Synthesis of 4-Amino-7-oxyindoles via Dearomatization of 4-Alkyl-2-alkynylanilines and Dual Fragment Incorporation with *O*-Benzoylhydroxylamines

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Supplementary Information

Content

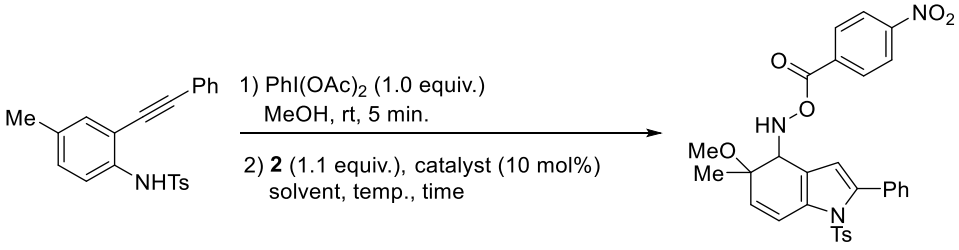
Supplementary Methods

1. General Information:

All reactions were performed in oven dried test tubes or Schlenk tube. 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. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. High Resolution Mass spectra was recorded by Waters G2-xs Tof (ESI+).

2. Evaluation of the Reaction Conditions

Table S1. Reaction Optimization with **Int-3a**.



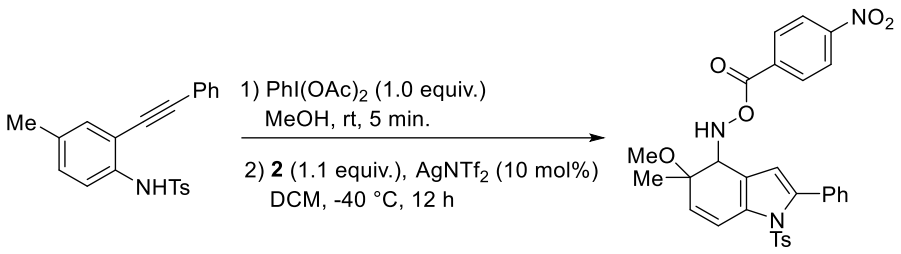
1a **Int-3a**

Entry	Catalyst	Solvent	Temp.	Time	Yield[a]
1	AgOTf	DCM	-40 °C	6 h	48%
2	$Zn(OTf)_2$	DCM	-40 °C	6 h	20%
3	$Bi(OTf)_3$	DCM	-40 °C	6 h	35%
4	$Sc(OTf)_3$	DCM	-40 °C	6 h	28%
5	$Yb(OTf)_3$	DCM	-40 °C	6 h	0%
6	$In(OTf)_3$	DCM	-40 °C	6 h	7%
7	$Cu(OTf)_2$	DCM	-40 °C	6 h	3%
8	$AgBF_4$	DCM	-40 °C	6 h	15%
9	$AgClO_4$	DCM	-40 °C	6 h	0%
10	AgF	DCM	-40 °C	6 h	18%
11	$AgOCOCF_3$	DCM	-40 °C	6 h	45%
12	AgOAc	DCM	-40 °C	6 h	8%
13	LiCl	DCM	-40 °C	6 h	10%
14	$Rh(PPh_3)Cl$	DCM	-40 °C	6 h	0%
15	$AgNTf_2$	DCM	-40 °C	6 h	63%
16	$AgNTf_2$	DCM	-30 °C	6 h	46%
17	$AgNTf_2$	DCM	-40 °C	8 h	73%
18	$AgNTf_2$	DCM	-40 °C	12 h	85%
19	$AgNTf_2$	THF	-40 °C	12 h	0%

20	$AgNTf_2$	CH_3CN	-40 °C	12 h	23%
21	$AgNTf_2$	DMF	-40 °C	12 h	0%
22	$AgNTf_2$	Acetone	-40 °C	12 h	0%

[a] NMR yield.

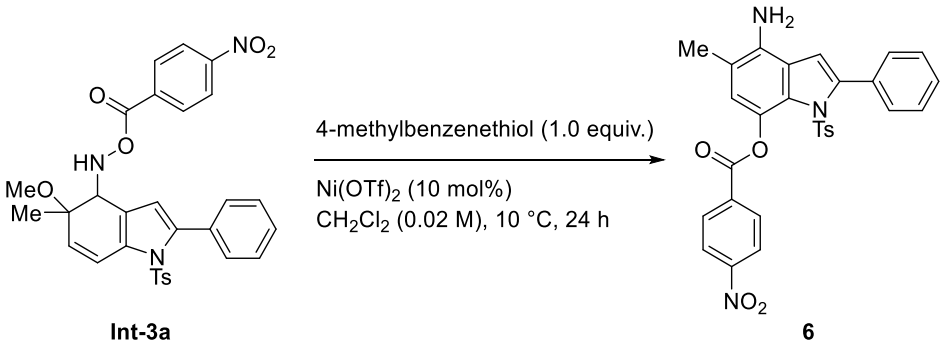
3. Representative Procedure



1a **Int-3a**

General Procedure for Synthesis of *N*-(5-methoxy-5-methyl-2-phenyl-1-tosyl-4,5-dihydro-1*H*-indol-4-yl)-*O*-(4-nitrobenzoyl)hydroxylamine:

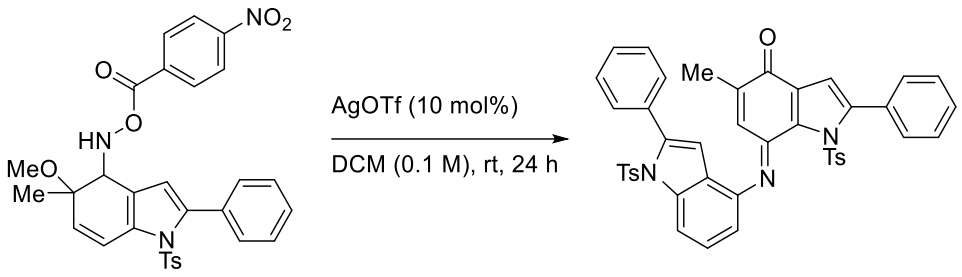
$PhI(OAc)_2$ (0.11 mmol) was added to a solution of 4-methyl-*N*-(4-methyl-2-(phenylethynyl)phenyl)benzenesulfonamide **1a** (0.1 mmol) in MeOH (2.0 mL) at 25 °C. After 5 min, the reaction mixture was concentrated in vacuo. The resulting mixture was mixed with *O*-(4-nitrobenzoyl)hydroxylamine **2** (0.11 mmol, 1.1 equiv., 20.0 mg) and anhydrous dichloromethane (1.0 mL) in a dry Schlenk tube. The solution was cooled to -40 °C and $AgNTf_2$ (0.01 mmol, 10 mol%, 3.8 mg) was added under nitrogen atmosphere. After stirring for 12 h, the reaction mixture was allowed to warm to room temperature and then passed through a short silica gel column. Solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1) to furnish the desired product.



Int-3a **6**

General Procedure for Synthesis of 4-amino-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate:

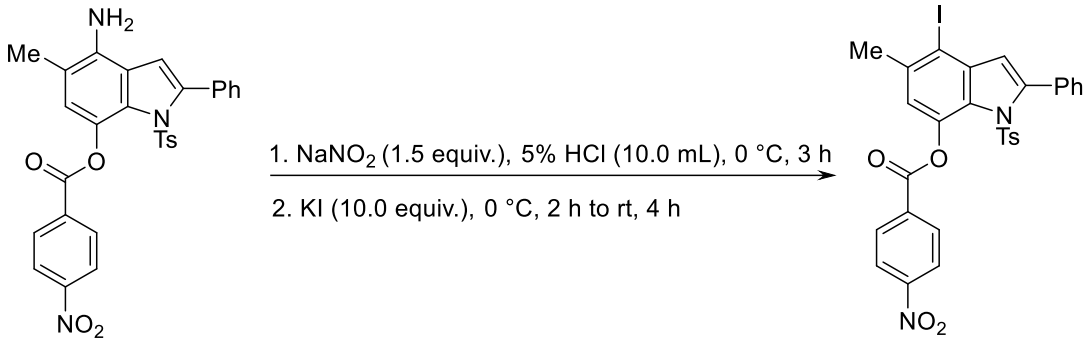
To a dried 25 mL round-bottom flask containing 4-methylbenzenethiol (0.10 mmol, 1.0 equiv., 12.4 mg), $Ni(OTf)_2$ (0.01 mmol, 10 mol%, 3.5 mg), *N*-(5-methoxy-5-methyl-2-phenyl-1-tosyl-4,5-dihydro-1*H*-indol-4-yl)-*O*-(4-nitrobenzoyl)hydroxylamine **Int-3a** (0.1 mmol, 1.0 equiv., 57.3 mg) and dichloromethane (5 mL) were added under nitrogen atmosphere. After stirred at 10 °C for 24 h, the mixture was allowed to warm to room temperature and then passed through a short silica gel column. Solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) to furnish the desired product.



Int-3a **4**

General Procedure for Synthesis of 5-methyl-2-phenyl-7-((2-phenyl-1-tosyl-1*H*-indol-4-yl)imino)-1-tosyl-1,7-dihydro-4*H*-indol-4-one:

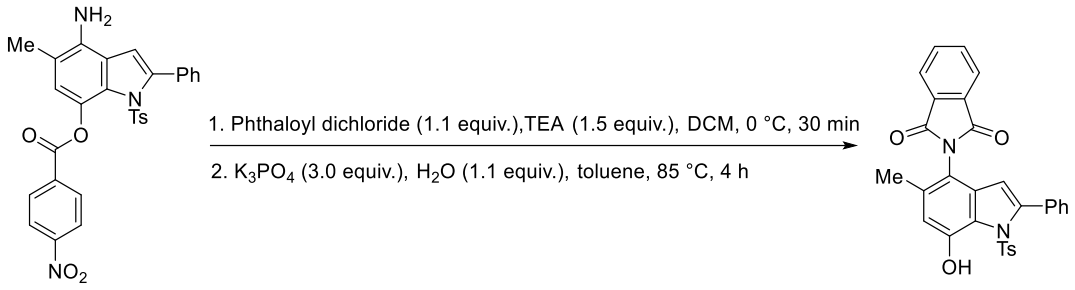
N-(5-methoxy-5-methyl-2-phenyl-1-tosyl-4,5-dihydro-1*H*-indol-4-yl)-*O*-(4-nitrobenzoyl)hydroxylamine **Int-3a** (0.1 mmol, 1.0 equiv., 57.3 mg) was dissolved in dichloromethane (10 mL), then added AgOTf (0.01 mmol, 10 mol%, 2.6 mg) under air atmosphere in a 25 mL round-bottom flask. The mixture was stirred at room temperature for 24 h and then passed through a short silica gel column. Solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1) to furnish the desired product.



6 **32**

General Procedure[1] for Synthesis of 4-iodo-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate:

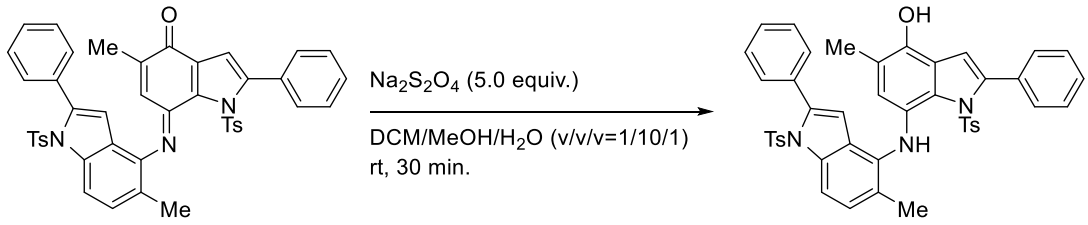
To a solution of 4-amino-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate **6** (0.1 mmol, 1.0 equiv., 54.1 mg) in water (2.0 mL) was added aqueous HCl (37%, 0.4 mL). This mixture was cooled to 0 °C and stirred for 2 min, and the $NaNO_2$ solution (0.3 mL) was then added. The $NaNO_2$ solution was prepared by dissolving 14 mg of $NaNO_2$ in water (0.3 mL). After stirred for another 2 h, KI (0.5 mmol, 5.0 equiv.) was added, and the mixture was allowed to warm to room temperature slowly. After being stirred for another 4 h, the solvent was extracted with ethyl acetate (5 mL × 3). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to furnish the desired product.



6 **33**

General Procedure for Synthesis of 4-(1,3-dioxoisoindolin-2-yl)-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate:

To a solution of 4-amino-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate **6** (0.2 mmol, 1.0 equiv., 108.2 mg) in dichloromethane (2 mL) was added triethylamine (0.3 mmol, 1.5 equiv., 41.6μL) and phthaloyl dichloride (0.22 mmol, 1.1 equiv., 31.9μL) by microsyringes. After stirred for 30 minutes in 0 °C, the reaction mixture was quenched with saturated $NaHCO_3$ (5 mL) and then extracted with ethyl acetate (5 mL × 3). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was added to a dried 25 mL round-bottom flask containing K_3PO_4 (0.6 mmol, 3.0 equiv., 127.2 mg), water (0.22mmol, 1.1 equiv., 4.0μL) and toluene (2 mL) under nitrogen atmosphere. After stirred at 85 °C for 4 h, the mixture was allowed to cool to room temperature and then quenched with saturated $NaHCO_3$ (5 mL), extracted with ethyl acetate (5 mL × 3). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4. Solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) to furnish the desired product.



4 **34**

General Procedure[2] for Synthesis of 5-methyl-7-((5-methyl-2-phenyl-1-tosyl-1*H*-indol-4-yl)amino)-2-phenyl-1-tosyl-1*H*-indol-4-ol:

To a mixed solvent of dichloromethane (0.5 mL), methanol (5.0 mL) and water (0.5 mL), 5-methyl-7-((5-methyl-2-phenyl-1-tosyl-1*H*-indol-4-yl)imino)-2-phenyl-1-tosyl-1,7-dihydro-4*H*-indol-4-one **4** (0.1 mmol, 1.0 equiv., 75.0 mg) and $Na_2S_2O_4$ (0.5 mmol, 5.0 equiv., 87 mg) were added. After stirred for 30 minutes , the reaction mixture was quenched with saturated $NaHCO_3$ (5 mL) and then extracted with ethyl acetate (5 mL × 3). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1) to furnish the desired product.

Supplementary References

1. J. Panteleev, R. Y. Huang, E. K. J. Lui, M. Lautens, *Org. Lett.*, 2011, **13**, 5314.
2. K. Navneet, K. Subodh, *Tetrahedron*, **2008**, 64, 14, 3168-3175.

4. Crystal details

Crystal details of compound 5

Sample preparation: A solution of compound **5** (0.1 mmol) in a mixed solvent of ether (1mL) and petroleum ether (1 mL) was placed in a vial (10 mL). The single crystal was obtained by slowly evaporating solvent at room temperature under the air conditions.

Crystal measurement: X-ray crystal structures of **5** were determined at 173 K by using D8 VENTURE Single Crystal X-Ray diffractometer.

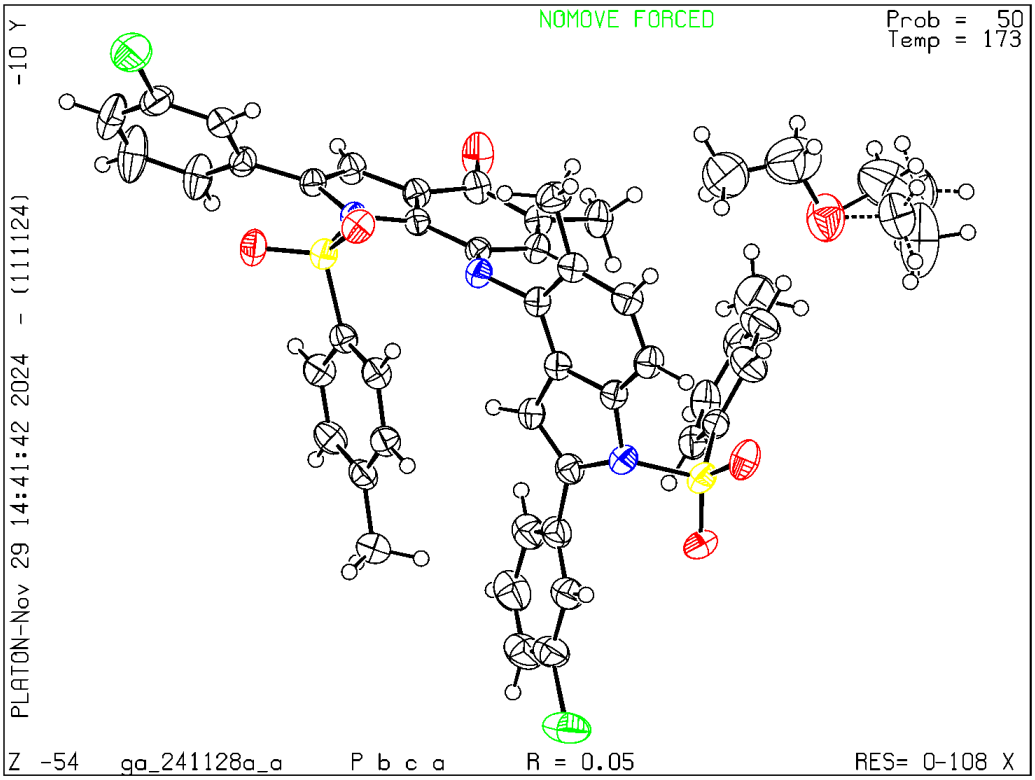


Figure S1. Crystal structure of compound **5**

Table S2. Crystal data and structure refinement for compound **5**

Identification code	ga_241128a_a
Empirical formula	$C_{48}H_{43}Cl_2N_3O_6S_2$
Formula weight	892.87
Temperature/K	173.0
Wavelength/Å	1.34138
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.2681(6)
b/Å	15.8022(6)
c/Å	34.5237(12)
α/°	90
β/°	90

γ/°	90
Volume/Å3	8875.1(6)
Z	8
ρcalcg/cm3	1.336
μ/mm-1	1.708
F(000)	3728.0
Crystal size/mm3	0.20 × 0.20 × 0.10
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.496 to 106.202
Index ranges	-18 ≤ h ≤ 19, -18 ≤ k ≤ 18, -40 ≤ l ≤ 41
Reflections collected	115884
Independent reflections	7864 [Rint = 0.0801, Rsigma = 0.0304]
Data/restraints/parameters	7864/35/576
Goodness-of-fit on F2	1.024
Final R indexes [I>=2σ (I)]	R1 = 0.0472, wR2 = 0.1233
Final R indexes [all data]	R1 = 0.0653, wR2 = 0.1347
Largest diff. peak/hole / e Å-3	0.54/-0.39

Crystal details of compound 16

Sample preparation: A solution of compound **16** (0.1 mmol) in a mixed solvent of ethyl acetate (1mL) and petroleum ether (2 mL) was placed in a vial (10 mL). The single crystal was obtained by slowly evaporating solvent at room temperature under the air conditions.

Crystal measurement: X-ray crystal structures of **16** were determined at 193 K by using D8 VENTURE Single Crystal X-Ray diffractometer.

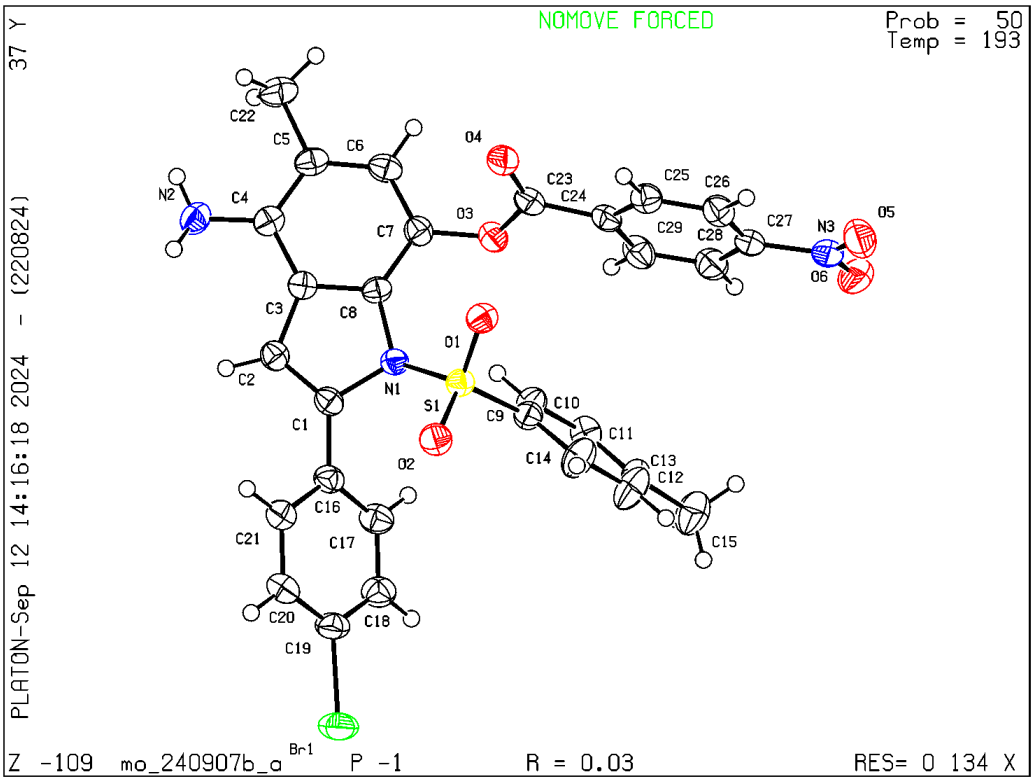


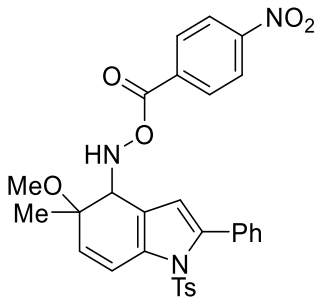
Figure S2. Crystal structure of compound **16**

Table S3. Crystal data and structure refinement for compound **16**

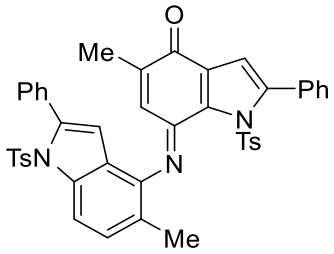
Identification code	mo_240907b_a
Empirical formula	$C_{29}H_{22}BrN_3O_6S$
Formula weight	620.46
Temperature/K	193.0
Wavelength/Å	0.71073
Crystal system	triclinic
Space group	P-1
a/Å	10.8071(12)
b/Å	11.4940(12)
c/Å	11.7684(12)
α/°	81.247(4)
β/°	67.573(3)
γ/°	79.206(4)
Volume/Å^3	1322.1(2)
Z	2
ρ_{calc}g/cm^3	1.559
μ/mm^{-1}	1.684
F(000)	632.0
Crystal size/mm^3	0.18 × 0.15 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.984 to 54.29

Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	11487
Independent reflections	5820 [R_{int} = 0.0231, R_{sigma} = 0.0374]
Data/restraints/parameters	5820/2/371
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0816
Final R indexes [all data]	R_1 = 0.0394, wR_2 = 0.0854
Largest diff. peak/hole / e $Å^{-3}$	0.68/-0.69

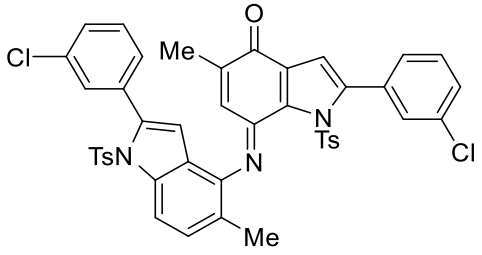
5. Characterization of Products



***N*-(5-methoxy-5-methyl-2-phenyl-1-tosyl-4,5-dihydro-1*H*-indol-4-yl)-*O*-(4-nitrobenzoyl)hydroxylamine (Int-3a)** (eluent: petroleum ether/ ethyl acetate 2:1), 48.7 mg, 85% yield; yellow solid; m.p. : 95-96 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.66 – 8.32 (m, 1H), 8.24 (d, *J* = 8.5 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.27 (m, 7H), 7.17 (d, *J* = 10.3 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.26 (s, 1H), 5.89 (d, *J* = 10.3 Hz, 1H), 4.08 (s, 1H), 3.30 (s, 3H), 2.35 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.32, 150.68, 144.99, 138.52, 135.61, 133.93, 132.07, 132.00, 130.49, 130.47, 129.91, 129.46, 128.46, 127.53, 126.90, 123.78, 123.08, 119.08, 116.68, 75.87, 62.24, 50.71, 22.54, 21.68. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}N_3NaO_7S$ 596.1462; Found: 596.1467.

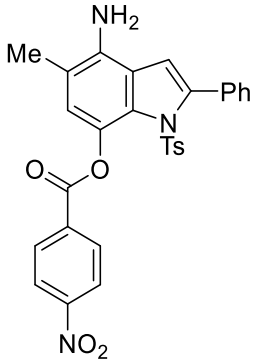


5-methyl-7-((5-methyl-2-phenyl-1-tosyl-1*H*-indol-4-yl)imino)-2-phenyl-1-tosyl-1,7-dihydro-4*H*-indol-4-one (4) (eluent: petroleum ether/ ethyl acetate 3:1), 34.9 mg, 93% yield; black solid; m.p. : 136-137 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.35 (m, 10H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 1H), 6.13 – 6.08 (m, 1H), 5.91 (s, 1H), 2.30 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 1.84 – 1.80 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 183.25, 150.22, 145.23, 144.81, 144.61, 142.61, 140.31, 139.98, 137.43, 137.09, 136.80, 134.53, 132.76, 132.42, 130.18, 129.56, 129.24, 129.13, 128.91, 128.77, 128.15, 127.98, 127.66, 127.09, 125.41, 123.04, 122.12, 113.35, 111.93, 110.83, 21.65, 21.44, 17.56, 15.61. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{44}H_{35}N_3O_5S_2$ 750.2091; Found: 750.2095.

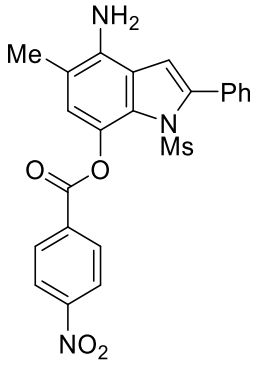


2-(3-chlorophenyl)-7-((2-(3-chlorophenyl)-5-methyl-1-tosyl-1*H*-indol-4-yl)imino)-5-methyl-1-tosyl-1,7-dihydro-4*H*-indol-4-one (5) (eluent: petroleum ether/ ethyl acetate 3:1),

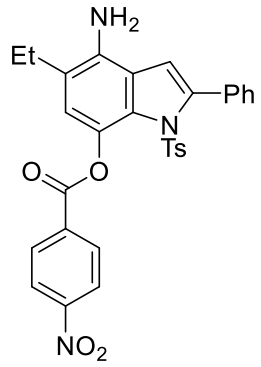
39.2 mg, 96% yield; black solid; m.p. : 151-152 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.25 (m, 11H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.70 (s, 1H), 6.17 – 6.11 (m, 1H), 6.03 (s, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 2.10 (s, 3H), 1.87 – 1.82 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 183.01, 150.39, 145.21, 144.91, 143.45, 140.81, 140.62, 140.16, 137.49, 137.20, 136.82, 134.51, 134.34, 134.11, 133.91, 133.58, 129.74, 129.41, 129.39, 129.34, 129.00, 128.91, 128.77, 128.69, 128.42, 128.11, 127.91, 127.88, 127.07, 125.37, 122.77, 121.86, 113.24, 112.38, 111.27, 21.69, 21.57, 17.55, 15.67. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{44}H_{34}Cl_2N_3O_5S_2$ 818.1312; Found: 818.1312.



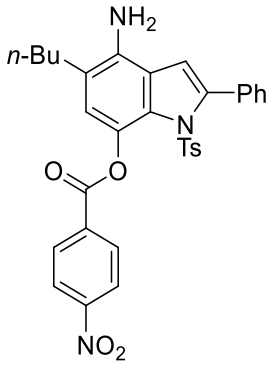
4-amino-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (6) (eluent: petroleum ether/ ethyl acetate 2:1), 33.0 mg, 61% yield; red solid; m.p. : 205-206 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 8.9 Hz, 2H), 8.31 (d, *J* = 9.0 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.38 – 7.33 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 1H), 6.46 (s, 1H), 3.99 – 3.48 (m, 2H), 2.28 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.19, 150.65, 144.59, 143.88, 135.92, 135.38, 133.64, 132.73, 131.88, 131.60, 130.28, 129.28, 129.00, 128.59, 127.83, 127.26, 123.58, 122.88, 122.44, 118.72, 111.87, 21.65, 16.88. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}N_3NaO_6S$ 564.1200; Found: 564.1204.



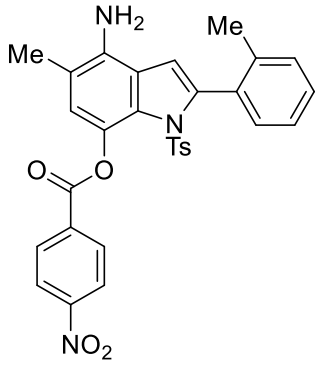
4-amino-5-methyl-1-(methylsulfonyl)-2-phenyl-1*H*-indol-7-yl 4-nitrobenzoate (7) (eluent: petroleum ether/ ethyl acetate 2:1), 29.2 mg, 60% yield; red solid; m.p. : 213-214 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.9 Hz, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.44 – 7.36 (m, 3H), 6.94 (s, 1H), 6.73 (s, 1H), 2.78 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.40, 150.84, 143.74, 135.73, 135.48, 132.87, 131.50, 130.89, 129.63, 129.04, 128.81, 128.13, 123.77, 123.05, 121.91, 118.77, 110.57, 39.12, 16.92. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}N_3NaO_6S$ 488.0887; Found: 488.0883.



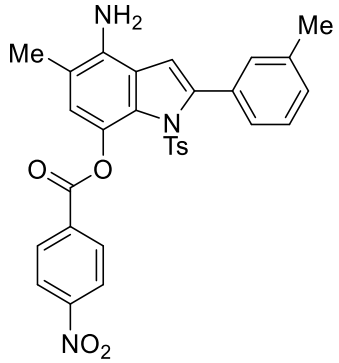
4-amino-5-ethyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (8) (eluent: petroleum ether/ ethyl acetate 2:1), 37.1 mg, 67% yield; red solid; m.p. : 209-210 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 9.0 Hz, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.32 (m, 3H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.96 (s, 1H), 6.55 (s, 1H), 2.61 (q, *J* = 7.5 Hz, 2H), 2.30 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.15, 150.70, 144.58, 143.95, 135.99, 134.54, 133.85, 132.74, 132.34, 131.65, 130.18, 129.35, 129.02, 128.63, 127.85, 127.30, 124.75, 123.63, 122.85, 120.97, 111.76, 23.60, 21.69, 13.26. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{26}N_3O_6S$ 556.1537; Found: 556.1545.



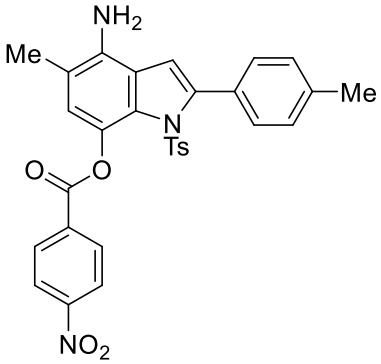
4-amino-5-butyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (9) (eluent: petroleum ether/ ethyl acetate 2:1), 29.0 mg, 50% yield; red solid; m.p. : 194-195 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, J = 8.9 Hz, 2H), 8.33 (d, J = 8.9 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.39 – 7.33 (m, 3H), 7.17 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 6.93 (s, 1H), 6.49 (s, 1H), 4.24 – 3.42 (m, 2H), 2.55 (t, J = 7.8 Hz, 2H), 2.29 (s, 3H), 1.62 (p, J = 7.5 Hz, 2H), 1.40 (h, J = 7.3 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.08, 150.76, 144.61, 135.97, 133.86, 131.68, 130.24, 129.36, 129.02, 128.70, 127.89, 127.34, 123.67, 121.98, 111.73, 31.21, 30.56, 22.75, 21.72, 14.12. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{30}N_3O_6S$ 584.1850; Found: 584.1860.



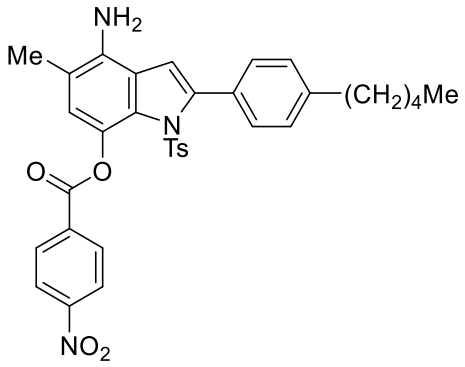
4-amino-5-methyl-2-(*o*-tolyl)-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (10) (eluent: petroleum ether/ ethyl acetate 2:1), 28.9 mg, 52% yield; red solid; m.p. : 213-214 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.9 Hz, 2H), 8.32 (d, *J* = 8.9 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.20 – 7.11 (m, 3H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.91 (s, 1H), 6.44 (s, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.20, 150.67, 144.62, 142.25, 138.57, 136.01, 135.04, 134.95, 132.45, 131.56, 131.23, 130.39, 130.05, 129.30, 129.24, 128.93, 127.04, 125.05, 123.61, 122.67, 122.21, 118.33, 111.30, 21.69, 20.78, 16.85. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{26}N_3O_6S$ 556.1537; Found: 556.1541.



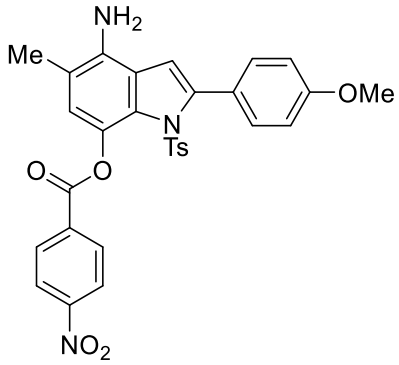
4-amino-5-methyl-2-(*m*-tolyl)-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (11) (eluent: petroleum ether/ ethyl acetate 2:1), 25.0 mg, 45% yield; red solid; m.p. : 215-216 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 8.9 Hz, 2H), 8.35 (d, *J* = 9.0 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.21 – 7.14 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 1H), 6.51 (s, 1H), 2.37 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.21, 150.71, 144.54, 144.24, 137.44, 135.97, 134.94, 133.83, 132.64, 132.12, 131.66, 130.31, 130.04, 129.46, 128.98, 127.77, 127.37, 126.45, 123.64, 122.81, 122.66, 118.91, 111.47, 21.69, 21.53, 16.97. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{26}N_3O_6S$ 556.1537; Found: 556.1536.



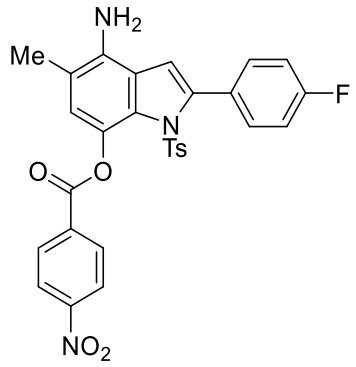
4-amino-5-methyl-2-(*p*-tolyl)-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (12) (eluent: petroleum ether/ ethyl acetate 2:1), 30.5 mg, 55% yield; red solid; m.p. : 217-218 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.9 Hz, 2H), 8.33 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.13 (m, 4H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.92 (s, 1H), 6.44 (s, 1H), 4.14 – 3.31 (m, 2H), 2.40 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.20, 150.64, 144.52, 144.08, 138.63, 135.95, 135.23, 133.59, 131.95, 131.60, 130.15, 129.94, 129.21, 128.96, 128.59, 127.28, 123.57, 122.70, 122.63, 118.74, 111.42, 21.65, 21.51, 16.88. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{26}N_3O_6S$ 556.1537; Found: 556.1544.



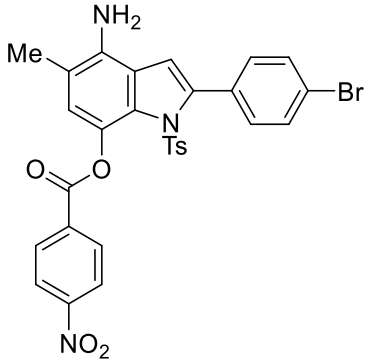
4-amino-5-methyl-2-(4-pentylphenyl)-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (13) (eluent: petroleum ether/ ethyl acetate 2:1), 28.7 mg, 47% yield; red solid; m.p. : 237-238 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 8.8 Hz, 2H), 8.35 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.13 (m, 4H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.94 (s, 1H), 6.50 (s, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.30 (s, 3H), 2.26 (s, 3H), 1.71 – 1.60 (m, 2H), 1.40 – 1.31 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.18, 150.61, 144.47, 144.05, 143.61, 135.94, 135.35, 133.69, 131.85, 131.58, 130.16, 130.04, 129.17, 128.92, 127.85, 127.28, 123.54, 122.64, 122.48, 118.57, 111.27, 35.87, 31.68, 31.09, 22.63, 21.62, 16.84, 14.14. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{34}N_3O_6S$ 612.2163; Found: 612.2172.



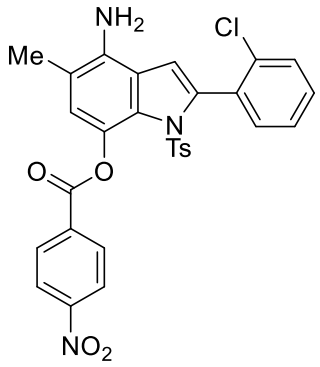
4-amino-2-(4-methoxyphenyl)-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (14) (eluent: petroleum ether/ ethyl acetate 1:1), 15.4 mg, 27% yield; red solid; m.p. : 244-245 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 9.0 Hz, 2H), 8.33 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.92 (s, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.40 (s, 1H), 3.85 (s, 3H), 2.29 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.20, 160.11, 150.68, 144.53, 143.90, 135.99, 134.96, 133.69, 132.14, 131.63, 130.71, 130.09, 128.97, 127.28, 125.24, 123.61, 122.80, 122.58, 118.85, 113.33, 110.74, 55.43, 21.68, 16.94. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{26}N_3O_7S$ 572.1486; Found: 572.1487.



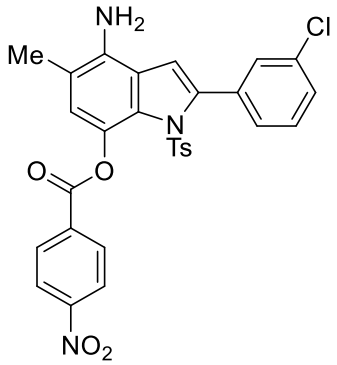
4-amino-2-(4-fluorophenyl)-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (15) (eluent: petroleum ether/ ethyl acetate 2:1), 41.3 mg, 74% yield; red solid; m.p. : 207-208 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 8.9 Hz, 2H), 8.35 (d, *J* = 8.9 Hz, 2H), 7.48 – 7.39 (m, 2H), δ 7.16 (d, *J* = 8.4 Hz, 2H), 7.10 – 7.00 (m, 4H), 6.95 (s, 1H), 6.50 (s, 1H), 2.31 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.16, 163.47 (d, $^{1}J_{C\text{-}F}$ = 248.8 Hz), 150.77, 144.79, 142.99, 135.87, 133.72, 132.37, 131.65, 131.11 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 130.28, 129.13, 128.84 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 127.23, 123.67, 123.05, 122.79, 119.44, 115.01 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 111.65, 21.72, 17.02. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.52. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ C alcd for $C_{29}H_{23}FN_3O_6S$ 560.1287; Found: 560.1289.



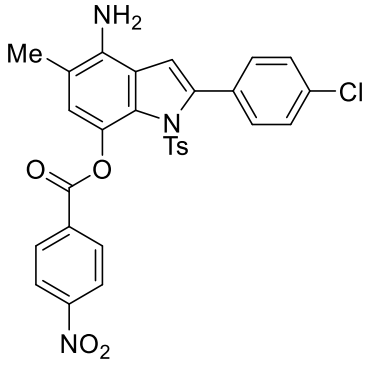
4-amino-2-(4-bromophenyl)-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (16) (eluent: petroleum ether/ ethyl acetate 2:1), 41.5 mg, 67% yield; red solid; m.p. : 230-231 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 9.0 Hz, 2H), 8.34 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.95 (s, 1H), 6.50 (s, 1H), 2.30 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.17, 150.73, 144.84, 142.74, 135.85, 135.18, 133.44, 132.07, 131.68, 131.63, 131.10, 130.72, 130.37, 129.13, 127.23, 123.65, 123.25, 122.96, 122.49, 119.16, 112.35, 21.71, 16.95. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}BrN_3O_6S$ 620.0486; Found: 620.0489.



4-amino-2-(2-chlorophenyl)-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (17) (eluent: petroleum ether/ ethyl acetate 2:1), 41.6 mg, 55% yield; red solid; m.p. : 223-224 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.34 (d, *J* = 8.8 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.45 – 7.38 (m, 1H), 7.35 – 7.28 (m, 4H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.91 (s, 1H), 6.75 (s, 1H), 2.32 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.21, 150.61, 144.64, 138.77, 135.86, 135.81, 134.54, 133.41, 132.94, 131.81, 131.50, 130.63, 129.69, 129.62, 129.31, 129.15, 127.04, 126.04, 123.53, 123.03, 121.51, 118.02, 113.05, 21.64, 16.74. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}ClN_3O_6S$ 576.0991; Found: 576.0996.

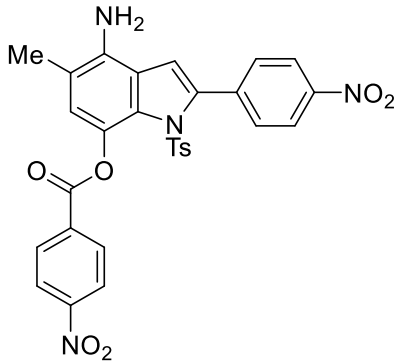


4-amino-2-(3-chlorophenyl)-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (18) (eluent: petroleum ether/ ethyl acetate 2:1), 27.0 mg, 47% yield; red solid; m.p. : 218-219 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 9.0 Hz, 2H), 8.34 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.27 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.95 (s, 1H), 6.51 (s, 1H), 4.25 – 3.27 (m, 2H), 2.31 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.16, 150.71, 144.90, 142.23, 135.85, 135.51, 134.44, 133.81, 133.51, 131.85, 131.63, 130.44, 129.13, 129.09, 128.79, 128.53, 127.73, 127.26, 123.64, 123.32, 122.14, 118.89, 112.58, 21.69, 16.91. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}ClN_3O_6S$ 576.0991; Found: 576.0992.

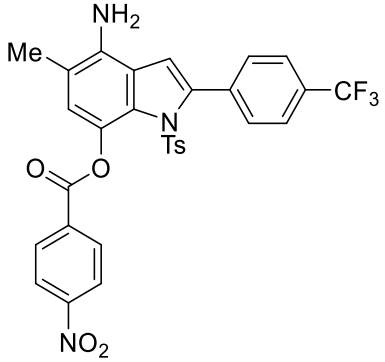


4-amino-2-(4-chlorophenyl)-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (19) (eluent:

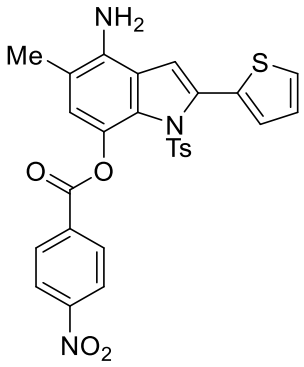
petroleum ether/ ethyl acetate 2:1), 35.1 mg, 61% yield; red solid; m.p. : 224-225 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 9.0 Hz, 2H), 8.33 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.94 (s, 1H), 6.49 (s, 1H), 4.38 – 3.30 (m, 2H), 2.30 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.16, 150.71, 144.82, 142.65, 135.85, 135.31, 134.66, 133.44, 131.98, 131.61, 131.23, 130.45, 130.34, 129.11, 128.14, 127.22, 123.63, 123.20, 122.40, 119.04, 112.33, 21.70, 16.92. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}ClN_3O_6S$ 576.0991; Found: 576.0994.



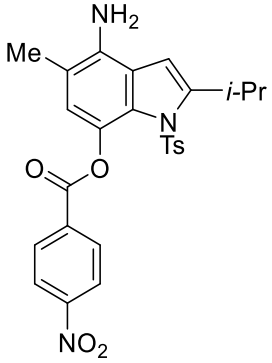
4-amino-5-methyl-2-(4-nitrophenyl)-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (20) (eluent: petroleum ether/ ethyl acetate 1:1), 22.8 mg, 39% yield; red solid; m.p. : 252-253 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.8 Hz, 2H), 8.35 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 6.70 (s, 1H), 2.32 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.12, 150.80, 147.48, 145.20, 141.41, 139.05, 135.70, 133.02, 131.89, 131.63, 130.86, 129.64, 129.30, 127.20, 124.16, 123.70, 123.27, 122.07, 119.43, 114.79, 21.74, 16.95. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}N_4O_8S$ 587.1232; Found: 587.1232.



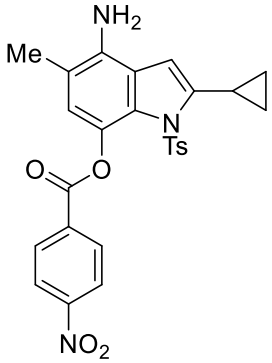
4-amino-5-methyl-1-tosyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indol-7-yl 4-nitrobenzoate (21) (eluent: petroleum ether/ ethyl acetate 2:1), 36.0 mg, 59% yield; red solid; m.p. : 226-227 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.9 Hz, 2H), 8.33 (d, *J* = 8.8 Hz, 2H), 7.65 – 7.58 (m, 4H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.97 (s, 1H), 6.58 (s, 1H), 4.33 – 3.38 (m, 2H), 2.30 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.17, 150.74, 144.97, 142.21, 136.25, 135.80, 135.66, 133.32, 131.84, 131.61, 130.55, 130.26 (q, $^2J_{C-F}$ = 32.7 Hz), 129.35, 129.18, 127.23, 124.85 (q, $^3J_{C-F}$ = 3.44 Hz), 124.23 (q, $^1J_{C-F}$ = 272.5 Hz), 123.65, 123.60, 122.14, 119.07, 113.48, 21.69, 16.90. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.49. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{23}F_3N_3O_6S$ 610.1255; Found: 610.1249.



4-amino-5-methyl-2-(thiophen-2-yl)-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (22) (eluent: petroleum ether/ ethyl acetate 2:1), 21.9 mg, 40% yield; red solid; m.p. : 207-208 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.8 Hz, 2H), 8.35 (d, *J* = 8.9 Hz, 2H), 7.32 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.28 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.07 (dd, *J* = 5.1, 3.7 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.97 (s, 1H), 6.60 (s, 1H), 2.30 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.16, 150.73, 144.66, 136.55, 135.88, 134.84, 133.91, 133.69, 132.09, 131.65, 130.21, 129.69, 129.13, 127.44, 127.27, 126.71, 123.64, 123.25, 122.37, 119.01, 111.80, 21.72, 16.98. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}N_3O_6S_2$ 548.0945; Found: 548.0950.

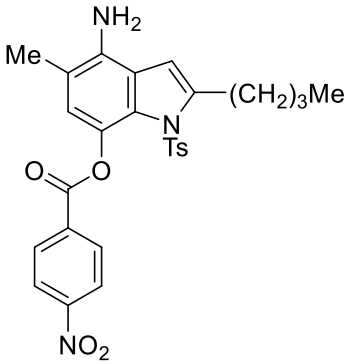


4-amino-2-isopropyl-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (23) (eluent: petroleum ether/ ethyl acetate 2:1), 18.8 mg, 37% yield; red solid; m.p. : 205-206 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 – 8.25 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.80 (s, 1H), 6.38 (s, 1H), 3.61 (hept, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 2.23 (s, 3H), 1.30 – 1.24 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.29, 151.30, 150.68, 144.40, 135.96, 135.65, 131.54, 129.54, 126.20, 123.55, 122.22, 106.10, 28.39, 23.42, 21.69, 16.88. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}N_3O_6S$ 508.1537; Found: 508.1540.

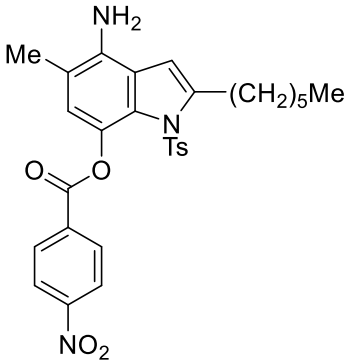


4-amino-2-cyclopropyl-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (24) (eluent:

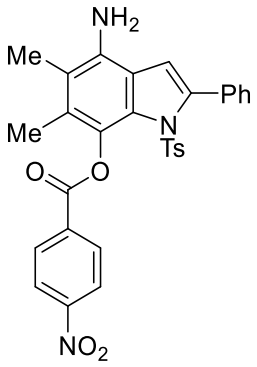
petroleum ether/ ethyl acetate 2:1), 22.7 mg, 45% yield; red solid; m.p. : 174-175 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.32 – 8.26 (m, 4H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.77 (s, 1H), 6.20 (s, 1H), 2.40 – 2.33 (m, 4H), 2.22 (s, 3H), 0.98 – 0.91 (m, 2H), 0.65 – 0.57 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.39, 150.68, 146.03, 144.40, 136.68, 135.95, 134.20, 131.47, 130.03, 129.63, 128.54, 126.39, 123.53, 122.10, 121.40, 117.74, 104.54, 21.70, 16.78, 10.65, 9.04. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}N_3O_6S$ 506.1381; Found: 506.1384.



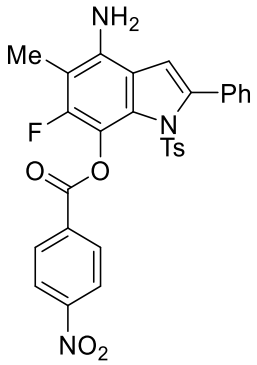
4-amino-2-butyl-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (25) (eluent: petroleum ether/ ethyl acetate 3:1), 27.2 mg, 52% yield; red solid; m.p. : 154-155 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 – 8.27 (m, 4H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 1H), 6.36 (s, 1H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 1.67 (p, *J* = 7.6 Hz, 2H), 1.39 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.35, 150.66, 144.41, 144.30, 136.23, 135.93, 134.25, 131.47, 130.31, 129.65, 128.70, 126.12, 123.51, 121.98, 121.77, 117.82, 107.24, 31.47, 29.90, 22.57, 21.68, 16.78, 14.01. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}N_3O_6S$ 522.1694; Found: 522.1691.



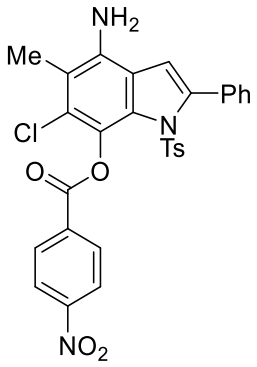
4-amino-2-hexyl-5-methyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (26) (eluent: petroleum ether/ ethyl acetate 3:1), 26.2 mg, 48% yield; red solid; m.p. : 138-139 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.33 – 8.22 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.75 (s, 1H), 6.35 (s, 1H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H), 2.20 (s, 3H), 1.68 (p, *J* = 7.5 Hz, 2H), 1.40 – 1.25 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.36, 150.65, 144.40, 144.28, 136.26, 135.95, 134.48, 131.46, 130.19, 129.65, 128.69, 126.12, 123.50, 121.97, 121.66, 117.65, 107.19, 31.72, 30.19, 29.32, 29.17, 22.70, 21.67, 16.75, 14.19. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{32}N_3O_6S$ 550.2007; Found: 550.2010.



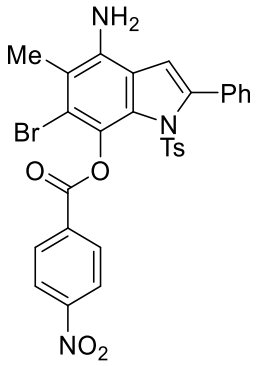
4-amino-5,6-dimethyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (28) (eluent: petroleum ether/ ethyl acetate 2:1), 19.4 mg, 35% yield; red solid; m.p. : 181-182 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 8.9 Hz, 2H), 8.34 (d, *J* = 8.9 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.38 – 7.30 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.44 (s, 1H), 4.09 – 3.30 (m, 2H), 2.28 (s, 3H), 2.19 (s, 3H), 2.12 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.50, 150.66, 144.46, 143.32, 135.86, 135.27, 133.78, 133.04, 131.62, 131.34, 130.73, 129.09, 128.96, 128.36, 128.10, 127.79, 127.22, 123.61, 120.63, 118.08, 112.08, 21.63, 14.54, 13.49. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{26}N_3O_6S$ 556.1537; Found: 556.1533.



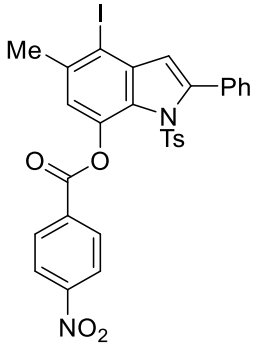
4-amino-6-fluoro-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (29) (eluent: petroleum ether/ ethyl acetate 2:1), 38.6 mg, 69% yield; red solid; m.p. : 164-165 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.9 Hz, 2H), 8.33 (d, *J* = 9.0 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.33 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.43 (s, 1H), 4.08 – 3.38 (m, 2H), 2.30 (s, 3H), 2.17 – 2.11 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.14, 152.50 (d, $^{1}J_{C\text{-}F}$ = 240.5 Hz), 150.76, 144.78, 143.38 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 135.76 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 135.27, 133.64, 132.56, 131.75, 130.43 (d, $^{3}J_{C\text{-}F}$ =6.0 Hz), 129.26, 129.11, 128.61, 127.86, 127.33, 123.63, 121.23 (d, $^{2}J_{C\text{-}F}$ = 20.2 Hz), 117.22, 111.40, 107.21 (d, $^{2}J_{C\text{-}F}$ = 20.0 Hz), 21.68, 9.00 (d, $^{3}J_{C\text{-}F}$ = 6.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -130.41. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}FN_3O_6S$ 560.1287; Found: 560.1284.



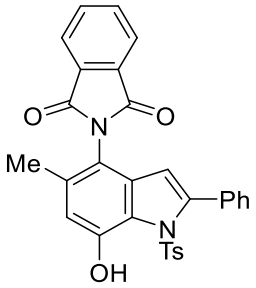
4-amino-6-chloro-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (30) (eluent: petroleum ether/ ethyl acetate 2:1), 35.6 mg, 62% yield; red solid; m.p. : 173-174 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 8.8 Hz, 2H), 8.37 (d, *J* = 8.8 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.40 – 7.36 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.46 (s, 1H), 2.37 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.04, 150.85, 144.80, 144.39, 135.69, 134.00, 132.77, 131.76, 131.14, 130.90, 130.25, 129.31, 129.23, 128.78, 127.91, 127.24, 123.72, 121.40, 118.86, 118.70, 111.27, 21.74, 17.55. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}ClN_3O_6S$ 576.0991; Found: 576.0997.



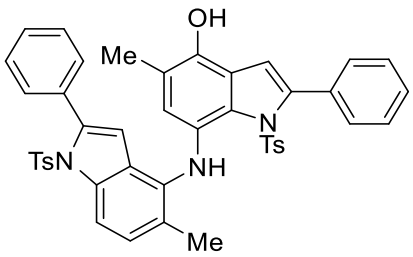
4-amino-6-bromo-5-methyl-2-phenyl-1-tosyl-1*H*-indol-7-yl 4-nitrobenzoate (31) (eluent: petroleum ether/ ethyl acetate 2:1), 39.6 mg, 64% yield; red solid; m.p. : 186-187 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 8.8 Hz, 2H), 8.37 (d, *J* = 8.8 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.40 – 7.36 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.50 (s, 1H), 2.33 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.03, 150.84, 144.83, 144.40, 135.63, 135.32, 133.97, 132.72, 131.75, 131.10, 130.36, 129.27, 129.23, 128.77, 127.91, 127.21, 123.71, 121.52, 118.80, 111.26, 21.72, 17.55. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}N_3O_6SBr$ 620.0486; Found: 620.0485.



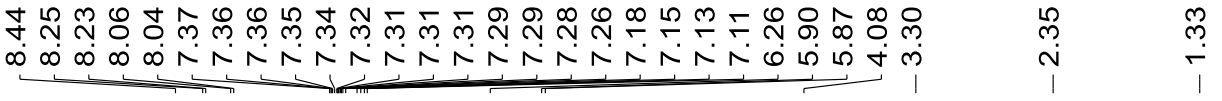
4-iodo-5-methyl-2-phenyl-1-tosyl-1H-indol-7-yl 4-nitrobenzoate (32) (eluent: petroleum ether/ ethyl acetate 5:1), 49.6 mg, 76% yield; white solid; m.p. : 174-175 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 8.8 Hz, 2H), 8.37 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.42 – 7.34 (m, 3H), 7.15 – 7.09 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.59 (s, 1H), 2.54 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.41, 150.93, 146.17, 145.07, 139.95, 139.85, 139.67, 135.37, 133.79, 132.00, 131.78, 129.61, 129.22, 128.47, 127.96, 127.25, 123.76, 121.41, 118.95, 90.48, 27.52, 21.75. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{22}IN_2O_6S$ 653.0238; Found: 653.0234.

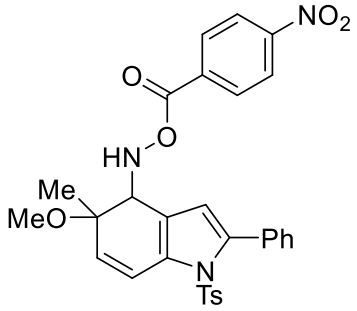


2-(7-hydroxy-5-methyl-2-phenyl-1-tosyl-1*H*-indol-4-yl)isoindoline-1,3-dione (33) (eluent: petroleum ether/ ethyl acetate 2:1), 72.3 mg, 73% yield; white solid; m.p. : 234-235 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.20 (s, 1H), 9.03 (s, 1H), 7.99 – 7.93 (m, 2H), 7.85 – 7.76 (m, 4H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.45 – 6.40 (m, 1H), 2.41 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.34, 147.07, 144.63, 142.45, 139.58, 134.60, 132.25, 132.15, 131.05, 129.98, 129.25, 129.07, 128.70, 126.85, 125.92, 125.41, 124.05, 115.46, 112.47, 98.27, 21.76, 15.21. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{23}N_2O_5S$ 523.1323; Found: 523.1327.

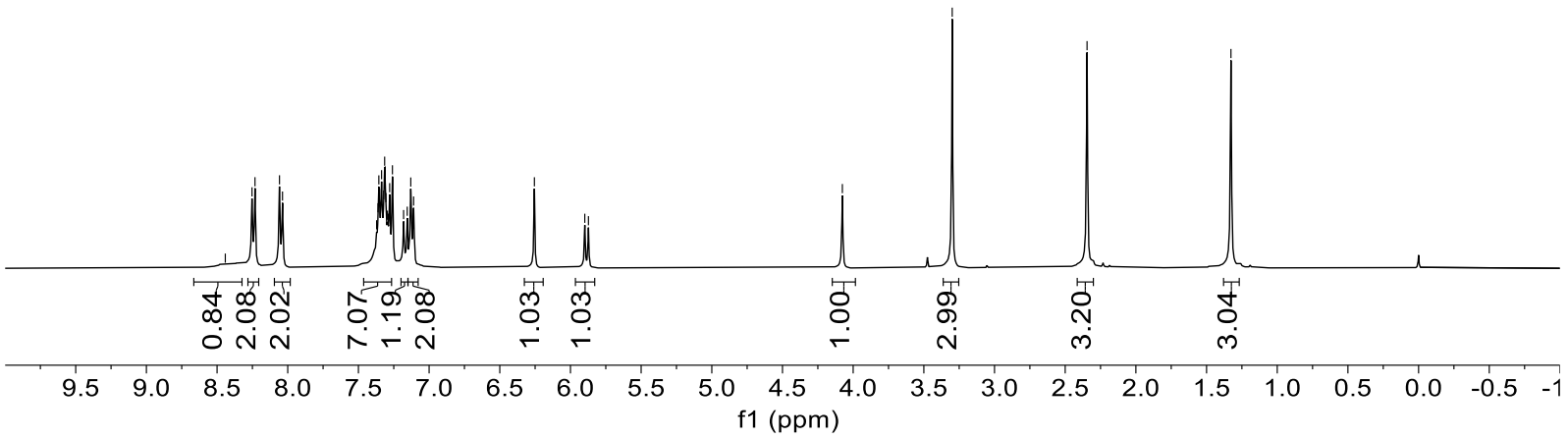


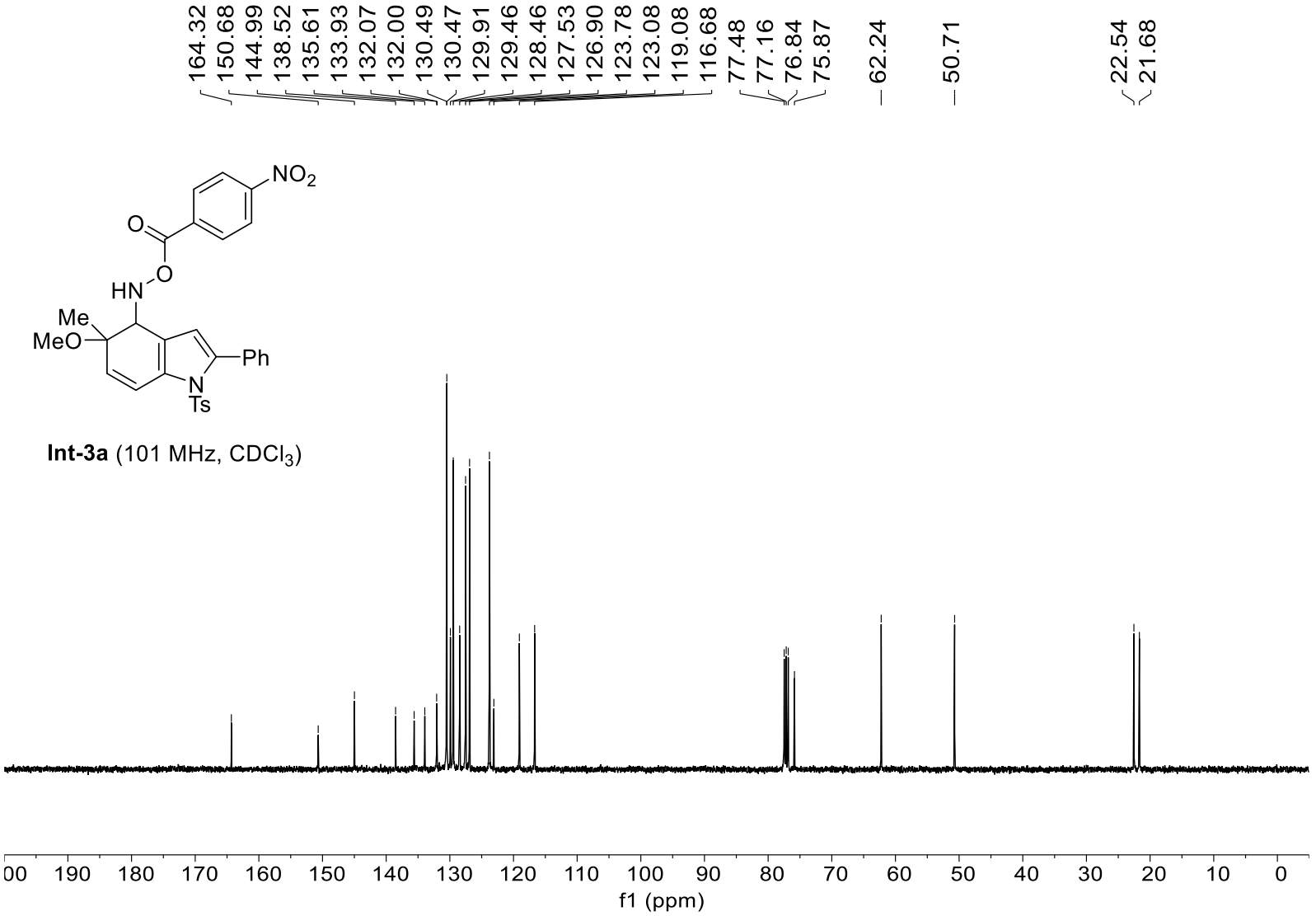
5-methyl-7-((5-methyl-2-phenyl-1-tosyl-1*H*-indol-4-yl)amino)-2-phenyl-1-tosyl-1*H*-indol-4-ol (34) (eluent: petroleum ether/ ethyl acetate 3:1), 67.3 mg, 90% yield; yellow solid; m.p. : 140-141 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.57 – 7.46 (m, 2H), 7.44 – 7.35 (m, 5H), 7.35 – 7.32 (m, 3H), 7.29 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.60 (s, 1H), 6.11 (s, 1H), 6.04 (s, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.24 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.87, 144.54, 134.57, 132.75, 130.28, 129.29, 128.92, 128.51, 127.98, 127.54, 127.41, 127.01, 113.19, 21.68, 21.66, 18.09. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{37}N_3NaO_5S_2$ 774.2067; Found: 774.2067.

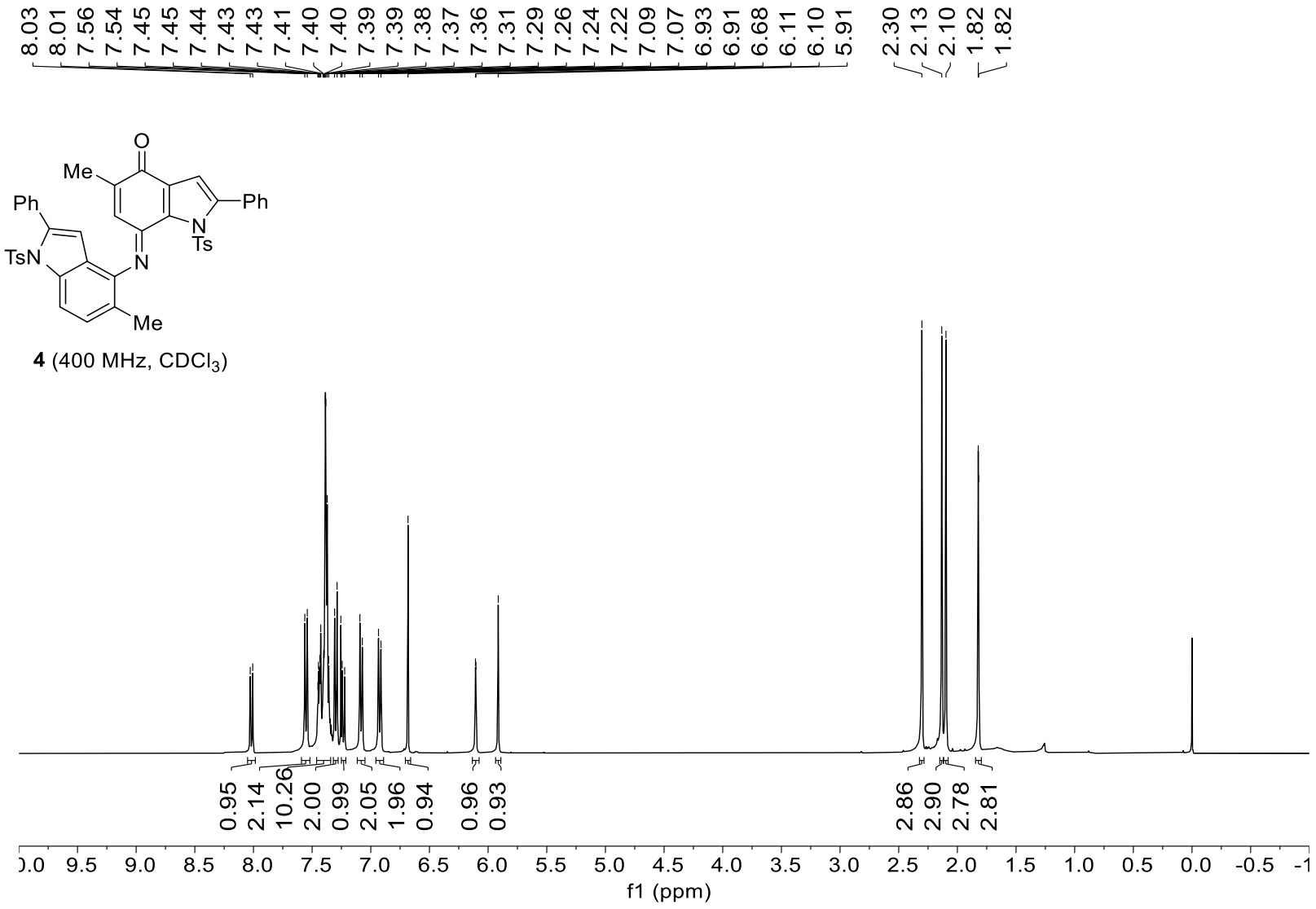


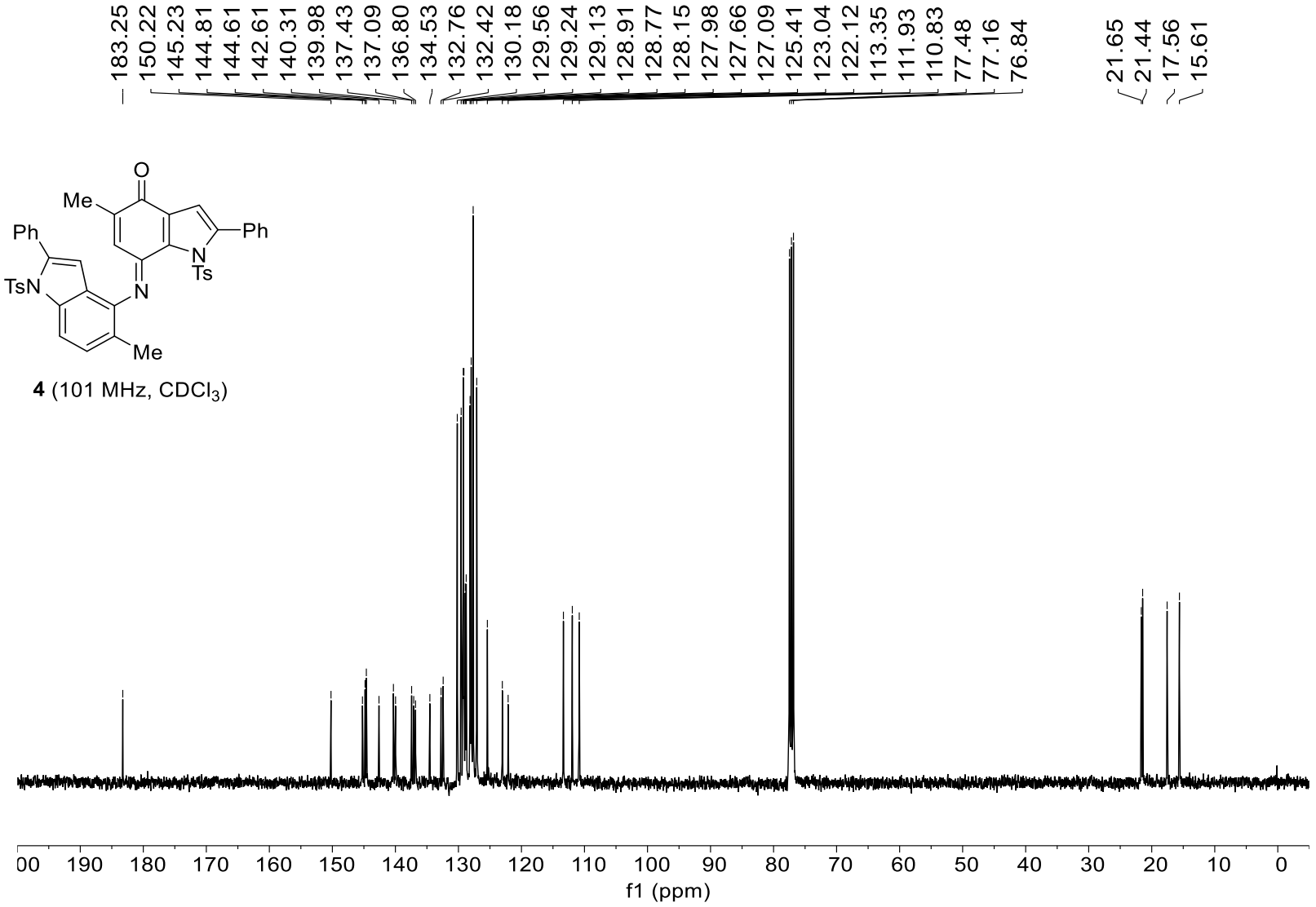


Int-3a (400 MHz, $CDCl_3$)

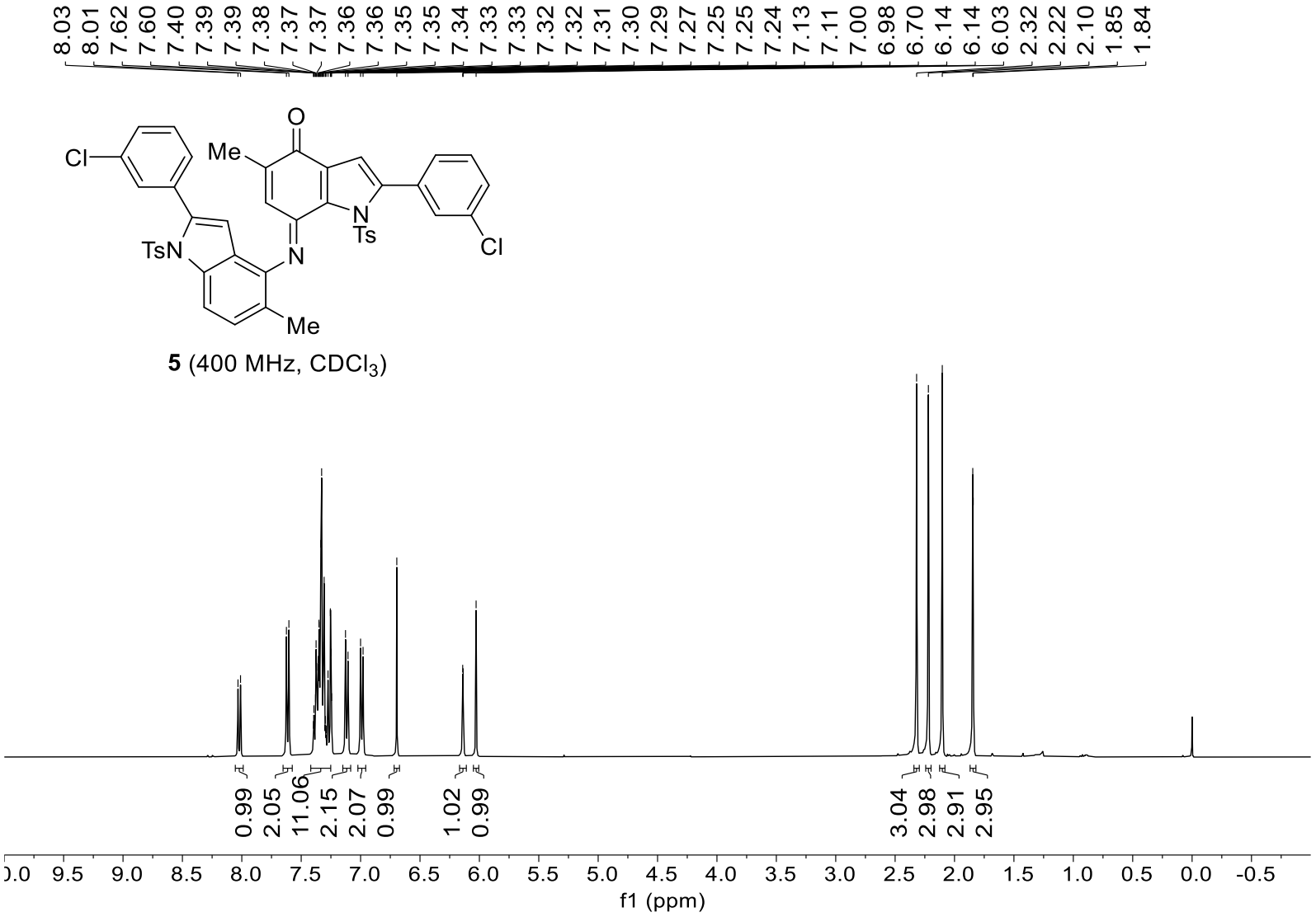



164.32
150.68
144.99
138.52
135.61
133.93
132.07
132.00
130.49
130.47
129.91
129.46
128.46
127.53
126.90
123.78
123.08
119.08
116.68
77.48
77.16
76.84
75.87
62.24
50.71
22.54
21.68
NO2
O
O
HN
Me
MeO
Ph
N
Ts
Int-3a (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

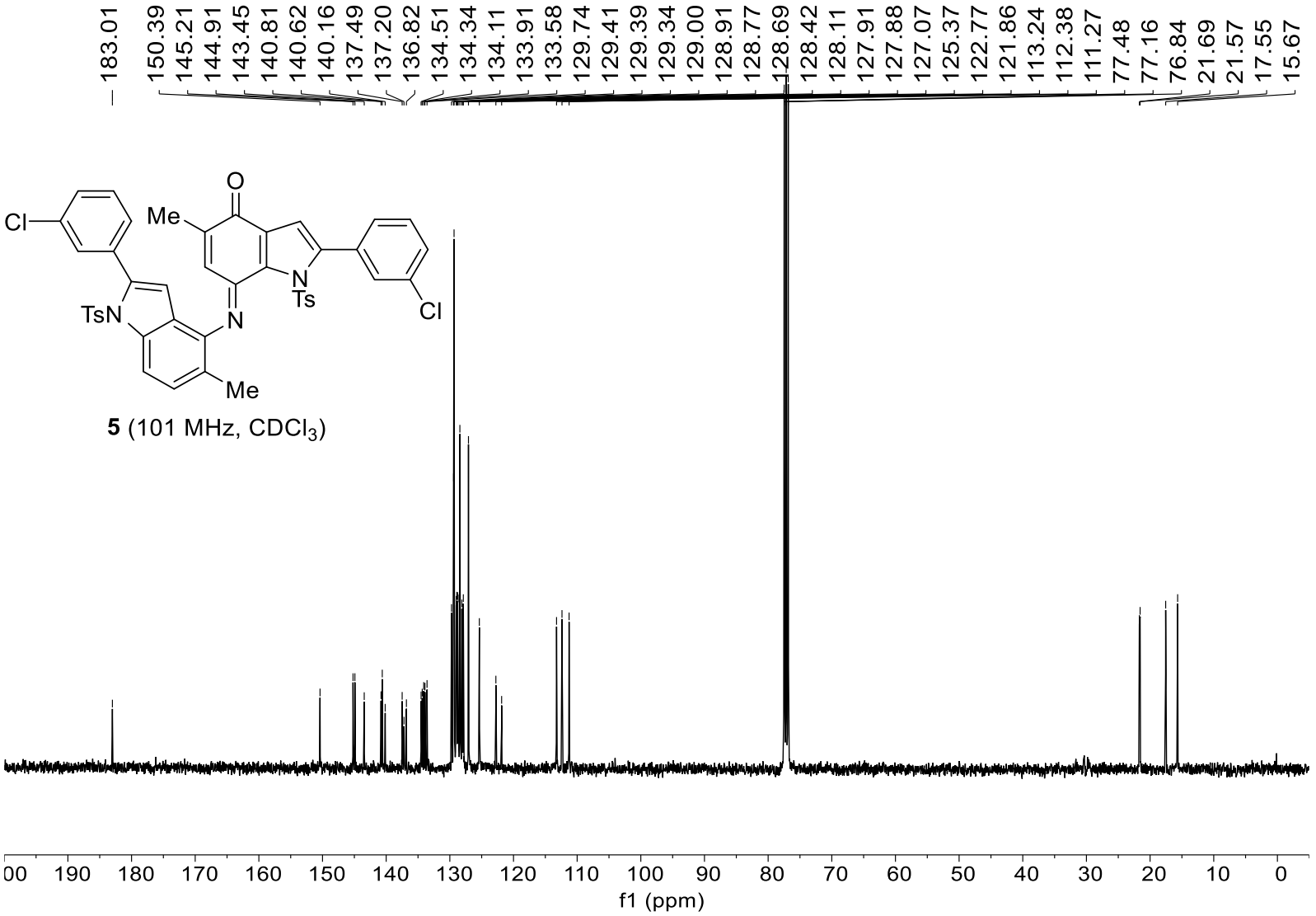

8.03
8.01
7.56
7.54
7.45
7.45
7.44
7.43
7.43
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.31
7.29
7.26
7.24
7.22
7.09
7.07
6.93
6.91
6.68
6.11
6.10
5.91
2.30
2.13
2.10
1.82
1.82
O
Me
Ph
Ph
N
Ts
TsN
N
Me
4 (400 MHz, CDCl3)
0.95
2.14
10.26
2.00
0.99
2.05
1.96
0.94
0.96
0.93
2.86
2.90
2.78
2.81
f1 (ppm)

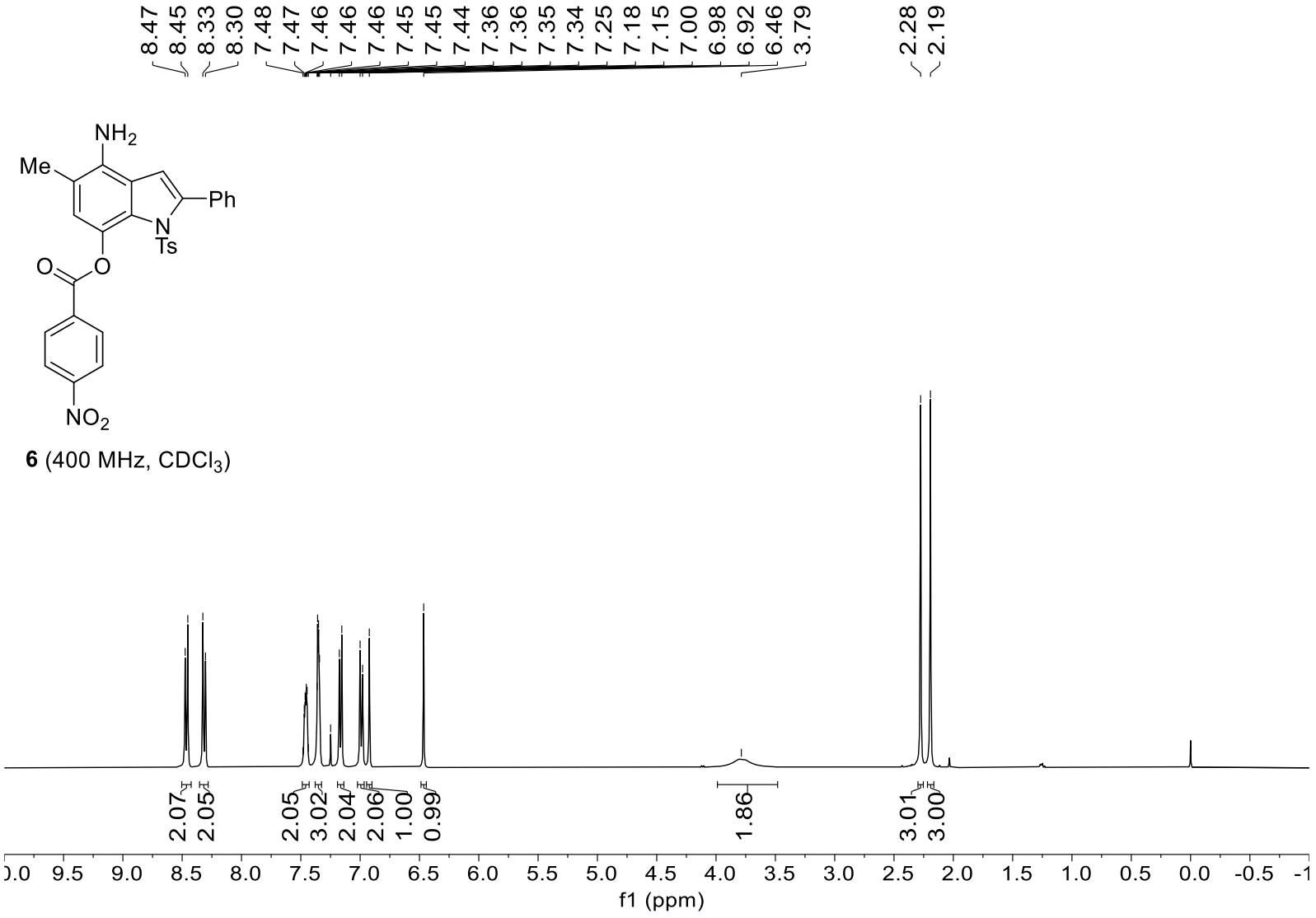


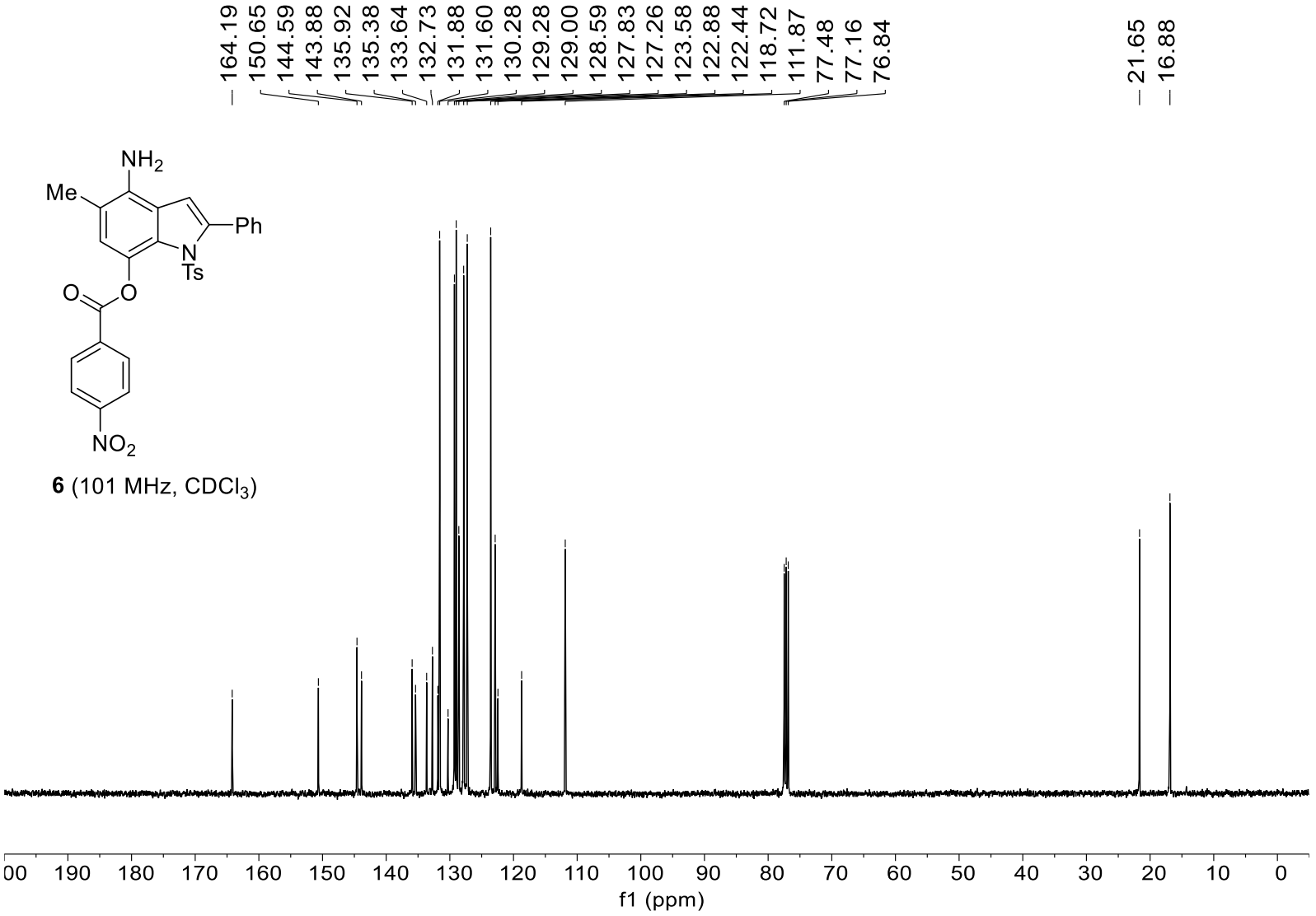
4 (101 MHz, $CDCl_3$)

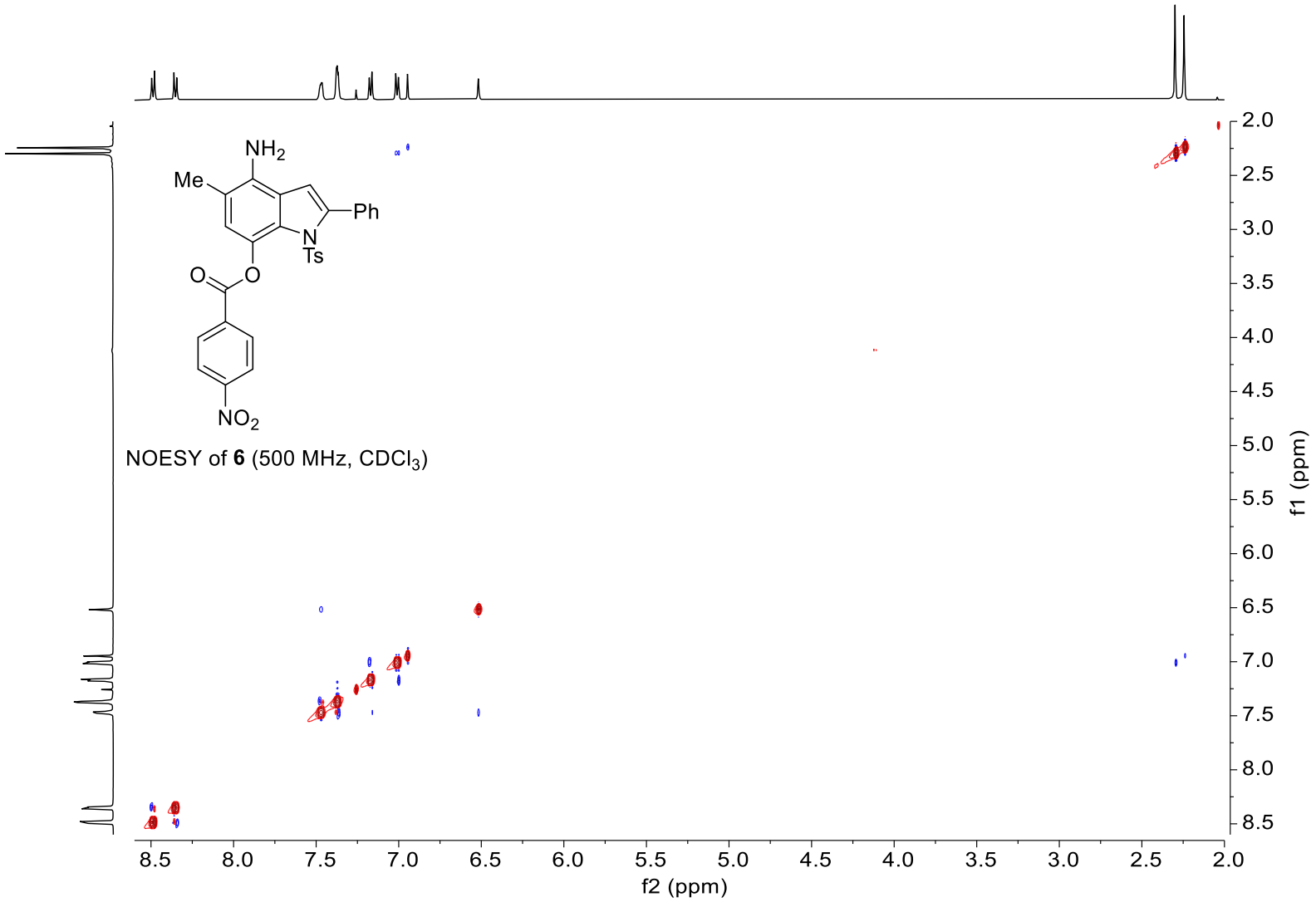


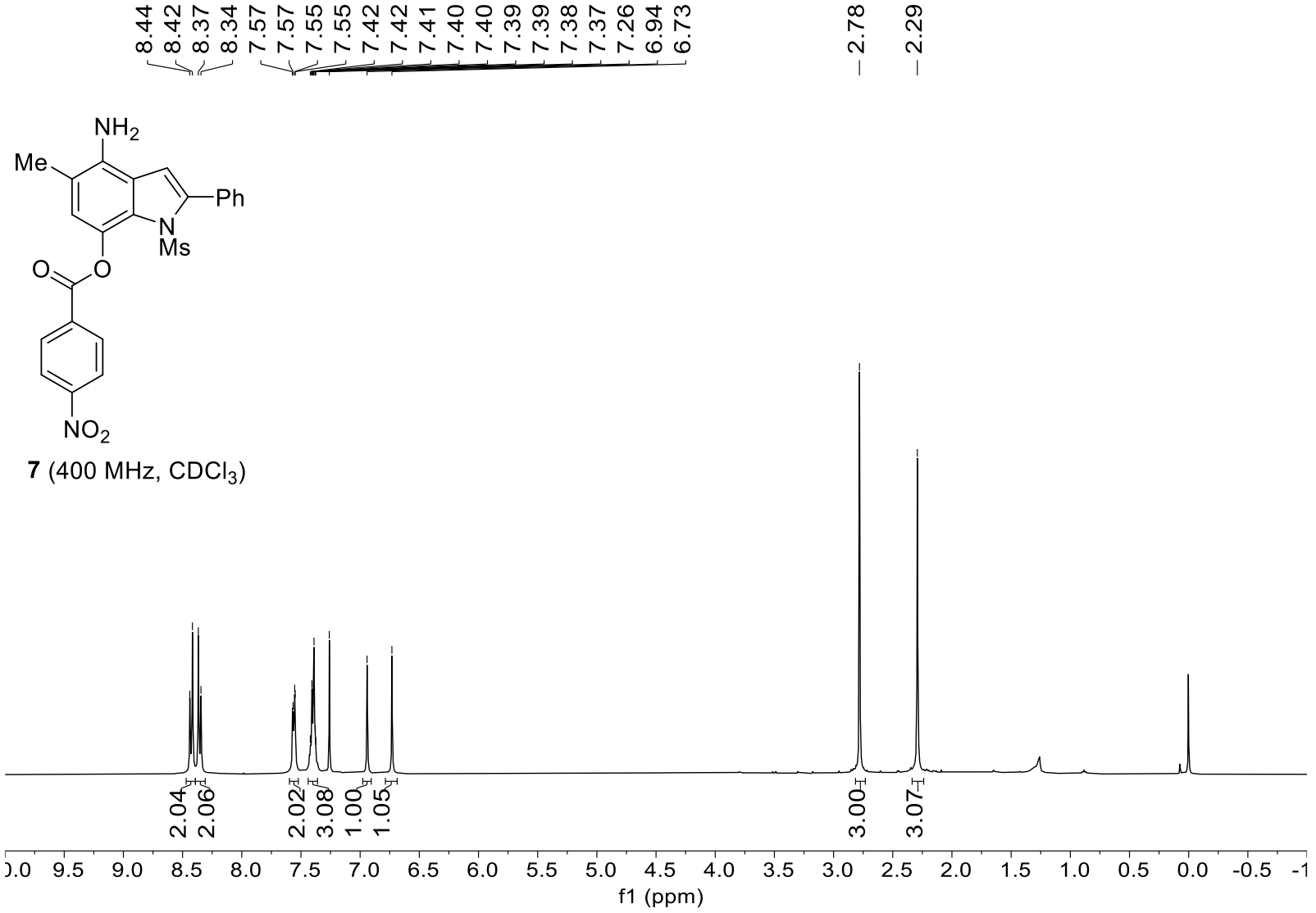
5 (400 MHz, $CDCl_3$)

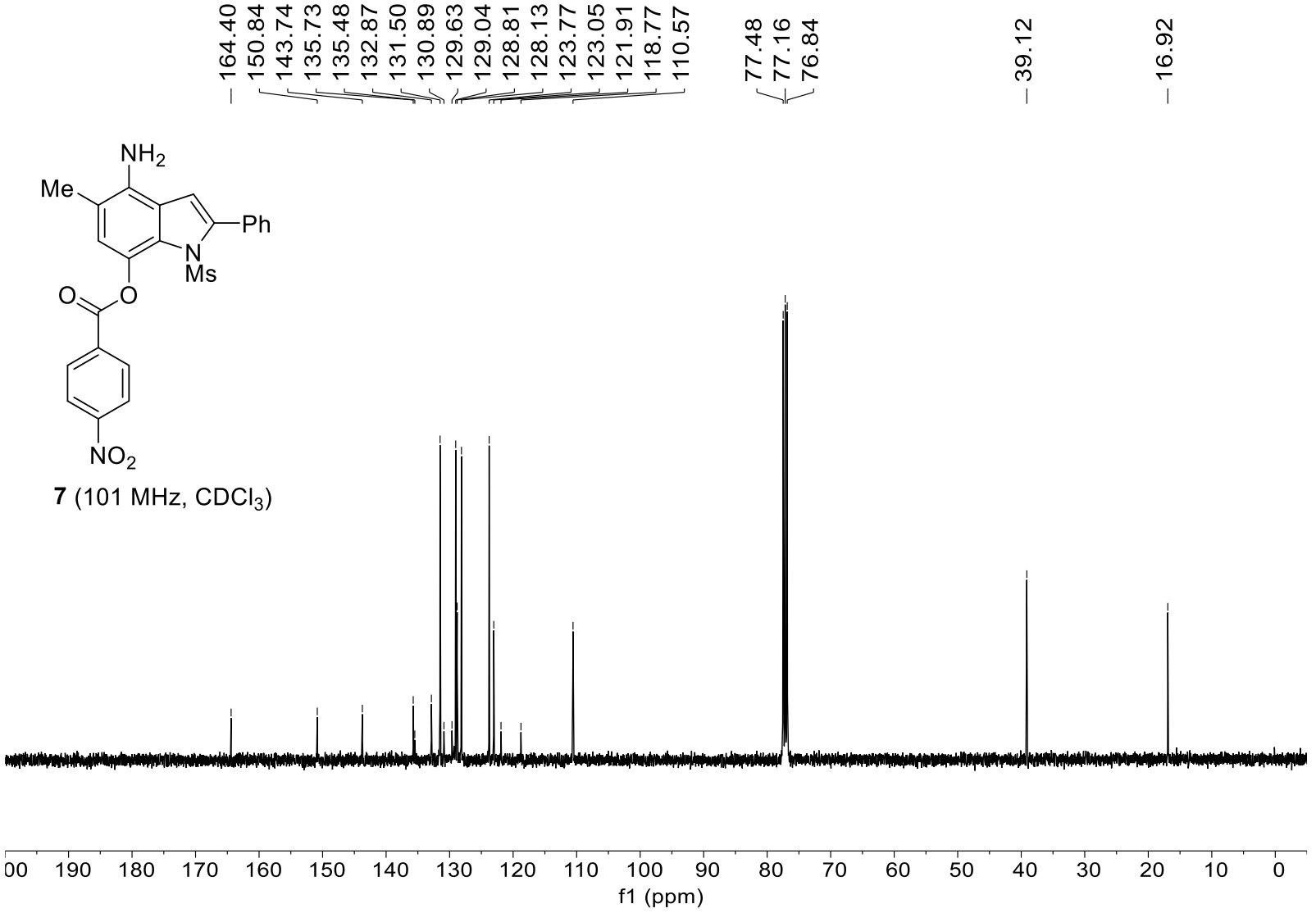

183.01
150.39
145.21
144.91
143.45
140.81
140.62
140.16
137.49
137.20
136.82
134.51
134.34
134.11
133.91
133.58
129.74
129.41
129.39
129.34
129.00
128.91
128.77
128.69
128.42
128.11
127.91
127.88
127.07
125.37
122.77
121.86
113.24
112.38
111.27
77.48
77.16
76.84
21.69
21.57
17.55
15.67
O
Me
Cl
N
Ts
TsN
N
Cl
Me
5 (101 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

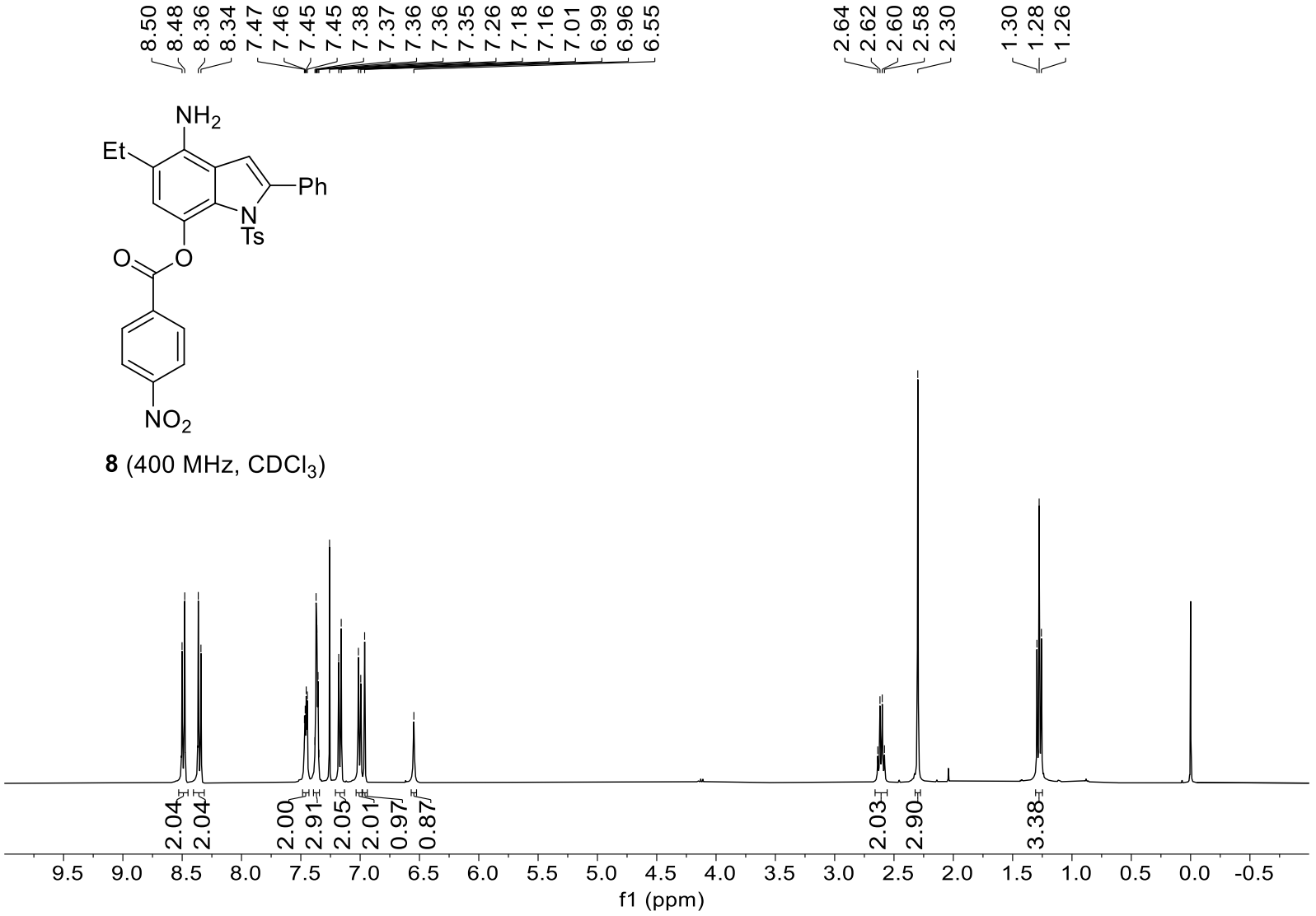

8.47
8.45
8.33
8.30
7.48
7.47
7.46
7.46
7.46
7.45
7.45
7.44
7.36
7.36
7.35
7.34
7.25
7.18
7.15
7.00
6.98
6.92
6.46
3.79
2.28
2.19
NH2
Me
Ph
N
Ts
O
O
NO2
6 (400 MHz, CDCl3)
2.07
2.05
2.05
3.02
2.04
2.06
1.00
0.99
1.86
3.01
3.00
f1 (ppm)

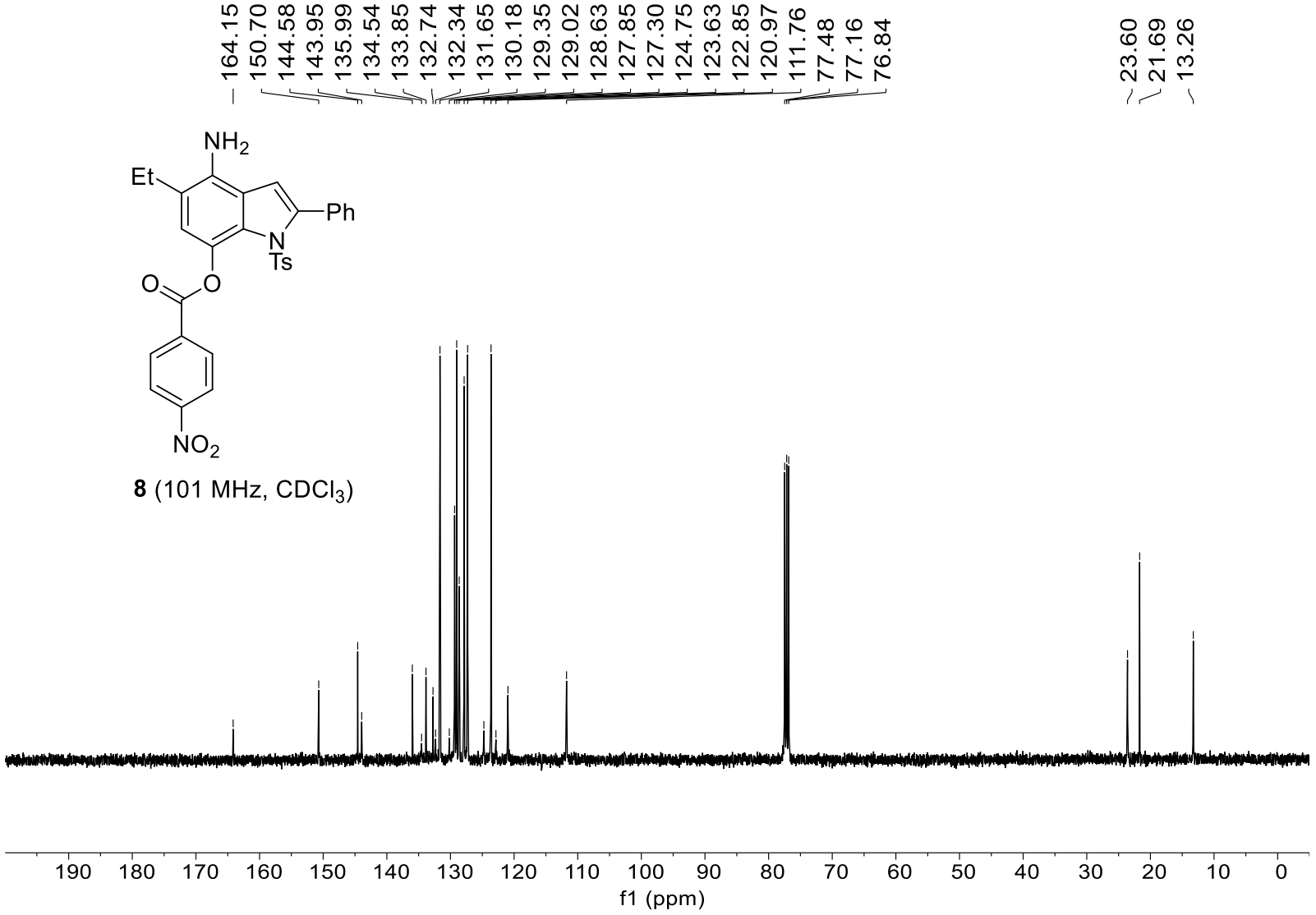

164.19
150.65
144.59
143.88
135.92
135.38
133.64
132.73
131.88
131.60
130.28
129.28
129.00
128.59
127.83
127.26
123.58
122.88
122.44
118.72
111.87
77.48
77.16
76.84
21.65
16.88
NH2
Me
Ph
N
Ts
O
O
NO2
6 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

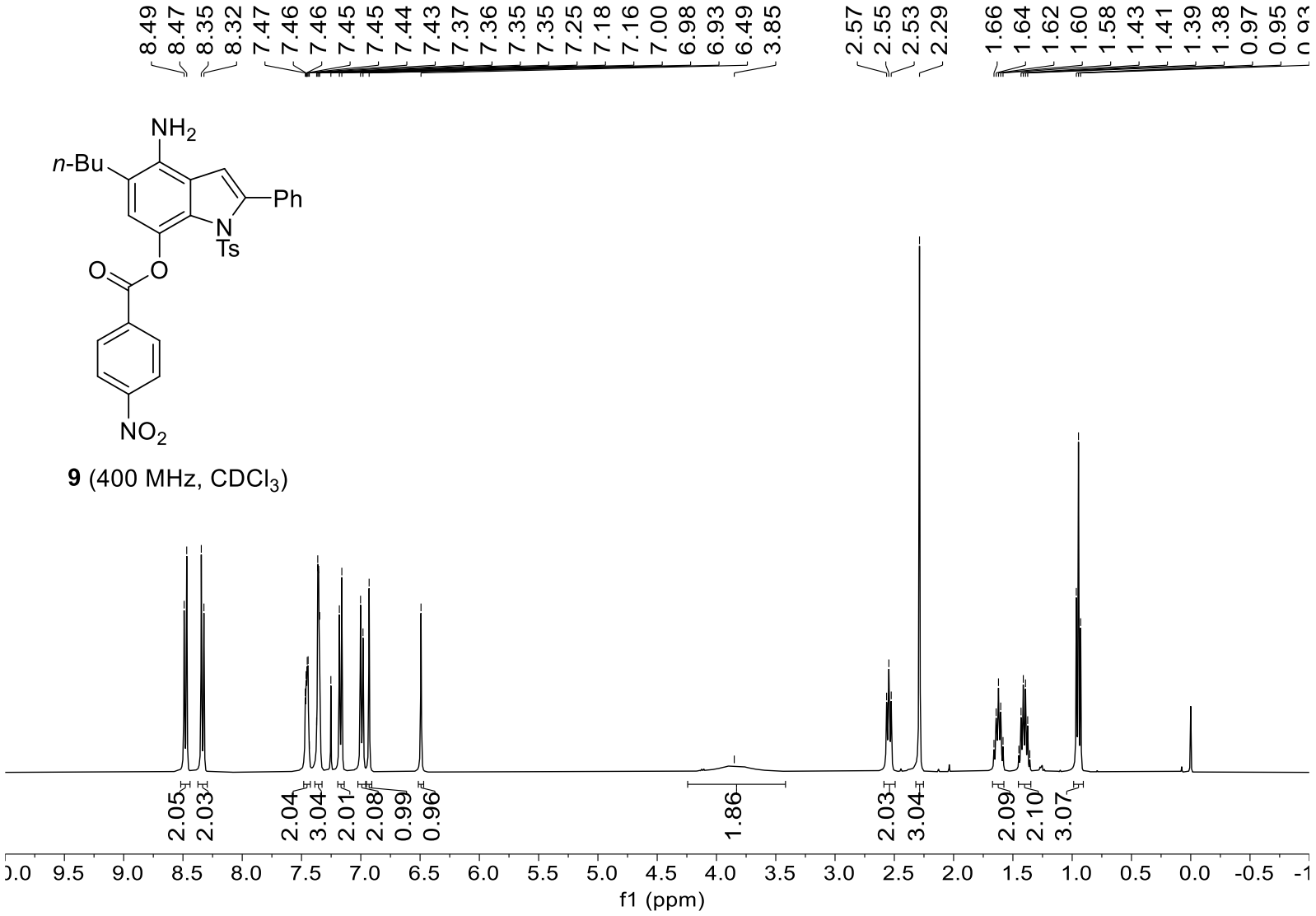

NH2
Me
Ph
N
Ts
O
O
NO2
NOESY of 6 (500 MHz, CDCl3)
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

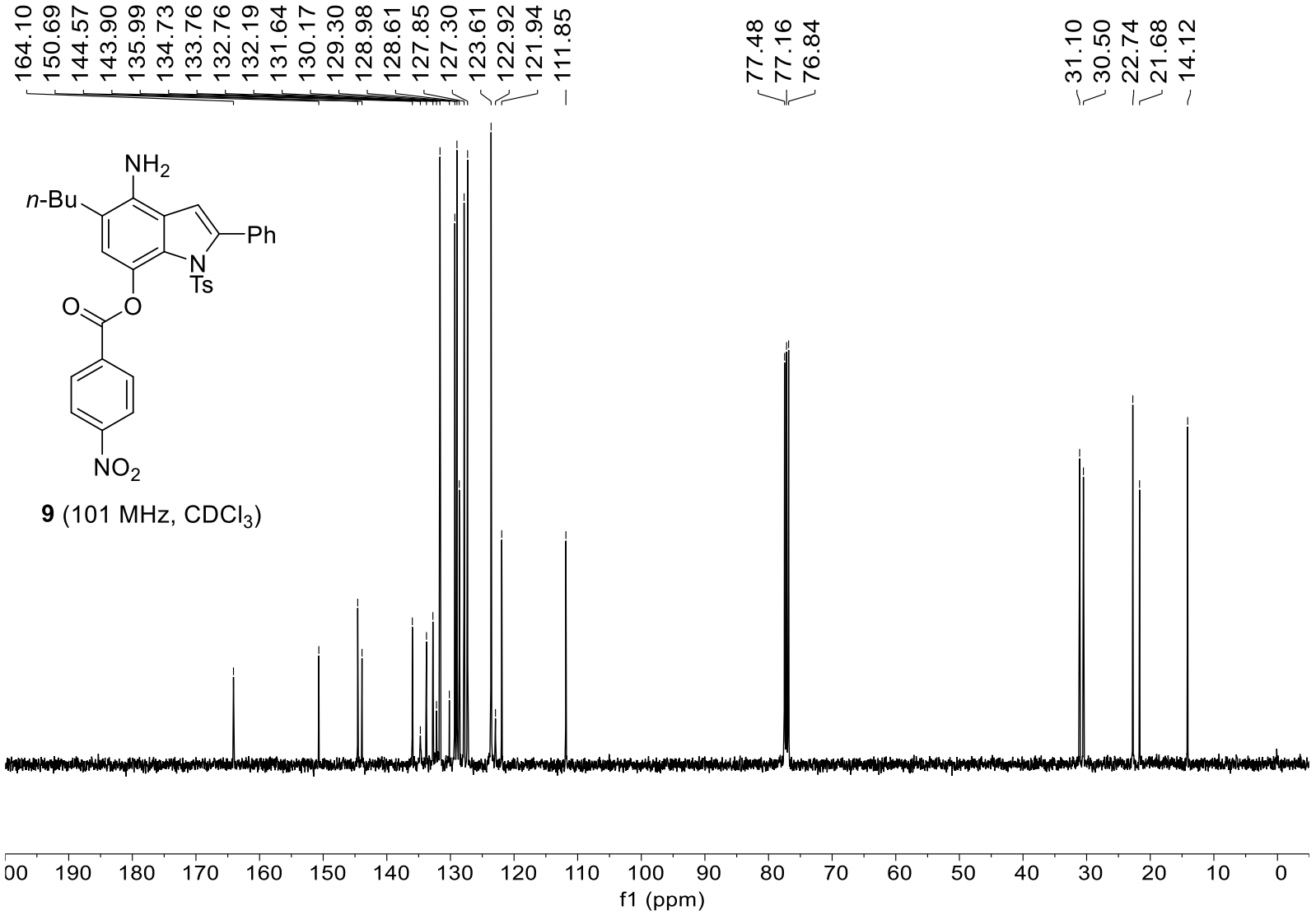

8.44
8.42
8.37
8.34
7.57
7.57
7.55
7.55
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.26
6.94
6.73
2.78
2.29
NH2
Me
Ph
N
Ms
O
O
NO2
7 (400 MHz, CDCl3)
2.04
2.06
2.02
3.08
1.00
1.05
3.00
3.07
f1 (ppm)

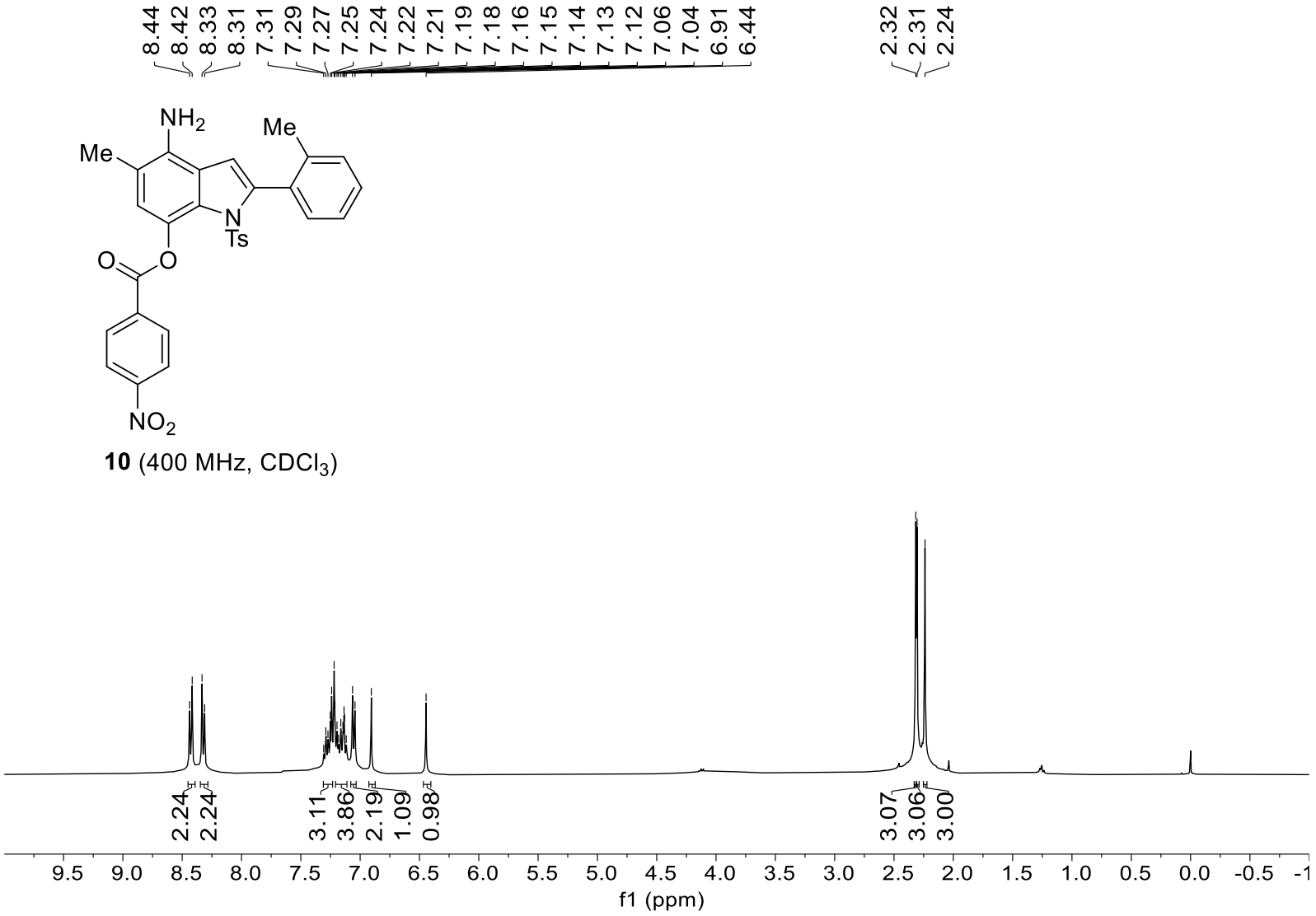

164.40
150.84
143.74
135.73
135.48
132.87
131.50
130.89
129.63
129.04
128.81
128.13
123.77
123.05
121.91
118.77
110.57
77.48
77.16
76.84
39.12
16.92
NH2
Me
Ph
N
Ms
O
O
NO2
7 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.50
8.48
8.36
8.34
7.47
7.46
7.45
7.45
7.38
7.37
7.36
7.36
7.35
7.26
7.18
7.16
7.01
6.99
6.96
6.55
2.64
2.62
2.60
2.58
2.30
1.30
1.28
1.26
NH2
Et
Ph
N
Ts
O
O
NO2
8 (400 MHz, CDCl3)
2.04
2.04
2.00
2.91
2.05
2.01
0.97
0.87
2.03
2.90
3.38
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

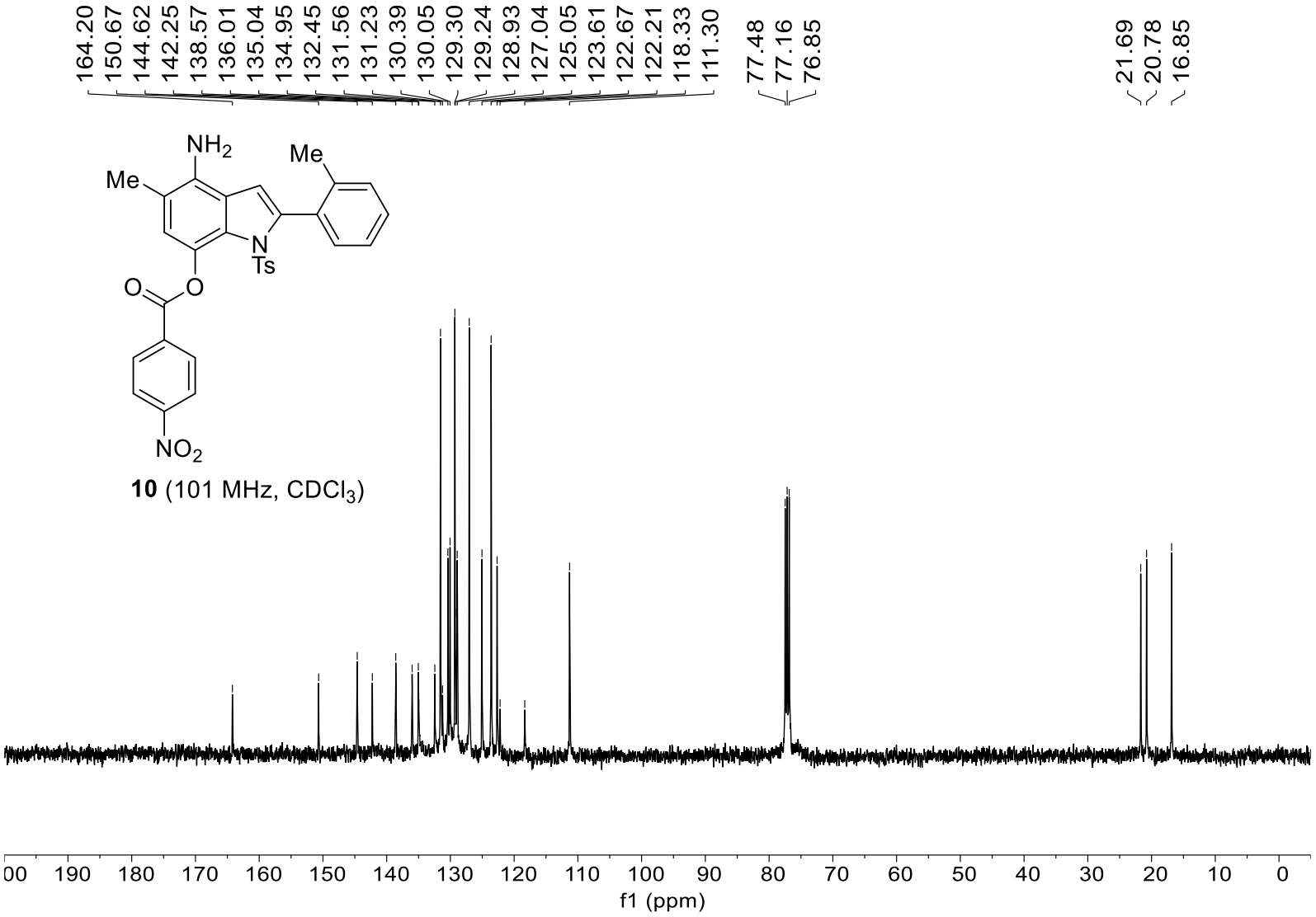

164.15
150.70
144.58
143.95
135.99
134.54
133.85
132.74
132.34
131.65
130.18
129.35
129.02
128.63
127.85
127.30
124.75
123.63
122.85
120.97
111.76
77.48
77.16
76.84
23.60
21.69
13.26
NH2
Et
Ph
N
Ts
O
O
NO2
8 (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

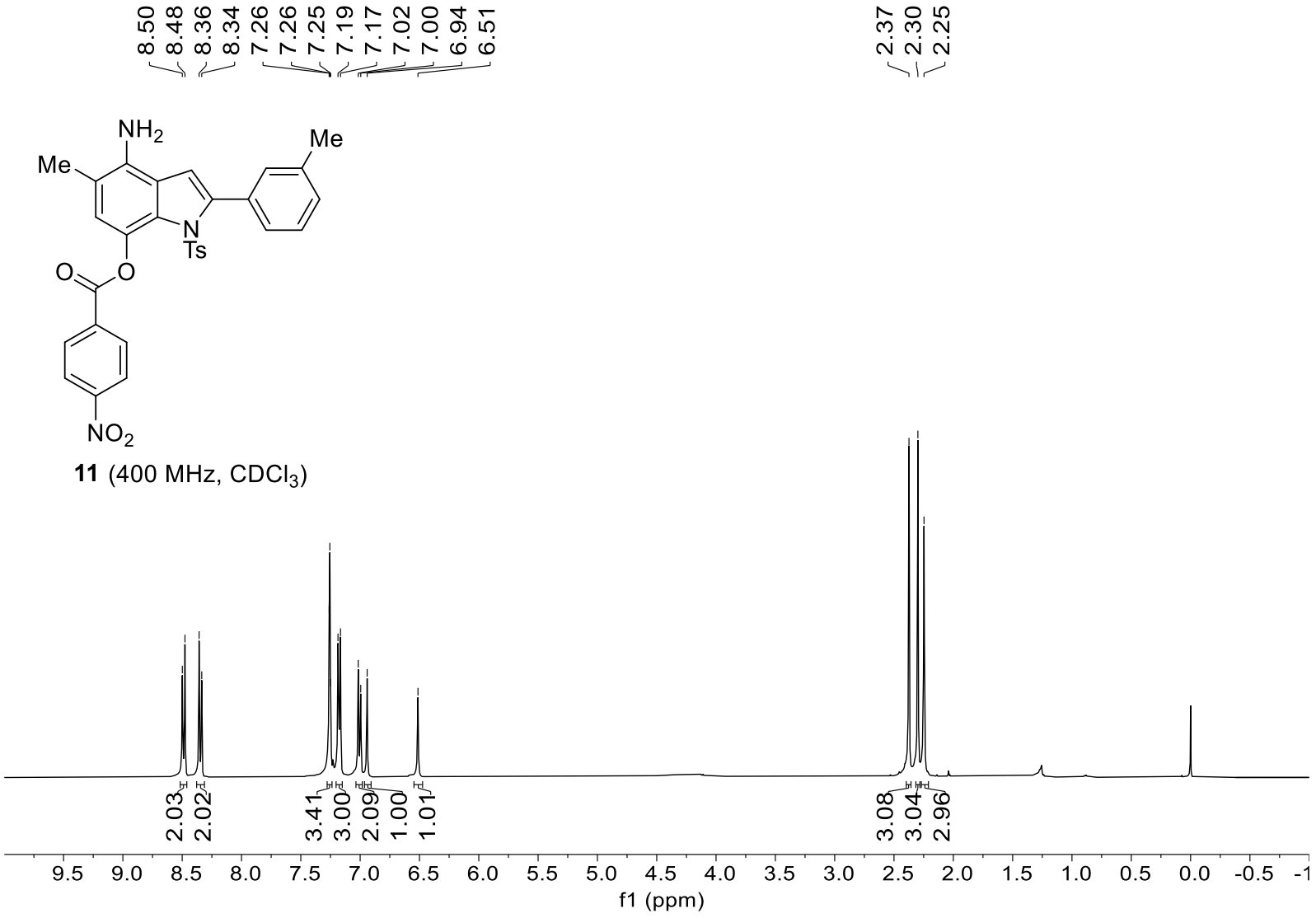

8.49
8.47
8.35
8.32
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.37
7.36
7.35
7.35
7.25
7.18
7.16
7.00
6.98
6.93
6.49
3.85
2.57
2.55
2.53
2.29
1.66
1.64
1.62
1.60
1.58
1.43
1.41
1.39
1.38
0.97
0.95
NH2
n-Bu
Ph
N
Ts
O
O
NO2
9 (400 MHz, CDCl3)
2.05
2.03
2.04
3.04
2.01
2.08
0.99
0.96
1.86
2.03
3.04
2.09
2.10
3.07
f1 (ppm)

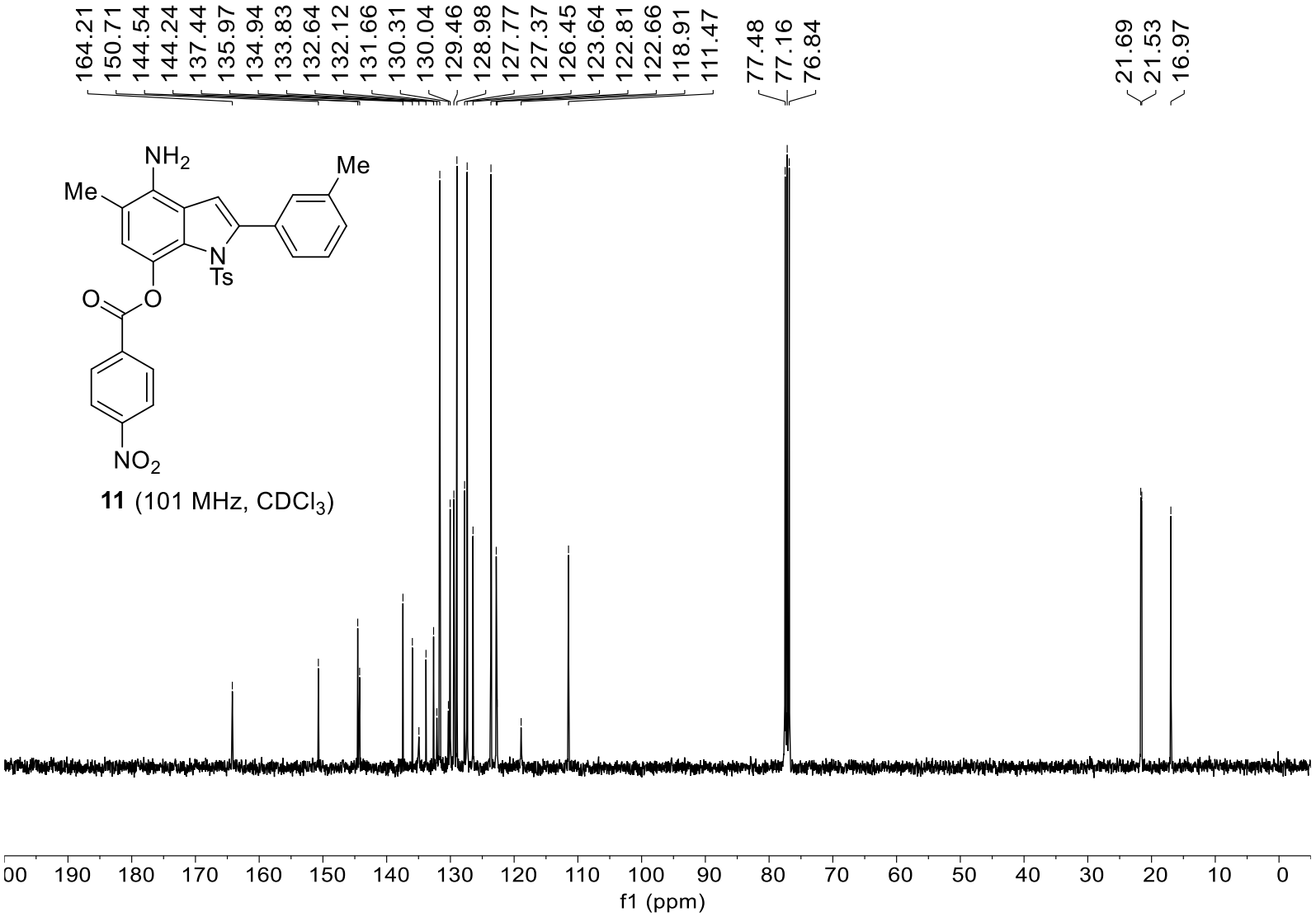

164.10
150.69
144.57
143.90
135.99
134.73
133.76
132.76
132.19
131.64
130.17
129.30
128.98
128.61
127.85
127.30
123.61
122.92
121.94
111.85
77.48
77.16
76.84
31.10
30.50
22.74
21.68
14.12
NH2
n-Bu
Ph
N
Ts
O
O
NO2
9 (101 MHz, CDCl3)
f1 (ppm)

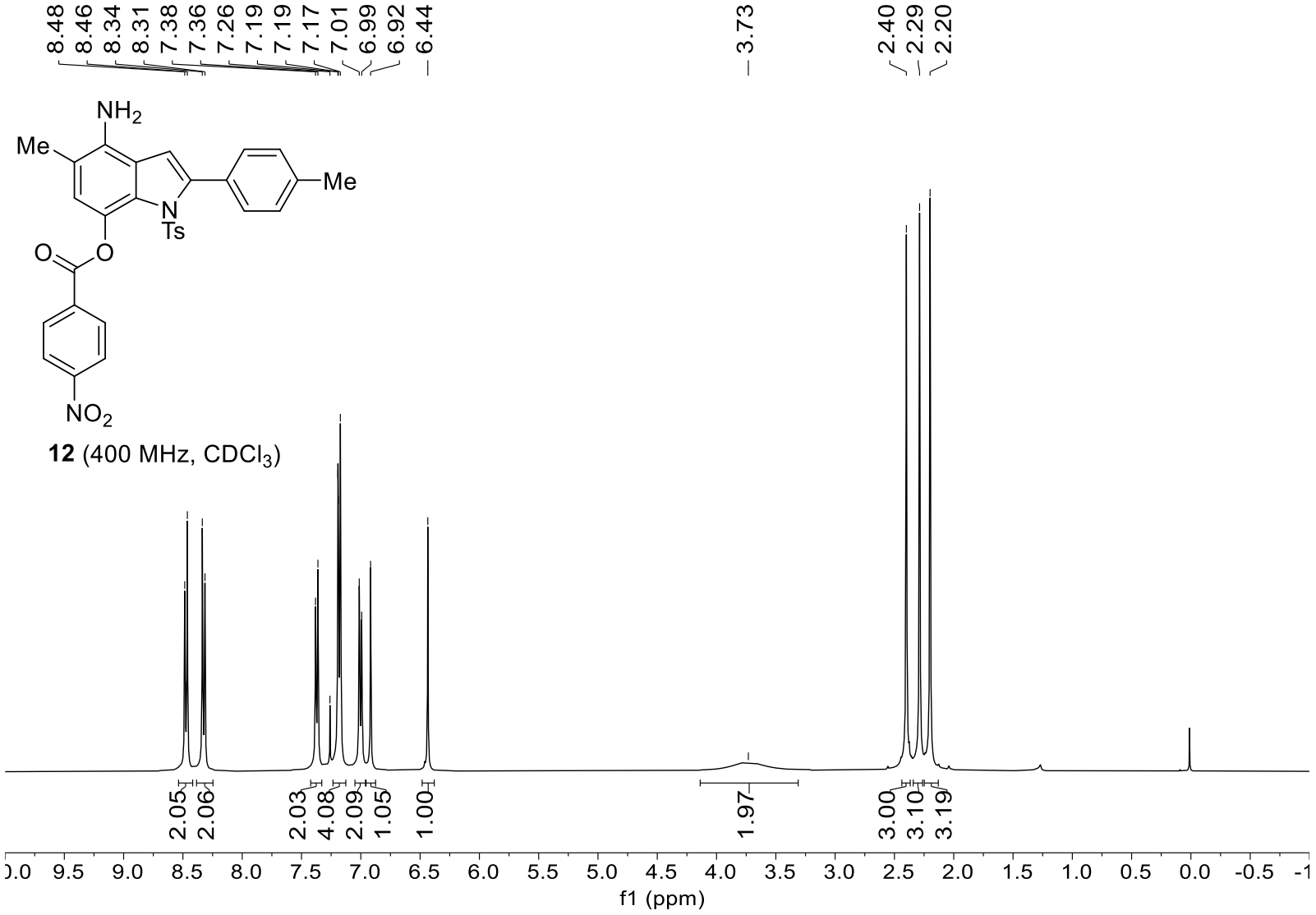


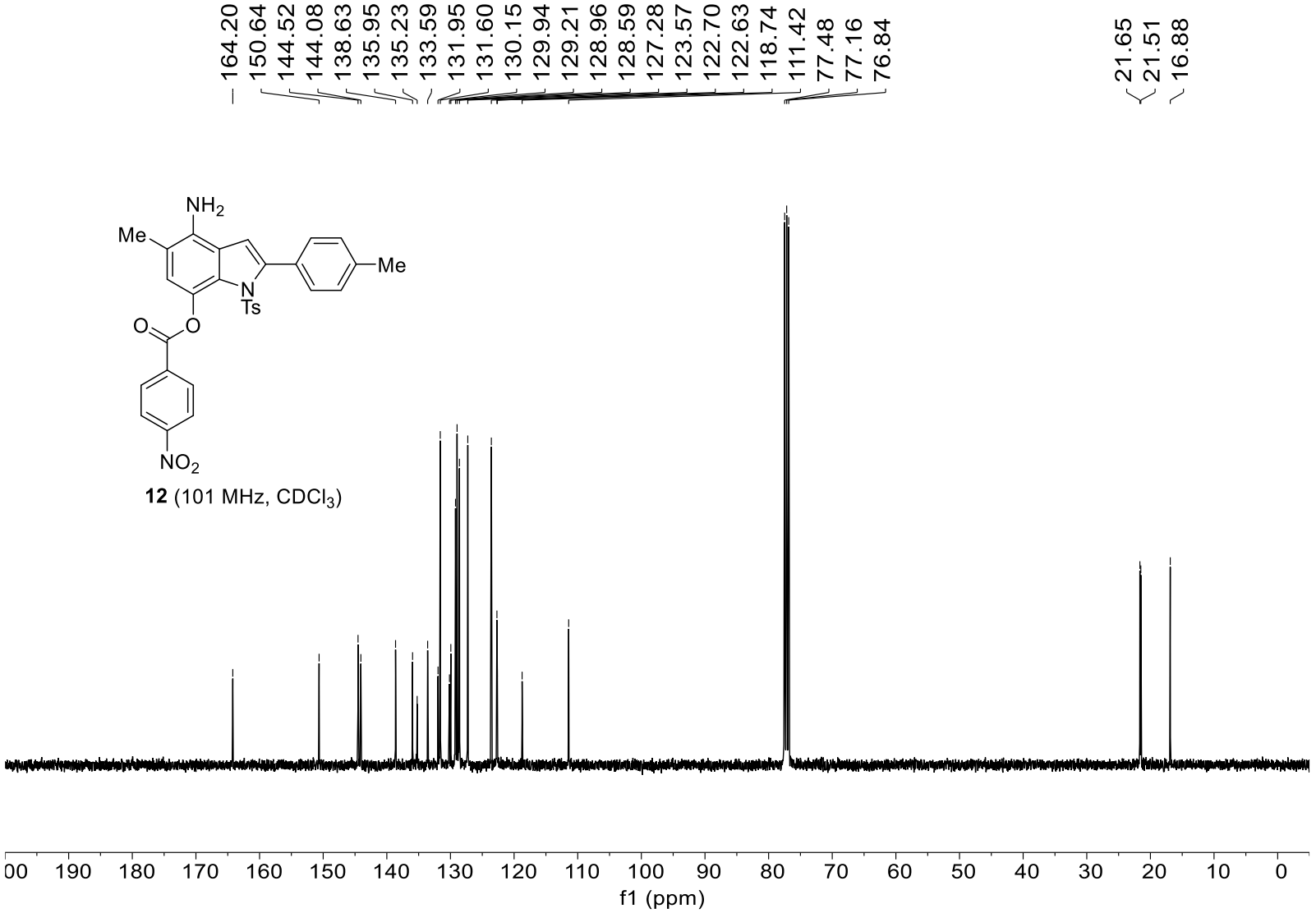
10 (400 MHz, $CDCl_3$)

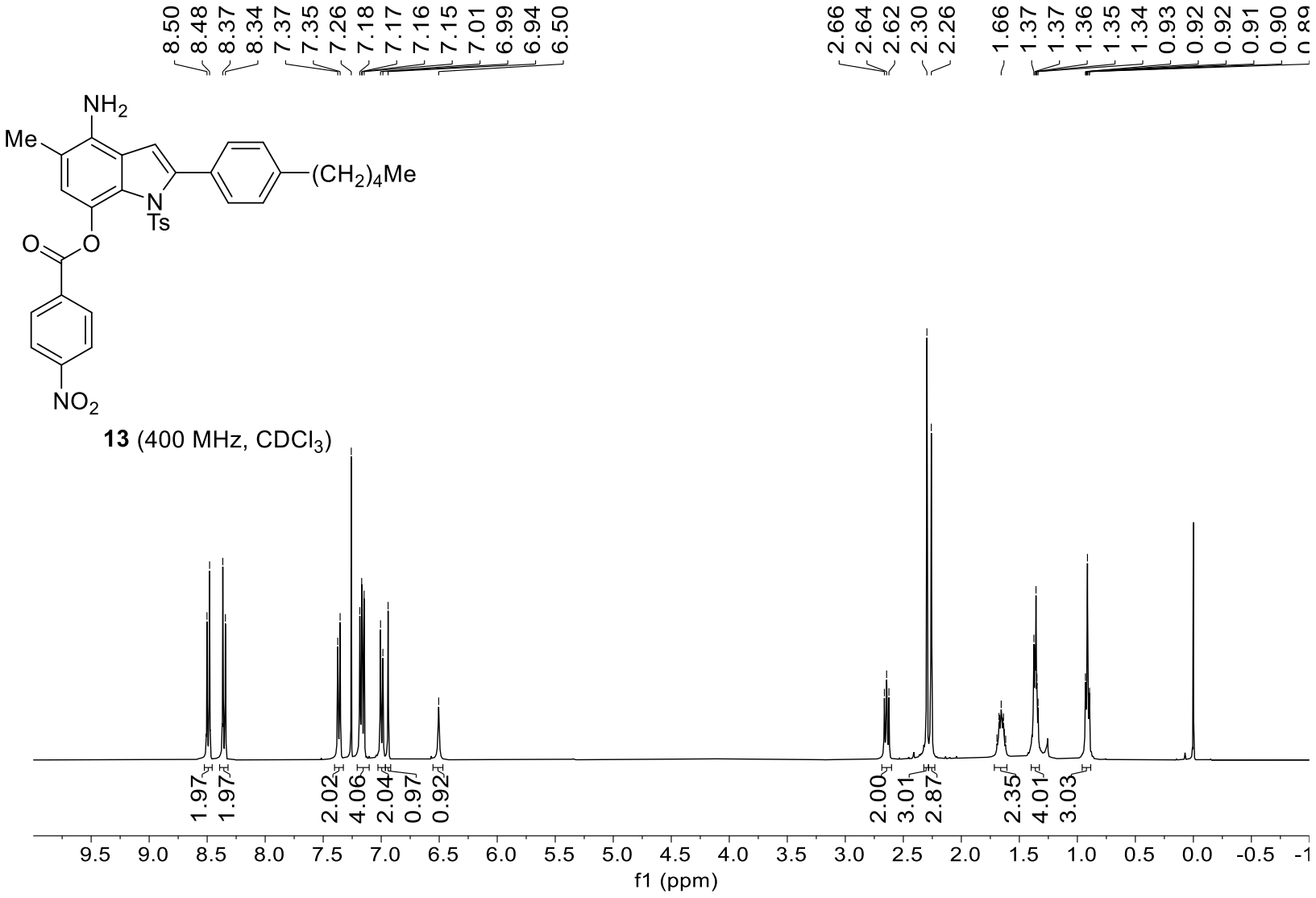

164.20
150.67
144.62
142.25
138.57
136.01
135.04
134.95
132.45
131.56
131.23
130.39
130.05
129.30
129.24
128.93
127.04
125.05
123.61
122.67
122.21
118.33
111.30
77.48
77.16
76.85
21.69
20.78
16.85
NH2
Me
Me
N
Ts
O
O
NO2
10 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

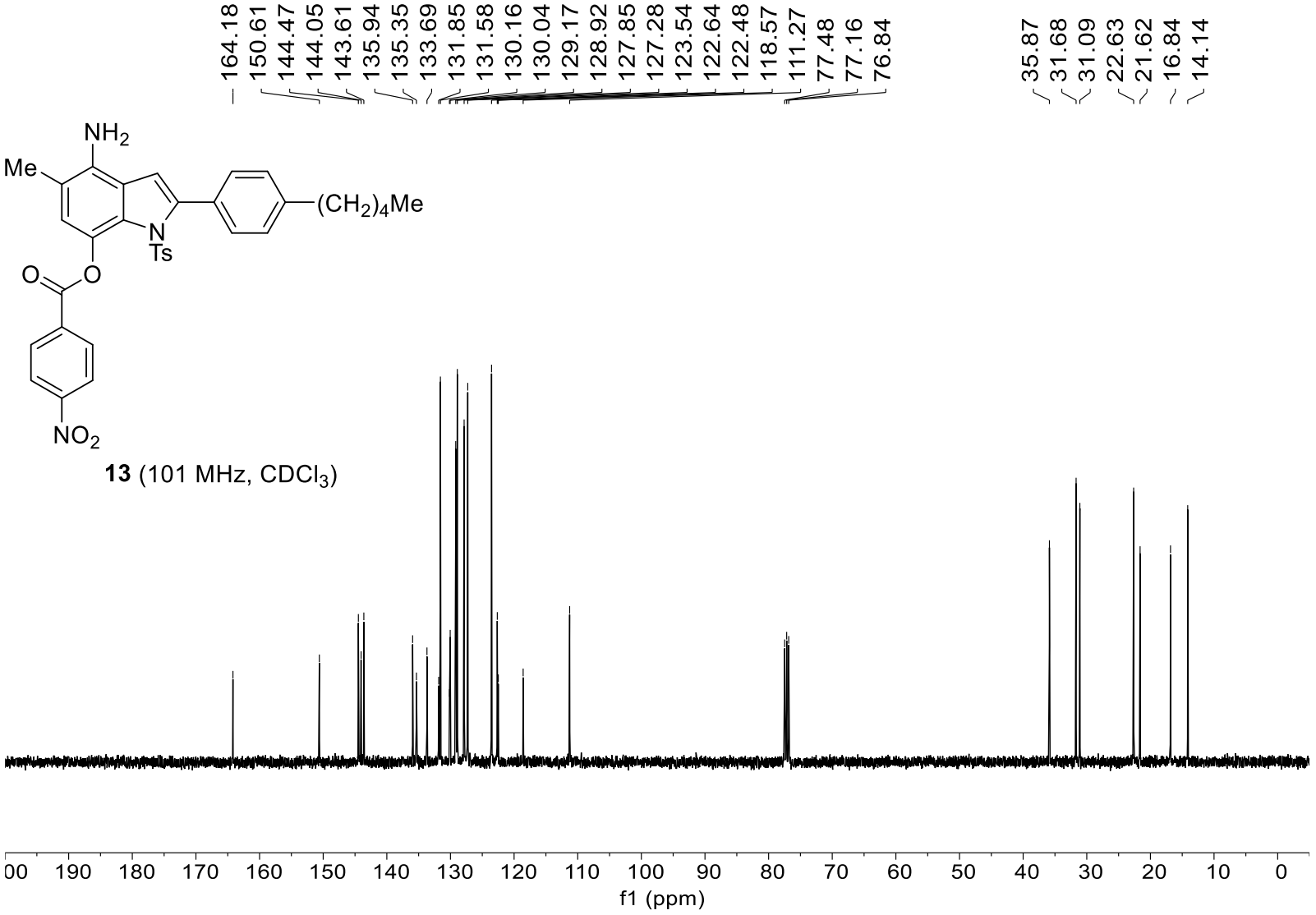

8.50
8.48
8.36
8.34
7.26
7.26
7.25
7.19
7.17
7.02
7.00
6.94
6.51
2.37
2.30
2.25
NH2
Me
Me
N
Ts
O
O
NO2
11 (400 MHz, CDCl3)
2.03
2.02
3.41
3.00
2.09
1.00
1.01
3.08
3.04
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

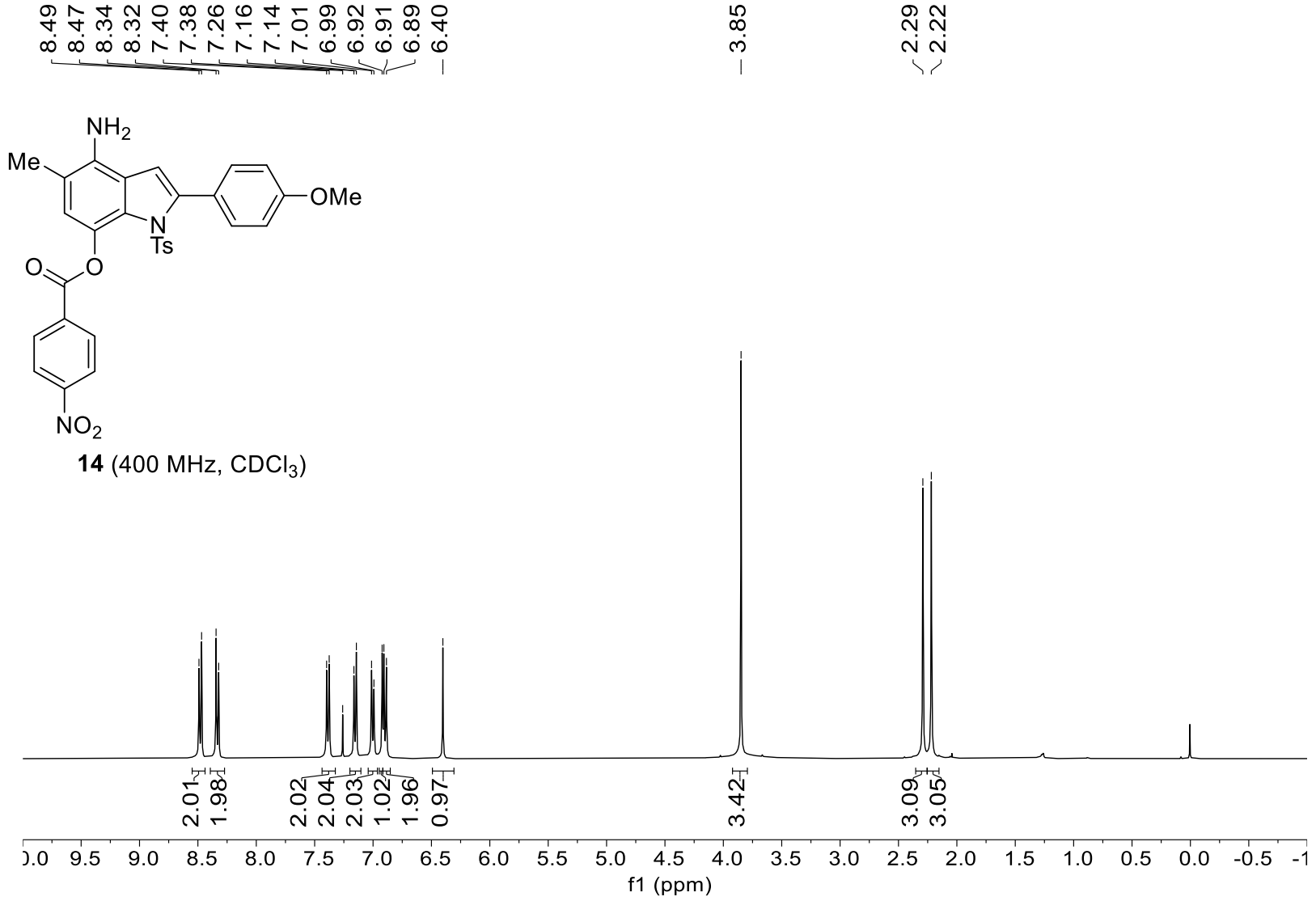

164.21
150.71
144.54
144.24
137.44
135.97
134.94
133.83
132.64
132.12
131.66
130.31
130.04
129.46
128.98
127.77
127.37
126.45
123.64
122.81
122.66
118.91
111.47
77.48
77.16
76.84
21.69
21.53
16.97
NH2
Me
Me
N
Ts
O
O
NO2
11 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.48
8.46
8.34
8.31
7.38
7.36
7.26
7.19
7.19
7.17
7.01
6.99
6.92
6.44
3.73
2.40
2.29
2.20
NH2
Me
Me
N
Ts
O
O
NO2
12 (400 MHz, CDCl3)
2.05
2.06
2.03
4.08
2.09
1.05
1.00
1.97
3.00
3.10
3.19
f1 (ppm)

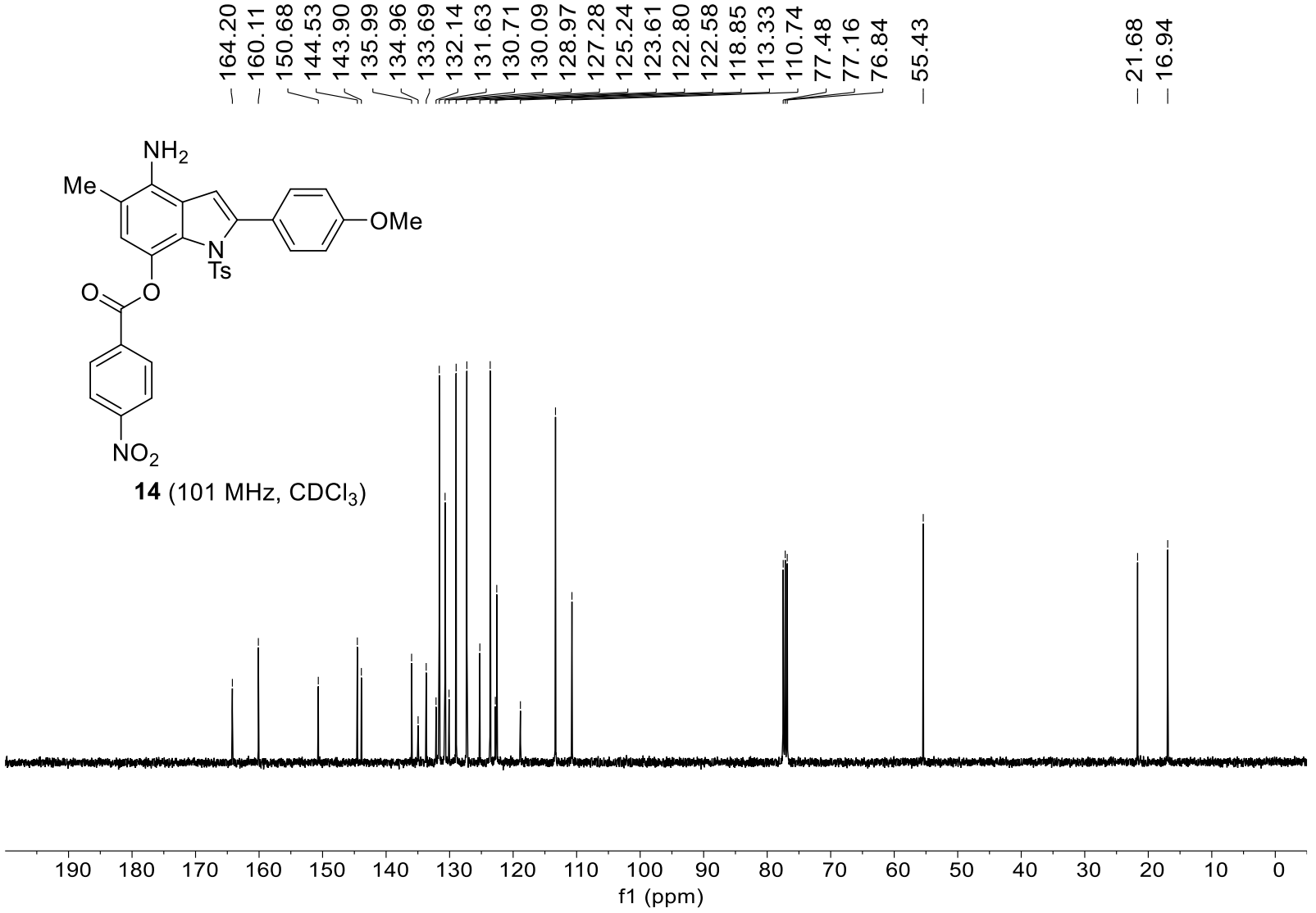

164.20
150.64
144.52
144.08
138.63
135.95
135.23
133.59
131.95
131.60
130.15
129.94
129.21
128.96
128.59
127.28
123.57
122.70
122.63
118.74
111.42
77.48
77.16
76.84
21.65
21.51
16.88
NH2
Me
Me
N
Ts
O
O
NO2
12 (101 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

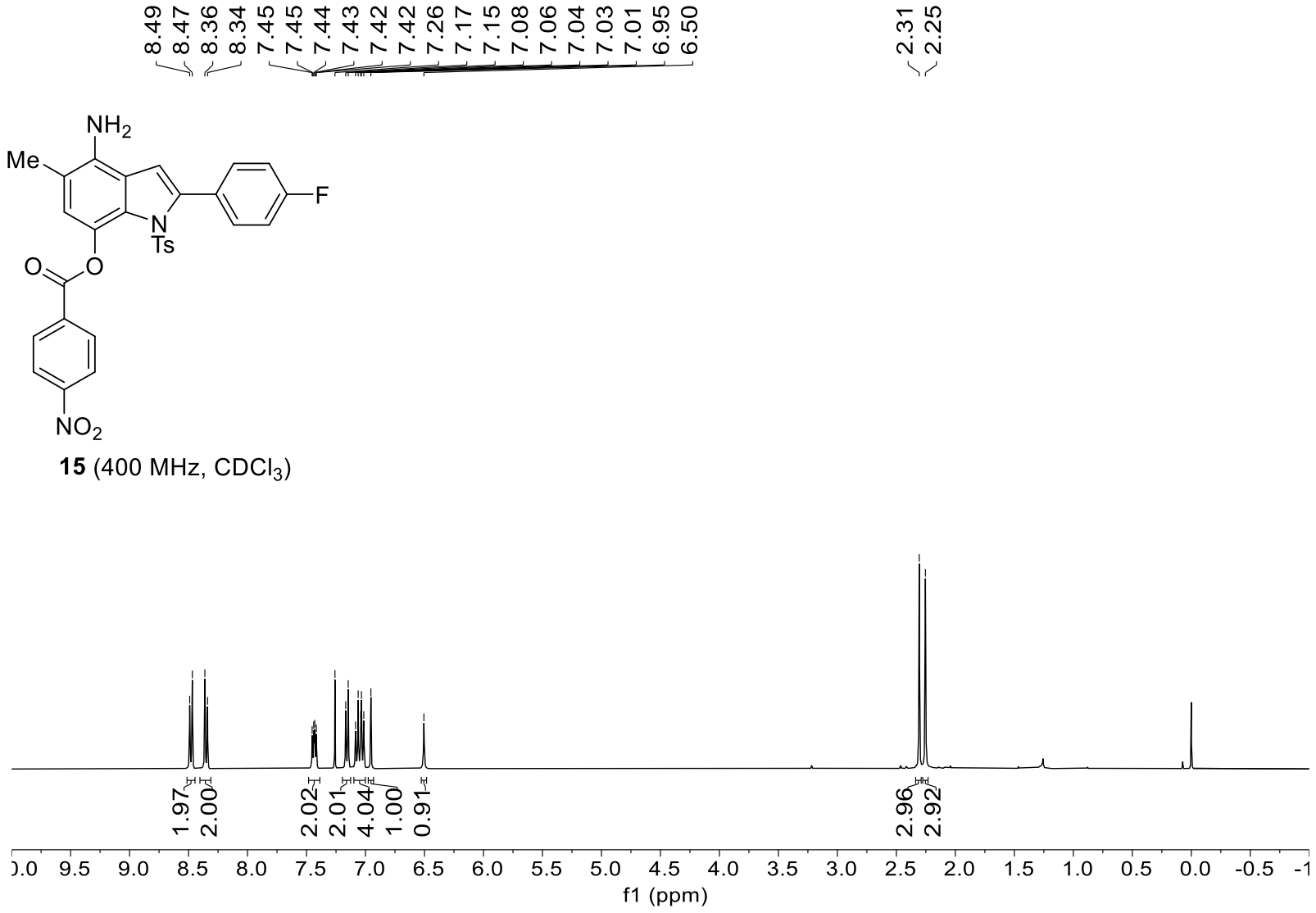

8.50
8.48
8.37
8.34
7.37
7.35
7.26
7.18
7.17
7.16
7.15
7.01
6.99
6.94
6.50
2.66
2.64
2.62
2.30
2.26
1.66
1.37
1.37
1.36
1.35
1.34
0.93
0.92
0.92
0.91
0.90
NH2
Me
(CH2)4Me
N
Ts
O
O
NO2
13 (400 MHz, CDCl3)
1.97
1.97
2.02
4.06
2.04
0.97
0.92
2.00
3.01
2.87
2.35
4.01
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


164.18
150.61
144.47
144.05
143.61
135.94
135.35
133.69
131.85
131.58
130.16
130.04
129.17
128.92
127.85
127.28
123.54
122.64
122.48
118.57
111.27
77.48
77.16
76.84
35.87
31.68
31.09
22.63
21.62
16.84
14.14
NH2
Me
(CH2)4Me
N
Ts
O
O
O
NO2
13 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

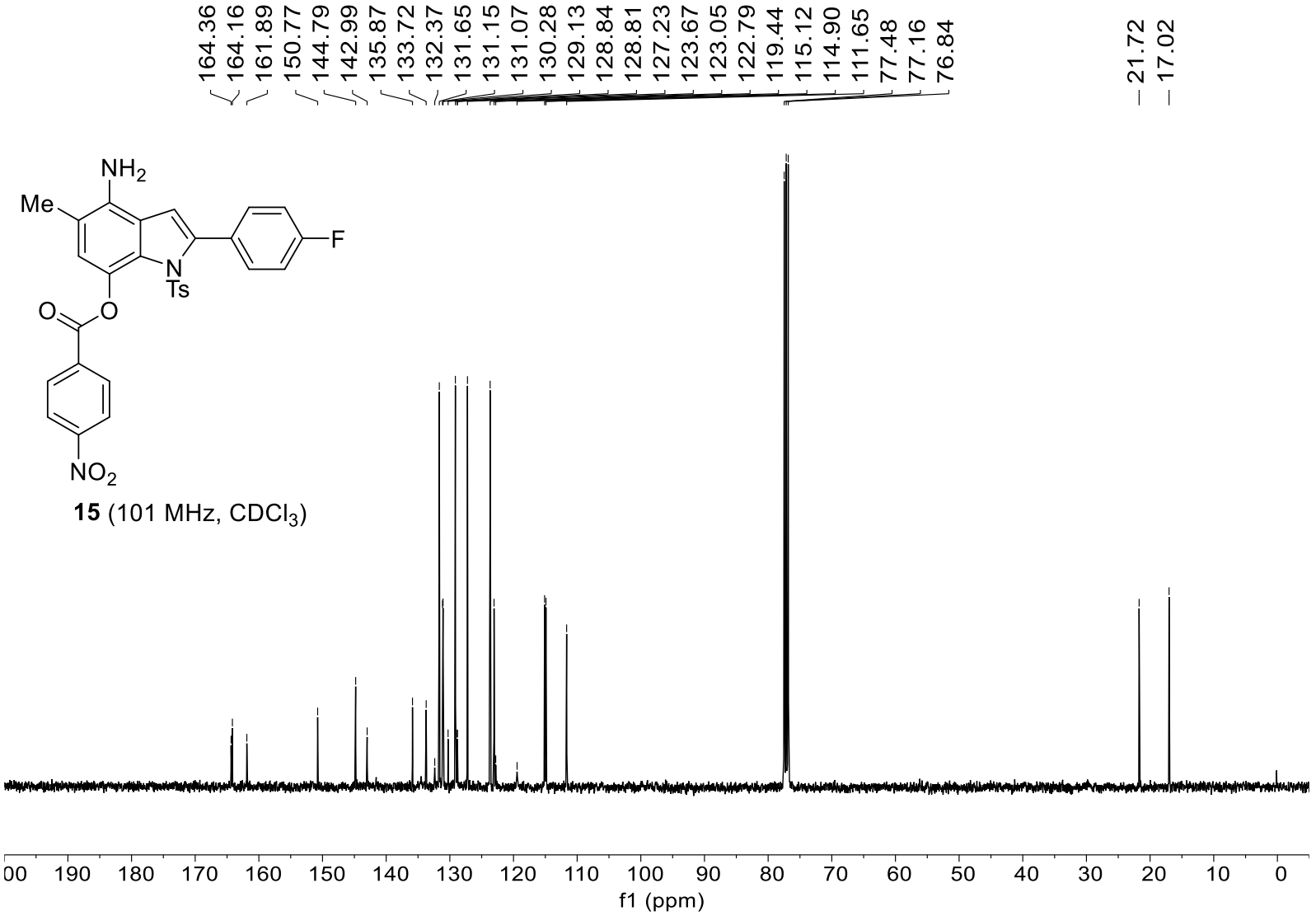


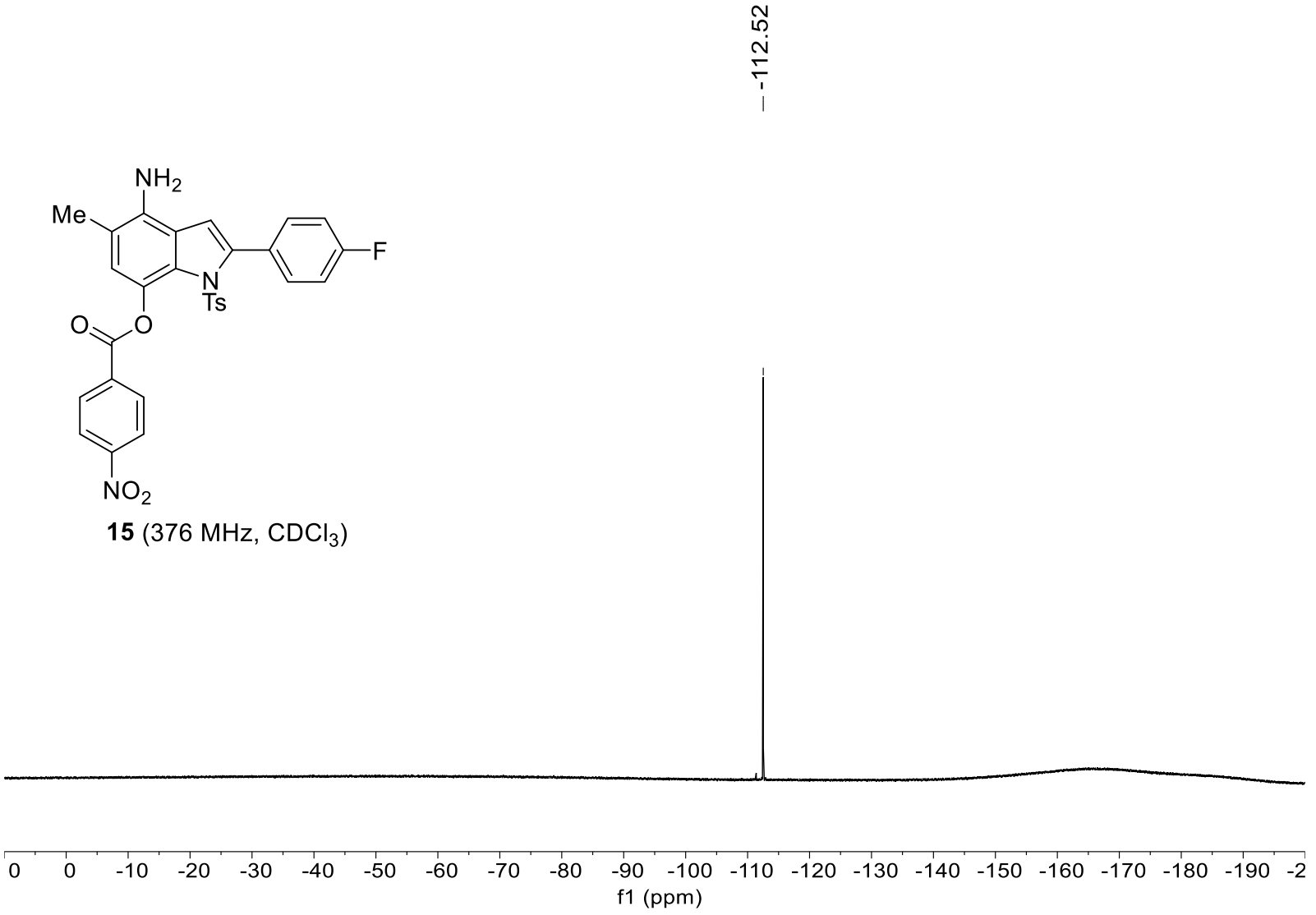
14 (400 MHz, $CDCl_3$)


164.20
160.11
150.68
144.53
143.90
135.99
134.96
133.69
132.14
131.63
130.71
130.09
128.97
127.28
125.24
123.61
122.80
122.58
118.85
113.33
110.74
77.48
77.16
76.84
55.43
21.68
16.94
NH2
Me
OMe
N
Ts
O
O
NO2
14 (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

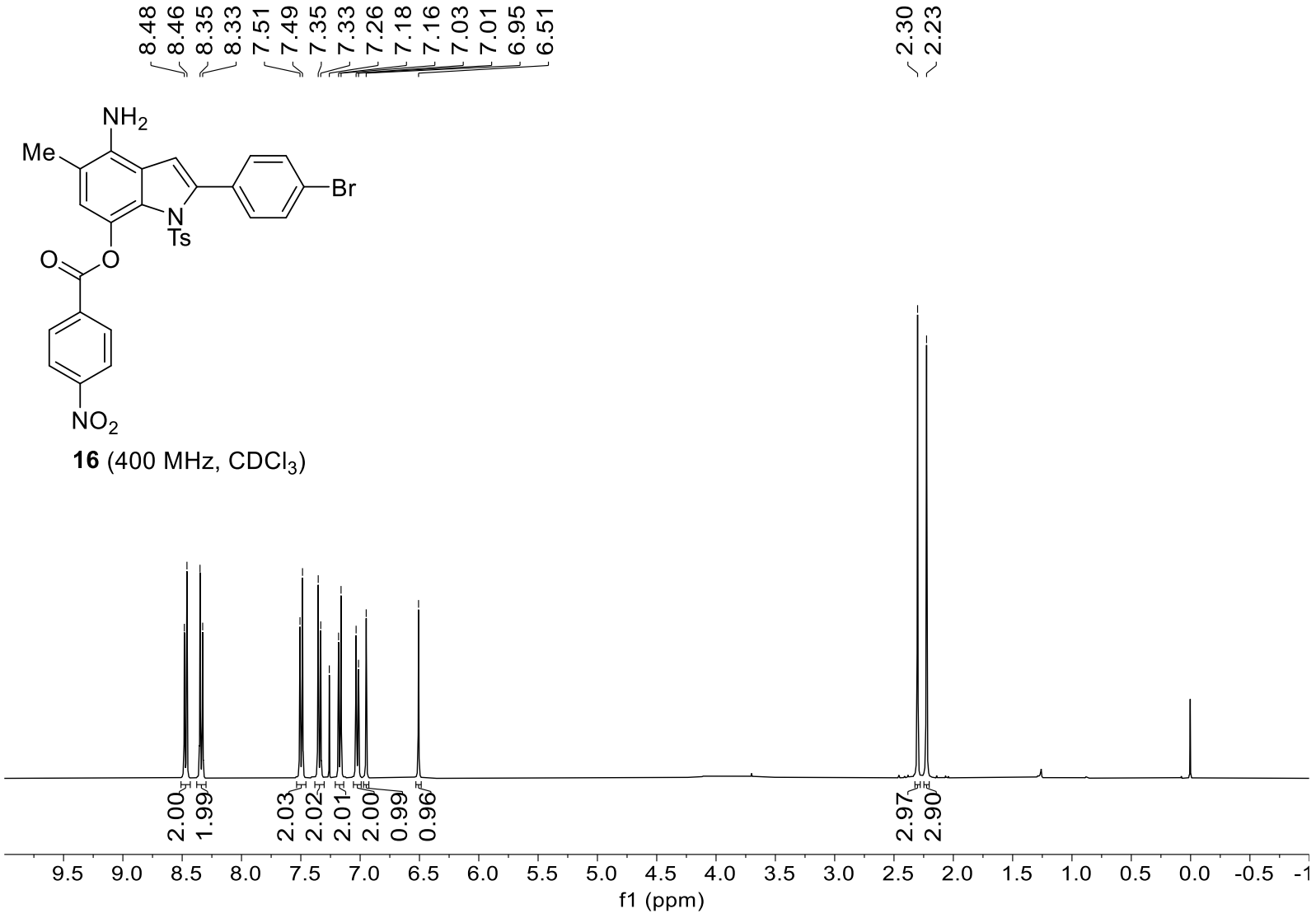


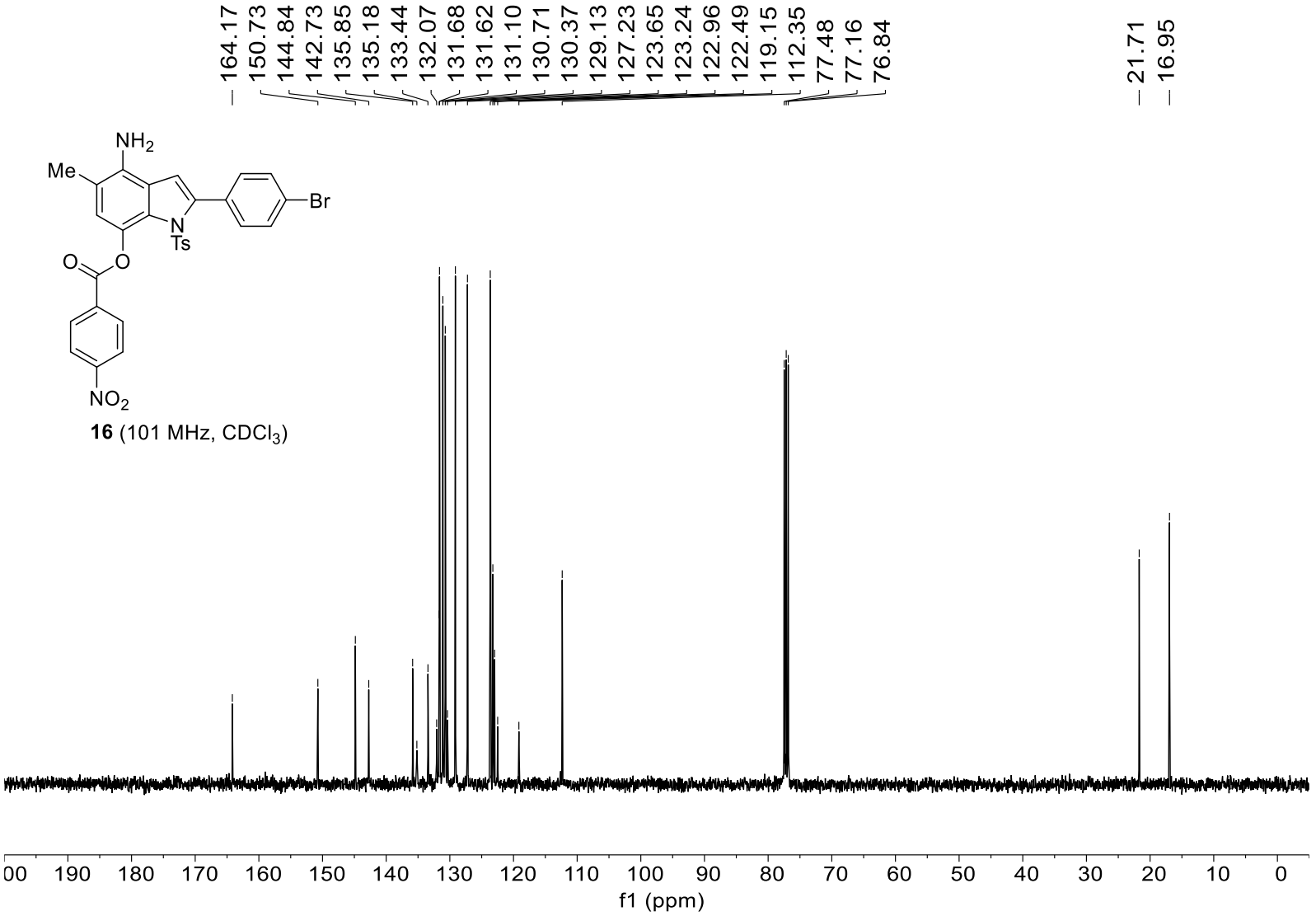
15 (400 MHz, $CDCl_3$)

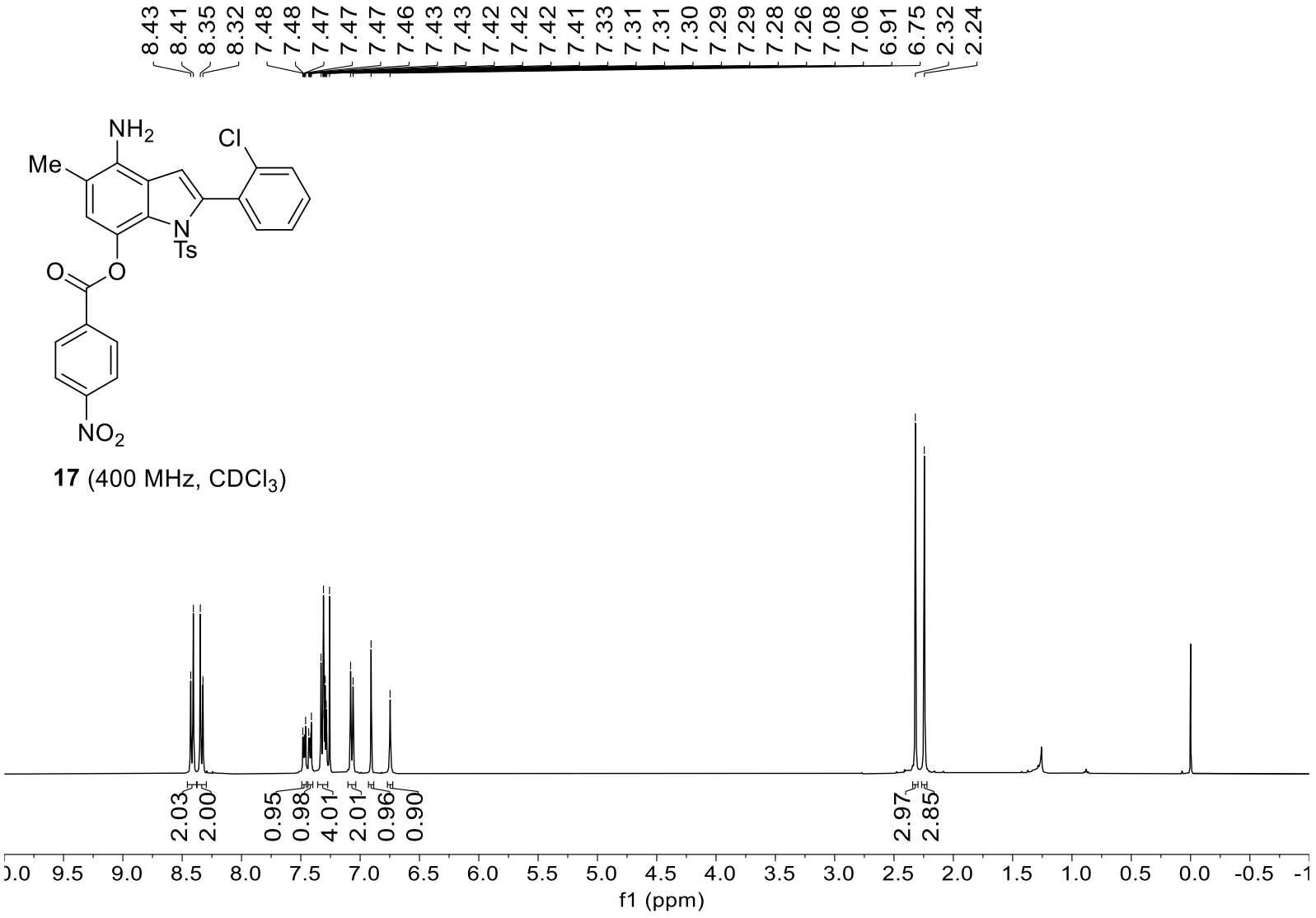

164.36
164.16
161.89
150.77
144.79
142.99
135.87
133.72
132.37
131.65
131.15
131.07
130.28
129.13
128.84
128.81
127.23
123.67
123.05
122.79
119.44
115.12
114.90
111.65
77.48
77.16
76.84
21.72
17.02
NH2
Me
F
N
Ts
O
O
NO2
15 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

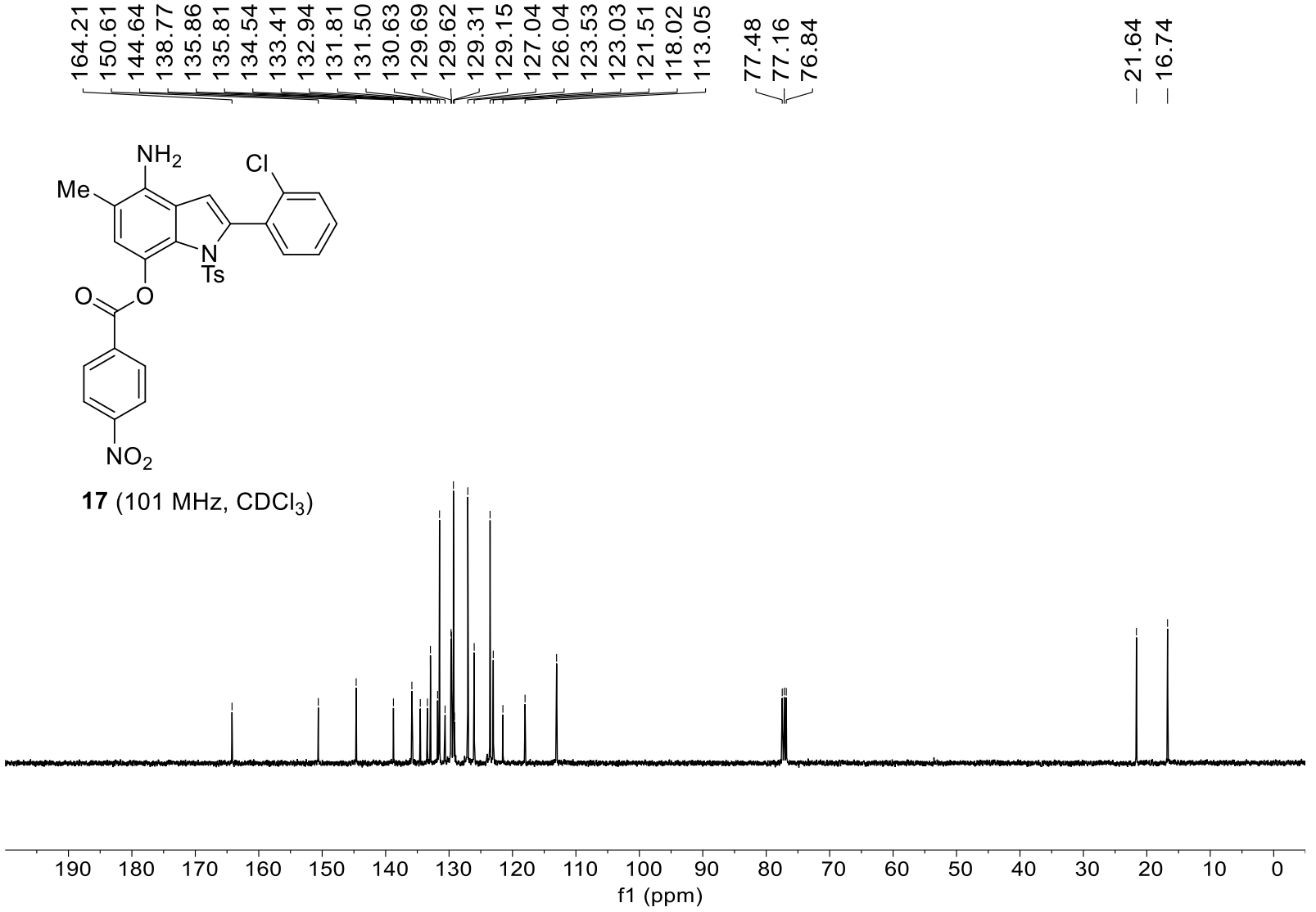


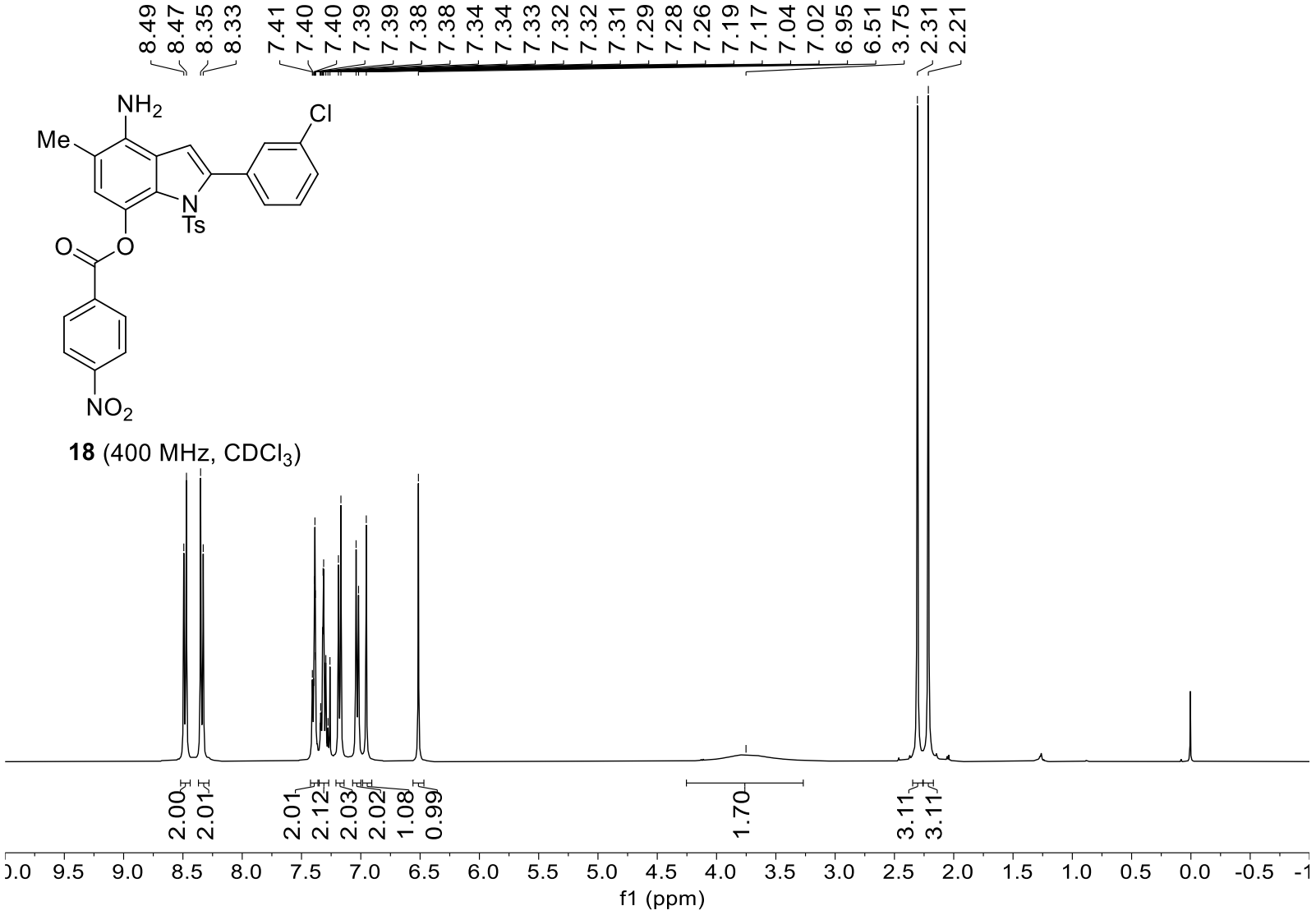
15 (376 MHz, $CDCl_3$)

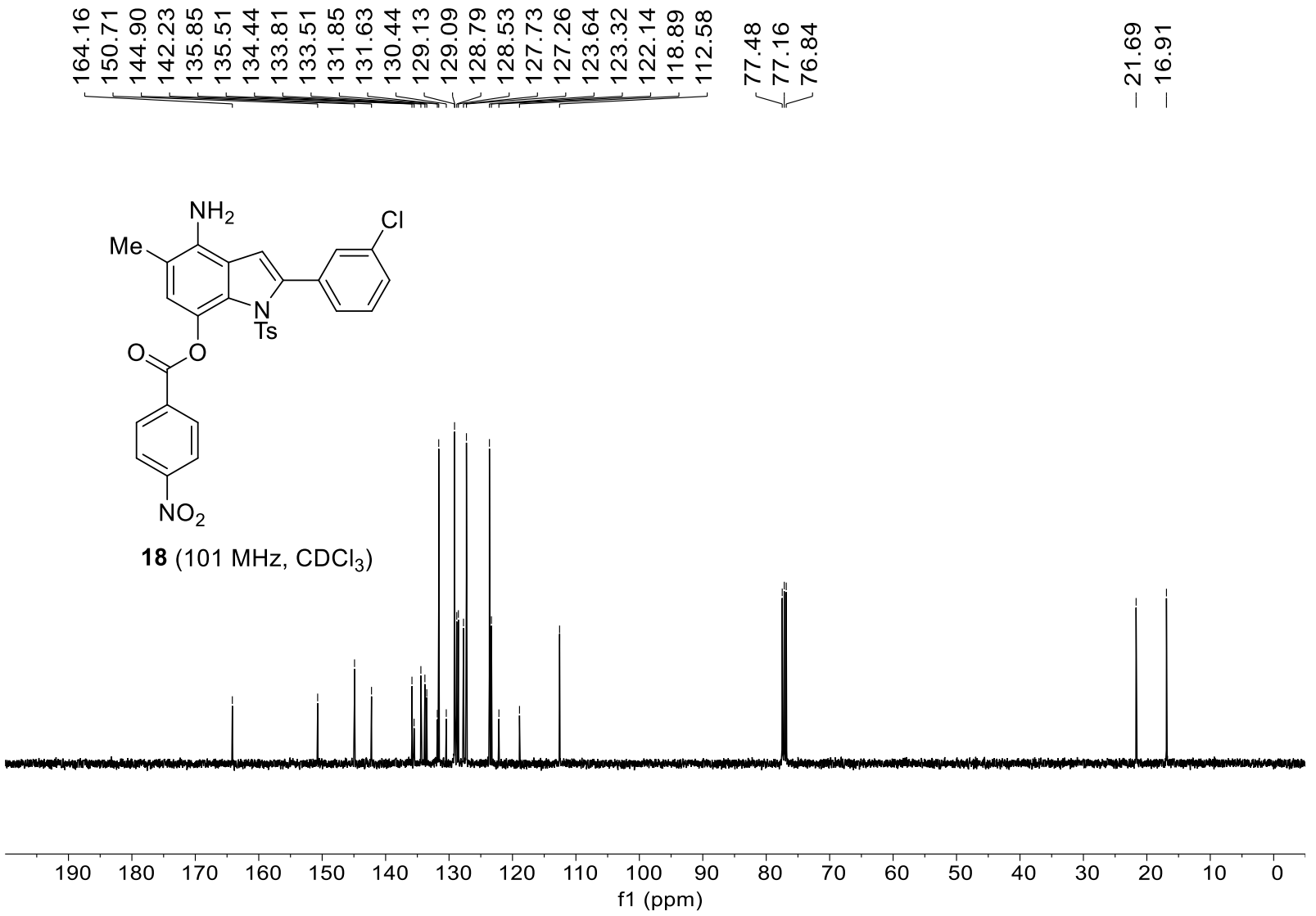

8.48
8.46
8.35
8.33
7.51
7.49
7.35
7.33
7.26
7.18
7.16
7.03
7.01
6.95
6.51
2.30
2.23
NH2
Me
Br
N
Ts
O
O
NO2
16 (400 MHz, CDCl3)
2.00
1.99
2.03
2.02
2.01
2.00
0.99
0.96
2.97
2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

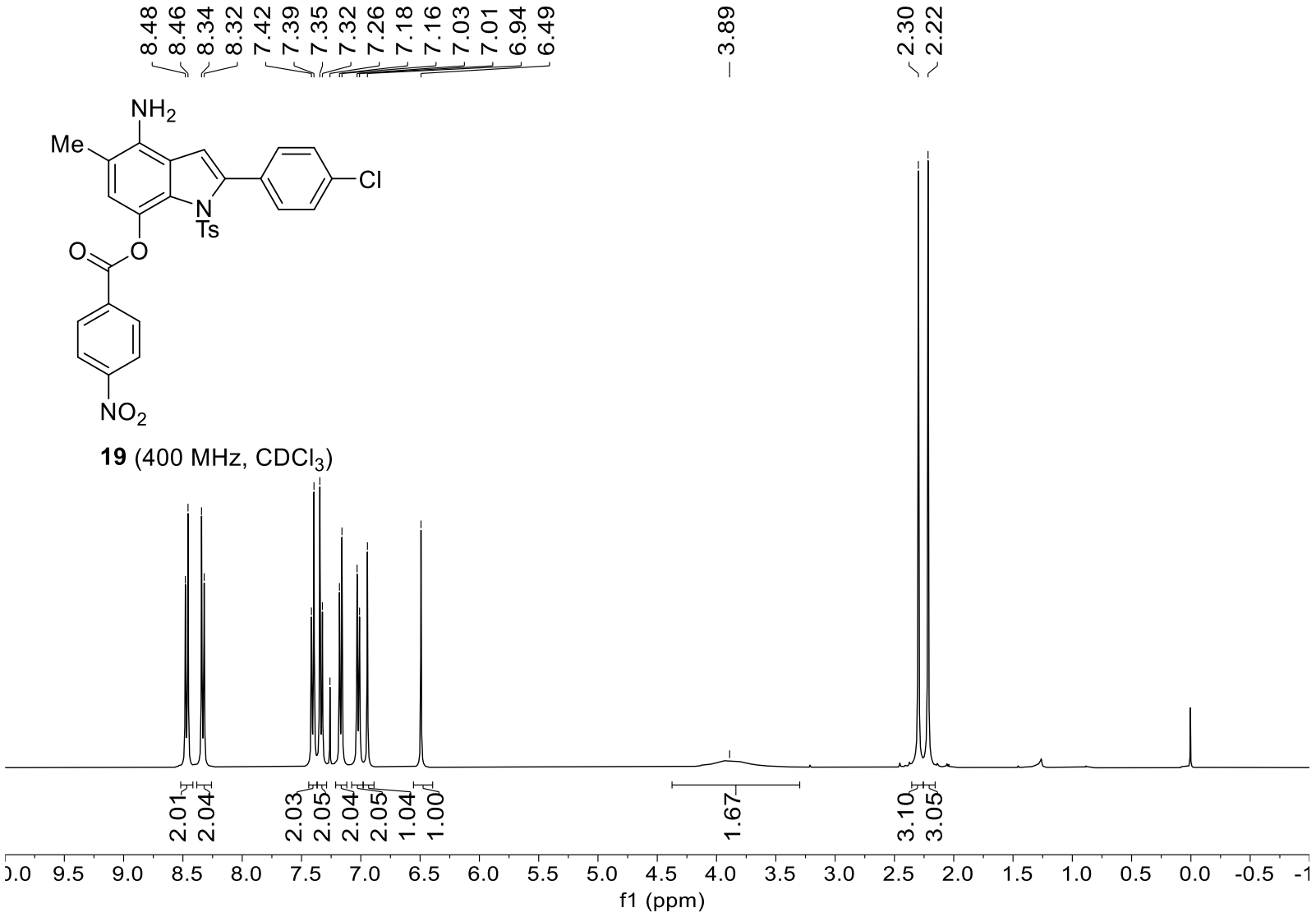

164.17
150.73
144.84
142.73
135.85
135.18
133.44
132.07
131.68
131.62
131.10
130.71
130.37
129.13
127.23
123.65
123.24
122.96
122.49
119.15
112.35
77.48
77.16
76.84
21.71
16.95
NH2
Me
Br
N
Ts
O
O
NO2
16 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

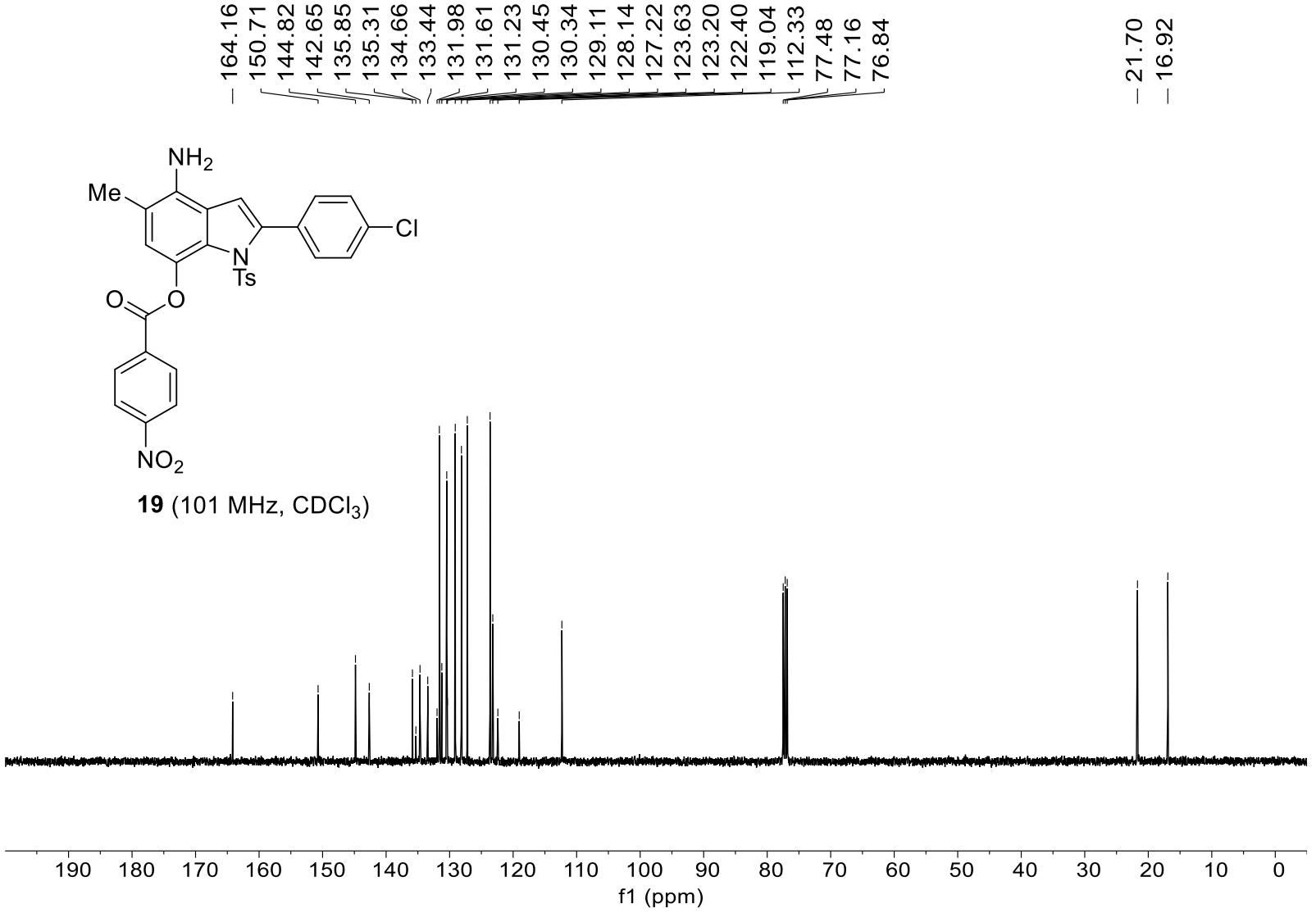

8.43
8.41
8.35
8.32
7.48
7.48
7.47
7.47
7.47
7.46
7.43
7.43
7.42
7.42
7.42
7.41
7.33
7.31
7.31
7.30
7.29
7.29
7.28
7.26
7.08
7.06
6.91
6.75
2.32
2.24
NH2
Me
Cl
N
Ts
O
O
O
NO2
17 (400 MHz, CDCl3)
2.03
2.00
0.95
0.98
4.01
2.01
0.96
0.90
2.97
2.85
f1 (ppm)

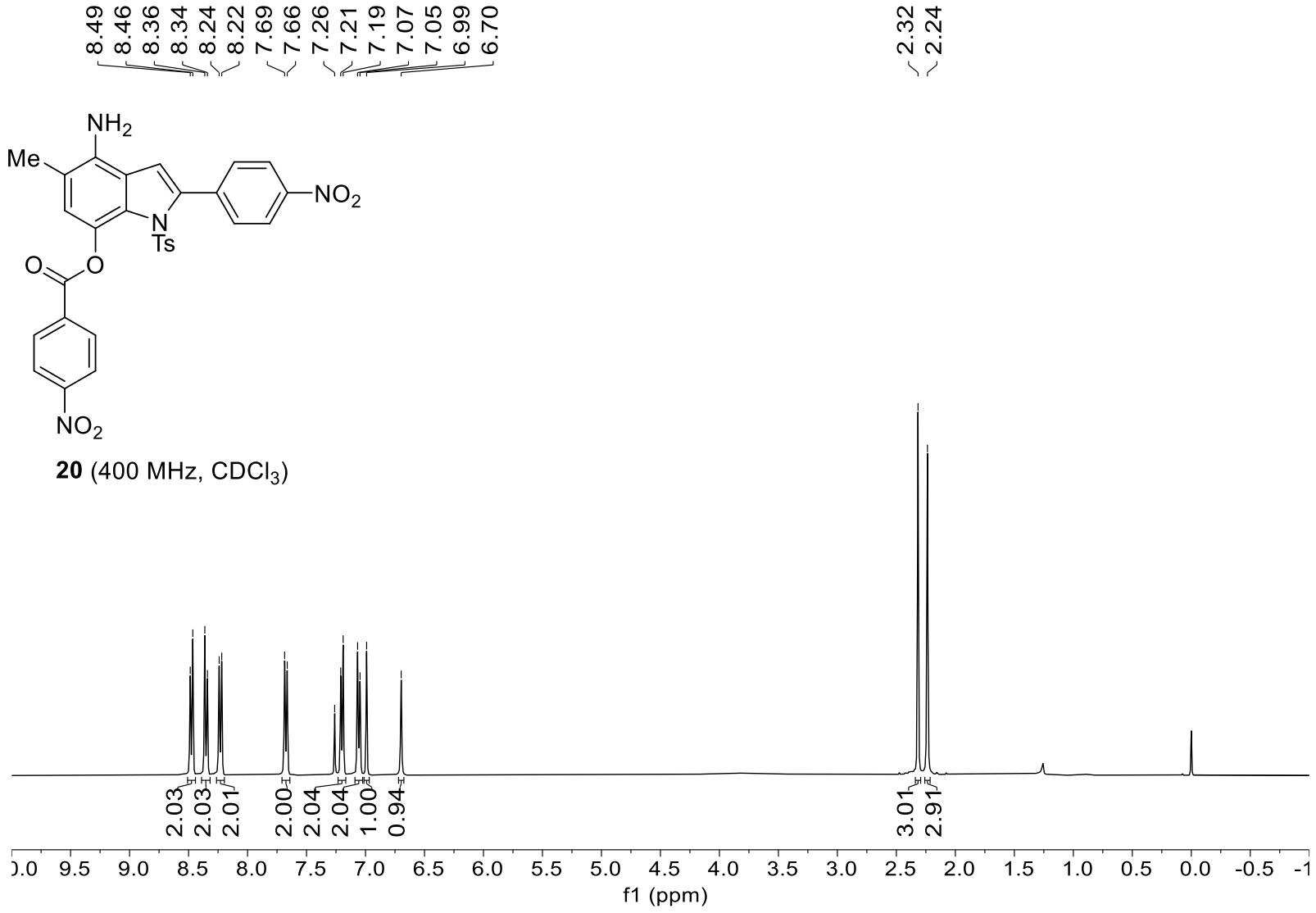

164.21
150.61
144.64
138.77
135.86
135.81
134.54
133.41
132.94
131.81
131.50
130.63
129.69
129.62
129.31
129.15
127.04
126.04
123.53
123.03
121.51
118.02
113.05
77.48
77.16
76.84
21.64
16.74
NH2
Cl
Me
N
Ts
O
O
NO2
17 (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

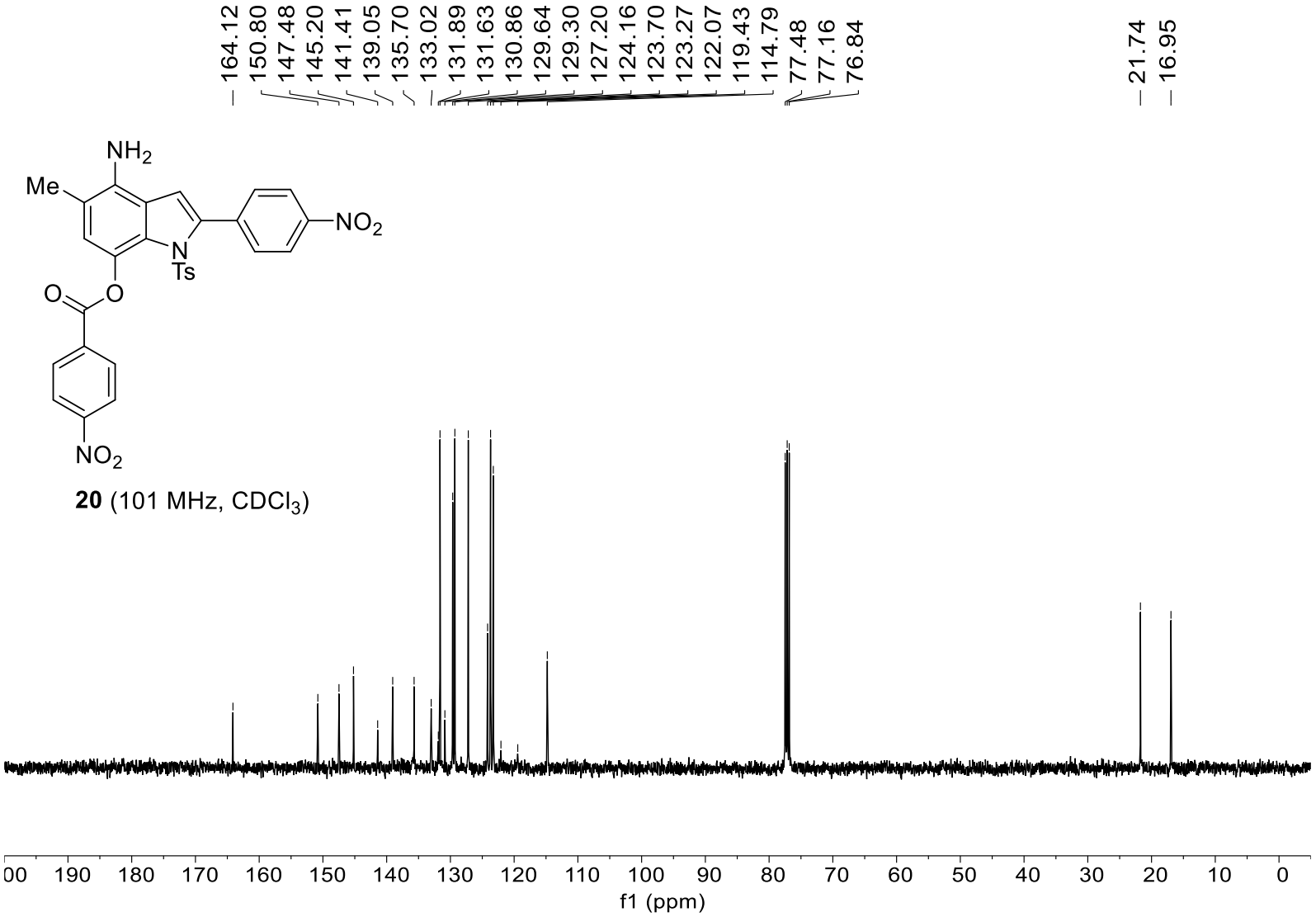

8.49
8.47
8.35
8.33
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.34
7.34
7.33
7.32
7.32
7.31
7.29
7.28
7.26
7.19
7.17
7.04
7.02
6.95
6.51
3.75
2.31
2.21
NH2
Me
Cl
N
Ts
O
O
O
NO2
18 (400 MHz, CDCl3)
2.00
2.01
2.01
2.12
2.03
2.02
1.08
0.99
1.70
3.11
3.11
f1 (ppm)

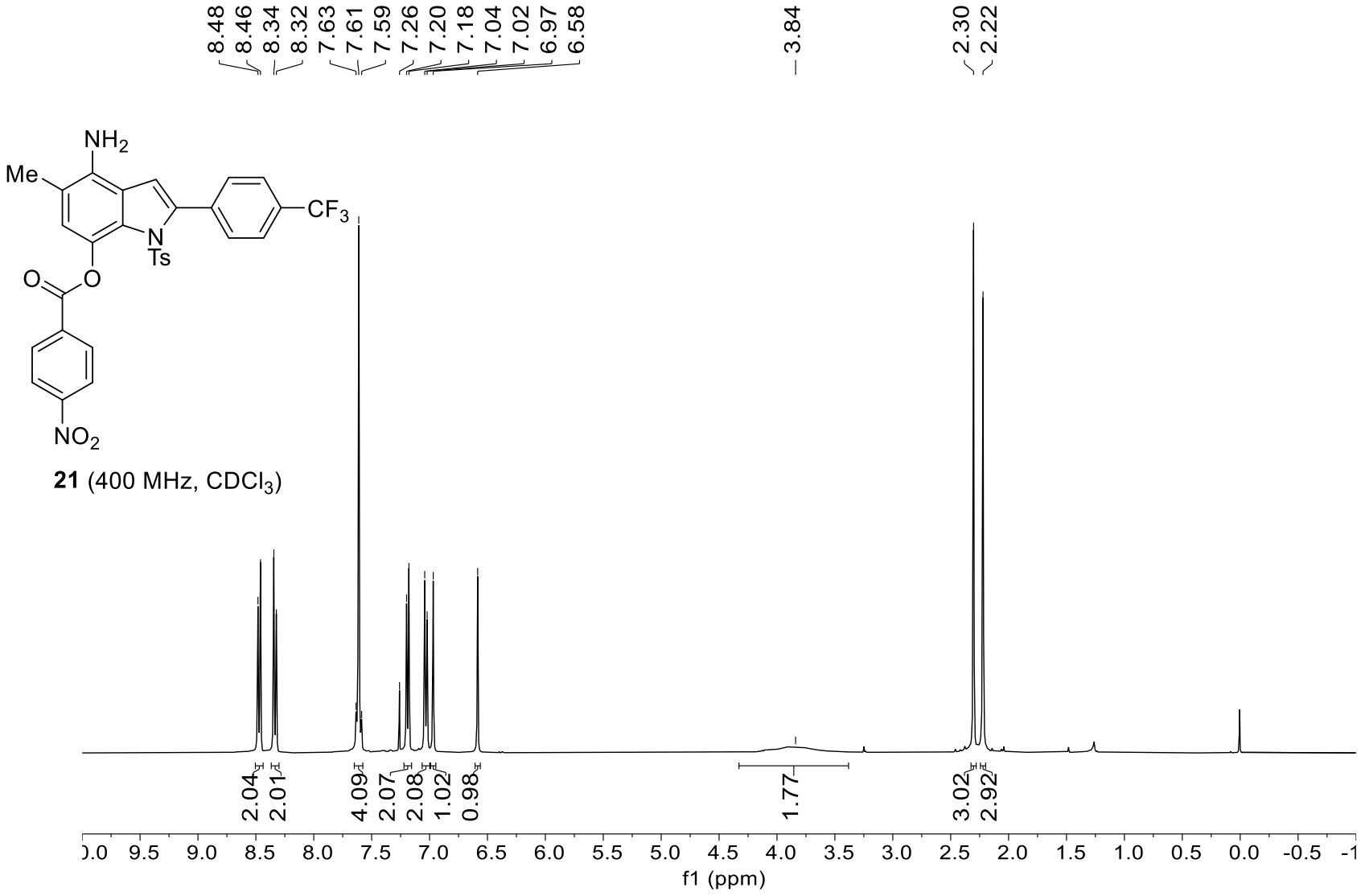

164.16
150.71
144.90
142.23
135.85
135.51
134.44
133.81
133.51
131.85
131.63
130.44
129.13
129.09
128.79
128.53
127.73
127.26
123.64
123.32
122.14
118.89
112.58
77.48
77.16
76.84
21.69
16.91
NH2
Me
Cl
N
Ts
O
O
NO2
18 (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

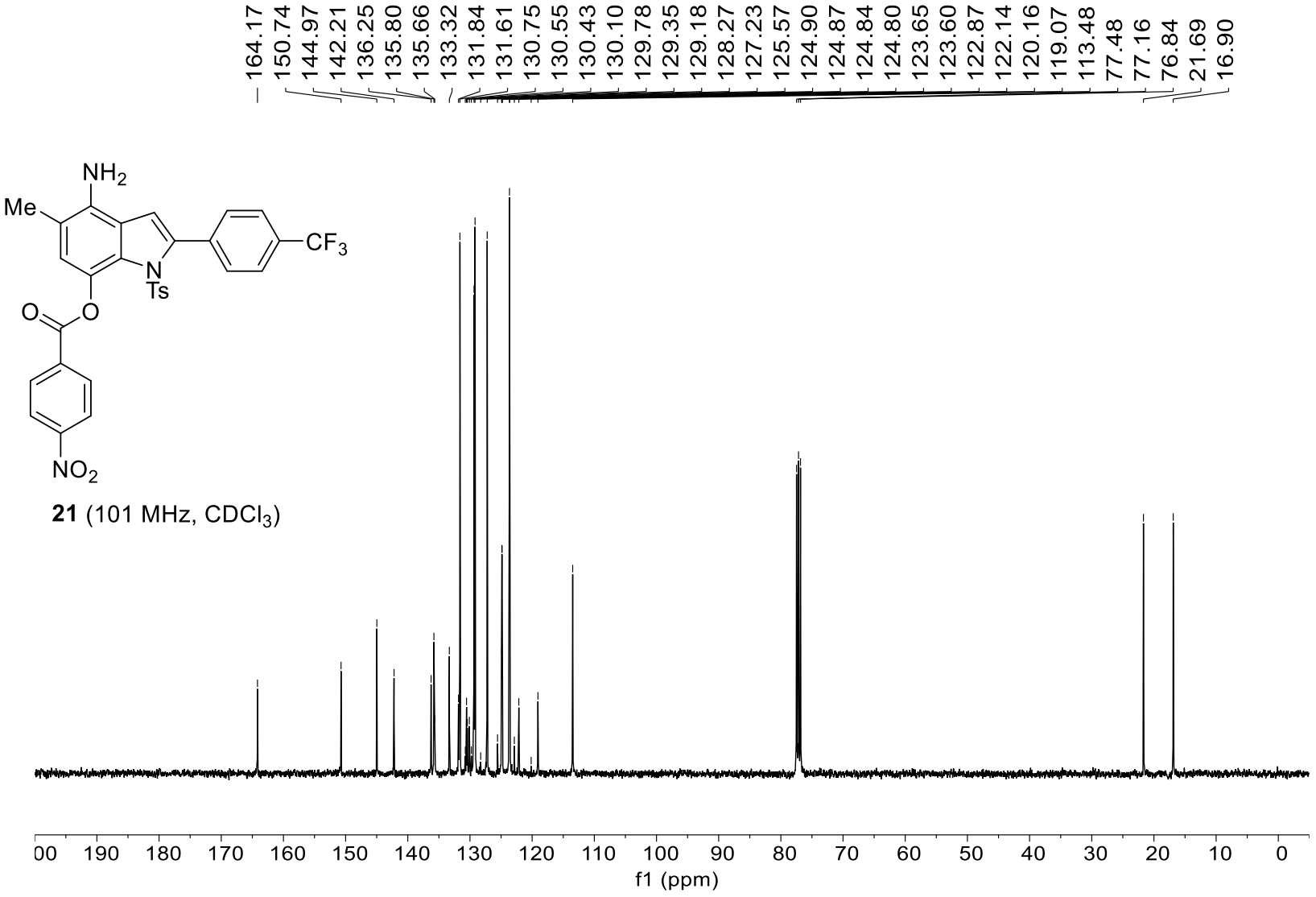

8.48
8.46
8.34
8.32
7.42
7.39
7.35
7.32
7.26
7.18
7.16
7.03
7.01
6.94
6.49
3.89
2.30
2.22
NH2
Me
Cl
N
Ts
O
O
NO2
19 (400 MHz, CDCl3)
2.01
2.04
2.03
2.05
2.04
2.05
1.04
1.00
1.67
3.10
3.05
f1 (ppm)

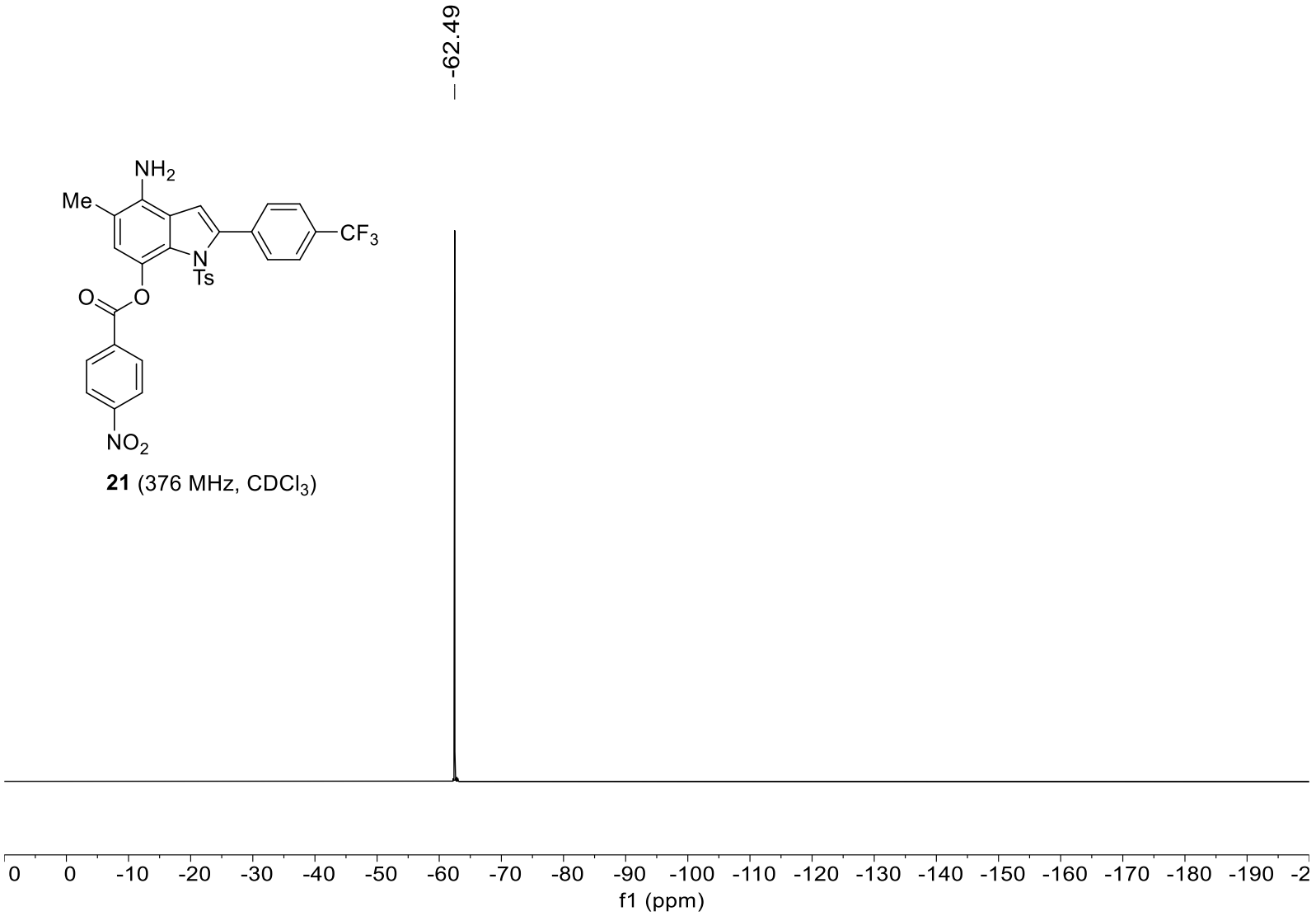

164.16
150.71
144.82
142.65
135.85
135.31
134.66
133.44
131.98
131.61
131.23
130.45
130.34
129.11
128.14
127.22
123.63
123.20
122.40
119.04
112.33
77.48
77.16
76.84
21.70
16.92
NH2
Me
Cl
N
Ts
O
O
NO2
19 (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.49
8.46
8.36
8.34
8.24
8.22
7.69
7.66
7.26
7.21
7.19
7.07
7.05
6.99
6.70
2.32
2.24
NH2
Me
NO2
N
Ts
O
O
NO2
20 (400 MHz, CDCl3)
2.03
2.03
2.01
2.00
2.04
2.04
1.00
0.94
3.01
2.91
f1 (ppm)

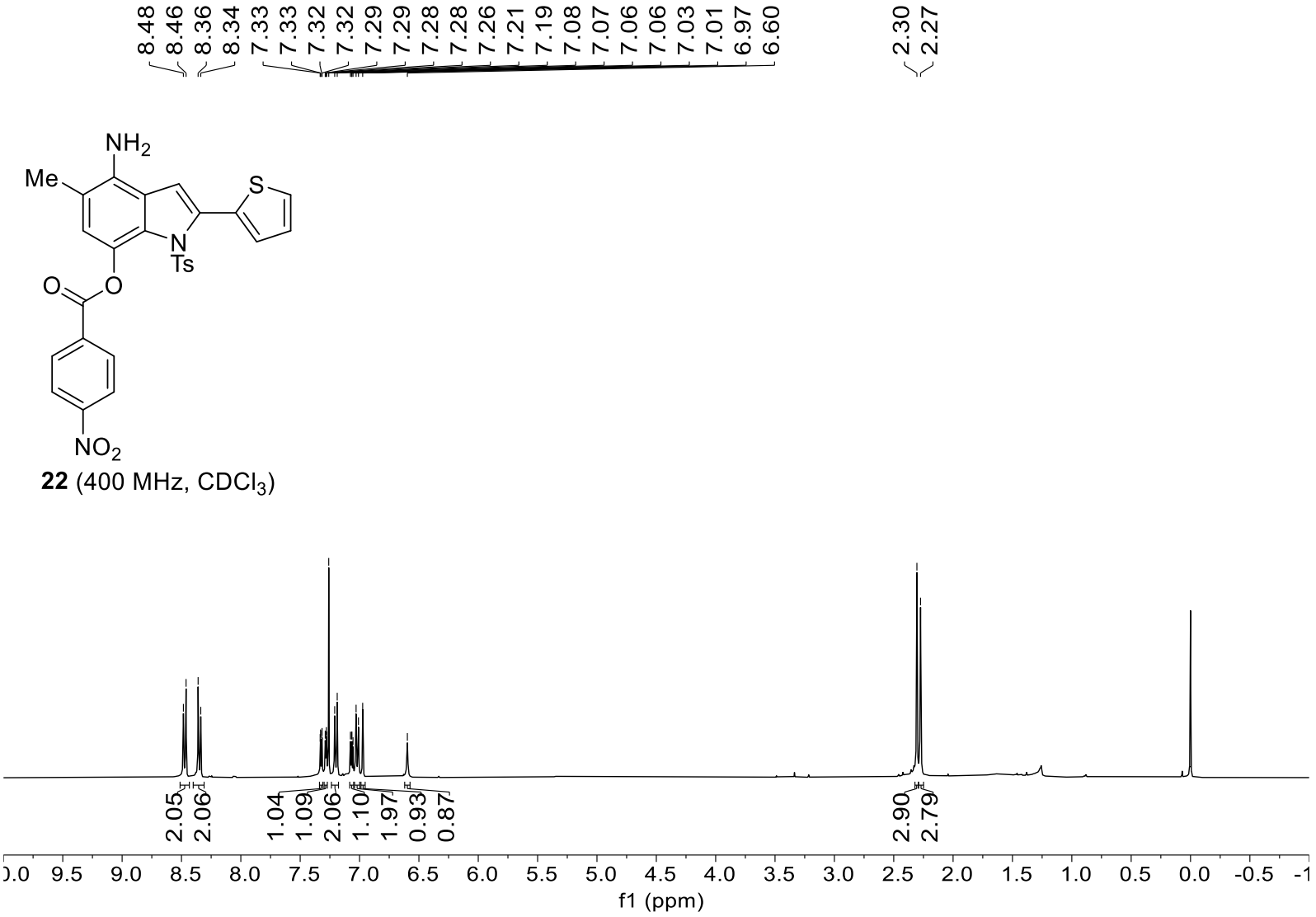

164.12
150.80
147.48
145.20
141.41
139.05
135.70
133.02
131.89
131.63
130.86
129.64
129.30
127.20
124.16
123.70
123.27
122.07
119.43
114.79
77.48
77.16
76.84
21.74
16.95
NH2
Me
NO2
N
Ts
O
O
NO2
20 (101 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.48
8.46
8.34
8.32
7.63
7.61
7.59
7.26
7.20
7.18
7.04
7.02
6.97
6.58
3.84
2.30
2.22
NH2
Me
CF3
N
Ts
O
O
NO2
21 (400 MHz, CDCl3)
2.04
2.01
4.09
2.07
2.08
1.02
0.98
1.77
3.02
2.92
f1 (ppm)

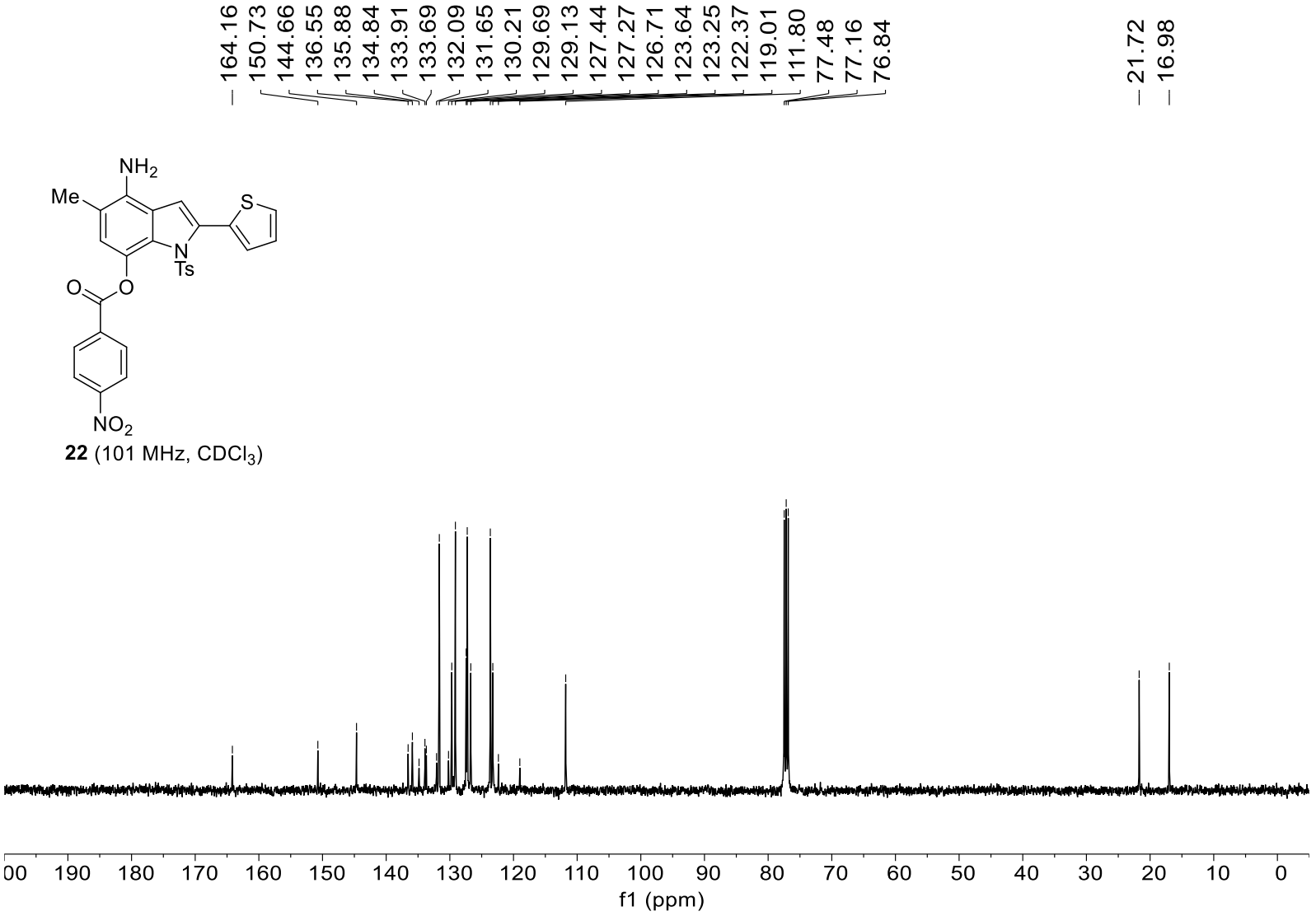

164.17
150.74
144.97
142.21
136.25
135.80
135.66
133.32
131.84
131.61
130.75
130.55
130.43
130.10
129.78
129.35
129.18
128.27
127.23
125.57
124.90
124.87
124.84
124.80
123.65
123.60
122.87
122.14
120.16
119.07
113.48
77.48
77.16
76.84
21.69
16.90
NH2
Me
CF3
N
Ts
O
O
O
NO2
21 (101 MHz, CDCl3)
f1 (ppm)



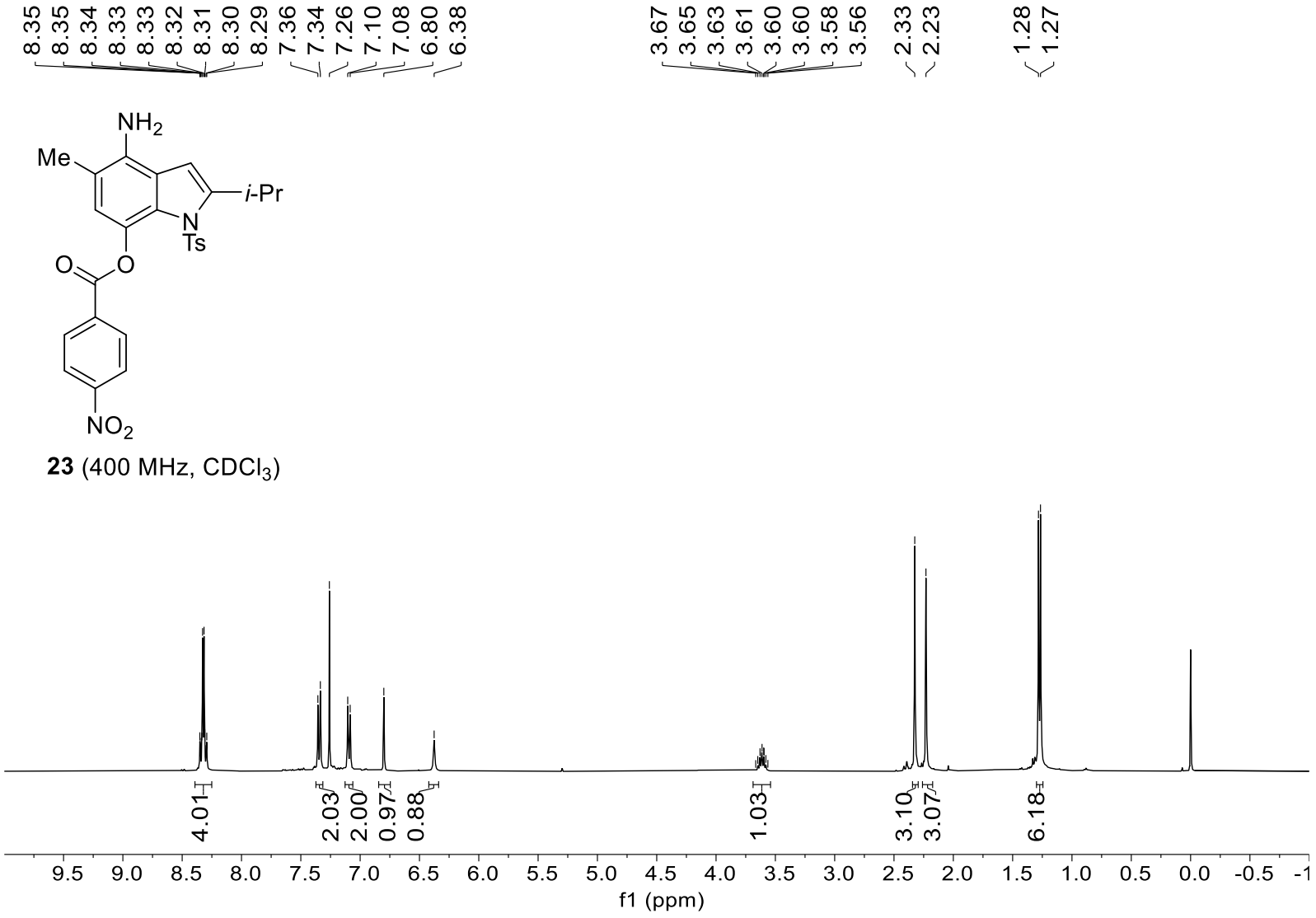
21 (376 MHz, $CDCl_3$)



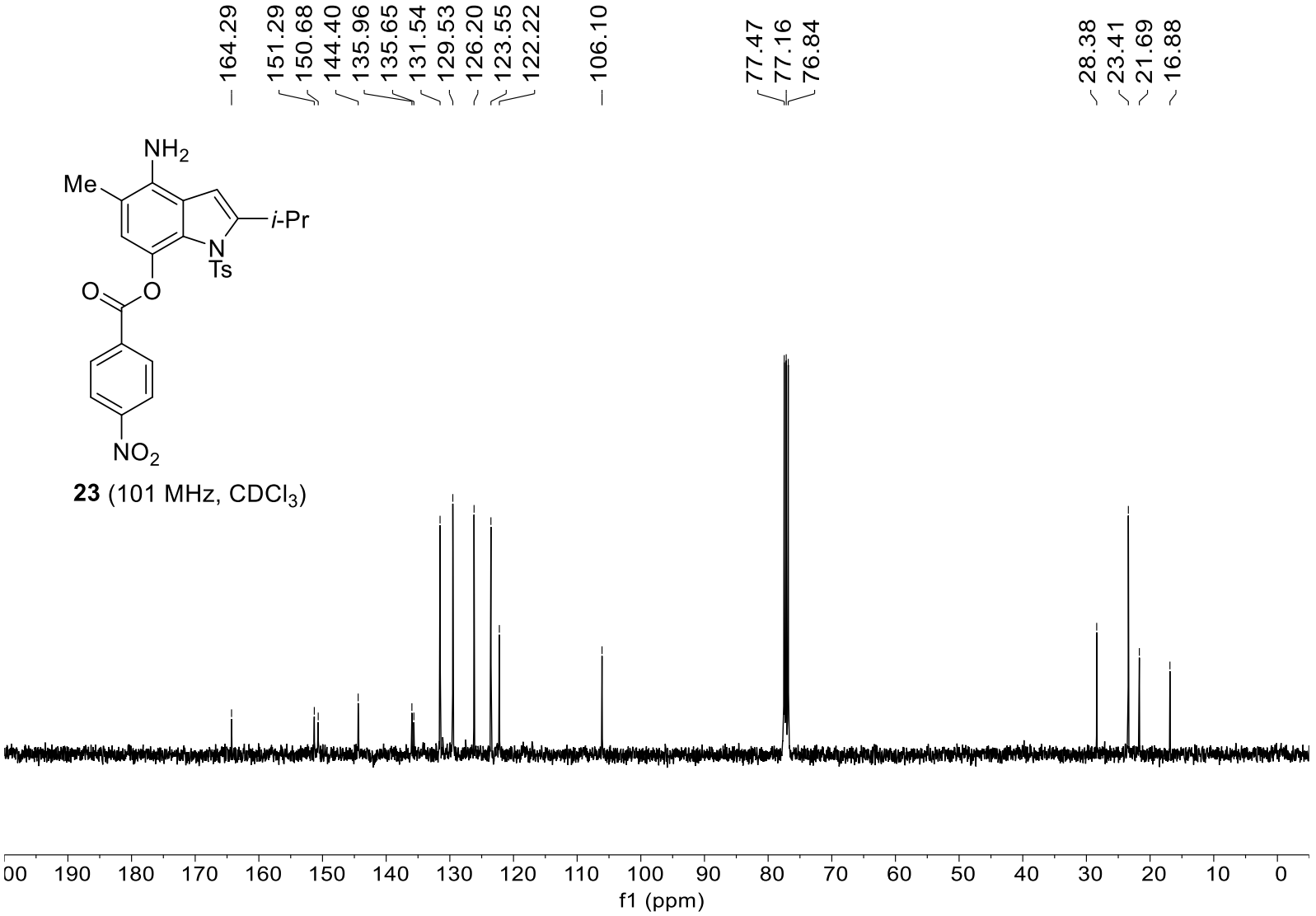
22 (400 MHz, $CDCl_3$)

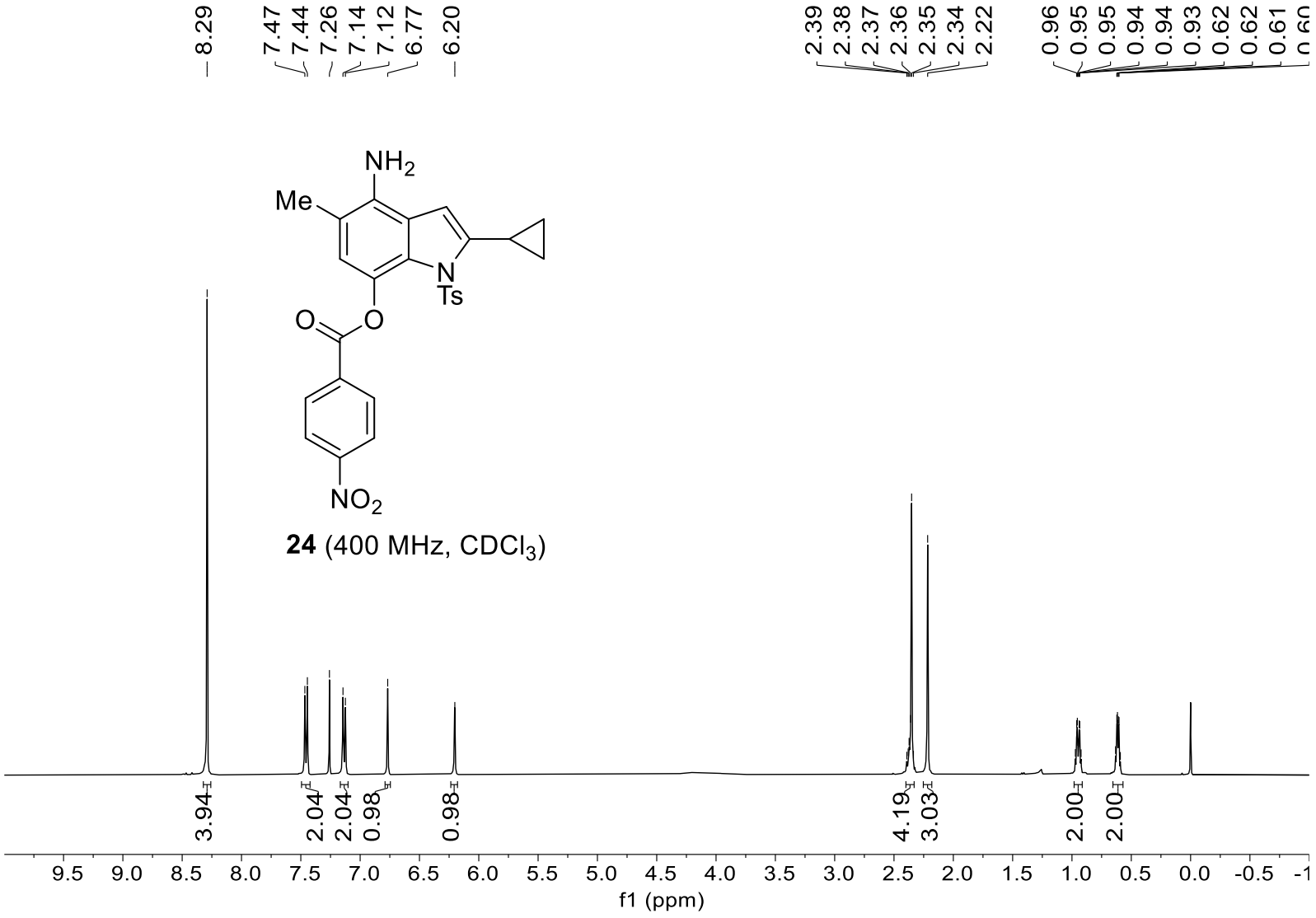


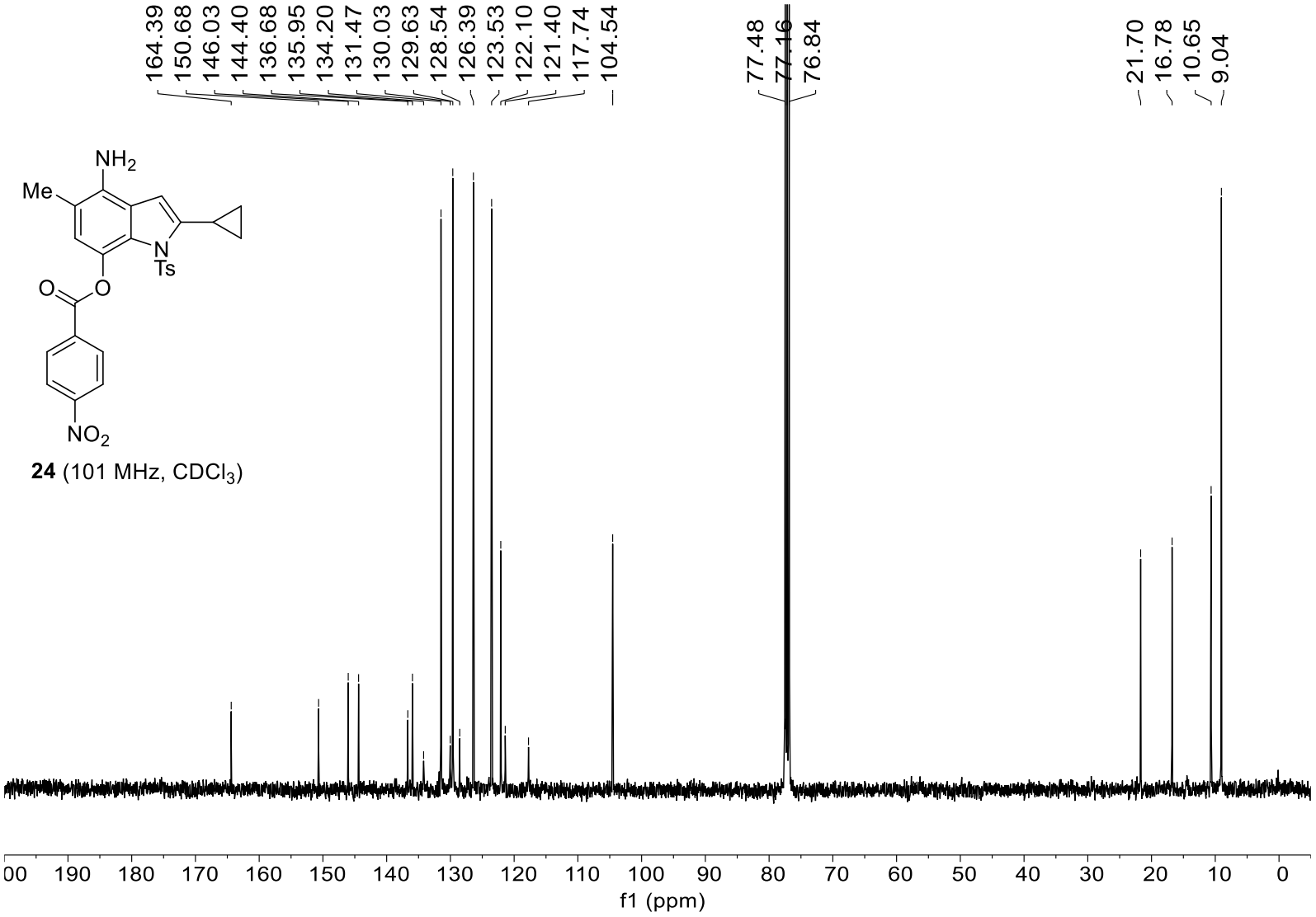
22 (101 MHz, $CDCl_3$)

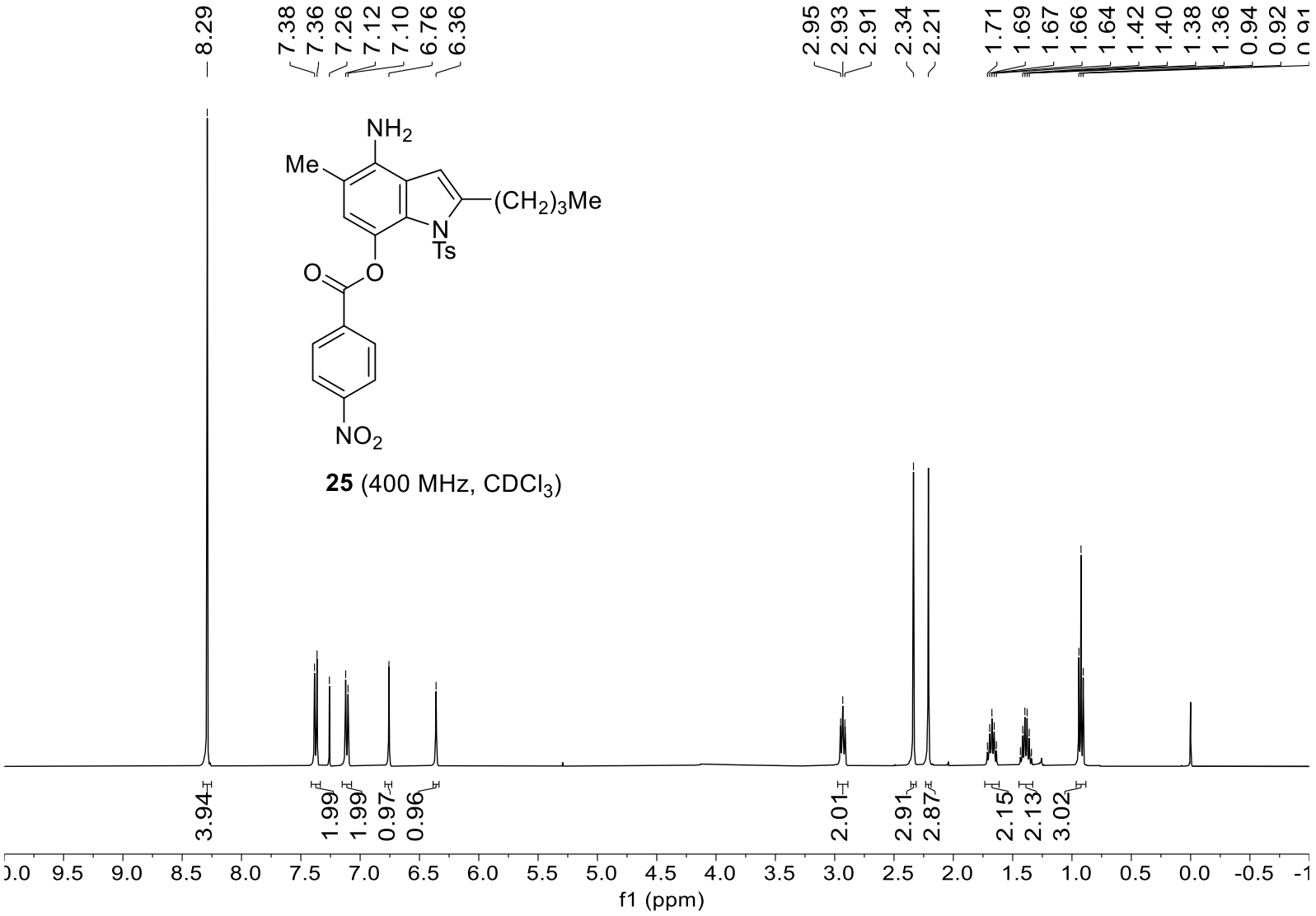


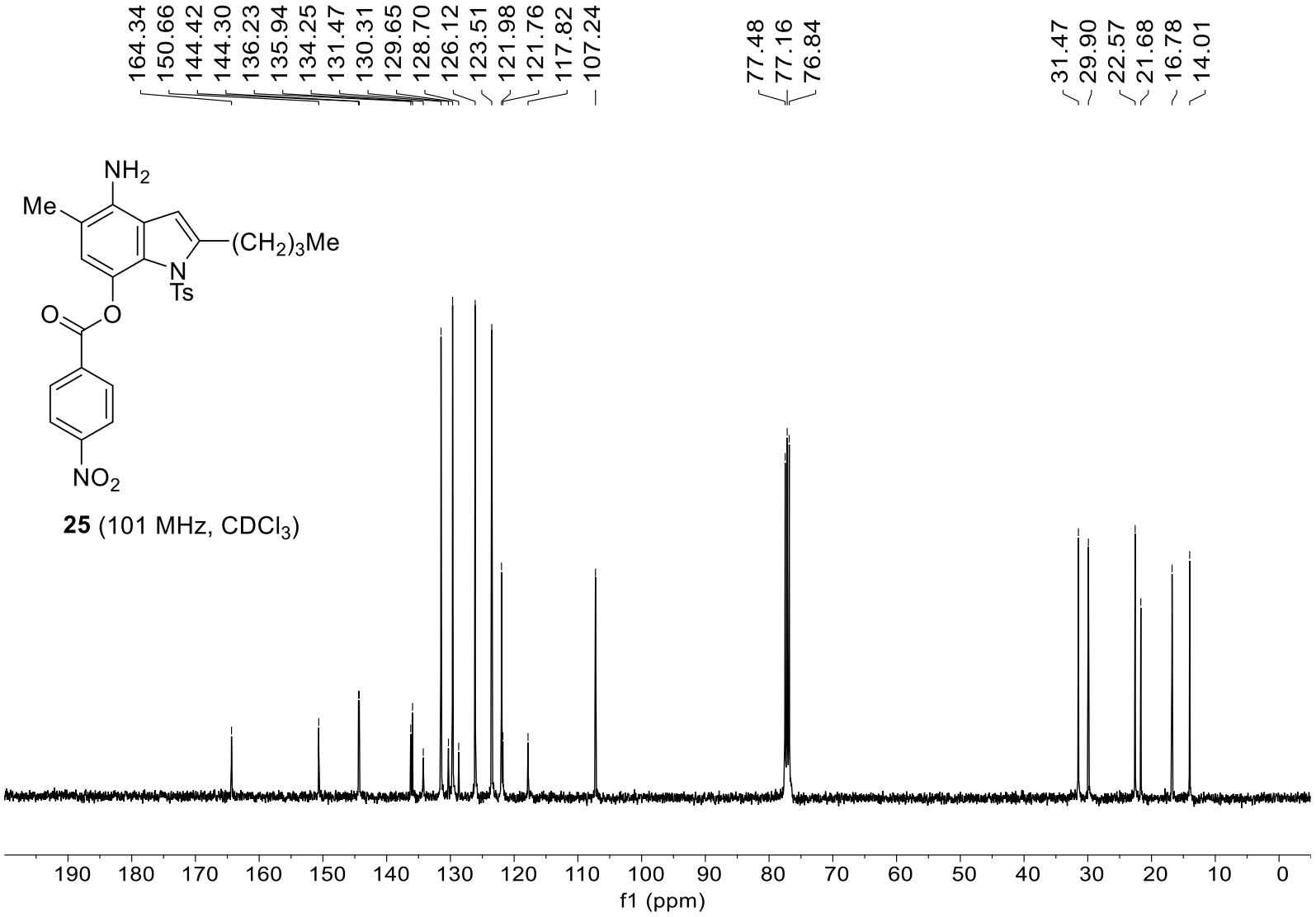
23 (400 MHz, $CDCl_3$)

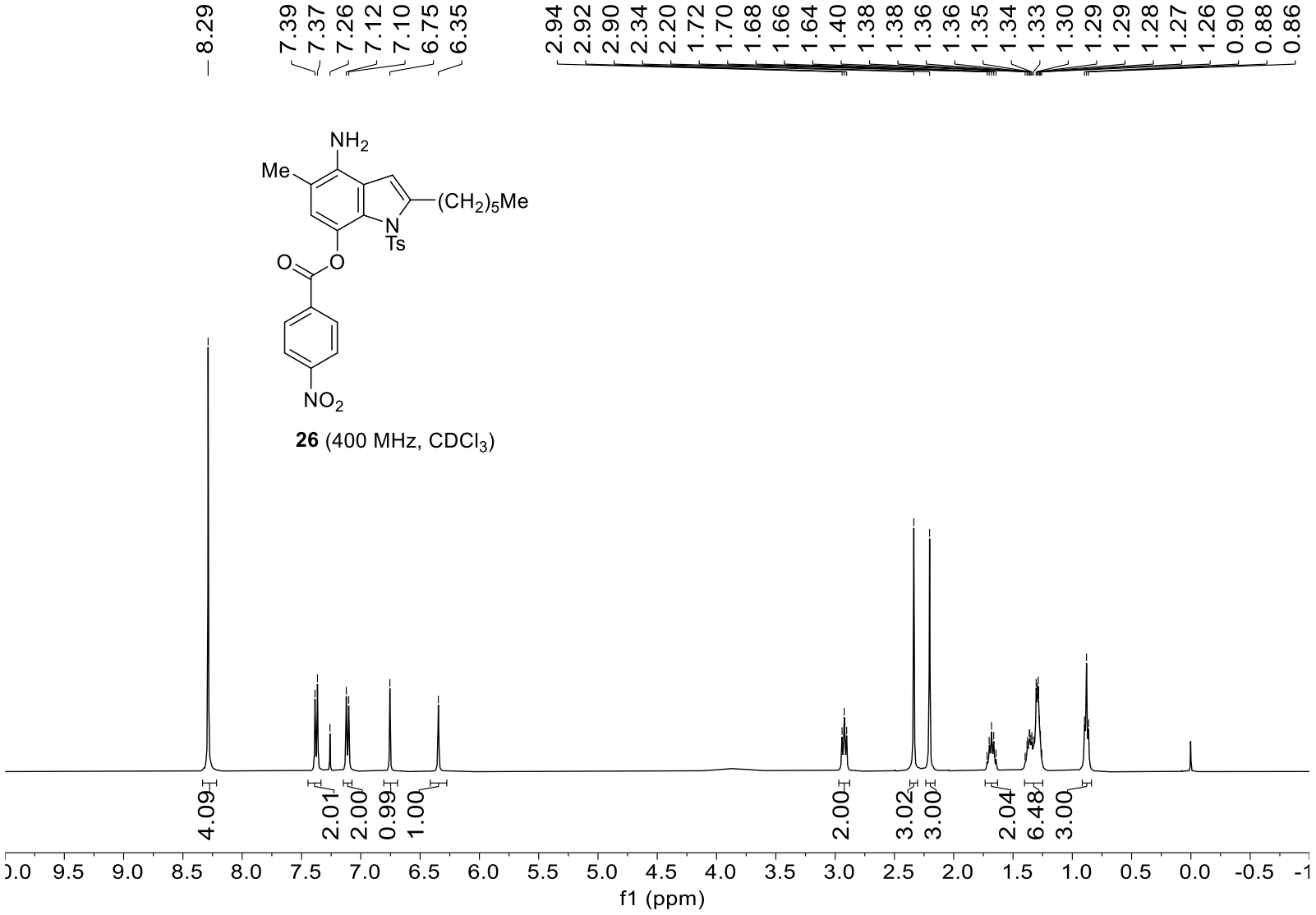

164.29
151.29
150.68
144.40
135.96
135.65
131.54
129.53
126.20
123.55
122.22
106.10
77.47
77.16
76.84
28.38
23.41
21.69
16.88
NH2
Me
i-Pr
N
Ts
O
O
NO2
23 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.29
7.47
7.44
7.26
7.14
7.12
6.77
6.20
2.39
2.38
2.37
2.36
2.35
2.34
2.22
0.96
0.95
0.95
0.94
0.94
0.93
0.62
0.62
0.61
NH2
Me
N
Ts
O
O
NO2
24 (400 MHz, CDCl3)
3.94
2.04
2.04
0.98
0.98
4.19
3.03
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

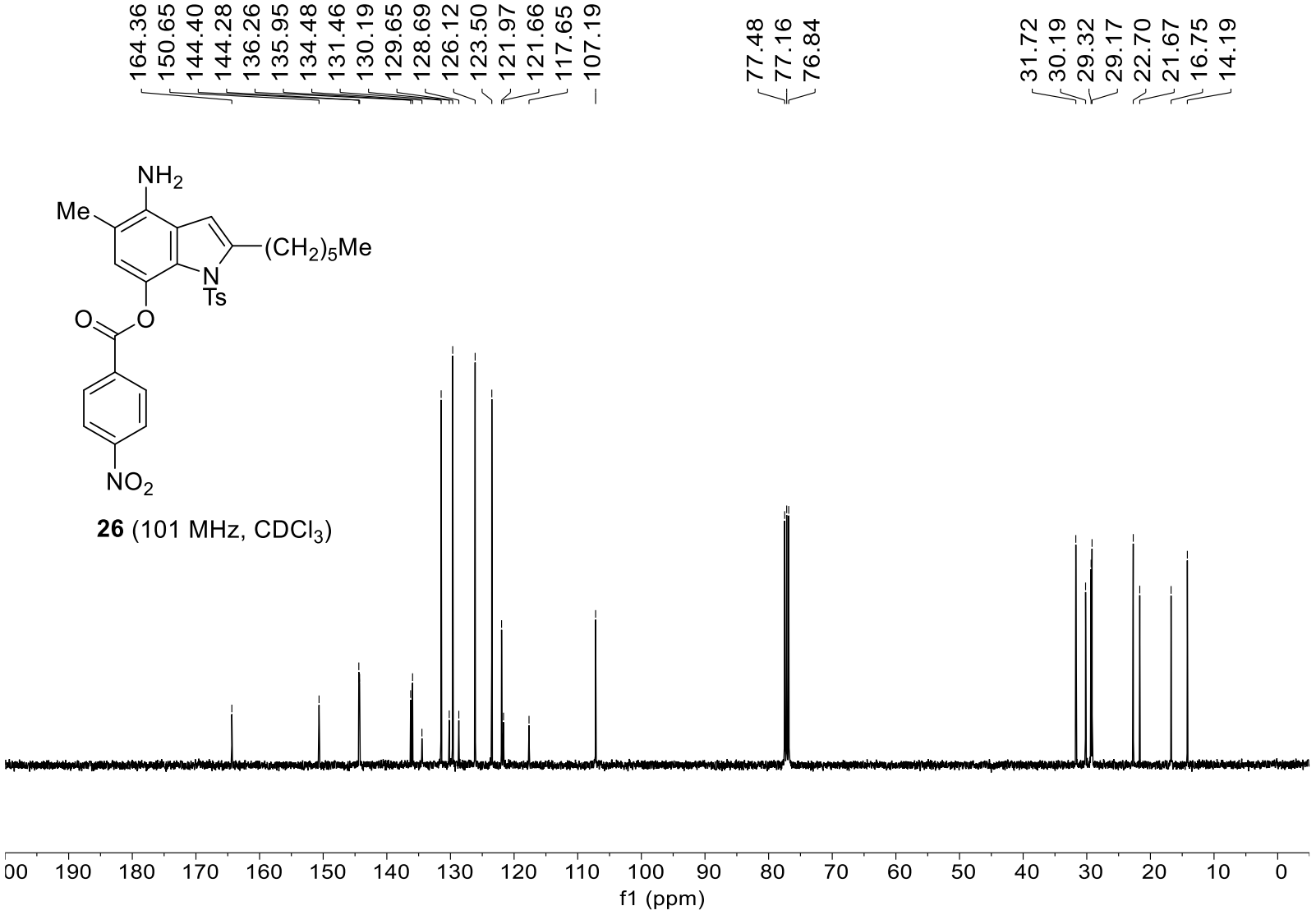

164.39
150.68
146.03
144.40
136.68
135.95
134.20
131.47
130.03
129.63
128.54
126.39
123.53
122.10
121.40
117.74
104.54
77.48
77.16
76.84
21.70
16.78
10.65
9.04
NH2
Me
N
Ts
O
O
NO2
24 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

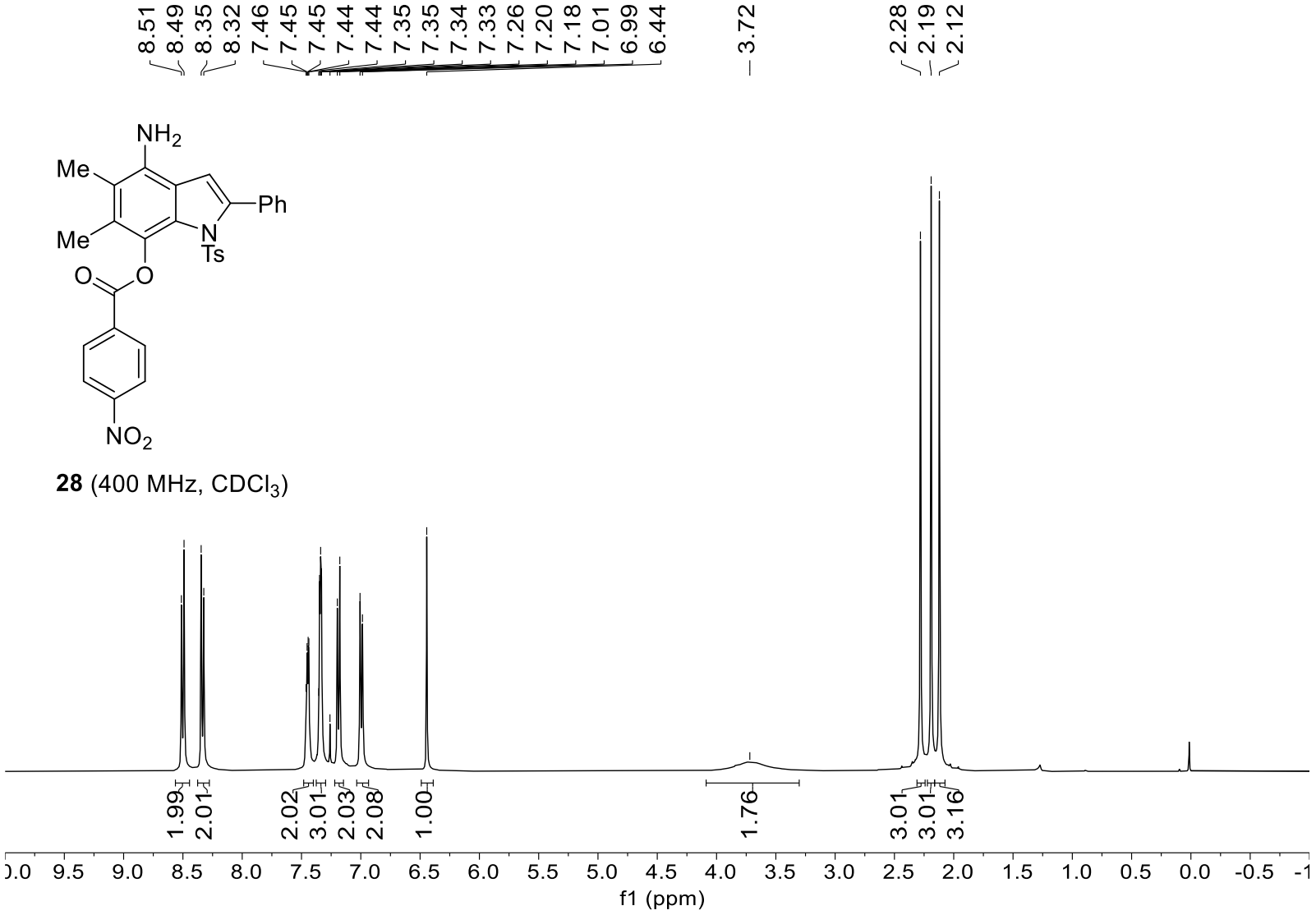

8.29
7.38
7.36
7.26
7.12
7.10
6.76
6.36
2.95
2.93
2.91
2.34
2.21
1.71
1.69
1.67
1.66
1.64
1.42
1.40
1.38
1.36
0.94
0.92
NH2
Me
(CH2)3Me
N
Ts
O
O
NO2
25 (400 MHz, CDCl3)
3.94
1.99
1.99
0.97
0.96
2.01
2.91
2.87
2.15
2.13
3.02
f1 (ppm)

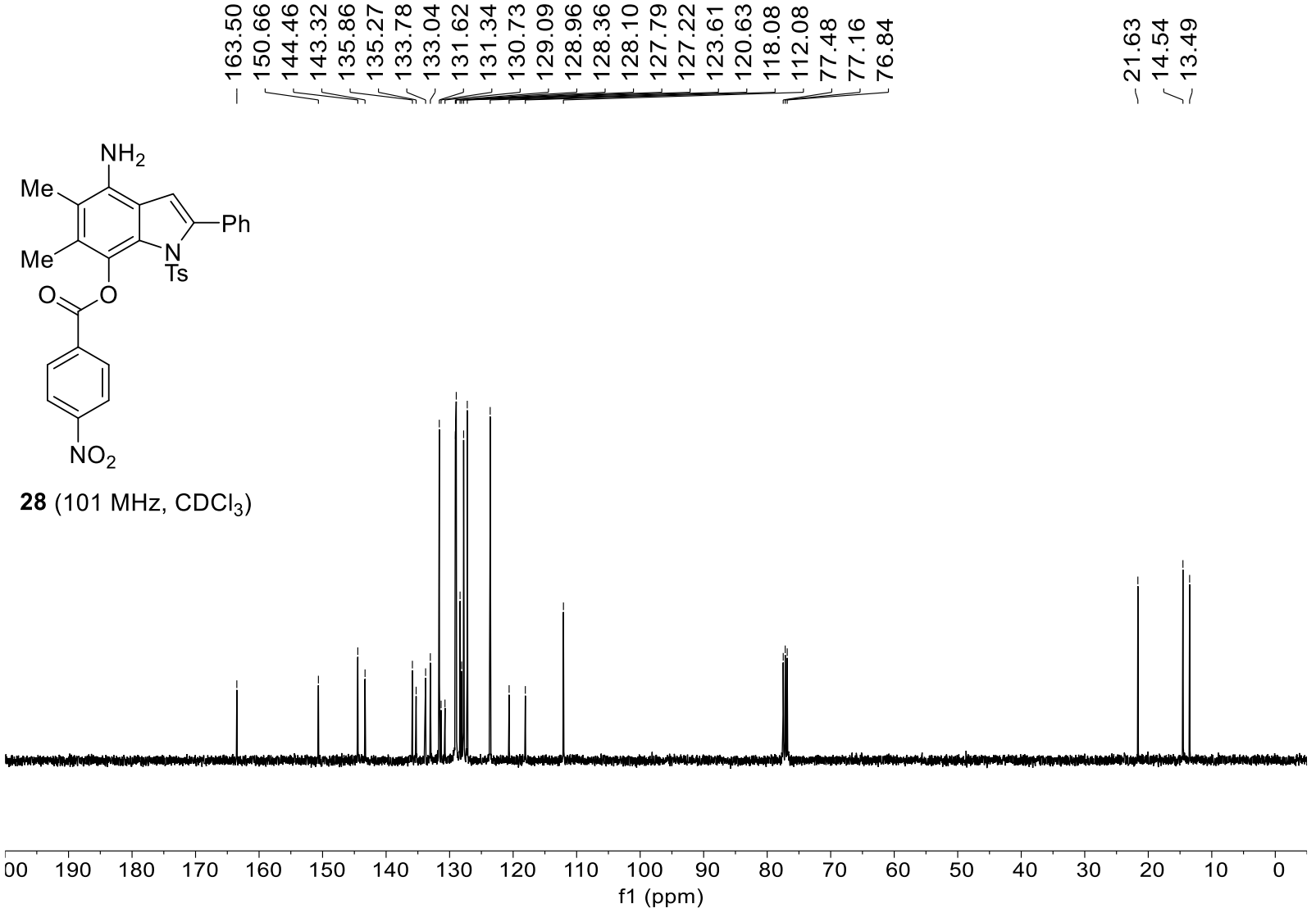

164.34
150.66
144.42
144.30
136.23
135.94
134.25
131.47
130.31
129.65
128.70
126.12
123.51
121.98
121.76
117.82
107.24
77.48
77.16
76.84
31.47
29.90
22.57
21.68
16.78
14.01
NH2
Me
(CH2)3Me
N
Ts
O
O
NO2
25 (101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



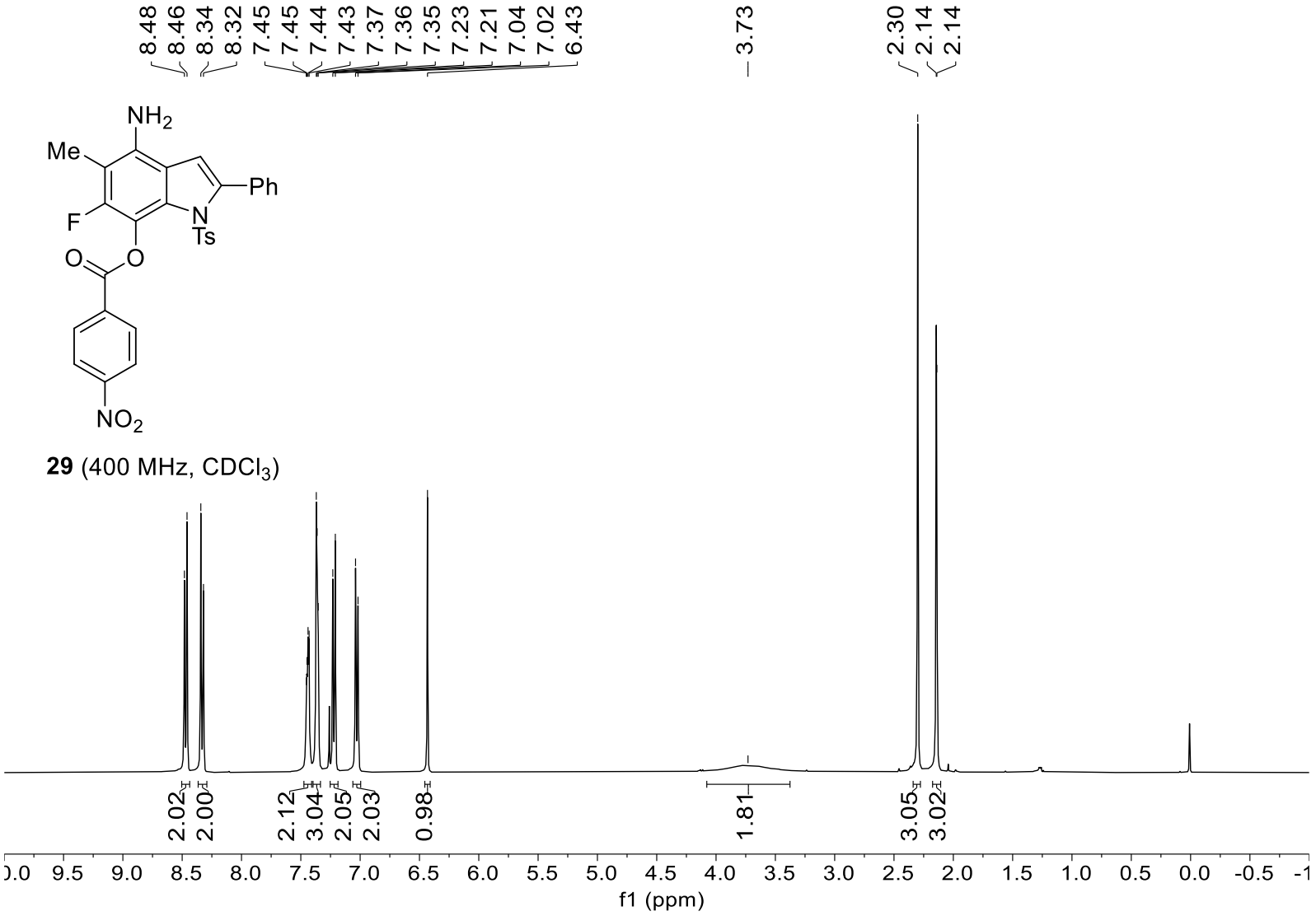
26 (400 MHz, $CDCl_3$)

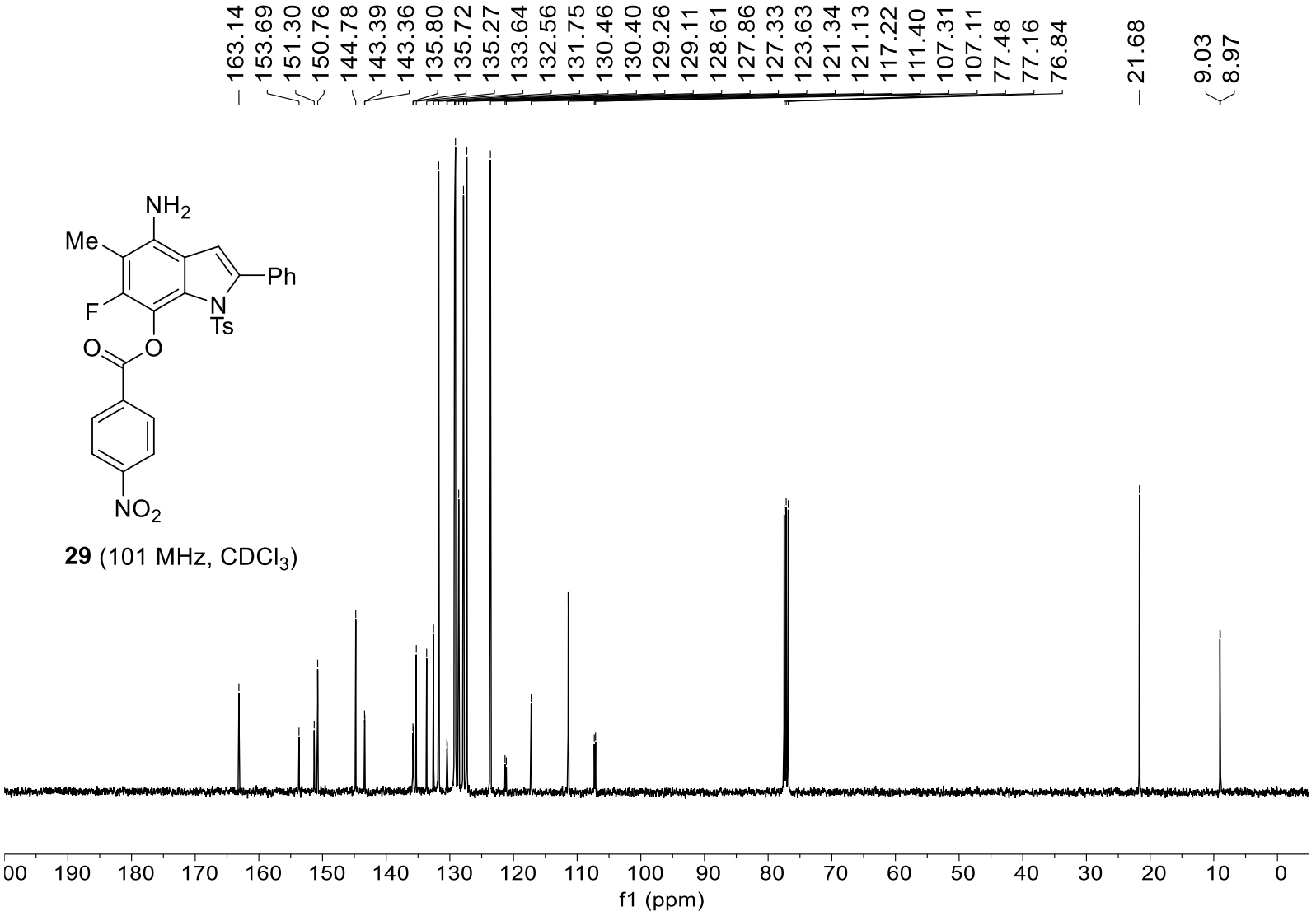

164.36
150.65
144.40
144.28
136.26
135.95
134.48
131.46
130.19
129.65
128.69
126.12
123.50
121.97
121.66
117.65
107.19
77.48
77.16
76.84
31.72
30.19
29.32
29.17
22.70
21.67
16.75
14.19
NH2
Me
(CH2)5Me
N
Ts
O
O
NO2
26 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

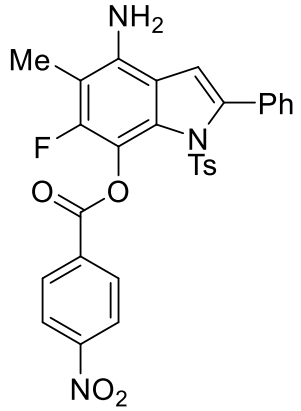

8.51
8.49
8.35
8.32
7.46
7.45
7.45
7.44
7.44
7.35
7.35
7.34
7.33
7.26
7.20
7.18
7.01
6.99
6.44
3.72
2.28
2.19
2.12
NH2
Me
Me
Ph
N
Ts
O
O
NO2
28 (400 MHz, CDCl3)
1.99
2.01
2.02
3.01
2.03
2.08
1.00
1.76
3.01
3.01
3.16
f1 (ppm)



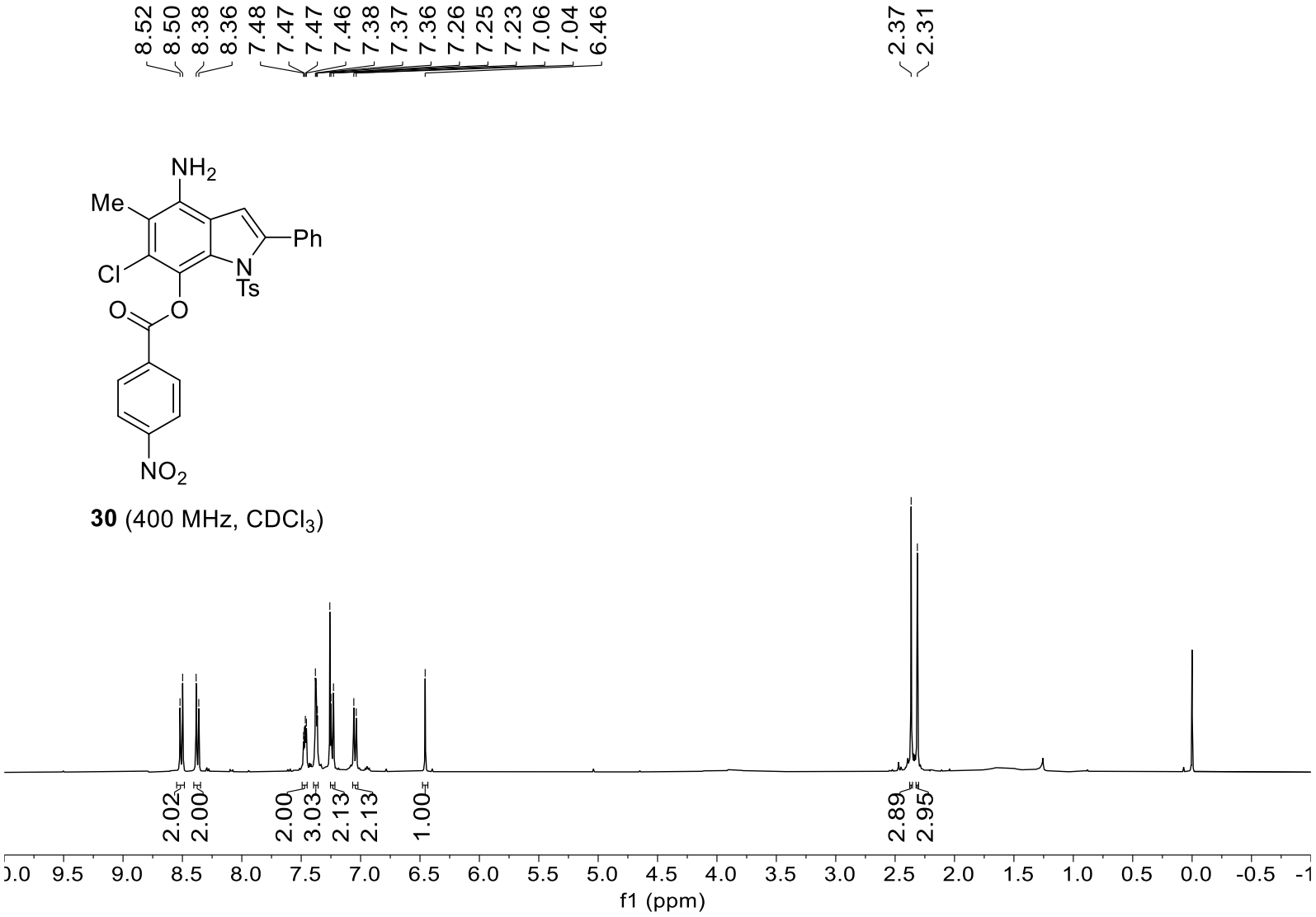
28 (101 MHz, $CDCl_3$)

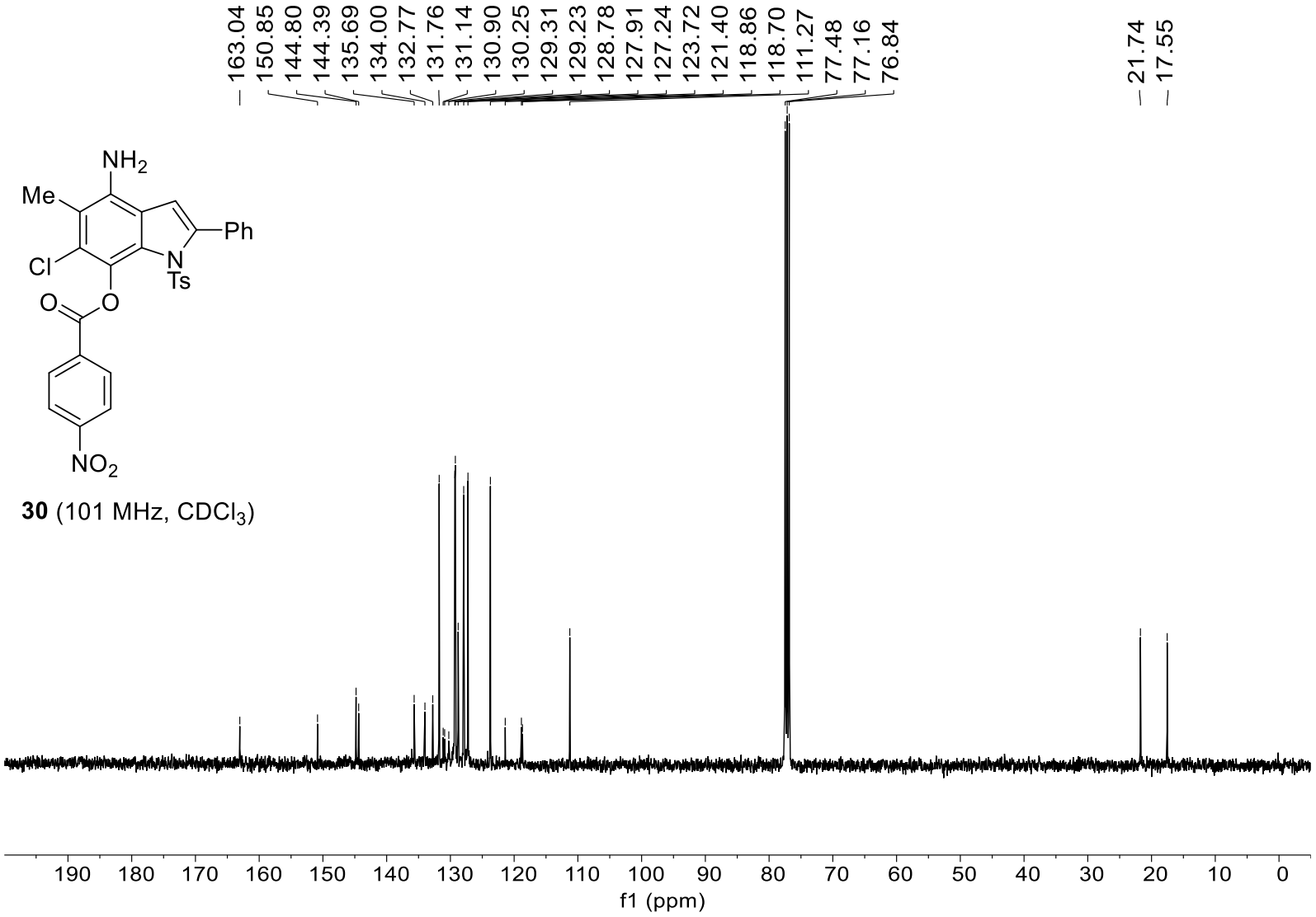

8.48
8.46
8.34
8.32
7.45
7.45
7.44
7.43
7.37
7.36
7.35
7.23
7.21
7.04
7.02
6.43
3.73
2.30
2.14
2.14
NH2
Me
Ph
F
N
Ts
O
O
O
NO2
29 (400 MHz, CDCl3)
2.02
2.00
2.12
3.04
2.05
2.03
0.98
1.81
3.05
3.02
f1 (ppm)

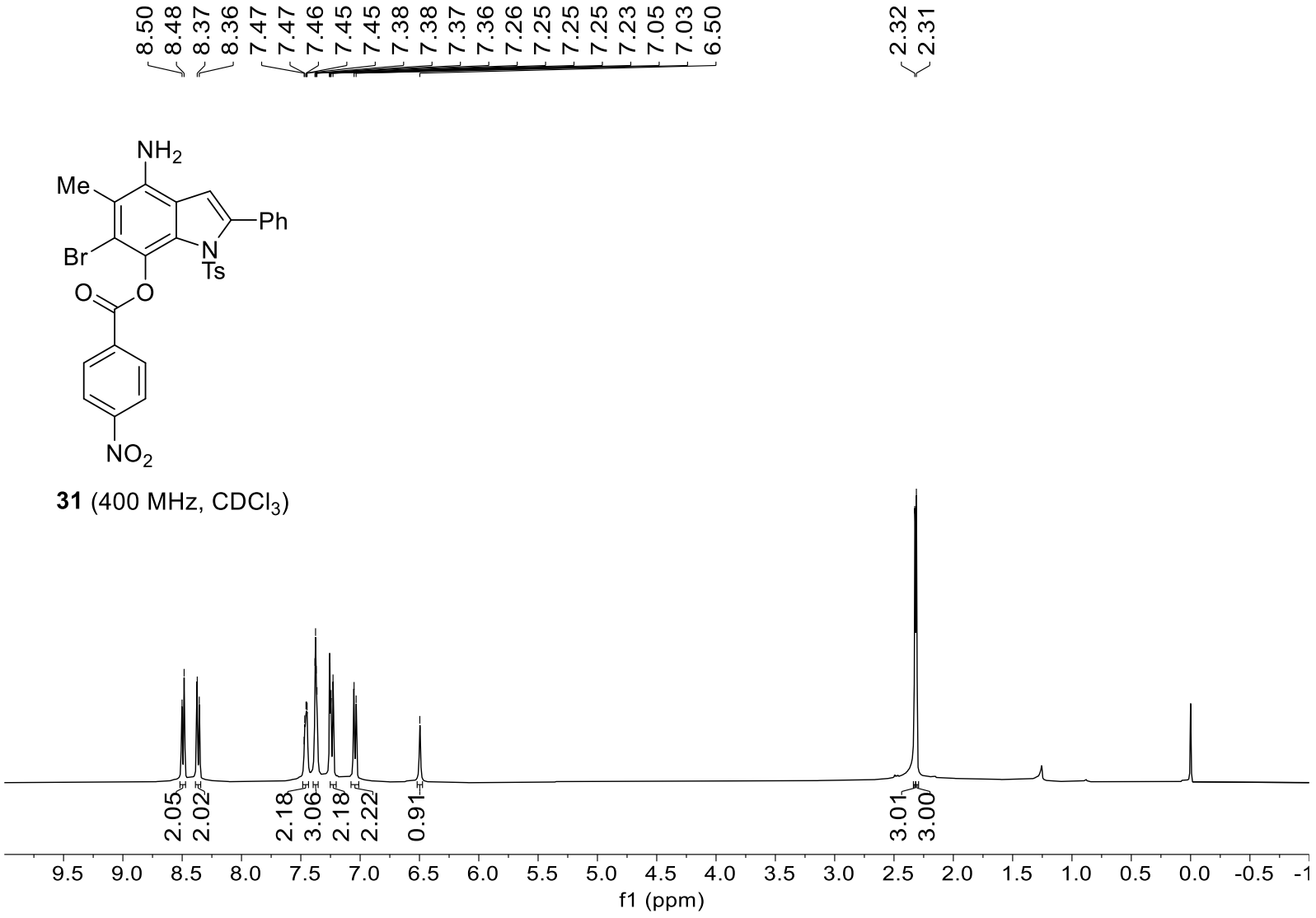

163.14
153.69
151.30
150.76
144.78
143.39
143.36
135.80
135.72
135.27
133.64
132.56
131.75
130.46
130.40
129.26
129.11
128.61
127.86
127.33
123.63
121.34
121.13
117.22
111.40
107.31
107.11
77.48
77.16
76.84
21.68
9.03
8.97
NH2
Me
Ph
F
N
Ts
O
O
NO2
29 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

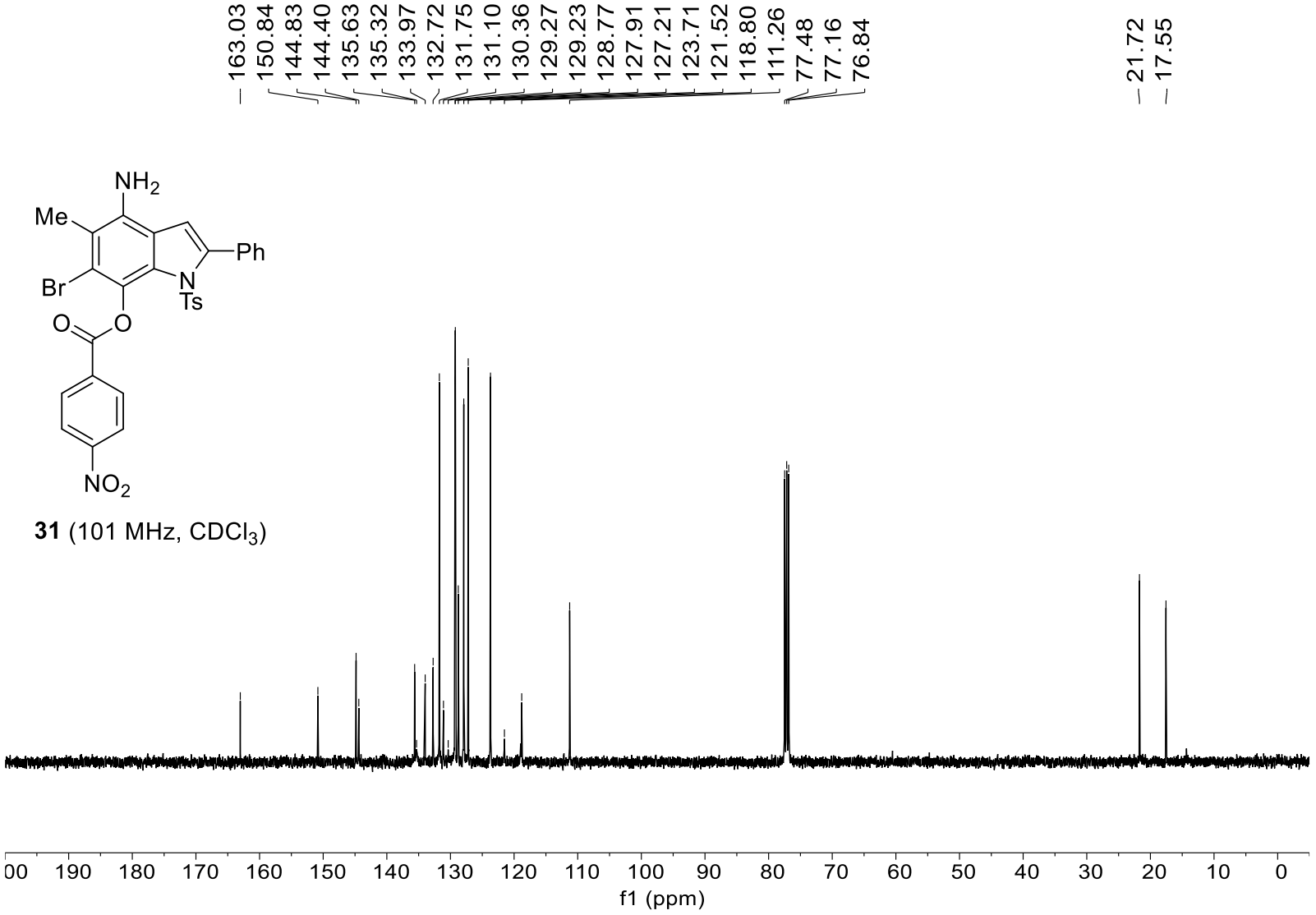


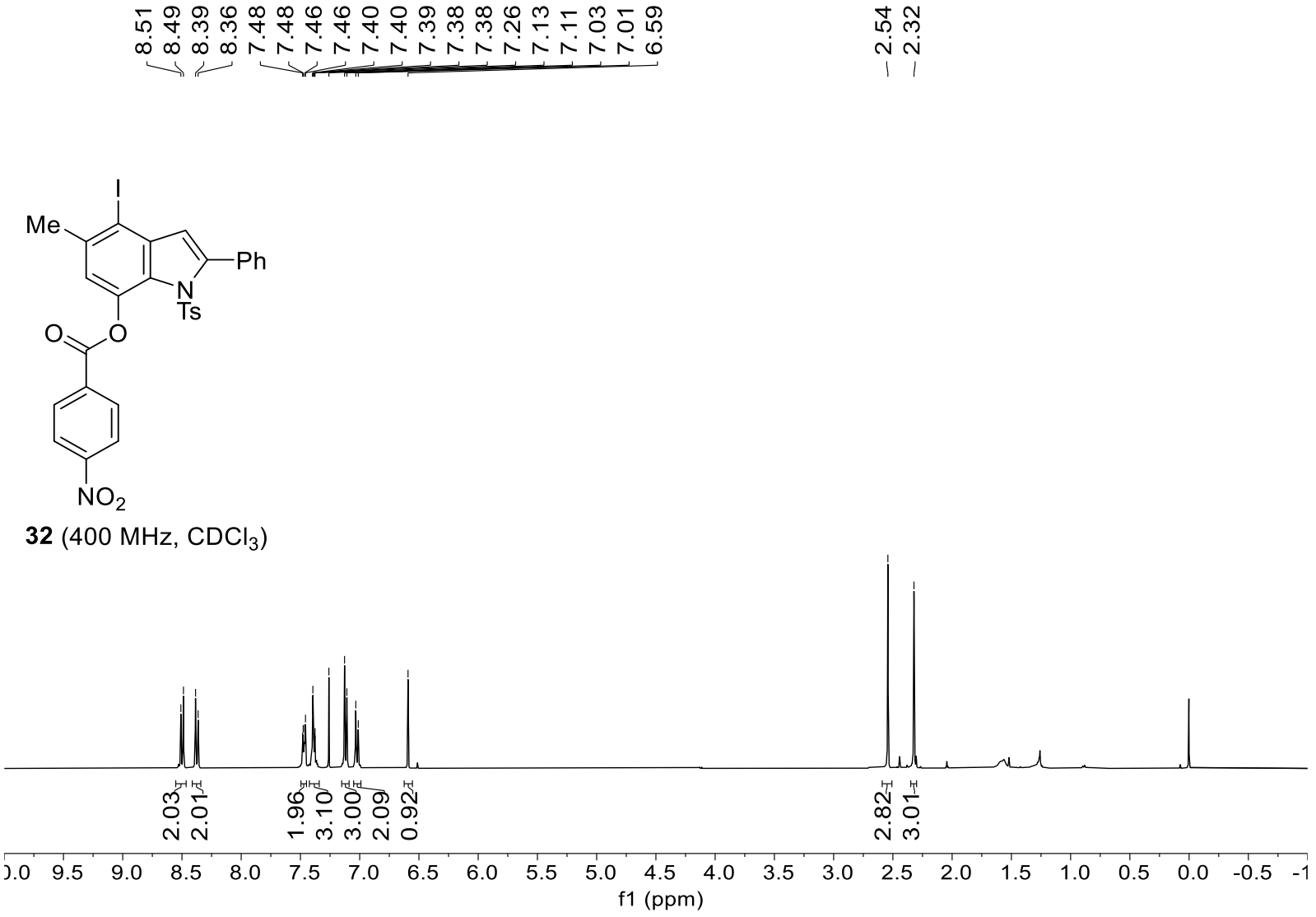
29 (376 MHz, $CDCl_3$)


8.52
8.50
8.38
8.36
7.48
7.47
7.47
7.46
7.38
7.37
7.36
7.26
7.25
7.23
7.06
7.04
6.46
2.37
2.31
NH2
Me
Ph
Cl
N
Ts
O
O
NO2
30 (400 MHz, CDCl3)
2.02
2.00
2.00
3.03
2.13
2.13
1.00
2.89
2.95
f1 (ppm)

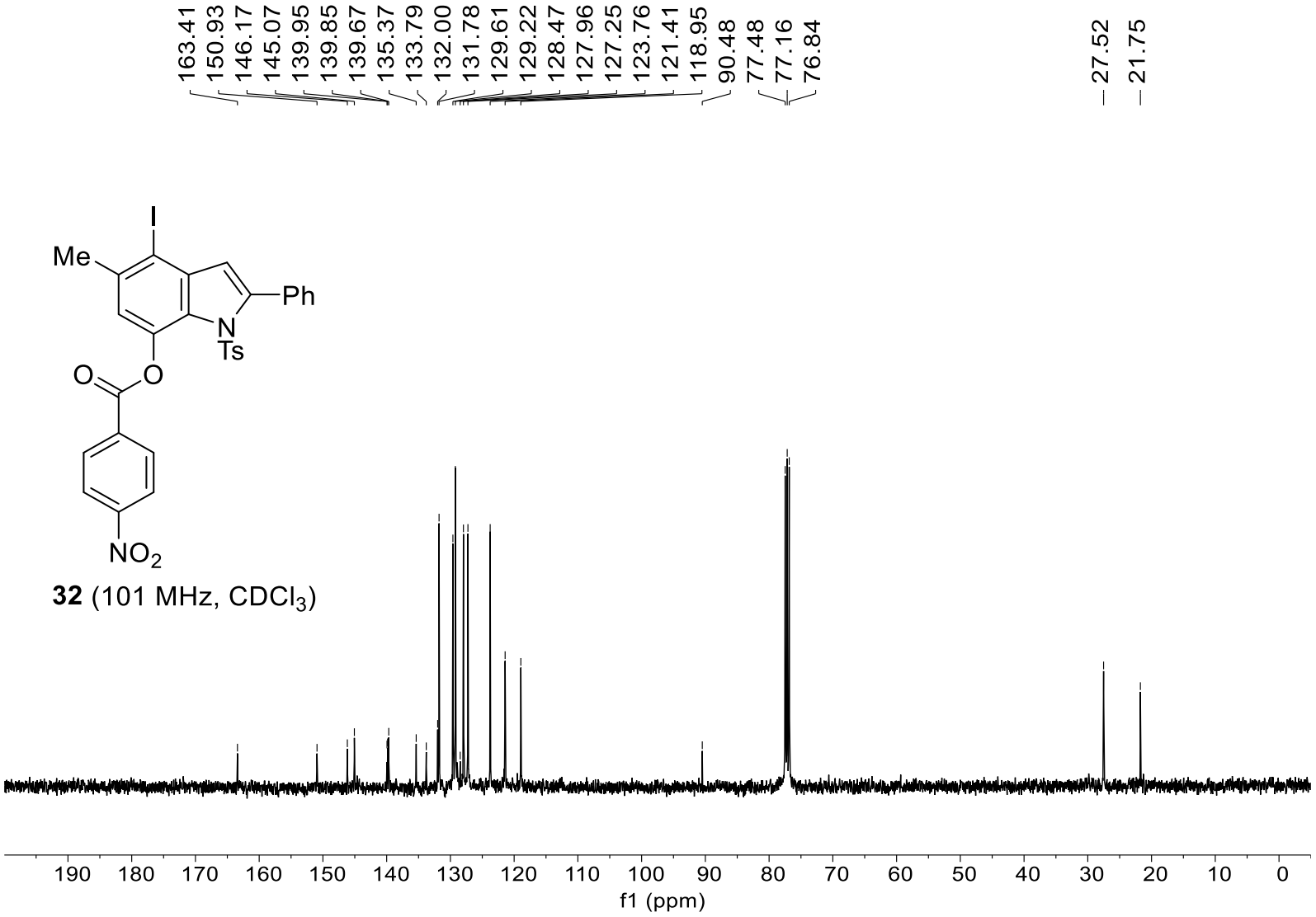

163.04
150.85
144.80
144.39
135.69
134.00
132.77
131.76
131.14
130.90
130.25
129.31
129.23
128.78
127.91
127.24
123.72
121.40
118.86
118.70
111.27
77.48
77.16
76.84
21.74
17.55
NH2
Me
Ph
Cl
N
Ts
O
O
NO2
30 (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

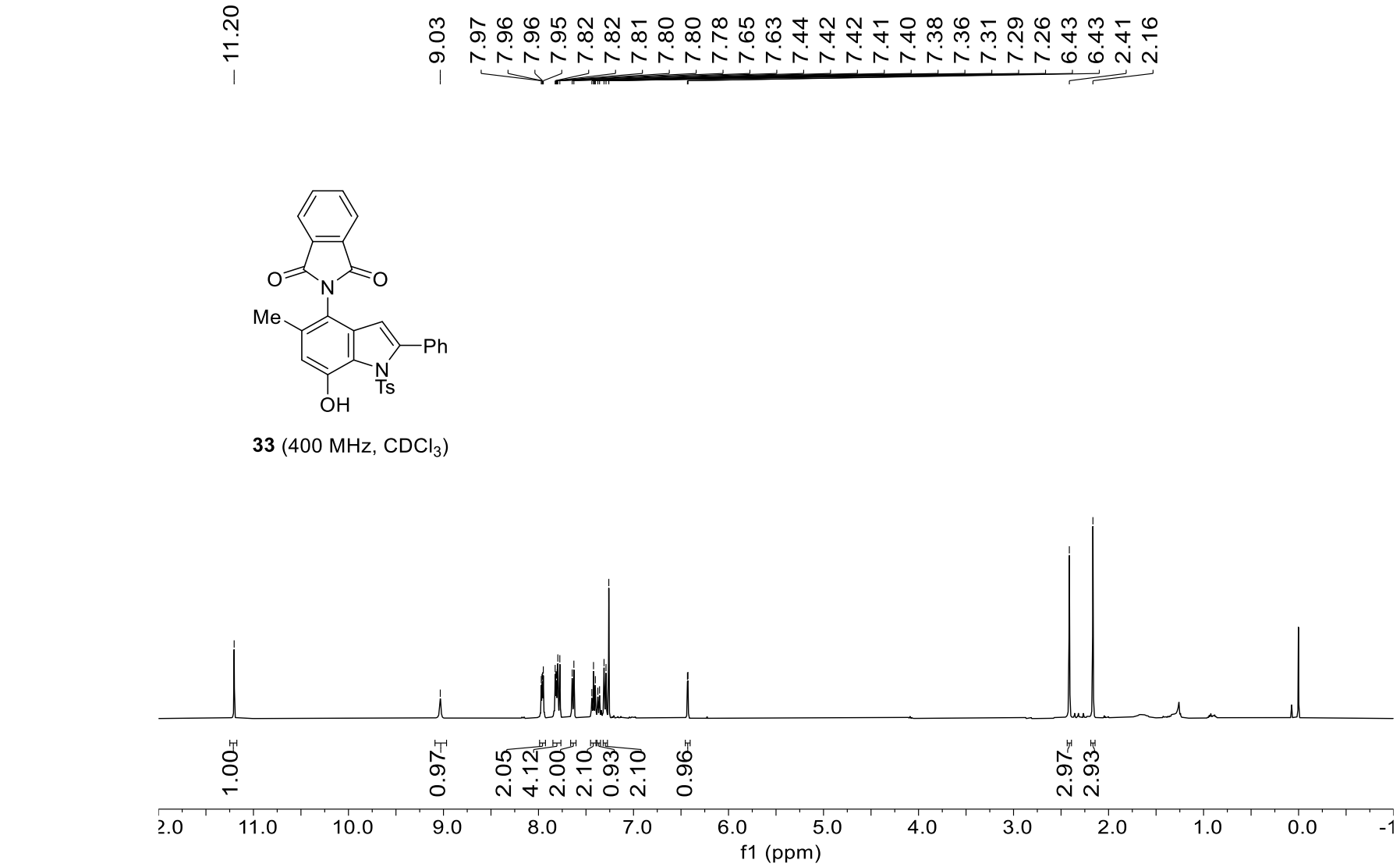

8.50
8.48
8.37
8.36
7.47
7.47
7.46
7.45
7.45
7.38
7.38
7.37
7.36
7.26
7.25
7.25
7.25
7.23
7.05
7.03
6.50
2.32
2.31
NH2
Me
Ph
Br
N
Ts
O
O
O
NO2
31 (400 MHz, CDCl3)
2.05
2.02
2.18
3.06
2.18
2.22
0.91
3.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


163.03
150.84
144.83
144.40
135.63
135.32
133.97
132.72
131.75
131.10
130.36
129.27
129.23
128.77
127.91
127.21
123.71
121.52
118.80
111.26
77.48
77.16
76.84
21.72
17.55
NH2
Me
Ph
Br
N
Ts
O
O
NO2
31 (101 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

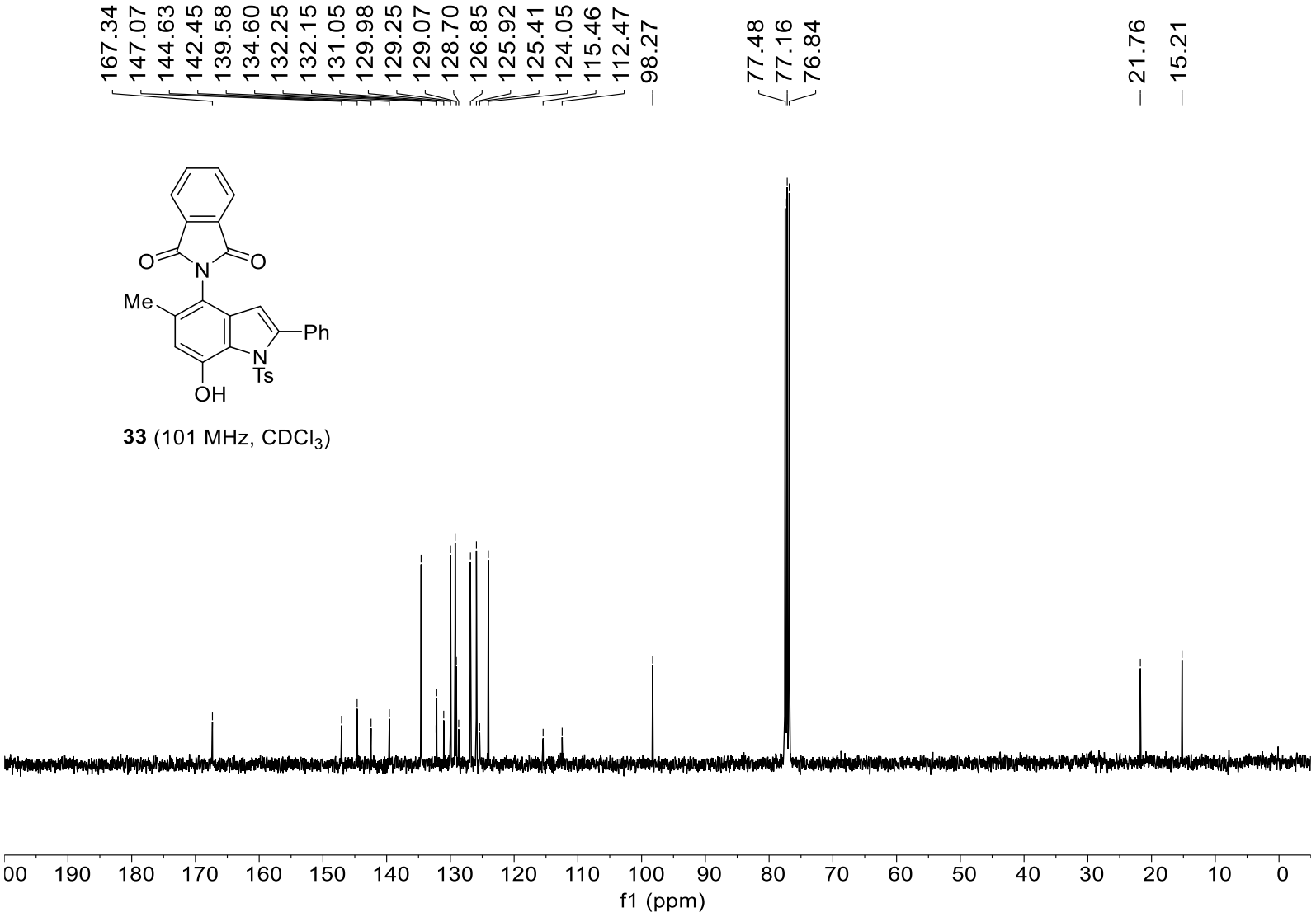


32 (400 MHz, $CDCl_3$)

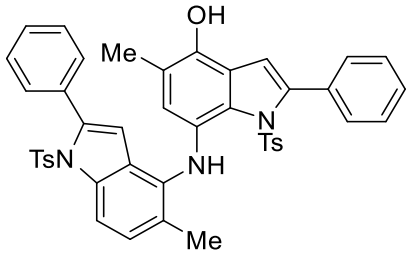

163.41
150.93
146.17
145.07
139.95
139.85
139.67
135.37
133.79
132.00
131.78
129.61
129.22
128.47
127.96
127.25
123.76
121.41
118.95
90.48
77.48
77.16
76.84
27.52
21.75
I
Me
Ph
N
Ts
O
O
NO2
32 (101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



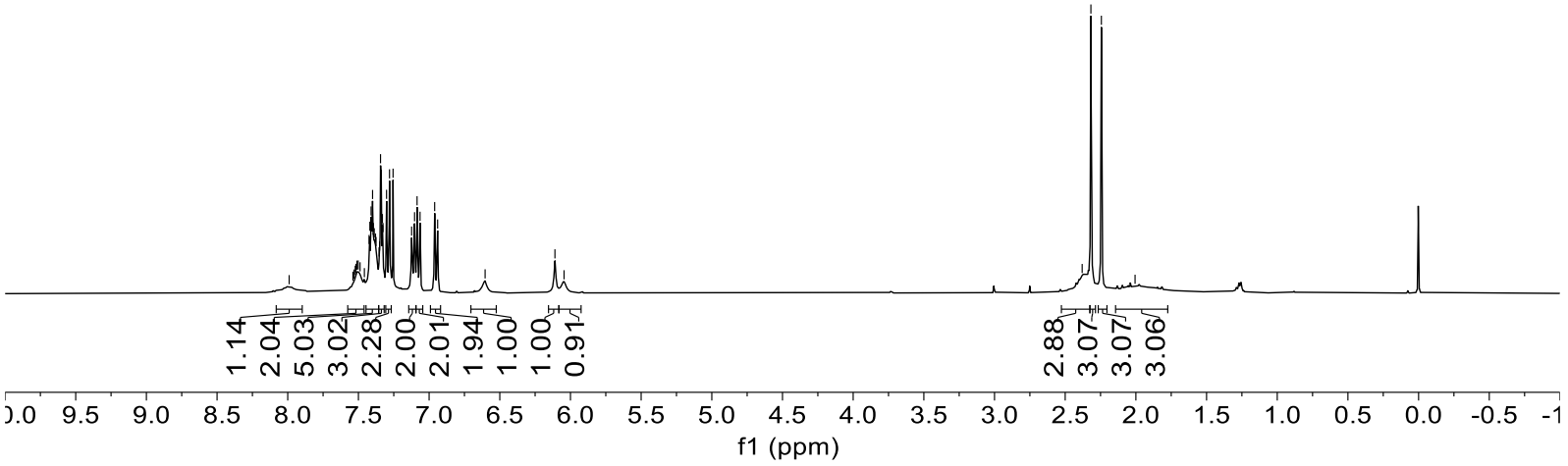
33 (400 MHz, $CDCl_3$)

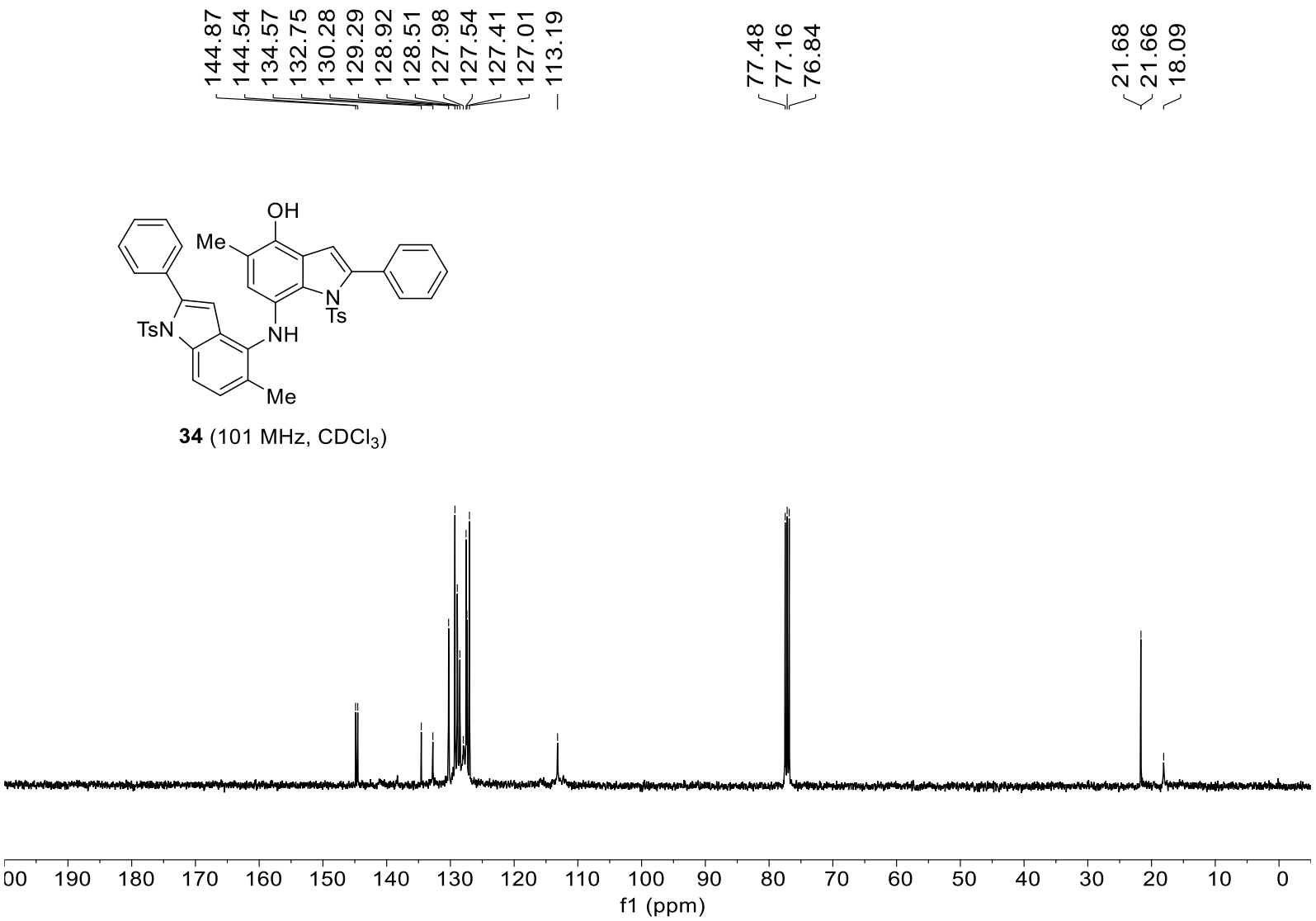


33 (101 MHz, $CDCl_3$)



34 (400 MHz, $CDCl_3$)





34 (101 MHz, $CDCl_3$)