Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

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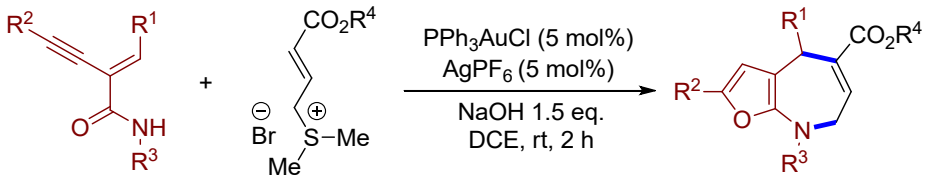
1. General Information

Commercially available materials purchased from Bidepharm or Energy Chemical was used as received. DCE was newly distilled over CaH_2. Unless otherwise specified, all reactions were carried out under an atmosphere of nitrogen in 10 mL Schlenk tube.

^1H NMR, ^{13}C NMR spectra were measured at 400 MHz and 151 MHz in $CDCl_3$. Data for ^1H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.16 ppm). High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with ESI.

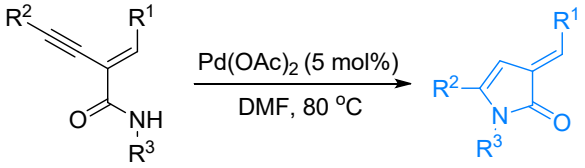
Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-300 mesh ASTM, purchased from Anhui Liangchen Silicon Material Co., Ltd.) and eluted with petroleum ether/ethyl acetate. Ynamides were prepared according to previous literature procedures. [1,2] Crotonate-derived sulfur ylides were prepared from dimethyl sulfide and 4-bromocrotonate according to the literature.[3]

2. General procedure for the synthesis of substrates and products



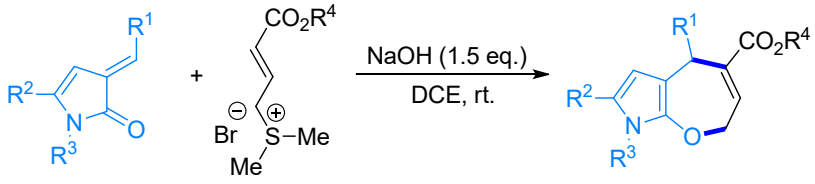
1 **2** (1.5 eq.) **3**

In a dried and nitrogen filled Schlenk flask, a mixture of PPh_3AuCl (5.0 mg, 0.01 mmol, 5 mol %), $AgPF_6$ (2.5 mg, 0.01mmol, 5 mol %) in DCE (2 mL) was stirred at room temperature under nitrogen for 15 mins to generate the gold catalyst. Immediately afterwards, ynamide (0.2 mmol, 1 equiv) was added to the above catalyst solution and stirred for 0.5 h to gain the intermediate. Then crotonate-derived sulfur ylide (0.3 mmol, 1.5 equiv) and NaOH (12 mg, 0.3 mmol, 1.5 equiv) were added. After that the mixture was stirred at room temperature until the reaction was complete (2 h, determined by TLC analysis). The mixture was concentrated under vacuum and purified by column chromatography on silica gel (hexanes:EtOAc = 8:1 to 20:1) to give the desired products **3** in good yields. All the products were confirmed by ^1H NMR, ^{13}C NMR spectra.



1 **4**

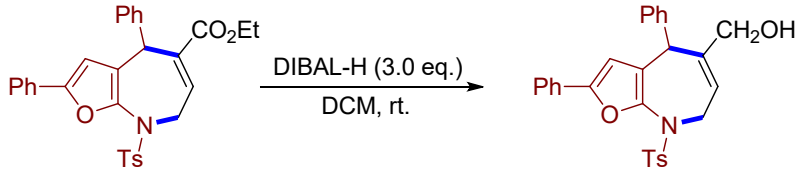
Under a nitrogen atmosphere, a mixture of ynamide (20 mmol), $Pd(OAc)_2$ (5 mol %) in DMF (20 mL) was stirred at 80 °C in a dry Schlenk tube for 8 h. The mixture was quenched with water, extracted with EA, dried over Na_2SO_4, and concentrated. The obtained residue was purified by silica gel column chromatography (hexanes:EtOAc = 17:1) to afford the desired intermediate.



4 **2** (1.5 eq.) **5**

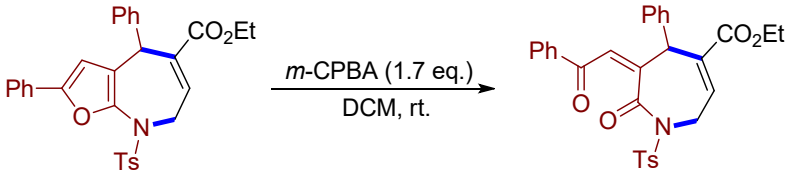
A mixture of intermediate **4** (0.2 mmol, 1.0 equiv), crotonate-derived sulfur ylide **2** (0.3 mmol, 1.5 equiv), and NaOH (12 mg, 0.3 mmol, 1.5 equiv) was stirred in 2 mL DCE at room temperature. The mixture was stirred at room temperature until the reaction was complete (2 h, determined by TLC analysis).The mixture was concentrated under vacuum and purified by column chromatography on silica gel (hexanes:EtOAc = 15:1) to give the desired products.

3. General procedure for the transformations of 3a.



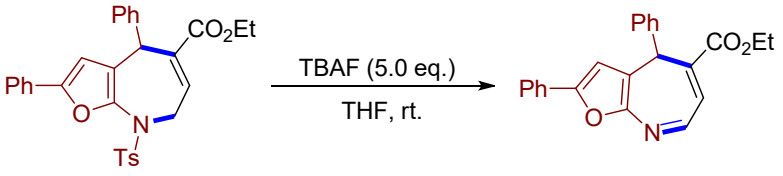
3a **7**, 72% yield

To a dry Schlenk tube with a magnetic stir bar, was added **3a** (0.15 mmol) and freshly distilled 1.5 mL DCM. Then slowly added diisobutyl aluminium hydride (DIBAL-H, 0.45 mmol) to the system. This solution was stirred at room temperature for 20 minutes until the **3a** was complete consumed (monitored by TLC). The mixture was concentrated under reduced pressure. The resulting crude residue was purified via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford the desired product **7** with 72% (51.2 mg) yield



3a **8**, 68% yield

To a dry Schlenk tube with a magnetic stir bar, was added **3a** (0.10 mmol), m-CPBA (0.17 mmol) and freshly distilled 1.0 mL DCM. This solution was stirred at room temperature until the **3a** was complete consumed (monitored by TLC). Then, the reaction was quenched with a saturated solution of $NaHCO_3$ (10 mL), and extracted with EtOAc (10 mL×3). The organic extracts were combined and dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude residue was purified via column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the desired product **8** with 68% (36.0 mg) yield.



3a **9**, 99% yield

To a dry Schlenk tube with a magnetic stir bar, was added **3a** (0.1 mmol) and freshly distilled 2.0 mL THF. Then slowly added tetrabutylammonium fluoride (TBAF, 0.5 mmol) to the system. This solution was stirred at room temperature for 10 minutes until the **3a** was complete consumed (monitored by TLC). The mixture was concentrated under reduced pressure. The resulting crude residue was purified via column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to give the desired product **9** with 99% (35.4 mg) yield.

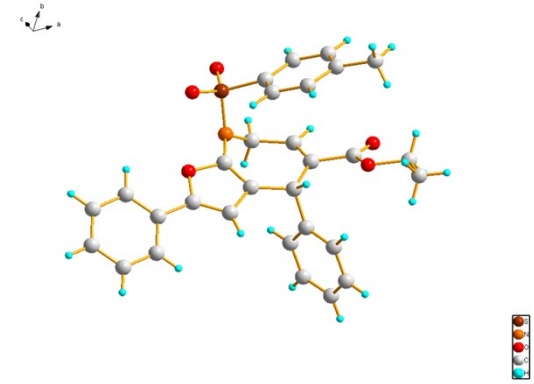
4. Reference

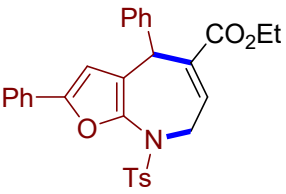
[1] R. Rossi, F. Bellina, C. Bechini, L. Mannina, P. Vergamini, *Tetrahedron* **1998***, 54*, 135.

[2] Y. Luo, K.-M. Qiu, X. Lu, K. Liu, J. Fu, H.-L. Zhu, *Bioorg. Med. Chem.* **2011***, 19*, 4730.

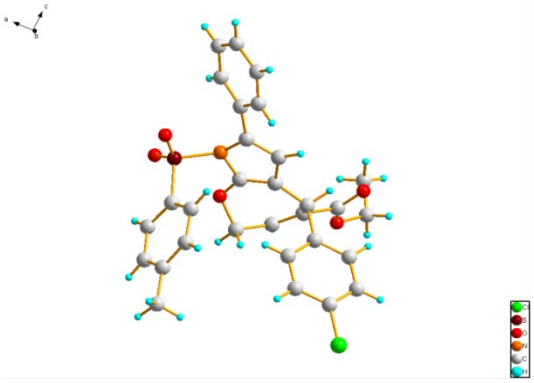
[3] W.-H. Yin, L. Fang, Z.-Y. Wang, F. Gao, Z.-F. Li, Z.-Y. Wang, *Org. Lett.* **2019***, 21*, 7361.

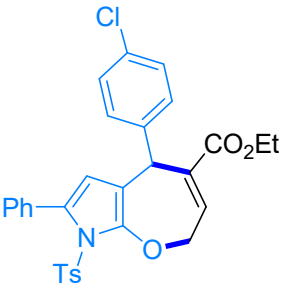
5. Crystal structures of 3a, 5d, 8



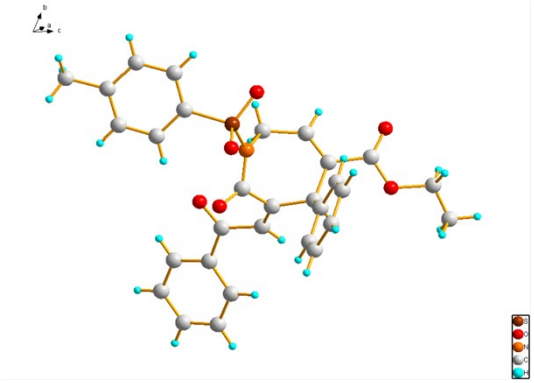


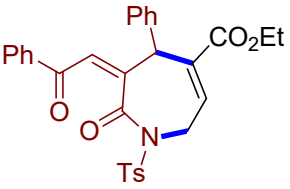
3a (CCDC: 2115221)





5d (CCDC: 2111119)





8 (CCDC: 2111092)

Crystal data and structure refinement for 3a.

CCDC number	2115221
Identification code	3a
Empirical formula	$C_{30}H_{27}NO_5S$
Formula weight	513.58
Temperature/K	160.00
Crystal system	triclinic
Space group	P-1
a/Å	9.9307(5)
b/Å	10.1799(5)
c/Å	14.9440(7)
α/°	74.8085(17)
β/°	82.4440(17)
γ/°	63.8588(15)
Volume/Å^3	1308.59(11)
Z	2
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	0.164
F(000)	540.0
Crystal size/mm^3	0.28 × 0.24 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.798 to 55.046
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 13$, $-19 \leq l \leq 19$
Reflections collected	27629
Independent reflections	5959 [R_{int} = 0.1059, R_{sigma} = 0.0525]
Data/restraints/parameters	5959/0/334
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.1267
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1348
Largest diff. peak/hole / e Å^{-3}	0.25/-0.30

Crystal data and structure refinement for 5d.

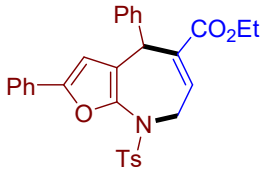
CCDC number	2111119
Identification code	5d
Empirical formula	$C_{30}H_{26}ClNO_5S$
Formula weight	548.03
Temperature/K	273.15
Crystal system	monoclinic
Space group	P2/n
a/Å	11.0616(5)
b/Å	11.8157(8)
c/Å	23.0833(15)
α/°	90
β/°	93.228(2)
γ/°	90
Volume/Å^3	3012.2(3)
Z	2
ρ_{calc}g/cm^3	0.604
μ/mm^{-1}	0.116
F(000)	572.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.048 to 55.032
Index ranges	$-14 \leq h \leq 13$, $-15 \leq k \leq 15$, $-29 \leq l \leq 29$
Reflections collected	32115
Independent reflections	6859 [R_{int} = 0.0445, R_{sigma} = 0.0333]
Data/restraints/parameters	6859/428/438
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1356
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.1574
Largest diff. peak/hole / e Å^{-3}	0.37/-0.18

Crystal data and structure refinement for 8.

CCDC number	2111092
Identification code	8
Empirical formula	$C_{30}H_{27}NO_6S$
Formula weight	529.58
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	10.2538(6)
b/Å	11.2736(6)
c/Å	13.5192(7)
α/°	66.045(2)
β/°	76.756(2)
γ/°	69.057(2)
Volume/Å^3	1327.35(13)
Z	2
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	0.167
F(000)	556.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.99 to 54.974
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-16 \leq l \leq 17$
Reflections collected	27624
Independent reflections	6021 [R_{int} = 0.0265, R_{sigma} = 0.0199]
Data/restraints/parameters	6021/0/345
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0496, wR_2 = 0.1304
Final R indexes [all data]	R_1 = 0.0602, wR_2 = 0.1398
Largest diff. peak/hole / e Å^{-3}	0.28/-0.28

6. Characterization of substrates and products

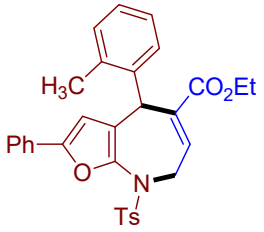
ethyl 2,4-diphenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3a)



Isolated in 87% yield (89.3 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.21 (m, 5H), 7.20 – 7.16 (m, 3H), 6.89 (t, *J* = 6.3 Hz, 1H), 6.25 (s, 1H), 4.95 (s, 1H), 4.56 (dd, *J* = 16.8, 7.1 Hz, 1H), 4.35 (dd, *J* = 16.8, 5.4 Hz, 1H), 4.12 – 3.96 (m, 2H), 2.41 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.30, 150.06, 144.42, 142.66, 142.13, 136.21, 135.97, 134.34, 129.96, 129.72, 128.78, 128.75, 128.14, 128.06, 127.78, 127.10, 123.75, 115.98, 108.03, 61.30, 46.65, 41.53, 21.75, 14.21. HRMS (ESI) calcd. for $C_{30}H_{28}NO_5S$ [M+H$^+$]: 514.1683, found: 514.1681.

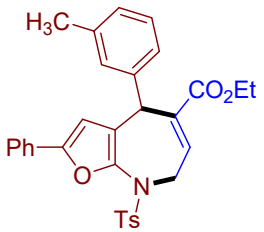
ethyl 2-phenyl-4-(o-tolyl)-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3b)



Isolated in 80% yield (84.3 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.23 (m, 5H), 7.09 – 7.06 (m, 3H), 6.94 (d, *J* = 6.4 Hz, 1H), 6.82 (s, 1H), 5.89 (s, 1H), 4.68 (s, 1H), 4.64 (d, *J* = 6.2 Hz, 1H), 4.41 (d, *J* = 17.9 Hz, 1H), 3.91 – 3.87 (m, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 1.03 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.74, 150.88, 144.48, 141.69, 140.33, 135.92, 135.54, 135.03, 134.07, 130.68, 129.90, 129.73, 128.65, 128.24, 128.20, 127.84, 127.12, 126.71, 123.84, 119.07, 107.44, 60.96, 47.23, 38.78, 21.72, 19.79, 13.96. HRMS (ESI) calcd. for $C_{31}H_{30}NO_5S$ [M+H$^+$]: 528.1839, found: 528.1842.

ethyl 2-phenyl-4-(m-tolyl)-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3c)

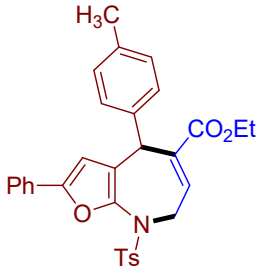


Isolated in 80% yield (84.3 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.16 – 7.10 (m, 1H)., 6.98 – 6.87 (m, 4H), 6.25 (s, 1H), 4.91 (s, 1H), 4.55 (dd, *J* = 16.6, 6.5 Hz, 1H), 4.36 (dd, *J* = 16.5, 3.8 Hz, 1H)., 4.16 – 3.94 (m, 2H), 2.41 (s, 3H), 2.28 (s, 3H), 1.20 (t, *J* = 6.3 Hz, 3H). ^{13}C

NMR (151 MHz, $CDCl_3$) δ 166.30, 149.96, 144.39, 142.61, 142.00, 138.40, 136.26, 135.98, 134.18, 130.00, 129.69, 128.73, 128.60, 128.12, 127.88, 127.74, 125.17, 123.73, 116.06, 108.09, 61.26, 46.66, 41.45, 21.74, 21.59, 14.21. HRMS (ESI) calcd. for $C_{31}H_{30}NO_5S$ [M+H$^+$]: 528.1839, found: 528.1843.

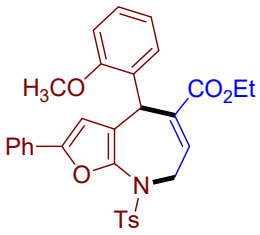
ethyl 2-phenyl-4-(p-tolyl)-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3d)



Isolated in 78% yield (82.2 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.25 – 7.21 (m, 3H), 7.05 (s, 4H), 6.86 (t, *J* = 5.8 Hz, 1H), 6.24 (s, 1H), 4.91 (s, 1H), 4.55 (dd, *J* = 16.5, 6.9 Hz, 1H), 4.35 (dd, *J* = 16.7, 5.0 Hz, 1H), 4.09 – 3.99 (m, 2H), 2.41 (s, 3H), 2.28 (s, 3H), 1.20 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.32, 150.01, 144.38, 142.63, 139.16, 136.74, 136.43, 136.00, 134.04, 130.02, 129.69, 129.46, 128.73, 128.14, 127.92, 127.74, 123.75, 116.13, 108.07, 61.25, 46.66, 41.17, 21.74, 21.14, 14.23. HRMS (ESI) calcd. for $C_{31}H_{30}NO_5S$ [M+H$^+$]: 528.1839, found: 528.1838.

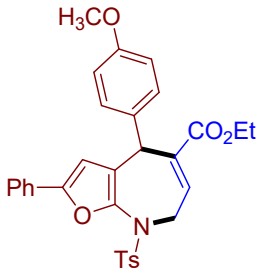
ethyl 4-(2-methoxyphenyl)-2-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3e)



Isolated in 82% yield (89.1 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 7.04 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.89 – 6.78 (m, 3H), 6.27 (s, 1H), 5.19 (s, 1H), 4.51 (dd, *J* = 16.8, 6.7 Hz, 1H), 4.40 (dd, *J* = 16.9, 6.4 Hz, 1H), 3.98 (qq, *J* = 10.8, 7.1 Hz, 2H), 3.80 (s, 3H), 2.41 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.55, 156.65, 149.90, 144.27, 142.23, 136.20, 135.55, 134.33, 130.21, 130.14, 129.72, 129.18, 128.69, 128.42, 128.13, 127.60, 123.72, 120.84, 116.83, 111.15, 108.00, 60.94, 55.57, 46.58, 36.49, 21.73, 14.16. HRMS (ESI) calcd. for $C_{31}H_{30}NO_6S$ [M+H$^+$]: 544.1788, found: 544.1792.

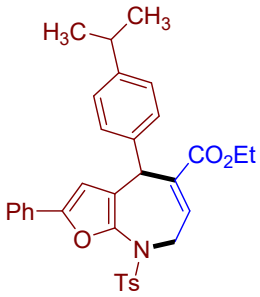
ethyl 4-(4-methoxyphenyl)-2-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3f)



Isolated in 87% yield (94.5 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.32 – 7.25 (m, 5H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.83 (t, *J* = 6.0 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 2H), 6.24 (s, 1H), 4.88 (s, 1H), 4.55 (dd, *J* = 16.4, 6.7 Hz, 1H), 4.34 (dd, *J* = 16.8, 4.3 Hz, 1H), 4.15 – 3.93 (m, 2H), 3.74 (s, 3H), 2.41 (s, 3H), 1.20 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.35, 158.59, 150.05, 144.39, 142.53, 136.40, 135.99, 134.25, 133.77, 130.00, 129.70, 129.12, 128.73, 128.13, 127.75, 123.74, 116.47, 114.10, 108.04, 61.23, 55.32, 46.68, 40.83, 21.72, 14.23. HRMS (ESI) calcd. for $C_{31}H_{30}NO_6S$ [M+H$^+$]: 544.1788, found: 544.1788.

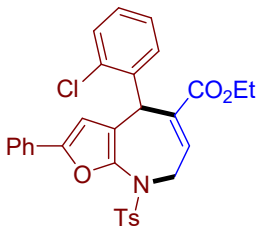
ethyl 4-(4-isopropylphenyl)-2-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3g)



Isolated in 79% yield (87.7 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.09 (s, 4H), 6.86 (t, *J* = 6.4 Hz, 1H), 6.27 (s, 1H), 4.95 (s, 1H), 4.55 (dd, *J* = 16.7, 7.2 Hz, 1H), 4.34 (dd, *J* = 16.7, 5.7 Hz, 1H), 4.13 – 3.97 (m, 2H), 2.83 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.40 (s, 3H), 1.21 – 1.18 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.32, 149.86, 147.58, 144.36, 142.72, 139.35, 136.62, 135.94, 133.96, 130.01, 129.66, 128.72, 128.12, 127.85, 127.70, 126.78, 123.71, 115.73, 108.16, 61.24, 46.57, 40.96, 33.71, 24.02, 24.01, 21.71, 14.19. HRMS (ESI) calcd. for $C_{33}H_{33}NNaO_5S$ [M+Na$^+$]: 578.1972, found: 578.1966.

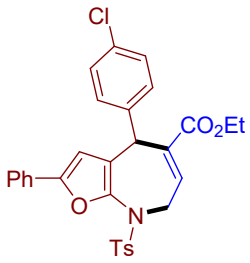
ethyl 4-(2-chlorophenyl)-2-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3h)



Isolated in 67% yield (73.3 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.32 (m, 5H), 7.27 – 7.20 (m, 1H), 7.16 (s, 3H), 7.01 (t, *J* = 4.3 Hz, 1H), 6.28 (s, 1H), 5.26 (s, 1H), 4.51 (s, 2H), 4.05 – 3.83 (m, 2H), 2.44 (s, 3H), 1.07 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.33, 150.70, 144.53, 141.70, 139.78, 136.14, 136.07, 133.66, 133.38, 129.96, 129.84, 129.79, 129.42, 128.69, 128.45, 128.11, 127.84, 127.61, 123.81, 118.17, 107.48, 61.24, 47.26, 38.93, 21.75, 13.97. HRMS (ESI) calcd. for $C_{30}H_{27}ClNO_5S$ [M+H$^+$]: 548.1293, found: 548.1292.

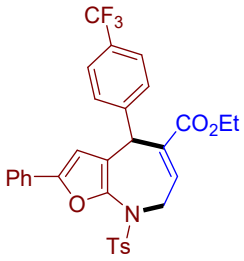
ethyl 4-(4-chlorophenyl)-2-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3i)



Isolated in 71% yield (77.7 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.21 (m, 5H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.92 (t, *J* = 6.0 Hz, 1H), 6.24 (s, 1H), 4.93 (s, 1H), 4.52 (dd, *J* = 17.1, 6.6 Hz, 1H), 4.35 (dd, *J* = 17.1, 5.3 Hz, 1H), 4.16 – 3.94 (m, 2H), 2.42 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.19, 150.29, 144.50, 142.65, 140.71, 136.07, 135.46, 134.90, 132.92, 129.86, 129.76, 129.45, 128.92, 128.79, 128.09, 127.91, 123.76, 115.98, 107.73, 61.42, 46.67, 41.03, 21.75, 14.23. HRMS (ESI) calcd. for $C_{30}H_{27}ClNO_5S$ [M+H$^+$]: 548.1293, found: 548.1243.

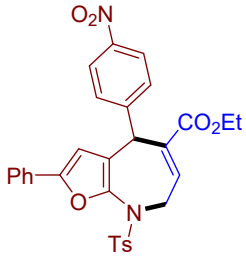
ethyl 2-phenyl-8-tosyl-4-(4-(trifluoromethyl)phenyl)-7,8-dihydro-4H-furo[2,3-b]azepine-5-carbox -ylate (3j)



Isolated in 71% yield (82.5 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.47 (m, 4H), 7.38 – 7.31 (m, 4H), 7.30 – 7.22 (m, 3H), 6.99 (t, *J* = 6.0 Hz, 1H), 6.26 (s, 1H), 5.05 (s, 1H), 4.52 (dd, *J* = 17.1, 6.5 Hz, 1H), 4.38 (dd, *J* = 18.0, 5.6 Hz, 1H), 4.14 – 3.98 (m, 2H), 2.42 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.11, 150.39, 146.18, 144.56, 142.75, 136.12, 135.55, 134.97, 129.80, 129.34 (q, *J* = 32.5 Hz), 128.80, 128.43, 128.07, 127.97, 125.76 (q, *J* = 3.6 Hz), 124.18 (q, *J* = 272.2 Hz), 123.76, 115.65, 107.59, 61.51, 46.67, 41.43, 21.73, 14.19. HRMS (ESI) calcd. for $C_{31}H_{27}F_3NO_5S$ [M+H$^+$]: 582.1557, found: 582.1532.

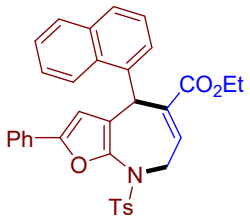
ethyl 4-(4-nitrophenyl)-2-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3k)



Isolated in 61% yield (68.1 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 7.07 (t, *J* = 5.7 Hz, 1H), 6.30 (s, 1H), 5.12 (s, 1H), 4.51 – 4.38 (m, 2H), 4.17 – 4.00 (m, 2H), 2.44 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.04, 150.63, 149.54, 146.98, 144.66, 142.72, 136.51, 136.25, 133.95, 129.86, 129.69, 128.94, 128.84, 128.09, 128.00, 124.07, 123.76, 115.79, 107.28, 61.67, 46.76, 41.46, 21.76, 14.22. HRMS (ESI) calcd. for $C_{30}H_{27}N_2O_7S$ [M+H$^+$]: 559.1533, found: 559.1504.

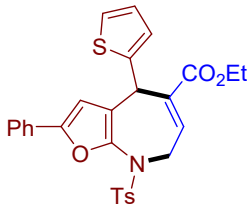
ethyl 4-(naphthalen-1-yl)-2-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3l)



Isolated in 82% yield (92.4 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.70 (m, 3H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.37 – 7.33 (m, 3H), 7.29 – 7.15 (m, 4H), 6.95 (t, *J* = 6.0 Hz, 1H), 5.91 (s, 1H), 5.44 (s, 1H), 4.69 (dd, *J* = 17.9, 6.0 Hz, 1H), 4.54 (dd, *J* = 17.9, 2.1 Hz, 1H), 3.88 – 3.63 (m, 2H), 2.45 (s, 3H), 0.74 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.71, 150.68, 144.55, 141.63, 138.41, 136.15, 135.44, 134.57, 134.14, 131.40, 129.87, 129.82, 129.12, 128.61, 128.30, 127.90, 127.80, 126.54, 126.15, 125.81, 125.78, 123.81, 123.41, 119.20, 107.63, 60.98, 47.25, 37.50, 21.78, 13.70. HRMS (ESI) calcd. for $C_{34}H_{30}NO_5S$ [M+H$^+$]: 564.1839, found: 564.1836.

ethyl 2-phenyl-4-(thiophen-2-yl)-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3m)

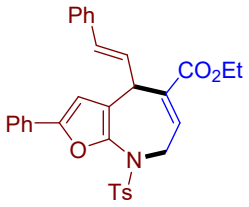


Isolated in 76% yield (78.9 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.23 (m, 3H), 7.12 (d, *J* = 5.0 Hz, 1H), 6.92 (t, *J* = 6.6 Hz, 1H), 6.88 – 6.77 (m, 2H), 6.46 (s, 1H), 5.33 (s, 1H), 4.54 (dd, *J* = 16.4, 7.2 Hz, 1H), 4.36 (dd, *J* = 16.3, 6.0 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H),

2.40 (s, 3H), 1.27 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.80, 149.72, 145.53, 144.42, 142.89, 136.41, 135.93, 134.75, 129.92, 129.66, 128.78, 128.07, 127.79, 126.72, 125.23, 124.66, 123.71, 114.42, 107.90, 61.51, 46.20, 36.19, 21.71, 14.29. HRMS (ESI) calcd. for $C_{28}H_{26}NO_5S_2$ [M+H$^+$]: 520.1247, found: 520.1245.

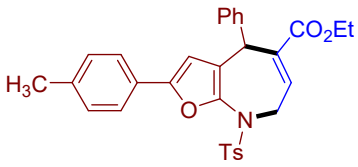
ethyl (E)-2-phenyl-4-styryl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3n)



Isolated in 77% yield (83.0 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.32 – 7.22 (m, 7H), 7.21 – 7.15 (m, 1H), 6.92 (t, J = 6.0 Hz, 1H), 6.51 (s, 1H), 6.41 (d, J = 15.7 Hz, 1H), 6.10 (dd, J = 15.6, 7.2 Hz, 1H), 4.61 (d, J = 6.9 Hz, 1H), 4.45 (dd, J = 16.9, 6.2 Hz, 1H), 4.36 (dd, J = 17.0, 6.1 Hz, 1H), 4.22 – 4.10 (m, 2H), 2.39 (s, 3H), 1.30 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.09, 149.90, 144.35, 142.89, 136.81, 136.16, 135.11, 134.80, 130.89, 130.07, 129.68, 129.04, 128.80, 128.62, 128.09, 127.75, 127.67, 126.54, 123.70, 114.99, 107.85, 61.39, 46.52, 38.77, 21.72, 14.37. HRMS (ESI) calcd. for $C_{32}H_{30}NO_5S$ [M+H$^+$]: 540.1839, found: 540.1832.

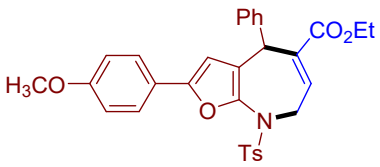
ethyl 4-phenyl-2-(p-tolyl)-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3o)



Isolated in 81% yield (85.4 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.26 – 7.21 (m, 4H), 7.21 – 7.10 (m, 5H), 6.88 (t, J = 6.2 Hz, 1H), 6.18 (s, 1H), 4.93 (s, 1H), 4.55 (dd, J = 16.9, 7.1 Hz, 1H), 4.34 (dd, J = 16.9, 5.4 Hz, 1H), 4.13 – 3.93 (m, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.31, 150.31, 144.36, 142.28, 142.18, 137.68, 136.23, 136.02, 134.33, 129.68, 129.42, 128.74, 128.15, 128.07, 127.31, 127.05, 123.73, 115.95, 107.28, 61.26, 46.68, 41.58, 21.73, 21.41, 14.20. HRMS (ESI) calcd. for $C_{31}H_{30}NO_5S$ [M+H$^+$]: 528.1839, found: 528.1857.

ethyl 2-(4-methoxyphenyl)-4-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3p)

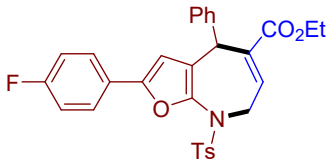


Isolated in 80% yield (86.9 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 7.29 – 7.14 (m, 7H), 6.87 (d, J = 7.4 Hz, 3H), 6.09 (s, 1H), 4.91 (s, 1H), 4.55 (dd, J = 16.7, 6.7 Hz, 1H), 4.35 (dd, J = 16.7,

4.5 Hz, 1H), 4.14 – 3.93 (m, 2H), 3.81 (s, 3H), 2.41 (s, 3H), 1.18 (t, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.31, 159.41, 150.23, 144.35, 142.21, 141.99, 136.17, 135.99, 134.31, 129.69, 128.74, 128.16, 128.10, 127.06, 125.28, 123.06, 116.11, 114.20, 106.40, 61.24, 55.46, 46.74, 41.66, 21.74, 14.20. HRMS (ESI) calcd. for $C_{31}H_{30}NO_6S$ [M+H$^+$]: 544.1788, found: 544.1784.

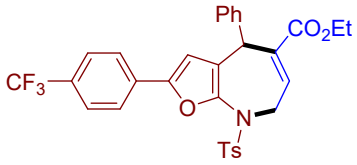
ethyl 2-(4-fluorophenyl)-4-phenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3q)



Isolated in 77% yield (81.8 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.58 – 7.47 (m, 2H), 7.28 – 7.14 (m, 7H), 7.03 (t, J = 8.7 Hz, 2H), 6.86 (dd, J = 6.9, 5.5 Hz, 1H), 6.17 (s, 1H), 4.93 (s, 1H), 4.56 (dd, J = 16.9, 7.1 Hz, 1H), 4.35 (dd, J = 16.8, 5.0 Hz, 1H), 4.13 – 3.92 (m, 2H), 2.41 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.23, 162.40 (d, J = 247.6 Hz), 149.29, 144.47, 142.62, 142.07, 136.08, 135.94, 134.25, 129.74, 128.79, 128.11, 128.07, 127.13, 126.37 (d, J = 3.1 Hz), 125.58 (d, J = 8.0 Hz), 116.22, 115.80 (d, J = 22.0 Hz), 107.67, 61.27, 46.67, 41.63, 21.72, 14.18. HRMS (ESI) calcd. for $C_{30}H_{27}FNO_5S$ [M+H$^+$]: 532.1588, found: 532.1585.

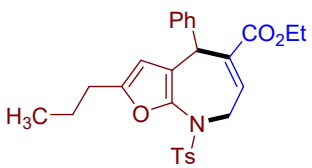
ethyl 4-phenyl-8-tosyl-2-(4-(trifluoromethyl)phenyl)-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3r)



Isolated in 70% yield (81.4 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 4H), 7.58 (d, J = 8.5 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.23 – 7.15 (m, 3H), 6.89 (dd, J = 7.0, 5.6 Hz, 1H), 6.38 (s, 1H), 4.98 (s, 1H), 4.56 (dd, J = 16.9, 7.1 Hz, 1H), 4.36 (dd, J = 16.8, 5.6 Hz, 1H), 4.13 – 3.97 (m, 2H), 2.42 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.19, 148.48, 144.62, 143.71, 141.92, 136.16, 135.96, 134.25, 133.09, 129.81, 129.32 (q, J = 32.5 Hz), 128.86, 128.08, 128.02, 127.23, 125.79 (q, J = 3.6 Hz), 124.20 (q, J = 272.0 Hz), 123.74, 116.17, 110.06, 61.36, 46.54, 41.47, 21.74, 14.19. HRMS (ESI) calcd. for $C_{31}H_{27}F_3NO_5S$ [M+H$^+$]: 582.1557, found: 582.1535.

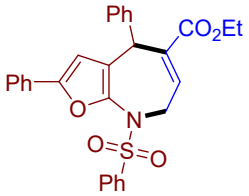
ethyl 4-phenyl-2-propyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3s)



Isolated in 58% yield (55.6 mg) as yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.18 – 7.14 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.80 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.56 (s, 1H), 4.78 (s, 1H), 4.51 (dd, *J* = 16.9, 7.2 Hz, 1H), 4.29 (dd, *J* = 17.7, 5.2 Hz, 1H), 3.99 (qq, *J* = 10.8, 7.1 Hz, 2H)., 2.55 – 2.44 (m, 2H), 2.40 (s, 3H), 1.65 – 1.57 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.31, 153.14, 144.21, 142.37, 141.12, 136.09, 135.79, 134.23, 129.59, 128.63, 128.14, 128.07, 126.92, 114.86, 108.30, 61.13, 46.85, 41.75, 30.06, 21.70, 21.21, 14.16, 13.78. HRMS (ESI) calcd. for $C_{27}H_{30}NO_5S$ [M+H$^+$]: 480.1839, found: 480.1836.

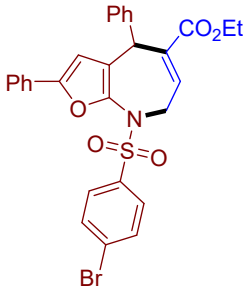
ethyl 2,4-diphenyl-8-(phenylsulfonyl)-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3t)



Isolated in 77% yield (76.9 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.52 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.14 (m, 6H), 6.89 (t, *J* = 6.2 Hz, 1H), 6.25 (s, 1H), 4.95 (s, 1H), 4.56 (dd, *J* = 16.8, 7.0 Hz, 1H), 4.37 (dd, *J* = 16.8, 5.4 Hz, 1H), 4.14 – 3.89 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.27, 150.09, 142.51, 142.04, 139.05, 136.29, 134.14, 133.37, 129.92, 129.12, 128.76, 128.74, 128.05, 128.03, 127.79, 127.10, 123.72, 116.07, 108.02, 61.27, 46.70, 41.49, 14.19. HRMS (ESI) calcd. for $C_{29}H_{26}NO_5S$ [M+H$^+$]: 500.1526, found: 500.1536.

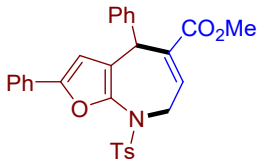
ethyl 8-((4-bromophenyl)sulfonyl)-2,4-diphenyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3u)



Isolated in 65% yield (75.0 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 4H), 7.58 – 7.52 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.22 – 7.14 (m, 3H), 6.86 (dd, *J* = 7.0, 5.7 Hz, 1H), 6.26 (s, 1H), 4.97 (s, 1H), 4.56 (dd, *J* = 16.9, 7.1 Hz, 1H), 4.38 (dd, *J* = 16.6, 5.2 Hz, 1H), 4.16 – 4.01 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.20, 150.38, 142.20, 141.89, 138.00, 136.49, 134.01, 132.44, 129.81, 129.58, 128.84, 128.82, 128.04, 127.97, 127.21, 123.79, 116.38, 108.04, 61.64, 46.81, 41.55, 14.24. HRMS (ESI) calcd. for $C_{29}H_{25}BrNO_5S$ [M+H$^+$]: 578.0631, found: 578.0625.

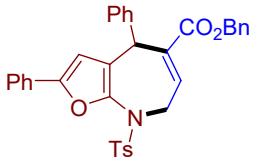
methyl 2,4-diphenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3v)



Isolated in 77% yield (76.9 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.14 (m, 8H), 6.88 (t, *J* = 6.2 Hz, 1H), 6.26 (s, 1H), 4.97 (s, 1H), 4.54 (dd, *J* = 16.7, 7.0 Hz, 1H), 4.35 (dd, *J* = 16.8, 5.4 Hz, 1H), 3.62 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.73, 150.06, 144.49, 142.73, 142.06, 135.98, 135.93, 134.72, 129.94, 129.70, 128.81, 128.75, 128.14, 128.00, 127.79, 127.14, 123.74, 115.83, 108.00, 52.31, 46.64, 41.48, 21.76. HRMS (ESI) calcd. for $C_{29}H_{26}NO_5S$ [M+H$^+$]: 500.1526, found: 500.1526.

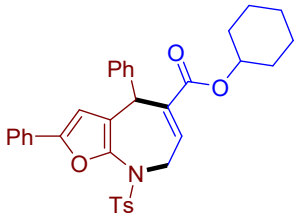
benzyl 2,4-diphenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3w)



Isolated in 80% yield (92.0 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.29 (m, 5H), 7.26 – 7.18 (m, 6H), 7.18 – 7.10 (m, 4H), 6.94 (dd, *J* = 6.8, 5.6 Hz, 1H), 6.23 (s, 1H), 5.02 (q, *J* = 12.4 Hz, 2H), 4.92 (s, 1H), 4.56 (dd, *J* = 17.0, 7.0 Hz, 1H), 4.36 (dd, *J* = 16.9, 5.4 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.13, 150.11, 144.49, 142.57, 141.95, 135.95, 135.80, 135.65, 134.81, 129.95, 129.68, 128.82, 128.75, 128.74, 128.50, 128.21, 128.09, 127.80, 127.15, 123.75, 116.14, 107.98, 67.07, 46.73, 41.71, 21.71. HRMS (ESI) calcd. for $C_{35}H_{30}NO_5S$ [M+H$^+$]: 576.1839, found: 576.1812.

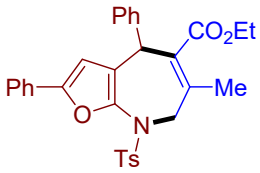
cyclohexylmethyl 2,4-diphenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3x)



Isolated in 80% yield (90.8 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 5H), 7.20 – 7.14 (m, 3H), 6.89 (dd, *J* = 6.9, 5.5 Hz, 1H), 6.24 (s, 1H), 4.92 (s, 1H), 4.69 – 4.60 (m, 1H), 4.57 (dd, *J* = 17.0, 7.1 Hz, 1H), 4.36 (dd, *J* = 16.9, 5.5 Hz, 1H), 2.41 (s, 3H), 1.78 – 1.60 (m, 4H), 1.56 – 1.47 (m, 1H), 1.39 – 1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.76, 150.04, 144.36, 142.56, 142.20, 136.61, 136.04, 133.99, 130.01, 129.76, 128.75, 128.10, 128.07, 127.77, 127.06, 123.75, 116.16, 108.08, 73.75, 46.66, 41.63, 31.63, 31.43, 25.44, 23.76, 21.76. HRMS (ESI) calcd. for $C_{34}H_{34}NO_5S$ [M+H$^+$]: 568.2152, found: 568.2124.

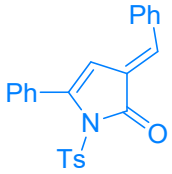
Ethyl-6-methyl-2,4-diphenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepine-5-carboxylate (3y)



Isolated in 43% yield (45.3 mg) as yellow solid.

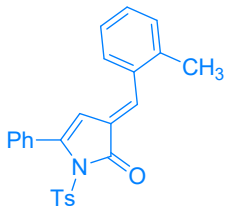
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.35-7.30 (m, 4H), 7.25 – 7.16 (m, 4H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.24 (s, 1H), 4.83 (s, 1H), 4.28 (q, *J* = 15.8 Hz, 2H), 4.12 – 3.98 (m, 2H), 2.46 (s, 3H), 2.11 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.79, 149.12, 144.38, 143.23, 142.33, 138.81, 136.41, 133.46, 130.07, 129.75, 128.76, 128.61, 128.01, 127.86, 127.53, 126.97, 123.49, 113.53, 108.35, 60.91, 52.85, 42.86, 23.43, 21.81, 14.21. HRMS (ESI) calcd. for $C_{31}H_{30}NO_5S$ [M+H$^+$]: 528.1839, found: 528.1821.

(E)-3-benzylidene-5-phenyl-1-tosyl-1,3-dihydro-2H-pyrrol-2-one (4a)



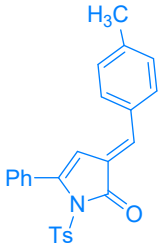
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.49 (m, 4H), 7.48 – 7.42 (m, 3H), 7.41 – 7.34 (m, 4H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.37 (d, *J* = 0.7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.69, 146.76, 145.26, 135.64, 135.25, 134.89, 132.24, 130.54, 130.47, 129.72, 129.69, 129.15, 128.41, 128.27, 128.04, 126.97, 108.56, 21.81. HRMS (ESI) calcd. for $C_{24}H_{20}NO_3S$ [M+H$^+$]: 402.1158, found: 402.1148.

(E)-3-(2-methylbenzylidene)-5-phenyl-1-tosyl-1,3-dihydro-2H-pyrrol-2-one (4b)



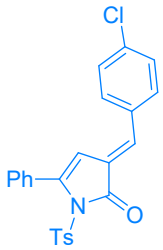
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.61 (s, 1H), 7.52 – 7.46 (m, 3H), 7.45 – 7.40 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.16 (m, 2H), 6.26 (d, *J* = 0.7 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.40, 146.68, 145.24, 139.15, 135.81, 133.84, 133.59, 132.29, 130.97, 130.37, 129.73, 129.62, 129.17, 128.38, 128.34, 128.03, 127.79, 126.36, 108.58, 21.85, 20.12. HRMS (ESI) calcd. for $C_{25}H_{22}NO_3S$ [M+H$^+$]: 416.1315, found: 416.1303.

(E)-3-(4-methylbenzylidene)-5-phenyl-1-tosyl-1,3-dihydro-2H-pyrrol-2-one (4c)



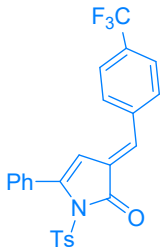
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.47 – 7.40 (m, 5H), 7.35 – 7.26 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.37 (d, *J* = 0.8 Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.82, 146.10, 145.18, 141.35, 135.68, 135.46, 132.36, 132.16, 130.59, 129.93, 129.69, 129.59, 128.42, 128.26, 128.02, 126.00, 108.72, 21.81, 21.71. HRMS (ESI) calcd. for $C_{25}H_{22}NO_3S$ [M+H$^+$]: 416.1315, found: 416.1307.

(E)-3-(4-chlorobenzylidene)-5-phenyl-1-tosyl-1,3-dihydro-2H-pyrrol-2-one (4d)



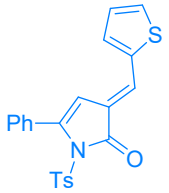
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.47 (m, 3H), 7.47 – 7.41 (m, 4H), 7.36 (d, J = 8.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 6.31 (d, *J* = 0.9 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.51, 147.38, 145.35, 136.56, 135.62, 133.48, 133.40, 132.11, 131.56, 129.85, 129.76, 129.49, 128.42, 128.32, 128.10, 127.33, 108.10, 21.86. HRMS (ESI) calcd. for $C_{24}H_{19}ClNO_3S$ [M+H$^+$]: 436.0769, found: 436.0759.

(E)-5-phenyl-1-tosyl-3-(4-(trifluoromethyl)benzylidene)-1,3-dihydro-2H-pyrrol-2-one (4e)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.66 (s, 4H), 7.57 – 7.51 (m, 2H), 7.51 – 7.44 (m, 3H), 7.39 – 7.31 (m, 3H), 6.35 (d, *J* = 0.8 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.29, 148.47, 145.49, 138.27, 135.53, 132.67, 131.89, 131.63 (q, *J* = 32.8 Hz), 130.38, 130.03, 129.81, 128.97, 128.41, 128.33, 128.15, 126.03 (q, *J* = 3.7 Hz), 123.81 (q, *J* = 272.3 Hz), 107.87, 21.85. HRMS (ESI) calcd. for $C_{25}H_{19}F_3NO_3S$ [M+H$^+$]: 470.1032, found: 470.1015.

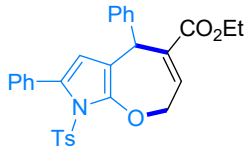
(E)-5-phenyl-3-(thiophen-2-ylmethylene)-1-tosyl-1,3-dihydro-2H-pyrrol-2-one (4f)



E/Z = 6:4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 0.8H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 3.6 Hz, 0.4H), 7.61 (d, *J* = 5.1 Hz, 0.4H), 7.54 (d, *J* = 2.2 Hz, 0.8H), 7.53 (d, *J* = 4.4 Hz, 2H), 7.47 – 7.43 (m, 5H), 7.42 - 7.34 (m, 1.2H), 7.35 (d, *J* = 3.7 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 0.8H), 7.17 (s, 0.4H), 7.12 (dd, *J* = 5.0, 3.8 Hz, 0.4H), 7.09 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.37 (d, *J* = 0.8 Hz, 1H), 5.93 (s, 0.4H), 2.40 (s, 3H), 2.39 (s, 1.2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.62, 166.01, 145.66, 145.21, 144.99, 141.76, 139.03, 138.08, 137.22, 135.79, 135.59, 134.87, 134.08, 132.43, 132.28, 131.79, 131.56, 129.69, 129.65, 129.17, 128.46, 128.42, 128.23, 128.14, 128.03, 127.95, 127.90, 127.12, 124.16, 123.39, 113.05, 108.85, 21.80, 21.78.

HRMS (ESI) calcd. for $C_{22}H_{18}NO_3S_2$ [M+H$^+$]: 408.0723, found: 408.0705.

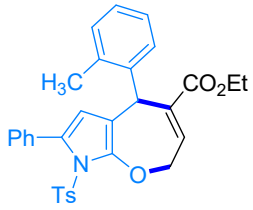
ethyl 5,7-diphenyl-8-tosyl-5,8-dihydro-2H-oxepino[2,3-b]pyrrole-4-carboxylate (5a)



Isolated in 61% yield (62.6 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.36 – 7.26 (m, 5H), 7.17 – 7.12 (m, 3H), 7.07 – 6.96 (m, 3H), 5.91 (s, 1H), 5.06 (s, 1H), 4.52 (d, *J* = 6.0 Hz, 2H), 4.19 (qq, *J* = 10.9, 7.1 Hz, 2H), 2.45 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.62, 146.46, 144.83, 143.02, 138.50, 135.93, 134.25, 133.21, 130.38, 129.62, 129.09, 128.39, 127.70, 127.56, 127.43, 126.63, 116.60, 107.21, 66.77, 61.58, 41.01, 21.84, 14.25. HRMS (ESI) calcd. for $C_{30}H_{28}NO_5S$ [M+H$^+$]: 514.1683, found: 514.1685.

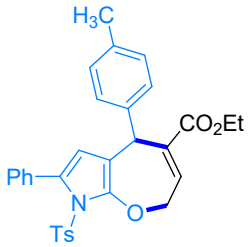
ethyl 7-phenyl-5-(o-tolyl)-8-tosyl-5,8-dihydro-2H-oxepino[2,3-b]pyrrole-4-carboxylate (5b)



Isolated in 50% yield (52.7 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 5H), 7.25 – 7.19 (m, 3H), 7.08 – 6.99 (m, 4H), 5.83 (s, 1H), 5.20 (s, 1H), 4.73 (dd, *J* = 16.9, 4.9 Hz, 1H), 4.60 (dd, *J* = 16.9, 2.8 Hz, 1H), 4.12 – 3.97 (m, 2H), 2.46 (s, 3H), 2.39 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.71, 145.00, 144.79, 141.34, 136.58, 136.00, 135.26, 135.00, 133.12, 130.48, 130.22, 129.66, 129.36, 128.07, 127.60, 127.56, 127.36, 126.58, 126.29, 114.34, 110.84, 68.98, 61.26, 38.71, 21.74, 20.04, 14.07. HRMS (ESI) calcd. for $C_{31}H_{30}NO_5S$ [M+H$^+$]: 528.1839, found: 528.1823.

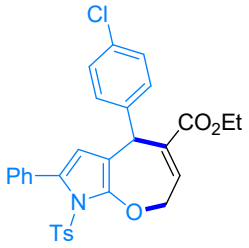
ethyl 7-phenyl-5-(p-tolyl)-8-tosyl-5,8-dihydro-2H-oxepino[2,3-b]pyrrole-4-carboxylate (5c)



Isolated in 48% yield (50.6 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.35 – 7.27 (m, 4H), 7.25 (d, *J* = 11.2 Hz, 1H), 7.01 – 6.87 (m, 5H), 5.90 (s, 1H), 5.02 (s, 1H), 4.51 (d, *J* = 5.9 Hz, 2H), 4.25 – 4.10 (m, 2H), 2.44 (s, 3H), 2.27 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.60, 146.42, 144.77, 140.01, 138.60, 136.18, 135.88, 134.01, 133.21, 130.29, 129.59, 129.06, 129.03, 127.64, 127.56, 127.48, 127.39, 116.64, 107.28, 66.72, 61.51, 40.63, 21.81, 21.09, 14.23. HRMS (ESI) calcd. For $C_{31}H_{30}NO_5S$ [M+H$^+$]: 528.1839, found: 528.1841.

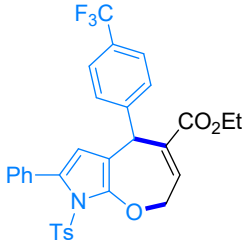
ethyl 5-(4-chlorophenyl)-7-phenyl-8-tosyl-5,8-dihydro-2H-oxepino[2,3-b]pyrrole-4-carboxylate (5d)



Isolated in 42% yield (46.1 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.29 (m, 3H), 7.29 – 7.25 (m, 2H), 7.15 – 7.07 (m, 2H), 7.04 – 6.96 (m, 3H), 5.88 (s, 1H), 4.99 (s, 1H), 4.62 – 4.48 (m, 2H), 4.26 – 4.09 (m, 2H), 2.45 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.44, 146.14, 144.94, 141.58, 137.17, 135.95, 134.98, 133.02, 132.40, 130.58, 129.63, 129.16, 129.08, 128.50, 127.70, 127.68, 127.40, 115.84, 107.89, 67.24, 61.65, 40.71, 21.83, 14.24. HRMS (ESI) calcd. For $C_{30}H_{27}ClNO_5S$ [M+H$^+$]: 548.1293, found: 548.1283.

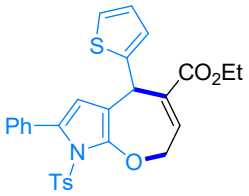
ethyl 7-phenyl-8-tosyl-5-(4-(trifluoromethyl)phenyl)-5,8-dihydro-2H-oxepino[2,3-b]pyrrole-4-car boxylate (5e)



Isolated in 53% yield (61.6 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.36 – 7.29 (m, 3H), 7.27 (s, 1H), 7.24 (d, *J* = 5.7 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.05 (t, *J* = 5.4 Hz, 1H), 5.90 (s, 1H), 5.07 (s, 1H), 4.65 – 4.50 (m, 2H), 4.26 – 4.10 (m, 2H), 2.42 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.31, 147.06, 146.12, 145.00, 136.48, 135.88, 135.55, 132.93, 130.65, 129.64, 129.15, 128.79 (q, *J* = 32.4 Hz), 128.02, 127.69, 127.67, 127.38, 125.30 (q, *J* = 3.6 Hz), 124.21 (q, *J* = 272.0 Hz), 115.58, 107.91, 67.38, 61.68, 41.13, 21.67, 14.17. HRMS (ESI) calcd. For $C_{31}H_{27}F_3NO_5S$ [M+H$^+$]: 582.1557, found: 582.1543.

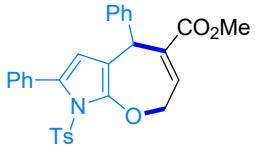
ethyl 7-phenyl-5-(thiophen-2-yl)-8-tosyl-5,8-dihydro-2H-oxepino[2,3-b]pyrrole-4-carboxylate (5f)



Isolated in 50% yield (51.9 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.37 – 7.27 (m, 4H), 7.25 (d, *J* = 8.7 Hz, 1H), 7.08 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.00 (t, *J* = 6.3 Hz, 1H), 6.78 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.45 (dt, *J* = 3.4, 1.1 Hz, 1H), 5.97 (s, 1H), 5.28 (s, 1H), 4.53 (d, *J* = 6.3 Hz, 2H), 4.33 – 4.14 (m, 2H), 2.42 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.03, 146.77, 146.69, 144.87, 138.85, 135.69, 134.16, 133.11, 130.20, 129.63, 129.03, 127.66, 127.53, 127.32, 126.40, 124.75, 124.38, 116.51, 106.13, 66.13, 61.70, 36.25, 21.75, 14.25. HRMS (ESI) calcd. For $C_{28}H_{26}NO_5S_2$ [M+H$^+$]: 520.1247, found: 520.1231.

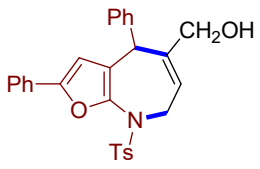
methyl 5,7-diphenyl-8-tosyl-5,8-dihydro-2H-oxepino[2,3-b]pyrrole-4-carboxylate (5g)



Isolated in 55% yield (54.9 mg) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.27 (m, 5H), 7.19 – 7.13 (m, 3H), 7.06 – 6.98 (m, 3H), 5.92 (s, 1H), 5.06 (s, 1H), 4.59 – 4.48 (m, 2H), 3.75 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.09, 146.44, 144.84, 142.91, 138.25, 135.87, 134.55, 133.17, 130.39, 129.62, 129.09, 128.41, 127.69, 127.65, 127.57, 127.42, 126.66, 116.56, 107.17, 66.71, 52.61, 40.98, 21.85. HRMS (ESI) calcd. for $C_{29}H_{26}NO_5S$ [M+H$^+$]: 500.1526, found: 500.1547.

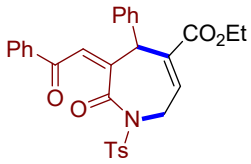
(2,4-diphenyl-8-tosyl-7,8-dihydro-4H-furo[2,3-b]azepin-5-yl)methanol (7)



Isolated in 72% yield (51.2 mg) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.35 – 7.26 (m, 7H), 7.25 – 7.16 (m, 4H), 6.17 (s, 1H), 5.77 (t, *J* = 6.0 Hz, 1H), 4.48 (dd, *J* = 16.3, 7.1 Hz, 1H), 4.38 – 4.24 (m, 2H), 3.60 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.02, 144.25, 143.77, 142.79, 142.14, 136.90, 130.03, 129.57, 129.01, 128.71, 128.51, 128.24, 127.71, 127.33, 123.73, 121.76, 117.04, 108.01, 67.00, 47.39, 43.62, 21.70. HRMS (ESI) calcd. for $C_{28}H_{26}NO_4S$ [M+H$^+$]: 472.1577, found: 472.1558.

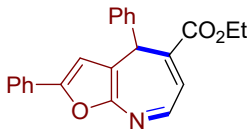
ethyl (Z)-7-oxo-6-(2-oxo-2-phenylethylidene)-5-phenyl-1-tosyl-2,5,6,7-tetrahydro-1H-azepine-4-carboxylate (8)



Isolated in 68% yield (36.0 mg) as yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 3H), 7.05 (d, *J* = 3.6 Hz, 2H), 6.87 (s, 1H), 4.98 (t, *J* = 12.7 Hz, 2H), 4.55 (dd, *J* = 17.7, 2.6 Hz, 1H), 4.19 – 3.95 (m, 2H), 2.45 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.25, 167.81, 165.59, 151.80, 144.86, 136.90, 136.58, 136.27, 135.89, 133.85, 129.45, 128.99, 128.83, 128.79, 128.03, 127.91, 126.57, 61.51, 50.48, 42.43, 21.84, 14.02. HRMS (ESI) calcd. for $C_{30}H_{28}NO_6S$ [M+H$^+$]: 530.1632, found: 530.1619.

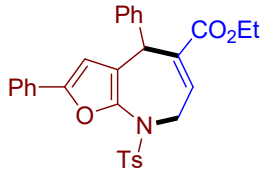
ethyl 2,4-diphenyl-4H-furo[2,3-b]azepine-5-carboxylate (9)



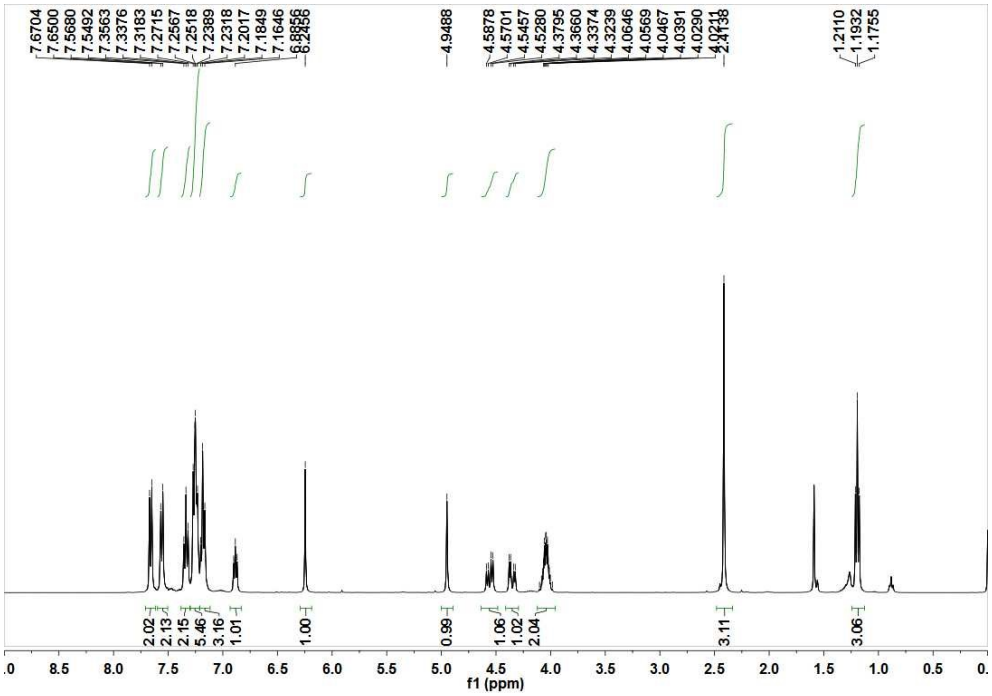
Isolated in 99% yield (35.4 mg) as orange solid.

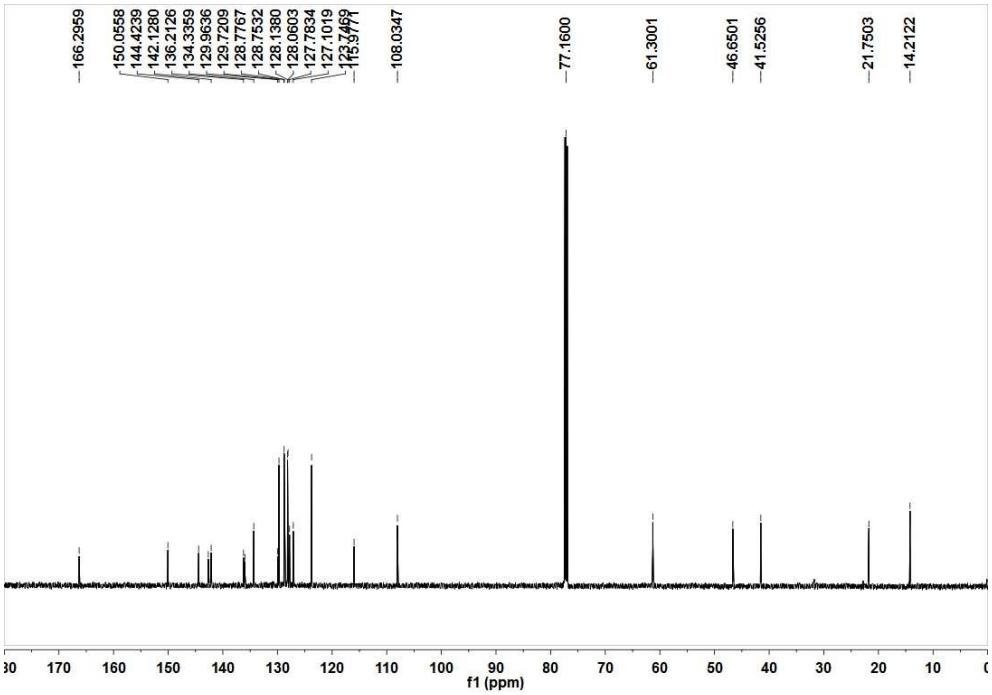
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.70 (d, *J* = 4.6 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.35 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 7.13 – 7.06 (m, 2H), 6.67 (s, 1H), 5.57 (s, 1H), 4.39 – 4.24 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.72, 156.21, 154.02, 147.90, 141.82, 136.15, 129.87, 128.97, 128.82, 128.76, 128.40, 127.31, 126.90, 124.36, 116.93, 108.47, 62.25, 39.73, 14.35. HRMS (ESI) calcd. for $C_{23}H_{20}NO_3$ [M+H$^+$]: 358.1438, found: 358.1432.

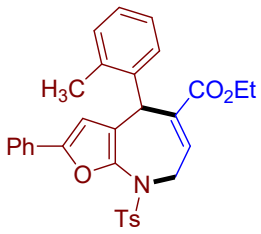
7. ^{1}H NMR, ^{13}C NMR and HPLC Spectra



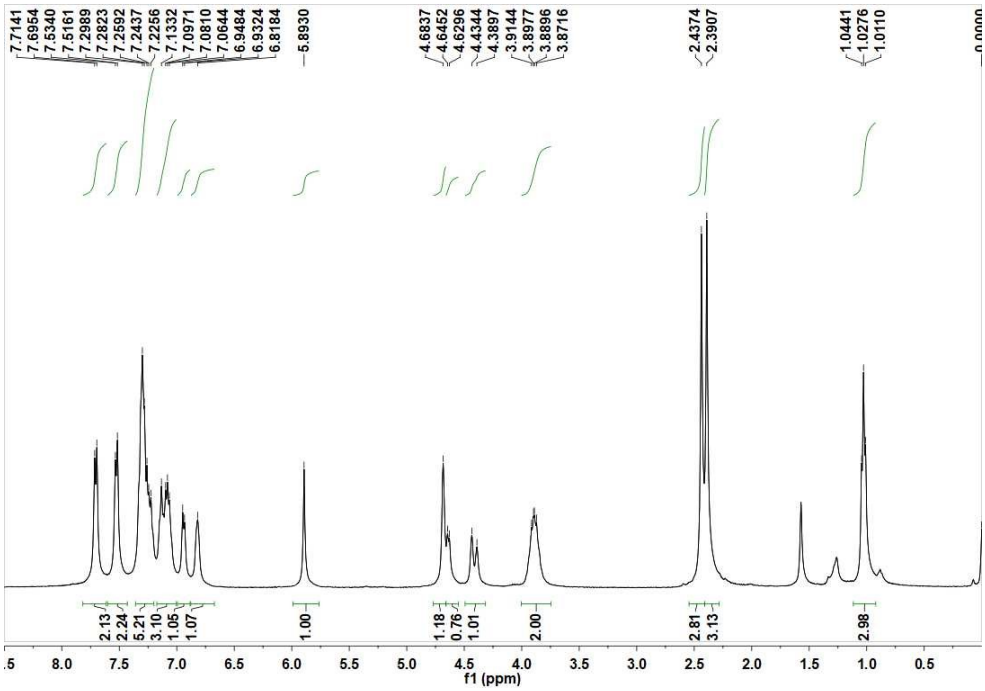
3a






H3C
CO2Et
Ph
O
N
Ts

3b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7.0971
7.0810
7.0644
6.9484
6.9324
6.8184
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4.4344
4.3897
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3.8977
3.8896
3.8716
2.4374
2.3907
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1.0276
1.0110
2.13
2.24
5.21
3.10
1.05
1.07
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1.01
2.00
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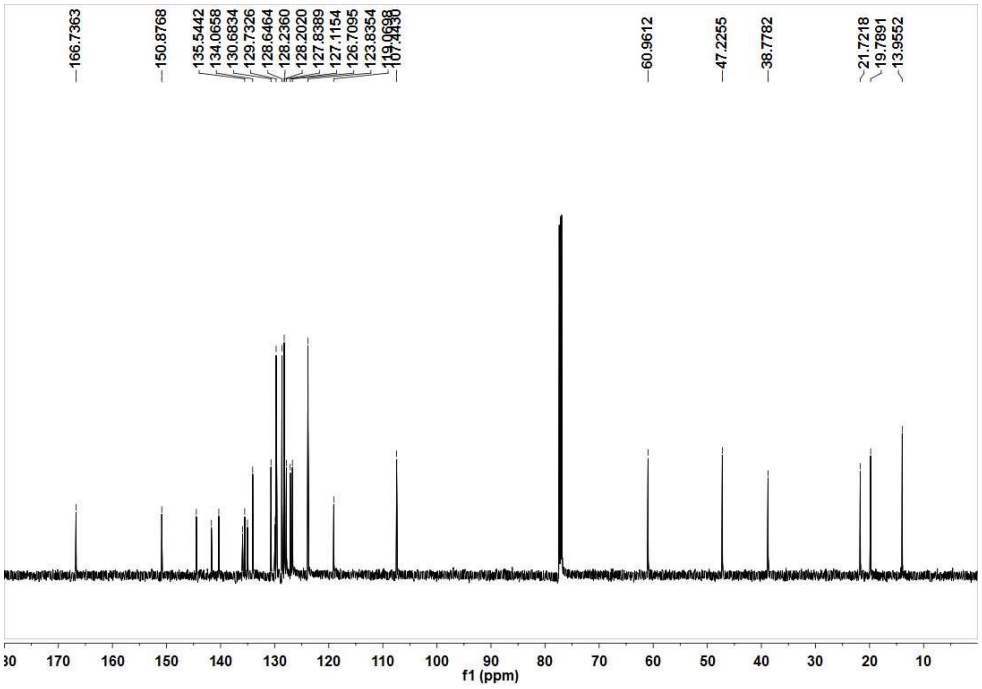
3.13
2.98
f1 (ppm)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123.8354
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47.2255
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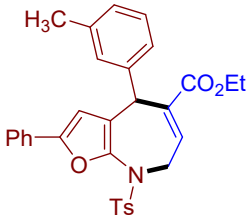
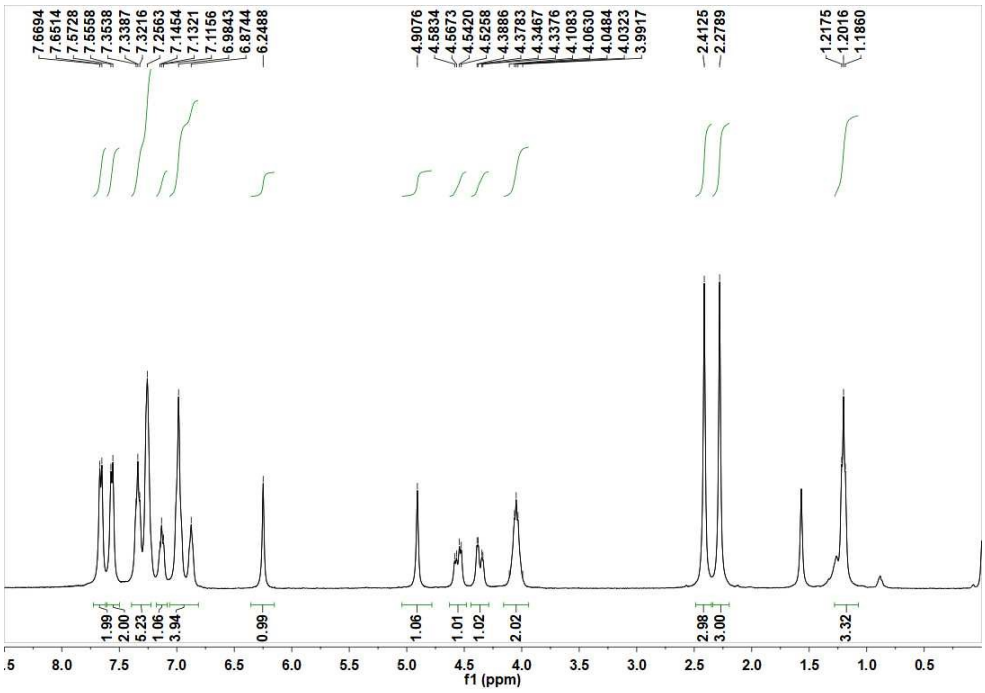
f1 (ppm)


H3C
CO2Et
Ph
O
N
Ts

3c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7.1454
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7.1156
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6.8744
6.2488
4.9076
4.5834
4.5673
4.5420
4.5258
4.3886
4.3783
4.3467
4.3376
4.1083
4.0630
4.0484
4.0323
3.9917
2.4125
2.2789
1.2175
1.2016
1.1860
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2.00
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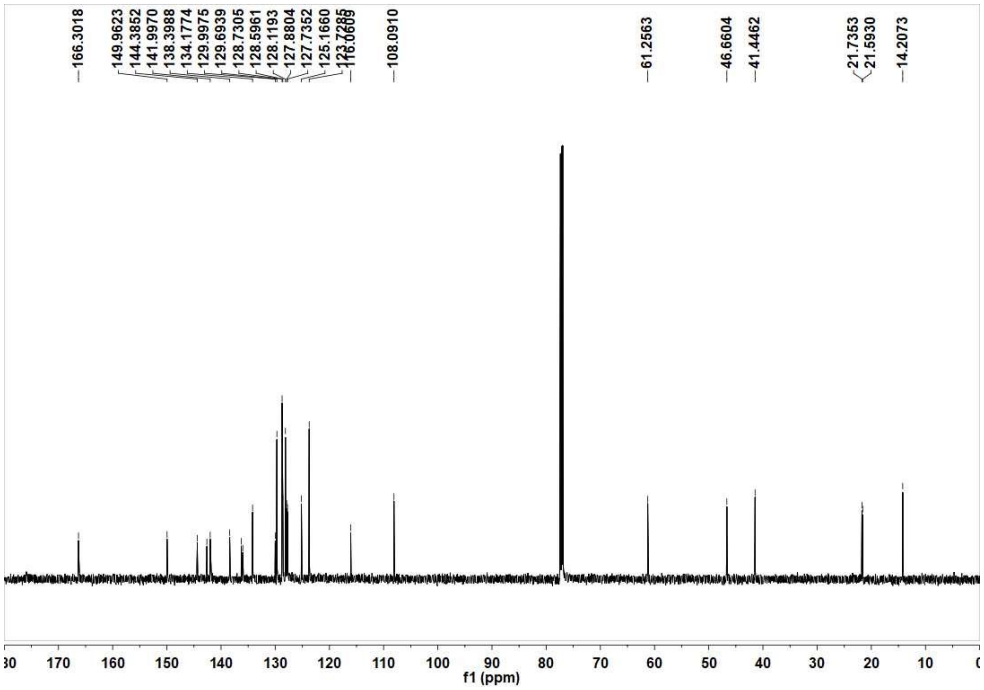
0.99
1.06
1.01
1.02
2.02
2.98
3.00
3.32
f1 (ppm)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129.9975
129.6939
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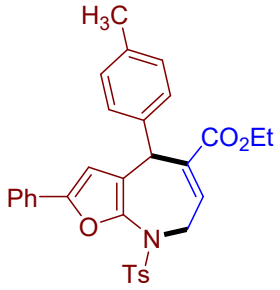
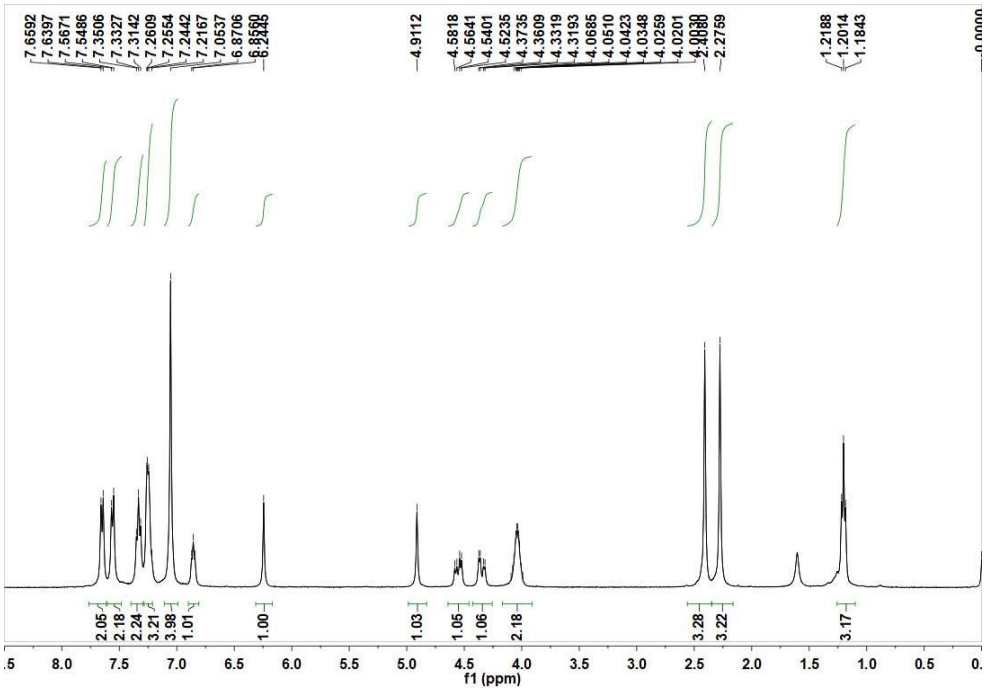
128.5961
128.1193
127.8804
127.7352
125.1660
108.0910
61.2563
46.6604
41.4462
21.7353
21.5930
14.2073
f1 (ppm)


H3C
CO2Et
Ph
O
N
Ts

3d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4.0259
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2.24
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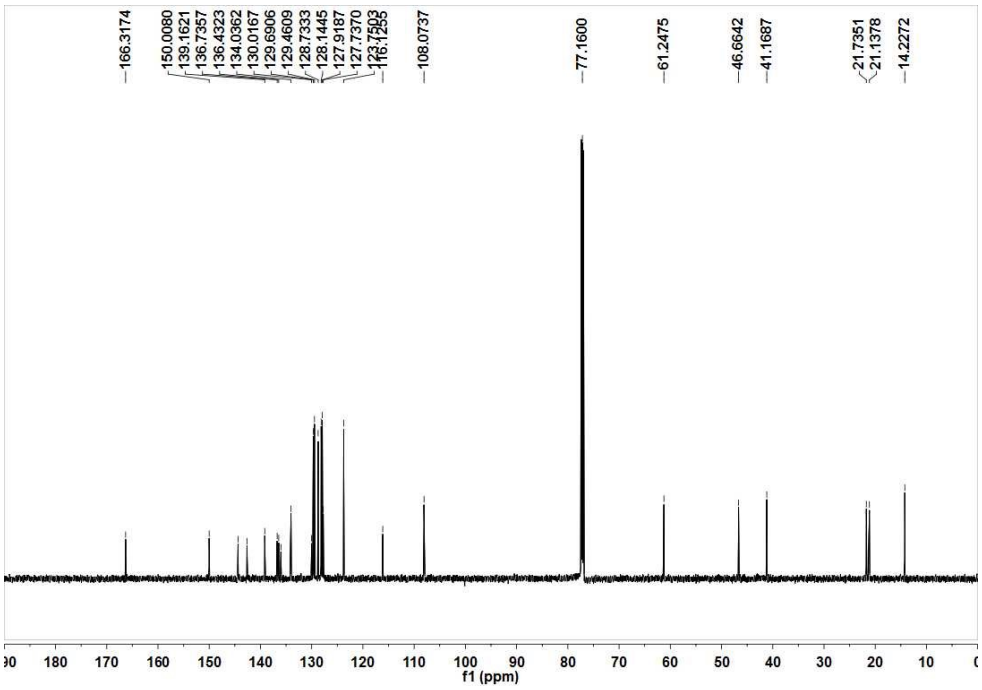
f1 (ppm)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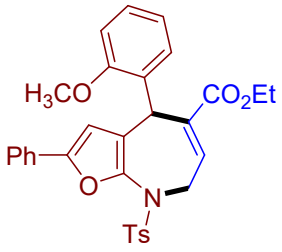
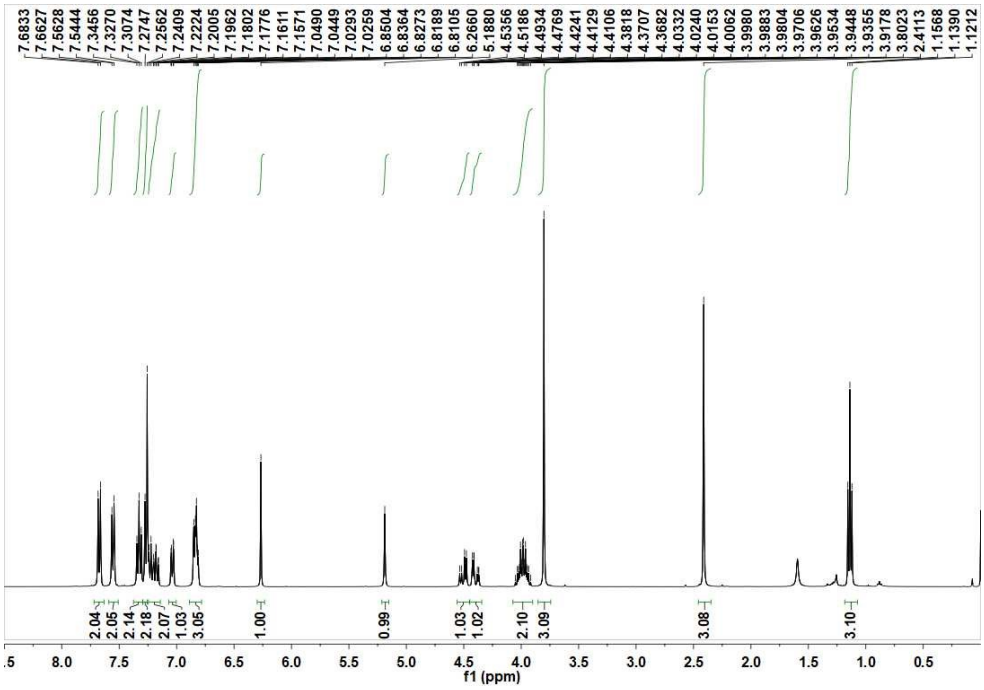
21.1378
14.2272
f1 (ppm)


H3CO
CO2Et
Ph
O
N
Ts

3e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7.1962
7.1802
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1.1390
1.1212
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2.05
2.14
2.18
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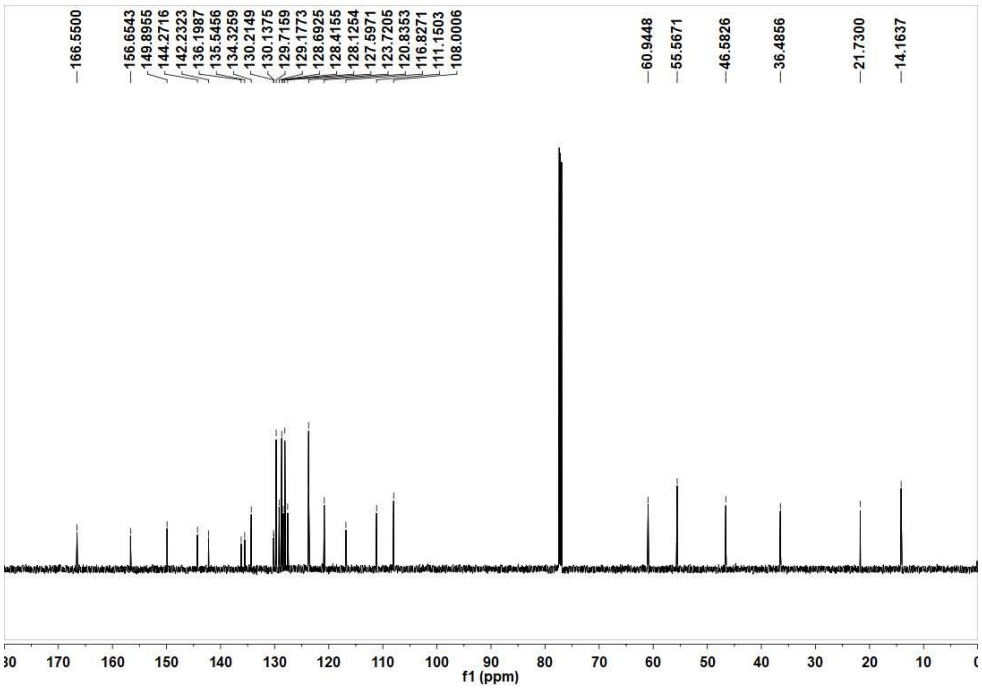
3.09
3.08
3.10
f1 (ppm)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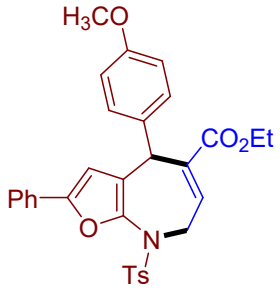
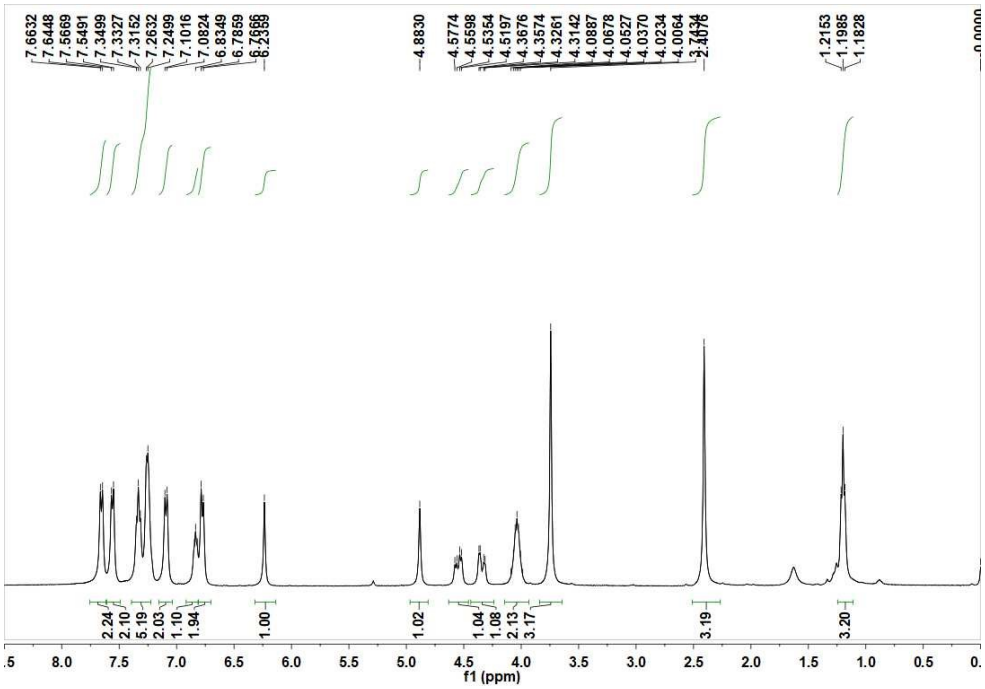
f1 (ppm)


H3CO
CO2Et
Ph
O
N
Ts

3f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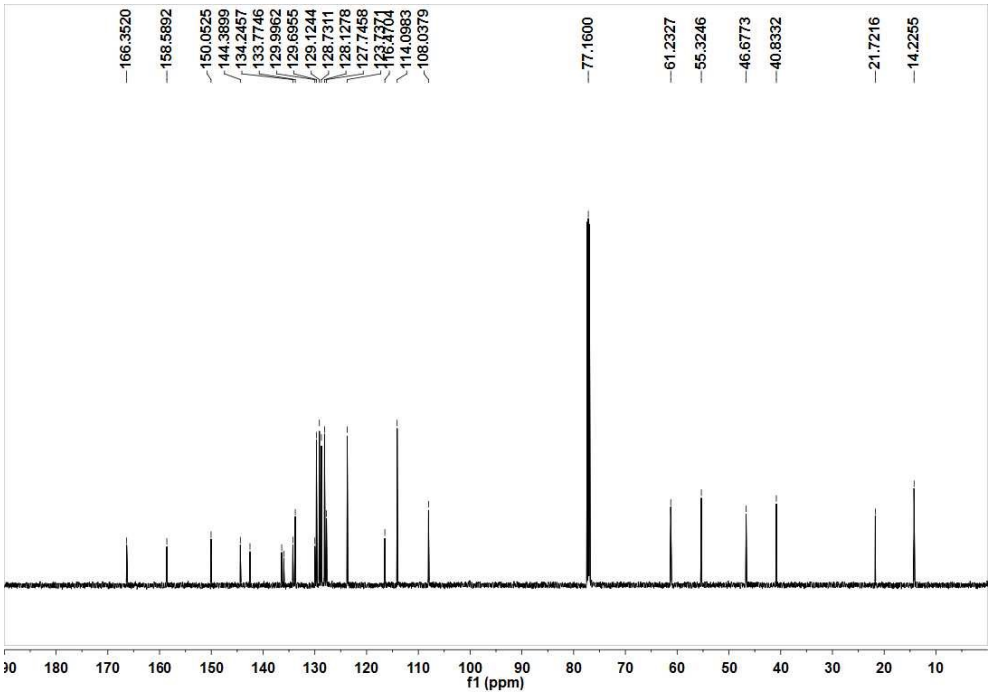
2.03
1.10
1.94
1.00
1.02
1.04
1.08
2.13
3.17
3.19
3.20
f1 (ppm)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150.0525
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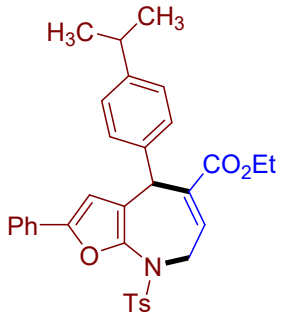
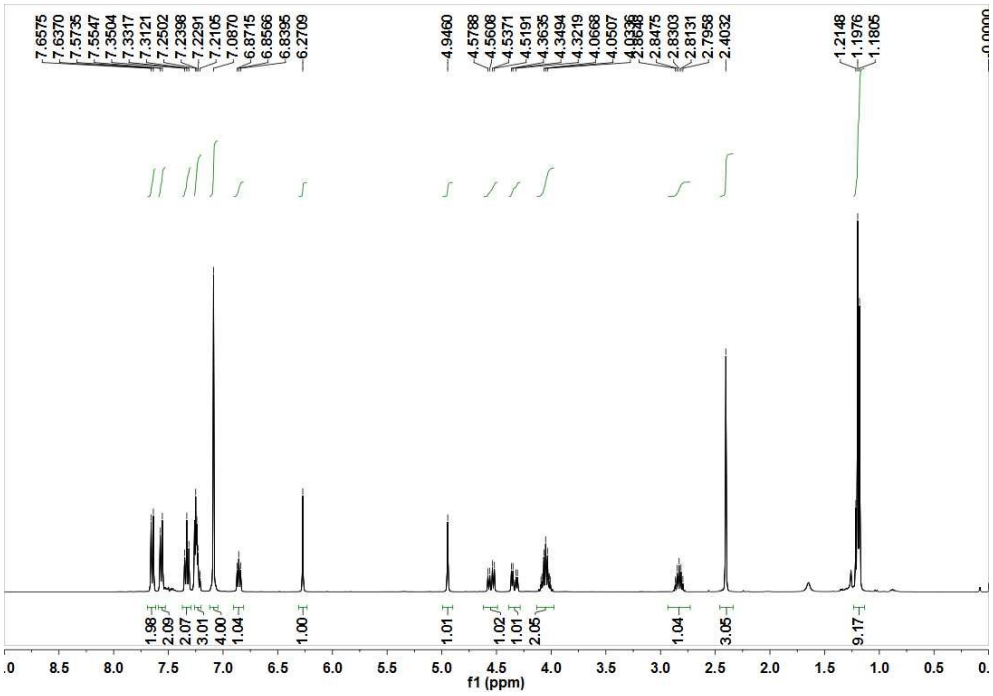
134.2457
133.7746
129.9962
129.6955
129.1244
128.7311
128.1278
127.7458
123.7371
123.4704
114.0983
108.0379
77.1600
61.2327
55.3246
46.6773
40.8332
21.7216
14.2255
f1 (ppm)


H3C
CH3
CO2Et
Ph
O
N
Ts

3g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7.2398
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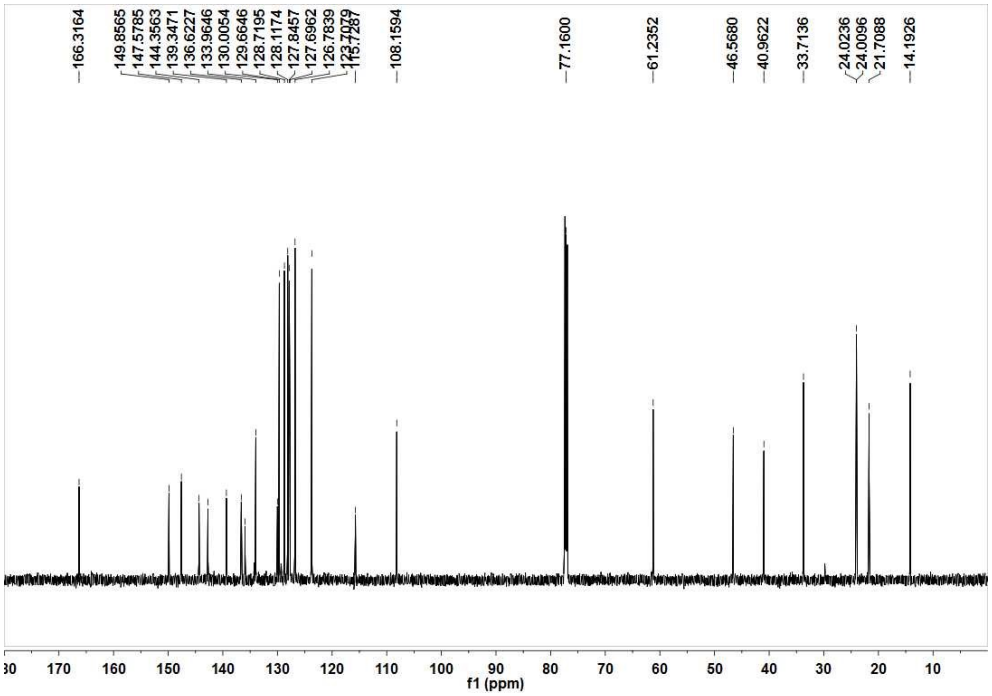
7.2105
7.0870
6.8715
6.8566
6.8395
6.2709
4.9460
4.5788
4.5608
4.5371
4.5191
4.3635
4.3494
4.3219
4.0668
4.0507
2.8475
2.8303
2.8131
2.7958
2.4032
1.2148
1.1976
1.1805
1.98
2.09
2.07
3.01
4.00
1.04
1.00
1.01
1.02
1.01
2.05
1.04
3.05
9.17
f1 (ppm)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129.6646
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127.8457
127.6962
126.7839
123.7079
115.7287
108.1594
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61.2352
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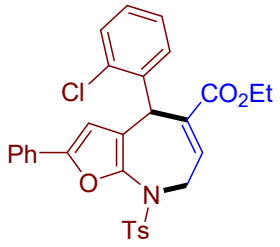
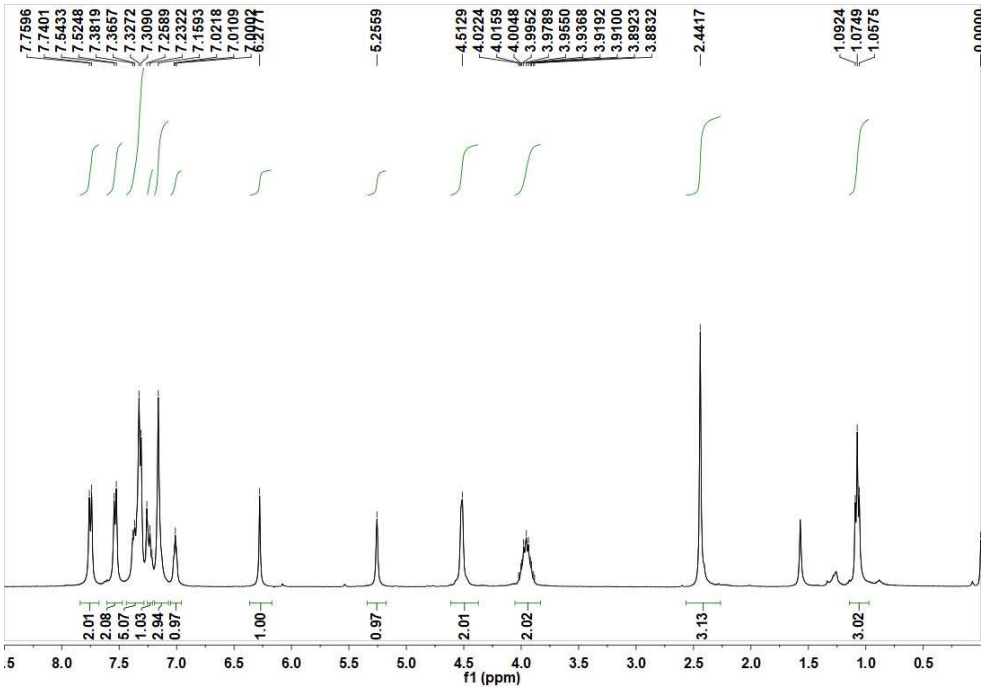
24.0236
24.0096
21.7088
14.1926
f1 (ppm)


Cl
CO2Et
Ph
O
N
Ts

3h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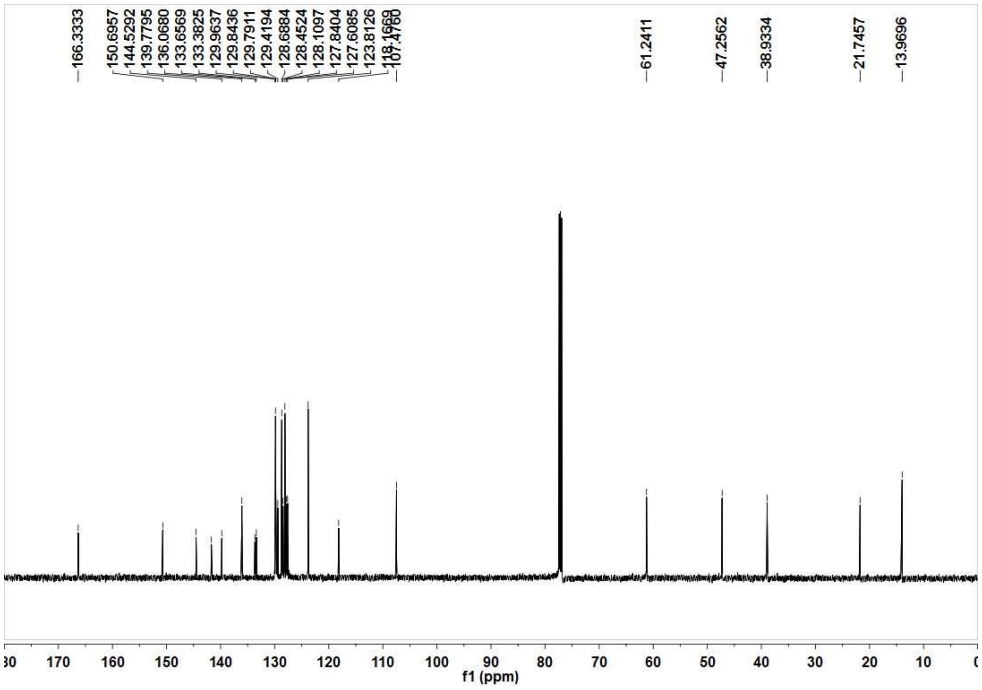
7.5248
7.3819
7.3657
7.3272
7.3090
7.2589
7.2322
7.1593
7.0218
7.0109
5.2559
4.5129
4.0224
4.0159
4.0048
3.9952
3.9789
3.9650
3.9368
3.9192
3.9100
3.8923
3.8832
2.4417
1.0924
1.0749
1.0575
2.01
2.08
5.07
1.03
2.94
0.97
1.00
0.97
2.01
2.02
3.13
3.02
f1 (ppm)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128.6884
128.4524
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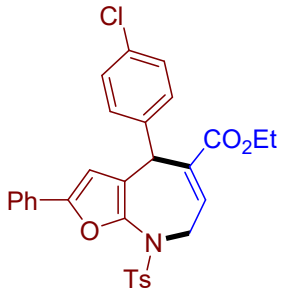
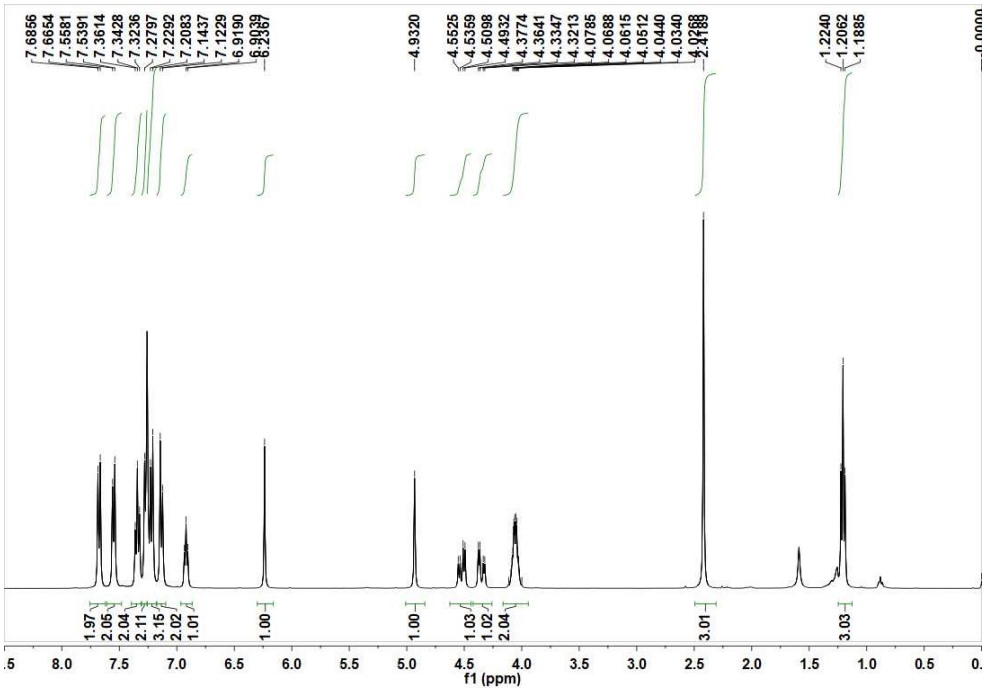
127.6085
123.8126
61.2411
47.2562
38.9334
21.7457
13.9696
f1 (ppm)


Cl
CO2Et
Ph
O
N
Ts

3i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7.3428
7.3236
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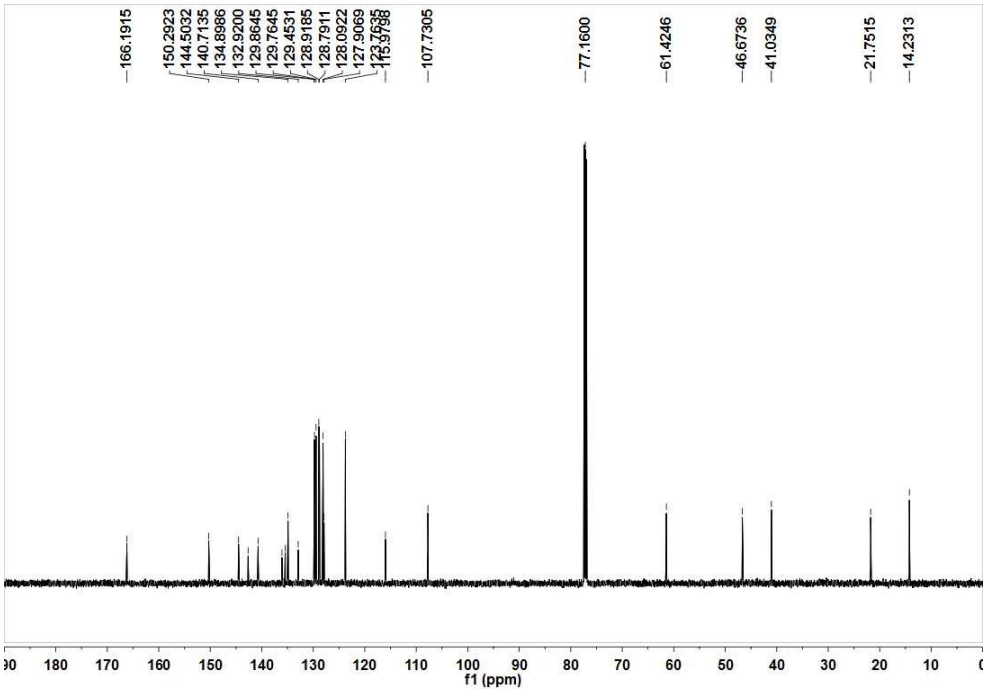
7.2292
7.2083
7.1437
7.1229
6.9190
4.9320
4.5525
4.5359
4.5098
4.4932
4.3774
4.3641
4.3347
4.3213
4.0785
4.0688
4.0615
4.0512
4.0440
4.0340
2.4189
1.2240
1.2062
1.1885
1.97
2.05
2.04
2.11
3.15
2.02
1.01
1.00
1.00
1.03
1.02
2.04
3.01
3.03
f1 (ppm)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140.7135
134.8986
132.9200
129.8645
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129.4531
128.9185
128.7911
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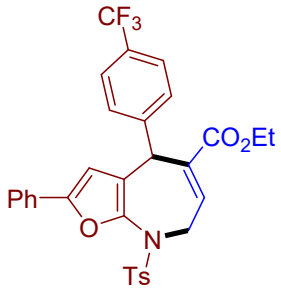
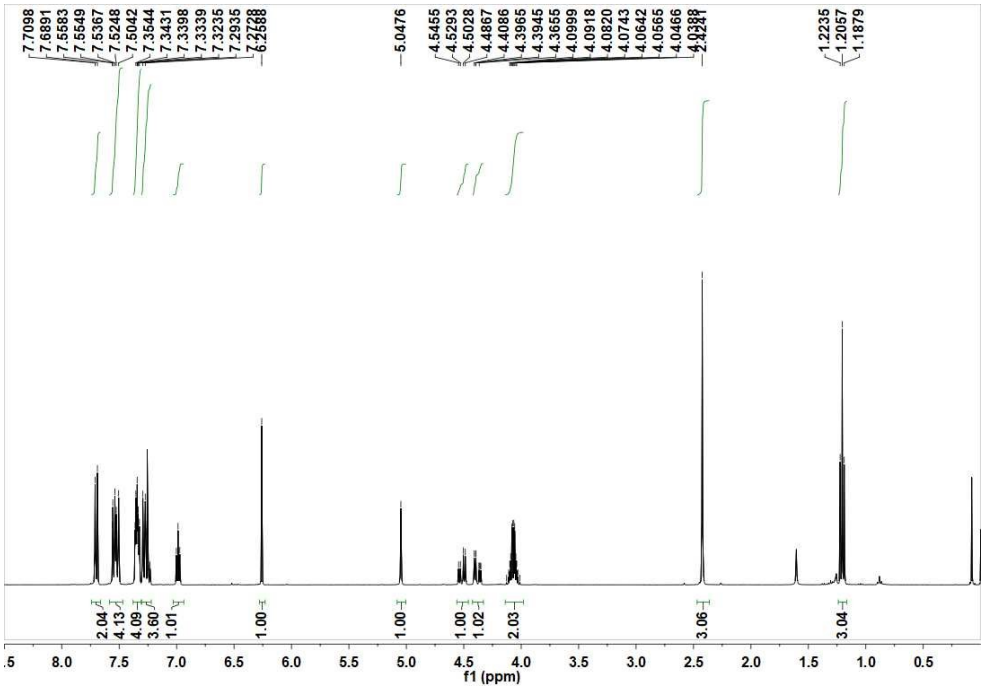
127.9069
107.7305
77.1600
61.4246
46.6736
41.0349
21.7515
14.2313
f1 (ppm)


CF3
CO2Et
Ph
O
N
Ts

3j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7.5248
7.5042
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7.3431
7.3398
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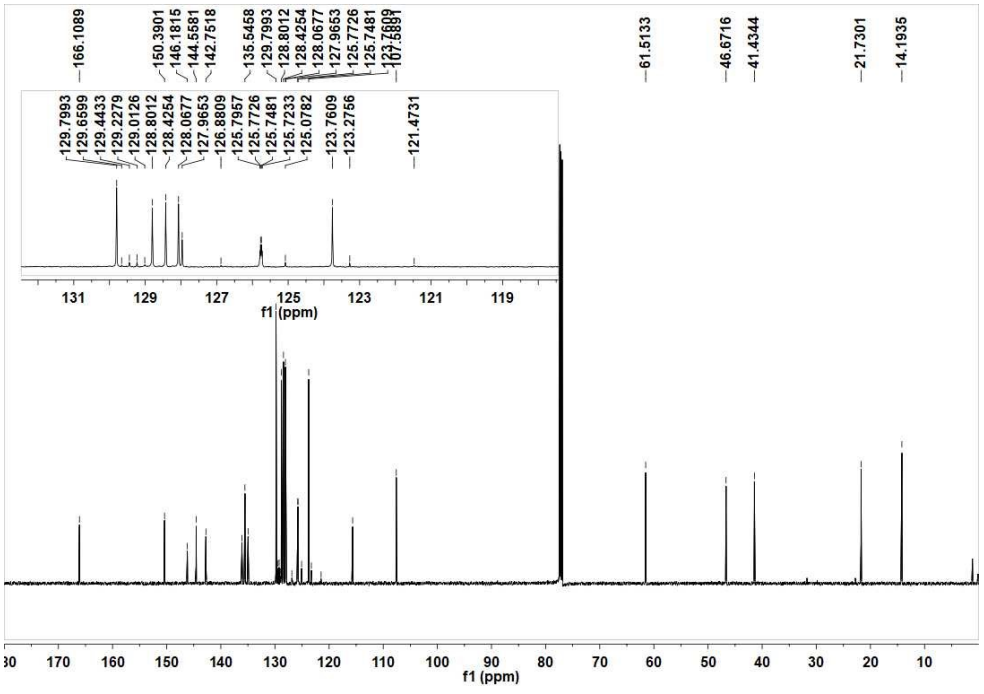
7.3235
7.2935
5.0476
4.5455
4.5293
4.5028
4.4867
4.4086
4.3965
4.3945
4.3655
4.0999
4.0918
4.0820
4.0743
4.0642
4.0565
4.0466
2.4241
1.2235
1.2057
1.1879
2.04
4.13
4.09
3.60
1.01
1.00
1.00
1.00
1.02
2.03
3.06
3.04
f1 (ppm)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128.4254
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125.7481
123.7609
107.5891
61.5133
46.6716
41.4344
21.7301
14.1935
129.7993
129.6599
129.4433
129.2279
129.0126
128.8012
128.4254
128.0677
127.9653
126.8809
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125.7233
125.0782
123.7609
123.2756
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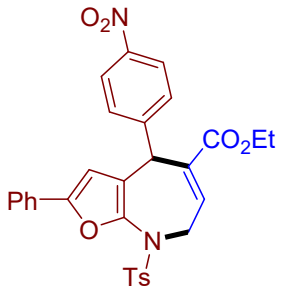
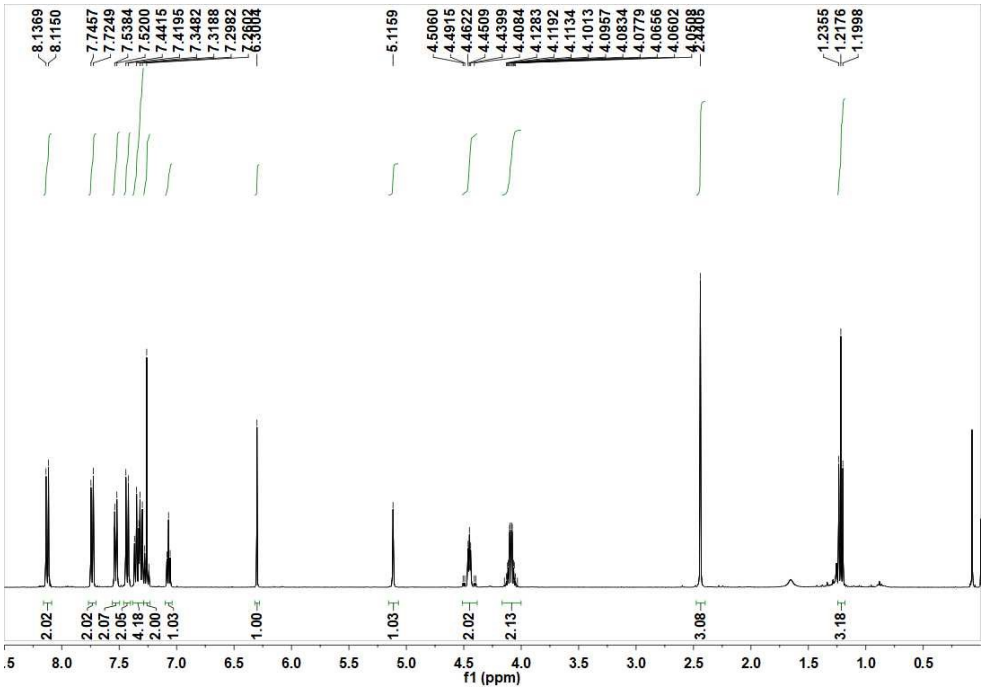
f1 (ppm)
f1 (ppm)


O2N
CO2Et
Ph
O
N
Ts

3k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7.3482
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7.2982
5.1159
4.5060
4.4915
4.4622
4.4509
4.4399
4.4084
4.1283
4.1192
4.1134
4.1013
4.0957
4.0834
4.0779
4.0656
4.0602
1.2355
1.2176
1.1998
2.02
2.02
2.07
2.05
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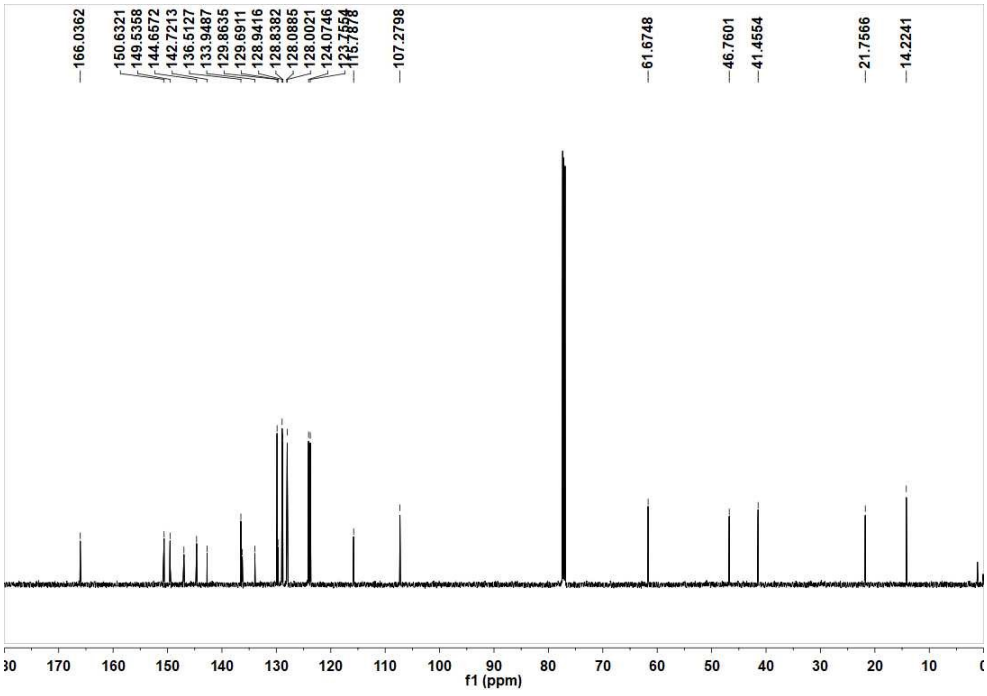
1.03
1.00
1.03
2.02
2.13
3.08
3.18
f1 (ppm)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129.6911
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124.0746
107.2798
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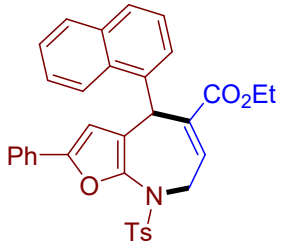
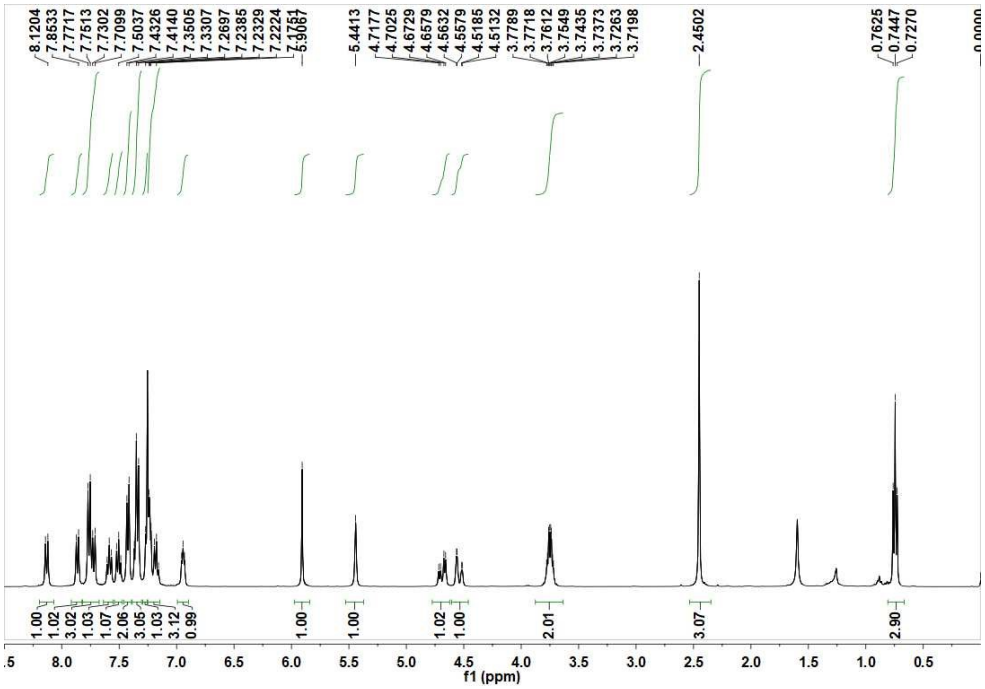
46.7601
41.4554
21.7566
14.2241
f1 (ppm)


CO2Et
Ph
O
N
Ts

3l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7.7099
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7.4326
7.4140
7.3505
7.3307
7.2697
7.2385
7.2329
7.2224
7.1751
5.9067
5.4413
4.7177
4.7025
4.6729
4.6579
4.5632
4.5579
4.5185
4.5132
3.7789
3.7718
3.7612
3.7549
3.7435
3.7373
3.7263
3.7198
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0.7447
0.7270
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1.02
3.02
1.03
1.07
2.06
3.05
1.03
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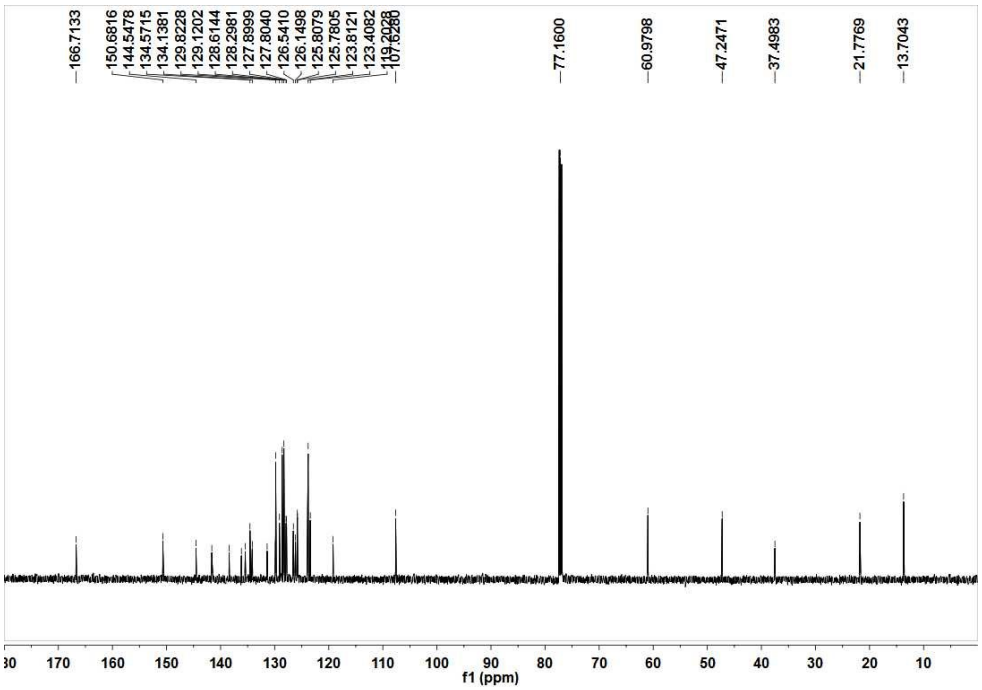
1.00
1.02
1.00
2.01
3.07
2.90
f1 (ppm)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128.2981
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127.8040
126.5410
126.1498
125.8079
125.7805
123.8121
123.4082
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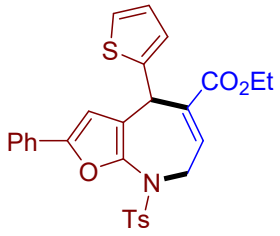
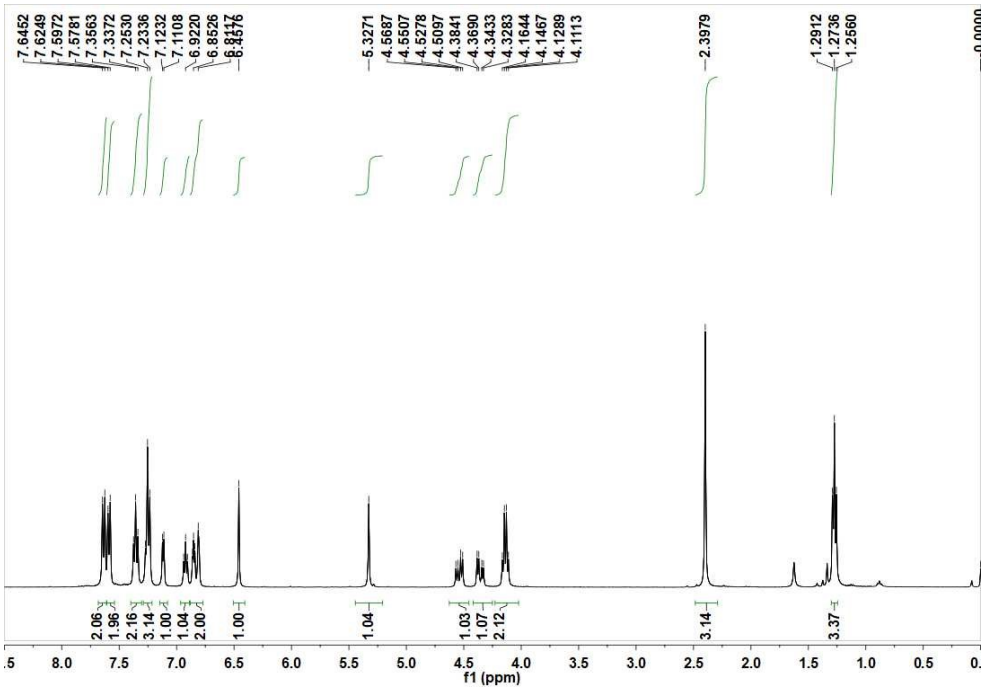
47.2471
37.4983
21.7769
13.7043
f1 (ppm)


S
CO2Et
Ph
O
N
Ts

3m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5.3271
4.5687
4.5507
4.5278
4.5097
4.3841
4.3690
4.3433
4.3283
4.1644
4.1467
4.1289
4.1113
2.3979
1.2912
1.2736
1.2560
2.06
1.96
2.16
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1.00
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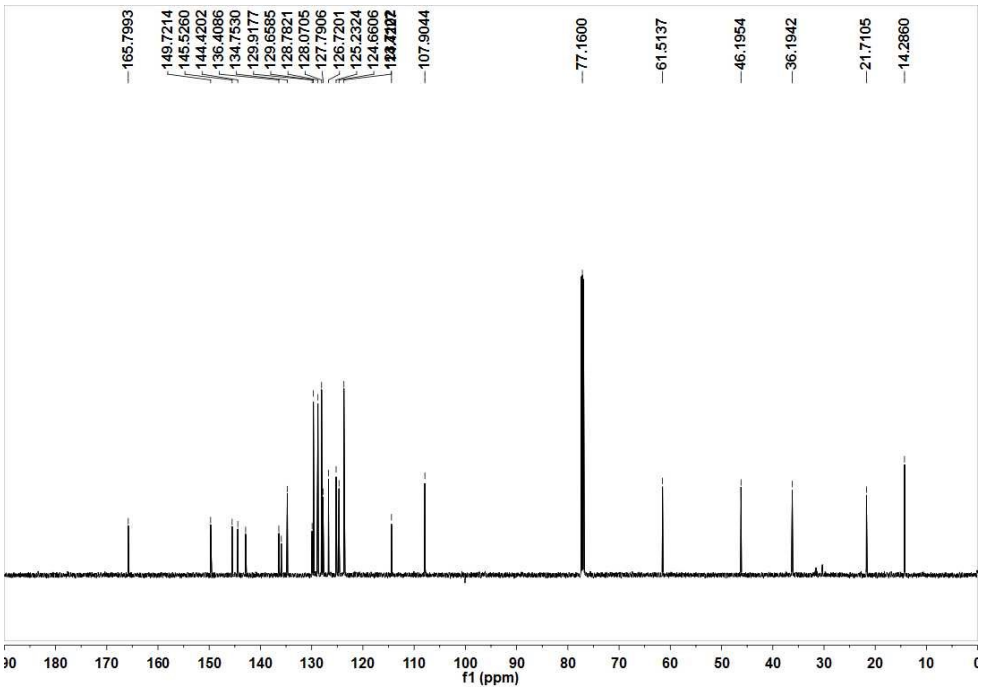
1.04
1.03
1.07
2.12
3.14
3.37
f1 (ppm)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128.7821
128.0705
127.7906
126.7201
125.2324
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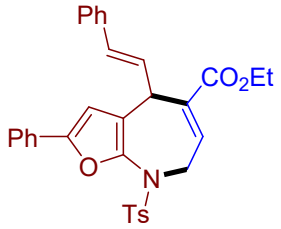
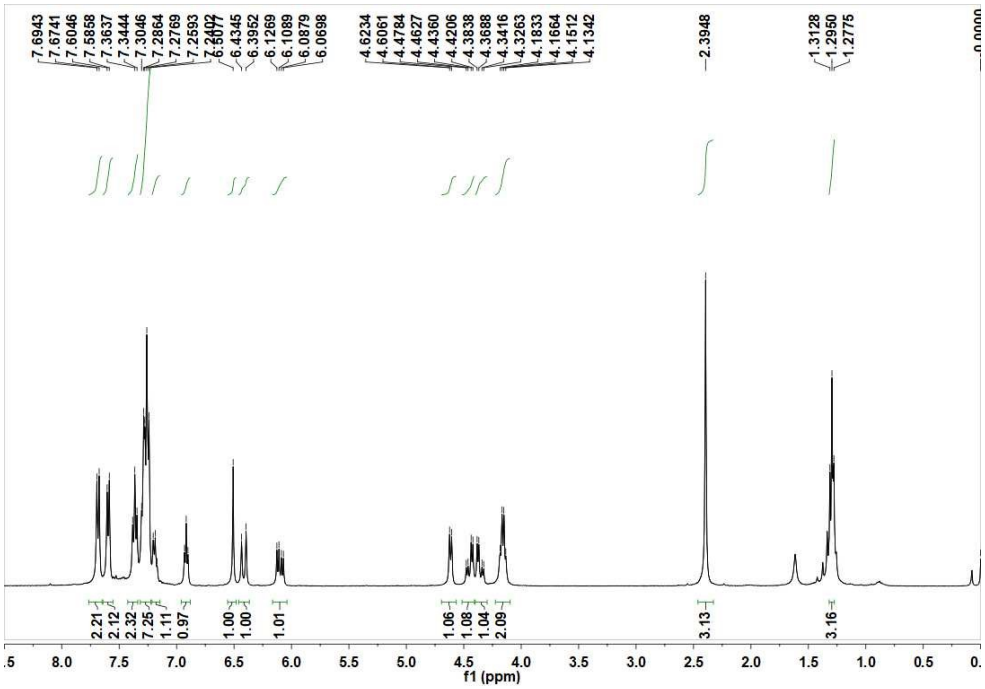
107.9044
77.1600
61.5137
46.1954
36.1942
21.7105
14.2860
f1 (ppm)


Ph
CO2Et
Ph
O
N
Ts

3n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4.3416
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4.1512
4.1342
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1.2950
1.2775
2.21
2.12
2.32
7.25
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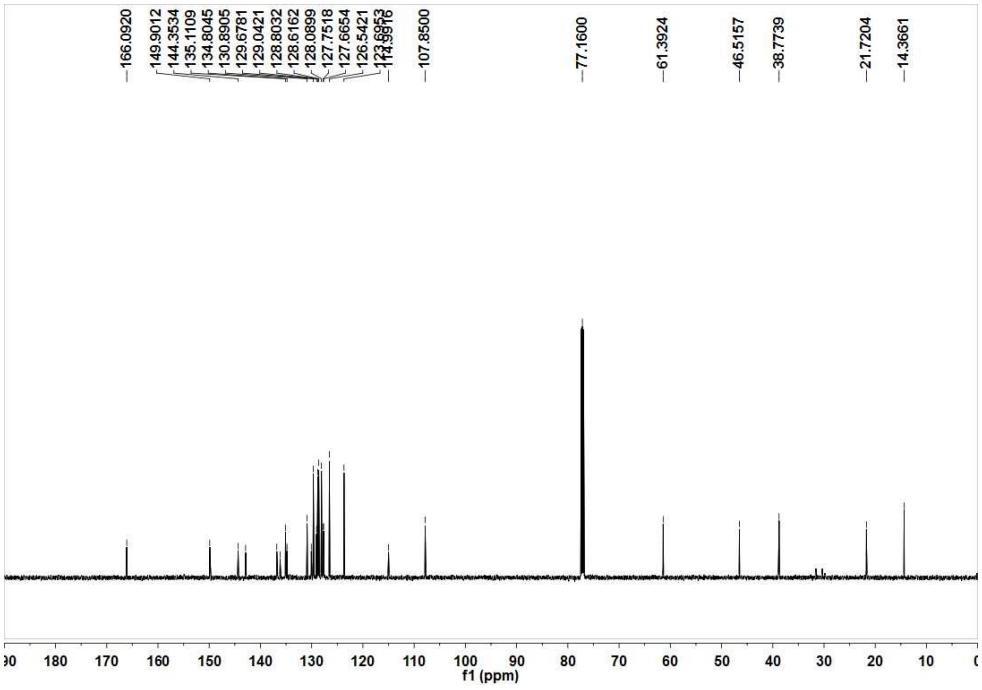
1.00
1.01
1.06
1.08
1.04
2.09
3.13
3.16
f1 (ppm)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127.7518
127.6654
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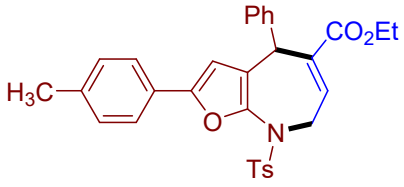
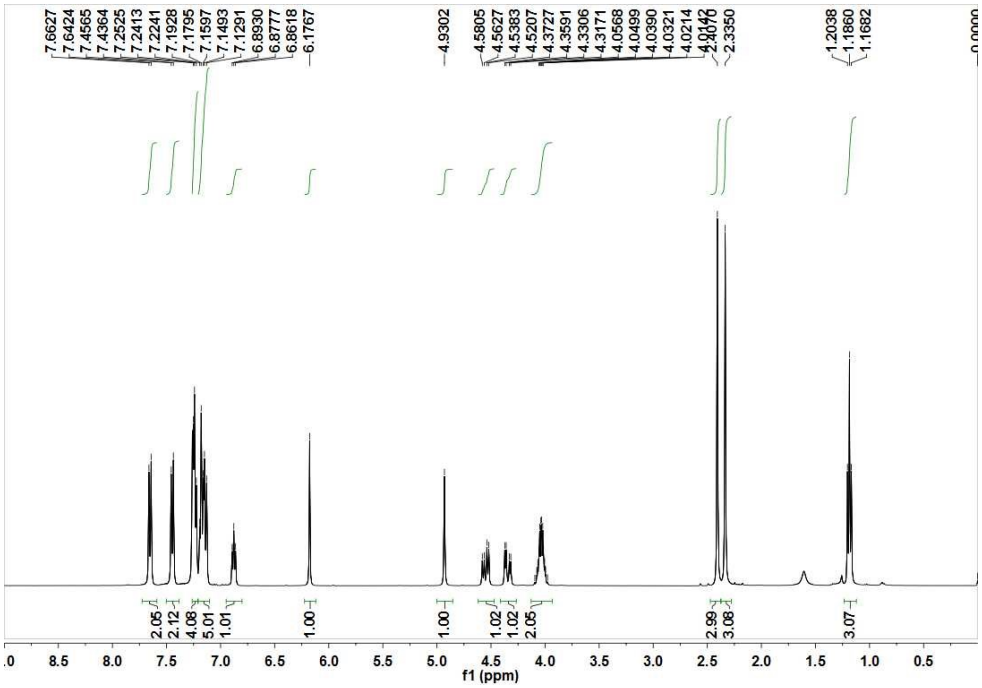
61.3924
46.5157
38.7739
21.7204
14.3661
f1 (ppm)


Ph
CO2Et
H3C
O
N
Ts

3o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7.1291
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6.1767
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4.5383
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4.0214
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1.2038
1.1860
1.1682
2.05
2.12
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1.00
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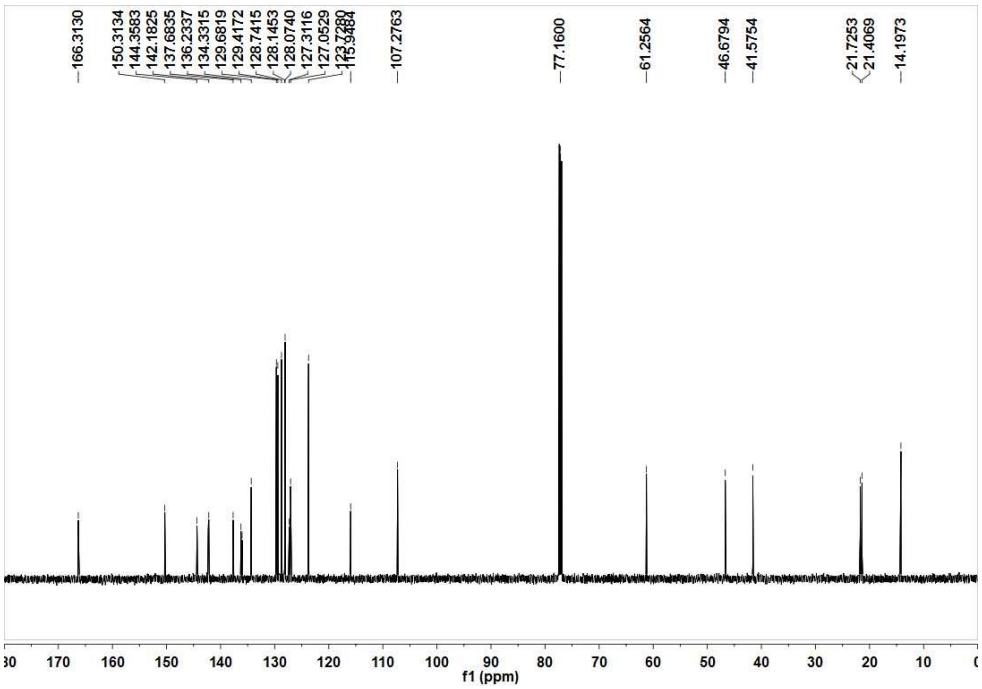
1.02
2.05
2.99
3.08
3.07
f1 (ppm)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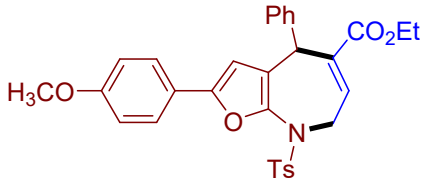
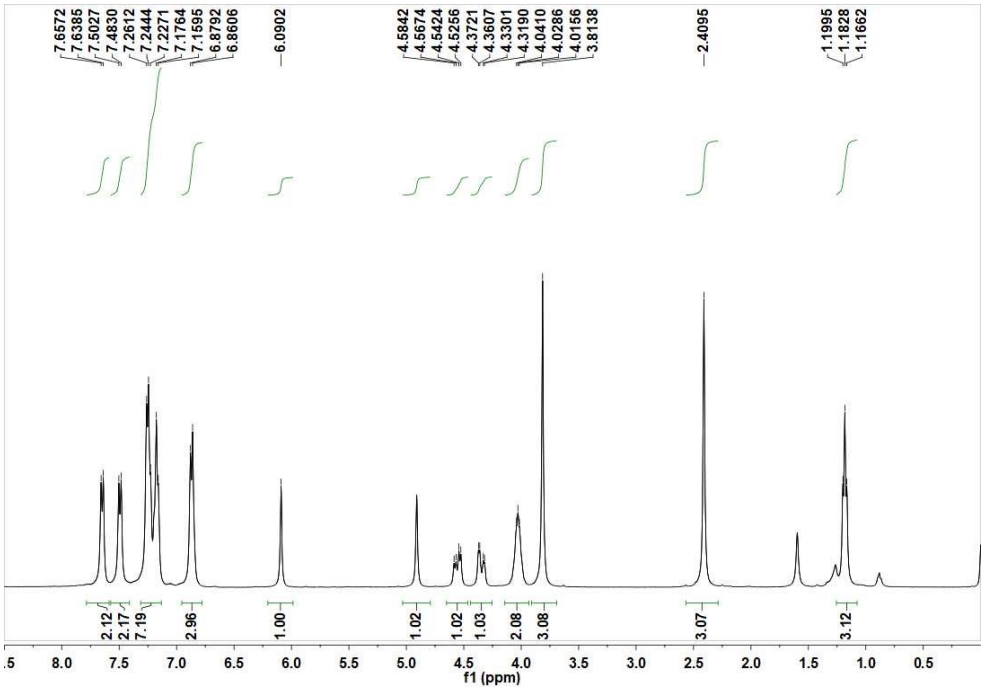
41.5754
21.7253
21.4069
14.1973
f1 (ppm)


Ph
CO2Et
H3CO
O
N
Ts

3p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7.2271
7.1764
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6.8792
6.8606
6.0902
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4.5256
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4.3301
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4.0410
4.0286
4.0156
3.8138
2.4095
1.1995
1.1828
1.1662
2.12
2.17
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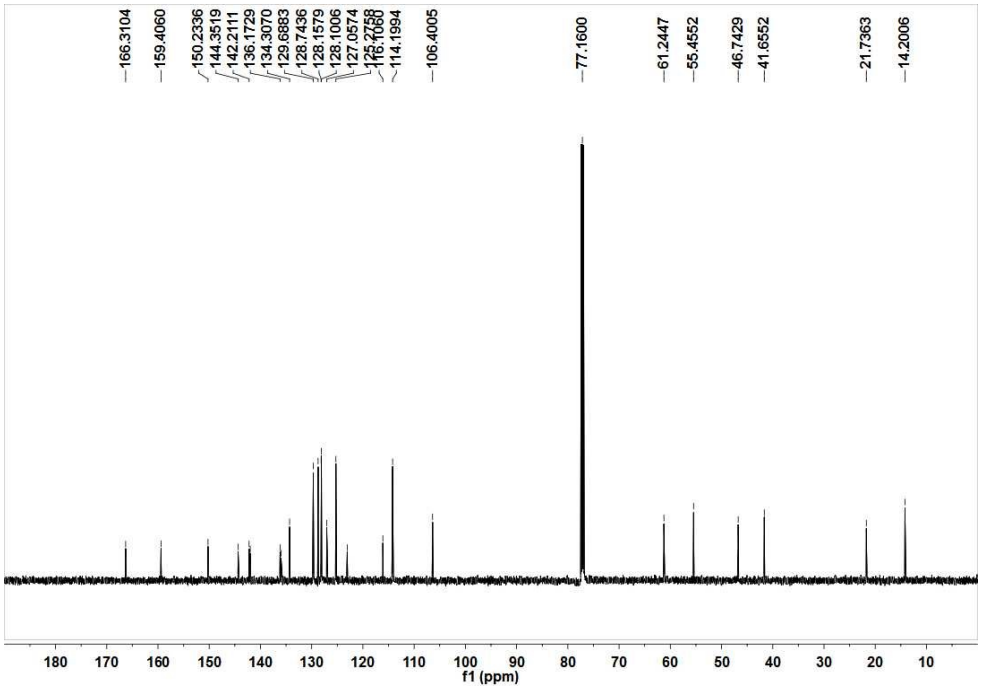
1.02
1.02
1.03
2.08
3.08
3.07
3.12
f1 (ppm)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127.0574
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41.6552
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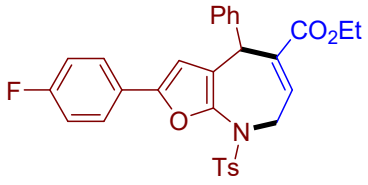
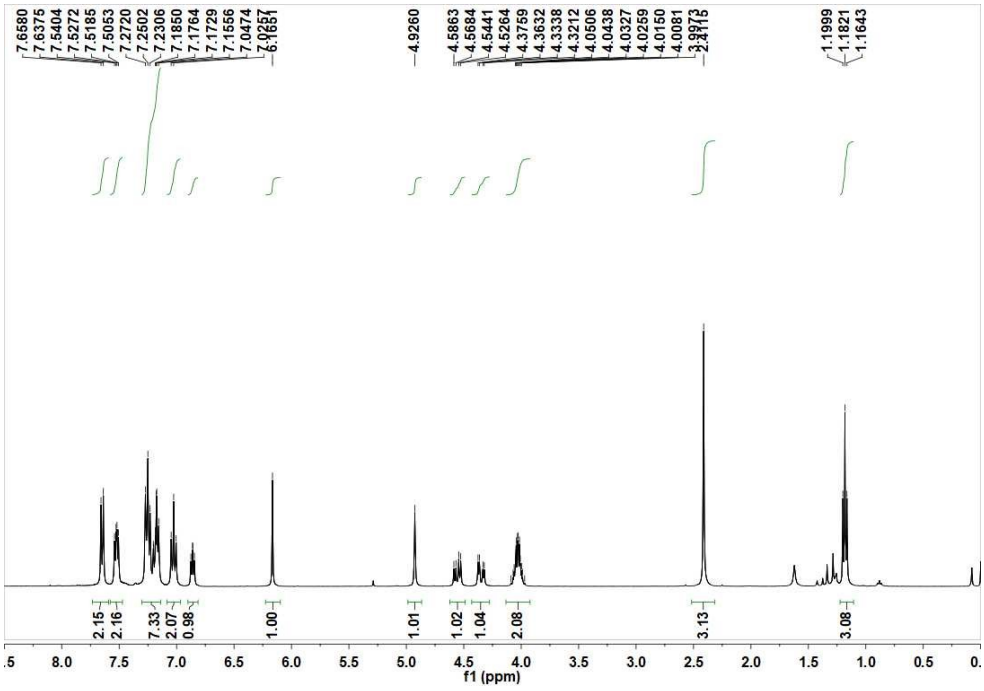
14.2006
f1 (ppm)


Ph
CO2Et
F
O
N
Ts

3q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7.2306
7.1850
7.1764
7.1729
7.1556
7.0474
7.0257
6.1651
4.9260
4.5863
4.5684
4.5441
4.5264
4.3759
4.3632
4.3338
4.3212
4.0506
4.0438
4.0327
4.0259
4.0150
4.0081
3.3973
2.4116
1.1999
1.1821
1.1643
2.15
2.16
7.33
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1.00
1.01
1.02
1.04
2.08
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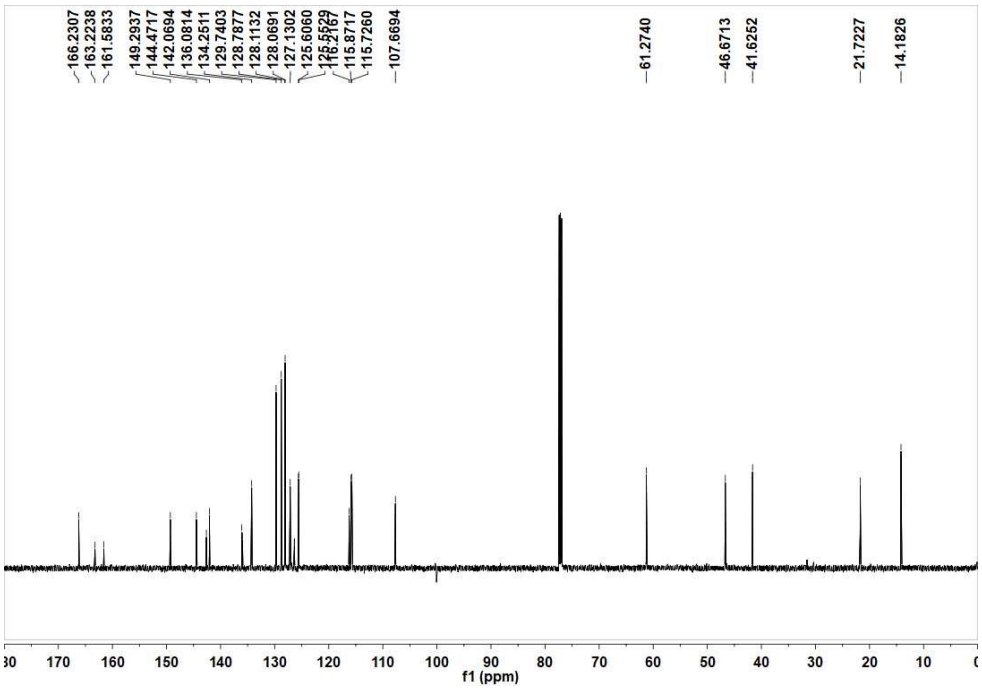
3.08
f1 (ppm)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128.0691
127.1302
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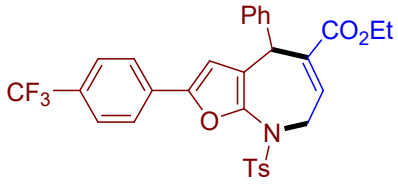
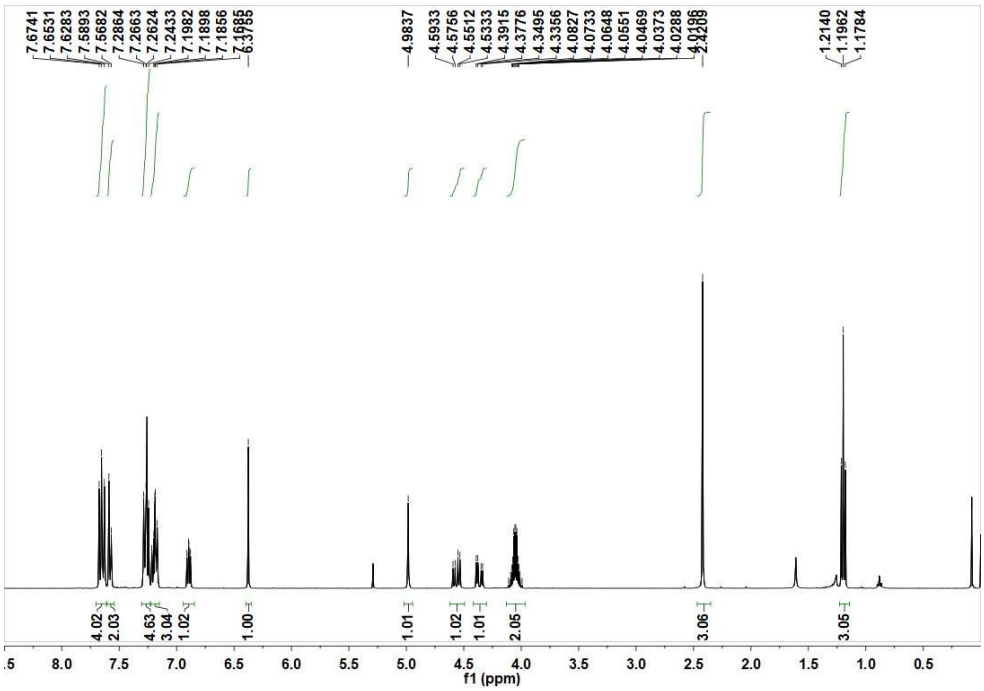
41.6252
21.7227
14.1826
f1 (ppm)


Ph
CO2Et
CF3
O
N
Ts

3r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7.2624
7.2433
7.1982
7.1898
7.1856
7.1685
6.3765
4.9837
4.5933
4.5756
4.5512
4.5333
4.3915
4.3776
4.3495
4.3356
4.0827
4.0733
4.0648
4.0551
4.0469
4.0373
4.0288
2.4209
1.2140
1.1962
1.1784
4.02
2.03
4.63
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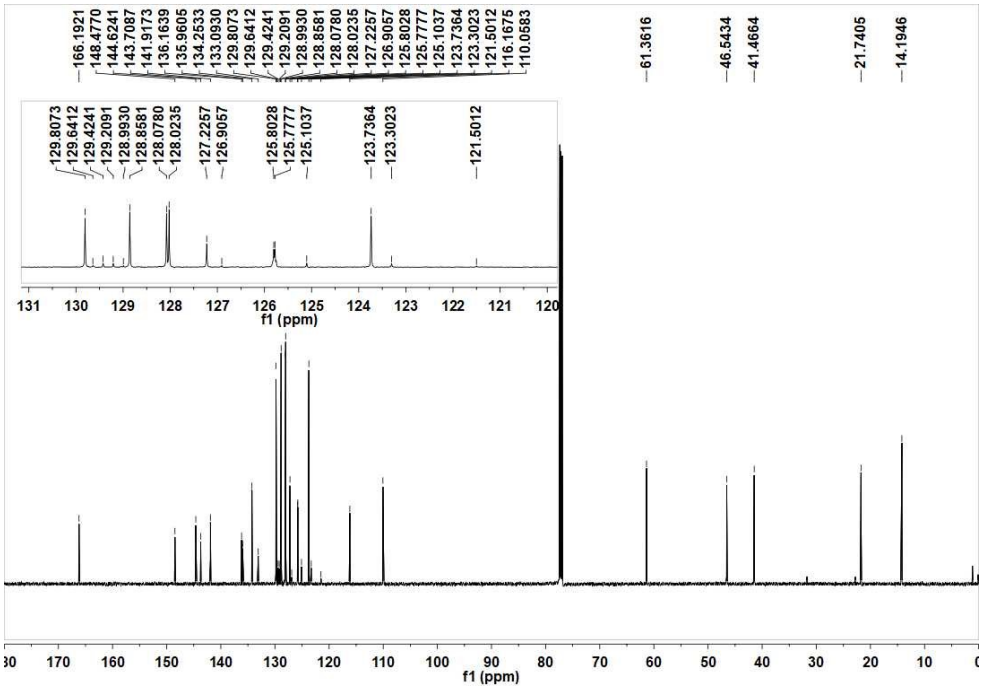
1.02
1.00
1.01
1.02
1.01
2.05
3.06
3.05
f1 (ppm)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141.9173
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133.0930
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129.6412
129.4241
129.2091
128.9930
128.8581
128.0780
128.0235
127.2257
126.9057
125.8028
125.7777
125.1037
123.7364
123.3023
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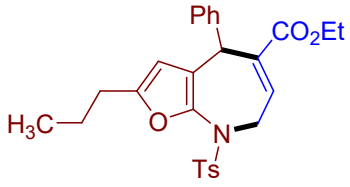
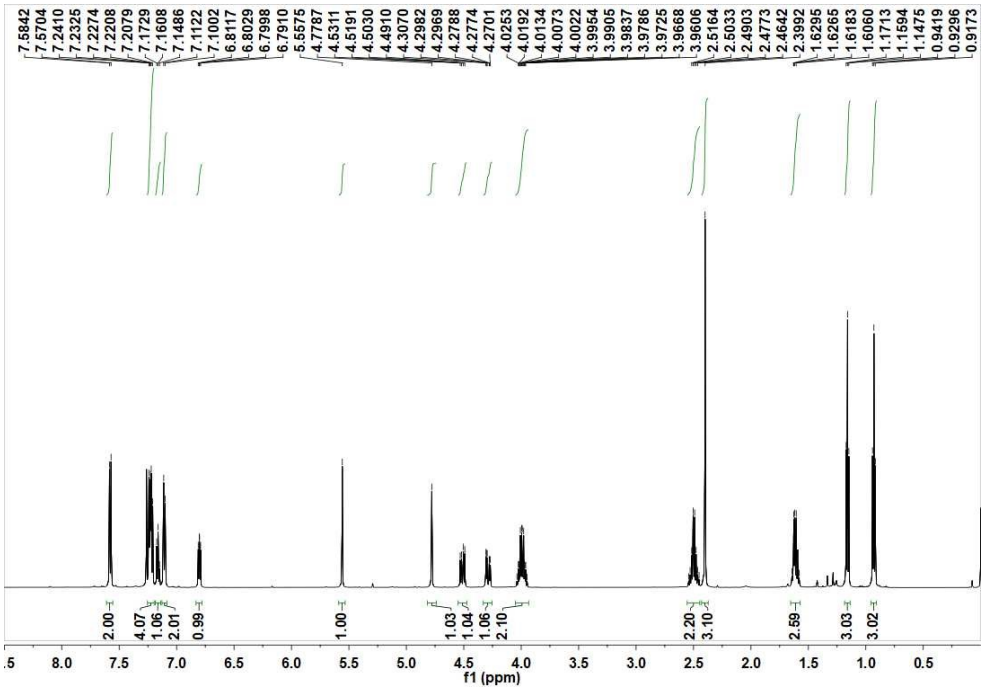
61.3616
46.5434
41.4664
21.7405
14.1946
f1 (ppm)


Ph
CO2Et
H3C
O
N
Ts

3s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7.1608
7.1486
7.1122
7.1002
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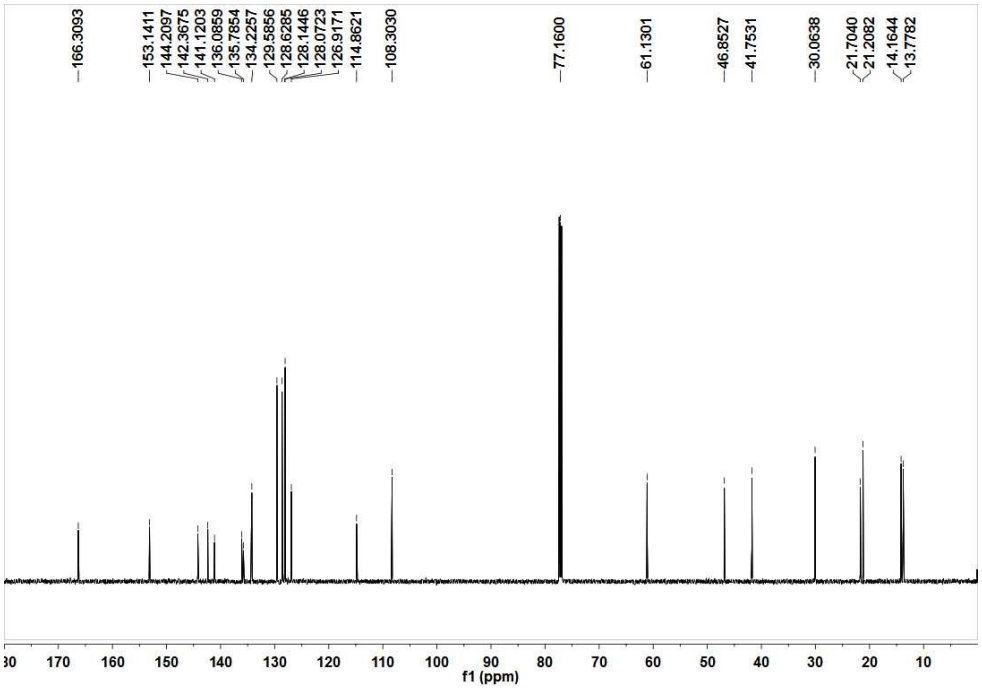
6.8029
6.7998
6.7910
5.5575
4.7787
4.5311
4.5191
4.5030
4.4910
4.3070
4.2982
4.2969
4.2788
4.2774
4.2701
4.0253
4.0192
4.0134
4.0073
4.0022
3.9954
3.9905
3.9837
3.9786
3.9725
3.9668
3.9606
2.5164
2.5033
2.4903
2.4773
2.4642
2.3992
1.6295
1.6265
1.6183
1.6060
1.1713
1.1594
1.1475
0.9419
0.9296
0.9173
2.00
4.07
1.06
2.01
0.99
1.00
1.03
1.04
1.06
2.10
2.20
3.10
2.59
3.03
3.02
f1 (ppm)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128.0723
126.9171
114.8621
108.3030
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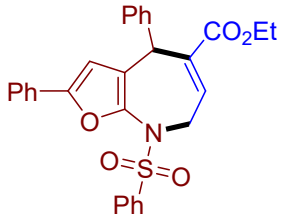
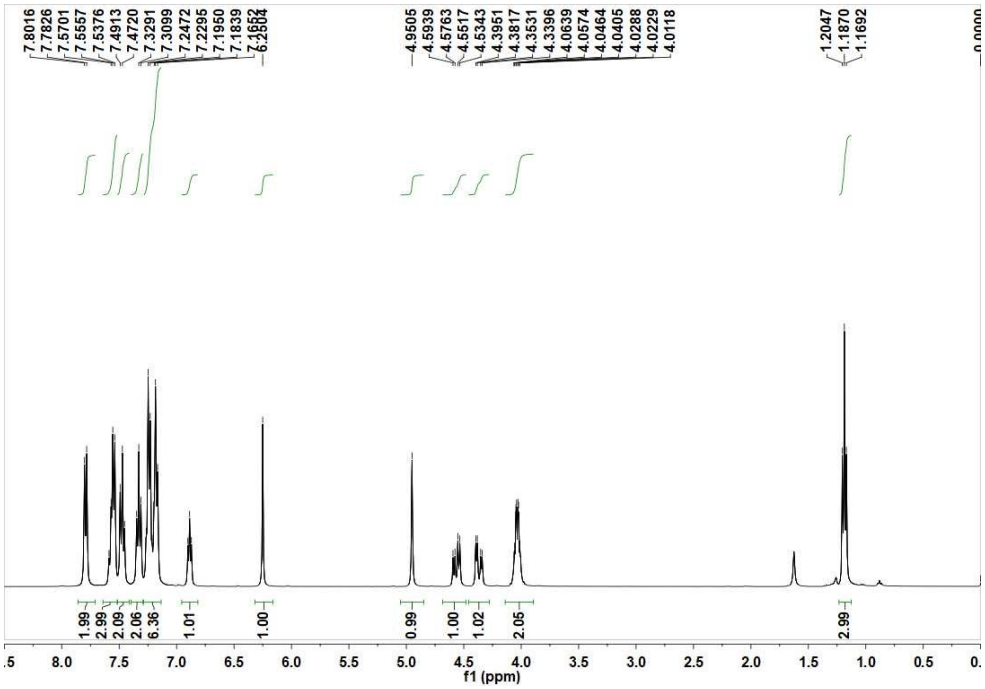
61.1301
46.8527
41.7531
30.0638
21.7040
21.2082
14.1644
13.7782
f1 (ppm)


Ph
CO2Et
Ph
O
N
O=S=O
Ph

3t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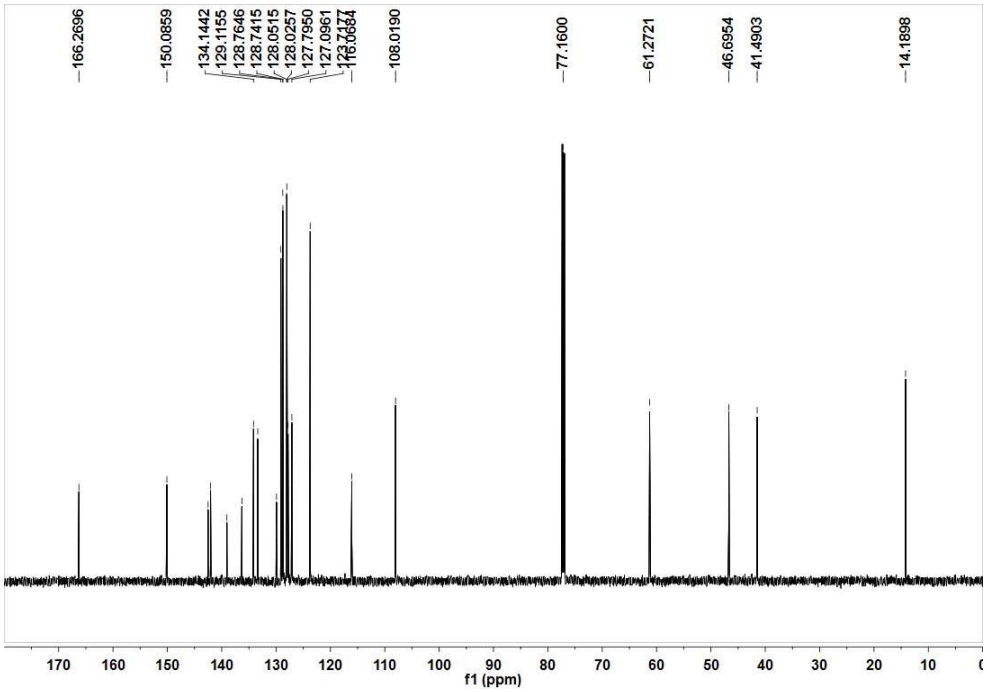
7.2295
7.1950
7.1839
4.9505
4.5939
4.5763
4.5517
4.5343
4.3951
4.3817
4.3531
4.3396
4.0639
4.0574
4.0464
4.0405
4.0288
4.0229
4.0118
1.2047
1.1870
1.1692
1.99
2.99
2.09
2.06
6.36
1.01
1.00
0.99
1.00
1.02
2.05
2.99
f1 (ppm)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127.0961
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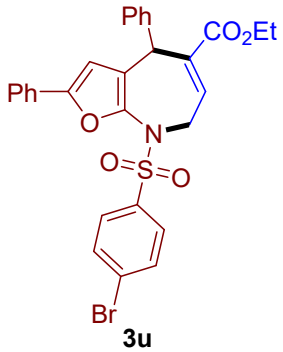
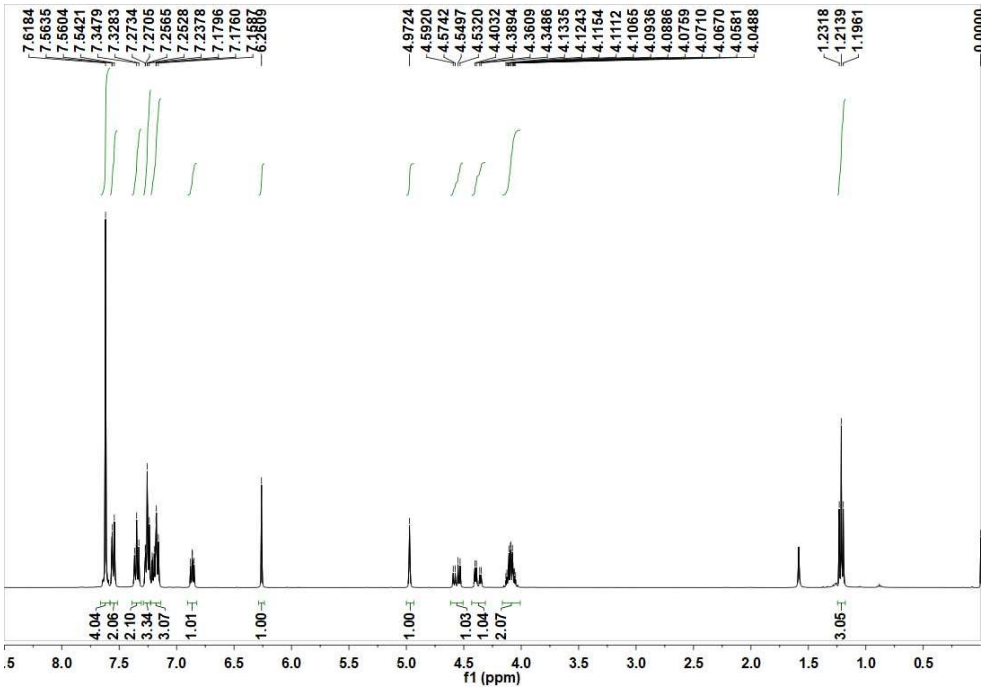
77.1600
61.2721
46.6954
41.4903
14.1898
f1 (ppm)


Ph
CO2Et
Ph
O
N
O=S=O
Br

3u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7.2378
7.1796
7.1760
4.9724
4.5920
4.5742
4.5497
4.5320
4.4032
4.3894
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4.1112
4.1065
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4.0886
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4.0710
4.0670
4.0581
4.0488
1.2318
1.2139
1.1961
4.04
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2.10
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3.07
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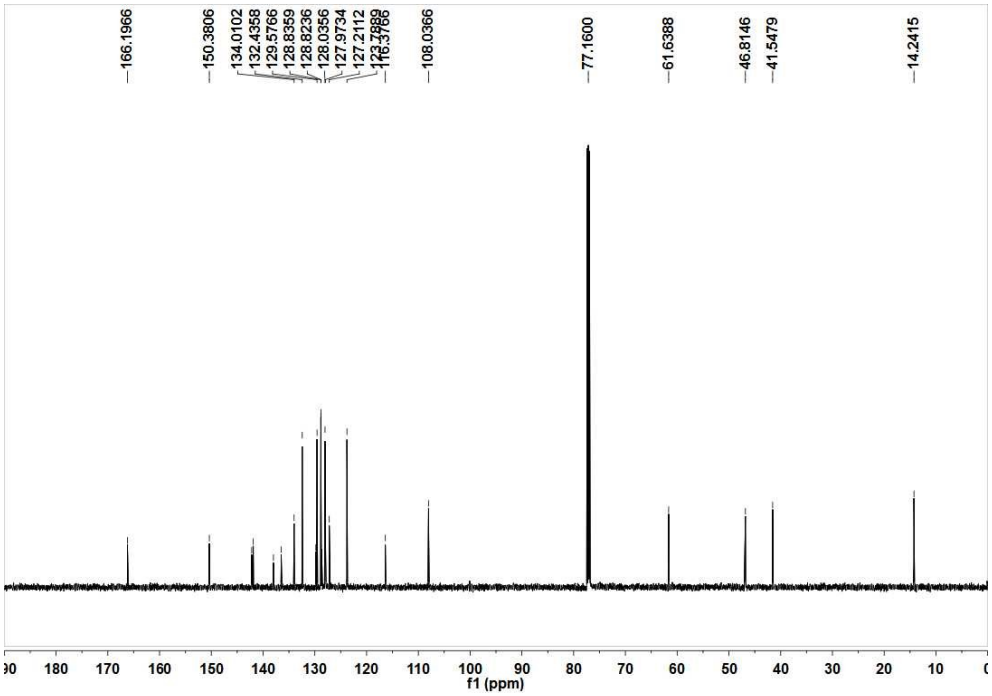
1.00
1.00
1.03
1.04
2.07
3.05
f1 (ppm)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128.8236
128.0356
127.9734
127.2112
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77.1600
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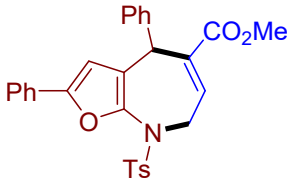
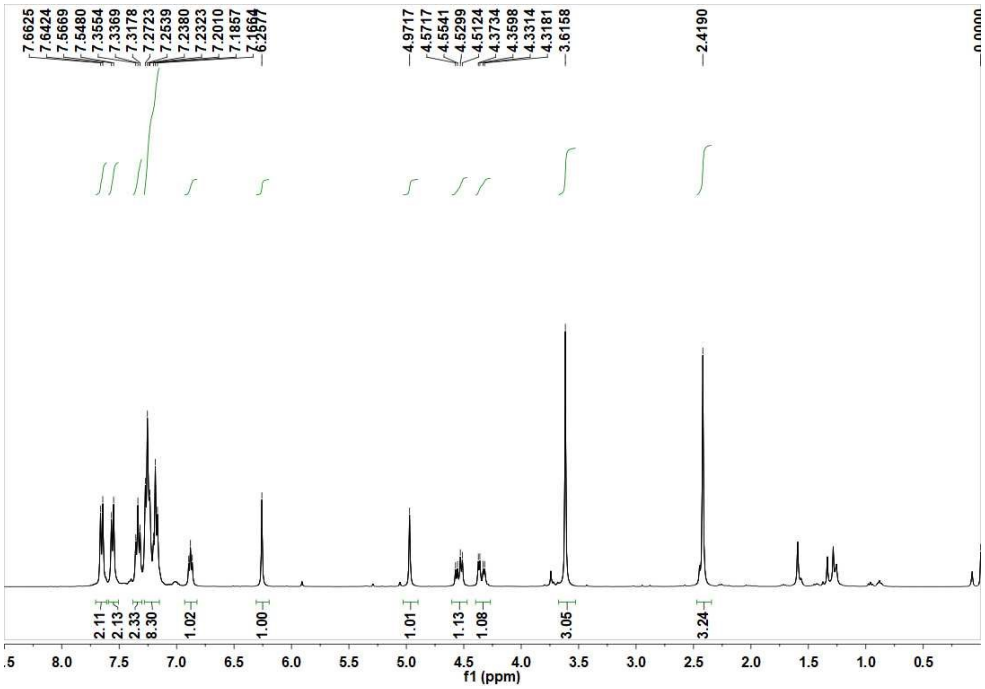
46.8146
41.5479
14.2415
f1 (ppm)


Ph
CO2Me
Ph
O
N
Ts

3v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4.3598
4.3314
4.3181
3.6158
2.4190
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2.13
2.33
8.30
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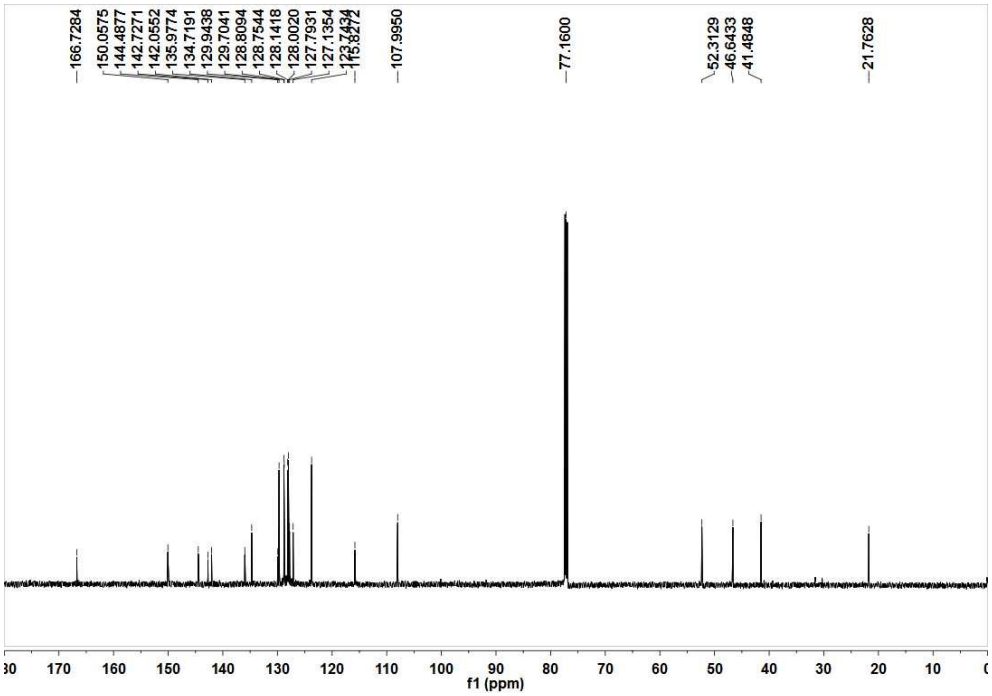
1.00
1.01
1.13
1.08
3.05
3.24
f1 (ppm)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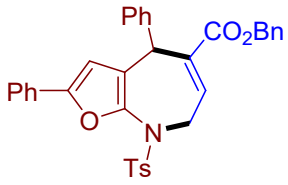
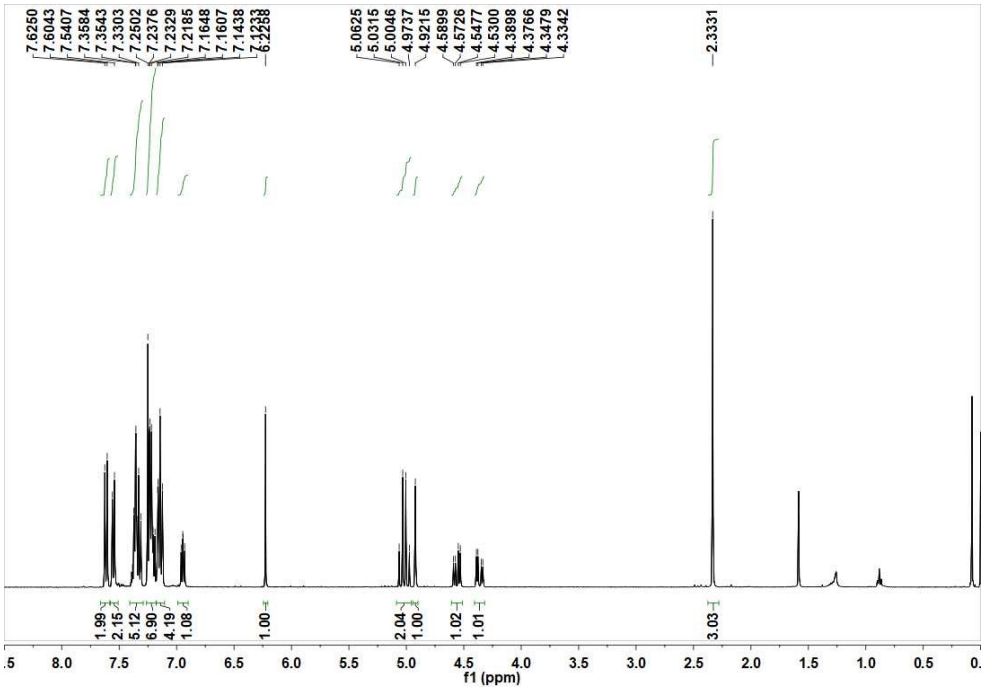
128.7544
128.1418
128.0020
127.7931
127.1354
107.9950
77.1600
52.3129
46.6433
41.4848
21.7628
f1 (ppm)


Ph
CO2Bn
Ph
O
N
Ts

3w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7.1607
7.1438
5.0625
5.0315
5.0046
4.9737
4.9215
4.5899
4.5726
4.5477
4.5300
4.3898
4.3766
4.3479
4.3342
2.3331
1.99
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5.12
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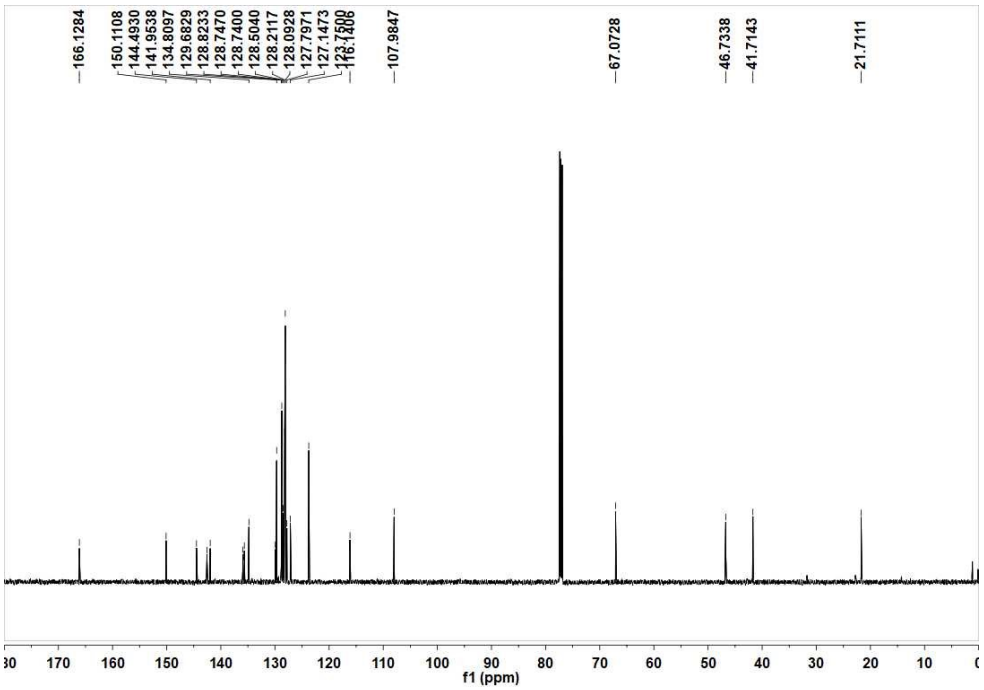
1.08
1.00
2.04
1.00
1.02
1.01
3.03
f1 (ppm)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128.5040
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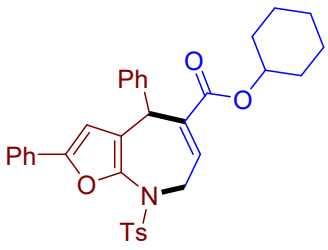
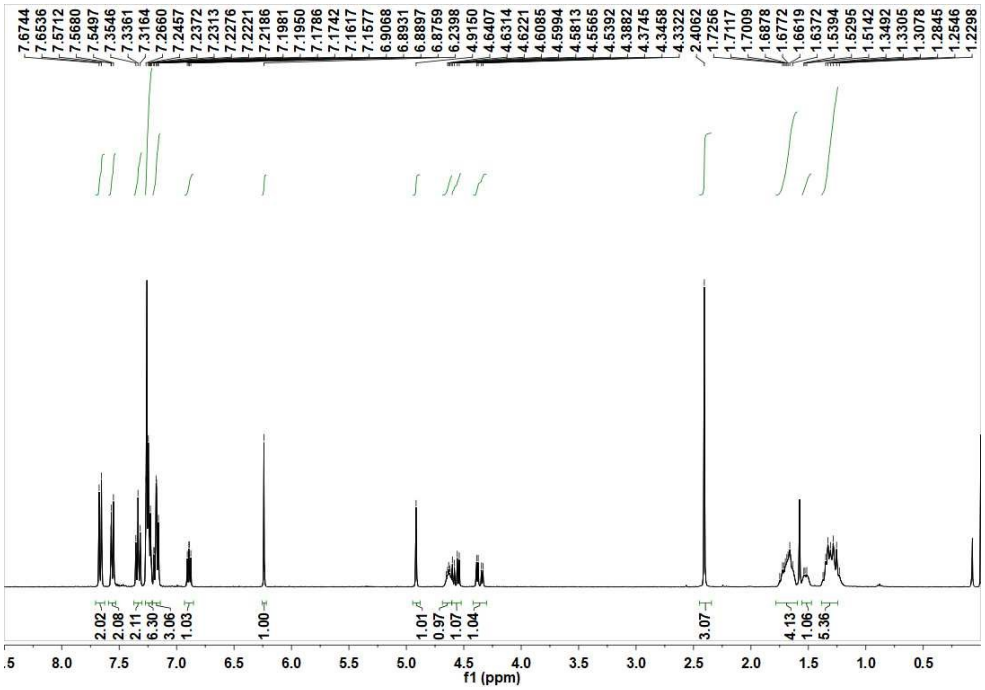
127.1473
107.9847
67.0728
46.7338
41.7143
21.7111
f1 (ppm)


Ph
O
O
Ph
O
N
Ts

3x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7.2372
7.2313
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7.2221
7.2186
7.1981
7.1950
7.1786
7.1742
7.1617
7.1577
6.9068
6.8931
6.8897
6.8759
6.2398
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4.6407
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4.6221
4.6085
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4.5392
4.3882
4.3745
4.3458
4.3322
2.4062
1.7256
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1.7009
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1.5295
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1.3492
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1.3078
1.2845
1.2546
1.2298
2.02
2.08
2.11
6.30
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1.01
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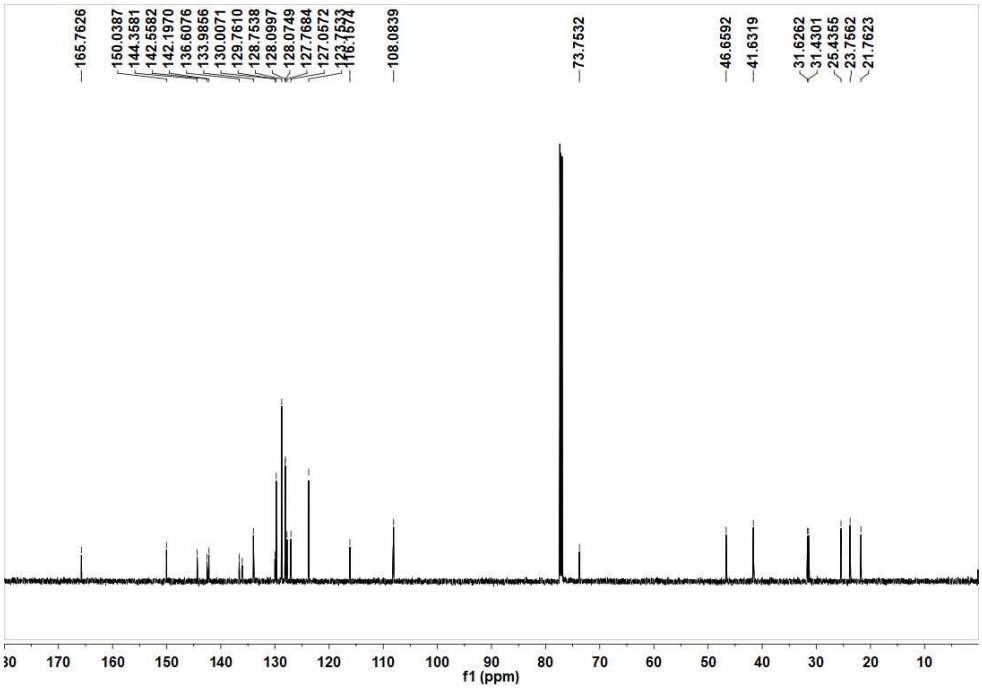
1.07
1.04
3.07
4.13
1.06
5.36
f1 (ppm)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133.9856
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128.0749
127.7684
127.0572
108.0839
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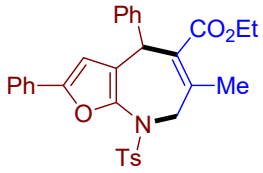
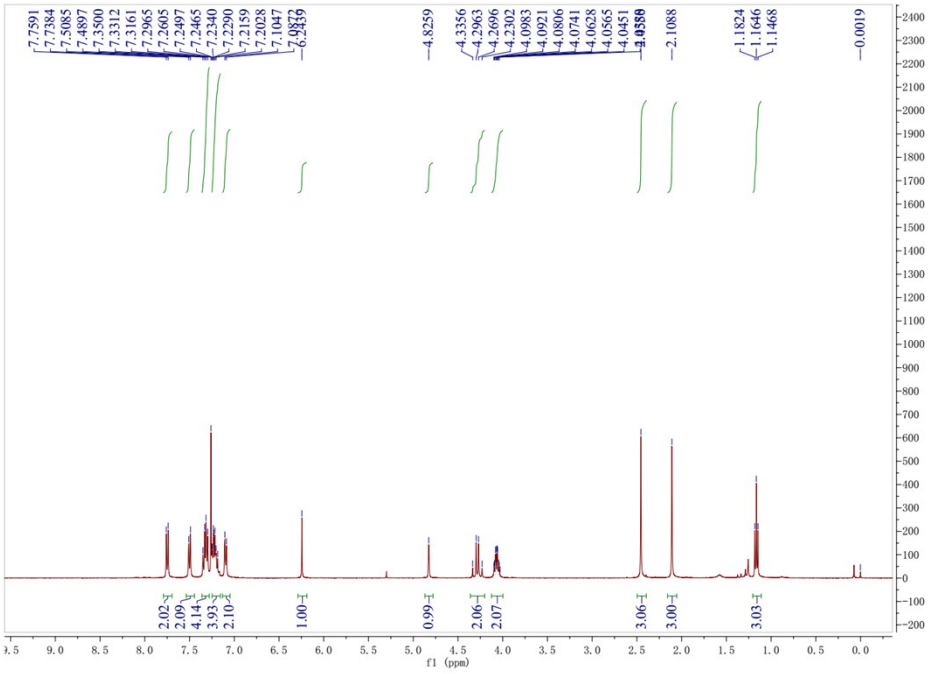
46.6592
41.6319
31.6262
31.4301
25.4355
23.7562
21.7623
f1 (ppm)


Ph
CO2Et
Ph
Me
O
N
Ts

3y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7.2340
7.2290
7.2159
7.2028
7.1047
4.8259
4.3356
4.2963
4.2696
4.2302
4.0983
4.0921
4.0806
4.0741
4.0628
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2.1088
1.1824
1.1646
1.1468
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2.02
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4.14
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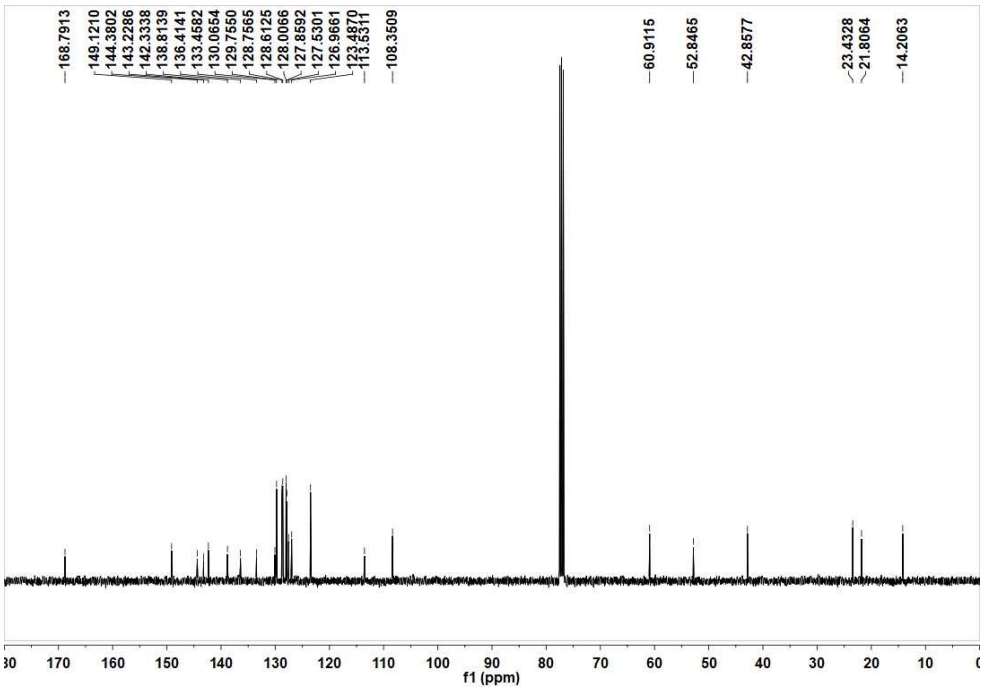
2.10
1.00
0.99
2.06
2.07
3.06
3.00
3.03
f1 (ppm)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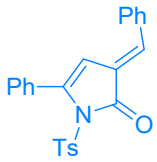
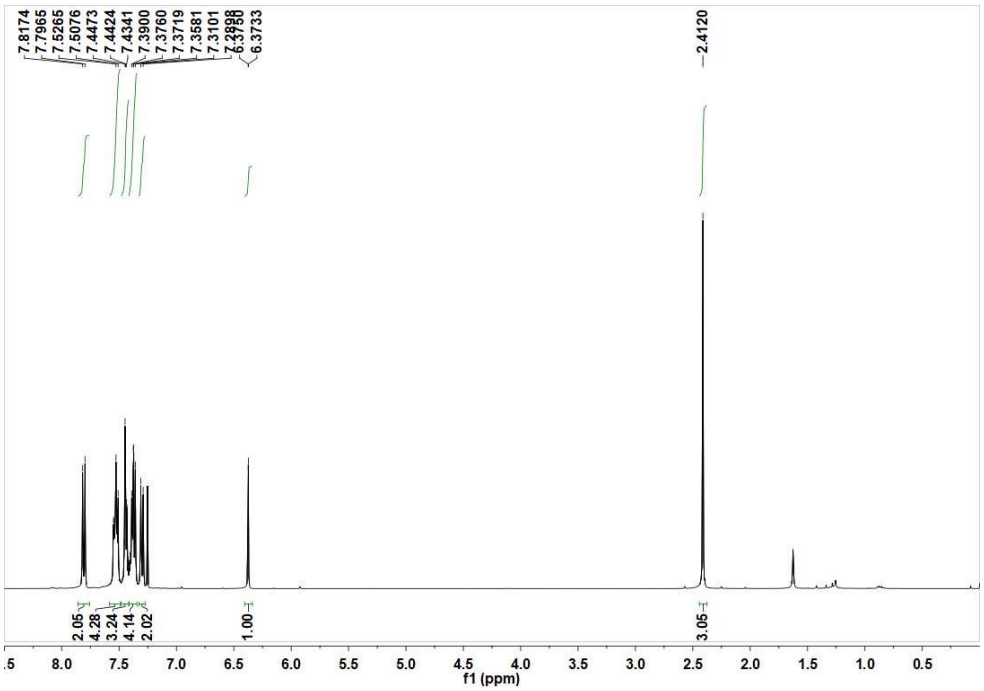
128.6125
128.0066
127.8592
127.5301
126.9661
123.4870
113.5311
108.3509
60.9115
52.8465
42.8577
23.4328
21.8064
14.2063
f1 (ppm)


Ph
Ph
N
O
Ts

4a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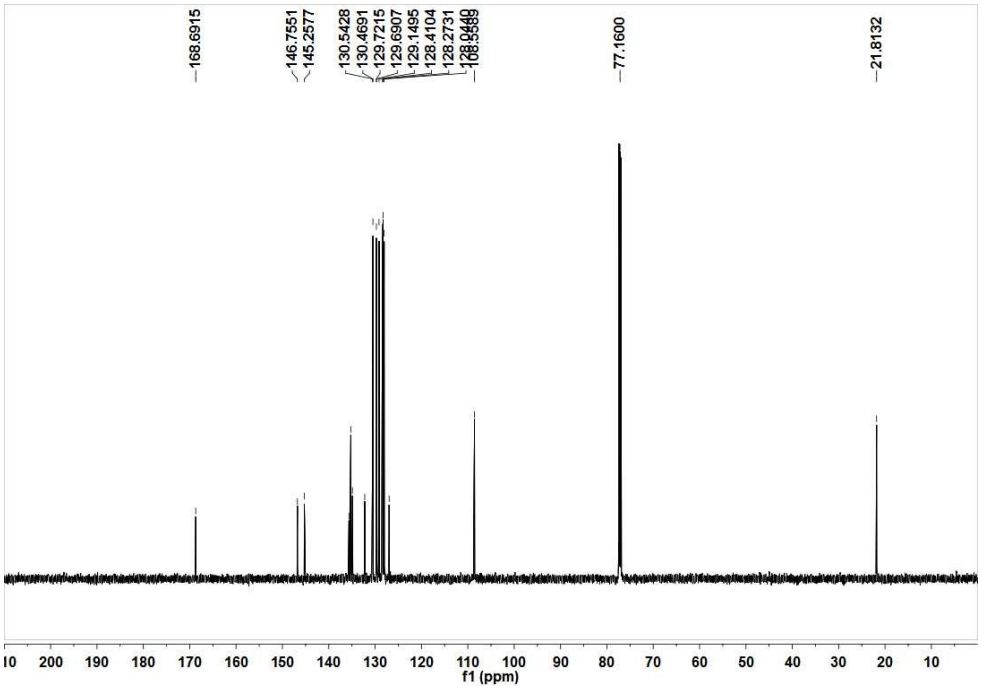
7.5265
7.5076
7.4473
7.4424
7.4341
7.3900
7.3760
7.3719
7.3581
7.3101
6.3733
2.4120
2.05
4.28
3.24
4.14
2.02
1.00
3.06
f1 (ppm)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145.2577
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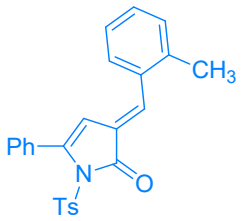
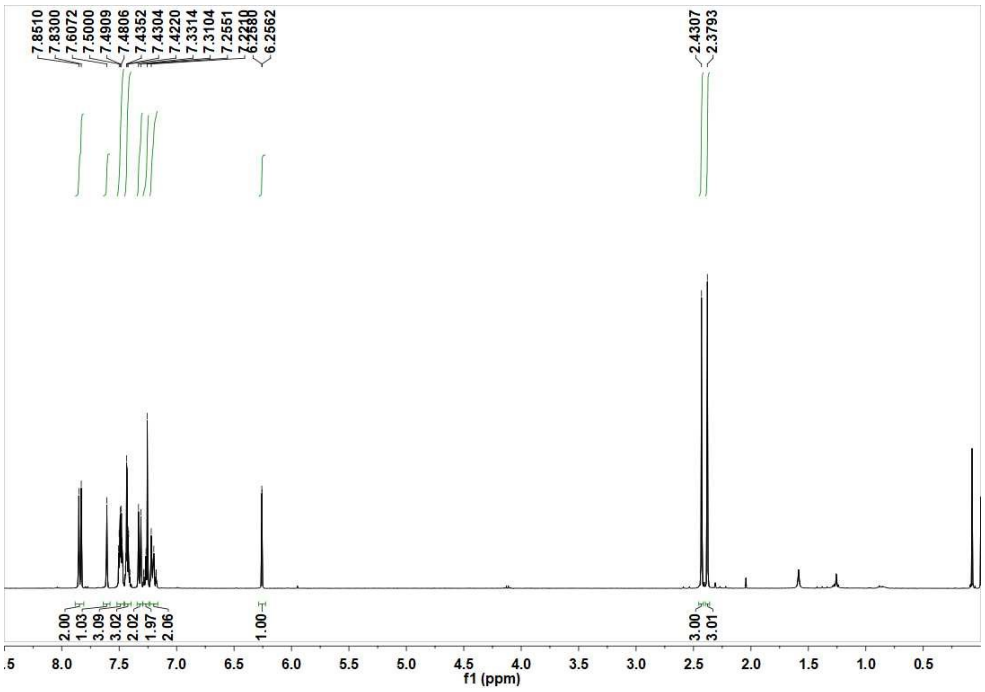
129.7215
129.6907
129.1495
128.4104
128.2731
77.1600
21.8132
f1 (ppm)


CH3
Ph
N
O
Ts

4b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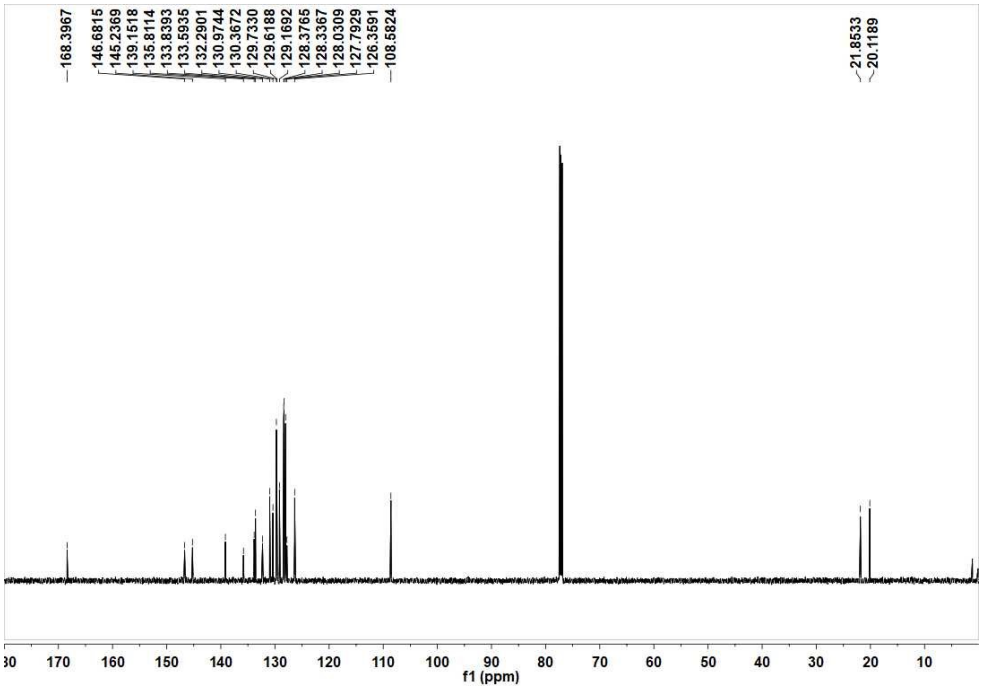
7.6072
7.5000
7.4909
7.4806
7.4352
7.4304
7.4220
7.3314
7.3104
7.2551
6.2562
2.4307
2.3793
2.00
1.03
3.09
3.02
2.02
1.97
2.06
1.00
3.00
3.01
f1 (ppm)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135.8114
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133.5935
132.2901
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129.7330
129.6188
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128.0309
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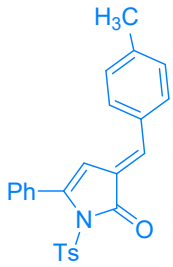
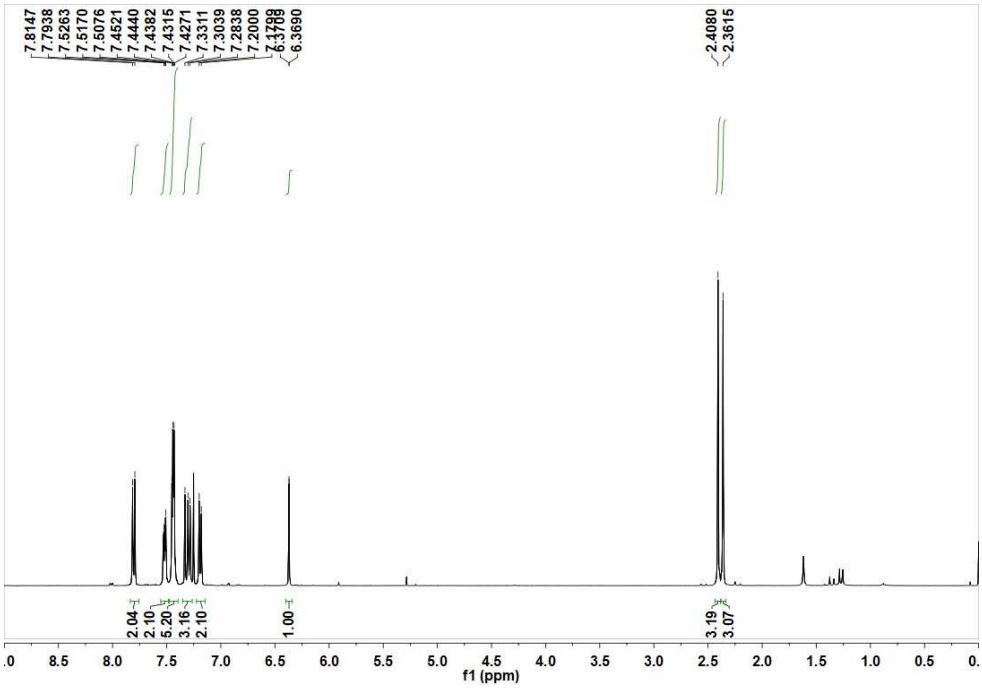
126.3591
108.5824
21.8533
20.1189
f1 (ppm)


H3C
Ph
N
O
Ts

4c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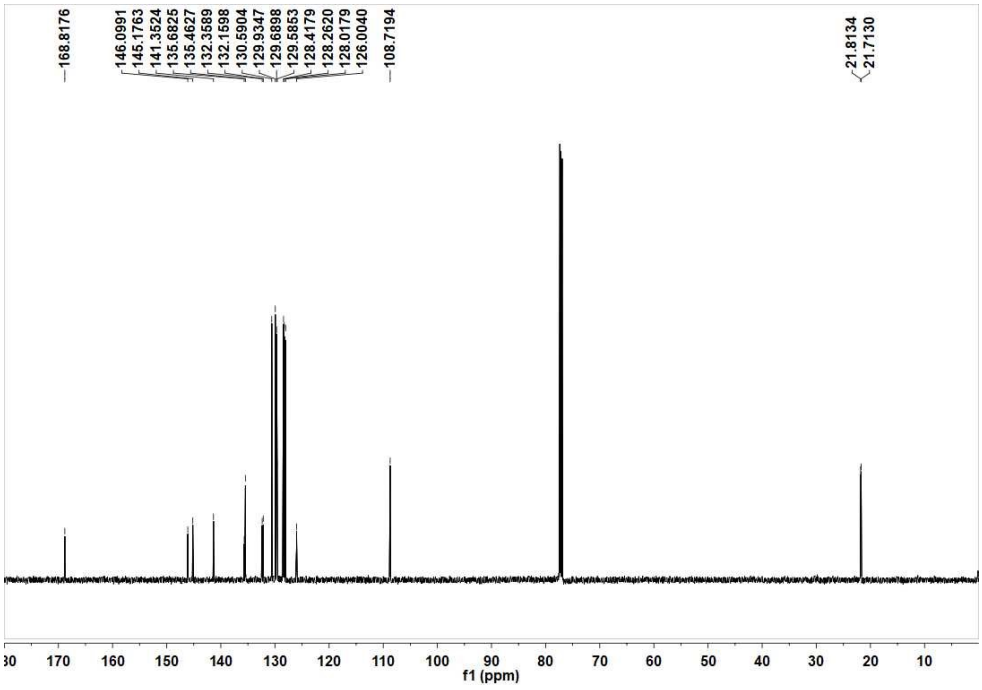
7.5263
7.5170
7.5076
7.4521
7.4440
7.4382
7.4315
7.4271
7.3311
7.3039
7.2838
7.2000
6.3690
2.4080
2.3615
2.04
2.10
5.20
3.16
2.10
1.00
3.19
3.07
f1 (ppm)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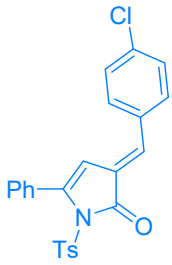
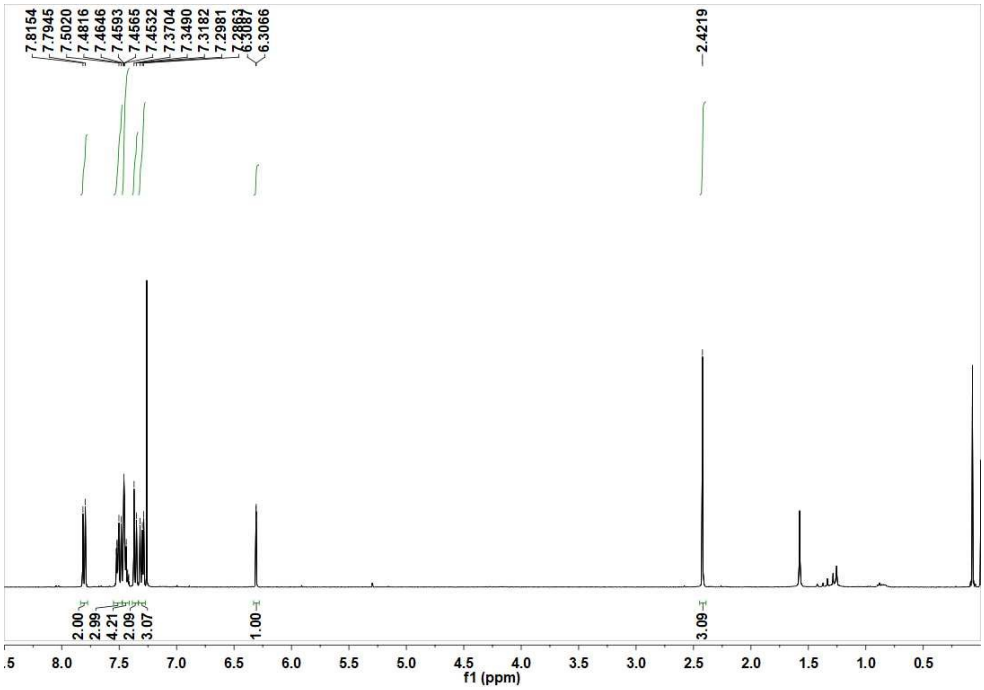
141.3524
135.6825
135.4627
132.3589
132.1598
130.5904
129.9347
129.6898
129.5853
128.4179
128.2620
128.0179
126.0040
108.7194
21.8134
21.7130
f1 (ppm)


Cl
Ph
N
O
Ts

4d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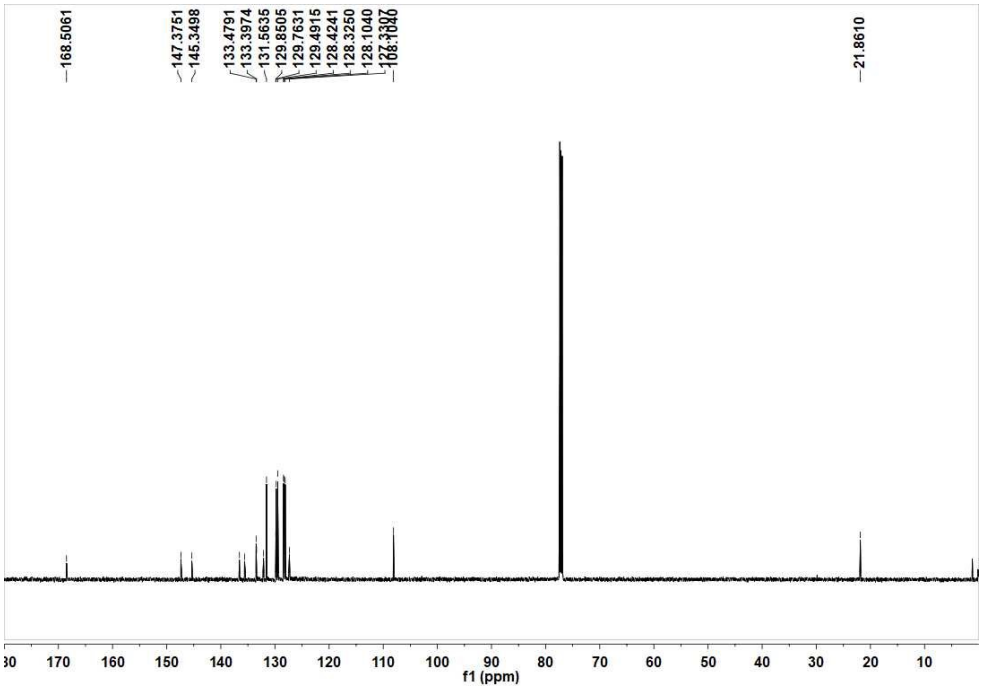
7.5020
7.4816
7.4646
7.4593
7.4565
7.4532
7.3704
7.3490
7.3182
7.2981
6.3087
6.3066
2.4219
2.00
2.99
4.21
2.09
3.07
1.00
3.09
f1 (ppm)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145.3498
133.4791
133.3974
131.5635
129.8505
129.7631
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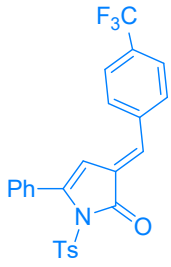
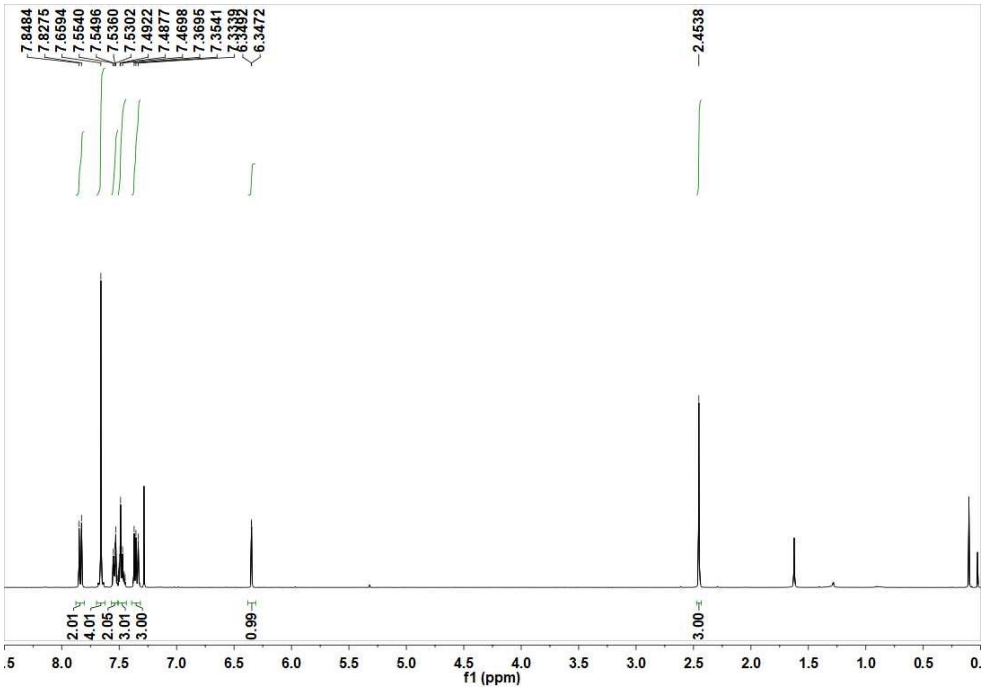
128.4241
128.3250
128.1040
21.8610
f1 (ppm)


F3C
Ph
N
O
Ts

4e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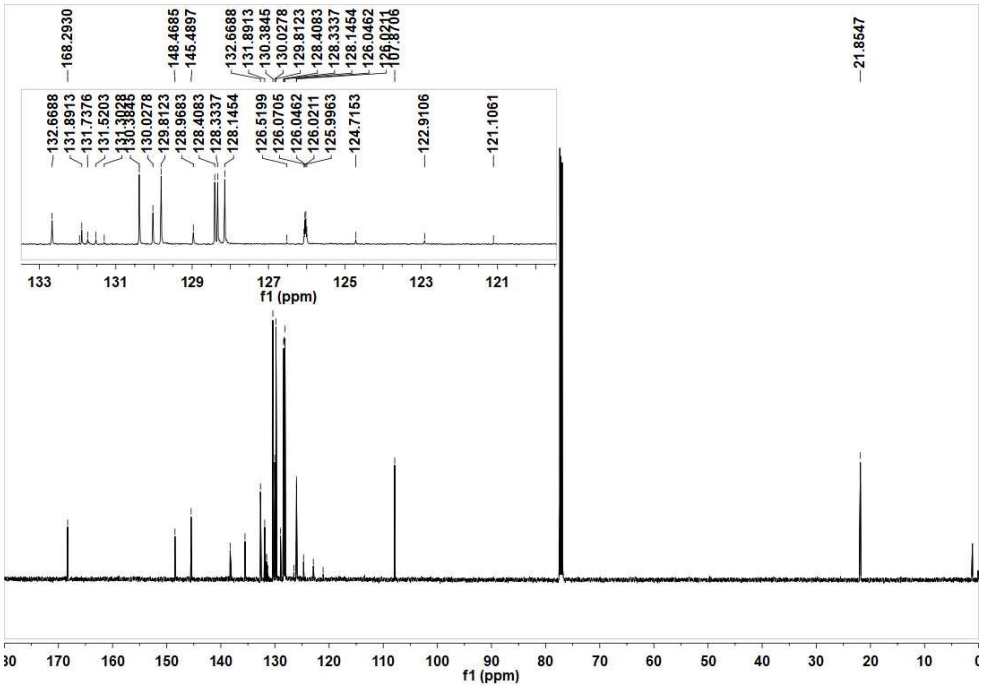
7.6594
7.5540
7.5496
7.5360
7.5302
7.4922
7.4877
7.4698
7.3695
7.3641
6.3492
6.3472
2.4538
2.01
4.01
2.05
3.01
3.00
0.99
3.00
f1 (ppm)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145.4897
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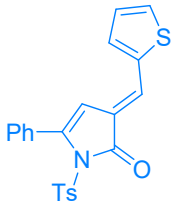
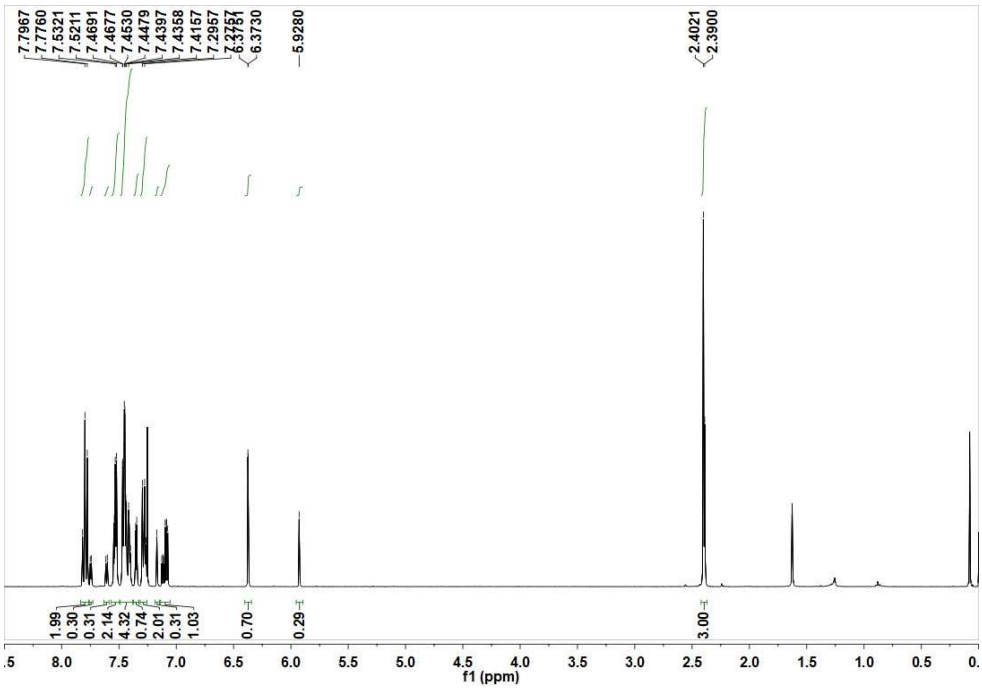
131.8913
130.3845
130.0278
129.8123
128.4083
128.3337
128.1454
126.0462
126.0211
107.8706
21.8547
132.6688
131.8913
131.7376
131.5203
130.0278
129.8123
128.9683
128.4083
128.3337
128.1454
126.5199
126.0705
126.0462
126.0211
125.9963
124.7153
122.9106
121.1061
f1 (ppm)
f1 (ppm)


S
Ph
N
O
Ts

4f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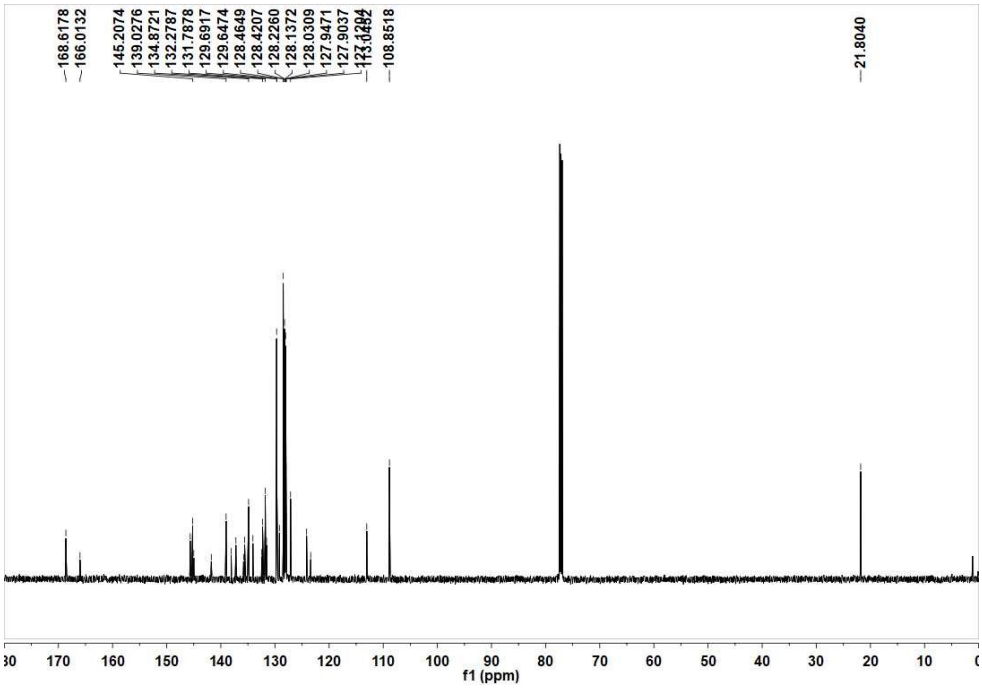
7.4397
7.4358
7.4157
7.2957
6.3730
5.9280
2.4021
2.3900
1.99
0.30
0.31
2.14
4.32
0.74
2.01
0.31
1.03
0.70
0.29
3.00
f1 (ppm)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132.2787
131.7878
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129.6474
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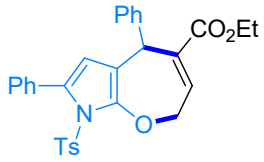
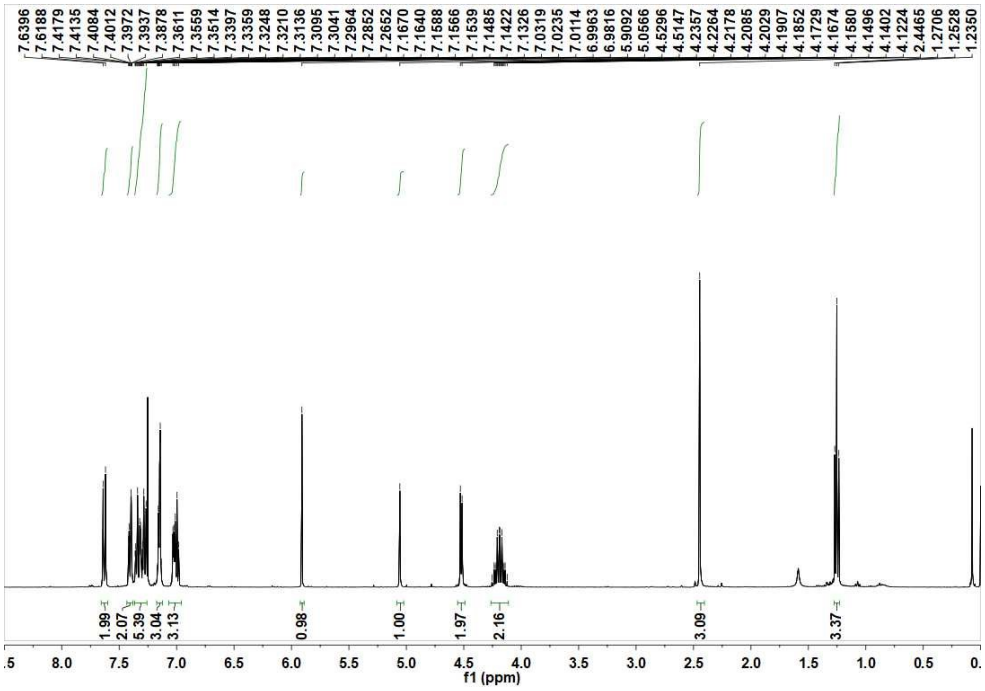
127.9037
108.8518
21.8040
f1 (ppm)


Ph
CO2Et
Ph
N
O
Ts

5a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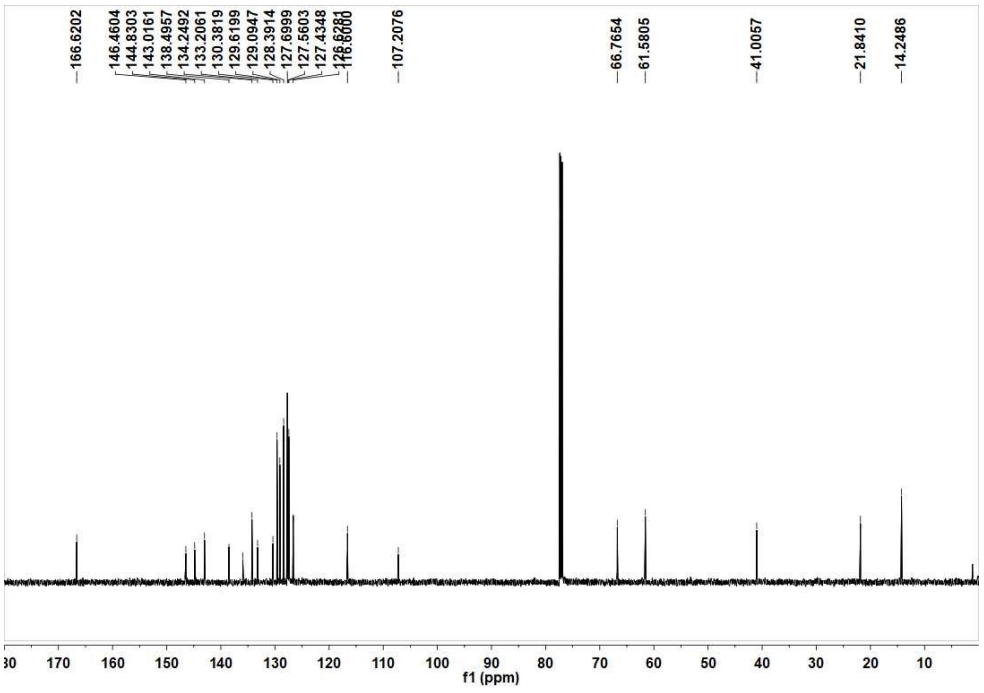
7.3611
7.3559
7.3514
7.3397
7.3359
7.3248
7.3210
7.3136
7.3095
7.3041
7.2964
7.2852
7.2652
7.1670
7.1640
7.1588
7.1566
7.1539
7.1485
7.1422
7.1326
7.0319
7.0235
7.0114
6.9963
6.9816
5.9092
5.0566
4.5296
4.5147
4.2357
4.2264
4.2178
4.2085
4.2029
4.1907
4.1852
4.1729
4.1674
4.1580
4.1496
4.1402
4.1224
2.4465
1.2706
1.2528
1.2350
1.99
2.07
5.39
3.04
3.13
0.98
1.00
1.97
2.16
3.09
3.37
f1 (ppm)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128.3914
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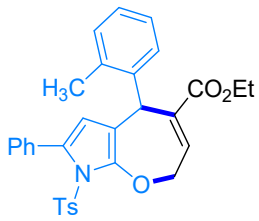
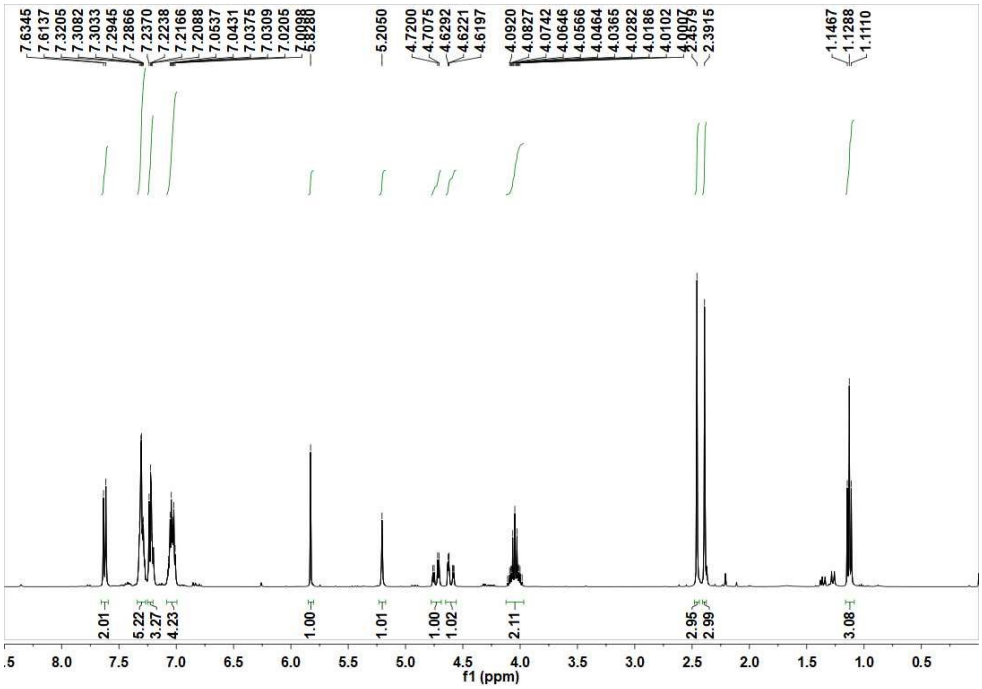
61.5805
41.0057
21.8410
14.2486
f1 (ppm)


H3C
CO2Et
Ph
N
O
Ts

5b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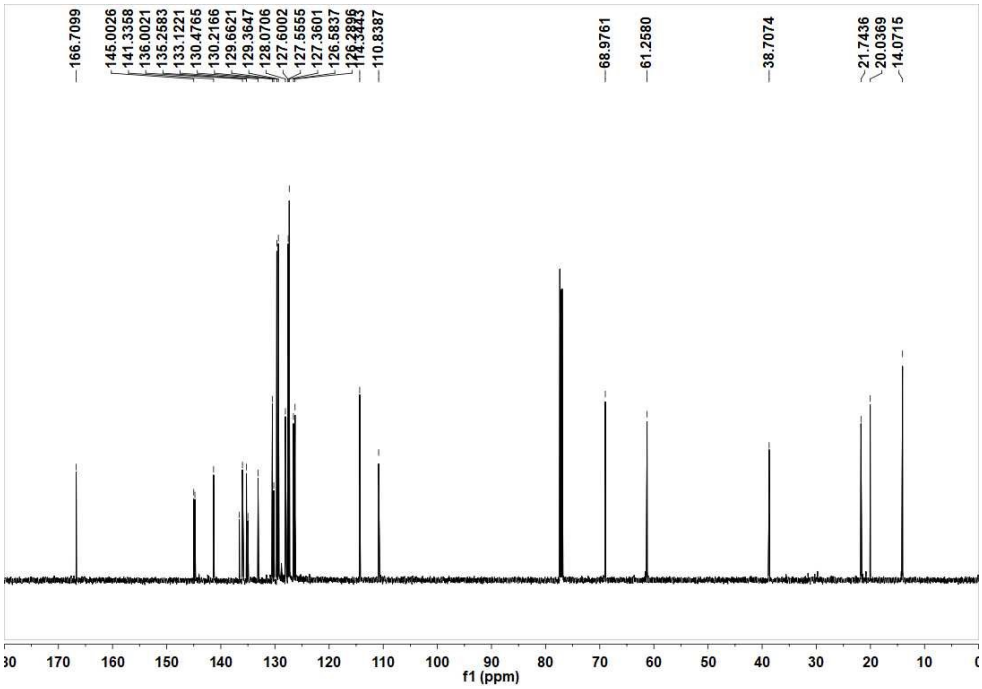
7.3033
7.2945
7.2866
7.2370
7.2238
7.2166
7.2088
7.0637
7.0431
7.0375
7.0309
7.0205
5.2050
4.7200
4.7075
4.6292
4.6221
4.6197
4.0920
4.0827
4.0742
4.0646
4.0566
4.0464
4.0365
4.0282
4.0186
4.0102
2.3915
1.1467
1.1288
1.1110
2.01
5.22
3.27
4.23
1.00
1.01
1.00
1.02
2.11
2.95
2.99
3.08
f1 (ppm)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128.0706
127.6002
127.5555
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126.5837
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68.9761
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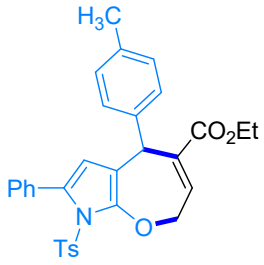
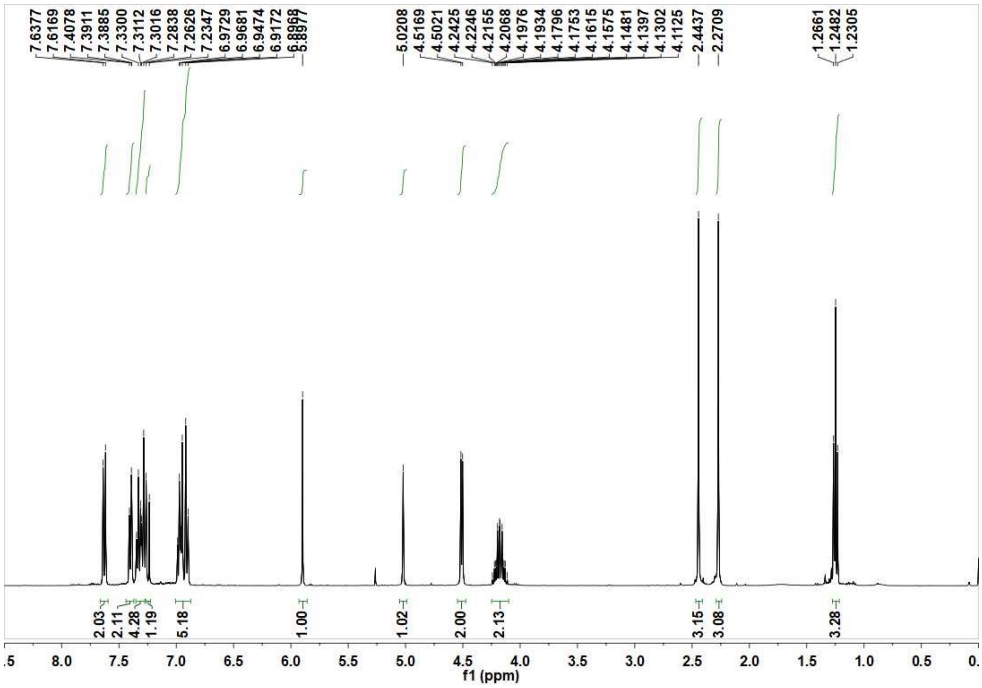
38.7074
21.7436
20.0369
14.0715
f1 (ppm)


H3C
CO2Et
Ph
N
O
Ts

5c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7.3112
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7.2838
7.2626
7.2347
6.9729
6.9681
6.9474
6.9172
6.8968
6.8977
5.0208
4.5169
4.5021
4.2425
4.2246
4.2155
4.2068
4.1976
4.1934
4.1796
4.1753
4.1615
4.1575
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4.1397
4.1302
4.1125
2.4437
2.2709
1.2661
1.2482
1.2305
2.03
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5.18
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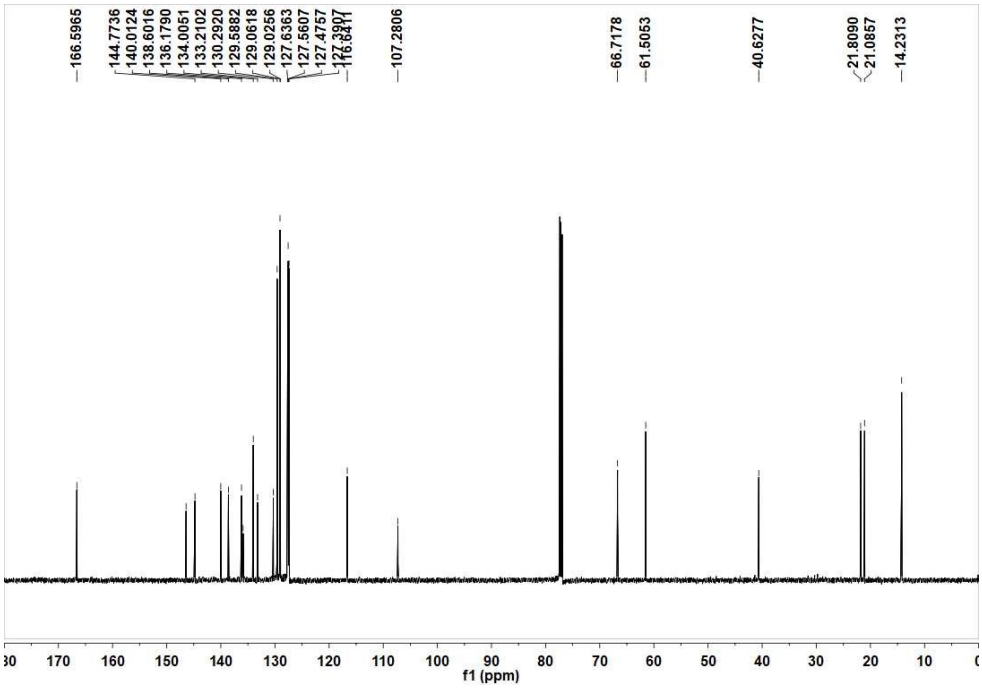
2.13
3.15
3.08
3.28
f1 (ppm)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127.6363
127.5607
127.4757
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61.5053
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21.8090
21.0857
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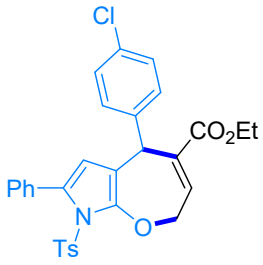
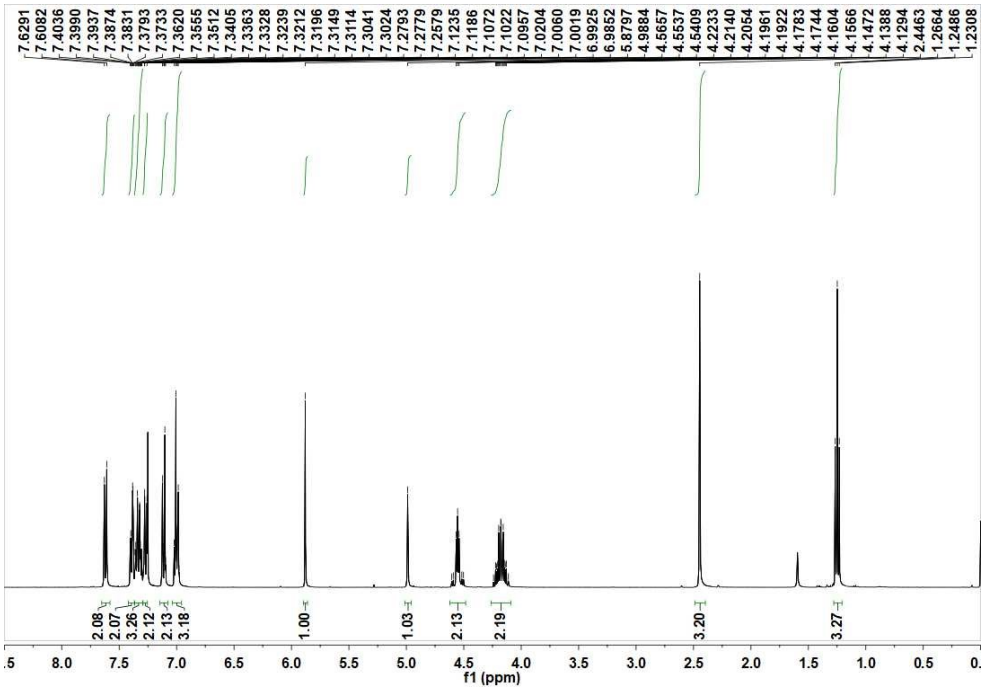
f1 (ppm)


Cl
CO2Et
Ph
N
O
Ts

5d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7.3831
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7.3733
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7.3512
7.3405
7.3363
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7.3212
7.3196
7.3149
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7.3041
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6.9852
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4.1922
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4.1472
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4.1294
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1.2664
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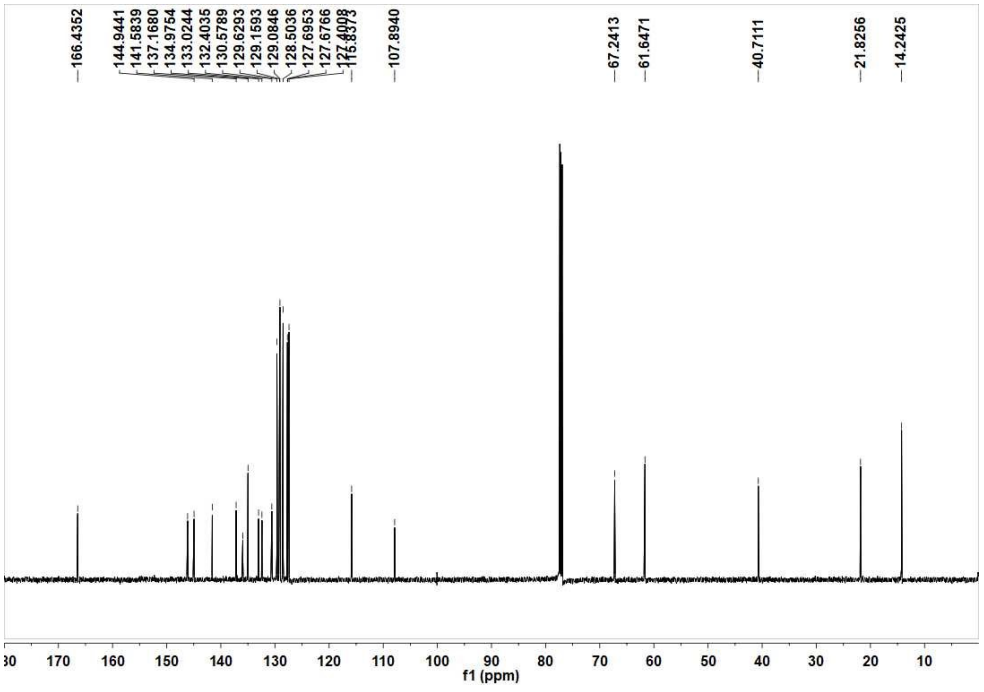
1.03
2.13
2.19
3.20
3.27
f1 (ppm)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128.5036
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107.8940
67.2413
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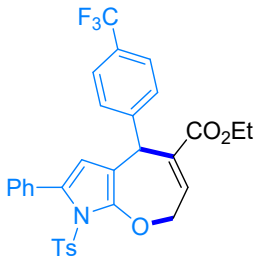
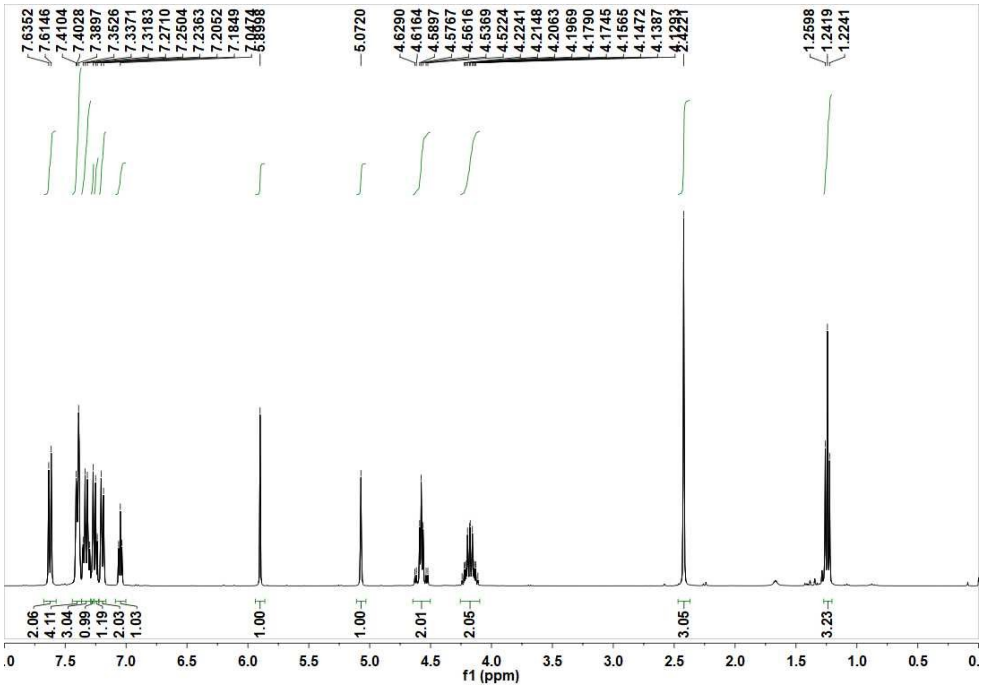
40.7111
21.8266
14.2425
f1 (ppm)


F3C
CO2Et
Ph
N
O
Ts

5e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7.2710
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7.2363
7.2052
7.1849
5.0720
4.6290
4.6164
4.5897
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4.5616
4.5369
4.5224
4.2241
4.2148
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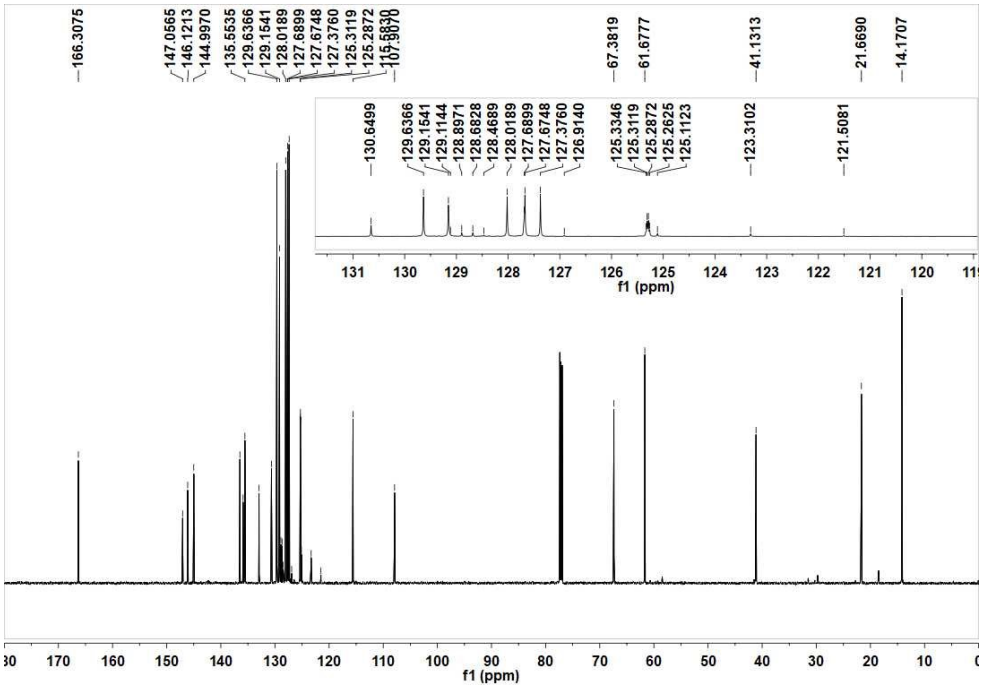
4.1565
4.1472
4.1387
1.2598
1.2419
1.2241
2.06
4.11
3.04
0.99
1.19
2.03
1.03
1.00
1.00
2.01
2.05
3.05
3.23
f1 (ppm)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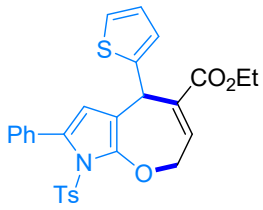
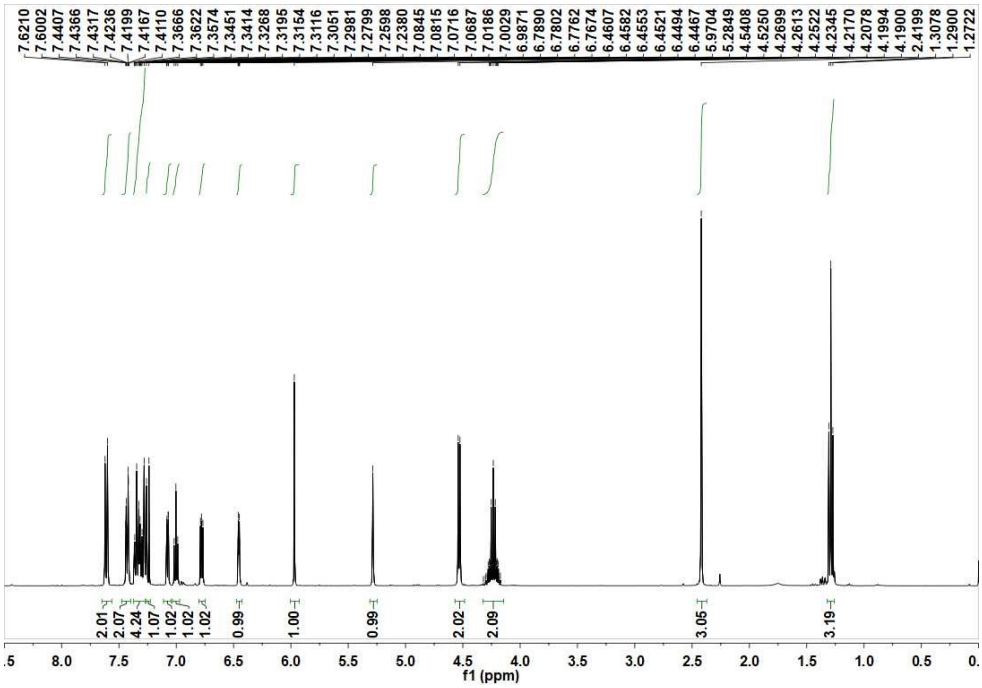
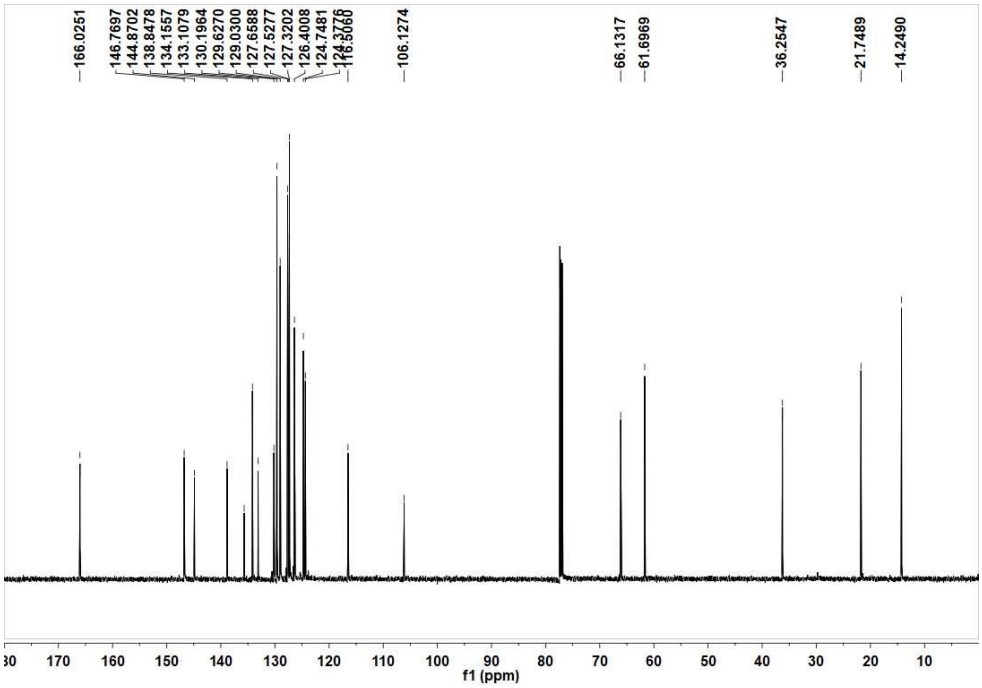
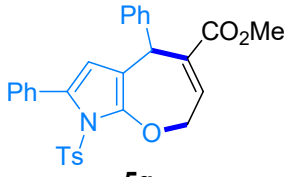
147.0565
146.1213
144.9970
135.5535
129.6366
129.1641
128.0189
127.6899
127.6748
127.3760
125.3119
125.2872
107.5070
67.3819
61.6777
41.1313
21.6690
14.1707
130.6499
129.6366
129.1641
129.1144
128.8971
128.6828
128.4689
128.0189
127.6899
127.6748
127.3760
126.9140
125.3346
125.3119
125.2872
125.2625
125.1123
123.3102
121.5081
f1 (ppm)


S
CO2Et
Ph
N
O
Ts

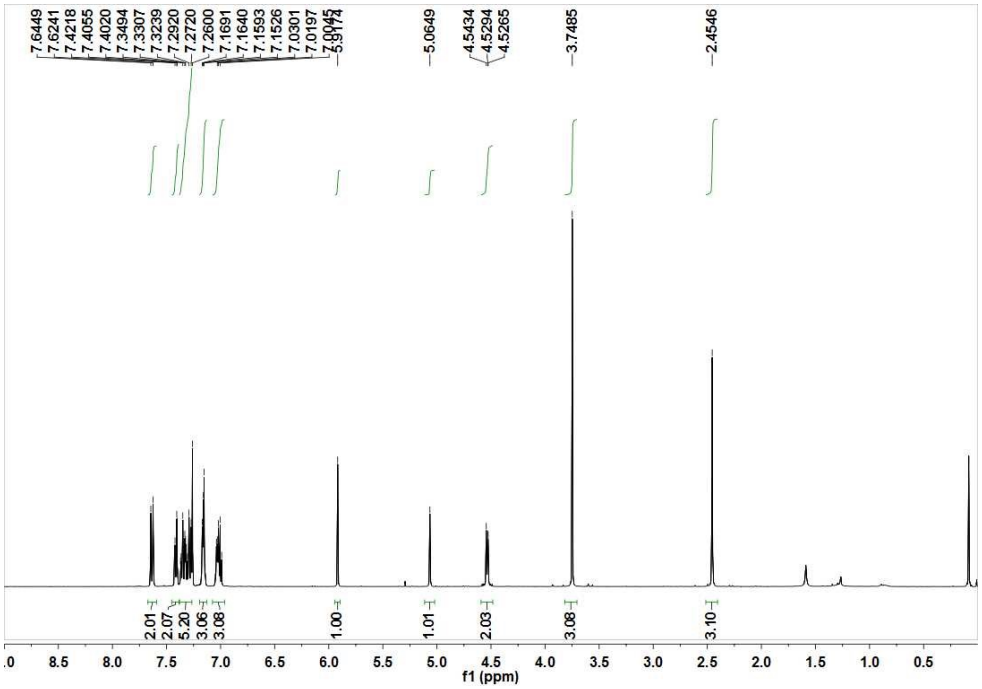
5f

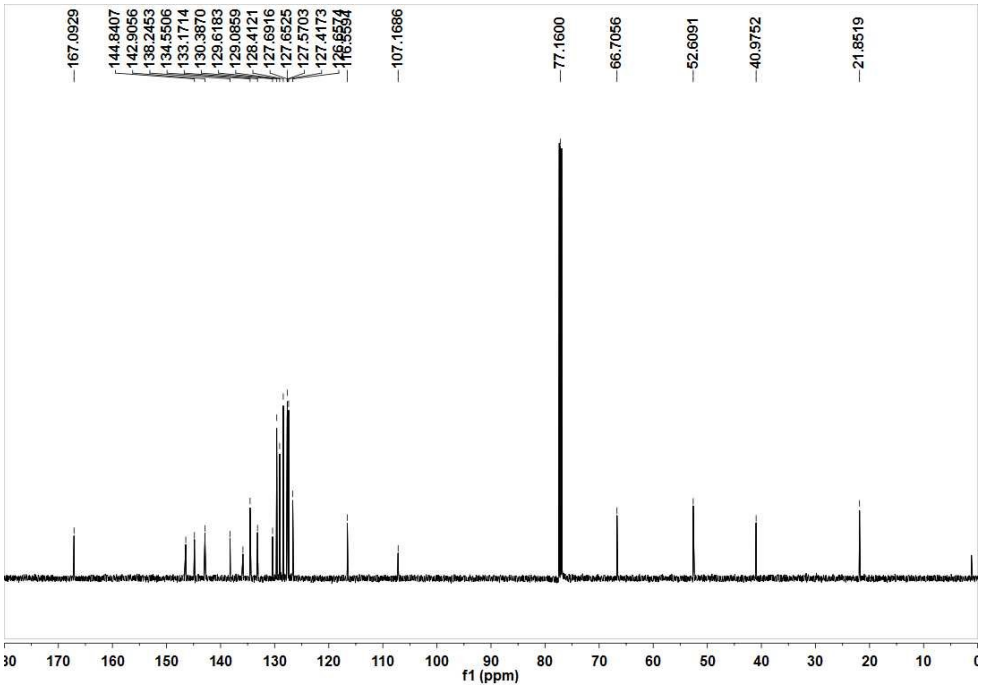

7.6210
7.6002
7.4407
7.4366
7.4317
7.4236
7.4199
7.4167
7.4110
7.3666
7.3622
7.3574
7.3451
7.3414
7.3268
7.3195
7.3154
7.3116
7.3051
7.2981
7.2799
7.2598
7.2380
7.0845
7.0815
7.0716
7.0687
7.0186
7.0029
6.9871
6.7890
6.7802
6.7762
6.7674
6.4607
6.4582
6.4553
6.4521
6.4494
6.4467
5.9704
5.2849
5.1408
4.5250
4.2699
4.2613
4.2522
4.2345
4.2170
4.2078
4.1994
4.1900
2.4199
1.3078
1.2900
1.2722
2.01
2.07
4.24
1.07
1.02
1.02
1.02
0.99
1.00
0.99
2.02
2.09
3.05
3.19
f1 (ppm)

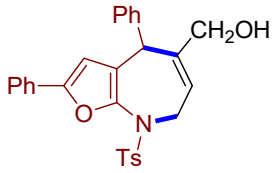

166.0251
146.7697
144.8702
138.8478
134.1557
133.1079
130.1964
129.6270
129.0300
127.6588
127.5277
127.3202
126.4008
124.7481
124.3776
116.8060
106.1274
66.1317
61.6969
36.2547
21.7489
14.2490
f1 (ppm)


Ph
CO2Me
Ph
N
O
Ts

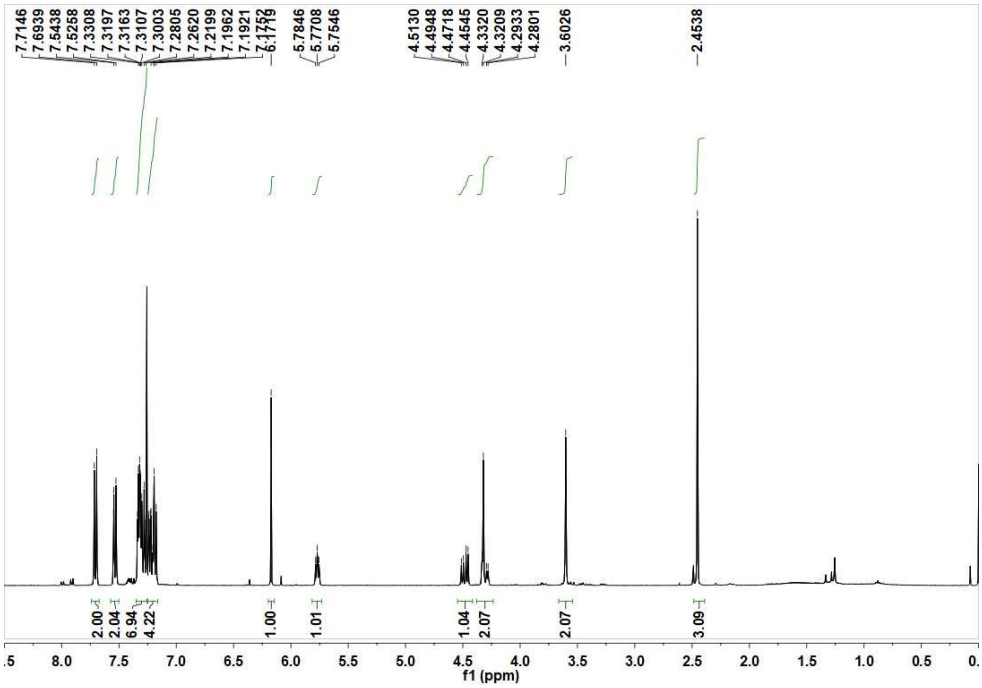
5g

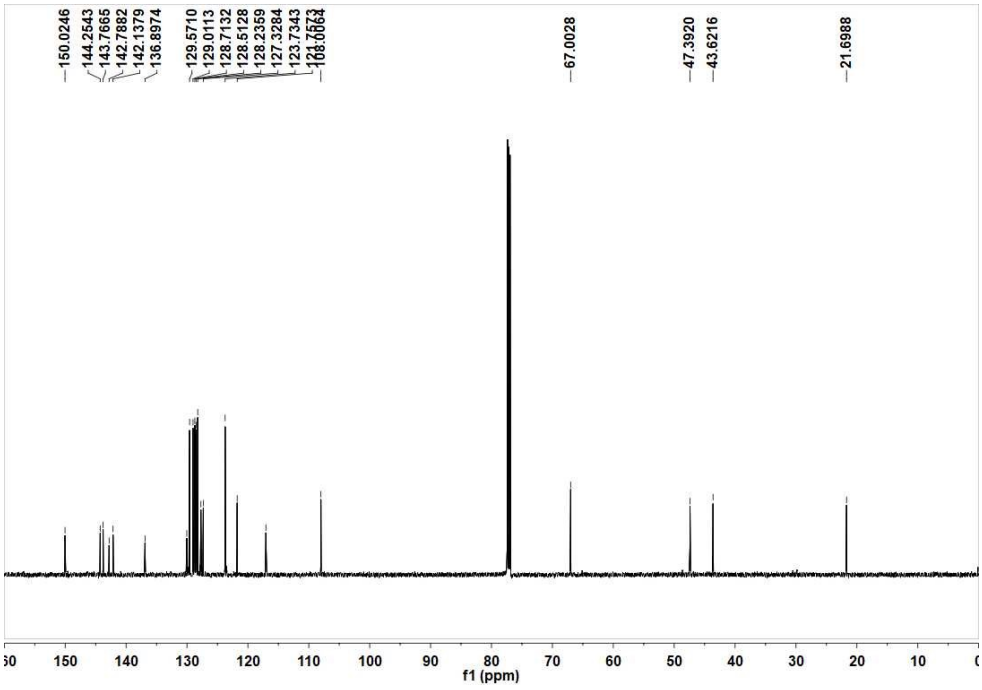

7.6449
7.6241
7.4218
7.4055
7.4020
7.3494
7.3307
7.3239
7.2920
7.2720
7.2600
7.1691
7.1640
7.1593
7.1526
7.0301
7.0197
5.0649
4.5434
4.5294
4.5265
3.7485
2.4546
2.01
2.07
5.20
3.06
3.08
1.00
1.01
2.03
3.08
3.10
f1 (ppm)


167.0929
144.8407
142.9056
138.2453
134.5506
133.1714
130.3870
129.6183
129.0859
128.4121
127.6916
127.6525
127.5703
127.4173
107.1686
77.1600
66.7056
52.6091
40.9752
21.8519
f1 (ppm)


Ph
CH2OH
Ph
O
N
Ts

7


7.7146
7.6939
7.5438
7.5258
7.3308
7.3197
7.3163
7.3107
7.3003
7.2805
7.2620
7.2199
7.1962
7.1921
5.7846
5.7708
5.7546
4.5130
4.4948
4.4718
4.4545
4.3320
4.3209
4.2933
4.2801
3.6026
2.4538
2.00
2.04
6.94
4.22
1.00
1.01
1.04
2.07
2.07
3.09
f1 (ppm)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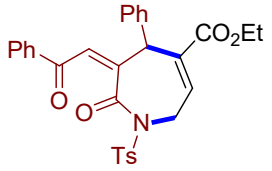
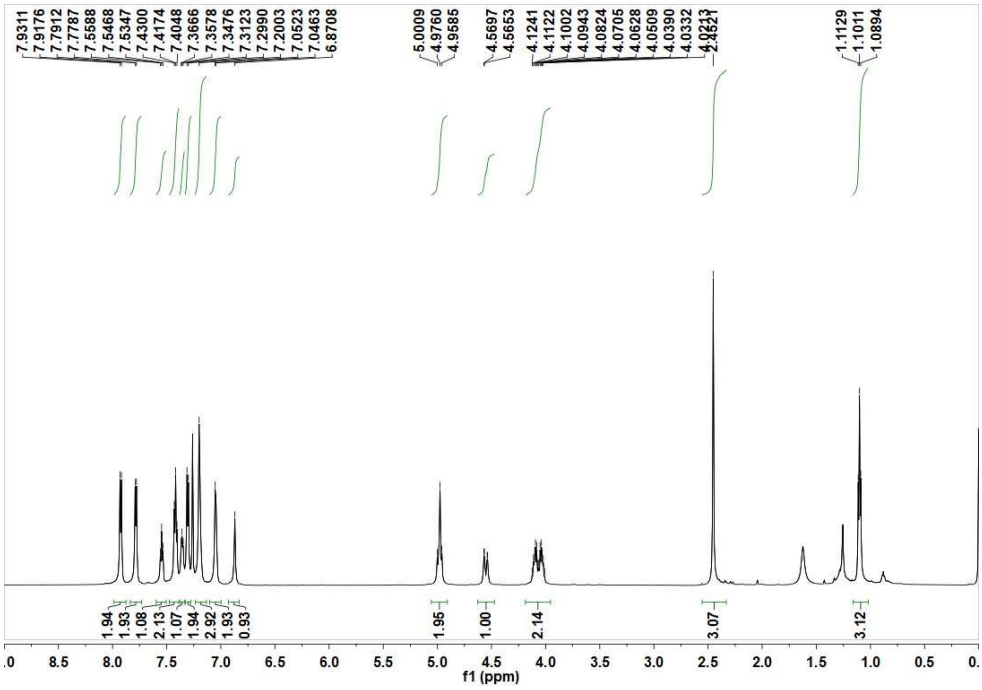
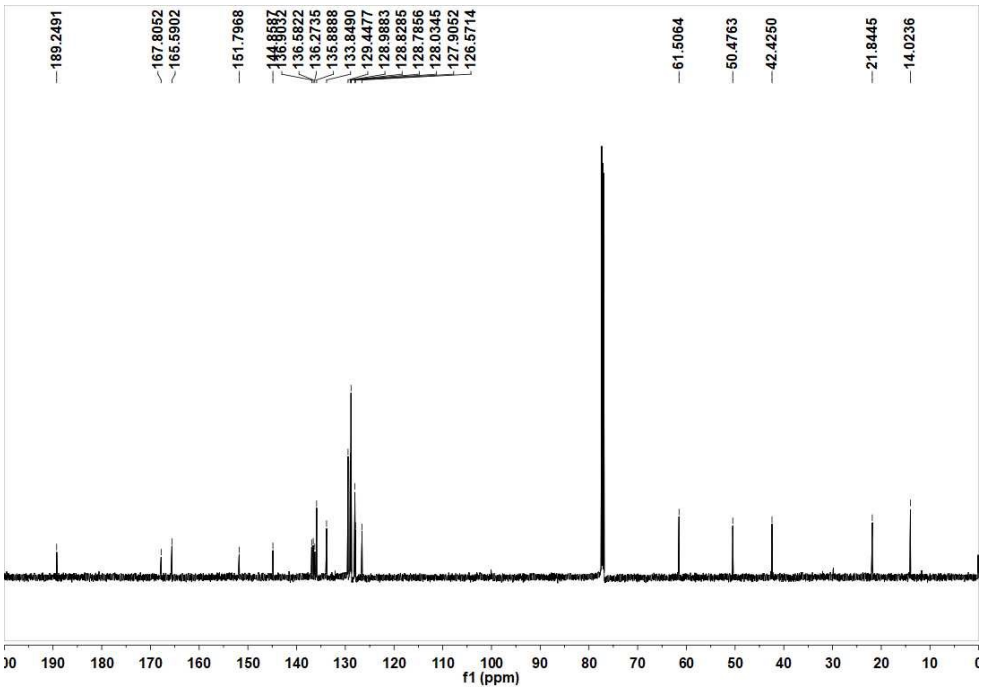
143.7665
142.7882
142.1379
136.8974
129.5710
129.0113
128.7132
128.5128
128.2359
127.3284
123.7343
67.0028
47.3920
43.6216
21.6988
f1 (ppm)


Ph
CO2Et
Ph
O
O
N
Ts

8


7.9311
7.9176
7.7912
7.7787
7.5588
7.5468
7.5347
7.4300
7.4174
7.4048
7.3666
7.3578
7.3476
7.3123
7.2990
7.2003
7.0523
7.0463
6.8708
5.0009
4.9760
4.9585
4.5697
4.5663
4.1241
4.1122
4.1002
4.0943
4.0824
4.0705
4.0628
4.0509
4.0390
4.0332
1.1129
1.1011
1.0894
1.94
1.93
1.08
2.13
1.07
1.94
2.92
1.93
0.93
1.95
1.00
2.14
3.07
3.12
f1 (ppm)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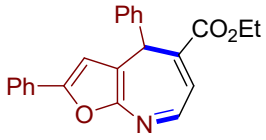
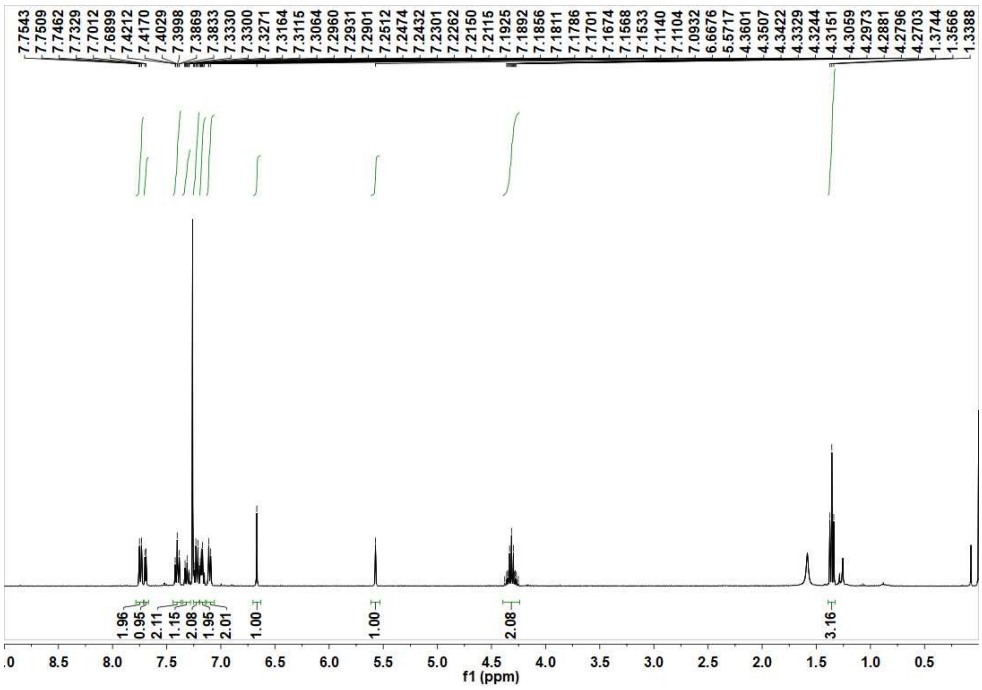
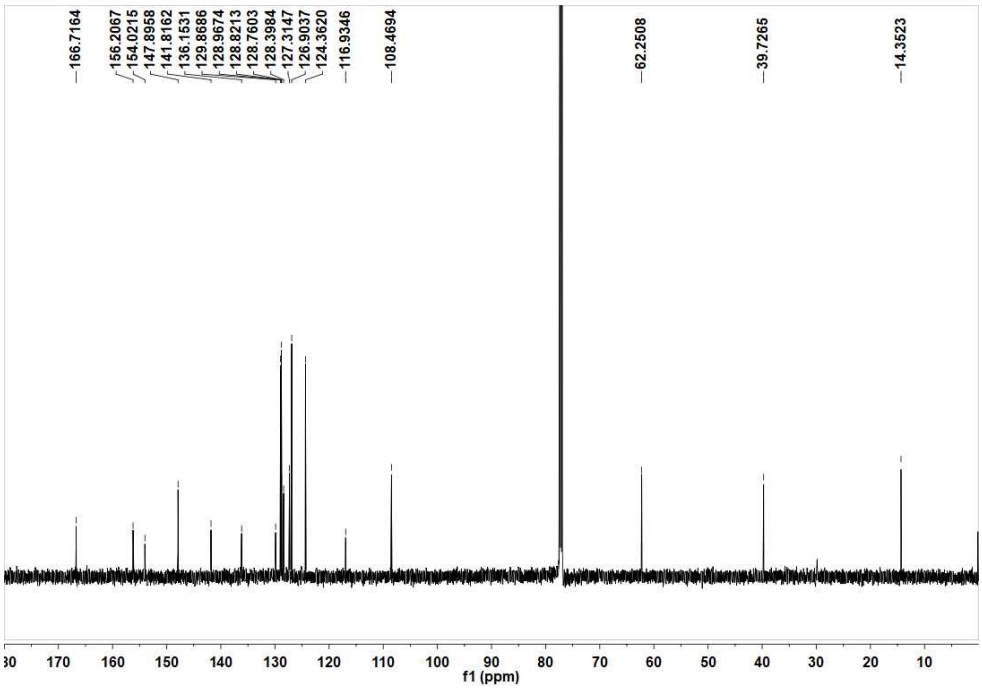
167.8052
165.5902
151.7968
136.5822
136.2735
135.8888
133.8490
129.4477
128.9883
128.8285
128.7856
128.0345
127.9052
126.5714
61.5064
50.4763
42.4250
21.8445
14.0236
f1 (ppm)

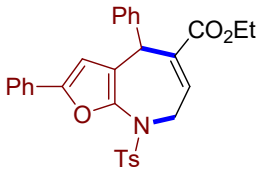

Ph
CO2Et
Ph
O
N

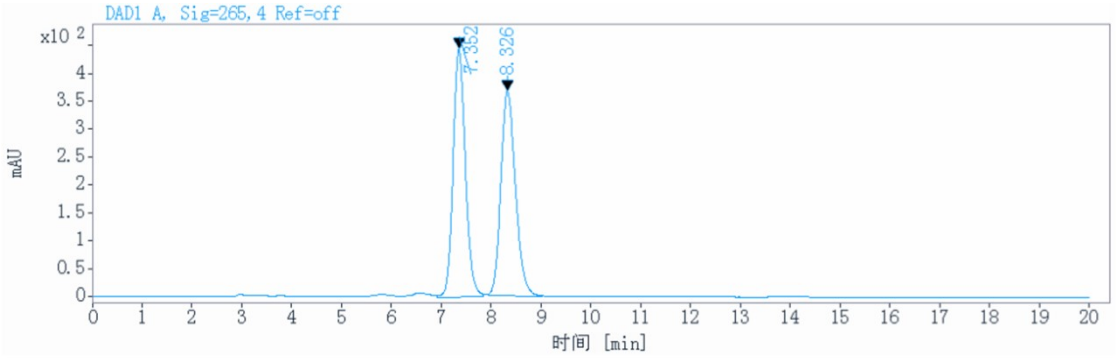
9


7.7543
7.7509
7.7462
7.7329
7.7012
7.6899
7.4212
7.4170
7.4029
7.3998
7.3869
7.3833
7.3330
7.3300
7.3271
7.3164
7.3115
7.3064
7.2960
7.2931
7.2901
7.2512
7.2474
7.2432
7.2301
7.2262
7.2150
7.2115
7.1925
7.1892
7.1856
7.1811
7.1786
7.1701
7.1674
7.1568
7.1533
7.1140
7.1104
7.0932
6.6676
5.5717
4.3601
4.3507
4.3422
4.3329
4.3244
4.3151
4.3059
4.2973
4.2881
4.2796
4.2703
1.3744
1.3566
1.3388
1.96
0.95
2.11
1.15
2.08
1.95
2.01
1.00
1.00
2.08
3.16
f1 (ppm)


166.7164
156.2067
154.0215
147.8958
141.8162
136.1531
129.8686
128.9674
128.8213
128.7603
128.3984
127.3147
126.9037
124.3620
116.9346
108.4694
62.2508
39.7265
14.3523
f1 (ppm)

HPLC Spectra of **3a**





信号: DAD1 A, Sig=265,4 Ref=off

RT	Area	Height	Area%	Height%
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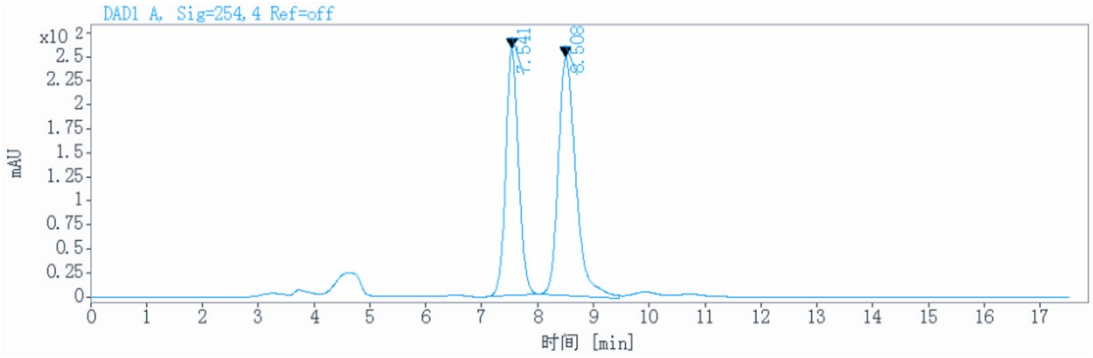
8.326	7531.3530	366.6086	49.4205	45.12
	15239.3198			



信号: DAD1 A, Sig=254,4 Ref=off

RT	Area	Height	Area%	Height%
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8.508	5432.4424	248.1743	57.2047	49.19
	9496.4922			