Journal of the Serbian Chemical Society
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J. Serb. Chem. Soc. 82 (12) S466–S479 (2017) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Synthesis of substituted allyl acetates from heterocyclic dienes by a Pd-promoted arylation–acetoxylation cascade

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J. Serb. Chem. Soc. 82 (12) (2017) 1335–1341

ANALYTICAL AND SPECTRAL DATA OF THE SYNTHESISED COMPOUNDS

*[2-(4-Methoxybenzyl)-1,6,7,11*b*-tetrahydro-4*H*-pyrido[2,1-*a*]isoquinolin-3-yl]methyl acetate (**5**).* IR (cm^{-1}): 1733, 1509, 1240, 1022, 736; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.11–7.03 (6H, *m*, Ar-H), 6.83 (1H, *s*, Ar-H), 6.81 (1H, *s*, Ar-H), 4.82 (1H, *d*, *J* = 12.5 Hz, H-3′), 4.70 (1H, *d*, *J* = 12.5 Hz, H-3′), 3.79 (3H, *s*, OCH_3), 3.57 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.50 (1H, *d*, *J* = 15.5 Hz, H-4), 3.45 (1H, *dd*, *J* = 11.0 & 3.5 Hz, H-11b), 3.38 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.19––3.11 (2H, *m*, H-7 & H-4), 3.10–3.08 (1H, *m*, H-6), 2.70 (1H, *d*, *J* = 15.0 Hz, H-7), 2.58–2.51 (2H, *m*, H-1 & H-6), 2.16–2.11 (1H, *m*, H-1), 2.08 (3H, *s*, CH_3CO); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 171.1 ($C{=}O_{ester}$), 158.1, 137.6, 135.3, 134.2, 129.5, 128.8, 126.0, 125.8, 125.4, 125.3, 113.9, 62.2 (C-3′), 59.0 (C-11b), 57.3 (C-4), 55.2 (OCH_3), 50.8 (C-6), 37.3 (C-2′), 36.7 (C-1), 29.2 (C-7), 21.3, 20.9 (**C**H_3CO); MS-EI (*m*/*z*): 270.1, 226.0, 210.1, 130.0. 59.9; HRMS--ESI): Calcd. for $[C_{24}H_{27}NO_3{+}H]^+$: 378.20637. Found: 378.20459.

*[2-(3,4-Dimethylbenzyl)-1,6,7,11*b*-tetrahydro-4*H*-pyrido[2,1-*a*]isoquinolin-3-yl]methyl acetate (**7a**).* IR (cm^{-1}): 1735, 1371, 1222, 1020, 735; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.11–7.03 (6H, *m*, Ar-H), 6.94 (1H, *s*, Ar-H), 6.90 (1H, *d*, *J* = 7.5 Hz, Ar-H), 4.82 (1H, *d*, *J* = 12.0 Hz, H-3′), 4.70 (1H, *d*, *J* = 12.0 Hz, H-3′), 3.57 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.50 (1H, *d*, *J* = 16.0 Hz, H-4), 3.45 (1H, *dd*, *J* = 10.5 & 3.5 Hz, H-11b), 3.36 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.19––3.08 (3H, *m*, H-7, H-6 & H-4), 2.70 (1H, *d*, *J* = 15.0 Hz, H-7), 2.61–2.51 (2H, *m*, H-1 & H-6), 2.23 (3H, *s*, Ar-CH_3), 2.22 (3H, *s*, Ar-CH_3), 2.14 (1H, *m*, H-1), 2.08 (3H, *s*, CH_3CO); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 171.1 ($C{=}O_{ester}$),

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137.6, 136.5, 136.3, 135.3, 134.3, 134.2, 129.9, 129.7, 128.7, 126.0, 125.9, 125.8, 125.4, 125.3, 62.2 (C-3′), 58.9 (C-11b), 57.3 (C-4), 50.8 (C-6), 37.7 (C-2′), 36.8 (C-1), 29.2 (C-7), 20.9 (**C**H_3CO), 19.7 (Ar-CH_3), 19.2 (Ar-CH_3); MS-EI (*m*/*z*): 374.2 (M^+–1), 315.2 (M^+–CH_3COO), 256.1, 196.1, 169.1, 132.0; HRMS-ESI: Calcd. for $[C_{25}H_{29}NO_2+H]^+$: 376.22711. Found: 376.22499.

*[2-(4-Methylbenzyl)-1,6,7,11*b*-tetrahydro-4*H*-pyrido[2,1-*a*]isoquinolin-3--yl]methyl acetate (**7b**).* IR (cm^{-1}): 2914, 1733, 1371, 1200, 1020, 736; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.11–7.04 (8H, *m*, Ar-H), 4.81 (1H, *d*, *J* = = 12.0 Hz, H-3′), 4.69 (1H, *d*, *J* = 12.0 Hz, H-3′), 3.59 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.50 (1H, *d*, *J* = 16.0 Hz, H-4), 3.46 (1H, *dd*, *J* = 10.5 & 3.5 Hz, H-11b), 3.39 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.16–3.11 (2H, *m*, H-4 & H-7), 3.10–3.08 (1H, *m*, H-6), 2.70 (1H, *d*, *J* = 15.0 Hz, H-7), 2.59–2.51 (2H, *m*, H-6 & H-1), 2.31 (3H, *s*, Ar-CH_3), 2.15 (1H, *t*, *J* = 14.0 Hz, H-1), 2.07 (3H, *s*, CH_3CO); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 171.1 (C=O_{ester}), 137.6, 135.9, 135.7, 135.2, 134.2, 129.2, 128.7, 128.4, 126.0, 125.8, 125.5, 125.3, 62.3 (C-3′), 58.9 (C-11b), 57.4 (C-4), 50.8 (C-6), 37.8 (C-2′), 36.8 (C-1), 29.2 (C-7), 20.9 (Ar-CH_3, **C**H_3CO); MS-EI (*m*/*z*): 346.2 (M^+–CH_3), 287.1 (M^+–CH_2OAc), 256.1, 196.1, 132.1; HRMS-ESI (*m*/*z*): Calcd. for $[C_{24}H_{27}NO_2+H]^+$: 362.21146. Found: 362.21292.

*[2-(Naphthalen-1-ylmethyl)-1,6,7,11*b*-tetrahydro-4*H*-pyrido[2,1-*a*]isoquinolin-3-yl]methyl acetate (**7c**).* IR (cm^{-1}): 1731, 1635, 1371, 1019, 783; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 8.05 (1H, *d*, *J* = 8.0 Hz, Ar-H), 7.86 (1H, *d*, *J* = 8.5 Hz, Ar-H), 7.73 (1H, *d*, *J* = 8.5 Hz, Ar-H), 7.54–7.47 (2H, *m*, Ar-H), 7.41 (1H, *t*, *J* = 8.0 Hz, Ar-H), 7.27 (1H, *d*, *J* = 7.0 Hz, Ar-H), 7.09–7.03 (3H, *m*, Ar-H), 6.94 (1H, *d*, *J* = 7.5 Hz, Ar-H), 4.79 (1H, *d*, *J* = 12.0 Hz, H-3′), 4.71 (1H, *d*, *J* = 12.5 Hz, H-3′), 4.07 (1H, *d*, *J* = 16.0 Hz, H-2′), 3.95 (1H, *d*, *J* = 16.5 Hz, H-2′), 3.65–3.59 (2H, *m*, H-4 & H-11b), 3.28 (1H, *d*, *J* = 15.5 Hz, H-4), 3.21–3.18 (2H, *m*, H-6 & H-7), 2.77–2.74 (1H, *m*, H-7), 2.64–2.60 (2H, *m*, H-6 & H-1), 2.23 (1H, *t*, *J* = 13.5 Hz, H-1), 2.04 (3H, *s*, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 171.1 (C=O_{ester}), 136.9, 134.5, 134.3, 133.9, 133.7, 132.3, 128.8, 128.7, 127.0, 126.4, 126.2, 126.1, 125.9, 125.6, 125.5, 125.3, 125.2, 123.3, 62.2 (C-3′), 58.9 (C-11b), 57.1 (C-4), 50.7 (C-6), 36.9 (C-1), 34.8 (C-2′), 28.9 (C-7), 20.9 (CH_3); MS-EI (*m*/*z*): 355.1, 281.1, 207.0, 73.1; HRMS-ESI: Calcd. for $[C_{27}H_{27}NO_2+H]^+$: 398.21146. Found: 398.21240.

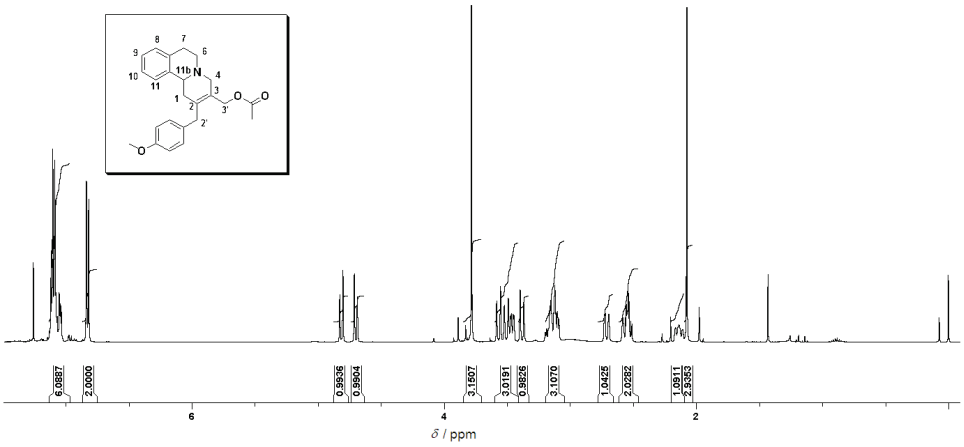
*[2-(4-Methylbenzyl)-1,4,6,7,12,12*b*-hexahydroindolo[2,3-*a*]quinolizin-3--yl]methyl acetate (**9**).* IR (cm^{-1}): 2907, 1732, 1451, 1375, 1223, 1020, 740; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.65 (1H, *brs*, N–H), 7.46 (1H, *d*, *J* = 8.0 Hz, Ar-H), 7.24 (1H, *m*, Ar-H), 7.08 (6H, *m*, Ar-H), 4.82 (1H, *d*, *J* = 12.5 Hz, H-3′), 4.69 (1H, *d*, *J* = 12.0 Hz, H-3′), 3.67 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.58 (1H, *d*, *J* = = 16.0 Hz, H-4), 3.49 (1H, *m*, H-12b), 3.35 (1H, *d*, *J* = 15.0 Hz, H-2′), 3.23–3.19 (2H, *m*, H-6 & H-4), 3.04–2.97 (1H, *m*, H-7), 2.75 (1H, *dt*, *J* = 15.5 & 2.5 Hz, H-7), 2.64 (1H, *dt*, *J* = 11.5 & 4.0 Hz, H-6), 2.38–2.35 (1H, *m*, H-1), 2.32 (3H, *s*,

Ar-CH_3), 2.27–2.22 (1H, *m*, H-1), 2.07 (3H, *s*, CH_3CO); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 171.1 ($C{=}O_{ester}$), 136.2, 135.9, 135.7, 134.1, 133.9, 129.3, 128.5, 127.1, 126.3, 121.5, 119.4, 118.2, 110.7, 108.5, 62.2 (C-3′), 56.4 (C-4), 55.5 (C-12b), 51.8 (C-6), 37.6 (C-2′), 34.6 (C-1), 21.3 (**C**H_3CO), 20.9 (Ar-CH_3); HRMS-ESI: Calcd. for $[C_{26}H_{28}N_2O_2{+}H]^+$: 401.22235. Found: 401.22364.

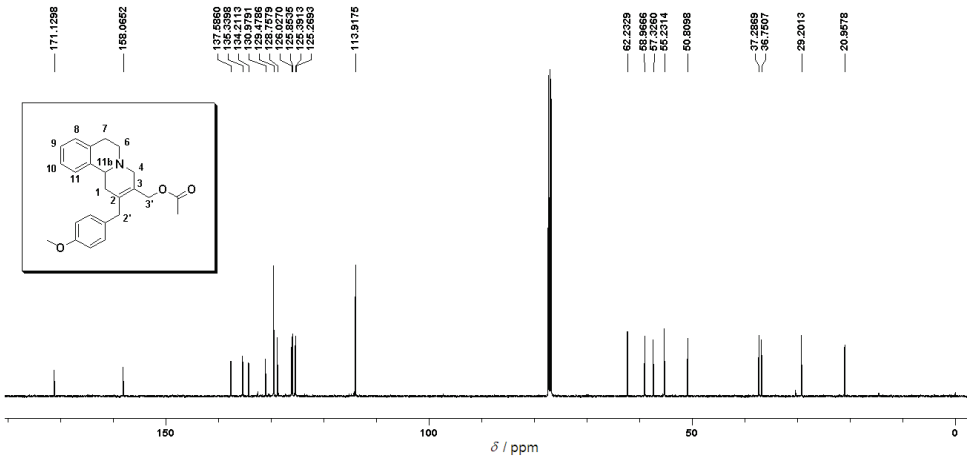
SELECTED SPECTRA

*[2-(4-Methoxybenzyl)-1,6,7,11*b*-tetrahydro-4*H*-pyrido[2,1-*a*]isoquinolin-3-yl]-methyl acetate (**5**)*

^{1}H-NMR



^{13}C-NMR



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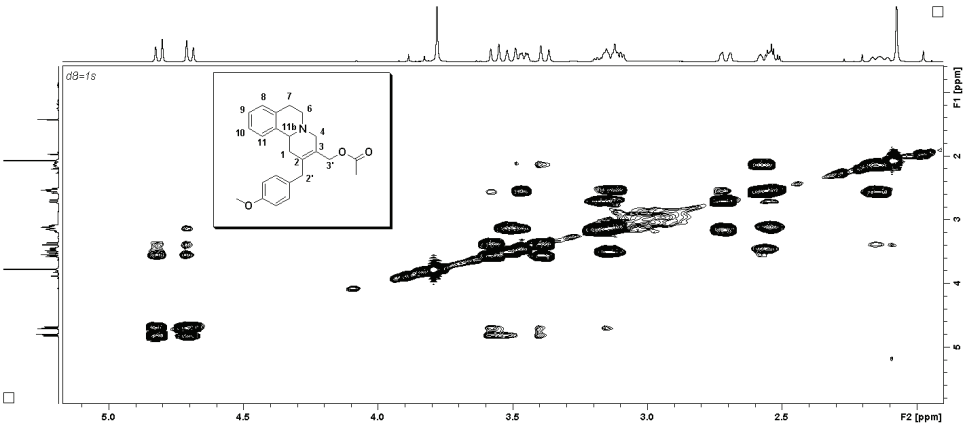
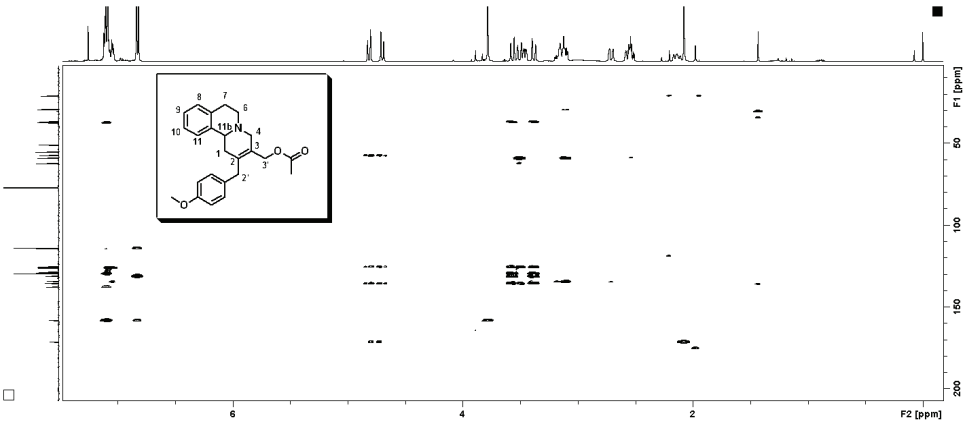
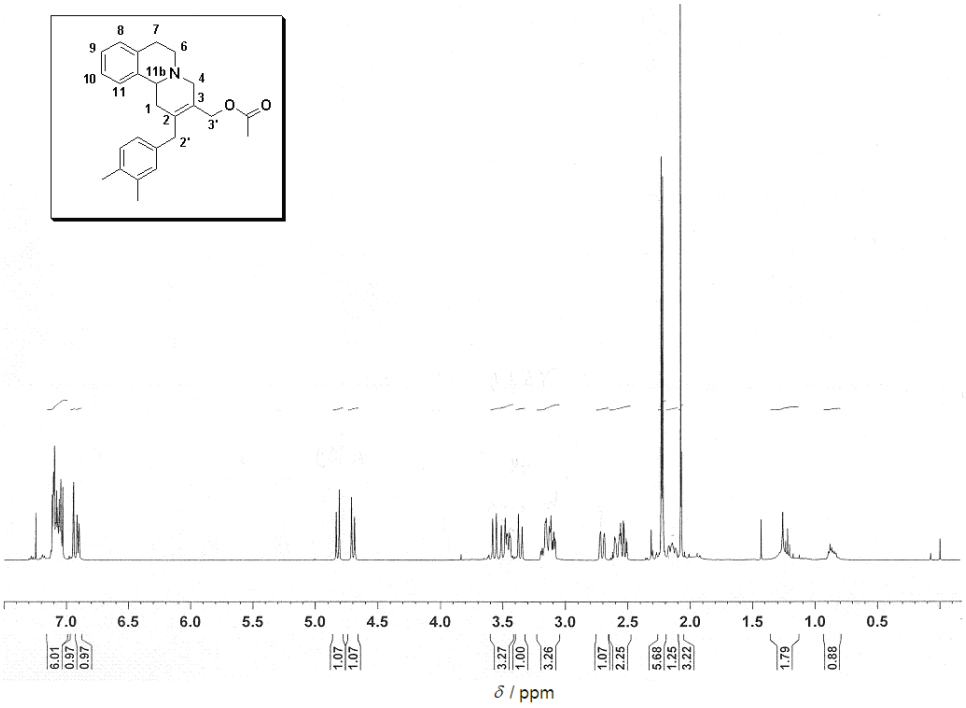


HMBC



*[2-(3,4-Dimethylbenzyl)-1,6,7,11*b*-tetrahydro-4*H*-pyrido[2,1-*a*]isoquinolin-3-yl]methyl acetate (**7a**)*

^{1}H-NMR



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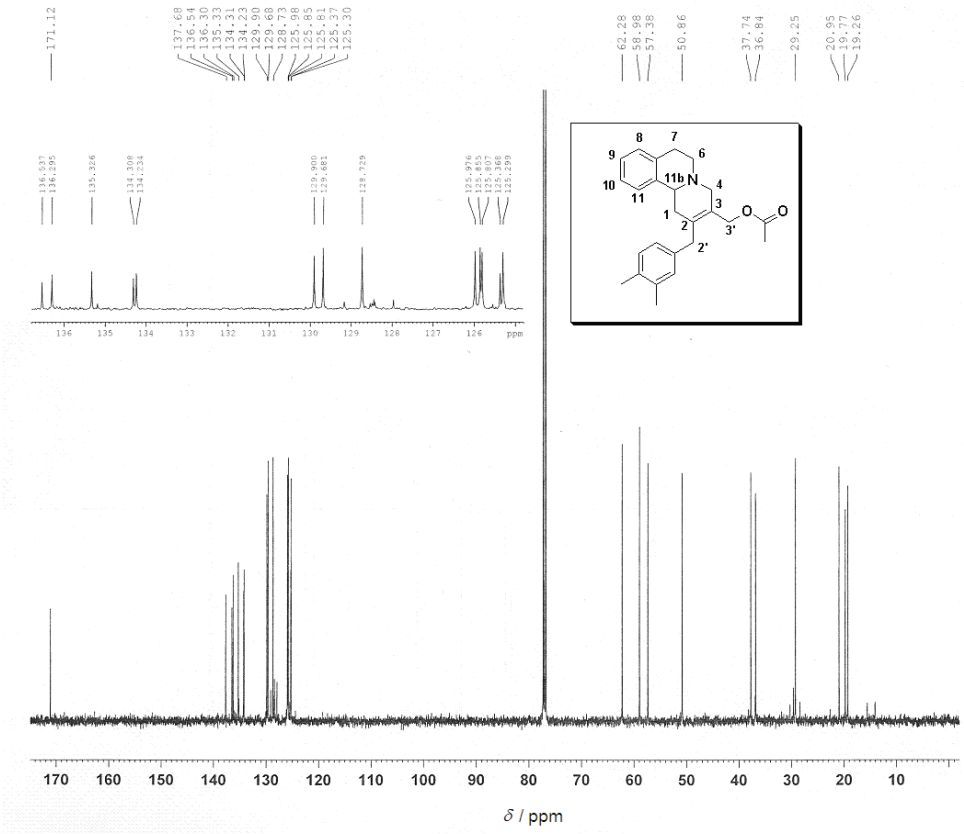

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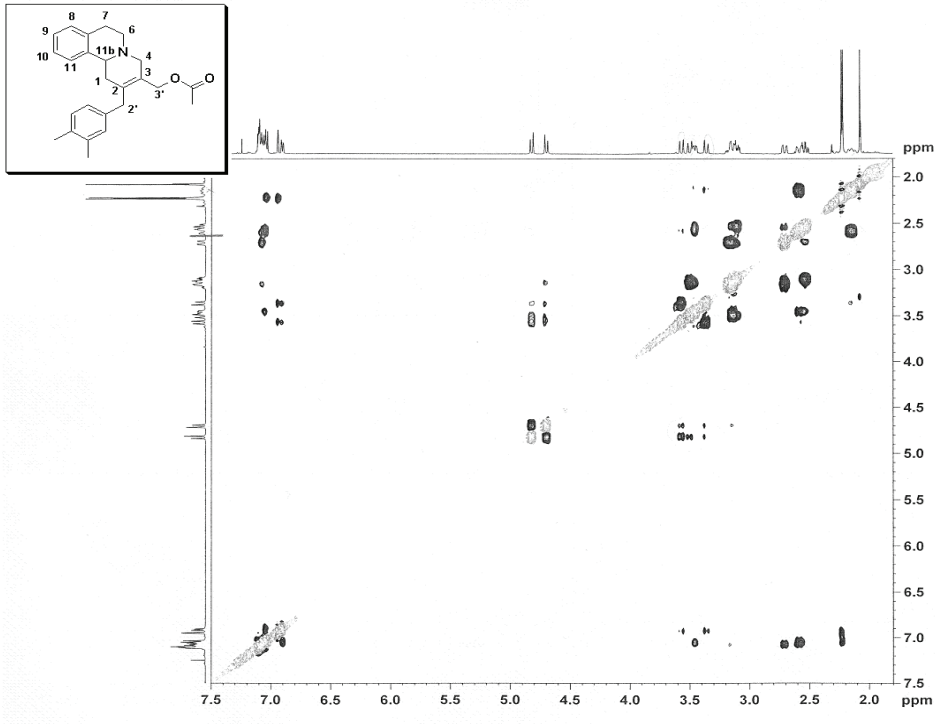
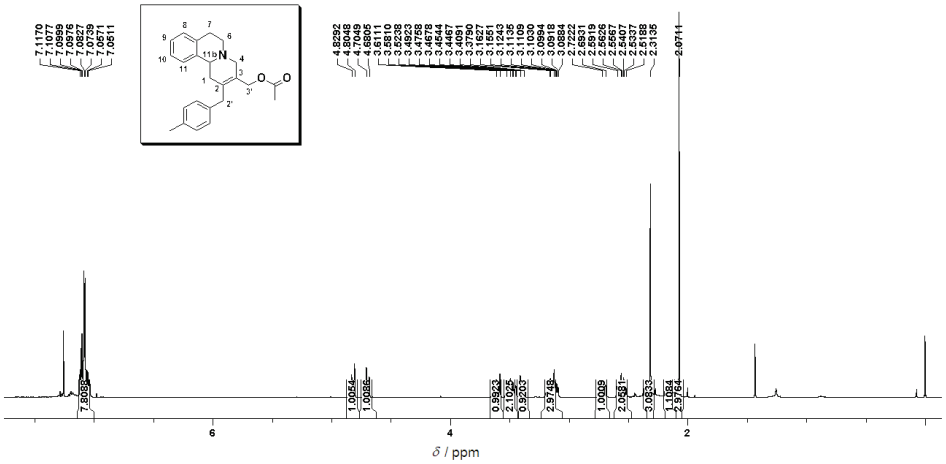


*[2-(4-Methylbenzyl)-1,6,7,11b-tetrahydro-4H-pyrido[2,1-a]isoquinolin-3-yl]-methyl acetate (**7b**)*

^{1}H-NMR



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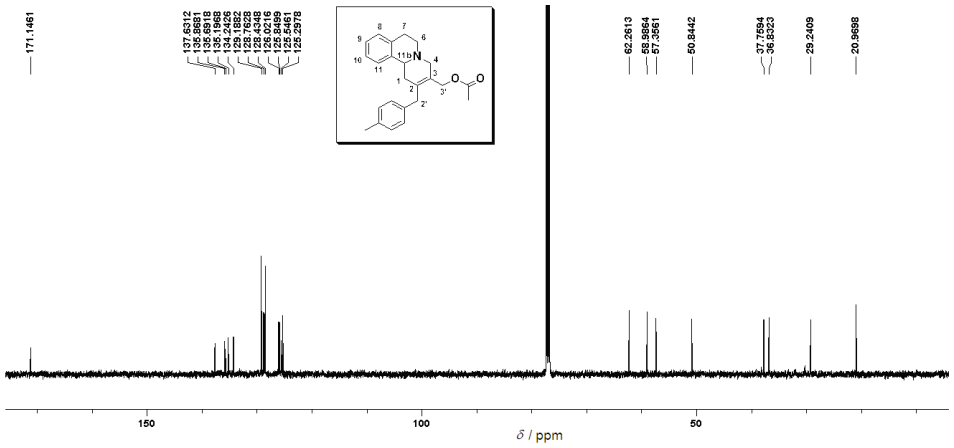

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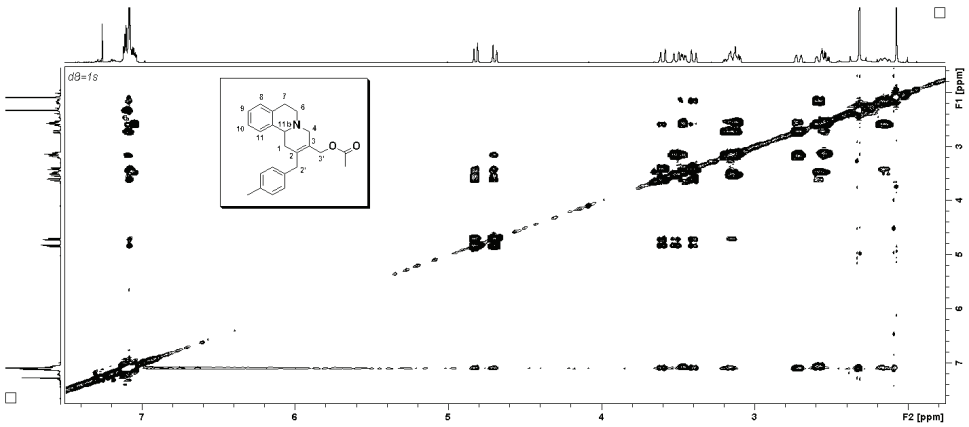
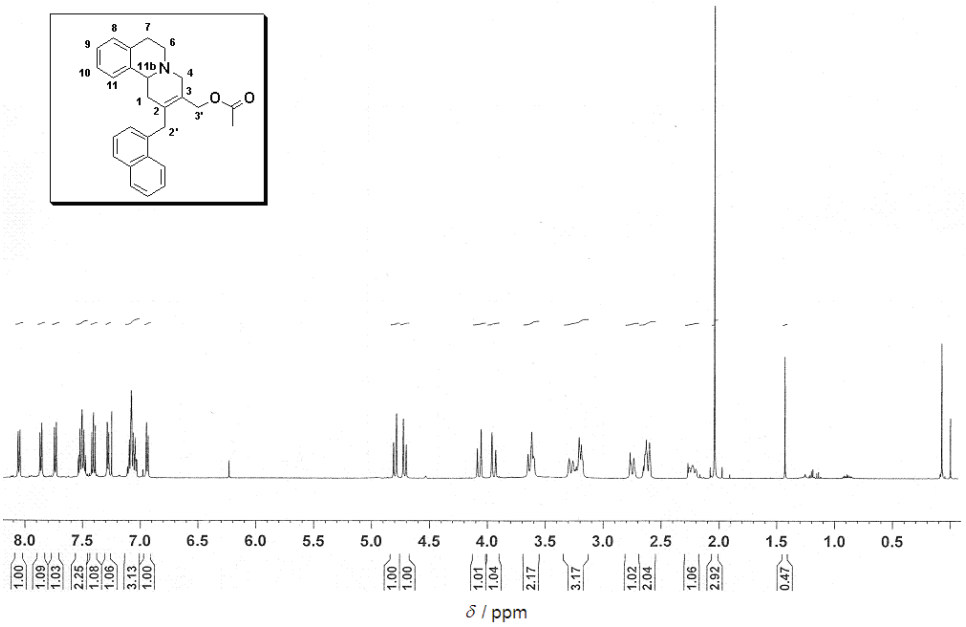


*[2-(Naphthalen-1-ylmethyl)-1,6,7,11*b*-tetrahydro-4*H*-pyrido[2,1-*a*]isoquinolin-3-yl]methyl acetate (**7c**)*

^{1}H-NMR



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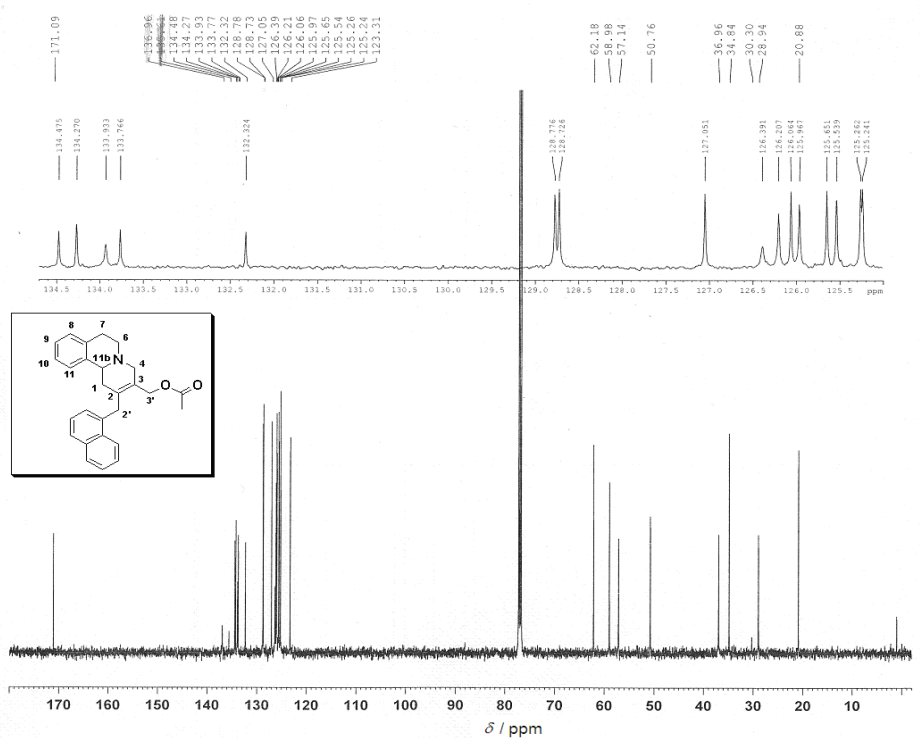

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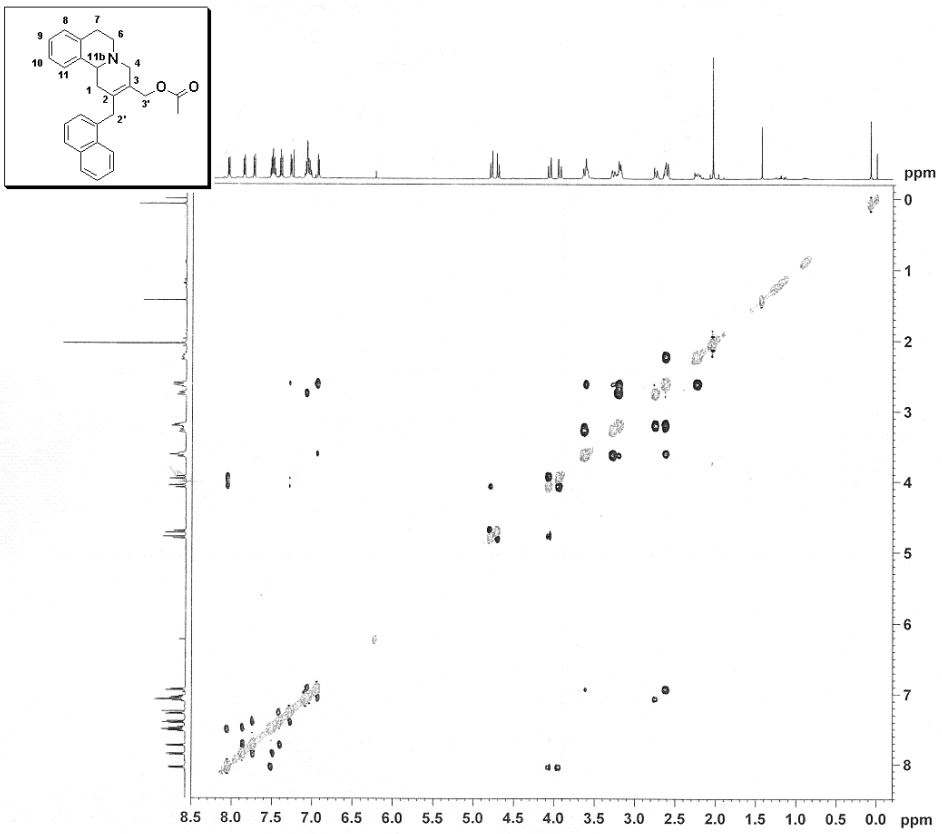
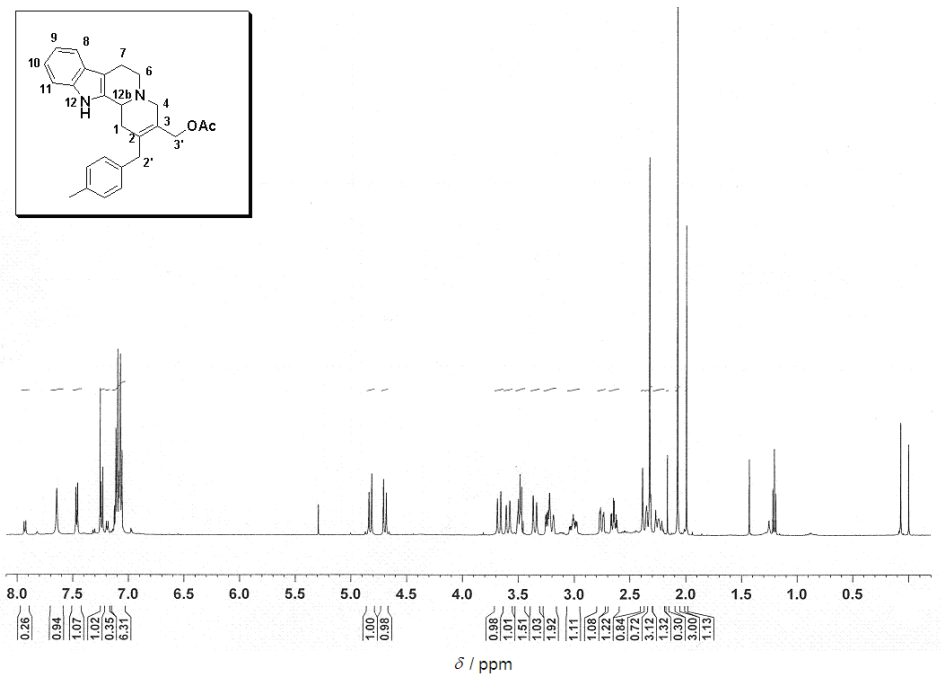


*[2-(4-Methylbenzyl)-1,4,6,7,12,12*b*-hexahydroindolo[2,3-*a*]quinolizin-3-yl]-methyl acetate (**9**)*

^{1}H-NMR



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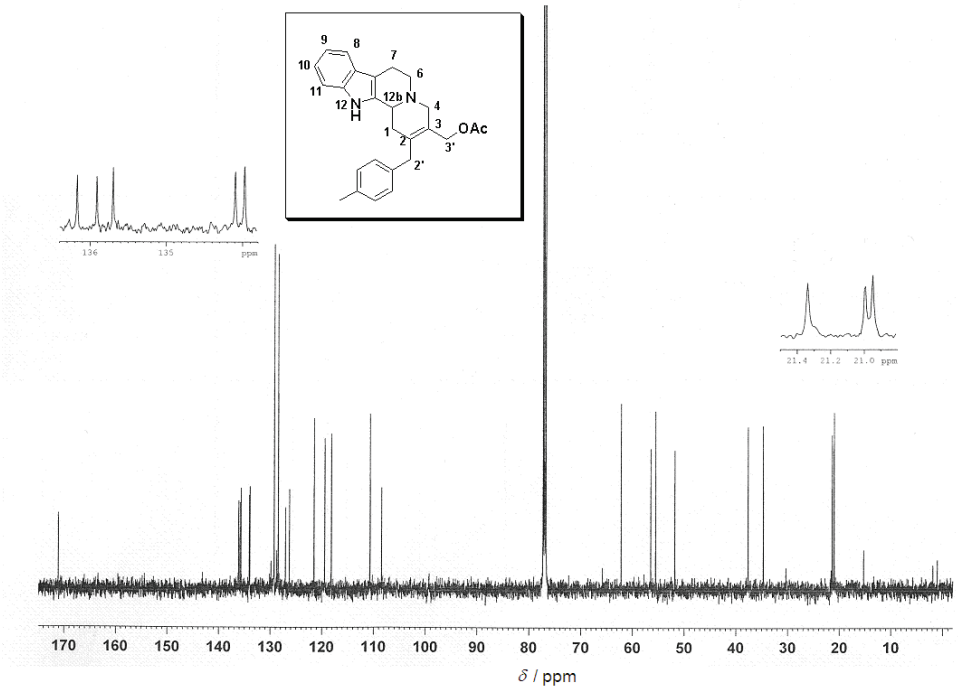

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