Palladium Catalyzed Dehydrogenative Coupling of Cyclic Enones with Thiophenes: A Rapid Access to β-Heteroarylated Cyclic Enones

Zhen-Kang Wen, *,† Ting-Ting Song†, Yu-Fang Liu† and Jian-Bin Chao‡

†School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China

‡Scientific Instrument Center, Shanxi University, Taiyuan 030006, China

E-mail: zkwen@sxu.edu.cn

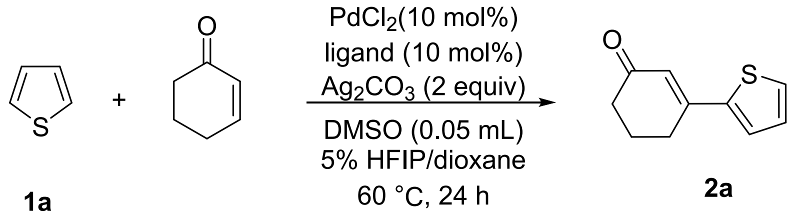
Supporting information

Table of Contents ....Page

General methods

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel. Commercial grade solvents and reagents were used without further purification. Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. High resolution mass spectral analysis (HRMS) was performed on an AB SCIEX TripleTOF 5600 Instruments.^{1}H NMR and ^{13}C NMR experiments were performed with a BRUKER AVANCE III HD 600 MHz and 151 MHz NMR spectrometer, respectively (Bruker, Billerica, MA). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet).

Optimization of Reaction Conditions

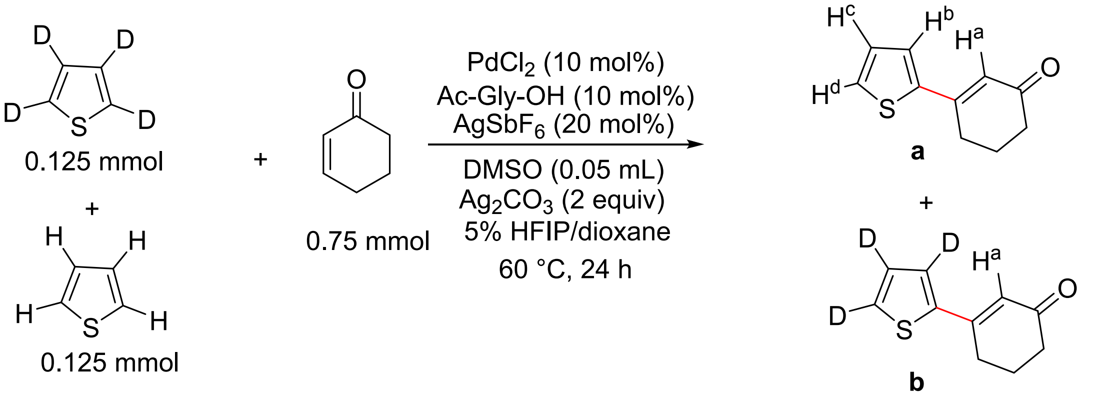


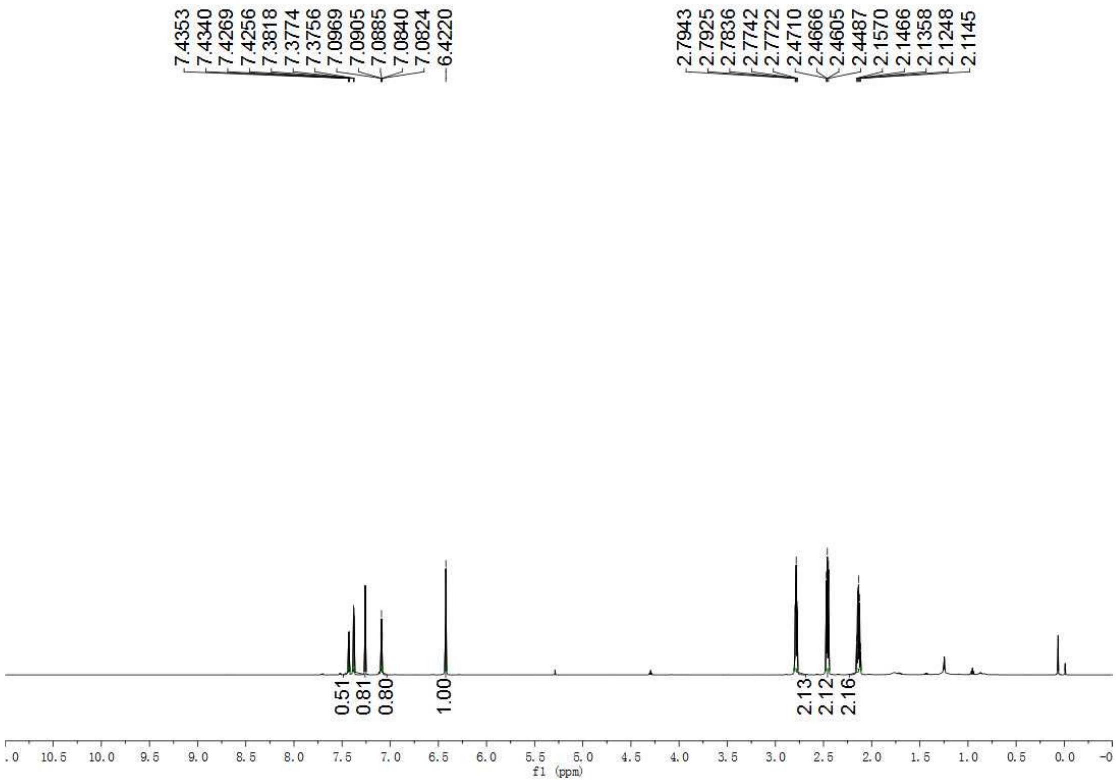
Screening of amino acid ligands effect of the reaction.[a]

entry	ligand	yield/%
1	Ac-Gly-OH	64%
2	Ac-Leu-OH	56%
3	Ac-Val-OH	54%
4	Ac-Ile-OH	50%
5	Ac-Phe-OH	48%
6[b]	Ac-Gly-OH	0
7[c]	-	0

[a] General conditions: **1a** (0.25 mmol), cyclohexenone (3.0 equiv), amino acid ligand (10 mol%), $Pd(OAc)_2$ (10 mol%), HFIP:1,4-dioxane =1:20 (0.05mL, 1 mL), 60 °C, 24 h. The yields indicated were determined upon isolation. [b]in the absence of $PdCl_2$ [c]in the absence of Ac-Gly-OH.

Competing Kinetic Isotope Effect (KIE) Experiment

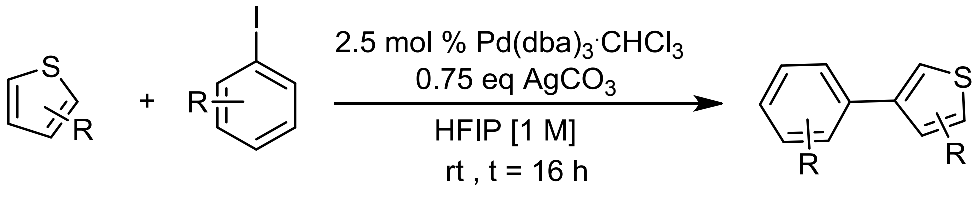




^{1}H NMR spectra of the mixture of compound **a** and **b**

Note: The value of k_H/k_D was calculated from the ^{1}H NMR spectra above which should be the mixture of compound **a** and **b** (the KIE scheme). The compound **a** was integrated as 0.8 (since the H^b and H^c was integrated as 0.8). Therefore, the compound **b** was integrated as 0.2 (since the mixed H^a of compound **a** and **b** with chemical shift 6.422 (s, 1H) was integrated as 1.0, so 1.0-0.8 = 0.2). Therefore, k_H/k_D = 0.8/(1.0-0.8) = 4.

General Procedure for the Synthesis of thiophene homologues.

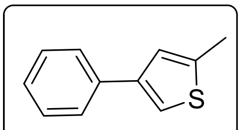


Thiophene homologues was synthesized according to the procedure of

Larrosa *et al.*[1] Thiophene homologues (2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (51.8 mg, 0.05 mmol, 0.025 equiv), silver carbonate (413.6 mg, 1.5 mmol, 0.75 equiv), aryl iodide (3 mmol, 1.5 equiv) and were stirred in hexafluoro-2-propanol (2 mL) at room temperature for 16 h. After this time, the resultant mixture was diluted with EtOAc (5 mL) and filtered through a plug of silica. The silica plug was flushed with EtOAc (30 mL) and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography to give the corresponding product.

Characterization data for the substituted thiophenes

2-methyl-4-phenylthiophene (1o)

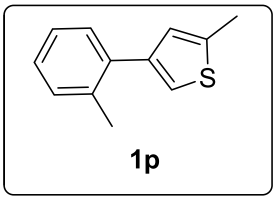


1o

The product **1o** was obtained via general procedure using 2-methylthiophene (0.194 mL, 2 mmol) and iodobenzene (0.334 mL, 3 mmol, 1.5 equiv) and isolated by column chromatography as a white solid in 70% yield (244 mg).

Rf (hexane): 0.65; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.22 (s, 1H), 7.08 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.05, 140.49, 136.12, 128.71, 126.92, 126.23, 124.62, 118.00, 15.43. This data is in accordance with the reported literature.[2]

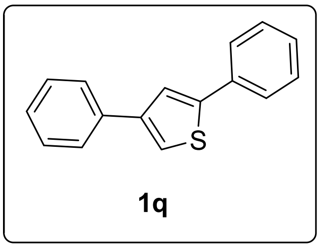
2-methyl-4-(o-tolyl)thiophene (1p)



The product **1p** was obtained via general procedure using 2-methylthiophene (0.194 mL, 2 mmol) and 1-iodo-2-methylbenzene (0.382 mL, 3 mmol, 1.5 equiv) and isolated by column chromatography as a colorless oil in 68% yield (256 mg).

Rf (hexane): 0.70; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.28 – 7.26 (m, 1H), 7.24 – 7.17 (m, 3H), 6.93 (s, 1H), 6.80 (s, 1H), 2.51 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 142.01, 139.08, 136.91, 135.59, 130.39, 129.59, 127.20, 127.11, 125.71, 120.33, 20.77, 15.30; HRMS (ESI) *m/z* calculated for $C_{12}H_{13}S$ $[M+H]^+$: 189.0732, found 189.0732.

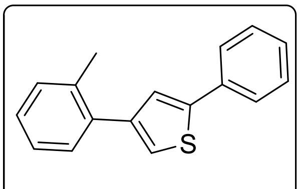
2,4-diphenylthiophene (1q)



The product **1q** was obtained via general procedure using 2-phenylthiophene 1h (320.5 mg, 2 mmol) and iodobenzene (0.334 mL, 3 mmol, 1.5 equiv) and isolated by column chromatography as a white solid in 45% yield (214 mg).

Rf (hexane): 0.55; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.67-7.61 (m, *J* = 21.7, 9.3 Hz, 4H), 7.60 (d, *J* = 1.0 Hz, 1H), 7.44-7.38 (m, 5H), 7.31 (dd, *J* = 15.2, 5.8 Hz, 2H). the data is in accordance with the reported literature.[3]

2-phenyl-4-(o-tolyl)thiophene (**1r**)

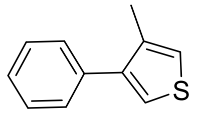


1r

The product **1r** was obtained via general procedure using 2-phenylthiophene (320.5 mg, 2 mmol) and 1-iodo-2-methylbenzene (0.382 mL, 3 mmol, 1.5 equiv) and isolated by column chromatography as a colorless oil in 54% yield (269 mg).

Rf (hexane): 0.50; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.67-7.65 (m, 2H), 7.40 (t, *J* = 9.1, 7.6 Hz, 4H), 7.33-7.26 (m, 4H), 7.17 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 143.80, 143.07, 136.58, 135.66, 134.34, 130.49, 129.59, 128.90, 127.55, 127.43, 127.40, 125.81, 124.99, 122.07, 20.77; HRMS (ESI) *m/z* calculated for $C_{17}H_{15}S$ [M+H]$^+$: 251.0889, found 251.0892.

3-methyl-4-phenylthiophene (**1s**)

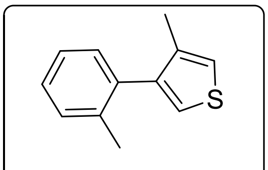


1s

The product **1s** was obtained via general procedure using 3-methylthiophene (0.193 mL, 2 mmol) and iodobenzene (0.334 mL, 3 mol, 1.5 equiv) and isolated by column chromatography as a colorless oil in 76% yield (265 mg).

Rf (hexane): 0.65; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43 (d, *J* = 5.6 Hz, 4H), 7.37-7.34 (m, 1H), 7.22 (d, *J* = 3.1 Hz, 1H), 7.04 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 143.11, 137.07, 136.13, 128.60, 128.28, 126.94, 122.93, 121.96, 15.51. The data is in accordance with the literature.[4]

3-methyl-4-(o-tolyl)thiophene (1t)

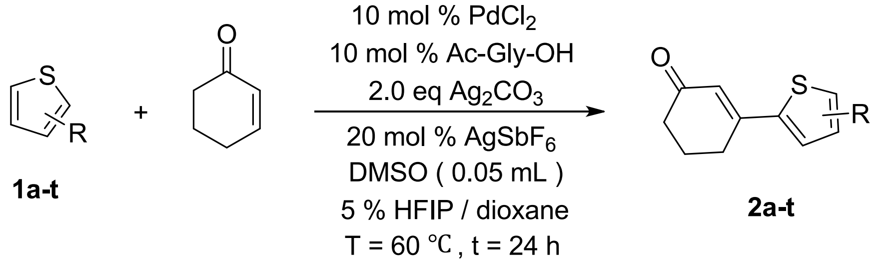


1t

The product **1t** was obtained via general procedure using 3-methylthiophene (0.193 mL, 2 mmol) and 1-iodo-2-methylbenzene (0.382 mL, 3 mmol, 1.5 equiv) and isolated by column chromatography as a colorless oil in 57% yield (216 mg).

Rf (hexane): 0.65; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 4.1 Hz, 2H), 7.22 (dt, *J* = 8.2, 4.3 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 7.02 (s, 1H), 2.15 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.73, 137.01, 136.87, 136.81, 130.03, 129.86, 127.45, 125.41, 122.58, 120.84, 19.93, 14.74. The data is in accordance with the literature.[4]

General procedure for the palladium-catalyzed cross-coupling of thiophenes with cyclic enones.

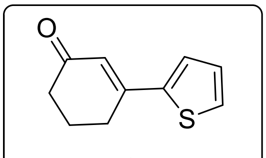


A 10 mL reaction tube equipped with a magnetic stirring bar was added thiophene derivative (0.25 mmol), $PdCl_2$ (0.025 mmol, 10 mol%), silver carbonate (0.75 mmol, 2 equiv), Ac-Gly-OH (0.025 mmol, 10 mol%), $AgSbF_6$ (0.05 mmol, 20 mol%), DMSO (0.05 mL), and 2-cyclohexen-1-one (0.75 mmol, 3.0 equiv) in 5% HFIP / 1,4-Dioxane (v/v, 1 mL) at 60

°C for 24 h. The reaction mixture was cooled to room temperature, followed by the addition of water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtrated and concentrated in *vacuo*, the residue was purified through column chromatography on silica gel to give the desired products.

Characterization data for the products

3-(thiophen-2-yl)cyclohex-2-enone (2a)



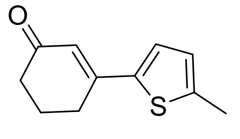
2a

This compound was prepared by the general procedure described above and was obtained as a yellow oil (28.6 mg) in 64% yield.

Rf (hexane:EtOAc = 5:1): 0.40; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 5.1 Hz, 1H), 7.37 (d, *J* = 3.7 Hz, 1H), 7.10-7.05 (m, 1H), 6.41 (s, 1H), 2.77 (t, *J* = 6.0 Hz, 2H), 2.48-2.42 (m, 2H), 2.15-2.09 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.39, 152.38, 142.70, 128.71, 128.22, 127.28, 122.68, 37.19, 27.96, 22.39; HRMS (ESI) *m/z* calculated for $C_{10}H_{11}OS$ $[M+H]^+$: 179.0525, found 179.0525. the data is in accordance with the literature.[5]

3-(5-methylthiophen-2-yl)cyclohex-2-enone (2b)

This compound was prepared by the general procedure described above

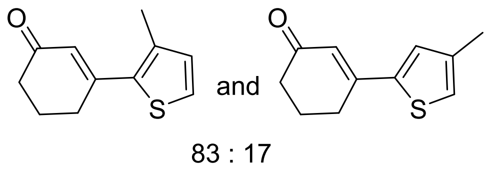


2b

and was obtained as a yellow oil (32.6 mg) in 68% yield.

Rf (hexane:EtOAc = 5:1): 0.45; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.71 (d, *J* = 0.9 Hz, 1H), 6.26 (s, 1H), 2.70 (t, *J* = 6.0 Hz, 2H), 2.45 (s, 3H), 2.39 (dd, *J* = 9.4, 3.8 Hz, 2H), 2.08-2.04 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.19, 152.56, 144.19, 140.13, 127.80, 126.61, 121.51, 37.07, 27.38, 22.27, 15.59; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}OS$ $[M+H]^+$: 193.0682, found 193.0681.

3-(4-methylthiophen-2-yl)cyclohex-2-enone (**2ca**)

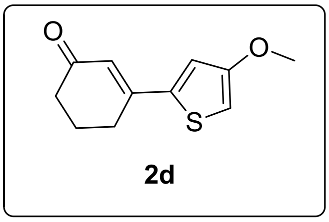


2ca **2cb**

This compound was prepared by the general procedure described above and was obtained as a yellow oil (33.6 mg) of inseparable mixture (**2ca**/**2ccb** = 83:17) in 70% yield.

Rf (hexane:EtOAc = 5:1): 0.45; ^{1}H and ^{13}C NMR are described for the **2ca** isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 5.1 Hz, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 6.24 (s, 1H), 2.72 (t, *J* = 11.2, 5.4 Hz, 2H), 2.45-2.40 (m, 2H), 2.36 (s, 3H), 2.10 (dt, *J* = 12.8, 6.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.19, 153.74, 137.64, 136.45, 132.58, 126.16, 125.24, 36.86, 30.76, 22.62, 16.93; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}OS$ $[M+H]^+$: 193.0682, found 193.0682.

3-(4-methoxythiophen-2-yl)cyclohex-2-enone (**2d**)

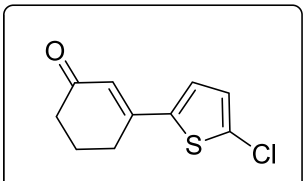


2d

This compound was prepared by the general procedure described above in the absence of $AgSbF_6$ and was obtained as a yellow solid (32.6 mg) in 63% yield.

Rf (hexane:EtOAc = 2:1): 0.40; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 5.6 Hz, 1H), 6.90 (d, *J* = 5.6 Hz, 1H), 6.78 (s, 1H), 3.92 (s, 3H), 2.74 (t, *J* = 5.9 Hz, 2H), 2.44-2.40 (m, 2H), 2.11-2.05 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.96, 158.43, 152.10, 126.81, 122.51, 118.54, 116.82, 58.54, 37.11, 29.29, 22.62; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}O_2S$ $[M+H]^+$: 209.0631, found 209.0631.

3-(5-chlorothiophen-2-yl)cyclohex-2-enone (2e)



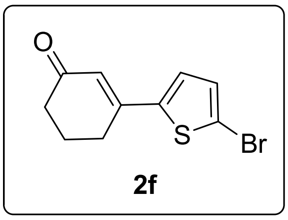
2e

This compound was prepared by the general procedure described above and was obtained as a white solid (31.2 mg) in 59% yield.

Rf (hexane:EtOAc = 5:1): 0.35; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 4.0 Hz, 1H), 6.26 (s, 1H), 2.71-2.68 (m, 2H), 2.46-2.44 (m, 2H), 2.14-2.10 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.00, 151.32, 141.08, 133.67, 127.49, 126.84, 122.63, 37.17, 27.24, 22.26; HRMS (ESI) *m/z* calculated for $C_{10}H_{10}ClOS$ $[M+H]^+$: 213.0135, found 213.0134.

3-(5-bromothiophen-2-yl)cyclohex-2-enone (2f)

This compound was prepared by the general procedure described above

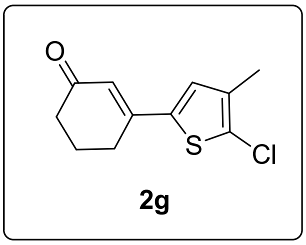


2f

and was obtained as a yellow solid (36.6 mg) in 57% yield.

Rf (hexane:EtOAc = 5:1): 0.35; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.12 (d, J = 4.0 Hz, 1H), 7.05 (d, J = 4.0 Hz, 1H), 6.29 (s, 1H), 2.71-2.69 (m, 2H), 2.46-2.44 (m, 2H), 2.16-2.10 (m, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 199.04, 151.17, 143.99, 131.20, 127.56, 122.81, 116.37, 37.17, 27.36, 22.29; HRMS (ESI) *m/z* calculated for $C_{10}H_{10}BrOS$ [M+H]$^+$: 256.9630, found 256.9623. Data is in accordance with the literature.[6]

3-(5-chloro-4-methylthiophen-2-yl)cyclohex-2-enone (**2g**)

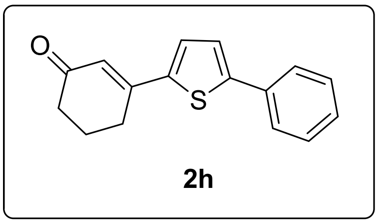


2g

This compound was prepared by the general procedure described above and was obtained as a yellow solid (37.9 mg) in 67% yield.

Rf (hexane:EtOAc = 5:1): 0.40; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.06 (s, 1H), 6.24 (s, 1H), 2.69-2.65 (m, 2H), 2.45-2.41 (m, 2H), 2.17 (s, 3H), 2.13-2.07 (m, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 199.02, 151.44, 138.42, 135.85, 129.04, 128.82, 122.23, 37.16, 27.14, 22.27, 13.59; HRMS (ESI) *m/z* calculated for $C_{11}H_{12}ClOS$ [M+H]$^+$: 227.0292, found 227.0290.

3-(5-phenylthiophen-2-yl)cyclohex-2-enone (**2h**)

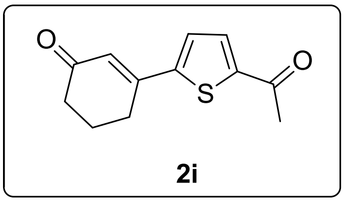


2h

This compound was prepared by the general procedure described above and was obtained as a yellow solid (47.7 mg) in 75% yield.

Rf (hexane:EtOAc = 5:1): 0.47; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.36-7.30 (m, 2H), 7.29 (d, *J* = 3.7 Hz, 1H), 6.43 (s, 1H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 6.6 Hz, 2H), 2.17-2.12 (m, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 199.26, 152.22, 147.66, 141.51, 133.42, 129.02, 128.54, 128.44, 125.91, 124.08, 122.32, 37.22, 27.61, 22.40; HRMS (ESI) *m/z* calculated for $C_{16}H_{15}OS$ [M+H]$^+$: 255.0838, found 255.0837.

3-(5-acetylthiophen-2-yl)cyclohex-2-enone (2i)

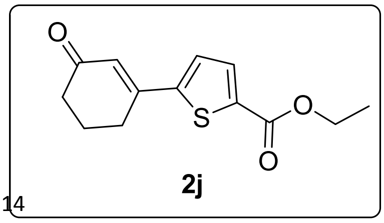


2i

This compound was prepared by the general procedure described above using 0.5 equivalent Ac-Gly-OH in HFIP/dioxane (0.5 mL/0.5 mL) instead of HFIP/dioxane (0.05 mL/1 mL) at 110 °C and was obtained as a yellow solid (24.4 mg) in 44% yield.

Rf (hexane:EtOAc = 2:1): 0.38; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.63 (d, *J* = 3.7 Hz, 1H), 7.36 (d, *J* = 3.7 Hz, 1H), 6.48 (s, 1H), 2.76 (t, *J* = 5.9 Hz, 2H), 2.56 (s, 3H), 2.48 (t, *J* = 6.6 Hz, 2H), 2.18-2.13 (m, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 199.04, 190.48, 151.13, 149.83, 145.52, 132.67, 127.20, 124.74, 37.14, 27.89, 26.74, 22.29; HRMS (ESI) *m/z* calculated for $C_{12}H_{13}O_2S$ [M+H]$^+$: 221.0631, found 221.0629.

ethyl 5-(3-oxocyclohex-1-en-1-yl)thiophene-2-carboxylate (2j)



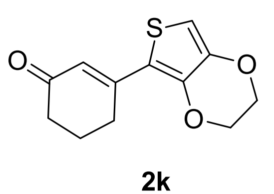
2j

This compound was prepared by the general procedure described above using 0.5

equivalent Ac-Gly-OH in HFIP/dioxane (0.5 mL/0.5 mL) instead of HFIP/dioxane (0.05 mL/1 mL) at 110 °C and was obtained as a yellow solid (37.4 mg) in 60% yield.

Rf (hexane:EtOAc = 5:1): 0.65; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 4.0 Hz, 1H), 7.33 (d, *J* = 4.0 Hz, 1H), 6.46 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 6.0 Hz, 2H), 2.49-2.46 (m, 2H), 2.17-2.13 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.00, 161.65, 151.23, 148.43, 135.64, 133.65, 126.91, 124.32, 61.52, 37.14, 27.83, 22.28, 14.23; HRMS (ESI) *m/z* calculated for $C_{13}H_{15}O_3S$ $[M+H]^+$: 251.0736, found 251.0735.

3-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)cyclohex-2-enone (2k)

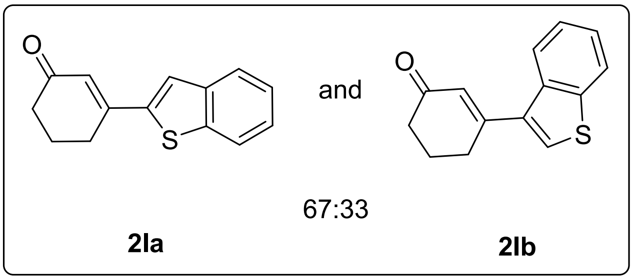


2k

This compound was prepared by the general procedure described above and was obtained as a white solid (17.2 mg) in 29% yield.

Rf (hexane:EtOAc = 2:1): 0.35; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (s, 1H), 6.51 (s, 1H), 4.32-4.29 (m, 2H), 4.23-4.21 (m, 2H), 2.71-2.68 (m, 2H), 2.45-2.42 (m, 2H), 2.11-2.06 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.75, 151.56, 142.41, 142.25, 122.65, 116.63, 102.93, 64.90, 64.17, 37.19, 28.16, 22.50; HRMS (ESI) *m/z* calculated for $C_{12}H_{13}O_3S$ $[M+H]^+$: 237.0580, found 237.0578.

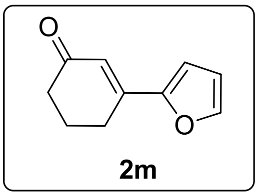
3-(benzo[b]thiophen-2-yl)cyclohex-2-enone (2la)



This compound was prepared by the general procedure described above and was obtained as a white solid (13.4 mg) of inseparable mixture (**2c**/**2c'** = 67:33) in 23% yield.

R^f(hexane:EtOAc = 5:1): 0.50; ^{1}H and ^{13}C NMR are described for the **2la** isomer:^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 16.4, 7.5 Hz, 2H), 7.60 (s, 1H), 7.40-7.35 (td, *J* = 13.6, 7.0 Hz, 2H), 6.48 (s, 1H), 2.87 (t, *J* = 5.9 Hz, 2H), 2.53-2.50 (m, 2H), 2.24-2.16 (m, *J* = 19.0, 6.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.34, 152.47, 142.45, 140.13, 139.68, 126.21, 124.88, 124.83, 124.73, 124.43, 122.37, 37.33, 27.53, 22.43; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}OS$ $[M+H]^+$: 229.0682, found 229.0681.Data is in accordance with the literature.[7]

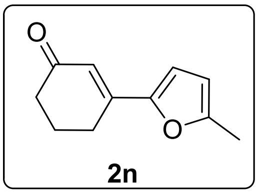
3-(furan-2-yl)cyclohex-2-enone (2m)



This compound was prepared by the general procedure described above and was obtained as a colorless oil (16.9 mg) in 42% yield.

Rf (hexane:EtOAc = 5:1): 0.40; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.74 (s, 1H), 6.49 (d, *J* = 14.2 Hz, 2H), 2.65 (t, *J* = 5.9 Hz, 2H), 2.46 (t, *J* = 6.2 Hz, 2H), 2.14 – 2.09 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.48, 152.18, 147.11, 145.00, 120.98, 112.49, 112.28, 37.50, 25.31, 22.39; HRMS (ESI) *m/z* calculated for $C_{10}H_{11}O_2$ $[M+H]^+$: 163.0754, found 163.0753.

3-(5-methylfuran-2-yl)cyclohex-2-enone (**2n**)

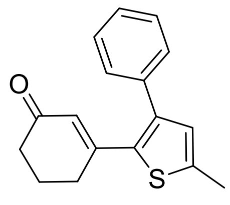


2n

This compound was prepared by the general procedure described above and was obtained as a white solid (24.7 mg) in 56% yield.

Rf (hexane:EtOAc = 5:1): 0.45; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.64 (d, *J* = 3.3 Hz, 1H), 6.41 (s, 1H), 6.12-6.09 (m, 1H), 2.62-2.59 (m, 2H), 2.45-2.42 (m, 2H), 2.34 (s, 3H), 2.11-2.05 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.45, 155.78, 150.53, 147.17, 119.60, 114.13, 108.85, 37.48, 25.13, 22.42, 13.87; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found 177.0909.The data is in accordance with the literature.[8]

3-(5-methyl-3-phenylthiophen-2-yl)cyclohex-2-enone (**2o**)

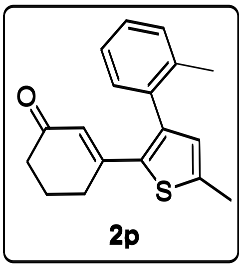


2o

This compound was prepared by the general procedure described above and was obtained as a white solid (57.2 mg) in 85% yield.

Rf (hexane:EtOAc = 5:1): 0.50; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 3H), 6.78 (s, 1H), 6.17 (s, 1H), 2.49 (s, 3H), 2.39-2.34 (m, 4H), 1.94-1.89 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.14, 155.36, 142.07, 140.90, 136.86, 134.37, 130.07, 128.50, 128.45, 127.65, 126.81, 37.18, 29.94, 22.90, 15.30; HRMS (ESI) *m/z* calculated for $C_{17}H_{17}OS$ $[M+H]^+$: 269.0995, found 269.0991.

3-(5-methyl-3-(o-tolyl)thiophen-2-yl)cyclohex-2-enone (2p)

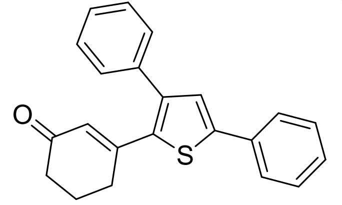


2p

This compound was prepared by the general procedure described above and was obtained as a colorless oil (67.8 mg) in 96% yield.

Rf (hexane:EtOAc = 5:1): 0.50; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 6.61 (s, 1H), 6.00 (s, 1H), 2.49 (s, 3H), 2.32-2.27 (m, 4H), 2.14 (s, 3H), 1.90-1.85 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.20, 154.42, 142.35, 141.19, 136.99, 135.71, 135.10, 130.52, 130.18, 129.10, 127.96, 125.85, 124.62, 36.98, 29.27, 22.77, 19.89, 15.38; HRMS (ESI) m/z calculated for $C_{18}H_{19}OS$ $[M+H]^+$: 283.1151, found 283.1150.

3-(3,5-diphenylthiophen-2-yl)cyclohex-2-enone (2q)

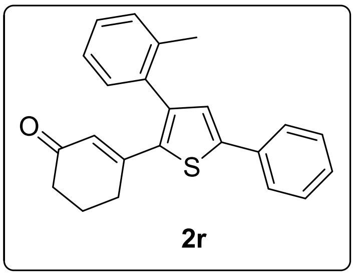


2q

This compound was prepared by the general procedure described above and was obtained as a yellow oil (43.8 mg) in 53% yield.

Rf (hexane:EtOAc = 5:1): 0.47; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63-7.62 (m, 2H), 7.44-7.31 (m, 8H), 7.30 (s, 1H), 6.27 (s, 1H), 2.44-2.39 (m, 4H), 1.96 (dt, J = 12.6, 6.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.03, 154.87, 144.50, 142.89, 136.63, 135.83, 133.27, 129.00, 128.62, 128.46, 128.28, 127.92, 127.35, 127.24, 125.77, 37.19, 29.89, 22.89; HRMS (ESI) *m/z* calculated for $C_{22}H_{19}OS$ $[M+H]^+$: 331.1151, found 331.1148.

3-(5-phenyl-3-(o-tolyl)thiophen-2-yl)cyclohex-2-enone (**2r**)

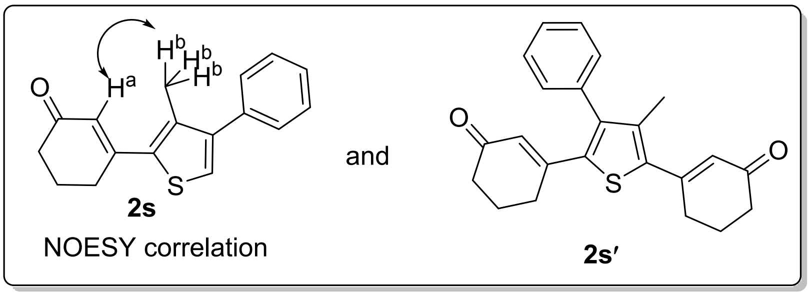


2r

This compound was prepared by the general procedure described above and was obtained as a yellow oil (43.4 mg) in 50% yield.

Rf (hexane:EtOAc = 5:1): 0.42; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64-7.61 (t, 2H), 7.41 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.35-7.27 (m, 3H), 7.24 (m, *J* = 11.5, 4.4 Hz, 1H), 7.22-7.19 (m, 1H), 7.18 (s, 1H), 6.10 (s, 1H), 2.39-2.34 (m, 4H), 2.20 (s, 3H), 1.96-1.91 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.12, 153.92, 144.66, 143.14, 136.77, 136.59, 135.83, 133.27, 130.37, 129.17, 129.03, 128.34, 128.28, 127.83, 126.05, 125.75, 125.25, 37.06, 29.33, 22.83, 19.99; HRMS (ESI) *m/z* calculated for $C_{23}H_{21}OS$ $[M+H]^+$: 345.1308, found 345.1305.

3-(3-methyl-4-phenylthiophen-2-yl)cyclohex-2-enone (**2s**) and **3,3'-(3-methyl-4-phenylthiophene-2,5-diyl)bis(cyclohex-2-enone)** (**2s'**)

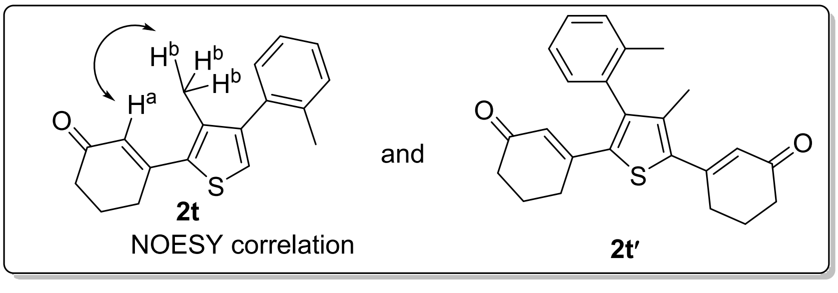


The use of **1s** as substrate following the general procedure, **2s** (30 mg, 45%) and **2s'** (42.0 mg, 46%) were obtained.

2s, Rf (hexane:EtOAc = 5:1): 0.40, green solid; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.31 (s, 1H), 6.32 (s, 1H), 2.80 (t, *J*= 5.9 Hz, 2H), 2.52 – 2.48 (t, 2H), 2.31 (s, 3H), 2.19 – 2.14 (m, 2H);^{13}C NMR (151 MHz, CDCl$_3$) δ 199.36, 154.22, 146.03, 137.95, 136.61, 135.80, 128.96, 128.39, 127.46, 126.23, 124.10, 37.08, 31.15, 22.78, 16.44; HRMS (ESI) *m/z* calculated for $C_{17}H_{17}OS$ [M+H]$^+$: 269.0995, found 269.0992.

2s', Rf (hexane:EtOAc = 2:1): 0.40, yellow oil; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.44-7.38 (m, 3H), 7.20-7.18 (m, 2H), 6.30 (s, 1H), 6.08 (s, 1H), 2.78 (t, *J* = 5.9 Hz, 2H), 2.51-2.48 (m, 2H), 2.33 (t, *J* = 6.6 Hz, 2H), 2.23 (t, *J* = 5.9 Hz, 2H), 2.17-2.14 (m, 2H), 2.10 (s, 3H), 1.89-1.84 (m, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 199.12, 198.92, 154.01, 153.31, 144.45, 138.96, 138.39, 137.86, 136.31, 129.40, 128.77, 128.20, 127.83, 127.10, 37.10, 37.02, 31.13, 29.80, 22.81, 22.75, 16.30; HRMS (ESI) *m/z* calculated for $C_{23}H_{23}O_2S$ [M+H]$^+$: 363.1413, found 363.1409.

3-(3-methyl-4-(o-tolyl)thiophen-2-yl)cyclohex-2-enone (**2t**) and **3,3'-(3-methyl-4-(o-tolyl)thiophene-2,5-diyl)bis(cyclohex-2-enone)** (**2t'**)



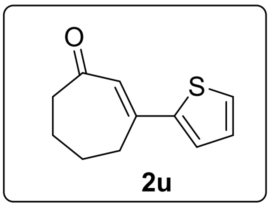
The use of **1t** as substrate following the general procedure, **2t** (31.7 mg, 45%) and **2t'** (48.1 mg, 40%) were obtained.

2t, Rf (hexane:EtOAc = 5:1): 0.42, white solid; ^{1}H NMR (600 MHz,

$CDCl_3$) δ 7.29 (q, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 6.9 Hz, 1H), 7.19 (s, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.34 (s, 1H), 2.82 (t, *J* = 5.7 Hz, 2H), 2.50 (t, *J* = 6.6 Hz, 2H), 2.17 (dt, *J* = 12.7, 6.2 Hz, 2H), 2.11 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.43, 154.22, 145.58, 137.12, 136.94, 136.79, 136.38, 130.08, 129.98, 127.93, 125.67, 125.62, 124.04, 37.08, 30.99, 22.81, 19.89, 15.89; HRMS (ESI) *m/z* calculated for $C_{18}H_{19}OS$ $[M+H]^+$: 283.1151, found 283.1148.

2t', Rf (hexane:EtOAc = 2:1): 0.40, yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 5.97 (s, 1H), 2.79 (t, *J* = 5.8 Hz, 2H), 2.51-2.48 (m, 2H), 2.33-2.26 (m, 4H), 2.20-2.14 (m, 2H), 2.04 (s, 3H), 1.98 (s, 3H), 1.92-1.87 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.16, 199.04, 153.25, 153.20, 144.50, 138.81, 138.65, 138.12, 136.32, 136.08, 130.50, 129.44, 128.63, 126.90, 126.43, 126.42, 37.05, 30.99, 29.36, 22.78, 22.77, 19.68, 15.84; HRMS (ESI) *m/z* calculated for $C_{24}H_{25}O_2S$ $[M+H]^+$: 377.1570, found 377.1565.

3-(thiophen-2-yl)cyclohept-2-en-1-one (2u)

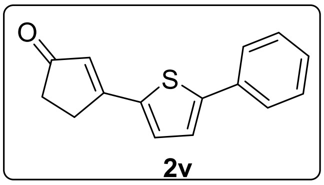


2u

This compound was prepared by the general procedure described above and was obtained as a yellow solid (13.5 mg) in 28% yield.

Rf (hexane:EtOAc = 5:1): 0.45; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 4.8 Hz, 1H), 7.32 (s, 1H), 7.05 (s, 1H), 6.50 (s, 1H), 2.93-2.90 (m, 2H), 2.68-2.65 (m, 2H), 1.97-1.92 (m, 2H), 1.89-1.84 (m, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 203.62, 149.66, 145.16, 128.24, 128.01, 127.18, 126.73, 41.89, 31.23, 24.90, 21.00; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}OS$ [M+H]$^+$：193.0682, found: 193.0683.

3-(5-phenylthiophen-2-yl)cyclopent-2-en-1-one (**2v**)

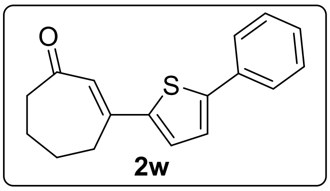


2v

This compound was prepared by the general procedure described above and was obtained as a yellow solid (25.6 mg) in 43% yield.

Rf (hexane:EtOAc = 2:1): 0.3; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.65-7.62 (m, 2H), 7.44-7.39 (m, 3H), 7.37-7.32 (m, 2H), 6.36 (t, *J* = 1.5 Hz, 1H), 3.04 (ddd, *J* = 6.7, 3.2, 1.6 Hz, 2H), 2.59 – 2.56 (m, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 208.36, 166.36, 149.31, 137.46, 133.28, 129.65, 129.09, 128.68, 126.01, 125.42, 124.12, 35.02, 29.02; HRMS (ESI) *m/z* calculated for $C_{15}H_{13}OS$ [M+H]$^+$: 241.0682, found 241.0682.

3-(5-phenylthiophen-2-yl)cyclohept-2-en-1-one (**2w**)



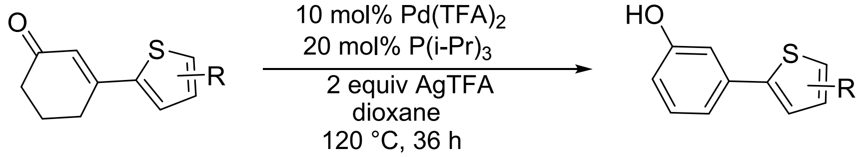
2w

This compound was prepared by the general procedure described above and was obtained as a yellow solid (28.2 mg) in 42% yield.

Rf (hexane:EtOAc = 5:1): 0.35; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.62-7.60 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34- 7.31 (m, 2H), 7.27 (d, *J* = 3.9 Hz, 1H), 6.53 (s, 1H), 2.94-2.91 (m, 2H), 2.70-2.67 (m, 2H), 1.99-1.94 (m, 2H), 1.89 (dt, *J* = 13.2, 6.5 Hz, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ

203.56, 149.58, 146.92, 143.97, 133.59, 129.00, 128.26, 127.97, 126.81, 125.84, 124.12, 41.87, 30.67, 24.89, 21.01; HRMS (ESI) *m/z* calculated for $C_{17}H_{17}OS$ $[M+H]^+$: 269.0995, found 269.0996.

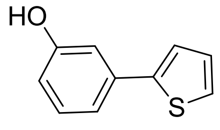
General procedure for the palladium-catalyzed dehydrogenation of β-thiophene-substituted cyclohexenone to *meta*-phenol derivatives



A 10 mL reaction tube equipped with a magnetic stirring bar was added β-thiophene-substituted cyclohexenone (0.15 mmol), $Pd(TFA)_2$ (10 mol%), silver trifluoroacetate (2.0 equiv), triisopropylphosphane (20 mol%) in 1,4-dioxane (0.75 mL) at 120 °C for 36 h. The reaction mixture was cooled to room temperature, followed by the addition of water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtrated and concentrated in *vacuo*, the residue was purified through column chromatography on silica gel to give the desired products.

Characterization data for the products

3-(thiophen-2-yl)phenol (3a)

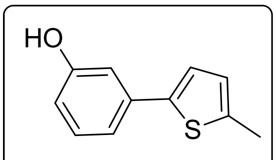


3a

This compound was prepared by the general procedure described above and was obtained as a yellow oil (14.7 mg) in 83% yield.

Rf (hexane:EtOAc = 5:1): 0.50; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.29-7.26 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.22-7.19 (m, 1H), 7.11-7.09 (m, 1H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.76 (m, 1H), 4.93 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.81, 143.86, 135.96, 130.13, 127.95, 124.95, 123.33, 118.64, 114.42, 112.79; HRMS (ESI) *m/z* calculated for $C_{10}H_7OS$ [M-H]$^-$: 175.0212, found 175.0217.

3-(5-methylthiophen-2-yl)phenol (**3b**)

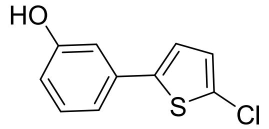


3b

This compound was prepared by the general procedure described above and was obtained as a white solid (9.4 mg) in 33% yield.

Rf (hexane:EtOAc = 5:1): 0.48; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.14-7.12 (m, 1H), 7.09 (d, *J* = 3.5 Hz, 1H), 7.03-7.02 (m, 1H), 6.73-6.70 (m, 2H), 4.83 (s, 1H), 2.50 (d, *J* = 0.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.80, 141.40, 139.71, 136.28, 130.03, 126.15, 123.16, 118.18, 113.94, 112.30, 15.45; HRMS (ESI) *m/z* calculated for $C_{11}H_9OS$ [M-H]$^-$: 189.0369, found 189.0375.

3-(5-chlorothiophen-2-yl)phenol (**3c**)

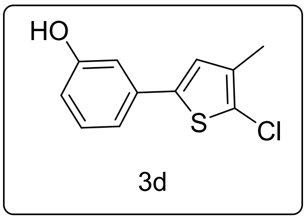


3c

This compound was prepared by the general procedure described above and was obtained as a white solid (22.9 mg) in 72% yield.

Rf (hexane:EtOAc = 5:1): 0.50; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.24 (t, *J* = 7.9 Hz, 1H), 7.10-7.07 (m, 1H), 7.05 (d, *J* = 3.9 Hz, 1H), 6.99-6.98 (m, 1H), 6.88 (d, *J* = 3.9 Hz, 1H), 6.78-6.75 (m, 1H), 4.99 (s, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 155.97, 142.37, 135.21, 130.26, 129.30, 127.06, 122.49, 118.18, 114.82, 112.39; HRMS (ESI) *m/z* calculated for $C_{10}H_6ClOS$ [M-H]$^-$: 208.9822, found 208.9831.

3-(5-chloro-4-methylthiophen-2-yl)phenol (3d)

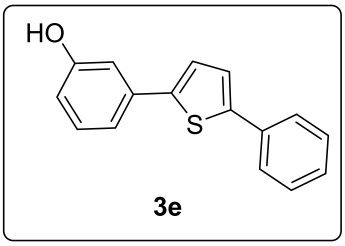


3d

This compound was prepared by the general procedure described above and was obtained as a white solid (23.5 mg) in 74% yield.

Rf (hexane:EtOAc = 5:1): 0.50; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.08-7.05 (m, 1H), 6.97-6.95 (m, 2H), 6.76-6.73 (m, 1H), 4.90 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 155.92, 139.74, 135.31, 135.29, 130.20, 124.87, 124.25, 118.02, 114.65, 112.20, 13.68; HRMS (ESI) *m/z* calculated for $C_{11}H_8ClOS$ [M-H]$^-$: 222.9979, found 222.9987.

3-(5-phenylthiophen-2-yl)phenol (3e)



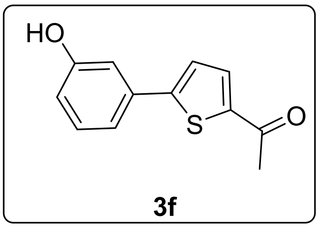
3e

This compound was prepared by the general procedure described above and was obtained as a white solid (20.8 mg) in 55% yield.

Rf (hexane:EtOAc = 5:1): 0.50; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.63 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.40 (dd, *J* = 10.6, 4.9 Hz, 2H), 7.31-7.24 (m, 4H), 7.23-7.21 (m, 1H), 7.12-7.11 (m, 1H), 6.78-6.75 (m, 1H), 4.94 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.90, 143.77, 143.04, 135.87, 134.22, 130.16, 128.92, 127.57, 125.64, 124.26, 123.94, 118.32, 114.49, 112.44; HRMS (ESI) *m/z* calculated for $C_{16}H_{11}OS$ [M-H]$^-$: 251.0525, found 251.0537.

1-(5-(3-hydroxyphenyl)thiophen-2-yl)ethanone (**3f**)

This compound was prepared by the general procedure described above and was obtained as a white solid (22.9 mg) in 70% yield.



3f

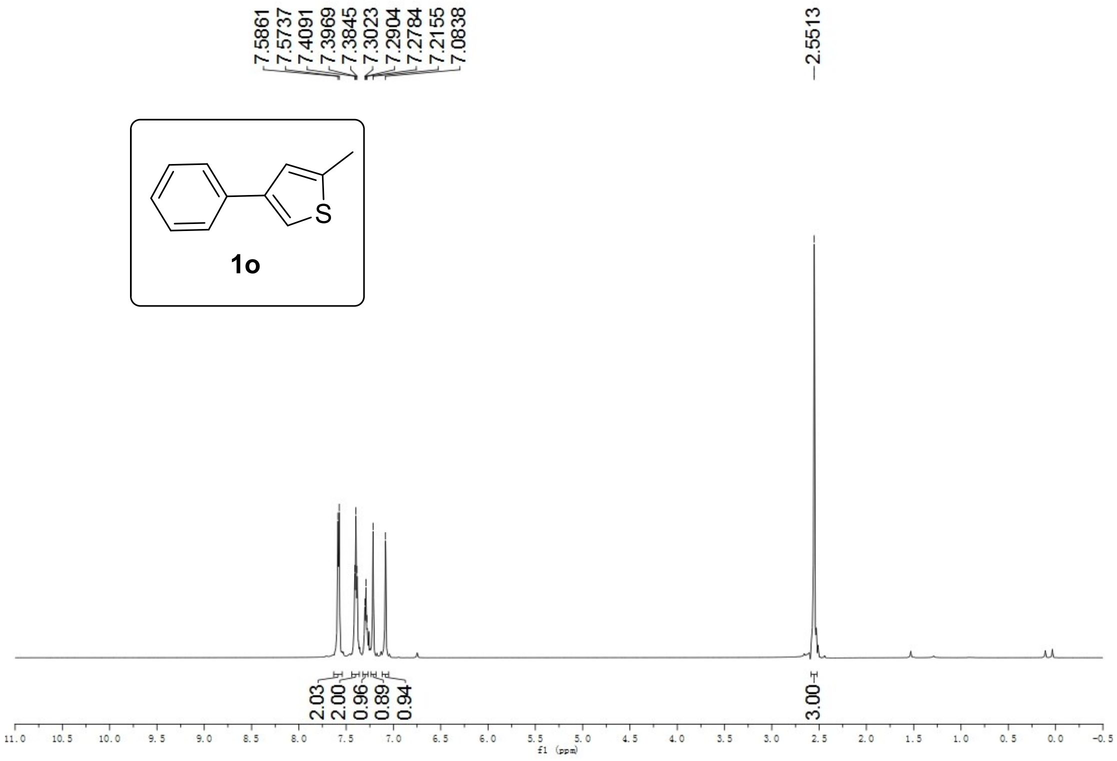
Rf (hexane:EtOAc = 2:1): 0.40; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 3.9 Hz, 1H), 7.32-7.30 (m, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.21 (s, 1H), 6.86 (dd, *J* = 8.0, 2.2 Hz, 1H), 5.62 (d, *J* = 12.4 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.09, 156.32, 152.78, 143.00, 134.71, 133.70, 130.38, 124.11, 118.63, 116.20, 113.25, 26.53;HRMS (ESI) *m/z* calculated for $C_{12}H_9O_2S$ [M-H]$^-$: 217.0318, found 217.0327.

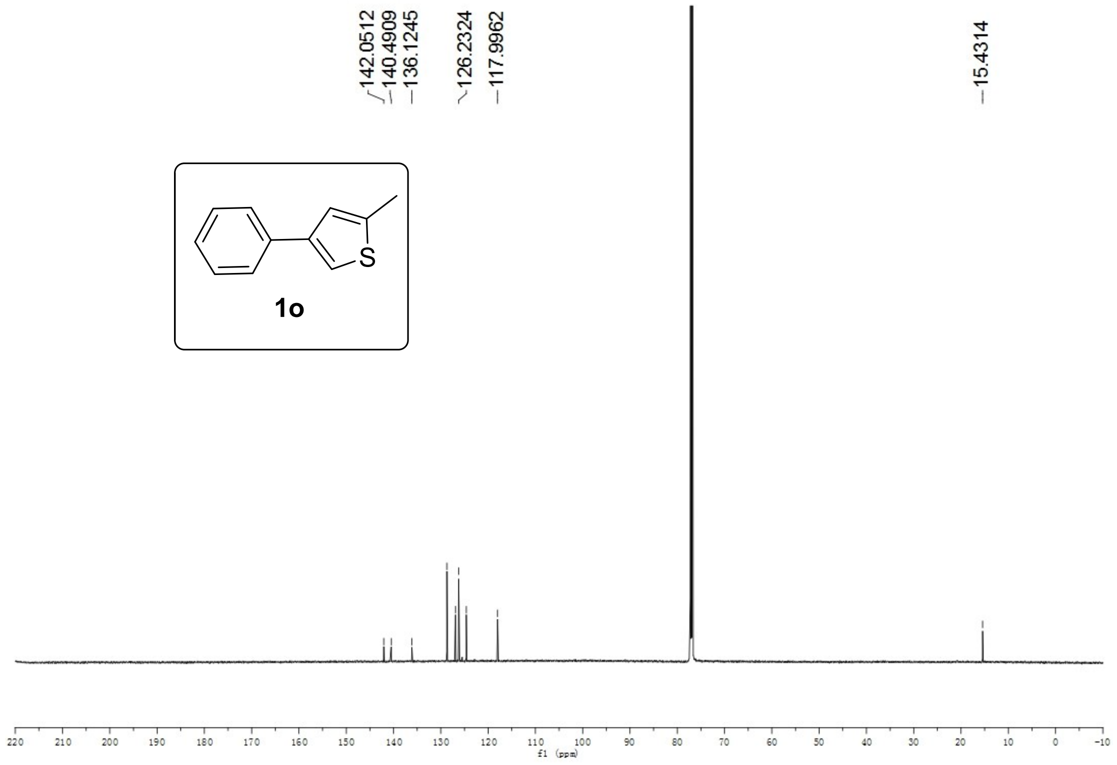
Reference:

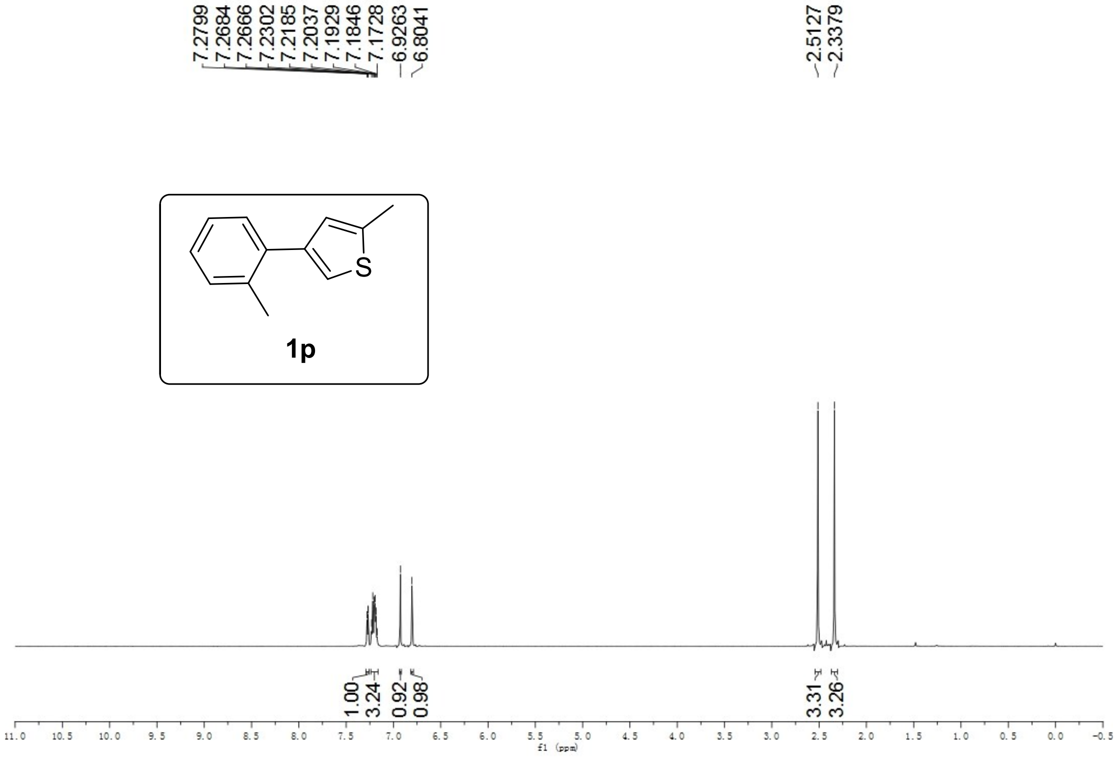
1. Colletto, C.; Islam, S.; Juliá-Hernández, F.; Larrosa, I. *J. Am. Chem. Soc.* **2016**, *138*, 1677.
2. Yuan, K. D.; Doucet, H. *Chem. Sci.*, **2014**, 5, 392.
3. Funaki,K.; Sato, T.; Oi, S. *Org. Lett.*, **2012**, 14, 6186.

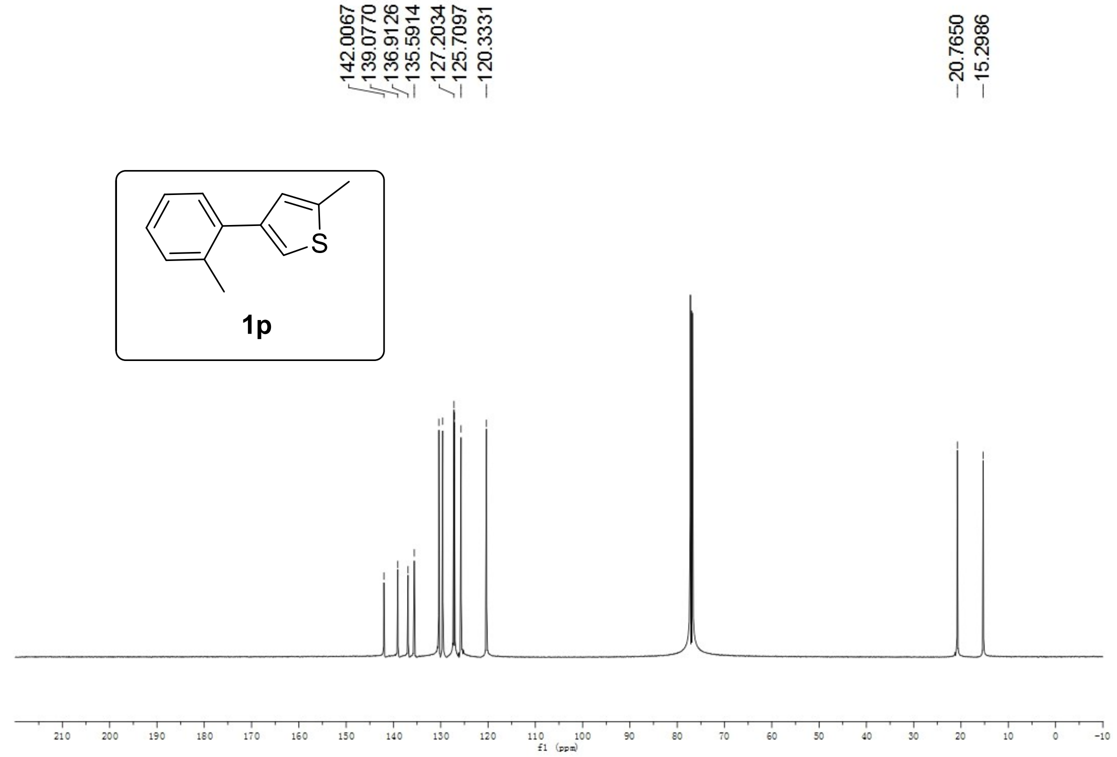
4. Mao, S. L.; Sun, Y.; Yu, G. A.; Zhao, C.; Han, Z. J.; Yuan, J.; Zhu, X. L.; Yang, Q. H.; Liu, S. H. *Org. Biomol. Chem.,* **2012**, *10*, 9410.
5. Kikushima, K.; Nishina, Y. *RSC Advances*, **2013**, 3, 20150.
6. Chen, K. F.; Hsu, Y. C.; Wu, Q. Y.; Yeh, M. C. P.; Sun, S. S. *Org. Lett.*, **2009**, 11, 377-380.
7. Jimenez, M. E.; Bush, K.; Pawlik, J.; Sower, L.; Peterson, J. W.; Gilbertson, S. R. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4215.
8. Moreno-Dorado, F. J.; Guerra, F. M.; Aladro, F. J.; Bustamante, J. M.; Jorge, Z. D.; Massanet, G. M. *Tetrahedron*, **1999**, 55, 6997.

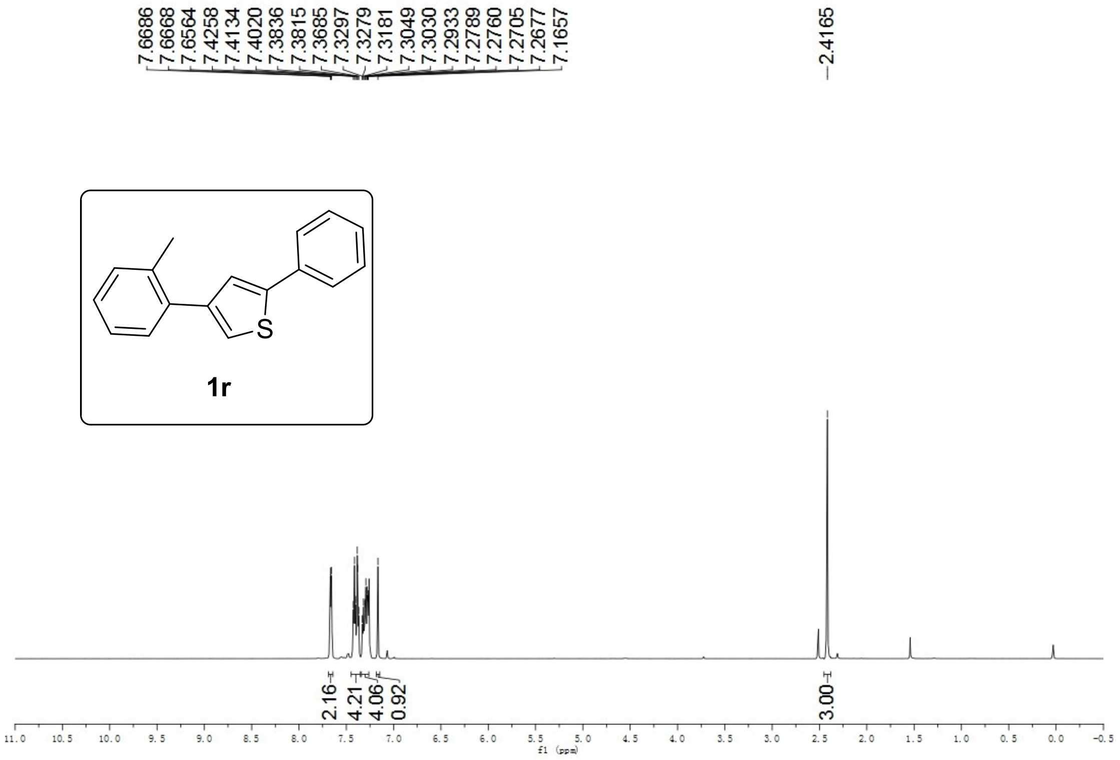
Copy of ^{1}H NMR, ^{13}C NMR Spectra

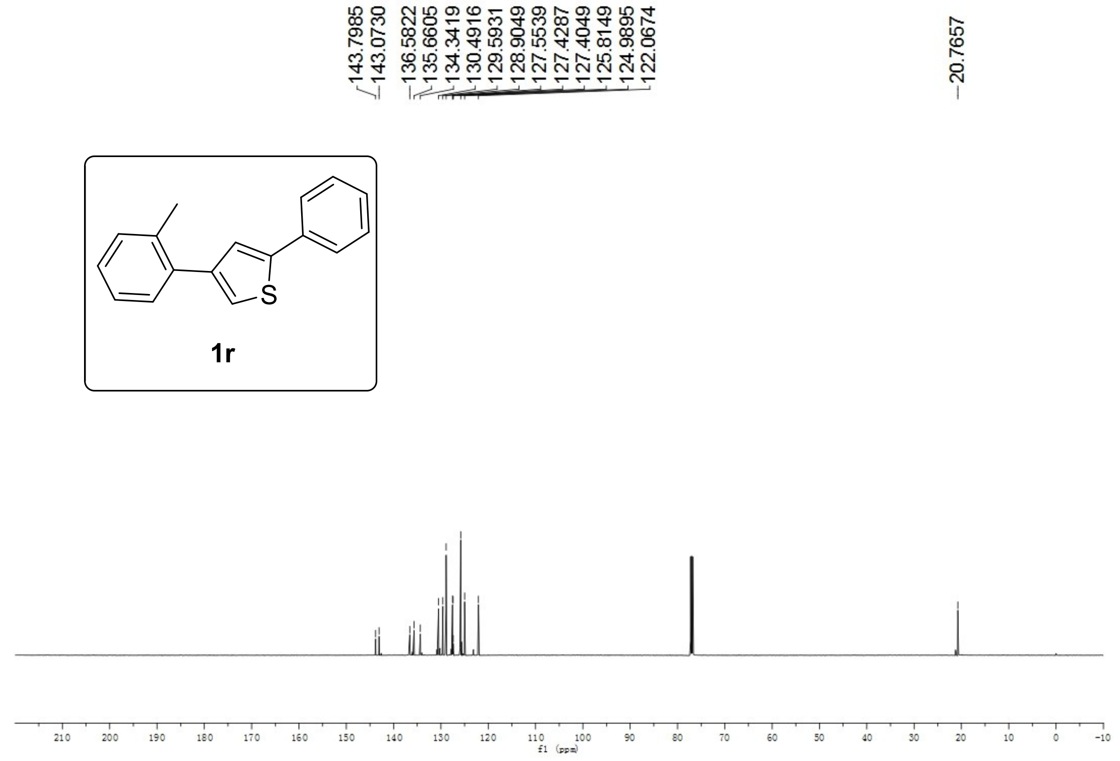


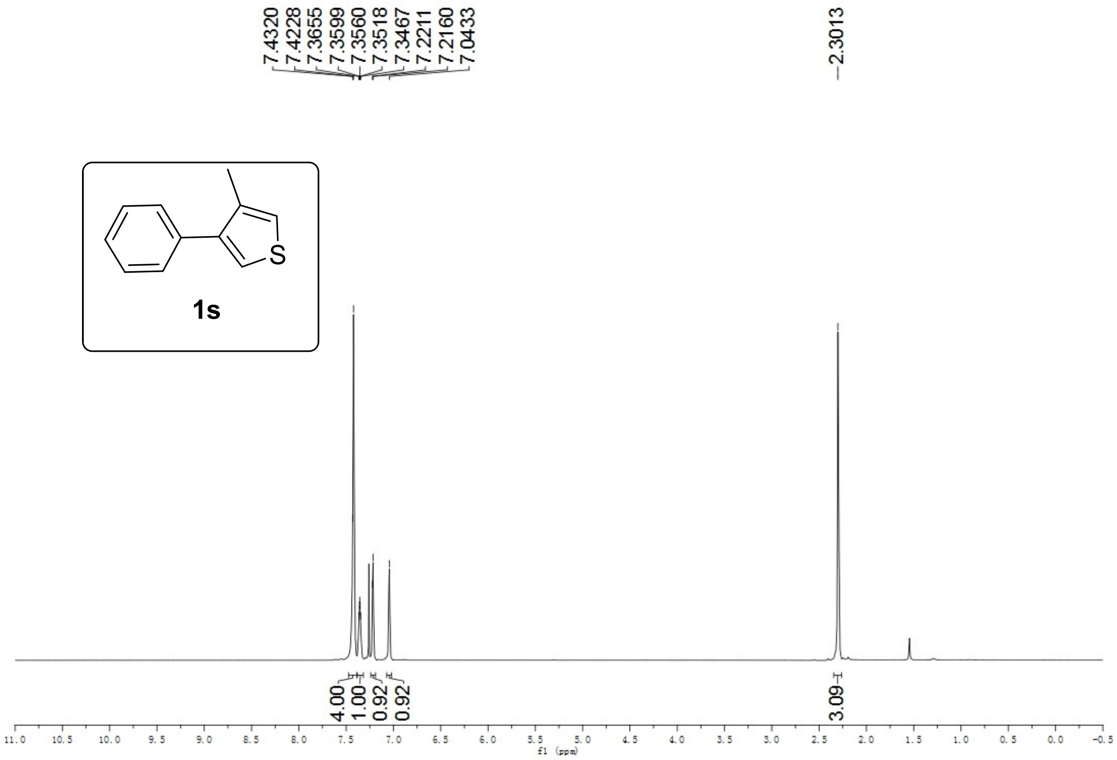


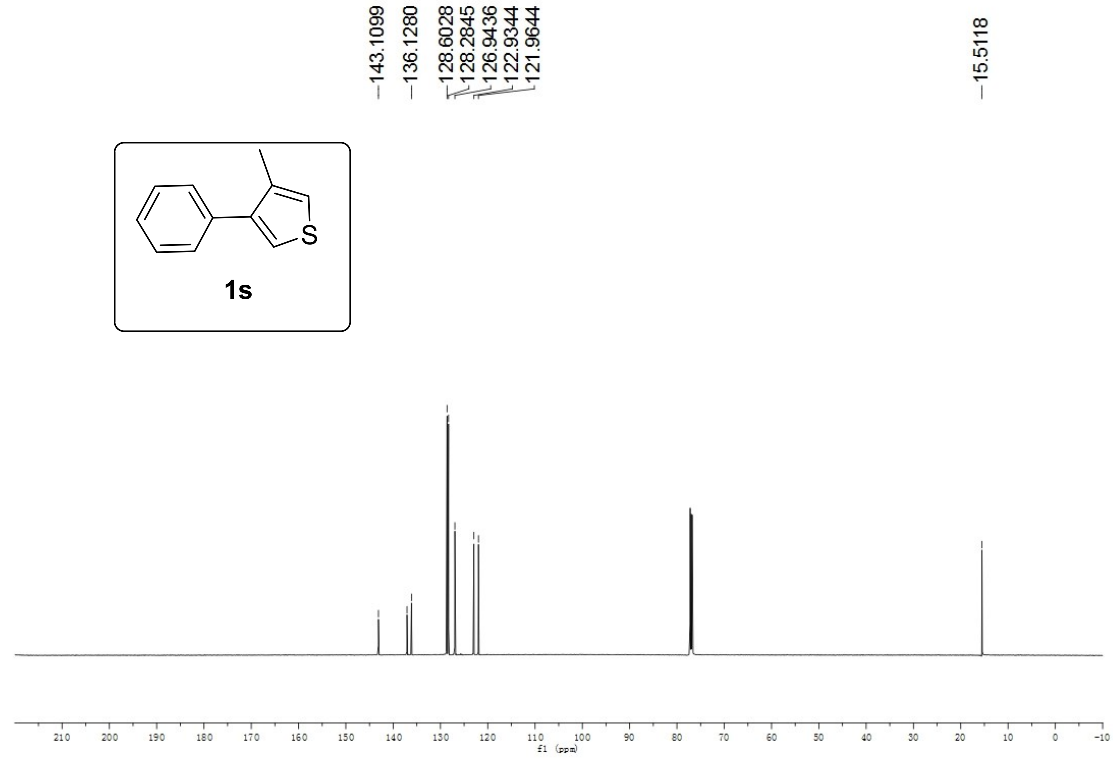

7.2799
7.2684
7.2666
7.2302
7.2185
7.2037
7.1929
7.1846
7.1728
6.9263
6.8041
2.5127
2.3379
S
1p
1.00
3.24
0.92
0.98
3.31
3.26
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

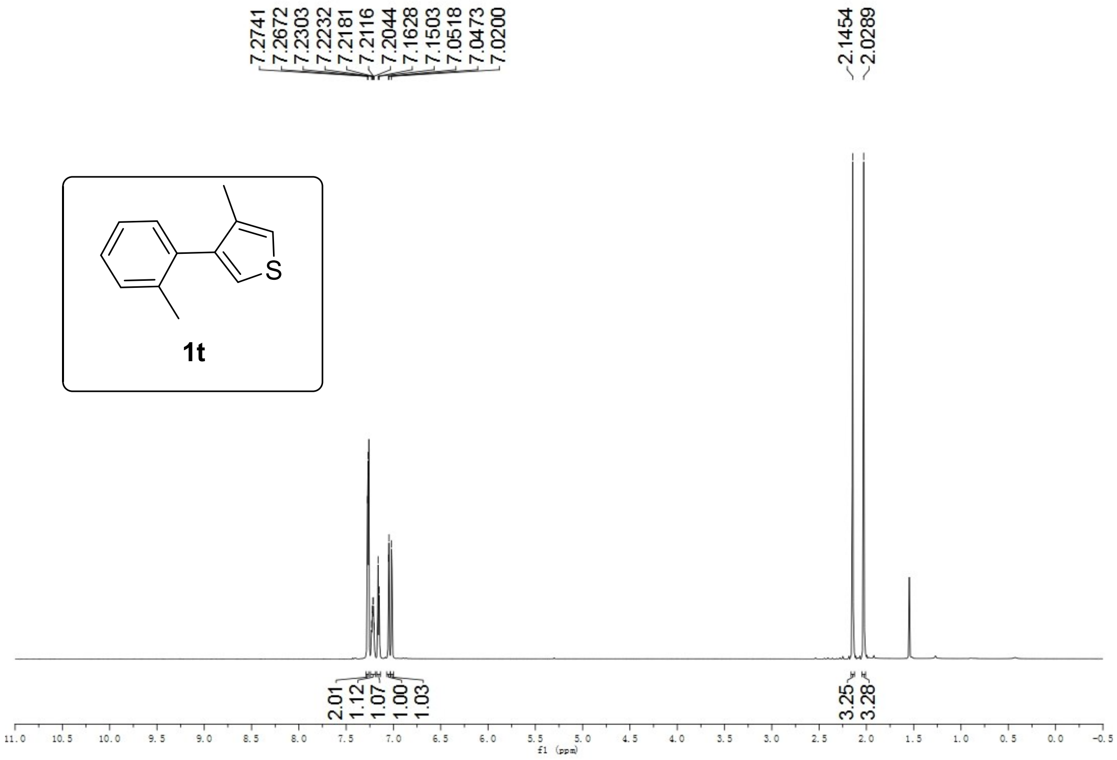

142.0067
139.0770
136.9126
135.5914
127.2034
125.7097
120.3331
20.7650
15.2986
S
1p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

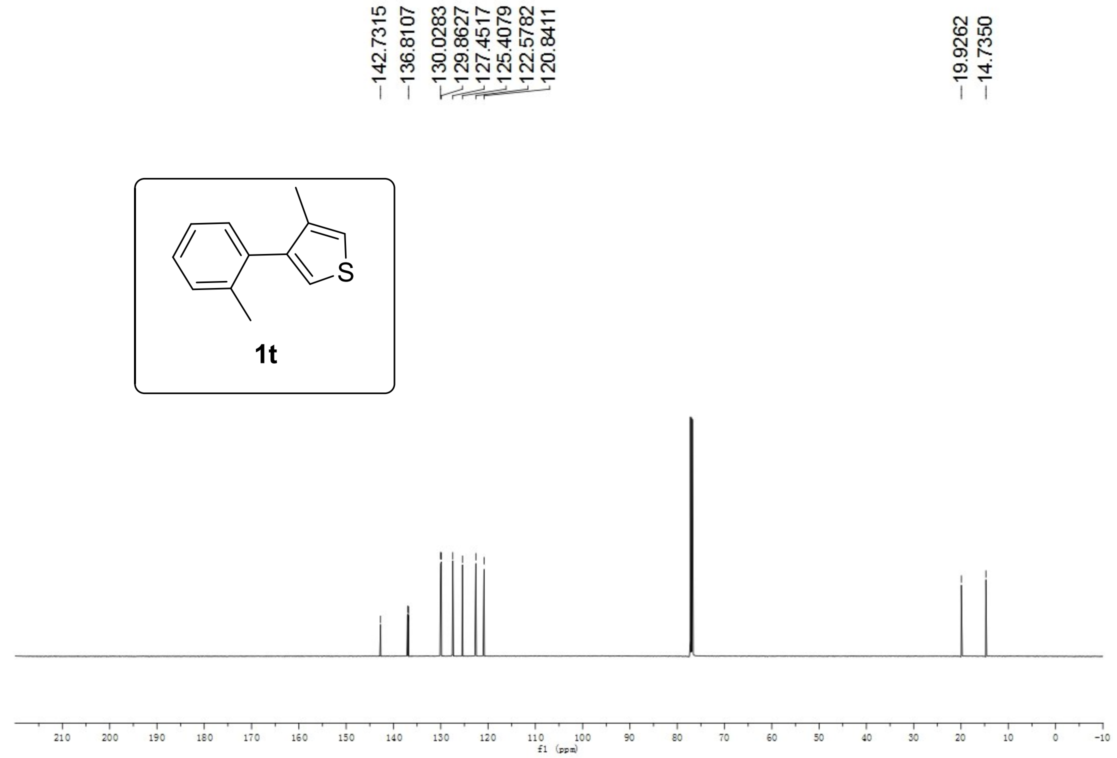

7.6686
7.6668
7.6564
7.4258
7.4134
7.4020
7.3836
7.3815
7.3685
7.3297
7.3279
7.3181
7.3049
7.3030
7.2933
7.2789
7.2760
7.2705
7.2677
7.1657
2.4165
S
1r
2.16
4.21
4.06
0.92
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

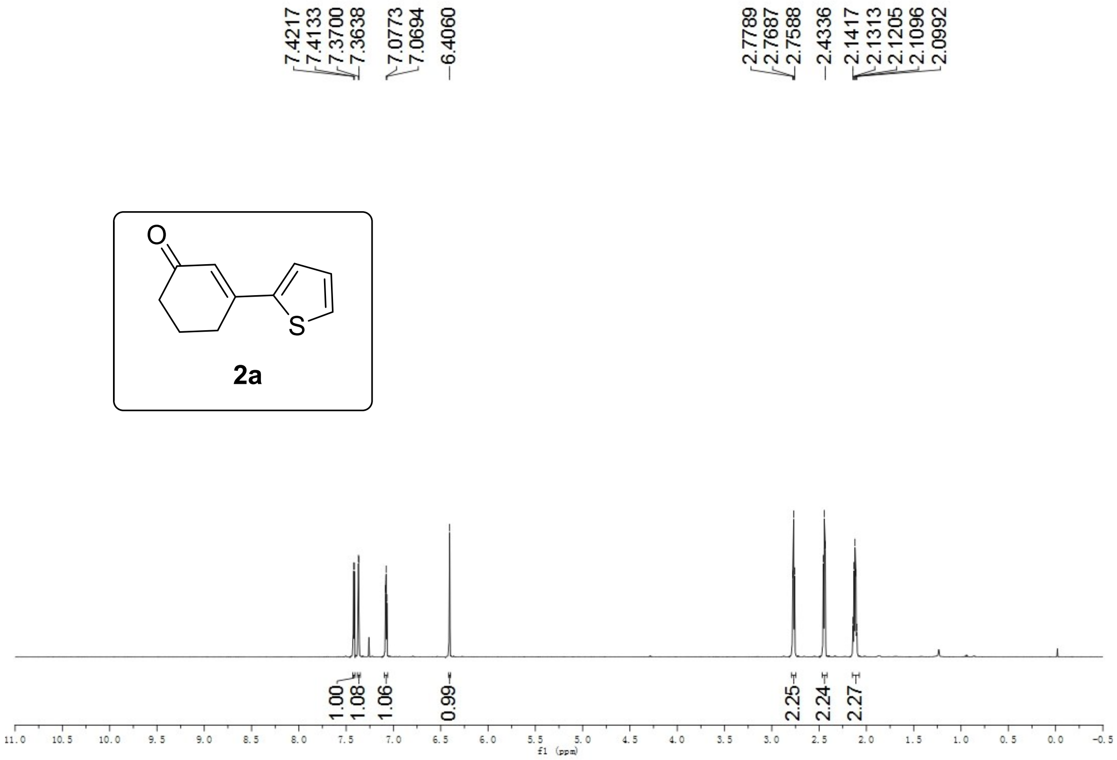

143.7985
143.0730
136.5822
135.6605
134.3419
130.4916
129.5931
128.9049
127.5539
127.4287
127.4049
125.8149
124.9895
122.0674
20.7657
S
1r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

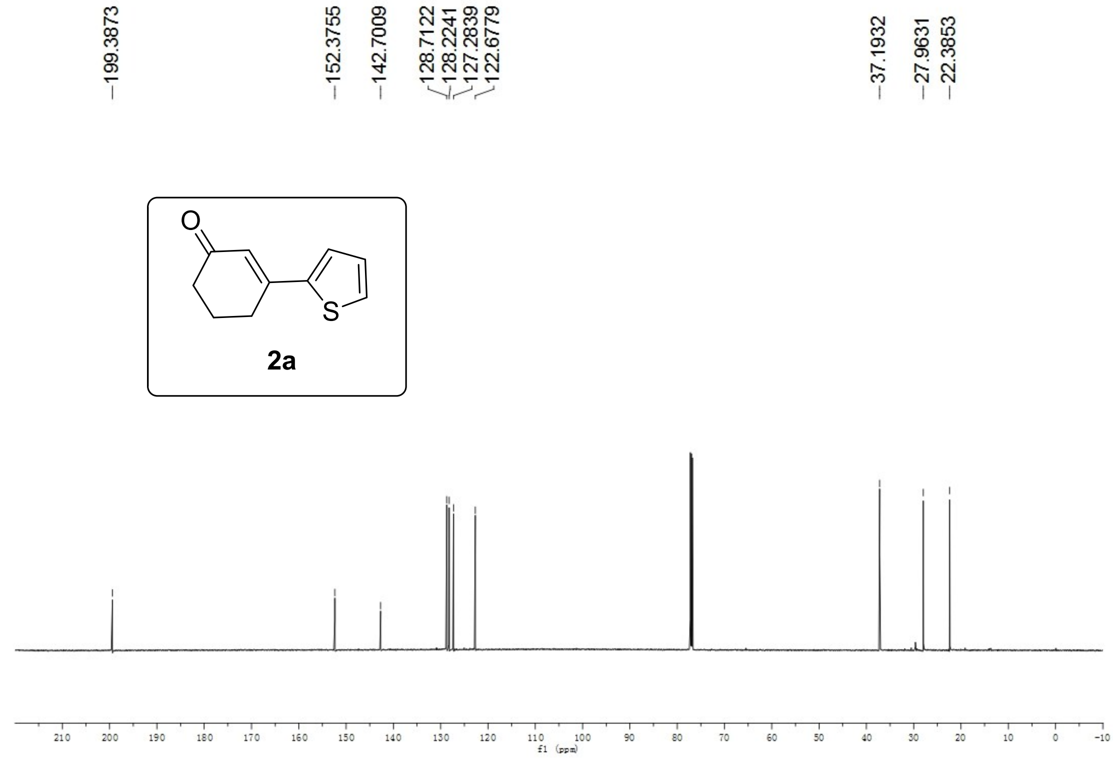

7.4320
7.4228
7.3655
7.3599
7.3560
7.3518
7.3467
7.2211
7.2160
7.0433
2.3013
S
1s
4.00
1.00
0.92
0.92
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

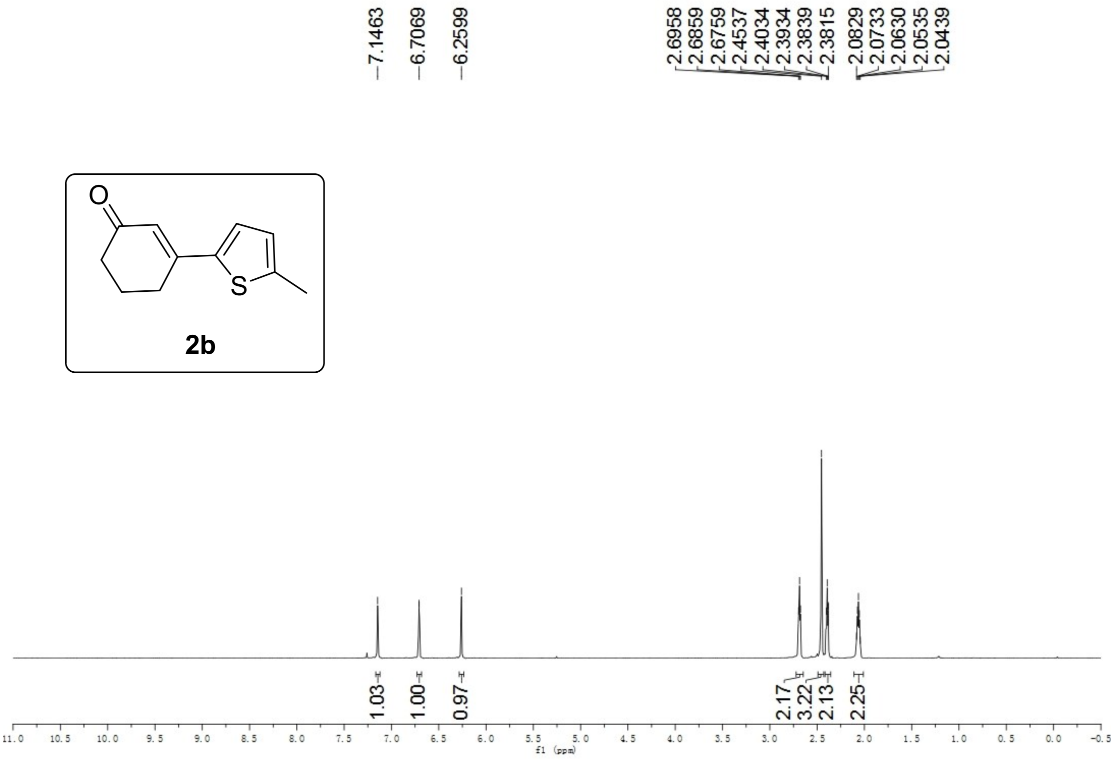

143.1099
136.1280
128.6028
128.2845
126.9436
122.9344
121.9644
15.5118
S
1s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

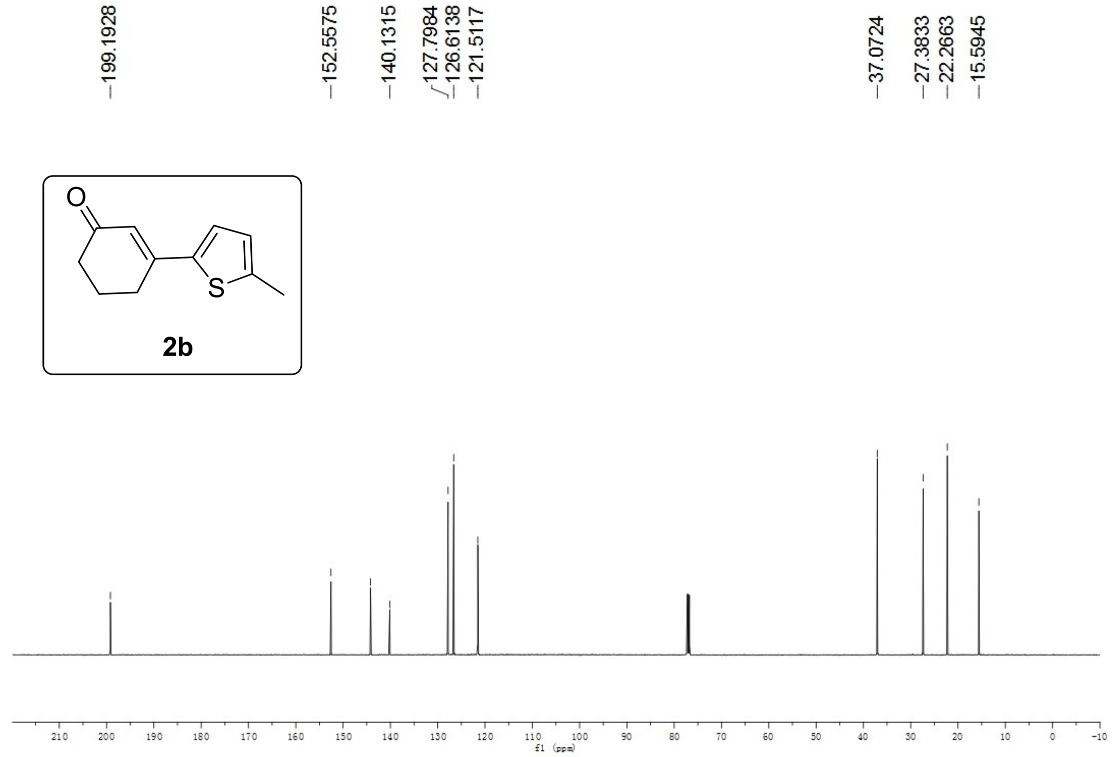

7.2741
7.2672
7.2303
7.2232
7.2181
7.2116
7.2044
7.1628
7.1503
7.0518
7.0473
7.0200
2.1454
2.0289
S
1t
2.01
1.12
1.07
1.00
1.03
3.25
3.28
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

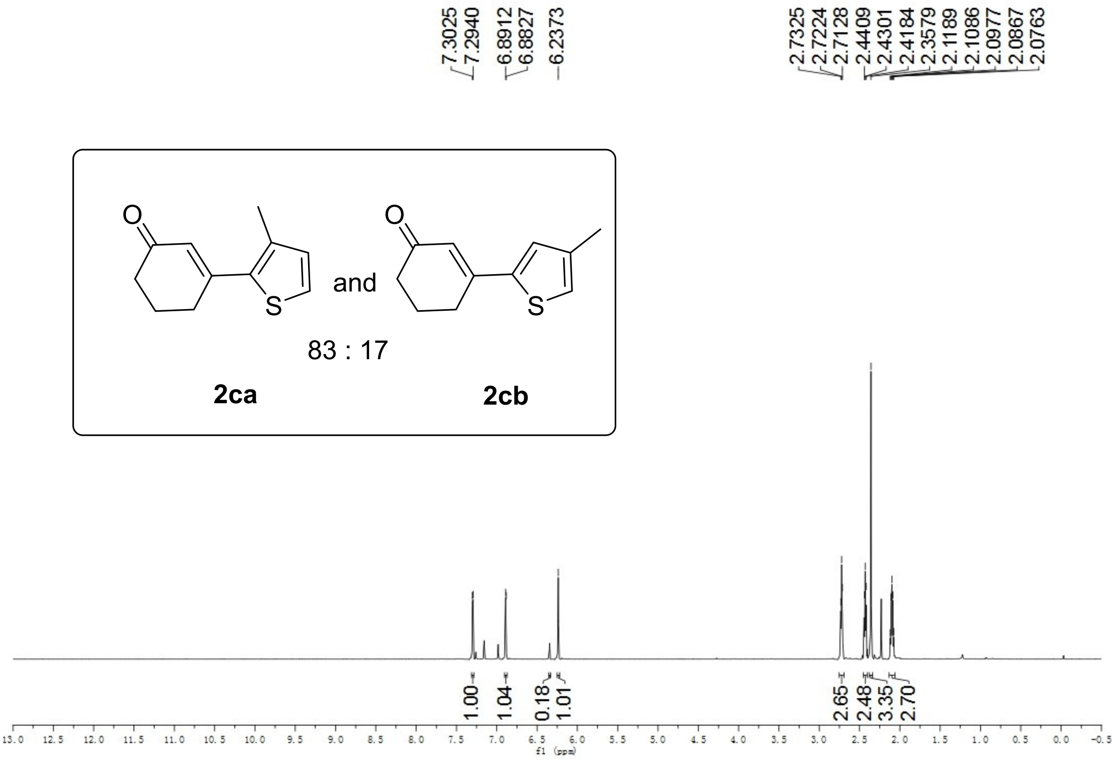

142.7315
136.8107
130.0283
129.8627
127.4517
125.4079
122.5782
120.8411
19.9262
14.7350
S
1t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

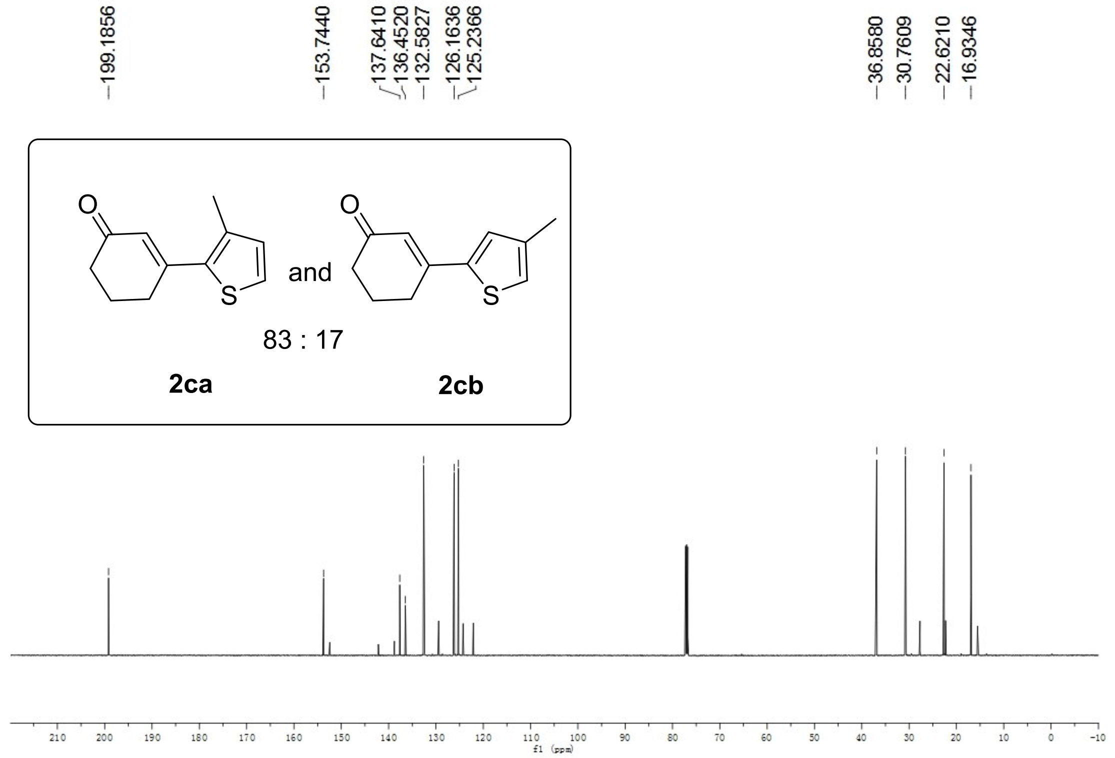

7.4217
7.4133
7.3700
7.3638
7.0773
7.0694
6.4060
2.7789
2.7687
2.7588
2.4336
2.1417
2.1313
2.1205
2.1096
2.0992
O
S
2a
1.00
1.08
1.06
0.99
2.25
2.24
2.27
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

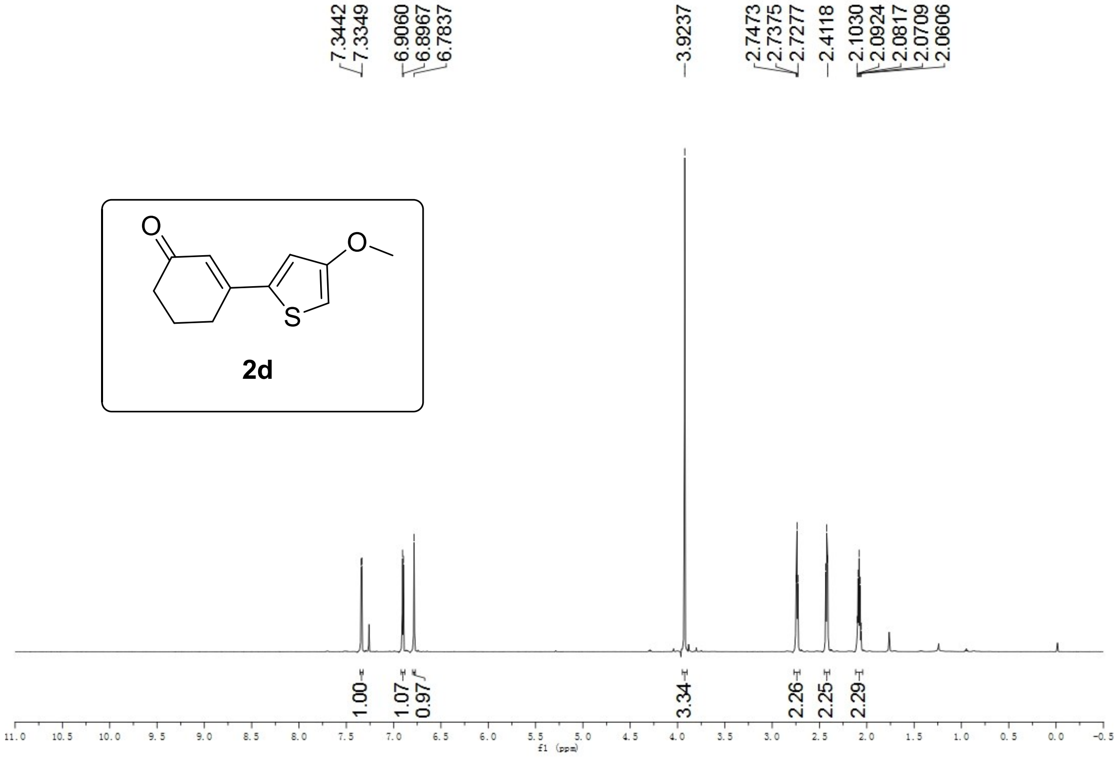

199.3873
152.3755
142.7009
128.7122
128.2241
127.2839
122.6779
37.1932
27.9631
22.3853
O
S
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

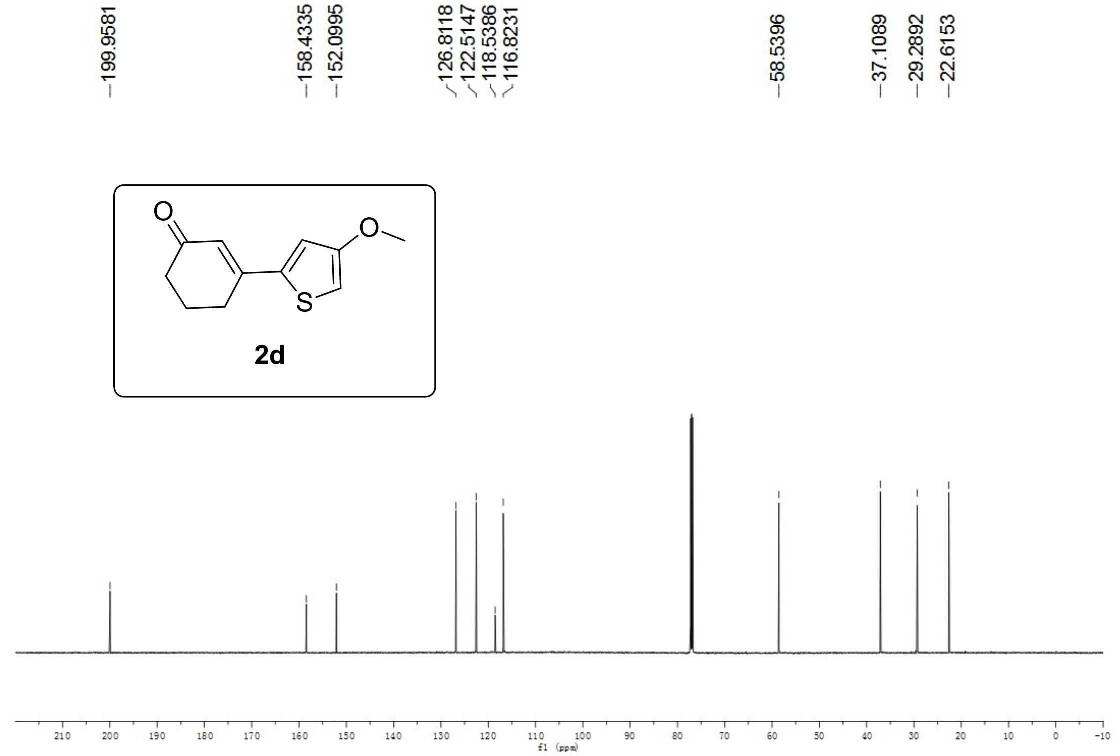

7.1463
6.7069
6.2599
2.6958
2.6859
2.6759
2.4537
2.4034
2.3934
2.3839
2.3815
2.0829
2.0733
2.0630
2.0535
2.0439
O
S
2b
1.03
1.00
0.97
2.17
3.22
2.13
2.25
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

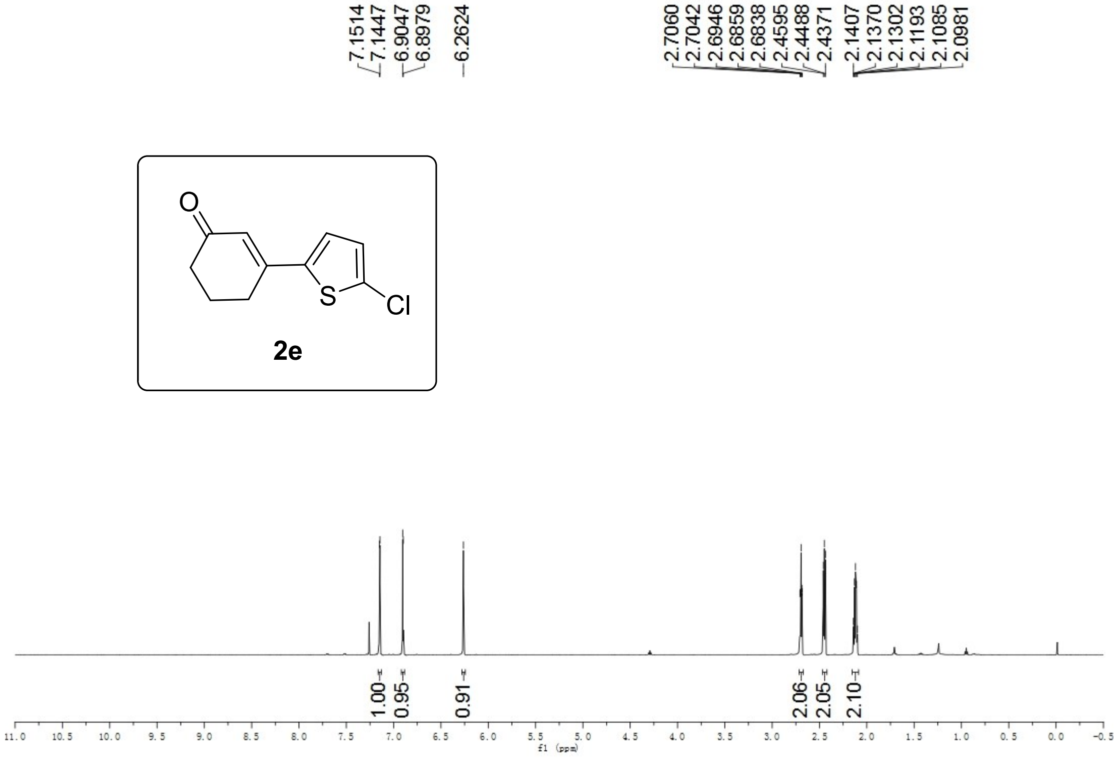

199.1928
152.5575
140.1315
127.7984
126.6138
121.5117
37.0724
27.3833
22.2663
15.5945
O
S
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

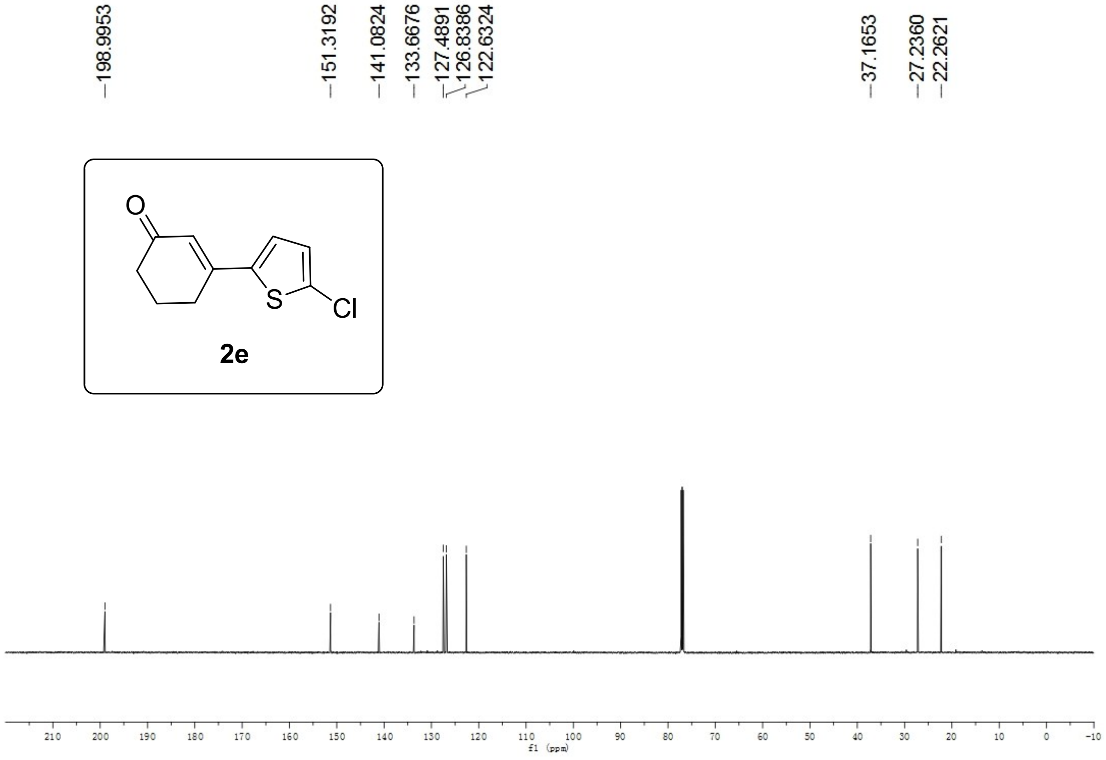

7.3025
7.2940
6.8912
6.8827
6.2373
2.7325
2.7224
2.7128
2.4409
2.4301
2.4184
2.3579
2.1189
2.1086
2.0977
2.0867
2.0763
O
S
and
O
S
83 : 17
2ca
2cb
1.00
1.04
0.18
1.01
2.65
2.48
3.35
2.70
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

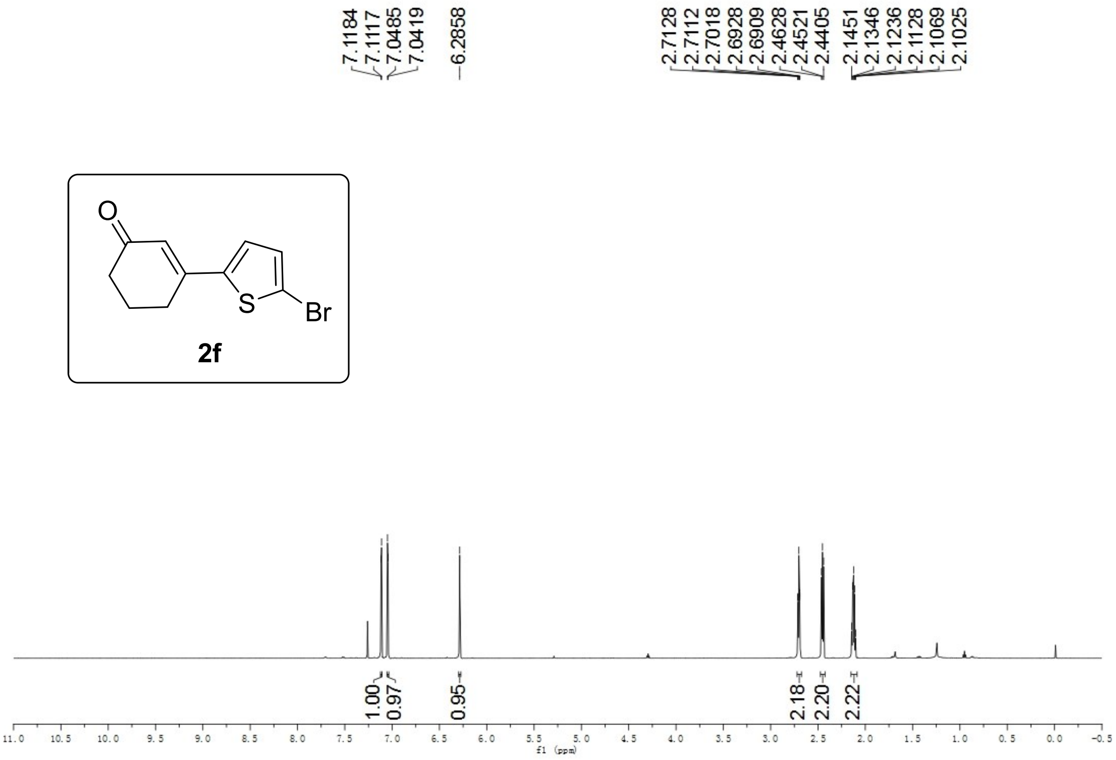

199.1856
153.7440
137.6410
136.4520
132.5827
126.1636
125.2366
36.8580
30.7609
22.6210
16.9346
O
S
and
O
S
83 : 17
2ca
2cb
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

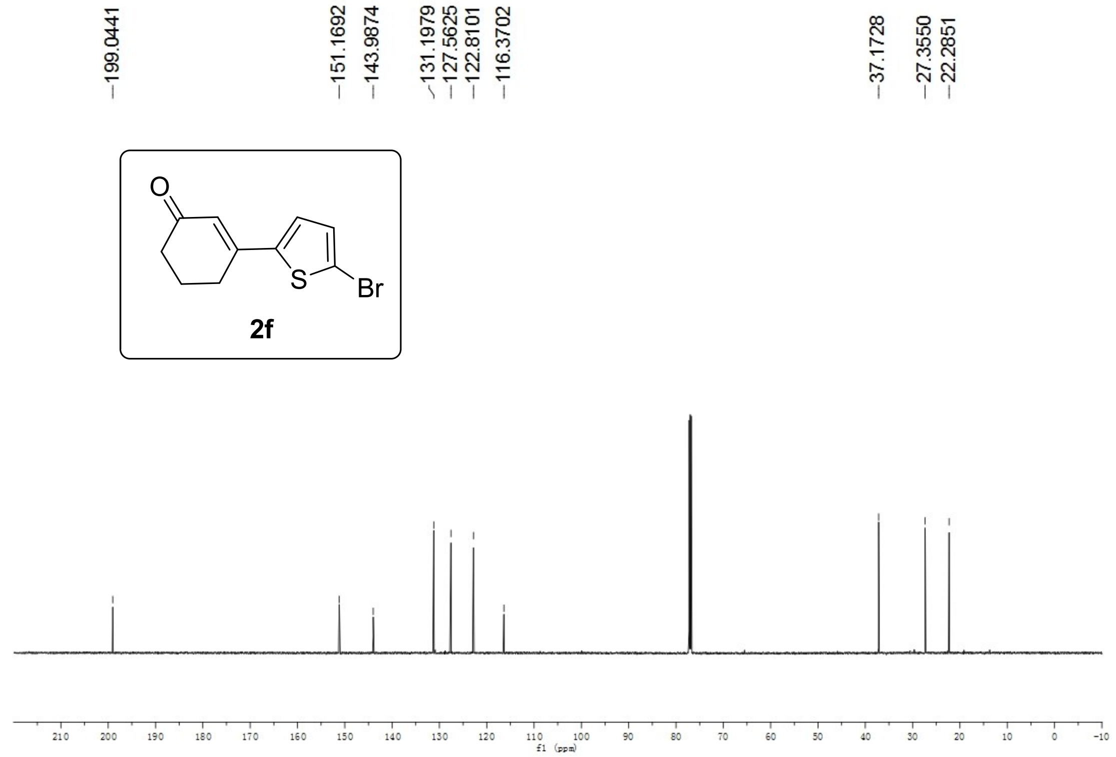

7.3442
7.3349
6.9060
6.8967
6.7837
3.9237
2.7473
2.7375
2.7277
2.4118
2.1030
2.0924
2.0817
2.0709
2.0606
O
S
2d
1.00
1.07
0.97
3.34
2.26
2.25
2.29
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

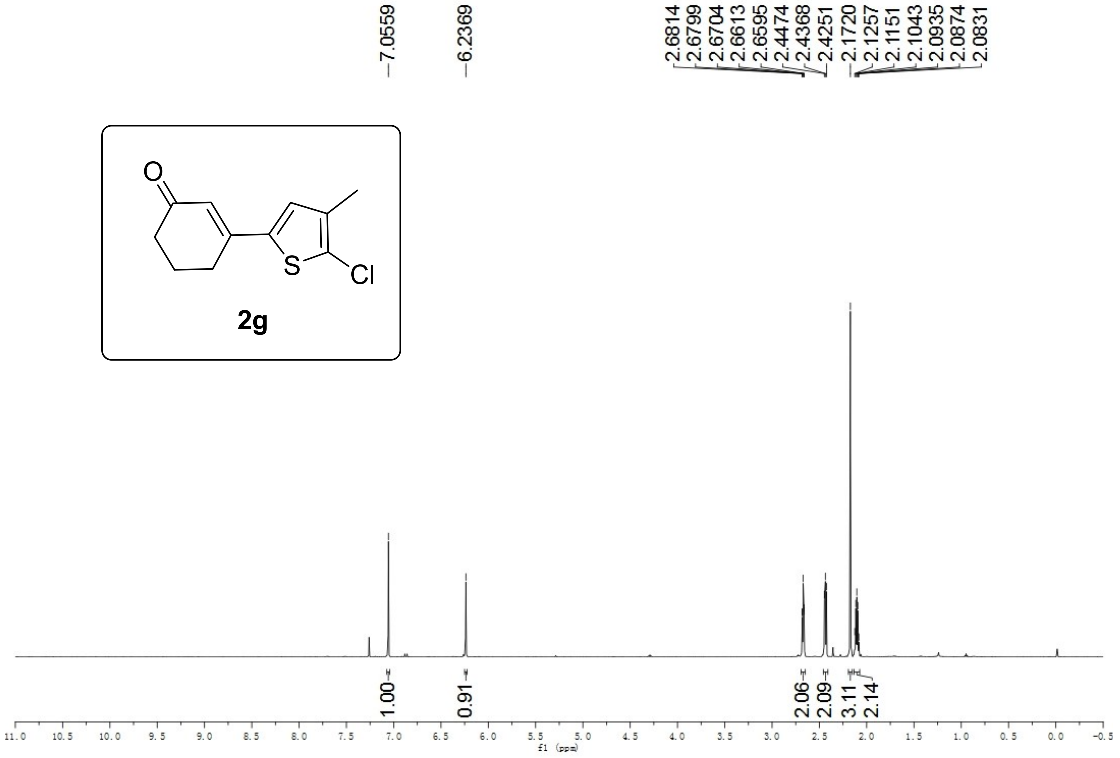

199.9581
158.4335
152.0995
126.8118
122.5147
118.5386
116.8231
58.5396
37.1089
29.2892
22.6153
O
S
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

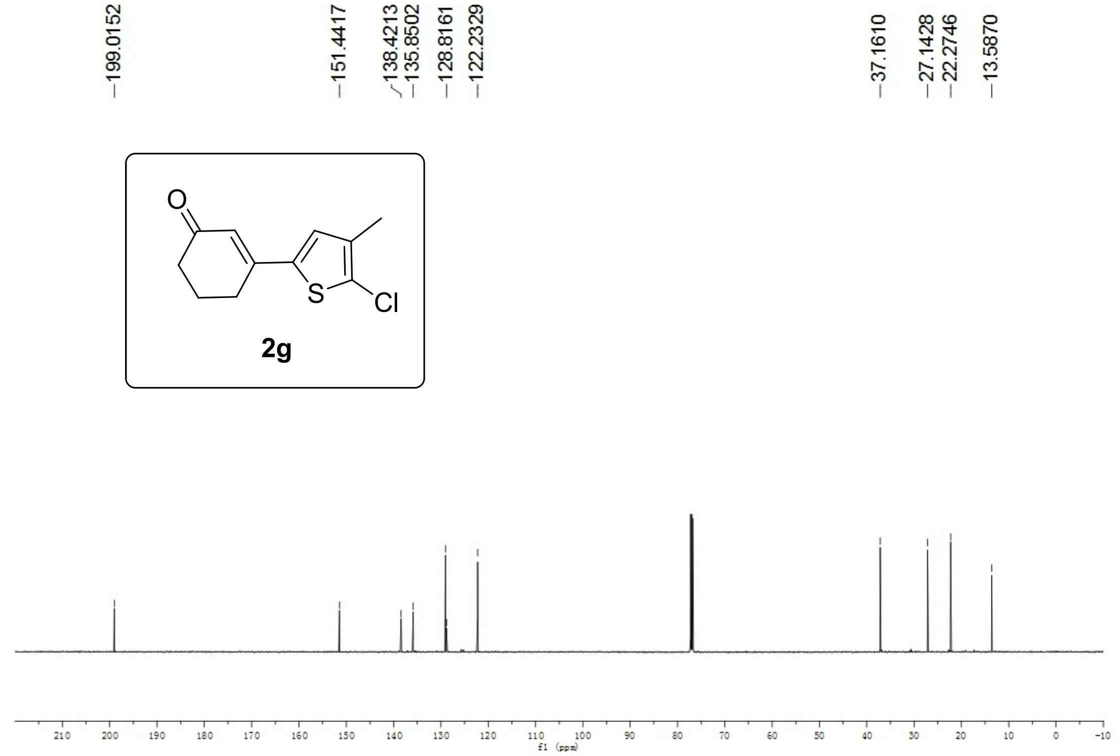

7.1514
7.1447
6.9047
6.8979
6.2624
2.7060
2.7042
2.6946
2.6859
2.6838
2.4595
2.4488
2.4371
2.1407
2.1370
2.1302
2.1193
2.1085
2.0981
O
S
Cl
2e
1.00
0.95
0.91
2.06
2.05
2.10
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

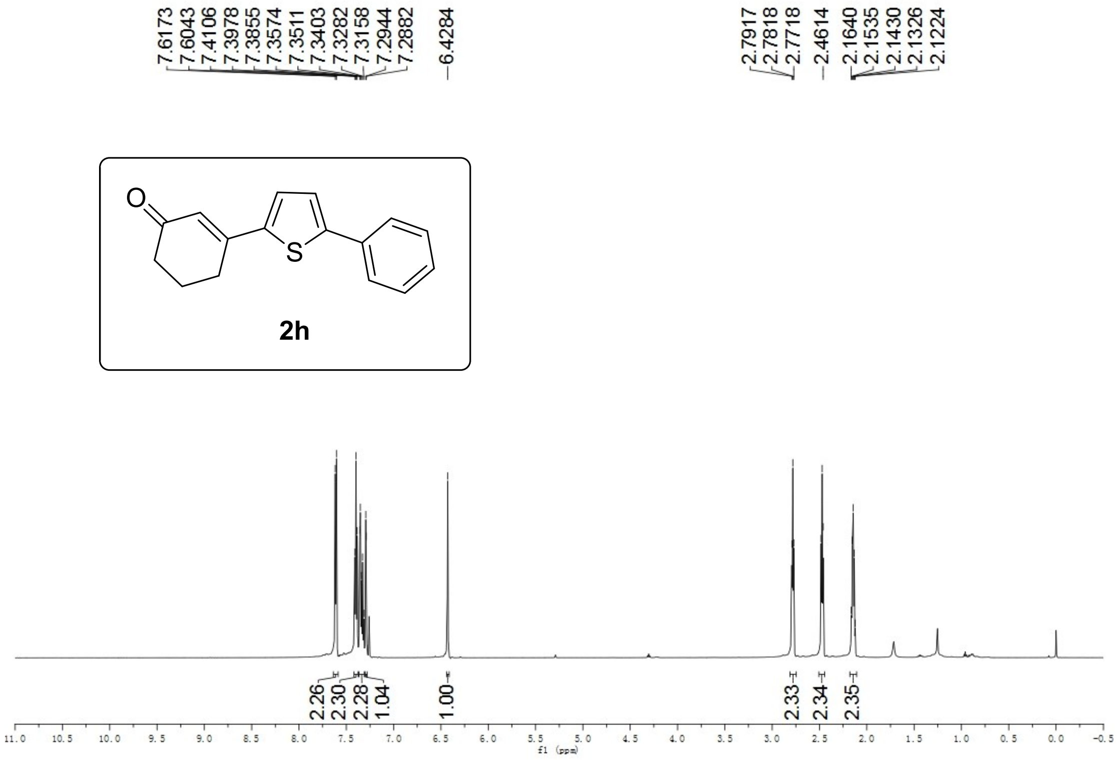

198.9953
151.3192
141.0824
133.6676
127.4891
126.8386
122.6324
37.1653
27.2360
22.2621
O
S
Cl
2e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

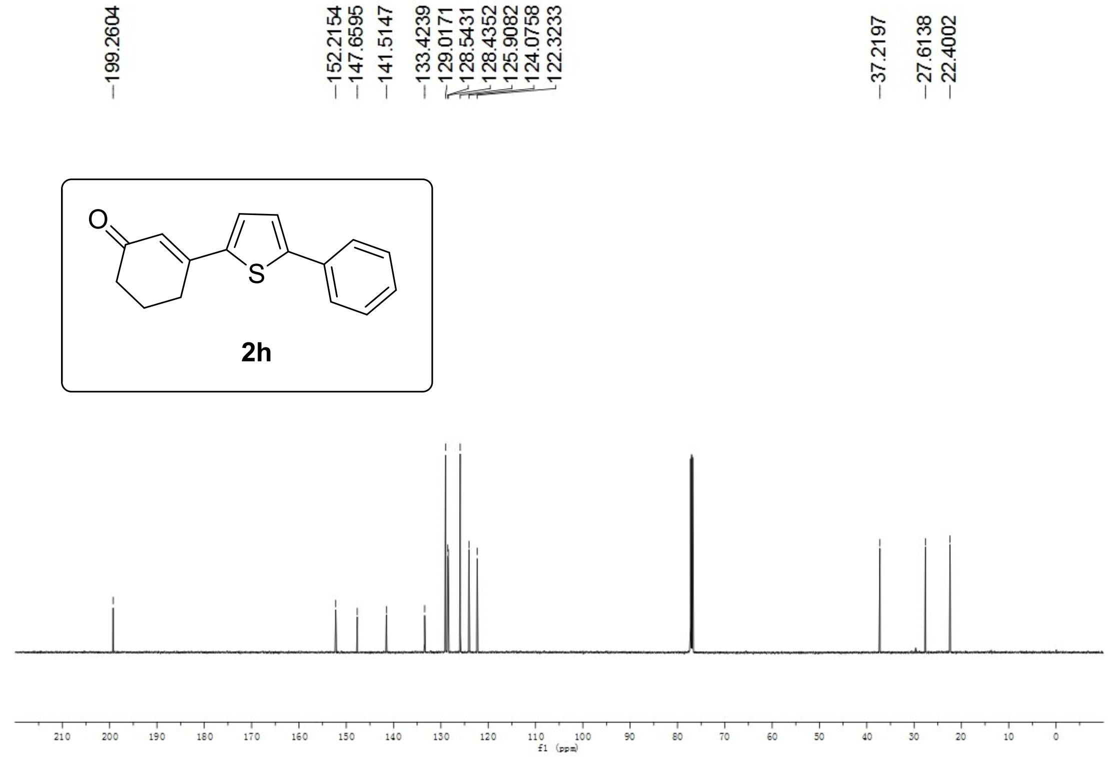

7.1184
7.1117
7.0485
7.0419
6.2858
2.7128
2.7112
2.7018
2.6928
2.6909
2.4628
2.4521
2.4405
2.1451
2.1346
2.1236
2.1128
2.1069
2.1025
O
S
Br
2f
1.00
0.97
0.95
2.18
2.20
2.22
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

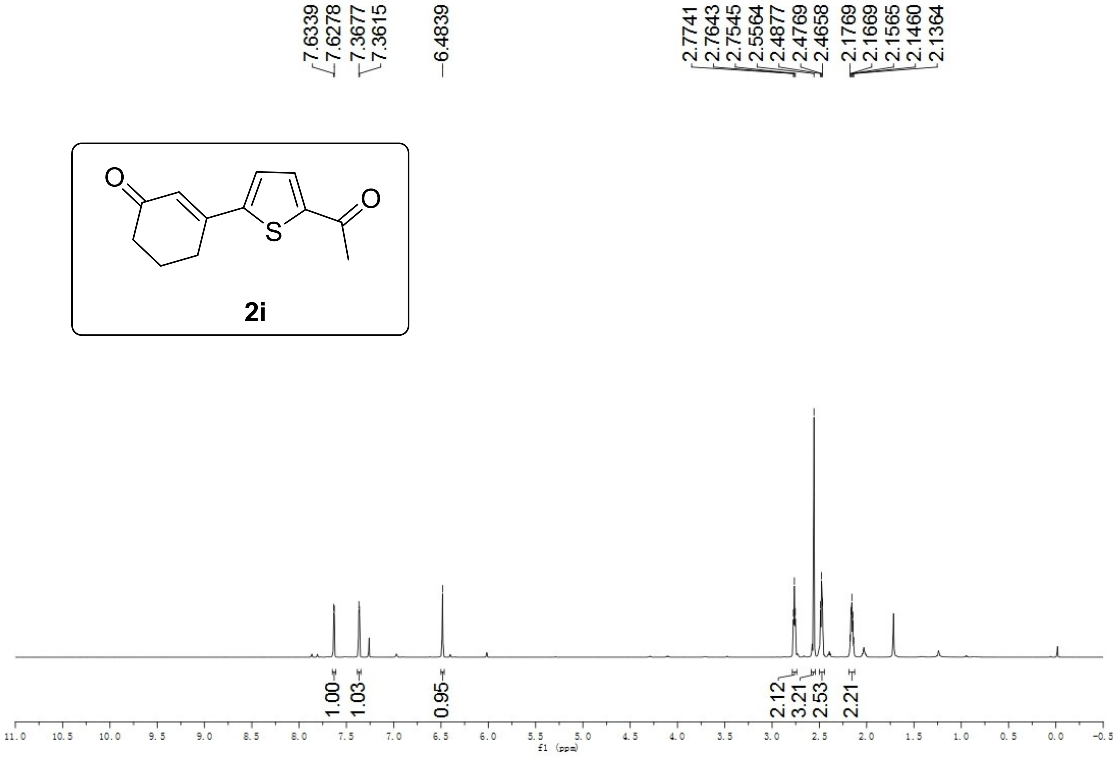

199.0441
151.1692
143.9874
131.1979
127.5625
122.8101
116.3702
37.1728
27.3550
22.2851
O
S
Br
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

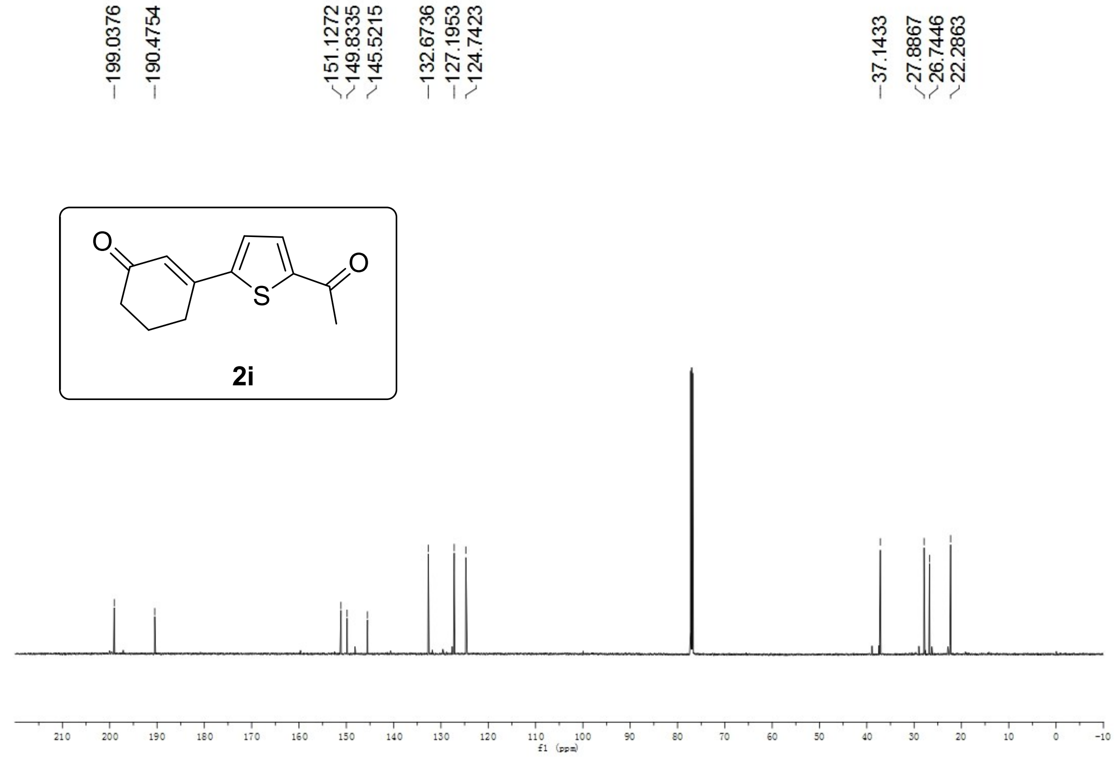

7.0559
6.2369
2.6814
2.6799
2.6704
2.6613
2.6595
2.4474
2.4368
2.4251
2.1720
2.1257
2.1151
2.1043
2.0935
2.0874
2.0831
O
S
Cl
2g
1.00
0.91
2.06
2.09
3.11
2.14
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

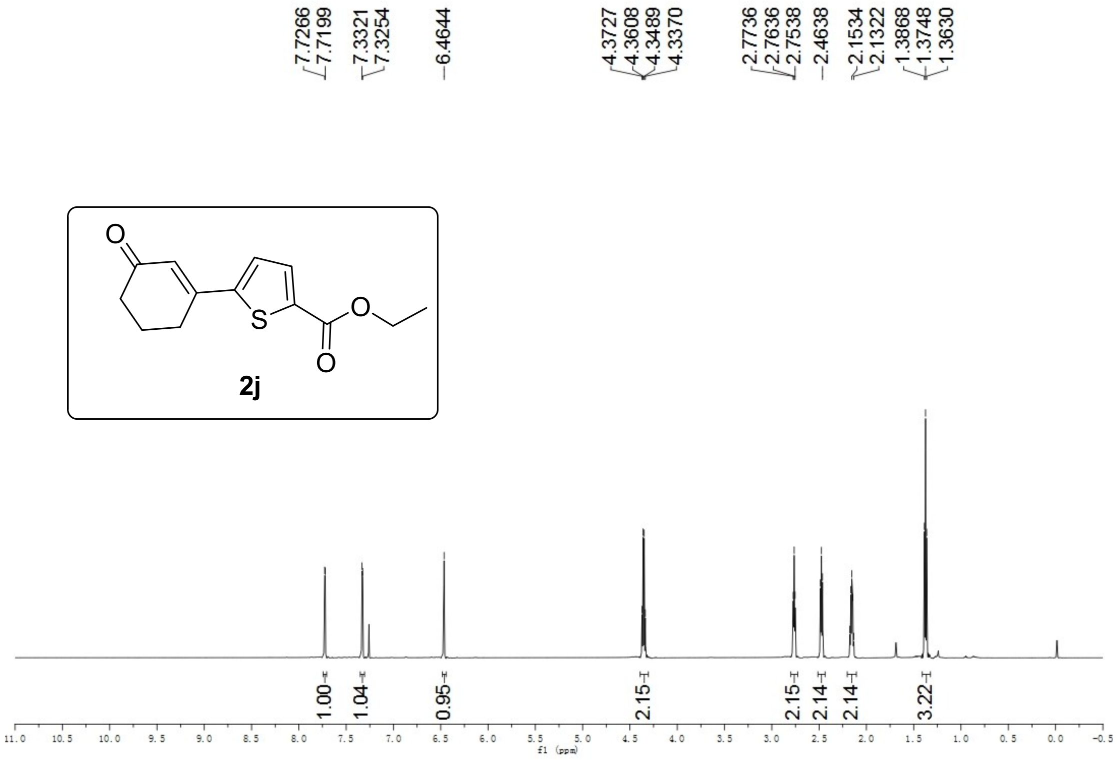

199.0152
151.4417
138.4213
135.8502
128.8161
122.2329
37.1610
27.1428
22.2746
13.5870
O
S
Cl
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

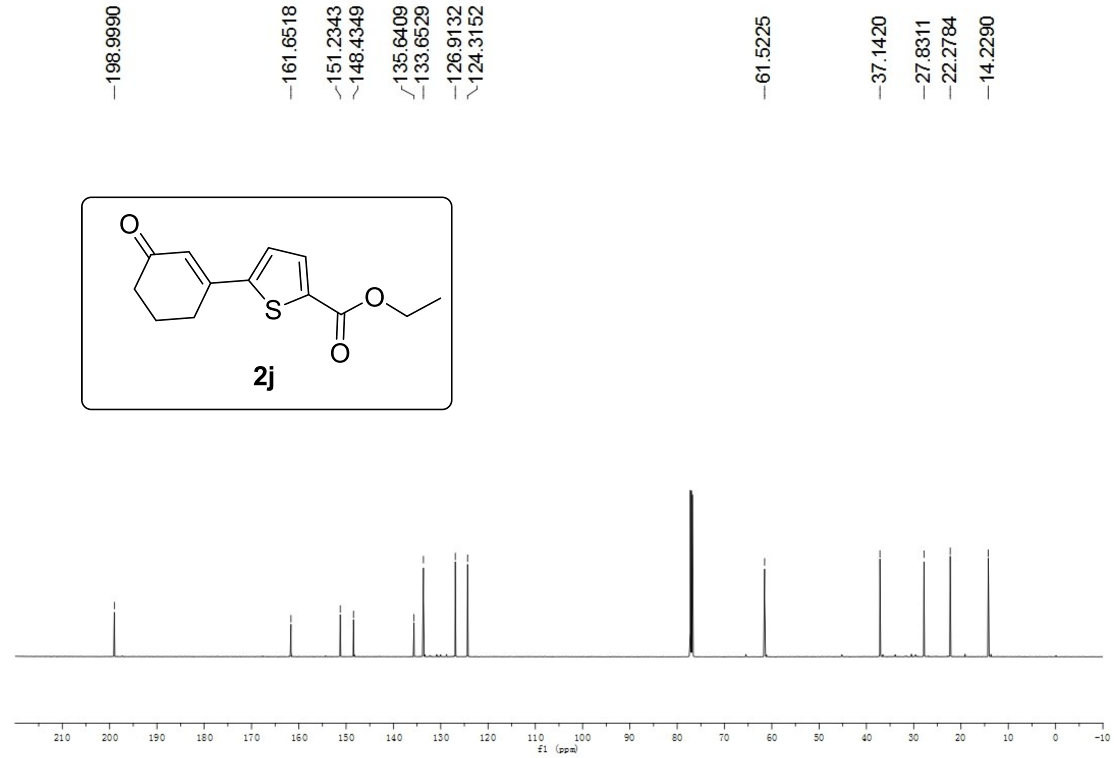

7.6173
7.6043
7.4106
7.3978
7.3855
7.3574
7.3511
7.3403
7.3282
7.3158
7.2944
7.2882
6.4284
2.7917
2.7818
2.7718
2.4614
2.1640
2.1535
2.1430
2.1326
2.1224
O
S
2h
2.26
2.30
2.28
1.04
1.00
2.33
2.34
2.35
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

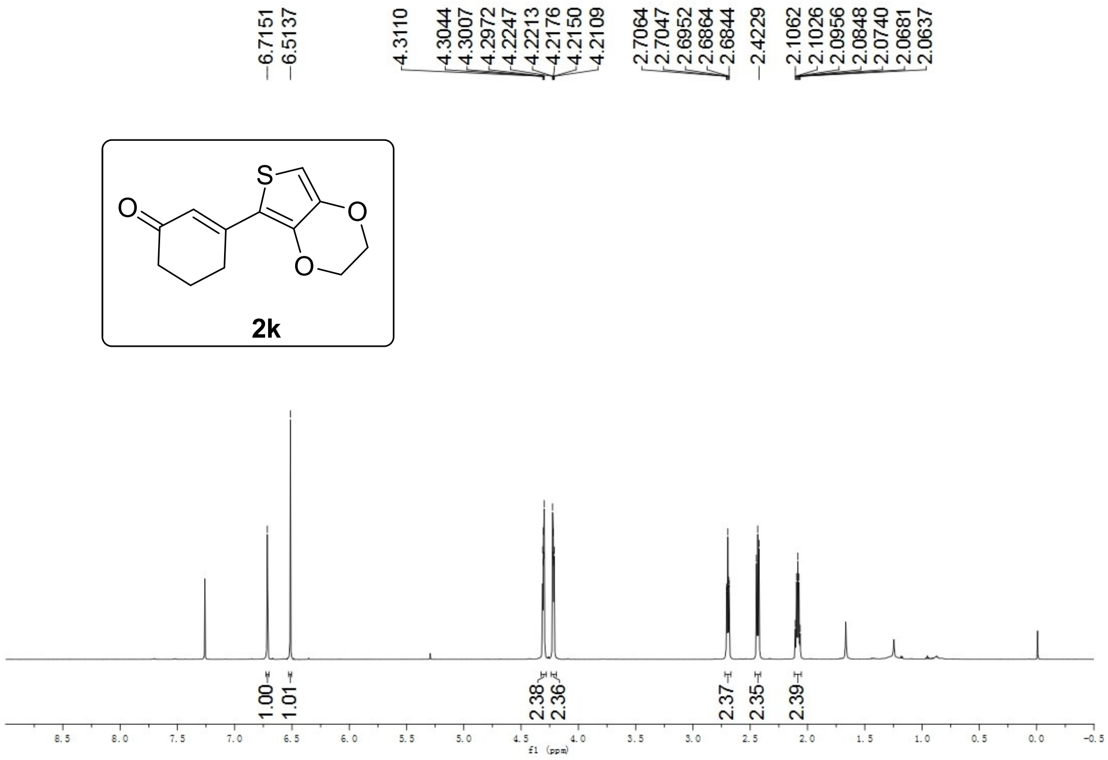

199.2604
152.2154
147.6595
141.5147
133.4239
129.0171
128.5431
128.4352
125.9082
124.0758
122.3233
37.2197
27.6138
22.4002
O
S
2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

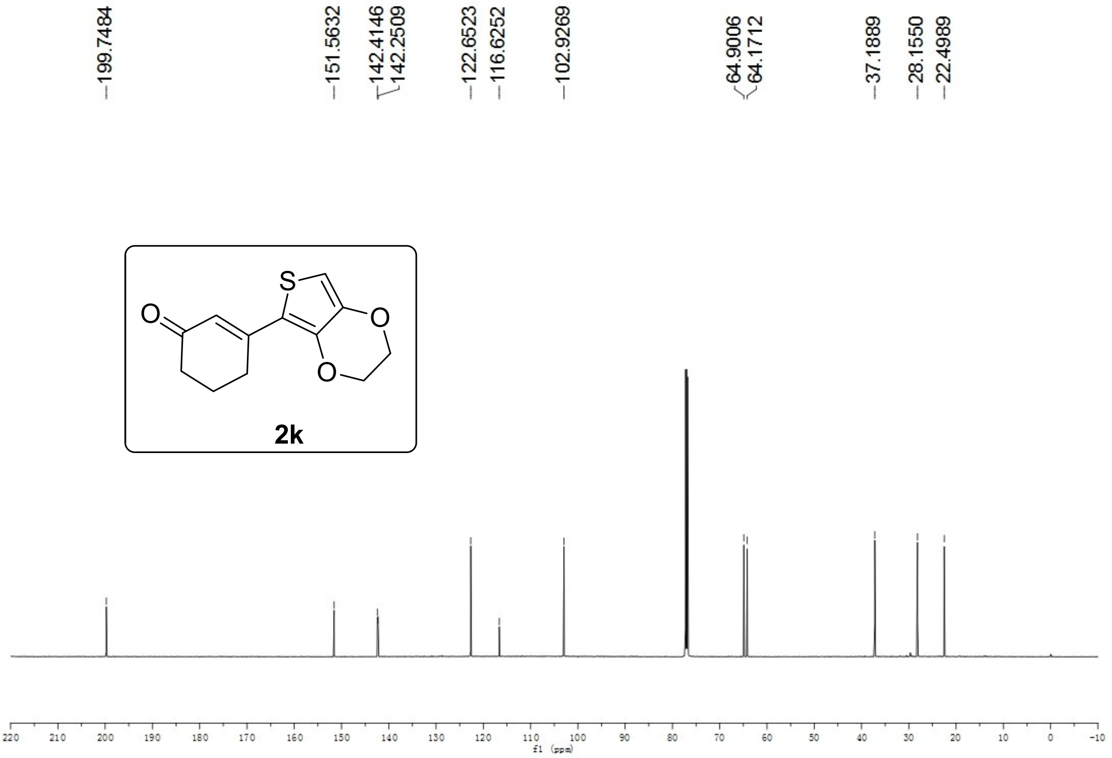

7.6339
7.6278
7.3677
7.3615
6.4839
2.7741
2.7643
2.7545
2.5564
2.4877
2.4769
2.4658
2.1769
2.1669
2.1565
2.1460
2.1364
O
S
O
2i
1.00
1.03
0.95
2.12
3.21
2.53
2.21
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

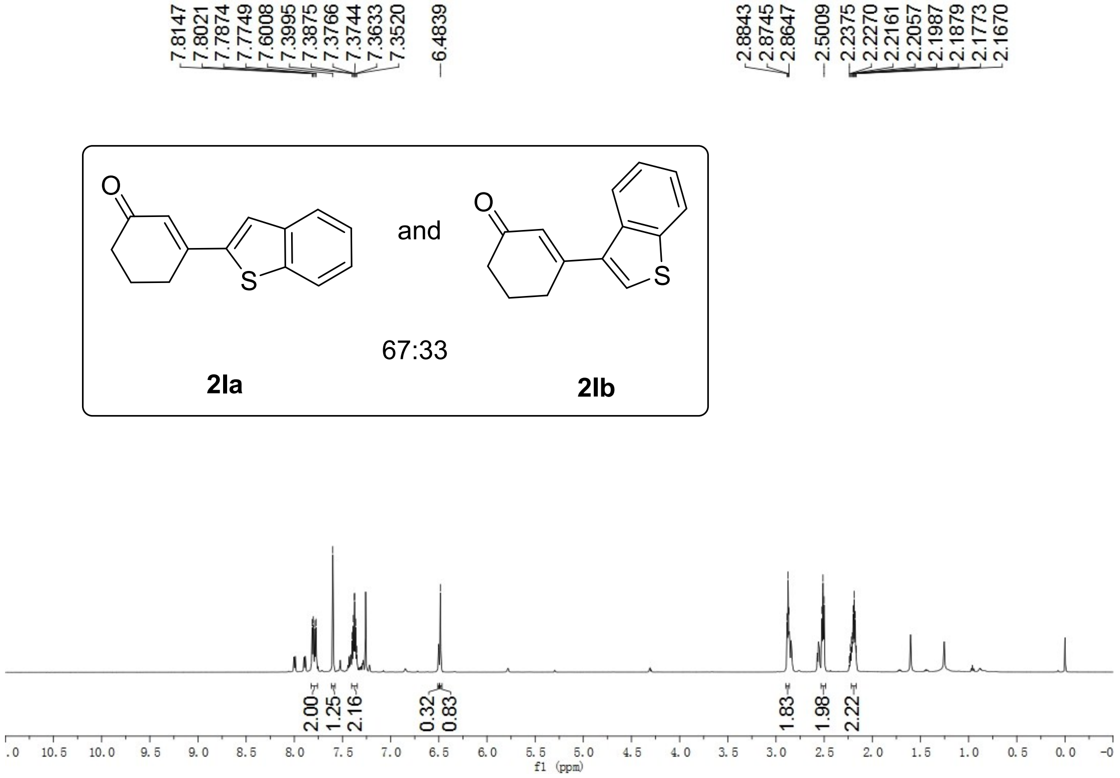

199.0376
190.4754
151.1272
149.8335
145.5215
132.6736
127.1953
124.7423
37.1433
27.8867
26.7446
22.2863
O
S
O
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

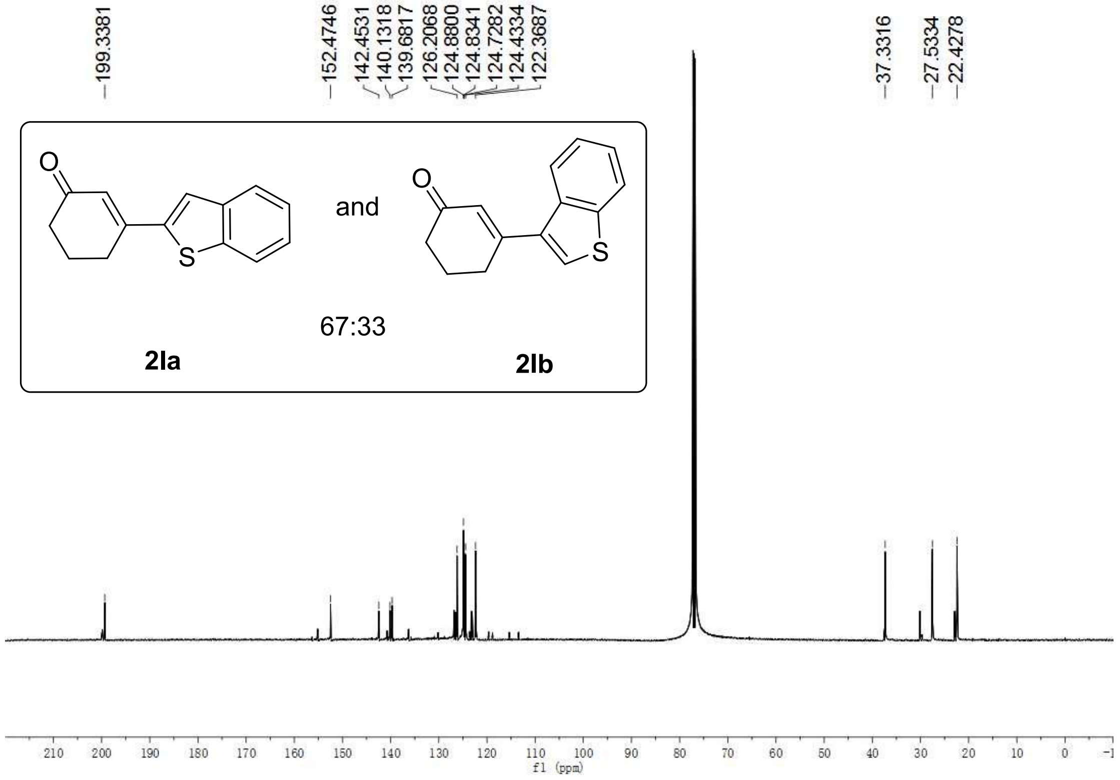

7.7266
7.7199
7.3321
7.3254
6.4644
4.3727
4.3608
4.3489
4.3370
2.7736
2.7636
2.7538
2.4638
2.1534
2.1322
1.3868
1.3748
1.3630
O
S
O
O
2j
1.00
1.04
0.95
2.15
2.15
2.14
2.14
3.22
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

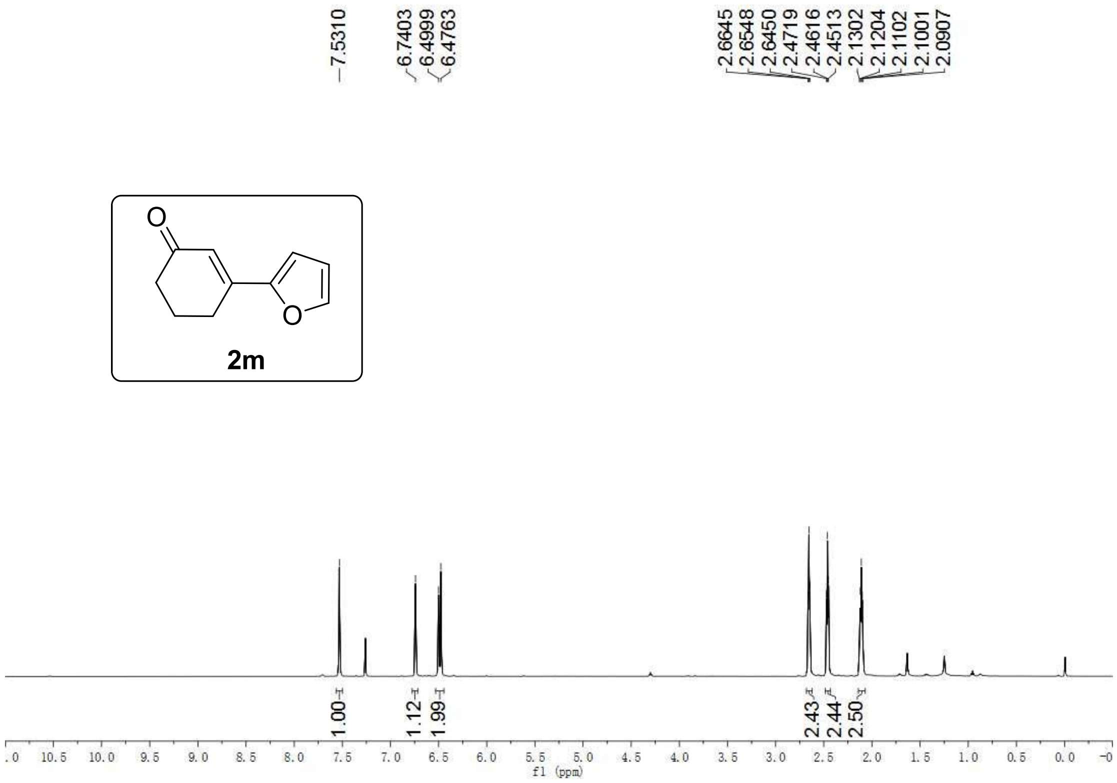

198.9990
161.6518
151.2343
148.4349
135.6409
133.6529
126.9132
124.3152
61.5225
37.1420
27.8311
22.2784
14.2290
O
S
O
O
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

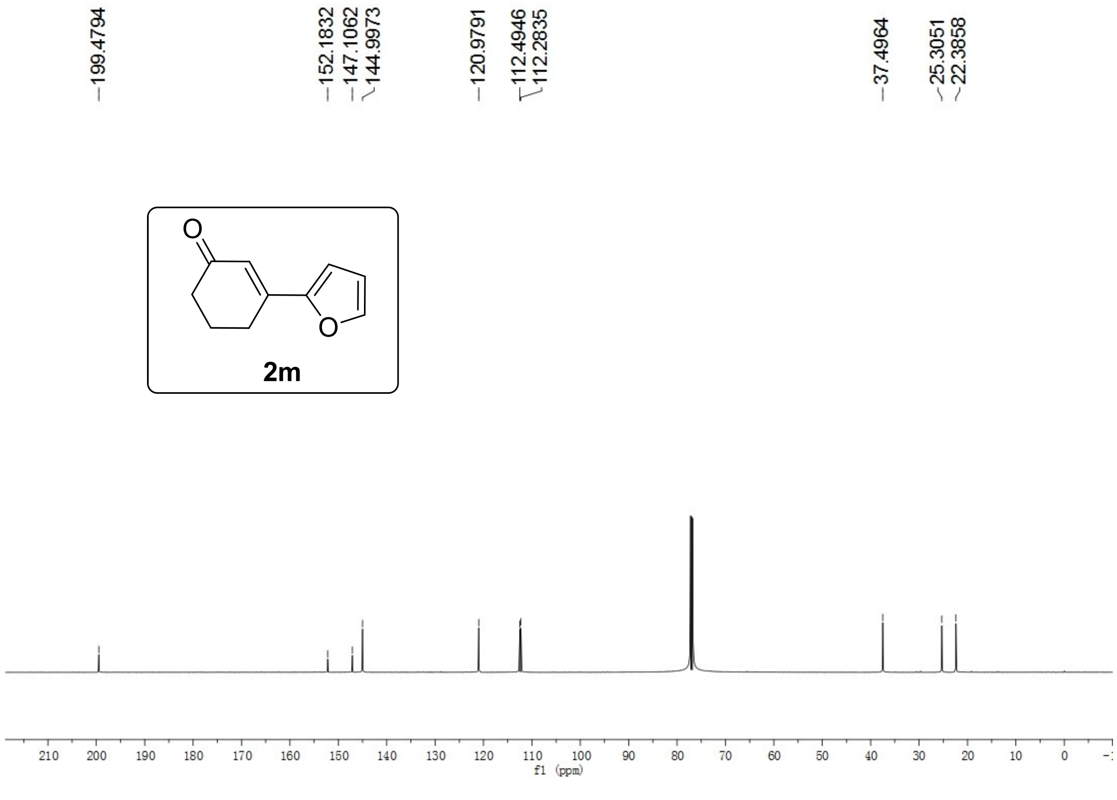

6.7151
6.5137
4.3110
4.3044
4.3007
4.2972
4.2247
4.2213
4.2176
4.2150
4.2109
2.7064
2.7047
2.6952
2.6864
2.6844
2.4229
2.1062
2.1026
2.0956
2.0848
2.0740
2.0681
2.0637
S
O
O
O
2k
1.00
1.01
2.38
2.36
2.37
2.35
2.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

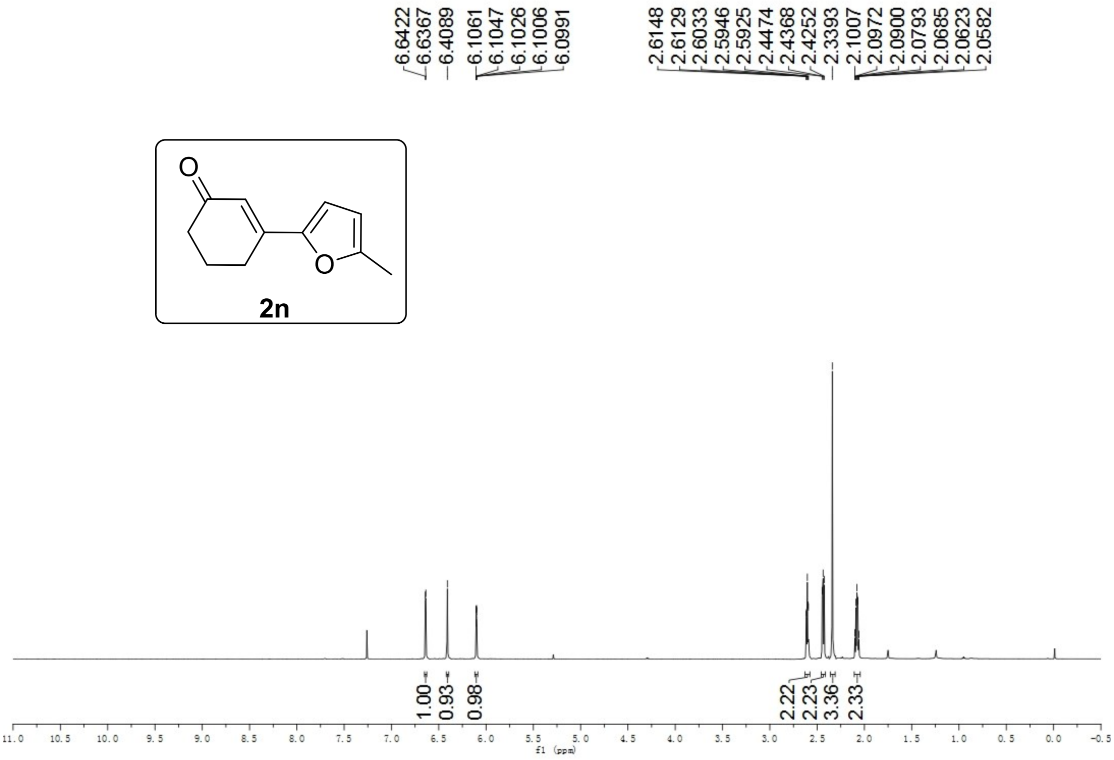

199.7484
151.5632
142.4146
142.2509
122.6523
116.6252
102.9269
64.9006
64.1712
37.1889
28.1550
22.4989
S
O
O
O
2k
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.8147
7.8021
7.7874
7.7749
7.6008
7.3995
7.3875
7.3766
7.3744
7.3633
7.3520
6.4839
2.8843
2.8745
2.8647
2.5009
2.2375
2.2270
2.2161
2.2057
2.1987
2.1879
2.1773
2.1670
O
S
and
O
S
67:33
2la
2lb
2.00
1.25
2.16
0.32
0.83
1.83
1.98
2.22
.0
10.5
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
f1 (ppm)

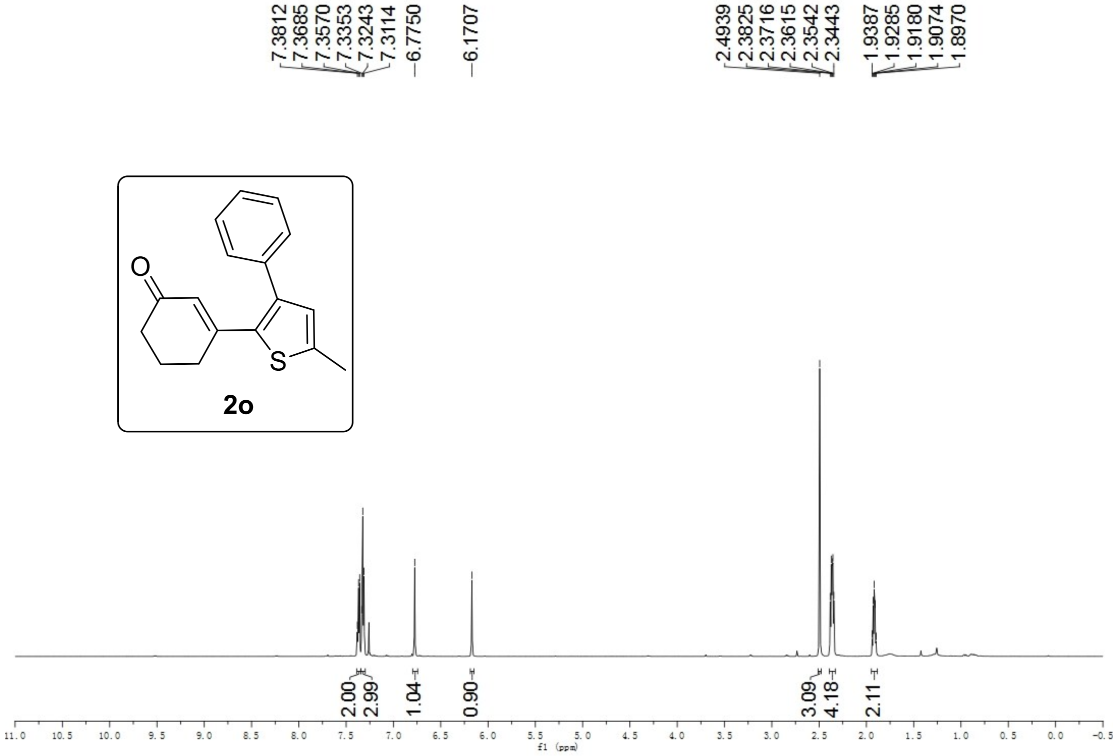

199.3381
152.4746
142.4531
140.1318
139.6817
126.2068
124.8800
124.8341
124.7282
124.4334
122.3687
37.3316
27.5334
22.4278
O
S
and
O
S
67:33
2la
2lb
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

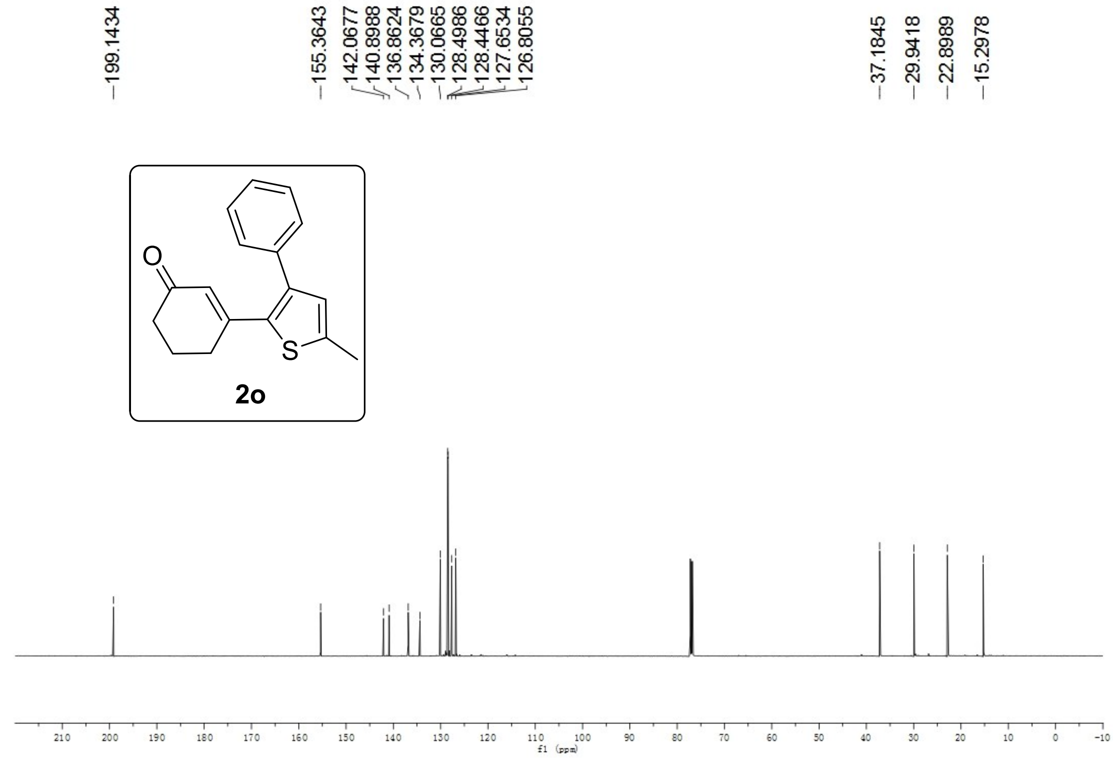

7.5310
6.7403
6.4999
6.4763
2.6645
2.6548
2.6450
2.4719
2.4616
2.4513
2.1302
2.1204
2.1102
2.1001
2.0907
O
O
2m
1.00
1.12
1.99
2.43
2.44
2.50
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

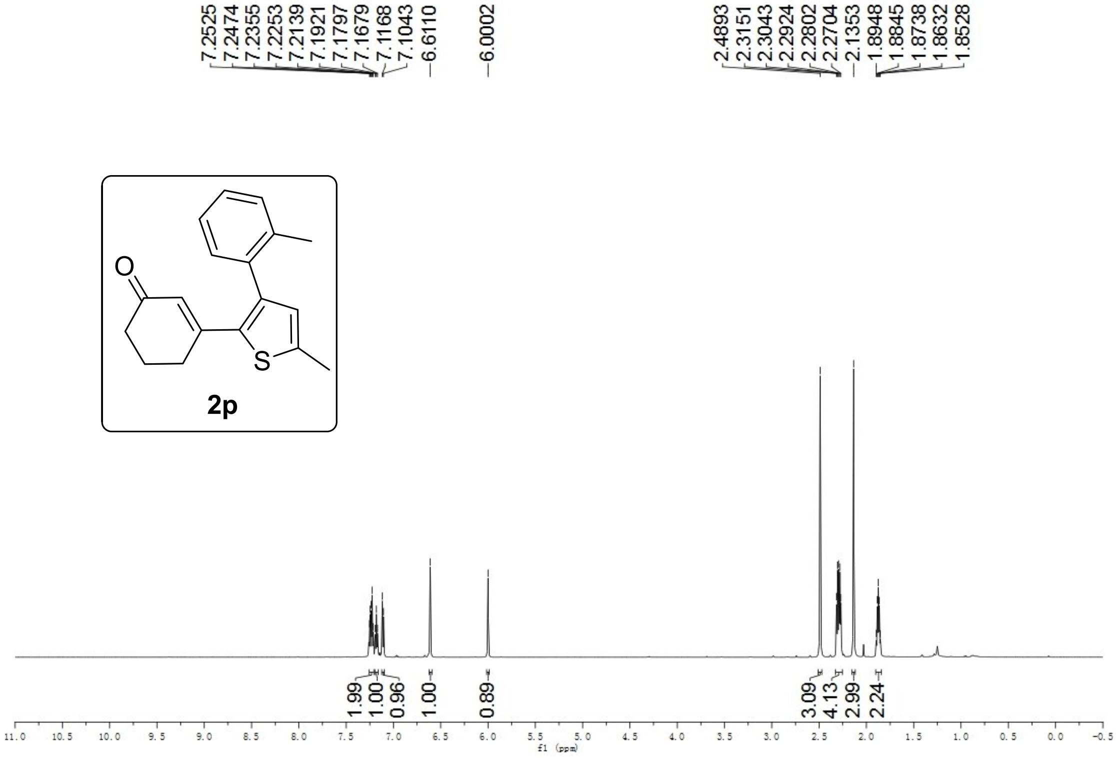

199.4794
152.1832
147.1062
144.9973
120.9791
112.4946
112.2835
37.4964
25.3051
22.3858
O
O
2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

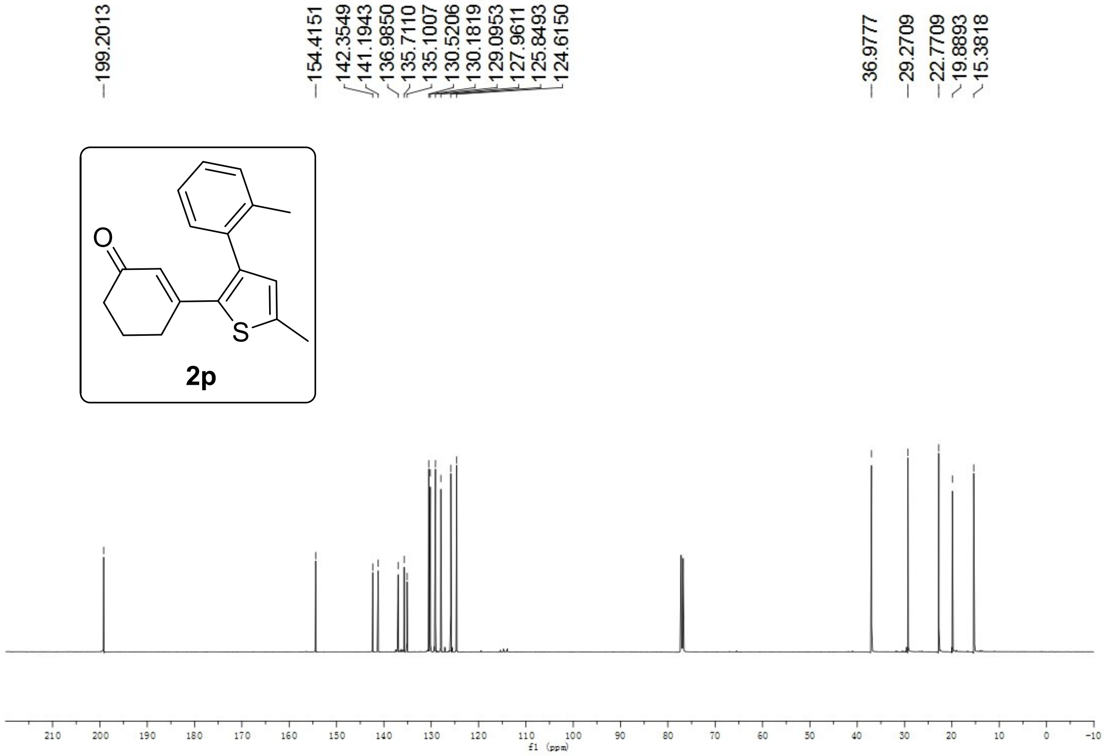

6.6422
6.6367
6.4089
6.1061
6.1047
6.1026
6.1006
6.0991
2.6148
2.6129
2.6033
2.5946
2.5925
2.4474
2.4368
2.4252
2.3393
2.1007
2.0972
2.0900
2.0793
2.0685
2.0623
2.0582
O
O
2n
1.00
0.93
0.98
2.22
2.23
3.36
2.33
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

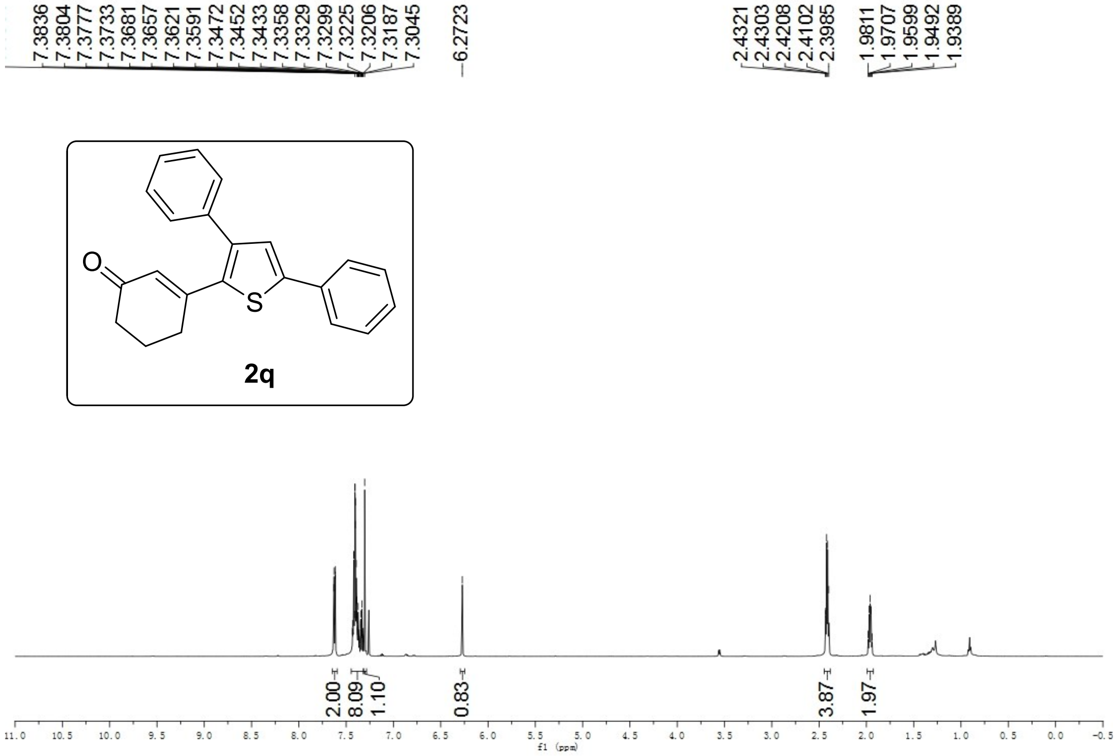

199.4481
155.7767
150.5288
147.1720
119.6001
114.1329
108.8476
37.4827
25.1283
22.4221
13.8663
O
O
2n
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

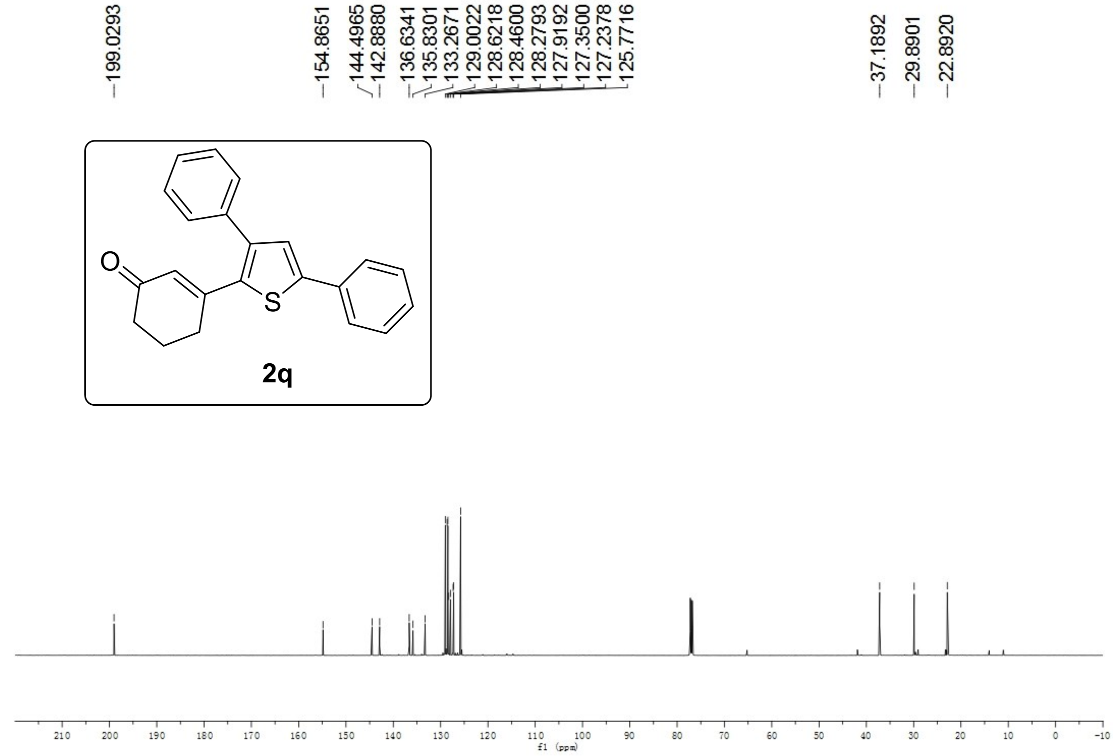

7.3812
7.3685
7.3570
7.3353
7.3243
7.3114
6.7750
6.1707
2.4939
2.3825
2.3716
2.3615
2.3542
2.3443
1.9387
1.9285
1.9180
1.9074
1.8970
O
S
2o
2.00
2.99
1.04
0.90
3.09
4.18
2.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

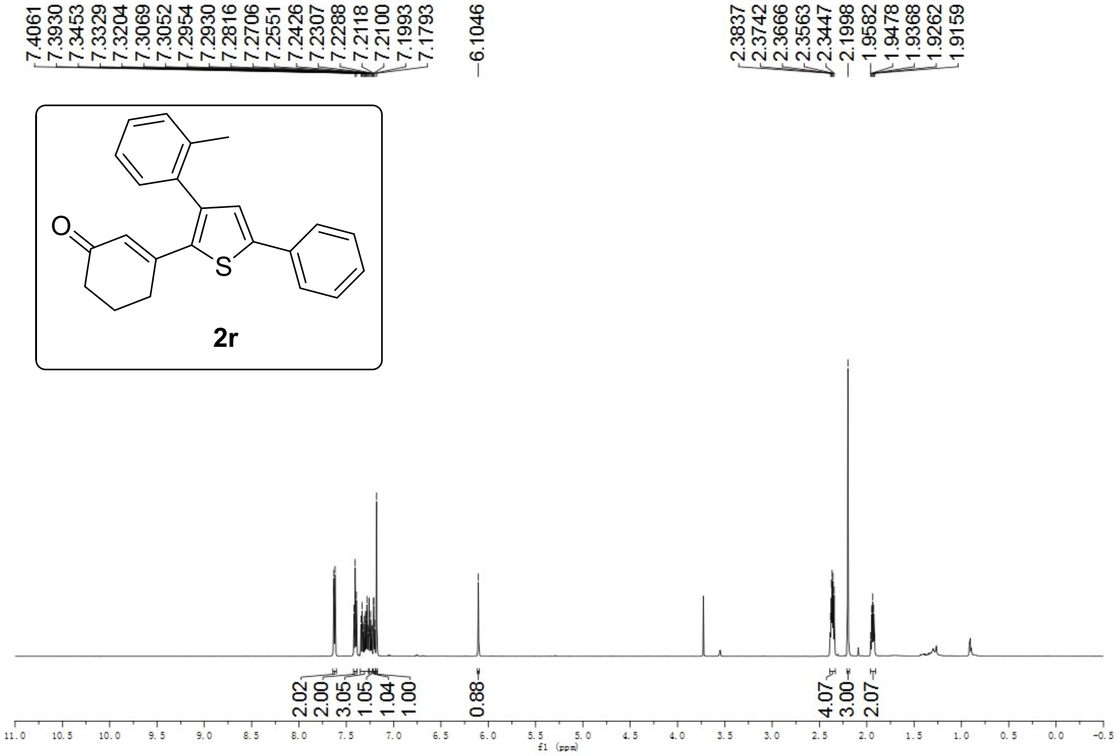

199.1434
155.3643
142.0677
140.8988
136.8624
134.3679
130.0665
128.4986
128.4466
127.6534
126.8055
37.1845
29.9418
22.8989
15.2978
O
S
2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

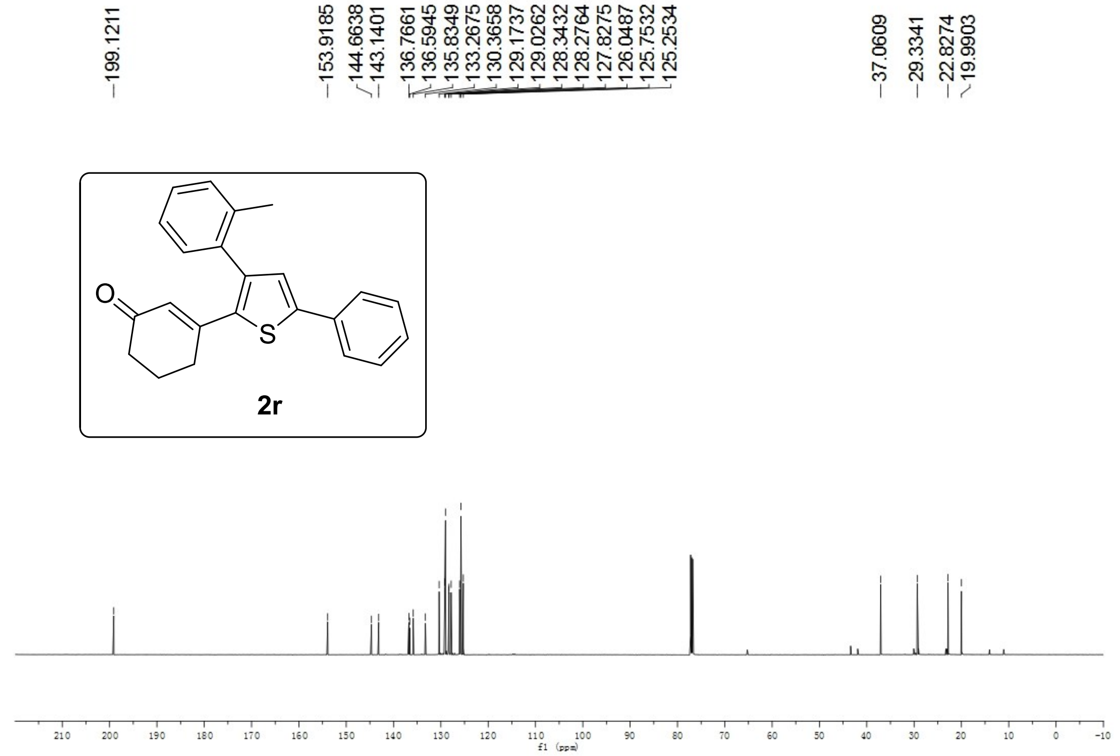

7.2525
7.2474
7.2355
7.2253
7.2139
7.1921
7.1797
7.1679
7.1168
7.1043
6.6110
6.0002
2.4893
2.3151
2.3043
2.2924
2.2802
2.2704
2.1353
1.8948
1.8845
1.8738
1.8632
1.8528
O
S
2p
1.99
1.00
0.96
1.00
0.89
3.09
4.13
2.99
2.24
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

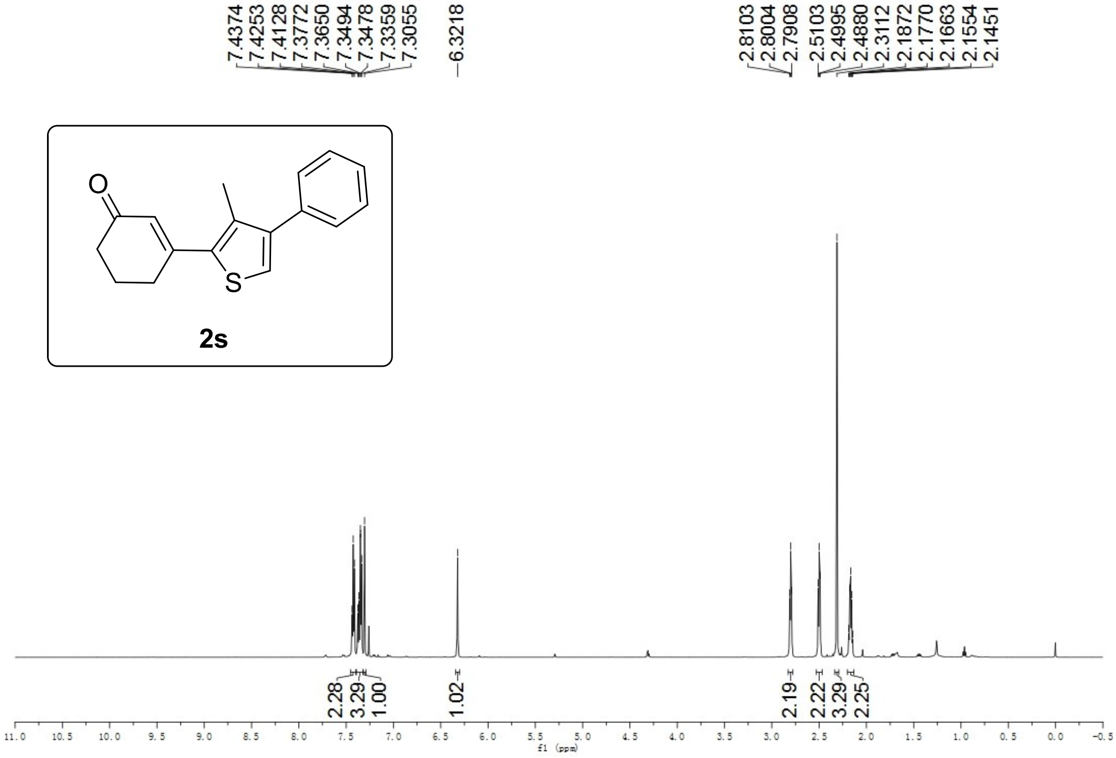

199.2013
154.4151
142.3549
141.1943
136.9850
135.7110
135.1007
130.5206
130.1819
129.0953
127.9611
125.8493
124.6150
36.9777
29.2709
22.7709
19.8893
15.3818
O
S
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

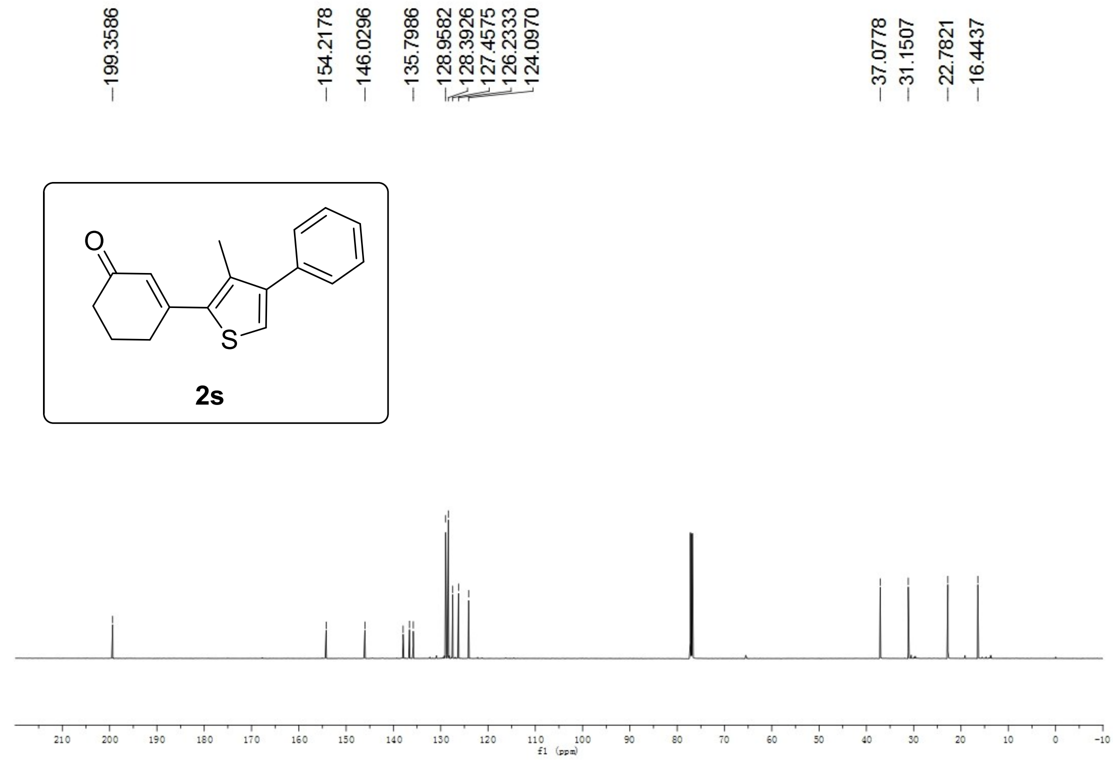

7.3836
7.3804
7.3777
7.3733
7.3681
7.3657
7.3621
7.3591
7.3472
7.3452
7.3433
7.3358
7.3329
7.3299
7.3225
7.3206
7.3187
7.3045
6.2723
2.4321
2.4303
2.4208
2.4102
2.3985
1.9811
1.9707
1.9599
1.9492
1.9389
O
S
2q
2.00
8.09
1.10
0.83
3.87
1.97
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

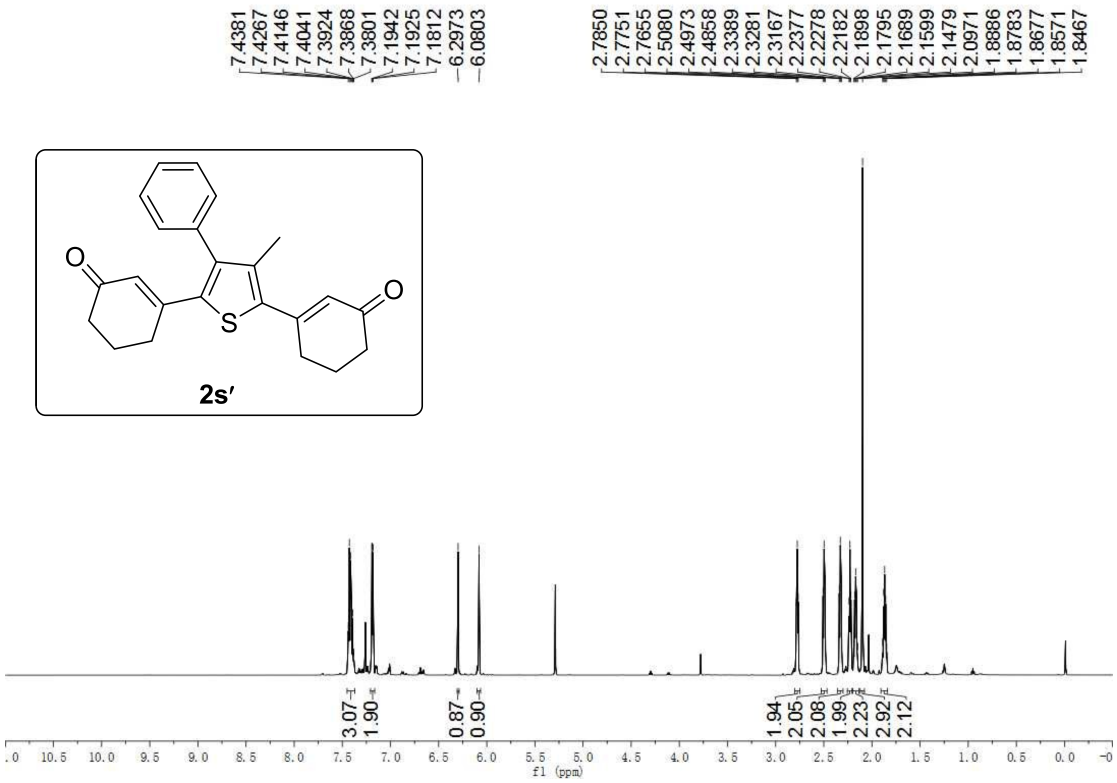

199.0293
154.8651
144.4965
142.8880
136.6341
135.8301
133.2671
129.0022
128.6218
128.4600
128.2793
127.9192
127.3500
127.2378
125.7716
37.1892
29.8901
22.8920
O
S
2q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

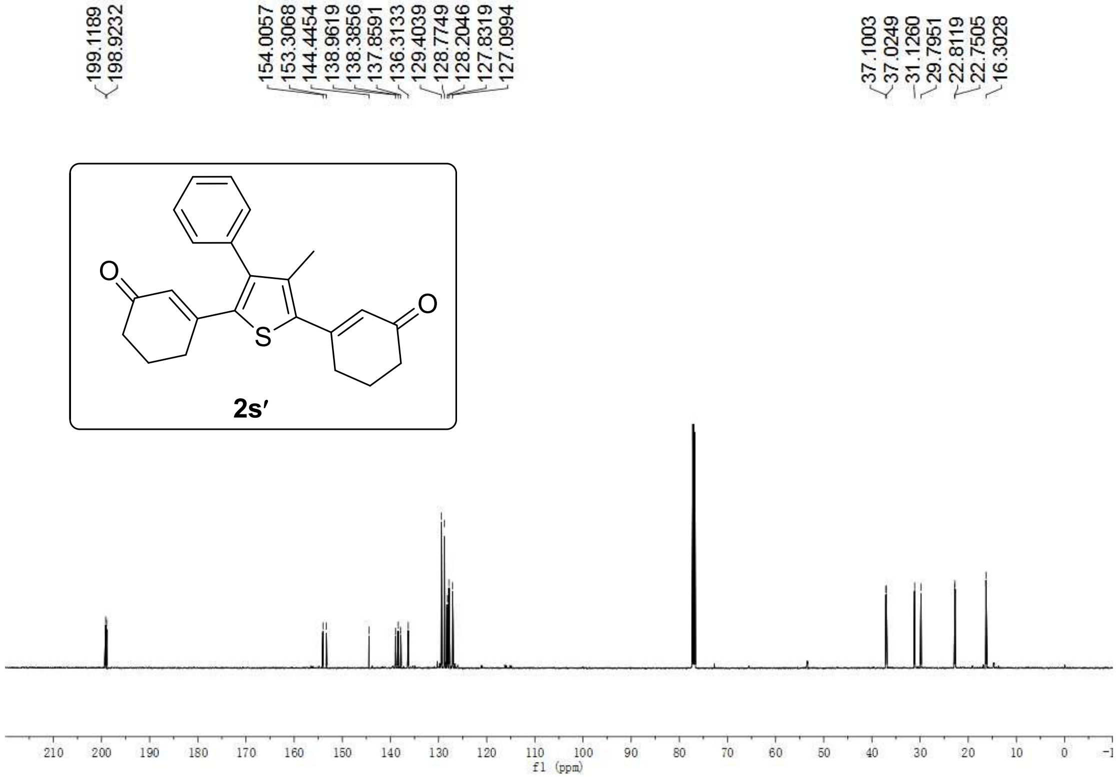

7.4061
7.3930
7.3453
7.3329
7.3204
7.3069
7.3052
7.2954
7.2930
7.2816
7.2706
7.2551
7.2426
7.2307
7.2288
7.2118
7.2100
7.1993
7.1793
6.1046
2.3837
2.3742
2.3666
2.3563
2.3447
2.1998
1.9582
1.9478
1.9368
1.9262
1.9159
O
S
2r
2.02
2.00
3.05
1.05
1.04
1.00
0.88
4.07
3.00
2.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

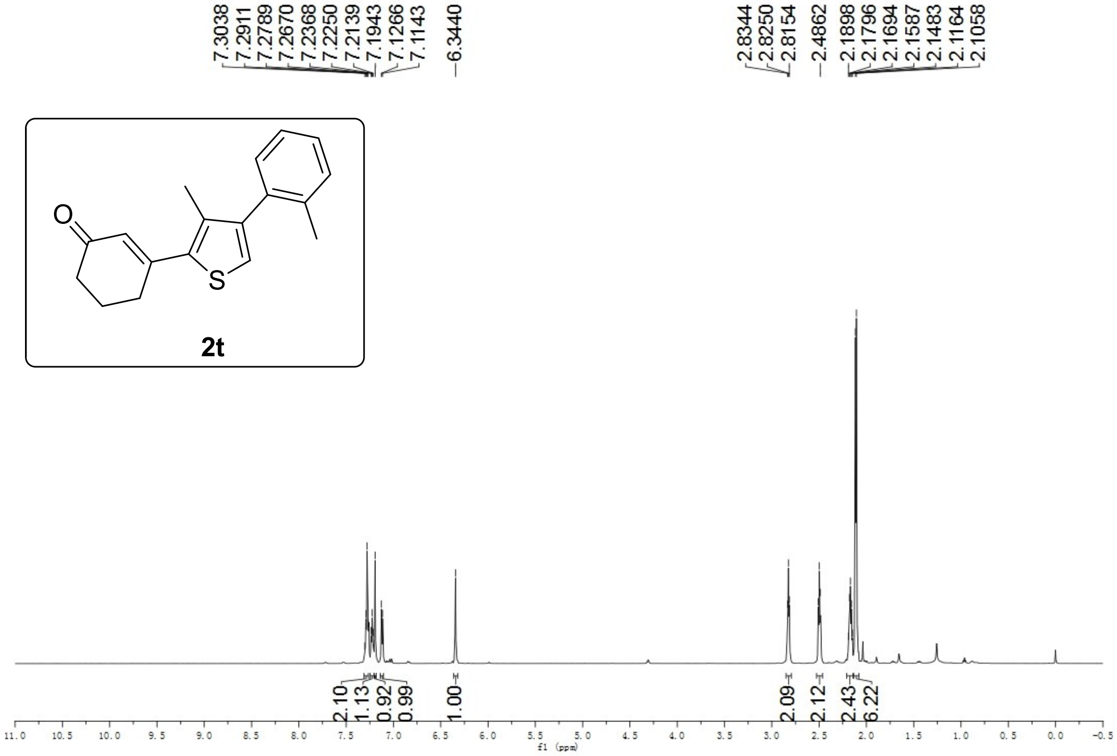

199.1211
153.9185
144.6638
143.1401
136.7661
136.5945
135.8349
133.2675
130.3658
129.1737
129.0262
128.3432
128.2764
127.8275
126.0487
125.7532
125.2534
37.0609
29.3341
22.8274
19.9903
O
S
2r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

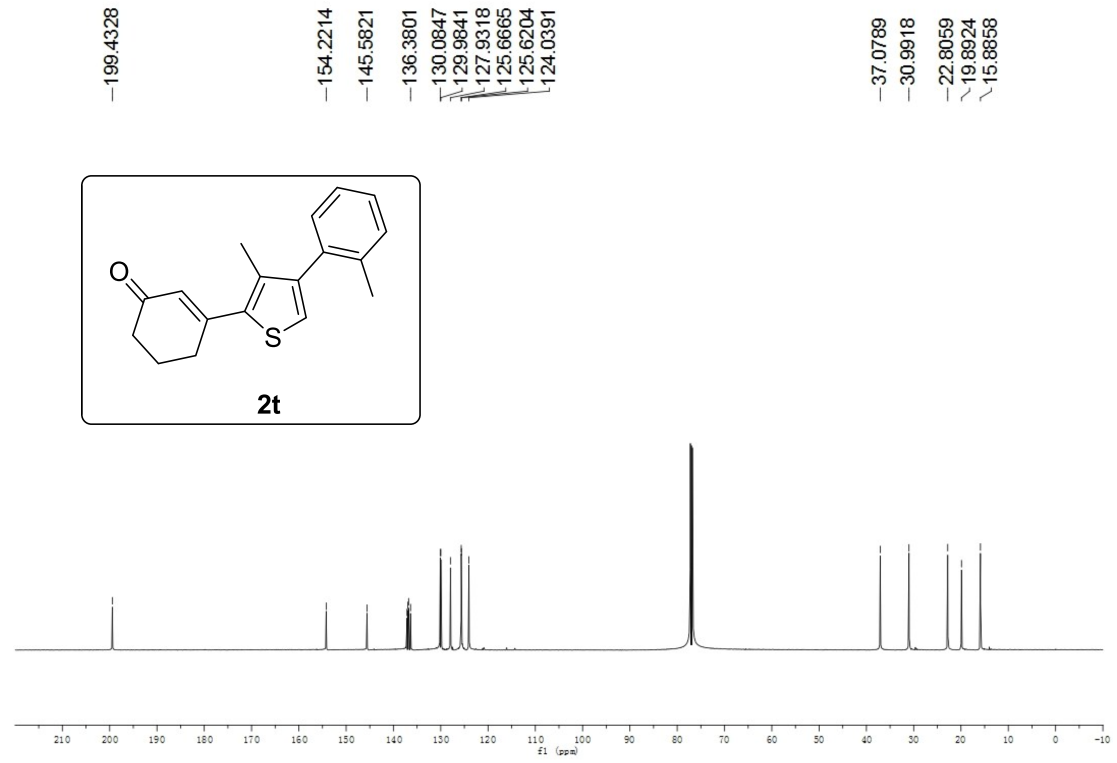

7.4374
7.4253
7.4128
7.3772
7.3650
7.3494
7.3478
7.3359
7.3055
6.3218
2.8103
2.8004
2.7908
2.5103
2.4995
2.4880
2.3112
2.1872
2.1770
2.1663
2.1554
2.1451
O
S
2s
2.28
3.29
1.00
1.02
2.19
2.22
3.29
2.25
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

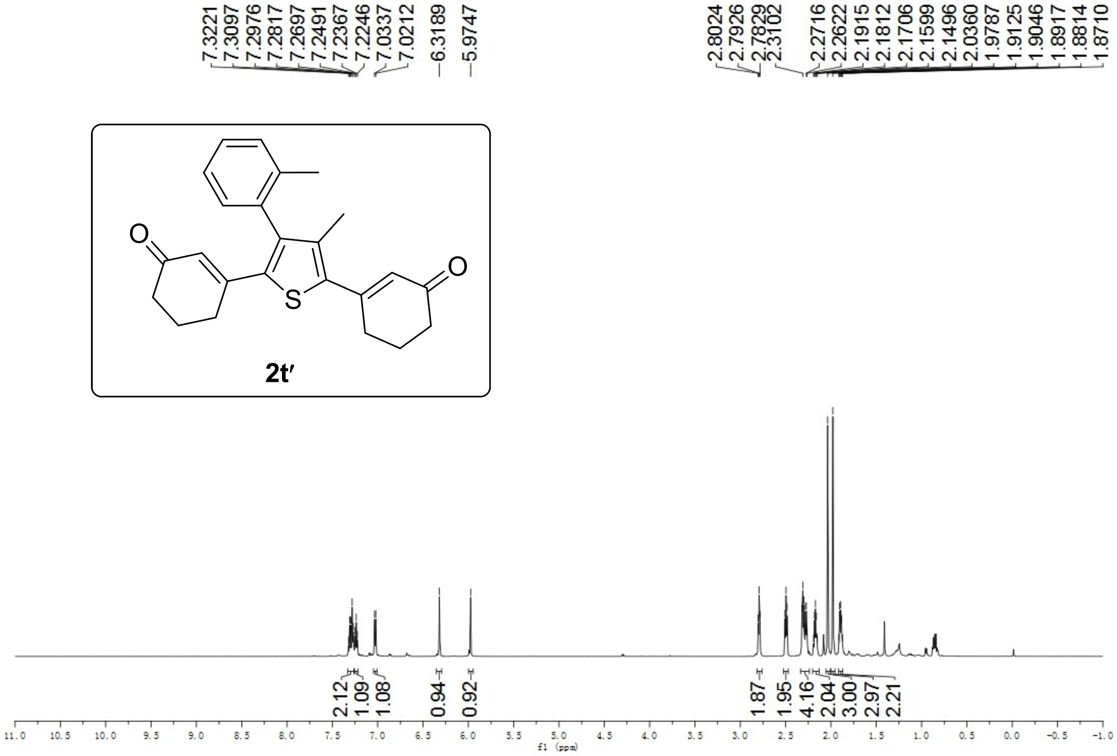

199.3586
154.2178
146.0296
135.7986
128.9582
128.3926
127.4575
126.2333
124.0970
37.0778
31.1507
22.7821
16.4437
O
S
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

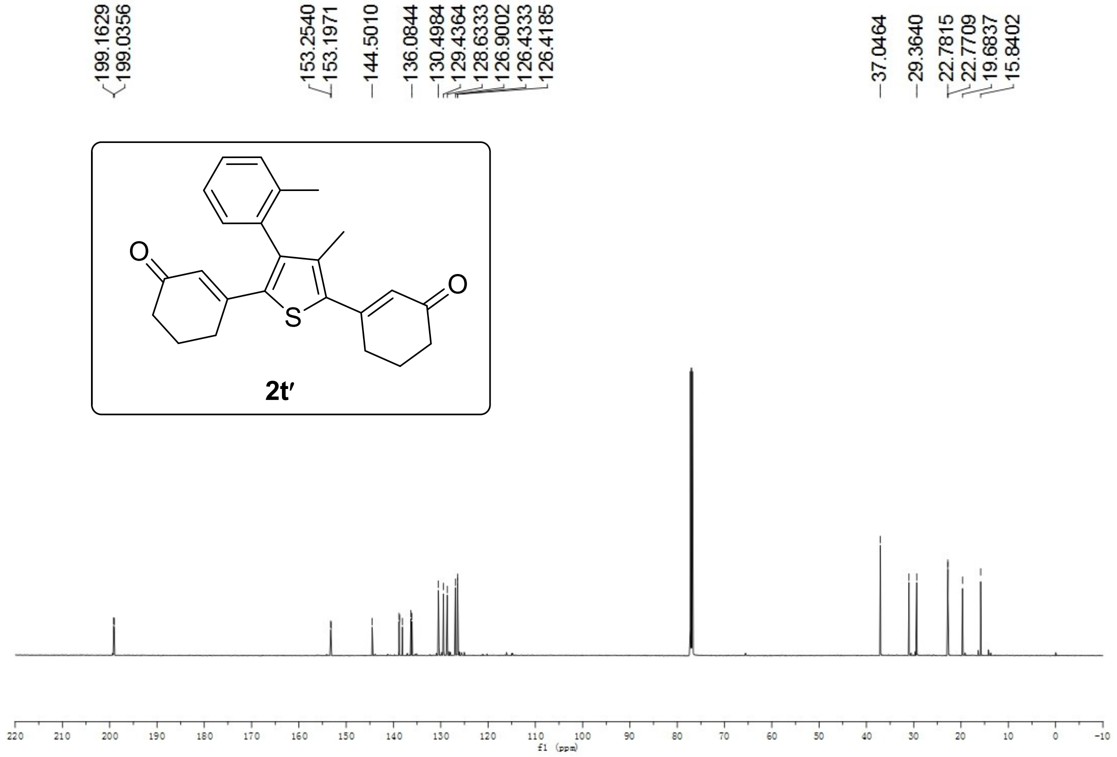

7.4381
7.4267
7.4146
7.4041
7.3924
7.3868
7.3801
7.1942
7.1925
7.1812
6.2973
6.0803
2.7850
2.7751
2.7655
2.5080
2.4973
2.4858
2.3389
2.3281
2.3167
2.2377
2.2278
2.2182
2.1898
2.1795
2.1689
2.1599
2.1479
2.0971
1.8886
1.8783
1.8677
1.8571
1.8467
O
O
S
2s′
3.07
1.90
0.87
0.90
1.94
2.05
2.08
1.99
2.23
2.92
2.12
.0
10.5
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
f1 (ppm)

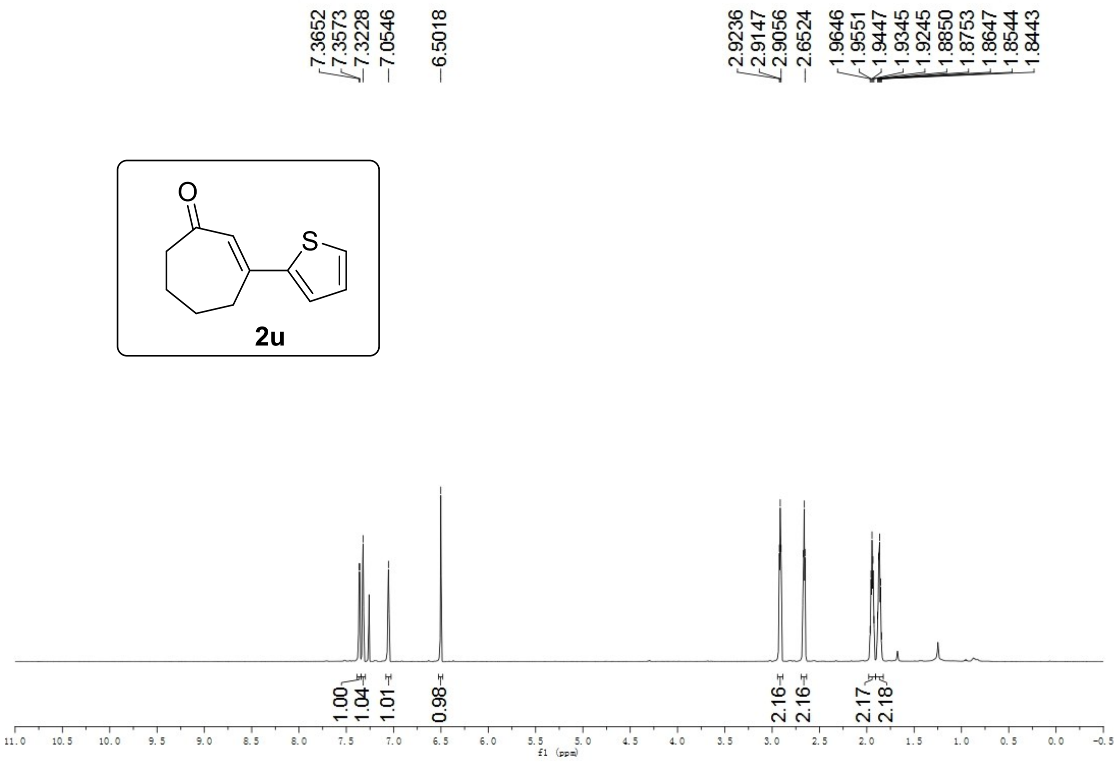

199.1189
198.9232
154.0057
153.3068
144.4454
138.9619
138.3856
137.8591
136.3133
129.4039
128.7749
128.2046
127.8319
127.0994
37.1003
37.0249
31.1260
29.7951
22.8119
22.7505
16.3028
O
O
S
2s′
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

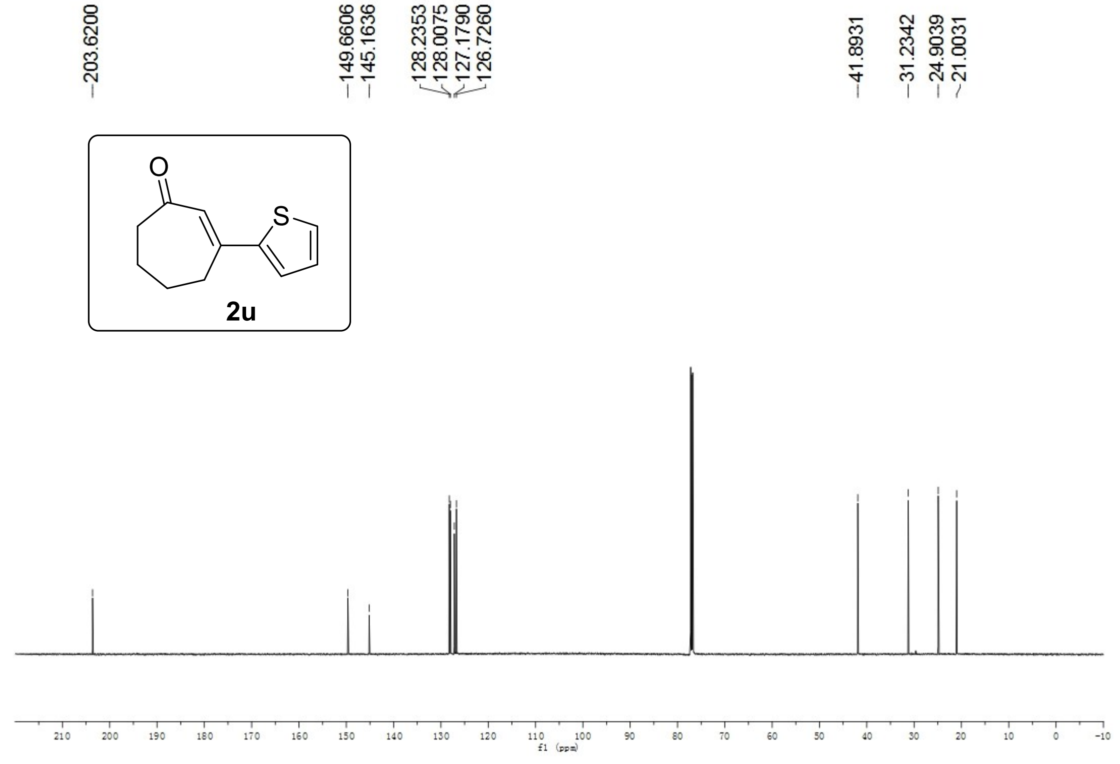

7.3038
7.2911
7.2789
7.2670
7.2368
7.2250
7.2139
7.1943
7.1266
7.1143
6.3440
2.8344
2.8250
2.8154
2.4862
2.1898
2.1796
2.1694
2.1587
2.1483
2.1164
2.1058
O
S
2t
2.10
1.13
0.92
0.99
1.00
2.09
2.12
2.43
6.22
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

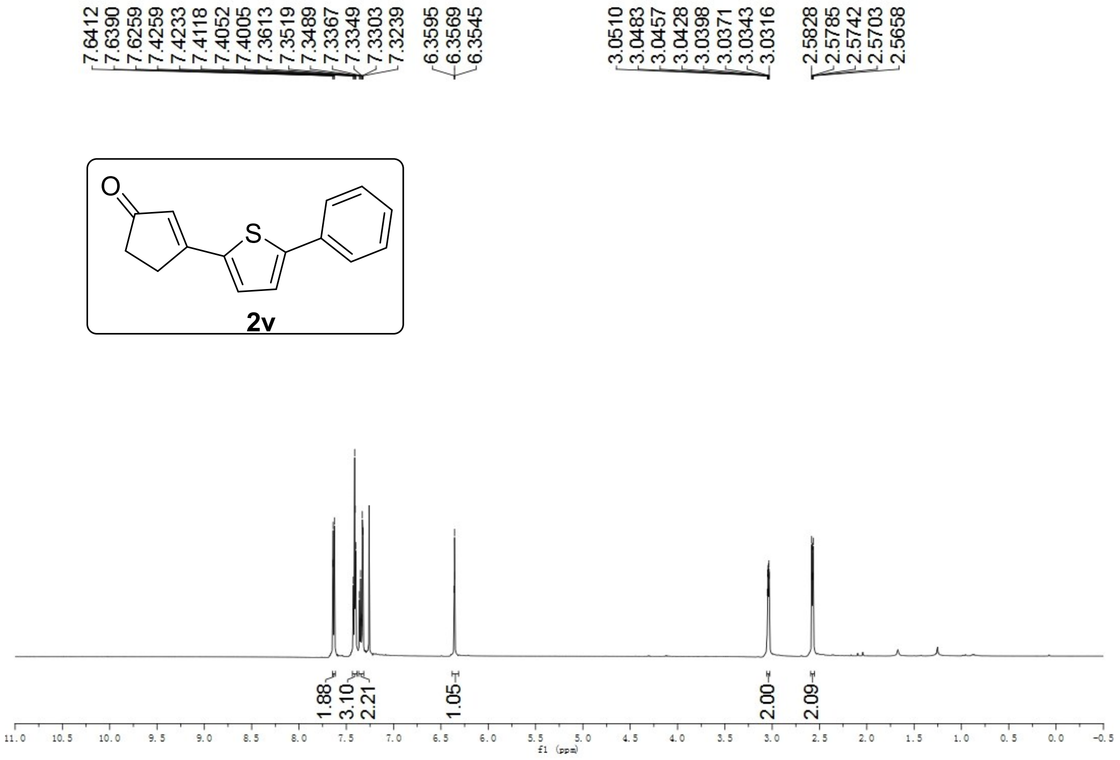

199.4328
154.2214
145.5821
136.3801
130.0847
129.9841
127.9318
125.6665
125.6204
124.0391
37.0789
30.9918
22.8059
19.8924
15.8858
O
S
2t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

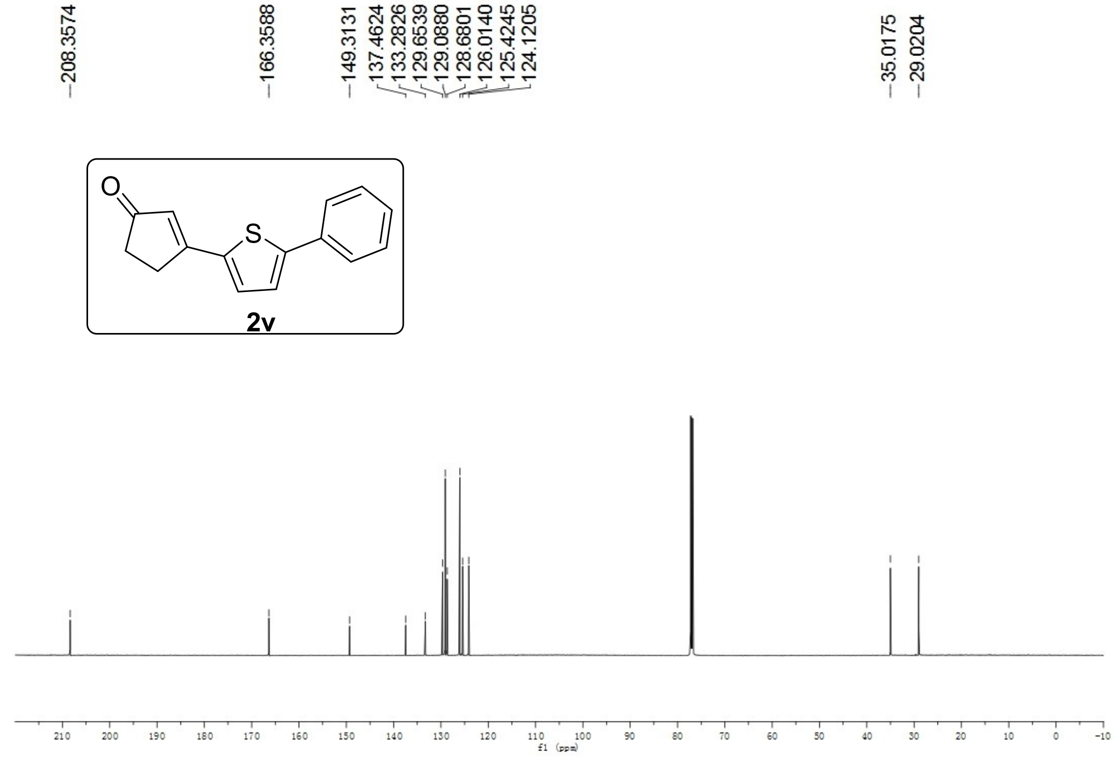

7.3221
7.3097
7.2976
7.2817
7.2697
7.2491
7.2367
7.2246
7.0337
7.0212
6.3189
5.9747
2.8024
2.7926
2.7829
2.3102
2.2716
2.2622
2.1915
2.1812
2.1706
2.1599
2.1496
2.0360
1.9787
1.9125
1.9046
1.8917
1.8814
1.8710
O
S
O
2t′
2.12
1.09
1.08
0.94
0.92
1.87
1.95
4.16
2.04
3.00
2.97
2.21
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

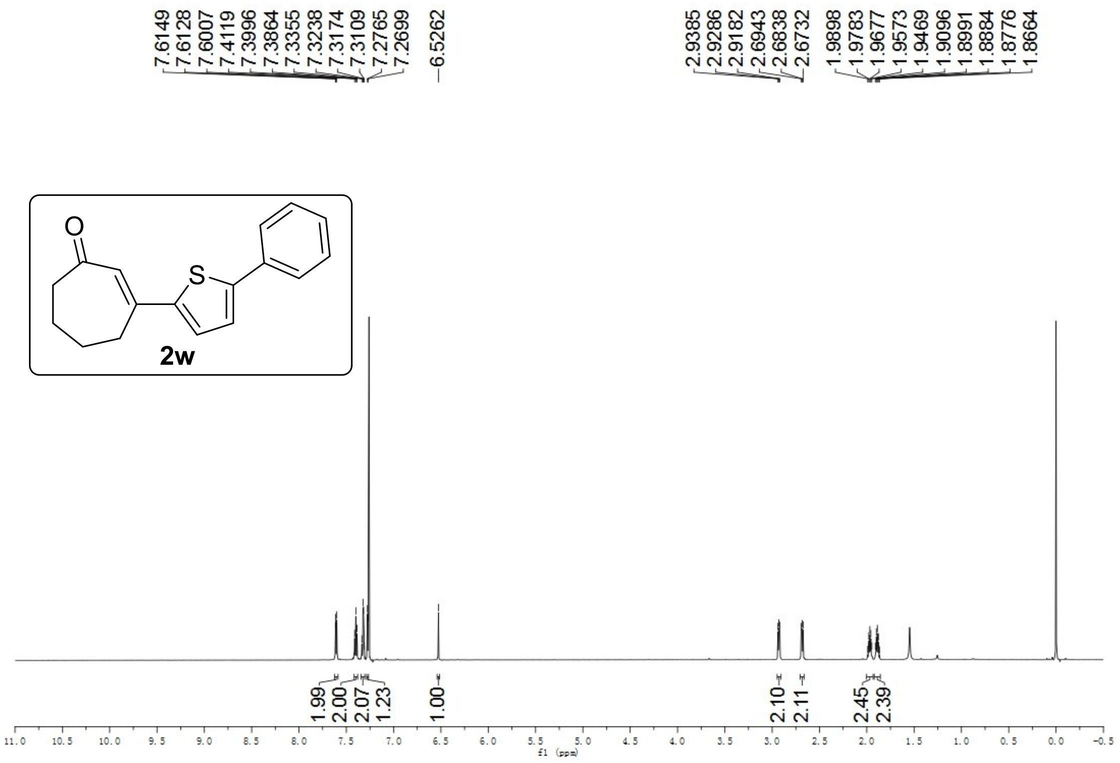

199.1629
199.0356
153.2540
153.1971
144.5010
136.0844
130.4984
129.4364
128.6333
126.9002
126.4333
126.4185
37.0464
29.3640
22.7815
22.7709
19.6837
15.8402
O
S
O
2t′
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

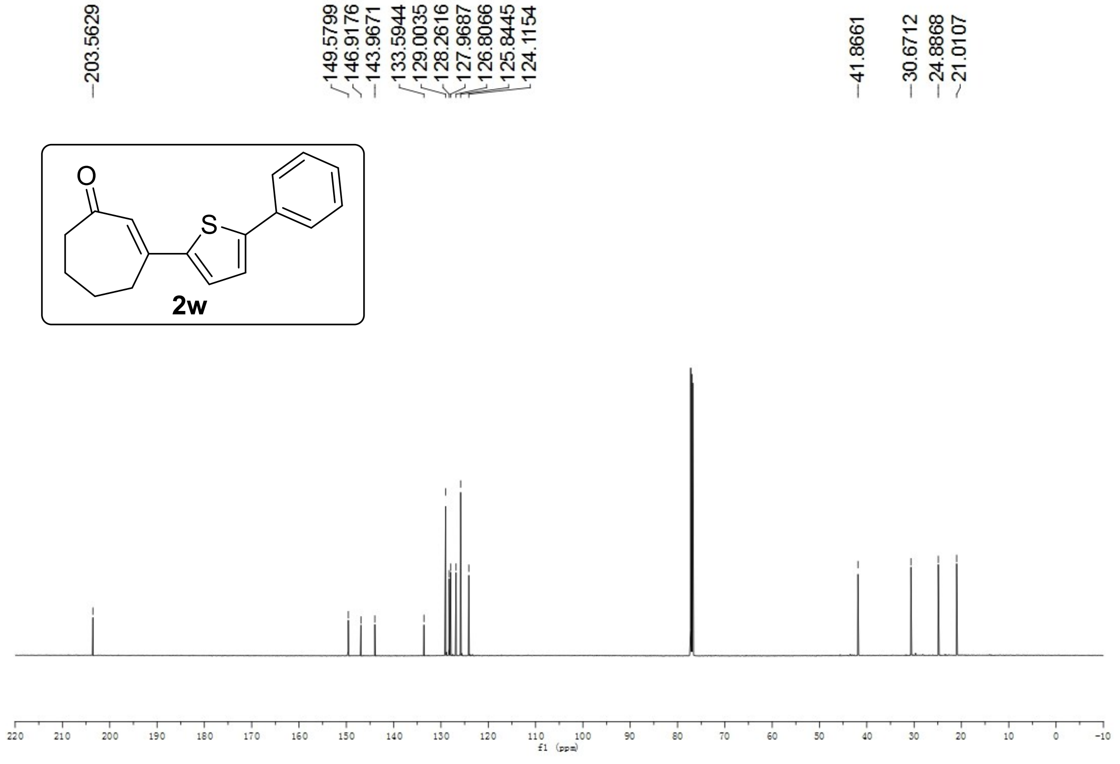

7.3652
7.3573
7.3228
7.0546
6.5018
2.9236
2.9147
2.9056
2.6524
1.9646
1.9551
1.9447
1.9345
1.9245
1.8850
1.8753
1.8647
1.8544
1.8443
O
S
2u
1.00
1.04
1.01
0.98
2.16
2.16
2.17
2.18
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

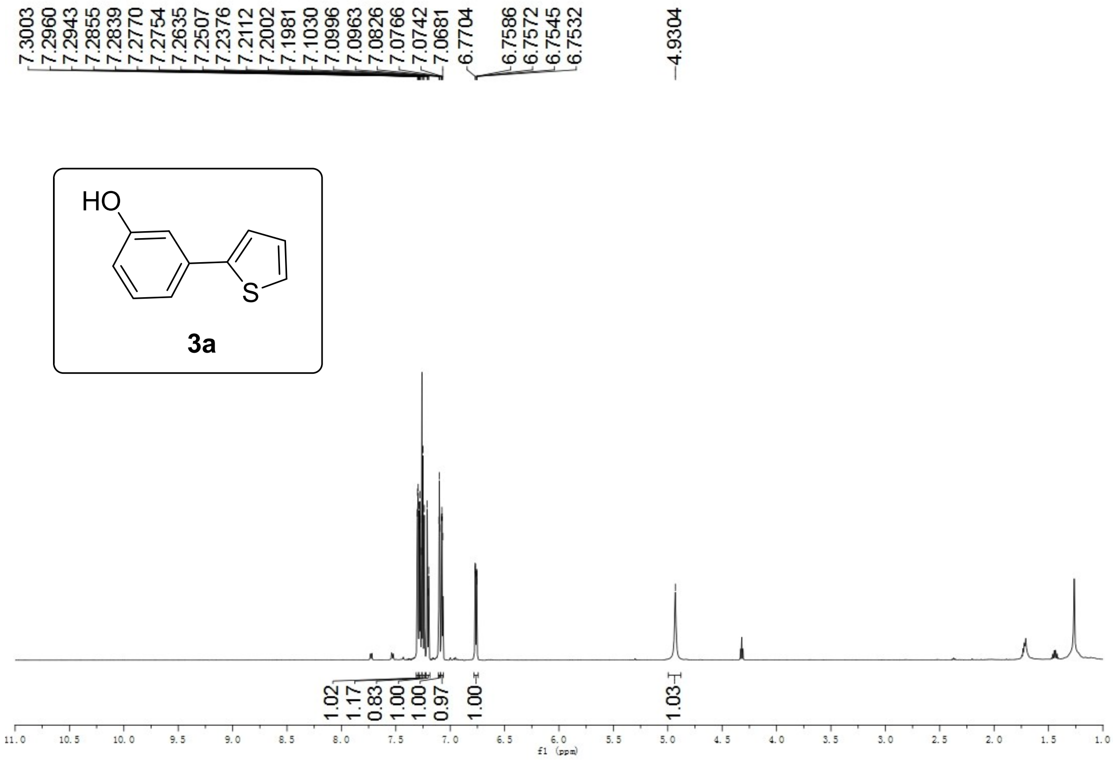

203.6200
149.6606
145.1636
128.2353
128.0075
127.1790
126.7260
41.8931
31.2342
24.9039
21.0031
O
S
2u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

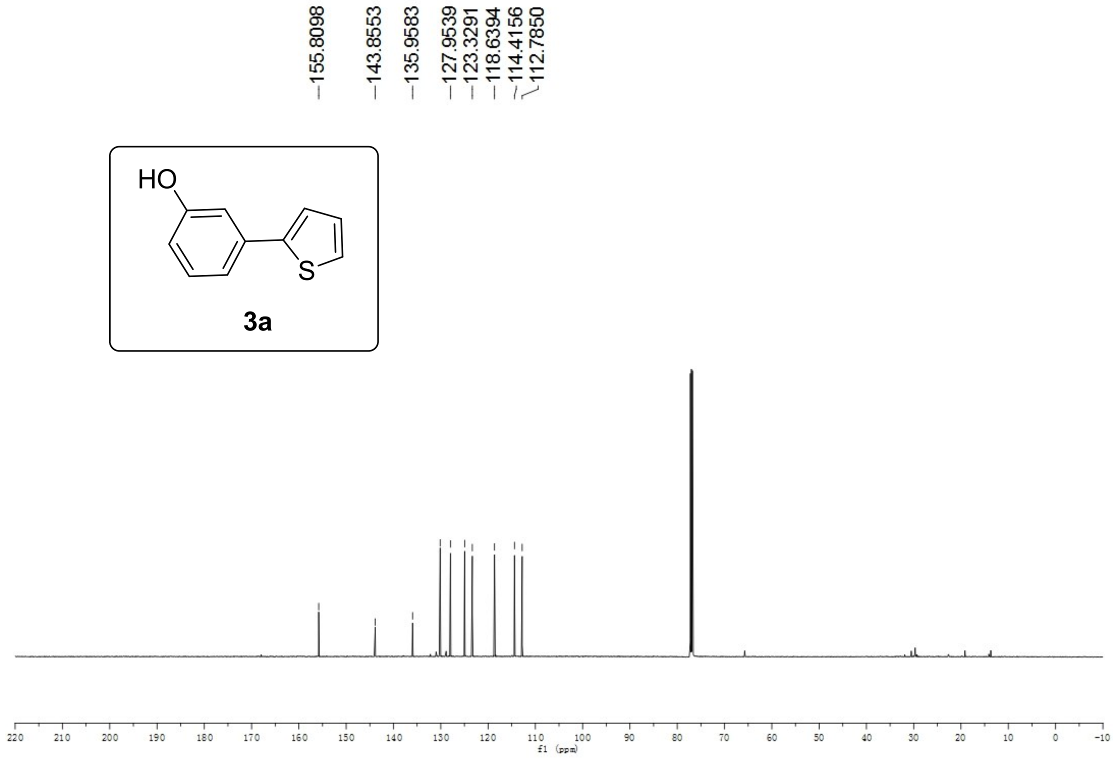

7.6412
7.6390
7.6259
7.4259
7.4233
7.4118
7.4052
7.4005
7.3613
7.3519
7.3489
7.3367
7.3349
7.3303
7.3239
6.3595
6.3569
6.3545
3.0510
3.0483
3.0457
3.0428
3.0398
3.0371
3.0343
3.0316
2.5828
2.5785
2.5742
2.5703
2.5658
O
S
2v
1.88
3.10
2.21
1.05
2.00
2.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

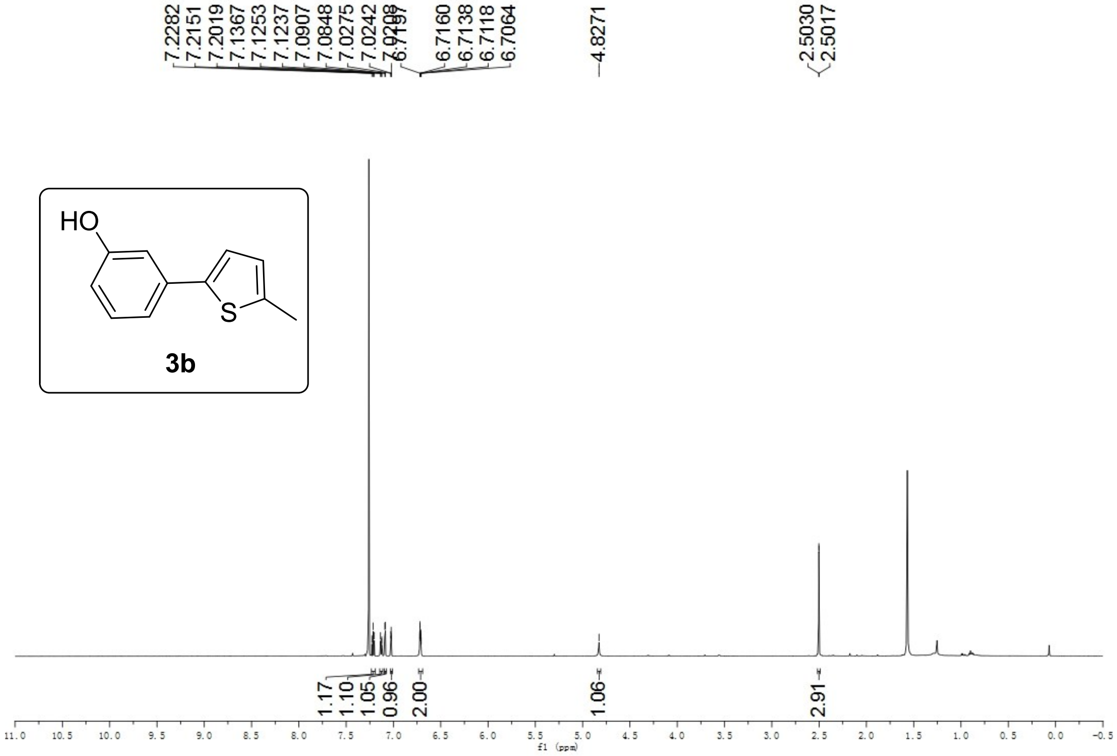

208.3574
166.3588
149.3131
137.4624
133.2826
129.6539
129.0880
128.6801
126.0140
125.4245
124.1205
35.0175
29.0204
O
S
2v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

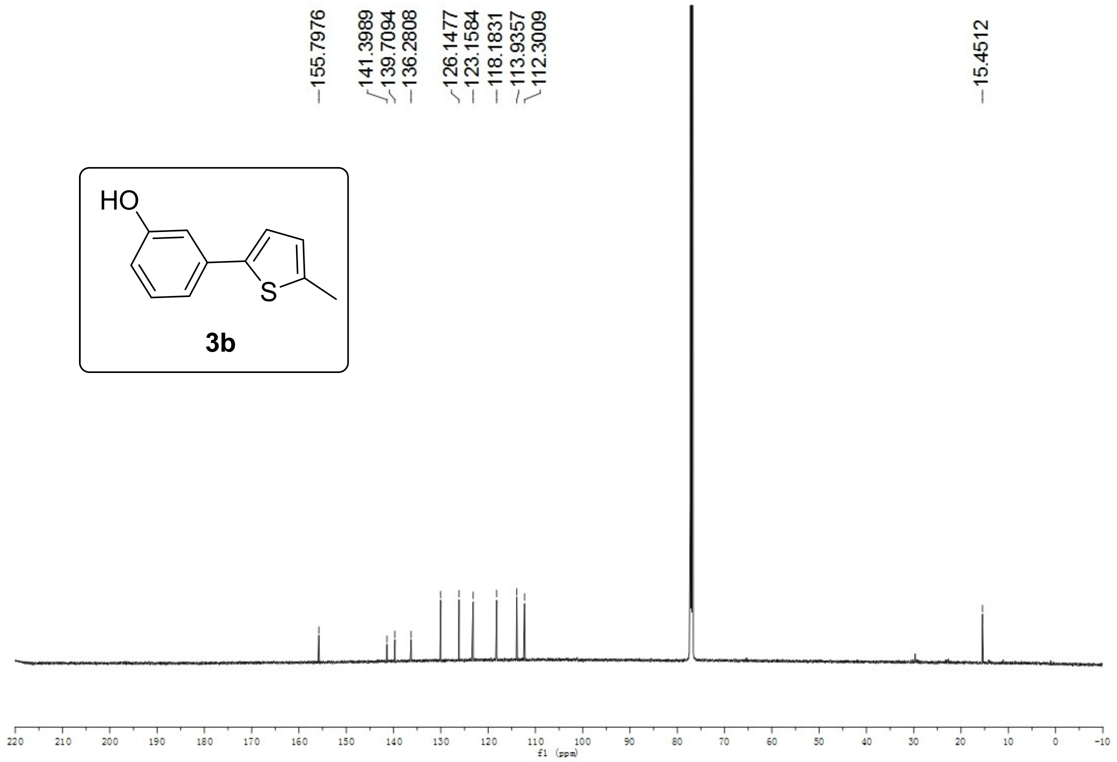

7.6149
7.6128
7.6007
7.4119
7.3996
7.3864
7.3355
7.3238
7.3174
7.3109
7.2765
7.2699
6.5262
2.9385
2.9286
2.9182
2.6943
2.6838
2.6732
1.9898
1.9783
1.9677
1.9573
1.9469
1.9096
1.8991
1.8884
1.8776
1.8664
O
S
2w
1.99
2.00
2.07
1.23
1.00
2.10
2.11
2.45
2.39
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

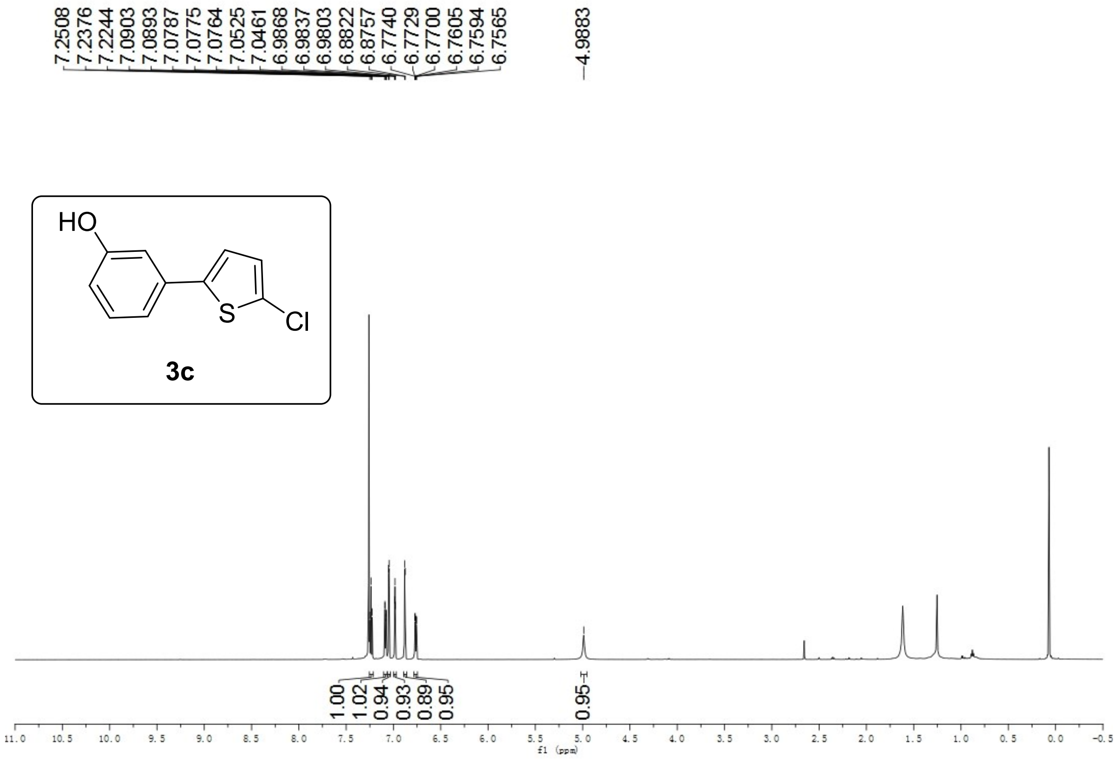

203.5629
149.5799
146.9176
143.9671
133.5944
129.0035
128.2616
127.9687
126.8066
125.8445
124.1154
41.8661
30.6712
24.8868
21.0107
O
S
2w
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

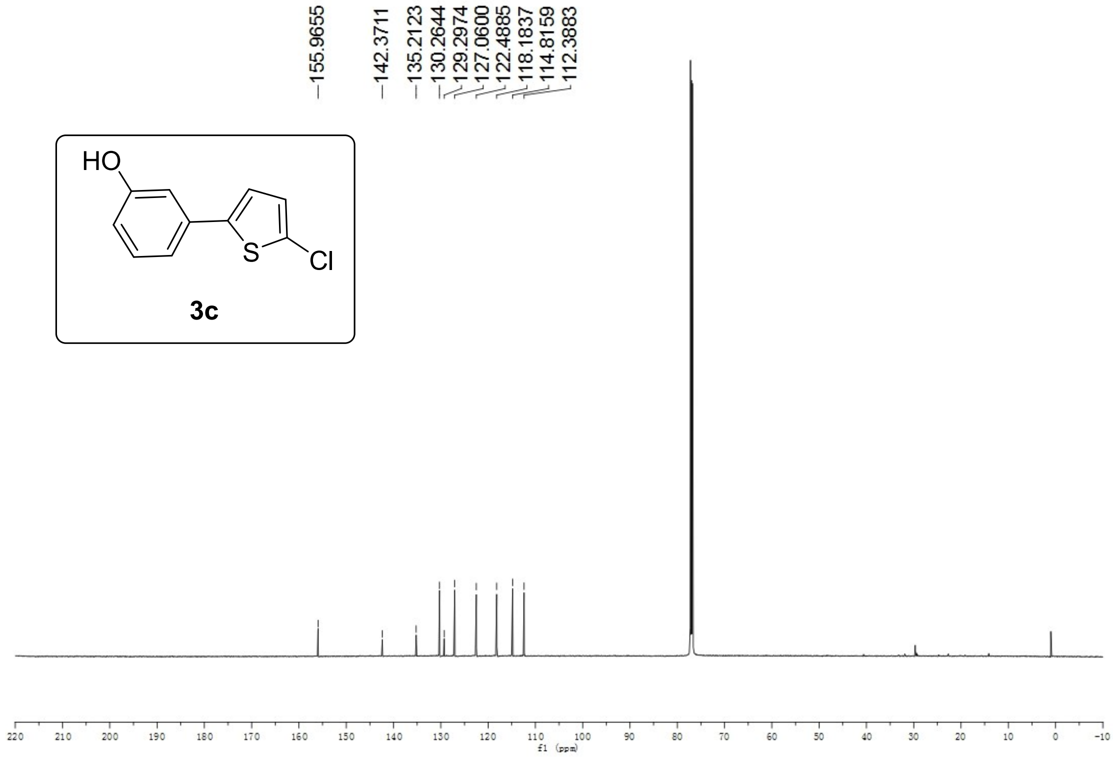

7.3003
7.2960
7.2943
7.2855
7.2839
7.2770
7.2754
7.2635
7.2507
7.2376
7.2112
7.2002
7.1981
7.1030
7.0996
7.0963
7.0826
7.0766
7.0742
7.0681
6.7704
6.7586
6.7572
6.7545
6.7532
4.9304
HO
S
3a
1.02
1.17
0.83
1.00
1.00
0.97
1.00
1.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

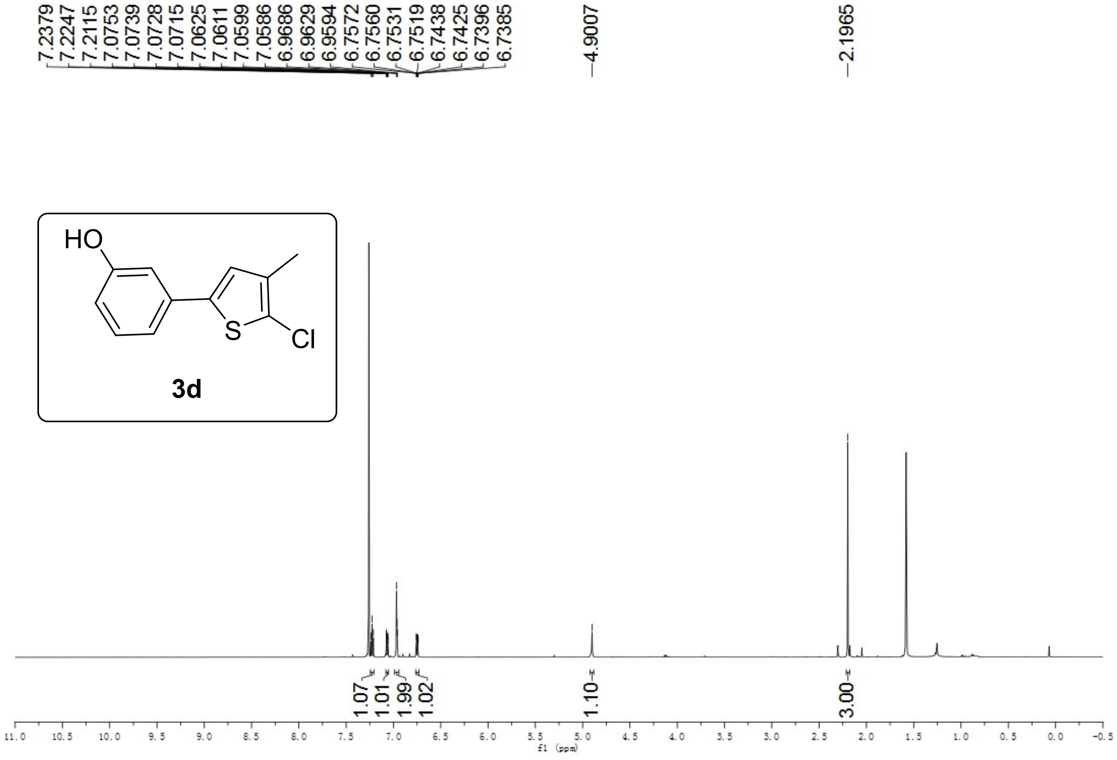

155.8098
143.8553
135.9583
127.9539
123.3291
118.6394
114.4156
112.7850
HO
S
3a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

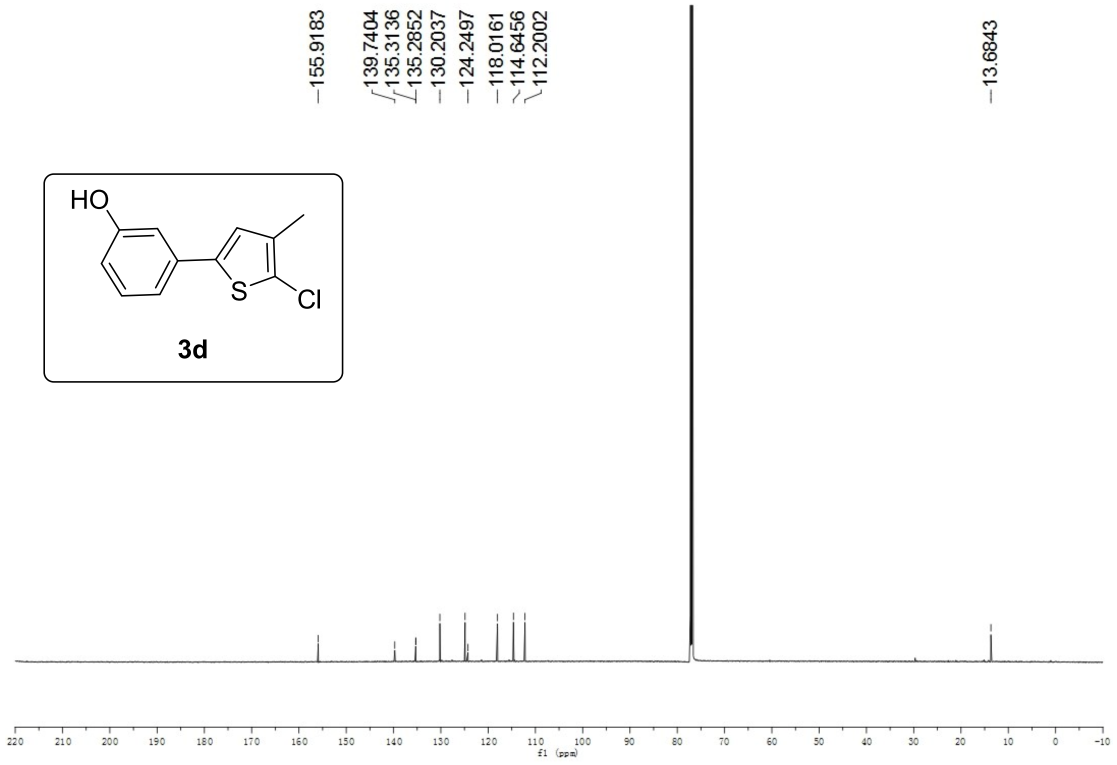

7.2282
7.2151
7.2019
7.1367
7.1253
7.1237
7.0907
7.0848
7.0275
7.0242
7.0208
6.7197
6.7160
6.7138
6.7118
6.7064
4.8271
2.5030
2.5017
HO
S
3b
1.17
1.10
1.05
0.96
2.00
1.06
2.91
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

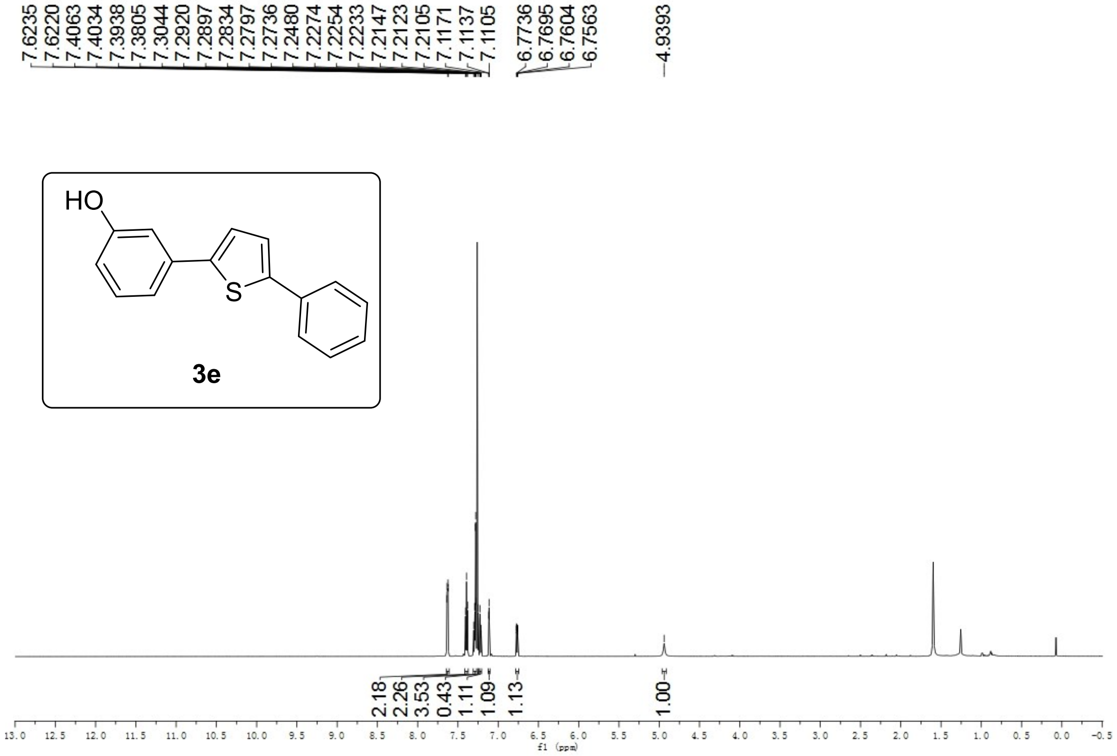

155.7976
141.3989
139.7094
136.2808
126.1477
123.1584
118.1831
113.9357
112.3009
15.4512
HO
S
3b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

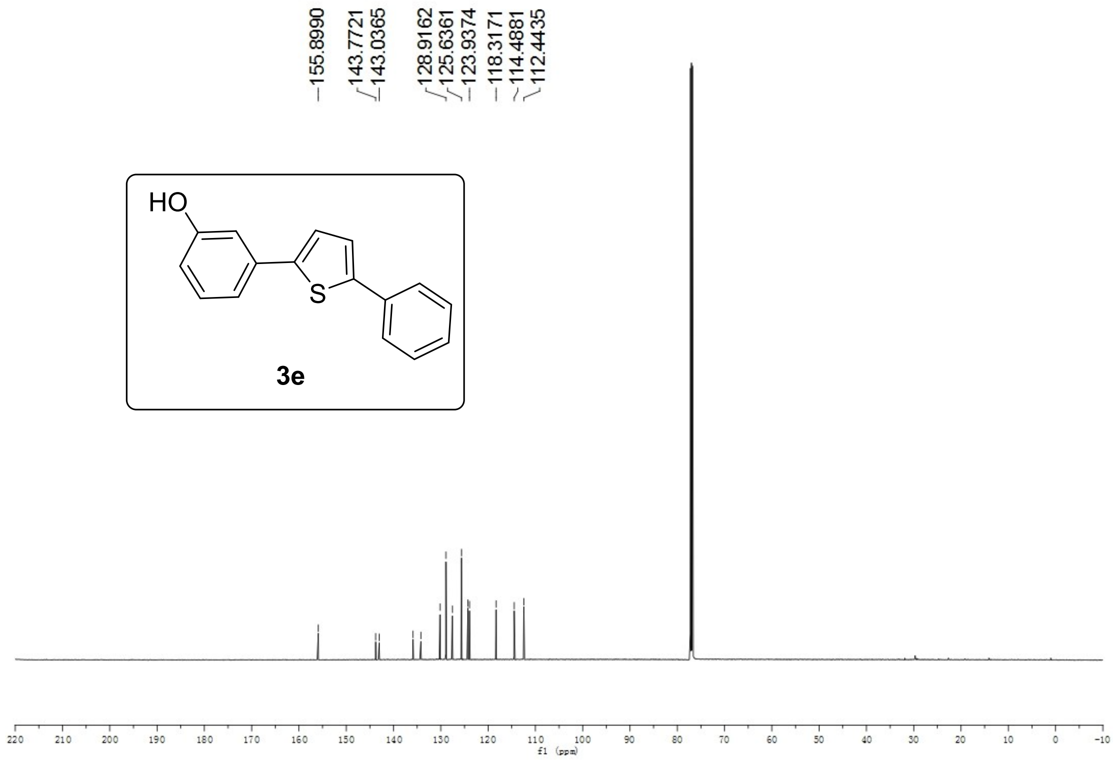

7.2508
7.2376
7.2244
7.0903
7.0893
7.0787
7.0775
7.0764
7.0525
7.0461
6.9868
6.9837
6.9803
6.8822
6.8757
6.7740
6.7729
6.7700
6.7605
6.7594
6.7565
4.9883
HO
S
Cl
3c
1.00
1.02
0.94
0.93
0.89
0.95
0.95
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

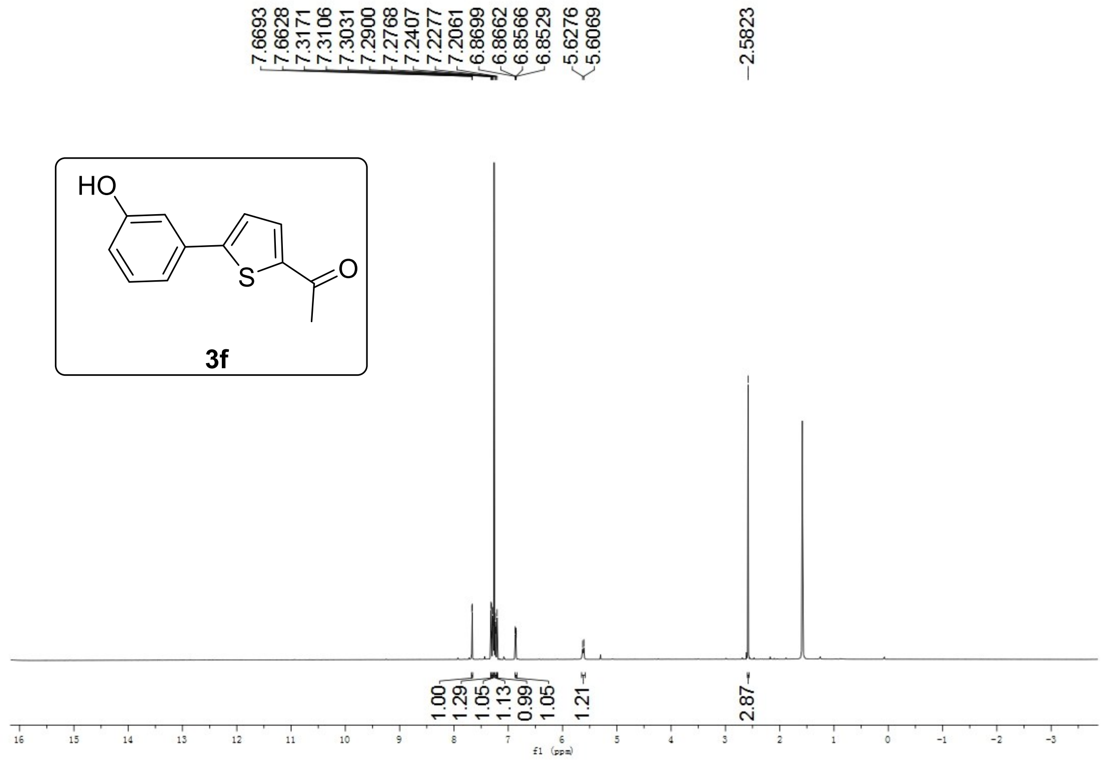

155.9655
142.3711
135.2123
130.2644
129.2974
127.0600
122.4885
118.1837
114.8159
112.3883
HO
S
Cl
3c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

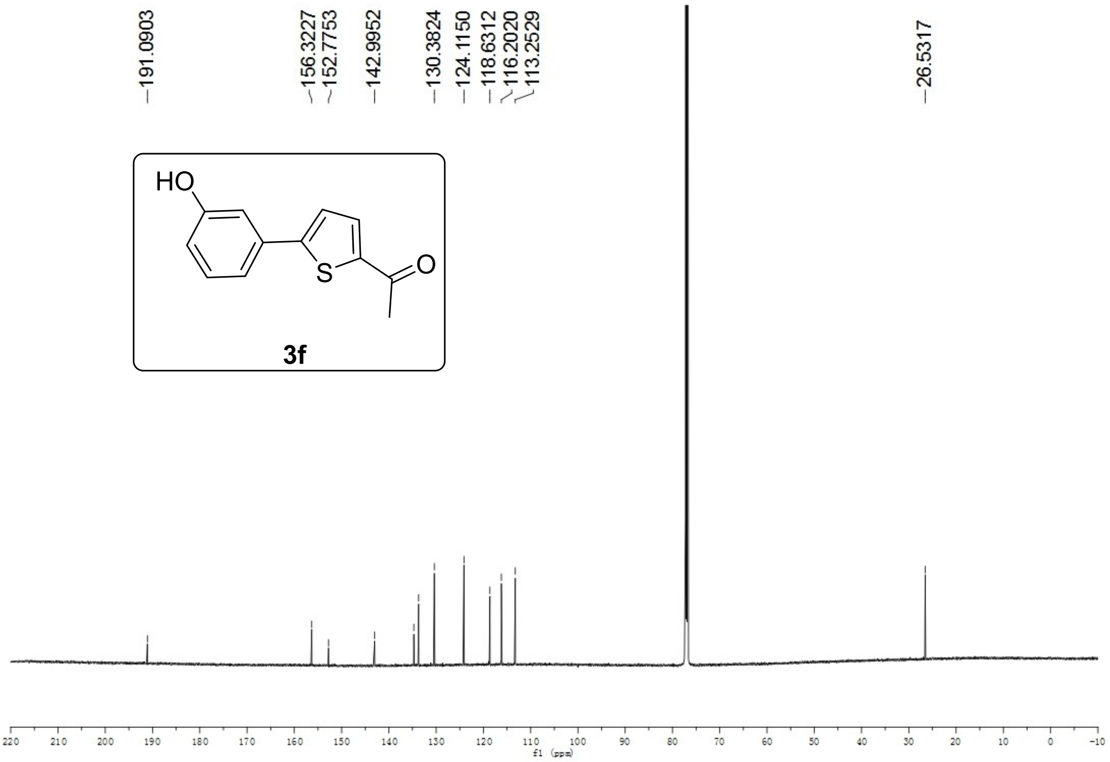

7.2379
7.2247
7.2115
7.0753
7.0739
7.0728
7.0715
7.0625
7.0611
7.0599
7.0586
6.9686
6.9629
6.9594
6.7572
6.7560
6.7531
6.7519
6.7438
6.7425
6.7396
6.7385
4.9007
2.1965
HO
S
Cl
3d
1.07
1.01
1.99
1.02
1.10
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


155.9183
139.7404
135.3136
135.2852
130.2037
124.2497
118.0161
114.6456
112.2002
13.6843
HO
S
Cl
3d
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)


7.6235
7.6220
7.4063
7.4034
7.3938
7.3805
7.3044
7.2920
7.2897
7.2834
7.2797
7.2736
7.2480
7.2274
7.2254
7.2233
7.2147
7.2123
7.2105
7.1171
7.1137
7.1105
6.7736
6.7695
6.7604
6.7563
4.9393
HO
S
3e
2.18
2.26
3.53
0.43
1.11
1.09
1.13
1.00
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


155.8990
143.7721
143.0365
128.9162
125.6361
123.9374
118.3171
114.4881
112.4435
HO
S
3e
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)


7.6693
7.6628
7.3171
7.3106
7.3031
7.2900
7.2768
7.2407
7.2277
7.2061
6.8699
6.8662
6.8566
6.8529
5.6276
5.6069
2.5823
HO
S
O
3f
1.00
1.29
1.05
1.13
0.99
1.05
1.21
2.87
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


191.0903
156.3227
152.7753
142.9952
130.3824
124.1150
118.6312
116.2020
113.2529
26.5317
HO
S
O
3f
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)