N-Heterocyclic carbene-catalyzed diastereoselective synthesis of β-lactone-fused cyclopentanes using homoenolate annulation reaction

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Supporting Information

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw cap. THF was dried by distillation over Na-benzophenone and was transferred under argon. The 2-acetylpyridine was purchased from commercial sources, 2-acetyl-6-bromopyridine was purchased from Alfa Aesar and they were used without any further purification. The unsaturated aldehydes were synthesized from corresponding aldehydes following the literature procedure.[1] DBU was purchased from Sigma Aldrich and was distilled, prior to use. The imidazolium salt **4** was synthesized following the literature procedure.[2]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. Melting points are uncorrected, and analyzed using Barnstead International MEL-TEMP (230 V, 50-60 Hz). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400, AV 500, and in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). Infrared spectra were recorded on a Bruker Alpha-E Infrared Spectrophotometer. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS mass spectra were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. HPLC analysis was performed on Shimadzu Class-VP V6.12 SP5 with UV detector. X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (Mo Kα=0.71073 Å) radiation at ambient temperature.

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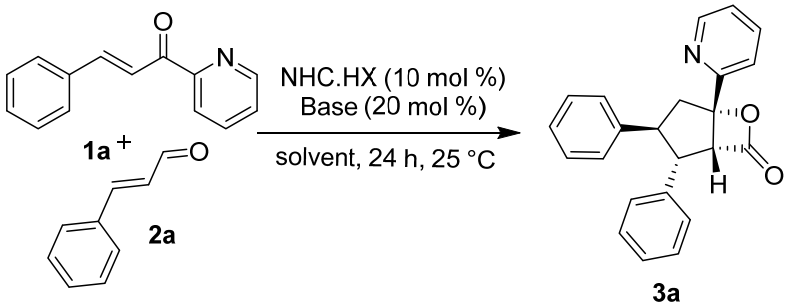
[1] (*a*) A. A. Wube, A. Hüfner, C. Thomaschitz, M. Blunder, M. Kollroser, R. Bauer and F. Bucar, *Bioorg. Med. Chem*., 2011, **19**, 567; (*b*) A. Orita, G. Uehara, K. Miwa and J. Otera, *Chem. Commun.,* 2006, 4729; (*c*) S. K. Gadakh, R. S. Reddy and A. Sudalai, *Tetrahedron: Asymmetry*, 2012, **23**, 898.

[2] (*a*) A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron,* 1999, **55**, 14523; (*b*) J. Cooke and O. C. Lightbody, *J. Chem. Educ.,* 2009, **86**, 610.

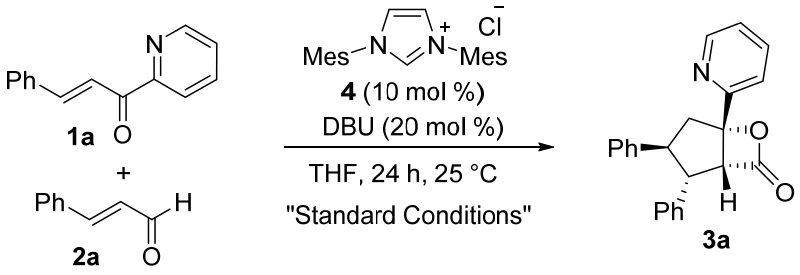
2. General Procedure for the Optimization of Reaction Conditions



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the azolium salt NHC.HX (0.025 mmol) and (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (52 mg, 0.25 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the *trans* cinnamaldehyde **2a** (33 mg, 31 μL, 0.25 mmol) followed by the addition of DBU (7.6 mg, 7.5 μL, 0.05 mmol). After 24 hours stirring, the reaction mixture was diluted with CH_2Cl_2 (2.0 mL), and concentrated under reduced pressure. The crude mixture was subsequently purified by silica gel flash column chromatography to afford the product **3a.**

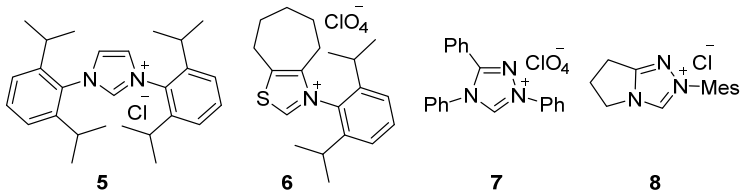
3. Optimization Studies

The optimization study commenced with treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** with *trans* cinnamaldehyde **2a**. Treatment of **1a** with **2a** in the presence of the carbene generated from **4** by deprotonation using DBU resulted in the formation of β-lactone-fused cyclopentane **3a** in 63% yield as a single diastereomer (after silica gel column chromatography). Notably, compared to this NHC, other common NHCs derived from precursors **5-8** are less effective (entries 2-5). Other bases such as NEt_3, DABCO, Cs_2CO_3, and KO*t*-Bu furnished the desired product in reduced yields (Table 1, entries 6-9). Among the various solvents screened, DME, 1,4-dioxane, toluene and DCM resulted in comparable result (entries 10-13). Finally, the reaction condition was optimized using 20 mol% of catalyst **4** and 1.2 equiv of **2a** leading to the formation of **3a** in 86% yield.



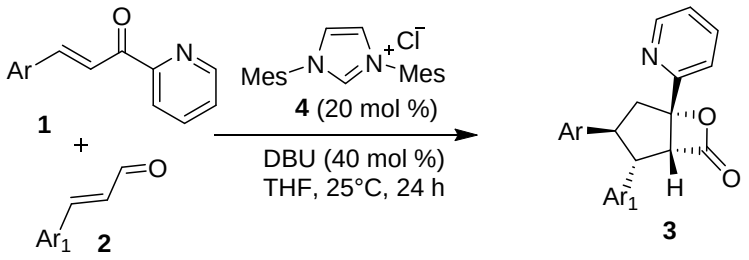
entry	variation of the standard conditions[a]	yield of **3a** (%)[b,c]
1	none	63
2	**5** instead of **4**	<5
3	**6** instead of **4**	<5
4	**7** instead of **4**	<5
5	**8** instead of **4**	32
6	Et_3N instead of DBU	15
7	DABCO instead of DBU	25
8	KO*t*-Bu instead of DBU	27
9	Cs_2CO_3 instead of DBU	35
10	DME instead of THF	57
11	1,4-dioxane instead of THF	41
12	toluene instead of THF	44
13	CH_2Cl_2 instead of THF	57
14[d]	20 mol % of **4** instead of 10 mol %	76
15[d]	*20 mol % of **4**, 1.2 equiv of **2a***	*86*

[a] Standard conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), **4** (10 mol %), DBU (20 mol %), THF (1.0 mL), 25 °C and 24 h. [b] Isolated yield after column chromatography. [c] A single diastereomer was observed in all cases. [d] 40 mol % of DBU was used.



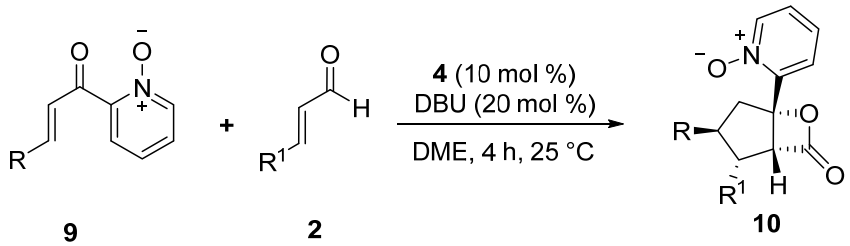
5 6 7 8

4. Procedure for the NHC-Catalyzed Synthesis of β-Lactone-Fused Cyclopentanes



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (0.034 g, 0.10 mmol) and the 2-enoylpyridine **1** (0.50 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added THF (2.5 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the aldehyde **2** (0.60 mmol) (*solid* aldehydes were transferred to the screw-capped tube by closing the argon flow and *liquid* aldehydes were transferred via syringe under argon flow) and the DBU (0.030 gm, 30 μL, 0.20 mmol) were successively added. Then the reaction mixture was stirred at 25° C for 24 h. When the reaction is complete, the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding functionalized β-lactone-fused cyclopentanes.

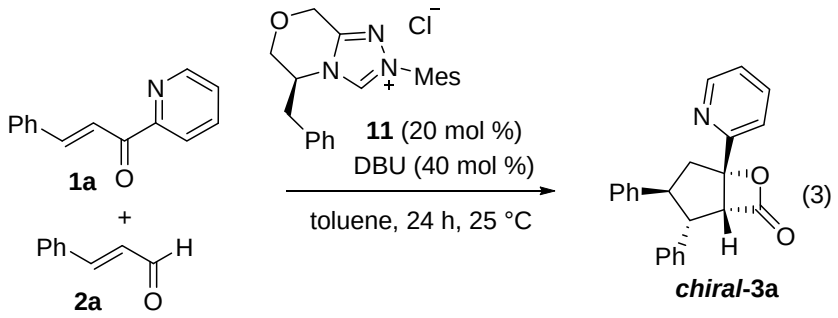
5. Procedure for the Annulation of Enal and 2-Enoylpyridine *N*-oxides



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (0.017 g, 0.05 mmol) and the 2-enoylpyridine *N*-oxides **9** (0.50 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this

mixture was added DME (2.5 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the aldehyde **2** (0.50 mmol) (*solid* aldehydes were transferred to the screw-capped tube by closing the argon flow and *liquid* aldehydes were transferred via syringe under argon flow) and the DBU (0.015 gm, 15 μL, 0.10 mmol) were successively added. Then the reaction mixture was stirred at 25° C for 24 h. When the reaction is complete, the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding functionalized β-lactones-fused cyclopentanes.

6. Procedure for the Enantioselective Synthesis of β-Lactone-Fused Cyclopentane

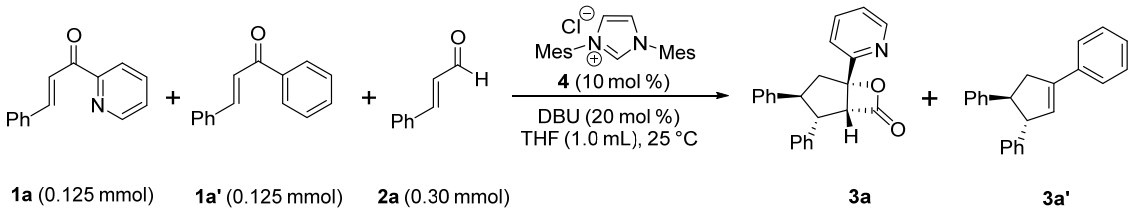


(3)

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **11** (0.018 g, 0.05 mmol) and the 2-enoylpyridine **1a** (0.25 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added THF (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the aldehyde **2a** (0.25 mmol) and the DBU (0.015 gm, 15 μL, 0.10 mmol) were successively added. Then the reaction mixture was stirred at 25 °C for 24 h. When the reaction is complete, the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel to afford the β-lactone-fused cyclopentane ***chiral*-3a** in high enantioselectivity (It may be noted that the absolute stereochemistry of ***chiral*-3a** was not determined).

7. Competition Experiment

Competition Experiments between 2-enoylpyridine (1a) and chalcone (1a')



1a (0.125 mmol) **1a'** (0.125 mmol) **2a** (0.30 mmol) **3a** **3a'**

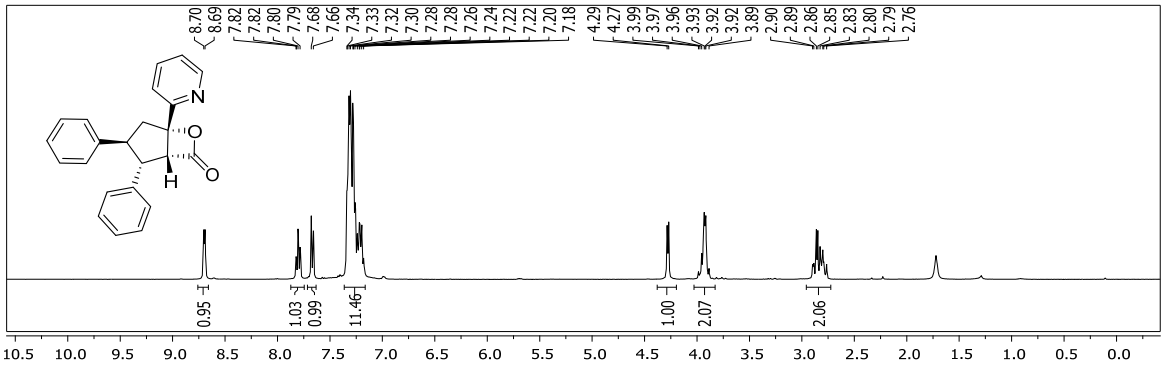
entry	Time (min)	Yield of **3a** (%)[a]	Yield of **3a'** (%)[a]
1	15	40	10
2	30	48	14

[a] The yields were determined by ^{1}H-NMR of the crude products using CH_2Br_2 as the internal standard.

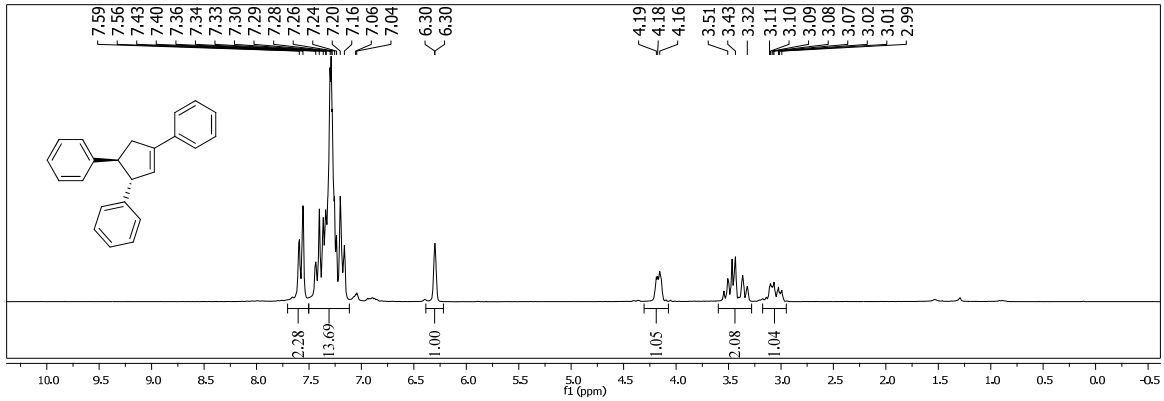
Both two reactions were carried out parallel. To each of the flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (8.5 mg, 0.025 mmol), (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (26 mg, 0.125 mmol) and (*E*)-chalcone **1a'** (26 mg, 0.125 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the *trans* cinnamaldehyde **2a** (39 mg, 38 μL, 0.30 mmol) followed by DBU (7.6 mg, 7.5 μL, 0.05 mmol). After 15 minutes stirring the first reaction was quenched and the mixture was diluted with CH_2Cl_2 (2.0 mL) and filtered through a short pad of silica gel and eluted with CH_2Cl_2 (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ^{1}H NMR using CH_2Br_2 (18.0 μL, 0.25 mmol) as the internal standard. The same procedure is followed for second reaction which was quenched after 30 min.

*From the competition experiments, it is clear that **1a** reacts almost four times faster than **1a'***

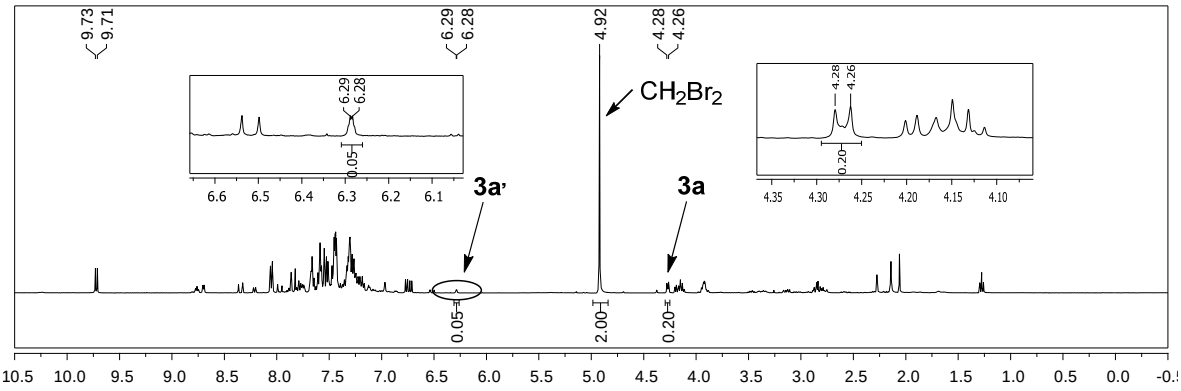
^{1}H-NMR of 2,3-diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3a)



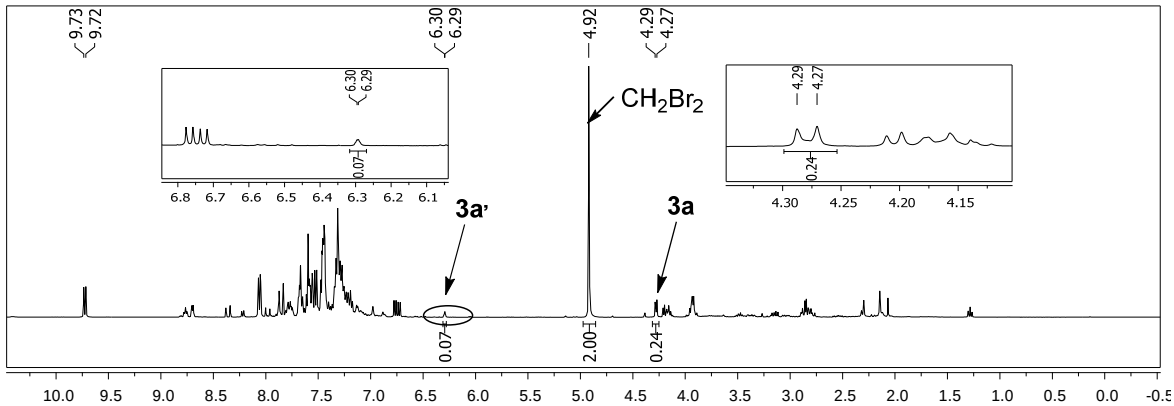
^{1}H-NMR of cyclopent-3-ene-1,2,4-triyltribenzene (3a')



^{1}H-NMR of Crude Reaction Mixture after 15 minutes ($CDCl_3$)

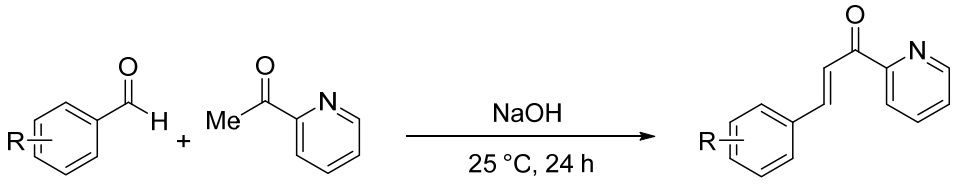


^{1}H-NMR of Crude Reaction Mixture after 30 minutes ($CDCl_3$)

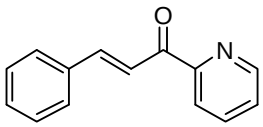


8. Synthesis and Characterization of 2-Enoylpyridines

The 2-enoylpyridines used in the present study were synthesized following the known procedure.[3]



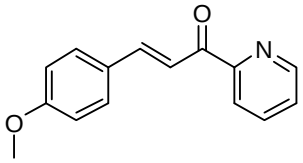
(*E*)-3-Phenyl-1-(pyridin-2-yl)prop-2-en-1-one (1a)[3]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (2.66 g, 2.46 mL, 22.0 mmol) and benzaldehyde (2.12 g, 2.03 mL, 20 mmol) were added to to distilled water (200 mL) cooled to 0°C and shaken vigorously. 20 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** as a crystalline pale green solid (3.6 g, 78%).

R_f (Pet. ether/EtOAc = 80/20): 0.47; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, *J* = 4.8 Hz 1H, H_{ar}), 8.31 (d, *J* = 16 Hz, 1H, H_{ar}), 8.19 (d, *J* = 7.8 Hz, 1H, H_{ar}), 7.94 (d, *J* = 16 Hz, 1H, H_{ar}), 7.86 (td, J_1 = 7.6 Hz, J_2= 1.7 Hz, 1H, H_{ar}), 7.74-7.71 (m, 2H, H_{ar}), 7.49-7.47 (m, 1H, H_{ar}), 7.42-7.40 (m, 3H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.59, 154.31, 148.97, 144.88, 137.12, 135.24, 130.68, 128.97, 128.95, 127.00, 123.03, 120.95. **FTIR (cm^{-1})** 3021, 1669, 1603, 1438, 1332, 1216, 1033, 991, 927, 767, 673.

(*E*)-3-(4-Methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1b)[4]



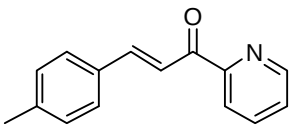
Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.33 g, 1.23 mL, 11 mmol) and 4-methoxybenzaldehyde (1.36 g, 10 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 15 mL of 10 % NaOH aqueous solution

[3] A. Ciupa, P. A. De Bank, M. F. Mahon, P. J. Wood and L. Caggiano, *Med. Chem. Commun*., 2013, **4**, 956.
[4] N. Molleti, N. K. Rana and V. K. Singh, *Org. Lett.,* 2012, **14**, 4322.

was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(4-methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1b** as a crystalline green solid (0.5 g, 21%).

R_f (Pet. ether/EtOAc = 80/20): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (d, *J* = 4.7 Hz 1H, H_{ar}), 8.19-8.15(m, 2H, H_{ar}), 7.91 (d, *J* = 16 Hz, 1H, H_{ar}), 7.84 (td, J_1 = 7.7 Hz, J_2= 1.7 Hz, 1H, H_{ar}), 7.67 (d, *J* = 8.7 Hz, 2H, H_{ar}), 7.47(ddd, J_1 = 7.4 Hz, J_2 = 4.8, J_3 = 1.1 Hz, 1H, H_{ar}), 6.92 (d, *J* = 8.8 Hz, 2H, H_{ar}), 3.83 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.48, 161.83, 154.56, 148.88, 144.79, 137.07, 130.76, 128.05, 126.82, 122.95, 118.60, 114.43, 55.48. **FTIR (cm^{-1})** 3357, 3018, 1666, 1595, 1572, 1511, 1421, 1336, 1257, 1215, 1032, 756, 668.

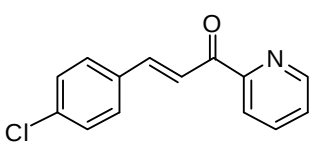
(*E*)-1-(Pyridin-2-yl)-3-(p-tolyl)prop-2-en-1-one (1c)[4]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.33 g, 1.23 mL, 11.0 mmol) and 4-methylbenzaldehyde (1.20 g, 1.2 mL, 10 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 10 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-1-(pyridin-2-yl)-3-(p-tolyl)prop-2-en-1-one **1c** as a crystalline pale green solid (0.56 g, 25%).

R_f (Pet. ether/EtOAc = 80/20): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, *J* = 4.7 Hz 1H, H_{ar}), 8.26 (d, *J* = 16 Hz, 1H, H_{ar}), 8.18 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.93 (d, *J* = 16 Hz, 1H, H_{ar}), 7.86 (td, J_1 = 7.7 Hz, J_2= 1.7 Hz, 1H, H_{ar}), 7.63 (d, *J* = 8 Hz, 2H, H_{ar}), 7.47(ddd, J_1 = 7.5 Hz, J_2 = 4.8, J_3 = 1.1 Hz, 1H, H_{ar}), 7.21 (d, *J* = 7.9 Hz, 2H, H_{ar}), 2.38 (s, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.62, 154.45, 148.93, 145.03, 141.24, 137.10, 132.53, 129.73, 129.00, 126.92, 123.00, 119.90, 21.68. **FTIR (cm^{-1})** 3019, 1669, 1600, 1582, 1466, 1335, 1215, 1180, 1029, 994, 758, 669.

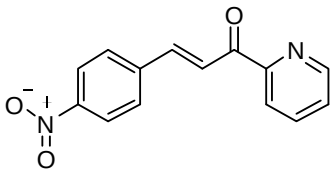
(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (1d)[4]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.99 g, 1.85 mL, 16.5 mmol) and 4-chlorobenzaldehyde (2.1 g, 15 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 15 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one **1d** as a crystalline gray solid (1.28 g, 35%).

R_f (Pet. ether/EtOAc = 80/20): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, *J* = 4.7 Hz 1H, H_{ar}), 8.27 (d, *J* = 16.1 Hz, 1H, H_{ar}), 8.18 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.89-7.85 (m, 2H, H_{ar}), 7.65 (d, *J* = 8.5 Hz, 2H, H_{ar}), 7.50-7.47 (m, 1H, H_{ar}), 7.38 (d, *J* = 8.4 Hz, 2H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.40, 154.16, 149.00, 143.31, 137.19, 136.55, 133.78, 130.08, 129.27, 127.14, 123.08, 121.45. **FTIR (cm^{-1})** 3019, 1672, 1609, 1566, 1491, 1437, 1331, 1215, 1090, 1027, 987, 764, 668.

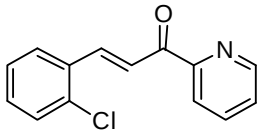
(*E*)-3-(4-Nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1e)[4]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.21 g, 1.1mL, 10 mmol) and 4-nitrobenzaldehyde (1.66 g, 11 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 10 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(4-nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1e** as a crystalline yellow solid (2.02 g, 79%).

R_f (Pet. ether/EtOAc = 80/20): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (d, *J* = 4.6 Hz 1H, H_{ar}), 8.42 (d, *J* = 16 Hz, 1H, H_{ar}), 8.26 (d, *J* = 8.7 Hz, 2H, H_{ar}), 8.20 (d, *J* = 7.8 Hz, 1H, H_{ar}), 7.93-7.85 (m, 4H, H_{ar}), 7.53(ddd, J_1 = 7.5 Hz, J_2 = 4.7, J_3 = 1.0 Hz, 1H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.09, 153.72, 149.12, 148.67, 141.44, 141.39, 137.34, 129.38, 127.49, 124.92, 124.26, 123.22. **FTIR (cm^{-1})** 3019, 1676, 1614, 1583, 1522, 1437, 1346, 1215, 1110, 1025, 987, 755, 668.

(*E*)-3-(2-Chlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one(1f)[5]



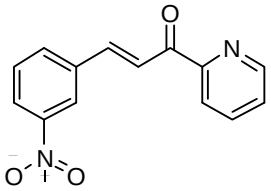
Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.21 g, 1.1mL, 10 mmol) and 2-chlorobenzaldehyde (1.54 g, 1.2mL, 11 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 10 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(2-chlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1f** as a crystalline green solid (0.51 g, 21%).

R_f (Pet. ether/EtOAc = 80/20): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, *J* = 4.6 Hz 1H, H_{ar}), 8.32 (q, *J* = 16.1 Hz, 2H, H_{ar}), 8.20 (d, *J* = 8.0 Hz, 1H, H_{ar}), 7.91-7.86 (m, 2H, H_{ar}),

[5] K. I. Bhat, A. Kumar, M. Nisar and P. Kumar, *Med. Chem. Res.,* 2014, **23**, 3458.

7.53-7.47 (m, 1H, H_{ar}), 7.45-7.42 (m, 1H, H_{ar}), 7.35-7.28 (m, 2H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.31, 154.16, 149.01, 140.40, 137.20, 135.93, 133.52, 131.36, 130.33, 128.17, 127.15, 127.12, 123.38, 123.15. **FTIR (cm^{-1})** 3019, 1672, 1603, 1470, 1329, 1215, 1026, 928, 756, 669.

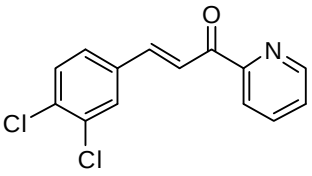
(*E*)-3-(3-Nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1g)[4]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.21 g, 1.1mL, 10 mmol) and 4-nitrobenzaldehyde (1.66 g, 11 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 10 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(3-nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1g** as a crystalline white solid (0.42 g, 17%).

R_f (Pet. ether/EtOAc = 80/20): 0.26; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (d, *J* = 4.6 Hz, 1H, H_{ar}), 8.57 (s, 1H, H_{ar}), 8.42 (d, *J* = 16.1 Hz, 1H, H_{ar}), 8.2 (dd, J_1 = 8.2 Hz J_2 = 1.3 Hz, 1H, H_{ar}), 8.19 (d, *J* = 7.8 Hz, 1H, H_{ar}), 8.0 (d, *J* = 7.7 Hz, 1H, H_{ar}), 7.94-7.88 (m, 2H, H_{ar}), 7.60 (t, *J* = 7.9 Hz, 1H, H_{ar}), 7.54-7.51 (m, 1H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.13, 153.76, 149.12, 148.84, 141.55, 137.30, 137.06, 134.58, 130.04, 129.27, 127.43, 124.78, 123.82, 123.17, 122.98. **FTIR (cm^{-1})** 3356, 3063, 3022, 1708, 1610, 1531, 1475, 1430, 1344, 1032, 865, 760, 666.

(*E*)-3-(3,4-Dichlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1h)[6]



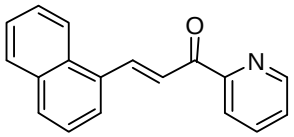
Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (0.62 g, 0.58 mL, 5.1 mmol) and 3,4-dichlorobenzaldehyde (1.0 g, 5.7 mmol) were added to to distilled water (50 mL) cooled to 0°C and shaken vigorously. 5 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(3,4-dichlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1h** as a crystalline green solid (0.65 g, 46%).

R_f (Pet. ether/EtOAc = 80/20): 0.44; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, *J* = 4.7 Hz 1H, H_{ar}), 8.27 (d, *J* = 16.2 Hz, 1H, H_{ar}), 8.17 (d, *J* = 8.0 Hz, 1H, H_{ar}), 7.87 (td, J_1 = 7.7 Hz, J_2= 1.7 Hz, 1H, H_{ar}), 7.78 (dd, J_1 = 8.9 Hz, J_2 = 7.1 Hz, 2H, H_{ar}), 7.53-7.45 (m, 1H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.13, 153.92, 149.03, 141.82, 137.23, 135.34, 134.46, 133.33,

[6] Z. Zhang, Y.-W. Dong and G.-W. Wang, *Chem. Lett.*, 2003, **32**, 966.

130.97, 130.22, 127.93, 127.27, 123.12, 122.58. **FTIR (cm^{-1})** 3021, 1668, 1602, 1471, 1423, 1326, 1216, 1031, 927, 763, 670.

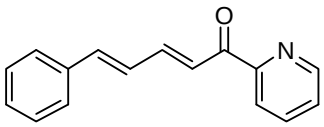
(*E*)-3-(Naphthalen-1-yl)-1-(pyridin-2-yl)prop-2-en-1-one (1i)[4]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.21 g, 1.1 mL, 10 mmol) and 1-naphthaldehyde (1.71 g, 1.5 mL, 11 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 10 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(naphthalen-1-yl)-1-(pyridin-2-yl)prop-2-en-1-one **1i** as a crystalline pale green solid (0.46 g, 17%).

***R*$_f$** (Pet. ether/EtOAc = 80/20): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (d, *J* = 15.8 Hz 1H, H_{ar}), 8.76 (d, *J* = 4.6 Hz, 1H, H_{ar}), 8.41 (d, *J* = 15.8 Hz, 1H, H_{ar}), 8.35 (d, *J* = 8.4 Hz, 1H, H_{ar}), 8.24 (d, *J* = 7.9 Hz, 1H, H_{ar}), 8.07 (d, *J* = 7.3 Hz, 1H, H_{ar}), 7.94-7.88 (m, 3H, H_{ar}), 7.63-7.59 (m, 1H, H_{ar}), 7.56-7.49 (m, 3H. H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.51, 154.40, 149.06, 141.51, 137.18, 133.89, 132.46, 132.08, 131.04, 128.90, 127.06, 126.33, 125.67, 125.62, 123.63, 123.39, 123.15. **FTIR (cm^{-1})** 3019**,** 1669, 1581, 1527, 1348, 1321, 1215, 1025, 928, 851, 761, 669.

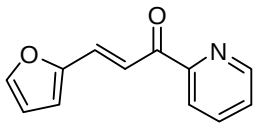
(2*E*, 4*E*)-5-Phenyl-1-(pyridin-2-yl)penta-2,4-dien-1-one (1j)[4]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.21 g, 1.1mL, 10 mmol) and cinnamaldehyde (1.71 g, 1.63mL, 11 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 10 mL of 10 % NaOH aqueous solution was added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (2*E*, 4*E*)-5-phenyl-1-(pyridin-2-yl)penta-2,4-dien-1-one **1j** as a crystalline green solid (0.44 g, 18%).

***R*$_f$** (Pet. ether/EtOAc = 80/20): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 4.7 Hz 1H, H_{ar}), 8.15 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.87-7.69 (m, 3H, H_{ar}), 7.51-7.45 (m, 3H, H_{ar}), 7.39-7.30 (m, 3H, H_{ar}), 7.13-7.02 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.65, 154.38, 148.94, 144.97, 142.23, 137.13, 136.31, 129.32, 128.97, 127.59, 127.44, 126.91, 124.64, 122.94. **FTIR (cm^{-1})** 3357, 3019, 1661, 1577, 1350, 1215, 1122, 1047, 1003, 756, 691, 667.

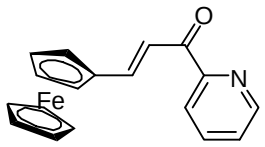
(*E*)-3-(Furan-2-yl)-1-(pyridin-2-yl)prop-2-en-1-one (1k)[4]



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (1.21 g, 1.1 mL, 10 mmol) and furan-2-carbaldehyde (1.05 g, 0.9 mL, 11 mmol) were added to to distilled water (100 mL) cooled to 0°C and shaken vigorously. 10 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(furan-2-yl)-1-(pyridin-2-yl)prop-2-en-1-one **1k** as a crystalline green solid (0.73 g, 37%).

R_f (Pet. ether/EtOAc = 80/20): 0.41; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, *J* = 4.7 Hz 1H, H_{ar}), 8.17-8.11(m, 2H, H_{ar}), 7.86 (td, J_1 = 7.8 Hz, J_2= 1.4 Hz, 1H, H_{ar}), 7.69 (d, *J* = 15.7 Hz, 1H, H_{ar}), 7.53 (s, 1H, H_{ar}), 7.48-7.45 (m, 1H, H_{ar}), 6.76 (d, *J* = 3.4 Hz, 1H, H_{ar}), 6.51-6.50 (m, 1H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.44, 154.33, 152.23, 149.04, 145.24, 137.08, 130.80, 126.93, 122.93, 118.85, 116.35, 112.77. **FTIR (cm^{-1})** 3019, 1667, 1599, 1474, 1324, 1218, 1022, 982, 929, 878, 762, 664.

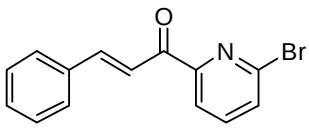
(*E*)-3-(Ferrocenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1l)



Following the known procedure, 1-(pyridin-2-yl)ethan-1-one (0.31 g, 0.28 mL, 2.56 mmol) and ferrocene carboxaldehyde (0.5g, 2.33 mmol) were added to to distilled water (23 mL) cooled to 0°C and shaken vigorously. 2.3 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(ferrocenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1l** as a crystalline red solid (0.45 g, 60%).

R_f (Pet. ether/EtOAc = 80/20): 0.41; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (d, *J* = 4.4 Hz, 1H, H_{ar}), 8.18 (d, *J* = 7.8 Hz, 1H, H_{ar}), 7.93-7.82 (m, 3H, H_{ar}), 7.46 (dd, *J* = 6.8, 5.1 Hz, 1H, H_{ar}), 4.67 (s, 2H), 4.49 (s, 2H), 4.18 (s, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.61, 154.81, 148.88, 147.33, 137.10, 126.67, 123.03, 117.88, 79.54, 77.48, 77.16, 76.84, 71.64, 69.97, 69.56. **HRMS** calculated $[M+H]^+$ for $C_{18}H_{16}ONFe$: 318.0576, found: 318.0567. **FTIR (cm^{-1})** 3356, 1653, 1584, 1420, 1354, 1311, 1117, 1028.

(*E*)-1-(6-Bromopyridin-2-yl)-3-phenylprop-2-en-1-one (1m)



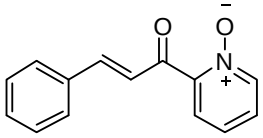
Following the known procedure, 1-(6-bromopyridin-2-yl)ethan-1-one (0.5 g, 2.49 mmol) and benzaldehyde (0.31 g, 2.99 mmol)

were added to to distilled water (24 mL) cooled to 0°C and shaken vigorously. 2.4 mL of 10 % NaOH aqueous solution was then added and reaction was continued for 24 h. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-1-(6-bromopyridin-2-yl)-3-phenylprop-2-en-1-one **1m** as a crystalline pale green solid (0.53 g, 74%).

R_f (Pet. ether/EtOAc = 80/20): 0.52; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22-8.14 (m, 2H, H_{ar}), 7.95 (d, *J* = 16 Hz, 1H, H_{ar}), 7.76-7.67 (m, 4H, H_{ar}), 7.44-7.43 (m, 3H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.98, 155.15, 145.78, 141.44, 139.44, 135.06, 131.71, 130.98, 129.13, 129.06, 121.93, 120.36. **HRMS** calculated $[M+H]^+$ for $C_{14}H_{11}ONBr$: 288.0019, found: 288.0018. **FTIR (cm^{-1})** 3360, 1663, 1598, 1562, 1419, 1329, 1215, 1117, 1037, 985, 768, 684.

9. Synthesis and Characterization of 2-Enoylpyridine *N*-oxides

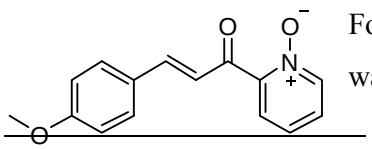
2-Cinnamoylpyridine 1-oxide (9a)[7]



Following the known procedure,[7] 1 (M) KOH (3.0 mL, 3 mmol) was added to a solution of 2-acetylpyridine 1-oxide (1.9 g, 13.85 mmol) and benzaldehyde (2.93 g, 2.8 mL, 27.7 mmol) in methanol (50 mL) at 0°C and reaction was continued for overnight at room temperature. Then methanol was evaporated and the residue was suspended in water (50 mL). The mixture was neutralized with 2(M) HCl (1.5 mL, 3 mmol) and extracted with CH_2Cl_2. The product was isolated by column chromatography to afford 2-cinnamoylpyridine 1-oxide **9a** as a crystalline yellow solid (1.85 g, 60%).

R_f (EtOAc): 0.26 ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 6.4 Hz, 1H, H_{ar}), 7.81-7.77 (m, 1H, H_{ar}), 7.72-7.61 (m, 4H, H_{ar}), 7.40-7.32(m, 5H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 186.47, 147.34, 147.34, 144.43, 144.43, 140.55, 140.55, 134.68, 134.68, 130.93, 130.93, 128.98, 128.98, 128.96, 128.96, 127.85, 127.85, 127.37, 127.37, 125.90, 125.90, 124.39, 124.39. **FTIR (cm^{-1})** 3018, 1663, 1604, 1433, 1329, 1216, 1037, 981, 850, 762, 669.

(*E*)-2-(3-(4-Methoxyphenyl)acryloyl)pyridine 1-oxide (9b)[7]



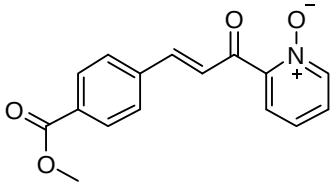
Following the known procedure, 1 (M) KOH (0.7 mL, 0.7 mmol) was added to a solution of 2-acetylpyridine 1-oxide (0.5 g, 3.66

[7] P. K. Singh, V. K. Singh, *Org. Lett.,* 2008, **10**, 4121.

mmol) and 4-methoxybenzaldehyde (0.99 g, 0.9 mL, 7.33 mmol) in methanol (17 mL) at 0°C and reaction was continued for overnight at room temperature. Then methanol was evaporated and the residue was suspended in water (15 mL). The mixture was neutralized with 2(M) HCl (0.35 mL, 0.7 mmol) and extracted with CH_2Cl_2. The product was isolated by column chromatography to afford (*E*)-2-(3-(4-methoxyphenyl)acryloyl)pyridine 1-oxide **9b** as a crystalline yellow solid (0.43 g, 46%).

R_f (EtOAc): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 6.3 Hz, 1H, H_{ar}), 7.71 (d, *J* = 15.9 Hz, 1H, H_{ar}), 7.60 (dd, J_1 = 7.4 Hz, J_2 = 2.2 Hz, 1H, H_{ar}), 7.55-7.51 (m, 3H, H_{ar}), 7.35-7.26 (m, 2H, H_{ar}), 6.85 (d, *J* = 8.7 Hz, 2H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 186.32, 161.97, 147.40, 144.50, 140.40, 130.73, 127.56, 127.28, 127.11, 125.77, 122.08, 114.37, 55.41. **FTIR (cm^{-1})** 3017, 1657, 1591, 1512, 1468, 1428, 1298, 1217, 1115, 1034, 980, 761, 667.

(*E*)-2-(3-(4-(Methoxycarbonyl)phenyl)acryloyl)pyridine 1-oxide (9c)

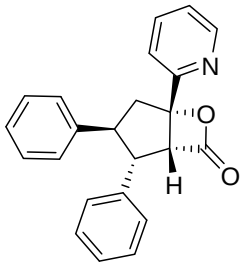


Following the known procedure, 1(M) KOH (0.7 mL, 0.7 mmol) was added to a solution of 2-acetylpyridine 1-oxide (0.5 g, 3.66 mmol) and 4-methoxybenzaldehyde (1.2 g, 7.33 mmol) in methanol (17 mL) at 0°C and reaction was continued for overnight at room temperature. Then methanol was evaporated and the residue was suspended in water (15 mL). The mixture was neutralized with 2(M) HCl (0.35 mL, 0.7 mmol) and extracted with CH_2Cl_2. The product was isolated by column chromatography to afford (*E*)-2-(3-(4-(methoxycarbonyl)phenyl)acryloyl)pyridine 1-oxide **9c** as a crystalline yellow solid (0.21 g, 20%).

R_f (EtOAc = 80/20): 0.27; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.22 (d, *J* = 6.1 Hz, 1H, H_{ar}), 8.01 (d, *J* = 8.0 Hz, 2H, H_{ar}), 7.78-7.65 (m, 5H, H_{ar}), 7.40-7.33 (m, 2H, H_{ar}), 3.90 (S, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 186.14, 166.50, 147.02, 142.27, 140.54, 138.94, 131.70, 130.11, 128.66, 128.12, 127.52, 126.38, 125.94, 52.36. **HRMS** calculated $[M+H]^+$ for $C_{16}H_{14}O_4N$: 284.0917, found: 284.0916. **FTIR (cm^{-1})** 3020, 1718, 1666, 1606, 1429, 1320, 1285, 1216, 1111, 1031, 761, 669.

10.Characterization of β-lactone-fused Cyclopentanes

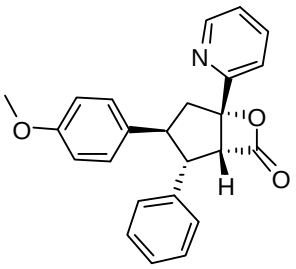
2,3-Diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3a)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 μL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2,3-diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3a** as a white solid (0.146 g, 86% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.47; Melting point: 163-165 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.69 (d, *J* = 4.8 Hz, 1H, H$_{ar}$), 7.81 (td, J_1 = 7.8 Hz, J_2= 1.2 Hz, 1H, H$_{ar}$), 7.67 (d, *J* = 7.8 Hz, 1H, H$_{ar}$), 7.34-7.18 (m, 11H, H$_{ar}$), 4.28 (d, *J* = 6.7 Hz, 1H), 3.98-3.88 (m, 2H), 2.90-2.76 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.46, 157.74, 149.68, 139.71, 137.09, 135.84, 128.73, 128.58, 128.50, 127.81, 127.52, 127.14, 123.33, 120.30, 86.60, 66.41, 52.81, 47.34, 44.59. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{20}NO_2$: 342.1489, found: 342.1486. **FTIR (cm^{-1})** 3359, 3166, 3021, 2926, 2859, 1823, 1661, 1604, 1418, 1074, 931,759, 666.

3-(4-Methoxyphenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3b)

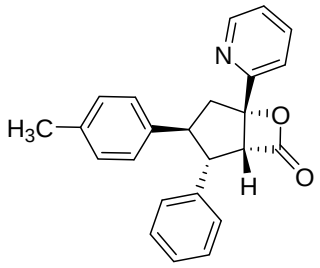


Following the general procedure, treatment of (*E*)-3-(4-methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1b** (0.119 g, 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 μL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(4-methoxyphenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3b** as yellow foam-type solid (0.159 g, 85% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.35; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.69 (d, *J* = 4.6 Hz, 1H, H$_{ar}$), 7.79 (td, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H, H$_{ar}$), 7.66 (d, *J* = 7.8 Hz, 1H, H$_{ar}$), 7.33-7.22 (m, 8H, H$_{ar}$), 6.80 (d, *J* = 8.66 Hz, 2H, H$_{ar}$), 4.26 (d, *J* = 7.1 Hz, 1H), 3.93-3.81 (m, 2H), 3.75 (s, 3 H), 2.86-2.72 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.51, 158.58, 157.74, 149.64, 137.06, 135.91, 131.58, 128.70, 128.54, 128.50, 127.46, 123.29, 120.26, 114.08, 86.52, 77.48, 77.16, 76.84, 66.29, 55.27, 52.98, 46.56, 44.55. **HRMS** calculated $[M+H]^+$ for

$C_{24}H_{22}O_3N$: 372.1594, found: 372.1592. **FTIR (cm^{-1})** 3062, 3017, 2961, 2934, 1824, 1612, 1591, 1438, 1250, 1126, 1037, 830, 758, 667.

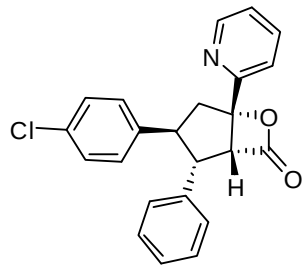
2-Phenyl-5-(pyridin-2-yl)-3-p-tolyl-6-oxa-bicyclo[3.2.0]heptan-7-one (3c)



Following the general procedure, treatment of (*E*)-3-*p*-tolyl-1-(pyridin-2-yl)prop-2-en-1-one **1c** (0.112 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-phenyl-5-(pyridin-2-yl)-3-p-tolyl-6-oxa-bicyclo[3.2.0]heptan-7-one **3c** as a white solid (0.135 g, 76% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.52; Melting point: 133-135 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, *J*= 4.7 Hz, 1H, H_{ar}), 7.80 (td, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H, H_{ar}), 7.33-7.27 (m, 5H, H_{ar}), 7.24-7.21 (m, 3H, H_{ar}), 7.09 (d, *J* = 7.9 Hz, 2H, H_{ar}), 4.28 (d, *J* = 6.8 Hz, 1H), 3.97-3.86 (m, 2H), 2.88-2.75 (m, 2H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.48, 157.72, 149.64, 137.04, 136.64, 136.55, 135.88, 129.39, 128.53, 128.48, 127.62, 127.44, 123.28, 120.26, 86.57, 66.34, 52.77, 46.85, 44.59, 21.10. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{22}O_2N$: 356.1645, found: 356.1643. **FTIR (cm^{-1})** 3019, 1824, 1658, 1593, 1516, 1494, 1438, 1216, 1125, 756, 669.

3-(4-Chlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3d)

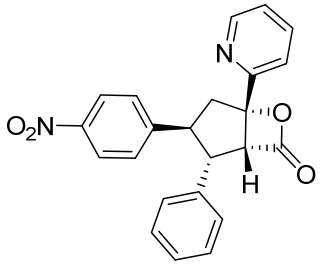


Following the general procedure, treatment of (*E*)-3-(4-chlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1d** (0.122 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(4-chlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3d** as a white solid (0.143 g, 76% yield).

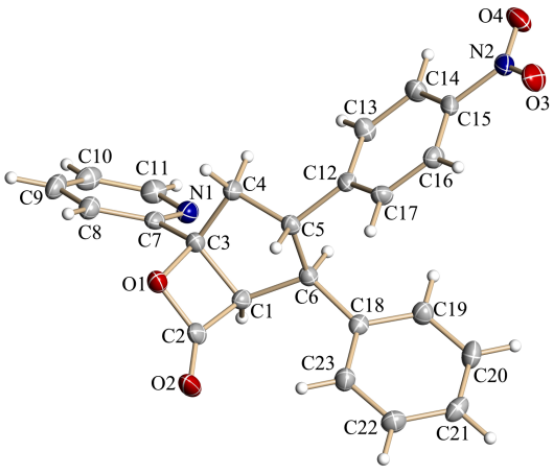
R_f (Pet. ether /EtOAc = 60/20): 0.44; Melting point: 136-138 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, *J* = 4.6 Hz, 1H, H_{ar}), 7.81 (td, *J* = 7.8 Hz, 1.6 Hz, 1H, H_{ar}), 7.66 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.35-7.23 (m, 10H, H_{ar}), 4.25 (d, *J* = 7.2 Hz, 1H), 3.94-3.80 (m, 2H), 2.87-2.74 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.25, 157.51, 149.68, 138.16, 137.13, 135.42, 132.85, 129.11, 128.89, 128.68, 128.43, 127.71, 123.40, 120.26, 86.45, 66.34, 53.00, 46.85,

44.31.**HRMS** calculated $[M+H]^+$ for $C_{23}H_{19}O_2NCl$: 376.1099, found: 376.1100. **FTIR (cm^{-1})** 3022, 1824, 1591, 1488, 1424, 1215, 1094, 1032, 930, 761, 668.

3-(4-Nitrophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3e)

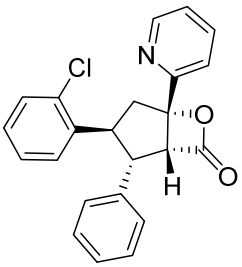


Following the general procedure, treatment of (*E*)-3-(4-nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1e** (0.127 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(4-nitrophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3e** as a yellow solid (0.120 g, 62% yield). CCDC 1057298 (For the further detail about crystal structure please visit http://www.ccdc.cam.ac.uk/deposit/)



R_f (Pet. ether /EtOAc = 60/40): 0.26; Melting point: 109-111 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68-8.67 (m, 1H, H_{ar}), 8.12-8.09 (m, 2H, H_{ar}), 7.81 (td, *J* = 7.7 Hz, 1.7 Hz, 1H, H_{ar}), 7.66 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.46 (d, *J* = 8.7 Hz, 2H, H_{ar}), 7.35-7.21 (m, 6H, H_{ar}), 4.26 (d, *J* = 7.5 Hz, 1H), 4.06-3.99 (m, 1H), 3.90-3.85 (m, 1H), 2.92-2.81 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.87, 157.16, 149.72, 147.42, 147.17, 137.22, 134.85, 128.84, 128.68, 128.33, 127.99, 123.98, 123.53, 120.24, 86.36, 66.41, 53.13, 47.42, 43.99. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{19}O_4N_2$: 387.1339, found: 387.1335. **FTIR (cm^{-1})** 3359, 3022, 2403, 1826, 1597, 1522, 1347, 1216, 761, 669.

3-(2-Chlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one (3f)

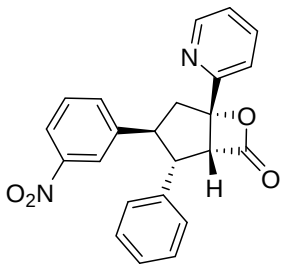


Following the general procedure, treatment of (*E*)-3-(2-chlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1f** (0.122 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography

afforded 3-(2-chlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one **3f** as a white solid (0.134 g, 71% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.32; Melting point: 137-139 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.67 (d, *J* = 4.3 Hz, 1H, H$_{ar}$), 7.79 (td, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H, H$_{ar}$), 7.66 (d, *J* = 7.9 Hz, 1H, H$_{ar}$), 7.43 (dd, J_1 = 7.7 Hz, J_2 = 1.2 Hz, 1H, H$_{ar}$), 7.36-7.27 (m, 6H, H$_{ar}$), 7.24-7.18 (m, 2H, H$_{ar}$), 7.12 (td, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H, H$_{ar}$), 4.57-4.49 (m, 1H), 4.31 (d, *J* = 7.7 Hz, 1H), 4.13-4.08 (m, 1H), 3.06-3.01 (m, 1H), 2.57-2.51 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.12, 157.53, 149.61, 137.19, 137.09, 135.23, 134.62, 129.93, 128.65, 128.36, 128.16, 127.66, 127.63, 127.36, 123.33, 120.31, 86.57, 65.99, 51.03, 43.52, 42.72. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{19}O_2NCl$: 376.1099, found: 376.1099. **FTIR (cm^{-1})** 3359, 3022, 2403, 1825, 1591, 1435, 1216, 1128, 1042, 931, 763, 669.

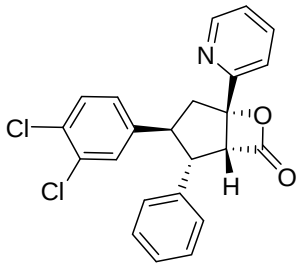
3-(3-Nitrophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one (3g)



Following the general procedure, treatment of (*E*)-3-(3-nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1g** (0.127 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(3-nitrophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one **3g** as a gray solid (0.147 g, 76% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.23; Melting point: 154-156 °C; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.70 (d, *J* = 4.8 Hz, 1H, H$_{ar}$), 8.24-8.23 (m, 1H, H$_{ar}$), 8.08-8.05 (m, 1H, H$_{ar}$), 7.82 (td, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H, H$_{ar}$), 7.69-7.67 (m, 1H, H$_{ar}$), 7.61 (d, *J* = 7.7 Hz, 1H, H$_{ar}$), 7.43 (t, *J* = 7.7 Hz, 1H, H$_{ar}$), 7.37-7.34 (m, 1H, H$_{ar}$), 7.31-7.29 (m, 4H, H$_{ar}$), 7.28-7.23 (m, 1H, H$_{ar}$), 4.28 (d, *J* = 7.5 Hz, 1H), 4.08-4.02 (m, 1H), 3.93-3.89 (m, 1H), 2.94-2.84 (m, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 167.91, 157.16, 149.74, 148.63, 141.94, 137.20, 134.84, 134.34, 129.69, 128.86, 128.40, 127.98, 123.53, 122.42, 122.39, 120.25, 86.33, 66.37, 53.10, 47.19, 44.05. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{19}O_4N_2$: 387.1339, found: 387.1341. **FTIR (cm^{-1})** 3019, 1827, 1658, 1593, 1494, 1414, 1351, 1216, 1127, 1042, 932, 756, 669.

3-(3,4-Dichlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one (3h)

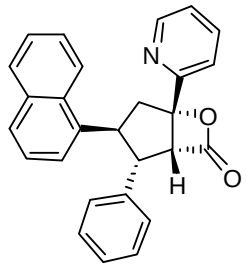


Following the general procedure, treatment of (*E*)-3-(3,4-dichlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one **1h** (0.139 g 0.5

mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(3,4-dichlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one **3h** as a gray solid (0.166 g, 81% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.44; Melting point: 147-149 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.68 (d, *J* = 4.3 Hz, 1H, H$_{ar}$), 7.79 (td, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H, H$_{ar}$), 7.65 (d, *J* = 7.8 Hz, 1H, H$_{ar}$), 7.41 (d, *J* = 1.9 Hz, 1H, H$_{ar}$), 7.34-7.23 (m, 7H, H$_{ar}$), 7.11 (dd, J_1 = 8.3 Hz, J_2 = 1.9 Hz, 1H, H$_{ar}$), 4.23 (d, *J* = 7.1 Hz, 1H), 3.91-3.78 (m, 2H), 2.86-2.72 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.00, 157.26, 149.69, 140.02, 137.17, 135.02, 132.72, 131.14, 130.65, 129.58, 128.78, 128.37, 127.88, 127.34, 123.46, 120.24, 86.32, 66.32, 52.91, 46.64, 44.16. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{18}O_2NCl_2$: 410.0709, found: 410.0712. **FTIR (cm^{-1})** 3683, 3622, 3019, 1826, 1593, 1572, 1498, 1476, 1438, 1216, 1134, 1066, 1042, 929, 757, 669.

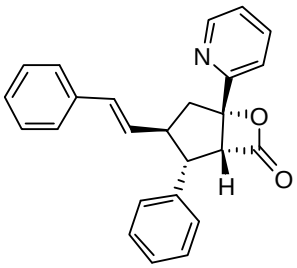
3-(Naphthalen-1-yl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3i)



Following the general procedure, treatment of (*E*)-3-(naphthalen-1-yl)-1-(pyridin-2-yl)prop-2-en-1-one **1i** (0.129 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(naphthalen-1-yl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3i** as a yellow solid (0.153 g, 78% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.41; Melting point: 57-59 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.64 (d, *J* = 4.61 Hz, 1H, H$_{ar}$), 8.29 (d, *J* = 8.65 Hz, 1H, H$_{ar}$), 7.84 (d, *J* = 8.28 Hz, 1H, H$_{ar}$), 7.75 (td, J_1 = 7.80 Hz, J_2 = 1.63 Hz, 1H, H$_{ar}$), 7.70 (d, *J* = 8.17 Hz, 1H, H$_{ar}$), 7.65 (d, *J* = 7.96 Hz, 1H, H$_{ar}$), 7.58 (t, *J* = 7.54 Hz, 1H, H$_{ar}$), 7.51-7.48 (m, 2H, H$_{ar}$), 7.38-7.31 (m, 3H, H$_{ar}$), 7.28-7.14 (m, 4H, H$_{ar}$), 4.80 (dt, J_1 = 6.02 Hz, J_2 = 11.94 Hz, 1H, H), 4.41-4.32 (m, 2H), 3.14 (dd, J_1 = 5.92 Hz, J_2 = 6.02 Hz, 1H), 2.62-2.55 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.48, 157.47, 149.63, 137.05, 135.68, 135.49, 133.98, 132.21, 129.06, 128.65, 128.29, 127.59, 127.49, 126.41, 125.76, 125.74, 123.41, 123.32, 123.05, 120.27, 86.66, 65.93, 49.93, 44.98, 41.27. **HRMS** calculated $[M+H]^+$ for $C_{27}H_{22}O_2N$: 392.1645, found: 392.1644. **FTIR (cm^{-1})** 3360, 3167, 3020, 2926, 2859, 1824, 1661, 1590, 1405, 1215, 1078, 931, 758, 665.

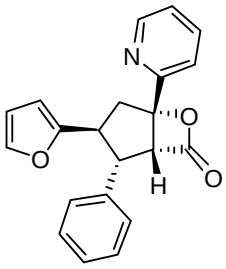
2-Phenyl-5-(pyridin-2-yl)-3-((*E*)-styryl)-6-oxabicyclo[3.2.0]heptan-7-one (3j)



Following the general procedure, treatment of (2*E*, 4*E*)-5-phenyl-1-(pyridin-2-yl)penta-2,4-dien-1-one **1j** (0.118 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-phenyl-5-(pyridin-2-yl)-3-((*E*)-styryl)-6-oxabicyclo[3.2.0]heptan-7-one **3j** as a white foam-type solid (0.170 g, 92% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.5; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.61 (d, *J* = 4.7 Hz, 1H, H_{ar}), 7.72 (td, *J* = 7.7 Hz, 1.7 Hz, 1H, H_{ar}), 7.58 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.32-7.17 (m, 10H, H_{ar}), 7.16-7.10 (m, 1H, H_{ar}), 6.41 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 15.9 Hz, 6.8 Hz, 1H), 4.10 (d, *J* = 6.8 Hz, 1H), 3.52-3.47(m, 2H), 2.69-2.64 (m, 1H), 2.59-2.53 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.39, 157.69, 149.65, 137.12, 136.98, 135.91, 132.00, 128.77, 128.70, 128.61, 128.56, 127.63, 127.55, 126.30, 123.32, 120.25, 86.81, 66.53, 52.40, 45.12, 42.44. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{22}O_2N$: 368.1645, found: 368.1641. **FTIR (cm^{-1})** 3021, 1824, 1655, 1591, 1433, 1215, 1041, 929, 763, 669.

3-(Furan-2-yl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3k)

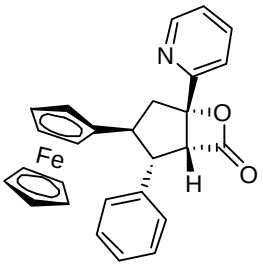


Following the general procedure, treatment of (*E*)-3-(furan-2-yl)-1-(pyridin-2-yl)prop-2-en-1-one (0.099 g, 0.5 mmol) **1k** and *trans* cinnamaldehyde **2** (0.079 g, 75 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(furan-2-yl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0] heptan-7-one **3k** as white solid (0.139 g, 84% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.55; Melting point: 117-119 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.68 (d, *J* = 4.71 Hz, 1H, H_{ar}), 7.79 (td, J_1 = 7.78 Hz, J_2 = 1.70 Hz, 1H, H_{ar}), 7.64 (d, *J* = 7.93 Hz, 1H, H_{ar}), 7.32-7.25 (m, 7H, H_{ar}), 6.22 (dd, J_1 = 1.89 Hz, J_2 = 1.89 Hz, 1H) 6.01 (d, *J* = 3.20 Hz, 1H, H_{ar}), 4.23 (d, *J* = 7.32 Hz, 1H), 4.03-3.89 (m, 2H), 2.94-2.81 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.16, 157.40, 153.38, 149.71, 141.77, 137.07, 135.79, 128.61, 128.30, 127.64, 123.38, 120.29, 110.32, 106.65, 86.54, 77.48, 77.16, 76.84, 66.03, 51.31, 41.65, 41.22. **HRMS** calculated $[M+H]^+$ for $C_{21}H_{18}O_3N$: 332.1281, found:

332.1283. **FTIR (cm^{-1})** 3361, 3117, 3066, 2934, 1824, 1591, 1571, 1497, 1343, 1216, 1202, 1039, 934, 836, 755, 667.

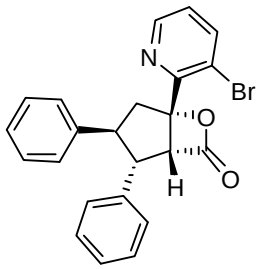
3-(Ferrocenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3l)



Following the general procedure, treatment of (*E*)-3- ferrocenyl -1-(pyridin-2-yl)prop-2-en-1-one **1l** (0.158 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 μL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-(ferrocenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3l** as a red solid (0.116 g, 52% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.61; Melting point: 134-136 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.68 (d, *J* = 4.7 Hz, 1H, H$_{ar}$), 7.80 (td, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H, H$_{ar}$), 7.67 (d, *J* = 7.8 Hz, 1H), 7.36-7.27 (m, 6H, H$_{ar}$), 4.12-4.10 (m, 6H), 4.02 (s, 1H), 3.98 (s, 2H), 3.79 (s, 1H), 3.70-3.63 (m, 1H), 3.51-3.46 (m, 1H), 2.96-2.82 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.71, 157.96, 149.73, 137.05, 136.58, 128.75, 128.58, 127.62, 123.25, 120.15, 88.43, 86.82, 77.48, 77.16, 76.84, 68.59, 68.46, 67.43, 67.13, 65.92, 54.57, 43.02, 41.67. **HRMS** calculated $[M+H]^+$ for $C_{27}H_{23}O_2NFe$: 449.1073, found: 449.1072. **FTIR (cm^{-1})** 3361, 3166, 3019, 1823, 1661, 1619, 1592, 1437, 1215, 1080, 930, 756, 668.

5-(3-Bromopyridin-2-yl)-2,3-diphenyl-6-oxabicyclo[3.2.0]heptan-7-one (3m)

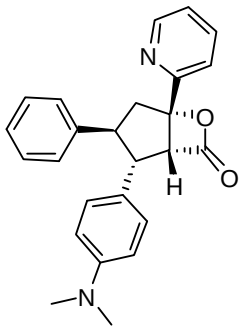


Following the general procedure, treatment of (*E*)-1-(3-bromopyridin-2-yl)-3-phenylprop-2-en-1-one **1m** (0.144 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.079 g, 75 μL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 5-(3-bromopyridin-2-yl)-2,3-diphenyl-6-oxabicyclo[3.2.0]heptan-7-one **3m** as a white solid (0.152 g, 72% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.81; Melting point: 173-175 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.65-7.60 (m, 2H), 7.49 (dd, J_1 = 7.1 Hz, J_2 = 1.7 Hz, 1H, H$_{ar}$), 7.31-7.25 (m, 8H, H$_{ar}$), 7.23-7.19 (m, 2H, H$_{ar}$),4.25 (d, *J* = 6.9 Hz, 1H), 3.95-3.85 (m, 2H), 2.85-2.72 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.01, 158.99, 142.18, 139.43, 139.32, 135.56, 128.76, 128.61, 128.46, 127.96, 127.79, 127.59, 127.21, 119.23, 85.93, 66.62, 52.43, 47.04, 44.17.

HRMS calculated $[M+H]^+$ for $C_{23}H_{19}O_2NBr$: 420.0594, found: 420.0594. **FTIR (cm^{-1})** 3361, 3169, 3021, 2926, 2860, 1826, 1660, 1589, 1408, 1216, 931, 760, 667.

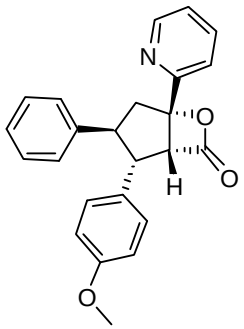
2-(4-(Dimethylamino)phenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3n)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(4-(dimethylamino)phenyl)acrylaldehyde **2n** (0.105 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-(4-(dimethylamino)phenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3n** as a gray solid (0.133 g, 69% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.35; Melting point: 143-145 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 (d, J = 4.8 Hz, 1H, H_{ar}), 7.78 (td, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H, H_{ar}), 7.65 (d, J = 7.9 Hz, 1H, H_{ar}), 7.33-7.24 (m, 5H, H_{ar}), 7.19-7.15 (m, 3H, H_{ar}), 6.64 (d, J = 8.8 Hz, 2H, H_{ar}), 4.20 (d, J = 7.1 Hz, 1H), 3.92-3.80 (m, 2H), 2.90 (s, 6 H), 2.86-2.72 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.82, 157.93, 149.81, 149.63, 140.13, 137.03, 129.09, 128.64, 127.85, 126.93, 123.22, 120.27, 112.57, 86.58, 66.52, 52.09, 47.34, 44.60, 40.59.**HRMS** calculated $[M+H]^+$ for $C_{25}H_{25}O_2N_2$: 385.1911, found: 385.1912. **FTIR (cm^{-1})** 3360, 3018, 1822, 1659, 1641, 1572, 1524, 1438, 1215, 1078, 817, 756, 668.

2-(4-Methoxyphenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3o)

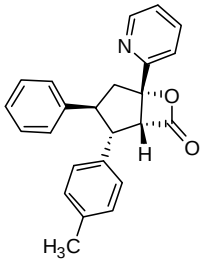


Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(4-methoxyphenyl)acrylaldehyde **2o** (0.097 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-(4-methoxyphenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3o** as a white solid (0.156 g, 84% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.38; Melting point: 107-109 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, J = 4.8 Hz, 1H, H_{ar}), 7.79 (td, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H, H_{ar}), 7.66 (d, J = 7.1 Hz, 1H, H_{ar}), 7.33-7.18 (m, 8H, H_{ar}), 6.62 (d, J = 8.6 Hz, 2H, H_{ar}), 4.24 (d, J = 6.9 Hz,

1H), 3.93-3.84 (m, 2H), 3.76 (s, 3 H), 2.89-2.75 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.64, 158.80, 157.66, 149.61, 139.73, 137.04, 129.43, 128.66, 127.76, 127.67, 127.06, 123.28, 120.23, 113.94, 86.56, 66.32, 55.17, 52.09, 47.47, 44.45. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{22}O_3N$: 372.1594, found: 372.1591. **FTIR (cm-1)** 3361, 3166, 3019, 2933, 1823, 1613, 1593, 1515, 1215, 1039, 828, 756, 668.

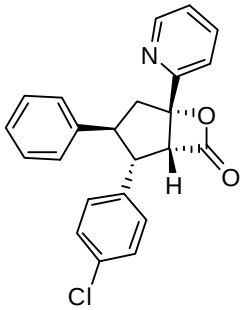
3-Phenyl-5-(pyridin-2-yl)-2-(p-tolyl)-6-oxabicyclo[3.2.0]heptan-7-one (3p)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(p-tolyl)acrylaldehyde **2p** (0.088 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2,3-diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3p** as a white solid (0.149 g, 84% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.5; Melting point: 44-46 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (d, *J* = 4.8 Hz, 1H, H_{ar}), 7.78 (td, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H, H_{ar}), 7.64 (d, *J* = 7.8 Hz, 1H, H_{ar}), 7.31-7.23 (m, 6H, H_{ar}), 7.17 (d, *J* = 8.2 Hz, 3H, H_{ar}), 7.06 (d, *J* = 7.9 Hz, 2H, H_{ar}), 4.22 (d, *J* = 6.9 Hz, 1H), 3.94-3.83 (m, 2H), 2.82-2.74 (m, 2H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.59, 157.76, 149.66, 139.81, 137.08, 132.64, 129.33, 128.71, 128.30, 127.81, 127.09, 123.31, 120.30, 86.64, 66.48, 52.36, 47.18, 44.66, 21.22. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{22}O_2N$: 356.1645, found: 356.1642. **FTIR (cm^{-1})** 3686, 3620, 3022, 1823, 1658, 1592, 1518, 1427, 1216, 1124, 1040, 928, 768, 670.

2-(4-Chlorophenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3q)

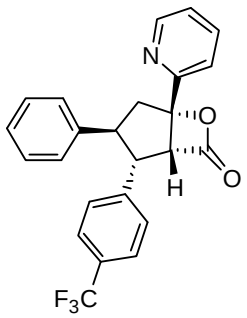


Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(4-chlorophenyl)acrylaldehyde **2q** (0.100 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-(4-chlorophenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3q** as a white solid (0.150 g, 80% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.41; Melting point: 113-115 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, *J* = 4.8 Hz, 1H, H_{ar}), 7.80 (td, *J* = 7.7 Hz, 1.7 Hz, 1H, H_{ar}), 7.66 (d, *J* = 7.9

Hz, 1H, H_{ar}), 7.35-7.28 (m, 5H, H_{ar}), 7.27-7.19 (m, 5H, H_{ar}), 4.27-4.25 (m, 1H), 3.90-3.83 (m, 2H), 2.89-2.76 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.35, 157.45, 149.68, 139.23, 137.12, 134.38, 133.33, 129.81, 128.81, 128.78, 127.73, 127.32, 123.40, 120.27, 86.58, 66.04, 52.26, 47.61, 44.45. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{19}O_2NCl$: 376.1099, found: 376.1100. **FTIR (cm^{-1})** 3683, 3620, 3019, 2976, 2400, 1823, 1593, 1521, 1429, 1216, 1127, 1043, 769, 669.

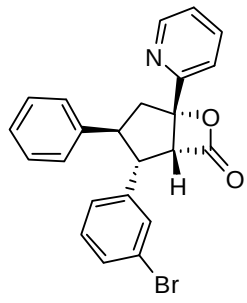
3-Phenyl-5-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)-6-oxabicyclo[3.2.0]heptan-7-one (3r)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde **2r** (0.120 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-Phenyl-5-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)-6-oxabicyclo[3.2.0]heptan-7-one **3r** as a light yellow solid (0.130 g, 64% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.32; Melting point: 95-97 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (d, *J* = 4.7 Hz, 1H, H_{ar}), 7.80-7.76 (m, 1H, H_{ar}), 7.62 (d, *J* = 7.8 Hz, 1H, H_{ar}), 7.50-7.48 (m, 2H, H_{ar}), 7.39-7.35 (m, 2H, H_{ar}), 7.32 – 7.23 (m, 5H, H_{ar}), 7.20-7.17 (m, 1H, H_{ar}), 4.26 (d, *J* = 6.5 Hz, 1H), 3.94-3.84 (m, 2H), 2.87 – 2.74 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.19, 157.35, 149.72, 140.06, 139.04, 137.18, 128.91, 128.86, 127.72, 127.45, 125.60, 125.56, 123.48, 120.30, 86.62, 65.96, 52.52, 47.58, 44.60. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.47. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{19}O_2NF_3$: 410.1362, found: 410.1361. **FTIR (cm^{-1})** 3022, 1823, 1590, 1425, 1326, 1216, 1125, 1031, 765, 668.

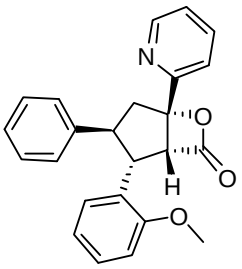
2-(3-Bromophenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3s)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(3-bromophenyl)acrylaldehyde **2s** (0.127 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-(3-bromophenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3s** as a white solid (0.150 g, 71% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.45; Melting point: 144-146 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (d, *J* = 4.7 Hz, 1H, H_{ar}), 7.79 (td, *J* = 7.7, 1.6 Hz, 1H, H_{ar}), 7.64 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.42 (s, 1H, H_{ar}), 7.35-7.19 (m, 8H, H_{ar}), 7.14 (t, *J* = 7.8 Hz, 1H, H_{ar}), 4.25 (d, *J* = 6.8 Hz, 1H), 3.91-3.81 (m, 2H), 2.88-2.73 (m, 2H) **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.12, 157.41, 149.69, 139.16, 138.24, 137.12, 131.81, 130.69, 130.13, 128.86, 127.74, 127.36, 126.86, 123.41, 122.63, 120.27, 86.54, 66.11, 52.28, 47.27, 44.50. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{19}O_2NBr$: 420.0594, found: 420.0594. **FTIR (cm^{-1})** 3685, 3619, 3022, 2402, 1823, 1589, 1523, 1480, 1216, 1041, 771, 672.

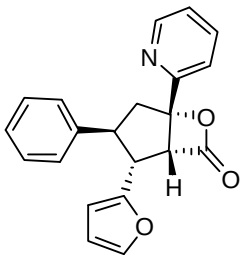
2-(2-Methoxyphenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3t)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(2-methoxyphenyl)acrylaldehyde **2t** (0.097 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-(2-methoxyphenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3t** as a white solid (0.102 g, 56% yield).

R_f (Pet. ether /EtOAc = 60/40): 0.44; Melting point: 151-153 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 4.8 Hz, 1H, H_{ar}), 7.77 (td, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H, H_{ar}), 7.65 (d, *J* = 7.9 Hz, 1H, H_{ar}), 7.38 (d, *J* = 7.4 Hz, 2H, H_{ar}), 7.33-7.26 (m, 4H, H_{ar}), 7.23-7.17 (m, 2H, H_{ar}), 6.90 (t, *J* = 7.6 Hz, 1H, H_{ar}), 6.84 (d, *J* = 8.3 Hz, 1H, H_{ar}), 4.46 (d, *J* = 7.6 Hz, 1H), 4.38-4.33 (m, 1H), 4.08-4.01 (m, 1H), 3.81 (s, 3H, CH_3), 2.90-2.74 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.83, 157.71, 157.58, 149.57, 140.05, 136.94, 128.65, 128.31, 127.95, 127.80, 126.92, 123.97, 123.20, 120.56, 120.29, 110.17, 86.70, 77.48, 77.16, 76.84, 64.56, 55.31, 44.97, 44.54, 44.46.**HRMS** calculated $[M+H]^+$ for $C_{24}H_{22}O_3N$: 372.1594 , found: 372.1594. **FTIR (cm^{-1})** 3361, 3167, 3018, 2928, 1823, 1662, 1592, 1437, 1311, 1245, 1215, 1053, 755,668.

2-(Furan-2-yl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3u)

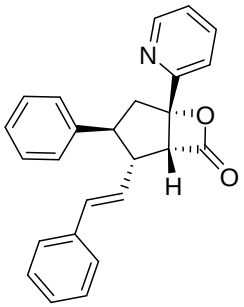


Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-3-(furan-2-yl)acrylaldehyde **2u** (0.073 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5

mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-(furan-2-yl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0] heptan-7-one **3u** as a white solid (0.127 g, 77% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.47; Melting point: 157-159 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.67-8.65 (m, 1H, H$_{ar}$), 7.78 (td, *J* = 7.7 Hz, 1.7 Hz, 1H, H$_{ar}$), 7.64 (d, *J* = 7.9 Hz, 1H, H$_{ar}$), 7.34-7.22 (m, 7H, H$_{ar}$), 6.26-6.17 (m, 2H, H$_{ar}$), 4.32 (d, *J* = 7.3 Hz, 1H), 3.96-3.81 (m, 2H), 2.83-2.73 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.77, 157.41, 150.63, 149.67, 142.09, 139.51, 137.08, 128.78, 127.65, 127.35, 123.37, 120.26, 110.40, 107.64, 86.70, 64.68, 47.23, 46.30, 44.14. **HRMS** calculated $[M+H]^+$ for $C_{21}H_{18}O_3N$: 332.1281 , found: 332.1277. **FTIR (cm^{-1})** 3022, 1827, 1592, 1425, 1216, 1123, 1037, 927, 751, 669.

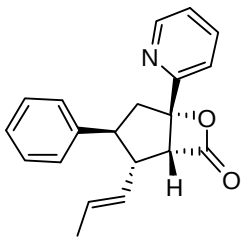
3-Phenyl-5-(pyridin-2-yl)-2-((*E*)-styryl)-6-oxabicyclo[3.2.0]heptan-7-one (3v)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (2*E*,4*E*)-5-phenylpenta-2,4-dienal **2v** (0.095 g, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 3-phenyl-5-(pyridin-2-yl)-2-((*E*)-styryl)-6-oxabicyclo[3.2.0] heptan-7-one **3v** as a light yellow foam (0.159 g, 87% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.52; Melting point: 93-95 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.65 (d, *J* = 4.7 Hz, 1H, H$_{ar}$), 7.77 (td, *J* = 7.8, 1.6 Hz, 1H, H$_{ar}$), 7.62 (d, *J* = 7.9 Hz, 1H, H$_{ar}$), 7.32-7.22 (m, 10H, H$_{ar}$), 7.19-7.15 (m, 1H, H$_{ar}$), 6.32-6.21 (m, 2H), 4.14 (d, *J* = 7.6 Hz, 1H), 3.50-3.43 (m, 1H), 3.36-3.30 (m, 1H), 2.79-2.71 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.73, 157.61, 149.67, 139.53, 137.08, 136.87, 133.68, 128.75, 128.55, 128.02, 127.64, 127.24, 126.55, 125.11, 123.33, 120.30, 87.05, 65.48, 51.79, 49.15, 43.77. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{22}O_2N$: 368.1645, found: 368.1643. **FTIR (cm^{-1})** 3022, 1821, 1591, 1428, 1215, 1096, 1039, 927, 765, 670.

3-Phenyl-2-((*E*)-prop-1-en-1-yl)-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3w)

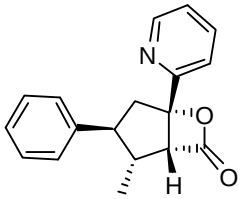


Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (2*E*,4*E*)-hexa-2,4-dienal **2w** (0.058 g, 64 µL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at

25 °C for 24 h followed by flash column chromatography afforded 3-phenyl-2-((*E*)-prop-1-en-1-yl)-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3w** as a white solid (0.127 g, 83% yield, dr determined by ^{1}H NMR analysis of crude reaction mixture is 5:1).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.58; Melting point: 96-98 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.65-8.61 (m, 1H, H$_{ar}$), 7.78-7.73 (m, 1H, H$_{ar}$), 7.62-7.58 (m, 1H, H$_{ar}$), 7.33-7.20 (m, 6H, H$_{ar}$), 5.59-5.36 (m 2H), 4.03 (d, *J* = 7.7 Hz, 1H), 3.35-3.26 (m, 1H), 3.17-3.10 (m, 1H), 2.80-2.59 (m, 2H), 1.56 (d, *J* = 5.5 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.03, 157.74, 149.61, 139.92, 137.02, 129.76, 128.61, 128.03, 127.06, 126.07, 123.24, 120.26, 86.95, 65.42, 51.25, 48.83, 43.85, 18.15. Representative Peaks of Minor Isomer: **^{1}H NMR** δ 4.00 (d, *J* = 7.8 Hz), 3.49-3.42 (m), 1.28-1.24 (m). **^{13}C NMR** δ 128.72, 127.97, 127.15, 125.56, 64.98, 49.43, 46.02, 43.12, 13.10. **HRMS** calculated $[M+H]^+$ for $C_{20}H_{20}O_2N$: 306.1489, found: 306.1487. **FTIR (cm^{-1})** 3019, 1818, 1593, 1437, 1215, 1103, 1036, 930, 763, 669.

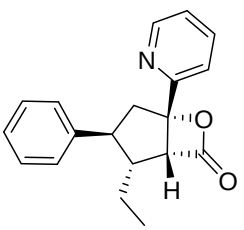
2-Methyl-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3x)



Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and *(E)*-but-2-enal **2x** (0.042 g, 49 μL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2-methyl-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3x** as a white solid (0.102 g, 73% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.5; Melting point: 77-79 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.65 (d, *J* = 4.3 Hz, 1H, H$_{ar}$), 7.77 (td, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H, H$_{ar}$), 7.62 (d, *J* = 7.8 Hz, 1H, H$_{ar}$), 7.39-7.33 (m, 4H, H$_{ar}$), 7.31-7.26 (m, 2H, H$_{ar}$), 4.04 (d, *J* = 7.6 Hz, 1H), 3.15-3.05 (m, 1H), 2.67 (d, *J* = 9.1 Hz, 2H), 2.64-2.55 (m, 1H), 1.15 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.29, 157.82, 149.54, 140.20, 136.95, 128.77, 127.87, 127.19, 123.18, 120.22, 87.17, 65.67, 50.47, 44.08, 42.94, 12.96. **HRMS** calculated $[M+H]^+$ for $C_{18}H_{18}O_2N$: 280.1332, found: 280.1329. **FTIR (cm^{-1})** 3360, 3019, 2969, 1824, 1661, 1592, 1437, 1339, 1215, 1082, 977, 756, 668.

2-Ethyl-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3y)

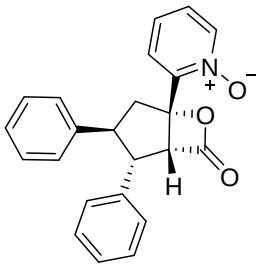


Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.104 g 0.5 mmol) and (*E*)-pent-2-enal **2y** (0.050 g, 58 μL, 0.6 mmol) with imidazolium salt **4** (0.034 g, 0.1

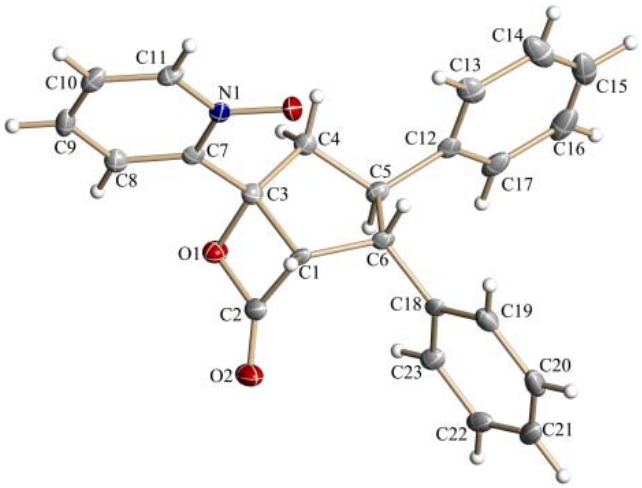
mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in THF (2.5 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2,3-diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **3y** as a red solid (0.089 g, 61% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.61; Melting point: 96-98 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.65 (d, *J* = 4.8 Hz, 1H, H$_{ar}$), 7.77 (td, *J*$_1$ = 7.7 Hz, *J*$_2$ = 1.7 Hz, 1H, H$_{ar}$), 7.62 (d, *J* = 7.9 Hz, 1H, H$_{ar}$),7.38-7.25 (m, 7H, H$_{ar}$), 4.17 (d, *J* = 7.7 Hz, 1H), 3.19-3.12 (m, 1H), 2.67-2.64 (m, 2H), 2.50-2.42 (m, 1H), 1.59-1.51 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.14, 157.96, 149.56, 140.58, 136.98, 128.78, 127.96, 127.18, 123.20, 120.28, 87.07, 63.62, 50.31, 49.73, 44.21, 22.16, 13.09. **HRMS** calculated $[M+H]^+$ for $C_{19}H_{20}O_2N$: 294.1489, found: 294.1487. **FTIR (cm^{-1})** 3022, 2970, 2931, 2885, 1822, 1591, 1467, 1429, 1216, 1164, 1094, 1033, 928, 762, 669.

2-(7-Oxo-2,3-diphenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10a)

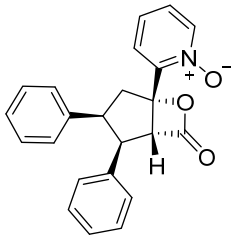


Following the general procedure, treatment of 2-cinnamoylpyridine 1-oxide **9a** (0.112 g, 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.066 g, 62 µL, 0.5 mmol) with imidazolium salt **4** (0.017 g, 0.05 mmol) and DBU (0.015 g, 15 µL, 0.1 mmol) in DME (2.5 mL) at 25 °C for 4 h followed by flash column chromatography afforded 2-(7-oxo-2,3-diphenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide **10a** as a white solid (0.11 g, 82% yield, 3:1 dr (62% of **10a** and 20% of **10a'**after isolation)). CCDC 1057299 (For the further detail about crystal structure please visit http://www.ccdc.cam.ac.uk/deposit/)



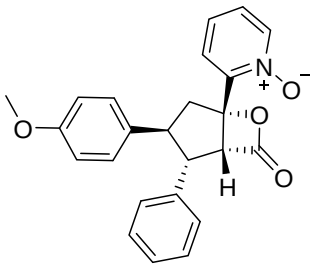
Major diastereomer (10a): ***R*$_f$** (EtOAc): 0.26; Melting point: 181-183 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.26 (d, *J* = 6.4 Hz, 1H, H$_{ar}$), 7.63 (dd, *J*$_1$ = 7.8 Hz, *J*$_2$ = 2.0 Hz, 1H, H$_{ar}$), 7.40(td, *J*$_1$ = 7.7 Hz, *J*$_2$ = 1.0 Hz, 1H, H$_{ar}$), 7.36-7.27 (m, 5H, H$_{ar}$), 7.25-7.12 (m, 6H, H$_{ar}$), 4.45 (d, *J* = 7.6 Hz, 1H), 4.29 (dd, *J*$_1$ = 12.3 Hz, *J*$_2$ = 7.5 Hz, 1H), 3.91-3.84 (m, 1H), 3.05 (dd, *J*$_1$ = 14.1 Hz, *J*$_2$ = 11.7 Hz, 1H), 2.52 (dd, *J*$_1$ = 14.1 Hz, *J*$_2$ = 6.7 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.44, 158.57, 147.78, 139.99, 136.04, 131.88, 128.83, 128.55, 128.46, 127.34,

126.54, 125.80, 124.34, 114.04, 83.68, 65.12, 55.24, 52.83, 47.25, 40.66. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{20}O_3N$: 358.1438, found: 358.1436. **FTIR (cm^{-1})** 3361, 3019, 2925, 2853, 1826, 1662, 1619, 1432, 1215, 1079, 756, 669.



Minor diastereomer (10a'): R_f (EtOAc): 0.33; Melting point: 132-134 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.36-8.32 (m, 1H, H_{ar}), 7.69 (dd, J_1 = 7.5 Hz, J_2 = 2.4 Hz, 1H, H_{ar}), 7.46-7.37 (m, 4H, H_{ar}), 7.26-7.17 (m, 8H, H_{ar}), 4.73 (td, J_1 = 11.3 Hz, J_2 = 8.7 Hz, 1H), 4.39 (d, J = 6.6 Hz, 1H), 3.86 (dd, J_1 = 11.3 Hz, J_2 = 6.6 Hz, 1H), 2.99 (dd, J_1 = 14.7 Hz, J_2 = 8.6 Hz, 1H), 2.73 (dd, J_1 = 14.7 Hz, J_2 = 11.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.14, 149.00, 141.19, 140.91, 139.75, 128.79, 128.68, 128.00, 127.66, 127.19, 127.06, 126.56, 125.89, 124.32, 86.47, 77.48, 77.16, 76.84, 68.40, 60.98, 56.06, 44.47. **HRMS** calculated $[M+H]^+$ for $C_{23}H_{20}O_3N$: 358.1438, found: 358.1436. **FTIR (cm^{-1})** 3021, 2980, 1830, 1722, 1601, 1488, 1432, 1216, 1132, 1040, 910, 765, 663.

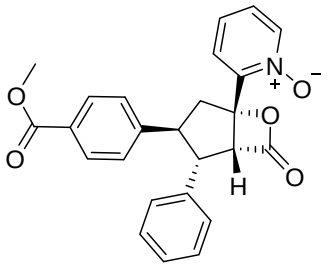
2-(3-(4-Methoxyphenyl)-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10b)



Following the general procedure, treatment of (*E*)-2-(3-(4-methoxyphenyl)acryloyl)pyridine 1-oxide **9b** (0.127 g, 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.066 g, 62 μL, 0.5 mmol) with imidazolium salt **4** (0.017 g, 0.05 mmol) and DBU (0.015 g, 15 μL, 0.1 mmol) in DME (2.5 mL) at 25 °C for 4 h followed by flash column chromatography afforded 2-(3-(4-methoxyphenyl)-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide **10b** as a yellow solid (0.113 g, 59% yield).

R_f (EtOAc): 0.27; Melting point: 102-104 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (d, J = 6.2 Hz, 1H, H_{ar}), 7.63 (dd, J_1 = 7.8 Hz, J_2 = 2.0 Hz, 1H, H_{ar}), 7.39(td, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H, H_{ar}), 7.35-7.16 (m, 8H, H_{ar}), 6.76 (d, J = 8.7 Hz, 2H, H_{ar}), 4.44 (d, J = 7.5 Hz, 1H), 4.24 (dd, J_1 = 12.3 Hz, J_2 = 7.5 Hz, 1H), 3.86-3.79 (m, 1H), 3.71 (S, 3H), 3.02 (dd, J_1 = 14.1 Hz, J_2 = 11.7 Hz, 1H), 2.49 (dd, J_1 = 14.1 Hz, J_2 = 6.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.44, 158.57, 147.78, 139.99, 136.04, 131.88, 128.83, 128.55, 128.46, 127.34, 126.54, 125.80, 124.34, 114.04, 83.68, 65.12, 55.24, 52.83, 47.25, 40.66. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{22}O_4N$: 388.1543, found: 388.1540. **FTIR (cm^{-1})** 3361, 3019, 2927, 2400, 1828, 1662, 1614, 1493, 1215, 1037, 756, 668.

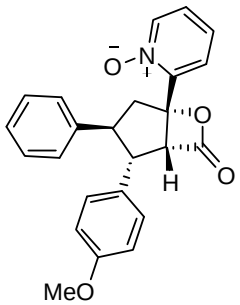
2-(3-(4-(Methoxycarbonyl)phenyl)-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10c)



Following the general procedure, treatment of (*E*)-2-(3-(4-(methoxycarbonyl) phenyl)acryloyl)pyridine 1-oxide **9c** (0.141 g, 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.066 g, 62 µL, 0.5 mmol) with imidazolium salt **4** (0.017 g, 0.05 mmol) and DBU (0.015 g, 15 µL, 0.1 mmol) in DME (2.5 mL) at 25 °C for 4 h followed by flash column chromatography afforded 2-(3-(4-(methoxycarbonyl)phenyl)-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide **10c** as a yellow solid (0.141 g, 69% yield).

R_f (EtOAc): 0.27; Melting point: 96-98 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 6.3 Hz, 1H, H_{ar}), 7.89 (d, *J* = 8.2 Hz, 2H, H_{ar}), 7.65-7.63 (m, 1H, H_{ar}), 7.43-7.34 (m, 4H, H_{ar}), 7.27-7.17 (m, 5H, H_{ar}), 4.47 (d, *J* = 7.5 Hz, 1H), 4.30 (dd, J_1 = 12.3 Hz, J_2 = 7.4 Hz, 1H), 3.96-3.90 (m, 1H), 3.85 (S, 3H), 3.08 (dd, J_1 = 14.1 Hz, J_2 = 11.7 Hz, 1H), 2.54 (dd, J_1 = 14.1 Hz, J_2 = 6.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.10, 166.90, 147.52, 145.36, 140.01, 135.46, 129.99, 129.07, 128.57, 128.44, 127.98, 127.59, 126.66, 125.93, 124.35, 83.66, 65.17, 52.85, 52.11, 48.21, 40.38. **HRMS** calculated $[M+H]^+$ for $C_{25}H_{22}O_5N$: 416.1492, found: 416.1488. **FTIR (cm^{-1})** 3685, 3619, 3022, 2403, 1832, 1716, 1607, 1431, 1216, 1118, 1036, 926, 765, 671.

2-(4-Methoxyphenyl)-7-oxo-3-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10d)

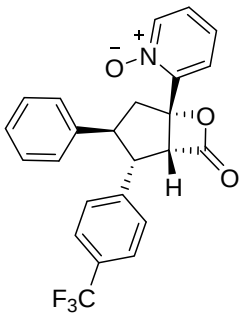


Following the general procedure, treatment of 2-cinnamoylpyridine 1-oxide **9a** (0.113 g 0.5 mmol) and (*E*)-3-(4-methoxyphenyl) acrylaldehyde **2o** (0.081 g, 0.5 mmol) with imidazolium salt **4** (0.017 g, 0.05 mmol) and DBU (0.015 g, 15 µL, 0.1 mmol) in DME (2.5 mL) at 25 °C for 4 h followed by flash column chromatography afforded 2-(4-methoxyphenyl)-7-oxo-3-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide **10d** as a white solid (0.152 g, 82% yield).

R_f (EtOAc): 0.27; Melting point: 157-159 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (d, *J* = 6.2 Hz, 1H, H_{ar}), 7.67 (dd, J_1 = 7.8 Hz, J_2 = 2.0 Hz, 1H, H_{ar}), 7.46-7.41 (m, 1H, H_{ar}), 7.40-7.37 (m, 1H, H_{ar}), 7.35-7.33 (m, 2H, H_{ar}), 7.28-7.22 (m, 4H, H_{ar}), 7.20-7.16 (m, 1H, H_{ar}), 6.80 (d, *J* = 8.8 Hz, 2H, H_{ar}), 4.44 (d, *J* = 7.5 Hz, 1H), 4.29-4.24 (m, 1H), 3.89-3.80 (m, 1H), 3.75 (s, 3H), 3.10-3.04 (m, 1H), 2.56-2.51 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.62,

158.80, 147.85, 140.04, 129.54, 128.69, 127.96, 127.85, 127.09, 126.59, 125.83, 124.41, 113.93, 83.79, 65.23, 55.22, 52.13, 48.27, 40.64. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{22}O_4N$: 388.1543, found: 388.1541. **FTIR (cm^{-1})**3022, 1829, 1658, 1604, 1518, 1426, 1216, 1124, 1038, 928, 763, 670.

2-(7-Oxo-3-phenyl-2-(4-(trifluoromethyl)phenyl)-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10e)

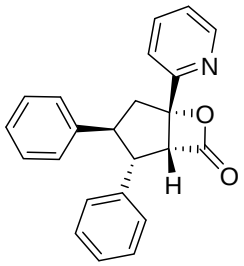


Following the general procedure, treatment of 2-cinnamoylpyridine 1-oxide **9e** (0.056 g 0.25 mmol) and (*E*)-3-(4-(trifluoromethyl) phenyl)acrylaldehyde **2r** (0.050 g, 0.25 mmol) with imidazolium salt **4** (0.008 g, 0.025 mmol) and DBU (0.008 g, 7.5 μL, 0.050 mmol) in DME (1 mL) at 25 °C for 24 h followed by flash column chromatography afforded 2,3-diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one **10e** as a white solid (0.076 g, 71% yield).

***R**f* (EtOAc): 0.27; Melting point: 161-163 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.29 (d, *J* = 6.1 Hz, 1H, H_{ar}), 7.66 (dd, *J* = 7.8 Hz, 1.9 Hz, 1H, H_{ar}), 7.52-7.50 (m, 2H, H_{ar}), 7.46-7.32 (m, 6H, H_{ar}), 7.28-7.25 (m, 2H, H_{ar}), 7.21-7.17 (m, 1H, H_{ar}), 4.49 (d, *J* = 7.4 Hz, 1H), 4.39-4.34 (m, 1H), 3.88 (td, *J* = 11.9 Hz, 6.6 Hz, 1H), 3.09 (dd, *J* = 14.1 Hz, 11.7 Hz, 1H), 2.57 (dd, *J* = 14.2 Hz, 6.7 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.16, 147.48, 140.24, 140.03, 139.37, 128.91, 128.88, 127.87, 127.42, 126.65, 125.99, 125.52, 125.48, 124.38, 83.76, 64.86, 52.47, 48.30, 40.72. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.56. **HRMS** calculated $[M+H]^+$ for $C_{24}H_{19}O_3NF_3$: 426.1312, found: 426.1308. **FTIR (cm^{-1})** 3019, 1827, 1657, 1592, 1421, 1326, 1216, 1069, 757, 669.

11.Characterization of Chiral β-lactone-fused Cyclopentane

2,3-Diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (*chiral*-3a)



Chiral-3a

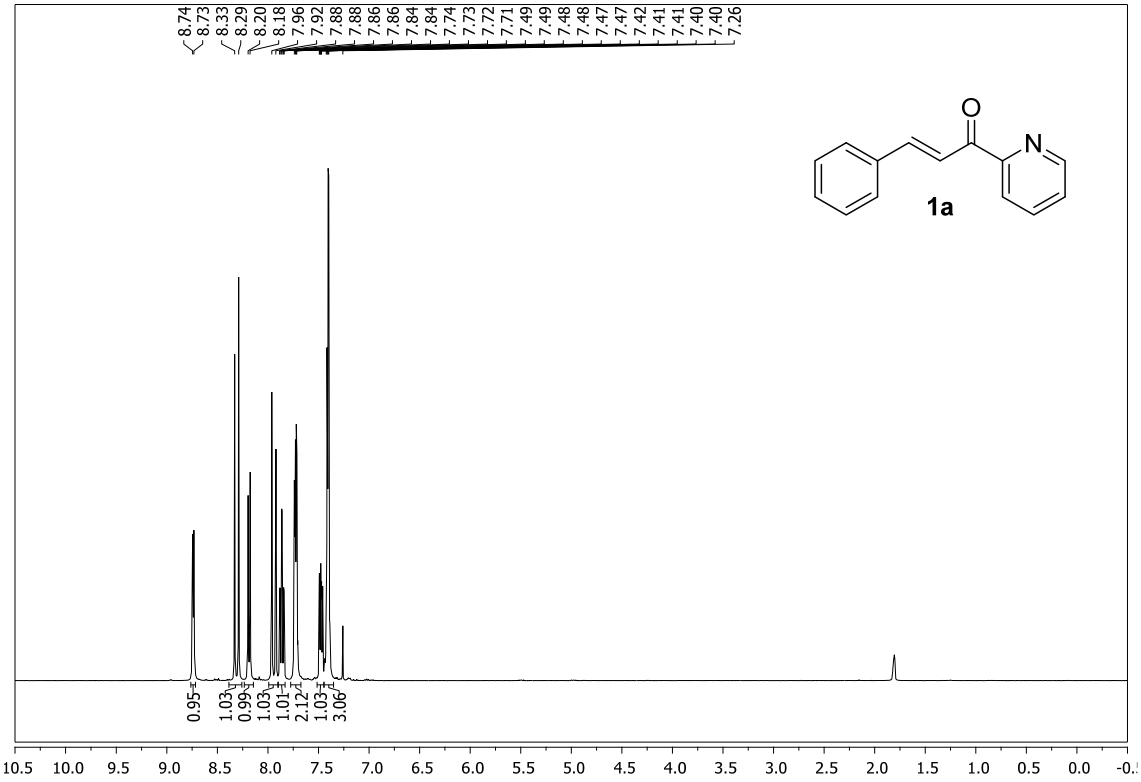
Following the general procedure, treatment of (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one **1a** (0.053 g 0.25 mmol) and *trans* cinnamaldehyde **2a** (0.033 g, 31 μL, 0.25 mmol) with triazolium salt **11** (0.018 g, 0.05 mmol) and DBU (0.015 g, 15 μL, 0.1 mmol) in Toluene (1.0 mL) at 25 °C for 24 h followed by flash column

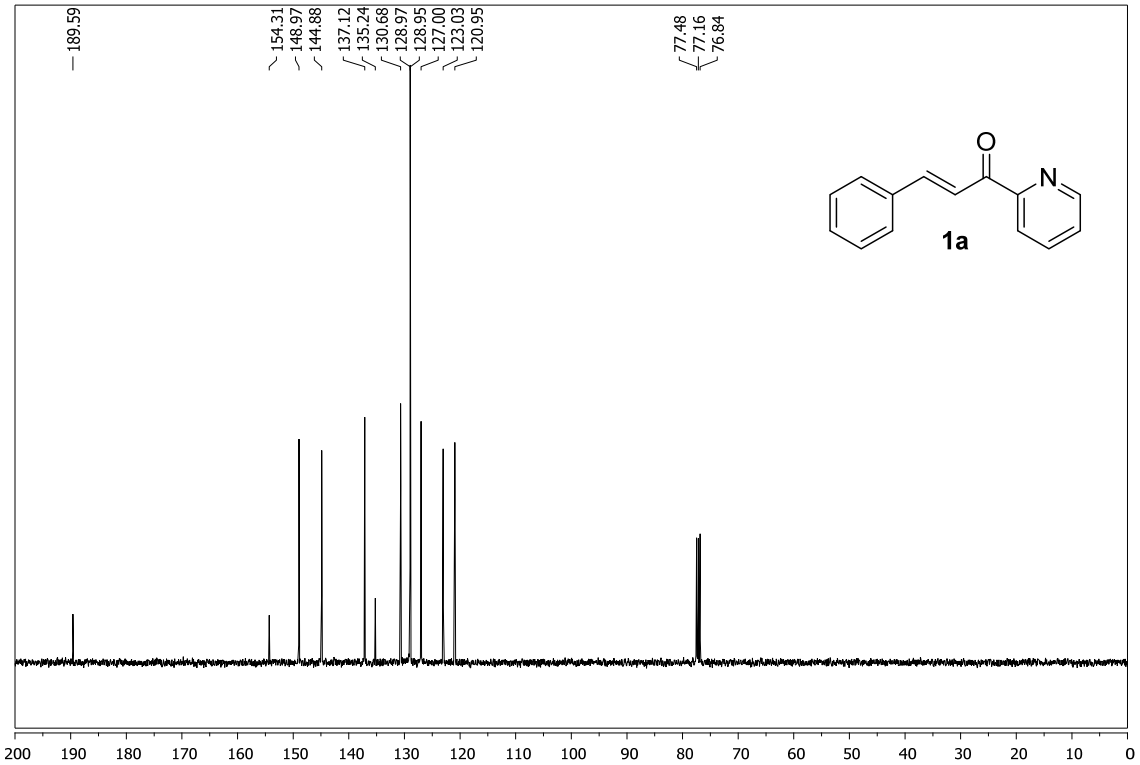
chromatography afforded 2,3-Diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (***Chiral*-3a**) as a white solid (0.048 g, 56% yield).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.47; 99% ee, $[\alpha]_D^{25}$ = +10.38 (c 0.1, $CHCl_3$). **HPLC** (Chiralcel OJ-H, 50:50 Pet ether / EtOH, 0.6 mL/min.) Major: 13.70 min, Minor: 37.89 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 4.6 Hz, 1H, H_{ar}), 7.82-7.79 (m, 1H, H_{ar}), 7.67 (d, *J* = 7.8 Hz, 1H, H_{ar}), 7.34-7.18 (m, 11H, H_{ar}), 4.28 (d, *J* = 6.4 Hz, 1H), 3.99-3.89 (m, 2H), 2.90-2.77 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.47, 157.67, 149.65, 139.66, 137.09, 135.79, 128.71, 128.56, 128.47, 127.79, 127.51, 127.12, 123.33, 120.28, 86.60, 66.37, 52.75, 47.27, 44.57.

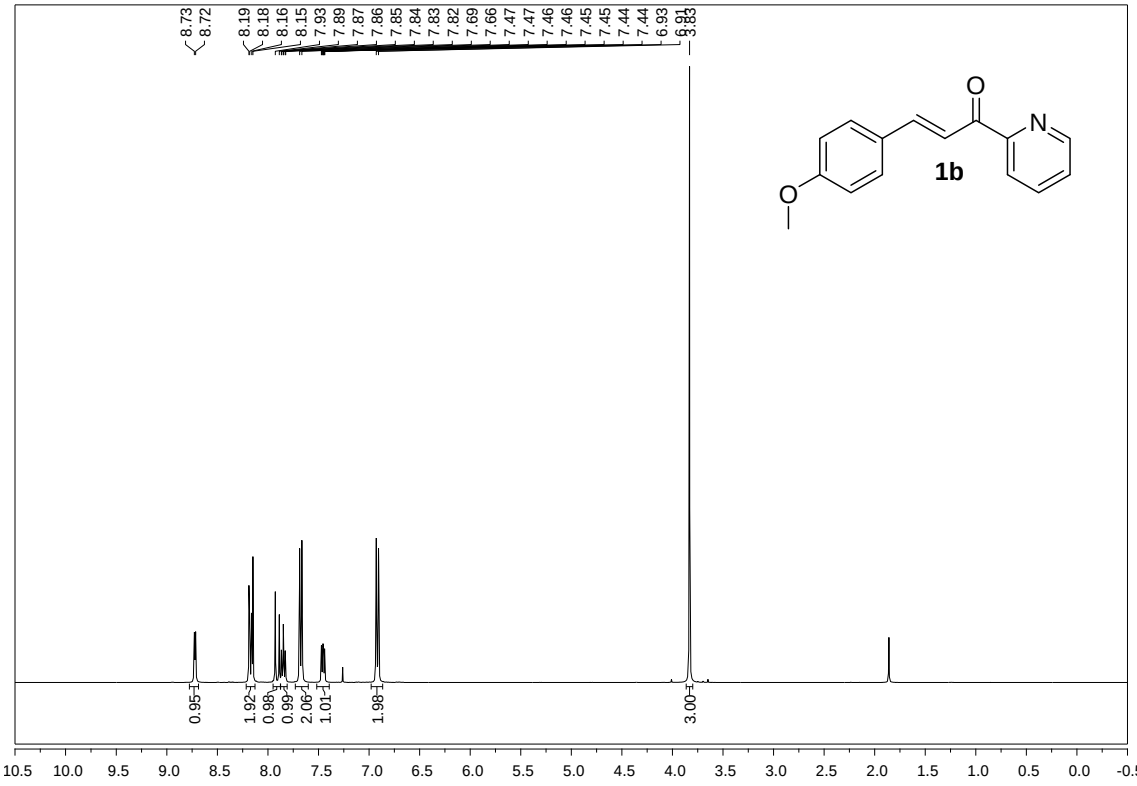
12. ^{1}H and ^{13}C NMR Spectra of 2-Enoylpyridines

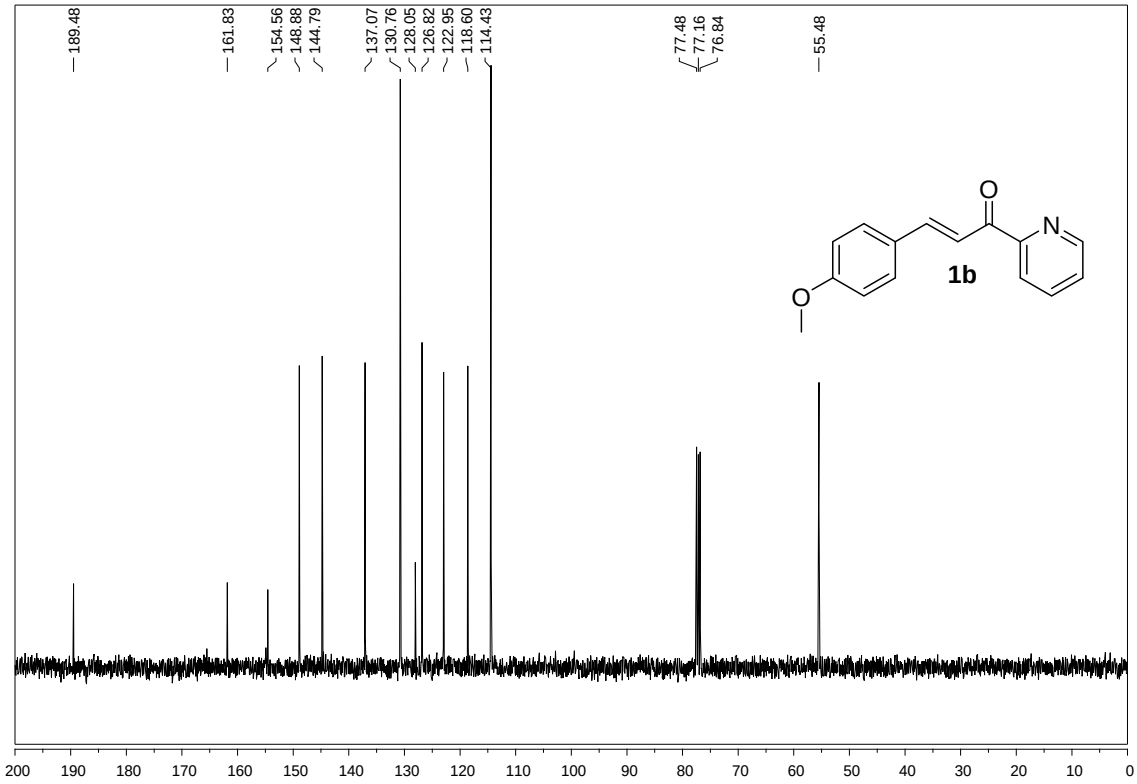
(*E*)-3-Phenyl-1-(pyridin-2-yl)prop-2-en-1-one (1a)



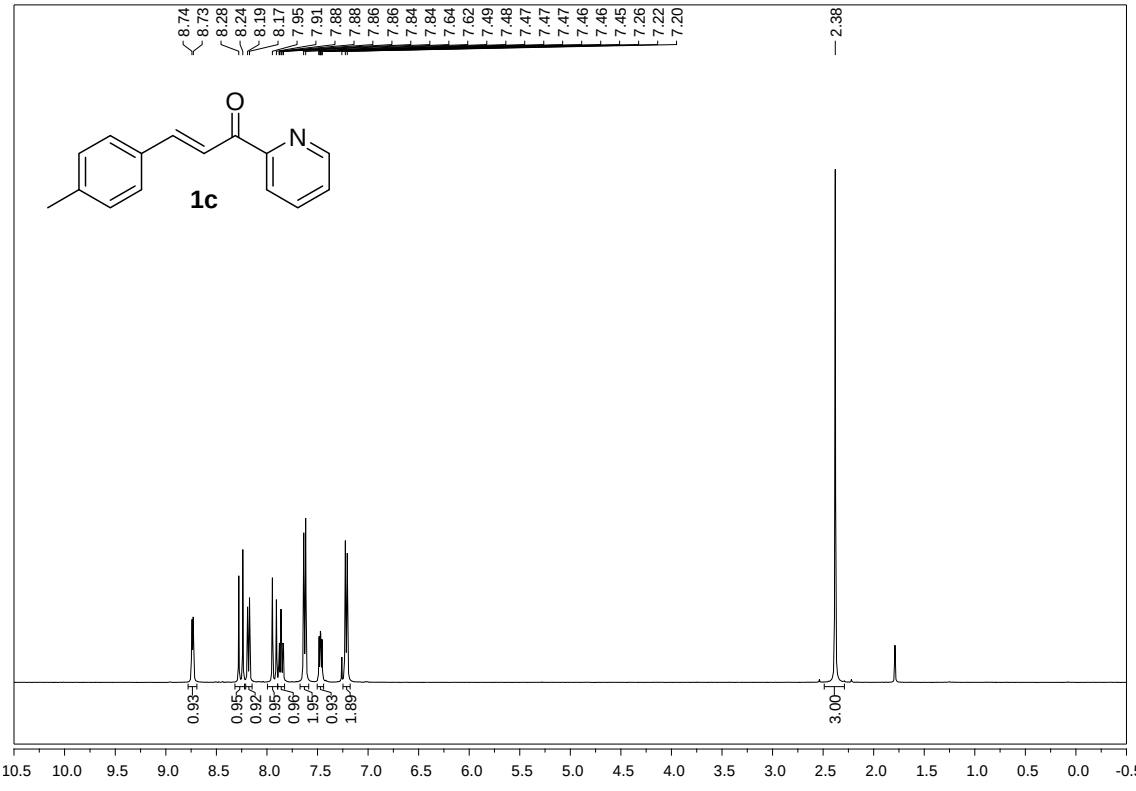


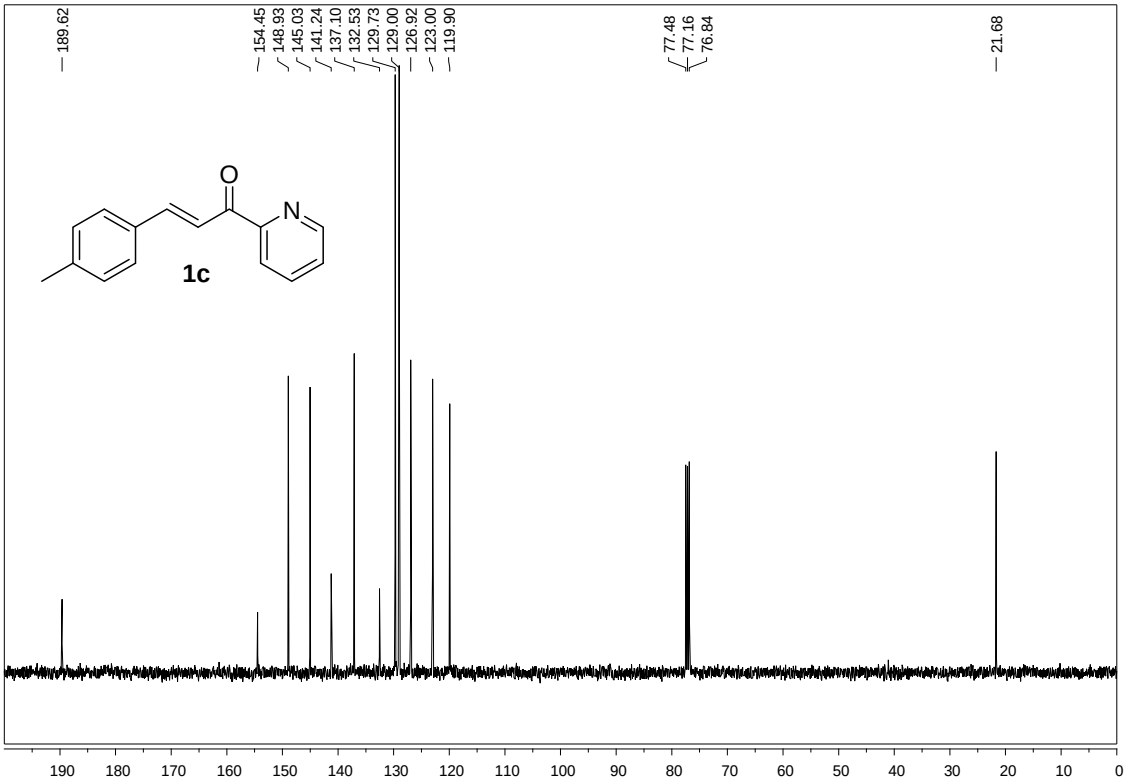
(*E*)-3-(4-Methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1b)



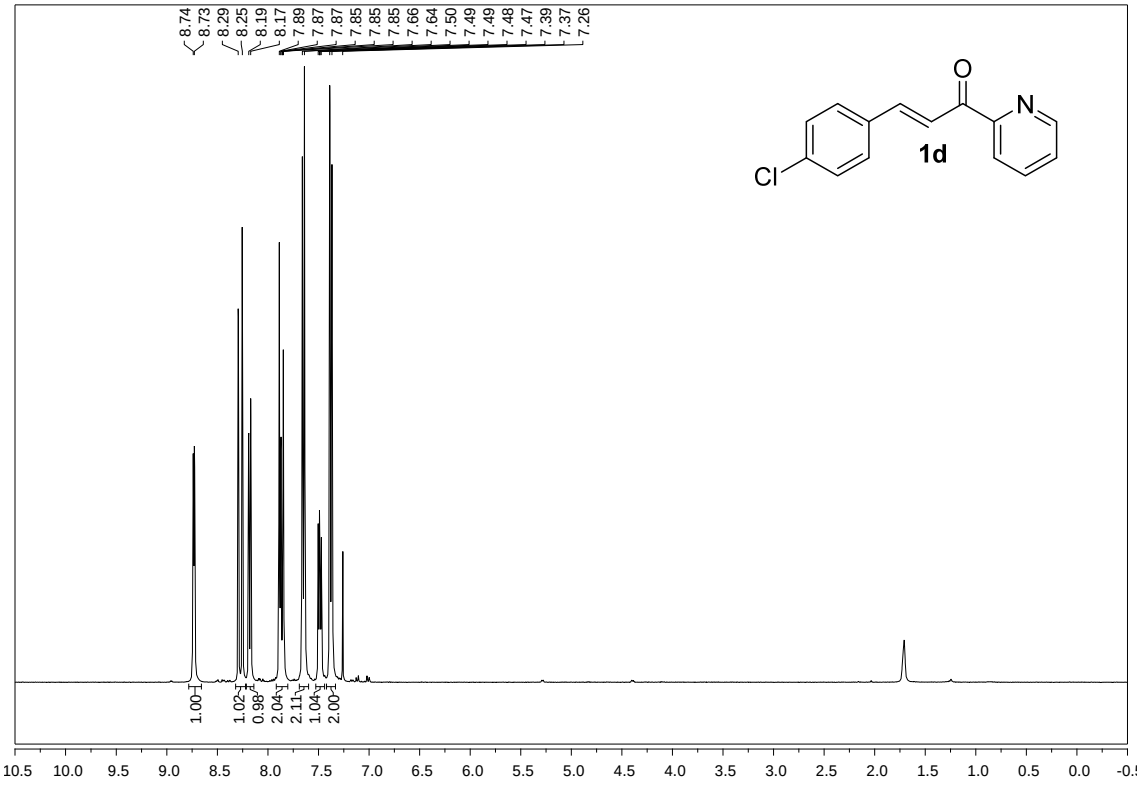


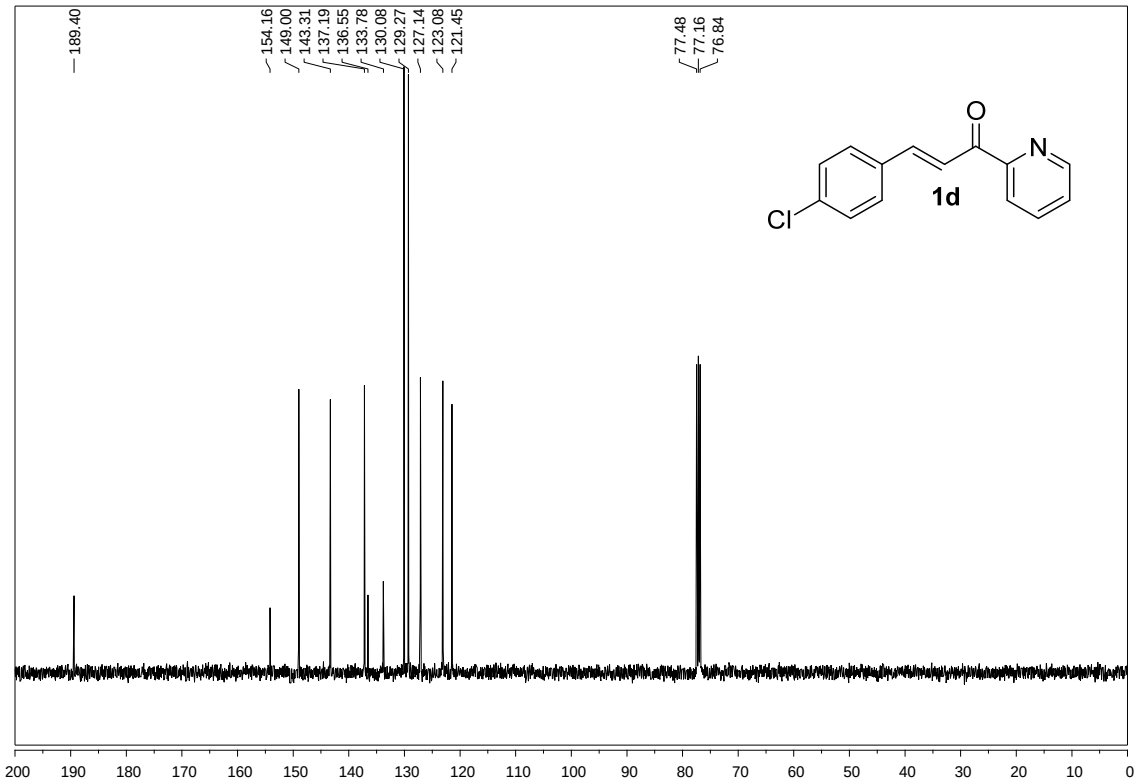
(*E*)-1-(Pyridin-2-yl)-3-(p-tolyl)prop-2-en-1-one (1c)



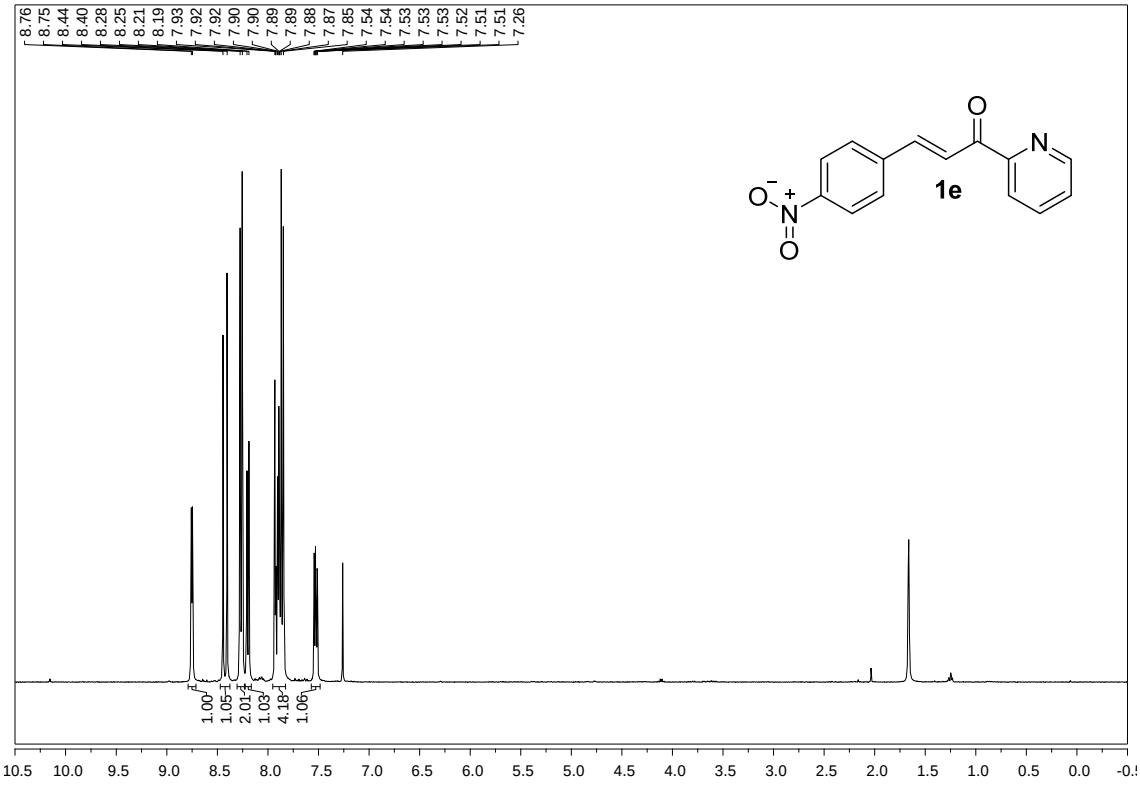


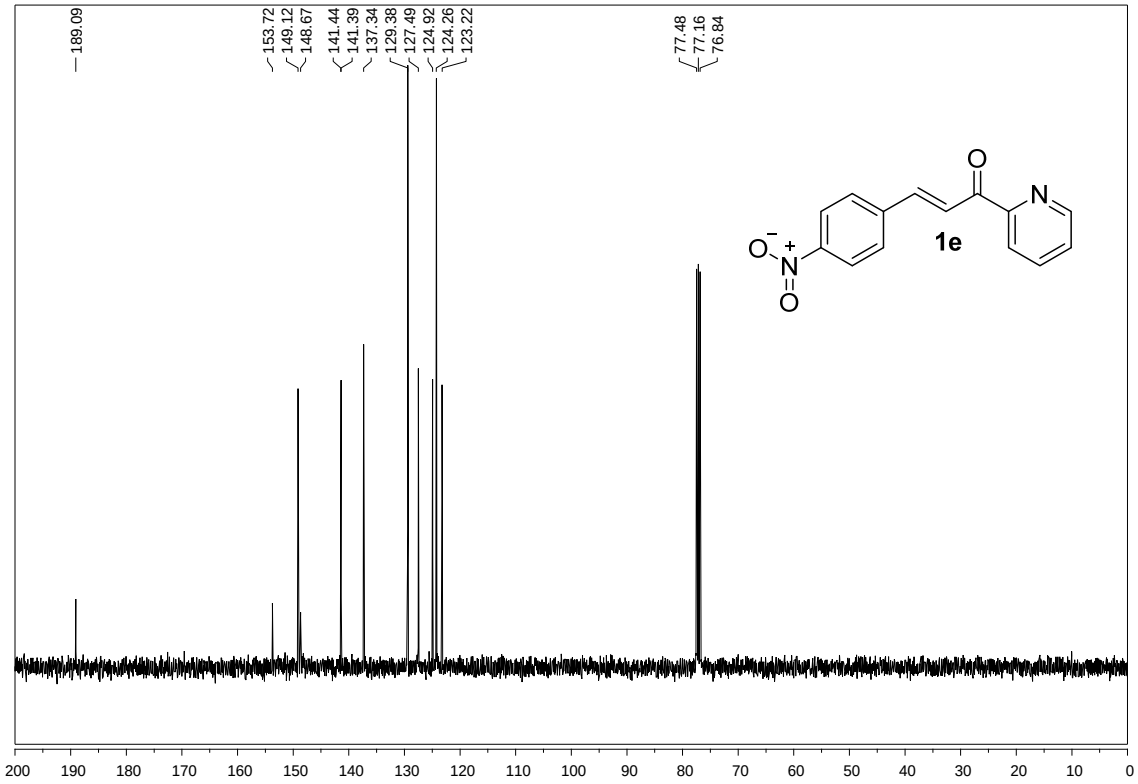
(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (1d)



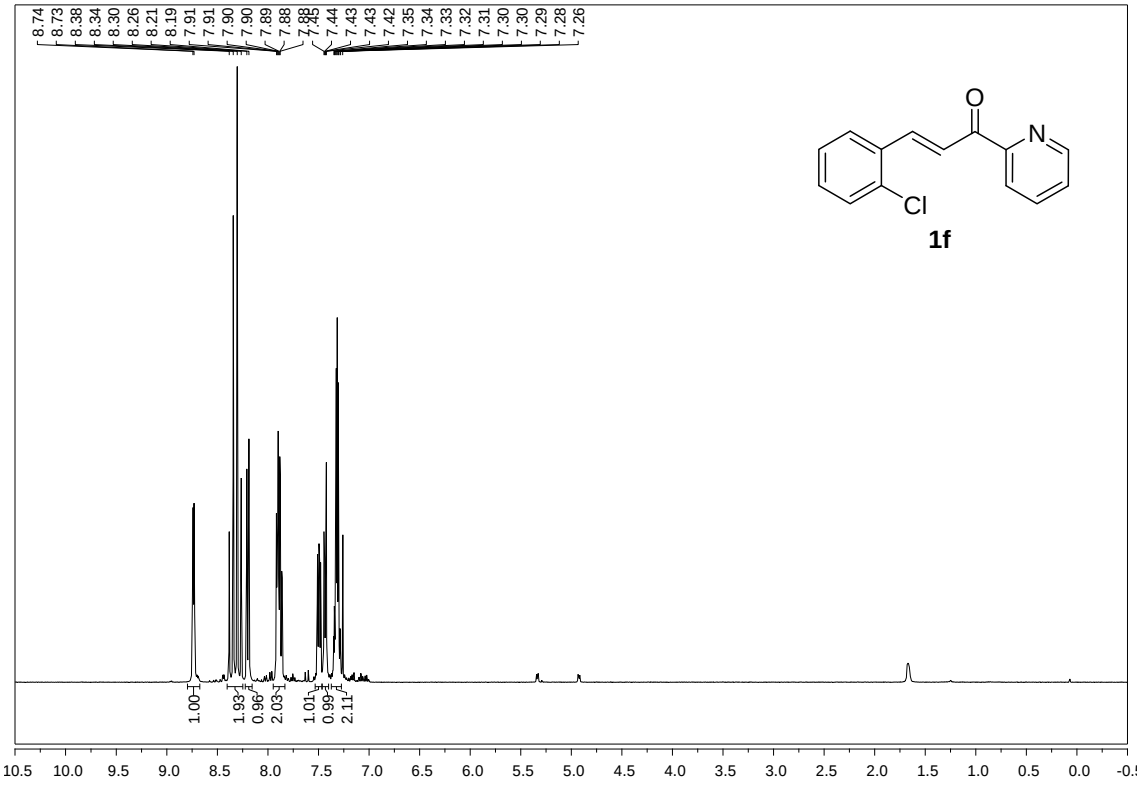


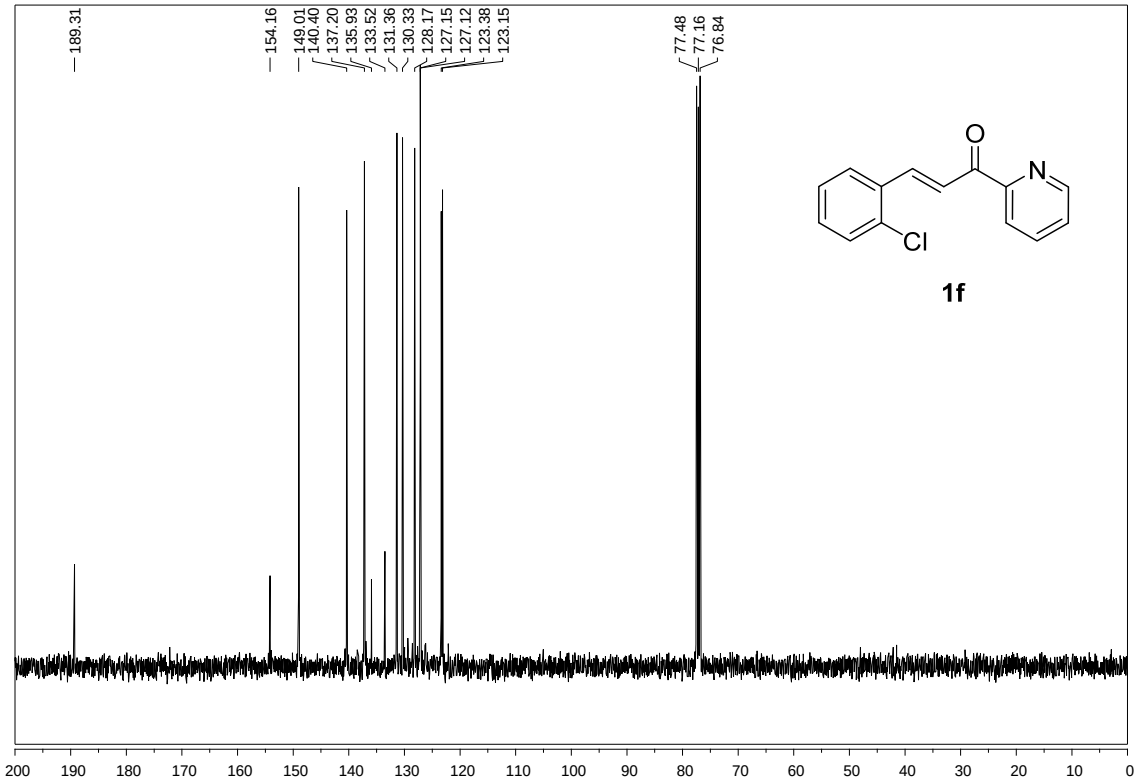
(*E*)-3-(4-Nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1e)



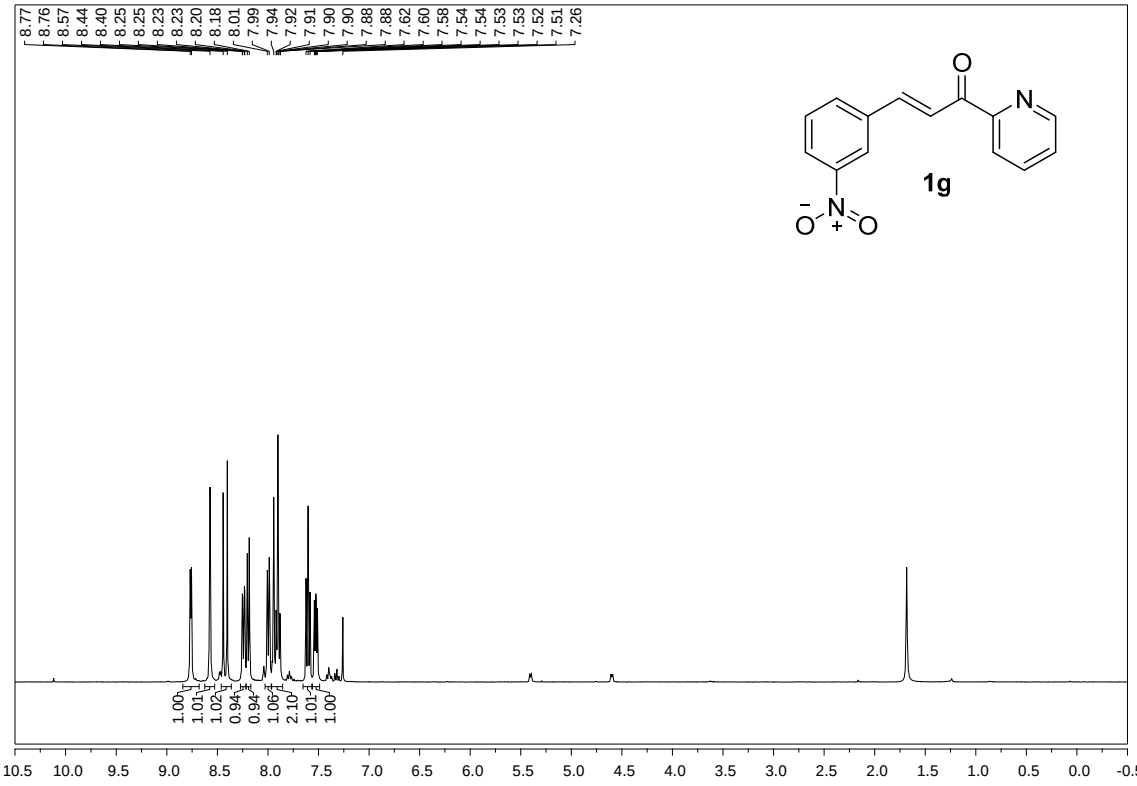


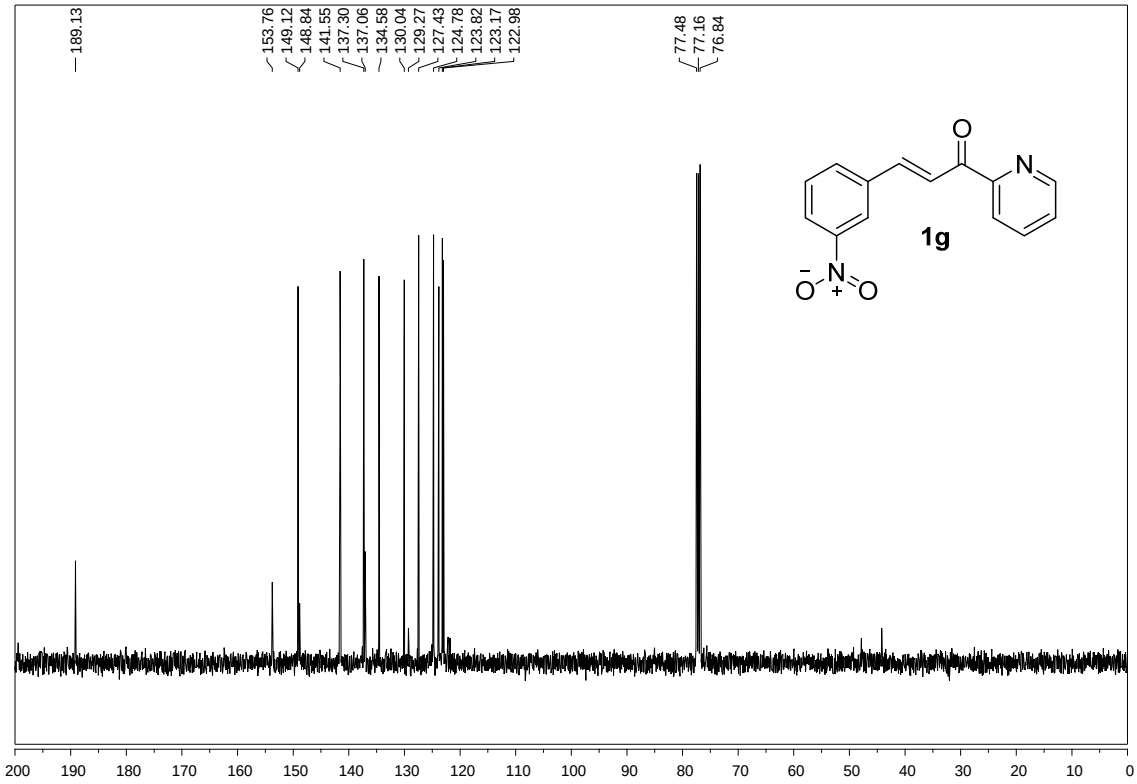
(*E*)-3-(2-Chlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1f)



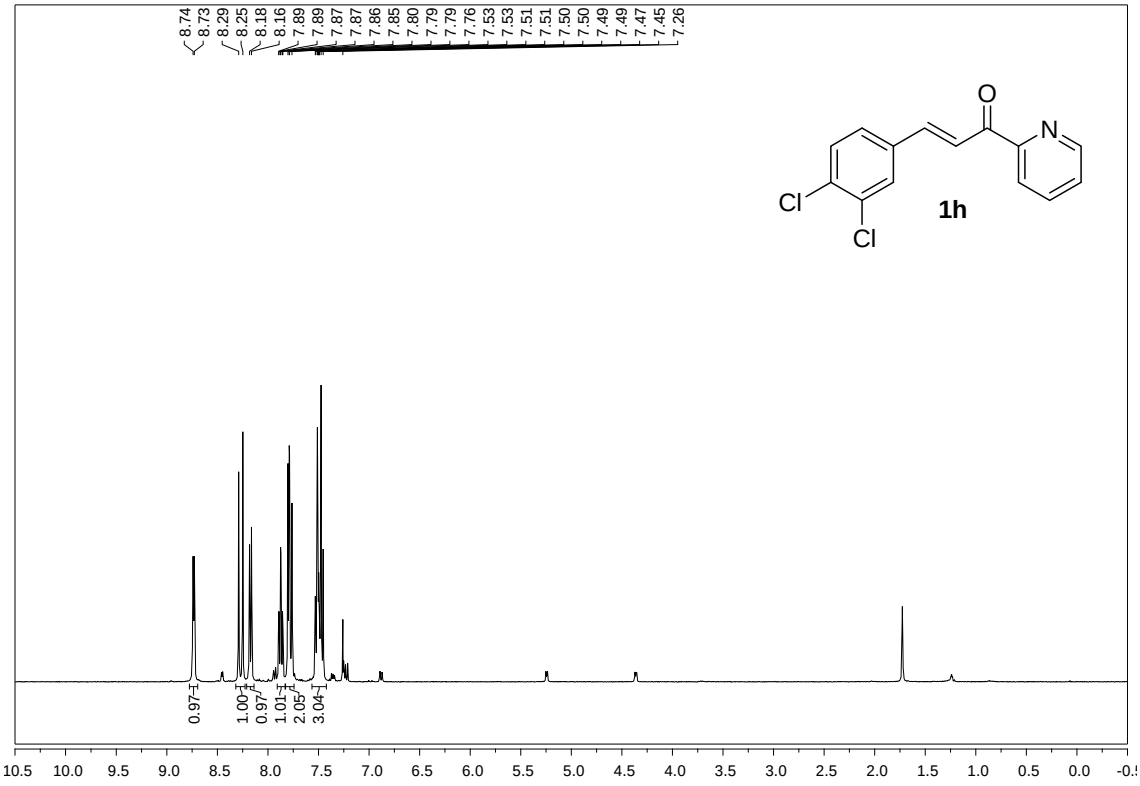


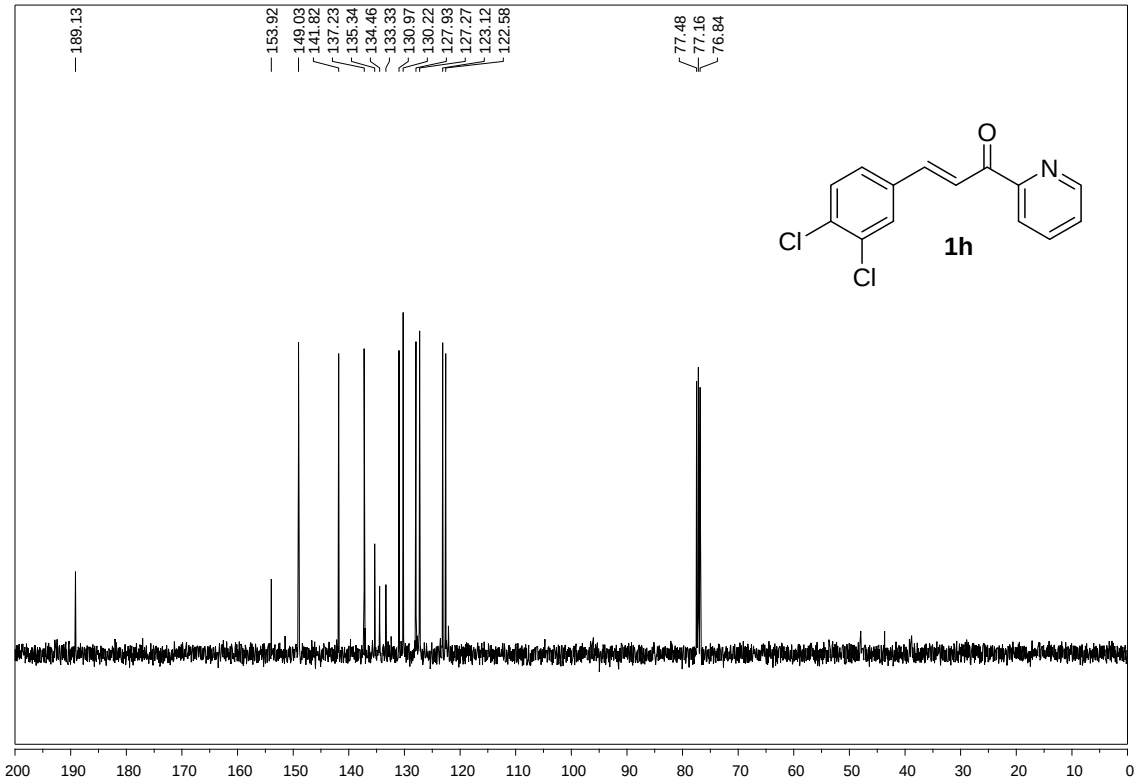
(*E*)-3-(3-Nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1g)



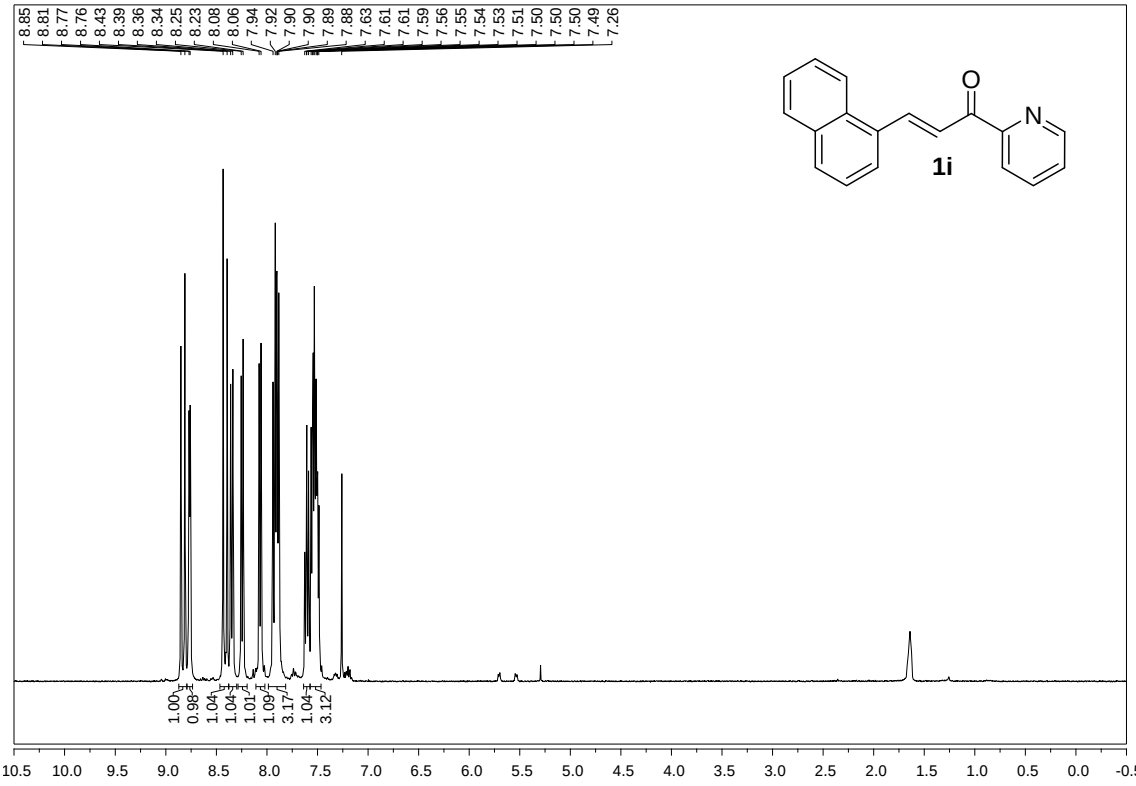


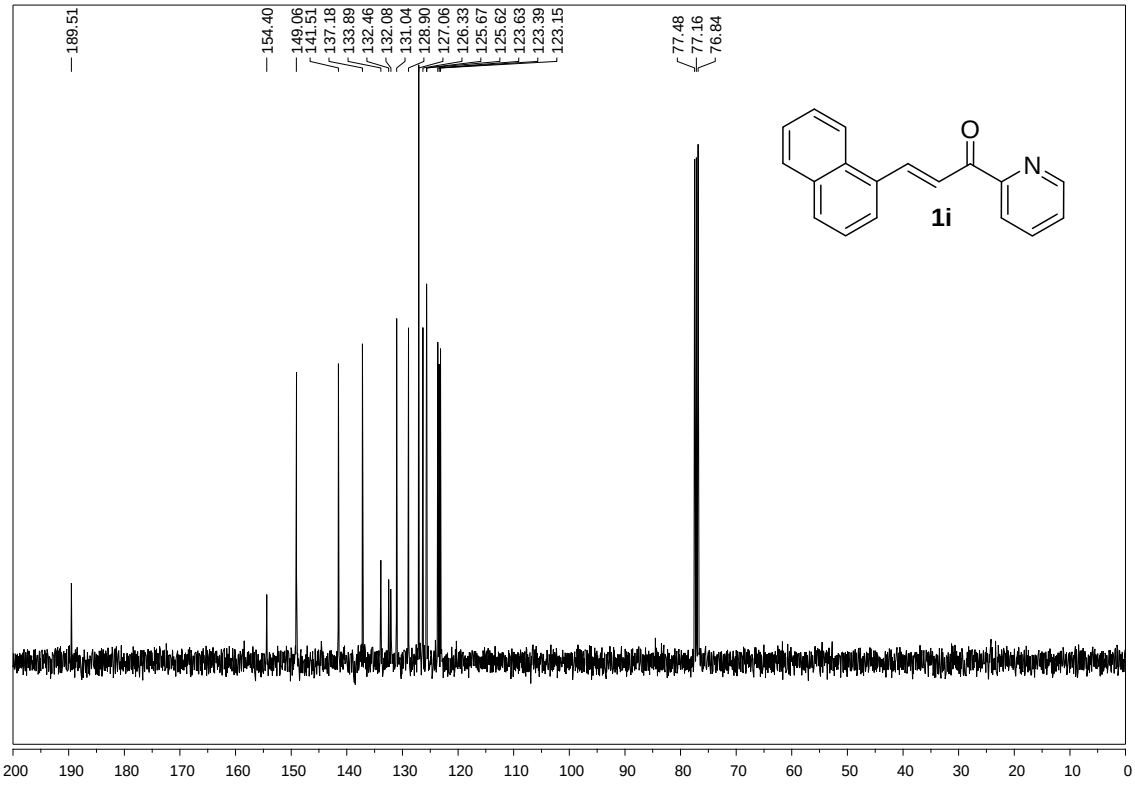
(*E*)-3-(3,4-Dichlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1h)



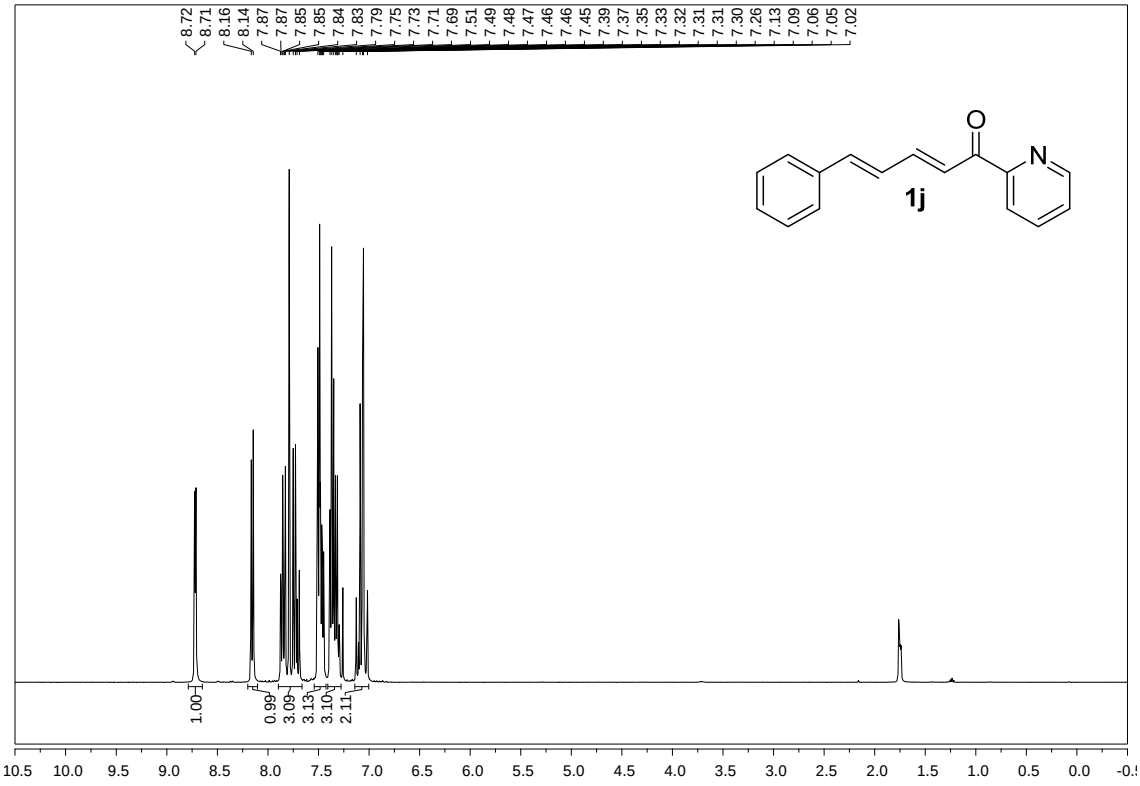


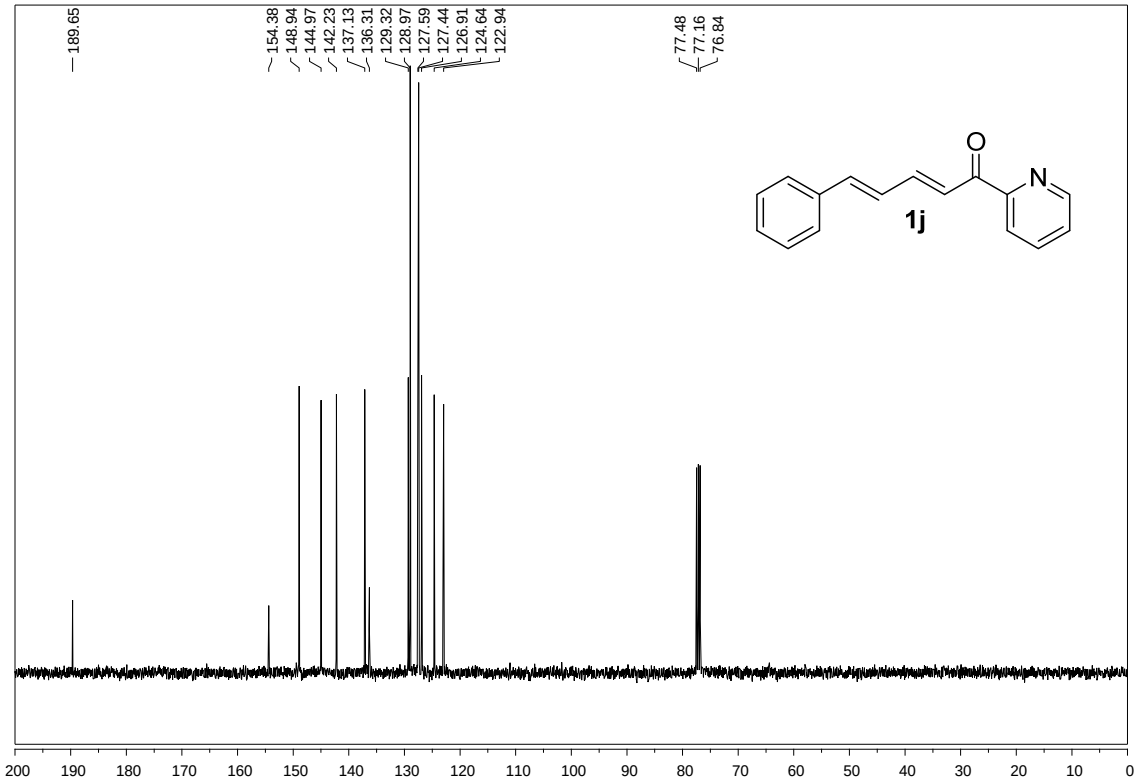
(*E*)-3-(Naphthalen-1-yl)-1-(pyridin-2-yl)prop-2-en-1-one (1i)



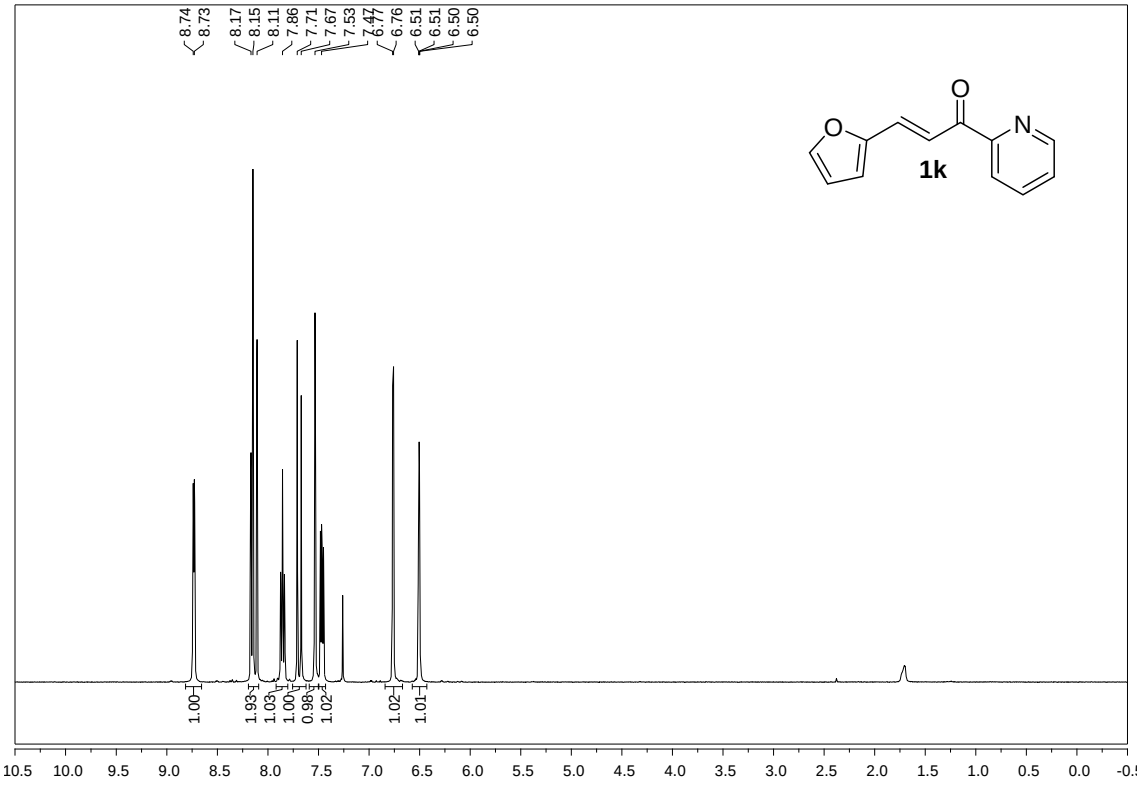


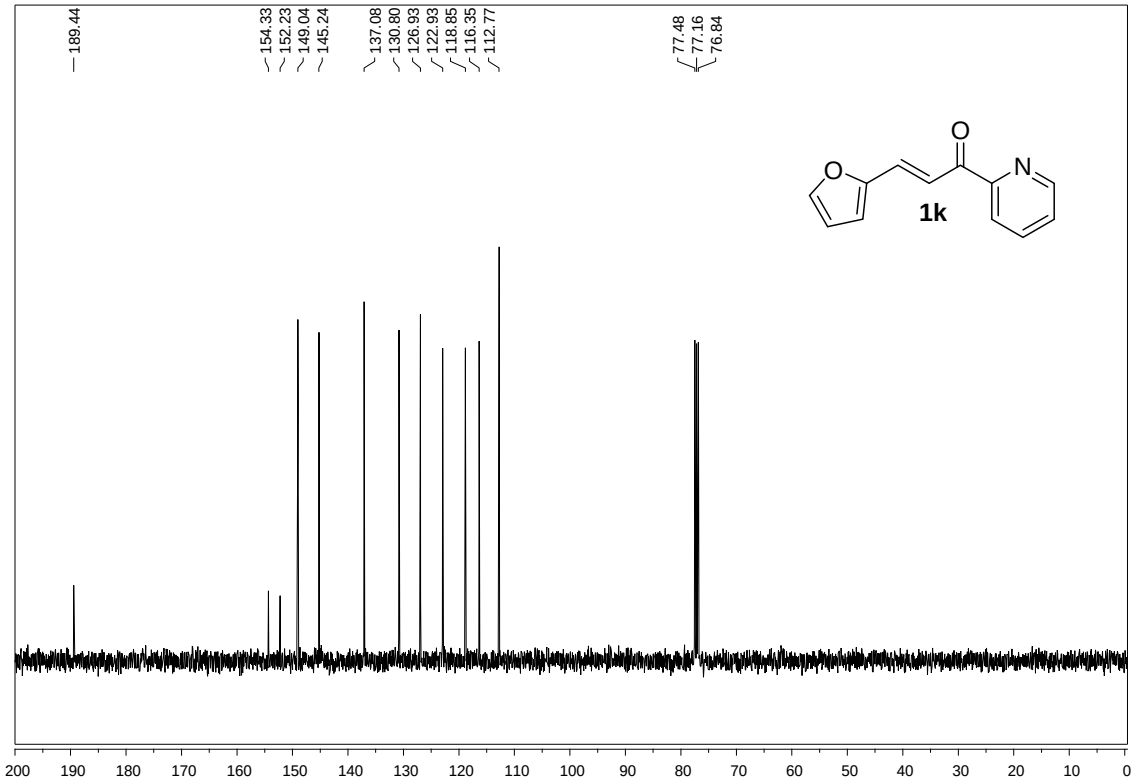
(2*E*,4*E*)-5-Phenyl-1-(pyridin-2-yl)penta-2,4-dien-1-one (1j)



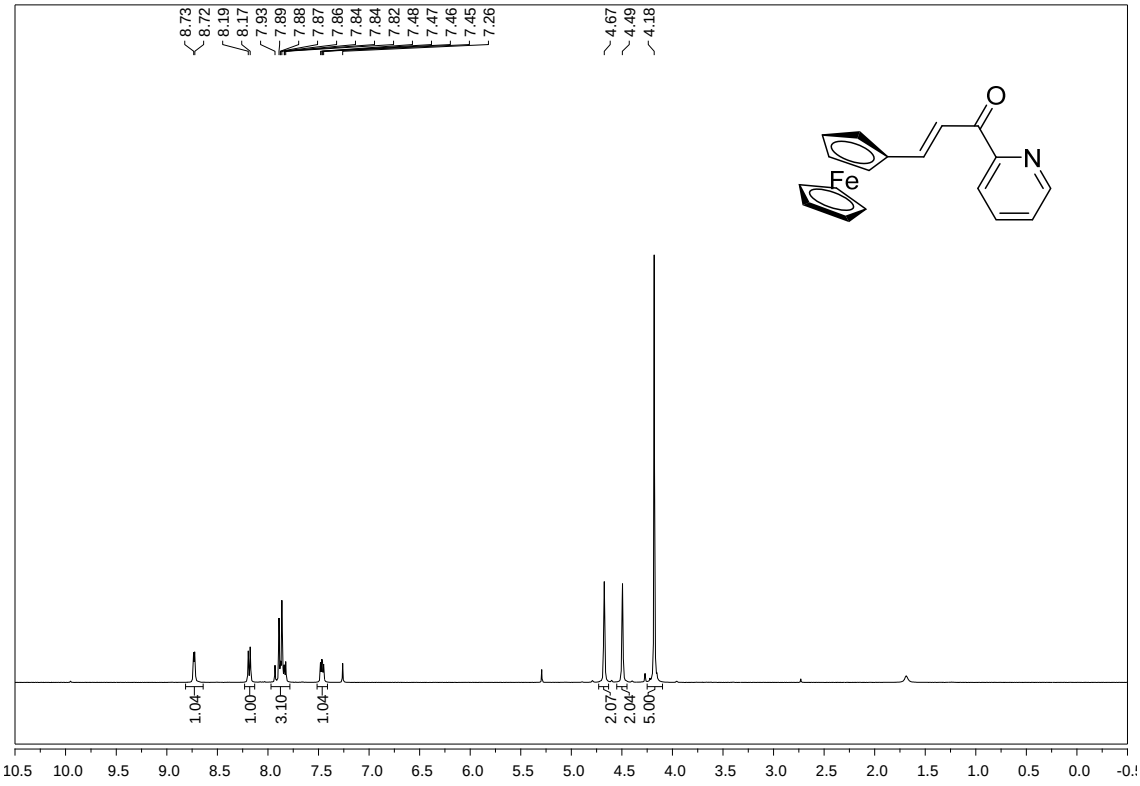


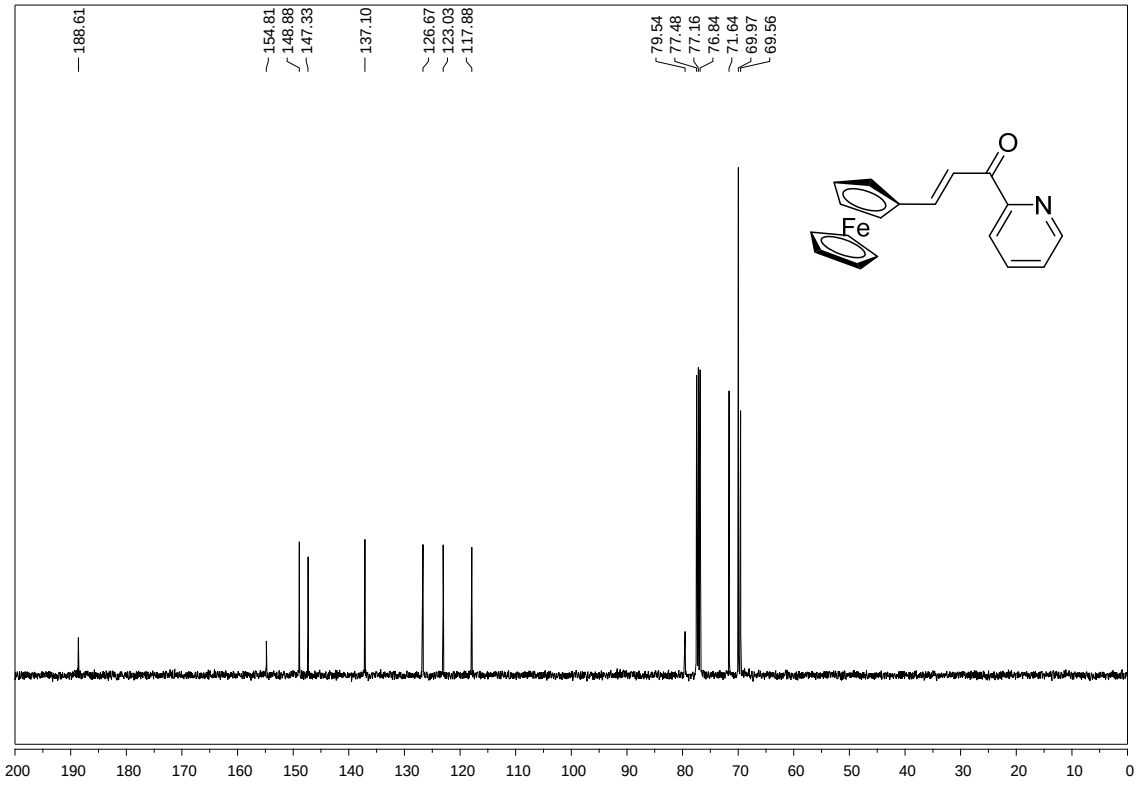
(*E*)-3-(Furan-2-yl)-1-(pyridin-2-yl)prop-2-en-1-one (1k)



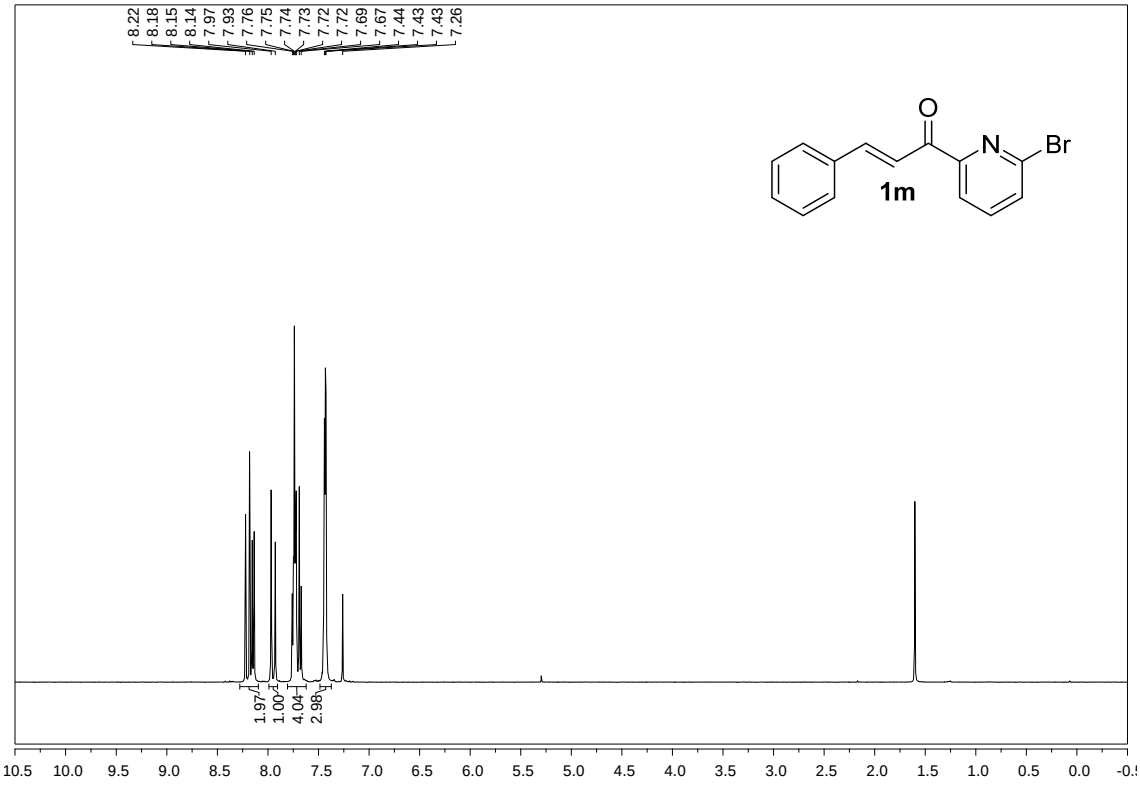


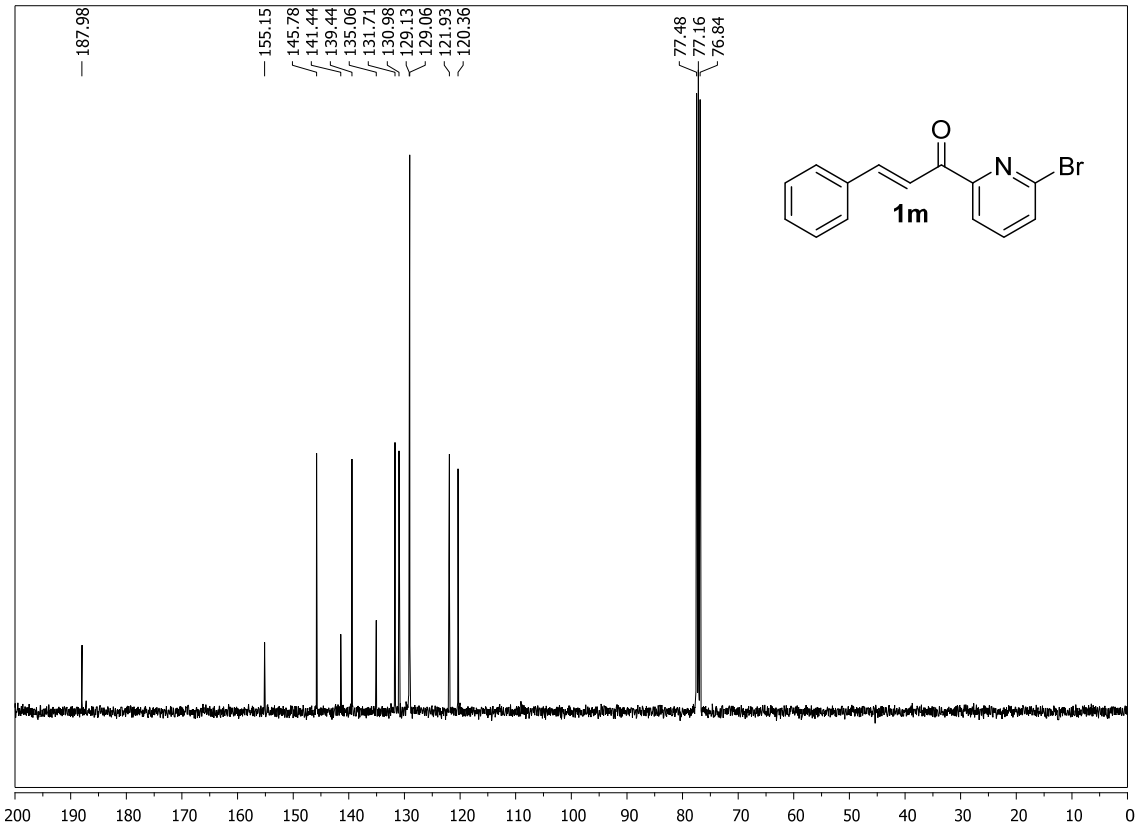
(*E*)-3-(Ferrocenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1l)





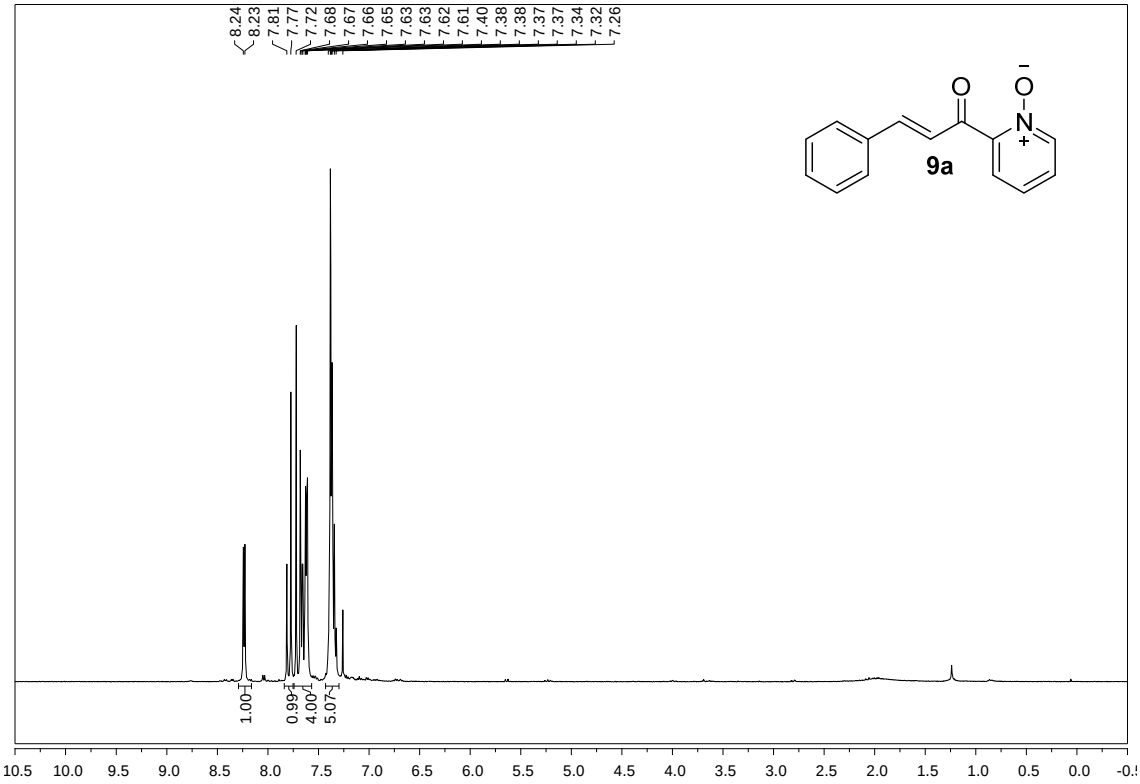
(*E*)-1-(6-Bromopyridin-2-yl)-3-phenylprop-2-en-1-one (1m)

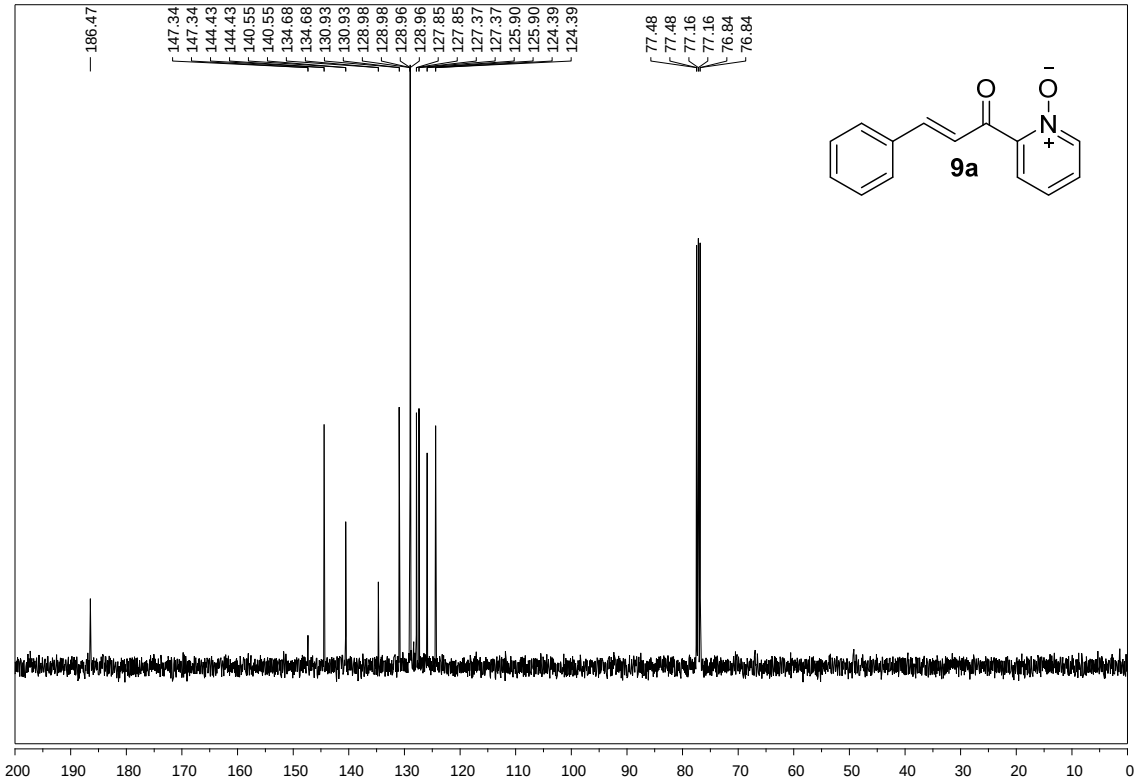




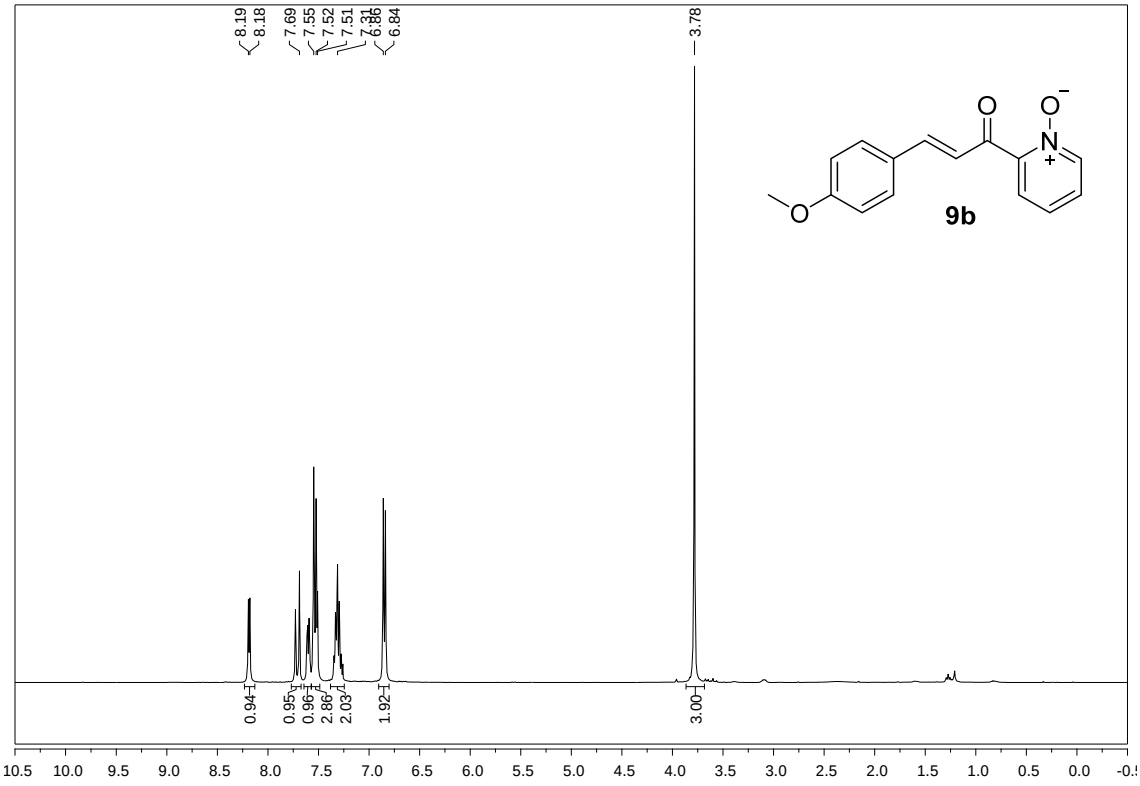
13.^{1}H and ^{13}C NMR Spectra of 2-Enoylpyridine *N*-Oxides

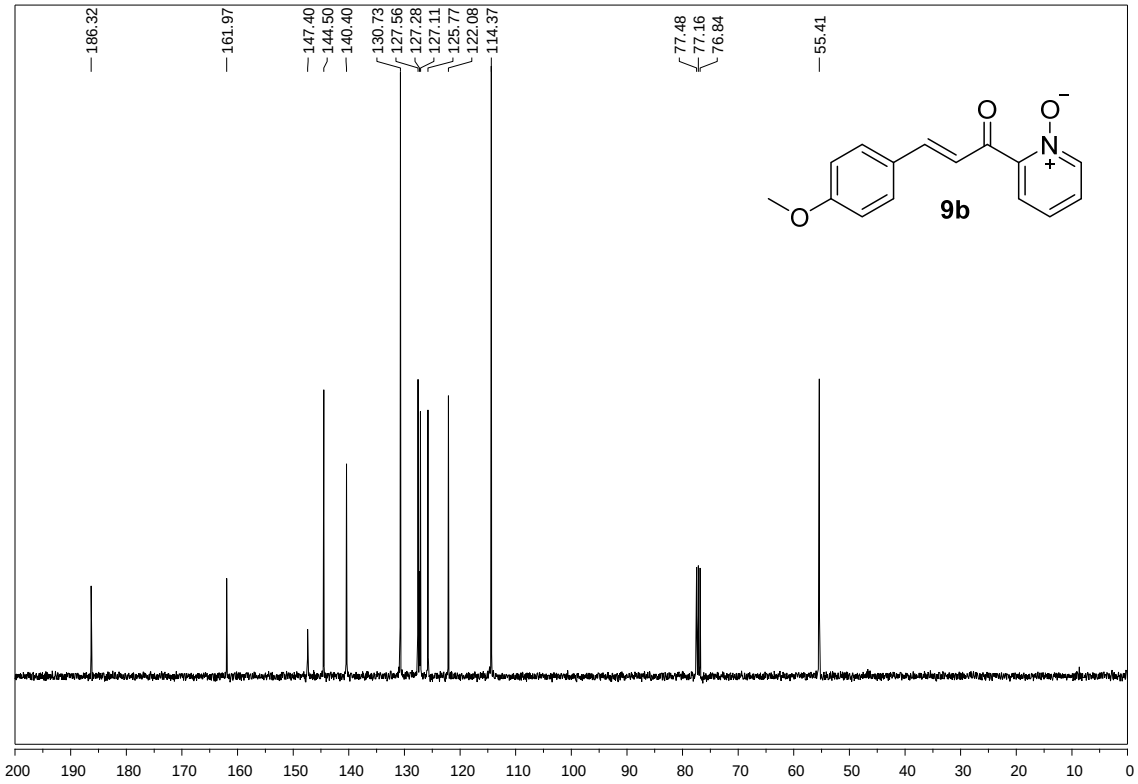
2-Cinnamoylpyridine 1-oxide (9a)



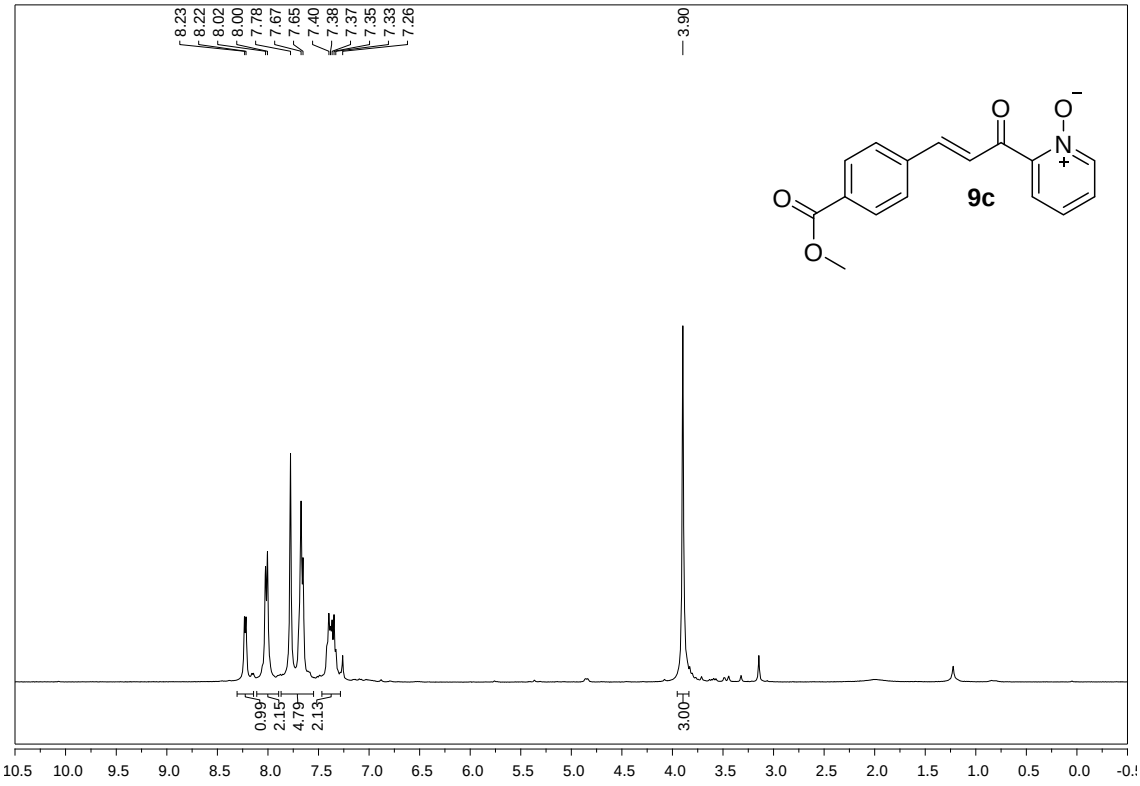


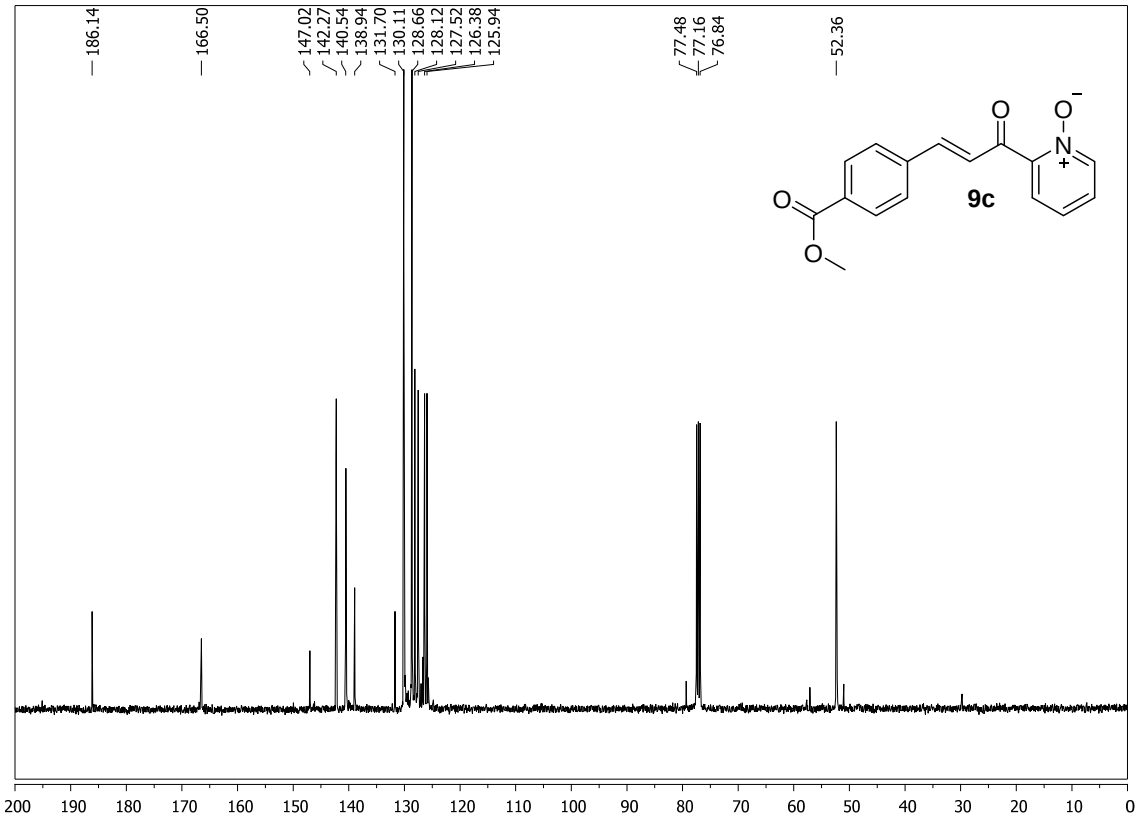
(*E*)-2-(3-(4-Methoxyphenyl)acryloyl)pyridine 1-oxide (9b)





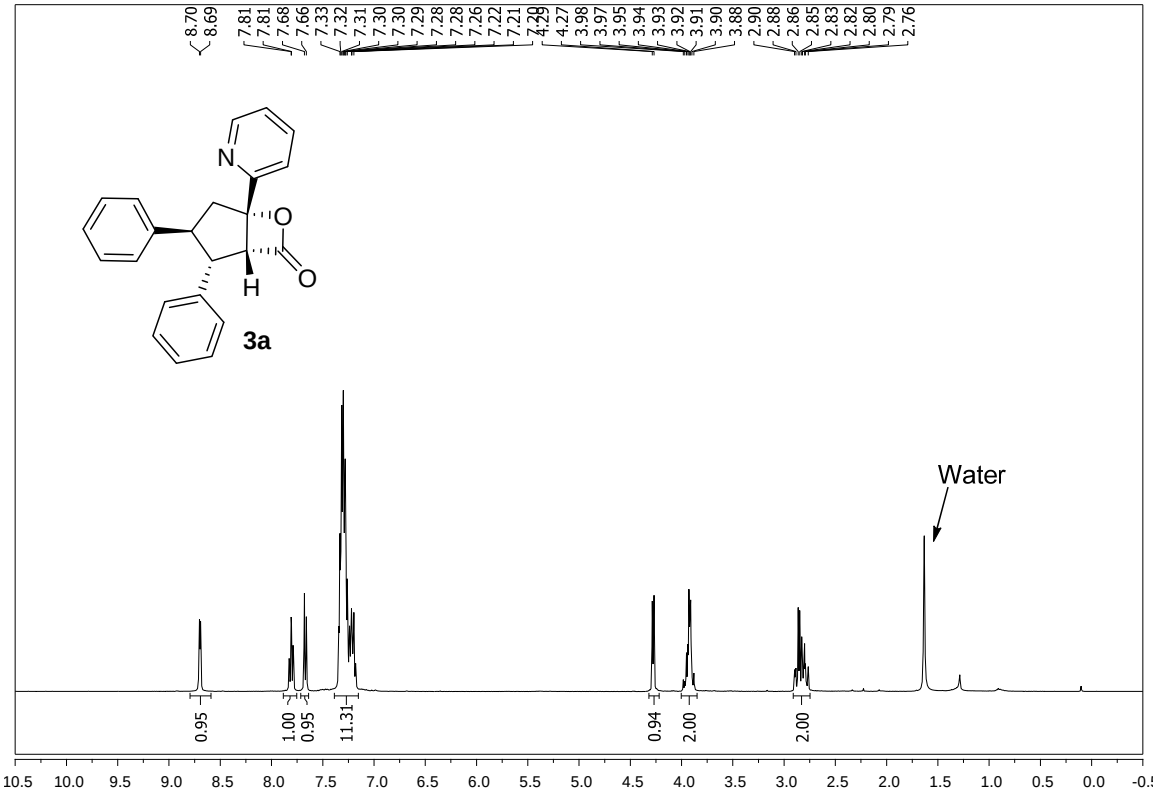
(*E*)-2-(3-(4-(Methoxycarbonyl)phenyl)acryloyl)pyridine 1-oxide (9c)

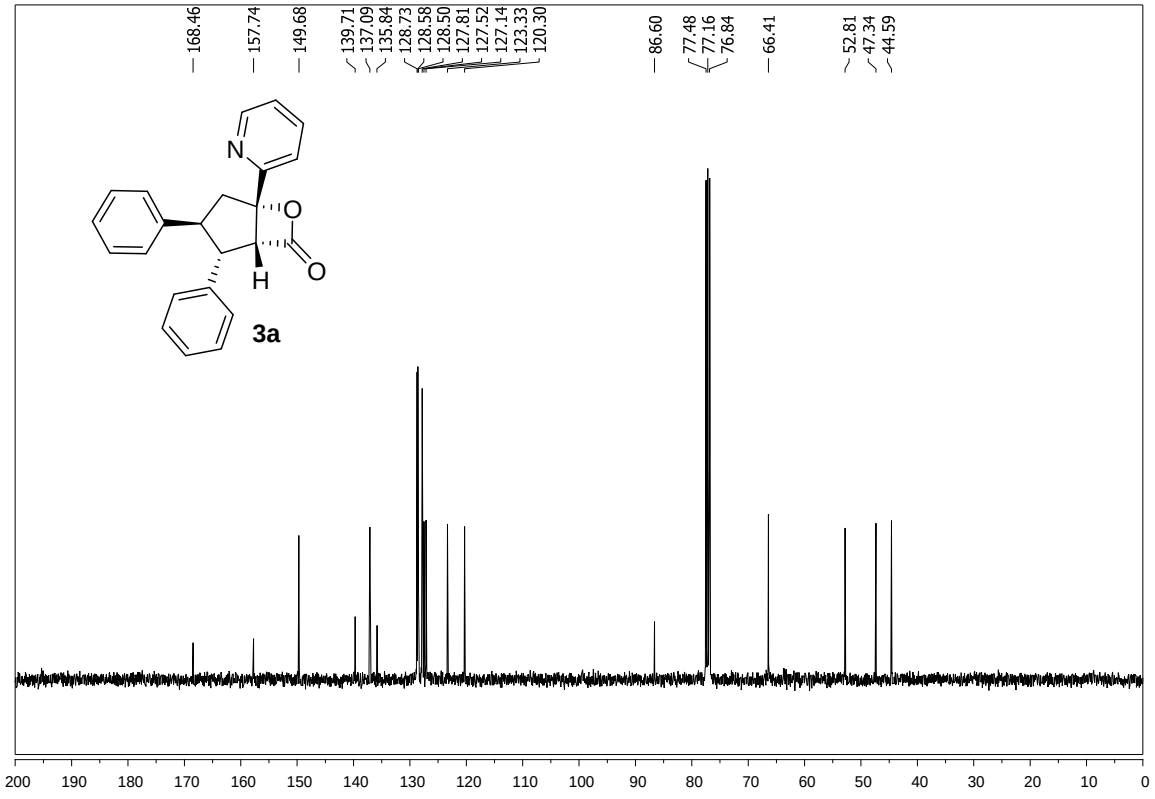




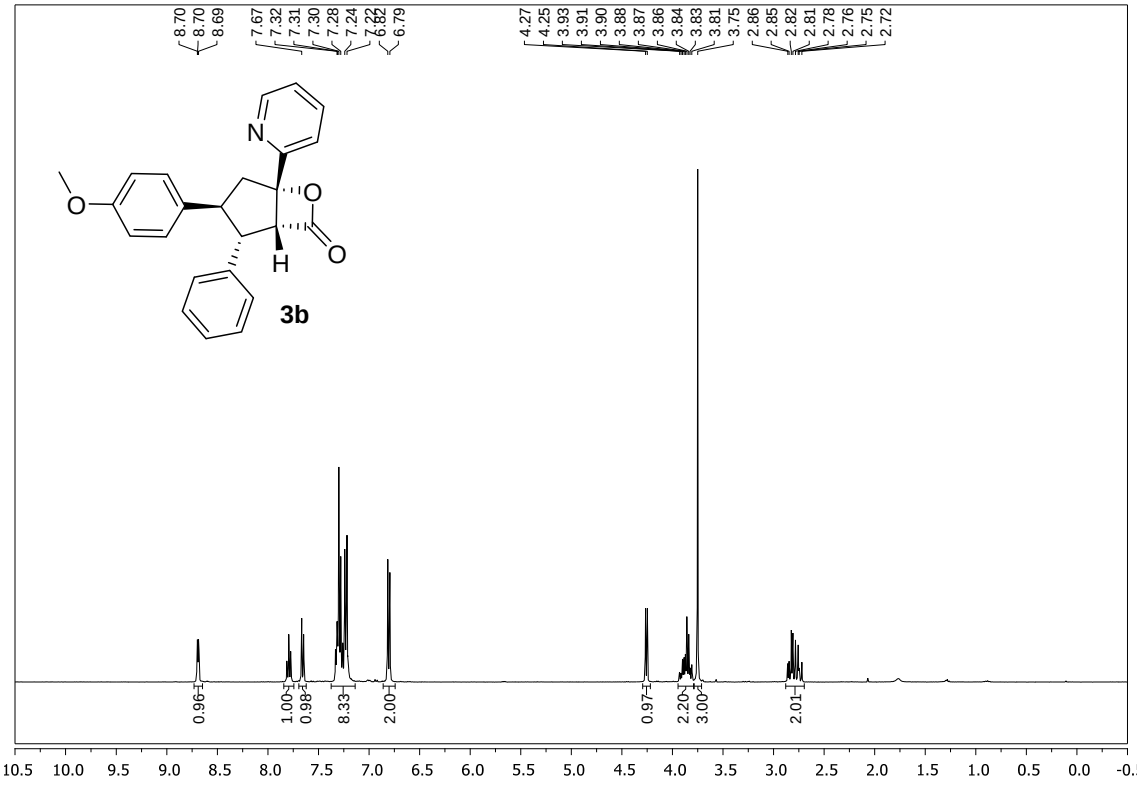
14.[1]H and [13]C NMR Spectra of β-Lactone-Fused Cyclopentanes

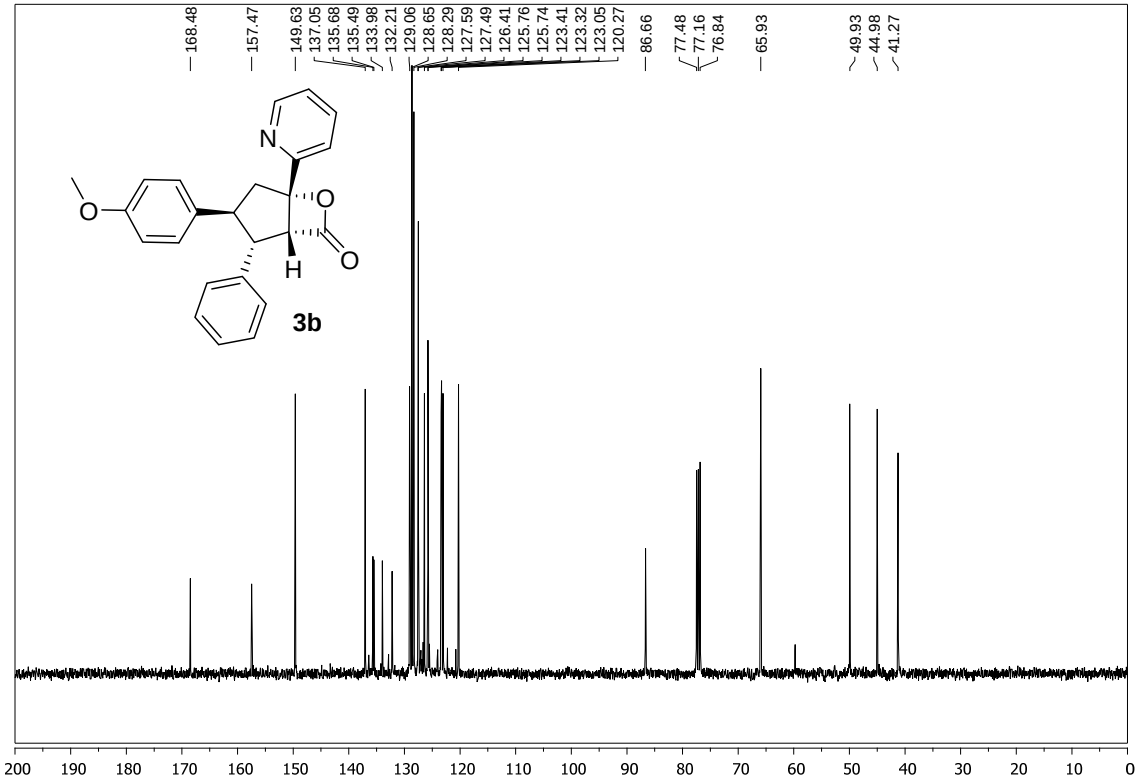
2,3-Diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3a)



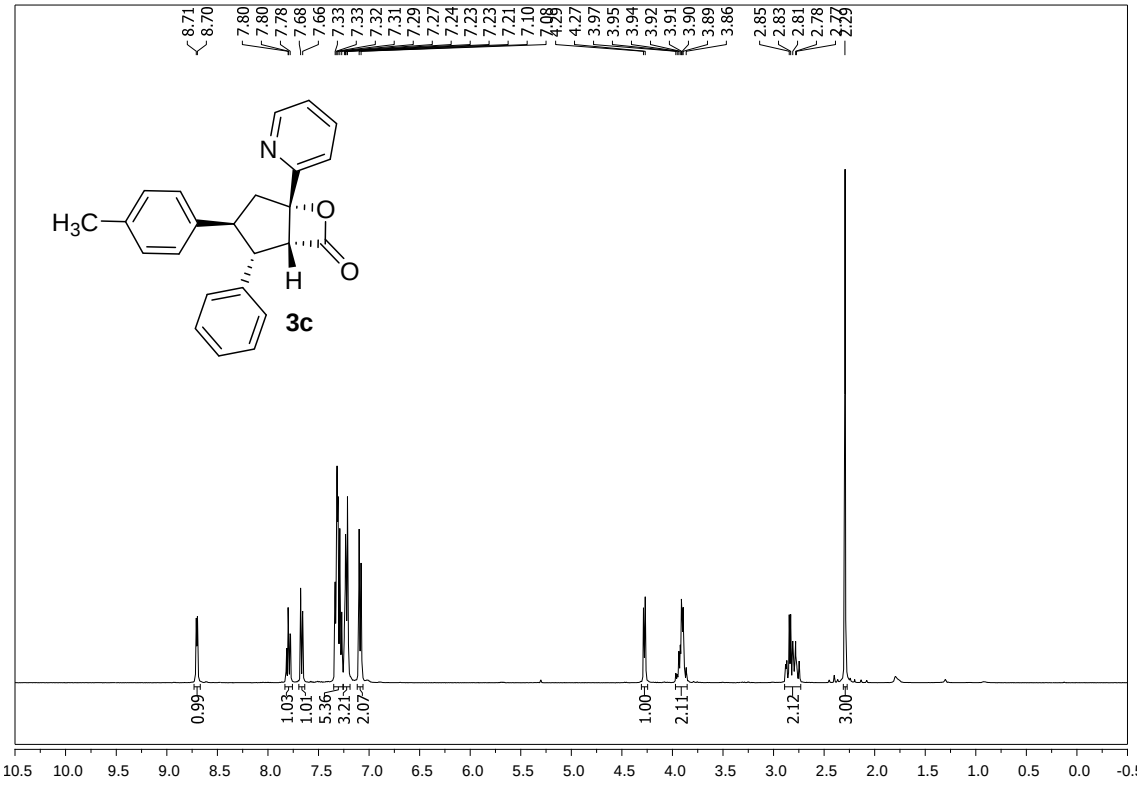


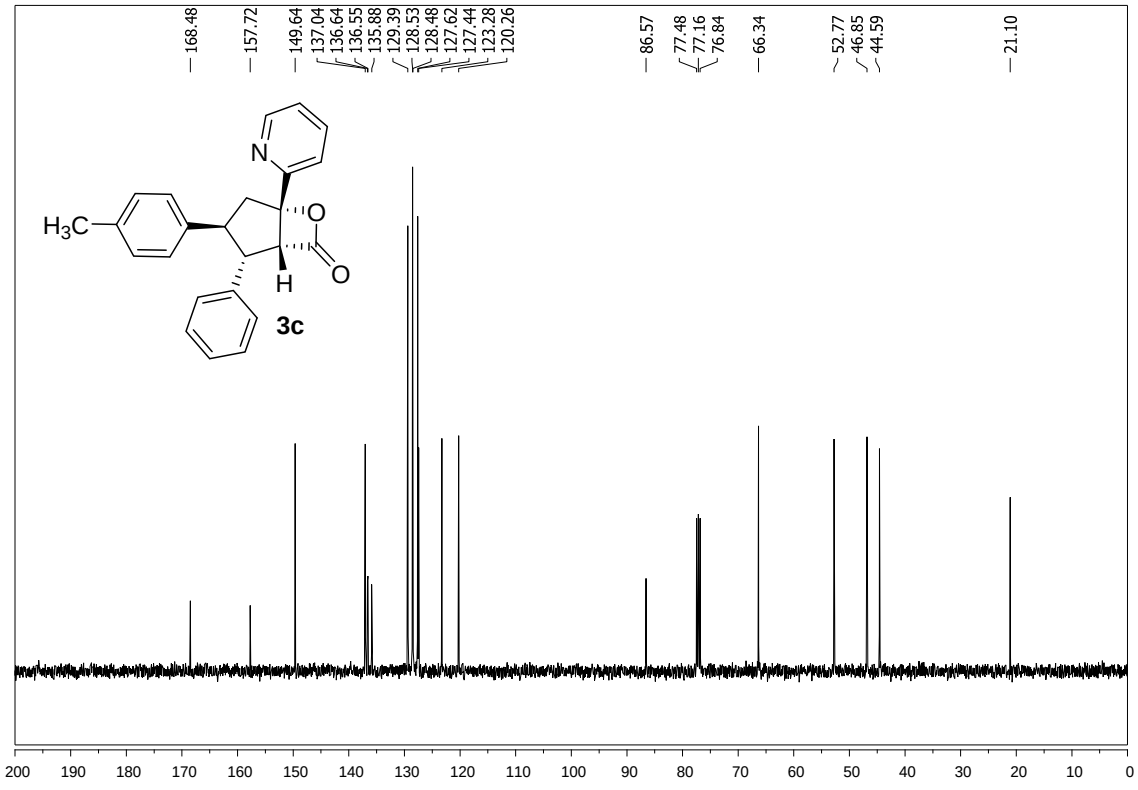
3-(4-Methoxyphenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3b)



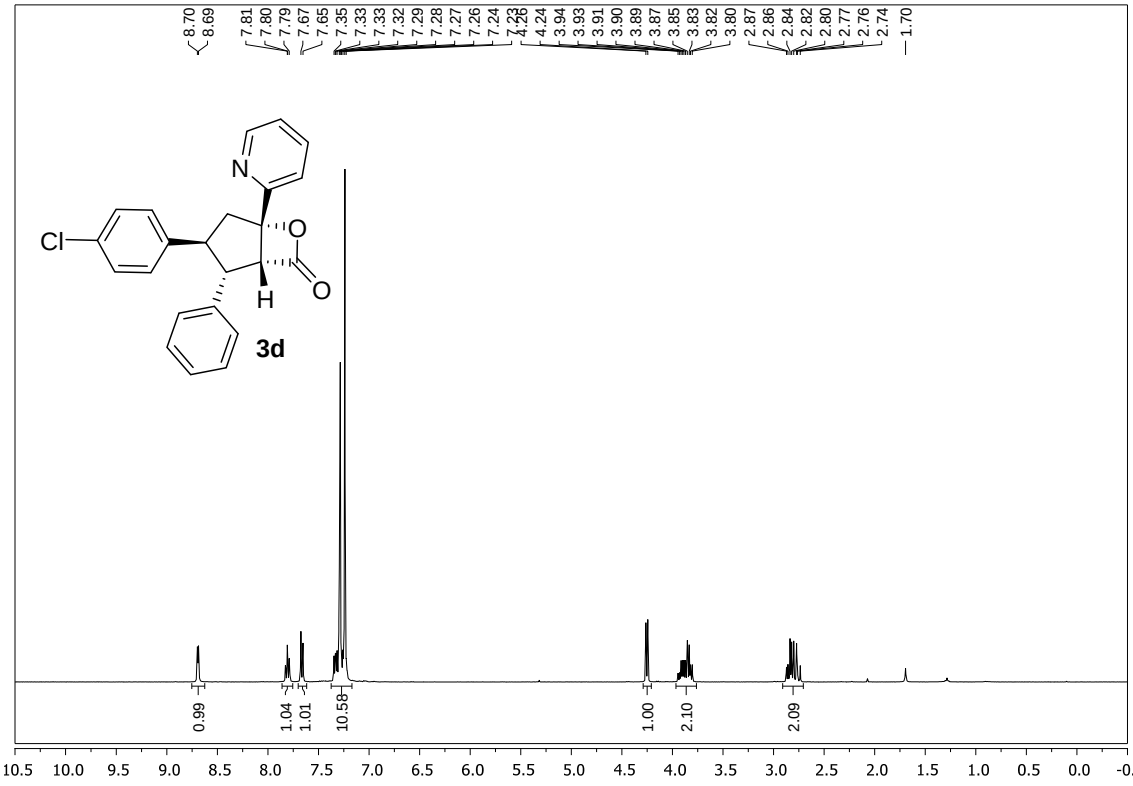


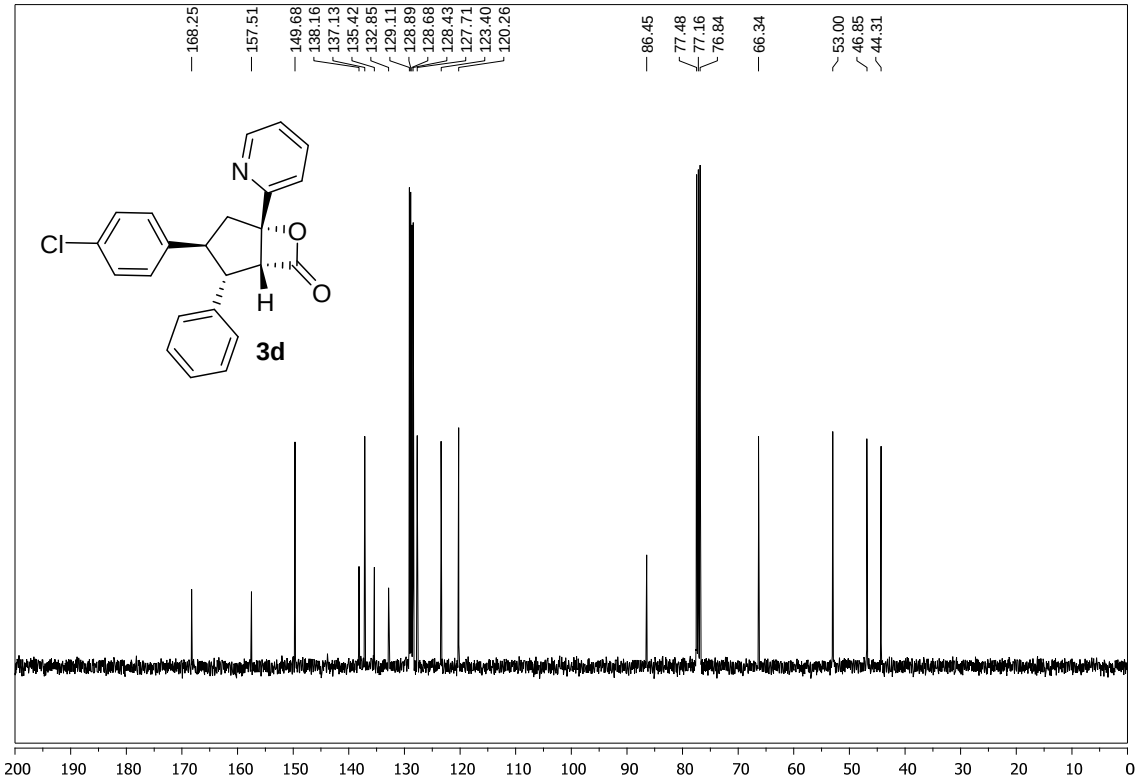
2-Phenyl-5-(pyridin-2-yl)-3-p-tolyl-6-oxa-bicyclo[3.2.0]heptan-7-one (3c)



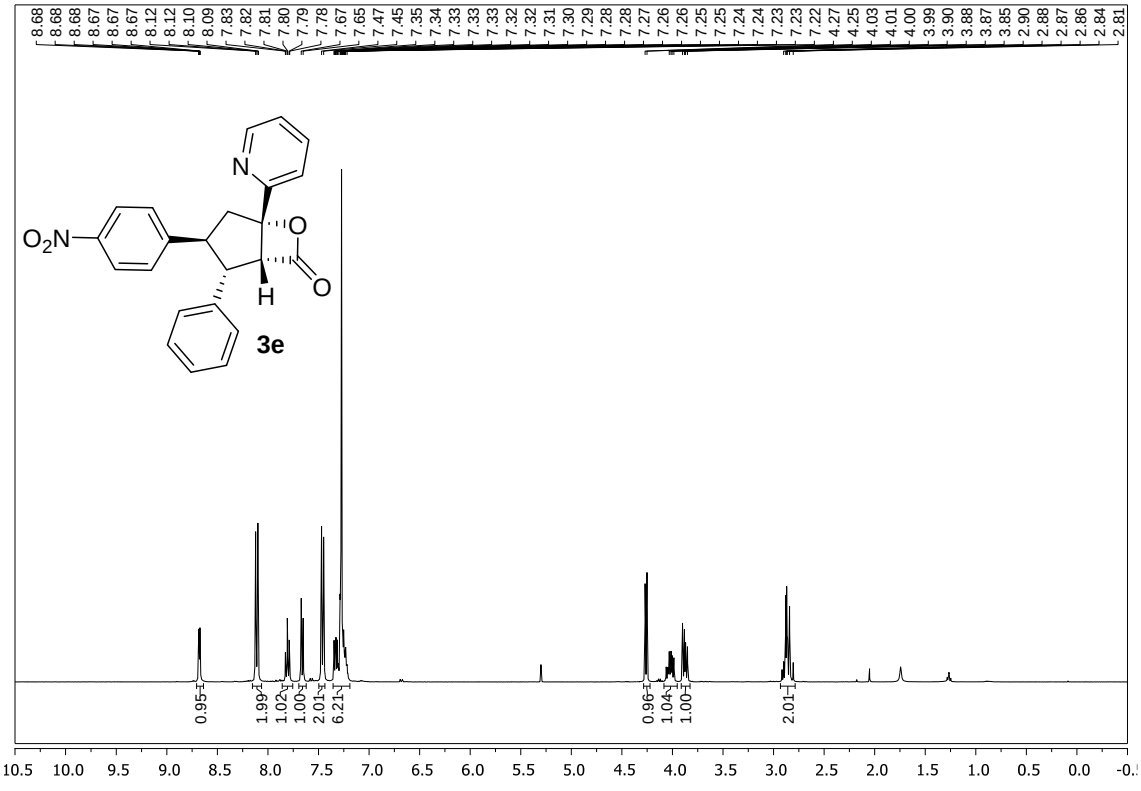


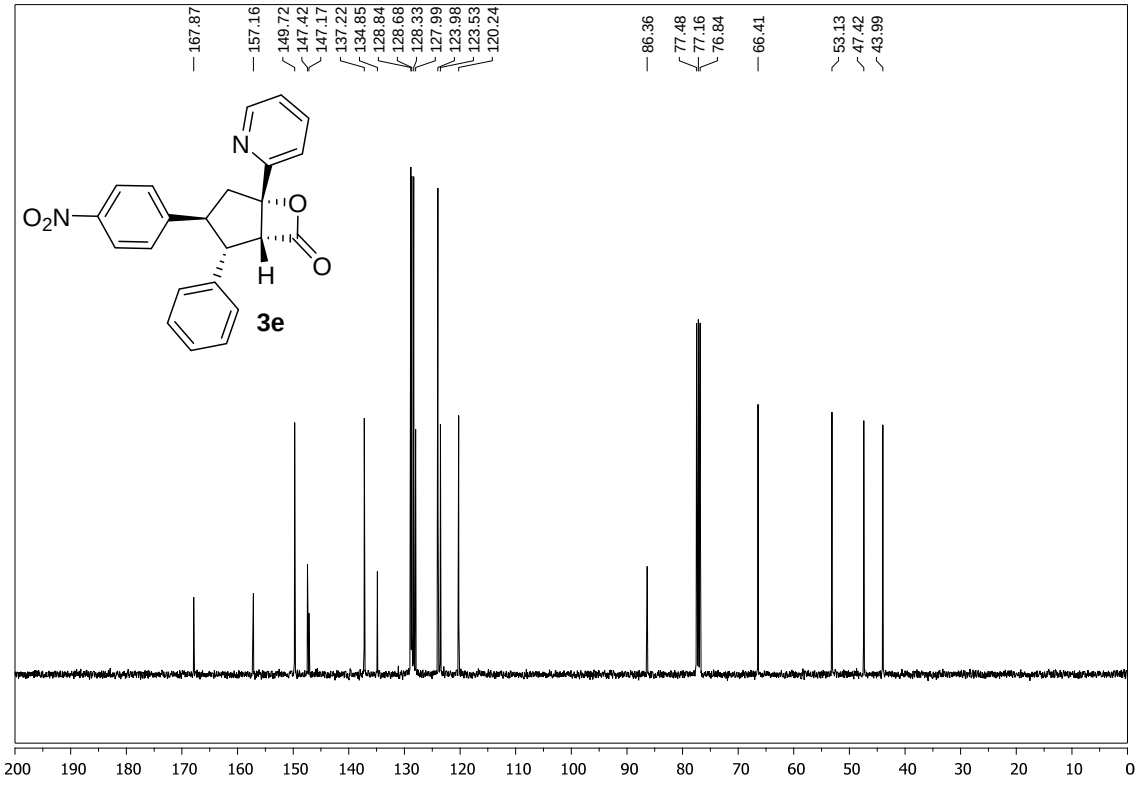
3-(4-Chlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3d)



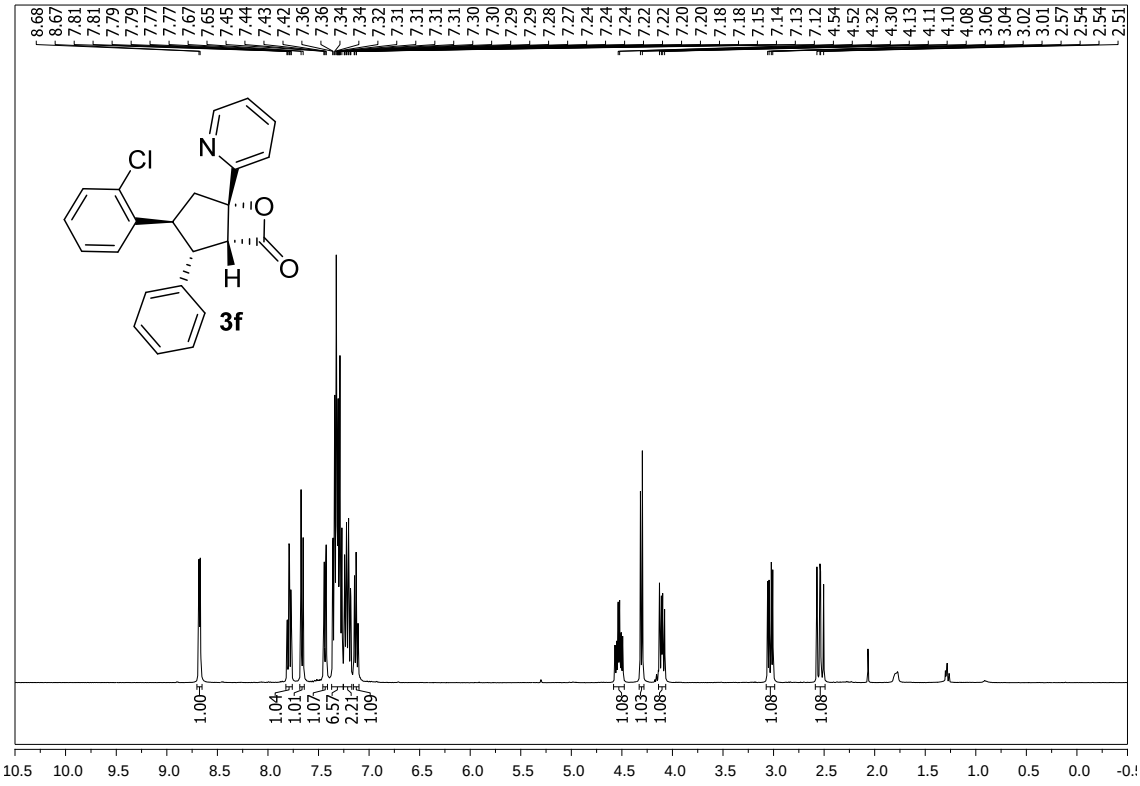


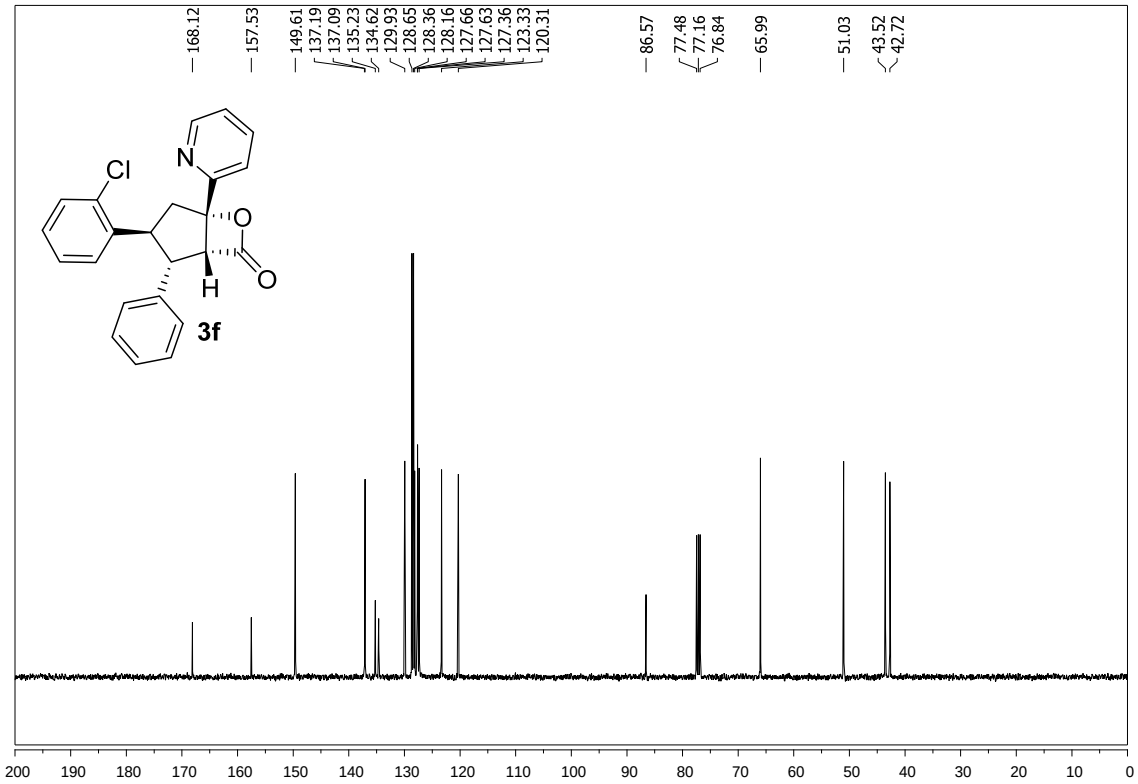
3-(4-Nitrophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3e)



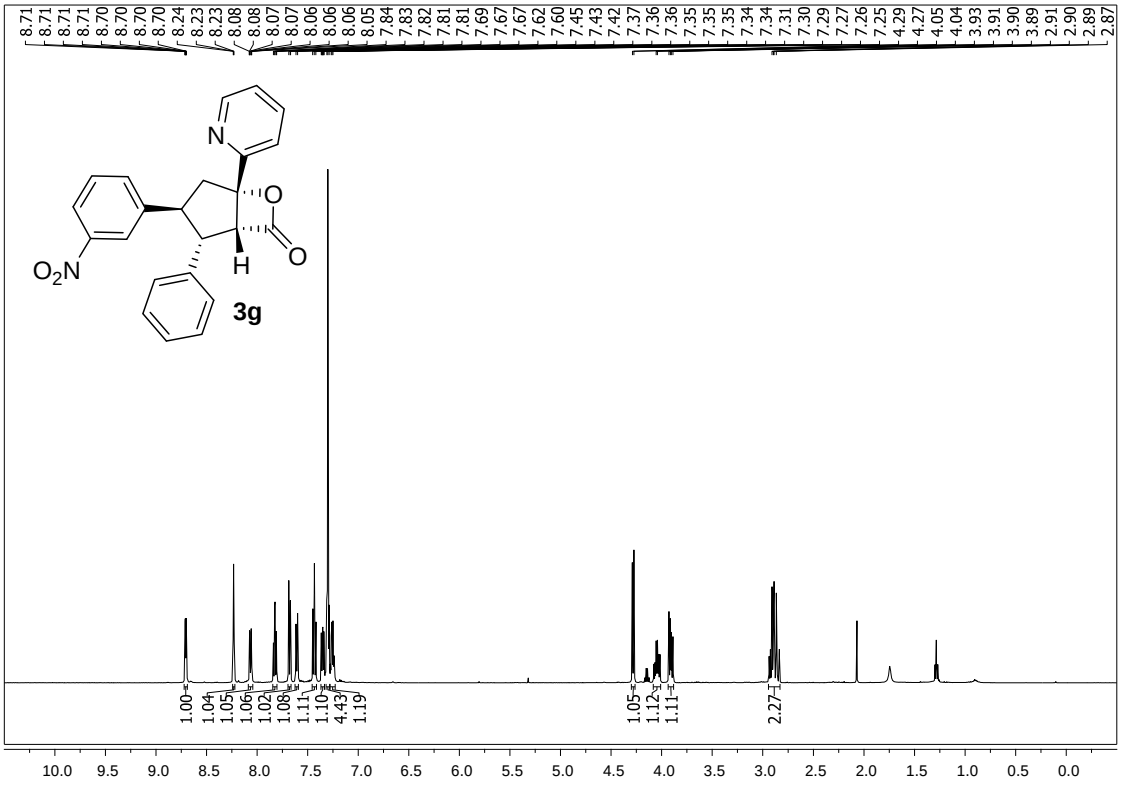


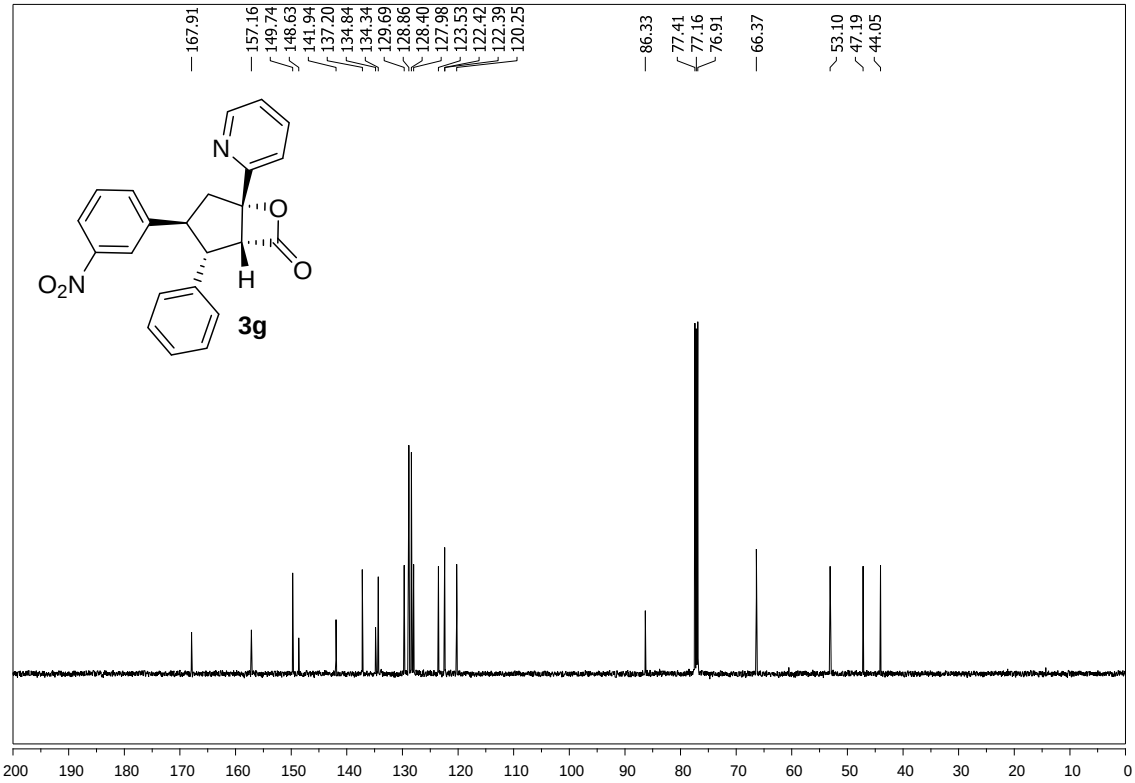
3-(2-Chlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one (3f)



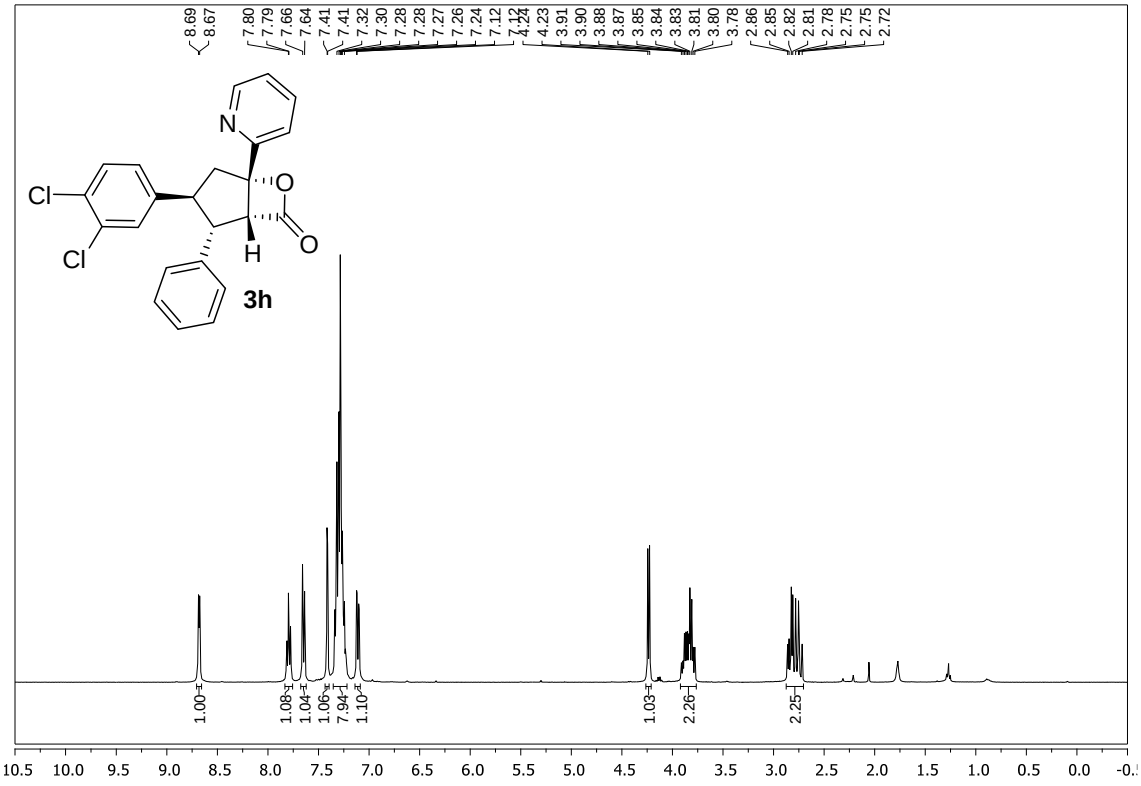


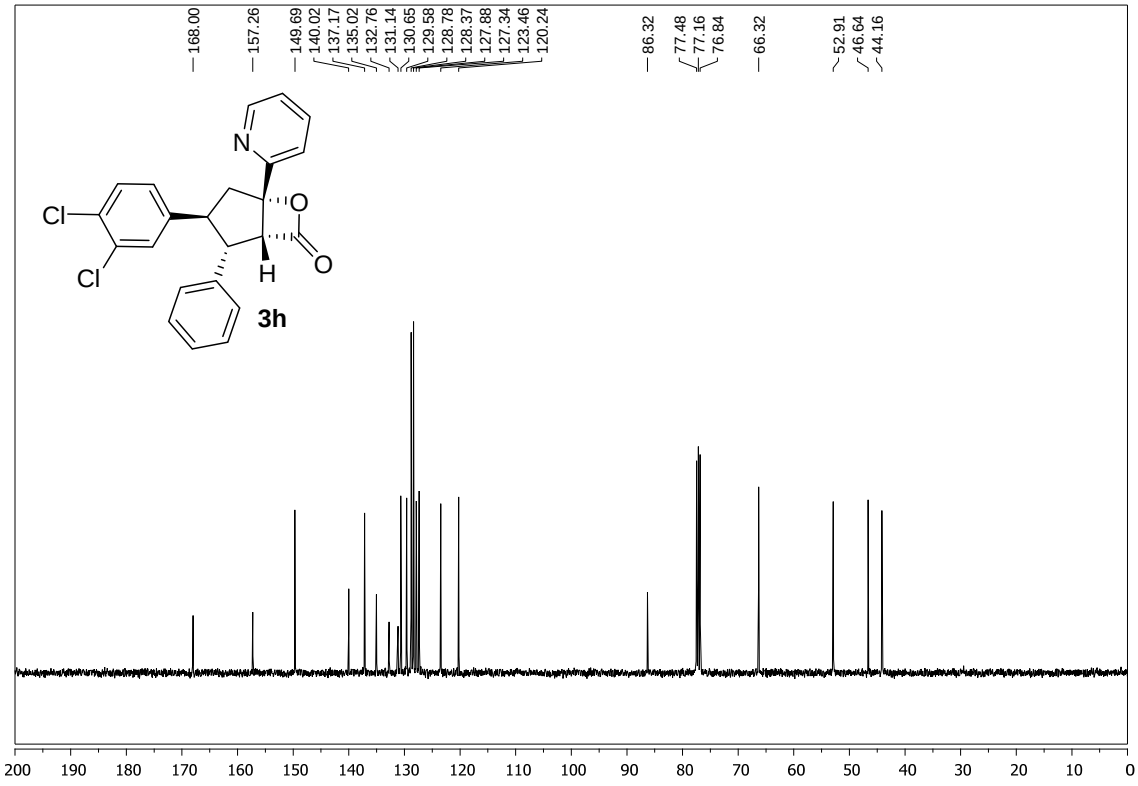
3-(3-Nitrophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one (3g)



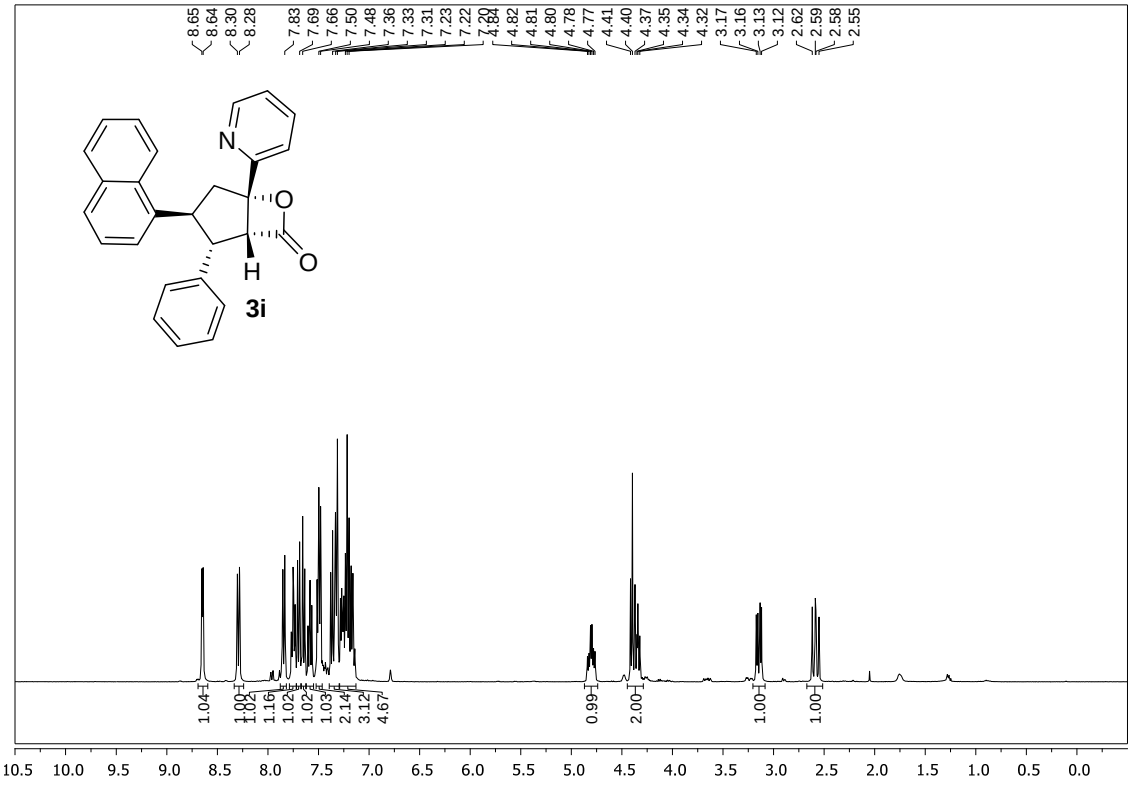


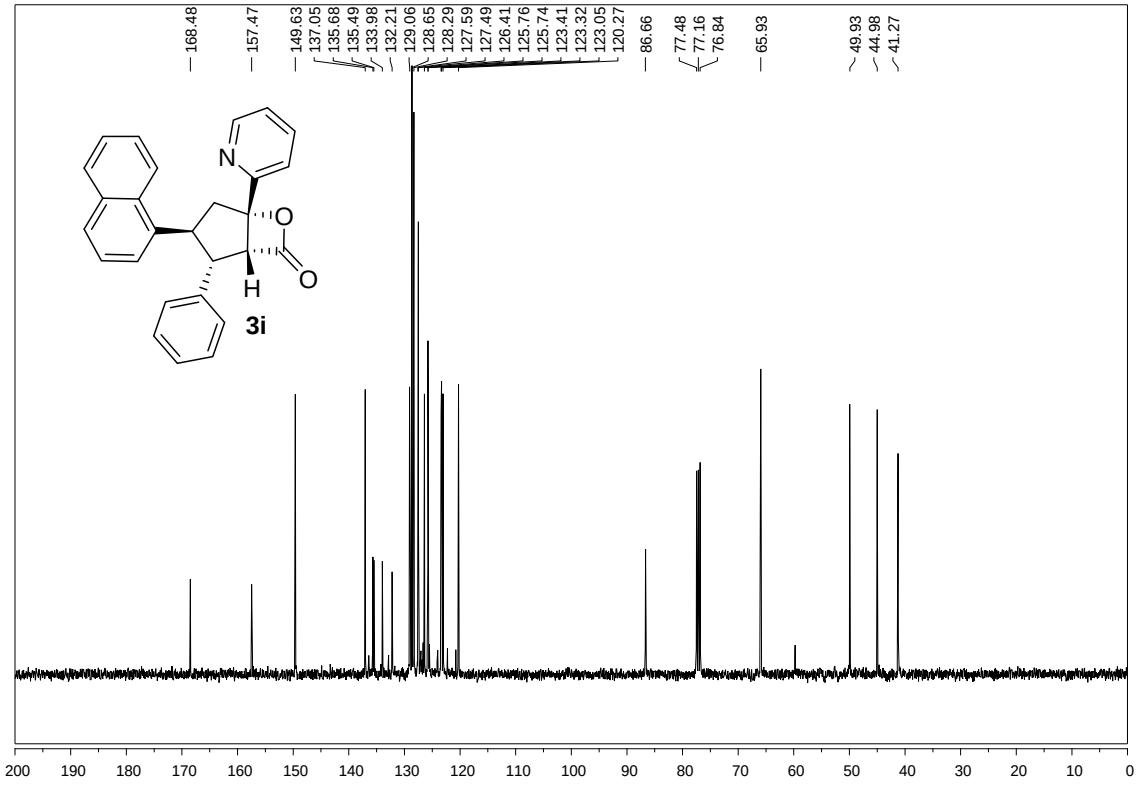
3-(3,4-Dichlorophenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxa-bicyclo[3.2.0]heptan-7-one (3h)



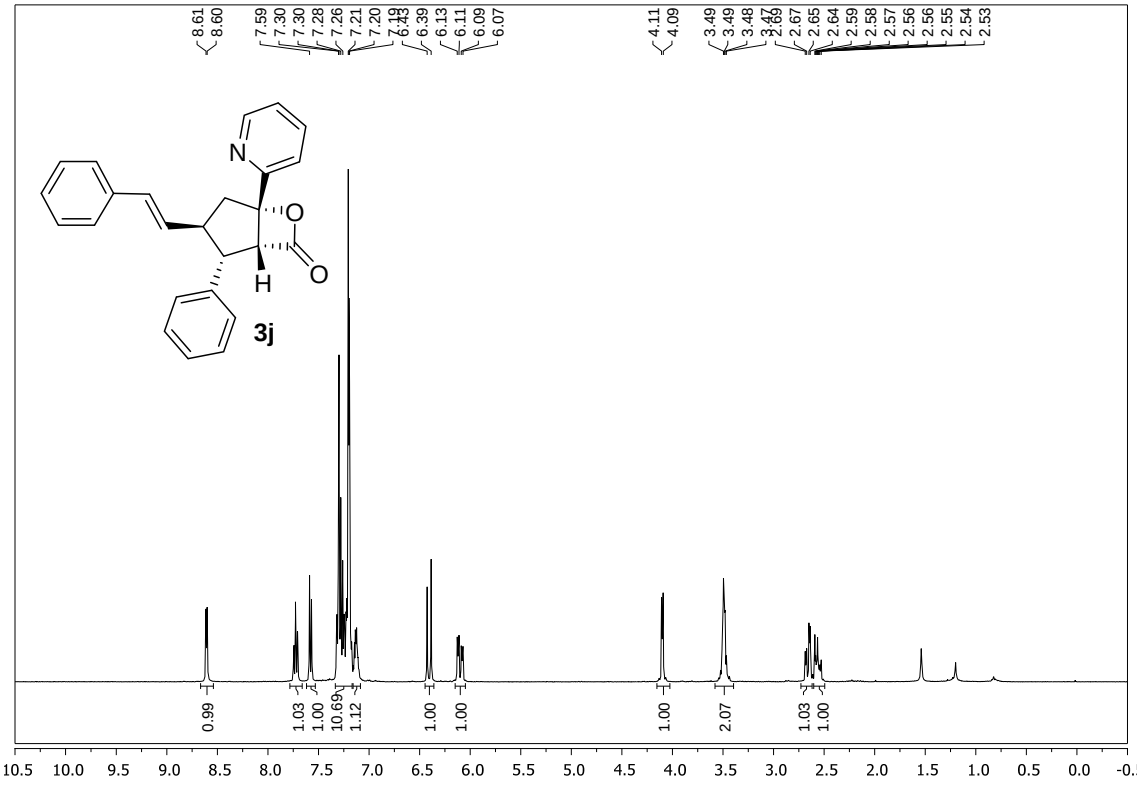


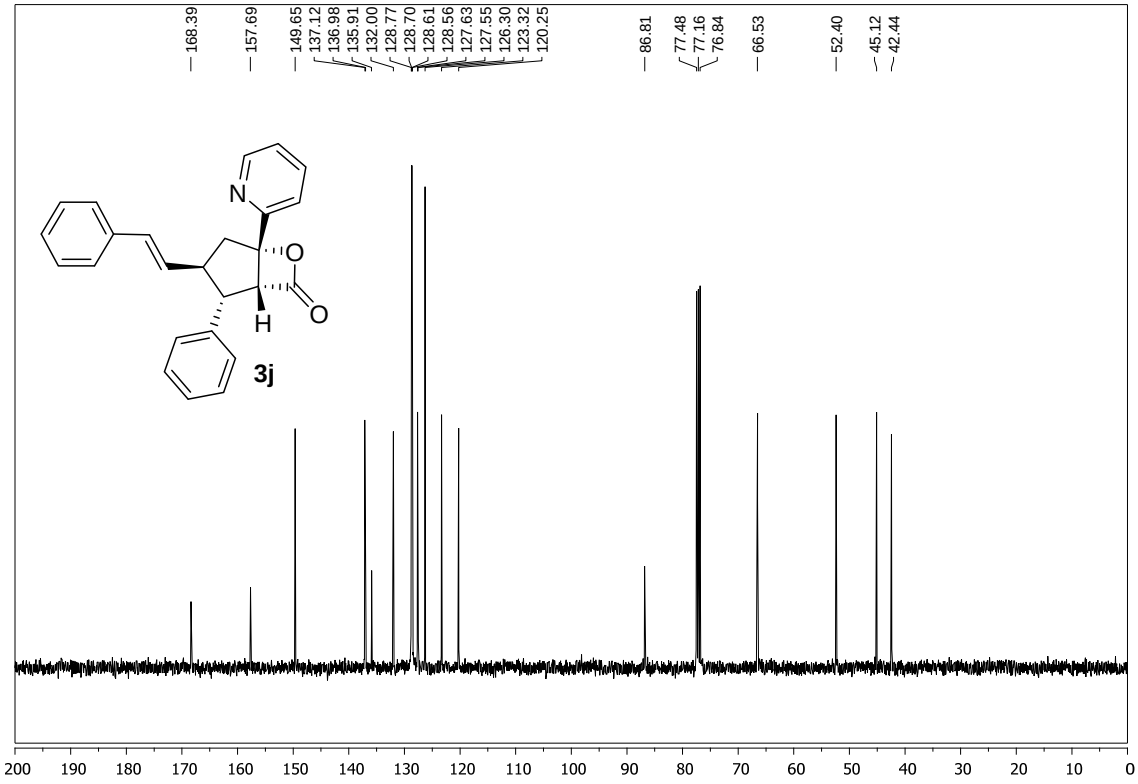
3-(Naphthalen-1-yl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3i)



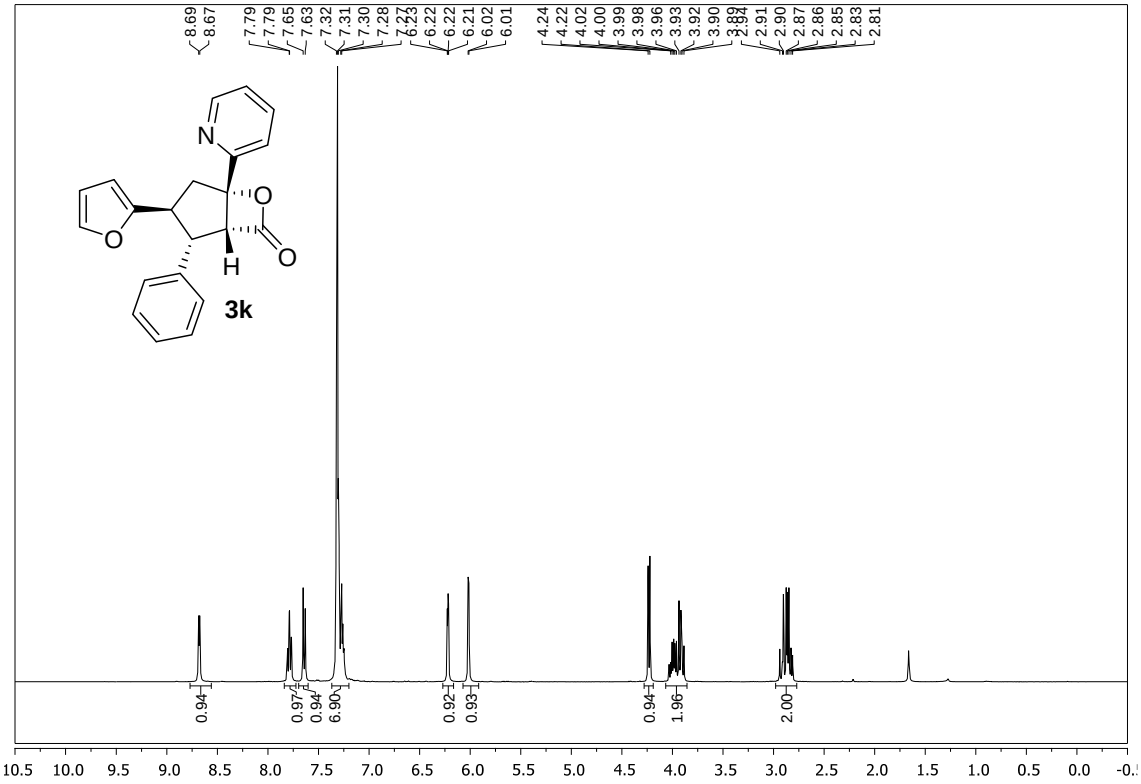


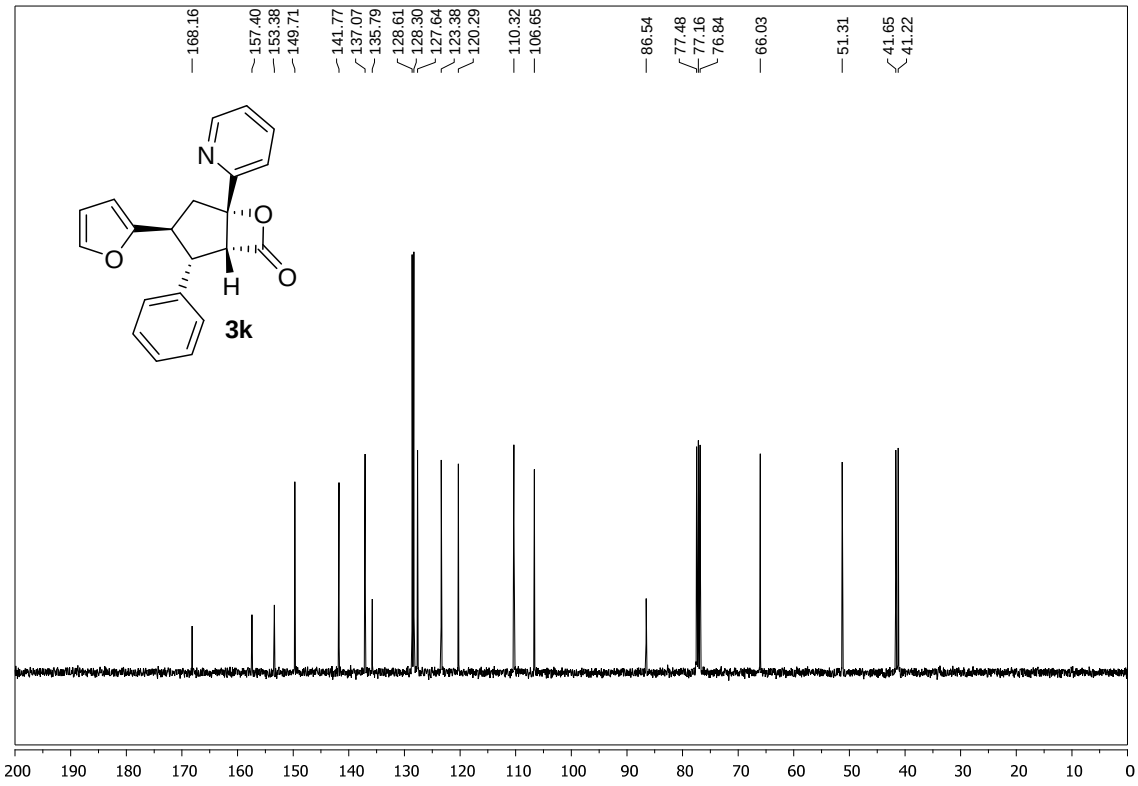
2-Phenyl-5-(pyridin-2-yl)-3-((*E*)-styryl)-6-oxabicyclo[3.2.0]heptan-7-one (3j)



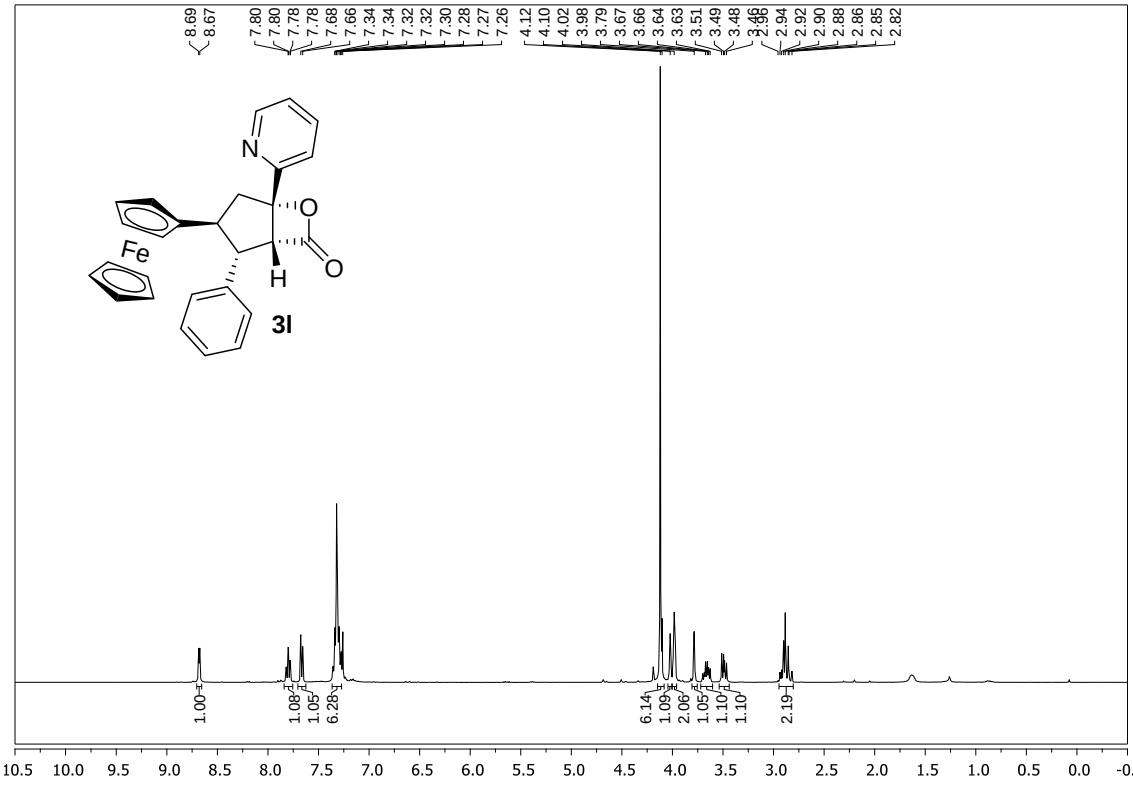


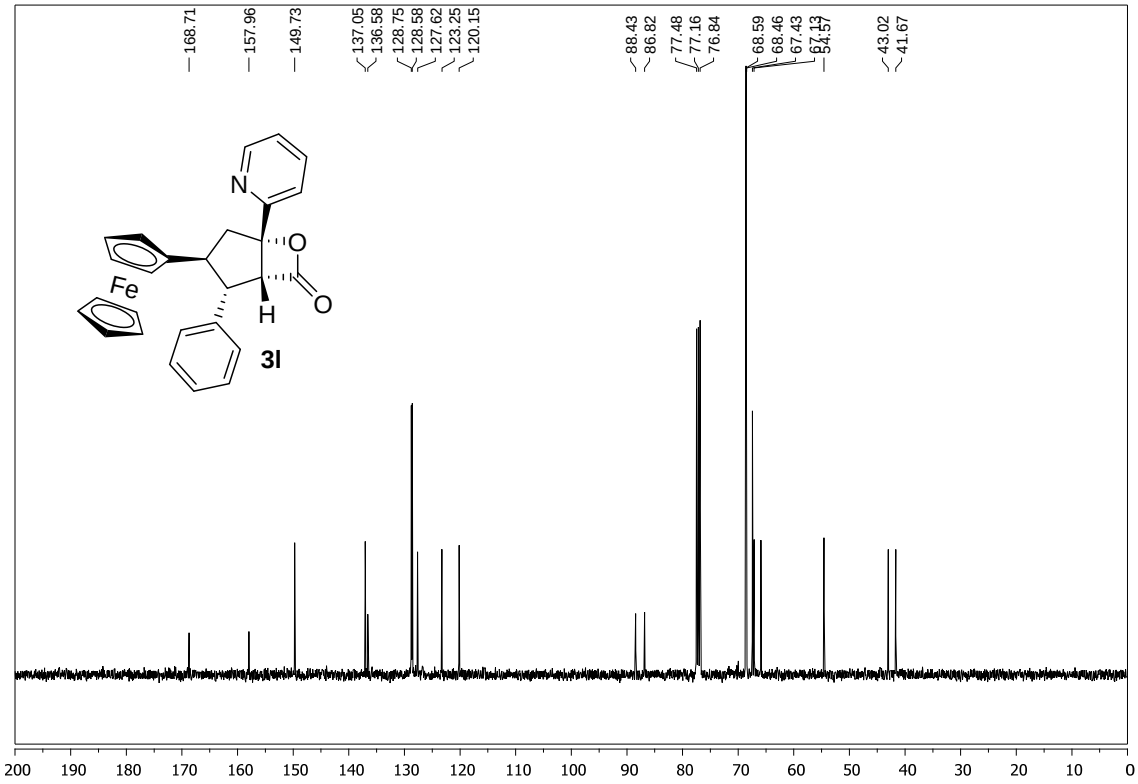
3-(Furan-2-yl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3k)



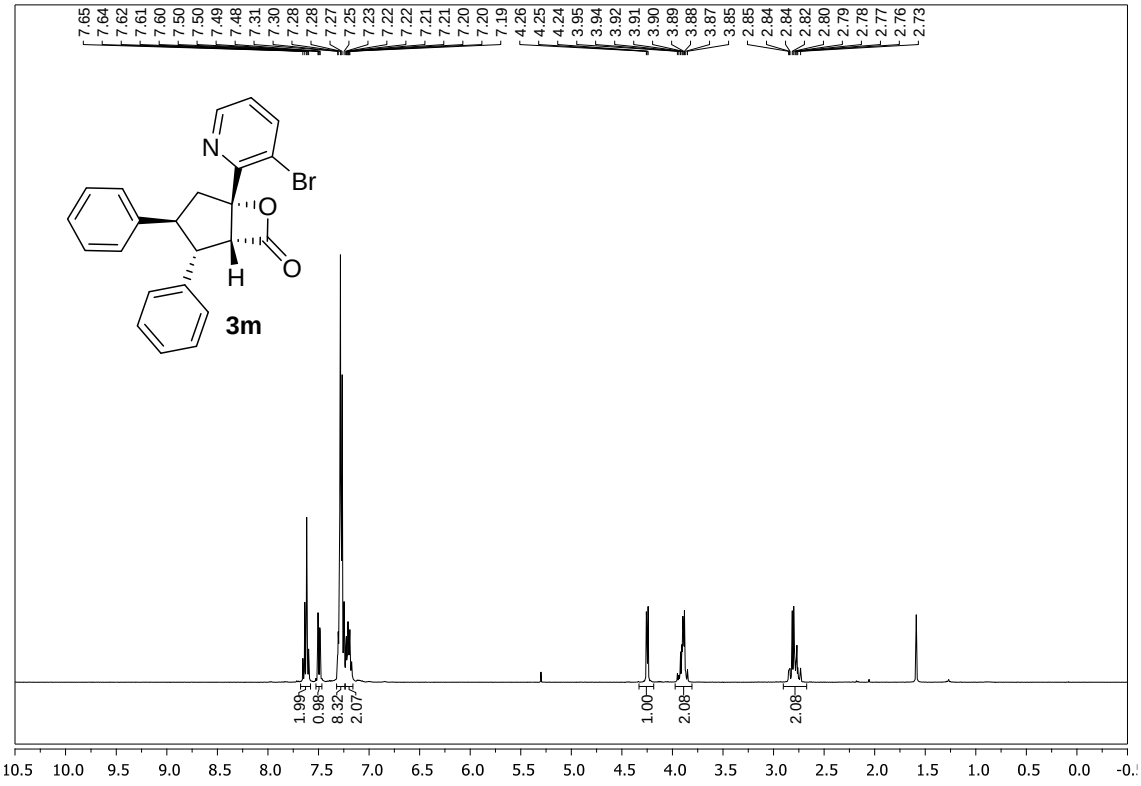


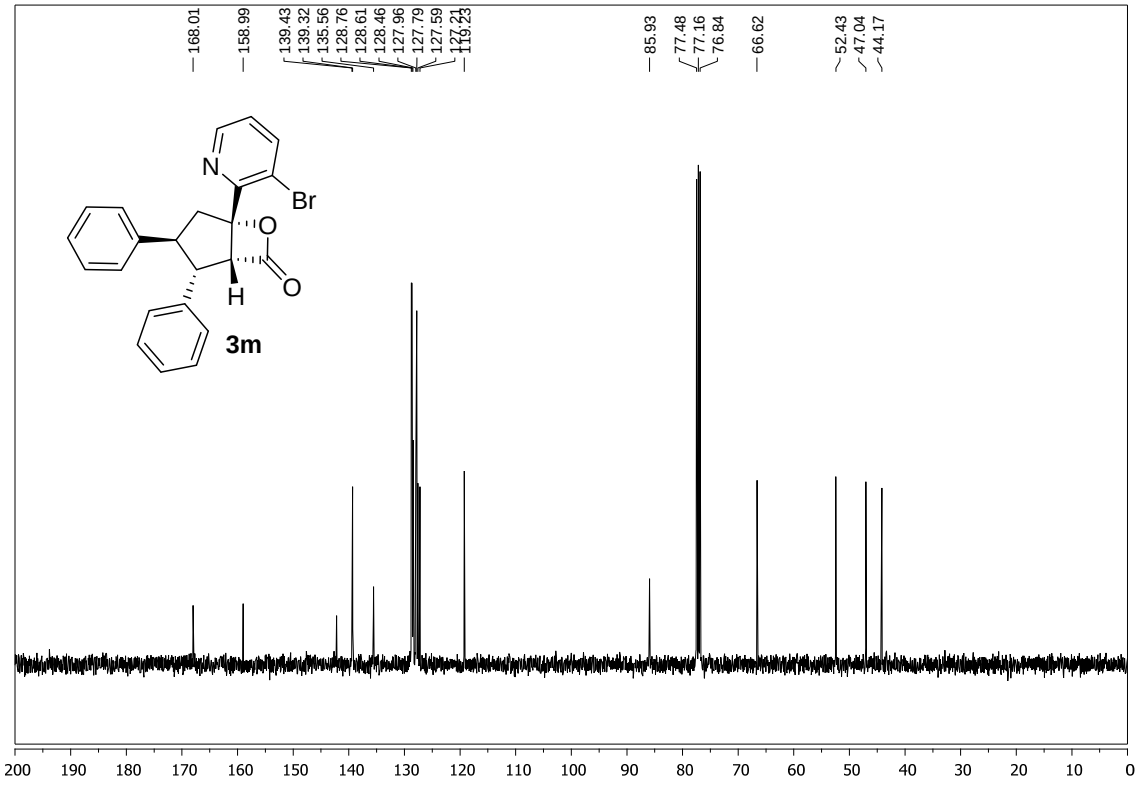
3-(Ferrocenyl)-2-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3l)



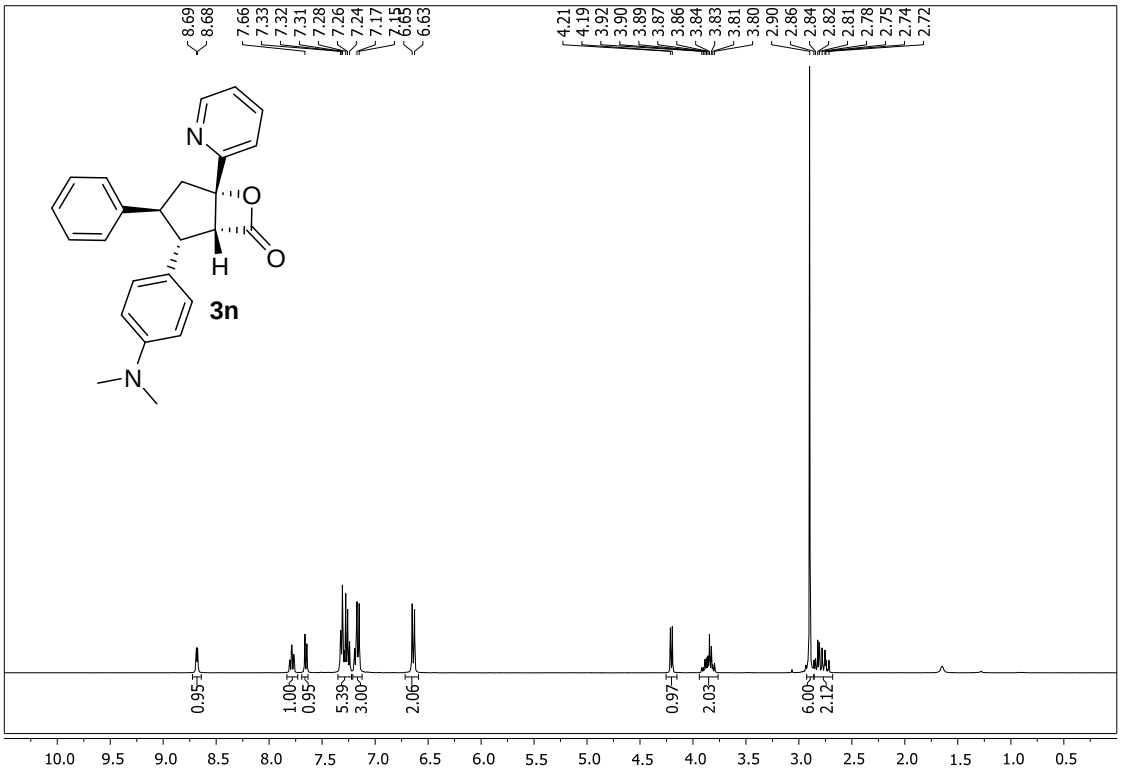


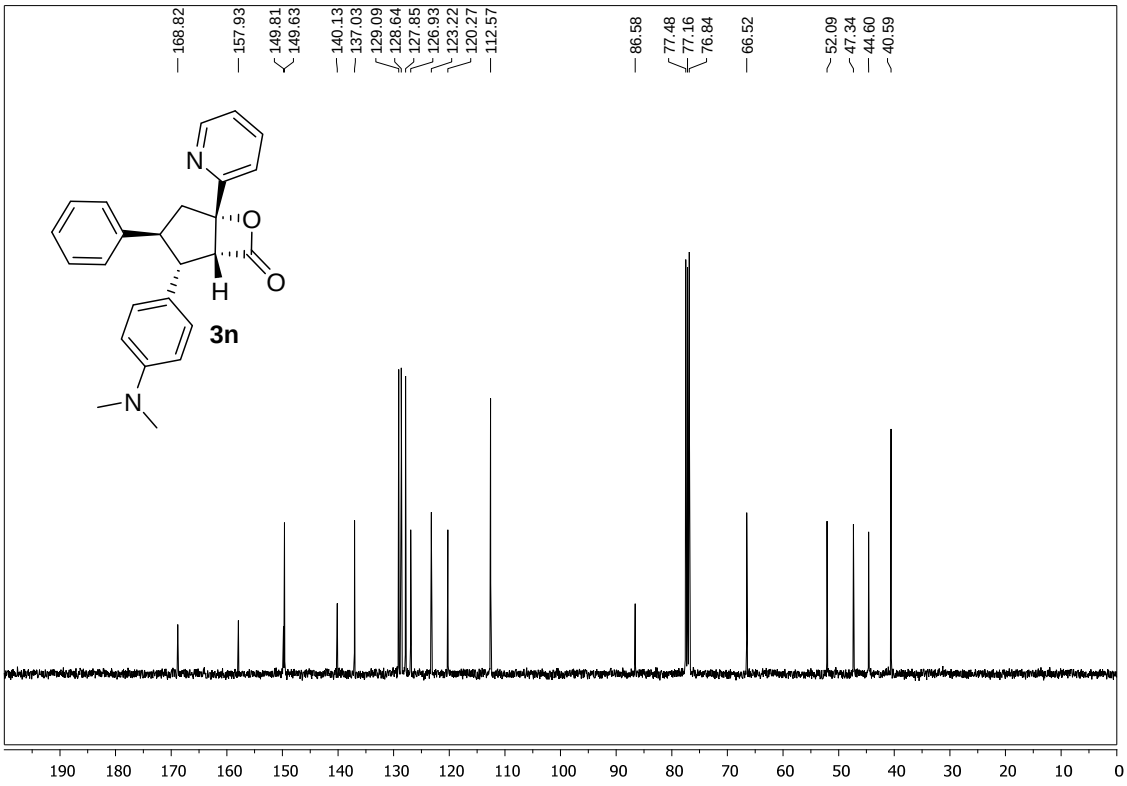
5-(3-Bromopyridin-2-yl)-2,3-diphenyl-6-oxabicyclo[3.2.0]heptan-7-one (3m)



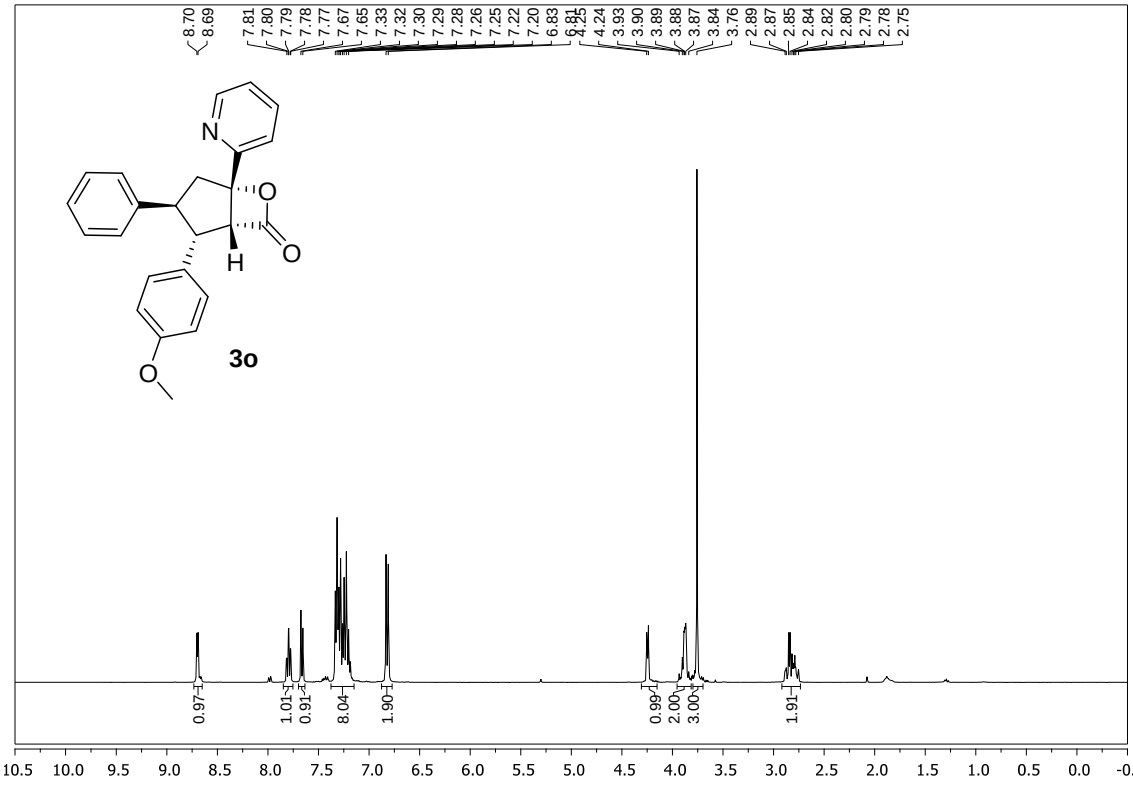


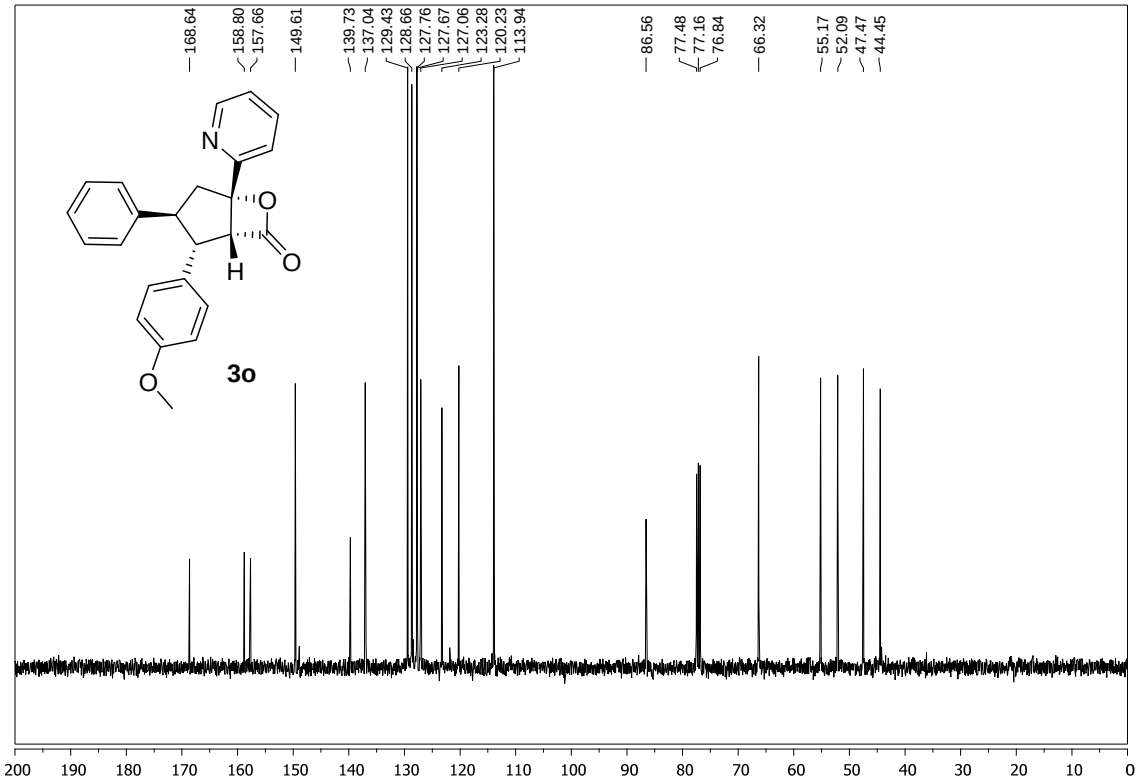
2-(4-(Dimethylamino)phenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3n)



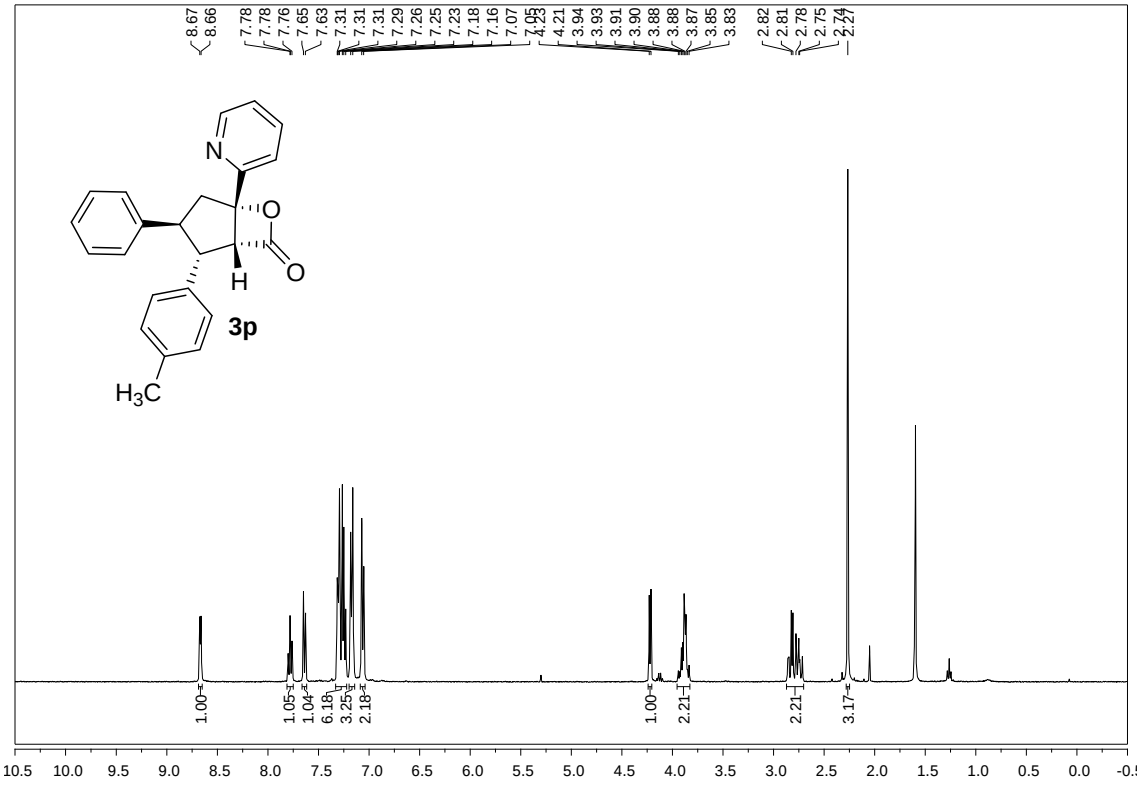


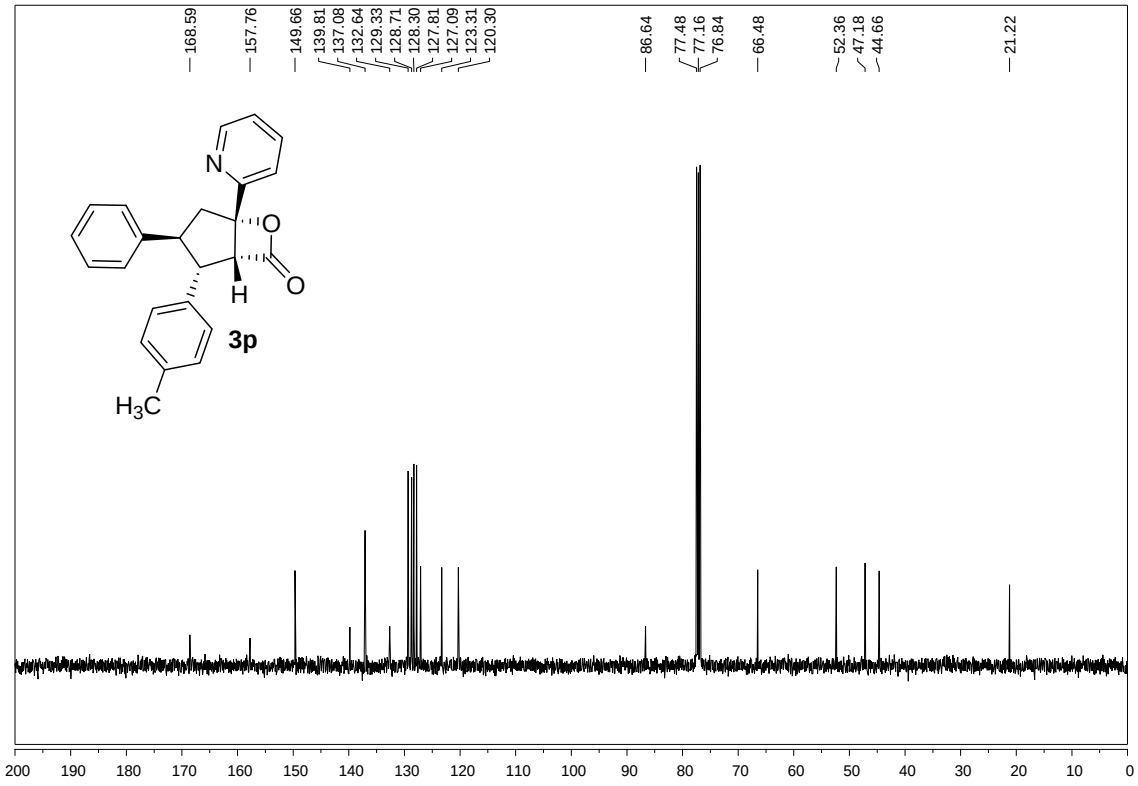
2-(4-Methoxyphenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3o)



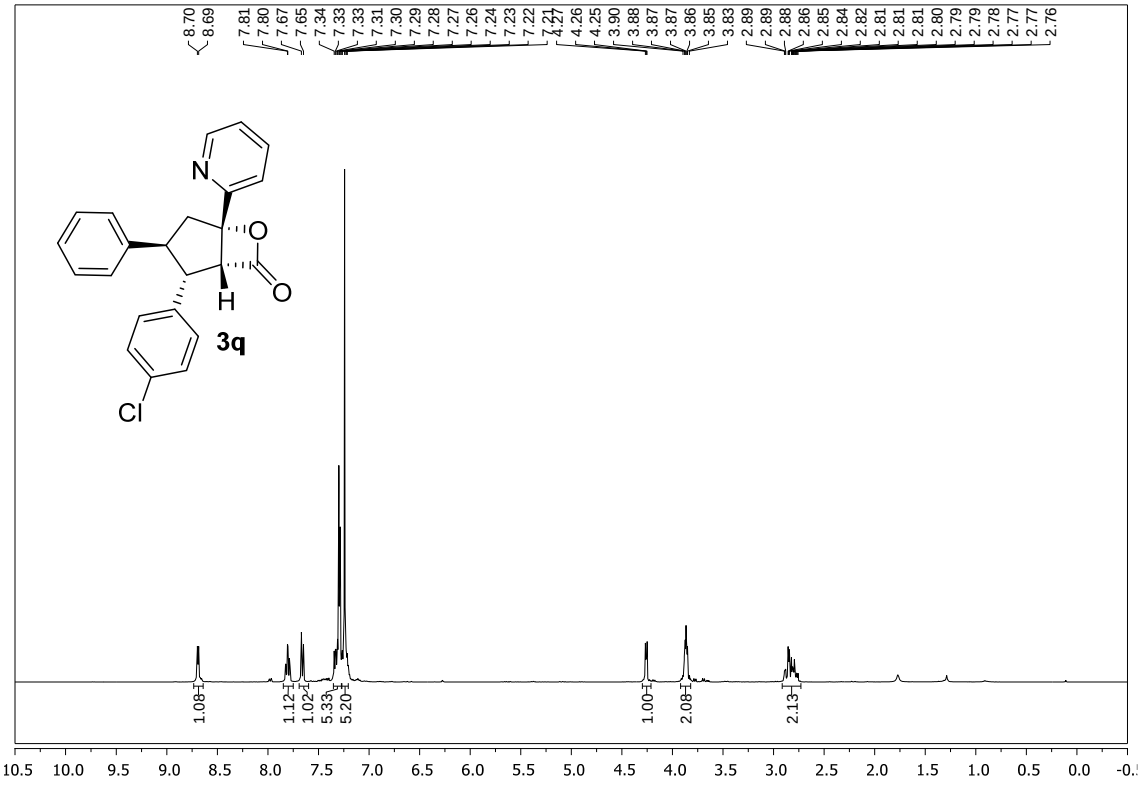


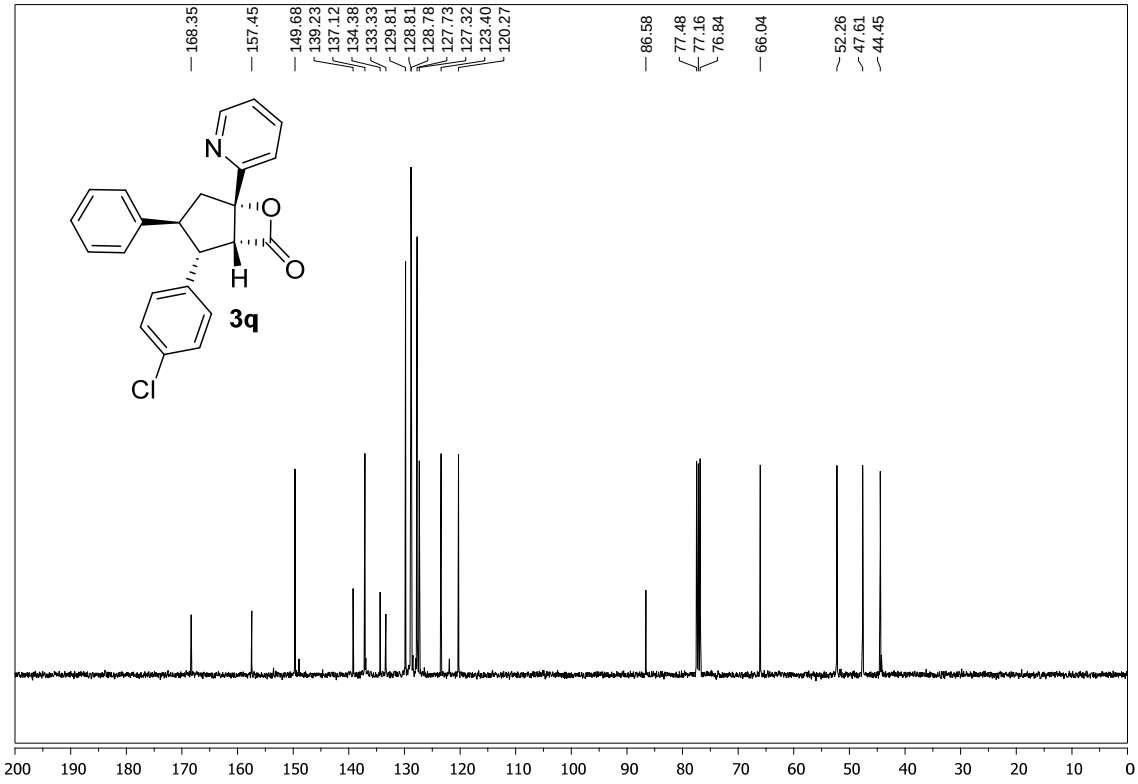
3-Phenyl-5-(pyridin-2-yl)-2-(p-tolyl)-6-oxabicyclo[3.2.0]heptan-7-one (3p)



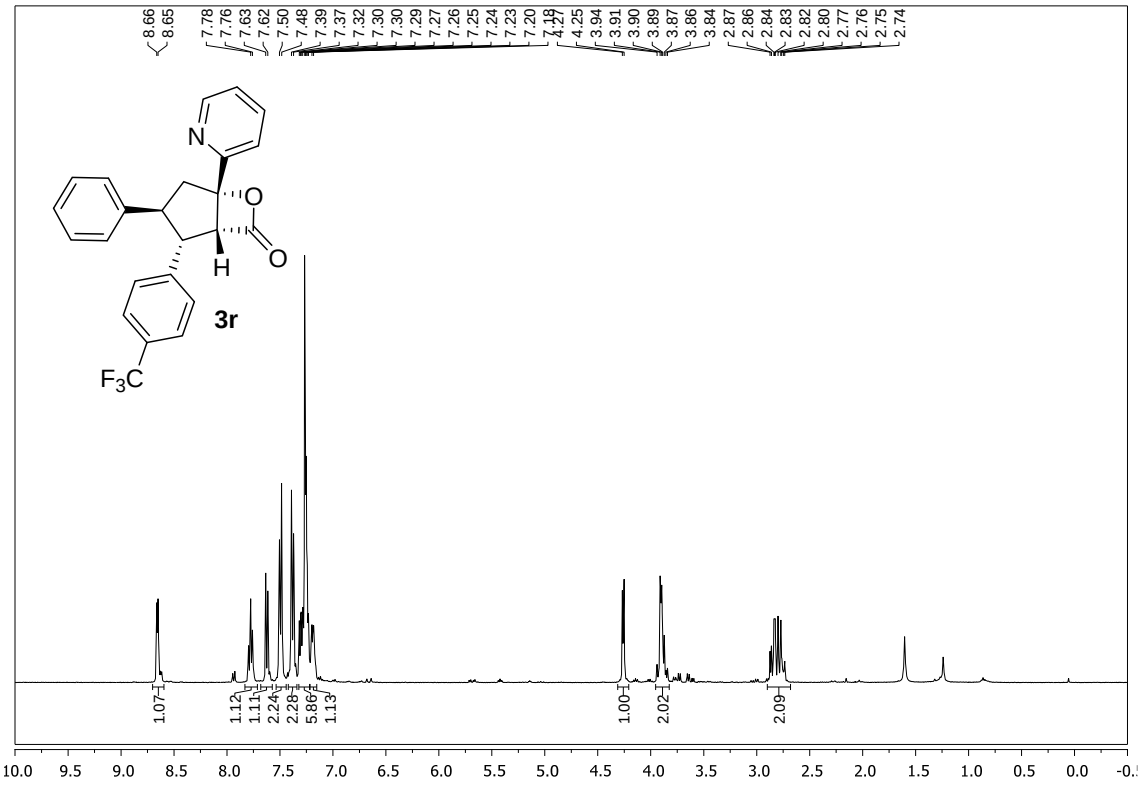


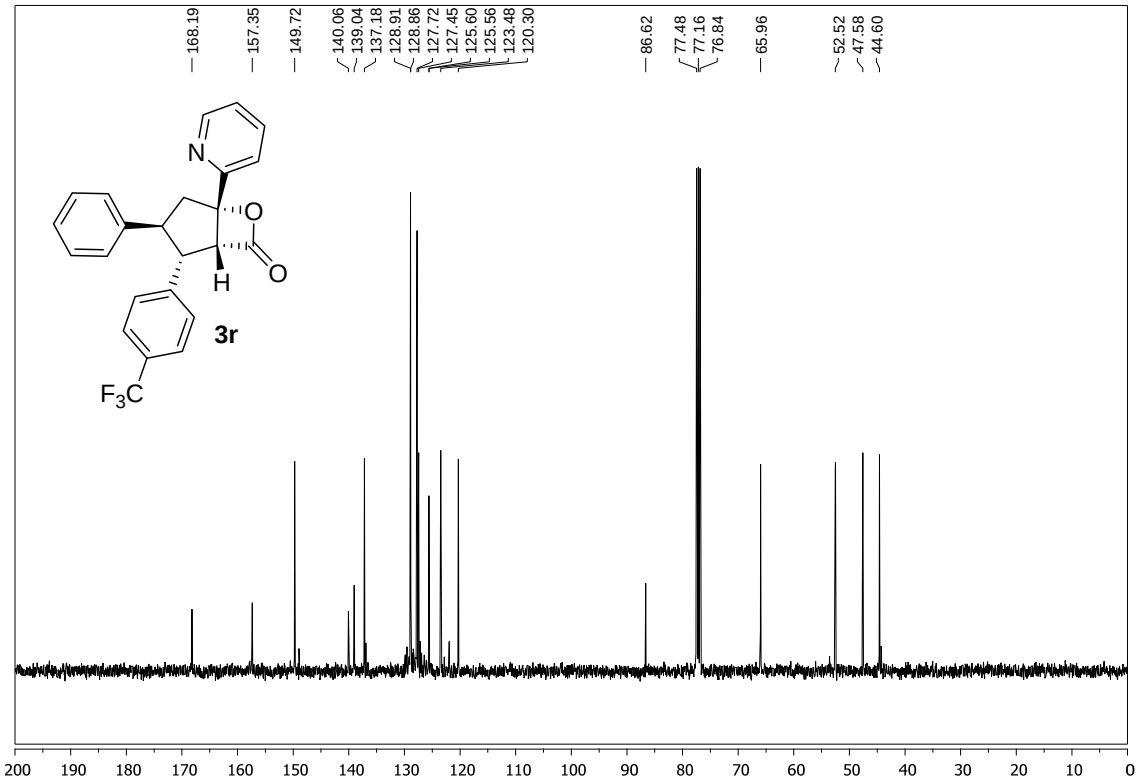
2-(4-Chlorophenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3q)



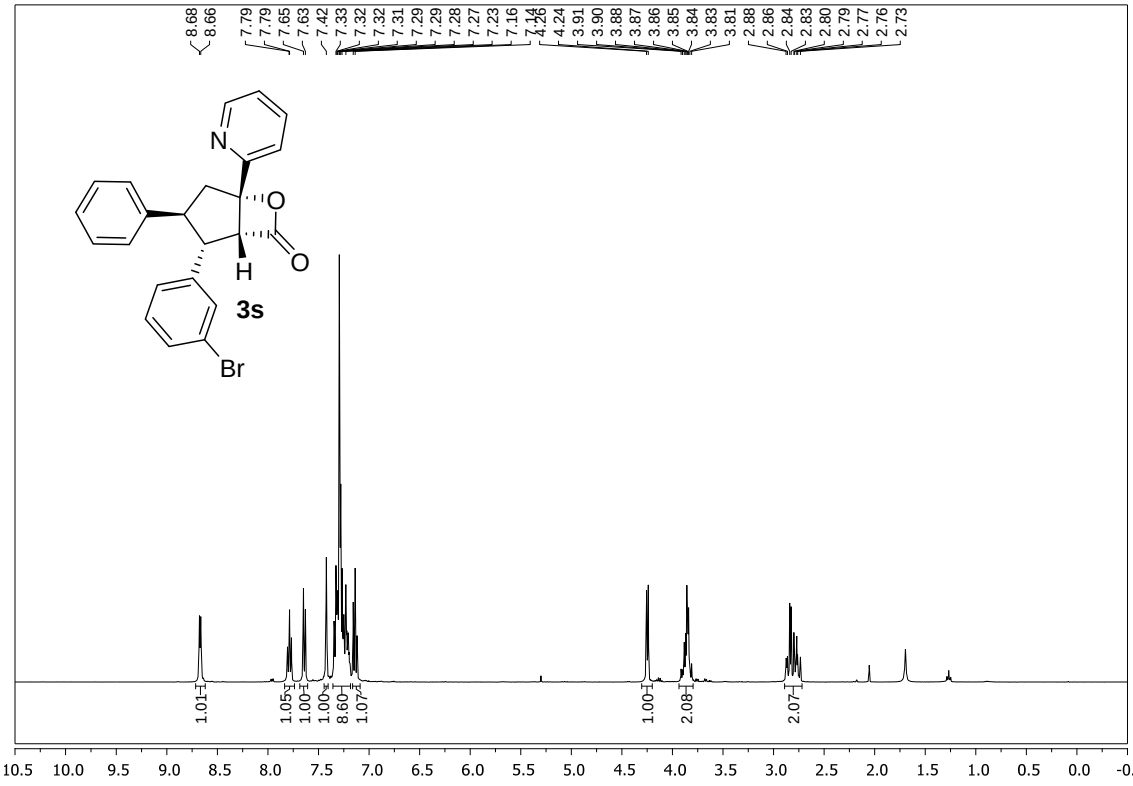


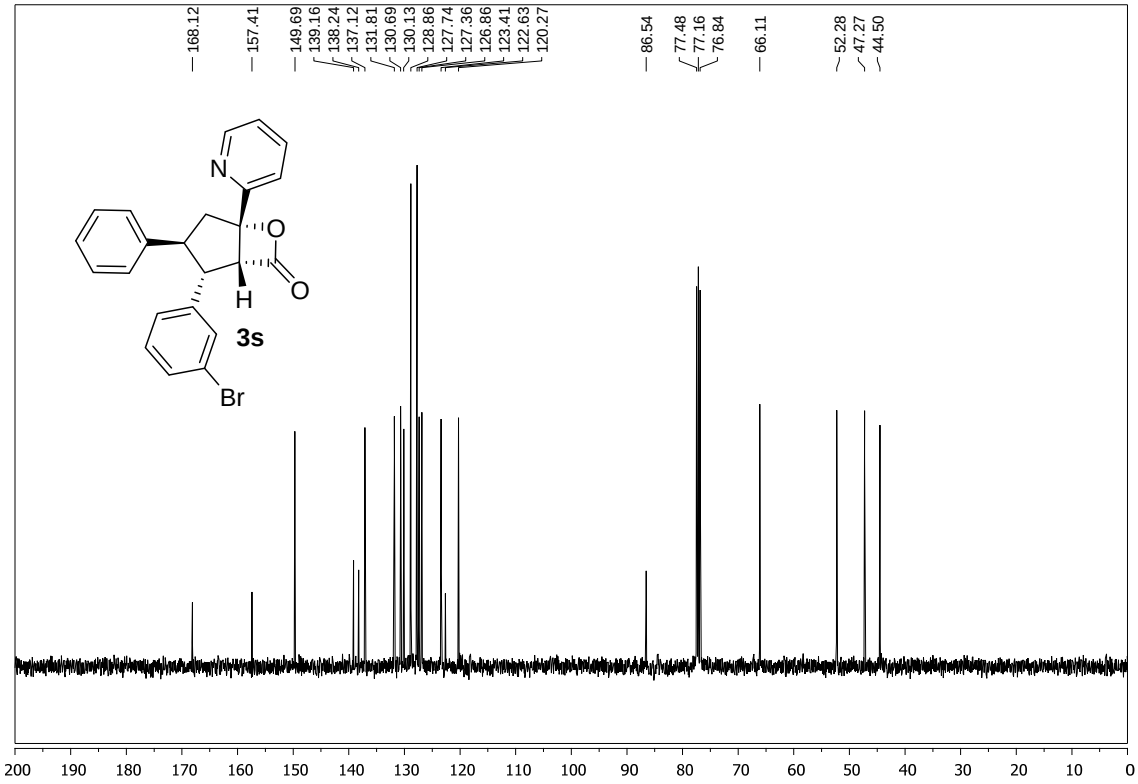
3-Phenyl-5-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)-6-oxabicyclo[3.2.0]heptan-7-one (3r)



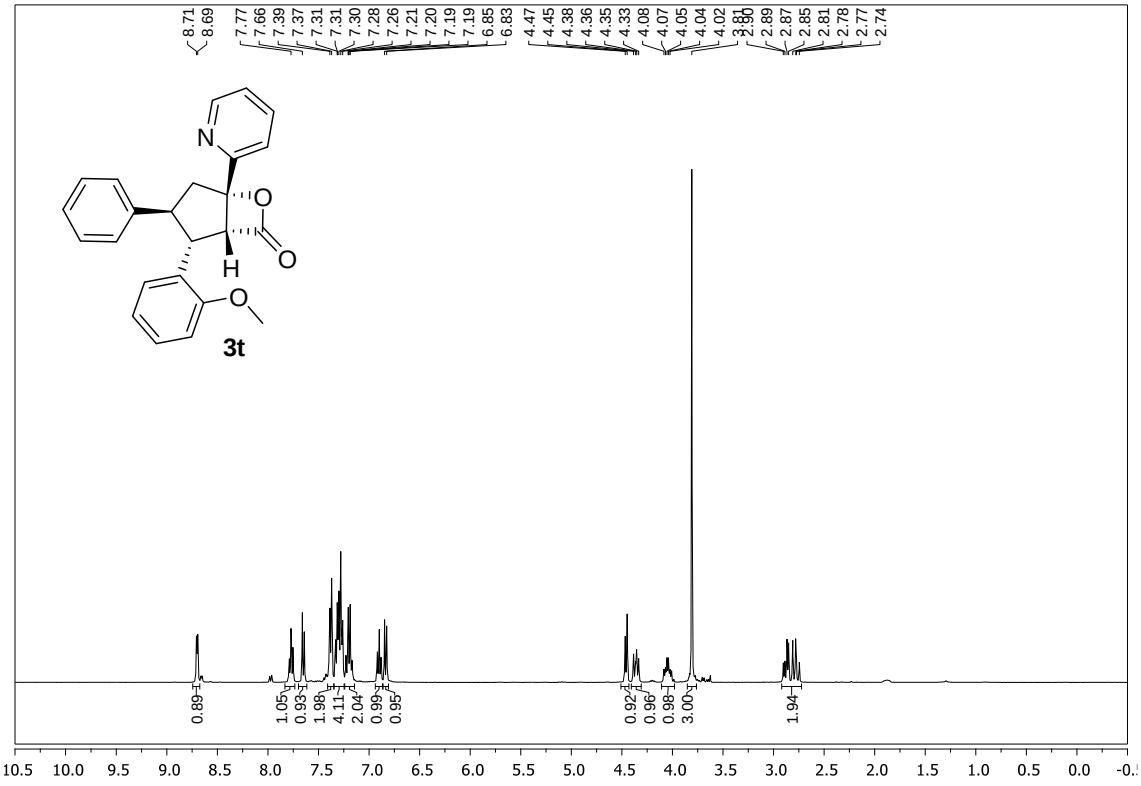


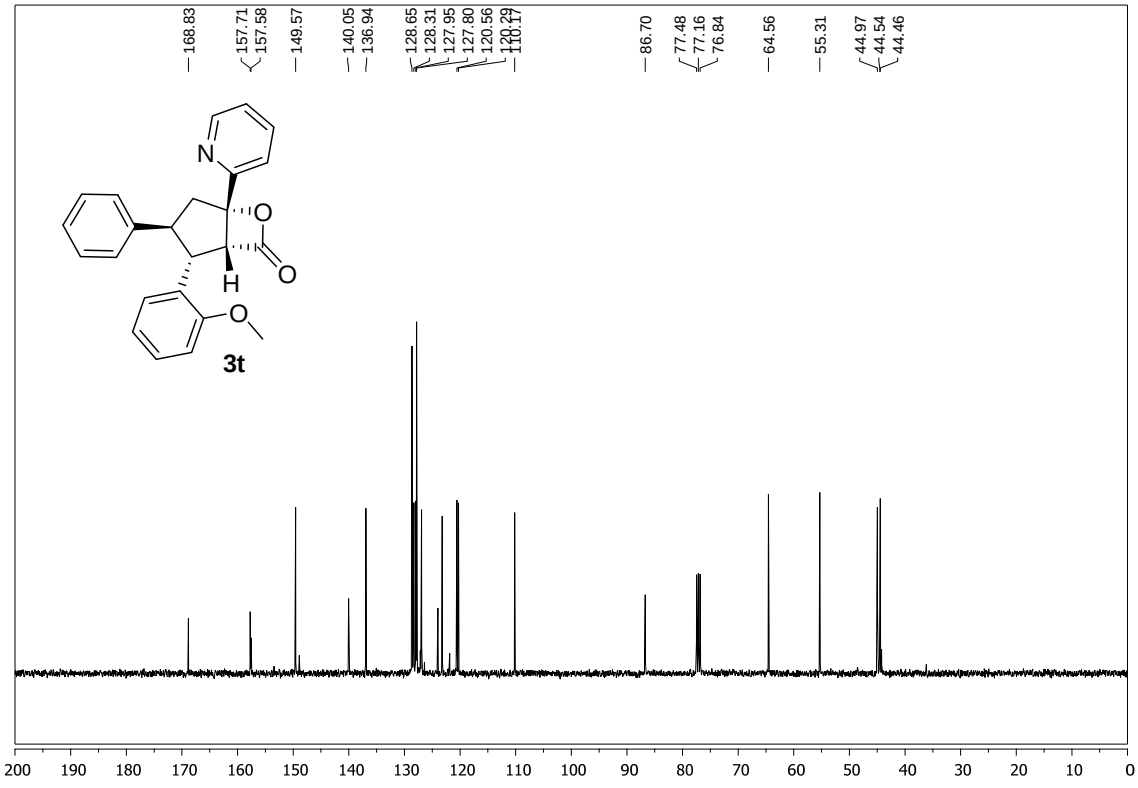
2-(3-Bromophenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3s)



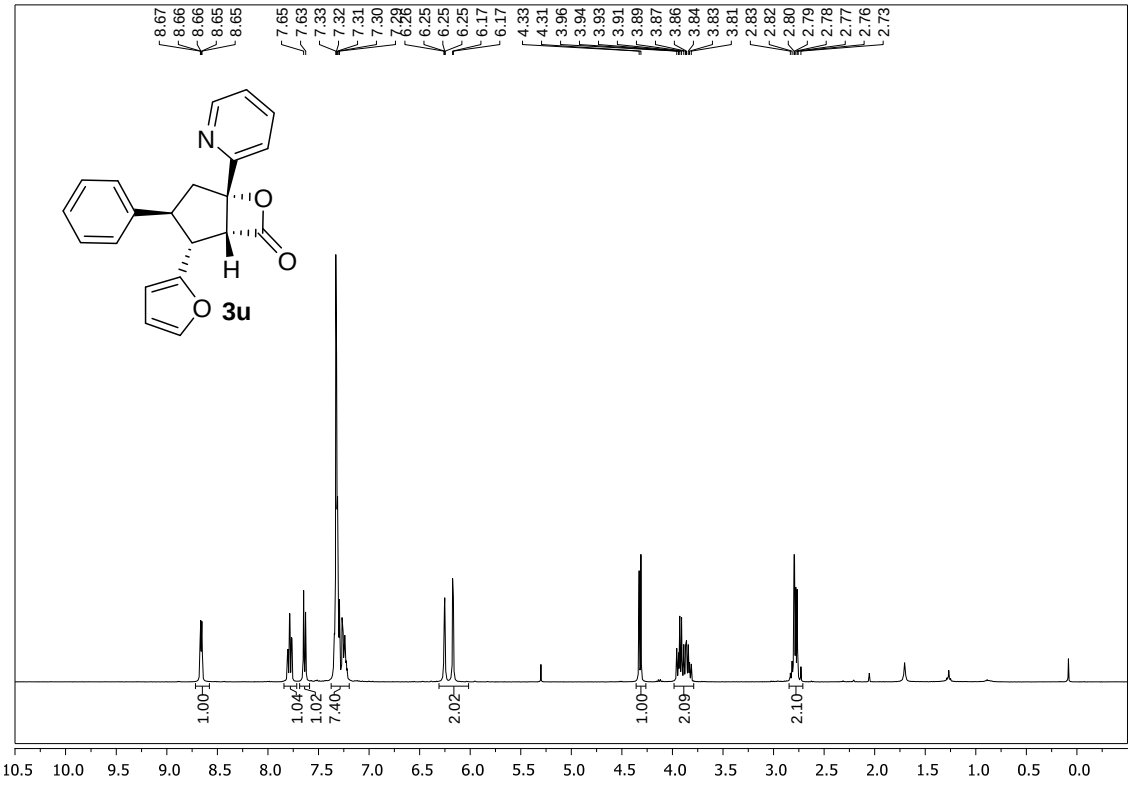


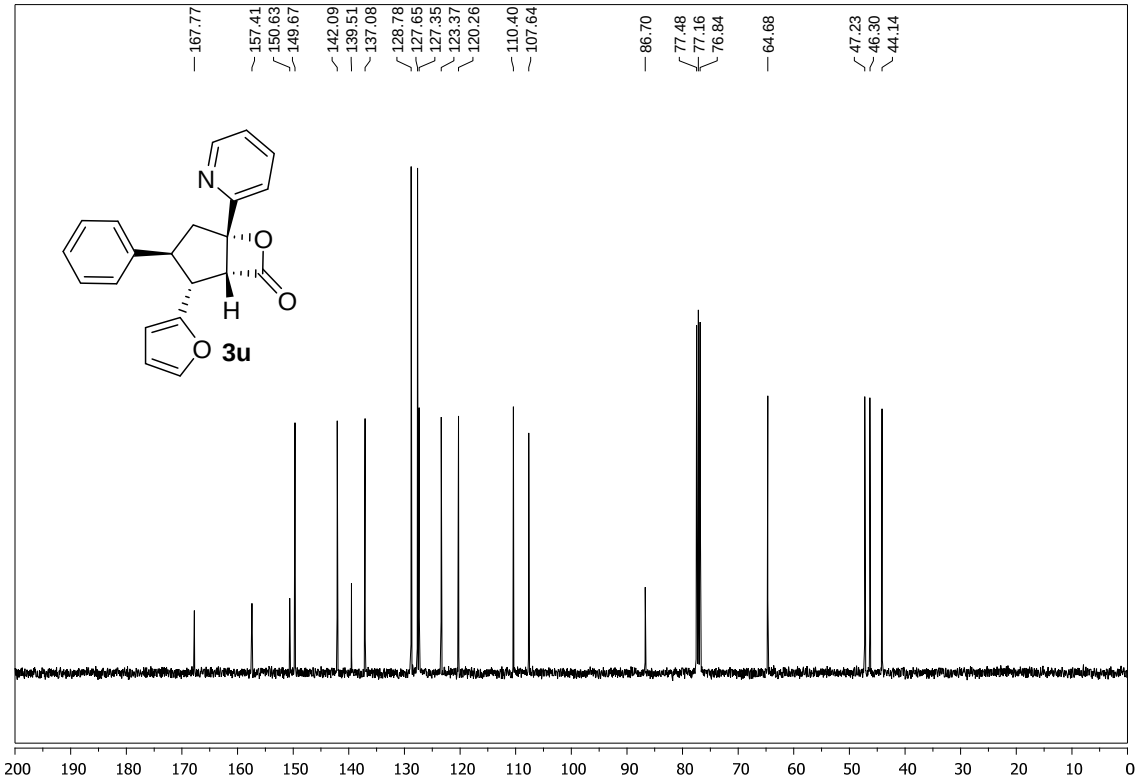
2-(2-Methoxyphenyl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3t)



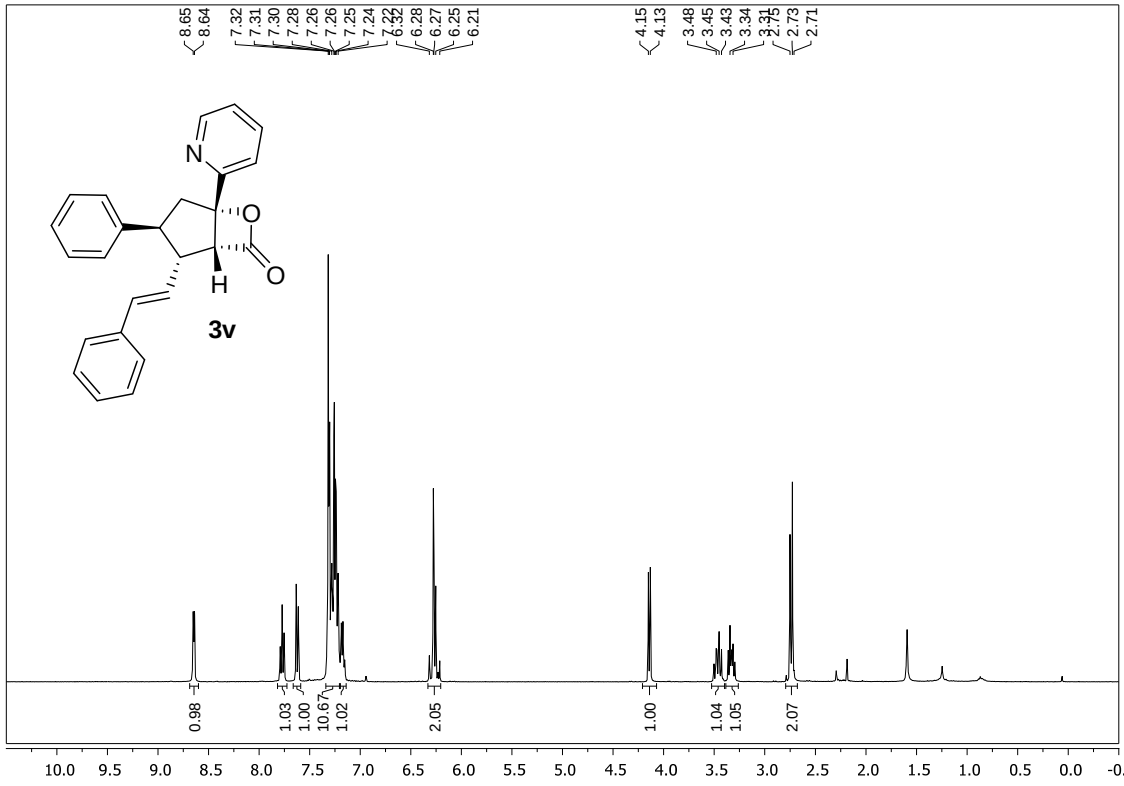


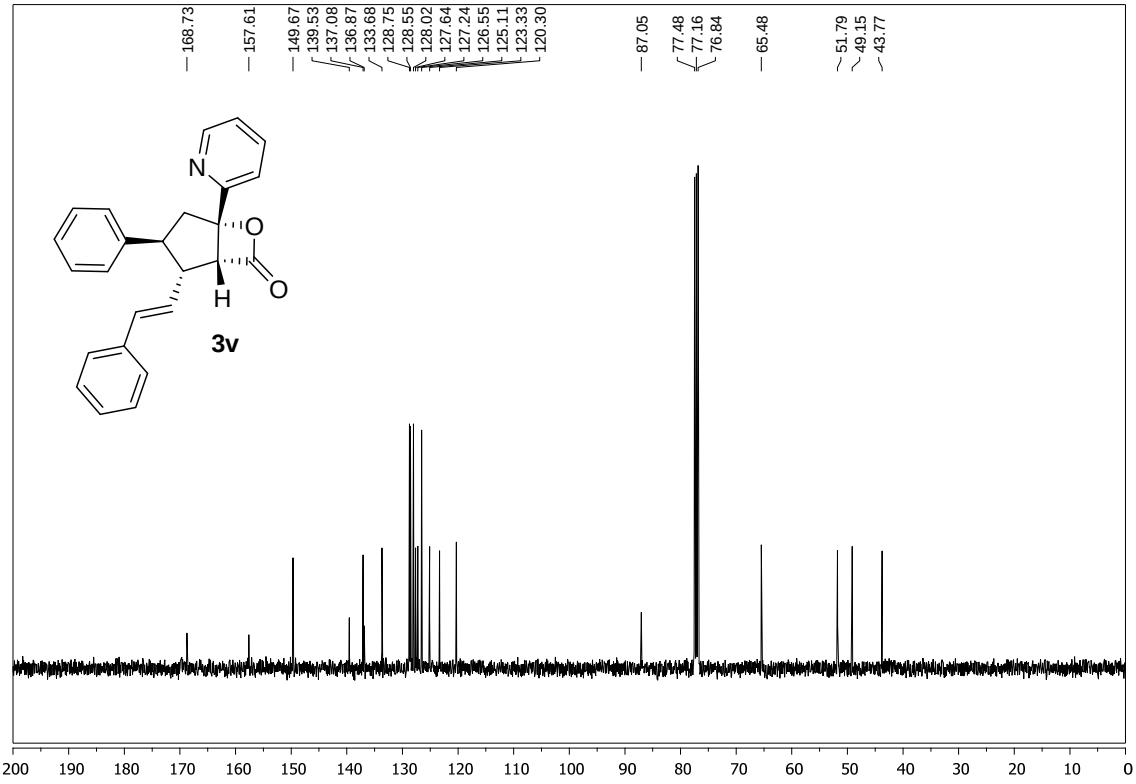
2-(Furan-2-yl)-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3u)



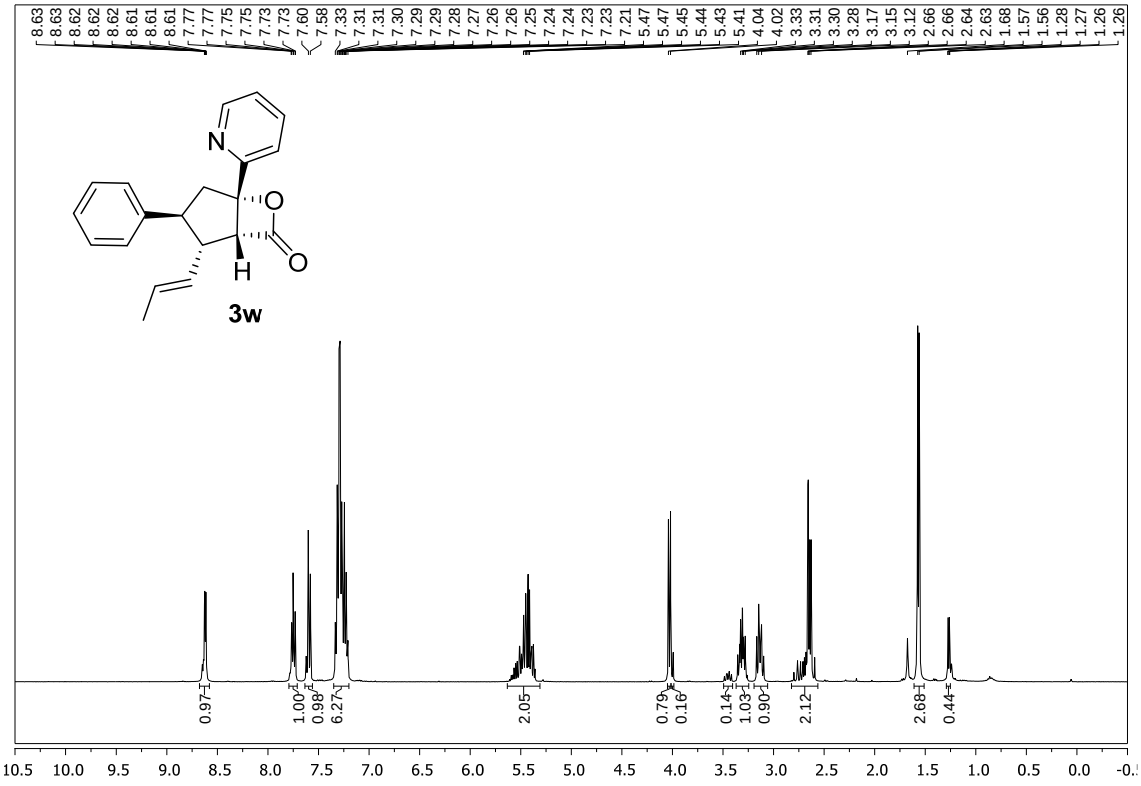


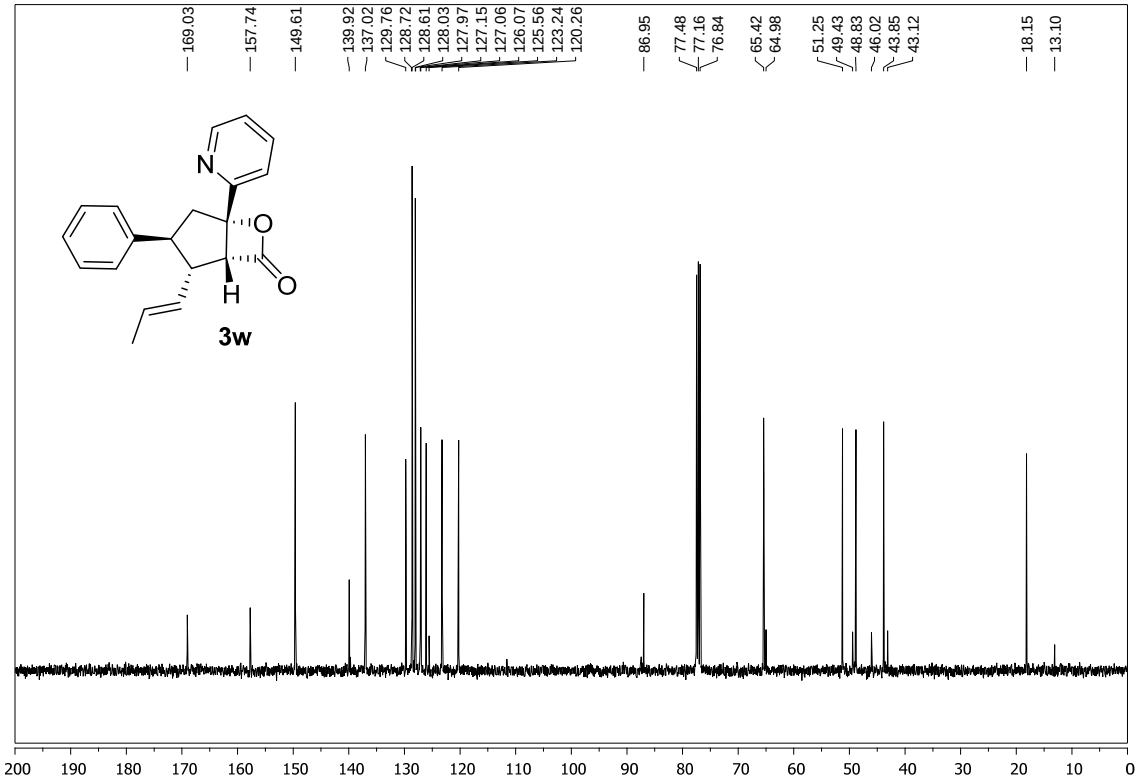
3-Phenyl-5-(pyridin-2-yl)-2-((*E*)-styryl)-6-oxabicyclo[3.2.0]heptan-7-one (3v)



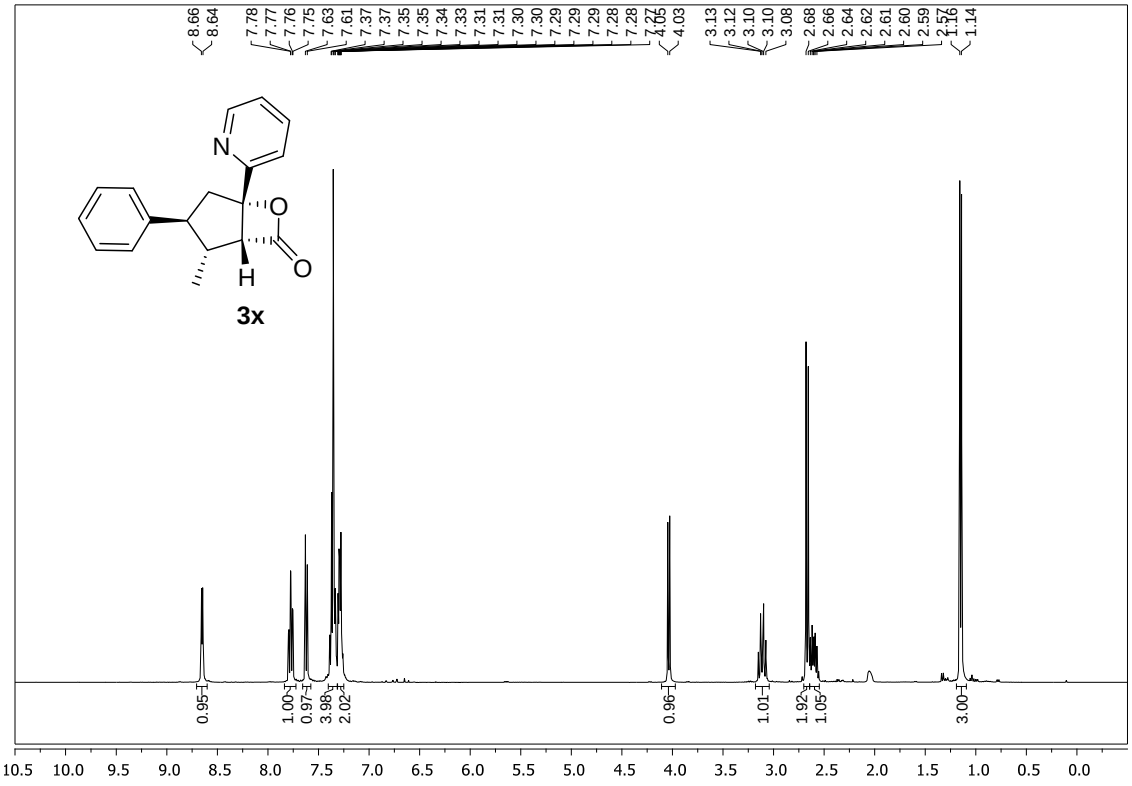


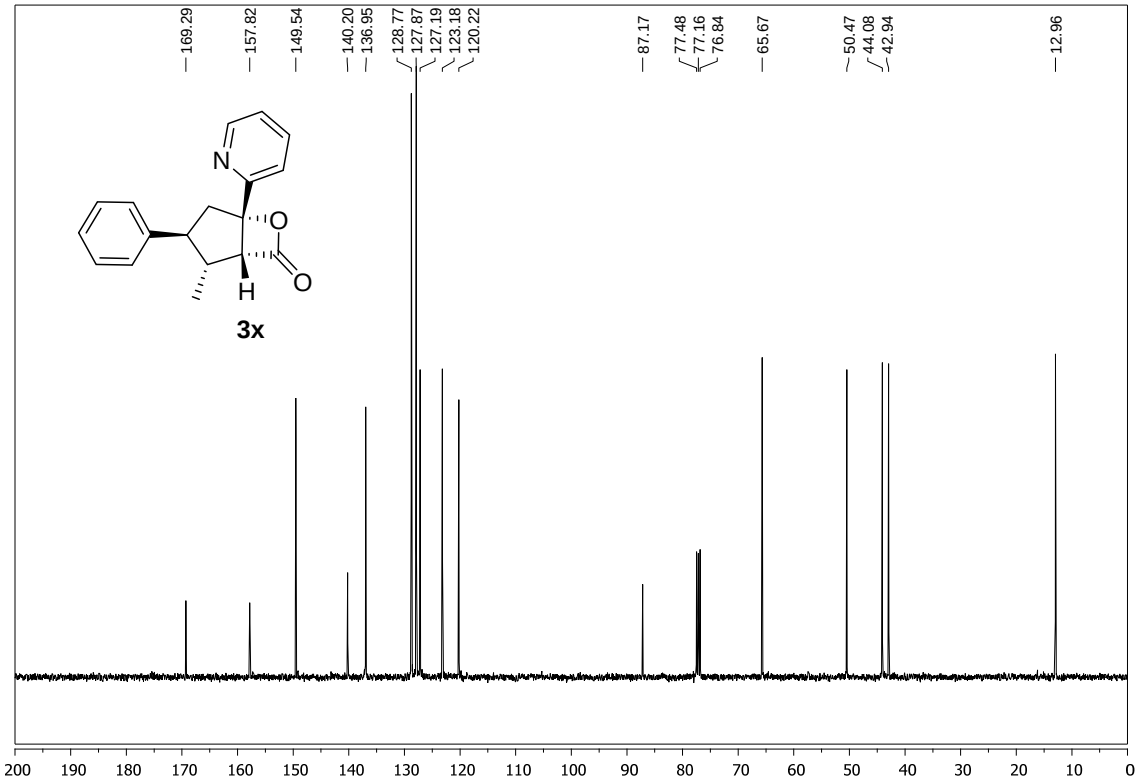
3-Phenyl-2-((*E*)-prop-1-en-1-yl)-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3w)



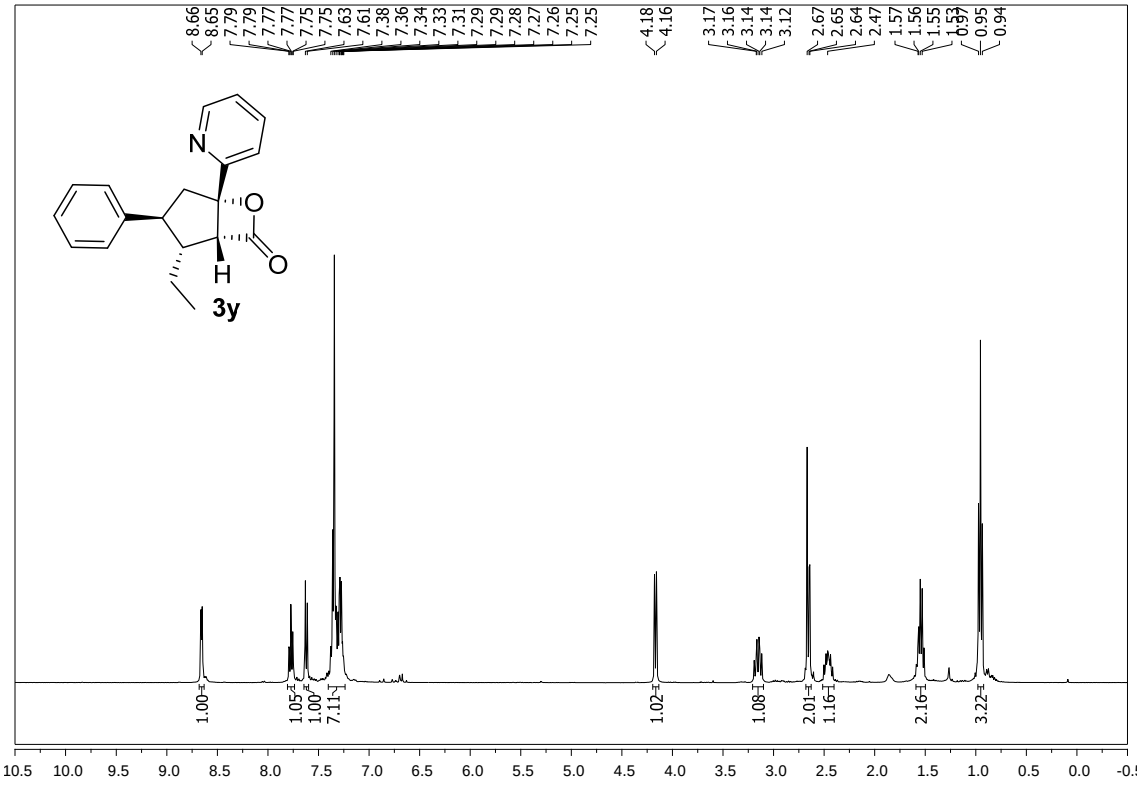


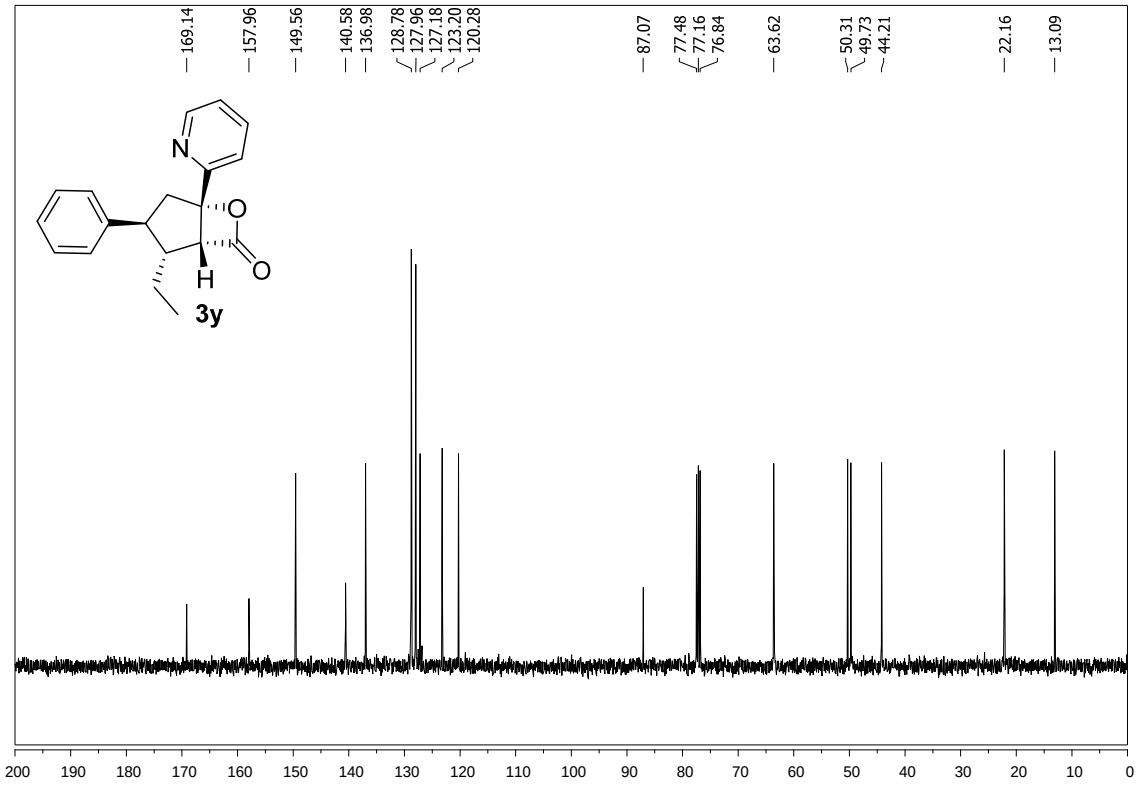
2-Methyl-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3x)



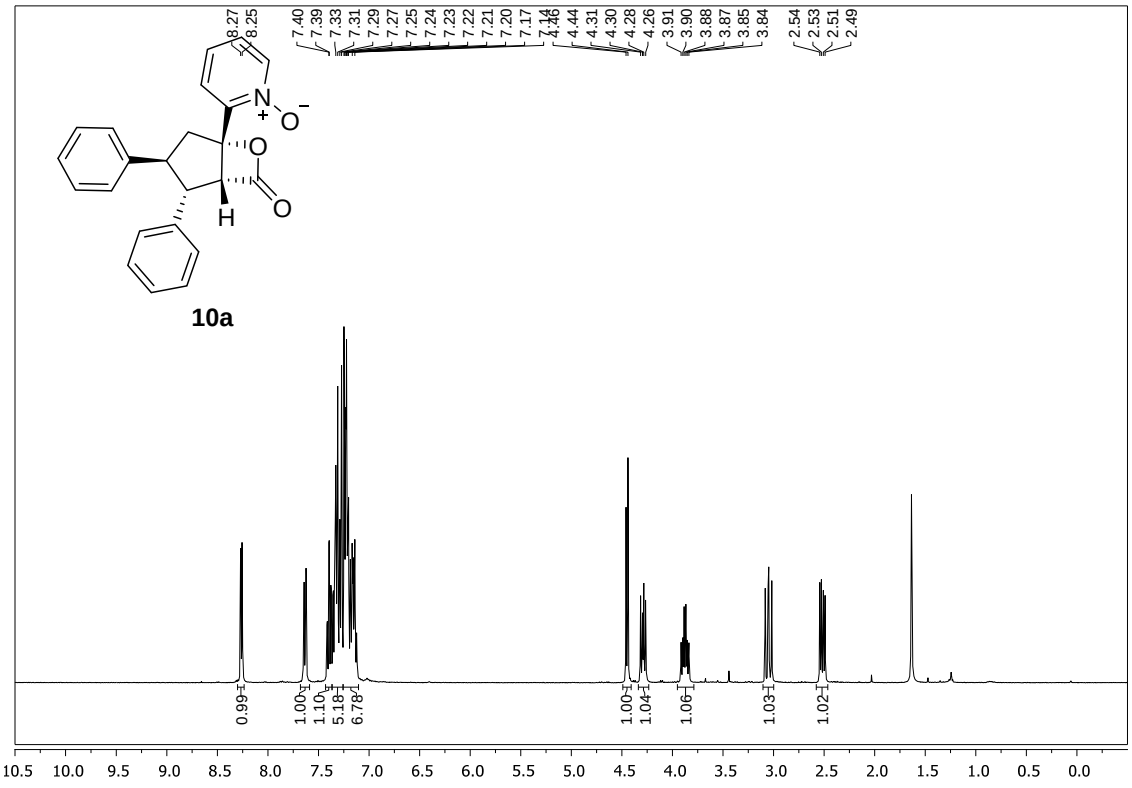


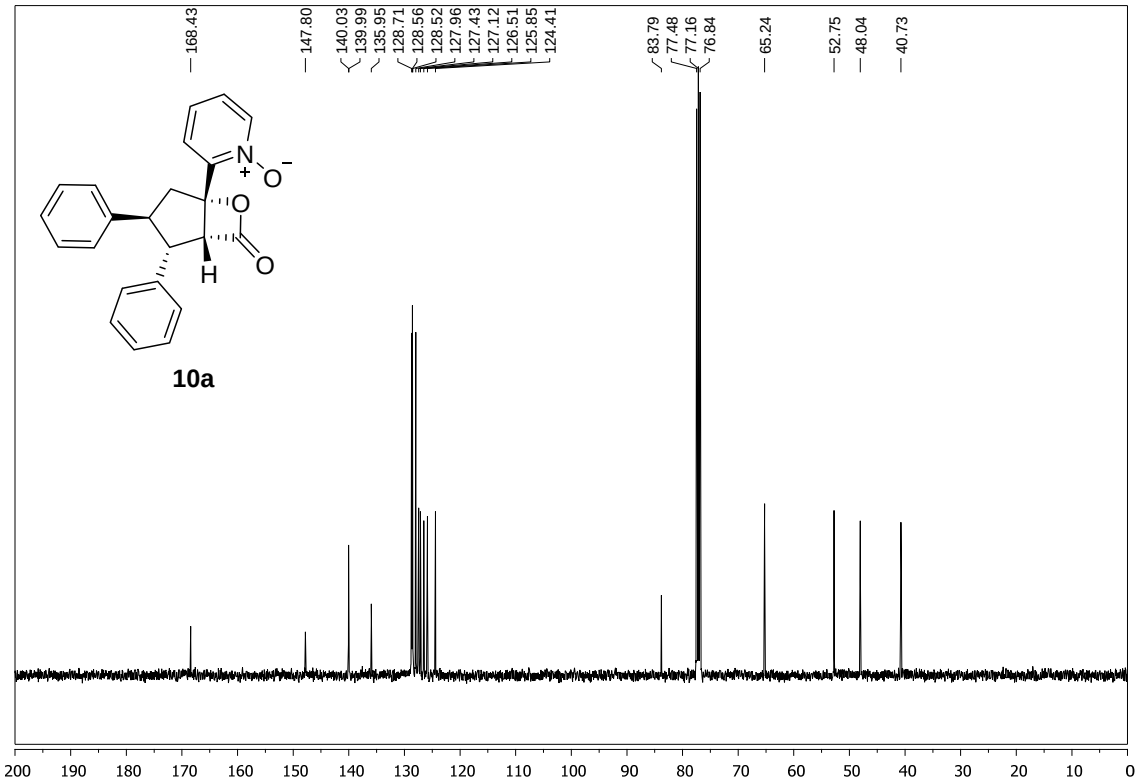
2-Ethyl-3-phenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (3y)



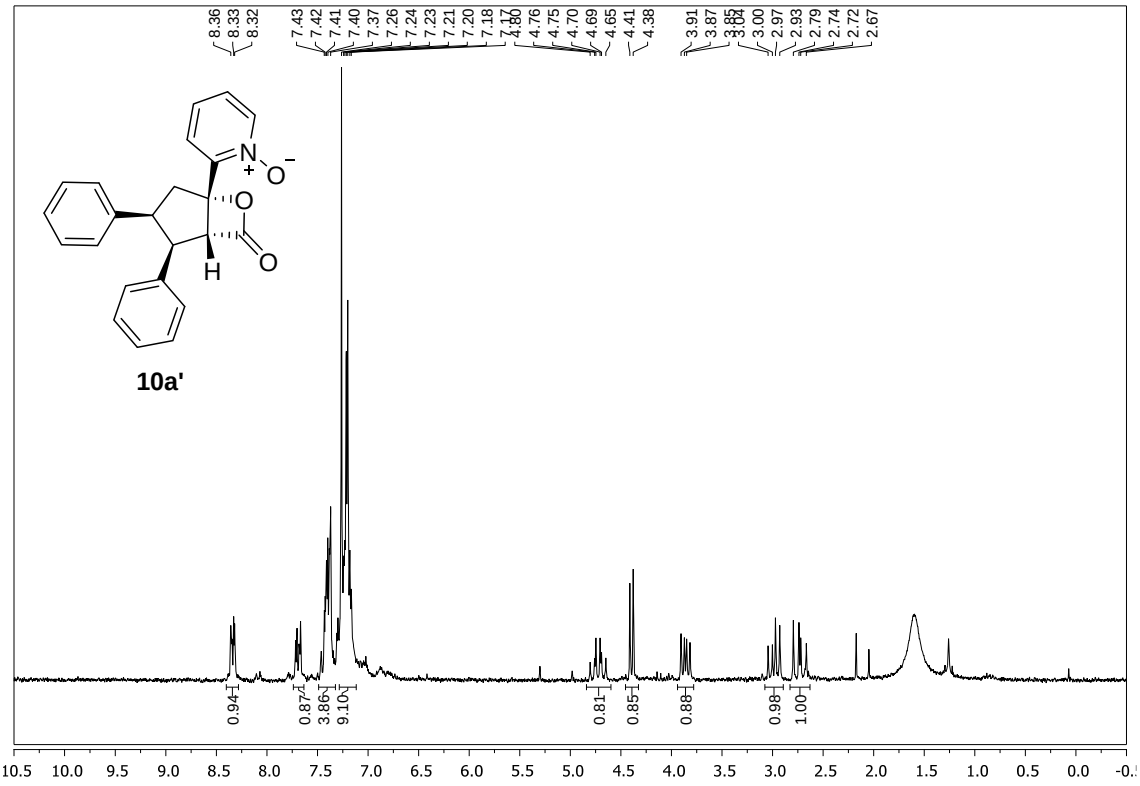


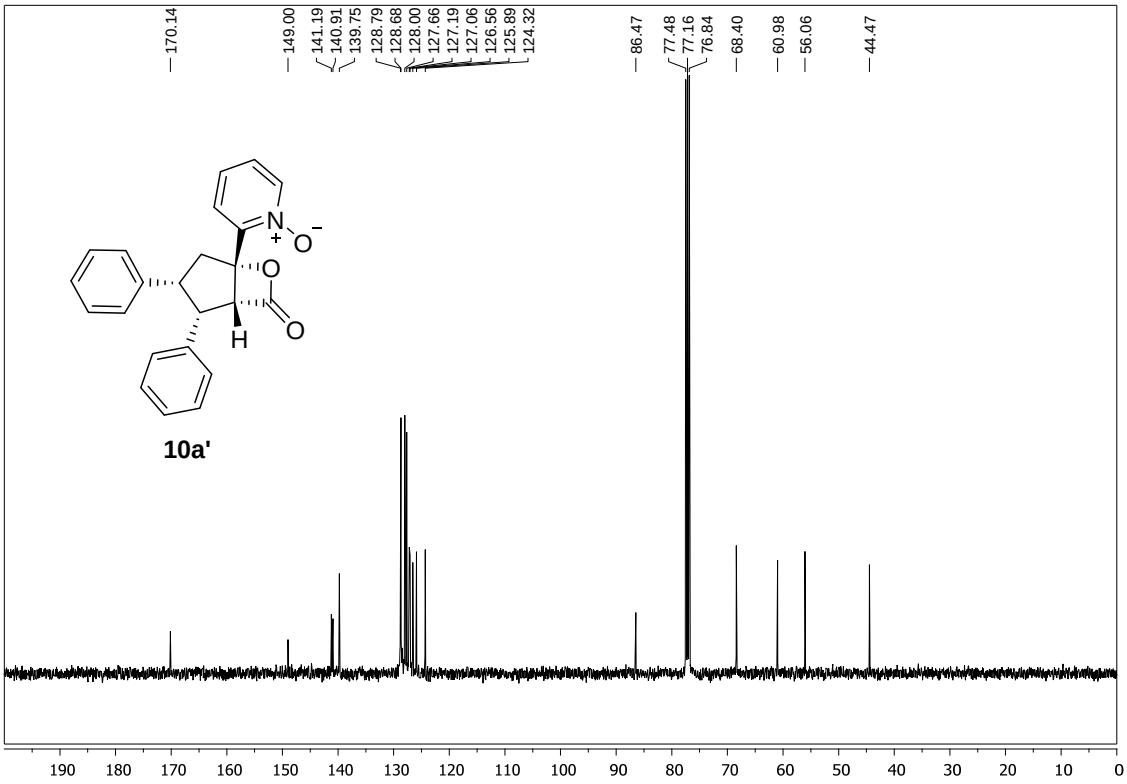
2-(7-Oxo-2,3-diphenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10a major isomer)



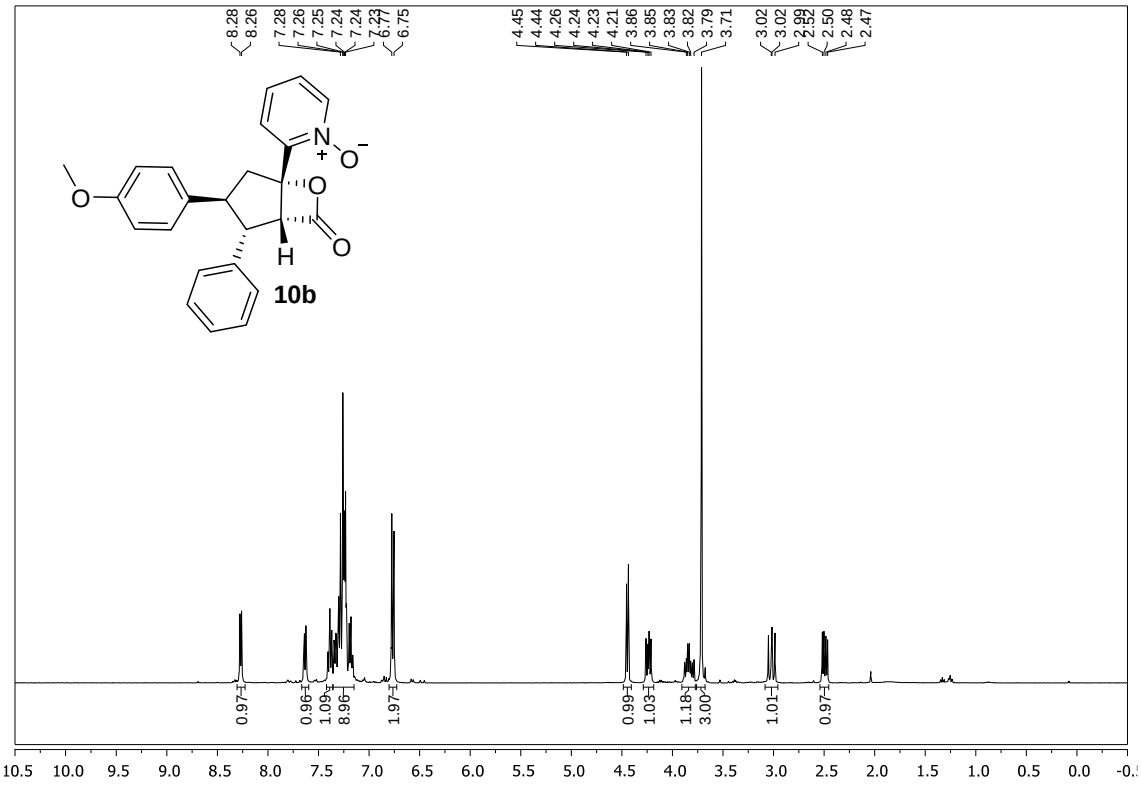


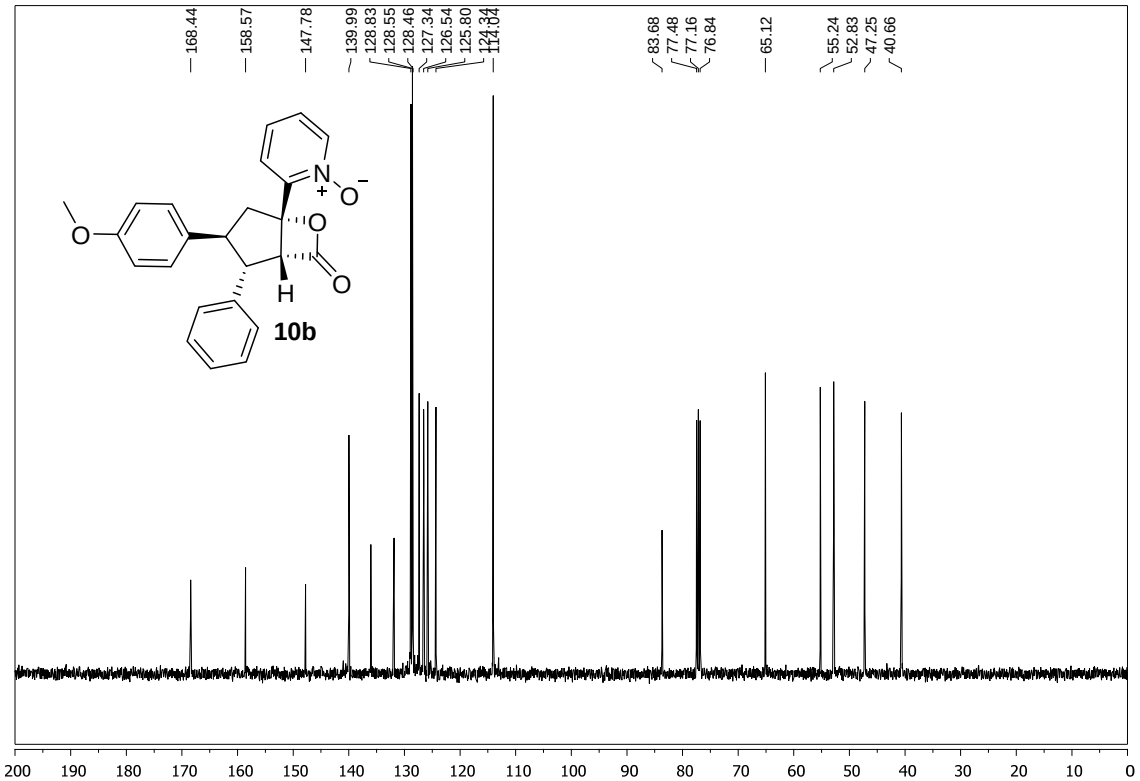
2-(7-Oxo-2,3-diphenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10a' minor isomer)



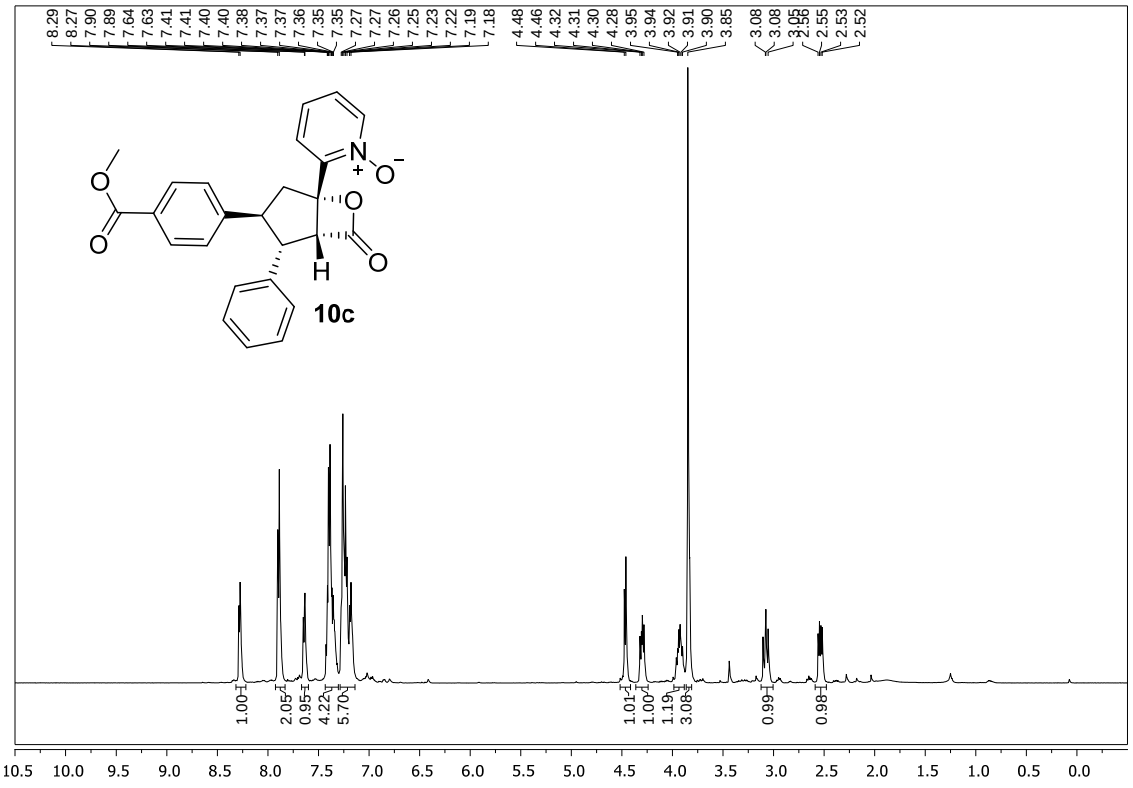


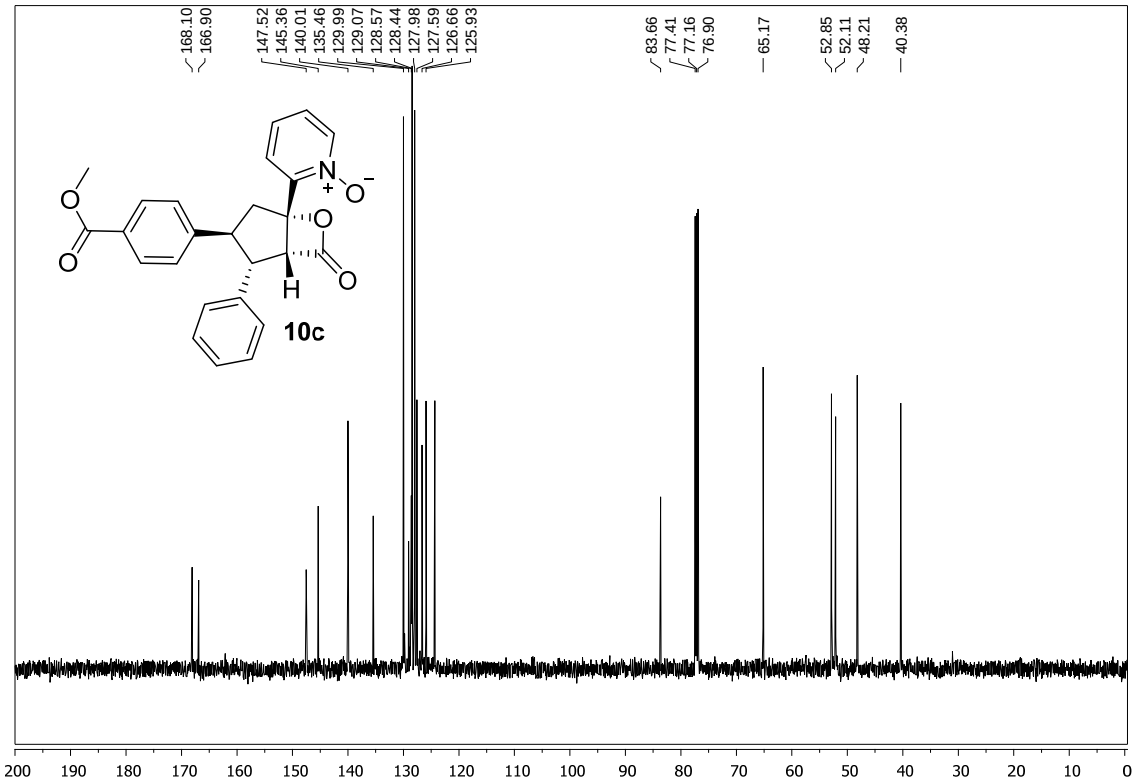
2-(3-(4-Methoxyphenyl)-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10b)



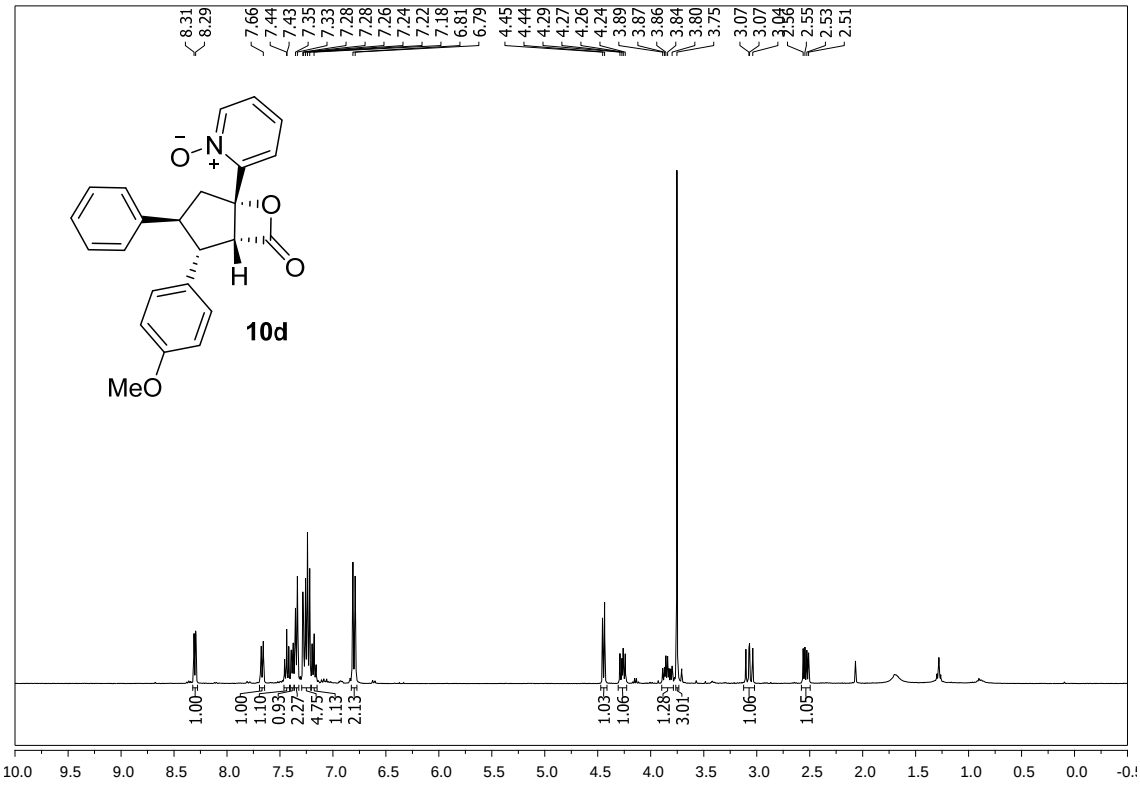


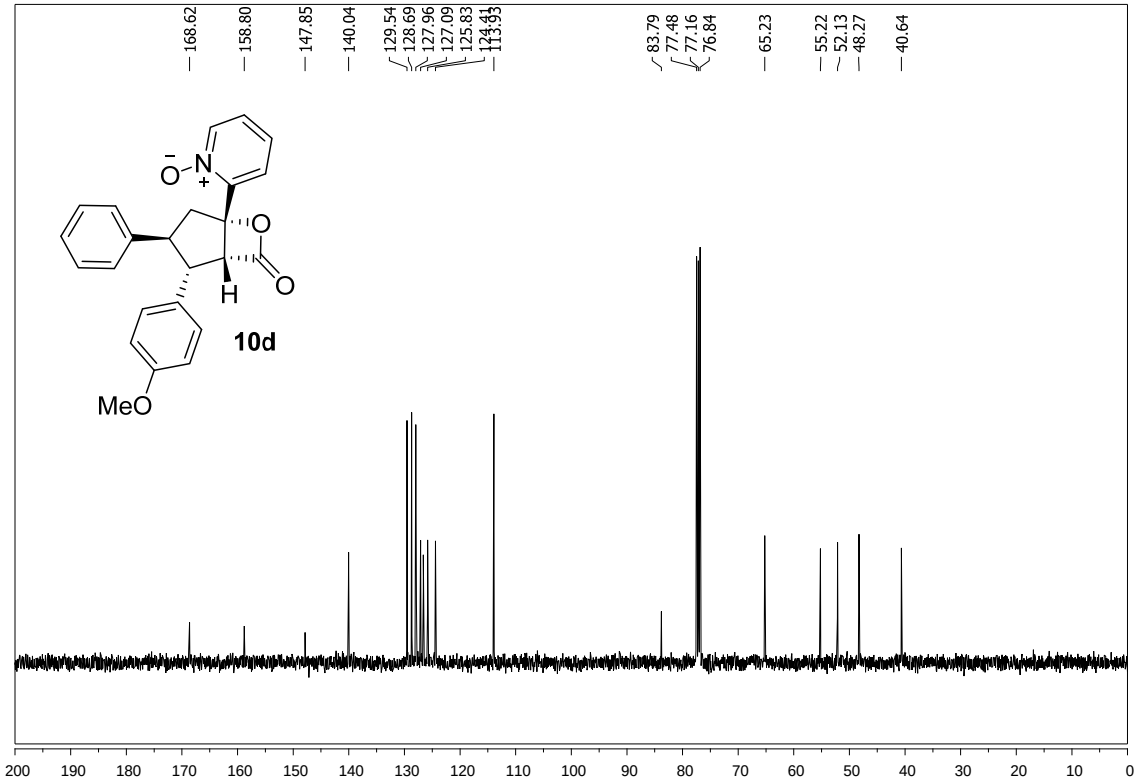
2-(3-(4-(Methoxycarbonyl)phenyl)-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10c)



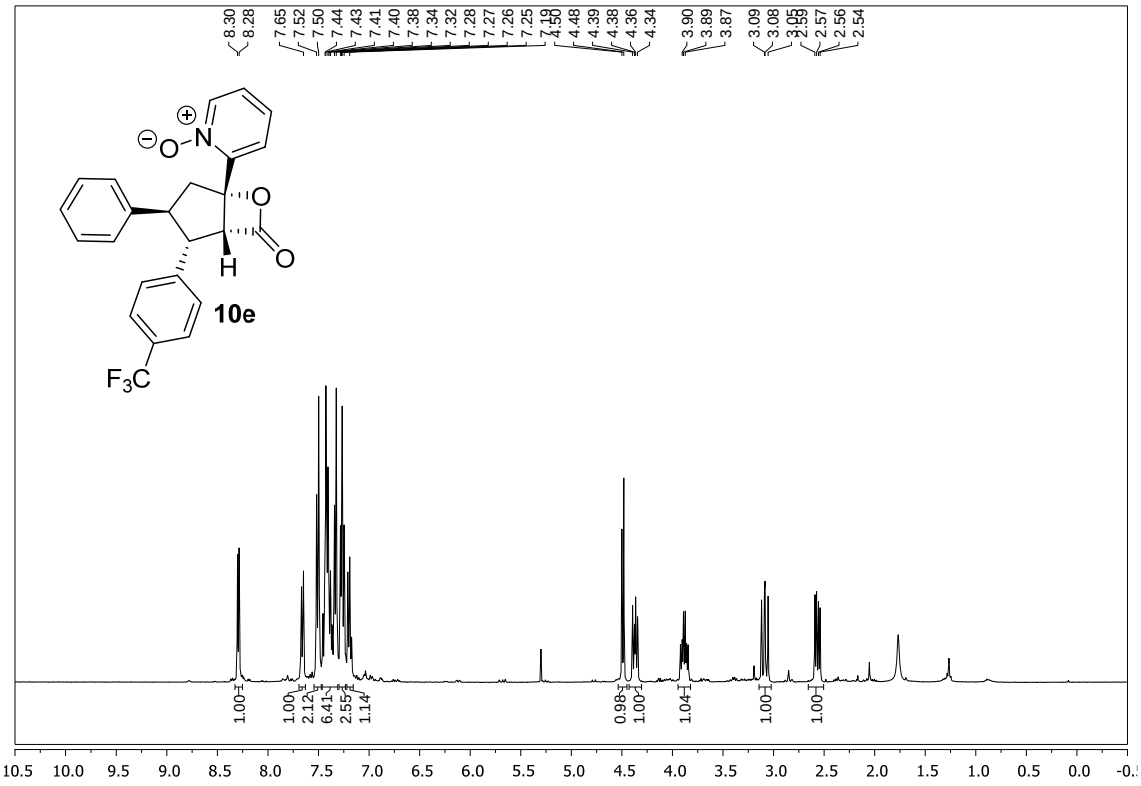


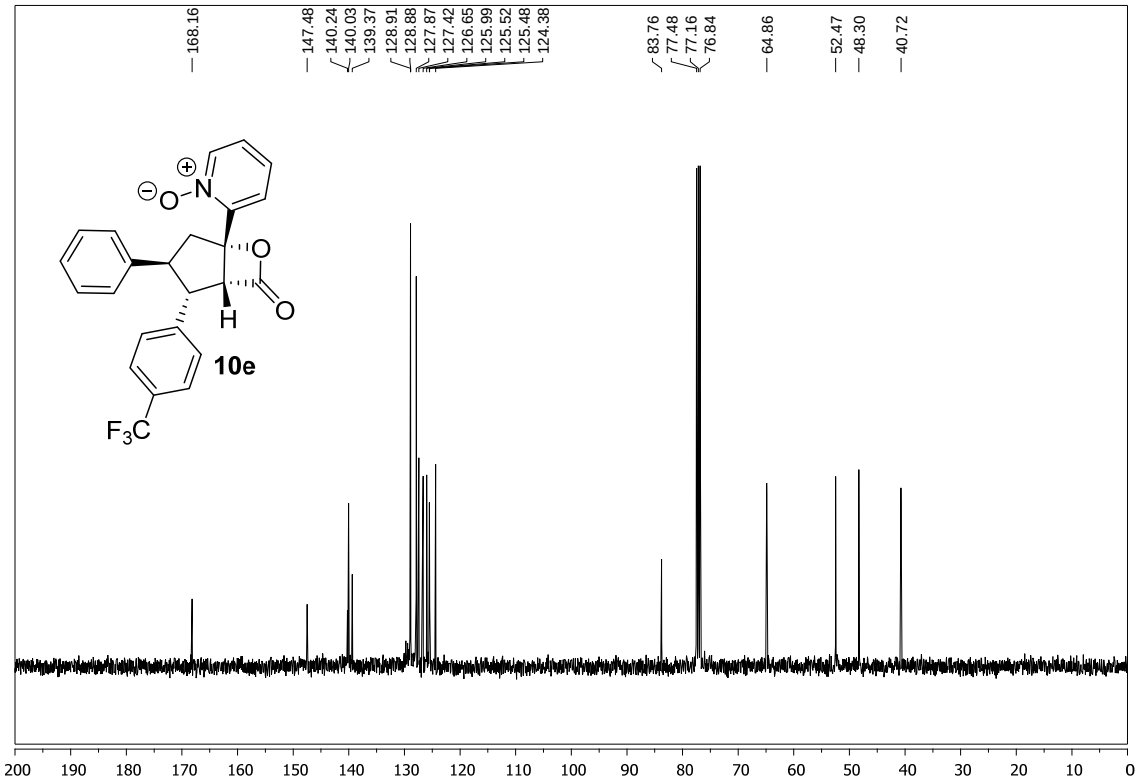
2-(4-Methoxyphenyl)-7-oxo-3-phenyl-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10d)





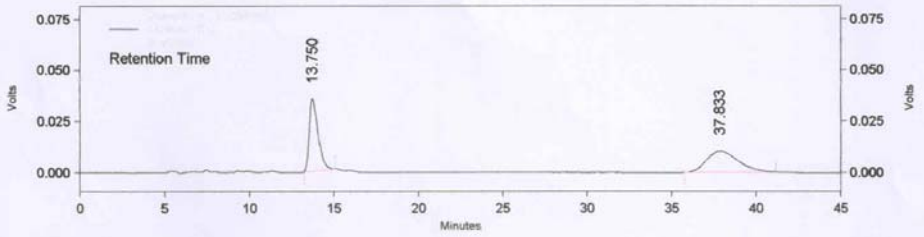
2-(7-Oxo-3-phenyl-2-(4-(trifluoromethyl)phenyl)-6-oxabicyclo[3.2.0]heptan-5-yl)pyridine 1-oxide (10e)





2,3-Diphenyl-5-(pyridin-2-yl)-6-oxabicyclo[3.2.0]heptan-7-one (*chiral*-3a)

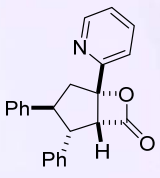
Method Name: C:\CLASS-VP\Method ch 2.met
Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr2168
User: System
Acquired: 1/7/15 11:40:32 AM
Printed: 4/6/15 4:55:22 PM
Sample Name SUM-SB-Rac



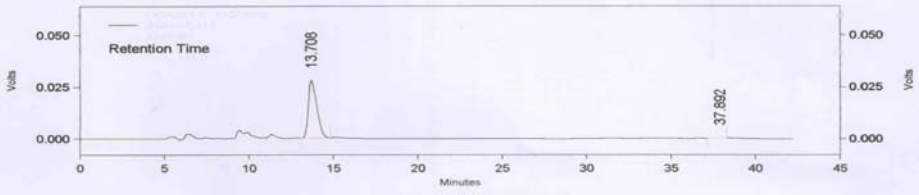
Detector A - 1 (254nm)

Retention Time	C Area	Area %
13.750	1244851	48.577
37.833	1317774	51.423
Totals	2562625	100.000

Method Name: C:\CLASS-VP\Method ch 2.met
Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr2184
User: System
Acquired: 1/15/15 4:39:10 PM
Printed: 4/6/15 5:11:03 PM
Sample Name SUM-SB-113



***chiral*-3a**



Detector A - 1 (254nm)

Retention Time	C Area	Area %
13.708	923171	99.548
37.892	4190	0.452
Totals	927361	100.000

Project Leader :Dr.A.T. Biju
Column :Chiralcel OJ-H (250mm x 4.6mm)
Mobile Phase :EtOH : Petether (50:50)
Wavelength : 254 nm
Flow Rate : 0.6ml/min
Conc. : 1mg/1ml
Inj vol- : 10ul