Supporting Information

Nickel-Catalyzed Cross-Coupling of Unactivated Alkyl Halides Using Bis(pinacolato)diboron as Reductant

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Experimental Section

Part 1. General Information

All reagents were reagent grade quality and used as received from Aladdin Co. (China), unless otherwise indicated. All reactions were carried out under an atmosphere of nitrogen unless otherwise indicated. Anhydrous THF and Toluene were distilled from sodium/benzophenone ketyl prior to use. Anhydrous DCM and MeOH were distilled over CaH_2. All other solvents were technical grade unless noted. The following anhydrous solvents, DMF, DMA (*N*,*N*-dimethylacetamide, 99.5% ultra pure), NMP (*N*-methylpyrrolidinone), DMSO, and 1,4-Dioxane were purchased from Acros; anhydrous MeCN (*J*&*K*) and DMI (*N*,*N*-1,3-dimethylimidazolidin-2-one, Aldrich) were purchased and used as received. The following reagents, $Ni(acac)_2$ (Acros), $NiCl_2$, $NiBr_2$, and anhydrous NiI_2 (Alfa Aesar), $Ni(COD)_2$ (Aldrich), KO^{t}Bu and (pin)B–B(pin) (TCI), LiOMe (*J*&*K*), KOEt (Aldrich), NaOMe and LiO^{t}Bu (Aladdin, China) were purchased, and used as received. The following ligands 1,10-phenanthroline (Alfa Aesar)，**6a** and **6b** (Aldrich), **6c** (Aladdin) were purchased. Pybox ligands **5a–e**,[1] **L2a–d,**[1, 2] **7a–7j**[3] **and L1a–L1c**,[4] were synthesized according to the literature procedures. The following alkyl halides *exo*-2-Bromonorbornane (Aldrich), 2-(2-Bromoethyl)-1,3-dioxolane (Aldrich), cyclohexyl bromide (Alfa Asear) were purchased, and used as received. Other alkyl halides

(1) (a) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991,** *10*, 500-508. (b) Yu, X.; Yang, T.; Wang, S.; Xu, H.; Gong, H. *Org. Lett.* **2011**, *13*, 2138. (c) Vermonden, T.; Branowska, D.; Marcelis, A. T. M.; Sudholter, E. J. R. *Tetrahedron*, **2003**, 59, 5039. (d) Iwasa,S.; Nakamura, H.; Nishiyama, H. *Heterocycles* **2000**, *52*, 939.

(2) (a) Müller, P.; Chappellet, S. *Helv. Chim. Acta* **2005**, *88*, 1010. (b) Nishiyama, H.; Soeda, N.;Naito, T.; Motoyama, Y. *Tetrahedron Asymm.* **1998**, *9*, 2865. (c) Graf, G. I.; Daniel Hastreiter, D.; da Silva, L. E.; Rebelo, R. A.; Montalbanb, A. G.; McKillop. A. *Tetrahedron* **2002**, *58*, 9095.

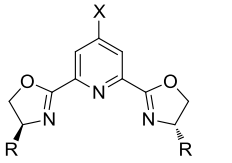
(3) (a) Kotaro Kikushima, Jeffrey C. Holder, Michele Gatti, and Brian M. Stoltz. *J. Am. Chem. Soc*. **2011**, *133*, 6902. (b) Rajaram, S.; Sigman, M. S. *Org. Lett.* **2002**, *4*, 3399. (c) Frauenlob, R.; McCormack, M. M.; Walsh, C. M.; Bergin, E. *Org. Biomol. Chem.* **2011**, *9*, 6934. (d) Ishihara, M.; Togo, H. *Tetrahedron* **2007**, *63*, 1474. (e) Henri, B.; Obermann, U. *Chem. Ber.* **1989**, *122*, 199. (f) Dodd, D. W.; Toews, H. E.; Trevail, M. J.; Jennings, M. C.; Hudson, R. H. E.; Jones, N. D. *Can. J. Chem.* **2009**, *87*, 321. (g) Michel, B. W.; Steffens, L. D.; Sigman., M. S. *J. Am. Chem. Soc.* **2011**, *133*, 8317.

(4) (a) Cheng, J.; Deming, T. J. *Macromolecules* **1999**, *32*, 4745. (b) Chelucci, G.; Deriu, S.; Pinna, G. A.; Saba, A.; Valenti, R. *Tetrahedron: Asymm* **1999**, *10*, 3803.

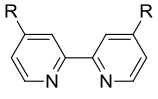
were synthesized according to the literature procedures.[1b] Column chromatography was performed using silica gel 300-400 mesh (purchased from Qingdao-Haiyang Co. China) as the solid support. All NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at STP unless otherwise indicated. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. NMR chemical shifts are reported in units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^{1}H NMR and ^{13}C NMR spectra were set at 7.28 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Low resolution mass spectra were recorded on GCMS-QP2010 SE (SHIMADZU). Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Details of Optimization and Control Experiments

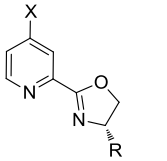
A typical procedure for optimization and control reactions: To a flame-dried Schlenk tube equipped with a stir bar was loaded alkyl halide, followed by addition of ligand and Bis(pinacolato)diboron. The tube was moved to a dry glove box, at which point Ni salt and bases were added. The tube was capped with a rubber septum, and it was moved out of the glove box. NMP were then added via syringe. After the reaction mixture was allowed to stir for 16 hours under N_2 atmosphere at 30 ℃ (or at 45 and 80 ℃), it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil.



5a, X = H, R = *i*Pr
5b, X = H, R = H
5c, X = H, R = CH_2OBn
5d, X = H, R = *s*Bu
5e, X = Cl, R = H

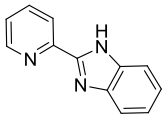


6a, R = *t*Bu
6b, R = CH_3
6c, R = H
6d, R = NO_2



7a, X = OMe, R = *i*Pr
7b, X = Cl, R = H
7c, X = Cl, R = *i*Pr
7d, X = H, R = *i*Pr
7e, X = OMe, R = H

7f, R = H,
7g, R = CH_3
7h, R = ^{s}Bu
7i, R = ^{t}Bu
7j, R = Bn



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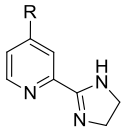
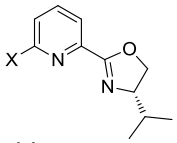
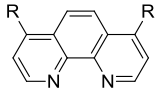


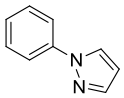
8a, R = H
8b: R = OMe
8c: R = Cl
8d: R = Me



L1a, X = Br
L1b, X = OMe
L1c, X = CN

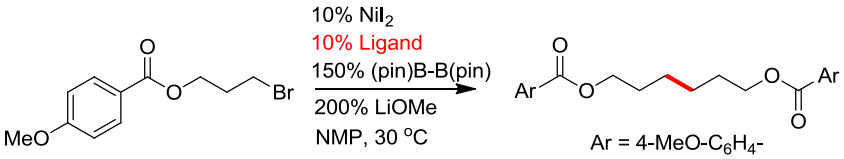


L2a, R = H
L2b, R = OMe
L2c, R = Ph
L2d, R = Cl



L3

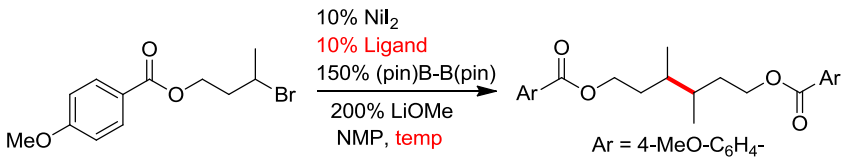
Table S1. Ligand screening for dimerization of **2a**.



Entry	Ligand	Yield (%)[a]
1	**7a**	86
2	**7b**	73
3	**7c**	66
4	**7d**	73
5	**7e**	70
6	**7g**	82
7	**8a**	99
8	**L3**	25

[a] Isolated yield.

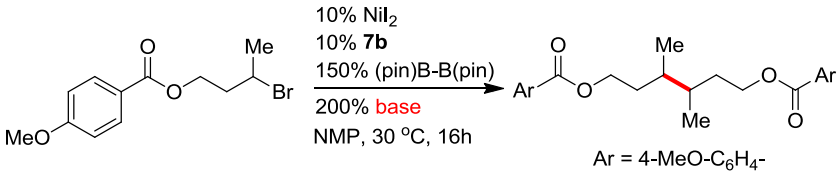
Table S2. Ligand screening for dimerization of **1a**.



entry	ligand	Temp (°C)	yield (%)	entry	ligand	Temp (°C)	yield (%)[a]
1	**5a**	30	4[b]	12	**7b**	30	58[a]
2	**5b**	30	6[b]	13	**7c**	30	49[b]
3	**5c**	30	4[b]	14	**7d**	30	51[b]
4	**6a**	30	22[b]	15	**7e**	30	30[a]
5	**6b**	30	13[b]	16	**7f**	30	31[b]
6	**6c**	30	5[b]	17	**7g**	30	50[a]
7	**6d**	30	5[b]	18	**7g**	30	37[b]
8	**L2a**	30	18[b]	19	**7i**	30	34[b]
9	**L2b**	30	21[b]	20	**7j**	30	45[a]
10	**7a**	30	66[a]	21	**8a**	30	50[a]
11	**7a**	**45**	**74**[a, c]	22	**L1a**	30	37[b]

[a] Isolated yield. [b] HPLC yield using propyl 4-methoxybenzoate internal standard (calibrated). [c] The concentration of **1a** in NMP was increased to 0.32 M

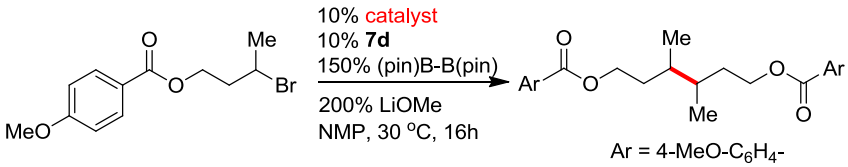
Table S3. Base screening for dimerization of **1a.**



entry	base	yield (%)[a]
1	LiOMe	56
2	NaOMe	29
3	KO*t*Bu	15
4	LiO*t*Bu	9
5	Et_3N	17
6	Na_2CO_3	4
7	DBU	ND[b]
8	NH_4OAc	<10
9	pyridine	ND

[a] HPLC yield using propyl 4-methoxybenzoate internal standard (calibrated). [b] ND = not detected.

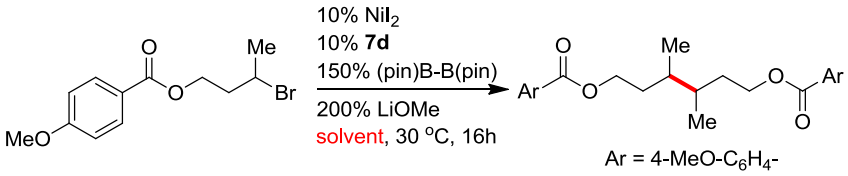
Table S4. Catalyst screening for dimerization of **1a**



entry	catalyst	yield (%)[a]
1	NiI_2	52
2	$Ni(acac)_2$	38
3	$Ni(cod)_2$	46
4	$NiBr_2$	16
5	$CoCl_2$	ND[b]
6	CoI_2	ND[b]
7	$NiCl_2$	ND[b]

[a] HPLC yield using propyl 4-methoxybenzoate internal standard (calibrated). [b] ND = not detected.

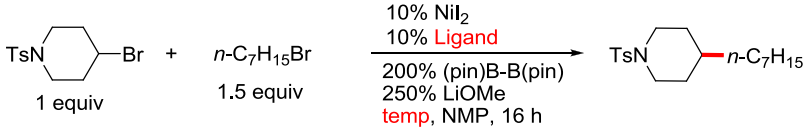
Table S5. Solvent screening for dimerization of **1a.**



entry	solvent	yield (%)[a]
1	DMF	46
2	DMA	39
3	MeCN	26
4	1,4-dioxane	15
5	THF	14
6	NMP	52
7	DMI	6

[a] HPLC yield using propyl 4-methoxybenzoate internal standard (calibrated).

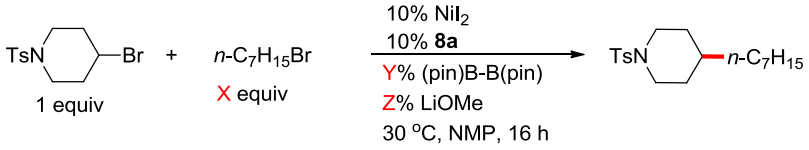
Table S6. Ligand screening for the coupling of **10a** and *n*-heptylbromide.



entry	ligand	Temp (°C)	yield (%)[a]	entry	ligand	Temp (°C)	yield (%)[a,b]
1	**5b**	30	20	13	**7d**	30	45
2	**5d**	30	20	14	**7e**	30	25
3	**5e**	30	48	15	**7f**	30	27
4	**6a**	30	45	16	**7g**	30	20
5	**6b**	30	24	17	**7h**	30	10
6	**6c**	30	33	18	**7i**	30	20
7	**L2a**	30	33	19	**7j**	30	10
8	**L2c**	30	26	20	**8a**	30	68
9	**L3**	30	41	21	**8a**	30	70[c]
10	**7a**	30	44	**22**	**8a**	**40**	**74**[c]
11	**7b**	30	36				
12	**7c**	30	24				

[a] Isolated yield. [b] The concentration of 18 in NMP is set as 0.16 M. [c] the concentration of **10a** in NMP was reduced to half (0.32 M).

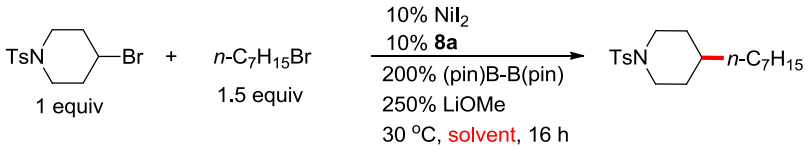
Table S7. Screening the ratio of n-heptylbromide, $(Bpin)_2$ and LiOMe for the coupling of **10a** with *n*-heptylbromide.



entry[a]	X	Y	Z	yield (%)[b]	entry	X	Y	Z	yield (%)[b]
1	1.2	2	2.5	60	5	1.5	2.5	2.5	65
2	1.5	2	2.5	68	6	1.8	2	2.5	66
3	1.5	2.25	2.5	62	7	2	2	2.5	71
4	1.5	1.5	2	50					

[a] The concentration of **10a** in NMP is set as 0.16 M. [b] Isolated yield.

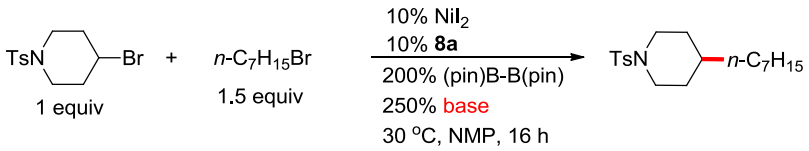
Table S8. Solvent screening for the coupling of **10a** and *n*-heptylbromide.



Entry	Solvent	Yield (%)[a,c]
1	NMP	68
2	DMA	50
3	DMF	59
4	MeCN	30
5	1,4-dioxane	ND[b]
6	DMSO	15

[a] Isolated yield. [b] ND = not detected. [c] The concentration of **10a** in NMP is set as 0.16 M.

Table S9. Base screening for the coupling of **10a** and *n*-heptylbromide.

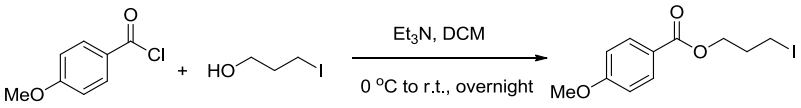


entry	base	yield (%)[a,b]
1	LiOMe	68
2	NaOMe	31
3	KO*t*Bu	30
4	LiO*t*Bu	< 15
5	Et_3N	23
6	KOEt	25

[a] Isolated yield. [b] The concentration of **10a** in NMP is set as 0.16 M.

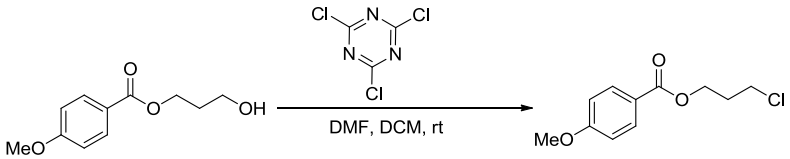
Part 3. Preparation of Alkyl Halides and Tosylates and Ligands.

(1) Preparation of compounds **2c**.



3-Iodopropyl 4-methoxybenzoate (2c). To an oven-dried round bottom flask charged with a mixture of 3-iodopropan-1-ol (0.93 g, 5.0 mmol, 100 mol %), Et_3N (0.84 mL, 6.0 mmol, 120 mol %) in DCM (10 mL) was added 4-Methoxybenzoyl chloride (0.85 g, 5.0 mmol, 100 mol %) at 0℃. The reaction mixture was warmed to room temperature, and was allowed to stir overnight. The reaction mixture was then partitioned with H_2O (2×10 mL) and brine (15 mL). The organic phase was collected, dried (over $MgSO_4$) and filtered, at which point silica gel was added. The mixture was concentrated under reduced pressure, and the residue was loaded onto a silica column. Flash chromatography (SiO2: 10% ethyl acetate in hexanes) afforded **2c** as a light yellow oil (1.44 g, 4.50 mmol, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01-7.99 (m, 2H), 6.95-6.92 (m, 2H), 4.38 (t, *J* = 6.1 Hz, 2H), 3.87 (s, 3H), 3.32 (t, *J* = 6.9 Hz, 2H), 2.31-2.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 163.4, 131.6, 122.3, 113.6, 64.1, 55.4, 32.6, 1.5.

(2) Preparation of compounds **2d**.



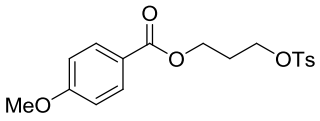
3-Chloropropyl 4-methoxybenzoate (2d). This compound was synthesized according to the literature procedures.[5] To a round bottom flask charged with DMF (1.0 mL) was added 2,4,6-Trichloro-[1,3,5]triazine (TCT) (0.92 g, 5.0 mmol). The mixture was stirred at 25 ℃. After the formation of a white solid, the reaction was monitored by TLC until complete consumption of TCT, at which point, DCM (15 mL) was added followed by 3-hydroxypropyl 4-methoxybenzoate (1.00 g, 4.75 mmol). The resulting mixture was stirred at room temperature for 6 h. The reaction was washed with water (15 mL) and a saturated solution of Na_2CO_3 (15 mL). After the organic phase was collected and

(5) Luca, L. D.; Giacomelli, G.; Porcheddu, A. *Org. Lett.* **2002**, *4*, 553.

washed by 1N HCl and brine, it was dried (Na_2SO_4), and filtered, at which point silica gel was added. The mixture was concentrated under reduced pressure, and the residue was loaded onto a silica column. Flash chromatography (SiO_2: 10% ethyl acetate in hexanes) afforded **2d** as a colorless oil (0.94 g, 4.13 mmol, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01-7.98 (m, 2H), 6.94-6.91 (m, 2H), 4.45 (t, *J* = 6.0 Hz, 2H), 3.87 (s, 3H), 3.70 (t, *J* = 6.5 Hz, 2H), 2.26-2.20 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 163.4, 131.5, 122.4, 113.6, 61.3, 55.4, 41.3, 31.7.

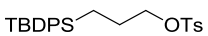
(3) Preparation of Alkyl Tosylates.

General Procedure for the Synthesis of Alkyl Tosylates. A solution of alcohol (100 mol %) in dry DCM (0.1 M) was treated with *p*-toluenesulfonyl chloride (110 mol %) and Et_3N (120 mol %). The solution was allowed to stir at rt overnight. It was then washed with water, saturated sodium bicarbonate, and brine. The organic layer was collected, dried (over sodium sulfate), filtered. The solvent was removed under reduced pressure. The residue was purified via column chromatography (ethyl acetate /hexanes) to give the alkyl tosylate.



3-(Tosyloxy)propyl 4-methoxybenzoate. According to the general method, this compound was obtained in 92% yield.

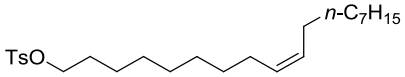
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.86 (m, 2H), 7.79-7.77 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.91-6.89 (m, 2H), 4.29 (t, *J* = 6.0 Hz, 2H), 4.20 (t, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 2.36 (s, 3H), 2.13-2.08 (m, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.8, 163.3, 144.8, 132.6, 131.5, 129.8, 127.8, 122.2, 113.5, 66.8, 60.1, 55.4, 28.2, 21.5. M.p. = 70-71 ℃.



3-(Tert-butyldiphenylsilyloxy)propyl 4-methylbenzenesulfonate. According to the general method, this compound was obtained in 90% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83-7.81 (m, 2H), 7.62-7.60 (m, 4H), 7.47-7.43 (m, 2H),

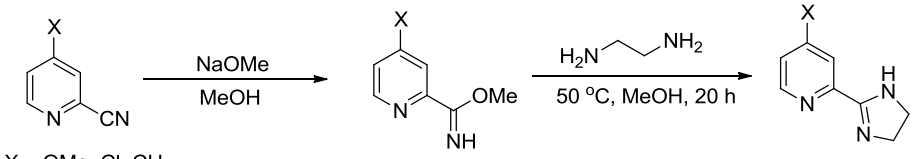
7.41-7.38 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.25 (t, *J* = 6.3 Hz, 2H), 3.70 (t, *J* = 5.8 Hz, 2H), 2.45 (s, 3H), 1.88 (m, *J* = 6.0 Hz, 2H), 1.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.6, 135.4, 133.4, 133.1, 129.8, 129.6, 127.9, 127.7, 67.5, 59.2, 31.8, 26.7, 21.6, 19.1.



(Z)-Octadec-9-en-1-yl 4-methylbenzenesulfonate. According to the general method, this compound was obtained in 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.39-5.32 (m, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.46 (s, 3H), 2.04-1.99(m, 3h), 1.67-1.61 (m, 2H), 1.32-1.24 (m, 22H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 133.2, 130.0, 129.7, 129.6, 127.8, 70.6, 31.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 29.2, 29.0, 28.9, 28.8, 27.2, 27.1, 25.3, 22.6, 21.6, 14.1.

(4) Peparation of ligands **8b-8d.**



2-(4, 5-Dihydro-1H-imidazol-2-yl)-4-methoxypyridine (8b). Following the literature procedures,[6] sodium methoxide (6.0 mg, 0.112 mmol, 10 mol %) was added to a solution of 4-chloropicolinonitrile (150 mg, 1.12 mmol, 100 mol %) in methanol (1.0 mL). After the reaction mixture was allowed to stir for 15 h under N_2 atmosphere at 25 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: 50% ethyl acetate in hexanes) provided methyl

(6) Malkov, A. V.; Liddon, A. J. P. S.; Ram ŕez-López, P.; Bendová, L.; Haigh, D.; Kočovský. P. *Angew. Chem. Int. Ed.* **2006**, *45*, 1432.

4-methoxypicolinimidate as a colorless oil (162 mg, 0.97 mmol, 87% yield).

Ethylene diamine (0.24 mL, 3.60 mmol, 493 mol %) was added to a mixture of methyl 4-methoxypicolinimidate (120 mg, 0.72 mmol, 100 mol %) in MeOH (2.5 mL). The reaction mixture was allowed to stir for 20 h under N_2 atmosphere at 50 ℃. The solution was cooled to room temperature and quenched with H_2O (10 mL) and diluted with CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure to provided **8b** as a light yellow solid (110 mg, 0.62 mmol, 86% yield).

^{1}H NMR (500 MHz, DMSO): δ 8.40 (d, *J* = 5.7 Hz, 1H), 7.55 (d, *J* = 2.7 Hz, 1H), 7.06 (dd, *J* = 5.7, 2.7 Hz, 1H), 3.86 (s, 3H), 3.62 (s, 4H). ^{13}C NMR (125 MHz, DMSO): δ 165.5, 163.6, 150.5, 150.0, 111.8, 107.3, 55.5. M.p. = 81-83 ℃. MS (EI) m/z (M^+) calcd for $C_9H_{11}N_3O$: 177, found: 177.

4-Chloro-2-(4,5-dihydro-1H-imidazol-2-yl)pyridine (8c). Following the literature procedures,[6] sodium methoxide (7.8 mg, 0.144 mmol, 10 mol %) was added to a solution of 4-chloropicolinonitrile (200 mg, 1.44 mmol, 100 mol %) in methanol (1.5 mL). After the reaction mixture was allowed to stir for 15 h under N_2 atmosphere at 25 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: 30% ethyl acetate in hexanes) provided methyl 4-chloropicolinimidate as a colorless oil (209 mg, 1.22 mmol, 85% yield).

Ethylene diamine (0.15 mL, 2.32 mmol, 493 mol %) was added to a mixture of methyl 4-chloropicolinimidate (80mg, 0.47 mmol, 100 mol %) in MeOH (1.5 mL). The reaction mixture was allowed to stir for 20 h under N_2 atmosphere at 50 ℃. The solution was cooled to room temperature and quenched with H_2O (5 mL) and diluted with CH_2Cl_2 (5 mL). The layers were separated and the aqueous layer was extracted with DCM (2 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure to provided **8c** as a light yellow solid (68 mg, 0.376 mmol, 80% yield).

^{1}H NMR (500 MHz, DMSO): δ 8.60 (dd, *J* = 5.5, 0.5 Hz, 1H), 8.03 (d, *J* = 2.2 Hz, 1H), 7.65 (dd,

J = 5.5, 2.2 Hz, 1H), 7.05 (s, 1H), 3.64 (s, 4H). ^{13}C NMR (125 MHz, DMSO): δ 162.7, 150.4, 150.4, 143.3, 125.2, 121.9. M.p. = 77-78 ℃. MS (EI) m/z (M^+) calcd for $C_8H_8ClN_3$: 181, found: 181.

2-(4,5-Dihydro-1H-imidazol-2-yl)-4-methylpyridine (8d). Following the literature procedures,[6] sodium methoxide (9.0 mg, 0.169 mmol, 10 mol %) was added to a solution of 4-chloropicolinonitrile (200 mg, 1.69 mmol, 100 mol %) in methanol (1.5 mL). After the reaction mixture was allowed to stir for 15 h under N_2 atmosphere at 25 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: 40% ethyl acetate in hexanes) provided methyl 4-chloropicolinimidate as a colorless oil (240 mg, 1.60 mmol, 94% yield).

Ethylene diamine (0.44 mL, 6.56 mmol, 493 mol %) was added to a mixture of methyl 4-chloropicolinimidate (200mg, 1.33 mmol, 100 mol %) in MeOH (4.0 mL). The reaction mixture was allowed to stir for 20 h under N_2 atmosphere at 50 ℃. The solution was cooled to room temperature and quenched with H_2O (15 mL) and diluted with CH_2Cl_2 (15 mL). The layers were separated and the aqueous layer was extracted with DCM (2 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure to provided **8d** as a light yellow solid (160 mg, 0.99 mmol, 75% yield).

^{1}H NMR (500 MHz, DMSO): δ 8.44 (d, *J* = 5.0 Hz, 1H), 7.87 (s, 1H), 7.29 (dd, *J* = 5.0, 0.9 Hz, 1H), 6.87 (s, 1H), 3.62 (s, 4H), 2.34(s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 165.5, 163.6, 150.5, 150.0, 111.8, 107.3, 55.5. M.p. = 92-93 ℃. MS (EI) m/z (M^+) calcd for $C_9H_{11}N_3$: 161, found: 161.

Part 4. Reductive Coupling Reactions

General Procedure 1 for Homo-Coupling of Primary Alkyl bromides: To a flame-dried Schlenk tube equipped with a magnetic stir bar was loaded primary alkyl bromide (0.16 mmol, 100 mol %), followed by addition of 2-(2-Pyridyl)imidazoline (**8a**) (1.2 mg, 0.008 mmol, 5 mol %), (pin)B–B(pin) (60.9 mg, 0.24 mmol, 150 mol %). The tube was moved into a dry glove box, at which point NiI_2 (2.5 mg, 0.008 mmol, 5 mol %) and LiOMe (12.2 mg, 0.32 mmol, 200 mol %) were added. The tube was capped with a rubber septum, and it was moved out of the glove box. NMP (1.0 mL) were then added via syringe. After the reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 30 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: ethyl acetate in hexanes) provided the coupling product.

General Procedure 2 for Homo-coupling Coupling of Primary Alkyl Tosylates: To a flame-dried Schlenk tube equipped with a magnetic stir bar was loaded primary alkyl tosylates (0.16 mmol, 100 mol %), followed by addition of 2-(2-Pyridyl)imidazoline (**8a**) (2.4 mg, 0.016 mmol, 10 mol %) and (pin)B–B(pin) (60.9 mg, 0.24 mmol, 150 mol %). The tube was moved into a dry glove box, at which point NiI_2 (5.0 mg, 0.016 mmol, 10 mol %), LiOMe (12.2 mg, 0.32 mmol, 200 mol %) were added. The tube was capped with a rubber septum, and it was moved out of the glove box. NMP (1.0 mL) were then added via a syringe. After the reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 45 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: ethyl acetate in hexanes) provided the coupling product.

General Procedure 3 for Homo-Coupling of Secondary Alkyl Bromides: To a flame-dried Schlenk tube equipped with a magnetic stir bar was loaded secondary alkyl bromide (0.16 mmol, 100 mol %), followed by addition of **7a** (3.5mg, 0.016 mmol, 10 mol %) and (pin)B–B(pin) (60.9 mg, 0.24 mmol, 150 mol %). The tube was moved into a dry glove box, at which point NiI_2 (5.0 mg, 0.016 mmol, 10

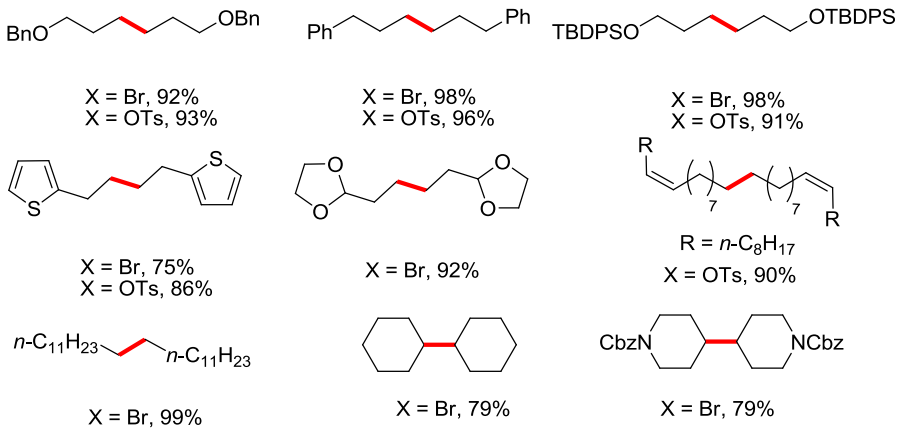
mol %) and LiOMe (12.2 mg, 0.32 mmol, 200 mol %) were added. The tube was capped with a rubber septum, and it was moved out of the glove box. NMP (0.5 mL) were then added via syringe. After the reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 45 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: ethyl acetate in hexanes) provided the coupling product.

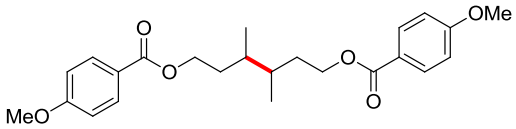
General Procedure 4 for the Coupling of Secondary and Primary Alkyl Bromides: To a flame-dried Schlenk tube equipped with a magnetic stir bar was loaded second alkyl bromide (0.16 mmol, 100 mol %), followed by addition of 2-(2-Pyridyl)imidazoline (**8a**) (2.4 mg, 0.016 mmol, 10 mol %) and (pin)B–B(pin) (81.3 mg, 0.32 mmol, 200 mol %). The tube was moved into a dry glove box, at which point NiI_2 (5.0 mg, 0.016 mmol, 10 mol %) and LiOMe (15.2 mg, 0.40 mmol, 250 mol %) were added. The tube was capped with a rubber septum, and it was moved out of the glove box. The primary alkyl bromide (0.24 mmol, 150 mol %) and NMP (0.5 mL) were then added via a syringe. After the reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 40 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: ethyl acetate in hexanes) provided the coupling product.

General Procedure 5 for the Coupling of Alkyl Iodides and Alkyl Bromides: To a flame-dried Schlenk tube equipped with a magnetic stir bar was loaded alkyl bromide (0.16 mmol, 100 mol %), followed by addition of 2-(2-Pyridyl)imidazoline (**8a**) (2.4 mg, 0.016 mmol, 10 mol %) and (pin)B–B(pin) (81.3 mg, 0.32 mmol, 200 mol %). The tube was moved into a dry glove box, at which point NiI_2 (5.0 mg, 0.016 mmol, 10 mol %) and LiOMe (15.2 mg, 0.40 mmol, 250 mol %) were added. The tube was capped with a rubber septum, and it was moved out of the glove box. The alkyl iodide (0.24 mmol, 150 mol %) and NMP (0.5 mL) were then added via a syringe. After the reaction mixture was allowed to stir for 16 h under N_2 atmosphere at 40 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash

column chromatography (SiO_2: ethyl acetate in hexanes) provided the coupling product.

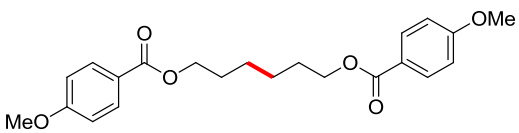
(1) Examples of Dimerization of Primary Halides.





3,4-Dimethylhexane-1,6-diyl bis(4-methoxybenzoate) (3). This compound was prepared according to the *General Procedure 3*, using **1a** (45.9 mg, 0.16 mmol, 100 mol %). After purification by column chromatography (SiO_2: 15% ethyl acetate in hexanes), the title compound was isolated as a colorless oil as a mixture of inseparable diastereomers (24.5 mg, 0.059 mmol, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01-7.98 (m, 4H), 6.94-6.89 (m, 4H), 4.41-4.29 (m, 4H), 3.87 (two singlets, 6H), 1.91-1.68 (m, 4H), 1.64-1.51 (m, 2H), 1.00-0.92 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 122.8, 113.5, 113.5, 64.7, 63.5, 63.4, 63.1, 55.4, 36.5, 35.5, 34.5, 33.8, 33.4, 31.8, 29.9, 29.7, 29.0, 23.4, 19.5, 16.2, 14.4. MS (EI) m/z (M^+) calcd for $C_{24}H_{30}O_6$: 414.5, found: 415.1.

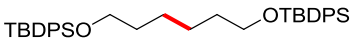


Hexane-1,6-diyl bis(4-methoxybenzoate) (4). This compound was prepared according to the

General Procedure 1, using **2a** (43.7 mg, 0.16 mmol, 100 mol %). After purification by column chromatography (SiO_2: 15% ethyl acetate in hexanes), the title compound was isolated as a white solid (30.6 mg, 0.079 mmol, 99% yield).

This compound can also be prepared according to the *General Procedure 2*, using **2b** (58.3 mg, 0.16 mmol, 100 mol %). After purification by column chromatography (SiO_2: 15% ethyl acetate in hexanes), the title compound was isolated as a white solid (29.1 mg, 0.075 mmol, 94% yield).

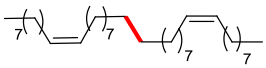
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02-7.99 (m, 4H), 6.94-6.91 (m, 4H), 4.32 (t, *J* = 6.6 Hz, 4H), 3.87 (s, 6H), 1.81 (m, 4H), 1.55-1.53 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 122.9, 113.5, 64.6, 55.4, 28.7, 25.8. M.p. = 88-89 ℃. MS (EI) m/z (M^+) calcd for $C_{22}H_{26}O_6$: 386.4, found: 387.0.



2,2,13,13-Tetramethyl-3,3,12,12-tetraphenyl-4,11-dioxa-3,12-disilatetradecane. This compound was prepared according to the *General Procedure 1*, using 1-Bromo-3-tert-butyldiphenylsilyloxypropane (60.4 mg, 0.16 mmol, 100 mol %). After purification by column chromatography (SiO_2: 3% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (46.6 mg, 0.078 mmol, 98% yield).

This compound can also be prepared according to the *General Procedure 2*, using 3-(tert-butyldiphenylsilyloxy)propyl 4-methylbenzenesulfonate (75.0 mg, 0.16 mmol, 100 mol %). After purification by column chromatography (SiO_2: 3% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (43.3 mg, 0.073 mmol, 91% yield).

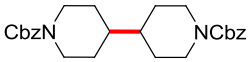
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.71 (m, 8H), 7.47-7.40 (m, 12H), 3.69 (t, *J* = 6.6 Hz, 4H), 1.63-1.57 (m, 4H), 1.39-1.36 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.6, 134.2, 129.5, 127.6, 63.9, 32.6, 26.9, 25.5, 19.2. MS (EI) m/z (M^+) calcd for $C_{38}H_{50}O_2Si_2$: 595.0, found: 597.0.



(9Z,27Z)-Hexatriaconta-9,27-diene. This compound was prepared according to the *General*

Procedure 2, using (Z)-octadec-9-enyl 4-methylbenzenesulfonate (67.6 mg, 0.16 mmol, 100 mol %). After purification by column chromatography (SiO_2: hexane), the title compound was isolated as a colorless oil (36.2 mg, 0.072 mmol, 90% yield).

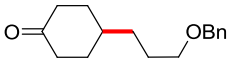
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.42-5.34 (m, 4H), 2.06-2.02 (m, 6H), 2.01-1.97 (m, 4H), 1.36-1.33 (m, 8H), 1.33-1.28 (m, 42H), 0.91 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 130.4, 129.9, 32.6, 32.0, 31.9, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.2, 27.2, 22.7, 14.1.



Dibenzyl 4,4'-bipiperidine-1,1'-dicarboxylate. This compound was prepared according to the *General Procedure 3*, using benzyl 4-bromopiperidine-1-carboxylate (47.7 mg, 0.16 mmol, 100 mol %). After purification by column chromatography (SiO_2: 3% ethyl acetate in hexanes), the title compound was isolated as a white solid (27.6 mg, 0.063 mmol, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.35 (m, 8H), 7.35-7.31 (m, 2H), 5.14 (s, 4H), 4.23 (s, 4H), 2.73 (s, 4H), 1.68 (s, 4H), 1.28 (s, 2H), 1.18 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 136.9, 128.4, 127.9, 127.8, 66.9, 44.3, 40.9, 29.6, 29.0. M.p. = 108-110 ℃. MS (EI) m/z (M^+) calcd for $C_{26}H_{24}N_2O_4$: 436.5, found: 437.1.

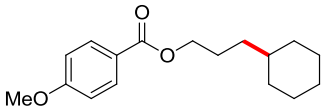
(2) Examples of cross-coupling products



4-(3-(Benzyloxy)propyl)cyclohexanone (18). This compound was prepared according to the *General Procedure 4*, using 4-bromocyclohexanone (28.3 mg, 0.16 mmol, 100 mol %), ((3-bromopropoxy)methyl)benzene (55.0 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 10% ethyl acetate in hexanes), the title compound was isolated as a light yellow oil (27.6 mg, 0.112 mmol, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.35 (m, 4H), 7.33-7.28 (m, 1H), 4.53 (s, 2H), 3.50 (t, *J* = 6.5 Hz, 2H), 2.41-2.29 (m, 4H), 2.07 (dq, *J* = 13.6 and 3.0 Hz, 2H), 1.77-1.68 (m, 3H), 1.45-1.39 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.3, 138.5, 128.3, 127.6, 127.5, 72.9, 70.4, 40.8, 35.9, 32.6, 32.0, 29.7, 27.5.

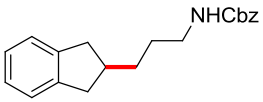
HRMS (ESI) m/z (M^+) calcd for $C_{16}H_{22}O_2$: 246.1620, found: 246.1622.



3-Cyclohexylpropyl 4-methoxybenzoate (19). This compound was prepared according to the *General Procedure 5*, using **2a** (43.7 mg, 0.16 mmol, 100 mol %), iodocyclohexane (50.4 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (34.0 mg, 0.123 mmol, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.94-6.92 (m, 2H), 4.28 (t, *J* = 7.0 Hz, 2H), 3.87 (s, 3H), 1.80-1.67 (m, 6H), 1.35-1.12 (m, 7H), 0.95-0.88 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 65.1, 55.4, 37.3, 33.7, 33.3, 26.6, 26.3, 26.1.

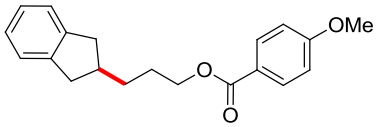
HRMS (ESI) m/z (M^+) calcd for $C_{17}H_{24}O_3$: 276.1725, found: 276.1728.



Benzyl 3-(2,3-dihydro-1H-inden-2-yl)propylcarbamate (22). This compound was prepared according to the *General Procedure 4*, using 2-bromo-2,3-dihydro-1H-indene (31.5 mg, 0.16 mmol, 100 mol %), benzyl 3-bromopropylcarbamate (65.3 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 15% ethyl acetate in hexanes), the title compound was isolated as a light yellow oil (36.6 mg, 0.118 mmol, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.37 (m, 4H), 7.37-7.33 (m, 1H), 7.22-7.19 (m, 2H), 7.17-7.14 (m, 2H), 5.13 (s, 2H), 4.83 (s, 1H), 3.25 (q, *J* = 6.4 Hz, 2H), 3.07 (dd, *J* = 15.4 and 7.8 Hz, 2H), 2.60 (dd, *J* = 9.0 and 15.4 Hz, 2H), 2.46 (dt, *J* = 15.1 and 7.6 Hz, 1H), 1.65-1.60 (m, 2H), 1.57-1.53 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.4, 143.3, 136.6, 128.5, 128.1, 126.1, 124.4, 66.6, 41.2, 39.8, 39.2, 32.7, 28.8.

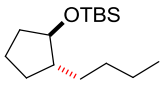
HRMS (ESI) m/z (M^+) calcd for $C_{20}H_{23}NO_2$: 309.1729, found: 309.1731.



3-(2,3-Dihydro-1H-inden-2-yl)propyl 4-methoxybenzoate (23). This compound was prepared according to the *General Procedure 4*, using 2-bromo-2,3-dihydro-1H-indene (31.5 mg, 0.16 mmol, 100 mol %), **2a** (65.5 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 6% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (36.8 mg, 0.118 mmol, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2H), 7.22-7.20 (m, 2H), 7.17-7.14 (m, 2H), 6.96-6.94 (m, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 3.89 (s, 3H), 3.10 (dd, *J* = 15.4 and 7.9 Hz, 2H), 2.65 (dd, *J* = 15.4 and 8.2 Hz, 2H), 2.53 (m, 1H), 1.91-1.85 (m, 2H), 1.71-1.66 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.3, 143.3, 131.5, 126.1, 124.4, 122.9, 113.6, 64.8, 55.4, 39.8, 39.3, 32.1, 27.7.

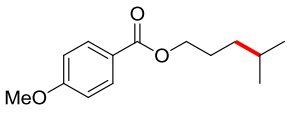
HRMS (ESI) m/z (M^+) calcd for $C_{20}H_{22}O_3$: 310.1569, found: 310.1566.



Tert-butyl((1R,2R)-2-butylcyclopentyloxy)dimethylsilane (24). This compound was prepared according to the *General Procedure 4*, using ((1R,2R)-2-bromocyclopentyloxy)(tert-butyl)dimethylsilane (44.7 mg, 0.16 mmol, 100 mol %), 1-bromobutane (32.9 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: hexane), the title compound was isolated as a colorless oil (25.0 mg, 0.098 mmol, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.71 (q, *J* = 6.2 Hz, 1H), 1.89-1.77 (m, 2H), 1.71-1.63 (m, 2H), 1.57-1.46 (m, 3H), 1.35-1.24 (m, 6H), 1.11-1.03 (m, 2H), 0.91-0.89 (m, 12H), 0.06 (d, *J* = 4.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 79.6, 47.9, 34.6, 33.3, 30.4, 29.7, 29.2, 25.9, 22.9, 21.4, 18.1, 14.1, -4.4, -4.6.

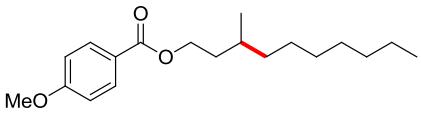
HRMS (ESI) m/z (M^+) calcd for $C_{15}H_{32}OSi$: 256.2222, found: 256.2223.



4-Methylpentyl 4-methoxybenzoate (25). This compound was prepared according to the *General Procedure 5*, using **2a** (43.7 mg, 0.16 mmol, 100 mol %), 2-iodopropane (40.8 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (18.9 mg, 0.080 mmol, 50% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.95-6.92 (m, 2H), 4.28 (t, *J* = 7.0 Hz, 2H), 3.87 (s, 3H), 1.80-1.74 (m, 2H), 1.65-1.58 (m, 1H), 1.35-1.31 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 65.1, 55.4, 35.1, 27.7, 26.7, 22.5.

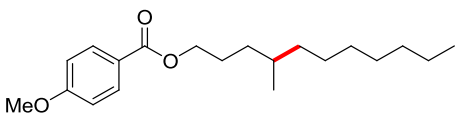
HRMS (ESI) m/z (M^+) calcd for $C_{14}H_{20}O_3$: 236.1412, found: 236.1415.



3-Methyldecyl 4-methoxybenzoate (26). This compound was prepared according to the *General Procedure 4*, using **1a** (45.9 mg, 0.16 mmol, 100 mol %), 1-bromoheptane (43.0 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (34.3 mg, 0.112 mmol, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.34 (qd, *J* = 11.0 and 6.8 Hz, 2H), 3.87 (s, 3H), 1.84-1.77 (m, 1H), 1.66-1.54 (m, 2H), 1.38-1.28 (m, 12H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 113.5, 63.3, 55.4, 36.9, 35.6, 31.9, 30.0, 29.8, 29.5, 29.3, 26.9, 22.7, 19.6, 14.1.

HRMS (ESI) m/z (M^+) calcd for $C_{19}H_{30}O_3$: 306.2195, found: 306.2200.

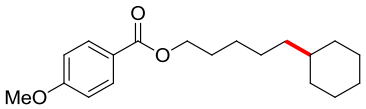


4-Methylundecyl 4-methoxybenzoate (27). This compound was prepared according to the *General Procedure 4*, using 4-bromopentyl 4-methoxybenzoate (48.2 mg, 0.16 mmol, 100 mol %),

1-bromoheptane (43.0 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (30.7 mg, 0.096 mmol, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.95-6.92 (m, 2H), 4.28 (t, *J* = 6.5 Hz, 2H), 3.88 (s, 3H), 1.85-1.69 (m, 2H), 1.49-1.41 (m, 2H), 1.33-1.21 (m, 14H), 1.17-1.12 (m, 1H), 0.91-0.88 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 65.1, 55.4, 36.9, 33.2, 32.5, 31.9, 29.9, 29.4, 27.0, 26.3, 22.7, 19.6, 14.1.

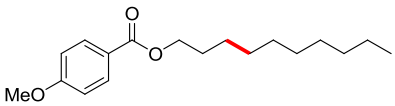
HRMS (ESI) m/z (M^+) calcd for $C_{20}H_{32}O_3$: 320.2351, found: 320.2350.



5- Cyclohexylpropyl 4-methoxybenzoate (29). This compound was prepared according to the *General Procedure 5*, using 5-bromopentyl 4-methoxybenzoate (48.2 mg, 0.16 mmol, 100 mol %), iodocyclohexane (50.4 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (32.3 mg, 0.106 mmol, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.94-6.92 (m, 2H), 4.30 (t, *J* = 7.0 Hz, 2H), 3.87 (s, 3H), 1.79-1.64 (m, 6H), 1.46-1.34 (m, 4H), 1.27-1.13 (m, 7H), 0.91-0.83 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4,163.2, 131.5, 123.0, 113.5, 64.8, 55.4, 37.6, 37.4, 33.4, 28.8, 26.7, 26.5, 26.4, 26.3.

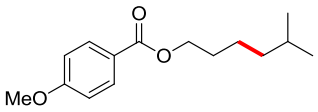
HRMS (ESI) m/z (M^+) calcd for $C_{19}H_{28}O_3$: 304.2038, found: 304.2037.



Decyl 4-methoxybenzoate (30). This compound was prepared according to the General Procedure 5, using 2a (43.7 mg, 0.16 mmol, 100 mol %), 1-bromoheptane (43.0 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title

compound was isolated as a colorless oil (25.7 mg, 0.088 mmol, 55% yield).

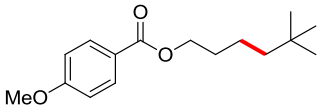
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.95-6.92 (m, 2H), 4.30 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 1.79-1.73 (m, 2H), 1.47-1.41 (m, 2H), 1.39-1.25 (m, 12H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 64.8, 55.4, 31.9, 29.5, 29.3, 28.7, 26.0, 22.6, 14.1.



5-Methylhexyl 4-methoxybenzoate (32). This compound was prepared according to the *General Procedure 5*, using **2a** (43.7 mg, 0.16 mmol, 100 mol %), 1-iodo-2-methylpropane (44.2 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (18.0 mg, 0.072 mmol, 45% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.94-6.92 (m, 2H), 4.30 (t, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 1.78-1.72 (m, 2H), 1.62-1.53 (m, 1H), 1.48-1.42 (m, 2H), 1.28-1.24 (m, 2H), 0.90 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 64.8, 55.4, 38.5, 29.0, 27.8, 23.8.

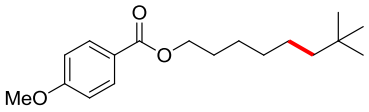
HRMS (ESI) m/z (M^+) calcd for $C_{15}H_{22}O_3$: 250.1569, found: 250.1567.



5,5-Dimethylhexyl 4-methoxybenzoate (33). This compound was prepared according to the *General Procedure 5*, using **2a** (43.7 mg, 0.16 mmol, 100 mol %), 1-iodo-2,2-dimethylpropane (47.5 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (31.2 mg, 0.118 mmol, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.95-6.92 (m, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 3.88 (s, 3H), 1.77-1.72 (m, 2H), 1.45-1.38 (m, 2H), 1.27-1.24 (m, 2H), 0.90 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 64.8, 55.4, 43.8, 30.3, 29.6, 29.3, 21.1.

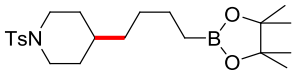
HRMS (ESI) m/z (M^+) calcd for $C_{16}H_{24}O_3$: 264.1725, found: 264.1724.



7,7-Dimethyloctyl 4-methoxybenzoate (34). This compound was prepared according to the *General Procedure 5*, using 5-bromopentyl 4-methoxybenzoate (48.2 mg, 0.16 mmol, 100 mol %), 1-iodo-2,2-dimethylpropane (47.5 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 4% ethyl acetate in hexanes), the title compound was isolated as a colorless oil (37.4 mg, 0.128 mmol, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 6.95-6.92 (m, 2H), 4.30 (t, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 1.80-1.74 (m, 2H), 1.49-1.43 (m, 2H), 1.37-1.25 (m, 4H), 1.20-1.16 (m, 2H), 0.88 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 163.2, 131.5, 123.0, 113.5, 64.8, 55.4, 44.1, 30.3, 30.2, 29.4, 28.8, 26.1, 24.4.

HRMS (ESI) m/z (M^+) calcd for $C_{18}H_{28}O_3$: 292.2038, found: 292.2033.



4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1-tosylpiperidine (39). This compound was prepared according to the *General Procedure 4*, using **18a** (50.9 mg, 0.16 mmol, 100 mol %), 2-(4-bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (63.1 mg, 0.24 mmol, 150 mol %). After purification by column chromatography (SiO_2: 12% ethyl acetate in hexanes), the title compound was isolated as a colorless oil containing inseparable **18a** (43.8 mg, 0.104 mmol, 65% yield). The yield was estimated based on the NMR ratio of these two compounds. Removal of **18a** was performed using our previous published procedure (Organic Letters, **2011**, *13*, 2138), but induced trace amount of inseparable hydrodehalogenation byproduct.

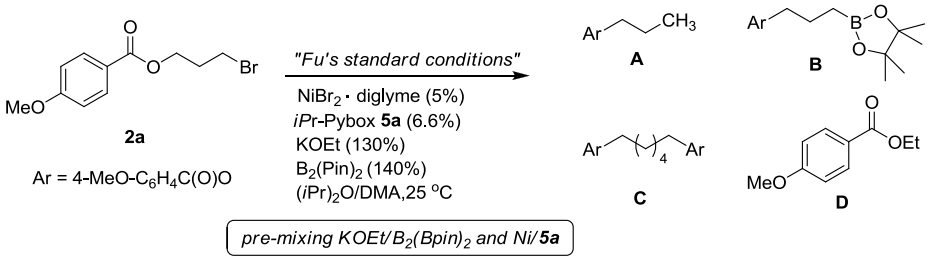
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.75 (d, *J* = 11.5 Hz, 2H), 2.44 (s, 3H), 2.20 (td, *J* = 12.0 and 2.0 Hz, 2H), 1.70 (d, *J* = 11.5 Hz, 2H), 1.38-1.32 (m, 2H), 1.28-1.19 (m, 18H), 1.15-1.10 (m, 1H), 0.75 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ

143.2, 133.2, 129.5, 127.7, 82.8, 46.5, 35.7, 34.8, 31.5, 29.2, 24.8, 23.9, 21.5.

HRMS (ESI) m/z (M^+) calcd for $C_{22}H_{36}BNO_3S$: 420.2494, found: 420.2497.

Part 5. Comparison of Fu's Borylation and Our Reductive Coupling Conditions

Table S10. Variation of the reaction parameters for Fu's borylation conditions.



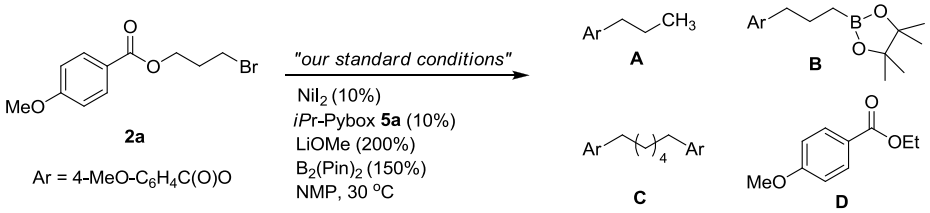
entry[a]	alternation from the standard conditions	2a	A	B (R-Bpin)	C	D
1	none	9%	6%	64%	21%	ND
2	LiOMe	76%	13%	ND	11%	ND
3	NiI_2	16%	7%	54%	23%	ND
4	NMP	23%	17%	31%	29%	ND
5	one-pot	5%	11%	17%	25%	42%
6	18-Crown-6 (130%)	13%	10%	44%	33%	ND
7	LiOMe (130%) 12-Crown-4 (130%)	20%	26%	ND	54%	ND
8	KOEt (130%+70%)	5%	7%	46%	15%	27%
9	$B_2(pin)_2$ (280%)	13%	11%	41%	35%	ND
10	NiI_2/LiOMe/NMP	34%	29%	10%	27%	ND
11	NiI_2/KOEt/NMP	36%	27%	24%	13%	ND

[a] Unless otherwise mentioned, yields refer to NMR yields determined without internal standard.

A comparison of the reaction parameters in Fu's alkyl borylation and our reductive coupling conditions (Table S10, entry 1) was performed using **2a** and (3-bromopropyl)benzene as the model substrate and **5a** as the ligand at 25 or 30 °C. Following Fu's $NiBr_2$•diglyme (5%) /KOEt (130%) /iPr$_2$O/DMA (0.078 M)conditions (featuring pre-mixing KOEt and $(Bpin)_2$, and Ni and **5a**), broylation of **2a** was obtained in 64% yield along with 21% of homocoupling product and 9% of unreacted **2a** (Table S10, entry 1). Replacement of KOEt with LiOMe led to majorly recovered **2a**, and failed to generate borylation product **B** possibly due to poor solubility of the Li(OMeBpin-Bpin) generated in the reaction (Table S10, entry 2). Change of $NiBr_2$•diglyme and iPr$_2$O/DMA with NiI_2 and NMP, generates 54% and 31% borylation product, 23% and 29% homocoupling product, and 16% and 23%

of recovered **2a**, respectively (Table S10, entries 3-4). Performance of Fu's reagent in one pot (our procedure) increased the ratio of B (R-Bpin) to **C** (homocoupling) along with 42% of **D**, suggesting pre-mixing of KOEt and $(Bpin)_2$ is crucial in Fu's method (Table S10, entry 5). Premixing 18-C-6/KOEt/$(Bpin)_2$, and 12-C-4/LiOMe/$(Bpin)_2$, indicate more homocoupling product **C** was produced, particularly no **B** was observed in the case of LiOMe (Table S10, entries 6-7). The effects of capture of the cations on the reaction results are not clear. Increase of the amount of KOEt to 2 equiv lead to formation of transesterificiation byproduct **D** (Table S10, entry 8). On the other hand, 2.8 equiv of $(Bpin)_2$ promoted homocoupling (Table S10, entry 9). Following Fu's procedure, but using NiI_2(5%)/LiOMe (130%)/NMP (0.078 M), and NiI_2 (5%)/KOEt (130%)/NMP significantly reduced borylation as compared to 64% in entry 1 (Table S10, entries 10-11)

Table S11. Variation of the reaction parameters for our reductive homocoupling conditions.



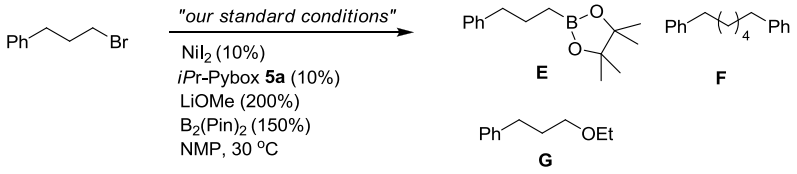
entry[a]	alternation from the standard conditions	2a	A	B (R-Bpin)	C	D
1	none	10%	9%	trace	80%[b]	ND
2	$NiBr_2$ · diglyme	8%	14%	trace	78%	ND
3	$(iPr)_2O$/DMA	6%	20%	trace	53%[b]	ND
4	KOEt (200%)	5%	4%	5%	27%	59%
5	LiOMe (130%)	14%	16%	trace	66%[b]	ND
6	12-crown-4 (200%)	8%	14%	trace	78%	ND
7	KOEt (200%) 18-Crown-6 (200%)	14%	10%	13%	36%	27%

[a] Unless otherwise mentioned, yields refer to NMR yields determined without internal standard. [b] isolated yield.

Following our one-pot procedure, replacement of NiI_2 and NMP with $NiBr_2$•diglyme and iPr_2O/DMA, respectively, only produced trace amount of borylation product where homocoupling is the major (Table S11, entries 1-3). Replacement of LiOMe with KOEt using our procedure, on the

other hand, generated 5% of borylation product although 27% of homocoupling product was observed (Table S11, entry 4). The transesterification product **D** was observed in 59% yield, suggesting a dramatic difference between LiOMe and KOEt in terms of nucleophilicity. The borylation yield could be promoted to 26% using KOEt when (3-bromopropyl)benzene was used as the substrate (Table S12, entry 2). Use of 1.3 equiv of LiOMe reduced the homocoupling yield and increased the amount of 2a and hydrodehalogenation product (Table S11, entry 5). Addition of 12-C-4 and 12-C-8 to the reaction of LiOMe and KOEt, respectively did not seem to alter the reaction result, although less transesterification byproduct **D** was generated (Table S11, entries 6-7).

Table 12. Use of KOEt in our reductive homocoupling conditions for phenylpropylbromide .

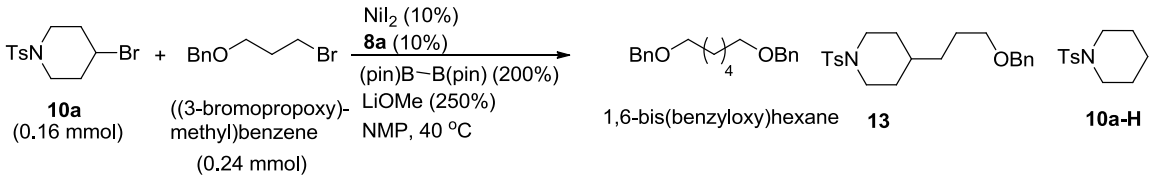


entry[a]	alternation from the standard conditions	**E** (R-Bpin)	**F**	**G**
1[b]	none	trace	98%	NA
2	KOEt	26%	26%	13%

[a] Unless otherwise mentioned, yields refer to NMR yields determined without internal standard. [b] isolated yield.

Part 6. Tracking the Reaction Progress

1. Tracking the Reaction Progress for the Coupling of **10a** with ((3-Bromopropoxy)methyl)benzene.



10a (0.16 mmol)

((3-bromopropoxy)-methyl)benzene (0.24 mmol)

1,6-bis(benzyloxy)hexane **13** **10a-H**

entry[a]	((3-bromopropoxy)-methyl)benzene	1,6-bis(benzyloxy)hexane[b]	**10a**	**10a-H**	**13**[c]
1 h	0.211 mmol (88%)	0.011 mmol (9%)	0.145 mmol (91%)	NA	0.010 mmol (53%)
3 h	0.134 mmol (56%)	0.028 mmol (23%)	0.083 mmol (53%)	NA	0.064mmol (53%)
5 h	0.088 mmol (37%)	0.037 mmol (31%)	0.064 mmol (41%)	0.003 mmol (2%)	0.083 mmol (53%)
8 h	0.051 mmol (22%)	0.043 mmol (36%)	0.034 mmol (22%)	0.0065 mmol (4%)	0.106 mmol (68%)
16 h	0.035 mmol (15%)	0.052 mmol (44%)	0.015 mmol (10%)	0.008 mmol (5%)	0.117 mmol (75%)
36 h	0.026 mmol (11%)	0.050 mmol 43%	0.012 mmol (7%)	0.011 mmol (7%)	0.121 mmol (77%)

[a] The quantity of 1,6-bis(benzyloxy)hexane and ((3-bromopropoxy)-methyl)benzene was determined by ^{1}H NMR from an isolated mixture of these two compounds, and the quantity of **10a**, **10a-H** and **13** was determined by ^{1}H NMR from an isolated mixture of these three compounds. [b] yields refer to the percentage of conversion of primary alkyl halides. [c] yields refer to (moles of product)/(1 equiv of **10a**)

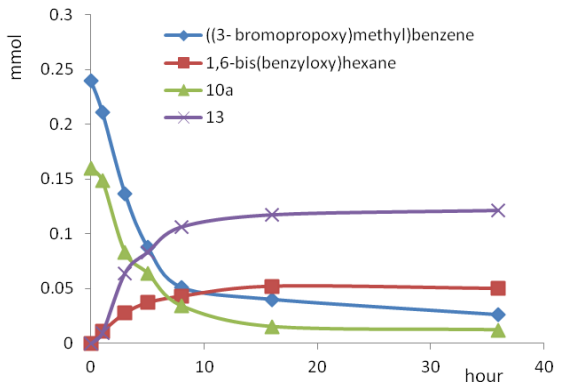


Figure 1. Tracking the Reaction Progress for the Coupling of **10a** with ((3-Bromopropoxy)methyl)benzene.

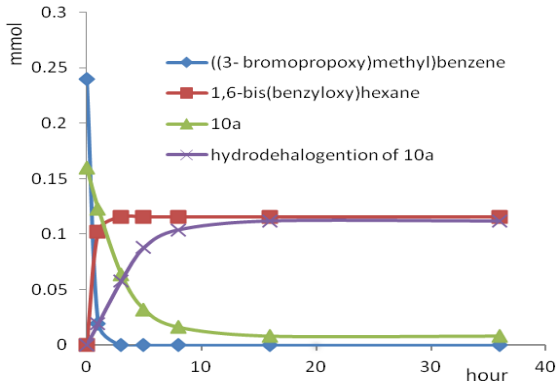


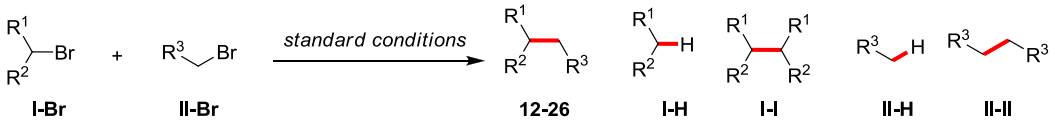
Figure 2. Tracking the reaction progress of ((3-bromopropoxy)methyl)benzene in the absence of 9a, and the reaction progress of **10a** in the absence of ((3-bromopropoxy)methyl)benzene under the standard cross-coupling reaction conditions.

2. Tracking the reaction progress of ((3- bromopropoxy)methyl)benzene in the absence of **10a**, and the reaction progress of **10a** in the absence of ((3-bromopropoxy)methyl)benzene under the standard cross-coupling reaction conditions.

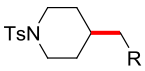
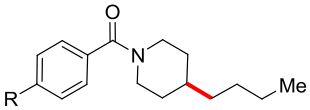
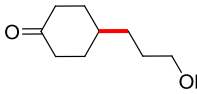
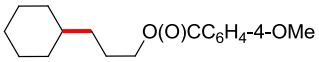
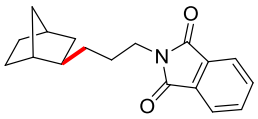
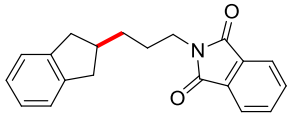
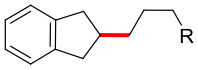
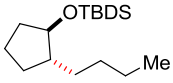
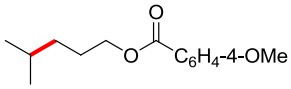
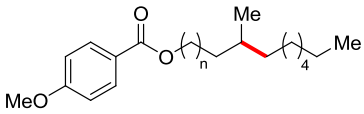
Time (h)	((3-bromopropoxy)methyl)benzene (mmol)	1,6-bis(benzyloxy)hexane (mmol)	**10a** (mmol)	Hydrodehalogenation of **10a (10a-H)** (mmol)
0	0.24	0	0.16	0
1	0.0196	0.102	0.1232	0.0192
3	0	0.1152	0.064	0.0576
5	0	0.1152	0.032	0.088
8	0	0.1152	0.016	0.104
16	0	0.1152	0.008	0.112
36	0	0.1152	0.008	0.112

Part 7. Determination of the Byproducts for Examples in Tables 3–5.

(1) **Table S13.** Data of product distribution obtained for Table 3:

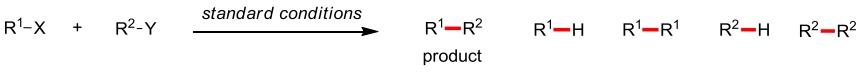


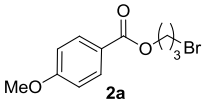
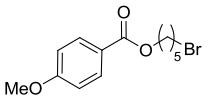
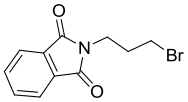
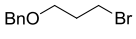
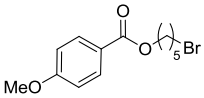
I-Br **II-Br** **12-26** **I-H** **I-I** **II-H** **II-II**

entry[a]	product		yield (%)	**I-H**	**I-Br**[b]	**I-I**[c]	**II-H**	**II-Br**[b]	**II-II**[c]	$(Bpin)_2$[b]
1		**12**:	79	5%	5%	NA[d]	trace	ND[e]	52%	>20%
2		**13**:	75	trace	10%	5%	trace	8%	49%	>30%
3		**14**:	80	NA[d]	NA	NA	NA	NA	NA	>30%
4		**15**:	40	52%	6%	NA	NA	NA	NA	>50%
5		**16**:	85	trace	~5%	NA	NA	NA	NA	32%
6		**17:**	83	trace	~5%	NA	NA	NA	NA	34%
7		**18**:	70	NA		NA	ND[e]	8%	47%	NA
8		**19**:	15	NA	5%	30%	NA	ND	82%	NA
9		**20**:	45	NA	NA	NA	ND	ND	65%	~40%
10		**21**:	63	NA	NA	NA	4%	trace	54%	33%
11		**22**:	74	NA	NA	NA	ND	8%	42%	~20%
12		**23**:	74	NA	NA	NA	2%	5%	44%	27%
13		**24**:	61	ND	32%	NA	NA	NA	NA	16%
14		**25**:	trace	NA	NA	NA	NA	NA	NA	NA
15		**26**, n = 1:	70	trace	9%	20%	NA	NA	52%	>31%

[a] Except for the products and $(Bpin)_2$, the quantities of other compounds were estimated by ^1H NMR from mixtures after column chromatography unless otherwise mentioned (similar to Part 6). [b] recovery% of the starting materials. [c] yilelds refer to conversion% of the starting materials to the dimerization products. [d] NA = availalble. [e] ND = not detected

(2) **Table S14.** Part of data for product distribution obtained for Table 4 and Table 5:



entry[a]	R^1-X	R^2-Y	R^1-X/ R^2-Y	product	yield[d]	R^1-**H**	(R^1-**X**)[e]	(**R^1-R^1**)[f]	**R^2-H**	(R^2-**Y**)[e]	(R^2-R^2)[f]	$(Bpin)_2$[d,e]
1[b]	 **2a**		1.5:1	**19**	60%	NA[g]	7%	55%	trace	7%	30%	~20%
2[b]			1:1.5		77%	NA[g]	3%	20%	trace	3%	20%	>40%
3[b]			1:1.5	**29**	66%	NA[g]	4%	29%	trace	5%	25%	NA[g]
4[b]			1:1.5	**20**	65%	trace	trace	NA[g]	56%	NA[g]	NA[g]	NA[g]
9[b]	**10a**	*n*-$C_7H_{15}I$	1:1.5	**11a**	20%	14%	42%	NA[g]	NA[g]	15%	58%	NA[g]
10[b]	**10b**	*n*-C_4H_9I	1:1.5	**11b**	43%	50%	trace	NA[g]	NA[g]	15%	60%	NA[g]
1[c]	**2a**	*n*-$C_7H_{15}Br$	1:1.5	**30**	55%	NA	5%	36%	trace	ND[h]	30%	NA[g]
2[c]	**2a**	*n*-$C_7H_{15}Br$	1.5:1	**30**	52%	2%	15%	48%	NA	ND[h]	25%	NA[g]
3[c]	**2a**		1:1.5	**31**	52%	NA	NA[g]	NA[g]	NA[g]	NA[g]	NA[g]	>28%
8[c]	**2a**		1:1.5	**32**	45%	3%	ND[h]	51%	NA[g]	NA[g]	NA[g]	~30%
10[c]			1:1.5	**34**	80%	trace	ND[h]	19%	NA	NA[g]	NA[g]	~15%
12[c]	 **10a**, X= Br		1:1.5	**35**	10%	70%	ND[h]	NA[g]	trace	ND[h]	20%	NA[g]
13[c]	**10b**, X = I		1:1.5		5%	70%	ND[h]	NA[g]	trace	ND[h]	20%	NA[g]

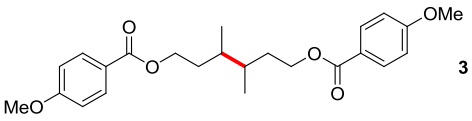
[a] Except for the products, the quantities of other compounds were estimated by ^{1}H NMR from mixtures after column chromatography unless otherwise mentioned (similar to Table S13). [b] entries in Table 4. [c] entries in Table 5. [d] ioslated yileds. [e] recovery% of starting materials. [f] yilelds refer to conversion% of the starting materials to the dimerization products. [g] not availalble. [h] not detected

In addition, tracking the reaction progress for the coupling of equimolar **10a** and $Ph(CH_2)_3Br$ indicated that the two alkyl halides remains a ratio of 1:1 during the course of reaction till disappearance after 16 h, at which point **12** was isolated in 55% yield. The major side reaction for **10a** was homocoupling (>20%) and hydrodehalogenation (10%), whereas the major byproducts isolated from $Ph(CH_2)_3Br$ was homocoupling (>40%).

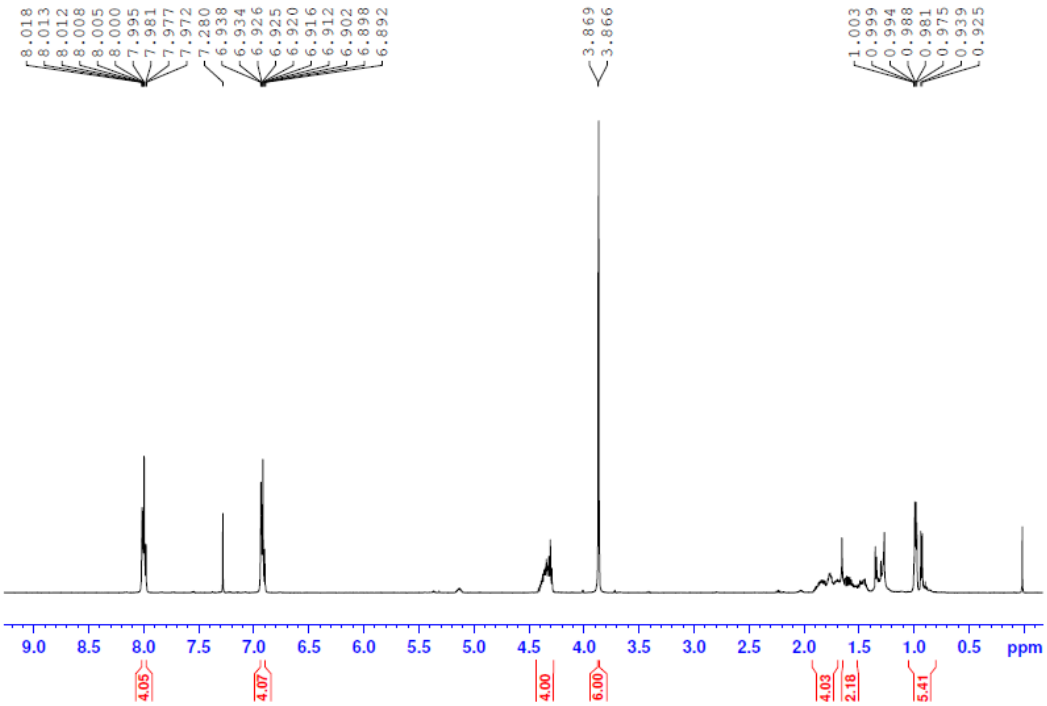
Analysis of the products arising from cyclohexyl iodide in Table 4, entry 1 and the less reactive cyclohexyl bromide in Table 3, entry 8 revealed that >0.3 equiv of cyclohexyl halides were converted into bi(cyclohexane) in both cases. The major side reactions arising from primary halide **2a** were attributed to homocoupling.

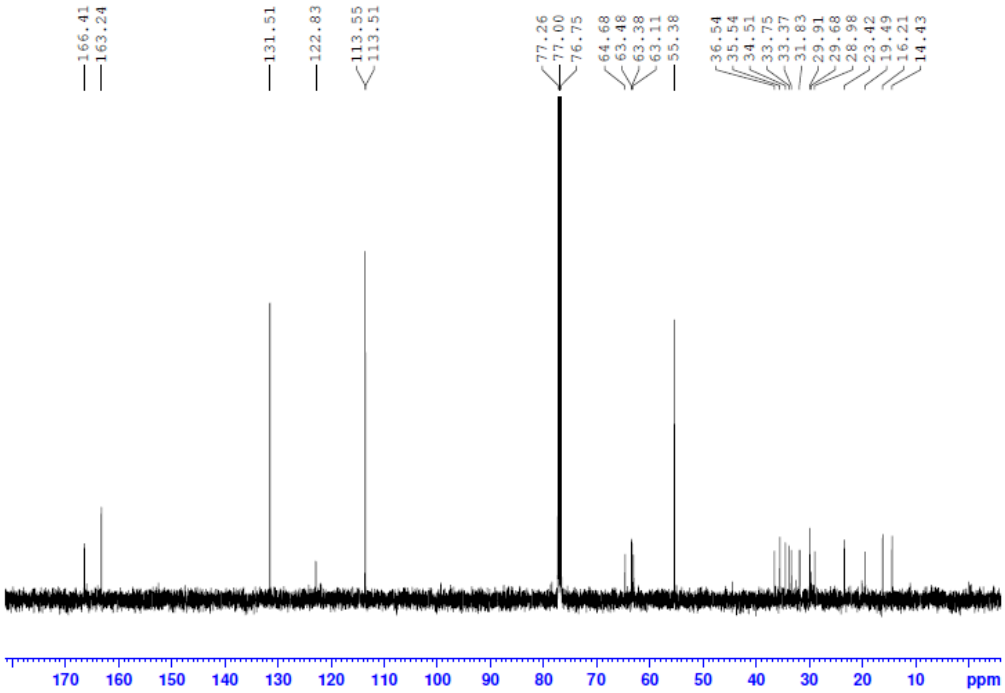
On the other hand, coupling of cyclohexyl iodide with **10a** and **10b** generated trace amount of product **35** (Table 5, entries 12–13). The side reactions of **10a** and **10b** were hydrodehalogenation (>70%), while less than 0.2 equiv of cyclohexyl iodide converting into bis(cyclohexane) were detected. For the cross-coupling of primary bromides **2a** and *n*-heptyl bromide (Table 5, entry 1), homocoupling of **2a** (36%) and tetradecane (30%, i.e. dimerization of 0.45 equiv of *n*-$C_7H_{15}Br$) were observed.

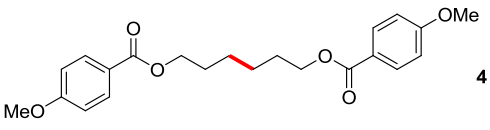
II. Spectral Data for New Compounds



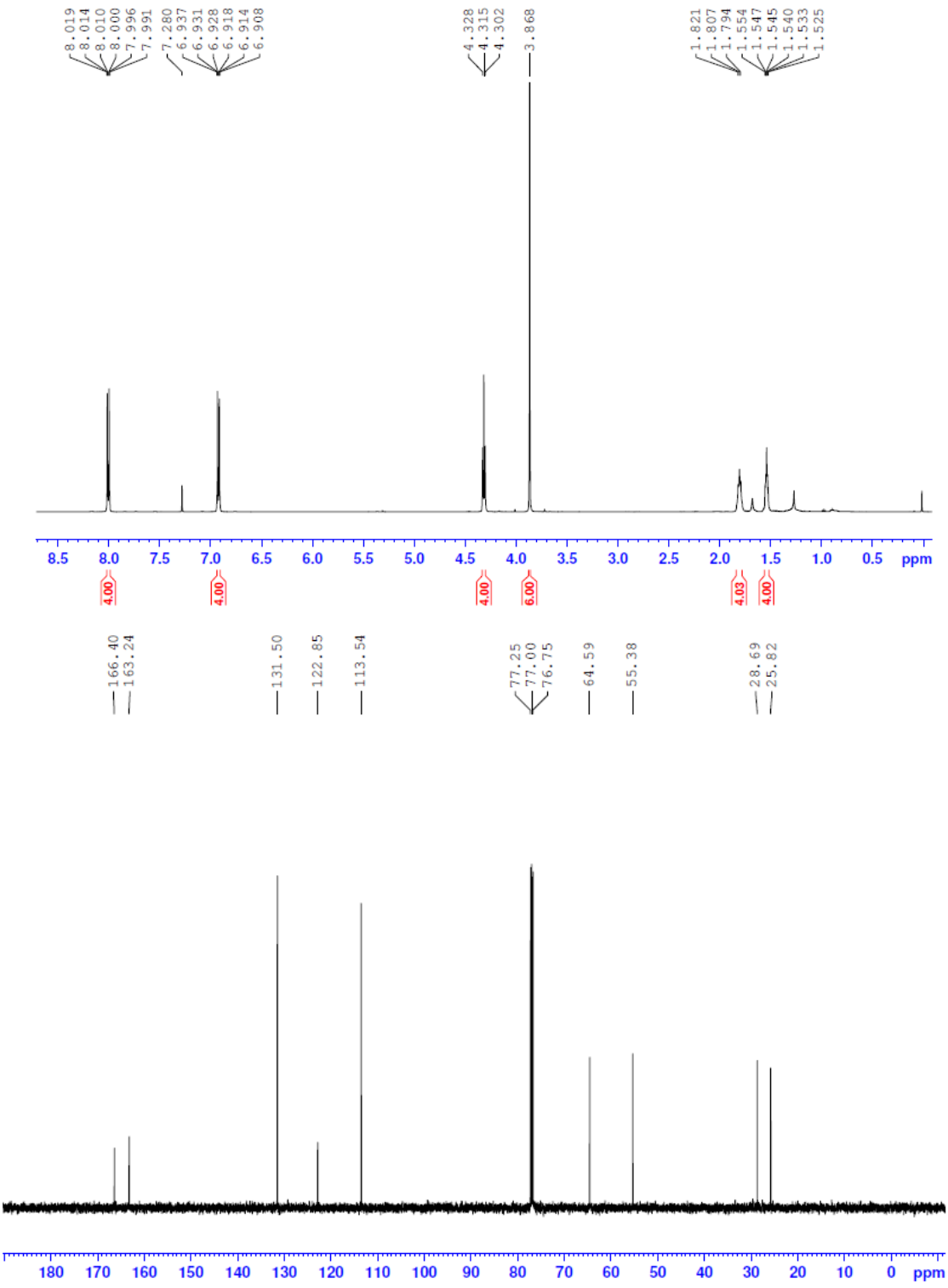
3






OMe
MeO
O
O
O
O

4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7.991
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6.931
6.928
6.918
6.914
6.908
4.328
4.315
4.302
3.868
1.821
1.807
1.794
1.554
1.547
1.545
1.540
1.533
1.525
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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4.00
6.00
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4.00
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122.85
113.54
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77.00
76.75
64.59
55.38
28.69
25.82
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170
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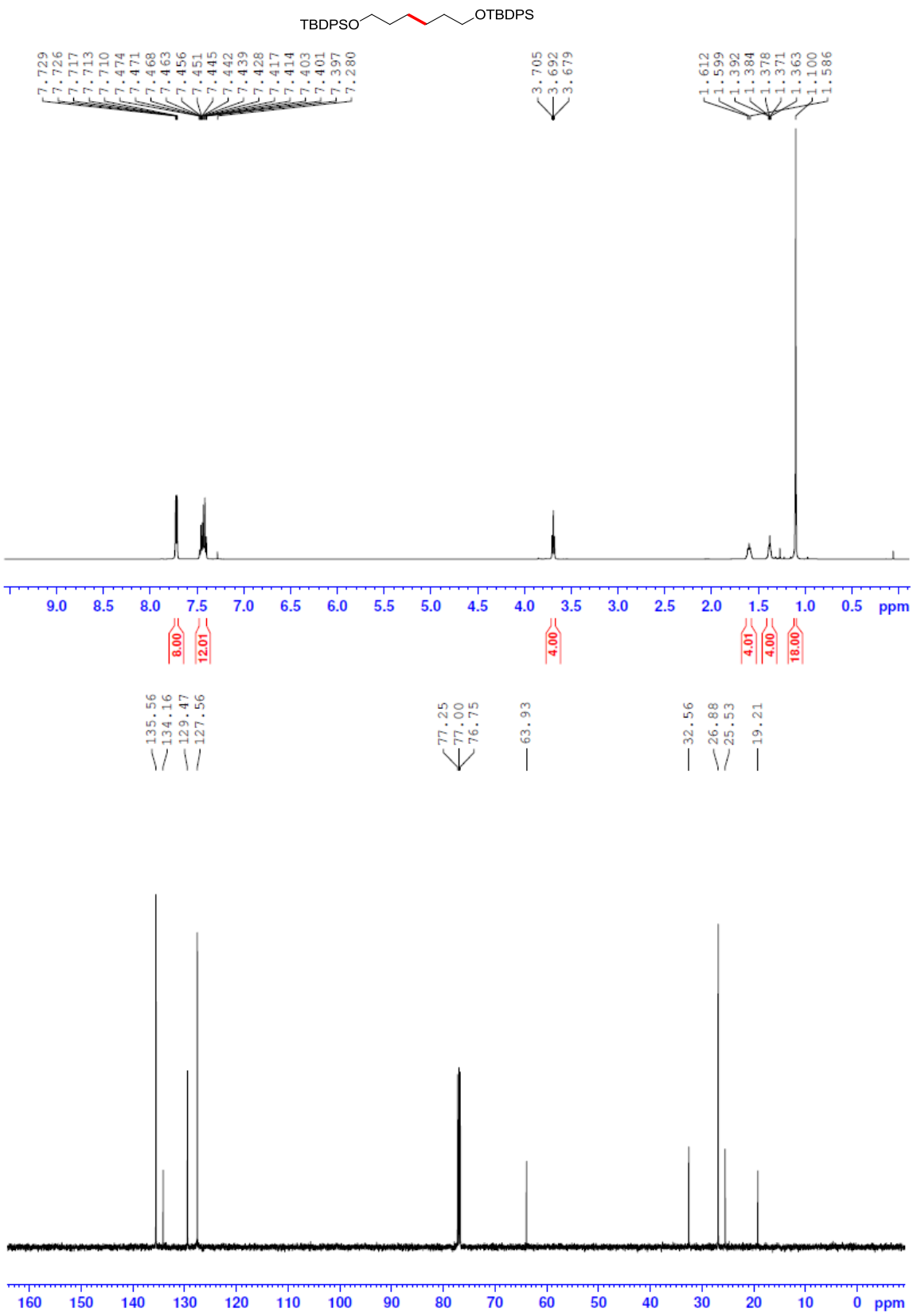
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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OTBDPS
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7.726
7.717
7.713
7.710
7.474
7.471
7.468
7.463
7.456
7.451
7.445
7.442
7.439
7.428
7.417
7.414
7.403
7.401
7.397
7.280
3.705
3.692
3.679
1.612
1.599
1.392
1.384
1.378
1.371
1.363
1.100
1.586
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
8.00
12.01
4.00
4.01
4.00
18.00
135.56
134.16
129.47
127.56
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76.75
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19.21
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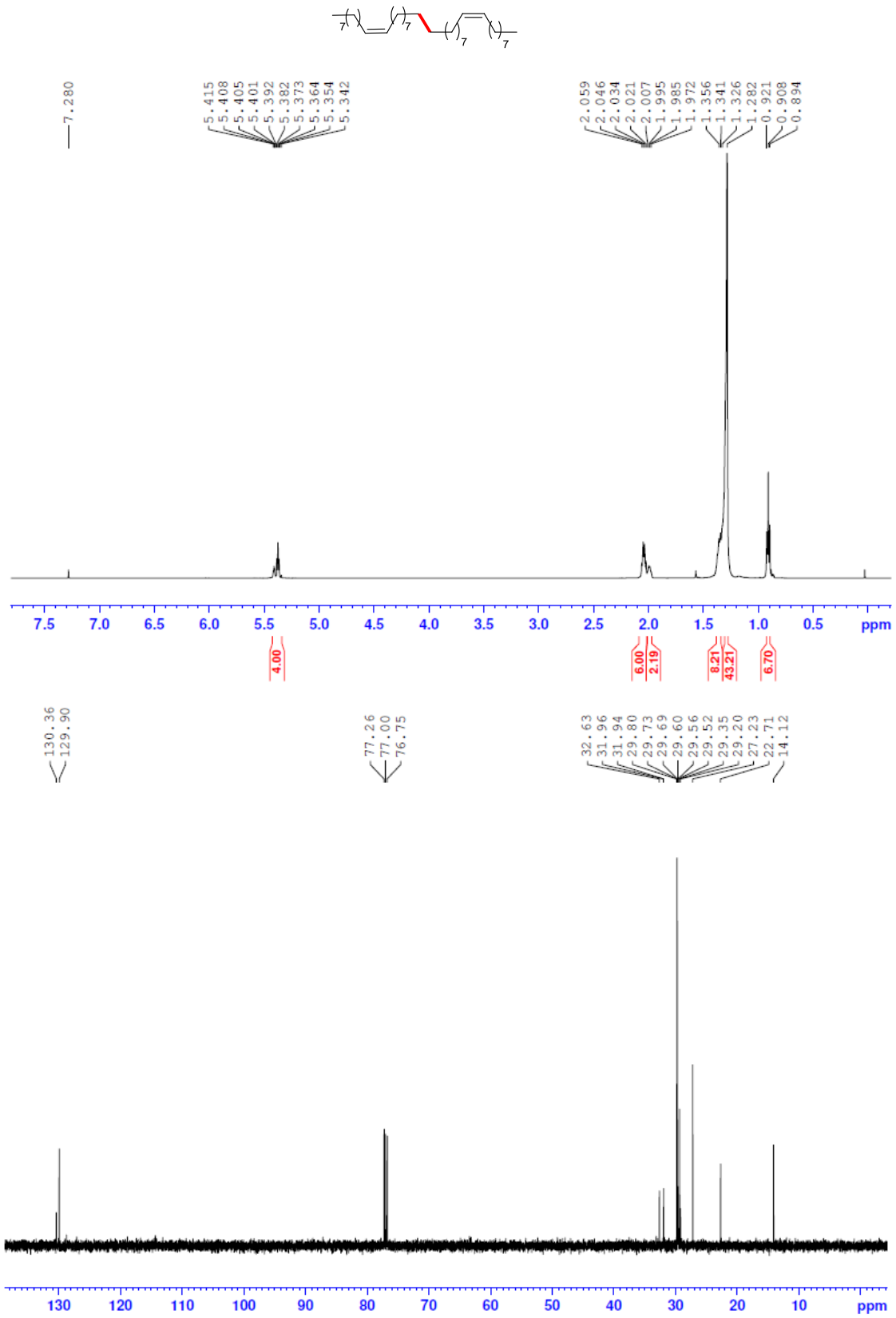
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5.405
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2.046
2.034
2.021
2.007
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1.985
1.972
1.356
1.341
1.326
1.282
0.921
0.908
0.894
ppm
4.00
6.00
2.19
8.21
43.21
6.70
130.36
129.90
77.26
77.00
76.75
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29.20
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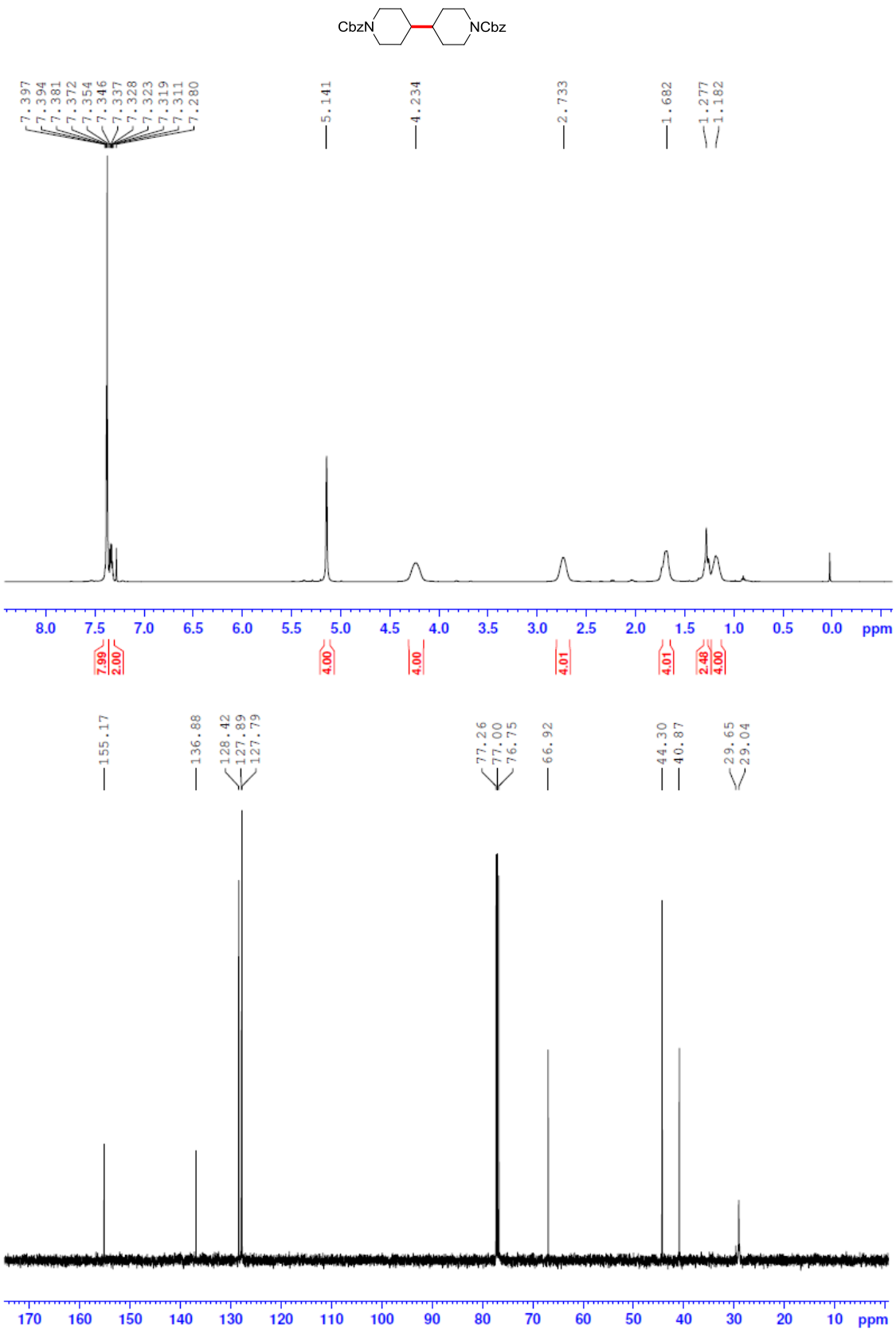
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7.280
5.141
4.234
2.733
1.682
1.277
1.182
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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ppm
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2.00
4.00
4.00
4.01
4.01
2.40
4.00
155.17
136.88
128.42
127.89
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77.26
77.00
76.75
66.92
44.30
40.87
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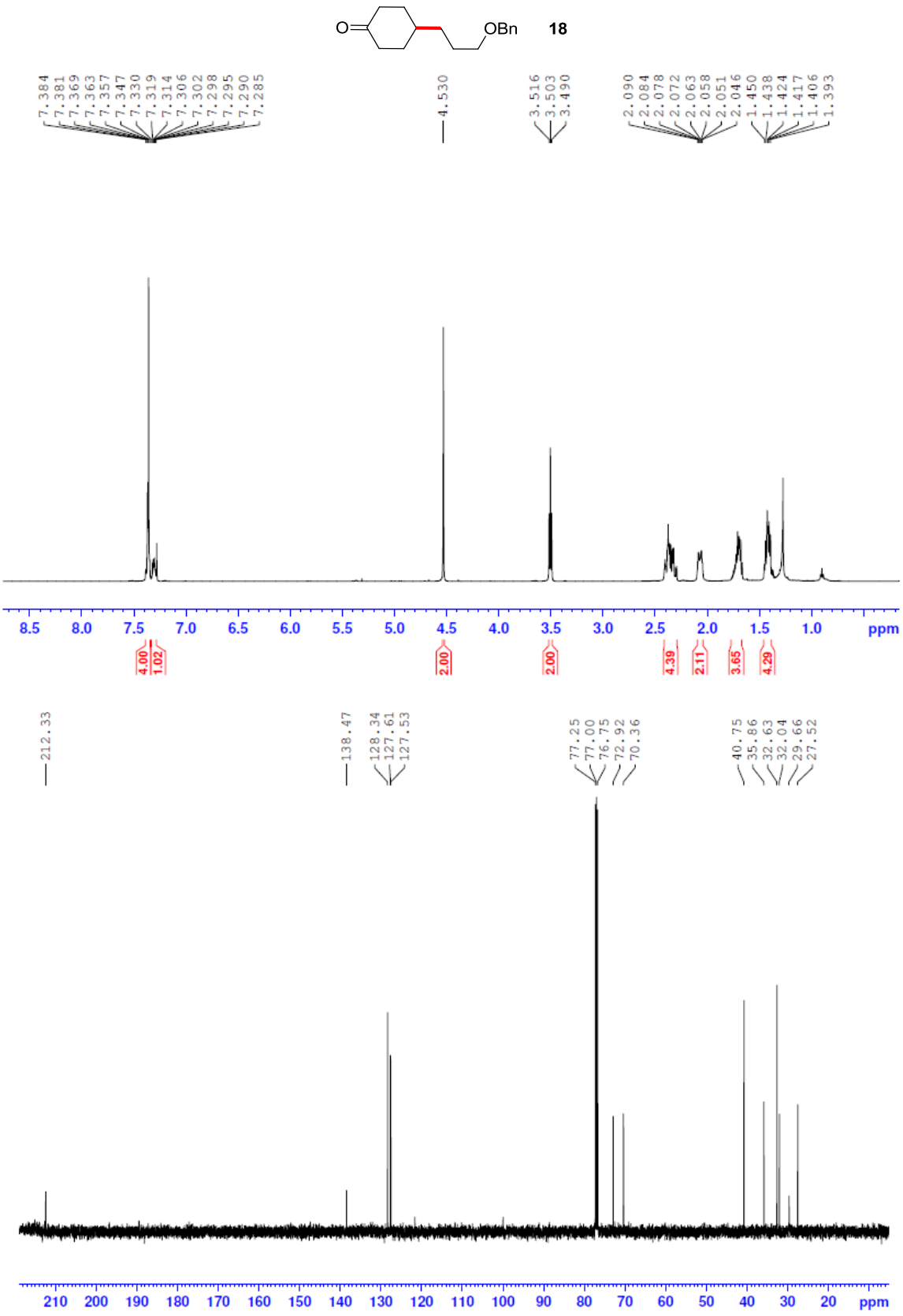
90
80
70
60
50
40
30
20
10
ppm


O
OBn
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7.319
7.314
7.306
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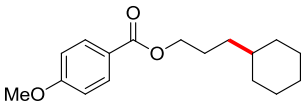
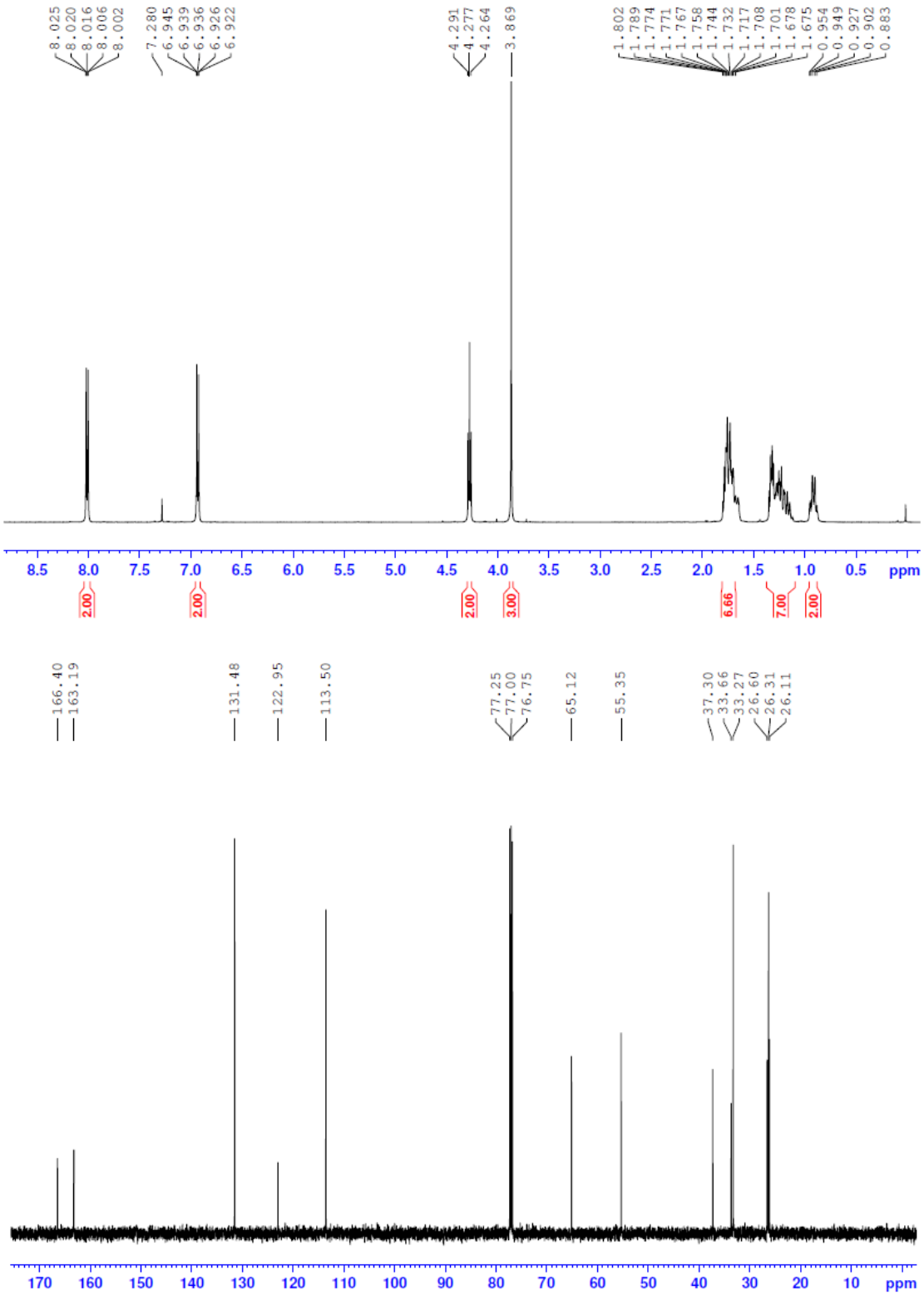
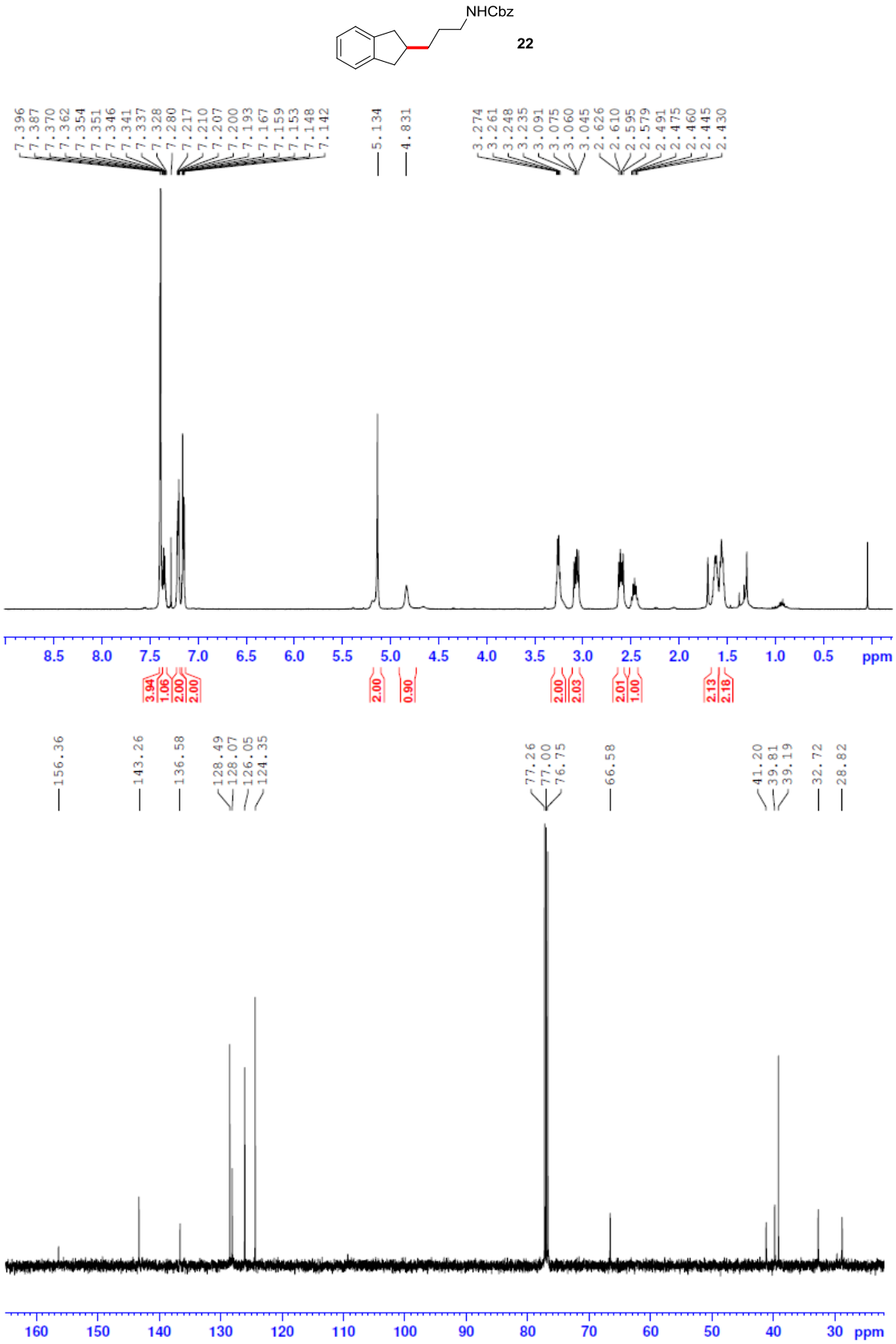
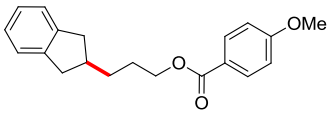
7.290
7.285
4.530
3.516
3.503
3.490
2.090
2.084
2.078
2.072
2.063
2.058
2.051
2.046
1.450
1.438
1.424
1.417
1.406
1.393
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.00
1.02
2.00
2.00
4.39
2.11
3.65
4.29
212.33
138.47
128.34
127.61
127.53
77.25
77.00
76.75
72.92
70.36
40.75
35.86
32.63
32.04
29.66
27.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



19



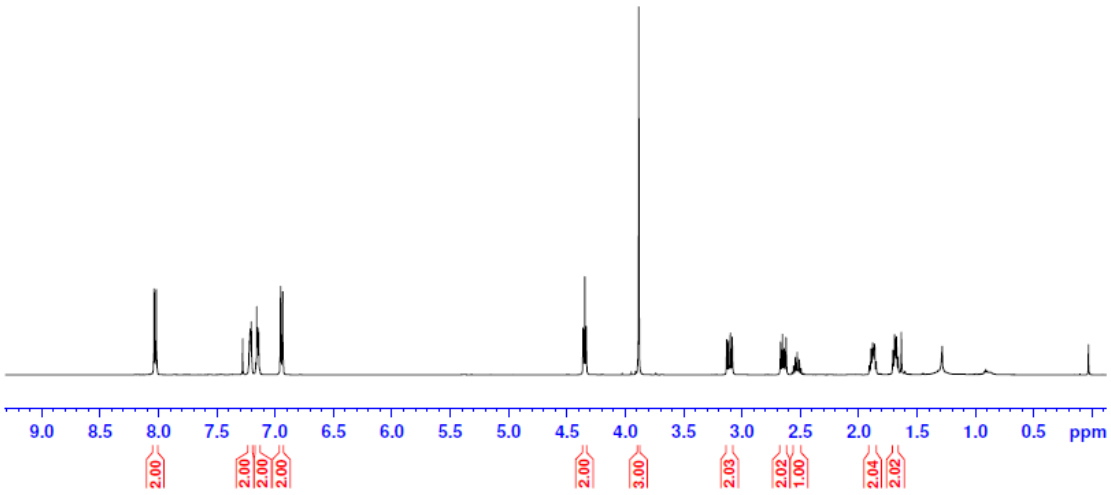

NHCbz
22
7.396
7.387
7.370
7.362
7.354
7.351
7.346
7.341
7.337
7.328
7.280
7.217
7.210
7.207
7.200
7.193
7.167
7.159
7.153
7.148
7.142
5.134
4.831
3.274
3.261
3.248
3.235
3.091
3.075
3.060
3.045
2.626
2.610
2.595
2.579
2.491
2.475
2.460
2.445
2.430
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.94
1.06
2.00
2.00
2.00
0.90
2.00
2.03
2.01
1.00
2.13
2.18
156.36
143.26
136.58
128.49
128.07
126.05
124.35
77.26
77.00
76.75
66.58
41.20
39.81
39.19
32.72
28.82
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm



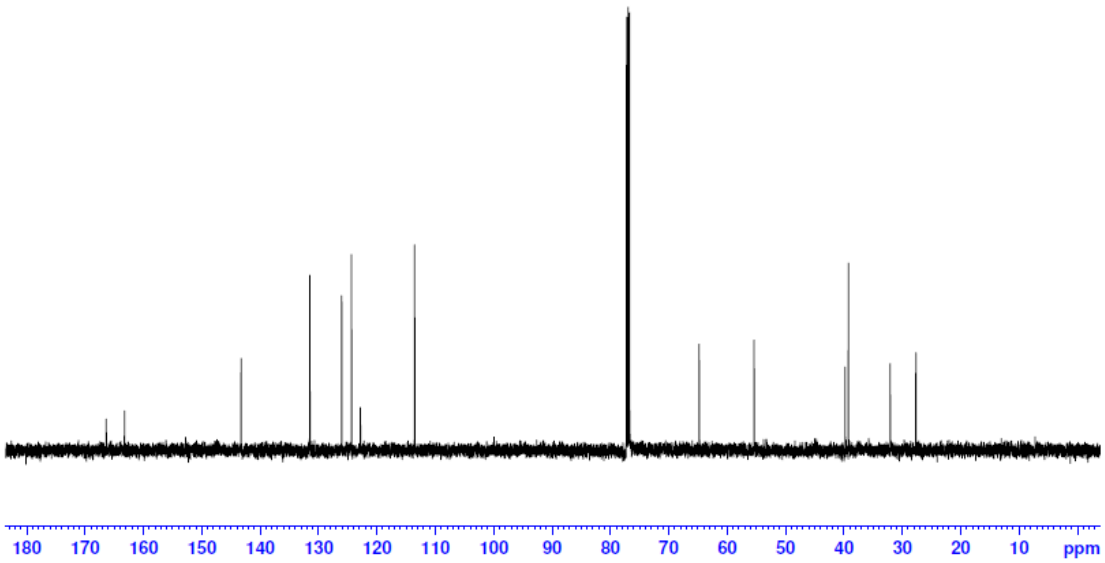
23

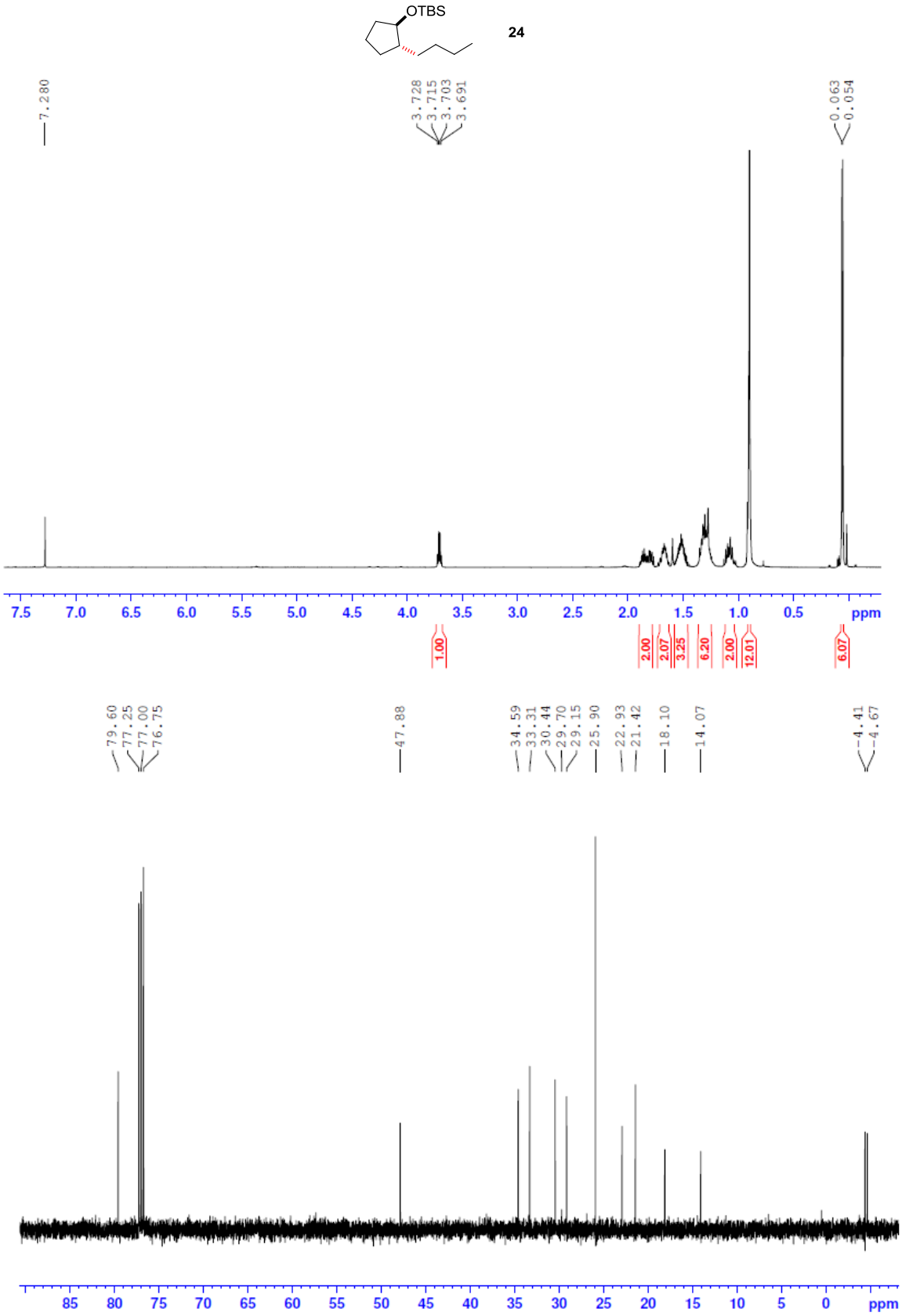
8.044
8.038
8.034
8.024
8.020
8.015
7.224
7.217
7.213
7.207
7.199
7.167
7.159
7.153
7.148
7.142
6.961
6.955
6.952
6.941
6.938

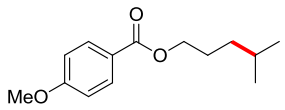
4.362
4.348
4.335
3.885
3.130
3.114
3.099
3.084
2.670
2.653
2.639
2.623
2.557
2.542
2.526
2.511
2.495
1.909
1.895
1.880
1.874
1.864
1.850
1.707
1.696
1.692
1.682
1.675
1.661



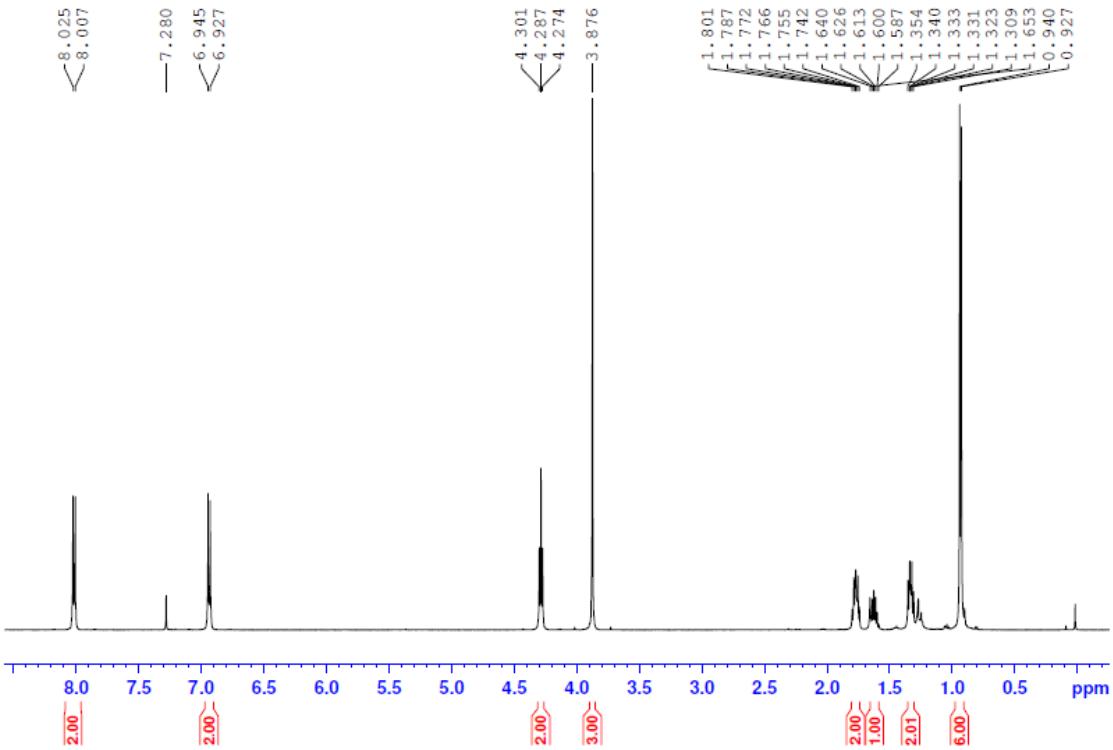
166.40
163.26
143.30
131.53
126.08
124.37
122.86
113.56
77.25
77.00
76.75
64.79
55.39
39.84
39.25
32.09
27.69

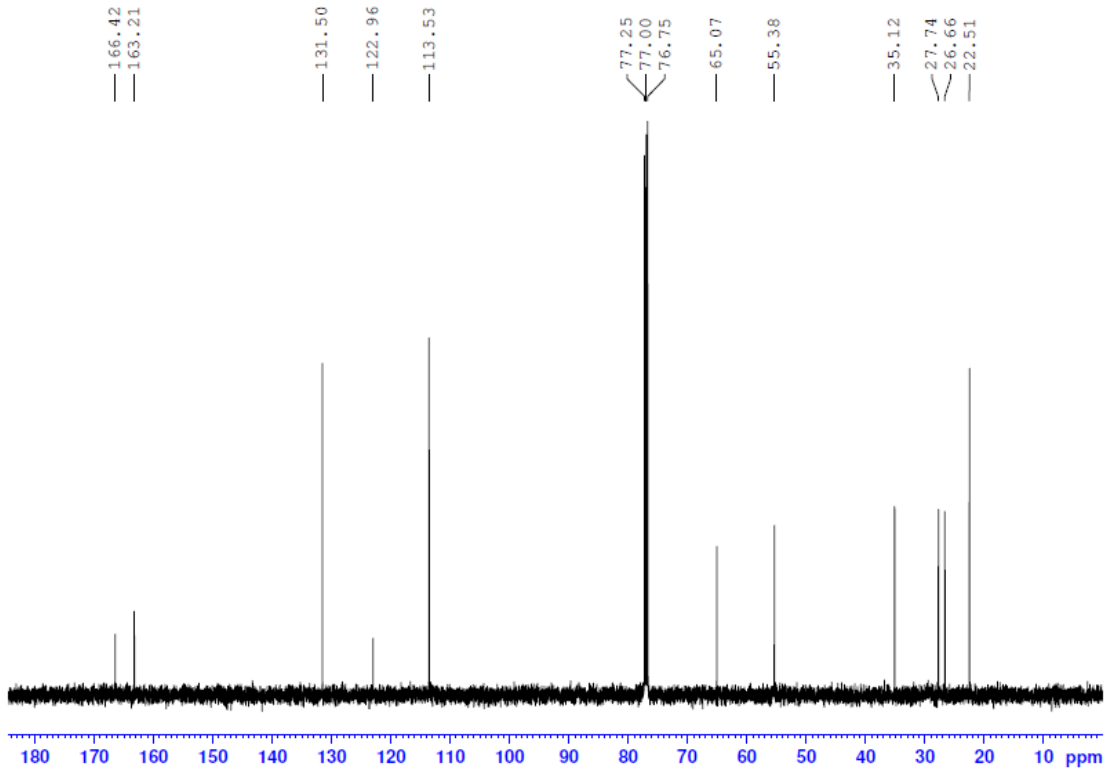


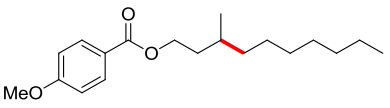



O
O
MeO

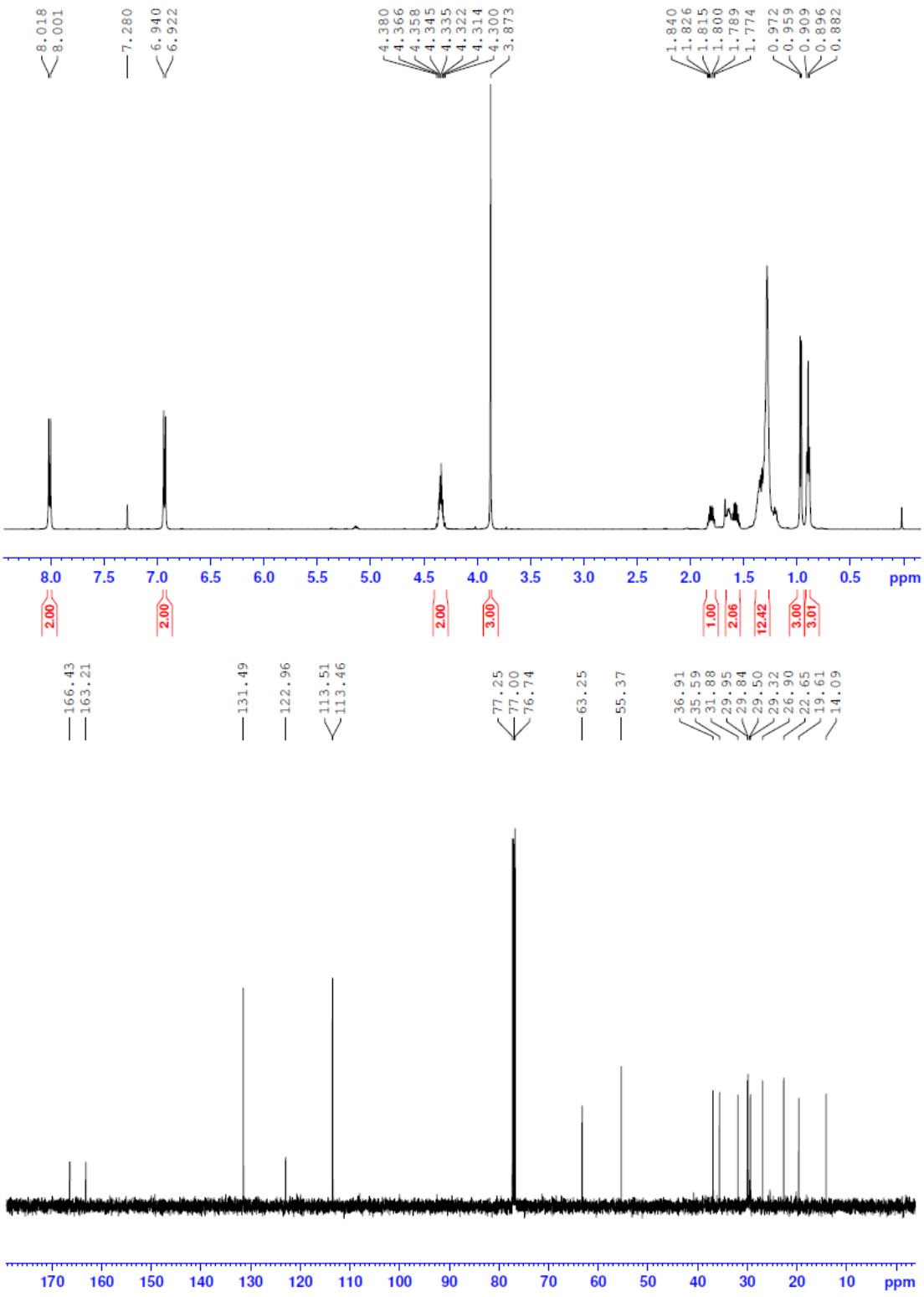
25


8.025
8.007
7.280
6.945
6.927
4.301
4.287
4.274
3.876
1.801
1.787
1.772
1.766
1.755
1.742
1.640
1.626
1.613
1.600
1.587
1.354
1.340
1.333
1.331
1.323
1.309
1.653
0.940
0.927
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
2.00
2.00
2.00
3.00
2.00
1.00
2.01
6.00


166.42
163.21
131.50
122.96
113.53
77.25
77.00
76.75
65.07
55.38
35.12
27.74
26.66
22.51
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
O
MeO

26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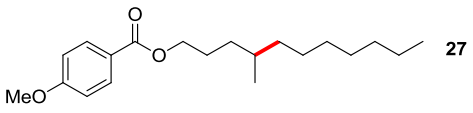
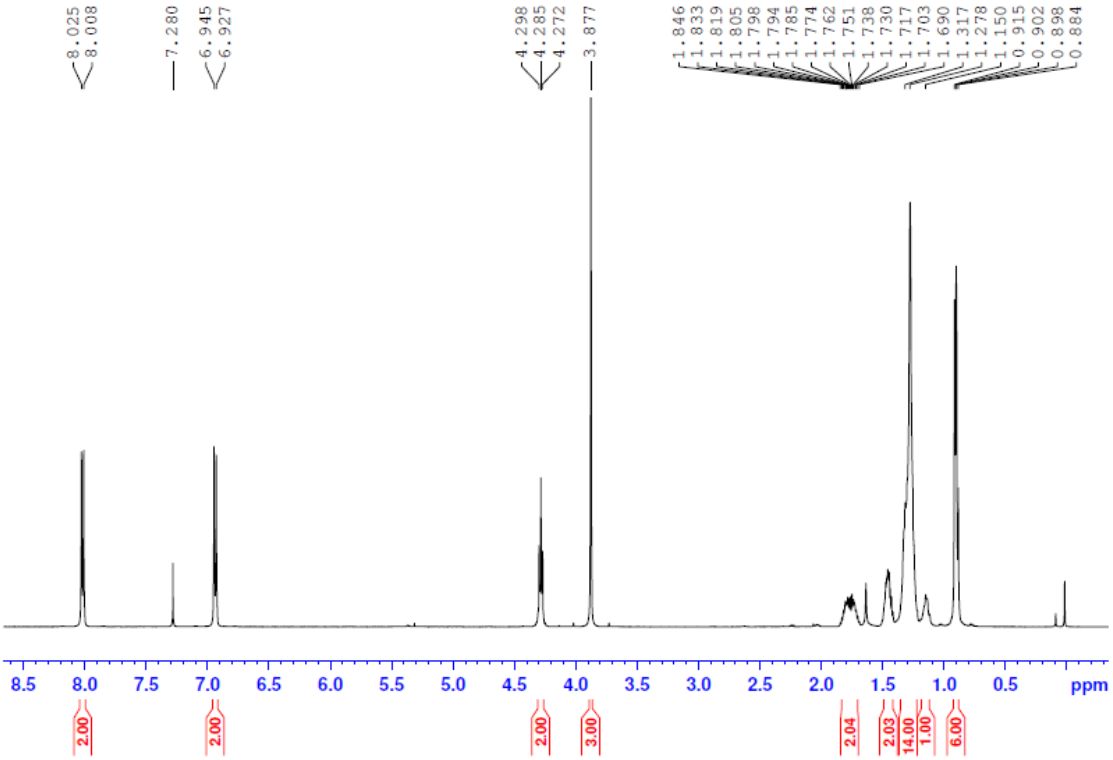
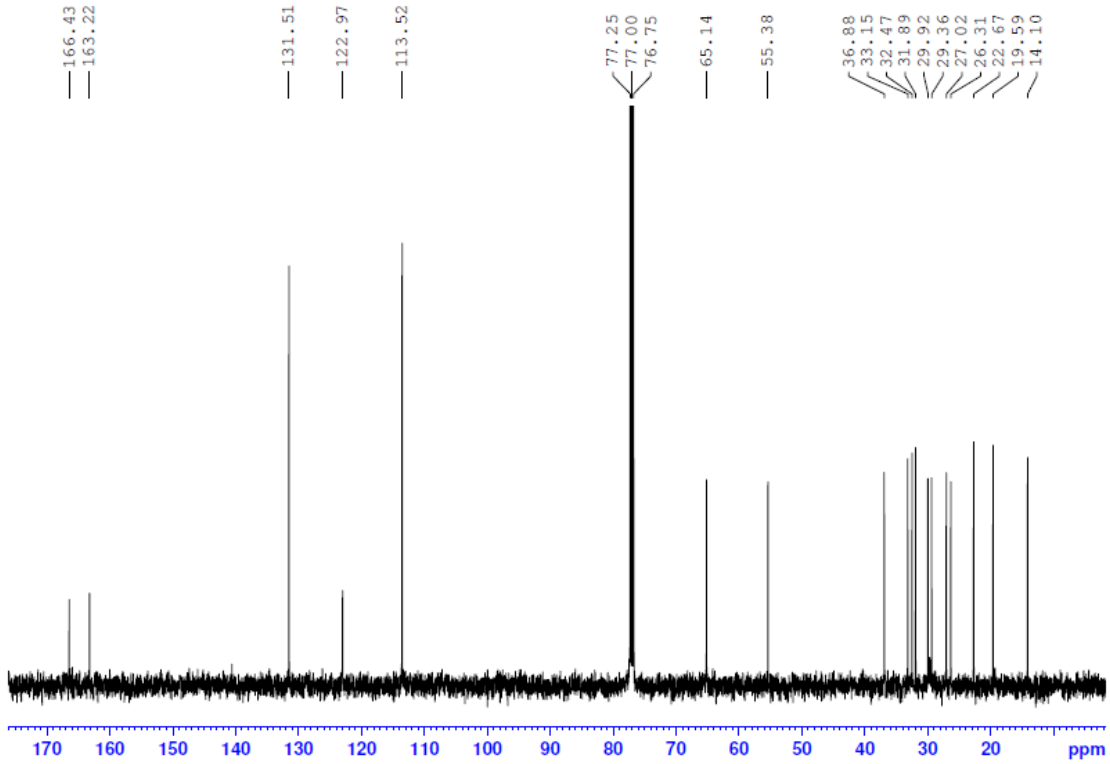
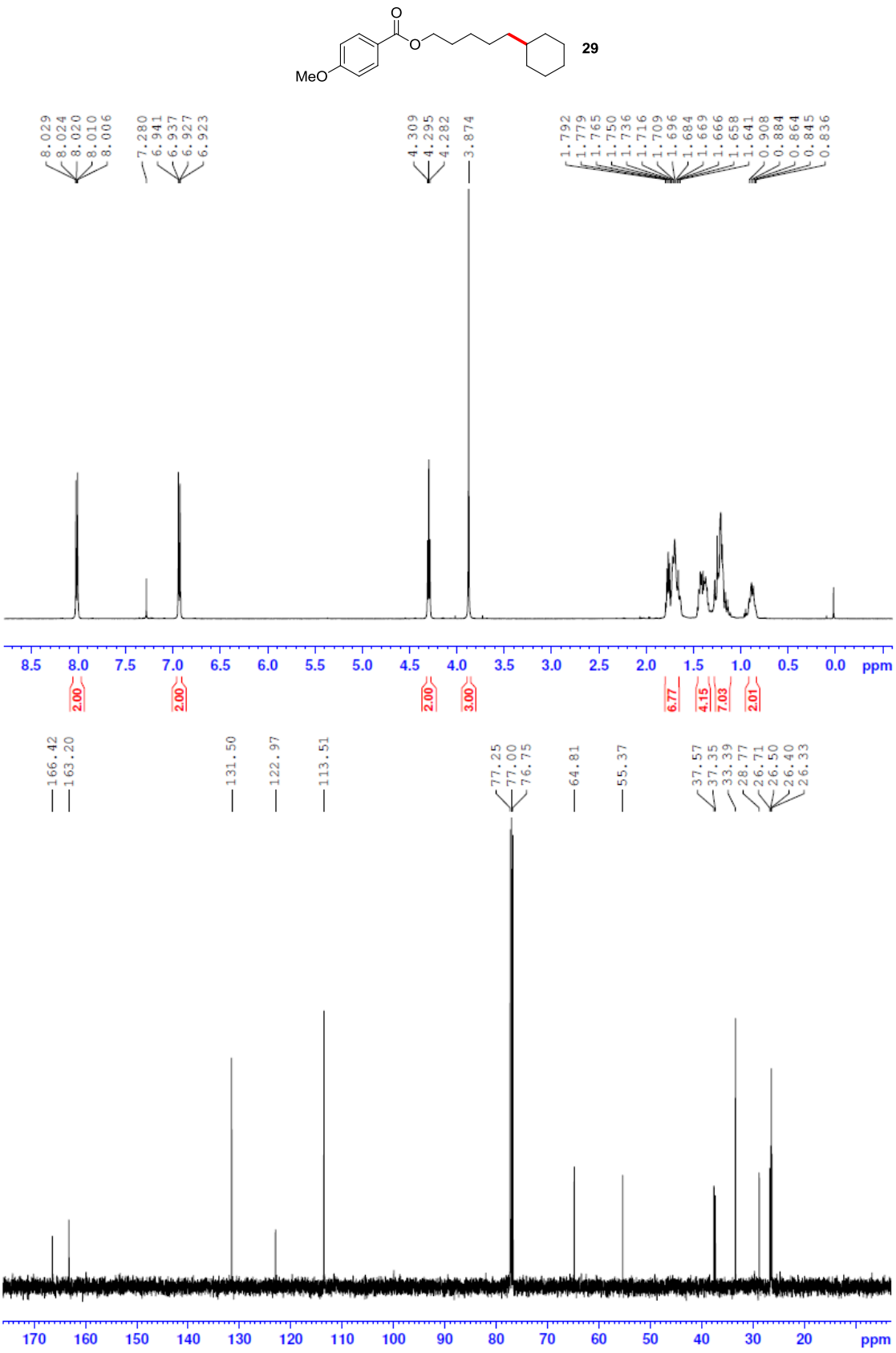
8.001
7.280
6.940
6.922
4.380
4.366
4.358
4.345
4.335
4.322
4.314
4.300
3.873
1.840
1.826
1.815
1.800
1.789
1.774
0.972
0.959
0.909
0.896
0.882
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.00
2.00
3.00
1.00
2.06
12.42
3.00
3.01
166.43
163.21
131.49
122.96
113.51
113.46
77.25
77.00
76.74
63.25
55.37
36.91
35.59
31.88
29.95
29.84
29.50
29.32
26.90
22.65
19.61
14.09
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

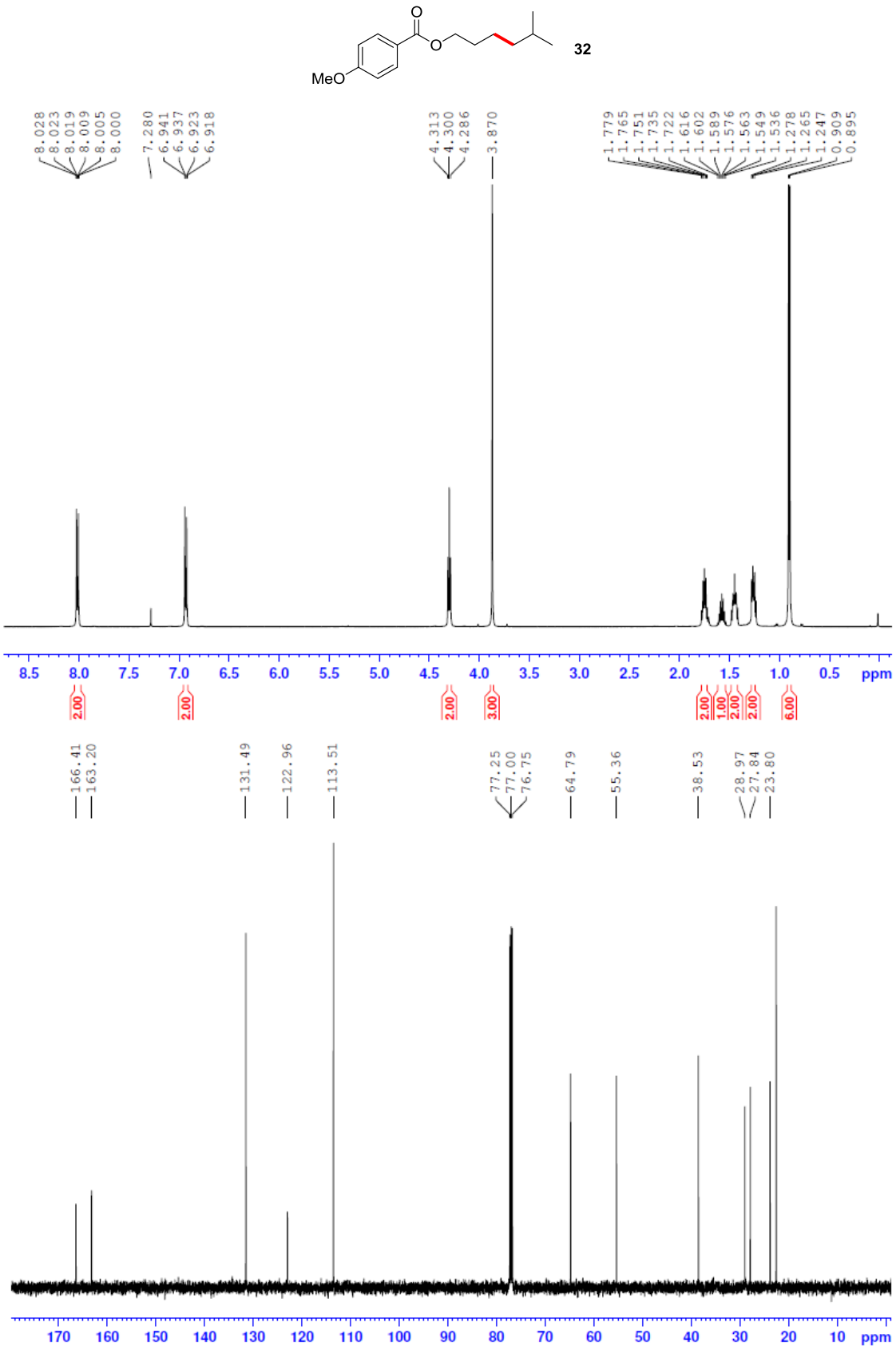


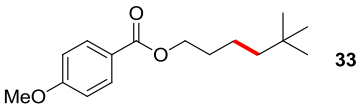
27



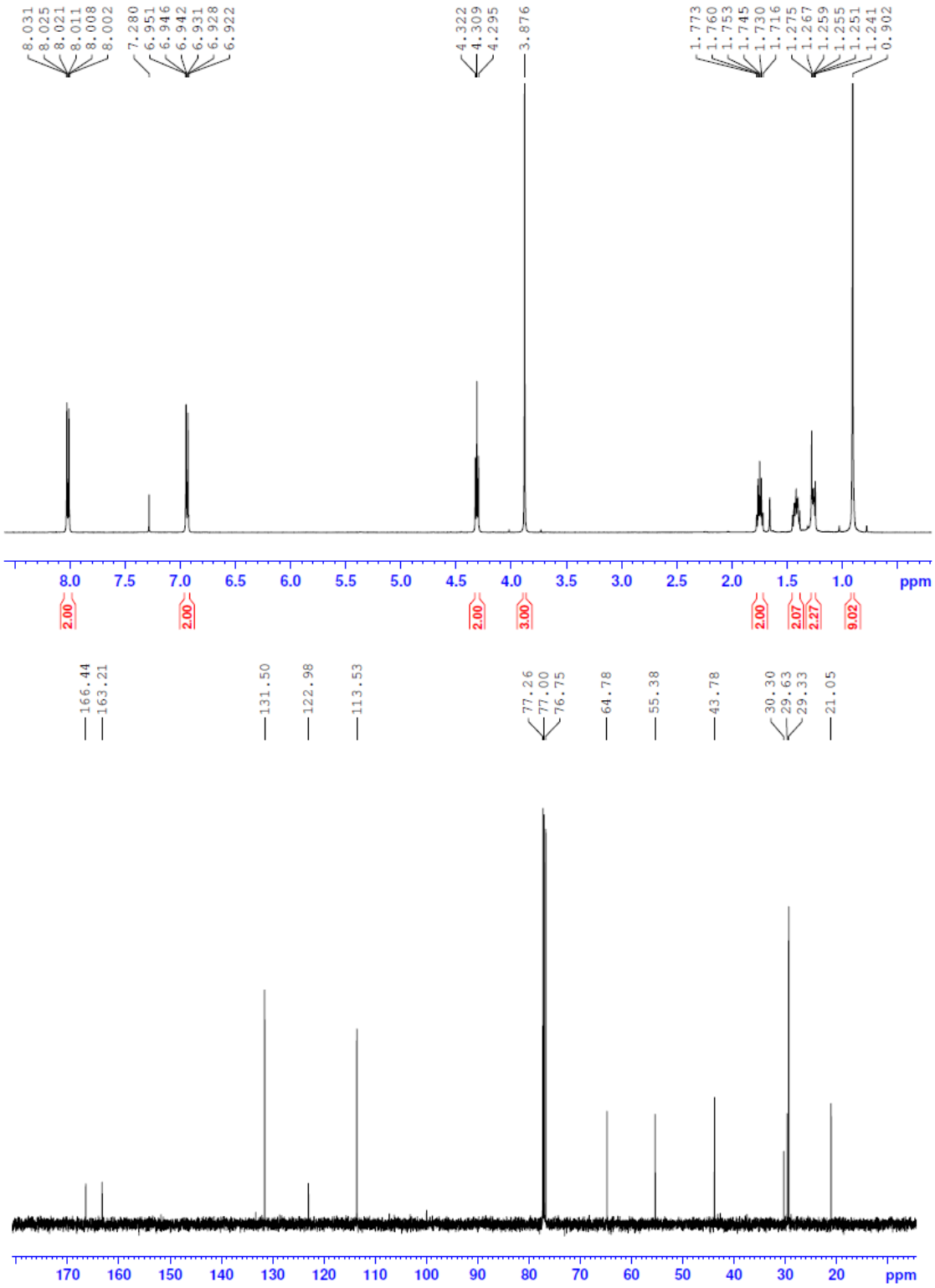


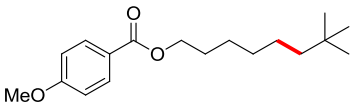



MeO
O
O
32
8.028
8.023
8.019
8.009
8.005
8.000
7.280
6.941
6.937
6.923
6.918
4.313
4.300
4.286
3.870
1.779
1.765
1.751
1.735
1.722
1.616
1.602
1.589
1.576
1.563
1.549
1.536
1.278
1.265
1.247
0.909
0.895
ppm
2.00
2.00
2.00
3.00
2.00
1.00
2.00
2.00
6.00
166.41
163.20
131.49
122.96
113.51
77.25
77.00
76.75
64.79
55.36
38.53
28.97
27.84
23.80
ppm

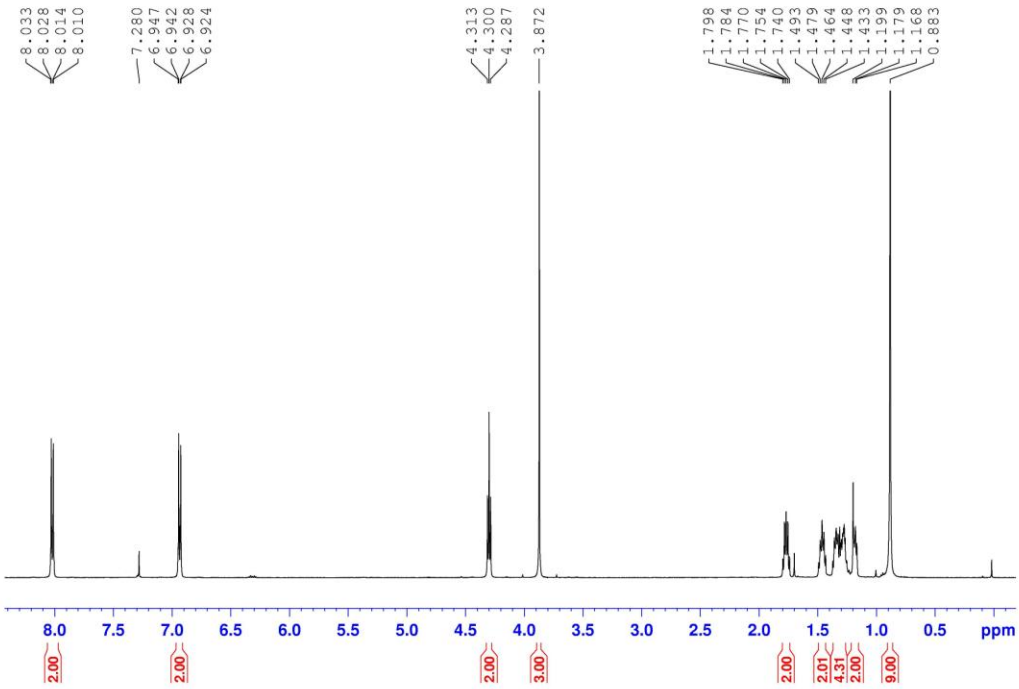


33




O
O
MeO

34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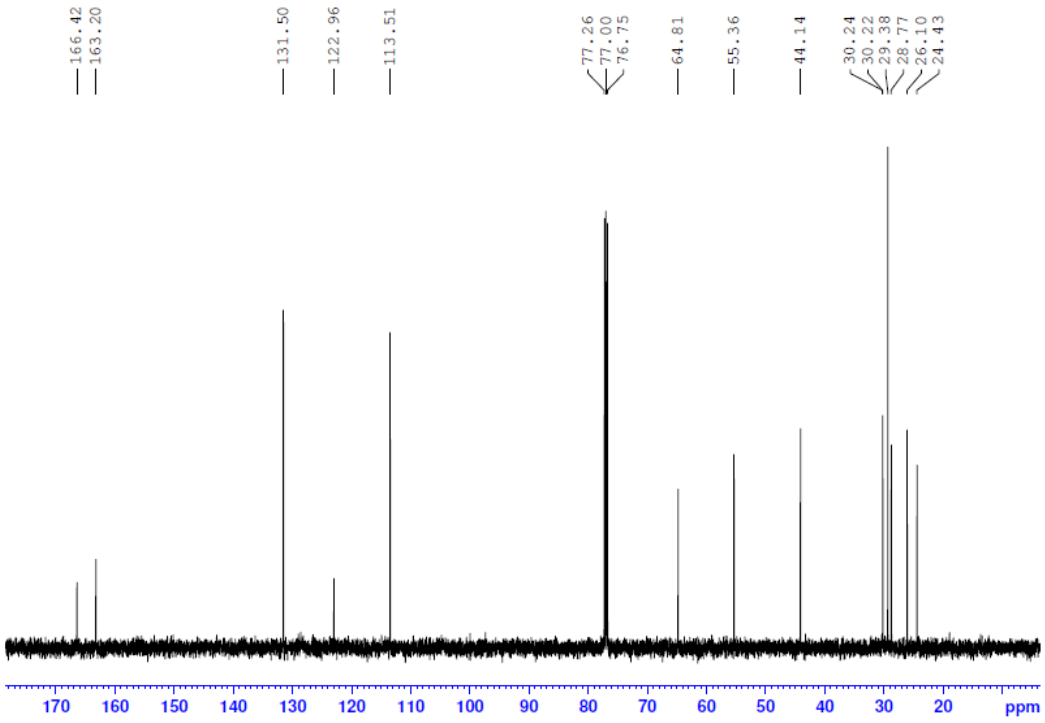
8.028
8.014
8.010
7.280
6.947
6.942
6.928
6.924
4.313
4.300
4.287
3.872
1.798
1.784
1.770
1.754
1.740
1.493
1.479
1.464
1.448
1.433
1.199
1.179
1.168
0.883
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.00
2.00
3.00
2.00
2.01
4.31
2.00
9.00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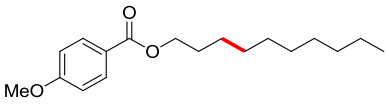
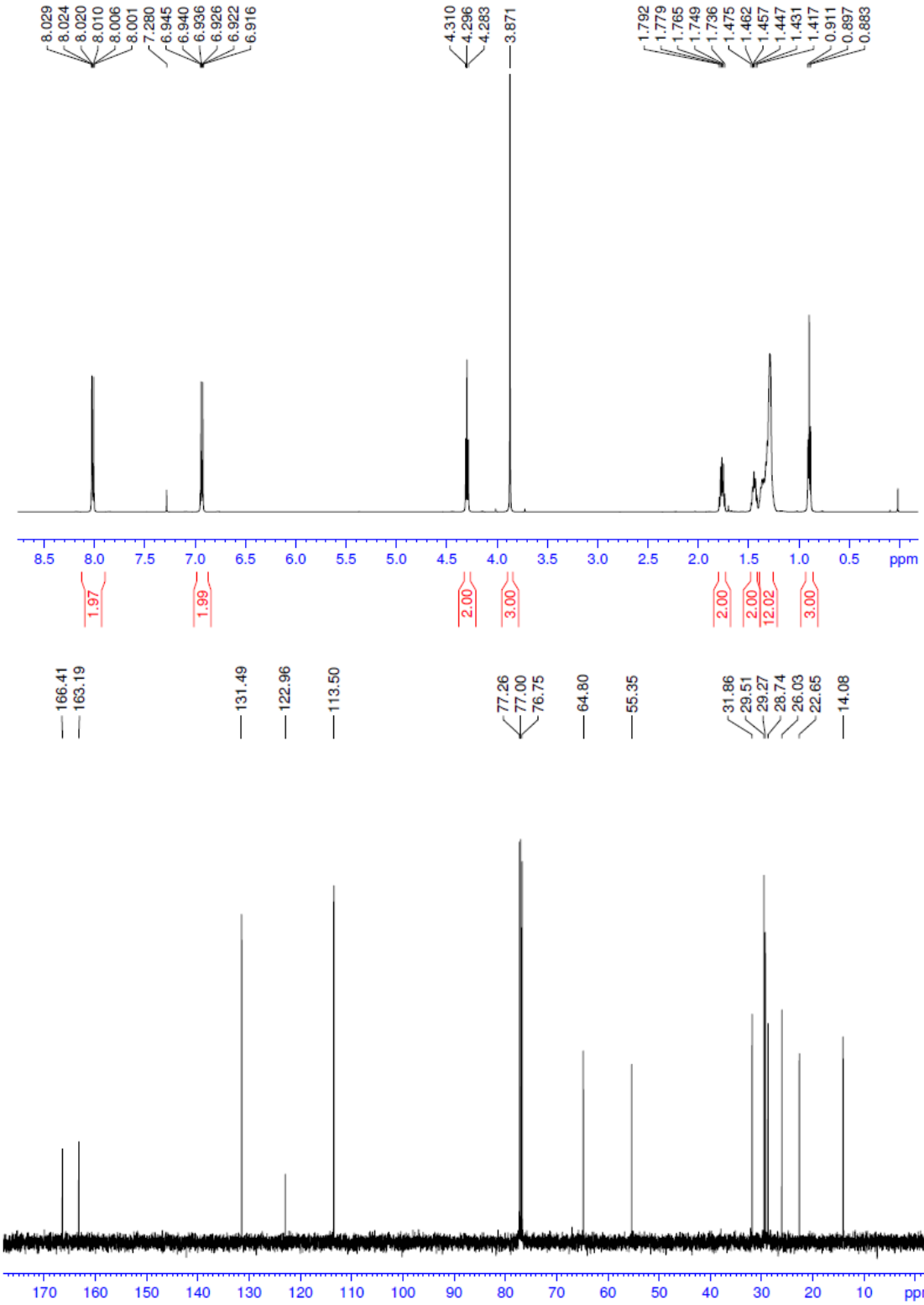
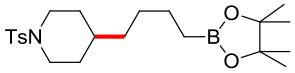
163.20
131.50
122.96
113.51
77.26
77.00
76.75
64.81
55.36
44.14
30.24
30.22
29.38
28.77
26.10
24.43
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

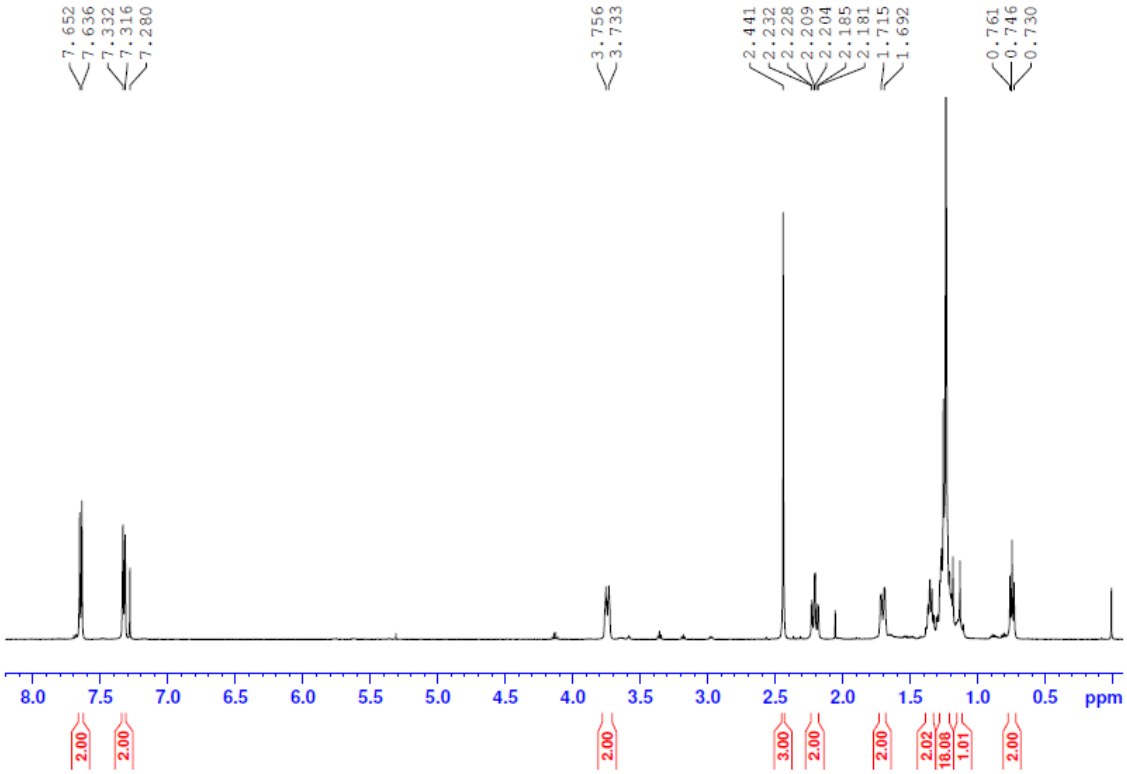

O
O
MeO

30


8.029
8.024
8.020
8.010
8.006
8.001
7.280
6.945
6.940
6.936
6.926
6.922
6.916
4.310
4.296
4.283
3.871
1.792
1.779
1.765
1.749
1.736
1.475
1.462
1.457
1.447
1.431
1.417
0.911
0.897
0.883
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
1.97
1.99
2.00
3.00
2.00
2.00
12.02
3.00
166.41
163.19
131.49
122.96
113.50
77.26
77.00
76.75
64.80
55.35
31.86
29.51
29.27
28.74
26.03
22.65
14.08
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


TsN
B
O
O

39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7.332
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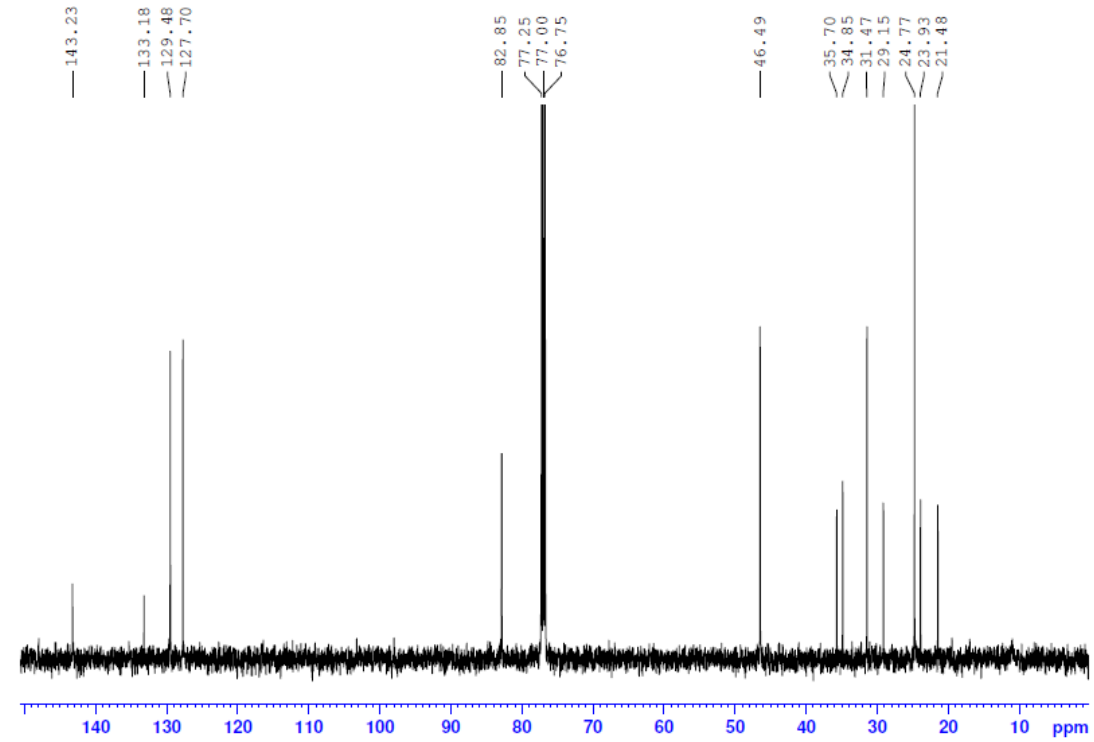
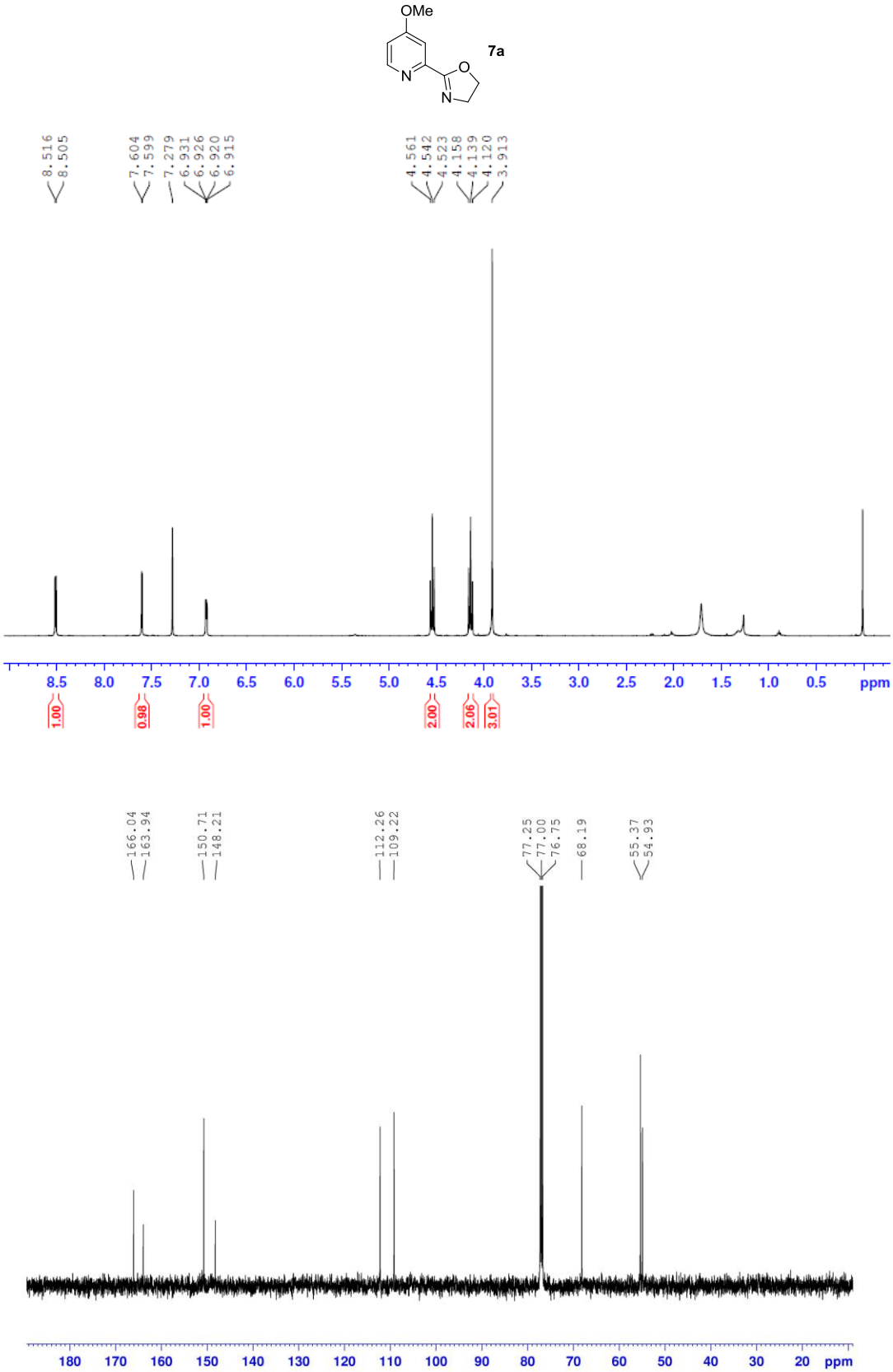
7.280
3.756
3.733
2.441
2.232
2.228
2.209
2.204
2.185
2.181
1.715
1.692
0.761
0.746
0.730
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.00
2.00
3.00
2.00
2.00
2.02
16.08
1.01
2.00


143.23
133.18
129.48
127.70
82.85
77.25
77.00
76.75
46.49
35.70
34.85
31.47
29.15
24.77
23.93
21.48
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OMe
7a
N
O
N
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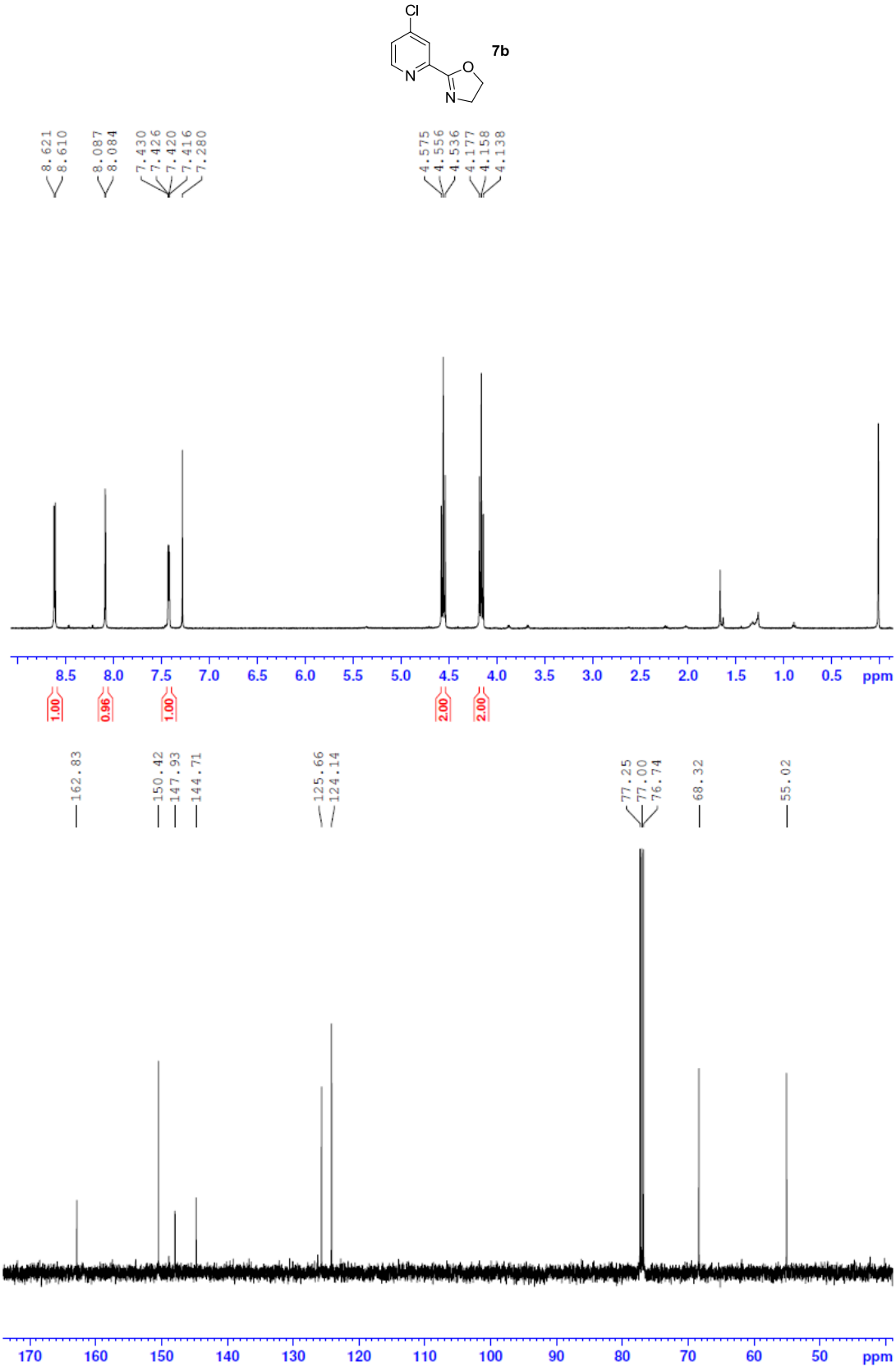
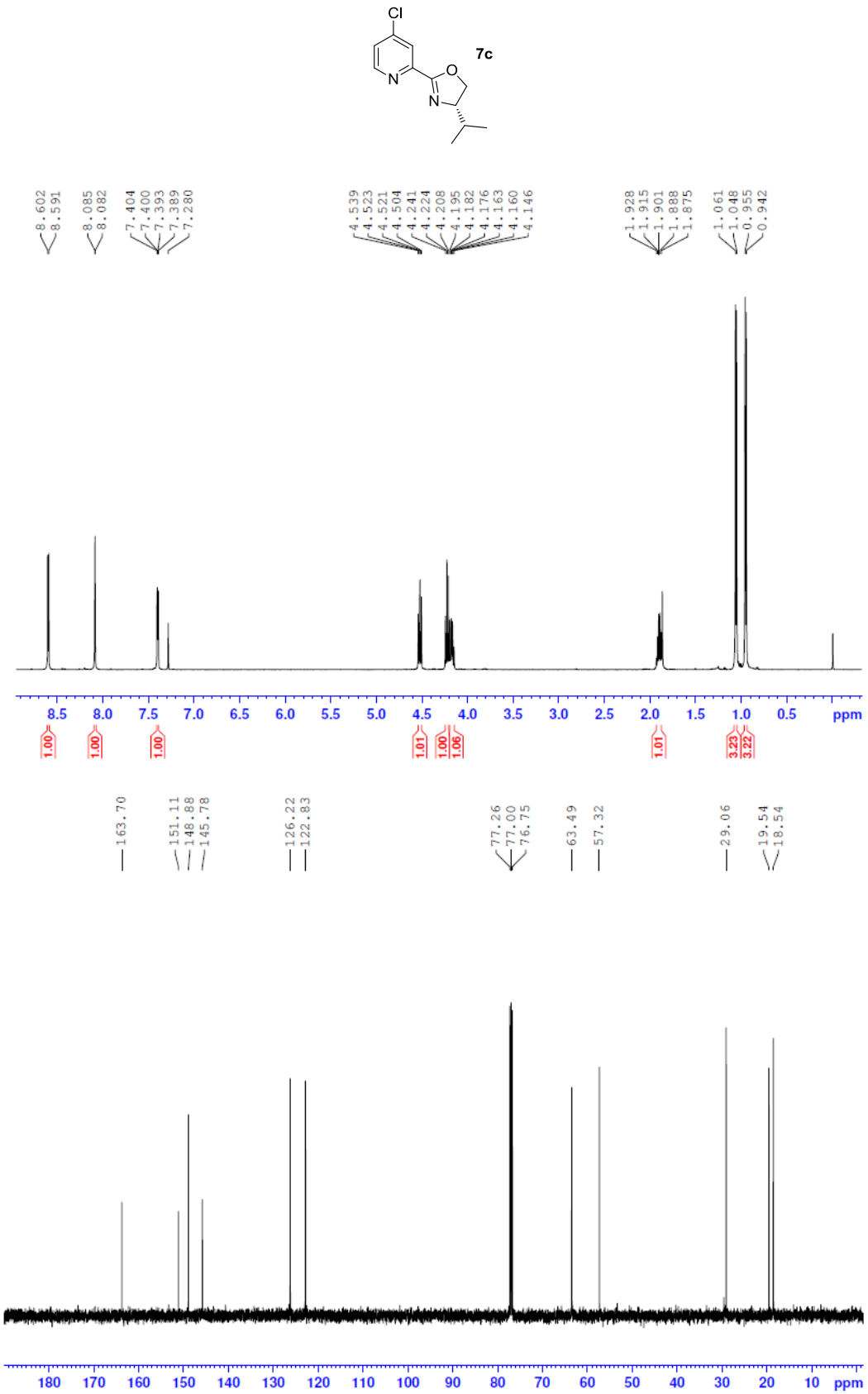
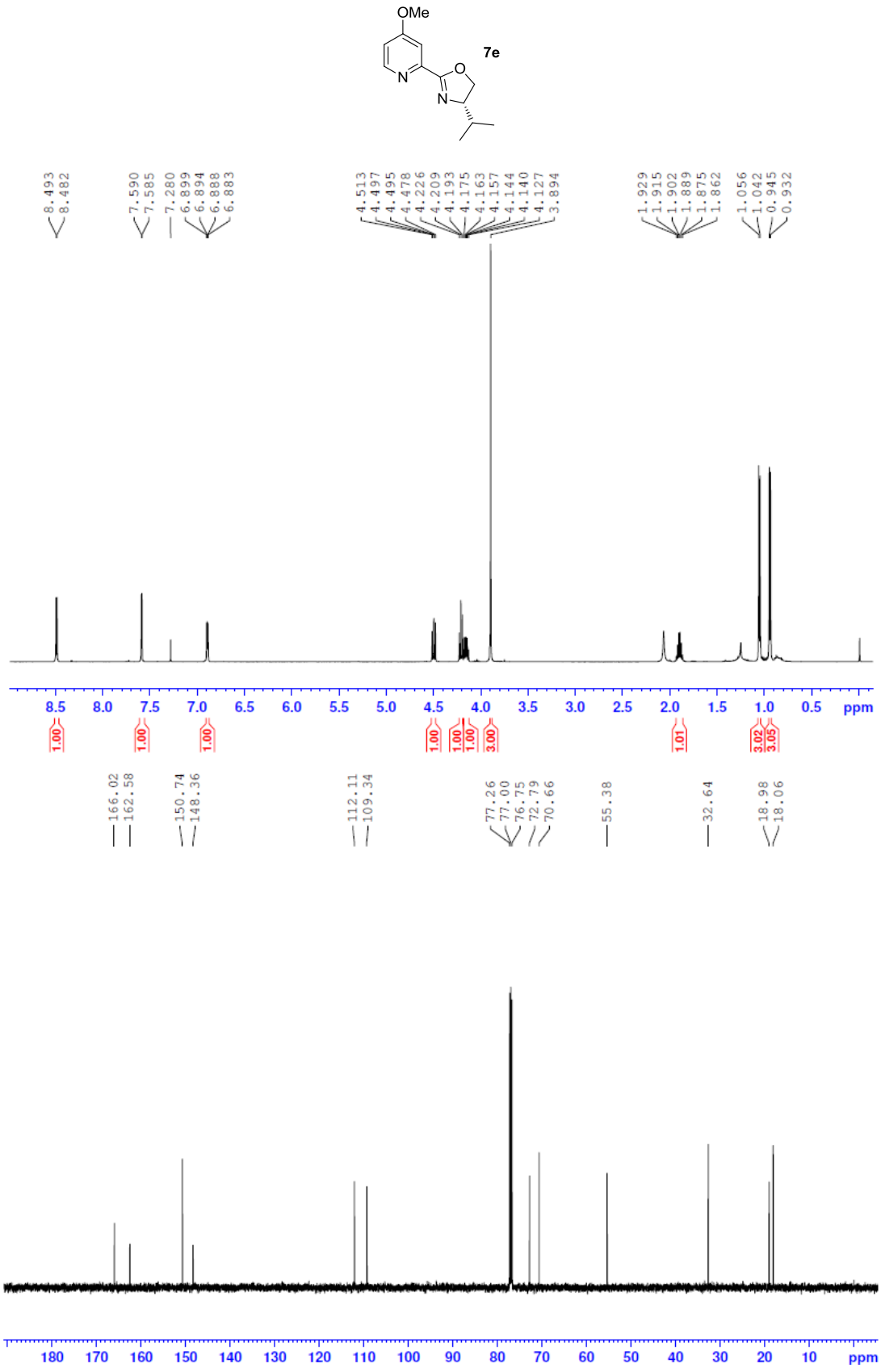
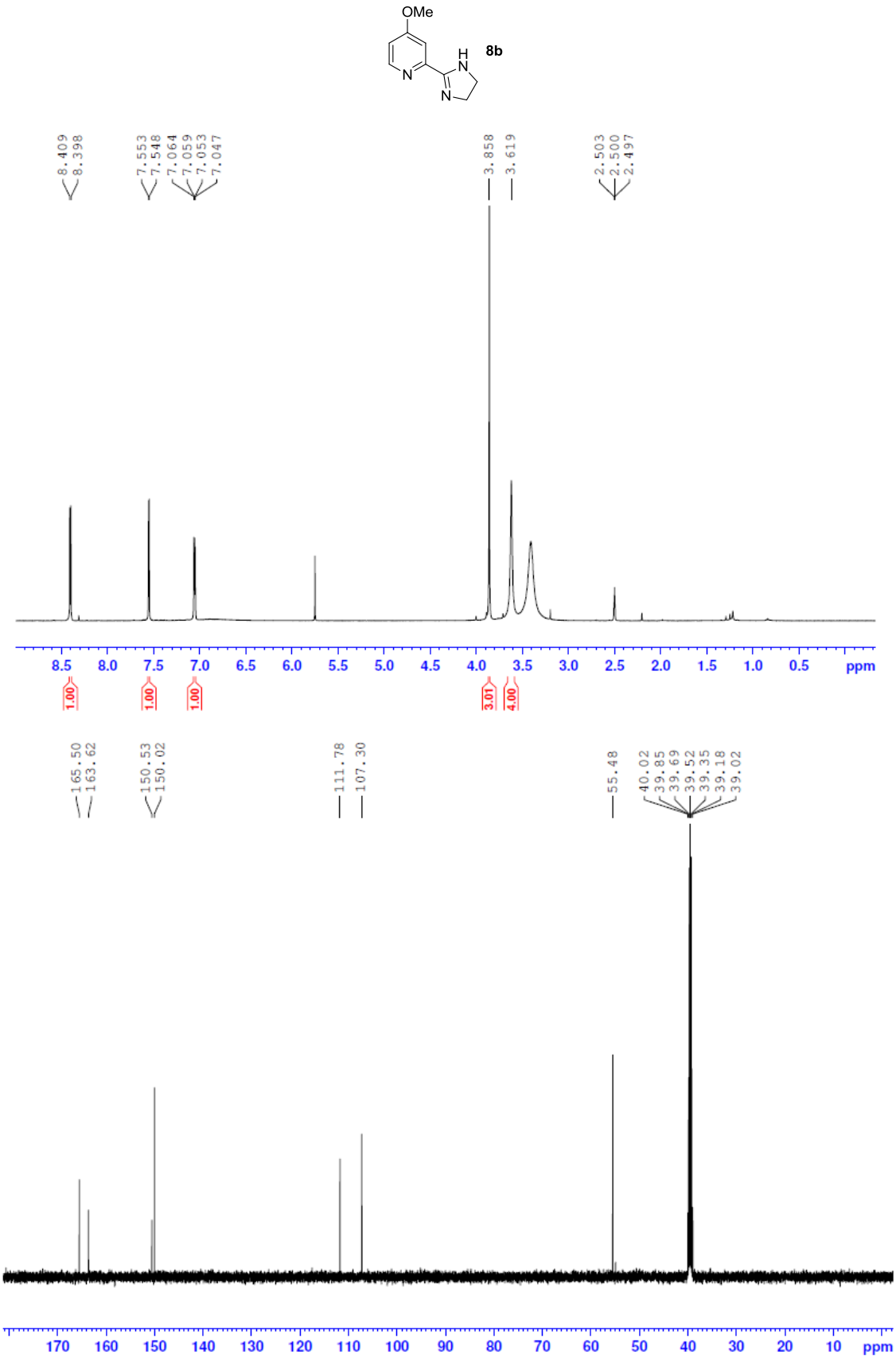
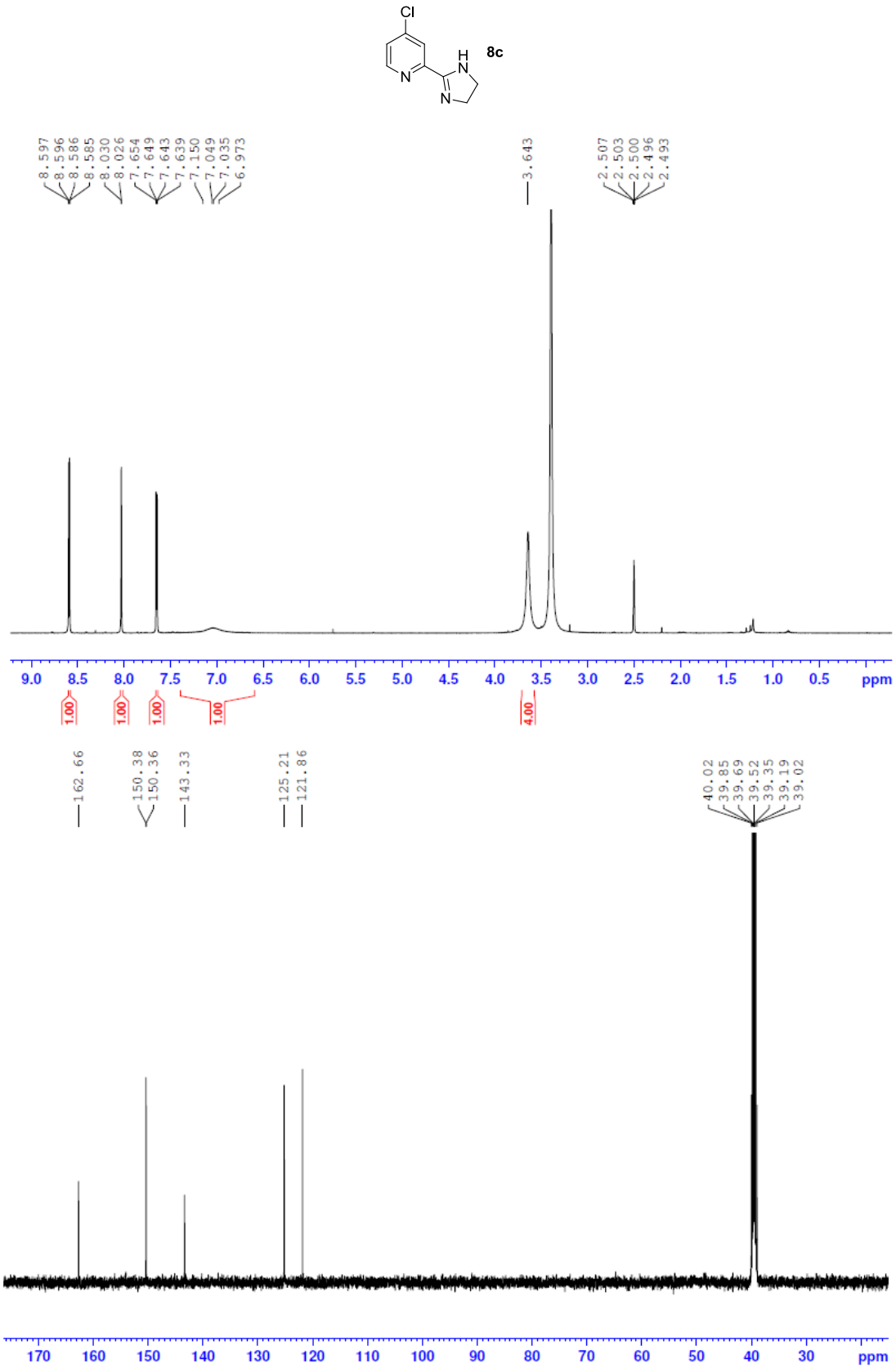
8.505
7.604
7.599
7.279
6.931
6.926
6.920
6.915
4.561
4.542
4.523
4.158
4.139
4.120
3.913
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.98
1.00
2.00
2.06
3.01
166.04
163.94
150.71
148.21
112.26
109.22
77.25
77.00
76.75
68.19
55.37
54.93
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

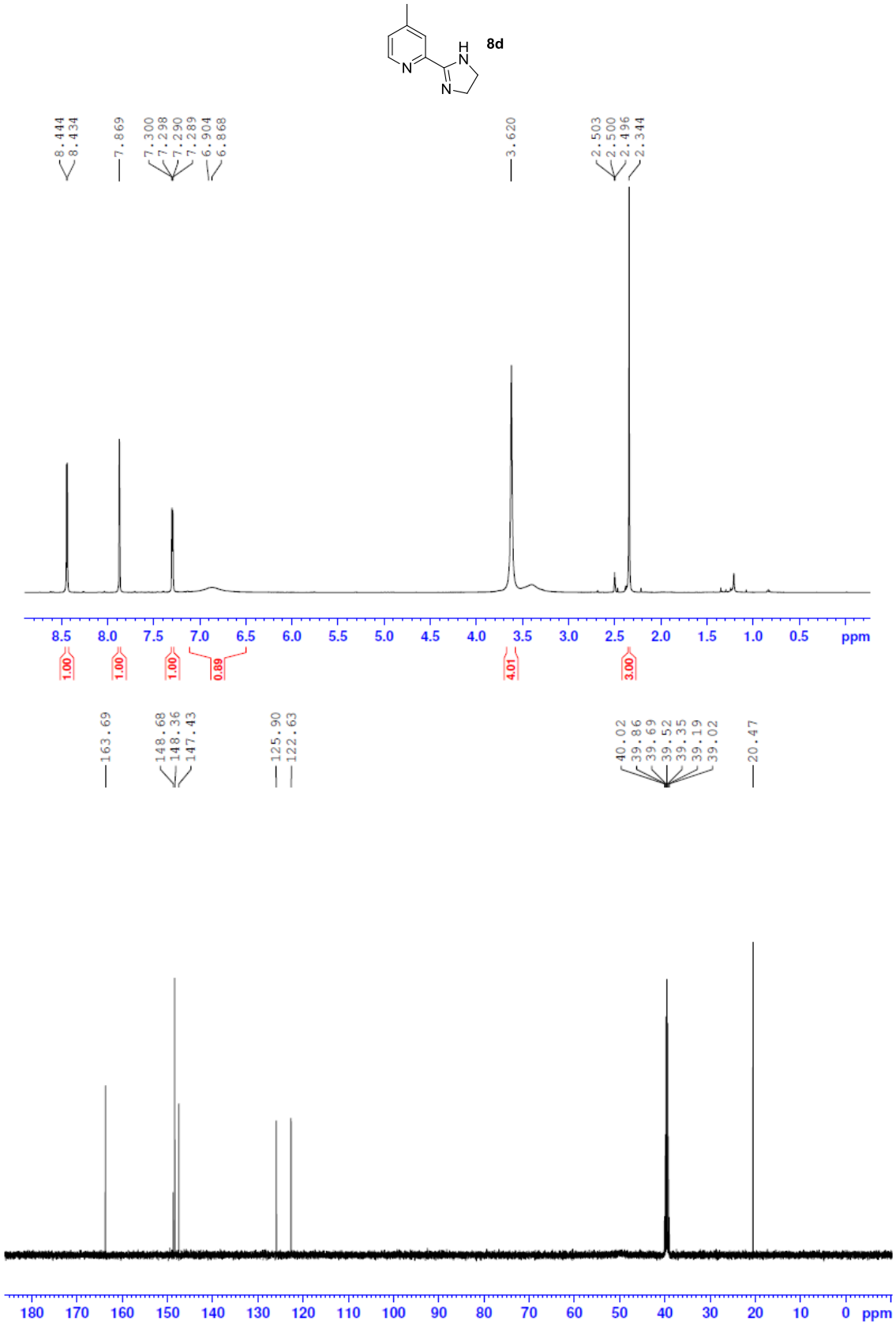


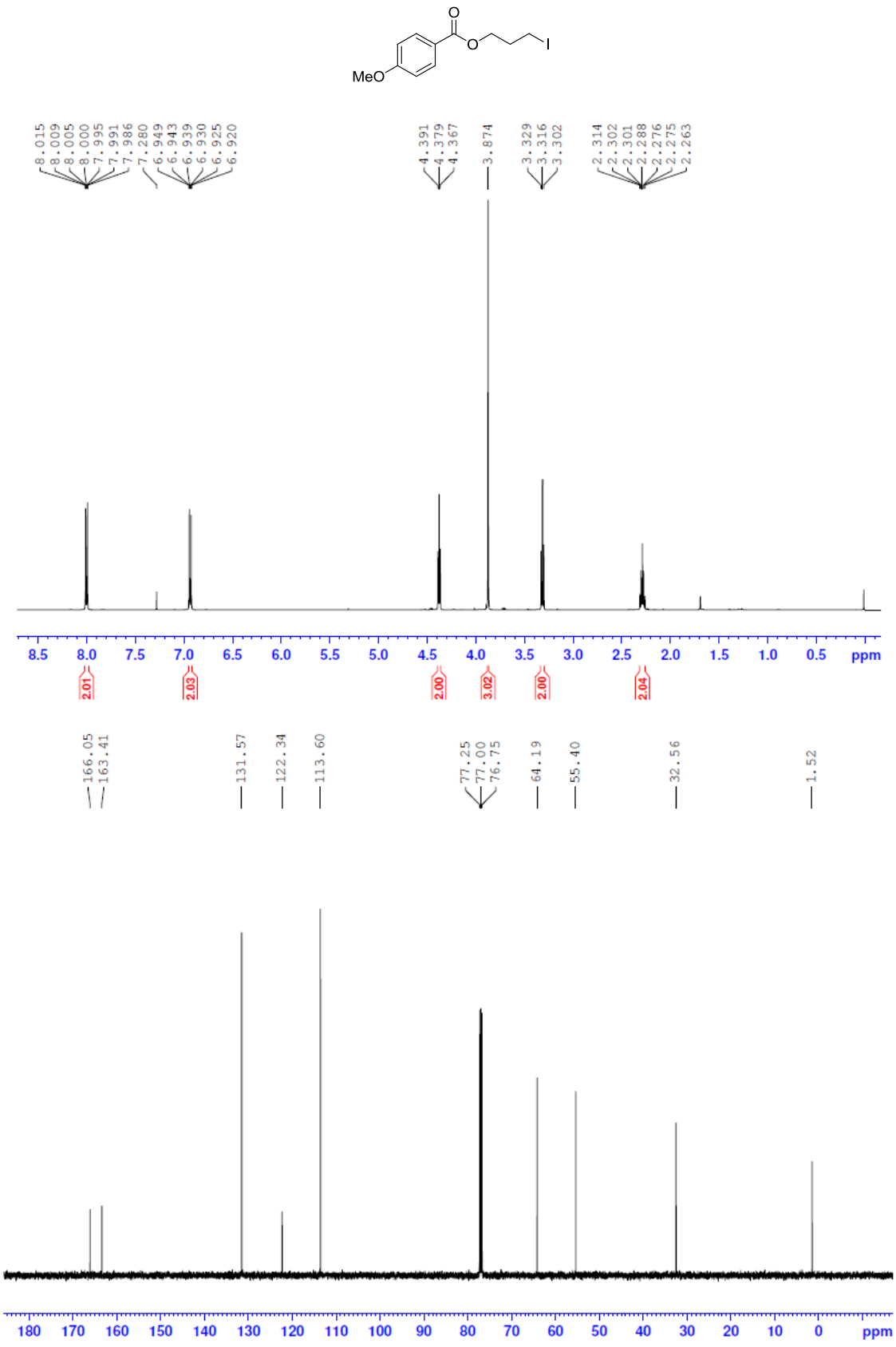











O
O
I
MeO
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8.009
8.005
8.000
7.995
7.991
7.986
7.280
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6.939
6.930
6.925
6.920
4.391
4.379
4.367
3.874
3.329
3.316
3.302
2.314
2.302
2.301
2.288
2.276
2.275
2.263
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
2.03
2.00
3.02
2.00
2.04
166.05
163.41
131.57
122.34
113.60
77.25
77.00
76.75
64.19
55.40
32.56
1.52
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140
130
120
110
100
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70
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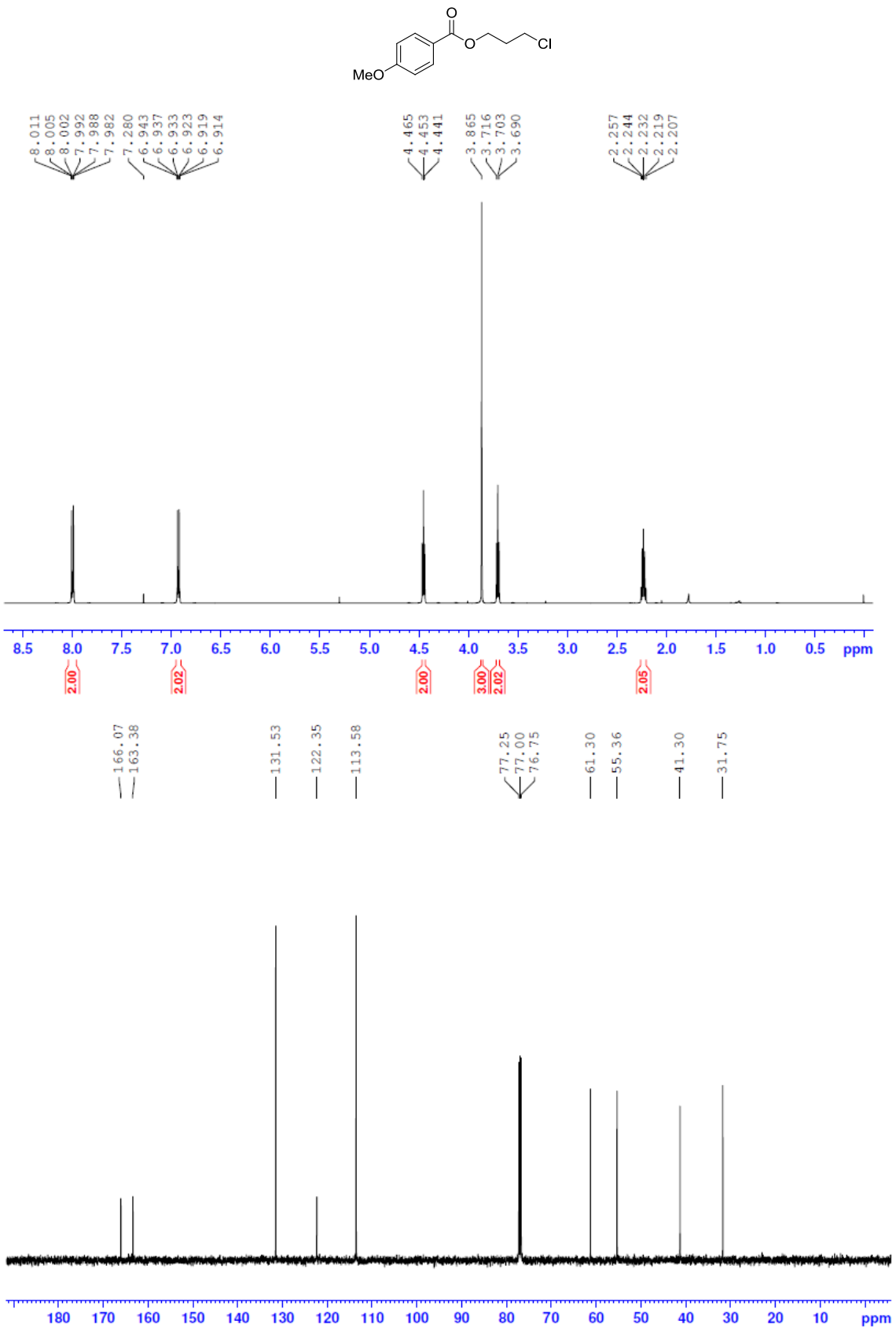
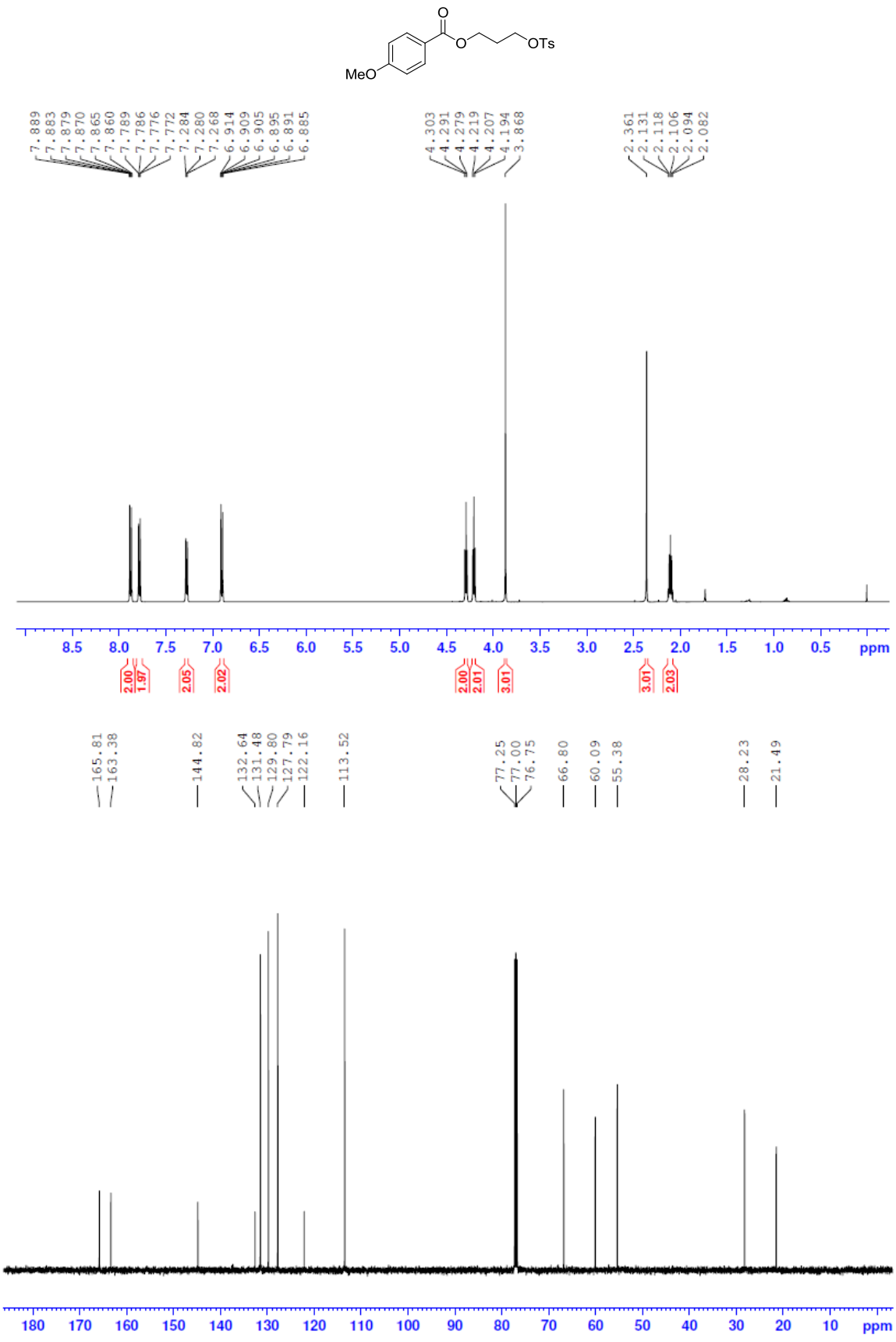
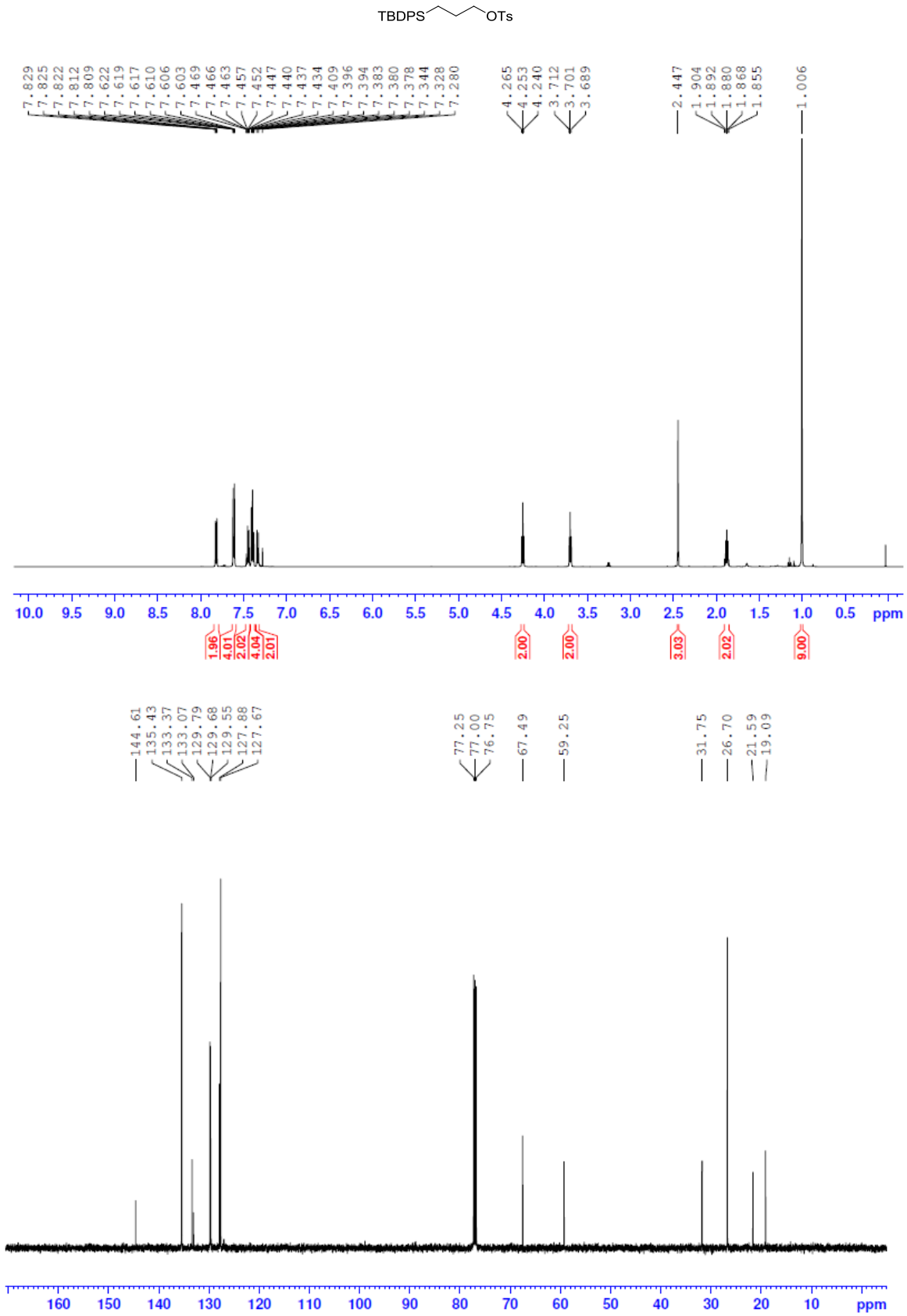
50
40
30
20
10
0
ppm






TBDPS
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7.622
7.619
7.617
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7.603
7.469
7.466
7.463
7.457
7.452
7.447
7.440
7.437
7.434
7.409
7.396
7.394
7.383
7.380
7.378
7.344
7.328
7.280
4.265
4.253
4.240
3.712
3.701
3.689
2.447
1.904
1.892
1.880
1.868
1.855
1.006
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 0.5 ppm
1.96
4.01
2.02
4.04
2.01
2.00
2.00
3.03
2.02
9.00
144.61
135.43
133.37
133.07
129.79
129.68
129.55
127.88
127.67
77.25
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59.25
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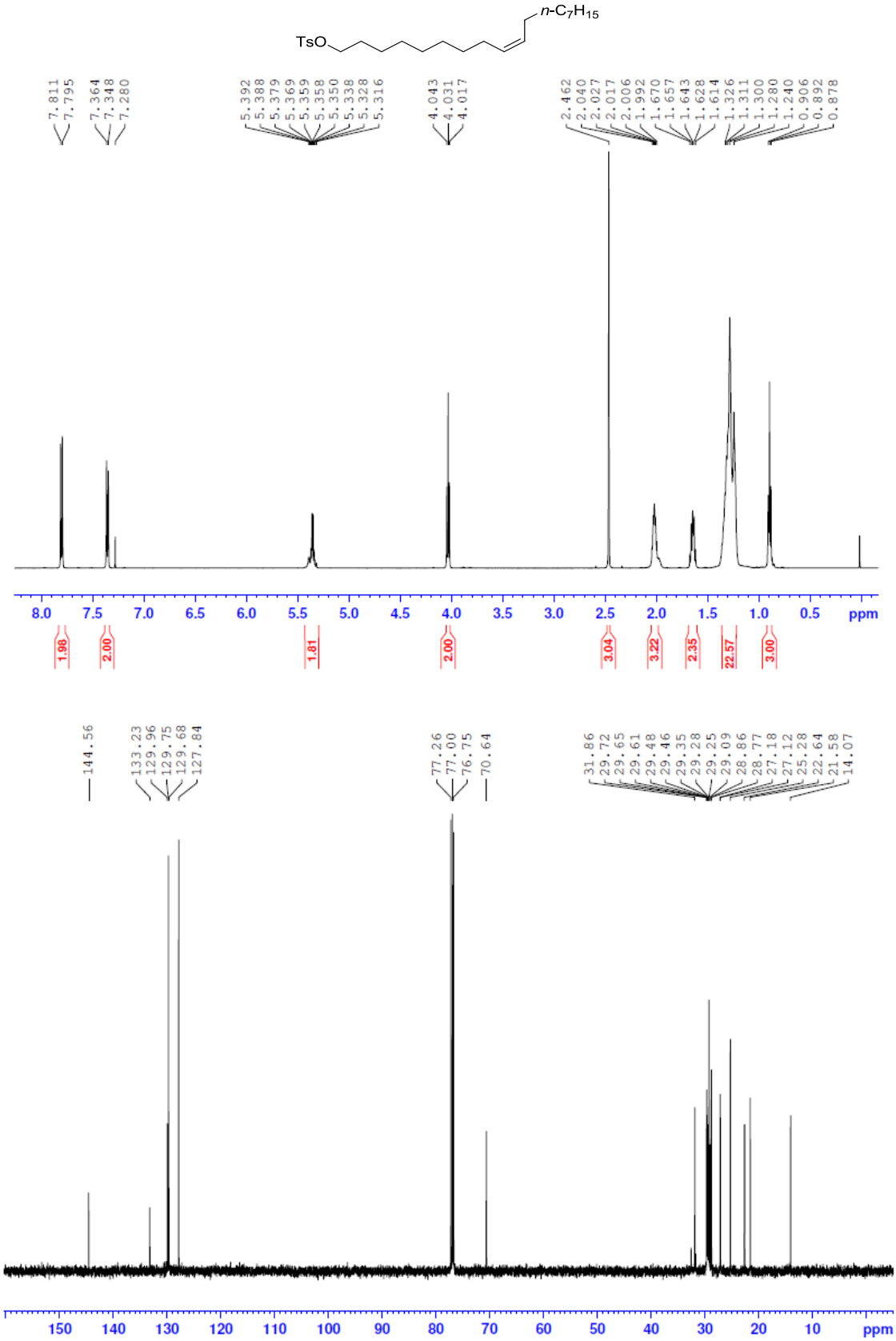
26.70
21.59
19.09
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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5.359
5.358
5.350
5.338
5.328
5.316
4.043
4.031
4.017
2.462
2.040
2.027
2.017
2.006
1.992
1.670
1.657
1.643
1.628
1.614
1.326
1.311
1.300
1.280
1.240
0.906
0.892
0.878
8.0
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
2.00
1.81
2.00
3.04
3.22
2.35
22.57
3.00
144.56
133.23
129.96
129.75
129.68
127.84
77.26
77.00
76.75
70.64
31.86
29.72
29.65
29.61
29.48
29.46
29.35
29.28
29.25
29.09
28.86
28.77
27.18
27.12
25.28
22.64
21.58
14.07
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm