Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for:

Diboron as Reductant for Nickel-Catalyzed Reductive Coupling: Rational Design and Mechanistic Studies

Guoying Zhang, Yinjun Xie, Zhengkun Wang, Yang Liu, and Hanmin Huang*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China.

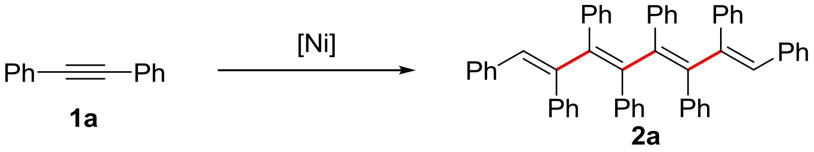
E-mail: hmhuang@licp.cas.cn

CONTENTS

1. General experiment details and materials

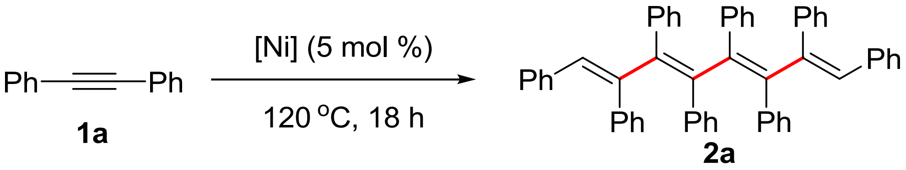
Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and refered to apparent peak multiplications. All the high-resolution mass spectrometry (HRMS) experiments were carried out using Bruker MicroTOF-QII mass instrument (ESI) or Agilent 6210 TOF mass spectrometer (APCI). IR spectra were recorded on a METTLER TOLEDO ReactIR 15 spectrometer. 1,2-Diphenylethyne were purchased from Alfa aesar. The other alkynes used here are known compounds and synthesized according to the reported methods.[1]

2. Optimization of the reaction conditions



1,2-Diphenylethyne **1a** (178.2 mg, 1.0 mmol), [Ni] (0.05 mmol, 5 mol %), additives and solvents (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvents was evaporated under reduced pressure, and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **2a** as a yellow solid.

Table S1. Optimization of the reaction conditions [a]

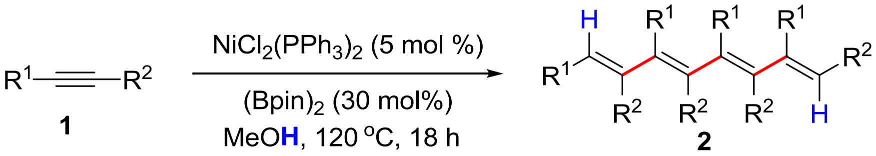


Entry	[Ni] (5 mol %)	Additive (equiv.)	Solvent	Yield (%)
1	$NiCl_2$	B_2pin_2 (1.0)	MeOH	<5
2	$NiCl_2(PPh_3)_2$	B_2pin_2 (1.0)	MeOH	87
3	$NiBr_2(PPh_3)_2$	B_2pin_2 (1.0)	MeOH	69
4	$NiI_2(PPh_3)_2$	B_2pin_2 (1.0)	MeOH	35
5	$NiCl_2$(dppe)	B_2pin_2 (1.0)	MeOH	37
6	$Ni(COD)_2$	B_2pin_2 (1.0)	MeOH	79[b]
7	$NiCl_2(PPh_3)_2$	$BF_3{\cdot}Et_2O$ (1.0)	MeOH	0
8	$NiCl_2(PPh_3)_2$	$B(OEt)_3$ (1.0)	MeOH	0
9	$NiCl_2(PPh_3)_2$	BEt_3 (1.0)	MeOH	0
10	$NiCl_2(PPh_3)_2$	HBpin (1.0)	MeOH	<5
11	$NiCl_2(PPh_3)_2$	$HSiEt_3$ (1.0)	MeOH	<5
12	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.6)	MeOH	86
13	**$NiCl_2(PPh_3)_2$**	**B_2pin_2 (0.3)**	**MeOH**	**89**
14	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.2)	MeOH	80
15	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.1)	MeOH	23

16	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.3)	EtOH	76
17	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.3)	PrOH	83
18	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.3)	*i*-PrOH	<5
19	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.3)	$MeNO_2$	0
20	$NiCl_2(PPh_3)_2$	B_2pin_2 (0.3)	DCE	0
21	--	B_2pin_2 (0.3)	MeOH	0
22	$NiCl_2(PPh_3)_2$	--	MeOH	0

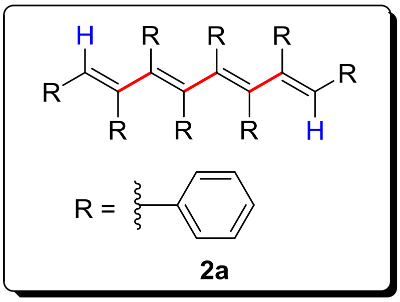
[a] General conditions: **1a** (178.2 mg, 1.0 mmol), [Ni] (0.05 mmol, 5 mol%), additive, solvent (1.0 mL), Ar, 120 °C for 18 h, isolated yield, unless otherwise noted. [b] Added PPh_3 (26.2 mg, 0.10 mmol, 10 mol%)

3. General procedure for the tetramerization



1,2-Diphenylethyne **1** (1.0 mmol), $NiCl_2(PPh_3)_2$ (32.7 mg, 0.05 mmol, 5 mol %), B_2pin_2 (76.2 mg, 0.3 mmol, 30 mol %) and MeOH (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvents were evaporated under reduced pressure, and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1 − 5/1) to afford the desired product **2**.

4. Experimental characterization data for products



(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octaphenyl-1,3,5,7-octatetraene (2a): The title compound was prepared according to the general procedure as a yellow solid, 158.7 mg, 89% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.33 (s, 2H), 6.86-6.92 (m, 6H), 7.00-7.11 (m, 30H), 7.58 (d, *J* = 7.6 Hz, 4H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 126.2, 126.5, 126.6, 126.7, 127.3, 127.4, 127.7, 127.8, 129.0, 129.7, 130.0, 130.3, 133.7, 137.8, 139.1, 141.3, 142.0, 142.5, 142.7, 145.3; **HRMS** (APCI) calcd. for $C_{56}H_{43}$ [M+H]: 715.3359, found: 715.3344.

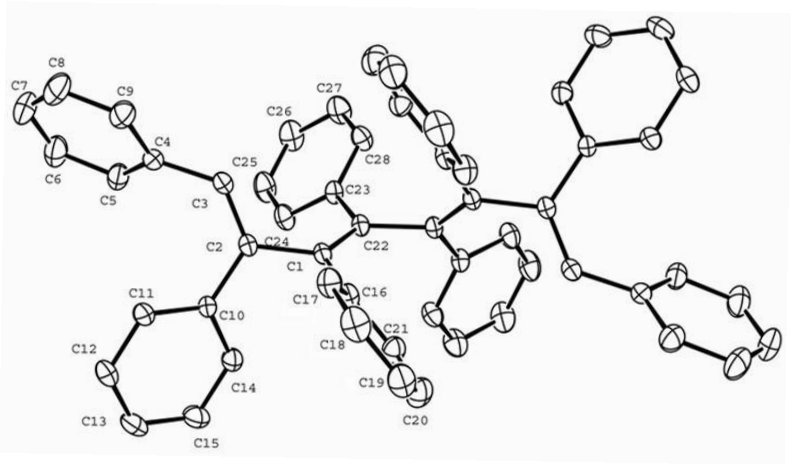
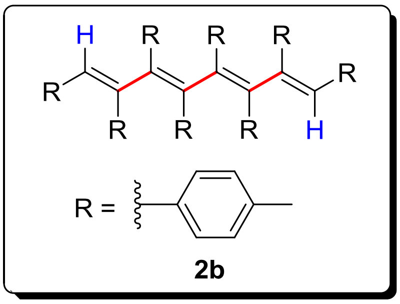
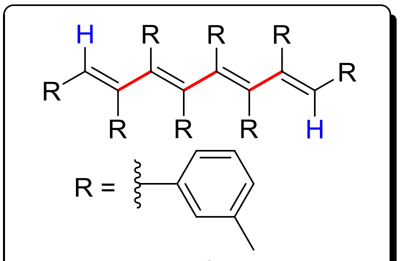


Figure S1. ORTEP drawing of product **2a**

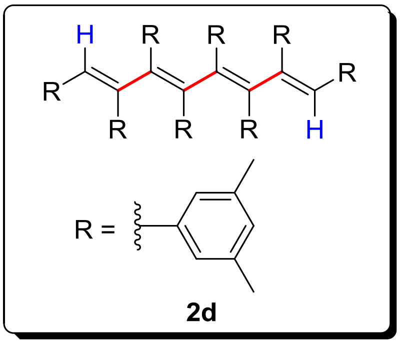


(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(4-methylphenyl)-1,3,5,7-octatetraene (2b): The title compound was prepared according to the general procedure as a yellow solid, 169.9 mg, 82% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 2.13-2.25 (s, 24H), 6.22 (s, 2H), 6.80-6.93 (m, 24H), 7.04 (d, *J* = 7.6 Hz, 4H), 7.58 (d, *J* = 7.6 Hz, 4H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 21.1, 21.2, 21.3, 127.2, 127.7, 128.1, 128.4, 128.5, 128.8, 129.5, 129.9, 130.1, 131.3, 131.9, 135.4, 135.5, 135.6, 135.9, 136.1, 136.2, 138.4, 138.8, 141.4, 141.7, 144.1; **HRMS** (APCI) calcd. for $C_{64}H_{59}$ [M+H]: 827.4611, found: 827.4601.



2c

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(3-methylphenyl)-1,3,5,7-octatetraene (2c): The title compound was prepared according to the general procedure as a yellow solid, 140.2 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.10-2.17 (s, 24H), 6.22 (s, 2H), 6.62-6.70 (m, 6H), 6.79-7.02 (m, 22H), 7.19-7.25 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.3, 21.3, 21.6, 126.0, 126.5, 126.8, 126.9, 126.9, 127.0, 127.0, 127.1, 127.2, 127.3, 127.5, 129.9, 130.2, 131.0, 131.2, 133.1, 135.8, 136.2, 136.6, 137.1, 138.0, 139.6, 141.8, 142.6, 143.1, 143.2, 145.2; **HRMS** (APCI) calcd. for $C_{64}H_{59}$ [M+H]: 827.4611, found: 827.4601



2d

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(3,5-dimethylphenyl)-1,3,5,7-octatetraene (2d): The title compound was prepared according to the general procedure as a yellow solid, 180.7 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.06 -2.07 (m, 36H), 2.15 (s, 12H), 6.08 (s, 2H), 6.41 (s, 2H), 6.48 (s, 4H), 6.55-6.63 (m, 10H), 6.68 (s, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.0, 21.1, 21.4, 126.7, 126.9, 127.4, 127.6, 127.7, 127.8, 128.0, 128.2, 132.6, 135.1, 135.8, 136.0, 136.7, 138.1, 140.1, 143.0, 143.4, 144.2, 144.8, 146.1; **HRMS** (APCI) calcd. for $C_{72}H_{75}$ [M+H]: 939.5863, found: 939.5894.

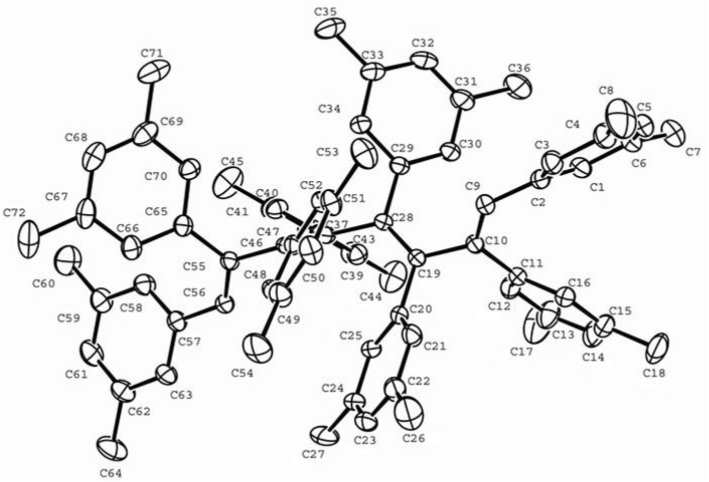
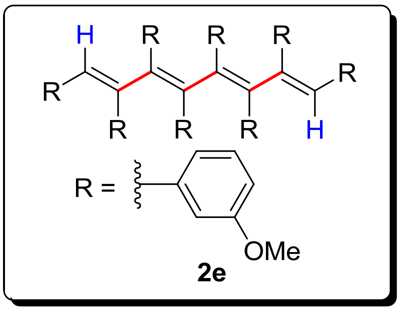


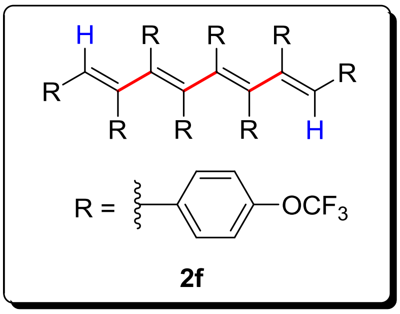
Figure S2. ORTEP drawing of product **2d**

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(4-methoxyphenyl)-1,3,5,7-octatetraene (2e):



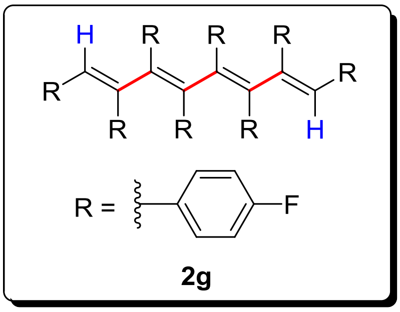
The title compound was prepared according to the general procedure as a yellow solid, 178.9 mg, 75% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 3.51-3.54 (m, 12H), 3.62-3.63 (m, 12H), 6.32 (s, 2H), 6.41 (s, 2H), 6.47-6.62 (m, 14H), 6.73 (d, J = 7.6 Hz, 2H), 6.90 (d, J = 5.6 Hz, 2H), 6.96-7.05 (m, 8H), 7.10 (s, 2H), 7.16 (d, J = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 54.8, 54.9, 55,0, 112.1, 112.2, 112.9, 113.1, 113.8, 115.1, 115.4, 115.8, 121.7, 122.4, 122.6, 128.0, 128.2, 128.7, 128.8, 133.6, 139.1, 140.4, 142.6, 142.6, 143.5, 145.0, 158.7, 158.8, 158.8, 159.0; **HRMS** (APCI) calcd. for $C_{64}H_{59}O_8$ [M+H]: 955.4204, found: 955.4203.

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(4-trifluoromethoxyphenyl)-1,3,5,7-octatetraene



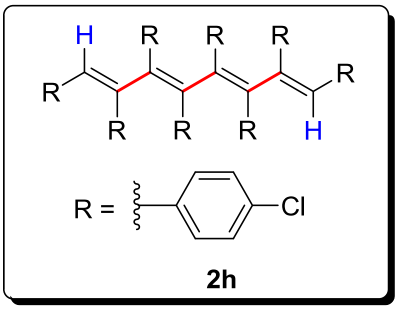
(2f): The title compound was prepared according to the general procedure as a yellow solid, 280.0 mg, 81% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.24 (s, 2H), 6.74-6.92 (m, 24H), 7.00-7.02 (m, 4H), 7.16-7.18 (m, 4H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 116.5, 116.5, 116.6, 119.0, 119.1, 119.2, 120.0, 120.4, 120.7, 121.6, 121.6, 121.7, 124.2, 124.2, 124.3, 130.2, 130.9, 131.1, 134.7, 135.0, 137.8, 141.5, 141.6, 143.1, 144.1, 147.2, 147.6, 147.6, 148.0, 148.0, 148.2, 148.2, 148.4, 148.5; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -58.2, -58.1, -58.0; **HRMS** (APCI) calcd. for $C_{64}H_{34}F_{24}O_8$ [M]: 1386.1876, found: 1386.1834.

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(4-fluorophenyl)-1,3,5,7-octatetraene (2g): The title compound was prepared according to the general procedure as a yellow solid, 117.4 mg, 83% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.20 (s, 2H), 6.72-6.83 (m, 20H), 6.86-6.89 (m, 4H), 7.02-7.06 (m, 4H), 7.25-7.29 (m, 4H); **^{13}C NMR** (100 MHz,



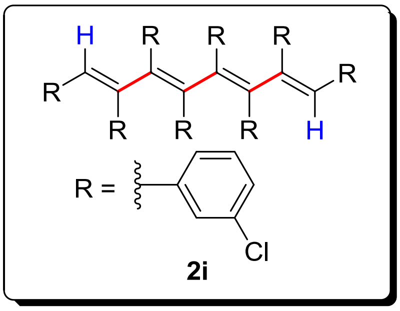
$CDCl_3$) δ 114.5, 114.8, 115.0, 115.2, 130.5, 130.6, 131.1, 131.1, 131.4, 131.5, 132.8, 132.8, 133.5, 134.7, 134.8, 137.5, 137.5, 138.0, 141.5, 142.2, 145.1, 160.0, 160.4, 160.5, 160.6, 162.4, 162.8, 163.0, 163.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.8, -114.2, -114.0, -114.0; **HRMS** (APCI) calcd. for $C_{56}H_{34}F_8$ [M]: 858.2538, found: 858.2529.

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(4-chlorophenyl)-1,3,5,7-octatetraene (2h): The title compound was prepared according to the general procedure as a yellow solid, 157.8 mg, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.18 (s, 2H), 6.73 (d, *J* = 8.4 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 4H), 6.95 (d, *J* = 8.4 Hz, 4H), 7.02-7.10 (m, 16H), 7.23-7.25 (d, *J* = 8.4 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 128.0, 128.0, 128.4, 128.5, 130.2, 130.7, 130.8, 131.1, 132.7, 133.3, 134.0, 134.9, 136.8, 139.4, 139.9, 141.6, 142.2, 145.3; **HRMS** (APCI) calcd. for $C_{56}H_{35}Cl_8$ [M+H]: 987.0247, found: 987.0245.



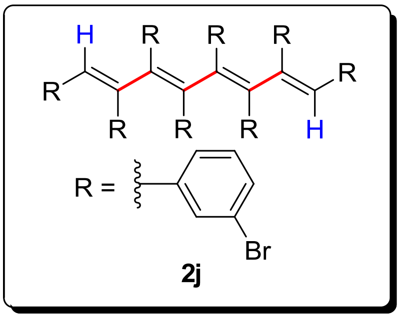
2h

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(3-chlorophenyl)-1,3,5,7-octatetraene (2i): The title compound was prepared according to the general procedure as a yellow solid, 197.1 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.27 (s, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.88-7.14 (m, 30H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 126.9, 127.1, 127.4, 127.5, 127.7, 128.0, 128.9, 129.1, 129.2, 129.3, 129.4, 129.8, 129.9, 133.5, 133.8, 134.0, 134.0, 134.8, 138.1, 140.3, 142.3, 143.0, 143.2, 143.5, 146.0; **HRMS** (APCI) calcd. for $C_{56}H_{35}Cl_8$ [M+H]: 987.0247, found: 987.0251.



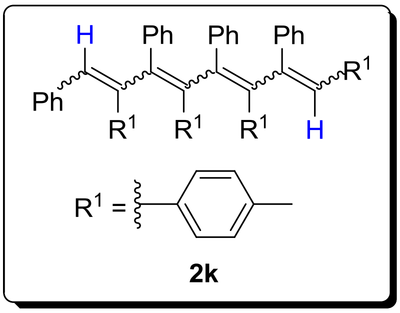
2i

(1*E*,3*E*,5*E*,7*E*)-1,2,3,4,5,6,7,8-Octa(4-brorophenyl)-1,3,5,7-octatetraene (2j): The title compound was prepared according to the general procedure as a yellow solid, 151.2 mg, 45% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.24 (s, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.86-7.11 (m, 21H), 7.18-7.20 (m, 4H), 7.25 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 121.7, 122.1, 122.1, 127.5, 127.7, 128.2, 128.4, 129.0, 129.4, 129.6, 129.6, 129.7, 130.3, 130.4, 130.6, 132.1, 132.3, 132.6, 133.0, 134.8, 138.3, 140.7, 142.6, 143.7, 143.8, 144.0, 146.4; **HRMS** (APCI) calcd. for $C_{56}H_{35}Br_8$ [M+H]: 1338.62, found: 1338.6155.



2j

1,2,3,4,5,6,7,8-Octa(4-brorophenyl)-1,3,5,7-octatetraene (2k): The title compound was prepared according to the general procedure as a yellow solid, 163.2 mg, 85% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 2.12-2.25 (m, 12H), 6.25-6.32 (m, 2H), 6.75-6.96 (m, 14H), 6.70-7.11 (m, 18H), 7.55-7.65 (m, 4H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 21.2, 126.3, 126.5, 127.1, 127.1, 127.4, 127.6, 127.7, 127.8, 128.2, 128.5, 128.5, 128.9, 129.0, 129.0, 129.6, 129.9, 129.9, 130.0, 130.2, 130.3, 132.2, 132.9, 135.8, 135.9, 136.2, 136.3, 138.2, 138.3, 138.6, 138.6, 139.4, 141.9, 142.3, 144.2; **HRMS** (APCI) calcd. for $C_{60}H_{51}$ [M+H]: 771.3985, found: 771.3993.

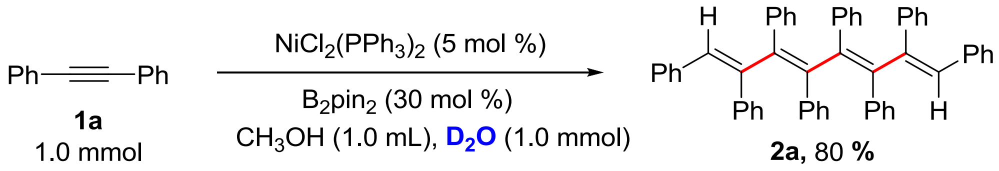


2k

5. Mechanistic studies

5.1 D-Labelled experiments

5.1.1 Tetramerization in CH_3OH with D_2O as additive



1,2-Diphenylethyne **1a** (178.2 mg, 1.0 mmol), $NiCl_2(PPh_3)_2$ (32.7 mg, 0.05 mmol, 5 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 30 mol%), CH_3OH (1.0 mL) and D_2O (20.0 mg, 1.0 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 ^oC for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **2a** as a yellow solid (142.6 mg, 80 %). The product was characterized by NMR and HRMS (APCI) (Figure S3 and S4).

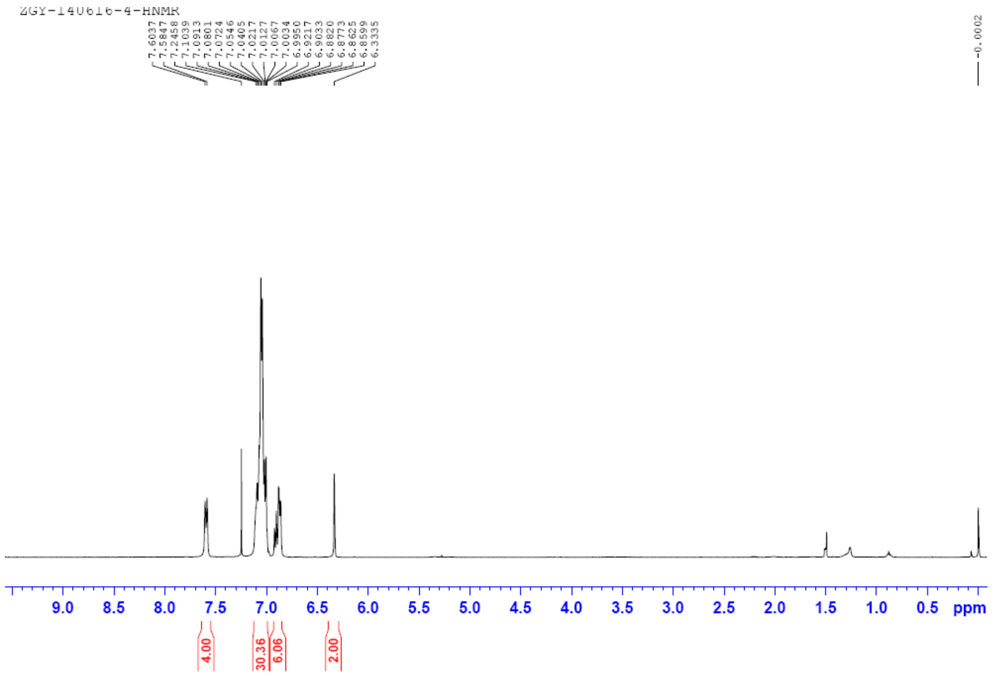


Figure S3. ^1H NMR of the product **2a**

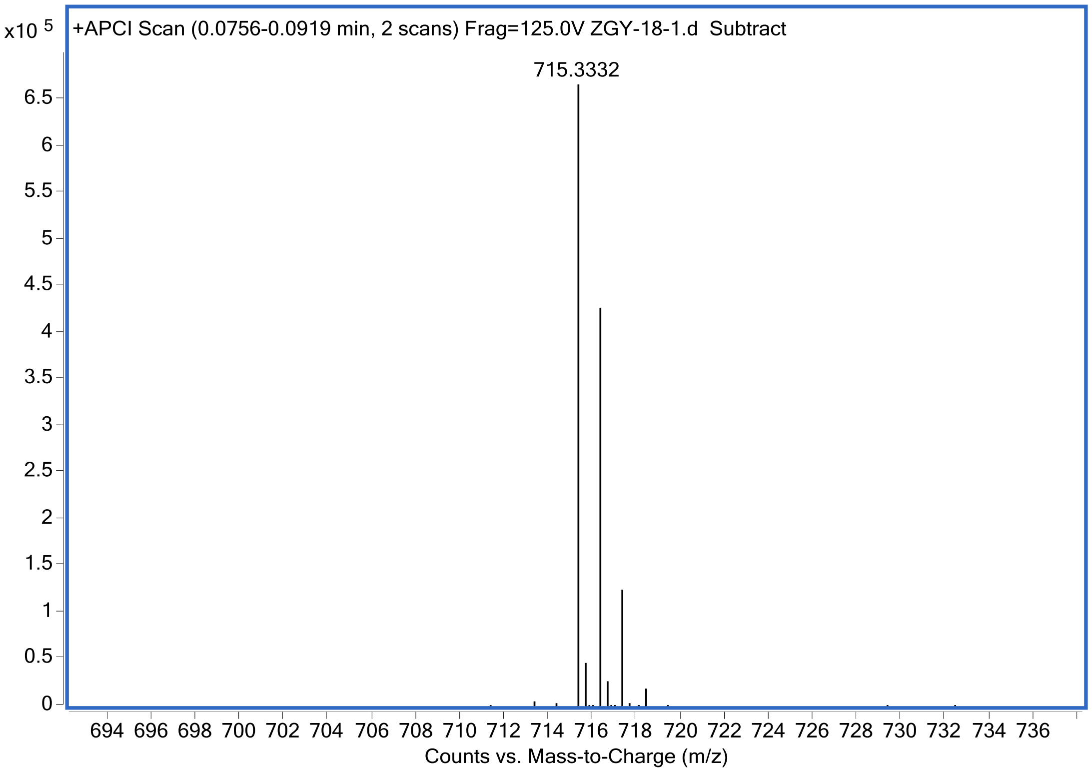
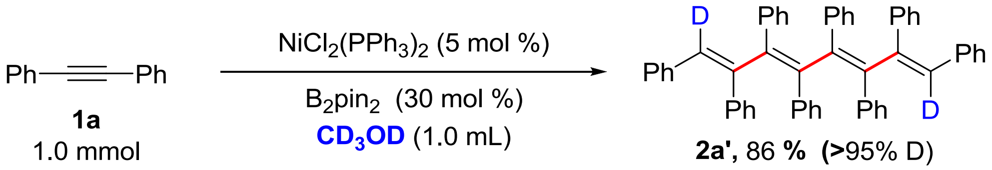


Figure S4. HRMS (APCI) of the product **2a**

5.1.2 Tetramerization in CD_3OD



1,2-Diphenylethyne **1a** (178.2 mg, 1.0 mmol), $NiCl_2(PPh_3)_2$ (32.7 mg, 0.05 mmol, 5 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 30 mol%) and CD_3OD (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **2a’** as a yellow solid (155.1 mg, 86 %, > 95% D). The compound was characterized by NMR and HRMS (APCI) (Figure S5 and S6).

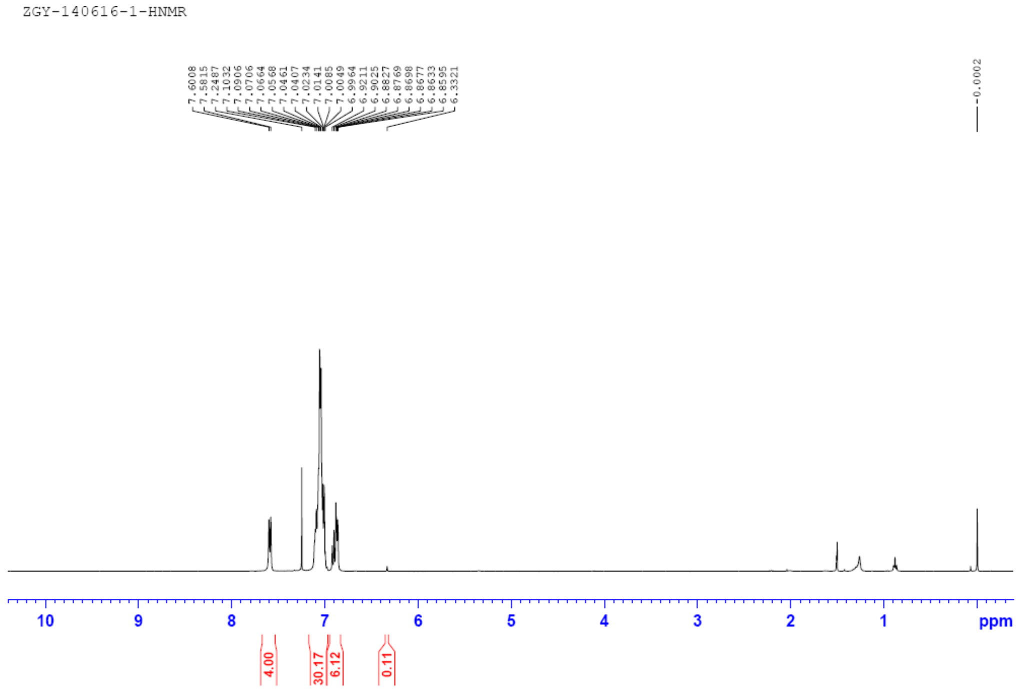


Figure S5. ^{1}H NMR of the product **2a’**

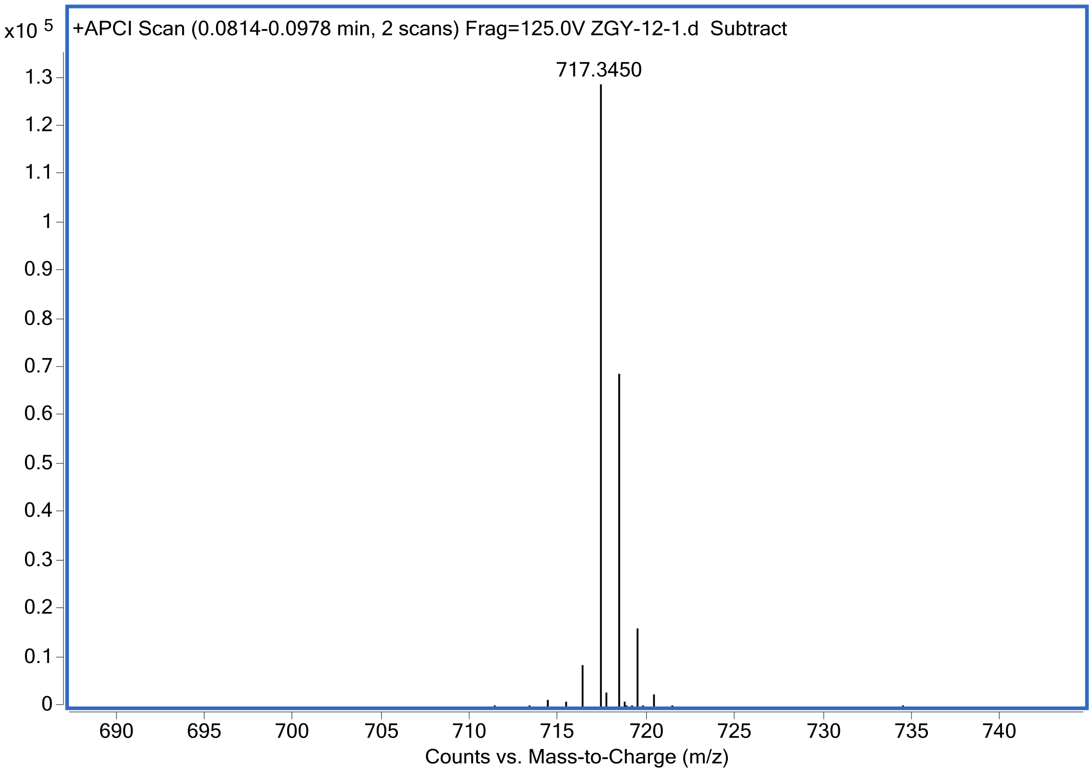
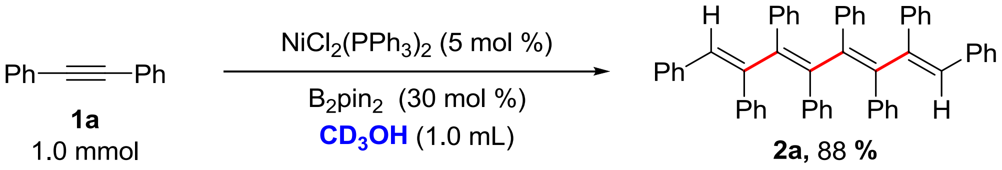


Figure S6. HRMS (APCI) of the product **2a’**

5.1.3 Tetramerization in CD_3OH



1,2-Diphenylethyne **1a** (178.2 mg, 1.0 mmol), $NiCl_2(PPh_3)_2$ (32.7 mg, 0.05 mmol, 5 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 30 mol%) and CD_3OH (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **2a** as a yellow solid (156.9 mg, 88 %). The compound was characterized by NMR and HRMS (APCI) (Figure S7 and S8).

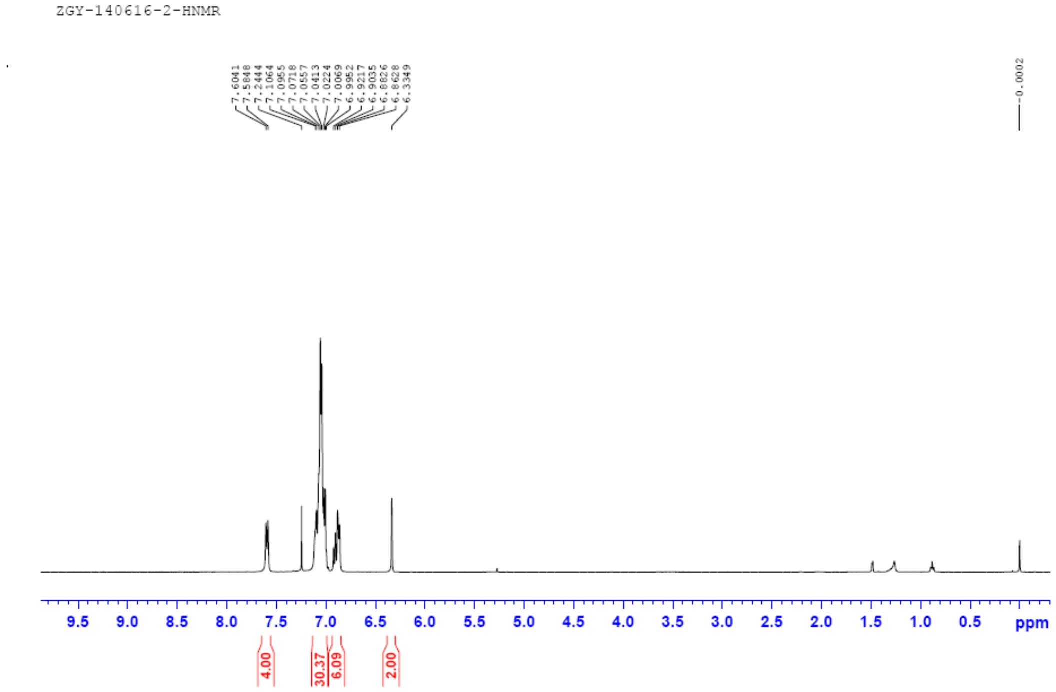


Figure S7. ^{1}H NMR of the product **2a**

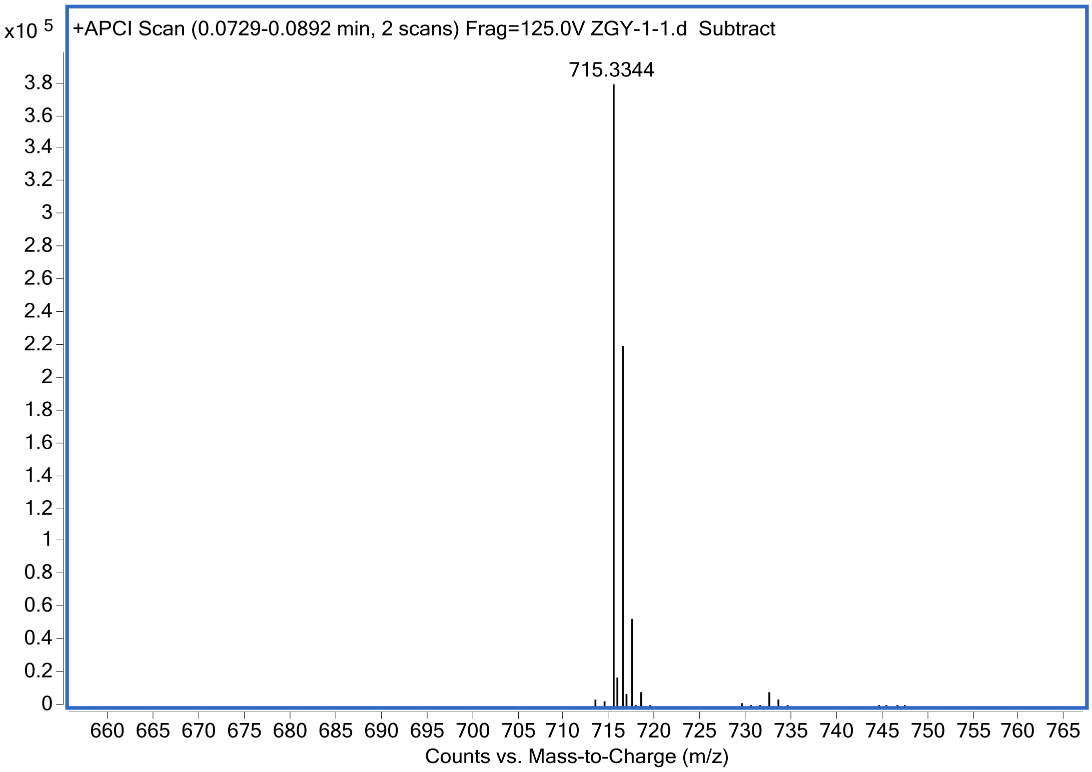
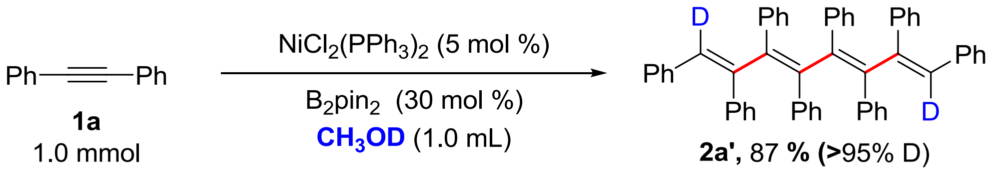


Figure S8. HRMS (APCI) of the product **2a**

5.1.4 Tetramerization in CH_3OD



1a
1.0 mmol

2a', 87 **%** (>95% D)

1,2-Diphenylethyne **1a** (178.2 mg, 1.0 mmol), $NiCl_2(PPh_3)_2$ (32.7 mg, 0.05 mmol, 5 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 30 mol%) and CH_3OD (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 ^{o}C for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **2a'** as a yellow solid (156.8 mg, 87 %, > 95% D). The compound was characterized by NMR and HRMS (APCI) (Figure S9 and S10).

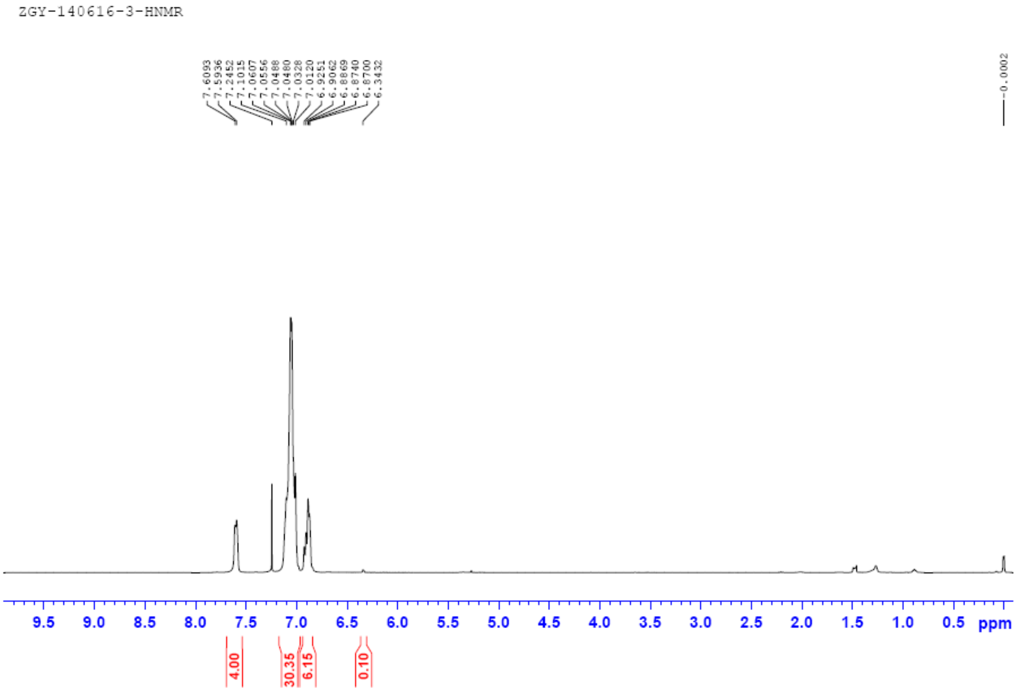


Figure S9. ^{1}H NMR of the product **2a’**

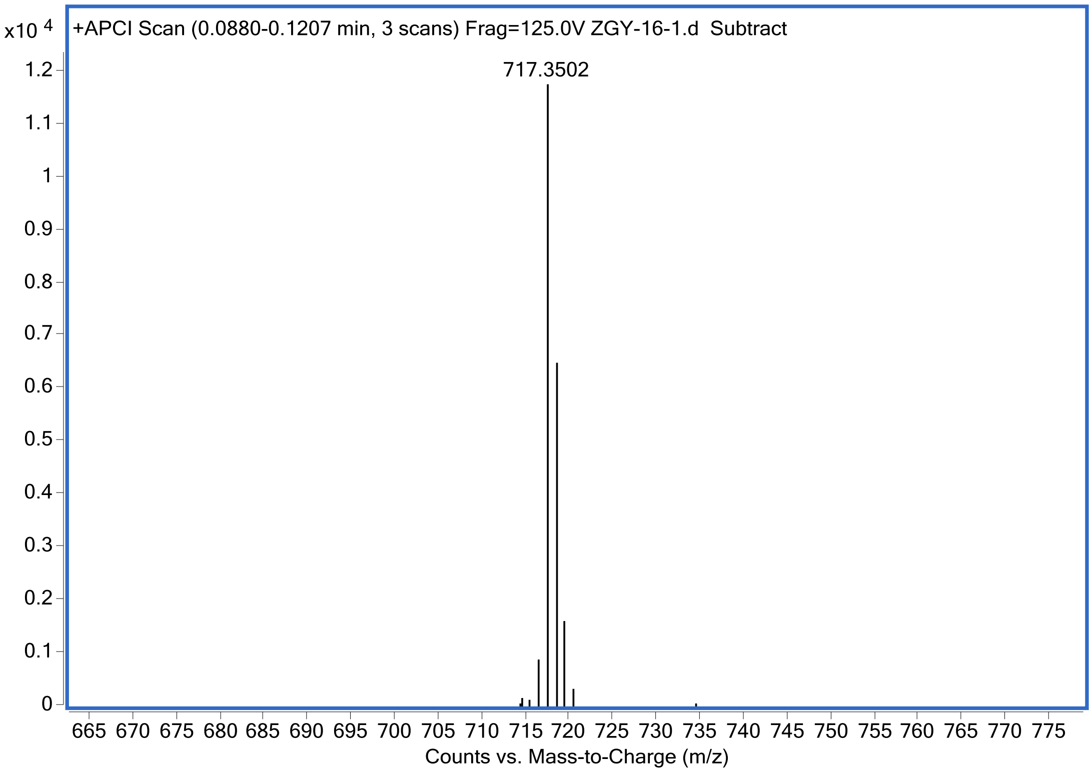
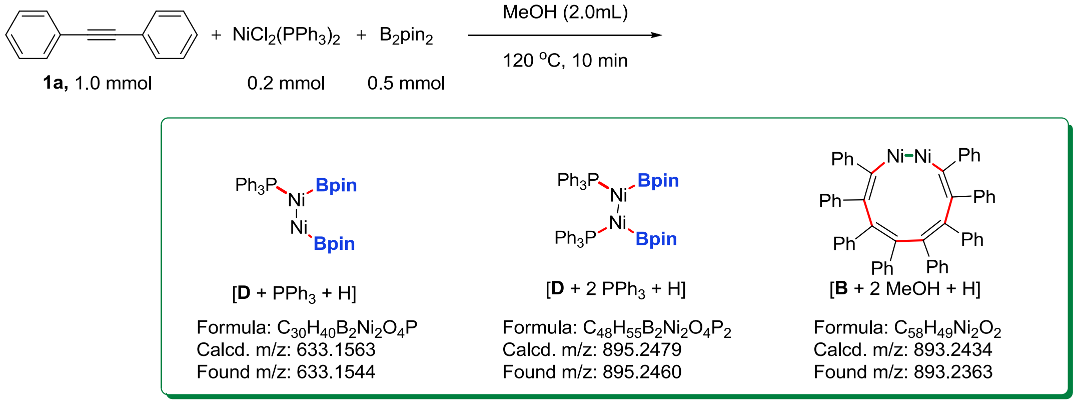


Figure S10. HRMS (APCI) of the product **2a’**

5.2 HRMS (ESI) studies:



Formula: $C_{30}H_{40}B_2Ni_2O_4P$
Calcd. m/z: 633.1563
Found m/z: 633.1544

Formula: $C_{48}H_{55}B_2Ni_2O_4P_2$
Calcd. m/z: 895.2479
Found m/z: 895.2460

Formula: $C_{58}H_{49}Ni_2O_2$
Calcd. m/z: 893.2434
Found m/z: 893.2363

1,2-Diphenylethyne **1a** (178.2 mg, 1.0 mmol), $NiCl_2(PPh_3)_2$ (130.8 mg, 0.2 mmol), B_2pin_2 (114.3 mg, 0.5 mmol) and MeOH (2.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 10 minutes, some reaction mixture was taken and inject to HRMS. The HRMS (ESI) spectrum was shown in Figure S11, Figure S13 and Figure S15. Three strong peaks at *m*/*z*= 633.1563, 893.2363 and 895.2460 were observed, which were correspond to the mass of dinuclear Ni-Ni complexes [**D** + PPh_3 + H]$^+$, [**B** + 2 MeOH+ H]$^+$ and [**D** + 2 PPh_3 + H]$^+$.

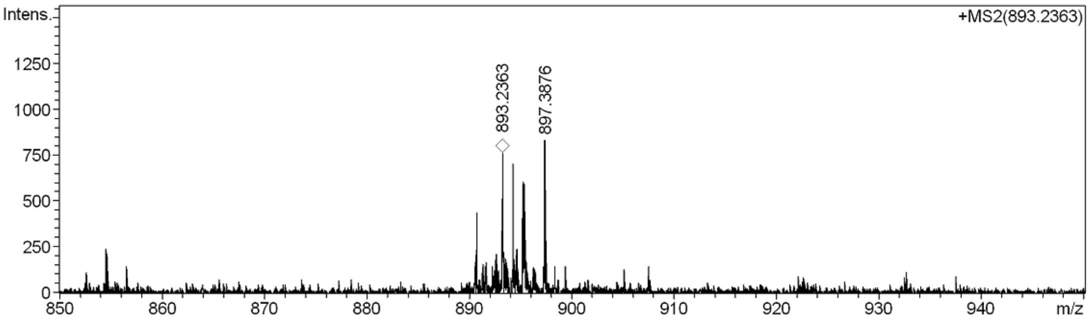


Figure S11. HRMS (ESI) spectrum of [**B** + 2 MeOH + H]$^+$.

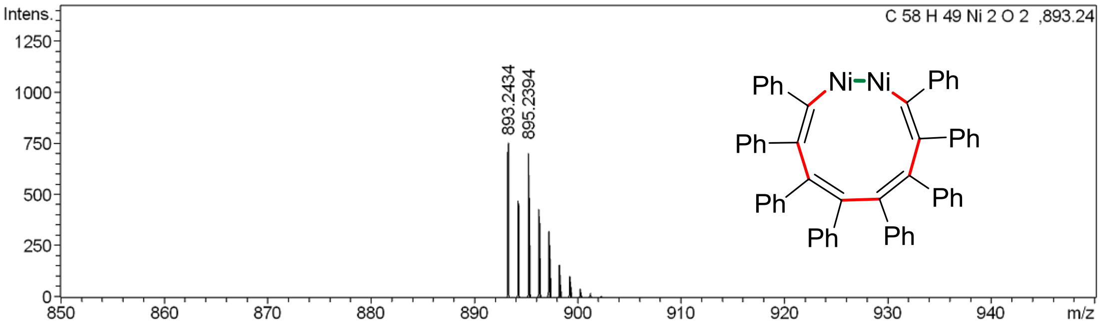


Figure S12. Calcd. HRMS (ESI) spectrum of [**B** + 2 MeOH + H]$^+$.

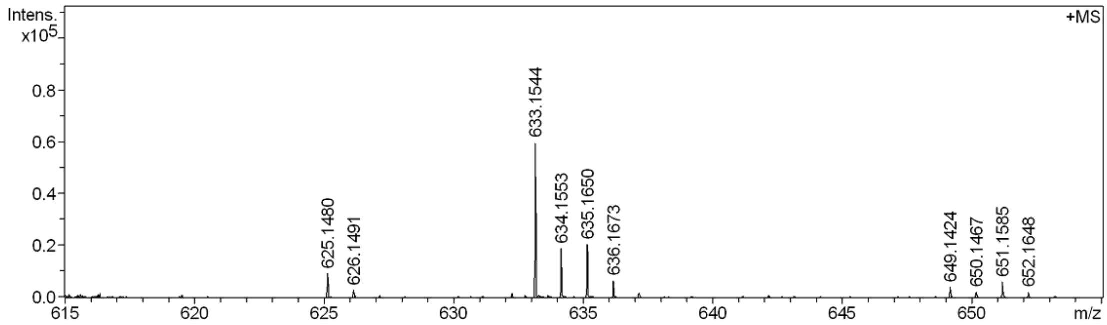


Figure S13. HRMS (ESI) spectrum of [**D** + PPh_3 + H]$^+$.

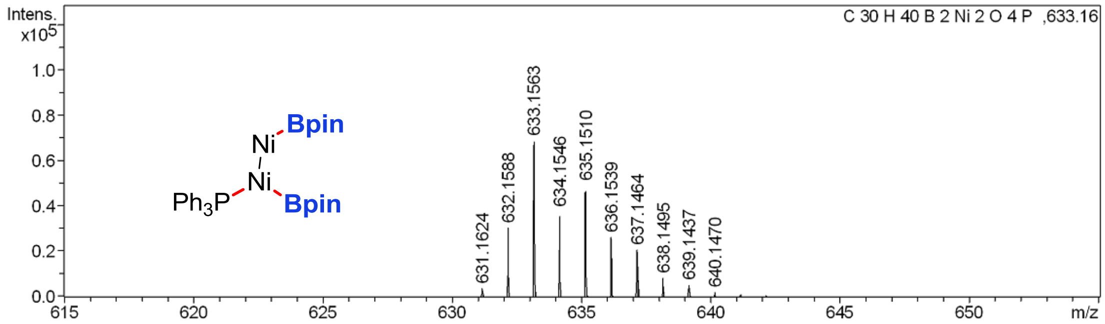


Figure S14. Calcd. HRMS (ESI) spectrum of [**D** + PPh_3 + H]$^+$.

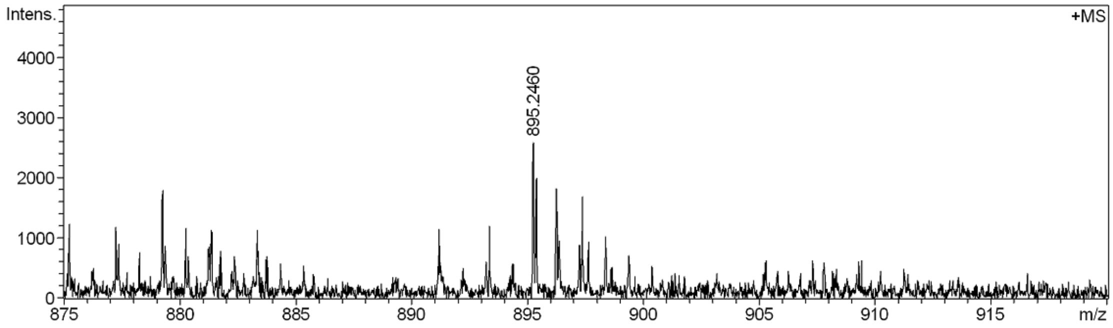


Figure S15. HRMS (ESI) spectrum of [**D** + 2 PPh_3 + H]$^+$.

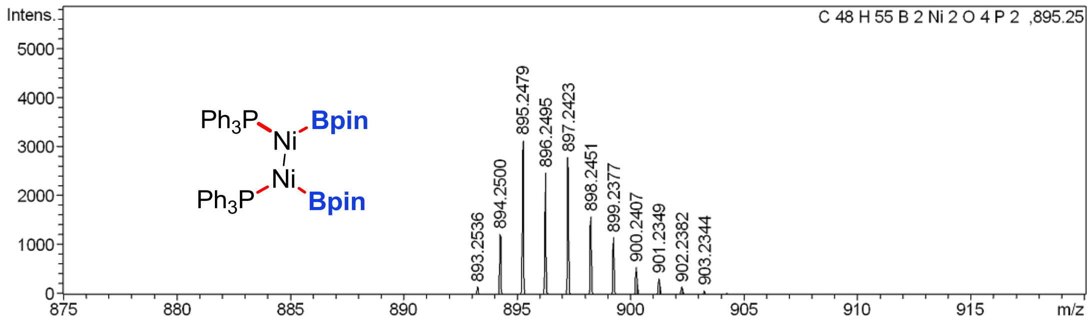


Figure S16. Calcd. HRMS (ESI) spectrum of [**D** + 2 PPh_3 + H]$^+$.

The result of two stage mass spectrometry indicated that the peak *m*/*z* = 633.1544 was recognized as [**D** + PPh_3 + H]$^+$.

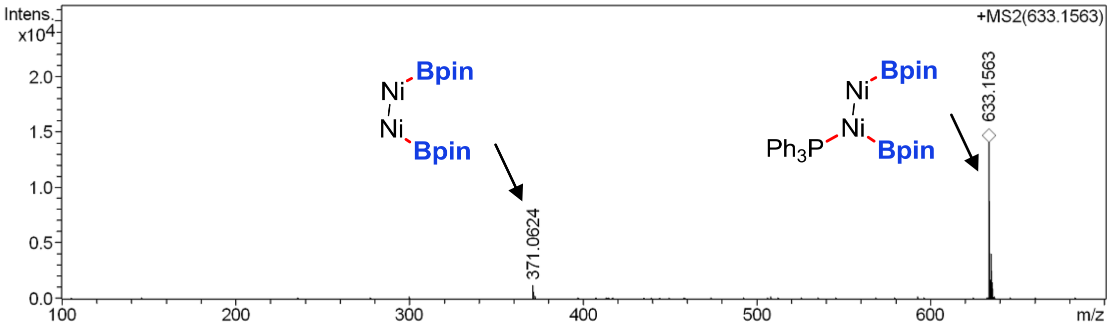


Figure S17. Two stage mass spectrum of the peak *m*/*z* = 633.1544.

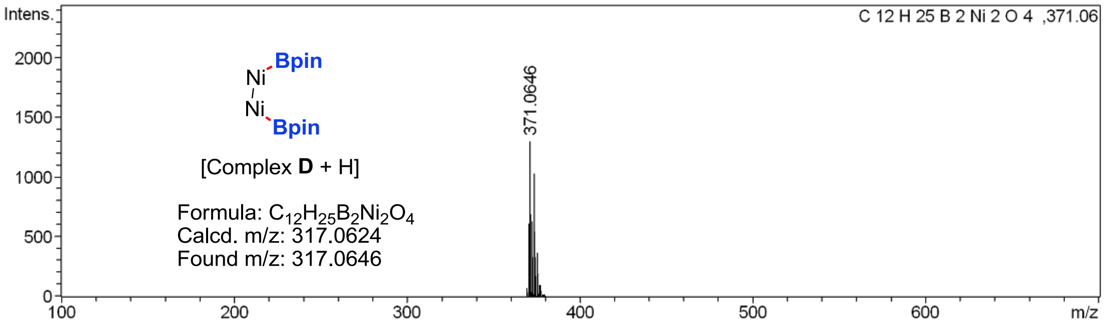


Figure S18. Calcd. HRMS (ESI) spectrum of [**D** + H]$^+$.

The result of two stage mass spectrometry indicated that the peak *m*/*z* = 895.2460 was recognized as [**D** + 2 PPh_3 + H]$^+$.

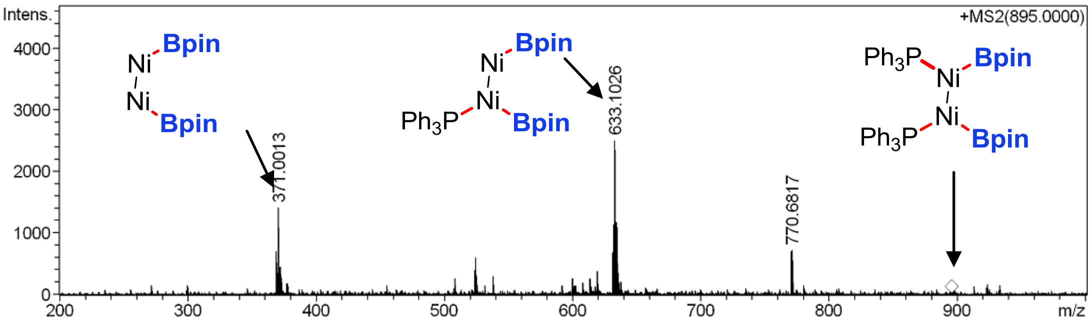
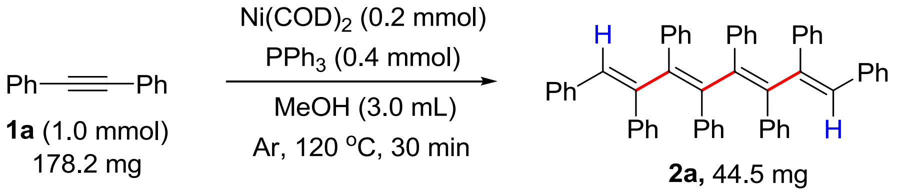


Figure S19. Two stage mass spectrum of the peak *m*/*z* = 895.2460

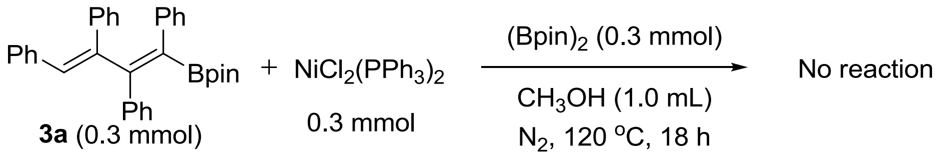
5.3 Stoichiometric reaction:

5.3.1 Stoichiometric reaction of 1a with Ni(COD)$_2$



Ni(COD)$_2$ (55.2 mg, 0.2 mmol), PPh$_3$ (104.8 mg, 0.4 mmol, 2.0 equiv) and CH$_3$OH (3.0 mL) were added to a 25 mL flame-dried Young-type tube in glove box. The mixture was stirred at 120 °C for 30 minutes. After cooling to room temperature, 1,2-diphenylethyne **1a** (178.2 mg, 1.0 mmol, 5.0 equiv) was added and stirred at 120 °C for 24 hours. After cooling to room temperature, the solvents was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **2a** as a yellow solid (44.5 mg).

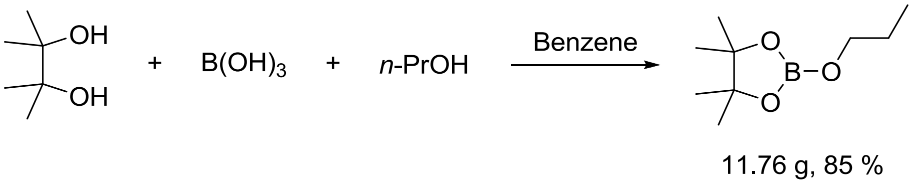
5.3.2 Stoichiometric reaction of 3a with NiCl$_2$(PPh$_3$)$_2$



3a (145.3 mg, 0.3 mmol), NiCl$_2$(PPh$_3$)$_2$ (196.2 mg, 0.3 mmol), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol%) and CH$_3$OH (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. No **2a** was detected.

6. Kinetic experiments

Synthesis of 2-propoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (*n*-PrOBpin)[2]

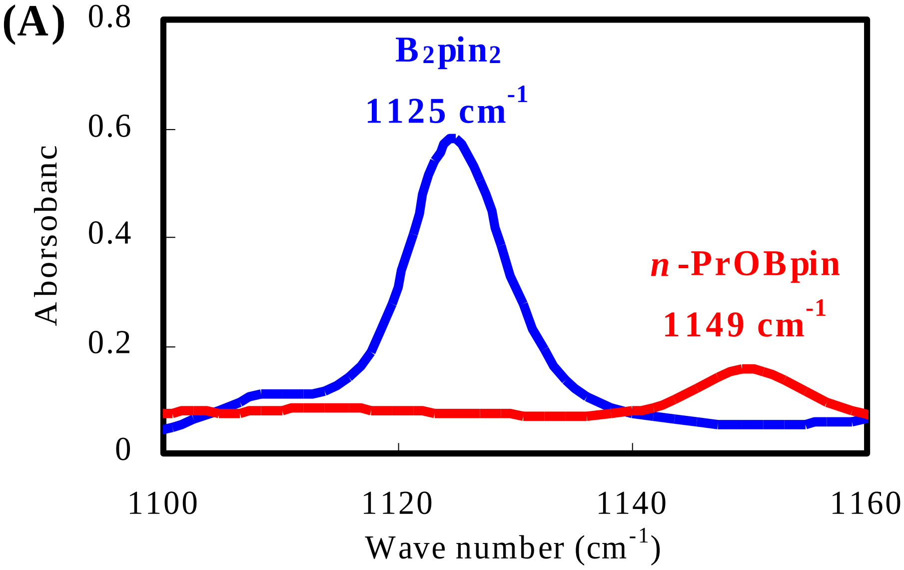


Boric acid (4.96 g, 80 mmol), dry *n*-propanol (24.04 g, 400 mmol), pinacol (9.44g, 80mmol) and benzene (50 mL) were added to a 100 mL flame-dried reactor. After stirring at room temperature for 30 minutes, the *n*-propanol/water/benzene ternary azeotrope was distilled off for 12 hours, and most of the residual benzene was removed *in vacuo* at 30 ℃. The crude product was distilled to give the title compound as a colourless liquid (11.76 g, 85%).

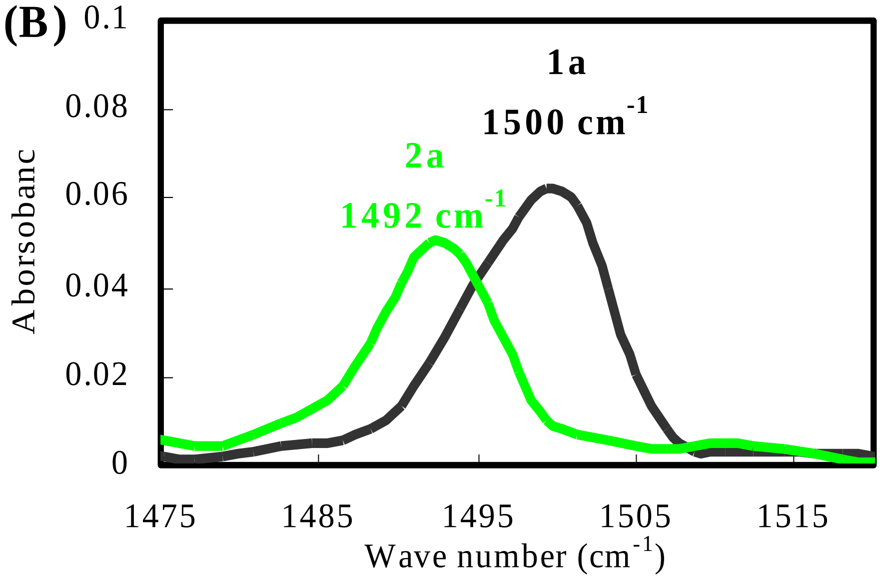
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 0.80-0.85 (m, 3H), 1.16-1.17 (m, 12H), 1.47-1.52 (m, 2H), 3.69-3.73 (m, 2H).

^{13}**C NMR** (100 MHz, $CDCl_3$) δ 10.0, 24.4, 24.6, 66.4, 82.4.

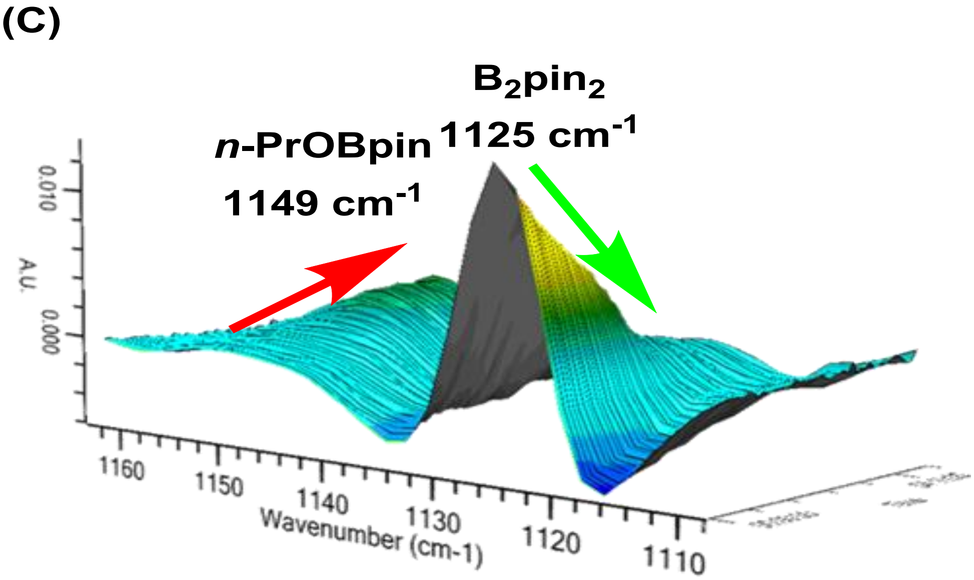
6.1 The standard IR spectra and the reactions in *n*-PrOH



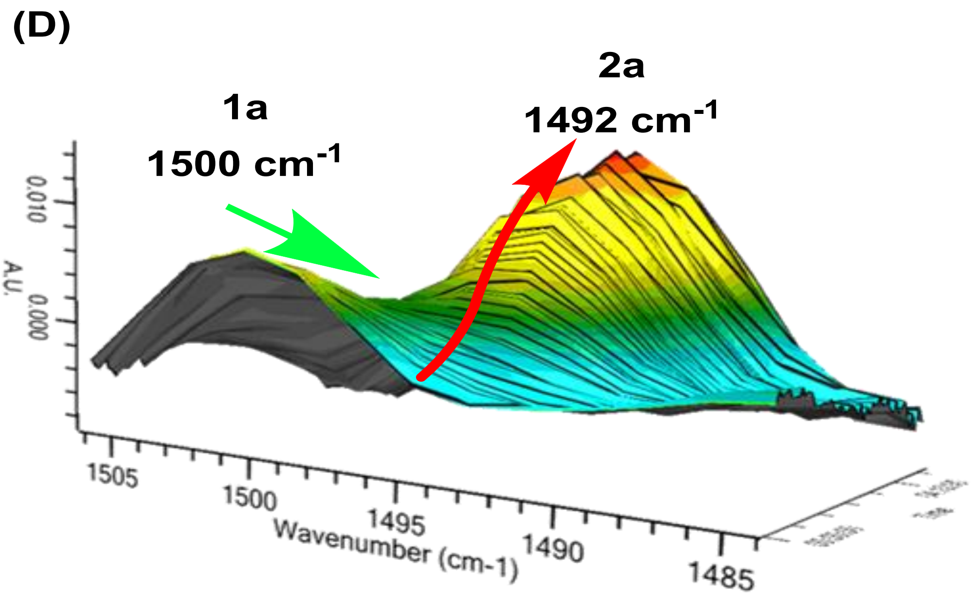
(A) Standard IR spectra of *n*-PrOBpin and B_2pin_2.



(B) Standard IR spectra of **1a** and **2a**.

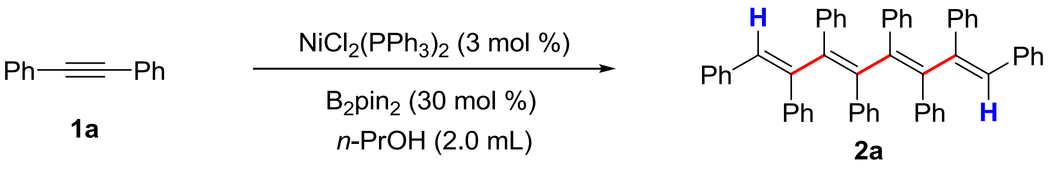


(C) Depletion of B_2pin_2 and formation of *n*-PrOBpin.

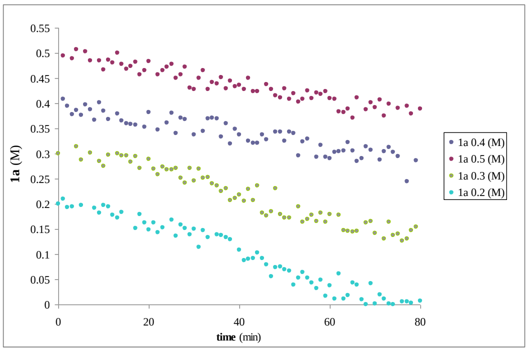


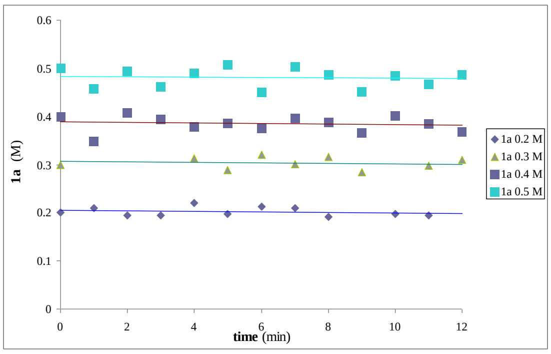
(D) Depletion of **1a** and formation of **2a**.

6.2 Different diphenylethyne (1a) loadings

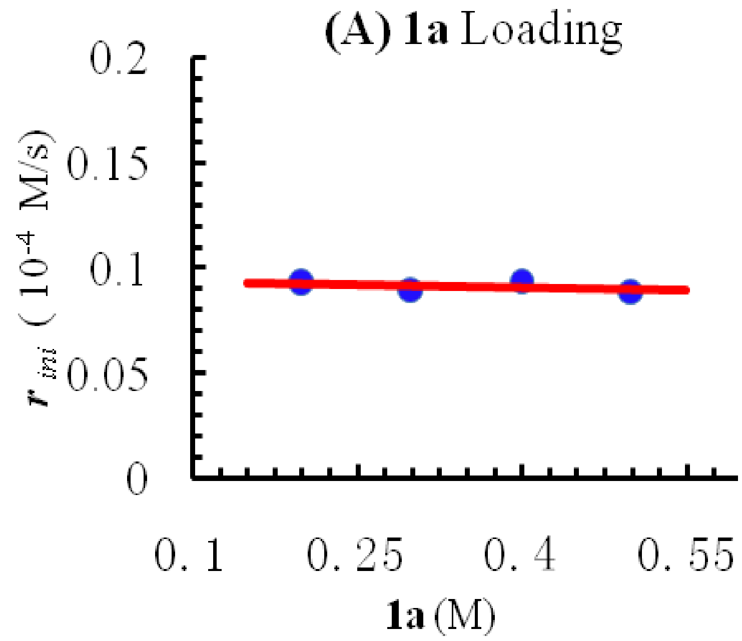


In a dried self-prepared three-necked micro reactor with a magnetic stirrer, $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) and B_2pin_2 (76.2 mg, 0.3 mmol, 30 mol%) were added. The reactor was allowed to be purged with nitrogen three times, *n*-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 ^{o}C and the different amount of 1,2-diphenylethyne **1a** (1.0 mmol, 0.8 mmol, 0.6 mmol, 0.4 mmol) was dissolved in *n*-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at 120 ^{o}C for 2-6 hours. After cooling to room temperature, *n*-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.

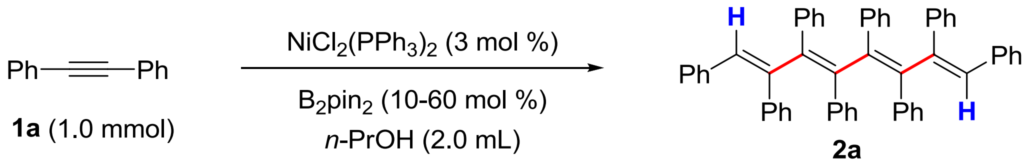




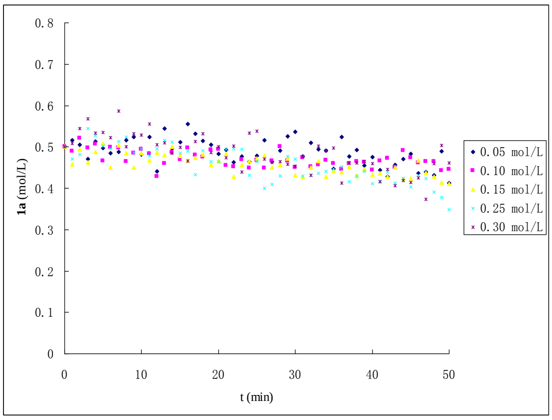
entry	1	2	3	4
1a loading (M)	0.2	0.3	0.4	0.5
r_{ini} (10^{-4} M/s)	0.093	0.09	0.094	0.089

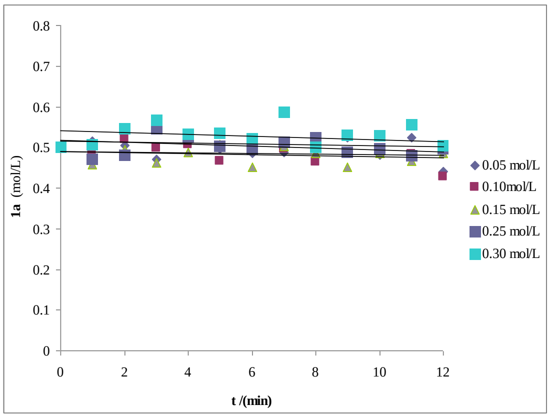


6.3 Different B_2pin_2 loadings

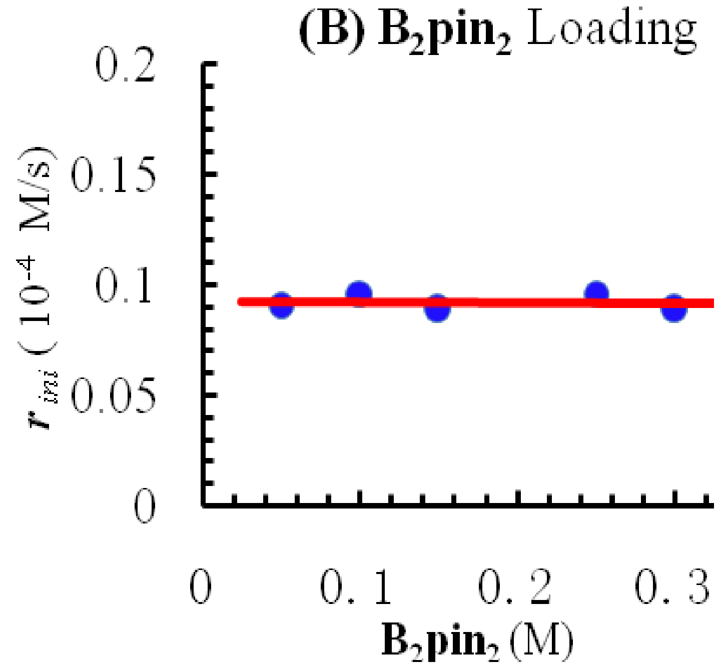


In a dried self-prepared three-necked micro reactor with a magnetic stirrer, $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) and the different amount of B_2pin_2 (0.1 mmol, 0.2 mmol, 0.3 mmol, 0.5 mmol, 0.6 mmol) were added. The reactor was allowed to be purged with nitrogen three times, *n*-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 °C, and the 1,2-diphenylethyne **1a** (178.2 mg, 1.0 mmol) was dissolved in *n*-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at 120 °C for 2-6 hours. After cooling to room temperature, *n*-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.

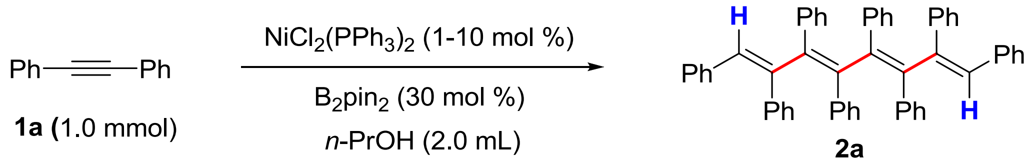




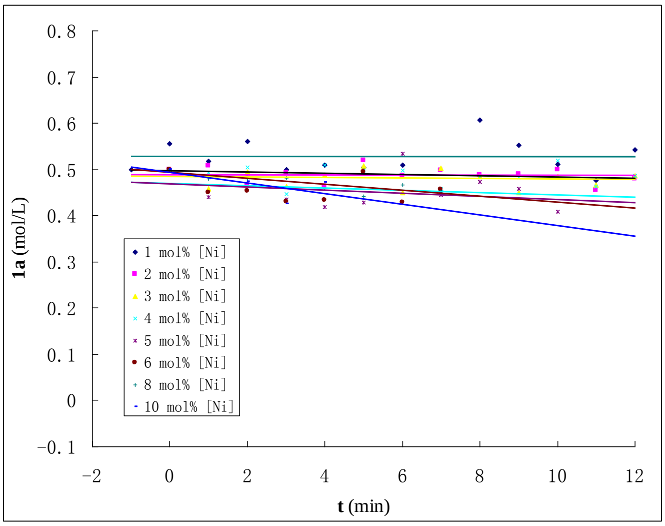
entry	1	2	3	4	5
$\mathbf{B_2pin_2}$ loading (M)	0.05	0.10	0.15	0.25	0.30
$\boldsymbol{r}_{\text{ini}}$ (10^{-4} M/s)	0.091	0.096	0.089	0.096	0.089



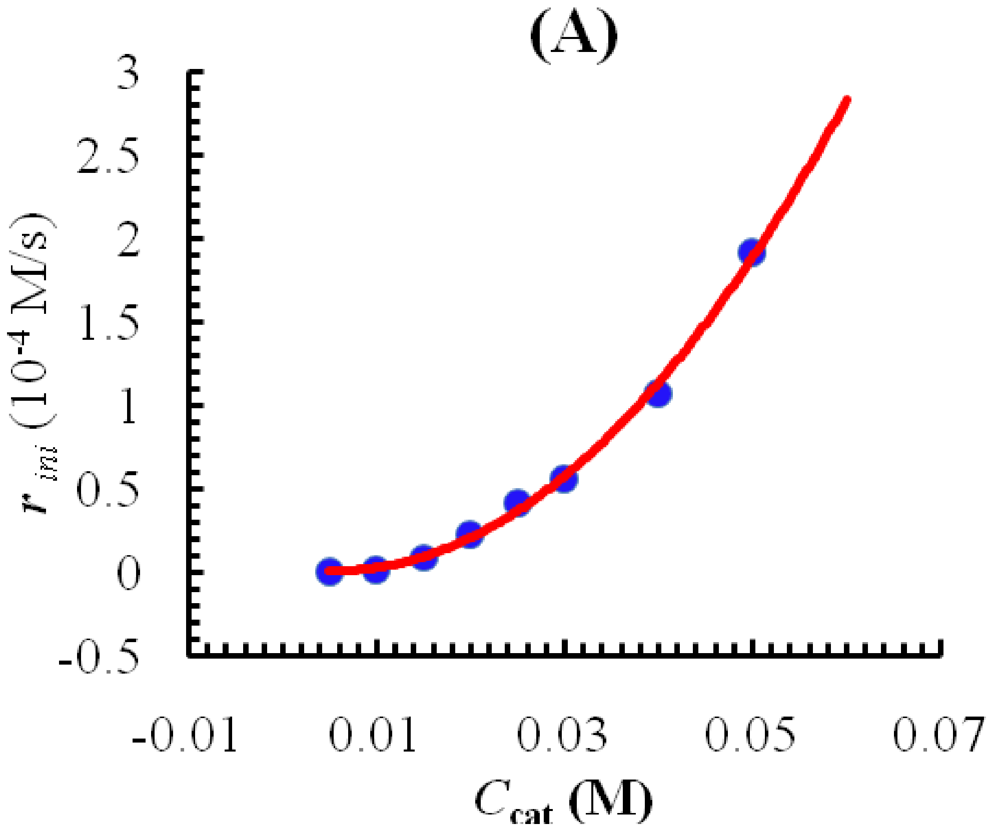
6.4 Different $NiCl_2(PPh_3)_2$ loadings

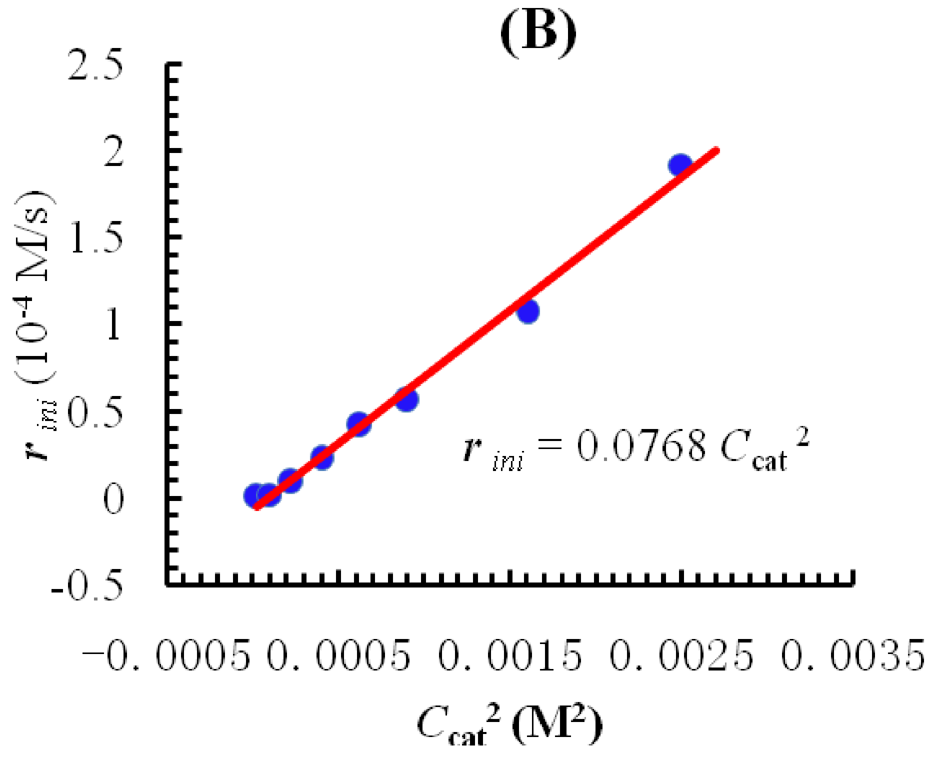


In a dried self-prepared three-necked micro reactor with a magnetic stirrer, the different amount of $NiCl_2(PPh_3)_2$ (0.01 mmol, 0.02 mmol, 0.03 mmol, 0.04 mmol, 0.05 mmol, 0.06 mmol, 0.08 mmol, 0.10 mmol) and B_2pin_2 (76.2 mg, 0.3 mmol, 30 mol%) were added. The reactor was allowed to be purged with nitrogen three times, *n*-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 ^{o}C, and the 1,2-diphenylethyne **1a** (178.2 mg, 1.0 mmol) was dissolved in *n*-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at 120 ^{o}C for 2-6 hours. After cooling to room temperature, *n*-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.



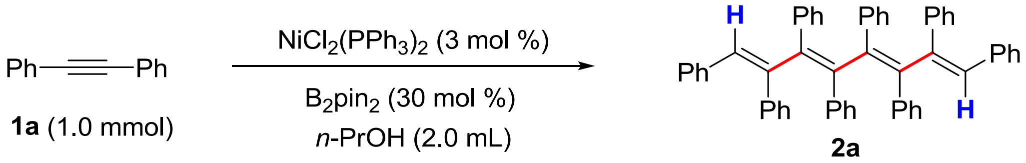
entry	1	2	3	4	5	6	7	8
$NiCl_2(PPh_3)_2$ (M)	0.005	0.01	0.015	0.02	0.025	0.03	0.04	0.05
C_{cat}^2 $(M)^2$	0.000025	0.0001	0.000225	0.0004	0.000625	0.0009	0.00016	0.0025
$\boldsymbol{r}_{ini}$ (10^{-4} M/s)	0.003	0.019	0.089	0.225	0.416	0.563	1.07	1.919



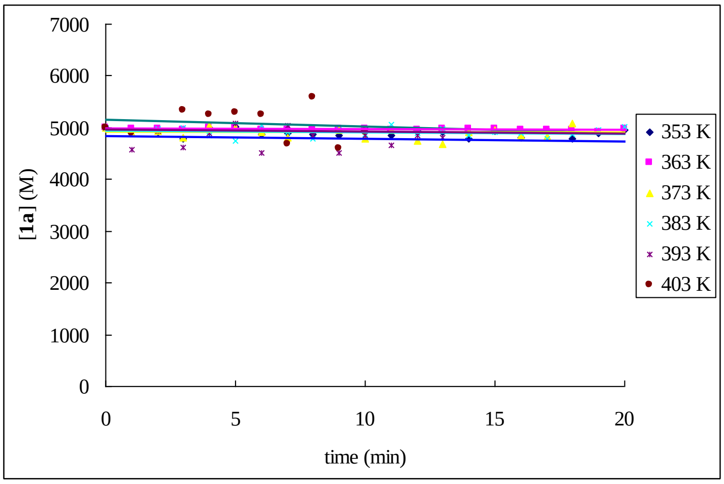


$$r_{ini} = 0.0768 c_{cat}^{2} - 7.43\times10^{-6} \quad R = 0.9968$$

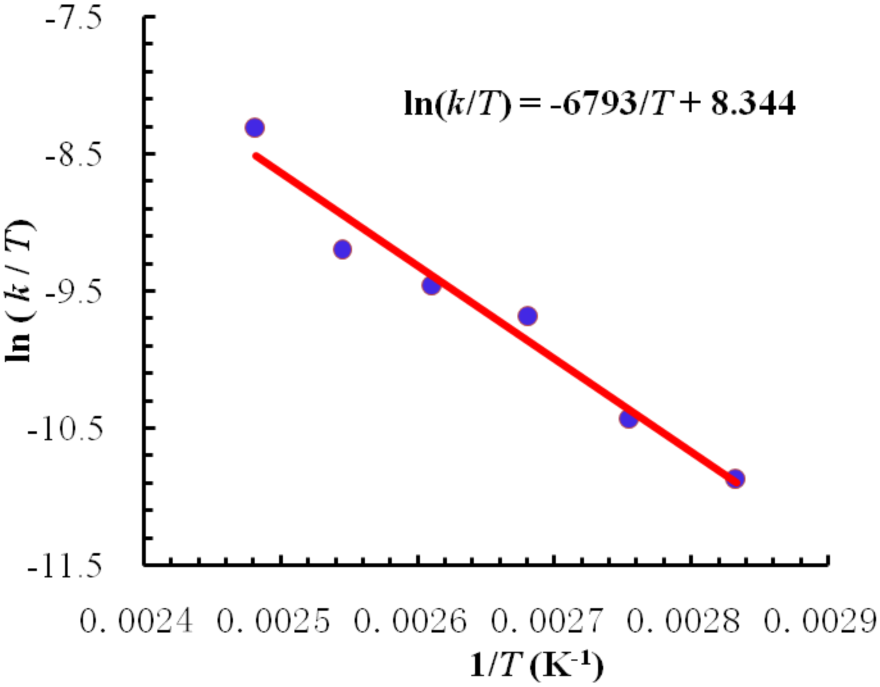
6.5 Arrhenius parameters of Nickel-catalyzed reductive coupling



In a dried self-prepared three-necked micro reactor with a magnetic stirrer, $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) and B_2pin_2 (76.2 mg, 0.3 mmol) were added. The reactor was purged with nitrogen for three times, *n*-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 ^{o}C, and was transferred to the different temperature (80 ^{o}C, 90 ^{o}C, 100 ^{o}C, 110 ^{o}C, 120 ^{o}C, 130 ^{o}C). And the 1,2-diphenylethyne **1a** (178.2 mg, 1.0 mmol) was dissolved in *n*-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at the different temperature for 2-6 hours. After cooling to room temperature, *n*-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.



T (K)	1/T (K^{-1})	*k* (mL mol^{-1} s^{-1})	$\ln(\frac{kc^{\ominus}}{T})$
353	0.002833	0.006666667	-10.88
363	0.002755	0.010666667	-10.44
373	0.002681	0.023111111	-9.69
383	0.002611	0.029777778	-9.46
393	0.002545	0.039555556	-9.20
403	0.002481	0.098666667	-8.31



$$k = \frac{k_{\mathrm{B}}T}{h}\left(c^{\ominus}\right)^{-1}\exp\left(\frac{\Delta_r^{\neq}S_m^{\ominus}(c^{\ominus})}{R}\right)\exp\left(-\frac{\Delta_r^{\neq}H_m^{\ominus}(c^{\ominus})}{RT}\right) \qquad (1)$$

$$\ln\left(\frac{kc^{\ominus}}{T}\right) = \ln\frac{k_{\mathrm{B}}}{h} + \frac{\Delta_r^{\neq}S_m^{\ominus}(c^{\ominus})}{R} - \frac{\Delta_r^{\neq}H_m^{\ominus}(c^{\ominus})}{R}\frac{1}{T} \qquad (2)$$

k_{B}: $1.38*10^{-23}$ J·K^{-1}

h: $6.626*10^{-34}$ J s

$c^{\ominus}$：1mol·mL^{-1}

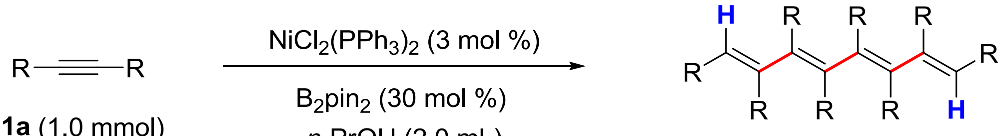
$[\mathrm{Ni}] = 0.015$ mol·L^{-1}， $k = \frac{r}{c_{cat}^{2}}$

$$\ln\frac{k}{T} = -\frac{6793}{T} + 8.344\,, \quad R = 0.9818 \qquad (3)$$

$$\Delta_r^{\neq}H_m^{\ominus} = 56.5\,\mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_r^{\neq}S_m^{\ominus} = -128\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$$

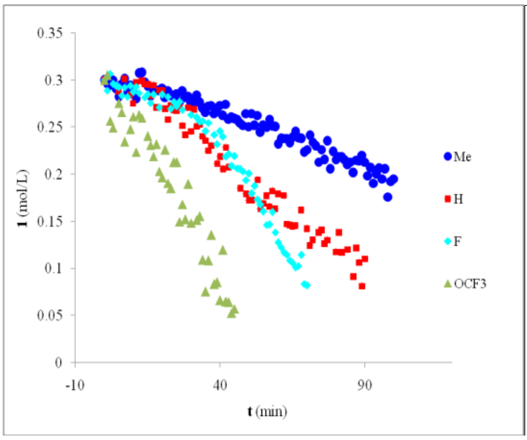
6.6 The role of diarylalkynes

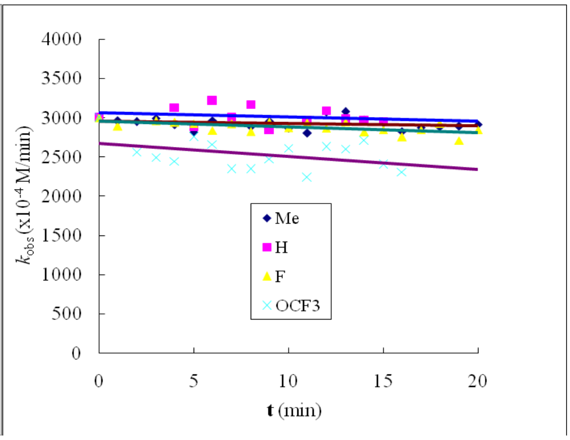


1a (1.0 mmol)

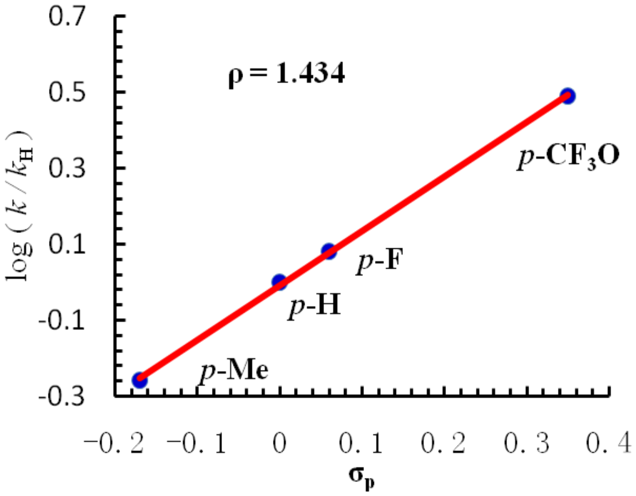
2a

In a dried self-prepared three-necked micro reactor with a magnetic stirrer, $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) and B_2pin_2 (76.2 mg, 0.3 mmol) were added. The reactor was purged with nitrogen for three times, *n*-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 °C, and the different of diarylethynes **1** (1.0 mmol) was dissolved in *n*-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at 120 °C for 2-6 hours. After cooling to room temperature, *n*-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.

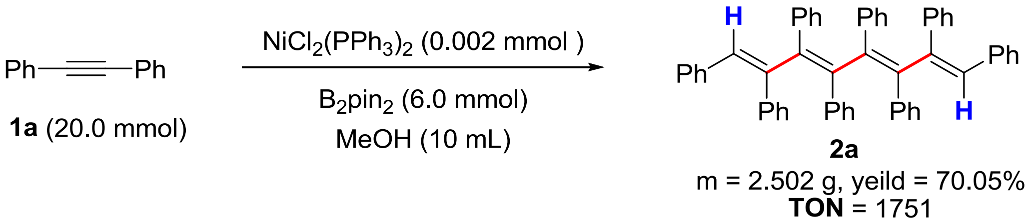




entry	1	2	3	4
para-	Me	H	F	OCF_3
k ($x10^{-4}$ M/min)	-2.941	-5.44	-6.4638	-16.508
σ_p	-0.17	0	0.06	0.35
log (k/k_H)	-0.2671	0	0.074889	0.482096



7. TON experiment



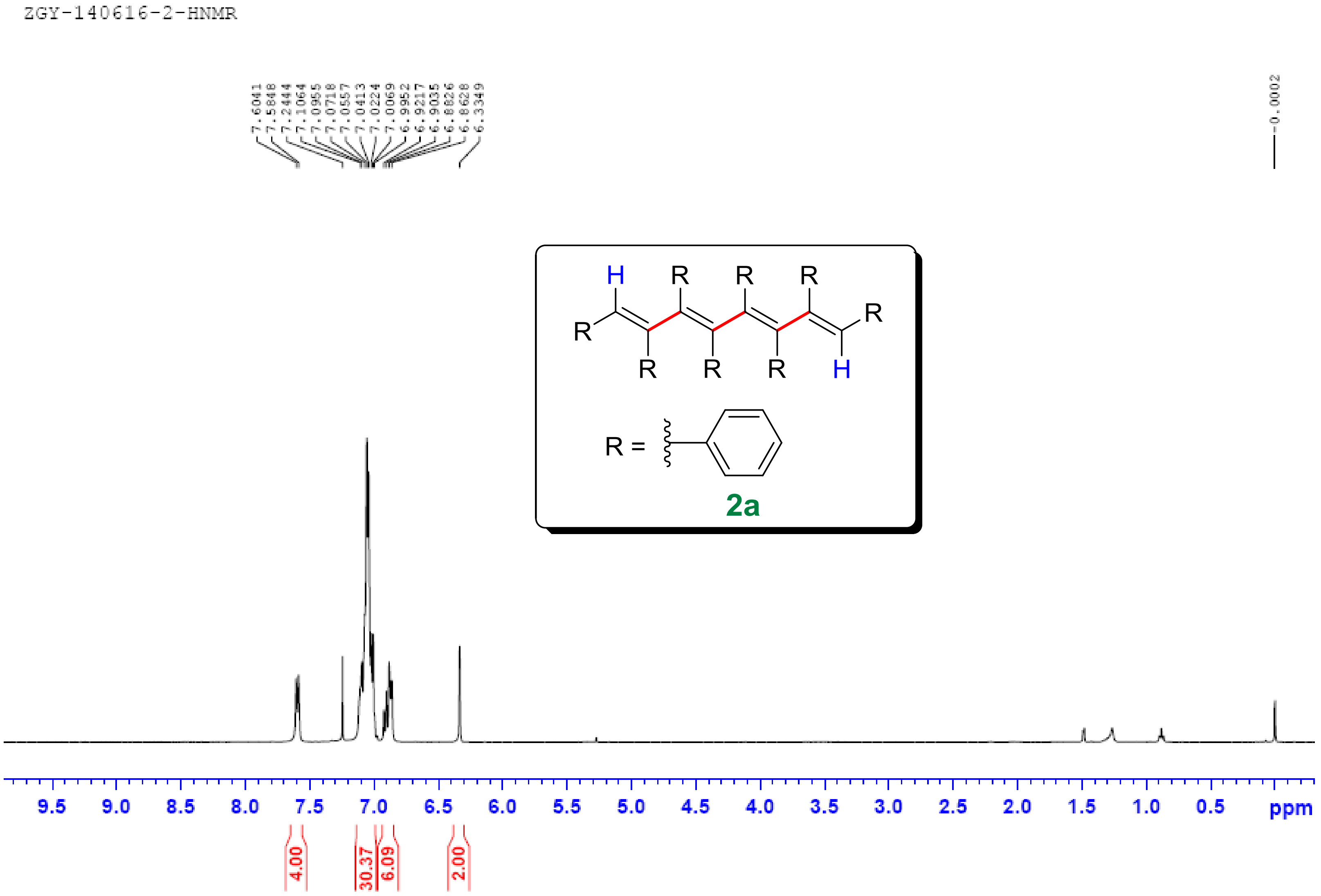
1,2-Diphenylethyne **1a** (3.564 g, 20.0 mmol), $NiCl_2(PPh_3)_2$ (1.3 mg, 0.002 mmol, 1 mol $^{0}/_{000}$), B_2pin_2 (1.5234 g, 6.0 mmol, 30 mol %) and MeOH (10.0 mL) were added to a 100 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 12 days. After cooling to room temperature, the solvents were evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **2a** (2.502 g, in 70.05 % yield, **TON** = 1751).

References:

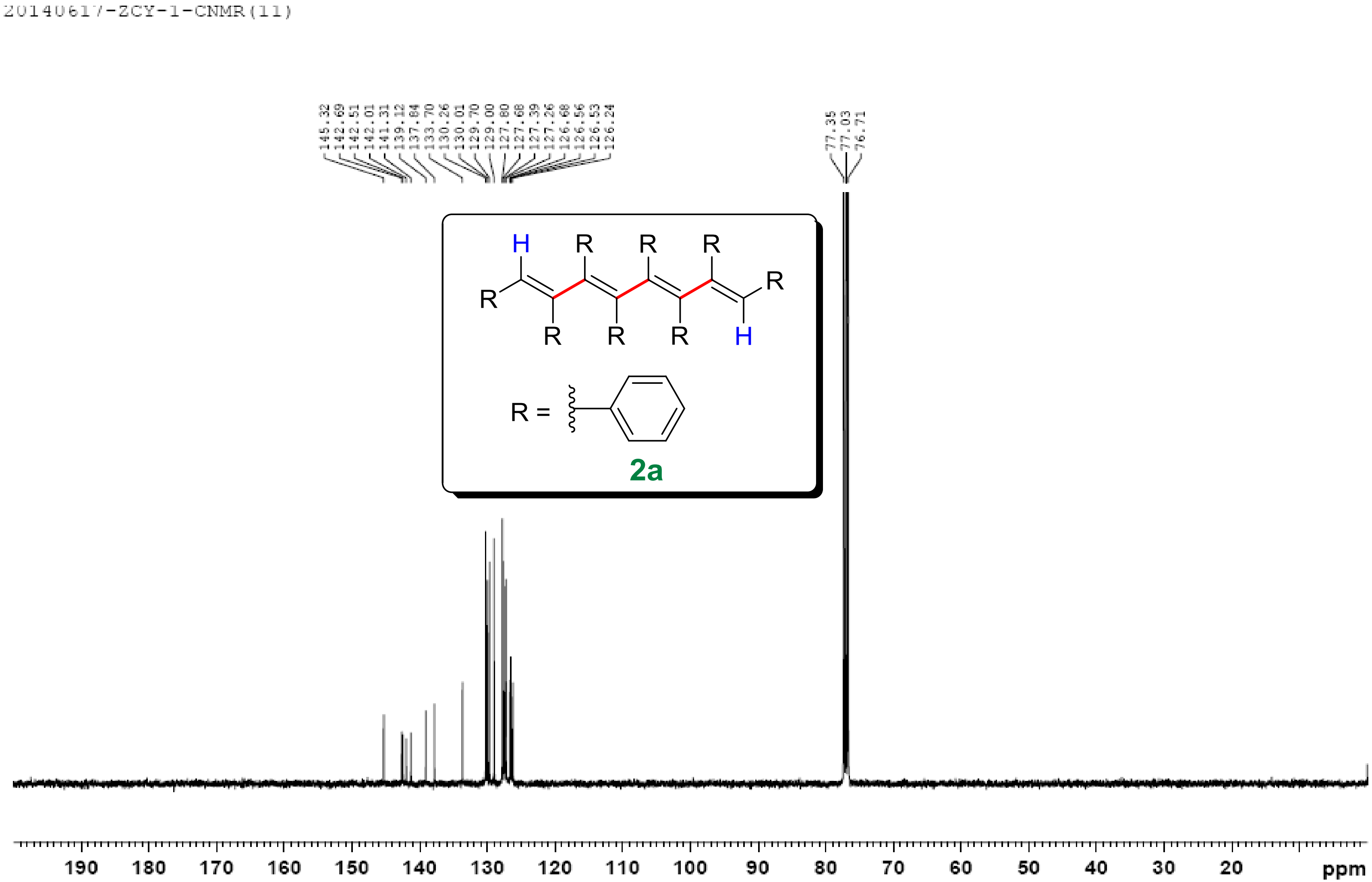
(1) P. Chuentragool, K. Vongnamb, P. Rashatasakhon, M. Sukwattanasinitt and S. Wacharasindhu, *Tetrahedron.* 2011, ***67***, 8177.

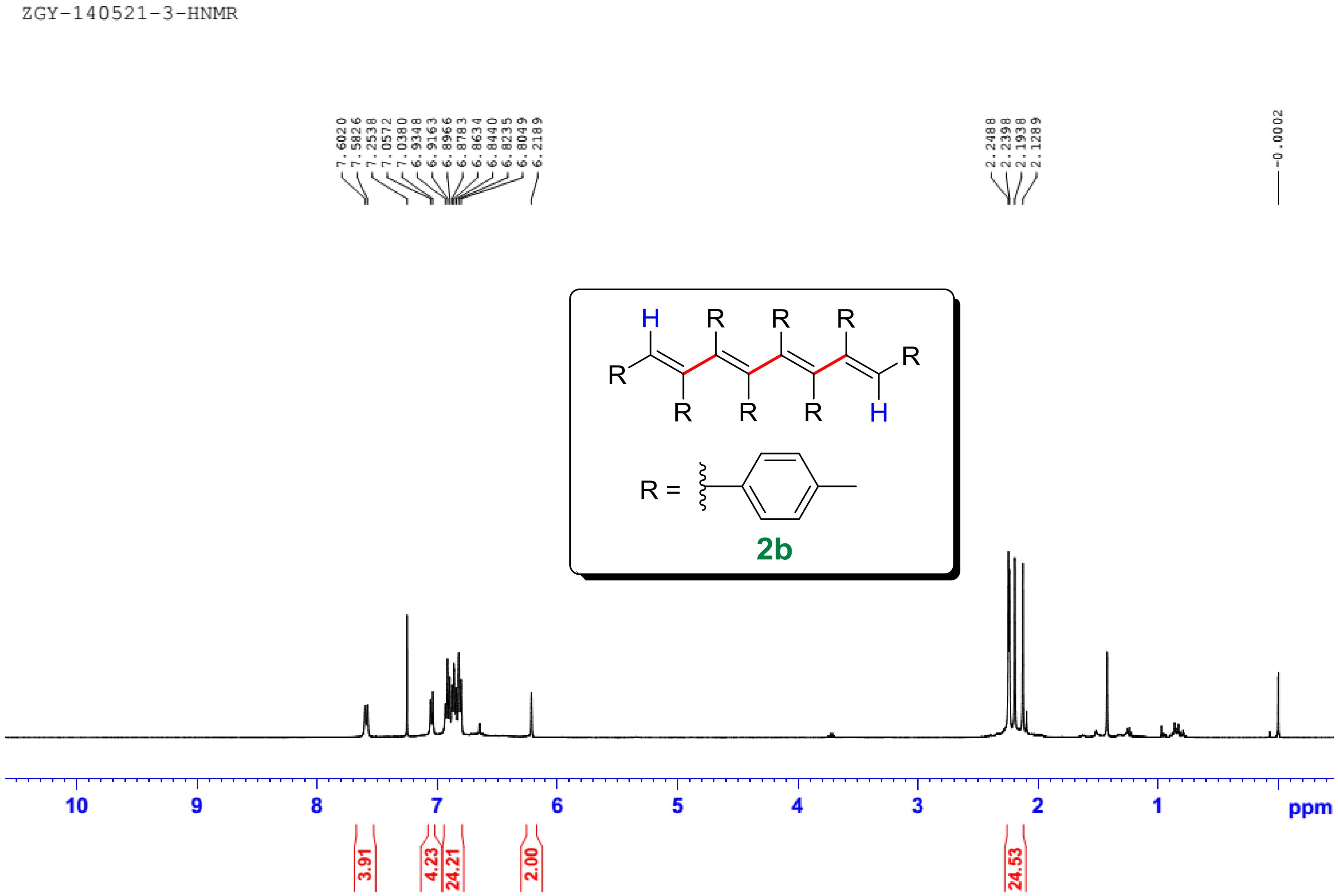
(2) N. Boudet, J. R. Lachs and P. Knochel, *Org. Lett.* 2007, ***9***, 5525.

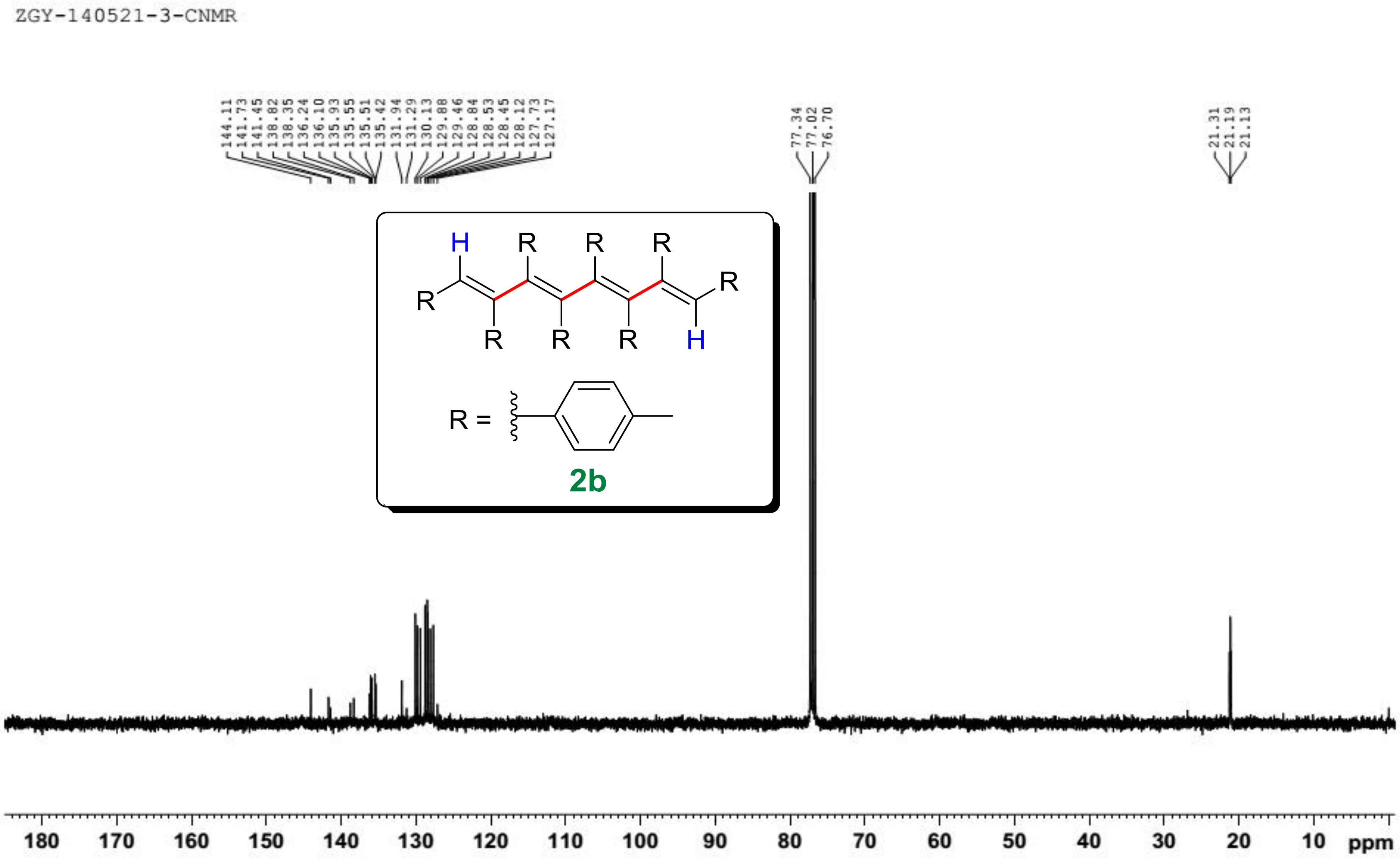
8. Copies for ^{1}H NMR and ^{13}C NMR

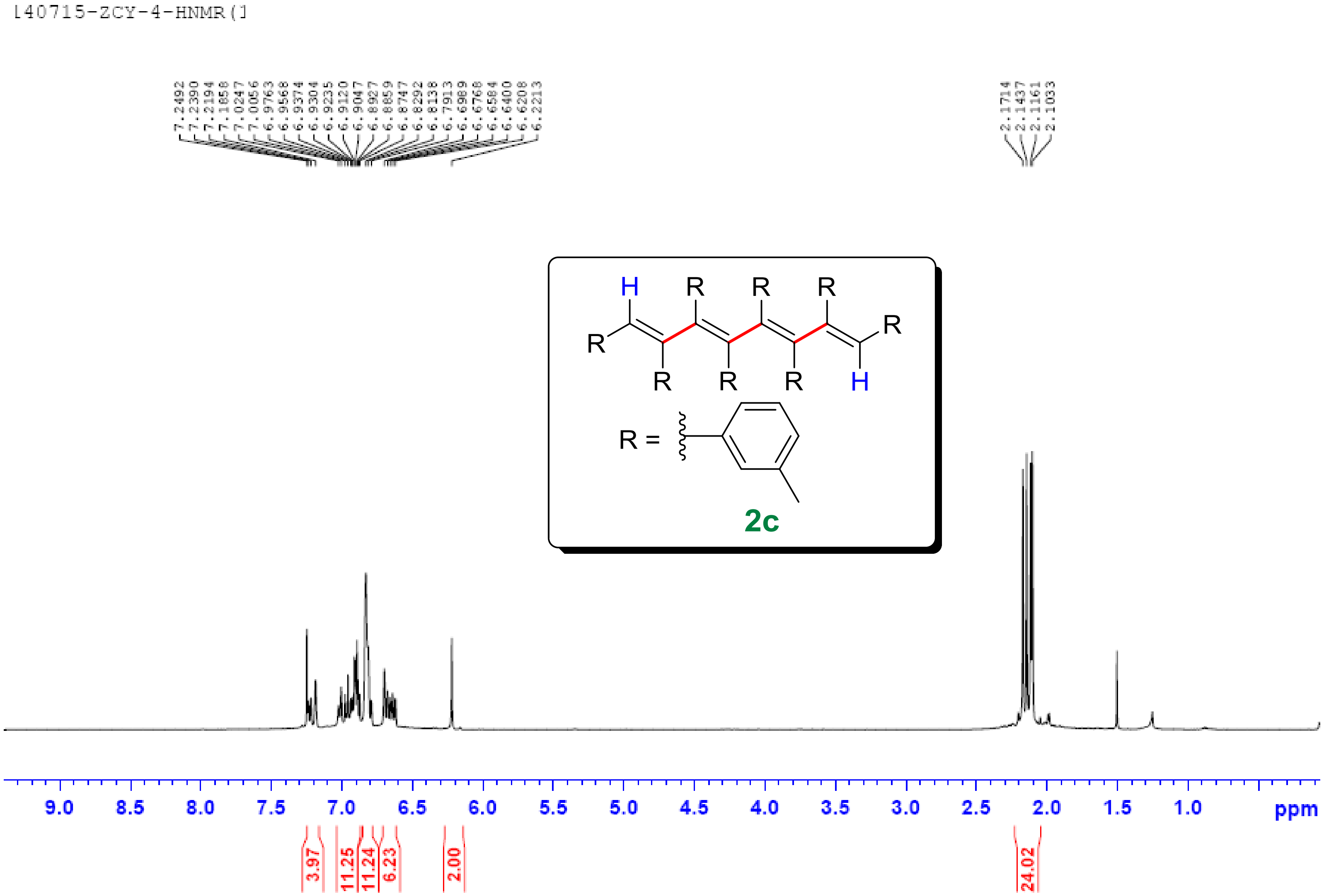

ZGY-140616-2-HNMR
7.6041
7.5848
7.2444
7.1064
7.0955
7.0718
7.0557
7.0413
7.0224
7.0069
6.9952
6.9217
6.9035
6.8826
6.8628
6.3349
-0.0002
H
R
R
R
R
R
R
R
H
R
R =
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
30.37
6.09
2.00

2a

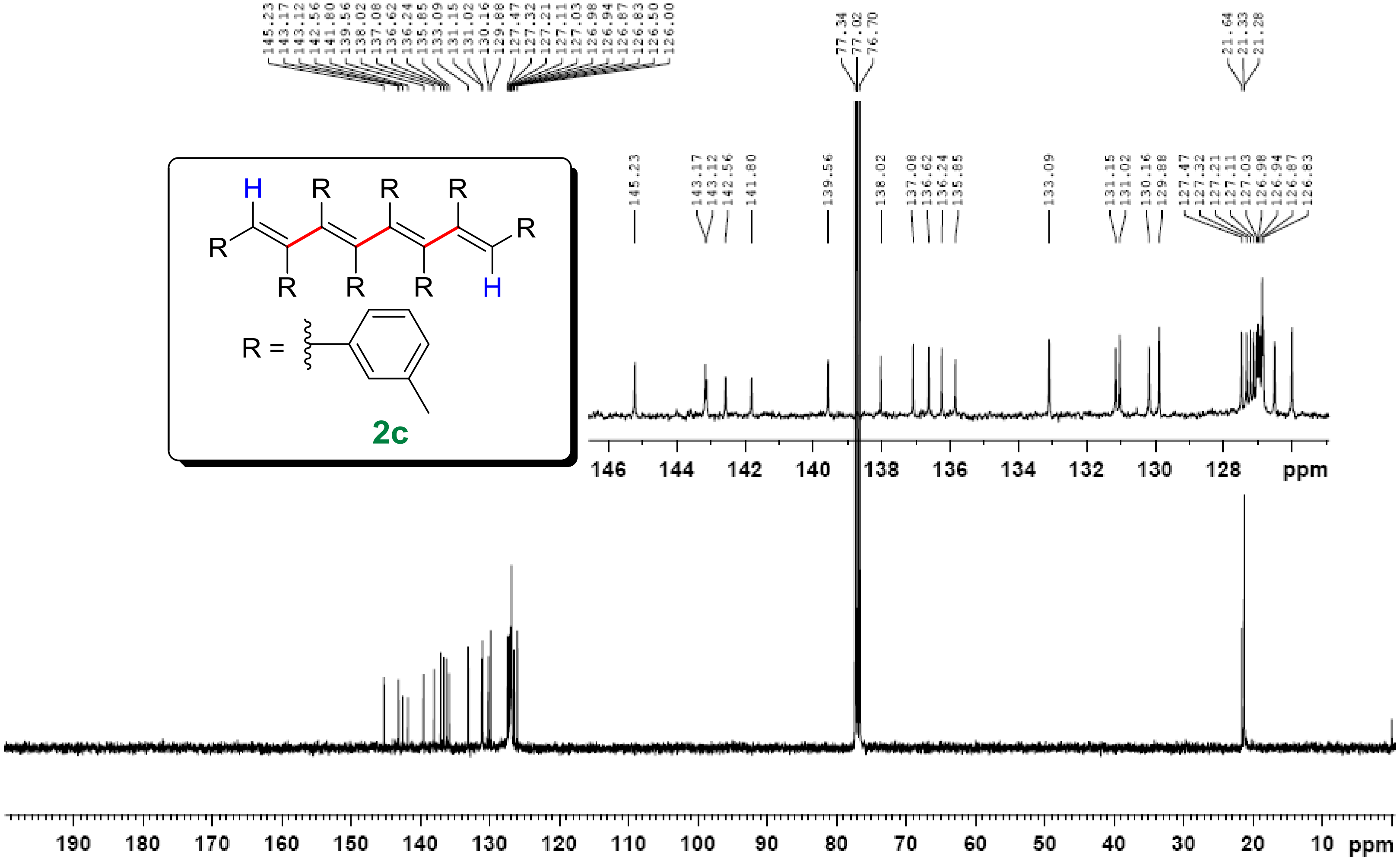

20140617-ZCY-1-CNMR(11)
145.32
142.69
142.51
142.01
141.31
139.12
137.84
133.70
130.26
130.01
129.70
129.00
127.80
127.68
127.39
127.26
126.68
126.56
126.53
126.24
77.35
77.03
76.71
H
R
R =
2a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

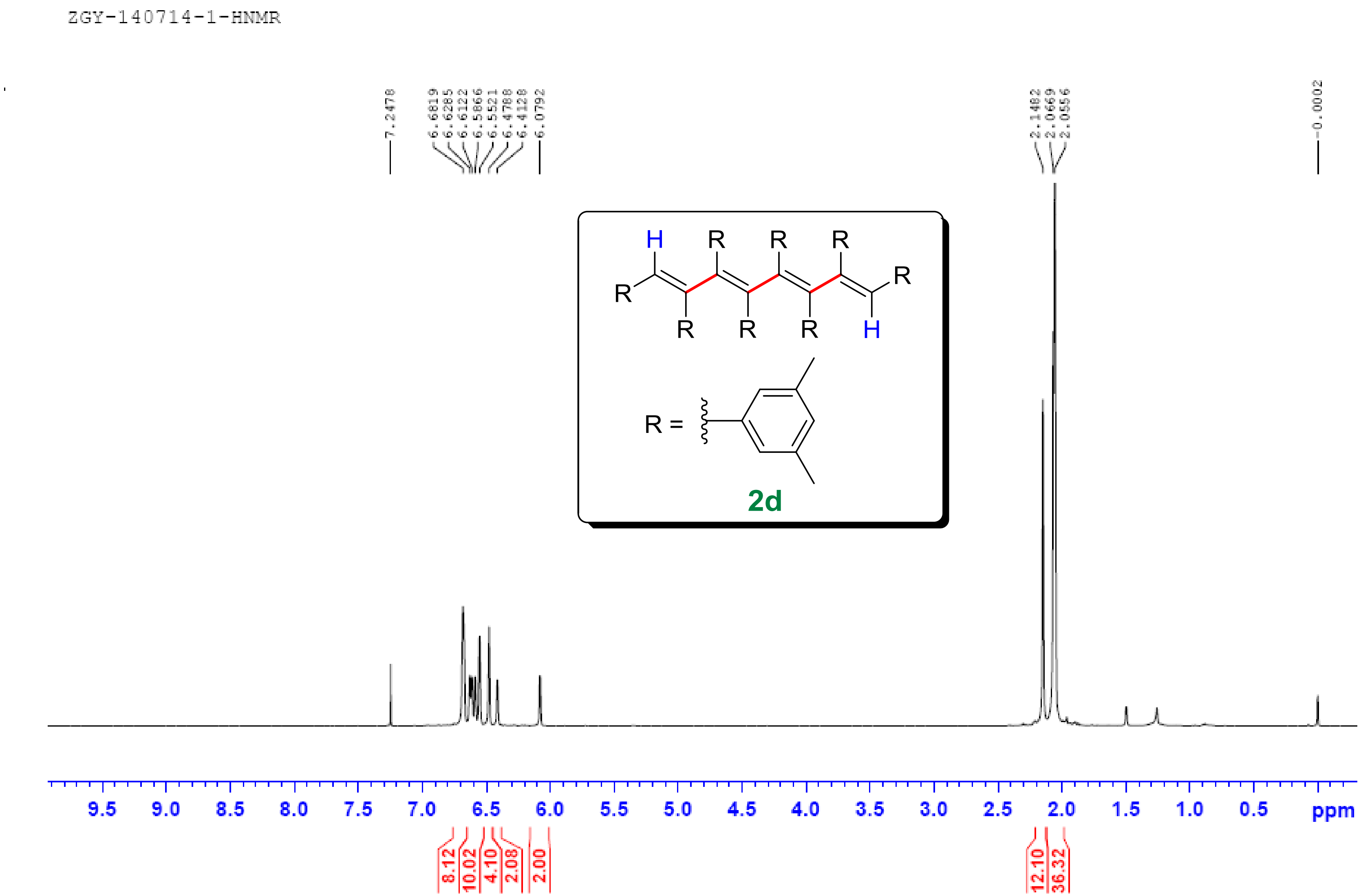

ZGY-140521-3-HNMR
7.6020
7.5826
7.2538
7.0572
7.0380
6.9348
6.9163
6.8966
6.8783
6.8634
6.8440
6.8235
6.8049
6.2189
2.2488
2.2398
2.1938
2.1289
-0.0002
H
R
R
R
R
R
R
R
R
H
R =
2b
10
9
8
7
6
5
4
3
2
1
ppm
3.91
4.23
24.21
2.00
24.53

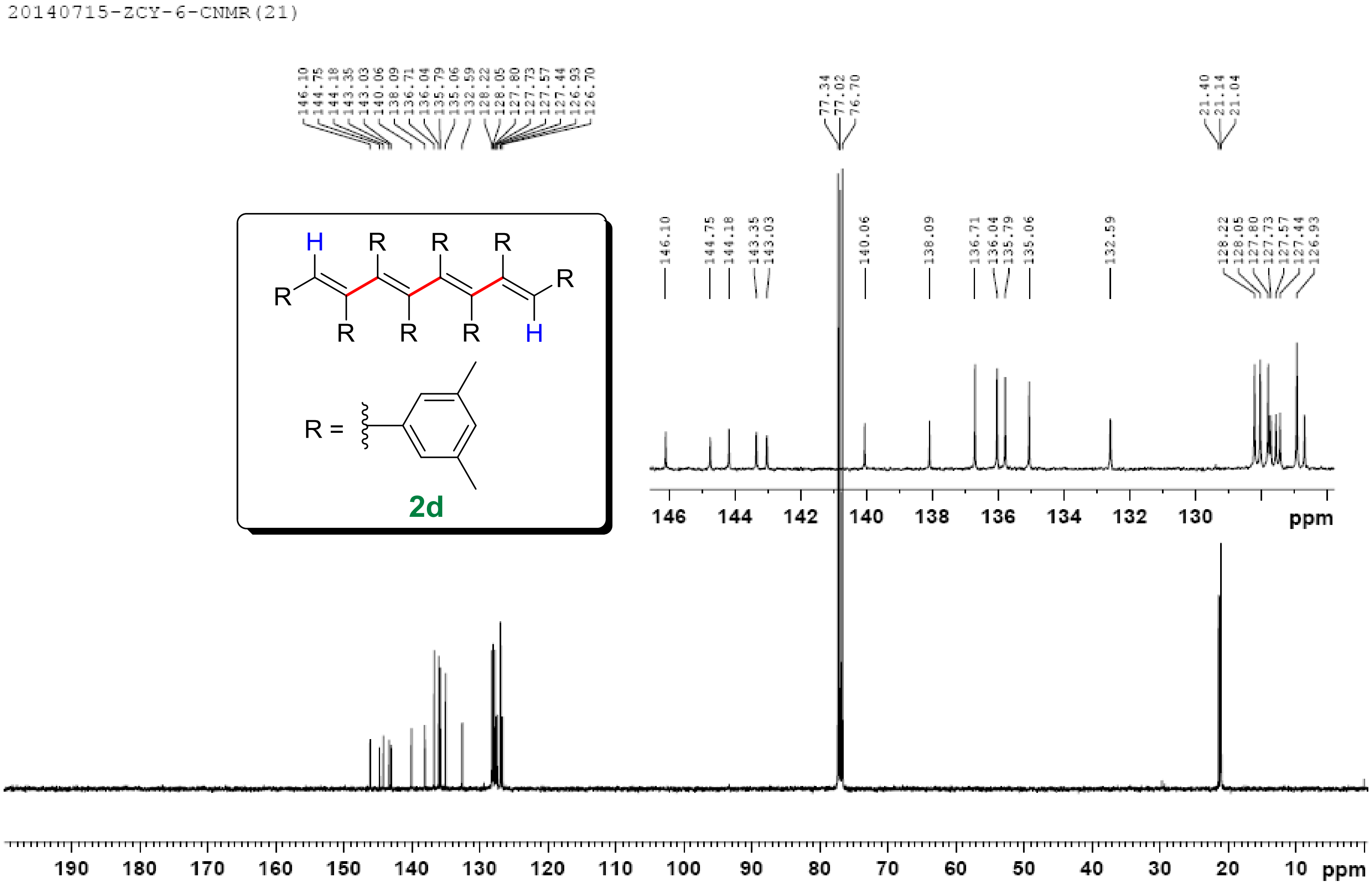
ZGY-140521-3-CNMR
144.11
141.73
141.45
138.82
138.35
136.24
136.10
135.93
135.55
135.51
135.42
131.94
131.29
130.13
129.88
129.46
128.84
128.53
128.45
128.12
127.73
127.17
77.34
77.02
76.70
21.31
21.19
21.13
H
R
R
R
R
R
R
R
R
H
R =
2b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

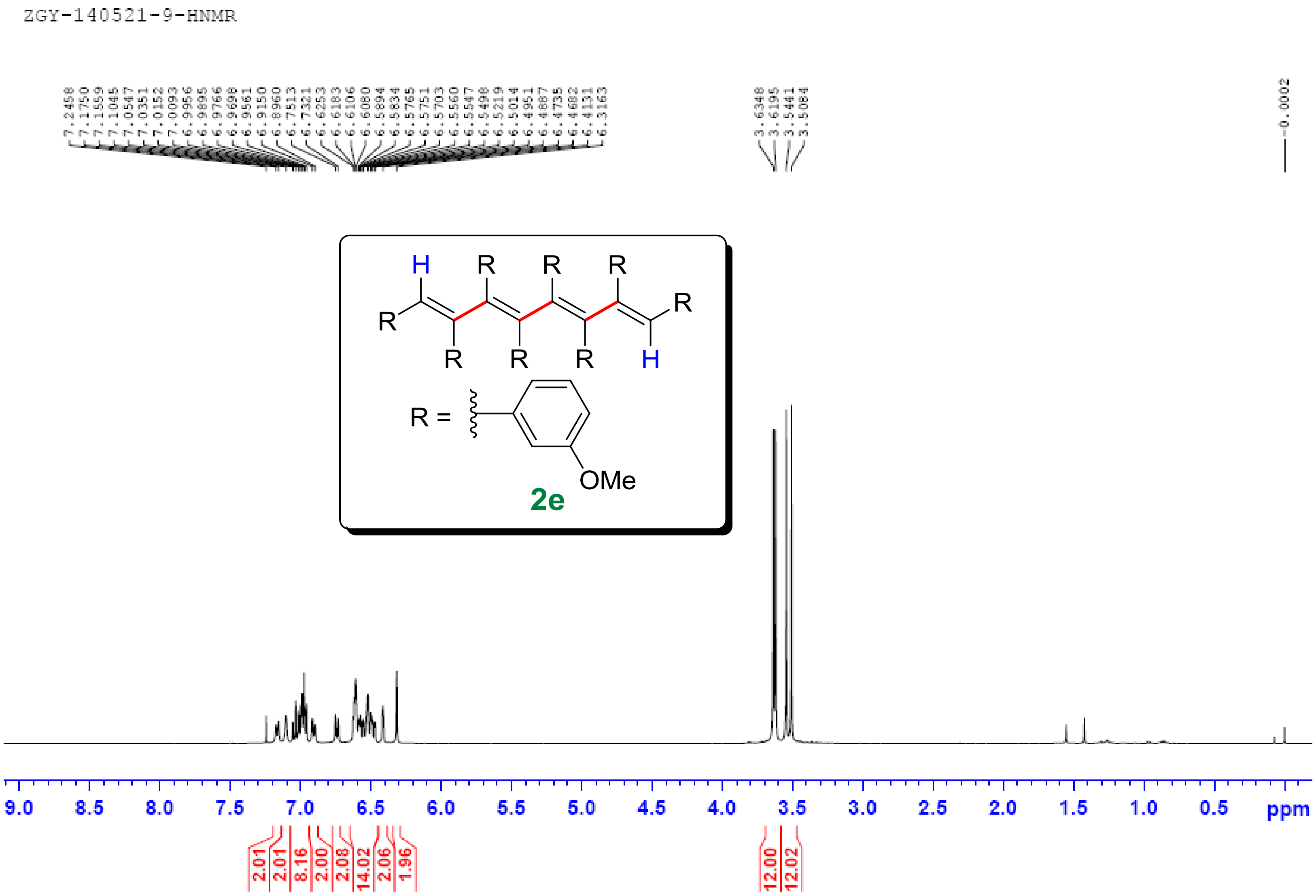

140715-ZCY-4-HNMR(1
7.2492
7.2390
7.2194
7.1858
7.0247
7.0056
6.9763
6.9568
6.9374
6.9304
6.9235
6.9120
6.9047
6.8927
6.8859
6.8747
6.8292
6.8138
6.7913
6.6989
6.6768
6.6584
6.6400
6.6208
6.2213
2.1714
2.1437
2.1161
2.1033
H
R
R
R
R
R
R
R
R
H
R =
2c
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.97
11.25
11.24
6.23
2.00
24.02

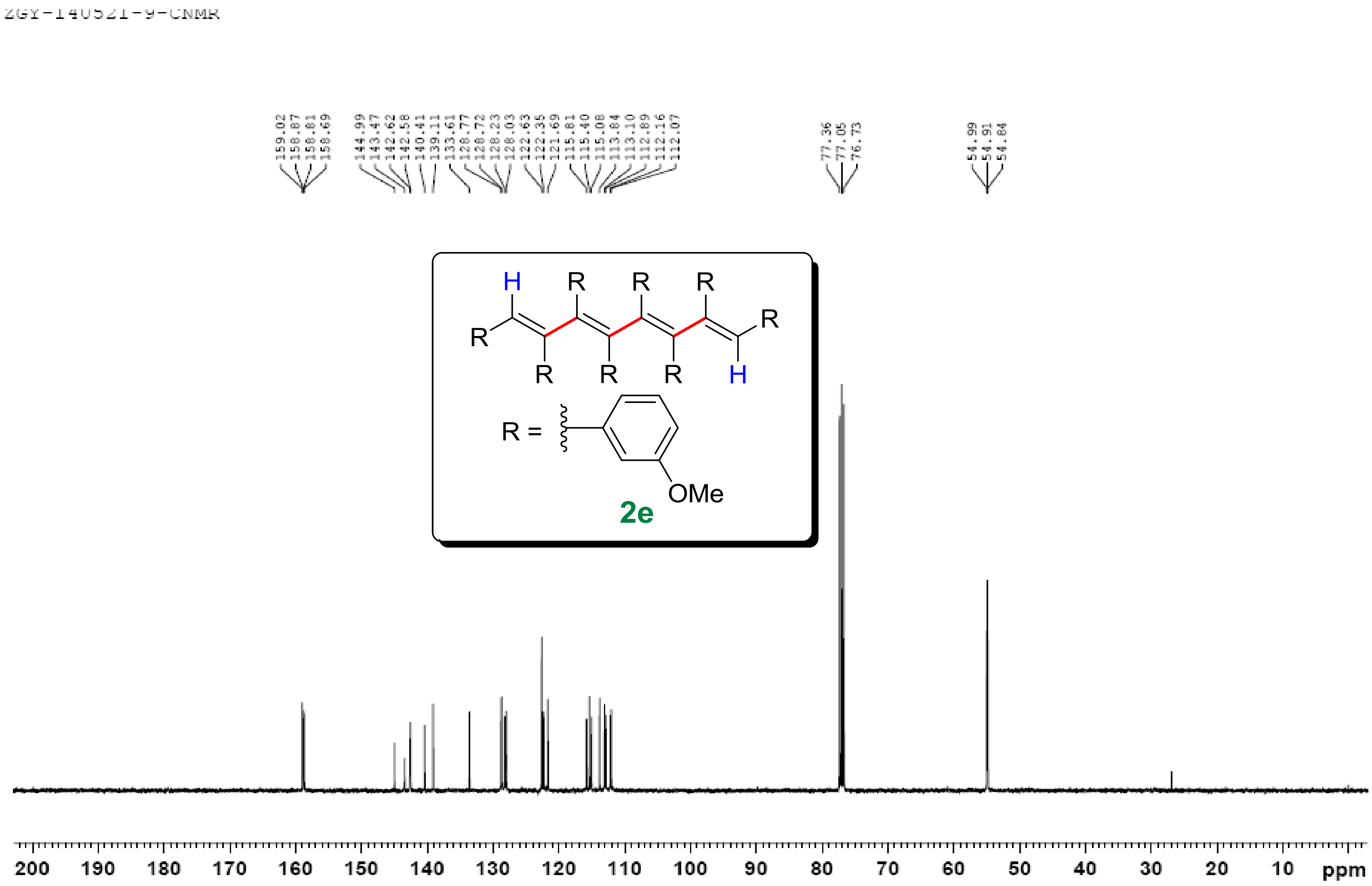
20140715-ZCY-4-CNMR(19)

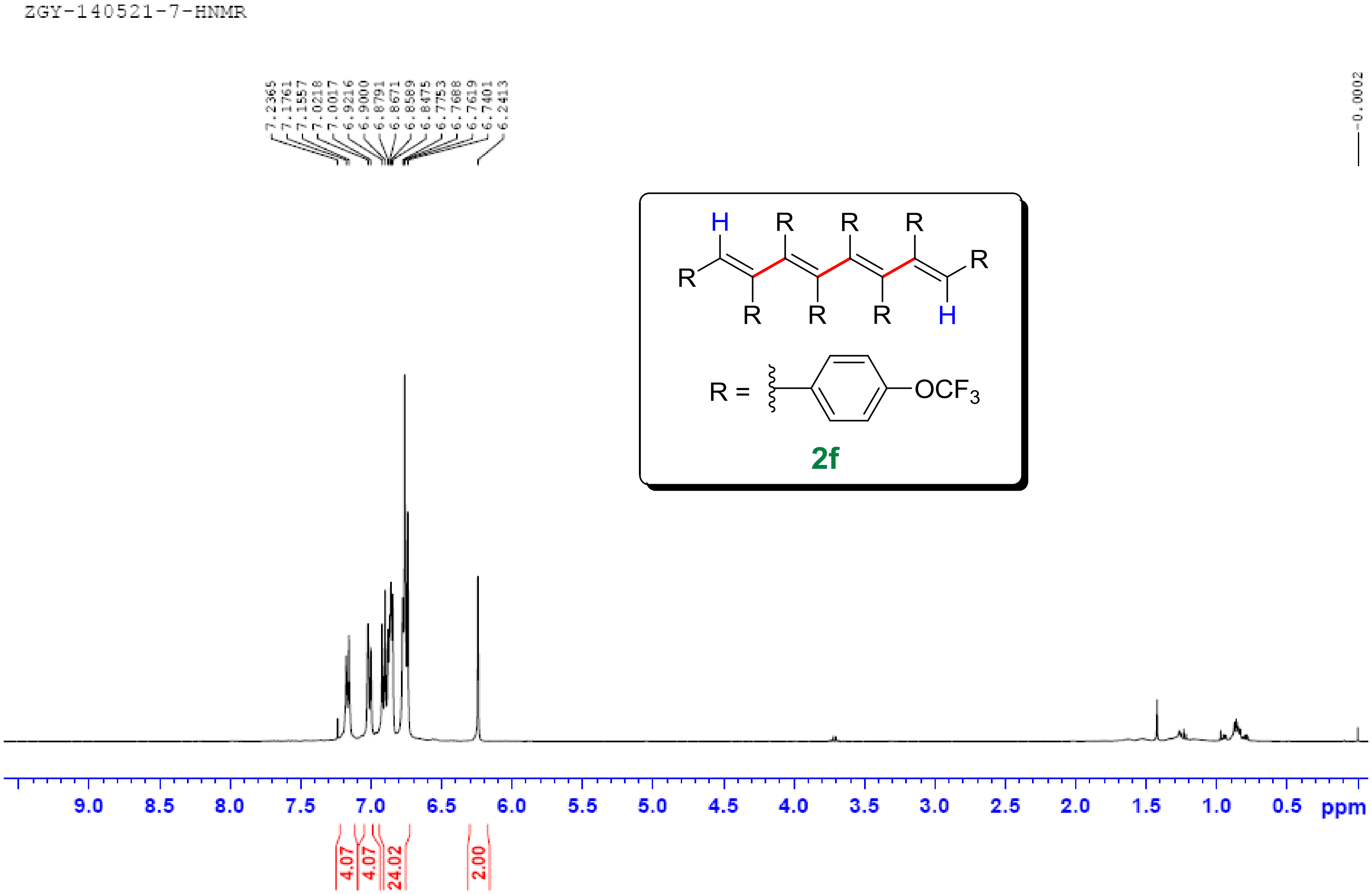


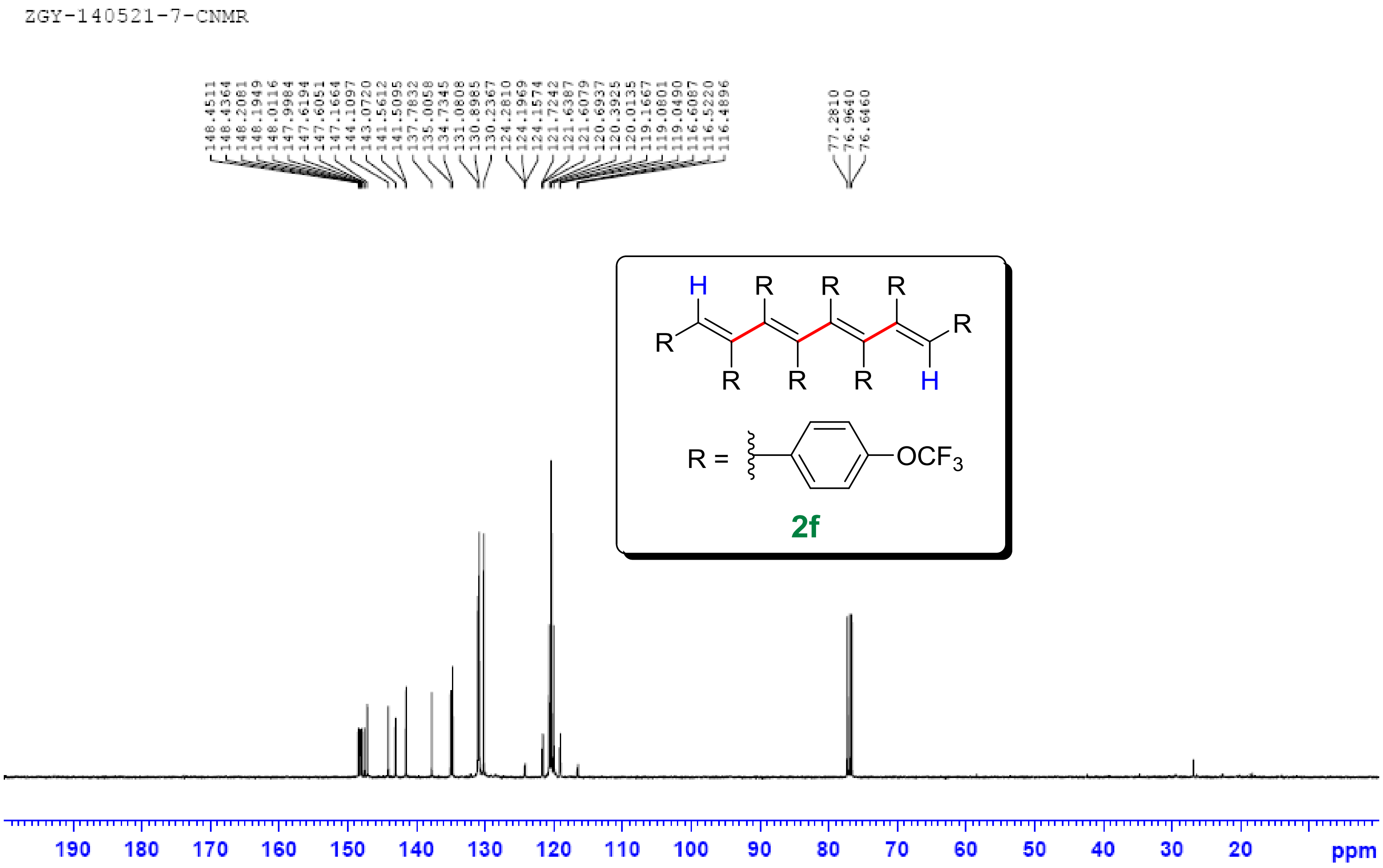

ZGY-140714-1-HNMR
7.2478
6.6819
6.6285
6.6122
6.5866
6.5521
6.4788
6.4128
6.0792
2.1482
2.0669
2.0556
-0.0002
H
R
R
R
R
R
R
R
R
H
R =
2d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
8.12
10.02
4.10
2.08
2.00
12.10
36.32

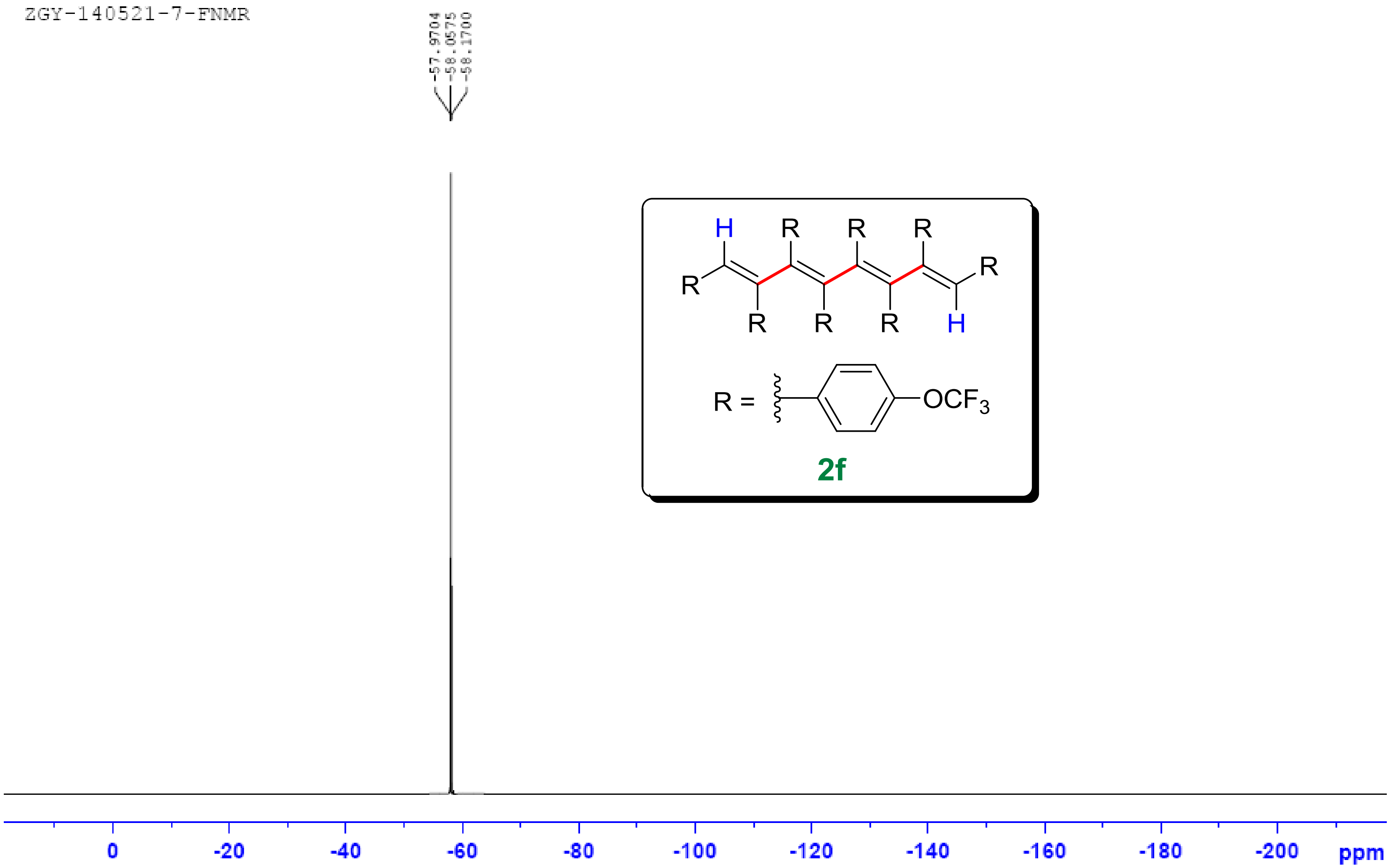

20140715-ZCY-6-CNMR(21)
146.10
144.75
144.18
143.35
143.03
140.06
138.09
136.71
136.04
135.79
135.06
132.59
128.22
128.05
127.80
127.73
127.57
127.44
126.93
126.70
77.34
77.02
76.70
21.40
21.14
21.04
H
R
R
R
R
R
R
R
R
H
R =
2d
146
144
142
140
138
136
134
132
130
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

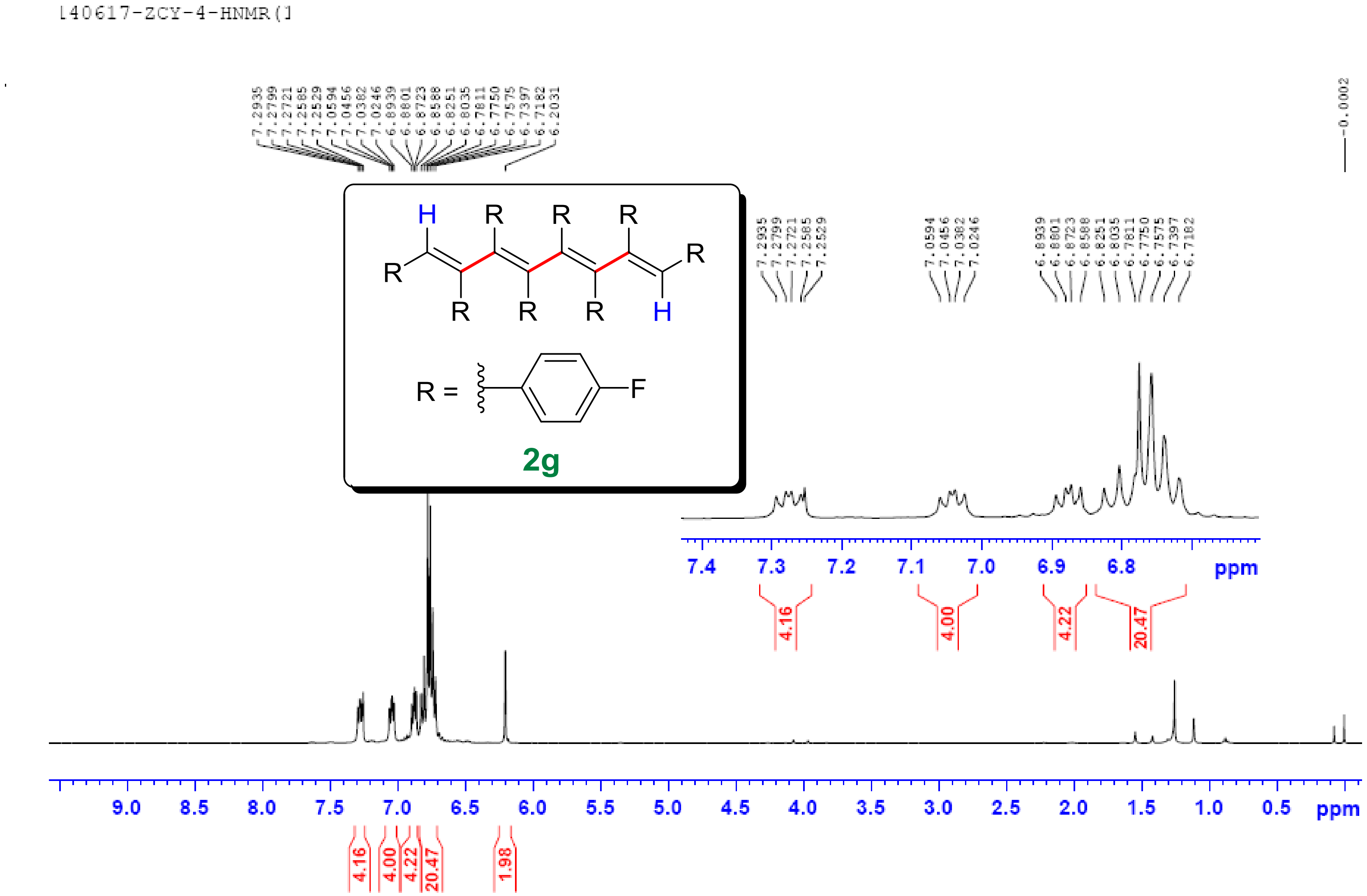

ZGY-140521-9-HNMR
7.2458
7.1750
7.1559
7.1045
7.0547
7.0351
7.0152
7.0093
6.9956
6.9895
6.9766
6.9698
6.9561
6.9150
6.8960
6.7513
6.7321
6.6253
6.6183
6.6106
6.6080
6.5894
6.5834
6.5765
6.5751
6.5703
6.5560
6.5547
6.5498
6.5219
6.5014
6.4951
6.4887
6.4735
6.4682
6.4131
6.3163
3.6348
3.6195
3.5441
3.5084
-0.0002
H
R
R
R
R
R
R
R
R
H
R =
OMe
2e
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
ppm
2.01
2.01
8.16
2.00
2.08
14.02
2.06
1.96
12.00
12.02

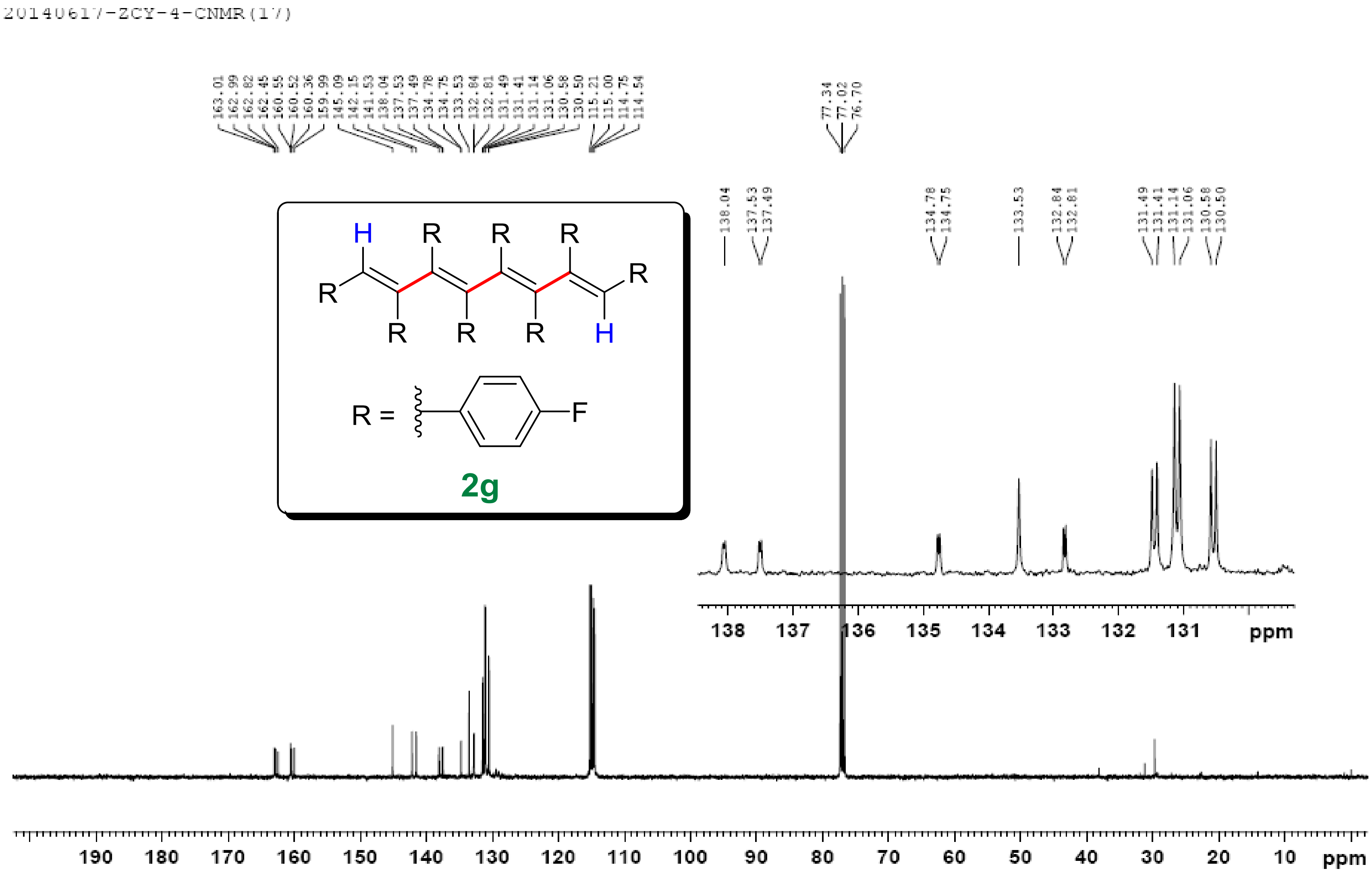

ZGY-140521-9-CNMR
159.02
158.87
158.81
158.69
144.99
143.47
142.62
142.58
140.41
139.11
133.61
128.77
128.72
128.23
128.03
122.63
122.35
121.69
115.81
115.40
115.08
113.84
113.10
112.89
112.16
112.07
77.36
77.05
76.73
54.99
54.91
54.84
H
R
R
R
R
R
R
R
R
H
R =
OMe
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

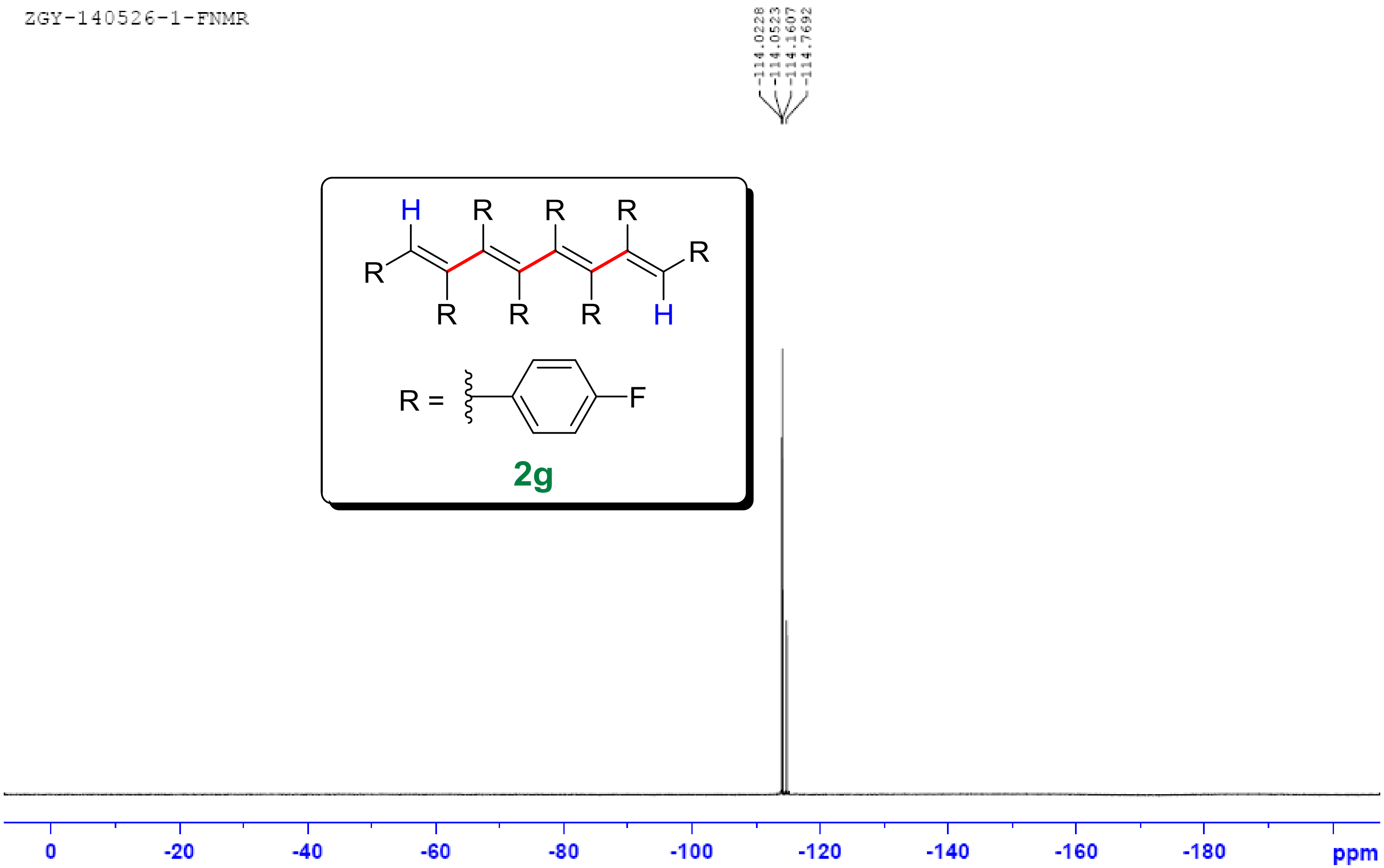

ZGY-140521-7-HNMR
7.2365
7.1761
7.1557
7.0218
7.0017
6.9216
6.9000
6.8791
6.8671
6.8589
6.8475
6.7753
6.7688
6.7619
6.7401
6.2413
-0.0002
H
R
R
R
R
R
R
R
R
H
R =
OCF$_3$
2f
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.07
4.07
24.02
2.00


ZGY-140521-7-CNMR
148.4511
148.4364
148.2081
148.1949
148.0116
147.9984
147.6194
147.6051
147.1664
144.1097
143.0720
141.5612
141.5095
137.7832
135.0058
134.7345
131.0808
130.8985
130.2367
124.2810
124.1969
124.1574
121.7242
121.6387
121.6079
120.6937
120.3925
120.0135
119.1667
119.0801
119.0490
116.6087
116.5220
116.4896
77.2810
76.9640
76.6460
H
R
R
R
R
R
R
R
R
H
R =
OCF$_3$
2f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

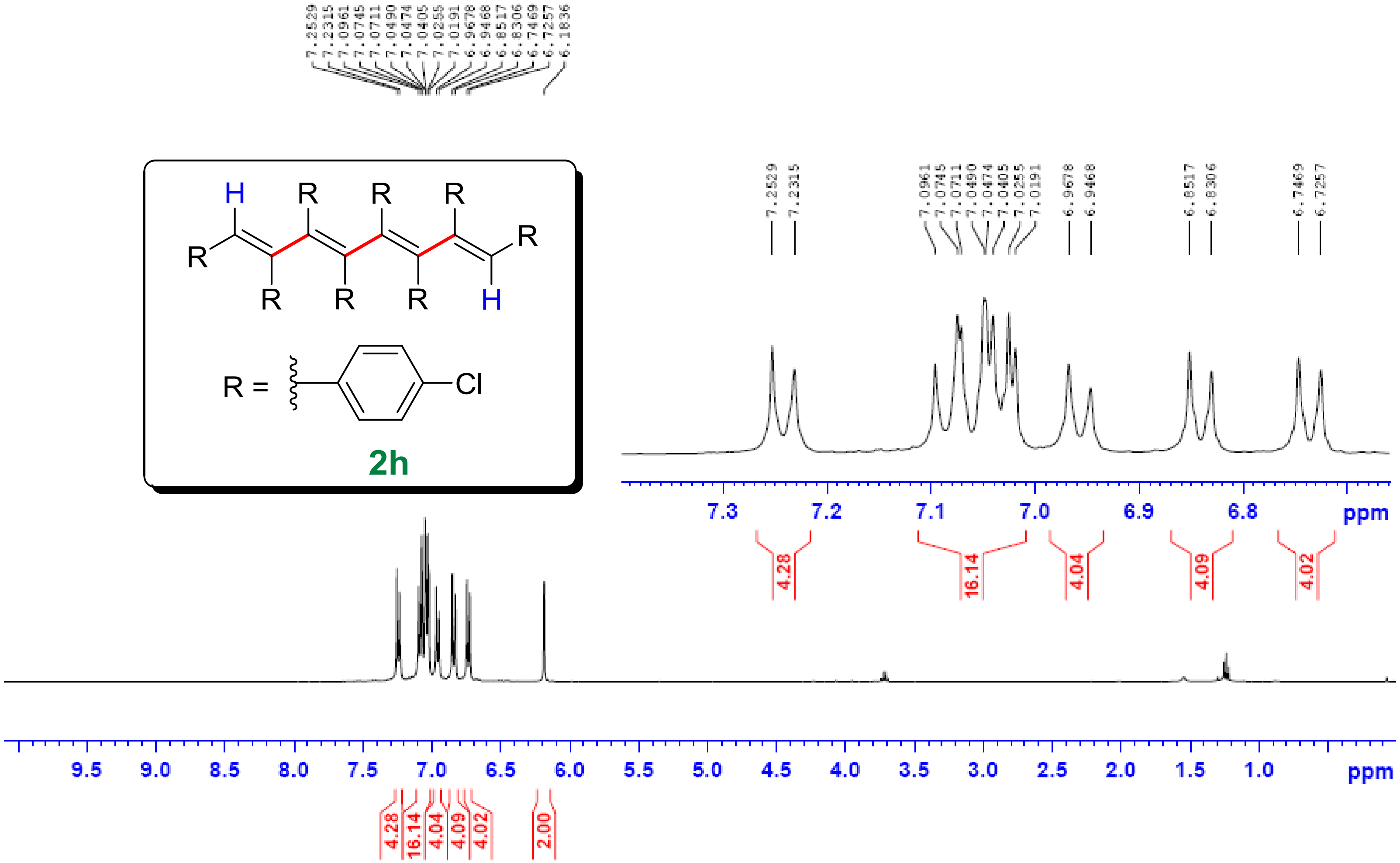

ZGY-140521-7-FNMR
-57.9704
-58.0575
-58.1700
H
R
R
R
R
R
R
R
R
H
R =
OCF3
2f
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


140617-ZCY-4-HNMR(1
7.2935
7.2799
7.2721
7.2585
7.2529
7.0594
7.0456
7.0382
7.0246
6.8939
6.8801
6.8723
6.8588
6.8251
6.8035
6.7811
6.7750
6.7575
6.7397
6.7182
6.2031
-0.0002
H
R
R =
F
2g
7.4
7.3
7.2
7.1
7.0
6.9
6.8
ppm
4.16
4.00
4.22
20.47
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
ppm
1.98

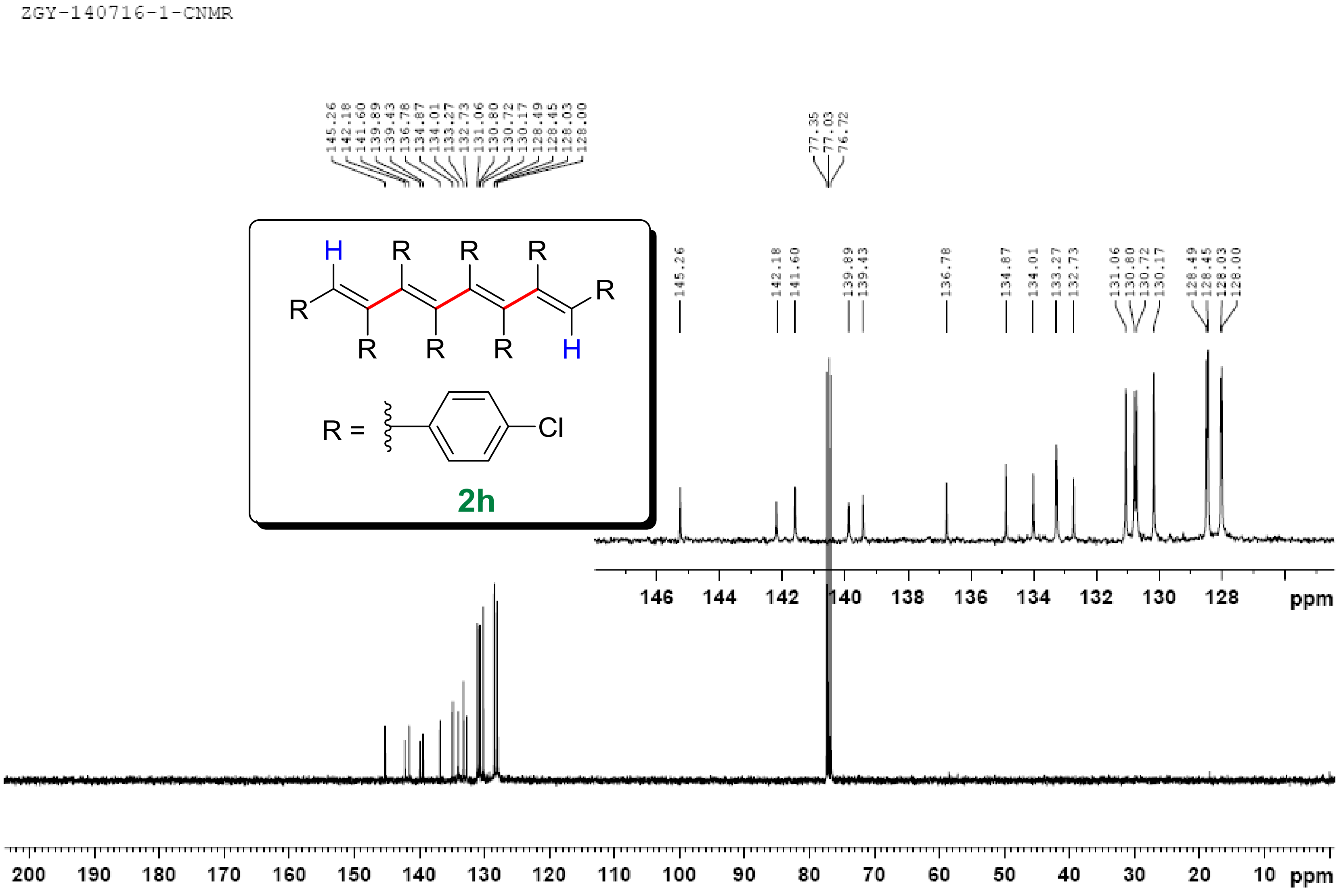

20140617-ZCY-4-CNMR(17)
163.01
162.99
162.82
162.45
160.55
160.52
160.36
159.99
145.09
142.15
141.53
138.04
137.53
137.49
134.78
134.75
133.53
132.84
132.81
131.49
131.41
131.14
131.06
130.58
130.50
115.21
115.00
114.75
114.54
77.34
77.02
76.70
H
R
R
R
R
R
R
R
R
H
R =
F
2g
138.04
137.53
137.49
134.78
134.75
133.53
132.84
132.81
131.49
131.41
131.14
131.06
130.58
130.50
138
137
136
135
134
133
132
131
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

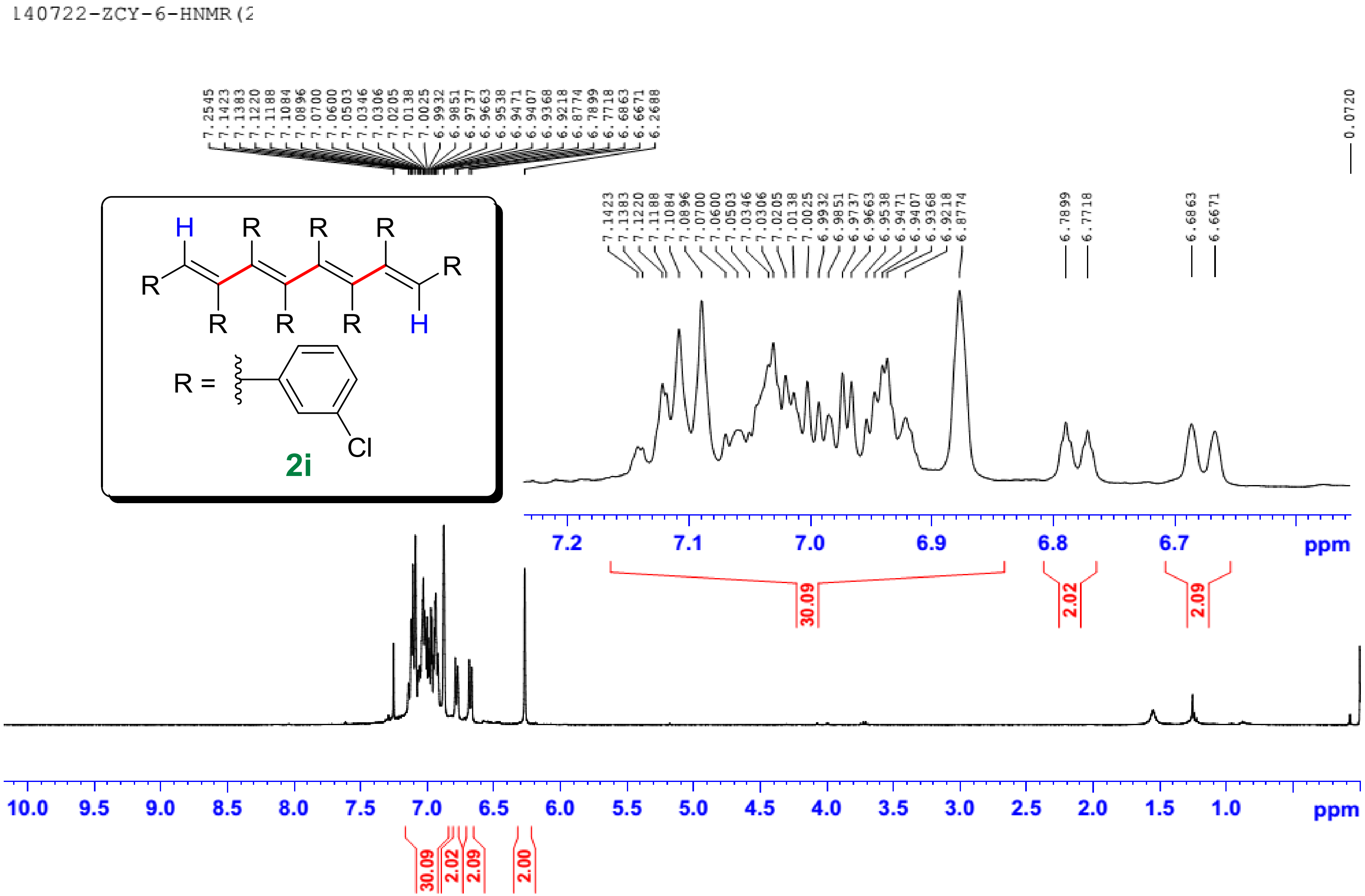

ZGY-140526-1-FNMR
-114.0228
-114.0523
-114.1607
-114.7692
H
R
R
R
R
R
R
R
R
H
R =
F
2g
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

ZGY-140716-1-HNMR

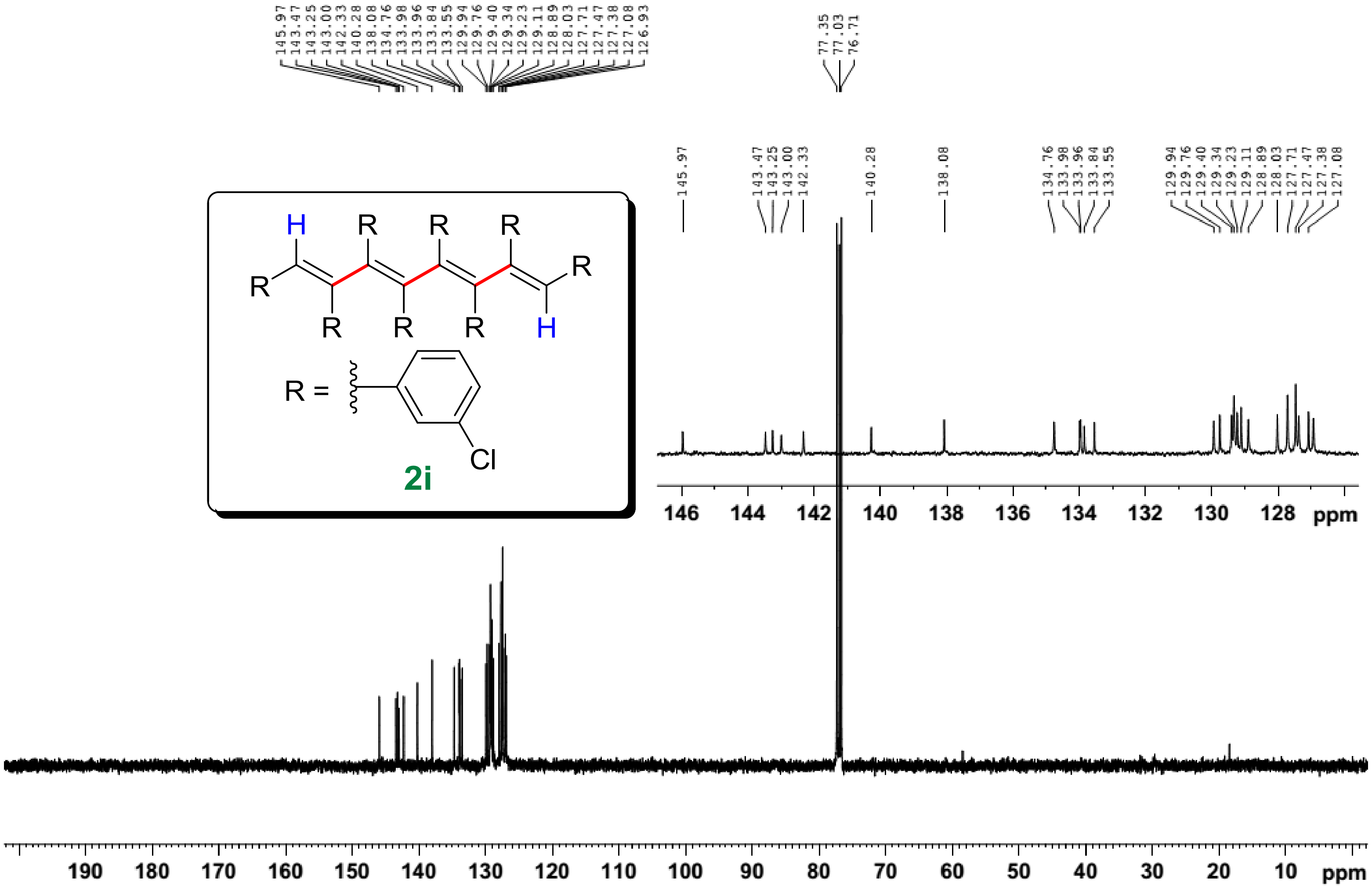


2h

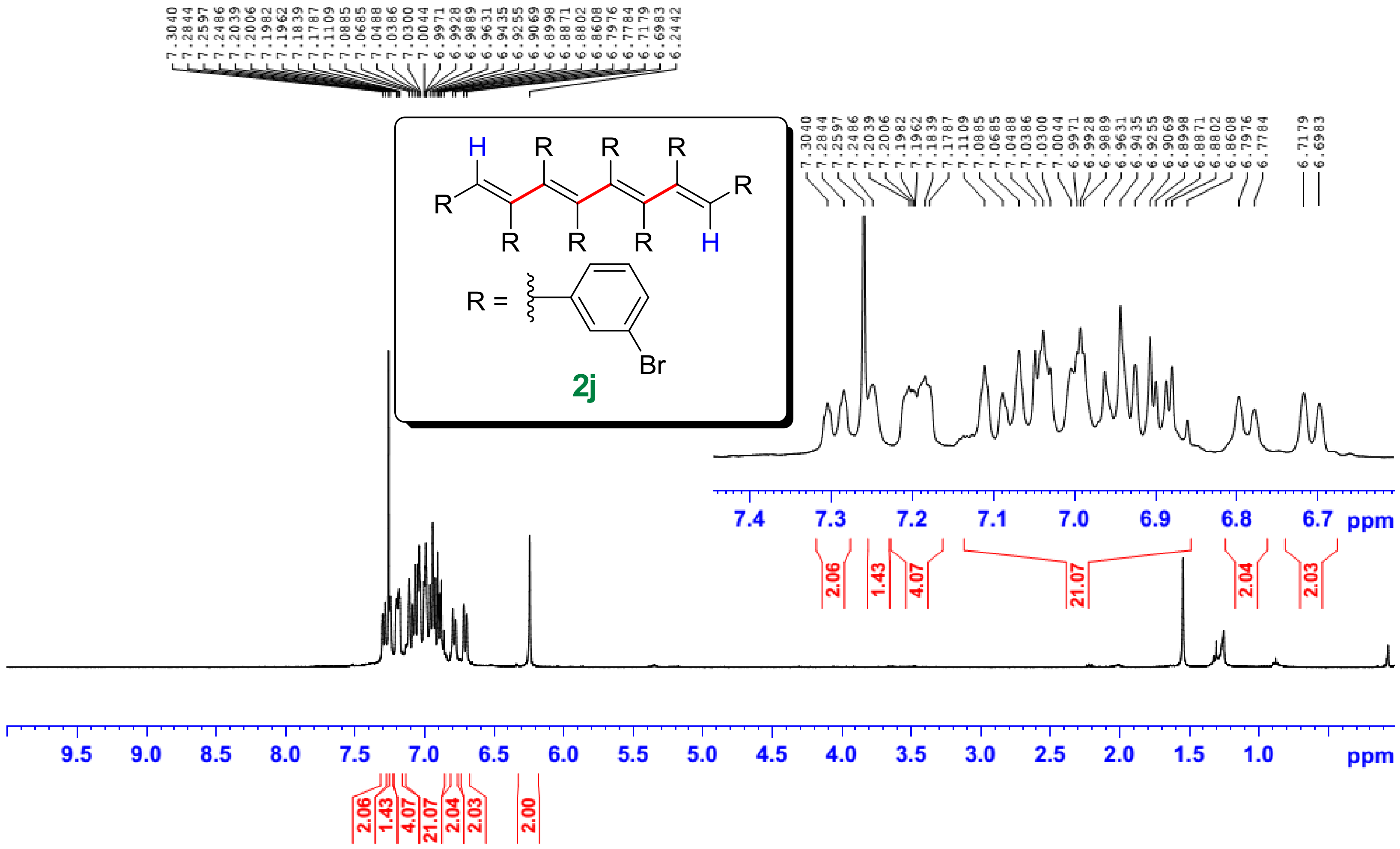

ZGY-140716-1-CNMR
145.26
142.18
141.60
139.89
139.43
136.78
134.87
134.01
133.27
132.73
131.06
130.80
130.72
130.17
128.49
128.45
128.03
128.00
77.35
77.03
76.72
H
R
R
R
R
R
R
R
R
H
R =
Cl
2h
146
144
142
140
138
136
134
132
130
128
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


140722-ZCY-6-HNMR(2
7.2545
7.1423
7.1383
7.1220
7.1188
7.1084
7.0896
7.0700
7.0600
7.0503
7.0346
7.0306
7.0205
7.0138
7.0025
6.9932
6.9851
6.9737
6.9663
6.9538
6.9471
6.9407
6.9368
6.9218
6.8774
6.7899
6.7718
6.6863
6.6671
6.2688
0.0720
H
R
R
R
R
R
R
R
R
H
R =
Cl
2i
7.2
7.1
7.0
6.9
6.8
6.7
ppm
30.09
2.02
2.09
10.0
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
ppm
30.09
2.02
2.09
2.00

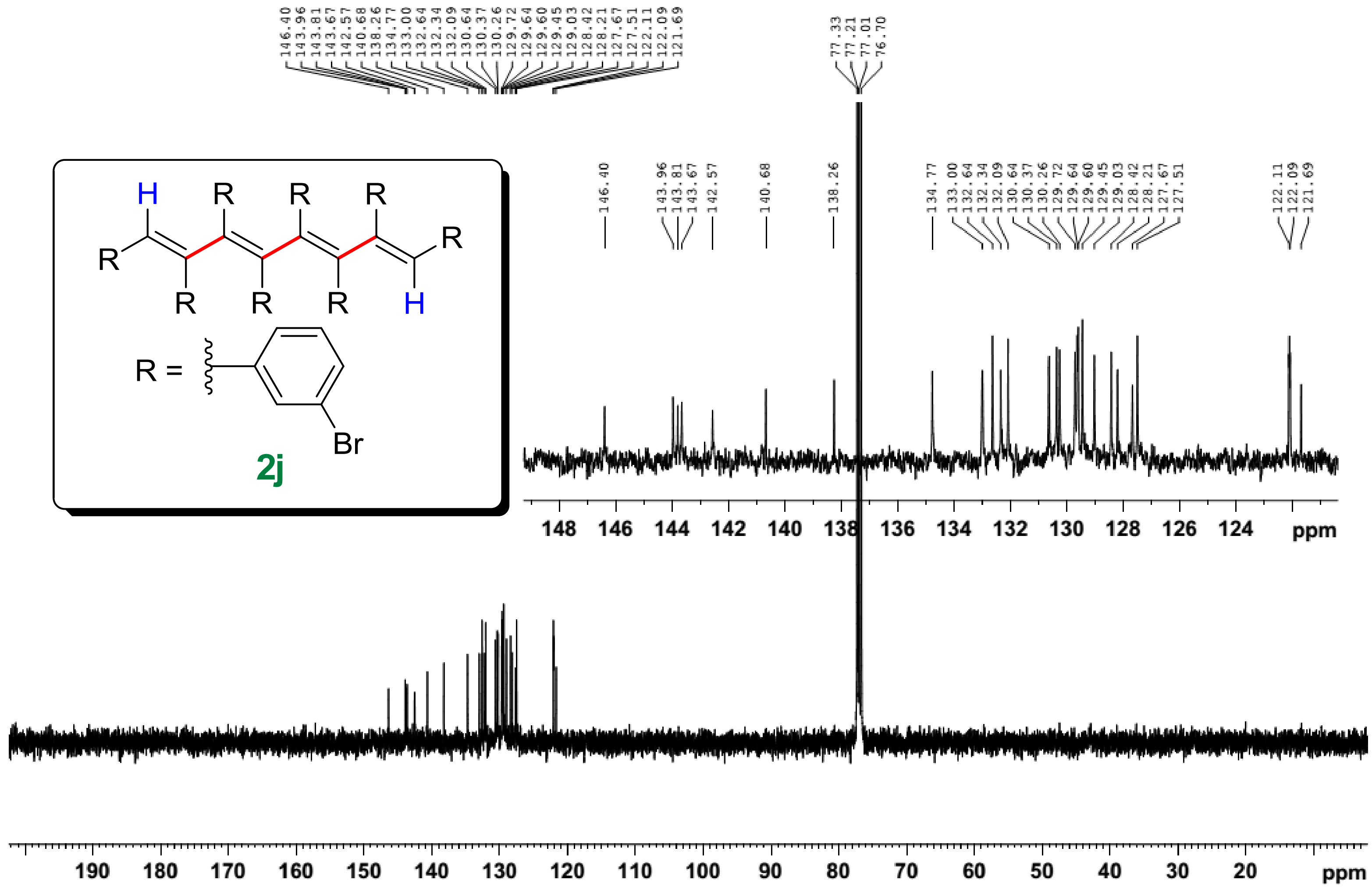
ZGY-140716-2-CNMR



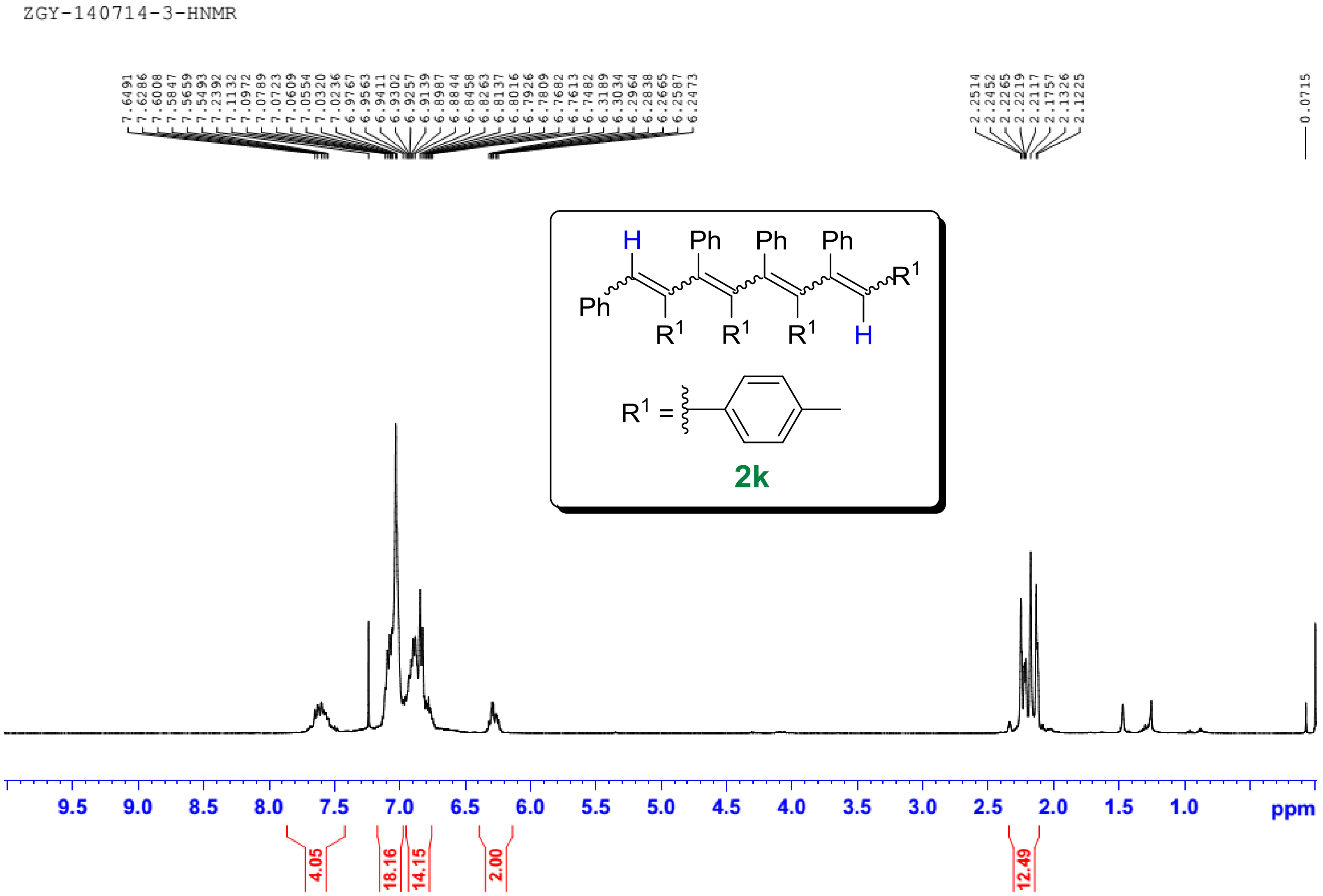
140715-ZCY-1-HNMR(1

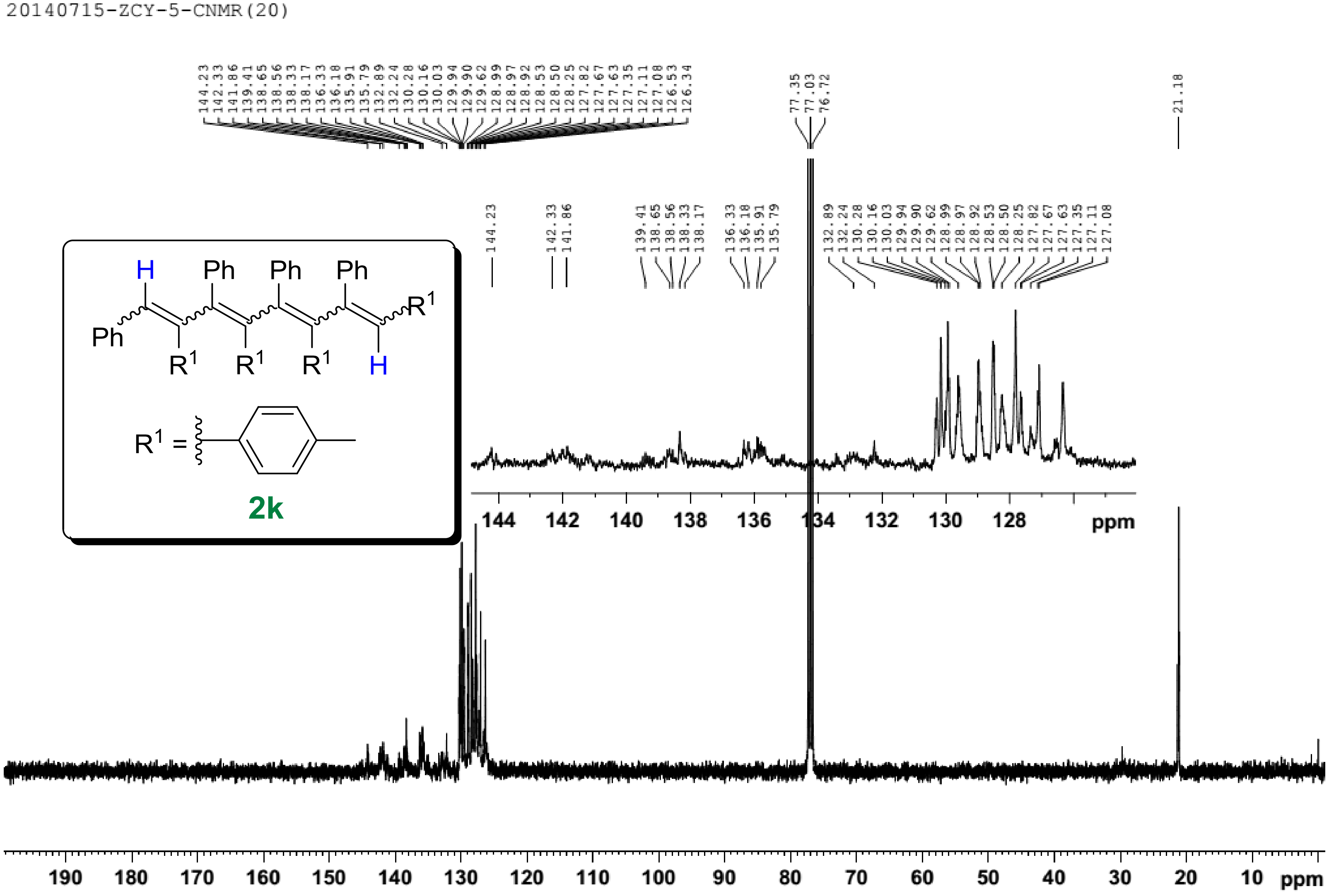


20140715-ZCY-1-CNMR(13)

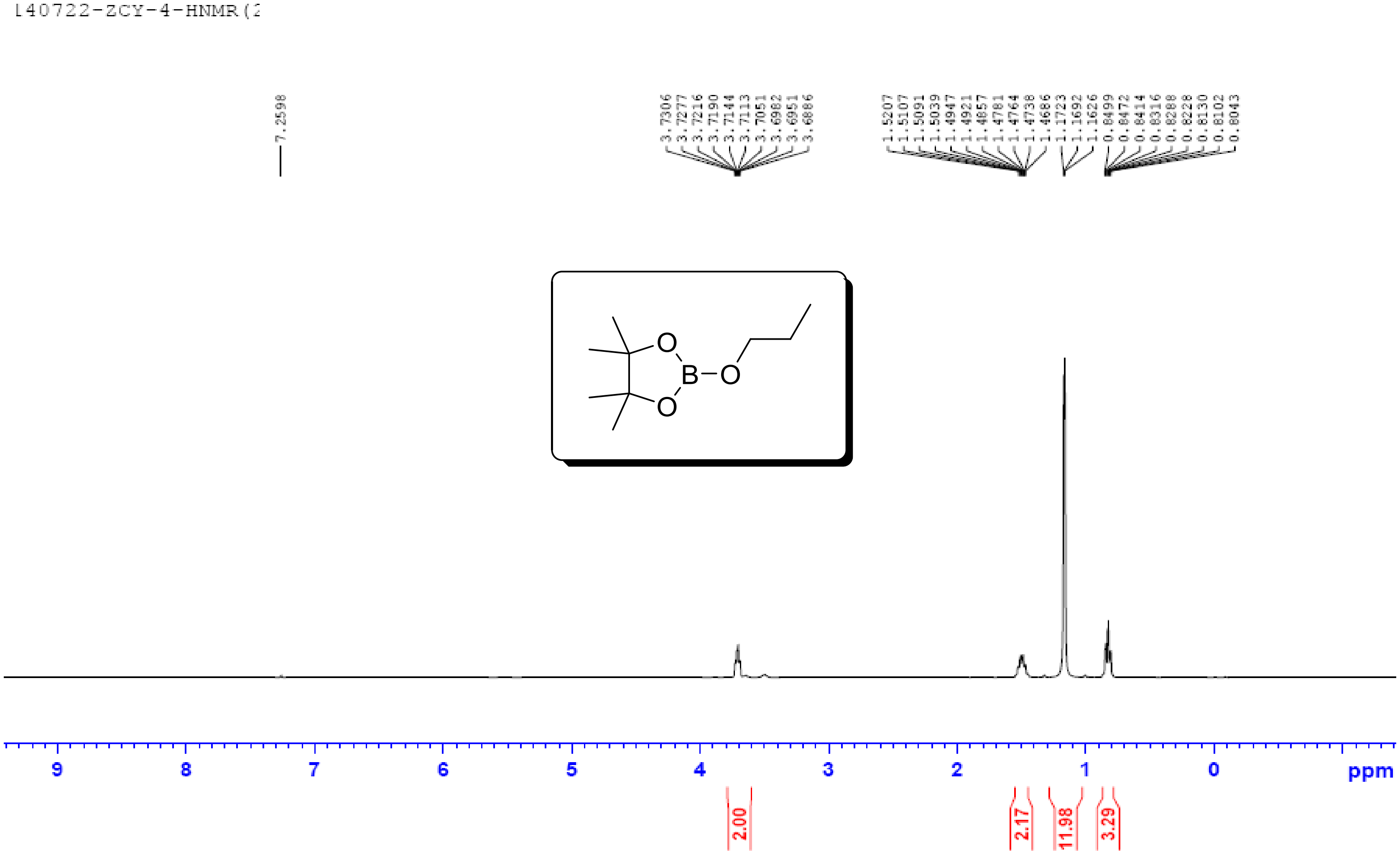


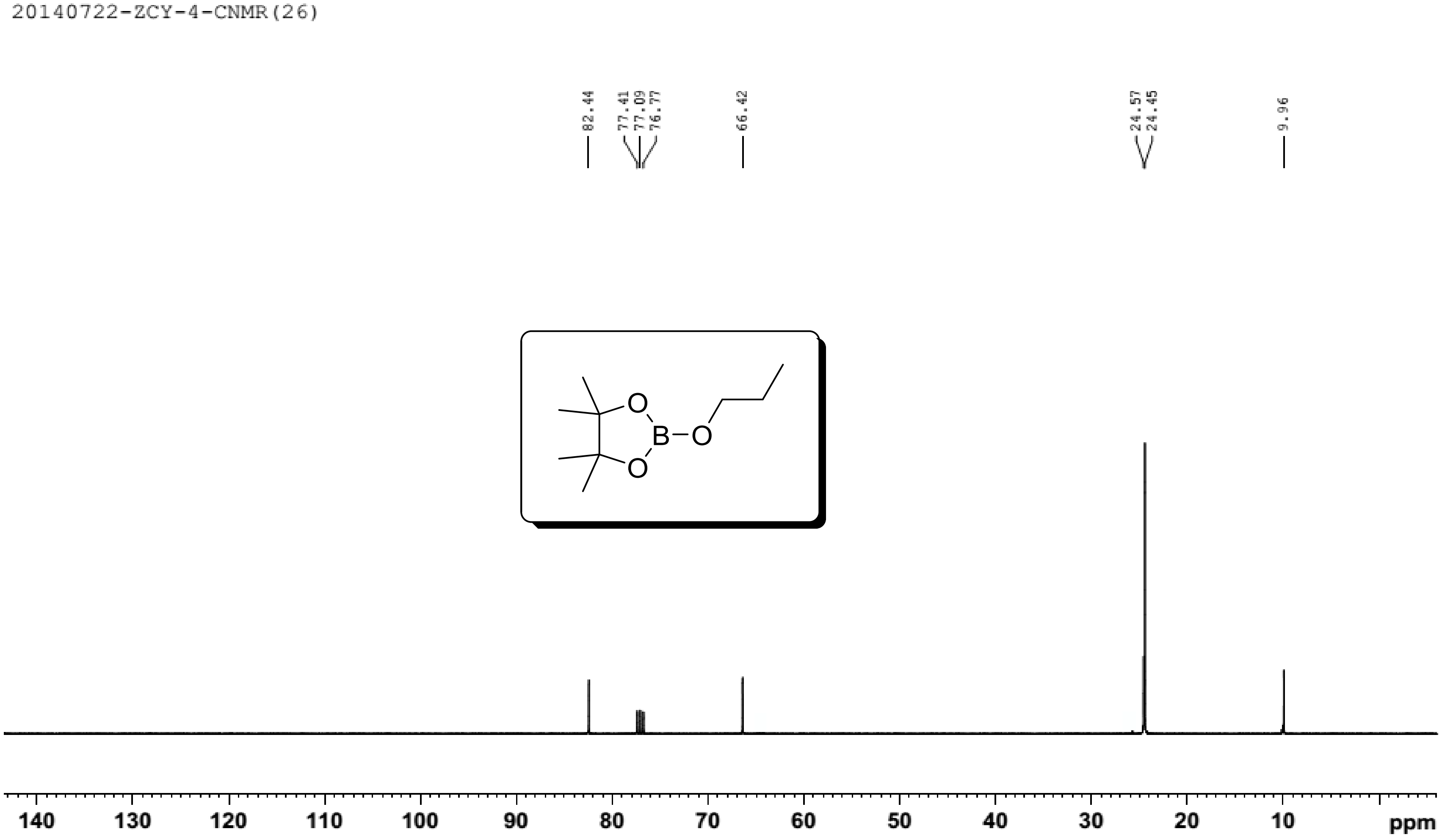
2j


ZGY-140714-3-HNMR
7.6491
7.6286
7.6008
7.5847
7.5659
7.5493
7.2392
7.1132
7.0972
7.0789
7.0723
7.0609
7.0554
7.0320
7.0236
6.9767
6.9563
6.9411
6.9302
6.9257
6.9139
6.8987
6.8844
6.8458
6.8263
6.8137
6.8016
6.7926
6.7809
6.7682
6.7613
6.7482
6.3189
6.3034
6.2964
6.2838
6.2665
6.2587
6.2473
2.2514
2.2452
2.2265
2.2219
2.2117
2.1757
2.1326
2.1225
0.0715
H
Ph
Ph
Ph
Ph
R1
R1
R1
R1
H
R1 =
2k
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
ppm
4.05
18.16
14.15
2.00
12.49

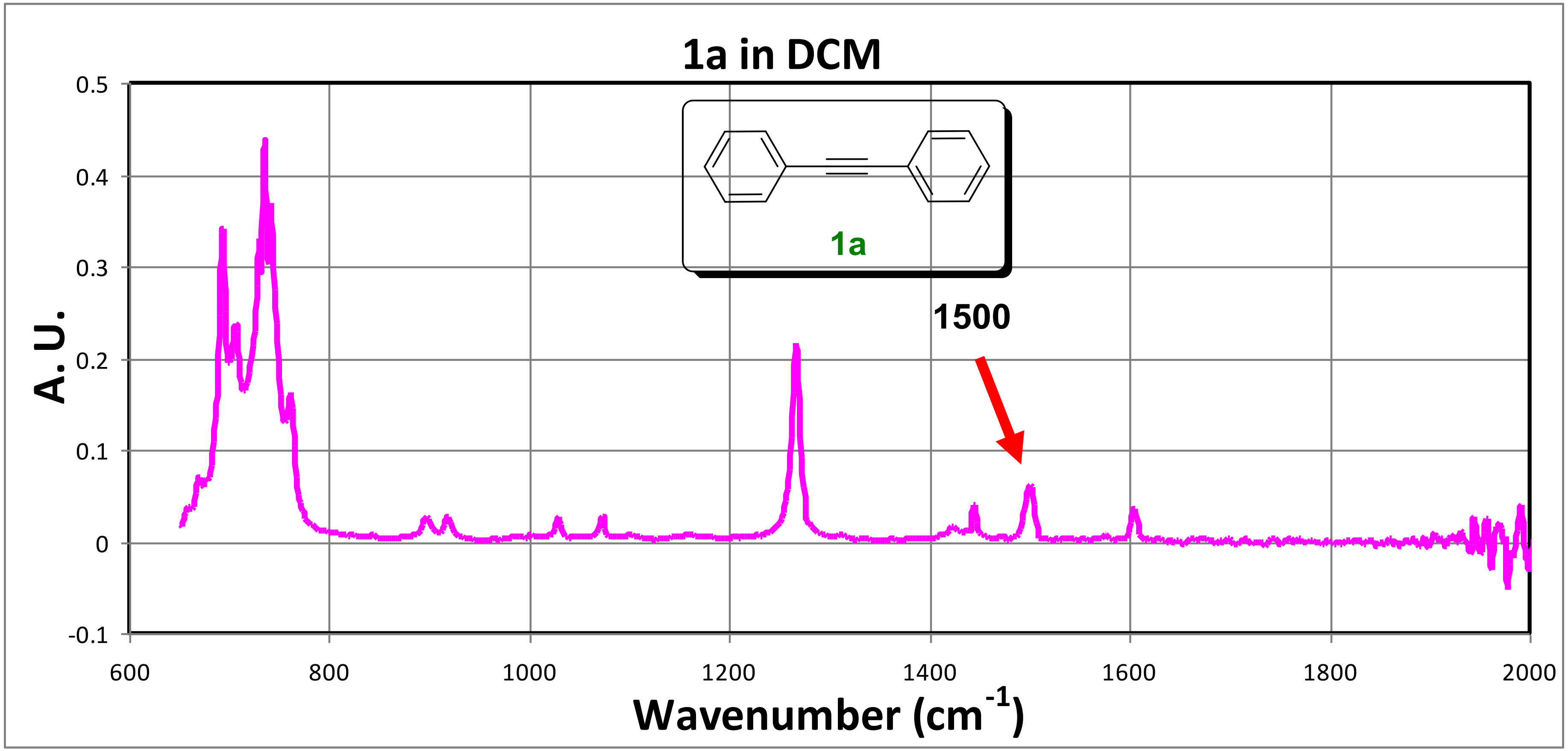

20140715-ZCY-5-CNMR(20)
144.23
142.33
141.86
139.41
138.65
138.56
138.33
138.17
136.33
136.18
135.91
135.79
132.89
132.24
130.28
130.16
130.03
129.94
129.90
129.62
128.99
128.97
128.92
128.53
128.50
128.25
127.82
127.67
127.63
127.35
127.11
127.08
126.53
126.34
77.35
77.03
76.72
21.18
H
Ph
Ph
Ph
Ph
R1
R1
R1
R1
H
R1 =
144
142
140
138
136
134
132
130
128
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

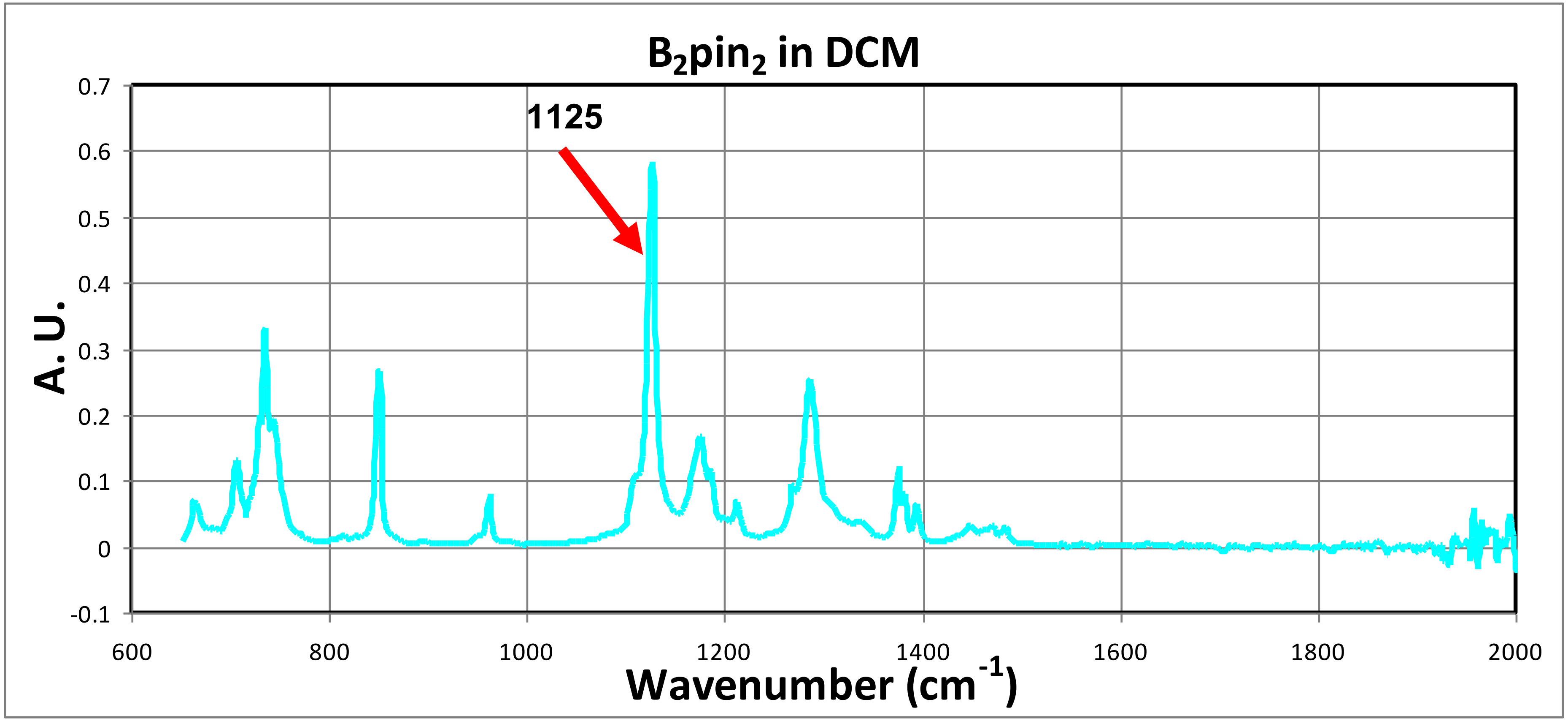
2k

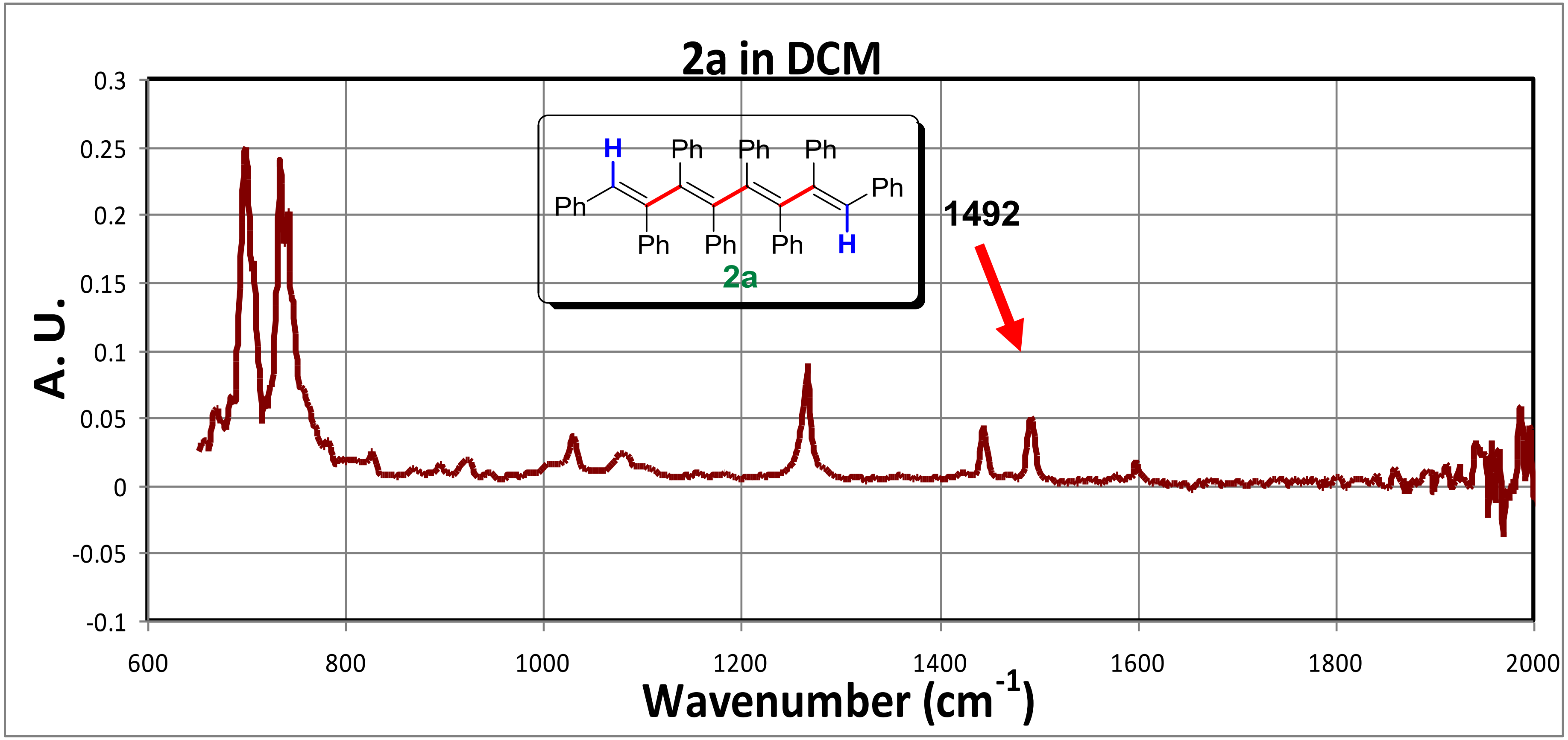

l40722-ZCY-4-HNMR(2
7.2598
3.7306
3.7277
3.7216
3.7190
3.7144
3.7113
3.7051
3.6982
3.6951
3.6886
1.5207
1.5107
1.5091
1.5039
1.4947
1.4921
1.4857
1.4781
1.4764
1.4738
1.4686
1.1723
1.1692
1.1626
0.8499
0.8472
0.8414
0.8316
0.8288
0.8228
0.8130
0.8102
0.8043
O
B
O
O
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.17
11.98
3.29

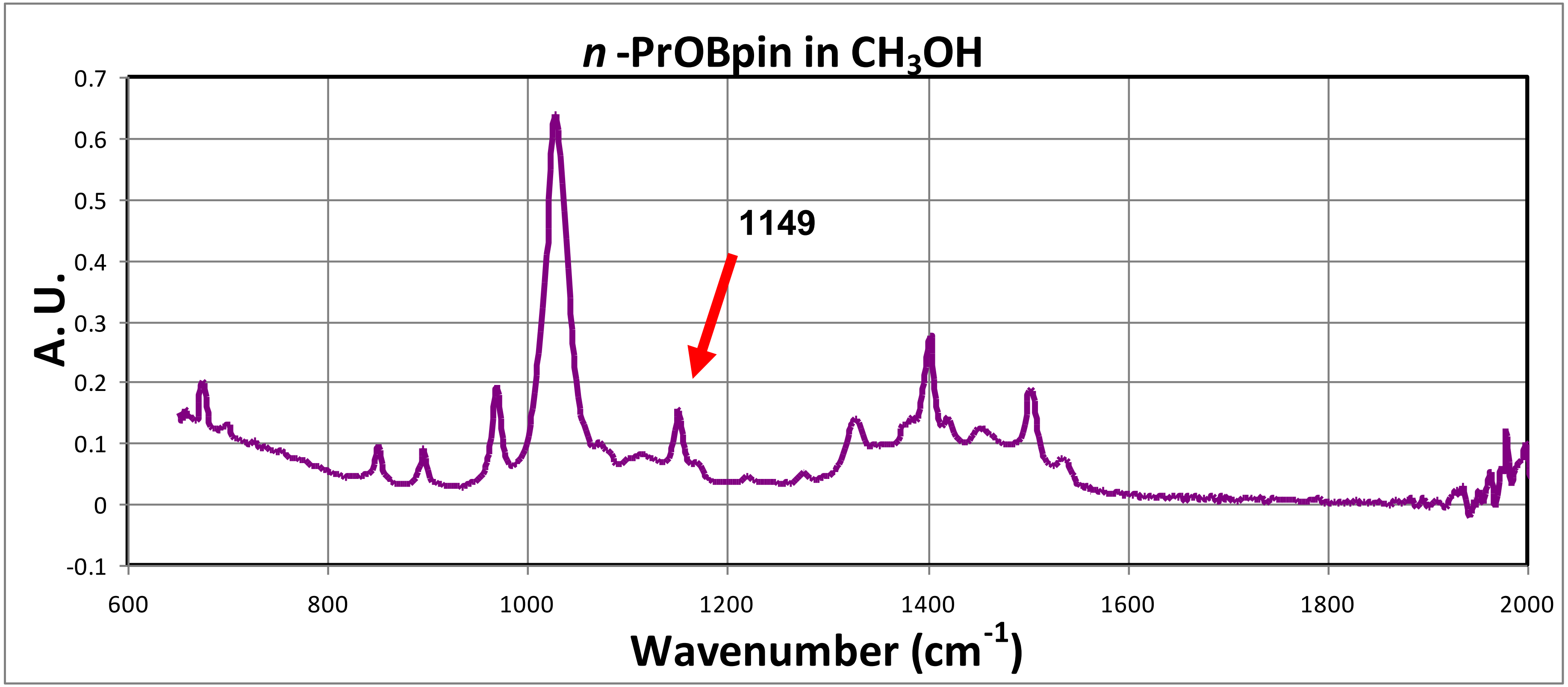

20140722-ZCY-4-CNMR(26)
82.44
77.41
77.09
76.77
66.42
24.57
24.45
9.96
O
B
O
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

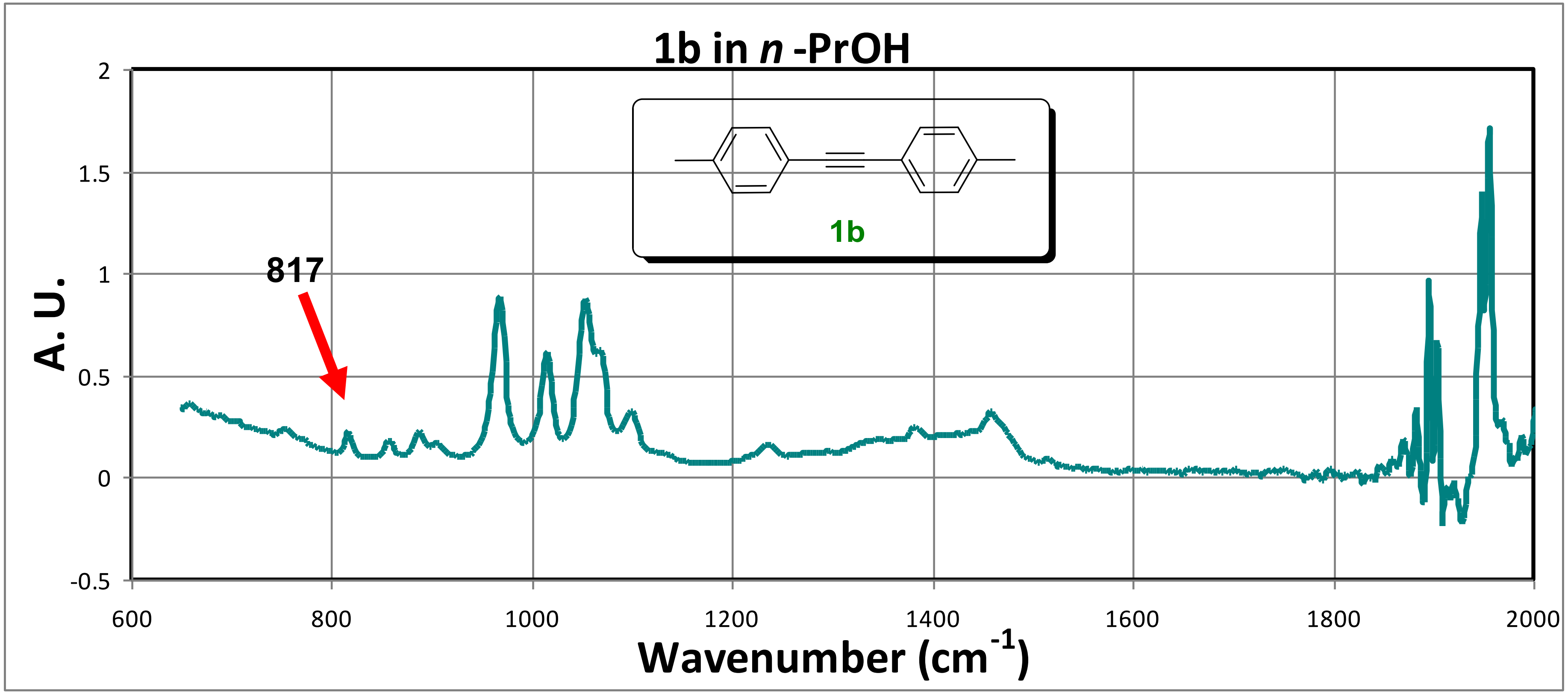
9. Copies for *In stiu* IR spectra

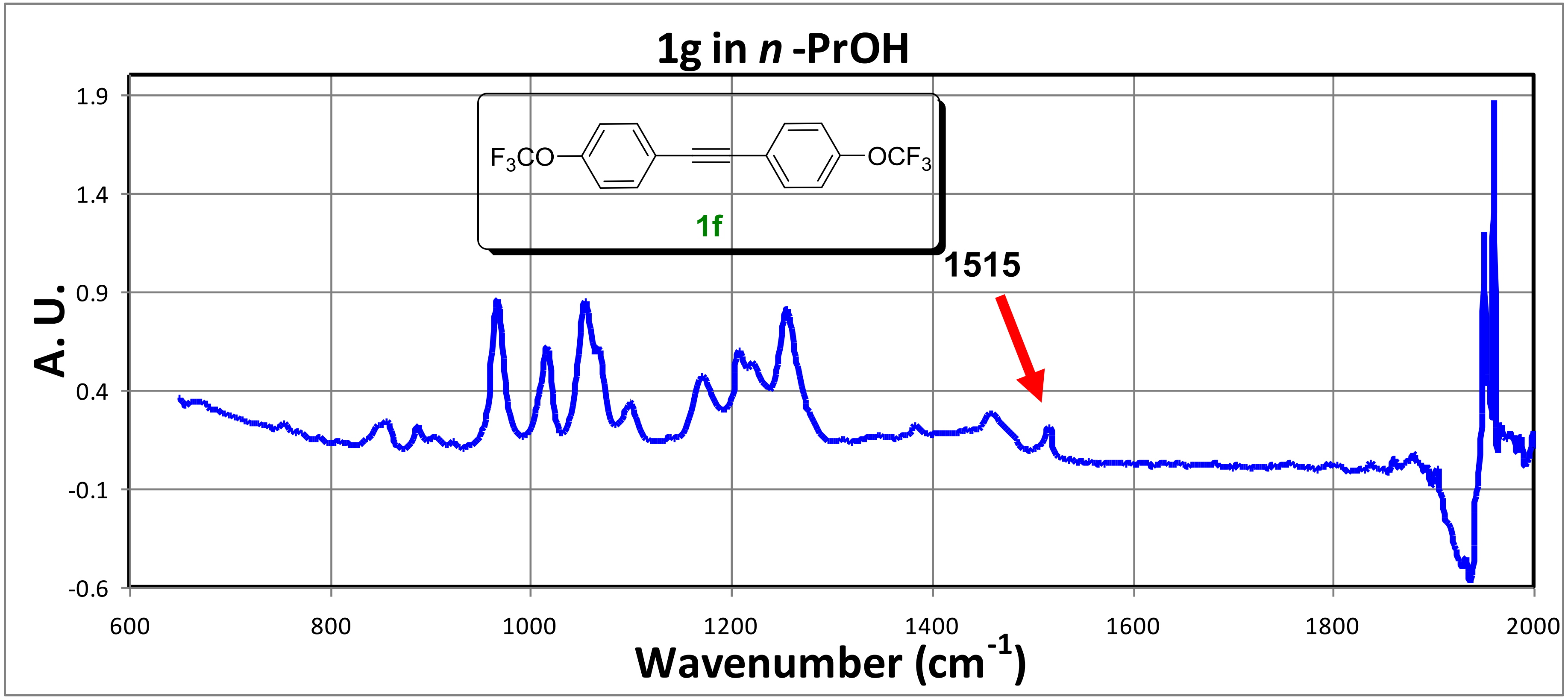


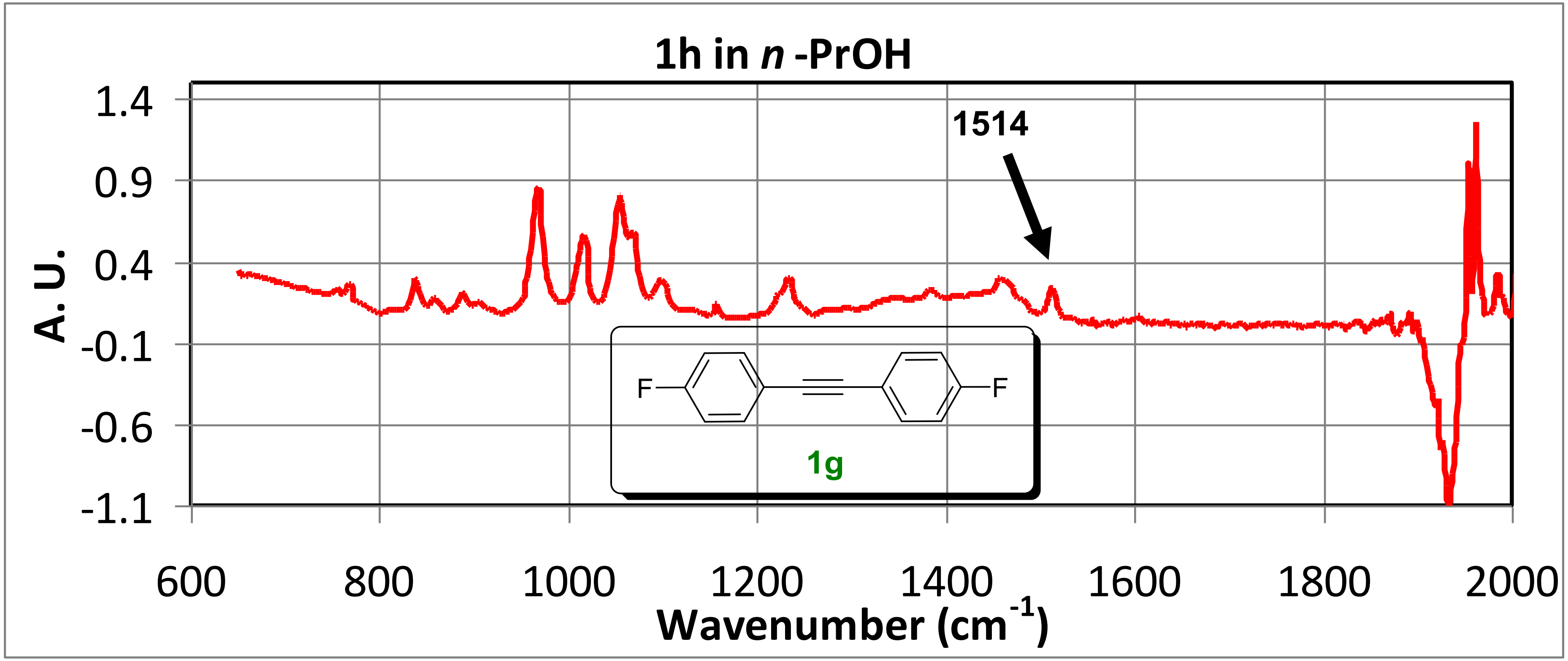

B_2pin_2 in DCM
1125
A. U.
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
600
800
1000
1200
1400
1600
1800
2000
Wavenumber (cm^{-1})


2a in DCM
H
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
H
2a
1492
A. U.
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
600
800
1000
1200
1400
1600
1800
2000
Wavenumber (cm-1)

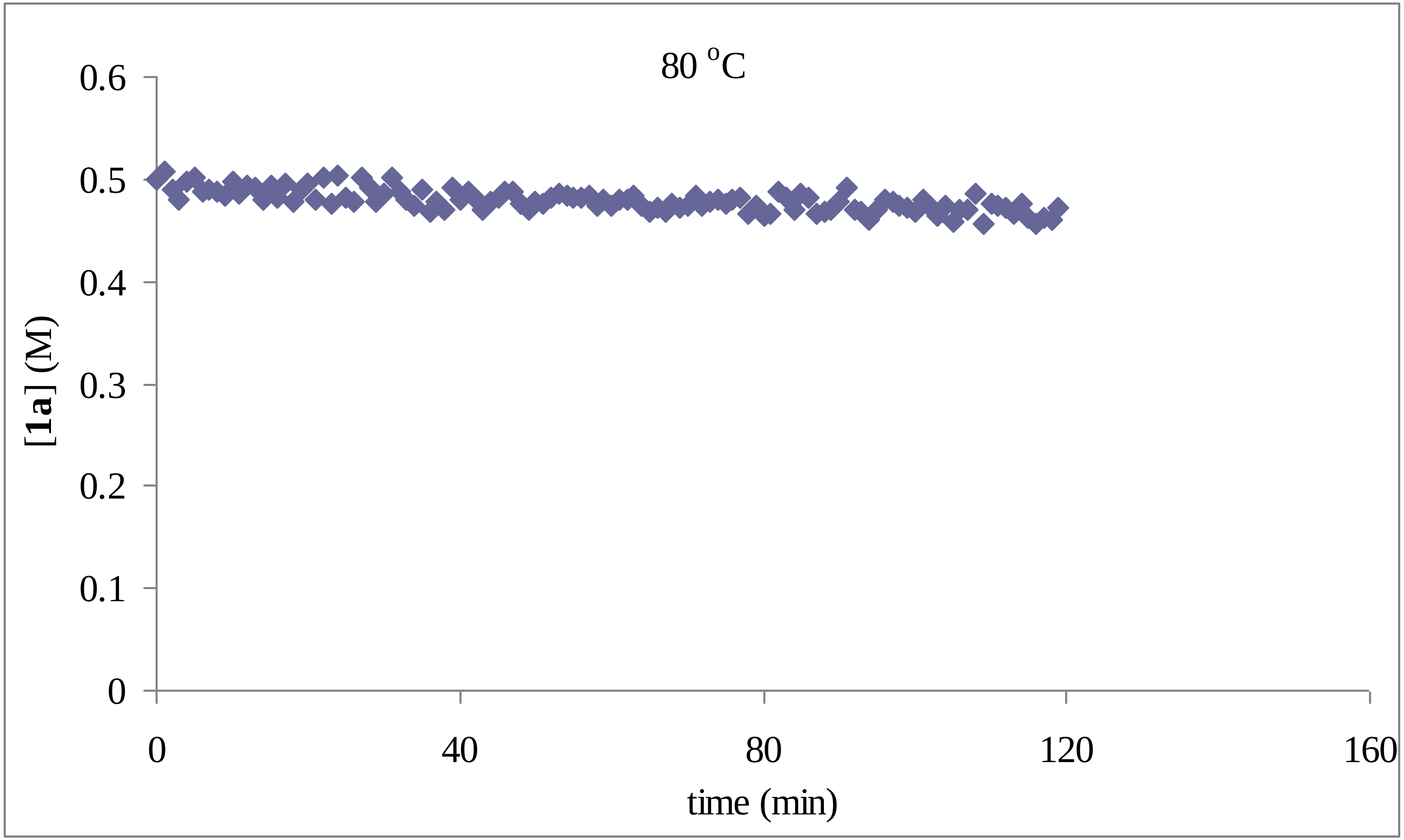

n -PrOBpin in CH_3OH
A. U.
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
600
800
1000
1200
1400
1600
1800
2000
Wavenumber (cm^{-1})
1149


1b in *n* -PrOH
2
1.5
1
0.5
0
-0.5
A. U.
817
1b
600
800
1000
1200
1400
1600
1800
2000
Wavenumber (cm^{-1})

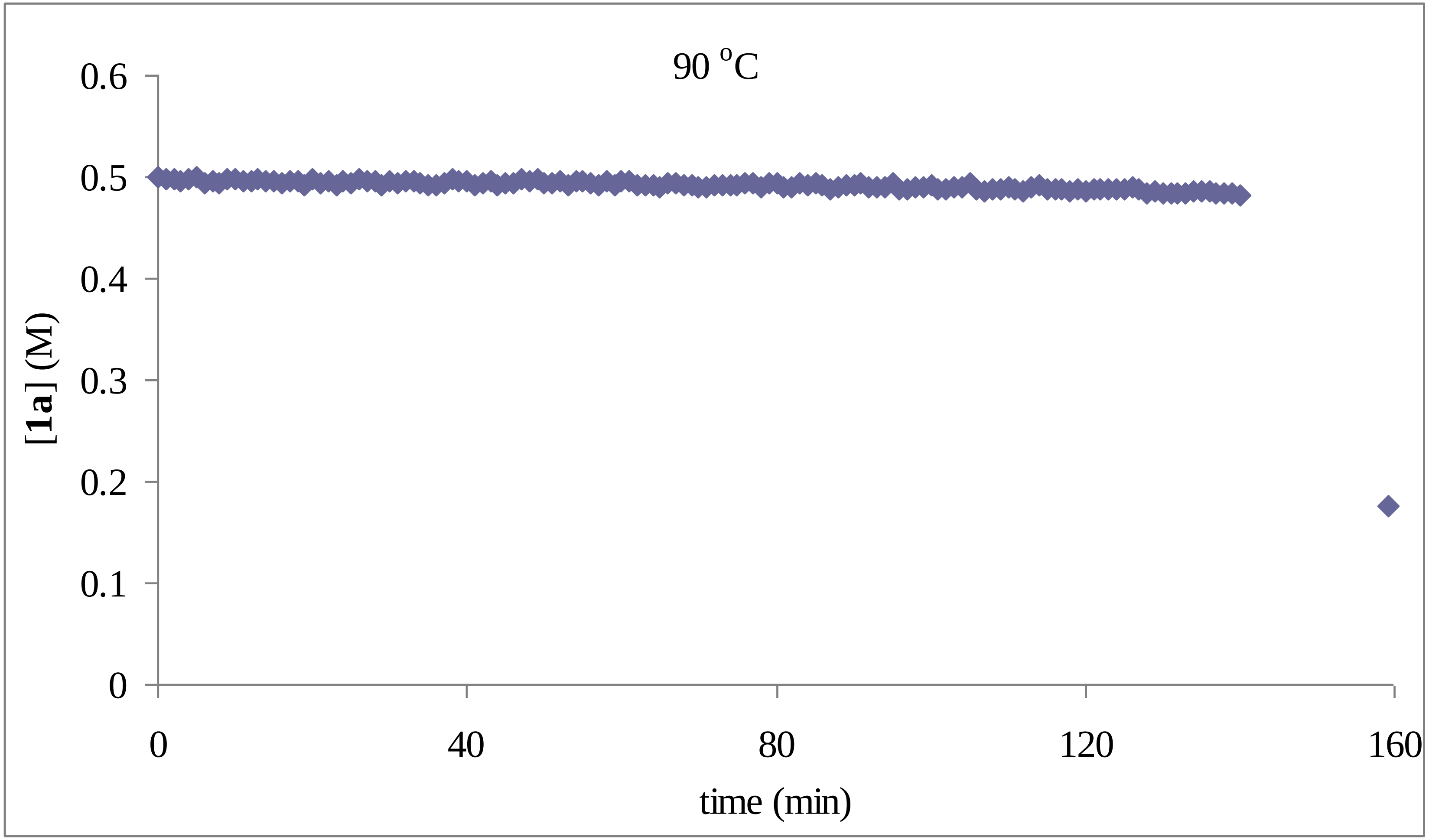

1g in *n* -PrOH
F3CO
OCF3
1f
1515
1.9
1.4
0.9
0.4
-0.1
-0.6
A. U.
600
800
1000
1200
1400
1600
1800
2000
Wavenumber (cm-1)



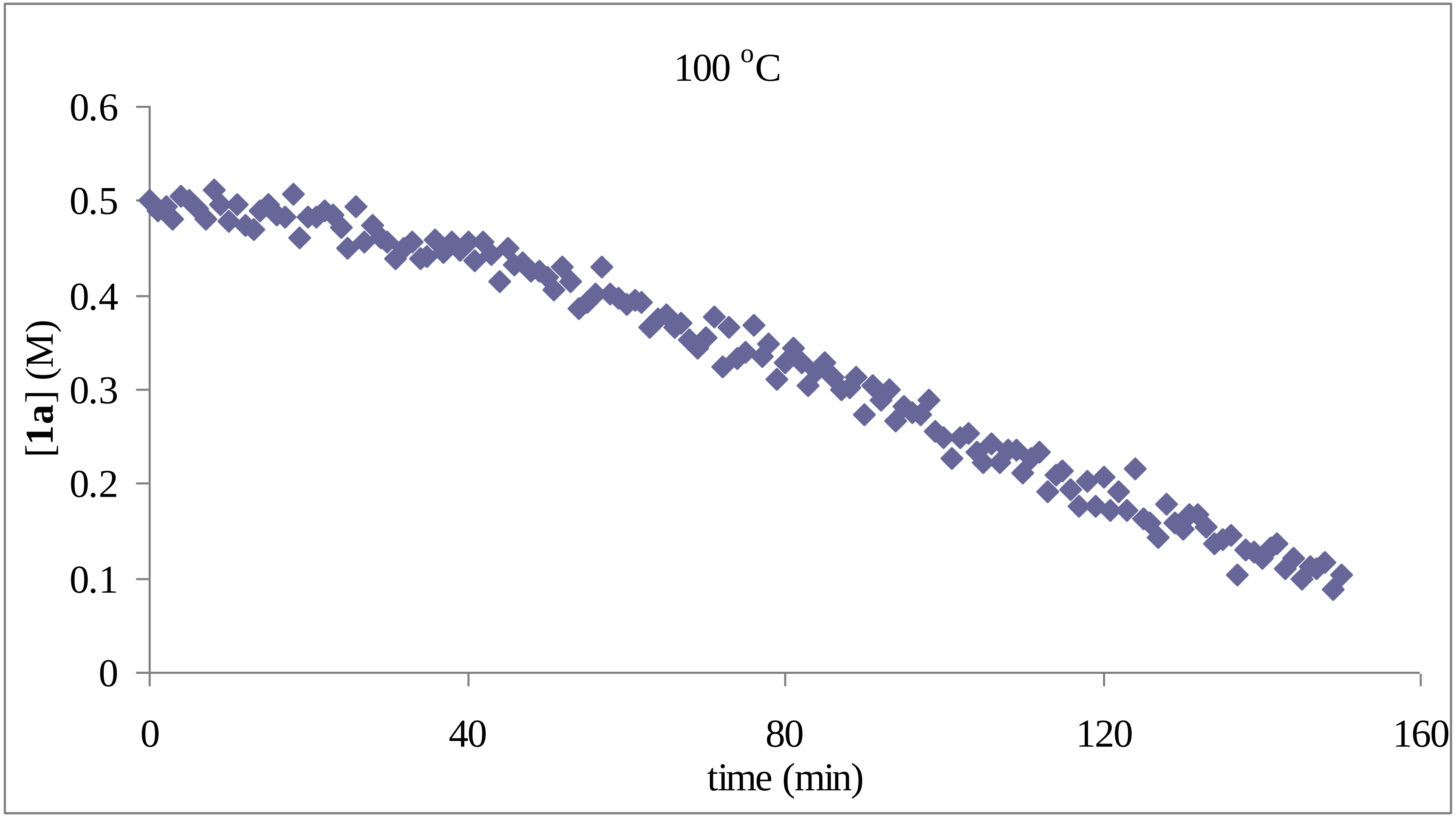
1h in *n* -PrOH
1.4
0.9
0.4
-0.1
-0.6
-1.1
A. U.
600
800
1000
1200
1400
1600
1800
2000
Wavenumber (cm^{-1})
1514
F
F
1g



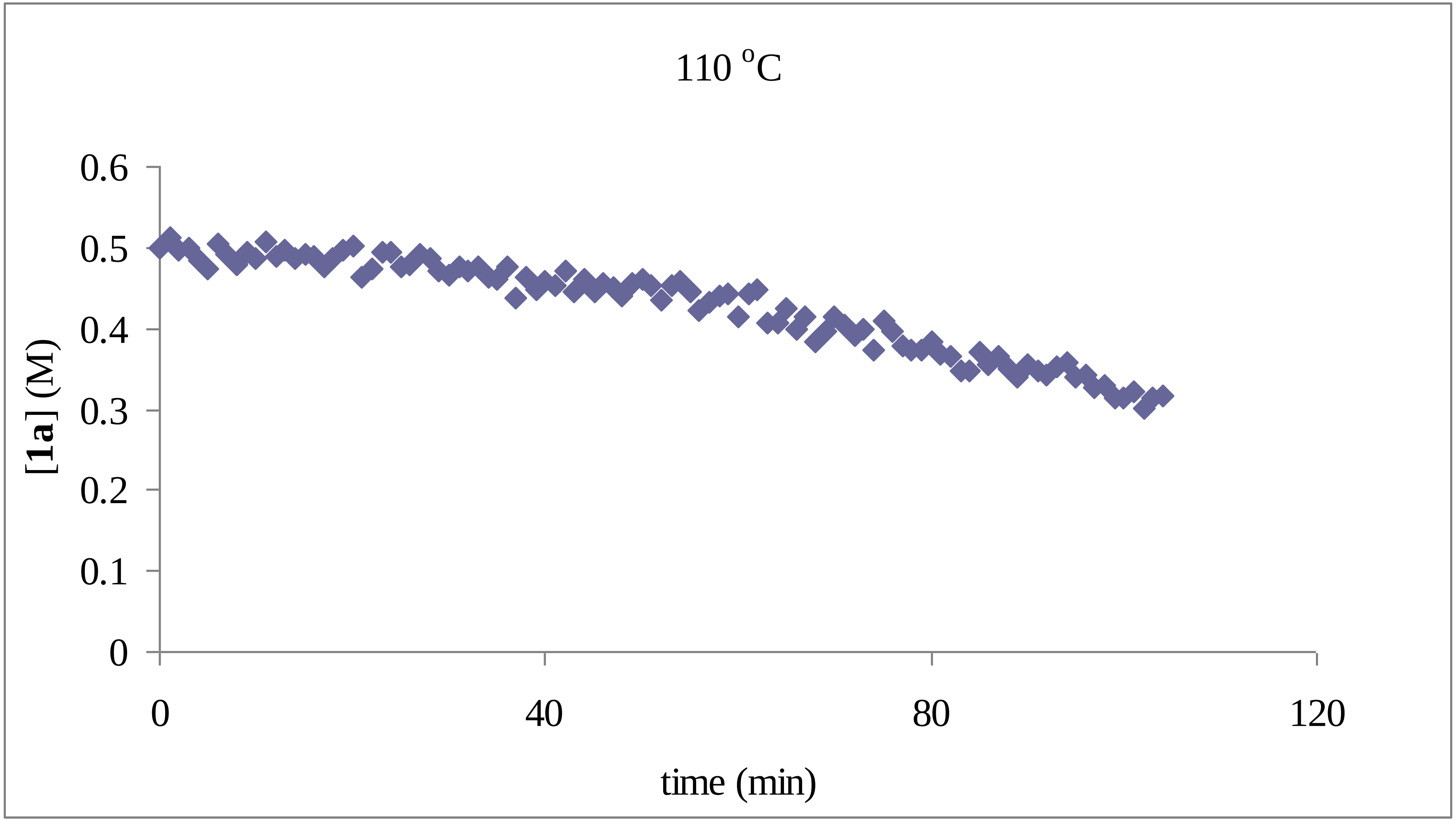
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 80 °C for 2 h.



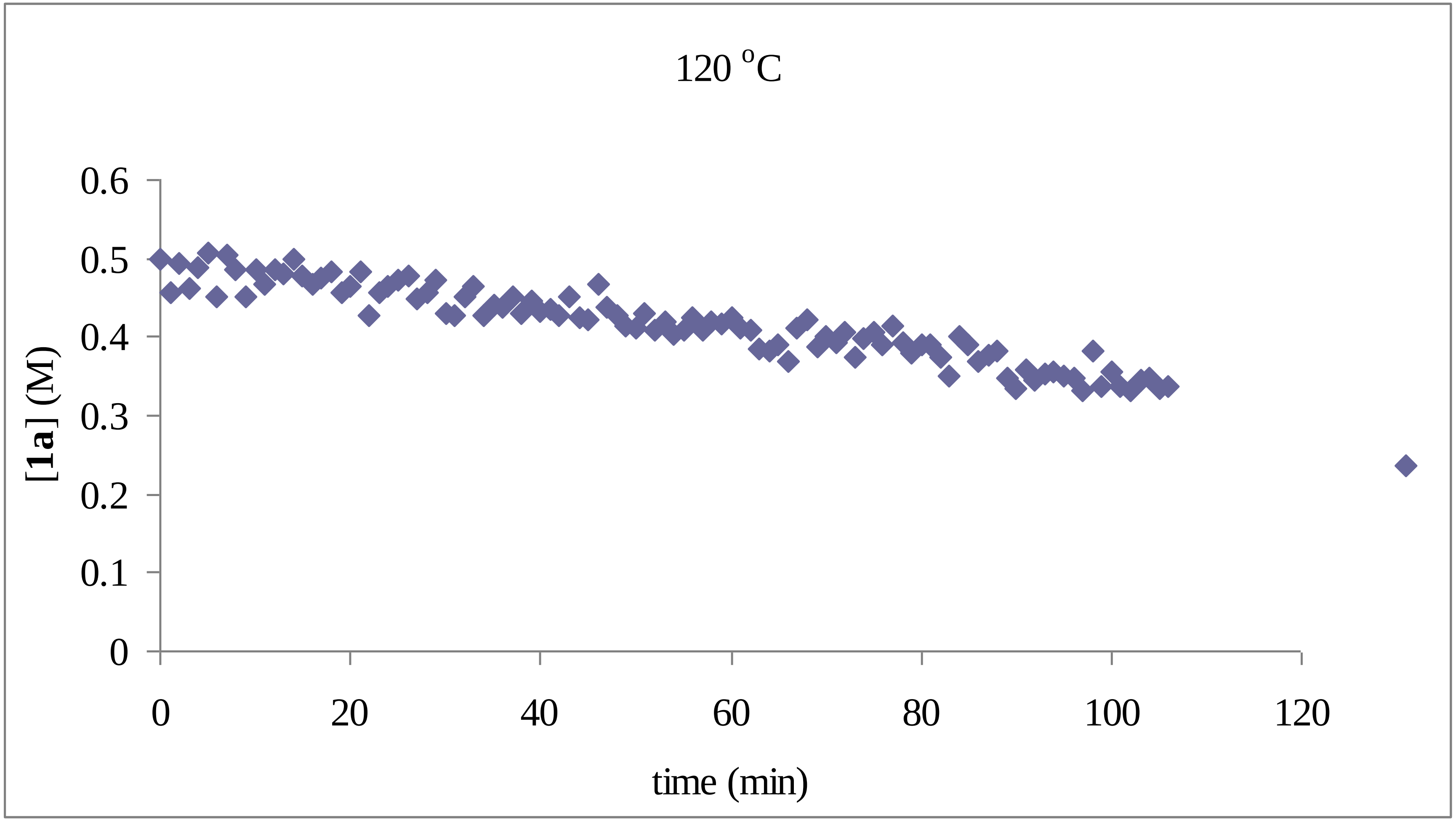
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 90 ^oC for 2 h.



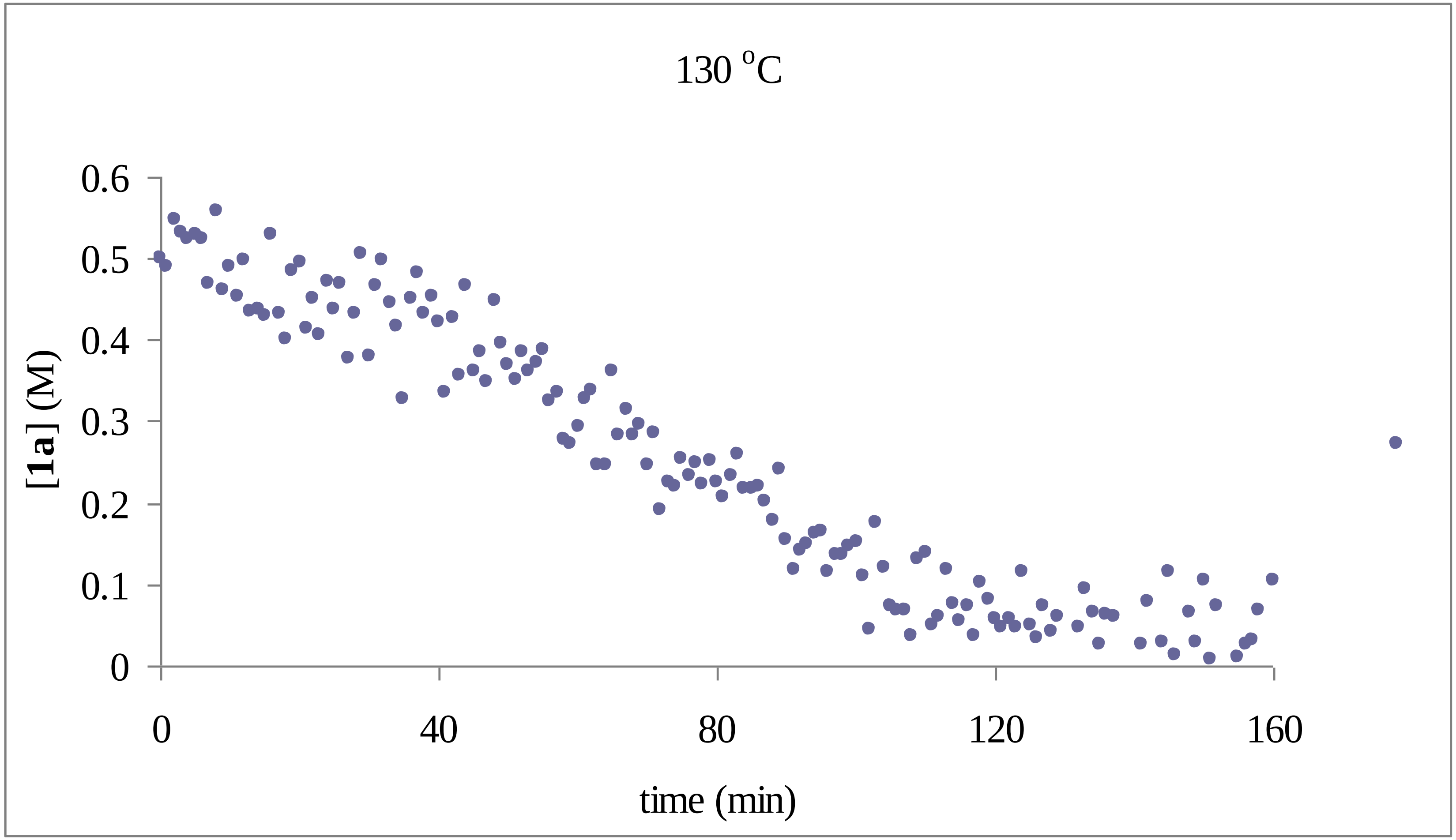
Reaction condition: **1a** (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 100 °C for 3 h.



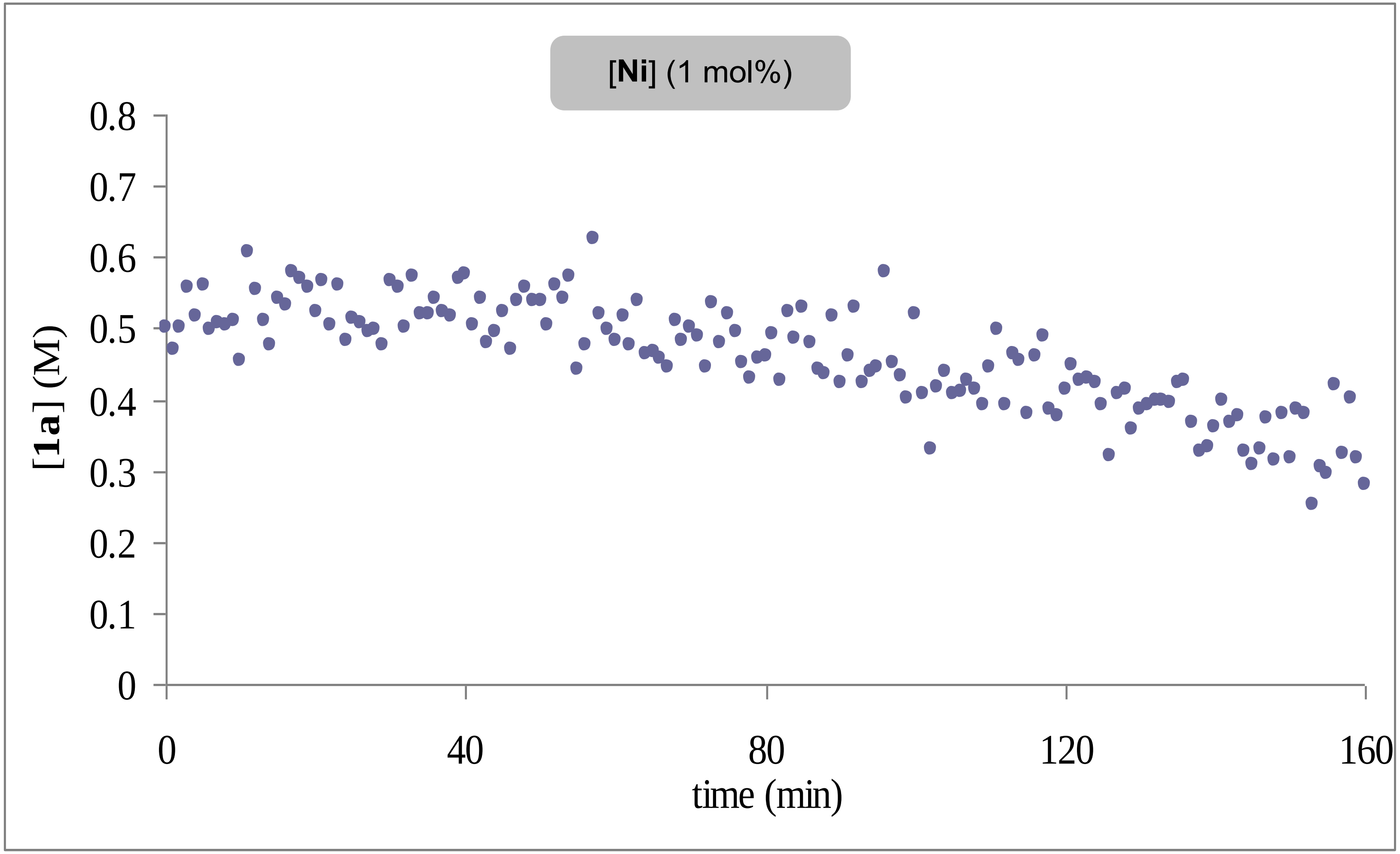
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 110 °C for 2 h.



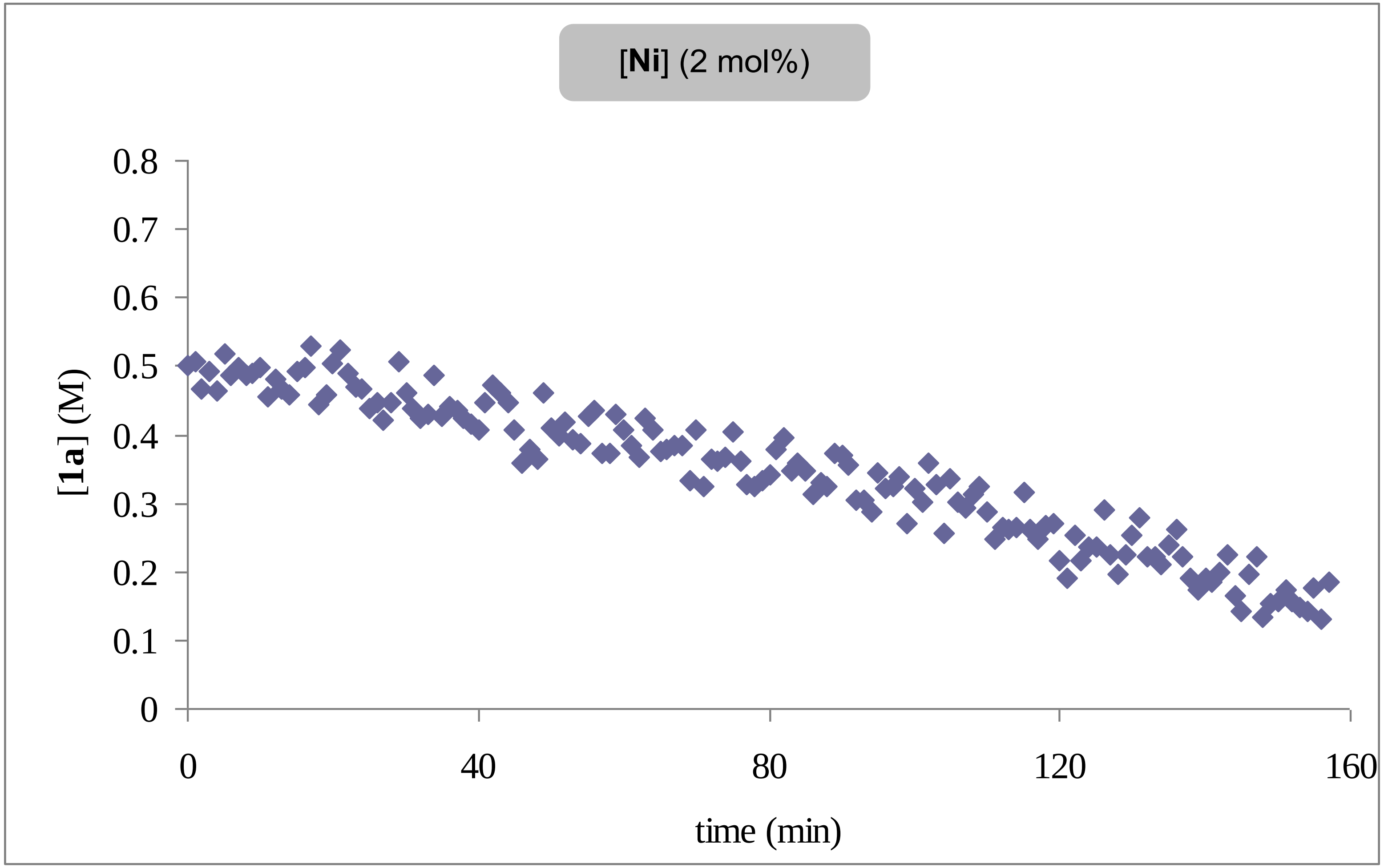
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 °C for 2 h.



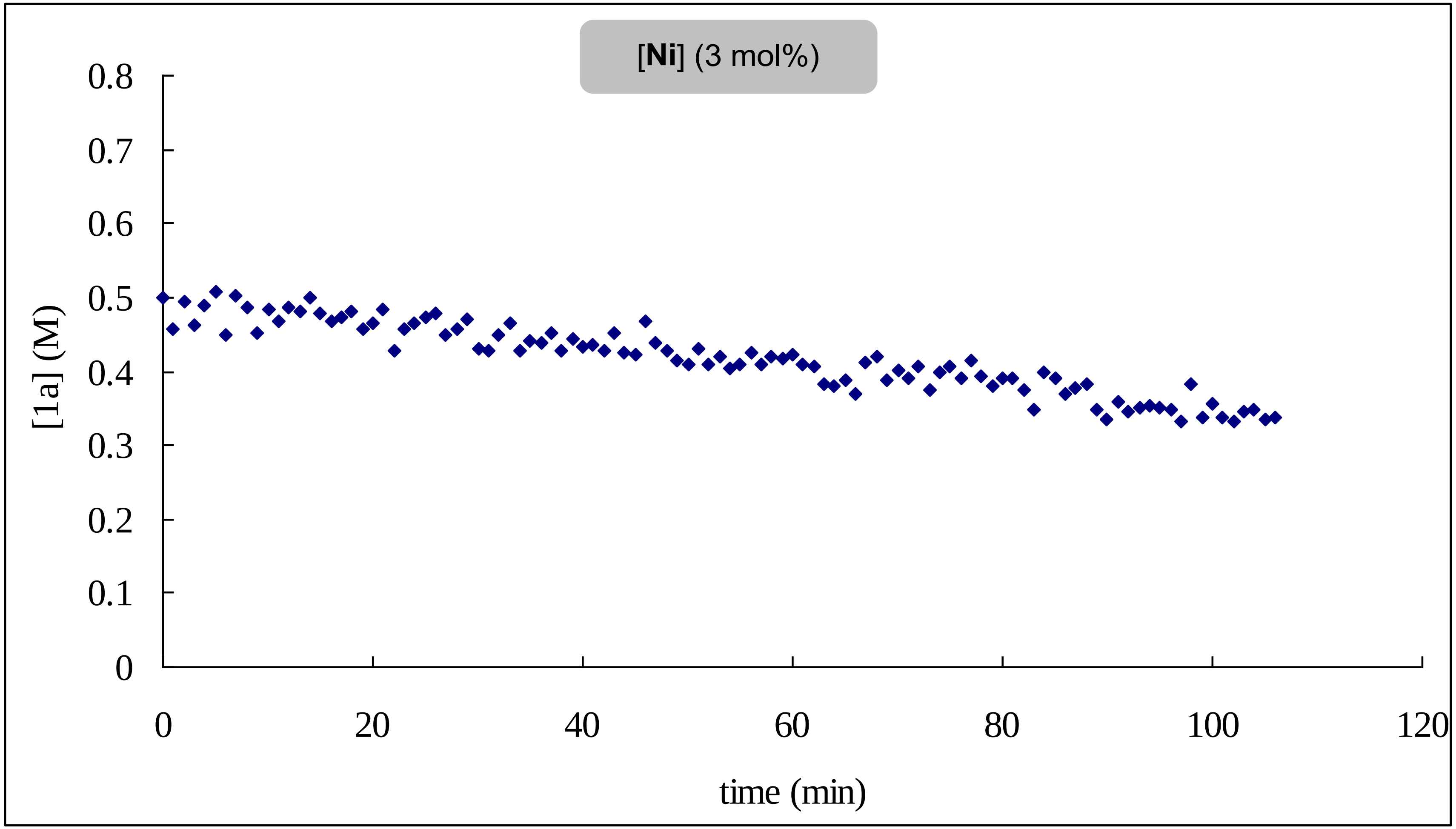
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 130 ^{o}C for 3 h.



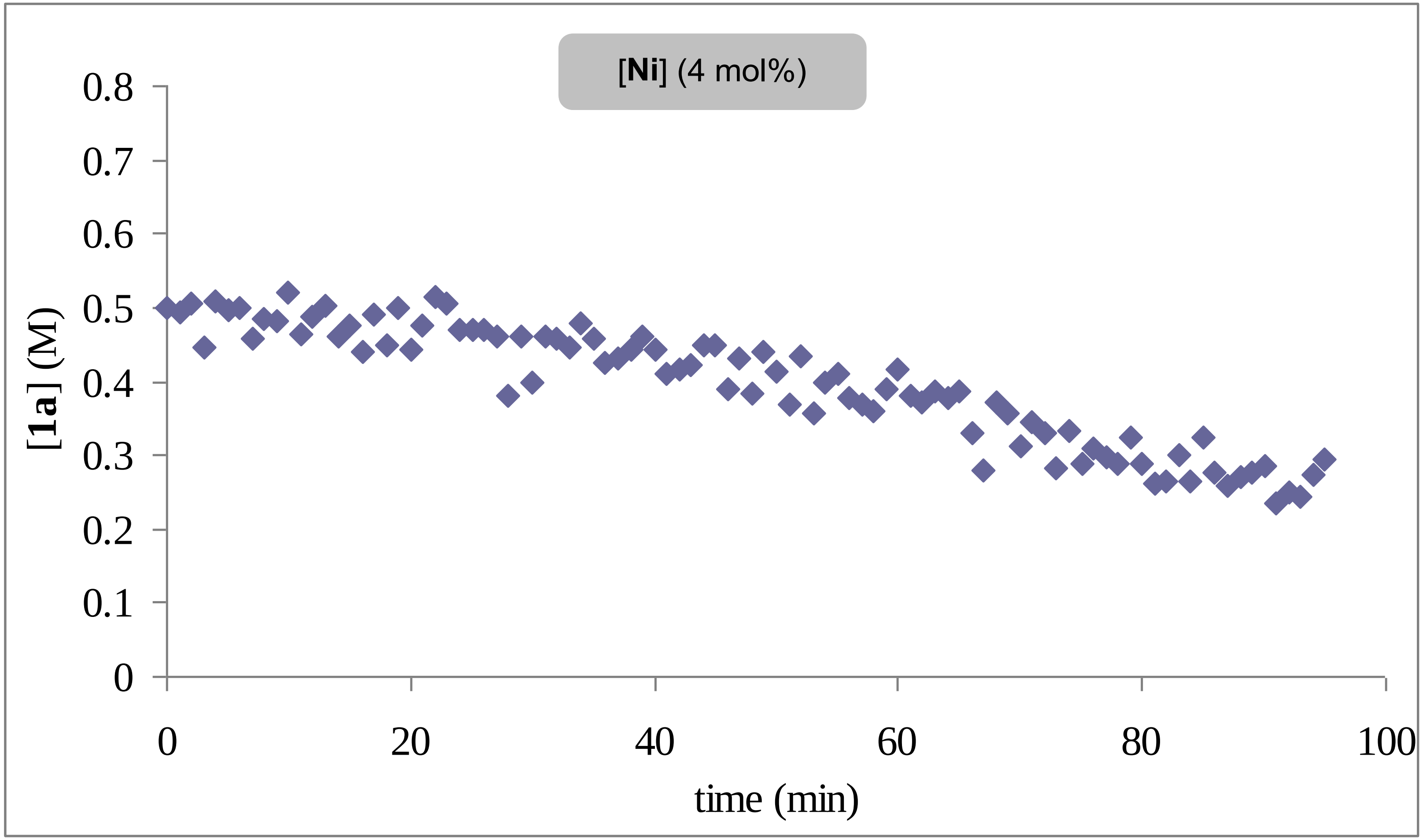
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.01 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 3 h.



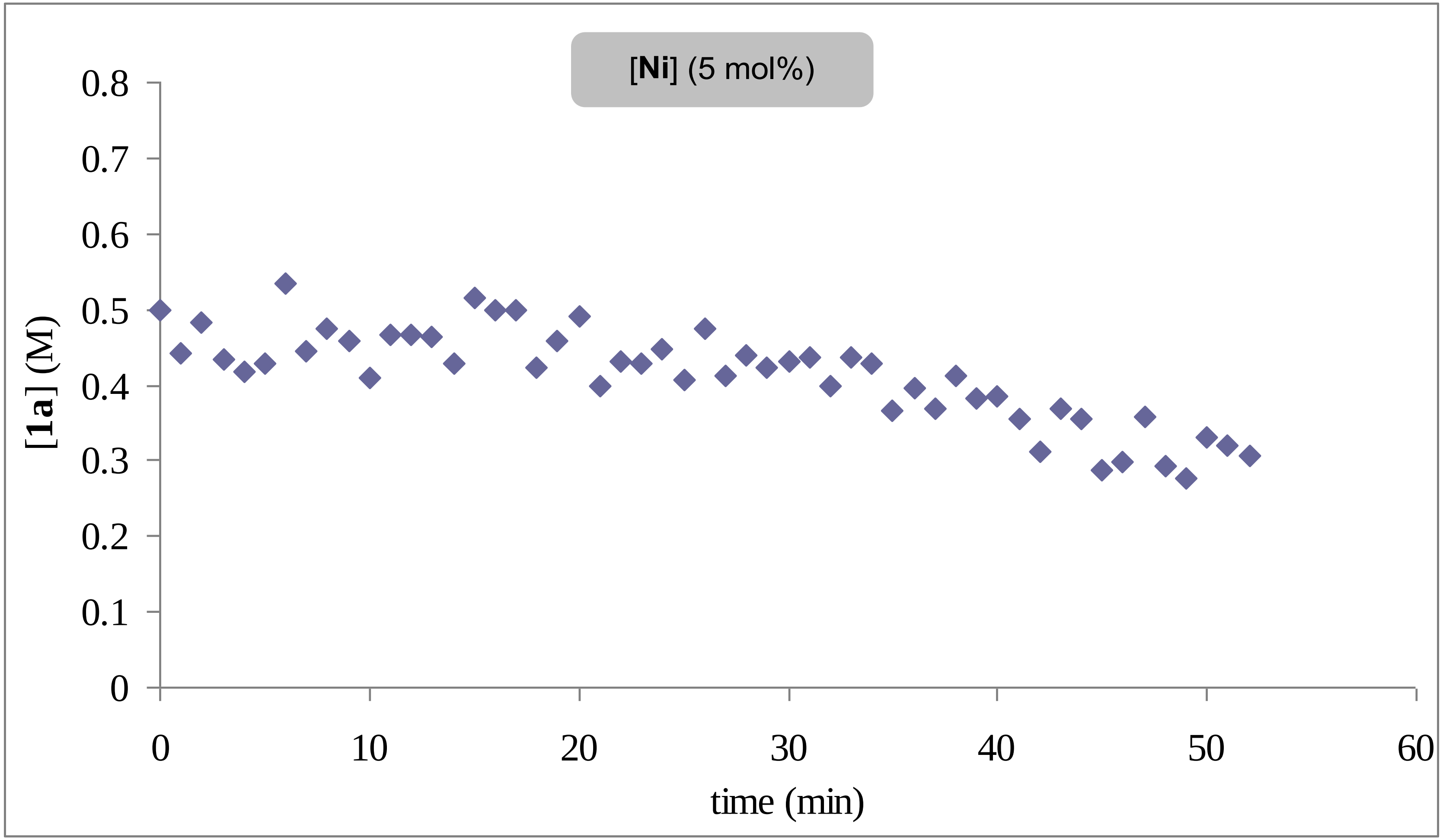
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.02 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^oC for 3 h.



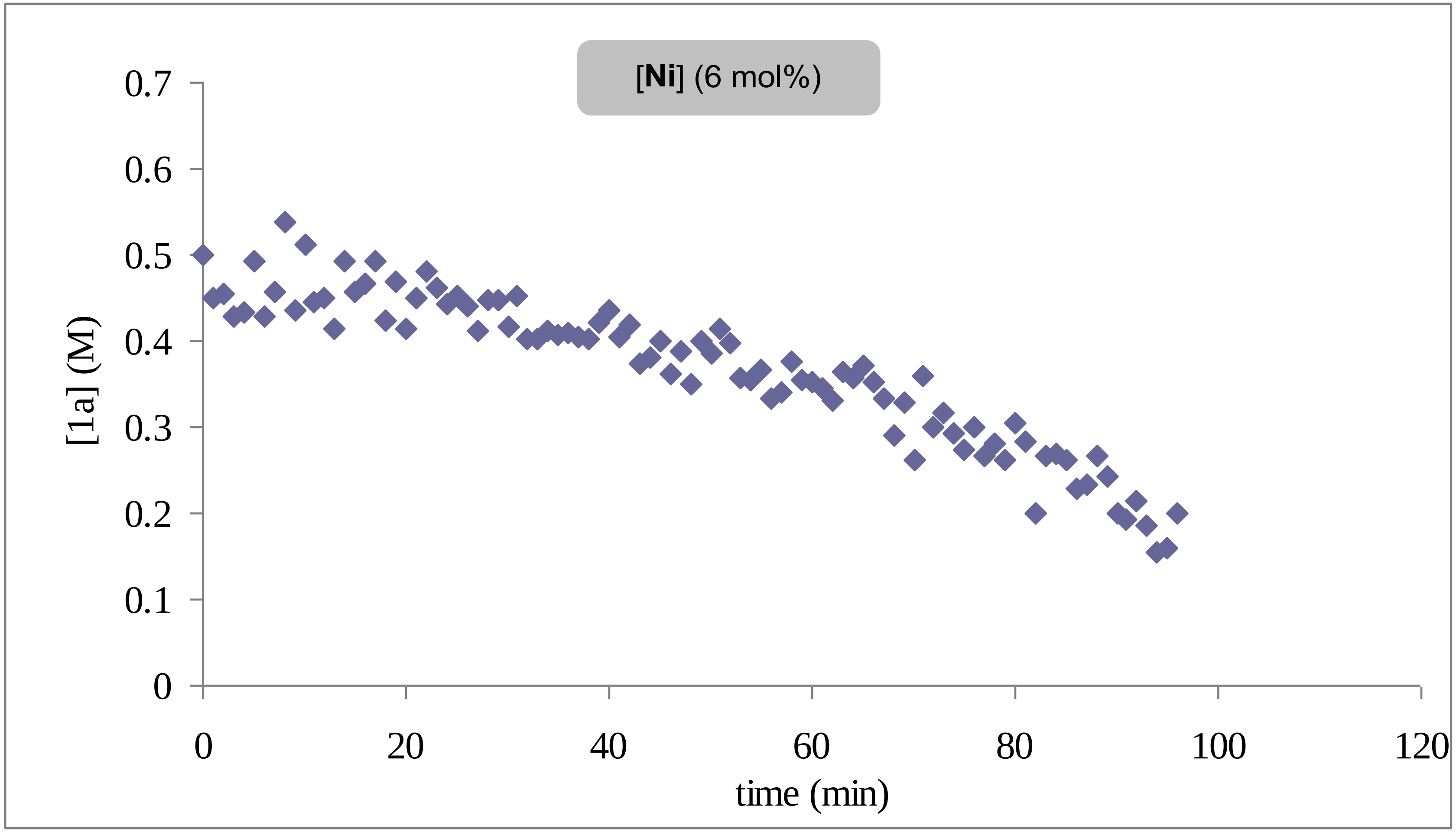
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 2 h.



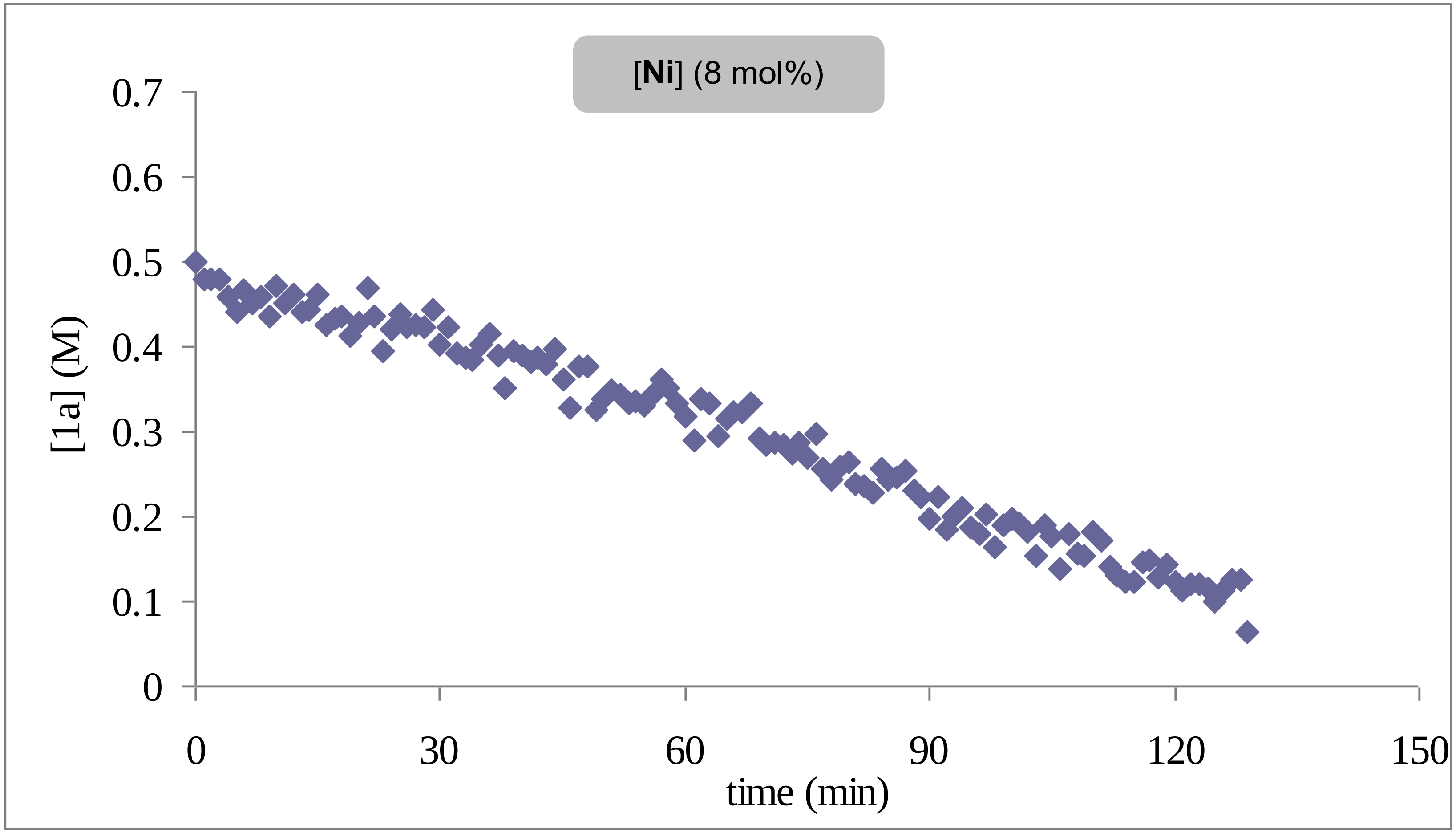
Reaction condition: **1a** (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.04 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^oC for 2 h.



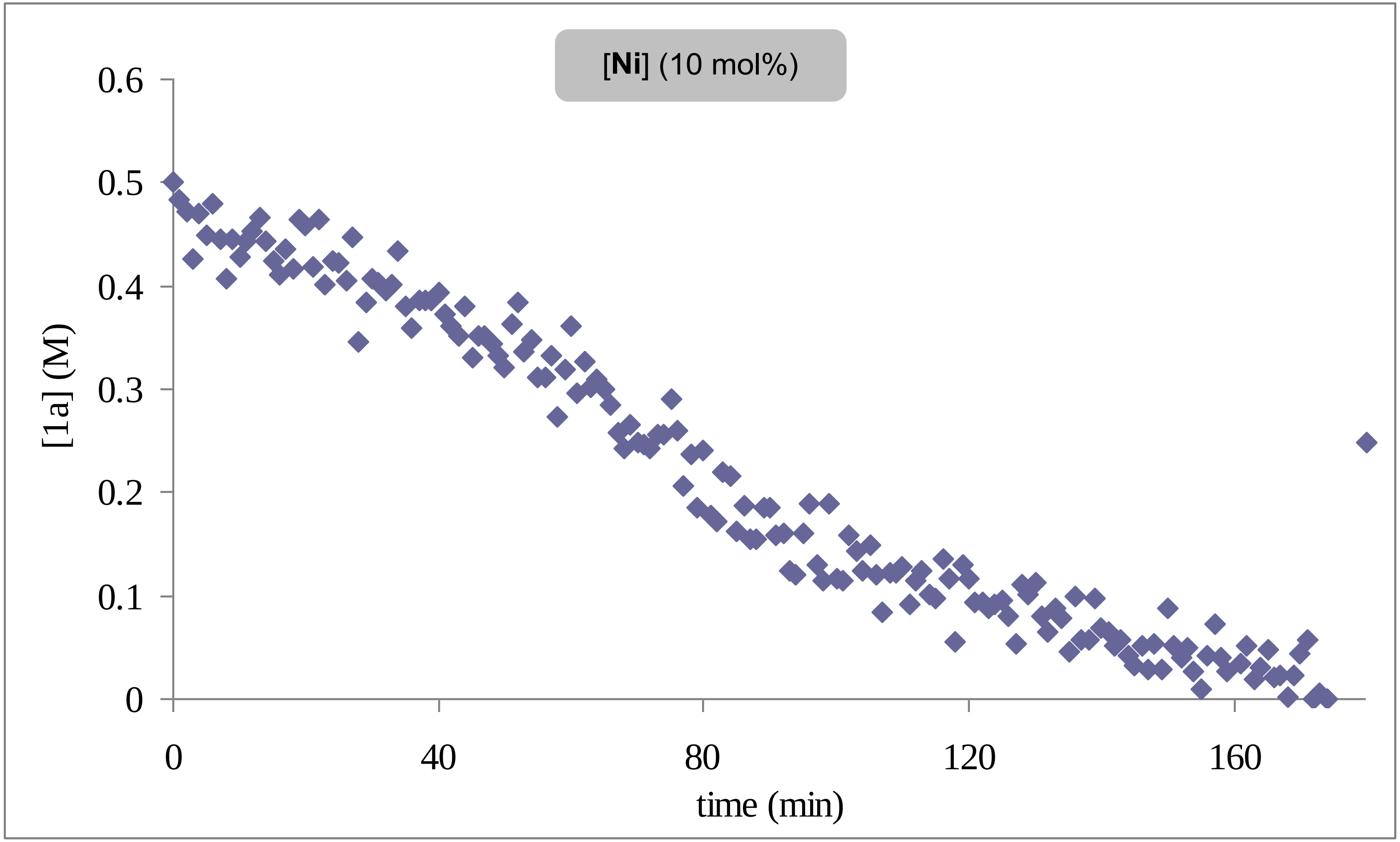
Reaction condition: **1a** (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.05 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 °C for 1 h.



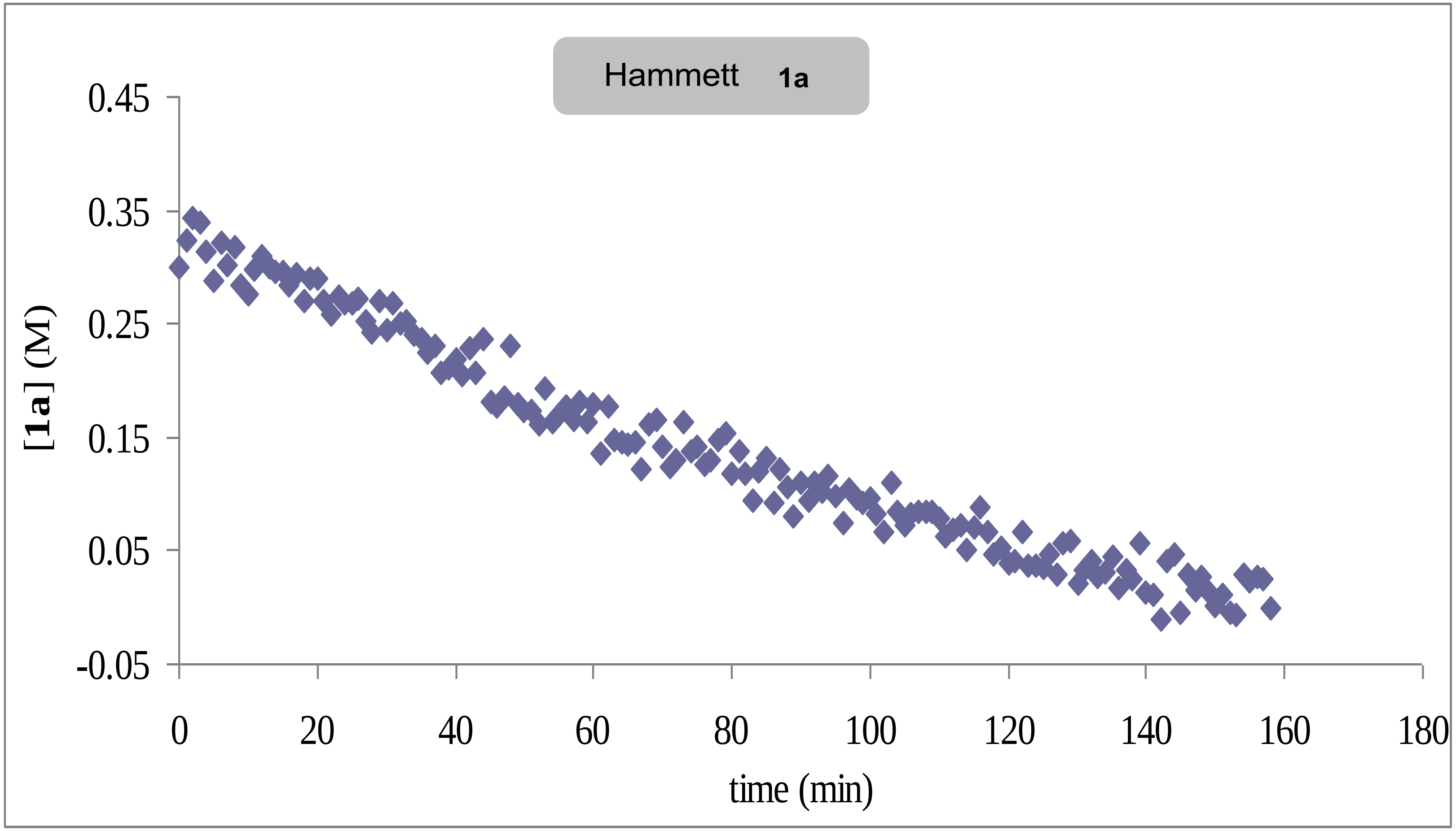
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.06 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 2 h.



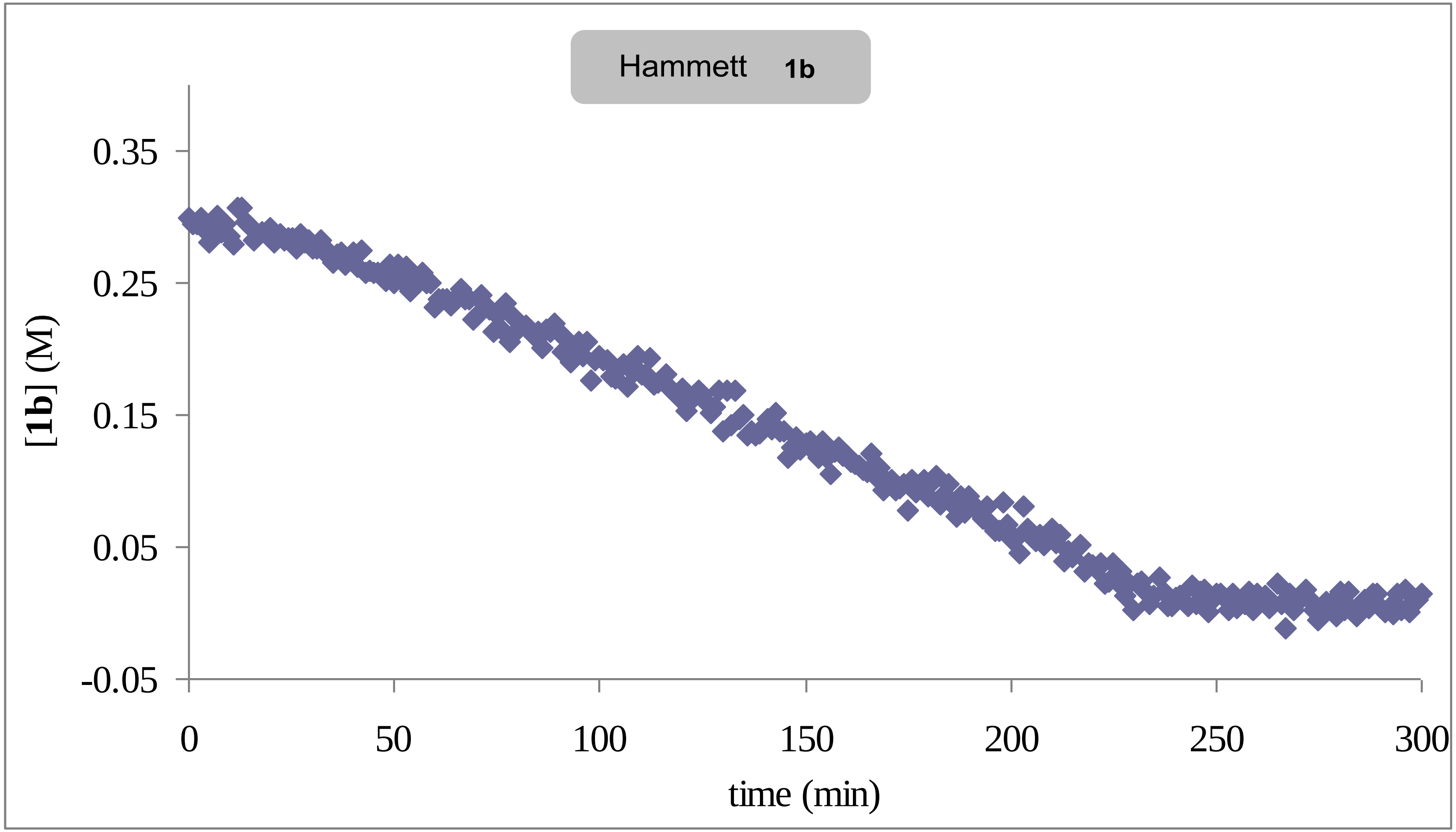
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.08 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 3 h.



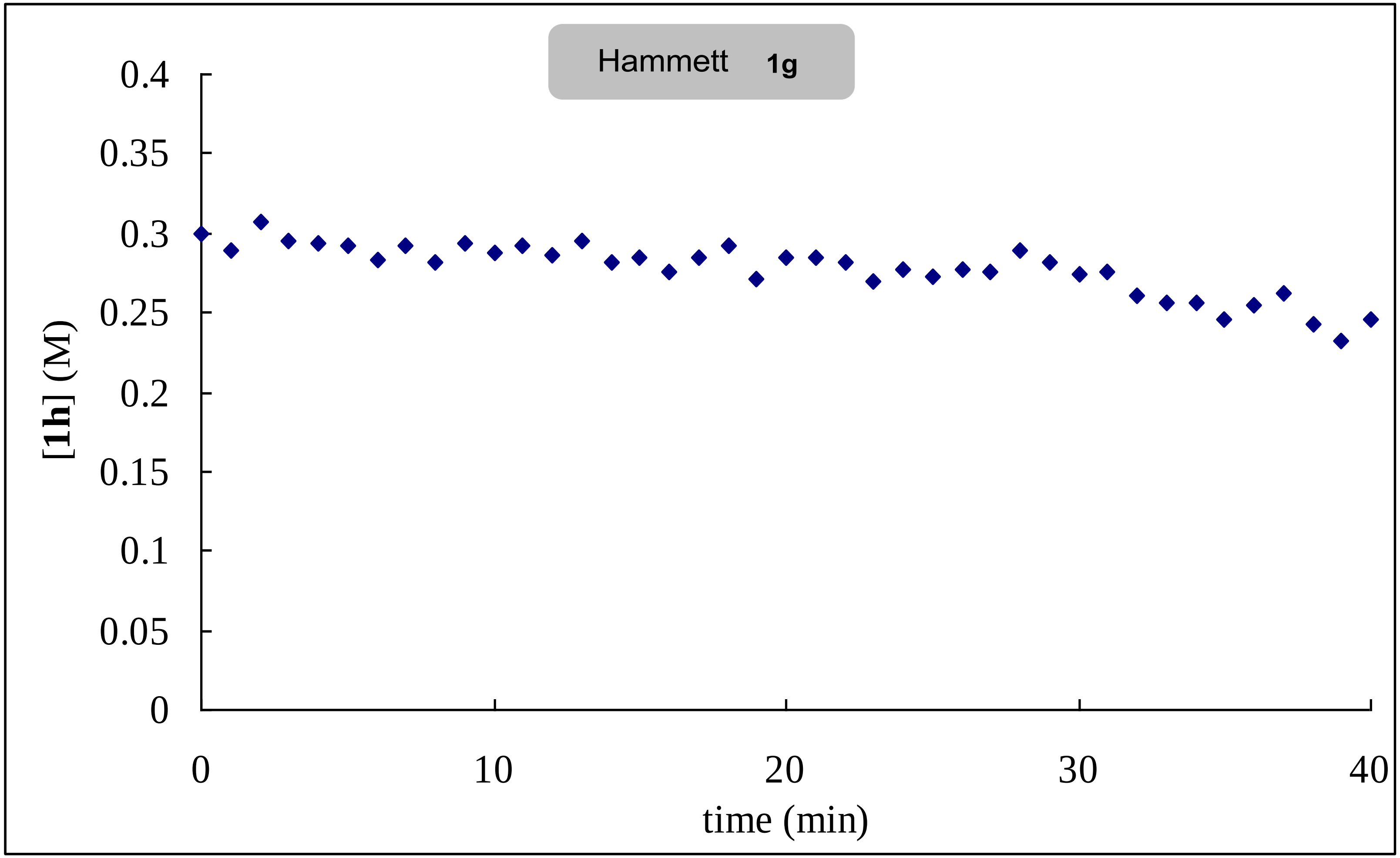
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.10 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^oC for 4 h..



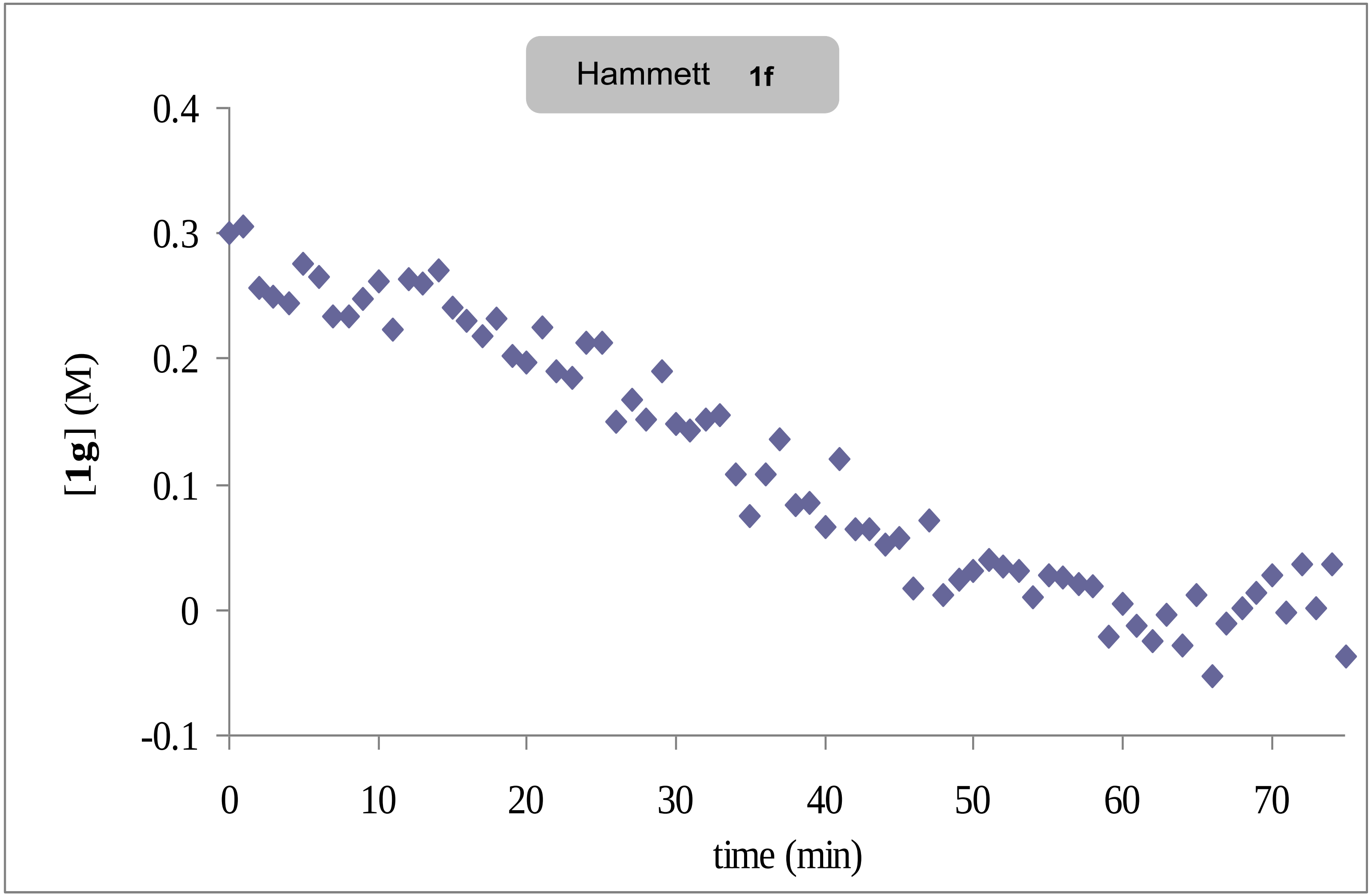
Reaction condition: 1a (0.6 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 3 h.



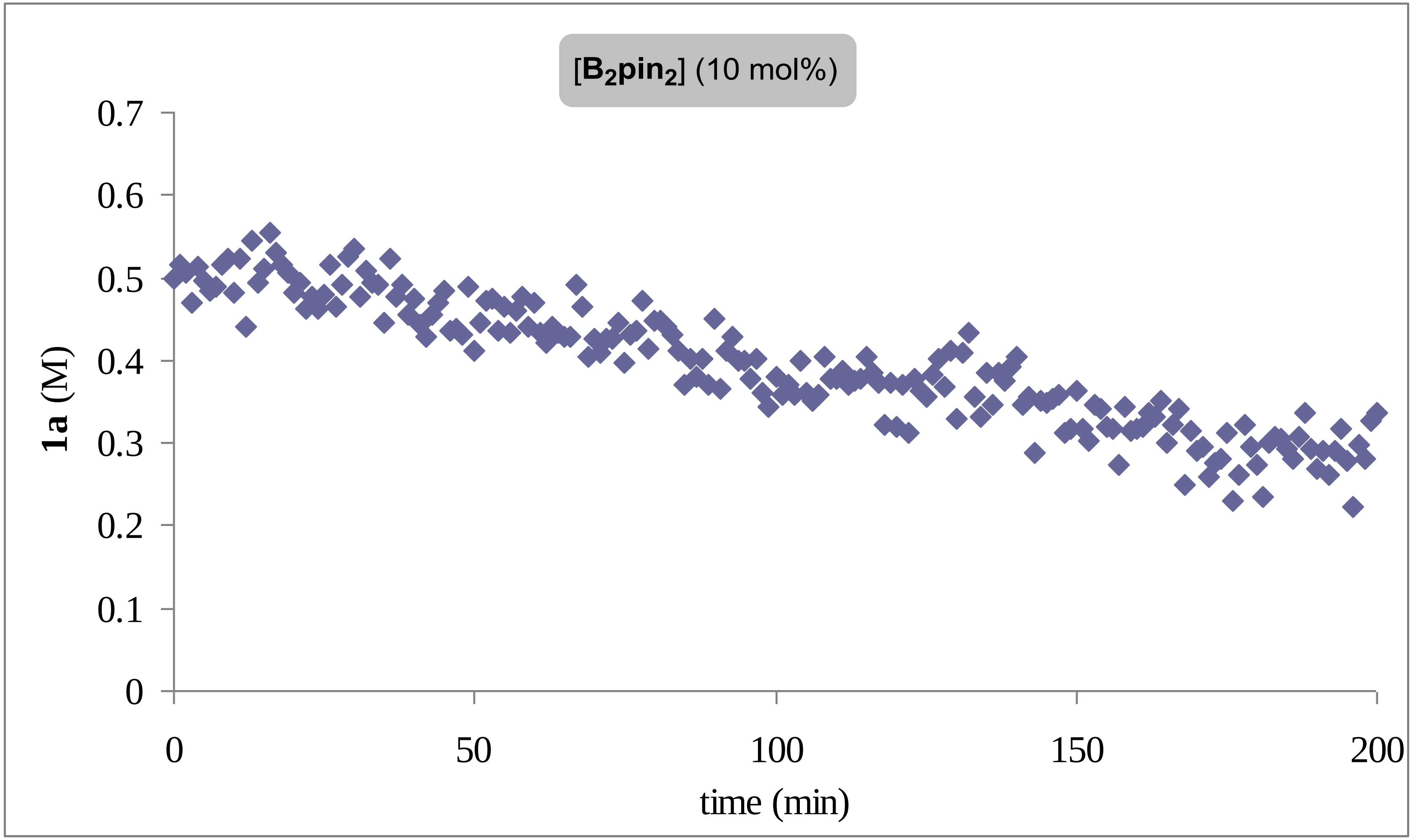
Reaction condition: 1b (0.6 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 °C for 7 h.



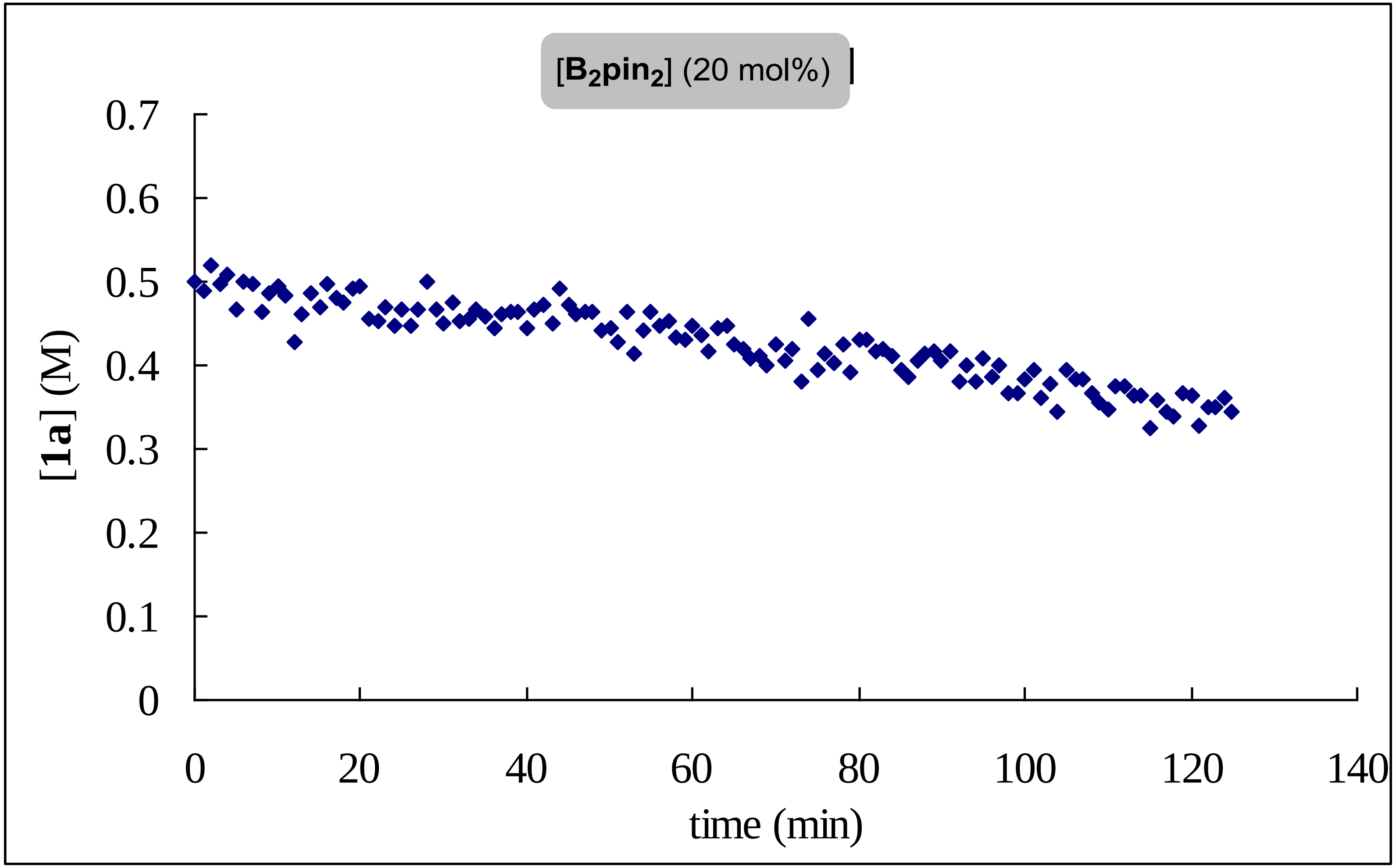
Reaction condition: 1h (0.6 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^oC for 1 h.



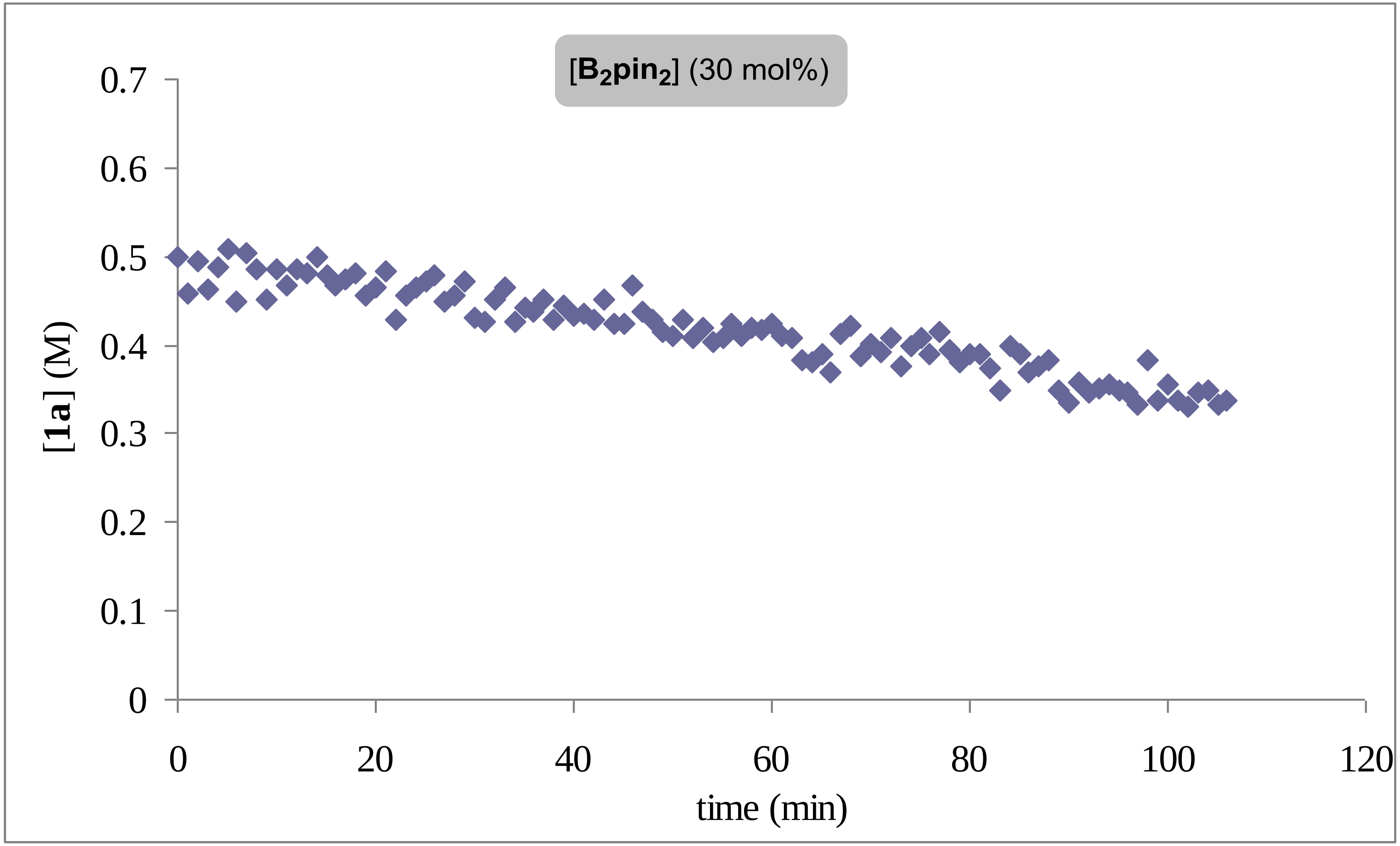
Reaction condition: 1g (0.6 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 2 h.



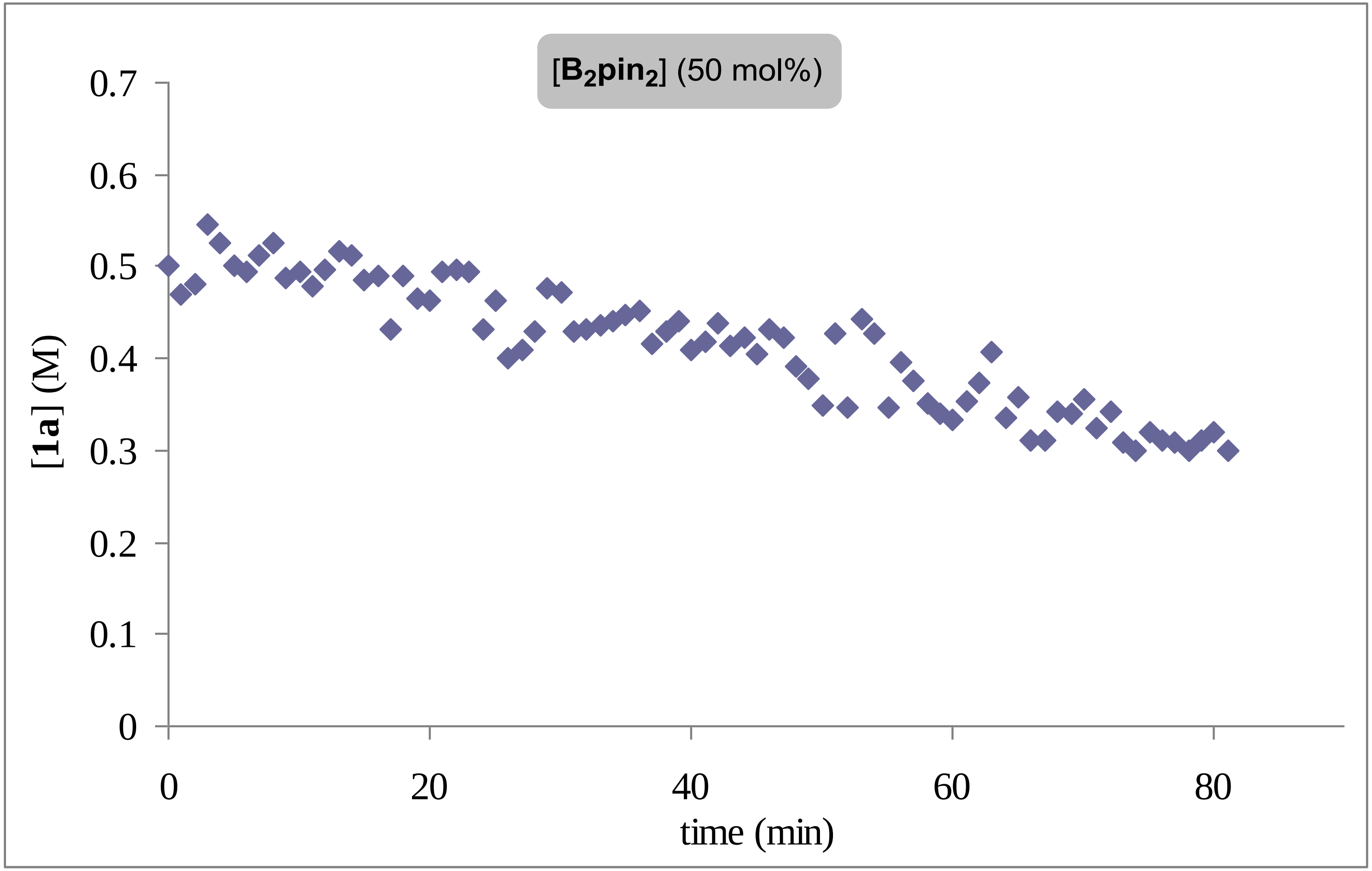
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.1 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 3 h.



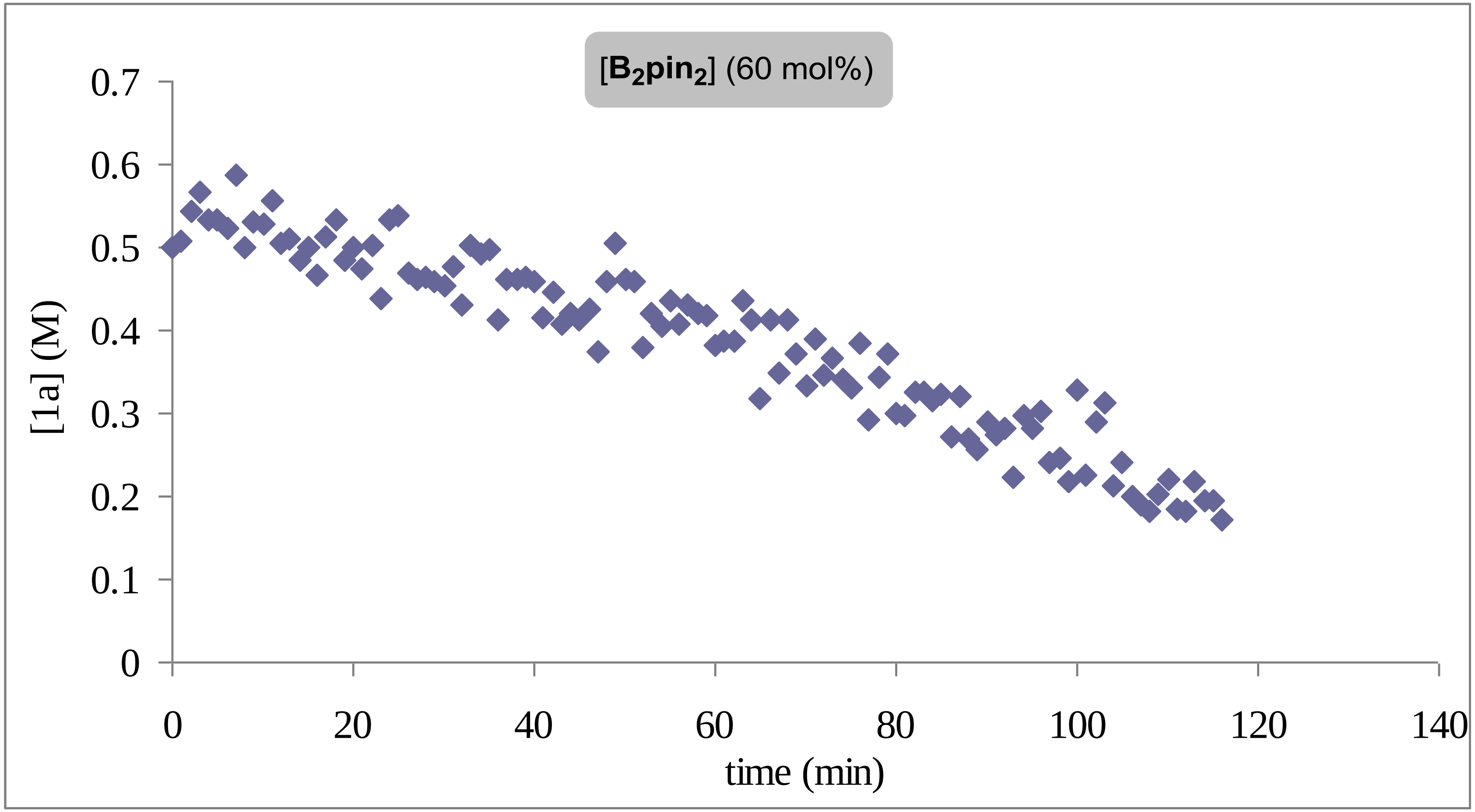
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.2 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 3 h.



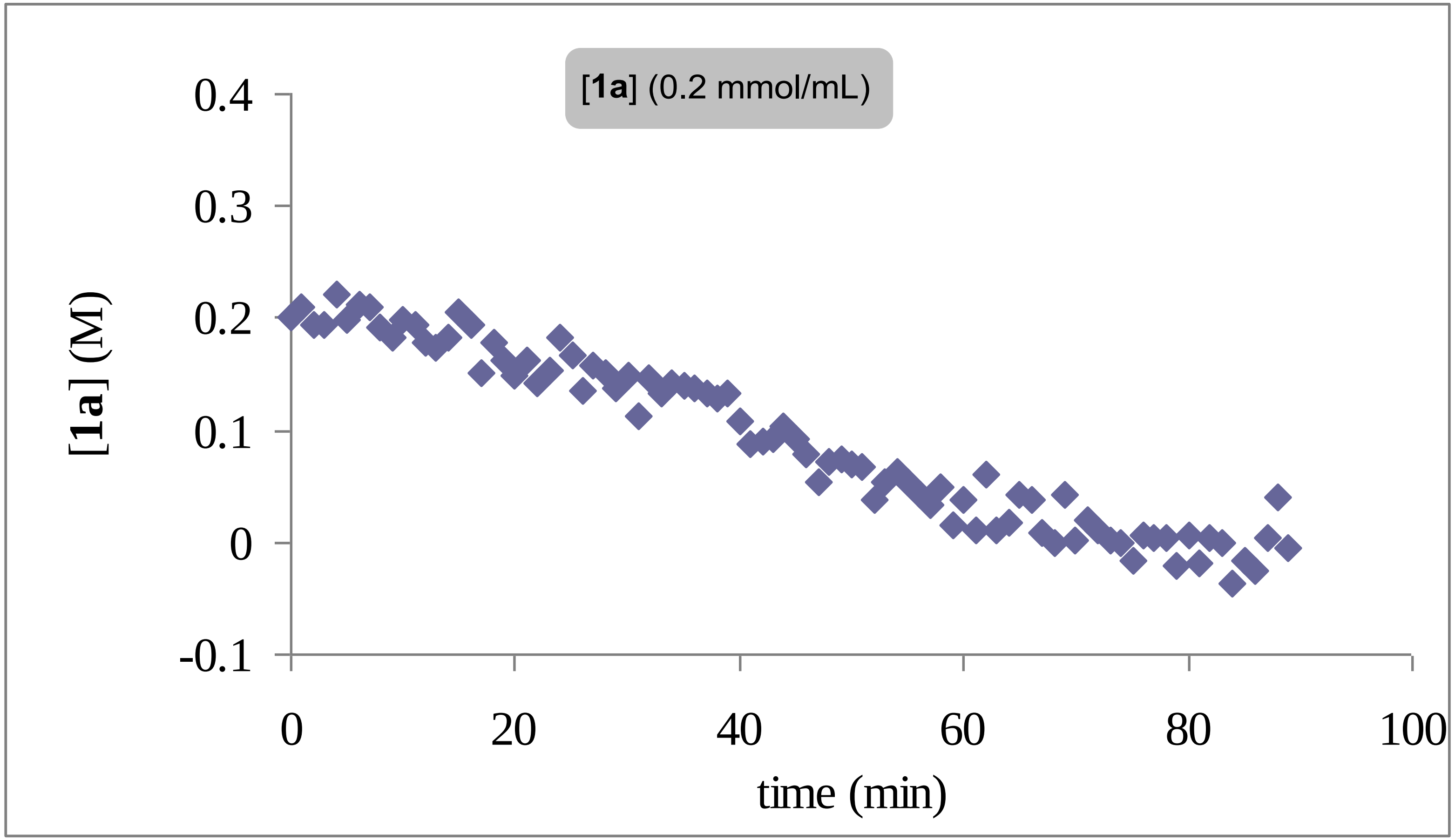
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.3 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^oC for 2 h.



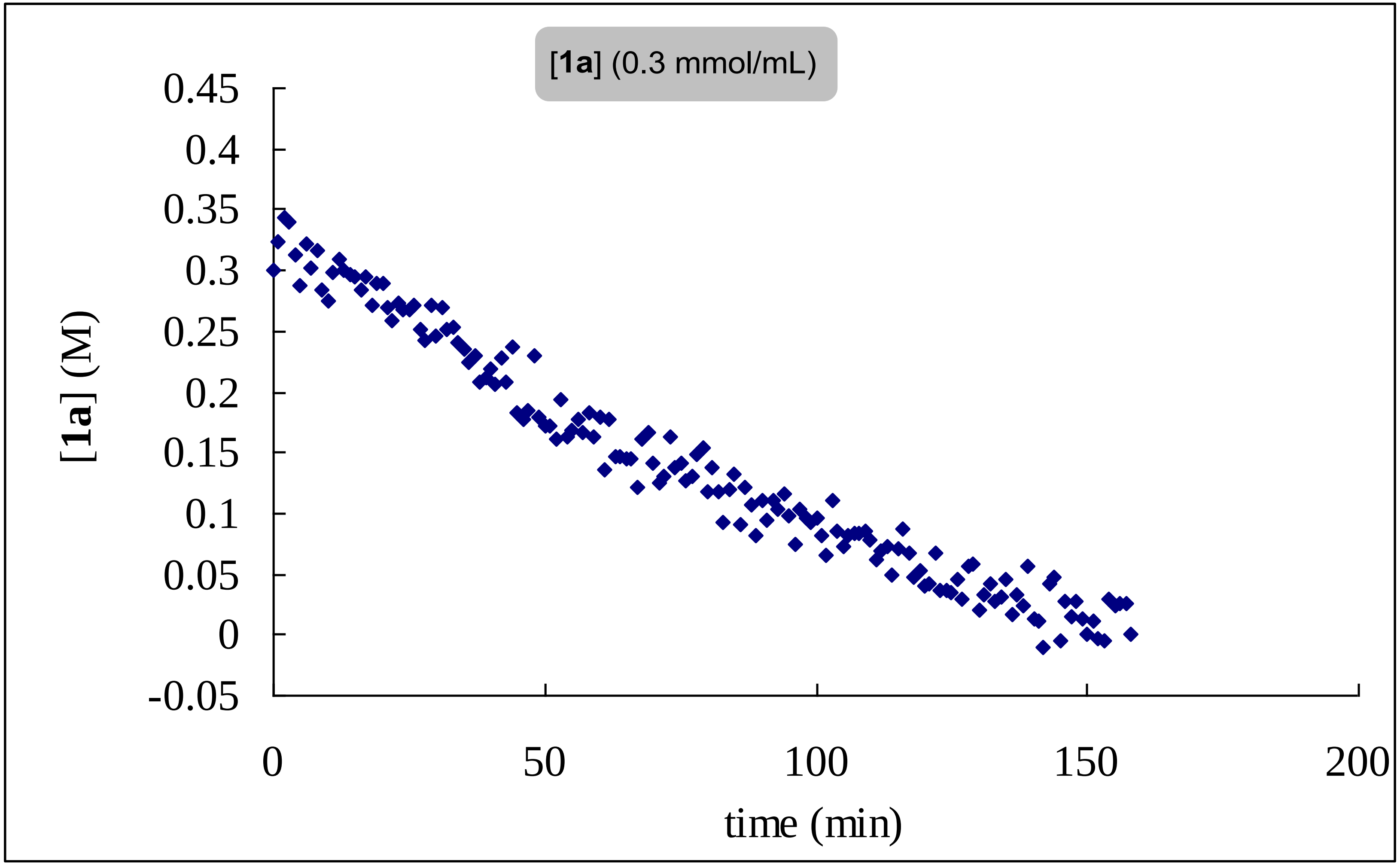
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.5 mmol), *n*-PrOH (2.0 mL), N_2, 120 °C for 2 h.



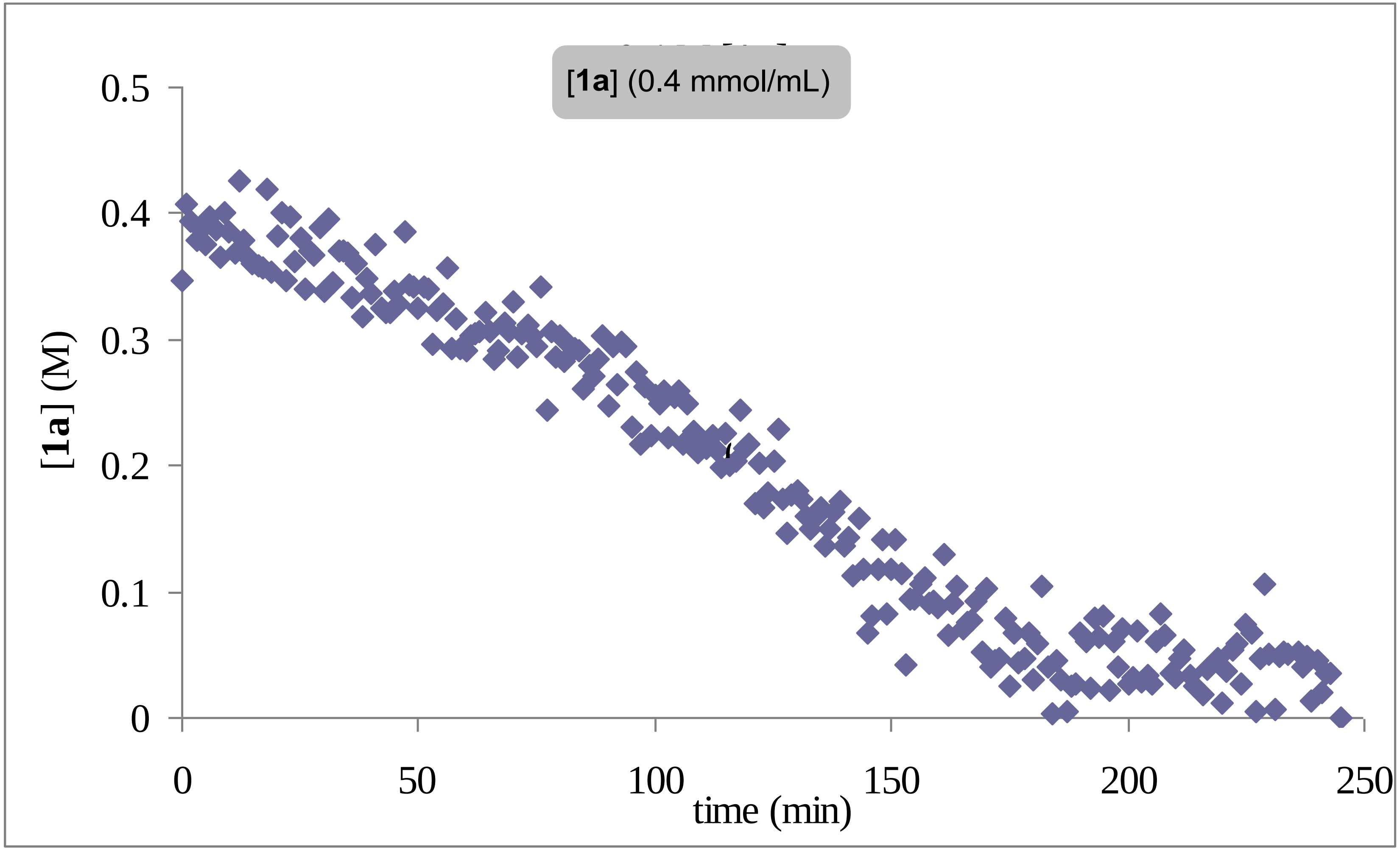
Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.6 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^oC for 2 h.



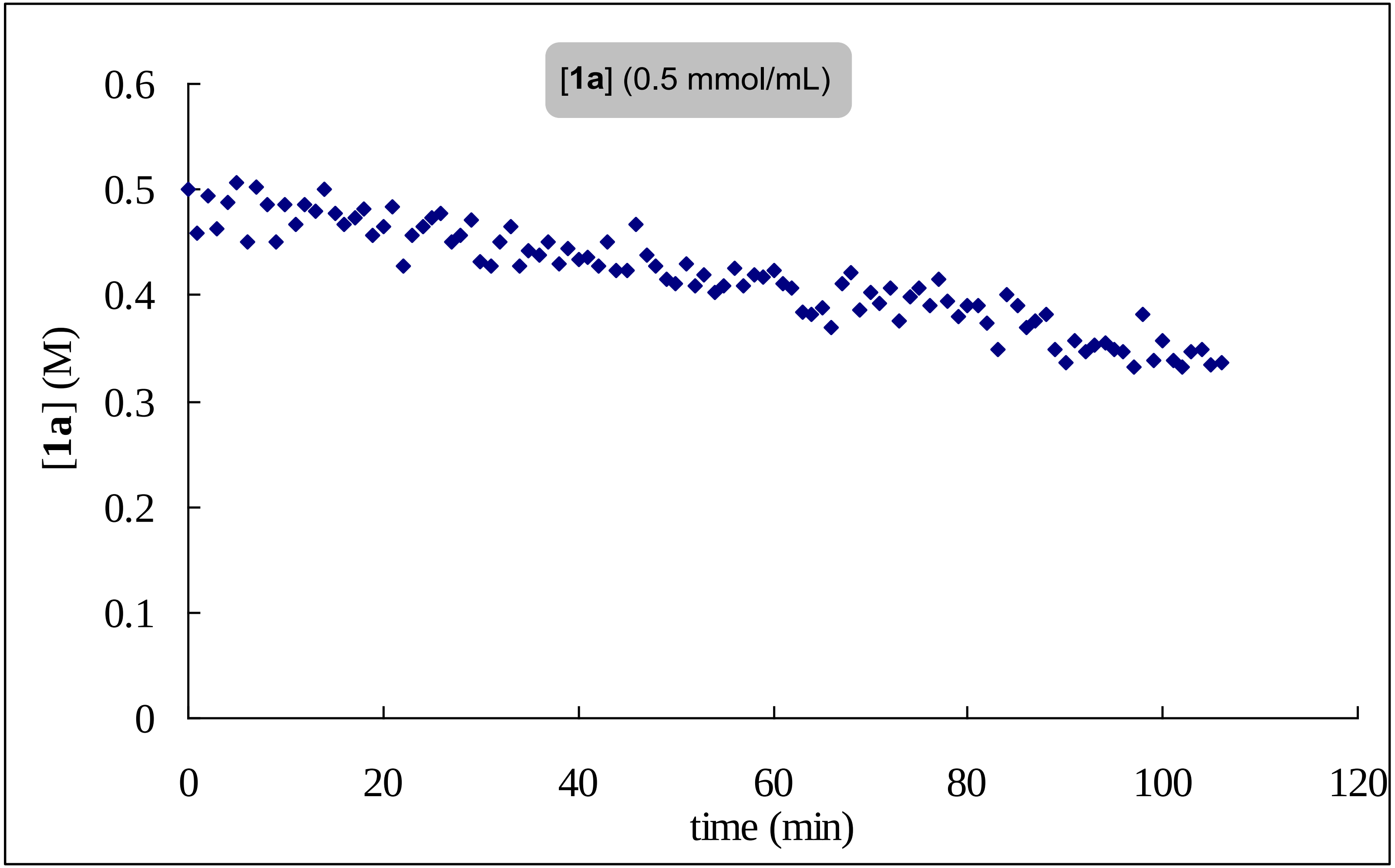
Reaction condition: 1a (0.20 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.6 mmol), *n*-PrOH (2.0 mL), N_2, 120 °C for 2 h.



Reaction condition: 1a (0.6 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.6 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 3 h.



Reaction condition: 1a (0.8 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.6 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^{o}C for 4 h.



Reaction condition: 1a (1.0 mmol), $NiCl_2(PPh_3)_2$ (0.03 mmol), B_2pin_2 (0.6 mmol), *n*-PrOH (2.0 mL), N_2, 120 ^oC for 2 h.