Supporting Information

PPh_3-Catalyzed [2+2+2] and [4+2] Annulations: Synthesis of Highly Substituted 1,2-Dihydropyridines (DHPs)

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Table of Contents

I. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

Nuclear magnetic resonance spectra. ^{1}H and ^{13}C spectra were recorded on a Bruker AVANCE 400 spectrometer, operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C, 161 MHz for ^{31}P. NMR were reported downfield from $CDCl_3$ (δ: 7.27 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) used as an internal reference.

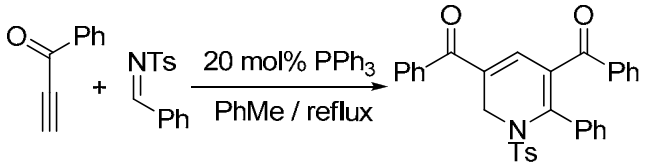
Mass spectroscopy. Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

Chromatography. Column chromatography was performed with silica gel (200-300 mesh ASTM).

II. Optimized Conditions for the [2+2+2] annulations

A number of different factors were considered in order to optimize the PPh_3-catalyzed [2+2+2] annulations of aryl *N*-tosylimines **2a** with 1-arylpropynone **1b**. The results were presented in Table S1.

Table S1: Optimized Conditions for Reaction of **1b** and **2a** in the presence of PPh_3.[a]

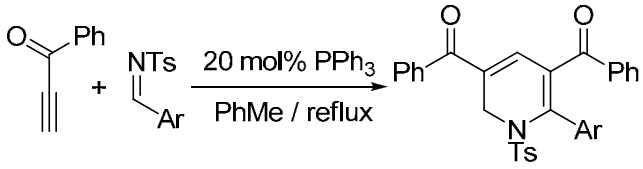


1b **2a** **4ba**

Entry	PPh_3 (%)	T (^oC)	Solvent	4ba Yield[b](%)
1	20	r. t.	toluene	trace
2	20	r. t.	acetonitrile	20
3	20	80	p-xylene	NR
4	20	r. t. to 80	toluene	42
5	20	80	toluene	53
6	20	80 to reflux	toluene	56
7	**20**	**reflux**	**toluene**	**75**
8	10	reflux	toluene	ND[c]
9	50	reflux	toluene	16

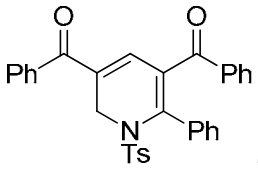
[a] Reaction Conditions: the solution of **1b** (1.5 mmol) in toluene (10 mL) was slowly added to a mixture of **2a** (0.5 mmol) and PPh_3 (0.1 mmol) in toluene (10 mL) under 120 ^{0}C within 1.5 hours. [b] Isolated yield. [c] ND = no detected product.

III. General procedure for [2+2+2] annulations between 1b and 2



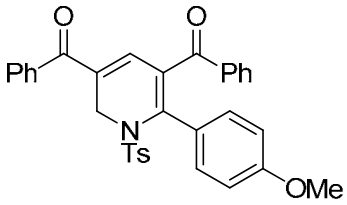
1b **2** **4**

General Procedure A: The PPh_3-Catalyzed Reactions of 1-Arylpropynone 1b and *N*-Tosylimine 2: N-tosylimine **2** (0.5 mmol), PPh_3 (26.2 mg, 20 mmol%) were added to toluene (10 mL) in a there-neck bottle. The mixture was stirred at 120 °C under nitrogen atmosphere. To this reaction mixture the solution of arylpropynone **1b** (1.5 mmol) in toluene (10 mL) was slowly added within 1.5 hours. The reaction mixture was monitored by TLC. Once the reaction was finished, the reaction mixture was cooled down to room temperature. The contents were transferred to a round-bottom flask, and volatiles were removed in vacuo. Then the mixture was directly subjected to silica gel column chromatography (petroleum ether : EtOAc 15:1 to 5:1 gradient) to give the product **4**.



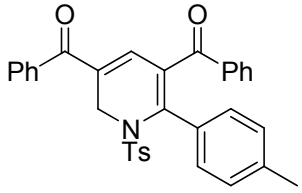
4ba (218 mg, 75%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.4 Hz, 2H), 7.53-7.49 (m, 3H), 7.40-7.36 (m, 4H), 7.28-7.23 (m, 5H), 7.20-7.13 (m, 5H), 6.85 (s, 1H), 5.01 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 106.8, 106.2, 95.0, 94.1, 92.3, 92.2, 92.0, 91.9, 91.8, 91.2, 91.0, 90.7, 90.4, 90.2, 90.1, 90.1, 90.0, 90.0, 89.7, 89.7, 89.5, 69.3, 63.2; MS (EI-m/z): 519 (M^+); HRMS Calcd for $C_{32}H_{25}NO_4S$ 519.6102, Found 519.6098.



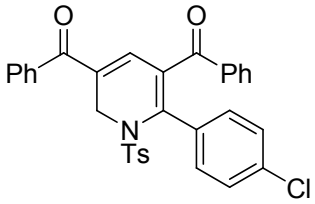
4bb (247 mg, 90%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.48 (m, 5H), 7.38-7.14 (m, 11H), 6.86 (s, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.05 (s, 2H), 3.71 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 192.6, 161.8, 148.1, 144.6, 137.4, 137.1, 136.4, 132.7, 132.6, 131.8, 129.7, 129.0, 128.7, 128.2, 128.1, 127.7, 127.1, 126.5, 113.6, 55,2, 45.8, 21.6; MS (EI-m/z): 549 (M^+); HRMS Calcd for $C_{33}H_{27}NO_5S$ 549.6362, Found 549.6361.



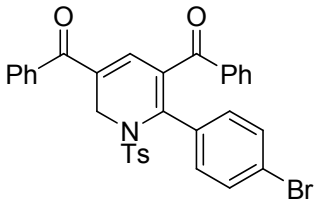
4bc (156 mg, 59%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.47 (m, 5H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31-7.22 (m, 7H), 7.15 (t, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 5.06 (s, 2H), 2.38 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 192.7, 148.2, 144.6, 141.3, 137.3, 137.1, 136.3, 136.1, 132.7, 132.5, 131.9, 130.8, 129.8, 129.1, 128.8, 128.7, 128.3, 128.1, 127.9, 127.0, 126.7, 45.7, 21.6, 21.4; MS (EI-m/z): 533 (M^+); HRMS Calcd for $C_{33}H_{27}NO_4S$ 533.6368, Found 533.6365.



4bd (185 mg, 67%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.48 (m, 5H), 7.38-7.31 (m, 5H), 7.27-7.17 (m, 6H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.80 (s, 1H), 5.05 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 192.6, 146.3, 144.8, 137.1, 136.9, 136.9, 136.1, 135.5, 133.8, 133.2, 132.0, 131.8, 129.8, 129.1, 128.8, 128.7, 128.4, 128.3, 127.4, 127.0, 45.7, 21.6; MS (EI-m/z): 553 (M^+); HRMS Calcd for $C_{32}H_{24}ClNO_4S$ 554.0553, Found 554.0556.

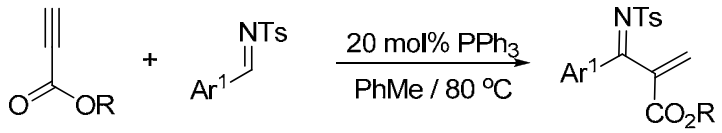


4be (255 mg, 85%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.49 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 3H), 7.30-7.18 (m, 10H), 6.80 (s, 1H), 5.05 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 192.6, 146.3, 144.9, 137.1, 136.8, 136.0, 135.5, 134.3, 133.2, 132.1, 132.0, 131.3, 129.9, 129.1, 128.8, 128.7, 128.3, 127.4, 127.0, 125.4, 45.7, 21.6; MS (EI-m/z): 597 (M^+); HRMS Calcd for $C_{32}H_{24}BrNO_4S$ 598,5063, Found 598,5061.

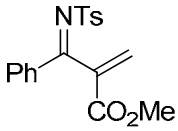
IV. General Procedure for [4+2] Annulations between 1b-d and 3

1. Synthesis of 3

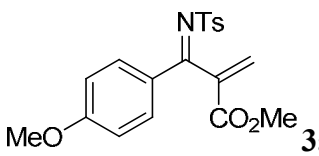


1 **2** **3**

General Procedure B: *N*-tosylimine **2** (1.0 mmol), PPh_3 (52.4 mg, 20 mmol%) were added to toluene (20 mL) in one-neck bottle. The mixture was stirred at 80 °C under nitrogen atmosphere. To this reaction mixture the solution of alkyl propiolate **1** (1.2 mmol) in toluene (20 mL) was slowly added within 3 hours. Once the addition was finished, the reaction mixture was cooled down to room temperature. Then the mixture was directly subjected to silica gel column chromatography to give the product **3**.

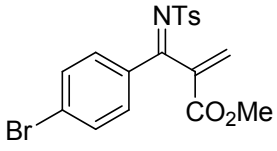


3aa Prepared according to General Procedure B (Note: the solvent toluene was 10ml + 10ml); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8. 4Hz, 2H), 6.85 (s, 1H), 5.94 (s, 1H), 3.80 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 163.3, 144.0, 137.5, 137.0, 135.5, 134.0, 130.5, 129.7, 129.5, 128.7, 127.4, 52.4, 21.4; MS (EI-m/z): 343 (M^+); HRMS Calcd for $C_{18}H_{17}NO_4S$ 343.3969, Found 343.3971.

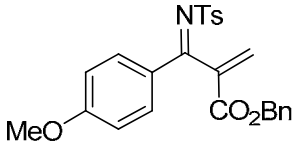


3ab Prepared according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* =

8.0 Hz, 2H), 6.90 (d, *J* = 9.2 Hz, 2H), 6.82 (s, 1H), 5.89 (s, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 164.6, 163.7, 143.7, 137.9, 137.3, 132.3, 130.2, 129.5, 128.1, 127.4, 114.1, 55.6, 52.6, 21.6; MS (EI-m/z): 373 (M^+); HRMS Calcd for $C_{19}H_{19}NO_5S$ 373.4229, Found 373.4228.

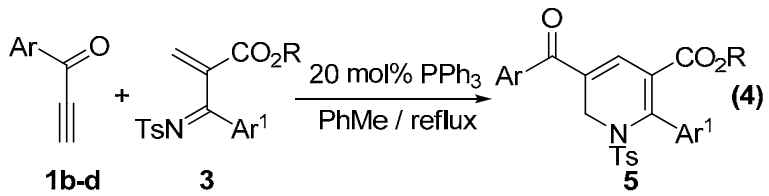


3ae Prepared according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 5.94 (s, 1H), 3.78 (s, 3H), 2.43(d, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 163.3, 144.2, 143.7, 137.2, 136.7, 134.5, 132.0, 131.1, 129.6, 128.3, 127.6, 52.7, 21.6; MS (EI-m/z): 421 (M^+, Br^{79}); HRMS Calcd for $C_{18}H_{16}BrNO_4S$ 420.9983, Found 420.9980.



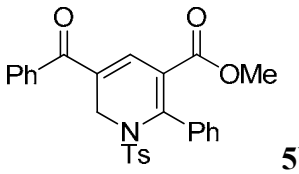
3ed Prepared according to General Procedure B; ^{1}H NMR (400 MHz, CDCl3): δ 7.85-7.82 (m, 4H), 7.29-7.25 (m, 7H), 6.87 (d, J = 8.4 Hz, 2H), 6.84 (s, 1H), 5.94 (s, 1H), 5.25 (s, 2H), 3.83 (s, 3H), 2.42 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 172.8, 164.6, 163.0, 143.7, 137.9, 137.5, 135.4, 132.2, 130.5, 129.5, 128.4, 128.2, 128.1, 127.9, 127.5, 114.1, 67.1, 55.6, 21.6; MS (EI-m/z): 449 (M+); HRMS Calcd for C25H23NO5S 449.1297, Found 449.1295.

2. The [4+2] annulations between 1b-d and 3



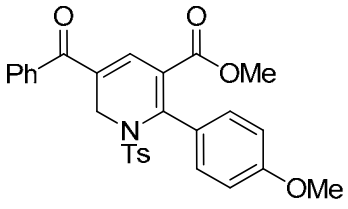
General Procedure C: The PPh_3-Catalyzed Reactions of 1-arylpropynones 1b-d and alkyl 2-[Aryl-(tosylimino)methyl] acrylate 3: 3 (0.3 mmol), PPh_3 (15.7 mg, 20

mmol%) were added to toluene (6 mL) in there-neck bottle. The mixture was stirred at 120 °C under nitrogen atmosphere. To this reaction mixture the solution of 1-arylpropynones **1b-d** (0.6 mmol) in toluene (6 mL) was slowly added within one hour. The reaction mixture was monitored by TLC. Once the reaction was finished, the reaction mixture was cooled down to room temperature. The contents were transferred to a round-bottom flask, and volatiles were removed in vacuo. Then the mixture was directly subjected to silica gel column chromatography (petroleum ether : EtOAc 15:1 to 5:1 gradient) to give the product **5**.



5ba (84 mg, 59%)

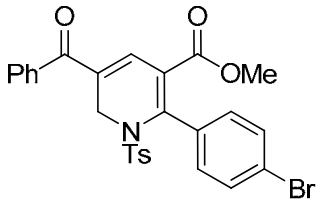
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.38 (m, 10H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.89 (s, 1H), 4.91 (s, 2H), 3.45 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 167.1, 150.7, 144.6, 137.3, 135.3, 135.2, 131.9, 130.7, 130.0, 129.7, 128.7, 128.3, 127.9, 127.0, 126.7, 120.3, 51.8, 45.6, 21.5; MS (EI-m/z): 473 (M^+); HRMS Calcd for $C_{27}H_{23}NO_5S$ 473.5402, Found 473.5404.



5bb (146 mg, 96%)

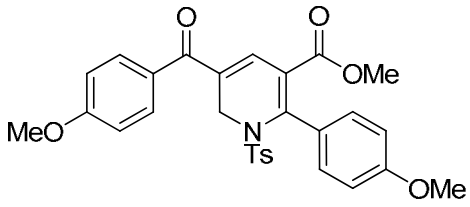
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 3H), 7.44-7.37 (m, 4H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.88 (s, 1H), 4.89 (s, 2H), 3.88 (s, 3H), 3.50 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 167.4, 161.9, 150.6, 144.5, 137.4, 137.3, 135.8, 131.9, 131.8, 129.7, 128.7, 128.2, 127.5, 126.9, 126.2, 119.0, 113.4, 55.3, 51.9, 45.5, 21.5; MS (EI-m/z): 503 (M^+);

HRMS Calcd for $C_{28}H_{25}NO_6S$ 503.5662, Found 503.5666.



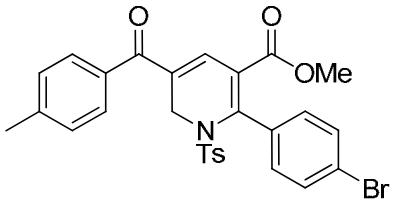
5bc (142 mg, 86%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.49 (m, 5H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 4.89 (s, 2H), 3.50 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 166.7, 149.4, 144.8, 137.2, 137.1, 134.9, 134.3, 132.0, 131.4, 131.2, 129.8, 128.7, 128.3, 127.1, 126.9, 125.3, 120.5, 52.0, 45.5, 21.6; MS (EI-m/z): 551 (M^+); HRMS Calcd for $C_{27}H_{22}BrNO_5S$ 552.4363, Found 552.4361.



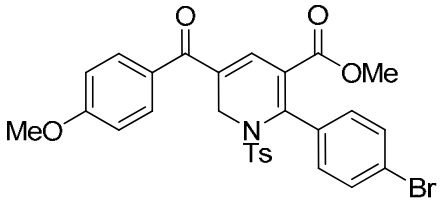
5cb (94 mg, 59%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.0 Hz, 2H), 7.40 (d, *J* = 8.8Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 4.86 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.50 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 167.4, 162.8, 161.8, 150.1, 144.4, 137.4, 134.6, 131.9, 131.1, 129.9, 129.6, 127.5, 127.0, 126.6, 119.1, 113.5, 113.4, 55.4, 55.3, 51.8, 46.0, 21.5; MS (EI-m/z): 533 (M^+); HRMS Calcd for $C_{29}H_{27}NO_7S$ 533.5922, Found 533.5925.



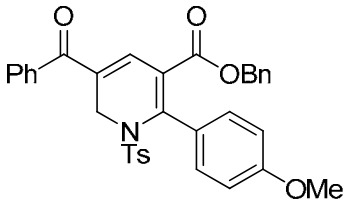
5de (102 mg, 60%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7,50 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25-7.18 (m, 6H), 6.86 (s, 1H), 4.88 (s, 2H), 3.50 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 166.7, 149.1, 144.2, 142.8, 137.1, 134.4, 134.4, 134.3, 131.4, 131.2, 129.8, 129.0, 128.9, 127.4, 126.9, 125.2, 120.6, 52.0, 45.6, 21.6; MS (EI-m/z): 565 (M^+); HRMS Calcd for $C_{28}H_{24}BrNO_5S$ 566.4629, Found 566.4633.



5cc (87mg, 50%)

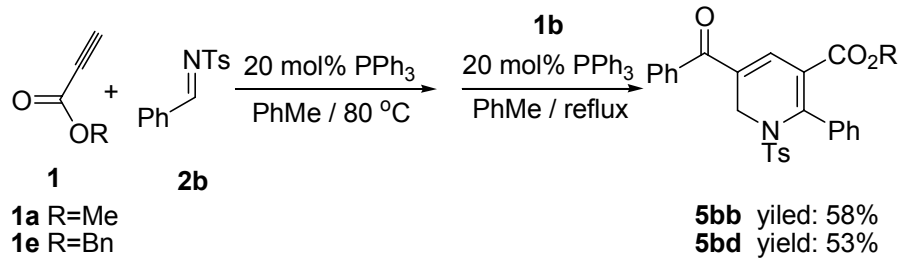
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.84 (s, 1H), 4.86 (s, 2H), 3.86 (s, 3H), 3.49 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 166.7, 163.0, 148.9, 144.7, 137.2, 134.3, 133.6, 131.5, 131.2, 131.2, 129.8, 129.6, 127.5, 126.9, 125.2, 120.6, 113.6, 55.5, 52.0, 45.9, 21.6; MS (EI-m/z): 581 (M^+); HRMS Calcd for $C_{28}H_{24}BrNO_6S$ 582.4623, Found 582.4626.



5bd (109 mg, 63%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 3H), 7.41-7.37 (m, 4H), 7.31-7.22 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.95 (s, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.95 (s, 2H), 4.90 (s, 2H), 3.84 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 166.9, 161.9, 150.8, 144.5, 137.4, 137.3, 135.9, 134.8, 131.9, 131.8, 129.7, 128.7, 128.3, 128.2, 128.2, 127.5, 127.0, 126.2, 119.1, 113.5, 66.9, 55.3, 45.5, 21.5; MS (EI-m/z): 579 (M^+); HRMS Calcd for $C_{34}H_{29}NO_6S$ 579.6622, Found 579.6621.

V. General Procedure for synthesis of 5ba and 5bd in one-pot way



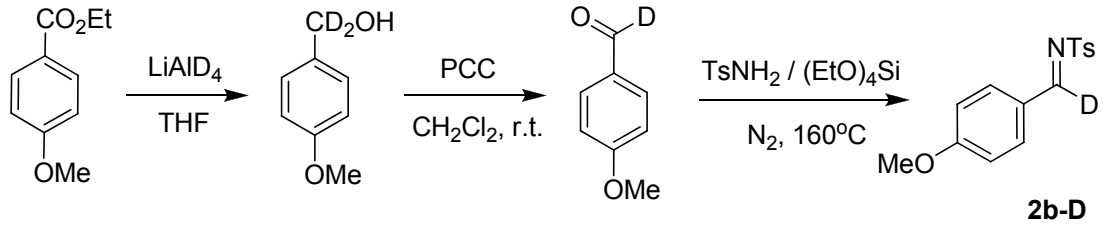
1 **2b**

1a R=Me
1e R=Bn

5bb yiled: 58%
5bd yield: 53%

N-tosylimine **2b** (1.0 mmol), PPh_3 (52.5 mg, 20 mmol%) were added to toluene (20 mL) in there-neck bottle. The mixture was stirred at 80 °C under nitrogen atmosphere. To this reaction mixture the solution of alkyl propiolate **1a (1e)** (1.2 mmol) in toluene (20 mL) was slowly added within 3.0 hours. Once the addition was finished, additional PPh_3 (52.5 mg, 20 mmol%) in toluene (5 mL) was added to the mixture. And the reaction mixture was heated up to 120 °C. Then, the solution of 1-arylpropynones **1b** (2.0 mmol) in toluene (10 mL) was slowly added within 1.5 hours. The reaction mixture was monitored by TLC. The contents were transferred to a round-bottom flask, and volatiles were removed in vacuum. Then the mixture was directly subjected to silica gel column chromatography (petroleum ether : EtOAc 15:1 to 5:1 gradient) to give the product **5bb (5bd).**

VI. Procedure for 2b-D



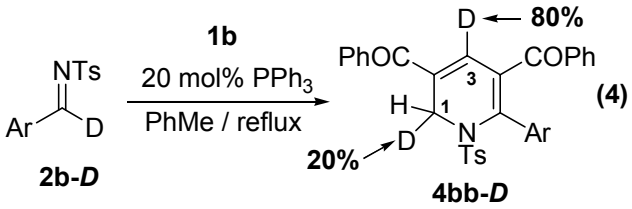
2b-D

$LiAlD_4$ (from Aldrich, >98% D) (1.51 g, 36 mmol) was added to 100 ml of dry THF in an ice bath. Ethyl 4-methoxybenzoate (7.90 g, 44.0 mmol) in 50 ml of THF was slowly added. The mixture was brought to room temperature and heated at refluxed for another 6 hrs. Then 10 ml of 10% aqueous NaOH and 5 ml water was cautiously added to the reaction mixture; the resulting salts were filtered, and filtrate was extracted with 3 × 50 ml portions of ethyl acetate. The ethyl acetate solutions were combined, dried over $NaSO_4$, and the solvent was removed under vacuum to obtain a color-less liquid (5.55 g, about 39.6 mmol). The liquid was used without any further purification.

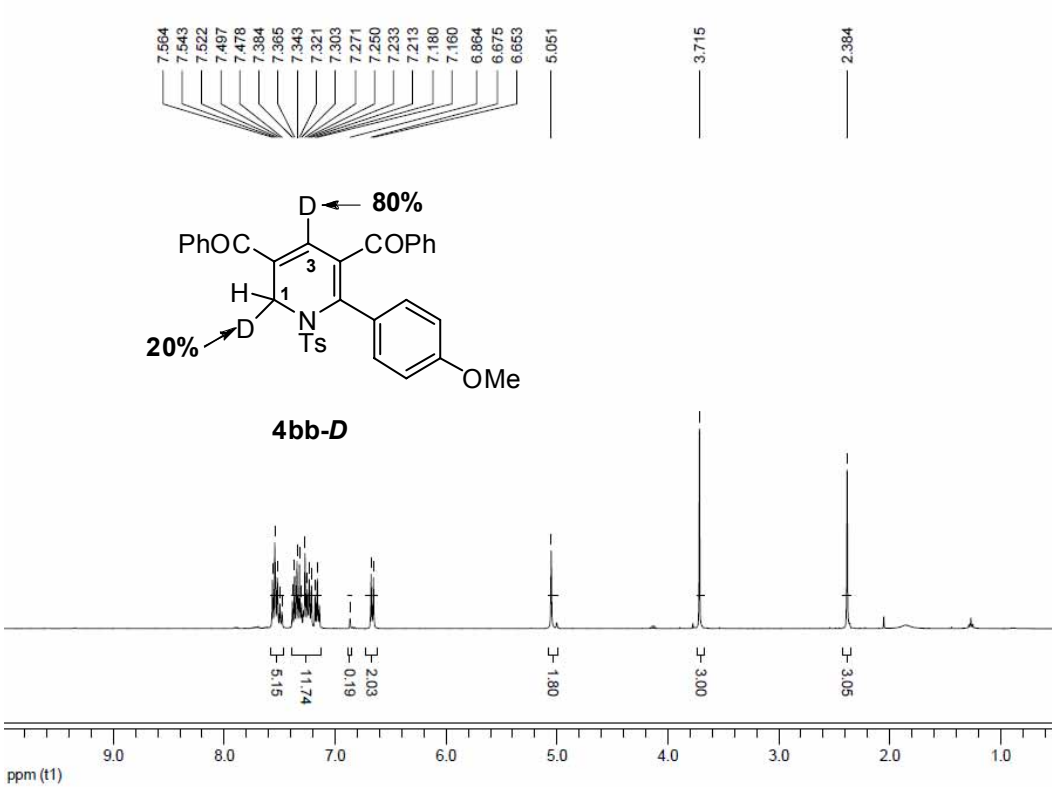
The liquid in 80 ml of CH_2Cl_2 was added to PCC (12.8g, 59.4 mmol) in 120 ml of CH_2Cl_2 in an ice bath. About an hour later, the mixture was brought to room temperature and stirred at room temperature until the starting material was disappeared. The mixture was directly subjected to FCG to offer a colorless liquid (3.79g, 63%).

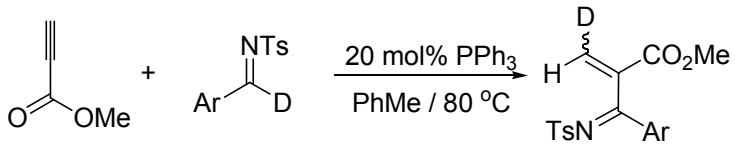
4-methoxybenzaldehyde-d_1 (3.79g, 27.7 mmol) and $TsNH_2$ (4.74g, 27.7 mmol) were added to $(EtO)_4Si$ (11.1 ml, 29.4 mmol). The mixture was heating to 160 ^oC for 6 hrs under nitrogen atmosphere. Then the reaction mixture was cooled down to room temperature. The solvent was removed under vacuum to obtain a white solid. This solid was purified with petroleum ether and ethyl acetate to give compound **2b-D** (5.95 g, 74%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 6.4 Hz, 2H), 7.88 (d, J = 5.6 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H), 2.44 (s, 3H).

VII. The data of eq 4 and eq 5



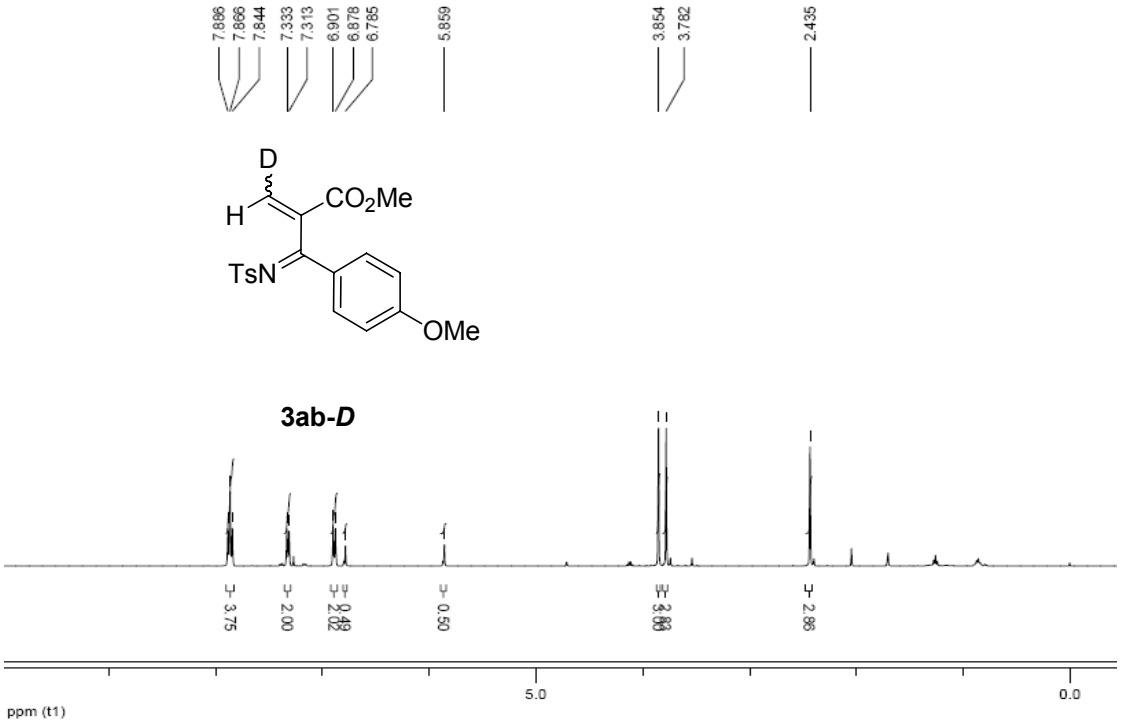
4bb-D was prepared according to General **Procedure A** (130mg, 47%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.48 (m, 5H), 7.38-7.16 (m, 11H), 6.86 (s, 0.2H), 6.66 (d, J = 8.8 Hz, 2H), 5.05 (s, 1.8H), 3.72 (s, 3H), 2.38 (s, 3H).

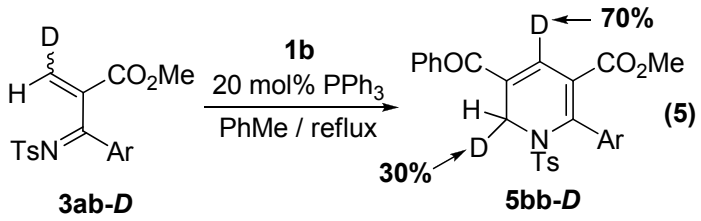




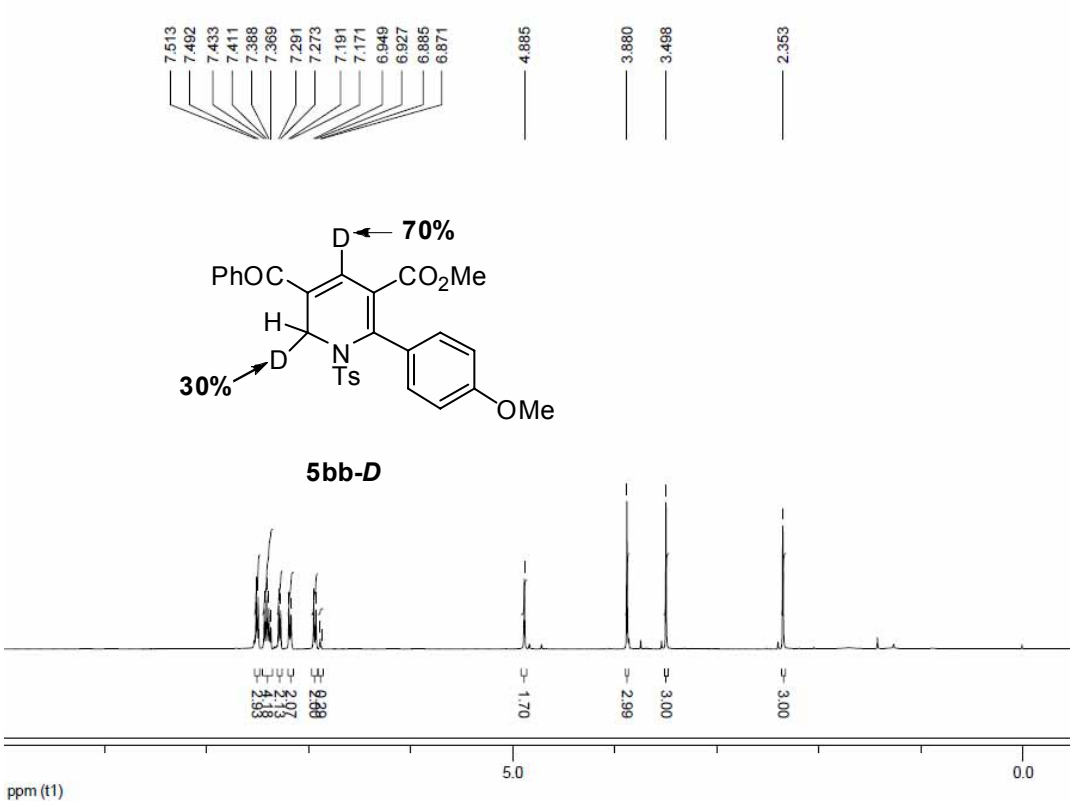
1a **2b-*D*** **3ab-*D***

3ab-D was prepared according to General **Procedure B** (75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 6.79(s, 0.5H), 5.86 (s, 0.5H), 3.85 (s, 3H), 3.78 (s, 3H), 2.44 (s, 3H); MS (m/z): 375 ($M + H^+$).



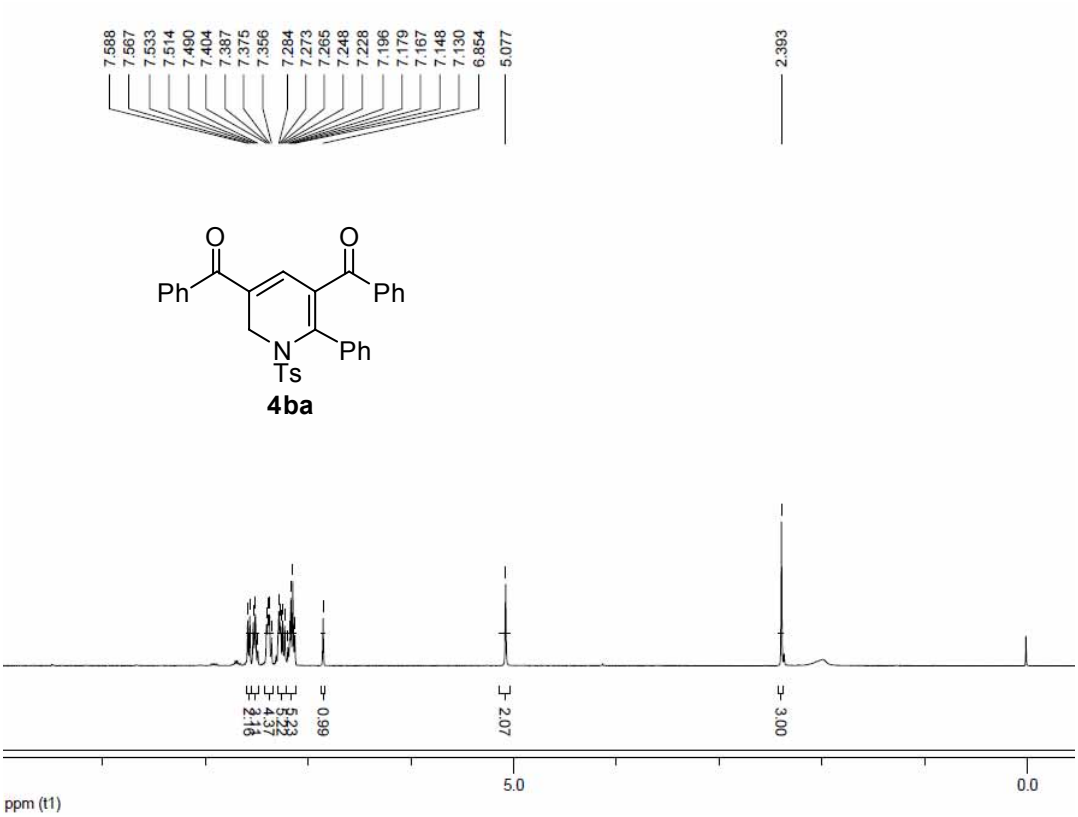


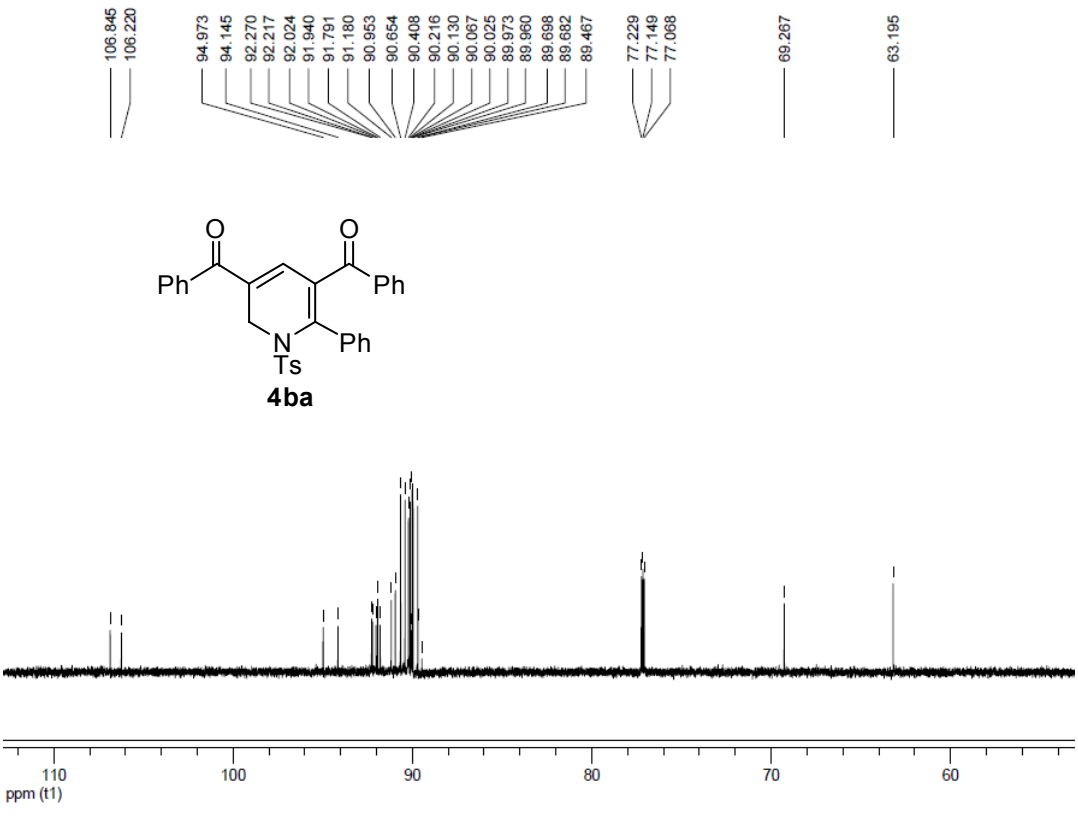
5bb-D was prepared according to General **Procedure C** (118mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 3H), 7.43-7.37 (m, 4H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.89 (s, 0.3H), 4.89 (s, 1.7 H), 3.88 (s, 3H), 3.50 (s, 3H), 2.35 (s, 3H).

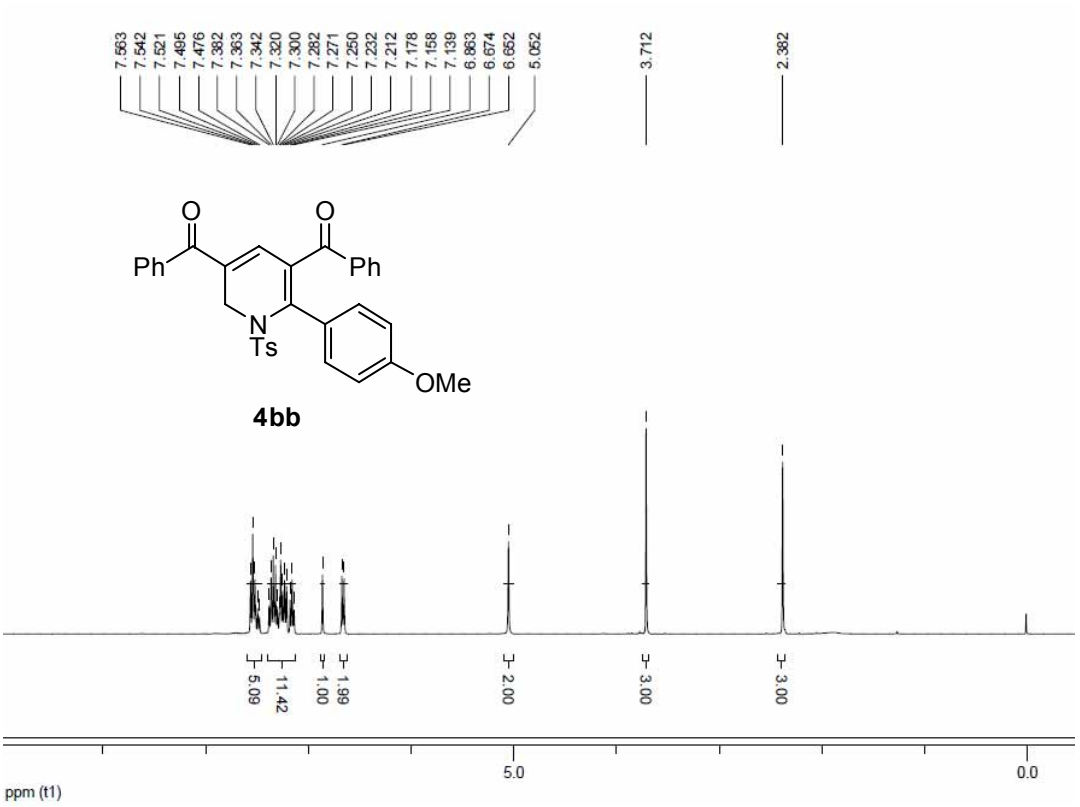


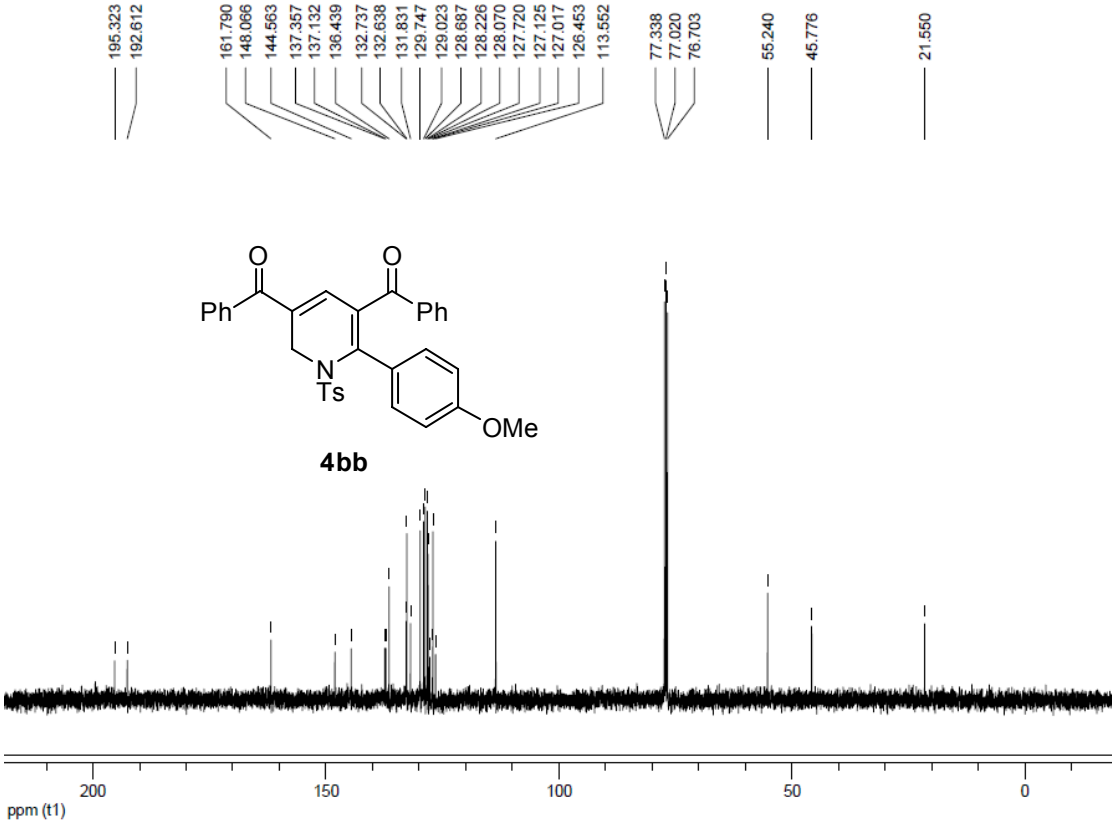
VIII. NMR Spectra

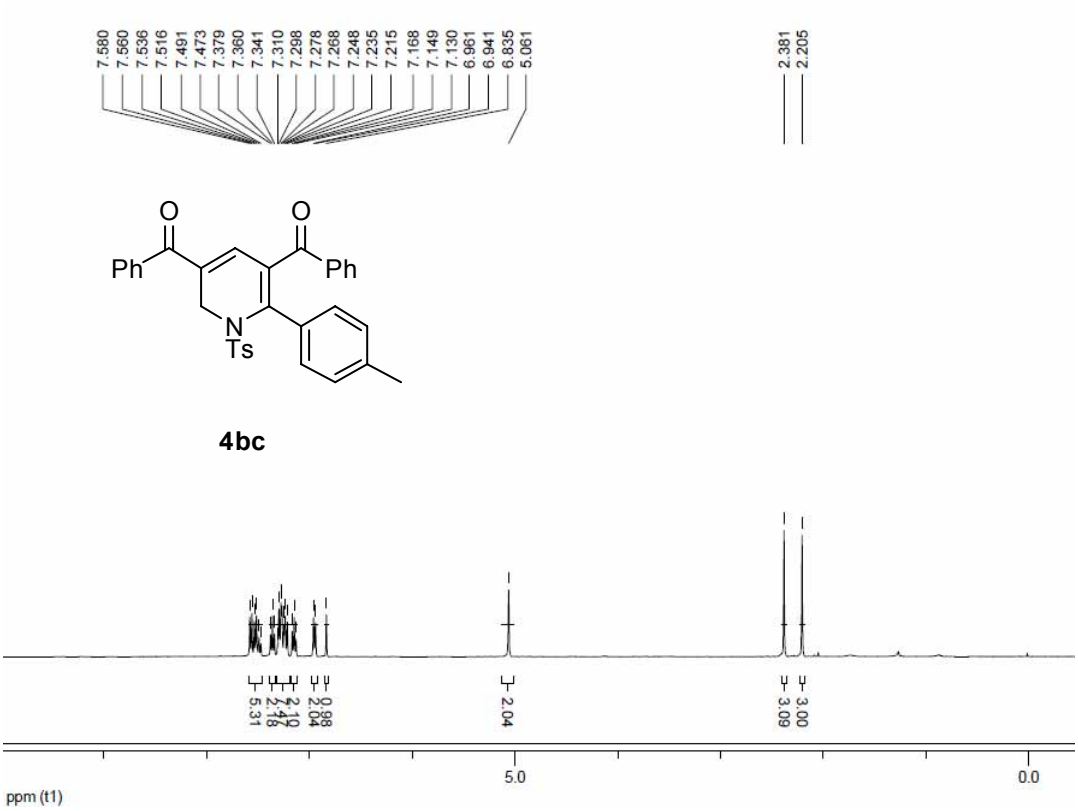
1. The [2+2+2] annulations products **4**



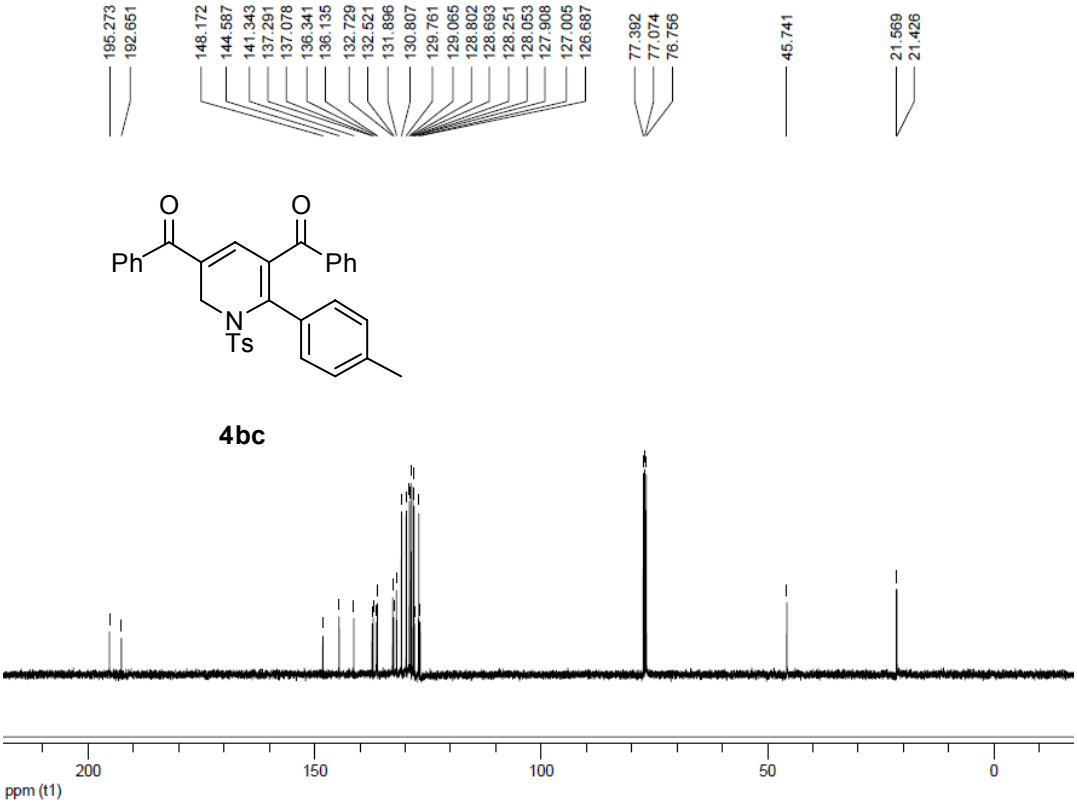



7.563
7.542
7.521
7.495
7.476
7.382
7.363
7.342
7.320
7.300
7.282
7.271
7.250
7.232
7.212
7.178
7.158
7.139
6.863
6.674
6.652
5.052
3.712
2.382
O
O
Ph
Ph
N
Ts
OMe
4bb
6.09
11.42
1.00
1.99
2.00
3.00
3.00
5.0
0.0
ppm (t1)

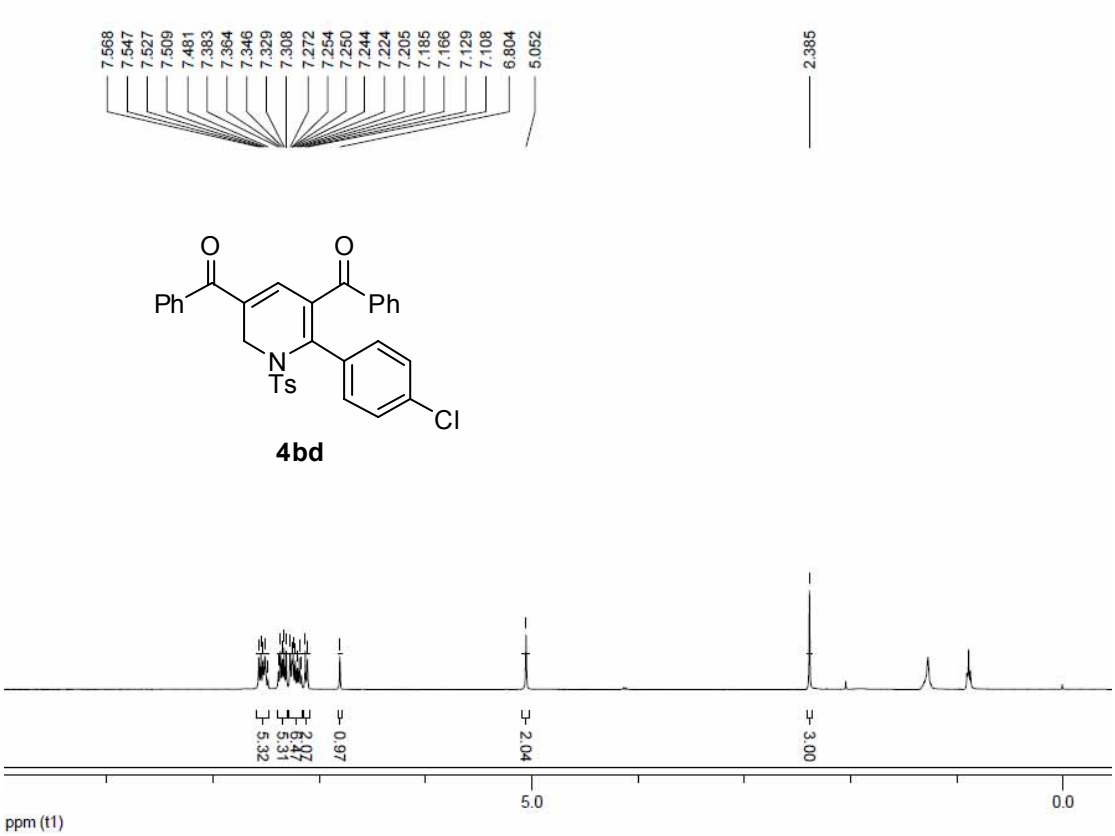

195.323
192.612
161.790
148.066
144.563
137.357
137.132
136.439
132.737
132.638
131.831
129.747
129.023
128.687
128.226
128.070
127.720
127.125
127.017
126.453
113.552
77.338
77.020
76.703
55.240
45.776
21.550
O
O
Ph
Ph
N
Ts
OMe
4bb
200
150
100
50
0
ppm (t1)


7.580
7.560
7.536
7.516
7.491
7.473
7.379
7.360
7.341
7.310
7.298
7.278
7.268
7.248
7.235
7.215
7.168
7.149
7.130
6.961
6.941
6.835
5.061
2.381
2.205
O
O
Ph
Ph
N
Ts
5.13
2.18
2.10
2.07
0.88
2.04
3.09
3.00
5.0
0.0
ppm (t1)

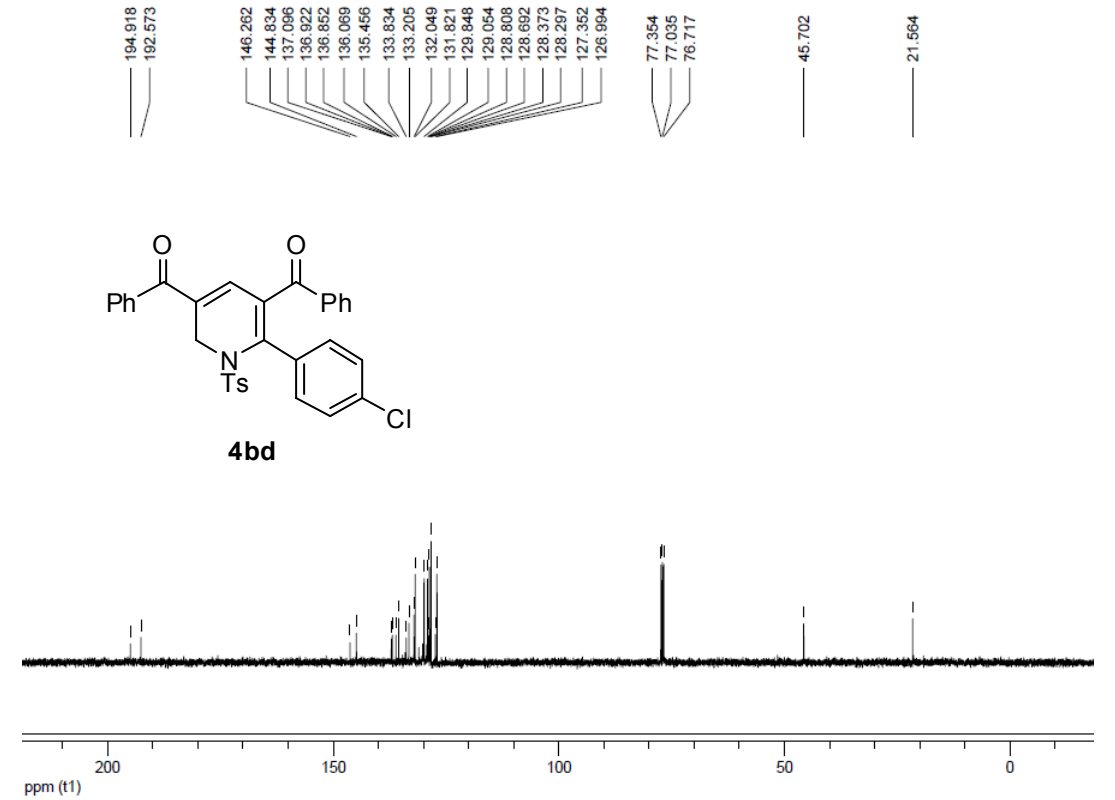
4bc


195.273
192.651
148.172
144.587
141.343
137.291
137.078
136.341
136.135
132.729
132.521
131.896
130.807
129.761
129.065
128.802
128.693
128.251
128.053
127.908
127.005
126.687
77.392
77.074
76.756
45.741
21.569
21.426
O
O
Ph
Ph
N
Ts
200
150
100
50
0
ppm (t1)

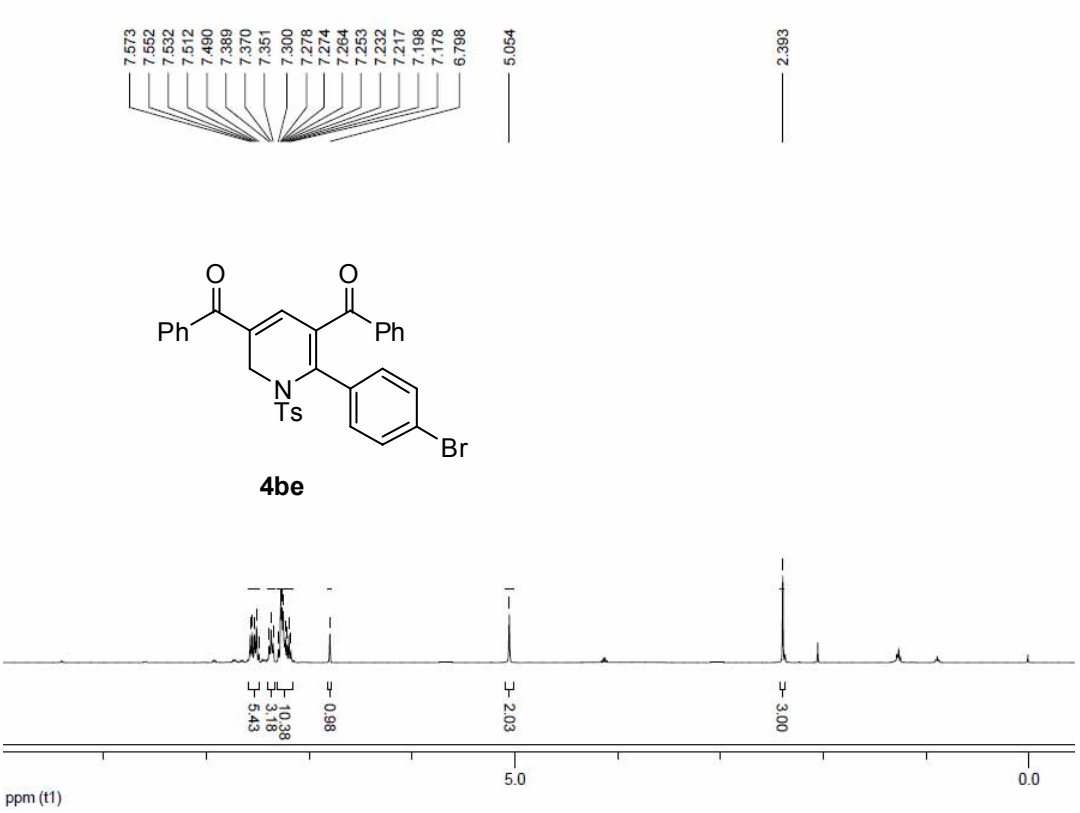
4bc


7.568
7.547
7.527
7.509
7.481
7.383
7.364
7.346
7.329
7.308
7.272
7.254
7.250
7.244
7.224
7.205
7.185
7.166
7.129
7.108
6.804
5.052
2.385
O
O
Ph
Ph
N
Ts
Cl
5.32
5.31
2.07
2.07
0.97
2.04
3.00
5.0
0.0
ppm (t1)

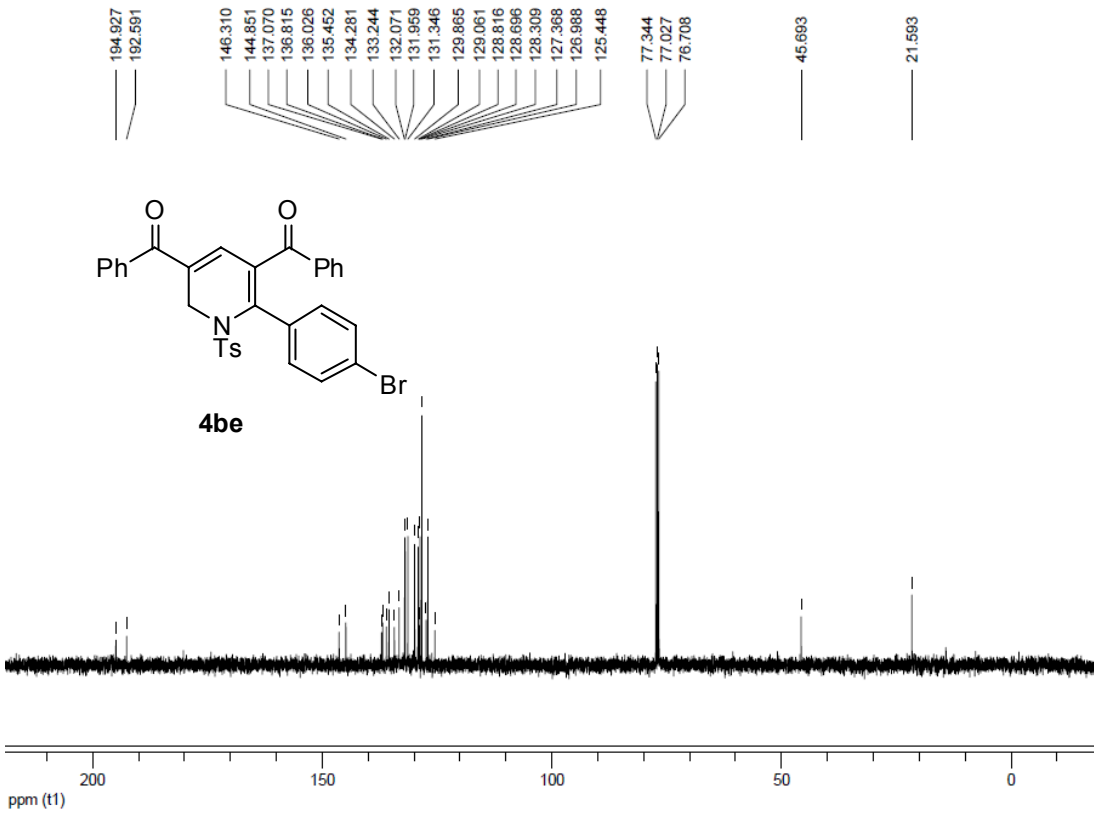
4bd


194.918
192.573
146.262
144.834
137.096
136.922
136.852
136.069
135.456
133.834
133.205
132.049
131.821
129.848
129.054
128.808
128.692
128.373
128.297
127.352
126.994
77.354
77.035
76.717
45.702
21.564
O
O
Ph
Ph
N
Ts
Cl
200
150
100
50
0
ppm (t1)

4bd

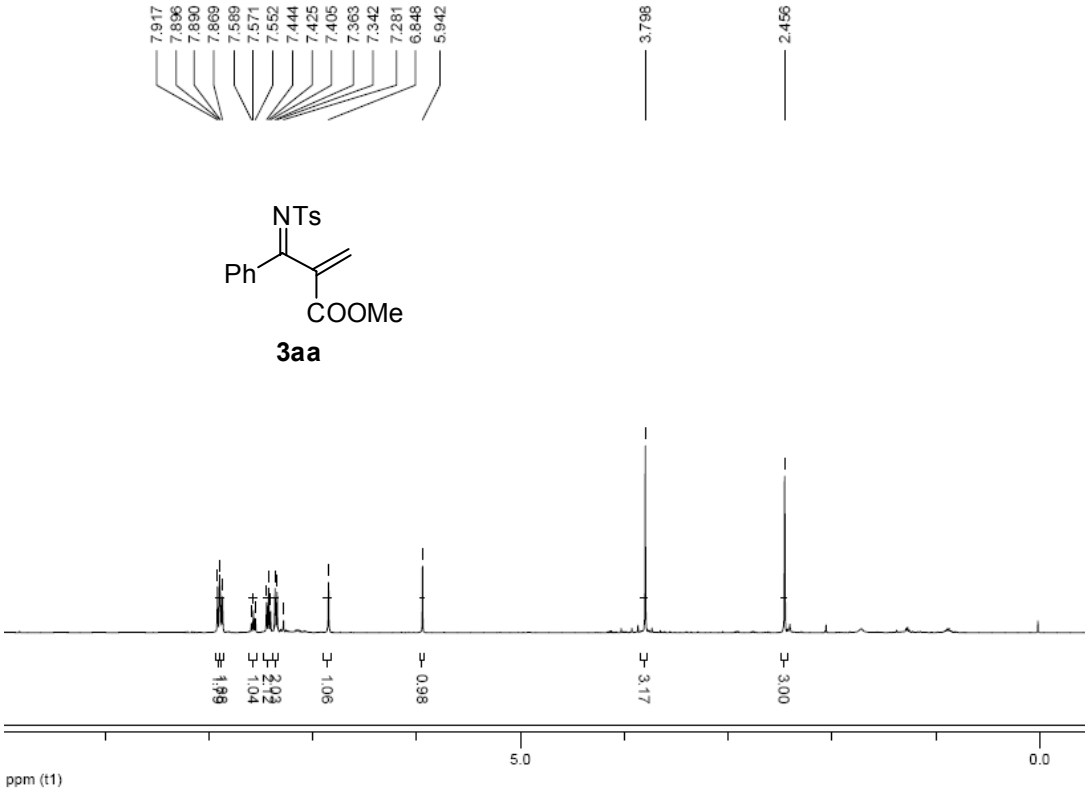

7.573
7.552
7.532
7.512
7.490
7.389
7.370
7.351
7.300
7.278
7.274
7.264
7.253
7.232
7.217
7.198
7.178
6.798
5.054
2.393
O
O
Ph
Ph
N
Ts
Br
5.43
3.18
10.38
0.98
2.03
3.00
5.0
0.0
ppm (t1)

4be

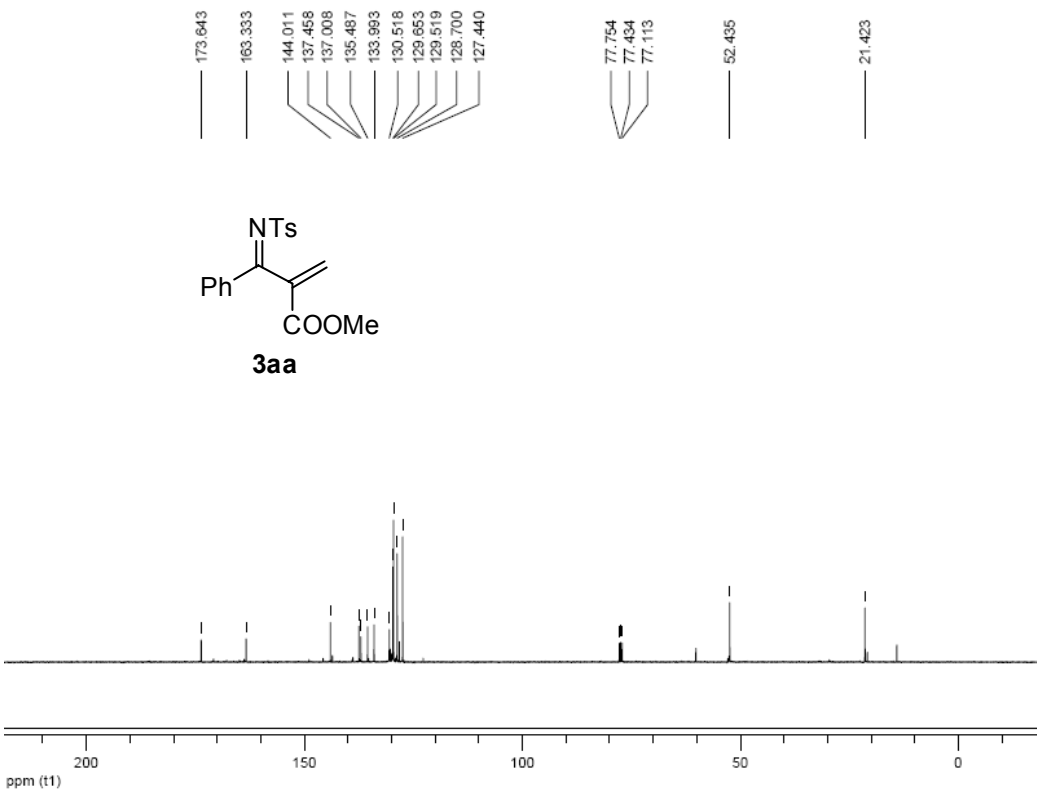

194.927
192.591
146.310
144.851
137.070
136.815
136.026
135.452
134.281
133.244
132.071
131.959
131.346
129.865
129.061
128.816
128.696
128.309
127.368
126.988
125.448
77.344
77.027
76.708
45.693
21.593
O
O
Ph
Ph
N
Ts
Br
200
150
100
50
0
ppm (t1)

4be

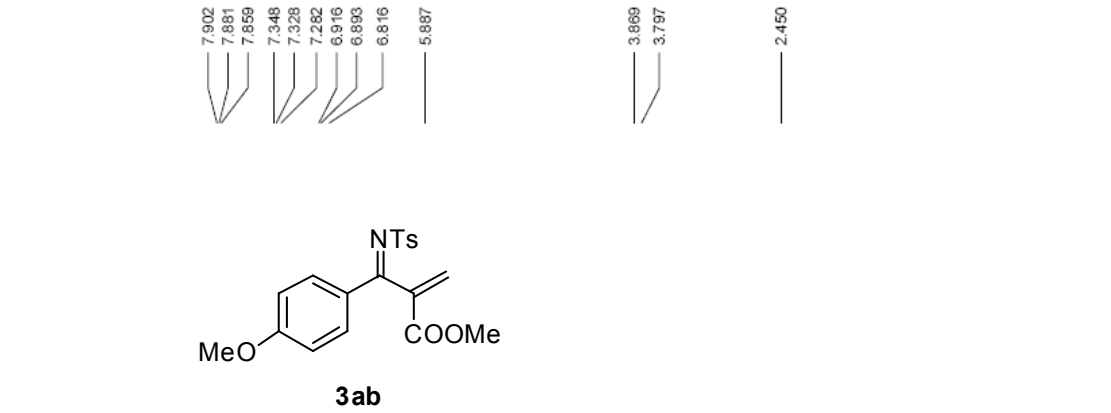
2. The NMR spectra of **3**



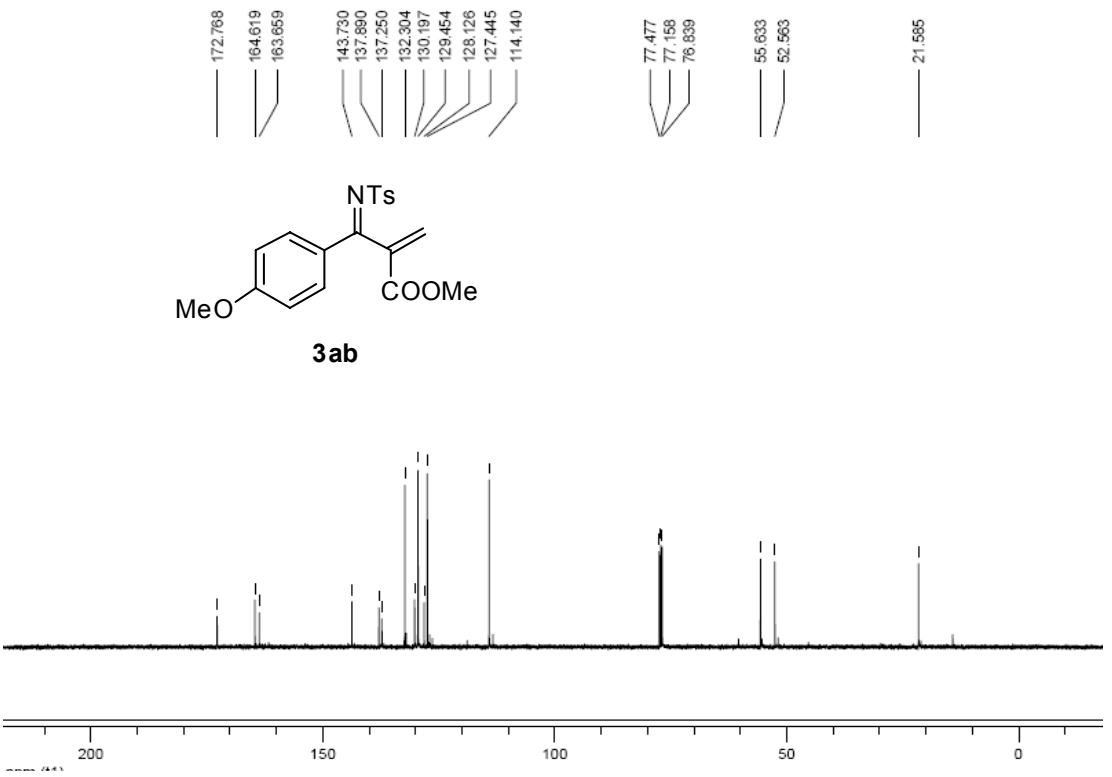
3aa



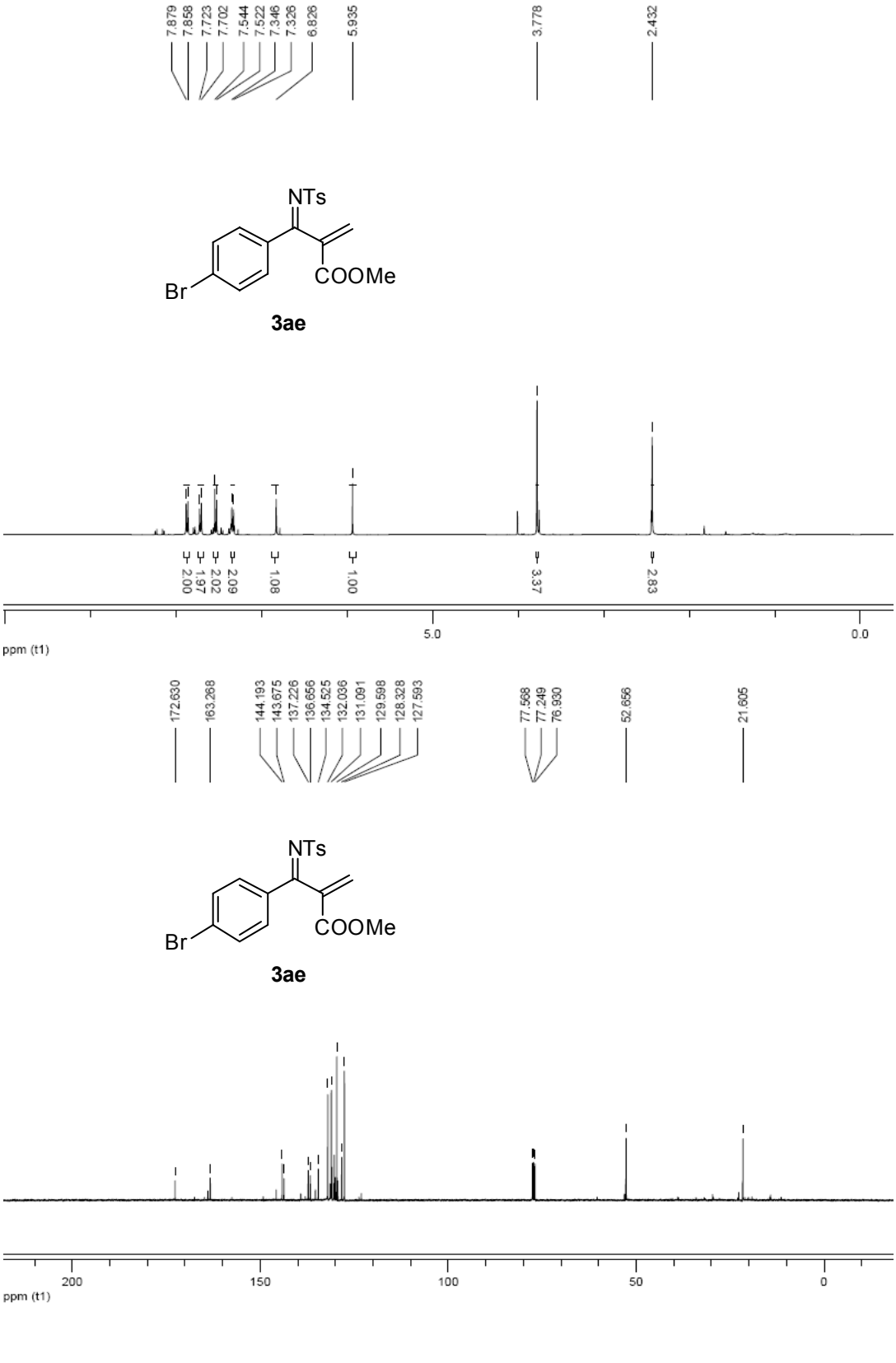
3aa


7.902
7.881
7.859
7.348
7.328
7.282
6.916
6.893
6.816
5.887
3.869
3.797
2.450
NTs
MeO
COOMe
2.22
1.88
0.98
3.01
5.0
0.0
ppm (t1)

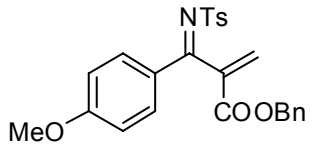
3ab


172.768
164.619
163.659
143.730
137.890
137.250
132.304
130.197
129.454
128.126
127.445
114.140
77.477
77.158
76.839
55.633
52.563
21.585
NTs
MeO
COOMe
200
150
100
50
0
ppm (t1)

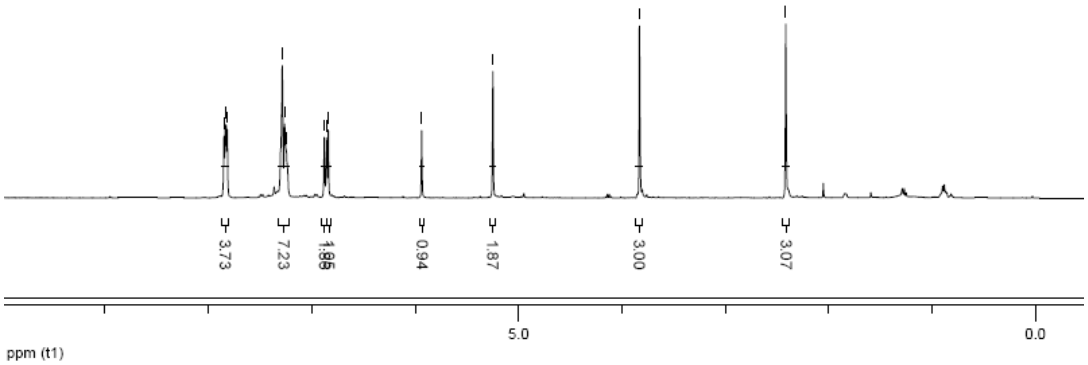
3ab

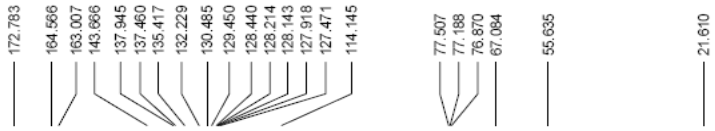

7.879
7.858
7.723
7.702
7.544
7.522
7.346
7.326
6.826
5.935
3.778
2.432
NTs
Br
COOMe
3ae
2.00
1.97
2.02
2.09
1.08
1.00
3.37
2.83
5.0
0.0
ppm (t1)
172.630
163.268
144.193
143.675
137.226
136.656
134.525
132.036
131.091
129.598
128.328
127.593
77.568
77.249
76.930
52.656
21.605
NTs
Br
COOMe
3ae
200
150
100
50
0
ppm (t1)

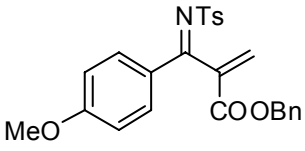

7.850
7.837
7.828
7.817
7.286
7.262
7.247
6.879
6.857
6.840
5.937
5.248
3.831
2.415


NTs
MeO
COOBn

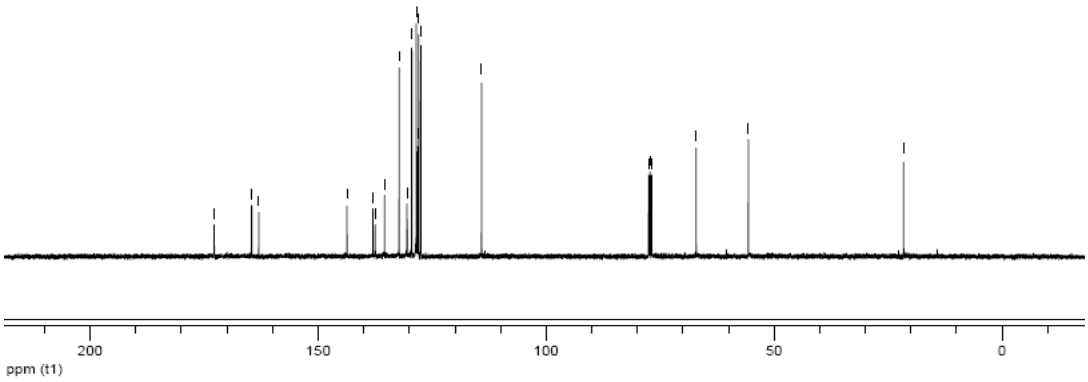
3eb

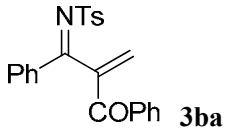

3.73
2.23
1.86
0.94
1.87
3.00
3.07
5.0
0.0
ppm (t1)


172.783
164.566
163.007
143.666
137.945
137.460
135.417
132.229
130.485
129.450
128.440
128.214
128.143
127.918
127.471
114.145
77.507
77.188
76.870
67.084
55.635
21.610

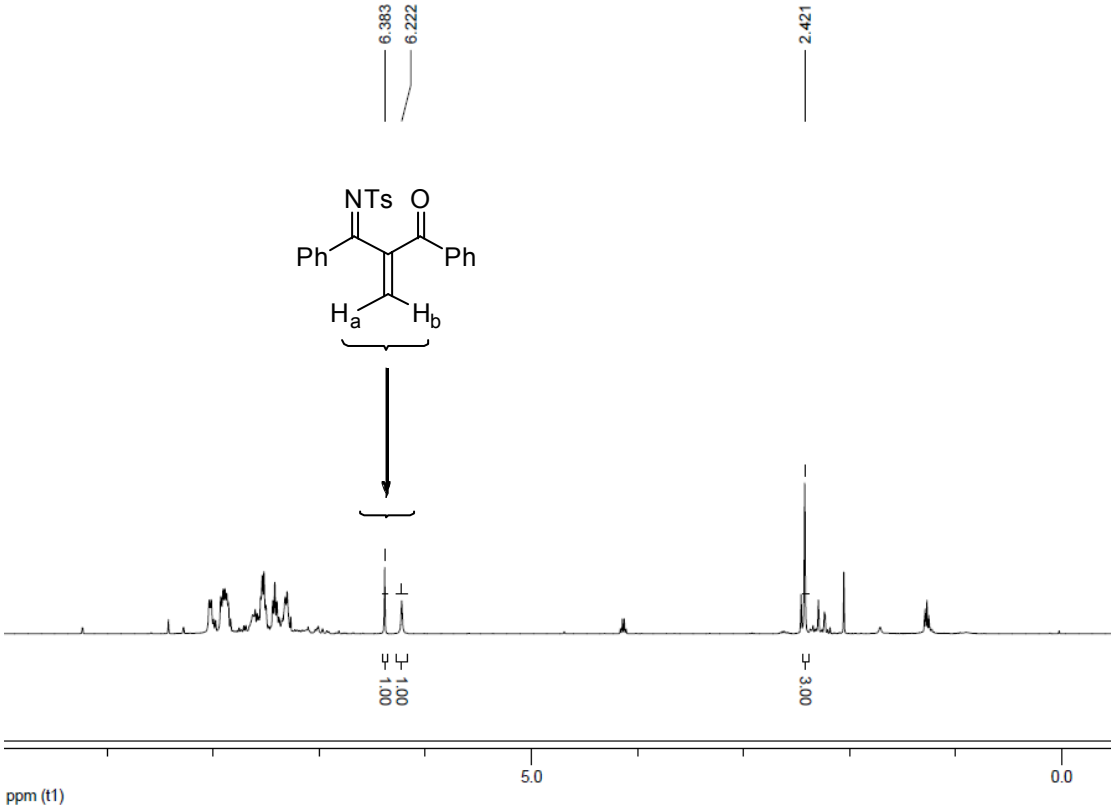

NTs
MeO
COOBn

3eb

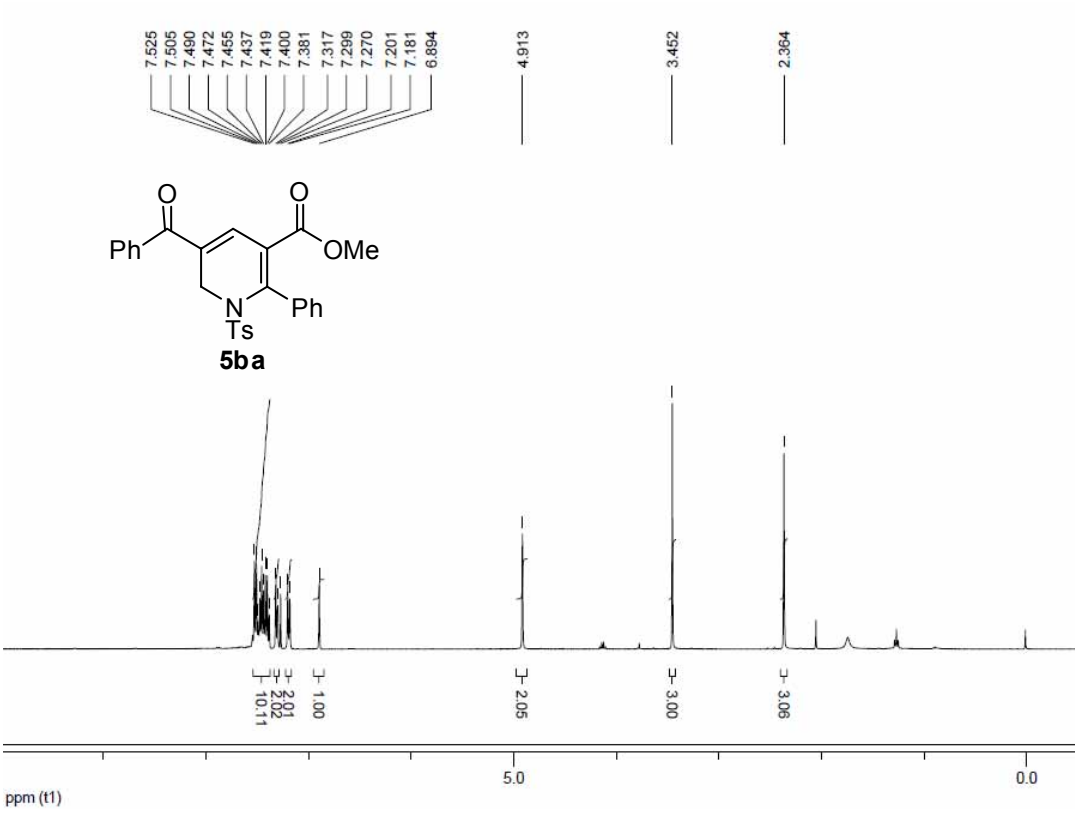

200
150
100
50
0
ppm (t1)

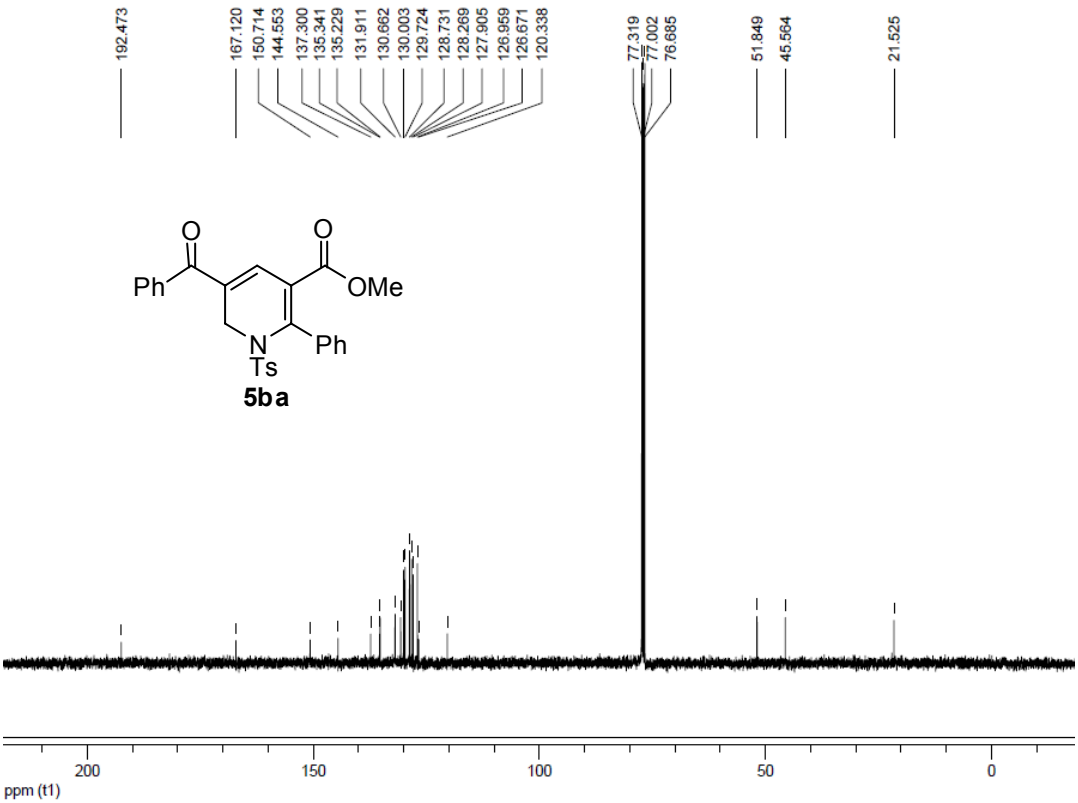

NTs
Ph
COPh

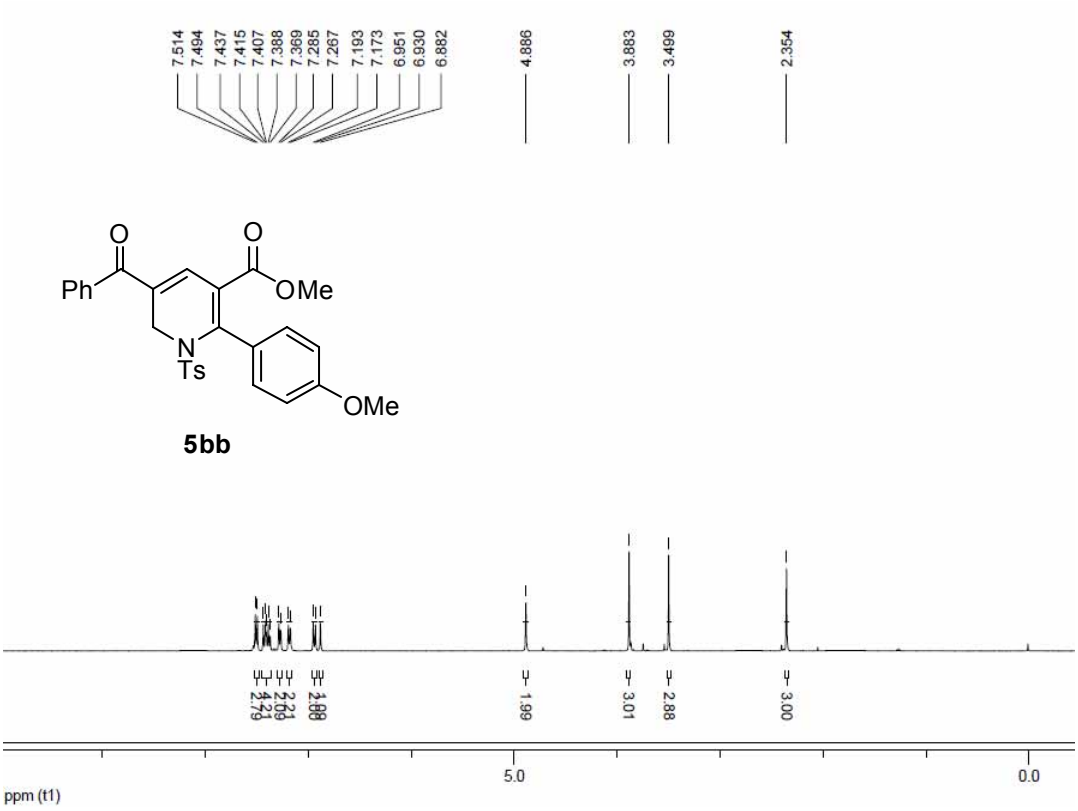
3ba

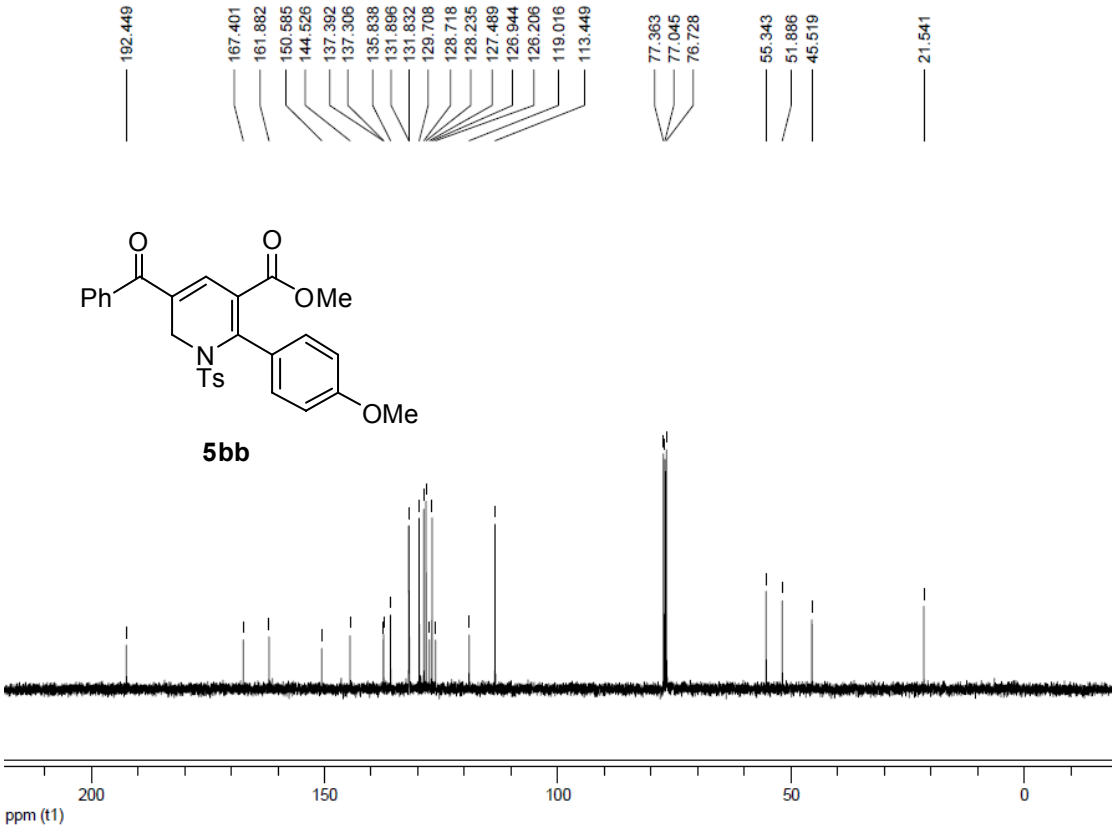

6.383
6.222
2.421
NTs
O
Ph
Ph
Ha
Hb
1.00
1.00
3.00
5.0
0.0
ppm (t1)

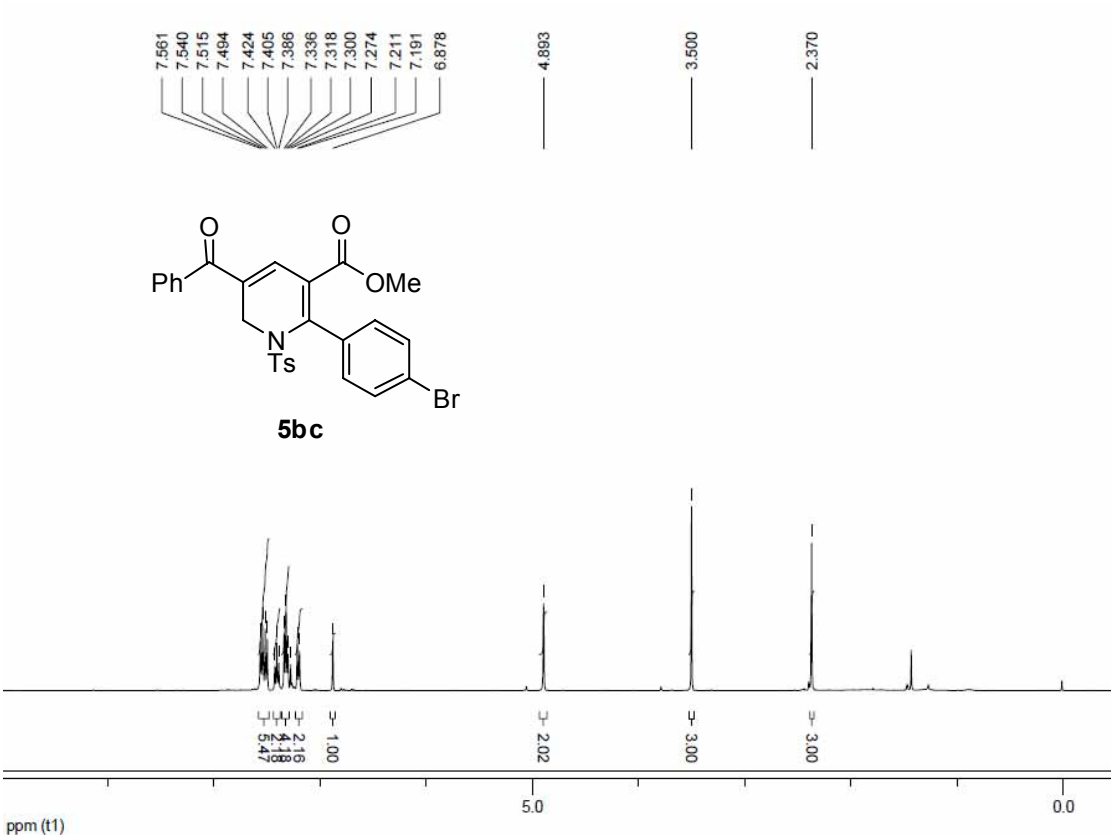
3. The [4+2] annulations products **5**



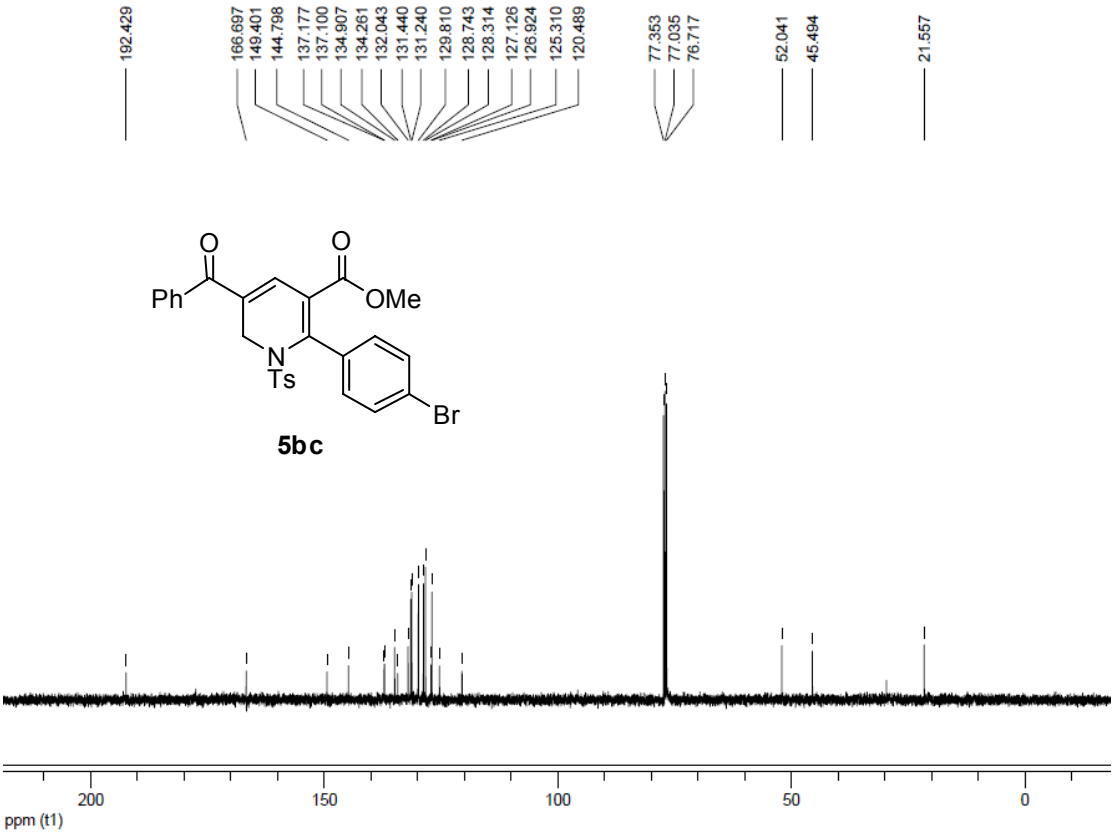



7.514
7.494
7.437
7.415
7.407
7.388
7.369
7.285
7.267
7.193
7.173
6.951
6.930
6.882
4.886
3.883
3.499
2.354
O
O
Ph
OMe
N
Ts
OMe
5bb
2.79
2.21
2.00
1.99
3.01
2.88
3.00
5.0
0.0
ppm (t1)

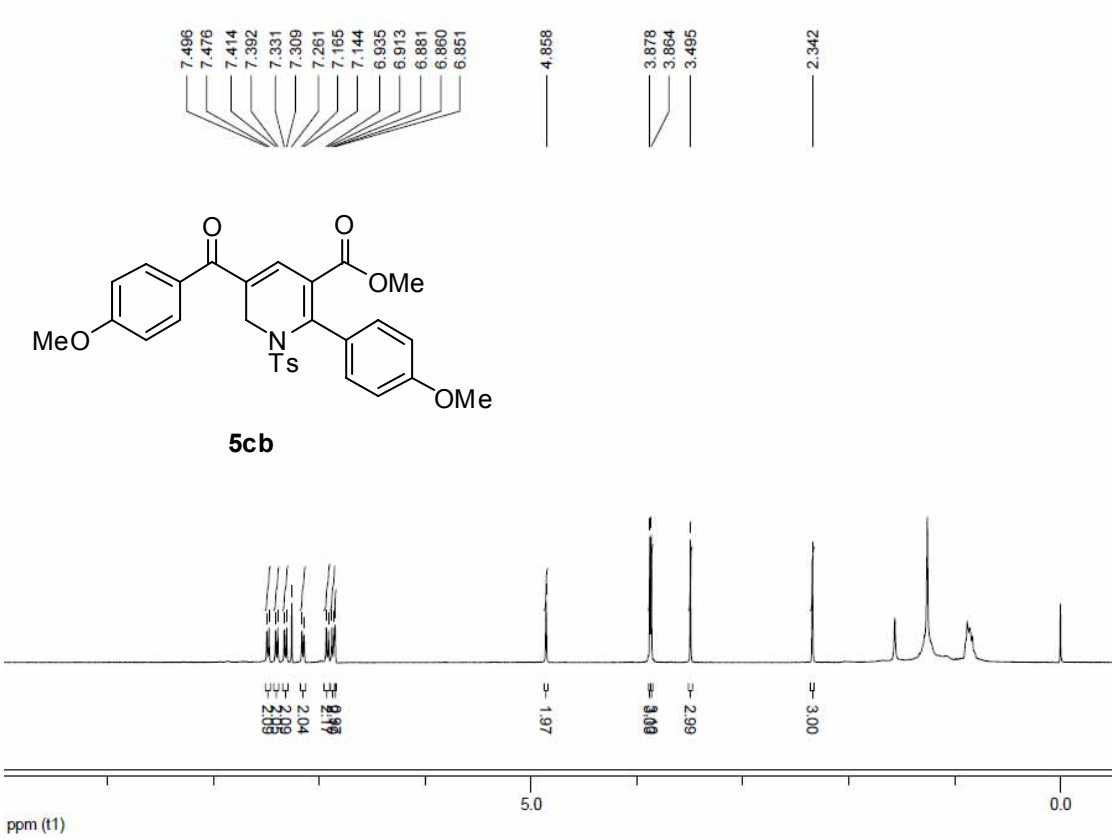

192.449
167.401
161.882
150.585
144.526
137.392
137.306
135.838
131.896
131.832
129.708
128.718
128.235
127.489
126.944
126.206
119.016
113.449
77.363
77.045
76.728
55.343
51.886
45.519
21.541
O
O
Ph
OMe
N
Ts
OMe
5bb
200
150
100
50
0
ppm (t1)


7.561
7.540
7.515
7.494
7.424
7.405
7.386
7.336
7.318
7.300
7.274
7.211
7.191
6.878
4.893
3.500
2.370
O
O
Ph
OMe
N
Ts
Br
5.47
2.18
2.16
1.00
2.02
3.00
3.00
5.0
0.0
ppm (t1)

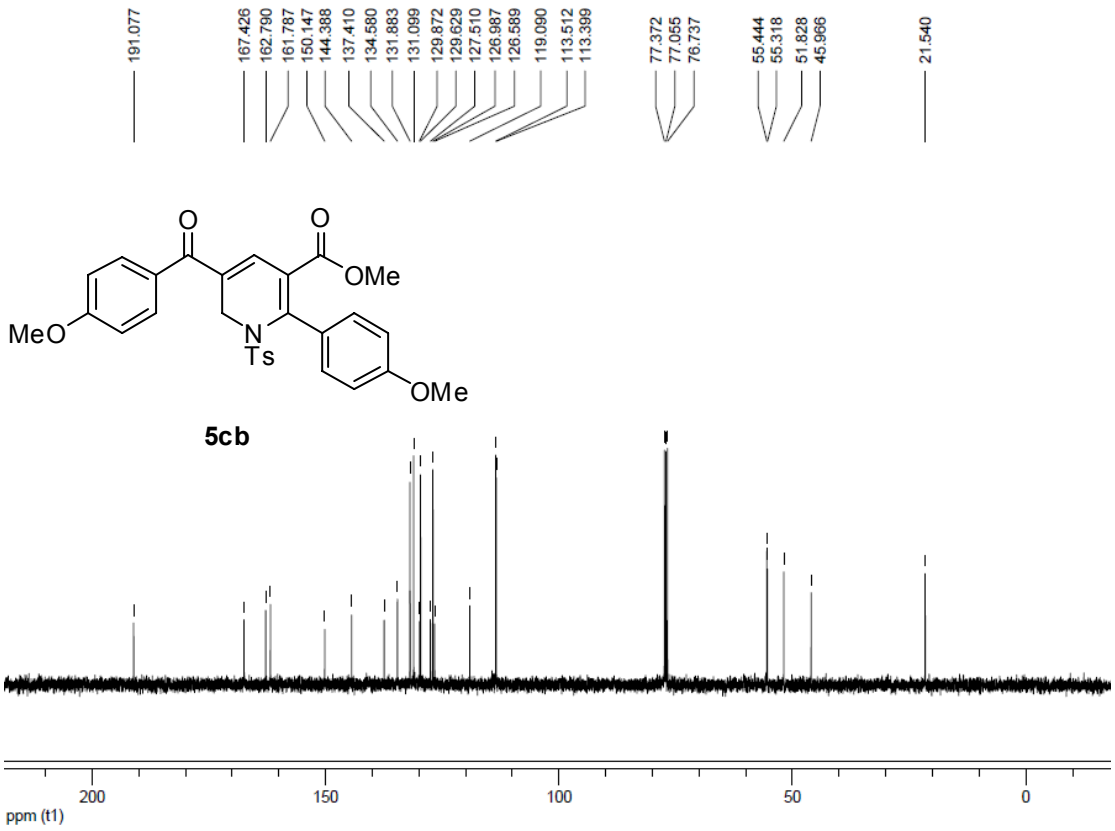
5bc


192.429
166.697
149.401
144.798
137.177
137.100
134.907
134.261
132.043
131.440
131.240
129.810
128.743
128.314
127.126
126.924
125.310
120.489
77.353
77.035
76.717
52.041
45.494
21.557
O
O
Ph
OMe
N
Ts
Br
200
150
100
50
0
ppm (t1)

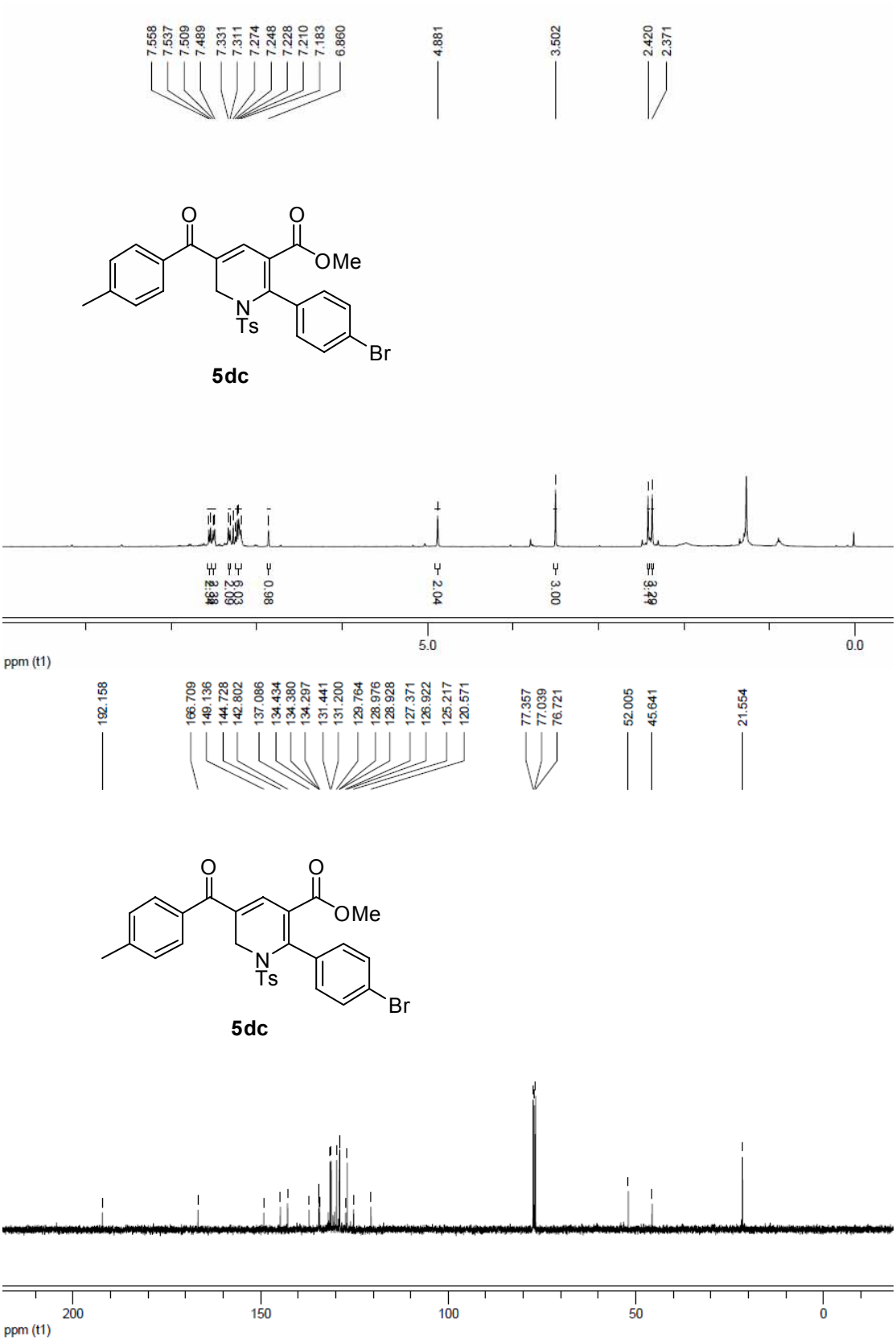
5bc

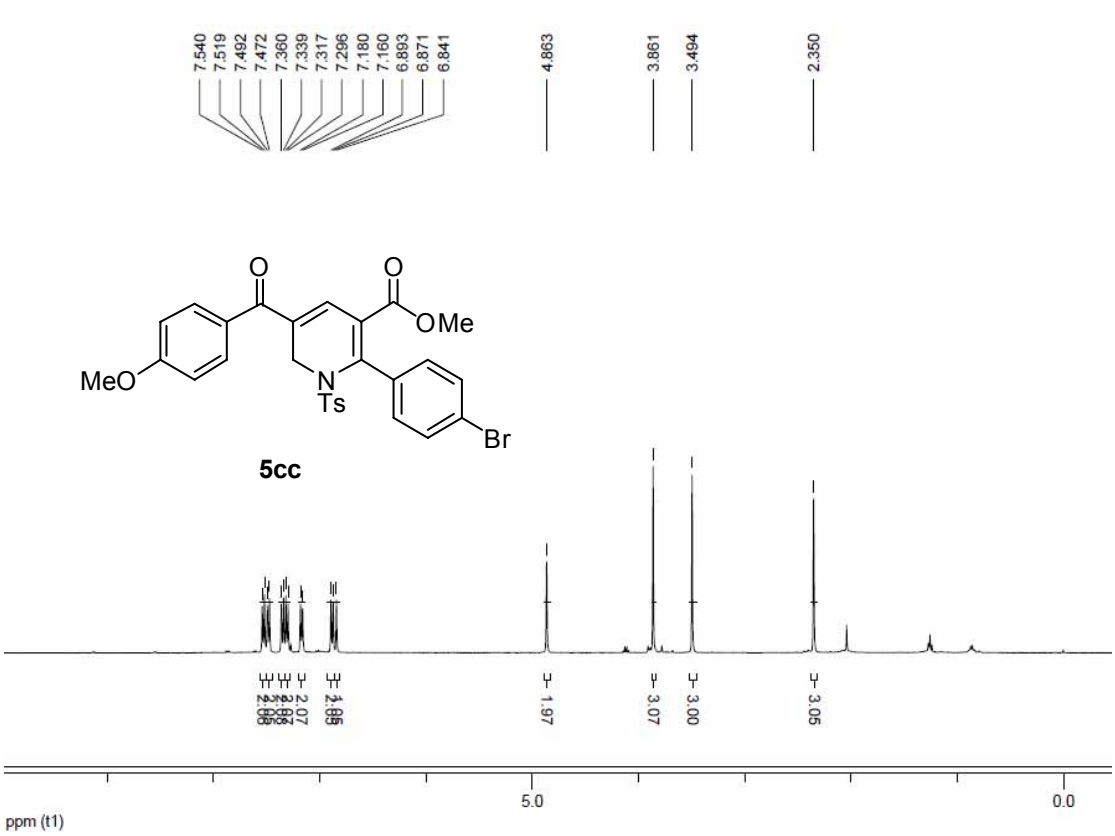

7.496
7.476
7.414
7.392
7.331
7.309
7.261
7.165
7.144
6.935
6.913
6.881
6.860
6.851
4.858
3.878
3.864
3.495
2.342
O
O
OMe
MeO
N
Ts
OMe
2.09
2.04
1.97
3.00
2.99
5.0
0.0
ppm (t1)

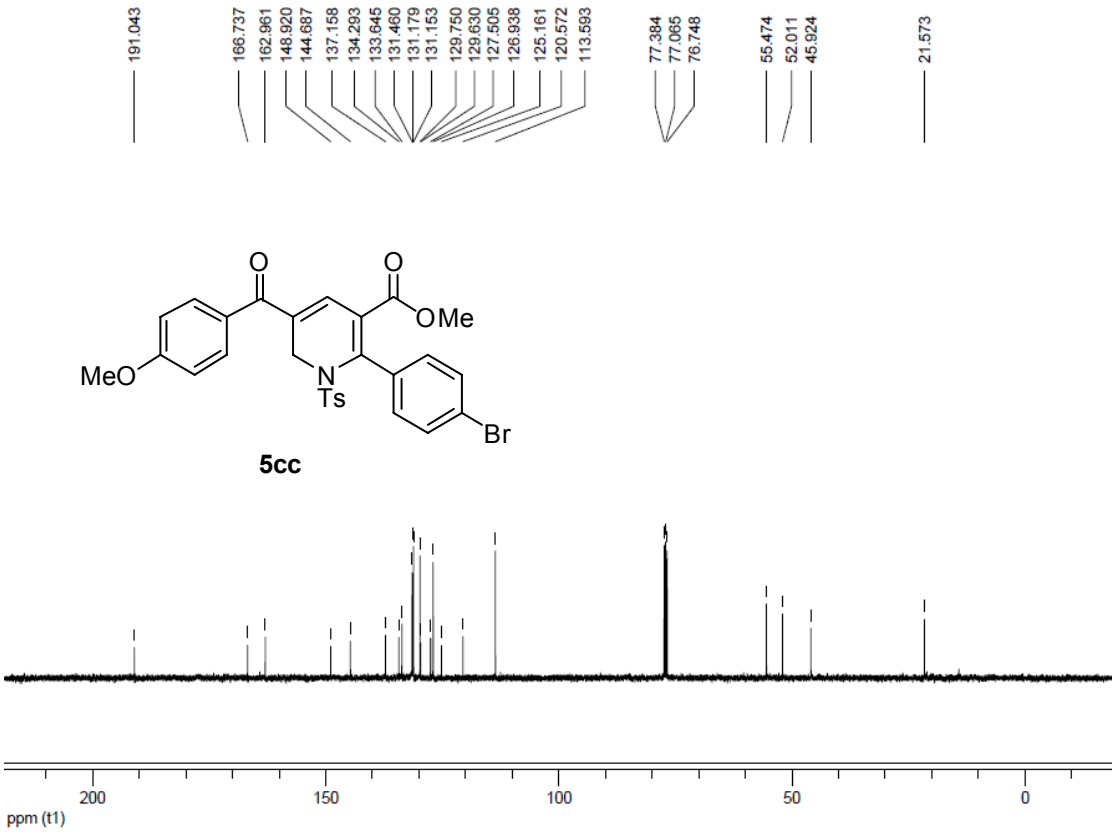
5cb

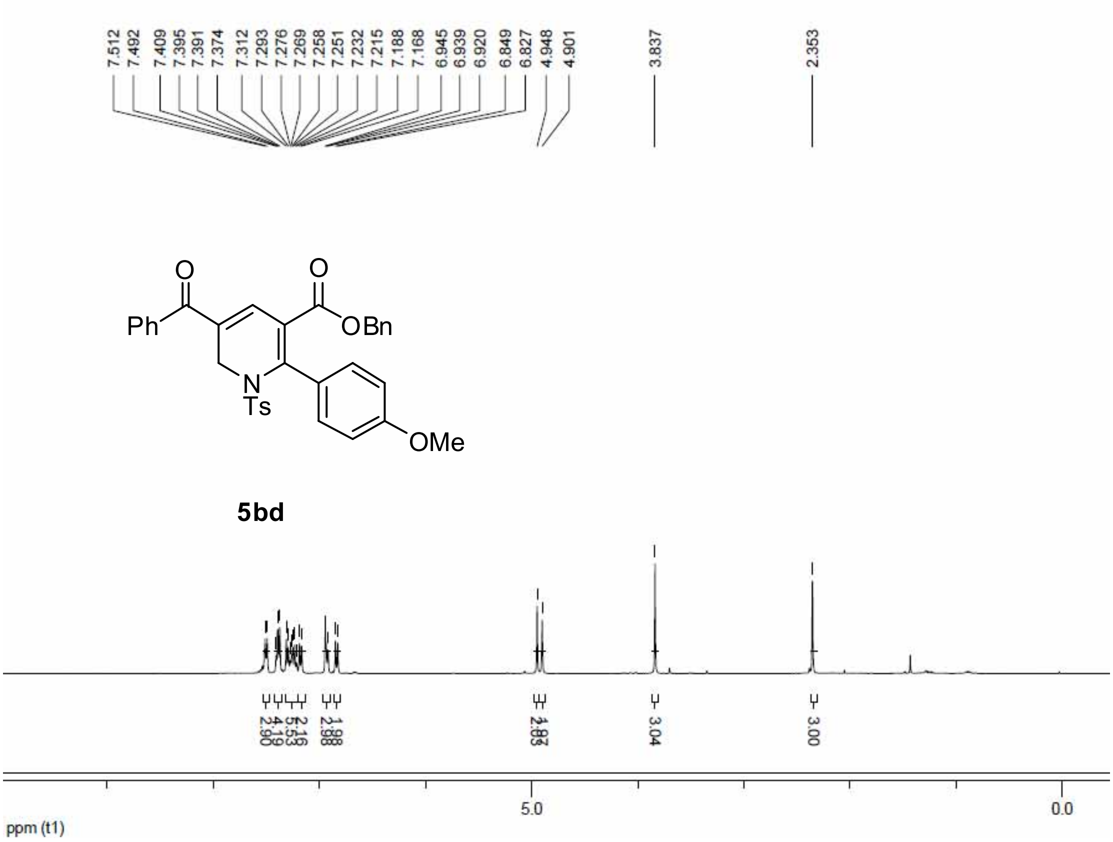

191.077
167.426
162.790
161.787
150.147
144.388
137.410
134.580
131.883
131.099
129.872
129.629
127.510
126.987
126.589
119.090
113.512
113.399
77.372
77.055
76.737
55.444
55.318
51.828
45.966
21.540
O
O
OMe
MeO
N
Ts
OMe
200
150
100
50
0
ppm (t1)

5cb

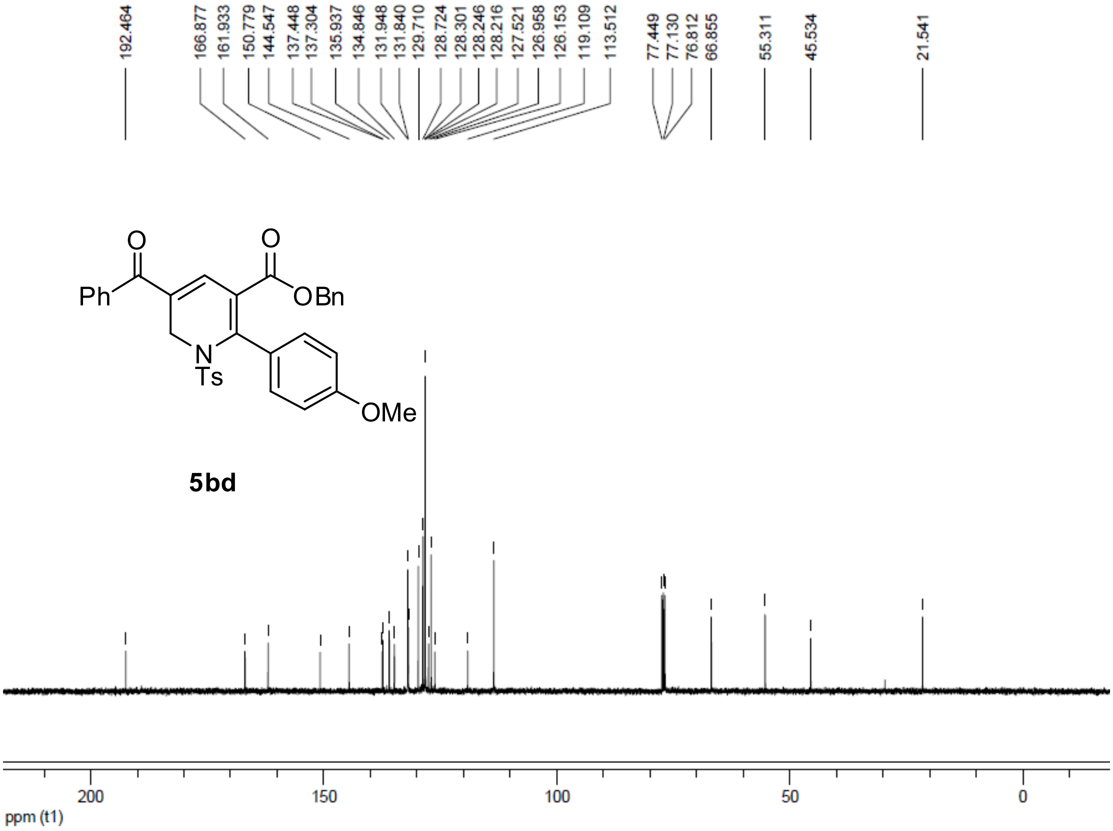

7.558
7.537
7.509
7.489
7.331
7.311
7.274
7.248
7.228
7.210
7.183
6.860
4.881
3.502
2.420
2.371
O
O
OMe
N
Ts
Br
5dc
2.38
2.08
3.03
0.98
2.04
3.00
3.24
5.0
0.0
ppm (t1)
192.158
166.709
149.136
144.728
142.802
137.086
134.434
134.380
134.297
131.441
131.200
129.764
128.976
128.928
127.371
126.922
125.217
120.571
77.357
77.039
76.721
52.005
45.641
21.554
O
O
OMe
N
Ts
Br
5dc
200
150
100
50
0
ppm (t1)


7.540
7.519
7.492
7.472
7.360
7.339
7.317
7.296
7.180
7.160
6.893
6.871
6.841
4.863
3.861
3.494
2.350
O
O
OMe
MeO
N
Ts
Br
5cc
2.07
2.15
1.97
3.07
3.00
3.05
5.0
0.0
ppm (t1)


191.043
166.737
162.961
148.920
144.687
137.158
134.293
133.645
131.460
131.179
131.153
129.750
129.630
127.505
126.938
125.161
120.572
113.593
77.384
77.065
76.748
55.474
52.011
45.924
21.573
O
O
OMe
MeO
N
Ts
Br
5cc
200
150
100
50
0
ppm (t1)

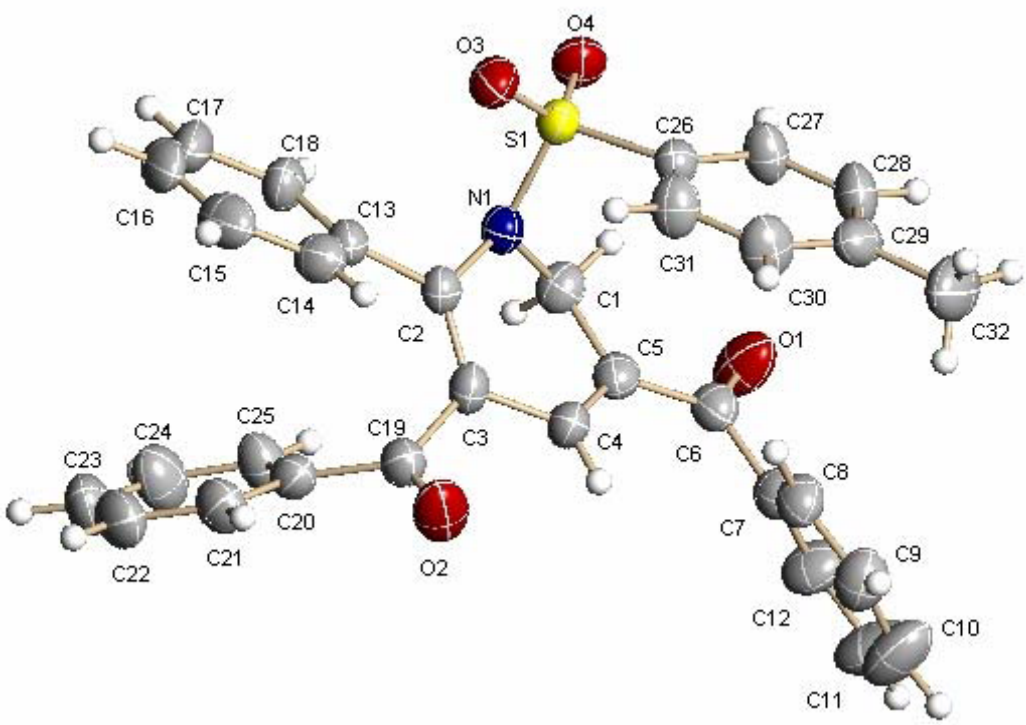

7.512
7.492
7.409
7.395
7.391
7.374
7.312
7.293
7.276
7.269
7.258
7.251
7.232
7.215
7.188
7.168
6.945
6.939
6.920
6.849
6.827
4.948
4.901
3.837
2.353
O
O
Ph
OBn
N
Ts
OMe
2.90
4.19
5.53
2.16
2.98
1.98
2.85
3.04
3.00
5.0
0.0
ppm (t1)

5bd


192.464
166.877
161.933
150.779
144.547
137.448
137.304
135.937
134.846
131.948
131.840
129.710
128.724
128.301
128.246
128.216
127.521
126.958
126.153
119.109
113.512
77.449
77.130
76.812
66.855
55.311
45.534
21.541
O
O
Ph
OBn
N
Ts
OMe
200
150
100
50
0
ppm (t1)

5bd

Ⅸ. Crystal Structure of 4ba



Chemical formula and formula weight (*M*)

C33H27Cl2NO4S, 604.52

Crystal system

Triclinic

Unit-cell dimensions (or pm, degrees) and volume, with estimated standard deviations, temperature

a = 6.7166(13) A alpha = 70.430(3) deg.

b = 12.567(3) A beta = 84.280(4) deg.

c = 18.230(4) A gamma = 81.087(4) deg.

Space group symbol

P-1

No. of formula units in unit cell (*Z*)

Z = 2. Calculated density = 1.404 Mg/m^3

Number of reflections measured and/or number of independent reflections, R_{int}

Final *R* values (and whether quoted for all or observed data)

[I>2sigma(I)] R1 = 0.0855, wR2 = 0.2767

CCDC 739301 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.