Lewis acid-catalyzed (3+2) annulation of bicyclobutanes with ynamides: Access to 2-amino bicyclo[2.1.1]hexenes

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Supporting Information

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in oven-dried reaction vessels with Teflon screw caps. 30 °C Corresponds to the room temperature (rt) of the lab when the experiments were carried out. CH_2Cl_2 was freshly purified by distillation over CaH_2 under argon atmosphere. All BCBs were prepared following the reported literature procedures.[1] All ynamides and their derivatives were prepared following the literature procedure.[2]

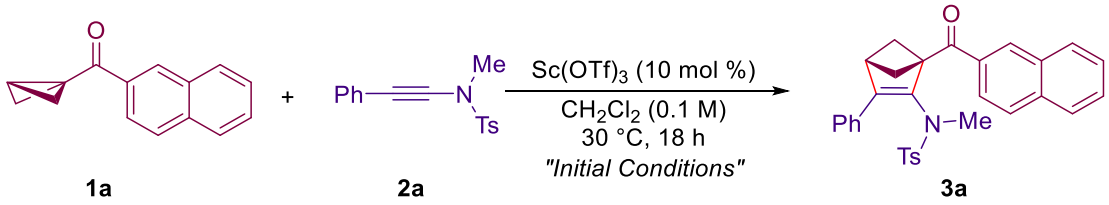
Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. All the isolated new compounds were confirmed to be a single spot on TLC. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Column chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker Ultrashield spectrometer in $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). Infrared (FT-IR) spectra were recorded on a Bruker Alfa FT-IR, ν-max in cm^{-1}. HRMS (ESI) data were recorded on a Waters Xevo G2-XS Q-TOF instrument.

[1] R. Guo, Y. Chang, L. Herter, C. Salome, S. E. Braley, T. C. Fessard and M. K. Brown, *J. Am. Chem. Soc*., 2022, **144**, 7988.

[2] (*a*) K. Murakami, J. Imoto, H. Matsubara, S. Yoshida, H. Yorimitsu and K. Oshima, *Chem. Eur. J.*, 2013, **19**, 5625. (*b*) M. Chen, N. Sun, H. Chen and Y. Liu, *Chem. Commun*., 2016, **52**, 6324.

2. General Procedure for the Optimization of the Reaction Conditions



1a **2a** **3a**

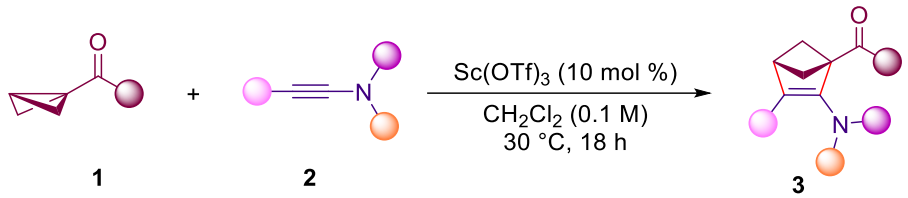
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (21 mg, 0.1 mmol) and CH_2Cl_2 (1.0 ml) under argon atmosphere. To this mixture, $Sc(OTf)_3$ (5 mg, 0.01 mmol) was added and then *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (57 mg, 0.2 mmol) was added and kept for stirring at 30 °C for 18 h under argon atmosphere. After the reaction completion (monitored by TLC), solvent was evaporated, and the crude mixture was passed through a pad of silica gel and eluted with EtOAc (3x10 mL). The reaction mixture was concentrated under reduced pressure and then the yield of **3a** was determined by the ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Table S1. Optimization Studies

entry	variation of the initial conditions[a]	yield of **3a** (%)[b]
1	None (**2a** added at the end)	62 (61)
2	$Yb(OTf)_3$ instead of $Sc(OTf)_3$	50
3	$Bi(OTf)_3$ instead of $Sc(OTf)_3$	20
4	TMS-OTf instead of $Sc(OTf)_3$	51
5	$Eu(OTf)_3$ instead of $Sc(OTf)_3$	38
6	$AlCl_3$ instead of $Sc(OTf)_3$	23
7	$CHCl_3$ instead of CH_2Cl_2	60
8	Toluene instead of CH_2Cl_2	53
9	MeCN instead of CH_2Cl_2	50
10	DCE instead of CH_2Cl_2	43
11	With 4 Å MS as the additive	56
12	50 °C instead of 30 °C	63
13	20 °C instead of 30 °C	51
14	12 h instead of 18 h	52
15	24 h instead of 18 h	61
16	2.0 equiv of **1a** and 1.0 of equiv **2a**	54
17	0.05 M CH_2Cl_2 instead of 0.1 M CH_2Cl_2	49
18	5 mol % $Sc(OTf)_3$ instead of 10 mol %	59
19	15 mol % $Sc(OTf)_3$ instead of 10 mol %	62
20[c]	*$Sc(OTf)_3$ added at the end*	*65 (65)*
21	reaction in the absence of $Sc(OTf)_3$	<5

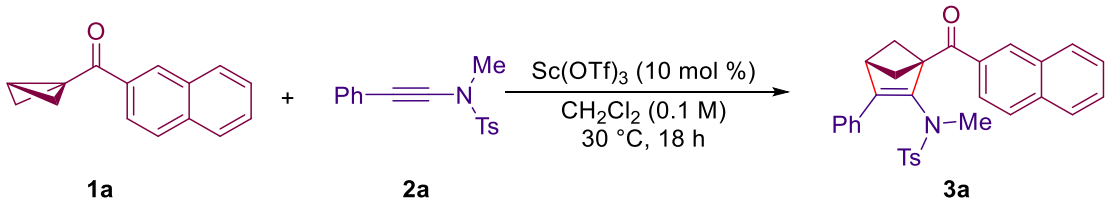
[a] Initial conditions: **1a** (0.1 mmol), **2a** (2.0 equiv), $Sc(OTf)_3$ (10 mol %), CH_2Cl_2 (0.1 M), 30 °C, 18 h. [b] The ^{1}H NMR yield of the crude products determined with the aid of 1,3,5-trimethoxybenzene as an internal standard. [c] $Sc(OTf)_3$ was added at the last.

3. General Procedure for the Lewis Acid-Catalyzed (3+2) Annulation of Bicyclobutanes with Ynamides



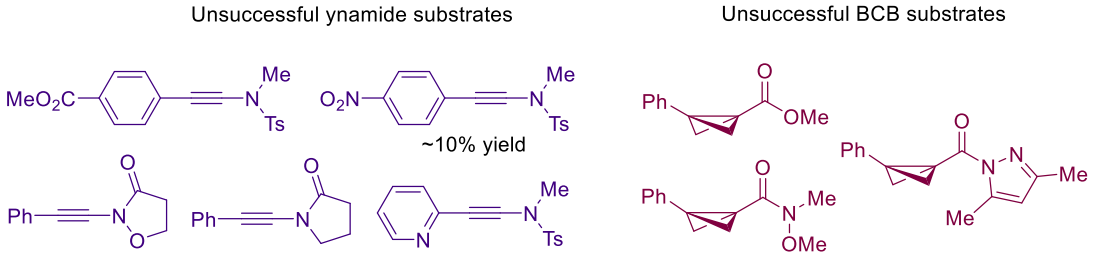
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added BCBs **1** (0.2 mmol) and CH_2Cl_2 (2.0 ml) under argon atmosphere. To this mixture, the ynamide derivatives **2** (0.4 mmol) was added, then $Sc(OTf)_3$ (0.02 mmol) was added to it and kept for stirring at 30 °C for 18 h under argon atmosphere. After the reaction completion (monitored by TLC), solvent was evaporated, and the crude residue was pre-adsorbed on silica and purified by column chromatography (Pet. Ether-EtOAc as the eluent) to afford **3** in good to excellent yields.

Procedure for the 2.0 mmol Scale Reaction for the synthesis of 3a



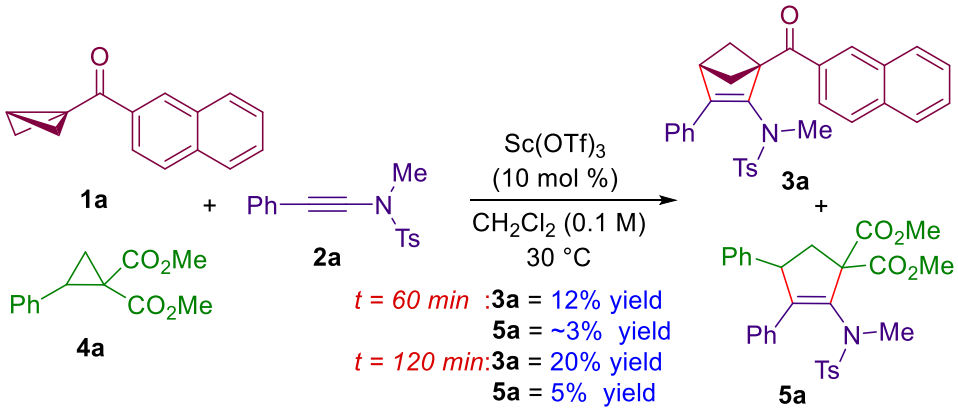
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (416 mg, 2.0 mmol) and CH_2Cl_2 (20 ml) under argon atmosphere. To this mixture, *N*,4-dimethyl-*N*-(phenylethynyl)benzene sulfonamide **2a** (1141 mg, 4.0 mmol) was added, then $Sc(OTf)_3$ (98 mg, 0.2 mmol) was added to it and kept for stirring at 30 °C for 18 h under argon atmosphere. After the reaction completion (monitored by TLC), solvent was evaporated, and the crude residue was pre-adsorbed on silica and purified by column chromatography (Pet. Ether-EtOAc as the eluent) to afford **3a** as a white solid (592 mg, 60% yield).

Unsuccessful substrates in this (3+2) annulation



4. Mechanistic Studies

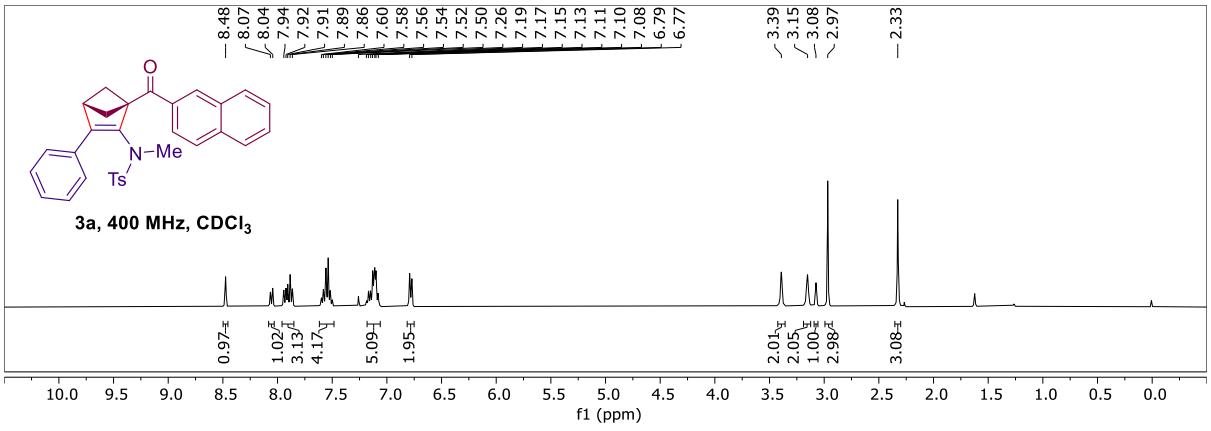
1. Competition experiment between BCB and donor-acceptor cyclopropane:



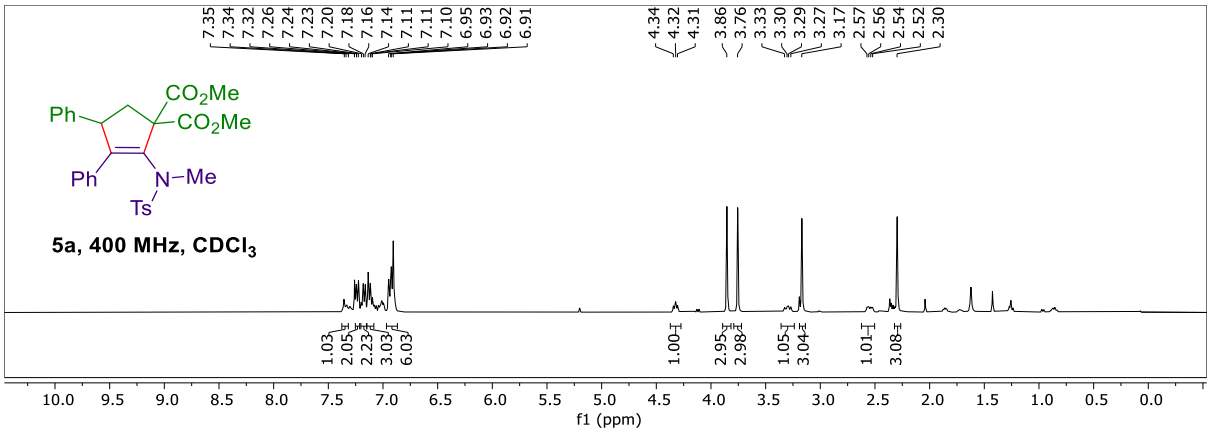
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (10.4 mg, 0.05 mmol) and CH_2Cl_2 (1.0 ml) under argon atmosphere. To this mixture, dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **4a** (11.7 mg, 0.05 mmol), *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (57.1 mg, 0.2 mmol) was added, then $Sc(OTf)_3$ (5 mg, 0.01 mmol) was added to it and purged with argon gas. The reaction mixture is then kept for stirring at 30 °C for different time intervals (see table below). The reaction mixture is diluted with CH_2Cl_2 (2.0 mL) and filtered through a short pad of silica gel and eluted with ethyl acetate (10 mL). The solvent was then evaporated, and the crude product was analyzed using ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) as the internal standard.

entry	time (min)	yield of **3a (%)**	yield of **5a (%)**
1	60	12	~3
2	120	20	5

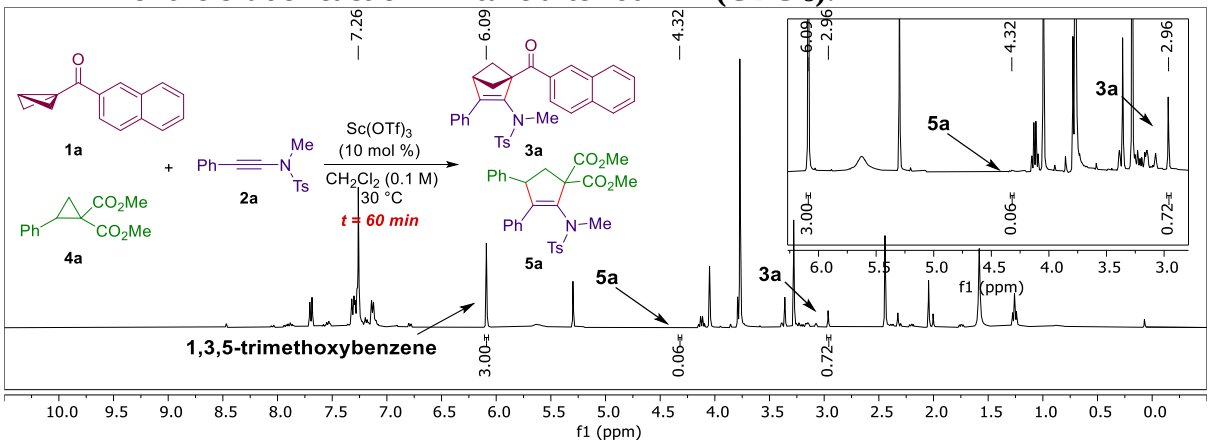
^{1}H NMR of 3a:



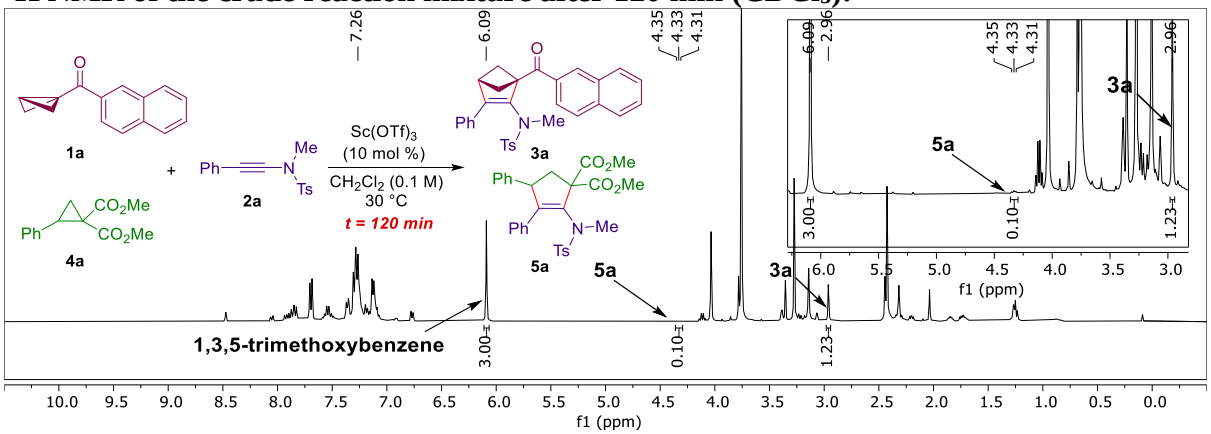
^{1}H NMR of 5a:



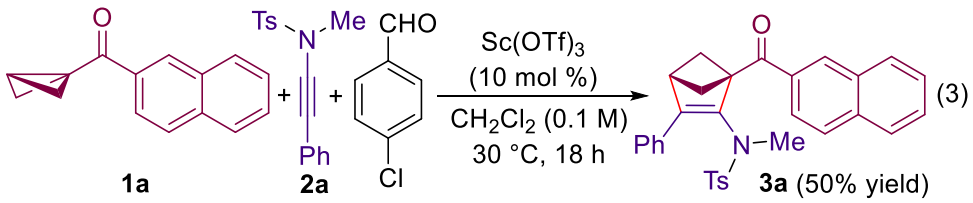
^{1}H NMR of the crude reaction mixture after 60 min ($CDCl_3$):



^{1}H NMR of the crude reaction mixture after 120 min ($CDCl_3$):

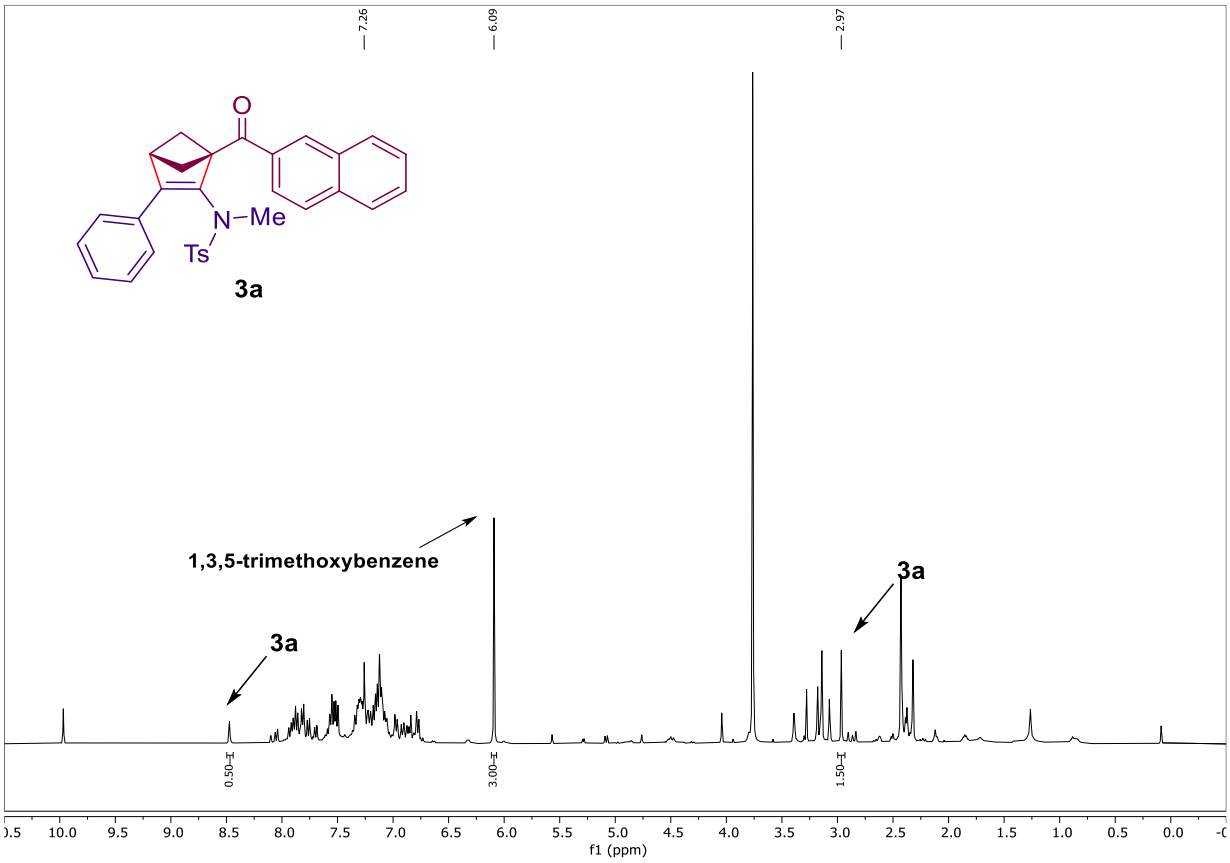


2. Attempt to intercept the enolate intermediate:



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (21 mg, 0.1 mmol) and CH_2Cl_2 (1.0 ml) under argon atmosphere. To this mixture, 4-chlorobenzaldehyde **4a** (14 mg, 0.1 mmol),

N,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (57 mg, 0.2 mmol) was added, then $Sc(OTf)_3$ (5 mg, 0.01 mmol) was added to it and purged with argon gas. The reaction mixture is then kept for stirring at 30 °C for different time intervals (see table below). The reaction mixture is diluted with CH_2Cl_2 (2.0 mL) and filtered through a short pad of silica gel and eluted with ethyl acetate (10 mL). The solvent was then evaporated, and the crude product was analyzed using ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) as the internal standard.



5. X-ray Data of 3a

Single crystal of **3a** (recrystallized from $CHCl_3$/*n*-hexane at 25 °C) was mounted and the diffraction data was collected at 120 K on a Bruker APEX-II CCD diffractometer using SMART/SAINT software. Intensity data were collected using MoKα radiation (λ=0.71073 A°). The single crystal was affixed to a Hampton Research cryoloop using Paratone-N oil. Data collection and reduction was performed using Bruker APEX2 and Bruker SAINT, respectively. The structure was solved by direct methods using the SHELX-97 and refined by full-matrix leastsquares on F2. Empirical absorption corrections were applied with SADABS. All Nonhydrogen atoms were refined anisotropically and hydrogen atoms were included in

geometric positions. Structure was drawn using Olex-2 and Mercury-3. CCDC 2358094 (**3a**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic refinement parameters are given below:

Compound	**3a**
Empirical formula	$C_{31}H_{27}NO_3S$
Formula weight	493.59
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monocyclic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.8078(18) Å, b = 31.102(8) Å, c = 12.122(3) Å, α = 90°, β = 99.747(8), γ = 90°
Volume	2529.7(11)Å^3
Z	4
Density (calculated)	1.296 g/cm^3
Absorption coefficient	0.162 mm^{-1}
F(000)	1040
Theta range for data collection	2.620 to 31.542°
Index ranges	$-9 \leq h \leq 10$, $-45 \leq k \leq 45$, $-17 \leq l \leq 17$
Reflections collected	94382
Independent reflections	8403 [R_{int} = 0.0445, R_{sigma} = 0.0206]
Data / restraints / parameters	8403/0/327
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R_1 = 0.0427, wR_2 = 0.1056
R indices (all data)	R_1 = 0.0475, wR_2 = 0.1083

Table S2 Crystal Data and structure refinement for **3a**

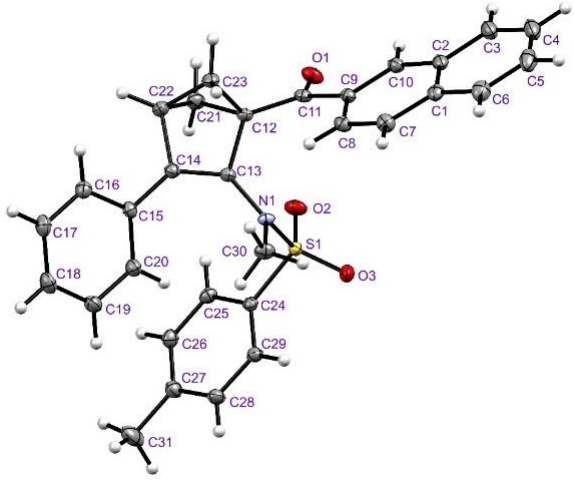
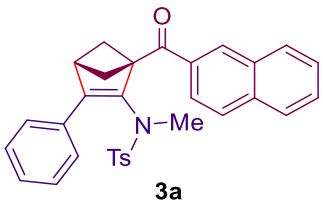


Figure S1. Crystal Structure of **3a**

6. Synthesis and Characterization of Substituted 2-Amino Bicyclo[2.1.1] hexene Derivatives

N-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3a)

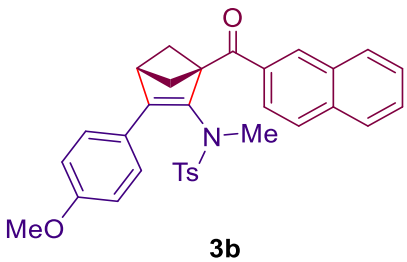


3a

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and N,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3a** as white solid (64 g, 65% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.60 – 7.50 (m, 4H), 7.19 – 7.08 (m, 5H), 6.78 (d, *J* = 8.5 Hz, 2H), 3.39 (s, 2H), 3.15 (s, 2H), 3.08 (s, 1H), 2.97 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.9, 148.1, 147.4, 143.7, 135.6, 135.5, 134.5, 133.1, 132.5, 131.3, 129.7, 128.3, 128.1, 127.9, 127.8, 127.5, 126.6, 126.5, 125.2, 65.8, 41.0, 37.9, 21.5 *(2 signals in the aromatic region and 2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{27}NO_3SNa$ 516.1604; found 516.1607. **FTIR (cm^{-1})** 2924, 2358, 1664, 1461, 1215, 752.

N-(1-(2-Naphthoyl)-3-(4-methoxyphenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide (3b)



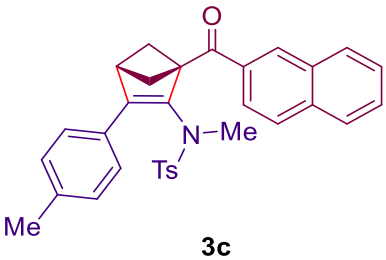
3b

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-((4-methoxyphenyl)phenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide **2b** (126 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-(4-methoxyphenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide **3b** as white solid (75 mg, 71% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.12; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.59 – 7.49 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 3.36 (s, 2H), 3.13 (s, 2H), 3.05 (s, 1H), 2.98

(s, 3H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.2, 159.2, 147.8, 145.2, 143.6, 135.9, 135.4, 134.5, 132.4, 131.2, 129.6, 129.6, 128.3, 128.0, 127.9, 127.8, 127.4, 126.6, 125.7, 125.2, 113.7, 65.5, 55.3, 40.9, 37.8, 21.5 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{29}NO_4SNa$ 546.1710; found 546.1714. **FTIR (cm^{-1})** 2988, 2357, 1662, 1506, 1346, 1155.

_N_-(1-(2-Naphthoyl)-3-(_p_-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3c)

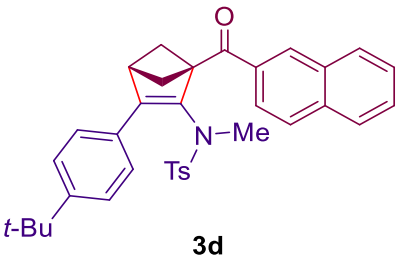


3c

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and _N_,4-dimethyl-_N_-(_p_-tolylethynyl)benzenesulfonamide **2c** (119 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded _N_-(1-(2-naphthoyl)-3-(_p_-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide **3c** as white solid (66 mg, 66% yield).

***R*$_f$** (Pet. ether/EtOAc = 85/15): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.60 – 7.50 (m, 4H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 2H), 3.38 (s, 2H), 3.14 (s, 2H), 3.05 (s, 1H), 2.97 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.0, 148.1, 146.4, 143.6, 137.8, 135.7, 135.4, 134.5, 132.4, 131.3, 130.3, 129.6, 128.9, 128.3, 128.0, 127.9, 127.4, 126.6, 126.4, 125.2, 65.7, 41.0, 37.9, 21.5, 21.3 *(1 signal in the aromatic region and 2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{29}NO_3SNa$ 530.1760; found 530.1761. **FTIR (cm^{-1})** 2990, 2358, 1663, 1463, 1350, 1159.

_N_-(1-(2-Naphthoyl)-3-(4-(*tert*-butyl)phenyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethyl benzenesulfonamide (3d)



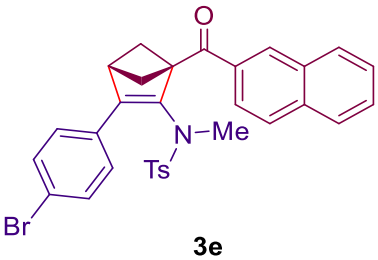
3d

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and _N_-((4-(*tert*-butyl)phenyl)ethynyl)-_N_,4-dimethylbenzene sulfonamide **2d** (137 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded _N_-(1-(2-

naphthoyl)-3-(4-(*tert*-butyl)phenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide **3d** as white solid (77 mg, 70% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.22; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.87 (m, 3H), 7.60 – 7.50 (m, 4H), 7.13 (d, *J* = 6.2 Hz, 4H), 6.77 (d, *J* = 8.2 Hz, 2H), 3.37 (s, 2H), 3.14 – 3.10 (m, 3H), 3.00 (s, 3H), 2.33 (s, 3H), 1.29 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 151.0, 148.0, 146.5, 143.5, 135.8, 135.4, 134.5, 132.4, 131.2, 130.0, 129.7, 129.6, 128.3, 128.0, 127.9, 127.4, 126.6, 126.3, 125.2, 125.2, 65.7, 40.7, 37.9, 34.6, 31.3, 21.5 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{35}H_{35}NO_3SNa$ 572.2230; found 572.2236. **FTIR (cm^{-1})** 2959, 2356, 1663, 1463, 1349, 1155.

_N_-(1-(2-Naphthoyl)-3-(4-bromophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3e)



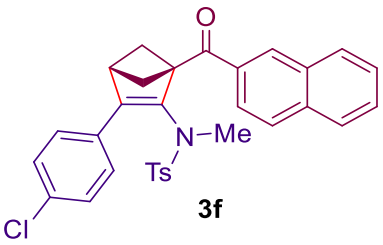
3e

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-((4-bromophenyl)ethynyl)-*N*,4-dimethylbenzene sulfonamide **2e** (146 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-(4-bromophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3e** as white solid (60 mg, 53% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.88 (t, *J* = 8.3 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 6.6 Hz, 2H), 3.39 (s, 2H), 3.14 (s, 2H), 3.02 (s, 1H), 2.97 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.9, 148.4, 147.3, 143.9, 135.8, 135.5, 134.3, 132.4, 132.0, 131.4, 131.3, 129.7, 128.4, 128.1, 128.0, 127.9, 127.3, 126.7, 125.1, 121.7, 65.7, 40.9, 38.0, 21.6 *(1 signal in the aromatic region and 2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{26}BrNO_3SNa$ 594.0709; found 530.0719. **FTIR (cm^{-1})** 2990, 2357, 1663, 1479, 1349, 1160.

_N_-(1-(2-Naphthoyl)-3-(4-chlorophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethyl benzene sulfonamide (3f)

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-((4-chlorophenyl)ethynyl)-*N*,4-dimethylbenzene

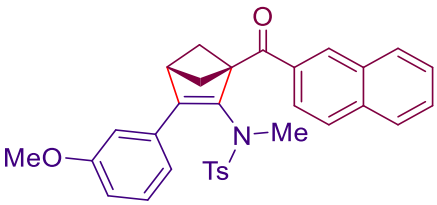


3f

sulfonamide **2f** (129 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-(4-chlorophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3f** as white solid (89 mg, 85% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.3; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 1H), 7.88 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 6.9 Hz, 1H), 7.54-7.50 (m, 3H), 7.11-7.05 (m, 4H), 6.75 (d, *J* = 8.3 Hz, 2H), 3.39 (s, 2H), 3.14 (s, 2H), 3.02 (s, 1H), 2.97 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.0, 148.2, 147.3, 143.9, 135.8, 135.5, 134.4, 133.6, 132.4, 131.6, 131.3, 129.7, 129.7, 128.5, 128.4, 128.1, 127.9, 127.7, 127.4, 126.7, 125.1, 65.7, 41.0, 38.0, 21.6 *(2 signals in the aliphatic region are overlapping).* **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{26}NClO_3SNa$ 550.1214; found 550.1227. **FTIR (cm^{-1})** 2994, 1762, 1664, 1594, 1488, 1352.

_N_-(1-(2-Naphthoyl)-3-(3-methoxyphenyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethyl benzenesulfonamide (3g)

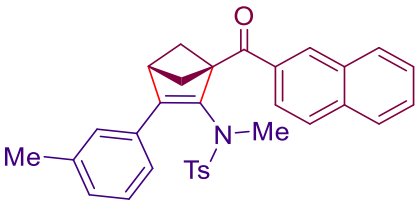


3g

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-((3-methoxyphenyl) phenyl)ethynyl)-*N*,4-dimethyl benzene sulfonamide **2g** (126 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL)s at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-(3-methoxyphenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3g** as white solid (85 mg, 81% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.11; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.59 – 7.50 (m, 4H), 7.08 – 7.0 (m, 3H), 6.75 – 6.73 (m, 1H), 6.54 (s, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 3.68 (s, 3H), 3.41 (s, 2H), 3.14 (s, 2H), 3.06 (s, 1H), 2.99 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.0, 159.5, 147.7, 143.7, 135.4, 134.5, 134.4, 132.4, 131.3, 129.7, 129.6, 129.2, 128.3, 128.0, 127.9, 127.4, 126.6, 125.2, 119.0, 113.5, 112.1, 65.7, 55.2, 41.1, 37.9, 21.5 *(2 signals in the aromatic region and 2 signals in the aliphatic region are overlapping).* **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{29}NO_4SNa$ 546.1710; found 546.1711. **FTIR (cm^{-1})** 2991, 2358, 1663, 1467, 1348, 1157.

***N*-(1-(2-Naphthoyl)-3-(*m*-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3h)**

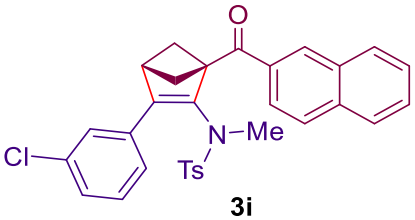


3h

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(*m*-tolylethynyl)benzenesulfonamide **2h** (119 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-(*m*-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3h** as white solid (71 mg, 70% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.38; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.94 – 7.87 (m, 3H), 7.60 – 7.56 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.43 (s, 1H), 3.38 (s, 2H), 3.16 (s, 2H), 3.07 (s, 1H), 2.95 (s, 3H), 2.35 (s, 3H), 2.08 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.8, 147.8, 147.2, 143.6, 137.8, 135.6, 135.5, 134.5, 133.2, 132.5, 131.3, 129.8, 129.7, 128.6, 128.3, 128.2, 128.1, 127.9, 127.5, 127.2, 126.6, 125.3, 123.6, 65.9, 41.1, 37.8, 21.6, 21.3 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{29}NO_3SNa$ 530.1760; found 530.1779. **FTIR (cm^{-1})** 2989, 2357, 1665, 1464, 1350, 1158.

***N*-(1-(2-Naphthoyl)-3-(3-chlorophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzene sulfonamide (3i)**



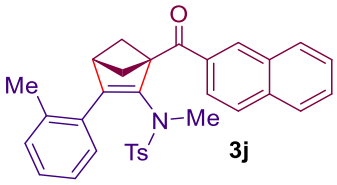
3i

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-((3-chlorophenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide **2i** (129 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-(3-chlorophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide **3i** as white solid (83 mg, 79% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.05 (d, *J* = 9.2 Hz, 1H), 7.95 – 7.86 (m, 3H), 7.56 – 7.50 (m, 4H), 7.17 – 7.12 (m, 3H), 7.09-7.05 (m, 1H), 6.80 (d, *J* = 6.9 Hz, 1H), 6.51 (s, 1H), 3.39 (s, 2H), 3.16 (s, 2H), 3.03 (s, 1H), 2.96 (s, 3H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.6, 149.0, 146.6, 144.1, 135.5, 135.3, 135.0, 134.4, 134.3, 132.5, 131.3, 130.0, 129.7, 129.5, 128.7, 128.1, 128.0, 127.7, 127.2, 126.7, 126.4, 125.2,

124.6, 65.9, 41.1, 38.0, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{26}NClO_3SNa$ 550.1214; found 550.1220. **FTIR (cm^{-1})** 2994, 2357, 1757, 1664, 1594, 1469.

_N_-(1-(2-Naphthoyl)-3-(_o_-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3j)

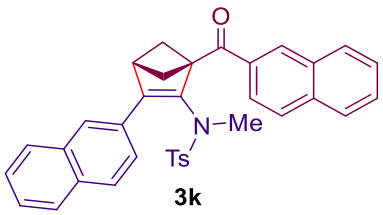


3j

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and _N_,4-dimethyl-_N_-(_o_-tolylethynyl)benzenesulfonamide **2j** (119 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded _N_-(1-(2-naphthoyl)-3-(_o_-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzenesulfonamide **3j** as white solid (60 mg, 59% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (s, 1H), 8.12 (dd, J_1 = 8.6 Hz, J_2 =1.8 Hz, 1H), 7.99 (d, J = 7.1 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.61 – 7.51 (m, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.14 – 7.08 (m, 4H), 6.79 – 6.74 (m, 1H), 6.16 (d, J = 7.6 Hz, 1H), 3.48 (dd, J_1 = 1.3 Hz, J_2 = 1.8 Hz, 2H), 3.13 (t, J = 3.1 Hz , 2H), 2.77 (s, 4H), 2.36 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.9, 149.1, 148.8, 143.5, 135.6, 135.0, 134.5, 133.9, 132.6, 131.9, 130.2, 129.9, 129.5, 128.9, 128.4, 128.2, 128.0, 127.9, 127.6, 126.6, 125.5, 125.1, 65.1, 42.3, 38.1, 21.6, 20.8 *(1 signal in the aromatic region and 2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{29}NO_3SNa$ 530.1760; found 530.1768. **FTIR (cm^{-1})** 2990, 2356, 1663, 1463, 1350, 1159.

_N_-(1-(2-Naphthoyl)-3-(naphthalen-2-yl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethyl benzenesulfonamide (3k)



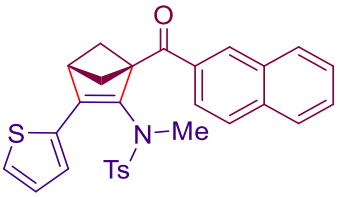
3k

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and _N_,4-dimethyl-_N_-(naphthalen-2-ylethynyl)benzene sulfonamide **2k** (135 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded _N_-(1-(2-naphthoyl)-3-(naphthalen-2-yl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzenesulfonamide **3k** as white solid (75 mg, 69% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.3; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (s, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.96 – 7.87 (m, 3H), 7.80 – 7.73 (m, 1H), 7.61 – 7.56 (m, 3H), 7.54 – 7.52 (m,

2H), 7.43 (s, 3H), 7.12 – 7.10 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.46 (s, 2H), 3.21 (s, 3H), 3.01 (s, 3H), 2.96 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.8, 149.7, 148.8, 148.7, 147.4, 147.0, 147.0, 143.5, 136.6, 136.5, 135.4, 134.1, 132.9, 132.2, 130.9, 129.6, 128.3, 128.3, 128.2, 128.2, 127.7, 127.6, 127.4, 126.5, 126.4, 126.3, 124.0, 66.5, 40.2, 37.9, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{35}H_{29}NO_3SNa$ 566.1760; found 566.1763. **FTIR (cm^{-1})** 2986, 2357, 1761, 1663, 1501, 1462.

_N_-(1-(2-Naphthoyl)-3-(thiophen-2-yl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3l)



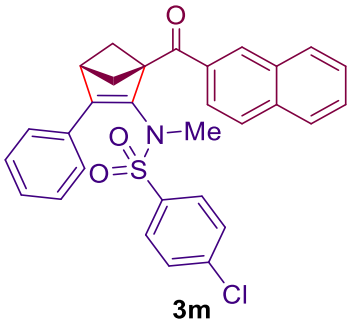
3l

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(thiophen-2-ylethynyl)benzenesulfonamide **2l** (117 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-(thiophen-2-yl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3l** as white solid (65 mg, 65% yield).

***R*$_f$** (Pet. ether/EtOAc = 90/10): 0.18; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (s, 1H), 7.98 – 7.86 (m, 5H), 7.60 – 7.51 (m, 4H), 7.19 (d, *J* = 5.1 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.88 (m, 1H), 6.65 (d, *J* = 3.5 Hz, 1H), 3.38 (s, 2H), 3.15 (s, 2H), 3.11 (s, 1H), 3.10 (s, 3H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 145.1, 143.6, 143.1, 136.7, 135.4, 135.0, 134.5, 132.4, 131.0, 129.6, 129.6, 128.4, 128.1, 127.9, 127.4, 127.2, 126.7, 126.4, 125.4, 125.1, 65.5, 41.9, 37.6, 21.5 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{29}H_{25}NO_3S_2Na$ 522.1168; found 522.1176. **FTIR (cm^{-1})** 2987, 2358, 1662, 1462, 1347, 1155.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-chloro-_N_-methylbenzene sulfonamide (3m)

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and 4-chloro-*N*-methyl-*N*-(phenylethynyl) benzenesulfonamide **2m** (122 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-

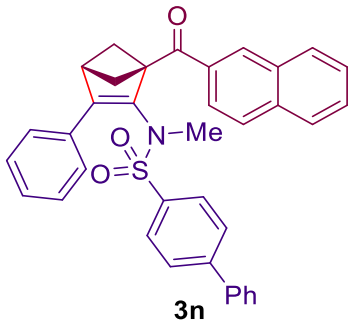


3m

phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-chloro-*N*-methylbenzenesulfonamide **3m** as white solid (60 mg, 59% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.24; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 8.02 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.89 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 3H), 7.23 – 7.14 (m, 5H), 6.92 (d, *J* = 7.0 Hz, 2H), 3.42 – 3.41 (m, 2H), 3.17 – 3.15 (m, 2H), 3.09 (t, *J* = 2.7 Hz, 1H), 3.03 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.2, 149.3, 147.2, 139.3, 137.6, 135.5, 134.4, 132.9, 132.5, 131.3, 129.7, 129.2, 128.8, 128.5, 128.5, 128.2, 128.1, 128.0, 126.8, 126.4, 125.0, 65.5, 41.0, 38.4 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{27}NO_3SNa$ 536.1058; found 536.1064. **FTIR (cm^{-1})** 3059, 2988, 1664, 1470, 1353, 1159, 753.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-methyl-[1,1'-biphenyl]-4-sulfonamide (3n)

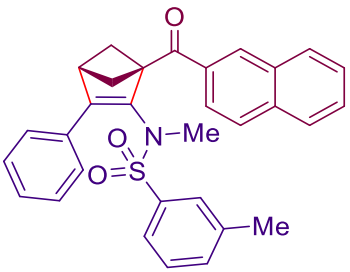


3n

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-methyl-*N*-(phenylethynyl)-[1,1'-biphenyl]-4-sulfonamide **2n** (139 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-methyl-[1,1'-biphenyl]-4-sulfonamide **3n** as white solid (59 mg, 53% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.26; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.54 – 7.41 (m, 8H), 7.14 – 7.06 (m, 3H), 6.85 (d, *J* = 8.1 Hz, 2H), 3.44 – 3.44 (m, 2H), 3.19 – 3.17 (m, 2H), 3.10 (t, *J* = 2.7 Hz, 1H), 3.04 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 148.6, 147.4, 145.8, 139.5, 137.3, 135.5, 134.5, 133.1, 132.2, 131.3, 129.7, 129.1, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.7, 127.4, 126.7, 126.5, 125.2, 65.7, 41.1, 38.2 *(1 signal in the aromatic region and 2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{36}H_{29}NO_3SNa$ 578.1760; found 578.1766. **FTIR (cm^{-1})** 3057, 2985, 1666, 1472, 1353, 1160, 759.

***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,3-dimethylbenzene sulfonamide (3o)**

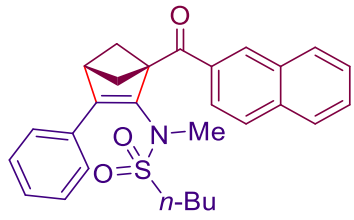


3o

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1x** (42 mg, 0.2 mmol) and *N*,3-dimethyl-*N*-(phenylethynyl)benzene sulfonamide **2o** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,3-dimethylbenzenesulfonamide **3o** as white solid (60 mg, 61% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.27; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.89 (t, *J* = 8.6 Hz, 2H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 (s, 1H), 7.26 – 7.23 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 2H), 6.84 (d, *J* = 6.9 Hz, 2H), 3.41 – 3.40 (m, 2H), 3.16 - 3.14 (m, 2H), 3.08 (t, *J* = 2.7 Hz, 1H), 2.98 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.0, 148.3, 147.4, 139.4, 138.5, 135.5, 134.5, 133.6, 133.1, 132.5, 131.3, 129.7, 128.9, 128.3, 128.1, 127.9, 127.9, 127.8, 126.6, 126.5, 125.2, 124.7, 65.7, 41.0, 38.0, 21.3 *(1 signal in the aromatic region and 2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{27}NO_3SNa$ 516.1604; found 516.1609. **FTIR (cm^{-1})** 3058, 2943, 1664, 1468, 1350, 1153, 756.

***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-methylbutane-1-sulfonamide (3p)**



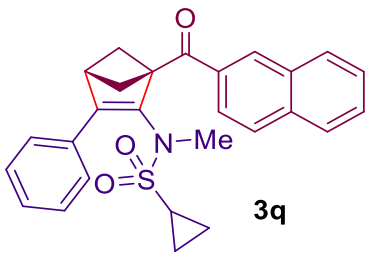
3p

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-methyl-*N*-(phenylethynyl)butane-1-sulfonamide **2p** (101 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 95/05) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-methylbutane-1-sulfonamide **3p** as white solid (51 mg, 55% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.58 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.62 – 7.53 (m, 4H), 7.41 (t, *J* = 6.7 Hz, 2H), 7.33 – 7.29 (m, 1H), 3.44 – 4.43 (m, 2H), 3.13 – 3.09 (m, 6H), 2.56 – 2.52 (m, 2H), 1.50 – 1.42 (m, 2H), 1.06 – 0.96 (m, 2H), 0.61 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**

δ 199.5, 149.4, 148.0, 135.6, 134.2, 133.2, 132.5, 131.7, 129.9, 128.8, 128.8, 128.4, 128.2, 127.9, 126.9, 126.8, 124.8, 65.0, 52.8, 40.7, 38.2, 25.1, 21.5, 13.3 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{29}NO_3SNa$ 482.1760; found 482.1766. **FTIR (cm^{-1})** 3276, 2957, 1693, 1403, 1349, 1155.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-methylcyclopropane sulfonamide (3q)

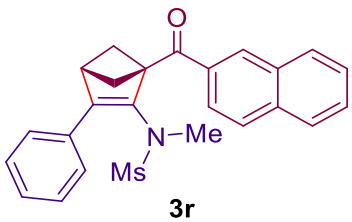


3q

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-methyl-*N*-(phenylethynyl)cyclopropane sulfonamide **2q** (94 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-methylcyclopropanesulfonamide **3q** as white solid (56 mg, 64% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.54 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.60 – 7.57 (m, 3H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 3.44 – 3.39 (m, 2H), 3.14 – 3.10 (m, 6H), 1.97 – 1.90 (m, 1H), 1.03 – 0.99 (m, 2H), 0.70 – 0.65 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.2, 148.3, 148.1, 135.5, 134.4, 133.2, 132.4, 131.4, 129.8, 128.7, 128.6, 128.3, 128.1, 127.8, 126.8, 126.8, 124.9, 65.1, 40.8, 38.3, 29.7, 5.5 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{25}NO_3SNa$ 466.1447; found 466.1454. **FTIR (cm^{-1})** 3056, 2944, 1661, 1464, 1340, 1141, 728.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-methylmethanesulfonamide (3r)

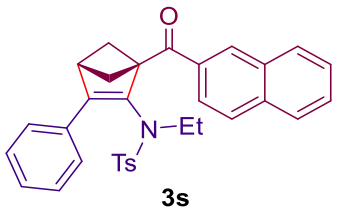


3r

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-methyl-*N*-(phenylethynyl)methanesulfonamide **2r** (84 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-methylmethanesulfonamide **3r** as white solid (60 mg, 72% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.24; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, J_1 = 13.2 Hz, J_2 = 8.4 Hz, 2H), 7.63 – 7.55 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 3.44 (s, 2H), 3.13 (s, 1H), 3.11 (s, 2H), 3.08 (s, 3H), 2.53 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.5, 149.0, 147.5, 135.5, 134.1, 133.0, 132.4, 131.5, 129.8, 128.8, 128.7, 128.4, 128.2, 127.9, 126.9, 126.7, 124.7, 67.9, 64.7, 40.6, 39.4, 37.5 *(1 signal in the aliphatic region is overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NO_3SNa$ 440.1291; found 440.1295. **FTIR (cm^{-1})** 3012, 2358, 1660, 1462, 1333, 1146.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-ethyl-4-methylbenzene sulfonamide (3s)

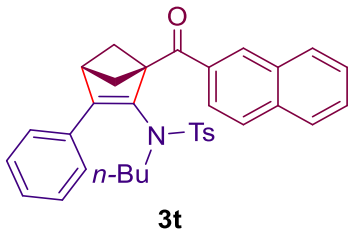


3s

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-ethyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide **2s** (120 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-ethyl-4-methylbenzene sulfonamide **3s** as white solid (64 mg, 63% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53 (s, 1H), 8.06 (dd, J_1 = 8.6 Hz, J_2 = 1.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 8.5 Hz, 2H), 7.61 – 7.50 (m, 4H), 7.20 – 7.11 (m, 5H), 6.90 – 6.88 (m, 2H), 3.45 (s, 2H), 3.29 – 3.13 (m, 4H), 3.04 (t, *J* = 2.5 Hz, 1H), 2.33 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.7, 135.4, 135.0, 133.6, 132.4, 131.2, 129.8, 129.7, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 126.7, 126.6, 125.3, 65.2, 43.8, 41.8, 21.5, 14.2 *(4 signals in the aromatic region and 2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{32}H_{29}NO_3SNa$ 530.1760; found 530.1761. **FTIR (cm^{-1})** 2984, 2358, 1662, 1449, 1371, 1157.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-butyl-4-methylbenzene sulfonamide (3t)



3t

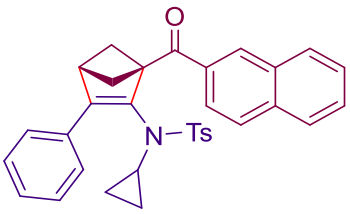
Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-butyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide **2t** (131 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30

°C for 18 h followed by column chromatography (Pet. ether/EtOAc = 95/05) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-butyl-4-methylbenzenesulfonamide **3t** as white solid (66 mg, 62% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.21; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.88 (t, *J* = 8.0 Hz, 2H), 7.62 – 7.50 (m, 4H), 7.18 – 7.10 (m, 5H), 6.84 (d, *J* = 8.3 Hz, 2H), 3.44 (s, 2H), 3.20 – 3.12 (m, 5H), 3.01 (s, 1H), 2.35 (s, 3H), 1.49 – 1.37 (m, 2H), 1.15 – 1.06 (m, 2H), 0.69 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.8, 148.1, 145.1, 143.7, 135.9, 135.4, 135.0, 133.7, 132.4, 131.2, 129.8, 129.7, 128.3, 128.2, 128.0, 127.9, 127.8, 126.8, 126.6, 125.4, 65.2, 48.5, 41.9, 30.8, 21.6, 19.9, 13.7 *(1 signal in the aromatic region and 2 signals in the aliphatic region are overlapping).* **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{34}H_{33}NO_3SNa$ 558.2073; found 558.2080. **FTIR (cm^{-1})** 3058, 2958, 1662, 1462, 1349, 1159, 731.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-cyclopropyl-4-methyl benzenesulfonamide (3u)

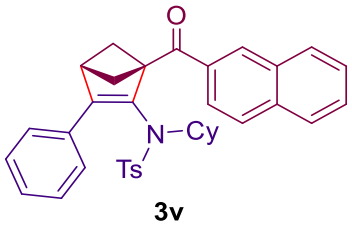
Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-cyclopropyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide **2u** (125 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 95/05) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-cyclopropyl-4-methylbenzenesulfonamide **3u** as white solid (61 mg, 59% yield).



3u

***R*f** (Pet. ether/EtOAc = 95/05): 0.27; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 8.3 Hz, 3H), 7.17 – 7.11 (m, 5H), 6.94 (d, J = 6.7 Hz, 2H), 3.51 – 3.40 (m, 2H), 3.19 (s, 1H), 3.05 – 3.01 (m, 2H), 2.40 – 2.36 (s, 4H), 0.73 (bs, 1H), 0.59 (bs, 2H), 0.34 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.4, 147.8, 147.1, 143.8, 135.5, 134.6, 134.3, 132.5, 131.5, 129.7, 129.4, 128.4, 128.4, 128.2, 128.1, 127.9, 127.6, 126.8, 126.7, 125.2, 65.2, 41.9, 31.5, 21.6, 9.7, 7.9 *(1 signal in the aromatic region and 1 signal in the aliphatic region are overlapping).* **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{33}H_{29}NO_3SNa$ 542.1760; found 542.1763. **FTIR (cm^{-1})** 3055, 2951, 1665, 1489, 1345, 1157, 731.

***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-cyclohexyl-4-methylbenzene sulfonamide (3v)**

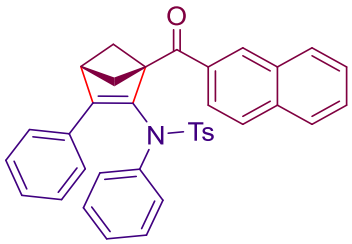


3v

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-cyclohexyl-4-methyl-*N*-(phenylethynyl) benzenesulfonamide **2v** (141 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-cyclohexyl-4-methylbenzenesulfonamide **3v** as white solid (75 mg, 67% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.41; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (s, 1H), 8.08 (d, *J* = 6.9 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.86 (t, *J* = 9.2 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.31 (m, 2H), 7.23 – 7.21 (m, 3H), 6.92 (d, *J* = 8.3 Hz, 2H), 3.78 – 3.74 (m, 1H), 3.60 – 3.53 (m, 1H), 3.35 – 3.31 (m, 1H), 3.22 (s, 1H), 3.04 (s, 1H), 2.95 (s, 1H), 2.24 (s, 3H), 2.02 – 1.99 (m, 1H), 1.84 – 1.83 (m, 1H), 1.71 – 1.68 (m, 1H), 1.57 – 1.54 (m, 1H), 1.49 - 1.46 (m, 1H), 1.38 – 1.27 (m, 2H), 1. 16 - 1.08 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.8, 153.1, 144.4, 142.9, 138.3, 135.4, 134.8, 134.1, 132.5, 132.0, 130.0, 129.2, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 127.2, 126.6, 125.2, 67.8, 67.3, 65.5, 62.6, 42.3, 32.6, 26.2, 25.4, 21.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{36}H_{35}NO_3SNa$ 584.2230; found 584.2235. **FTIR (cm^{-1})** 2986, 2357, 1657, 1329, 1198, 1153.

***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-methyl-*N*-phenylbenzene sulfonamide (3w)**



3w

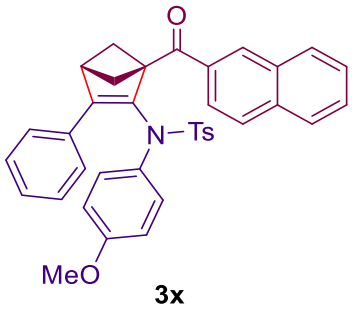
Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and 4-methyl-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide **2w** (139 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-methyl-*N*-phenylbenzenesulfonamide **3w** as white solid (74 mg, 67% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.28; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 7.97 (dd, J_1 = 8.6 Hz, J_2 = 1.5 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 7.3 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.53 – 7.49 (m, 1H), 7.41 – 7.34 (m, 6H), 7.20 – 7.18 (m, 3H), 7.05 (t, *J* = 7.8 Hz, 2H),

6.95 (t, *J* = 7.7 Hz, 3H), 3.58 (s, 2H), 3.14 – 3.11 (m, 3H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.0, 150.0, 146.7, 143.6, 140.6, 136.8, 135.4, 134.4, 133.2, 132.5, 131.7, 130.0, 129.2, 128.8, 128.5, 128.3, 128.0, 128.0, 127.9, 127.7, 126.9, 126.5, 126.2, 125.1, 124.9, 65.0, 41.5, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{36}H_{29}NO_3SNa$ 578.1760; found 578.1766. **FTIR (cm^{-1})** 2921, 2356, 1657, 1488, 1350, 1158.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-(4-methoxyphenyl)-4-methyl benzenesulfonamide (3x)

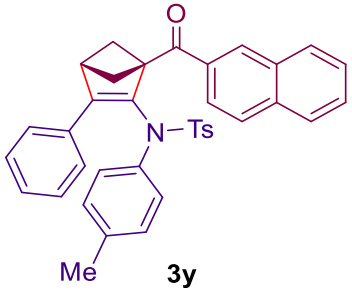
Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and *N*-(4-methoxyphenyl)-4-methyl-*N*-(phenylethynyl)benzene sulfonamide **2x** (152 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-(4-methoxyphenyl)-4-methylbenzene sulfonamide **3x** as white solid (64 mg, 55% yield).



3x

***R*$_f$** (Pet. ether/EtOAc = 90/10): 0.3; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (s, 1H), 7.96-7.94 (m, 1H), 7.90– 7.86 (m, 2H), 7.84 – 7.82 (m, 1H), 7.60 – 7.56 (m, 1H), 7.53-7.49 (m, 1H), 7.46-7.44 (m, 2H), 7.27-7.26 (m, 1H), 7.24-7.22 (m, 4H), 7.16-7.14 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.50-6.47 (m, 2H), 3.56 (s, 3H), 3.51 (s, 2H), 3.08-3.06 (m, 3H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.0, 158.2, 155.3, 149.4, 147.3, 143.4, 137.0, 135.4, 134.3, 133.6, 133.1, 132.5, 131.8, 130.1, 129.1, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 127.0, 126.6, 124.8, 113.9, 67.8, 64.9, 55.2, 41.6, 27.1, 21.6. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{37}H_{31}NO_4SNa$ 608.1866; found 608.1874. **FTIR (cm^{-1})** 2991, 2359, 1659, 1602, 1505, 1457.

_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-methyl-_N_-(_p_-tolyl)benzene sulfonamide (3y)



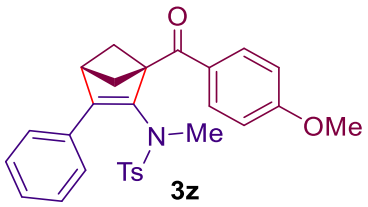
3y

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-2-yl)methanone **1a** (42 mg, 0.2 mmol) and 4-methyl-*N*-(phenylethynyl)-*N*-(*p*-tolyl)benzene sulfonamide **2y** (145 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction

mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-methyl-*N*-(*p*-tolyl)benzenesulfonamide **3y** as white solid (61 mg, 54% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.55; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.40 (s, 1H), 7.92 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 7.85 – 7.79 (m, 3H), 7.56 (t, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.42 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.19 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.54 (s, 2H), 3.10 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.9, 149.8, 146.8, 143.4, 137.9, 137.2, 136.3, 135.4, 134.3, 133.4, 132.4, 131.7, 130.0, 129.5, 129.1, 128.4, 128.4, 128.0, 128.0, 127.9, 127.7, 127.0, 126.4, 125.5, 124.8, 67.7, 65.1, 41.4, 21.6, 20.9 *(1 signal in the aliphatic region is overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{37}H_{31}NO_3SNa$ 592.1917; found 592.1925. **FTIR (cm^{-1})** 2987, 2377, 1658, 1505, 1351, 1161.

_N_-(1-(4-Methoxybenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3z)



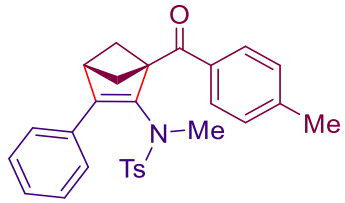
3z

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(4-methoxyphenyl)methanone **1b** (37 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl) benzene sulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(4-methoxybenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide **3z** as white solid (63 mg, 66% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.2; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.17 – 7.13 (m, 3H), 7.08 (t, *J*= 7.8 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 7.7 Hz, 2H), 3.87 (s, 3H), 3.29 (s, 2H), 3.06 (s, 2H), 3.01 (s, 1H), 2.97 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.7, 163.2, 148.1, 147.7, 143.7, 135.7, 133.2, 131.8, 130.2, 129.7, 128.3, 127.7, 127.6, 126.5, 113.5, 65.5, 55.5, 40.9, 38.0, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{27}NO_4SNa$ 496.1553; found 496.1555. **FTIR (cm^{-1})** 2984, 1753, 1658, 1596, 1506, 1454.

_N_,4-Dimethyl-_N_-(1-(4-methylbenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide (3aa)

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(*p*-tolyl)methanone **1c** (35 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by

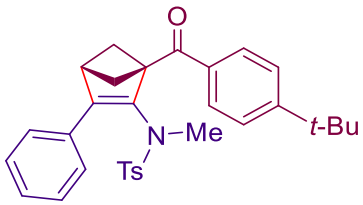


3aa

column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*,4-dimethyl-*N*-(1-(4-methylbenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide **3aa** as white solid (66 mg, 73% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.32; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.18 – 7.13 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 3.29 (s, 2H), 3.07 (s, 2H), 3.02 (s, 1H), 2.96 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 197.7, 148.0, 147.5, 143.7, 143.3, 135.7, 134.6, 133.2, 129.7, 129.6, 128.9, 128.2, 127.7, 127.5, 126.5, 65.6, 40.9, 37.9, 21.8, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{27}NO_3SNa$ 480.1604; found 480.1610. **FTIR (cm^{-1})** 2988, 2356, 1664, 1446, 1345, 1158.

_N_-(1-(4-(_tert_-Butyl)benzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3ab)

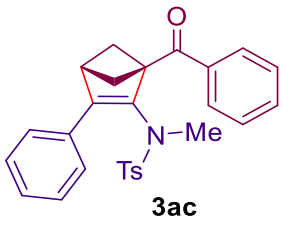


3ab

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(4-(*tert*-butyl)phenyl)methanone **1d** (43 mg, 0.2 mmol) and N,4-dimethyl-*N*-(phenylethynyl) benzenesulfonamide **2a** (114 mg, 0.4 mmol) with Sc(OTf)$_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(4-(*tert*-butyl)benzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3ab** as white solid (71 mg, 71% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.24; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.08 (m, 5H), 6.82 (d, *J* = 7.4 Hz, 2H), 3.30 (s, 2H), 3.06 (s, 2H), 3.02 (m, 1H), 3.00 (m, 3H), 2.36 (s, 3H), 1.35 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 197.8, 156.2, 148.2, 147.6, 143.6, 135.8, 134.5, 133.1, 129.6, 129.5, 128.3, 127.7, 127.5, 126.4, 125.1, 65.4, 40.9, 38.0, 35.2, 31.2, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{33}NO_3SNa$ 522.2073; found 522.2076. **FTIR (cm^{-1})** 2961, 2357, 1663, 1456, 1345, 1156.

***N*-(1-Benzoyl-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide (3ac)**

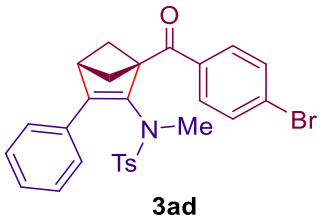


3ac

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(phenyl)methanone **1e** (32 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-benzoyl-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3ac** as white solid (58 mg, 65% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.22; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 – 7.96 (m, 2H), 7.59 – 7.52 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.13 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.73 – 6.71 (m, 2H), 3.30 (s, 2H), 3.09 (s, 2H), 3.03 (s, 1H), 2.95 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 147.9, 147.3, 143.7, 137.2, 135.6, 133.0, 132.6, 129.7, 129.4, 128.2, 128.1, 127.7, 127.4, 126.4, 65.6, 40.9, 37.8, 21.5 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{25}NO_3SNa$ 466.1447; found 466.1450. **FTIR (cm^{-1})** 2988, 2358, 1667, 1490, 1345, 1156.

***N*-(1-(4-Bromobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3ad)**

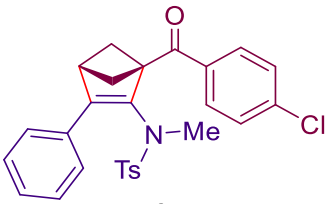


3ad

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(4-bromophenyl)methanone **1f** (47 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzene sulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(4-bromobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide **3ad** as white solid (78 mg, 75% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.32; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.66 (d, *J* = 7.1 Hz, 2H), 3.27 (s, 2H), 3.07 (s, 2H), 3.02 (s, 1H), 2.95 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.1, 147.8, 147.1, 143.9, 136.0, 135.4, 132.9, 131.5, 130.9, 129.8, 128.2, 127.8, 127.7, 127.5, 126.4, 65.4, 41.0, 37.9, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}BrNO_3SNa$ 544.0552; found 544.0555. **FTIR (cm^{-1})** 2989, 2356, 1672, 1446, 1350, 1160.

***N*-(1-(4-Chlorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3ae)**

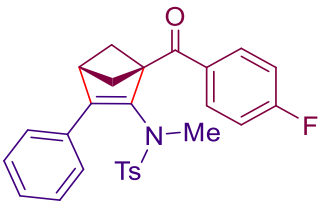


3ae

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(4-chlorophenyl)methanone **1g** (38 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzene sulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(4-chlorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide **3ae** as white solid (87 mg, 90% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.27; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.66 (d, *J* = 7.8 Hz, 2H), 3.28 (s, 2H), 3.07 (s, 2H), 3.02 (s, 1H), 2.95 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.9, 147.8, 147.1, 143.9, 138.9, 135.6, 135.4, 133.0, 130.8, 129.8, 128.5, 128.2, 127.8, 127.5, 126.4, 65.4, 41.0, 37.9, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}ClNO_3SNa$ 500.1058; found 500.1066. **FTIR (cm^{-1})** 2991, 2357, 1671, 1590, 1350, 1160.

***N*-(1-(4-Fluorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3af)**



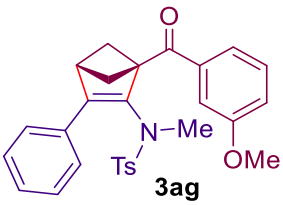
3af

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(4-fluorophenyl)methanone **1h** (35 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(4-fluorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3af** as white solid (74 mg, 80% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.21; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 (q, J_1 = 8.7 Hz, J_2 = 7.5 Hz, 3H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.66 – 6.64 (m, 2H), 3.28 (s, 2H), 3.08 (s, 2H), 3.02 (s, 1H), 2.95 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.5, 165.4 (*J* = 254.8 Hz), 147.8, 147.1, 143.9, 135.3, 133.6 (*J* = 3.0 Hz), 132.9, 132.0 (*J* = 8.9 Hz), 129.8, 128.2, 127.8, 127.4, 126.4, 115.2 (*J* = 21.8 Hz), 65.4, 41.0, 37.8, 21.6 *(2 signals in the aliphatic region are*

overlapping). **^{19}F NMR (376 MHz, $CDCl_3$)** δ = -106.0. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}FNO_3SNa$ 484.1353; found 484.1360. **FTIR (cm^{-1})** 3020, 2359, 1667, 1598, 1349, 1156.

_N_-(1-(3-Methoxybenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethyl benzene sulfonamide (3ag)

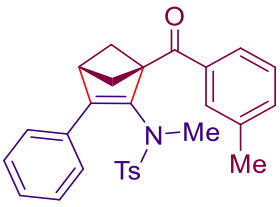


3ag

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(3-methoxyphenyl)methanone **1i** (37 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzene sulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(3-methoxybenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3ag** as white solid (62 mg, 65% yield).

***R*$_f$** (Pet. ether/EtOAc = 90/10): 0.2; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58-7.55 (m, 2H), 7.53-7.31 (m, 1H), 7.37 – 7.31 (m, 2H), 7.17 (d, *J*= 8.2 Hz, 2H), 7.13 (d, *J*= 7.9 Hz, 1H), 7.09-7.04 (m, 3H), 6.73 (d, *J*= 7.1 Hz, 2H), 3.86 (s, 3H) 3.29 (s, 2H), 3.08 (s, 2H), 3.02 (s, 1H), 2.95 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.9, 159.6, 147.4, 143.7, 138.5, 135.7, 133.1, 129.7, 129.1, 128.5, 128.2, 127.8, 127.5, 126.4, 122.1, 119.1, 113.8, 65.6, 55.5, 40.9, 37.9, 21.6 *(2 signals in the aliphatic region are overlapping).* **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{27}NO_4SNa$ 496.1553; found 496.1558. **FTIR (cm^{-1})** 2989, 2357, 1752, 1668, 1589, 1484.

_N_,4-Dimethyl-_N_-(1-(3-methylbenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide (3ah)



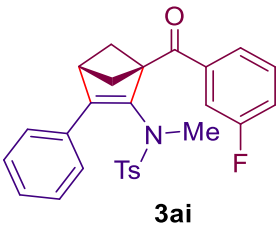
3ah

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(*m*-tolyl)methanone **1j** (35 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*,4-dimethyl-*N*-(1-(3-methylbenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)benzenesulfonamide **3ah** as white solid (63 mg, 70% yield).

***R*$_f$** (Pet. ether/EtOAc = 90/10): 0.28; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (s, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.18 – 7.15 (m, 3H), 7.07 (t, *J* = 6.2 Hz, 2H), 6.74 (d, *J*

= 8.6 Hz, 2H), 3.29 (s, 2H), 3.08 (s, 2H), 3.02 (s, 1H), 2.94 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.2, 148.0, 147.4, 143.7, 137.9, 137.2, 135.7, 133.4, 133.1, 130.0, 129.7, 128.3, 128.0, 127.8, 127.5, 126.7, 126.4, 65.7, 40.9, 37.9, 21.6, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{27}NO_3SNa$ 480.1604; found 480.1609. **FTIR (cm^{-1})** 2941, 2357, 1668, 1448, 1347, 1159.

_N_-(1-(3-Fluorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3ai)

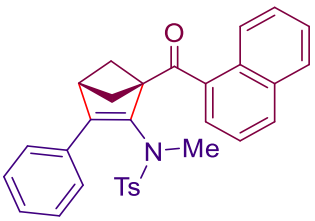


3ai

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(3-fluorophenyl)methanone **1k** (35 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N* -(1-(3-fluorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3ai** as white solid (70 mg, 76% yield).

***R*$_f$** (Pet. ether/EtOAc = 90/10): 0.19; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.59 (m, 3H), 7.43 (q, *J* = 7.9 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 3.28 (s, 2H), 3.09 (s, 2H), 3.03 (s, 1H), 2.95 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.7 (*J* = 2.0 Hz), 162.6 (*J* = 246.5 Hz), 147.8, 147.0, 143.9, 139.3 (*J* = 6.3 Hz), 135.4, 132.9, 129.8, 129.7, 128.2, 127.9, 127.5, 126.4, 125.2 (*J* = 2.9 Hz), 119.5 (*J* = 21.4 Hz), 116.1 (*J* = 22.5 Hz), 65.5, 41.0, 37.9, 21.6 *(2 signals in the aliphatic region are overlapping)*. **^{19}F NMR (376 MHz, $CDCl_3$)** δ = -112.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}FNO_3SNa$ 484.1353; found 484.1363. **FTIR (cm^{-1})** 2986, 1674, 1589, 1486, 1347, 1159.

_N_-(1-(1-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3aj)



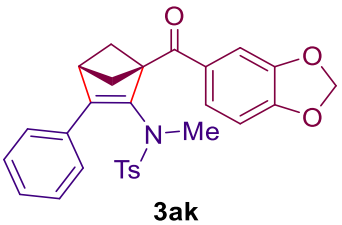
3aj

Following the general procedure, treatment of bicyclo[1.1.0] butan-1-yl(naphthalen-1-yl)methanone **1l** (42 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl) benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(1-naphthoyl)-3-

phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide **3aj** as white solid (51 mg, 51% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.3; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.58 (d, *J* = 8.9 Hz, 1H), 8.04 (d, *J* = 7.1 Hz, 1H), 7.98 (d, *J*= 8.9 Hz, 1H), 7.88 (d, *J*= 8.5 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.53-7.49 (m, 2H), 7.14-7.03 (m, 5H), 6.82 (d, *J* = 6.8 Hz, 2H), 3.30 (s, 2H), 3.09 (s, 2H), 3.02 (s, 4H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.8, 148.8, 147.0, 143.5, 136.5, 135.4, 134.1, 132.9, 132.2, 130.9, 129.6, 128.3, 128.3, 128.2, 127.7, 127.6, 127.3, 126.5, 126.4, 126.3, 124.0, 66.5, 40.2, 37.9, 21.5 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI) m/z: [M+Na]+** calcd for $C_{31}H_{27}NO_3SNa$ 516.1604; found 516.1607. **FTIR (cm^{-1})** 2924, 1664, 1461, 1352, 1215.

_N_-(1-(Benzo[_d_][1,3]dioxole-5-carbonyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzenesulfonamide (3ak)



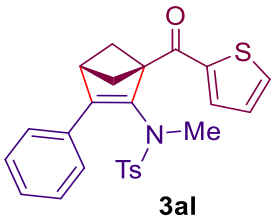
3ak

Following the general procedure, treatment of benzo[*d*][1,3]dioxol-5-yl(bicyclo[1.1.0]butan-1-yl)methanone **1m** (41 mg, 0.2 mmol) and N,4-dimethyl-*N*-(phenylethynyl) benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(benzo[*d*][1,3]dioxole-5-carbonyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide **3ak** as white solid (53 mg, 65% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.2; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J*=7.5 Hz, 3H), 7.46 (s, 1H), 7.19 – 7.12 (m, 3H), 7.07 (t, *J*=7.4 Hz, 2H), 6.84 (d, *J*= 7.9 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 6.03 (s, 2H), 3.27 (s, 2H), 3.06 (s, 2H), 3.00 (s, 1H), 2.97 (s, 3H), 2.38 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.0, 151.4, 148.0, 147.9, 147.5, 143.7, 135.7, 133.1, 131.8, 129.7, 128.3, 127.7, 127.5, 126.5, 126.0, 109.3, 107.6, 101.8, 65.4, 40.9, 38.0, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}NO_5SNa$ 510.1346; found 510.1351. **FTIR (cm^{-1})** 2904, 2357, 1659, 1604, 1490, 1439.

***N*,4-Dimethyl-*N*-(3-phenyl-1-(thiophene-2-carbonyl)bicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide (3al)**

Following the general procedure, treatment of bicyclo[1.1.0]butan-1-yl(thiophen-2-yl)methanone **1n** (33 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction

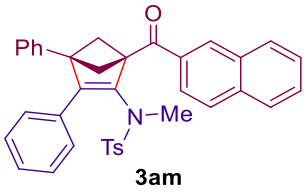


3al

mixture using silica gel afforded *N*,4-dimethyl-*N*-(3-phenyl-1-(thiophene-2-carbonyl)bicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide **3al** as white solid (69 mg, 77% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 3.9 Hz, 1H), 7.64 (d, *J* = 4.9 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.12 (m, 6H), 6.89 (d, *J* = 8.4 Hz, 2H), 3.30 (s, 2H), 3.08 (s, 2H), 3.05 – 3.03 (m, 4H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.7, 148.5, 147.4, 143.8, 143.6, 135.8, 133.6, 133.4, 133.0, 129.6, 128.3, 128.0, 127.8, 127.6, 126.5, 64.9, 40.8, 38.0, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NO_3S_2Na$ 472.1012; found 472.1016. **FTIR (cm^{-1})** 2988, 2356, 1746, 1450, 1350, 1157.

_N_-(1-(2-Naphthoyl)-3,4-diphenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3am)

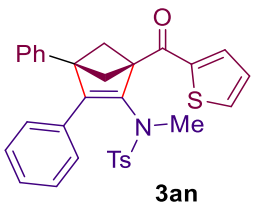


3am

Following the general procedure, treatment of naphthalen-2-yl(3-phenylbicyclo[1.1.0]butan-1-yl)methanone **1o** (57 mg, 0.2 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzene sulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-(1-(2-naphthoyl)-3,4-diphenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide **3am** as white solid (40 mg, 35% yield).

***R*f** (Pet. ether/EtOAc = 90/10): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (s, 1H), 8.13 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.59 (t, *J* = 6.8 Hz, 1H), 7.53 (t, *J* = 6.8 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.13 (m, 5H), 7.03 – 7.00 (m, 3H), 6.86 (t, *J* = 7.8 Hz, 2H), 6.31 (d, *J* = 7.1 Hz, 2H), 3.91 – 3.90 (m, 2H), 3.28 – 3.27 (m, 2H), 2.83 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.7, 149.6, 148.9, 143.7, 139.7, 135.6, 134.9, 134.3, 132.7, 132.5, 131.6, 129.8, 129.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.4, 127.0, 126.8, 126.7, 125.2, 60.5, 55.1, 38.4, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{37}H_{31}NO_3SNa$ 592.1917; found 592.1922. **FTIR (cm^{-1})** 3026, 2952, 1731, 1441, 1341, 1249, 1157, 757.

***N*-(3,4-Diphenyl-1-(thiophene-2-carbonyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide (3an)**



3an

Following the general procedure, treatment of 3-phenylbicyclo[1.1.0]butan-1-yl)(thiophen-2-yl)methanone **1p** (41 mg, 0.2 mmol) and *N*-((4-chlorophenyl)ethynyl)-*N*,4-dimethylbenzene sulfonamide **2a** (114 mg, 0.4 mmol) with $Sc(OTf)_3$ (10 mg, 0.02 mmol) in CH_2Cl_2 (2.0 mL) at 30 °C for 18 h followed by column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded *N*-3,4-diphenyl-1-(thiophene-2-carbonyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide **3an** as yellow sticky-solid (58 mg, 55% yield).

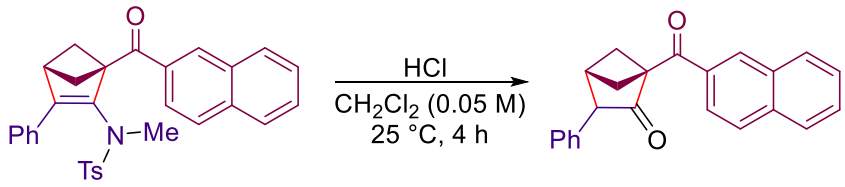
***R*f** (Pet. ether/EtOAc = 90/10): 0.4; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.88 (m, 1H), 7.67 (d, *J* = 5.0 Hz, H), 7.49 (d, *J* =7.5 Hz, 2H), 7.20-7.15 (m, 6H), 7.00 (d, *J*= 8.0 Hz, 3H), 6.87 (t, *J* = 7.2 Hz, 2H), 6.37 (d, *J* = 8.1 Hz, 2H), 3.82 (s, 2H), 3.21-3.20 (m, 2H), 2.87 (s, 3H), 2.39-2.35 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.6, 149.9, 148.9, 143.7, 143.6, 139.6, 135.2, 133.7, 133.6, 132.6, 129.6, 128.3, 128.1, 128.1, 127.8, 127.7, 127.4, 127.0, 126.8, 59.9, 55.0, 38.5, 21.6 *(2 signals in the aliphatic region are overlapping)*. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{31}H_{27}NO_3S_2Na$ 548.1325; found 548.1326. **FTIR (cm^{-1})** 3059, 2940, 1697, 1447, 1352, 1161, 730.

7. Product Functionalization

a) Hydrolysis of 3a

Following the modified literature procedure,[3] to a Schlenk tube equipped with a magnetic stir bar was added **3a** (49.4 mg, 0.10 mmol, 1.0 equiv) and dry CH_2Cl_2 (2 mL). Then, HCl (37 w%, 20 µL, 2.0 equiv) was added slowly to it. The reaction was then stirred at 25 °C for 4 h. Then aqueous saturated $NaHCO_3$ solution (1.0 mL) was added to quench the reaction. The organic layer was extracted with CH_2Cl_2 (3 x 5 mL), washed with brine (8 mL), dried over Na_2SO_4, filtered and concentrated on rotavapor under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 85/15) to afford the corresponding product **8a** as white solid (28.3 mg, 90% yield).

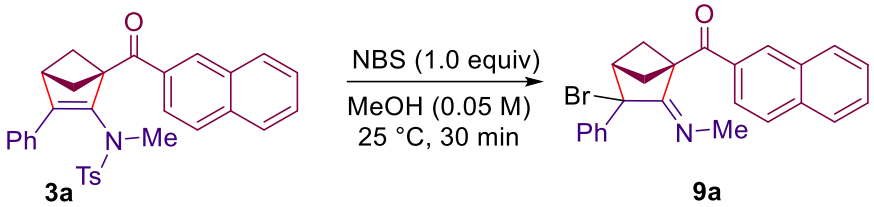
[3] E.-i. Negishi and K. Akiyoshi, *Chem. Lett.*, 1987, **16**, 1007.



3a **8a**, 90%

***R*f** (Pet. ether/EtOAc = 85/15): 0.41; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.25 (s, 1H), 7.91 – 7.85 (m, 4H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 3.91 (s, 1H), 3.19 (s, 1H), 2.78 – 2.75 (m, 1H), 2.67 – 2.63 (m, 1H), 2.59 (t, *J* = 8.6 Hz, 1H), 2.46 (t, *J* = 8.6 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 207.6, 197.1, 136.13, 135.8, 133.1, 132.5, 131.2, 129.9, 128.9, 128.8, 128.6, 127.9, 127.7, 127.3, 126.9, 124.4, 72.9, 55.6, 44.1, 42.6, 35.7. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{23}H_{18}NaO_2$ 349.1199; found 349.1206. **FTIR (cm^{-1})** 2994, 1753, 1661, 1318, 1232, 1180.

b) Bromination of 3a



3a **9a**

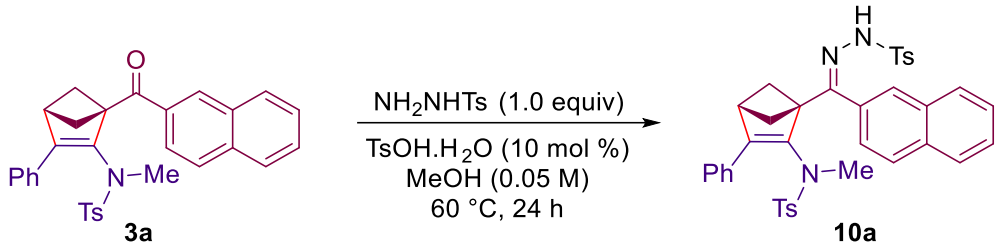
According to the modified literature procedure,[4] to a Schlenk tube containing **3a** (49.4 mg, 0.10 mmol, 1.0 equiv), MeOH (2.0 mL) was added, followed by the addition of NBS (18 mg, 0.10 mmol, 1.0 equiv) to it. The reaction was stirred at 25 °C for 30 min. After reaction completion (monitored by TLC), MeOH is removed by rotavapor. The crude reaction mixture was extracted with ethyl acetate (3 x 5 mL), washed with brine (8 mL), dried over Na_2SO_4, filtered and concentrated on rotavapor under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 90/10) to afford the corresponding product **9a** as white solid (29 mg, 70% yield).

***R*f** (Pet. ether/EtOAc = 85/15): 0.41; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.43 (s, 1H), 8.00 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.60 – 7.53 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.34 (m, 1H), 3.39 (s, 3H), 3.13 (t, *J* = 3.2 Hz, 1H), 2.94 (dd, *J* = 9.9, 7.4 Hz, 1H), 2.63 (dd, *J* = 7.4, 3.2 Hz, 1H), 2.28 (dd, *J* = 7.9, 3.4 Hz, 1H), 2.18 – 2.14 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 198.1, 170.4, 139.8, 135.8, 133.3, 132.6, 131.7, 129.9, 128.7, 128.4, 128.1, 127.9, 126.8, 124.9, 68.7, 67.1, 49.9, 46.6, 42.2, 40.3. **HRMS (ESI)** m/z:

[4] V. M. Lyubchanskaya, T. I. Mukhanova, L. M. Alekseeva and V. G. Granik, *Pharm Chem J.*, 1995, **29**, 780.

$[M+H]^+$ calcd for $C_{24}H_{21}BrNO$ 418.0801; found 418.0804. **FTIR (cm^{-1})** 2893, 1669, 1360, 1180, 992, 764.

c) Hydrazone formation from 3a



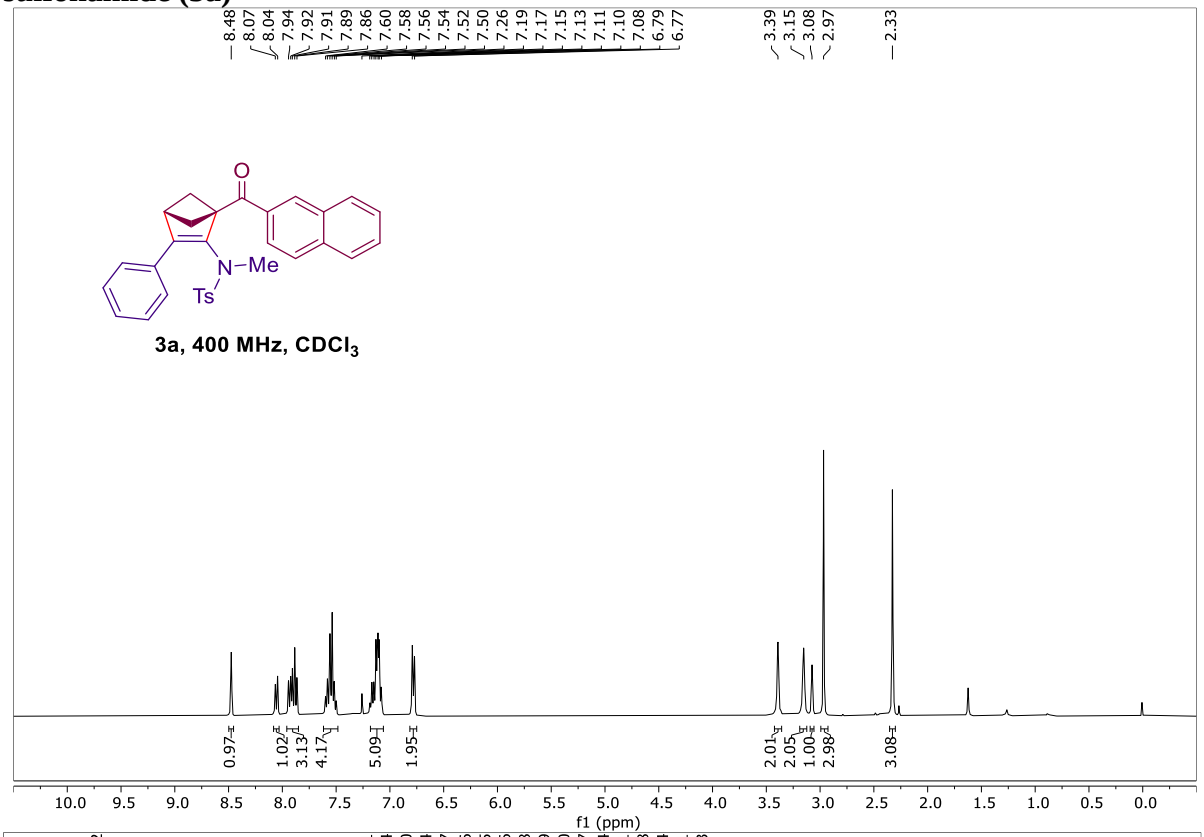
Following the literature procedure,[5] to a Schlenk tube equipped with a magnetic stir bar was added with **3a** (49.4 mg, 0.10 mmol, 1.0 equiv), *p*-toluenesulfonyl hydrazide (19 mg, 0.1 mmol) and methanol (2 ml). To this, *p*-toluenesulfonic acid monohydrate (10 mol%) was added and the reaction mixture was stirred at 60 °C for 24 h and the reaction was monitored by TLC. After reaction completion, the crude reaction mixture concentrated on rotavapor under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 85/15) to afford the corresponding product **10a** as white solid (45 mg, 68% yield).

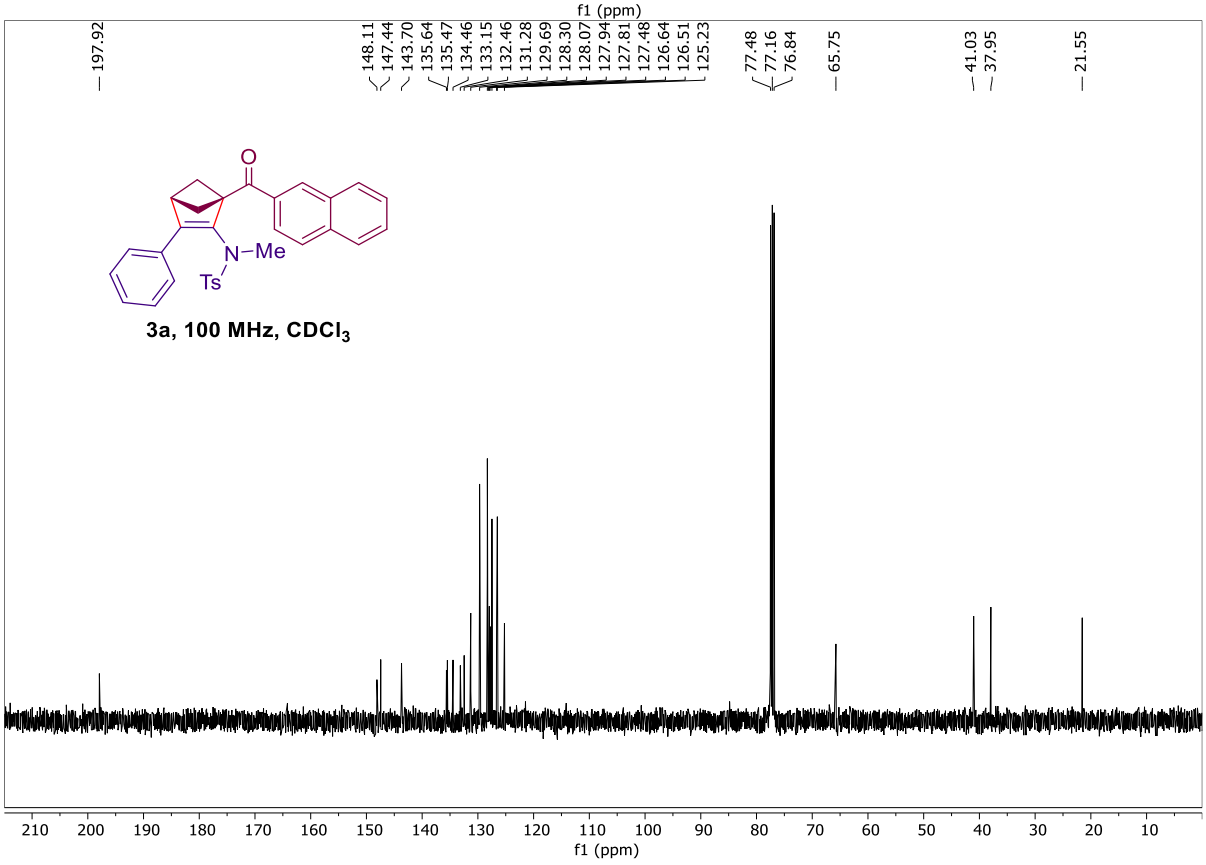
***R*f** (Pet. ether/EtOAc = 80/20): 0.21; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.79 (m, 4H), 7.59 – 7.50 (m, 6H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.20 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.08 – 7.05 (m, 3H), 7.03 – 7.00 (m, 2H), 6.88 – 6.85 (m, 2H), 3.09 – 2.97 (m, 3H), 2.82 – 2.80 (m, 2H), 2.57 (s, 3H), 2.44 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0, 150.5, 147.1, 144.0, 143.2, 137.3, 136.0, 133.4, 133.2, 132.9, 129.6, 129.5, 128.6, 128.2, 128.1, 128.0, 127.5, 127.5, 127.3, 127.1, 126.1, 124.6, 62.0, 39.9, 37.9, 21.8, 21.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{38}H_{35}N_3O_4S_2Na$ 684.1961; found 684.1970. **FTIR (cm^{-1})** 3056, 2868, 2255, 1598, 1444, 1344, 1180, 726.

[5] Z. Huang, Y. Yang, Q. Xiao, Y. Zhang and J. Wang, *Eur. J. Org. Chem.*, 2012, 6586.

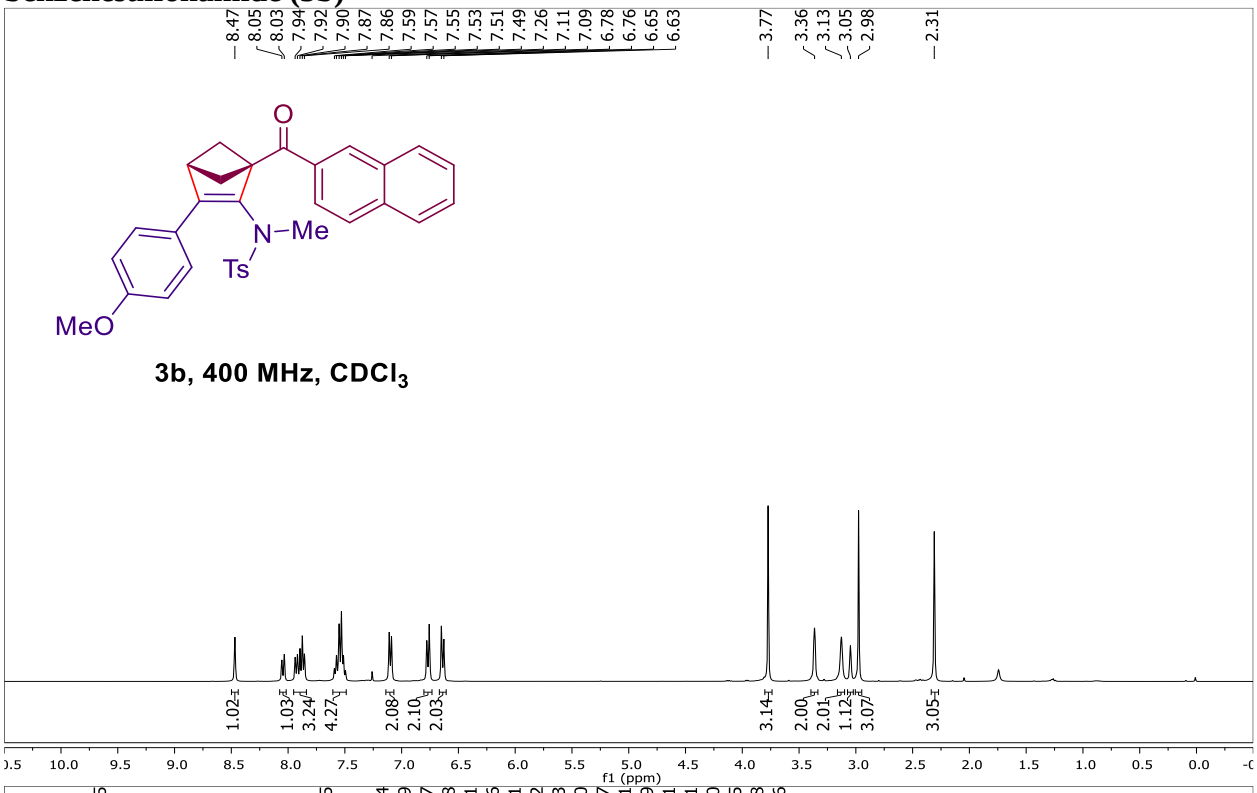
8. ^{1}H and ^{13}C NMR Spectra of 2-Amino Bicyclo[2.1.1]hexenes

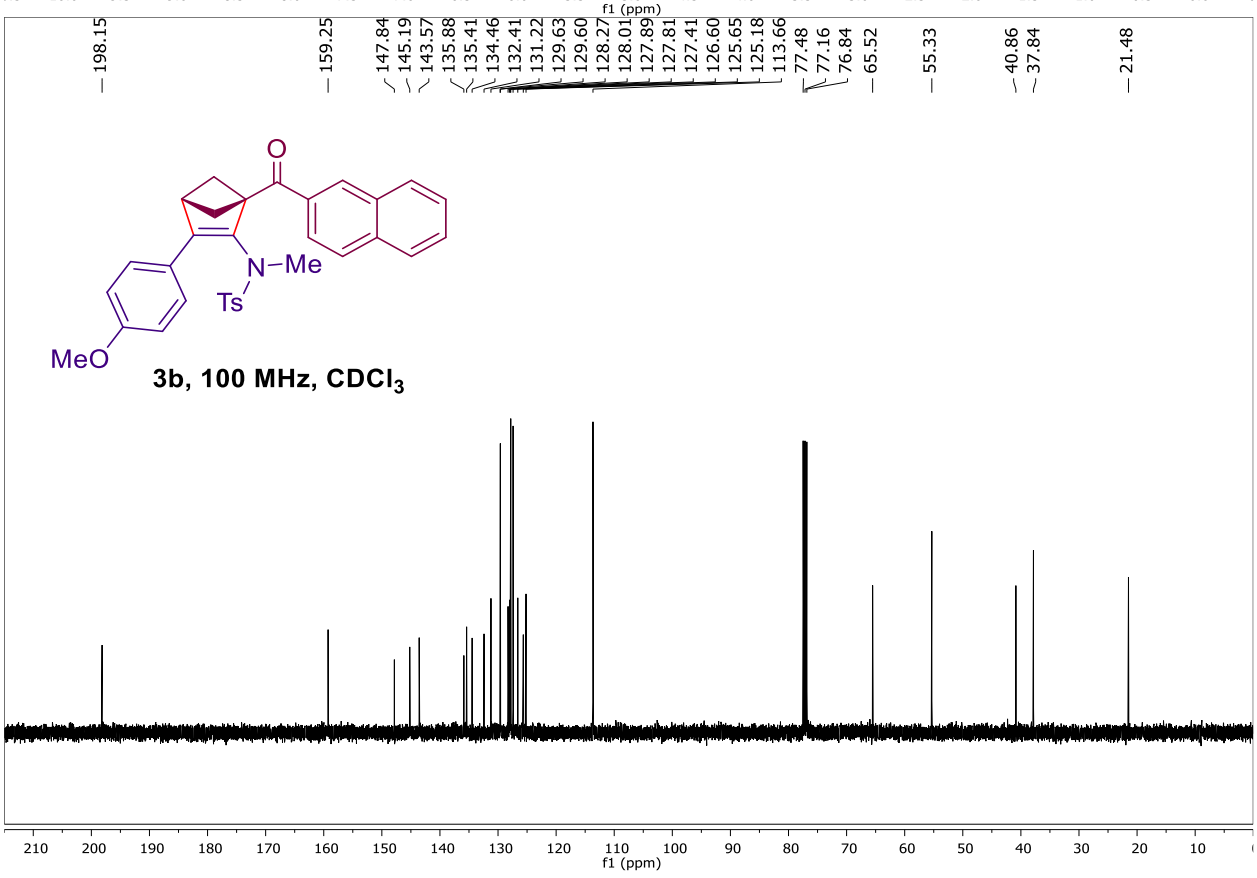
N-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3a)



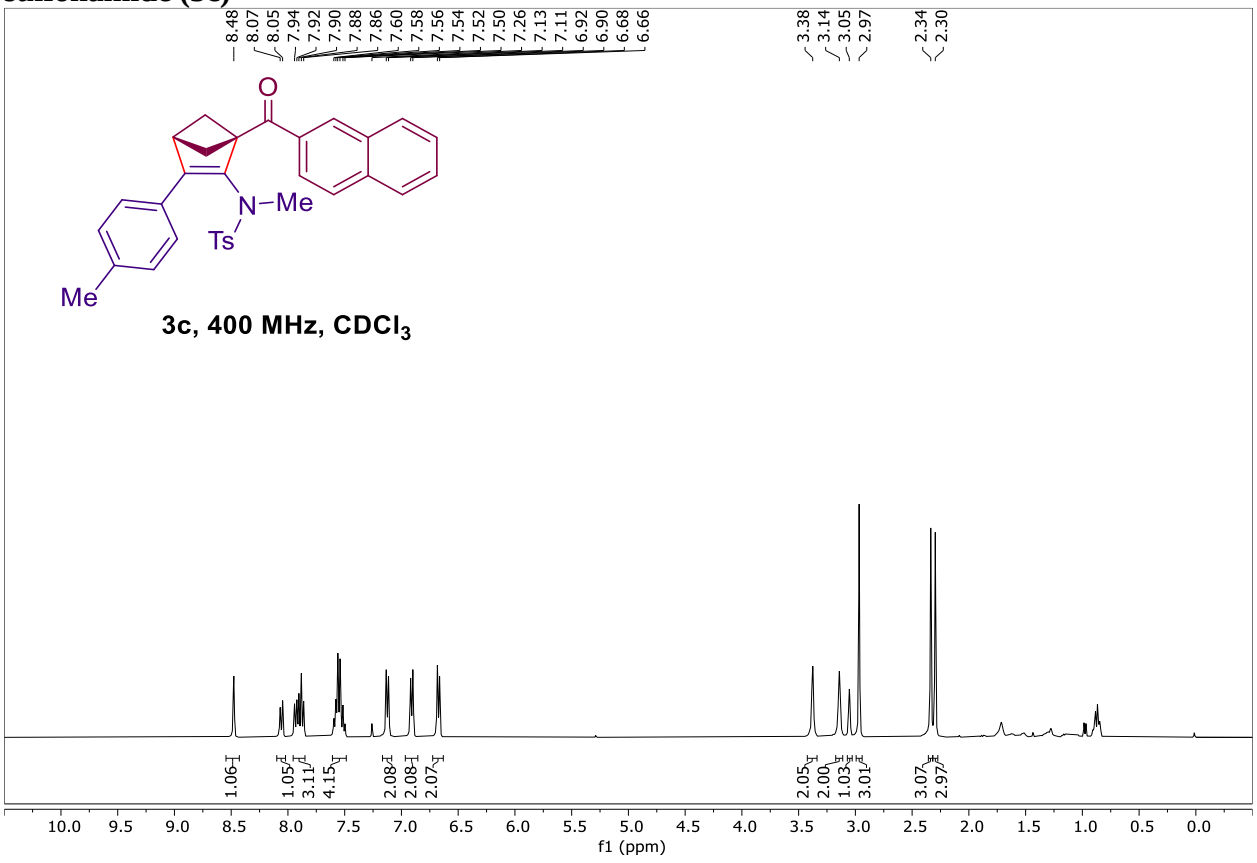


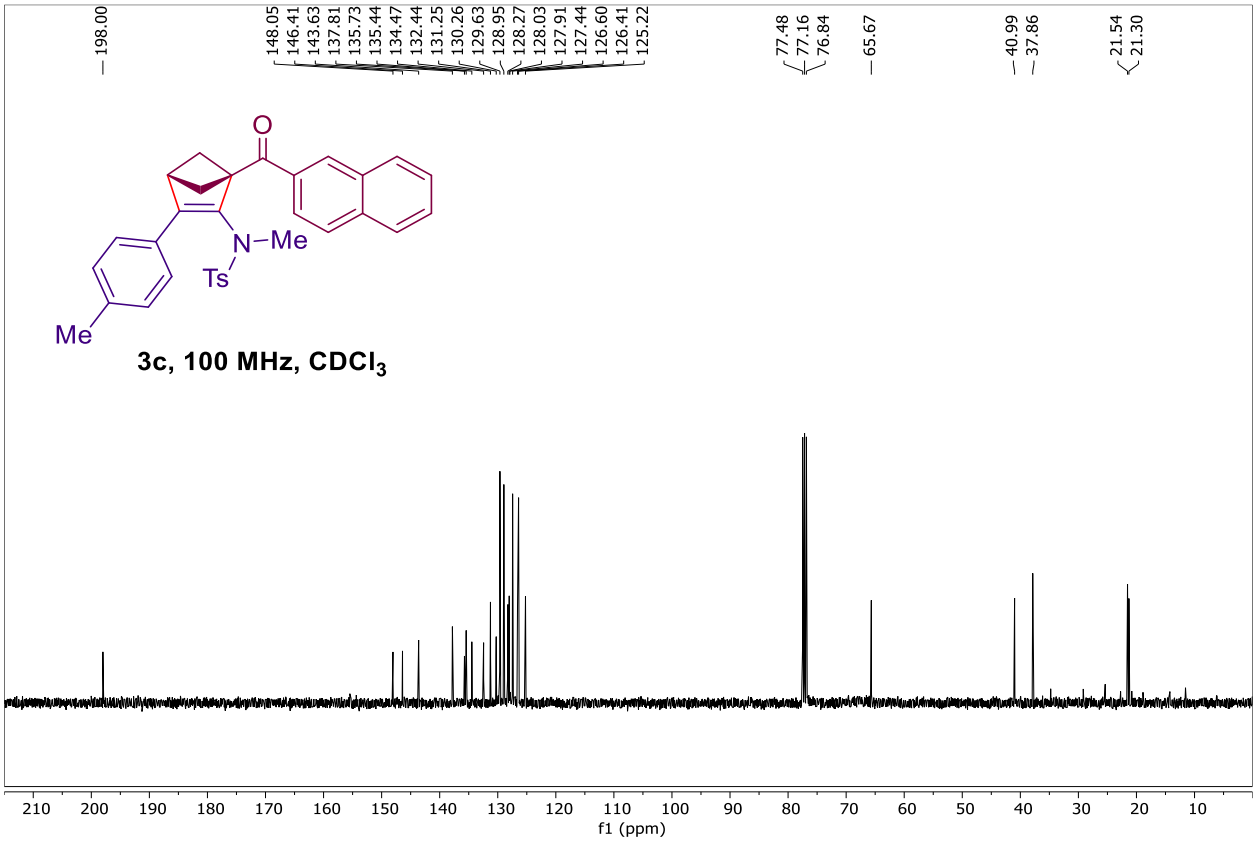
***N*-(1-(2-Naphthoyl)-3-(4-methoxyphenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide (3b)**



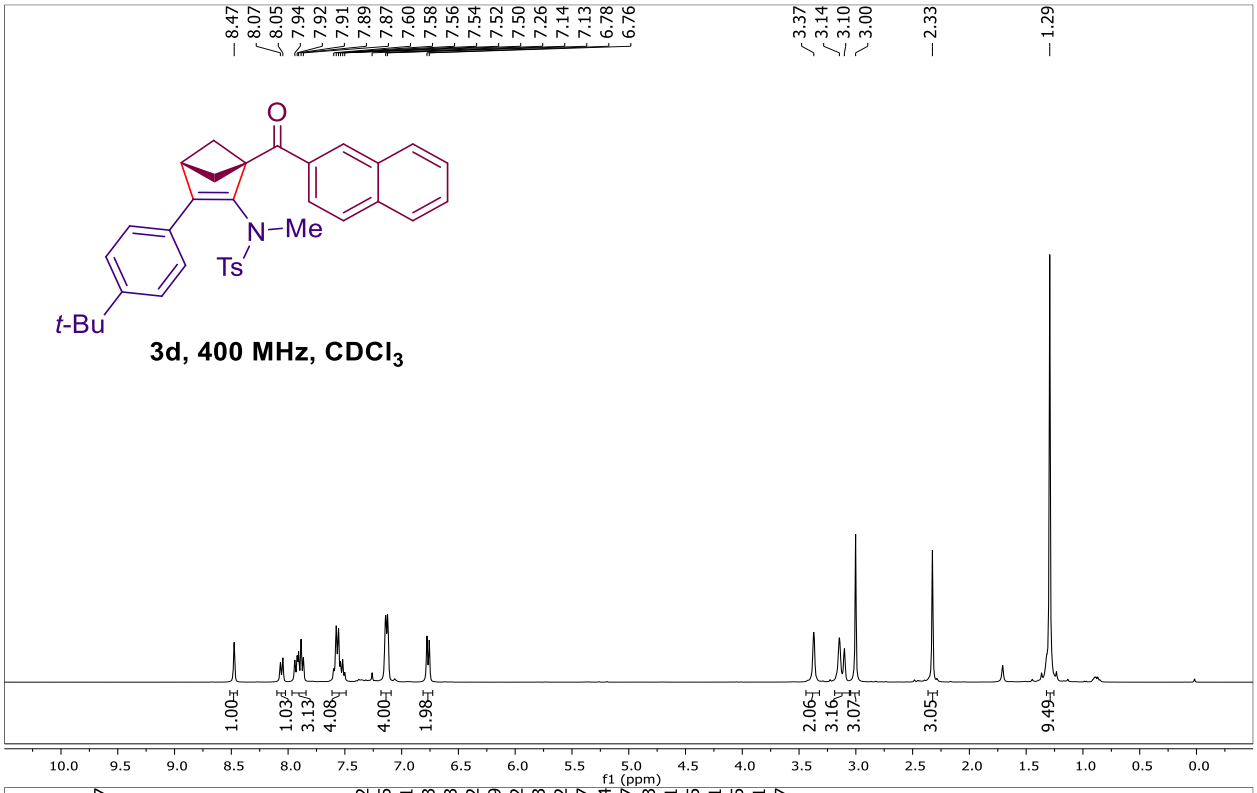


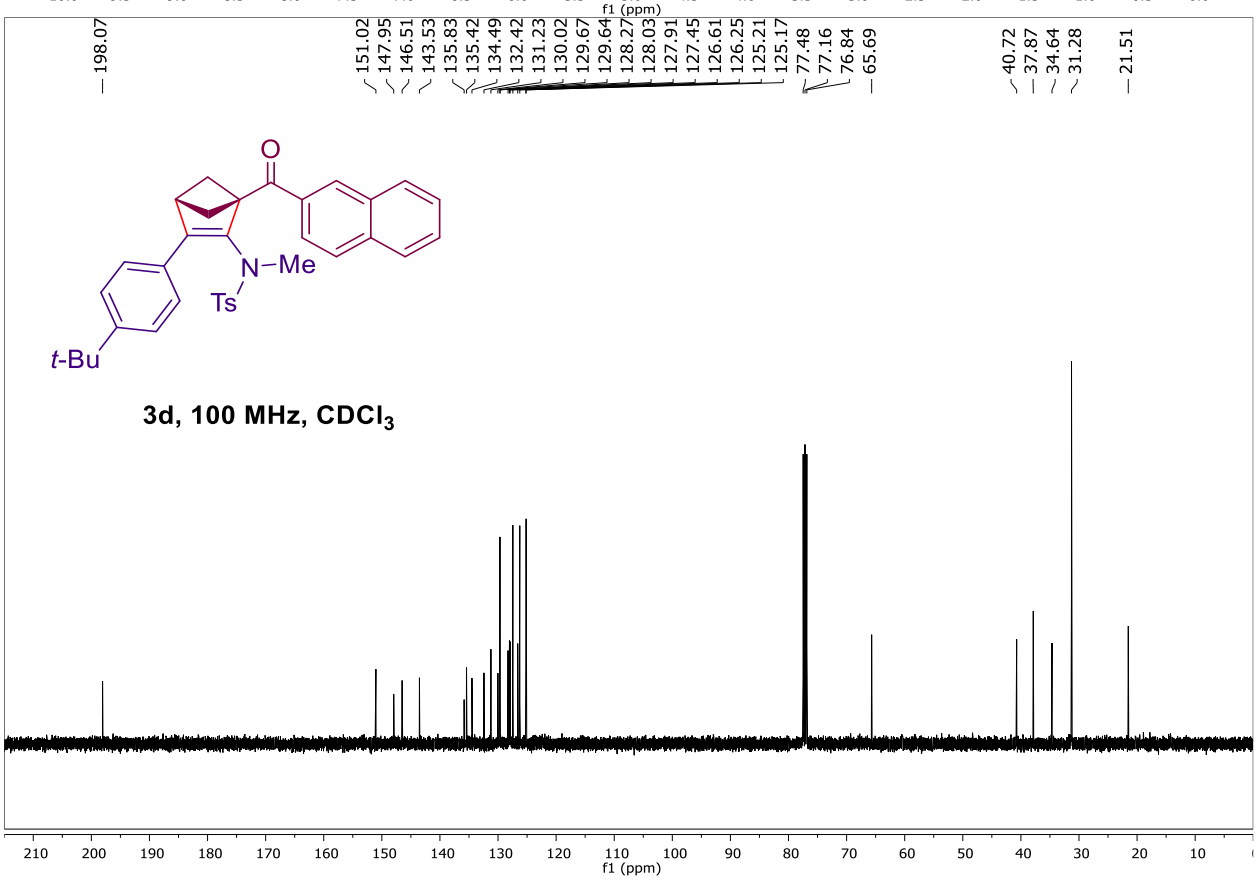
_N_-(1-(2-Naphthoyl)-3-(_p_-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3c)



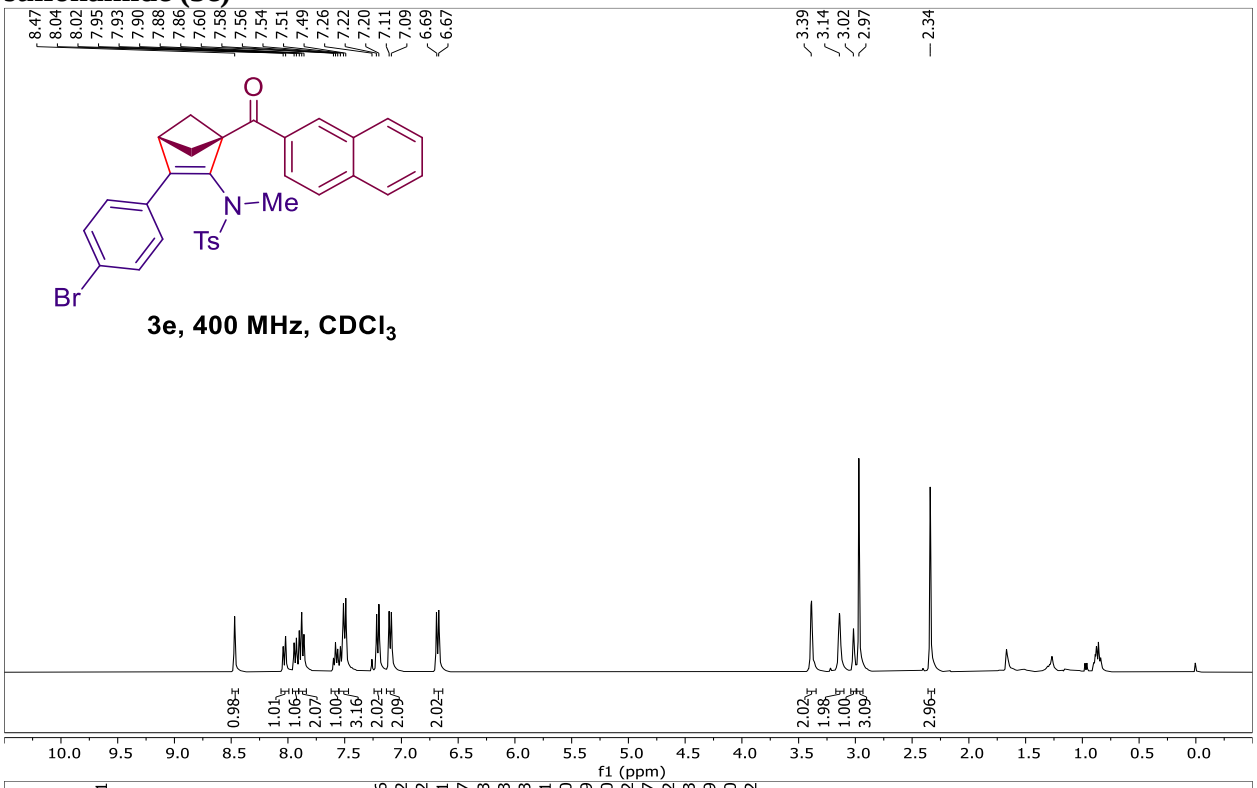


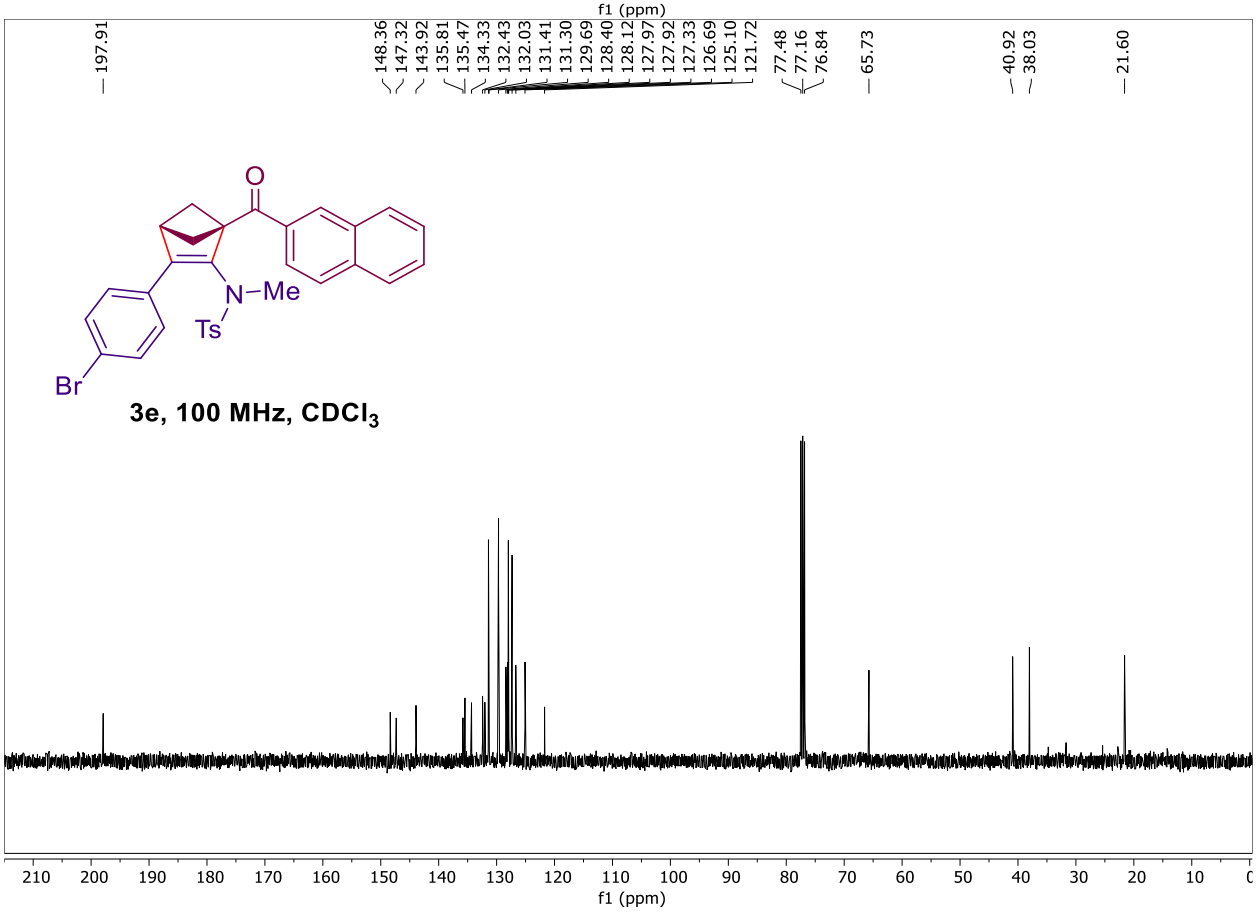
_N_-(1-(2-Naphthoyl)-3-(4-(*tert*-butyl)phenyl)bicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethyl benzenesulfonamide (3d)



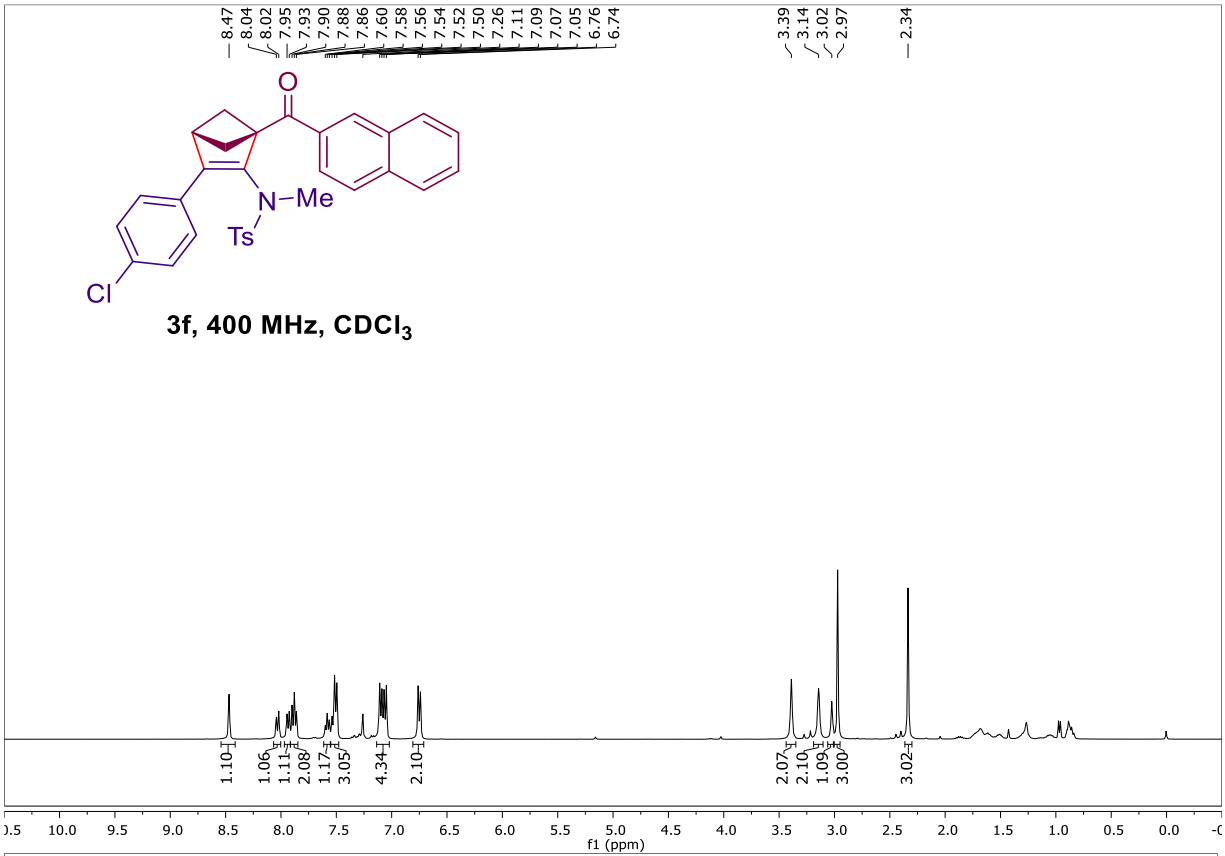


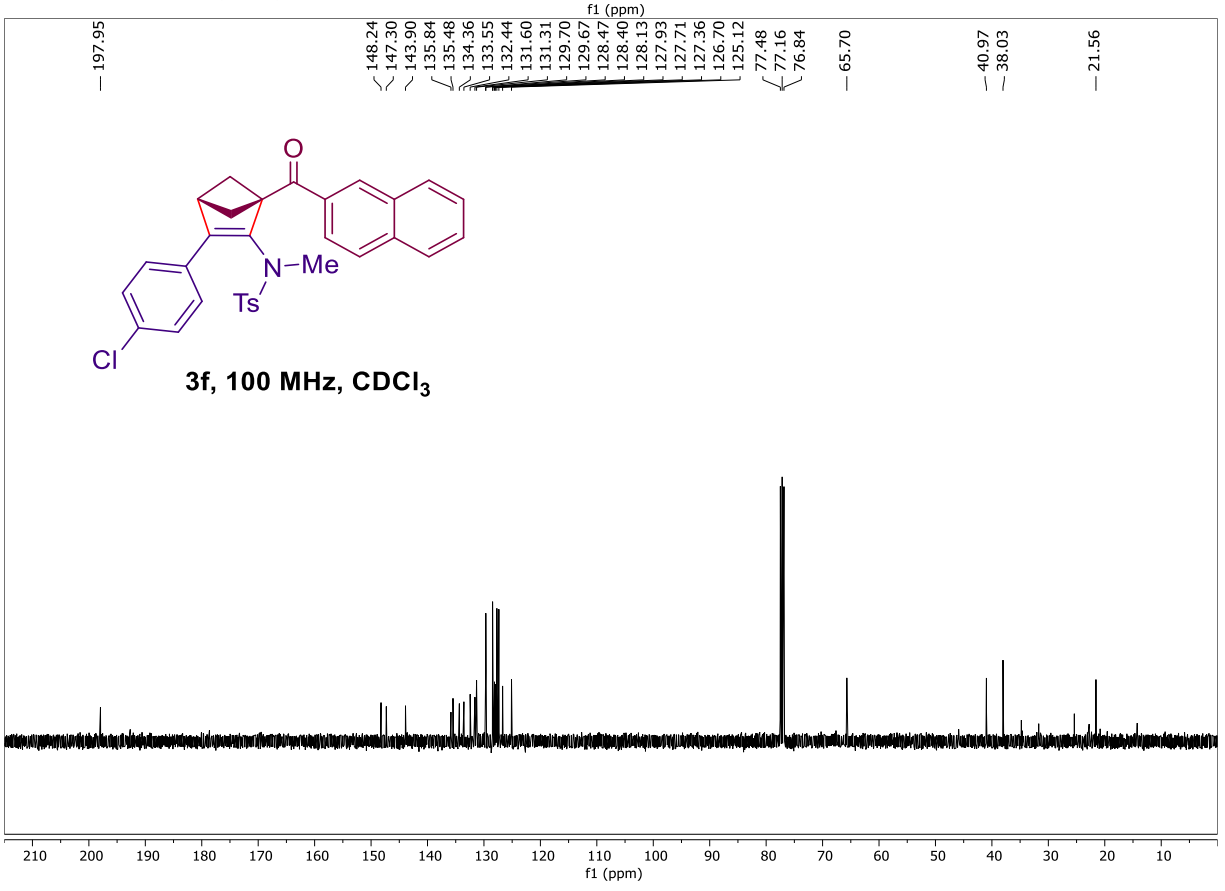
***N*-(1-(2-naphthoyl)-3-(4-bromophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3e)**



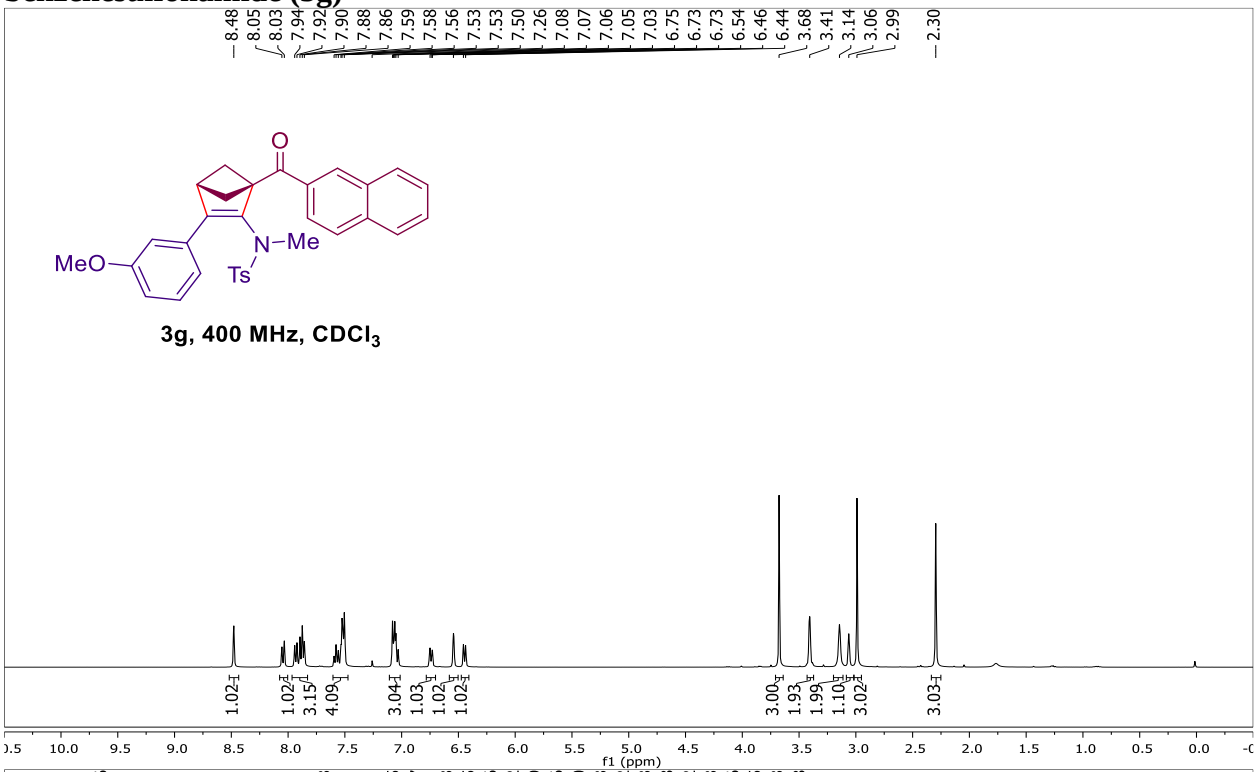


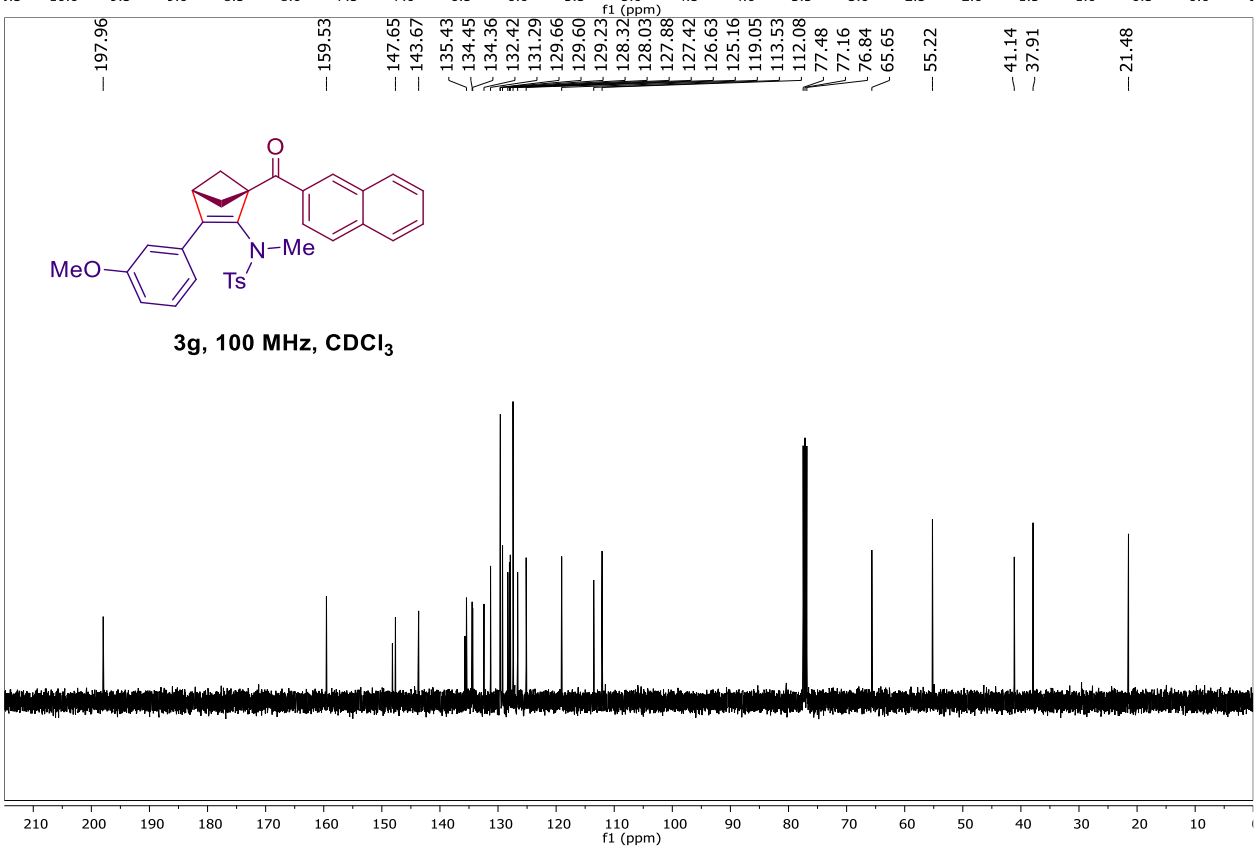
***N*-(1-(2-Naphthoyl)-3-(4-chlorophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide (3f)**



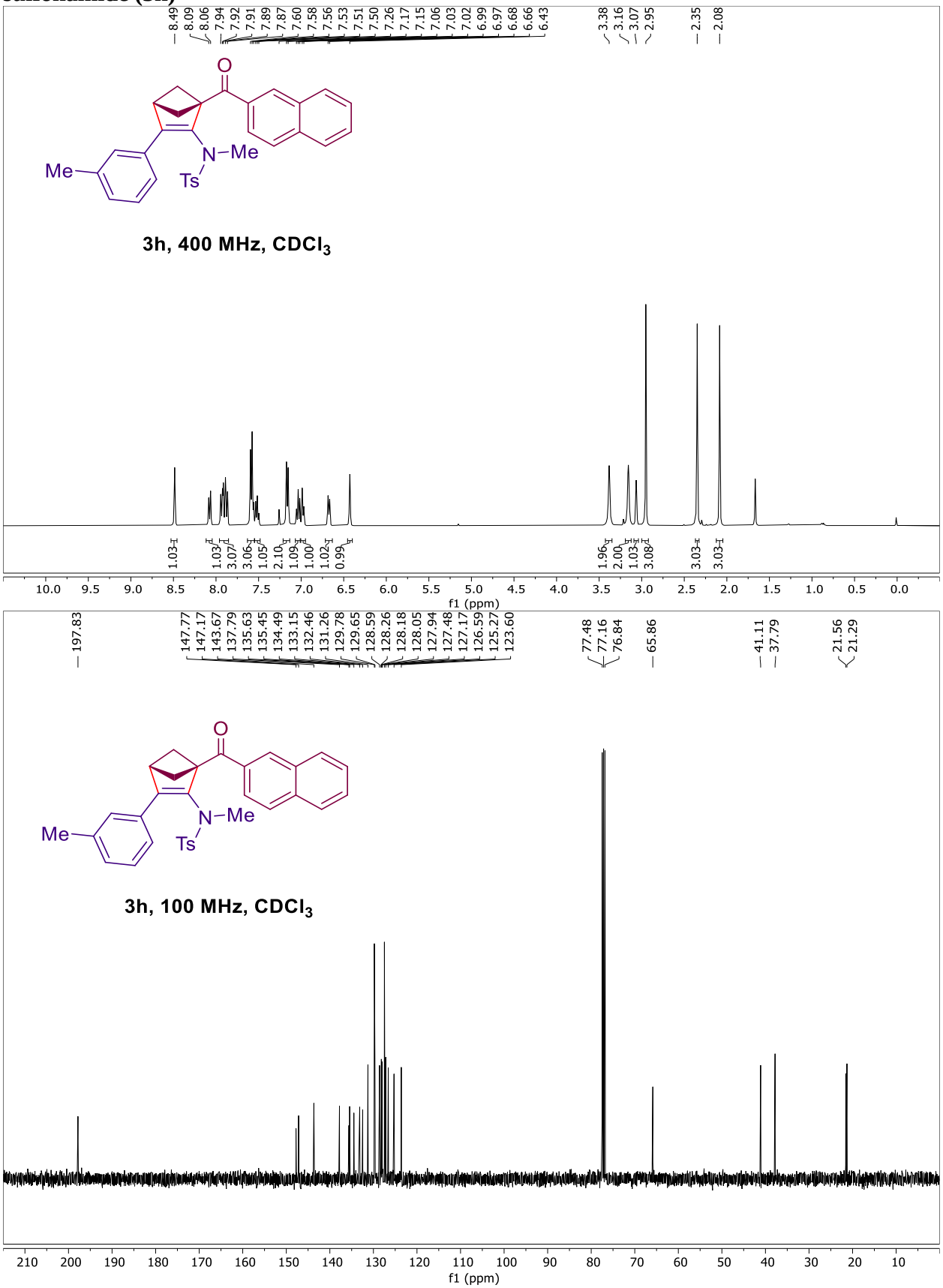


***N*-(1-(2-Naphthoyl)-3-(3-methoxyphenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide (3g)**

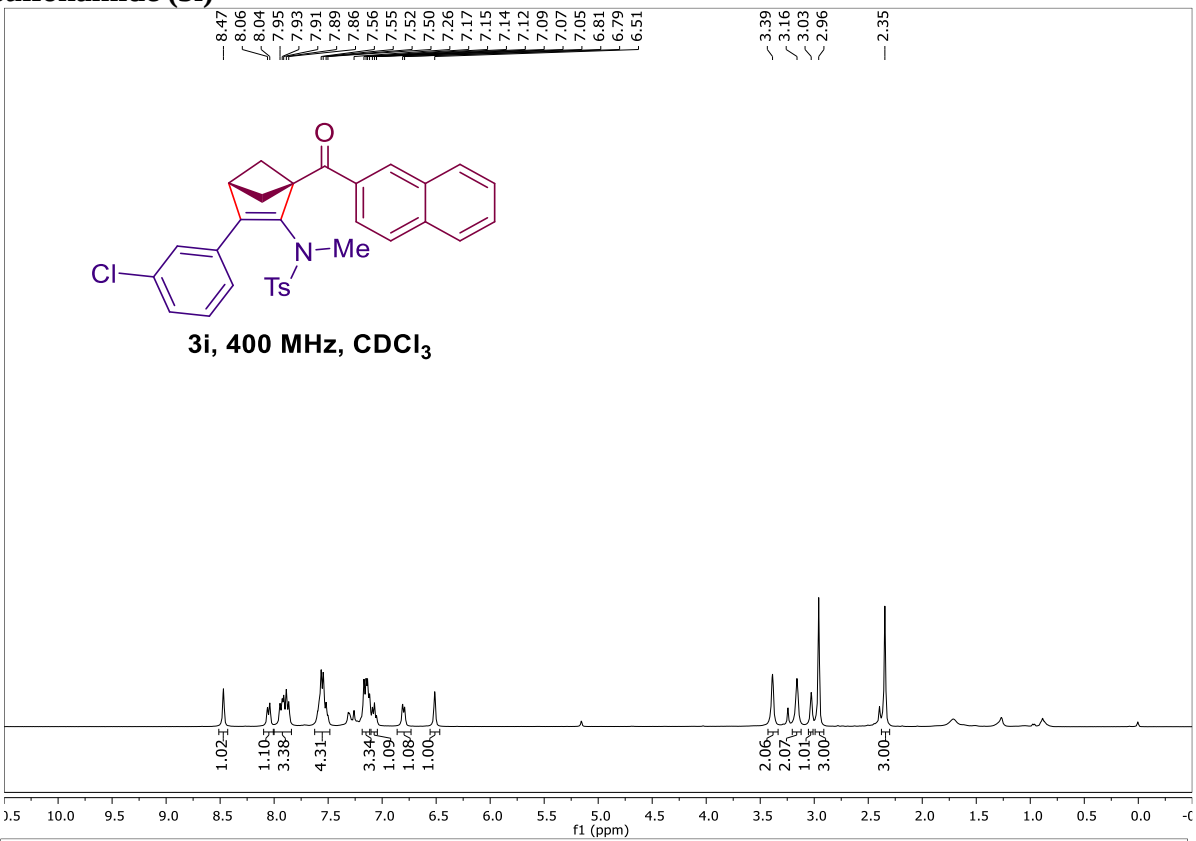


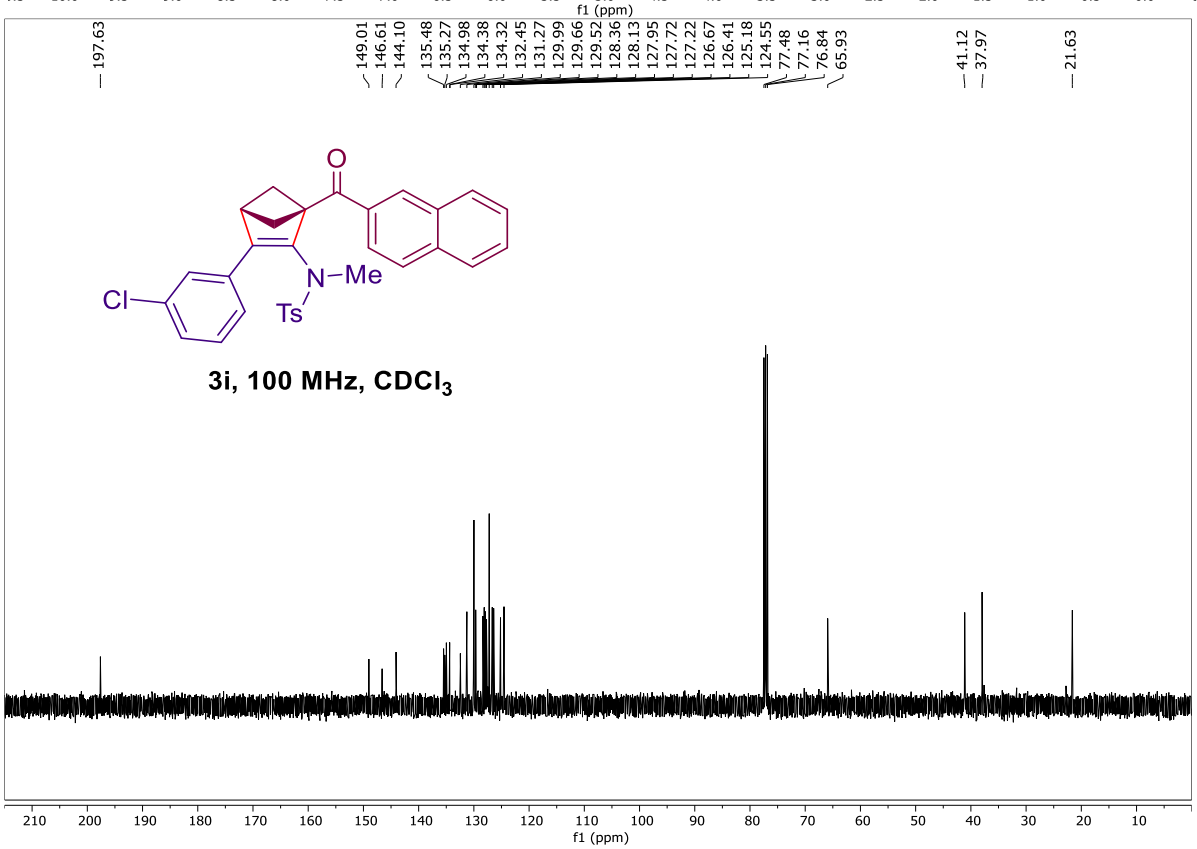


***N*-(1-(2-Naphthoyl)-3-(*m*-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3h)**

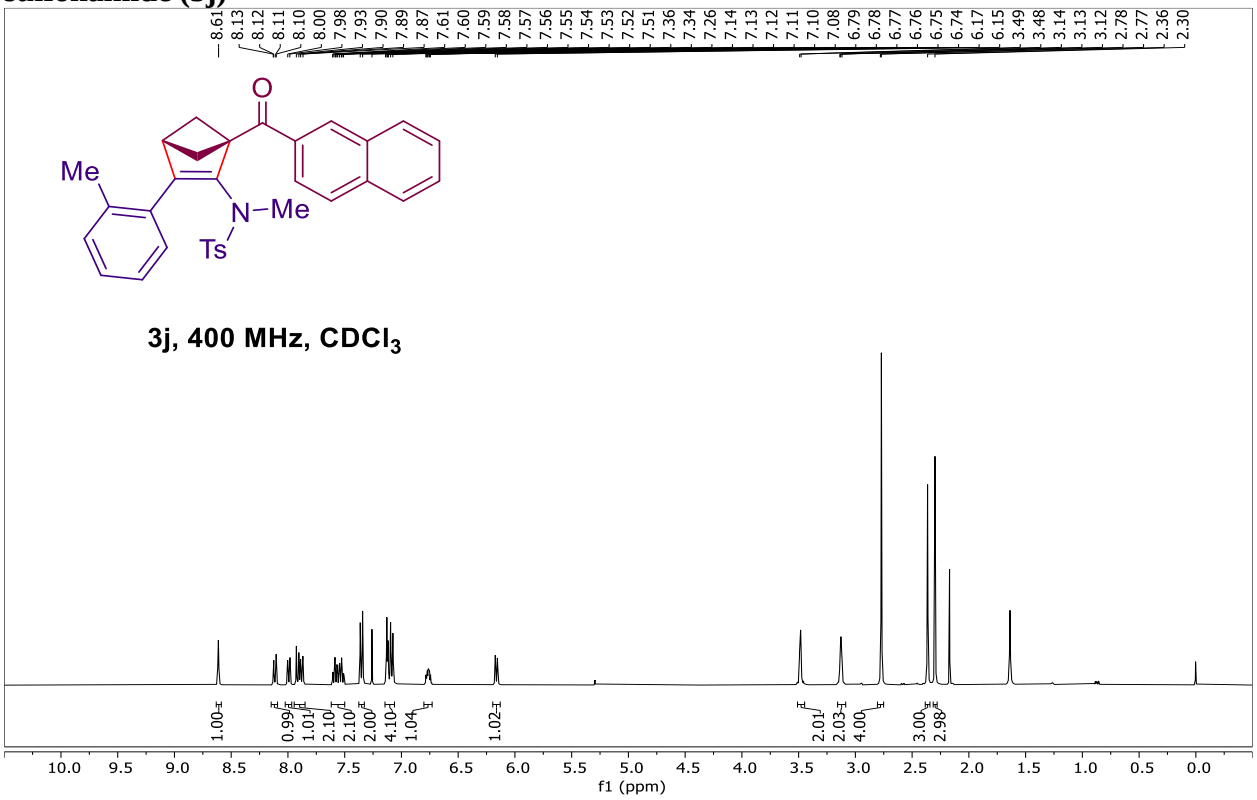


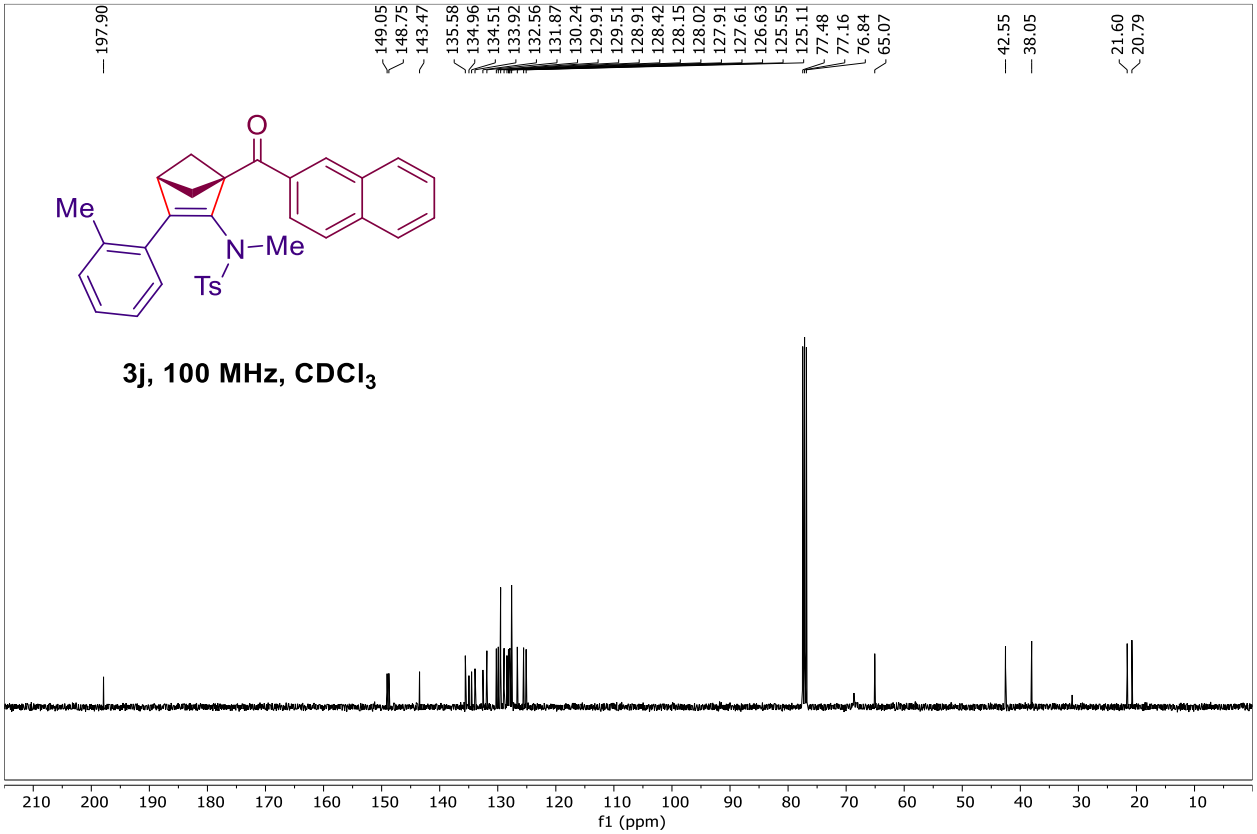
***N*-(1-(2-naphthoyl)-3-(3-chlorophenyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzene sulfonamide (3i)**



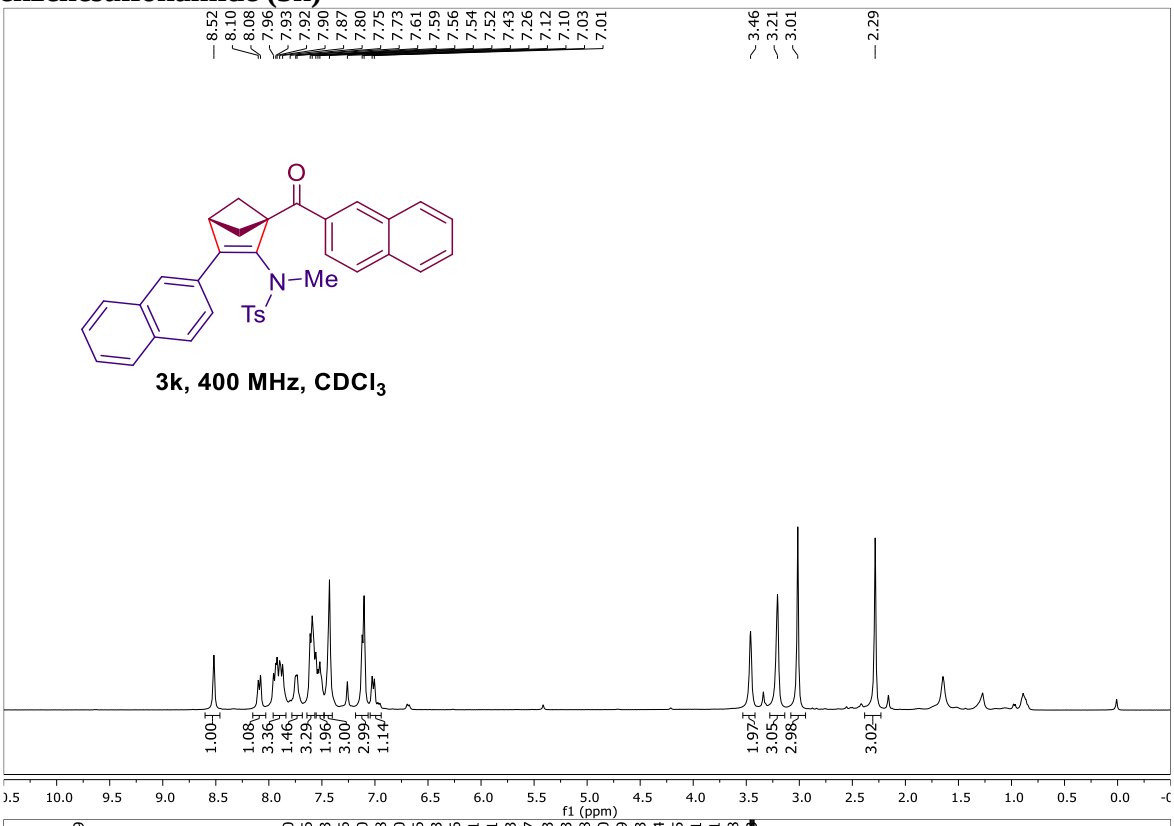


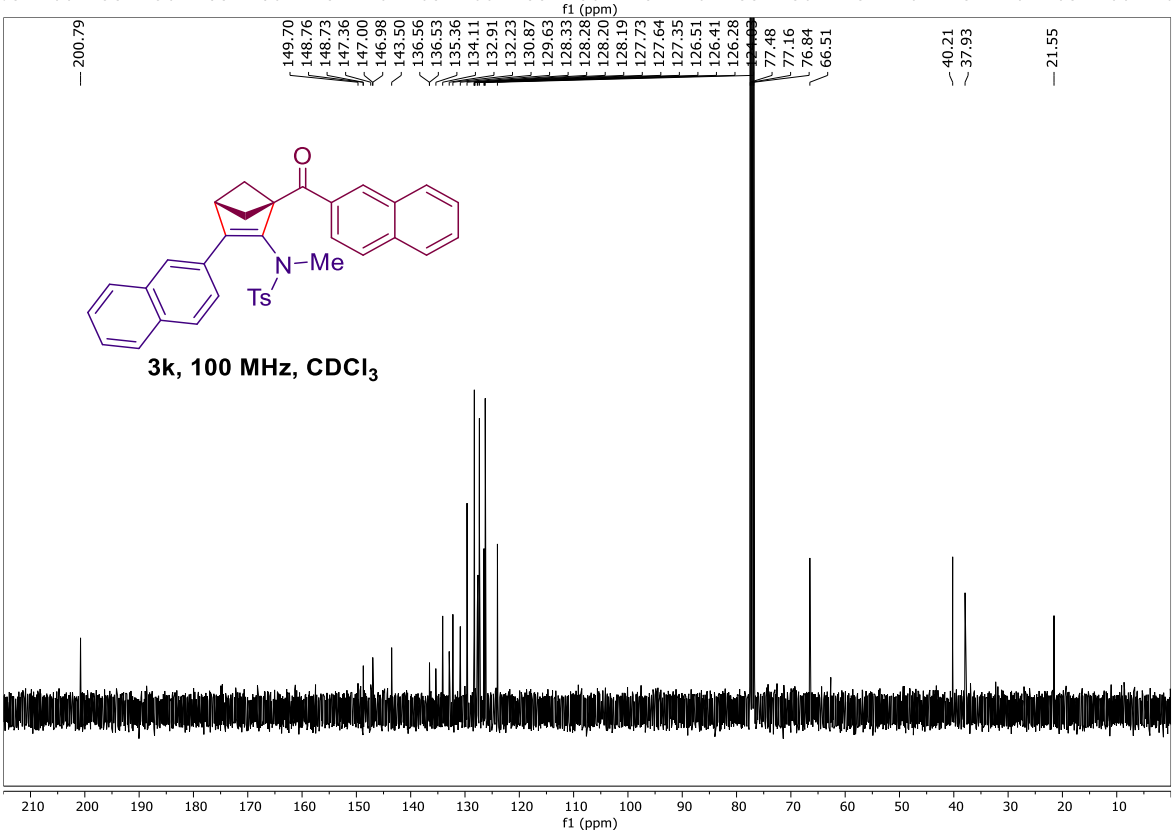
***N*-(1-(2-Naphthoyl)-3-(*o*-tolyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3j)**



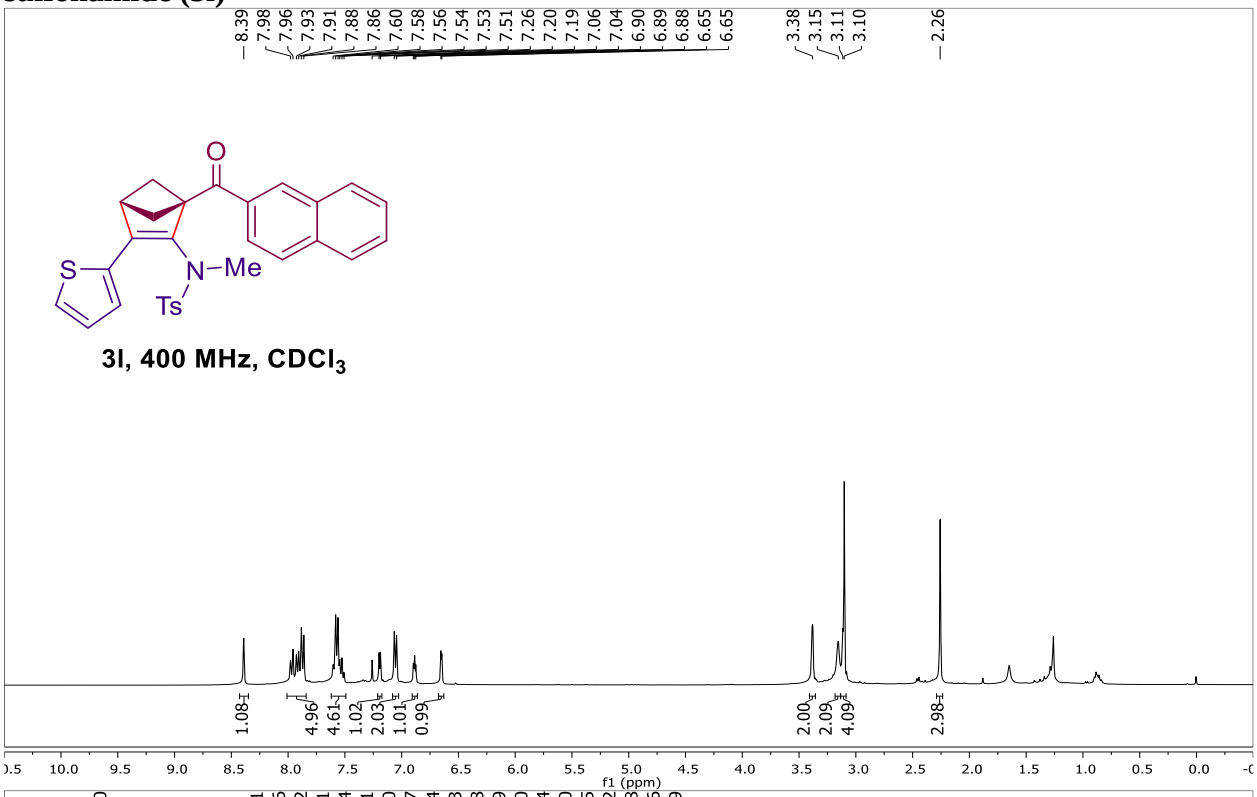


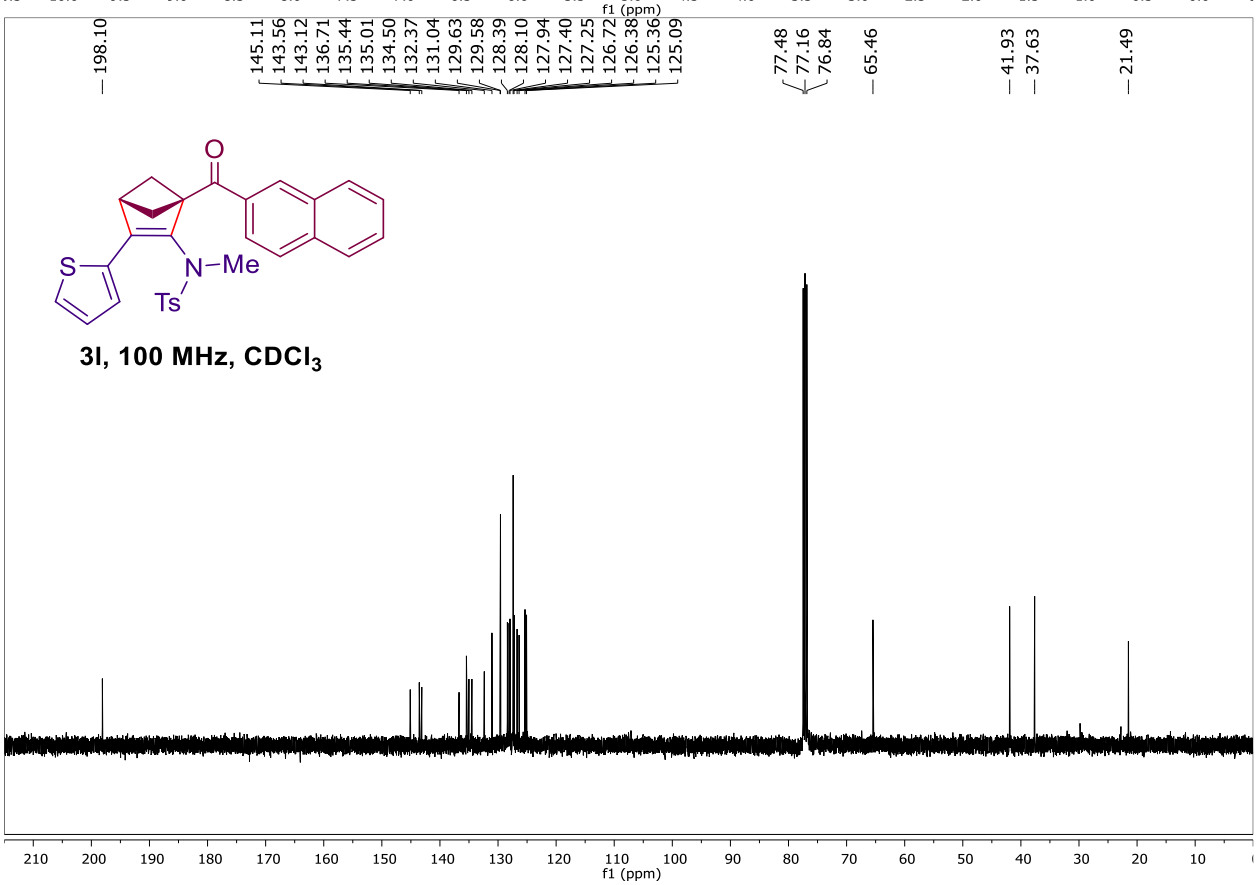
***N*-(1-(2-naphthoyl)-3-(naphthalen-2-yl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide (3k)**



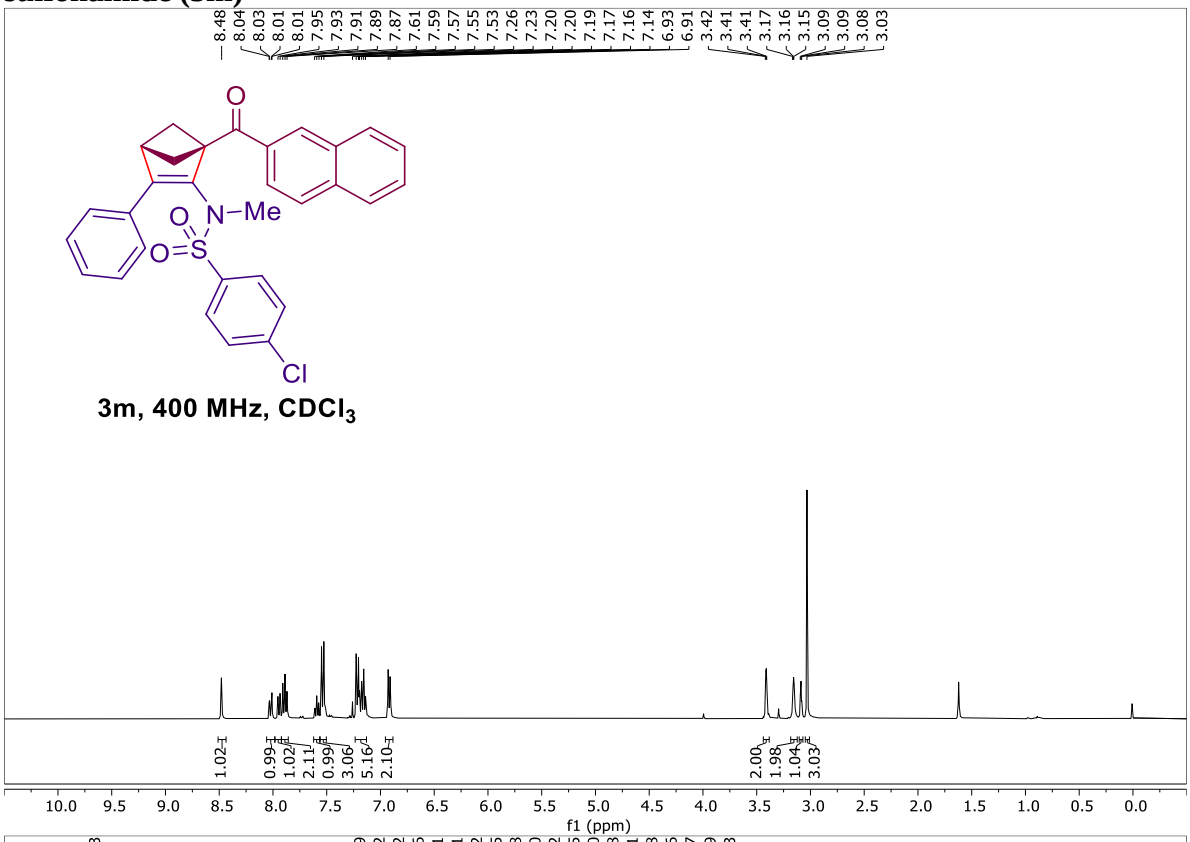


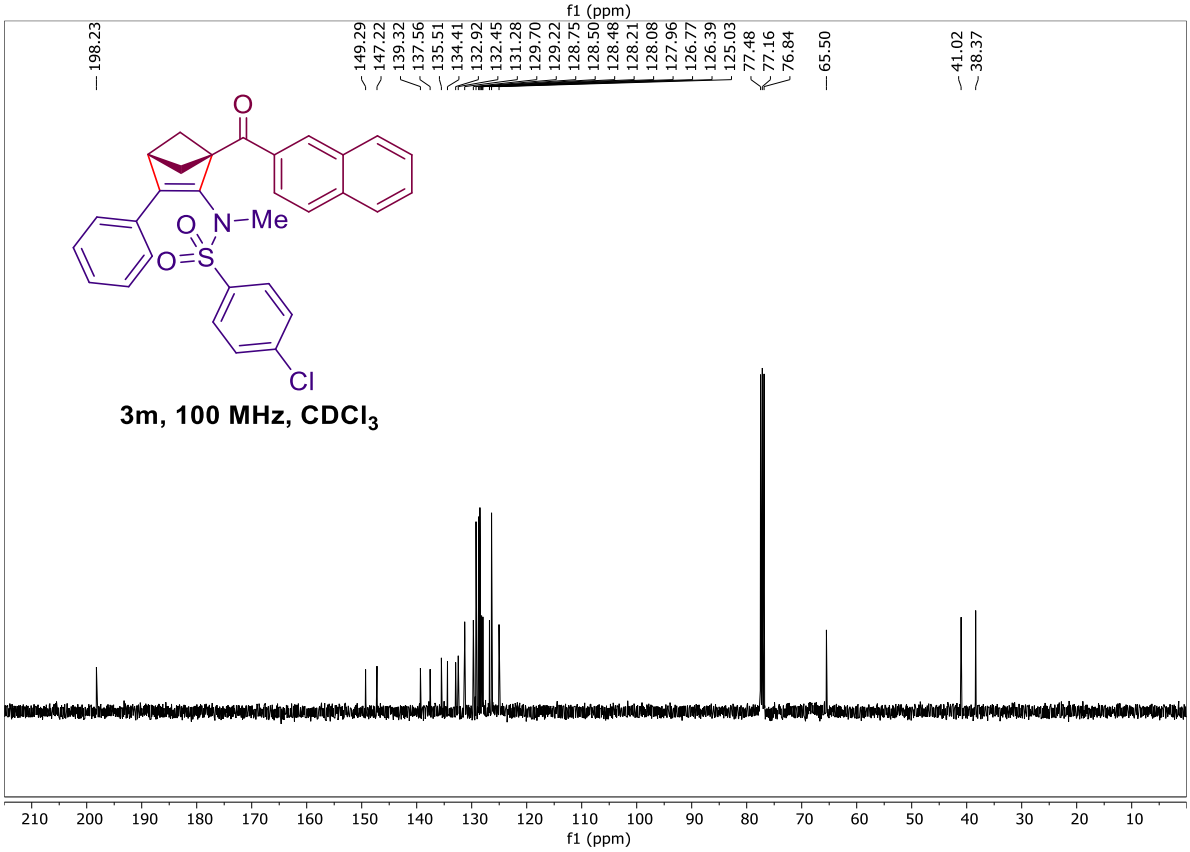
***N*-(1-(2-Naphthoyl)-3-(thiophen-2-yl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3l)**



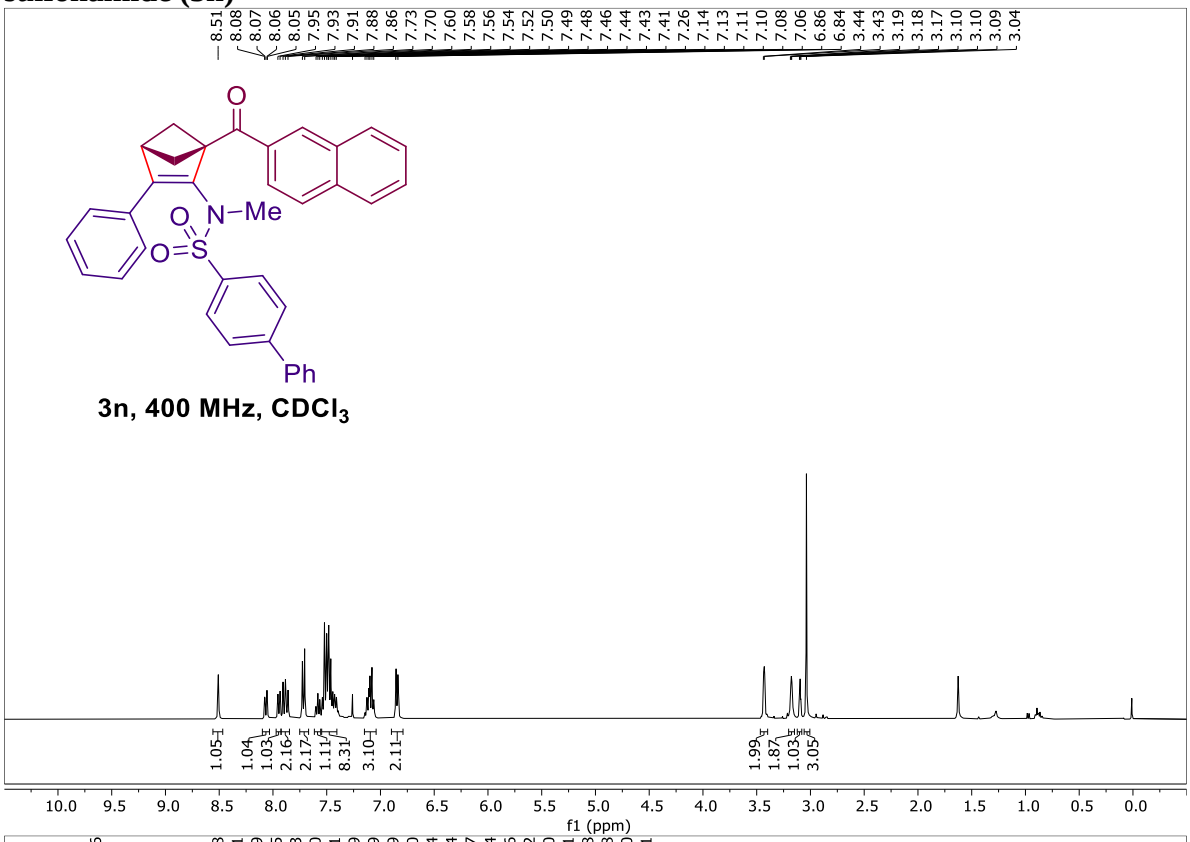


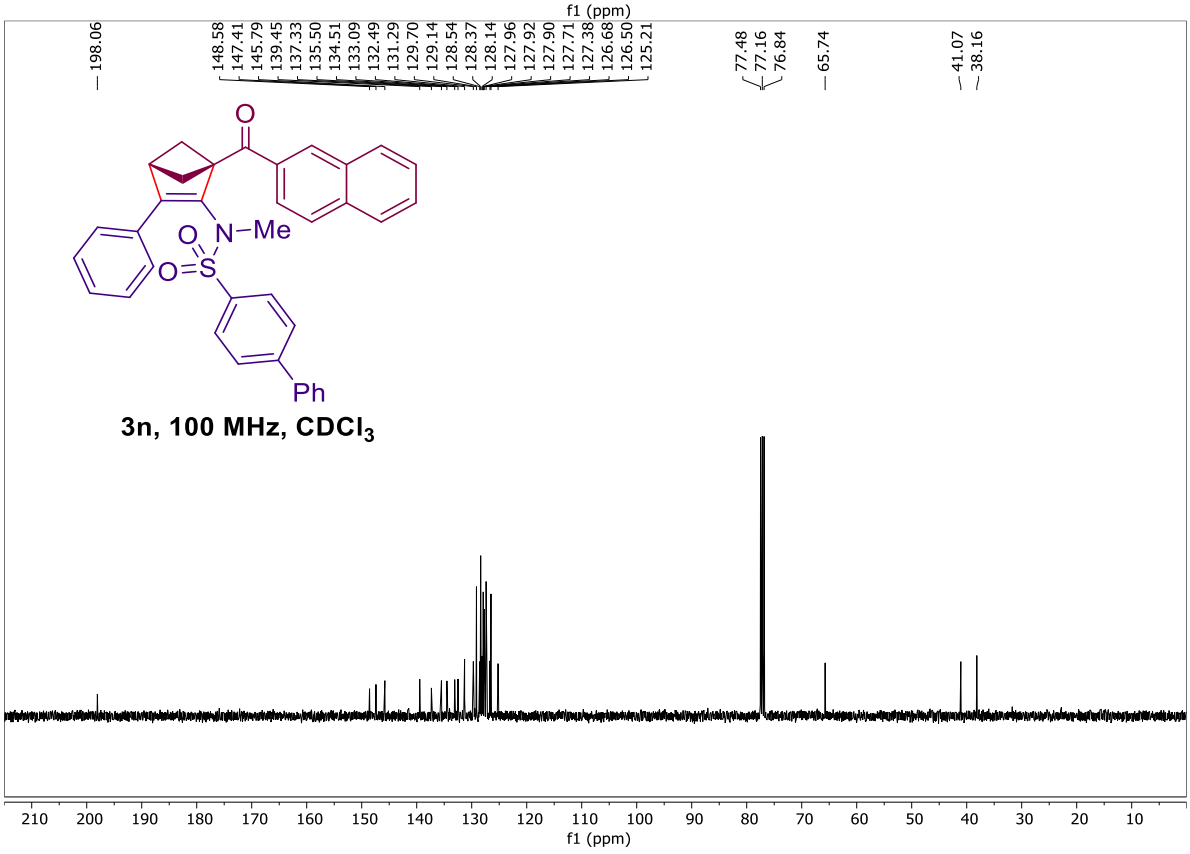
_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-chloro-_N_-methylbenzene sulfonamide (3m)



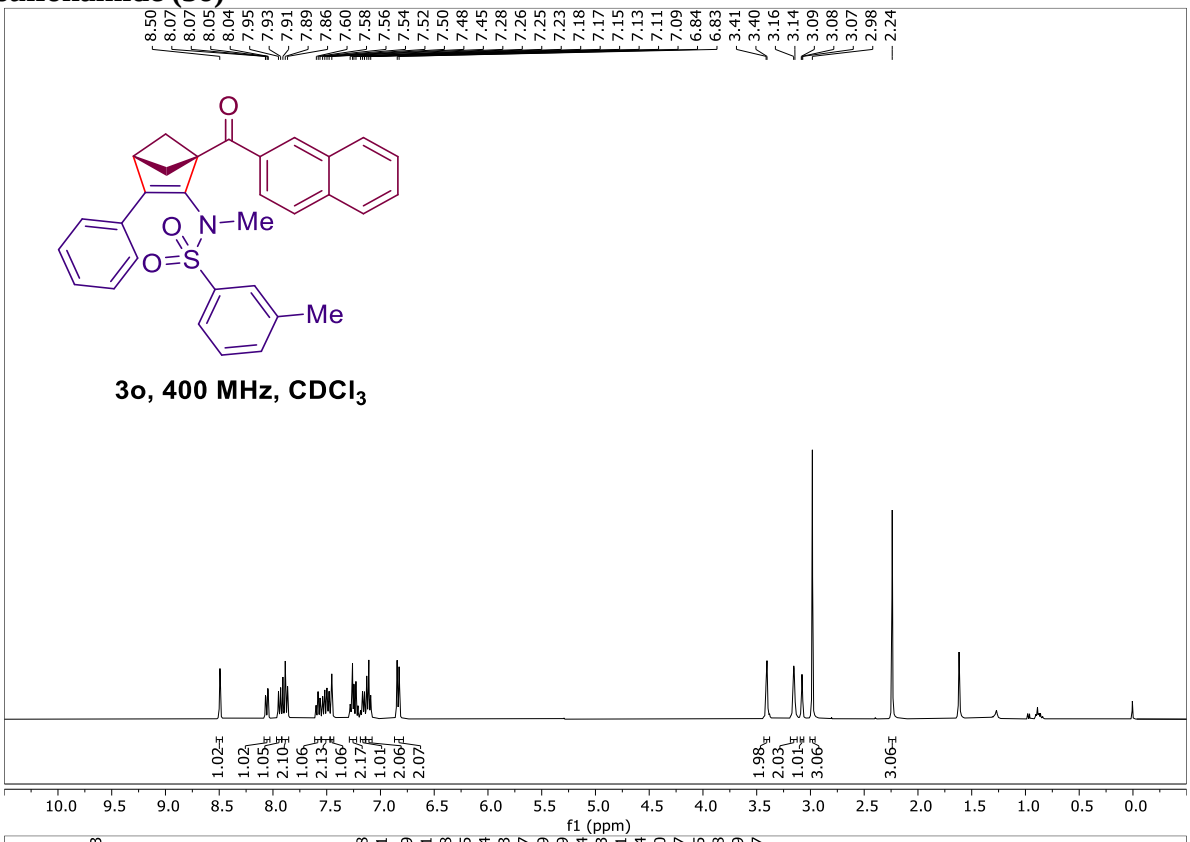


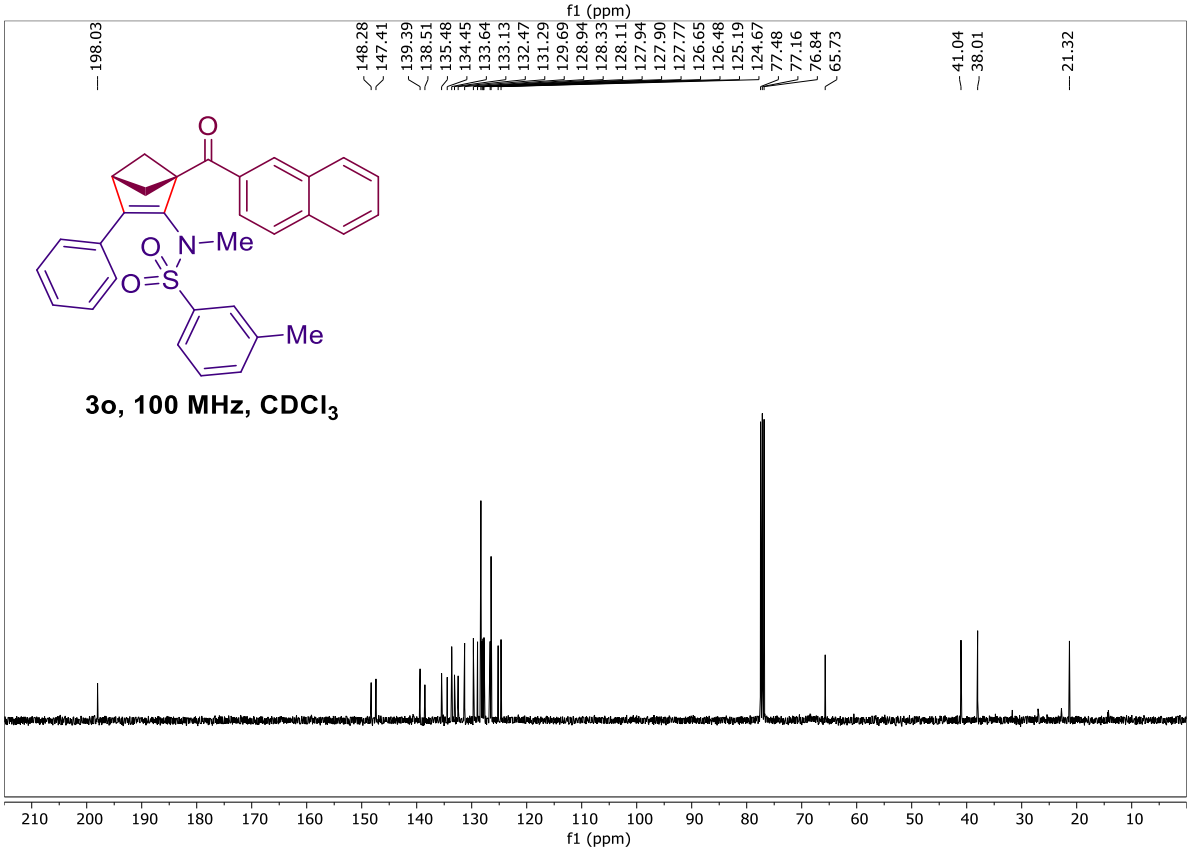
_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-methyl-[1,1'-biphenyl]-4-sulfonamide (3n)



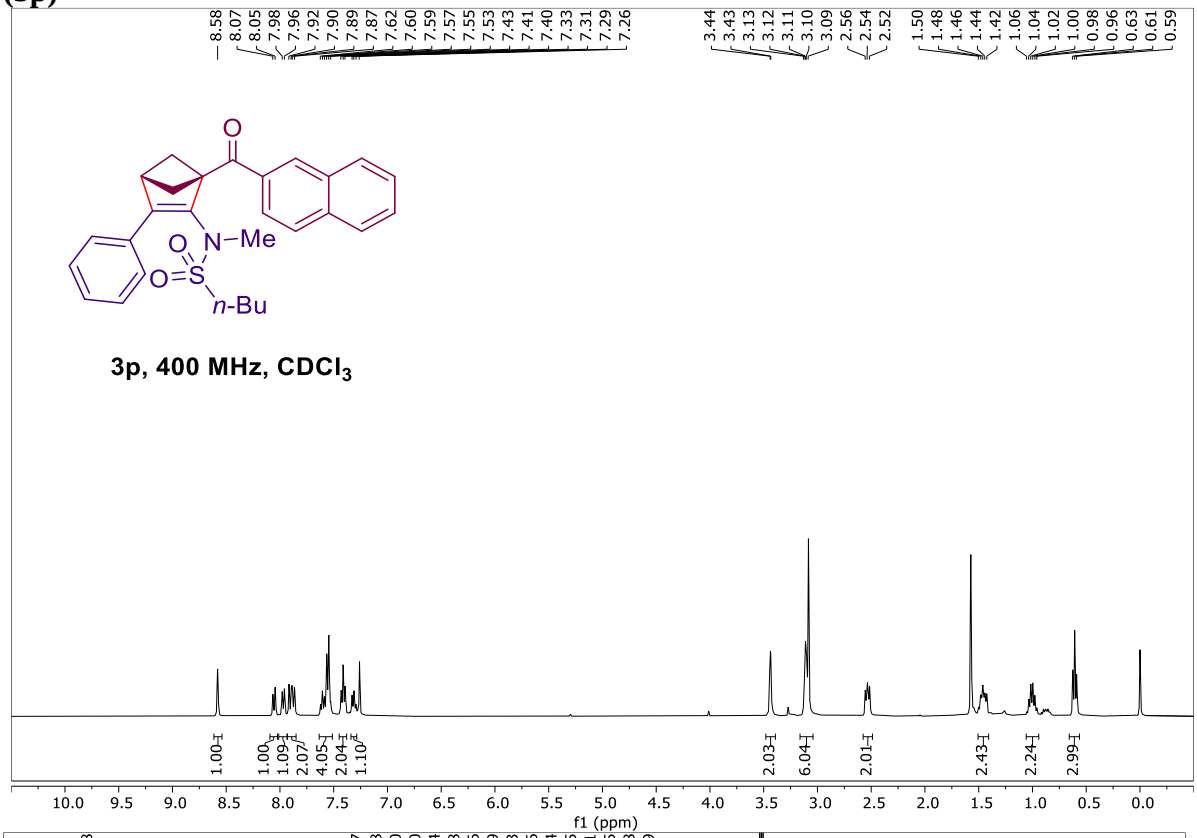


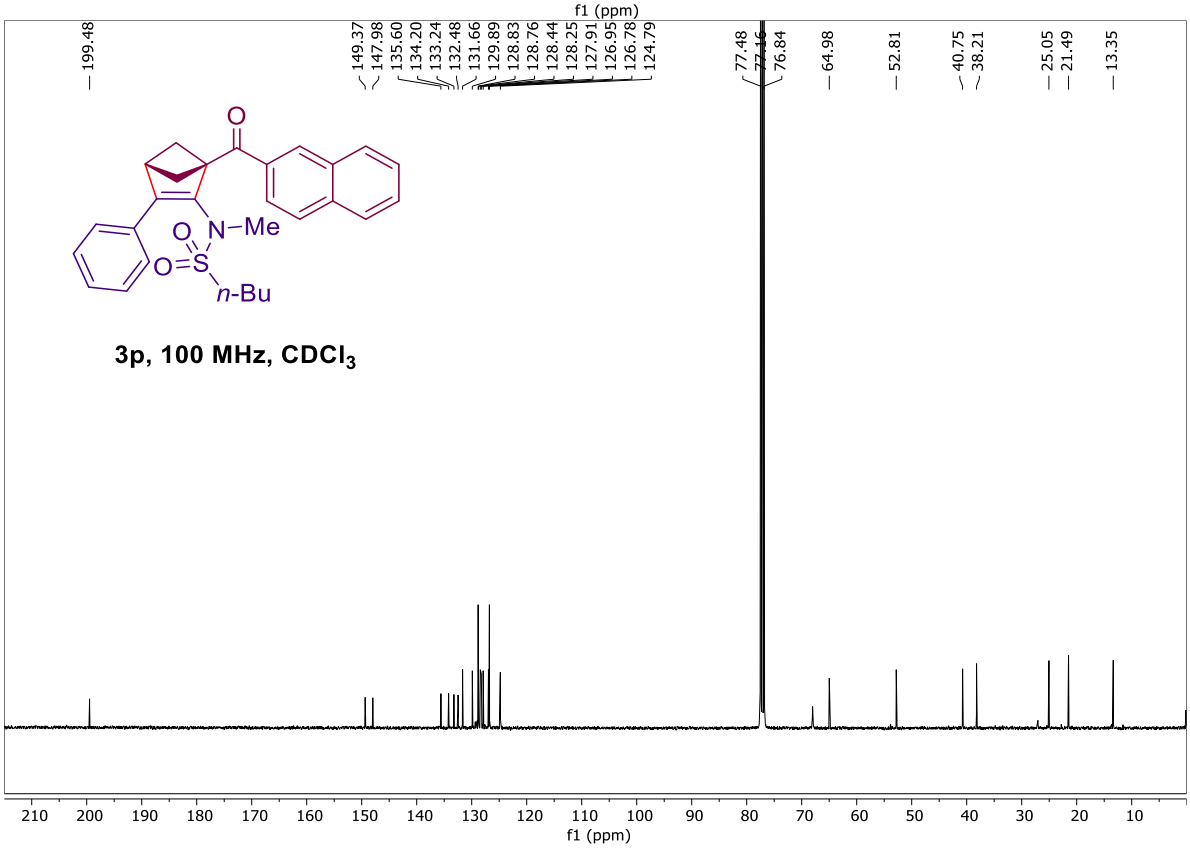
***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,3-dimethylbenzene sulfonamide (3o)**



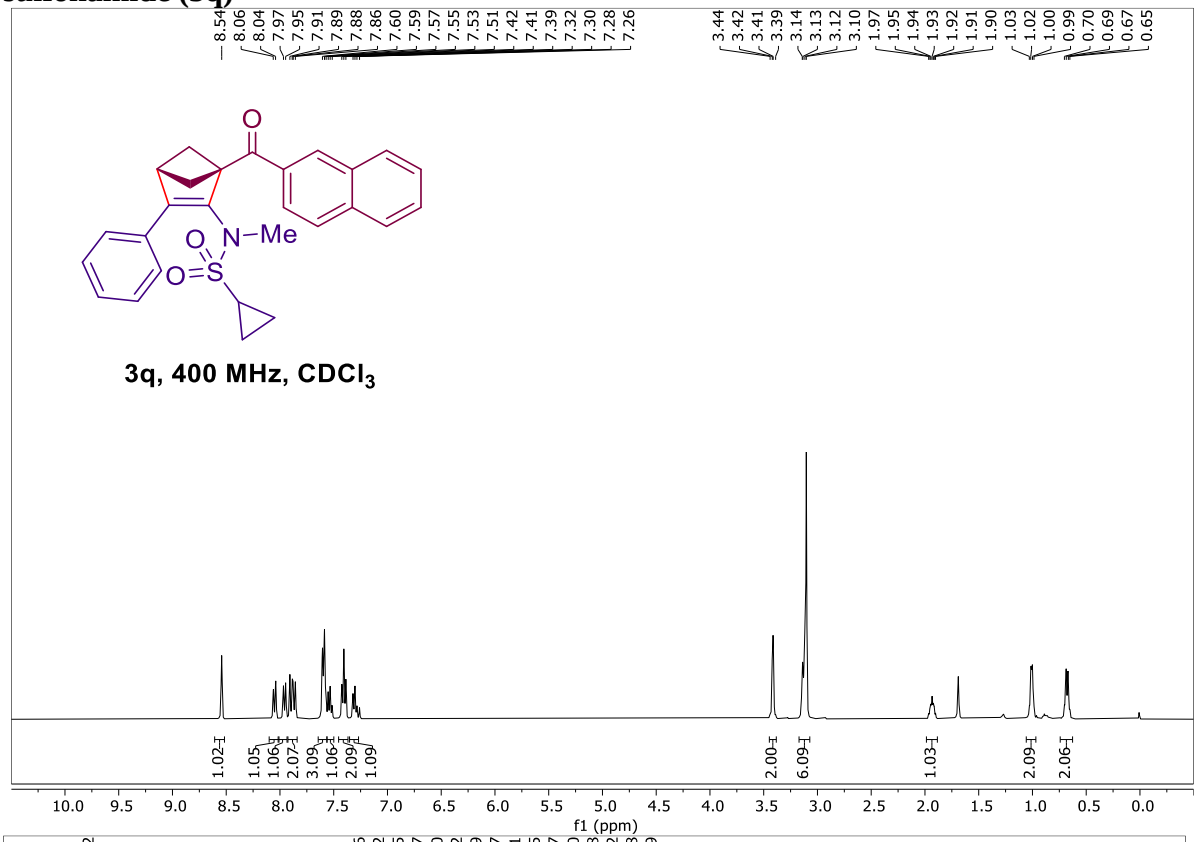


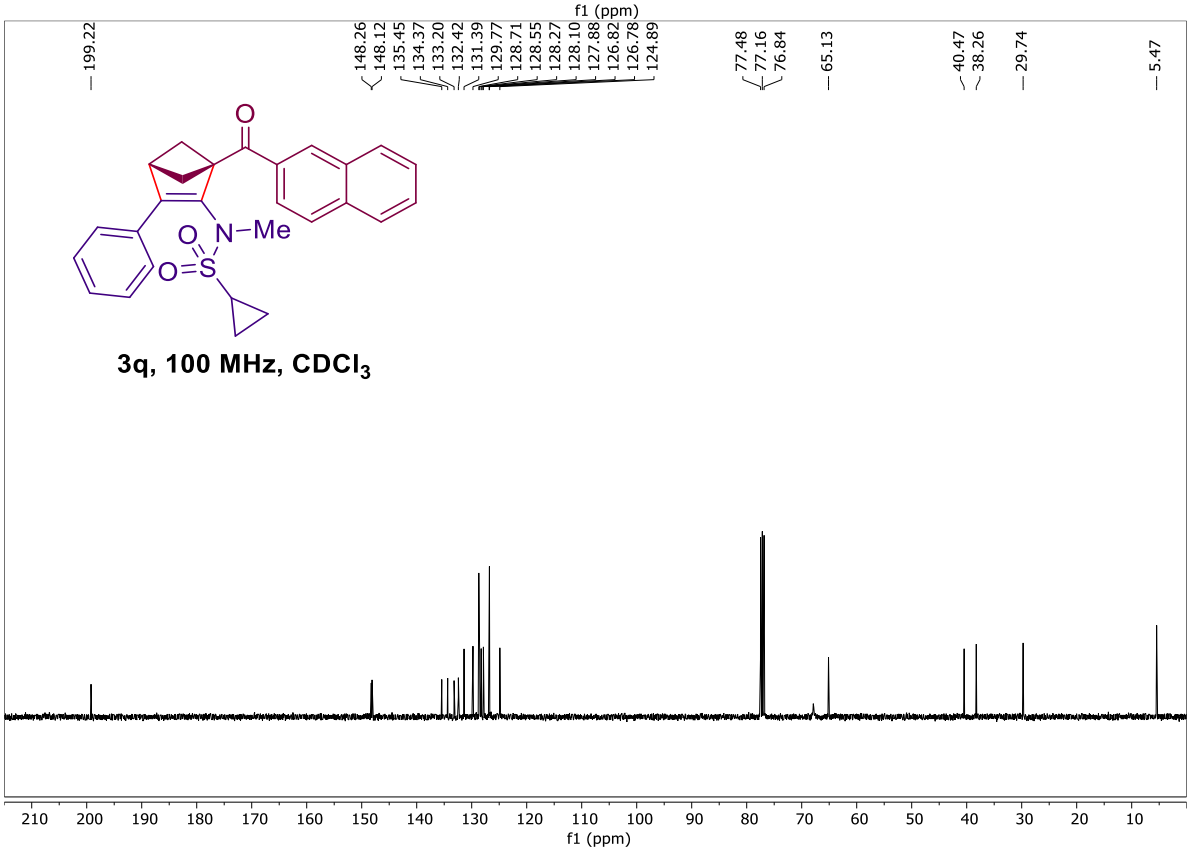
***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-methylbutane-1-sulfonamide (3p)**



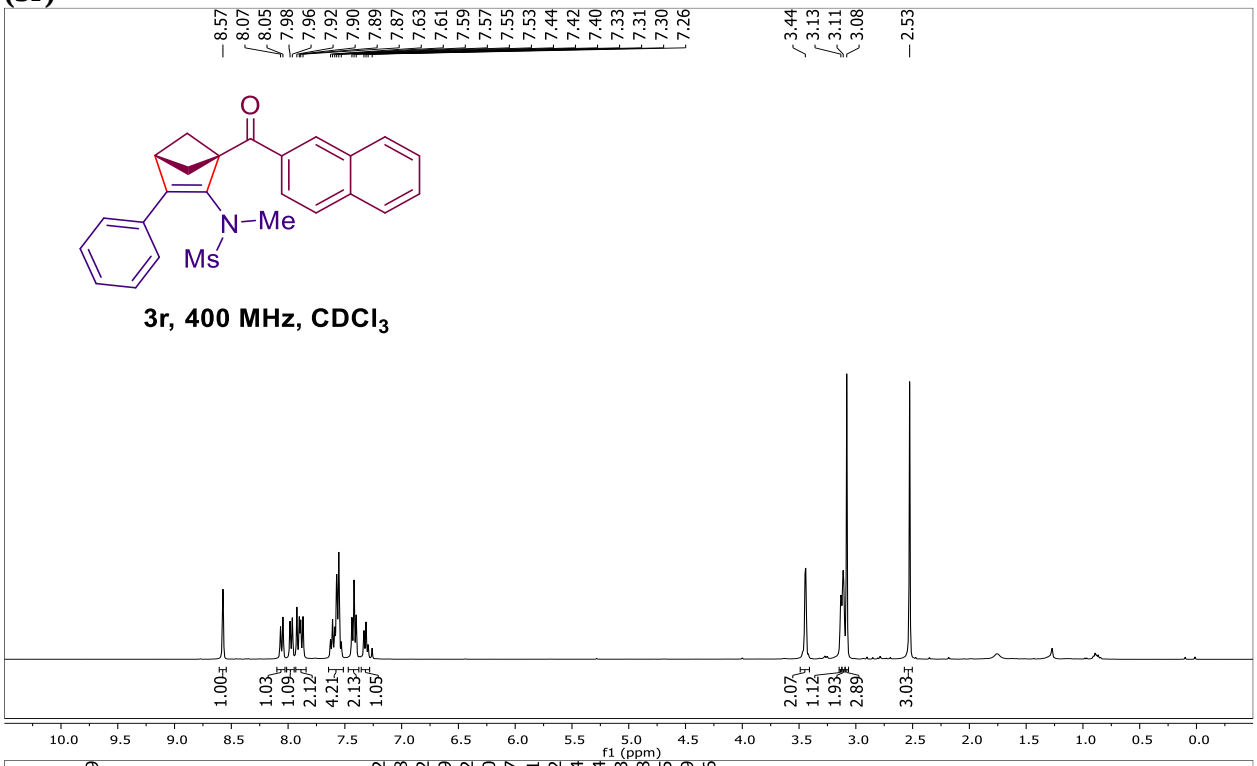


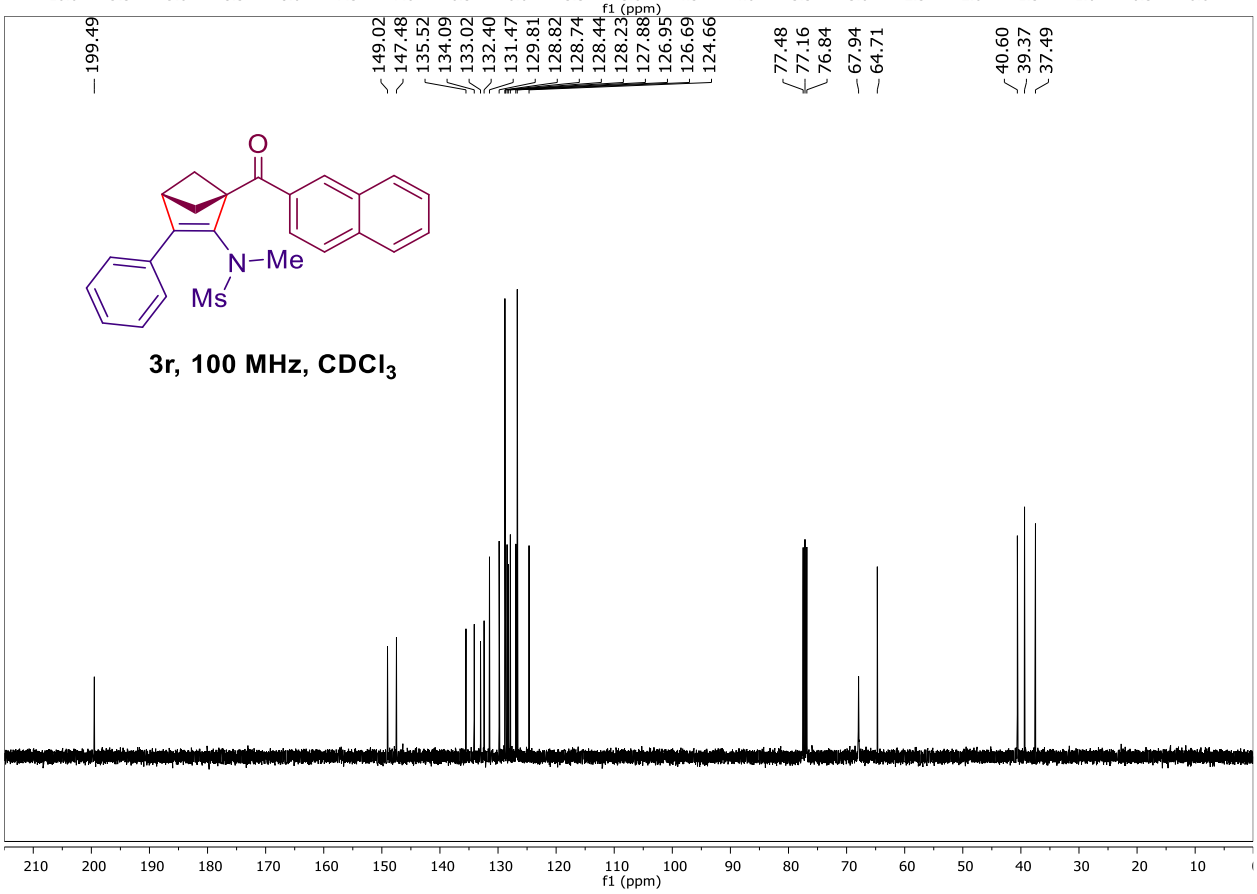
***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-methylcyclopropane sulfonamide (3q)**



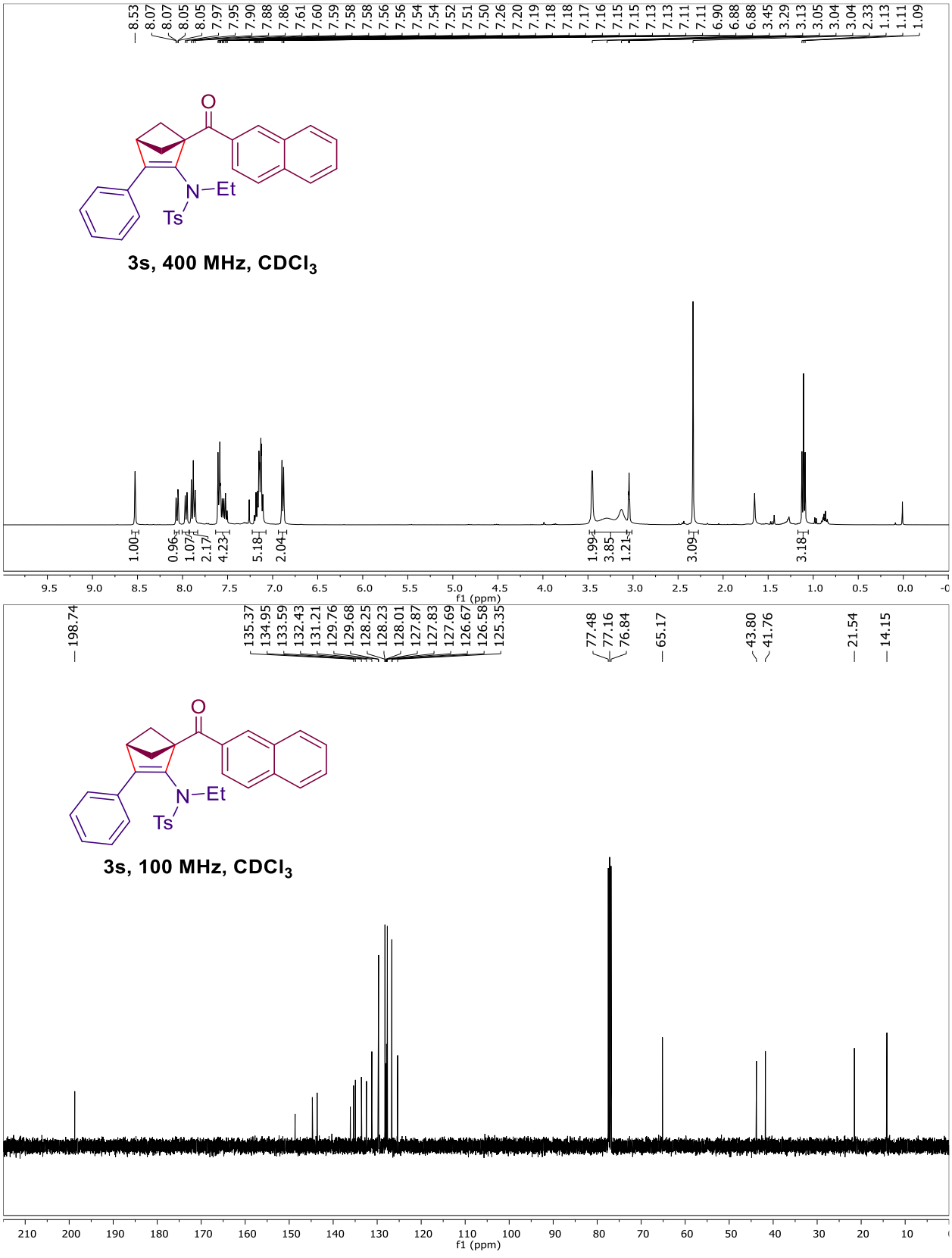


_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-methylmethanesulfonamide (3r)

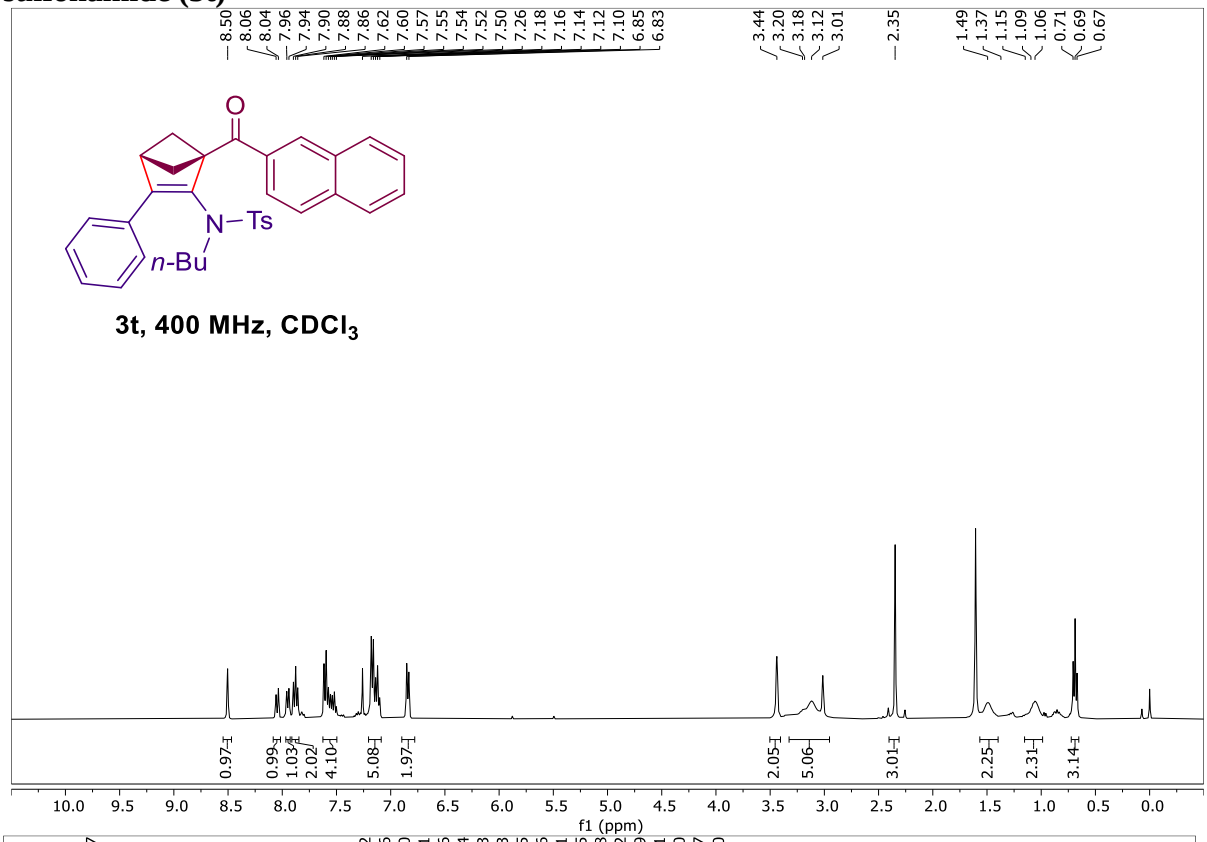


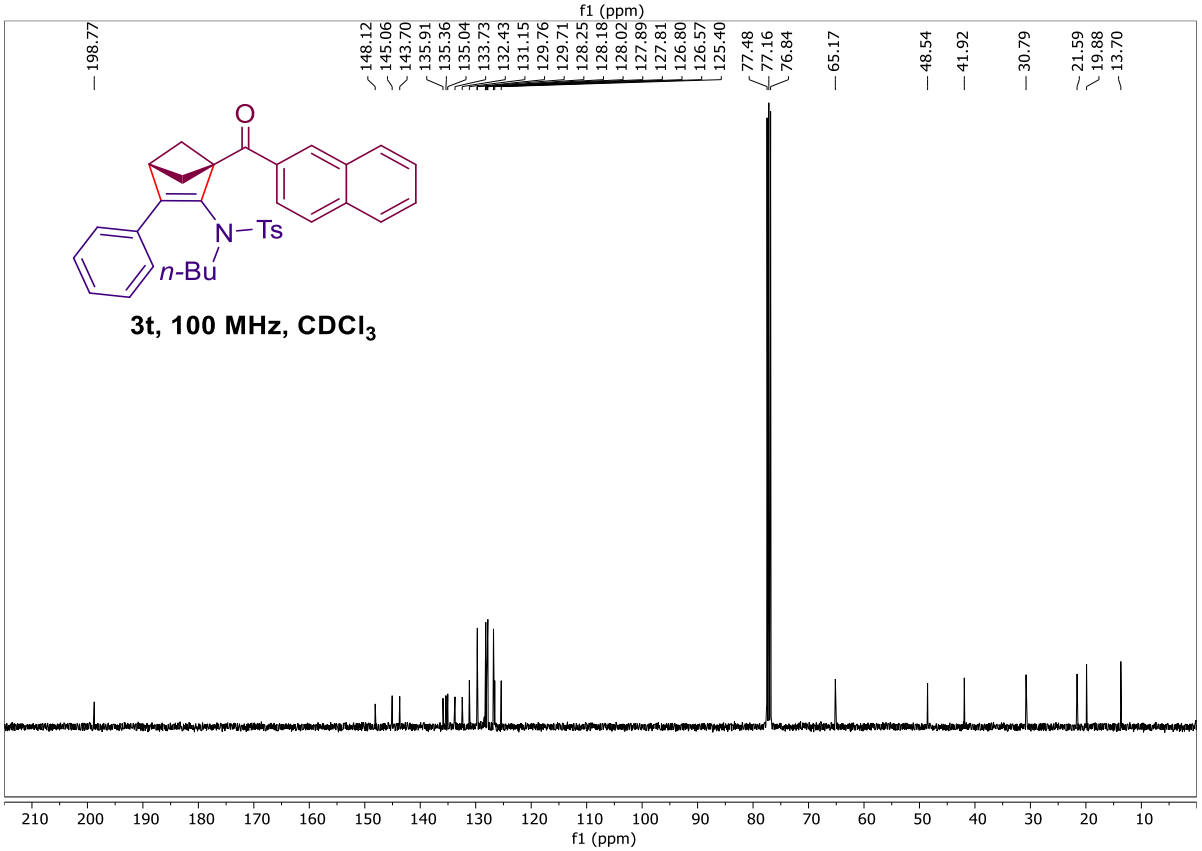


_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-ethyl-4-methylbenzene sulfonamide (3s)

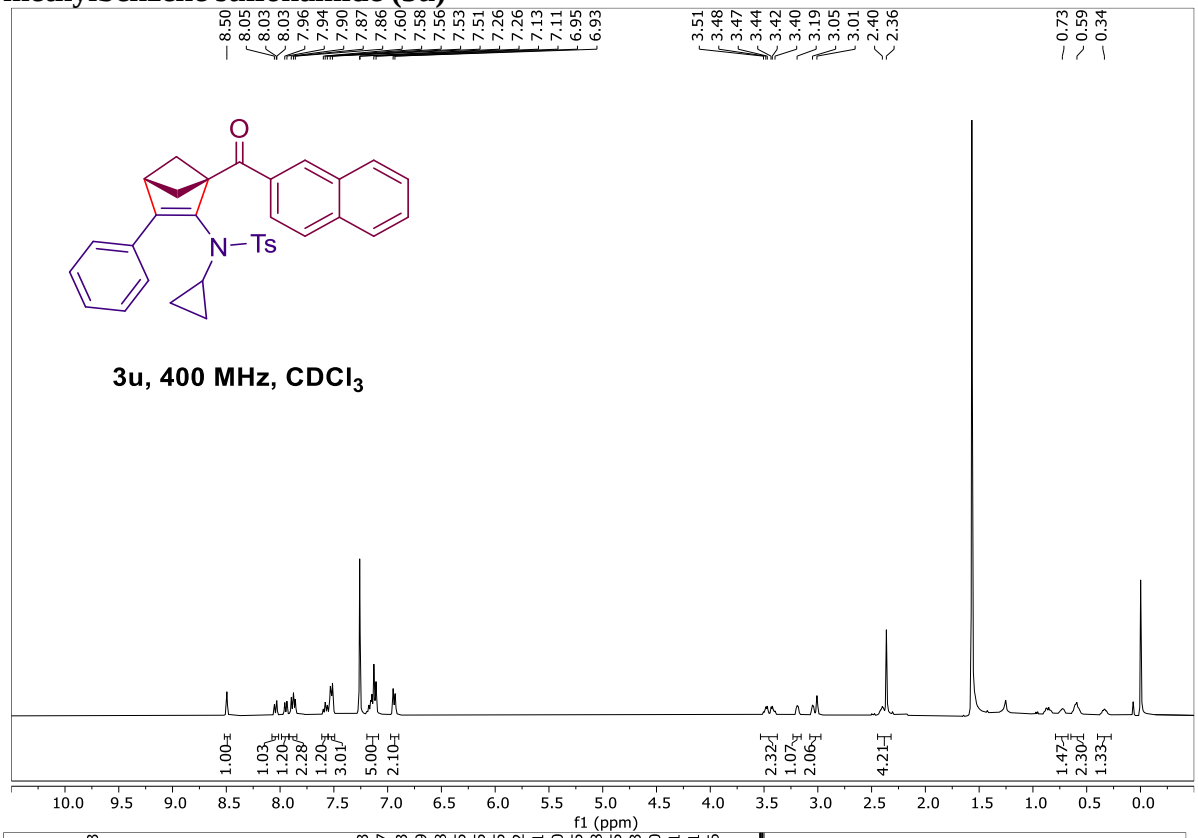


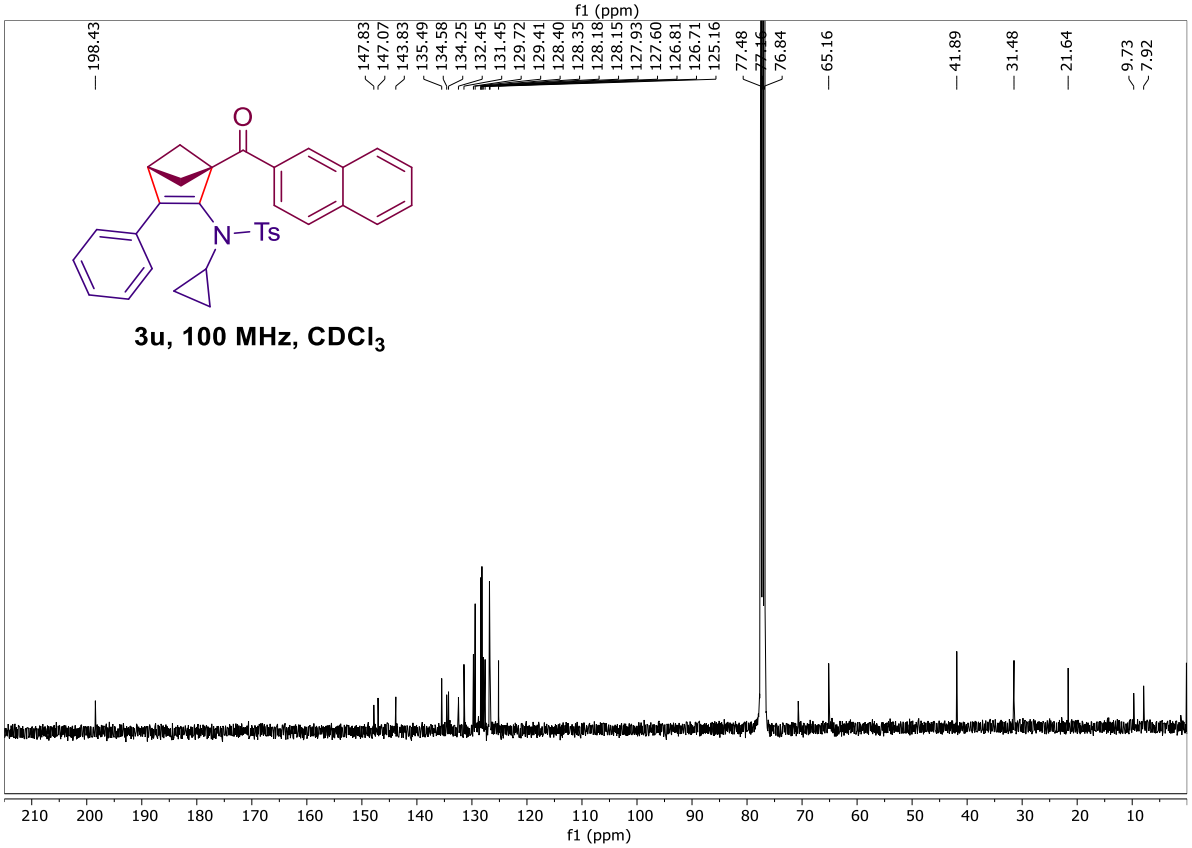
***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-butyl-4-methylbenzene sulfonamide (3t)**



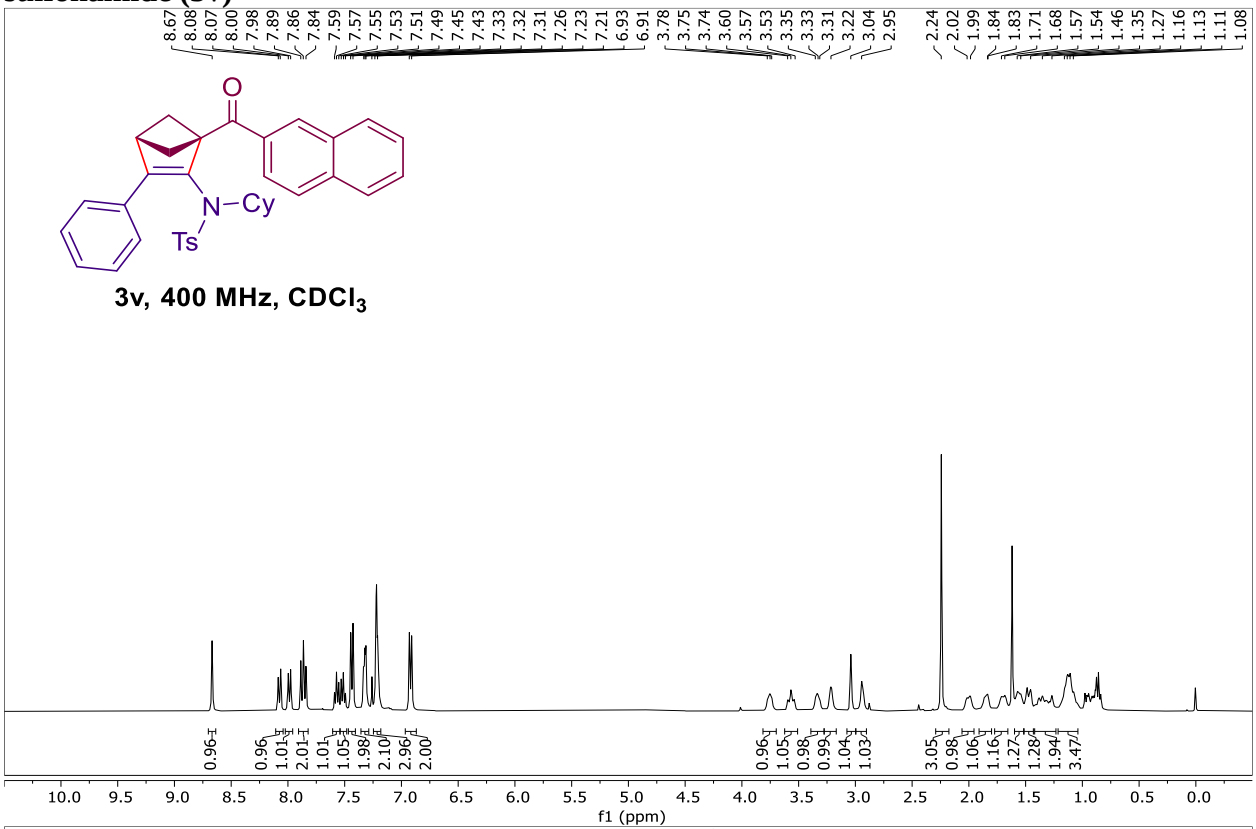


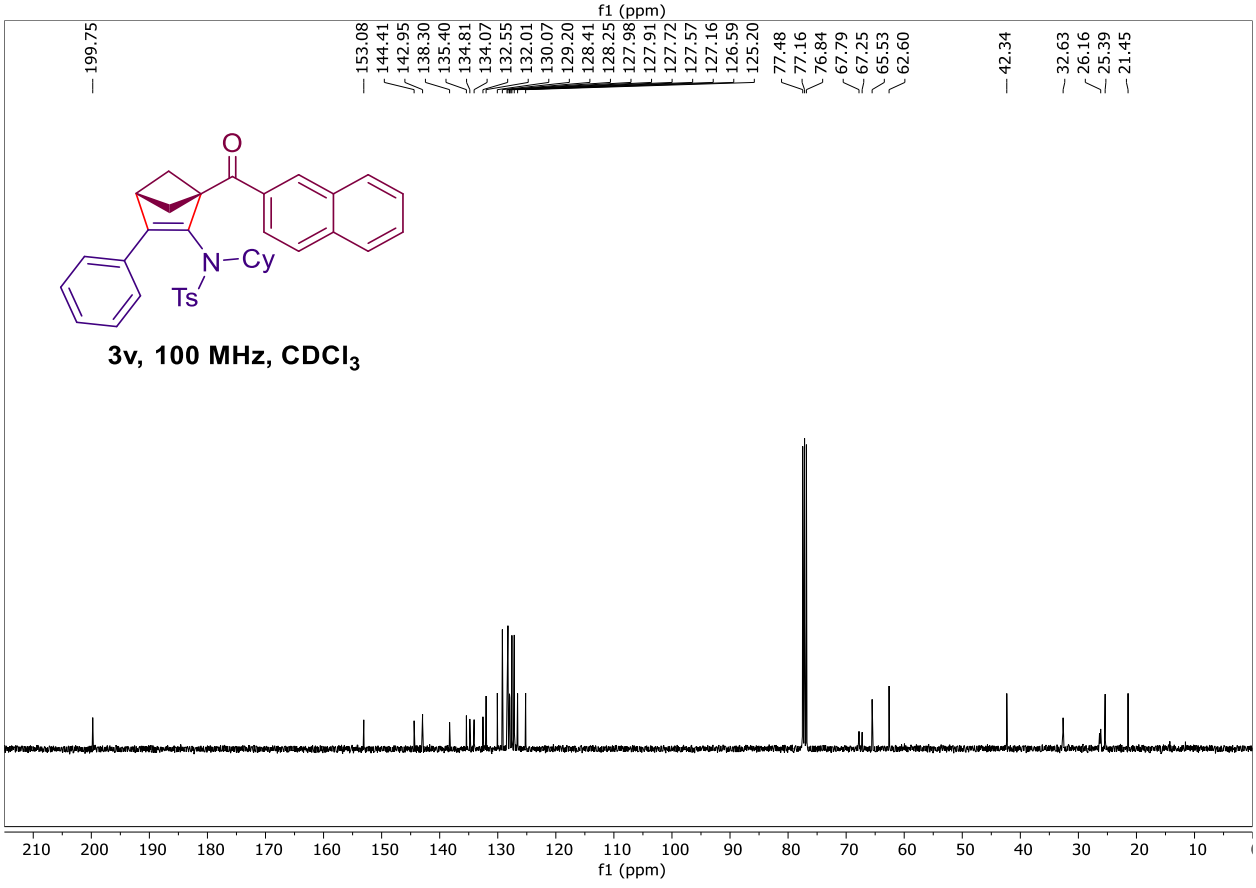
***N*-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*-cyclopropyl-4-methylbenzene sulfonamide (3u)**



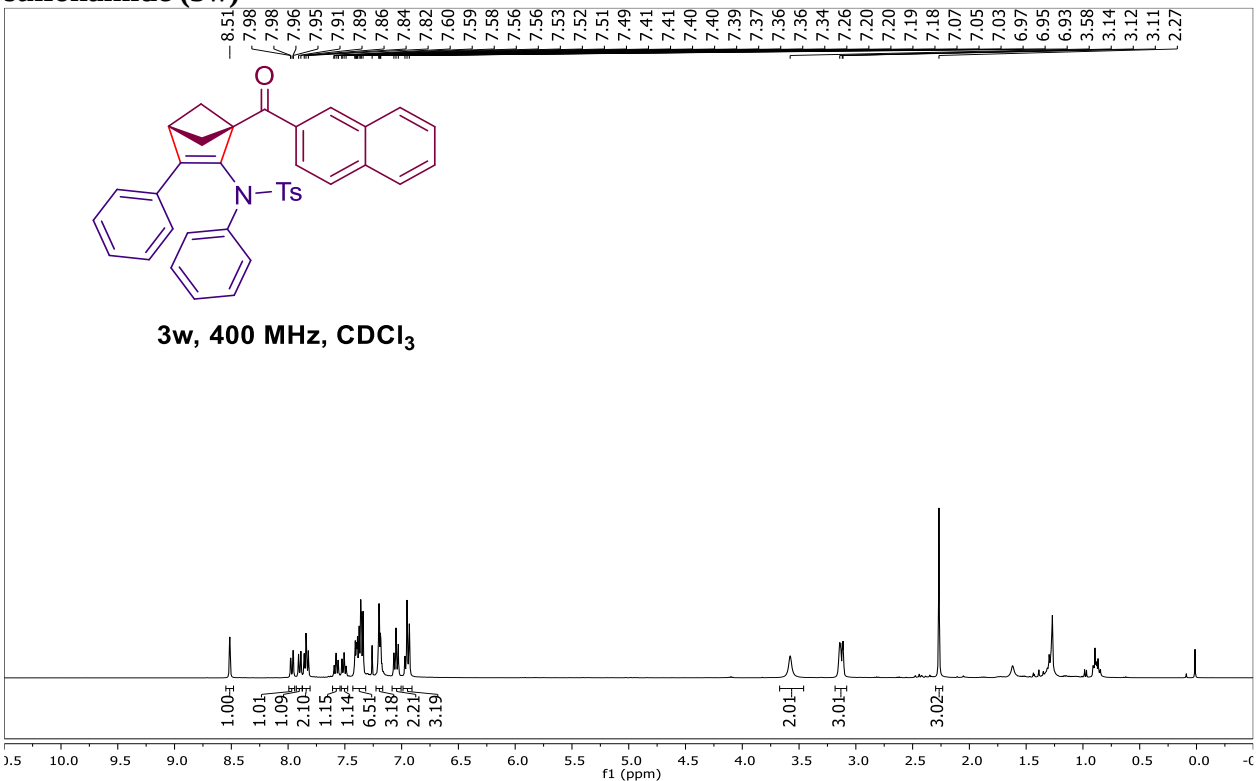


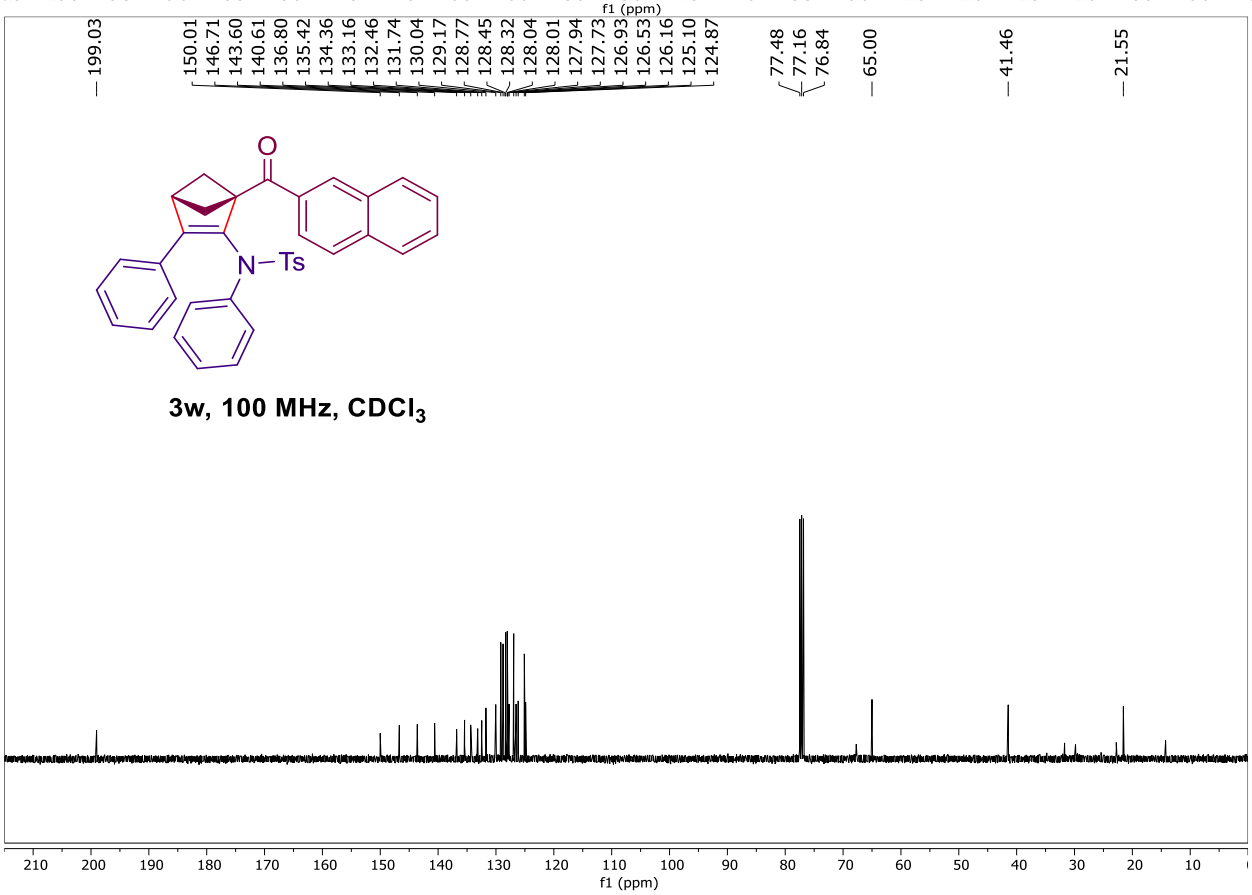
_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-cyclohexyl-4-methylbenzene sulfonamide (3v)



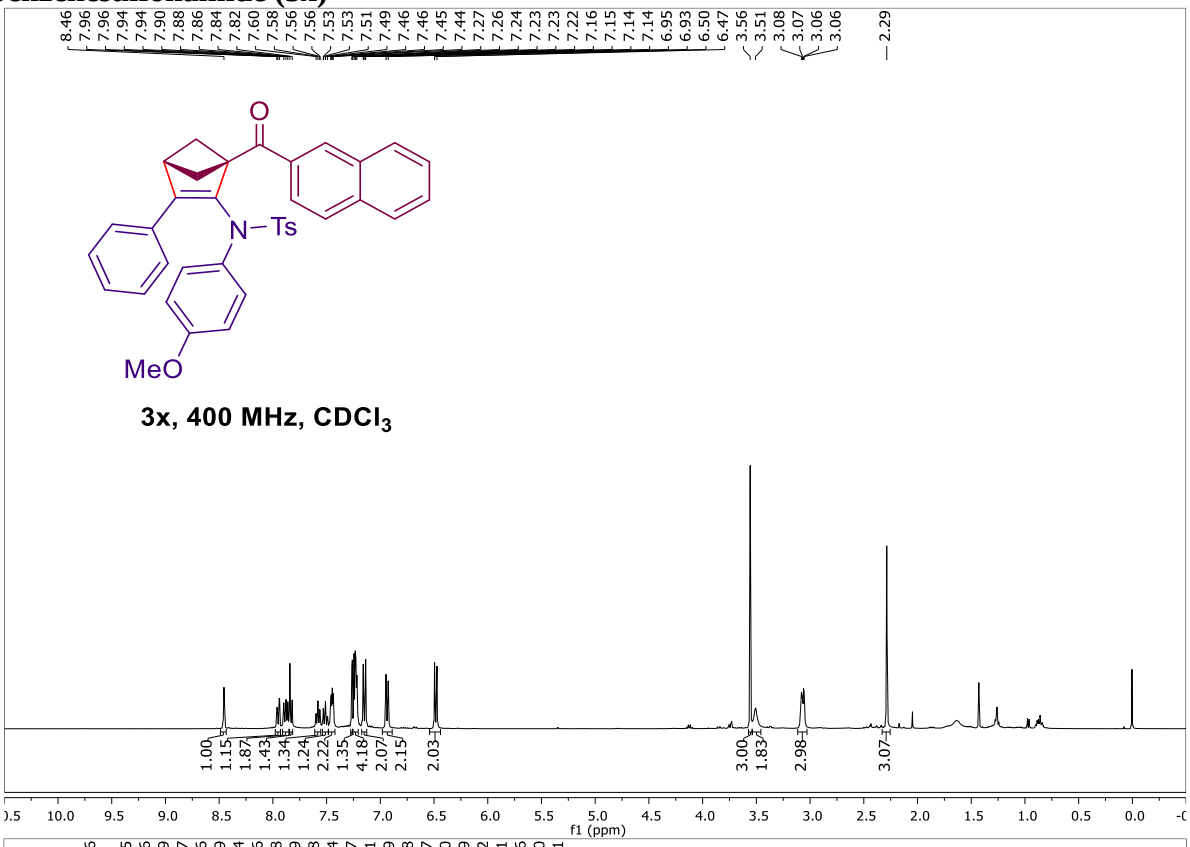


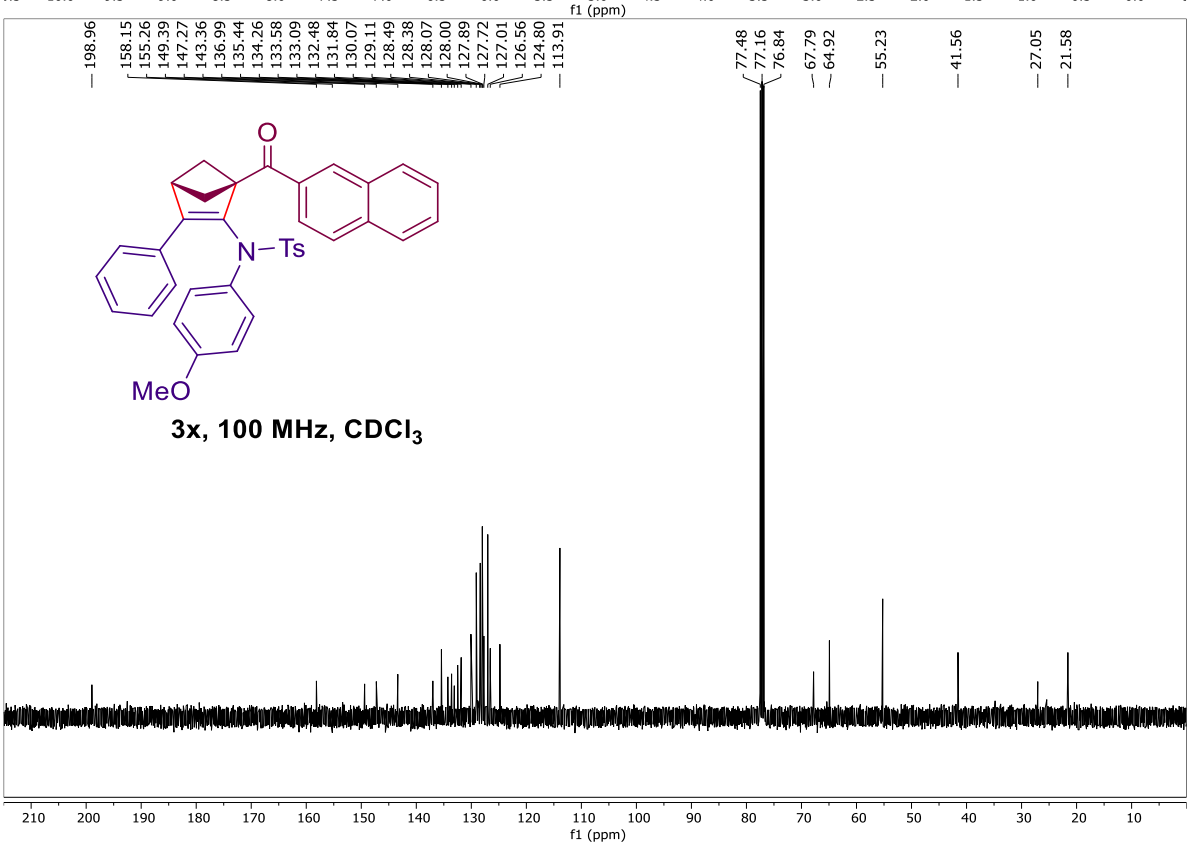
_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-methyl-_N_-phenylbenzene sulfonamide (3w)



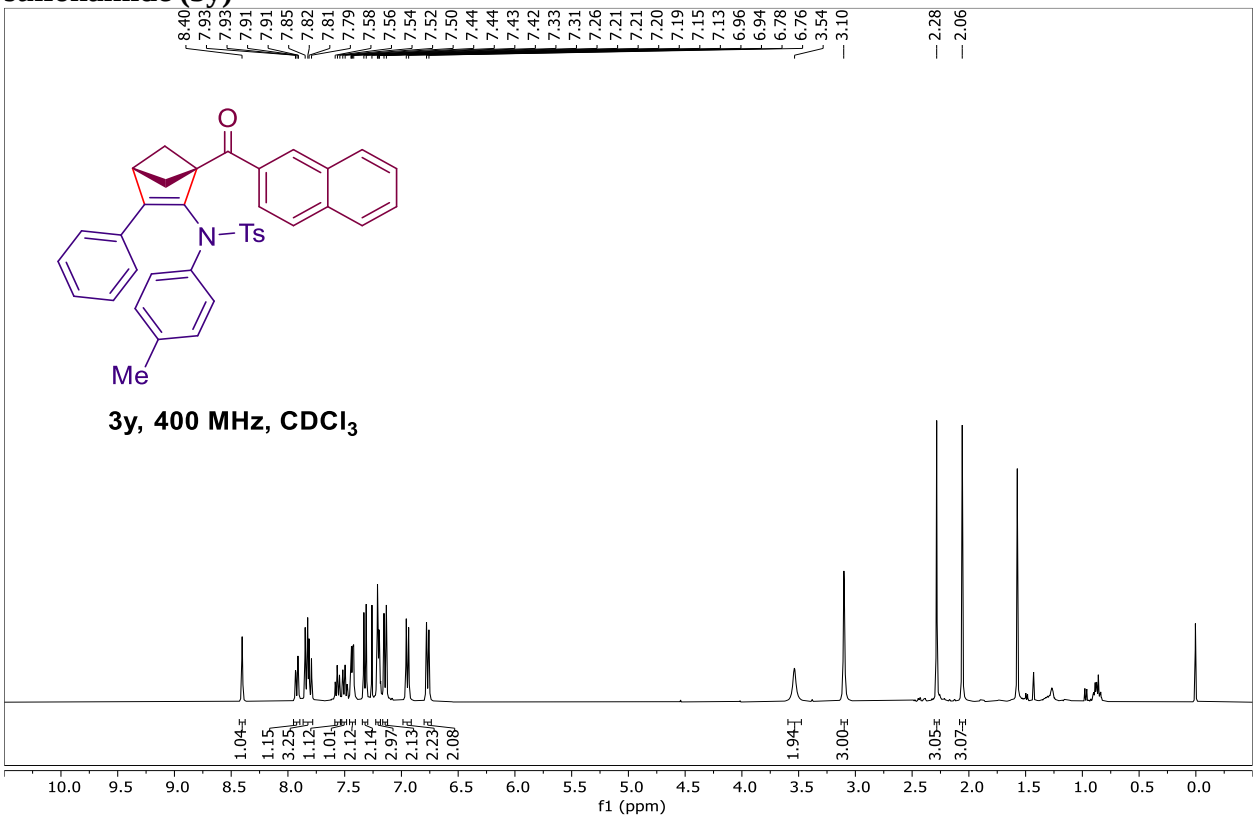


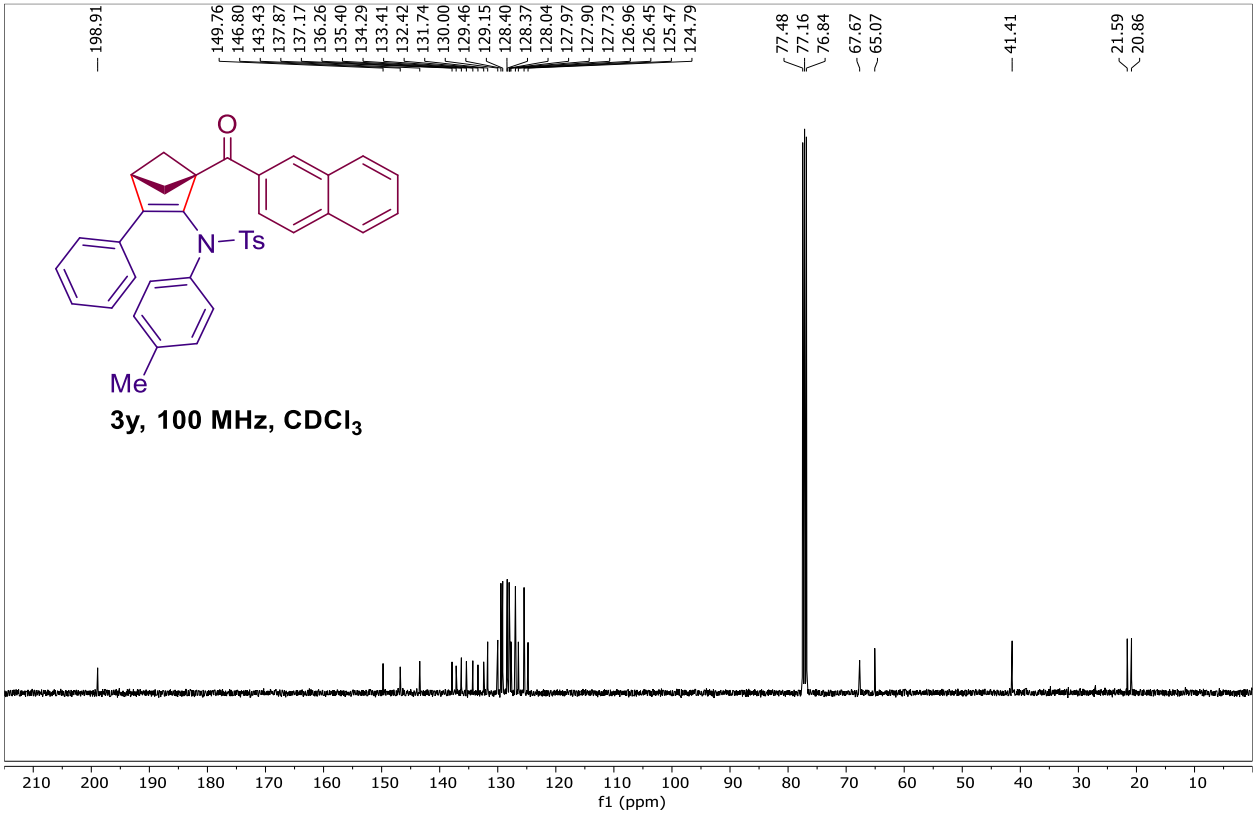
_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_-(4-methoxyphenyl)-4-methyl benzenesulfonamide (3x)



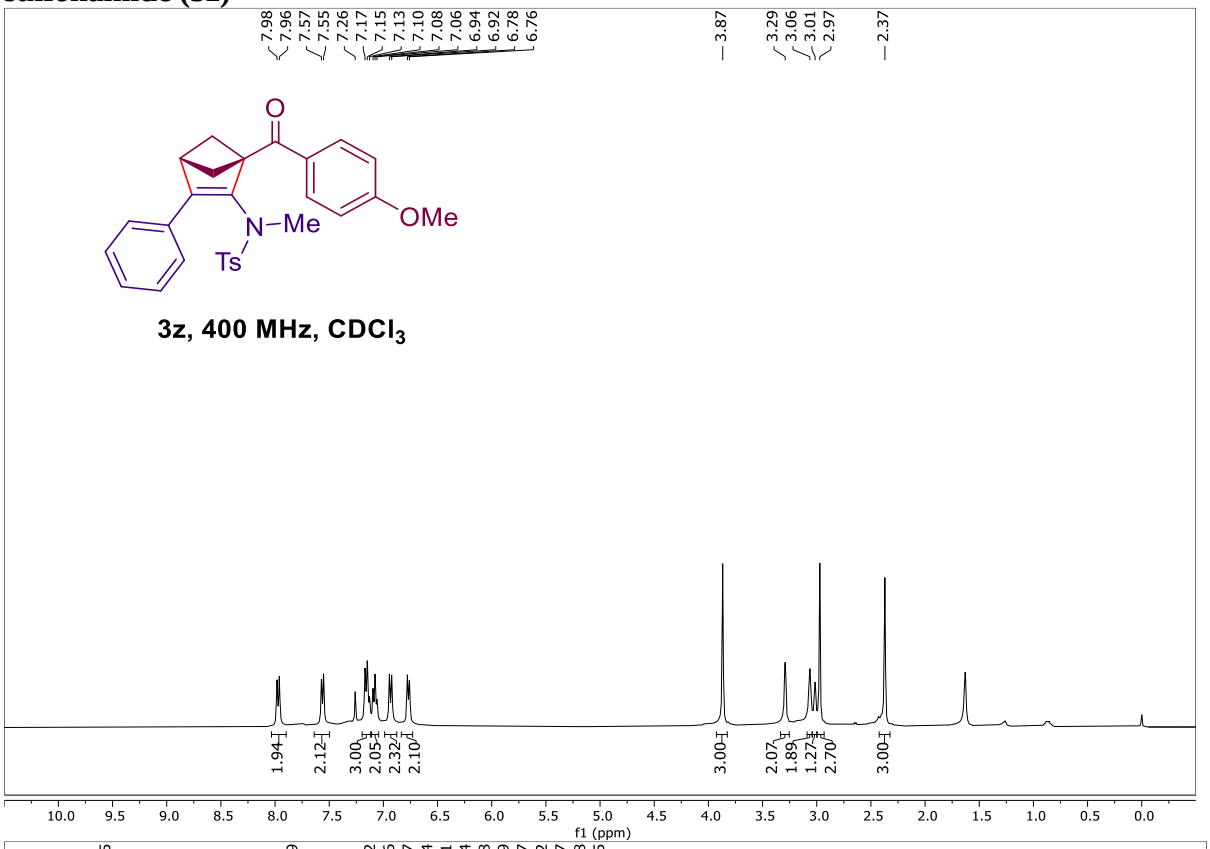


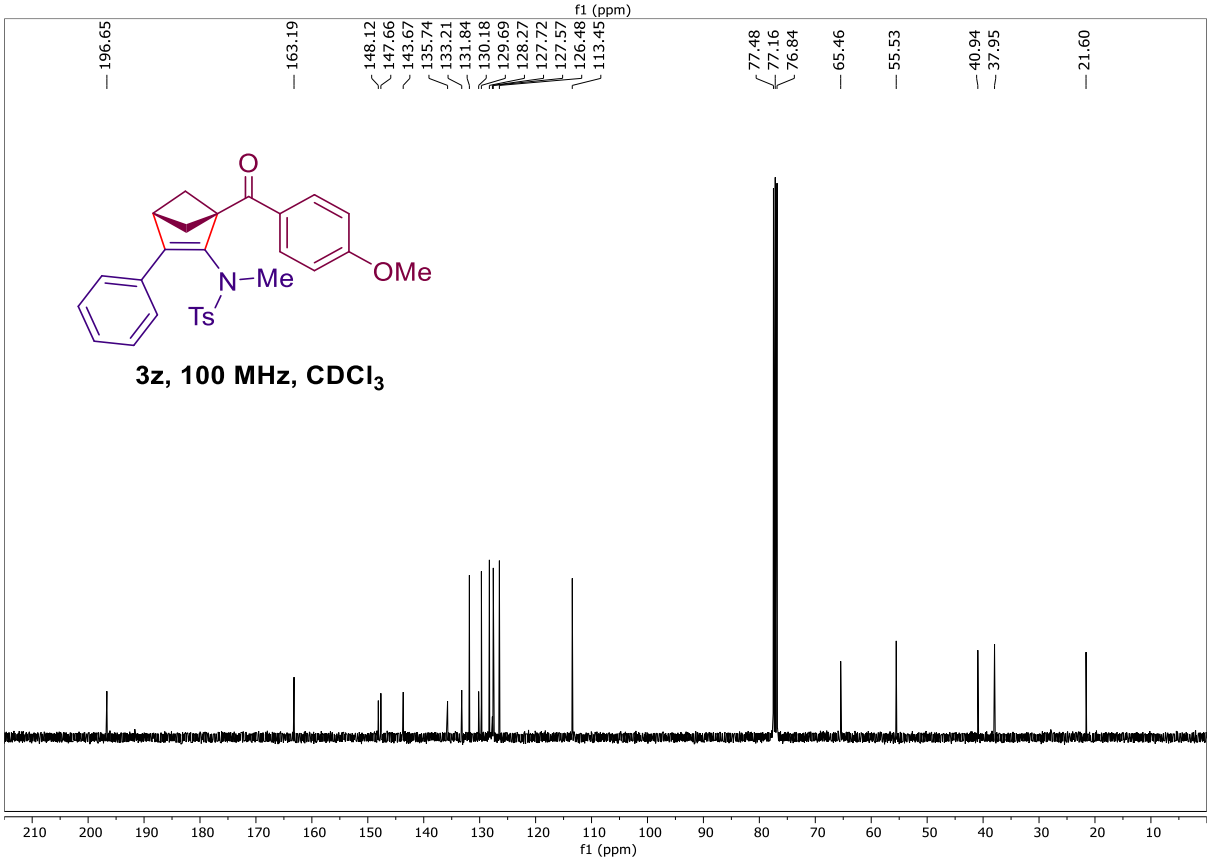
_N_-(1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-4-methyl-_N_-(_p_-tolyl)benzene sulfonamide (3y)



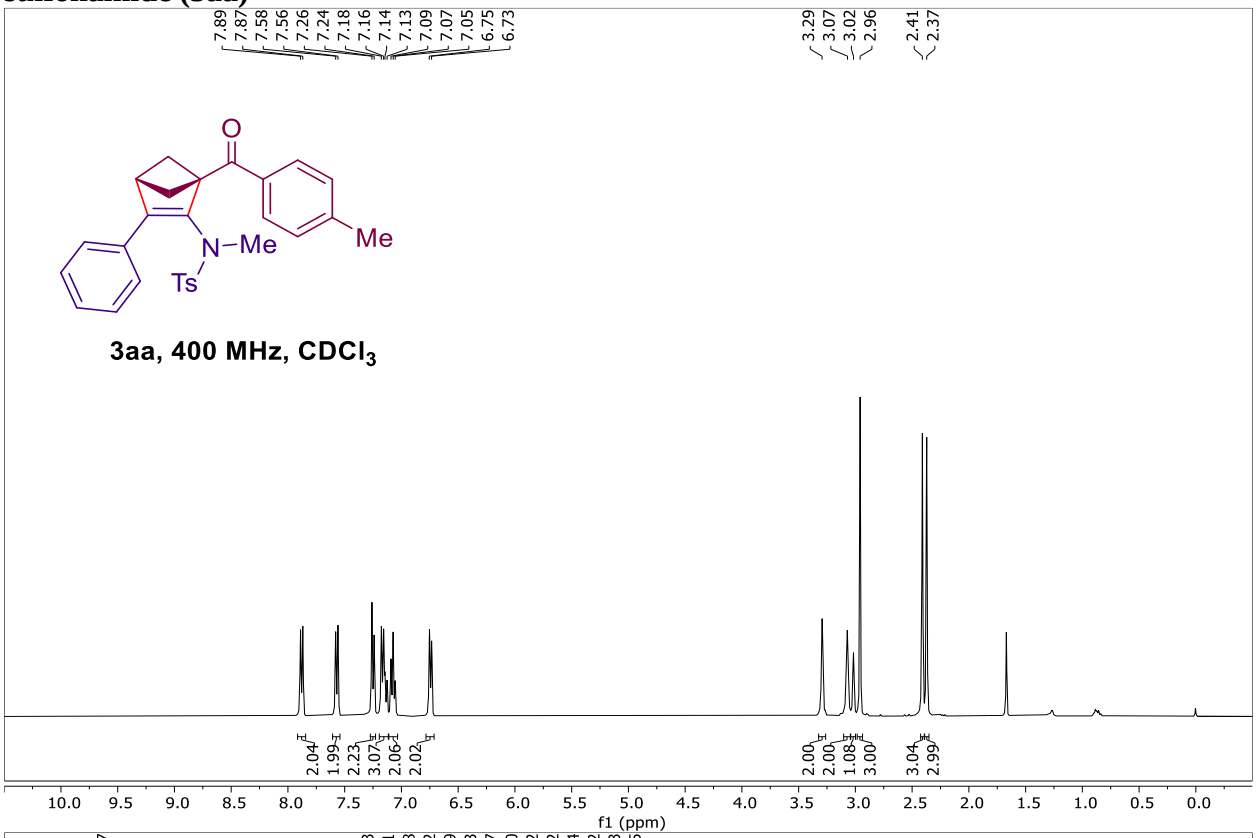


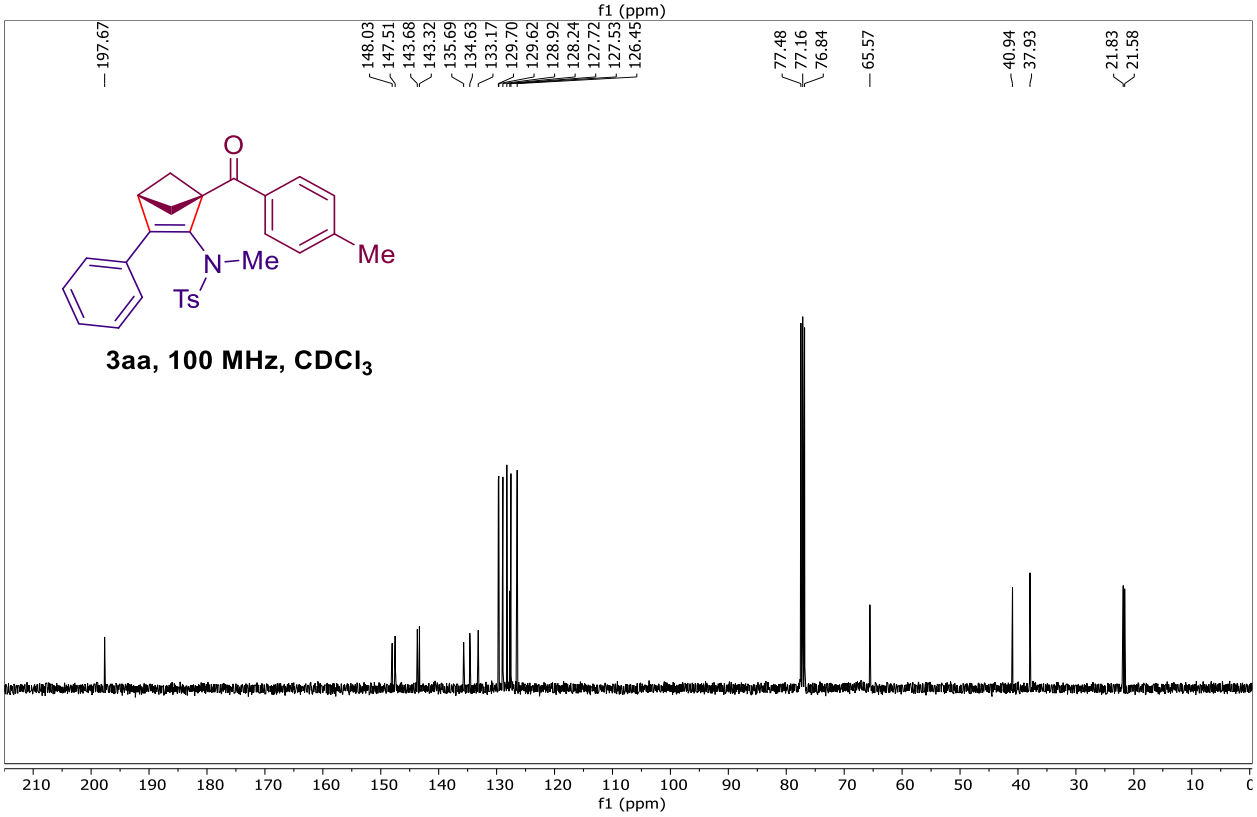
***N*-(1-(4-Methoxybenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzene sulfonamide (3z)**



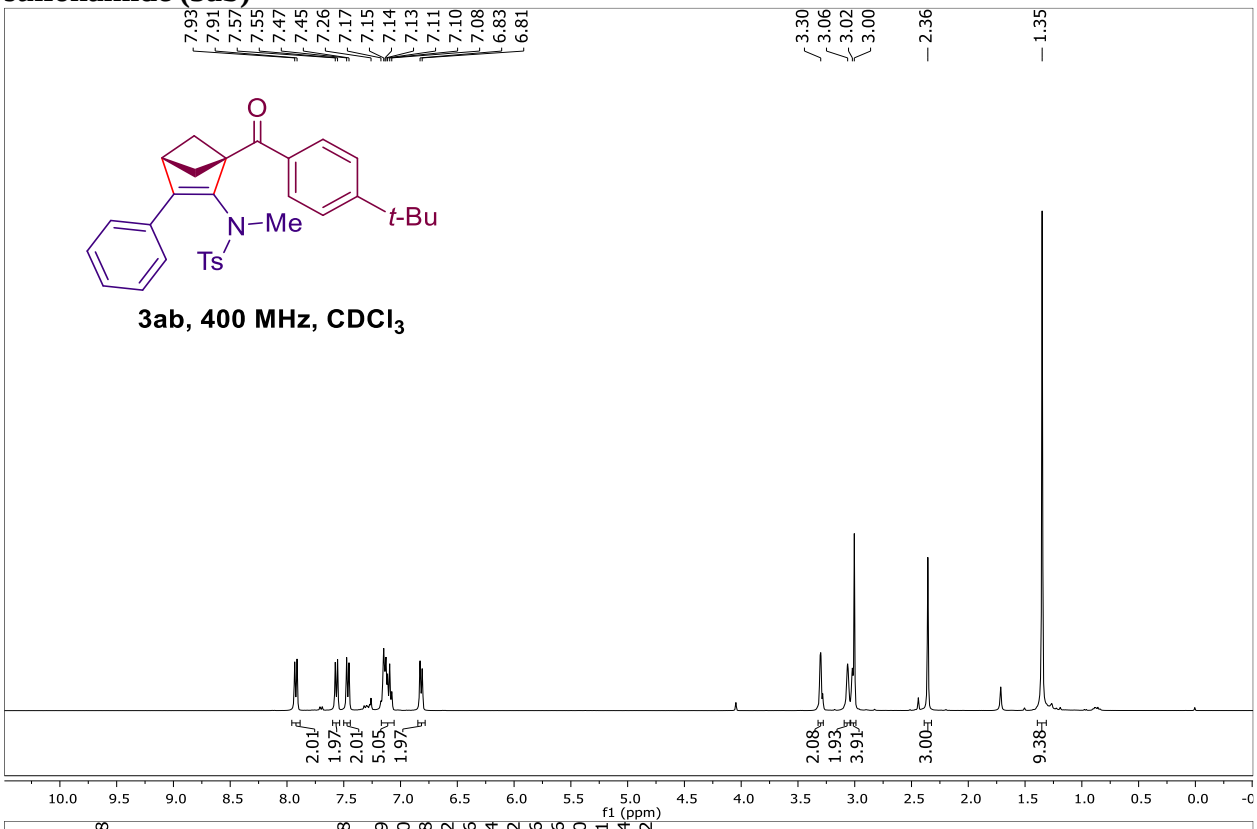


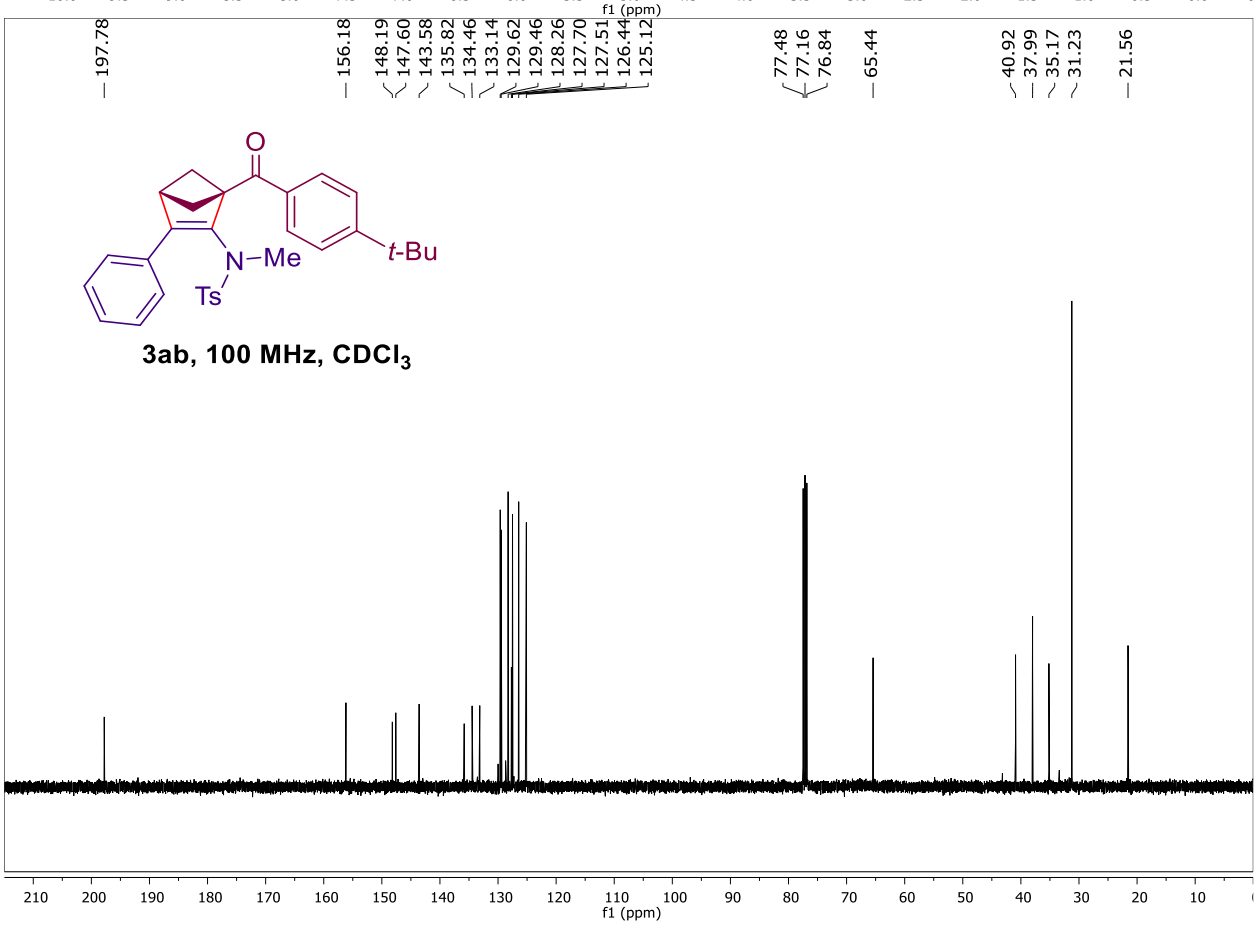
_N_,4-Dimethyl-_N_-(1-(4-methylbenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide (3aa)



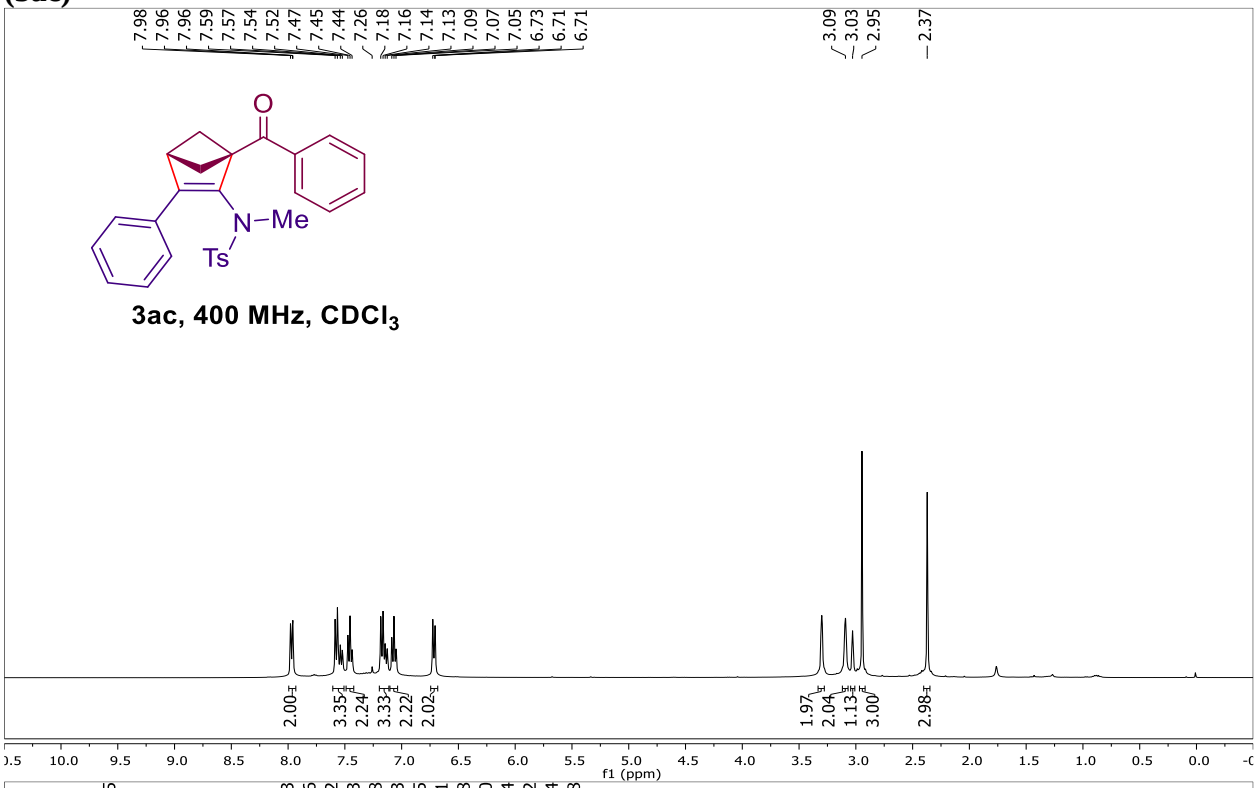


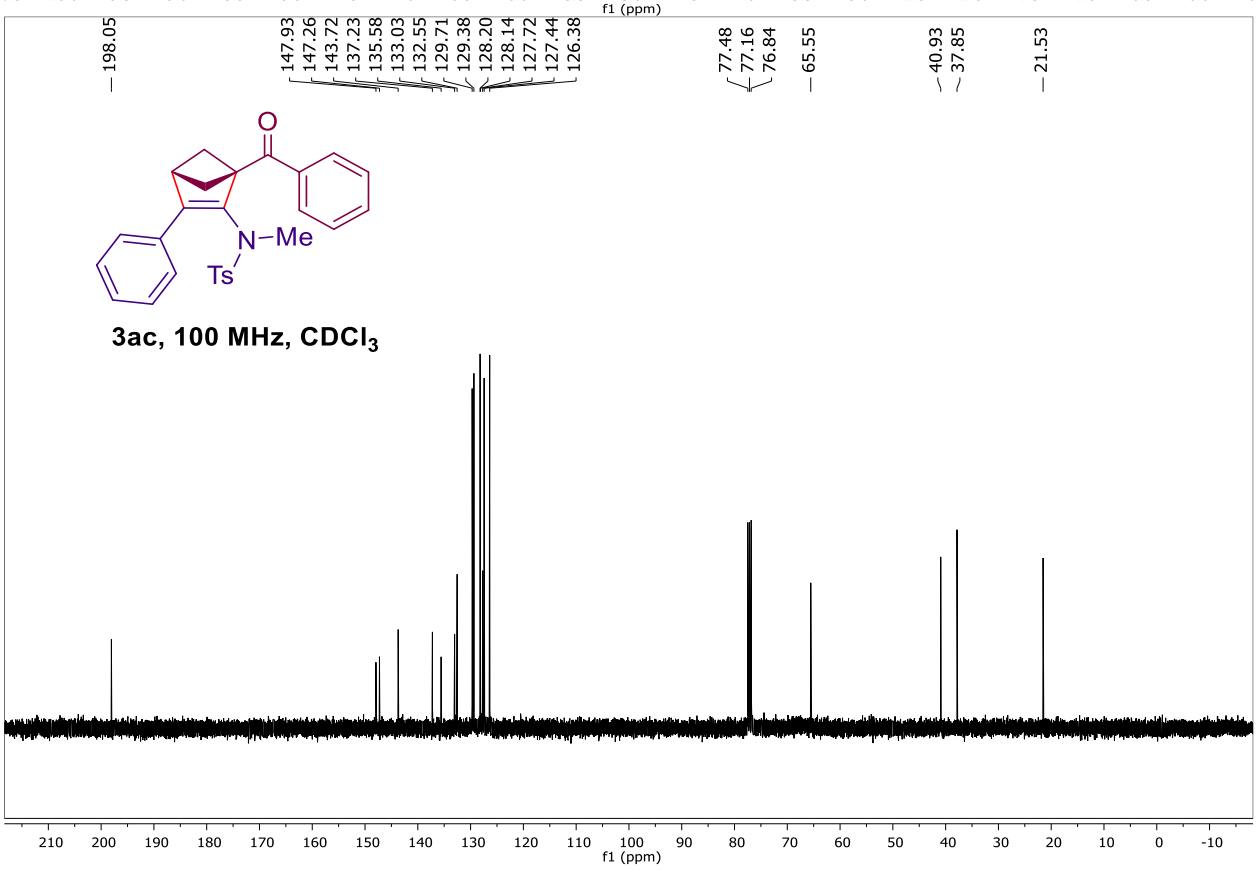
***N*-(1-(4-(*tert*-Butyl)benzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3ab)**



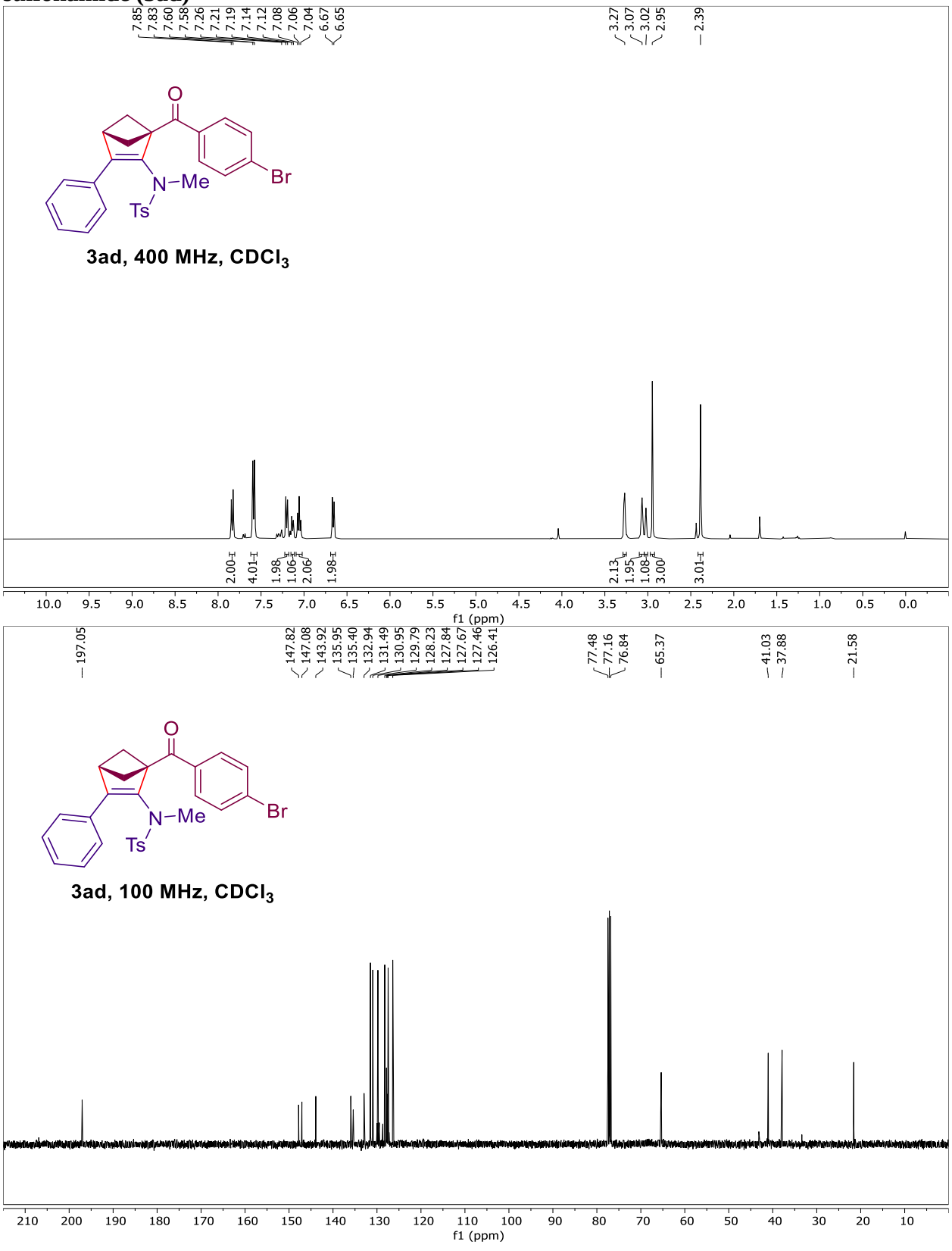


***N*-(1-Benzoyl-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide (3ac)**

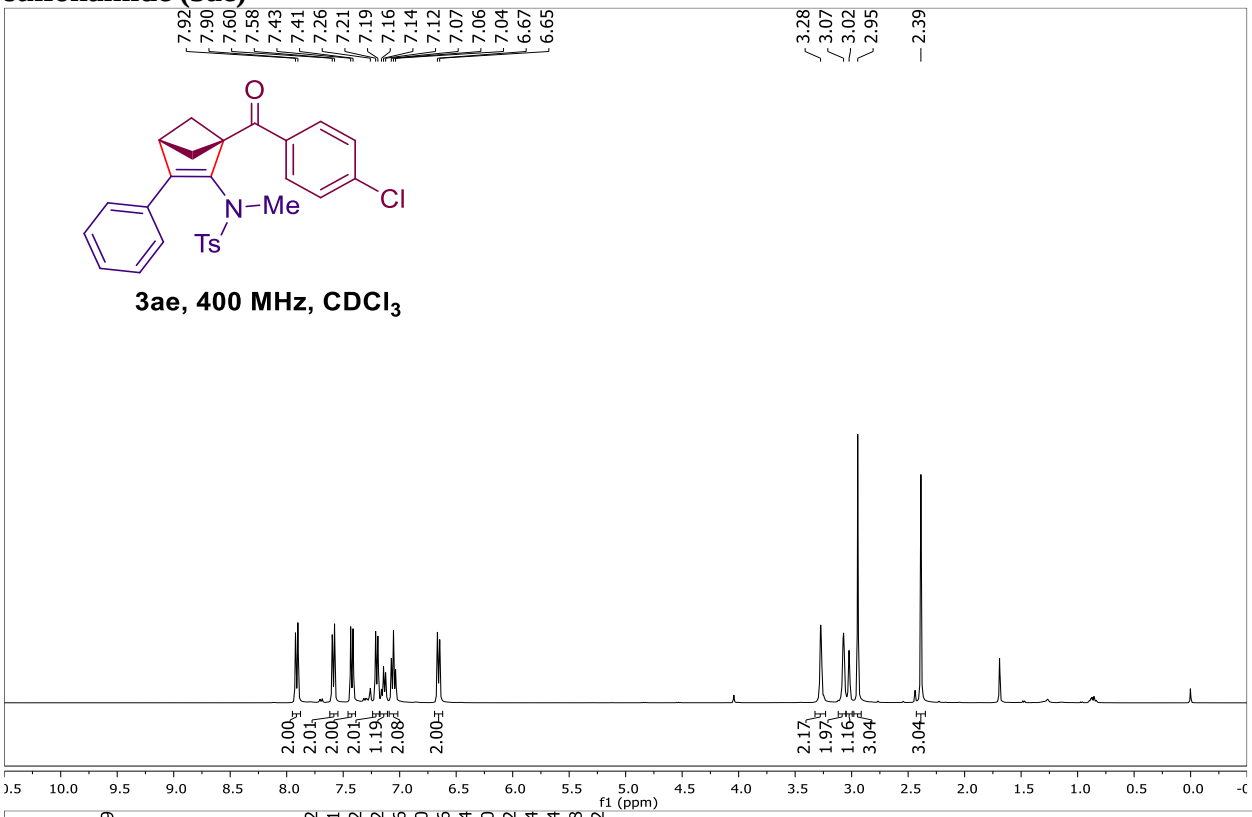


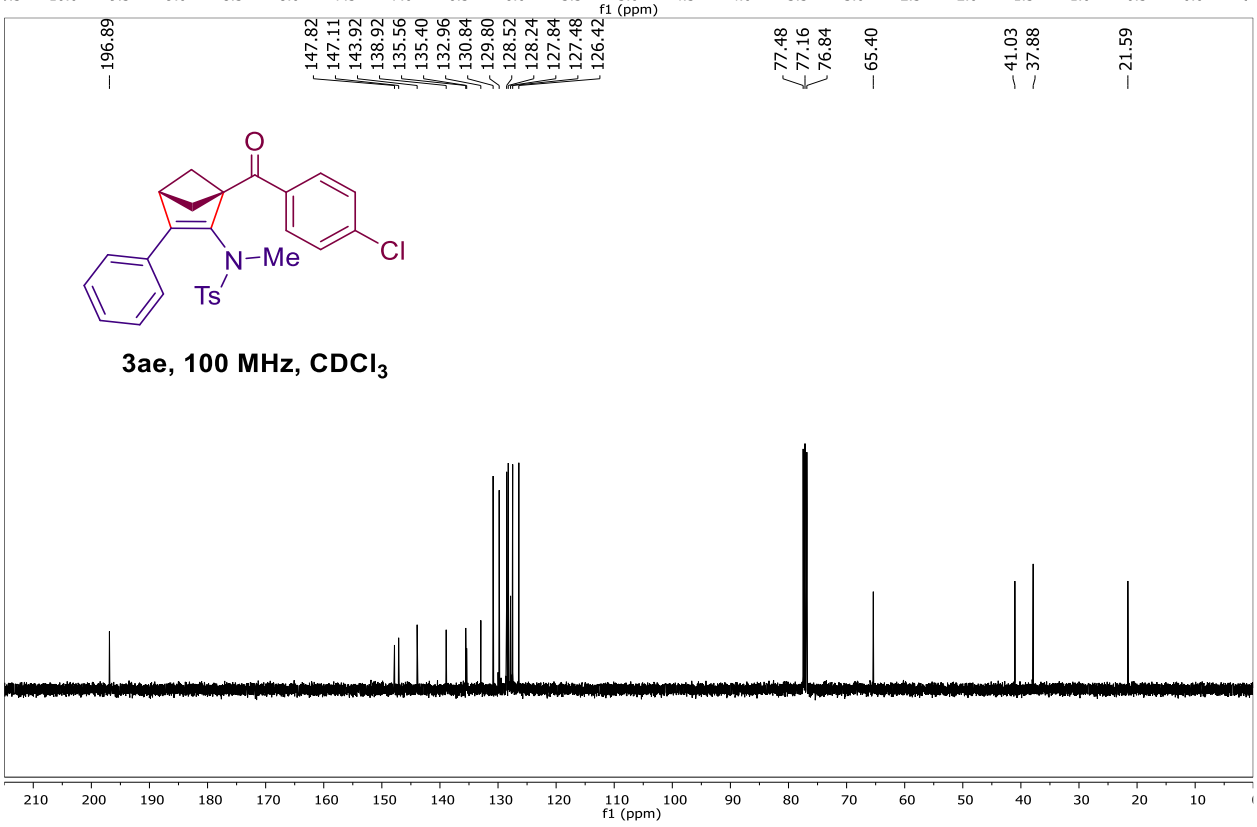


***N*-(1-(4-Bromobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3ad)**

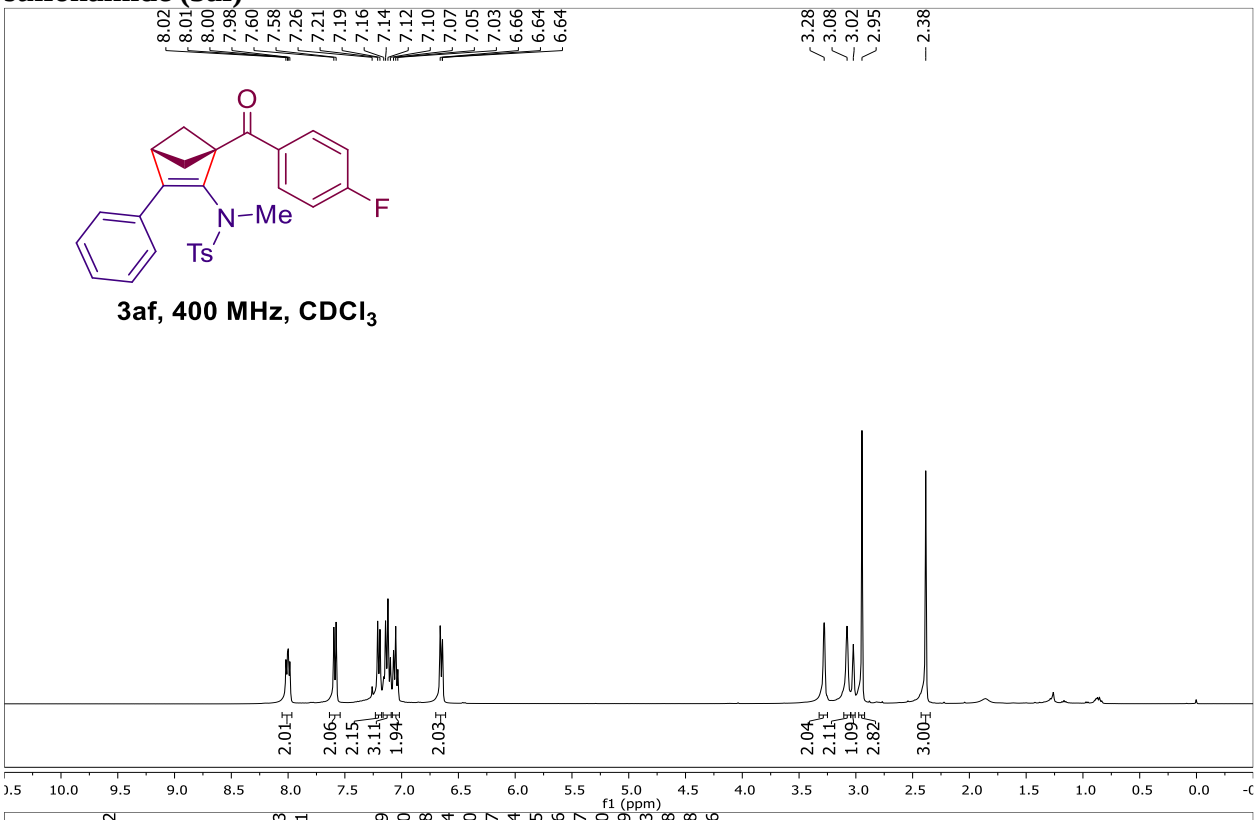


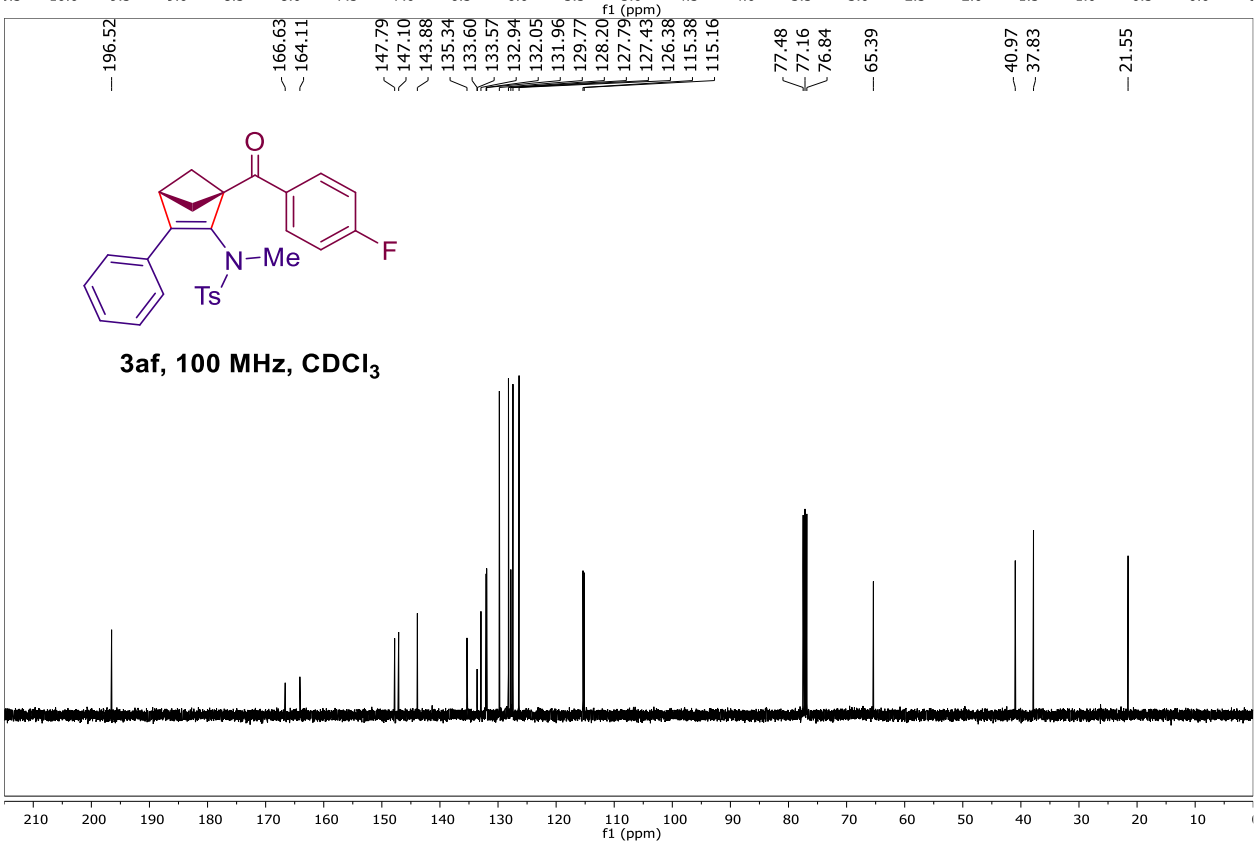
_N_-(1-(4-Chlorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3ae)

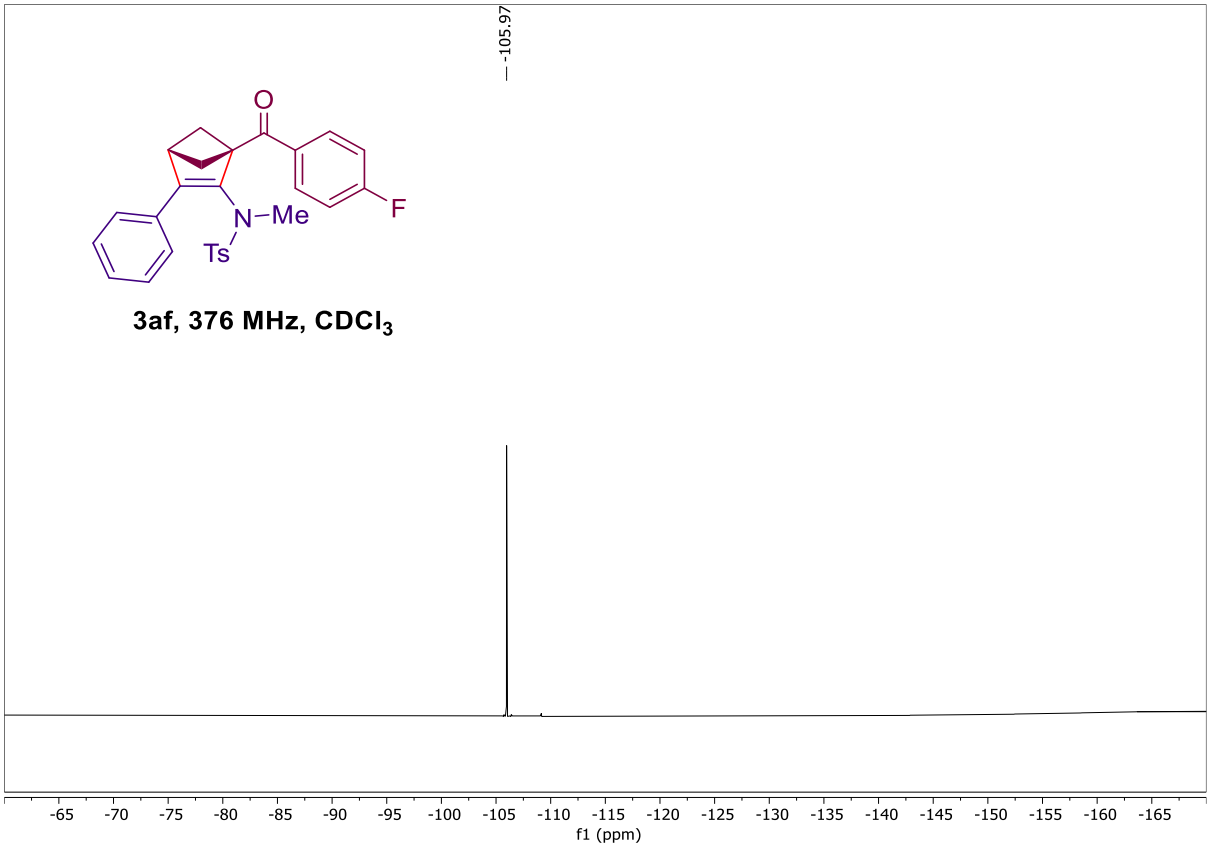




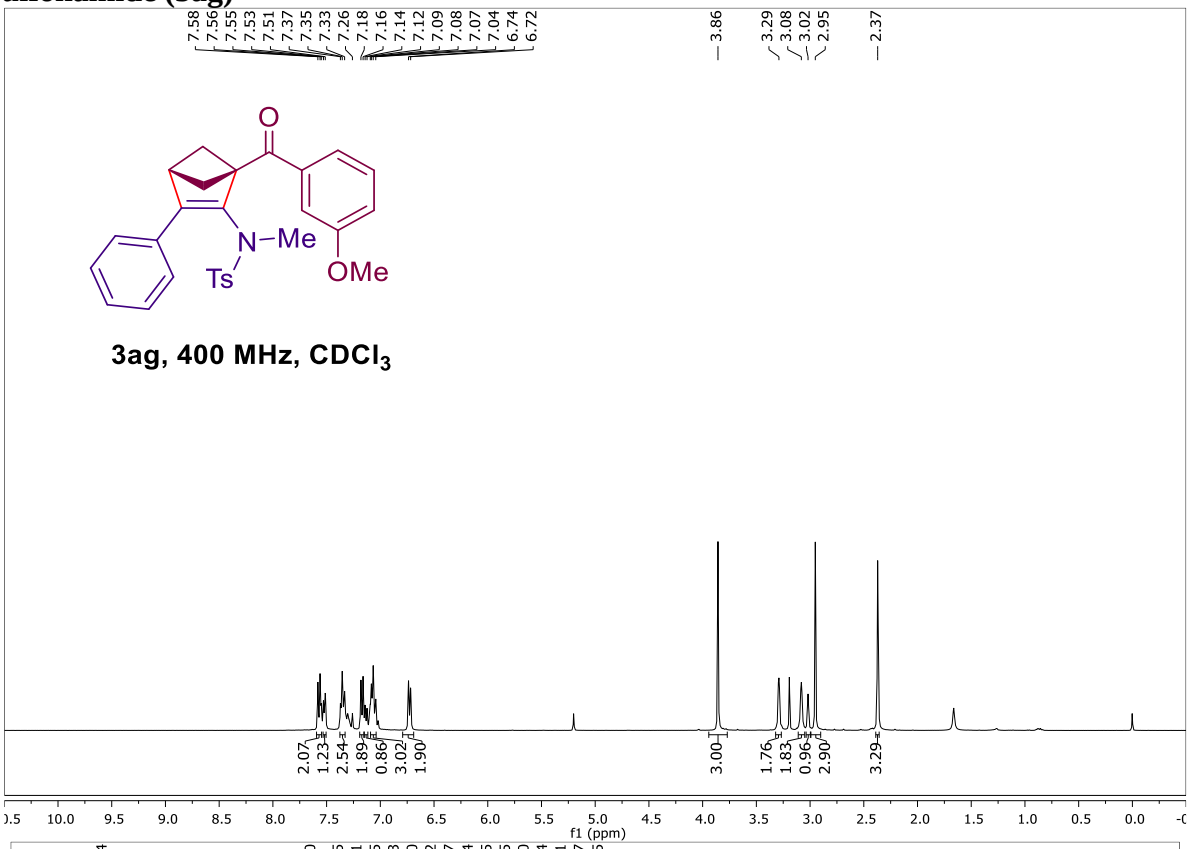
***N*-(1-(4-Fluorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3af)**

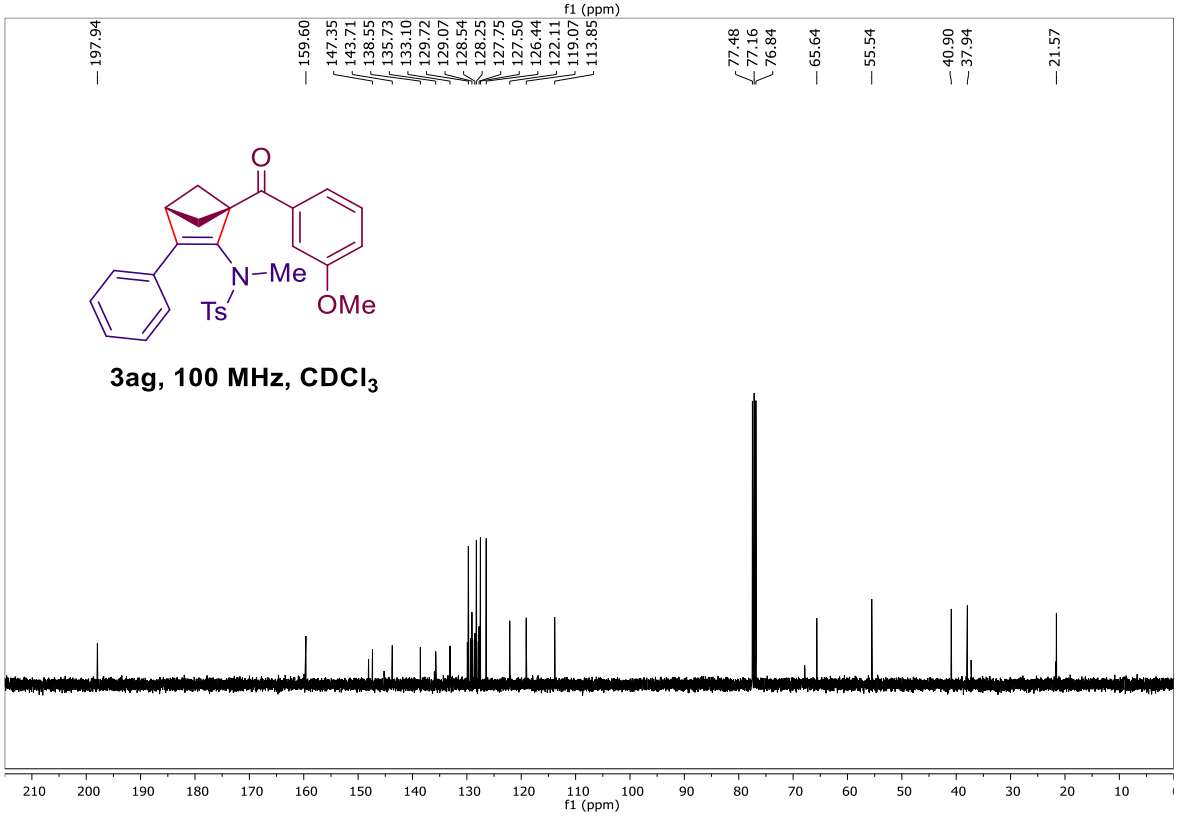




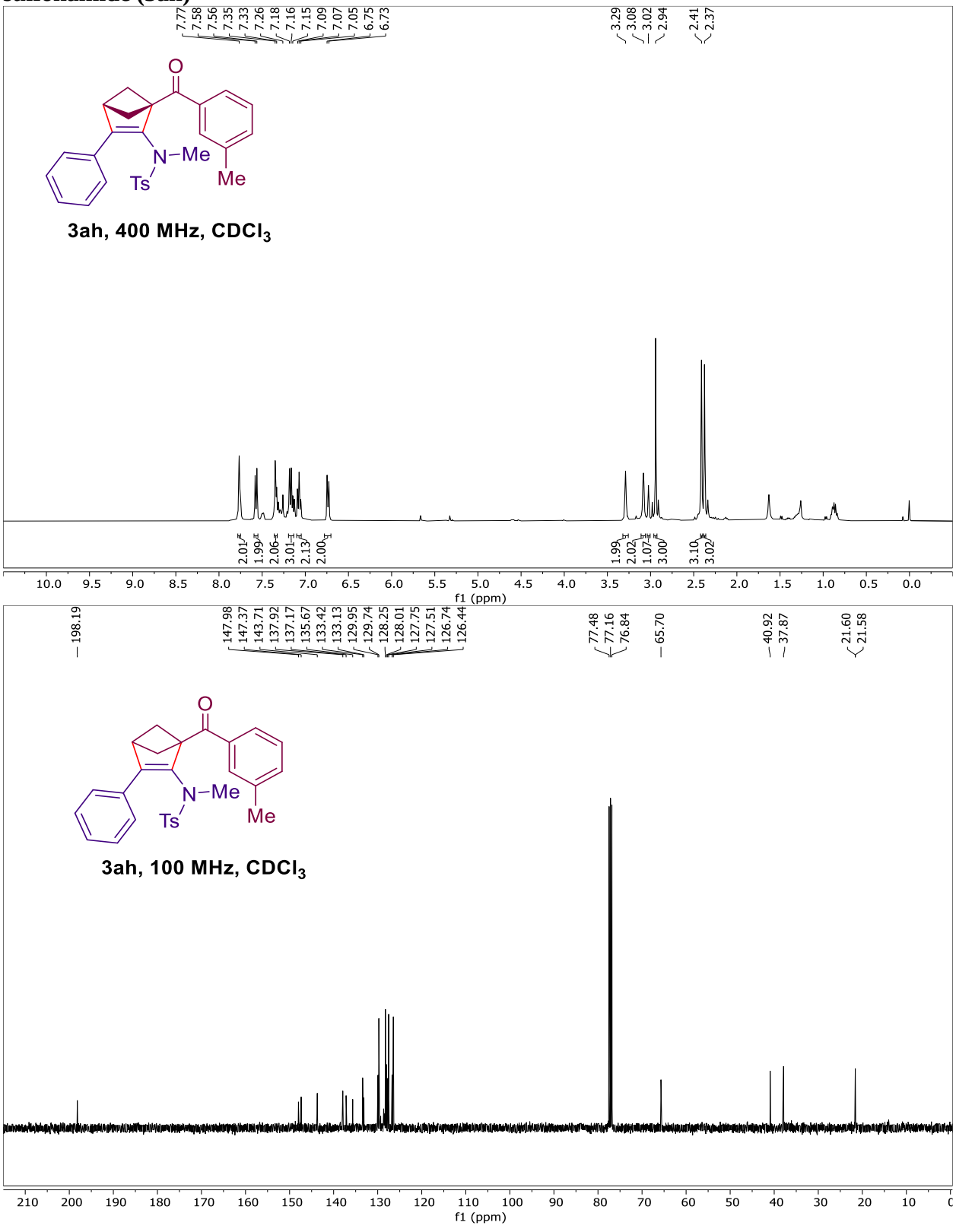

-105.97
O
F
N–Me
Ts
3af, 376 MHz, CDCl3
-65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)

_N_-(1-(3-Methoxybenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3ag)

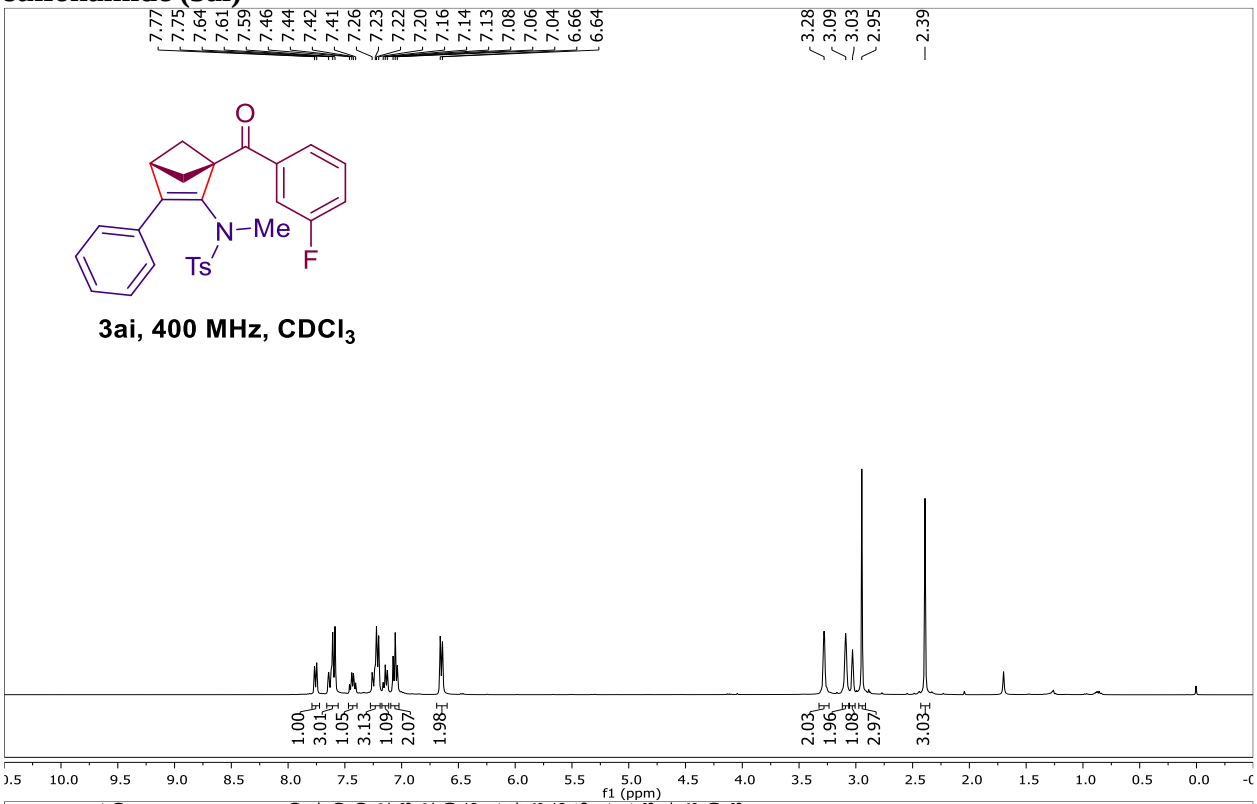


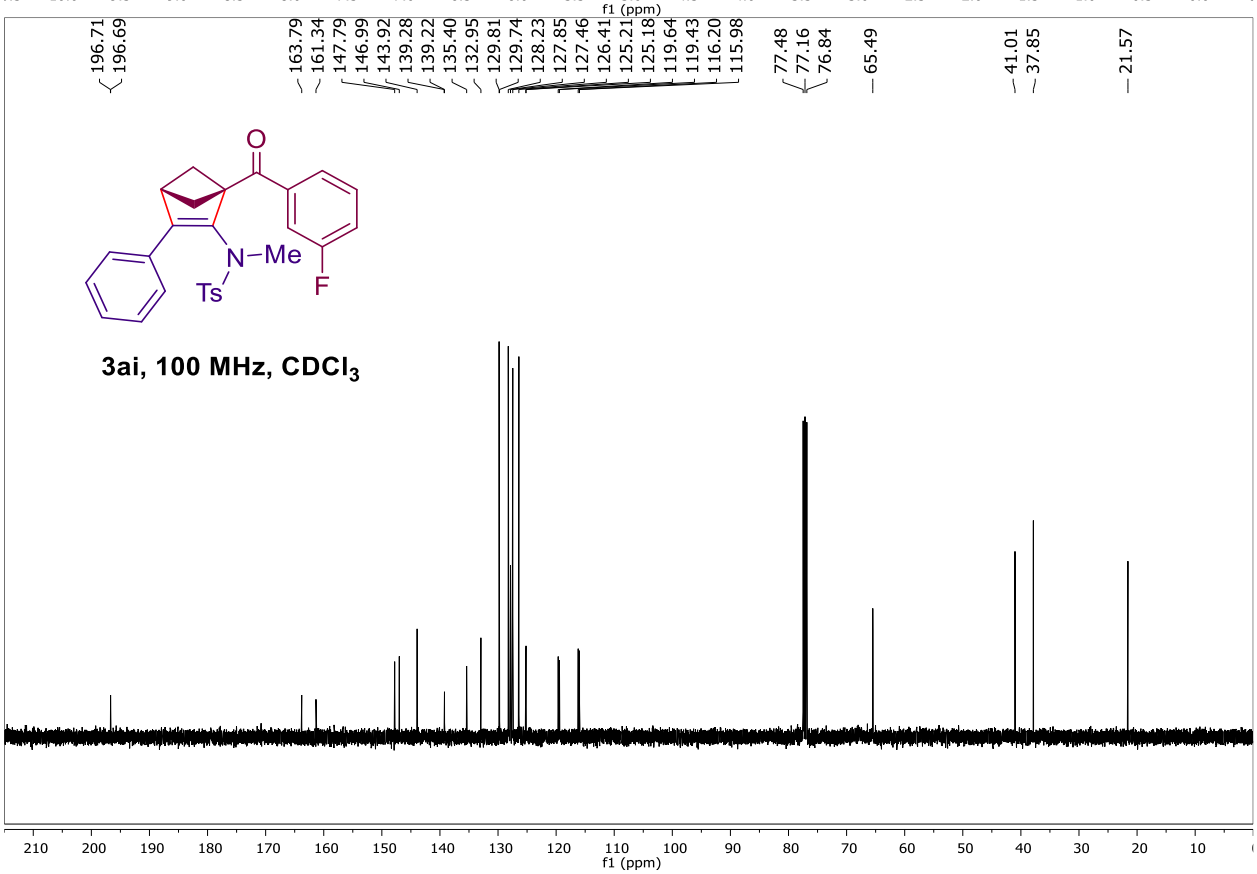


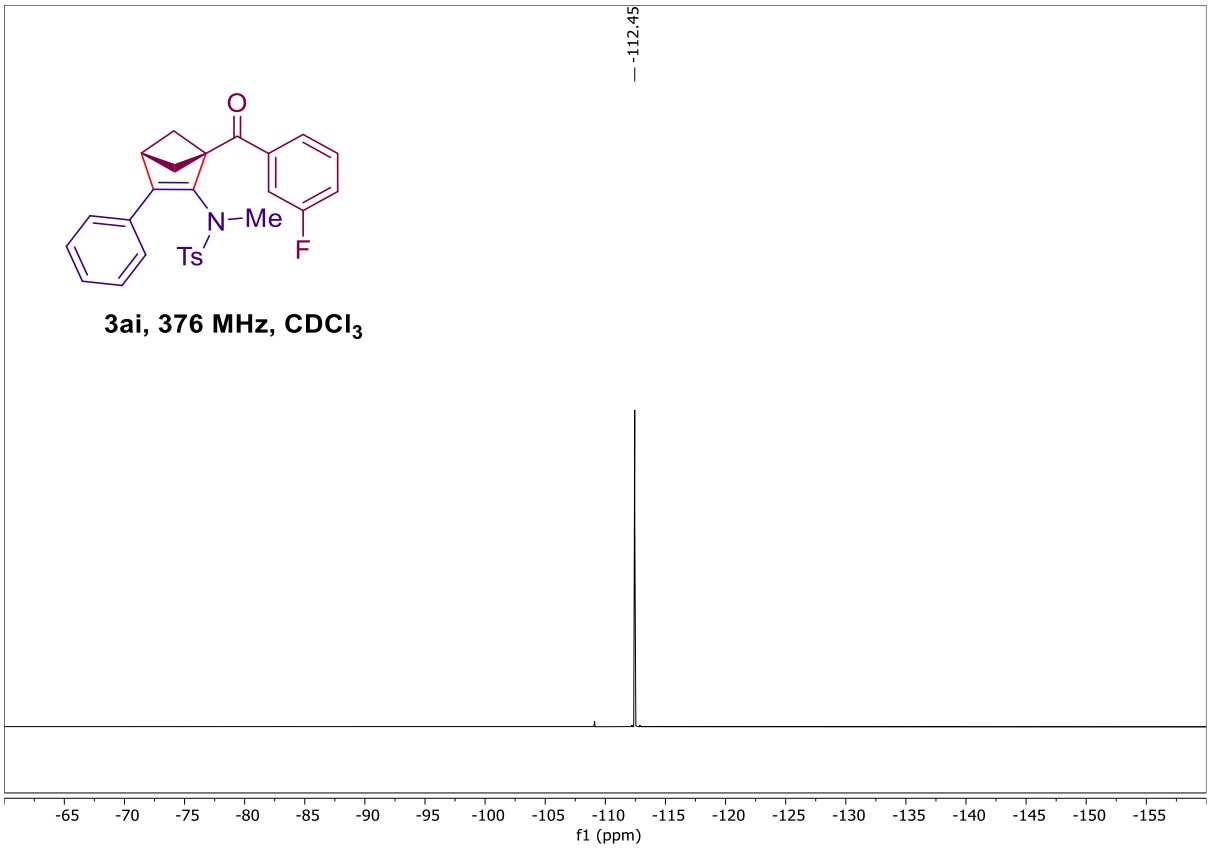
_N_,4-Dimethyl-_N_-(1-(3-methylbenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide (3ah)



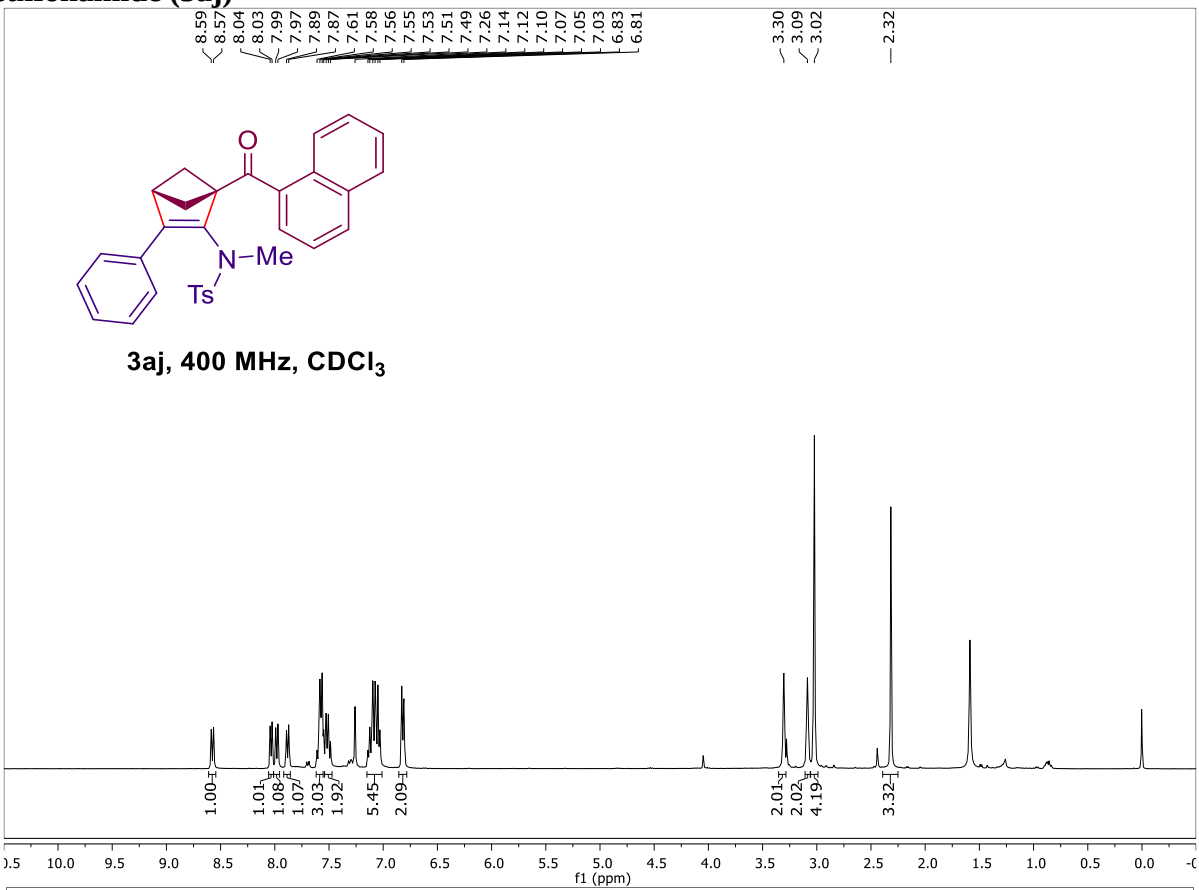
_N_-(1-(3-Fluorobenzoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-_N_,4-dimethylbenzene sulfonamide (3ai)

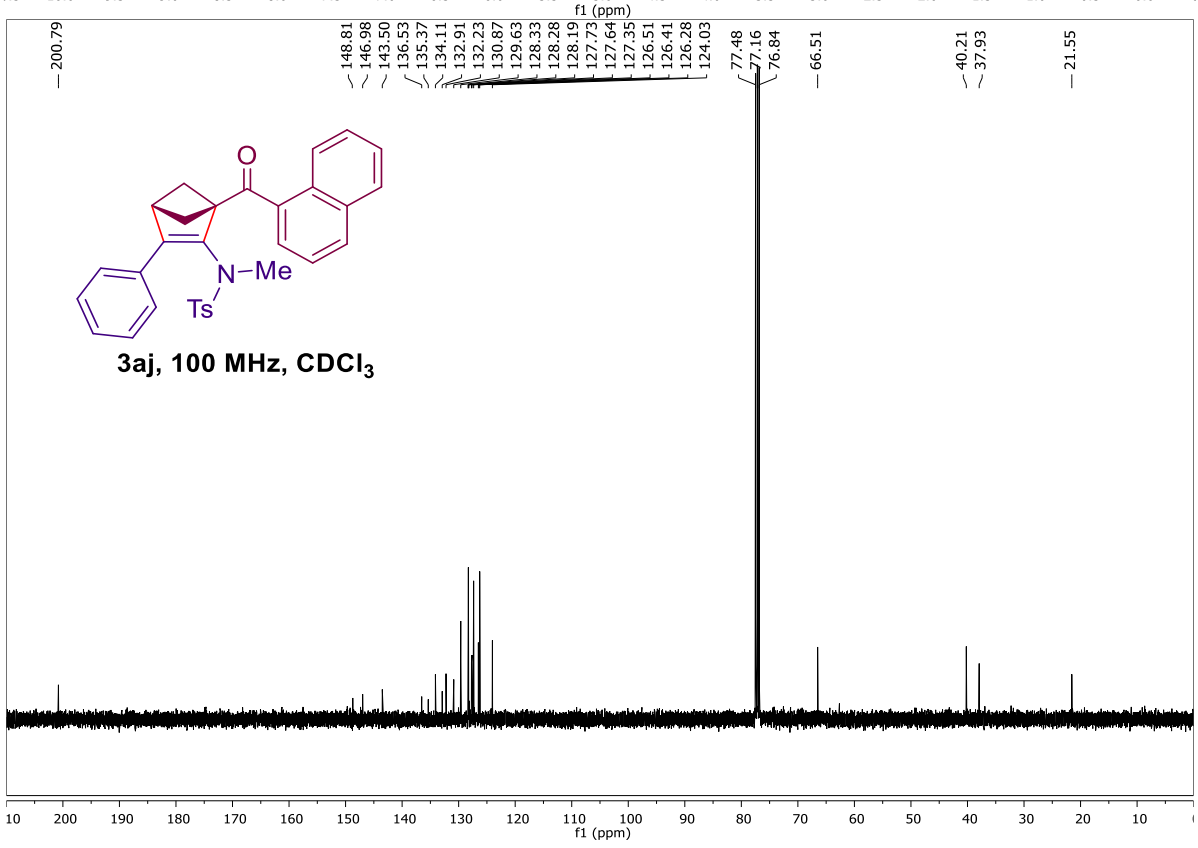




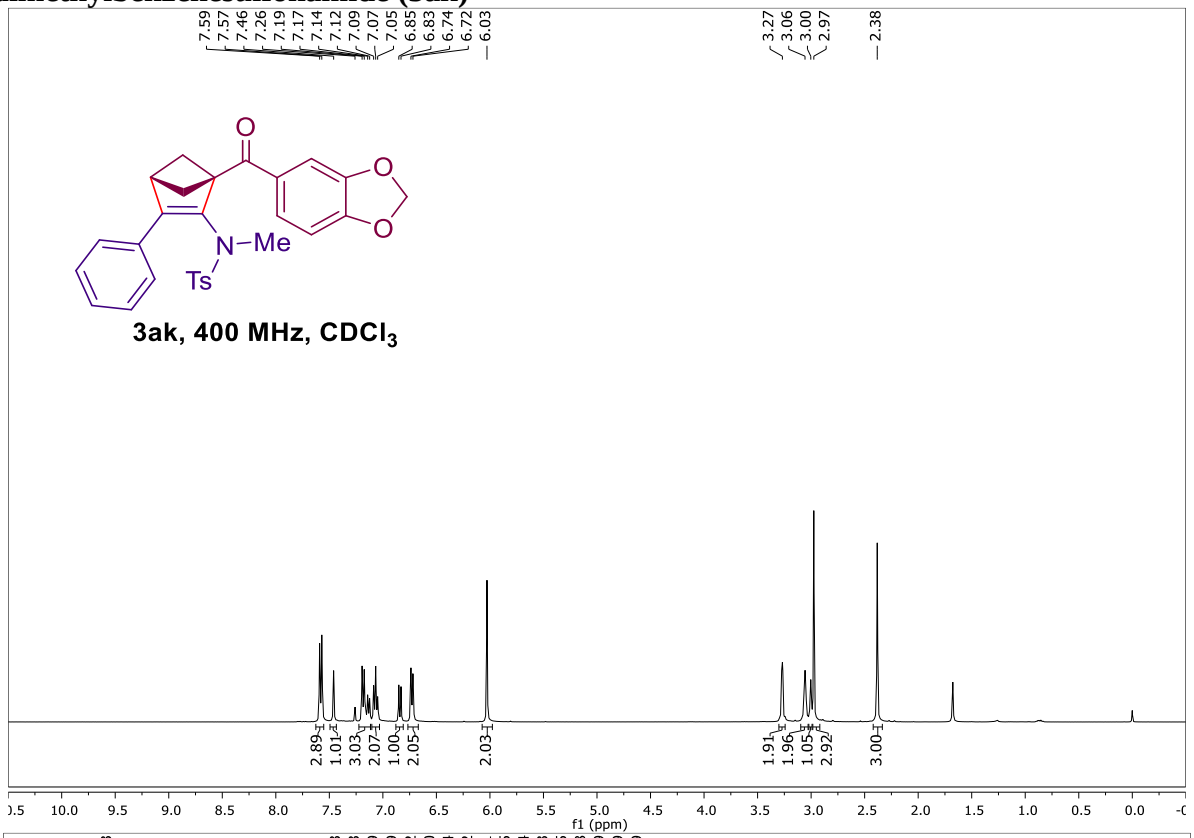

-112.45
O
N–Me
Ts
F
3ai, 376 MHz, CDCl3
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

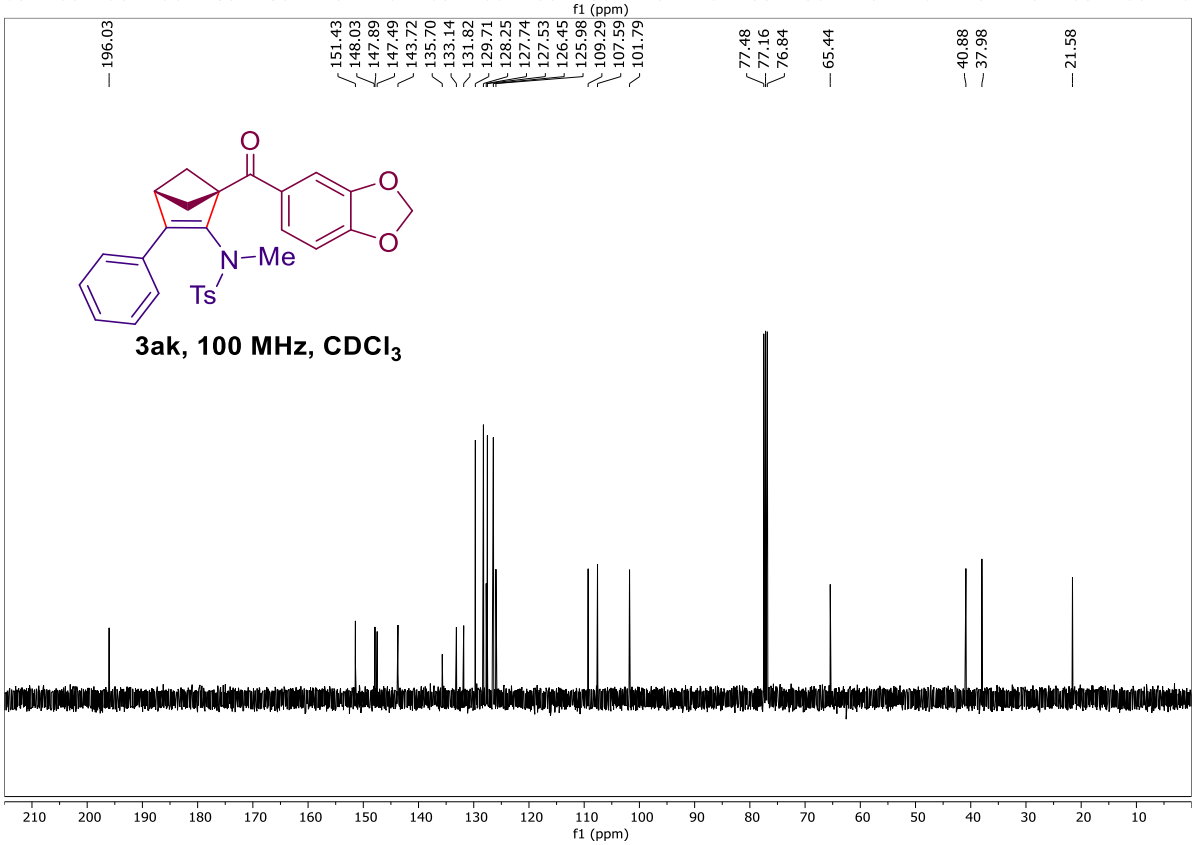
***N*-(1-(1-Naphthoyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3aj)**



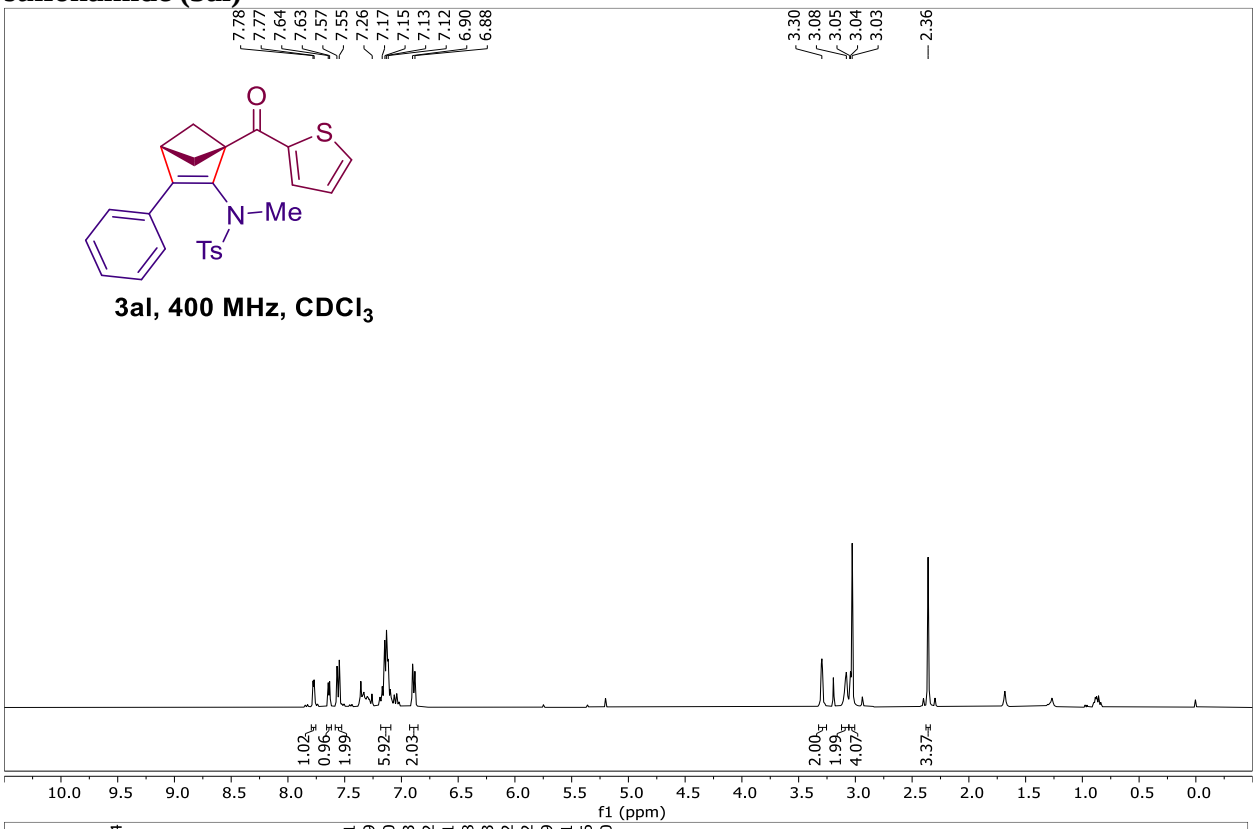


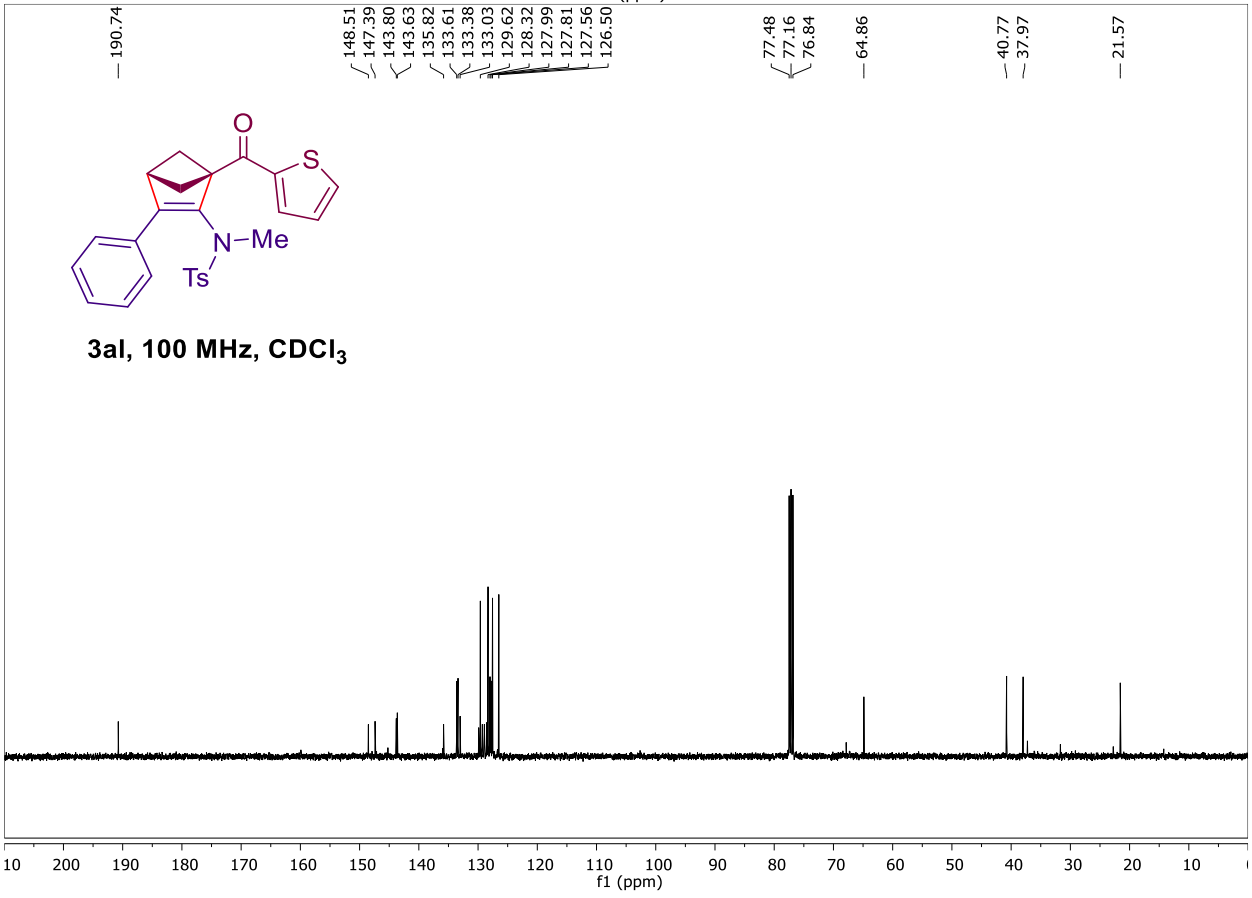
***N*-(1-(Benzo[*d*][1,3]dioxole-5-carbonyl)-3-phenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzenesulfonamide (3ak)**



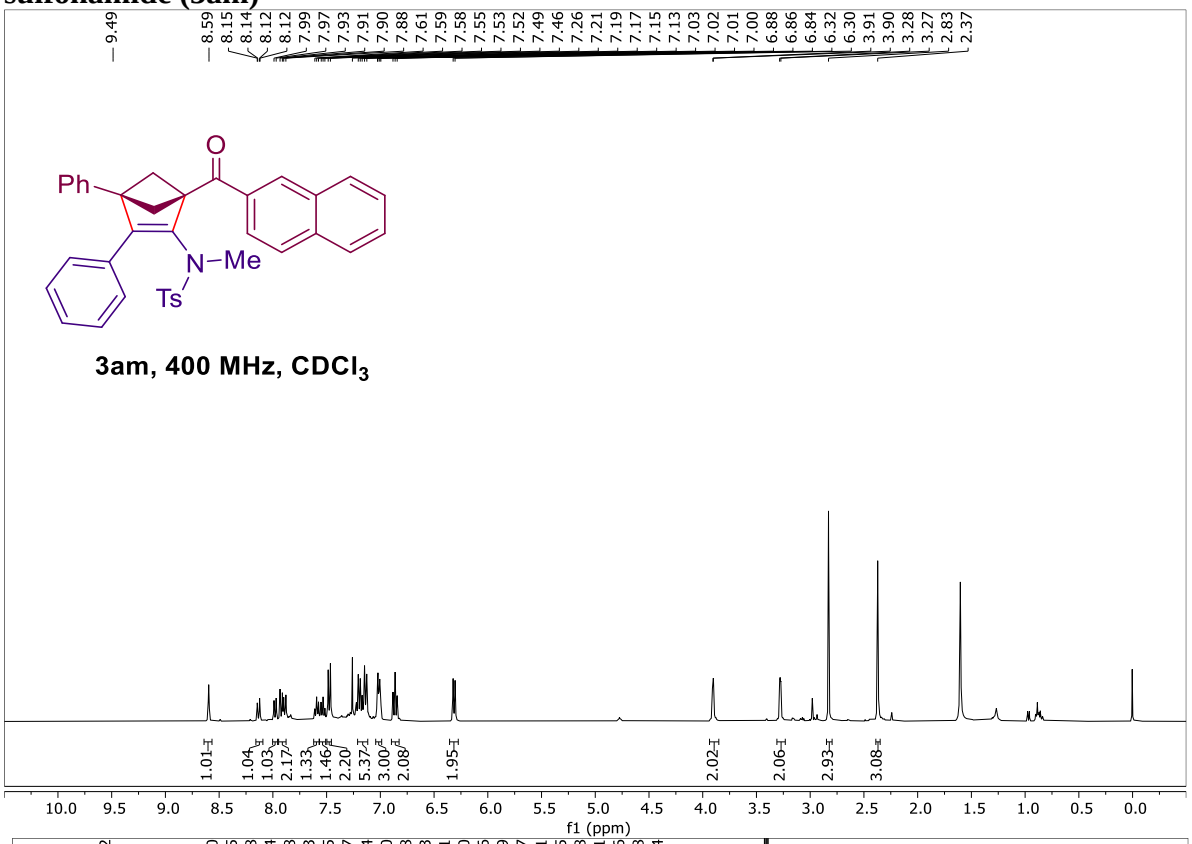


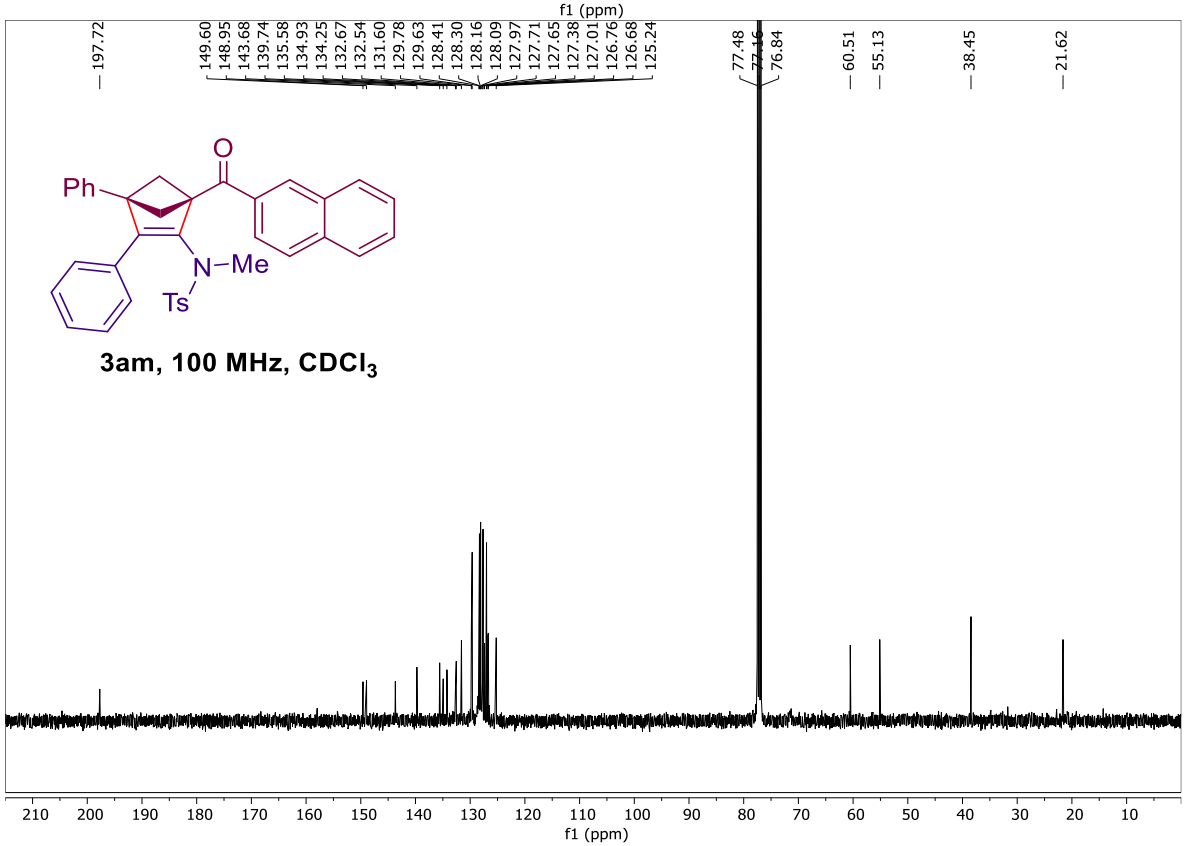
***N*,4-Dimethyl-*N*-(3-phenyl-1-(thiophene-2-carbonyl)bicyclo[2.1.1]hex-2-en-2-yl)benzene sulfonamide (3al)**



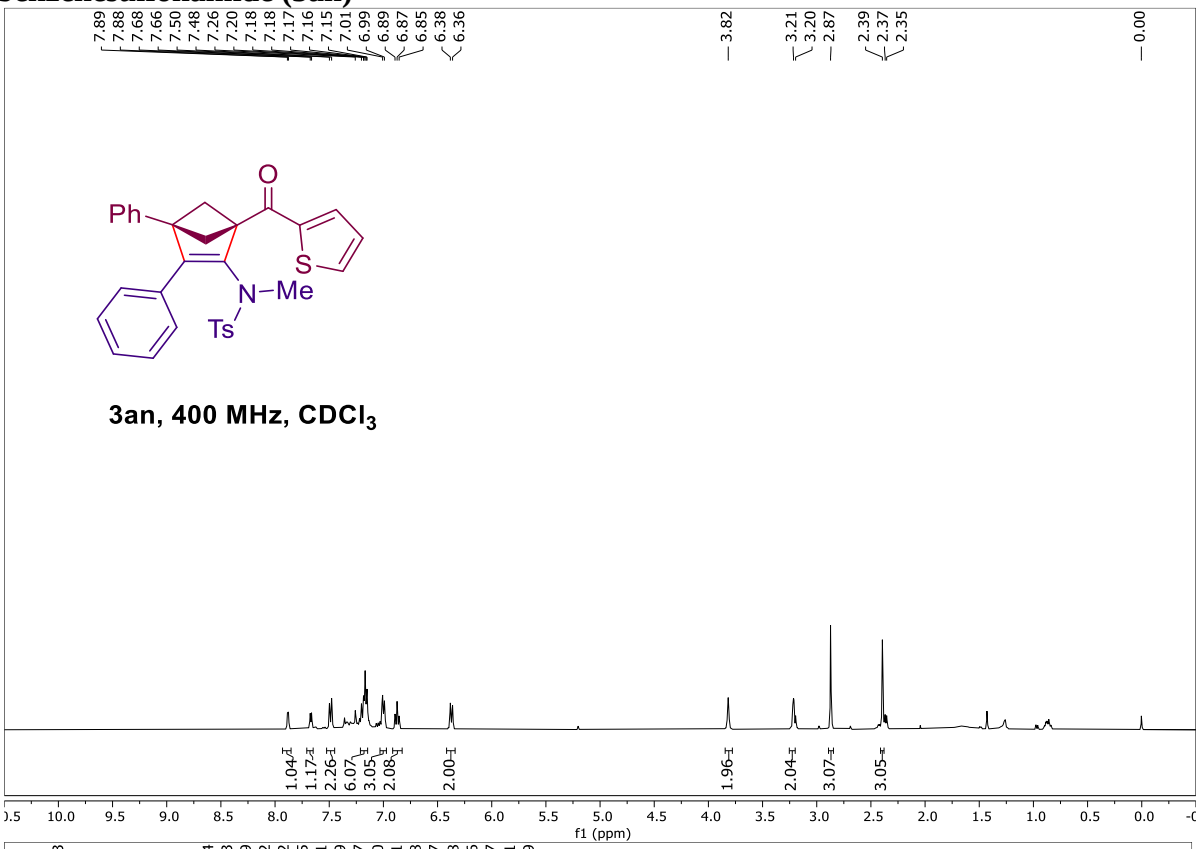


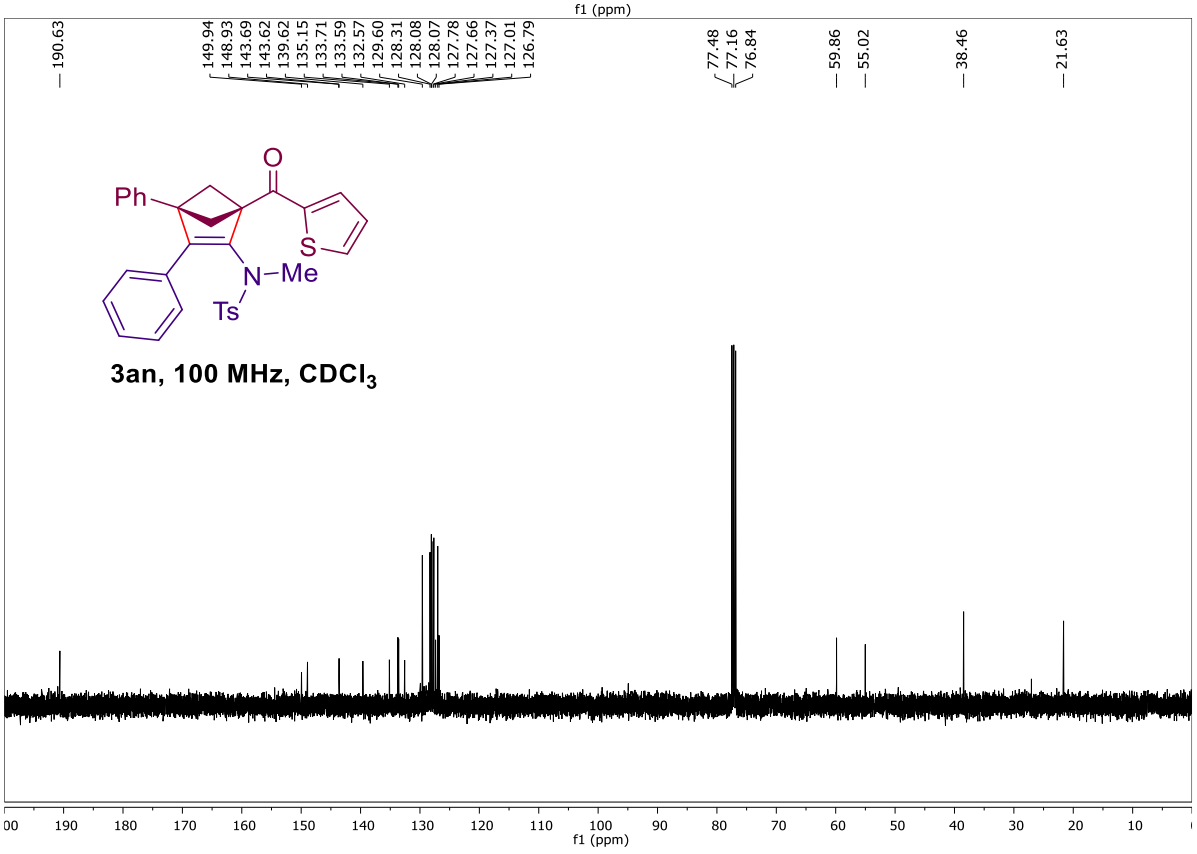
***N*-(1-(2-Naphthoyl)-3,4-diphenylbicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethylbenzene sulfonamide (3am)**



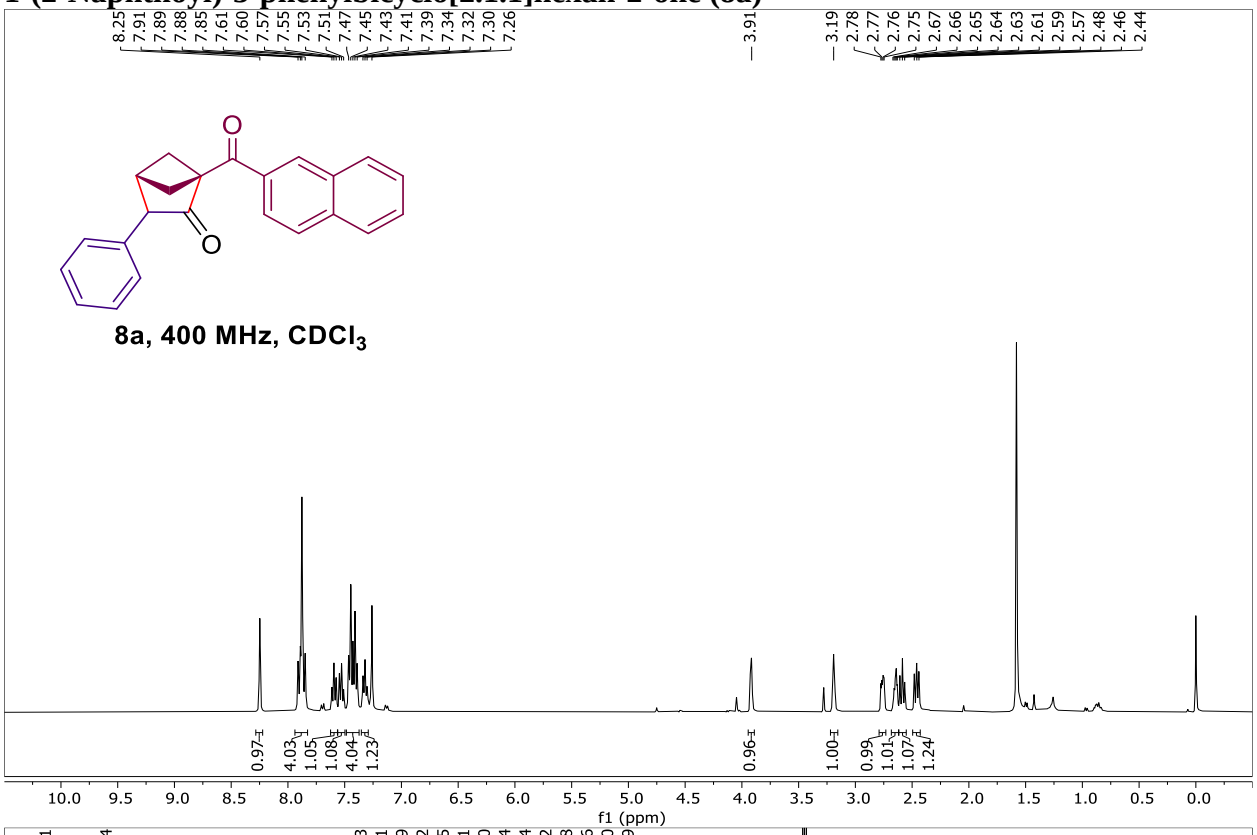


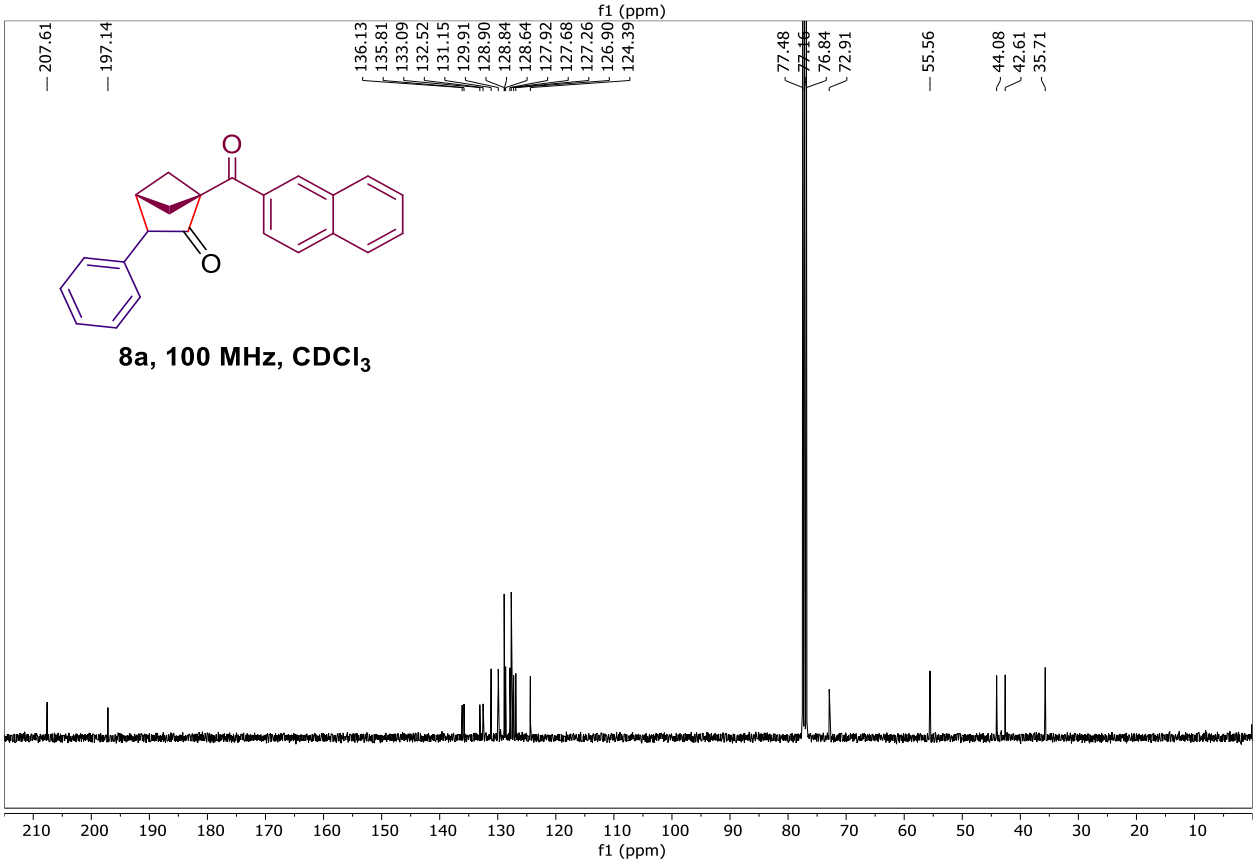
***N*-(3,4-Diphenyl-1-(thiophene-2-carbonyl)bicyclo[2.1.1]hex-2-en-2-yl)-*N*,4-dimethyl benzenesulfonamide (3an)**



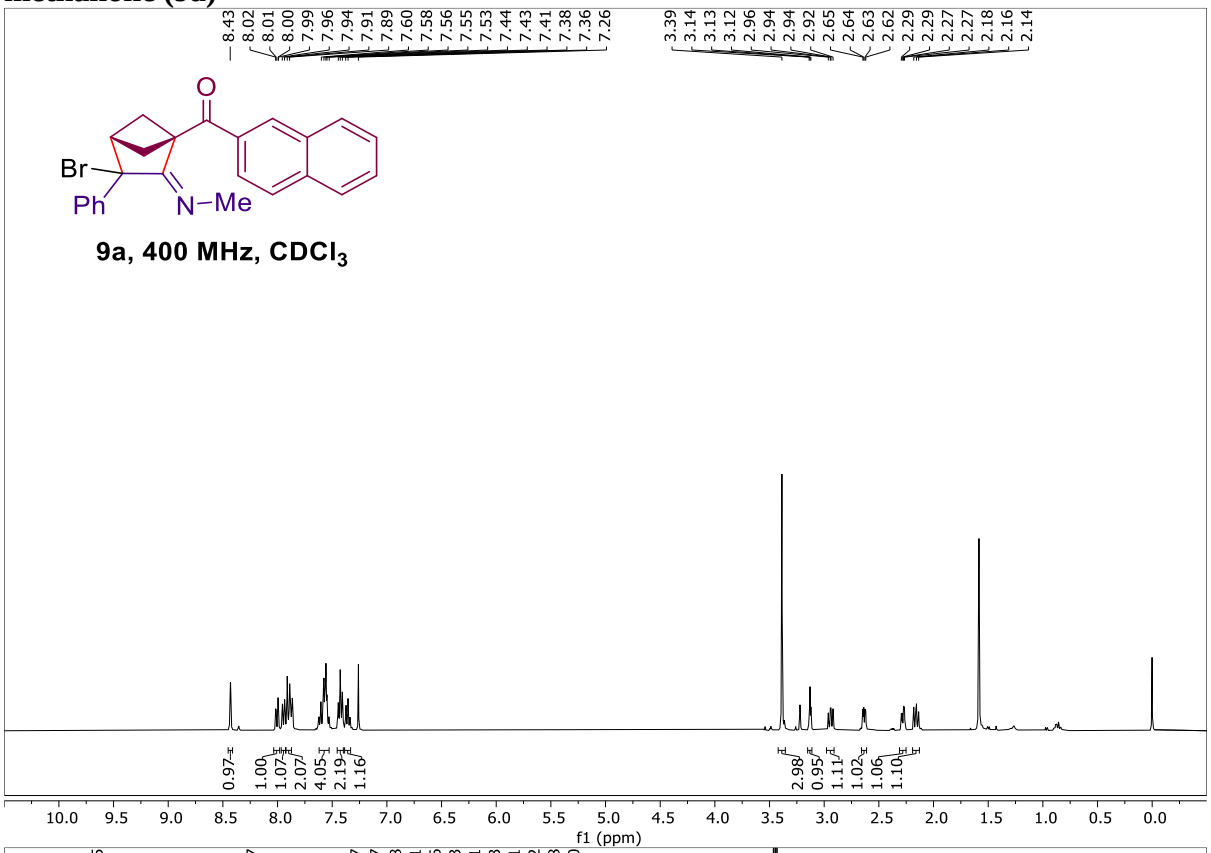


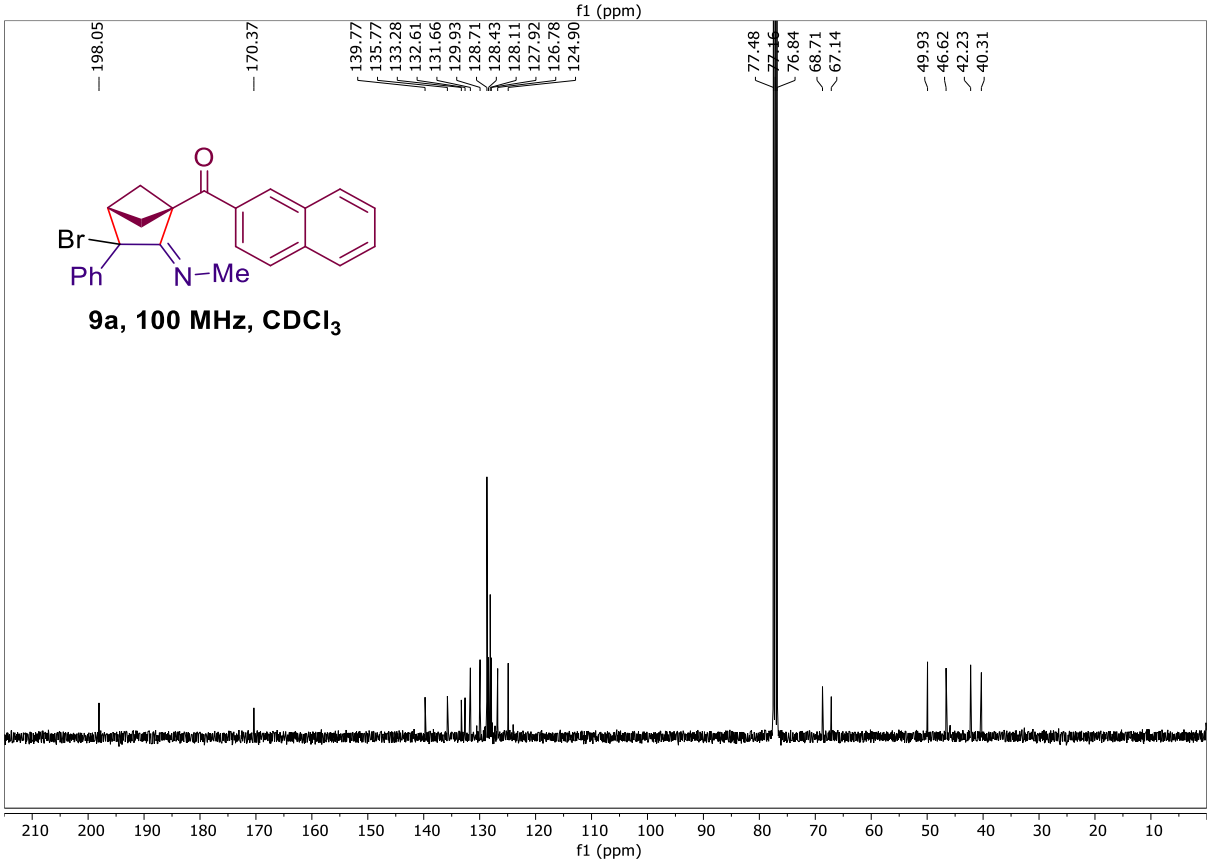
1-(2-Naphthoyl)-3-phenylbicyclo[2.1.1]hexan-2-one (8a)





(3-Bromo-2-(methylimino)-3-phenylbicyclo[2.1.1]hexan-1-yl)(naphthalen-2-yl) methanone (9a)





***N*,4-Dimethyl-*N*-(1-(naphthalen-2-yl(2-tosylhydrazineylidene)methyl)-3-phenylbicyclo [2.1.1]hex-2-en-2-yl)benzenesulfonamide (10a)**