Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 41–43

C,N-Palladacycle based on *N*,*N*-dimethyl-*N*-(diphenylmethyl)amine as an effective phosphine-free (pre)catalyst for the Suzuki–Miyaura cross-coupling

Margarita P. Timerkaeva, Konstantin A. Kochetkov and Olga N. Gorunova

Materials and methods

NMR spectra were recorded on an Agilent 300-MR spectrometer with an operating frequency of 300.0 MHz (for ^{1}H nuclei) in $CDCl_3$ at 20 °C. Chemical shifts are given relative to the residual signals of $CDCl_3$ (δ 7.26 for ^{1}H nuclei). The reactions were carried out without protection from light, moisture, and atmospheric oxygen. The reaction was monitored by TLC on Merck F-254 plates with UV detection. All reagents and solvents utilized in the experimental procedures were procured from commercial suppliers and were of analytical grade, used without the need for additional purification or drying. The particle size study was carried out with the particle analyzer Malvern Zeta-Sizer Ultra (Malvern Instruments Ltd., UK) by the dynamic light scattering method (DLS). Relaxation time distribution functions and hydrodynamic radii were calculated using the analysis package CONTIN data. All the DLS experiments were held under scattering angles from 40 to 150°.

Synthesis of the di-μ-chloro-bis[2-{1′-(dimethylamino)benzyl}phenyl*C*,*N*]dipalladium(II) **11** was carried out according to the procedure reported previously [S1].

Preparation of a catalyst solution of a given concentration.

To a (pre)catalyst **11** (8.02×10^{-3} mmol) placed into a graduated flask (10 mL), dichloromethane was added. An aliquot of this solution in 1 mL contained 8.02×10^{-4} mmol of catalyst, which corresponded to 1 mol% [Pd]. If necessary, additional dilutions were performed to obtain the appropriate amount of catalyst in 1.0 ml of solvent. Then, the necessary amount of the catalyst solution in dichloromethane was transferred to a reaction vessel, and the solvent was removed.

The Suzuki–Miyaura reaction catalyzed by palladacycle 11 (general procedure).

A mixture of both corresponding arylboronic acid (**13a-g**) (1.5 eq., 0.240 mmol) and aryl bromide (**12a-i**) or aryl chloride (**12j-l**) (1 eq., 0.160 mmol), KF (5 eq., 0.802 mmol, 46.6 mg), and dimeric (pre)catalyst **11** (8.02×10^{-5} or 8.02×10^{-4} mmol, 0.056 mg or 0.56 mg to obtain 0.1 or 1 mol% [Pd], respectively) in MeOH (1 mL) was stirred at a specified temperature for a specified time in air. The mixture was evaporated to dryness, and CH_2Cl_2 (10 mL) was added to the residue. The resulting solution was washed with water (3×5 mL). The filtrate was dried over $MgSO_4$ and evaporated to dryness at reduced pressure (1 Torr). The resultant residue obtained

was purified using column chromatography in a hexane/CH_2Cl_2 solvent system (the gradient is from 10:1 to 1:1) to afford the desired products. The ^{1}H NMR chemical shifts are consistent with previously reported literature data [S2-S3].

4-Methoxybiphenyl (**14a**, 92%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3H), 7.01 (d, J = 8.7 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.53-7.61 (m, 4H). [S2]

4-Methylbiphenyl (**14b**, 96% in reaction with aryl bromide and 92% in reaction with aryl chloride): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 7.1 Hz, 2H), 7.35 (m, 1H), 7.28 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H). [S3]

4-Acetylbiphenyl (**14c**, 94% in reaction with aryl bromide and 85% in reaction with aryl chloride): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.7 Hz, 2H), 7.62-7.73 (m, J = 8.1 Hz, 4H), 7.52-7.42 (m, 3H), 2.66 (s, 3H). [S2]

4-Cyanobiphenyl (**14d**, 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.55 (m, 3H), 7.61 (d, J = 7.4 Hz, 2H), 7.69-7.77 (m, 4H). [S3]

4-Nitrobiphenyl (**14e**, 71%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.57 (m, 3H), 7.65 (d, J = 7 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 8.32 (d, J = 8.4 Hz, 2H). [S2]

Ethyl 4-phenylbenzoate (**14f**, 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.71-7.62 (m, 4H), 7.47 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H). [S4]

2-Methoxybiphenyl (**14g**, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (m, 2H), 7.44 (ddd, J = 8.1, 6.6, 1.5 Hz, 2H), 7.39-7.31 (m, 3H), 7.10-6.98 (m, 2H), 3.84 (s, 3H). [S3]

2-Formylbiphenyl (**14h**, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.43-7.56 (m, 5H), 7.40 (d, J = 7.6 Hz, 2H). [S5]

3-Methylbiphenyl (**14i**, 97%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.32-7.51 (m, 6H), 7.20 (d, J = 7.6 Hz, 1H), 2.46 (s, 3H). [S6]

Methyl 4-phenylbenzoate (**14j**, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, 2H), 7.70-7.62 (m, 4H), 7.39-7.52 (m, 3H), 3.94 (s, 3H). [S2]

1-(4'-Methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (**14k**, 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.66 (s, 3H, $COCH_3$), 2.43 (s, 3H, CH_3). [S7]

1-(4'-Methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**14l**, 97%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H; ArH), 7.66 (d, J = 8.5 Hz, 2H; ArH), 7.59 (d, J = 8.8 Hz, 2H; ArH), 7.02 (d, J = 8.8 Hz, 2H; ArH), 3.88 (s, 3H; OCH_3), 2.65 (s, 3H; $COCH_3$). [S8]

1-(4'-Bromo-[1,1'-biphenyl]-4-yl)ethan-1-one (**14m**, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 2.66 (s, 3H; $COCH_3$). [S8]

1-(4'-Chloro-[1,1'-biphenyl]-4-yl)ethan-1-one (**14n**, 93%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 2.66 (s, 3H; $COCH_3$). [S8]

1-(1,1':4',1"-Terphenyl)-4-ylethan-1-one (**14o**, 89%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H), 7.78-7.68 (m, 6H), 7.65 (d, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 2.67 (s, 3H; $COCH_3$). [S9]

1-(4-Acetylphenyl)naphthalene (**14p**, 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.3 Hz, 2H), 7.94 (t, J = 8.2 Hz, 2H), 7.87 (d, J = 8.3 Hz, 1H), 7.63 (m, 2H), 7.60 - 7.42 (m, 4H), 2.72 (s, 3H). [S9]

Procedure for Carbon Disulfide (CS_2) Poisoning Study.

A solution of (pre)catalyst **11** (8.02×10^{-5} mmol, 0.056 mg, 0.1 mol% [Pd]) in MeOH (1.0 mL) was stirred for 5 min at ambient temperature. Thereafter, phenylboronic acid (**13**) (1.5 eq., 0.240 mmol, 29.3 mg), 4-bromoacetophenone (**12c**) (1 eq., 0.160 mmol, 31.8 mg) was added along with KF (5 eq., 0.802 mmol, 46.6 mg). Carbon disulfide (CS_2) (2 eq., 0.320 mmol, 0.019 mL) was then added (at the start of the reaction), and the reaction mixture was stirred at ambient temperature for 3 h. On completion of the stipulated time, a TLC analysis of the reaction mixture revealed no progress in the reaction, thus suggesting complete inhibition of the catalytic reaction.

General procedure for Tetrabutylammonium bromide (TBAB) Study.

A solution of (pre)catalyst **11** (8.02×10^{-5} mmol, 0.056 mg, 0.1 mol% [Pd]) in MeOH (1.0 mL) was stirred for 5 min at ambient temperature. Thereafter, phenylboronic acid (13) (1.5 eq., 0.240 mmol, 29.3 mg), 4-bromoacetophenone (**12c**) (1 eq., 0.160 mmol, 31.8 mg) was added along with KF (5 eq., 0.802 mmol, 46.6 mg). TBAB (1 eq., 0.160 mmol, 51.6 mg or 0.1 eq., 0.016 mmol, 5.16 mg) was added to the reaction mixture and the resulting solution was then stirred at ambient temperature for 3.0 h. On completion of the stipulated time the mixture was evaporated to dryness, and CH_2Cl_2 (10 mL) was added to the residue. The resulting solution was washed with water (3×5 mL). The filtrate was dried over $MgSO_4$ and evaporated to dryness at reduced pressure (1 Torr). The sample were then dissolved in $CDCl_3$ and transferred to NMR ampoules. Conversion was determined by ^{1}H NMR spectroscopy.

Procedure for Polyvinylpyrrolidone (PVP) Study.

A solution of (pre)catalyst **11** (8.02×10^{-5} mmol, 0.056 mg, 0.1 mol% [Pd]) in MeOH (1.0 mL) was stirred for 5 min at ambient temperature. Thereafter, phenylboronic acid (13) (1.5 eq., 0.240 mmol, 29.3 mg), 4-bromoacetophenone (**12c**) (1 eq., 0.160 mmol, 31.8 mg) was added along with KF (5 eq., 0.802 mmol, 46.6 mg). PVP (M = 10 000, 0.1 eq., 0.016 mmol, 160 mg) was added to the reaction mixture and the resulting solution was then stirred at ambient temperature

for 3.0 h. On completion of the stipulated time the mixture was evaporated to dryness, and CH_2Cl_2 (10 mL) was added to the residue. The resulting solution was washed with water (3×5 mL). The filtrate was dried over $MgSO_4$ and evaporated to dryness at reduced pressure (1 Torr). The sample were then dissolved in $CDCl_3$ and transferred to NMR ampoules. Conversion was determined by ^1H NMR spectroscopy.

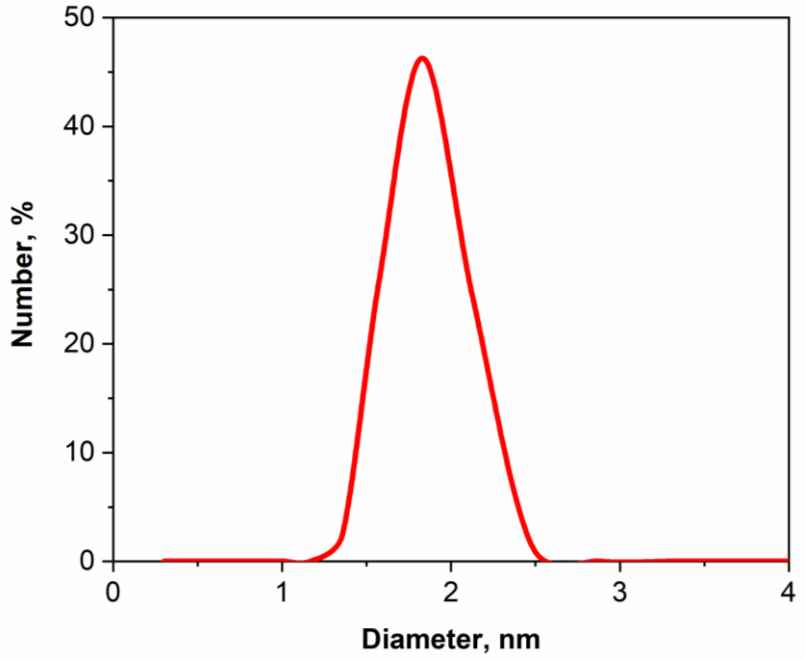


Figure S1 Particle size distribution by number (%) obtained by DLS.

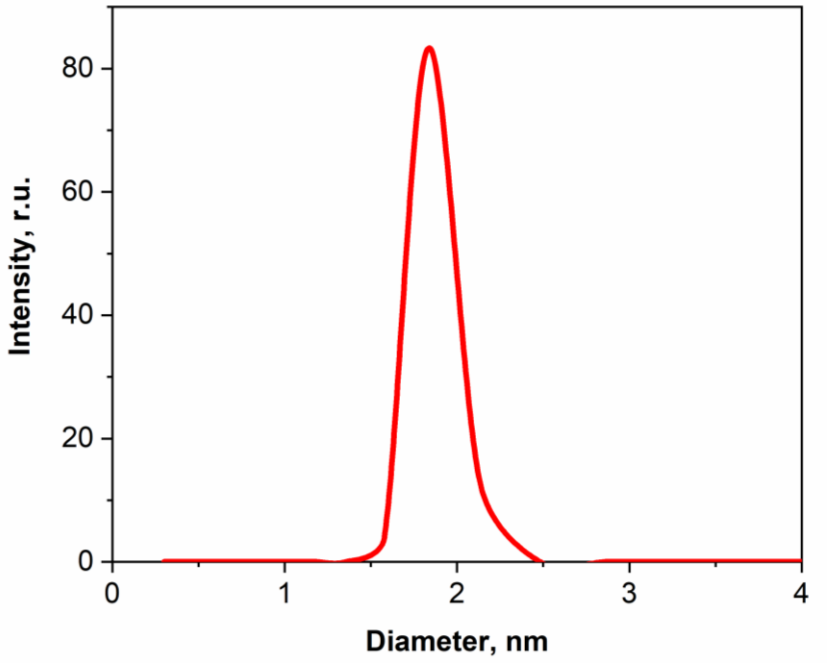
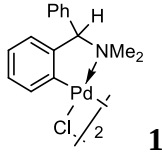
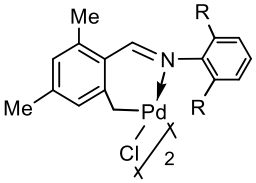
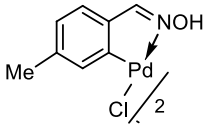
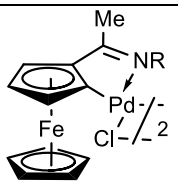
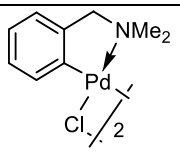
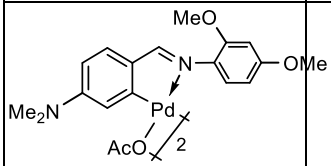
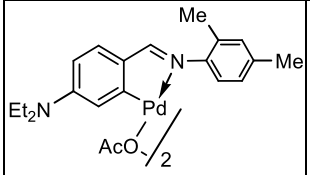
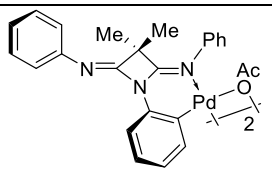
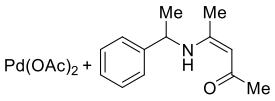
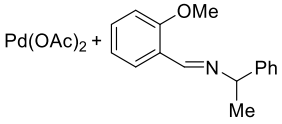
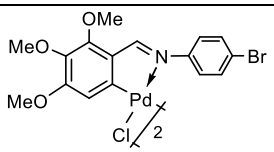


Figure S2 Particle size distribution by intensity obtained by DLS.

Table S1 Comparison of the effectiveness in the Suzuki-Miyaura reaction of 4-bromoacetophenone with $PhB(OH)_2$ palladacycle **11** from this article with the catalytic activity of known phosphine-free palladacycles.

Catalyst	[Pd], mol%	Solvent	Base	T, °C	Time	Yield, %	Ref.
 **11**	**0.1**	**MeOH**	**KF**	**20**	**5**	**94**	**This work**
	0.0001	EtOH	K_2CO_3	80	2	99	S10
	0.01	H_2O	K_2CO_3	100	15 min	93	S11
	0.01	$MeOH/H_2O$	KOH	20	4 days	100	
 $R = n\text{-}C_{12}H_{25}$	0.1	$MeOH/H_2O$	K_2CO_3	20	2	99	S12
	0.5	MeOH	KF	20	1	99	S13
	0.5	$^{i}PrOH$	Cs_2CO_3	82	0.5 h	99	S14
	0.5	$^{i}PrOH$	Cs_2CO_3	82	0.5 h	75	S14

	1.0	THF	KF	25	1 h	96%	S15
	1.0	THF	KF	25	50 min	85%	S16
	2.0	THF	KF	35	1.5 h	99%	S17
	2.0	THF/H_2O	K_2CO_3	25	2 h	88%	S18

References

S1. V. V. Dunina, E. D. Razmyslova, L. G. Kuz'mina, A. V. Churakov, M. Yu. Rubina, Yu. K. Grishin, *Tetrahedron: Asymmetry*, 1999, **10**, 3147; https://doi.org/10.1016/S0957-4166(99)00319-5.

S2. F. Izquierdo, C. Zinser, Y. Minenkov, D. B. Cordes, A. M. Z. Slawin, L. Cavallo, F. Nahra, C. S. J. Cazin and S. P. Nolan, *ChemCatChem*, 2018, **10**, 601; https://doi.org/10.1002/cctc.201701279.

S3. S.-J. Park, H.-J. Cho, S.-M. Lee and Y.-S. Lee, *Tetrahedron Lett.*, 2017, **58**, 2670; https://doi.org/10.1016/j.tetlet.2017.05.080.

S4. V. Pascanu, Q. Yao, A. B. Gómez, M. Gustafsson, Y. Yun, W. Wan, L. Samain, X. Zou and B. Martín-Matute, *Chem. - Eur. J*, 2013, **19**, 17221; https://doi.org/10.1002/chem.201302621.

S5. A. Dadras, M. R. Naimi-Jamal, F. M. Moghaddam and S. E. Ayati, *Appl. Organomet. Chem*., 2017, **32**, e3993; https://doi.org/10.1002/aoc.3993.

S6. X. Li, W. Chen, H. Chang, Z. Shao and W. Wei, *Synthesis*, 2014, **46**, 1593; https://doi.org/10.1055/s-0033-1341084.

S7. R. Takahashi, K. Kubota and H. Ito, *Chem. Commun*., 2020, **56**, 407; https://doi.org/10.1039/C9CC06946A.

S8. S. Sharma, M. Kaur, Ch. Sharma, Sh. Sharma and S. Paul, *ChemistrySelect*, 2021, **6**, 12280; https://doi.org/10.1002/slct.202103088.

S9. B. Guo, H.-X. Li, C.-H. Zha, D. J. Young, H.-Y. Li, J.-P. Lang, *ChemSusChem*, 2019, **12**, 1421; https://doi.org/10.1002/cssc.201802918.

S10. C.-L. Chen, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Organometallics*, 2005, **24**, 1075; https://doi.org/10.1021/om049125t.

S11. L. Botella and C. Nájera, *J. Organomet. Chem*., 2002, **663**, 46; https://doi.org/10.1016/S0022-328X(02)01727-8.

S12. B. Mu, T. Li, J. Li and Y. Wu, *J. Organomet. Chem*., 2008, **693**, 1243; https://doi.org/10.1016/j.jorganchem.2008.01.012.

S13. M. P. Timerkaeva, K. A. Kochetkov and O. N Gorunova, *INEOS Open*, 2025, **8**, 5; https://doi.org/10.32931/io2517a.

S14. I. Babahan, R. Firinci, N. Ozdemir and G. M. Emin, *Inorg. Chim. Acta*, 2021, **522**, 120360; https://doi.org/10.1016/j.ica.2021.120360.

S15. M.-T. Chen, C.-A. Huang and C.-T. Chen, *Eur. J. Inorg. Chem*., 2008, 3142; https://doi.org/10.1002/ejic.200800195.

S16. Y.-C. Lai, H.-Y. Chen, W.-C. Hung, C.-C. Lin and F.-E. Hong, *Tetrahedron*, 2005, **61**, 9484; https://doi.org/10.1016/j.tet.2005.08.005.

S17. D. Srimani and A. Sarkar, *Tetrahedron Lett*., 2008, **49**, 6304; https://doi.org/10.1016/j.tetlet.2008.08.056.

S18. B. Bermudez-Puente, L. A. Adrio, F. Lucio-Martinez, F. Reigosa, J. M. Ortigueira and J. M. Vila, *Molecules*, 2022, **27**, 3146; https://doi.org/10.3390/molecules27103146.

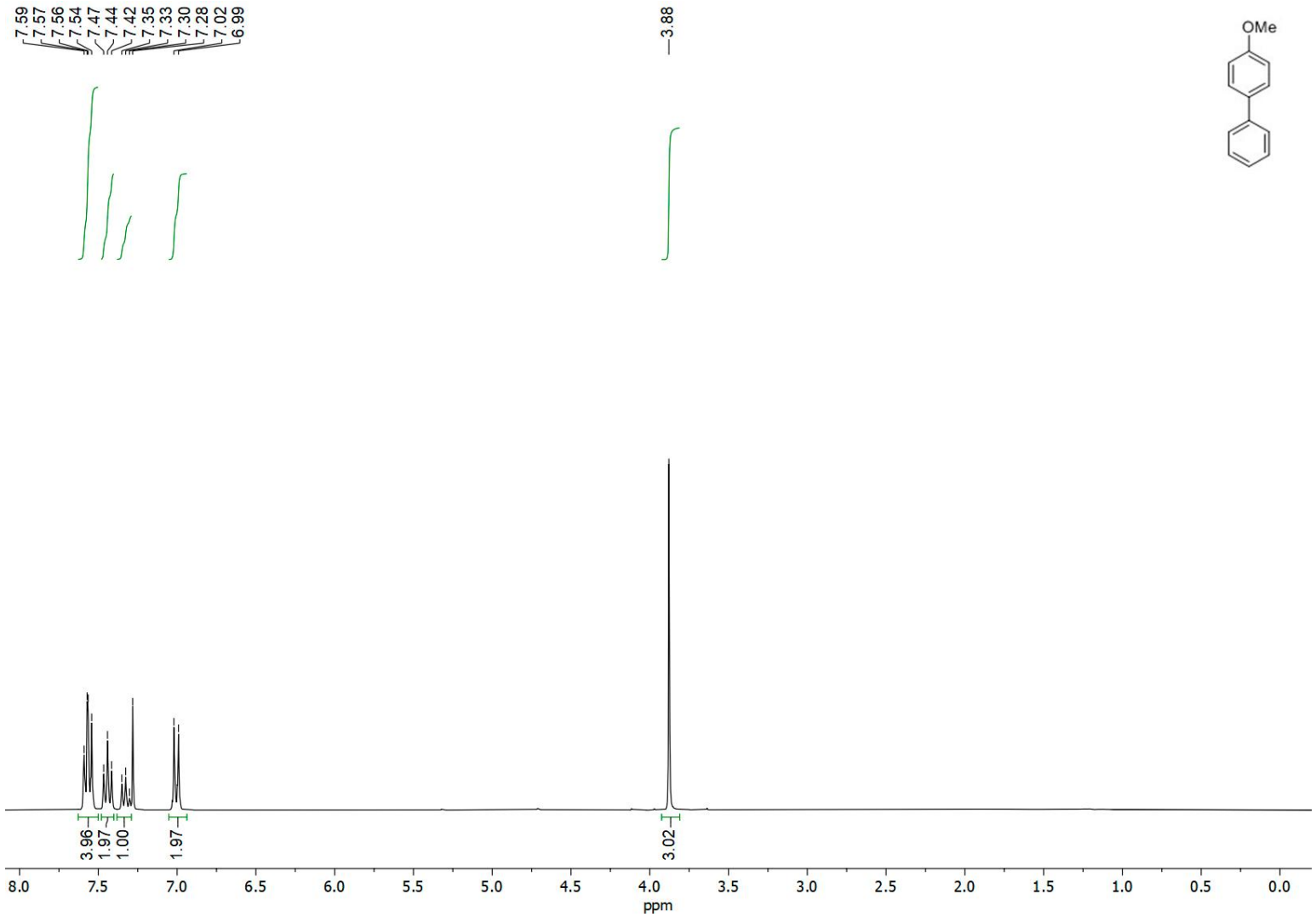


Figure S3 ^{1}H NMR spectrum of 4-methoxybiphenyl (**14a**).

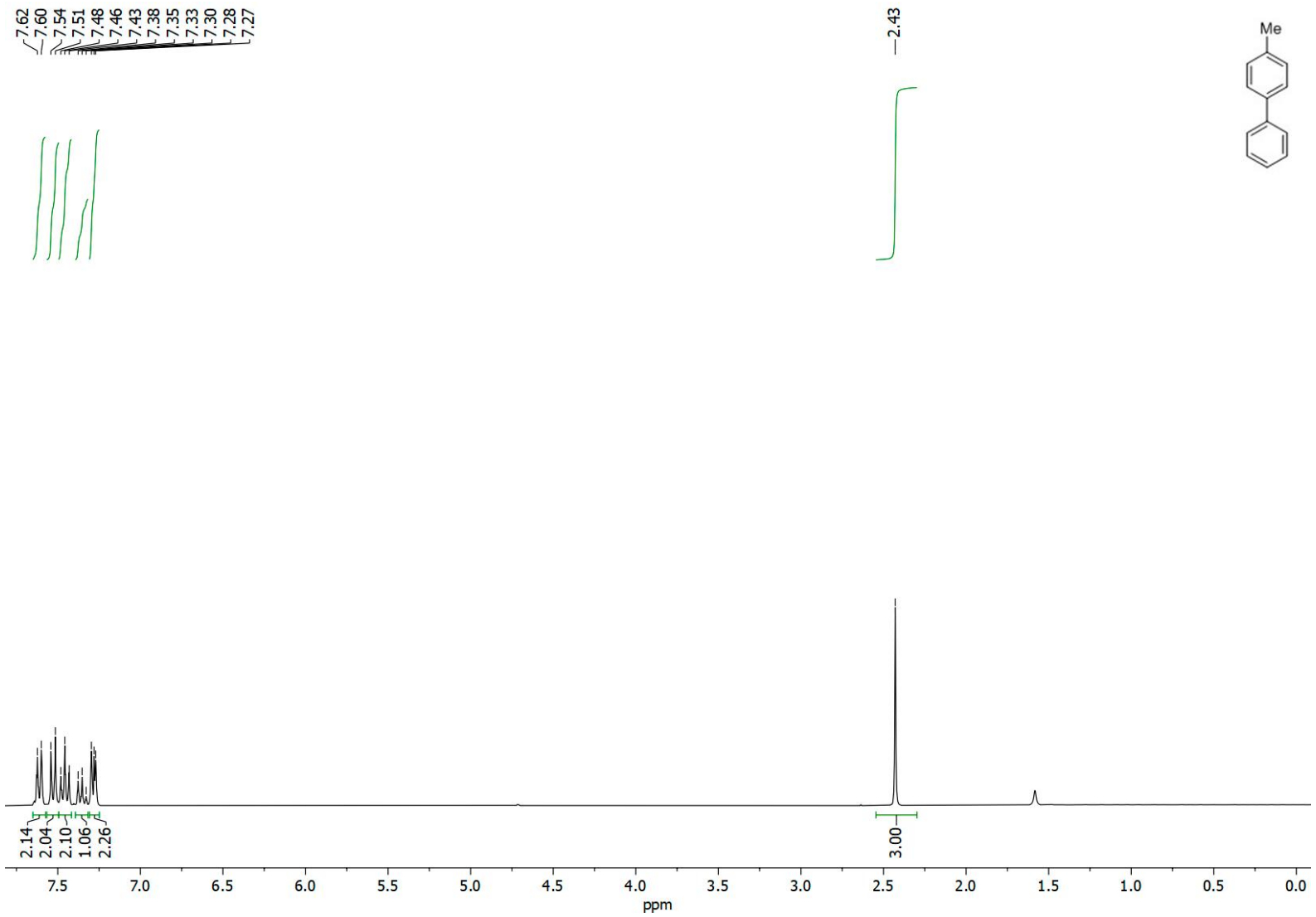


Figure S4 ^{1}H NMR spectrum of 4-methylbiphenyl (**14b**).

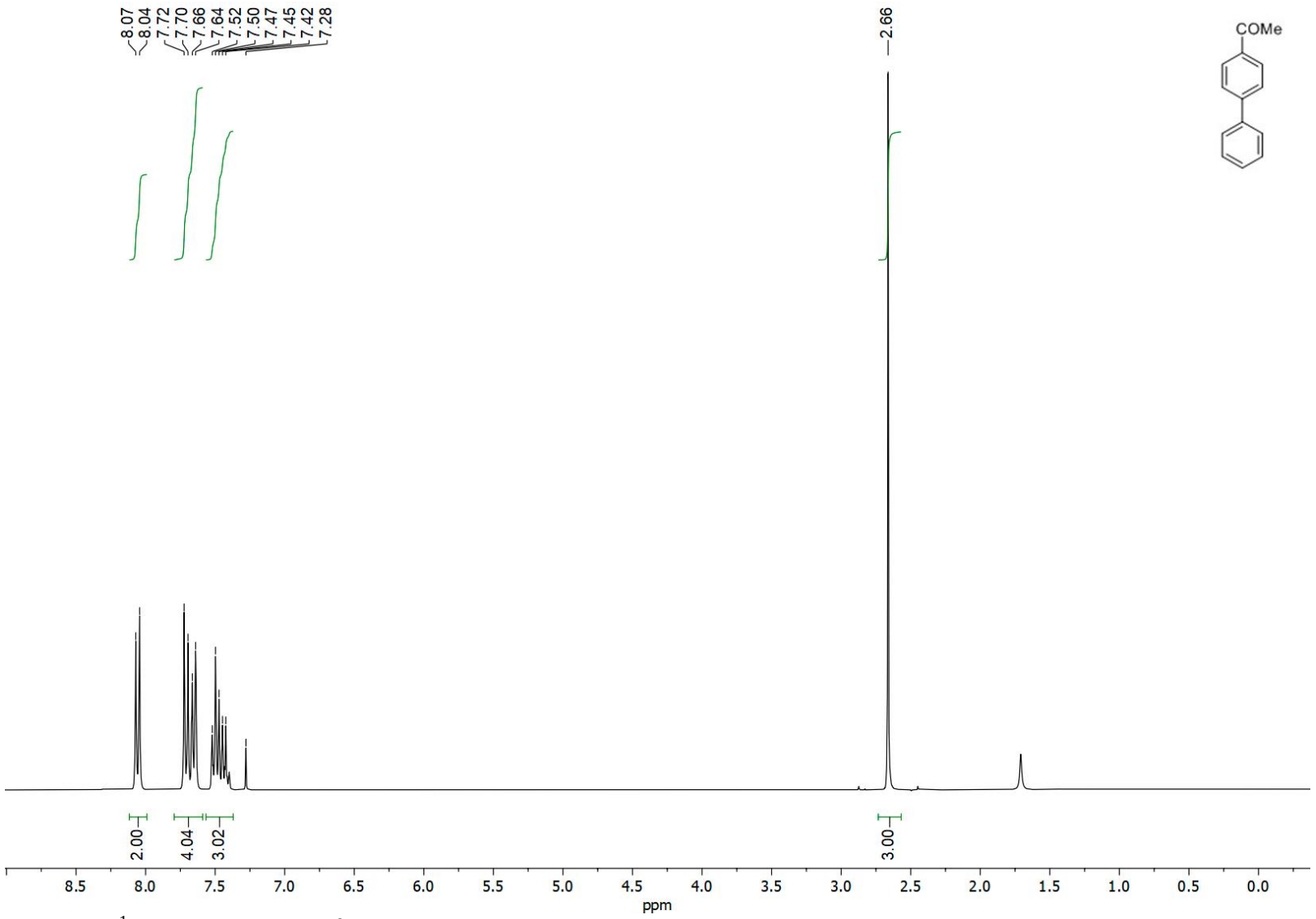


Figure S5 ^{1}H NMR spectrum of 4-acetylbiphenyl (**14c**).

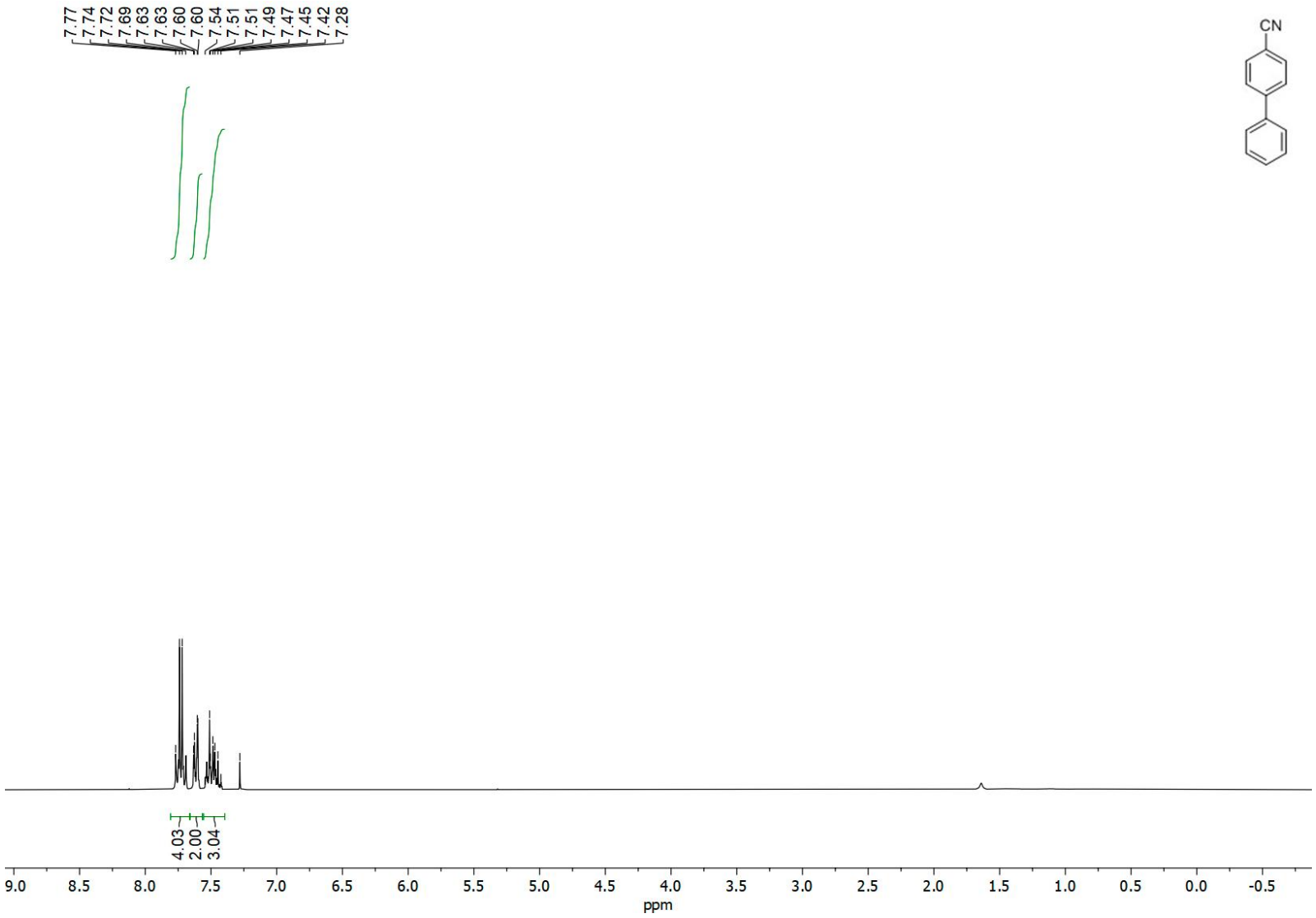


Figure S6 ^{1}H NMR spectrum of 4-cyanobiphenyl (**14d**).

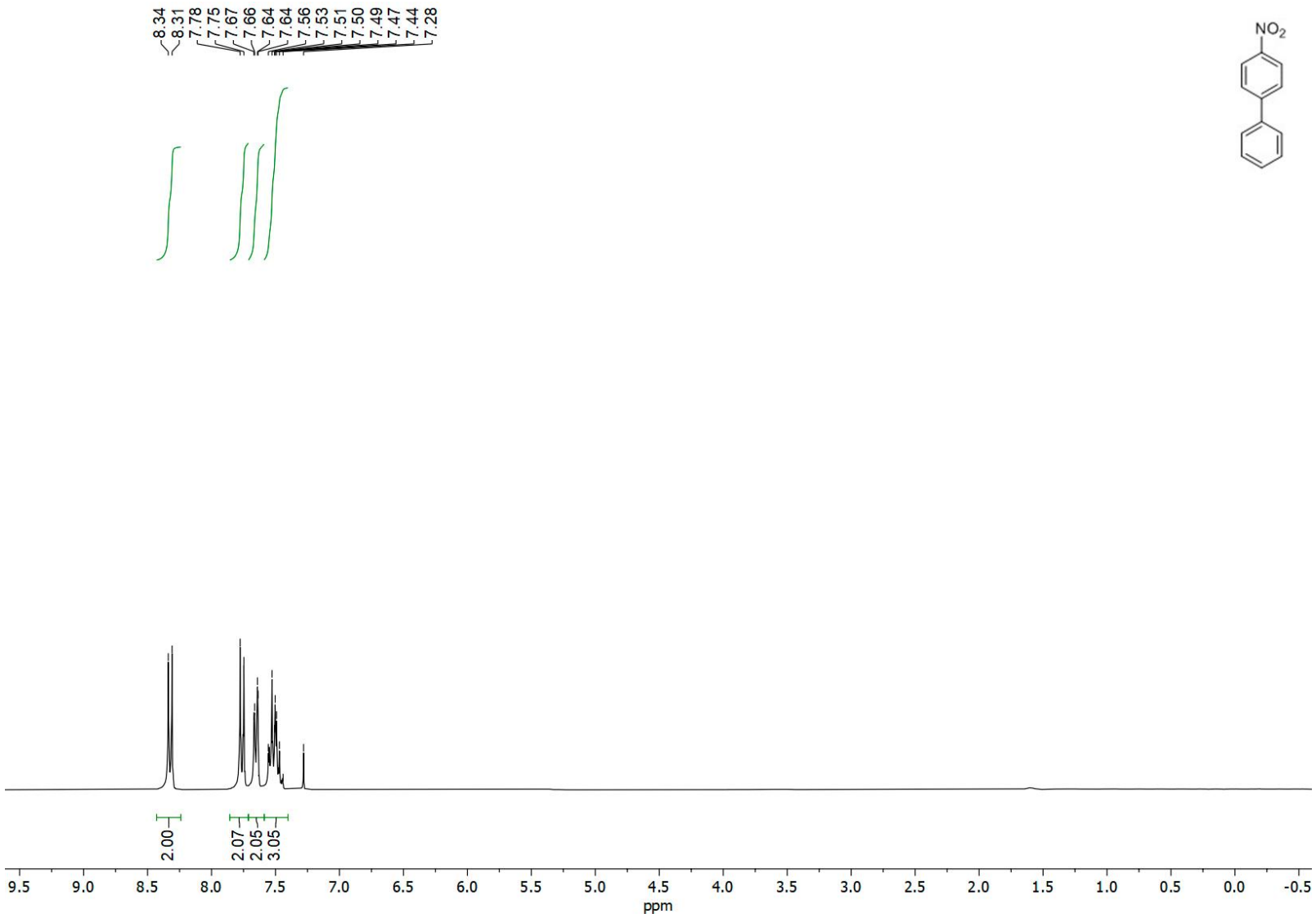


Figure S7 ^{1}H NMR spectrum of 4-nitrobiphenyl (**14e**).

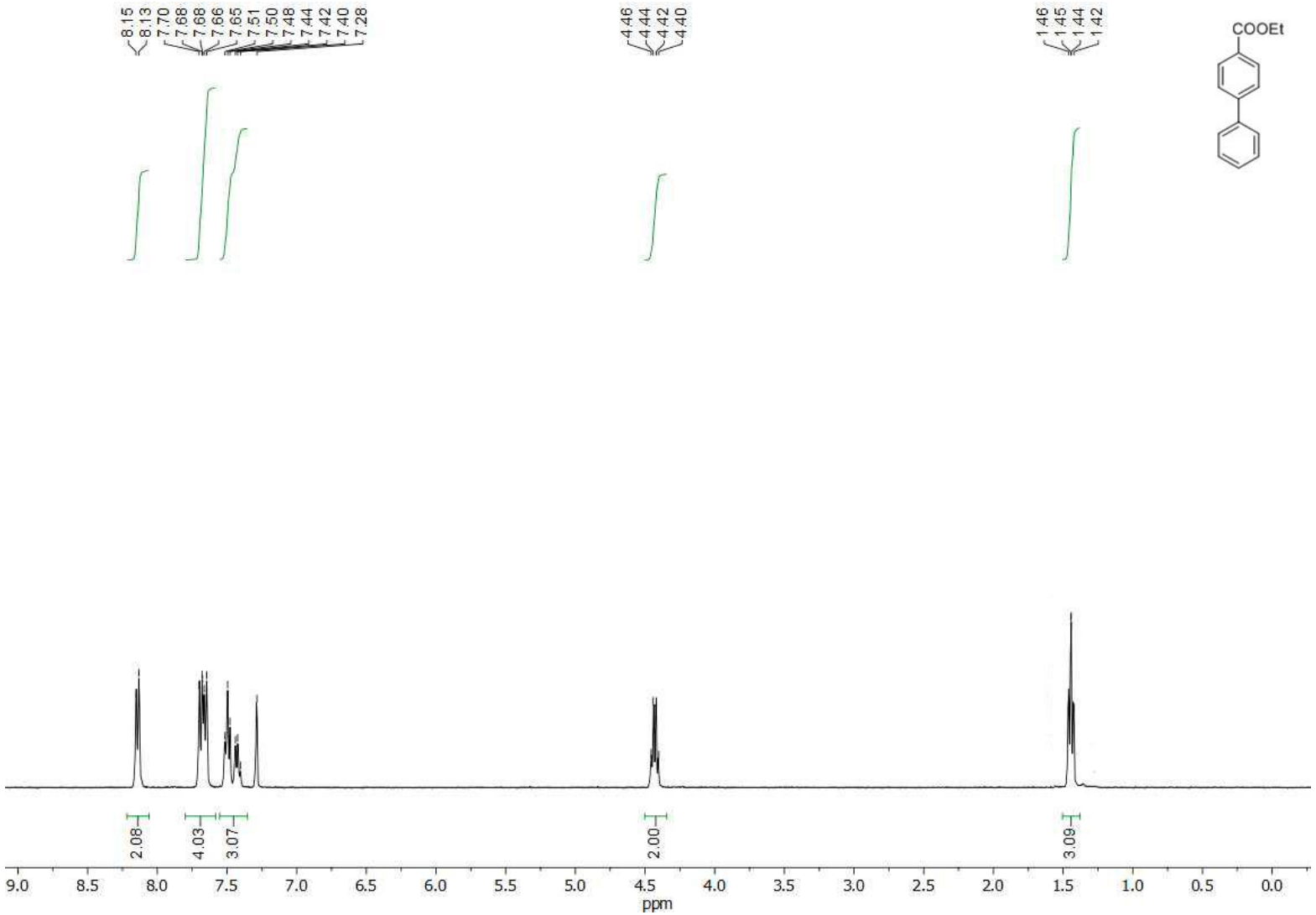


Figure S8 ^{1}H NMR spectrum of ethyl 4-phenylbenzoate (**14f**).

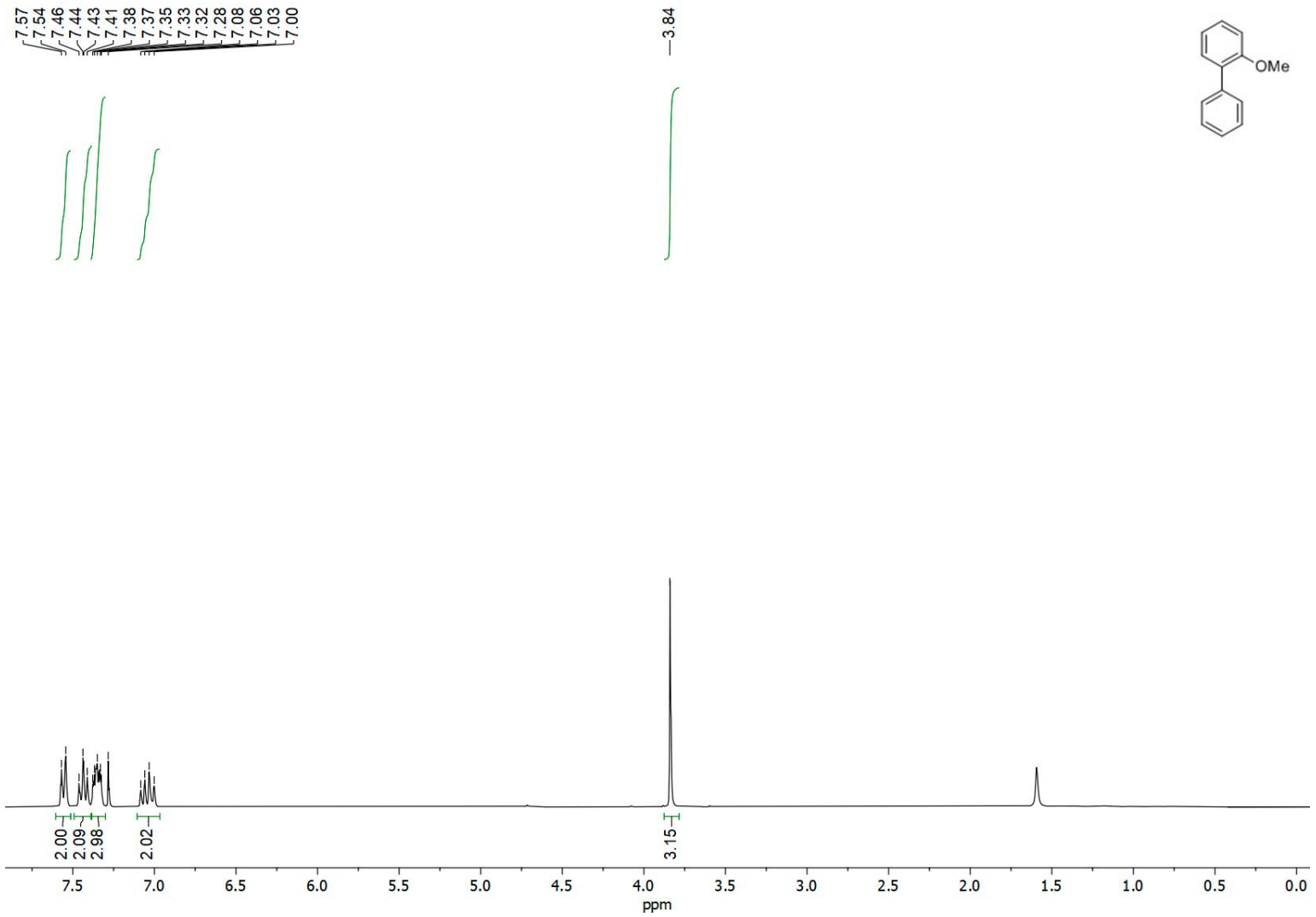


Figure S9 ^{1}H NMR spectrum of 2-methoxybiphenyl (**14g**).

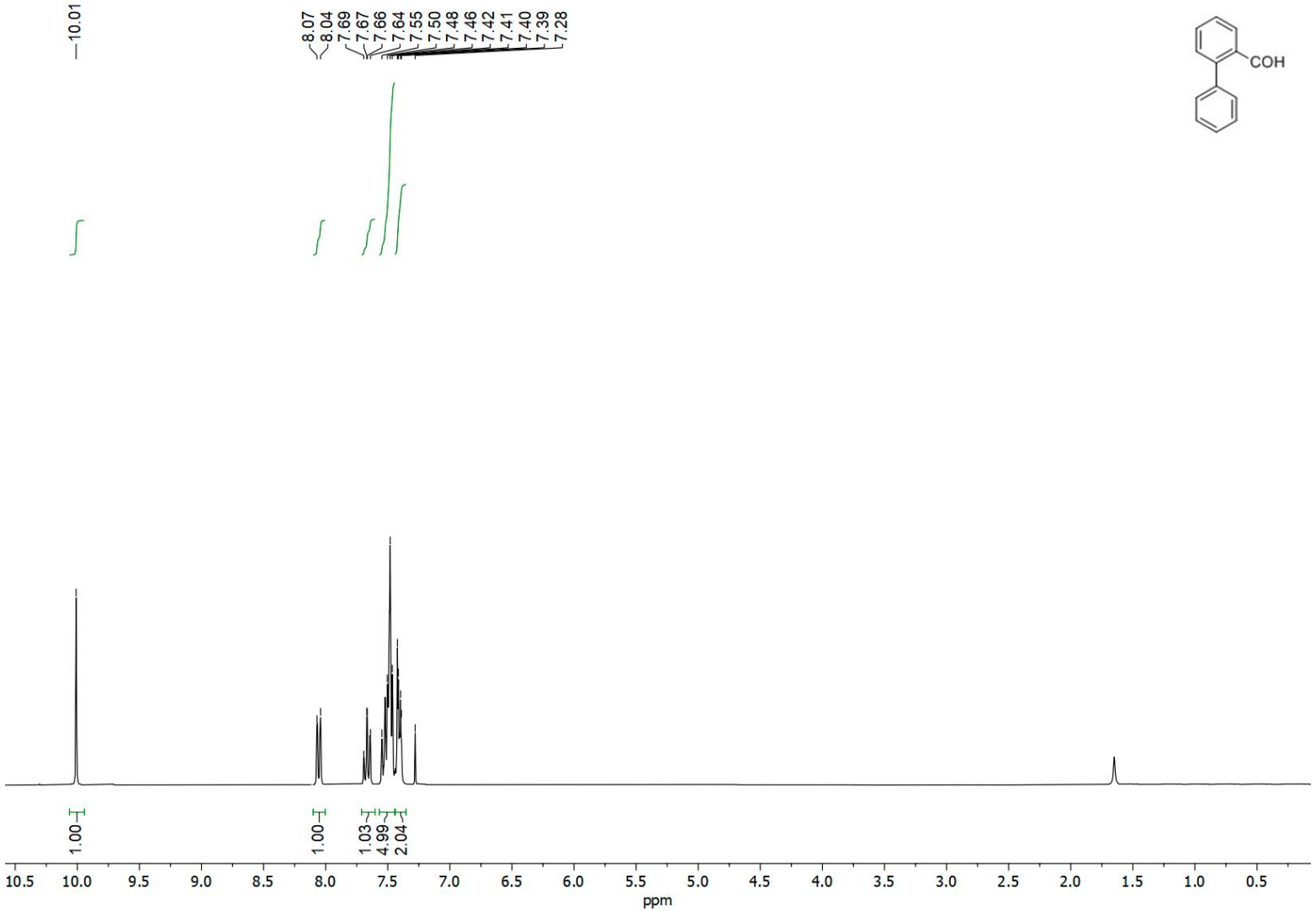


Figure S10 ^{1}H NMR spectrum of 2-formylbiphenyl (**14h**).

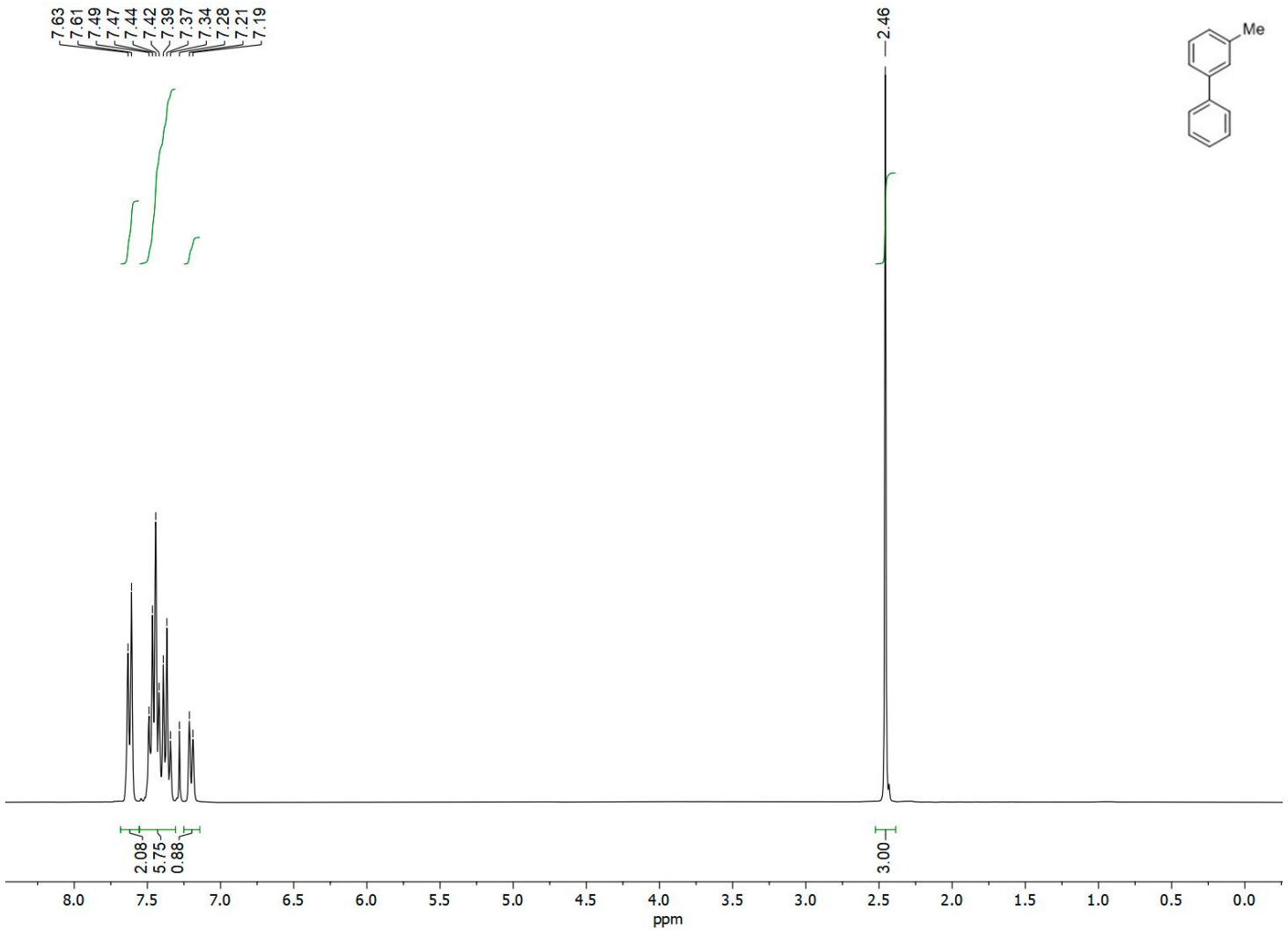


Figure S11^{1}H NMR spectrum of 3-methylbiphenyl (**14i**).

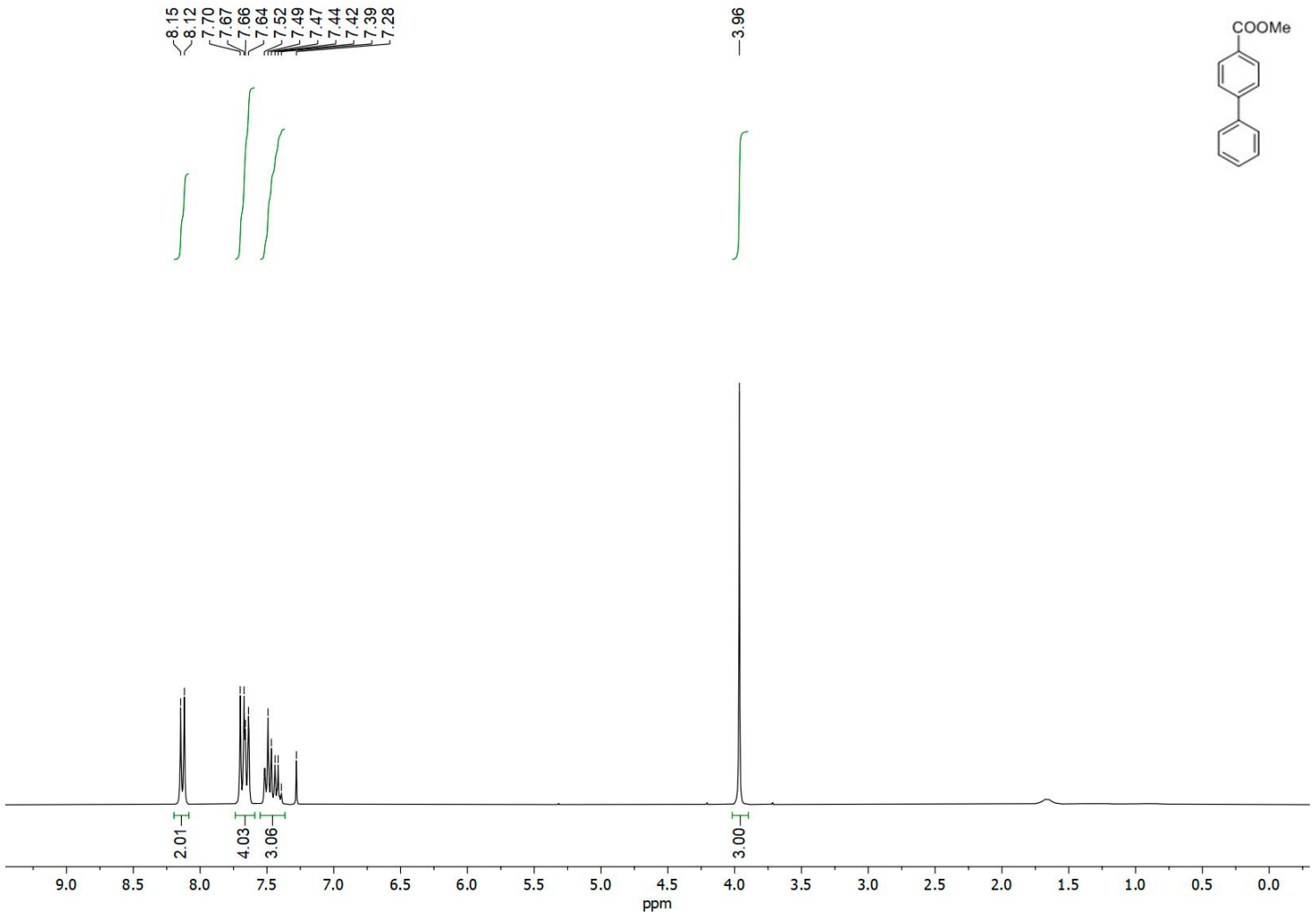


Figure S12 ^{1}H NMR spectrum of methyl 4-phenylbenzoate (**14j**).

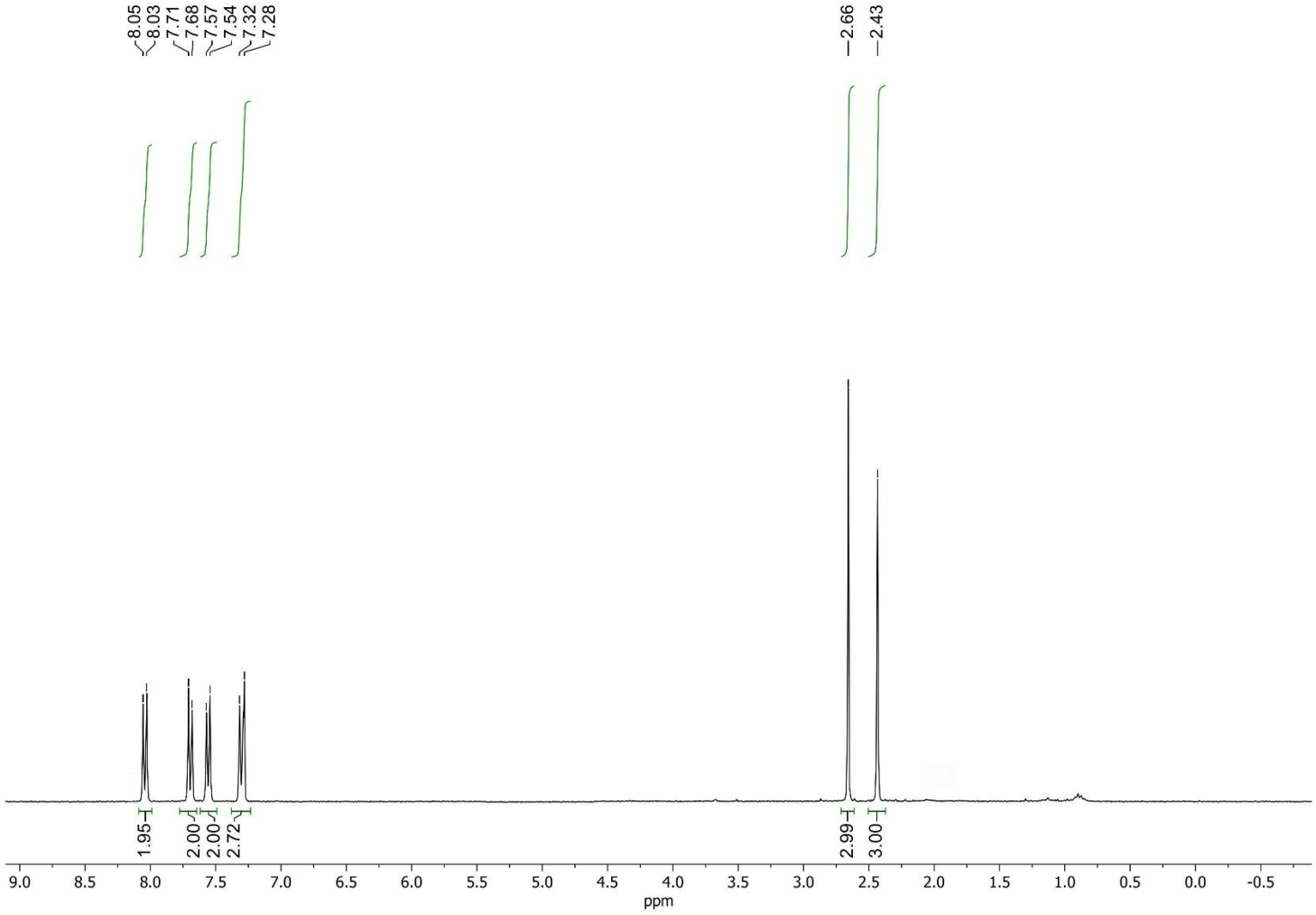


Figure S13 ^{1}H NMR spectrum of 1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (**14k**).

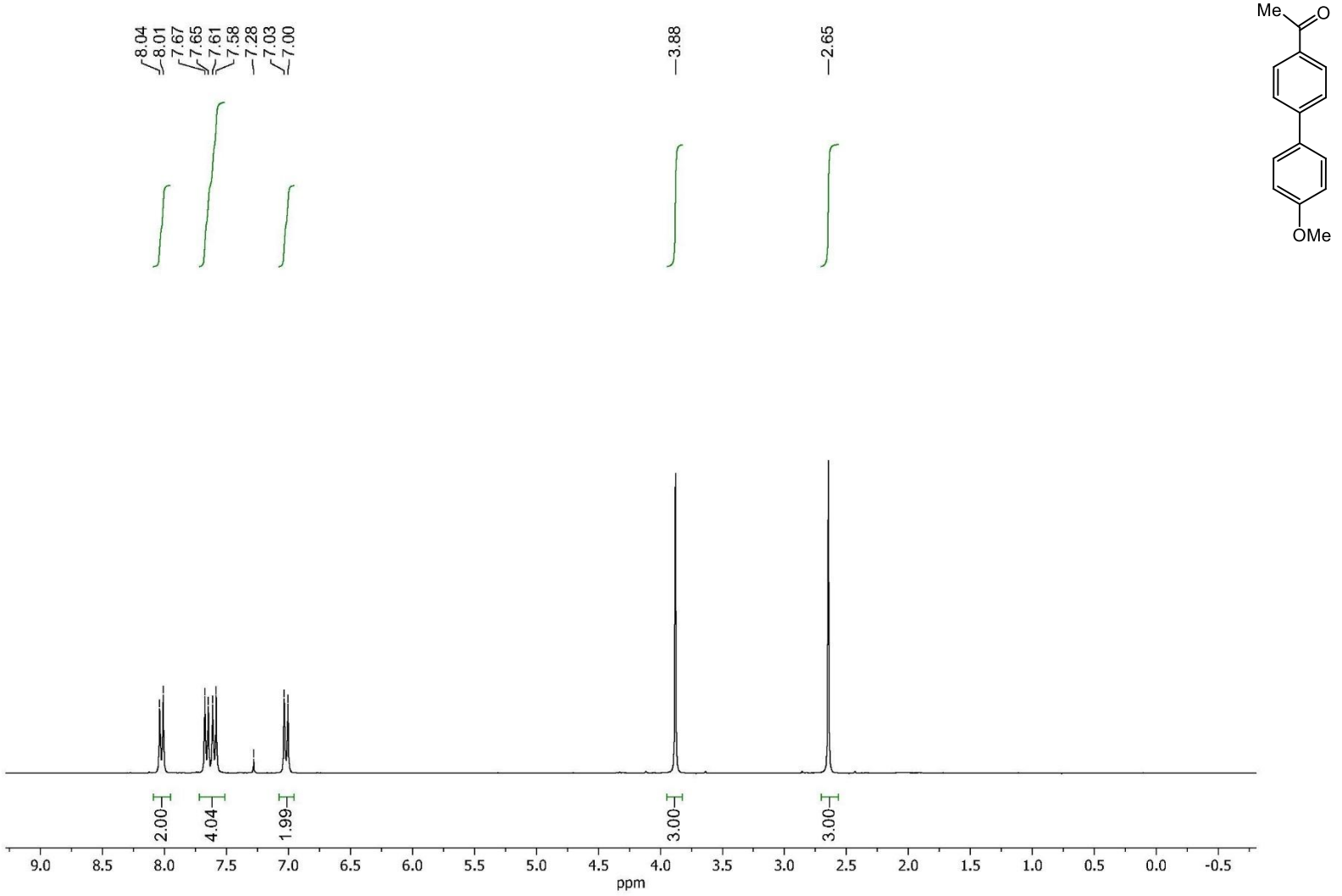


Figure S14 ^{1}H NMR spectrum of 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**14l**).

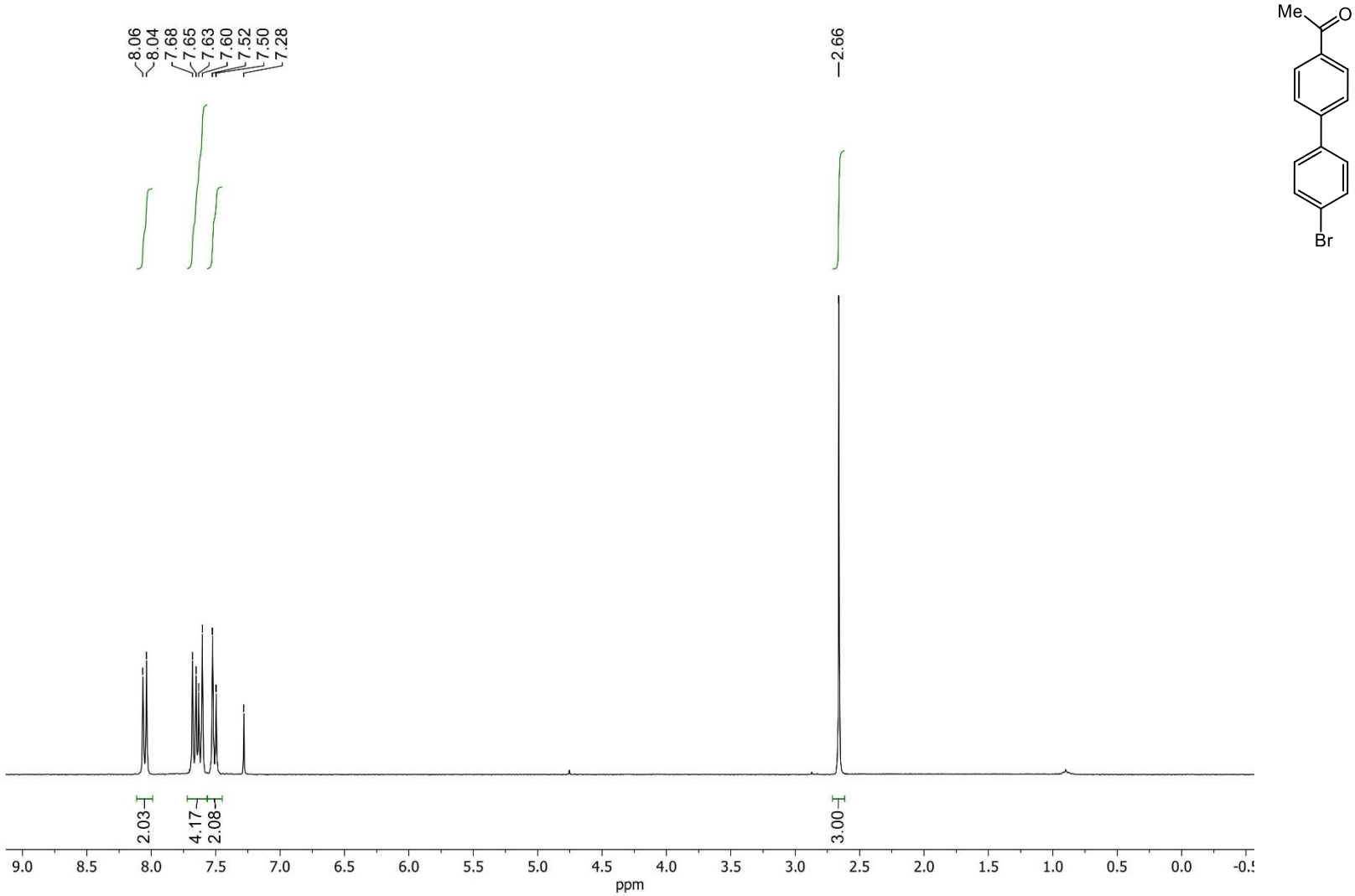


Figure S15 ^{1}H NMR spectrum of 1-(4'-bromo-[1,1'-biphenyl]-4-yl)ethan-1-one (**14m**).

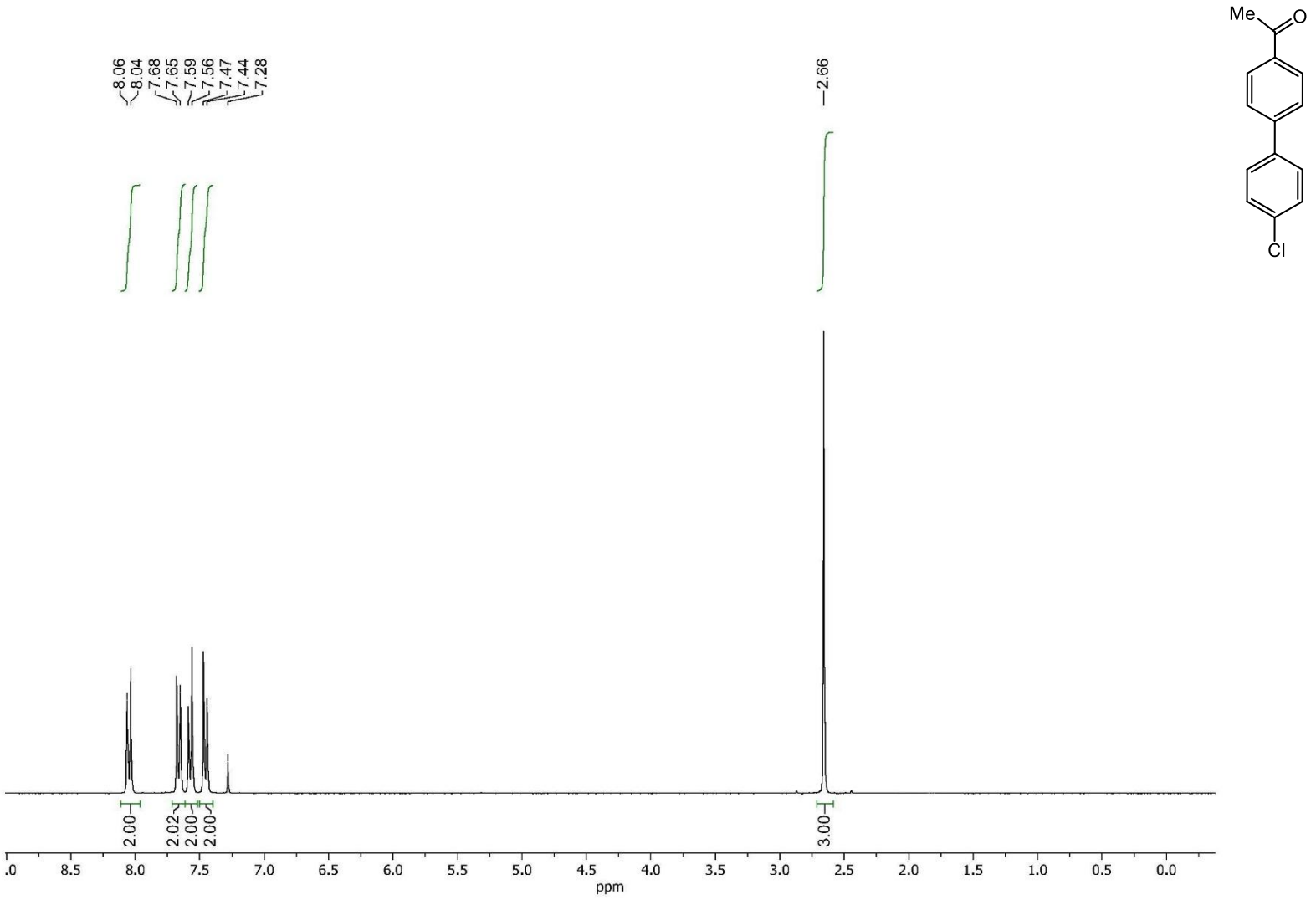


Figure S16 ^{1}H NMR spectrum of 1-(4'-chloro-[1,1'-biphenyl]-4-yl)ethan-1-one (**14n**).

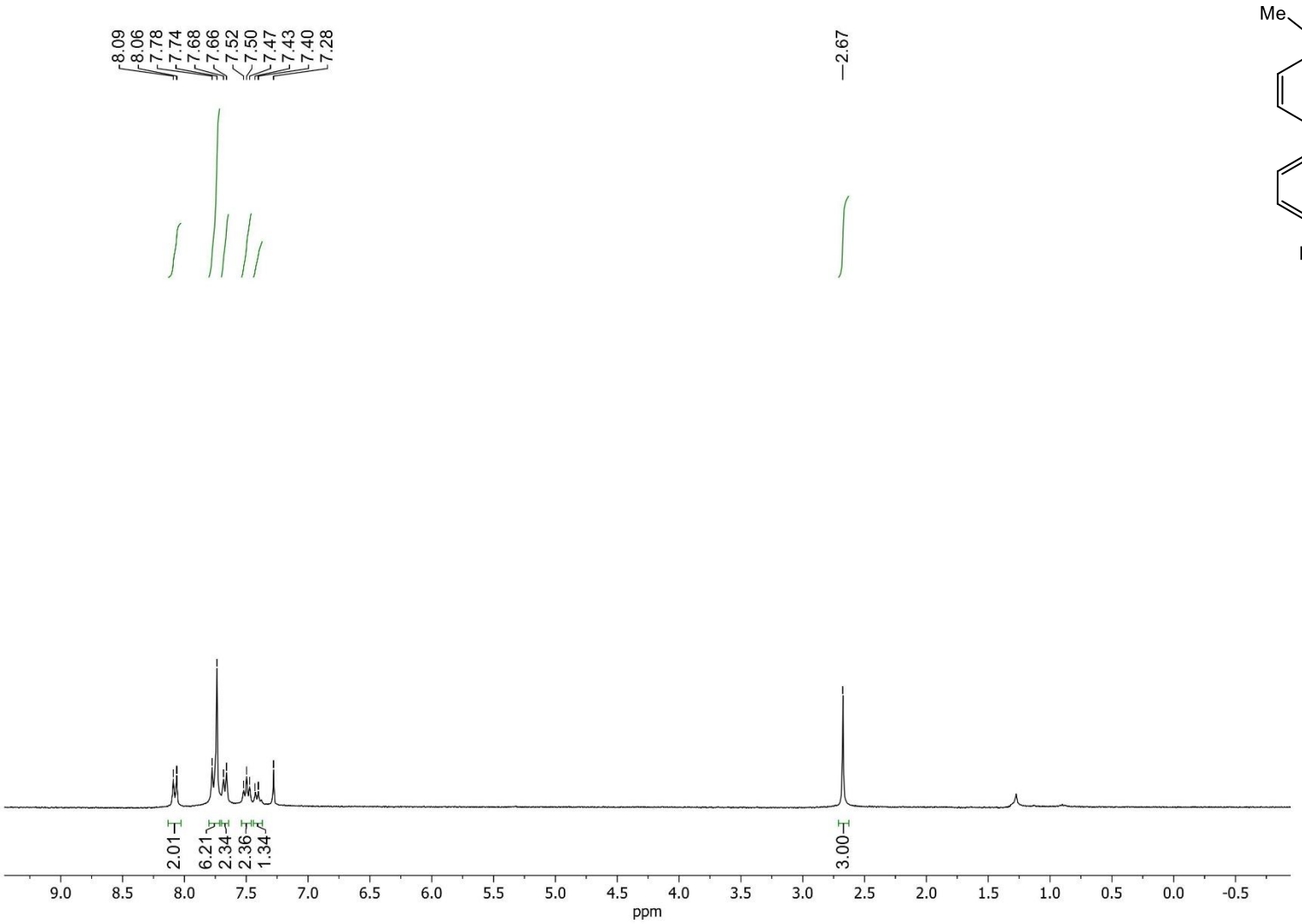
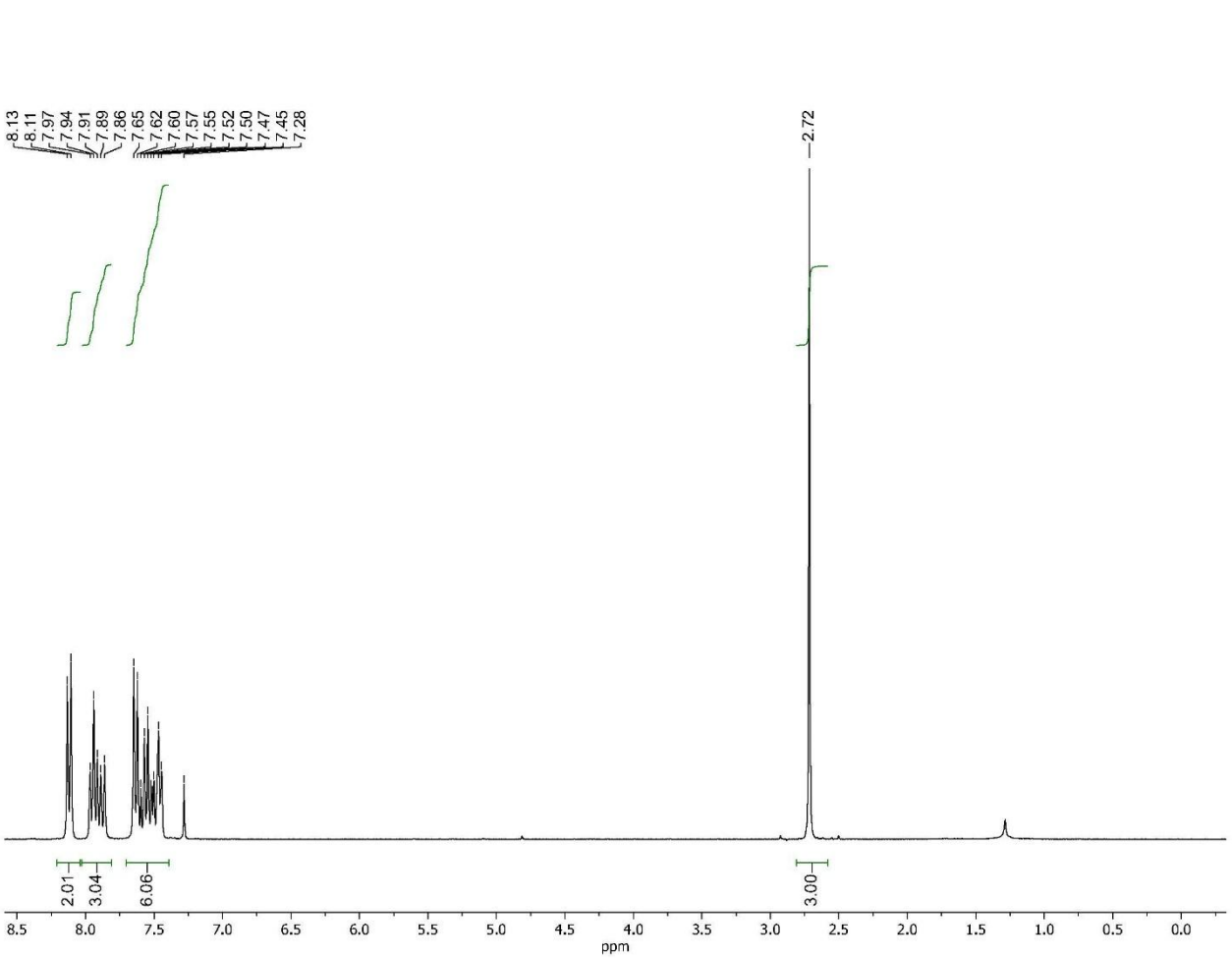


Figure S17 ^{1}H NMR spectrum of 1-(1,1':4',1''-terphenyl)-4-ylethan-1-one (**14o**).



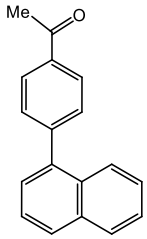


Figure S18 ^{1}H NMR spectrum of 1-(4-acetylphenyl)naphthalene (**14p**).