*Supporting Information*

# Synthesis of *o*-Benzyl Benzamides via NaH-Mediated Aryne Insertion into *N*-Sulfonylacetimidates

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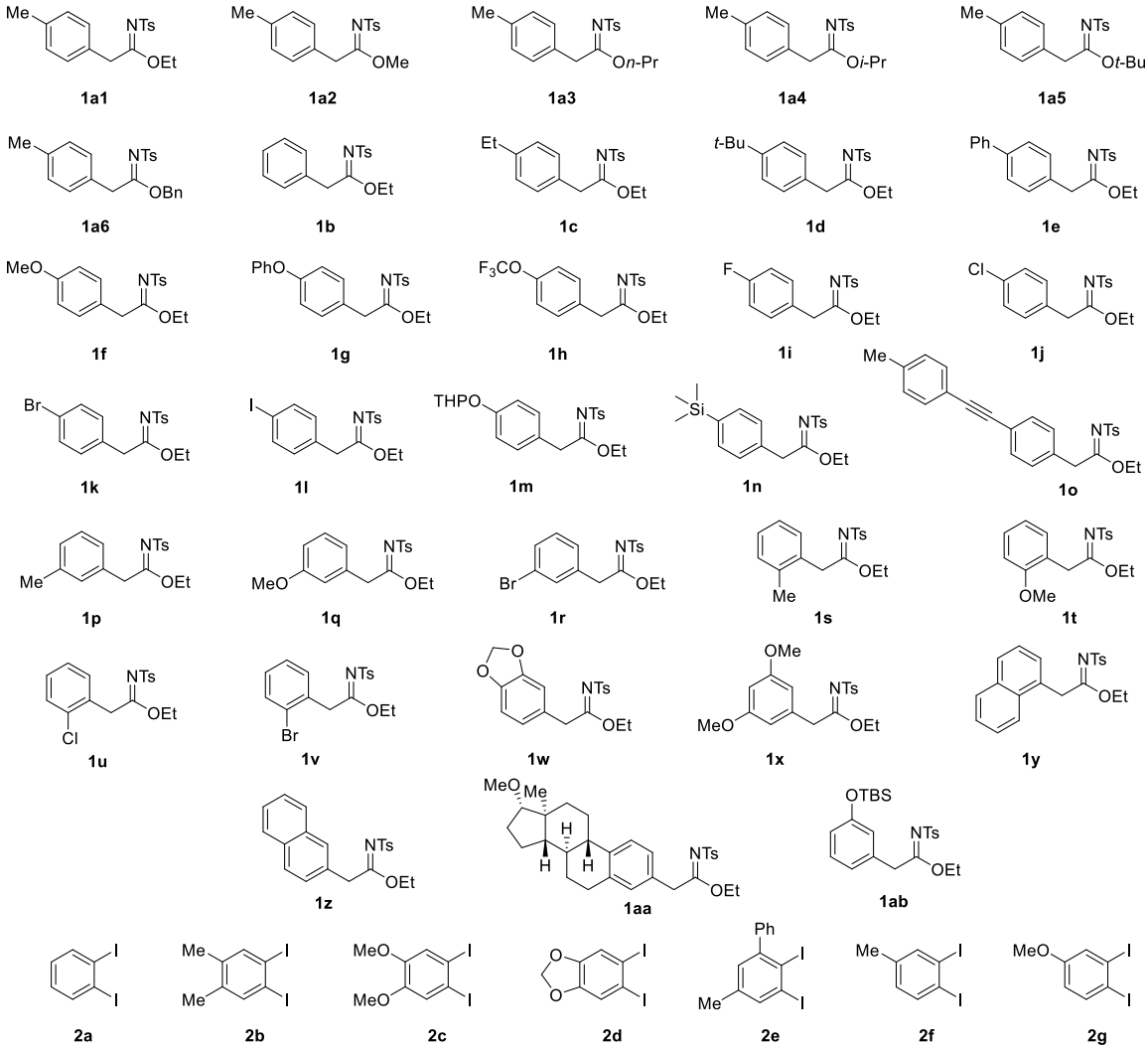
## 1. General information

Unless otherwise indicated, all glassware was oven dried by a heat gun before use and all reactions were performed under an atmosphere of nitrogen. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on glass plates coated with silica gel GF254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (200-300 mesh). Mass spectra were obtained using a TOF MS instrument EI or ESI source. All $^{1}H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR spectra were recorded on Bruker AV-400 or AV-600. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 ($^{1}H$ NMR), δ = 77.16 ($^{13}C$ NMR). Coupling constants were quoted in Hz (*J*). $^{1}H$ NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t) and quadruplet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m).

## 2. General procedure for the synthesis of starting materials



*o*-Diiodoarenes **2a** and **2f** are commercially available. *N*-sulfonylacetimidates **1a2**[1], **1a6**[2], **1b**[3], **1e**[3], **1s**[3], **1v**[3] and *o*-diiodoarenes **2b**[4], **2c**[4], **2d**[5], **2e**[6], **2g**[7] are known compounds and synthesized according to reported literatures. The other *N*-sulfonylacetimidates were synthesized as detailed below.

References:


[1] Y. Liu, P. Xie, J. G. Li, W. J. Bai and J. Jiang, Nickel-Catalyzed Coupling of N-Sulfonyl-1,2,3-triazole with H-Phosphine Oxides: Stereoselective and Site-Selective Synthesis of *α*-Aminovinylphosphoryl Derivatives, *Org. Lett.*, 2019, **21**, 4944–4949.

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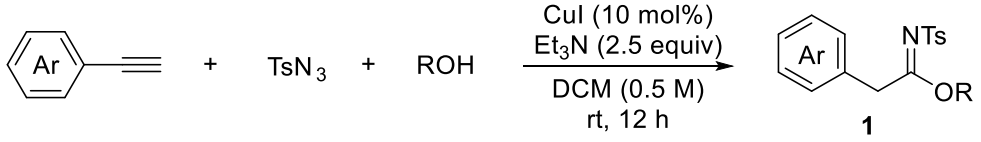
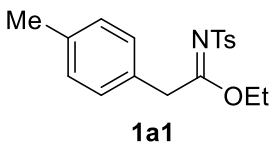
**General procedure for the synthesis of *N*-sulfonylacetimidates 1**




To a vigorously stirred solution alkyne (1.3 to 5.0 mmol), 4-methylbenzenesulfonyl azide (1.2 equiv), alcohol (1.2 equiv), and CuI (10 mol%) in DCM (0.5 M) was slowly added $Et_3N$ (12.5 mmol, 2.5 equiv) at ambient temperature under nitrogen atmosphere and stirred for 12 h. Then the mixture was quenched with saturated aqueous $NH_4Cl$ solution and the resulting mixture was extracted with DCM. The combined extracts were dried over $Na_2SO_4$ and concentrated under vacuum. The obtained residue was purified by silica gel chromatography eluting with an eluent (PE/EtOAc) to afford the corresponding *N*-sulfonylacetimidates **1**.



1a1

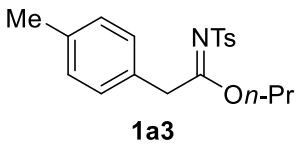
**ethyl (*Z*)-2-(*p*-tolyl)-*N*-tosylacetimidate (1a1)**

Following the general procedure, the title compound was prepared from 1-ethynyl-4-methylbenzene (581 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as yellow solid, 1.37 g, 83% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.18 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 173.4, 143.2, 139.2, 136.8, 130.6, 129.5, 129.4, 129.3, 126.7, 64.8, 39.3, 21.6, 21.1, 13.6.

**HRMS (ESI-TOF):** calculated for $[C_{18}H_{21}NO_3SNa\ (M + Na)]^+$: 354.1134, found: 354.1135.



1a3

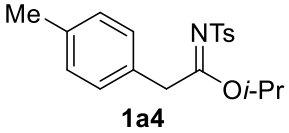
**propyl (*Z*)-2-(*p*-tolyl)-*N*-tosylacetimidate (1a3)**

Following the general procedure, the title compound was prepared from 1-ethynyl-4-methylbenzene (581 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and *n*-PrOH (360.6 mg, 6 mmol), and it was obtained as light-yellow solid, 1.22 g, 71% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 4.19 (s, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 1.63 – 1.56 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.6, 143.3, 139.3, 136.9, 130.7, 129.6, 129.5, 129.3, 126.8, 70.4, 39.4, 21.7, 21.5, 21.2, 10.4.

**HRMS (ESI-TOF):** calculated for $[C_{19}H_{23}NO_3SNa\ (M + Na)]^+$: 368.1291, found: 368.1290.



1a4

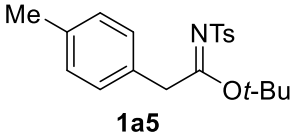
**isopropyl (*Z*)-2-(*p*-tolyl)-*N*-tosylacetimidate (1a4)**

Following the general procedure, the title compound was prepared from 1-ethynyl-4-methylbenzene (581 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and *i*-PrOH (360.6 mg, 6 mmol), and it was obtained as yellow solid, 1.31 g, 76% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 5.04 – 4.97 (m, 1H), 4.15 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 1.16 (d, *J* = 6.2 Hz, 6H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.9, 143.2, 139.4, 136.8, 130.8, 129.5, 129.3, 126.7, 72.5, 39.6, 21.7, 21.23, 21.20.

**HRMS (ESI-TOF):** calculated for $[C_{19}H_{23}NO_3SNa\ (M + Na)]^+$: 368.1291, found: 368.1292.



1a5

***tert*-butyl (*Z*)-2-(*p*-tolyl)-*N*-tosylacetimidate (1a5)**

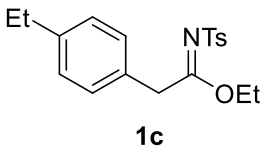
Following the general procedure, the title compound was prepared from 1-ethynyl-4-methylbenzene (581 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and *t*-BuOH (445 mg, 6 mmol), and it was obtained as yellow solid, 754.8 mg, 42% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 4.10 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 1.36 (s, 9H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.1, 143.0, 139.7, 136.7, 131.3, 129.5, 129.3, 126.5, 85.3,

40.6, 27.8, 21.7, 21.2.

**HRMS (ESI-TOF):** calculated for $[C_{20}H_{25}NO_3SNa\ (M + Na)]^+$: 382.1447, found: 382.1448.




**1c**

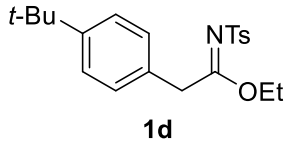
**ethyl (*Z*)-2-(4-ethylphenyl)-*N*-tosylacetimidate (1c)**

Following the general procedure, the title compound was prepared from 1-ethyl-4-ethynylbenzene (651 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as yellow oil, 1.3 g, 75% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.19 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.22 (q, *J* = 7.3 Hz, 6H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.4, 143.29, 143.25, 139.3, 130.9, 129.6, 129.5, 128.2, 126.8, 64.9, 39.4, 28.6, 21.6, 15.6, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{19}H_{23}NO_3SNa\ (M + Na)]^+$: 368.1291, found: 368.1290.




**1d**

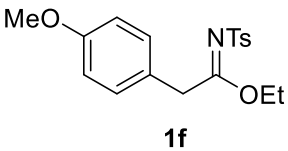
**ethyl (*Z*)-2-(4-(*tert*-butyl)phenyl)-*N*-tosylacetimidate (1d)**

Following the general procedure, the title compound was prepared from 1-(*tert*-butyl)-4-ethynylbenzene (790 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as white solid, 895.2 mg, 48% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.25 (m, 6H), 4.19 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.31 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.4, 150.2, 143.3, 139.3, 130.7, 129.5, 129.3, 126.8, 125.6, 64.9, 39.3, 34.6, 31.5, 21.7, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{27}NO_3SNa\ (M + Na)]^+$: 396.1604, found: 396.1603.




**1f**

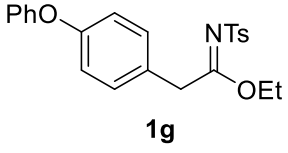
**ethyl (Z)-2-(4-methoxyphenyl)-*N*-tosylacetimidate (1f)**

Following the general procedure, the title compound was prepared from 1-ethynyl-4-methoxybenzene (665 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as yellow solid, 1.44 g, 83% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.28 (t, *J* = 6.3 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.16 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.42 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.6, 158.9, 143.3, 139.3, 130.8, 129.5, 126.8, 125.8, 114.1, 64.9, 55.4, 39.0, 21.7, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{18}H_{22}NO_4S\ (M + H)]^+$: 348.1264, found: 348.1263.

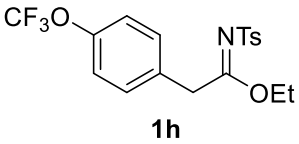



**1g**

**ethyl (*Z*)-2-(4-phenoxyphenyl)-*N*-tosylacetimidate (1g)**

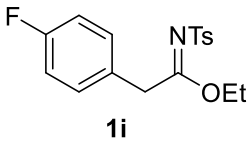
Following the general procedure, the title compound was prepared from 1-ethynyl-4-phenoxybenzene (250 mg, 1.29 mmol), 4-methylbenzenesulfonyl azide (304 mg, 1.55 mmol) and EtOH (71 mg, 1.55 mmol), and it was obtained as light-yellow solid, 409 mg, 77% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.28 (m, 6H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.01 (dd, *J* = 8.6, 0.9 Hz, 2H), 6.97 – 6.92 (m, 2H), 4.20 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.2, 157.2, 156.6, 143.4, 139.2, 131.1, 129.9, 129.5, 128.5, 126.8, 123.5, 119.1, 118.9, 65.0, 39.1, 21.7, 13.7.
**HRMS (ESI-TOF):** calculated for $[C_{23}H_{24}NO_4S\ (M + H)]^+$: 410.1241, found: 410.1240.



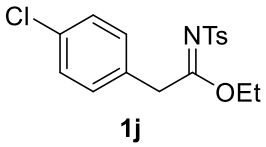
**1h**

**ethyl (*Z*)-*N*-tosyl-2-(4-(trifluoromethoxy)phenyl)acetimidate (1h)**
Following the general procedure, the title compound was prepared from 1-ethynyl-4-(trifluoromethoxy)benzene (930 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as white solid, 1.43 g, 72% yield.
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.23 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.5, 148.6, 143.5, 139.0, 132.5, 131.2, 129.6, 126.8, 121.2, 120.6 (dd, *J* = 514.3, 257.2 Hz), 65.2, 39.1, 21.7, 13.7.
**$^{19}$F NMR (565 MHz, $CDCl_3$):** δ -57.86 (s).
**HRMS (ESI-TOF):** calculated for $[C_{18}H_{18}F_3NO_4SNa\ (M + Na)]^+$: 424.0801, found: 484.0802.



**1i**

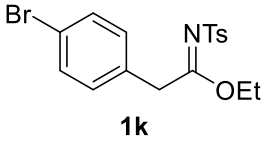
**ethyl (*Z*)-2-(4-fluorophenyl)-*N*-tosylacetimidate (1i)**
Following the general procedure, the title compound was prepared from 1-ethynyl-4-fluorobenzene (601 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as white solid, 1.20 g, 71% yield.
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.22 (m, 4H), 7.00 (t, *J* = 7.6 Hz, 2H), 4.20 (s, 2H), 4.13 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.20 (t, *J* = 6.3 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.9, 162.2 (d, *J* = 245.7 Hz), 143.5, 139.1, 131.3 (d, *J* = 8.0 Hz), 129.5, 129.2 (d, *J* = 168.8 Hz), 126.8, 115.56 (d, *J* = 21.2 Hz), 65.05, 39.0, 21.7, 13.7.
**$^{19}$F NMR (565 MHz, $CDCl_3$):** δ -115.36 – -115.44 (m).
**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}FNO_3SNa\ (M + Na)]^+$: 358.0884, found: 358.0883.



**1j**

**ethyl (*Z*)-2-(4-chlorophenyl)-*N*-tosylacetimidate (1j)**
Following the general procedure, the title compound was prepared from 1-ethynyl-4-chlorobenzene (683 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as yellow solid, 970.3 mg, 55% yield.
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 6H), 4.22 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.6, 143.5, 139.0, 133.3, 132.2, 131.1, 129.5, 128.8, 126.8, 65.1, 39.1, 21.7, 13.6.

**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}ClNO_3SNa\ (M + Na)]^+$: 374.0588, found: 374.0588.



**1k**

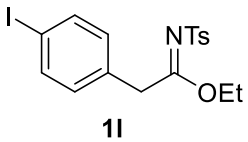
**ethyl (*Z*)-2-(4-bromophenyl)-*N*-tosylacetimidate (1k)**

Following the general procedure, the title compound was prepared from 1-ethynyl-4-bromobenzene (895 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as yellow solid, 920.6 mg, 47% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.85 – 7.78 (m, 2H), 7.48 – 7.40 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.18 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.4, 143.5, 139.0, 132.7, 131.8, 131.4, 129.5, 126.7, 121.5, 65.1, 39.2, 21.7, 13.6.

**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}BrNO_3SNa\ (M + Na)]^+$: 418.0083, found: 418.0081.



**1l**

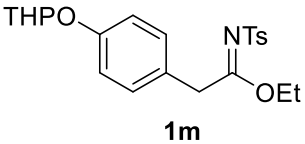
**ethyl (*Z*)-2-(4-iodophenyl)-*N*-tosylacetimidate (1l)**

Following the general procedure, the title compound was prepared from 1-ethynyl-4-iodobenzene (1.14 g, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as white solid, 1.68 g, 76% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.17 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.5, 143.5, 139.0, 137.8, 133.4, 131.7, 129.5, 126.8, 93.0, 65.1, 39.3, 21.7, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}INO_3SNa\ (M + Na)]^+$: 465.9944, found: 465.9944.



**1m**

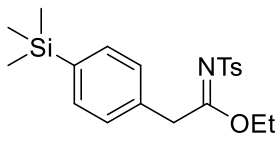
**ethyl (*Z*)-2-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)-*N*-tosylacetimidate (1m)**

Following the general procedure, the title compound was prepared from 2-(4-ethynylphenyl)tetrahydro-2*H*-pyran (808 mg, 4 mmol), 4-methylbenzenesulfonyl azide (944 mg, 4.8 mmol) and EtOH (221mg, 4.8 mmol), and it was obtained as light-yellow oil, 1.10 g, 66% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.23 (m, 4H), 6.98 (d, *J* = 7.4 Hz, 2H), 5.40 – 5.36 (m, 1H), 4.16 (s, 2H), 4.12 (q, *J* = 6.8 Hz, 2H), 3.91 (t, *J* = 10.5 Hz, 1H), 3.63 – 3.56 (m, 1H), 2.41 (s, 3H), 2.04 – 1.95 (m, 1H), 1.89 – 1.80 (m, 2H), 1.72 – 1.63 (m, 2H), 1.62 – 1.56 (m, 1H), 1.20 (t, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.5, 156.4, 143.2, 139.3, 130.7, 129.4, 126.8, 126.7, 116.6, 96.6, 64.9, 62.2, 39.0, 30.5, 25.3, 21.6, 19.0, 13.6.

**HRMS (ESI-TOF):** calculated for $[C_{22}H_{27}NO_5SNa\ (M + Na)]^+$: 440.1502, found: 440.1503.



**1n**

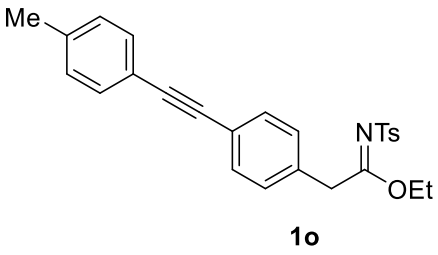
**ethyl (*Z*)-*N*-tosyl-2-(4-(trimethylsilyl)phenyl)acetimidate (1n)**

Following the general procedure, the title compound was prepared from (4-ethynylphenyl)trimethylsilane (870 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as light-yellow solid, 1.33 g, 69% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.25 (m, 2H), 4.22 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.26 (s, 9H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.1, 143.3, 139.3, 139.2, 134.3, 133.7, 129.5, 129.0, 126.8, 65.0, 39.7, 21.7, 13.7, -1.0.

**HRMS (ESI-TOF):** calculated for $[C_{20}H_{27}NO_3SSiNa\ (M + Na)]^+$: 412.1373, found: 412.1372.



**1o**

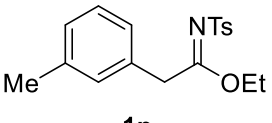
**ethyl (Z)-2-(4-(*p*-tolylethynyl)phenyl)-N-tosylacetimidate (1o)**

Following the general procedure, the title compound was prepared from 4-ethynyl-4'-methyl-1,1'-biphenyl (588 mg, 2.72 mmol), 4-methylbenzenesulfonyl azide (642 mg, 3.26 mmol) and EtOH (150.4 mg, 3.26 mmol), and it was obtained as light-yellow solid, 510.5 mg, 44% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.34 – 7.27 (m, 4H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.24 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.37 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.7, 143.4, 139.1, 138.6, 133.8, 131.8, 131.6, 129.8, 129.5, 129.3, 126.8, 122.6, 120.3, 90.0, 88.6, 65.1, 39.7, 21.7, 21.7, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{26}H_{25}NO_3SNa\ (M + Na)]^+$: 454.1447, found: 454.1445.



**1p**

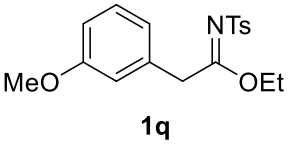
**ethyl (Z)-2-(*m*-tolyl)-*N*-tosylacetimidate (1p)**

Following the general procedure, the title compound was prepared from 1-ethynyl-3-methylbenzene (580 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as white solid, 1.29 g, 77% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.08 (s, 1H), 4.19 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.3, 143.3, 139.3, 138.3, 133.7, 130.4, 129.5, 128.5, 128.0, 126.8, 126.7, 64.9, 39.6, 21.6, 21.5, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}BrNO_3SNa\ (M + Na)]^+$: 418.0083, found: 418.0081.

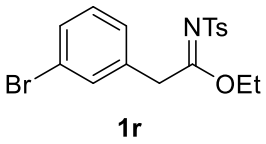


**1q**

**ethyl (*Z*)- 2-(3-methoxyphenyl)-*N*-tosylacetimidate (1q)**

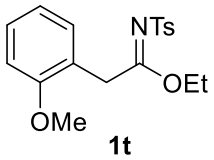
Following the general procedure, the title compound was prepared from 1-ethynyl-3-methoxybenzene (660 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as white solid, 1.32 g, 76% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.83 – 6.77 (m, 1H), 4.20 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.42 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.1, 159.8, 143.4, 139.2, 135.2, 129.6, 129.5, 126.8, 122.1, 115.2, 113.1, 65.0, 55.4, 39.8, 21.7, 13.7.
**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}BrNO_4SNa$ (M + Na)$]^+$: 370.1083, found: 370.1082.



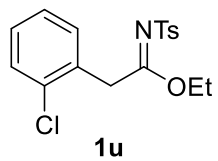
**1r**

**ethyl (*Z*)- 2-(3-methoxyphenyl)-*N*-tosylacetimidate (1r)**
Following the general procedure, the title compound was prepared from 1-bromo-3-ethynylbenzene (895 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as white solid, 995.2 mg, 50% yield.
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 4.20 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.3, 143.5, 139.0, 135.9, 132.6, 130.5, 130.2, 129.6, 128.4, 126.8, 122.6, 65.2, 39.3, 21.7, 13.7.
**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}BrNO_3SNa$ (M + Na)$]^+$: 418.0083, found: 418.0081.



**1t**

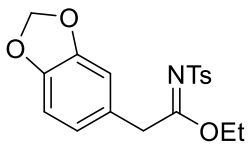
**ethyl (*Z*)-2-(2-methoxyphenyl)-*N*-tosylacetimidate (1t)**
Following the general procedure, the title compound was prepared from 1-ethynyl-2-methoxybenzene (660 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as light-yellow oil, 950.7 mg, 55% yield.
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.12 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.23 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 2.42 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 174.2, 157.4, 143.1, 139.4, 130.6, 129.4, 128.6, 126.9, 123.0, 120.5, 110.4, 64.7, 55.4, 35.0, 21.6, 13.6.
**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}BrNO_4SNa$ (M + Na)$]^+$: 370.1083, found: 370.1084.



**1u**

**ethyl (*Z*)-2-(2-chlorophenyl)-*N*-tosylacetimidate (1u)**
Following the general procedure, the title compound was prepared from 1-chloro-2-ethynylbenzene (683 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as light-yellow oil, 800.4 mg, 46% yield.
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.20 (m, 3H), 4.39 (s, 2H), 4.16 (d, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.5, 143.4, 139.0, 134.7, 132.4, 131.3, 129.5, 129.5, 128.8, 127.0, 126.9, 65.2, 38.2, 21.7, 13.5.

**HRMS (ESI-TOF):** calculated for $[C_{17}H_{18}ClNO_3SNa\ (M + Na)]^+$: 374.0588, found: 374.0588.



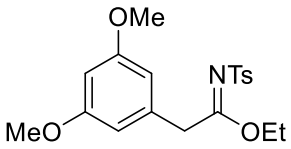
**1w**

**ethyl (*Z*)-2-(benzo[*d*][1,3]dioxol-5-yl)-*N*-tosylacetimidate (1w):**
Following the general procedure, the title compound was prepared from 5-ethynylbenzo[*d*][1,3]dioxole (1.0 g, 6.85 mmol), 4-methylbenzenesulfonyl azide (1.62 g, 8.2 mmol) and EtOH (276.4 mg, 8.2 mmol), and it was obtained as light-yellow oil, 1.85 g, 75% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.87– 6.81 (m, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 2H), 4.16 – 4.10 (m, 4H), 2.42 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.2, 147.8, 146.9, 143.3, 139.2, 129.5, 127.3, 126.8, 123.1, 110.1, 108.4, 101.2, 65.0, 39.4, 21.7, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{18}H_{19}NO_5SNa\ (M + Na)]^+$: 384.0876, found: 384.0875.



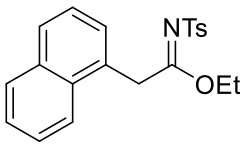
**1x**

**ethyl (*Z*)-2-(3,5-dimethoxyphenyl)-*N*-tosylacetimidate (1x):**
Following the general procedure, the title compound was prepared from 1-ethynyl-3,5-dimethoxybenzene (810 g, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as light-yellow oil, 1.29 g, 68% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 2H), 6.36 (s, 1H), 4.18 – 4.11 (m, 4H), 3.77 (s, 6H), 2.41 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 172.9, 160.8, 143.3, 139.2, 135.7, 129.4, 126.7, 107.7, 99.5, 64.9, 55.4, 39.8, 21.6, 13.6.

**HRMS (ESI-TOF):** calculated for $[C_{19}H_{23}NO_5SNa\ (M + Na)]^+$: 400.1189, found: 400.1188.



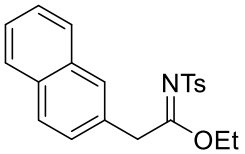
**1y**

**ethyl (*Z*)-2-(naphthalen-1-yl)-*N*-tosylacetimidate (1y):**
Following the general procedure, the title compound was prepared from 1-ethynylnaphthalene (761 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as light-yellow solid, 982.1 mg, 54% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.94 – 7.84 (m, 4H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.43 – 7.35 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.7, 143.4, 139.2, 133.9, 132.2, 130.3, 129.6, 128.8, 128.2, 128.1, 126.9, 126.5, 125.9, 125.5, 123.9, 65.1, 37.6, 21.7, 13.5.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{21}NO_3SNa\ (M + Na)]^+$: 390.1134, found: 390.1134.



**1z**

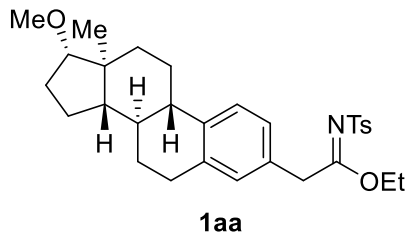
**ethyl (*Z*)-2-(naphthalen-2-yl)-*N*-tosylacetimidate (1z):**
Following the general procedure, the title compound was prepared from 2-ethynylnaphthalene (761 mg, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as light-yellow solid, 1.06 g, 58% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.84 – 7.75 (m, 6H), 7.50 – 7.43 (m,

3H), 7.28 – 7.24 (m, 2H), 4.40 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.2, 143.4, 139.2, 133.6, 132.6, 131.3, 129.5, 128.6, 128.3, 127.9, 127.8, 127.7, 126.8, 126.3, 126.0, 65.1, 39.9, 21.7, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{21}NO_3SNa\ (M + Na)]^+$: 390.1134, found: 390.1135.



**1aa**

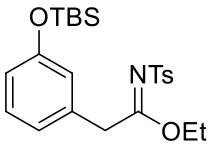
**ethyl (*Z*)-2-((8*R*,9*S*,13*S*,14*S*,17*S*)-17-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)-N-tosylacetimidate (1aa)**

Following the general procedure, the title compound was prepared from corresponding aryl acetylene (382 mg, 1.3 mmol), 4-methylbenzenesulfonyl azide (306.8 mg, 1.56 mmol) and EtOH (72 mg, 1.56 mmol), and it was obtained as light-yellow solid, 510.4 mg, 44% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.02 (s, 1H), 4.18 – 4.11 (m, 4H), 3.38 (s, 3H), 3.32 (t, *J* = 8.3 Hz, 1H), 2.85 – 2.80 (m, 2H), 2.42 (s, 3H), 2.33 – 2.26 (m, 1H), 2.26 – 2.17 (m, 1H), 2.12 – 2.01 (m, 2H), 1.91 – 1.85 (m, 1H), 1.74 – 1.66 (m, 1H), 1.55 – 1.47 (m, 2H), 1.47 – 1.43 (m, 1H), 1.41 – 1.30 (m, 3H), 1.25 – 1.18 (m, 4H), 0.79 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.2, 143.0, 139.2, 139.1, 136.7, 130.6, 129.9, 129.2, 126.7, 126.5, 125.4, 90.6, 64.7, 57.7, 50.3, 44.1, 43.1, 39.0, 38.2, 37.9, 29.3, 27.6, 27.1, 26.1, 23.0, 21.4, 13.5, 11.5.

**HRMS (ESI-TOF):** calculated for $[C_{30}H_{39}NO_4SNa\ (M + Na)]^+$: 532.2492, found: 532.2491.



**1ab**

**ethyl (Z)-2-(3-((*tert*-butyldimethylsilyl)oxy)phenyl)-*N*-tosylacetimidate (1ab)**

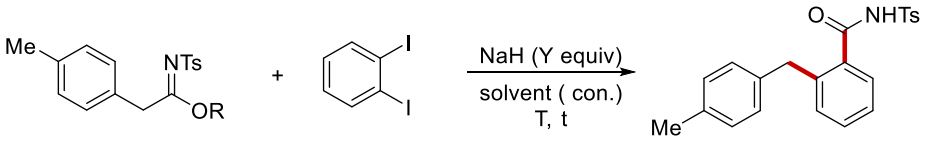
Following the general procedure, the title compound was prepared from *tert*-butyl(3-ethynylphenoxy)dimethylsilane (1.16 g, 5 mmol), 4-methylbenzenesulfonyl azide (1.18 g, 6 mmol) and EtOH (276.4 mg, 6 mmol), and it was obtained as yellow oil, 1.23 g, 55% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 6.74 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.17 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.98 (s, 9H), 0.19 (s, 6H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 173.1, 155.9, 143.3, 139.3, 135.1, 129.6, 129.5, 126.8, 122.7, 121.5, 119.1, 64.9, 39.6, 25.8, 21.7, 18.4, 13.7, -4.3.

**HRMS (ESI-TOF):** calculated for $[C_{23}H_{33}NO_4SSiNa\ (M + Na)]^+$: 470.1792, found: 470.1793.

## 3. Optimization of reaction conditions (Table S1)



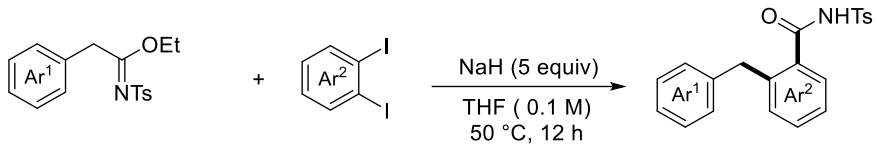

**1a1-1a8**, 0.2 mmol **2a**, X equiv **3a**

| Entry | **1a** (R group) | **2a** (X equiv) | NaH (Y equiv) | temp (°C) | solvent | con. | time | yield (%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 55 |
| 2 | Me (**1a2**) | 2.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 0[b] |
| 3 | *n*-Pr (**1a3**) | 2.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 20 |
| 4 | *i*-Pr (**1a4**) | 2.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 35 |
| 5 | *t*-Bu (**1a5**) | 2.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 45 |
| 6 | Bn (**1a6**) | 2.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 40 |
| 7 | Et (**1a1**) | 2.0 | 3.0 | 50 | THF | 0.05 M | 12 h | 18 |
| 8 | Et (**1a1**) | 2.0 | 4.0 | 50 | THF | 0.05 M | 12 h | 43 |
| 9 | Et (**1a1**) | 2.0 | 6.0 | 50 | THF | 0.05 M | 12 h | 53 |
| 10 | Et (**1a1**) | 2.0 | 5.0 | rt(25) | THF | 0.05 M | 12 h | NR |
| 11 | Et (**1a1**) | 2.0 | 5.0 | 40 | THF | 0.05 M | 12 h | 43 |
| 12 | Et (**1a1**) | 2.0 | 5.0 | 60 | THF | 0.05 M | 12 h | 53 |
| 13 | Et (**1a1**) | 2.0 | 5.0 | 50 | DMA | 0.05 M | 12 h | 25 |
| 14 | Et (**1a1**) | 2.0 | 5.0 | 50 | DMA-THF | 0.05 M | 12 h | 25[c] |
| 15 | Et (**1a1**) | 2.0 | 5.0 | 50 | DMF | 0.05 M | 12 h | 22 |
| 16 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.2 M | 12 h | 45 |
| **17** | **Et (1a1)** | **2.0** | **5.0** | **50** | **THF** | **0.1 M** | **12 h** | **65(60)** |
| 18 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.067 M | 12 h | 54 |
| 19 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.04 M | 12 h | 53 |
| 20 | Et (**1a1**) | 1.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 39 |
| 21 | Et (**1a1**) | 3.0 | 5.0 | 50 | THF | 0.05 M | 12 h | 45 |
| 22 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.1 M | 4 h | 20 |
| 23 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.1 M | 6 h | 50 |
| 24 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.1 M | 8 h | 55 |
| 25 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.1 M | 16 h | 60 |
| 26 | Et (**1a1**) | 2.0 | 5.0 | 50 | THF | 0.1 M | 24 h | 50 |

[a] NMR yield with mesitylene as internal standard, isolated yield from 0.5 mmol scale of **1a** in parentheses. [b] *N*-Sulfonylacetimidate **1a2** decomposed after the reaction. [c] The solvent volume ratio of THF to DMA is 4 : 1. DMA = *N*,*N*-Dimethylacetamide, DMF = *N*,*N*-Dimethylformamide.

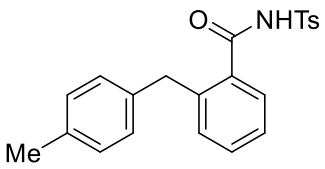
**General procedure for optimization of reaction conditions**: To a suspension of NaH (60% dispersion in mineral oil) in anhydrous solvent was added *N*-sulfonylacetimidates **1a** (0.5 mmol) and *o*-diiodoarene **2a** respectively at ambient temperature stirring for 5 min. After that, the mixture was warmed to indicated temperature. After stirring for the indicated time, the reaction was quenched with saturated aqueous $NH_4Cl$ (6 mL) solution at 0 °C. The mixture was then extracted with EtOAc (8 mL × 4). The combined extracts were dried over $Na_2SO_4$, concentrated under vacuum and prepared for NMR analysis with methylene as internal standard.

## 4. General procedure for the synthesis of *o*-benzyl-*N*-sulfonylbenzamides




**1a1-1ai** (0.5 mmol) **2a-2g** (2 equiv) **3, 4**

**General procedure:** To a suspension of NaH (60% dispersion in mineral oil, 101 mg, 2.5 mmol) in anhydrous THF (5 mL) was added *N*-sulfonylacetimidate **1** (0.5 mmol) and *o*-diiodoarene **2** (2.0 equiv) respectively at ambient temperature. The mixture was warmed to 50 °C for 12 h. After that, the reaction was quenched with saturated aqueous $NH_4Cl$ (6 mL) solution at 0 °C. The mixture was then extracted with EtOAc (8 mL × 4). The combined extracts were dried over $Na_2SO_4$, concentrated under vacuum. The resulting residue was purified by silica gel chromatography affording *o*-benzyl-*N*-sulfonylbenzamide **3** or **4**.




**3a**

**2-(4-methylbenzyl)-*N*-tosylbenzamide (3a)**

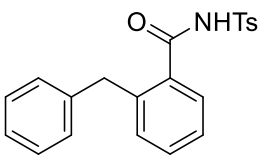
Following the general procedure, the title compound was obtained as colorless oil, 113.8 mg, 60% yield.

Following the general procedure, when **1a** (3.31 g, 10 mmol) and THF (100 mL) were used in this reaction, **3a** was obtained 1.86 g, 49% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.47 (brs, 1H), δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.18 (m, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 4.02 (s, 2H), 2.46 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.6, 145.2, 140.9, 137.1, 135.8, 135.7, 132.7, 131.9, 131.5, 129.7, 129.3, 128.8, 128.7, 127.8, 126.6, 38.1, 21.8, 21.1.

**HRMS (ESI-TOF):** calculated for $[C_{22}H_{21}NO_3SNa\ (M + Na)]^+$: 402.1140, found: 402.1139.




**3b**

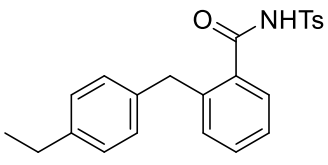
**2-benzyl-*N*-tosylbenzamide (3b):**

Following the general procedure, the title compound was obtained as colorless oil, 115.0 mg, 63% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.48 (brs, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.28 (td, *J* = 4.8, 2.4 Hz, 1H), 7.22 (t, *J* = 8.2 Hz, 2H), 7.15 – 7.08 (m, 2H), 7.06 – 7.02 (m, 3H), 6.88 – 6.84 (m, 2H), 3.96 (s, 2H), 2.35 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.5, 145.2, 140.7, 140.2, 135.5, 132.6, 132.0, 131.6, 129.7, 128.9, 128.64, 128.59, 127.8, 126.6, 126.3, 38.5, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{20}NO_3S\ (M + H)]^+$: 366.1164, found: 366.1165.




**3c**

**2-(4-ethylbenzyl)-*N*-tosylbenzamide (3c)**

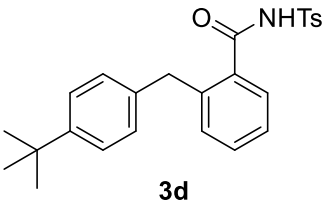
Following the general procedure, the title compound was obtained as colorless oil, 98.1 mg, 50% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.40 (brs, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H),

6.88 (d, *J* = 8.0 Hz, 2H), 4.02 (s, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.6, 145.1, 142.2, 140.9, 137.3, 135.6, 132.6, 131.9, 131.5, 129.7, 128.8, 128.7, 128.1, 127.8, 126.5, 38.0, 28.5, 21.8, 15.6.

**HRMS (ESI-TOF):** calculated for $[C_{23}H_{23}NO_3SNa\ (M + Na)]^+$: 416.1296, found: 416.1295.




**3d**

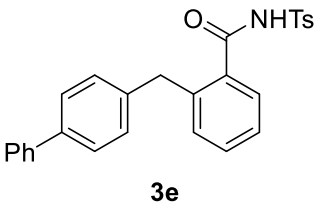
**2-(4-(*tert*-butyl)benzyl)-*N*-tosylbenzamide (3d)**

Following the general procedure, the title compound was obtained as colorless oil, 67.3 mg, 32% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.37 (brs, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.25 – 7.21 (m, 2H), 7.18 – 7.15 (m, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 4.02 (s, 2H), 2.46 (s, 3H), 1.27 (s, 9H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.5, 149.2, 145.2, 140.9, 137.1, 135.7, 132.7, 132.0, 131.6, 129.7, 128.8, 128.5, 127.8, 126.6, 125.6, 38.0, 34.5, 31.5, 21.9.

**HRMS (ESI-TOF):** calculated for $[C_{25}H_{27}NO_3SNa\ (M + Na)]^+$: 444.1609, found: 444.1610.




**3e**

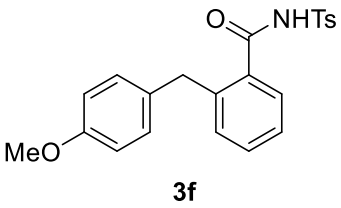
**2-([1,1'-biphenyl]-4-ylmethyl)-*N*-tosylbenzamide (3e)**

Following the general procedure, the title compound was obtained as colorless oil, 145.6 mg, 66% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.51 (brs, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.47 – 7.37 (m, 4H), 7.35 – 7.30 (m, 3H), 7.27 – 7.23 (m, 4H), 7.00 (d, *J* = 8.3 Hz, 2H), 4.10 (s, 2H), 2.37 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.4, 145.2, 140.9, 140.8, 139.3, 139.1, 135.6, 132.6, 132.1, 131.7, 129.7, 129.3, 128.9, 128.6, 127.9, 127.3, 127.2, 127.0, 126.8, 38.2, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{27}H_{24}NO_3S\ (M + H)]^+$: 442.1477, found: 442.1478.




**3f**

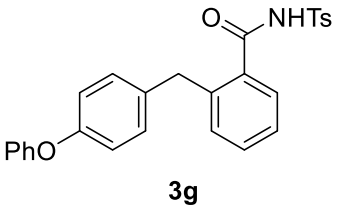
**2-(4-methoxybenzyl)-*N*-tosylbenzamide (3f)**

Following the general procedure, the title compound was obtained as colorless oil, 104.6 mg, 53% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.60 (brs, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.25 – 7.16 (m, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 3.99 (s, 2H), 3.74 (s, 3H), 2.45 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.5, 158.1, 145.2, 141.1, 135.6, 132.6, 132.3, 132.0, 131.5, 129.8, 129.7, 128.7, 127.8, 126.6, 114.0, 55.3, 37.7, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{22}H_{21}NO_4SNa\ (M + Na)]^+$: 418.1089, found: 418.1088.



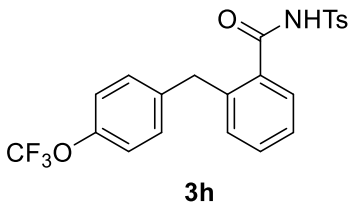

**3g**

**2-(4-phenoxybenzyl)-*N*-tosylbenzamide (3g)**

Following the general procedure, the title compound was obtained as colorless oil, 121.2 mg, 53% yield.

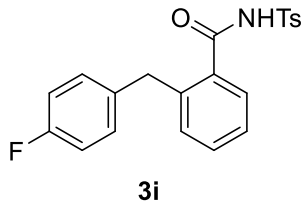
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.29 (m, 4H), 7.28 – 7.23 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.8 Hz,

2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 4.07 (s, 2H), 2.42 (s, 3H).
**$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 166.5, 157.4, 155.6, 145.3, 141.0, 135.6, 135.1, 132.6, 132.0, 131.6, 130.1, 129.8, 129.7, 128.7, 127.9, 126.7, 123.3, 119.0, 118.8, 37.8, 21.8.
**HRMS (ESI-TOF):** calculated for $[C_{27}H_{24}NO_4S\ (M + H)]^+$: 458.1426, found: 458.1424.



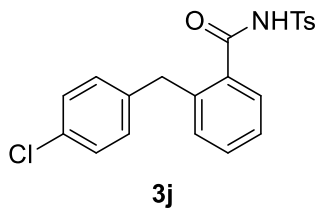
**3h**

***N*-tosyl-2-(4-(trifluoromethoxy)benzyl)benzamide (3h)**
Following the general procedure, the title compound was obtained as colorless oil, 96.4 mg, 43% yield.
**$^{1}$H NMR (400 MHz, CDCl$_3$):** δ 8.62 (brs, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.89 (m, 4H), 4.08 (s, 2H), 2.46 (s, 3H).
**$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 166.3, 147.6, 145.4, 140.6, 139.0, 135.5, 132.4, 132.3, 131.7, 130.1, 129.7, 128.7, 127.9, 127.0, 120.9, 120.57 (q, *J* = 256.6 Hz), 37.8, 21.8.
**$^{19}$F NMR (565 MHz, CDCl$_3$)**: δ -116.92(s).
**HRMS (ESI-TOF):** calculated for $[C_{22}H_{19}F_3NO_4S\ (M + H)]^+$: 450.0987, found: 450.0986.



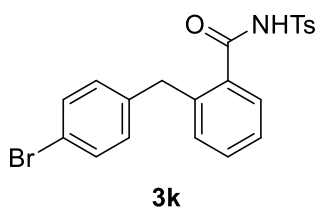
**3i**

**2-(4-fluorobenzyl)-*N*-tosylbenzamide (3i)**
Following the general procedure, the title compound was obtained as colorless oil, 76.5 mg, 40% yield.
**$^{1}$H NMR (400 MHz, CDCl$_3$):** δ 8.52 (brs, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.77 (dd, *J* = 12.0, 5.4 Hz, 2H), 4.05 (s, 2H), 2.46 (s, 3H).
**$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 166.4, 161.4 (d, *J* = 244.2 Hz), 145.3, 140.8, 135.9 (d, *J* = 2.6 Hz), 135.6, 132.1, 131.7, 130.3 (d, *J* = 8.0 Hz), 129.7, 128.6, 127.9, 126.8, 126.6, 115.2 (d, *J* = 21.7 Hz), 37.8, 21.8.
**$^{19}$F NMR (565 MHz, CDCl$_3$):** δ -57.84(s).
**HRMS (ESI-TOF):** calculated for $[C_{21}H_{18}FNO_3SNa\ (M + Na)]^+$: 406.0889, found: 406.0892.



**3j**

**2-(4-chlorobenzyl)-*N*-tosylbenzamide (3j)**
Following the general procedure, the title compound was obtained as colorless oil, 94.2 mg, 47% yield.
**$^{1}$H NMR (600 MHz, CDCl$_3$):** δ 9.04 (brs, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.38 (td, *J* = 7.6, 1.0 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 4.04 (s, 2H), 2.47 (s, 3H).
**$^{13}$C NMR (150 MHz, CDCl$_3$):** δ 166.5, 145.2, 140.4, 138.8, 135.4, 132.3, 132.1, 131.8, 131.6, 130.1, 129.7, 128.5, 128.4, 128.0, 126.9, 37.9, 21.8.
**HRMS (ESI-TOF):** calculated for $[C_{21}H_{19}ClNO_3S\ (M + H)]^+$: 400.0074, found: 400.0072.




**3k**

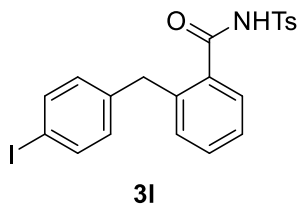
**2-(4-bromobenzyl)-*N*-tosylbenzamide (3k)**

Following the general procedure, the title compound was obtained as colorless oil, 115.2 mg, 52% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.75 (brs, 1H)7.89 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 3H), 6.77 (d, *J* = 8.1 Hz, 2H), 4.02 (s, 2H), 2.48 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.3, 145.3, 140.4, 139.3, 135.5, 132.4, 132.2, 131.7, 131.4, 130.6, 129.7, 128.6, 128.0, 126.9, 120.0, 38.05, 21.9.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{18}BrNO_3SNa$ (M + Na)$]^+$: 468.0068, found: 468.0072.




**3l**

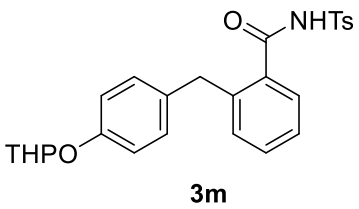
**2-(4-iodobenzyl)-*N*-tosylbenzamide (3l)**

Following the general procedure, the title compound was obtained as colorless oil, 127.4 mg, 52% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.41 (brs, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.39 (m, 1H), 7.38 – 7.32 (m, 4H), 7.29 – 7.24 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 2H), 4.02 (s, 2H), 2.49 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.2, 145.3, 140.5, 139.9, 137.5, 135.5, 132.4, 132.2, 131.8, 130.9, 129.8, 128.7, 127.9, 127.0, 91.5, 38.1, 21.9.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{18}INO_3SNa$ (M + Na)$]^+$: 513.9950, found: 513.9952.




**3m**

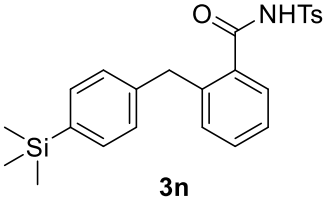
**2-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)benzyl)-*N*-tosylbenzamide (3m)**

Following the general procedure, the title compound was obtained as colorless oil, 93.2 mg, 40% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.32 (brs, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.37 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 12.7, 7.6 Hz, 2H), 6.88 – 6.80 (m, 4H), 5.33 (t, *J* = 3.2 Hz, 1H), 3.99 (s, 2H), 3.92 – 3.84 (m, 1H), 3.60 – 3.53 (m, 1H), 2.46 (s, 3H), 2.03 – 1.95 (m, 1H), 1.86 – 1.82 (m, 1H), 1.69 – 1.56 (m, 4H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.4, 155.6, 145.3, 141.1, 135.6, 133.2, 132.6, 132.0, 131.6, 129.8, 129.7, 128.7, 127.8, 126.6, 116.7, 96.6, 62.2, 37.7, 30.5, 25.3, 21.9, 19.0.

**HRMS (ESI-TOF):** calculated for $[C_{26}H_{28}NO_5S$ (M + H)$]^+$: 466.1688, found: 466.1687.




**3n**

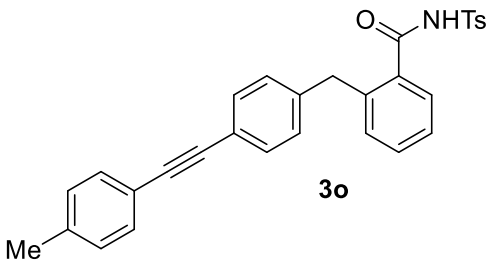
***N*-tosyl-2-(4-(trimethylsilyl)benzyl)benzamide (3n)**

Following the general procedure, the title compound was obtained as colorless oil, 109.3 mg, 50% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 2H), 4.05 (s, 2H), 2.47 (s, 3H), 0.23 (s, 9H).

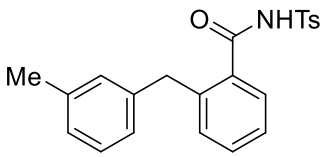
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.4, 145.3, 140.8, 140.7, 138.2, 135.7, 133.7, 132.7,

132.0, 131.6, 129.7, 128.8, 128.3, 127.7, 126.7, 38.4, 21.9, -1.0.
**HRMS (ESI-TOF):** calculated for $[C_{24}H_{28}NO_3SSi\ (M + H)]^+$: 438.1559, found: 438.1558.



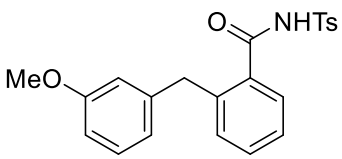
**3o**

**2-(4-(*p*-tolylethynyl)benzyl)-*N*-tosylbenzamide (3o)**
Following the general procedure, the title compound was obtained as colorless oil, 93.2 mg, 39% yield.
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.27 (brs, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.41 (m, 4H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.20 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 4.09 (s, 2H), 2.48 (s, 3H), 2.37 (s, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.1, 145.3, 140.5, 140.3, 138.5, 135.4, 132.5, 132.2, 131.9, 131.6, 131.6, 129.8, 129.3, 128.8, 128.7, 127.9, 127.0, 121.3, 120.3, 89.5, 88.8, 38.5, 21.9, 21.7.
**HRMS (ESI-TOF):** calculated for $[C_{30}H_{25}NO_3SNa\ (M + Na)]^+$: 502.1453, found: 502.1455.



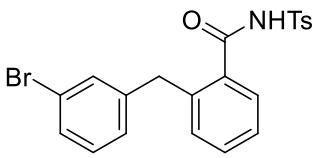
**3p**

**2-(3-methylbenzyl)-*N*-tosylbenzamide (3p)**
Following the general procedure, the title compound was obtained as colorless oil, 68.3 mg, 36% yield.
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.72 (brs, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 4.03 (s, 2H), 2.45 (s, 3H), 2.26 (s, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.6, 145.2, 140.6, 140.0, 138.2, 135.6, 132.6, 131.9, 131.5, 129.7, 128.6, 128.5, 127.8, 127.1, 126.6, 125.9, 38.4, 21.8, 21.5.
**HRMS (ESI-TOF):** calculated for $[C_{22}H_{21}NO_3SNa\ (M + Na)]^+$: 402.1140, found: 402.1141.



**3q**

**2-(3-methoxybenzyl)-*N*-tosylbenzamide (3q)**
Following the general procedure, the title compound was obtained as colorless oil, 73.2 mg, 37% yield.
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.87 (brs, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.58 (s, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 4.03 (s, 2H), 3.71 (s, 3H), 2.43 (s, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.6, 159.7, 145.1, 141.7, 140.3, 135.6, 132.6, 131.9, 131.5, 129.6, 129.5, 128.5, 127.9, 126.6, 121.2, 114.6, 111.7, 55.2, 38.4, 21.8.
**HRMS (ESI-TOF):** calculated for $[C_{22}H_{21}NO_4SNa\ (M + Na)]^+$: 418.1089, found: 418.1091.



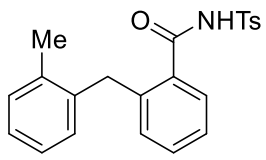
**3r**

**2-(3-bromobenzy)-*N*-tosylbenzamide (3r)**
Following the general procedure, the title compound was obtained as colorless oil, 90.8 mg, 41% yield.
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.59 (brs, 1H), 7.93 (d, *J* = 8.2

Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.13 (s, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 4.04 (s, 2H), 2.45 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.2 145.3, 142.6, 139.9, 135.5, 132.5, 132.2, 131.78, 131.77, 130.1, 129.8, 129.4, 128.6, 127.8, 127.5, 127.0, 122.6, 38.1, 21.9.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{18}BrNO_3SNa\ (M + Na)]^+$: 468.0068, found: 468.0071.




**3s**

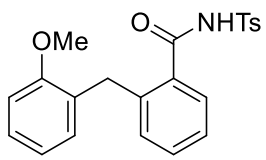
**2-(2-methylbenzyl)-*N*-tosylbenzamide (3s)**

Following the general procedure, the title compound was obtained as colorless oil, 98.6 mg, 52% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.54 (brs, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.33– 7.22 (m, 4H), 7.12 – 7.08 (m, 2H), 7.06 – 7.00 (m, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 4.00 (s, 2H), 2.44 (s, 3H), 2.08 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 166.4, 145.2, 139.8, 138.2, 136.7, 135.5, 132.9, 132.0, 131.1, 130.4, 129.7, 129.2, 128.6, 127.7, 126.7, 126.6, 126.2, 36.1, 21.8, 19.6.

**HRMS (ESI-TOF):** calculated for $[C_{22}H_{22}NO_3S\ (M + H)]^+$: 380.1320, found: 380.1318.




**3t**

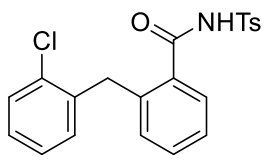
**2-(2-methoxybenzyl)-*N*-tosylbenzamide (3t)**

Following the general procedure, the title compound was obtained as colorless oil, 84.8 mg, 43% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 9.75 (brs, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.96 – 6.91 (m, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.95 (s, 2H), 3.83 (s, 3H), 2.44 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 167.1, 157.0, 145.1, 138.5, 135.9, 133.3, 131.5, 131.3, 130.5, 129.7, 129.5, 128.7, 128.5, 128.2, 126.6, 121.2, 111.0, 55.6, 33.9, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{22}H_{21}NO_4SNa\ (M + Na)]^+$: 418.1089, found: 418.1086.




**3u**

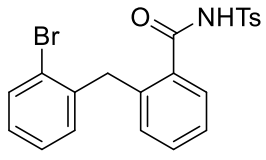
**2-(2-chlorobenzyl)-*N*-tosylbenzamide (3u)**

Following the general procedure, the title compound was obtained as colorless oil, 75.8 mg, 38% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.63 (brs, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.24 (s, 1H), 7.15 – 7.06 (m, 3H), 6.92 (dd, *J* = 7.4, 1.6 Hz, 1H), 4.13 (s, 2H), 2.44 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.3, 145.3, 140.4, 139.3, 135.5, 132.4, 132.2, 131.7, 131.4, 130.6, 129.7, 128.6, 128.0, 126.9, 120.0, 38.0, 21.9.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{19}ClNO_3S\ (M + H)]^+$: 400.0074, found: 400.0076.




**3v**

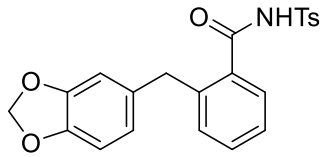
**2-(2-bromobenzyl)-*N*-tosylbenzamide (3v)**

Following the general procedure, the title compound was obtained as colorless oil, 99.6 mg, 45% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.56 (brs, 1H), 7.93 (t, *J* = 8.2 Hz, 2H), 7.48 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.36 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.14 (td, *J* = 7.5, 1.2 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.91 (dd, *J* = 7.6, 1.5 Hz, 1H), 4.12 (s, 2H), 2.44 (d, *J* = 3.5 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.3, 145.3, 139.6, 139.1, 135.4, 133.0, 132.9, 132.0, 131.2, 131.1, 129.8, 128.6, 128.2, 127.7, 127.5, 126.8, 125.0, 38.7, 21.9.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{18}BrNO_3SNa\ (M + Na)]^+$: 468.0068, found: 468.0072.




**3w**

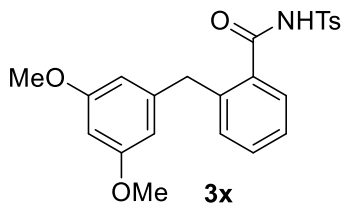
**2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-*N*-tosylbenzamide (3w)**

Following the general procedure, the title compound was obtained as colorless oil, 137.2 mg, 67% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 8.74 (brs, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.45 (s, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 5.85 (s, 2H), 3.96 (s, 2H), 2.45 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.5, 147.7, 146.0, 145.2, 140.7, 135.6, 134.0, 132.6, 132.0, 131.5, 129.7, 128.6, 127.9, 126.7, 121.8, 109.3, 108.2, 100.9, 38.1, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{22}H_{19}NO_5SNa\ (M + Na)]^+$: 432.0082, found: 432.0085.




**3x**

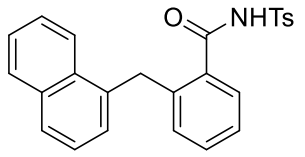
**2-(3,5-dimethoxybenzyl)-*N*-tosylbenzamide (3x)**

Following the general procedure, the title compound was obtained as colorless oil, 87.1 mg, 41% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.88 (brs, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.17 (m, 2H), 6.26 (t, *J* = 2.2 Hz, 1H), 6.17 (d, *J* = 2.2 Hz, 2H), 4.01 (s, 2H), 3.71 (s, 6H), 2.43 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.5, 160.9, 145.1, 142.5, 139.8, 135.6, 132.8, 131.9, 131.6, 129.8, 129.7, 128.5, 127.9, 126.7, 126.5, 107.0, 98.4, 55.4, 38.7, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{23}H_{23}NO_5SNa\ (M + Na)]^+$: 448.1195, found: 448.1197.




**3y**

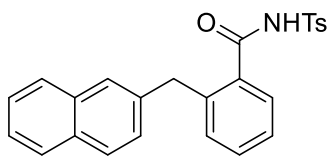
**2-(naphthalen-1-ylmethyl)-*N*-tosylbenzamide (3y)**

Following the general procedure, the title compound was obtained as colorless oil, 105.9 mg, 51% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.69 (brs, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.71 (m, 3H), 7.54 – 7.46 (m, 2H), 7.46 – 7.41 (m, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 1H), 4.47 (s, 2H), 2.32 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.6, 145.1, 139.5, 136.1, 135.3, 133.9, 133.0, 132.02, 131.97, 131.3, 129.5, 128.8, 128.3, 127.6, 127.4, 126.8, 126.7, 126.3, 125.9, 125.6, 124.0, 35.6, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{25}H_{21}NO_3SNa\ (M + Na)]^+$: 438.1140, found: 438.1141.




**3z**

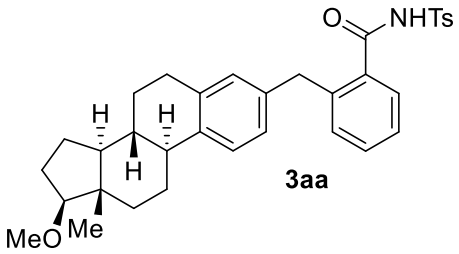
**2-(naphthalen-2-ylmethyl)-*N*-tosylbenzamide (3z)**

Following the general procedure, the title compound was obtained as colorless oil, 122.3 mg, 59% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.72 (brs, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.77 – 7.73 (m, 1H), 7.67 – 7.63 (m, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.43 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.28 – 7.20 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.11 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.23 (s, 2H), 2.37 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.5, 145.1, 140.4, 137.8, 135.4, 133.6, 132.7, 132.1, 131.8, 129.6, 128.4, 128.2, 127.9, 127.8, 127.7, 127.4, 127.0, 126.8, 126.5, 126.1, 125.6, 38.6, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{25}H_{21}NO_3SNa\ (M + Na)]^+$: 438.1140, found: 438.1142.




**3aa**

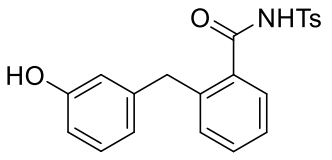
**2-(((8*R*,9*S*,13*S*,14*S*,17*S*)-17-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)methyl)-*N*-tosylbenzamide (3aa)**

Following the general procedure, the title compound was obtained as colorless oil, 100.1 mg, 36% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.39 (s, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.13 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.97 (s, 2H), 3.37 (s, 3H), 3.30 (t, *J* = 8.3 Hz, 1H), 2.74 (dd, *J* = 9.4, 6.3 Hz, 2H), 2.41 (d, *J* = 5.3 Hz, 3H), 2.24 (dd, *J* = 12.9, 3.5 Hz, 1H), 2.16 (dd, *J* = 17.6, 7.6 Hz, 1H), 2.08 – 2.00 (m, 2H), 1.87 – 1.79 (m, 1H), 1.71 – 1.63 (m, 1H), 1.50 – 1.28 (m, 6H), 1.22 – 1.14 (m, 1H), 0.76 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 167.4, 144.9, 140.7, 138.5, 137.3, 137.0, 136.0, 133.1, 131.7, 131.4, 129.6, 129.5, 128.6, 127.9, 126.5, 126.2, 125.6, 90.9, 58.0, 50.5, 44.3, 43.3, 38.5, 38.2, 38.1, 29.6, 27.8, 27.3, 26.3, 23.2, 21.8, 11.7.

**HRMS (ESI-TOF):** calculated for $[C_{34}H_{39}NO_4SNa\ (M + Na)]^+$: 580.2497, found: 580.2494.




**3ab**

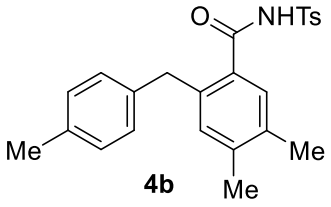
**2-(3-hydroxybenzyl)-*N*-tosylbenzamide (3ab)**

Following the general procedure, the title compound was obtained as colorless oil, 91.5 mg, 48% yield.

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 9.03 (brs, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 9.2 Hz, 2H), 7.18 – 7.10 (m, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 7.3 Hz, 1H), 6.43 (s, 1H), 3.96 (s, 2H), 2.40 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 167.2, 156.0, 145.3, 141.9, 140.1, 135.2, 132.7, 131.9, 131.6, 129.7, 128.5, 127.8, 126.6, 120.9, 115.8, 113.5, 38.3, 21.8.

**HRMS (ESI-TOF):** calculated for $[C_{21}H_{19}NO_4SNa\ (M + Na)]^+$: 404.0932, found: 404.0933.



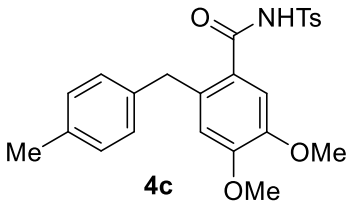

**4,5-dimethyl-2-(4-methylbenzyl)-*N*-tosylbenzamide (4b)**

Following the general procedure, the title compound was obtained as colorless oil, 65.0 mg, 32% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.28 (brs, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 1H), 6.98 – 6.91 (m, 3H), 6.85 (d, *J* = 7.9 Hz, 2H), 3.97 (s, 2H), 2.45 (s, 3H), 2.27 (s, 3H), 2.20 (s, 6H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.4, 145.0, 141.3, 138.4, 137.6, 135.8, 135.6, 135.1, 133.0, 129.8,129.6, 129.3, 129.2, 128.7, 37.7, 21.8, 21.1, 19.9, 19.2.

**HRMS (ESI-TOF):** calculated for $[C_{24}H_{25}NO_3SNa\ (M + Na)]^+$: 430.1453, found: 430.1454.



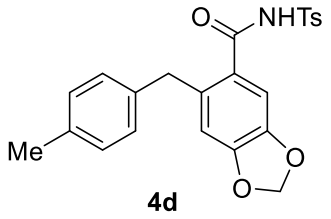

**4,5-dimethoxy-2-(4-methylbenzyl)-*N*-tosylbenzamide (4c)**

Following the general procedure, the title compound was obtained as colorless oil, 76.6 mg, 35% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 9.08 (brs, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.05 (s, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 2H), 6.60 (s, 1H), 4.00 (s, 2H), 3.77 (d, *J* = 4.3 Hz, 6H), 2.43 (s, 3H), 2.27 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 166.0, 151.7, 147.0, 144.9, 137.4, 135.7, 135.6, 135.0, 129.7, 129.5, 129.2, 128.49, 128.46, 126.4, 123.7, 114.0, 111.2, 56.1, 55.9, 37.8, 21.7, 21.1.

**HRMS (ESI-TOF):** calculated for $[C_{24}H_{25}NO_5SNa\ (M + Na)]^+$: 462.1351, found: 462.1350.



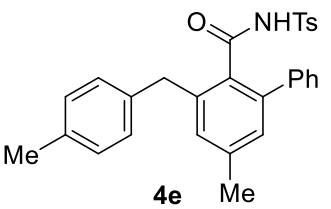

**6-(4-methylbenzyl)-*N*-tosylbenzo[d][1,3]dioxole-5-carboxamide (4d)**

Following the general procedure, the title compound was obtained as colorless oil, 84.5 mg, 40% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.37 (brs, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.90 (s, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 5.95 (s, 2H), 3.93 (s, 2H), 2.45 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 165.6, 150.6, 146.2, 145.2, 137.1, 136.8, 136.0, 135.7, 129.7, 129.4, 128.7, 128.6, 125.4, 111.5, 107.8, 102.0, 38.0, 21.9, 21.1.

**HRMS (ESI-TOF):** calculated for $[C_{23}H_{21}NO_5SNa\ (M + Na)]^+$: 446.1038, found: 446.1041.



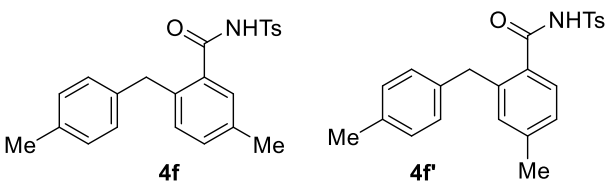

**5-methyl-3-(4-methylbenzyl)-*N*-tosyl-[1,1'-biphenyl]-2-carboxamide (4e)**

Following the general procedure, the title compound was obtained as colorless oil, 96.1 mg, 41% yield.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.19 – 7.16 (m, 2H), 7.15 – 7.10 (m, 2H), 7.07 – 7.01 (m, 5H), 6.98 (s, 1H), 3.95 (s, 2H), 2.47 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 167.0, 144.8, 140.6, 139.9, 139.6, 139.3, 137.0, 135.9, 135.2, 130.5, 130.3, 129.6, 129.4, 129.03, 128.97, 128.8, 128.7, 128.4, 127.8, 38.3, 21.9, 21.5, 21.2.

**HRMS (ESI-TOF):** calculated for $[C_{29}H_{28}NO_3S\ (M + H)]^+$: 470.1790, found: 470.1789.




53/47

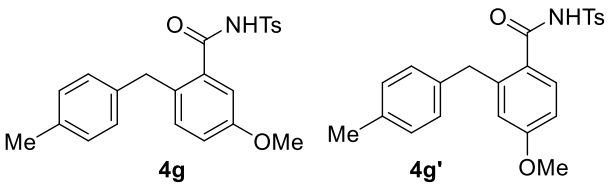
**5-methyl-2-(4-methylbenzyl)-*N*-tosylbenzamide (4f) and 4-methyl-2-(4-methylbenzyl)-*N*-tosylbenzamide (4f')**

Following the general procedure, the title compound was obtained as colorless oil, 94.2 mg, 48% yield.

**$^1$H NMR (400 MHz, $CDCl_3$),** mixture of **4f** and **4f':** δ 8.48 (brs, 1H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.30 (m, 2.53H), 7.25 (s, 0.47H), 7.18 (d, *J* = 7.8 Hz, 0.53H), 7.07 (d, *J* = 7.8 Hz, 0.47H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.89 – 6.82 (m, 2H), 4.01 (s, 1.06H), 3.97 (s, 0.94H), 2.46 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$),** mixture of **4f** and **4f':** δ 166.7, 166.5, 145.1, 145.0, 142.6, 141.1, 137.8, 137.4, 137.3, 136.4, 135.77, 135.73, 135.66, 132.7, 132.5, 132.4, 131.5, 129.66, 129.63, 129.61, 129.3, 128.73, 128.69, 128.64, 128.4, 128.1, 127.2, 38.1, 37.7, 21.8, 21.6, 21.1, 20.9.

**HRMS (ESI-TOF):** calculated for $[C_{23}H_{23}NO_3SNa\ (M + Na)]^+$: 416.1296, found: 416.1298.




50/50

**5-methoxy-2-(4-methylbenzyl)-*N*-tosylbenzamide (4g) and 4-methoxy-2-(4-methylbenzyl)-*N*-tosylbenzamide (4g')**

Following the general procedure, the title compound was obtained as colorless oil, 69.3 mg, 34% yield.

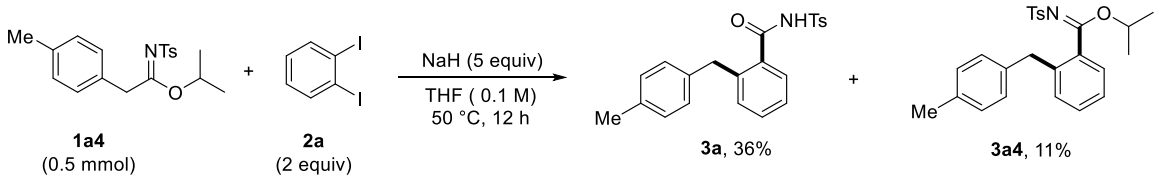
**$^1$H NMR (400 MHz, $CDCl_3$),** mixture of **4g** and **4g':** δ 8.44 (brs, 1H), 7.95 (dd, *J* = 8.4 Hz, 2.0 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 0.50H), 7.35 – 7.31(m, 2H), 7.10 (d, *J* = 8.5 Hz, 0.50H), 6.98 – 6.90 (m, 3H), 6.89 – 6.82 (m, 2H), 6.73– 6.68 (m, 1.0H), 4.05 (s, 1.0H), 3.92 (s, 1H), 3.76 (s, 1.50H), 3.75 (s, 1.50H), 2.46 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$),** mixture of **4g** and **4g':** δ 166.2, 165.8, 162.3, 158.0, 145.2, 145.0, 144.0, 137.5, 136.9, 135.80, 135.76, 135.5, 133.4, 132.8, 132.4, 130.3, 129.7, 129.6, 129.34, 129.31, 128.8, 128.69, 128.66, 128.6, 124.5, 117.9, 117.6, 112.9, 111.2, 55.7, 55.5, 38.4, 37.3, 21.9, 21.1.

**HRMS (ESI-TOF):** calculated for $[C_{23}H_{23}NO_4SNa\ (M + Na)]^+$: 432.1245, found: 432.1246.

## 5. Mechanism study

### 5.1 The observation of imidate intermediate




To a suspension of NaH (60% dispersion in mineral oil, 101 mg, 2.5 mmol) in anhydrous THF (5 mL) was added *N*-sulfonylacetimidate **1a4** (172.7 mg, 0.5 mmol) and *o*-diiodoarene **2a** (330 mg, 1 mmol) respectively at ambient temperature. The mixture was warmed to 50 °C for 12 h. After that, the reaction was quenched with saturated aqueous $NH_4Cl$ (6 mL) solution at 0 °C. The mixture was then extracted with EtOAc (8 mL × 4). The combined extracts were dried over $Na_2SO_4$, concentrated under vacuum. The resulting residue was purified by silica gel chromatography to afford *o*-benzyl benzimidate **3a**, 68.1 mg, 37% yield, and the imidate intermediate **3a4** as white solid, 23.5 mg, 11% yield.

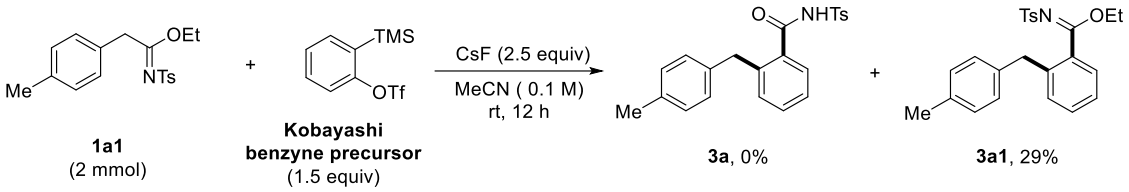
**isopropyl (*Z*)-2-(4-methylbenzyl)-*N*-tosylbenzimidate (3a4)**

**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.19 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 3H), 5.27 – 5.19 (m, 1H), 3.82 (s, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.26 (d, *J* = 6.3 Hz, 6H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.3, 143.2, 139.0, 138.4, 136.8, 135.9, 132.7, 130.6, 129.9, 129.4, 129.3, 129.2, 127.8, 127.1, 125.8, 73.4, 38.5, 21.7, 21.4, 21.2.

**HRMS (ESI-TOF):** calculated for $[C_{25}H_{28}NO_3S\ (M + H)]^+$: 422.1784, found: 422.1785.

### 5.2 The preformed imidate intermediate undergoes a NaH mediated hydrolysis



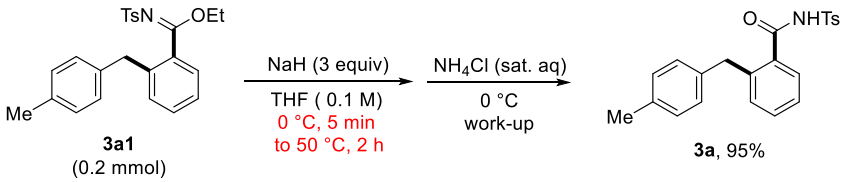

Following a literature procedures.[3] An oven-dried round-bottom flask equipped with a magneticstirring bar was charged with *N*-sulfonylacetimidates **1a1** (663 mg, 2 mmol), **Kobayashi benzyne precursor** (895mg, 3 mmol), and CsF (760 mg, 5 mmol) in $CH_3CN$ (10 mL) under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 12 h. After the reaction was finished, the solvent was evaporated and the residue was purified by flash column chromatography to give imidate intermediate **3a1** as white solid, 235.8 mg, 29% yield.

**ethyl (*Z*)-2-(4-methylbenzyl)-*N*-tosylbenzimidate (3a1)**

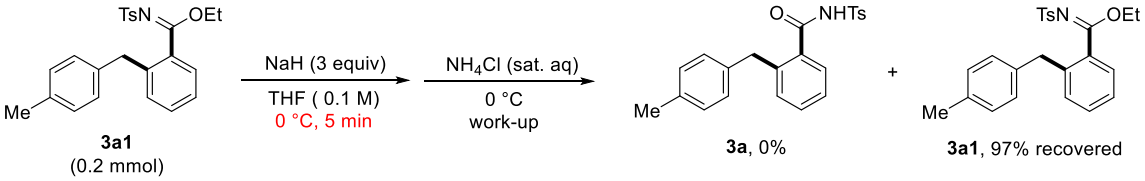
**$^1$H NMR (600 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 8.1 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.05 (m, 3H), 7.01 (d, *J* = 7.9 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 2H), 2.41 (s, 3H), 2.30 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** δ 171.8, 143.2, 138.9, 138.7, 136.8, 135.8, 132.4, 130.7, 130.1, 129.31, 129.27, 129.2, 128.0, 127.2, 125.8, 65.5, 38.9, 21.7, 21.1, 13.7.

**HRMS (ESI-TOF):** calculated for $[C_{24}H_{26}NO_3S\ (M + H)]^+$: 408.1628, found: 408.1631.



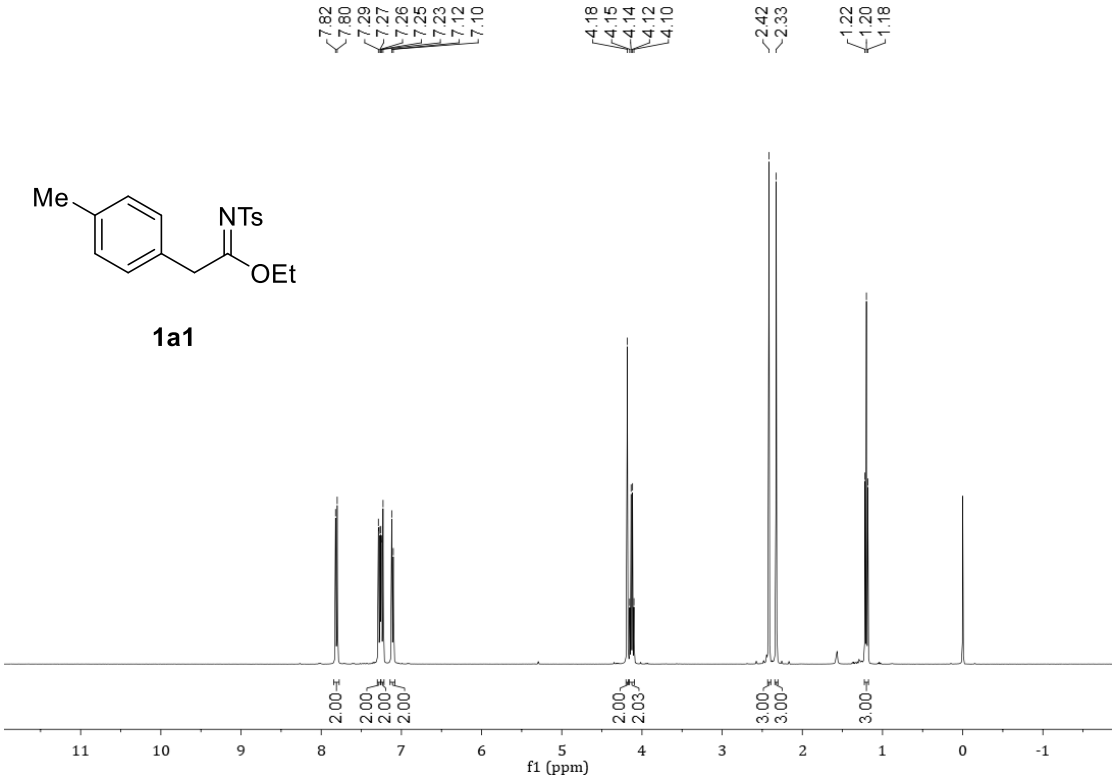

To a suspension of NaH (60% dispersion in mineral oil, 24 mg, 0.6 mmol) in anhydrous THF (2 mL) was added imidate intermediate **3a1** (81.5 mg, 0.2 mmol) at 0 °C and stirred for 5 min. Then the mixture was warmed to 50 °C for 2 h. After that, the reaction was quenched with saturated aqueous $NH_4Cl$ (2 mL) solution at 0 °C. The mixture was then extracted with EtOAc (3 mL × 4). The combined extracts were dried over $Na_2SO_4$, concentrated under vacuum. The resulting residue was purified by silica gel chromatography to afford *o*-benzyl benzimidate **3a**, 71.8 mg, 95% yield.



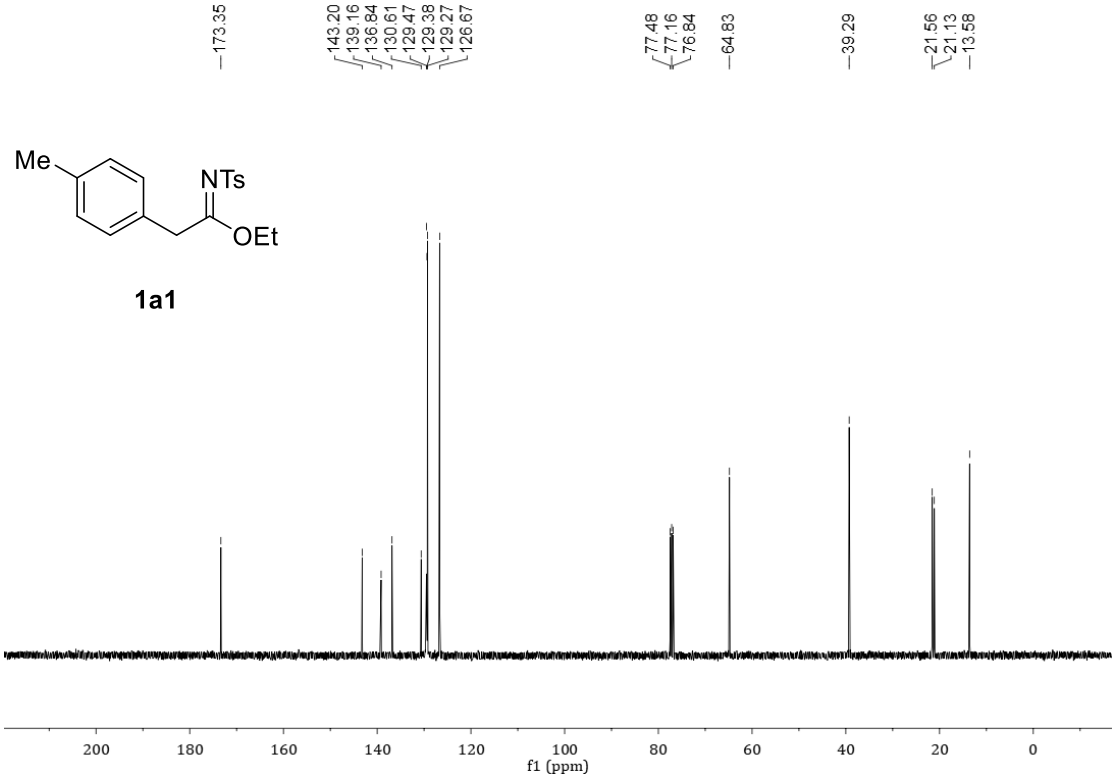

To a suspension of NaH (60% dispersion in mineral oil, 24 mg, 0.6 mmol) in anhydrous THF (2 mL) was added imidate intermediate **3a1** (81.5 mg, 0.2 mmol) at 0 °C and stirred for 5 min. Then the mixture was quenched with saturated aqueous $NH_4Cl$ (2 mL) solution at the same temperature. The mixture was then extracted with EtOAc (3 mL × 4). The combined extracts were dried over $Na_2SO_4$, concentrated under vacuum. This procedure resulted in the recovery of **3a1** (79.2 mg, 97%), with no detectable formation of **3a**.

## 6. NMR spectra

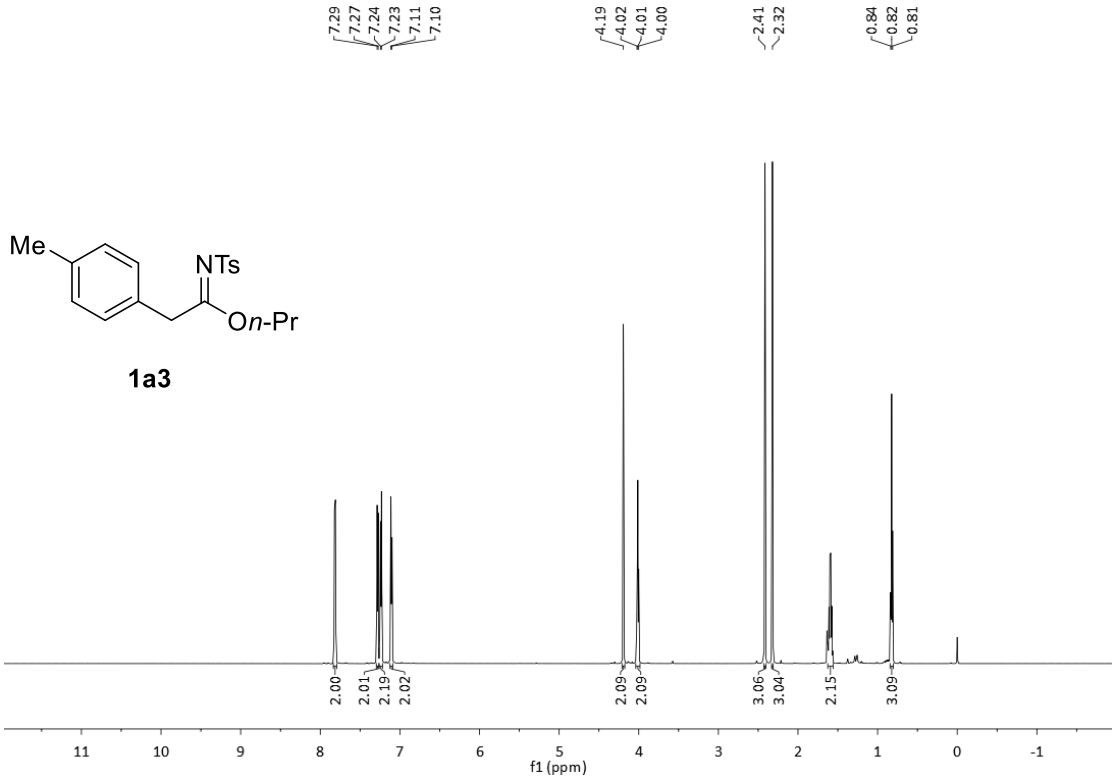
### $^{1}$H NMR (400 MHz, $CDCl_3$)



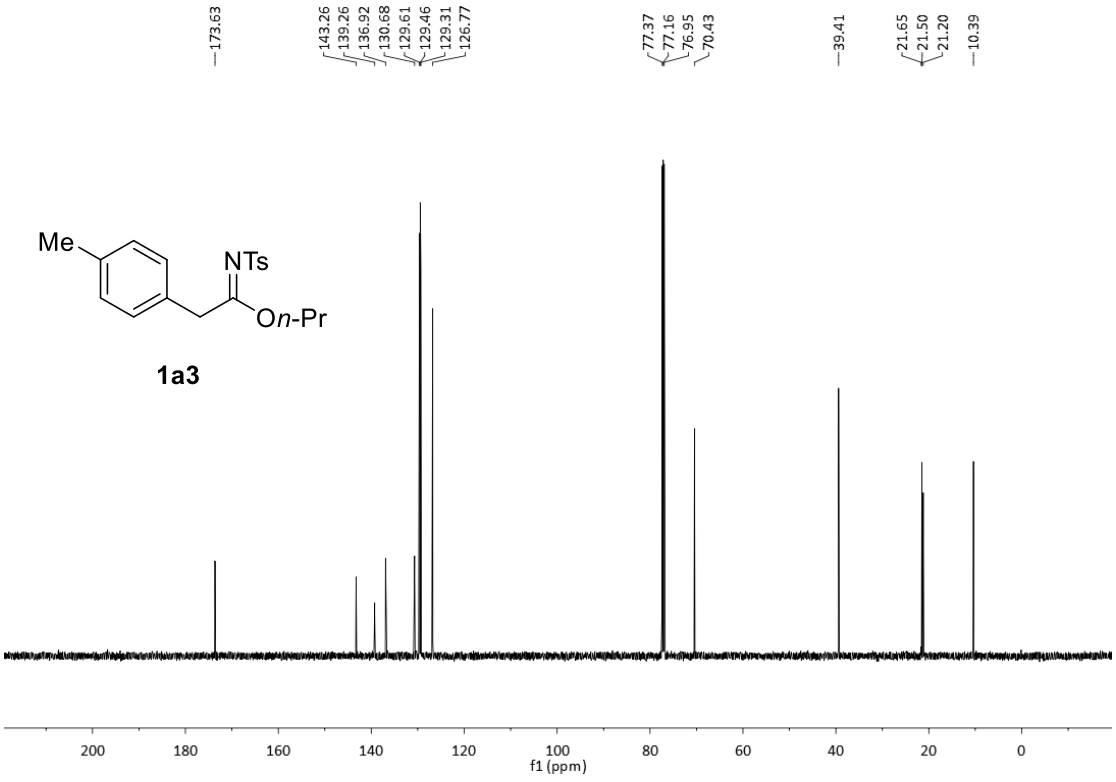

### $^{13}$C NMR (100 MHz, $CDCl_3$)



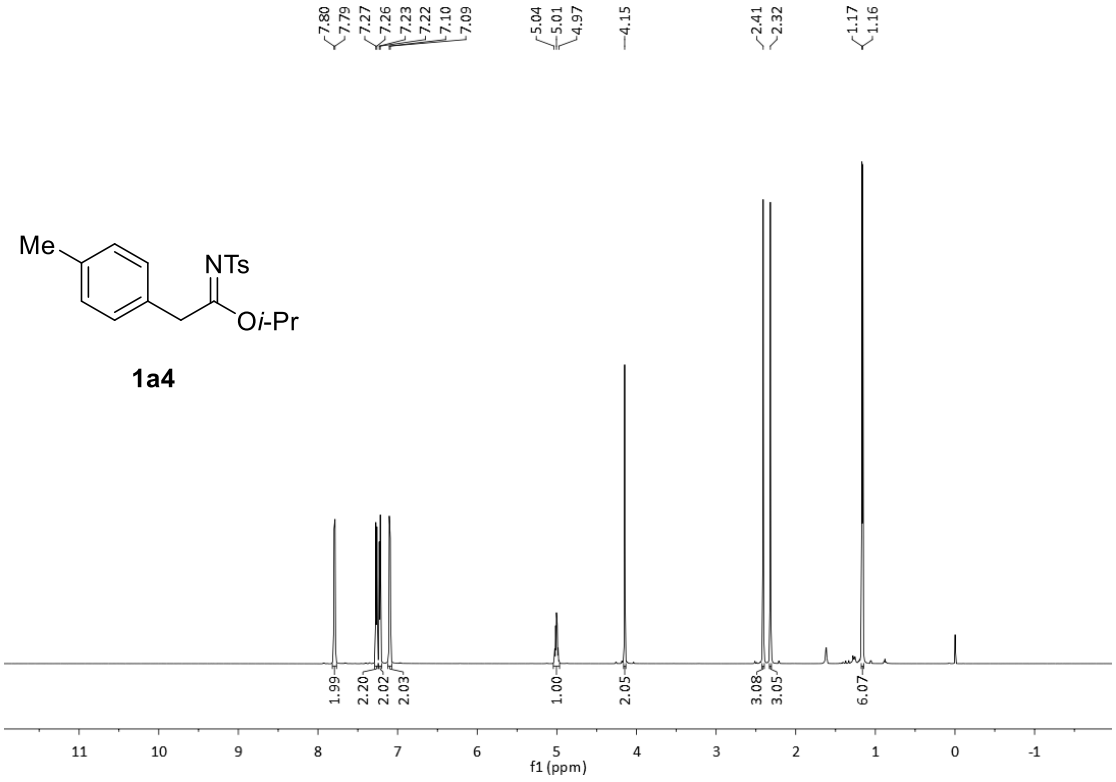
**$^{1}$H NMR (600 MHz, $CDCl_3$)**



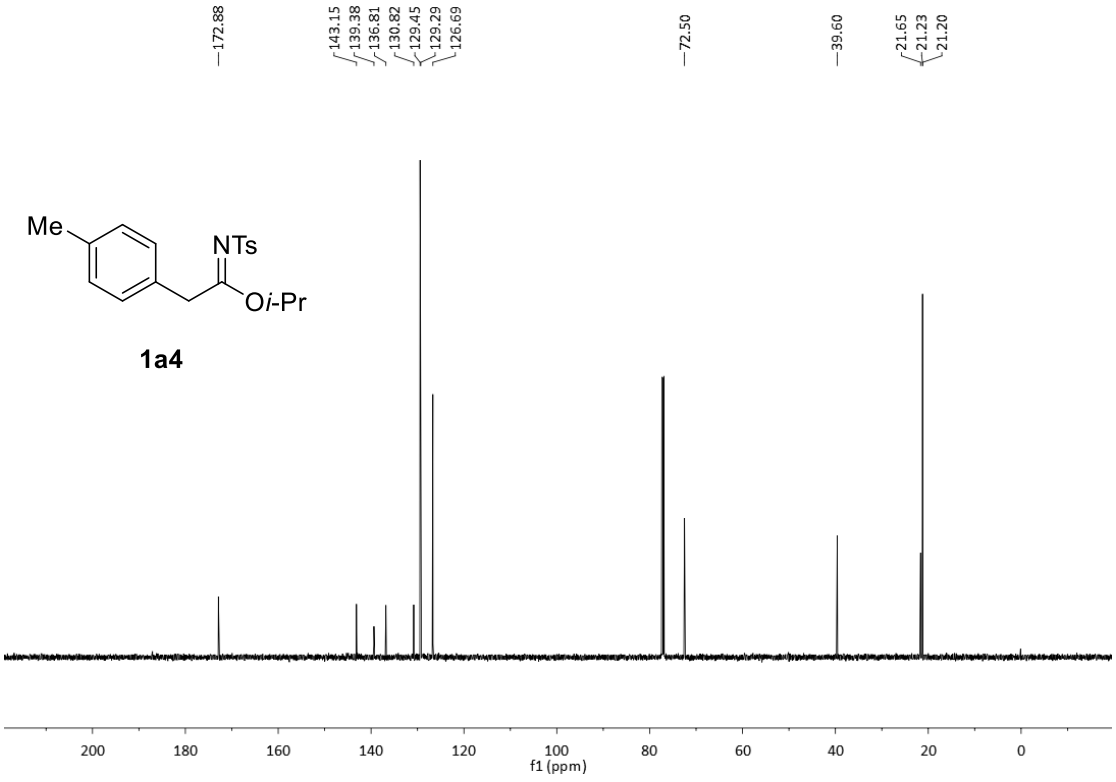

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



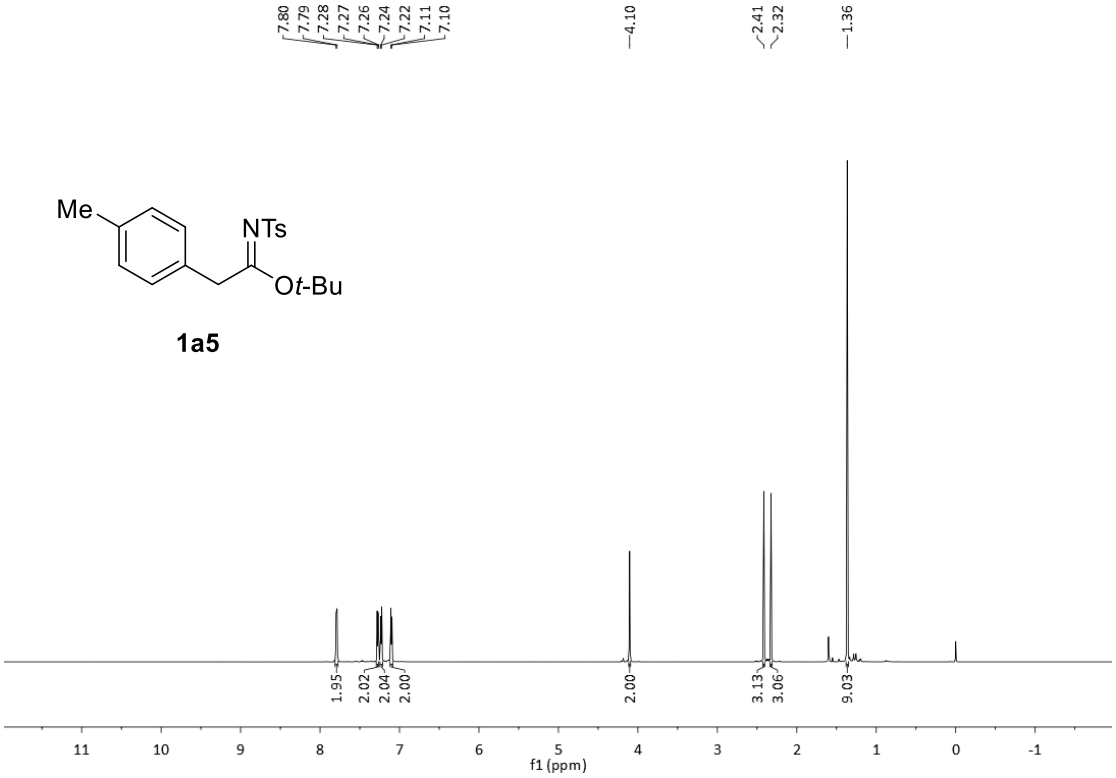
**$^{1}$H NMR (600 MHz, $CDCl_3$)**



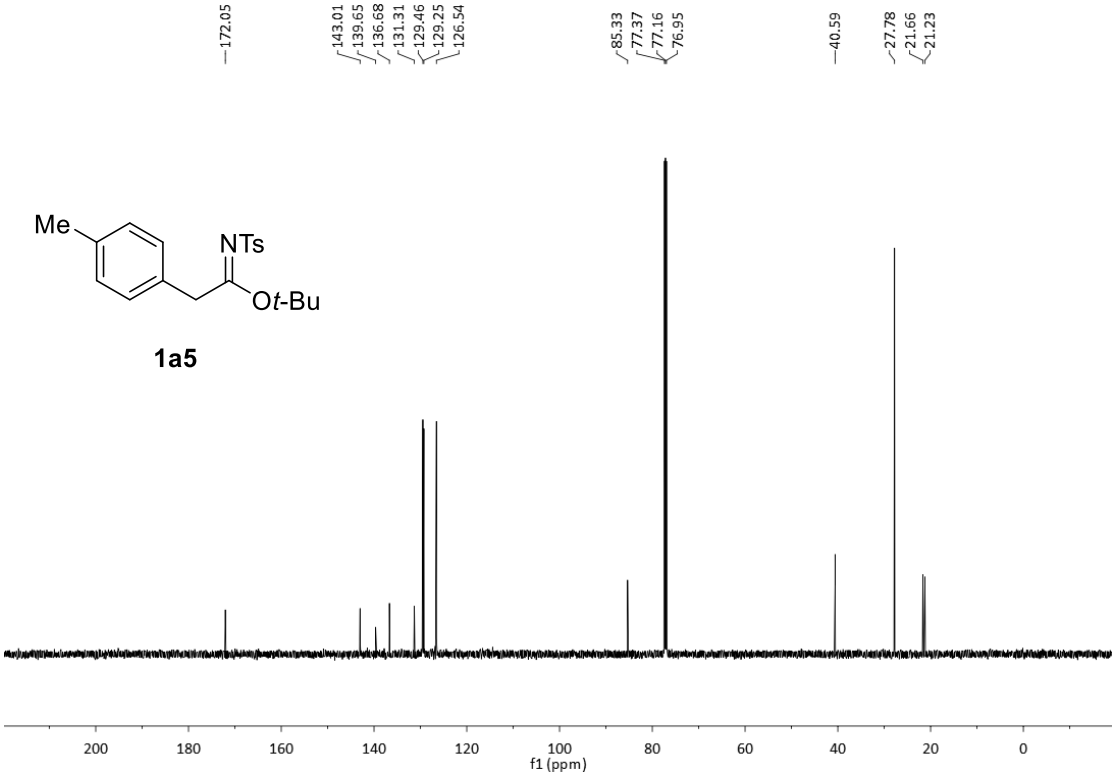

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



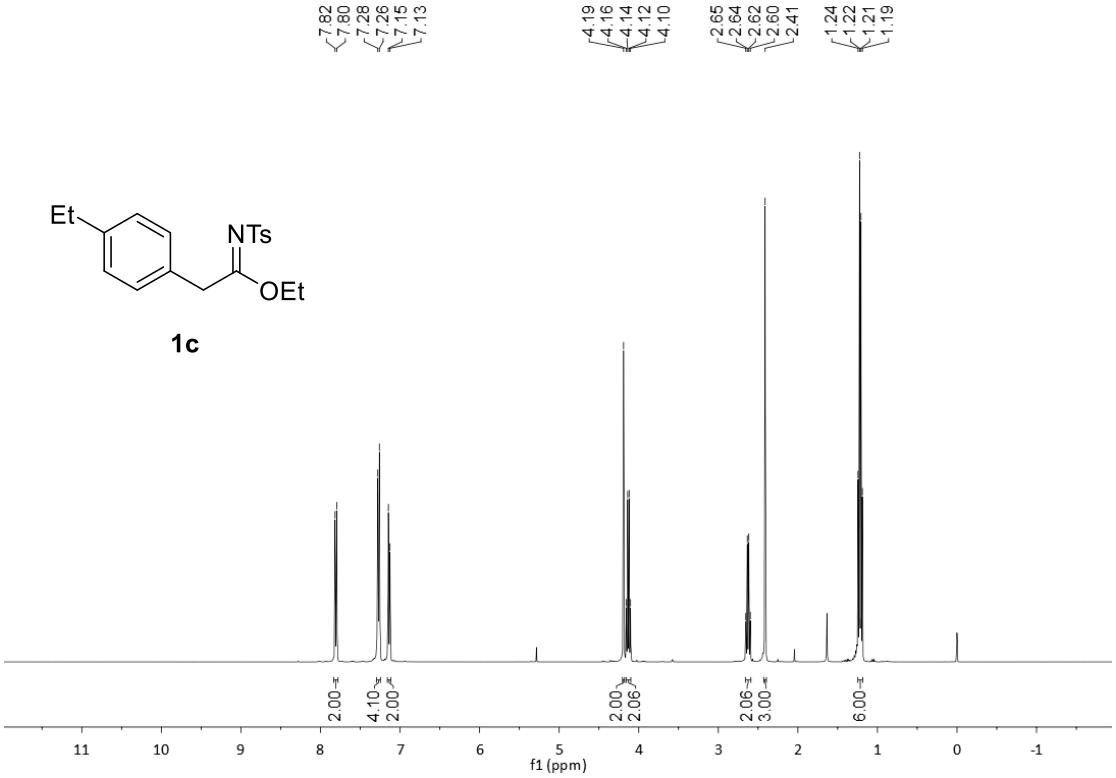
**$^{1}$H NMR (600 MHz, $CDCl_3$)**



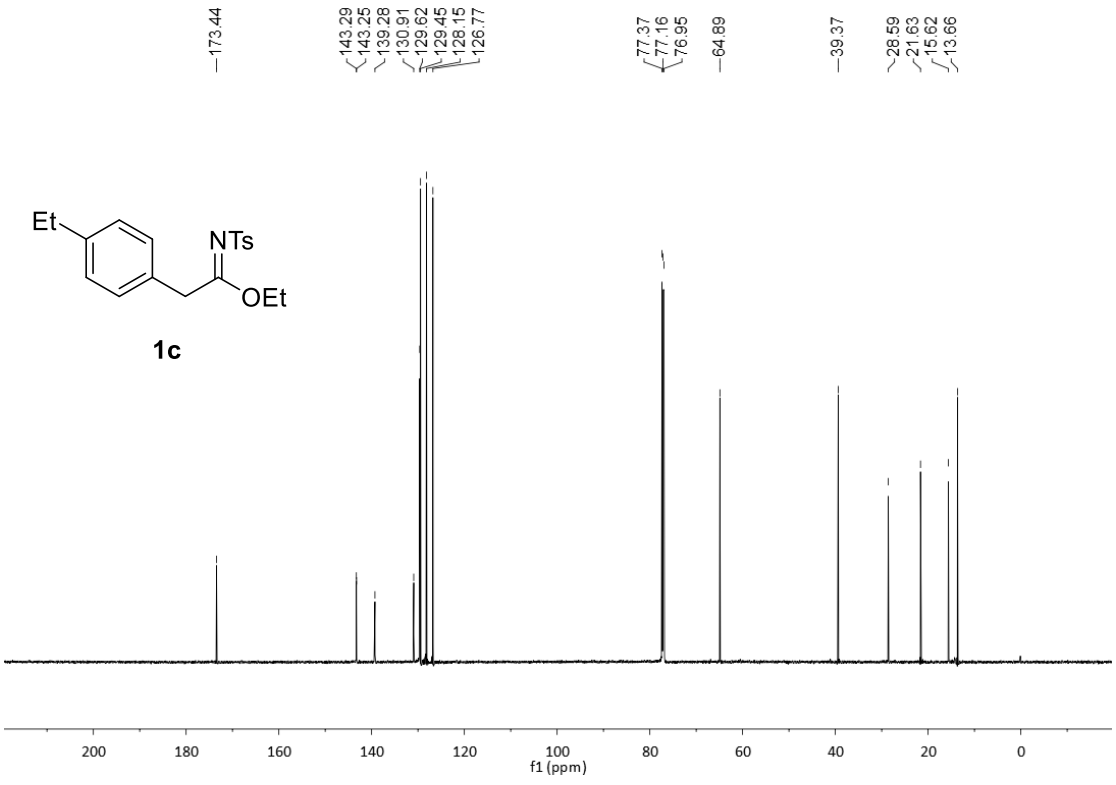

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



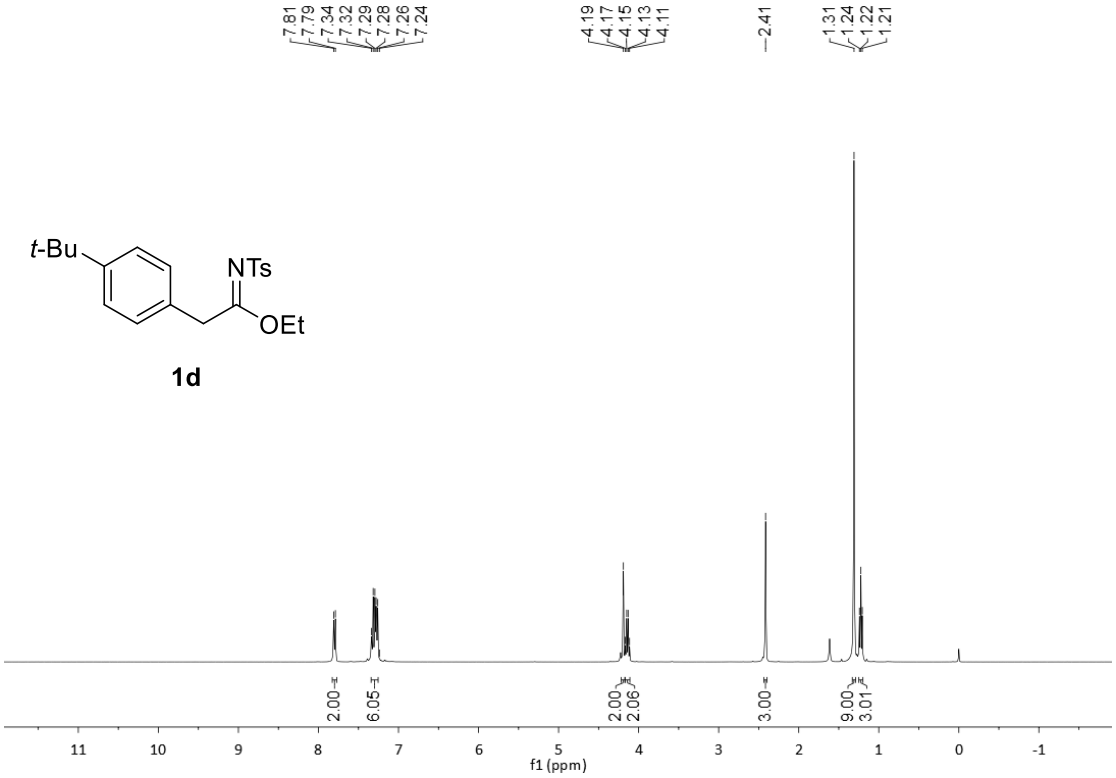
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



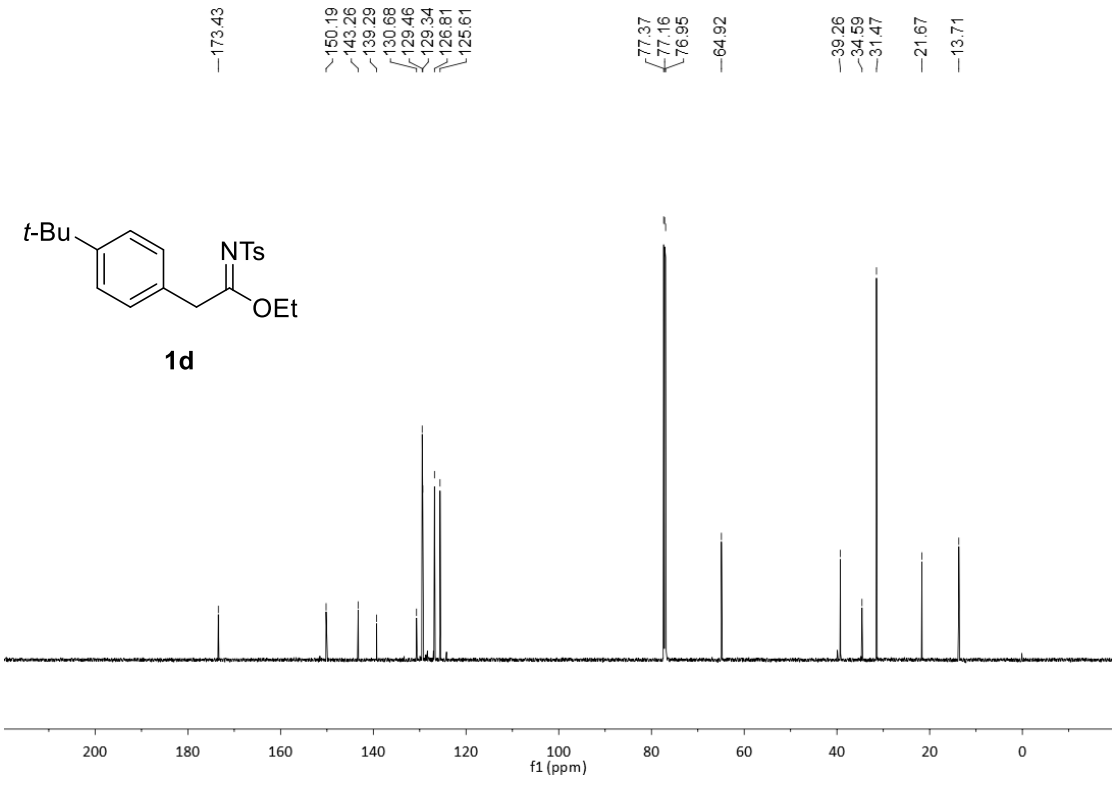

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



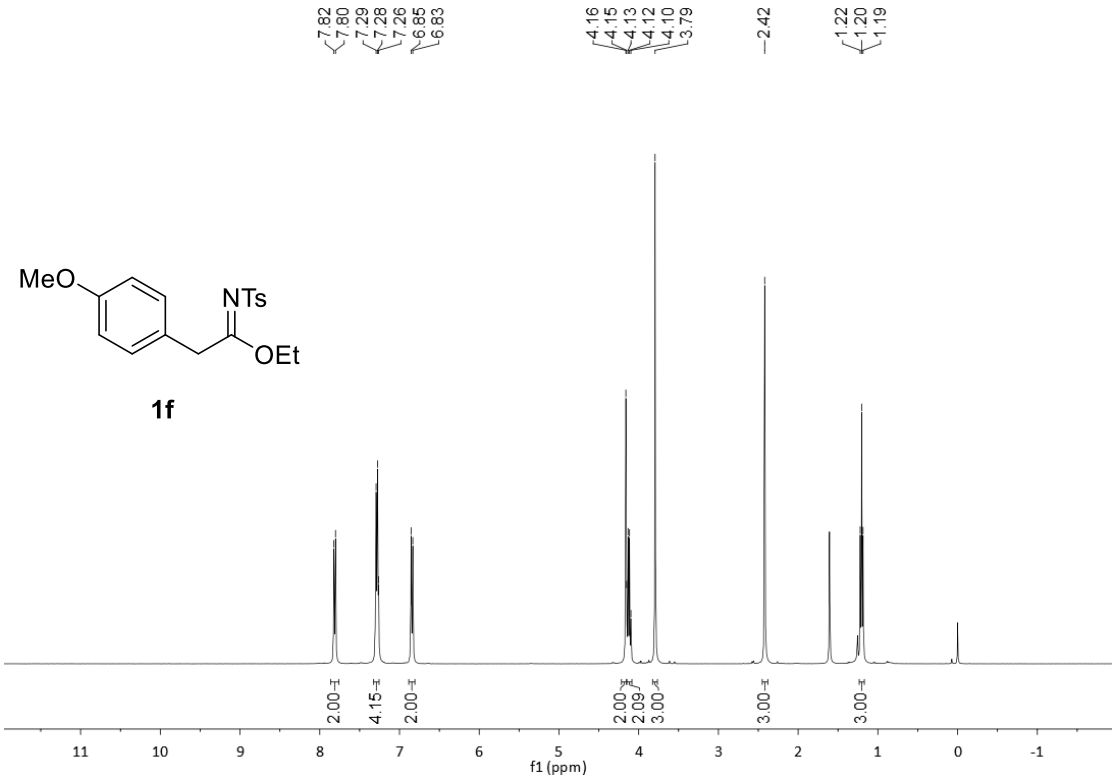
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



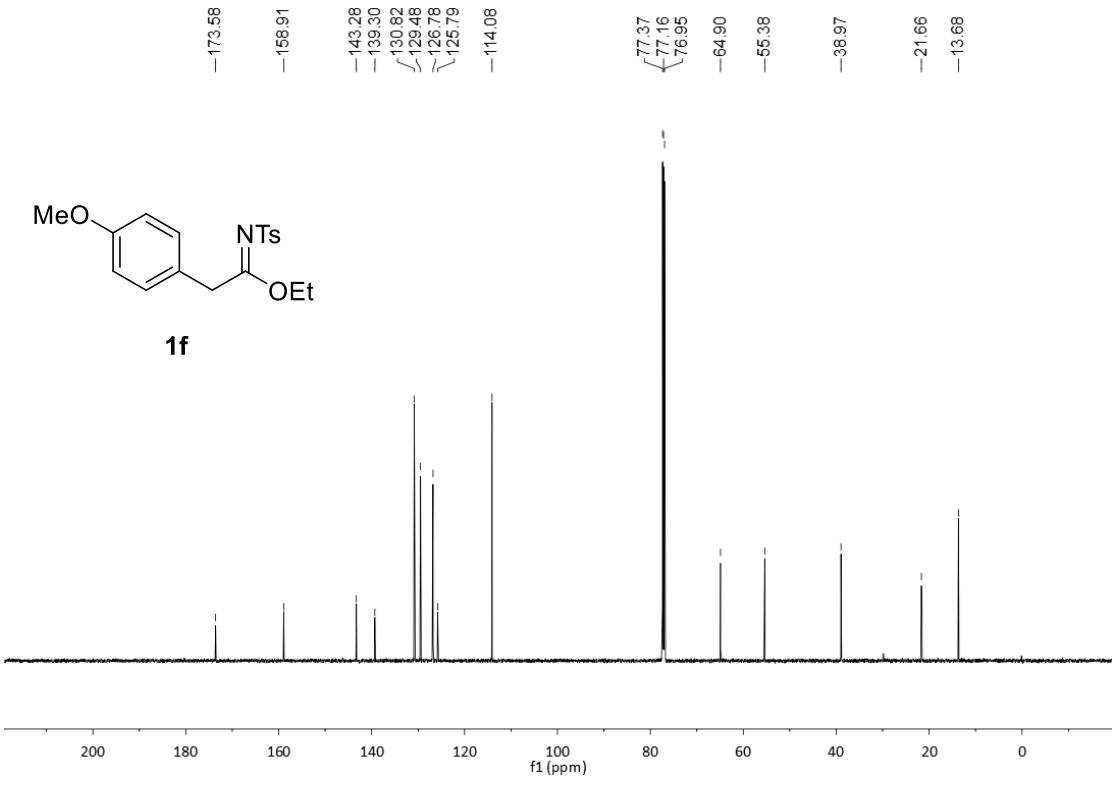

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**




**$^{13}$C NMR (150 MHz, $CDCl_3$)**



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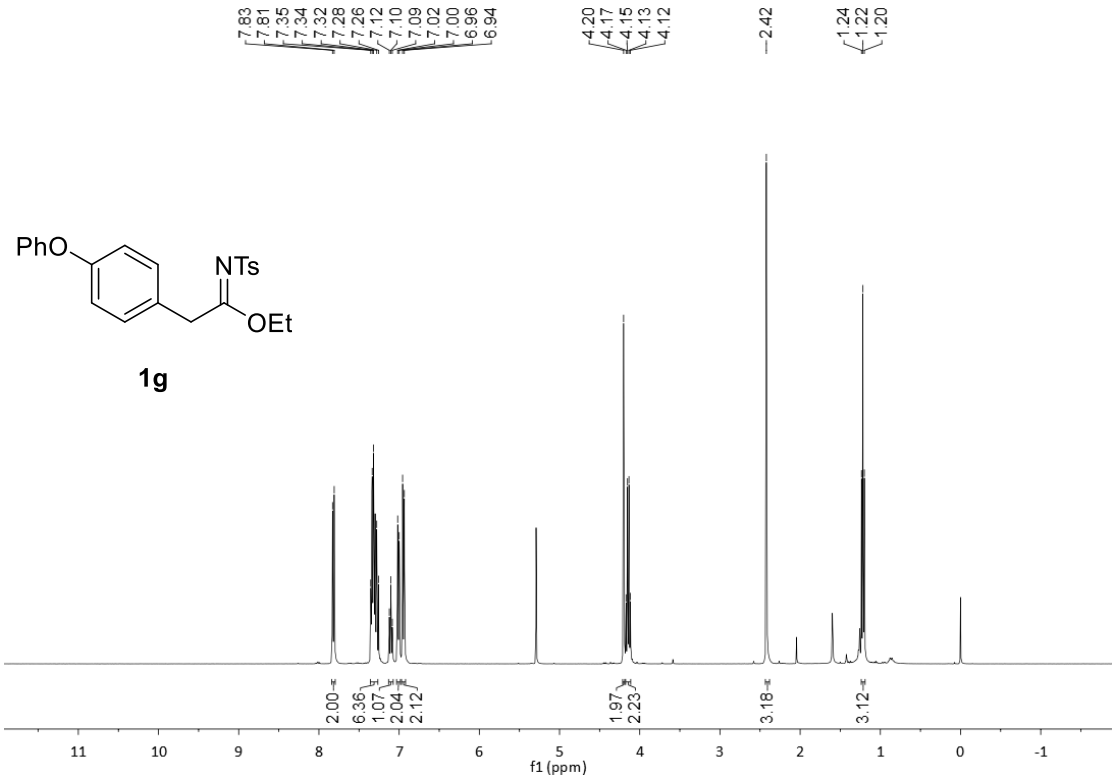
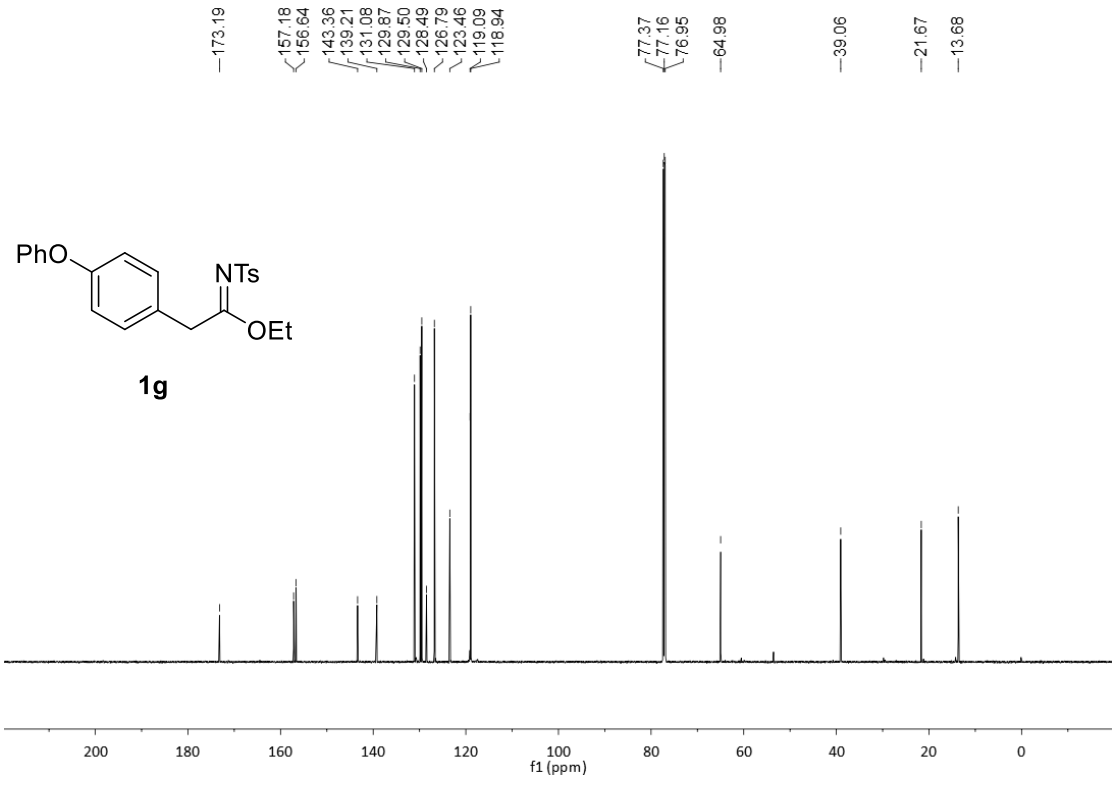
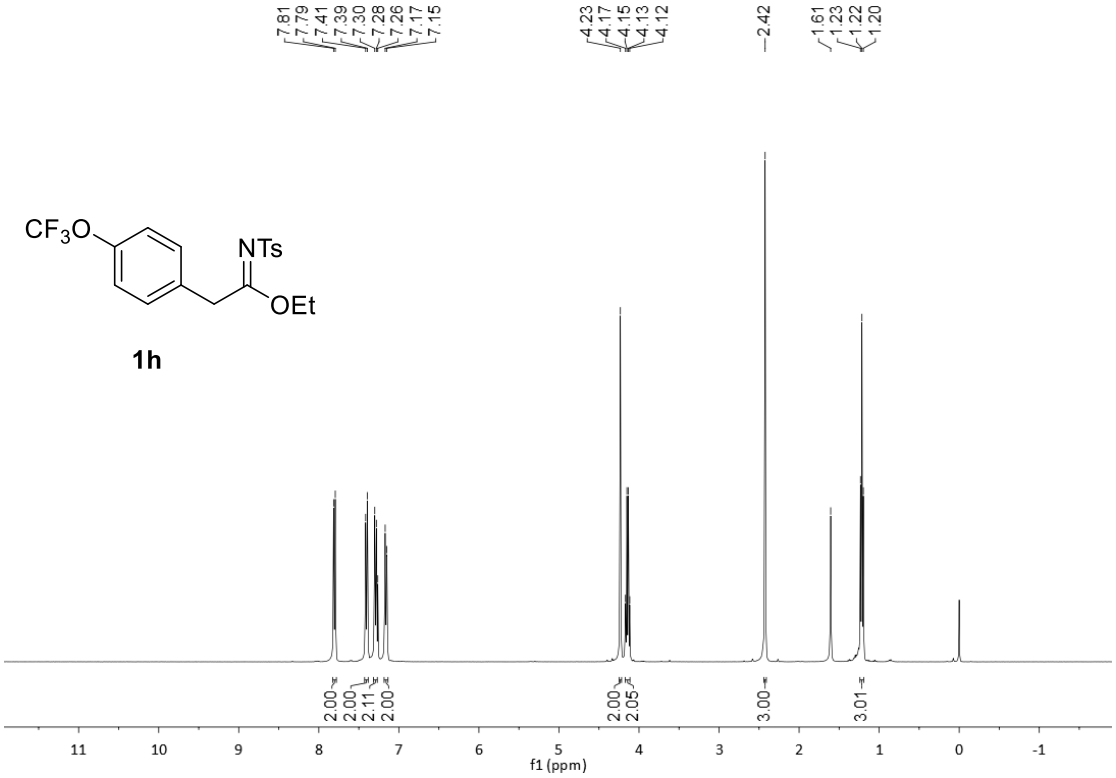


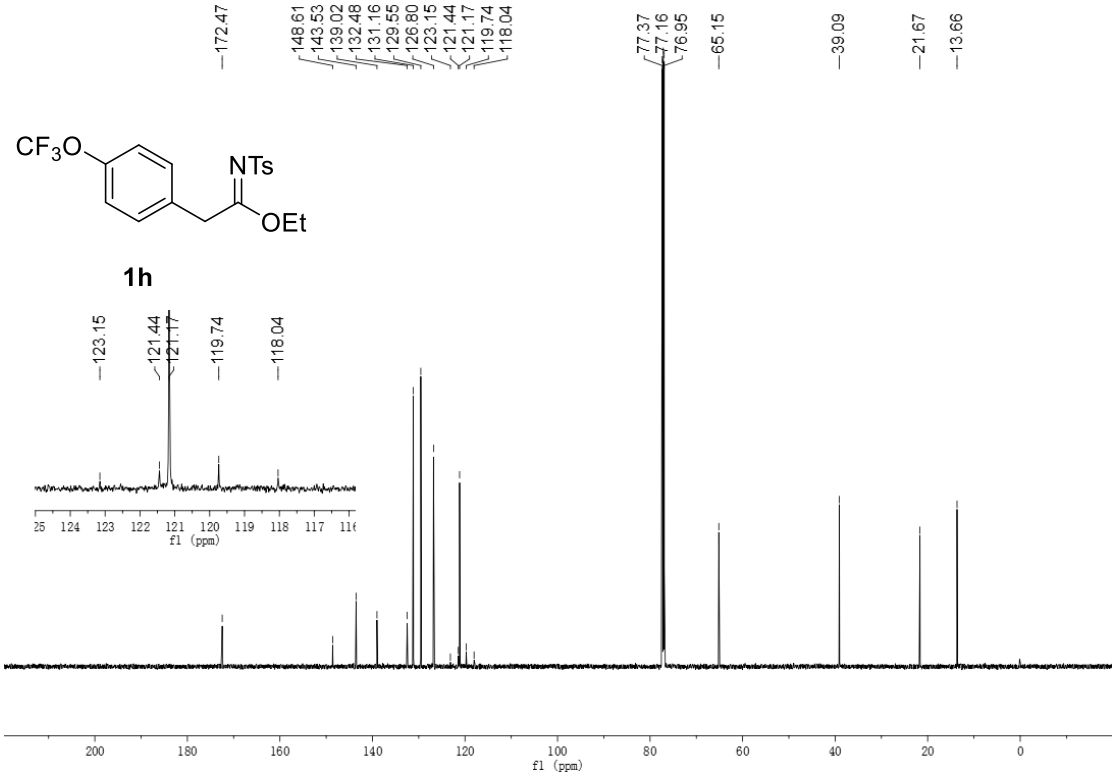

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



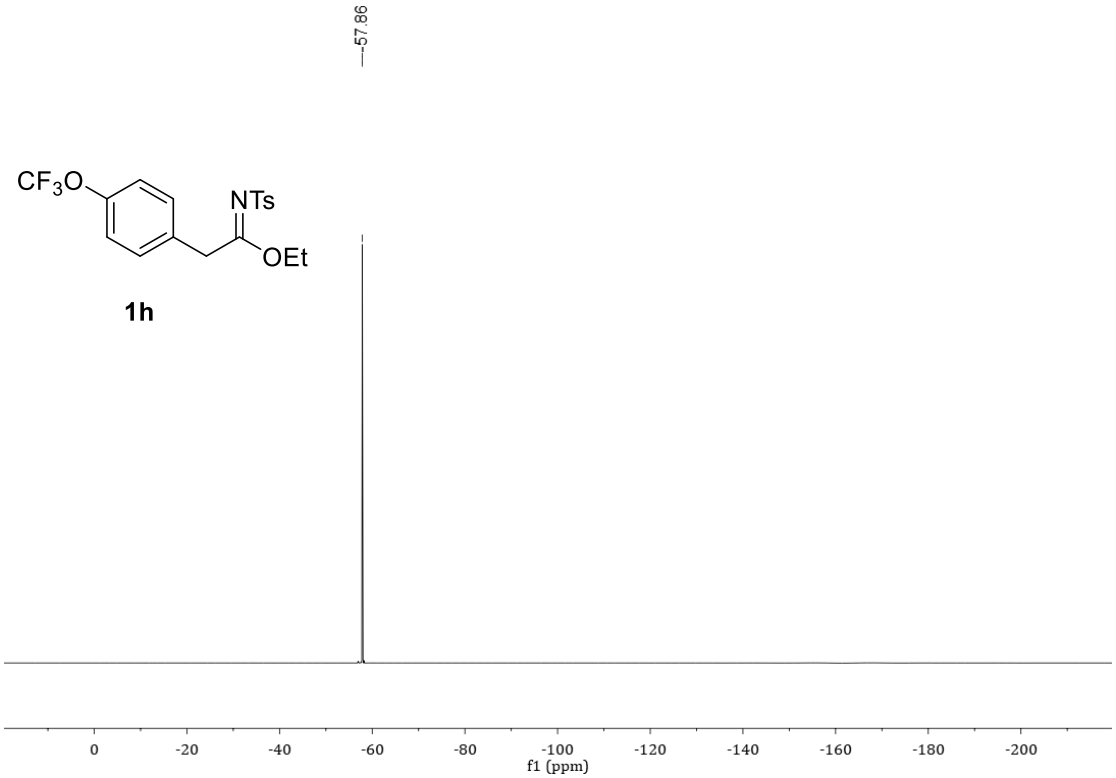
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



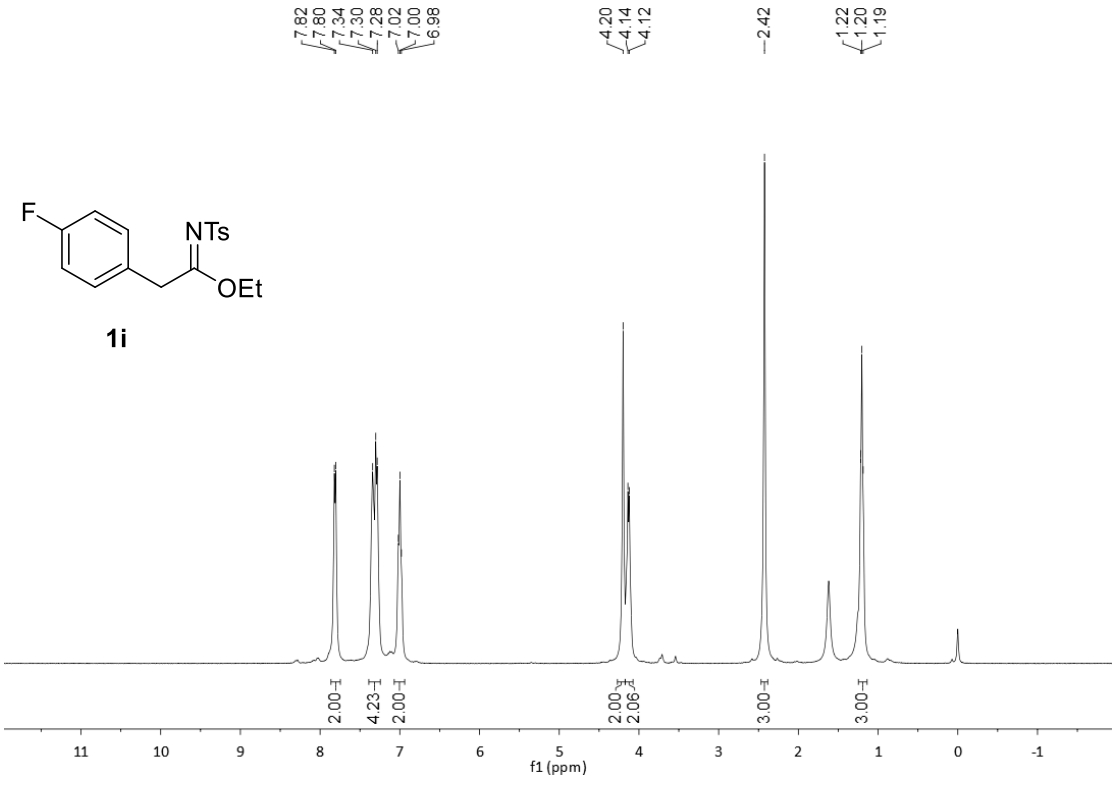

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



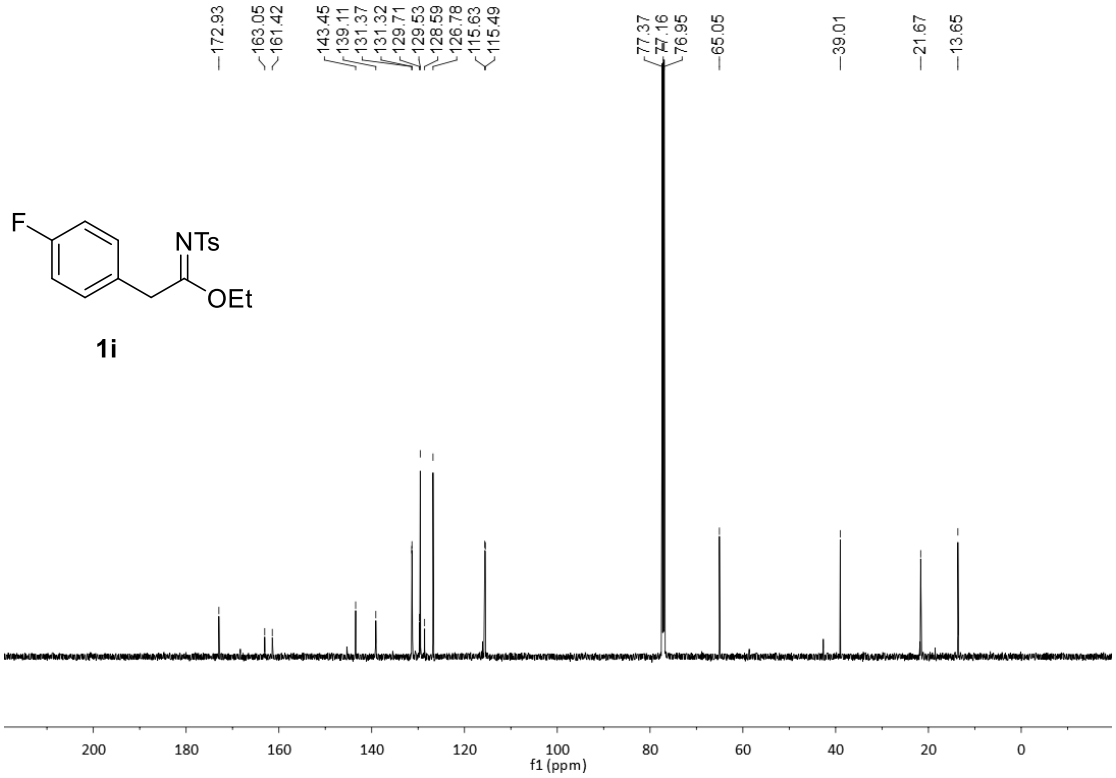
**$^{19}$F NMR (565 MHz, $CDCl_3$)**



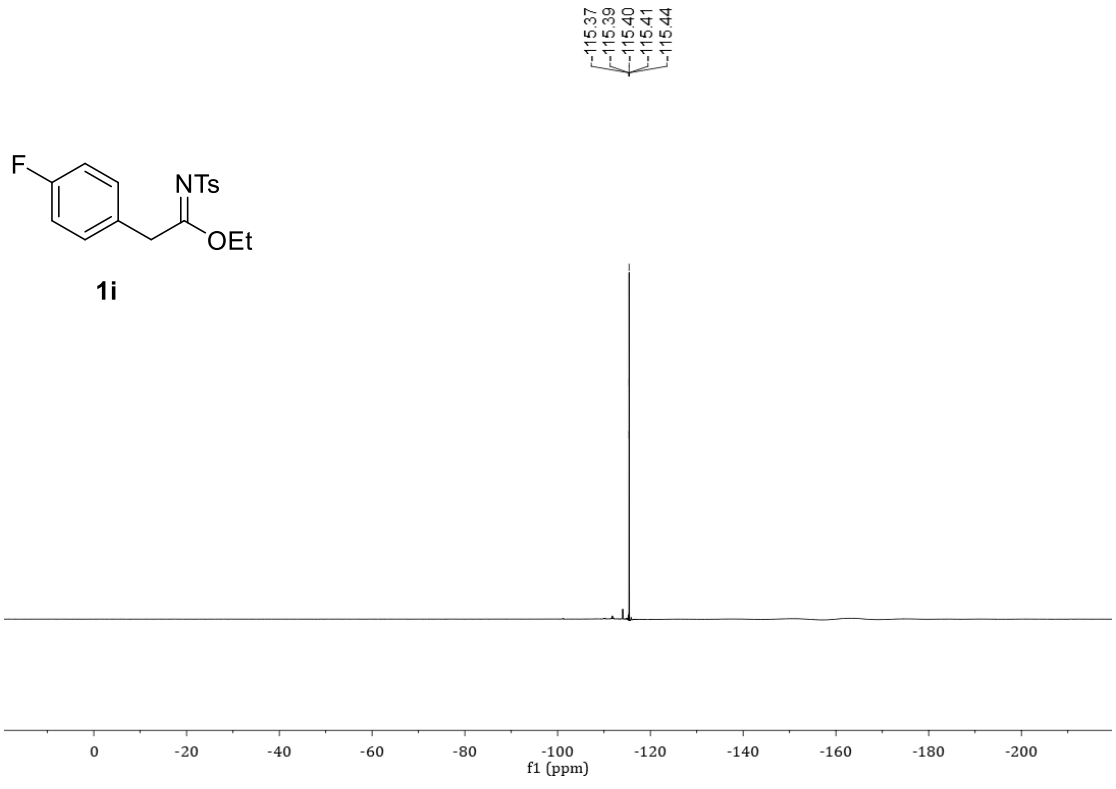

**$^{1}$H NMR (400 MHz, $CDCl_3$)**



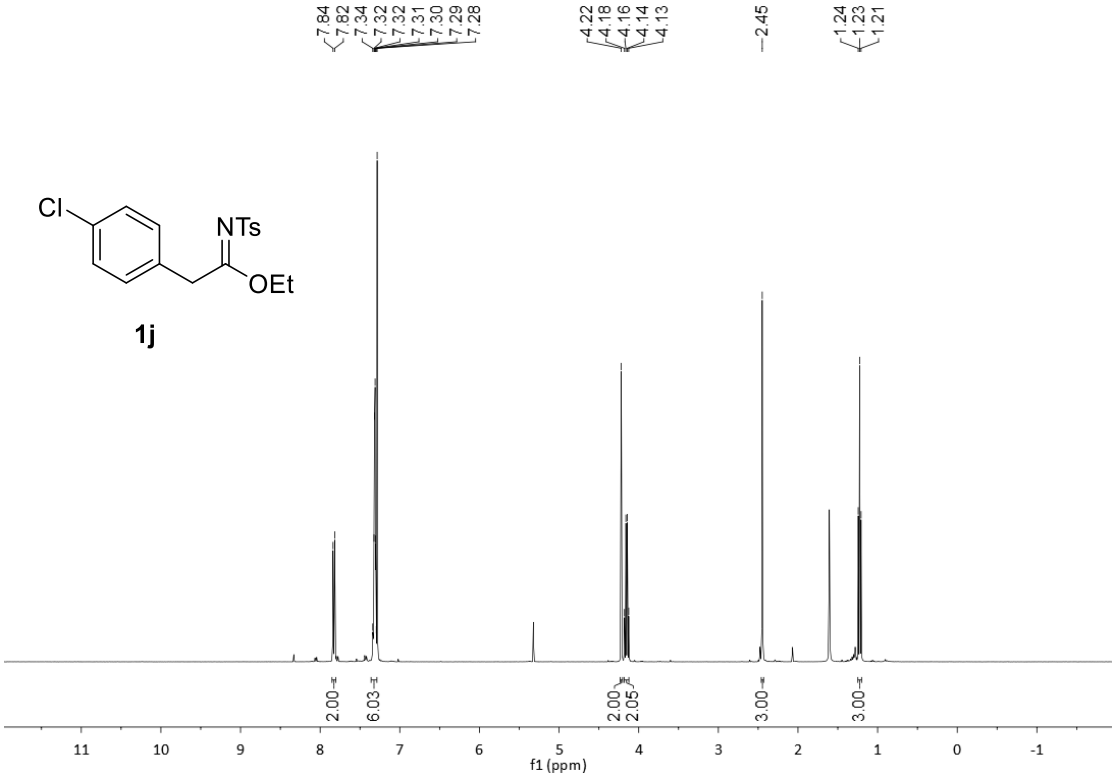
**$^{13}$C NMR (150 MHz, $CDCl_3$)**



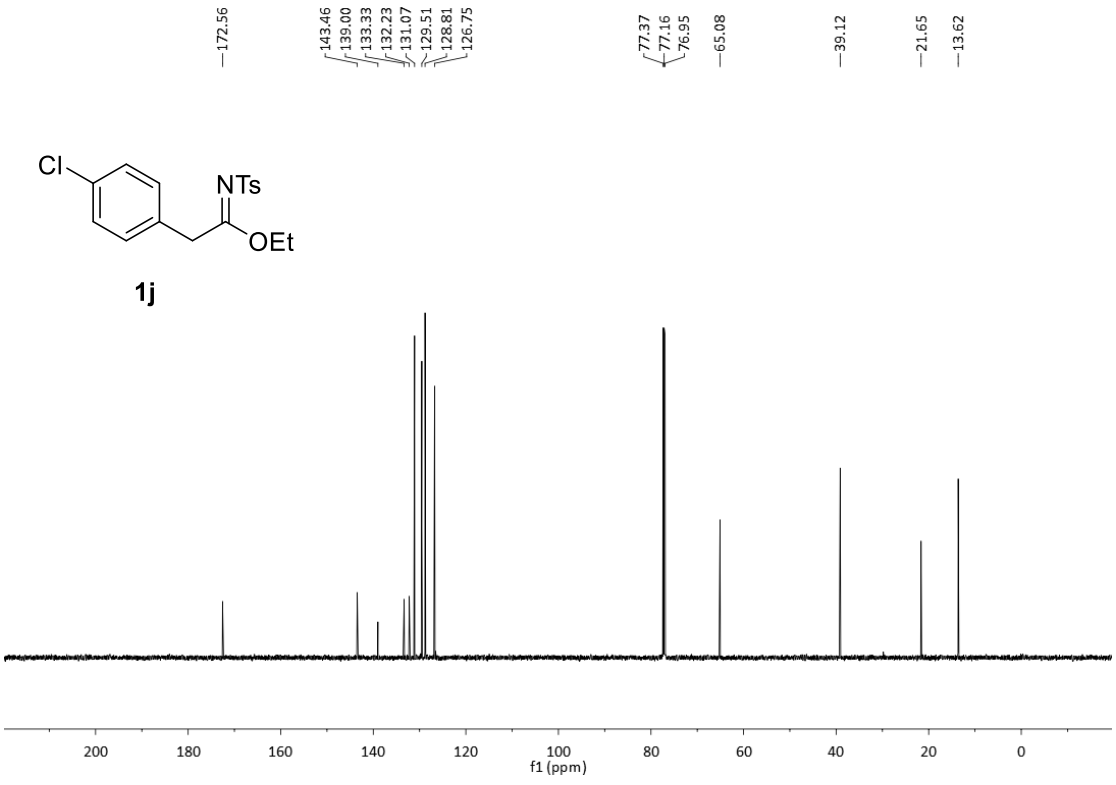

**$^{19}$F NMR (565 MHz, $CDCl_3$)**



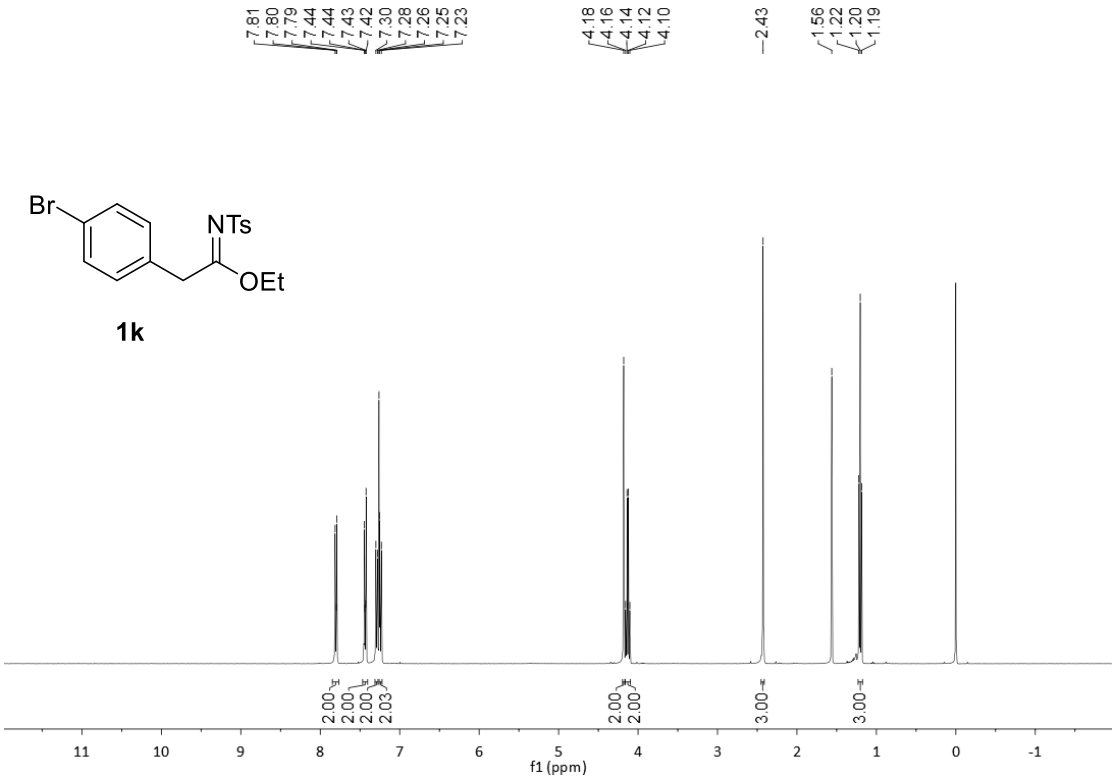
**$^{1}$H NMR (400 MHz, $CDCl_3$)**




**$^{13}$C NMR (150 MHz, $CDCl_3$)**



## $^{1}$H NMR (400 MHz, $CDCl_3$)

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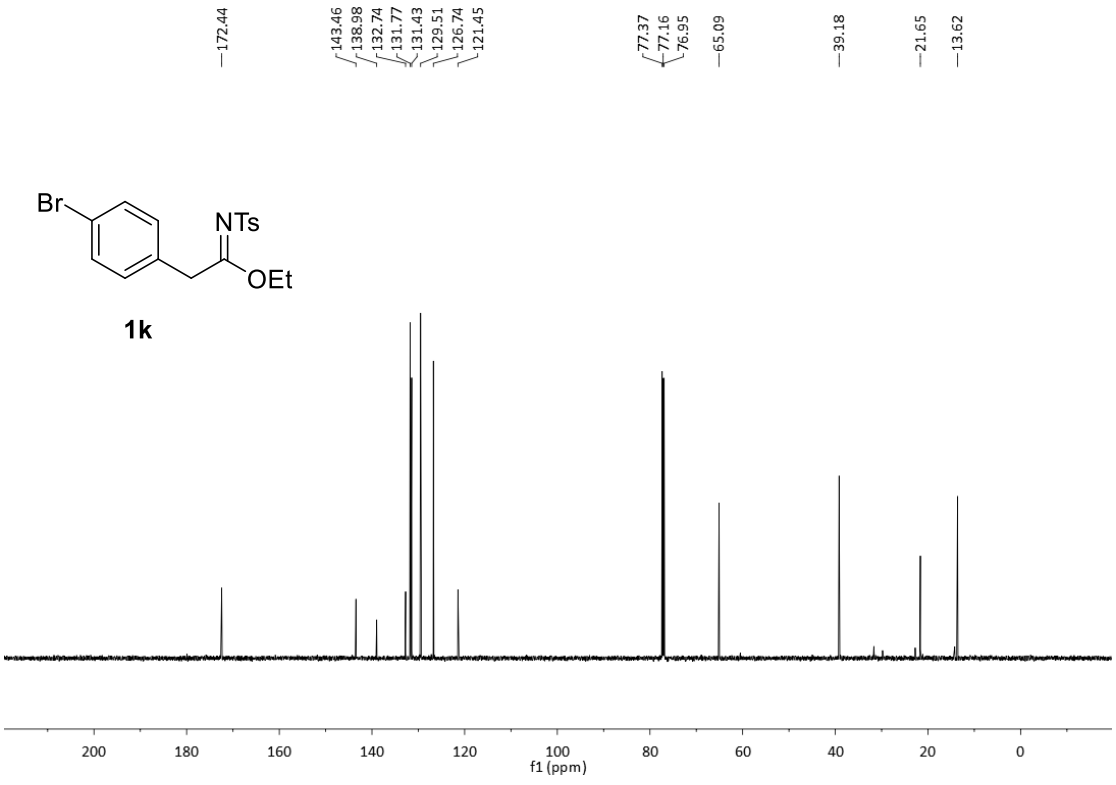

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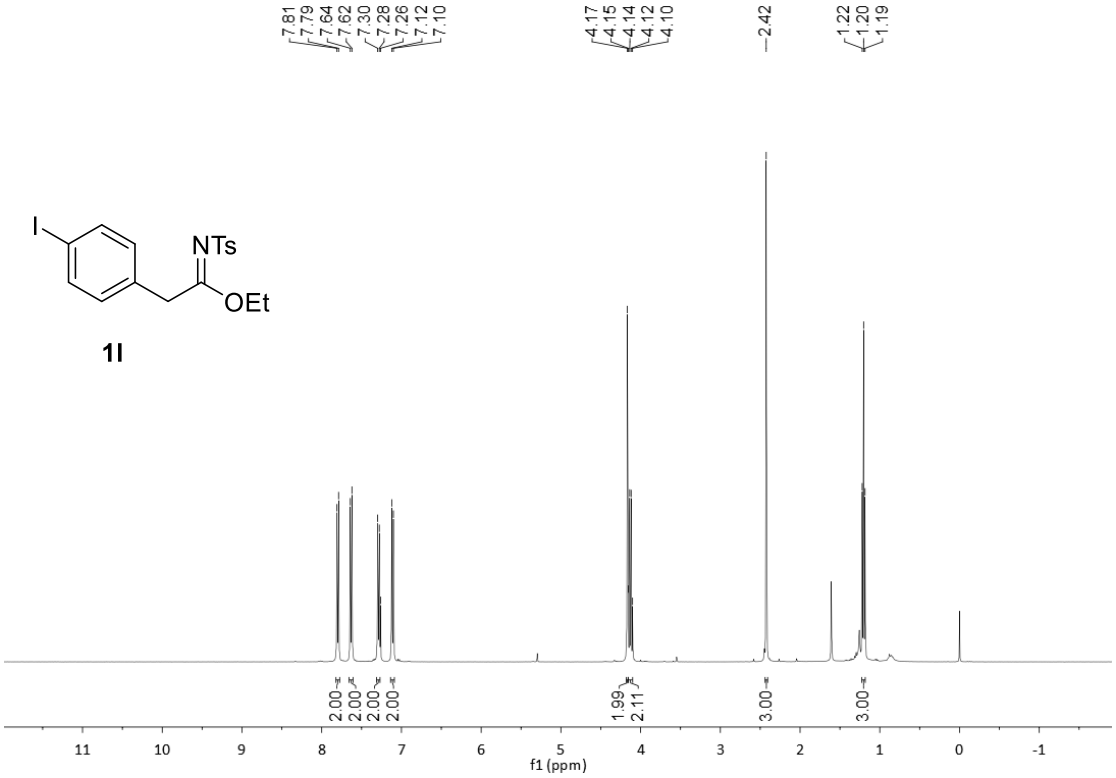
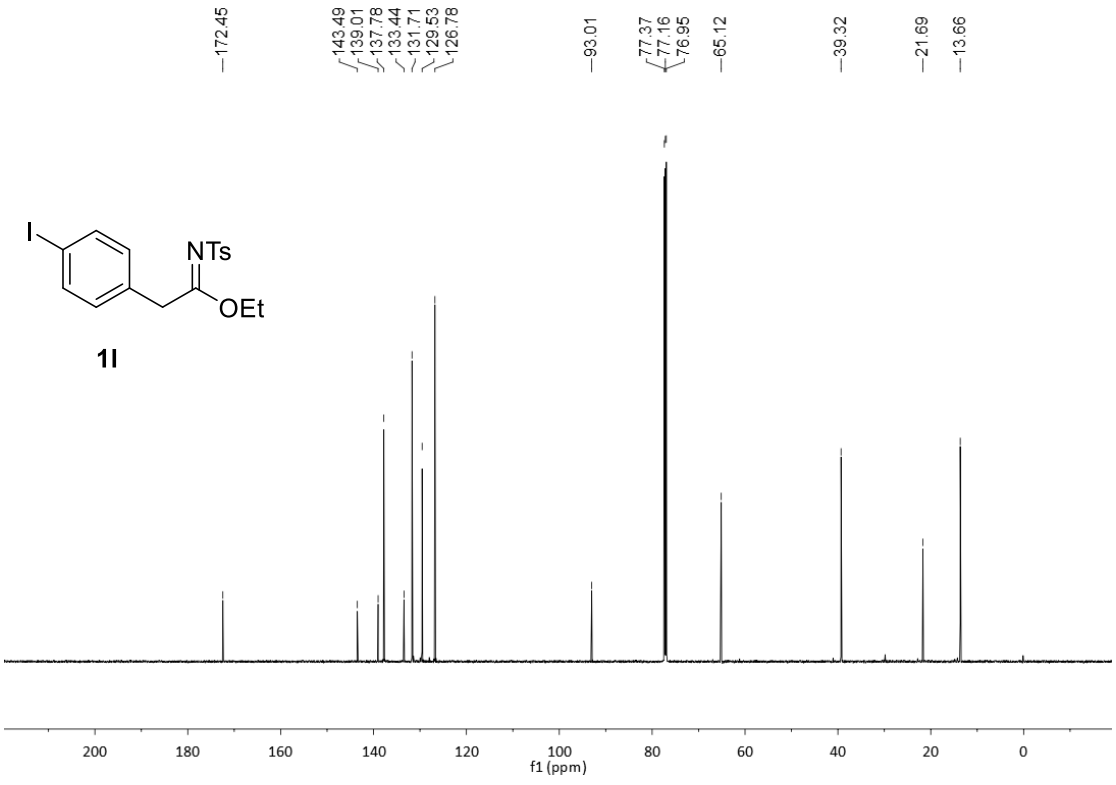
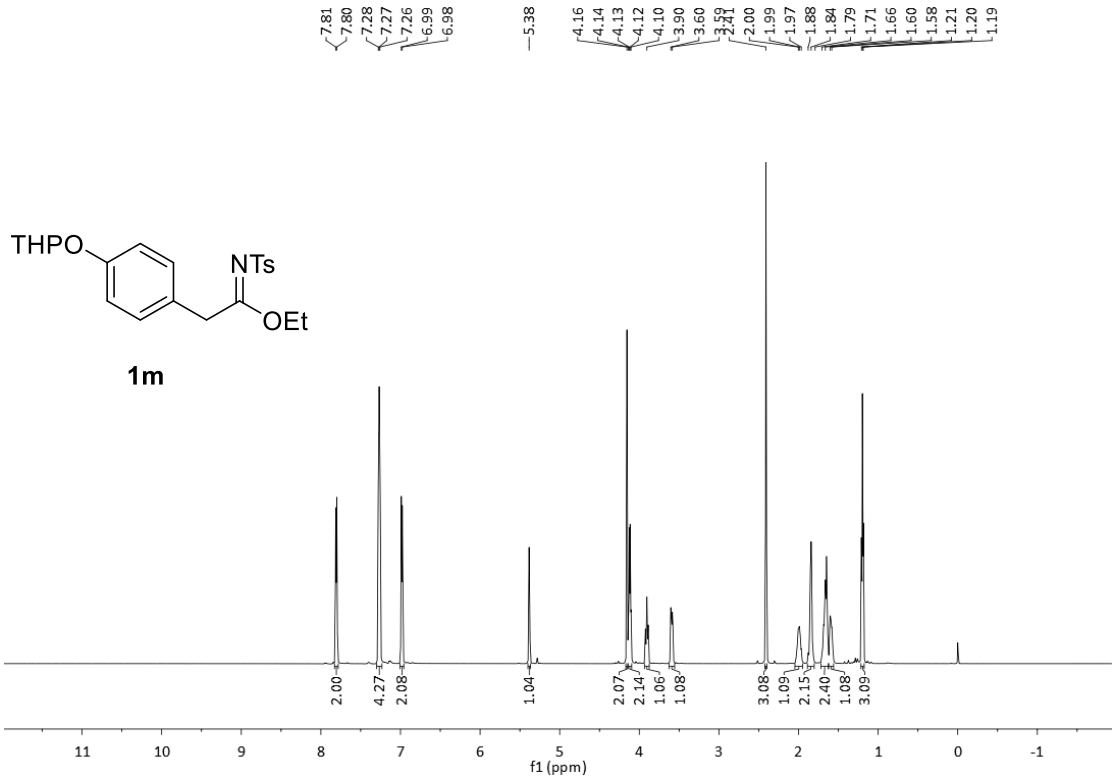


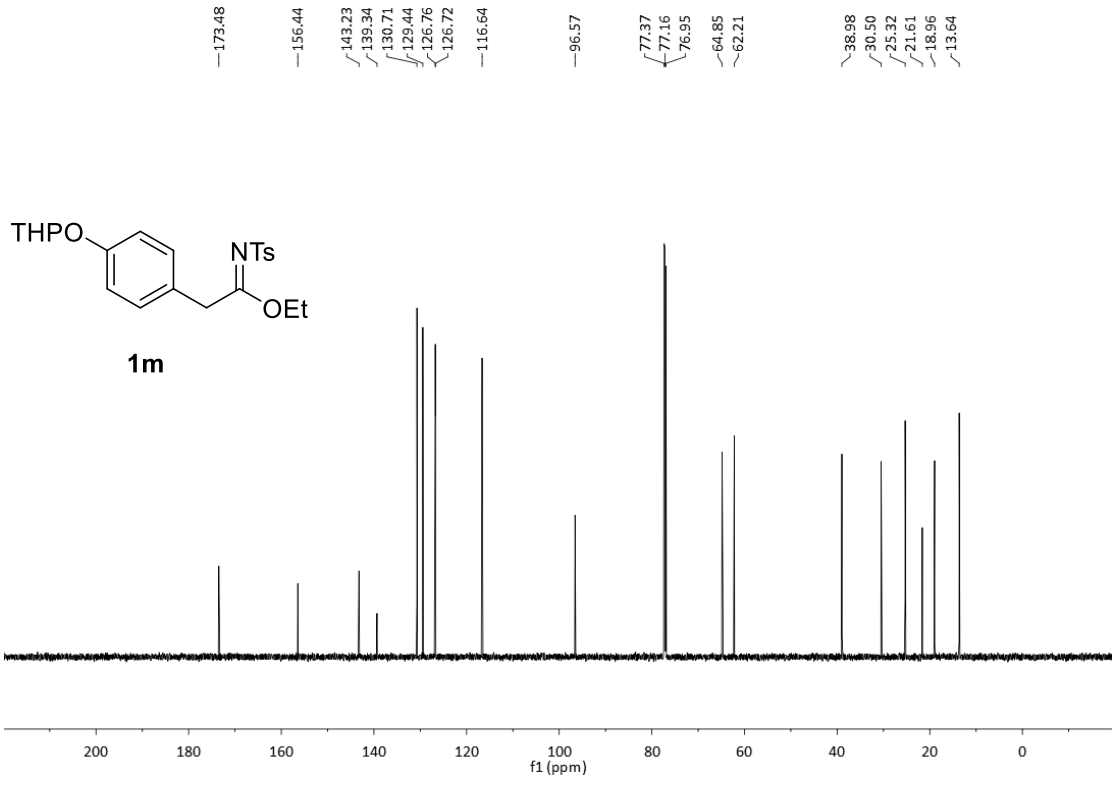

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



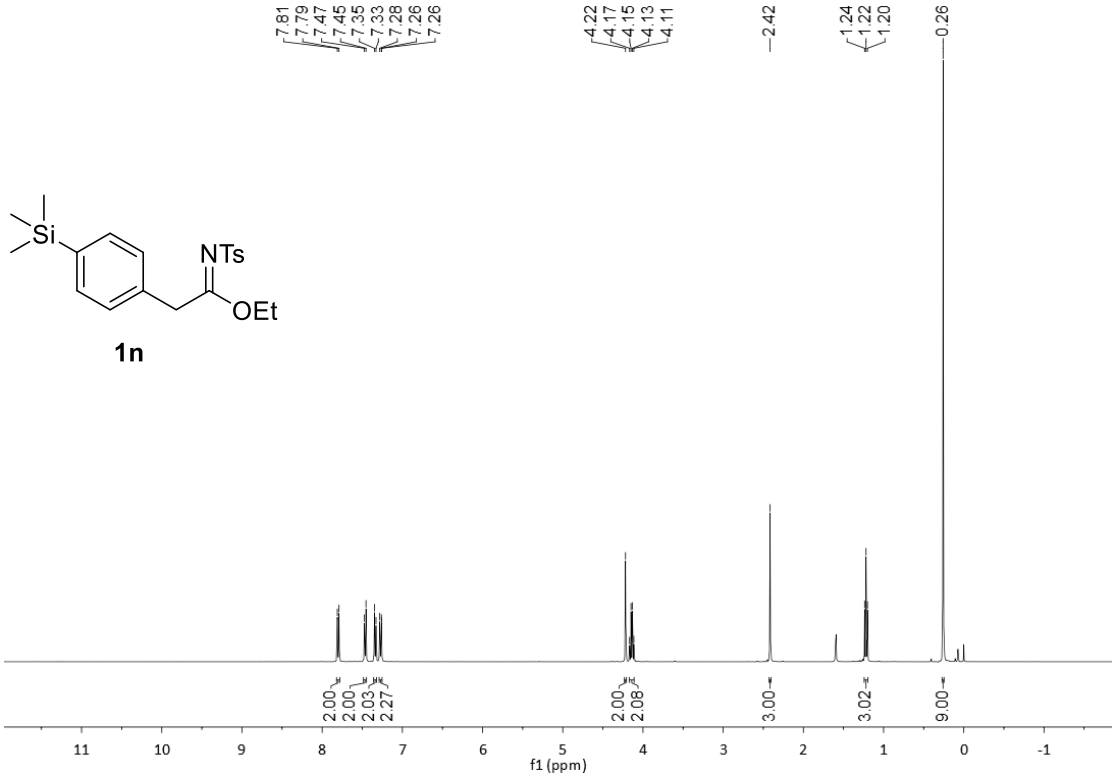
**$^{1}$H NMR (600 MHz, $CDCl_3$)**




**$^{13}$C NMR (150 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**

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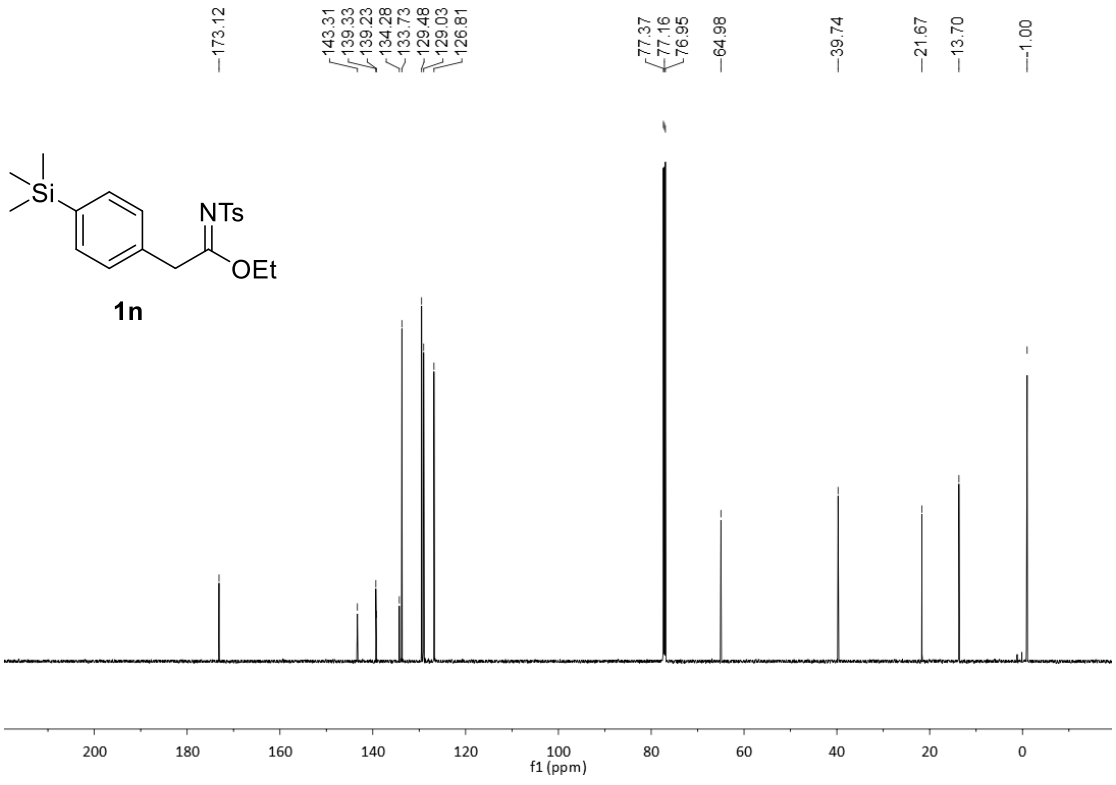

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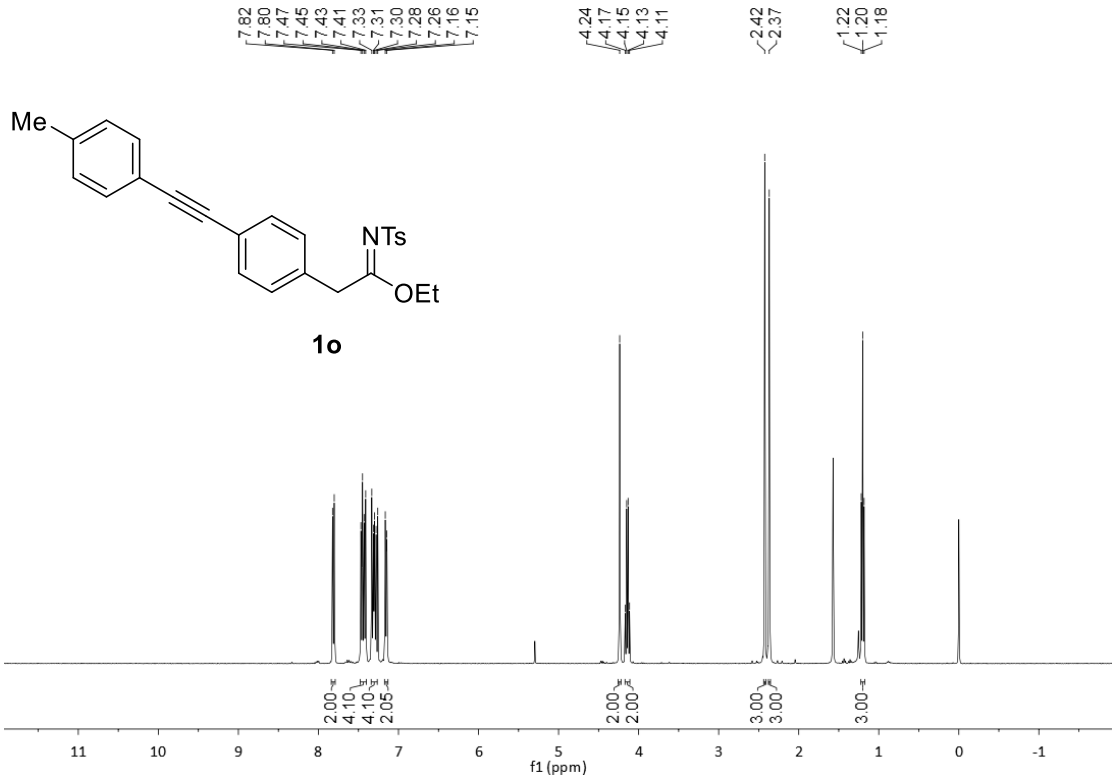


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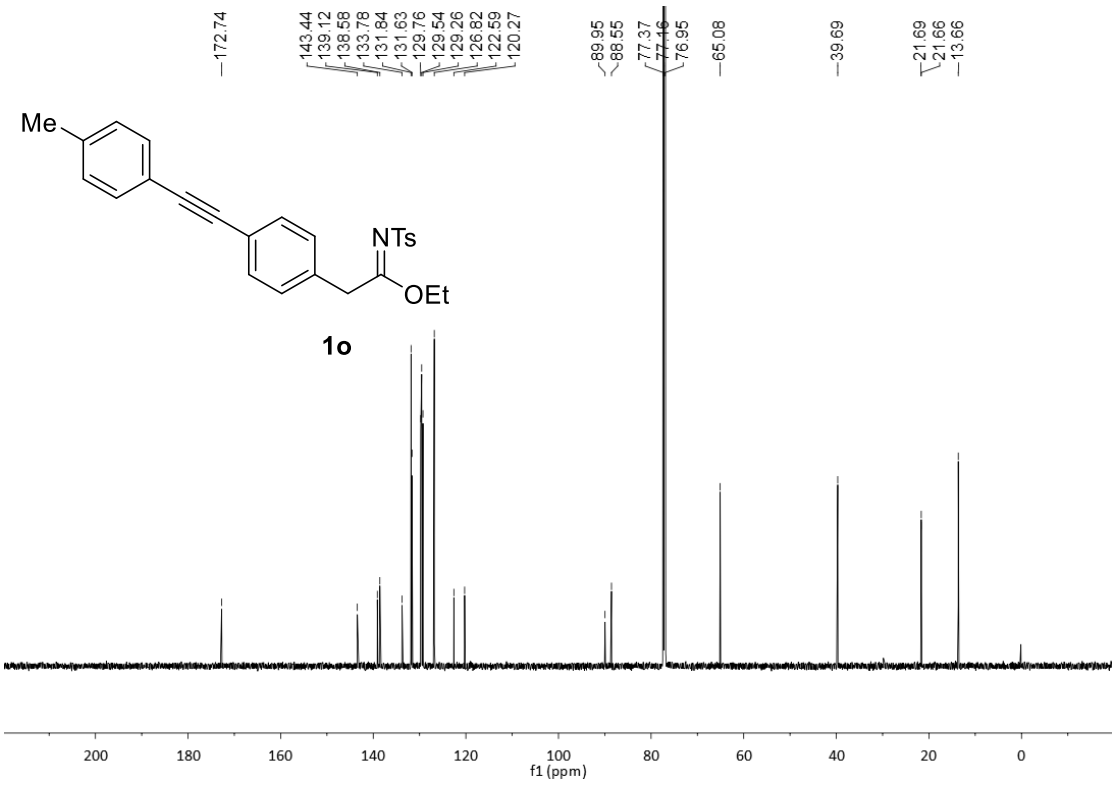

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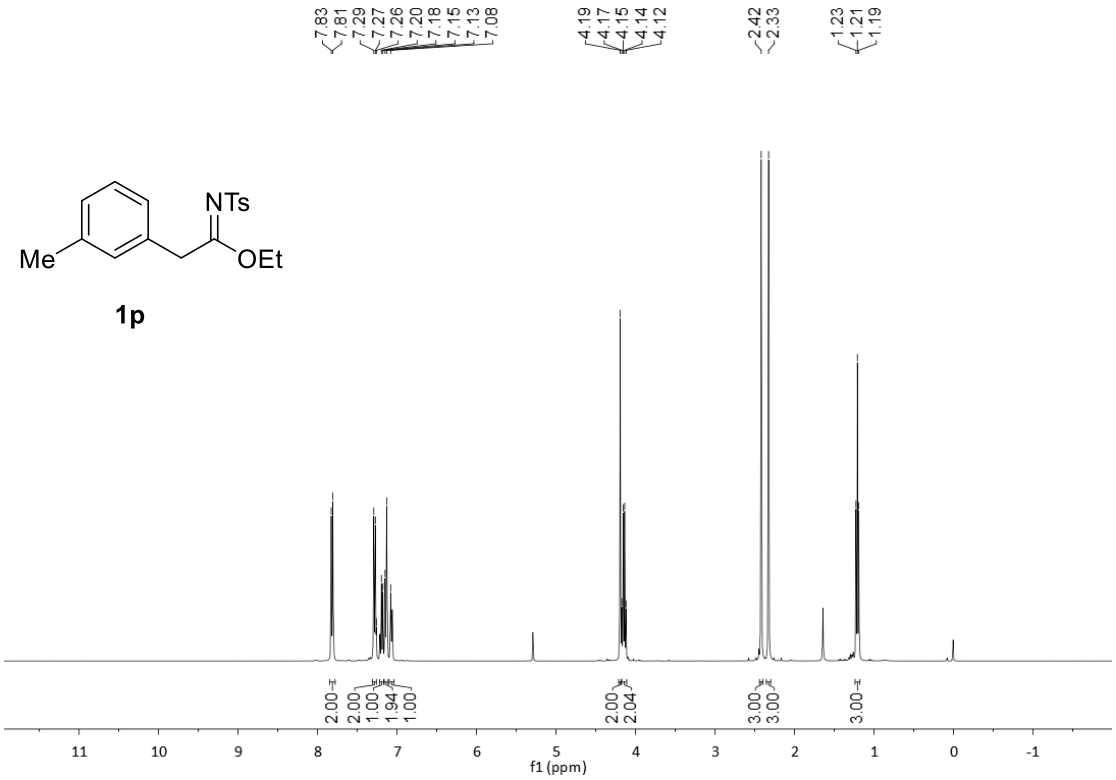


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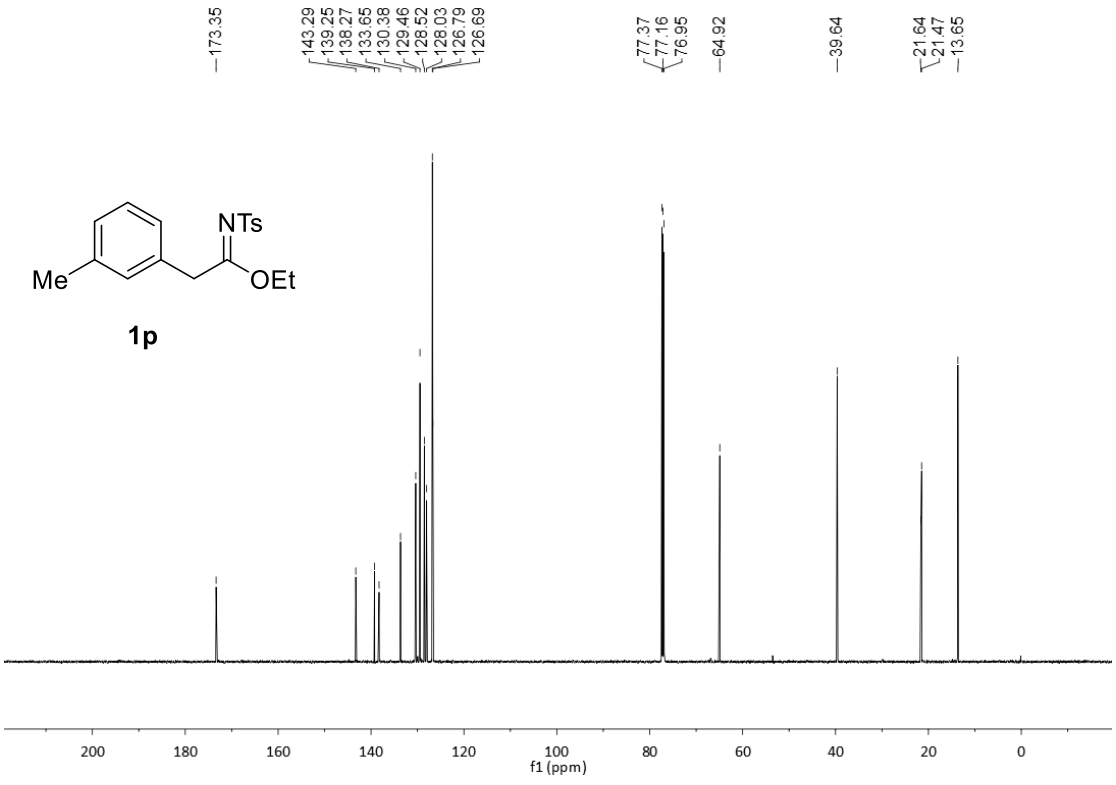

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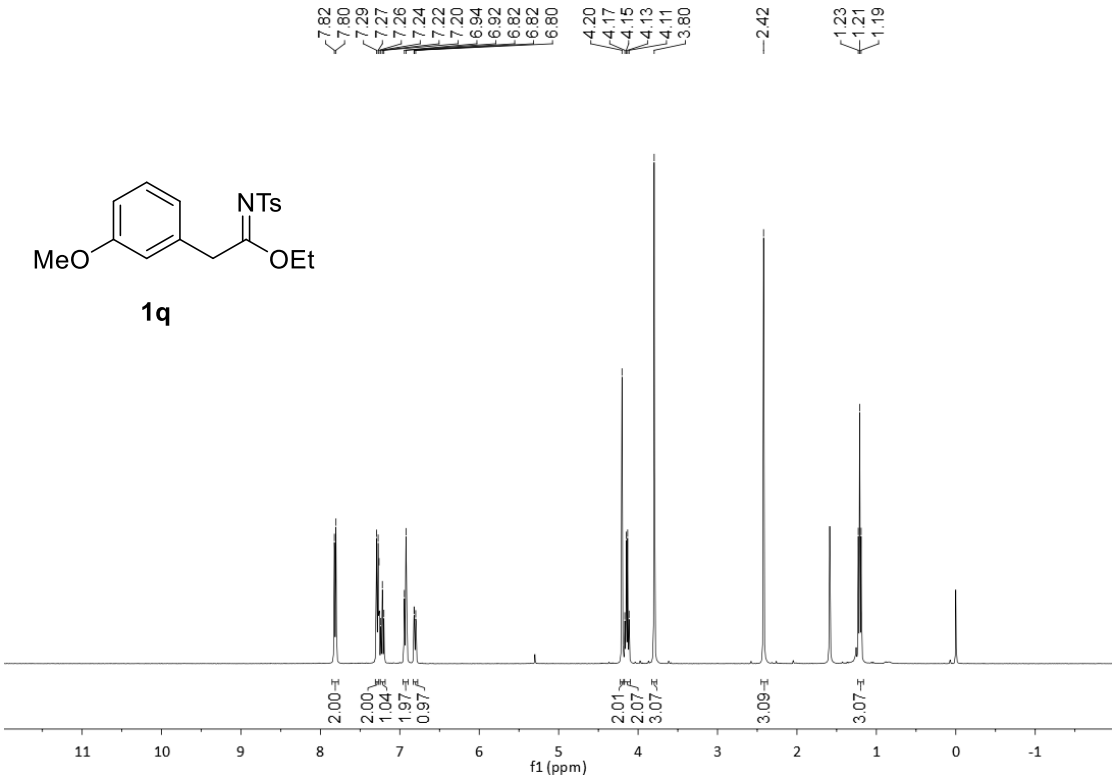


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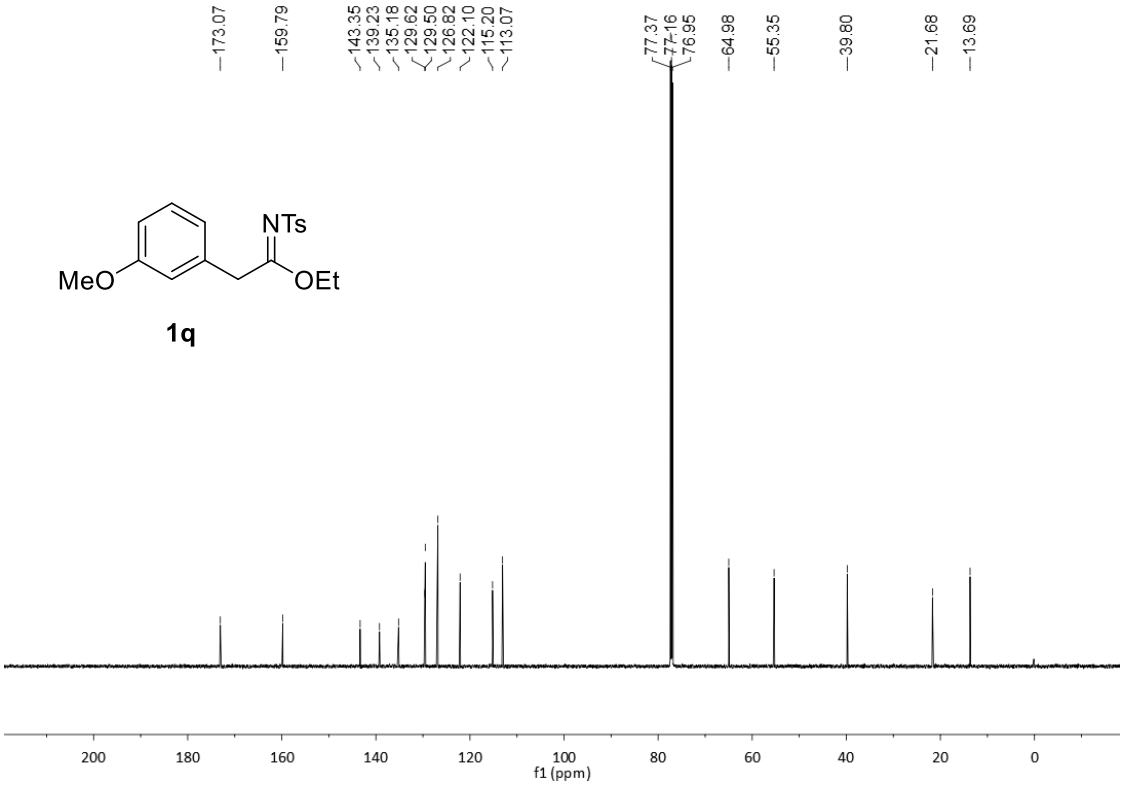

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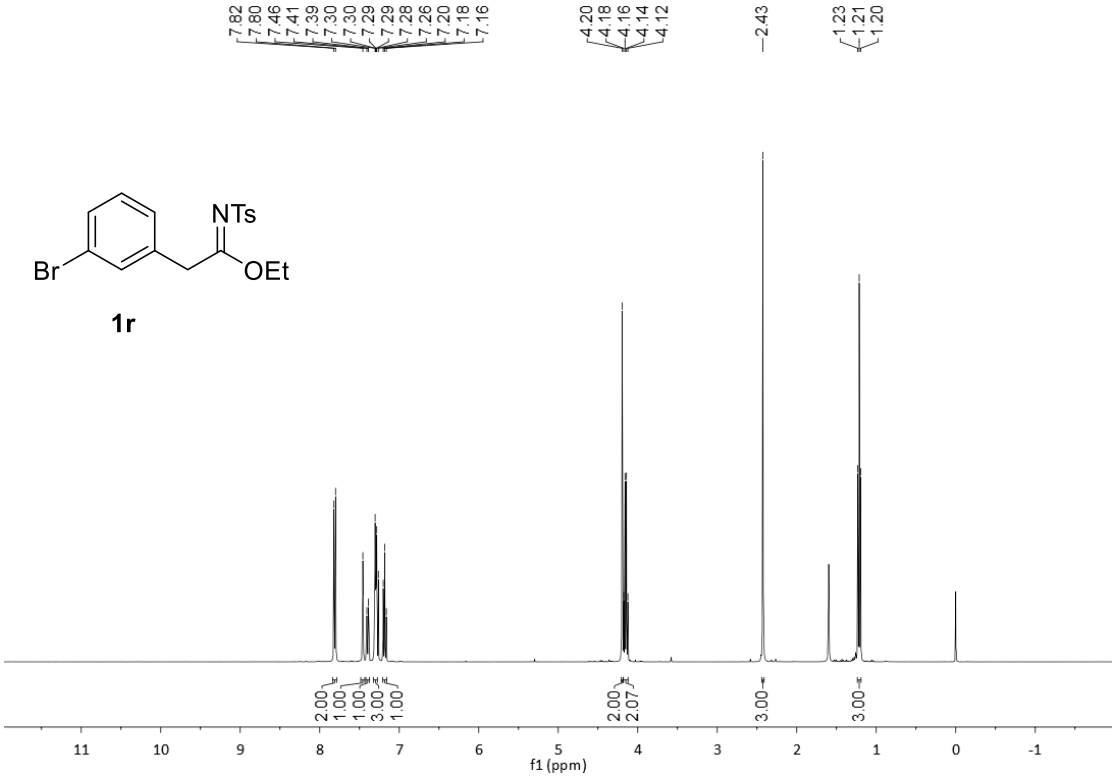


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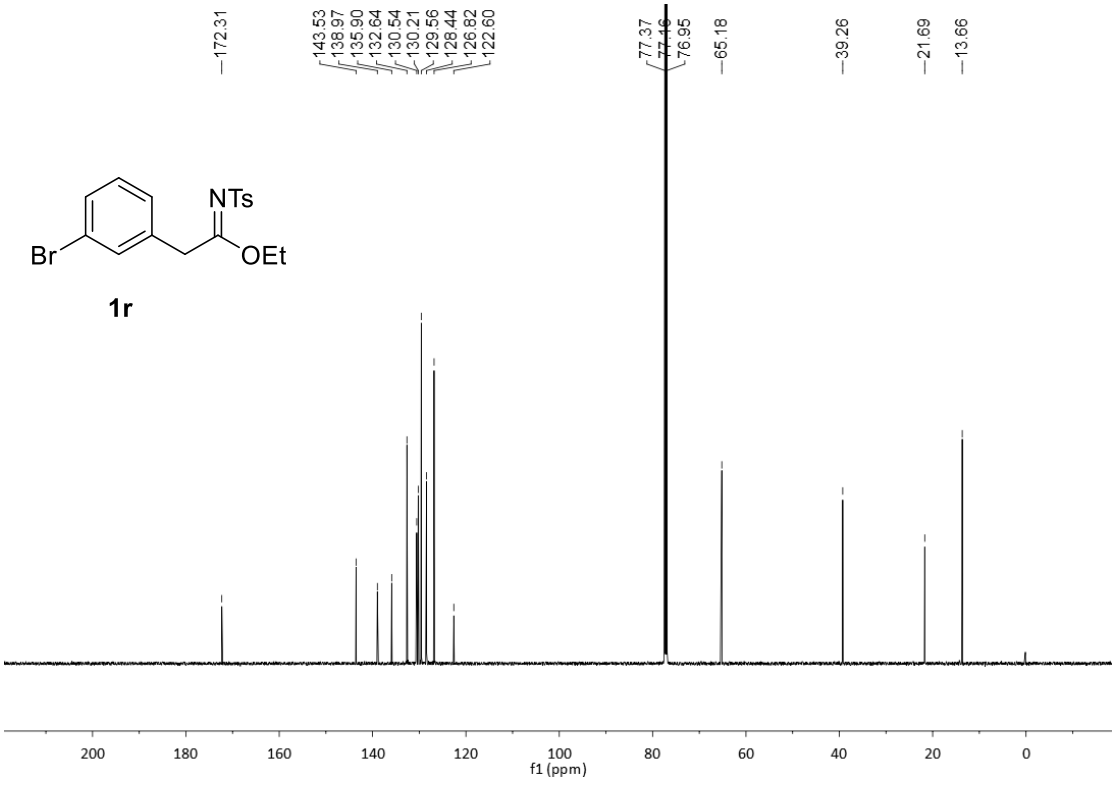

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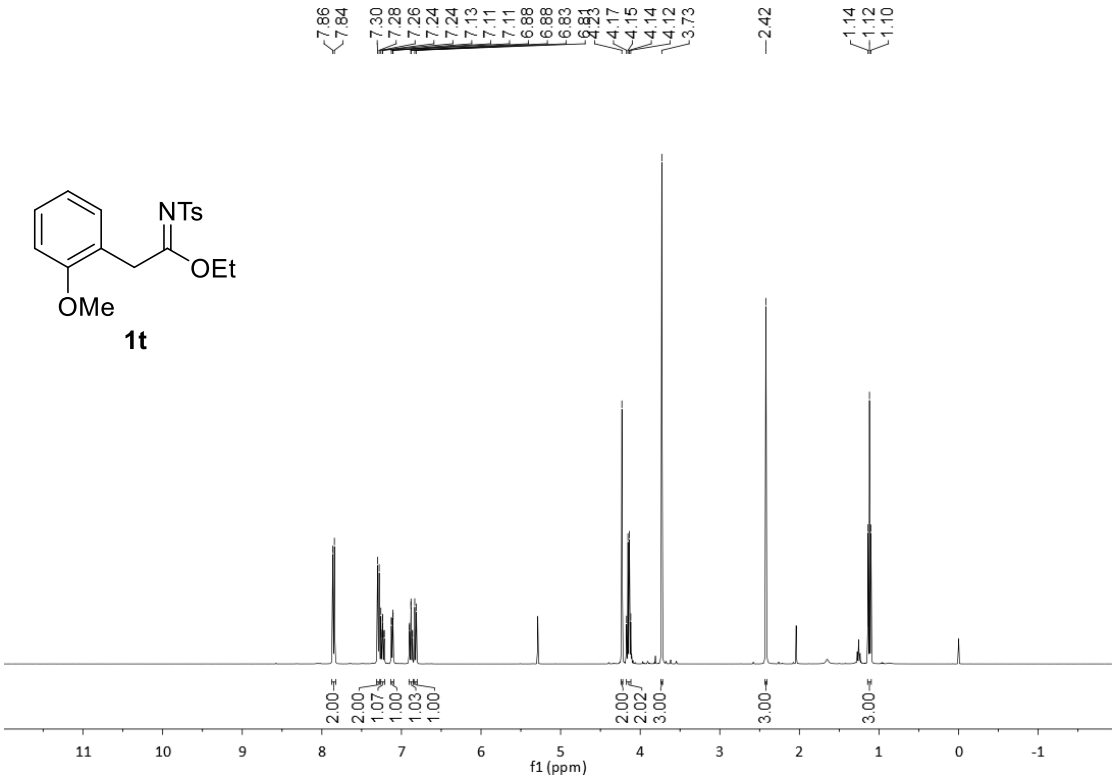


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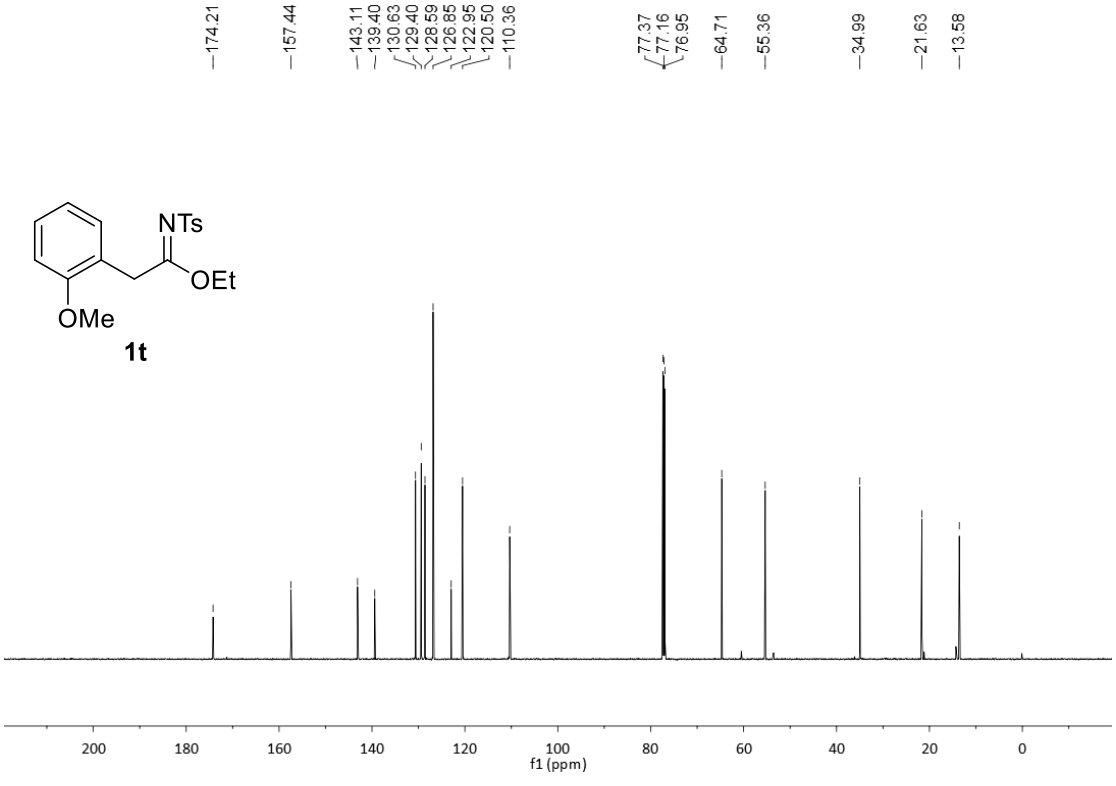

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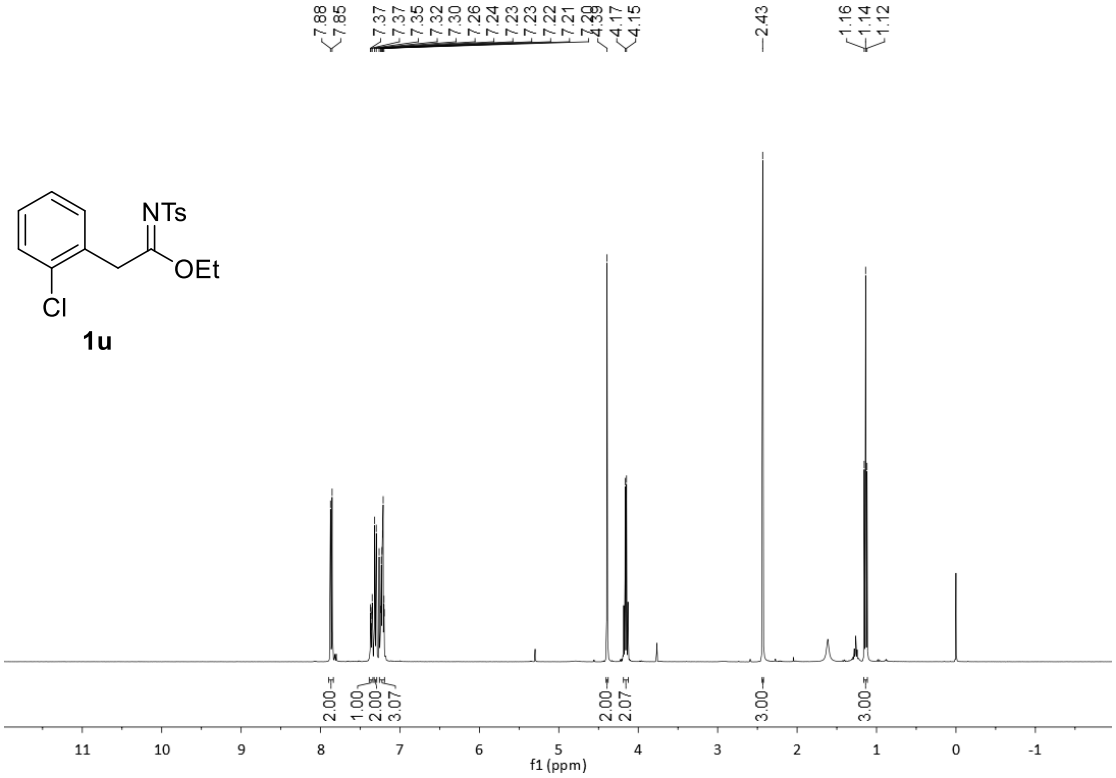


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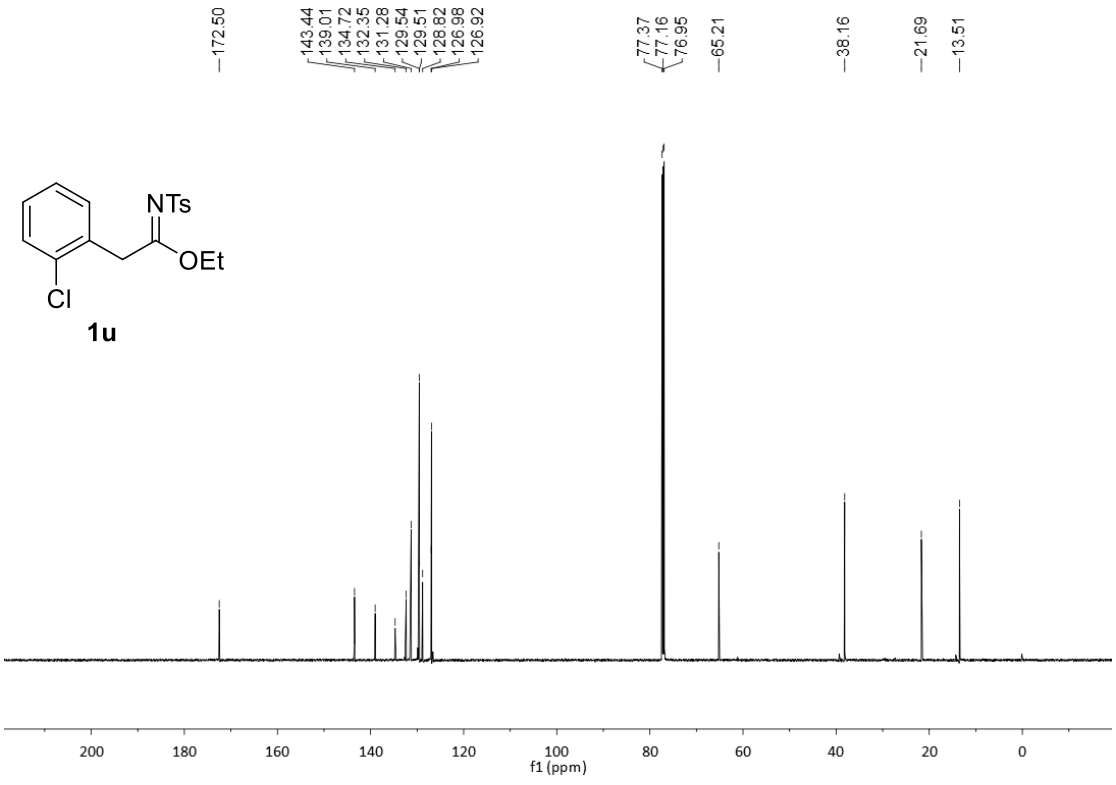

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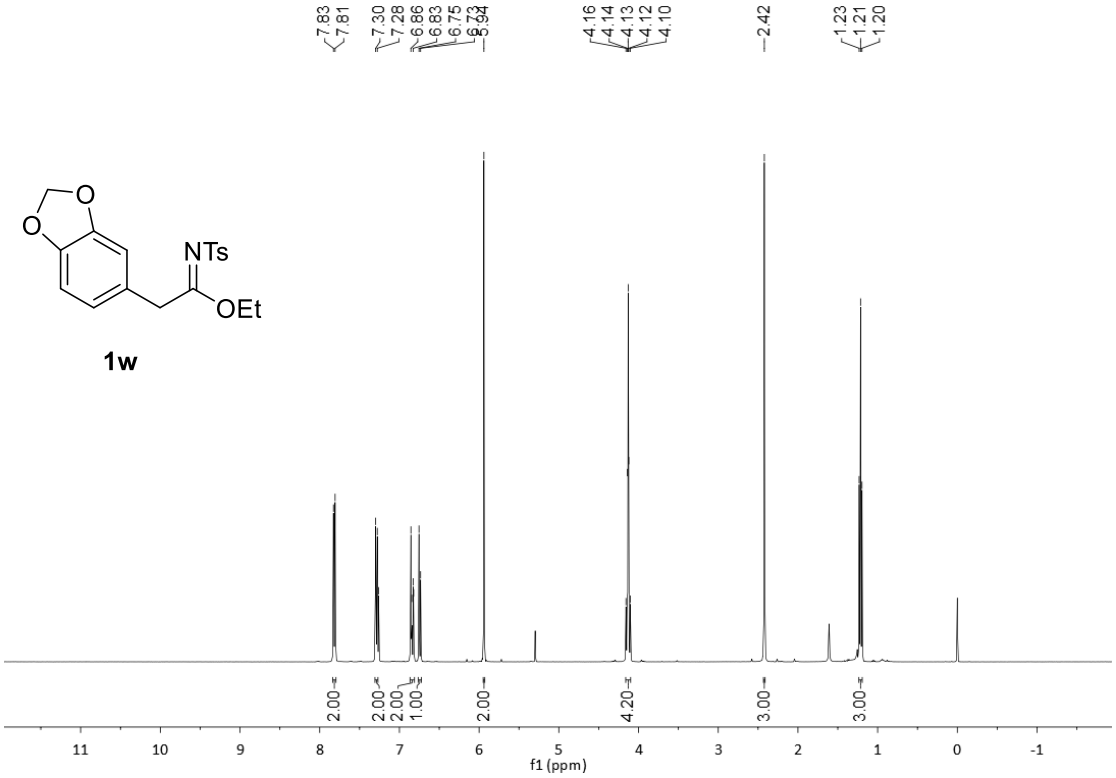


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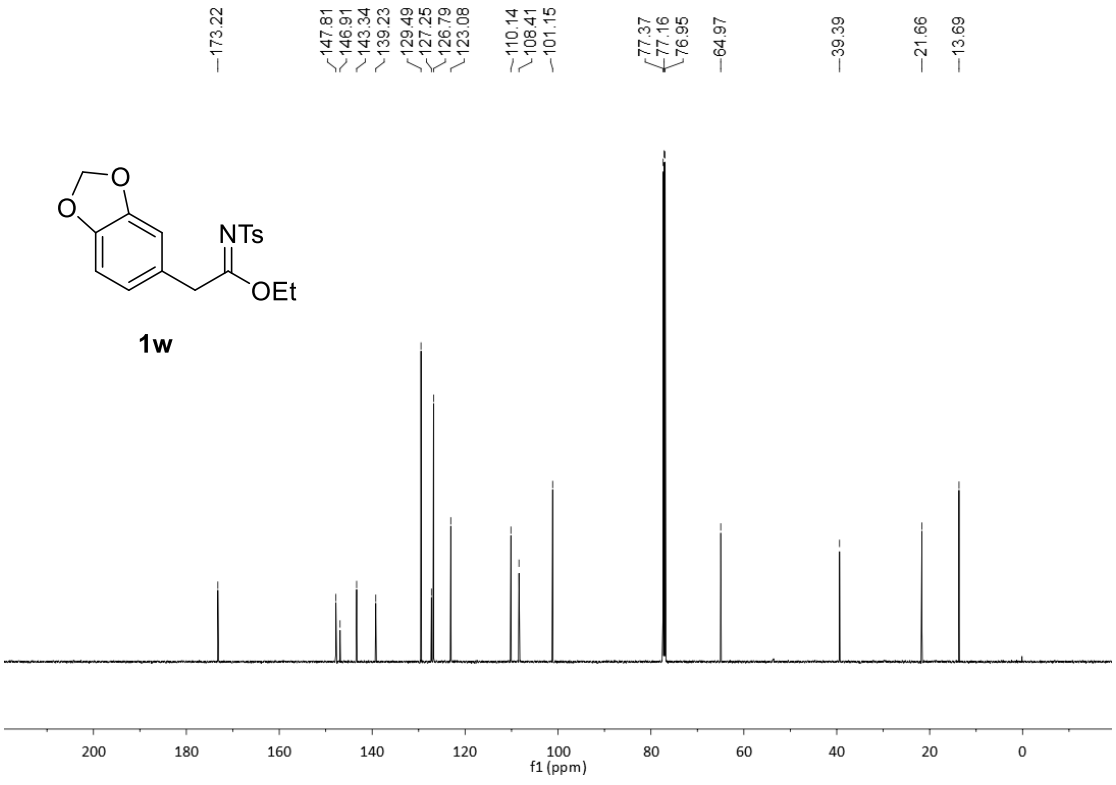

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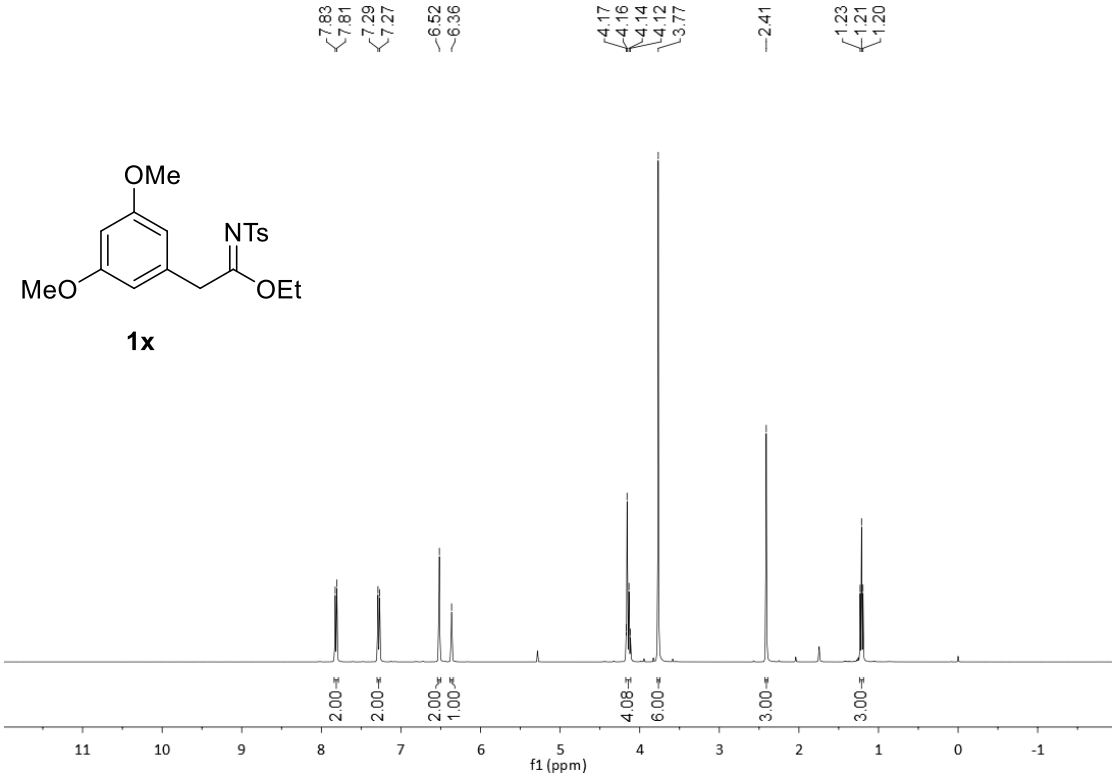


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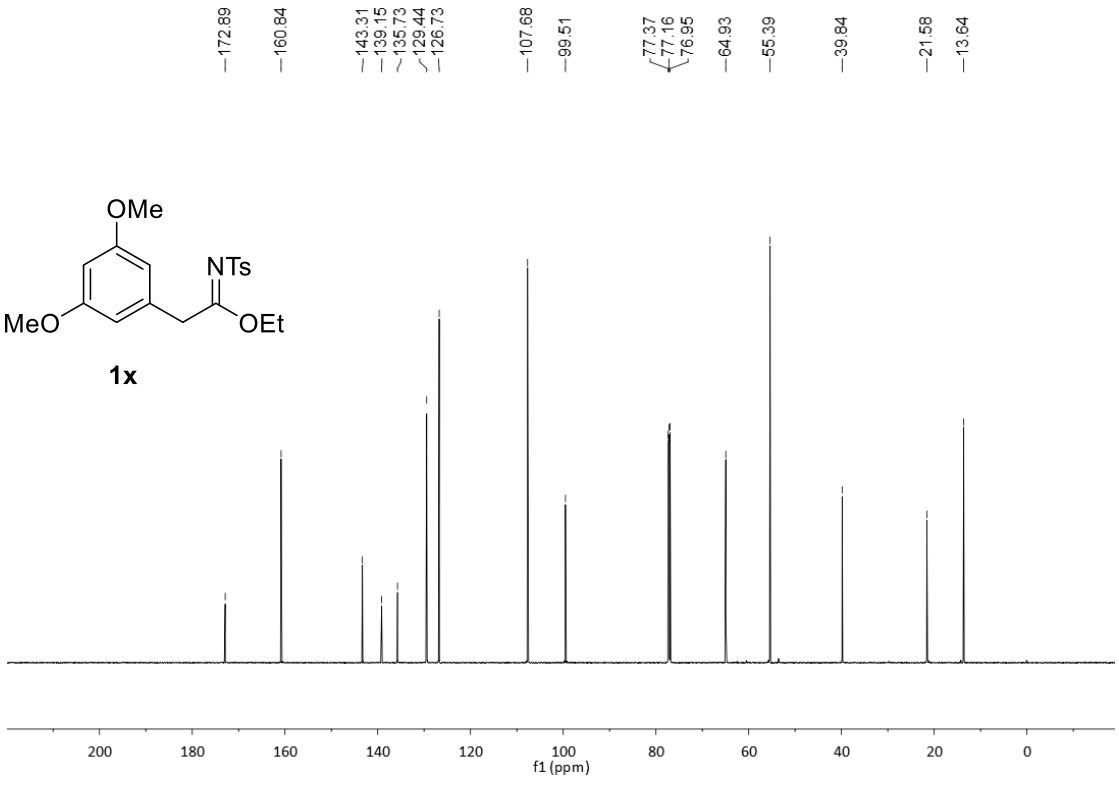

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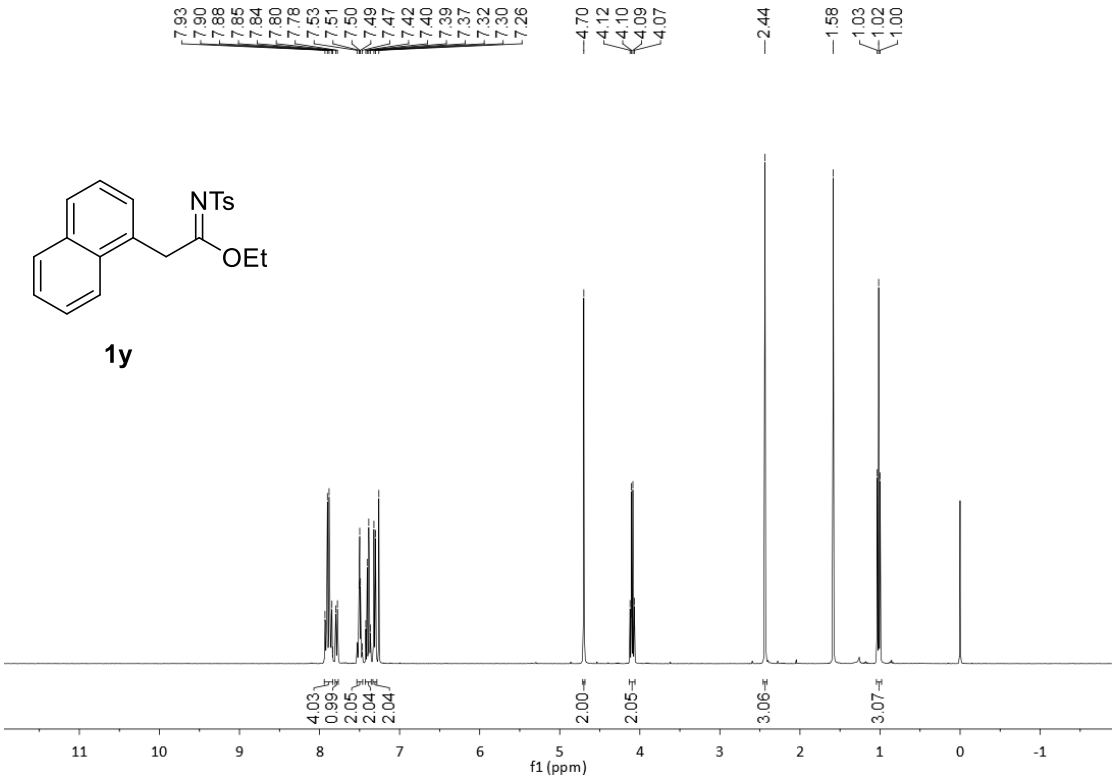


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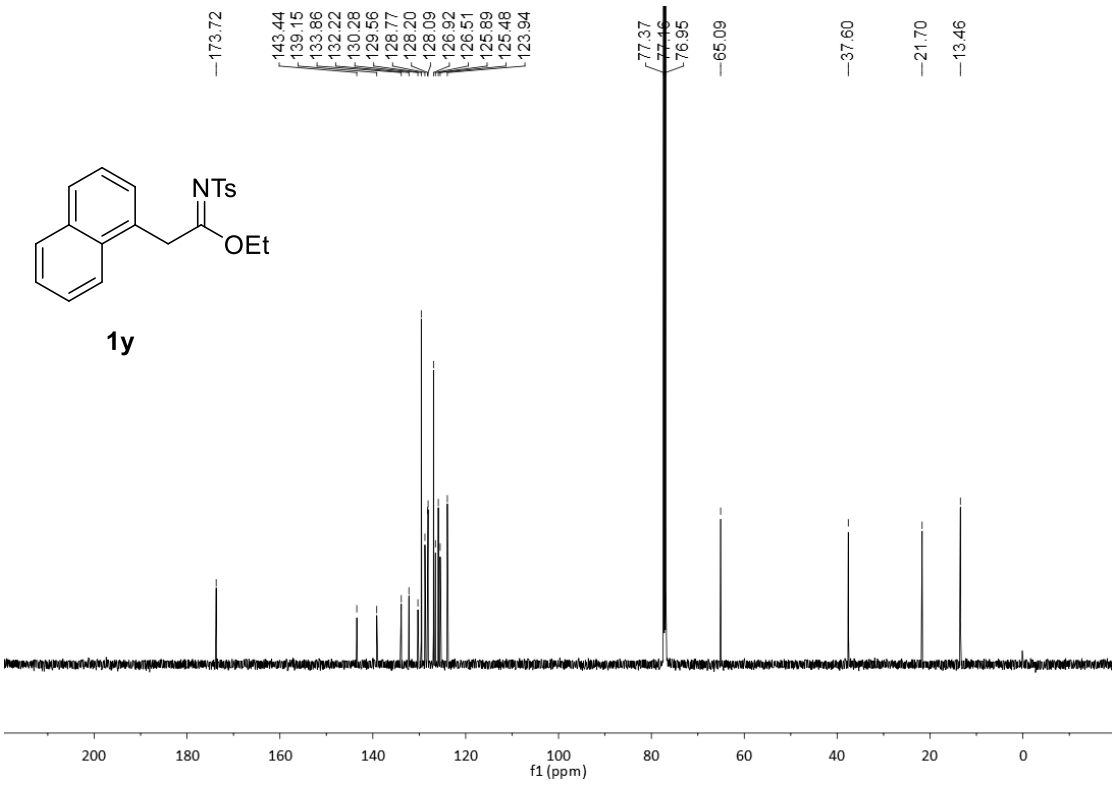
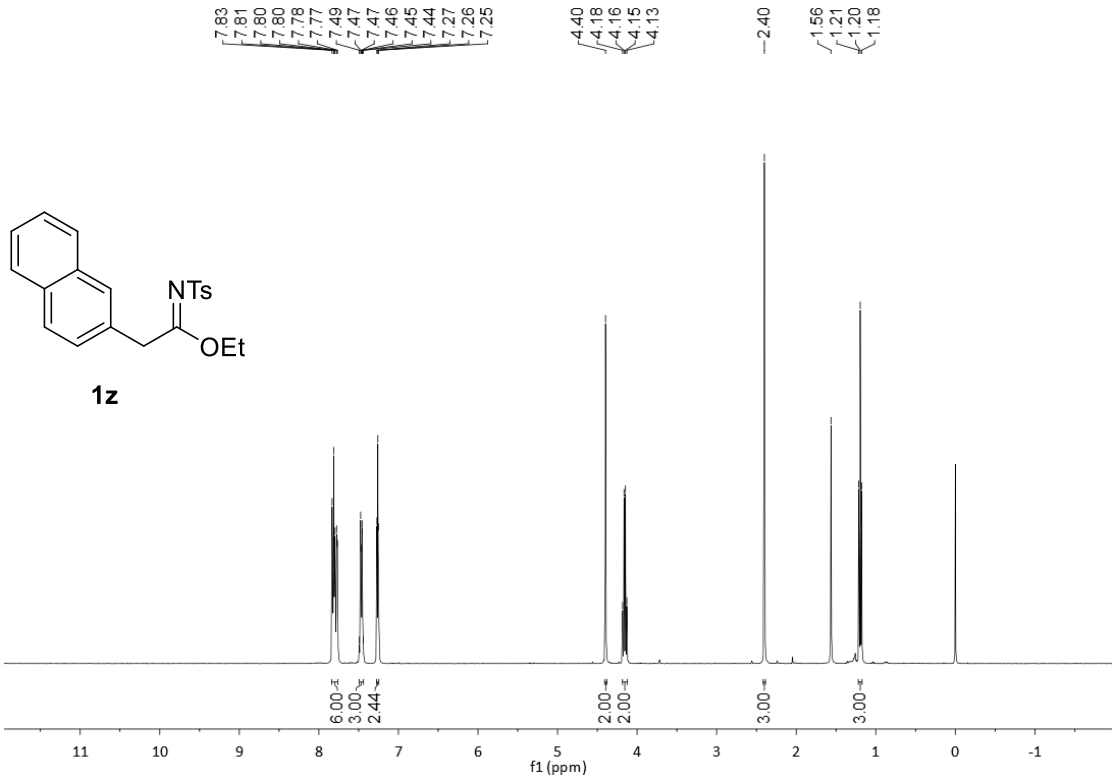
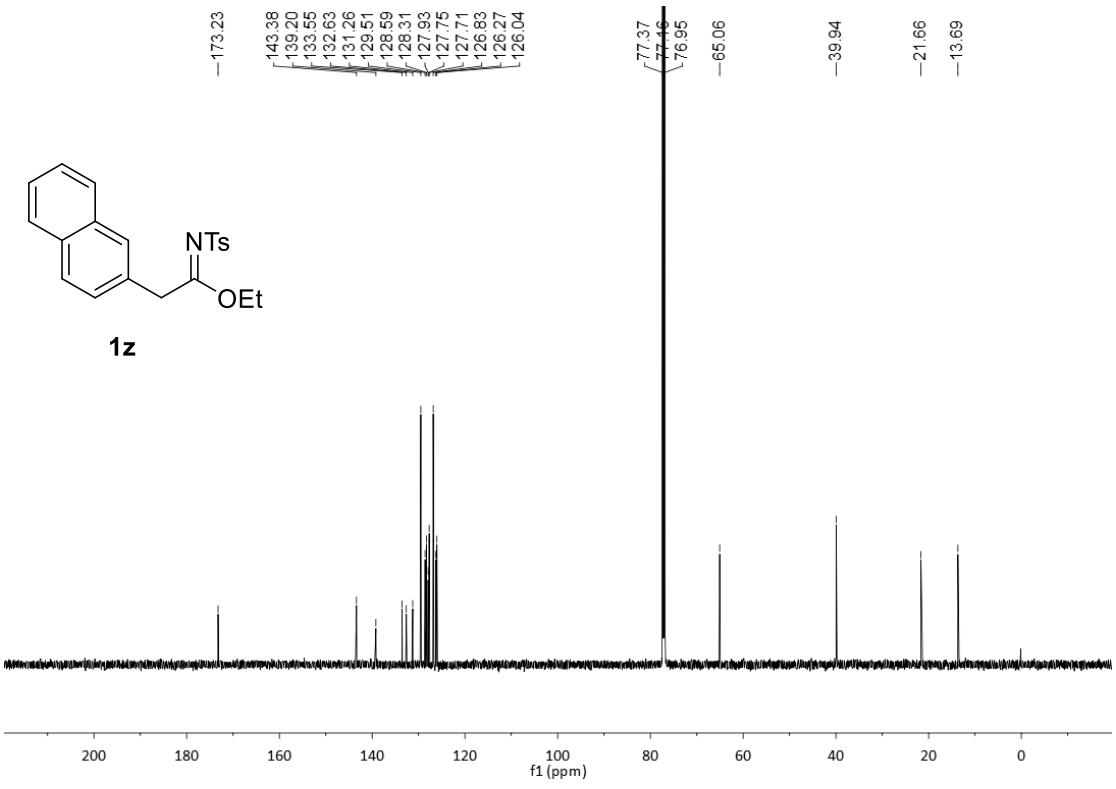


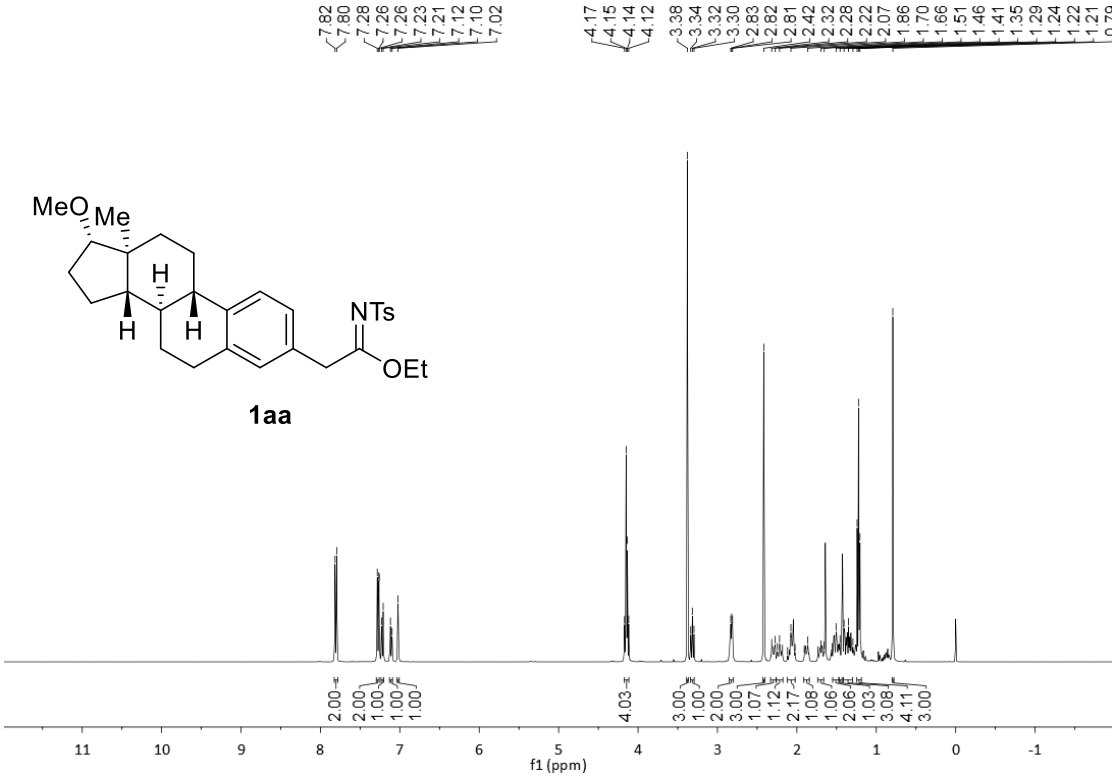
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



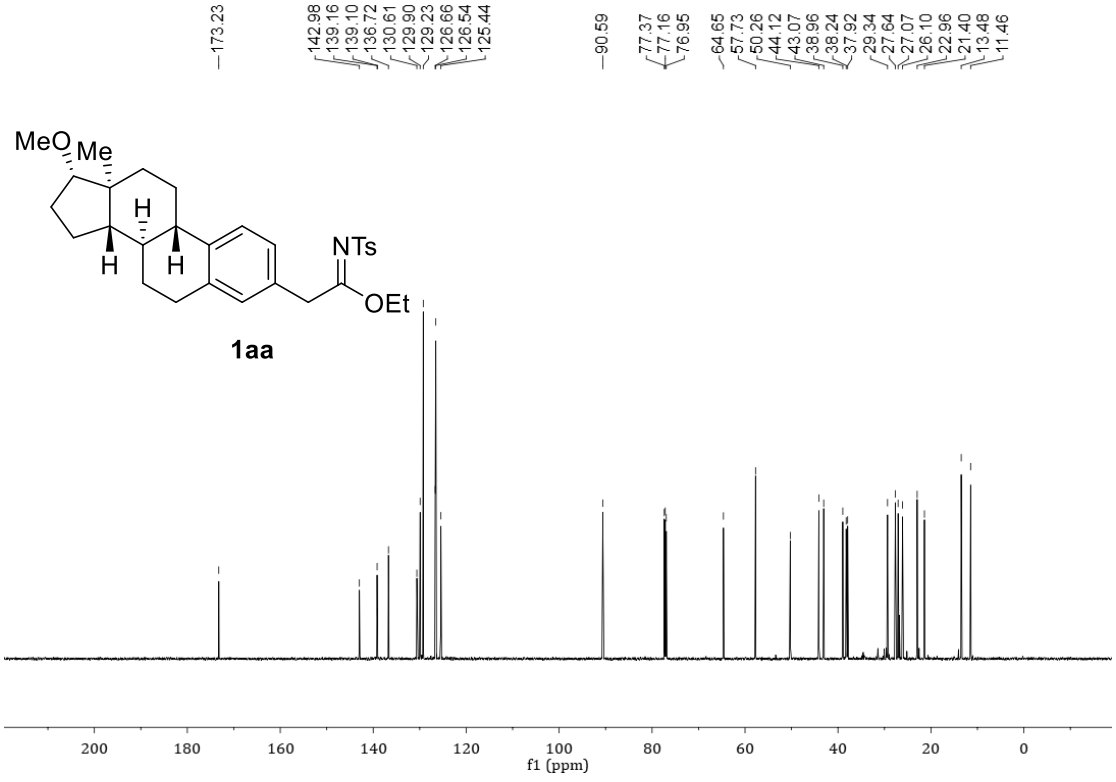

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



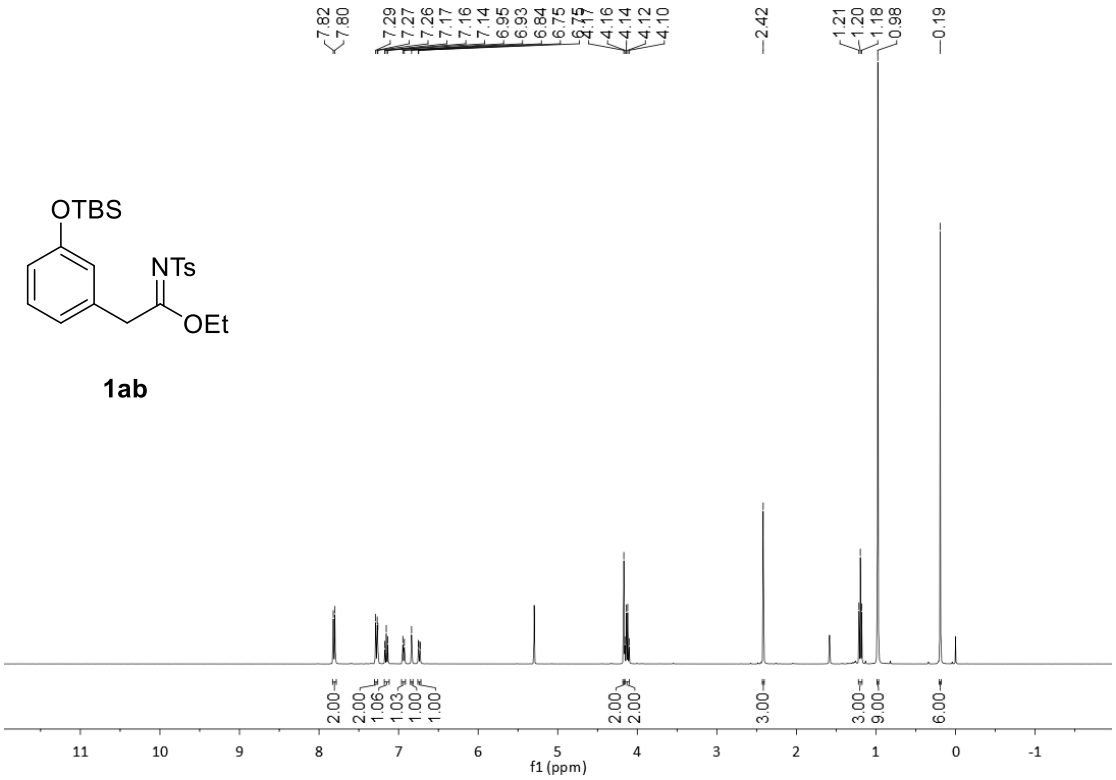
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



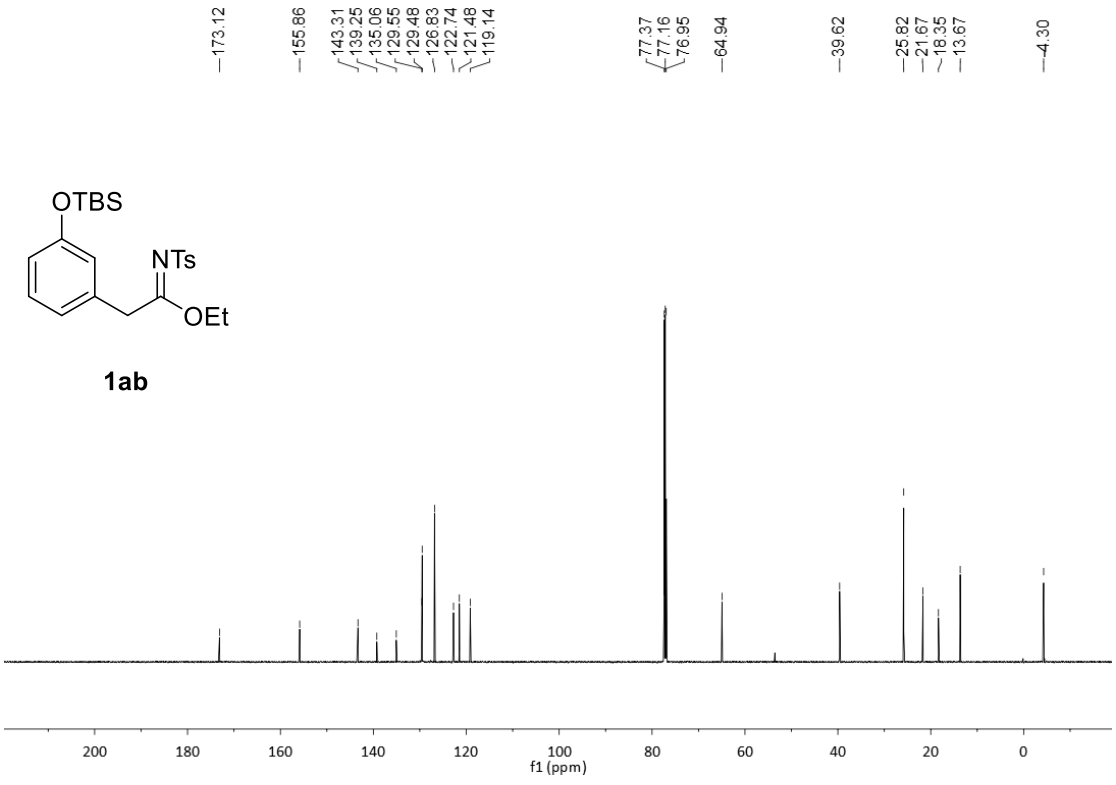

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



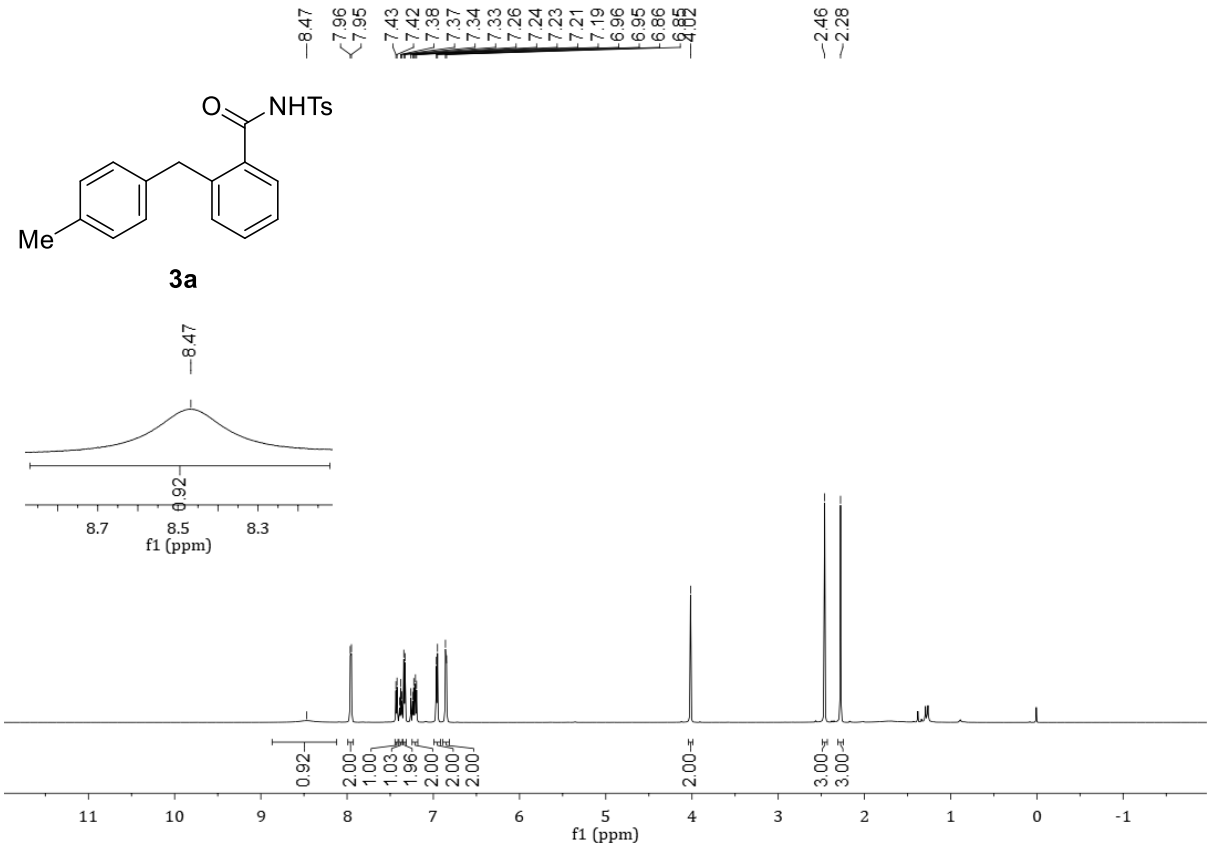
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



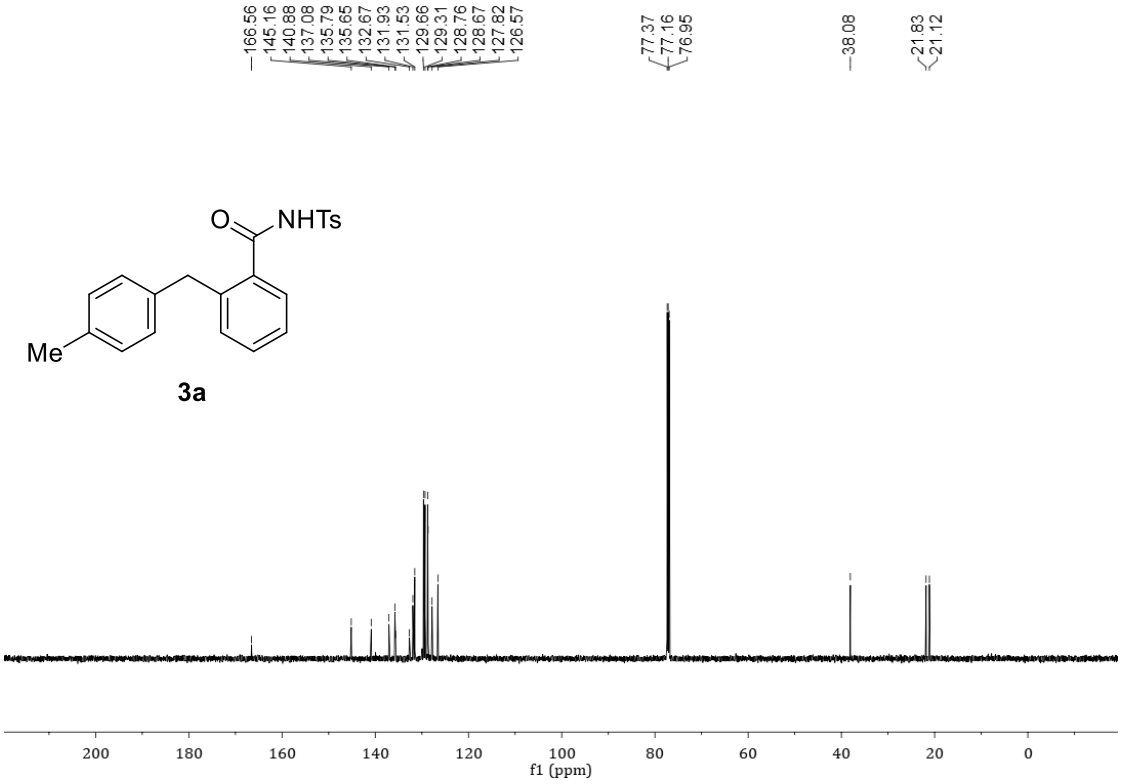

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



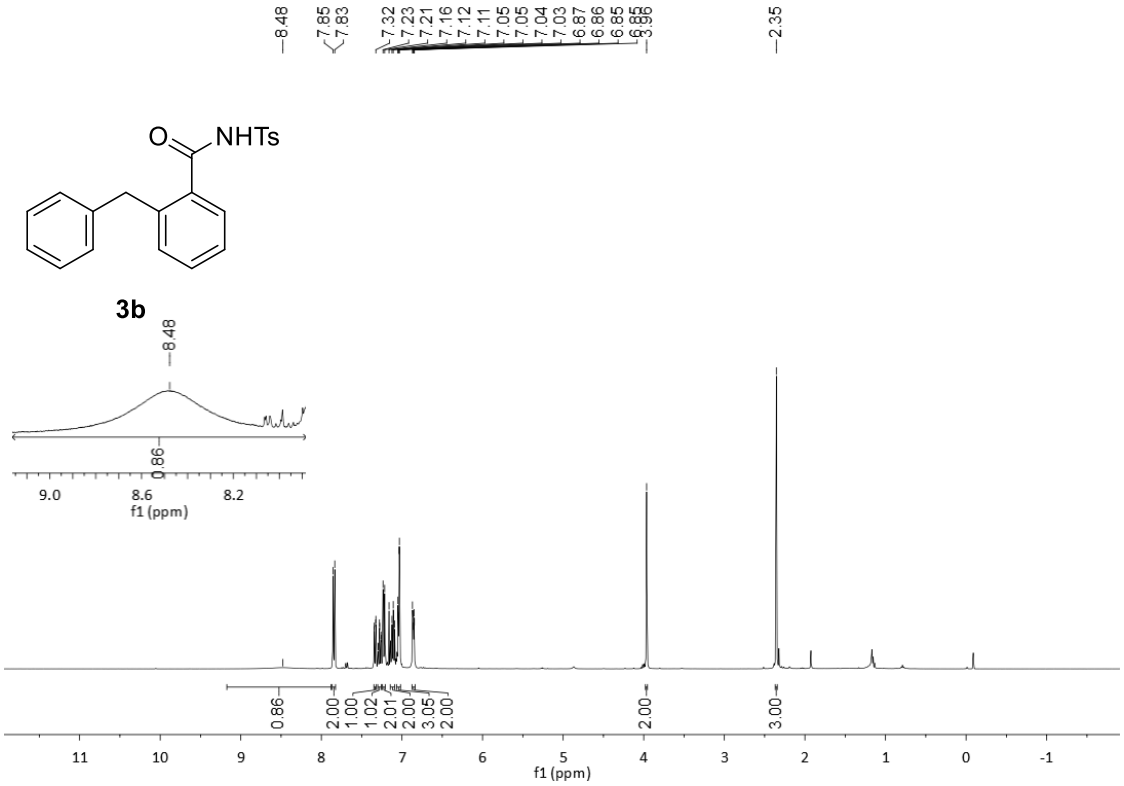
**$^{1}$H NMR (600 MHz, $CDCl_3$)**



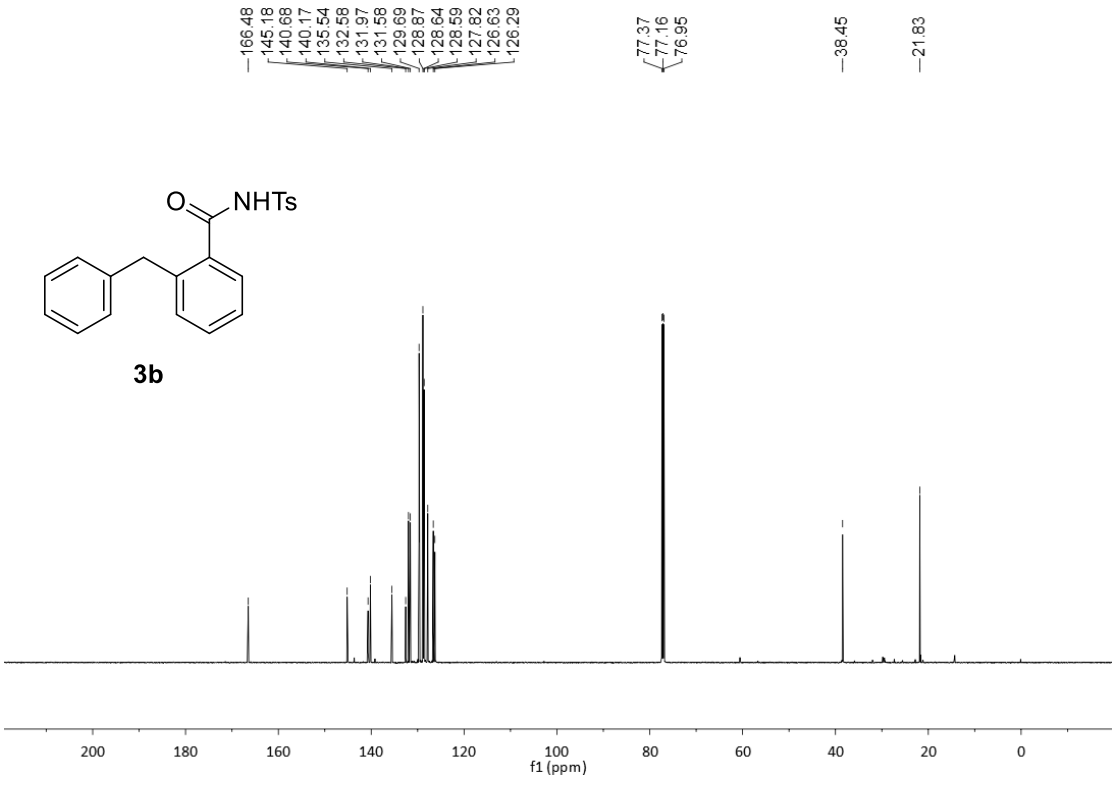

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



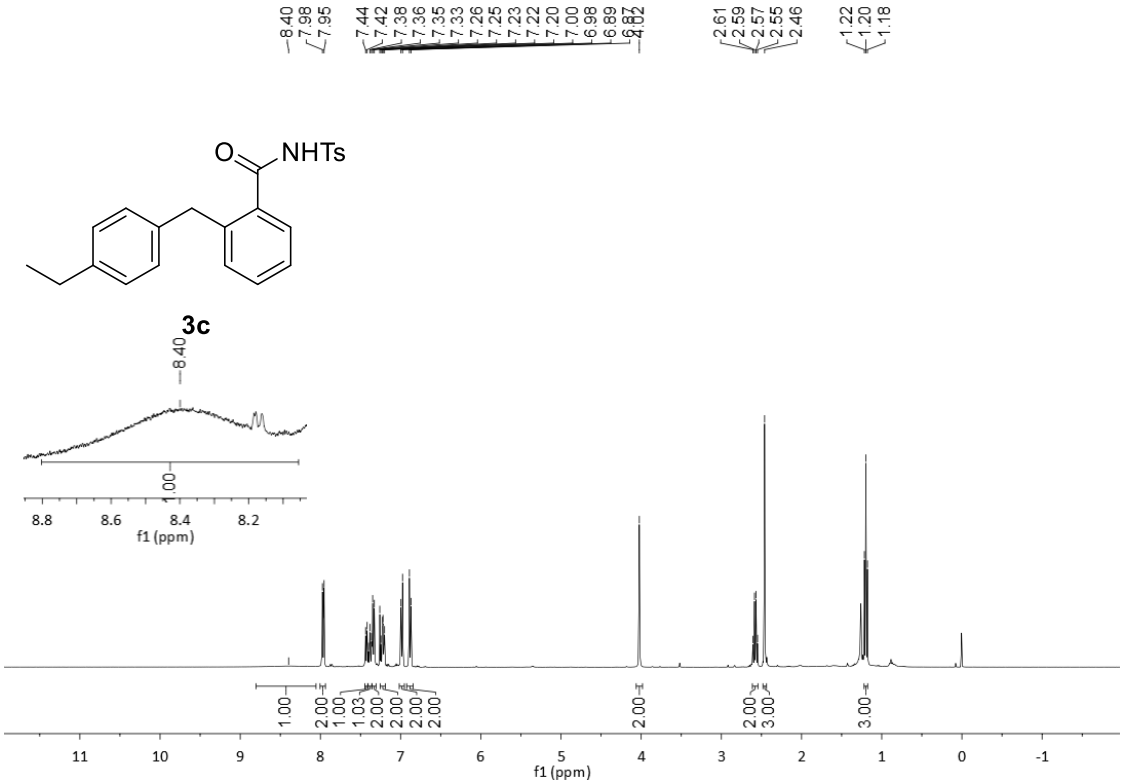
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



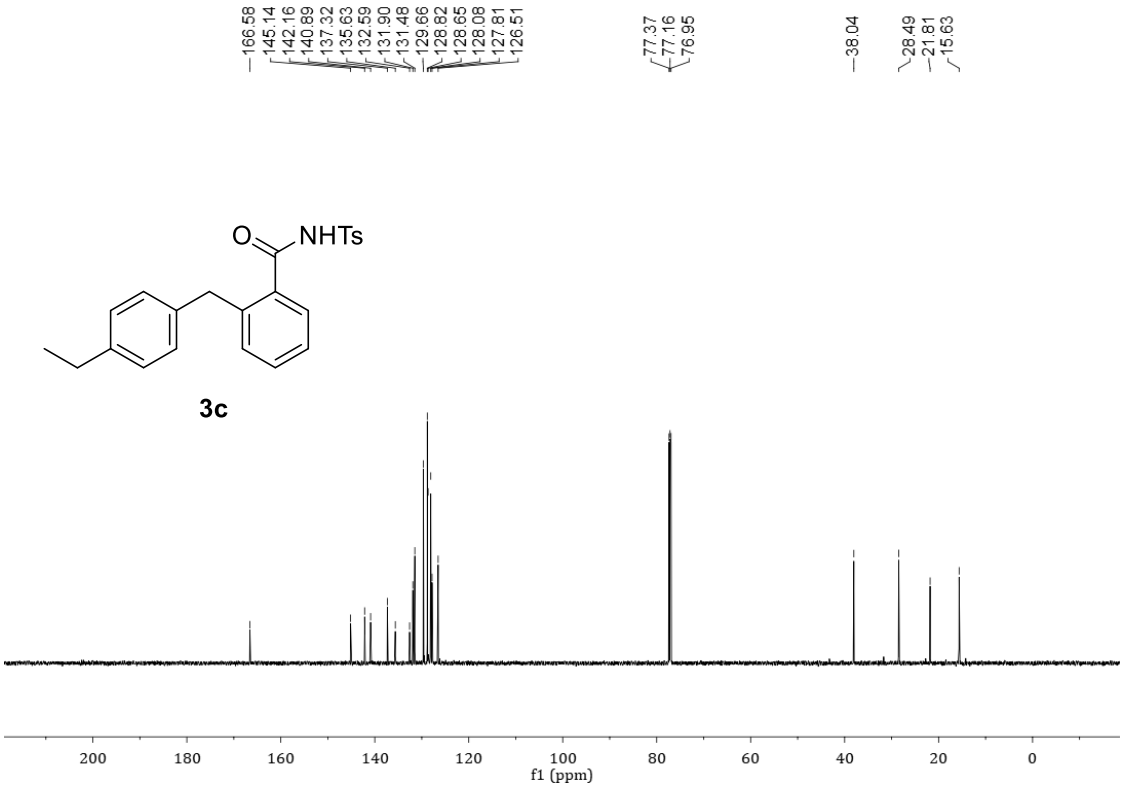

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



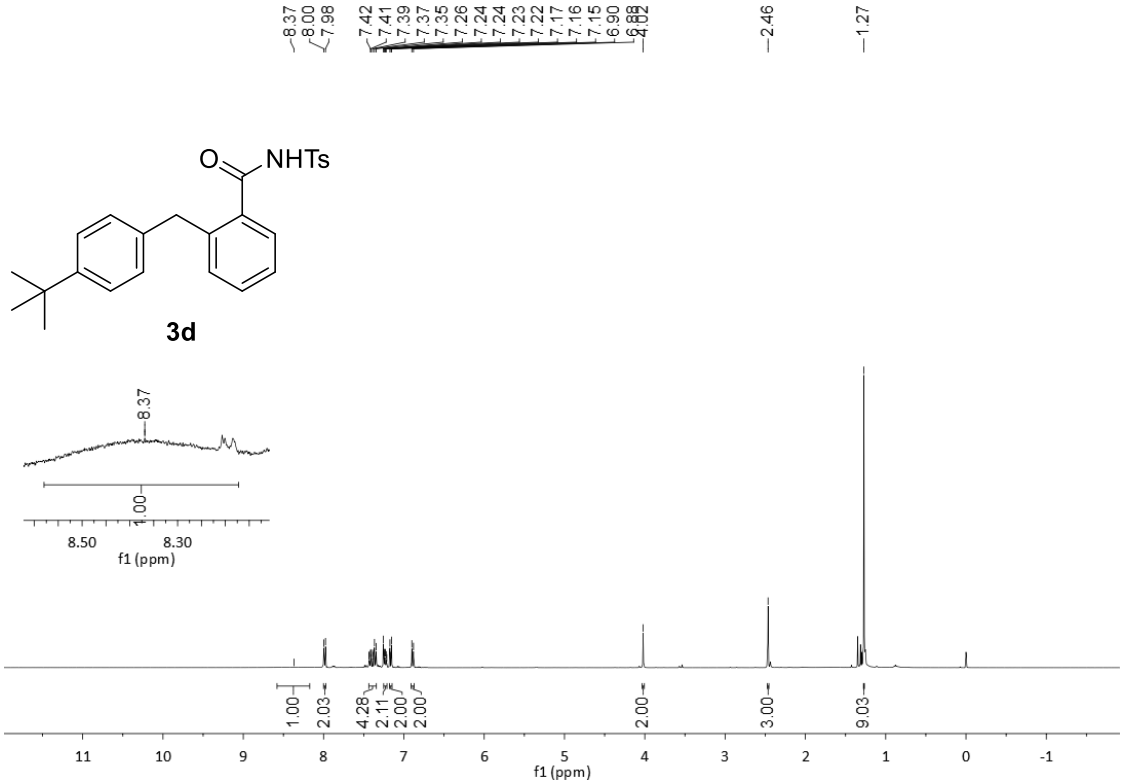
## $^{1}$H NMR (400 MHz, $CDCl_3$)



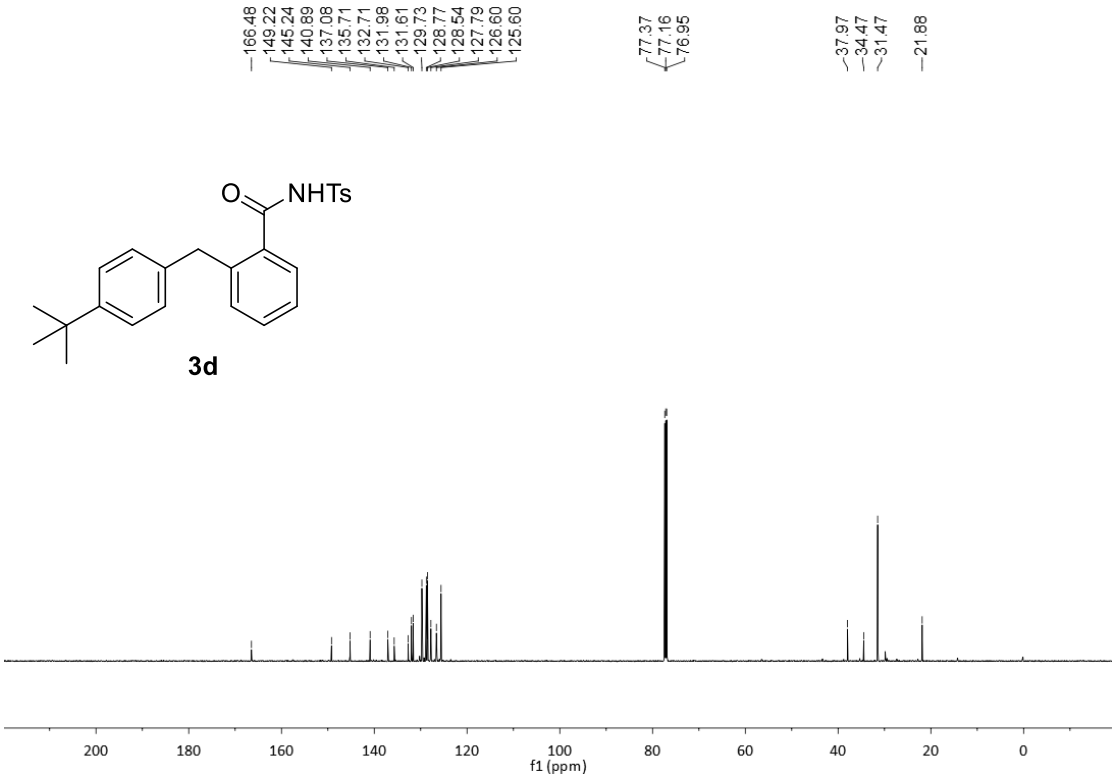

## $^{13}$C NMR (150 MHz, $CDCl_3$)



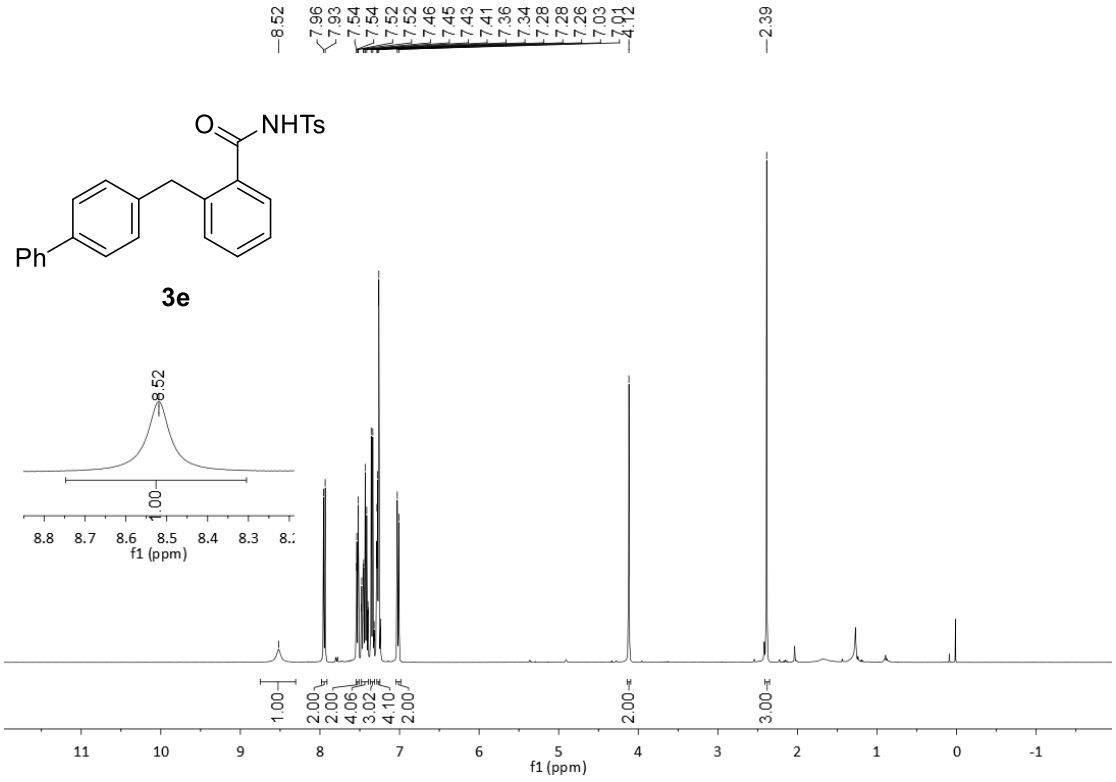
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



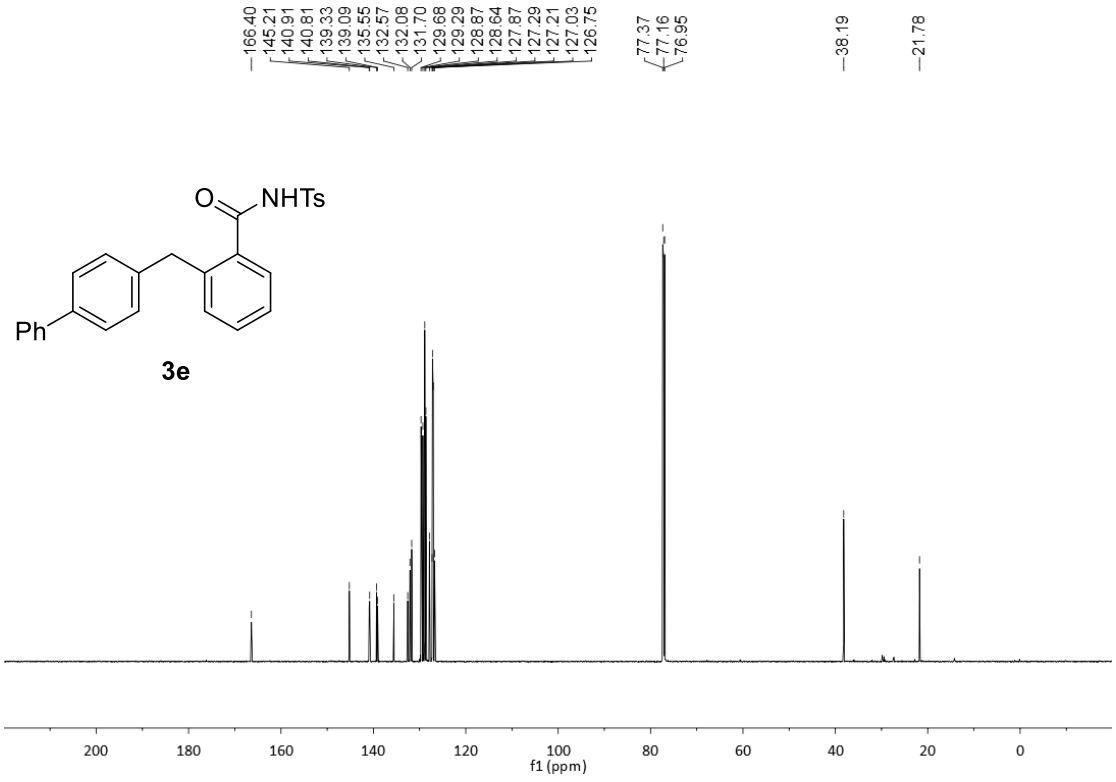

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



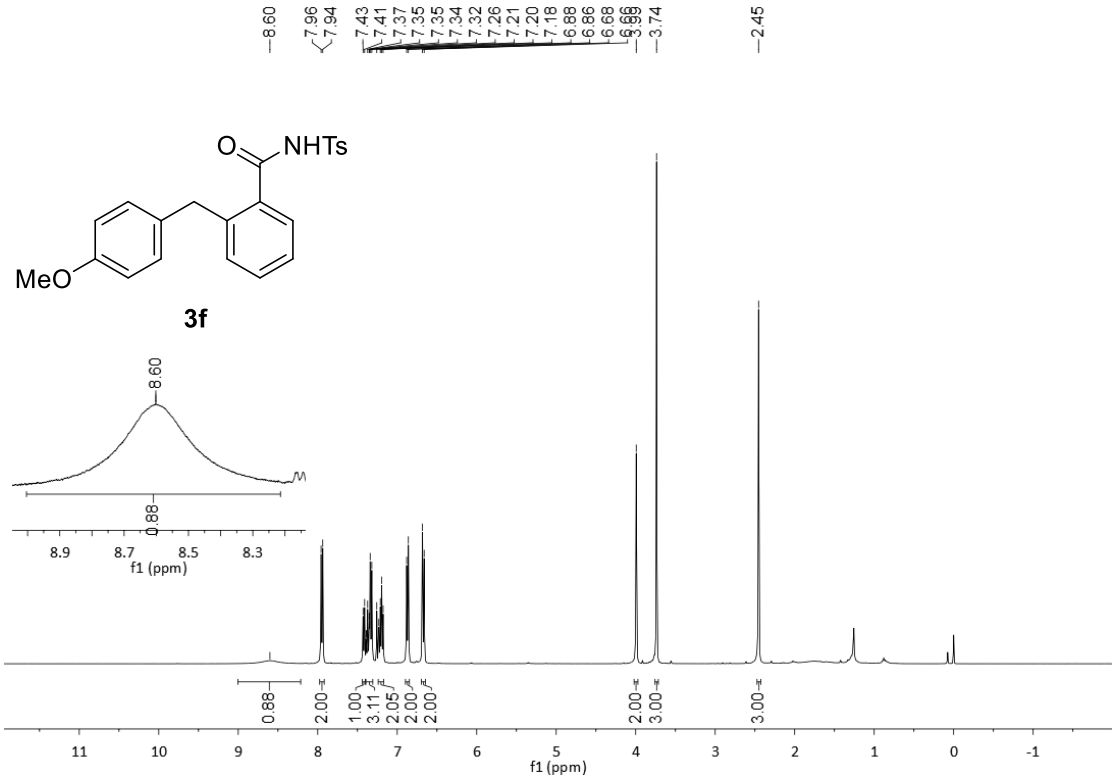
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



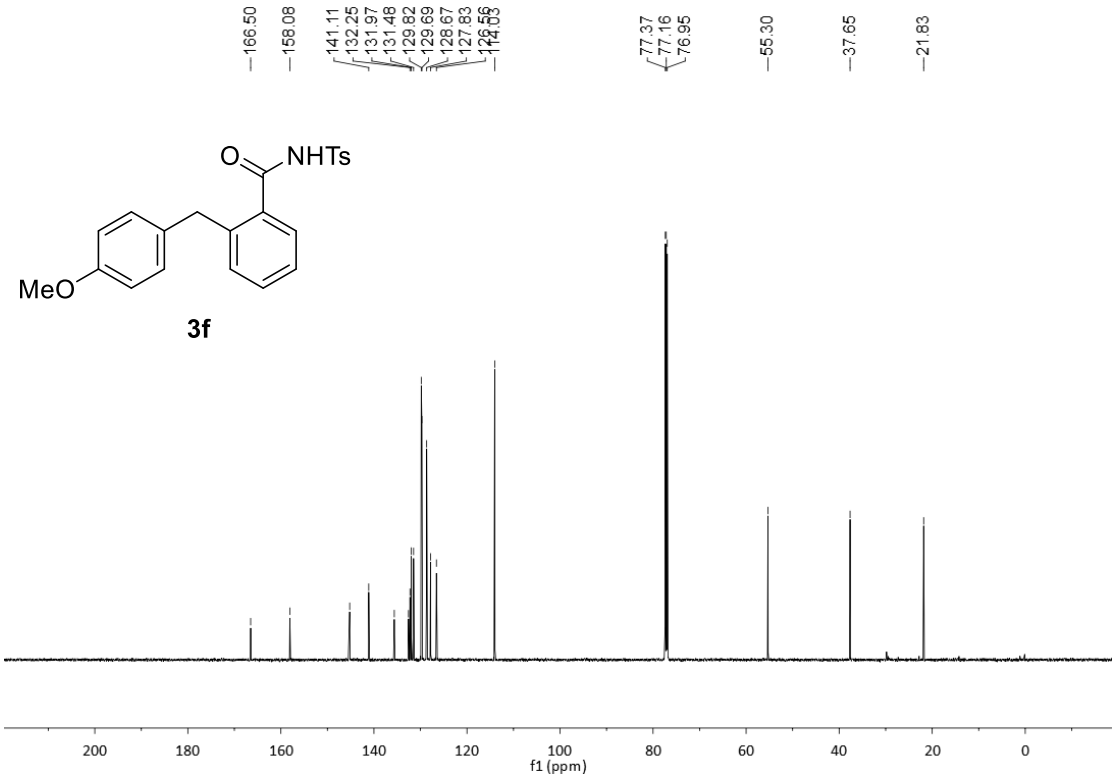

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



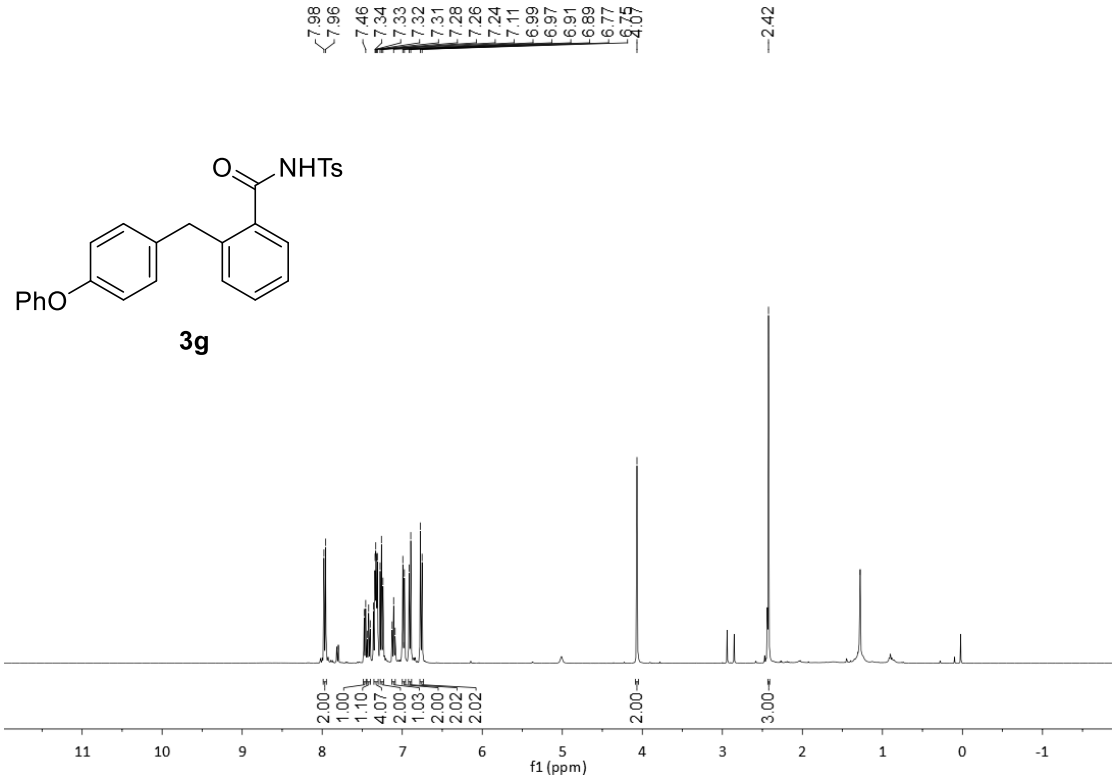
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



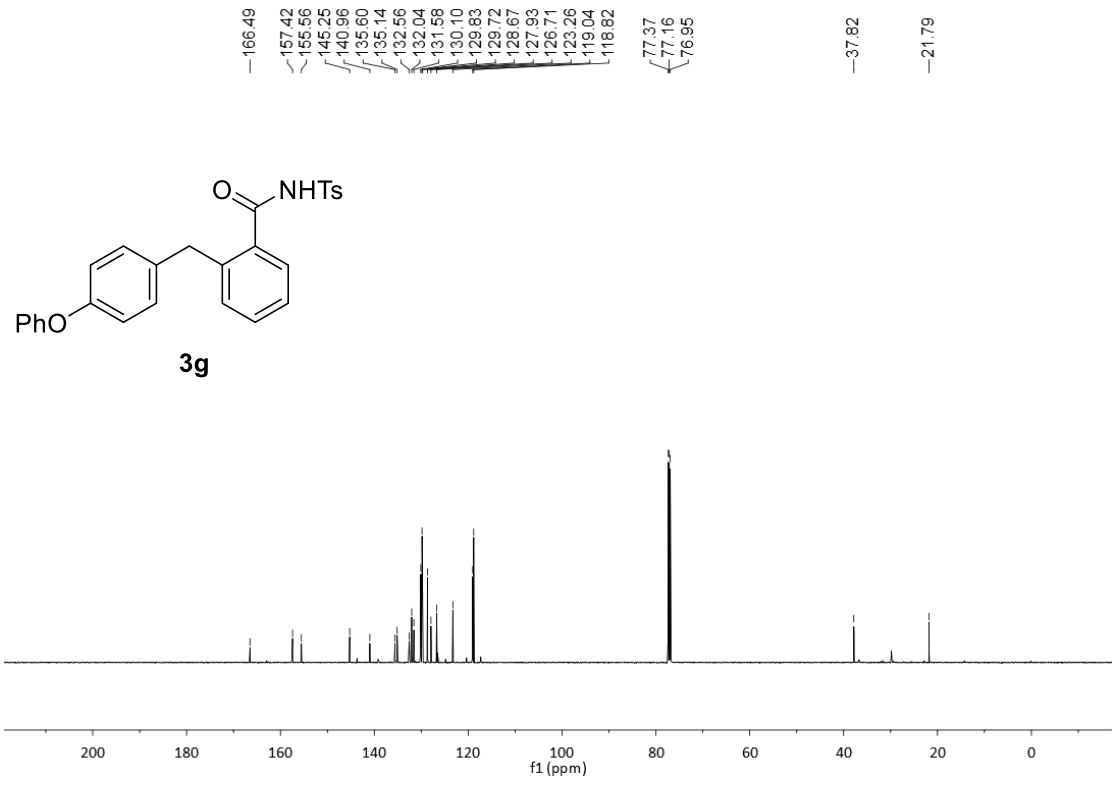

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



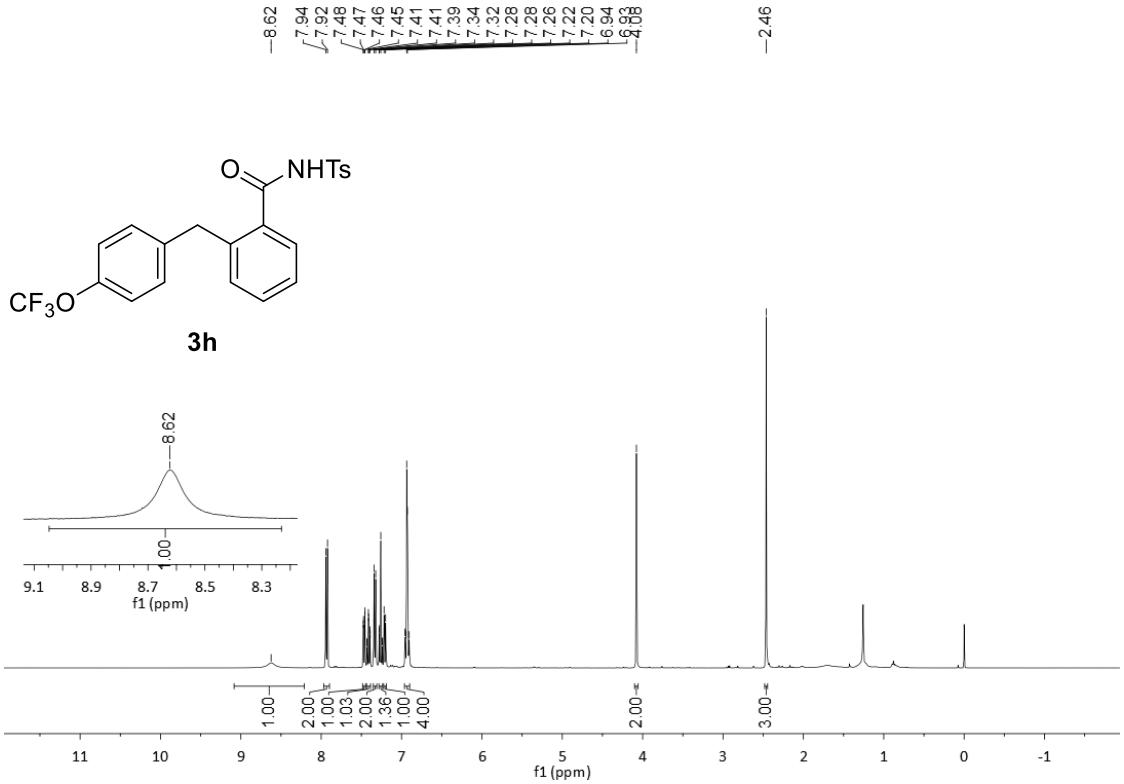
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



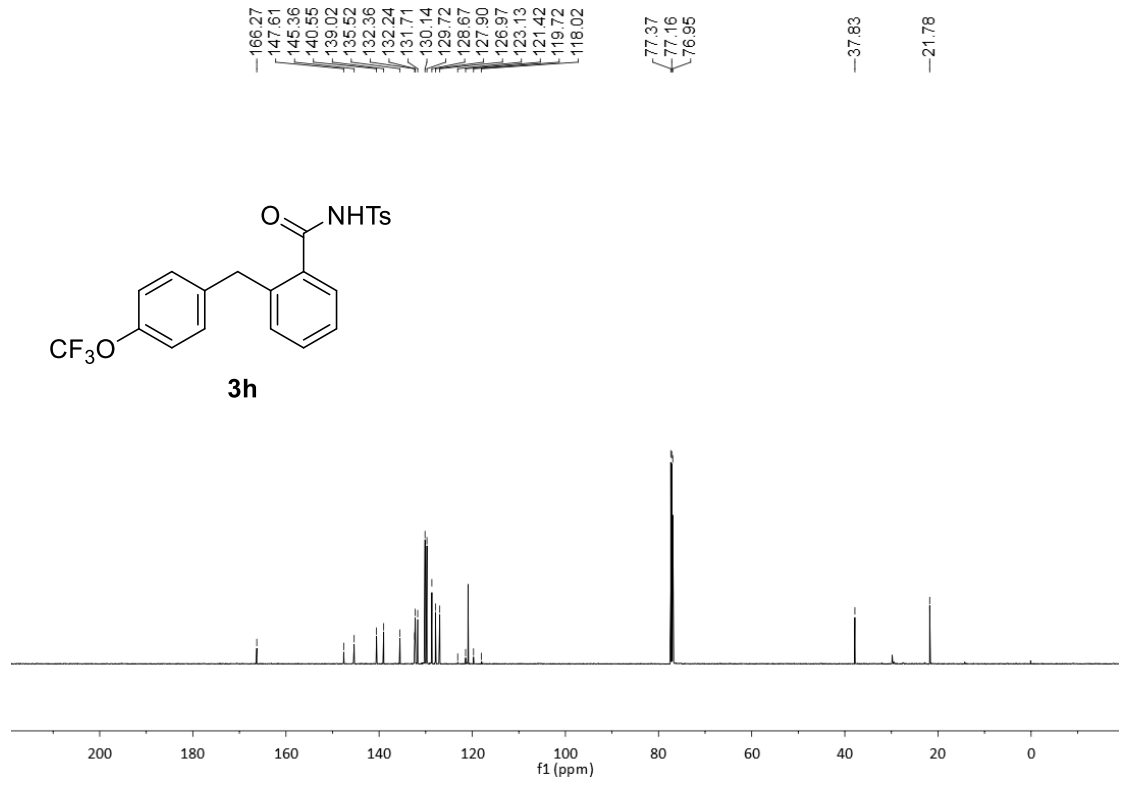

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



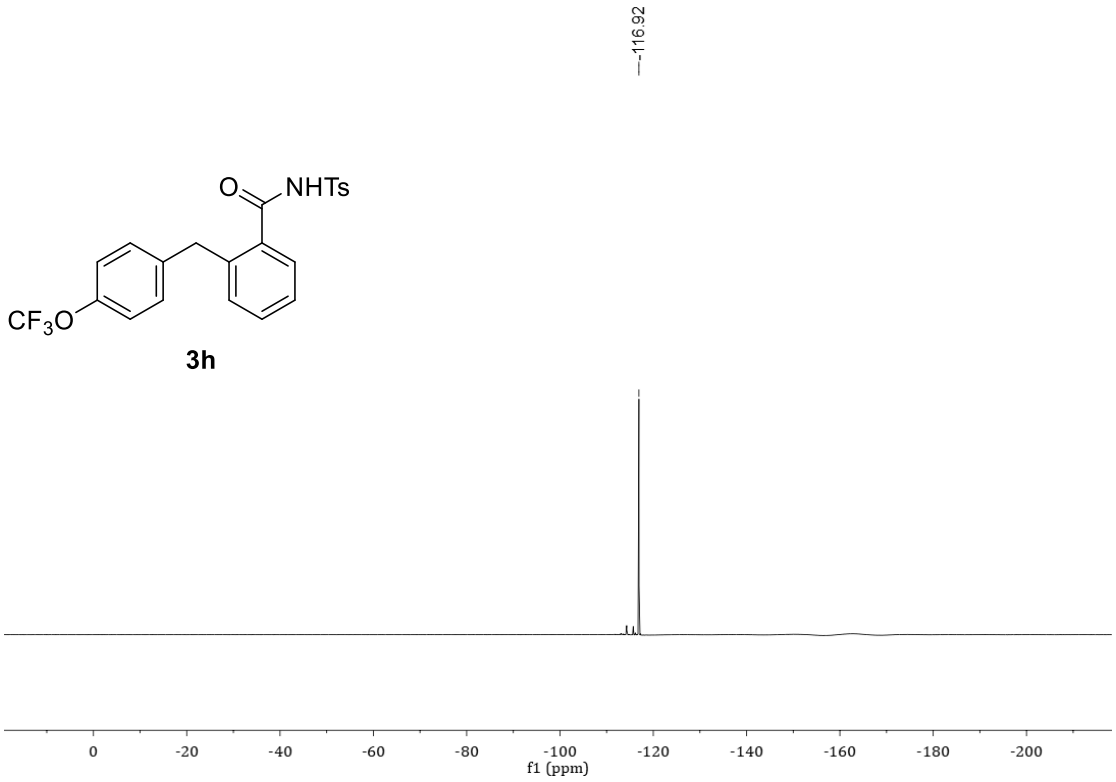
## $^{1}$H NMR (400 MHz, $CDCl_3$)



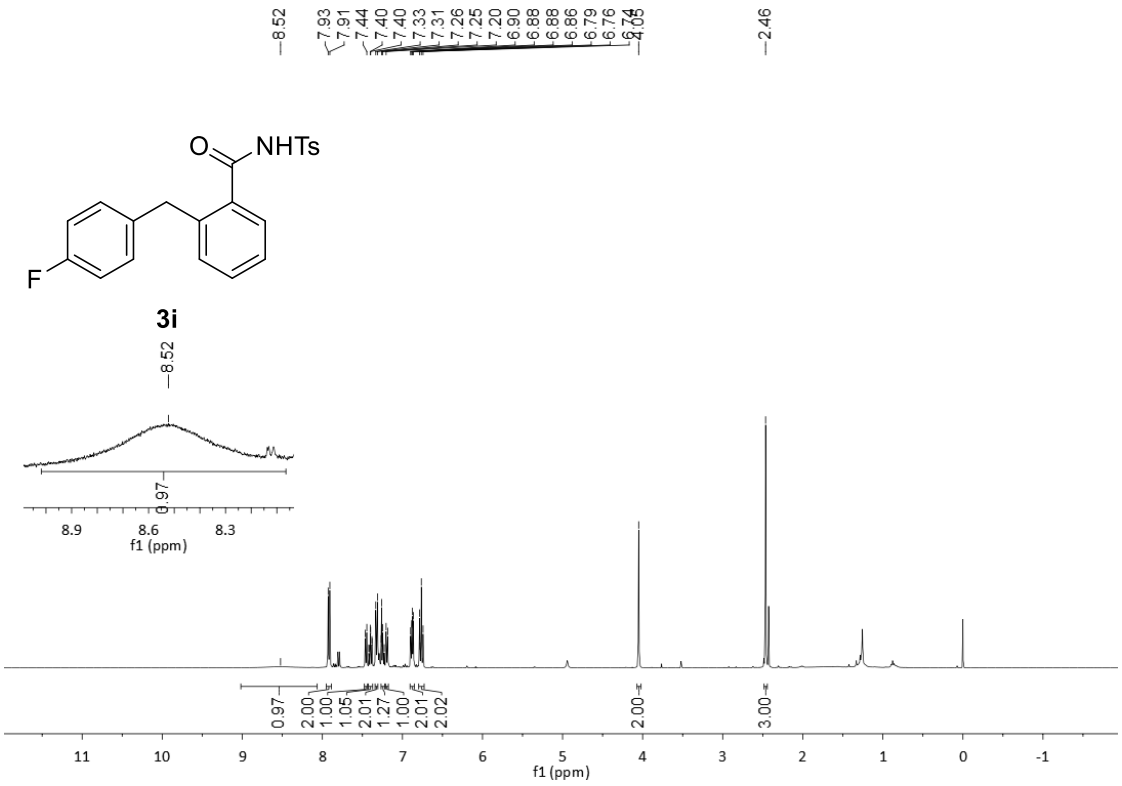

## $^{13}$C NMR (150 MHz, $CDCl_3$)



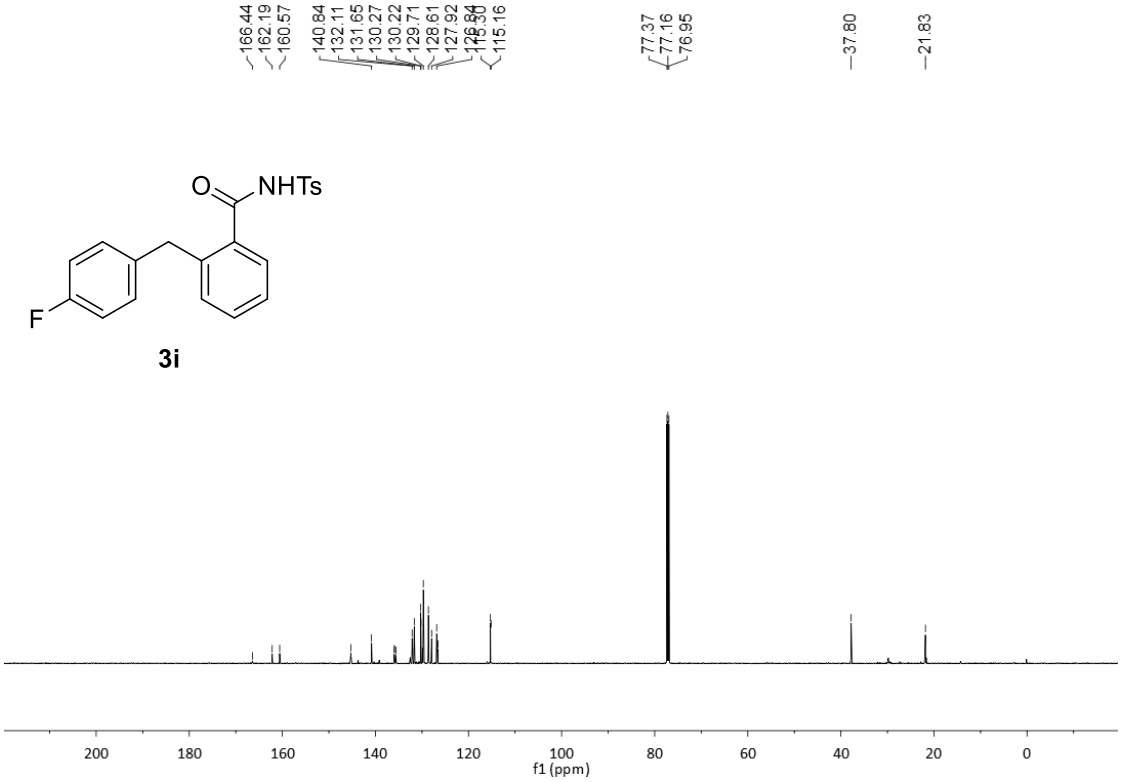
**$^{19}$F NMR (565 MHz, $CDCl_3$)**



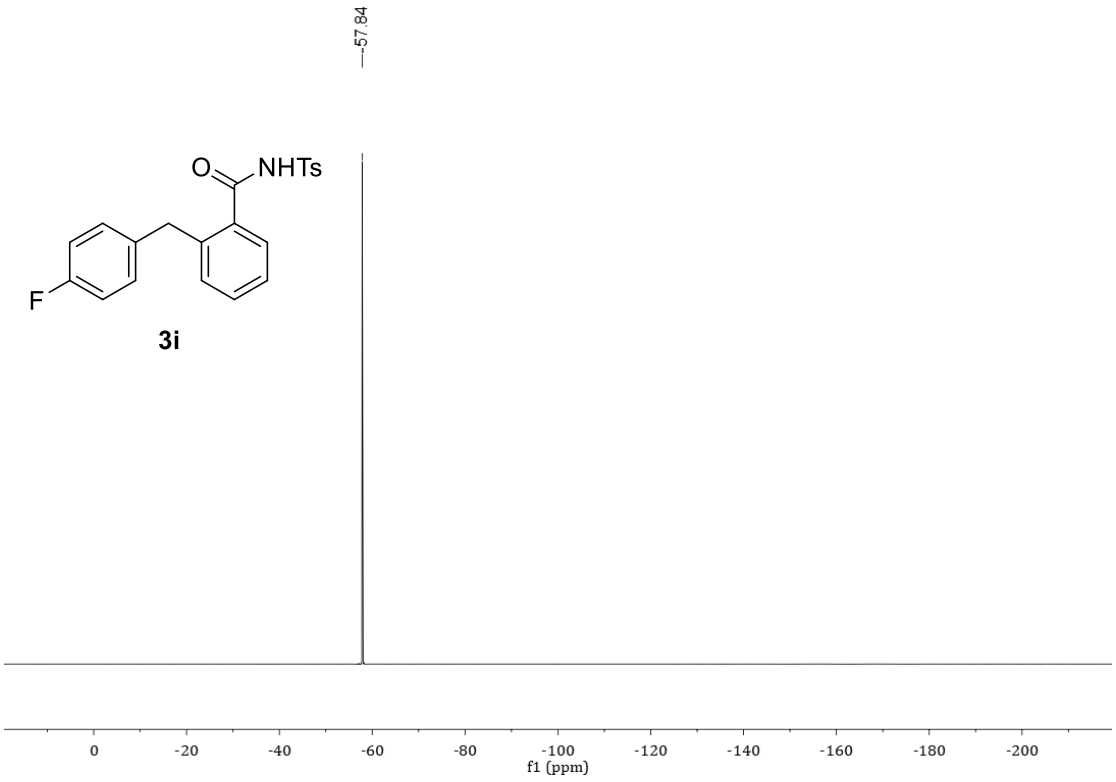

**$^{1}$H NMR (400 MHz, $CDCl_3$)**



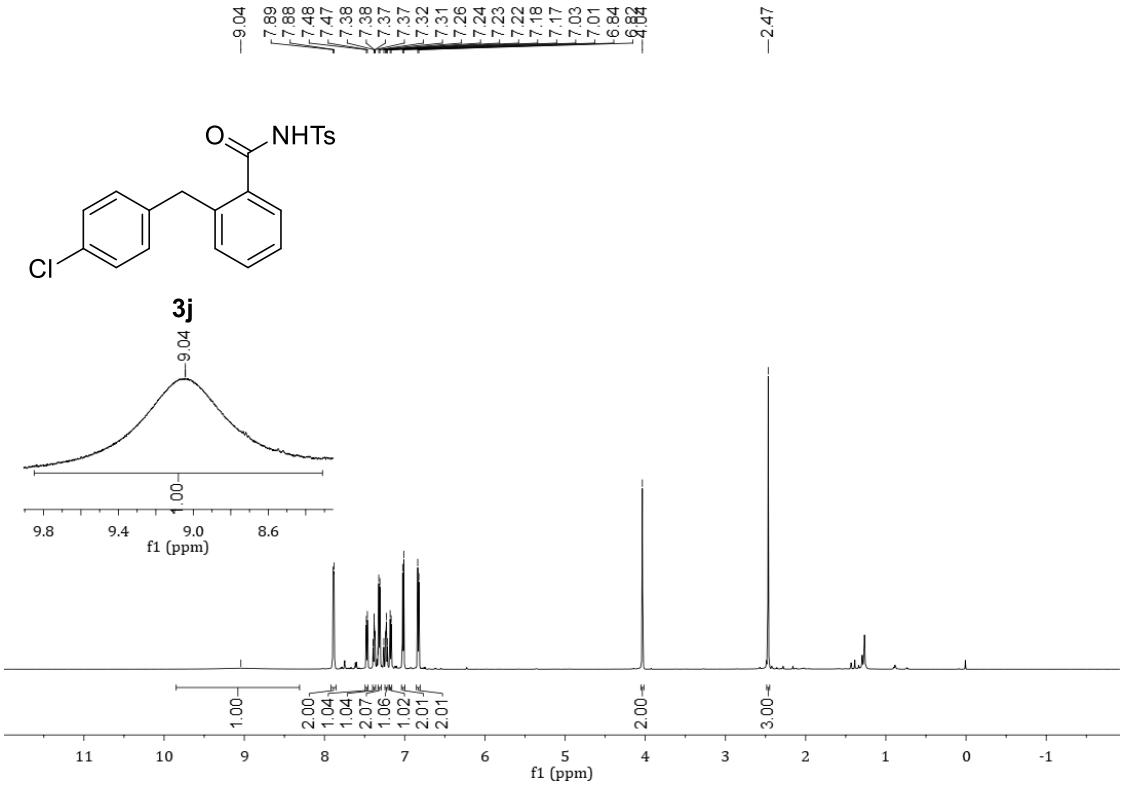
**$^{13}$C NMR (150 MHz, $CDCl_3$)**



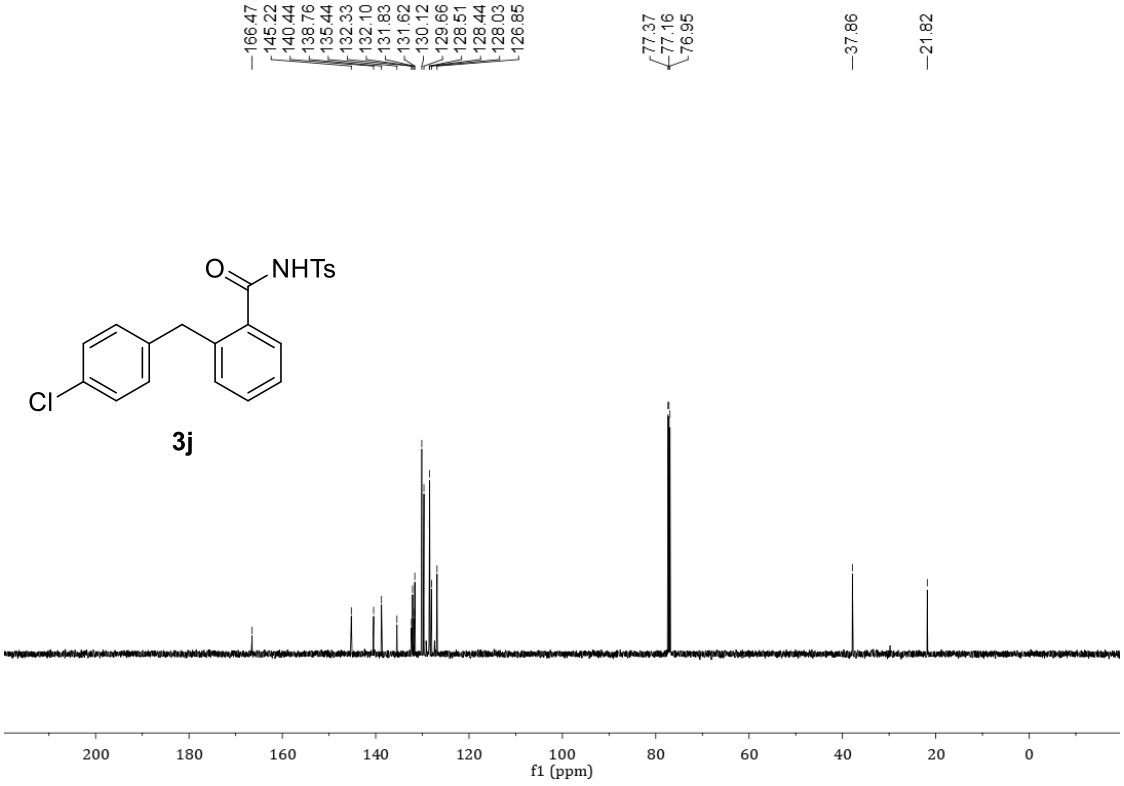

**$^{19}$F NMR (565 MHz, $CDCl_3$)**



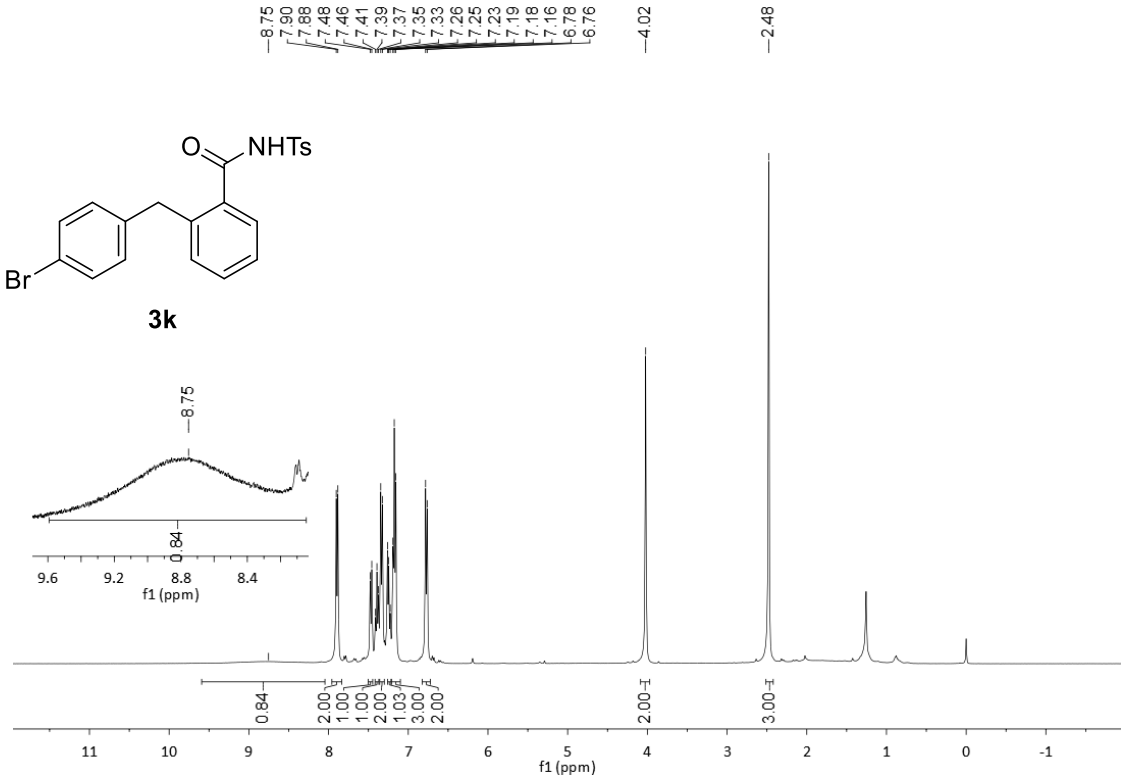
## $^{1}$H NMR (600 MHz, $CDCl_3$)



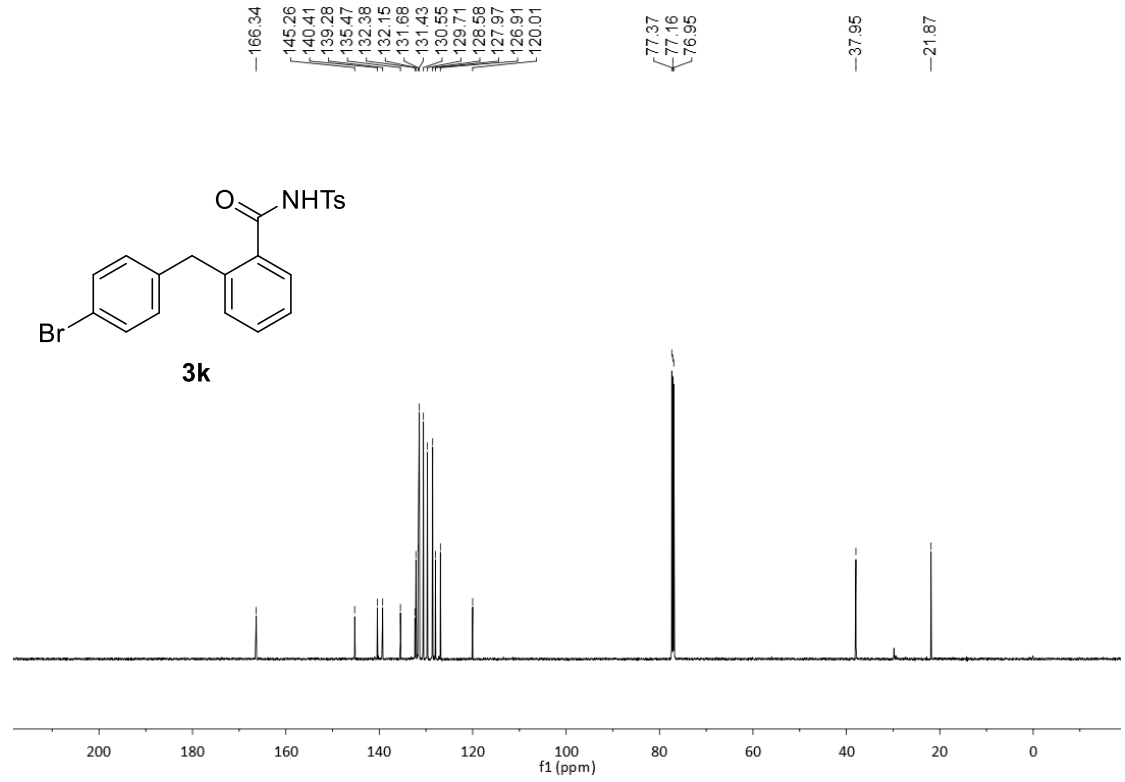

## $^{13}$C NMR (150 MHz, $CDCl_3$)



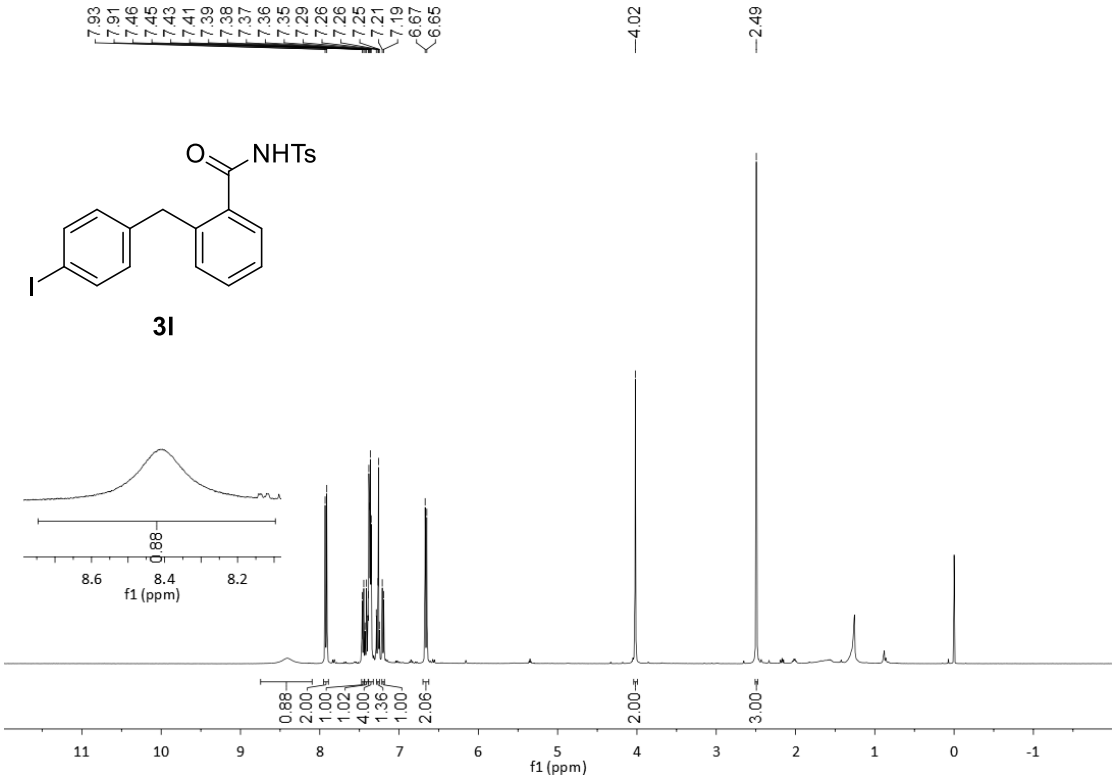
**$^{1}$H NMR (400 MHz, $CDCl_3$)**




**$^{13}$C NMR (150 MHz, $CDCl_3$)**



## $^{1}$H NMR (400 MHz, $CDCl_3$)

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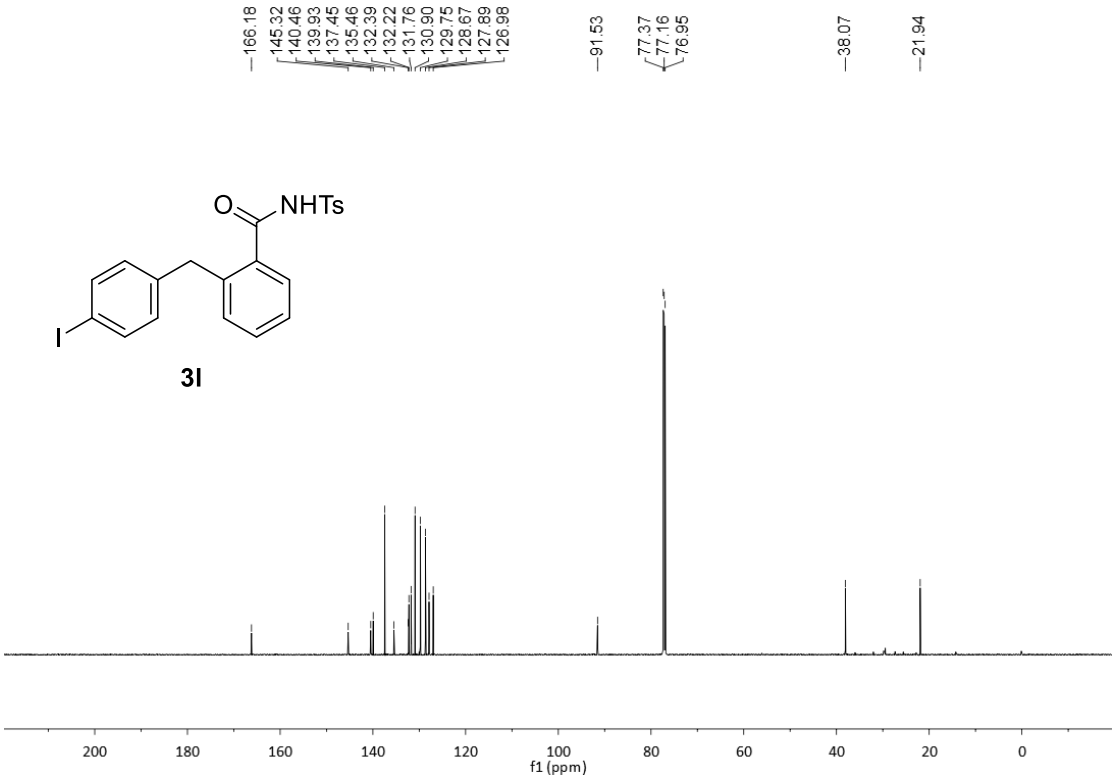

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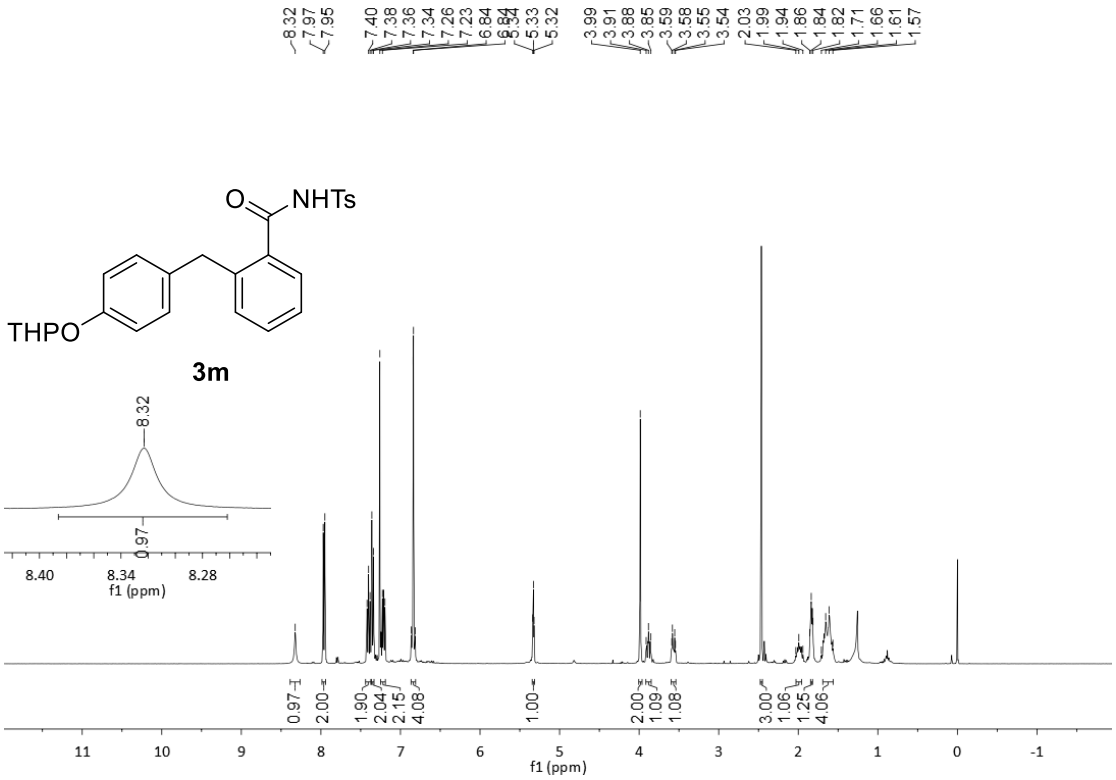
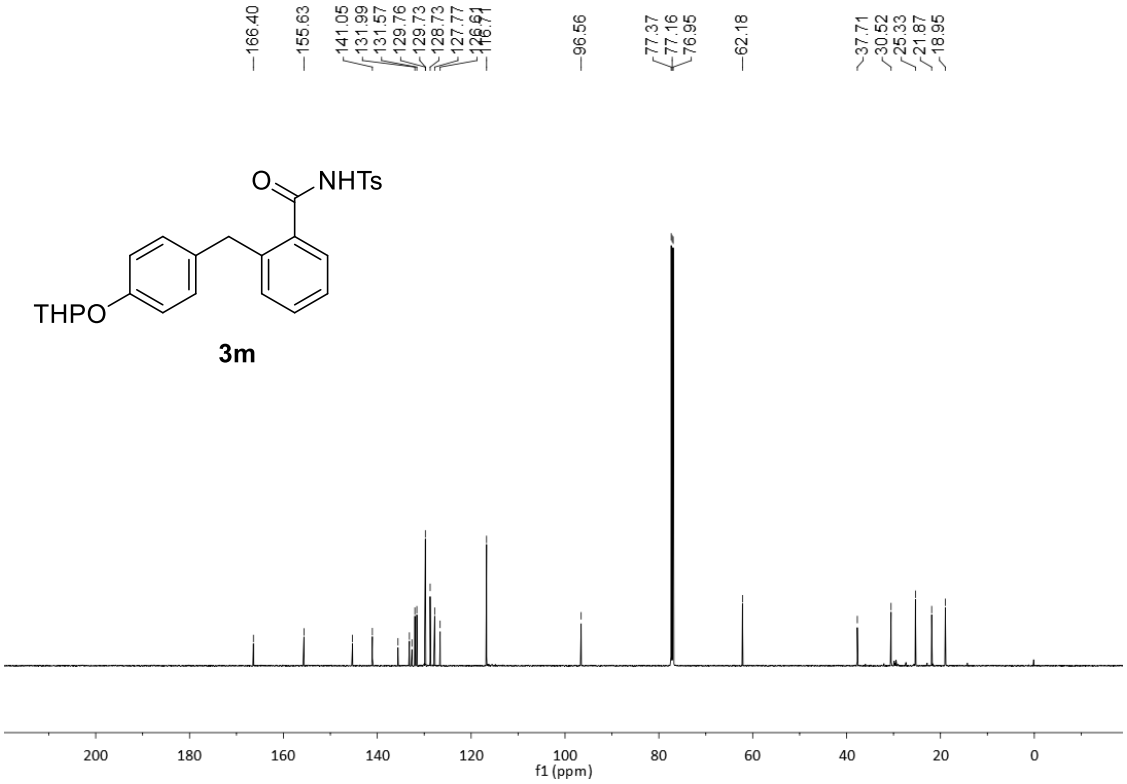
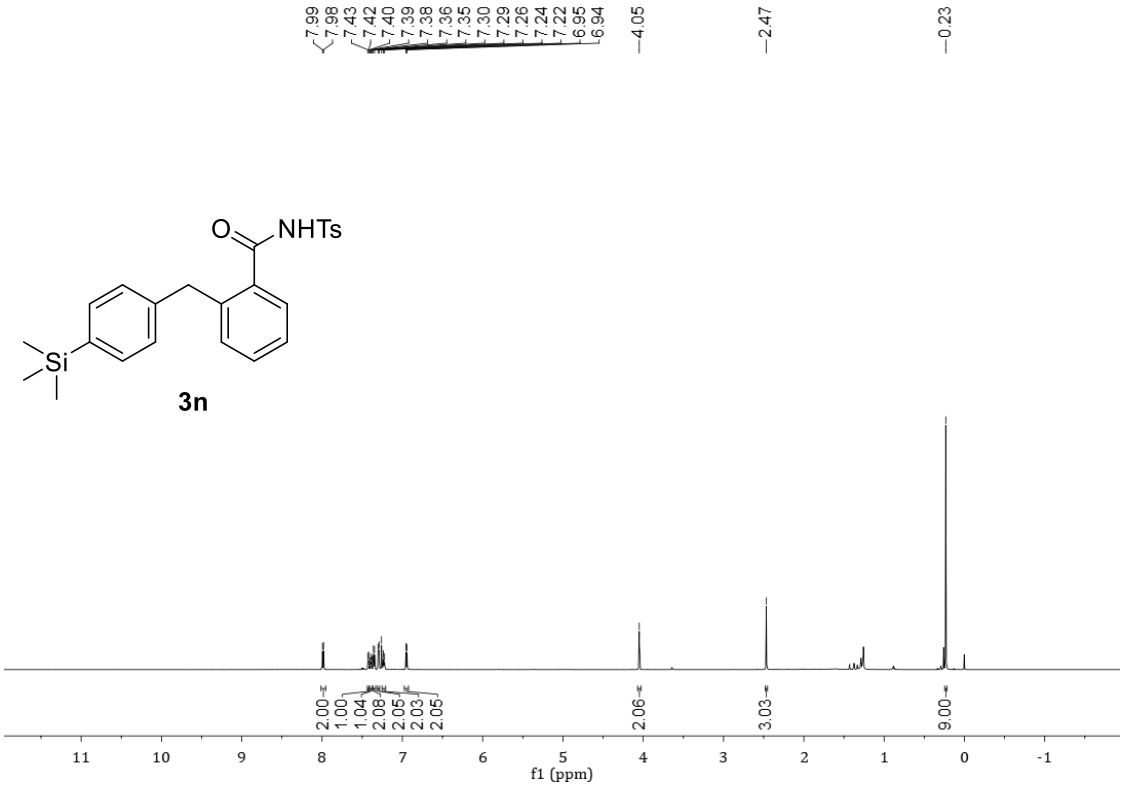


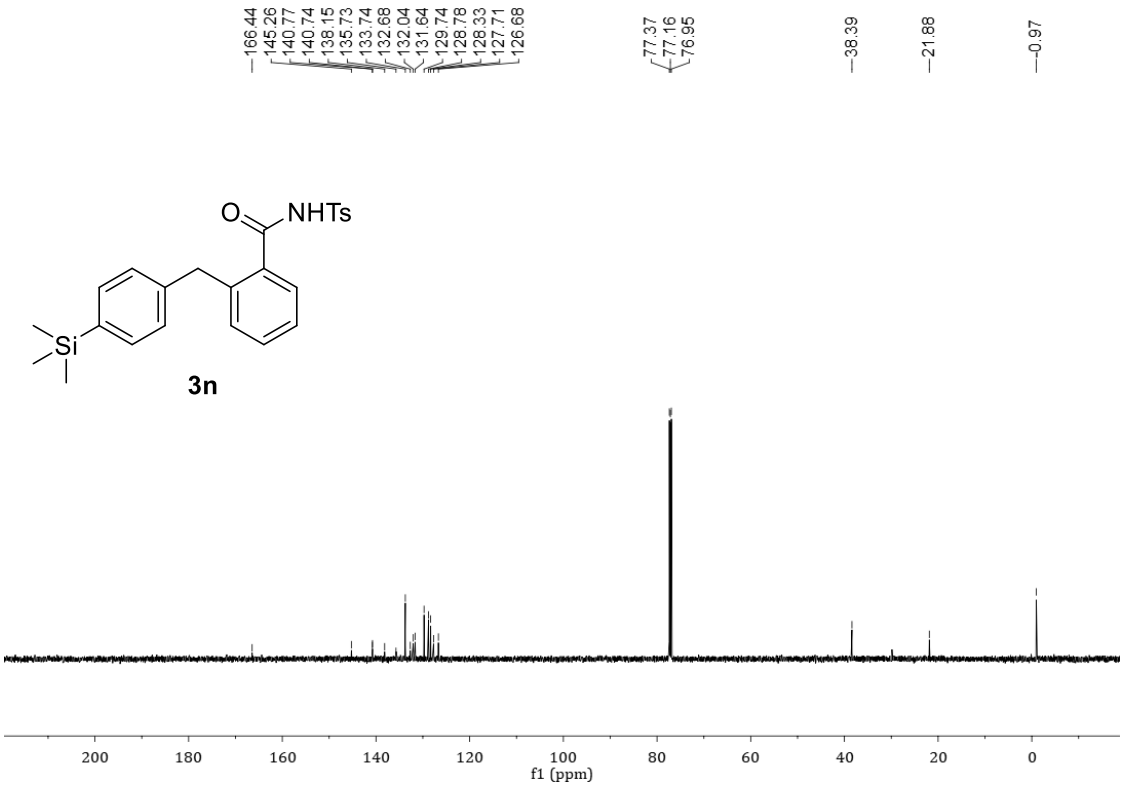

## $^{13}$C NMR (150 MHz, $CDCl_3$)



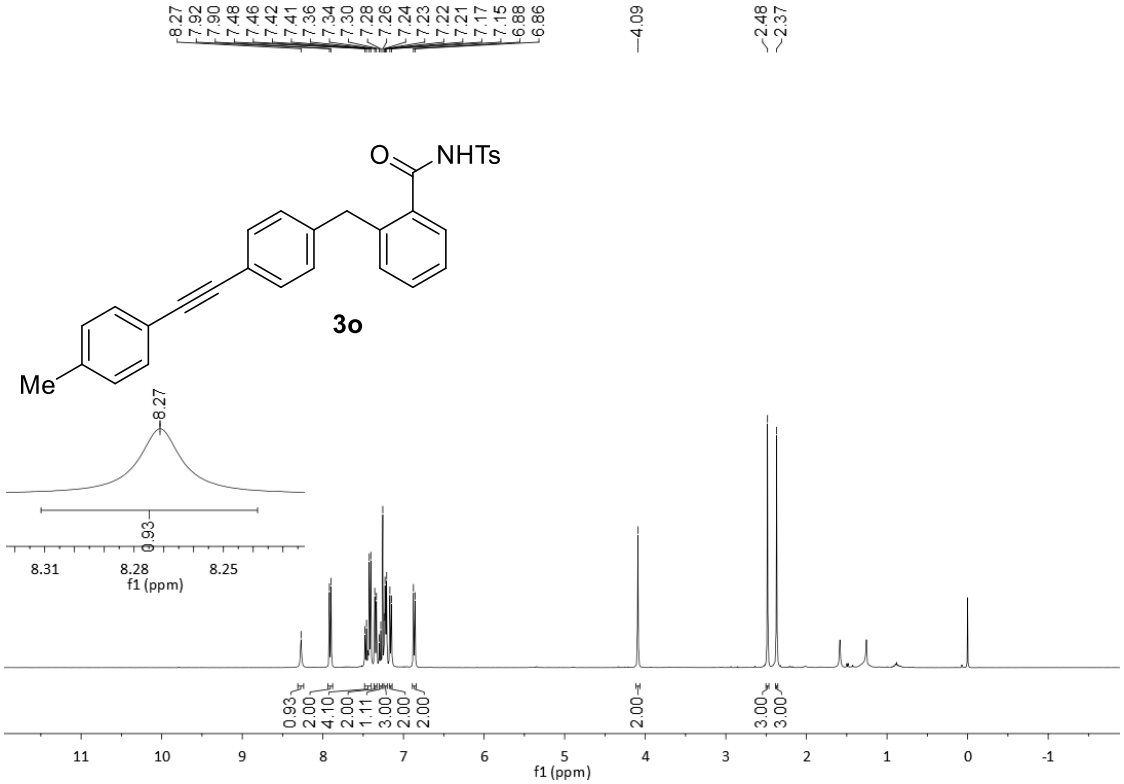
**$^{1}$H NMR (600 MHz, $CDCl_3$)**



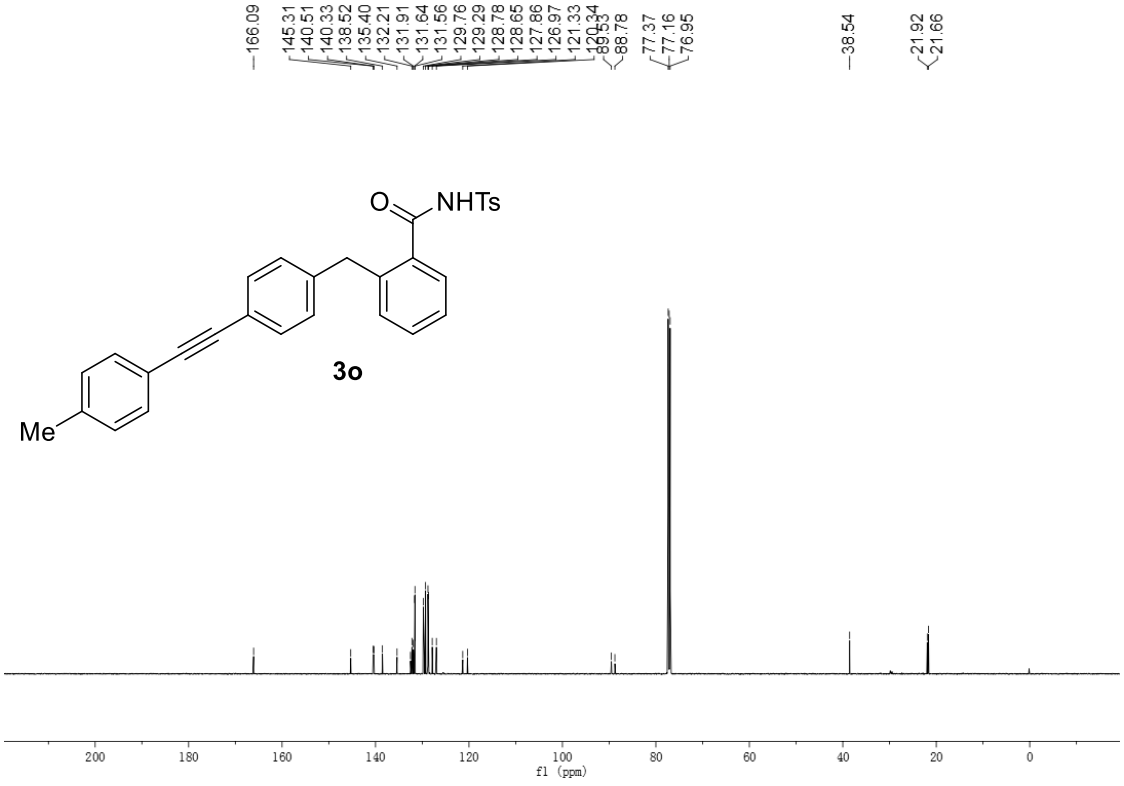

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



**$^{1}$H NMR (400 MHz, $CDCl_3$)**




**$^{13}$C NMR (150 MHz, $CDCl_3$)**



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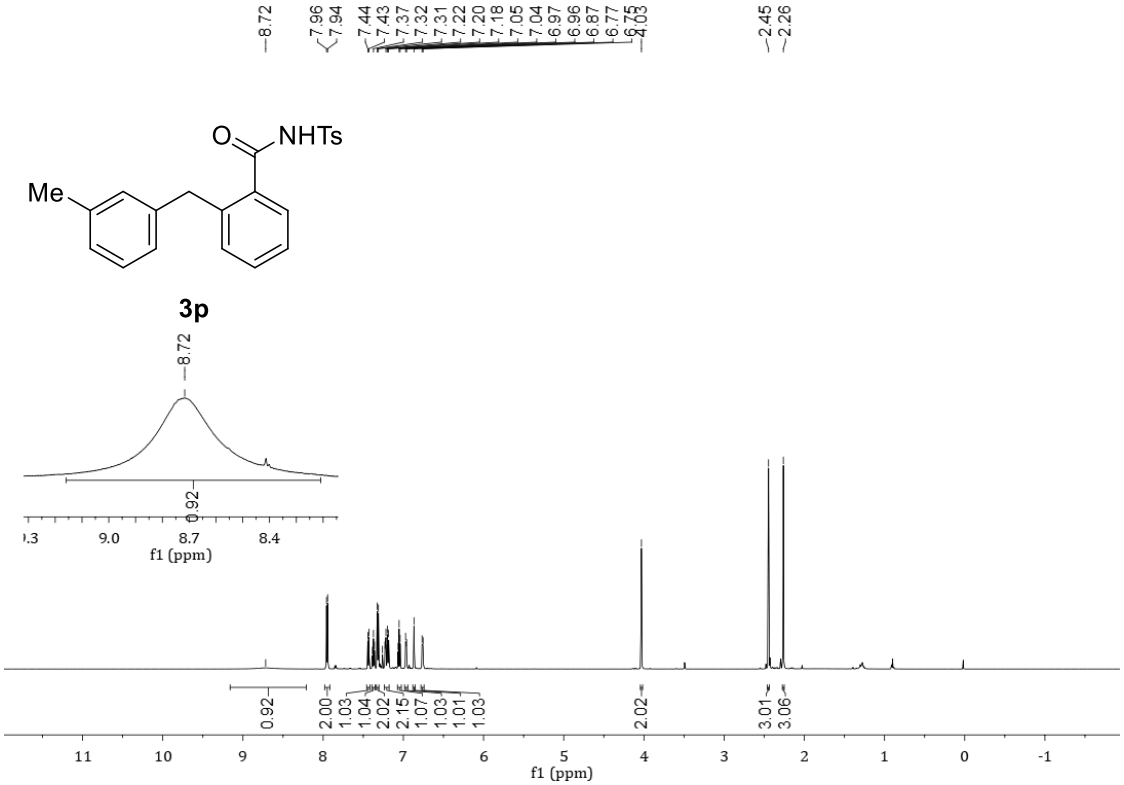


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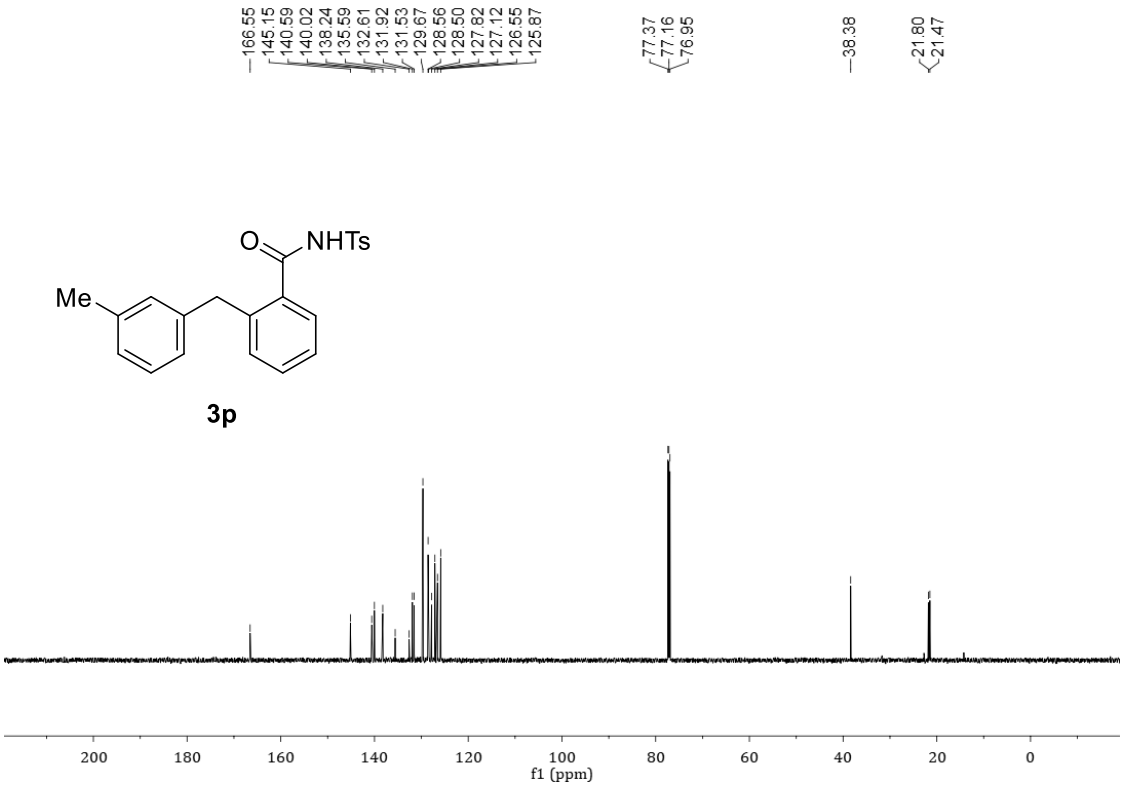

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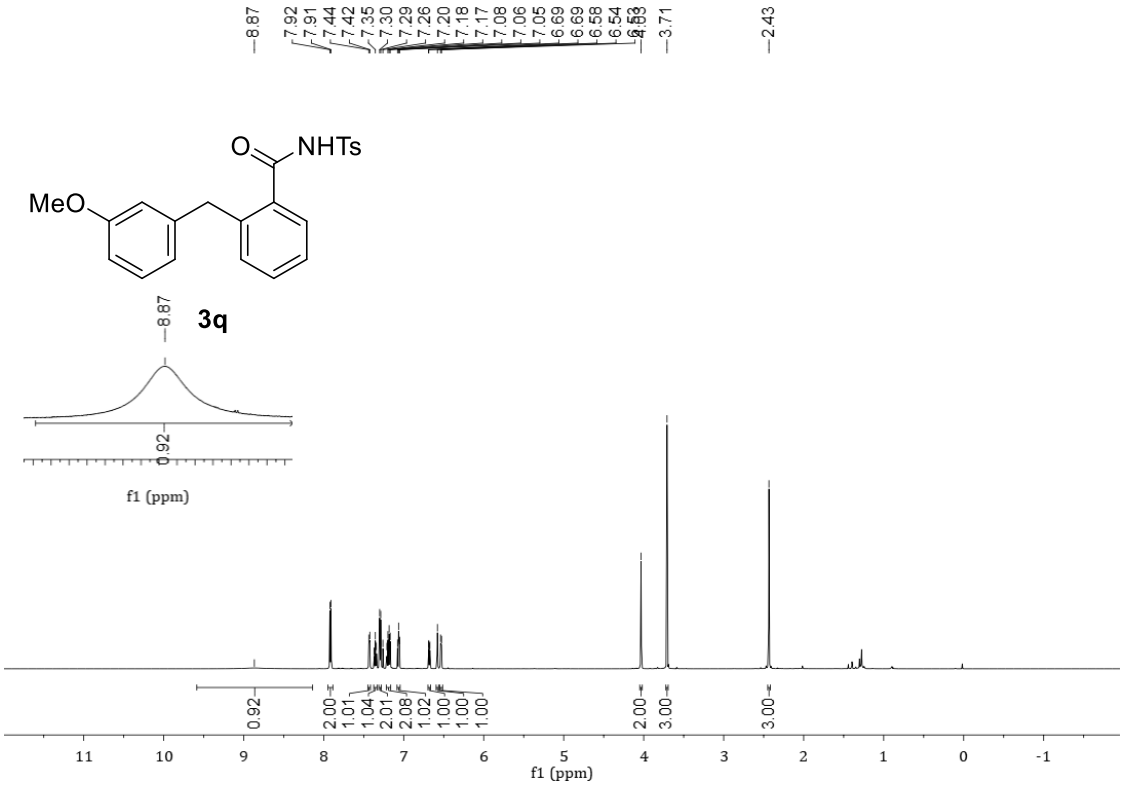
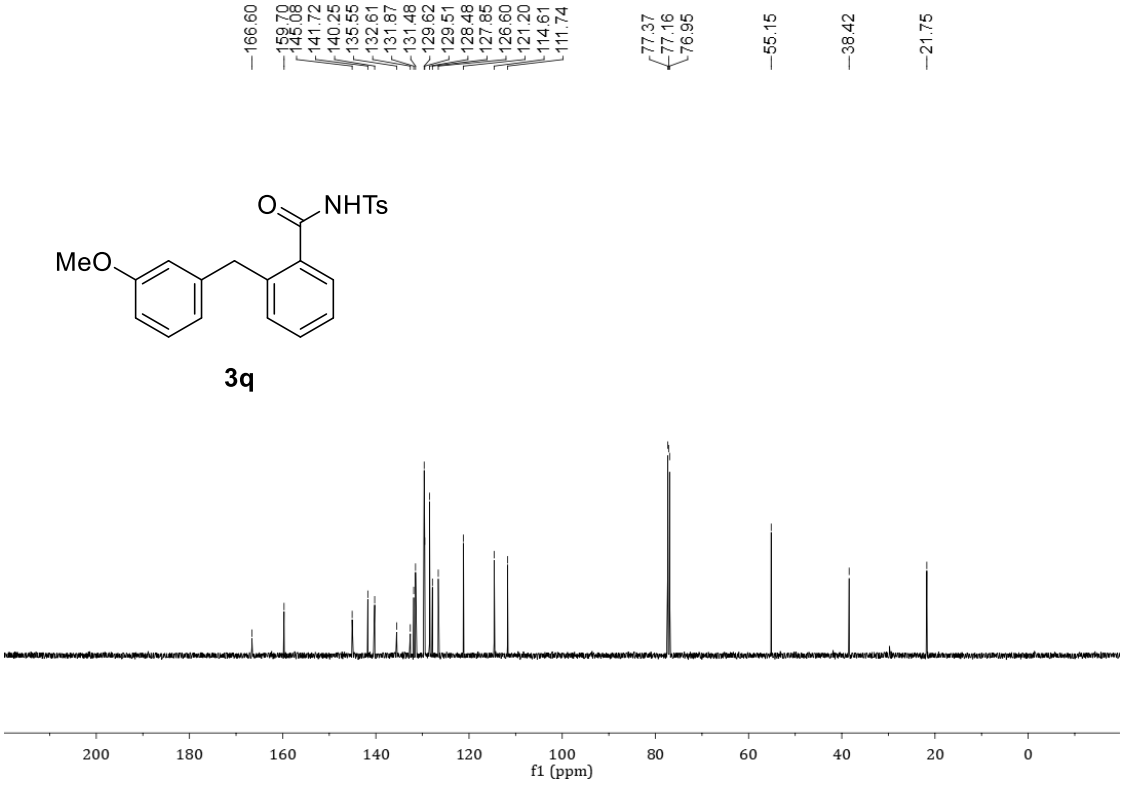



## $^{13}$C NMR (150 MHz, $CDCl_3$)



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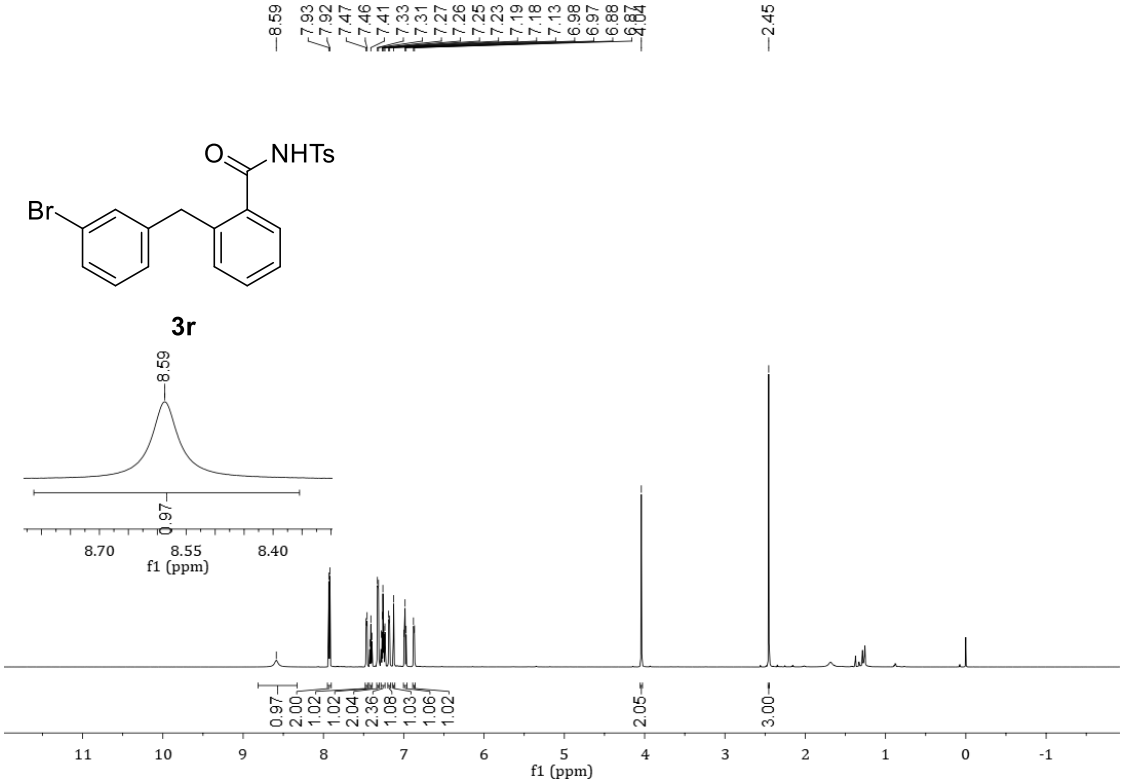
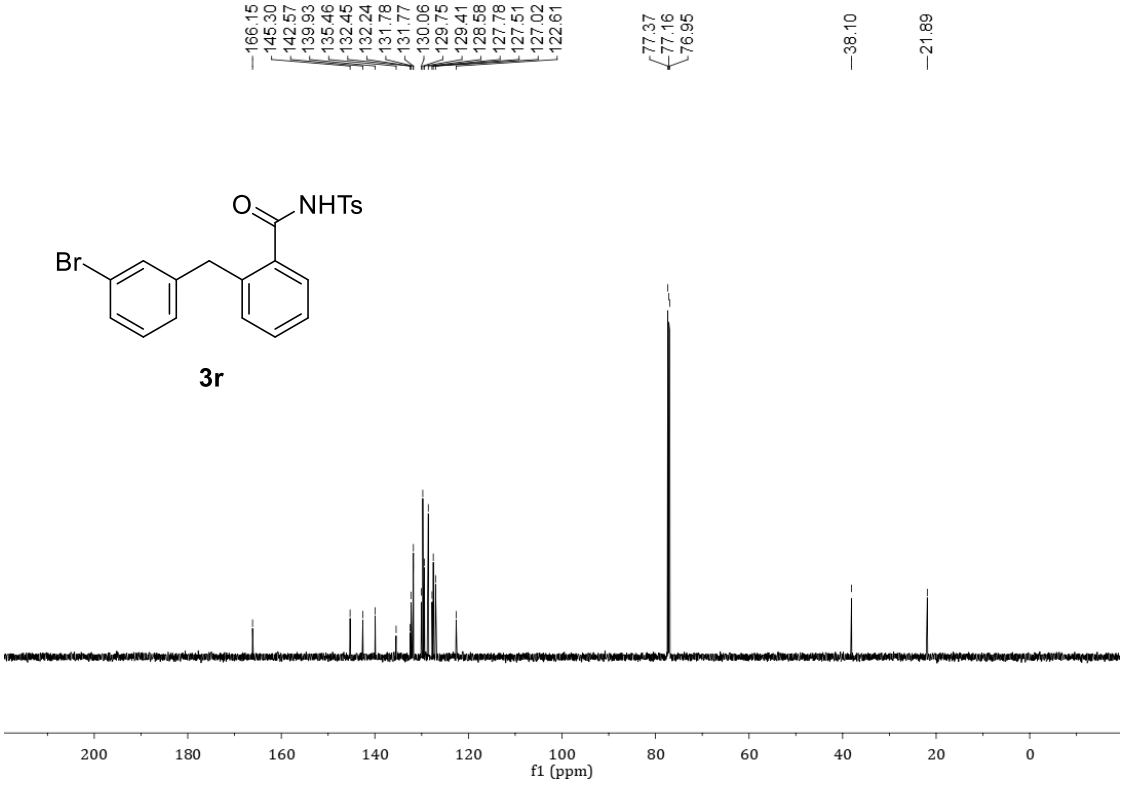
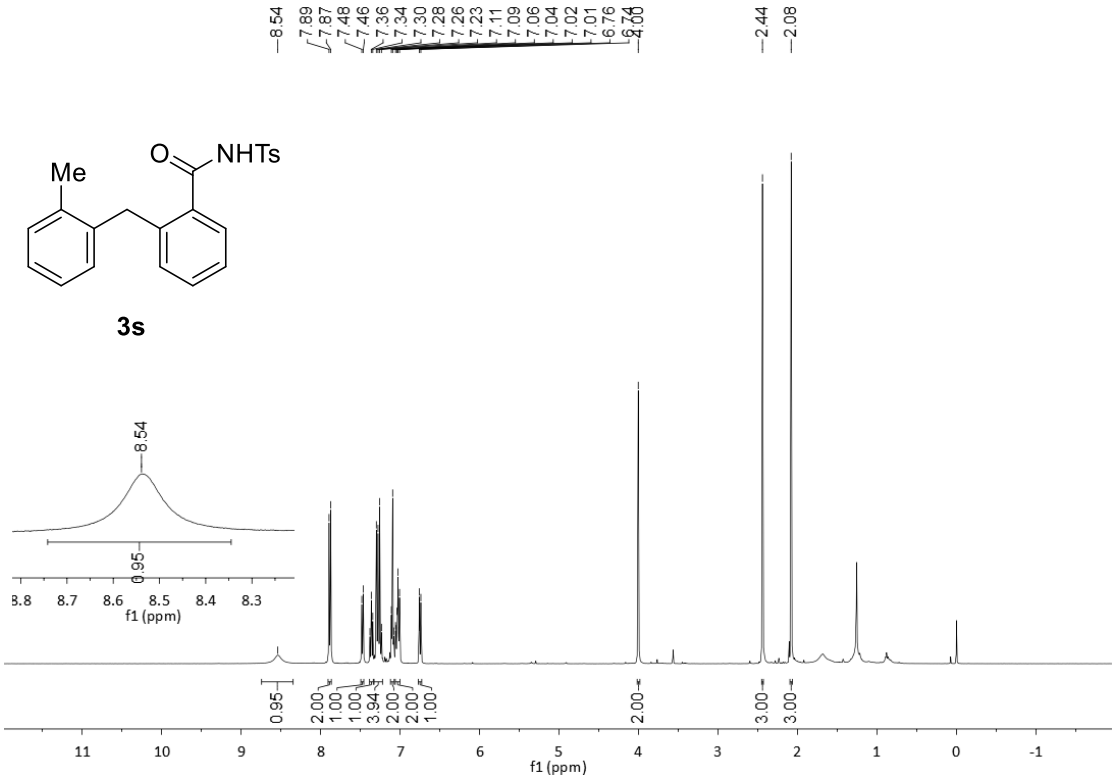


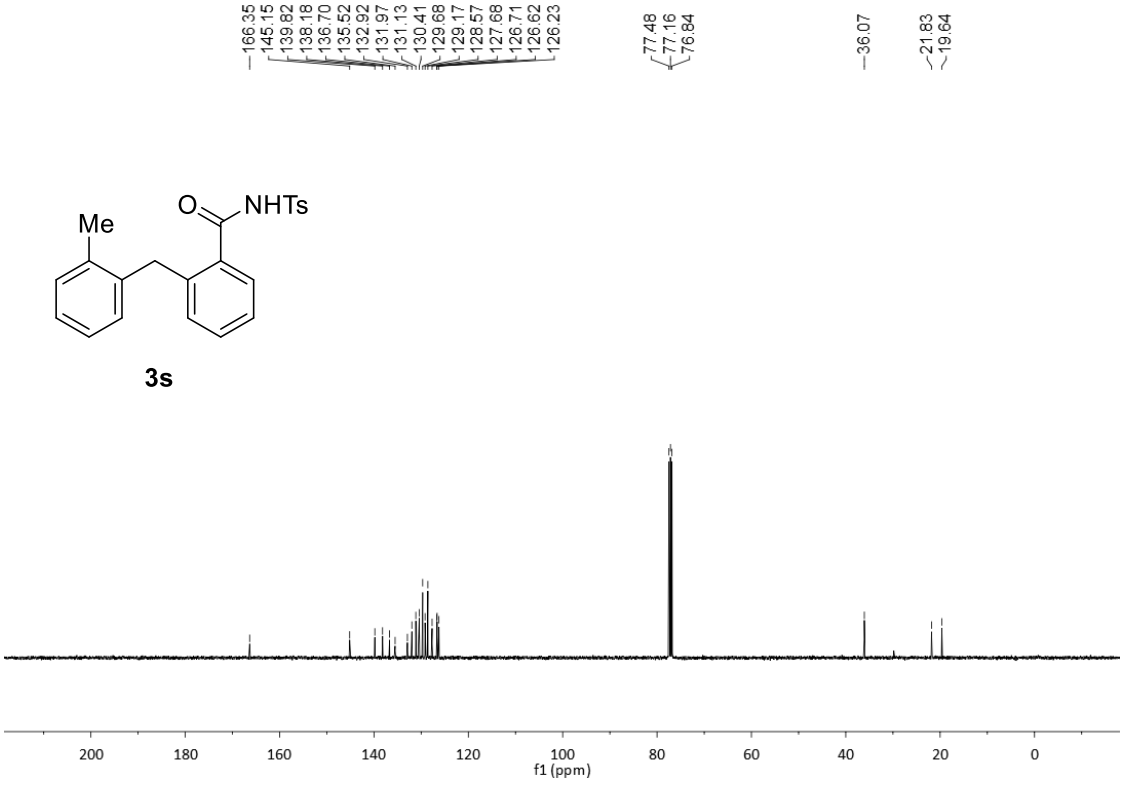

## $^{13}$C NMR (150 MHz, $CDCl_3$)



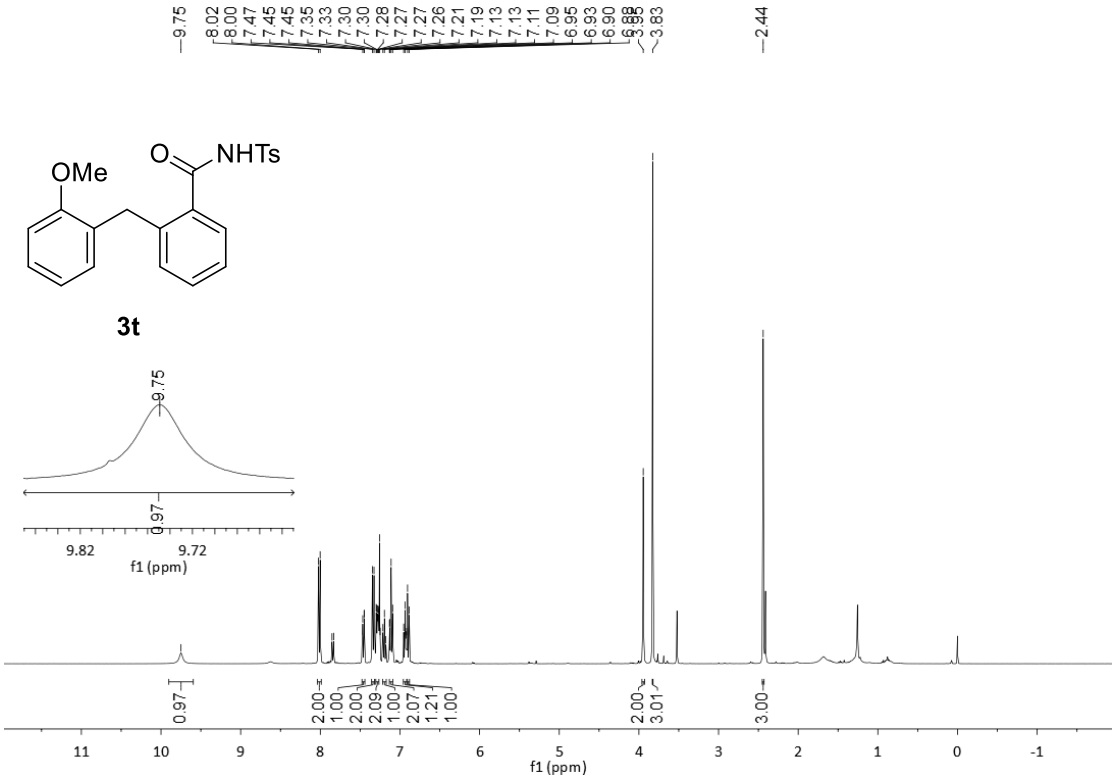
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



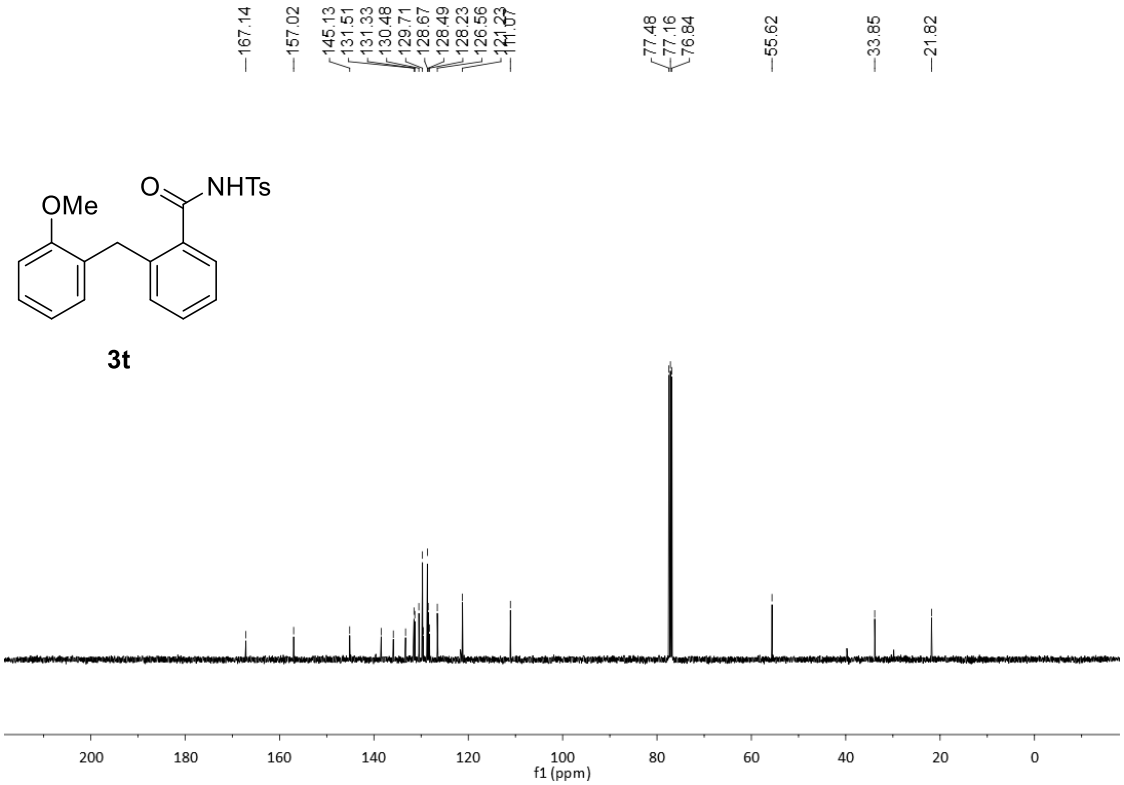

**$^{13}$C NMR (100 MHz, $CDCl_3$)**



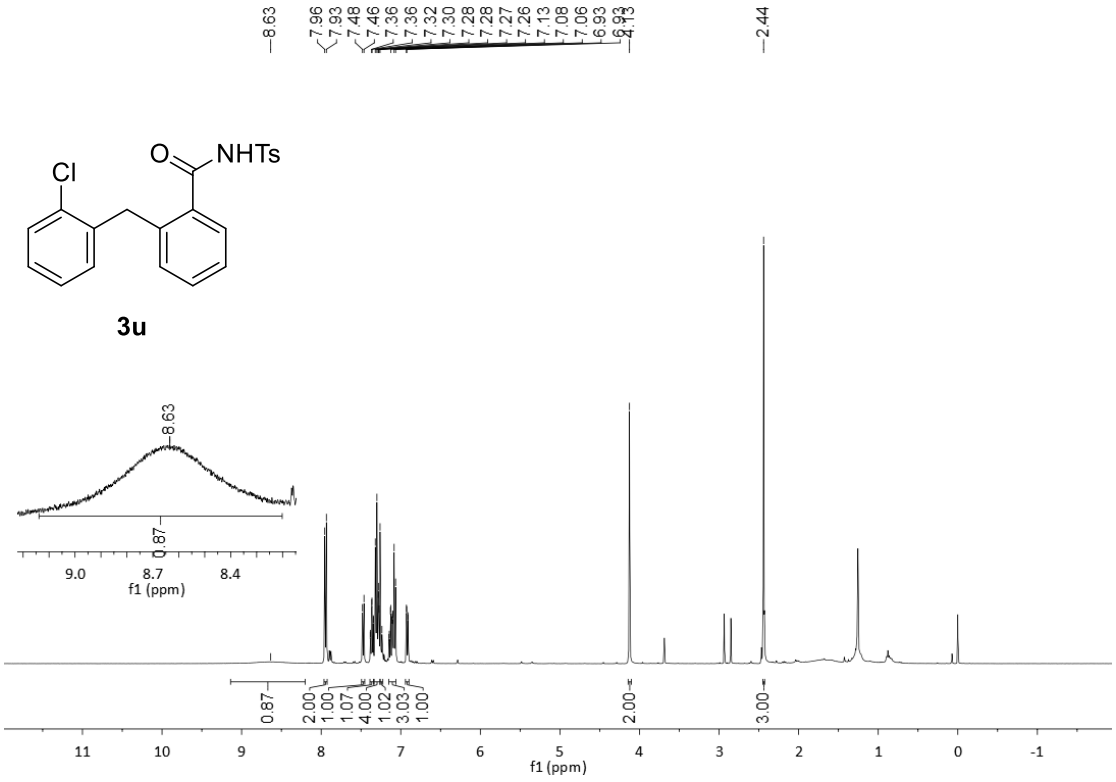
## $^{1}$H NMR (400 MHz, $CDCl_3$)



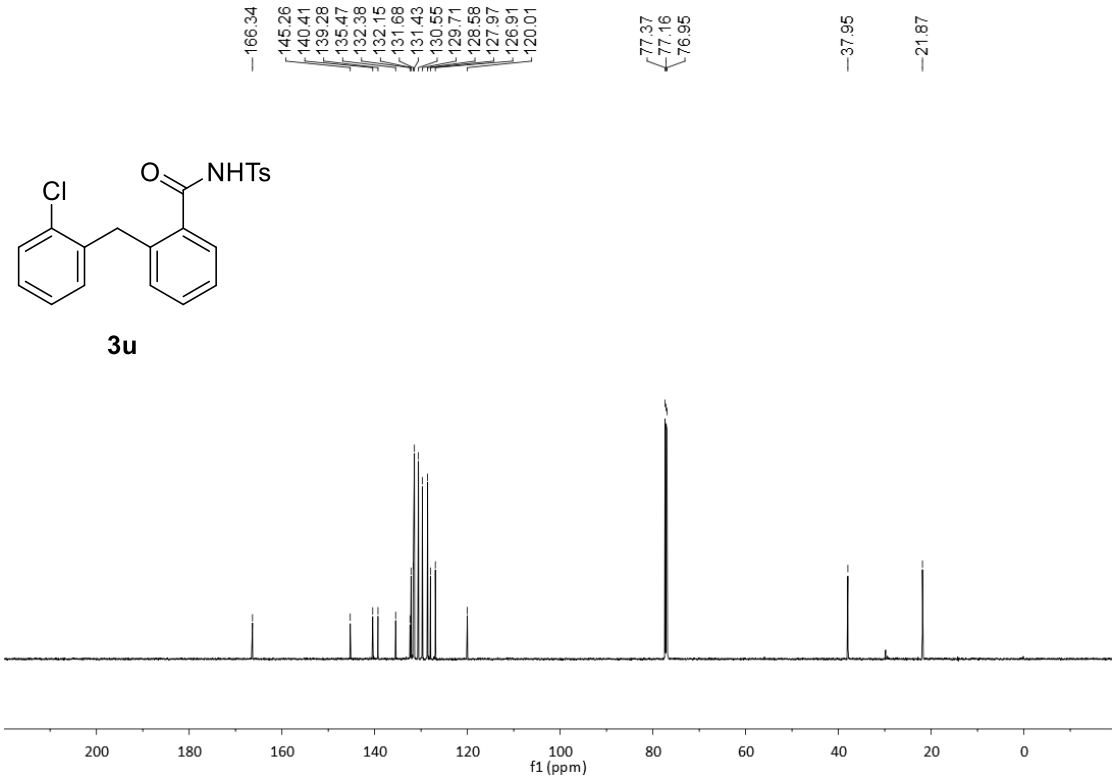

## $^{13}$C NMR (100 MHz, $CDCl_3$)



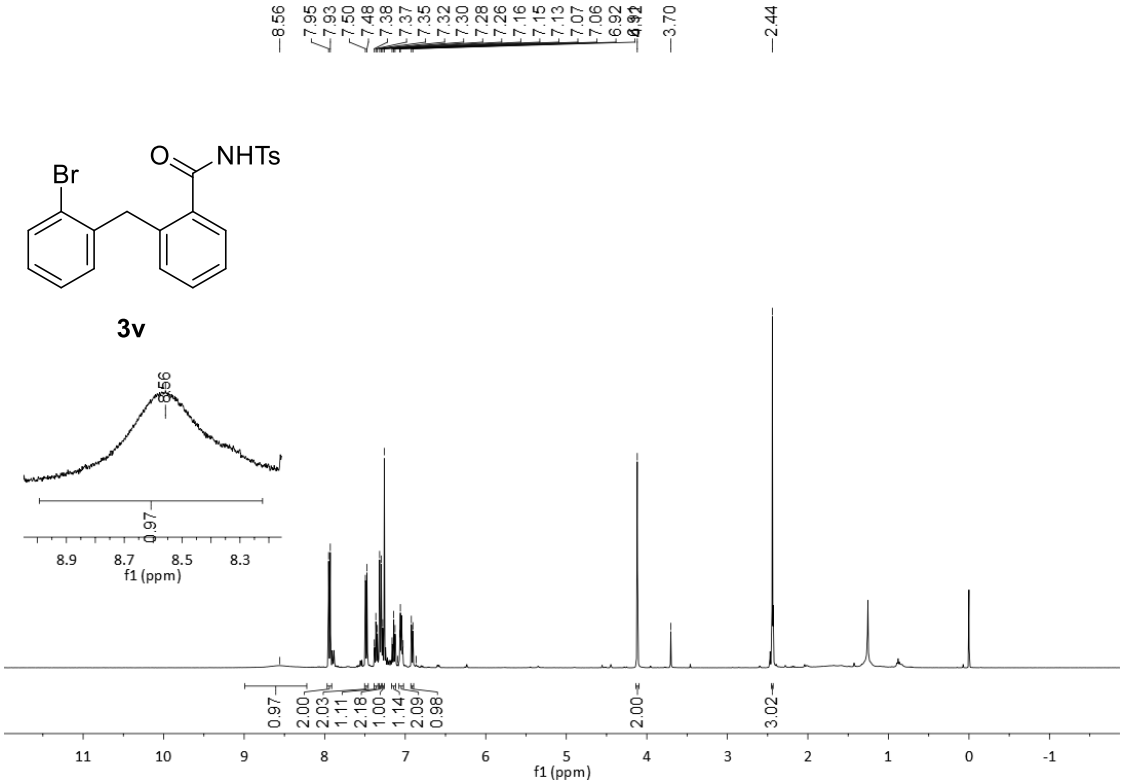
## $^{1}$H NMR (400 MHz, $CDCl_3$)



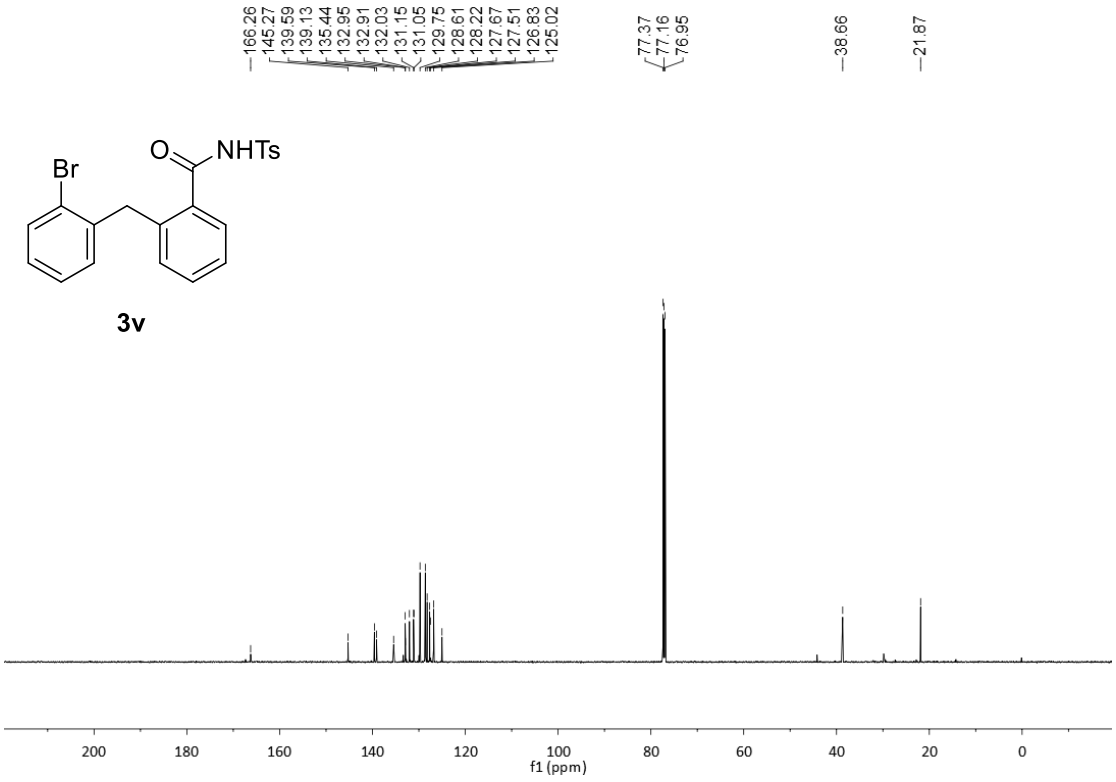

## $^{13}$C NMR (150 MHz, $CDCl_3$)



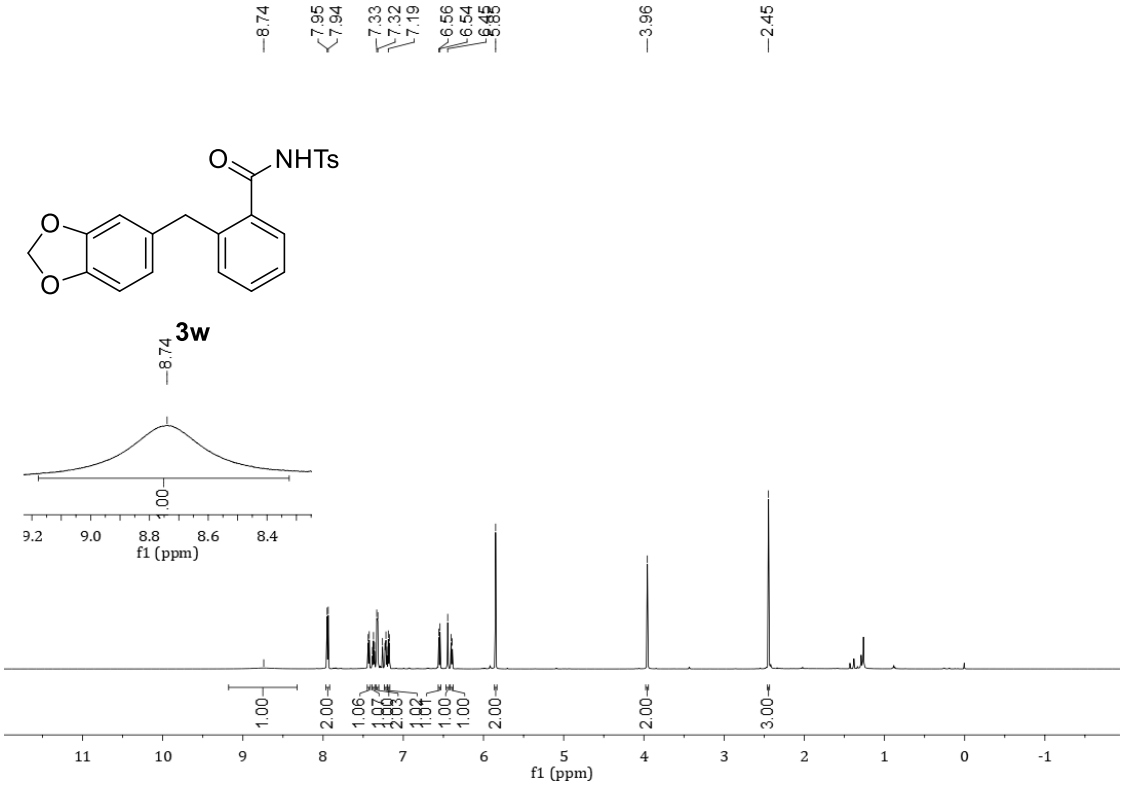
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



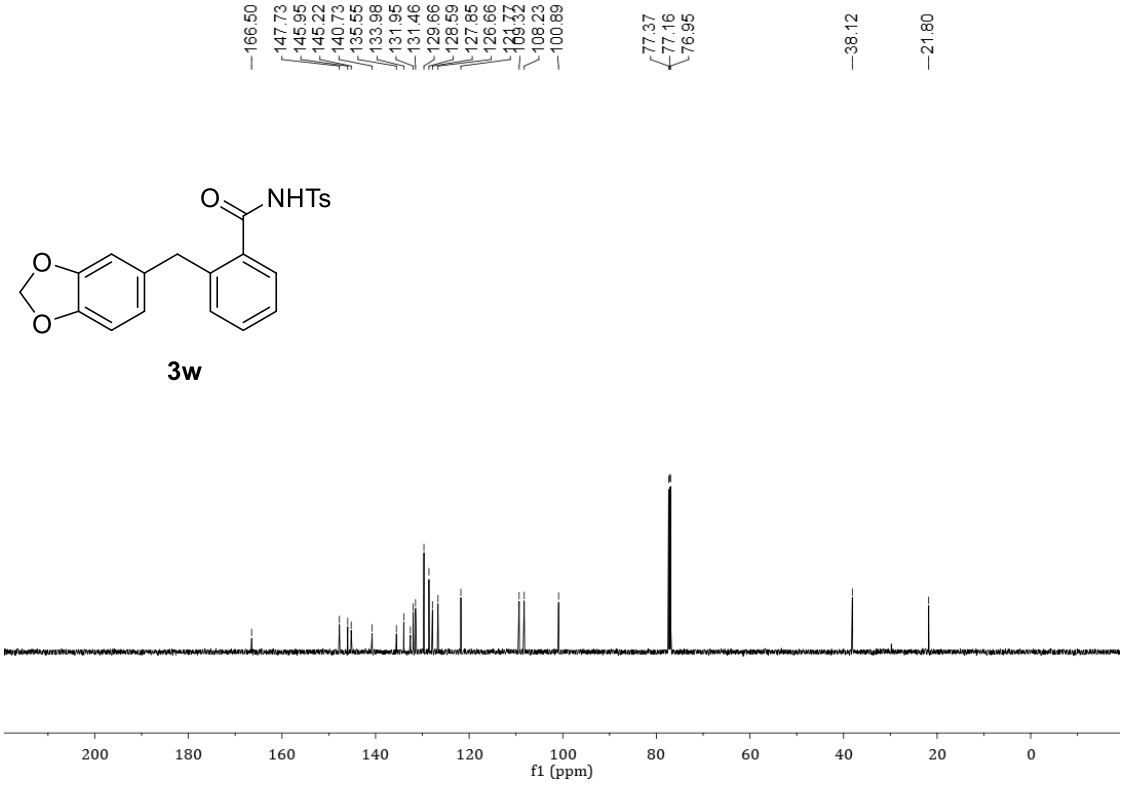

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



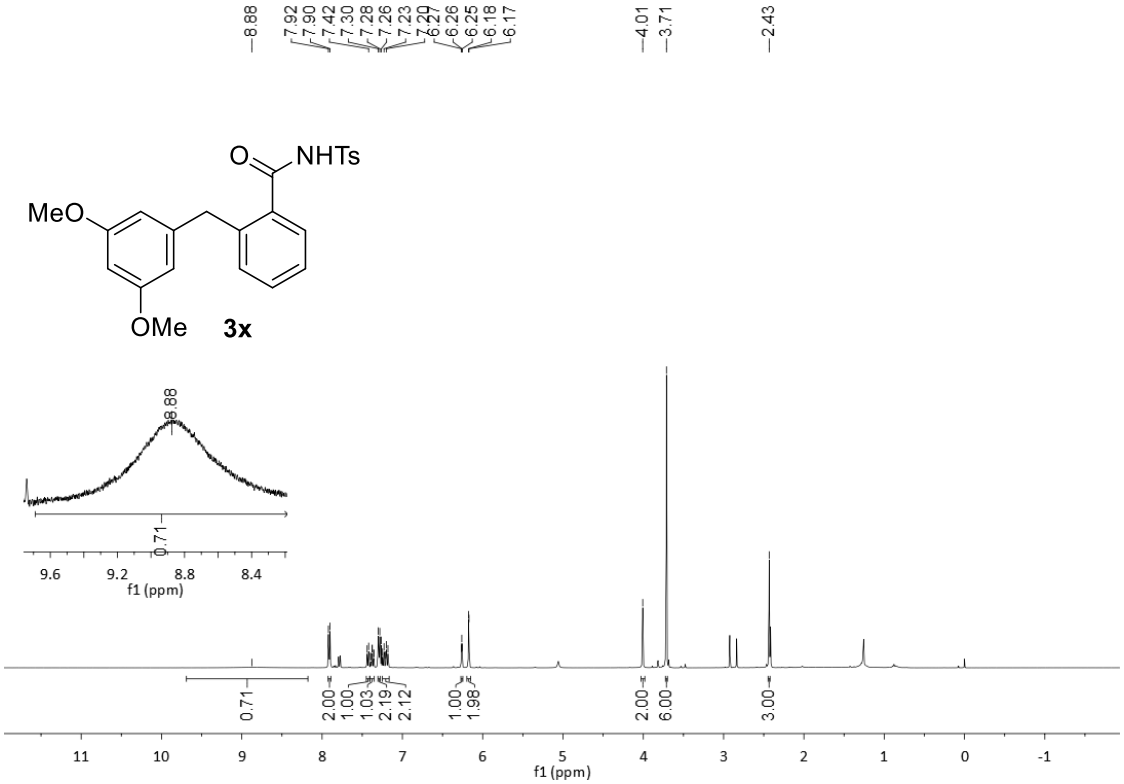
## $^{1}$H NMR (600 MHz, $CDCl_3$)




## $^{13}$C NMR (150 MHz, $CDCl_3$)



## $^{1}$H NMR (400 MHz, $CDCl_3$)

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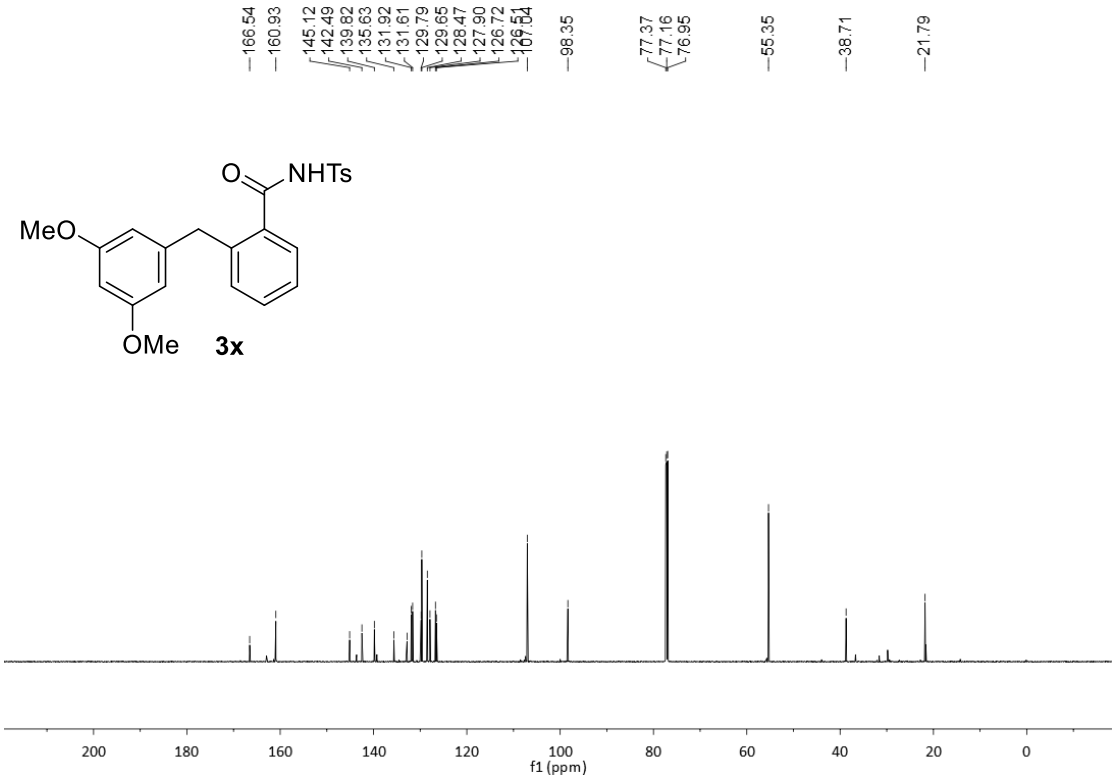
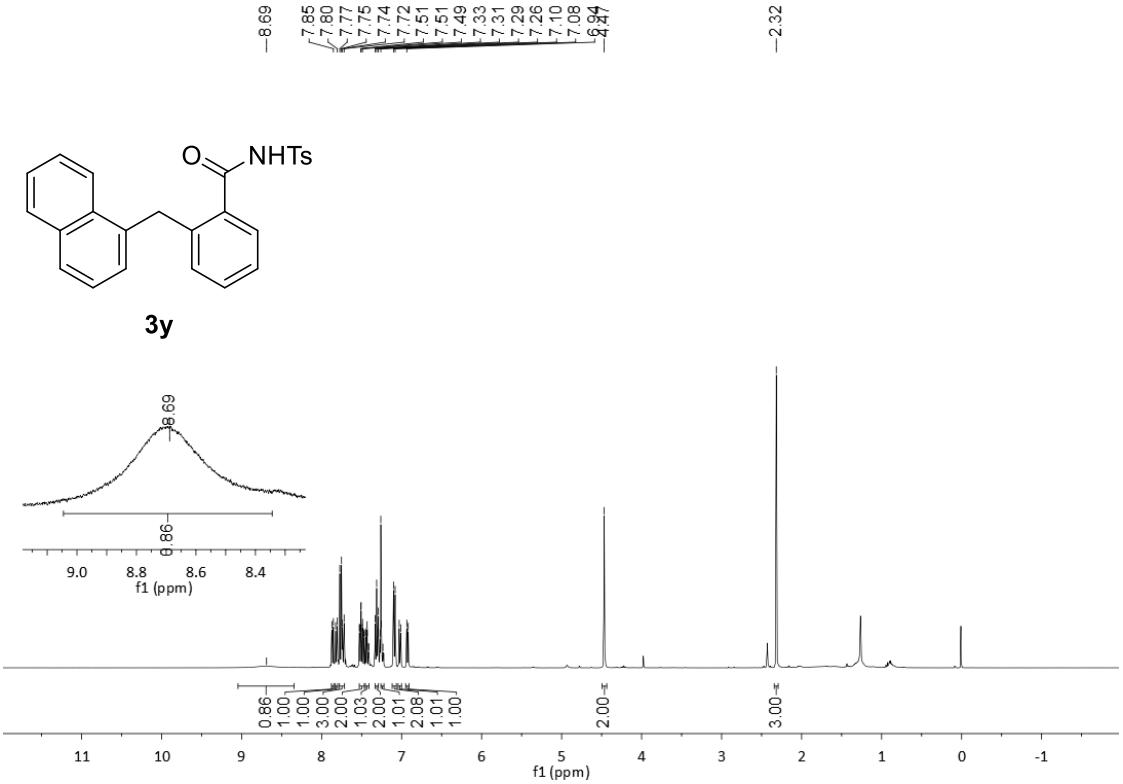
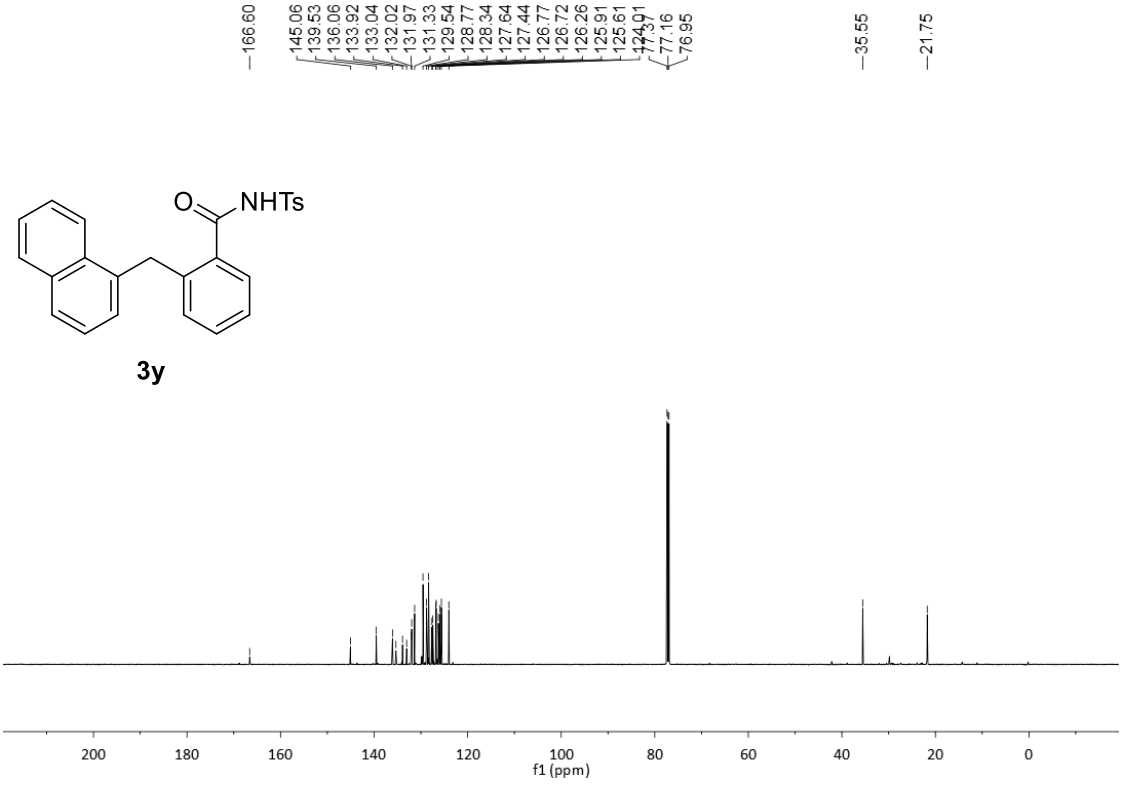


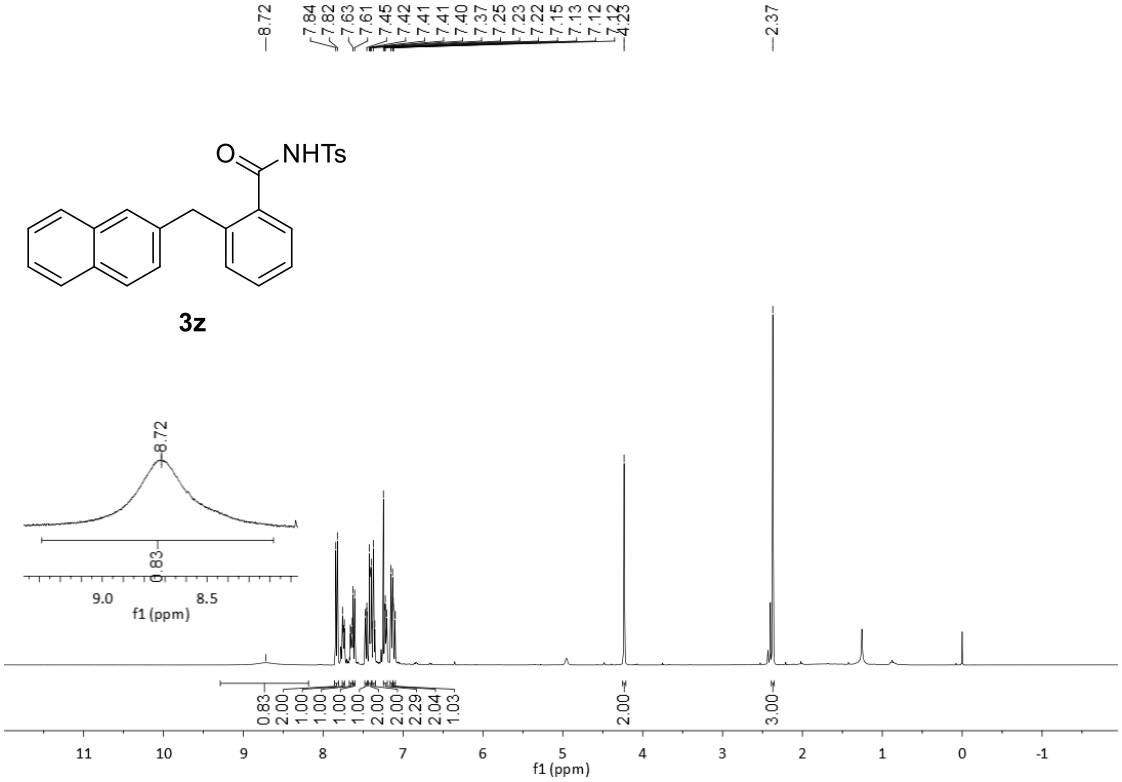
## $^{1}$H NMR (400 MHz, $CDCl_3$)



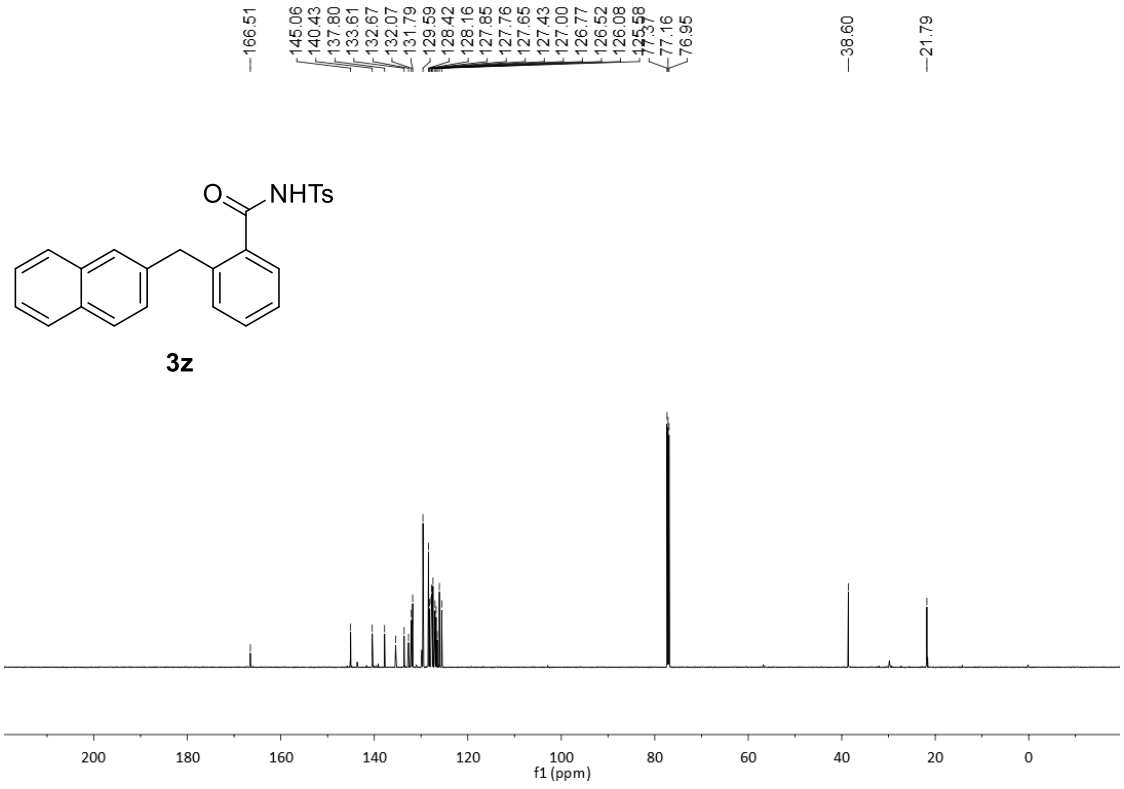

## $^{13}$C NMR (150 MHz, $CDCl_3$)



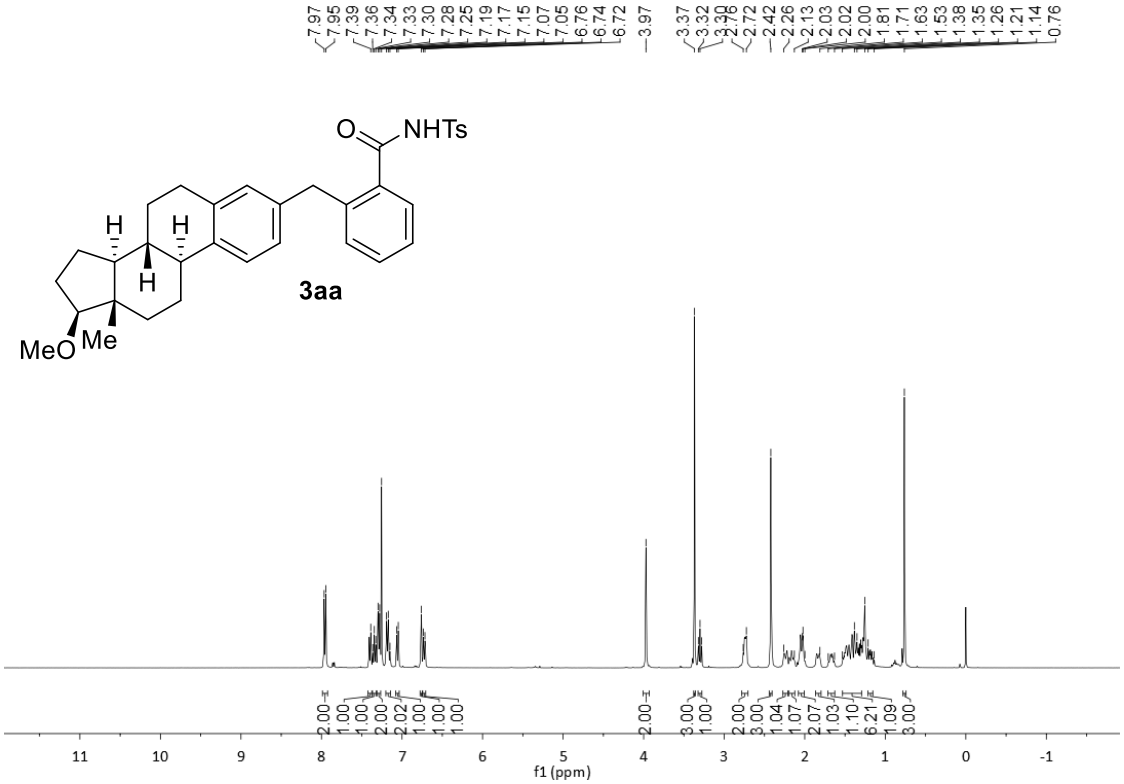
## $^{1}$H NMR (400 MHz, $CDCl_3$)



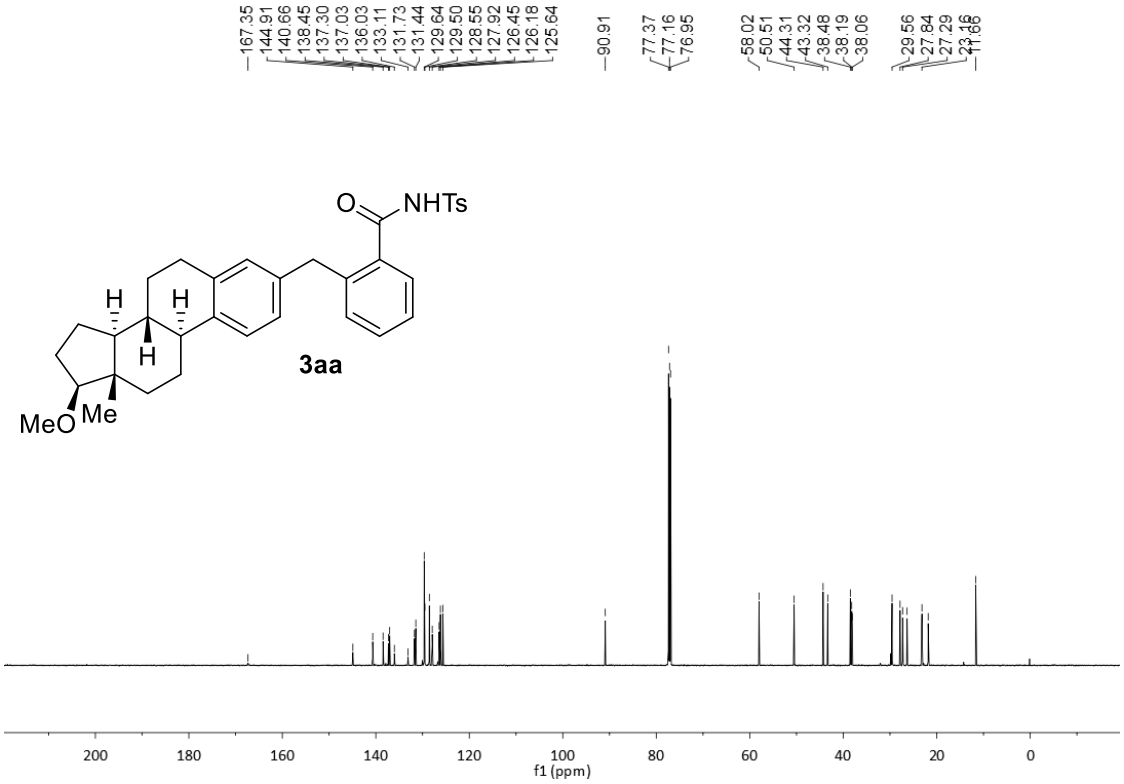

## $^{13}$C NMR (150 MHz, $CDCl_3$)



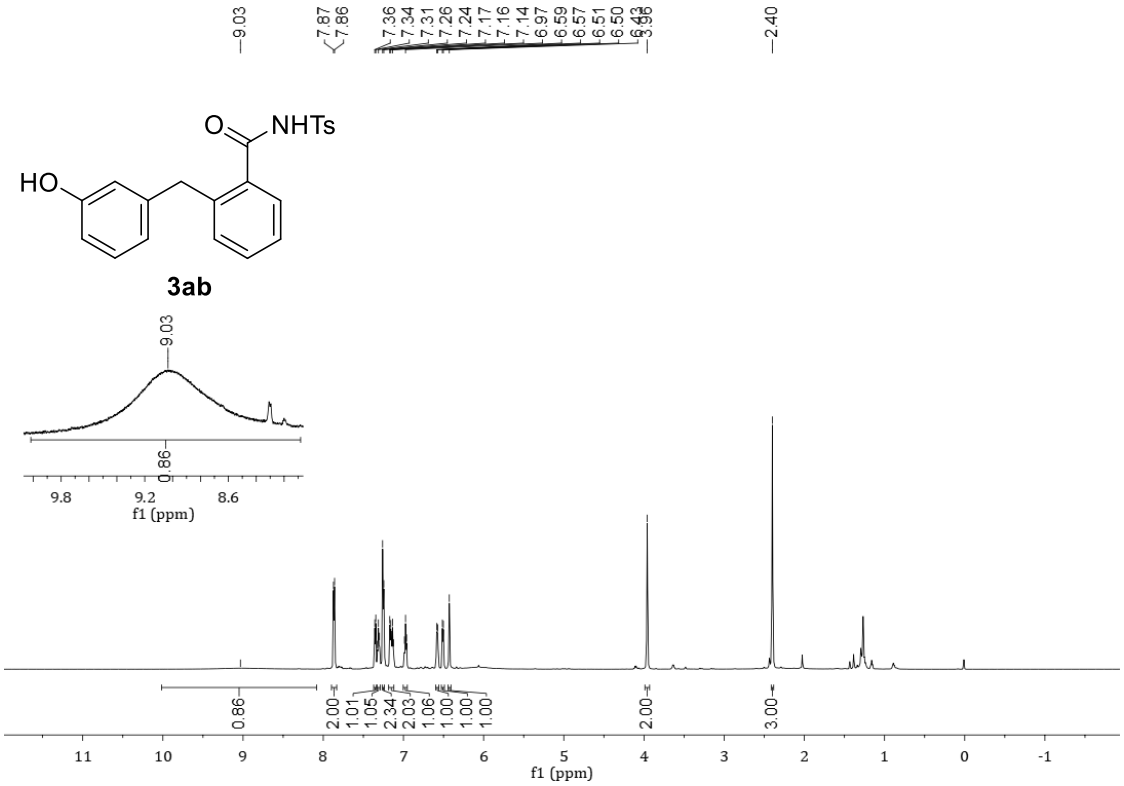
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



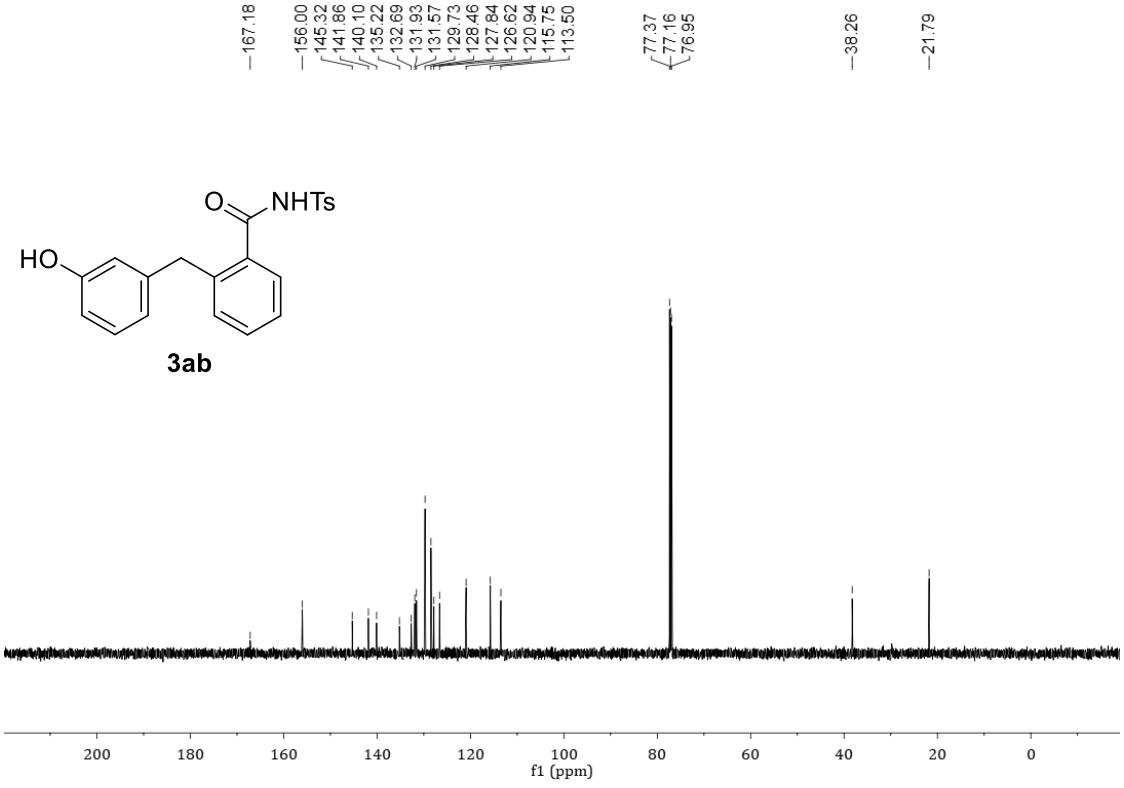

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



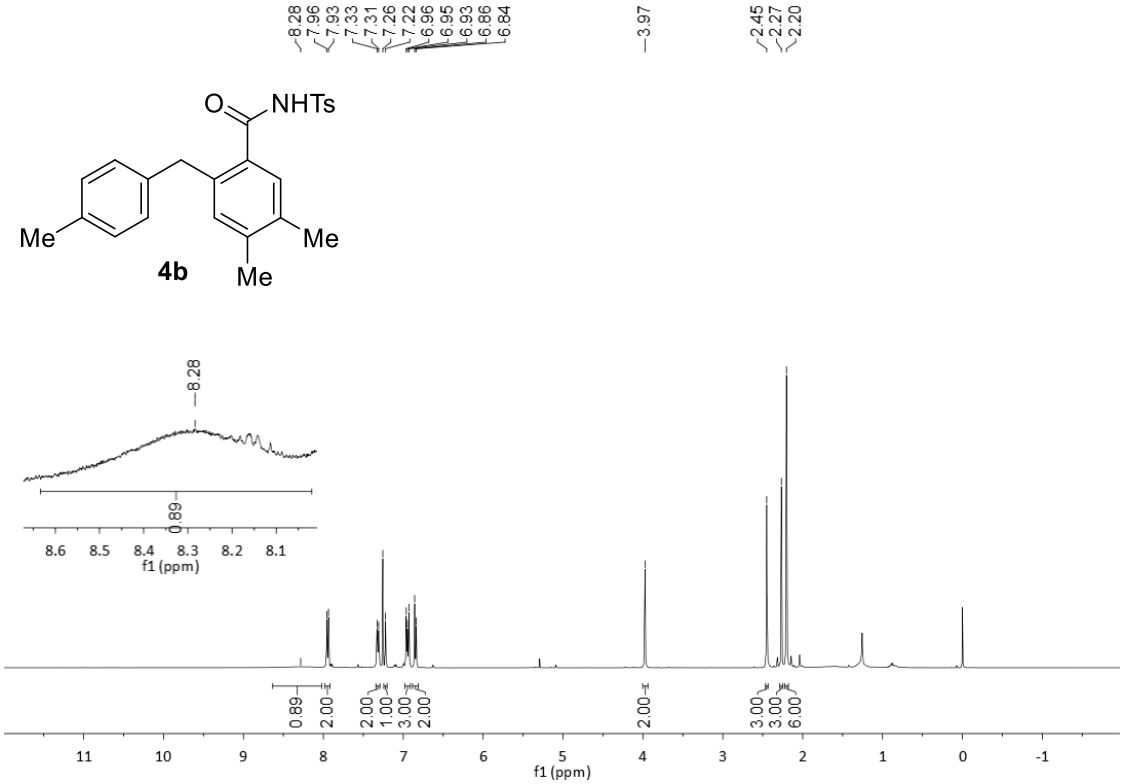
## $^{1}$H NMR (600 MHz, $CDCl_3$)



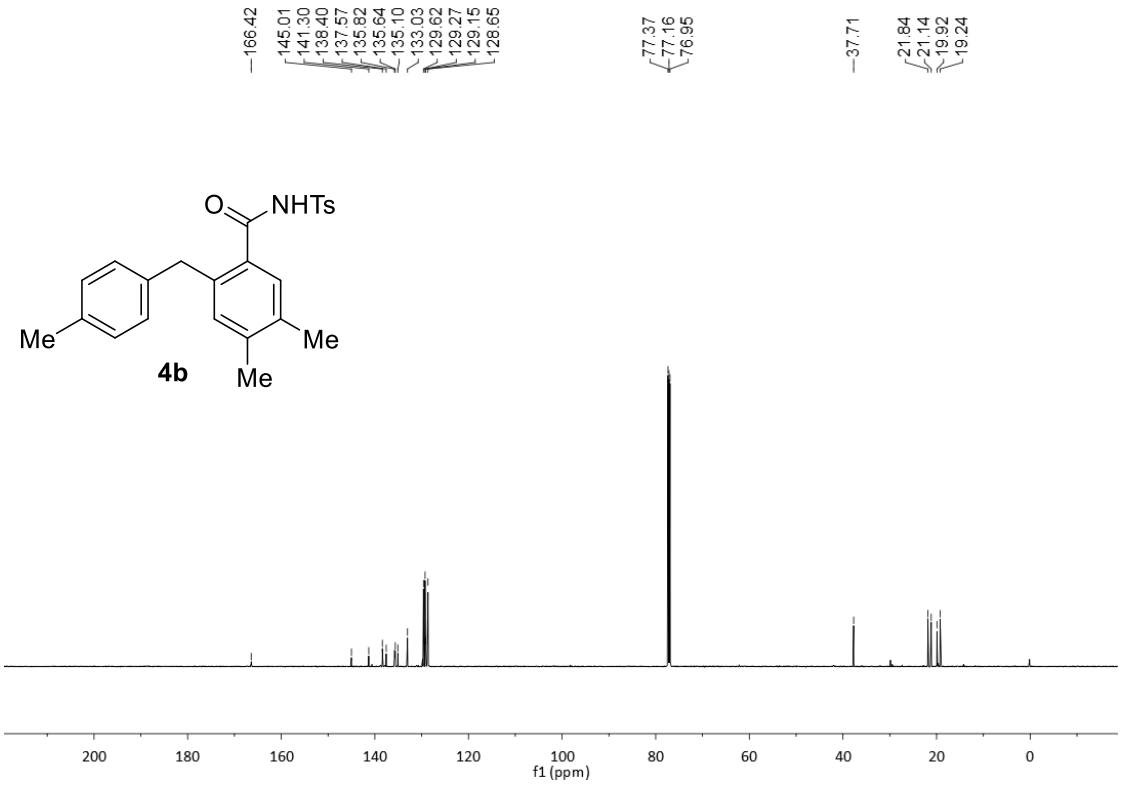

## $^{13}$C NMR (150 MHz, $CDCl_3$)



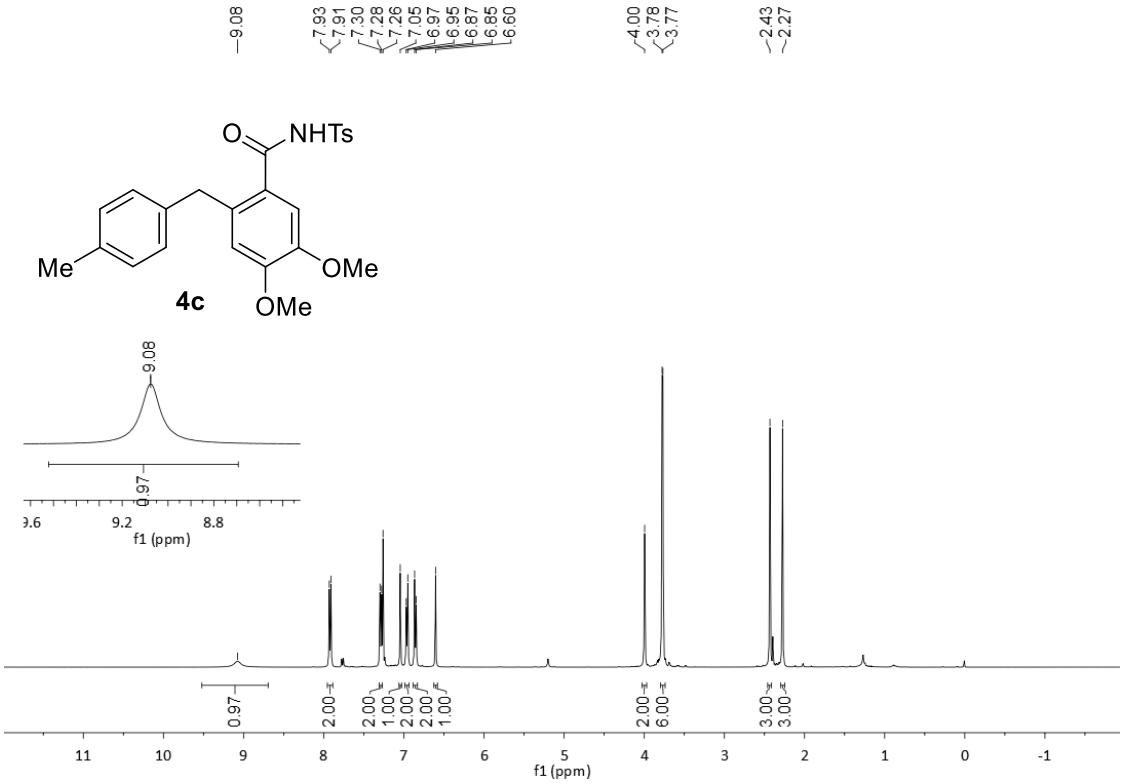
**$^{1}$H NMR (400 MHz, $CDCl_3$)**



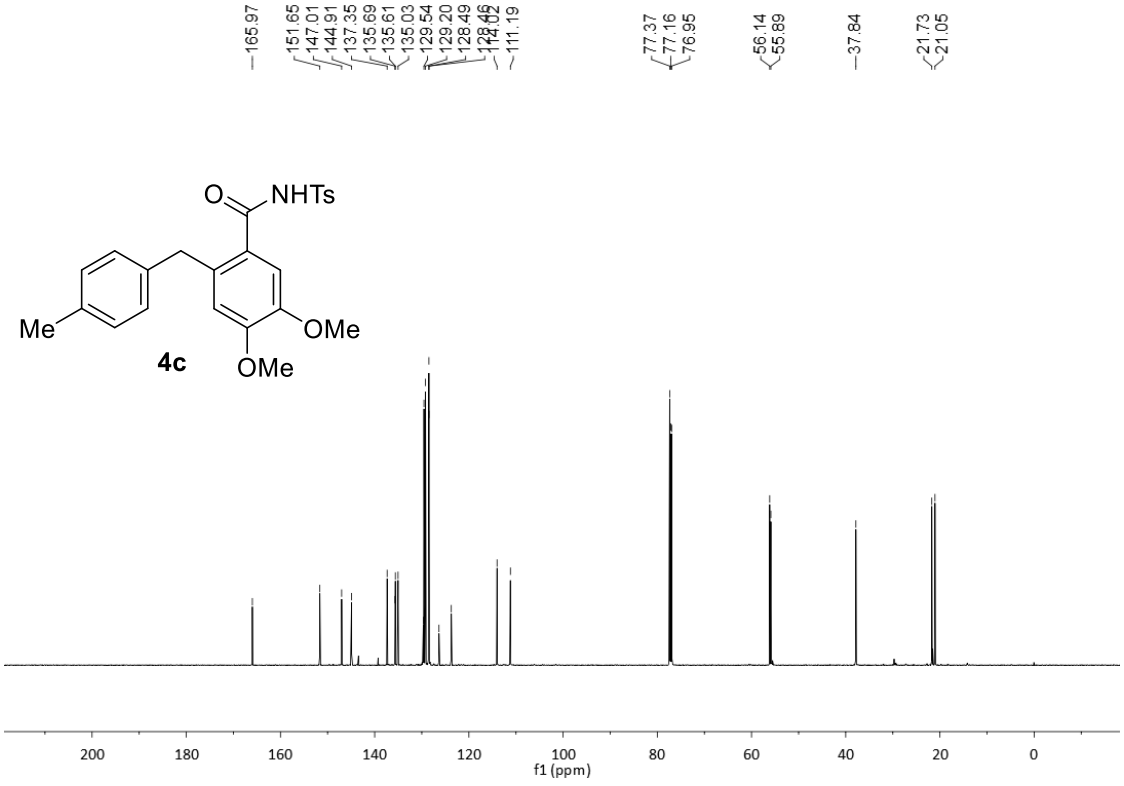

**$^{13}$C NMR (150 MHz, $CDCl_3$)**



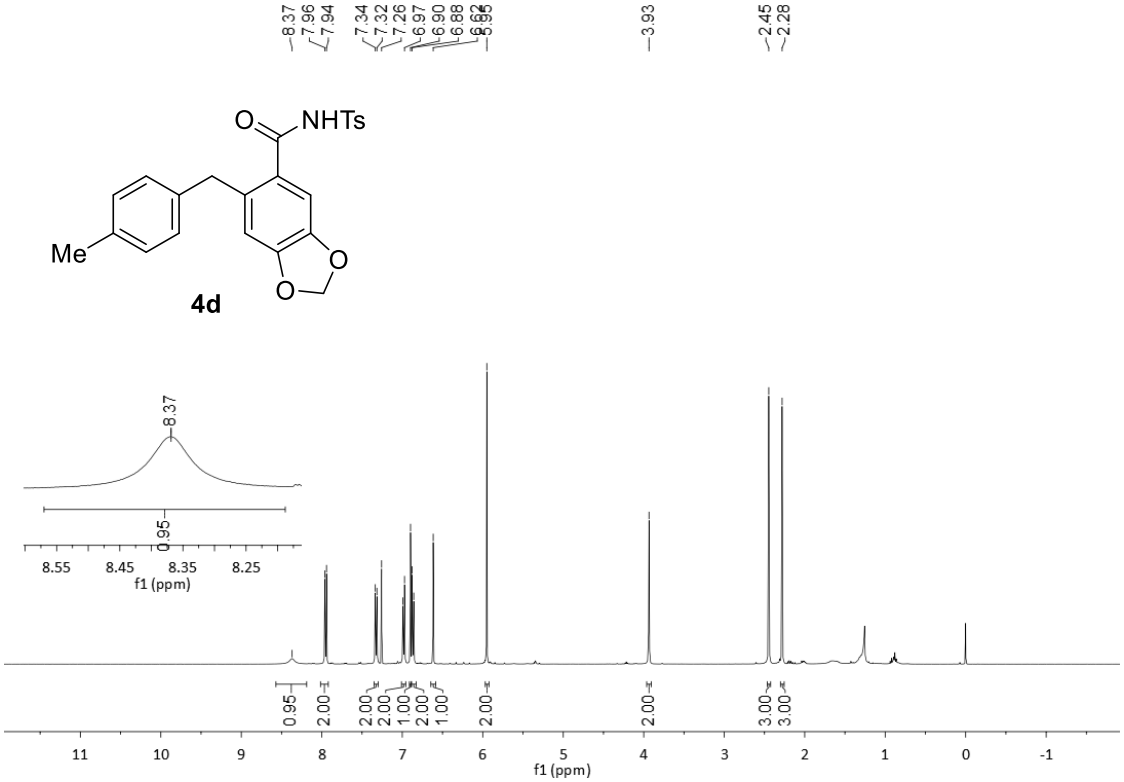
## $^{1}$H NMR (400 MHz, $CDCl_3$)



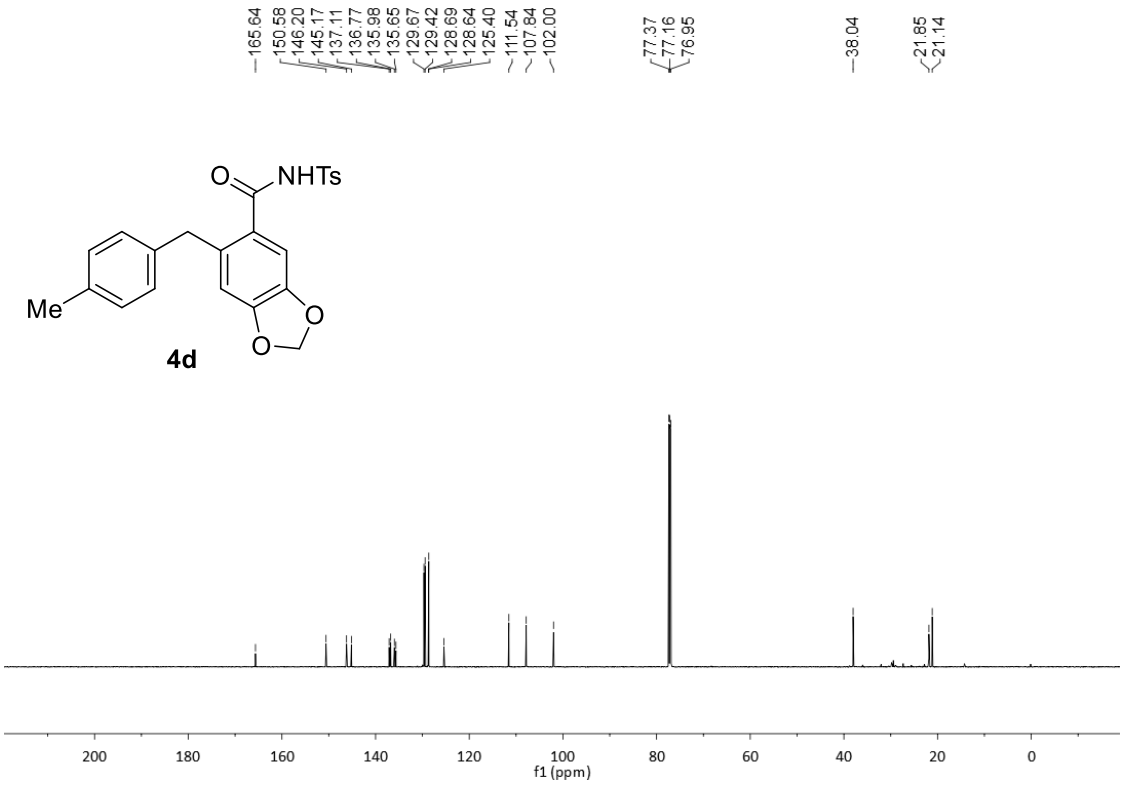

## $^{13}$C NMR (150 MHz, $CDCl_3$)



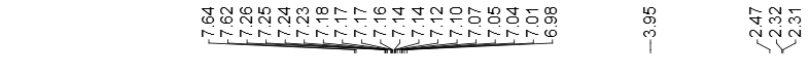
**$^{1}$H NMR (400 MHz, $CDCl_3$)**

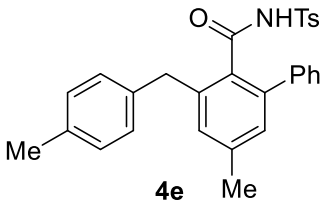



**$^{13}$C NMR (150 MHz, $CDCl_3$)**

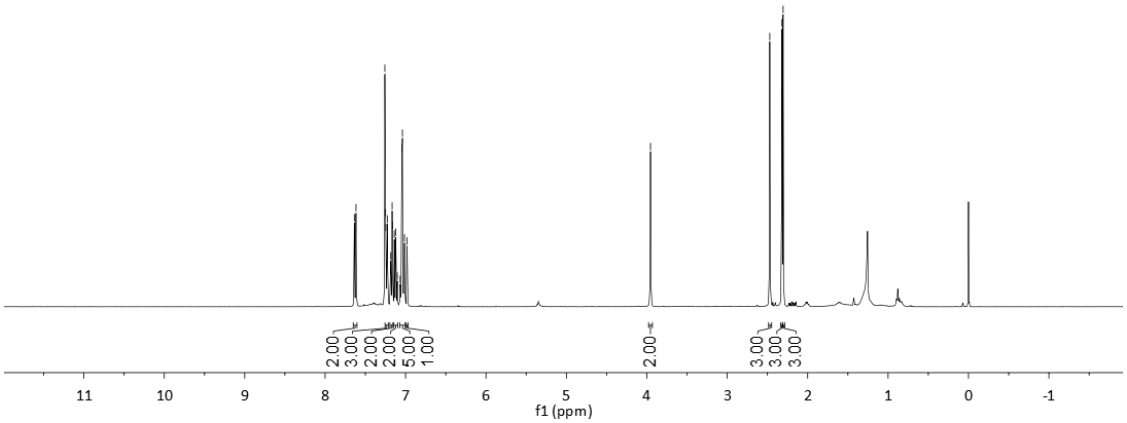


## $^{1}$H NMR (400 MHz, $CDCl_3$)

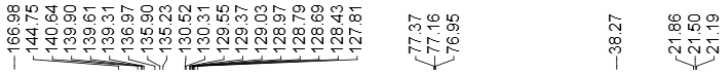


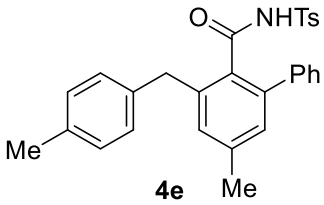




**4e**

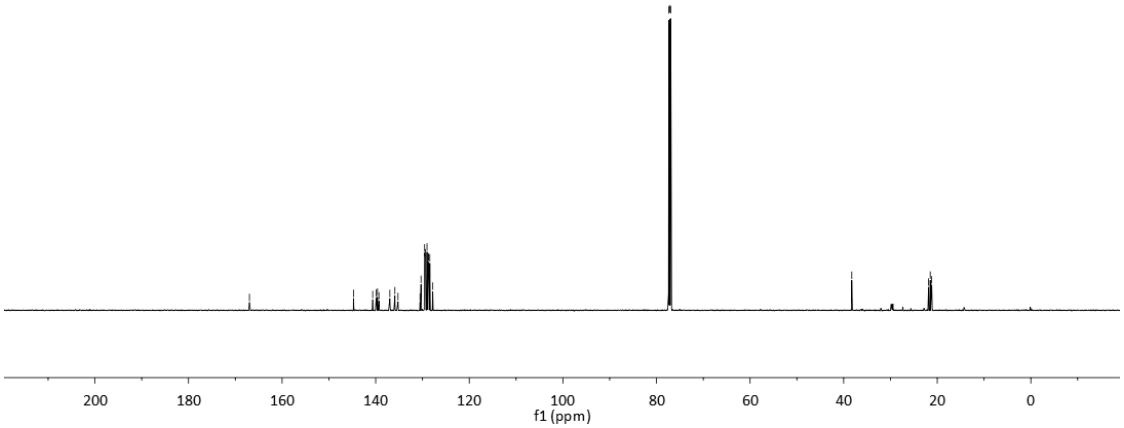



## $^{13}$C NMR (150 MHz, $CDCl_3$)

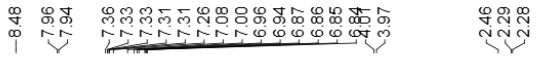


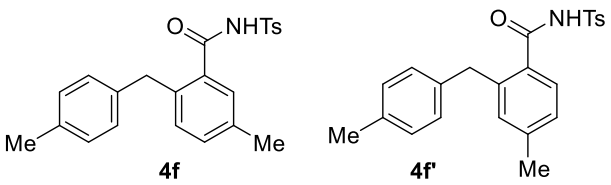




**4e**



## $^{1}$H NMR (400 MHz, $CDCl_3$)

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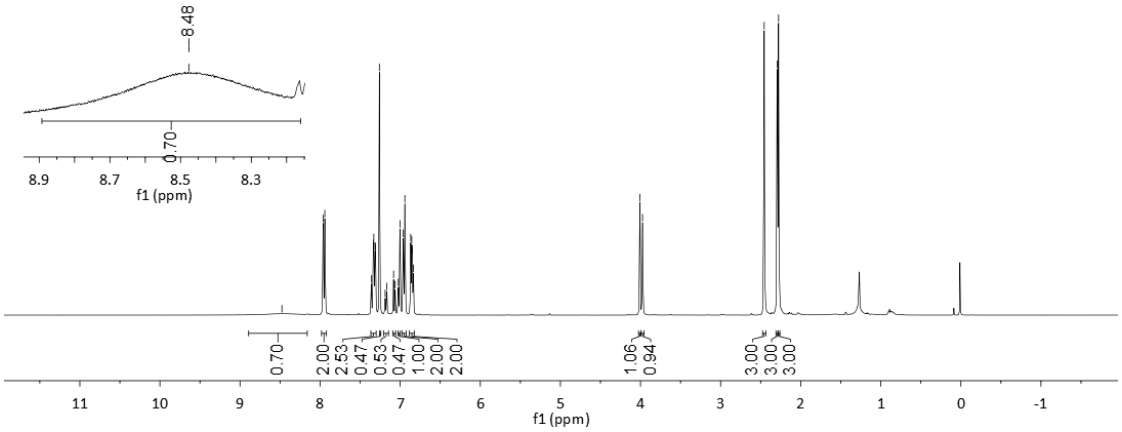
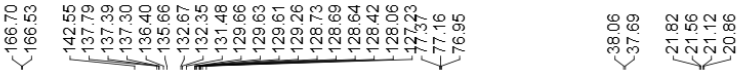
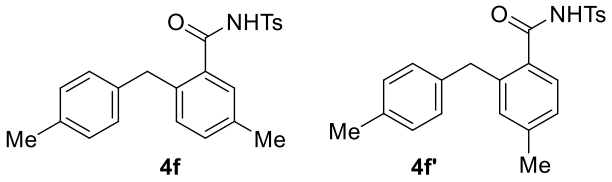



## $^{13}$C NMR (150 MHz, $CDCl_3$)

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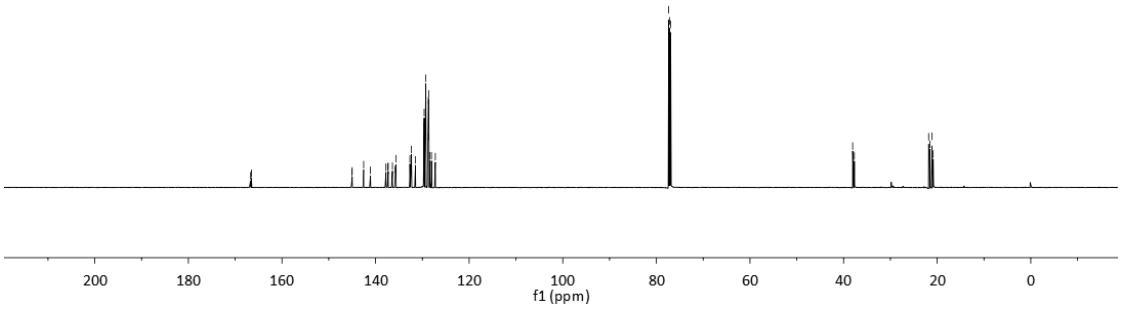
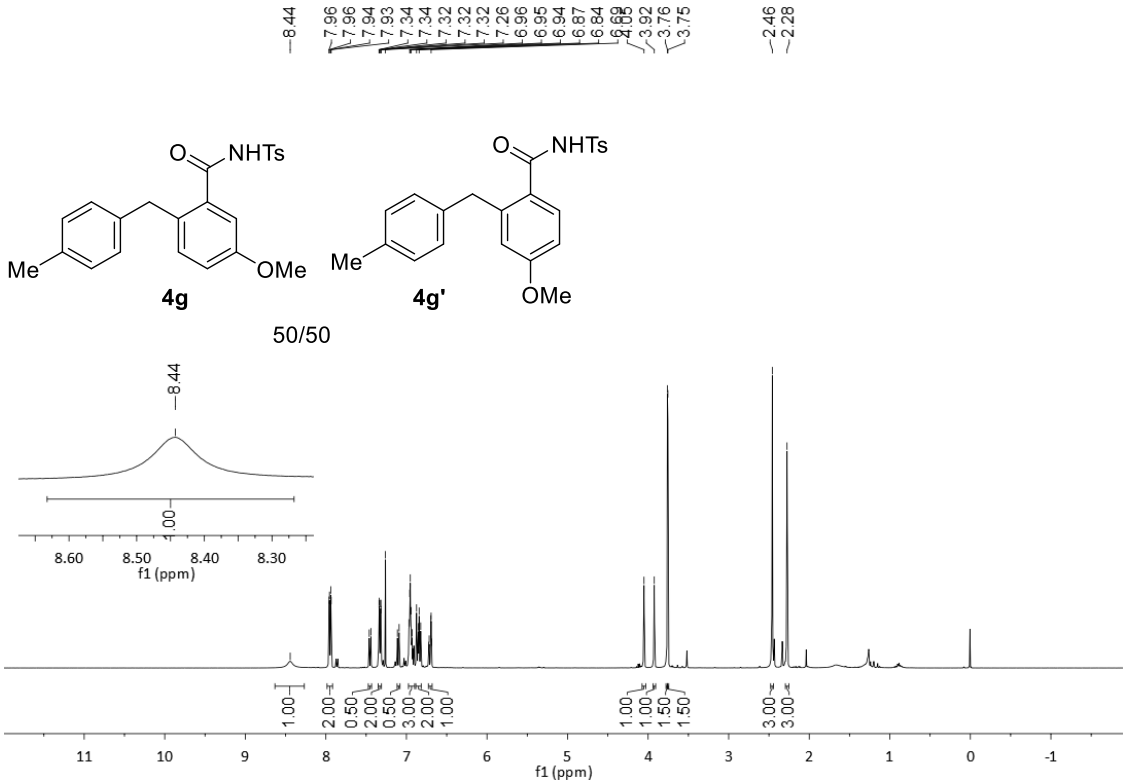
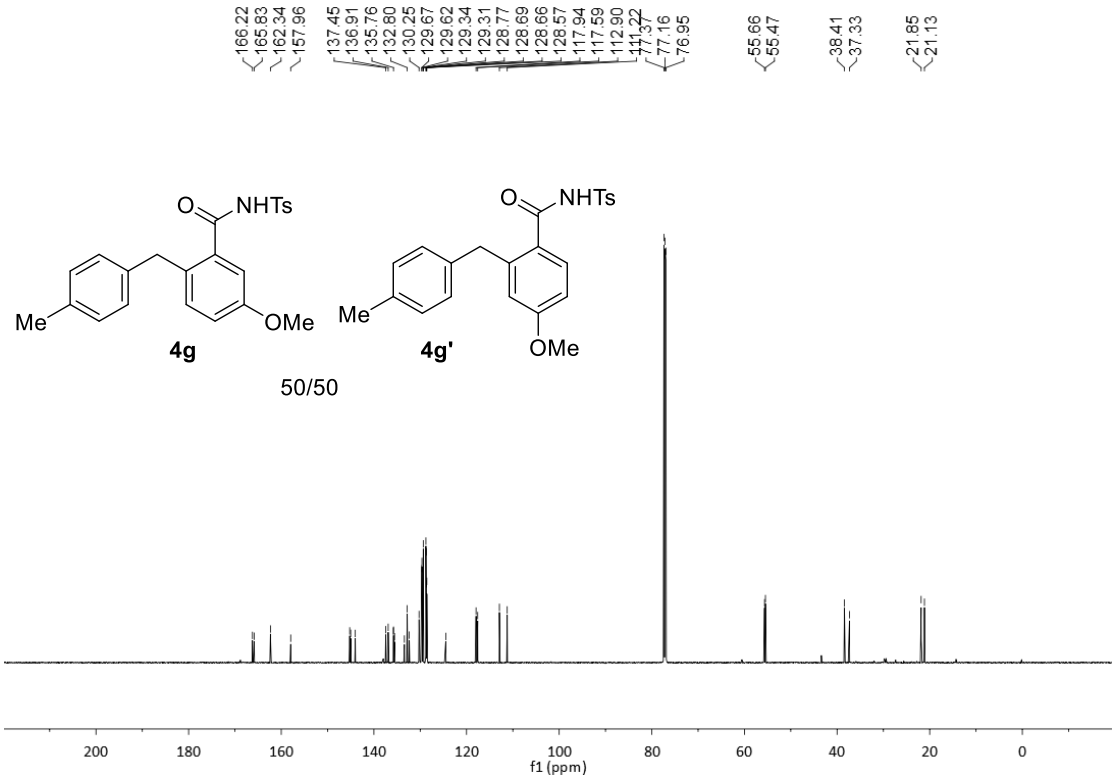


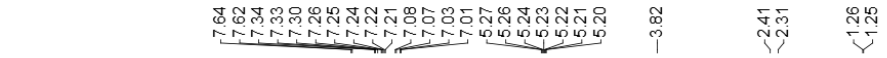
## $^{1}$H NMR (400 MHz, $CDCl_3$)

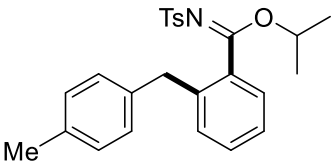



## $^{13}$C NMR (150 MHz, $CDCl_3$)

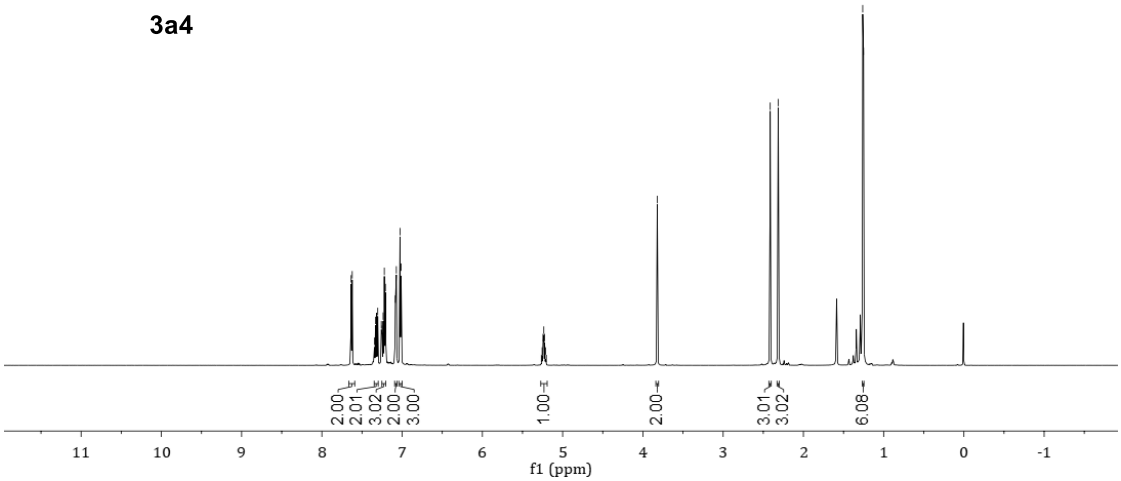


## $^{1}$H NMR (600 MHz, $CDCl_3$)

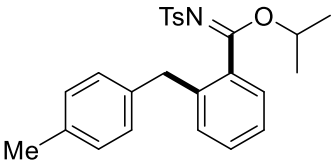


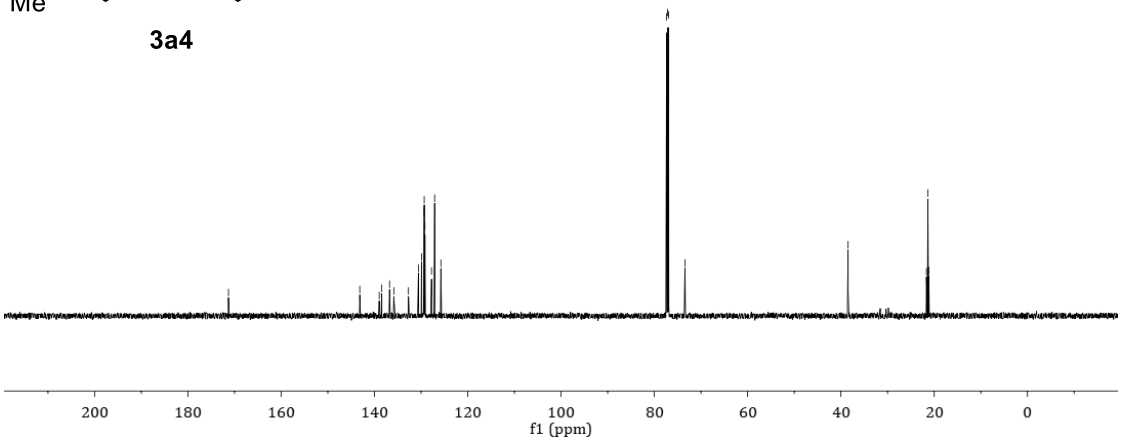

**3a4**



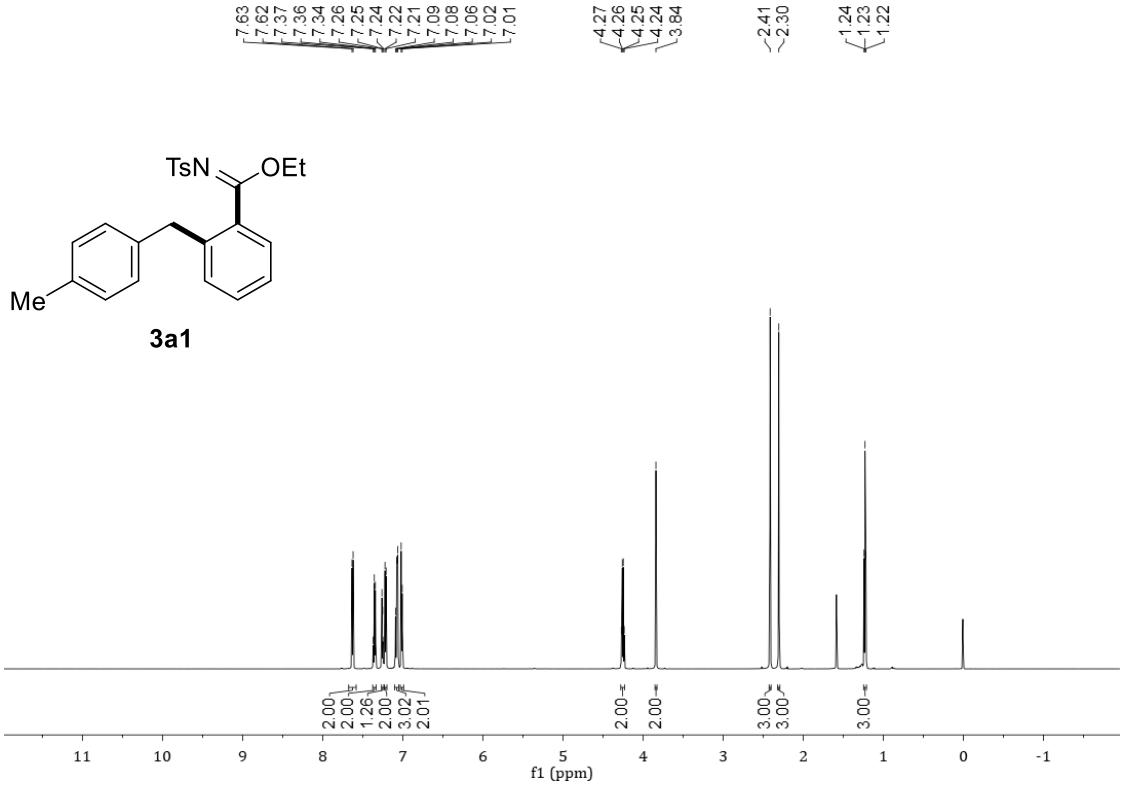

## $^{13}$C NMR (150 MHz, $CDCl_3$)


**3a4**



## $^{1}$H NMR (600 MHz, $CDCl_3$)




## $^{13}$C NMR (150 MHz, $CDCl_3$)