Diversity-Oriented Approach to 1,2-Dihydroisoquinolin-3(4*H*)-imines via Copper(I)-Catalyzed Reaction of (*E*)-2-Ethynylphenylchalcone, Sulfonyl Azide, and Amine

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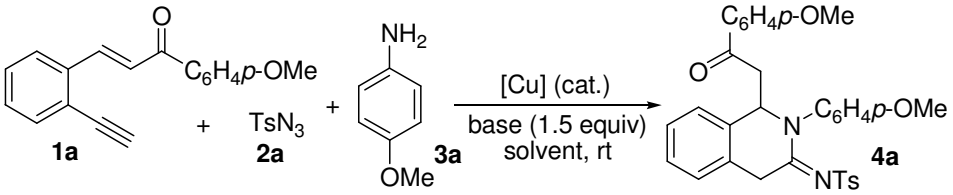
Supporting Information

General experimental methods:

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All reactions were performed in reaction tubes under N_2. The Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25-35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane (TMS) on the δ scale.

X-ray Crystallographic Analysis. Suitable crystals were selected under a microscope. Data collections were performed on a Bruker SMART APEX (at 293K) diffractometer with CCD area detector using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using SAINT (*SAINTPlus Data Reduction and Correction Program* v. 6.02 a; Bruker AXS: Madison, WI, **2000**.) and SADABS (Sheldrick, G. M. *SADABS*, A Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, **1998**.) to yield the reflection data file. The structure was solved by using SHELXTL program (Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, **1997**.). Refinement was performed on F^2 anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. CCDC 815165 (compound **4a**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336033; or deposit@ccdc.cam.ac.uk).

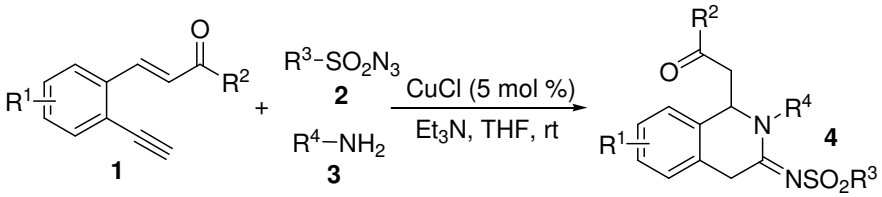
Table 1 Initial studies for the copper-catalyzed three-component reaction of (*E*)-2-ethynylphenylchalcone **1a**, tosyl azide **2a**, and *p*-anisidine **3a**.



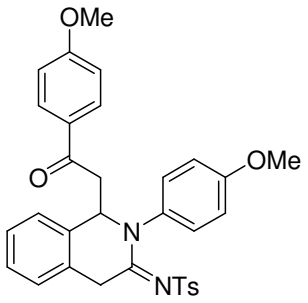
entry	[Cu] cat	base / equiv	solvent	Yield (%)[a]
1	CuI (10 mol %)	Et_3N / 3.0	CH_3CN	62
2	CuBr (10 mol %)	Et_3N / 3.0	CH_3CN	78
3	CuCl (10 mol %)	Et_3N / 3.0	CH_3CN	81
4	$Cu(OTf)_2$ (10mol %)	Et_3N / 3.0	CH_3CN	16
5	IPr/CuCl (10 mol%)	Et_3N / 3.0	CH_3CN	7
6	CuCl (5 mol %)	Et_3N / 3.0	CH_3CN	82
7	CuCl (2 mol %)	Et_3N / 3.0	CH_3CN	71
8	none	Et_3N / 3.0	CH_3CN	0
9	CuCl (5 mol %)	$^iPr_2NEt$ / 3.0	CH_3CN	65
10	CuCl (5 mol %)	DBU / 3.0	CH_3CN	trace
11	CuCl (5 mol %)	DABCO / 3.0	CH_3CN	48
12	CuCl (5 mol %)	pyridine / 3.0	CH_3CN	35
13	CuCl (5 mol %)	K_2CO_3 / 3.0	CH_3CN	23
14	CuCl (5 mol %)	NaOAc / 3.0	CH_3CN	37
15	CuCl (5 mol %)	KOH / 3.0	CH_3CN	n.r.
16	CuCl (5 mol %)	Et_3N / 1.5	CH_3CN	81
17	CuCl (5 mol %)	none	CH_3CN	0
18	CuCl (5 mol %)	Et_3N / 1.5	THF	92
19	CuCl (5 mol %)	Et_3N / 1.5	DMSO	31
20	CuCl (5 mol %)	Et_3N / 1.5	Toluene	69
21	CuCl (5 mol %)	Et_3N / 1.5	1,4-dioxane	80
22	CuCl (5 mol %)	Et_3N / 1.5	DCM	42

[a] Isolated yield based on (*E*)-2-ethynylphenylchalcone **1a**.

General procedure for the synthesis of 1,2-dihydroisoquinolin-3(4H)-imines via a copper(I)-catalyzed reaction of (E)-2-ethynylphenylchalcone, sulfonyl azide, and amine.

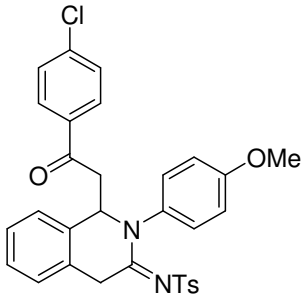


A solution of 2-ethynylphenylchalcone **1** (0.20 mmol) in anhydrous THF (0.5 mL) was added a mixture of sulfonyl azide **2** (0.24 mmol, 1.2 equiv), amine **3** (0.22 mmol, 1.1 equiv) and CuCl (0.01 mmol, 5 mol %) in THF (0.5 mL) at room temperature under N_2 atmosphere. Subsequently triethylamine (43 μL, 0.30 mmol, 1.5 equiv) was slowly added by a syringe. The resulting suspension was stirred at room temperature for about 12hs and the reaction might become clear as a dark yellow solution. After completion of the reaction as indicated by TLC, the reaction mixture was concentrated in vacuum. The crude residue was purified by flash column chromatograph (EtOAc/*n*-hexane, 1:3) to give the desired product **4** as a light yellow solid.



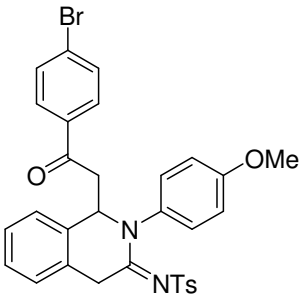
N-(2-(4-Methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4a**

Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.73 (m, 2H), 7.64-7.62 (m, 2H), 7.37-7.28 (m, 3H), 7.25-7.15 (m, 5H), 6.92-6.85 (m, 4H), 5.55-5.52 (m, 1H), 5.04 (d, *J* = 19.60 Hz, 1H), 4.25 (d, *J* = 19.60 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.55-3.44 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 34.2, 42.6, 55.5,5 55.57, 62.3, 113.8, 114.6, 126.0, 126.2, 127.2, 128.0, 128.41, 128.47, 128.9, 129.4, 129.8, 130.3, 134.3, 134.39, 140.8, 141.8, 138.9, 163.9, 165.4, 194.3; HRMS calcd. for $C_{32}H_{31}N_2O_5S^+$ $[M+H]^+$: 555.1954, found 555.1950.



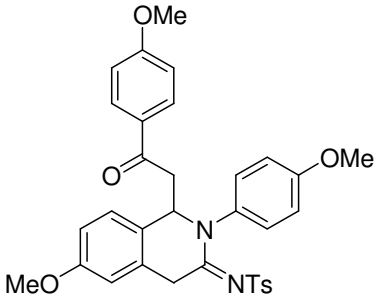
N-(1-(2-(4-Chlorophenyl)-2-oxoethyl)-2-(4-methoxyphenyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4b**

Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.66 (m, 2H), 7.61-7.59 (m, 2H), 7.35-7.29 (m, 5H), 7.24-7.16 (m, 1H), 7.14-7.13 (m, 4H), 6.90-6.88 (m, 2H), 5.51-5.48 (m, 1H), 5.02 (d, *J* = 20.0 Hz, 1H), 4.25 (d, *J* = 20.0 Hz, 1H), 3.81 (s, 3H), 3.54-3.45 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 34.1, 43.0, 55.5, 62.1, 114.6, 126.0, 126.1, 127.2, 128.1, 128.4, 128.5, 128.9, 129.0, 129.3, 129.8, 134.0, 134.2, 134.5, 140.1, 140.7, 141.8, 158.9, 165.3, 194.8; HRMS calcd. for $C_{31}H_{28}ClN_2O_4S^+$ $[M+H]^+$: 559.1458, found 559.1478.



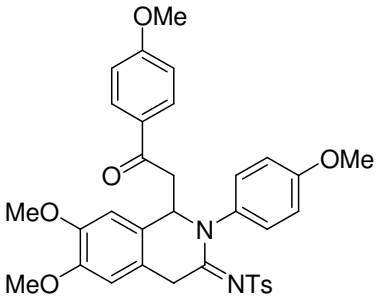
N-(1-(2-(4-Bromophenyl)-2-oxoethyl)-2-(4-methoxyphenyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4c**

Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 4H), 7.52-7.50 (m, 2H), 7.33-7.29 (m, 3H), 7.24-7.21 (m, 1H), 7.16-7.13 (m, 4H), 6.89-6.88 (m, 2H), 5.50-5.48 (m, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.54-3.44 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 34.1, 43.0, 55.5, 62.1, 114.6, 126.0, 126.1, 127.2, 128.1, 128.4, 128.5, 128.9, 129.4, 129.8, 130.9, 132.0, 134.0, 134.2, 134.9, 140.7, 141.8, 158.9, 165.3, 195.0; HRMS calcd. for $C_{31}H_{28}BrN_2O_4S^+$ $[M+H]^+$: 603.0953, found 603.0971.



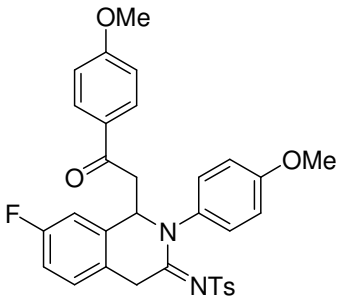
N-(6-Methoxy-2-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4d**

Yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.70 (m, 2H), 7.61-7.60 (m, 2H), 7.24-7.23 (m, 1H), 7.16-7.12 (m, 4H), 6.88-6.87 (m, 2H), 6.84-6.79 (m, 3H), 6.74-6.72 (m, 1H), 5.46-5.44 (m, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 4.24 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.50-3.39 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 34.4, 42.7, 55.3, 55.5, 62.0, 112.4, 113.4, 113.8, 114.5, 125.9, 126.4, 127.4, 128.4, 128.9, 129.4, 130.3, 131.1, 134.4, 140.8, 141.7, 158.9, 159.5, 163.8, 165.2, 194.6; HRMS calcd. for $C_{33}H_{33}N_2O_6S^+$ $[M+H]^+$: 585.2059, found 585.2068.



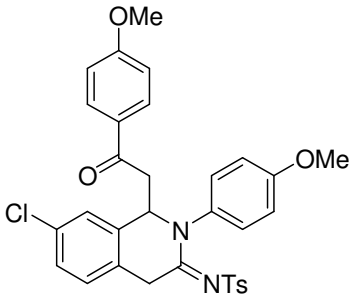
N-(6,7-Dimethoxy-2-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4e**

Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.61-7.59 (m, 2H), 7.18-7.11 (m, 5H), 6.89-6.82 (m, 4H), 6.75 (s, 1H), 5.44-5.42 (m, 1H), 4.93 (d, *J* = 16.4 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.796 (s, 3H), 3.790 (s, 3H), 3.51-3.39 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 33.6, 42.9, 55.48, 55.49, 56.00, 56.01, 62.2, 109.4, 110.5, 113.8, 114.5, 121.6, 125.9, 126.2, 128.4, 128.9, 129.5, 130.3, 134.3, 140.8, 141.7, 147.9, 149.0, 158.9, 163.8, 165.5, 194.8; HRMS calcd. for $C_{34}H_{35}N_2O_7S^+$ $[M+H]^+$: 615.2165, found 615.2168.



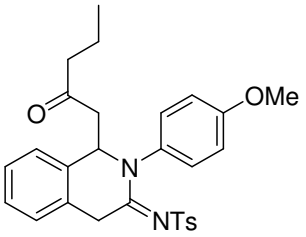
N-(7-Fluoro-2-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4f**

Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.74 (m, 2H), 7.60-7.58 (m, 2H), 7.23-7.20 (m, 1H), 7.15-7.11 (m, 5H), 6.98-6.94 (m, 1H), 6.88-6.83 (m, 4H), 5.49-5.44 (m, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.21(d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.56-3.44 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 33.5, 42.3, 55.4, 55.5, 61.9, 113.3, 113.5, 113.8, 114.6, 115.3, 115.5, 125.5, 125.9, 126.2, 126.3, 128.4, 128.9, 129.2, 129.5, 129.6, 130.3, 134.1, 136.2, 136.3, 140.7, 141.8, 159.0, 160.5, 162.5, 163.9, 165.2, 194.1; HRMS calcd. for $C_{32}H_{29}FN_2NaO_5S^+$ $[M+Na]^+$: 595.1679, found 595.1680.



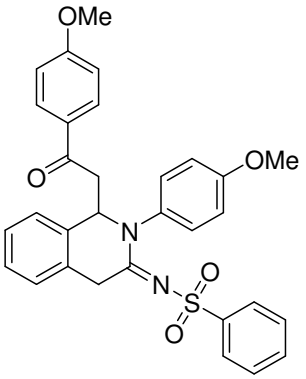
N-(7-Chloro-2-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydrois oquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4g**

Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.74 (m, 2H), 7.60-7.58 (m, 2H), 7.39 (d, *J* = 1.60 Hz, 1H), 7.25-7.12 (m, 6H), 6.89-6.84 (m, 4H), 5.48-5.45 (m, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.54-3.44 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 33.6, 42.3, 55.4, 55.5, 61.7, 113.8, 114.6, 125.9, 126.3, 128.3, 128.4, 128.5, 128.9, 129.1, 129.2, 130.3, 132.9, 134.0, 136.0, 140.6, 141.8, 159.0, 163.9, 164.9, 194.0; HRMS calcd. for $C_{32}H_{29}ClN_2NaO_5S^+$ $[M+Na]^+$: 611.1383, found 611.1408.



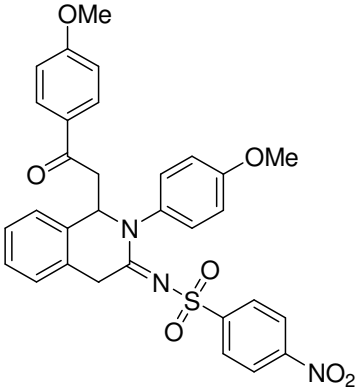
N-(2-(4-Methoxyphenyl)-1-(2-oxopentyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-m ethylbenzenesulfonamide **4h**

Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.70 (m, 2H), 7.28-7.16 (m, 8H), 6.85-6.83 (m, 2H), 5.41 (s, 1H), 4.98 (d, *J* = 2.40 Hz, 1H), 3.76 (s, 3H), 3.62 (s, 1H), 2.43-2.35 (m, 5H), 1.66-1.58 (m, 1H), 1.43-1.40 (m, 1H), 1.29-1.22 (m, 2H), 0.85 (t, *J* = 5.60 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 16.2, 21.4, 42.5, 43.6, 55.4, 63.9, 75.0, 114.3, 121.6, 126.2, 126.3, 126.7, 127.8, 128.2, 129.1, 129.5, 133.2, 134.2, 138.8, 140.7, 142.1, 158.6, 168.3; HRMS calcd. for $C_{28}H_{31}N_2O_4S^+$ $[M+H]^+$: 491.2005, found 491.2001.



N-(2-(4-Methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)benzenesulfonamide **4i**

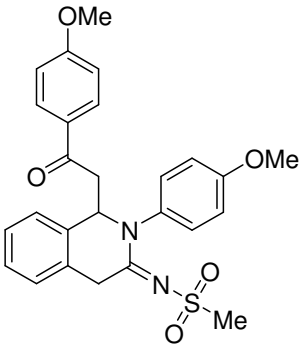
Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 4H), 7.43-7.31 (m, 5H), 7.25-7.24 (m, 1H), 7.21-7.14 (m, 3H), 6.88-6.86 (m, 2H), 6.83-6.81 (m, 2H), 5.52-5.50 (m, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.53-3.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.2, 42.5, 55.5, 55.52, 62.4, 113.8, 114.6, 125.9, 126.2, 126.3, 127.2, 127.9, 128.3, 128.4, 128.6, 129.3, 129.7, 130.3, 131.3, 134.2, 143.6, 158.9, 163.8, 165.5, 194.3; HRMS calcd. for $C_{31}H_{29}N_2O_5S^+$ $[M+H]^+$: 541.1797, found 541.1801.



N-(2-(4-Methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-nitrobenzenesulfonamide **4j**

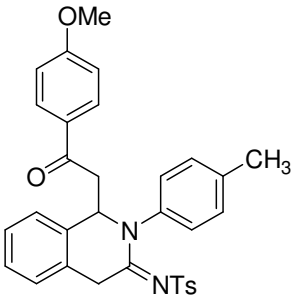
Yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.13 (m, 2H), 7.85-7.83 (m, 2H), 7.72-7.71 (m, 2H), 7.35-7.22 (m, 4H), 7.16-7.14 (m, 2H), 6.91-6.82 (m, 4H), 5.53-5.51 (m, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.34 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.54-3.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.5, 42.3, 55.5, 62.5, 113.8, 114.7, 123.6, 126.1, 127.2, 127.4, 127.9, 128.2, 128.5, 129.2, 130.3, 133.8,

133.9, 149.1, 149.2, 159.2, 163.9, 166.0, 194.2; HRMS calcd. for $C_{31}H_{27}N_3NaO_7S^+$ $[M+Na]^+$: 608.1467, found 608.1478.



N-(2-(4-Methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)methanesulfonamide **4k**

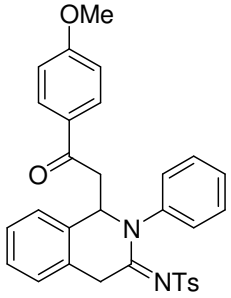
Yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.32-7.16 (m, 6H), 6.92-6.90 (m, 2H), 6.86-6.83 (m, 2H), 5.49-5.47 (m, 1H), 4.91 (d, *J* = 16.0 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.51-3.41 (m, 2H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.2, 42.6, 43.3, 55.4, 55.5, 62.3, 113.8, 114.5, 126.1, 126.8, 127.1, 127.9, 128.3, 128.4, 129.4, 129.7, 130.3, 134.3, 158.8, 163.8, 165.2, 194.3; HRMS calcd. for $C_{26}H_{26}N_2NaO_5S^+$ $[M+Na]^+$: 501.1460, found 501.1465.



N-(1-(2-(4-Methoxyphenyl)-2-oxoethyl)-2-*p*-tolyl-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4l**

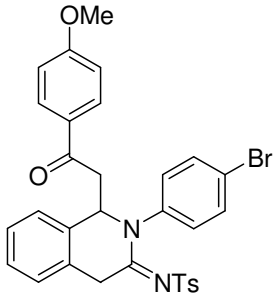
Yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.70 (m, 2H), 7.61-7.59 (m, 2H), 7.34 (d, *J* = 6.00 Hz, 1H), 7.26-7.25 (m, 1H), 7.20-7.14 (m, 4H), 7.12-7.10 (m, 4H), 6.82-6.80 (m, 2H), 5.53-5.51 (m, 1H), 5.01 (d, *J* = 16.00 Hz, 1H), 4.26 (d, *J* = 16.00 Hz, 1H), 3.78 (s, 3H), 3.54-3.43 (m, 2H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 21.6, 34.4, 42.7, 55.7, 62.4, 114.0, 126.2, 126.5, 127.2, 127.3, 128.1, 128.5, 129.2, 129.4, 130.0, 130.2, 130.5, 134.5, 138.1, 139.2, 141.0, 142.0,

164.0, 165.6, 194.6; HRMS calcd. for $C_{32}H_{31}N_2O_4S^+$ $[M+H]^+$: 539.2005, found 539.2019.



N-(1-(2-(4-Methoxyphenyl)-2-oxoethyl)-2-phenyl-1,2-dihydroisoquinolin-3(4*H*)-ylid ene)-4-methylbenzenesulfonamide **4m**

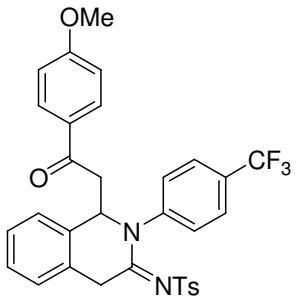
Yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.73 (m, 2H), 7.61-7.59 (m, 2H), 7.43-7.33 (m, 5H), 7.31-7.24 (m, 4H), 7.14-7.11 (m, 2H), 6.86-6.84 (m, 2H), 5.60-5.57 (m, 1H), 5.05 (d, *J* = 20.00 Hz, 1H), 4.31 (d, *J* = 20.00 Hz, 1H), 3.83 (s, 3H), 3.59-3.46 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 34.2, 42.6, 55.5, 62.1, 113.8, 126.0, 126.3, 127.2, 127.4, 128.0, 128.1, 128.4, 128.9, 129.3, 129.5, 129.8, 130.3, 134.3, 140.7, 141.7, 141.8, 163.9, 165.3, 194.3; HRMS calcd. for $C_{31}H_{29}N_2O_4S^+$ $[M+H]^+$: 525.1848, found 525.1847.



N-(2-(4-Bromophenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3 (4*H*)-ylidene)-4-methylbenzenesulfonamide **4n**

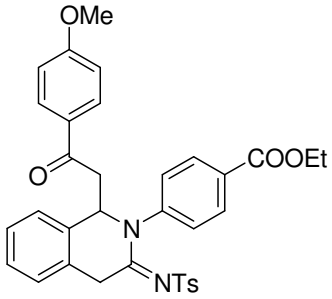
Yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.64-7.62 (m, 2H), 7.57-7.56 (m, 2H), 7.39-7.35 (m, 3H), 7.30-7.12 (m, 5H), 6.84-6.82 (m, 2H), 5.60-5.57 (m, 1H), 5.05 (d, *J* = 15.60 Hz, 1H), 4.28 (d, *J* = 16.00 Hz, 1H), 3.81 (s, 3H), 3.52-3.47 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 34.0, 42.5, 55.4, 61.9, 113.7, 121.7, 125.9, 126.1, 127.2, 127.9, 128.4, 129.0, 129.1, 129.2, 129.5, 130.3, 132.5, 134.1, 140.2, 140.5, 142.0, 163.8, 165.3, 194.2; HRMS calcd. for

$C_{31}H_{28}BrN_2O_4S^+$ $[M+H]^+$: 603.0953, found 603.0946.



N-(1-(2-(4-Methoxyphenyl)-2-oxoethyl)-2-(4-(trifluoromethyl)phenyl)-1,2-dihydroiso quinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4o**

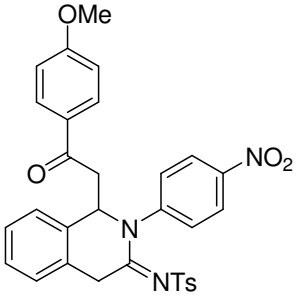
Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.74 (m, 2H), 7.69-7.65 (m, 2H), 7.61-7.58 (m, 2H), 7.44-7.39 (m, 3H), 7.34-7.32 (m, 2H), 7.29-7.25 (m, 1H), 7.18-7.16 (m, 2H), 6.88-6.85 (m, 2H), 5.63-5.60 (m, 1H), 5.07 (d, *J* = 20.00 Hz, 1H), 4.32 (d, *J* = 19.60 Hz, 1H), 3.85 (s, 3H), 3.60-3.45 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 34.4, 42.9, 55.7, 62.0, 114.0, 126.1, 126.4, 126.6, 126.7, 126.83, 128.86, 127.6, 128.3, 128.8, 129.3, 129.7, 130.6, 134.3, 140.4, 142.5, 145.0, 164.1, 165.6, 194.3; HRMS calcd. for $C_{32}H_{28}F_3N_2O_4S^+$ $[M+H]^+$: 593.1722, found 593.1729.



Ethyl 4-(1-(2-(4-methoxyphenyl)-2-oxoethyl)-3-(tosylimino)-3,4-dihydroisoquinolin-2(1*H*)-yl)benzoate **4p**

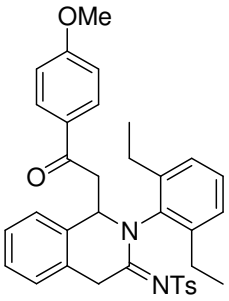
Yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.21 (m, 2H), 7.76-7.73 (m, 2H), 7.62-7.60 (m, 2H), 7.46-7.43 (m, 2H), 7.40-7.37 (m, 1H), 7.34-7.28 (m, 3H), 7.20-7.17 (m, 2H), 6.87-6.85 (m, 2H), 5.67-5.64 (m, 1H), 5.09 (d, *J* = 20.0 Hz, 1H), 4.31 (d, *J* = 20.0 Hz, 1H), 3.90-3.84 (m, 5H), 3.52-3.50 (m, 2H), 2.37 (s, 3H), 1.41-1.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 21.6, 34.4, 42.9, 55.7, 61.5,

62.0, 114.0, 126.1, 126.4, 127.5, 127.6, 128.3, 128.7, 129.3, 129.4, 129.8, 130.1, 130.5, 130.9, 134.4, 142.3, 145.8, 164.1, 165.5, 165.9, 194.3; HRMS calcd. for $C_{34}H_{32}N_2NaO_6S^+$ $[M+Na]^+$: 619.1879, found 619.1896.



N-(1-(2-(4-Methoxyphenyl)-2-oxoethyl)-2-(4-nitrophenyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4q**

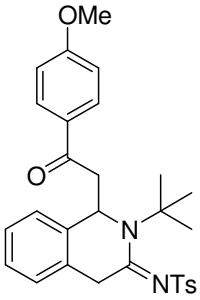
Yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.05 (m, 2H), 7.74-7.72 (m, 2H), 7.61-7.59 (m, 2H), 7.39-7.30 (m, 6H), 7.16-7.14 (m, 2H), 6.85-6.83 (m, 2H), 5.62-5.59 (m, 1H), 5.07 (d, *J* = 20.00 Hz, 1H), 4.30 (d, *J* = 20.00 Hz, 1H), 3.82 (s, 3H), 3.57-3.44 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 34.2, 46.0, 55.6, 61.8, 113.9, 124.7, 126.0, 127.0, 127.6, 128.2, 128.5, 128.7, 129.2, 129.4, 130.4, 130.8, 134.1, 139.9, 142.5, 146.6, 147.4, 164.1, 165.4, 193.9**;** HRMS calcd. for $C_{31}H_{27}N_3NaO_6S^+$ $[M+Na]^+$: 592.1518, found 592.1539.



N-(2-(2,6-Diethylphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4r**

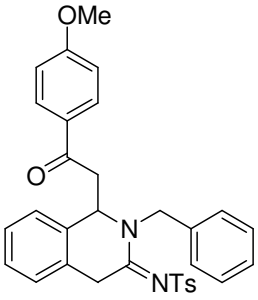
Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.53-7.51 (m, 2H), 7.33-7.28 (m, 4H), 7.21-7.17 (m, 3H), 7.11-7.09 (m, 2H), 6.86-6.83 (m, 2H), 5.31-5.28 (m, 1H), 5.06 (d, *J* = 19.20 Hz, 1H), 4.35 (d, *J* = 19.20 Hz, 1H), 3.82 (s, 3H), 3.61-3.36 (m, 2H), 2.57-2.46 (m, 2H), 2.32 (s, 3H), 2.29-2.23 (m, 2H), 1.15 (t, *J* = 7.60 Hz, 3H), 1.03 (t, *J* = 7.60 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.4,

21.4, 24.2, 24.3, 34.0, 41.8, 55.5, 62.0, 113.9, 125.9, 126.0, 126.2, 127.3, 127.4, 128.1, 128.4, 128.6, 128.9, 129.4, 129.8, 130.2, 134.9, 138.4, 139.7, 140.6, 140.8, 141.7, 163.8, 165.2, 194.3; HRMS calcd. for $C_{35}H_{37}N_2O_4S$ $[M+H]^+$: 581.2474, found 581.2473.



N-(2-*tert*-butyl-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4s**

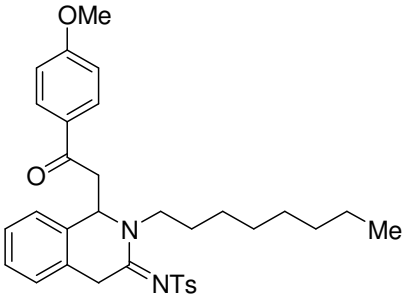
Yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.01 (m, 2H), 7.93-7.70 (m, 4H), 7.41-7.36 (m, 2H), 7.28-7.24 (m, 2H), 6.98-6.95 (m, 2H), 5.29-5.08 (d, 1H), 4.42-4.28 (m, 2H), 3.87 (s, 3H), 3.73-3.71 (m, 2H), 2.41-2.37 (m, 3H), 1.23-1.19 (d, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 28.0, 28.2, 38.8, 38.9, 53.9, 55.8, 55.9, 114.2, 114.3, 125.8, 126.4, 128.4, 128.7, 128.8, 129.2, 129.3, 129.4, 129.5, 130.7, 131.0, 131.1, 131.30, 131.34, 132.2, 133.1, 135.3, 137.4, 140.2, 140.4, 140.9, 142.2, 142.3, 163.8, 164.2, 164.3, 165.1, 188.5, 190.5; HRMS calcd. for $C_{29}H_{33}N_2O_4S^+$ $[M+H]^+$: 505.2161, found 505.2171.



N-(2-Benzyl-1-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4t**

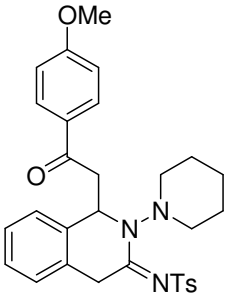
Yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.75 (m, 4H), 7.29-7.18 (m, 11H), 6.89-6.87 (m, 2H), 5.37-5.30 (m, 2H), 5.05 (d, *J* = 19.60 Hz, 1H), 4.97 (d, *J* = 14.80 Hz, 1H), 4.12-4.06 (m, 1H), 3.84 (s, 3H), 3.40-3.25 (m, 2H), 2.39 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 22.4, 34.7, 44.3, 52.8, 56.5, 58.4, 114.8, 126.7, 127.1, 128.2, 128.8, 128.9, 129.2, 129.7, 130.1, 130.2, 130.4, 131.3, 135.9, 136.3, 141.7, 143.0, 164.9, 166.1, 195.5; HRMS calcd. for $C_{32}H_{31}N_2O_4S^+$ $[M+H]^+$: 539.2005, found 539.2029.



N-(1-(2-(4-Methoxyphenyl)-2-oxoethyl)-2-octyl-1,2-dihydroisoquinolin-3(4*H*)-yliden e)-4-methylbenzenesulfonamide **4u**

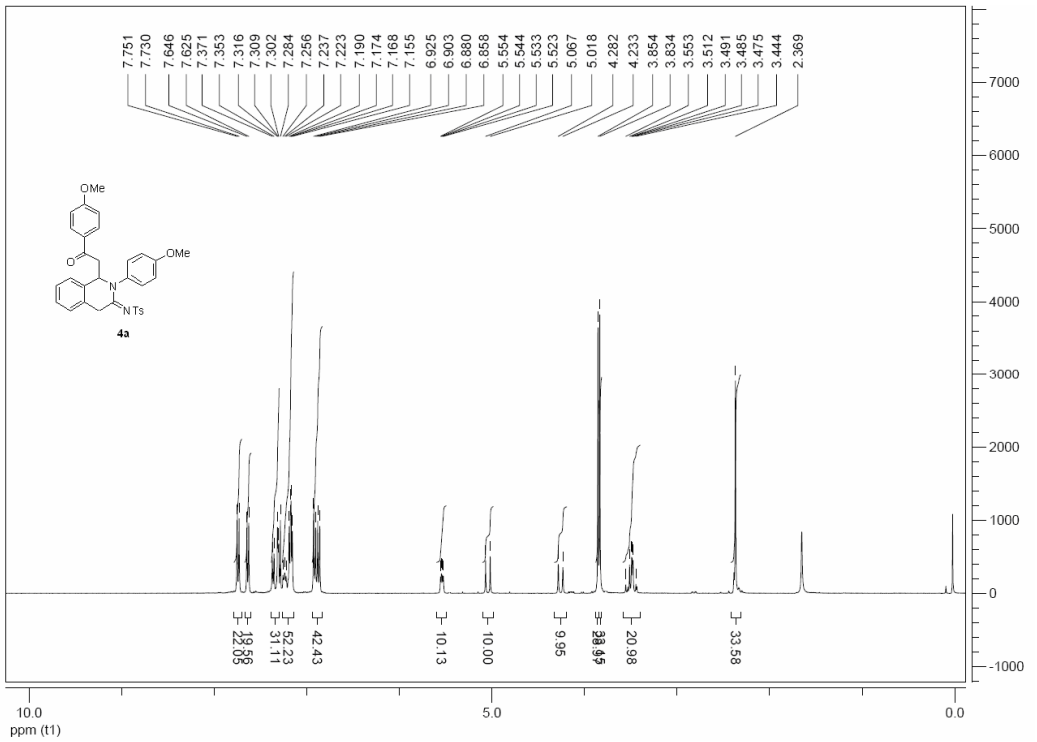
Yield: 82%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (m, 2H), 7.80-7.78 (m, 2H), 7.31-7.17 (m, 6H), 6.88-6.87 (m, 2H), 5.29-5.27 (m, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.09-4.06 (m, 1H), 3.97 (d, *J* = 15.6 Hz 1H), 3.83 (s, 3H), 3.41-3.26 (m, 2H), 3.08-3.05 (m, 1H), 2.39 (s, 3H), 1.56-1.55 (m, 1H), 1.26-1.17 (m, 11H), 0.85 (t, *J* = 5.60 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 21.8, 22.9, 27.0, 27.2, 29.2, 32.0, 34.0, 43.7, 49.7, 55.8, 58.5, 114.2, 126.2, 126.4, 127.5, 128.1, 128.5, 129.4, 129.5, 130.1, 130.7, 135.2, 141.3, 142.2, 164.3, 164.6, 195.1; HRMS calcd. for $C_{33}H_{41}N_2O_4S^+$ $[M+H]^+$: 561.2787, found 561.2772.



N-(1-(2-(4-Methoxyphenyl)-2-oxoethyl)-2-(piperidin-1-yl)-1,2-dihydroisoquinolin-3(4*H*)-ylidene)-4-methylbenzenesulfonamide **4v**

Yield: 86%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 4H), 7.27-7.15 (m, 6H), 6.90-6.88 (m, 2H), 4.72 (d, *J* = 15.60 Hz, 1H), 4.18 (d, *J* = 15.60 Hz, 1H), 3.84-3.81 (m, 4H), 3.53-3.39 (m, 3H), 2.86-2.81 (m, 2H), 2.41-2.37 (m, 4H), 1.64-1.37 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 23.5, 26.5, 34.8, 42.9, 55.5, 62.5, 113.8, 125.5, 126.1, 126.3, 127.0, 127.5, 128.0, 129.1, 129.3, 129.5, 130.4, 134.5, 141.1, 142.0, 163.0, 163.7, 194.7; HRMS calcd. for $C_{30}H_{34}N_3O_4S^+$ $[M+H]^+$: 532.2270, found 532.2289.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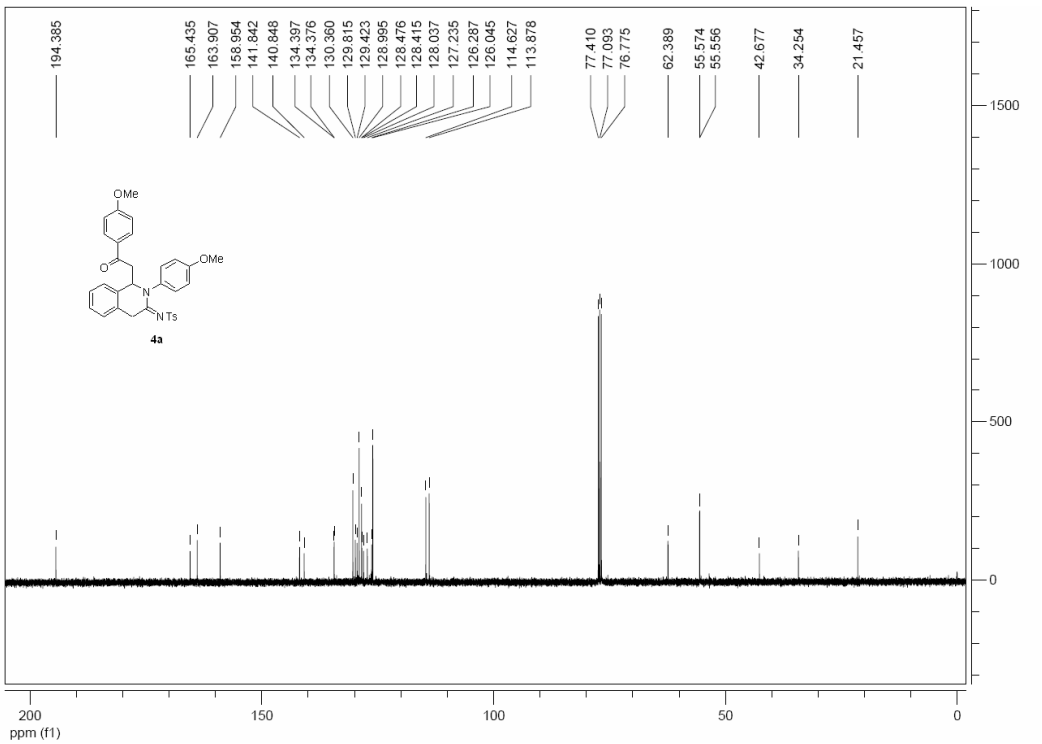
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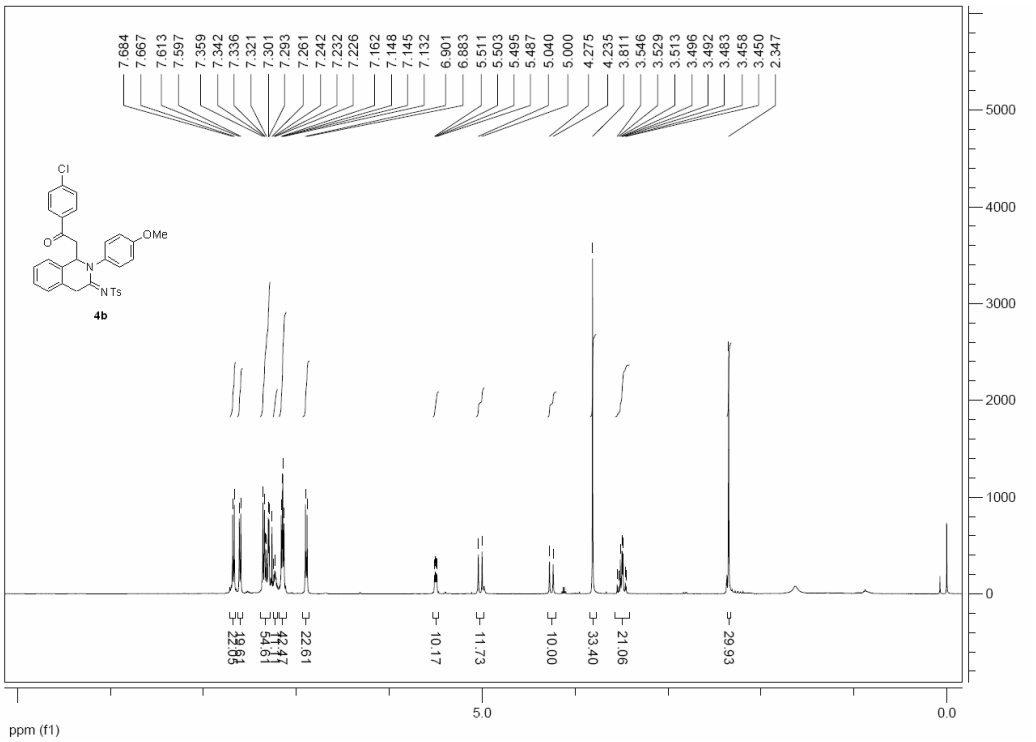
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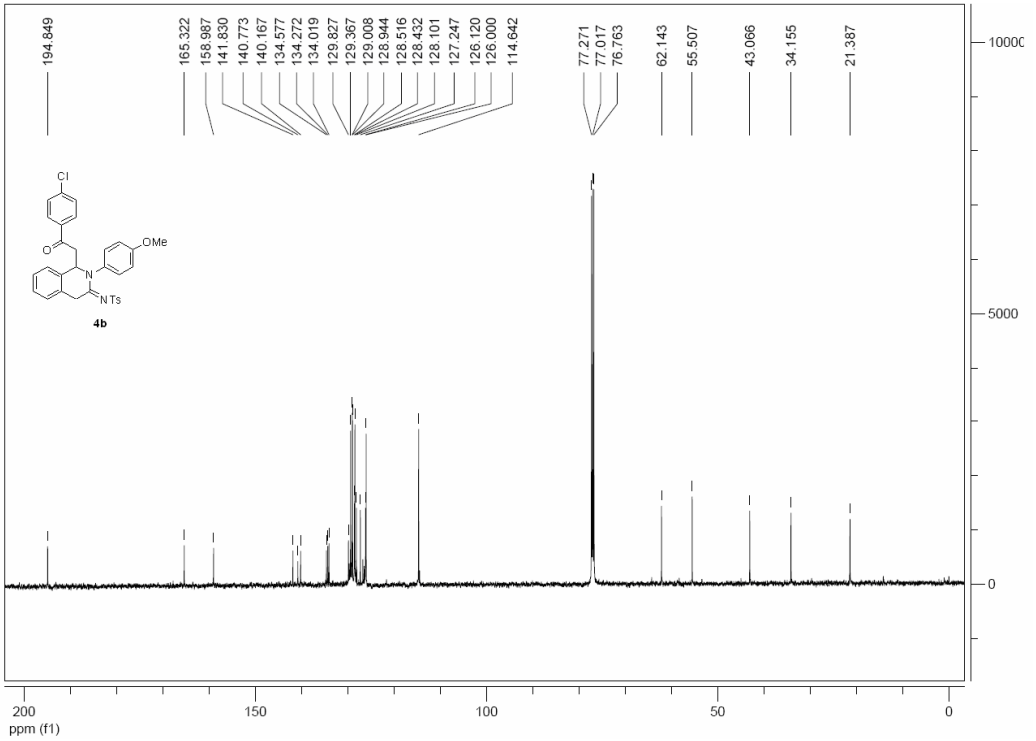
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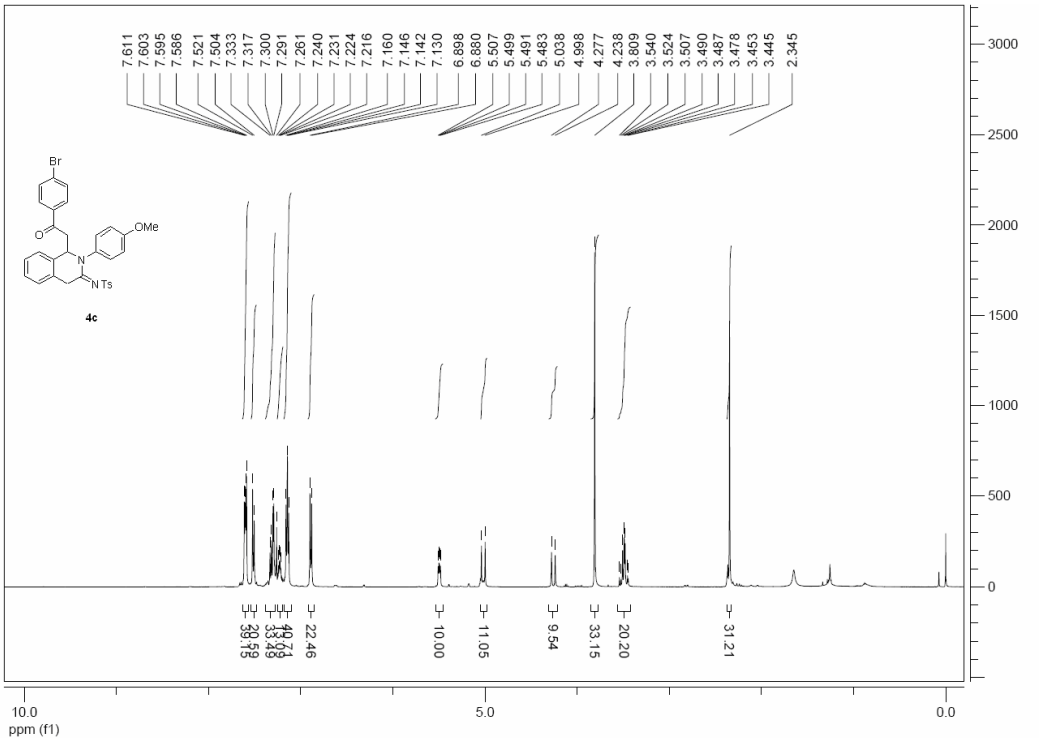
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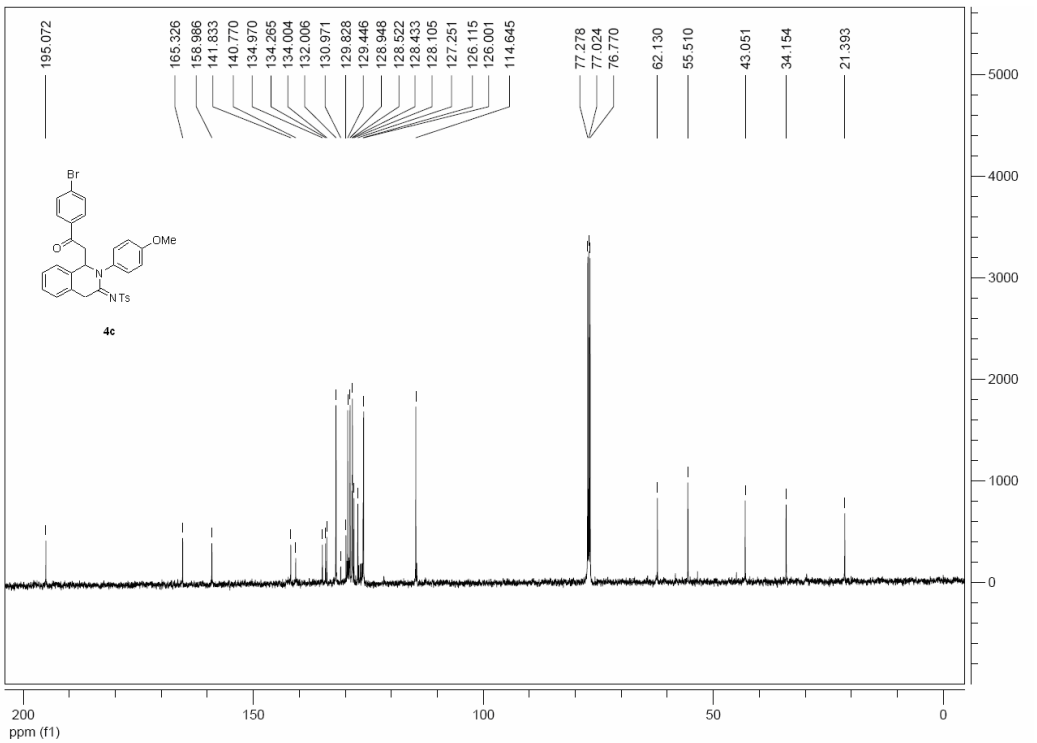
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132.006
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128.433
128.105
127.251
126.115
126.001
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77.278
77.024
76.770
62.130
55.510
43.051
34.154
21.393
Br
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NTs
4c
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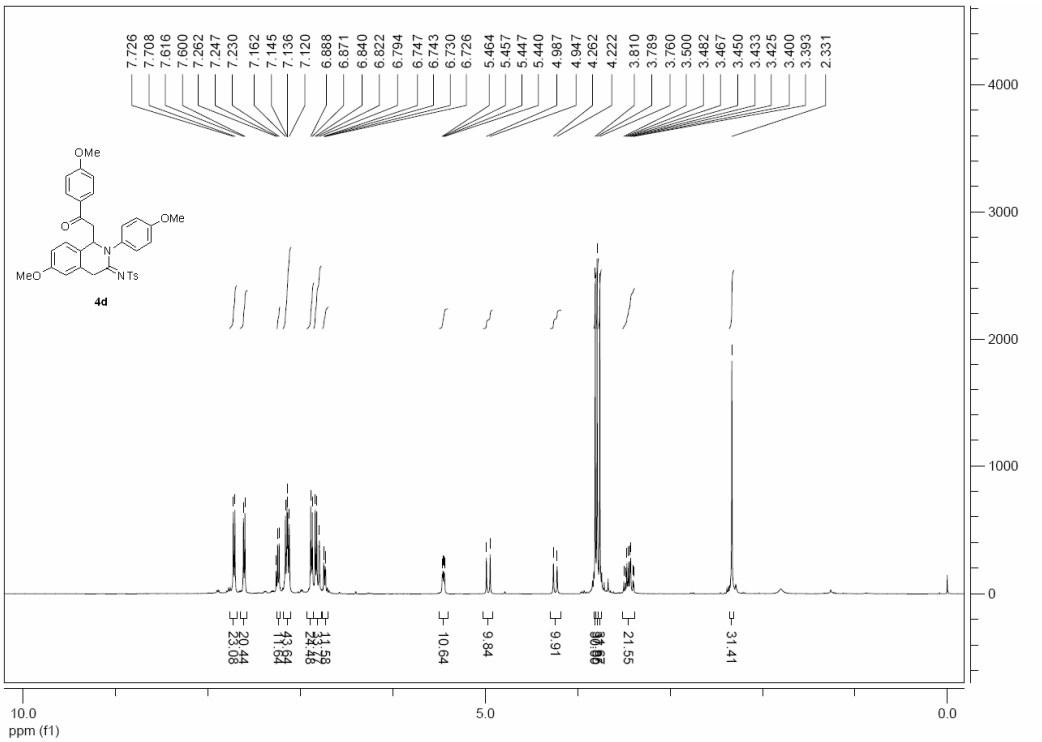
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6.822
6.794
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6.730
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5.457
5.447
5.440
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4.947
4.262
4.222
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3.482
3.467
3.450
3.433
3.425
3.400
3.393
2.331
OMe
OMe
MeO
N Ts
4d
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20.44
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11.58
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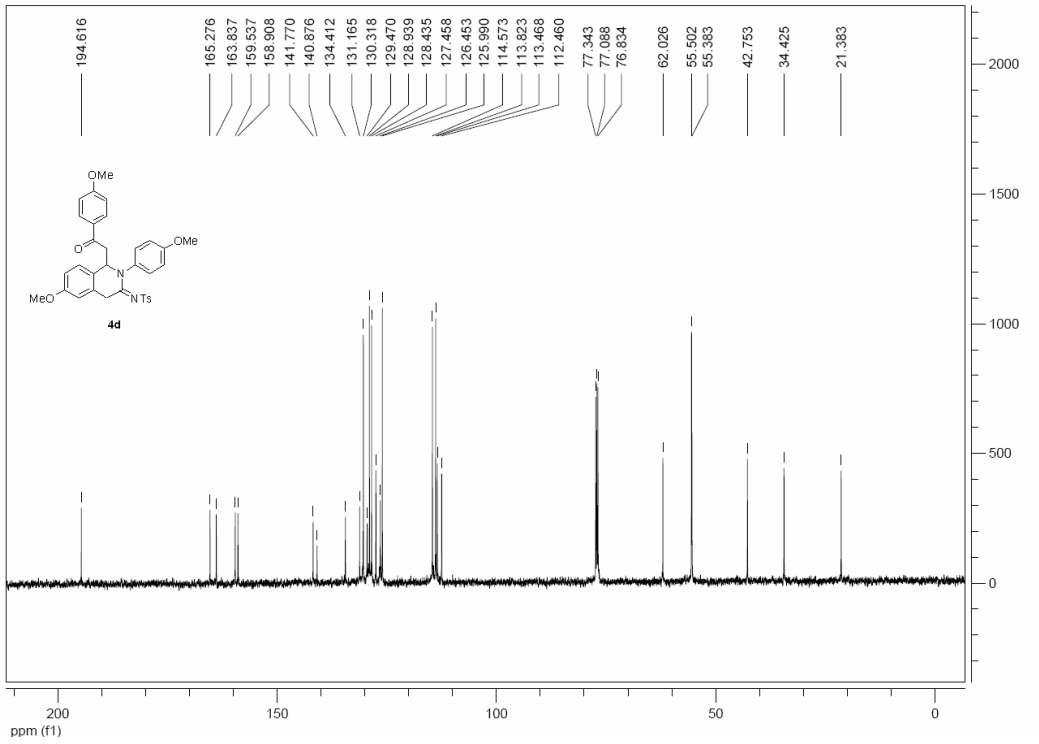
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126.453
125.990
114.573
113.823
113.468
112.460
77.343
77.088
76.834
62.026
55.502
55.383
42.753
34.425
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OMe
MeO
N Ts
4d
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1000
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0
200
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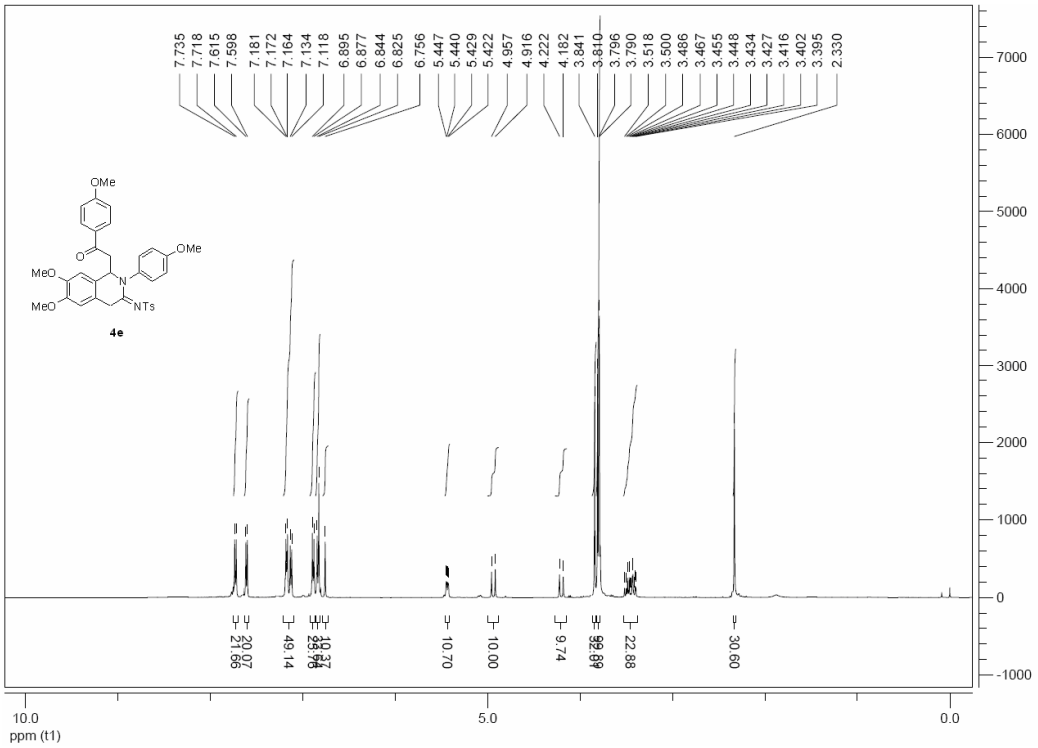
100
50
0
ppm (f1)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6.825
6.756
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5.429
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4.957
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4.222
4.182
3.841
3.810
3.796
3.790
3.518
3.500
3.486
3.467
3.455
3.448
3.434
3.427
3.416
3.402
3.395
2.330
OMe
MeO
MeO
OMe
NTs
4e
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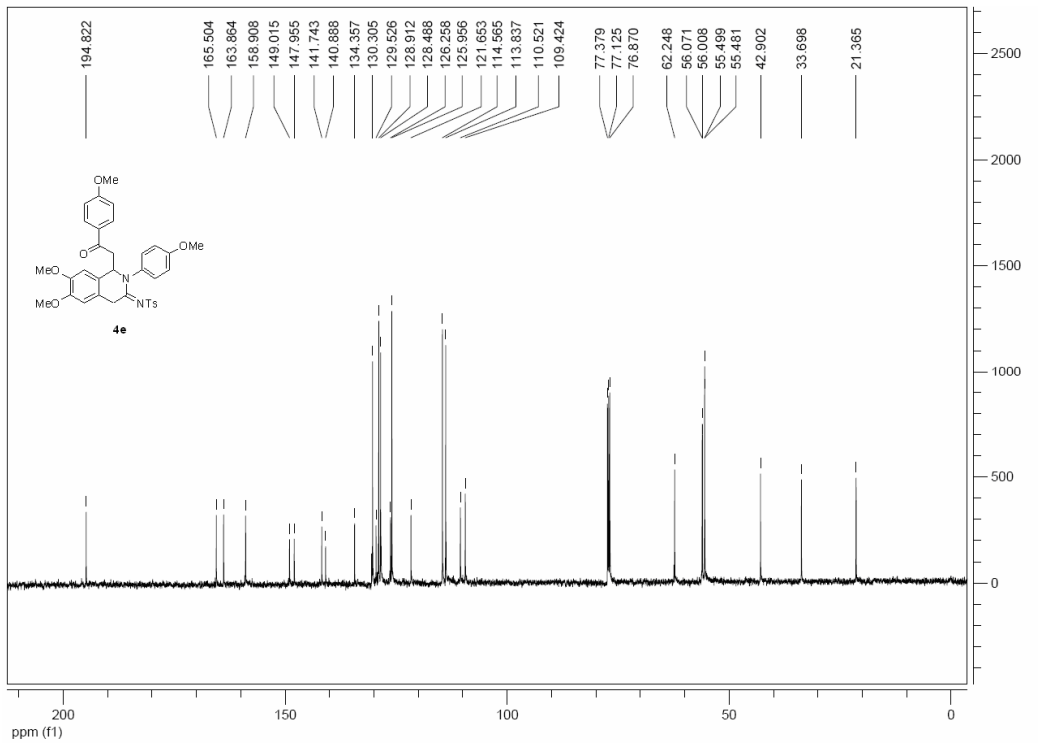
ppm (t1)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121.653
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109.424
77.379
77.125
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56.008
55.499
55.481
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OMe
MeO
MeO
OMe
NTs
4e
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50
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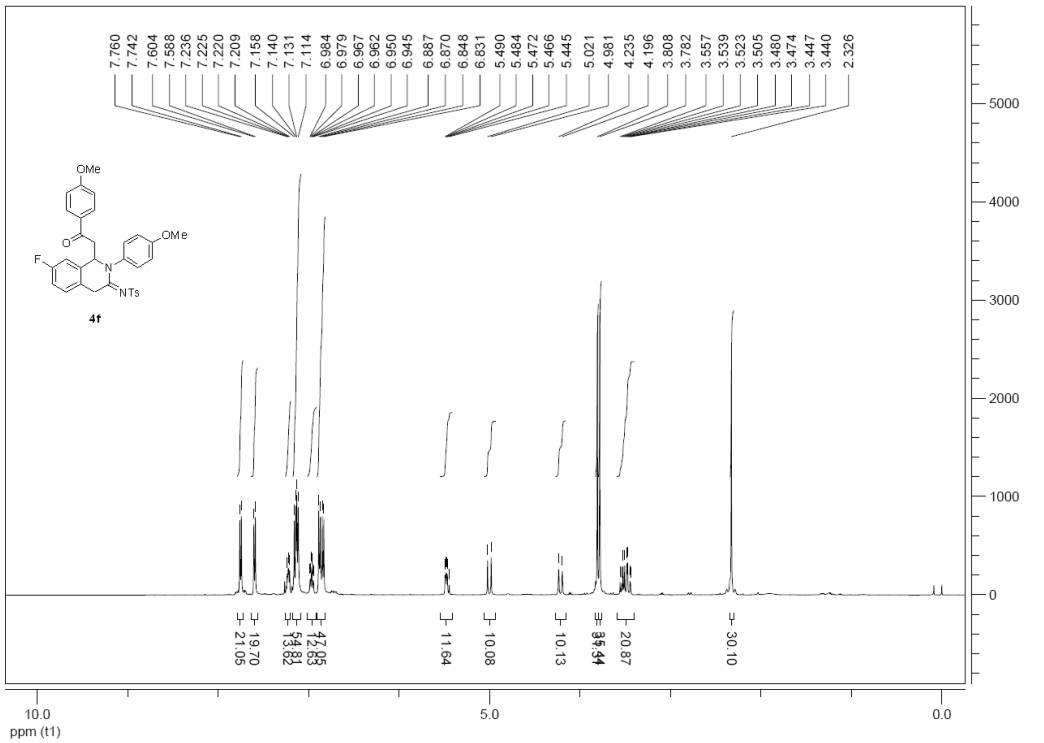
ppm (f1)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6.979
6.967
6.962
6.950
6.945
6.887
6.870
6.848
6.831
5.490
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5.472
5.466
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3.480
3.474
3.447
3.440
2.326
OMe
OMe
F
N
NTs
O
4f
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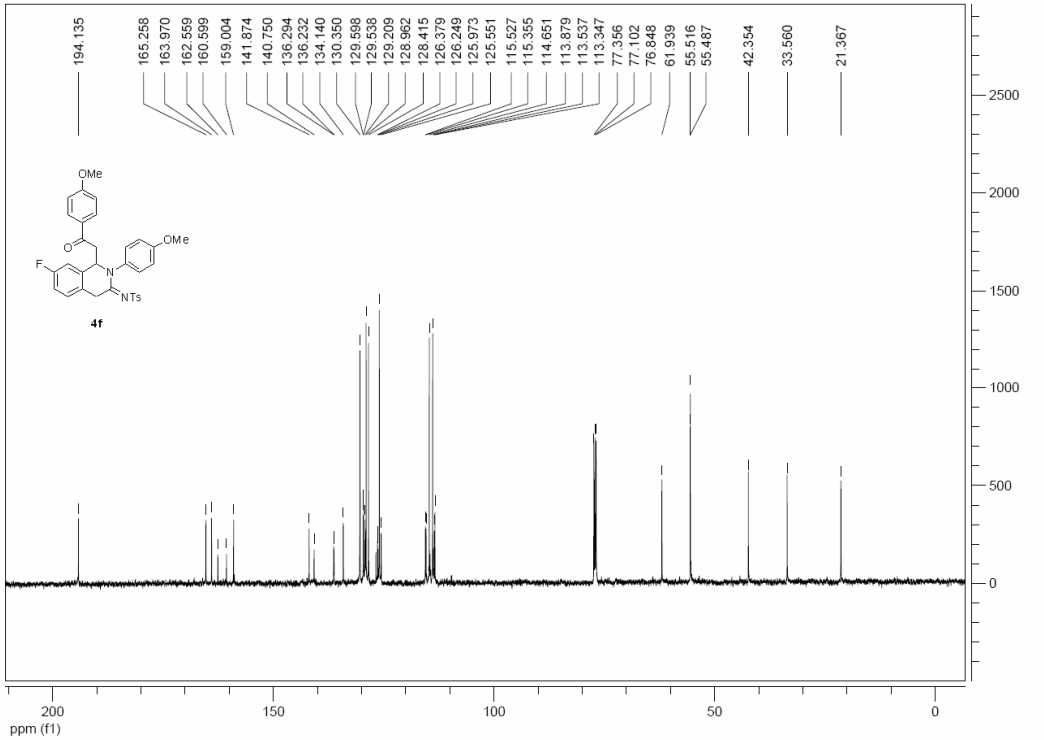
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129.598
129.538
129.209
128.962
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126.249
125.973
125.551
115.527
115.355
114.651
113.879
113.537
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77.356
77.102
76.848
61.939
55.516
55.487
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OMe
OMe
F
N
NTs
O
4f
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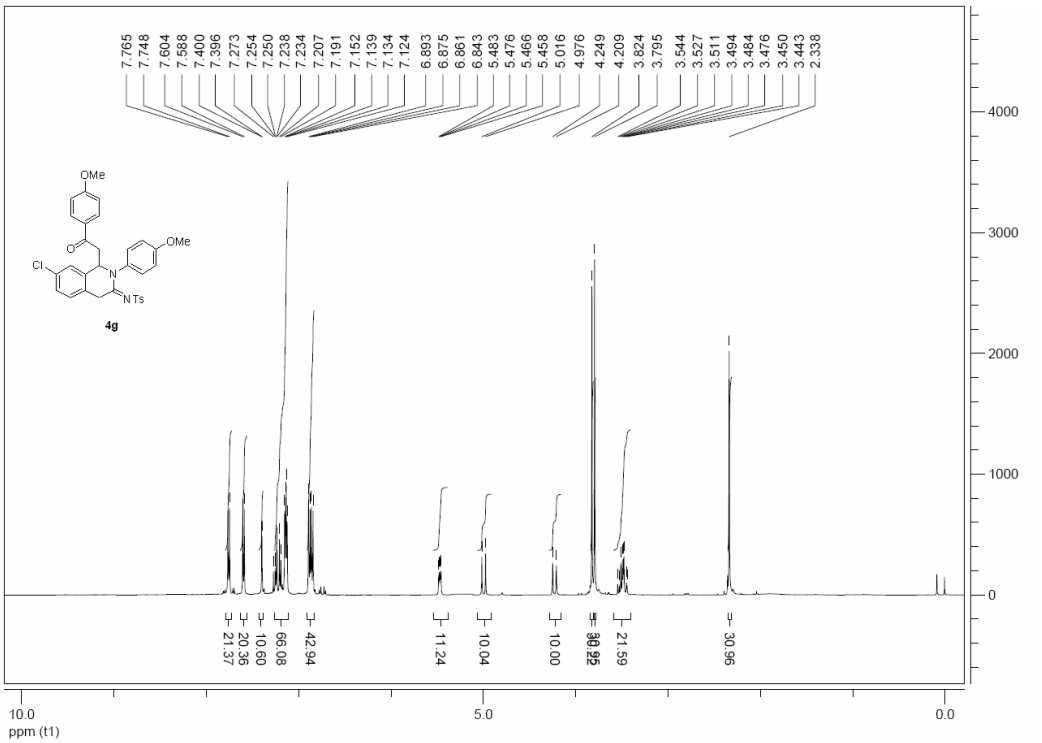
150
100
50
0
ppm (f1)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7.191
7.152
7.139
7.134
7.124
6.893
6.875
6.861
6.843
5.483
5.476
5.466
5.458
5.016
4.976
4.249
4.209
3.824
3.795
3.544
3.527
3.511
3.494
3.484
3.476
3.450
3.443
2.338
OMe
OMe
Cl
N
NTs
4g
21.37
20.36
10.90
66.08
42.94
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12.59
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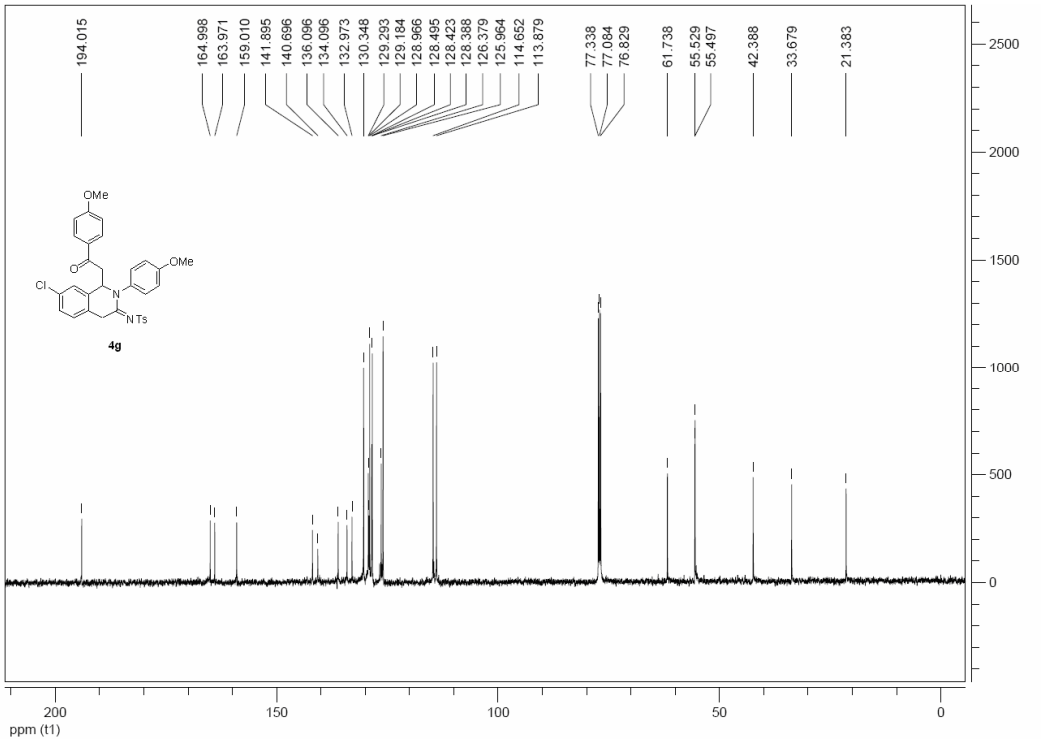
ppm (t1)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77.338
77.084
76.829
61.738
55.529
55.497
42.388
33.679
21.383
OMe
OMe
Cl
N
NTs
4g
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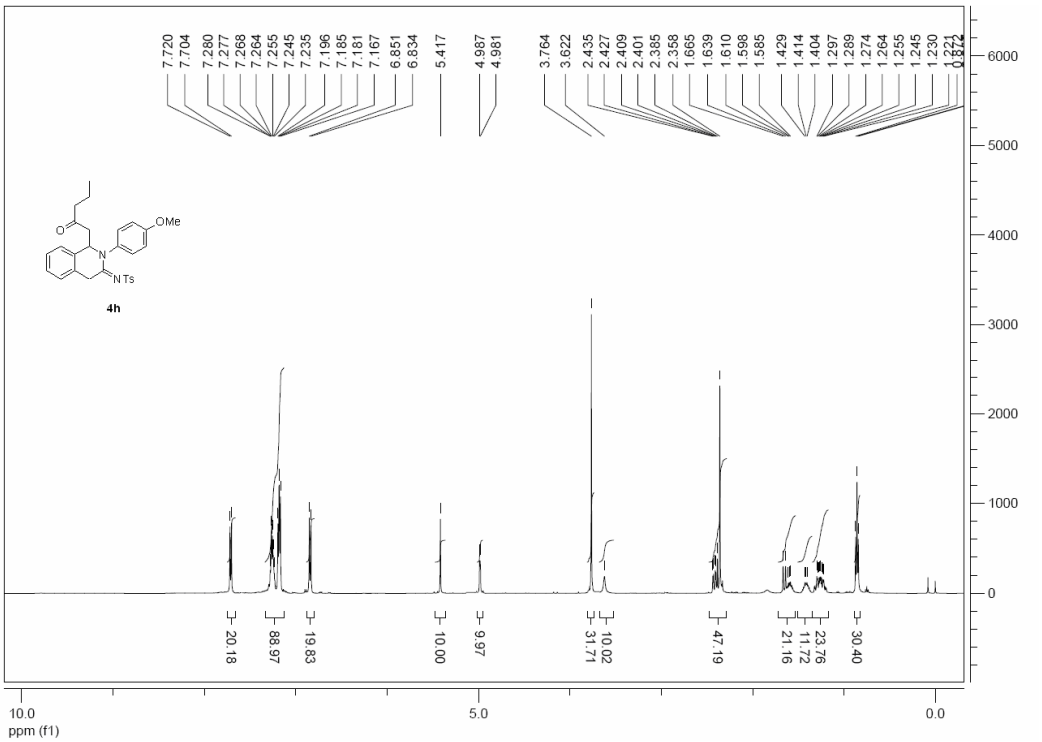
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)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7.167
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6.834
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4.981
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3.622
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2.427
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2.401
2.385
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1.639
1.610
1.598
1.585
1.429
1.414
1.404
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1.289
1.274
1.264
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1.245
1.230
1.221
0.872
OMe
N
NTs
4h
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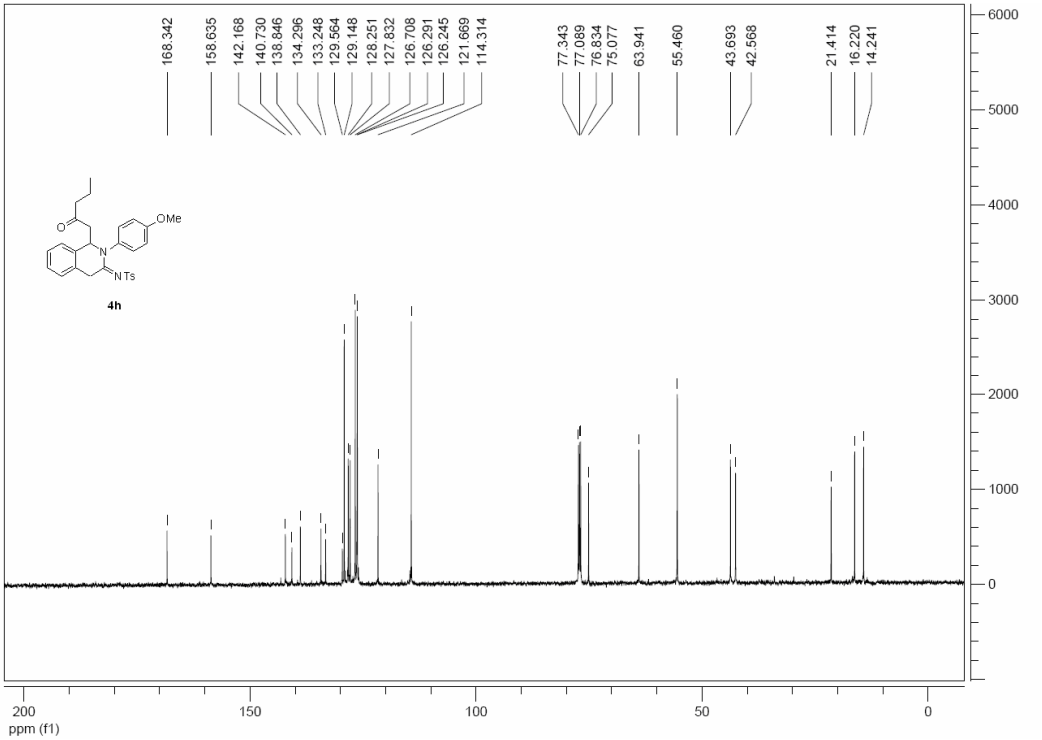
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126.291
126.245
121.669
114.314
77.343
77.089
76.834
75.077
63.941
55.460
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N
NTs
4h
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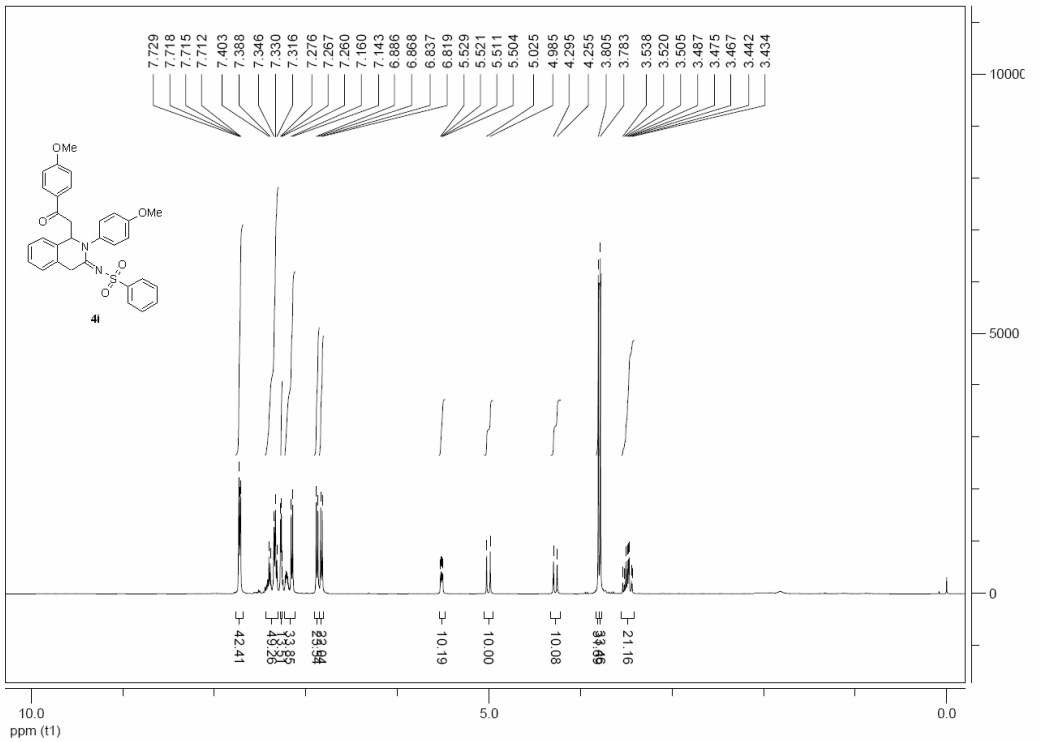
ppm (f1)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5.504
5.025
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4.295
4.255
3.805
3.783
3.538
3.520
3.505
3.487
3.475
3.467
3.442
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OMe
OMe
4l
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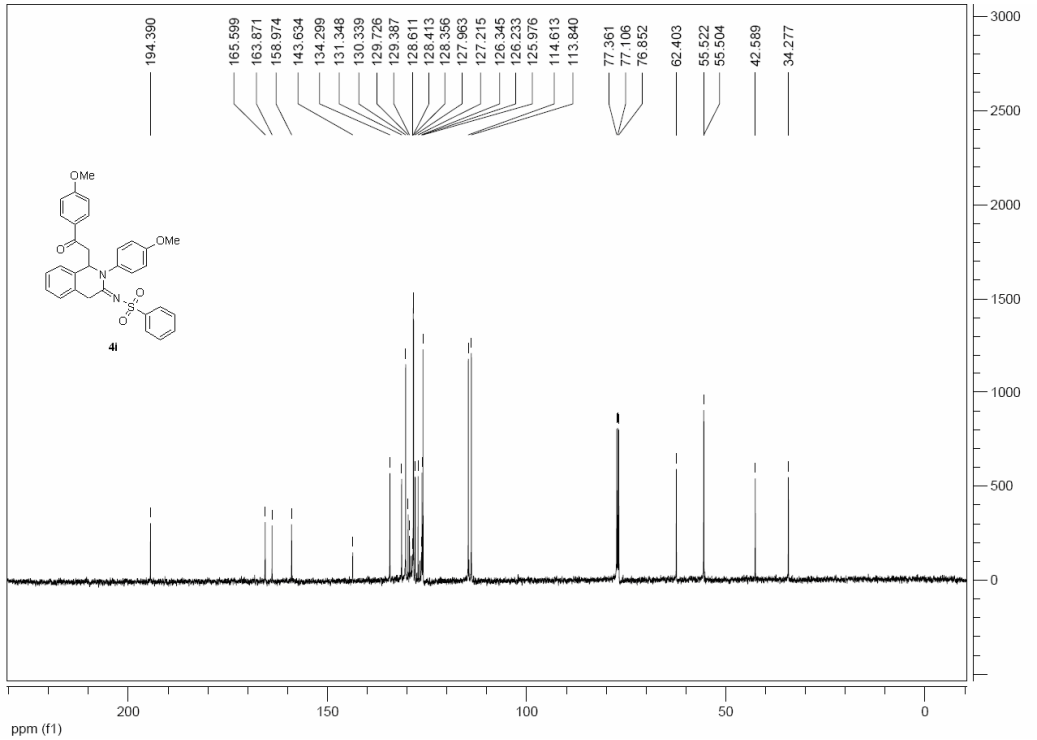
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128.356
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127.215
126.345
126.233
125.976
114.613
113.840
77.361
77.106
76.852
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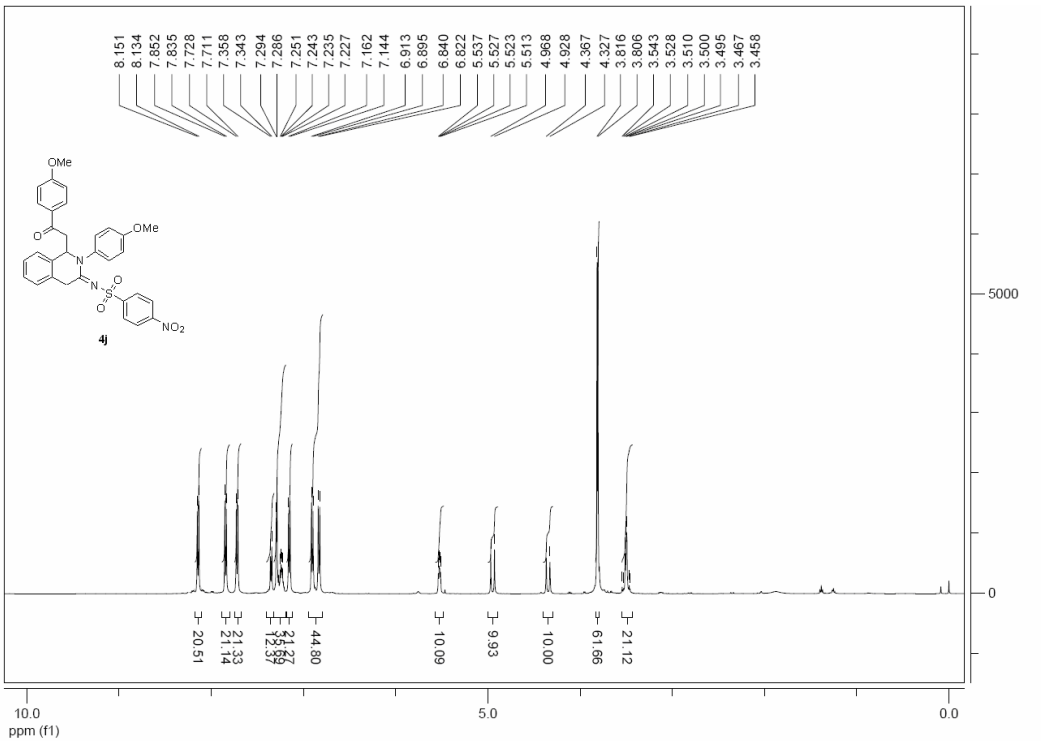
55.504
42.589
34.277
OMe
OMe
4l
200
150
100
50
0
ppm (f1)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7.162
7.144
6.913
6.895
6.840
6.822
5.537
5.527
5.523
5.513
4.968
4.928
4.367
4.327
3.816
3.806
3.543
3.528
3.510
3.500
3.495
3.467
3.458
OMe
OMe
NO2
4j
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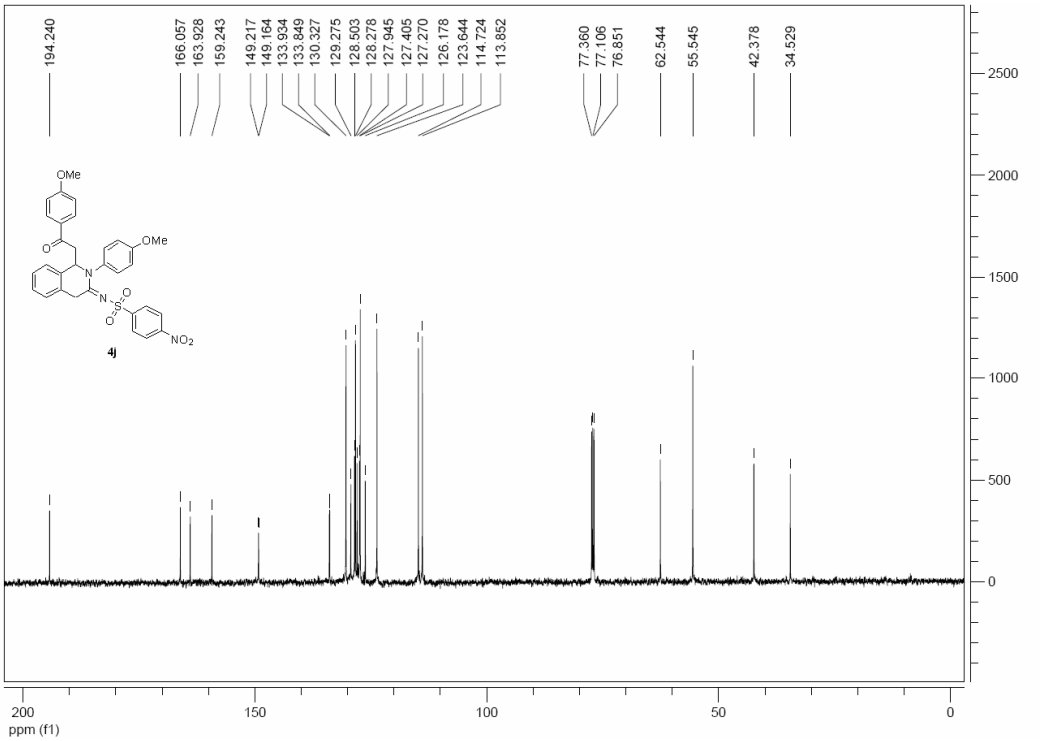
ppm (f1)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OMe
NO2
4j
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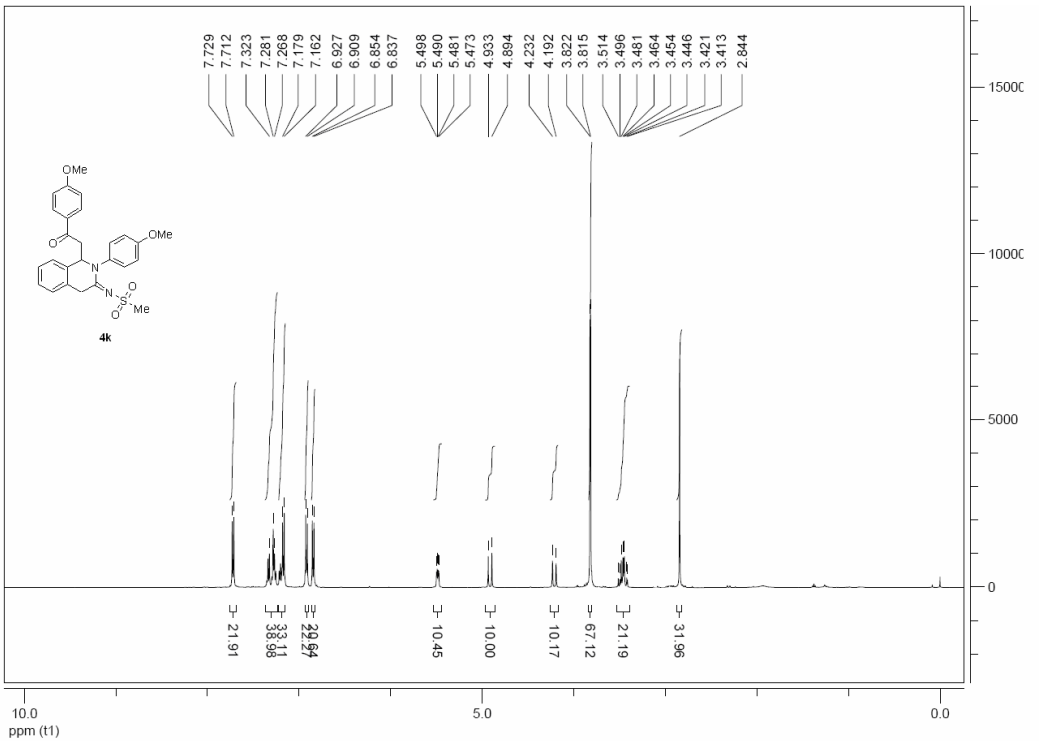
ppm (f1)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5.490
5.481
5.473
4.933
4.894
4.232
4.192
3.822
3.815
3.514
3.496
3.481
3.464
3.454
3.446
3.421
3.413
2.844
OMe
OMe
Me
4k
21.91
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ppm (t1)
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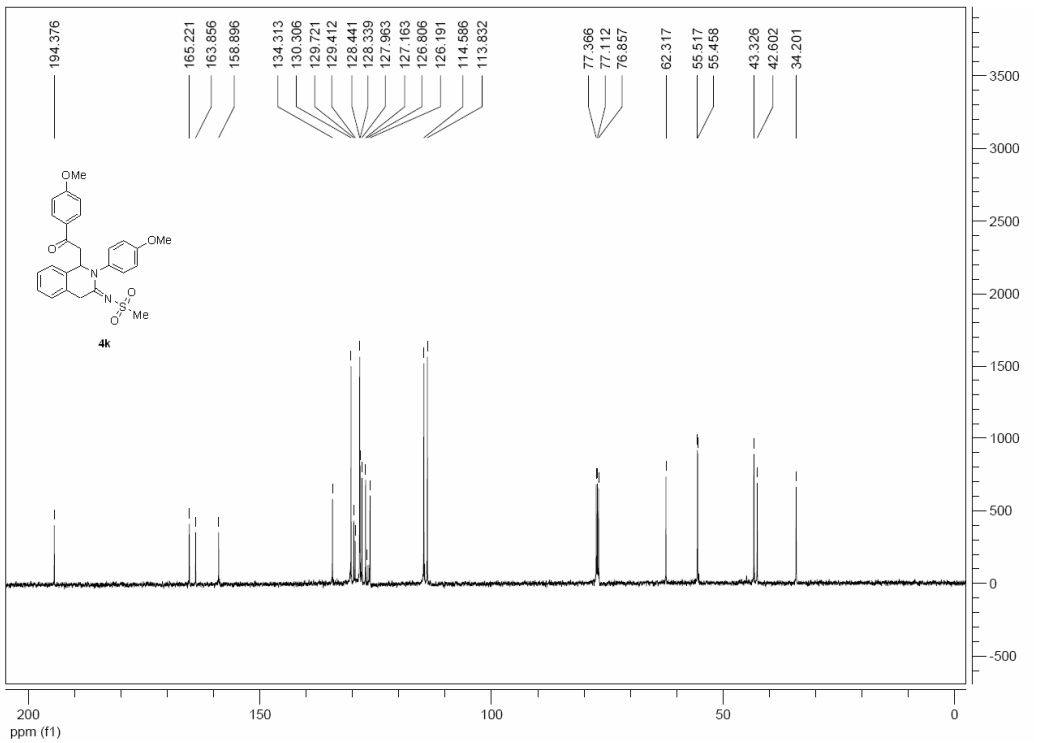
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126.806
126.191
114.586
113.832
77.366
77.112
76.857
62.317
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OMe
OMe
Me
4k
200
ppm (f1)
150
100
50
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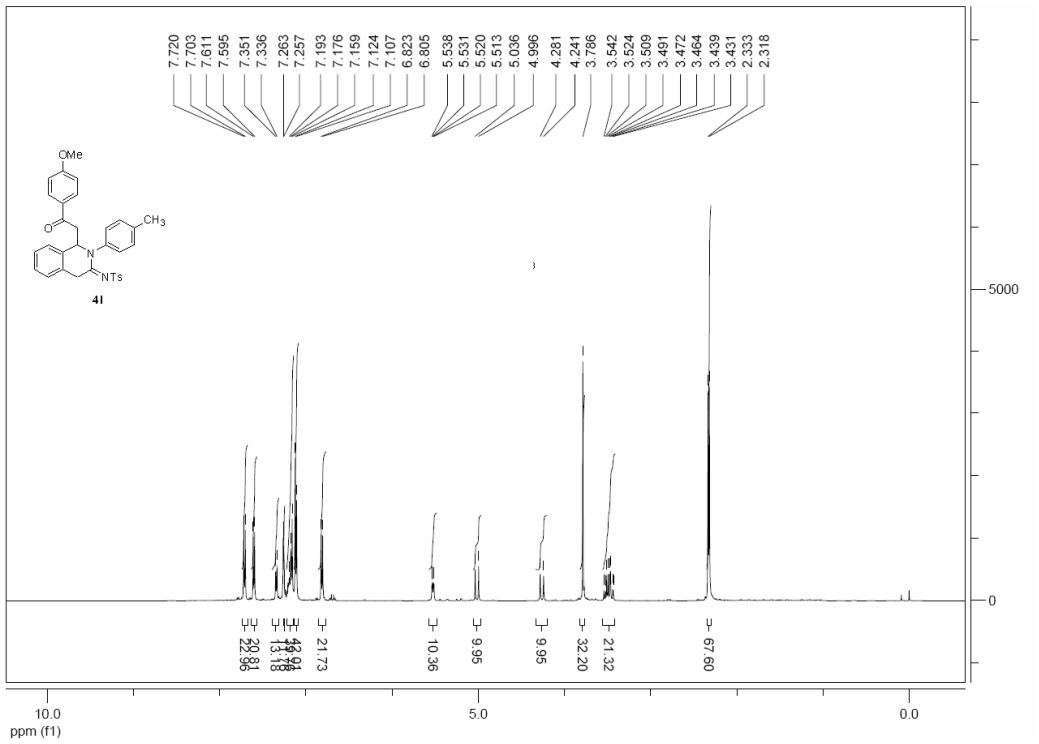
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3.509
3.491
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3.464
3.439
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OMe
CH3
N
NTs
4l
5000
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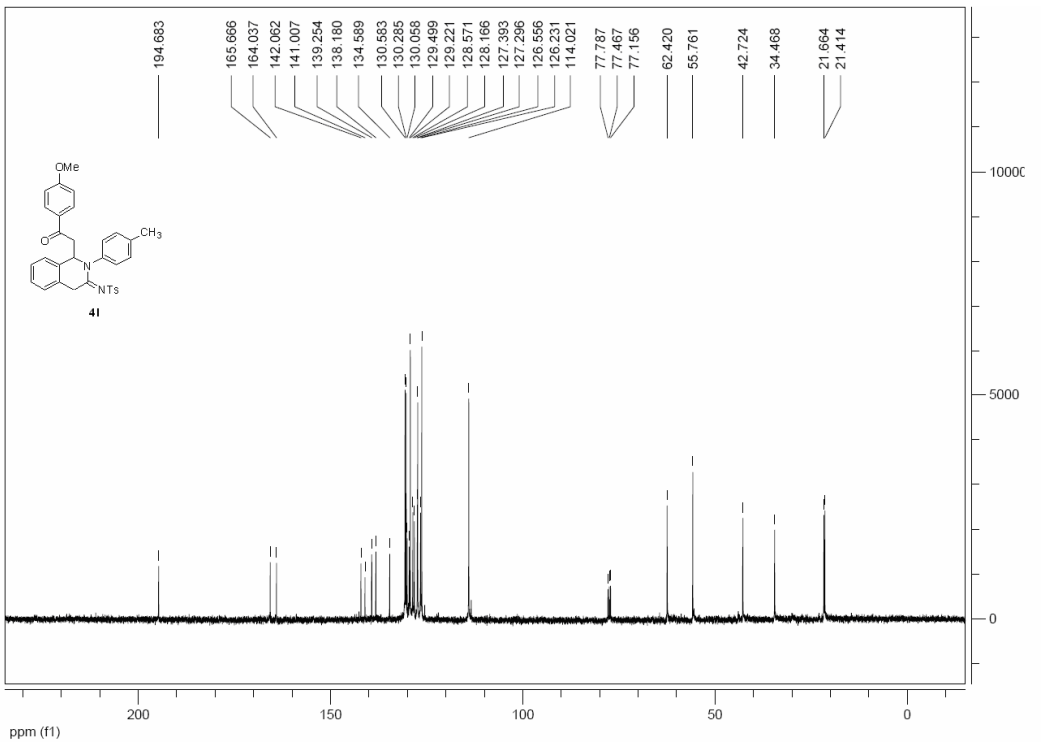
ppm (f1)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126.556
126.231
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77.787
77.467
77.156
62.420
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CH3
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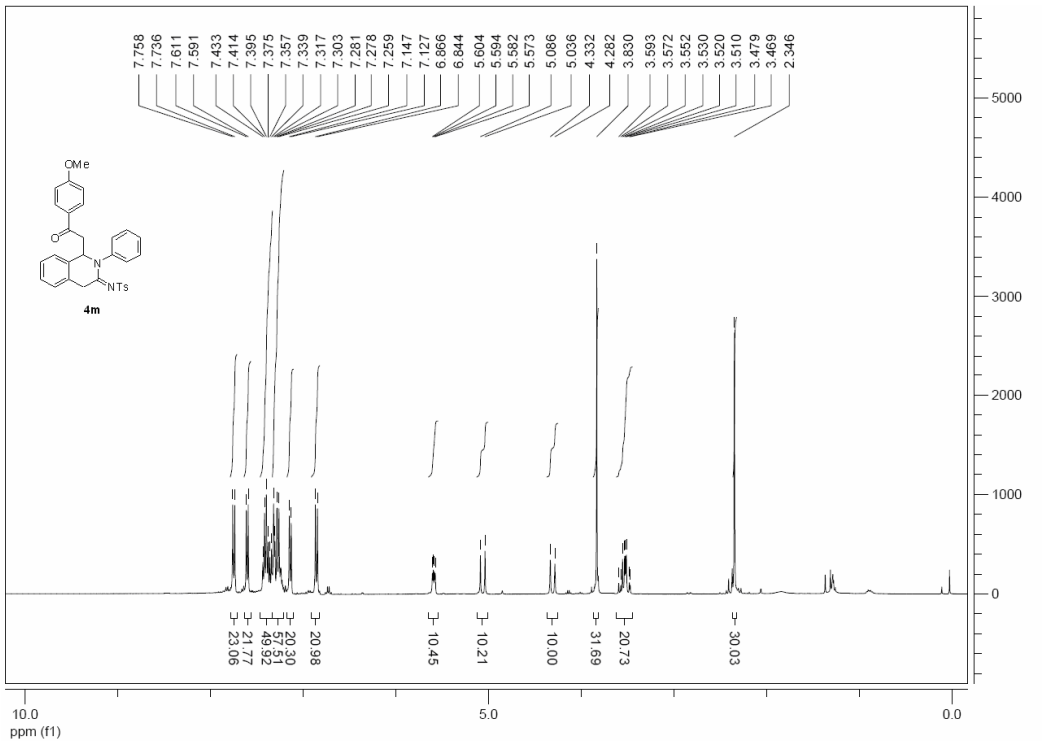
ppm (f1)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3.469
2.346
OMe
O
N
NTs
4m
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10.45
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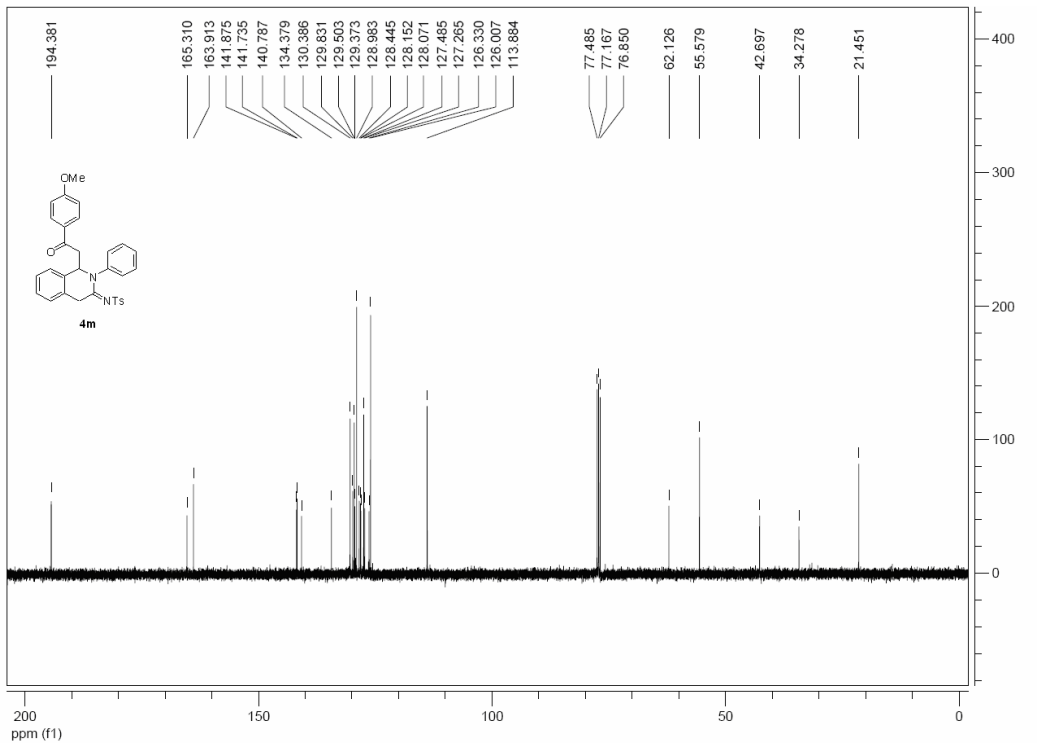
ppm (f1)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42.697
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N
NTs
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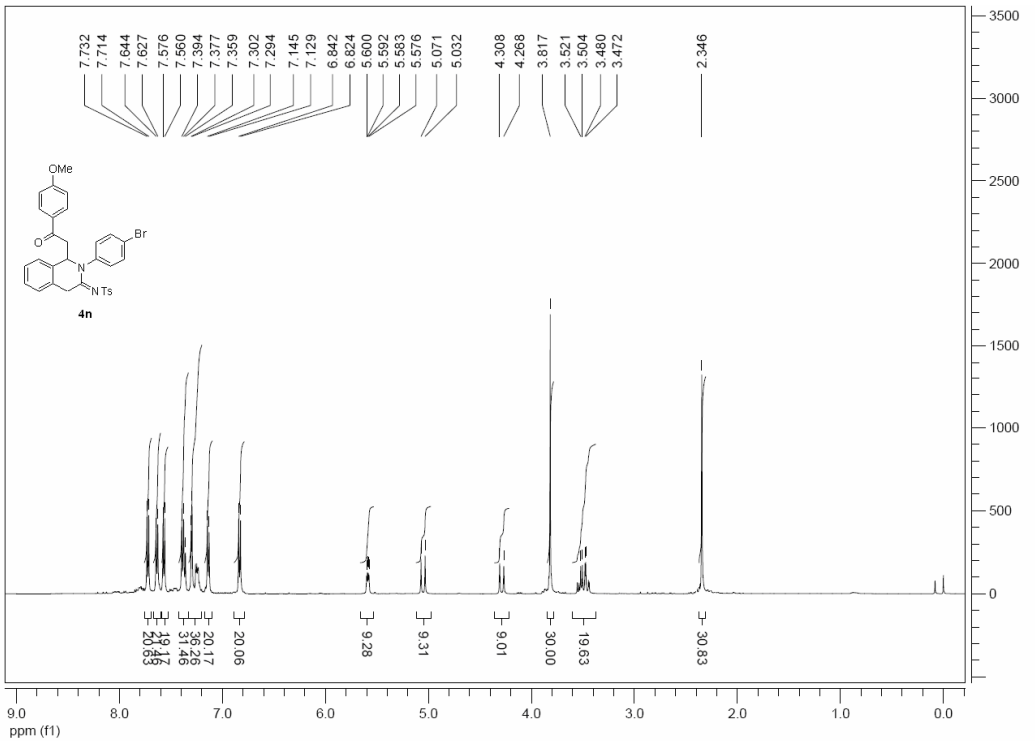
ppm (f1)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Br
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NTs
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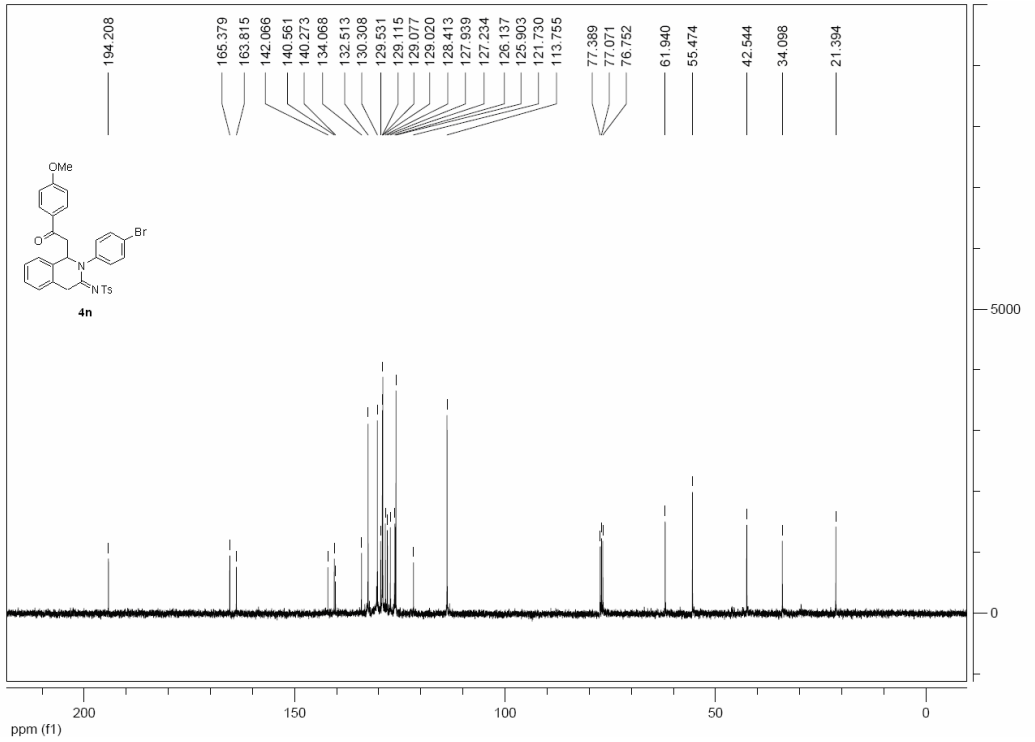
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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163.815
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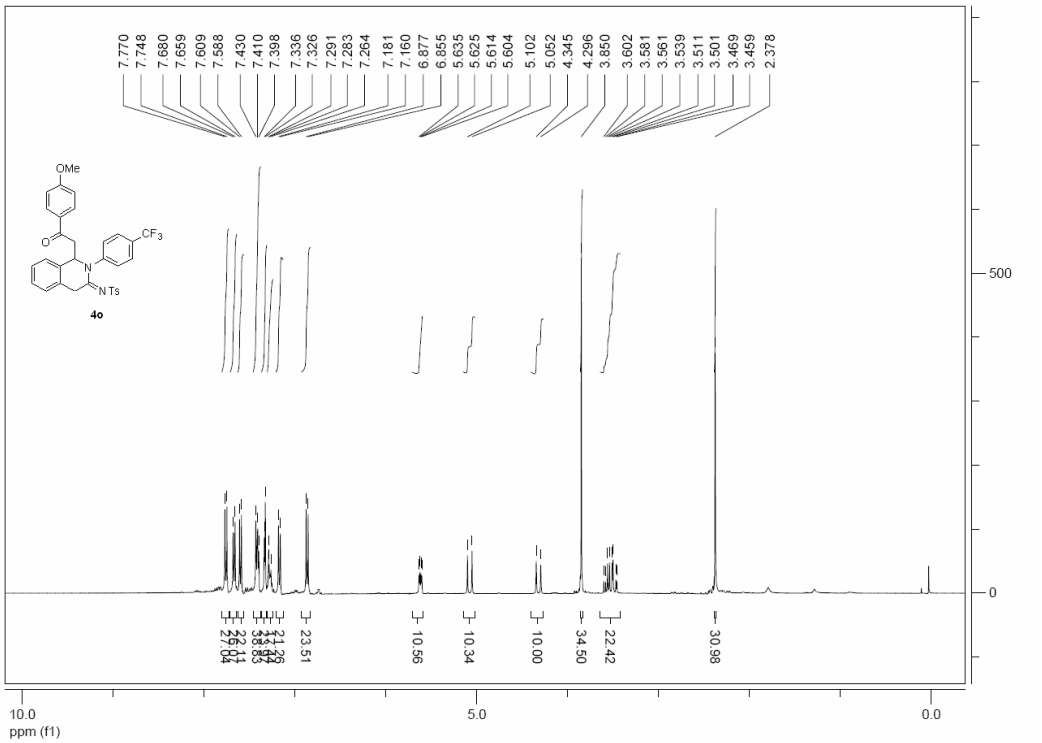
140.273
134.068
132.513
130.308
129.531
129.115
129.077
129.020
128.413
127.939
127.234
126.137
125.903
121.730
113.755
77.389
77.071
76.752
61.940
55.474
42.544
34.098
21.394
OMe
Br
N
NTs
4n
5000
0
200
150
100
50
0
ppm (f1)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7.748
7.680
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7.609
7.588
7.430
7.410
7.398
7.336
7.326
7.291
7.283
7.264
7.181
7.160
6.877
6.855
5.635
5.625
5.614
5.604
5.102
5.052
4.345
4.296
3.850
3.602
3.581
3.561
3.539
3.511
3.501
3.469
3.459
2.378
OMe
CF3
O
N
NTs
4o
500
0
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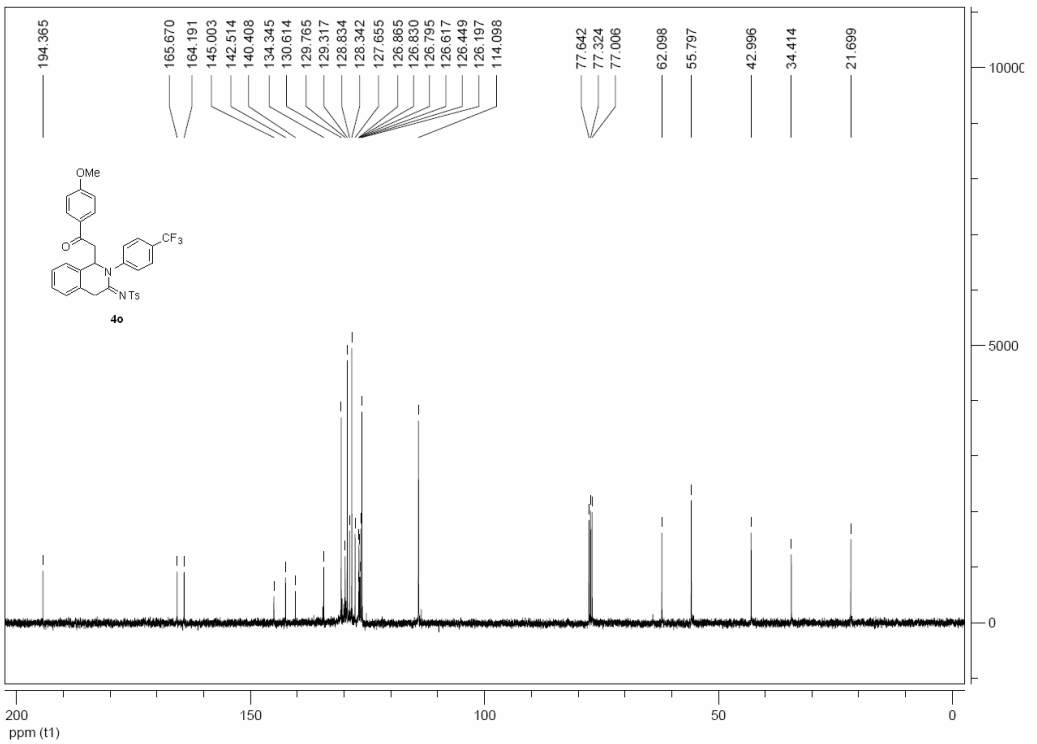
10.34
10.00
34.50
22.42
30.98
10.0
5.0
0.0
ppm (f1)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164.191
145.003
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134.345
130.614
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128.834
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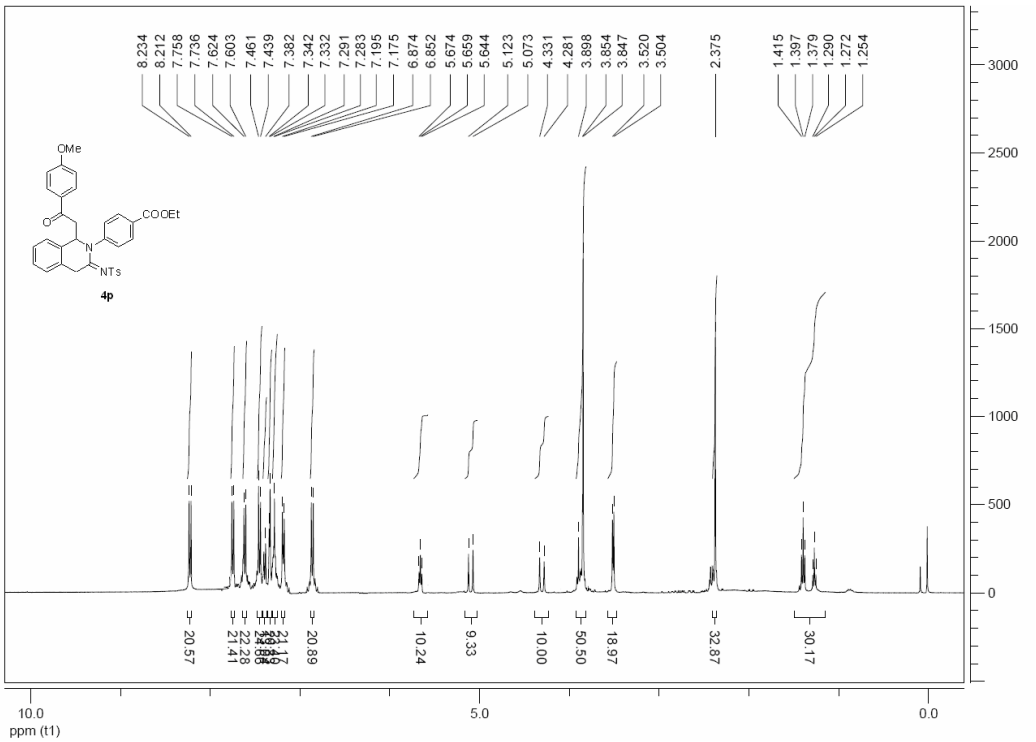
127.655
126.865
126.830
126.795
126.617
126.449
126.197
114.098
77.642
77.324
77.006
62.098
55.797
42.996
34.414
21.699
OMe
CF3
O
N
NTs
4o
10000
5000
0
200
150
100
50
0
ppm (t1)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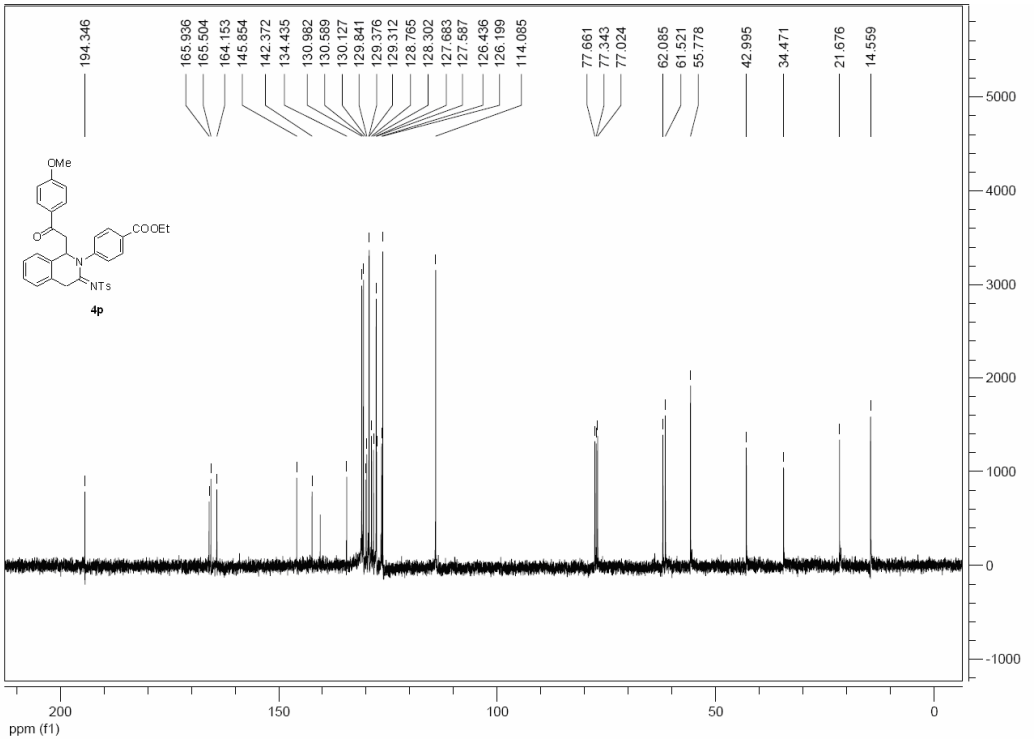
8.212
7.758
7.736
7.624
7.603
7.461
7.439
7.382
7.342
7.332
7.291
7.283
7.195
7.175
6.874
6.852
5.674
5.659
5.644
5.123
5.073
4.331
4.281
3.898
3.854
3.847
3.520
3.504
2.375
1.415
1.397
1.379
1.290
1.272
1.254
OMe
COOEt
NTs
4p
20.57
20.89
10.24
9.33
10.00
50.50
18.67
32.87
30.17
10.0
5.0
0.0
ppm (t1)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165.936
165.504
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130.982
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129.841
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129.312
128.765
128.302
127.683
127.587
126.436
126.199
114.085
77.661
77.343
77.024
62.085
61.521
55.778
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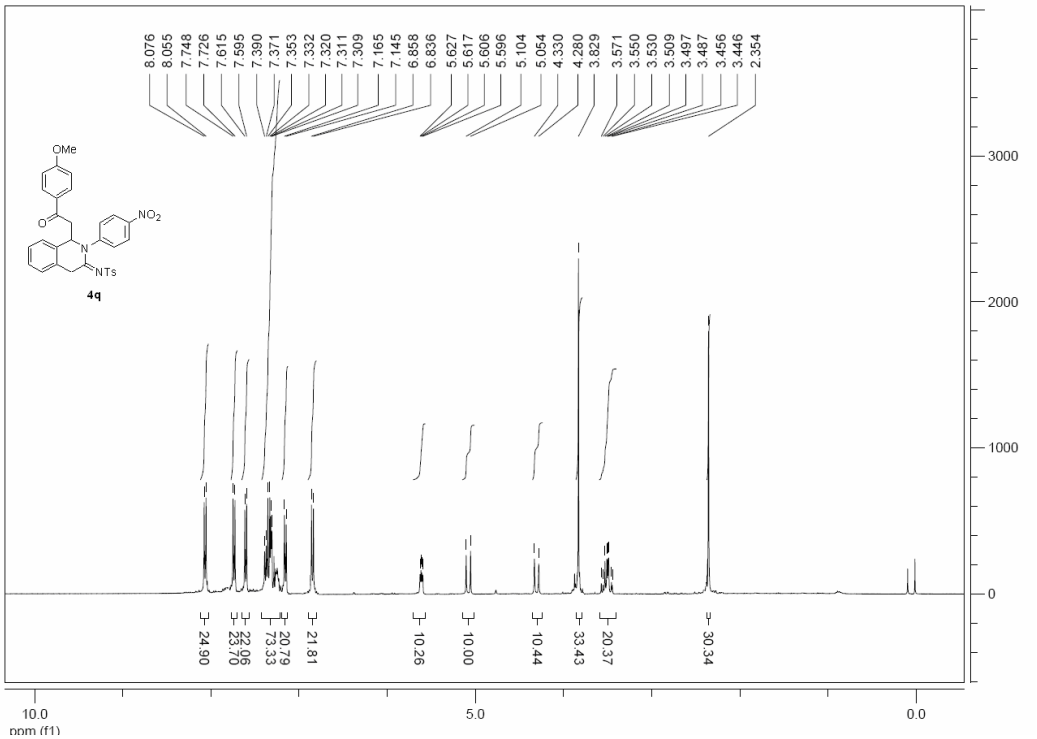
21.676
14.559
OMe
COOEt
NTs
4p
200
150
100
50
0
ppm (f1)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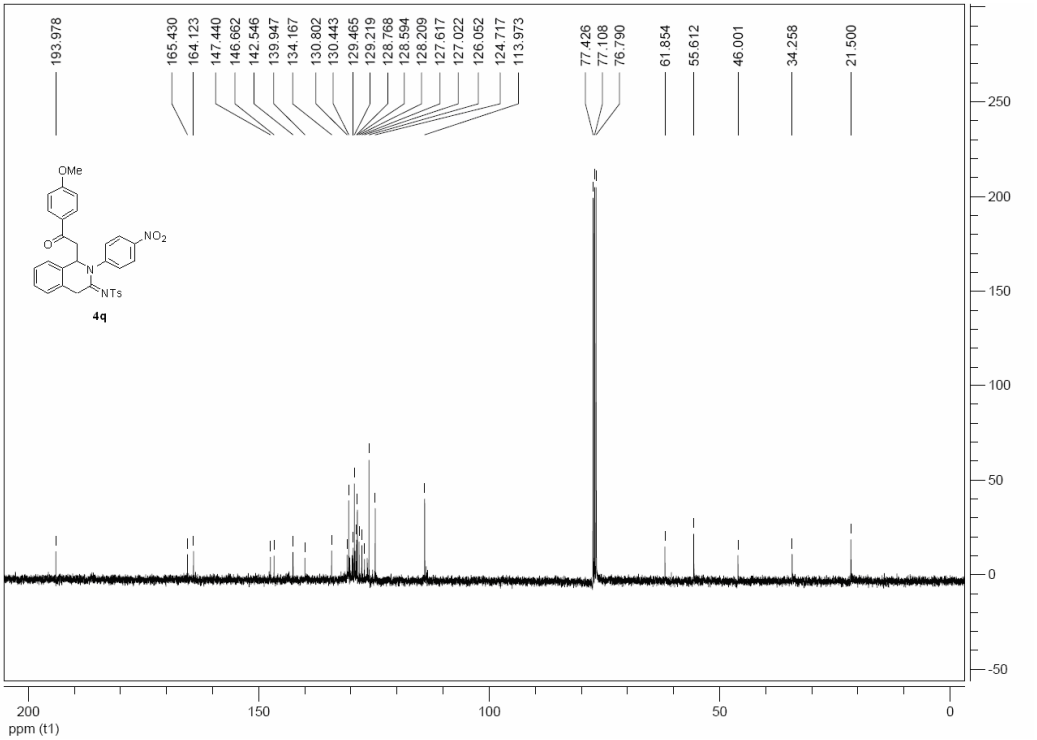
7.615
7.595
7.390
7.371
7.353
7.332
7.320
7.311
7.309
7.165
7.145
6.858
6.836
5.627
5.617
5.606
5.596
5.104
5.054
4.330
4.280
3.829
3.571
3.550
3.530
3.509
3.497
3.487
3.456
3.446
2.354
OMe
O
N
NTs
NO2
4q
24.90
23.70
22.06
73.33
20.79
21.81
10.26
10.00
10.44
33.43
20.37
30.34
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)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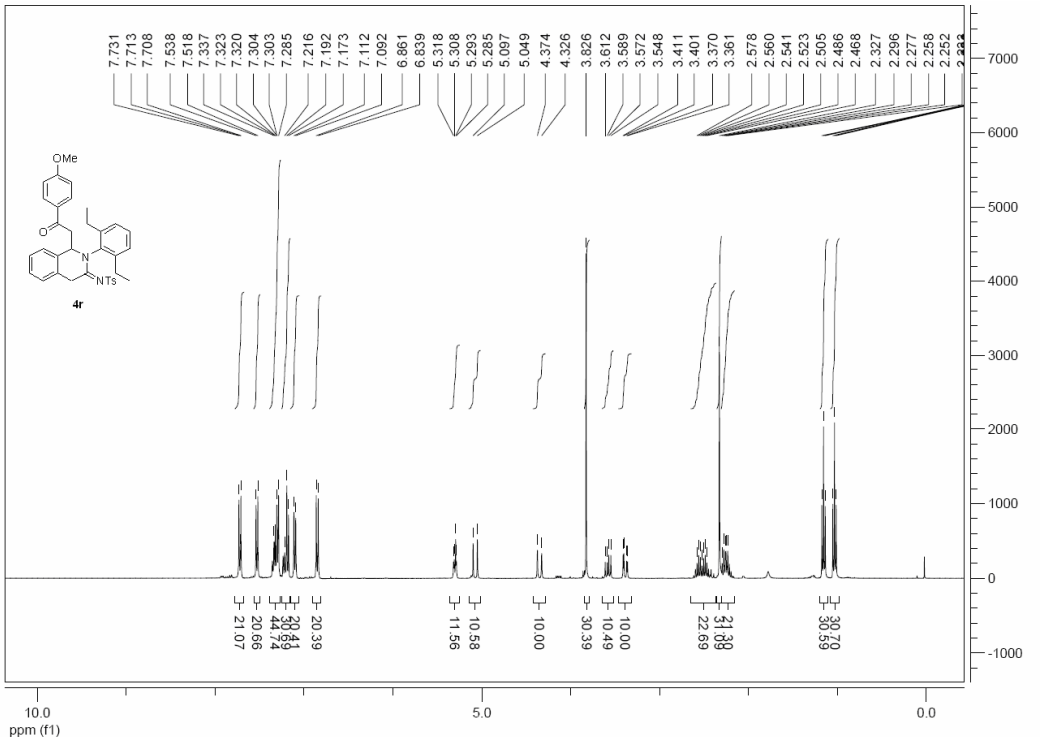
147.440
146.662
142.546
139.947
134.167
130.802
130.443
129.465
129.219
128.768
128.594
128.209
127.617
127.022
126.052
124.717
113.973
77.426
77.108
76.790
61.854
55.612
46.001
34.258
21.500
OMe
O
N
NTs
NO2
4q
250
200
150
100
50
0
-50
200
150
100
50
0
ppm (t1)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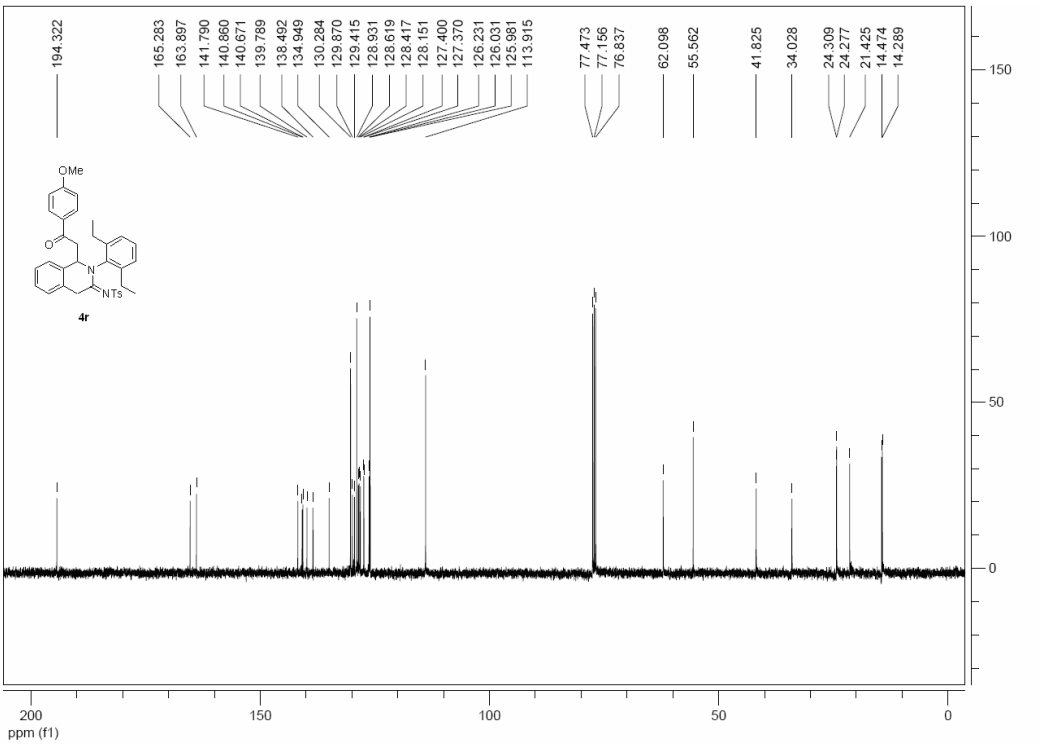
7.518
7.337
7.323
7.320
7.304
7.303
7.285
7.216
7.192
7.173
7.112
7.092
6.861
6.839
5.318
5.308
5.293
5.285
5.097
5.049
4.374
4.326
3.826
3.612
3.589
3.572
3.548
3.411
3.401
3.370
3.361
2.578
2.560
2.541
2.523
2.505
2.486
2.468
2.327
2.296
2.277
2.258
2.252
OMe
O
N
NTs
4r
21.07
20.96
44.74
20.39
11.56
10.58
10.00
30.39
10.00
22.99
31.39
30.70
10.0
ppm (f1)
5.0
0.0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140.671
139.789
138.492
134.949
130.284
129.870
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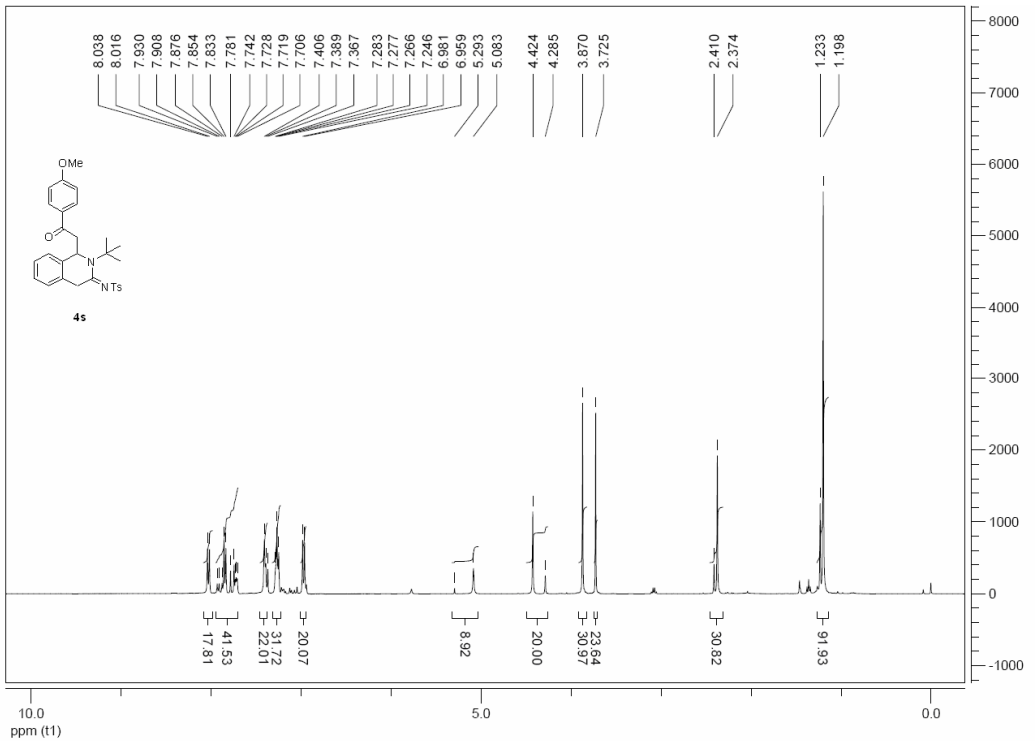
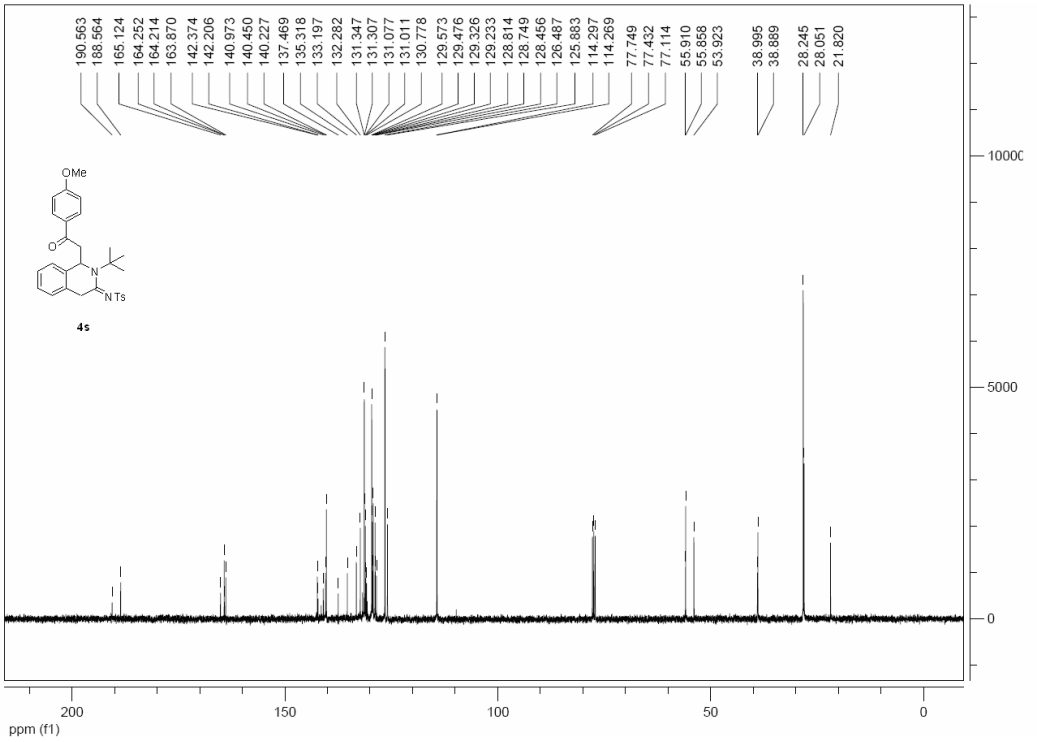
128.931
128.619
128.417
128.151
127.400
127.370
126.231
126.031
125.981
113.915
77.473
77.156
76.837
62.098
55.562
41.825
34.028
24.309
24.277
21.425
14.474
14.289
OMe
O
N
NTs
4r
200
ppm (f1)
150
100
50
0


8.038
8.016
7.930
7.908
7.876
7.854
7.833
7.781
7.742
7.728
7.719
7.706
7.406
7.389
7.367
7.283
7.277
7.266
7.246
6.981
6.959
5.293
5.083
4.424
4.285
3.870
3.725
2.410
2.374
1.233
1.198
OMe
O
N
NTs
4s
17.81
41.53
22.01
13.72
20.07
8.92
20.00
36.47
22.94
30.82
91.93
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
5.0
0.0
ppm (t1)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163.870
142.374
142.206
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140.450
140.227
137.469
135.318
133.197
132.282
131.347
131.307
131.077
131.011
130.778
129.573
129.476
129.326
129.233
128.814
128.749
128.456
126.487
125.883
114.297
114.269
77.749
77.432
77.114
55.910
55.858
53.923
38.995
38.889
28.245
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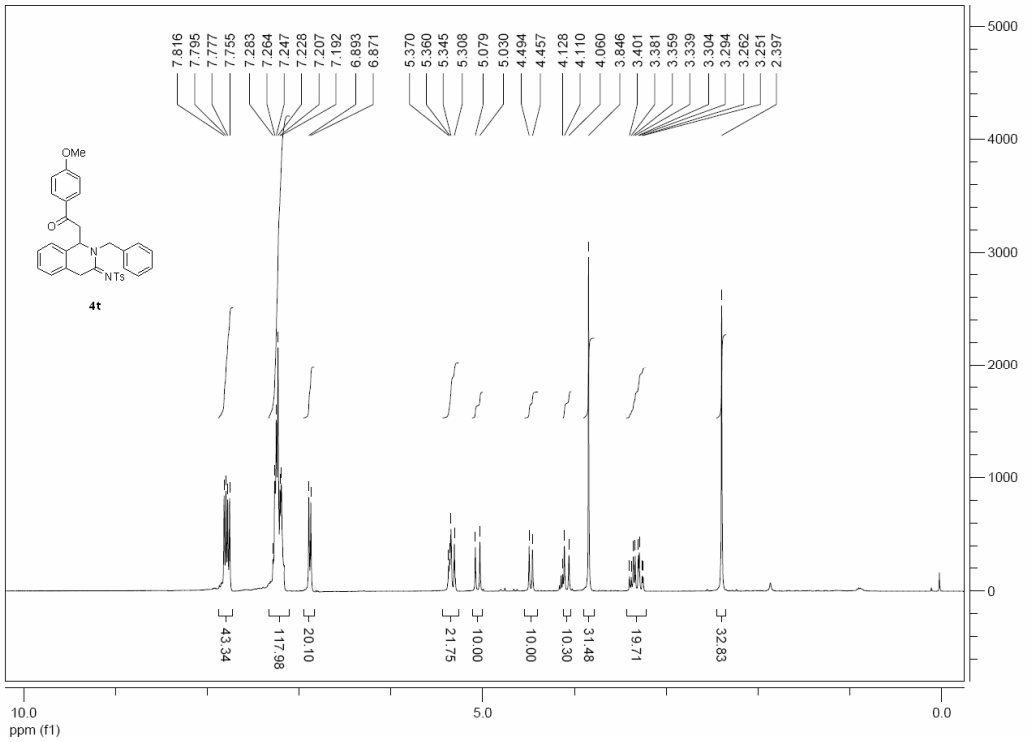
OMe
O
N
NTs
4s
10000
5000
0
200
150
100
50
0
ppm (f1)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7.247
7.228
7.207
7.192
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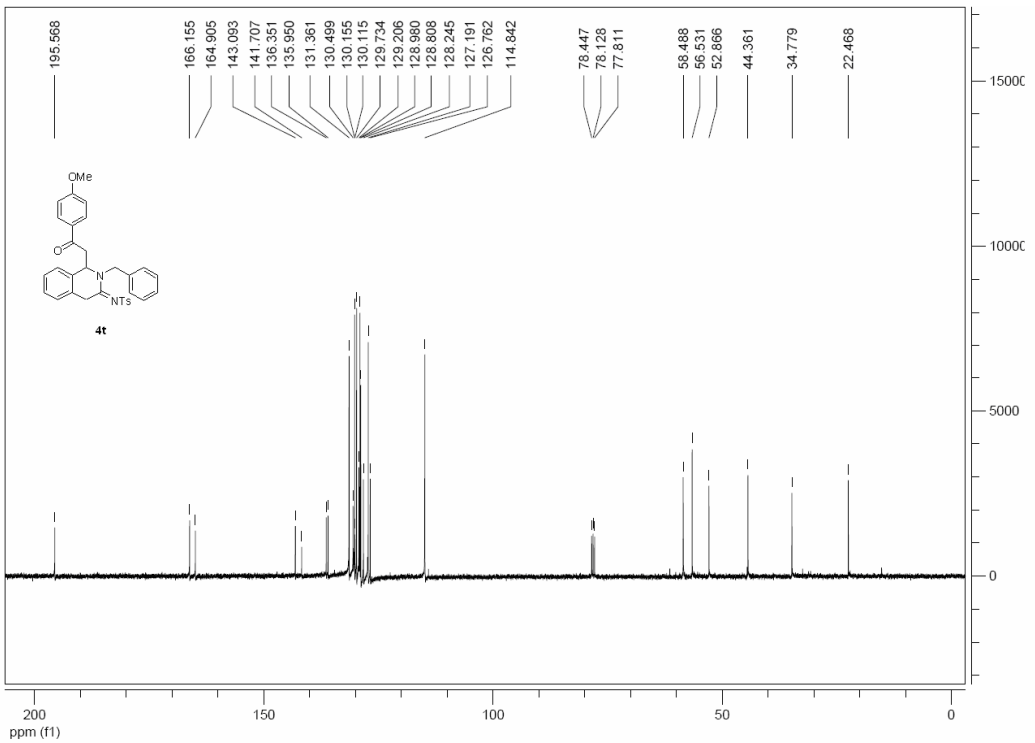
6.871
5.370
5.360
5.345
5.308
5.079
5.030
4.494
4.457
4.128
4.110
4.060
3.846
3.401
3.381
3.359
3.339
3.304
3.294
3.262
3.251
2.397
OMe
O
N
NTs
4t
43.34
117.98
20.10
21.75
10.00
10.00
10.30
31.48
19.71
22.83
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)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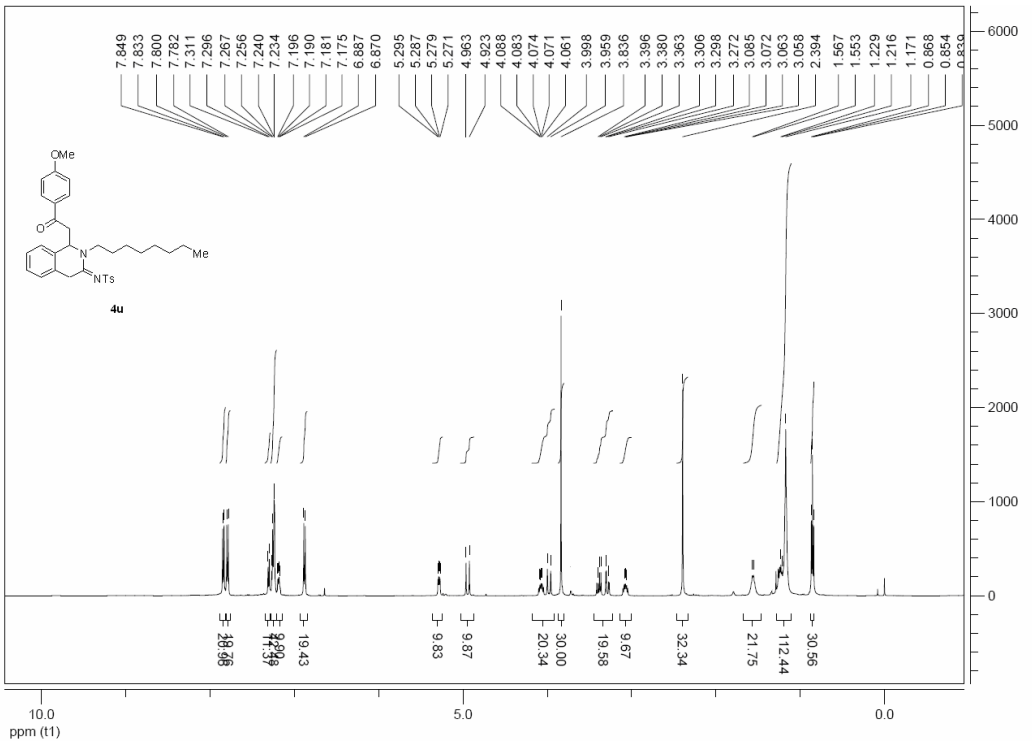
135.950
131.361
130.499
130.155
130.115
129.734
129.206
128.980
128.808
128.245
127.191
126.762
114.842
78.447
78.128
77.811
58.488
56.531
52.866
44.361
34.779
22.468
OMe
O
N
NTs
4t
15000
10000
5000
0
200
150
100
50
0
ppm (f1)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7.256
7.240
7.234
7.196
7.190
7.181
7.175
6.887
6.870
5.295
5.287
5.279
5.271
4.963
4.923
4.088
4.083
4.074
4.071
4.061
3.998
3.959
3.836
3.396
3.380
3.363
3.306
3.298
3.272
3.085
3.072
3.063
3.058
2.394
1.567
1.553
1.229
1.216
1.171
0.868
0.854
OMe
O
N
Me
NTs
4u
19.43
6.83
6.87
20.34
30.00
19.58
9.67
32.34
21.75
112.44
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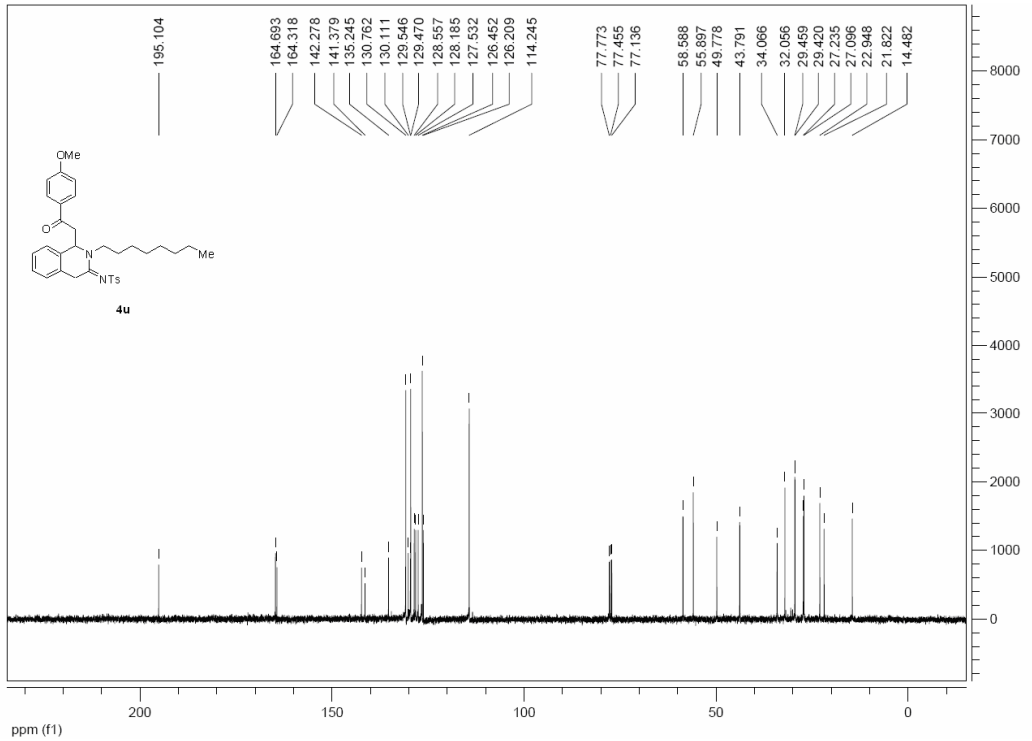
10.0
5.0
0.0
ppm (t1)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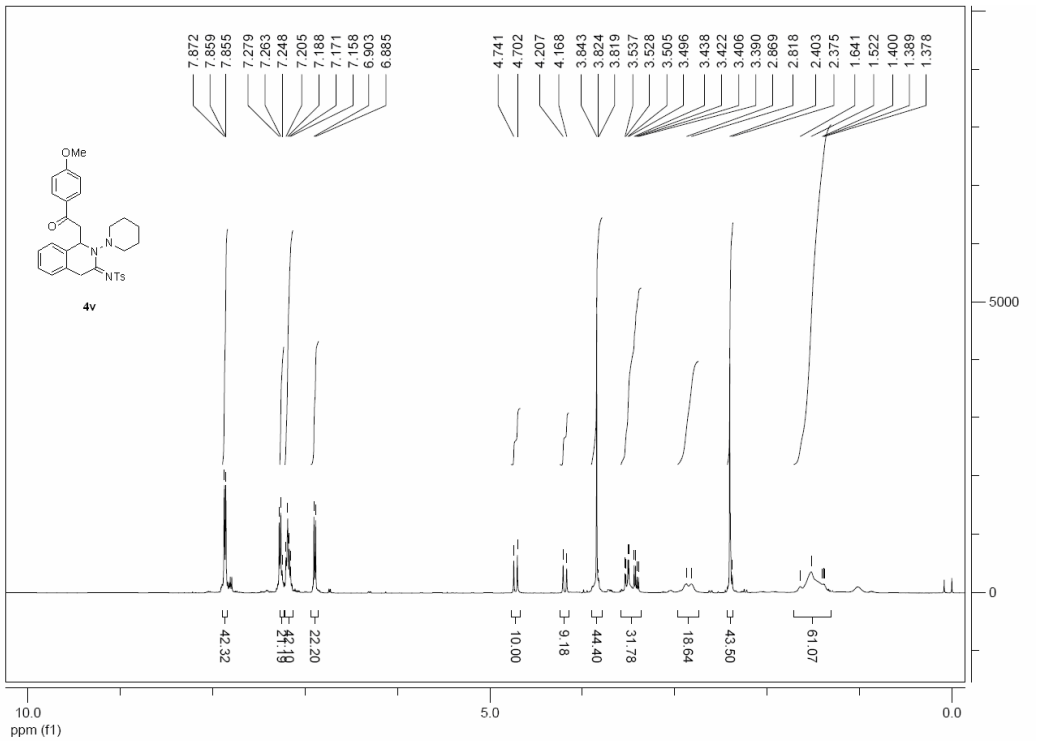
129.470
128.557
128.185
127.532
126.452
126.209
114.245
77.773
77.455
77.136
58.588
55.897
49.778
43.791
34.066
32.056
29.459
29.420
27.235
27.096
22.948
21.822
14.482
OMe
O
N
Me
NTs
4u
200
150
100
50
0
ppm (f1)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7.158
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6.885
4.741
4.702
4.207
4.168
3.843
3.824
3.819
3.537
3.528
3.505
3.496
3.438
3.422
3.406
3.390
2.869
2.818
2.403
2.375
1.641
1.522
1.400
1.389
1.378
OMe
O
N
N
NTs
4v
42.32
22.20
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10.0
5.0
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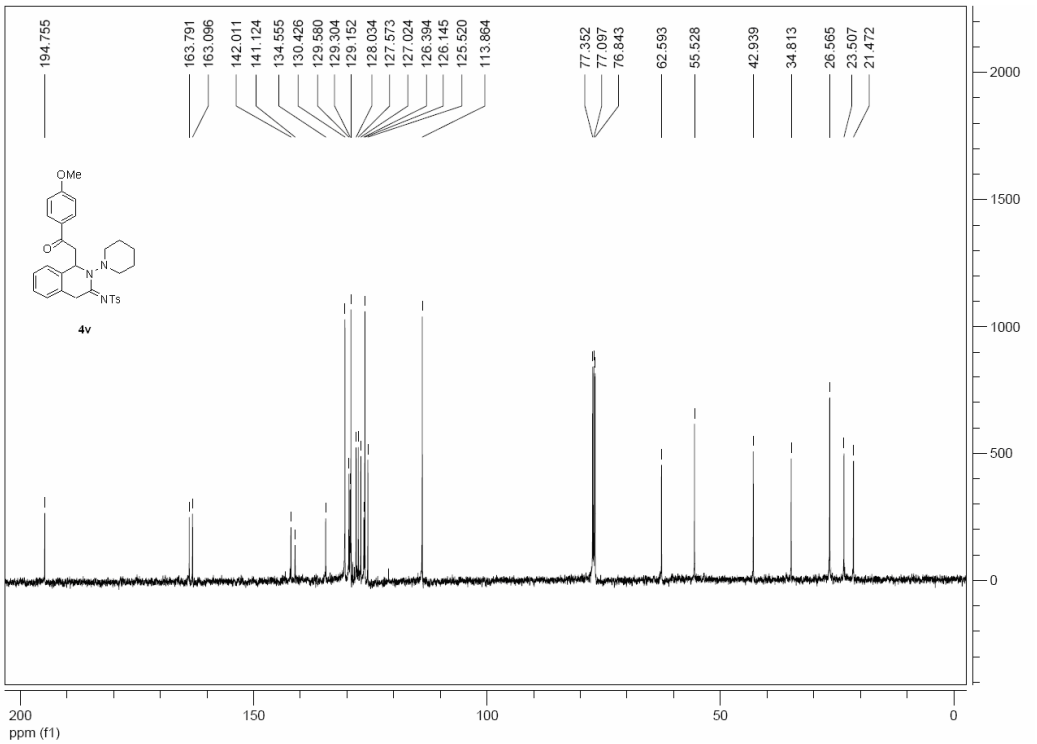
ppm (f1)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163.096
142.011
141.124
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129.580
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129.152
128.034
127.573
127.024
126.394
126.145
125.520
113.864
77.352
77.097
76.843
62.593
55.528
42.939
34.813
26.565
23.507
21.472
OMe
O
N
N
NTs
4v
2000
1500
1000
500
0
200
150
100
50
0
ppm (f1)