freshly distilled solvents. All solvents were purified and dried using standard methods. Analytical thin layer chromatography (TLC) plates were purchased from EM Science (silica gel 60 F_{254} plates). High-resolution mass spectra (HRMS) were performed on a microTOF-ESI mass spectrometer using CsI as the standard. Accurate masses are reported for the molecular ion $[M+Cs]^+$, $[M+Na]^+$, or $[M+H]^+$. Melting points were determined on an Electrothermo Mel-Temp DLX 104 device and were uncorrected. Column chromatography was performed on CombiFlash® Rf 200 purification system using normal phase disposable columns. IR spectra were recorded using a Bruker Vector 22 spectrometer. The gold signals were imaged using Hitachi SU-70 Schottky field emission gun Scanning Electron Microscope (FEG-SEM) at an operation voltage 10 kV. All NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) or an Agilent spectrometer at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). The HPLC analyses for the kinetic studies were carried on Agilent Technologies HPLC (1260 series). Chemical shifts are reported in ppm with the solvent signals as reference (in $CDCl_3$ as solvent), and coupling constants (*J*) are given in Hertz (Hz). The peak information was described as: br = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite of magnetically non-equivalent protons. The wavelength of maximum absorbance and molar extinction coefficients measurements were performed on a Carey 50 Bio UV-Vis spectrometer (200-800 nm) in DCM at room temperature.

Materials: $AuCl(PPh_3)$, $Au(JohnPhos)SbF_6$, $IPrAuBF_4$ (IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene), and $PicAuCl_2$ (Pic = 2-pyridinecarboxylato) were purchased from Sigma-Aldrich; AuCl and $AuCl_3(Pyr)$ and other gold catalysts were purchased from Strem Chemicals. Unsaturated imines[1] and propargylic diazoesters[2] were prepared according to the literature procedures. All other chemicals were obtained from commercial sources and used as received without further purification.

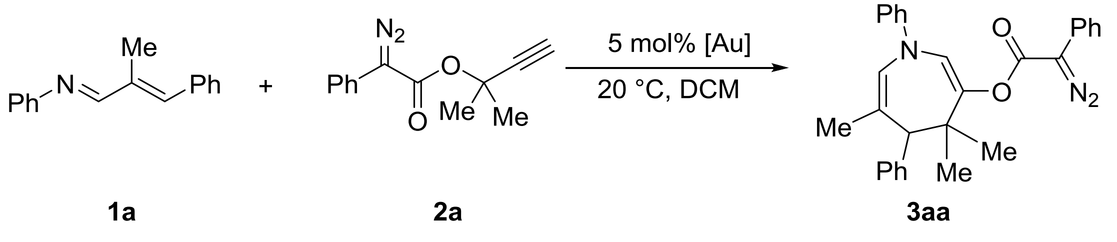
Initial Surveys and General Procedures

Initial attempts to form 3aa by the gold-catalyzed cycloaddition reaction of 1,1-dimethylpropargyl phenyldiazoacetate with unsaturated imines.



Procedure: To a flame-dried 10-mL Schlenk flask charged with a magnetic stirring bar, *N*-arylimine **1a** (or **1b**) (0.20 mmol), the stated solvent (2.0 mL) and catalyst (0.01 mmol) were sequentially added under a nitrogen atmosphere. Propargyl phenyldiazoester **2a** (0.24 mmol) dissolved in 2.0 mL of DCE was added in one portion into the solution under a flow of nitrogen. The reaction mixture was stirred for the stated time at the stated temperature. The color of the reaction mixture turned dark yellow to red as the reaction progressed; NMR spectral analyses portray a complex mixture of reaction products. The yield of **4ba** (or **3aa**) was determined by ^{1}H NMR spectroscopy using 2,4,6-trimethoxybenzaldehyde as an internal standard. Other catalysts that included $Pd(OAc)_2$, $(cod)_2(IrCl)_2$, $(Ph_3P)_3RuCl_2$, $Ru(acac)_3$ and $NiCl_2$ did not exhibit any reaction with **2a** in the presence of **1d** over 4 h.

Table S1. Catalyst survey in attempts to form **3aa**.

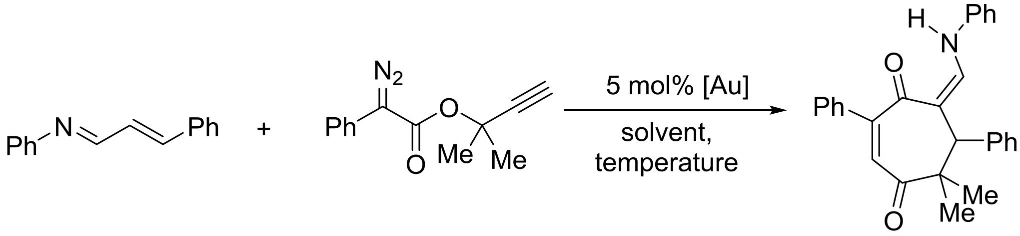


entry[a]	[Au]	time (h)	conversion of **2a**[b] (%)	yield of **3aa**[c] (%)
1	$PicAuCl_2$	0.5	>95	<5
2	$Au(JohnPhos)SbF_6$	2	>95	<5

3	IPrAuBF$_4$	2	>95	<5
4	AuCl$_3$(Pyr)	6	75	20
5	AuCl	2	>95	<5

[a]Reactions were performed with 5.0 mol% of the selected catalyst in 2.0 mL of solvent under a nitrogen atmosphere at 20 ºC, and the resulting reaction mixture was stirred for the stated time. [b]The percent conversion of **2a** was determined by ^{1}H NMR spectroscopy using 2,4,6-trimethoxy-benzaldehyde as an internal standard. [c]The yield of **3aa** was determined by ^{1}H NMR analyses of characteristic absorptions.

Table S2. Optimization of the gold-catalyzed reaction of propargyl phenyldiazoacetate **2a** with *trans*-cinnamyl-*N*-phenylimine **1b** for the formation of **4ba**.



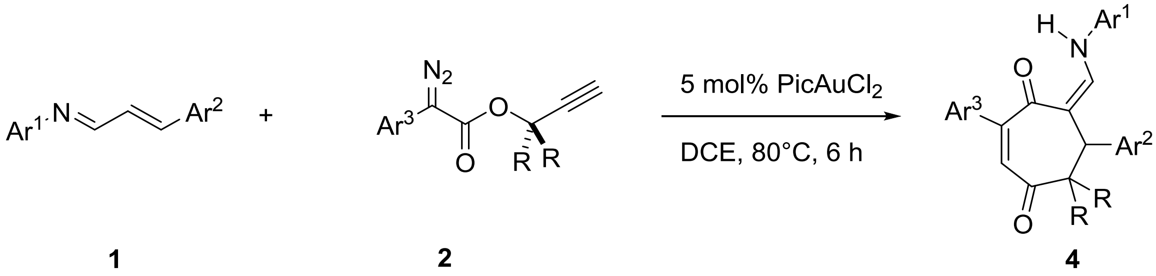
1b **2a** **4ba**

entry[a]	[Au]	temperature(ºC) /time (h)	solvent	conversion of **2a**[b] (%)	yield of **4ba**[c] (%)
1	PicAuCl$_2$	20/72	DCM	40	10
2	PPh$_3$AuSbF$_6$[d]	20/24	DCM	<10	<5
3	IPrAuBF$_4$[d]	20/24	DCM	<10	<5
4	[(2,4-^{t}Bu)$_2$C$_6$H$_3$O]$_3$PAuSbF$_6$[d]	20/24	DCM	<10	<5
5	AuCl	20/72	DCM	25	8
6	PicAuCl$_2$	40/48	DCE	60	31
7	PicAuCl$_2$	60/12	DCE	85	47
8	**PicAuCl$_2$**	**80/6**	**DCE**	**>95**	**65 (62)**[e]
9	PicAuCl$_2$	100/2	DCE	>95	57
10	PicAuCl$_2$	80/6	toluene	>95	25
11	PicAuCl$_2$	80/6	CH$_3$CN	80	38

12	$PicAuCl_2$	80/6	DMF	<20	<5

[a] Reactions were performed with 5.0 mol% of selected catalyst in 2.0 mL of the solvent under a nitrogen atmosphere at the stated temperature, and the resulting reaction mixture was stirred for the stated time. [b] The percent conversion of **2a** was determined by ^1H NMR spectroscopy using 2,4,6-trimethoxybenzaldehyde as an internal standard. [c] The yield of **4ba** was determined by ^1H NMR analyses of its characteristic absorptions. [d] Reactions performed at higher temperatures resulted in complex product mixtures.

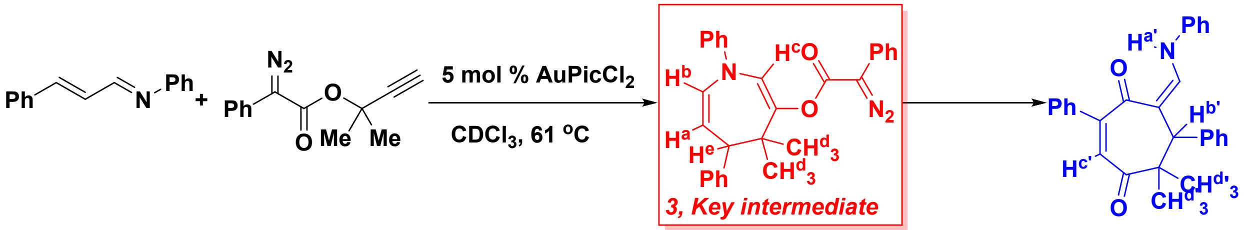
General procedure for the reactions of propargylic diazoesters with *N*-arylcinnamylimines catalyzed by $PicAuCl_2$:



To a flame-dried 10-mL Schlenk flask charged with a magnetic stirring bar, *N*-arylcinnamylimine **2** (0.20 mmol), DCE (2.0 mL) and $AuPicCl_2$ (3.9 mg, 0.010 mmol) were added sequentially under a nitrogen atmosphere. Propargyl diazoester **1** (0.24 mmol) dissolved in 2.0 mL of DCE was added in one portion into the solution under a flow of nitrogen. As the reaction progressed the color of the reaction mixture darkened considerably, and the presence of metallic gold was evident. The mixture was stirred for 6 h at 80 °C after which the solvent was evaporated, and products were purified by column chromatography (100:1 to 10:1 gradient of hexanes: ethyl acetate as eluents) to afford pure **4** as red solids or liquids.

Mechanistic Investigations

^{1}H-NMR study of the gold-catalyzed reaction of propargyl phenyldiazoacetate 2a with *N*-phenylcinnamylimine 1a.



1b **2a** **3ba** **4ba**

Procedure: To a clean 5 mm NMR tube, imine **1b** (0.050 mmol), CDCl$_3$ (0.30 mL) and AuPicCl$_2$ (0.95 mg, 0.0025 mmol) were sequentially added under a nitrogen atmosphere. Propargyl phenyldiazoacetate **2a** (0.060 mmol) dissolved in 0.3 mL of CDCl$_3$ was added in one portion into the solution. The resulting reaction mixture was heated to 61°C and monitored by ^{1}H NMR spectroscopy. The observed NMR spectral characterization data corresponds to those for the compounds reported by Toste and co-workers.[1]

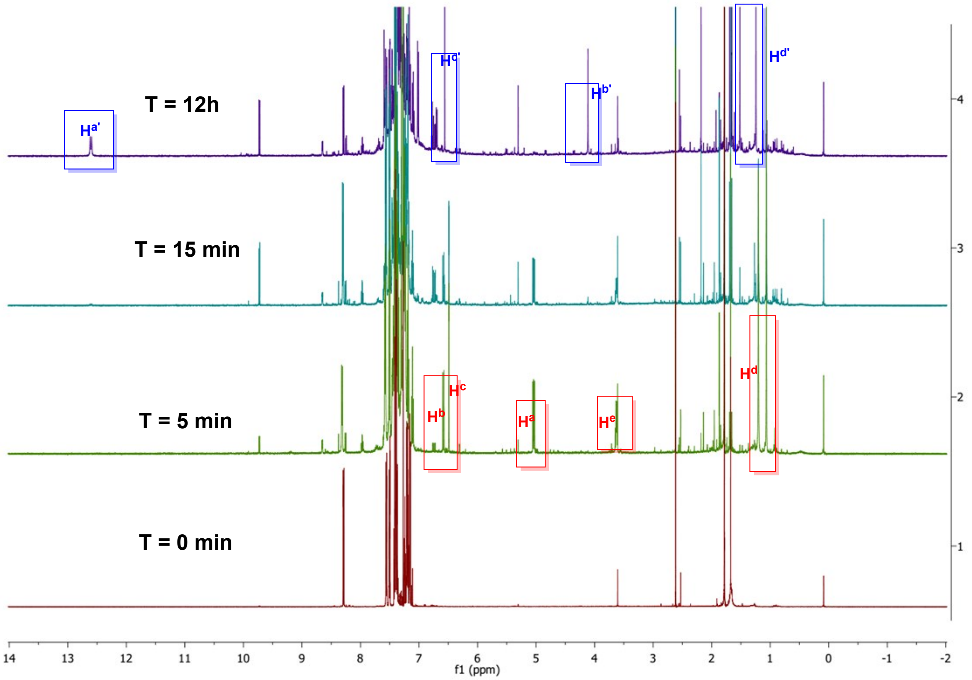
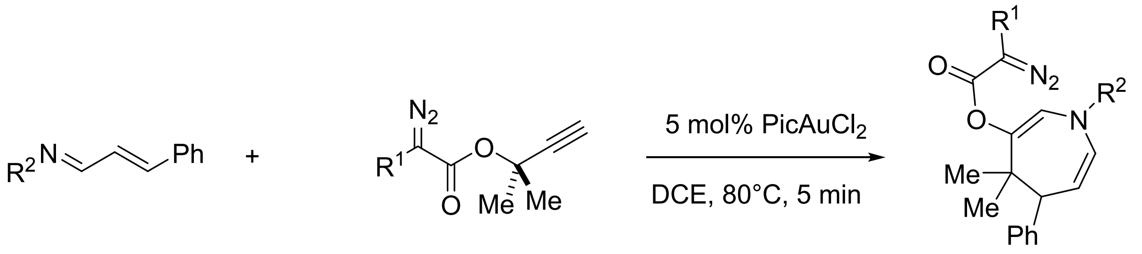


Figure S1. ^{1}H NMR Progress of the Gold-Catalyzed Reaction. Box Colors Denote the Compound Being Observed.

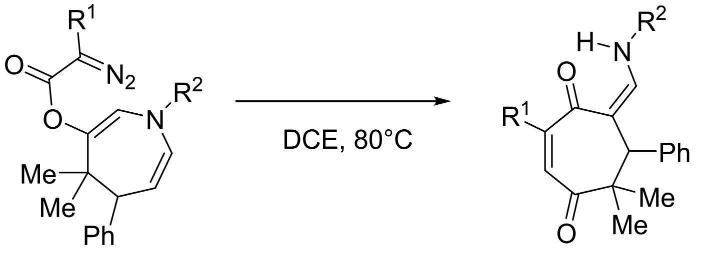
Isolation of 3cb and control experiment



1c **2b** **3cb**

R^1 = 4-MeOC$_6$H$_4$
R^2 = 4-HOC$_6$H$_4$

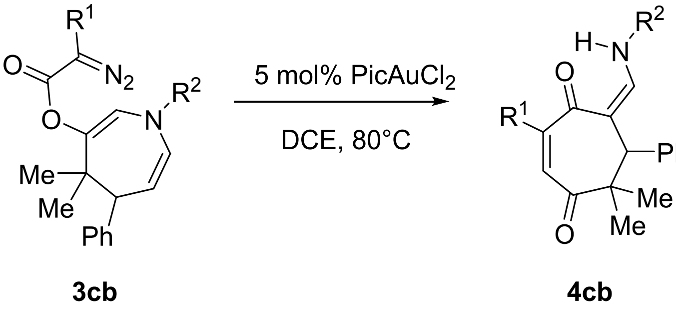
Procedure: To a flame-dried 10-mL Schlenk flask charged with a magnetic stir bar, *N*-arylcinnamylimine **1c** (0.20 mmol), DCE (2.0 mL) and AuPicCl$_2$ (3.9 mg, 0.010 mmol) were sequentially added under a nitrogen atmosphere. Propargyl diazoester **2b** (0.24 mmol) dissolved in 2.0 mL of DCE was added in one portion into the solution under the flow of nitrogen. The mixture was stirred for 5 min at 80 °C. As the reaction progressed the color of the reaction mixture darkened considerably, and the presence of metallic gold was evident. The reaction mixture was directly purified by column chromatography (100:1 to 10:1 gradient of hexanes: ethyl acetate as eluents) to afford pure **3cb** as a light-yellow oil in 36% isolated yield.



3cb **4cb**

R^1 = 4-MeOC$_6$H$_4$
R^2 = 4-HOC$_6$H$_4$

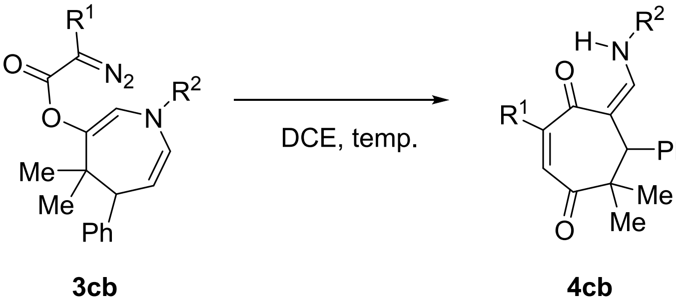
Procedure: To a flame-dried 10-mL Schlenk flask charged with a magnetic stir bar, **3cb** (0.10 mmol) dissolved in 2.0 mL of DCE was added under a nitrogen atmosphere. The reaction mixture was stirred for 6 h at 80 °C during which time the reaction solution turned the deep red color of the reaction product **4cb**. Solvent was evaporated, and the product was purified by column chromatography on a CombiFlash R_f instrument (100:1 to 10:1 gradient of hexanes: ethyl acetate as eluents) to afford pure **4cb** in 90% isolated yield.



R^1 = 4-MeOC$_6$H$_4$
R^2 = 4-HOC$_6$H$_4$

Procedure: To a flame-dried 10-mL Schlenk flask charged with a magnetic stir bar, **3cb** (0.1 mmol) dissolved in 2.0 mL of DCE and AuPicCl$_2$ (2.0 mg, 0.0050 mmol) were added under a nitrogen atmosphere. After 5 min at 80°C the reaction turned dark black, and the starting material **3cb** was completely consumed according to TLC analyses. The isolated yield of **4cb** was only 10%.

Kinetic Measurements



R^1 = 4-MeOC$_6$H$_4$
R^2 = 4-HOC$_6$H$_4$

Procedure: To a flame-dried 10.0 mL Schlenk flask charged with a magnetic stir bar, **3cb** (0.20 mmol) and 2,4,6-trimethoxybenzaldehyde (internal standard, 0.20 mmol) dissolved in 4.0 mL of DCE was added under nitrogen atmosphere. The reaction temperature stated here was the temperature of solvent. For every 5 (or 10) minutes, 0.05 mL was removed from the reaction mixture and dissolved in 1.0 mL of CH$_3$CN for HPLC analysis. The amount of **3cb** was determined by the analysis of HPLC traces of each aliquot. HPLC conditions: ZORBAX-C_{18}, ACN:H_2O = 90:10; 254 nm, 1 mL/min, 20 ºC, t_R for **3cb** was 2.50 min; t_R for 2,4,6-trimethoxybenzaldehyde was 0.82 min (normalized as “1000”); t_R for **4cb** was 1.54 min. [3]

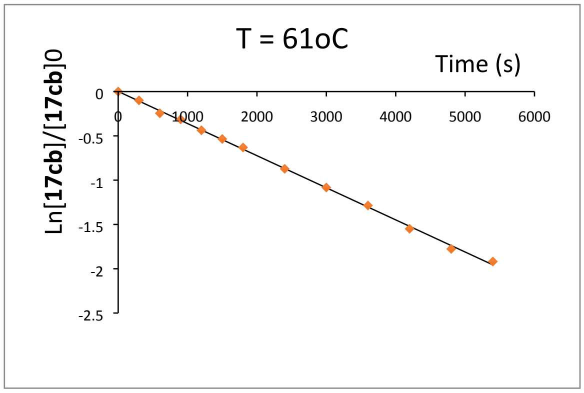


Figure S2 First-order Rate Determination at 61 ºC.

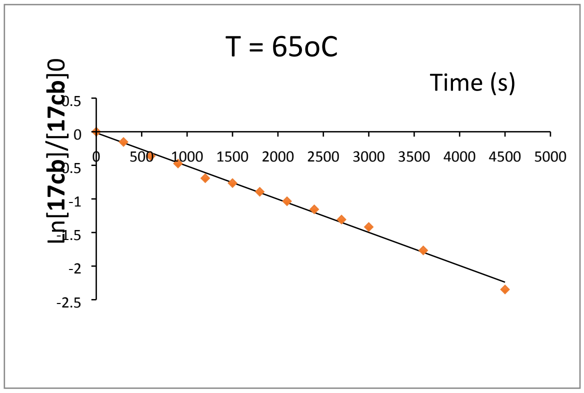


Figure S3 First-order Rate Determination at 65ºC.

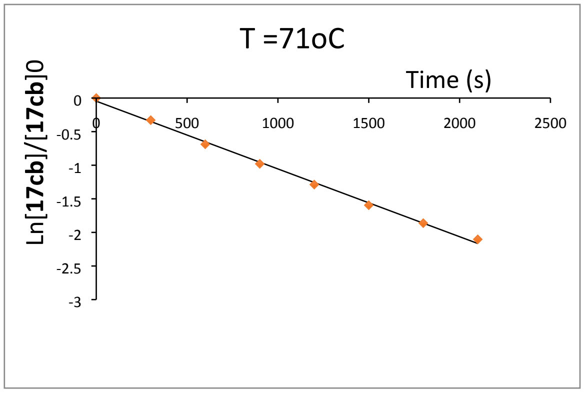


Figure S4 First-order Rate Determination at 71 ºC.

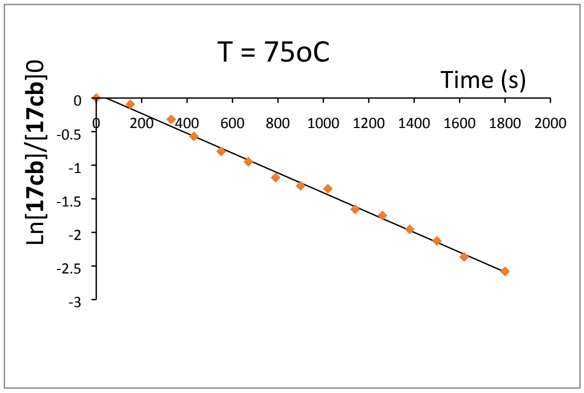


Figure S5 First-order Rate Determination at 75ºC.

Table S3. Data for Arrhenius plot.

lnk	-6.5225	-6.8978	-7.6211	-7.9294
1/T	0.002864	0.002906	0.002957	0.002993

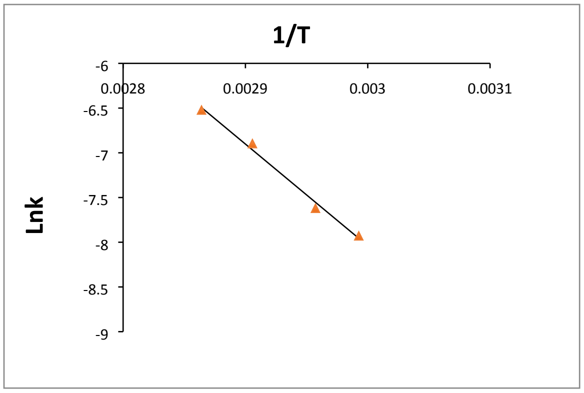


Figure S6. Arrhenius Plot: Activation Energy for the conversion of **3cb** to **4cb**.

The Role of the Unsaturated Imines in Cycloheptene-1,4-dione-enamine Formation

The [4+3]-cycloaddition product **3cb** undergoes a metal free rearrangement to form **4b**. However, the AuPicCl$_2$ catalyst, which is capable of undergoing dinitrogen extrusion from the [4+3]-cycloaddition product **3cb** or reacting with **3cb** by other means, exists in the reaction mixture. We speculated that there is a base, whose coordination with the catalyst prevented the gold species from decomposing the [4+3]-cycloaddition product **3cb**. Several control experiments were carried out, and four types of bases were tested in the presence of 5 mol% AuPicCl$_2$. From the results in Table S4 the following conclusions can be made: (a) adding base increased the yields of **4cb**; and (b) decreasing the amount of base resulted in a decreasing the yield of **4cb**. These results supported the conclusion that the imines also served as a ligand for gold, which assists in the formation of **4cb** in presence of 5.0 mol% AuPicCl$_2$. We also found the formation of metallic gold in the presence of imines (**A$_2$** to **A$_4$**), which was confirmed by a SEM (Scanning Electron Microscope) of the solid obtained from the reaction mixture after filtration.

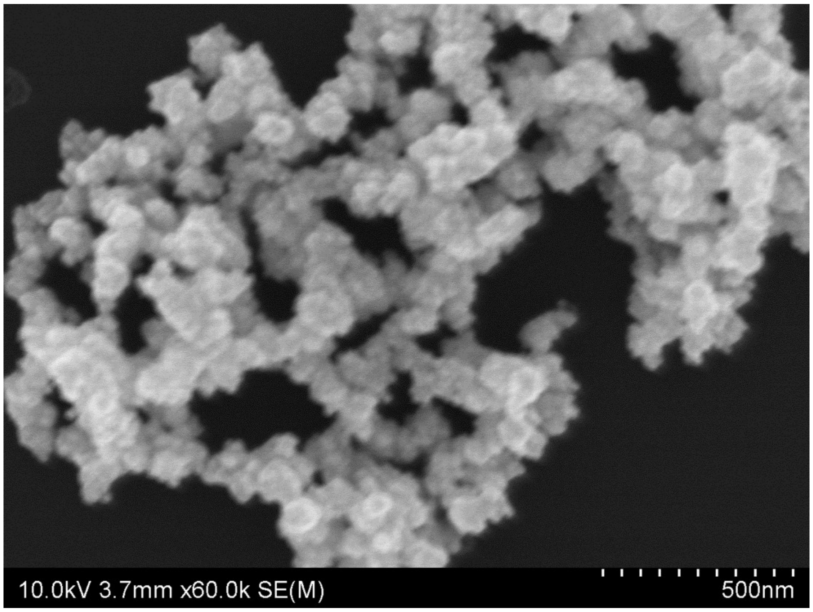
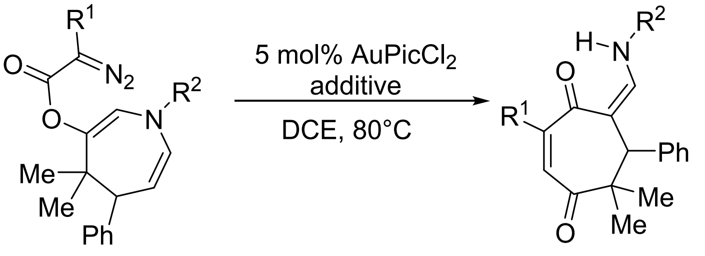


Figure S7. Representative SEM of metallic gold obtained from the reaction of **1b** and **2a** under optimized reaction conditions (Table S2, entry 8). After the reaction solution was cooled to roon temperature for 1h, the reaction mixture was filtered, and washed with methanol for 3 times. The black solid (metallic gold) was submitted to SEM analysis.

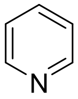
Table S4. Control Experiments



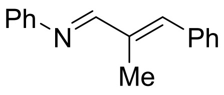
3cb

4cb

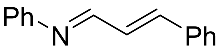
R^1 = 4-MeOC$_6$H$_4$
R^2 = 4-HOC$_6$H$_4$



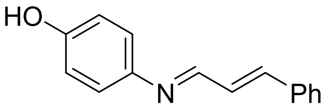
A1



A2



A3

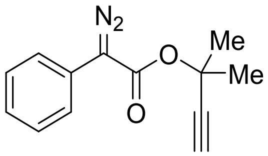


A4

entry[a]	additive	equiv of additive (mol%)	^{1}H NMR yield (%)
1	A1	50	56
2	A2	50	40
3	A3	50	72
4	A4	50	73
5	A4	40	69
6	A4	30	63
7	A4	20	55
8	A4	10	45

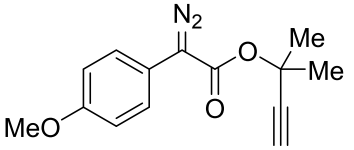
[a]Reactions were performed on a 0.05 mmol scale: a solution of **3cb** (0.05 mmol) in 0.5 mL DCE was added to a solution of the stated amount of additive and 5.0 mol% of $PicAuCl_2$ in 0.5 mL of DCE under a nitrogen atmosphere at 20 °C. The resulting reaction mixture was stirred at 80 ºC for 6 h. Yield was determined by ^{1}H NMR analyses of characteristic absorptions.

Characterization Data for New Compounds



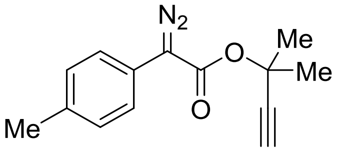
2a

2-Methylbut-3-yn-2-yl Phenyldiazoacetate 2a: 80% yield. Yellow solid, m.p. 70.2 – 71.4℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 1H), 2.62 (s, 1H), 1.78 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.45, 128.84, 125.75, 125.44, 123.96, 84.51, 72.84, 72.77, 29.21. IR (neat) 2082, 1701, 1286, 1145 cm^{-1}; HRMS (ESI) m/z calculated for $C_{13}H_{12}N_2O_2Na^+$ [M+Na]+ 251.0791, found: 251.0796.



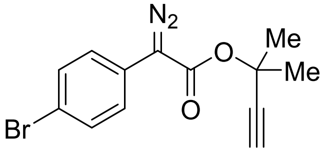
2b

2-Methylbut-3-yn-2-yl (4-Methoxyphenyl)diazoacetate 2b: 75% yield. Red solid, 67.0 – 68.5℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 9.1 Hz, 2H), 6.93 (d, *J* = 9.1 Hz, 2H), 3.80 (s, 3H), 2.59 (s, 1H), 1.76 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.03, 158.00, 125.89, 116.87, 114.54, 84.62, 72.71, 72.68, 55.34, 29.24. IR (neat) 2084, 1702, 1127, 903 cm^{-1}; HRMS (ESI) m/z calculated for $C_{14}H_{14}N_2O_3Na$ [M+Na]$^+$ 281.0897, found: 281.0900.



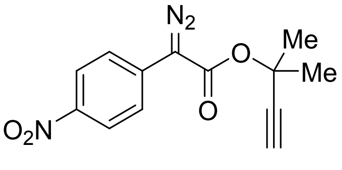
2c

2-Methylbut-3-yn-2-yl *p*-Tolyldiazoacetate 2c: 78% yield. Yellow solid, 58.0 – 59.2℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 2.61 (s, 1H), 2.35 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.70, 135.60, 129.57, 124.08, 122.07, 84.58, 72.70, 29.22, 20.95. IR (neat) 2083, 1702, 1124, 906 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{14}N_2O_2Na^+$ [M+Na]$^+$ 265.0947, found 265.0953.



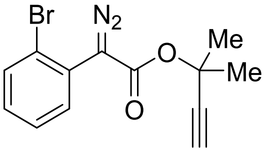
2d

2-Methylbut-3-yn-2-yl (4-Bromophenyl)diazoacetate 2d: 82% yield. Yellow solid, 90.1 – 91.5℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 2.62 (s, 1H), 1.77 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.08, 131.93, 125.33, 124.69, 119.28, 84.35, 73.12, 72.93, 29.20. IR (neat) 2087, 1703, 1126, 907 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{12}N_2O_2BrNa^+$ [M+Na]$^+$ 328.9896, found 328.9891.



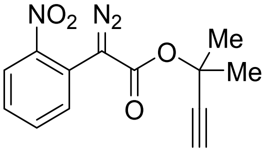
2e

2-Methylbut-3-yn-2-yl (4-Nitrophenyl)diazoacetate 2e: 65% yield. Yellow solid, 107.2 – 108.5℃. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.22 (d, *J* = 7.1 Hz, 2H), 7.68 (d, *J* = 7.1 Hz, 2H), 2.64 (s, 1H), 1.80 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.98, 145.00, 133.85, 124.19, 123.18, 84.00, 73.78, 73.28, 29.14. IR (neat) 2095, 1710, 1334, 904 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}N_3O_4Na^+$ [M+Na]$^+$ 296.0642, found 296.0634.



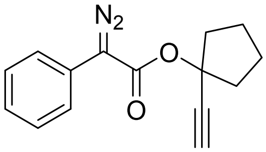
2f

2-Methylbut-3-yn-2-yl (2-Bromophenyl)diazoacetate 2f: 65% yield. Yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.35 (dd, *J* = 8.0, 7.7 Hz, 1H), 7.18 (dd, *J* = 7.8, 7.7 Hz, 1H), 2.60 (s, 1H), 1.74 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.58, 133.16, 132.73, 129.81, 127.44, 125.55, 124.13, 84.39, 72.88, 72.68, 29.05. IR (neat) 2091, 1699, 1117, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{12}N_2O_2BrNa^+$ [M+Na]$^+$ 328.9896, found 328.9893.



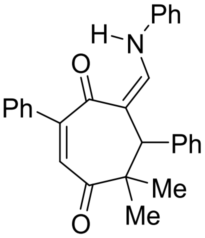
2g

2-Methylbut-3-yn-2-yl (2-Nitrophenyl)diazoacetate 2g: 52% yield. Yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.63 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.46 (dd, *J* = 8.2, 2.3 Hz, 1H), 2.58 (s, 1H), 1.70 (s, 7H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 162.94, 147.17, 133.12, 130.96, 128.74, 125.60, 121.01, 84.18, 73.74, 72.94, 28.97. IR (neat) 2085, 1702, 1513, 1259, 903 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}N_3O_4Na^+$ [M+Na]$^+$ 296.0642, found 296.0637.



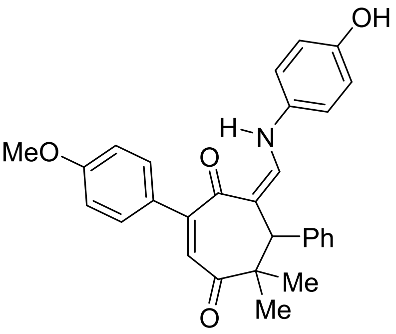
2h

1-Ethynylcyclopentyl Phenyldiazoacetate 2h: 81% yield. Yellow solid, m.p. 31.8 – 33.0°C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.52 – 7.47 (m, 2H), 7.39 – 7.35 (m, 2H), 7.20 – 7.15 (m, 1H), 2.64 (s, 1H), 2.37 – 2.30 (m, 2H), 2.27 – 2.20 (m, 2H), 1.82 – 1.76 (m, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.64, 128.84, 125.75, 125.37, 123.91, 83.97, 81.27, 73.36, 40.59, 23.32. IR (neat) 2081, 1701, 1598, 1286, 907 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{14}N_2O_2Na^+$ [M+Na]$^+$ 277.0947, found 277.0946.



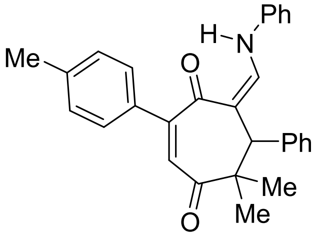
4ba

(*Z*)-5,5-Dimethyl-2,6-diphenyl-7-[(phenylamino)methylene]cyclohept-2-ene-1,4-dione 4ba: 63% yield. Red viscous oil. TLC R$_f$ = 0.3 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.60 (d, *J* = 12.3 Hz, 1H), 7.58 (d, *J* = 12.3 Hz, 1H), 7.41 – 7.34 (comp, 5H), 7.34 – 7.27 (comp, 6H), 7.26 – 7.21 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.55 (s, 1H), 4.10 (s, 1H), 1.50 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 206.6, 189.7, 149.2, 147.1, 140.0, 139.8, 138.9, 131.1, 129.8, 129.8, 128.7, 128.4, 128.3, 126.8, 124.2, 116.7, 111.4, 54.5, 52.5, 27.9, 23.2. IR (neat) 2977, 2248, 1625, 1596 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{28}H_{26}NO_2^+$ [M+H]$^+$ 408.1958, found: 408.1944. UV/Vis absorption spectrum of **4ba** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 308 nm, 411 nm, and corresponding molar extinction coefficients are ε_{308} = 10362 M^{-1} cm^{-1}, ε_{411} = 9534 M^{-1} cm^{-1}.



4cb

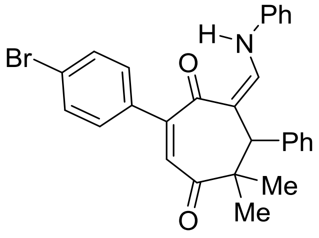
(Z)-7-[(4-hydroxyphenyl)amino]methylene-2-(4-methoxyphenyl)-5,5-dimethyl-6-phenylcyclohept-2-ene-1,4-dione 4cb: 68% yield. Red viscous oil. TLC R_f = 0.15 (5:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, CDCl$_3$) δ 12.72 (d, *J* = 12.3 Hz, 1H), 7.47 (d, *J* = 12.3 Hz, 1H), 7.36 – 7.28 (comp, 4H), 7.28 – 7.23 (comp, 4H), 6.91 – 6.83 (comp, 4H), 6.78 – 6.73 (comp, 2H), 6.53 (d, *J* = 1.1 Hz, 1H), 5.86 (s, 1H), 4.10 (s, 1H), 3.81 (s, 3H), 1.48 (s, 3H), 1.21 (s, 3H).^{13}C NMR (125 MHz, CDCl$_3$) δ 207.32, 189.05, 160.19, 153.08, 149.13, 148.13, 140.06, 133.10, 131.12, 129.89, 129.88, 129.47, 128.35, 126.72, 118.49, 116.55, 113.82, 110.71, 55.34, 54.35, 52.77, 27.87, 23.06. HRMS (ESI) *m/z* calculated for $C_{29}H_{28}NO_4^+$ $[M+H]^+$ 454.2018, found: 454.2014; UV/vis absorption spectrum of **4cb** recorded at 20 °C in dichloromethane (DCM): UV (λ max) = 303 nm, 419 nm, and corresponding molar extinction coefficients are ε_{303} = 9762 M^{-1} cm^{-1}, ε_{419} = 8121 M^{-1} cm^{-1}.



4bc

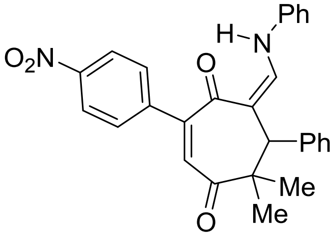
(*Z*)-5,5-Dimethyl-6-phenyl-7-[(phenylamino)methylene]-2-(*p*-tolyl)cyclohept-2-ene-1,4-dione 4bc: 65% yield. Red viscous oil. TLC R_f = 0.25 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.61 (d, *J* = 12.2 Hz, 1H), 7.56 (d, *J* = 12.2 Hz, 1H), 7.37 – 7.28 (comp, 6H), 7.25 – 7.22 (m, 1H), 7.19 – 7.15 (comp, 4H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.54 (s, 1H), 4.09 (s, 1H), 2.36 (s, 3H), 1.49 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 206.8, 189.9, 149.3, 147.0, 140.0, 139.9, 138.9, 136.0, 130.5, 129.8, 129.8, 129.0, 128.4, 128.3, 126.7, 124.2, 116.7, 111.5, 54.5, 52.5, 27.9, 23.2, 21.3. IR (neat) 2973, 1628, 1598 cm^{-1}. HRMS

(ESI) *m/z* calculated for $C_{29}H_{28}NO_2^+$ $[M+H]^+$ 422.2115, found: 422.2118. UV/Vis absorption spectrum of **4bc** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 311 nm, 405 nm, and corresponding molar extinction coefficients are $\varepsilon_{311} = 9517\ M^{-1}\ cm^{-1}$, $\varepsilon_{405} = 8119\ M^{-1}\ cm^{-1}$.



4bd

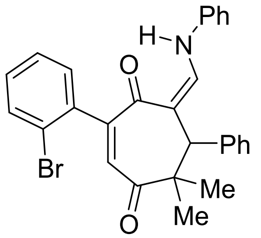
(*Z*)-2-(4-Bromophenyl)-5,5-dimethyl-6-phenyl-7-[(phenylamino)-methylene]-cyclohept-2-ene-1,4-dione 4bd: 55% yield. Red viscous oil. TLC R_f = 0.3 (10:1 hexanes/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 12.60 (d, *J* = 12.3 Hz, 1H), 7.59 (d, *J* = 12.3 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.28 (comp, 6H), 7.25 – 7.21 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.50 (s, 1H), 4.04 (s, 1H), 1.50 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 188.9, 148.2, 147.4, 139.9, 139.6, 137.8, 131.4, 131.3, 130.0, 129.8, 129.7, 128.4, 126.8, 124.4, 123.1, 116.8, 111.4, 54.6, 52.3, 27.9, 23.5. IR (neat) 2975, 1625, 1597 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{25}BrNO_2^+$ $[M+H]^+$ 486.1063, found: 486.1052; UV/Vis absorption spectrum of **4bd** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 311 nm, 411 nm, and corresponding molar extinction coefficients are $\varepsilon_{311} = 14924\ M^{-1}\ cm^{-1}$, $\varepsilon_{411} = 11984\ M^{-1}\ cm^{-1}$.



4be

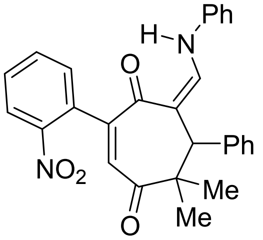
(*Z*)-5,5-Dimethyl-2-(4-nitrophenyl)-6-phenyl-7-[(phenylamino)-methylene]-cyclohept-2-ene-1,4-dione 4be: 43% yield. Red viscous oil. TLC R_f = 0.4 (5:1 hexanes/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 12.61 (d, *J* = 12.4 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 12.4 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.30 (comp, 6H), 7.29 – 7.22 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.53 (s, 1H), 4.00 (s, 1H), 1.53 (s, 3H), 1.27 (s, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 205.6, 187.9, 148.0, 147.7, 147.3, 145.7, 139.8, 139.4, 132.8, 129.9, 129.6, 129.5, 128.5, 126.9, 124.7, 123.4, 117.0, 111.5, 54.7, 52.2, 27.9, 23.8; IR (neat) 2926, 1626, 1596 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_{28}H_{25}N_2O_4^+$ $[M+H]^+$ 453.1809, found: 408.1813; UV/Vis absorption spectrum of **4be** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 288 nm, 420 nm, and corresponding molar extinction coefficients are $\varepsilon_{288} = 14841$ M^{-1} cm^{-1}, $\varepsilon_{420} = 6549$ M^{-1} cm^{-1}.



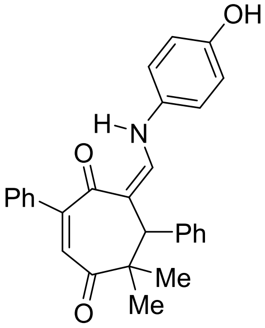
4bf

(*Z*)-2-(2-Bromophenyl)-5,5-dimethyl-6-phenyl-7-[(phenylamino)-methylene]-cyclohept-2-ene-1,4-dione 4bf: 52% yield. Red viscous oil. TLC R_f = 0.2 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.44 (d, *J* = 12.3 Hz, 1H), 7.59 (s, 2H), 7.43 – 7.37 (comp, 3H), 7.37 – 7.34 (comp, 2H), 7.34 – 7.27 (comp, 4H), 7.25 – 7.21 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.46 (s, 1H), 4.37 (s, 1H), 1.49 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 188.2, 149.5, 147.4, 140.7, 139.9, 139.8, 132.9, 132.5, 131.1, 130.0, 129.9, 129.7, 128.5, 127.5, 126.9, 124.1, 122.0, 116.6, 110.4, 54.3, 52.6, 27.5, 22.2. IR (neat) 2975, 1759, 1624, 1597 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{25}BrNO_2^+$ $[M+H]^+$ 486.1063, found: 486.1020. UV/Vis absorption spectrum of **4bf** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 311 nm, 410 nm, and corresponding molar extinction coefficients are $\varepsilon_{311} = 8329$ M^{-1} cm^{-1}, $\varepsilon_{410} = 8494$ M^{-1} cm^{-1}.



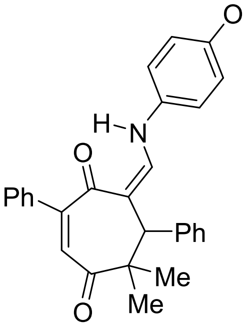
4bg

(*Z*)-5,5-Dimethyl-2-(2-nitrophenyl)-6-phenyl-7-[(phenylamino)-methylene]-cyclohept-2-ene-1,4-dione 4bg: 55% yield. Red viscous oil. TLC R_f = 0.3 (5:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (d, *J* = 12.4 Hz, 1H), 8.19 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.72 (td, *J* = 7.5, 1.3 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.52 – 7.44 (comp, 4H), 7.40 – 7.34 (comp, 2H), 7.31 – 7.26 (comp, 2H), 7.26 – 7.23 (m, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 2H), 6.58 (s, 1H), 1.49 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 187.0, 148.4, 147.7, 147.5, 140.2, 139.6, 135.0, 134.0, 132.2, 131.5, 129.8, 129.7, 129.6, 128.6, 127.0, 124.6, 124.3, 116.8, 110.2, 27.2; IR (neat) 2976, 1623, 1597 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{25}N_2O_4^+$ $[M+H]^+$ 453.1809, found: 453.1802. UV/Vis absorption spectrum of **4bg** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 292 nm, 413 nm, and corresponding molar extinction coefficients are ε_{292} = 9321 M^{-1} cm^{-1}, ε_{413} = 7601 M^{-1} cm^{-1}.



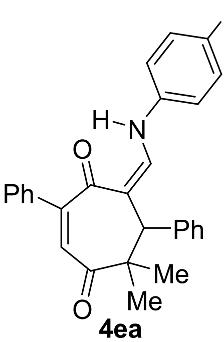
4ca

(*Z*)-7-[(4-Hydroxyphenyl)amino]methylene-5,5-dimethyl-2,6-diphenylcyclohept-2-ene-1,4-dione 4ca: 64% yield. Red viscous oil. TLC R_f = 0.2 (5:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.71 (d, *J* = 12.3 Hz, 1H), 7.47 (d, *J* = 12.3 Hz, 1H), 7.39 – 7.32 (comp, 6H), 7.31 – 7.27 (comp, 3H), 7.26 – 7.21 (m, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.53 (s, 1H), 5.23 (br, 1H), 4.06 (s, 1H), 1.49 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 188.8, 152.8, 149.5, 148.2, 140.1, 139.1, 133.3, 130.9, 129.8, 128.7, 128.4, 128.4, 128.3, 126.7, 118.5, 116.5, 110.8, 54.6, 52.6, 27.8, 23.2. IR (neat) 3321, 2975, 1733, 1620 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{26}NO_3^+$ $[M+H]^+$ 424.1907, found: 424.1889. UV/Vis absorption spectrum of **4ca** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 305 nm, 418 nm, and corresponding molar extinction coefficients are ε_{305} = 9592 M^{-1} cm^{-1}, ε_{418} = 8307 M^{-1} cm^{-1}.



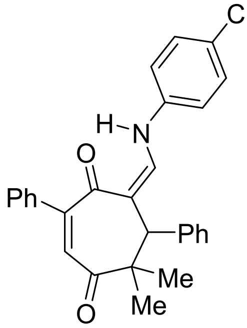
4da

(*Z*)-7-[(4-Methoxyphenyl)amino]methylene-5,5-dimethyl-2,6-diphenylcyclohept-2-ene-1,4-dione 4da: 65% yield. Red viscous oil. TLC R_f = 0.5 (5:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.71 (d, *J* = 12.3 Hz, 1H), 7.47 (d, *J* = 12.3 Hz, 1H), 7.39 – 7.32 (comp, 6H), 7.31 – 7.27 (comp, 3H), 7.26 – 7.21 (m, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.53 (s, 1H), 5.23 (br, 1H), 4.06 (s, 1H), 1.49 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 188.8, 152.8, 149.5, 148.2, 140.1, 139.1, 133.3, 130.9, 129.8, 128.7, 128.4, 128.4, 128.3, 126.7, 118.5, 116.5, 110.8, 54.6, 52.6, 27.8, 23.2. IR (neat) 2919, 2850, 1622 cm^{-1}.. HRMS (ESI) *m/z* calculated for $C_{29}H_{28}NO_3^+$ $[M+H]^+$ 438.2064, found: 438.2057. UV/Vis absorption spectrum of **4da** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 305 nm, 420 nm, and corresponding molar extinction coefficients are $\varepsilon_{305} = 10691$ M^{-1} cm^{-1}, $\varepsilon_{420} = 9478$ M^{-1} cm^{-1}.



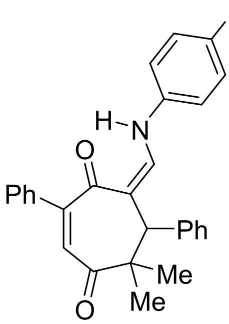
4ea

(*Z*)-7-[(4-Bromophenyl)amino]methylene-5,5-dimethyl-2,6-diphenylcyclohept-2-ene-1,4-dione 4ea: 61% yield. Red viscous oil,. TLC R_f = 0.2 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.55 (d, *J* = 12.2 Hz, 1H), 7.49 (d, *J* = 12.2 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.39 – 7.31 (comp, 7H), 7.31 – 7.27 (comp, 2H), 7.26 – 7.22 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 1H), 4.09 (s, 1H), 1.50 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 190.2, 149.0, 146.4, 139.8, 139.0, 138.8, 132.7, 131.3, 129.8, 128.8, 128.4, 128.4, 128.3, 126.9, 118.2, 116.7, 111.9, 54.5, 52.4, 27.9, 23.2. IR (neat) 2976, 1623, 1590 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{25}BrNO_2^+$ $[M+H]^+$ 486.1063, found: 486.1035. UV/Vis absorption spectrum of **4ea** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 301 nm, 413 nm, and corresponding molar extinction coefficients are $\varepsilon_{301} = 12017\ M^{-1}\ cm^{-1}$, $\varepsilon_{413} = 11837\ M^{-1}\ cm^{-1}$.



4fa

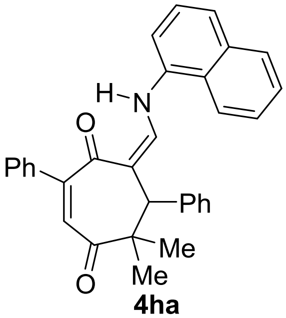
(*Z*)-7-[(4-Chlorophenyl)amino]methylene-5,5-dimethyl-2,6-diphenylcyclohept-2-ene-1,4-dione 4fa: 60% yield. Red viscous oil. TLC R_f = 0.2 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.57 (d, *J* = 12.1 Hz, 1H), 7.49 (d, *J* = 12.1 Hz, 1H), 7.39 – 7.36 (comp, 3H), 7.35 – 7.31 (comp, 4H), 7.31 – 7.27 (comp, 3H), 7.26 – 7.23 (comp, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.56 (s, 1H), 4.10 (s, 1H), 1.50 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 190.1, 149.0, 146.6, 139.8, 138.8, 138.5, 131.3, 129.8, 129.8, 129.3, 128.8, 128.4, 128.4, 128.3, 126.9, 117.8, 111.8, 54.5, 52.4, 27.9, 23.2. IR (neat) 2976, 1623, 1595 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{25}ClNO_2^+$ $[M+H]^+$ 442.1568, found: 442.1573. UV/Vis absorption spectrum of **4fa** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 300 nm, 410 nm, and corresponding molar extinction coefficients are $\varepsilon_{300} = 6217\ M^{-1}\ cm^{-1}$, $\varepsilon_{410} = 5461\ M^{-1}\ cm^{-1}$.



4ga

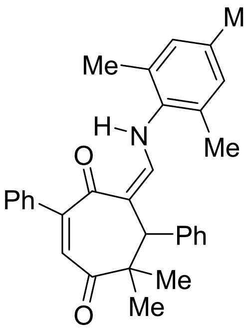
(*Z*)-7-[(4-Fluorophenyl)amino]methylene-5,5-dimethyl-2,6-diphenylcyclohept-2-ene-1,4-dione 4ga: 56% yield. Red viscous oil. TLC R_f = 0.2 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (d, *J* = 12.2 Hz, 1H), 7.47 (d, *J* = 12.2 Hz, 1H), 7.39 – 7.36 (comp, 3H), 7.35 – 7.33 (comp, 2H), 7.32 – 7.31 (m, 1H), 7.31 – 7.26 (comp, 3H), 7.25 – 7.22 (m, 1H), 7.06 –

6.98 (comp, 2H), 6.98 – 6.92 (comp, 2H), 6.55 (s, 1H), 4.09 (s, 1H), 1.50 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 206.5, 189.7, 159.55 (d, *J* = 244.2 Hz), 149.1, 147.5, 139.9, 138.9, 136.2 (d, *J* = 2.8 Hz), 131.2, 129.8, 128.8, 128.4, 128.4, 128.3, 126.8, 118.25 (d, *J* = 8.0 Hz), 116.59 (d, *J* = 23.1 Hz), 111.4, 54.5, 52.5, 27.9, 23.2. IR (neat) 2975, 1735, 1624, 1600 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{25}FNO_2^+$ [M+H]$^+$ 426.1864, found: 426.1867. UV/Vis absorption spectrum of **4ga** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 299 nm, 408 nm, and corresponding molar extinction coefficients are ε_{299} = 8565 M^{-1} cm^{-1}, ε_{408} = 7098 M^{-1} cm^{-1}.



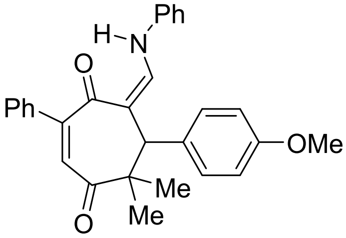
4ha

(*Z*)-5,5-Dimethyl-7-(naphthalen-1-ylamino)methylene-2,6-diphenylcyclohept-2-ene-1,4-dione 4ha: 68% yield. Red solid, 62.6 - 63.4 ºC. TLC R_f = 0.3 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, CDCl$_3$) δ 13.43 (d, *J* = 11.8 Hz, 1H), 8.16 – 8.08 (m, 1H), 7.89 – 7.81 (m, 1H), 7.77 (d, *J* = 11.8 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.50 (comp, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.31 (comp, 9H), 7.29 – 7.23 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 4.22 (s, 1H), 1.54 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 206.9, 190.2, 149.2, 148.3, 139.9, 138.8, 136.2, 134.2, 131.0, 129.9, 128.9, 128.5, 128.5, 128.4, 128.4, 126.8, 126.8, 126.8, 125.7, 124.9, 124.8, 121.1, 112.3, 111.7, 54.4, 52.8, 27.9, 23.0. IR (neat) 2975, 2268, 1616 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{32}H_{28}NO_2^+$ [M+H]$^+$ 458.2115, found: 458.2088. UV/Vis absorption spectrum of **4ha** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 325 nm, 424 nm, and corresponding molar extinction coefficients are ε_{325} = 3967 M^{-1} cm^{-1}, ε_{424} = 4629 M^{-1} cm^{-1}.



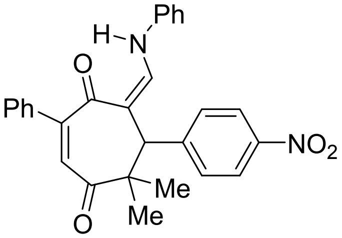
4ia

(*Z*)-7-(Mesitylamino)methylene-5,5-dimethyl-2,6-diphenylcyclohept-2-ene-1,4-dione 4ia: 70% yield. Red viscous oil. TLC R_f = 0.3 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.13 (d, *J* = 12.5 Hz, 1H), 7.41 – 7.34 (comp, 5H), 7.34 – 7.26 (comp, 4H), 7.24 – 7.18 (m, 1H), 7.06 (d, *J* = 12.5 Hz, 1H), 6.87 (s, 2H), 6.57 (s, 1H), 4.19 (s, 1H), 2.26 (s, 3H), 2.16 (s, 6H), 1.49 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 207.8, 189.1, 155.2, 149.0, 140.3, 138.8, 135.9, 135.9, 131.7, 130.3, 129.9, 129.5, 128.7, 128.4, 128.4, 128.3, 126.6, 109.3, 53.8, 53.2, 27.7, 22.3, 20.8, 18.5. IR (neat) 2974, 1622, 1602 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{31}H_{32}NO_2^+$ $[M+H]^+$ 450.2428, found: 450.2401. UV/Vis absorption spectrum of **4ia** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 300 nm, 393 nm, and corresponding molar extinction coefficients are ε_{300} = 12797 M^{-1} cm^{-1}, ε_{393} = 7917 M^{-1} cm^{-1}.



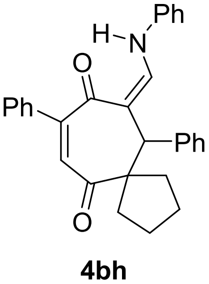
4ja

(Z)-6-(4-methoxyphenyl)-5,5-dimethyl-2-phenyl-7-[(phenylamino)methylene]-cyclohept-2-ene-1,4-dione 4ja: 67% yield. Red viscous oil. TLC R_f = 0.30 (10:1 hexanes/EtOAc.). ^{1}H NMR (500 MHz, CDCl$_3$) δ 12.60 (d, *J* = 12.1 Hz, 1H), 7.57 (d, *J* = 12.1 Hz, 1H), 7.41 – 7.36 (comp., 3H), 7.35 – 7.30 (comp., 4H), 7.30 – 7.25 (comp., 4H), 7.10 – 7.07 (m, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.56 (s, 1H), 4.10 (s, 1H), 3.81 (s, 3H), 1.48 (s, 3H), 1.21 (s, 3H).. ^{13}C NMR (125 MHz, CDCl$_3$) δ 206.90, 189.82, 158.22, 149.17, 147.05, 139.87, 138.91, 131.88, 130.96, 130.85, 129.79, 128.76, 128.44, 128.33, 124.21, 116.76, 113.76, 111.56, 55.25, 53.71, 52.79, 27.83, 22.85. IR (neat) 2927, 1621, 1427 cm^{-1}.. HRMS (ESI) *m/z* calculated for $C_{29}H_{28}NO_3^+$ $[M+H]^+$ 438.2064, found: 438.2061.UV/Vis absorption spectrum of **4ja** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 301 nm, 391 nm, and corresponding molar extinction coefficients are $\varepsilon_{296} = 17213$ M^{-1} cm^{-1}, $\varepsilon_{413} = 16721$ M^{-1} cm^{-1}.



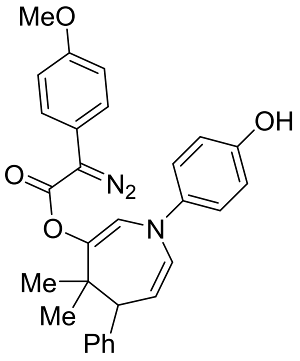
4ka

(*Z*)-5,5-Dimethyl-6-(4-nitrophenyl)-2-phenyl-7-[(phenylamino)methylene]cyclohept-2-ene-1,4-dione 4ka: 59% yield. Red viscous oil. TLC R_f = 0.15 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.66 (d, *J* = 12.3 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 12.3 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.32 (comp, 5H), 7.25 – 7.20 (comp, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.53 (s, 1H), 4.01 (s, 1H), 1.52 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 188.9, 149.9, 148.1, 147.5, 146.4, 139.4, 138.8, 131.4, 130.3, 129.9, 129.0, 128.4, 128.3, 124.8, 123.4, 117.0, 110.6, 55.1, 51.6, 28.0, 24.4; IR (neat) 2925, 1625, 1595 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{28}H_{25}N_2O_4^+$ $[M+H]^+$ 453.1809, found: 453.1810. UV/Vis absorption spectrum of **4ka** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 296 nm, 413 nm, and corresponding molar extinction coefficients are $\varepsilon_{296} = 36223$ M^{-1} cm^{-1}, $\varepsilon_{413} = 23233$ M^{-1} cm^{-1}.



4bh

(*Z*)-8,11-Diphenyl-10-[(phenylamino)methylene]spiro[4.6]undec-7-ene-6,9-dione 4bh: 65% yield. Red viscous oil. TLC R_f = 0.2 (10:0 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.53 (d, *J* = 12.3 Hz, 1H), 7.61 (d, *J* = 12.3 Hz, 1H), 7.40 – 7.33 (comp, 2H), 7.31 – 7.28 (m, 1H), 7.27 – 7.21 (comp, 6H), 7.17 – 7.11 (comp, 4H), 7.06 – 7.01 (comp, 2H), 6.21 (s, 1H), 3.72 (s, 1H), 2.89 – 2.79 (m, 1H), 2.08 – 1.96 (m, 1H), 1.93 – 1.83 (comp, 3H), 1.78 – 1.67 (comp, 2H), 1.66 – 1.55 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 205.0, 189.2, 149.8, 147.1, 141.5, 139.8, 139.7, 132.2, 129.8, 128.3, 128.3, 128.3, 128.1, 128.0, 126.2, 124.2, 116.7, 112.5, 62.2, 54.9, 40.0, 38.2, 26.3, 24.8. IR (neat) 2949, 1625, 1595 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{30}H_{28}NO_2^+$ [M+H]$^+$ 434.2115, found: 434.2134. UV/Vis absorption spectrum of **4bh** recorded at 20°C in dichloromethane (DCM): UV (λ max) = 298 nm, 419 nm, and corresponding molar extinction coefficients are $\varepsilon_{298} = 8390\ M^{-1}\ cm^{-1}$, $\varepsilon_{419} = 5328\ M^{-1}\ cm^{-1}$.

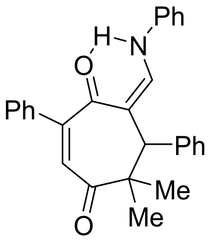
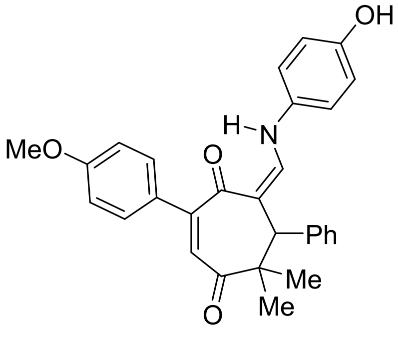
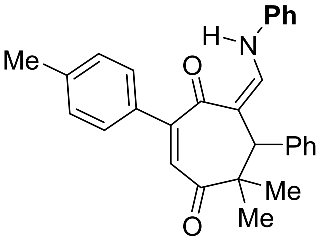
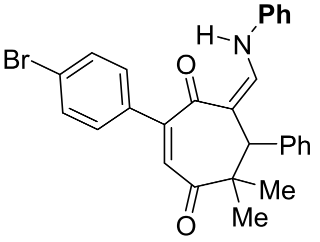
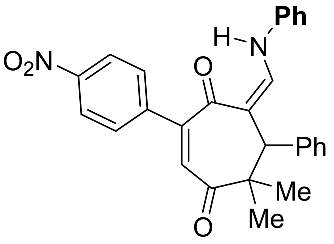


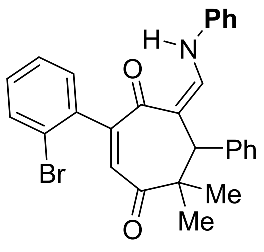
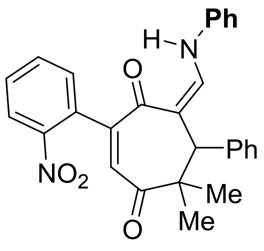
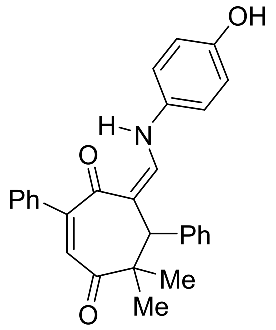
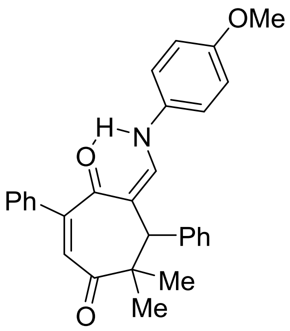
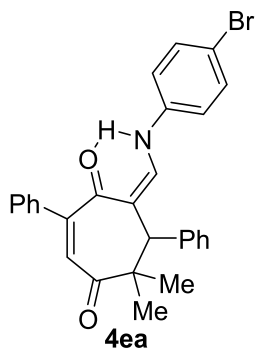
3cb

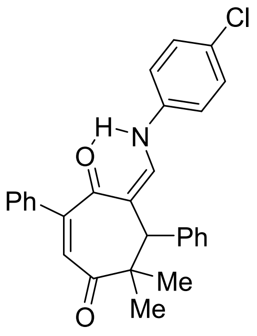
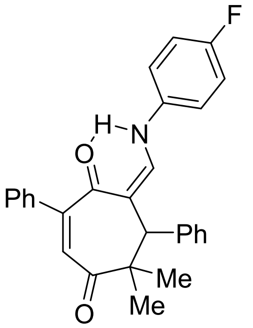
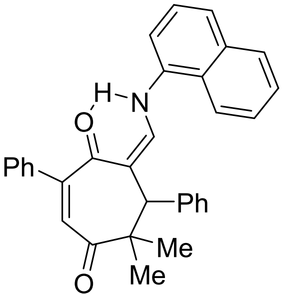
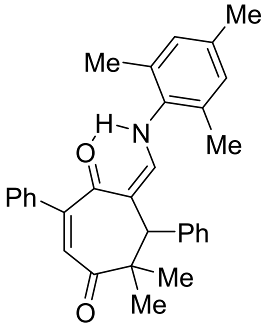
1-(4-Hydroxyphenyl)-4,4-dimethyl-5-phenyl-4,5-dihydro-1H-azepin-3-yl (4-Methoxyphenyl)diazoacetate 3cb: 36% yield. Yellow oil.^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33-7.21 (comp., 7H), 7.09 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H) . 6.39 (d, *J* = 9.9 Hz, 1H), 6.37 (s, 1H), 5.33 (br, 1H), 4.92 (dd, *J* = 9.9, 6.6 Hz, 1H), 3.80 (s, 3H), 3.57 (d, *J* = 6.6 Hz, 1H), 1.19 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.96, 158.08, 152.62, 144.09, 140.75, 138.84, 129.65, 129.17, 127.69, 126.27, 125.86, 124.75, 122.96, 116.62, 115.85, 114.63, 107.79, 55.35, 54.90, 43.75, 28.36, 25.01. IR (neat) 3406, 2086, 1671, 1152, 1253 cm^{-1}. HRMS (ESI) *m/z* calculated for $C_{29}H_{28}N_3O_4^+$ [M+H]$^+$ 482.2080, found: 482.2086.

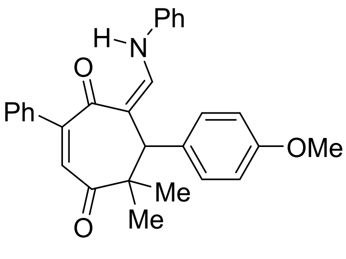
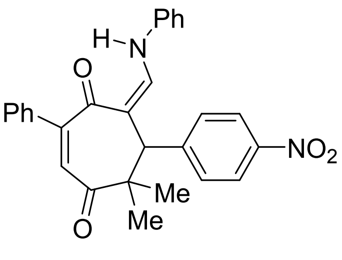
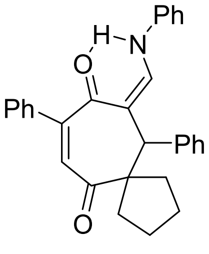
Table S5. Maximum absorption wavelengths and molar absorptivities for 1,4-enedione-ketoenamines[a]

Structure	λ_{1max} (nm)	$\xi_{\lambda 1max}$ ($M^{-1}\ cm^{-1}$)	λ_{2max}(nm)	$\xi_{\lambda 2max}$ ($M^{-1}\ cm^{-1}$)

 **4ba**	308	1.04×10^4	411	0.953×10^4
 **4cb**	303	0.976×10^4	8121	0.546×10^4
 **4bc**	311	0.952×10^4	405	0.812×10^4
 **4bd**	311	1.49×10^4	411	$1,20\times10^4$
 **4be**	298	0.839×10^4	419	0.533×10^4

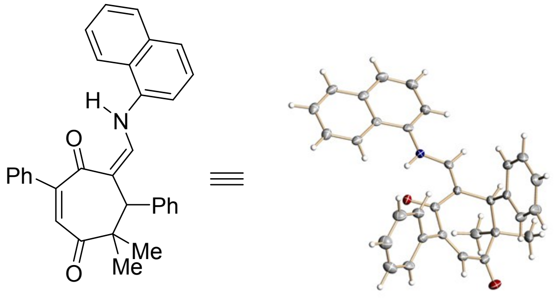
 **4bf**	311	0.833×10^4	410	0.849×10^4
 **4bg**	292	0.932×10^4	413	0.760×10^4
 **4ca**	305	0.959×10^4	418	0.831×10^4
 **4da**	305	1.07×10^4	420	0.948×10^4
 **4ea**	301	1.20×10^4	413	1.18×10^4

 **4fa**	300	0.622×10^{4}	410	0.546×10^{4}
 **4ga**	299	0.856×10^{4}	408	0.710×10^{4}
 **4ha**	325	0.397×10^{4}	424	0.463×10^{4}
 **4ia**	300	1.28×10^{4}	393	0.792×10^{4}

 **4ja**	292	0.932×10^4	413	0.760×10^4
 **4ka**	296	3.62×10^4	413	2.32×10^4
 **4bh**	288	1.48×10^4	420	0.655×10^4

The maximum absorption wavelengths for **4** were recorded by a Carey 50 Bio UV-Vis spectrometer, and according to the Beer–Lambert law, the molar absorptivities were calculated via the equation ξ= A/*cl*. *Procedure*: 0.05 mmol of Compounds **4** and 5.0 mL of DCM were added in a 5.0 mL oven-dried volumetric flask, and 1.0mL of red solution was 249.0 mL of DCM were added into a 250.0 mL oven-dried volumetric flask, and then the resulting solution was directly used in further analysis.

X-ray Crystal Structure Information for 4ha



Crystal Structure Report for 4ha

A specimen of $C_{32}H_{27}NO_2$, approximate dimensions 0.07 mm × 0.08 mm × 0.47 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube ($\lambda = 0.71073$ Å). Data collection temperature was 150 K.

The total exposure time was 17.78 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinicunit cell yielded a total of 15657 reflections to a maximum θ angle of 24.99° (0.84 Å resolution), of which 4299 were independent (average redundancy 3.642, completeness = 100.0%, R_{int} =7.86%) and 2251 (52.36%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 18.041(4)$ Å, $b = 12.292(3)$ Å, $c = 11.066(2)$ Å, $\beta = 94.663(3)°$, $V = 2445.9(9)$ Å^3, are based upon the refinement of the XYZ-centroids of 1326 reflections above 20 σ(I) with $5.328° < 2\theta < 41.67°$. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8840 and 0.9940. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{32}H_{27}NO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 404 variables converged at $R_1 = 5.44\%$, for the observed data and $wR_2 = 9.80\%$ for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was 0.199 $e^-/Å^3$ and the largest hole was -0.182 $e^-/Å^3$ with an RMS deviation of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was1.243 g/cm^3 and F(000), 968 e^-.

APEX2 Version 2010.11-3 (Bruker AXS Inc.). SAINT Version 7.68A (Bruker AXS Inc., 2009). SADABS Version 2008/1 (G. M. Sheldrick, Bruker AXS Inc.). XPREP Version 2008/2 (G. M. Sheldrick, Bruker AXS Inc.). XS Version 2008/1 (G. M. Sheldrick, *Acta Cryst.* (2008). A**64**, 112-122). L Version 2012/4 (G. M. Sheldrick, (2012) University of Gottingen, Germany). Platon (A. L. Spek, *Acta Cryst.* (1990). A**46**, C-34).

Table S6. Sample and crystal data for 4ha.

Identification code	2608	
Chemical formula	$C_{32}H_{27}NO_2$	
Formula weight	457.54	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.07 × 0.08 × 0.47 mm	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 18.041(4) Å	$\alpha = 90°$
	b = 12.292(3) Å	$\beta = 94.663(3)°$
	c = 11.066(2) Å	$\gamma = 90°$
Volume	2445.9(9) $Å^3$	
Z	4	
Density (calculated)	1.243 Mg/cm^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	968	

Table S7. Data collection and structure refinement for 4ha.

Diffractometer	Bruker APEX-II CCD
Radiation source	sealed tube, MoKα
Theta range for data collection	2.01 to 24.99°
Index ranges	$-20 \le h \le 21$, $-14 \le k \le 14$, $-13 \le l \le 13$

Reflections collected	15657	
Independent reflections	4299 [R(int) = 0.0786]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9940 and 0.8840	
Structure solution technique	direct methods	
Structure solution program	ShelXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	ShelXL-2014 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4299 / 0 / 404	
Goodness-of-fit on F^2	1.069	
Final R indices	2251 data; $I>2\sigma(I)$	$R_1 = 0.0544$, $wR_2 = 0.0797$
	all data	$R_1 = 0.1294$, $wR_2 = 0.0980$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0150P)^2+0.7500P]$, $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.199 and -0.182 eÅ^{-3}	
R.M.S. deviation from mean	0.043 eÅ^{-3}	

$R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$

$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

$GOOF = S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

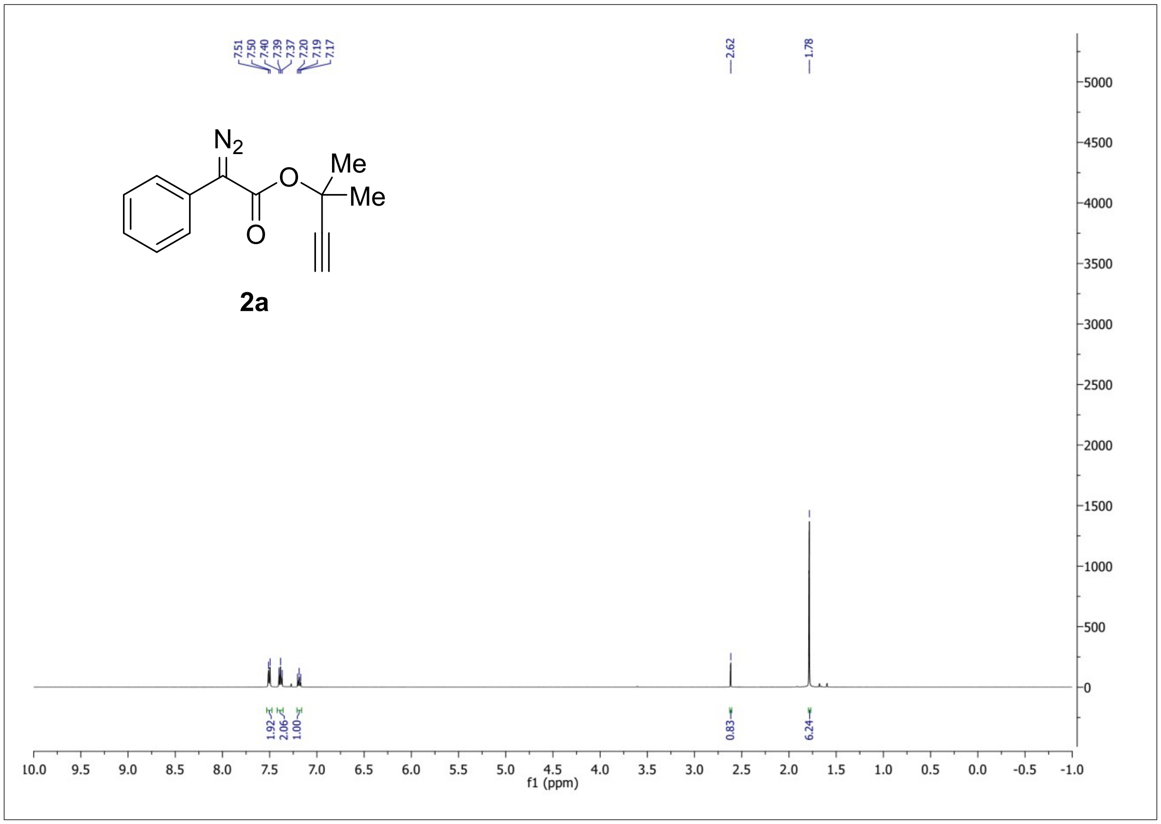
References

[1] (a) M. P. Doyle, W. Hu, D. J. Timmons, *Org. Lett.* 2001, **3**, 3741; (b)Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* 2008, **130**, 9244.

[2] Qiu, H.; Srinivas, H. D.; Zavalij, P. Y.; Doyle, M. P. *J. Am. Chem. Soc.* 2016, **138**, 1808.

[3] Eyring, H. *J. Chem. Phys.* 1935, **3**, 107.

^{1}H- and ^{13}C-NMR Spectra of New Compounds



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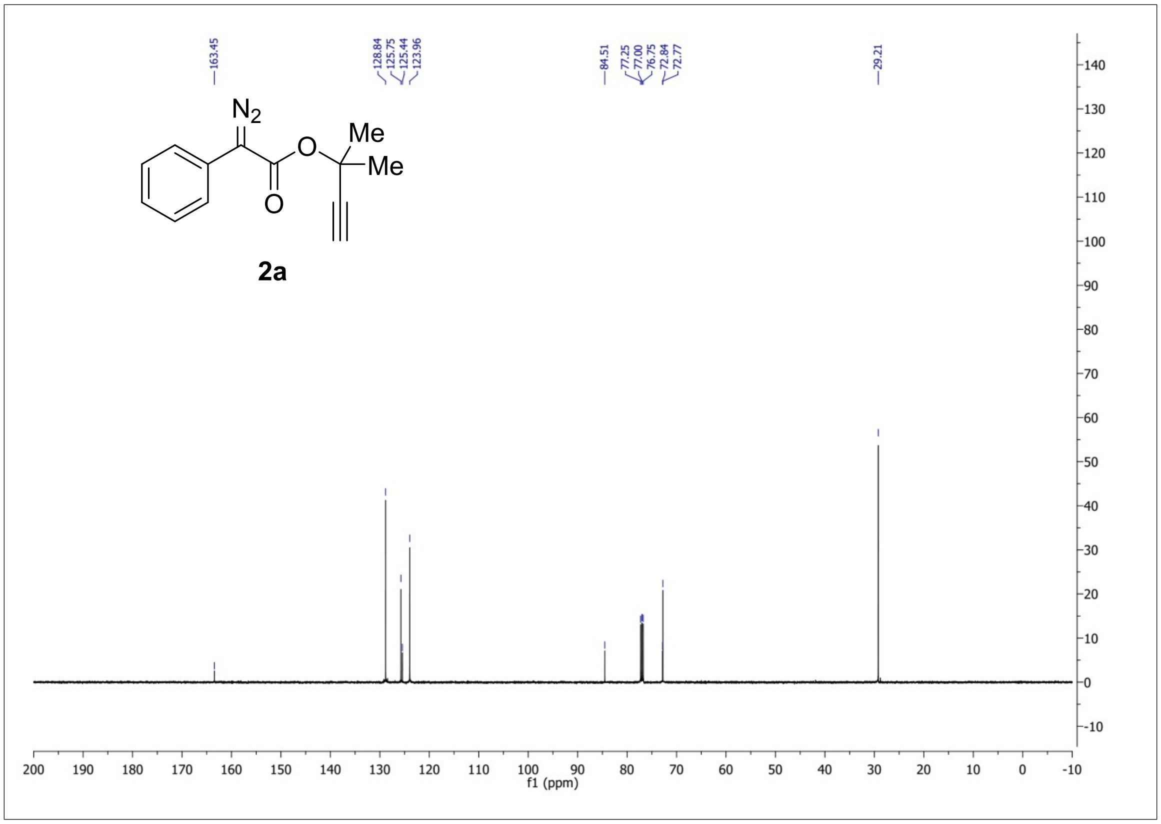
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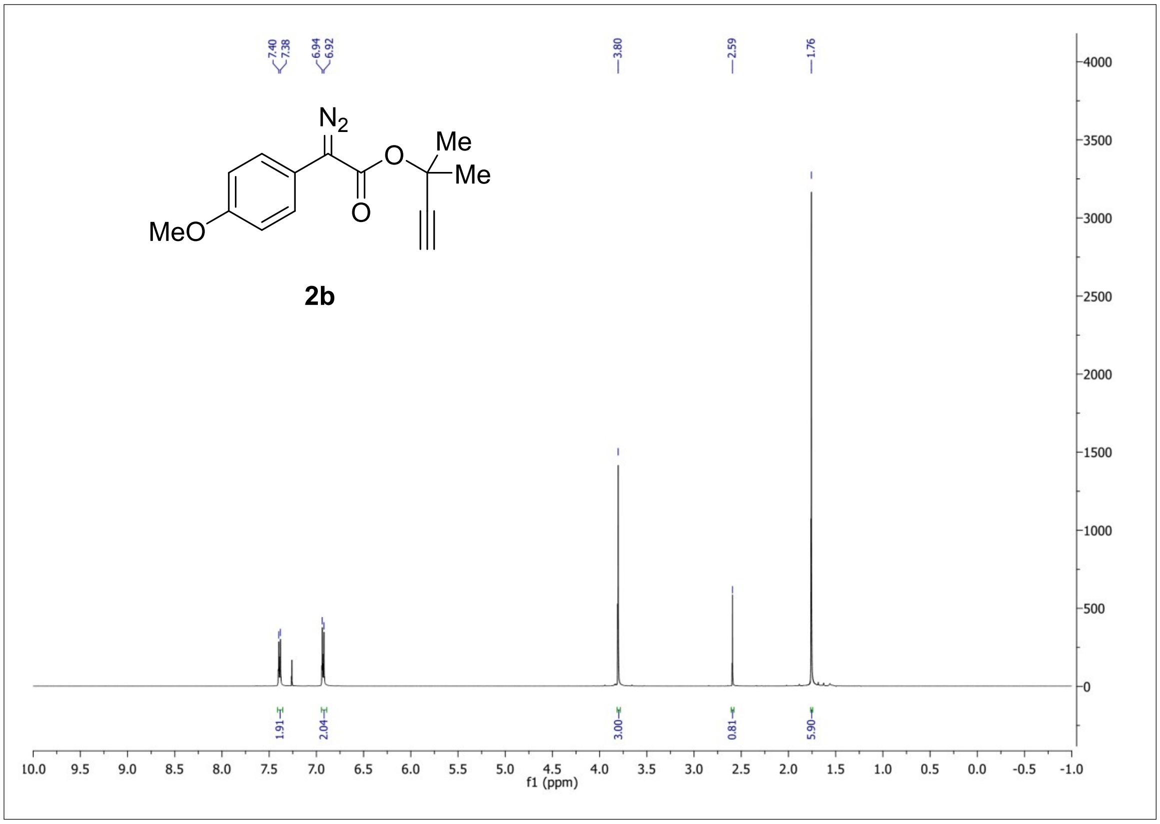
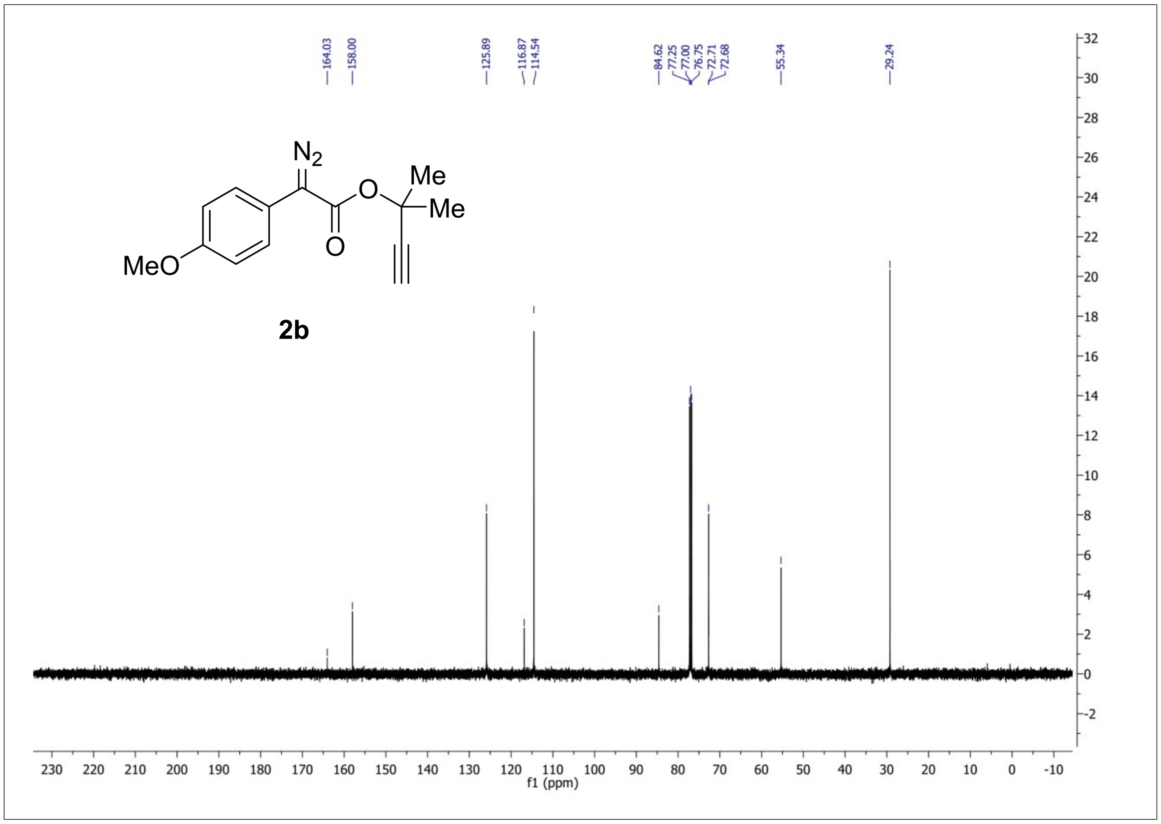
163.45
128.84
125.75
125.44
123.96
84.51
77.25
77.00
76.75
72.84
72.77
29.21
N2
O
Me
Me
O
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


2b

7.40
7.38
6.94
6.92
3.80
2.59
1.76
N2
O
Me
Me
MeO
O
1.91
2.04
3.00
0.81
5.90
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
4000
3500
3000
2500
2000
1500
1000
500
0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158.00
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114.54
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77.25
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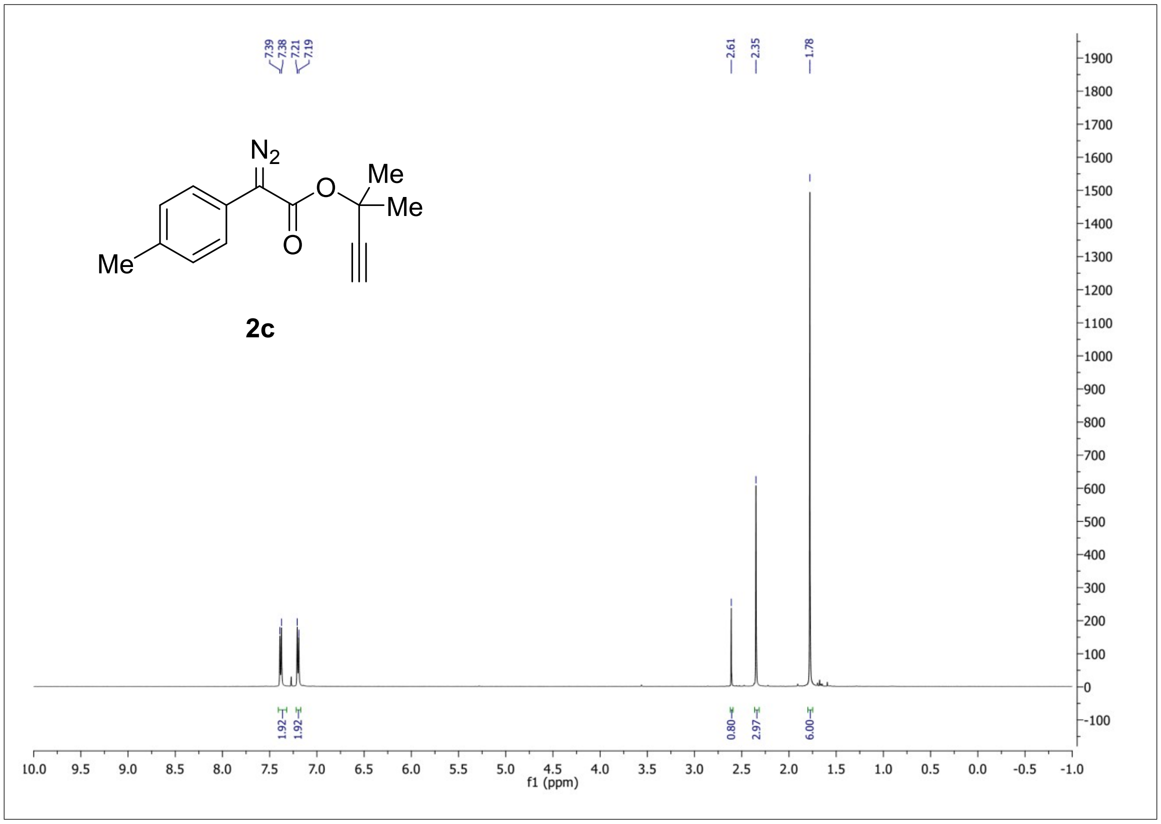
O
MeO
f1 (ppm)

2b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7.38
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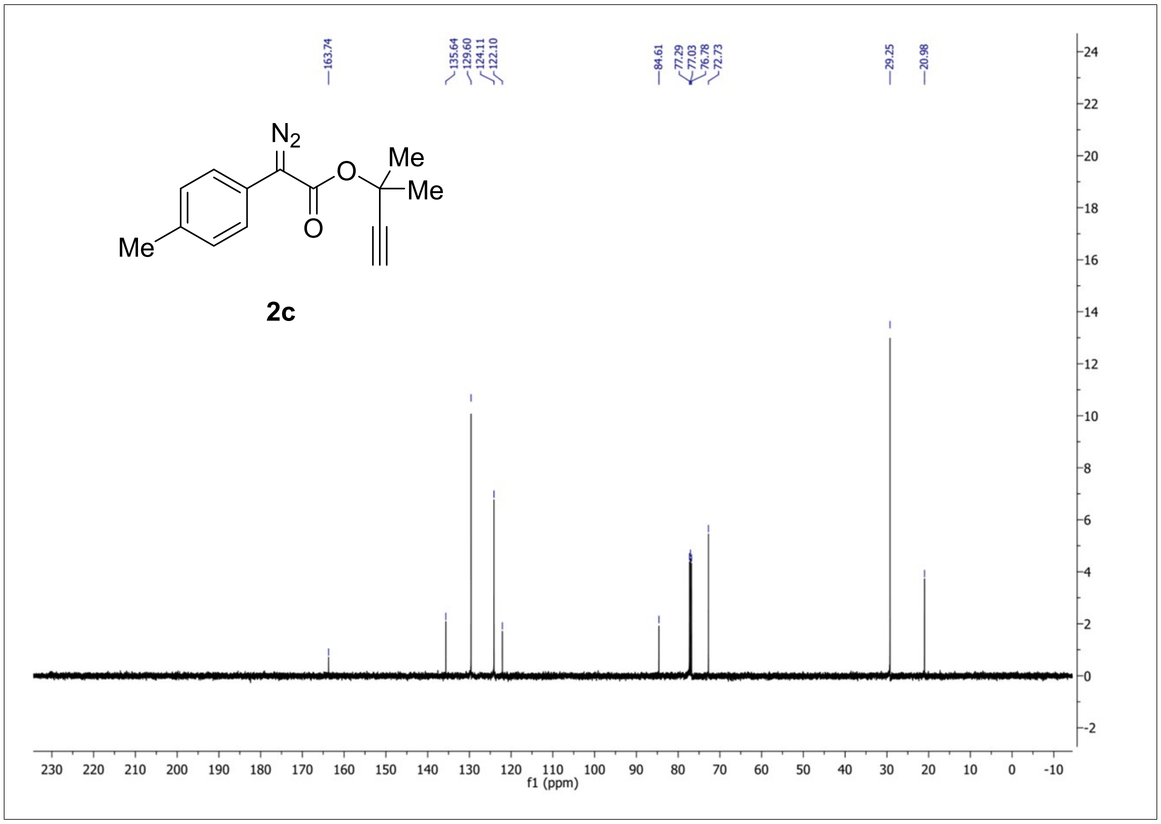
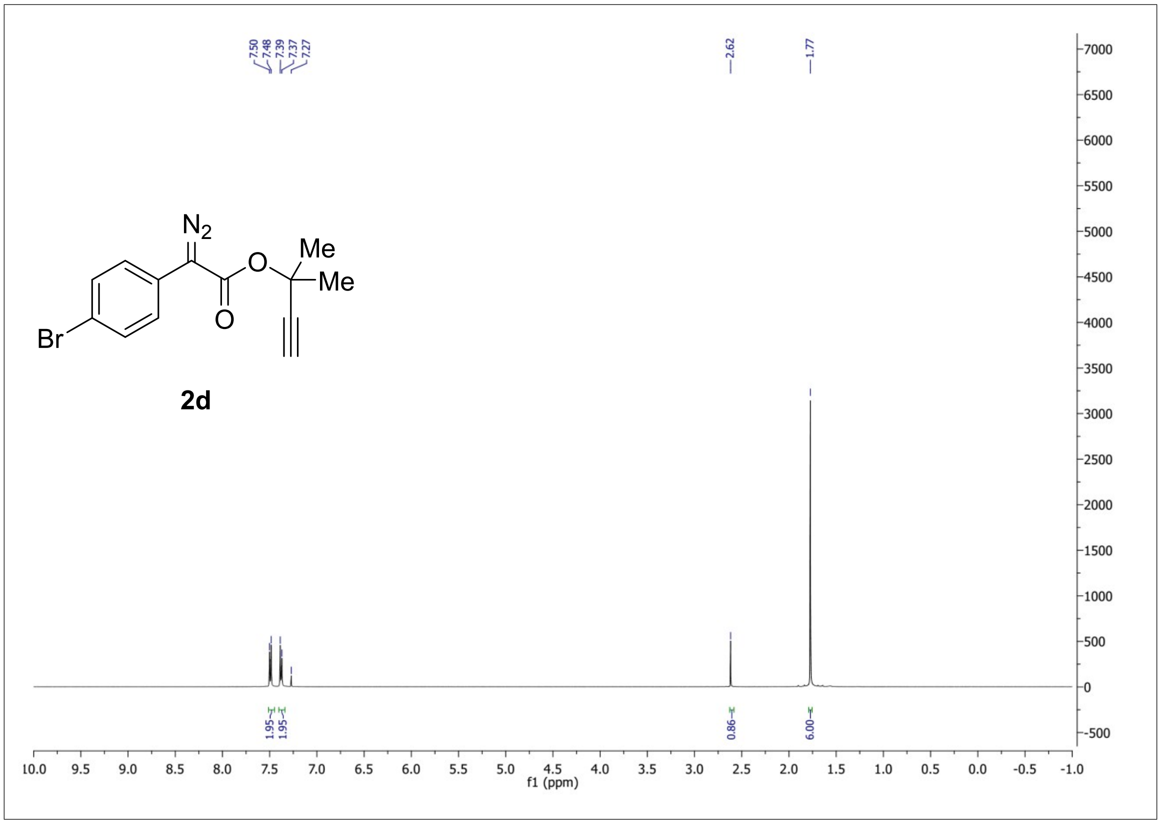
2.61
2.35
1.78
1.92
1.92
0.80
2.97
6.00
N2
Me
Me
O
O
Me
f1 (ppm)

2c


2c

163.74
135.64
129.60
124.11
122.10
84.61
77.29
77.03
76.78
72.73
29.25
20.98
N2
O
O
Me
Me
Me
f1 (ppm)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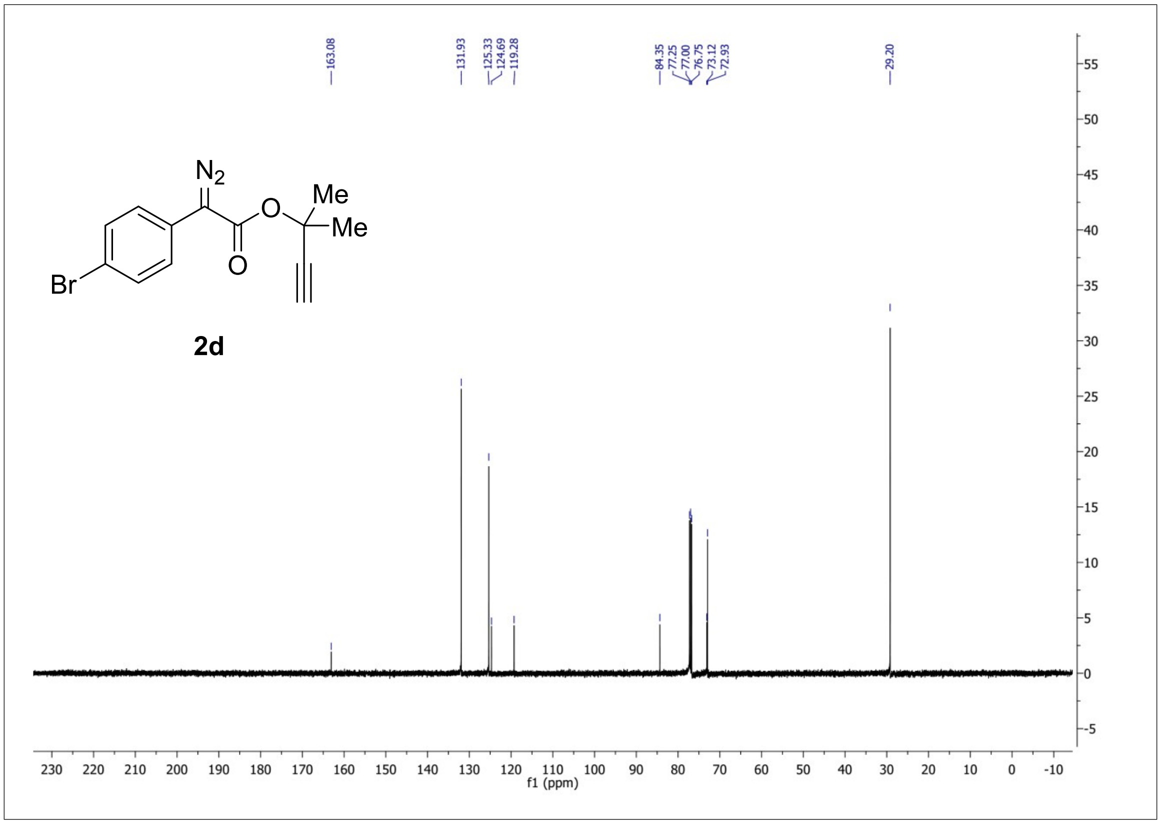
7.48
7.39
7.37
7.27
2.62
1.77
1.95
1.95
0.86
6.00
N2
O
O
Me
Me
Br
f1 (ppm)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131.93
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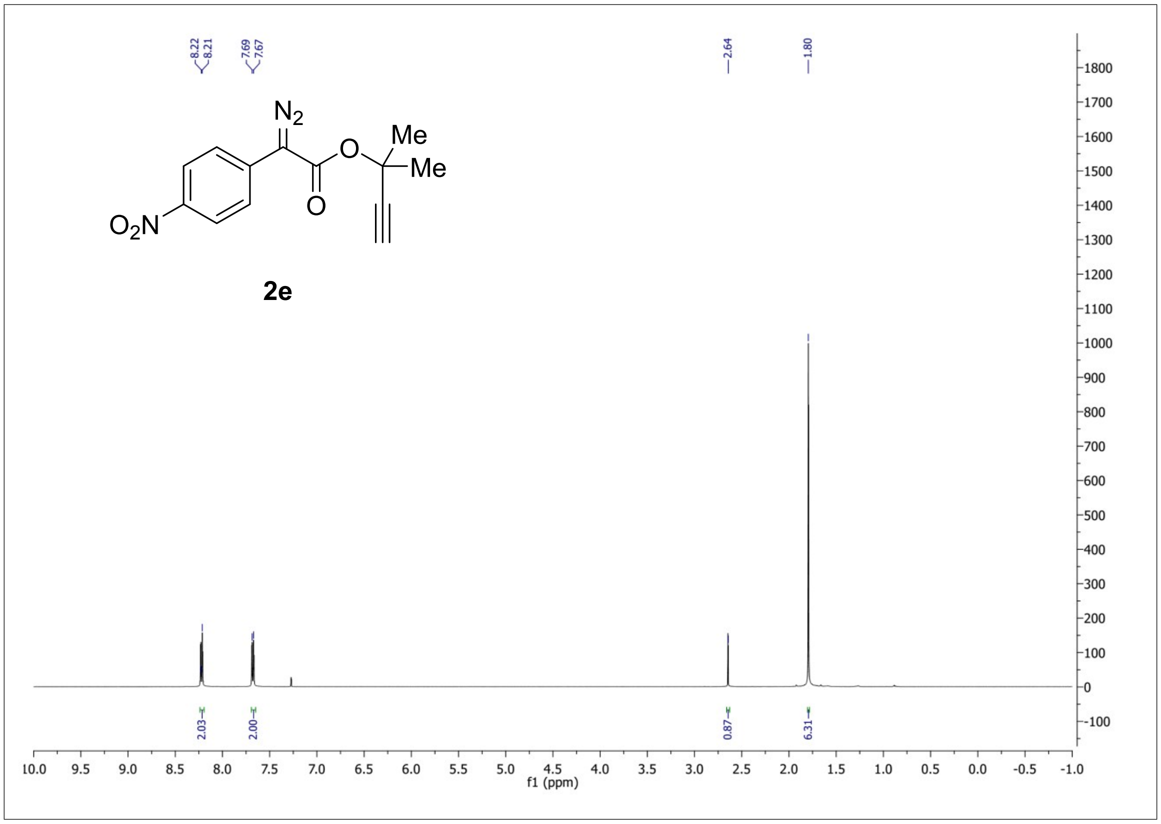
Me
Me
Br
O
f1 (ppm)

2d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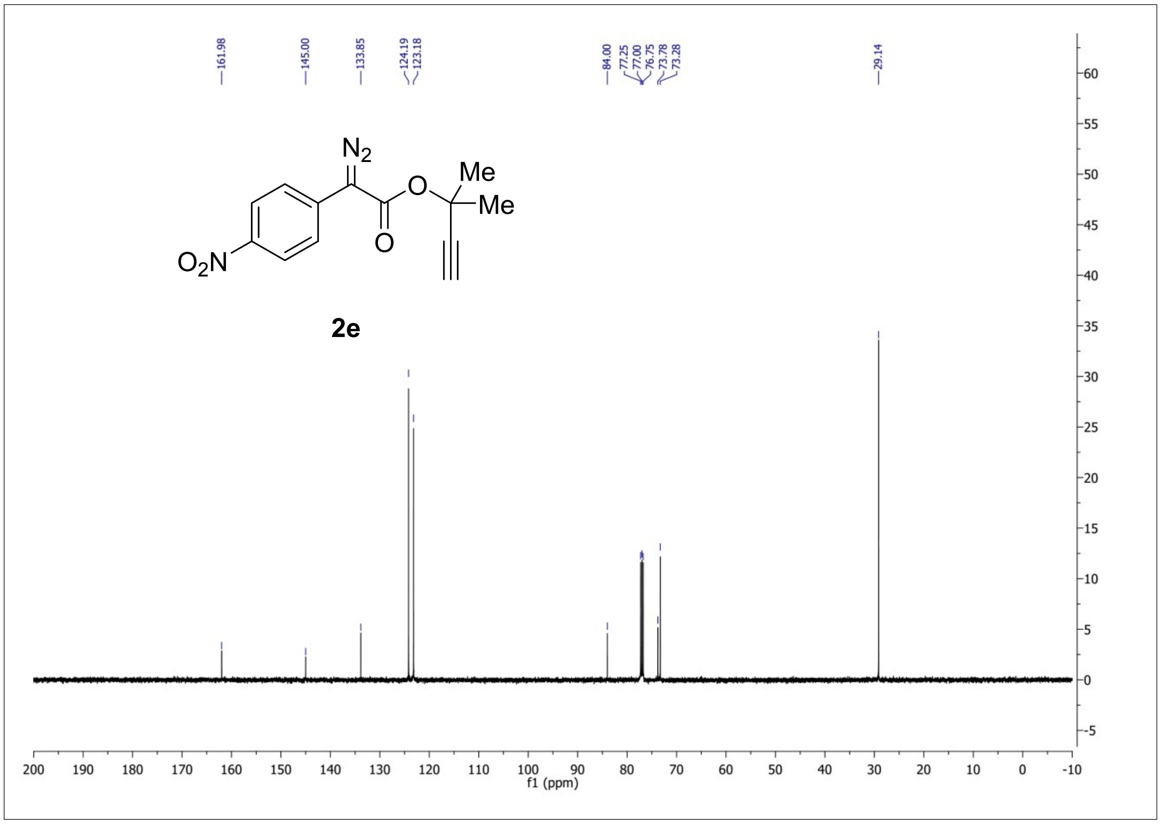
6.31
f1 (ppm)

2e



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133.85
124.19
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84.00
77.25
77.00
76.75
73.78
73.28
29.14
N2
O
Me
Me
O
O2N
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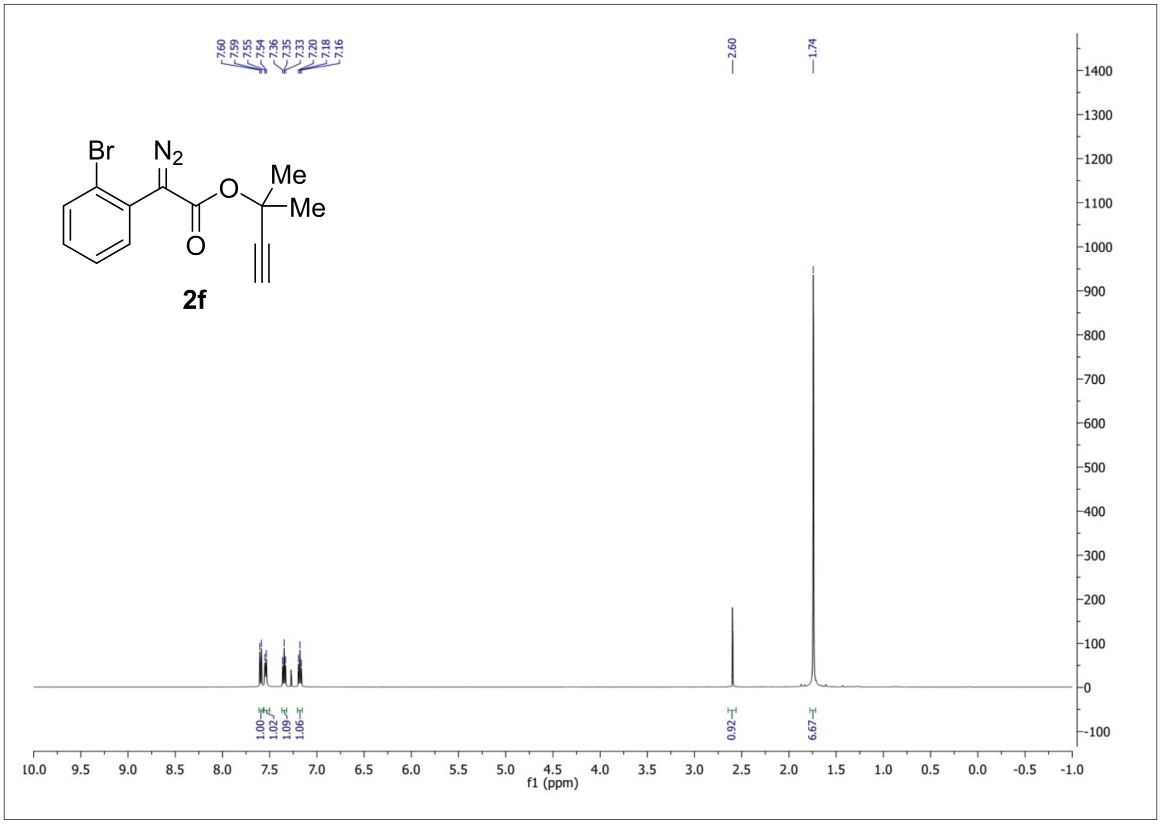
60 55 50 45 40 35 30 25 20 15 10 5 0 -5

2e



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7.59
7.55
7.54
7.36
7.35
7.33
7.20
7.18
7.16
2.60
1.74
Br
N2
O
Me
Me
O
1.00
1.02
1.09
1.06
0.92
6.67
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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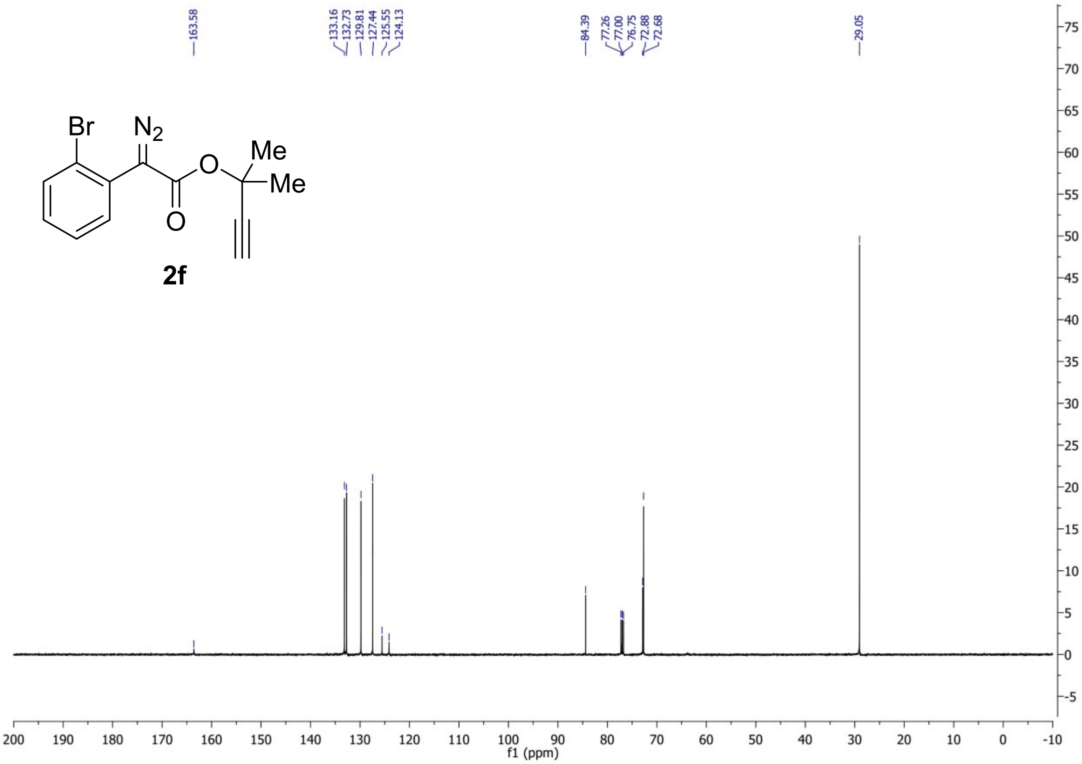
2f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77.00
76.75
72.88
72.68
29.05
Br
N2
O
Me
Me
O
2f
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
200
190
180
170
160
150
140
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120
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100
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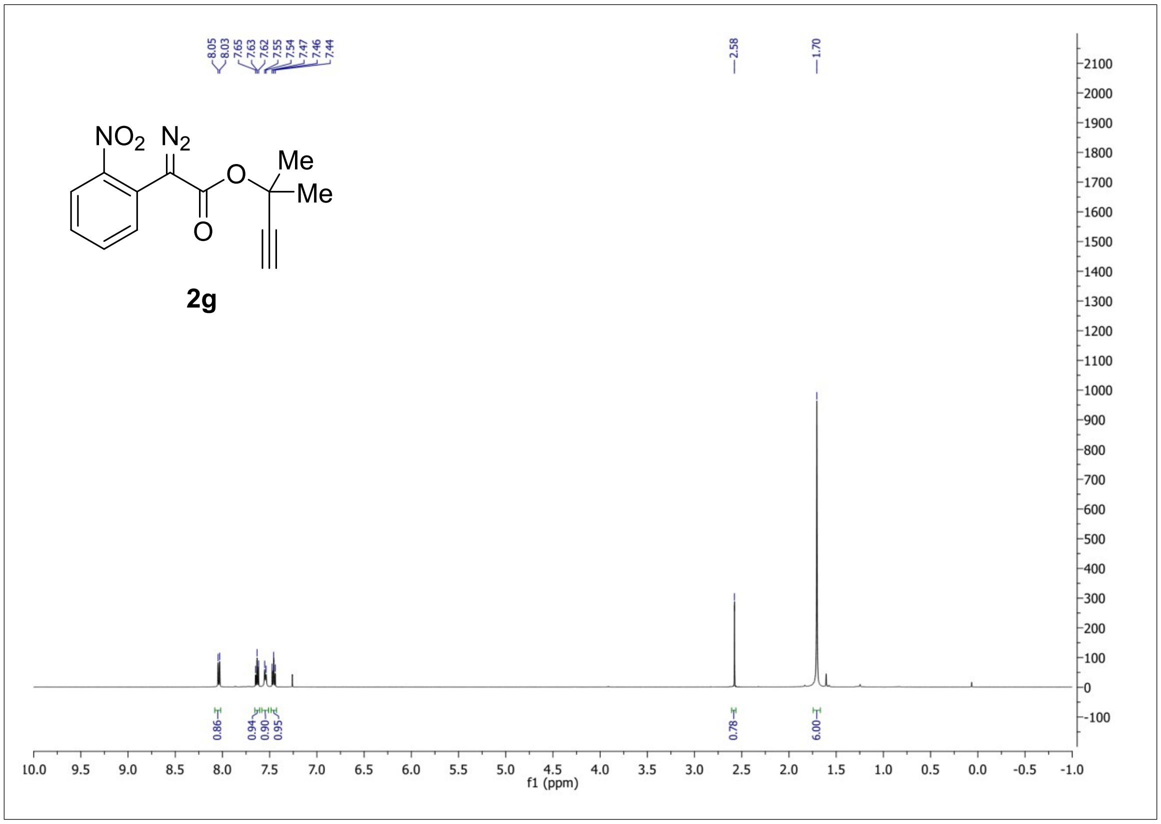
50
40
30
20
10
0
-10
f1 (ppm)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7.54
7.47
7.46
7.44
2.58
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NO2
N2
O
Me
Me
O
2g
0.86
0.94
0.90
0.95
0.78
6.00
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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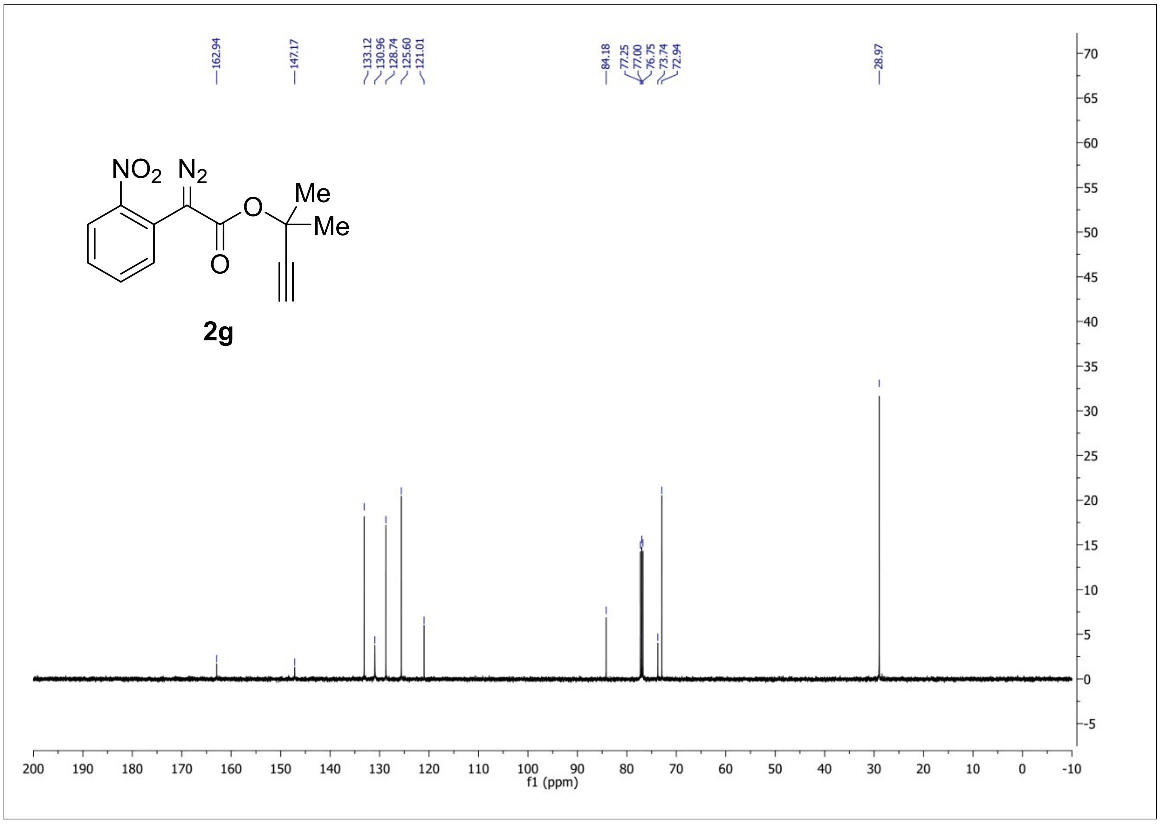
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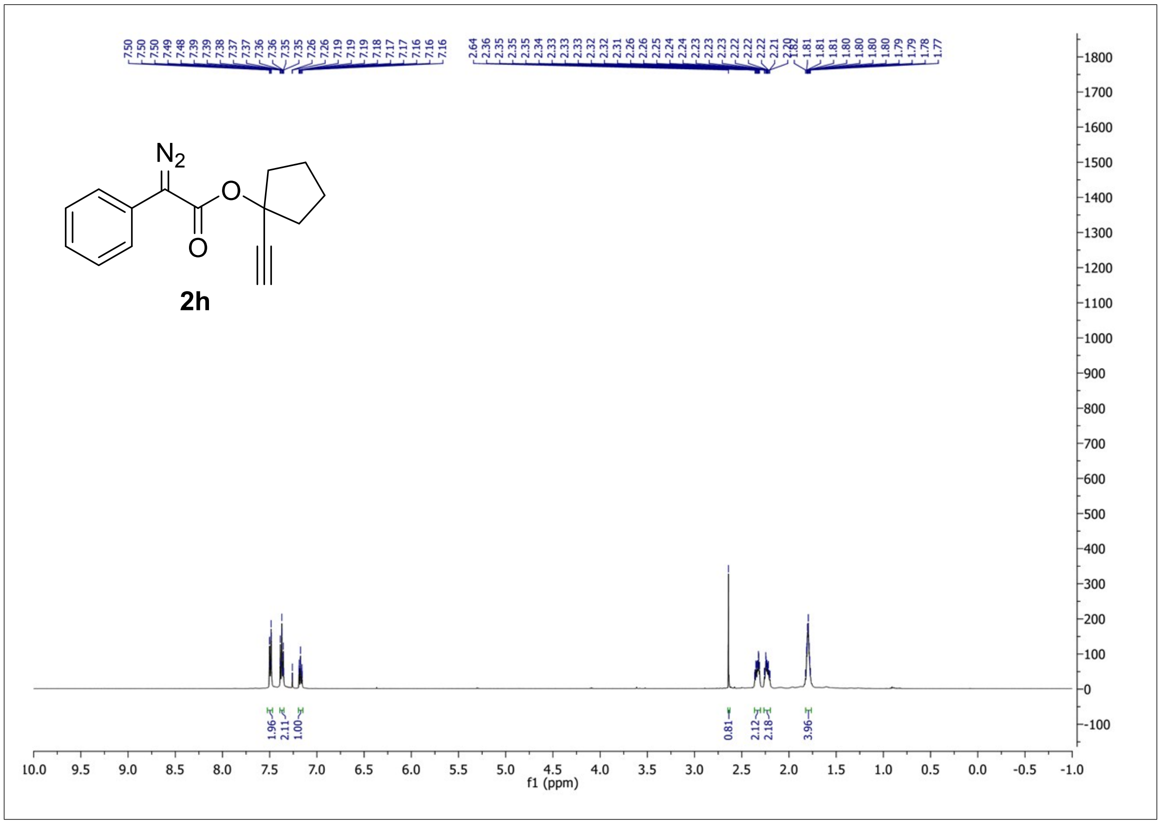
130.96
128.74
125.60
121.01
84.18
77.25
77.00
76.75
73.74
72.94
28.97
NO2
N2
O
Me
Me
O
2g
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5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2.64 2.36 2.35 2.35 2.35 2.34 2.33 2.33 2.33 2.32 2.31 2.26 2.26 2.25 2.24 2.24 2.23 2.23 2.23 2.22 2.22 2.21 2.20 1.82 1.81 1.81 1.80 1.80 1.80 1.80 1.79 1.78 1.77
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O
2h
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1.00
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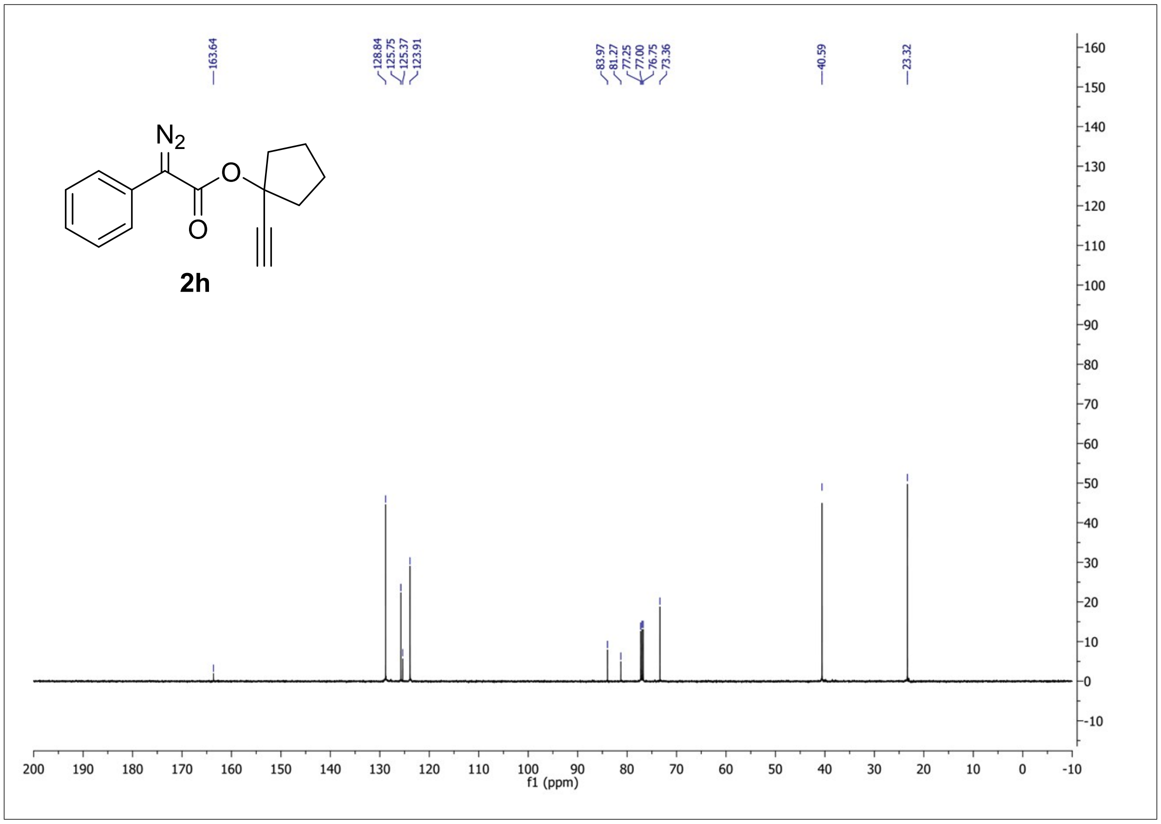
2.12
2.18
3.96
f1 (ppm)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23.32
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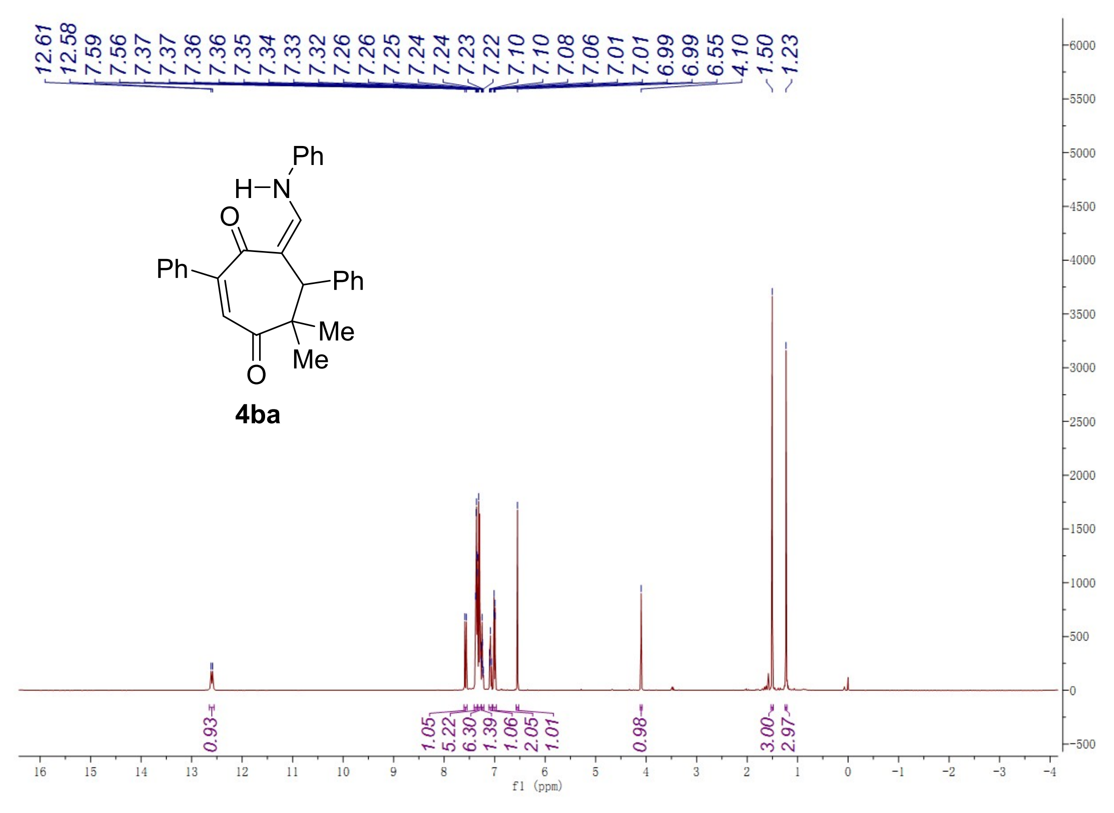
O
2h
f1 (ppm)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7.26
7.25
7.24
7.24
7.23
7.22
7.10
7.10
7.08
7.06
7.01
7.01
6.99
6.99
6.55
4.10
1.50
1.23
Ph
H−N
O
Ph
Ph
Me
Me
O
4ba
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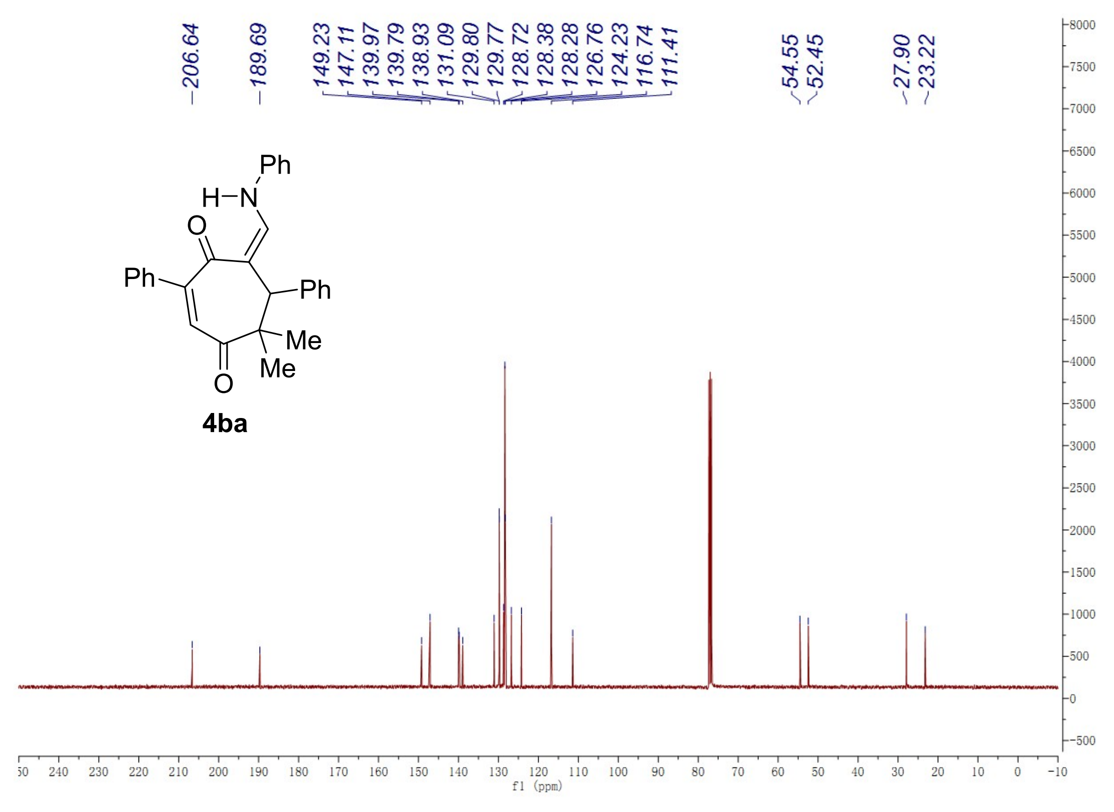
2.97
f1 (ppm)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131.09
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128.72
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128.28
126.76
124.23
116.74
111.41
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52.45
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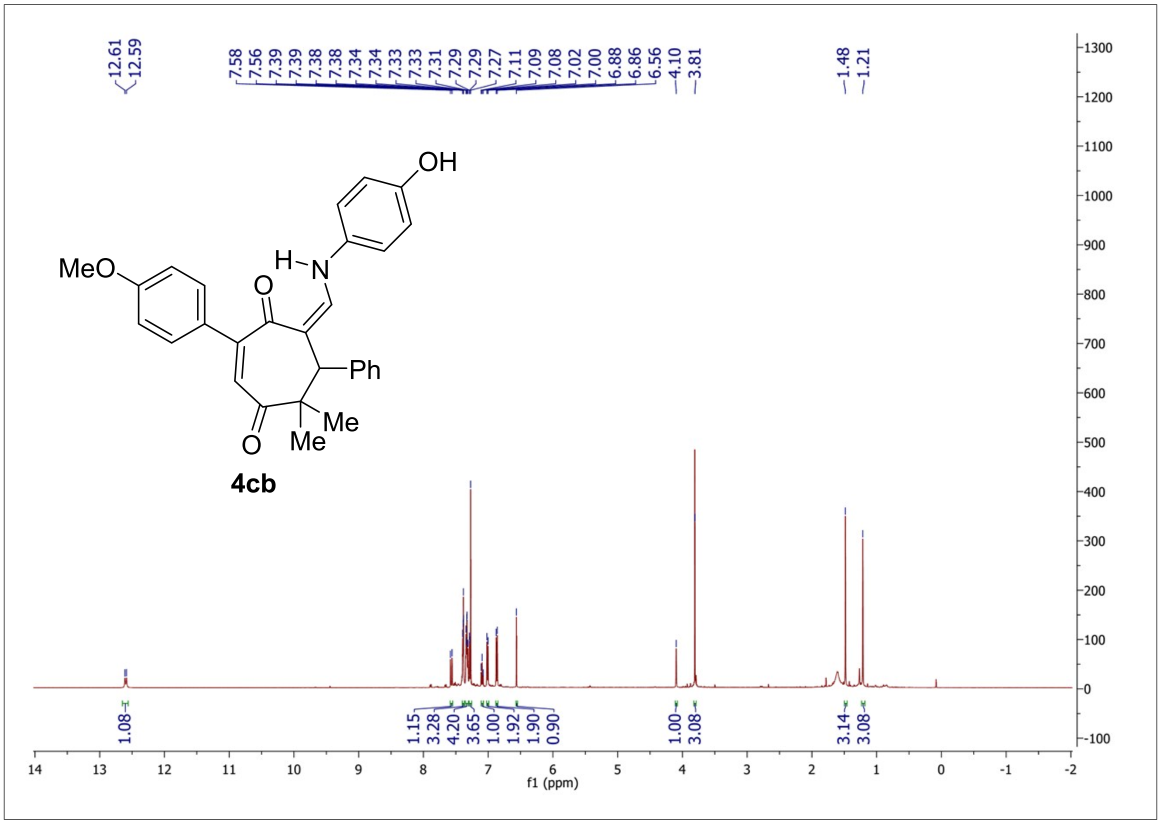
23.22
Ph
H−N
O
Ph
Ph
Me
Me
O
4ba
f1 (ppm)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7.56
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7.39
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7.34
7.33
7.33
7.31
7.29
7.29
7.27
7.11
7.09
7.08
7.02
7.00
6.88
6.86
6.56
4.10
3.81
1.48
1.21
OH
H
N
MeO
O
Ph
Me
O
Me
4cb
1.08
1.15
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1.00
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1.00
3.08
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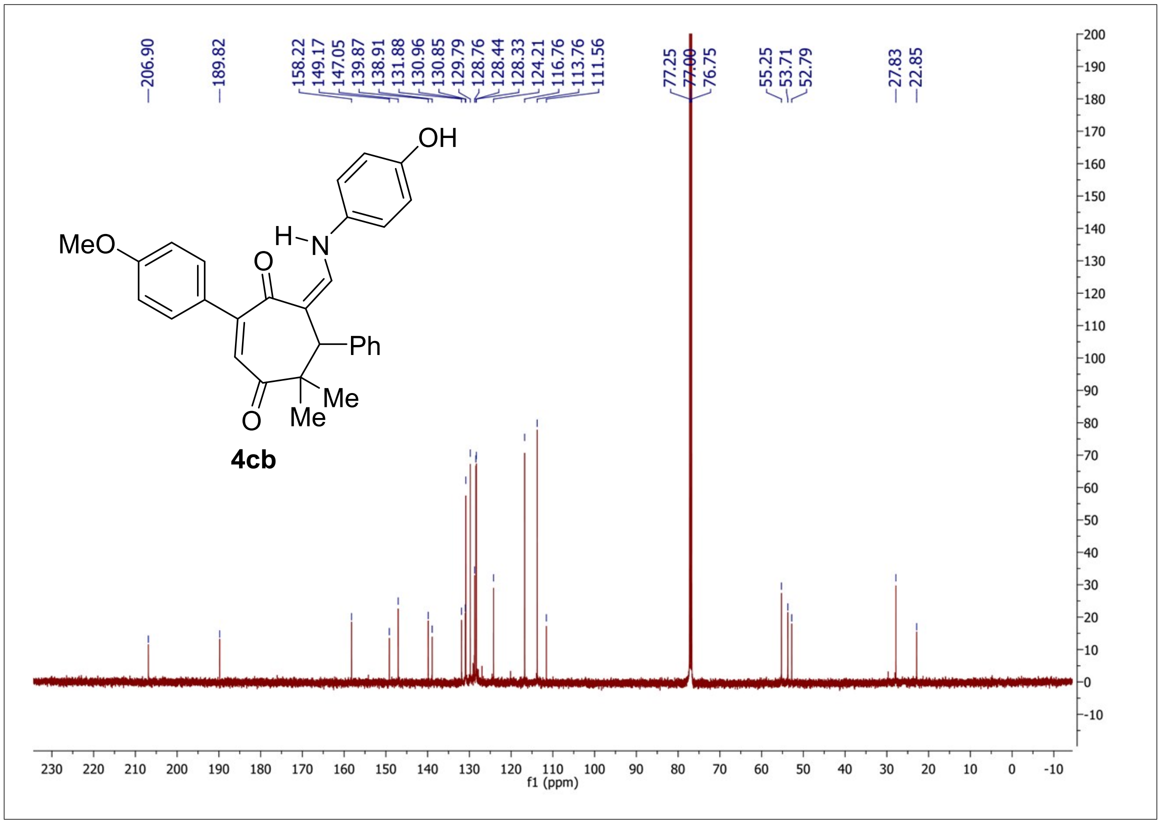
f1 (ppm)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128.44
128.33
124.21
116.76
113.76
111.56
77.25
77.00
76.75
55.25
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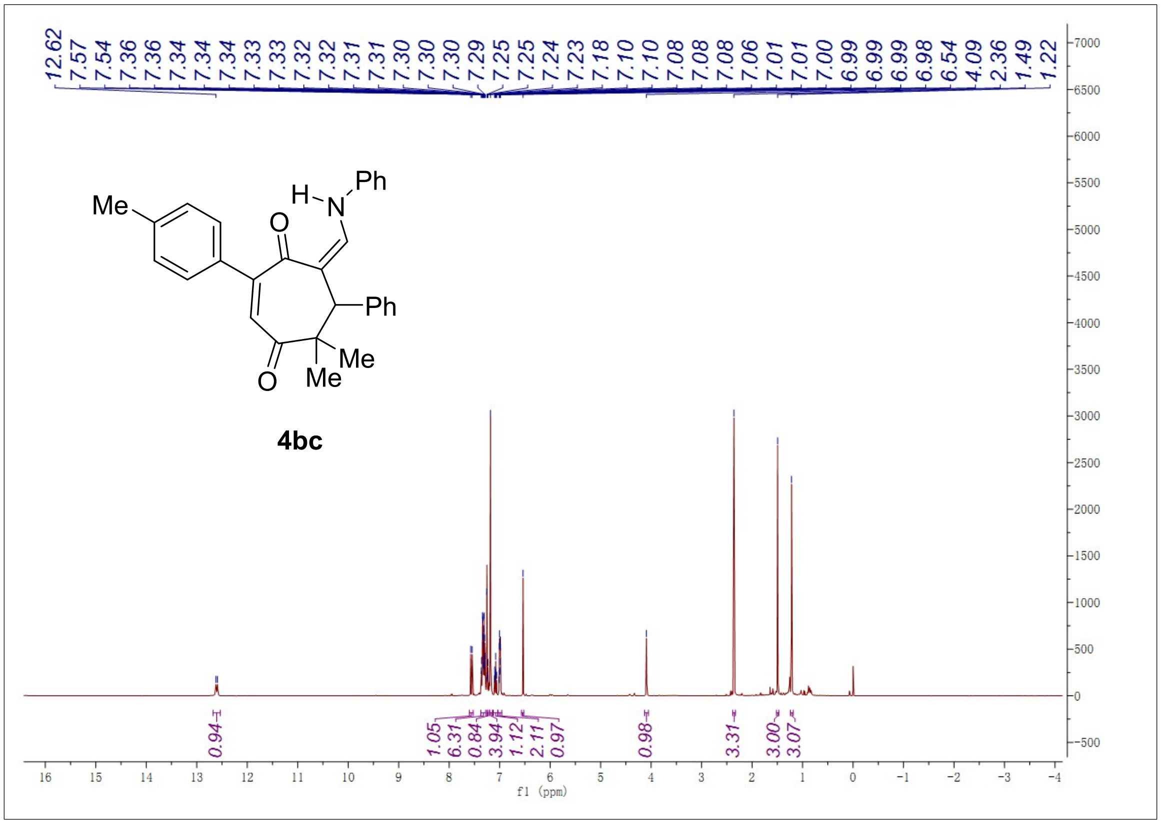
4cb
f1 (ppm)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7.31
7.30
7.30
7.30
7.29
7.25
7.25
7.24
7.23
7.18
7.10
7.10
7.08
7.08
7.08
7.06
7.01
7.01
7.00
6.99
6.99
6.99
6.98
6.54
4.09
2.36
1.49
1.22
Me
O
H
N
Ph
Ph
O
Me
Me
4bc
0.94
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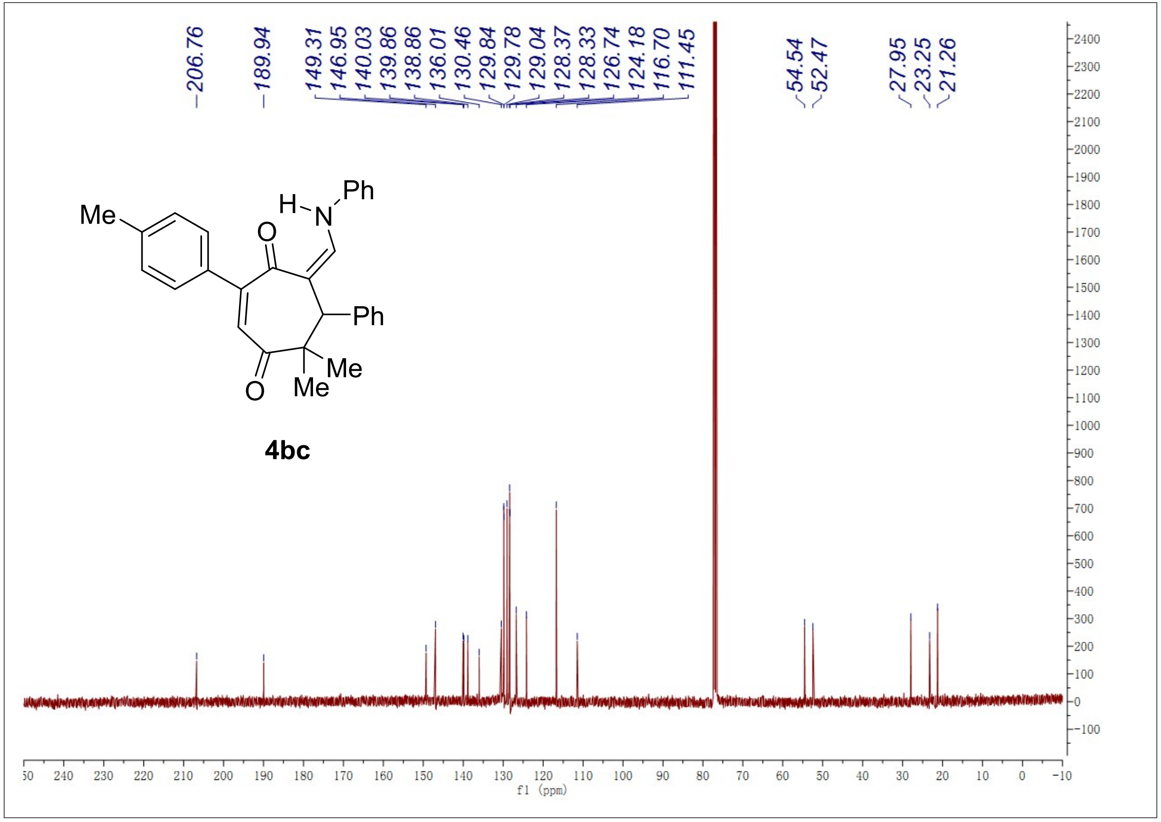
f1 (ppm)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130.46
129.84
129.78
129.04
128.37
128.33
126.74
124.18
116.70
111.45
54.54
52.47
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23.25
21.26
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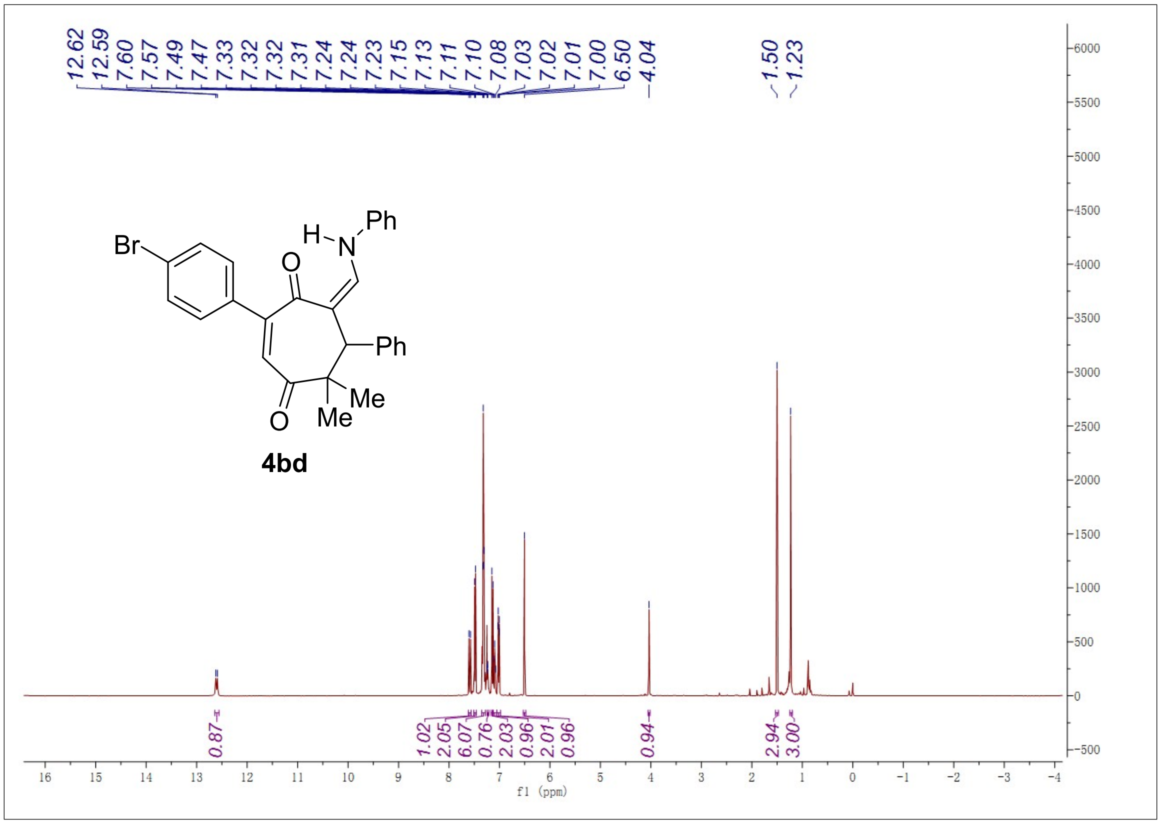
N
Ph
Ph
O
Me
Me
4bc
f1 (ppm)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Br
H
N
Ph
O
Ph
O
Me
Me
4bd
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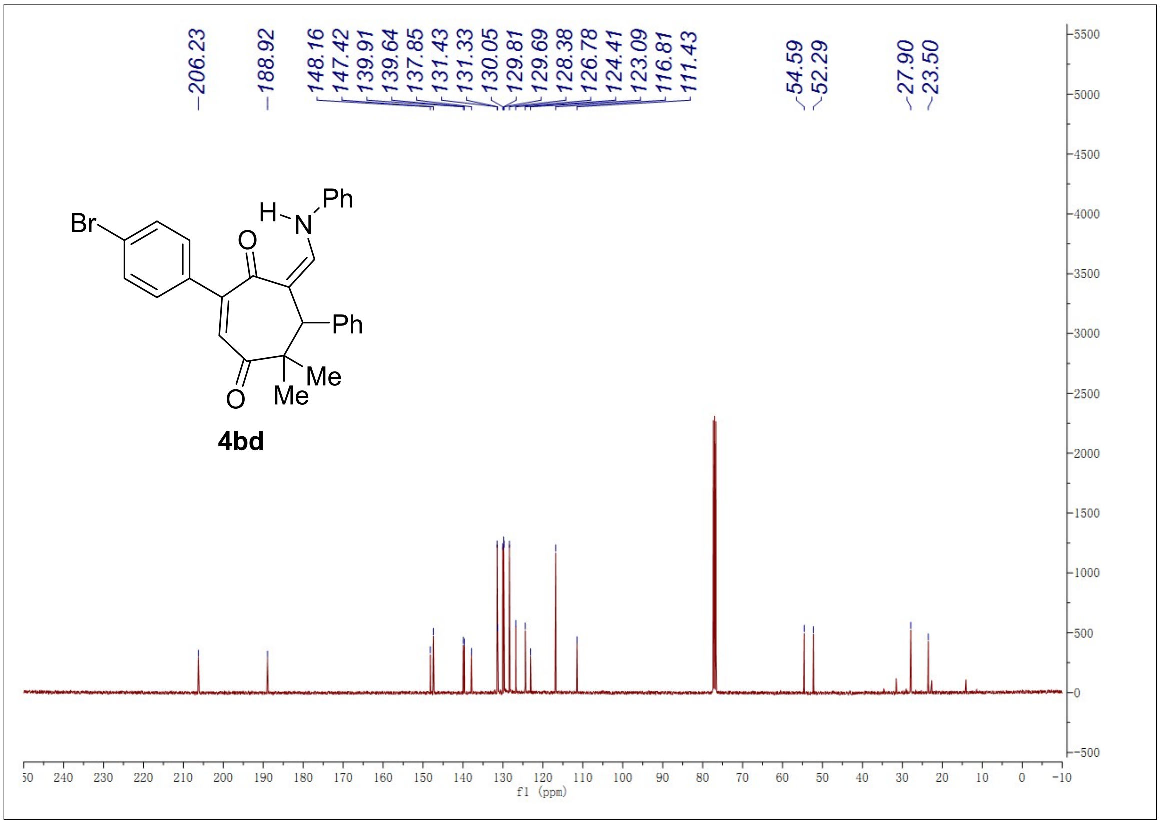
f1 (ppm)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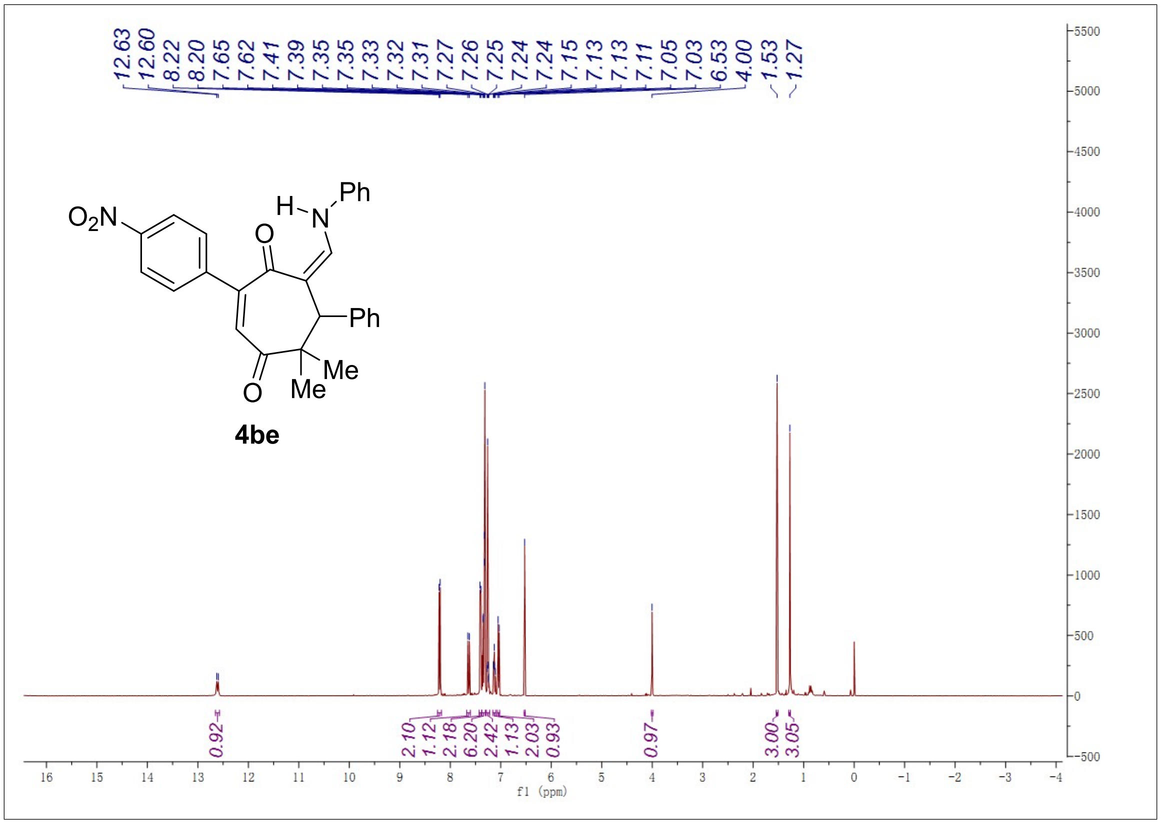
N
Ph
O
Ph
O
Me
Me
4bd
f1 (ppm)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7.31
7.27
7.26
7.25
7.24
7.24
7.15
7.13
7.13
7.11
7.05
7.03
6.53
4.00
1.53
1.27
O2N
H
N
Ph
O
Ph
O
Me
Me
4be
0.92
2.10
1.12
2.18
6.20
2.42
1.13
2.03
0.93
0.97
3.00
3.05
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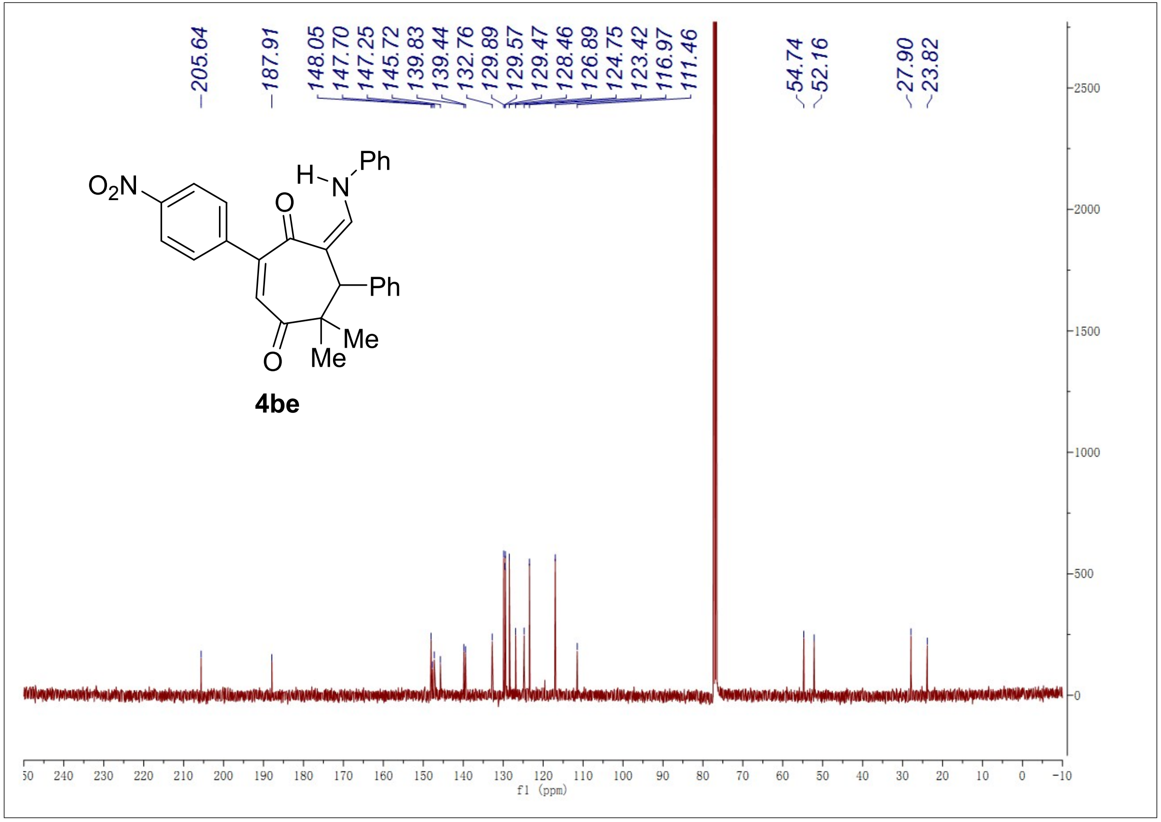
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116.97
111.46
54.74
52.16
27.90
23.82
O2N
H
N
Ph
O
Ph
O
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Me
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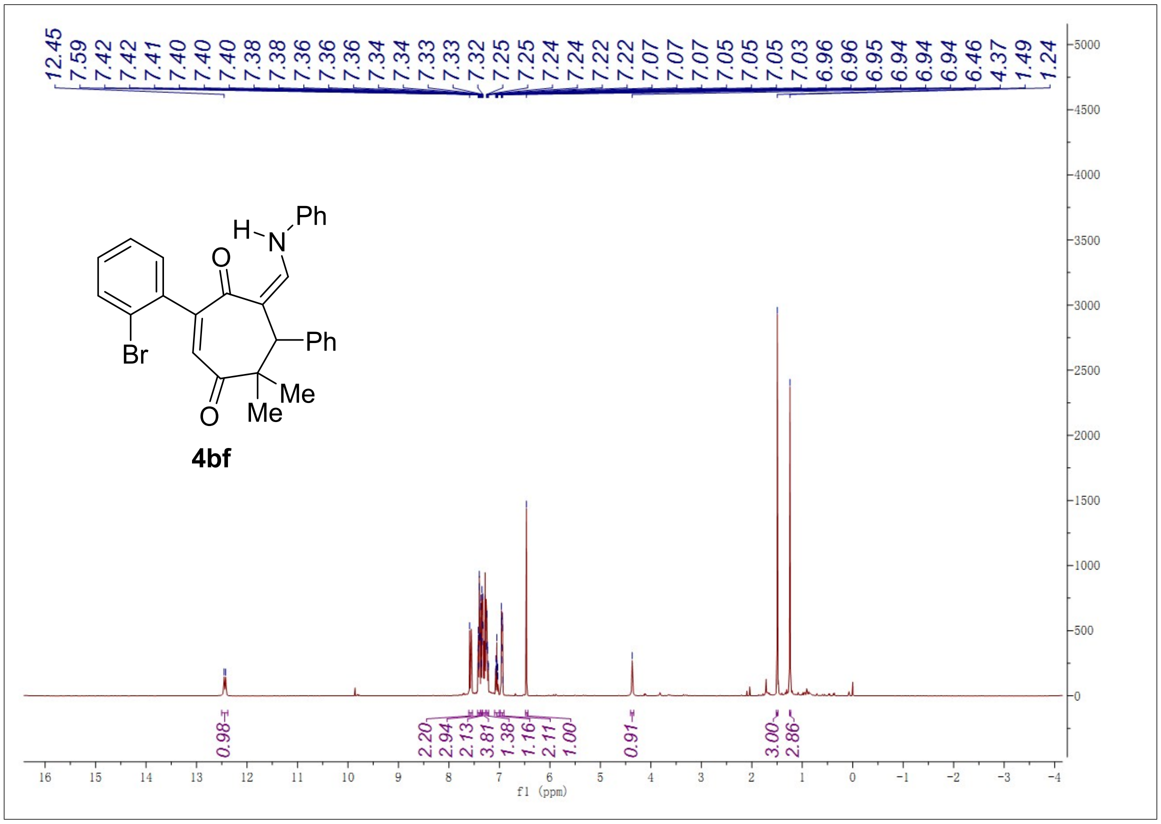
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2500 2000 1500 1000 500 0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7.36
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7.34
7.34
7.33
7.33
7.32
7.25
7.25
7.24
7.24
7.22
7.22
7.07
7.07
7.05
7.05
7.05
7.03
6.96
6.96
6.95
6.94
6.94
6.94
6.46
4.37
1.49
1.24
H
N
Ph
O
Ph
Br
O
Me
Me
4bf
0.98
2.20
2.94
2.13
3.81
1.38
1.16
2.11
1.00
0.91
3.00
2.86
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)
5000
4500
4000
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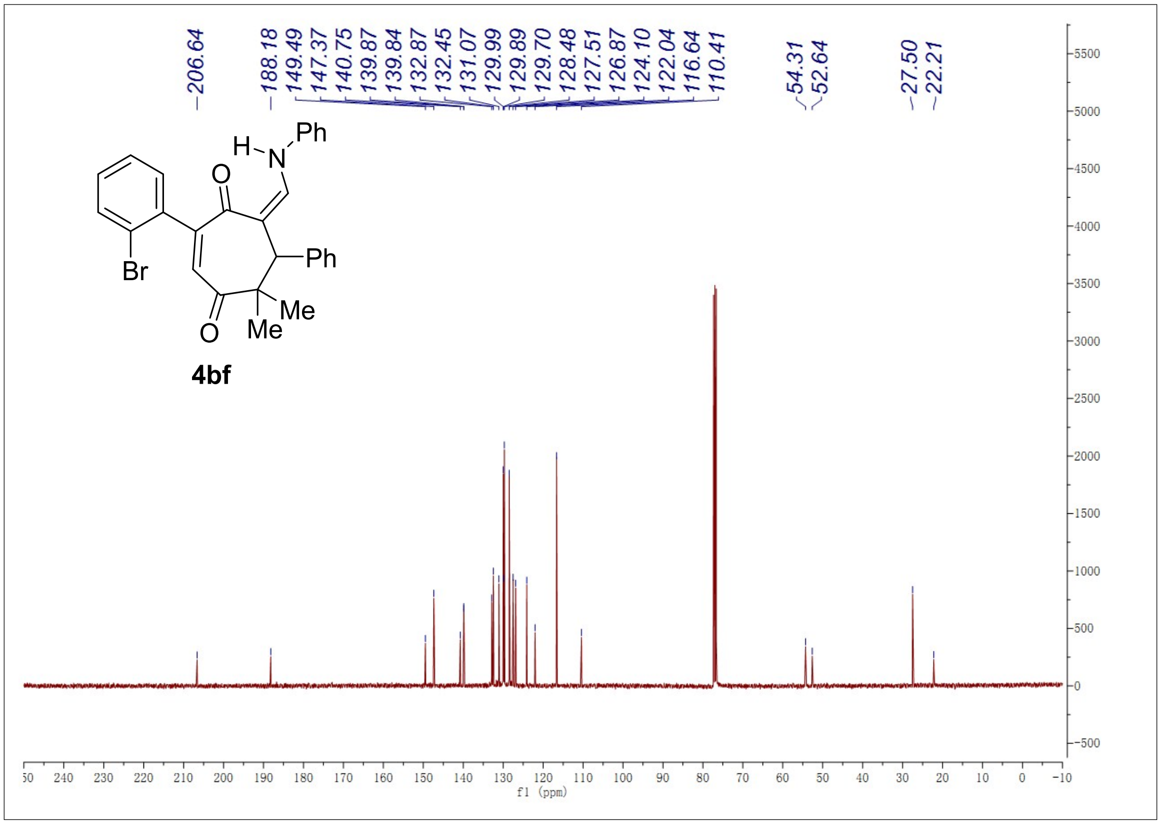
3000
2500
2000
1500
1000
500
0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129.70
128.48
127.51
126.87
124.10
122.04
116.64
110.41
54.31
52.64
27.50
22.21
H
N
Ph
O
Ph
Br
O
Me
Me
4bf
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
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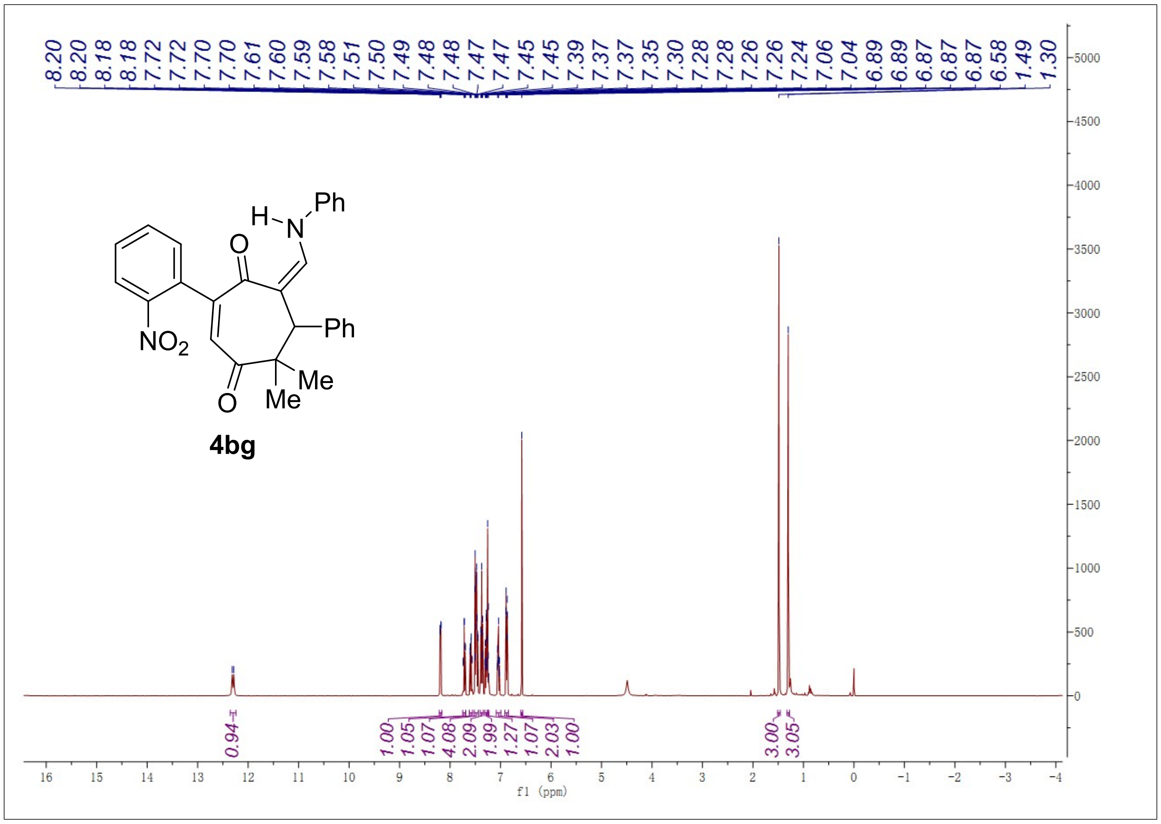
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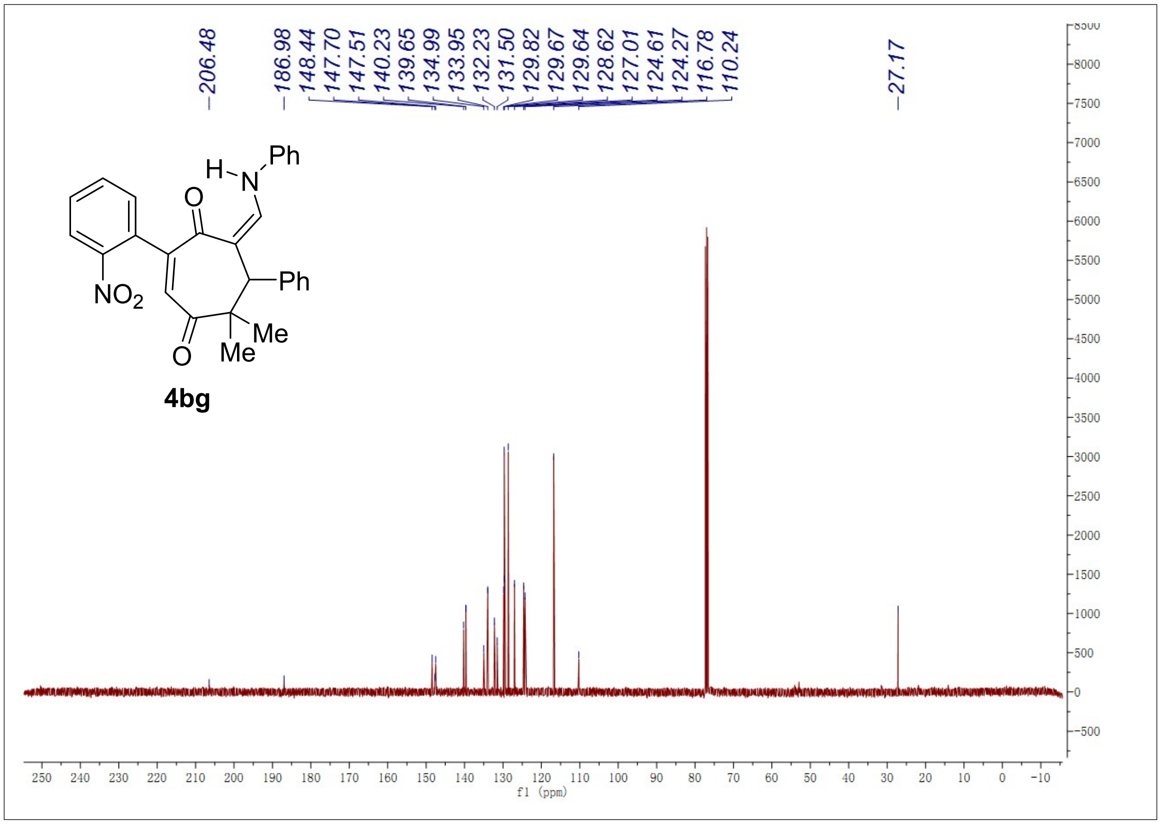
H
N
Ph
O
Ph
NO2
O
Me
Me
4bg
0.94
1.00 1.05 1.07 4.08 2.09 1.99 1.27 1.07 2.03 1.00
3.00 3.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0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186.98 148.44 147.70 147.51 140.23 139.65 134.99 133.95 132.23 131.50 129.82 129.67 129.64 128.62 127.01 124.61 124.27 116.78 110.24
27.17
H
N
Ph
O
Ph
NO2
O
Me
Me
4bg
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
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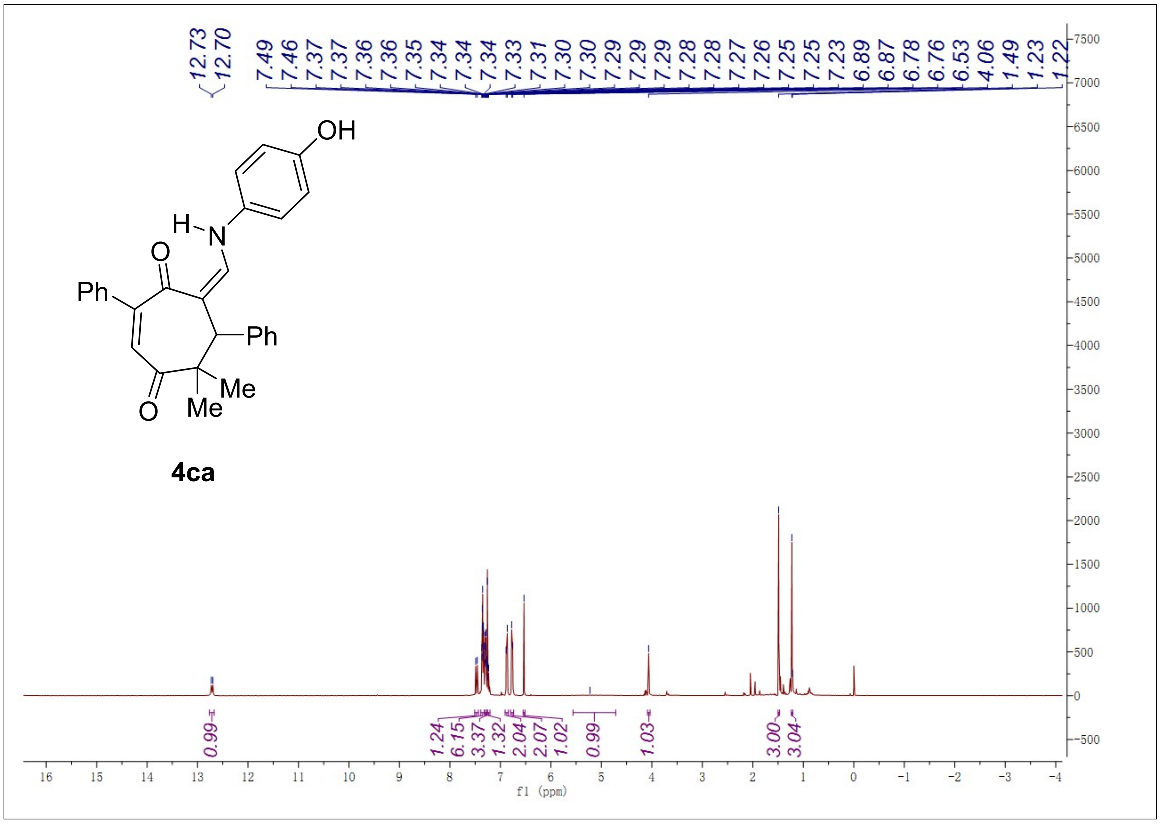
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7.34
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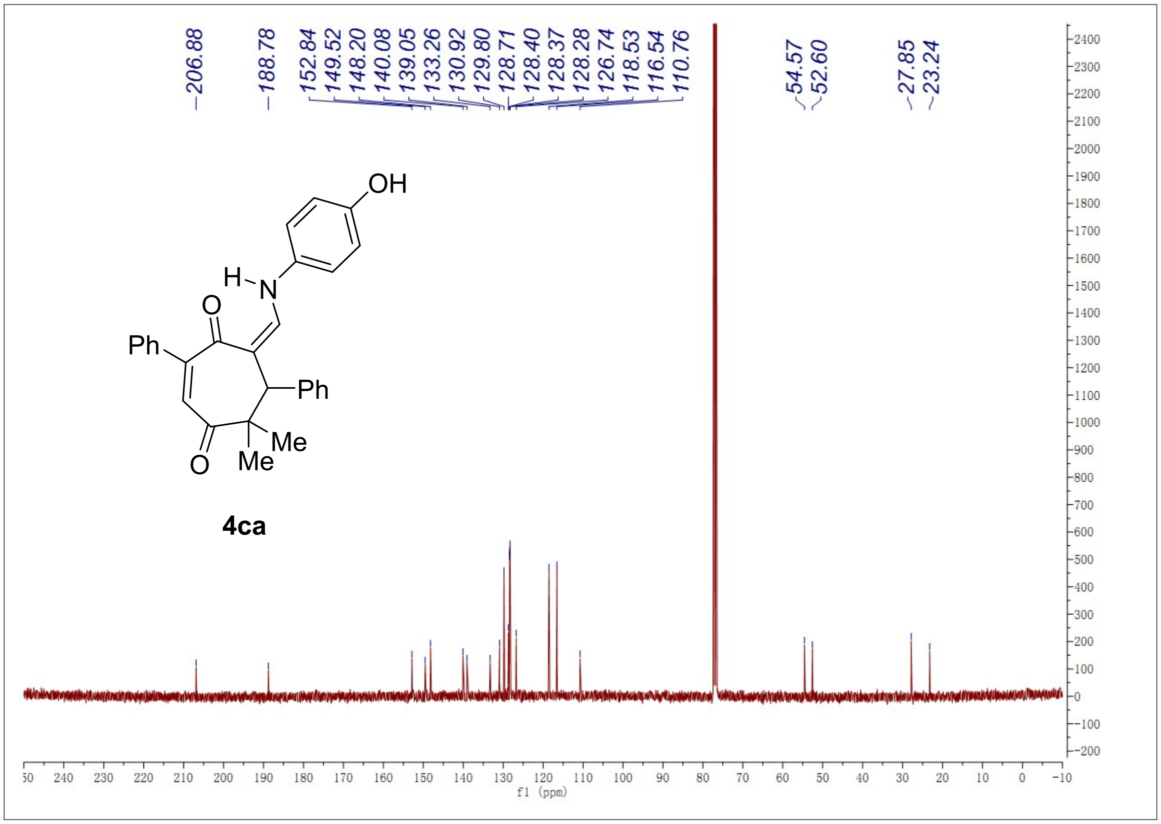
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.25
7.23
6.89
6.87
6.78
6.76
6.53
4.06
1.49
1.23
1.22
OH
H
N
O
Ph
Ph
O
Me
Me
0.99
1.24
6.15
3.37
1.32
2.04
2.07
1.02
0.99
1.03
3.00
3.04
f1 (ppm)

4ca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133.26
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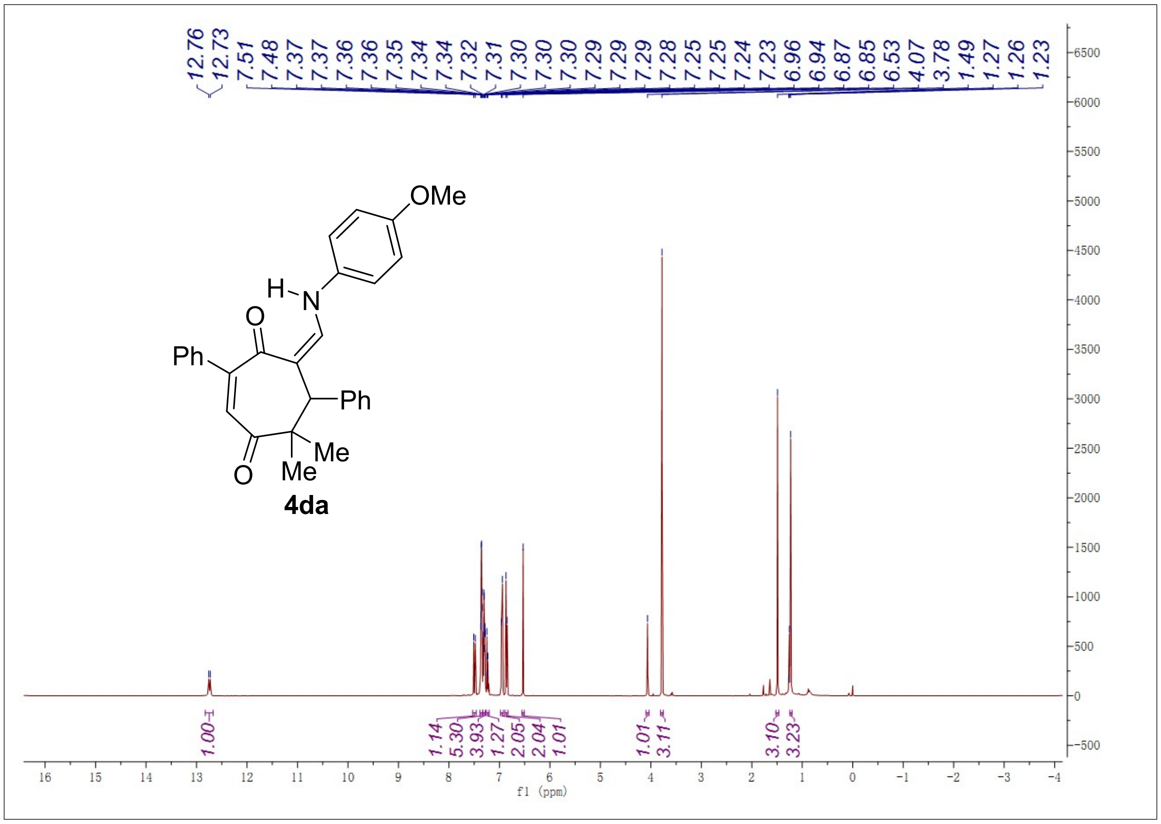
128.71
128.40
128.37
128.28
126.74
118.53
116.54
110.76
54.57
52.60
27.85
23.24
OH
H
N
O
Ph
Ph
O
Me
Me
f1 (ppm)

4ca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7.31
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.25
7.25
7.24
7.23
6.96
6.94
6.87
6.85
6.53
4.07
3.78
1.49
1.27
1.26
1.23
OMe
H
N
O
Ph
Ph
Me
Me
O
4da
1.00
1.14
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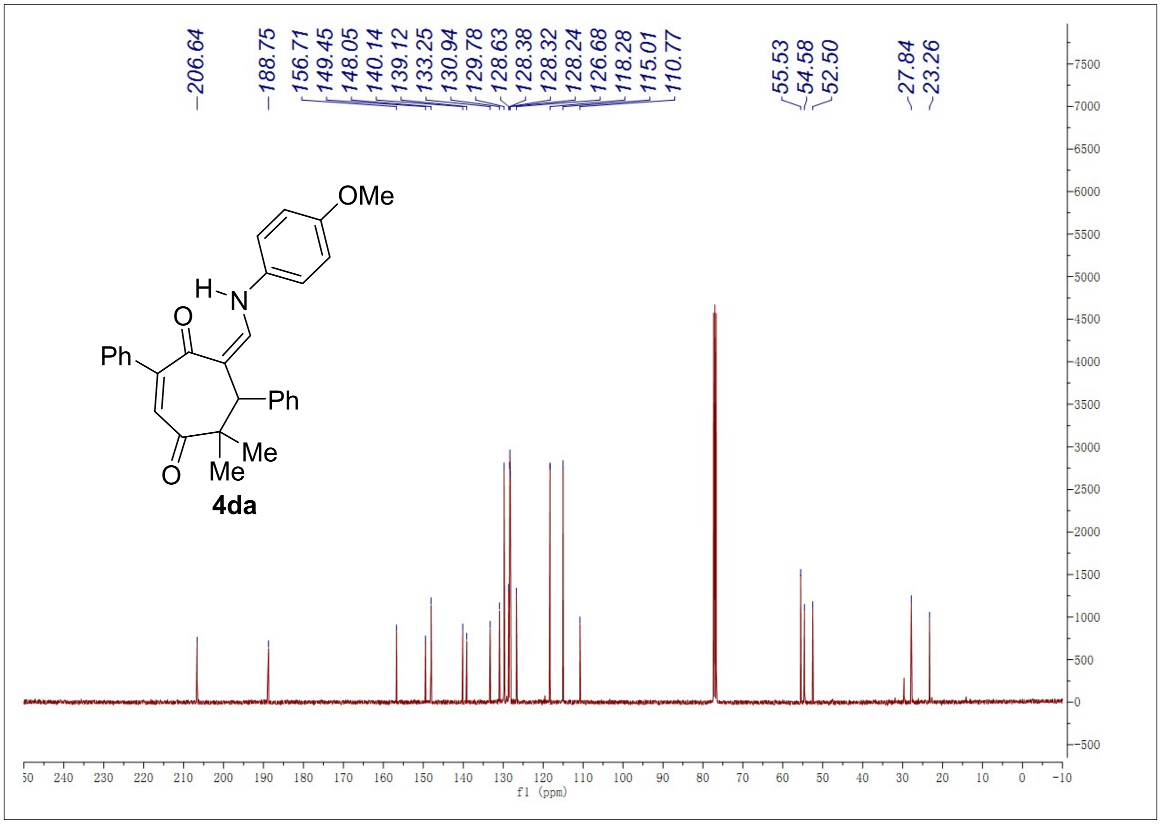
3.93
1.27
2.05
2.04
1.01
1.01
3.11
3.10
3.23
f1 (ppm)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128.24
126.68
118.28
115.01
110.77
55.53
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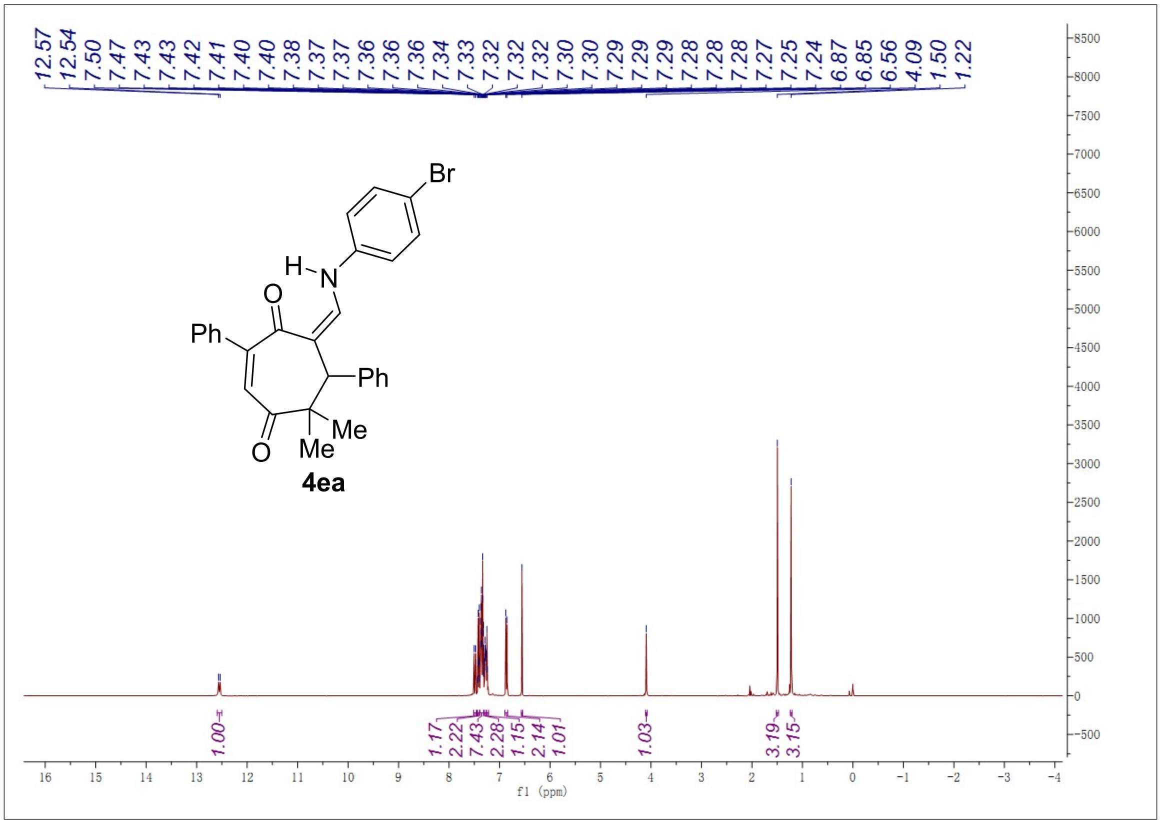
23.26
OMe
H
N
O
Ph
Ph
Me
Me
O
4da
f1 (ppm)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7.37
7.36
7.36
7.36
7.34
7.33
7.32
7.32
7.32
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.27
7.25
7.24
6.87
6.85
6.56
4.09
1.50
1.22
Br
H
N
O
Ph
Ph
Me
Me
O
4ea
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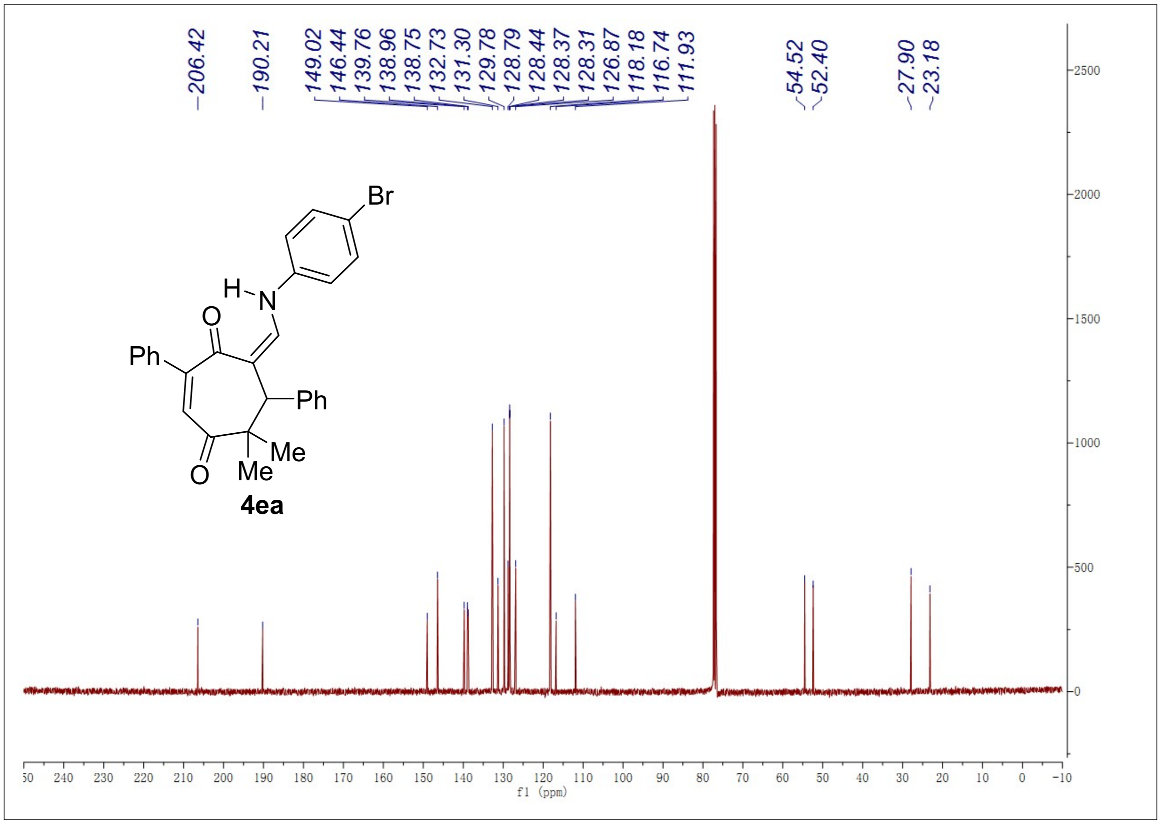
1.17
2.22
7.43
2.28
1.15
2.14
1.01
1.03
3.19
3.15
f1 (ppm)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138.75
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131.30
129.78
128.79
128.44
128.37
128.31
126.87
118.18
116.74
111.93
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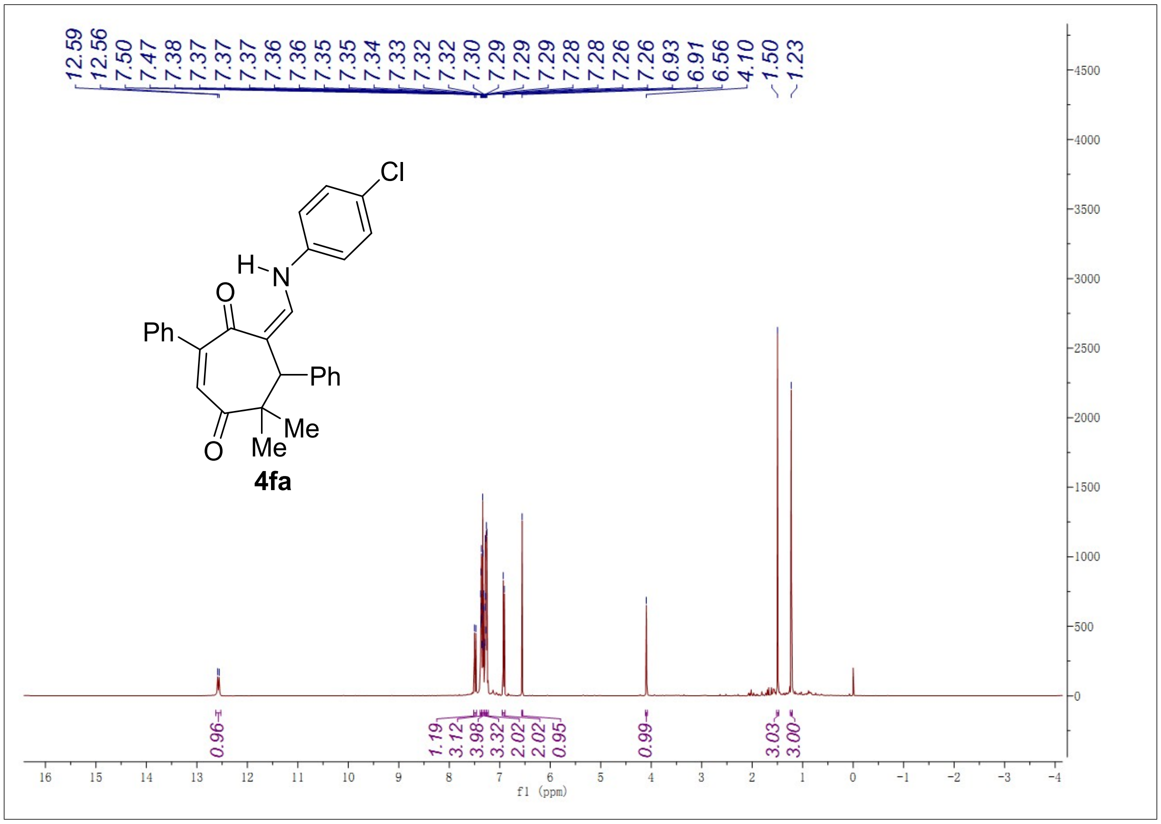
52.40
27.90
23.18
Br
H
N
O
Ph
Ph
Me
Me
O
4ea
f1 (ppm)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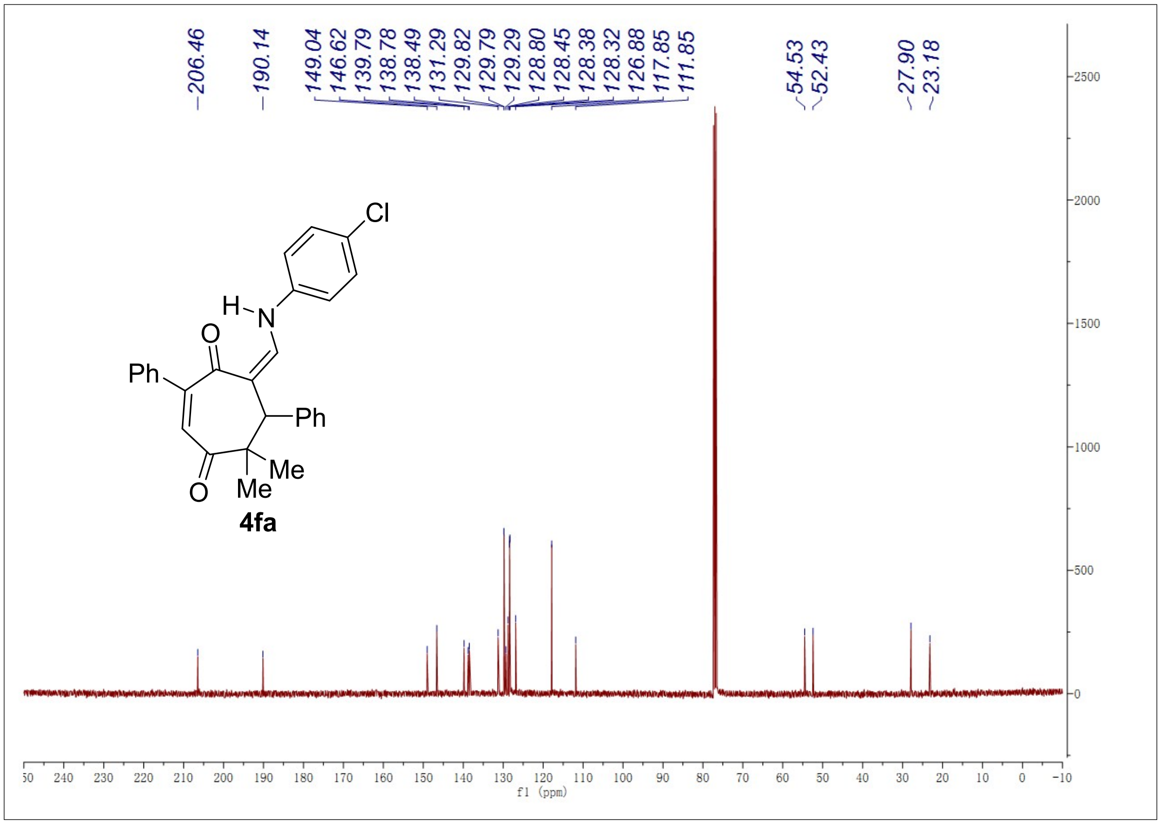
7.33
7.32
7.32
7.30
7.29
7.29
7.29
7.28
7.28
7.26
7.26
6.93
6.91
6.56
4.10
1.50
1.23
Cl
H
N
O
Ph
Ph
Me
Me
O
4fa
0.96
1.19
3.12
3.98
3.32
2.02
2.02
0.95
0.99
3.03
3.00
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
4500 4000 3500 3000 2500 2000 1500 1000 500 0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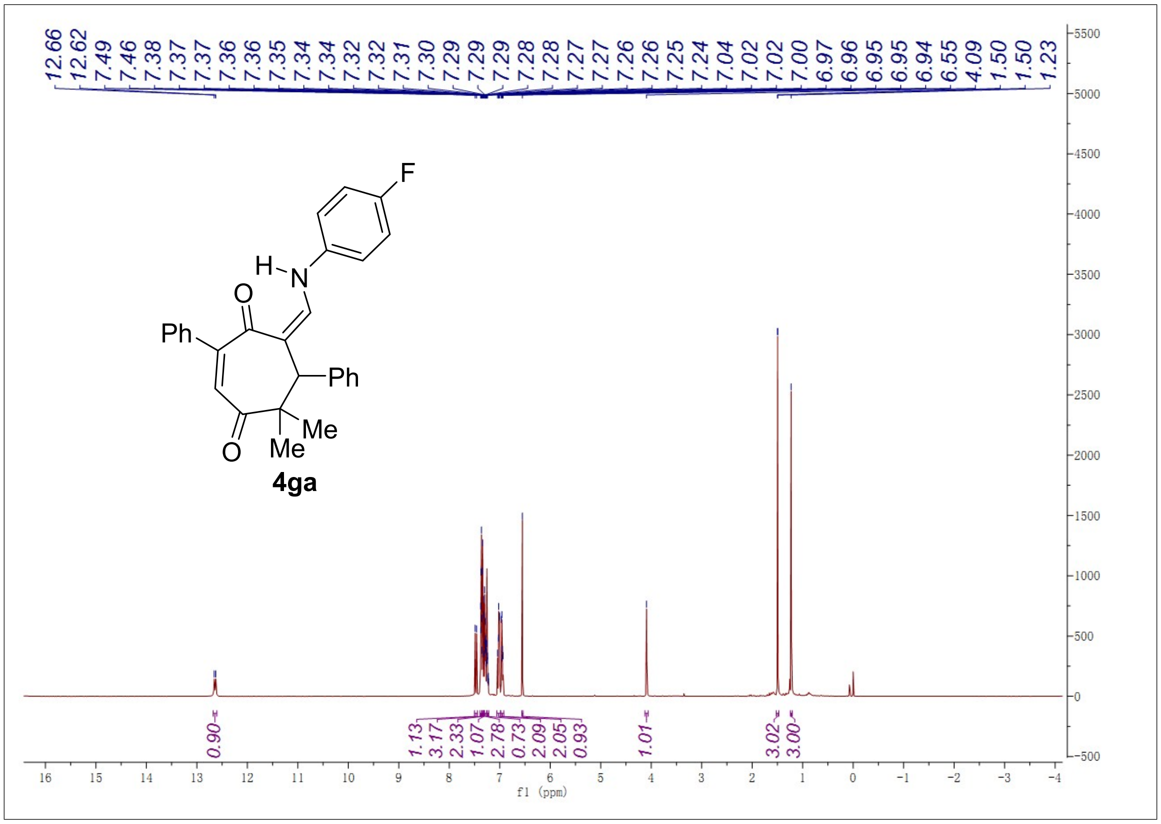
138.49
131.29
129.82
129.79
129.29
128.80
128.45
128.38
128.32
126.88
117.85
111.85
54.53
52.43
27.90
23.18
Cl
H
N
O
Ph
Ph
Me
Me
O
4fa
f1 (ppm)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
2500 2000 1500 1000 500 0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7.36
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7.35
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7.31
7.30
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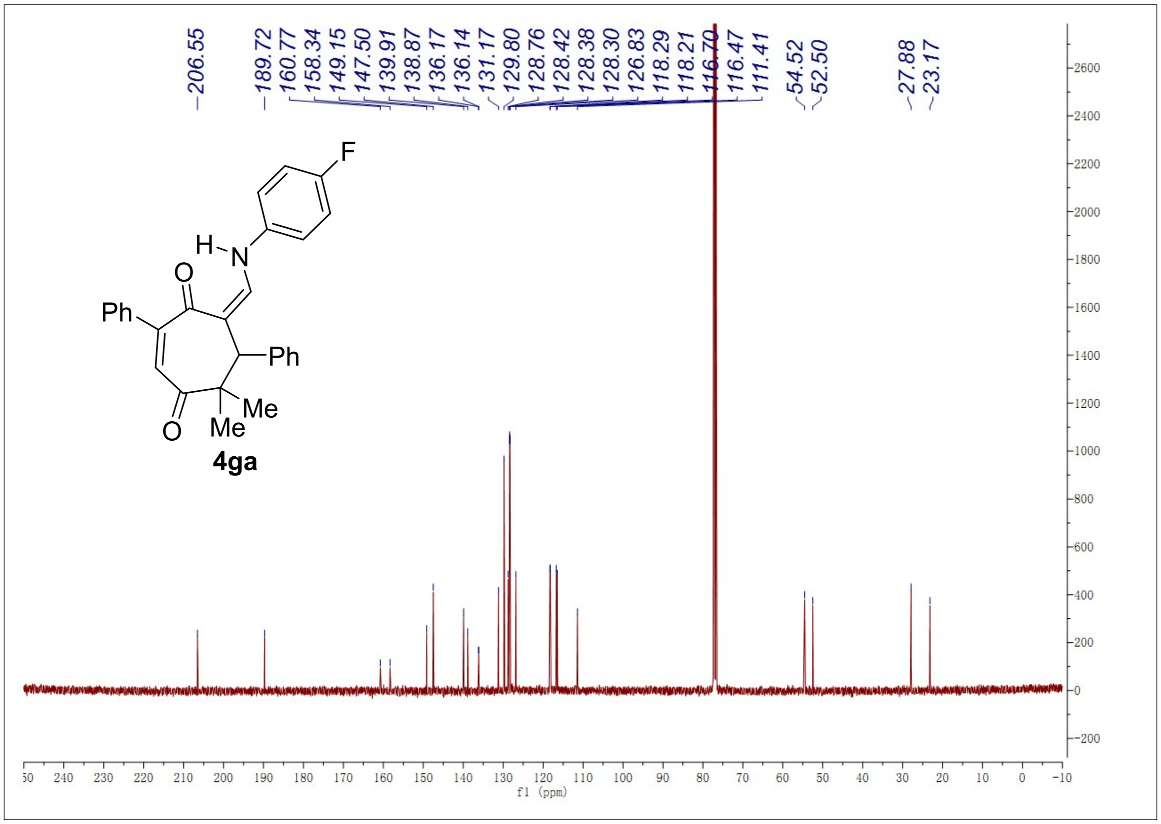
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.04
7.02
7.02
7.00
6.97
6.96
6.95
6.95
6.94
6.55
4.09
1.50
1.50
1.23
F
H
N
O
Ph
Ph
O
Me
Me
4ga
0.90
1.13
3.17
2.33
1.07
2.78
0.73
2.09
2.05
0.93
1.01
3.02
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)
5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500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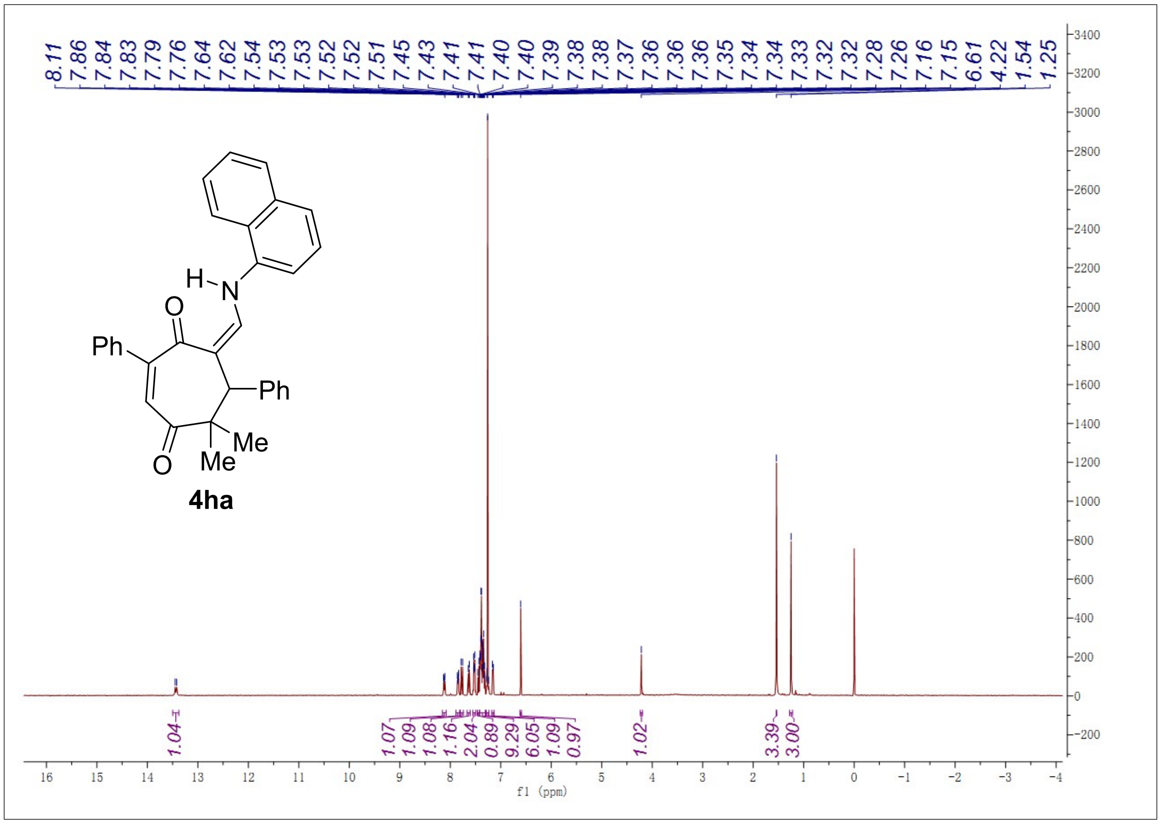
138.87
136.17
136.14
131.17
129.80
128.76
128.42
128.38
128.30
126.83
118.29
118.21
116.70
116.47
111.41
54.52
52.50
27.88
23.17
F
H
N
O
Ph
Ph
O
Me
Me
4ga
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200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7.86
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7.79
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7.53
7.52
7.52
7.51
7.45
7.43
7.41
7.41
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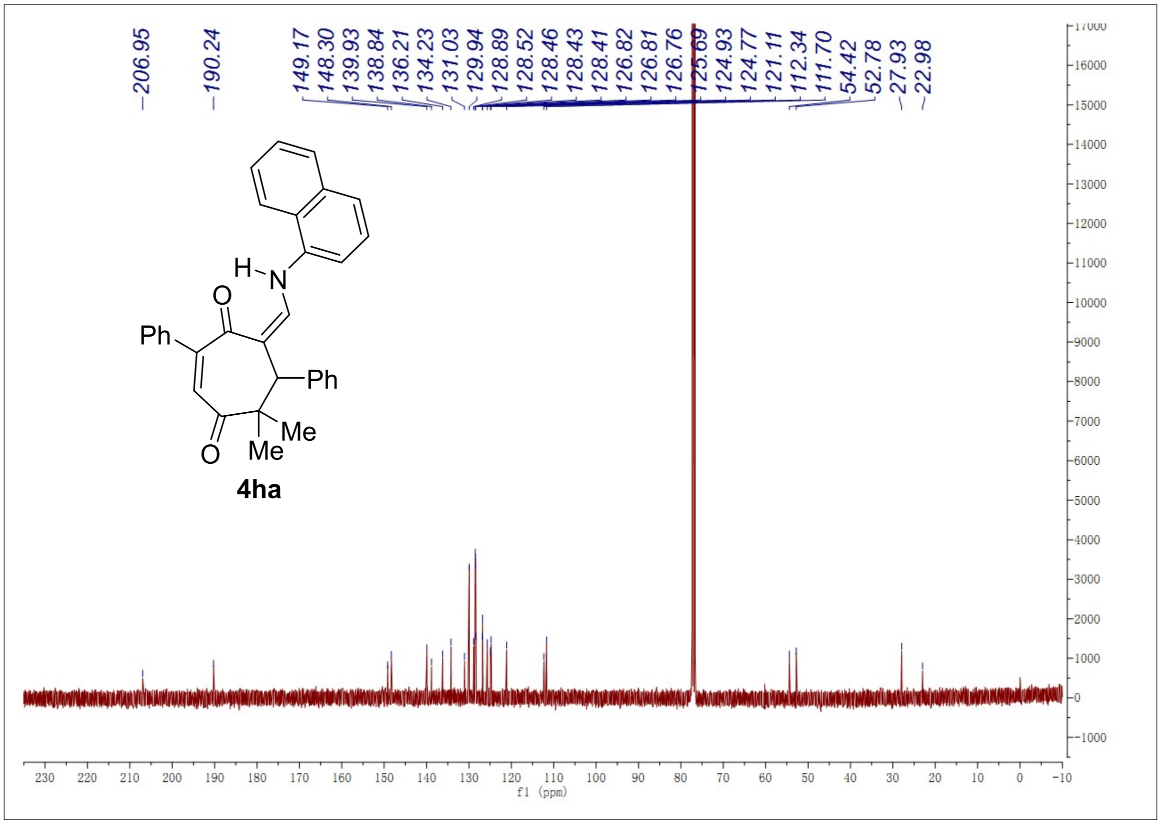
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.28
7.26
7.16
7.15
6.61
4.22
1.54
1.25
H
N
O
Ph
Ph
Me
O
Me
4ha
1.04
1.07
1.09
1.08
1.16
2.04
0.89
9.29
6.05
1.09
0.97
1.02
3.39
3.00
f1 (ppm)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128.52
128.46
128.43
128.41
126.82
126.81
126.76
125.69
124.93
124.77
121.11
112.34
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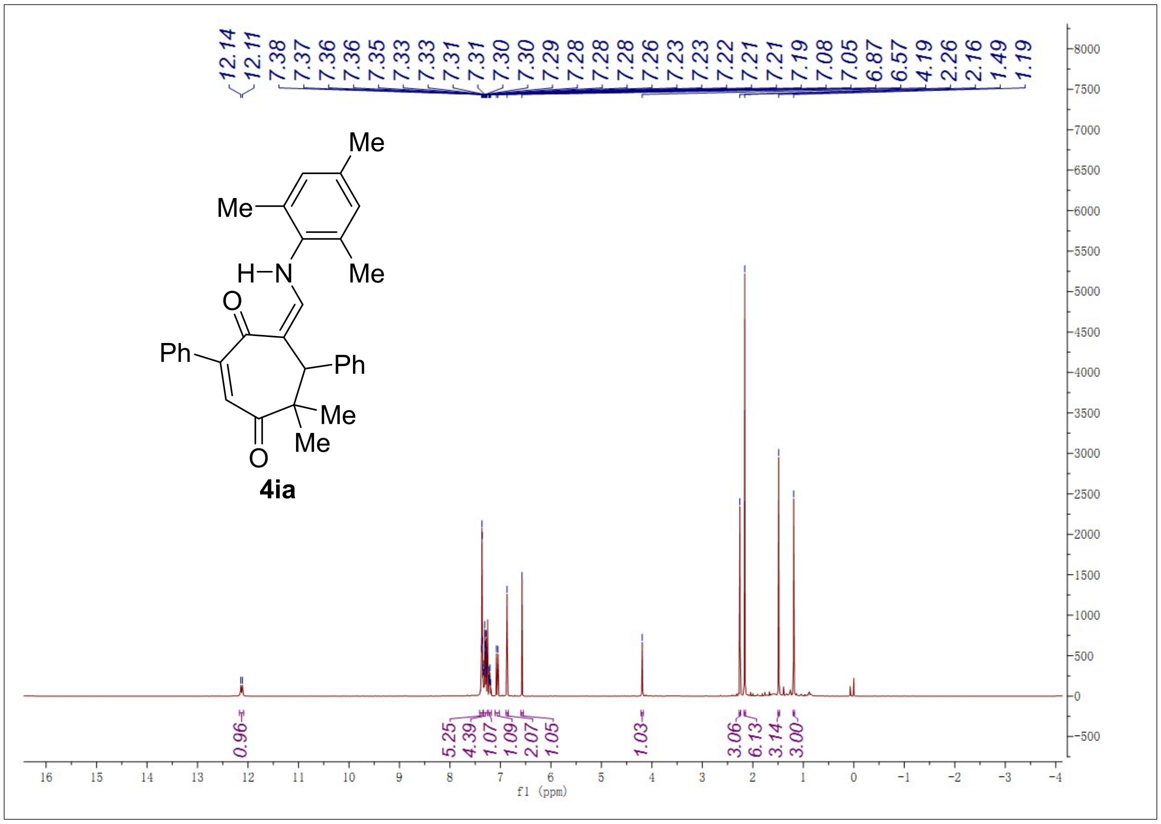
54.42
52.78
27.93
22.98
H
N
O
Ph
Ph
Me
O
Me
4ha
f1 (ppm)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7.30
7.29
7.28
7.28
7.28
7.26
7.23
7.23
7.22
7.21
7.21
7.19
7.08
7.05
6.87
6.57
4.19
2.26
2.16
1.49
1.19
Me
Me
H−N
Me
O
Ph
Ph
Me
Me
O
4ia
0.96
5.25
4.39
1.07
1.09
2.07
1.05
1.03
3.06
6.13
3.14
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)
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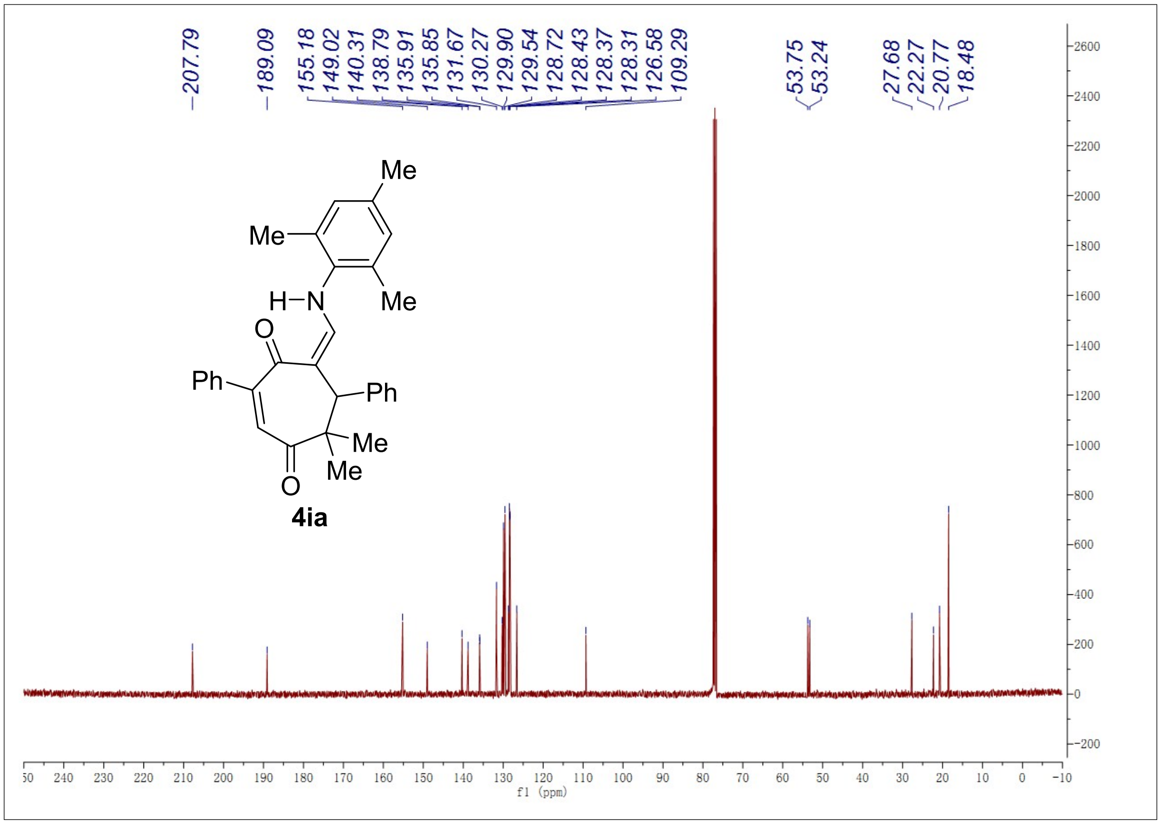
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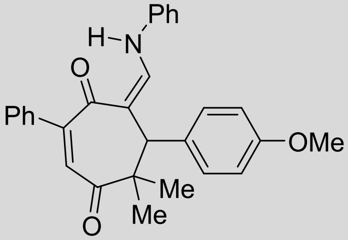
128.72
128.43
128.37
128.31
126.58
109.29
53.75
53.24
27.68
22.27
20.77
18.48
Me
Me
H−N
Me
O
Ph
Ph
Me
Me
O
4ia
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 −200



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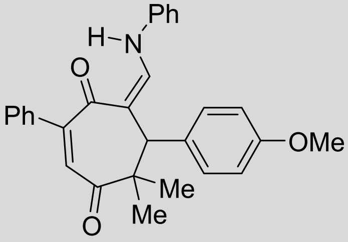

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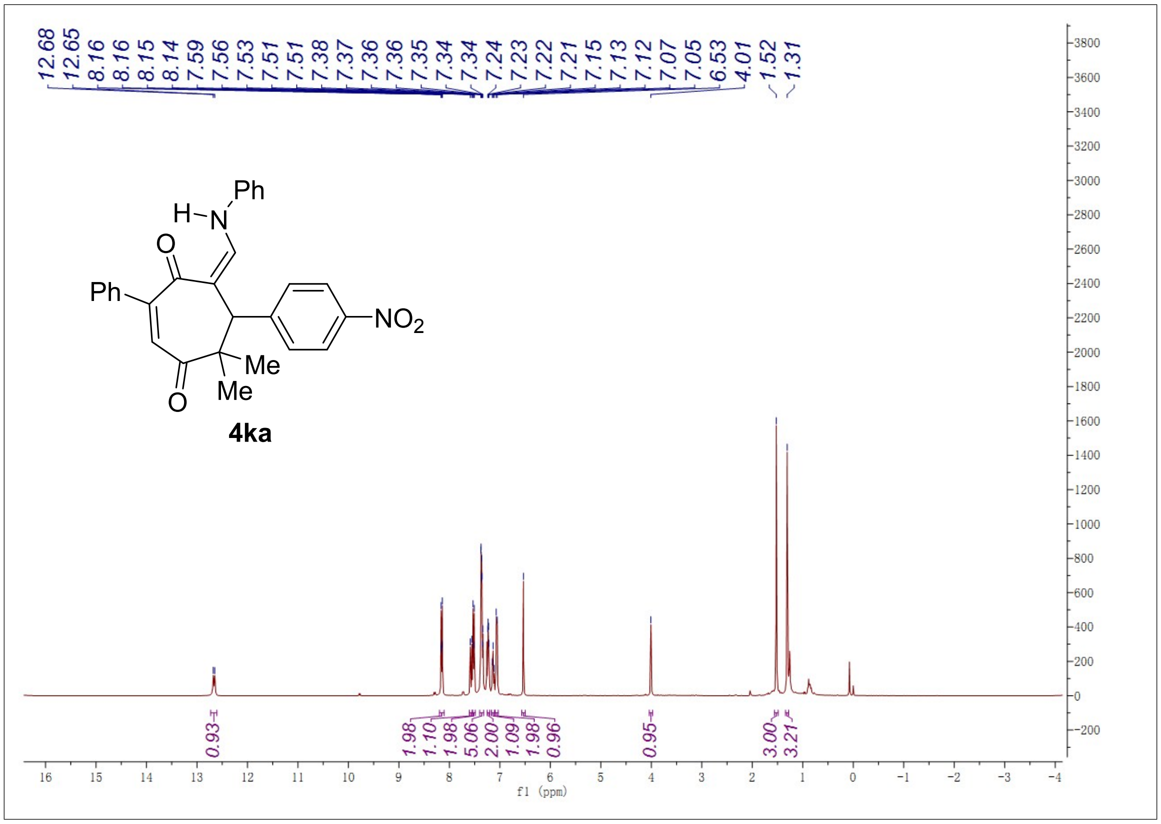
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7.36
7.36
7.35
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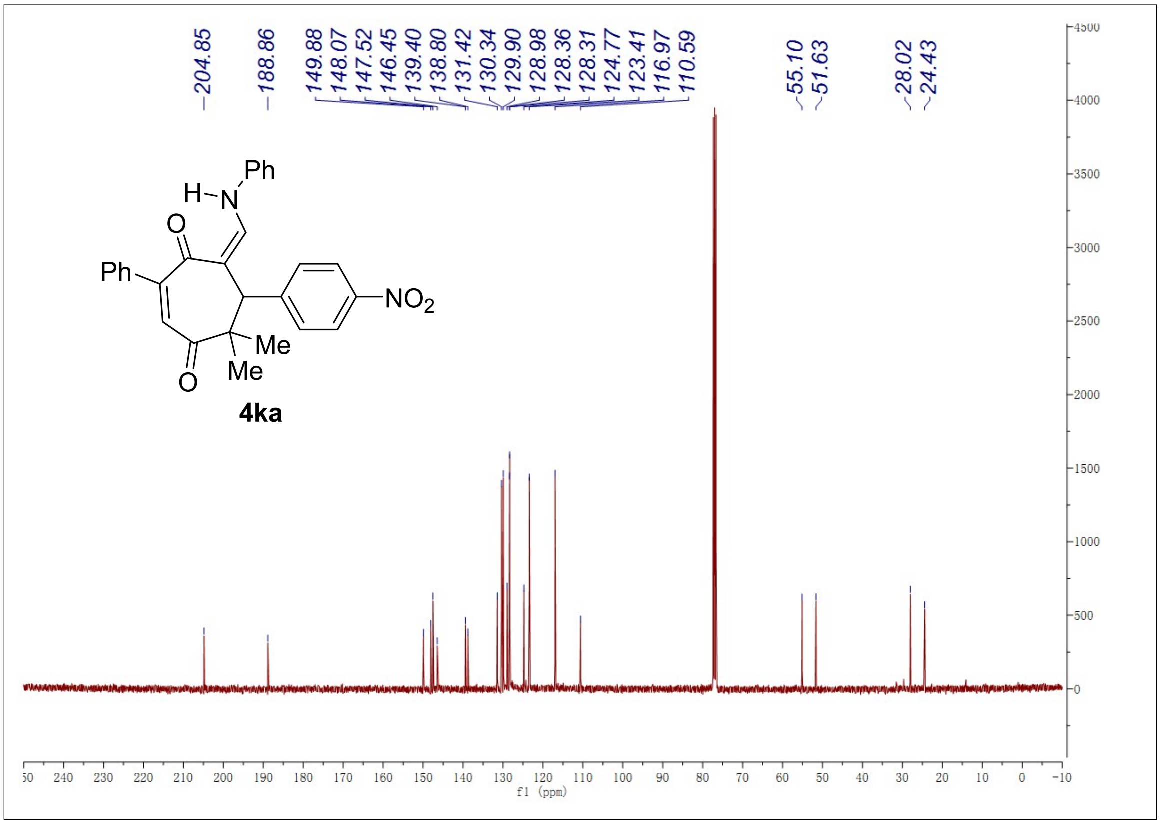
7.24
7.23
7.22
7.21
7.15
7.13
7.12
7.07
7.05
6.53
4.01
1.52
1.31
Ph
H
N
O
Ph
NO2
Me
Me
O
4ka
0.93
1.98
1.10
1.98
5.06
2.00
1.09
1.98
0.96
0.95
3.00
3.21
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200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130.34
129.90
128.98
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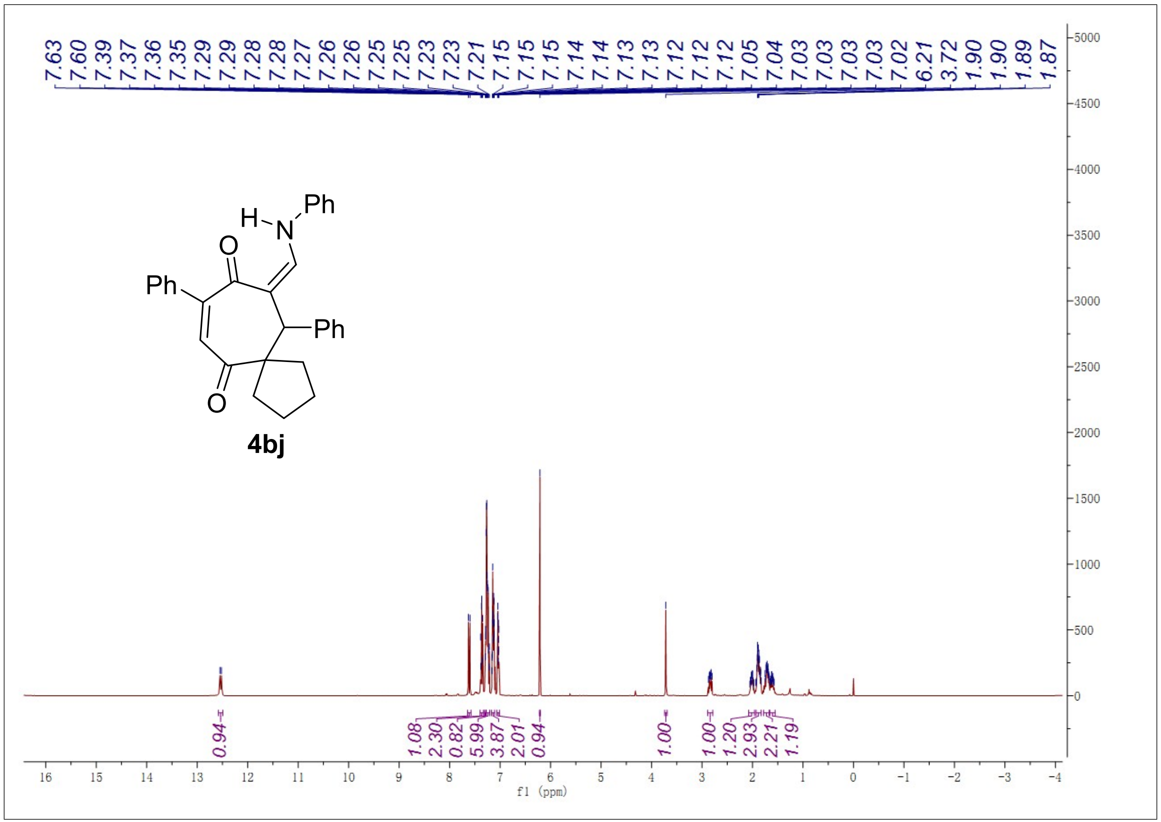
128.31
124.77
123.41
116.97
110.59
55.10
51.63
28.02
24.43
Ph
H
N
O
Ph
NO2
Me
Me
O
4ka
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
4500 4000 3500 3000 2500 2000 1500 1000 500 0


4bj

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7.15
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7.14
7.13
7.13
7.12
7.12
7.12
7.05
7.04
7.03
7.03
7.03
7.03
7.02
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1.90
1.89
1.87
H
N
Ph
O
Ph
Ph
O
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1.08
2.30
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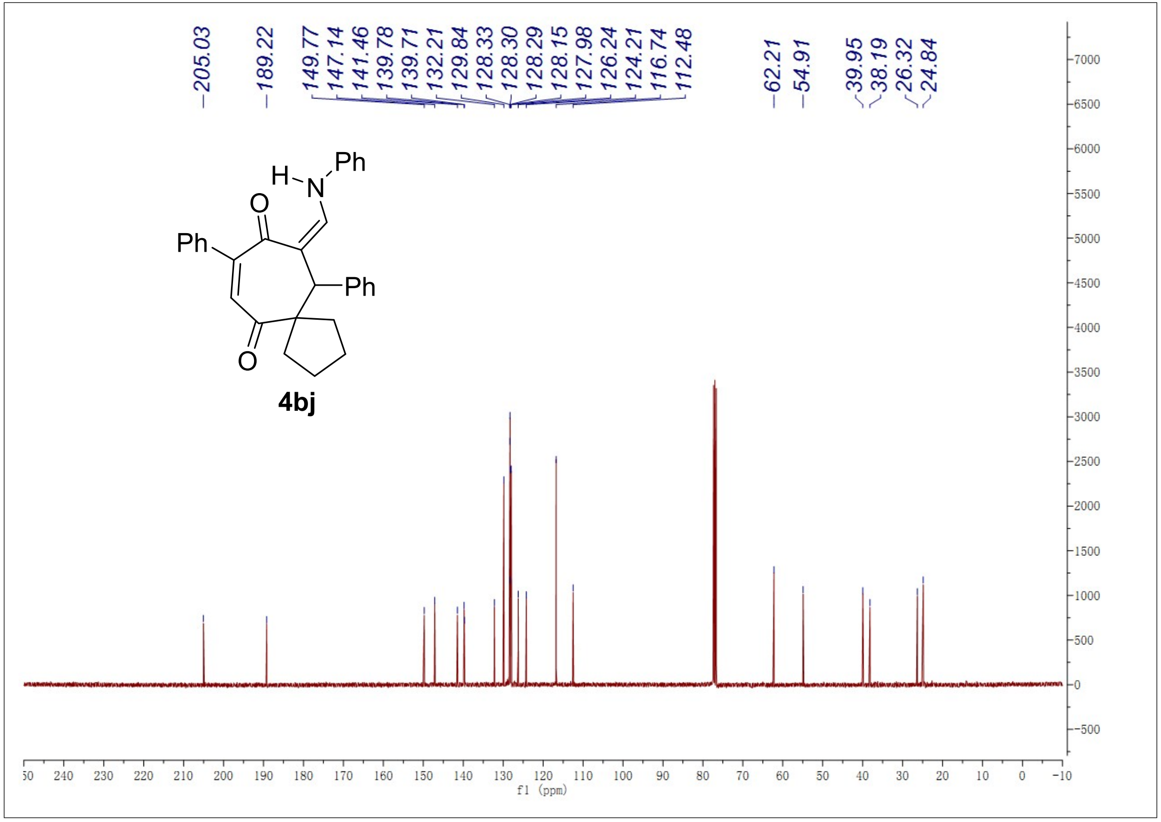
2.01
0.94
1.00
1.00
1.20
2.93
2.21
1.19
f1 (ppm)


4bj

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129.84
128.33
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128.29
128.15
127.98
126.24
124.21
116.74
112.48
62.21
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39.95
38.19
26.32
24.84
H
N
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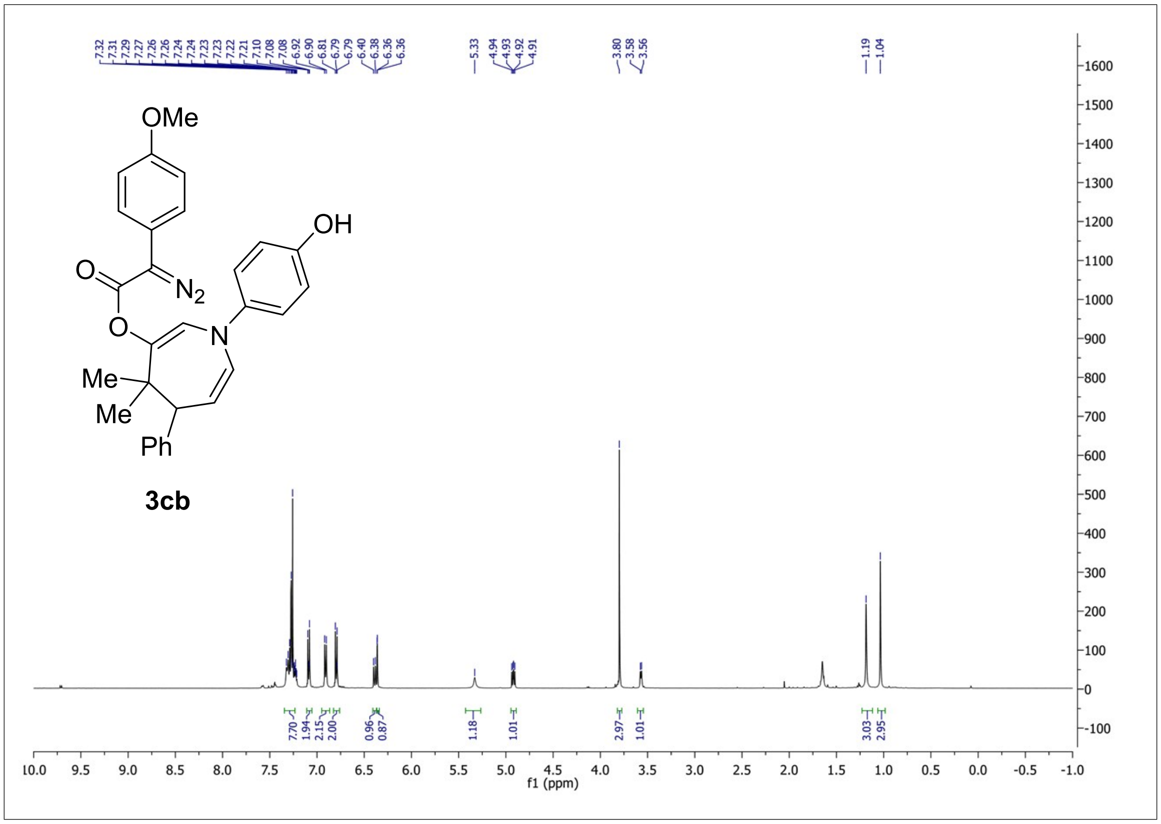
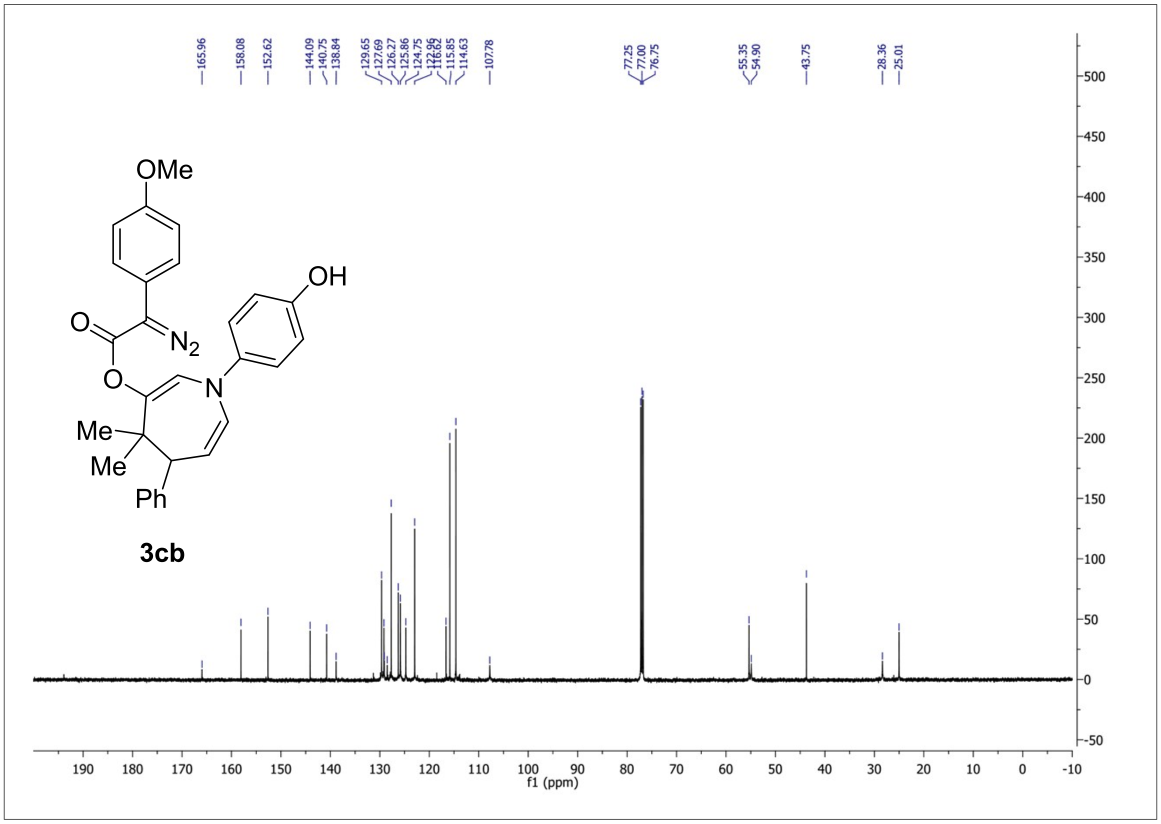
O
Ph
Ph
O
f1 (ppm)


3cb
7.32 7.31 7.29 7.27 7.26 7.26 7.24 7.23 7.23 7.22 7.21 7.10 7.08 7.08 6.92 6.90 6.81 6.79 6.79 6.40 6.38 6.36 6.36
5.33 4.94 4.93 4.92 4.91
3.80 3.58 3.56
1.19 1.04
7.70 1.94 2.15 2.00 0.96 0.87 1.18 1.01 2.97 1.01 3.03 2.95
OMe
OH
O
N2
O
N
Me
Me
Ph
f1 (ppm)


3cb
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77.25 77.00 76.75 55.35 54.90 43.75 28.36 25.01
OMe
OH
O
N2
O
N
Me
Me
Ph
f1 (ppm)